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SOME SULPHUR-NITROGEN RING TRANSFORMATIONS

USING TETRASULPHUR TETRANITRIDE

AND TRICHLOROTRITHIATRIAZENE AS PRECURSORS
A Thesis Submitted to
The University of Durham

by

Richard G. Hey, B.Sc.
(Grey College)

For The Degree of
Doctor of Philosophy
March 1980

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To the Heys, past, present and future
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MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Departments of the University of Durham and New Brunswick between October 1976 and September 1979. I declare that this work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

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"Producing Sulphur-Nitrogen Groups"

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"The crystal structure of 4-phenyl-1,2-dithia-3,5-diazole"
by A. Vegas, A. Perez-Salazar, A.J. Banister and R.G. Hey
"The preparation of thiazyl hexachloroantimonate (V) \( \text{NS}^+\text{SbCl}_6^- \)"

by A.J. Banister, R.G. Hey and J. Passmore


"Reactions of Chlorine Monofluoride with Tetrasulphur Tetranitride, Trichlorotrithiatriazene and Thiazyl chloride"

by A.J. Banister, R.G. Hey, J. Passmore and G. Sutherland

ABSTRACT

As part of a general study of 1,2,3,5-dithiadiazolium cations, a series of 4-phenyl-1,2,3,5-dithiadiazolium salts were produced by anion exchange reactions, both in the solid phase and in solution. The reduction of the 4-phenyl-1,2,3,5-dithiadiazolium cation gave the previously unreported, 4-phenyl-1,2-dithia-3,5-diazole, the crystal structure of which indicates that the dithiaazole exists as an eclipsed dimer.

By analogy with the solid phase exchange reactions which occur between 4-phenyl-1,2,3,5-dithiadiazolium chloride and Group I metal halides, the metathetical reactions between $S_2N_2Cl$ and metal halides were investigated. The product isolated from the reaction of $S_2N_2Cl$ with CsI was identified as tetrasulphur tetranitride. The reductions of $S_4N_2Cl$, $S_4N_2Cl_2$, and $(NSCl)_3$ were studied using a variety of reducing agents. The majority of the reduction reactions gave tetrasulphur tetranitride but the reduction of trichlorothiatriazene by iron using sulphur dioxide as a solvent provided a convenient synthesis of the cyclopentathiapentazenium cation ($S_5N_5^+$). The reduction of chlorothiodithiazyl chloride by iron using sulphur dioxide as a solvent produced the previously unreported salt ($S_{10}N_8^{2+}$)(FeCl$_4^-$)$_2$.

The synthesis of the cations $S_xN^+$ (x>1) was approached from two angles, that of reacting sulphur polycations ($S_8^{2+}$(AsF$_6^-$)$_2$) with nitrogen containing species (MN$_3$ and $S_4N_4$) and that of reacting the thionitrosyl cation (NS$^+$) with sulphur.

The reactions of $S_8^{2+}$(AsF$_6^-$)$_2$ with azides and tetrasulphur tetranitride led to the formation of the $S_2N^+$ cation and with
excess tetrasulphur tetranitride to the production of 
$S_{10}N_8^{2+}\text{(AsF}_6^-)_{2}$.

Some preliminary investigative reactions of selenium ($\text{Se}_4^{2+}\text{(AsF}_6^-)_{2}$) and tellurium ($\text{Te}_4^{2+}\text{(AsF}_6^-)_{2}$) polycations with both azides and tetrasulphur tetranitride were carried out and a selenium analogue of $S_N^{2+}$ isolated.

In an attempt to prepare thiazyl fluoride (as a precursor to thionitrosyl salts) by a simple single stage process, chlorine monofluoride was reacted with $S_4N_4$ and $(\text{NSCl})_3$. The reactions did not produce NSF in high yields, the main products being sulphur tetrafluoride $(\text{SF}_4)$, nitrogen and chlorine. The mechanisms of the reactions of $\text{ClF}$ with $S_4N_4$ and $(\text{NSCl})_3$ are discussed.

NSF was synthesised by the metathesis reaction between thiazyl chloride and cesium fluoride.

A facile route to the thionitrosyl cation via the oxidation of $(\text{NSCl})_3$ and $S_4N_4$ using Group V Lewis acids (AsF$_5$, SbF$_5$) at 100-150°C failed. However a convenient route to thionitrosyl hexachloroantimonate (V) has been found in the vapour phase reaction of thiazyl chloride with antimony pentachloride.
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(i) Reaction of \( \text{S}_8^{2+}(\text{AsF}_6^-)_2 \) with \( \text{NaN}_3 \) using \( \text{SO}_2 \) as a solvent 269
(ii) Reaction of \( \text{S}_8^{2+}(\text{AsF}_6^-)_2 \) with \( \text{NaN}_3 \) using \( \text{AsF}_3 \) as a solvent 270
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(v) Reaction of Se$_8^{2+}$($\text{AsF}_6^-$)$_2$ with Et$_4$N$^+$$\text{N}_3^-$ using SO$_2$ as a solvent

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using SO$_2$ as a solvent

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(vii) Reaction of Te$_4^{2+}$($\text{AsF}_6^-$)$_2$ with Et$_4$N$^+$$\text{N}_3^-$ using SO$_2$ as a solvent

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6.3 Discussion

6.3.1 The Reaction of Group VI Polycations with Azides

(i) Reaction of Sulphur Polycations with Azides

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(ii) Reaction of Selenium and Tellurium Polycations with Azides

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6.3.2 The Reactions of Group VI Polycations with Tetrasulphur Tetranitride

(i) The Reaction of S$_8^{2+}$($\text{AsF}_6^-$)$_2$ with Tetrasulphur Tetranitride

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(ii) The Reactions of Selenium Polycations with Tetrasulphur Tetranitride

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(iii) The Reaction of Te$_4^{2+}$($\text{AsF}_6^-$)$_2$ with Tetrasulphur Tetranitride (Ratio 1:2)

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6.3.3 Suggested mechanism by which Group VI Polycations react with Tetrasulphur Tetranitride

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NOMENCLATURE

The nomenclature used for sulphur-nitrogen heterocycles throughout this thesis is that adopted by Chemical Abstracts. A systematic nomenclature has recently been published by Banister and Heal* but is not, as yet, in general use.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_5N_5^+$</td>
<td>Cyclopentathiapentazenium</td>
</tr>
<tr>
<td>$S_4N_4$</td>
<td>Tetrasulphur Tetrannitride</td>
</tr>
<tr>
<td>$S_4N_4F_4$</td>
<td>Tetrafluorotetrathiatetrazocine</td>
</tr>
<tr>
<td>$S_4N_3^+$</td>
<td>Thiotrithiazyl</td>
</tr>
<tr>
<td>$S_4N_2$</td>
<td>Tetrasulphur dinitride</td>
</tr>
<tr>
<td>$S_3N_3X_3$</td>
<td>Trihalotrithiaziene</td>
</tr>
<tr>
<td>$S_3N_2^+$</td>
<td>Thiodithiazyl</td>
</tr>
<tr>
<td>$S_2N_2Cl^+$</td>
<td>Chlorothiodithiazyl</td>
</tr>
<tr>
<td>NSX</td>
<td>Thiazyl halide</td>
</tr>
<tr>
<td>NS$^+$</td>
<td>Thionitrosyl</td>
</tr>
</tbody>
</table>

* H.G. Heal and A.J. Banister

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The work in this thesis has been carried out in two Universities;

(i) University of Durham, Durham, England.

(ii) University of New Brunswick, Fredericton, New Brunswick, Canada.

The experimental techniques adopted in each University were somewhat different and thus the University is specified when referring to specific techniques or apparatus.

1.1 Handling Techniques

The majority of compounds handled throughout this thesis were moisture sensitive. The species were, therefore, manipulated in dry-box conditions, under a top pressure of dry nitrogen or \textit{in vacuo}.

A. \textbf{Nitrogen Supply (University of Durham)}

The nitrogen was obtained as boil off from the liquid nitrogen generation plant and was dried by passing it through (in series), a concentrated sulphuric acid bubbler, a liquid nitrogen cold trap, a phosphorus pentoxide column and a potassium hydroxide column. The removal of oxygen was not found necessary for the work carried out in Durham.

The nitrogen supply at the University of New Brunswick was from high pressure cylinders (equivalent to White Spot Nitrogen supplied by B.O.C. Ltd. (U.K.)).

B. \textbf{Dry-Boxes}

(i) \textbf{Dry-box in the University of Durham}

The dry-box in Durham operated with an atmosphere
of dry nitrogen (dried as in 1.1.A) which was continuously recycled through a phosphorus pentoxide column. The port was purged by dry nitrogen for at least 45 min. after each opening to the external atmosphere. At least one dish of phosphorus pentoxide was kept in the box at all times to monitor the efficiency of the drying columns. All samples for infra-red, Raman and mass spectra and analyses were prepared inside the box.

(ii) **Dry-box in the University of New Brunswick**

A vacuum atmospheres H.E-43-2 dry-box operating with a nitrogen or argon atmosphere was employed. The nitrogen and argon were obtained from high pressure cylinders, the nitrogen being used directly, whereas the argon was dried by passage over an active metal surface.

Access to the box was via a 70 dm$^3$ port (60 cm in length, 40 cm dia.) which could be evacuated. The port was pumped down for 20 min. and then the atmosphere inside the box allowed into the port, the total pressure in the box being maintained by nitrogen from the high pressure cylinder. The pressure inside the box was automatically controlled to within $\pm$ 10 torr of atmospheric pressure by a Pedatrol HE-63-P. The atmosphere inside the box was continuously recycled through an HE 493 DRI-TRAIN, which is essentially a molecular sieve/copper purifier. A water content of better than 2 ppm. was generally obtained.

C. **Apparatus used for Fluorine containing compounds and High Pressure Reactions**

(i) **Vacuum line**

For non-fluorinated compounds a glass vacuum line with high vacuum, hand ground taps and Apiezon grease
was used. For fluorinated species a Monel line fitted with stainless steel Whitey valves (1KS4) using swagelock fittings with teflon ferrules was employed. The Monel line was connected via a glass muck trap to a rotary oil pump. The Monel line was passivated by flaming the line with either an atmosphere of fluorine or sulphur tetrafluoride contained within. Pressures within the line were measured in torr using a diaphragm gauge (0 torr - 1500 torr).

(ii) Apparatus used for reactions involving fluorinated species or pressures greater than one atmosphere.

(a) Pyrex vessels fitted with sinters

Various types of vessels were used which fall under this heading. The simplest vessel is that shown in figure 1.1 (page 14) in which there is one teflon valve, through which the reactants and solvents may be loaded. More complex versions of the same basic design were used (figure 1.2, page 14) in which the solid reactants could be added to both bulbs and one bulb sealed off with respect to the other bulb. This allows moisture sensitive materials to be sealed in one section whilst operations are carried out in the other section under normal atmospheric conditions. Vessels with up to two sealable sections and two sinters were used in the work with Group VI polycations (Chapter Six, page 269).

(b) F.E.P. Tubes fitted with Swagelock Joints

F.E.P. tubing $\frac{1}{2}$" o.d. was purchased in 50' rolls. 20 cm lengths of this tubing were taken and one end sealed using a moderately hot glass tube. The tubing was then placed in a swagelock compression joint which was connected to a stainless steel Whitey valve (1KS4) (figure 1.3,
The mode of operation using these vessels was to passivate them by pumping under reduced pressure for 2h.
or by condensing in ca. 300 torr pressure of SF$_4$. Solid reactants were added to the tube by separating the swagelock joint. Gases and volatiles were condensed into the vessel by cryogenic pumping.

(c) **High Pressure Monel Vessels**

High pressure reactions (≥3 atmospheres) were carried out using Monel vessels (maximum working pressure ca. 20 atmospheres), (figure 1.4, page 15). The vessels were made leak tight by progressively tightening the Allen screws, with the resulting deformation of the teflon "O" ring. The vessels were passivated by heating them with a Bunsen flame whilst they contained sulphur tetrafluoride. Solids were placed in the vessels by removing the lid and volatiles by condensation via the Whitey valve.

1.1.1 Spectroscopic Data

(i) **Infra-red Spectra**

Infra-red spectra were recorded using nujol mulls, between KBr or AgCl plates and as discs using KBr or KCl as dispersants. Gas phase infra-red spectra of fluorine containing species were recorded using a passivated stainless steel cell with AgCl windows, whereas the spectra of non-fluorine containing compounds were recorded using a glass cell with KBr windows (figure 1.5, page 16). Perkin-Elmer 457, 577 and 467 prism grating spectrometers were used to obtain the spectra.

(ii) **Raman Spectra**

Raman spectra were obtained using a Cary 82 spectrometer with a Spectra Physics 125 (632.8 nm exciting
line) or a Spectra Physics 164 (514.5 nm, exciting line) laser (University of Durham). Spectra were also recorded using a Raman lab. machine with a Spectra Physics 125 laser (University of New Brunswick).

(iii) Mass Spectra

Mass spectra were obtained using an A.E.I. (MS9) spectrometer interfaced with a PDP 8 mini-computer. Samples were run at 120-180°C and 70 eV with an accelerating potential of 8kV. Samples were introduced by direct insertion into the ion source.

(iv) $^{19}$F-Nuclear Magnetic Resonance Spectra

$^{19}$F-n.m.r. were obtained using a Varian H.A 100 (94.08 MHz) or a Varian H.A. 60 (56.4 MHz) spectrometer. Perfluorobenzene and Freon 11 (CCl$_3$F) were used as reference compounds.

1.1.2 Analyses

Carbon, hydrogen and nitrogen were determined using a Perkin-Elmer 240 Elemental Analyser. Nitrogen was also determined by the Kjeldhal method.

Sulphur and the halogens were determined by oxygen flask combustion followed by visual and potentiometric titration of the sulphate and halide anions respectively.

All metals were determined using a Perkin-Elmer 403 Atomic Adsorption Spectrometer.

Arsenic and tellurium were analysed by Butterworth Laboratories Ltd., Teddington, Middlesex.

** PDP is a registered trade name.
* Raman lab. is a registered trade name.
1.2 Preparation and Purification of Starting Materials

1.2.1 Inorganic Liquids, as both Starting Materials and Solvents

(i) Sulphur Dichloride (S\(_{2}\)Cl\(_{2}\))

Sulphur dichloride was purified by fractional distillation, the middle fraction (bp 50-62°C) was retained and re fractionated, the purified species being collected at 60°C.

(ii) Disulphur Dichloride (S\(_{2}\)Cl\(_{2}\))

Disulphur dichloride was distilled from sulphur and decolourising charcoal at atmospheric pressure and fraction collected between 130°C-140°C redistilled in vacuo.²

(iii) Thionyl Chloride (SOCl\(_{2}\))

Thionyl chloride was stored in the dark with teflon sleeves on the ground joints, as grease is attacked by thionyl chloride.

(iv) Sulphuryl Chloride (SO\(_{2}\)Cl\(_{2}\))

Analar sulphuryl chloride was distilled under nitrogen, the fraction collected between 69-70°C being used.

(v) Sulphur Dioxide (SO\(_{2}\))

Sulphur dioxide was condensed on to either calcium dihydride or phosphorus pentoxide and stored for 4
days prior to use. The solvent was always distilled off the dehydrating agent.

(vi) **Arsenic Trifluoride (AsF$_3$)**

Arsenic trifluoride was distilled on to sodium fluoride and stored for 4 days prior to use. The solvent was always vacuum distilled off the sodium fluoride.

(vii) **Sulphuryl Chloride Fluoride (SO$_2$ClF)**

Sulphuryl chloride fluoride was dried over phosphorus pentoxide for 4 days prior to use. The solvent was always distilled off the dehydrating agent.

1.2.2 **Organic Liquids as both Starting Materials and Solvents**

(i) **Hexafluorobenzene (C$_6$F$_6$)**

Hexafluorobenzene was distilled *in vacuo* on to activated molecular sieve (4.A) and stored for 24h. The solvent was then distilled (*in vacuo*) on to a second batch of activated molecular sieve (4.A) and stored for ca. 60h. prior to use. The solvent was distilled off the molecular sieve (*in vacuo*) into the required vessel.

(ii) **Tetrahydrofuran (THF) and Monoglyme (CH$_3$OCH$_2$CH$_2$OCH$_3$)**

Tetrahydrofuran and monoglyme were refluxed for 8h. with sodium-potassium alloy and then fractionally distilled.

(iii) **Benzonitrile (PhCN)**

Benzonitrile was refluxed with magnesium sulphate for 12h. and then distilled on to and stored over activated molecular sieve (4.A).
(iv) The following solvents were dried using sodium wire

(a) 1,4-dioxan, (b) diethyl ether, (c) toluene, (d) benzene, (e) pentane, (f) hexane.

If a high degree of dryness was required for the above solvents, they were refluxed with metallic sodium for 3h. and then distilled.

(v) The following solvents were dried by refluxing with phosphorus pentoxide

(a) Nitromethane, (b) Freon 11 (CFCl₃), (c) carbon tetrachloride, (d) 1,2-dichloroethane, (e) dichloromethane.

1.2.3 Purification of Lewis Acids

(i) Boron trichloride (BCl₃)

Boron trichloride was distilled, in vacuo into the required vessel.

(ii) Aluminium Trichloride (Al₂Cl₆)

Aluminium trichloride was purified by sublimation at 130°C, in vacuo, on to a cold finger at -78°C.

(iii) Tin(IV)Chloride (SnCl₄)

Tin (IV)chloride was distilled in vacuo prior to use.

(iv) Iron(III)Chloride (Fe₂Cl₆)

Iron(III) chloride was purified by refluxing in thionyl chloride for 2h., filtering off the thionyl chloride and drying in vacuo.
(v) **Antimony Pentafluoride ($\text{SbF}_5$)**

Antimony pentafluoride was distilled four times, *in vacuo*, to remove all traces of HF, and stored *in vacuo*.

(vi) **Antimony Pentachloride ($\text{SbCl}_5$)**

Antimony pentachloride was purified by double distillation *in vacuo*.

(vii) **Arsenic Pentafluoride ($\text{AsF}_5$) (Monel Apparatus)**

Arsenic trifluoride was condensed into the bottom of a bomb and fluorine added in small aliquots. The vessel was allowed to warm slowly to room temperature between each addition of fluorine. A slight excess of fluorine was added to the system to ensure complete conversion. After all the fluorine had been added and the fluorination was complete the bomb was cooled to $-196^\circ C$ and the excess fluorine removed. The arsenic pentafluoride was used directly from the bomb.

1.2.4 Gaseous Reactants

(i) **Chlorine and Bromine**

Chlorine and bromine were distilled on to phosphorus pentoxide and stored for two days prior to use. The halogens were distilled, *in vacuo*, into the required vessels.

(ii) **Chlorine Monofluoride ($\text{ClF}$) (Monel Apparatus)**

The gas was condensed at $-196^\circ C$ and pumped on to remove nitrogen and/or fluorine. No attempt was made to remove any chlorine present.
1.2.5 **Solid Reactants**

All solid reactants were dried, in *vacuo*, at either room temperature or elevated temperatures as required. Salts that decompose in *vacuo* or on heating were used from a freshly opened sample.

1.2.6 **Sulphur-Nitrogen Starting Materials**

(i) **Tetrasulphur Tetranitride (\(\text{S}_4\text{N}_4\))**

Tetrasulphur tetranitride was prepared by the method described by Jolly, in which chlorine gas was passed through a carbon tetrachloride solution of disulphur dichloride until saturated, followed by ammonia gas. The solid was washed with water, then ether and extracted with 1,4-dioxan finally being recrystallised from benzene.

(ii) **Trichlorothriatriazene (\(\text{S}_3\text{N}_2\text{Cl}_3\))**

(a) Excess sulphuryl chloride was added to powdered chlorothiodithiazyl chloride and stirred at room temperature for 24h. The reaction mixture was filtered and the residue recrystallised from carbon tetrachloride.

(b) A higher melting and thermally more stable compound was formed when chlorine gas was passed over chlorothiodithiazyl chloride for 30 min. producing a deep red slurry. The sulphur dichloride formed was removed in *vacuo* and the process repeated until no further sulphur dichloride was produced. The crude material was then recrystallised from anhydrous carbon tetrachloride (2.5 cm³ gram⁻¹).

(iii) **Chlorothiodithiazyl Chloride \(\text{S}_3\text{~N~}_2\text{Cl}_2\)**

Dry ammonium chloride (200g) and sulphur (40g), were mixed in a 1000 cm³ *flask* fitted with an air
condenser (100 cm in length, 2 cm diameter) on top of which was attached a calcium chloride drying tube. Disulphur dichloride (200 cm$^3$, 336g) was added to the reactants and the reaction mixture heated (using an isomantle) to reflux. The reflux point was controlled and stabilised about 2/3rds of the way up the air condenser. Over a period of 10h. the reflux level dropped and large orange crystals formed on the condenser walls. It was found essential to use a fume cupboard with a high extraction rate, in order to increase the temperature gradient up the column. The temperature gradient should not be altered throughout the course of the experiment. After ca. 10h. the reaction was cooled down, the air condenser was removed and pumped down to remove all traces of SCl$_2$. The condenser was then filled with dry nitrogen and the product stored in a dry-box.

(iv) Thiodithiazyl Chloride$^7$ (S$_2$N$_2$Cl)

Thiodithiazyl chloride was prepared from chlorothiodithiazyl chloride (S$_3$N$_2$Cl$_2$) by heating the latter at 80°C, in vacuo, for ca. 1h. The orange-red S$_3$N$_2$Cl$_2$ gradually turned very deep green. The system was filled with dry nitrogen and the product stored in a dry-box.

(v) Thiotrichiazyl Chloride$^7$ (S$_4$N$_3$Cl)

Powdered chlorothiodithiazyl chloride was added to a mixture of excess disulphur-dichloride in dry carbon tetrachloride. The system was refluxed for 6h. until all the orange S$_3$N$_2$Cl$_2$ had reacted yielding the fine yellow S$_4$N$_3$Cl product. The product was isolated and the impurities present extracted from it with refluxing pentane. The purified S$_4$N$_3$Cl was dried in vacuo and stored in a dry-box.
Although the above procedure is reported to give quantitative yields of $S_4N_3Cl^7$, yields of only 60% were normally obtained.

1.2.7 Preparation of Group VI Polycations

(i) $S_8^{2+}(\text{AsF}_6^-)_2$

$S_8^{2+}(\text{AsF}_6^-)_2$ was prepared by the action of arsenic pentafluoride on sulphur. 8

\[
S_8 + 3\text{AsF}_5 \xrightarrow{\text{SO}_2} S_8^{2+}(\text{AsF}_6^-)_2 + \text{AsF}_3
\]

Pre-dried sulphur was placed in a vacuum tight pyrex vessel and sulphur dioxide condensed in. The correct volume of AsF$_5$ to satisfy the above equation was then condensed in and the reaction stirred for two days at room temperature. The deep blue product was then filtered off and dried in vacuo. The compound was stored in a dry-box.

(ii) $\text{Se}_8^{2+}(\text{AsF}_6^-)_2$

The same procedure was adopted as for the preparation of $S_8^{2+}(\text{AsF}_6^-)_2$. 9

(iii) $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$

The same procedure was adopted as for the preparation of $S_8^{2+}(\text{AsF}_6^-)_2$. 10

(iv) $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$. 11

$\text{Se}_4^{2+}(\text{AsF}_6^-)_2$ was produced by essentially the same procedure as $S_8^{2+}(\text{AsF}_6^-)_2$ but the system was heated to 80°C for 4 days and the solubles removed ($\text{Se}_8^{2+}(\text{AsF}_6^-)_2$). The $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$ is relatively insoluble in SO$_2$ and thus a slight excess of AsF$_5$ was used to ensure complete conversion of the elemental selenium.
Figure 1.1

Pyrex reaction vessel

Figure 1.2

Pyrex reaction vessel
High Pressure Monel Vessel

Figure 1.3.
F. E. P. Reaction Vessel and Assorted Valves
Figure 1.5.

Modified Infra-red Gas Cell

Figure 1.6.

Sealed system Soxhlet Extraction Apparatus
REFERENCES


CHAPTER TWO

THE PREPARATION AND REACTIONS OF THE
4-PHENYL-1,2,3,5-DITHIADIAZOLIUM CATION

2.1 Introduction

Carbon-Sulphur-Nitrogen Heterocycles containing
\((4n + 2)\) electrons (Hückel Aromatic Species)

There is a vast chemistry of heterocyclic five and
six membered rings containing carbon, sulphur and nitrogen.
There is no comprehensive review of all the permutations
and combinations of cyclic C/S/N species, although Barton
and Ollis in their excellent series "Comprehensive Organic
Chemistry" (Volume 4, Heterocyclic Chemistry)\(^1\) do discuss
some of these species. The Specialist Periodical Reports
on the organic compounds of Sulphur, Selenium and Tellurium
also provide useful lead references into this area of
chemistry. (2a-d, 3a,b, 4a-i, 5)

Heterocyclic C/S/N compounds can be categorised into
groups depending on the number of atoms in the heterocyclic
ring and by the charge on the ring. Figures 2.4-7 (pages
81 - 84) indicate the skeletal arrangements of the majority
of known C/S/N heterocycles containing a \((4n + 2)\) system.

2.1.1 Meso-ionic C/S/N Heterocycles

There is a class of compounds named "meso-ionic"
compounds, of which a large proportion of known examples con-
tain a five membered carbon-sulphur-nitrogen ring. Although
these compounds are not discussed at length in this thesis it
is worth noting their existence when discussing examples of
cationic C/N/S heterocycles.\(^1\) (figure 2.1)
"A compound may be appropriately called meso-ionic if it is a five-membered heterocycle which cannot be represented satisfactorily by any one covalent or polar structure and possesses a sextet of electrons in association with the five atoms comprising the ring".  

Figure 2.1 Some examples of C/S/N meso-ionic compounds

2.1.2 Neutral C/S/N Heterocycles containing a Five Membered Ring

All the C/N/S heterocycles containing 6π-electrons are known up to and including -CN₂S₂ in either neutral or cationic forms. Rings containing more than two atoms of either sulphur or nitrogen are generally not known except for 5 substituted 1,2,3,4 thiatriazole (compound 2.13, figure 2.4 page 81 ).

The thiazoles ("C₃NS" compounds 2.1, 2.3 figure 2.4 page 81 ) and benzothiazoles (compounds 2.2, 2.4 figure 2.4 page 81 ) have been known for many years and are of great
pharmaceutical interest as diuretics, antihistamines, mito-
statics\(^2\) and inflammatories.\(^2\) Recent industrial uses
have included the use as vulcanisation accelerators,\(^2\) anti-
oxidants,\(^2\) as photochromics\(^2\), as dyestuffs \(^2\) and
in polymeric applications.\(^2\)

2.1.3 Neutral C/S/N Heterocycles containing
a Six Membered Ring

There are fewer C/S/N six membered Hückel aromatic
ring systems than would, at first, be anticipated. All the
"C\(_4\)NS" rings are known, including examples with sulphur in the \(S^{IV}\)
and \(S^{VI}\) states due to bonding of an oxygen and a further group
to the sulphur (compounds 2.14-16, figure 2.5, page 82). Of
the three possible isomers of the dithiazine ring system only
the 1,4,2-isomer has been isolated (compound 2.17, figure 2.5,
page 82). The ring systems of the form "C\(_3\)SN\(_2\)" (thia-
diazines) are well documented\(^1\) and the chemistry of the S,S-
dioxides has been widely studied.\(^1\) Not all the isomers of
the thiadiazine rings are known and those that are tend to
be stabilised by coordination to a benzo or naphtho ring
(compounds 2.18-23, figure 2.5, page 82). The chemistry
of the heterocycles containing two sulphur-atoms and two
nitrogen atoms (dithiadiazines) has not been widely studied
and only the 1,3,2,4-isomer (compound 2.22, figure 2.5,
page 82) has been synthesised. Heterocycles of the form
"C\(_2\)SN\(_3\)" and "CS\(_2\)N\(_3\)" have been synthesised (compounds 2.23, 24,
figure 2.5, page 82) but as yet their uses and chemistry
have not been systematically investigated.

2.1.4 Neutral C/S/N Heterocycles containing
other than Five or Six Membered Rings

Although rings of other sizes than 5 or 6 do exist
they do not, in general, exist without one or more bonds in
the ring being fully saturated (i.e. an incomplete delocalised
system). The only exceptions to this are the 1,4,5-thiadiazepine, and 1,2-thiazepine ring systems (compounds 2.25, 26, figure 2.6, page 83).

2.1.5 Cationic Five Membered C/S/N Heterocycles with no substituents on Nitrogen or Sulphur

Although there are quite a few C/S/N cationic heterocycles with a five membered ring the majority are substituted at nitrogen (compounds 2.27-32, 35, 36, figure 2.7, pages 83, 84).

There are however four five membered C/S/N heterocyclic cations without the nitrogen being substituted (compounds 2.33, 34, 37, 38, figure 2.7, page 84).

(i) The 1,2,4-dithiazolium cation (comp. 2.33)

(ii) The 3,5-benzo-1,2,3-dithiazolium cation (Herz compound: 2.34)

(iii) The 4-substituted-1,2,3,5-dithiadiazolium cation (compound 2.37)

(iv) The 4-substituted-1,3,2,5-dithiadiazolium cation (comp. 2.38).

The 1,2,4-dithiazolium salts are, by far, the most investigated species of the four cations. Many salts have been synthesised with a large range of substituents at the 3 and 5 positions. The dithiazolium cations have found pharmaceutical and industrial uses as sterilizers, male contraceptives, and photographic development accelerators. Although the derivatives of the 1,2,4-dithiazolium cation are of significant industrial interest they are not discussed further in this thesis as there is no sulphur-nitrogen bond in the ring.
The only salts of the 1,2,3-dithiazolium cation synthesised are the 3,5-benzo derivatives, known as Herz compounds. The Herz compounds were first synthesised by Richard Herz in 1914 and a patent was published in 1922. The mechanism by which aniline hydrochloride or any aromatic amine reacts with disulphur dichloride to form the benzodithiazolium ring system has been an area of much interest for many years. Bezzubets et al (1939, 22 194823) showed that the rate of formation of the Herz compounds was much greater in polar solvents and hence suggested a series of initial reaction sequences. Gompper et al (1964)24 were however the first to postulate a plausible initial reaction sequence (figure 2.2).

Figure 2.2 Initial reaction sequence in the reaction of aniline with disulphur dichloride suggested by Gompper24

Gompper suggested that the $S_2Cl_2$ subsequently chlorinated position 6. This was however disputed by Hope and Wiles (1967)25 who, due to their observation of molecular chlorine in the reaction, postulated the mechanism presented in figure 2.3.
Figure 2.3 Subsequent mechanism (suggested by Hope and Wiles) to the initial reaction of S₂Cl₂ with amines (Figure 2.2)

Steps ii-iv outlined in Figure 2.3 indicate the probable route by which chlorine is produced for the subsequent chlorination of the carbon at position 6 and of the sulphur. (cf. the chlorination of sulphenyl chlorides; RSCl to RSCl₂)

The mechanism suggested by Hope and Wiles is generally accepted to be substantially correct.

The main interest in Herz compounds was shown by the dye industry. The compounds were hydrolysed by alkali providing a valuable synthetic route to \( \sigma \)-aminobenzenethiols which in
turn opened the way for the systematic, large scale production of a variety of dyes. During the past two decades the potential synthetic value of the cations in general hetero-cyclic chemistry has been realised. 27-31 Evdokimov et al. 32 have synthesised the 1,2,3-thiaseseleniazolium and 1,2,3-benzo-diselenazolium chloride analogues.

Although many different benzo-substituted Herz compounds have been produced relatively few salts with anions other than chloride have been synthesised. The first salt containing an anion other than chloride was 6-methoxy-8-bromo-1,2,3-benzothiadiazolium bromide 25 and subsequently salts containing the tetrafluoroborate, 33 perchlorate 34 and trichlorozincate 10 anions were prepared. The hydrolysis and substitution of these salts with primary 35 and secondary 31 amines have been areas of great interest over the past decade due to the formation of substituted 3-H-1,2,3-benzodithiazole-2-oxides, which are of considerable importance as herbicides.

2.1.5b The Dithiadiazolium Cations (R-CN₂S₂⁺)

Two isomers of the dithiadiazolium ring system have been synthesised, the 1,2,3,5-isomer 36-38 and the 1,3,2,5 39 isomer (equations 2.1-5).

\[ R - C \equiv N + (\text{NSCl})_3 \rightarrow R - C \begin{array}{c} \text{N} \\ \text{S} \end{array} \begin{array}{c} \text{O} \\ \text{Cl} \end{array} \text{(ref.37)} \quad (2.1) \]

\[(R = \text{CCl}_3, \text{Ph}, \text{tBu})\]

\[ \text{Cl}_2\text{O} = \text{CCl}_2 + (\text{NSCl})_3 \rightarrow \text{CCl}_3 - C \begin{array}{c} \text{N} \\ \text{S} \end{array} \begin{array}{c} \text{O} \\ \text{Cl} \end{array} \text{(ref.37)} \quad (2.2) \]

\[ 3\text{RCH} = N - N = \text{CHR} + 4(\text{NSCl})_3 \rightarrow 6 R - C \begin{array}{c} \text{N} \\ \text{S} \end{array} \begin{array}{c} \text{O} \\ \text{Cl} \end{array} + \]

\[ 3\text{N}_2 + 3\text{Cl}_2 \quad (\text{ref.38}) \quad (2.3) \]
The chemistry of these cations is still in its infancy. The preparation of the 1,3,2,4-isomer has been reported by Neidlein et al.\textsuperscript{39} but none of its chemistry has, as yet, been published. The only chemistry reported for the 1,2,3,5-dithiadiazolium cation is that of varying the substituent at position 4 (Ph, CCl\textsubscript{3}, tBu)\textsuperscript{37,38} and the anions (SbCl\textsubscript{6}\textsuperscript{−}, CF\textsubscript{3}SO\textsubscript{6}\textsuperscript{−}, N(SO\textsubscript{2}F\textsubscript{2}, BF\textsubscript{4}\textsuperscript{−} and PF\textsubscript{6}\textsuperscript{−}).\textsuperscript{38}

2.1.6 Cationic C/S/N Heterocycles containing (4n + 2) π-electrons, with ring sizes other than five

There are only two cations that fall into this category the 1,3-thiazinium\textsuperscript{1} and the 1,4-thiadiazinium cations.\textsuperscript{40}

(FIGURE 2.7, page 84). Both species have a six membered heterocyclic ring containing 6π-electrons. The 1,3-thiazinium cation is known to react readily with oxygen, sulphur and carbon nucleophiles cleaving the 5,6 bond to give thioacyl derivatives of vinylamines. Reduction of
the salts with sodium borohydride yields 2H-, 4H-, and 6H-thiazines. 1

Very little work has been reported on the 1,4-thiadiazinium cations, the only compounds produced being four 2,4,6-trisubstituted derivatives stabilised as either the iodide 40 or the perchlorate. 41

2.2 Experimental

2.2.1 Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

Ammonium chloride (105g, 1.96 mole), benzonitrile (250cm³, 2.45 mole) and sulphur dichloride (250cm³, 3.93 mole) were stirred at 140°C for 16h. Further aliquots of sulphur dichloride (SCl₂) (each of 100cm³, 1.57 mole) were added until no further evolution of hydrogen chloride was noted. The slurry was then cooled slowly to room temperature, filtered, washed with anhydrous ether (4 x 100cm³) and dried in vacuo. The crude product was then recrystallised from a number of solvents. The most successful results were obtained by recrystallisation from a 4:1 mixture (by volume) of dichloroethane:thionyl chloride and using sulphur dioxide.

Analysis for a double dichloroethane: thionyl chloride recrystallisation;

Found: C, 38.46; N, 12.57; H, 2.42; S, 29.23; Cl, 16.88%. C₇H₅ClN₂S₂ requires: C, 38.8; N, 12.9; H, 2.3; S, 29.6; Cl, 16.4%.

The crude material was extracted using sulphur dioxide in a sealed system (Figure 6, page 16). The product obtained was heated at 50°C in vacuo for 4h. to remove any
traces of trapped sulphur dioxide.

Analysis of the product recrystallised from sulphur dioxide;

Found: C, 38.58; N, 12.44; H, 2.64; S, 29.82; Cl, 16.18%.

The infra-red, Raman and mass spectra for the product recrystallised from sulphur dioxide are given below:

Infra-red spectrum (nujol mull): 1600m, 1582vw, 1495w, 1444s,
1396vs, 1345w, 1295w, 1260vw, 1212w, 1172w, 1150m, 1145w(sh),
1070w, 1031m, 1000w, 935m, 895s, 845vs, 795m, 785m, 740w,
708m, 698vs, 686w(sh), 670vw, 554s, 532w, 475w cm⁻¹.

Raman Spectrum (red line): 1600m, 1500w, 1392m, 1160m, 1004m,
927w, 845vs, 664vw, 512vs, 383m, 318w, 290w, 152m, 64s,
35s, cm⁻¹.

Mass Spectrum (m/e (abundance) assignment ): 181(100) PhCN⁺;
135(12) PhCNS⁺; 104(12) PhCNH; 103(98) PhCN⁺;
78(29) NS₂⁺; 77(13) Ph⁺; 76(29) CS₂⁺; 64(4) S₂⁺;
52(5) C₄H₄; 51(13) C₄H₃; 50(13) C₄H₂; 46(27) NS⁺;
39(6) C₃H₃; 38(7) HCl³⁷; 36(19) HCl³⁵;

(A diagrammatic representation of the above spectrum is shown in figure 2.8a, page 85. * Denotes the main peaks of interest in the spectrum and those used for comparison with spectra of other dithiadiazolium salts).

Crystals suitable for X-ray crystal studies of 4-phenyl-1,2,3,5-dithiadiazolium chloride were produced by slowly cooling a saturated refluxing solution of the salt in toluene, to room temperature. Needle shaped crystals of approximately 2mm, in length and 0.5mm diameter were formed which contained one mole­
cole of toluene of crystallisation for every six molecules of 4-phenyl-1,2,3,5-dithiadiazolium chloride.
2.2.2 Preparation of the 4-Phenyl-1,2,3,5-Dithiadiazolium Halides

(1) Preparation of 4-Phenyl-1,2,3,5-Dithiadiazolium Bromide

The exchange reactions between 4-phenyl-1,2,3,5-dithiadiazolium chloride (PhCN$_2$S$_2$Cl) and sodium bromide or potassium bromide using toluene, nitromethane, 1,4-dioxan, monoglyme, T.H.F., acetic anhydride, dichloromethane and dichloroethane as solvents, were unsuccessful yielding only starting materials. The reaction of PhCN$_2$S$_2$Cl with KBr in the solid state and with LiBr or AgBr in a variety of solvents (monoglyme, T.H.F., 1,2-dichloroethane, and sulphur dioxide) produced the desired dithiadiazolium bromide.

(a) Solid state reaction between PhCN$_2$S$_2$Cl and KBr

On grinding together KBr and PhCN$_2$S$_2$Cl it was noted that a deep red mixture was obtained which when pressed into an infra-red disc gave a spectrum of similar form to that recorded for a KCl/PhCN$_2$S$_2$Cl disc (orange in colour).

Infra-red spectrum of the (KBr/PhCN$_2$S$_2$Cl disc): 1600m, 1495w, 1455s, 1398vs, 1345w, 1295w, 1215w, 1180vw, 1165w, 1150m, 1070w, 1032m, 1005w, 924m, 892s, 842s, 795w, 782m, 760w, 708m(sh), 696vs, 680w(sh), 658vw, 610vw, 550m, 536w(sh), 330m cm$^{-1}$.

A preparative scale solid phase reaction was carried out by grinding together PhCN$_2$S$_2$Cl (4.36g, 20.14 mmoles) with anhydrous KBr (15.23g, 0.13 moles), under dry box conditions, and subliming the deep red product on to a liquid nitrogen cold finger, the system being heated to 220°C at 2.5 x 10$^{-2}$ torr. The infra-red spectrum recorded of the sublimed product was identical to that observed for the PhCN$_2$S$_2$Cl/KBr disc.
Analysis of the sublimed product.

Found: S, 22.69; N, 11.08; C, 31.21; Br, 29.16%

C₇Η₅Ν₂S₂Br requires: S, 24.52; N, 10.73; C, 32.18; Br, 30.65%.

(b) Reaction of PhCN₂S₂Cl with LiBr in various solvents

In a typical reaction anhydrous LiBr (0.20g, 2.3 mmole) was added to a stirred suspension of PhCN₂S₂Cl (0.5g, 2.3 mmole) in T.H.F. (30 cm³). A deep red solution was immediately formed. The reaction mixture was allowed to stir at room temperature for 16h. to ensure complete reaction. The reaction was then brought to reflux and the deep red solution filtered off. On cooling a bright red microcrystalline product was obtained which was washed with ether (2 x 10 cm³) and dried in vacuo.

The crude product was recrystallised from toluene and also from sulphur dioxide. The recrystallisation of the bromide from toluene yielded deep red needle shaped crystals which from their analyses indicated that toluene of crystallisation was present.

Analysis of the toluene recrystallised product:

Found: C, 41.93; N, 8.83; H, 3.36; S, 21.19; Br, 26.0%

C₇Η₅Ν₂S₂Br·PhCH₃ requires: C, 41.04; N, 9.12; H, 2.93; S, 20.88; Br, 26.06%.

The product from the sulphur dioxide recrystallisation was paler in colour and after heating to 50°C in vacuo for 2h., gave analyses consistent with the formulation C₇Η₅Ν₂S₂Br.

Analysis of the sulphur dioxide recrystallised product.
Found:  C, 32.49; N, 10.36; H, 2.21; S, 24.86; Br, 29.92%.

C\textsubscript{7}H\textsubscript{5}N\textsubscript{2}S\textsubscript{2}Br requires:  C, 32.18; N, 10.73; H, 1.92; S, 24.52; Br, 30.61%.

The infra-red spectra of the above products were identical to that observed for the PhCN\textsubscript{2}S\textsubscript{2}Cl/KBr disc.

(c) Reaction of KBr and PhCN\textsubscript{2}S\textsubscript{2}Cl using S\textsubscript{O}\textsubscript{2} as a solvent.

PhCN\textsubscript{2}S\textsubscript{2}Cl (0.5621g, 2.60 mmole) and KBr (0.3241g, 2.72 mmole) were placed in two separate bulbs of a pre-dried, vacuum tight, pyrex vessel (Figure 1.2, page 14) and sulphur dioxide (7.1344g) condensed into both bulbs. The KBr solution was then filtered on to the PhCN\textsubscript{2}S\textsubscript{2}Cl solution and an immediate reaction occurred forming a deep red solution. The sulphur dioxide was repeatedly recondensed on to the remaining KBr until all the reactant had been dissolved and then the KBr solution filtered into the bulb originally containing the PhCN\textsubscript{2}S\textsubscript{2}Cl. The reaction was agitated for 12h. and then the sulphur dioxide solubles filtered off. The solvent was slowly evaporated from the solution and bright red platelets of PhCN\textsubscript{2}S\textsubscript{2}Br were produced. The product was heated at 60°C in vacuo for 2h. to remove any occluded solvent.

Analysis of the product:

Found:  C, 31.98; N, 10.46; H 1.74; S, 24.93; Br, 30.12%.

C\textsubscript{7}H\textsubscript{5}N\textsubscript{2}S\textsubscript{2}Br requires:  C, 32.18; N, 10.73; H, 1.92; S, 24.52; Br, 30.61%.

The infra-red spectrum of the product was identical to that observed for the PhCN\textsubscript{2}S\textsubscript{2}Cl/KBr disc.
(ii) Preparation of 4-Phenyl-1,2,3,5-Dithiadiazolium Iodide

(a) Solid phase Reactions between PhCN$_2$S$_2$Cl and Iodides

An infra-red disc of PhCN$_2$S$_2$Cl was made using cesium iodide as the dispersant. A very deep purple disc resulted which gave an infra-red spectrum significantly different from that of either KCl/PhCN$_2$S$_2$Cl or KBr/PhCN$_2$S$_2$Cl discs.

Infra-red spectrum (CsI/PhCN$_2$S$_2$Cl disc): 1600w, 1498w, 1455s, 1358vs, 1212w, 1176m, 1130s, 1028m, 1005w, 930w, 904m, 860m, 848w(sh), 828m, 775vs, br, 692s, 600w, 536w, 525s, 460s cm$^{-1}$.

A preparative scale solid phase reaction was carried out by grinding together PhCN$_2$S$_2$Cl (1.26g, 5.82 mmole) with anhydrous NaI (1.5g, 10 mmole), under dry box conditions and subliming the purple-black product on to a liquid N$_2$ cold finger, the system being heated to 160$^\circ$C at 10$^{-2}$ torr. The infra-red spectrum of the sublimed product was identical to that observed for the PhCN$_2$S$_2$Cl/CsI disc.

Analysis of the sublimed product.

Found: S, 22.63; N, 8.79; C, 25.23; H, 1.18%.

C$_7$H$_5$N$_2$S$_2$I requires: S, 20.78; N, 9.09; C, 27.27; H, 1.62%.

(b) Reaction of PhCN$_2$S$_2$Cl with Iodides using Organic Solvents

The reaction of NaI with PhCN$_2$S$_2$Cl was studied in a variety of organic solvents.

(i) Toluene, dichloroethane, dichloromethane, ether and 1,4-dioxan.

(ii) Nitromethane, monoglyme, T.H.F. and acetonitrile.

The solvents listed in category (i) did not facilitate halide transport, whilst virtually immediate reaction occurred
in those solvents in category (ii).

In a typical reaction \( \text{PhCN}_2S_2Cl \) (1.06g, 4.90 mmole) and sodium iodide (0.75g, 5.00 mmoles) were stirred in T.H.F. (25 cm\(^3\)) for 60h. An immediate reaction occurred yielding a deep purple solution which did not change in appearance over the 60h. The reaction mixture was filtered at room temperature and the filtrate pumped to dryness. The deep purple residue was washed with ether and the product dried \textit{in vacuo}.

Analysis of the deep purple product.

Found: N, 9.29; S, 22.58; I, 30.67; C, 29.41; H, 2.33\%.

\( C_7H_5N_2S_2I \) requires N, 9.09; S, 20.78; I, 41.23; C, 27.27, H, 1.62\%.

The infra-red spectrum of the product was identical to that observed for the CsI/\( \text{PhCN}_2S_2Cl \) disc.

(c) Reaction of \( \text{PhCN}_2S_2Cl \) with KI using \( \text{SO}_2 \) as a solvent

\( \text{PhCN}_2S_2Cl \) (0.6057g, 2.798 mmole) and KI (0.4763g, 2.869 mmole) were placed in separate bulbs of a pre-dried vacuum tight pyrex vessel (figure 1.2 , page 14 ) and sulphur dioxide (7.1321g) condensed into both bulbs. The potassium iodide was completely dissolved and to this yellow-orange solution was added the solution of \( \text{PhCN}_2S_2Cl \). An immediate reaction occurred yielding a brown-green precipitate which was only sparingly soluble. The \( \text{PhCN}_2S_2Cl \) was completely washed on to the KI solution and then the \( \text{SO}_2 \) was removed and the crude product isolated. The crude product was then extracted from the potassium chloride by-product using \( \text{SO}_2 \) (figure 1.6 , page 16 ).

Analysis of the extracted product.
Found: C, 21.48; H, 1.25; N, 6.9; S, 16.9; I, 32.6%.

The recrystallised product was then sublimed in a sealed system (120°C, 10⁻³ torr) yielding a deep purple-black sublimate and a white residue. No iodine vapour was noted.

Analysis of the sublimed product.

Found: C, 27.19; H, 1.47; N, 9.30; S, 21.21%.

C₇H₅N₂S₂I requires: C, 27.27; H, 1.62; N, 9.09; S, 20.78%

The infra-red spectrum of the sublimed and the recrystallised product was identical to that recorded for the PhCN₂S₂Cl/CsI disc.

Mass spectrum (m/e, (abundance), assignment): 181(24)

PhCN₂S₂; 135(9) PhCNS; 104(9) PhCNH; 103(100) PhCN;
78(24) NS₂; 77(9) Ph; 76(26) CS₂; 51(8) C₄H₃; 50(11) C₄H₂;
46(2) NS.

(A diagrammatic representation of the above spectrum is given in Figure 2.8b(page 86)).

2.2.3 Formation of the Pseudo-Halides and Organic Acid salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation

(a) Metathesis reactions using Organic Solvents

It is believed that the PhCN₂S₂⁺ NCS⁻ salt is produced as an intermediate in the metathesis reaction between PhCN₂S₂⁺Cl⁻ and sodium thiocyanate. However a subsequent reaction occurs (see Section 2.2.5, page 40) and the thiocyanate salt was not isolated.

(b) Metathesis reactions using liquid Sulphur Dioxide as a Solvent

PhCN₂S₂Cl (0.26g, 1.20 mmole) and NH₄⁺NCS⁻ (0.097g, 1.28 mmole) were placed in two separate bulbs of a
pre-dried, vacuum tight pyrex vessel, and sulphur dioxide (6.13 g condensed in). The PhCN$_2$S$_2$Cl solution was then added to the NH$_4$NCS solution. An immediate reaction occurred forming an intense purple-red solution. The SO$_2$ was recon­
densed on to the PhCN$_2$S$_2$Cl until all the reactant had been filtered on to the NH$_4$NCS. The product was highly soluble in the solvent and this solution was filtered off leaving a white residue (0.07 g) behind. The solvent was slowly removed from the filtrate yielding a black, deep purple crystalline product.

Infra-red spectrum of the crystalline product (nujol mull):
2200 vs, 1592 m, 1585 w (sh), 1577 w (sh), 1495 w, 1449 vs, 1395 vs, 1335 w, 1312 w, 1289 w, 1235 w, 1208 m, 1178 m, 1158 w, 1148 m, 1090 vw, 1064 vw, 1023 m, 1000 w, 972 w, 923 m, 900 s, 843 s, 780 s, 763 w, 690 vs, 688 s (sh), 679 m, 662 w, 614 w, 552 s, 509 w cm$^{-1}$.

Analysis of the crystalline product.

Found: C, 40.64; N, 17.3; S, 41.2; H, 1.89%.

C$_8$H$_5$N$_3$S$_2$ requires: C, 40.17; N, 17.57; S, 40.17; H, 2.09%.

Mass Spectrum (m/e, (abundance), assignment). 181 (38) PhCN$_2$S$_2$ ; 135 (14) PhCNNS ; 104 (12) PhCNH ; 103 (100) PhCN ; 78 (45) NS$_2$ ; 77 (13) Ph ; 76 (39) CS$_2$ ; 50 (12) C$_4$H$_2$ ; 48 (17) SO.

(A diagrammatic representation of the above spectrum is given in Figure 2.8c, (page 87)).

(ii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Benzoate

Ammonium benzoate (0.89 g, 6.40 mmoles) and PhCN$_2$S$_2$Cl (0.64 g, 2.96 mmole) were placed in two separate bulbs of a pre-dried vacuum tight pyrex vessel (Figure 1.2, page 14) and SO$_2$ (12.33 g) condensed on to both reactants. The solvent was warmed to room temperature and the solution of ammonium benzoate
filtered on to the solution of PhCN$_2$S$_2$Cl. No reaction occurred. Suspecting that the solubility of PhCOO$^-$NH$_4^+$ was low on SO$_2$ the solution of PhCN$_2$S$_2$Cl was filtered on to the PhCOO$^-$NH$_4^+$. Immediate reaction occurred forming a deep purple slurry. The reaction was agitated for 2h. and then a second aliquot of PhCN$_2$S$_2$Cl was filtered in to the reaction bulb. The process was repeated until no further PhCN$_2$S$_2$Cl remained. The system was then agitated overnight (16h.) and the soluble product filtered off. The solvent was slowly evaporated off, with the resulting deposition of black-purple needle shaped crystals.

Infra-red spectrum of the crystalline product (nujol mull):

1690s,br, 1605 w(sh), 1598m, 1584m, 1575w(sh), 1495w,
1450vs, 1398s, 1372vs, 1124s, 1290s,br, 1182m, 1178m(sh),
1144m, 1135m, 1128m(sh), 1100w, 1070m, 1032w(sh), 1028m,
1015w(sh), 1000w, 933w, 922w, 895w, 842m, 800s, 790s,
788s(sh), 780s, 772w, 768m, 709s, 706s(sh), 700s(sh),
690m(sh), 685s, 682s(sh), 668m, 660m, 652m, 614w, 550m,
530w, 520w, 508m cm$^{-1}$.

Analysis of the crystals.

Found: C, 54.84; N, 8.88; S, 22.4; H, 3.54%.

C$_{14}$H$_{10}$S$_2$N$_2$O$_2$ requires C, 55.63; N, 9.27; S, 21.19; H, 3.31%.

Mass spectrum of the crystals run at 200°C and 70eV (m/e (abundance)) assignment:

181(10) PhCN$_2$S$_2$ , 135(6) PhCN ,
104(12) PhCNH , 103(100) PhCN , 78(20) NS$_2$ ; 77(64) Ph ;
76(28) CS$_2$ ; 64(22) S$_2$ , SO$_2$ ; 52(7) C$_4$H$_4$ ; 51(14) C$_4$H$_3$ ;
50(15) C$_4$H$_2$ ; 46(15) NS ; 44(73) CO$_2$ , CS .

(iii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Acetate

PhCN$_2$S$_2$Cl (0.44g, 2.03 mmole) and ammonium acetate (0.16g, 2.08 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1.1, page 14) and sulphur dioxide
condensed on to the reactants. A rapid reaction occurred on warming the system to room temperature yielding a deep purple-red solution. The reaction was agitated for 5h. at room temperature and then the solubles were filtered off. The insolubles were washed with recondensed sulphur dioxide to remove all traces of the solubles. The solvent was then slowly removed from the filtrate resulting in the deposition of a black-purple microcrystalline material.

Infra-red spectrum of the product (nujol mull): 1698s, 1595m, 1580w, 1495w, 1455vs, 1400vs, 1375vs, 1315m, 1290m, 1210w, 1165w, 1150s, 1064w, 1045w (sh), 1025m, 1000w, 920s, 892s, 840vs, 834m, 800w, 782s, 762w, 698vs, 680s, 660w, 650w, 548s, 520m, 508w cm⁻¹

The product was dissolved in T.H.F. but the product isolated after removing the T.H.F. was not the acetate but a species with an infra-red spectrum considerably different from that of the dithiadiazolium cation (section 2.2.5(v), page 42).

2.2.4 Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Lewis Acids

(i) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Tetrachloroborate (III)

PhCN₂S₂Cl (0.4373g, 2.020 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14). Sulphur dioxide (3.4819g) and BCl₃ (0.2775g, 2.566 mmole) were condensed on to the dithiadiazolium salt and the reaction warmed to room temperature. The reaction occurred readily forming a slightly deeper orange compound than the parent chloride. The volatiles at room temperature were completely removed and the product weighed (0.5524g). From the weight of product it was deduced that incomplete reaction had occurred (48% conversion). Therefore SO₂ (0.5118g) and BCl₃ (0.2513g,
2.142 mmole) were condensed on to the reaction mixture and the system stirred at room temperature for 4h. The volatiles present at room temperature were then removed and the product (0.6655g corresponds to 97% conversion) isolated.

Infra-red spectrum of the product (nujol mull): 1595m, 1498m, 1451s, 1392vs, 1345w, 1325vw, 1295w, 1195w, 1182m, 1165w(sh), 1160m, 1156w(sh), 1070vw, 1026m, 1000w, 935w, 922s(sh), 919s, 841s, 779s, 725m(sh), 770s(sh), 695vs, 675m(sh), 662s, 632m, 558s cm⁻¹.

Mass spectrum (m/e, (abundance) assignment): 181(28) PhCN₂S₂; 135(14) PhCNS; 103(100) PhCN; 83(18) BⁿCl³⁵Cl³⁷; 81(26) BⁿCl₂³⁵; 80(9) B¹⁰Cl₂³⁵; 78(84) NS; 77(55) Ph; 76(50) CS₂; 47(10) BⁿCl³⁷; 46(77) NS, BⁿCl³⁵; 45(7) B¹⁰Cl³⁵; 38(24) HCl³⁷; 36(70) HC₁³⁵; 32(15) S₂.

Analysis of the BC₁⁴⁻ salt.

Found: C, 24.23; N, 7.64; S, 19.40; Cl, 40.65; H, 1.40%.

C₇H₅N₂S₂BC₁₄ requires C, 25.16; N, 8.39; S, 19.17; Cl, 42.54; H, 1.50%.

(ii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Hexachloroantimonate(V).

(a) Using Thionyl Chloride as the Solvent

SbCl₅ (2.8g, 9.4 mmole) was added to a stirred solution of PhCN₂S₂Cl (1.8g, 8.3 mmole) in refluxing SOCl₂ (25 cm³). An immediate reaction occurred forming a bright red precipitate. After refluxing for 10 min. the reaction mixture was cooled to room temperature and the product filtered off. The salt was recrystallised from dry nitromethane (50 cm³) and dried in vacuo.

Infra-red spectrum of the product (KCl disc): 1600m, 1505m, 1459m, 1400s, 1268w, 1190m, 1168m, 1035w, 939w, 928s, 845s, 784m, 698s, 675s, 629m, 566s, 355s(sh) 348s cm⁻¹.
Major mass spectral peaks (m/e, (abundance), assignment ).

191(78) SbCl₂ ; 181(28) PhCN₂S₂ ; 156(10) SbCl ; 135(8) PhCNS ; 121(4) Sb ; 104(13) PhCNH ; 103(100) PhCN ; 78(52) NS₂ ; 77(34) Ph ; 76(51) CS₂ ; 46(28) NS .

Analysis of the product.

Found: C, 16.18; N, 5.38; S, 12.80; Cl, 40.61; Sb, 22.69; H, 1.10%.

C₇H₅N₂S₂SbCl₆ requires: C, 16.29; N, 5.43; S, 12.41; Cl, 41.30; Sb, 23.61; H, 0.97%.

(b) Using Sulphur Dioxide as a Solvent

PhCN₂S₂Cl (0.7557g, 3.491 mmole) was loaded into a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14). SbCl₅ (6.9875g, 23.35 mmole) and SO₂ (8.4519g) were condensed on to the salt and the reaction warmed to room temperature. An immediate reaction occurred forming a bright red precipitate that was virtually insoluble in the solvent. The excess antimony pentachloride was removed from the product by washing the salt with recondensed SO₂. The product was then isolated and dried in vacuo.

Infra-red spectrum of the product (nujol mull): 1600m, 1505m, 1395vs, 1345w, 1295w, 1194m, 1189m, 1172w(sh), 1164m, 1030w, 972vw, 935m, 924s, 840w, 780s, 692vs, 680s, 562s, 430vs, br, cm⁻¹.

Analysis of the product.

Found: C, 15.94; N, 5.05; S, 13.1; Cl, 42.1; H, 1.23%.

C₇H₅N₂S₂SbCl₆ requires: C, 16.29; N, 5.43; S, 12.41; Cl, 41.30; H, 0.97%.

The PhCN₂S₂⁺SbCl₆⁻ was found to be very soluble in arsenic trifluoride (AsF₃). However it was found that the hexachloroantimonate(V) salt crystallises from the solvent with AsF₃ of crystallisation.
Infra-red spectrum of PhCN$_2$S$_2^+$SbCl$_6^-$:xAsF$_3$ (nujol mull):

1595m, 1500m, 1395vs, 1295w, 1185m(sh), 1162m, 1030w,
932m(sh), 920s, 842m, 775s, 720m*, 699vs, 662w(sh)*, 645s(sh)*,
630vs*, 620s*, 585s, 560s, 370m, 340vs cm$^{-1}$.

(* Denotes peaks assignable to AsF$_3$).

(iii) Formation of 4-Phenyl-1,2,3,5-Dithiadiazolium Hexachlorostannate(IV).

SnCl$_4$ (0.4 cm$^3$, 3.4 mmole) was added to a stirred suspension of PhCN$_2$S$_2$Cl (1.32g, 6.1 mmole) in SOCl$_2$ (60 cm$^3$), at room temperature. An immediate reaction occurred yielding a bright yellow precipitate. The precipitate was filtered off, washed with pentane (3 x 20 cm$^3$) and dried in vacuo.

Infra-red spectrum of product (KCl disc): 1602w, 1595m, 1502m,
1469s, 1400vw, 1340vw, 1320vw, 1298vw, 1209m, 1184w(sh),
1175m, 1160m, 1072vw, 1026m, 1000w, 935m, 920s, 958vw(sh),
946s, 790s, 700vs, 670w, 617vw, 560s, 322vs, 315s(sh),
290m(sh) cm$^{-1}$.

Analysis of the product.

Found:  C, 23.51; N, 7.93; H, 1.32; S, 18.93; Cl, 30.14%.

C$_{14}$H$_{10}$N$_4$S$_4$SnCl$_6$ requires:  C, 24.22; N, 8.07; H, 1.44; S, 18.45,
Cl, 30.70%.
2.2.5 Reactions in which the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation is Reduced forming 4-Phenyl-1,2-Dithia-3,5-Diazole

(1) Reaction 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Sodium Thio­cyanate using Organic Solvents

Anhydrous NaNCS (1.42g, 17.5 mmole) was added to a stirred suspension of PhCN₂S₂Cl (3.8g, 17.6 mmole) in dry monoglyme (50 cm³). An immediate reaction occurred forming a deep purple solution, which after refluxing for 10 min. (stirring for 6h. at room temperature has the same effect), yielded a dense orange precipitate. The reaction was re­fluxed for 6h. and the reaction mixture filtered hot. The deep purple filtrate was cooled slowly to -20°C and the re­sulting deep purple-black needle shaped crystals isolated. The crystals were then recrystallised from dry 1,2-dichlo­roethane (15 cm³) and reprecipitated by slowly cooling the solution in a -78°C slush bath. The combined filtrates were pumped to dryness and the residue recrystallised from dry dichloroethane (20 cm³), crystals being obtained as above.

Analysis of the purple-black crystals:

Found: C, 46.60; N, 15.64; S, 34.92; H, 2.84%.

\[
[C_7H_5N_2S_2]^x \text{ requires; C, 46.41; N, 15.47; S, 35.36; H, 2.76% .}
\]

Infra-red spectrum of the crystals (nujol mull): 1600w, 1496w, 1450s, 1322w, 1240w, 1228w, 1186vw, 1181vw, 1178vw, 1161vw, 1159vw, 1145w, 1139m, 1077w, 1025w, 982w, 932vw, 923vw, 901vw, 858vw, 842w, 838m, 830w, 776s, 770m, 690s, 688m, 685m, 660w, 653s, 618vw, 512s cm⁻¹.

Major mass spectral peaks (m/e (abundance), assignment):

181(86) PhCN₂S₂⁻, 135(65) PhCNS⁻, 103(90) PhCN⁻, 78(100) NS₂⁻, 77(56) Ph⁻, 76(72) CS₂⁻, 46(20) NS⁻.
The mass and infra-red spectra listed above were used for identification of the 4-phenyl-1,2-dithia-3,5-diazole produced in all the reactions presented in this section.

(ii) The Thermal Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Thiocyanate.

PhCN$_2$S$_2$$^+$NCS$^-$ (1.23g, 5.15 mmole, see experiment 2.2.3(i,b), page 33) was placed in a pre-dried pyrex sublimation tube and sealed off, (vacuum: 1 x 10$^{-3}$ torr). The lower portion of the tube was then heated to 80°C and a black sublimate was noted to form above the oil bath level. After ca. 3h. it was noted that the residue was deep orange and no further sublimation was occurring. The system was cooled to room temperature and the sealed system separated in an atmosphere of dry nitrogen. The infra-red and mass spectra of the sublimate (0.91g) were recorded and found to be identical to those recorded in experiment 2.2.5(i), (page 40).

(iii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Azides

In a typical reaction lithium azide (1.1g, 22.5 mmole) was added to a slurry of PhCN$_2$S$_2$Cl (3.52g, 16.26 mmole) at room temperature. An immediate, highly exothermic reaction occurred with evolution of nitrogen and the formation of a deep purple solution with a pale coloured precipitate. The reaction was stirred for 6h. at room temperature. No nitrogen was evolved after ca. 10 min. The reaction mixture was filtered and cooled (using a dry-ice acetone slush bath) a white precipitate (lithium chloride) precipitating out of the solution. The solution was filtered at ca. -78°C and pumped to dryness. The residue was recrystallised from dry 1,2-dichloroethane (30 cm$^3$) and the crystals formed, on cooling this solution, were isolated. The crystals were identified by their infra-red
and mass spectra and found to be identical to the product obtained in experiment 2.2.5(i), (page 40).

Sodium azide does not react readily with phenyl dithia-diazolium chloride in organic solvents but does so in sulphur dioxide.

(iv) **Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Potassium Cyanide**

PhCN$_2$S$_2$Cl (0.9612g, 4.44 mmole) and KCN (0.3461g, 5.32 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14) and AsF$_3$ (8.1246g) condensed on to the reactants. On warming to room temperature a rapid reaction occurred yielding an intensely coloured solution and a brown precipitate. The product was recrystallised using arsenic trifluoride. However it was noted that either KCN or KCl was also soluble in the AsF$_3$ and thus the solvent was removed and $3O_2$ (6.3148g) was condensed into the vessel as the recrystallisation solvent. The product was recrystallised from sulphur dioxide yielding a purple-brown microcrystalline material which was identified as 4-phenyl-1,2-dithia-3,5-diazole by the analysis and infra-red and mass spectra (experiment 2.2.5(i), page 40).

Analysis of the microcrystalline product:

Found: C, 45.92; N, 14.83; H, 2.96%.

C$_7$H$_5$N$_2$S$_2$ requires: C, 46.41; N, 15.47; H, 2.76%.

(v) **Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Acetate**

PhCN$_2$S$_2$Cl$^+$ CH$_3$COO$^-$ (0.41g, 1.7 mmole, experiment 2.2.3(iii), page 35) was stirred for 12h. at room temperature in dry T.H.F. (4.32g). The resulting purple solution was filtered off from the residue and pumped to dryness. The infra-red and mass spectra of the species were recorded.
and found to be consistent with 4-phenyl-1,2-dithia-3,5-diazole (experiment 2.2.5(i), page 40).

(vi) Decomposition of 4-Phenyl-1,2,3,5-Dithiadiazolium Benzoate

PhCN$_2$S$_2$$^+$PhCOO$^-$ (0.59g, 1.95 mmole, experiment 2.2.3(ii)) was stirred in dry monoglyme (5 cm$^3$), at room temperature for 12h. The solvent was then removed and the residue identified by its infra-red spectrum as 4-phenyl-1,2,3,5-dithiadiazolium benzoate. Monoglyme (10 cm$^3$) was added to the residue and the solution was refluxed for 8h. The solvent was then removed by pumping at reduced pressure and the resulting residue was identified as being a mixture, in which 4-phenyl-1,2-dithia-3,5-diazole was present (experiment 2.2.5(i), page 40). Purification of the product was not attempted.

(vii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Phenyl Magnesium Bromide

A solution of PhMgBr in ether (23.10 mmoles of PhMgBr in 14.26 cm$^3$ of solution) was added to a stirred suspension of PhCN$_2$S$_2$Cl (5.06g, 23.37 mmole) in toluene (60 cm$^3$). A slow reaction occurred at room temperature which, over a period of 6h., produced a deep purple solution. The solution was filtered off from the pale coloured precipitate and pumped to dryness. The residue was sublimed at a pressure of 1 x 10$^{-2}$ torr and a temperature of 120°C, yielding a black sublimate. The sublimate was identified by its infra-red spectrum as 4-phenyl-1,2-dithia-3,5-diazole (experiment 2.2.5(i), page 40).

(viii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with n-Butyl Lithium

In a typical reaction n-butyl lithium (2.4 cm$^3$, 3.96 mmole) was syringed into a suspension of PhCN$_2$S$_2$Cl (0.85, 3.93 mmole) in toluene (60 cm$^3$), cooled to -196°C. The reaction was warmed slowly to room temperature via -95°C and
-78°C slush baths. No reaction was noted at temperatures below room temperature and even at room temperature the reaction was relatively slow. The reaction was stirred at room temperature for 16h. during which time a deep purple solution and a white precipitate were formed. The reaction mixture was then filtered and the filtrate pumped to dryness. The resulting residue was identified as 4-phenyl-1,2-dithia-3,5-diazole from its infra-red and mass spectra (experiment 2.2.5(i), page 40).

(ix) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Methyl Lithium

Methyl lithium (7.2 cm³, 12.56 mmole) was syringed into a pre-cooled (-196°C) suspension of PhCN₂S₂Cl (2.7g, 12.47 mmole) in monoglyme (30 cm³) contained in a pre-dried vacuum tight, pyrex vessel (figure 1.2, page 14). The reaction was warmed slowly to room temperature. Reaction occurred at ca. -50°C forming a deep purple solution and a pale precipitate. The reaction was agitated at room temperature for 4h.

The volatiles present at room temperature were then removed and the residue obtained was identified as 4-phenyl-1,2-dithia-3,5-diazole from its infra-red spectrum (experiment 2.2.5(i), page 40).

(x) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Tin(II) Chloride

Anhydrous tin (II) chloride (0.71g, 3.7 mmole) was added to a stirred suspension of PhCN₂S₂Cl (0.52g, 2.4 mmole) in monoglyme (20 cm³) at room temperature. An immediate reaction occurred forming a deep purple solution. The reaction was refluxed for 15 min. and the reaction mixture filtered hot. The filtrate was then pumped to dryness and the resulting residue extracted with refluxing pentane (50 cm³). The pentane
solution was pumped to dryness and the product thus obtained identified, by its infra-red spectrum (ex experiment 2.2.5(i), page 40) as 4-phenyl-1,2-dithia-3,5-diazole.

(x) Reduction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride by Metals

No reduction of the phenyl dithiadiazolium cation occurred on refluxing PhCN₂S₂Cl with sodium, sodium-mercury amalgam, or potassium using toluene as the solvent.

Reaction of PhCN₂S₂Cl with Transition Metals in Polar or Coordinating Aprotic Solvents

In a typical reaction iron powder (1.12g, 20.00 mmole) was added to a stirred solution of PhCN₂S₂Cl (0.48g, 2.22 mmole) in T.H.F. (10 cm³). An immediate reaction took place producing a deep purple-red solution. The reaction was stirred at room temperature for 2h. and then the solubles filtered off. The filtrate was pumped to dryness and the infra-red spectrum of the residue recorded. From the infra-red spectrum of the residue it was deduced that 4-phenyl-1,2-dithia-3,5-diazole had been produced. (Experiment 2.2.5(i), page 40).

A series of reactions with various metals using ethers as solvents were investigated and found to yield 4-phenyl-1,2-dithia-3,5-diazole (table 2.1).

TABLE 2.1 Reduction reactions of PhCN₂S₂Cl by Metals

<table>
<thead>
<tr>
<th>PhCN₂S₂Cl</th>
<th>Metal</th>
<th>Solvent</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>(weight, mmole)</td>
<td>(excess)</td>
<td>(cm³)</td>
<td></td>
</tr>
<tr>
<td>1.8g, 8.31 mmole</td>
<td>Zn/Cu</td>
<td>T.H.F.(30cm³)</td>
<td>R.T.</td>
</tr>
<tr>
<td>0.93g, 4.30 mmole</td>
<td>K</td>
<td>Monoglyme(30cm³)</td>
<td>Reflux</td>
</tr>
<tr>
<td>0.91g, 4.20 mmole</td>
<td>Hg</td>
<td>T.H.F. (40cm³)</td>
<td>R.T.</td>
</tr>
</tbody>
</table>
(xii) Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Hydrogen

PhCN₂S₂Cl (0.41g, 1.89 mmole) was partially dissolved in T.H.F. (10 cm³) and pre-dried hydrogen bubbled through the system at room temperature. The reaction was terminated after ca. 1h. as no apparent reaction had occurred. The infra-red spectrum of the residue indicated only the presence of 4-phenyl-1,2,3,5-dithiadiazolium chloride (experiment 2.2.1, page 26).

2.2.6 Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole

(1) Reactions with the Halogens and Halogenated Species

(a) Reaction with Sulphuryl Chloride and Thionyl Chloride

4-Phenyl-1,2-dithia-diazole (PhCN₂S₂)ₓ (0.33g, 1.82 mmole) was added to SO₂Cl₂ (4 cm³, 49.4 mmole). An immediate reaction occurred yielding a very bright yellow-orange precipitate. The precipitate was isolated, washed with pentane (3 x 10 cm³) and dried in vacuo.

Infra-red spectrum of the bright yellow product (nujol mull):

1602m, 1586w, 1455s, 1395s, 1300w, 1225w, 1180w, 1158m, 1075w, 1035m, 1008w, 930m, 900s, 850s, 800w, 790m, 715m(sh), 702vs, 670w, 555s cm⁻¹. (cf. PhCN₂S₂Cl, experiment 2.2.1, page 26).

Analysis of the product.

Found: C, 38.34; N, 12.86; H, 1.64; S, 29.18; Cl, 17.54%.

C₇H₅N₂S₂Cl requires: C, 38.80; N, 12.93; H, 2.31; S, 29.56; Cl, 16.40%.

An analogous reaction occurred on adding 4-phenyl-1,2-dithia-3,5-diazole to thionyl chloride, 4-phenyl-1,2,3,5-dithiadiazolium chloride being produced.
(b) **Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Trichlorotrithiatriazene.**

Trichlorotrithiatriazene ((NSCl)$_3$)(0.15g, 0.61 mmole) was added to a stirred solution of (PhCN$_2$S$_2$)$_x$ (0.28g, 1.55 mmole) in benzene (30 cm$^3$). An immediate reaction occurred yielding a flocculent orange precipitate in an orange solution. The precipitate was isolated and dried in vacuo.

Infra-red spectrum of the precipitate (nujol mull): 1600w, 1582w(sh), 1455vs, 1400vs, 1318w, 1295w, 1220w, 1175w, 1155m, 1150m, 1069w, 1029m, 1002w, 925m, 892s, 844s, 780s, 702s(sh), 698vs, 551s cm$^{-1}$ (cf. PhCN$_2$S$_2$Cl, experiment 2.2.1, page 26).

A thin layer chromatogram of the toluene solution using an $S_4N_4$ standard for comparison was run.

T.L.C. (benzene eluant): $R_f = 0.84$, $S_4N_4$ standard $R_f = 0.84$. The toluene solution was slowly evaporated to dryness and the infra-red spectrum of the residue recorded.

Infra-red spectrum of the residue (nujol mull): 928s, 730m, 700s, 555s, 355s cm$^{-1}$. (cf. $S_4N_4$).

(c) **Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Bromine**

Bromine (0.5 cm$^3$, 9.76 mmole) was added to a stirred solution of (PhCN$_2$S$_2$)$_x$ (0.8g, 4.42 mmole) in carbon tetrachloride (10 cm$^3$). An immediate reaction occurred forming a bright red insoluble compound. The product was filtered off, washed with carbon tetrachloride (2 x 10 cm$^3$) and pentane (2 x 10 cm$^3$) and dried in vacuo.

Infra-red spectrum of the product (nujol mull): 1595m, 1495w, 1455s, 1395s, 1150m, 1022w, 918m, 895s, 837s, 779m, 692vs, 658w, 610w, 545s cm$^{-1}$. (experiment 2.2.2(i)(a), page 28).
Analysis of the bright red product:

Found:  C, 32.64; N, 10.44; H, 2.06%.

C7H5N2S2Br requires:  C, 32.18; N, 10.73; H, 1.92%

Yield of PhCN2S2Br = 1.13g.  98% based on (PhCN2S2)X

(d) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Iodine

Iodine (0.48g, 1.89 mmole) was dissolved in toluene (15 cm³). To this solution was added (PhCN2S2) x (0.68, 3.76 mmole). An immediate reaction occurred yielding a green-brown precipitate. The reaction was stirred overnight without further observed change. The product was filtered off, washed with toluene (2 x 10 cm³), (to remove excess iodine) and by pentane (3 x 10 cm³) and dried in vacuo. The infra-red spectrum and analysis of the product was recorded.

Analysis of the product.

Found:  C, 27.60; N, 9.01; H, 1.21; S, 20.4%.

C7H5N2S2I requires:  C, 27.27; N, 9.09; H, 1.62; S, 20.78%.

Infra-red spectrum (nujol mull):  1598m, 1494w, 1450vs, 1375vs, 1255w, 1220w, 1172w, 1162m(sh), 1135s, 1070w, 1025m, 1000w, 938w, 922 , 904m, 868m, 852m, 840m, 826m, 792vs, 776s, 765s, 686s, 680m, 675w, 550w, 536w, 520m, 462m cm⁻¹

(cf. PhCN2S2I experiment 2.2.2(ii)(a), page 31 ).

(ii) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Lewis acids

(a) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Tin(IV) Chloride

SnCl₄ (0.22 cm³, 1.88 mmole) was added to a stirred solution of (PhCN2S2) x (0.34g, 1.88 mmole) in toluene (20 cm³). An immediate reaction occurred forming a yellow-orange precipitate. The precipitate was isolated and washed with pentane (2 x 10 cm³) and dried in vacuo.
Infra-red spectrum (nujol mull): 1600w, 1495w, 1398s, 1340m(sh), 1295w, 1265w, 1208w, 1182w(sh), 1172m, 1160m, 1071w, 1024m, 1000w, 932m, 918s, 844s, 789s, 752s, 738m(sh), 698vs, 660w, 558m, 320s cm\(^{-1}\). (cf. \((\text{PhCN}_2S_2)_2\) SnCl\(_6\), experiment 2.2.4(iii), page 39).

(b) **Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Antimony(V) Chloride**

A solution of SbCl\(_5\) (2.5 cm\(^3\), 19.52 mmole in 3.14g of SO\(_2\)) was filtered on to a slurry of \((\text{PhCN}_2S_2)_x\) (0.72g, 3.98 mmole in 4.36g of SO\(_2\)). An immediate reaction occurred forming a bright salmon pink precipitate which was virtually insoluble in the solvent. The excess SbCl\(_5\) was filtered off and the precipitate washed several times to remove all traces of SbCl\(_5\). The solvent was then removed and the product isolated.

Infra-red spectrum of the product: 1600w, 1495w, 1395vs, 1182w, 1160m(sh), 1155m, 1025w, 1000w, 929m, 911s, 841s, 785m, 770m(sh), 700vs, 696s(sh), 555m, 340s cm\(^{-1}\).

Analysis of the product:
Found: C, 15.84; N, 5.02; H, 1.62%.
\(c_7H_5N_2S_2SbCl_6\) requires: C, 16.29; N, 5.43; H, 0.97%.

(iii) **Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole with Group VI Polycations**

(a) **Reaction of \((\text{PhCN}_2S_2)_x\) with \(S_8^{2+}(\text{AsF}_6^-)_2\)**

\(S_8^{2+}(\text{AsF}_6^-)_2\) (0.72g, 1.136 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1.2 , page 14 ) and \((\text{PhCN}_2S_2)_x\) (0.41g, 2.27 mmole) in the second bulb. Sulphur dioxide (12.38g) was then condensed into the vessel (some into each bulb) and the deep blue \(S_8^{2+}(\text{AsF}_6^-)_2\) solution slowly filtered on to the \((\text{PhCN}_2S_2)_x\)
slurry. An immediate reaction occurred forming an orange-red solution and a pale yellow precipitate. After all the polycation had been added the reaction was agitated for 4h. The soluble product was then filtered off leaving the pale yellow residue behind (0.28g). The solvent was removed from the system and the infra-red spectrum of the solubles and Raman spectrum of the insolubles recorded.

Infra-red spectrum of the solubles (nujol mull): 1595m, 1560w, 1500m, 1445s, 1395vs, 1320w, 1296w, 1275w, 1195m, 1185m, 1170w(sh), 1168m(sh), 1162m, 1105vw, 1075vw, 1029m, 1004m, 990vw, 978vw, 965vw, 942vw, 928s, 858m, 854m(sh), 845s, 784s, 720-680vs,br, (AsF$_6^-$), 615vw, 609vw, 580vw, 560s, 464w, 395vs, 368m cm$^{-1}$. (c.f. PhCN$_2$S$_2$Cl, experiment 2.2.1, page 26).

Raman spectrum of the insolubles (red line) 472, 434, 243, 220m 152 cm$^{-1}$. (c.f. S$_8$ 475, 471, 437, 248, 243, 218, 191, 152, 86 cm$^{-1}$).

(Theoretical weight of sulphur if oxidation of PhCN$_2$S$_2$ to PhCN$_2$S$_2$$^+$AsF$_6^-$ and deposition of S$_8$ occurs = 0.29g).

(b) Reaction of (PhCN$_2$S$_2$)$_x$ with Se$_4^{2+}$(AsF$_6^-$)$_2$

In a similar reaction to that in experiment 2.2.6 iii(a), (page 49 ) Se$_4^{2+}$(AsF$_6^-$)$_2$ (1.41g, 2.03 mmole) was reacted with (PhCN$_2$S$_2$)$_x$ (0.74g, 4.09 mmole) in SO$_2$. (Due to the low solubility of Se$_4^{2+}$(AsF$_6^-$)$_2$ in SO$_2$ both reactants were placed in the same bulb). A green-brown solution was quickly formed, with deposition of a black precipitate. The solubles were extracted from the residue, the solvent removed from the system and the infra-red spectra of both solubles and insolubles (0.56g) recorded.

The infra-red spectrum of the solubles is identical to that recorded for the solubles in experiment 2.2.6, iii(a).
No infra-red spectrum was obtained for the insolubles, the only peaks present being those of the mulling agent.

The theoretical weight of selenium deposited if the reaction was

\[ (\text{PhCN}_2S_2)_2^+ \text{Se}_4(\text{AsF}_6)_2 \rightarrow 2\text{PhCN}_2S_2^+\text{AsF}_6^- + 4\text{Se} \]

would be 0.64g therefore 87% of the selenium is present as elemental selenium in the insolubles.

(iv) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Unsaturated Systems

(a) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Diphenyl Acetylene

Diphenyl acetylene (0.38g, 2.13 mmole) was added to a stirred suspension of \((\text{PhCN}_2S_2)_x\) (0.39g, 2.15 mmole) in toluene (30 cm\(^3\)) at room temperature. No immediate reaction occurred. The reaction was brought to reflux and refluxed for 16h. The presence of diphenyl acetylene in the reaction was monitored using T.L.C., with hexane as the elutant and a standard diphenyl acetylene solution as a reference. The chromatogram indicated that diphenyl acetylene was still remaining in high concentration after refluxing for 16h. The reaction was cooled to room temperature and the solvent removed by pumping at reduced pressure. The infra-red spectrum of the residue indicated that only 4-phenyl-1,2-dithia-3,5-diazole and diphenyl acetylene were present.

(b) Reaction of 4-Phenyl-1,2-Dithia-3,5-Diazole with Tetrasulphur Tetranitride \((\text{S}_4\text{N}_4)\)

\(\text{S}_4\text{N}_4\) (0.27g, 1.47 mmole) was added to a stirred solution of \((\text{PhCN}_2S_2)_x\) (1.06g, 5.86 mmole) in T.H.F. (30 cm\(^3\)) at room temperature. The reaction was stirred for 4h. at room temperature but no change was noted. (The \(\text{S}_4\text{N}_4\) concen-
tration was monitored using T.L.C.). The reaction was then refluxed for 16h. but no reaction appeared to occur. ($S_4N_4$ was still present in high concentration in the solution and no other species were detected on the T.L.C. plate). The reaction was pumped to dryness and the infra-red spectrum of the residue recorded. From the infra-red spectrum it was deduced that the only species present were $S_4N_4$ and $(PhCN_2S_2)_x$.

2.2.7 Reaction to produce Benzene-1,4-(di-1,2,3,5-Dithiadiazolium) Dichloride ($C_6H_4(CN_2S_2Cl)_2$)

(i) The Reaction of 1,4-Dicyanobenzene ($C_6H_4(CN)_2$), with Sulphur Dichloride ($SCl_2$) and Ammonium Chloride ($NH_4Cl$)

NH$_4$Cl (20g, 37.4 mmole), C$_6$H$_4$(CN)$_2$ (5.12g, 40.00 mmole), SCl$_2$ (50 cm$^3$, 78.69 mmole) and toluene (150 cm$^3$) were placed in a 500 cm$^3$ flask and the temperature slowly raised to reflux. The reaction evolved a gas which was identified as HCl. The evolution of HCl was used to monitor the reaction. After 24h. of refluxing no further gas was evolved. SCl$_2$ (30 cm$^3$) was added to the reaction and the system allowed to reflux until no further HCl was evolved. Aliquots of SCl$_2$ (20 cm$^3$) were added to the system until no further evolution of HCl was noted when SCl$_2$ was added to the reaction mixture (4 aliquots). The reaction was then cooled to room temperature. The orange precipitate formed on cooling was filtered off, washed with ether (4 x 25 cm$^3$) and recrystallised from benzene (50 cm$^3$). The product was then recrystallised from SO$_2$ (5.62g) (figure 1.2, page 14) and the bright orange product (1.14g) dried in vacuo.

Infra-red spectrum of the orange product (nujol mull): 2230w, 1598m, 1580w(sh), 1495w, 1455s, 1398vs, 1320s, 1310m(sh), 1295w(sh), 1210w, 1170w, 1150m, 1138m, 1028m, 1018m(sh), 921m, 895s, 845s, 785s, 700vs, 564w, 550m, 520w cm$^{-1}$. 


The product was heated to 200°C at a pressure of $1 \times 10^{-2}$ torr and the infra-red and analysis of the non-sublimed residue recorded.

Infra-red spectrum of the residue (KCl disc): 3090w, 3040w, 2235s, 1415m, 1395vs, 1380s, 1302vw, 1289m, 1156m, 1020w, 925m, 896m, 862s, 855s, 845m(sh), 745s, 694s, 564m(sh), 558s, 532w cm$^{-1}$.

Analysis of the product after subliming out the impurities.

Found: C, 38.37; H, 2.22; N, 17.0; S, 25.46; Cl, 14.4%.

C$_8$H$_4$N$_2$S$_2$Cl requires: C, 39.75; H, 1.66; N, 17.39; S, 26.50; Cl, 14.70%.

(ii) Reaction of C$_6$H$_4$(CN)$_2$ with (NSCl)$_3$.

C$_6$H$_4$(CN)$_2$ (1.28g, 10 mmole) was added to an apple green, refluxing solution of (NSCl)$_3$ (6.55g, 26.77 mmole) in benzene (30 cm$^3$). After refluxing for 24h, a bright yellow precipitate formed in a deep orange solution. The reaction mixture was filtered, the precipitate washed with pentane (4 x 20 cm$^3$) and dried in vacuo.

Infra-red spectrum of the precipitate (nujol mull): 1164s, 1000vs, 680s, 568s, 472vs, 466s(sh), 332s (cf. S$_4$N$_2$Cl$_4$).

The benzene solution was pumped to dryness and the resulting pale yellow residue dissolved in T.H.F. (10 cm$^3$). A T.L.C. plate (benzene elutant) was run of the T.H.F. solution and standard samples of S$_4$N$_4$ and C$_6$H$_4$(CN)$_2$. S$_4$N$_4$ and C$_6$H$_4$(CN)$_2$ were identified as being present. A third compound giving a red spot that faded with time was also observed which is believed to be S$_4$N$_2$. 
2.3 Discussion

Although the dithiadiazolium system was first synthesised by Banister et al in ca. 1970, little or no subsequent work had been reported at the commencement of the investigations described in this chapter (October 1976). In an attempt to find a salt (or salts) of the phenyl dithiadiazolium cation that was relatively moisture insensitive, and thus of potential industrial use, phenyl dithiadiazolium chloride was reacted with various ionic salts. A wide range of dithiadiazolium salts was produced and the previously unreported 4-phenyl-1,2-dithia-3,5-diazole. All the species produced were found to be moisture sensitive.

2.3.1 Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride (PhCN₂S₂Cl⁻)

Banister et al reported the synthesis of PhCN₂S₂Cl⁻ from NH₄Cl, PhCN and SCl₂ using PhNO₂ as a solvent. The salt was then recrystallised from PhNO₂ (50 cm³ gram⁻¹). Due to the very high toxicity of PhNO₂ (TLV-TWA: 1 ppm) a synthetic route and purification procedure were sought not involving the solvent. It was found that the synthetic route described by Banister et al still gave good yields if the nitrobenzene was omitted and 25% excess benzonitrile was added. The yields recorded were improved by the addition of aliquots of sulphur dichloride to the reaction mixture until no further hydrogen chloride gas was evolved.

Many methods of purifying the crude phenyl dithiadiazolium chloride were investigated. It was found that recrystallisation of the salt from thionyl chloride gave a product of reasonable purity but the analytical results were
invariably high in chlorine. The purification procedure was adapted by using a mixture (4:1 by volume) of 1,2-
dichloroethane (CH₂ClCH₂Cl) and thionyl chloride as the re-
crystallisation solvent and washing the purified material with refluxing hexane to remove any residual thionyl chloride. Double purification by the above method yielded a compound with good analytical results and this procedure was the one generally used throughout the work in this thesis. However, recently it was found that sulphur dioxide provides a facile single stage purification solvent as sulphur, ammonium chloride and ammonium sulphate are virtually insoluble in the solvent, whereas 4-phenyl-1,2,3,5-dithiadiazolium chloride is highly soluble.

Crystals of 4-phenyl-1,2,3,5-dithiadiazolium chloride were produced by slowly cooling a refluxing toluene solution of the salt to room temperature. The crystals are bright orange and needle shaped, containing toluene of crys-
tallisation. The X-ray crystal structure of the salt was determined using these crystals by Hazell (1979).

2.3.2 The Reactions of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

The reactions of 4-phenyl-1,2,3,5-dithiadiazolium chloride reported by Bell, Durrant and Roesky are presented in table 2.2.

From table 2.2 it can be seen that with the exception of the results published by Roesky little progress had been made in the field of dithiadiazolium chemistry since 1970. (The anion exchange reactions reported by Roesky were published after the majority of the work in this chapter had been completed).
TABLE 2.2  Reported Reactions of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Solvent</th>
<th>Product</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>-</td>
<td>PhCN₂S₂S₀₆H₃</td>
<td>49</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>-</td>
<td>PhCN₂S₂S₀₆H₃</td>
<td>49</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>SOCl₂</td>
<td>PhCN₂S₂⁺FeCl₄⁻</td>
<td>49</td>
</tr>
<tr>
<td>Iron (III) Chloride</td>
<td>SO₂</td>
<td>Hydrolysis Products</td>
<td>49</td>
</tr>
<tr>
<td>Sodium Iodide</td>
<td>CH₂Cl₂</td>
<td>Postulated to be PhCN₂S₂⁺I⁻</td>
<td>49</td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>C₆H₁₄</td>
<td>Hydrolysis Products</td>
<td>48</td>
</tr>
<tr>
<td>Cyclohexene oxide</td>
<td>-</td>
<td>PhCN₂S₂Cl</td>
<td>48</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>-</td>
<td>PhCN₂S₂Cl</td>
<td>48</td>
</tr>
<tr>
<td>Antimony (V) Chloride</td>
<td>CCl₄</td>
<td>Postulated to be PhCN₂S₂⁺SbCl₆⁻</td>
<td>48</td>
</tr>
<tr>
<td>Phenyl Lithium</td>
<td>C₂H₅OC₂H₅</td>
<td>PhCN₂S₂Cl</td>
<td>48</td>
</tr>
<tr>
<td>Diphenyl Mercury</td>
<td>C₆H₆</td>
<td>Postulated as Ph₂CN₂S₂</td>
<td>48</td>
</tr>
<tr>
<td>Antimony (V) Chloride</td>
<td>CH₂Cl₂</td>
<td>PhCN₂S₂⁺SbCl₆⁻</td>
<td>38</td>
</tr>
<tr>
<td>Trifluoromethyl sulphonico acid</td>
<td>CH₂Cl₂</td>
<td>PhCN₂S₂⁺CF₃SO₃⁻</td>
<td>38</td>
</tr>
<tr>
<td>Bis(fluorosulphonyl)imide</td>
<td>CH₂Cl₂</td>
<td>PhCN₂S₂⁺N(SO₂F)₂⁻</td>
<td>38</td>
</tr>
<tr>
<td>Triethyl oxonium tetrafluoroborate</td>
<td>CH₂Cl₂</td>
<td>PhCN₂S₂⁺BF₄⁻</td>
<td>38</td>
</tr>
<tr>
<td>Nitrosyl Hexafluorophosphate</td>
<td>CH₂Cl₂</td>
<td>PhCN₂S₂⁺PF₆⁻</td>
<td>38</td>
</tr>
</tbody>
</table>

From the work reported by Durrant and Bell in their theses, four new phenyl-dithiadiazolium salts and derivatives have been formulated. Of these four species, three of the formulations (PhCN₂S₂I⁴⁹, PhCN₂S₂SbCl₆⁴⁸ and Ph₂CN₂S₂⁴⁸) have been brought into question by subsequent work in this chapter, the other PhCN₂S₂⁺FeCl₄⁻⁴⁹ was not reinvestigated.
2.3.2(i) The Preparation and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Halides

The formation of the bromide and iodide salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation was first noted by the colour of the infra-red discs of PhCNS₂Cl using KBr and CsI dispersants (experiments 2.2.2(ia)(iia), pages 28,31). The infra-red spectra of the discs was recorded and although the spectrum of the PhCNS₂Cl/KBr was very similar to that of PhCNS₂Cl, that of the PhCNS₂Cl/CsI disc was significantly different (table 2.3).

**TABLE 2.3 Infra-red Spectrum of PhCNS₂Cl⁺Cl⁻ using a series of Dispersion Salts**

<table>
<thead>
<tr>
<th>KCl Dispersant</th>
<th>KBr Dispersant</th>
<th>CsI Dispersant</th>
<th>PhCNS₂Cl⁺Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1604m</td>
<td>1604m</td>
<td>1600m</td>
<td>1600w</td>
</tr>
<tr>
<td>1585w</td>
<td>1588w</td>
<td>1494m</td>
<td></td>
</tr>
<tr>
<td>1498w</td>
<td>1500w</td>
<td>1480m</td>
<td></td>
</tr>
<tr>
<td>1450s</td>
<td>1458s</td>
<td>1455s</td>
<td>1460vs</td>
</tr>
<tr>
<td>1395vs, br</td>
<td>1402vs, br</td>
<td>1380s</td>
<td>1378s</td>
</tr>
<tr>
<td>1305w</td>
<td>1295w</td>
<td>1255w</td>
<td></td>
</tr>
<tr>
<td>1222w</td>
<td>1220w</td>
<td>1220w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1190w</td>
<td>1210w (sh)</td>
<td></td>
</tr>
<tr>
<td>1182w</td>
<td>1180w</td>
<td>1173m</td>
<td>1181w</td>
</tr>
<tr>
<td>1158s</td>
<td>1164s</td>
<td>1135s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1080vw</td>
<td>1080w</td>
</tr>
<tr>
<td>1078w</td>
<td>1074w</td>
<td>1068w</td>
<td></td>
</tr>
<tr>
<td>1036m</td>
<td>1036m</td>
<td>1024s</td>
<td>1028m</td>
</tr>
<tr>
<td>1009w</td>
<td>1009w</td>
<td>1005w</td>
<td>972m</td>
</tr>
<tr>
<td>930m</td>
<td>920m</td>
<td>928w</td>
<td></td>
</tr>
<tr>
<td>900s</td>
<td>899s</td>
<td>905m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>868m</td>
<td>860m</td>
</tr>
<tr>
<td>850vs</td>
<td>850vs</td>
<td>852m</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>830w</td>
<td>832vs</td>
</tr>
<tr>
<td>802m</td>
<td>802m</td>
<td>826m</td>
<td></td>
</tr>
<tr>
<td>792m</td>
<td>790m</td>
<td>795vs</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>778s</td>
<td>782vs</td>
</tr>
<tr>
<td>705vs</td>
<td>702vs</td>
<td>690s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>682s</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>676s</td>
<td>676s</td>
</tr>
<tr>
<td>670w</td>
<td>670w</td>
<td>670m (sh)</td>
<td></td>
</tr>
<tr>
<td>610vw.</td>
<td></td>
<td>610vw</td>
<td></td>
</tr>
<tr>
<td>558s</td>
<td>556s</td>
<td>538w</td>
<td></td>
</tr>
<tr>
<td>520w</td>
<td>470w</td>
<td>472m (sh)</td>
<td></td>
</tr>
<tr>
<td>410w</td>
<td>410w</td>
<td>408w</td>
<td></td>
</tr>
<tr>
<td>318m</td>
<td>328m</td>
<td>325w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>286w</td>
<td>285w</td>
<td></td>
</tr>
</tbody>
</table>
(A photographic comparison of the chloride and iodide salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation is given in Figure 2.9).

From the infra-red data presented in table 2.3, it appears as though the deep red PhCN$_2$S$_2$Br and PhCN$_2$S$_2$Cl adopt the same configuration with possibly slightly more anion-cation interaction in the case of the bromide than the chloride. However the infra-red spectrum of the presumed iodide is significantly different and will be discussed later (page 76). It can be seen from table 2.3 that the infra-red spectrum reported by Durrant$^{49}$ for PhCN$_2$S$_2$I is significantly different from that of the PhCN$_2$S$_2$Cl/CsI disc. Hence doubt is thrown on the identity of the species postulated as PhCN$_2$S$_2$I by Durrant.

Initially the bromide and iodide salts were isolated in a reasonable pure state by subliming the product out of the ground mixture of either PhCN$_2$S$_2$Cl and KBr or PhCN$_2$S$_2$Cl and NaI (experiments 2.2.2(ia),(iia), page 28,31). However as yields achieved by this method were low, the synthesis of the salts by solution reactions were investigated.

(a) Synthesis of 4-Phenyl-1,2,3,5-Dithiadiazolium Bromide

The reactions of sodium and potassium bromides with phenyl-dithiadiazolium chloride using toluene, benzene, 1,4-dioxan, dichloromethane and nitromethane were unsuccessful almost certainly due to the relatively low solubility of the alkali metal bromides in the aforementioned solvents. The exchange reaction did however occur with Et$_4$N$^+Br^-$, NH$_4^+Br^-$ and LiBr using the solvents nitromethane, dichloroethane, monoglyme, tetrahydrofuran and sulphur dioxide. The reaction probably proceeds in the above examples due to the bromides having a reasonable solubility in the solvents listed.
Of all the reactions that yield 4-phenyl-1,2,3,5-dithiadiazolium bromide the best route is probably that in which phenyl dithiadiazolium chloride is reacted with lithium bromide using tetrahydrofuran as a solvent, the crude product thus produced being recrystallised from sulphur dioxide (experiment 2.2.2(1,b), page 29).

(b) Synthesis and Purification of 4-Phenyl-1,2,3,5-Dithiadiazolium Iodide

Reaction of phenyl dithiadiazolium chloride with sodium iodide was found to occur in numerous solvents (\(\text{CH}_3\text{NO}_2\), \(\text{CH}_2\text{ClCH}_2\text{Cl}\), \(\text{C}_6\text{H}_5\text{CH}_3\), T.H.F., \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3\), 1,4-dioxan and sulphur dioxide) producing a deep purple solution from which a green-brown precipitate was isolated. The infra-red spectrum of this precipitate was identical to that recorded for the PhCN\(_2\)S\(_2\)Cl/CSI disc (table 2.3, page 57). Great difficulty was however experienced in purifying the product to give consistent, good analytical results. Recrystallisation from a variety of solvents was investigated but invariably poor analytical results were obtained. Initially this was thought to be due to hydrolysis products but after the reaction using sulphur dioxide as the synthetic and recrystallisation solvent, it was deduced that the basic impurity was the alkali metal chloride by-product (experiment 2.2.2(ii,c), page 32). The metal chloride, although virtually insoluble in all the recrystallisation solvents used, therefore appears to pass through the sinters (grade 4) thus affecting the recorded analysis of the product. The reason for the metal chloride passing through the sinter must be due to the fact that the particle size of the metal chloride is smaller than the pore size of the sinter used. Hence it seems likely that the metal chloride produced in the reaction is so insoluble in the synthetic solvent, that precipitation of the salt
occurs in a very fine form. Consequently virtually no recrystallisation process except that using a very fine sinter (very small pore size) will purify the product. Purification of the salt was however achieved by the use of vacuum sublimation, consistent analytical results being recorded.

2.3.2(ii) The Reaction of 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride with Lewis Acids

As would be anticipated for an ionic chloride containing a large cation, reactions of 4-phenyl-1,2,3,5-dithiadiazolium chloride with the Lewis acids boron trichloride, tin tetrachloride and antimony pentachloride readily occur (section 2.2.4, page 36). All the products are brightly coloured, (SnCl$_6^{2-}$ yellow; BCl$_4^-$ orange and SbCl$_6^-$ bright red). Hence the SbCl$_6^-$ salt of the phenyl dithiadiazolium cation synthesised by Bell$^{48}$ which is reported to be white must be regarded with some suspicion, especially as Roesky$^{38}$ also reports that the PhCN$_2S_2^+$/SbCl$_6^-$ is red. All the salts give infra-red and mass spectra consistent with the species containing the PhCN$_2S_2^+$ cation (cf. PhCN$_2S_2^+$/FeCl$_4^-$$^{49}$).

2.3.2(iii) Formation of other salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation

(a) Salts containing Fluoro-anions

Both the tetrafluoroborate and hexafluorophosphate salts were prepared but not isolated in purified forms, such that consistent analytical data could be obtained. (These reactions are not reported in the experimental section).

The tetrafluoroborate salt was obtained from the reaction of silver tetrafluoroborate with phenyl dithiadiazolium
chloride using nitromethane as a solvent. The salt obtained was deep red and gave infra-red and mass spectra consistent with the formulation PhCN$_2$S$_2$$^+$/BF$_4^-$. The hexafluorophosphate salt was synthesised by the reaction of ammonium hexafluorophosphate with phenyl dithiadiazolium chloride using sulphur dioxide as a solvent. The infra-red spectrum of the soluble product indicated that the hexafluorophosphate salt of the phenyl dithiadiazolium cation had been produced ($\text{NH}_4$$^+$/PF$_6^-$ only very slightly soluble in SO$_2$).

No further investigations into the synthesis and purification of the above salts were made due to the isolation and characterisation of the compounds by Roesky.$^{38}$

(b) Formation of the Acetate and Benzoate Salts of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation (experiments 2.2.311, 311, pages 34, 35).

Attempts to produce the benzoate and acetate salts of the 4-phenyl-1,2,3,5-dithiadiazolium cation from the reaction of sodium benzoate and acetate with phenyl dithiadiazolium chloride using organic solvents, failed. However both salts were produced on reacting excess ammonium benzoate or acetate with PhCN$_2$S$_2$Cl using sulphur dioxide as a solvent. The resulting products were very deeply coloured (black/purple). The acetate was found to be unstable decomposing in tetrahydrofuran solution at room temperature yielding another carbon-sulphur-nitrogen heterocycle (see section 2.3.3, page 62).

The infra-red spectra of the isolated benzoate and acetate salts were consistent with them containing the phenyl dithiadiazolium cation and the acetate or benzoate anion. Although the colour is very deep, probably implying a relatively high degree of anion-cation interaction, little or no
shifting of the basic infra-red bands associated with the dithiadiazolium cation (reference PhCN₂S₂Cl, table 2.3, page 57) is observed. Hence the degree of interaction required to modify the observed colour of the salts must be much less than that required to effect the vibrational spectrum.

(c) The Formation of the Thiocyanate salt of the 4-Phenyl-1,2,3,5-Dithiadiazolium Cation (experiment 2.2.3(1,a,b), page 33,34).

The reaction of sodium thiocyanate with phenyl dithiadiazolium chloride using monoglyme, tetrahydrofuran, or dichloroethane as solvents produced a deep purple solution virtually immediately. However after refluxing for ca. 20 min. or stirring at room temperature for 6h. an orange precipitate was formed which was identified as (NCS)ₓ. Hence a reaction subsequent to the metathesis reaction occurs.

The intermediate 4-phenyl-1,2,3,5-dithiadiazolium thiocyanate was however isolated from the reaction of sodium thiocyanate with 4-phenyl-1,2,3,5-dithiadiazolium chloride using sulphur dioxide as a solvent. The salt is very deeply coloured (cf. acetate and benzoate salts) and gives an infra-red and mass spectrum (figure 2.8c) consistent with the formulation PhCN₂S₂⁺NCS⁻.

2.3.3 The Formation and Reactions of 4-Phenyl-1,2,-Dithia-3,5-Diazole (PhCN₂S₂)²

(1) 4-Phenyl-1,2,-dithia-3,5-diazole was first synthesised by the reaction of sodium thiocyanate with phenyl dithiadiazolium chloride using monoglyme as a solvent (experiment 2.2.5(1), page 40). The compound was isolated in a high state of purity as deep purple, needle shaped crystals. The crystals gave excellent analyses and mass
and infra-red spectra which enabled the species to be identified, with ease, in the products of other reactions. (The infra-red spectrum is shown in figure 2.9, page 88).

The crystals obtained from the NaNCS/PhCN₂S₂Cl reaction were sent for X-ray structural determination studies to Vegas (Instituto de Quimica Inorganica "Elhuyar" Madrid), the results of which are discussed in section 2.3.4, page 72.

It was found that 4-phenyl-1,2-dithia-3,5-diazole is formed in many reactions of the phenyl dithia-diazolium cation with organo-metallic species, metals, and reducing anions.

Equations 2.6-13

\[
\begin{align*}
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{LiN}_3 \xrightarrow{(\text{CH}_3\text{OCH}_2)_2} & (\text{PhCN}_2\text{S}_2)_2 + 2\text{LiCl} + 3\text{N}_2 \quad (2.6) \\
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{KCN} \xrightarrow{\text{SO}_2} & (\text{PhCN}_2\text{S}_2)_2 + 2\text{KCl} + (\text{CN})_2 \quad (2.7) \\
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{CH}_3\text{COONa} \xrightarrow{\text{SO}_2} & 2\text{PhCN}_2\text{S}_2^+\text{CH}_3\text{COO}^- + 2\text{NaCl} \\
& \xrightarrow{\text{THF}} (\text{PhCN}_2\text{S}_2)_2 + \text{C}_2\text{H}_6 + 2\text{CO}_2 \quad (2.8) \\
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{PhMgBr} \xrightarrow{(\text{C}_6\text{H}_4\text{OCH}_2)_2} & (\text{PhCN}_2\text{S}_2)_2 + \text{MgBr}_2 \\
& + \text{MgCl}_2 + \text{C}_{12}\text{H}_{10} \quad (2.9) \\
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{CH}_3\text{Li} \xrightarrow{\text{C}_6\text{H}_{14}/(\text{CH}_3\text{OCH}_2)_2} & (\text{PhCN}_2\text{S}_2)_2 \\
& + 2\text{LiCl} + \text{C}_2\text{H}_6 \quad (2.10) \\
2\text{PhCN}_2\text{S}_2\text{Cl} + 2\text{C}_4\text{H}_9\text{Li} \xrightarrow{\text{C}_6\text{H}_{14}/(\text{C}_6\text{H}_5\text{CH}_3)_2} & (\text{PhCN}_2\text{S}_2)_2 \\
& + 2\text{LiCl} + \text{C}_8\text{H}_{18} \quad (2.11)
\end{align*}
\]
2PhCN₂S₂Cl + SnCl₂ (CH₂OCH₂)₂ → (PhCN₂S₂)₂ + SnCl₄ (2.12)

xPhCN₂S₂Cl + M \text{T.H.F. or (CH₂OCH₂)} \rightarrow \frac{x}{2} (\text{PhCN₂S₂})₂ + MClₓ (2.13)

(M = Zn, Hg : table 2.1, page 45)

Therefore, as can be seen from the above equations, 4-phenyl-1,2,3,5-dithia-1,2-diazole is a thermodynamically stable species.

Particular note is made of the reactions of phenyl dithiadiazolium chloride with Grignard and organolithium species. Bell⁴⁸ reported the reactions of diphenyl mercury and phenyl lithium with 4-phenyl-1,2,3,5-dithiadiazolium chloride and from the diphenyl mercury reaction isolated PhHgCl and a compound postulated to be Ph₂CN₂S₂ (figure 2.10).

Figure 2.10 Postulated structure of Ph₂CN₂S₂.

The product obtained by Bell from both the reactions of PhCN₂S₂Cl with Ph₂Hg and PhLi was black and by analogy with the reactions of PhCN₂S₂Cl with PhMgBr, C₄H₉Li and CH₃Li (experiments 2.2.5(vii-ix), pages 43, 44) it is believed that Bell isolated partially hydrolysed 4-phenyl-1,2-dithia-3,5-diazole, with a biphenyl impurity.

The mechanism by which 4-phenyl-1,2-dithia-3,5-diazole is formed in the reactions of phenyl dithiadiazolium chloride with Grignard and organolithium species is believed to proceed via an intermediate in which the organo grouping is bonded to one or both of the sulphurs in the "CN₂S₂" ring.
The intermediate then dissociates yielding phenyl dithia-
diazole (figure 2.11).

Figure 2.11 Suggested mechanism by which \( \text{CH}_3\text{Li} \) reacts with \( \text{PhCN}_2\text{S}_2\text{Cl} \).

\[
\begin{align*}
\text{Ph-C} & \quad \text{N} \quad \text{S} \\
\text{Cl} + \text{CH}_3\text{Li} & \quad \rightarrow \quad (\text{PhCN}_2\text{S}_2)_{\text{2}} + \text{C}_2\text{H}_6
\end{align*}
\]

The colours of all the known phenyl dithia-
diazolium salts fall into two categories, those that are brightly coloured, (red, orange and yellow), and those that are purple-black (table 2.4). With the exception of phenyl dithiadiazolium iodide (which is discussed separately in section 2.3.4(iv), page 75) all purple-black salts decompose on heating to yield phenyl dithiadiazole, whereas the brightly coloured salts do not. It is suggested that the degree of anion-cation interaction is greatest in the purple-black salts and thus they are more prone to decomposition than the brightly coloured salts in which the degree of anion-cation interaction is much less. The anions of the black-purple salts are those anions which are generally regarded as being "soft", i.e. relatively highly polarisable. Thus with a large cyclic cation the degree of interaction is expected to be significant. There are various salts (e.g.
TABLE 2.4  Colours of the 4-Phenyl-1,2,3,5-Dithiadiazolium Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCN₂S₂Cl</td>
<td>Orange</td>
</tr>
<tr>
<td>PhCN₂S₂Br</td>
<td>Red</td>
</tr>
<tr>
<td>PhCN₂S₂I</td>
<td>Black-Purple</td>
</tr>
<tr>
<td>PhCN₂S₂BF₄</td>
<td>Red</td>
</tr>
<tr>
<td>PhCN₂S₂BCl₄</td>
<td>Orange</td>
</tr>
<tr>
<td>PhCN₂S₂SbCl₆</td>
<td>Red</td>
</tr>
<tr>
<td>PhCN₂S₂PF₆</td>
<td>Orange</td>
</tr>
<tr>
<td>(PhCN₂S₂)₂(SnCl₆)</td>
<td>Yellow</td>
</tr>
<tr>
<td>PhCN₂S₂FeCl₄&lt;sup&gt;45&lt;/sup&gt;</td>
<td>Orange</td>
</tr>
<tr>
<td>PhCN₂S₂CF₃SO₃&lt;sup&gt;38&lt;/sup&gt;</td>
<td>Yellow</td>
</tr>
<tr>
<td>PhCN₂S₂NCS&lt;sup&gt;*&lt;/sup&gt;</td>
<td>Black-Purple</td>
</tr>
<tr>
<td>PhCN₂S₂CH₂COO&lt;sup&gt;*&lt;/sup&gt;</td>
<td>Black-Purple</td>
</tr>
<tr>
<td>PhCN₂S₂PhCOO&lt;sup&gt;*&lt;/sup&gt;</td>
<td>Black-Purple</td>
</tr>
</tbody>
</table>

(*) Denotes the salts that decompose yielding phenyl dithiadiazo

zole).

SbCl₆<sup>-</sup> and Br<sup>-</sup>) in which a lesser degree of anion-cation-

interaction is noted. The SbCl₆<sup>-</sup> and Br<sup>-</sup> ions are spheri-
cally symmetrical and thus the degree of cation-anion inter-

action is not as great as in the cases of NCS<sup>-</sup>, CH₃COO<sup>-</sup> and

PhCOO<sup>-</sup>, consequently the SbCl₆<sup>-</sup> and Br<sup>-</sup> salts are red not

black-purple.

Both the acetate and thiocyanate salts decompose

in T.H.F. or monoglyme at room temperature. However the

benzoate does not decompose in the above solvents at room

temperature but requires refluxing for 8h. in monoglyme to

achieve the decomposition. It is thought likely that the
relative stability of the benzoate salt is derived from the fluidity of the \( \pi \)-electrons associated with the phenyl ring, which maintain a relatively strong carbon-carbon bond between the "\( \text{CO}_2 \)" and "\( \text{C}_6\text{H}_5 \)" fragments, even when there is significant anion-cation interaction draining electron density away from the anion.

In the reactions of the phenyl dithiadiazolium cation with thiocyanates, cyanides and azides it is believed that the mechanism proceeds via an intermediate in which the anion interacts strongly with the sulphur-sulphur bond in the dithiadiazolium ring. Complete one electron transfer from the anion to the cation then occurs with the formation of two radical species which dimerise with their own kind forming 4-phenyl-1,2-dithia-3,5-diazole and the by-product (e.g. (CN)_2 and (NCS)_2). Due to the highly exothermic nature of the reaction of the dithiadiazolium cation with azides it is not thought likely that an intermediate cage species of the form PhCN_2S_2 (Figure 2.12) will be isolated.

Figure 2.12 Postulated Mechanism by which PhCN_2S_2Cl reacts with LiN_3

2Ph-C\( ^\theta \) N\( ^\theta \) S \( ^\theta \) Cl+2LiN_3 \( \rightarrow \) 2 \( \begin{array}{c} \text{Ph-C} \\ N \_ S \_ N \_ S \\ \text{N} \\ \text{Cl+2LiCl+2N}_2 \\ \end{array} \) (PhCN_2S_2)_2 + N_2

2.3.3(i1) Purification of 4-Phenyl-1,2-dithia-3,5-diazole
Phenyl dithiadiazole is highly soluble in most organic solvents and is soluble to a limited extent in hexane and pentane. Two main procedures for the purification of the
compound have been found. The first is by the extraction of the material using refluxing pentane and the second is by sublimation in \textit{vacuo}.$^{50}$ The purified product obtained by the above methods, although in a high state of purity, is recommended to be recrystallised from a solvent such as refluxing monoglyme, dichloroethane or T.H.F., the solvent being cooled slowly to room temperature, so as to form reasonably large crystals. The reason for the above recommendation is that the phenyl dithiadiazole, obtained by extraction with pentane or by sublimation, has a very high surface area and as the salt is highly moisture sensitive the degree of hydrolysis on exposure to the atmosphere for only a few seconds is very significant. In the case of crystals the surface area is much less, per unit mass, and consequently so is the percentage hydrolysis if exposed to moisture.

2.3.3(iii) \textbf{Reactions of 4-Phenyl-1,2-Dithia-3,5-Diazole}

(a) \textbf{The Reactions of Phenyl-Dithiadiazole with the Halogens and Lewis acids}

4-Phenyl-1,2-dithia-3,5-diazole reacts readily with chlorine, bromine and iodine (Experiments 2.2.6(i)(a,c,d), pages 46 - 48) yielding compounds which are the same colour and give the same analyses, mass and infra-red spectra as the 4-phenyl-1,2,3,5-dithiadiazolium chloride, bromide and iodide salts (Table 2.3, page 57). Hence it appears as though phenyl dithiadiazole is oxidised back to the phenyl dithiadiazolium cation by chlorine, bromine and iodine.

A similar style of reaction was found in the reactions of excess tin(IV) chloride and antimony(V) chloride with phenyl-dithiadiazole (Experiments 2.2.6(ii),(a,b), pages 48,49). The dithiadiazole appears to abstract a halogen from the Lewis acid, forming phenyl dithiadiazolium chloride which
then reacts with the excess Lewis acid to produce either
\((\text{PhCN}_2\text{S}_2)_2\text{SnCl}_6\) or \(\text{PhCN}_2\text{S}_2\text{SbCl}_6\). It is thought likely that
the reduced species \(\text{SnCl}_2\) and \(\text{SbCl}_3\) are formed which are not
able to reduce the respective \(\text{SnCl}_6^{2-}\) and \(\text{SbCl}_6^{-}\) salts back
to the dithiadiazole.

2.3.3(iv) Reactions designed to substitute atoms,
or groups of atoms, into the basic
five membered "CN\(_2\)S\(_2\)" ring

(a) The Reactions of Phenyl Dithiadiazole with Group VI
Polycations

Phenyl dithiadiazole was reacted with \(S_8^{2+}(\text{AsF}_6^-)\)_2
and \(Se_4^{2+}(\text{AsF}_6^-)\)_2 (experiments 2.2.6(iii),(a,b), page 50)
in an attempt to synthesise \(\text{PhCN}_2\text{S}_4^{+}\text{AsF}_6^-\) and \(\text{PhCN}_2\text{S}_2\text{Se}_2^{+}\text{AsF}_6^-\),
respectively. The reactions occurred virtually immediately
on mixing the two components. From the infra-red spectrum
of the soluble product and the weight of insolubles it was
readily deduced that oxidation of the dithiadiazole to the
hexafluoroarsenate(V) salt of the dithiadiazolium cation occurs,
with deposition of elemental sulphur and selenium (equations
2.14,15).

\[
(\text{PhCN}_2\text{S}_2)_2 + S_8^{2+}(\text{AsF}_6^-)_2 \rightarrow 2\text{PhCN}_2\text{S}_2^{+}\text{AsF}_6^- + S_8
\]  
\[(\text{PhCN}_2\text{S}_2)_2 + Se_4^{2+}(\text{AsF}_6^-)_2 \rightarrow 2\text{PhCN}_2\text{S}_2^{+}\text{AsF}_6^- + 4\text{Se}\]

(b) Reactions of Phenyl Dithiadiazole with Unsaturated Species

No reaction was noted to occur in the reactions of phenyl
dithiadiazole with diphenyl acetylene or tetrasulphur tetra-
nitride in refluxing solutions. Fielder\(^{50}\) also investigated
the photolytic reaction of tetrasulphur tetranitride with
phenyl dithiadiazole but no reaction was found to occur.

A reaction did occur between phenyl dithiadiazole and
trichlorotrithiatriazene but by analogy with the reactions
of the dithiadiazole with the halogens and Lewis acids (SnCl₄, SbCl₅), the main product isolated was that of phenyl dithiadiazolium chloride with tetrasulphur tetranitride as the by-product (cf. Chapter Three, page 101).

It is therefore concluded that the basic five membered CN₂S₂ ring, in the conformation found in 1,2,3,5-dithiadiazoles and 1,2,3,5-dithiadiazolium species, is highly stable with respect to ring expansion. It is, therefore, thought somewhat unlikely, that cations containing larger ring sizes are formed in the reaction of ammonium chloride with sulphur dichloride and benzonitrile, (experiment 2.2.1, page 26; synthetic route to PhCN₂S₂Cl).

2.3.4 The X-ray Crystal Structures of 4-Trichloromethyl and 4-Phenyl-1,2,3,5-Dithiadiazolium Chlorides compared with that of 4-Phenyl-1,2-Dithia-3,5-Diazole

(1) 4-Trichloromethyl-1,2,3,5-Dithiadiazolium Chloride

The crystal structure of 4-trichloromethyl-1,2,3,5-dithiadiazolium chloride has been determined by Andreasen et al. 51 (1977) (figure 2.15, page 93). The cation is a five membered planar ring with the trichloromethyl group co-planar with it. From the relatively short bond lengths within the ring, it is concluded that there is extensive delocalisation of the π-system. The cation is probably best regarded as an aromatic 6π-system.52 A notable feature of the structure is the strong interaction between the chloride ion and the cation. The anion is almost symmetrically situated across the disulphide linkage, the contact distance being some 75pm. shorter than that using Pauling’s formula, assuming a +1/2 charge on each sulphur and a -1 charge on the chlorine.53
(ii) 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

The X-ray crystal structure of 4-phenyl-1,2,3,5-dithiadiazolium chloride has been determined by Hazel47 (figure 2.16 and tables 2.7-2.9, pages 94,89-90).

It would be anticipated that the "CN$_2$S$_2" ring in both CCl$_3$CN$_2$S$_2$Cl and PhCN$_2$S$_2$Cl has the same basic configuration, possibly with slightly modified bond lengths due to the different inductive effects of the CCl$_3$ and Ph groups. From the crystal structures of CCl$_3$CN$_2$S$_2$Cl and PhCN$_2$S$_2$Cl it is noted that the rings are virtually identical, the main differences being that the angle at carbon closes slightly in PhCN$_2$S$_2$Cl relative to CCl$_3$CN$_2$S$_2$Cl (N-CCl-N : CCl$_3$CN$_2$S$_2$Cl = 122.2°; PhCN$_2$S$_2$Cl = 119.0°) whereas the angle at nitrogen opens out marginally (C-N-S : CCl$_3$CN$_2$S$_2$Cl : 113.5°; PhCN$_2$S$_2$Cl : 1145°).

There are three marginally different PhCN$_2$S$_2$ units in the crystal structure, the main difference being the position of the chlorine relative to the S-S linkage. In all cases the chlorine is virtually symmetrically placed across the disulphide linkage (on average, 291.8pm from one sulphur and 289.4pm from the other). The degree of interaction between anion and cation, as quantified by the S⋅⋅⋅⋅⋅⋅Cl contact distances, is slightly less in PhCN$_2$S$_2$Cl than in CCl$_3$CN$_2$S$_2$Cl (average S⋅⋅⋅⋅⋅⋅Cl distance PhCN$_2$S$_2$Cl = 290.6pm; CCl$_3$CN$_2$S$_2$Cl = 285.6pm). Hence the most significant effects on the "CN$_2$S$_2" ring of changing the substituent at position 4 from CCl$_3$ to Ph is the closure of the N-CCl-N angle and the slight drop in anion cation interaction. The decrease in the N-CCl-N angle is probably due to the minimisation of the interaction of the hydrogens at positions 2 and 6 with the nitrogens in the heterocyclic ring.
The bond lengths and angles in benzene have been accurately determined from rotational Raman and neutron diffraction spectra and also by crystallographic methods. It can be seen that the C-C bond lengths in the phenyl group of PhCN₂S₂Cl are some 1.8pm shorter than those in benzene (C₆H₆: 139.7pm; PhCN₂S₂Cl: 137.9pm). Hence it would appear as though there is some delocalisation of the positive charge into the phenyl ring.

(iii) 4-Phenyl-1,2-Dithia-3,5-Diazole

The X-ray crystal structure of 4-phenyl-1,2-dithia-3,5-diazole was determined by Vegas (figures 2.17-19, tables 2.10-13, pages 95, 93, 90, 92).

Using the π-electron counting rules set out by Banister, the species PhCN₂S₂ would be postulated to be an odd electron 7π-aromatic and would, therefore, be expected to dimerise (cf. S₃N₂⁺ figure 3.2 page 107). The structure of (PhCN₂S₂)₂ was therefore postulated to be basically the same as in S₆N₄²⁺, with two 6π-rings being held together by a two electron four centre bridge in an opposed geometry (related through a centre of symmetry). However from the crystal structure it is seen that the units are in fact eclipsed. The difference in conformation between the S₆N₄²⁺ dimer unit and that of (PhCN₂S₂)₂ is almost certainly a function of the inherent positive charge on the S₃N₂⁺ rings which therefore arrange themselves, so as to minimise the electrostatic repulsions. However in the case of the (PhCN₂S₂)₂ dimer the eclipsed arrangement is preferred due to the increased interaction of the singly occupied H.O.M.Os of the monomeric units.
The unit cell of phenyl dithiadiazole contains 16 "PhCN$_2$S$_2"$ units, all of which are grouped into pairs, the asymmetric unit being four "PhCN$_2$S$_2"$ units or two pairs. Each dimer has an average $S \cdots \cdots S$ inter-ring contact distance of 310.9 pm as compared with 302.7 pm in S$_{6}$N$_{4}$$^{2+}$ (sum of the van der Waals' radii = 360 pm). Hence the strength of the four centre interaction in the (PhCN$_2$S$_2$)$_2$ and (S$_6$N$_4$$^{2+}$) dimers is similar but slightly less in the case of (PhCN$_2$S$_2$)$_2$.

All the phenyl groups, as well as the S$_{31}$-N$_{31}$-C$_{31}$-N$_{32}$-S$_{32}$ and S$_{41}$-N$_{41}$-C$_{41}$-N$_{42}$-S$_{42}$ rings are completely coplanar. The atom groups C$_1$-C$_2$-C$_3$-C$_7$ for all four PhCN$_2$S$_2$ units in the asymmetric unit are also coplanar. However the rings S$_{11}$-N$_{11}$-C$_{11}$-N$_{12}$-S$_{12}$ and S$_{21}$-N$_{21}$-C$_{21}$-N$_{22}$-S$_{22}$ are not coplanar due to the significant deviations of N$_{12}$ and N$_{21}$ (81 pm and 54 pm, respectively), from the plane described by the other four atoms in the ring.

The two PhCN$_2$S$_2$ units which form the dimer unit are almost parallel but are slightly twisted with respect to each other. The dihedral angles formed by the least squares planes through the two molecules are 6.56° and 7.04° for the dimers 1-4 and 2-3 respectively. The twist of one PhCN$_2$S$_2$ unit relative to the other (figure 2.19, page 93) can be quantified by the values of the torsion angles at the intermolecular S-S bonds (table 2.11, page 91).

The bond lengths and angles within the phenyl group are similar to those observed in benzene. A comparison of the C-N, S-N and S-S bond distances in the PhCN$_2$S$_2$ unit with various related systems is given in table 2.5.
TABLE 2.5 Comparison of C-N, S-N and S-S distances of phenyl-dithiadiazole with related species

<table>
<thead>
<tr>
<th></th>
<th>(PhCN₂S₂)₂</th>
<th>PhCN₂S₂Cl</th>
<th>CCl₃CN₂S₂Cl</th>
<th>C₅H₅N⁵⁹</th>
<th>NH₂SO₂H⁶⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N (pm)</td>
<td>133.4 (av)</td>
<td>134.0 (av)</td>
<td>131.8 (av)</td>
<td>134.0</td>
<td>-</td>
</tr>
<tr>
<td>S-N (pm)</td>
<td>162.5 (av)</td>
<td>159.0 (av)</td>
<td>158.4 (av)</td>
<td>-</td>
<td>177.1</td>
</tr>
<tr>
<td>S-S (pm)</td>
<td>208.9 (av)</td>
<td>199.1 (av)</td>
<td>200.9 (av)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(αv = average)

It can be seen from table 2.5 that all the C-N bond lengths compared are similar, as are the S-N bonds, except for that in NH₂SO₂H which is a formal single bond and is noted for comparison, to show the evident multiple bond character of the S-N bonds within the ring. The main area of difference noted in table 2.5 is the S-S bond distances which increase by some 8 pm in (PhCN₂S₂)₂ relative to PhCN₂S₂Cl and CCl₃CN₂S₂Cl. It would therefore appear as though the molecular orbital into which the extra electron is placed, on reducing a dithiadiazolium salt, is of such a symmetry as to be antibonding across the S-S linkage. Hence on reducing the dithiadiazolium salt to the dithiadiazole an increase in S-S bond distance is observed.

Due to the "CN₂S₂" ring being heteronuclear the π-electron density will not be evenly distributed around the ring (cf. pyridine⁶¹ (figure 2.13)).

Figure 2.13 π-electron densities in pyridine⁶¹

![Pyridine π-electron densities](image)
The greatest $\pi$-electron densities are, therefore, found at the hetero-atoms of greatest electronegativity. Hence in the case of $(\text{PhCN}_2\text{S}_2)_2$ the $\pi$-electron density will be greatest at the 3,5 nitrogens and least at the 1,2 sulphurs. It may therefore be suggested that the sulphurs of one monomer unit interact the $\pi$-system of the other thus leading to the observed sulphur-sulphur interring interactions. The relatively high $\pi$-electron density at nitrogen and the relatively low density at sulphur could also be the reason for the long range inter-dimer interactions, e.g. $(\text{N}_{12} \cdots \cdots \cdots \text{S}_{32}$ and $\text{S}_{12} \cdots \cdots \cdots \text{S}_{21})$. Both the $\text{N}_{12} \cdots \cdots \cdots \text{S}_{32}$ and $\text{S}_{12} \cdots \cdots \cdots \text{S}_{21}$ contact distances (315pm and 340.2pm respectively) are only slightly less than the sum of the van der Waals' radii ($\text{N} \cdots \cdots \cdots \text{S}$ assuming $sp^2$ hybridisation of the nitrogen = 315pm, $\text{S} \cdots \cdots \cdots \text{S}$ = 360pm). It is likely that the deviations of $\text{N}_{12}$ and $\text{N}_{21}$ from the plane of the rings towards $\text{S}_{32}$ and $\text{S}_{42}$ respectively, as well as the twist in the rings forming the dimers (Figure 2.19, page 93) are related to these long range interactions.

(iv) The Postulated Structures of 4-Phenyl-1,2,3,5-Dithiadiazolium Salts deduced from their Infra-red, Mass and E.S.C.A. Spectra

From the pattern and position of bands in the infra-red and mass spectra it was deduced that the following salts contain a dithiadiazolium cation with the same configuration as observed in PhCN$_2$S$_2$Cl.

(a) Bromide; (b) Thiocyanate; (c) Hexachloroantimonate(\text{V}); (d) Hexachlorostannate(\text{IV}); (e) Tetrachloroborate(\text{III}); (g) Tetrafluoroborate(\text{VI}); (h) Benzoate; (i) Acetate.

There is insufficient anion-cation interaction in the above salts to perturb the observed vibrational spectrum of the cation.
The iodide salt does however have a significantly different infra-red spectrum to those observed for the aforementioned salts. The iodide is black but does not decompose on heating to yield phenyl dithiadiazole. It is soluble in non-polar and non-coordinating solvents and sublimes readily at 120°C. The "salt" therefore, has the apparent physical properties of a non-ionic species. In order to determine whether the iodine was covalently bound, the E.S.C.A. spectrum was recorded: (A. Harrison and P.J. Stephenson, University of Durham). The binding energy of the $I_{3d}$ orbital in $\text{PhCN}_2S_2I$ was compared with the binding energies of the $I_{3d}$ orbitals in iodobenzene and with the $I^-$ anion of $\text{Ph}_2I^+I^-$; (table 2.6)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$I_{3d}$ binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PhCN}_2S_2I$</td>
<td>620.7</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_4I^-$</td>
<td>622.1</td>
</tr>
<tr>
<td>$(\text{C}_6\text{H}_5)_2I^+I^-$</td>
<td>619.7</td>
</tr>
</tbody>
</table>

Hence from table 2.6 it would appear as though the iodine in $\text{PhCN}_2S_2I$ is essentially anionic but with significant interaction with the cation, thus raising the observed binding energy relative to that of a non-interacting iodide.

Comparison of the infra-red spectra of $\text{PhCN}_2S_2Cl$, $\text{PhCN}_2S_2I$ and $(\text{PhCN}_2S_2)_2$ indicates that there are similarities between that of $(\text{PhCN}_2S_2)_2$ and $\text{PhCN}_2S_2I$ (Figure 2.9, page 88). It is thought likely that the basic difference in the infra-red spectra of $(\text{PhCN}_2S_2)_2$ and $\text{PhCN}_2S_2^+X^-$ is due to the neutralisation of the positive charge on the
ring and not the interactions caused by the \([\text{PhCN}_2S_2^2\cdot] \)
dimerising. Thus \(\text{PhCN}_2S_2I\) could be regarded as the mid
point between \(\text{PhCN}_2S_2^+\) and \([\text{PhCN}_2S_2^2\cdot]\), the degree of anion-
cation interaction being high. It is suggested that the
"soft", highly polarizable iodide anion (ionic radius \(\text{ca.} 212\text{pm}\))
is of the correct size to interact strongly with the relativ­ely electropositive disulphide linkage in the "CN\(_2\)S\(_2^+\)
ring (\(\text{PhCN}_2S_2^+\text{Cl}^-; S-S: 199.1\) pm). The strong cation-anion
interaction will almost certainly decrease the effective
positive charge on the \(\text{CN}_2\)S\(_2\) ring and hence cause an increase
in the \(S-S\) bond distance (\((\text{PhCN}_2S_2)^2\) \(S-S\) (average) = 208.9 pm).

It is therefore concluded that although
the infra-red spectrum of \(\text{PhCN}_2S_2I\) is distinctly different
from that of either \(\text{PhCN}_2S_2\text{Cl}\) or \((\text{PhCN}_2S_2)^2\) and may there­fore be regarded, at first sight, to be consistent with that
of a completely different ring system, the compound does
exist as \(\text{PhCN}_2S_2^+I^-\) but with a high degree of cation-anion
interaction thus significantly changing the basic \(\text{PhCN}_2S_2^+\)
spectrum.

2.3.5 Attempts to produce 1,4-di-1,2,3,5-
Dithiadiazolium Benzene Dichloride

\[
\text{Cl}^- \quad \text{N} \quad \text{C} \quad \text{N} \quad \text{Cl}^-
\]

The mechanism by which 4-phenyl-1,2,3,5-dithia-
diazolium chloride is postulated\(^{49}\) to be formed in the re-
action of \((\text{NSCl})_3\) with PhCN is via the nucleophilic attack of NSCl
on the carbon of the nitrile group (Figure 2.14).
It was, therefore, thought likely that in the reaction of 1,4-dicyanobenzene with NSCl, one cyano group would activate the other, to attack by the NSCl unit. Hence the first intermediate in the reaction sequence would be expected to be $\text{NCC}_6\text{H}_4\text{CN}_2\text{S}_2^+\text{Cl}^-$. The dithiadiazolium ring para to the second cyano group would then activate the cyano group to attack by the thiazyl chloride entity. However the cyano group in $\text{NCC}_6\text{H}_4\text{CN}_2\text{S}_2^+\text{Cl}^-$ destabilizes the dithiadiazolium ring relative to that in $\text{PhCN}_2\text{S}_2^+\text{Cl}^-$ and if $(\text{S}_2\text{N}_2\text{CC}_6\text{H}_4\text{CN}_2\text{S}_2^{2+})(\text{Cl}^-)_2$ is formed as an intermediate, the effect of one dithiadiazolium ring on the other is such that the species decomposes yielding $\text{NCC}_6\text{H}_4\text{CN}_2\text{S}_2^+\text{Cl}^-$. The destabilization of the $\text{NCC}_6\text{H}_4\text{CN}_2\text{S}_2^+\text{Cl}^-$ salt relative to $\text{PhCN}_2\text{S}_2^+\text{Cl}^-$ is seen in the ease with which the $\text{PhCN}_2\text{S}_2^+\text{Cl}^-$ salt is produced as compared with the cyano derivative. $\text{PhCN}_2\text{S}_2^+\text{Cl}^-$ can be produced by the reaction of benzonitrile with trichlorothiatriazene in carbon tetrachloride at $60^\circ\text{C}$, whereas on reacting 1,4-
dicyano benzene with trichlorotrithiatriazene in benzene at 80°C, no dithiadiazolium product was isolated (experiment 2.2.7(ii), page 53).

Hence it is concluded that \((C_8H_4N_2S_2^{2+})(Cl^-)_2\) cannot be readily synthesised due to the mutual destabilization of the two dithiadiazolium rings.

2.3.6 Comparison of the Known Chemistry of the 4-Trichloromethyl and 4-Phenyl-1,2,3,5-Dithiadiazolium Chloride

Quite an extensive chemistry of the 4-phenyl-1,2,3,5-dithiadiazolium cation has been developed in this thesis and by Roesky. There is however little or no analogous chemistry of the trichloromethyl derivative. In investigations, carried out concurrently with work reported in this thesis, Fielder failed to produce the reduced form of the trichloromethyl derivative or any salts by analogous reactions to those reported in this thesis for the phenyl derivative. It is suggested that the reduced form of the trichloromethyl derivative is not formed due to the repulsive interactions of the freely rotating \(CCl_3\) groups. In the anion exchange reactions of \(CCl_3CN_2S_2^{+}Cl^-\) the chlorines of the \(CCl_3\) group may also participate to some extent, thus leading to the mixtures of products reported by Fielder.

Hence it is concluded that the most extensive chemistry of any of the possible derivatives of the 1,2,3,5-dithiadiazolium cation will be for the case where the substituent at position 4 is phenyl or some other planar delocalised system (e.g. naphtho). No interference with anion exchange reactions will be observed for such a derivative and the eclipsed dimer system can be produced without
destructive interaction from freely rotating substituents at position 4.
Figure 2.4

2.1 1,3-Thiazole

2.2 1,3-Benzothiazole

2.3 1,2-Thiazole

2.4 1,2-Benzothiazole

2.5 1,2,3-Thiadiazole

2.6 1,2,3-Benzothiadiazole

2.7 1,2,3-Thia-S-diazole

2.8 1,2,5-Thiadiazole

2.9 1,2,5-Benzothiadiazole

2.10 1,2,5-Thia-S-diazole

2.11 1,2,4-Thiadiazole

2.12 1,3,4-Thiadiazole

2.13 1,3,4,5-Thiadiazole
Figure 2.5

1,2-Thiazine

1,2-Thiazine-1-oxide

1,4-Thiazine-1-oxide

1,4,2-Dithiazine

1,2,4-Benzothiadiazine

1,2,4-Benzothiadiazine-1-oxide

Naptho-[1,8-d,e]-1,2,3-Thiadiazine-1,1-Dioxide

Naptho-[1,8-c,d]-1,2,6-Thiadiazine

1,3,2,4-Dithiadiazine

1,2,4,6-Thiatriazine

1,3,2,4,6-Dithiatriazine-3,3-Dioxide
**Figure 2.6**

2·25  
1,4-Thiazepine

2·26  
1,4,5-Thiadiazepine

**Figure 2.7**

2·27  
1,2-Thiazolium Cation

2·28  
1,3-Benzothiazolium Cation

2·29  
1,3,4-Thiadiazolium Cation

2·30  
1,2,3-Benzothiadiazolium Cation

2·31  
1,2,4-Thiadiazolium Cation

2·32  
1,2,5-Thiadiazolium Cation
2.33  
\[ \text{1,2,4-Dithiazolium Cation} \]

2.34  
\[ \text{1,2,4-Benzodiazolium Cation} \]

2.35  
\[ \text{3-sub-1,2,3,4-Thiatriazolium Cation} \]

2.36  
\[ \text{2-sub-1,2,3,4-Thiatriazolium Cation} \]

2.37  
\[ \text{1,2,3,5-Dithiadiazolium Cation} \]

2.38  
\[ \text{1,3,2,5-Dithiadiazolium Cation} \]

2.39  
\[ \text{1,3-Thiazinium Cation} \]

2.40  
\[ \text{1,3,5-Thiadiazinium Cation} \]
Figure 2.8.a

PhCN$S^+Cl^-$
Figure 2.8.b

$\text{PhCN}_2 S^+ I^-$
FIGURE 2.9

Infra-red Spectra of 4-Phenyl-1,2,3,5-Dithiadiazonium salts and 4-Phenyl-1,2-Dithia-3,5-Diazole.

- $\text{PhCN}_2\text{S}_2\text{Cl}$
- $\text{PhCN}_2\text{S}_2\text{I}$
- $\left[\text{PhCN}_2\text{S}_2\right]_2$
TABLE 2.7 Crystal Data for PhCN₂S₂Cl₂

<table>
<thead>
<tr>
<th></th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>6C₆H₅CN₂S₂Cl₂</td>
<td>C₆H₅CH₃</td>
</tr>
<tr>
<td>Triclinic</td>
<td>Space Group P</td>
</tr>
<tr>
<td>a = 1577.0(13)pm</td>
<td></td>
</tr>
<tr>
<td>b = 756.5(6)pm</td>
<td></td>
</tr>
<tr>
<td>c = 1379.1(11)pm</td>
<td></td>
</tr>
<tr>
<td>α = 100.25°(4)</td>
<td></td>
</tr>
<tr>
<td>β = 109.81°(5)</td>
<td></td>
</tr>
<tr>
<td>γ = 95.25°(5)</td>
<td></td>
</tr>
<tr>
<td>R = 0.056</td>
<td></td>
</tr>
<tr>
<td>1535 reflections</td>
<td>172 parameters</td>
</tr>
</tbody>
</table>

TABLE 2.8 Mean Standard Deviations in the Crystal Structure of PhCN₂S₂Cl₂

<table>
<thead>
<tr>
<th>Lengths</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>σ(S-S) = 0.5pm</td>
<td>σ(S - Cl - S) = 0.10°</td>
</tr>
<tr>
<td>σ(S-Cl) = 0.5pm</td>
<td>σ(Cl - S - S) = 0.15°</td>
</tr>
<tr>
<td>σ(N-C) = 1pm</td>
<td>σ(S - S - N) = 0.40°</td>
</tr>
<tr>
<td>σ(C-C) = 1pm</td>
<td>σ(S - N - C) = 0.70°</td>
</tr>
<tr>
<td>σ(C-H) = 5pm</td>
<td>σ(C - C - C) = 0.70°</td>
</tr>
<tr>
<td>σ(S-N) = 1pm</td>
<td>σ(N - C - N) = 0.8°</td>
</tr>
<tr>
<td></td>
<td>σ(C - C - H) = 3°</td>
</tr>
</tbody>
</table>
TABLE 2.9  S-Cl contact distances between Molecules in the Crystal Structure of \textit{PhCN}_2S_2Cl

<table>
<thead>
<tr>
<th>Molecule</th>
<th>S-Cl distance (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1).....</td>
<td>S(1) = 318.8 pm</td>
</tr>
<tr>
<td></td>
<td>Cl(2)..... S(2) = 318.1 pm</td>
</tr>
<tr>
<td>Cl(1).....</td>
<td>S(3) = 320.9 pm</td>
</tr>
<tr>
<td>Cl(1).....</td>
<td>S(5) = 326.3 pm</td>
</tr>
<tr>
<td>Cl(1).....</td>
<td>S(6) = 333.4 pm</td>
</tr>
<tr>
<td>Cl(1).....</td>
<td>S(5) = 319.8 pm</td>
</tr>
<tr>
<td>Cl(1).....</td>
<td>S(6) = 332.5 pm</td>
</tr>
</tbody>
</table>

(Numbering system the same as used in figure 2.16)

TABLE 2.10  Crystal Data for 4-Phenyl-1,2-Dithia-3,5-Diazole

\textit{C}_7\textit{H}_5\textit{N}_2\textit{S}_2 \quad \text{MW} : \ 181.25

Orthorhombic, Space Group \textit{P}_2_1\textit{P}_2_1\textit{P}_2_1 (No.19)

- \textit{a} = 1606.1(1) pm
- \textit{b} = 3298.4(5) pm
- \textit{c} = 5774.0(4) pm
- \text{V} = 3.0429(5) \times 10^9 \text{ pm}^3
- \text{Z} = 16
- \text{R} = 0.082
- \text{D}_x = 1.58 \text{ g cm}^{-3}
- \text{F}(000) = 1488
- \text{X} = 71.07 \text{ pm}
- \text{\nu}_\text{Mo} = 5.99 \text{ cm}^{-1}
- 2513 reflections
- 132 positional parameters  264 thermal parameters
### TABLE 2.11 Torsion angles in (PhCN$_2$S$_2$)$_x$ (figure 2.19)

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$<em>{11}$ - S$</em>{11}$ - S$<em>{42}$ - N$</em>{42}$</td>
<td>8.43</td>
</tr>
<tr>
<td>N$<em>{12}$ - S$</em>{12}$ - S$<em>{41}$ - N$</em>{41}$</td>
<td>6.91</td>
</tr>
<tr>
<td>N$<em>{21}$ - S$</em>{21}$ - S$<em>{31}$ - N$</em>{31}$</td>
<td>3.61</td>
</tr>
<tr>
<td>N$<em>{22}$ - S$</em>{22}$ - S$<em>{32}$ - N$</em>{32}$</td>
<td>2.81</td>
</tr>
</tbody>
</table>

(Numbering system same as used in figure 2.18)

### TABLE 2.12 Mean Standard Deviations in the Crystal Structure of (PhCN$_2$S$_2$)$_2$

<table>
<thead>
<tr>
<th>Standard deviations lengths (pm)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.5</td>
</tr>
<tr>
<td>N</td>
<td>1.0</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
</tr>
</tbody>
</table>
TABLE 2.13  

Geometry of the Intermolecular Contacts in (PhCN$_2$S$_2$)$_2$

(a) Symmetry code

\[ \begin{align*}
\gamma &= x - \frac{1}{2}, \frac{3}{2} - y, -z \\
\gamma' &= x + \frac{1}{2}, \frac{3}{2} - y, -z
\end{align*} \]

Lengths (pm)

<table>
<thead>
<tr>
<th>Contact</th>
<th>Length (pm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$<em>{12}$ - S$</em>{21}$</td>
<td>340.2</td>
</tr>
<tr>
<td>S$<em>{32}$ - N$</em>{12}$</td>
<td>315.0</td>
</tr>
<tr>
<td>S$<em>{31}$ - N$</em>{12}$</td>
<td>338.0</td>
</tr>
<tr>
<td>S$<em>{41}$ - N$</em>{21}$</td>
<td>309.0</td>
</tr>
<tr>
<td>S$<em>{42}$ - N$</em>{21}$</td>
<td>317.0</td>
</tr>
</tbody>
</table>

(b) Angles (°)

<table>
<thead>
<tr>
<th>Contact</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S$<em>{12}$ - S$</em>{21}$ - S$_{22}$</td>
<td>137.9</td>
</tr>
<tr>
<td>S$<em>{12}$ - S$</em>{21}$ - S$_{31}$</td>
<td>128.6</td>
</tr>
<tr>
<td>S$<em>{12}$ - S$</em>{21}$ - N$_{21}$</td>
<td>101.9</td>
</tr>
<tr>
<td>S$<em>{32}$ - N$</em>{12}$ - S$_{12}$</td>
<td>100.1</td>
</tr>
<tr>
<td>S$<em>{32}$ - N$</em>{12}$ - C$_{11}$</td>
<td>109.7</td>
</tr>
<tr>
<td>S$<em>{31}$ - S$</em>{32}$ - N$_{12}$</td>
<td>77.3</td>
</tr>
<tr>
<td>S$<em>{22}$ - S$</em>{32}$ - N$_{12}$</td>
<td>102.0</td>
</tr>
<tr>
<td>N$<em>{32}$ - S$</em>{32}$ - N$_{12}$</td>
<td>163.9</td>
</tr>
<tr>
<td>S$<em>{32}$ - S$</em>{31}$ - N$_{12}$</td>
<td>65.5</td>
</tr>
<tr>
<td>S$<em>{21}$ - S$</em>{31}$ - N$_{12}$</td>
<td>97.7</td>
</tr>
<tr>
<td>N$<em>{31}$ - S$</em>{31}$ - N$_{12}$</td>
<td>156.2</td>
</tr>
<tr>
<td>N$<em>{41}$ - S$</em>{41}$ - N$_{21}$</td>
<td>162.5</td>
</tr>
</tbody>
</table>

(Numbering system same as used in Figure 2.17.)
Figure 2.15

X-ray crystal structure of 4-Trichloromethyl-1,2,3,5-
Dithiadiazolium Chloride

Figure 2.19

![Diagram of molecular structure]
Figure 2.16

X-ray crystal structure of 4-Phenyl-1,2,3,5-

Dithiadiazolium Chloride
Figure 2.17

Stereogram of 4-Phenyl-1,2-Dithia-3,5-Diazole
Figure 2.18

X-ray crystal structure of 4-Phenyl-1,2-Dithia-3,5-Diazole.
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CHAPTER THREE
THE REDUCTION OF SULPHUR-NITROGEN SPECIES

3.1 Introduction

There are four main sulphur-nitrogen species with which chlorine is associated in the form of the chloride anion or as covalently bound chlorine.

1. Thiotrichiazyl chloride ($S_4N_3^+Cl^-$)
2. Thiodithiazyl chloride ($S_3N_2^+Cl^-$)
3. Chlorothiodithiazyl chloride ($S_3N_2Cl^+Cl^-$)
4. Trichlorotrithiatriazene ($\left((NSCl)\right)_3$).

The four compounds form a series, in which the first two species ($S_4N_3^+Cl^-$ and $S_3N_2^+Cl^-$) contain cyclic sulphur-nitrogen cations with no covalent sulphur-chlorine linkages. The species $S_3N_2Cl^+Cl^-$ represents the sole example of a cationic compound containing a covalently bound chlorine and an anionic chlorine. This compound may therefore be regarded as the mid-point of the series listed above, as $(NSCl)_3$ contains three covalently bound chlorine atoms and is therefore not ionic.

The chemistry of the aforementioned sulphur-nitrogen cations and trichlorotrithiatriazene, although investigated by a number of research groups throughout the world, over a period of two decades, is still largely unexplored. Few potential industrial uses of the species have been found and their application to organic synthetic chemistry has been, in the main, undeveloped.
3.1.1 Thiotrithiazyl Chloride ($S_4N_3Cl$)

The thiotrithiazyl cation is probably the least moisture sensitive of all the cationic sulphur-nitrogen species and is far more stable to moisture than any sulphur-nitrogen species containing a covalently bound chlorine (e.g. $S_2N_2Cl_2$ and $(NSCl)_3$). The cation is often formed by the thermal decomposition and rearrangement of other sulphur-nitrogen species both in the vapour phase and in solution.

(a) Preparation of Thiotrithiazyl Chloride

\[ 3S_4N_4 + 2S_2Cl_2 \rightarrow 4S_4N_3Cl \quad \text{Yield; 90\% (ref.2.4)} \]  
(3.1)

\[ 3S_2N_2Cl_2 + S_2Cl_2 \rightarrow 2S_4N_3Cl + 3SCl_2 \quad \text{Yield; Quantitative (ref.5)} \]  
(3.2)

The above two routes are those normally used to synthesize $S_4N_3Cl$. Various other routes via trichlorotri-thiatriazene and by the use of other chlorinating agents e.g. $SOCl_2$ and $CH_3C(O)Cl$, are known. Direct synthesis by the reaction of sulphur-chlorides with ammonia or lithium azide does not provide a high yield of product.

(b) Physical Properties

Due to the insolubility of $S_4N_3Cl$ in non-polar solvents, the compound is normally isolated as a fine yellow powder. The finely divided form of the compound can cause irritation of the nasal system and mild dermatitis. The salt is soluble in highly polar or coordinating solvents, e.g. acetonitrile, nitromethane, thionyl chloride, tetrahydrofuran, monoglyme and to a lesser extent in sulphur dioxide.
(c) The Structure of the Thiotrithiazyl cation

$S_4N_3\text{Cl}$ was first prepared in 1880 and was shown to be ionic by salt formation, cryoscopy and conductivity measurements. The crystal structure of the ring was first determined by Weiss (1962)\textsuperscript{13,14} and later by Cordes (1964)\textsuperscript{15}, Kruss (1972)\textsuperscript{16,17}, Row (1978)\textsuperscript{18} and Street (1979)\textsuperscript{19}.

The structure of the $S_4N_3^+$ cation in $S_4N_3\text{NO}_3^-$ (1978)\textsuperscript{18} is shown in Figure 3.1.

Figure 3.1 Structure of the $S_4N_3^+$ cation.\textsuperscript{18}

![Diagram of $S_4N_3^+$ cation]

The bonding in the $S_4N_3^+$ cation has been the subject of much debate over the past decade. However, Friedman\textsuperscript{20} concluded from the U.V spectrum that the bonding was "a 10\pi-system, conjugated throughout the entire ring, though limited in extent across the S-S bond". This view was confirmed by Adams \textit{et al}\textsuperscript{21} who concluded from S.C.F.M.O. and E.S.C.A. calculations that the cation contained a 10\pi-delocalised ring.
(d) **The Reactions of Thiotrithiazyl chloride**

(i) **Salt Formation Reactions**

Due to its ionic nature, the majority of the reported chemistry of the thiotrithiazyl ring system is that of salt formation reactions. The salts are almost invariably synthesised from thiotrithiazyl chloride by one of three routes:

(a) Metathesis in polar solvents, e.g. \( \text{Br}_{22,25}^2 \text{SCN}_{22,25}^2 \text{BPh}_4^{22} \) and \( I_{25}^2 \).

(b) Reactions with liquid or concentrated acids with the evolution of hydrogen chloride, e.g. \( \text{NO}_3^{13,14,18,23} \), \( \text{ClO}_4^{24} \), \( \text{F}_26 \) and salts of the oxy-acids of sulphur\(^{24,27-30} \).

(c) Reactions with Lewis acids, e.g. \( \text{SbCl}_6^{11} \), \( \text{FeCl}_4^{31} \), \( \text{AlCl}_4^{31} \), \( \text{HgCl}_3^{32} \) and the bromo analogues\(^{33-36} \).

(ii) **Ring expansion**

Thiotrithiazyl chloride is reported to react with both lithium and aluminium azide forming tetrasulphur tetranitride\(^ {12} \).

(iii) **Reactions with Triphenyl Phosphine**

Thiotrithiazyl chloride reacts readily with triphenyl phosphine forming a series of compounds containing both phosphorous-nitrogen and sulphur-nitrogen bonds, e.g. \( \text{[Ph}_3\text{P} = \text{N} - \text{PPh}_3^\text{Cl}, \text{[Ph}_3\text{P} - \text{NH}_2^\text{Cl and [}(\text{Ph}_3\text{P} = \text{N})_3\text{S}]^\text{Cl}_3^{37}.} \)

(iv) **Reactions with Amines**

Thiotrithiazyl chloride reacts with trace amounts of amines to form very highly coloured species which decompose within short periods of time. The reaction has been suggested as a possible method of observing amines in low concentrations\(^ {38} \).
The potential application of $S_4N_2Cl$ to organic heterocyclic chemistry was investigated by Barton and Bubb$^{39}$, who discovered that the salt reacted readily with benzophenone hydrazone to give benzophenone azine and with benzophenone phenylhydrazone to give N-(phenylthio) diphenyl methylenamine (Ph$_2$C=N-S-Ph). No further work in this area has been reported by Barton, who concluded from his investigations that, "thiotri-thiazyl chloride leads to a variety of interesting products in reactions with electron rich organic substrates. However the crude product is usually a complex mixture and yields of pure substances are generally low. The multiplicity of pathways by which these reagents can react, although mechanistically fascinating, imposes limitations on their synthetic utility."

3.1.2 Thiodithiazyl Monochloride ($S_3N_2Cl$)

The chemistry of the thiodithiazyl cation is by far the least studied of all the sulphur-nitrogen ring systems.

(a) Preparation of the Thiodithiazyl Cation

The thiodithiazyl cation has been prepared by five routes:

(i) $3S_3N_2Cl_2 \rightarrow 2S_3N_2Cl + 2NCl + SCl_2$ (ref.5) (3.3)
(ii) $2S_3N_2Cl_2 + HCOOH \rightarrow 2S_3N_2Cl + 2HCl + CO_2$ (ref.40)(3.4)
(iii) $S_4N_4 + S_2Cl_2 \rightarrow 2S_3N_2Cl$ (ref.41)(3.5)

(iv) $S_4N_4 + 2NOC1 \rightarrow S_3N_2Cl + \frac{1}{2}S_2Cl_2 + NO + N_2$ (ref.42)(3.6a)

(ivb) $2(SNCI)_3 + 24NO \rightarrow 6S_3N_2Cl + 12NOC1 + 3S_2Cl_2 + 12N_20$ (ref.42)(3.6b)

(v) $4S_4N_4 + 7.5AsF_5 \rightarrow 4S_3N_2AsF_6 + N_2 + \frac{1}{2}S_8^{2+}(AsF_6)^{-} + 2.5AsF_3$ (ref.43) (3.7)
(b) Physical properties

Thiodithiazyl chloride is normally obtained as a deep green powder which is mildly moisture sensitive. It is insoluble in the majority of solvents but can be dissolved to a small extent in sulphur dioxide although decomposition to thiotrichiazyl chloride does occur if the solution is warmed above ca. 35°C for prolonged periods.\(^4^4\)

(c) Structure of thiodithiazyl chloride

N.Q.R. measurements on thiodithiazyl chloride indicate that the chlorine exists as a chloride ion.\(^4^5\) Thus the \(\text{S}_2\text{N}^+\) cation is postulated to be a \(7\pi\)-electron cation in either a monomeric or polymeric form. The crystal structures of both the hexafluoroarsenate\(^4^3\) and chloro-disulphate\(^4^6\) salts have been determined and a \(\text{S}_2\text{N}_2\) ring of similar dimensions deduced. The existence of the species as a monomer or dimer was however in dispute for a period of time. Banister et al determined the chloro-disulphate salt to be dimeric whereas Gillespie et al believed that the hexafluoroarsenate\(^4\) salt was a monomer having a five line E.S.R. spectrum. Recent work by Gillespie has however concluded that the system is dimeric with a low concentration (approx. 1 in \(10^6\)) of monomer units, which cause the observed E.S.R. spectrum.

The crystal structure of the chloro-disulphate salt is presented in figure 3.2.
(d) The Reactions of Thiodithiazyl Chloride

To date there are only two types of reactions that have been studied.

(i) The thermal decomposition of thiodithiazyl chloride:

\[
\begin{align*}
S_3N_2Cl_2 & \xrightarrow{\Delta \text{ at } 80^\circ C} S_3N_2Cl \\
& \text{in vacuo}
\end{align*}
\]

\[
\begin{align*}
S_3N_2Cl & \xrightarrow{\Delta \text{ at } 120-140^\circ C} S_4N_3Cl \\
& \text{in vacuo}
\end{align*}
\]

(ii) The formation of salts:

\[
\begin{align*}
2S_3N_2Cl+2HSO_3Cl & \rightarrow (S_3N_2^+)_2(S_2O_6Cl^-)_2+2HCl \\
& \text{(ref.46)} (3.9)
\end{align*}
\]

\[
\begin{align*}
S_3N_2Cl+5H_2S_2O_7 & \rightarrow S_3N_2^+HS_3O_10^-+HSO_3Cl+2H_2SO_4 \\
& \text{(ref.47) (3.10)}
\end{align*}
\]

\[
\begin{align*}
S_3N_2Cl + MCl_3 & \rightarrow S_3N_2Cl^+MCl_4^- \\
& \text{(ref.46) (3.11)
\end{align*}
\]

(M = Fe, Al)
(e) Formation of Related Species

Recent work by Street et al.$^{48}$ has produced two closely related compounds, $\text{SSE}_2\text{N}_2^+\text{Cl}^-$ and $\text{SSE}_2\text{N}_2^+\text{Br}^-$ (equation 3.12). Both these compounds are postulated to be dimeric with a 4 centre (seleniums), 2 electron bridge (c.f. figure 3.2, page 107).

$$2\text{SeX}_4 + 2\text{Se}_2\text{X}_2 + 2\left[(\text{SiMe}_3)_2\text{N}\right]_2 \xrightarrow{\text{S}} (\text{SSE}_2\text{N}_2\text{X})_2 + 3\text{Me}_2\text{SiX} \text{ (Equ. 3.12)}$$

3.1.3 Chlorothiodithiazyl Chloride ($S_3N_2Cl_2$)

Chlorothiodithiazyl chloride can be regarded as the pivot point in the series of sulphur-nitrogen compounds with associated chlorine atoms. It is the only cyclic sulphur-nitrogen species known that possesses both covalently bound and ionic chlorine.

(a) Preparation of Chlorothiodithiazyl Chloride

$$\text{4S}_2\text{Cl}_2 + 2\text{NH}_4\text{Cl} \rightarrow S_3\text{N}_2\text{Cl}_2 + 8\text{HCl} + 5\text{S} \quad \text{(ref. 1,5) \ (3.13)}$$

$$S_3\text{N}_2\text{Cl} + \text{MC}_3 \rightarrow S_3\text{N}_2\text{Cl}^+\text{MC}_4^+ \quad \text{(ref. 46) \ (3.14)}$$

$M = \text{Al, Fe}$

The primary synthetic route to $S_3\text{N}_2\text{Cl}_2$ is via disulphur dichloride and ammonium chloride, the product crystallising out on the walls of the air condenser. Jolly$^{1}$ quotes a yield of 12g of product from 100g $\text{NH}_4\text{Cl}$ and 100cm$^3 S_2\text{Cl}_2$.

Yields of $>25g$ per 100g $\text{NH}_4\text{Cl}$ and 100cm$^3 S_2\text{Cl}_2$ have been obtained in this thesis (ca. 40-50% yield based on $S_2\text{Cl}_2$).

(b) Physical properties

Chlorothiodithiazyl chloride is normally obtained as large orange-red crystals which conglomerate forming a solid
mass. It is highly moisture sensitive, rapidly darkening to give a black surface coating on exposure to moisture. Chlorothiodithiazyl chloride is only slightly soluble in the majority of polar and coordinating solvents and is insoluble in non-polar organic solvents.

(c) Structure of the Chlorothiodithiazyl Cation

The X-ray crystal structure of the chlorothiodithiazyl cation was determined by Zalkin et al (1966). The structure showed that \( S_2N_2Cl_2 \) was an ionic species with one chlorine covalently bound to a sulphur and the other anionic. The sulphur atom to which the chlorine is covalently bonded is out of plane with the remaining \( S_2N_2 \) fragment which is itself virtually planar. The structure of the chlorothiodithiazyl cation is shown in Figure 3.3.

Figure 3.3 Structure of the Chlorothiodithiazyl Cation
(d) Reactions of Chlorothiodithiazyl Chloride

The chemistry of the chlorothiodithiazyl cation is not highly developed, even though it is probably the most readily synthesised sulphur-nitrogen compound. It is however a key material in the production of the other cyclic sulphur-nitrogen cations and trichlorotrithiatriazene.

(i) Formation of other Sulphur-Nitrogen Ring Systems:

\[ 3S_2N_2Cl_2 + S_2Cl_2 \rightarrow 2S_4N_3Cl + 3SCl_2 \quad \text{(ref.5)} \quad (3.15) \]

\[ 3S_2N_2Cl_2 \xrightarrow{\Delta} 2S_2N_2Cl + 2NCl_3 + SCl_2 \quad \text{(ref.5)} \quad (3.16) \]

\[ 3S_2N_2Cl_2 + 3Cl_2 \rightarrow 2(NCl_3) \text{Cl}_2 + 3SCl_2 \quad \text{(ref.5)} \quad (3.17) \]

(ii) Salt Formation:

\[ S_2N_2Cl_2 + \text{MCl}_3 \overset{\text{SOCl}_2}{\rightarrow} S_2N_2\text{Cl}^+ \text{MCl}_4^- \quad \text{(M = Al, Fe)} \quad (3.18) \]

\[ S_2N_2\text{Cl}_2 + \text{HSO}_3^- \overset{\text{ref.50}}{\rightarrow} S_2N_2\text{Cl}^+ \text{SO}_3^- \text{F}^- + \text{HCl} \quad (3.18) \]

(iii) Reactions with Organometallic compounds:

\[ S_2N_2\text{Cl}_2 + 2\text{PhMgCl} \rightarrow S_2N_2\text{Ph}_2 + 2\text{MgCl}_2 \quad \text{(ref.51)} \quad (3.19) \]

\[ \text{P}^3\text{N}_3\text{F}_5\text{N}(\text{SiMe}_3)_2 + S_2N_2\text{Cl}_2 \rightarrow \text{P}^3\text{N}_3\text{F}_5\text{S}_3\text{N}_3 \text{Cl} + 2\text{Me}_3\text{SiCl} \quad \text{(ref.53)} \quad (3.21) \]

3.1.4 Trichlorotrithiatriazene (NCl)_3

Trichlorotrithiatriazene is the trimeric form of thiazylic chloride (NCl) and is a neutral species, all the chlorines being covalently bound to sulphurs.
(a) **Preparation of Trichlorotrithiatriazene**

(i) **From other Sulphur-Nitrogen Heterocycles:**

\[
3S_4N_4 + 6Cl_2 \rightarrow 4(\text{NSCl})_3 \quad \text{(ref.54)} \quad (3.22)
\]

\[
3S_3N_2Cl_2 + 3Cl_2 \rightarrow 2(\text{NSCl})_3 + 3SCl_2 \quad \text{(ref.4)} \quad (3.23)
\]

\[
3S_4N_4 + 6SO_2Cl_2 \rightarrow 4(\text{NSCl})_3 + 6SO_2 \quad \text{(ref.55)} \quad (3.24)
\]

\[
3S_3N_2Cl_2 + 3SO_2Cl_2 \rightarrow 2(\text{NSCl})_3 + 3SO_2 + 3SCl_2 \quad \text{(ref.55)} \quad (3.25)
\]

(ii) **From Ammonium Chloride and Disulphur Dichloride:**

\[
6S_2Cl_2 + 3\text{NH}_4\text{Cl} \rightarrow (\text{NSCl})_3 + \frac{3}{2}S_8 + 12\text{HCl} \quad \text{(ref.1)} \quad (3.26)
\]

(b) **Physical Properties**

\( (\text{NSCl})_3 \) forms yellow platelets of density 2.09g cm\(^{-3} \). It is highly moisture sensitive, decomposing with the evolution of sulphur dioxide and the formation of ammonium chloride. The trimer is highly soluble in carbon tetrachloride and benzene, forming a mint green solution above ca.60\(^\circ\)C. If however chlorine is bubbled through a refluxing solution of \((\text{NSCl})_3 \) in carbon tetrachloride, the green colouration is not observed. It is recommended by Jolly\(^{56} \) that chlorine be passed through the recrystallisation solvent if a very high purity product is required.

(c) **Structure of Trichlorotrithiatriazene**

The crystal structure of \((\text{NSCl})_3 \) was first determined by Wiegers *et al* (1962)\(^{57} \) who later refined the structure (1966).\(^{58} \) The structure of trichlorotrithiatriazene is presented in figure 3.4.
It is concluded from the relatively short, equi-distant, S-N bond lengths that a delocalised $\pi$-system is present in trichlorotrithiatrazene.\textsuperscript{58}

(d) The reactions of Trichlorotrithiatrazene

(i) The reactions of trichlorotrithiatrazene with alkenes and nitriles have been discussed in Chapter Two (page 24).

(ii) The fluorination of trichlorotrithiatrazene is discussed in Chapter Four (page 158).

(iii) The reactions of trichlorotrithiatrazene with Lewis acids are discussed in Chapter Five (page 225).

(iv) The formation and reactions of thiazyl chloride are discussed in Chapter Five (page 228).
(v) The reaction of trichlorotrithiatriazene with transition metal complexes:

\[
\text{Mo(CO)}_6 + (\text{NSCl})_3 \rightarrow \text{MoS}_2\text{N}_3\text{Cl}_3 + 6\text{CO} \quad \text{(ref. 59)} \quad (3.27)
\]

\[
\text{Na}\left[\left(n^5\text{C}_5\text{H}_5\right)\text{Cr(CO)}_3\right] + (\text{NSCl})_3 \rightarrow \left(n^5\text{C}_5\text{H}_5\right)\text{Cr(CO)}_2\text{NS} \quad \text{(ref. 60)}
\]

(vi) The reaction of trichlorotrithiatriazene with N-H groups:

(a) With Sulphur Imides:

\[
\begin{align*}
4(\text{NSCl})_3 + 3\text{S}_4\text{N}_4\text{H}_4 & \rightarrow 6\text{S}_4\text{N}_4 + 12\text{HCl} \quad \text{(ref. 61)} \quad (3.29) \\
(\text{NSCl})_3 + 3\text{S}_4\text{NH} & \rightarrow 3\text{S}_4\text{N}_2 + 3\text{HCl} + \frac{12}{8}\text{S}_8 \quad \text{(ref. 62)} (3.30) \\
2(\text{NSCl})_3 + 6\text{S}_4\text{NH} & \rightarrow 3\text{S}_4\text{N}_4 + 6\text{HCl} + \frac{9}{2}\text{S}_8 \quad \text{(ref. 3)} \quad (3.31)
\end{align*}
\]

(b) With Organic Imides:

\[
\begin{align*}
\text{C}_6\text{F}_5\text{SN(H)}\text{SC}_6\text{F}_5 + (\text{NSCl})_3 & \rightarrow \text{C}_6\text{F}_5\text{SN:S:NSC}_6\text{F}_5 \quad \text{(ref. 62)} \quad (3.32) \\
(\text{Me}_3\text{Si})_2\text{NH} + (\text{NSCl})_3 & \rightarrow \text{Me}_3\text{SiN:S:NSiMe}_3 \quad \text{(ref. 63)} \quad (3.33)
\end{align*}
\]

(c) Reaction with Ammonia:

\[
(\text{NSCl})_3 + \text{NH}_3 \xrightarrow{-78^\circ C} \text{NH}_4^+ (\text{S}_4\text{N}_5^-) \quad \text{(ref. 64)} \quad (3.34)
\]

(vii) Reaction of trichlorotrithiatriazene with trimethyl silane derivatives:

\[
(\text{NSCl})_3 + \text{Me}_3\text{SiNSNSiMe}_3 \rightarrow \text{S}_4\text{N}_5^+\text{Cl}^- + 2\text{Me}_3\text{SiCl} \quad \text{(ref. 65)} \quad (3.35)
\]
3.2 Experimental

3.2.1 Reductions of Sulphur-Nitrogen Species by Iodide

(i) The solid phase halide transport reaction between $S_2N_2Cl$ and KI

Approximately 0.1g (0.63 mmole) of $S_2N_2Cl$ was ground with dry potassium iodide (0.2g, 1.2 mmole) under dry box conditions. The mixture was then pressed into a disc (3000 lb. in$^2$) and the infra-red spectrum recorded. A control disc was also made from potassium chloride and thiadiazyl chloride. No shifting in peaks was noted for the $KCl/S_2N_2Cl$ disc relative to the infra-red spectrum of $S_2N_2Cl$ recorded using a nujol mull. Distinct and substantial shifts were however noted in the $S_2N_2Cl/KI$ disc relative to the $S_2N_2Cl/KCl$ disc.

Infra-red spectrum of the $S_2N_2Cl/KI$ disc: 1400 w.br, 928s, 728m, 700s, 552s, 348s cm$^{-1}$.

(cf. $S_4N_4$ (main peaks) 925s, 719s, 696s, 557s, 552s, 347s cm$^{-1}$).

(ii) Solid phase reaction between $S_2N_2Cl$ and NaI

$S_2N_2Cl$ (4.83g, 30.28 mmole) was ground with dry NaI (10.29g, 68.66 mmole) at room temperature, under dry box conditions. The mixture was then loaded into a soxhlet extraction thimble and extracted with 1,4-dioxan (100 cm$^3$). A deep brown solution was obtained which, after cooling and evaporating down to 20 cm$^3$, yielded a brown precipitate.

Infra-red spectrum of the brown precipitate (nujol mull): 928s, 728m, 700s, 555s, 345s cm$^{-1}$ (cf. $S_4N_4$)
(iii) Reaction of S$_2$N$_2$Cl with NaI in nitromethane (CH$_3$NO$_2$)

To a slurry of S$_2$N$_2$Cl (2.13g, 13.4 mmole) in refluxing CH$_3$NO$_2$ (40 cm$^3$) was added dry, powdered NaI (4.00g, 26.7 mmole). The reaction was refluxed for 6h. and the resulting deeply coloured solution filtered hot and allowed to cool slowly to room temperature. The solvent was then removed, by the passage of dry nitrogen across the surface of the solution, and a red-brown residue obtained (1.51g). The crude material was recrystallised from benzene (15 cm$^3$) and the orange crystals formed on cooling were isolated and their infra-red spectrum recorded.

Infra-red spectrum of the crystalline material (nujol mull):

930s, 726m, 700s, 550s, 350s cm$^{-1}$ (cf. S$_4$N$_4$)

(yield of S$_4$N$_4$: 0.62g, 50% based on S$_2$N$_2$Cl)

(iv) Reaction of S$_4$N$_3$Cl with NaI in CH$_3$NO$_2$

To a slurry of S$_4$N$_3$Cl (1.46g, 7.1 mmole) in refluxing CH$_3$NO$_2$ (30 cm$^3$) was added pre-dried, powdered, NaI (1.52, 10.1 mmole). The solution rapidly deepened in colour forming a very deep red-purple solution. A purple haze was noted in the flask. After refluxing for 40 min. the system was filtered hot and the filtrate evaporated to dryness using a stream of dry nitrogen across the surface of the solution. The crude product (1.24g) was recrystallised from benzene (20 cm$^3$) and the resulting orange needles isolated. The infra-red spectrum of the crystals was recorded.

Infra-red spectrum of the crystals (nujol mull):

930s, 728m, 700s, 555s, 350s cm$^{-1}$ (cf. S$_4$N$_4$)
(v) Reduction of $S_3N_2Cl$ by saturated aqueous solution of NaI

NaI (1.93g, 12.87 mmole) was dissolved in ice cold distilled water (10 cm$^3$) and the resulting solution poured on to carbon tetrachloride (30 cm$^3$). To the vigorously stirred two phase system was added $S_3N_2Cl$ (0.8lg, 5.08 mmole). A rapid reaction occurred forming a deeply coloured solution. After stirring for 10 min. the two phases were allowed to separate and it was noted that the CC$1_4$ phase was deep purple-red in colour. The carbon tetrachloride phase was isolated and the solvent removed. The resulting residue was washed with methanol (2 x 10 cm$^3$) and dried in vacuo.

Infra-red of the product (nujol mull): 3200 m.br, 1415m, 1240m, 1200m, 1020m, 930s, 730s, 700s, 660w, 602m, 560s, 350s cm$^{-1}$ (cf. $S_4N_4$)$^6$

(vi) Reaction of $S_4N_3Cl$ with NaI in Sulphur Dioxide (SO$_2$)

$S_4N_3Cl$ (1.24g, 6.03 mmole) and NaI (1.86g, 12.40 mmole) were placed in a 100 cm$^3$ flask and SO$_2$ (15 cm$^3$) condensed in. The reaction was stirred at -12°C for 4h. The initial yellow colouration deepened slowly to an intense orange-red over the 4h. The SO$_2$ was then removed and part of the residue (ca.0.1g) shaken with CC$1_4$ (2 cm$^3$). No purple colouration in the CC$1_4$ was seen.

Infra-red spectrum of the red product (nujol mull): 1165s, 1000vs, 675s, 562m, 470vs cm$^{-1}$ (cf. $S_4N_3Cl$)$^6$
3.2.2 Reduction of Sulphur-Nitrogen Species by the Sodium salts of the Oxy-acids of Sulphur

(i) Reduction of $S_2N_2Cl$ by Sodium Metabisulphite ($Na_2S_2O_5$)

To a stirred, refluxing, slurry of $S_2N_2Cl$ (10.58g, 66.33 mmole) in nitromethane (100 cm$^3$) was added $Na_2S_2O_5$ (14.23g, 74.9 mmole). An immediate reaction occurred evolving a gas (identified as $SO_2$). The system was refluxed for 4h. until no further evolution of gas was noted and filtered hot. On cooling the filtrate orange crystals were deposited. These crystals were isolated and the filtrate pumped to dryness. The resulting residue was then washed with ice cold water (3 x 10 cm$^3$), ethanol (2 x 5 cm$^3$) and ether (2 x 5 cm$^3$) and dried in vacuo. The crude product was then recrystallised from benzene (45 cm$^3$) yielding orange crystals.

Infra-red spectrum of the product (nujol mull): 1170vw, 930s, 732m, 704vs, 555s, 350s cm$^{-1}$ (cf. $S_4N_4$) $^{66}$

(yield of $S_4N_4$ : 3.24g, 53% based on $S_2N_2Cl$)

(ii) Reduction of $S_2N_2Cl_2$ by $Na_2S_2O_5$ in CH$_3$NO$_2$

To a stirred, refluxing, slurry of $S_2N_2Cl_2$ (6.13g, 31.44 mmole) in CH$_3$NO$_2$ (50 cm$^3$) was added $Na_2S_2O_5$ (10.14g, 53.37 mmole). A deep red solution was rapidly formed as was a green-black residue. The reaction was refluxed for 16h, filtered hot and cooled slowly to room temperature. The large orange crystals formed on cooling the filtrate were filtered off and the filtrate evaporated to dryness using a stream of dry nitrogen. The residue was washed and dried as in experiment 3.2.2(i) and the product recrystallised from 1,4-dioxan, the product being deposited as orange needle shaped crystals.
Infra-red spectrum of the product (nujol mull): 932s, 733m, 706s, 560s, 355s cm\(^{-1}\) (cf. \(S_4N_4\))\(^{66}\)

Analysis found; \(N\), 28.13\%, \(S_4N_4\) requires; \(N\), 30.43\%

(yield of \(S_4N_4\) 1.06g, 37\% based on \(S_2N_2Cl_2\))

(iii) Reduction of \(S_4N_3Cl\) by \(Na_2S_2O_5\) in \(CH_3NO_2\)

To a refluxing solution of \(S_4N_3Cl\) (2.33g, 11.34 mmole) in \(CH_3NO_2\) (25 cm\(^3\)) was added \(Na_2S_2O_5\) (2.41g, 12.68 mmole). A rapid reaction occurred producing a deep red solution and gradually over a period of 20 min. all traces of \(S_4N_3Cl\) disappeared. The reaction was refluxed for 2h., filtered hot and allowed to cool slowly to room temperature. Orange crystals were deposited on cooling and these were filtered off. The filtrate was evaporated to dryness and the residue washed as in Experiment 3.2.2(i). The resulting product was soxhlet extracted using benzene (25 cm\(^3\)) and an orange crystalline material obtained.

Infra-red spectrum of the product (nujol mull): 930s, 731m, 705s, 555s, 348s cm\(^{-1}\) (cf. \(S_4N_4\))\(^{66}\)

Analysis found; \(N\), 26.84\%, \(S_4N_4\) requires 30.43\%.

(yield of \(S_4N_4\), 0.83g, based on \(S_4N_4Cl\), 40\%)

(iv) Reduction of \(S_4N_3Cl\) by a Saturated Aqueous solution of \(Na_2S_2O_5\)

\(Na_2S_2O_5\) (4.23g, 22.26 mmole) was dissolved in ice cold water (20 cm\(^3\)) and \(S_4N_3Cl\) (1.94g, 9.44 mmole) added to the vigorously stirred solution. A rapid reaction occurred forming a deep green suspension. The reaction was stirred for 15 min., filtered and the residue washed with ice cold water (4 x 10 cm\(^3\)), ethanol (2 x 5 cm\(^3\)) and ether (2 x 10 cm\(^3\)) and dried in \textit{vacuo}. 
Infra-red spectrum of the product (nujol mull): 3150 mbr, 1415 s, 1235 s, 1205 s, 1050 m, 1015 s, 930 s, 730 s, 702 s, 662 w, 605 m, 560 s, 528 s, 350 s cm$^{-1}$ (cf. $S_4N_4$) 66

(v) Reaction of $S_3N_2Cl$ with Sodium Dithionite

To a refluxing suspension of $S_3N_2Cl$ (4.32 g, 27.08 mmole) in CH$_2$NO$_2$ (100 cm$^3$) was added sodium dithionite (6.16 g, 35.4 mmole). A rapid reaction occurred yielding a deep orange-red solution and a finely divided yellow precipitate. The system was refluxed for 4 h., filtered hot and cooled to room temperature. The precipitate was washed with ice cold water to remove any Na$_2$S$_2$O$_4$ and then by ethanol (2 x 10 cm$^3$) and ether (2 x 10 cm$^3$). The yellow product was then dried in vacuo and its infra-red spectrum recorded.

Infra-red spectrum of the product (nujol mull): 1165 m, 1000 s, 685 m, 570 m, 475 m cm$^{-1}$. (cf. $S_4N_2Cl^6$)

3.2.3 Reduction of Sulphur-Nitrogen Systems by Metals

(a) The Reduction of S/N compounds by Metals using Organic Solvents

The reductions of S/N compounds by metals using organic solvents involved essentially the same experimental technique in each case, the results of which are presented in table 3.1.

Experimental technique

To a stirred slurry/solution of the S/N species was added excess metal powder. The reaction was monitored by T.L.C., using a standard $S_4N_4$ sample for comparison. If the rate of reaction was low at room temperature the system was refluxed until complete reaction had occurred. The reaction mixture was then filtered and the precipitate and excess metal washed.
with 1,4-dioxan. The filtrate was evaporated to dryness and the residue obtained extracted with benzene. The product was isolated and the infra-red spectrum, yield and analyses obtained where applicable.

**TABLE 3.1 The reduction of S/N compounds by metals using organic solvents**

<table>
<thead>
<tr>
<th>S/N compound</th>
<th>Metal</th>
<th>Solvent (cm³)</th>
<th>Conditions</th>
<th>Product</th>
<th>Yield (S₄N₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₄N₂Cl</td>
<td>Fe</td>
<td>CH₃NO₂</td>
<td>R.T.</td>
<td>S₄N₄, S₄N₂</td>
<td>28%</td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Zn</td>
<td>T.H.F.</td>
<td>R.T.</td>
<td>S₄N₄, S₄N₂</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Hg</td>
<td>CH₃NO₂</td>
<td>R.T.</td>
<td>S₄N₄</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Al</td>
<td>CH₃NO₂</td>
<td>R.T.</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Mg</td>
<td>CH₃NO₂</td>
<td>R.T.</td>
<td>S₄N₄, S₄N₂</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Cu</td>
<td>CH₃NO₂</td>
<td>R.T.</td>
<td>Not identified</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Zn</td>
<td>THF</td>
<td>Reflux</td>
<td>S₄N₄, S₄N₂</td>
<td>60%</td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Fe</td>
<td>T.H.F.</td>
<td>Reflux</td>
<td>S₄N₄</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Mg</td>
<td>T.H.F.</td>
<td>Reflux</td>
<td>S₄N₄</td>
<td></td>
</tr>
<tr>
<td>S₄N₂Cl</td>
<td>Fe</td>
<td>CH₃NO₂</td>
<td>Reflux</td>
<td>S₄N₄</td>
<td></td>
</tr>
<tr>
<td>(NSCl)₃</td>
<td>Fe</td>
<td>Monoglyme</td>
<td>R.T.</td>
<td>S₄N₄</td>
<td>67%</td>
</tr>
</tbody>
</table>

(* Activated magnesium isolated from a Grignard reaction).
(b) Reaction of Potassium with $S_3N_2Cl$ using 1,4-Dioxan as a solvent

To a refluxing slurry of $S_3N_2Cl$ (1.84g, 11.54 mmole) in 1,4-dioxan (50 cm$^3$) was added small freshly cut pieces of potassium. A rapid reaction occurred yielding a deep red solution. The thin layer chromatogram was run of this solution using a standard $S_4N_4$ sample for comparison (eluting solvent benzene; $R_f$ values of the spots = 0.93 ($S_4N_2$) and 0.84 ($S_4N_4$)). Addition of excess potassium to the system caused the solution colour to change to deep blue-purple and then with more potassium to a very deep purple. The thin layer chromatogram indicated that no $S_4N_4$ remained in solution. The reaction was terminated at this point.

(c) The Reduction of S/N compounds by Metals using Sulphur Dioxide as a Solvent

1. Reduction of $S_4N_3Cl$ by Iron powder

$S_4N_3Cl$ (1.06g, 5.16 mmole) and Fe powder (1.28g, 22.86 mmole) were placed in a pre-dried, vacuum tight pyrex vessel, (figure 1.1, page 14) and sulphur dioxide (12.43g) condensed in. An orange-red solution was formed which did not alter over 22h. of agitation. The sulphur dioxide solubles were filtered off and the insolubles washed ca. 20 times to remove all the soluble fraction. The solvent was then slowly evaporated off leaving an orange-red residue (0.98g).

Infra-red spectrum of the residue (nujol mull): 1165w, 1000m, 930s, 730m, 700s, 675w, 550s, 470w, 370s, 355s cm$^{-1}$.

(cf. $S_4N_4$, $S_4N_3Cl$)

2. Reaction of ($NSCl)_3$ with Fe powder

($NSCl)_3$ (0.69g, 2.82 mmole) and Fe (1.57g, 28.04 mmole) were loaded in to a pre-dried, vacuum tight, pyrex vessel
(figure 1.1, page 14), and sulphur dioxide (7.19g) condensed in. Initially a pale green solution was formed but after agitating at room temperature for 30 min. a deep orange-red solution was produced. The reaction was agitated at room temperature for a further 5h. to ensure complete reaction and then the solubles filtered off. The residue was washed with SO₂ until no further evidence of any solubles was noted and then the solvent slowly removed, resulting in the formation of a deep orange-red microcrystalline product (0.52g).

Infra-red spectrum of the product (nujol mull): 1130s,br, 1050w,br, 730m(sh), 720m, 529s, 515m(sh), 370vs, cm⁻¹.

Raman spectrum of the product (red line) 736w, 675m, 650m(sh), 610s, 385s, 330s, 268m, 335vs, 186vs, 133m cm⁻¹.

(cf. Infra-red spectrum $S_2N_2Cl_2$: 1143s, 1047w, 1017vw, 731m, 721m(sh), 685m, 608m, 528s, 370s, 327s cm⁻¹). 31

(iii) Reaction of $S_2N_2Cl_2$ with Fe powder

$S_2N_2Cl_2$ (0.65g, 3.33 mmole) and Fe powder (1.16g, 20.7 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1.1, page 14) and SO₂ (8.43g) condensed in. A deep orange solution was immediately formed which did not change in appearance over the period of 6h. of agitation. The solubles were completely filtered off from the excess iron and the sulphur dioxide slowly removed, yielding a bright orange-red microcrystalline species (0.63g).

Infra-red of the orange product (nujol mull): 1165w, 1028m, 990m, 925m(sh), 914m, 864vs,br, 750m(sh), 730s, 710m, 685s, 680m(sh), 675m(sh), 668w(sh), 580m, 570w, 555w, 490m, 470m, 430m, 370vs cm⁻¹.

Analysis: found: S, 38.9; N, 14.15; Fe, 13.67; Cl, 33.6%.

$S_2N_2FeCl_4$ requires: S, 38.65; N, 13.53; Fe, 13.53; Cl, 34.30%
(iv) Reaction of (NSCl)₃ with Zn/Cu couple

(NSCl)₃ (0.53g, 2.17 mmole) and Zn/Cu powder (1.56g, 23.86 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1.1, page 14), and SO₂ (9.13g) condensed in. A very deep red solution was formed on warming to room temperature and this was agitated for 4h. The solubles were then removed and the residue washed with recondensed SO₂. During one washing of the insolubles an exothermic reaction occurred, in which the zinc was seen to burn in the atmosphere of sulphur dioxide producing a white compound (ZnO/ZnS). The reaction was terminated at this point.

(v) Reaction of (NSCl)₃ with Ag wool

(NSCl)₃ (0.59g, 2.41 mmole) and Ag wool (0.47g, 4.35 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1.1, page 14). The vessel was then evacuated. On evacuation it was noted that the silver became black in colour and a blue film was formed around the top of the containing bulb. The bulb was cooled to liquid nitrogen temperatures and the blue coloration took on a bronze metallic appearance. Sulphur dioxide (5.32g) was then added to the system and the film dissolved yielding a very deep green solution. The vessel was agitated at room temperature for 28h., during which time the colour of the solution changed to pale orange. The solution was filtered and the residue washed with recondensed solvent to remove all the solubles. The solvent was then slowly evaporated leaving an intractable tar from which it proved impossible to remove all the sulphur dioxide. The experiment was thus abandoned.

The reaction of thiazyl chloride (NSCl) with silver metal was investigated and is reported in Chapter Five (page 238).
(vi) Reaction of \((\text{N}_8\text{Cl})_3\) with Hg.

\((\text{N}_8\text{Cl})_3\) (0.64g, 2.6~ mmole) and Hg (28.42g, 141.7 mmole) were placed in a pre-dried, vacuum tight pyrex vessel (figure 1.1, page 14) and \(\text{SO}_2\) (9.13g) condensed in. The reaction was agitated for 16h. at room temperature and the resulting orange-red solution filtered off. The residue was washed with recondensed solvent to remove all the solubles. The solvent was then slowly evaporated from the filtrate leaving an orange residue.

Infra-red spectrum of the residue (nujol mull): 928s, 728m, 700s, 550s, 350s cm\(^{-1}\) (cf. \(\text{S}_4\text{N}_4\)) \(^{66}\)

T.L.C. (benzene elutant) \(R_f\) of product = 0.84 (cf. \(\text{S}_4\text{N}_4\); \(R_f\) = 0.84)

(vii) Reaction of \(\text{S}_2\text{N}_2\text{Cl}_2\) with Hg

\(\text{S}_2\text{N}_2\text{Cl}_2\) (1.72g, 8.82 mmole) and Hg (4.16g, 20.75 mmole) were placed in a pre-dried vacuum tight pyrex vessel (figure 1.1, page 14) and \(\text{SO}_2\) (12.63g) condensed in. The system was warmed to room temperature and the resulting orange-red solution agitated with the metal for 4h. The solubles were then completely removed into the second bulb and the solvent slowly removed from the system yielding an orange product. The \(\text{SO}_2\) insoluble species was essentially excess mercury but had a pinkish tinge to it. The infra-red spectra and thin layer chromatograms of both \(\text{SO}_2\) soluble and insoluble components were recorded.

Infra-red spectrum of the soluble product (nujol mull): 1165w, 920s, 725m, 695s, 545s, 340s cm\(^{-1}\) (cf. \(\text{S}_4\text{N}_4\)) \(^{66}\)

T.L.C. of soluble product (eluting solvent benzene) \(R_f\) = 0.84 (cf. \(\text{S}_4\text{N}_4\); \(R_f\) = 0.84).
Infra-red spectrum of the SO₂ insoluble product (nujol mull):
1015m, 970s, 959s, 945s, 715vs, 585m, 570m, 480m,br,
446m, 435m, 370s cm⁻¹.

The solubility of the pinkish SO₂ insolubles was tested in benzene, hexane and ether, in which it was found to be essentially insoluble. However with D.M.S.O., nitromethane and T.H.F. a red solution was formed. The compound was therefore extracted from the excess mercury using refluxing T.H.F. (20 cm³) and the resulting deep red solution pumped to dryness. The infra-red spectrum and thin layer chromatogram of the product were recorded.

Infra-red spectrum (nujol mull): 1165w, 1022s, 928s, 726m,
700s, 650w, 629s, 550s, 373s, 345s cm⁻¹ (cf. S₄N₄ ⁶₆ and S₄N₂ ⁶₇). T.L.C. (eluting solvent benzene) Rᶠ = 0.93 and 0.84.
(cf.S₄N₄ Rᶠ = 0.84; S₄N₂ Rᶠ = 0.92).

3.2.4 Reduction of Sulphur-Nitrogen Compounds by Molten Salts

S₄N₃Cl (1.86g, 9.05 mmole) and pre-dried KCNS (2.13g,
21.96 mmole) were ground together in dry box conditions and the resulting mixture placed in a sublimation tube fitted with a liquid nitrogen cold finger. The tube was then evacuated and the temperature slowly raised to the melting point of the KCNS (oil bath temperature of 165°C). The volatile species produced at this temperature were sublimed on to the cold finger over a period of 4h. A deeply coloured sublimate was obtained which did not change in appearance on warming to room temperature. The vessel was left under vacuum for four months to allow any polymerisation to occur. The vessel was then opened under dry box conditions and the infra-red spectrum of the sublimate recorded.
Infra-red spectrum (nujol mull): 1165w, 1000w, 928s, 728m, 705vs, 675w, 552s, 348vs cm\(^{-1}\) (cf. \(S_4N_4\)\(^{66}\) and \(S_4N_3Cl\)\(^6\))

3.3 Discussion

It has been noted in this thesis (Chapter Two, page 28) that solid phase halide transport reactions occur on grinding potassium bromide or cesium iodide with 4-phenyl-1,2,3,5-dithiadiazolium chloride. Hence due to the similarities in the heterocyclic ring between the dithiadiazolium cation and the thiodithiazyl cation (both have a 5-membered ring, the \(-CN_2S_2^+\) ring having 6\(\pi\)-electrons and the \(S_3N_2^+\) cation having 7\(\pi\)-electrons), the solid phase halide transport reactions of \(S_3N_2Cl\) were investigated.

KCl, KBr and CsI discs of \(S_3N_2Cl\) were made and their infra-red spectra compared, using the KCl/\(S_3N_2Cl\) disc as a control. Little or no shifting of the peaks in the KBr/\(S_3N_2Cl\) disc relative to the KCl/\(S_3N_2Cl\) disc were noted whereas significant shifting in the bands occurred in the CsI/\(S_3N_2Cl\) disc, relative to the KCl/\(S_3N_2Cl\) disc. The infra-red spectrum of the CsI/\(S_3N_2Cl\) was compared with a series of standard infra-red spectra of sulphur-nitrogen systems and was concluded to be consistent with that of \(S_4N_4\)\(^{66}\). Thus a reduction of the thiodithiazyl cation appeared to have occurred.

There are very few examples of the reduction of sulphur-nitrogen cations, the only one being that reported by Muthmann and Clever (1896)\(^{68}\) in which they reduced \(S_4N_2Cl\) to \(S_4N_4\) and \(S_5N_2\) with zinc using methanol as a solvent. Reductions of \(S_4N_3Cl\) by HI and KI (in conc. HCl) were reported by Padma and Muthy (1971) who reduced the \(S_4N_2^+\) cation to sulphur or hydrogen sulphide, ammonia, hydrogen chloride and iodine.
It was therefore decided to investigate the reductions of the readily available sulphur-nitrogen cations (\(S_3N_2^+\)Cl\(^-\), \(S_2N_2^+\)Cl\(^-\) and \(S_2N_2Cl^+\)Cl\(^-\)) and trichlorotrithiatriazene (NSC\(_3\)).

3.3.1 The Reduction of Sulphur-Nitrogen Species by Iodide

Having observed the solid phase reduction of thiodithiazylic chloride (\(S_3N_2Cl\)) by iodide in an infra-red disc (experiment 3.2.1(i), page 114) preparative scale, solid phase reductions were investigated (experiment 3.2.1(ii), page 114). The product was separated by extraction using 1,4-dioxan, yielding a brown precipitate which was identified from its infra-red spectrum, to be \(S_4N_4\). Due to the low yield of product obtained by the solid phase reaction technique, solvents were sought in which solution reductions could be investigated. The relatively high dielectric constant of nitromethane (\(\varepsilon = 35.9\))\(^{70}\) and the absence of unsaturated centres and hydroxylic hydrogens, indicated that nitromethane would be a suitable solvent for the reduction of sulphur-nitrogen cations by iodides. Both \(S_3N_2Cl\) and \(S_2N_2Cl\) were successfully reduced by iodide in nitromethane solution yielding tetrasulphur tetranitride (experiments 3.2.1(iii), (iv), page 115). The yields recorded were not as high as initially expected. However these were improved by evaporating the solvent off using a stream of dry nitrogen, rather than pumping off the solvent under reduced pressure. The pumping off of the solvent under reduced pressure lowered the recorded yields due to \(S_4N_4\) being removed with the solvent into the muck traps.

In an attempt to obtain high yields of \(S_4N_4\) using cheap easily obtainable solvents, sulphur-nitrogen cations were reacted with saturated solutions of \(NaI\) in ice cold water, ethanol and methanol. In all cases hydrolysis of the S/N species
occurred but some $\text{S}_4\text{N}_4$ was isolated. In the reaction of $\text{S}_2\text{N}_2\text{Cl}$ with NaI in ice cold water (experiment 3.2.1(v), page 116), reduction was shown to occur by the formation of a red-purple carbon tetrachloride phase. The yield of $\text{S}_4\text{N}_4$ from experiment 3.2.1(v) was approximately 15% thus being a synthetically non-viable route to $\text{S}_4\text{N}_4$.

Sulphur dioxide was investigated as a possible solvent for the reduction of $\text{S}_4\text{N}_2\text{Cl}$ by NaI (experiment 3.2.1(vi), page 116). The solubility of NaI in $\text{SO}_2$ is high (1.5g in 10g of $\text{SO}_2$ at $0^\circ\text{C}$)\textsuperscript{71} and thus the NaI should be completely dissolved under the conditions employed in experiment 3.2.1(vi). The expected reduction did not however occur under these mild conditions, $\text{S}_4\text{N}_3\text{I}$ being the only $\text{S}/\text{N}$ product.

Although the reduction of $\text{S}/\text{N}$ cations by iodide in nitromethane solution provided a useful route to crude $\text{S}_4\text{N}_4$, difficulty was found in separating the iodine, produced as a by-product of the reduction reactions, from the tetrasulphur tetranitride. Therefore reducing agents not producing a by-product that was difficult to separate from the reduced $\text{S}/\text{N}$ species were sought.

### 3.3.2 Reduction of Sulphur-Nitrogen Species by the Sodium Salts of the Oxy-acids of Sulphur

The reduction of the sulphur-nitrogen cations ($\text{S}_3\text{N}_3^{+}\text{Cl}^-$, $\text{S}_3\text{N}_2^{+}\text{Cl}^-$ and $\text{S}_3\text{N}_2\text{Cl}^{+}\text{Cl}^-$) by sodium metabisulphite ($\text{Na}_2\text{S}_2\text{O}_5$) were investigated predominantly in nitromethane ($\text{CH}_3\text{NO}_2$) solutions (experiments 3.2.2(i)-(iii), pages 117-118). In all cases reduction of the cations to $\text{S}_4\text{N}_4$ occurred with the evolution of sulphur dioxide. The yields of $\text{S}_4\text{N}_4$ recorded were generally in the region 45-55%. Again yields of $\text{S}_4\text{N}_4$
were improved by the evaporation of the solvent at atmospheric pressure rather than at reduced pressure due to the removal of $S_4N_4$ into the muck traps with the solvent at reduced pressures. The lower than expected yields for the reduction reactions using sodium metabisulphite are thought to be due to the water of crystallisation possessed by the reducing agent ($Na_2S_2O_5\cdot7H_2O$), which is difficult to remove without dissociating the salt into $Na_2SO_3$ and $SO_2$.

It is also noted that although sodium metabisulphite and sodium dithionite are generally regarded as reasonably strong reducing agents in aqueous solution, their reducing power is likely to be significantly modified in other solvents. This is typified by the reaction of $S_3N_2Cl$ with sodium dithionite ($Na_2S_2O_4\cdot2H_2O$) in $CH_3NO_2$, (experiment 3.2.2(v), page 119). No reduction reaction occurred using sodium dithionite as the reducing agent, the only reaction being the thermal cracking of $S_3N_2Cl$ into $S_4N_3Cl$.5

The reduction of various sulphur-nitrogen systems by saturated, ice cold, aqueous solutions of sodium metabisulphite were investigated. The reaction of $S_4N_2Cl$ with the aqueous reducing solution (experiment 3.2.2(iv), page 118) was the most successful, almost certainly due to the relative stability of the $S_4N_2^+$ cation to hydrolysis w.r.t. $S_3N_2^+$ and $S_3N_2Cl^+$. Tetrasulphur tetranitride was obtained in approximately 15% yields which, although significant due to the lack of complete hydrolysis of the reduction intermediates, was of little synthetic value.

Due to the problems of drying the metabisulphite and dithionite salts without their decomposition and due to their modified reducing power in aprotic solvents, no further
investigations using these reducing agents were done. In order to avoid problems with water and unwanted side products the investigations were switched to the use of metals as reducing agents. Smith\textsuperscript{72} and Fielder did however continue to study the reductions of S/N species by reducing anions e.g. \( S_2O_3^{2-} \), \( C_2O_4^{2-} \) and \( H_2PO_2^- \), and recorded yields of \( S_4N_4 \) in the region of 40-60%.

3.3.3 The Reduction of Sulphur-Nitrogen Systems by Metals

There are numerous examples, in both main group and transition metal chemistry, of metals reacting with halogen containing organic species, forming the organometallic compound and the metal halide (equations 3.36-3.34):\textsuperscript{73}

\[
\begin{align*}
R X + 2Li & \rightarrow RLi + LiX \\
4MeI + 2As & \rightarrow Me_4As^+I^- + AsI_3 \\
ClSiMe_2CH_2Cl + Mg & \rightarrow (Me_2SiCH_2)_2 + MgCl_2 \\
2CrCl_3 + 3Zn + 12CO & \rightarrow 2Cr(CO)_6 + 3ZnCl_2 \\
3CrCl_3 + 2Al + AlCl_3 + 6C_6H_6 & \rightarrow 3 (\pi-C_6H_6)_2Cr^+AlCl_4^+ 
\end{align*}
\]

Hence it seemed likely that both main group and transition metals would reduce the sulphur-nitrogen cations and also trichlorotrithiatriazene, to \( S_4N_4 \) and the metal chloride. The postulated advantages of using metals as reducing agents were:

(a) the ease of removing all traces of moisture;
(b) the ease of separation of the excess metal and metal chloride from the reduced product;
(c) the expected non-participation of the metal chlorides in the reaction.
Various transition metals were successfully employed as reducing agents (Fe, Zn and Hg) in a number of organic solvents (CH$_3$NO$_2$, monoglyme, T.H.F. and 1,2-dichloroethane). Group I metals (Na and K) reacted with the sulphur-nitrogen species (experiment 3.2.3(a), page 119) initially producing $S_4N_4^-$ (identified from T.L.C.). Further reduction then occurred yielding initially a deep blue solution, then a purple solution which did not change colour on adding more reducing metal. It is likely that the blue and purple solutions observed are due to the presence of the $S_3N_3^-$ and $S_4N_5^-$ anions. Due to their previous isolation and the highly explosive nature of the sulphur-nitrogen anions the salts were not isolated.

Probably the best synthetic routes to $S_4N_4^-$ by the reductions of S/N species using metals in organic solvents are:

1. Reduction of (NSCl)$_3$ by Fe using monoglyme as a solvent.
2. Reduction of $S_4N_3Cl$ by Fe using nitromethane as a solvent.
3. Reduction of $S_4N_3Cl$ by Zn using T.H.F. as a solvent.
4. Reduction of $S_3N_2Cl$ by Zn using T.H.F. as a solvent.

The reduction of S/N species by transition metals does therefore present a convenient synthetic route to $S_4N_4^-$. There is however one major yield reducing factor. In certain cases the metal chloride produced as a by-product is Lewis acidic in nature. Thus it reacts with the chlorine containing S/N starting material, or an intermediate, forming the MCl$_4^-$ anion which stabilises the S/N cation making the S/N species less prone to reduction (equation 3.41).

$$S_4N_3^+Cl^- + FeCl_3 \rightarrow S_4N_3^{+}FeCl_4^-$$ (3.41)
The formation of such salts is known to occur particularly when using CH$_3$NO$_2$ as a solvent, due to the isolation and characterisation of the salts from their infra-red spectra. Hence in the case of the reduction of S$_4$N$_3$Cl with Fe in CH$_3$NO$_2$, 25% of the S/N starting material is stabilised, w.r.t. reduction, as the FeCl$_4^-$ salt.

A second by-product formed in the reduction of S$_3$N$_2^+$, S$_3$N$_2$Cl$^+$ and S$_4$N$_3^+$ by metals is tetrasulphur dinitride (S$_4$N$_2$). Hence sulphur is not, as originally believed, formed in the primary reaction sequence. The overall equation for the reduction of S$_4$N$_3^+$ by Fe (in CH$_3$NO$_2$) must therefore take into account the formation of S$_4$N$_4^-$, S$_4$N$_2^-$ and S$_4$N$_3^+$FeCl$_4^-$ (equation 3.42).

$$\frac{16}{3} S_4N_3Cl + \frac{4}{3} Fe \xrightarrow{CH_3NO_2} 2S_4N_4 + 2S_4N_2 + \frac{4}{3} S_4N_3^+FeCl_4^-$$ (3.42)

The reduction of S$_4$N$_3$Cl by Fe using a coordinating ether as the solvent (monoglyme or T.H.F.) does not however produce an identical series of products. S$_4$N$_4^-$ and S$_4$N$_2^-$ are isolated but one species present in the insoluble products appears, from its infra-red spectrum (1280m, 1240m, 1180m, 1115m, 1065s, 1015s, 980m, 860s(sh), 850s, 800m, 555s, 410m, 370s, 355s cm$^{-1}$) to be the 1:1 adduct between FeCl$_3$ and monoglyme (CH$_3$OCH$_2$CH$_2$OCH$_3$).

(Infra-red spectrum of FeCl$_3$:C$_4$H$_{10}$O$_2$: 1282m, 1240m, 1200mw, 1181m, 1112m, 1065s, 1014vs, 980m, 862ms, 850s, 804m, 555m cm$^{-1}$). 75

Hence the formation of the S$_4$N$_3^+$FeCl$_4^-$ salt is not observed due to the sequestering of the iron (III) chloride by the solvent. The effect of the solvent in determining the nature of the products is highlighted in the reduction of
trichlorotrithiatriazene \((\text{NSCl}_3)\) by iron, using as a solvent (i) monoglyme \((\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3)\) and (ii) nitromethane \((\text{CH}_3\text{NO}_2)\). 

\((\text{NSCl}_3)\) was initially reduced by iron using monoglyme as the solvent and good yields of \(S_4N_4\) were obtained (table 3.1, page 120). However subsequent work by Fielder, whilst attempting to increase the yield of \(S_4N_4\) using \(\text{CH}_3\text{NO}_2\) as the solvent, produced cyclopentathiapentazenium tetrachloroferrate \((\text{III})\)(\(S_5N_5^{+}\text{FeCl}_4^-\)) in yields of ca. 55%.

Hence the nature of the final product of the reaction was determined solely by the coordinating power of the monoglyme sequestering out the \(\text{FeCl}_3\) which, in the case of the \(\text{CH}_3\text{NO}_2\) reduction, entered into the reaction mechanism (equations 3.43, 44).

\[
4(\text{NSCl})_3 + 4\text{Fe}_{\text{monoglyme}} \rightarrow 3S_4N_4 + 4\text{C}_4\text{H}_10\text{O}_2\cdot\text{FeCl}_3 \quad (3.43)
\]

\[
5(\text{NSCl}) + 4\text{Fe}_{\text{CH}_3\text{NO}_2} \rightarrow 3S_5N_5^{+}\text{FeCl}_4^- + \text{FeCl}_3 \quad (3.44)
\]

The reaction of trichlorotrithiatriazene with tetrasulphur tetranitride and iron \((\text{III})\) chloride, has been reported by Banister and Dainty (1972),\(^{31}\) to produce cyclopentathiapentazenium tetrachloroferrate \((\text{III})\). It can therefore be suggested that the initial reaction of iron with trichlorotrithiatriazene produces tetrasulphur tetranitride and iron \((\text{III})\) chloride, which in the presence of \((\text{NSCl})_3\) reacts, by an identical mechanism postulated by Banister and Dainty, forming \(S_5N_5^{+}\text{FeCl}_4^-\).

The reductions of \(S_4N_3\text{Cl}\) and \(S_3N_2\text{Cl}\) by metals are believed to follow essentially the same mechanistic route. It has been observed that on extracting \(S_3N_2\text{Cl}\) with refluxing \(\text{CH}_3\text{NO}_2\), \(S_4N_3\text{Cl}\) is isolated as a fine yellow precipitate and \((\text{NSCl})_3\) from solution. Hence it is concluded that the reductions of \(S_3N_2\text{Cl}\) in refluxing solvents probably proceed via \(S_4N_3\text{Cl}\), the
rate determining step being the rate at which $S_4N_3Cl$ is produced. The first step in the mechanism in which both $S_3N_2Cl$ and $S_4N_3Cl$ are reduced by metals is, therefore, postulated to be a one electron reduction of the $S_4N_3^+$ cation.

A suggested mechanism for the reduction of the $S_4N_3^+$ cation and subsequent formation of $S_4N_4$ and $S_4N_2$ is given in Figure 3.5.

**FIGURE 3.5** A possible mechanism for the reduction of $S_3N_2^+$ and $S_4N_3^+$ by metals and the subsequent rearrangement reactions.

\[
\begin{align*}
2S_3N_2Cl(s) & \rightarrow 2S_3N_2Cl(_{\text{soln}}) \rightarrow S_4N_3^+Cl^- + NSCl + \frac{1}{2}S_8 \\
S_4N_3^+ + e^- & \rightarrow [S_4N_3]^+ \\
2S_2N_2 & \rightarrow S_4N_4 \\
2[NS'] & \rightarrow S_2N_2 \rightarrow \frac{1}{2}S_4N_4
\end{align*}
\]
Smith \(^{72}\) has shown that thermal cracking of \(S_4N_3Cl\) occurs in refluxing solutions of nitromethane, yielding \(S_4N_4\) (cf. vapour phase cracking \(^{76}\)).

The reactions of metals with sulphur-nitrogen species were, therefore, carried out in liquid sulphur dioxide at ambient temperatures in order to show that \(S_4N_4\) is produced via a reduction mechanism and not via a thermal rearrangement process (section 3.2.3c, page 121). The main experiments of interest in this series of experiments are the reactions of chlorothiodithiazyl chloride (\(S_3N_2Cl_2\)) and trichlorotriazia- triazene (\(S_3N_3Cl_3\)) with the metals iron and mercury. Sulphur dioxide does not form stable isolatable complexes with Lewis acid chlorides (cf. monoglyme, THF \(^{75}\)) and hence the formation of Lewis acidic chlorides will affect the course of the re-

\[
\begin{align*}
4\text{NSCl} & \xrightarrow{\text{Metal}} S_4N_4 \\
2S_4N_2 & \underset{\text{in solution}}{\xrightarrow{\Delta}} S_4N_4 + 4S \quad (\text{ref. 44})
\end{align*}
\]
action to a greater or lesser extent depending upon the strength of the Lewis acid.

3.3 The Reactions of Sulphur Nitrogen Species with Metals using Sulphur Dioxide as a Solvent

The reaction of trichlorotrithiatriazene with iron produced $S_5N_5^{+}FeCl_4^{-}$ (experiment 3.2.3(c,ii), page 121) in approximately 60% yields. The reaction was quite rapid being essentially complete within 30 min. The $S_5N_5^{+}$ salt is isolated in a virtually pure state, there being no $S_4N_4$ or $S_4N_2$ impurities. The salt is highly soluble in $SO_2$ crystallising out of the solvent as deep orange crystals.

The reaction of $S_3N_3Cl_3$ with excess mercury (experiment 3.2.3(c,vi), page 124) was very rapid, possibly due to the high surface area presented by the mercury. The product was filtered off from the excess mercury and identified by T.L.C. and infra-red spectroscopy as $S_4N_4$.

From the above results it is surmised that, as stated previously, the nature of the final products in the reduction of sulphur-nitrogen species by metals is a function of the Lewis acidic strength of the chloride formed as the by-product. The iron (III) chloride is a strong enough Lewis acid, in sulphur dioxide solution, to abstract chloride ions from either the sulphur-nitrogen starting material or an intermediate, thus forming an ionic product ($S_5N_5^{+}FeCl_4^{-}$). However mercury chloride is not a powerful enough Lewis acid, in sulphur dioxide, to affect the basic reduction reaction and thus $S_4N_4$ is the sole sulphur-nitrogen product (figure 3.6).
As observed in the reaction of trichlorothri印花学iene with iron, the formation of the iron (III) chloride intermediate plays a significant role in the determination of the overall mechanism of the reaction. The compound produced in the reaction of chlorothiothri印花学iene chloride with iron is, as expected, by analogy with \( S_3N_2Cl \) reaction, the tetrachloroferrate (III) salt of a sulphur-nitrogen cation. The infra-red spectrum of the cation is however, significantly different from that of any of the sulphur-nitrogen cations previously synthesised. The compound was analysed as having the stoichiometry, \( S_5N_4FeCl_4 \). Using the guidelines set down by Banister for calculating the number of \( \pi \)-electrons associated with sulphur-nitrogen heterocycles, it can be seen that the cation \( S_5N_4^+ \) is an odd electron species (cf. \( S_3N_2^+ \)) and therefore the cation will probably exist as \( S_{10}N_8^{2+} \).
There are at least three possible structures for \( S_{10}N_8^{2+} \). Two structures based on two \( S_4N_4^+ \) units connected by a disulphide bridge (Figures 3.7a, b) and one structure based on a \( S_4N_4 \) cage and two \( S_2N_2^+ \) units (Figure 3.7c).

**Figure 3.7** Structures based on two \( S_4N_4^+ \) rings and a disulphide bridge

(a) **Structure 1**

(b) **Structure 2** (cf. \( S_4N_5^{+} \))
Without an X-ray crystal structure of the compound it is impossible to arrive at a firm conclusion as to the configuration of the postulated $S_{10}N_8^{2+}$ cation. However certain structures seem more likely than others purely by virtue of the synthetic route used to prepare the species. In structure 3 the basic units upon which the structure is based are postulated to be $S_3N_2^+$ and $S_4N_4$. The $S_3N_2^+$ unit is readily formed by the dechlorination of the $S_3N_2Cl^+$ cation and the $S_4N_4$ unit by the subsequent reduction of the $S_3N_2^+$ cation by the metal, (cf. the reductions of $S_3N_2Cl$ by metals, table 3.1, page 120). An overall reaction scheme may therefore be postulated for the reaction of $S_3N_2Cl_2$ with iron forming a species with structure 3 (equation 3.45).
Mechanisms by which structures 1 or 2 could be formed can be devised. However due to the ease with which the reaction proceeds, it would appear unlikely that significant breakdown of the "S\textsubscript{2}N\textsubscript{2}" ring occurs, which would probably have to be invoked for a structure containing a disulphide bridge. Further support for the conclusion that S\textsubscript{10}N\textsubscript{8}\textsuperscript{2+} is based upon an S\textsubscript{4}N\textsubscript{4} cage and two S\textsubscript{2}N\textsubscript{2}\textsuperscript{+} rings is drawn from the reactions of Group VI polycations with S\textsubscript{4}N\textsubscript{4} (Chapter Six, page 276).

The basic unit around which all of the products are based in the reactions of Se\textsubscript{4}\textsuperscript{2+}(AsF\textsubscript{6}\textsuperscript{-})\textsubscript{2}/S\textsubscript{4}N\textsubscript{4} (ratios 1:2 and 2:1) and in the reaction of S\textsubscript{8}\textsuperscript{2+}(AsF\textsubscript{6}\textsuperscript{-})\textsubscript{2}/S\textsubscript{4}N\textsubscript{4} (ratio 1:2) is the S\textsubscript{3}N\textsubscript{2}\textsuperscript{+} or Se\textsubscript{2}SN\textsubscript{2}\textsuperscript{+} unit.

The soluble product isolated from both the reactions of S\textsubscript{8}\textsuperscript{2+}(AsF\textsubscript{6}\textsuperscript{-})\textsubscript{2} and Se\textsubscript{4}\textsuperscript{2+}(AsF\textsubscript{6}\textsuperscript{-})\textsubscript{2} with S\textsubscript{4}N\textsubscript{4} (ratio 1:2) gave the same infra-red spectrum as that noted for the S\textsubscript{10}N\textsubscript{8}\textsuperscript{2+} cation. In the case of the selenium reaction the analytical result implied a low selenium substitution into the cation. This is almost certainly due to the substitution of one or both of the "S\textsubscript{2}N\textsubscript{2}" units by "S\textsubscript{2}S\textsubscript{2}N\textsubscript{2}" units. The low percentage
substitution of \( \text{SSe}_2\text{N}_2 \) rings for \( \text{S}_3\text{N}_2 \) rings in the \( \text{S}_{10}\text{N}_8^{2+} \) cation (structure 3) is probably due to a sulphur-sulphur inter-ring bond being more favoured than a sulphur-selenium inter-ring linkage and thus the former is more prevalent.

The structure postulated for \( \text{S}_{10}\text{N}_8^{2+} \) (structure 3) is based on two previously reported species, \( \text{S}_3\text{N}_2\text{Cl}^+ \) \(^49\) and \( \text{S}_4\text{N}_4\text{F}_2 \) \(^78\). The \( \text{S}_3\text{N}_2 \) rings will adopt the same structure as in \( \text{S}_3\text{N}_2\text{Cl}^+ \), the sulphur to which the chlorine would be attached in \( \text{S}_3\text{N}_2\text{Cl}^+ \) being bonded to the sulphur of the \( \text{S}_4\text{N}_4 \) ring.

The \( \text{S}_4\text{N}_4 \) ring will adopt the same conformation as in \( \text{S}_4\text{N}_4\text{F}_2 \) \(^78\) the sulphurs to which the fluorines would be attached in \( \text{S}_4\text{N}_4\text{F}_2 \) being bonded to the \( \text{S}_3\text{N}_2 \) units (figure 3.8).

Figure 3.8 A Diagrammatic representation of the structural units from which \( \text{S}_{10}\text{N}_8^{2+} \) may be regarded as being constructed.
Interpretation of the infra-red spectrum observed for the species \((S_{10}N_8^{2+})(FeCl_4^-)_{2}\), using the known infra-red spectra of the basic units \((S_2N_2Cl^+\) and \(S_4N_4F_2\)) is not feasible, due to the mass of the substituents on each ring. Hence whereas \(S_4N_4F_2\) is an \(S_4N_4\) ring with two substituents of M.W. = 19, in \(S_{10}N_8^{2+}\) the substituents can be regarded as cations of M.W. = 124. The effects of the increase in mass of the substituents and the inherent charge will change the basic infra-red spectrum of \(S_4N_4F_2\) very significantly but it is not possible to determine the overall effects of this change.

(iii) Reaction of Chlorothiodithiazyl Chloride with Mercury

The reaction of \(S_2N_2Cl_2\) with mercury as the reducing metal and sulphur dioxide as the solvent, was studied with first, a great excess of mercury and second, with only a slight excess of mercury (experiment 3.2.3(c,vii), page 124). The reaction with a great excess of mercury proceeded rapidly producing \(S_4N_4\) and \(S_4N_2\) (cf. table 3.1, page 120). However in the second reaction in which less mercury was used, two distinct products were formed, one soluble and the other insoluble. The soluble product was readily identified from its infra-red spectrum and by its thin layer chromatogram (compared with standard \(S_4N_4\) sample) as \(S_4N_4\). However the insoluble component contained a species which gave an infra-red spectrum significantly different to any of the products previously isolated from the reductions of sulphur-nitrogen species by metals. By analogy with the reaction of mercury with trichlorotrithiatriazene it seems likely that the mercury chloride produced in the reaction will not affect the reduction mechanism by abstracting chloride ions from the sulphur-nitrogen.
starting material or an intermediate. Hence it is concluded that the species must either be a neutral sulphur-nitrogen species or a mercury thionitrosyl. The solubility of the species was tested in various solvents and was found to be, to all intents and purposes, negligible in non-polar or non-coordinating solvents (benzene, di-ethyl ether and hexane). Hence it is suspected that the species is not a neutral sulphur-nitrogen compound (cf. solubility of $S_4N_4$, $S_4N_2$ and $(\text{NSCl})_3$ in benzene). It therefore appears as though the species is either a mercury thionitrosyl or a mercury chloride/sulphur-nitrogen heterocycle adduct. From the colour of the compound, pink-red, it can be deduced that the species is not $\text{Hg(NS}_7\text{)}_2$ (cream)\textsuperscript{79} or $\text{Hg}_5(\text{NS})_8$(green)\textsuperscript{3}. It is known that the compound dissociates yielding $S_4N_2$ and $S_4N_4$ in tetrahydrofuran at room temperature. It may therefore be suggested that the compound is an $\text{HgCl}_2$ adduct which dissociates in T.H.F. with the formation of an $\text{HgCl}_2\cdot\text{THF}$ adduct\textsuperscript{80}, $S_4N_4$, and $S_4N_2$. It has however been reported by Heal that $\text{Hg(NS}_7\text{)}_A$ dissociates, on heating, yielding $S_4N_2$. Hence the decomposition of both an adduct and a thionitrosyl can be postulated to give the observed products.

3.3 Attempts to product $(\text{SN})_x$ by the Reduction of Sulphur-Nitrogen Species

Reactions of $S_4N_3\text{Cl}$ with activated metal surfaces, (e.g. with Mg isolated from a Grignard reaction and with molten alkali metals) using solvents failed to produce $(\text{SN})_x$. The reported methods of producing $(\text{SN})_x$ are by the vapour phase cracking of $S_4N_4$\textsuperscript{81}. Hence the reduction of $S_4N_3\text{Cl}$ by molten KNCS, in vacuo, was attempted (experiment 3.2.4, page 125). It was hoped that the S/N fragments formed in
the reduction process would sublime on to a cold finger and thus polymerise. Although a very deeply coloured sublimate was formed the infra-red spectrum, recorded four months after its formation, indicated the presence of \( \text{S}_4\text{N}_2\text{Cl} \) and \( \text{S}_4\text{N}_4 \) only.

3.4 Conclusions

From work reported in this thesis and that of Smith,\(^7^2\) it can be seen that \( \text{S}_4\text{N}_2\text{Cl}, \text{S}_3\text{N}_2\text{Cl}, \text{S}_3\text{N}_2\text{Cl}_2 \) and \( (\text{NSCl})_3 \) are all reduced with ease by a wide range of reducing agents, yielding \( \text{S}_4\text{N}_4 \) and \( \text{S}_4\text{N}_2 \) as an impurity.

The formation of \( \text{S}_4\text{N}_4 \) by an \textit{in situ} method allows a considerable number of synthetic reactions involving \( \text{S}_4\text{N}_4 \) to be done without the isolation of the intrinsically explosive nitride. The reduction of sulphur-nitrogen species forming \( \text{S}_4\text{N}_4 \) \textit{in situ} may therefore, represent a useful industrial method of preparing the nitride for organic synthetic reactions.\(^8^2\)

The use of sulphur dioxide as a solvent has facilitated the isolation of a series of intermediates and the determination of various aspects of the mechanism by which metals reduce sulphur-nitrogen species.

In work, subsequent to that reported in this thesis, Hauptman\(^8^3\) and Smith\(^8^4\) have concentrated on the vapour phase reduction of \( \text{S}_4\text{N}_2\text{Cl} \) using metals and sodium iodide and have isolated various halogen doped sulphur-nitrogen polymers. Although solution reductions are no longer being investigated, the vapour phase work is continuing in earnest, as the route represents the first synthetically viable procedure for preparing analogues of \( (\text{SN})_x \) without the use of the potentially hazardous \( \text{S}_4\text{N}_4 \).
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CHAPTER FOUR

THE INVESTIGATION OF SYNTHETICALLY VIABLE ROUTES TO SULPHUR-NITROGEN-FLUORINE COMPOUNDS

4.1 Introduction

Little work had been done in the field of sulphur-nitrogen-fluorine chemistry until 1955 when Glemser synthesised a series of compounds, \((S_4N_4F_4, SN_2F_2,\) and NSF), by reacting tetrasulphur tetranitride with silver difluoride. Since then, a range of S/N/F compounds have been prepared, (mainly by Glemser et al.) and their spectral properties studied by many groups throughout the world. Structural studies indicate that these species adopt both cyclic and acyclic configurations, in which delocalisation across the sulphur-nitrogen bonds occurs. There are two main reviews by Mews and Glemser (1972, 1976) which cover most aspects of sulphur-nitrogen-fluorine chemistry to date.

4.1.1 Thiazyl fluoride \((N=S-F)\)

Preparation

Thiazyl fluoride has been prepared by a variety of routes:

(a) NSF is produced by the oxidative fluorination of systems containing S-N bonds.

Tetrasulphur tetranitride is fluorinated by several powerful fluorinating agents, e.g. silver difluoride, cobalt trifluoride \(^{15}\), and mercury difluoride \(^{17}\) (equation 4.1).

\[
S_4N_4 + 4HgF_2 \rightarrow 4NSF + 2Hg_2F_2
\]

\(S_4N_4\) may also be fluorinated using selenium tetrafluoride \((SeF_4)\) \(^{18}\), sulphur tetrafluoride \((SF_4)\) \(^{19}\) or
iodine pentafluoride (IF₅)¹⁸, or in a low temperature reaction with elemental fluorine²⁰, generally giving NSF in low yields (figure 4.1).

(b) Ammonia reacts with sulphur-fluoride species to produce thiazyl fluoride (equation 4.3)¹⁸,²¹

\[
\text{SF}_4 + 4\text{NH}_3 \xrightarrow{20^\circ\text{C} \text{ flow system}} \text{NSF} + 3\text{NH}_4\text{F} \tag{4.2}
\]

(c) Reactions of nitrogen trifluoride with sulphur²¹ or metal sulphides²³ (equations 4.3 and 4.4).
Thiazyl fluoride has also been observed as a product in flash photolysis reactions between nitrogen trifluoride and carbon disulphide or carbon oxide sulphide (COS)\textsuperscript{24}.

(d) Reactions of sulphur tetrafluoride (SF\textsubscript{4}) with nitrogen containing species:

\[
\text{Ph}_3\text{P} = \text{N-R} + \text{SF}_4 \quad \rightarrow \quad \text{F}_2\text{S} = \text{N-R} + \text{Ph}_3\text{PF}_2 \\
\downarrow \\
\text{N = S-F + RF} \\
71\% \text{ when R = Si(CH}_3)_3; (\text{ref.}\textsuperscript{25})
\]

\[
\text{H}_2\text{N-C-NH}_2 + 2\text{SF}_4 \quad \rightarrow \quad \text{F-C-NSF}_2 + \text{NSF} + 4\text{HF} \quad (\text{ref.}\textsuperscript{26})
\]

(e) Thiazyl fluoride is produced by the decomposition of S/N/F compounds, (equations 4.7 - 4.9).

\[
\text{S}_4\text{N}_4\text{F}_4 \quad \xrightarrow{\text{CCl}_4, \text{reflux}} \quad 4\text{NSF} \quad (\text{ref.}\textsuperscript{15})
\]

\[
\text{F-C-N = SF}_2 \quad \xrightarrow{\text{CsF, 20°C}} \quad \text{COF}_2 + \text{NSF} \quad (\text{ref.}\textsuperscript{26,27})
\]

\[
\text{Hg(\text{NSF}_2)_2} \quad \xrightarrow{110°C, \text{high vacuum}} \quad \text{HgF}_2 + 2\text{NSF} \quad (\text{ref.}\textsuperscript{30})
\]

Most of the reactions cited above produce thiazyl fluoride in relatively low yields, although reactions 4.5 and 4.9 are synthetically viable. Equation 4.9 is the route cited in most recent papers.\textsuperscript{28,29} The production of thiazyl
fluoride by the decomposition of the mercury salt is virtually quantitative, and little purification is required as no other volatile species are formed.

The mercury derivative, \( \text{Hg(\text{NSF}_2)}_2 \), was first prepared in 1969 by Glemser et al.\(^\text{30}\) from the reaction of mercury difluoride with N-fluoroformyliminosulphur difluoride (\( \text{SF}_2 = \text{NC(0)F} \)); the latter was synthesised by Clifford and Kobayashi\(^\text{31}\) using silicon tetraisocyanate with \( \text{SF}_4 \):

\[
\text{SF}_4 + \text{Si(}\text{NCO}\text{)}_4 \quad \xrightarrow{100^\circ\text{C}} \quad \frac{4}{\text{hr}} \quad \text{sealed tube} \quad \text{SF}_2 = \text{NCOF}
\]

\[
2\text{SF}_2 = \text{NC(}\text{O}\text{)}\text{F}+ \xrightarrow{24}{\text{hr}} \quad \text{HgF}_2 \quad \xrightarrow{\text{room temp.}} \quad \text{Hg(\text{NSF}_2)}_2 + \text{COF}_2
\]

The mercury derivative can be recrystallised from chloroform, yielding colourless, monoclinic needles, which decompose slowly in glass at room temperature.

The thermal cracking of the mercury species (equation 4.9), at 110\(^\circ\text{C in vacuo}\) is the preferred route to thiazyl fluoride, being essentially quantitative. It is known that thiazyl fluoride cannot be stored at room temperature without decomposition.\(^\text{13}\) Thus, the above method provides a useful synthetic route, as the mercury derivative may be stored indefinitely at low temperatures under nitrogen.

**Structure**

The structure of thiazyl fluoride (Figure 4.2) has been elucidated from infra-red\(^\text{32}\) and microwave spectra\(^\text{33}\), and the force constants calculated\(^\text{34}\) (Table 4.1).
Figure 4.2 Structure of thiazyl fluoride; (distances in pm).33

![Image of thiazyl fluoride structure]

Table 4.1 Force constants, bond lengths and X-S-N bond angles for various sulphur-nitrogen species.34

<table>
<thead>
<tr>
<th>Species</th>
<th>S-N stretching force constant $k_{SN}$ (N m$^{-1}$)</th>
<th>S-N bond length (pm)</th>
<th>S-X stretching force constant $k_{SX}$ (N m$^{-1}$)</th>
<th>S-X bond length (pm)</th>
<th>X-S-N bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N\equivSF_3$</td>
<td>1255</td>
<td>141.6</td>
<td>449</td>
<td>155.2</td>
<td></td>
</tr>
<tr>
<td>$N\equivS^+$</td>
<td>1185</td>
<td>(143)</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>$N\equivS-Cl$</td>
<td>1070.9</td>
<td>144.6</td>
<td>287.1</td>
<td>164.6</td>
<td>116° ± 52'</td>
</tr>
<tr>
<td>$N\equivS-Br$</td>
<td>987.5</td>
<td>(145)</td>
<td>138.0</td>
<td>216.1</td>
<td>117° ± 46'</td>
</tr>
</tbody>
</table>

Peake and Down34 noted that the S-N stretching force constant ($k_{SN}$) was high in all thiazyl halides, the value of $k_{SN}$ decreasing with decreasing electronegativity of the halide. The value of $k_{SX}$ (the S-X stretching force constant) was noted as being low relative to that found in comparable systems. A simple qualitative molecular orbital treatment was invoked to explain these values, (figure 4.3). The interaction of the halogen with $S\equivN$ causes partial delocalisation of the odd electron of the $[S\equivN]$ radical.
Figure 4.3 Molecular orbital scheme for NSX

Br (4p)  ----  ----  ----
Cl (3p)  ----  ----  ----

F (2p)  ----  ----  ----

X  XSN  SN

σ*  π*  σ
(contained in the $p_{\pi}^*$ orbital), into the sulphur-halogen molecular orbital. The degree of delocalisation is directly related to the electronegativity of the halogen. Thus, when the halogen is fluorine, the sulphur-fluorine bonding MO is similar in energy to that of the $p_z$ atomic orbital of fluorine. It is therefore suggested that there is a significant ionic contribution to the sulphur-fluorine bond. Hence, the S-F bond will have a rather low stretching force constant, whereas the partial removal of an electron from the $p_{\pi}^*$ orbital of $[S=\mathbf{N}]^-$ has the effect of enhancing the sulphur-nitrogen stretching force constant.

**Spectral and Thermodynamic Data**

(a) **Gas phase infra-red spectrum**

<table>
<thead>
<tr>
<th>Branch</th>
<th>Frequency (cm$^{-1}$)</th>
<th>Intensity</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>P</td>
<td>356</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>380</td>
<td>s</td>
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</tr>
<tr>
<td>P</td>
<td>627</td>
<td>vs</td>
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</tr>
<tr>
<td>R</td>
<td>651</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>640</td>
<td>vs</td>
<td>$v_2$</td>
</tr>
<tr>
<td>R</td>
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<td>$v_2 + v_3$</td>
</tr>
<tr>
<td>P</td>
<td>1270</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1283</td>
<td>m</td>
<td>$v_2 + v_2$</td>
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<td>1295</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td>P</td>
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<td>s</td>
<td>$v_1$</td>
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<td>Q</td>
<td>1372</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>1387</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1720</td>
<td>vw</td>
<td>$v_3 + v_1$</td>
</tr>
<tr>
<td></td>
<td>1920</td>
<td>vw</td>
<td>$v_2 + v_2 + v_2$</td>
</tr>
<tr>
<td></td>
<td>2020</td>
<td>vw</td>
<td>$v_1 + v_2$</td>
</tr>
<tr>
<td></td>
<td>2730</td>
<td>w</td>
<td>$v_1 + v_1$</td>
</tr>
</tbody>
</table>

**TABLE 4.2 Gas phase infra-red data for thiazyl fluoride**
(b) $^{19}_{32}\text{F}_{n.m.r.}$

$\nu = 24071080 \text{ Hz}$

$\nu_{\text{reference (KF)}} = 24062460 \text{ Hz}$

Chemical shift, ($\delta$) = $3.58 \times 10^4 \text{ ppm}$

**Standard Heats of Formation and Bond Dissociation Energies**

<table>
<thead>
<tr>
<th>Date</th>
<th>$\Delta H^0_{\text{f298}}$ NSF(g)</th>
<th>$D^0(\text{N-S})$</th>
<th>$D^0(\text{S-F})$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1968</td>
<td>$+125$</td>
<td>$339$</td>
<td>$-$</td>
<td>35</td>
</tr>
<tr>
<td>1970</td>
<td>$(+172 \pm 8)$</td>
<td>$297 \pm 21$</td>
<td>$-$</td>
<td>36</td>
</tr>
<tr>
<td>1973</td>
<td>$(-20.9 \pm 3.7)$</td>
<td>$526 \pm 13.8$</td>
<td>$380 \pm 25.1$</td>
<td>37</td>
</tr>
</tbody>
</table>

**Chemical Reactions**

Thiazyl fluoride (m.p. = $-89^\circ \text{C}$; b.p. = $0.4^\circ \text{C}$) is highly moisture sensitive. It is recommended that the synthesis of NSF be carried out in quartz or polythene apparatus due to the reaction of thiazyl fluoride with glass to form silicon tetrafluoride.$^{15}$

Due to the instability and difficulty of handling NSF, only a few reactions have been reported. (figure 4.4, page 159)

4.1.2 Oligmeric Forms of Thiazyl Fluoride: $\text{Trifluorotrithiatriazene (S}_3\text{N}_3\text{F}_3)$

Preparation

Trifluorotrithiatriazene ($S_3N_3F_3$) may be prepared by three routes:

(a) fluorination of $S_4N_4$ with fluorine at low temperatures$^{38}$

(b) the exchange reaction between trichlorotrithiatriazene with silver difluoride (equation 4.10)

$$S_3N_3Cl_3 + AgF_2 \rightarrow S_3N_3F_3 \quad (\text{ref.}^{39}) \quad (4.10)$$
Figure 4.4 Réactions of Thiazyl Fluoride

\[
\begin{align*}
\text{NSF}^+ & \text{MF}_6 \quad (87) \\
\text{AsF}_5 & \quad \text{SbF}_5 \\
\text{AgF}_2 & \\
(2)_\text{NSF}_3 & \\
\text{Cl}_2 & \\
(15)_{\text{NSC}_1} & \\
\text{CF}_3\text{CFCF}_2 & \\
\text{HF} & \\
\text{H}_2\text{NSF}_3 & \\
(\text{CF}_3)_2\text{CFSN}:\text{NSC} & \\
\text{NH}_4\text{F} + \text{SF}_4 & (14)
\end{align*}
\]
(c) polymerisation of thiazyl fluoride.\textsuperscript{22}

Structure

Trifluorotrithiatriazene forms colourless, highly reactive crystals, which crystallise in the space group $R_3\overline{1} - C_{31}$ with a hexagonal cell,\textsuperscript{40} (Figure 4.5).

Figure 4.5 Crystal Structure of $\text{N}_3\text{S}_3\text{F}_3$.\textsuperscript{40}

The equivalence of bond lengths implies extensive delocalisation of the $\pi$-system,\textsuperscript{40} as observed in $(\text{NSCl})_3$.\textsuperscript{41}

Spectral Data

(a) Infra-red spectrum\textsuperscript{17}

1080s, 720s, 650s cm\textsuperscript{-1}

(b) $^{19}\text{F} \text{nmr}$

$\nu = 24066220$ Hz

$\bar{\nu}_{\text{ref.}}(\text{KF}) = 24062680$ Hz

Chemical shift (8) = $1.47 \times 10^4$ ppm

Chemical shift with CFC\textsubscript{13} as external reference = -44.1 ppm.
Chemical Reactions

(a) Reactions with Lewis acids$^{42-44}$ are summarised in equations 4.11 to 4.14.

\[ S_3N_2F_3 + BF_3 \xrightarrow{\text{liquid SO}_2} S_3N_2F_2^{+}BF_4^{-} \quad (4.11) \]

\[ S_3N_2F_3 + AsF_5 \xrightarrow{\text{liquid SO}_2} S_3N_2F_2^{+}AsF_6^{-} \quad (4.12) \]

\[ S_3N_2F_3 + SbF_5 \xrightarrow{\text{liquid SO}_2} S_3N_2F_2^{+}SbF_6^{-} \quad (4.13) \]

\[ S_3N_2F_2^{+} AsF_6^{-} \xrightarrow{85^\circ C} \text{NS}^+\text{AsF}_6^{-} + 2\text{NSF} \]

(b) Hydrolysis of $S_3N_2F_3$\textsuperscript{13}

\[ \begin{align*}
\text{N} & \equiv \text{S} - \text{F} \\
\text{O} & \\
\text{H} & \\
\end{align*} \quad \xrightarrow{\text{H-N=S=O}} \quad \begin{align*}
\text{N} & \equiv \text{S} - \text{OH} \\
\end{align*} \]

4.1.3 Oligmeric Forms of Thiazyl Fluoride: Tetrafluorotetrathiatetrazocine ($S_4N_4F_4$)

Preparation

Tetrafluorotetrathiatetrazocine ($S_4N_4F_4$) is prepared by the fluorination of $S_4N_4$, using (a) Silver fluoride, (equation 4.15)

\[ S_4N_4 + 4 \text{AgF}_2 \xrightarrow{\text{CCl}_4} S_4N_4F_4 + 4 \text{AgF} \quad (4.15) \]
or

(b) fluorine at low temperatures, (equation 4.16)\textsuperscript{38}

\[ S_4N_4 + 2F_2 \xrightarrow{-78^\circ C} S_4N_4F_4 \] (4.16)

(It should be noted that, unlike \( S_3N_3F_3 \), \( S_4N_4F_4 \) cannot be prepared by the polymerisation of NSF).

**Structure\textsuperscript{11}**

\( S_4N_4F_4 \) crystallises as white needles from carbon tetrachloride. The space group is \( P_{4_2} \).

**Figure 4.6 Structure of \( S_4N_4F_4 \)**

From the X-ray structure (figure 4.6), it is seen that the \( \pi \)-system is localised in tetrafluorotetrathiatetrazoGine.
This contrasts with the delocalised systems of trifluoro-
and trichlorotrithiatriazene.

Physical Properties

Some physical properties of \( \text{S}_4\text{N}_4\text{F}_4 \) are summarised in table 4.3.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>153°C; (decomposes at 128°C)</td>
</tr>
<tr>
<td>Sublimation temp.</td>
<td>80°C (high vacuum)</td>
</tr>
<tr>
<td>Solubility in ( \text{CCl}_4 )</td>
<td>3.448 g dm(^{-3}) at 20°C</td>
</tr>
<tr>
<td>Density</td>
<td>2.326 g cm(^{-3}) at 20°C</td>
</tr>
</tbody>
</table>

Spectral Data

(a) \text{Infra-red spectrum} \(^\text{46}\)

\[ \text{1117, 786, 760, 645, 520 cm}^{-1} \]

(b) \( ^{19}\text{F n.m.r.} \)

\[ \bar{\nu} = 24066420 \text{ Hz} \]

\[ \bar{\nu} \text{ reference (KF) = 24062680 Hz} \]

Chemical shift (\( \delta \)) = \( 1.55 \times 10^4 \) ppm

Singlet at \(-35\) ppm; (\( \text{CFC}1_3 \) as external reference) (ref.\(^\text{13}\))

Reactions

(a) \text{Thermal decomposition (equation 4.17)}

\[ \text{S}_4\text{N}_4\text{F}_4 \xrightarrow{250°C} 4 \text{ NSF} \quad \text{(ref.13)} \]

(b) \text{Hydrolysis (equation 4.18)}

\[ \text{S}_4\text{N}_4\text{F}_4 + 12 \text{ H}_2\text{O} \rightarrow 4\text{NH}_4\text{F} + 4\text{H}_2\text{SO}_3 \quad \text{(ref.13)} \]
Reactions with Lewis acids are summarised in equations 4.19 and 4.20.

\[
\text{excess} \quad S_4N_4F_4 + 4\text{BF}_3 \rightarrow 4\text{NSF} + 4\text{BF}_3 \quad \text{(ref.} \quad ^{42} \text{)} \quad (4.19)
\]

\[
\begin{align*}
S_4N_4F_4 + 2\text{AsF}_5 & \rightarrow \text{NS}^+ \; \text{AsF}_6^- + S_2N_3F_2^+ \text{AsF}_6^- \quad \text{(ref.} \quad ^{45} \text{)} \\
\text{AsF}_5 & \downarrow \\
S_4N_4F_3^+ \text{AsF}_6^- & \rightarrow \text{NS}^+ \; \text{AsF}_6^- + N_2S_2F_3
\end{align*} 
\quad (4.20)
\]

4.1.4 N-substituted Imido-Sulphurous Difluorides, \((R-N=SF_2)\)

(I) \(R = \text{Halogen} ; \) N-halo-imido-sulphurous difluoride

Preparation

All the N-halo-imido-sulphurous difluorides have been reported. The most synthetically viable route is via the mercury bis-imido-sulphurous difluoride, (Figure 4.7)\(^{30,47}\).

Figure 4.7 Formation of \(X-N=SF_2\) (\(X = \text{Halogen}\))

\[
\begin{align*}
\text{Hg(} \text{NSF}_2 \text{)}_2 & \quad \rightarrow \text{FN} = \text{SF}_2 \quad \text{(ref.} \quad ^{47} \text{)} \\
\text{F}_2 ; -78^\circ \text{C} & \quad \rightarrow \text{ClN} = \text{SF}_2 \quad \text{(ref.} \quad ^{30} \text{)} \\
\text{Cl}_2 & \rightarrow \text{BrN} = \text{SF}_2 \quad \text{(ref.} \quad ^{30} \text{)} \\
\text{Br}_2 & \rightarrow \text{IN} = \text{SF}_2 \quad \text{(ref.} \quad ^{30} \text{)} \\
\text{I}_2 ; 50^\circ \text{C} & \rightarrow \text{IN} = \text{SF}_2 \quad \text{(ref.} \quad ^{30} \text{)}
\end{align*}
\]

N-chloro- and N-bromo-imido-sulphurous difluorides may also be synthesised from N-halo-hexamethylsilanes and sulphur tetrafluoride, \(^{48}\) (equation 4.21).

\[
X - N < \text{SiMe}_3^{-} \; \text{SF}_4 \quad \rightarrow \quad X - N = S_{F}^{-} < \text{SiMe}_3 + 2\text{Me}_3\text{SiF} \quad (4.21)
\]
Structure

By comparing the electron diffraction results of N-chloro-imido-sulphurous difluoride \(^4\) with results of an X-ray crystallographic study of \(\text{Hg(NSF}_2\text{)}_2\) \(^5\), it is deduced that both species adopt very similar configurations, (figure 4.8). The S-N bond distance in \(\text{Hg(NSF}_2\text{)}_2\) is very short and is comparable with that in thiazyl trifluoride (141.6 pm) \(^5\) and thiazyl fluoride (144.6 pm). \(^3\) The S-R bond angle in \(\text{Hg(NSF}_2\text{)}_2\) is 130.6\(^\circ\) which is significantly larger than the angle of 120.0\(^\circ\) in the N-chloro-derivative. This is explained by the degree of participation of the nitrogen lone pair in the bonding which opens out the angle. \(^1\)

Figure 4.8 Structures of \(\text{Hg(NSF}_2\text{)}_2\) and \(\text{ClNSF}_2\)
Spectral Data

(a) Infra-red and Raman spectra for the N-Fluoro, N-Chloro-, N-Bromo-, and N-Iodo-Imido· Sulphurous Difluorides.52

The infra-red and Raman frequencies are summarised in table 4.4.

TABLE 4.4 Raman and Infra-red Data for X-N=SF₂;
(I.R. frequencies are in brackets);
(all frequencies in cm⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>F-N=SF₂</th>
<th>Cl-N=SF₂</th>
<th>Br-N=SF₂</th>
<th>IN=SF₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1133(1150)</td>
<td>1176(1200)</td>
<td>1208(1214.7)</td>
<td>(1235)</td>
<td></td>
</tr>
<tr>
<td>770(770)</td>
<td>741(752)</td>
<td>735(745)</td>
<td>(735)</td>
<td></td>
</tr>
<tr>
<td>809(822)</td>
<td>539(548.5)</td>
<td>465(468)</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>611(615)</td>
<td>640(644.5)</td>
<td>593</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>409(409.6)</td>
<td>405</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>165</td>
<td>135</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>696(712)</td>
<td>694</td>
<td>660(699)</td>
<td>(675)</td>
<td></td>
</tr>
<tr>
<td>435</td>
<td>409(409.6)</td>
<td>405</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>145</td>
<td>135</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

Assignments

A vs (N=S)

v_s (S-F)

v (N-X)

δ_s (SF₂)

ω (SF₂)

δ_s (X-N-S)

A v_as (S-F)

ρ (SF₂)

δ_as (S-N-S)

(b) ¹⁴ N n.m.r. spectrum53

¹⁴ N chemical shifts relative to aqueous NH₄⁺ are positive (i.e. downfield); = 127 ppm for Cl-N=SF₂.

Reactions

Reactions with unsaturated systems are summarised in equations 4.22 to 4.28.

\[
\text{Cl-N=SF}_2 + F_2C = CF_2 \xrightarrow{hv} \text{ClF}_2CF_2NSF_2 \quad \text{(ref.}^{54} \text{)} \quad (4.22)
\]

\[
\text{Cl-N = SF}_2 + 2F_2C = CF_2 \xrightarrow{hv} \text{ClF}_2CCF_2CF_2NSF_2 \quad \text{(ref.}^{54} \text{)} \quad (4.23)
\]

\[
\text{Br-N = SF}_2 + F_2C = CF_2 \xrightarrow{90^oC} \text{BrF}_2CCF_2NSF_2 \quad \text{(ref.}^{54} \text{)} \quad (4.24)
\]
\[
2\text{Cl-N} = \text{SF}_2 + 2\text{F}_3\text{C-CP} = \text{CP}_2 \xrightarrow{\text{hv}} \text{P}_3\text{CCFOClCF}_2\text{NSF}_2 \\
\text{(77\%)}
\]

\[
\text{F}_3\text{C} \text{C-N=N} + \text{Cl-N} = \text{SF}_2 \xrightarrow{120^\circ \text{C}} \frac{2 \text{hr.}}{2} \text{Cl-C-N} = \text{SF}_2 \quad \text{(ref. 55)}
\]

\[
\text{Br-N = SF}_2 + \text{F}_3\text{C} \xrightarrow{60^\circ \text{C}} \frac{5 \text{hr.}}{2} \text{Br-C-N} = \text{SF}_2 \quad \text{(ref. 55)}
\]

\[
\text{Br-N = SF}_2 + \text{F}_3\text{CO} \xrightarrow{120^\circ \text{C}} \frac{2 \text{hr.}}{2} \text{Br-C-N} = \text{SF}_2
\]

Reactions 4.27 and 4.28 are believed to proceed by one of two mechanisms:

(i) via homolytic fission of the N-X bond and subsequent free radical attack.\(^56\)

(ii) by an addition mechanism.\(^57\)

R = Alkyl or Aryl; N-Substituted-Alkyl and Aryl Imido-Sulphurous-Difluorides

This large and varied group of compounds is covered in an excellent review by Glemser and Mews\(^39\) (1972) and is therefore not discussed in detail in this thesis. Some reactions of the R-N = SF\(_2\) system with various R groups are summarised in equations 4.29 to 4.32.

\[
\text{R-N} = \text{SF}_2 + 2\text{ClF} \rightarrow \text{RCl}_2 + \text{SF}_4 \quad \text{(ref. 29)}
\]

\[
\text{(R = FCO, CF}_3\text{CO, CF}_3, \text{CF}_3\text{O}_2\text{CF, and F}_2\text{SN(CF}_2)_2)}
\]

\[
\text{R-N} = \text{SF}_2 + 3\text{HF} \rightarrow \text{SF}_4 + \text{R-NH}_2\text{F}^- \quad \text{(ref. 14)}
\]

\[
\text{R-N} = \text{SF}_2 + 2\text{F}_2 \xrightarrow{\text{CsF}} \text{R-N-SF}_5 \quad \text{(ref. 59)}
\]
\[
CH_3N = SF_2 + Cl_2 \xrightarrow{-HCl} CH_2ClN = SF_2 \\
\quad + CHCl_2N = SF_2 \\
\quad + CF_3N = SCl_2 \text{ (ref.}60) \quad (4.32)
\]

(Note that chlorine does not add across the double bond).

4.1.5 Thiazyl Trifluoride (N\(\equiv\)SF\(_3\))

**Preparation**

There are four main preparative routes to thiazyl trifluoride (N\(\equiv\)SF\(_3\)), (equations 4.33 to 4.36).

\[
S_4N_4 + 12 AgF_2 \xrightarrow{\text{reflux, CCl}_4} NSF_3 \text{ (refs.}15,17) \quad (4.33)
\]

\[
NSF + 2 AgF_2 \xrightarrow{38^\circ C, 16 \text{ hr.}} NSF_3 \text{ (ref.}61) \quad (4.34)
\]

\[
OCFNSF_2 + 2 AgF_2 \xrightarrow{150^\circ C} \text{ (COF}_2 \text{)} \\
\]

\[
S_2F_{10} + NH_3 \xrightarrow{\text{flow system}} NSF_3 + SF_4 + 3HF \text{ (ref.}62) \quad (4.35)
\]

**Structure**

The structure of thiazyl trifluoride has been determined from infra-red,\(^3^2\) n.m.r.,\(^3^2\) microwave\(^5^1\) and photoelectron\(^6^3\) spectra, (figure 4.9).

Figure 4.9  Structure of N\(\equiv\)SF\(_3\)\(^5^1\)
Spectral Data

(a) Vibrational spectrum\textsuperscript{32,64}

The vibrational spectrum is summarised in Table 4.5.

<table>
<thead>
<tr>
<th>Branch</th>
<th>Frequency (cm\textsuperscript{-1})</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Calculated Frequency (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>324</td>
<td>m</td>
<td>( \delta_{\text{NSF}} : \nu_6 ) (E)</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>332</td>
<td>m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>342 (340 dp)</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>351</td>
<td>m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>415</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>429 (430 dp)</td>
<td>s</td>
<td>( \delta_{\text{SF}_3} : \nu_5 ) (E)</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>441</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>510</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>521 (520 dp)</td>
<td>s</td>
<td>( \delta_{\text{S(SF}_3)) : \nu_3 ) (A\textsubscript{1})</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>535</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>667</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>678</td>
<td>w</td>
<td>( \delta + \nu_6 )</td>
<td>684</td>
</tr>
<tr>
<td>R</td>
<td>690</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>769 (768 p)</td>
<td>s</td>
<td>( \delta_{\text{S(SF}_3}) ) (A\textsubscript{1})</td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>775</td>
<td>s</td>
<td>( \nu_2 ) (A\textsubscript{1})</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>782</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>811 (812 dp)</td>
<td>vs</td>
<td>( \nu_{\text{as(SF)}} : \nu_4 ) (E)</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>861</td>
<td>m</td>
<td>( \nu_5 + \nu_5 )</td>
<td>858</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>( \nu_3 + \nu_6 )</td>
<td>863</td>
</tr>
<tr>
<td>P</td>
<td>940</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>952</td>
<td>w</td>
<td>( \nu_3 + \nu_5 )</td>
<td>950</td>
</tr>
<tr>
<td>R</td>
<td>965</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1155</td>
<td>w</td>
<td>( \nu_4 + \nu_6 )</td>
<td>1153</td>
</tr>
</tbody>
</table>
### TABLE 4.5 (contd.)

<table>
<thead>
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<th>Branch</th>
<th>Frequency (cm(^{-1}))</th>
<th>Intensity</th>
<th>Assignment</th>
<th>Calculated Frequency (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>1241</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>1256</td>
<td>w</td>
<td>(v_4 + v_5)</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>1504</td>
<td>s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1515 (1512 p)</td>
<td>s</td>
<td>(v_1(A_1) : v_{SN})</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>1530</td>
<td>s</td>
<td></td>
<td></td>
</tr>
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<td>P</td>
<td>1540</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1551</td>
<td>sh</td>
<td>(v_2 + v_2)</td>
<td>1550</td>
</tr>
<tr>
<td>R</td>
<td>1566</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1582</td>
<td>m</td>
<td>(v_1 + v_4)</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1615</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1625</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1635</td>
<td>m</td>
<td>(v_4 + v_4)</td>
<td>1622</td>
</tr>
<tr>
<td>-</td>
<td>1643</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>1860</td>
<td>w</td>
<td>(v_1 + v_6)</td>
<td>1857</td>
</tr>
<tr>
<td>P</td>
<td>1930</td>
<td>sh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q</td>
<td>1950</td>
<td>w</td>
<td>(v_1 + v_5)</td>
<td>1944</td>
</tr>
<tr>
<td>R</td>
<td>1966</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>2040</td>
<td>w</td>
<td>(v_1 + v_3)</td>
<td>2036</td>
</tr>
<tr>
<td>-</td>
<td>2300</td>
<td>w</td>
<td>(v_1 + v_4)</td>
<td>2290</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(v_1 + v_2)</td>
<td>2326</td>
</tr>
<tr>
<td>-</td>
<td>2420</td>
<td>vw</td>
<td>(v_4 + v_4 + v_4)</td>
<td>2433</td>
</tr>
<tr>
<td>-</td>
<td>3040</td>
<td>vw</td>
<td>(v_1 + v_1)</td>
<td>3030</td>
</tr>
</tbody>
</table>

(dp = depolarised; p = polarised)

(b) \(^{19}F\) n.m.r.

\[ \bar{v} = 2406623 \text{ Hz for NSF}_3 \]

\[ \bar{v}_{\text{reference}}(KF) = 24062128 \text{ Hz} \]

Chemical shift (\(\delta\)) = 1.87 x 10\(^4\) ppm.
Thermodynamic and Physical Data

Some physical\textsuperscript{13} and thermodynamic\textsuperscript{36} properties of thiazyl trifluoride are summarised in table 4.6.

**TABLE 4.6 Some physical and thermodynamic properties of N=S\textsubscript{SF}._{3}**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>$-72.6 \pm 0.5^\circ C$</td>
</tr>
<tr>
<td>b.p.</td>
<td>$-27.1 \pm 1.0^\circ C$</td>
</tr>
<tr>
<td>$\Delta H^\circ_{f298}(g)$</td>
<td>$-356.5 \pm$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$D^\circ$ (N-S)</td>
<td>$418 \pm 8.4$ kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$D^\circ$ (S-F)</td>
<td>$318 \pm 29$ kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

---

Selected Reactions of Thiazyl Trifluoride

NSF$_3$ is both chemically and thermally very stable; (c.f. sulphur hexafluoride as opposed to thiazyl fluoride). It does not react with dilute acids,\textsuperscript{13} and reacts only at 300$^\circ$C with metallic sodium.\textsuperscript{13}

(a) Addition reactions to the sulphur-nitrogen multiple bond

Some addition reactions to the S=N triple bond in thiazyl trifluoride are summarised in equations 4.37 to 4.43.

$$\text{N}=\text{SF}_3 + 2\text{HF} \xrightarrow{20^\circ C} \text{H}_2\text{N} - \text{SF}_5$$ (ref.\textsuperscript{65}) \hspace{1cm} (4.37)

$$\text{N}=\text{SF}_3 + 2\text{ClF} \xrightarrow{-78^\circ C} \text{Cl}_2\text{N-SF}_5$$ (ref.\textsuperscript{67}) \hspace{1cm} (4.38)

$$\text{N}=\text{SF}_3 + \text{SF}_4 \xrightarrow{180^\circ C} \text{BF}_3$$ \hspace{1cm} (4.39)

$$2 \text{N}=\text{SF}_3 + 3\text{BCl}_3 \xrightarrow{20^\circ C} \left[\text{N(SCl}_2\right] + \left[\text{BCl}_4\right]^-$$

$$+ \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{Cl}_2 + 2\text{BF}_3$$ (ref.\textsuperscript{68}) (4.40)
Thiazyl trifluoride forms adducts with BF₃, AsF₅ and SbF₅ (equations 4.44). The structures of the products have been elucidated from their vibrational spectra, there being no evidence of fluoride ion abstraction by the Lewis acids.

\[ \text{N} \equiv \text{SF}_3 + 2 \text{LiN} (\text{CR}_3) \text{SiR}_3 \overset{-70^\circ \text{C}}{\text{THF}} \rightarrow \text{Me}_3 \text{Si} - \text{N} = \text{S} = \text{N} - \text{CMe}_3 \quad (\text{ref. } 69) (4.41) \]

\[ \text{N} \equiv \text{SF}_3 + \text{CF}_3 \text{-CF} = \text{CF}_2 \overset{90^\circ \text{C}}{\text{CsF}} \rightarrow (\text{CF}_3)_2 \text{CF} - \text{N} = \text{SF}_2 \quad (\text{ref. } 70) \quad (4.42) \]

\[ \text{N} \equiv \text{SF}_3 + \text{COF}_2 \rightarrow \text{O} = \text{C} = \text{N} - \text{SF}_5 \quad (\text{ref. } 71) \quad (4.43) \]

(b) **Adduct chemistry**
4.2 Experimental

**Fluorination of Sulphur-Nitrogen Species with Chlorine Monofluoride**

(a) **Tetrasulphur Tetranitride and Chlorine Monofluoride**

(1) **Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:6)**

Chlorine monofluoride (0.3267g, 5.99 mmole) was condensed, (in three aliquots) onto tetrasulphur tetranitride (0.1808g, 0.983 mmole) contained in a predried, vacuum tight, teflon vessel. The reaction was held at -78°C for 15 minutes between additions to allow a controlled reaction to occur. The system was warmed slowly, (over a period of 6 hours), to room temperature and kept there for 10 hours. The volatiles were sampled at various slush bath temperatures, and identified by their infra-red, Raman, and $^{19}$F n.m.r. spectra (Table 4.7). (The volatiles identified at one slush bath temperature were removed before sampling at a higher temperature).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>N$_2$</td>
</tr>
<tr>
<td>-78</td>
<td>SF$_5$Cl; SF$_4$; (SOF$_2$); Cl$_2$</td>
</tr>
<tr>
<td>Room temp.</td>
<td>NSF; SF$_4$</td>
</tr>
</tbody>
</table>

*(Standard spectra referenced in Appendix A, page 313)*

The volatiles present at room temperature were completely removed and the infra-red and Raman spectra of the residue (0.1853g) were recorded.
Infra-red spectrum (nujol mull): 1100 m, br(sh), 1052 s, br(sh), 1015 vs, 970 s, br(sh), 695 s, 618 w, 588 m, 500 s, br, 465 m, 422 w, 388 m cm⁻¹.

Raman spectrum (green line): 1022 vs, 964 s, 718 w, 694 w, 595 m, 488 m, 482 m, 460 w, 432 w, 406 w, 380 m, 340 s, 324 m, 212 m, 208 m, 188 m, 182 m, 178 m, 110 s cm⁻¹.

¹⁹F n.m.r. of the volatiles present at -78°C (reference CCl₃F):

Chemical shifts = 75.9 ppm and 81.1 ppm.

(ii) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:5)

Chlorine monofluoride (0.16g, 2.94 mmole) was condensed, (in four aliquots), on to S₄N₄ (0.11g, 0.60 mmole) contained in a Monel vessel. The system was warmed to -95°C for 15 minutes, and to -78°C for a further 30 minutes, between additions. After all the ClF had been added, the reaction was warmed slowly, (over a period of 6 hours), to room temperature. This temperature was maintained for 12 hours. The gas phase infra-red and Raman spectra of the volatiles were recorded at different slush bath temperatures (table 4.8). (At each slush bath temperature, the observed products were removed before further sampling).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>N₂</td>
</tr>
<tr>
<td>-95</td>
<td>SF₄; SO₂F₂; SF₅Cl</td>
</tr>
<tr>
<td>-78</td>
<td>SF₄; Cl₂; SO₂F₂; SF₅Cl</td>
</tr>
<tr>
<td>-22</td>
<td>SO₂F₂; NSF; SO₂ClF</td>
</tr>
<tr>
<td>Room temp.</td>
<td>NSF; SO₂ClF; SO₂F₂</td>
</tr>
</tbody>
</table>

(Standard spectra referenced in Appendix A, page 31)
The volatiles present at room temperature were completely removed and the infra-red spectrum of the residue (0.16g) recorded.

Infra-red spectrum (nujol mull): 1050 s, br(sh), 1017 vs, 970 s, 800 w, 698 s, 660 w, 632 m, 590 s, 553 w, 520 s, 508 m(sh), 468 m, 465 m, 422 w, 410 vw, 390 s cm⁻¹.

(iii) Tetrasulphur tetranitride and chlorine monofluoride (ratio 1:1.1)

ClF (0.12g, 2.20 mmole) was condensed on to $S_4N_4$ (0.37g, 2.01 mmole) contained in a predried, vacuum tight, Monel vessel. The reaction was warmed slowly from -78°C to room temperature (over a period of 4 hours) and maintained at room temperature for 10 hours. The volatiles were identified at various slush bath temperatures and the weight loss, on removal of the volatiles at each slush bath temperature recorded (table 4.9).

**TABLE 4.9 Volatiles observed at various slush bath temperatures after the reaction between $S_4N_4$ and ClF (1:1.1)**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Species identified</th>
<th>Weight of volatiles (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>$N_2$</td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>-78</td>
<td>$SF_4$</td>
<td>0.04</td>
</tr>
<tr>
<td>-22</td>
<td>$SF_4$; NSF</td>
<td>0.05</td>
</tr>
<tr>
<td>Room temp.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(Standard spectra referenced in Appendix A, page 313)

All the volatiles present at room temperature were removed and the infra-red spectrum of the residue (0.38g) recorded.
Infra-red spectrum (nujol mull): 1080 m, 1018 s, 952 m(sh), 922 s, 895 m, 791 w, 776 w, 722 m, 700 s(sh), 698 s, 690 s(sh), 687 s(sh), 662 m, 630 w, 582 w, 558 s(sh), 550 s, 520 w, 510 w, 464 s cm$^{-1}$.

$^{19}$F n.m.r. (reference perfluorobenzene): no signals.

(iv) **Tetrasulphur tetranitride and chlorine monofluoride** (ratio 1:16)

$S_4N_4$ (0.1988g, 1.08 mmole) was placed in a predried vacuum tight, Monel vessel and pumped on for 2 hours. ClF (2 line atmos., 0.2740g, 5.03 mmole) was condensed into the vessel and the reaction warmed to -78°C for 20 minutes. On addition of a second aliquot of ClF (2 line atmos.) a reaction was observed to occur forming an incondensable gas. This gas was removed from the system and the reaction warmed to -55°C for 30 minutes. No further incondensable gas was formed. A third aliquot of ClF (2 line atmos.) was added and the formation of the same gas was noted. This was removed and the system held at -55°C for 30 minutes. The final aliquot of ClF (0.5 line atmos.) was then added, with the production of the non-condensable gas. After removal of this product, the system was warmed to room temperature and maintained there for 12 hours. The pressure, gas phase spectra, and weight loss on removal of the volatiles at the various slush bath temperatures were recorded (table 4.10).

Sulphur dioxide was added to the volatiles present at -78°C to test for ClF by the formation of sulphuryl chloride fluoride ($SO_2ClF$) which has a strong and distinctive infra-red spectrum. No $SO_2ClF$ was formed, implying that no chlorine monofluoride was present.

No residue was obtained from the reaction.
TABLE 4.10 Volatiles observed at various slush bath temperatures after the reaction between $\text{S}_4\text{N}_4$ and $\text{ClF}$ (1:16)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
<th>Species identified</th>
<th>Weight of volatiles (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>730</td>
<td>$\text{N}_2$</td>
<td>0.06</td>
</tr>
<tr>
<td>-78</td>
<td>290</td>
<td>$\text{SF}_4$; $\text{Cl}_2$</td>
<td>1.06</td>
</tr>
<tr>
<td>Room temp.</td>
<td>10</td>
<td>$\text{SF}_4$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

(Standard spectra referenced in Appendix A, page 313).

(b) Trichlorotrithiatriazene and Chlorine Monofluoride

(i) Trichlorotrithiatriazene and chlorine monofluoride (ratio 1:3)

Chlorine monofluoride, (0.09g, 1.65 mmole), was condensed, (in three aliquots), onto trichlorotrithiatriazene ($\text{(NSCl)}_3$), (0.13g, 0.53 mmole), contained in a predried, vacuum tight, Monel vessel. The reaction was warmed to -78°C for 45 minutes between additions. After the final addition, the system was warmed to room temperature over a period of 6 hours. This temperature was maintained for 10 hours and the volatiles sampled at various slush bath temperatures (table 4.11).

TABLE 4.11 Volatiles observed at various slush bath temperatures after the reaction of $\text{(NSCl)}_3$ and $\text{ClF}$ (1:3)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>40</td>
<td>$\text{N}_2$</td>
</tr>
<tr>
<td>-78</td>
<td>220</td>
<td>$\text{Cl}_2$; $\text{SF}_4$; $\text{SOF}_2$</td>
</tr>
<tr>
<td>Room temp.</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>

(Standard spectra referenced in Appendix A, page 313)
The volatiles present at room temperature were completely removed, and the infra-red and Raman spectra of the residue (0.10 g) were recorded.

**Infra-red spectrum (nujol mull):** 1017 vs, 698 m, 646 w, 618 w, 554 w, 519 s, 390 s cm\(^{-1}\).

**Raman spectrum** (green line): 700 vw, 620 w, 495 m, 432 w, 376 s, 336 vs, 320 s, 211 w, 192 vs, 178 vs, 107 vs cm\(^{-1}\).

(ii) **Trichlorotrithiatriazene and chlorine monofluoride (ratio 1:3) at elevated temperatures**

ClF (0.97 g, 17.80 mmole) was condensed onto (NSC1)_3 (1.33 g, 5.44 mmole) contained in a predried Monel vessel. The temperature of the vessel was increased slowly to room temperature and then to 60°C. This temperature was maintained for 35 hours. The system was cooled to -196°C, -78°C, -22°C and 0°C using a series of slush baths. The pressure, gas infra-red phase spectra, and weight of the volatiles present at each temperature were recorded (table 4.12).

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
<th>Weight of volatiles (g)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>100</td>
<td>0.03</td>
<td>N(_2) (by discharge)</td>
</tr>
<tr>
<td>-78</td>
<td>200</td>
<td>1.09</td>
<td>{SF(_4)<em>; SF(_5)Cl; SF(_6)</em>; Cl(_2)}</td>
</tr>
<tr>
<td>-22</td>
<td>35</td>
<td>0.11</td>
<td>{SF(_4)<em>; SOF(_2)</em>}</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>0.03</td>
<td>SF(_4)*; NSF</td>
</tr>
</tbody>
</table>

*Main product*

(Standard spectra referenced in Appendix A, page 313)
The volatiles present at room temperature were completely removed and the infra-red and Raman spectra of the residual pale yellow, sublimed, crystals (1.03g) were recorded.

**Infra-red spectrum** (nujol mull): 1017 vs, 698 s, 514 s, 389 s cm\(^{-1}\).

**Raman spectrum** (green line): 702 w, 691 w, 619 w, br, 495 m, 456 w, 438 w (sh), 432 m, 376 s, 336 vs, 320 s, 211 m, 192 vs, 178 vs, 107 vs cm\(^{-1}\).

(iii) **Trichlororothiatriazene and chlorine monofluoride (ratio 1:3) at prolonged elevated temperature**

ClF (1.07g, 19.63 mmole) was condensed, (in two aliquots), on to (NSCl\(_3\)) (1.42g, 5.81 mmole). The temperature was slowly raised from -78°C to 80°C. This final temperature was maintained for 94 hours. The system was then cooled and the volatiles collected in slush baths of varying temperatures. The pressure, gas phase infra-red spectra and weight of the volatiles at each temperature were recorded (table 4.13). There was no residue.

**TABLE 4.13 Volatiles observed at various slush bath temperatures after the reaction of (NSCl\(_3\)) and ClF (1:3) at 80°C**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr)</th>
<th>Weight of volatiles (g)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>820</td>
<td>0.22</td>
<td>N(_2)</td>
</tr>
<tr>
<td>-78</td>
<td>165</td>
<td>0.39</td>
<td>SF(_4)*; SOF(_2); SF(_6); SF(_5)Cl</td>
</tr>
<tr>
<td>-22</td>
<td>80</td>
<td>0.16</td>
<td>SF(_4)<em>; S(_2)Cl(_2)</em></td>
</tr>
<tr>
<td>0</td>
<td>440</td>
<td>1.21</td>
<td>S(_2)Cl(_2)<em>; SCl(_2)</em></td>
</tr>
<tr>
<td>Room temp.</td>
<td>210</td>
<td>0.50</td>
<td>SCl(_2)</td>
</tr>
</tbody>
</table>

(* Main product)

(Standard spectra referenced in Appendix A, page 313)
(c) Investigation of the Mechanism of the Reaction of Chlorine Monofluoride with Tetrasulphur Tetranitride and Trichlorotrithiatriazene

(1) Thiazyl fluoride and chlorine monofluoride

Thiazyl fluoride (NSF) (100 torr, 0.33 mmole) was condensed into an infra-red gas cell. The spectrum was then recorded, the pressure in the cell being controlled by the condensation of the NSF into an isolatable side arm. The thiazyl fluoride was completely condensed into the side arm, isolated, and ClF (300 torr, 0.99 mmole) expanded into the cell. The valve on the side arm was opened to allow reaction between the gases to occur. The gas phase infra-red spectrum was recorded after 5 and 15 minutes. The spectra were identical.

Infra-red spectrum (gas phase): 894 m(sh), 884 s(sh), 870 s, 862 s, 856 s(sh), 858 s(sh), 732 vs, 723 vs, 712 vs(sh).

From the spectral data, the main infra-red active product was identified as SF₄ (standard spectrum referenced in Appendix A).

(ii) Thiazyl chloride and chlorine monofluoride

Thiazyl chloride (18 torr, 0.06 mmole) was expanded into an infra-red gas cell and the spectrum recorded. Aliquots of ClF were condensed into the cell and the gas phase infra-red spectrum was recorded after each addition. The variations in the spectrum were used to identify the products and hence the mechanistic pathway of the reaction (table 4.14).
TABLE 4.14 Species observed as products in the reaction between NSCl and ClF

<table>
<thead>
<tr>
<th>Total pressure of ClF added (torr)</th>
<th>Approximate ratio of ClF: NSCl</th>
<th>Species observed in the gas phase infra-red spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 : 1</td>
<td>NSCl</td>
</tr>
<tr>
<td>20</td>
<td>1 : 1</td>
<td>NSCl; NSF*, ClNSF₂*</td>
</tr>
<tr>
<td>40</td>
<td>2 : 1</td>
<td>SF₄*; ClNSF₂*</td>
</tr>
<tr>
<td>65</td>
<td>3.5 : 1</td>
<td>SF₄*; ClNSF₂*; NC1₃*</td>
</tr>
<tr>
<td>90</td>
<td>5 : 1</td>
<td>SF₄*; NC1₃*</td>
</tr>
<tr>
<td>165</td>
<td>9 : 1</td>
<td>SF₄*; NC1₃*; ClF</td>
</tr>
</tbody>
</table>

(* Main product)

(Standard spectra referenced in Appendix A, page 313).

(iii) Thiazyl fluoride and chlorine

Thiazyl fluoride (10 torr, 0.033 mmole) was condensed into an infra-red gas cell and the spectrum was recorded. Three aliquots of chlorine were expanded into the gas cell, giving total pressures of (a) 20 torr, (b) 100 torr, and (c) 300 torr. The infra-red spectrum was recorded after each addition, but no change from the spectrum of NSF was observed.

(Standard spectrum of NSF referenced in Appendix A, page 313).

(iv) Thiazyl fluoride and chlorine in the presence of sulphur dioxide

NSF (10 torr, 0.033 mmole) was expanded into a gas cell and its infra-red spectrum recorded. Sulphur dioxide (50 torr) was expanded into the same cell and the spectrum of the NSF/SO₂ mixture recorded. Chlorine (100 torr) was condensed into the gas cell and the infra-red spectrum of the reaction mixture was run 8 times over a period of 28 hours. The intensity of the bands due to sulphuryl chloride
fluoride ($\text{SO}_2\text{ClF}$), thiazyl fluoride and thiazyl chloride were used as an empirical measure of their relative concentrations at any particular time. It was noted that a slow reaction occurred in which $\text{SO}_2\text{ClF}$ and $\text{NSCl}$ were produced, and the concentration of NSF decreased.

(Standard spectra referenced in Appendix A, page 313).
4.3 Discussion

4.3.a Fluorination of Sulphur-Nitrogen Species with Chlorine Monofluoride

Chlorine monofluoride is known to act as a mild fluorinating agent in a number of reactions. It has been particularly successful in the preparation of perfluoroalkyl derivatives of sulphur (IV), sulphur (VI), selenium (IV) and selenium (VI). The fluorination of certain sulphur-nitrogen species by chlorine monofluoride was therefore investigated as a possible route to thiazyl fluoride (NSF).

The envisaged reaction between tetrasulphur tetranitride ($S_4N_4$) and chlorine monofluoride (ClF) was the formation of thiazyl fluoride and chlorine (equation 4.3a),

$$S_4N_4 + 4\text{ClF} \rightarrow 4\text{NSF} + 2\text{Cl}_2$$

$\Delta H^0 = -503 \text{ kJ mol}^{-1}$ (4.3a)

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).

It was however found that on reacting $S_4N_4$ with ClF, in an approximate ratio of 1:4 (experiments 4.2a(i,ii), pages 173, 174), sulphur tetrafluoride ($SF_4$) and trichlorothithiatriazene ((NSCl)$_3$) were the main products. The presence of large volumes of $SF_4$ and the low yield of NSF suggested that ClF was reacting by a mechanism in which one sulphur was completely fluorinated. The lack of fluorine in the residue and the presence of (NSCl)$_3$ and (NSCl)$_4$ (identified by their infrared spectra) indicate that the only fluorinated product is $SF_4$. The weight of residue is consistent with the total fluorine component reacting with $S_4N_4$ forming $SF_4$ and nitrogen and the chlorine component reacting in the ratio 1:1 with the remaining NS units forming thiazyl chloride (NSCl), which then oligomerises producing (NSCl)$_3$ and (NSCl)$_4$, the observed products.
Due to the low yield of thiazyl fluoride from the reactions of chlorine monofluoride with tetrasulphur tetranitride, the exchange-fluorination reactions of chlorine monofluoride with trichloroethatriazine were investigated.

The proposed reaction of ClF with (NSCl)₃ (ratio 3:1) was the formation of trifluorothiatriazene with chlorine as the by-product (equation 4.3b).

\[(\text{NSCl})_3 + 3\text{ClF} \rightarrow (\text{NSF})_2 + 3\text{Cl}_2\]  

\[(4.3b)\]

The initial reaction between (NSCl)₃ and ClF in the ratio 1:3 was carried out under moderate conditions, the temperature not rising above 22°C (experiment 4.2b(i) page 177). The products obtained indicated that the reaction had not gone to completion due to the presence of unreacted (NSCl)₃ and sulphuryl chloride fluoride (SO₂ClF). The presence of SO₂ClF was taken to indicate that ClF remained unreacted, as SO₂ClF is formed by the reaction of SO₂ with ClF,\(^\text{74}\) (The SO₂ being produced as a hydrolysis product of SF₄, a major volatile product of the fluorination reaction). Hence in subsequent investigations the reaction temperature was raised in an attempt to ensure complete reaction. If however too high a temperature is employed for too long a period of time then complete degradation of the sulphur-nitrogen system occurs (experiment 4.2b(iii), page 179). Heating the reaction to 60°C for 35h (experiment 4.2b(ii), page 178) did not cause thermal degradation of the sulphur-nitrogen system but did ensure that complete reaction of the chlorine monofluoride occurred. The major products observed in experiment 4.2b(ii) (table 4.12, page 178) were identified by their vibrational spectra as
Hence it was concluded that the proposed reaction (equation 4.3b) does not occur. It was noted that, in both the reactions of $S_4N_4$ and $(NSCl)_3$ with ClF, the main volatile products were $SF_4$ and $N_2$ and the main product in the residue was $(NSCl)_3$. Thus it is suggested that the reaction of $(NSCl)_3$ with ClF should be regarded as a subsequent reaction to that of $S_4N_4$ with ClF (equation 4.3c,d).

$$S_4N_4 + 4ClF \rightarrow SF_4 + (NSCl)_3 + \frac{1}{2}Cl_2 + \frac{1}{2}N_2$$  \hspace{1cm} (4.3c)

$$\Delta H^\circ = -1155 \text{kJ mol}^{-1}$$

$$\frac{1}{3}(NSCl)_3 + 4ClF \rightarrow SF_4 + \frac{5}{2}Cl_2 + \frac{1}{2}N_2$$  \hspace{1cm} (4.3d)

$$\Delta H^\circ = -585 \text{kJ mol}^{-1}$$

Therefore if the ratio of ClF : $S_4N_4$ is greater than 4 : 1 then the reaction proceeds via equation 4.3d producing $SF_4$ (equation 4.3e).

$$S_4N_4 + 8ClF \rightarrow 2SF_4 + \frac{2}{3}(NSCl)_3 + 3Cl_2 + N_2$$  \hspace{1cm} (4.3e)

$$\Delta H^\circ = -1740 \text{kJ mol}^{-1}$$

(Heats of reaction calculated from standard heats of formation of the gaseous species. See Appendix B, page 319).

The above postulate may be checked by calculating the theoretical weight of the residue from the known number of mmoles of both ClF and $S_4N_4$ or $(NSCl)_3$(assuming that the ratio of ClF : $S_4N_4 \approx 4 : 1$ and the ratio of ClF : $(NSCl)_3 \approx 3:1$) (equation 4.3f,g).

Weight of residue in $S_4N_4$/ClF reactions =

$$\left( No \text{ moles } NS - \frac{No \text{ mole } ClF}{4} \right) \times \text{M.W. of NSCl}$$  \hspace{1cm} (4.3f)
Weight of residue in \((\text{NSCl})_3/\text{ClF}\) reactions =
\[
\left\{ \frac{\text{No moles NSCl} - \text{No mole ClF}}{4} \right\} \times \text{M.W. of NSCl} \quad (4.3g)
\]
and comparing the theoretical weight with the observed (table 4.15):

<table>
<thead>
<tr>
<th>Sulphur-Nitrogen reactant (Expt. No.)</th>
<th>No moles S/N reactant</th>
<th>No moles ClF</th>
<th>Calculated Weight of residue</th>
<th>Observed Weight of residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{S}_4\text{N}_4 (4.2a(ii)))</td>
<td>0.60</td>
<td>2.94</td>
<td>0.14g</td>
<td>0.16g</td>
</tr>
<tr>
<td>((\text{NSCl})_3 (4.2b(i)))</td>
<td>0.53</td>
<td>1.65</td>
<td>0.10g</td>
<td>0.10g</td>
</tr>
<tr>
<td>((\text{NSCl})_3 (4.2b(ii)))</td>
<td>5.46</td>
<td>17.80</td>
<td>0.97g</td>
<td>1.03g</td>
</tr>
</tbody>
</table>

From the results listed in table 4.15 it can be seen that there is close agreement between the calculated and observed residue weights. The observed weights are marginally greater than the calculated. This is believed to be due to a low concentration of \((\text{NSF})_3\) being present. Evidence for this is drawn from the presence of NSF in the volatiles of all the listed reactions. Hence it is suggested that on cooling the vessel to \(-196^\circ\text{C}\) to test for nitrogen in the volatiles, polymerisation of the NSF occurs yielding \((\text{NSF})_3\) which is not completely removed on pumping at room temperature.

If the postulate expressed in equation 4.3f and g is taken to its conclusion then when the ratio of ClF to \(\text{S}_4\text{N}_4\) is greater than or equal to 16 : 1 and the ratio of ClF to \((\text{NSCl})_3\) is greater than or equal to 12 : 1, no residue will be obtained, the only products being \(\text{SF}_4\), \(\text{N}_2\) and \(\text{Cl}_2\) (equation 4.3h,i).

\[
\text{S}_4\text{N}_4 + 16 \text{ClF} \rightarrow 4\text{SF}_4 + 2\text{N}_2 + 8\text{Cl}_2 \quad \Delta H^0 = -2900 \text{ kJ mol}^{-1} \quad (4.3h)
\]
(NSCl)$_3$ + 12ClF $\rightarrow$ 3SF$_4$ + $\frac{3}{2}$ N$_2$ + $\frac{15}{2}$ Cl$_2$

$$\Delta H^0 = -1755 \text{ kJ mol}^{-1}$$ (4.31)

(Heats of reaction calculated from the standard heats of formation of the gaseous compounds. See Appendix B, page 319).

In order to verify that using excess ClF would produce only the gaseous products SF$_4$, N$_2$ and Cl$_2$ (equation 4.3h,i), ClF was reacted with S$_4$N$_4$ in a ratio of 17 : 1 (experiment 4.2a(iv) page 176). A highly exothermic reaction occurred yielding an incondensable gas (nitrogen), chlorine (identified from its Raman spectrum) and sulphur tetrafluoride (identified from its infra-red spectrum). No residue was obtained. From the weights of the volatiles and the lack of residue it was concluded that the reaction proceeds as outlined in equation 4.3h.

If the heat of reaction for the initially postulated reaction of S$_4$N$_4$ with ClF, in a ratio of 1 : 4 (equation 4.3a), is compared with that of the observed reaction (equation 4.3c), then it can be seen that the observed reaction is some 650 kJ mol$^{-1}$ more exothermic than the postulated. Thus the primary reason for the difference between the postulated and observed reactions is the formation of the highly thermodynamically favoured sulphur tetrafluoride.

4.3.b Mechanism by which Thiazyl units react with Chlorine Monofluoride

It is known that chlorine monofluoride adds to unsaturated centres 29, 58, 67, 79, the fluorine attacking the more electropositive end of the multiple bond. Thus it seems likely the ClF would react with NSF by a multistage addition mechanism (cf. ClF/NSF$_3$ 67) forming SF$_4$ as the final fluorinated product (equation 4.3j).
NSF + 3ClF $\rightarrow \frac{1}{2} N_2 + \frac{3}{2} Cl_2 + SF_4$

$\Delta H^0 = -600 \text{kJ mol}^{-1}$

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).

In order to verify that NSF and ClF do react as postulated in equation 4.3j, NSF* and ClF, in a ratio of 1 : 3, were reacted in an infra-red gas cell. The reaction was very rapid forming SF$_4$ as the only infra-red active species. Hence it is believed that any NSF produced in a fluorination reaction will react readily with ClF forming SF$_4$, Cl$_2$ and N$_2$, as indicated by equation 4.3j.

If the reaction of chlorine monofluoride with thiazyl fluoride proceeds via an addition mechanism then the first addition product would be Cl-N = SF$_2$, a known compound, and the second would be Cl$_2$N-SF$_3$ analogous to the species Cl$_2$N-SF$_5$.

Therefore a reaction was devised to observe the intermediates formed in the reaction of thiazyl chloride with chlorine monofluoride ultimately producing sulphur tetrafluoride. The reaction (experiment 4.2c(ii) page 180) was done in a gas phase infra-red cell, aliquots of ClF being added to the NSCl and the species produced being monitored by their infra-red spectra (table 4.14 page 181). After the addition of the first aliquot of ClF to NSCl (ratio 1 : 1), the species observed were NSCl, NSF and ClN = SF$_2$. Hence it is concluded that the mechanism must proceed by an exchange process followed by addition of ClF across the multiple bond of N = S-F (equation 4.3k).

(SF was produced by the chlorine-fluorine exchange of thiazyl chloride on a cesium fluoride column, see experiment 4.4b, (v) page 205).
The presence of NSCl and ClNSF₂ in the gas phase infra-red spectrum indicates that step (a) and (b) must be of similar rates, rather than step (a) being very much faster than step (b). The presence of NSF in the volatiles implies that step (b) is not very much faster than step (a).

After the addition of the second aliquot of ClF (NSCl : ClF = 1 : 2) the main product was ClNSF₂ with traces of SF₄. Thus it is suggested that the thiazyl halides are more activated to attack by chlorine monofluoride than ClN = SF₂. If the rate of addition of ClF to ClNSF₂ was similar or faster than the rate of addition of ClF to N=S-X then a higher concentration of SF₄ would be observed in the gas phase infra-red spectrum. Further addition of ClF to the system caused fluorination of the sulphur and chlorination of the nitrogen producing SF₄ and NCl₂. No Cl₂N-SF₃ was observed. (equation 4.3.l)

\[ \text{ClN} = \text{SF}_2 \xrightarrow{\text{ClF}} [\text{Cl}_2\text{N} - \text{SF}_3] \xrightarrow{\text{ClF}} \text{Cl}_2\text{N} + \text{SF}_4 \quad (4.3.l) \]

Hence an overall reaction mechanism can be suggested for the reaction of chlorine monofluoride with thiazyl chloride (figure 4.10).

The overall reaction of NSCl with ClF is therefore the formation of sulphur tetrafluoride, nitrogen and chlorine (equation 4.3m).

\[ \text{NSCl} + 4\text{ClF} \rightarrow \text{SF}_4 + \frac{5}{2} \text{Cl}_2 + \frac{1}{2} \text{N}_2 \]

\[ \Delta H^\circ = -650 \text{ kJ mol}^{-1} \quad (4.3m) \]

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B, page 319).
4.3.c The reaction of Thiazyl Fluoride with Chlorine

It has been reported by Glemser et al.\textsuperscript{15} that the reaction of thiazyl fluoride with chlorine, in a glass vessel, over a period of ten days, yields silicon tetrafluoride (SiF\textsubscript{4}), thionyl fluoride (SOF\textsubscript{2}), and thionyl chloride (SOCl\textsubscript{2}) as volatiles and trichlorotrithiatriazene (NSCl\textsubscript{3}) as the residue.

Hence from the above information it is concluded that the first step in the reaction sequence must be the formation of thiazyl chloride (equation 4.3n).

\[
\text{NSF} + \text{Cl}_2 \rightarrow \text{NSCl} + \text{ClF} \quad \Delta H^\circ = +50 \text{ kJ mol}^{-1} \quad (4.3n)
\]

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B page 319).

As can be seen from equation 4.3n the proposed reaction step is thermodynamically unfavoured. It is also known from this thesis (experiment 4.2c(ii) page 180) that the reverse reaction occurs readily. Hence initially it would...
appear unlikely that NSF reacts with chlorine, as suggested by Glemser. If however equation 4.3n is regarded as an equilibrium lying in favour of thiazyl fluoride and chlorine, then it could be regarded as the first step in a multistage reaction sequence in which ClF, produced in the first step, reacts with the NSF forming SF$_4$ (equation 4.3.0).

\[
\begin{align*}
\text{3NSF} + 3\text{Cl}_2 & \rightleftharpoons \text{3NSCl} + 3\text{ClF} \\
\text{NSF} + \frac{3}{2} \text{Cl}_2 & \rightarrow \text{SF}_4 + \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{Cl}_2
\end{align*}
\]

(4.3.0)

(The heat of reaction is calculated from the standard heats of formation of the gaseous species. See Appendix B page 319).

In order to show whether ClF is produced, as suggested by equation 4.3.0, a large excess of sulphur dioxide was added to the NSF/Cl$_2$ reaction (Experiment 4.2c(iv) page 181). It is known that there is a rapid reaction between SO$_2$ and ClF$^+$ thus, any ClF produced by the reaction of NSF with Cl$_2$ will be removed as SO$_2$ClF which is readily identifiable by its strong characteristic infra-red spectrum (equation 4.3p).

\[
\begin{align*}
\text{NSF} + \text{Cl}_2 & \rightarrow \text{NSCl} + \text{ClF} & \Delta H^o = +50 \text{ kJ mol}^{-1} \\
\text{ClF} + \text{SO}_2 & \rightarrow \text{SO}_2\text{ClF} & \Delta H^o = -119 \text{ kJ mol}^{-1} (4.3p)
\end{align*}
\]

The heats of reaction are calculated from the standard heats of formation of the gaseous species. See Appendix B page 319.

The rapid formation of SO$_2$ClF by the reaction of ClF with SO$_2$ will cause the equilibrium (equation 4.3n) to be constantly moved in favour of the production of NSCl and ClF.
Thus the observed concentration of $\text{SO}_2\text{ClF}$ should increase with time. The above postulate was borne out by the results obtained from experiment 4.2c(iv) (page 181), in which the concentrations of both $\text{SO}_2\text{ClF}$ and $\text{NSCl}$ increased with time and the concentration of $\text{NSF}$ decreased. Hence it is concluded that the gaseous products observed by Glemser were the products of hydrolysis, and the reaction with glass, of $\text{SF}_4$. The rate of the reaction between thiazyl fluoride and chlorine is very low, as indicated by both experiments 4.2c(iii, iv) (page 181). The low rate of reaction is probably due to the rate determining step being the thermodynamically unfavoured formation of $\text{ClF}$ (Equation 4.3n).

4.3. d The Mechanism by which Chlorine Monofluoride reacts with Tetrasulphur Tetranitride

The reactions of $\text{S}_4\text{N}_4$ with halogens and interhalogens have been widely studied\textsuperscript{39,78,80-83} and compounds of various skeletal arrangements synthesised. Recent work by Zborilova and Gebauer\textsuperscript{83} has shown that the initial product in the chlorination of $\text{S}_4\text{N}_4$ by chlorine is $\text{S}_4\text{N}_4\text{Cl}_2$ and that the initial product in the fluorination of $\text{S}_4\text{N}_4$ by $\text{IF}_5$ is $\text{S}_4\text{N}_4\text{F}_2$. Hence it was postulated that the initial product in the reaction of $\text{S}_4\text{N}_4$ with $\text{ClF}$ would be $\text{S}_4\text{N}_4\text{ClF}$.

In the reaction of $\text{ClF}$ with $\text{S}_4\text{N}_4$, in a molar ratio of 1:1, (experiment 4.2a(iii) page 175), at low temperatures, no evidence was found for the existence of $\text{S}_4\text{N}_4\text{ClF}$ as a stable isolatable species. From the weight and infra-red and $^{19}\text{F}$ n.m.r. spectra of the residue it was concluded that the species present in the residue were $\text{S}_4\text{N}_4$ and $\text{S}_4\text{N}_4\text{Cl}_2$. The presence of $\text{SF}_4$ in the volatiles implies that complete fluorination of one sulphur atom occurs at a
higher rate than the addition of ClF to $S_4N_4$. Using basically the same equation as equation 4.3j but with modifications, (due to lack of chlorine to convert all "SN" units into NSCl), the theoretical weight of residue is calculated as 0.42g (observed = 0.38g). The discrepancy is believed to be due to prolonged pumping at room temperature removing all the $(NSF)_x$ species.

It is suggested that $S_4N_4Cl_2$ is formed by the reaction of chlorine, produced as a by-product of the fluorination reactions of ClF, with $S_4N_4$, (c.f. Zborilova 83). A proposed reaction mechanism for the reaction of chlorine monofluoride with tetrasulphur tetranitride is presented in figure 4.11.

Step (a) in the mechanism is the addition of ClF to the $S_4N_4$ bridge in $S_4N_4$. It seems likely that fluorine, chlorine and chlorine monofluoride will all add 1,5 across the relatively electropositive sulphurs rather than 1,2 across a sulphur-nitrogen bond. Thus the most stable disubstituted $S_4N_4X_2$ ring is formed with the least interaction between highly electronegative substituents. It is not known whether $S_4N_4ClF$ (intermediate I) reacts with ClF by an exchange mechanism (step (b)) followed by an addition mechanism step (c), or by a single addition step (step (d)), to form intermediate III. It can only be surmised that because $S_4N_4Cl_2$ can be fluorinated to $S_4N_4F_2$ 83 without the formation of $SF_4$, then step (b) and (c) may well be preferred to step (d). It is however likely that both routes operate to some extent in the actual mechanism. Intermediate III is then postulated as dissociating into substituted thiazy1 units. Intermediate IV then reacts by an addition mechanism with chlorine mono-
Figure 4.11 Proposed Mechanism by which ClF reacts with $S_4N_4$

\[
\text{X} - S \equiv N + \text{Cl} - S \equiv N + [N \equiv S - N = SF_2] (IV)
\]

\[
\text{ClF} (f) \\
N \equiv S - F + \text{Cl} - N = SF_2
\]
fluoride forming NSF and ClN = SF₂. These latter species then react as previously indicated in equations 4.3k,l forming SF₄, N₂ and Cl₂.

The species observed in the residue are, therefore, formed by the reaction of S₄N₄ with chlorine. It is suggested that once S₄N₄Cl₂ has been produced, then it is this compound that reacts with ClF in preference to S₄N₄ due to the substituted sulphurs being activated to attack by ClF, relative to the sulphurs in S₄N₄. Hence the initial step in the mechanism becomes the chloro-fluoro exchange between S₄N₄Cl₂ and ClF forming S₄N₄ClF (intermediate I) which subsequently reacts by the same mechanism as presented in figure 4.11. Therefore due to the homogeneous gas phase steps in the mechanism having a higher rate than the heterogeneous gas solid steps, a sufficient chlorine concentration is built up to maintain the presence of S₄N₄Cl₂ in the system (figure 4.12). However due to the basic reaction being heterogeneous and the concentration of ClF being initially much greater than that of Cl₂, the actual reaction mechanism will involve both attack on S₄N₄ and S₄N₄Cl₂ by ClF.

Figure 4.12 The Overall Reaction Cycle for the Reaction of S₄N₄ with ClF
4.3.e The Mechanism by which Chlorine Monofluoride reacts with Trichlorotrithiatriazene (\((\text{NSCl})_3\))

In the reactions of \((\text{NSCl})_3\) with ClF the main products observed are \(\text{SF}_4\), \(\text{Cl}_2\), \(\text{N}_2\) and approximately 75% of the \((\text{NSCl})_3\) starting material (experiment 4.2b(i,ii) pages 177, 178). It therefore appears as though the chlorine monofluoride reacts in such a way as to completely fluorinate one sulphur. A mechanism for the reaction of ClF and \((\text{NSCl})_3\) is presented in figure 4.13.

**Figure 4.13 Proposed Mechanism by which ClF reacts with \((\text{NSCl})_3\)**

\[
2\text{N}=\text{S}-\text{Cl} + \text{Cl}-\text{N}=\text{SF}_2
\]
It is, therefore, suggested that the initial attack of ClF on \((\text{NSCl})_3\) is by an exchange mechanism. The chlorine monofluoride attacks a sulphur from the opposite side to chlorines (probably an \(S_{N2}\) mechanism). The effect of the equatorial S-F bond is to activate the fluorine substituted sulphur, relative to the chlorine substituted sulphurs, to further attack by ClF forming the intermediate VII. The intermediate VII then dissociates into two thiazyl chloride units and N-chloro-imido-disulphurous difluoride \(^8\), which then react with ClF as indicated by figure 4.10. As postulated previously, the rate of the homogeneous gas phase reactions will be, on the whole, greater than the heterogeneous gas-solid reactions. Hence it seems likely that the majority of the ClF will react with NSCl\((g)\) and ClNSF\(_2\) forming SF\(_4\), N\(_2\) and Cl\(_2\) thus leaving approximately 75\% of the \((\text{NSCl})_3\) starting material unreacted.

4.3.5 Overall Conclusion to the Reactions of ClF with S/N Compounds

The reactions of chlorine monofluoride with sulphur-nitrogen species do not provide a synthetically viable route to thiazyl fluoride. However should thiazyl chloride become a readily available starting material, then the reaction of NSCl with ClF in a 1 : 2 ratio might present a very useful synthetic route to N-chloro-imido-sulphurous difluoride \((\text{Cl-N=SF}_2)\).

The over-riding factor which prevents the isolation of synthetically viable yields of NSF is the formation of SF\(_4\) by the highly thermodynamically favoured addition of ClF across the multiple bond. Hence if any multiply-bonded sulphur-nitrogen species is formed in the presence of ClF, then addition across the multiple bond occurs with the eventual
formation of SF$_4$.

An overall reaction scheme is presented in figure 4.14 for all the reactions investigated.

Figure 4.14. Overall Reaction Scheme for the Reactions of ClF with S/N Compounds

* Denotes species observed.

Roman numerals refer to intermediates postulated in figures 4.11 and 4.13.
4.4 Experimental

Exchange Reactions of Trichlorotrithiatrazene with Cesium Fluoride

4.4.a Exchange reactions using solvents

(i) Trichlorotrithiatrazene and Cesium Fluoride in Sulphur Dioxide

Trichlorotrithiatrazene (0.533g, 2.180 mmole) and powdered, anhydrous, cesium fluoride (3.300g, 21.71 mmole) were placed in a pre-dried, vacuum tight F.E.P. vessel (figure 1.3, page 15), and sulphur dioxide (12.136g) condensed in. The vessel was maintained at room temperature for 48h. and the high pressure infra-red spectrum of the volatiles present at room temperature recorded. The spectrum indicated that only sulphur dioxide and a very low concentration of sulphuryl chloride fluoride ($SO_2ClF$) were present. The volatiles present at room temperature were condensed into a holding vessel and the infra-red spectrum of the residue recorded.

Infra-red spectrum of the residue (nujol mull) 1296m,br, 1230 m(sh), 1185 s,br, 1105 s, 1174 m, 925 w, 750 w, 700 w, 650vw, 600 m(sh), 592 s, 500 s,br, cm$^{-1}$.

(ii) (NSC1)$_3$ and CsF in Arsenic trifluoride (AsF$_3$)

AsF$_3$ (10.134g) was condensed on to (NSC1)$_3$ (0.907g, 3.710 mmole) and powdered, anhydrous CsF (2.567g, 16.89 mmole), contained in a pre-dried vacuum tight pyrex vessel (figure 1.1, page 14). The reaction was warmed to room temperature. At ca. 0°C a vigorous reaction occurred in which the CsF bonded together forming a solid mass. The AsF$_3$ solution was filtered off and the insolubles washed several times with AsF$_3$ to remove all the solubles. On standing for 10h. at
room temperature large colourless crystals were formed in the AsF$_3$ solution. The solvent was filtered off these crystals and the gas phase infra-red spectrum of the volatiles present at room temperature recorded prior to the removal of the solvent. The infra-red spectrum indicated that a low concentration of NSF was present, the predominant species being the solvent. On removal of the solvent in vacuo the large colourless crystals gradually disappeared.

(iii) (NSCl)$_3$ and CsF in AsF$_3$ (Repeat of expt. 4.4a(ii))

AsF$_3$ (7.312g) was condensed on to (NSCl)$_3$ (0.614g, 2.54 mmole) and powdered, anhydrous, CsF (1.22g, 8.026 mmole) contained in a pre-dried vacuum tight F.E.P. vessel. The reaction was warmed slowly to room temperature from $-22^\circ$C over a period of 2h, and maintained at room temperature for 60h. The gas phase infra-red spectra of the volatiles, at various slush bath temperatures were recorded and assigned (table 4.16).

**TABLE 4.16 Volatiles at various slush bath temperatures for the reaction of (NSCl)$_3$ with CsF in AsF$_3$**

<table>
<thead>
<tr>
<th>Slush bath temperature ($^\circ$C)</th>
<th>Pressure (torr)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>10</td>
<td>N$_2$</td>
</tr>
<tr>
<td>-78</td>
<td>50</td>
<td>SF$_4$, AsF$_3$</td>
</tr>
<tr>
<td>-22</td>
<td>50</td>
<td>AsF$_3$, NSF</td>
</tr>
<tr>
<td>r.t.</td>
<td>160</td>
<td>SO$_2$ClF, AsF$_3$, NSF</td>
</tr>
</tbody>
</table>

Species identified from their infra-red spectra. Standard spectra referenced in Appendix A, page 31.

The volatiles present at room temperature were removed but it was noted that on pumping the residue, AsF$_3$ was being
constantly removed. Thus an accurate residue weight could not be recorded.

Infra-red spectrum of the residue (nujol mull) 1300 w, 925 w, 715 m, 695 m(sh), 672 s, 640 s, 596 s(sh), 675 vs, 383 s, 340 s, cm\(^{-1}\).

(iv) (NSC\(_3\)) and CsF in Freon 11 (CCl\(_2\)F)

Freon 11 (5.043g) was condensed into a pre-dried F.E.P. tube (figure 1.3, page 15) containing (NSC\(_3\)) (0.376g, 1.538 mmole) and powdered, anhydrous CsF (1.124g, 7.395 mmole). The reaction was warmed slowly to room temperature and maintained at this temperature for 24h. The gas phase infra-red spectra of the volatiles at various slush bath temperatures were then recorded and assigned (table 4.17).

<table>
<thead>
<tr>
<th>Slush bath temperature (°C)</th>
<th>Species observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>-78</td>
<td>CCl(_2)F</td>
</tr>
<tr>
<td>-22</td>
<td>CCl(_2)F, SOF(_2)</td>
</tr>
<tr>
<td>r.t.</td>
<td>CCl(_2)F, NSF, SOF(_2)</td>
</tr>
</tbody>
</table>

(Species identified from their infra-red spectra. Standard spectra referenced in Appendix A, page 313).

Sulphur dioxide was added to the volatiles present at -78°C to test for the presence of ClF by the formation of SO\(_2\)ClF, which is readily identified from its infra-red spectrum. No evidence for the formation of ClF was noted.

The volatiles (5.163g) present at room temperature were removed and the infra-red spectrum of the residue (1.364g) recorded.
Infra-red spectrum of the residue (nujol mull) 2020 s, br, 1230 vs, br, 1130 w, 1090 w, 925 m, 830 w, br, 718 m, 698 m, 660 m, 607 m, 550 m, cm$^{-1}$.

(v) (NSCl)$_3$ and CsF in perfluorobenzene ($C_6F_6$)

Perfluorobenzene (3.33g) was condensed on to (NSCl)$_3$ (1.270g, 5.19 mmole) and CsF (2.730g, 17.96 mmole) contained in a pre-dried, vacuum tight, Monel vessel (figure 1. 4, page 15). The reaction was warmed slowly to room temperature and maintained at this temperature for 1h. The infra-red spectrum of the volatiles present at room temperature, was recorded indicating that only $C_6F_6$ was present. The reaction was then heated to 80$^\circ$C for 2h. and the volatiles present at room temperature were retested for the presence of NSF. The infra-red spectrum indicated that NSF had been produced and thus the reaction was heated at 80$^\circ$C for a further 40h. to ensure complete reaction. The gas phase infra-red spectrum of the volatiles was recorded at various slush bath temperatures and the species present identified by comparison with standard infra-red spectra (table 4.18), (standard spectra are referenced in Appendix A, page 313).

<table>
<thead>
<tr>
<th>Slush bath temperature ($^\circ$C)</th>
<th>Species identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>-196</td>
<td>$N_2$</td>
</tr>
<tr>
<td>-95</td>
<td>$SF_4$, $SOF_2$, NSF$_3$</td>
</tr>
<tr>
<td>-78</td>
<td>$SOF_2$, $SF_4$</td>
</tr>
<tr>
<td>-55</td>
<td>NSF, $C_6F_6$</td>
</tr>
<tr>
<td>-45</td>
<td>NSF, $C_6F_6$</td>
</tr>
<tr>
<td>-22</td>
<td>$C_6F_6$, NSF, $SOF_2$, $SF_4$</td>
</tr>
<tr>
<td>r.t.</td>
<td>$C_6F_6$, NSF</td>
</tr>
</tbody>
</table>

(Species listed in order of concentration in the gas phase infra-red spectrum)
The volatiles were completely removed at room temperature and the infra-red spectrum of the residue (3.34g) recorded. Infra-red spectrum of the residue (nujol mull) 922 m, 917 m(sh), 720 s, 698 m, 550 s, 342 s, cm\(^{-1}\).

4.4.b Exchange Reactions of Thiazyl Chloride with cesium fluoride without solvents

(i) The effect of temperature on the solid phase reaction between trichlorotrithiatriazene and cesium fluoride

\((\text{NSCl})_3\) (0.845g, 3.46 mmole) and CsF (1.832g, 12.05 mmole), were placed in a pre-dried, vacuum tight Monel vessel (figure 1.4, page 15). The vessel was then connected to a Monel vacuum line, equipped with a vacuum-pressure gauge and the line and vessel put under static vacuum. The temperature was slowly raised and the pressure was then monitored with respect to both time and temperature (table 4.19).

**TABLE 4.19 Variation in pressure w.r.t. temperature on heating the \((\text{NSCl})_3/\text{CsF}\) system**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Observed pressure (torr)</th>
<th>Time from commence-ment of experiment (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>r.t.</td>
<td>45</td>
<td>40</td>
</tr>
<tr>
<td>30</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>40</td>
<td>75</td>
<td>65</td>
</tr>
<tr>
<td>43</td>
<td>1170</td>
<td>67</td>
</tr>
<tr>
<td>45</td>
<td>1040</td>
<td>75</td>
</tr>
</tbody>
</table>

As is noted in table 4.19 a large increase in pressure occurs at 43° C. The vessel was cooled to -196° C to observe the pressure of incondensable gas (470 torr, nitrogen). The incondensable gas was then removed and the reaction warmed to room temperature, at which temperature the gas phase infra-red spectrum of the volatiles present, was recorded. The
infra-red spectrum indicated that SF$_4$, SOF$_2$ and NSF were the major volatile products.

The above experiment was repeated bringing the temperature very slowly up to the 43°C area. The same style of reaction occurred with the rapid increase on pressure occurring in the range 43-44°C.

(ii) The variation in observed pressure at a constant temperature for the solid phase reaction between trichlorotrithiatriazene and cesium fluoride.

Trichlorotrithiatriazene (0.700g, 2.86 mmole) and powdered anhydrous cesium fluoride were placed in a pre-dried, vacuum tight, F.E.P. vessel and the system put under a static vacuum (c f. experiment 4.4b(i)). The reaction was then heated to 35°C and the pressure within the system measured with time (table 4.20).

<table>
<thead>
<tr>
<th>Pressure (torr)</th>
<th>Time from start of Expt. (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>20</td>
<td>25</td>
</tr>
<tr>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>40</td>
<td>120</td>
</tr>
</tbody>
</table>

(volume of system = 60 cm$^3$)

(iii) Solid phase reaction between (NSC1)$_3$ and KF

(NSC1)$_3$ (0.432g, 1.77 mmole) and KF (0.942g, 16.24 mmole) were placed in a pre-dried, vacuum tight F.E.P. tube and placed under static vacuum (c f. experiment 4.4b(i)). The system was then heated and the volatiles produced were monitored by their pressure and gas phase infra-red spectrum. The
reaction was heated to 120°C but no thiazyl fluoride was produced, the only product observed in the gas phase infrared spectrum being NSCl.

(iv) Reaction of thiazyl chloride with cesium fluoride

\[(\text{NSCl})_3\] (0.683g, 2.793 mmole) was placed in a pre-dried, vacuum tight, F.E.P. vessel and on top of this was placed a one inch layer of passivated F.E.P. chippings. A layer of powdered, anhydrous, cesium fluoride (7.073g, 46.53 mmole), 3 cm in length, was then placed on top of the F.E.P. chippings (figure 4.15, page 216). The vessel was then placed under static vacuum (cf. experiment 4.4b(i)) and heated slowly to 70°C. The gas phase infra-red spectra of the volatiles were monitored over a period of 4h. but no evidence for the formation of NSF was noted. Thiazyl chloride was the only species observed in the gas phase infra-red spectrum.

(v) The reaction of thiazyl chloride with cesium fluoride at 110°C

In a typical reaction \[(\text{NSCl})_3\] (2.436g, 9.96 mmole) was placed in a pre-dried pyrex vessel and connected to a Monel column (1" diam. 25 cm. in length) packed with powdered anhydrous CsF (8.10g, 53.29 mmole). The column was then connected to a vacuum line and the whole system evacuated (figure 4.16, page 217). The column was then heated to 160°C for 1h. in a dynamic vacuum to remove any water and then cooled to 110°C for the reaction. The system was then placed under static vacuum and the \[(\text{NSCl})_3\] heated slowly to 70°C, the thiazyl chloride being cryogenically pumped through the column, at 110°C, in to the collecting vessel at -196°C. The volatiles formed on the column were monitored by their gas phase infra-red spectrum. Initially the main products
were SF\textsubscript{4} and NSF but after ca. 10 minutes the concentration of SF\textsubscript{4} in the volatiles had dropped to virtually zero. For the majority of the reaction the main product produced on the column was NSF but after approximately 75\% of the (NSCl)\textsubscript{3} had sublimed, it was noted that the NSCl was passing through the column unreacted. The reaction was, therefore, terminated. The gas phase infra-red spectrum of the volatiles condensed in the collection vessel (1.66g) was recorded and indicated the presence of NSF, SOF\textsubscript{2} and SO\textsubscript{2}ClF. The weight loss of the column and (NSCl)\textsubscript{3} bulb was recorded (1.64g) and also the weight of unreacted (NSCl)\textsubscript{3} (0.213g). Hence, assuming that all the volatiles are of the form (NSF)\textsubscript{x} (x = 1 or 3), a yield of 85\% thiazyl fluoride is calculated.

(vi) The exchange reaction between thiazyl chloride and KF on a column

Experiment 4.4b(v) was essentially repeated using a KF column. The column was heated to 130\degree C in an attempt to obtain an exchange reaction. However, little or no exchange occurred, the major volatile products coming off the end of the column being NSCl, SF\textsubscript{4}, N\textsubscript{2} and some NSF. A yield of only about 10\% was obtained using KF as the exchange reagent.

4.5 Discussion

Exchange reactions of Trichlorotrithiatrazene with Cesium Fluoride

Thiazyl fluoride and its trimeric and tetrameric oligomers have been synthesised by the oxidation-fluorination of both tetrasulphurtetranitride (S\textsubscript{4}N\textsubscript{4}) and trichlorotrithiatrazene (NSCl)\textsubscript{3} by silver difluoride (AgF\textsubscript{2}).\textsuperscript{15-18,39,80} The direct exchange reaction of the chlorines in (NSCl)\textsubscript{3} for
fluorines by the use of an ionic fluoride has, however, not been previously investigated (equation 4.5a).

\[(\text{NSCl})_3 + 3\text{MF} \rightarrow (\text{NSF})_3 + 3\text{MCl} \quad (4.5a)\]

In all the reactions of \((\text{NSCl})_3\) at elevated temperatures there is a significant concentration of \(\text{NSCl}\) monomer.\(^8\)

Hence depending upon the temperature at which the exchange reaction occurs, the mechanism is either predominantly that of exchange with the trimer (equation 4.5a) or with the monomer (equation 4.5b).

\[3\text{NSCl} + 3\text{MF} \rightarrow 3\text{NSF} + 3\text{MCl} \quad (4.5b)\]

In order to find the most suitable metal fluoride for the exchange reactions (4.5a,b) it is necessary to be able to calculate the difference between the heats of formation of the chlorinated and fluorinated sulphur-nitrogen species. The heats of formation of the trihalotrithiatriazenes have not been reported and thus it is possible only to estimate the heat of reaction of the monomer exchange mechanism. The heat of formation of \(\text{NSF}\) is known but that of \(\text{NSCl}\) has been calculated from known S-Cl bond energies and the N=S bond energy in thiazyl fluoride (see Appendix B, page 319). Hence in determining which ionic fluoride to use as the exchange reagent the criterion presented in equation 4.5c was used (table 4.21).

\[
\begin{align*}
\text{NSCl}(g) + \text{MF}(c) & \rightarrow \text{NSF}(g) + \text{MCl}(c) \\
\Delta H^o &= \Delta H^o_{\text{NSF}}(g) + \Delta H^o_{\text{MCl}}(c) - \Delta H^o_{\text{NSCl}}(g) - \Delta H^o_{\text{MF}}(c) \\
\Delta H^o &= \Delta H^o_{\text{MCl}}(c) - \Delta H^o_{\text{MF}}(c) > 100 \text{ kJ mol}^{-1} \\
\end{align*}
\]

for the exchange reaction to proceed readily.
TABLE 4.21 Thermodynamic comparison of a series of ionic fluorides w.r.t. the exchange reaction:

\[
\text{NSCl}_3 (g) + \text{MF} (c) \rightleftharpoons \text{NSF} (g) + \text{MCl} (c)
\]

<table>
<thead>
<tr>
<th>Cation</th>
<th>( \Delta H_f^{\text{MF}} (c) ) (kJ mol(^{-1}))</th>
<th>( \Delta H_f^{\text{MCl}} (c) ) (kJ mol(^{-1}))</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(^I)</td>
<td>-612</td>
<td>-408</td>
<td>+ 103</td>
</tr>
<tr>
<td>Na(^I)</td>
<td>-569</td>
<td>-411</td>
<td>+ 58</td>
</tr>
<tr>
<td>K(^I)</td>
<td>-562</td>
<td>-436</td>
<td>+ 27</td>
</tr>
<tr>
<td>Cs(^I)</td>
<td>-531</td>
<td>-433</td>
<td>-2</td>
</tr>
<tr>
<td>NH(_4)^I</td>
<td>-467</td>
<td>-315</td>
<td>+ 52</td>
</tr>
<tr>
<td>Ag(^I)</td>
<td>-203</td>
<td>-127</td>
<td>-24</td>
</tr>
<tr>
<td>Ba(_{II})</td>
<td>-1200</td>
<td>-860</td>
<td>+ 71</td>
</tr>
<tr>
<td>Pb(_{II})</td>
<td>-663</td>
<td>-359</td>
<td>+ 20</td>
</tr>
<tr>
<td>Tl(^I) (g)</td>
<td>-138</td>
<td>-67</td>
<td>-28</td>
</tr>
</tbody>
</table>

(Standard heats of formation are referenced in Appendix B, page 319)

From Table 4.21 it can be seen that, even allowing for a miscalculation of the heat of formation of thiazyl chloride of ca. 10 kJ mol\(^{-1}\) there are still only three feasible ionic fluorides for the exchange reaction, CsF, AgF and TlF. In no case is the exchange highly favoured but relatively speaking, AgF and TlF would be noticeably better exchange reagents than CsF. Due to the unavailability of both thalium and silver fluorides at the time of this work (though both are available from Alfa Vertron) the exchange reactions using cesium fluoride were investigated.

4.5.a *The exchange reactions between Trichlorotrithia-thiazene and Cesium Fluoride in solvents*

The exchange reactions between (NSCl\(_3\)) and CsF using sulphur dioxide (4.4a(i) page 199) and arsenic tri-
fluoride (experiments 4.4a(ii,iii) pages 199, 200) proved unsatisfactory due to reaction of the solvent with the cesium fluoride forming CsSO\(_2\)F and CsAsF\(_4\). The reaction of cesium fluoride with arsenic trifluoride was highly exothermic (experiment 4.4a(ii), page 199) and it was found necessary to control the temperature of the reaction. Large colourless crystals were formed from the resulting AsF\(_3\) solution in experiment 4.4a(ii) which disappeared on removal of the solvent from the system under reduced pressure. It is suggested that the crystals observed were (NSF)\(_3\) which is known to sublime easily at room temperature\(^{13}\) thus being removed with the solvent (AsF\(_3\); Bpt. 65°C, vapour pressure at 13.4°C = 100 torr).\(^8\) Low concentrations of thiazyl fluoride were observed in the gas phase infra-red spectrum of the volatiles present at room temperature. Hence it is believed that exchange does occur, forming (NSF)\(_3\) but due to the similarities in vapour pressure of (NSF)\(_3\) and the solvent, the isolation of the product is difficult.

In order to minimise the reaction of cesium fluoride with the exchange solvent, Freon II (CCl\(_2\)F) (experiment 4.4a(iv) page 201) and perfluorobenzene (C\(_6\)F\(_6\)) (experiment 4.4a(v) page 202) were employed. The exchange reaction between cesium fluoride and trichlorotrithiathiaceene in these solvents was, however, slow. The low rate of reaction is almost certainly due to the low solubility of cesium fluoride in the solvents. However with sufficiently finely ground cesium fluoride and long reaction times significant yields of thiazyll fluoride and trifluorotrithiatriazene were obtained \((\text{yield } (\text{CCl}_2\text{F}) : 41\% ; (\text{C}_6\text{F}_6) : 65\% )\). The yield of product is however artificially low due to the presence of
a small quantity of a sulphur-nitrogen species in the residue. The sulphur-nitrogen compound in the residue appears, from its infra-red spectrum (925 s, 720 s, 698 s, 550 s, and 342 s cm\(^{-1}\)) to be \(S_4N_4\). The mechanism by which both \(S_4N_4\) and \(SF_4\) (seen in the infra-red spectrum of the volatiles) are formed is thought to be highly complex involving the formation of ClF at some stage.

As can be seen from tables 4.17 and 4.18 the separation of thiazyl fluoride from the solvent presented a decided problem. During the evacuation of a vessel containing CsF and \((NSCl)_3\), prior to condensing in the solvent, it was noted that a gas was released that gave a blue discharge. The concentration of this gas was very low but it was suggested that it was thiazyl chloride or thiazyl fluoride. Hence due to this observation and the difficulty in separating thiazyl fluoride from solvents, the solid phase reaction of cesium fluoride with trichlorotrithiatriazene was investigated.

4.5.b The Solid Phase Exchange Reactions between Cesium Fluoride and Trichlorotrithiatriazene ((NSCl)_3) or Thiazyl Chloride (NSCl)

In the initial investigative reaction, the mixture of cesium fluoride and trichlorotrithiatriazene was heated slowly, under static vacuum and the pressure above the solids monitored (experiment 4.4b(i) page 203). The pressure rose quite slowly up to approximately 43°C at which temperature a highly exothermic reaction occurred with the release of a considerable volume of gas, (table 4.19 page 203). The experiment was repeated to check whether the vigorous reaction was solely temperature dependent or if it was temperature and time dependent. The rate of heating in the second
experiment was very much lower than that in the first experiment but it was noted that the reaction occurred at the same temperature (43-44°C). Thus it is concluded that the vigorous reaction occurs at ca. 43°C and is not dependent on how long the reaction has been at a certain temperature. The volatiles present after the sudden increase in pressure were identified as nitrogen, sulphur tetrafluoride and thiazy1 fluoride. Hence the "solid phase" exchange had occurred. In order to observe the reaction products without the reaction going critical, the temperature was raised to only 35°C, some 7-8°C lower than that at which the decomposition reaction occurs. The pressure of volatiles above the reactants was monitored with respect to time at a constant temperature (35°C) (experiment 4.4b(ii) page 203). A very low rate of reaction occurred, the volatiles being identified, by infra-red spectroscopy as, NSF and NSCl.

In an attempt to avoid the highly exothermic reaction between cesium fluoride and trichlorotrithiatrazene, on which thermal breakdown of the S/N species occurs with the formation of nitrogen, potassium fluoride was employed as the exchange reagent (experiment 4.4b(iii) page 204). No exchange reaction was observed to occur. Hence it was concluded that exchange does occur between trichlorotrithiatrazene and cesium fluoride ($\Delta H^0 = -2$ kJ mol$^{-1}$) but not with potassium fluoride ($\Delta H^0 = +27$ kJ mol$^{-1}$).

It is believed that the very high rate of reaction at 43°C is due to the rate of production of heat by a mildly exothermic reaction exceeding the activation barrier of a much more exothermic reaction. Hence once the second reaction has been initiated, a chain process
is set up in which very high temperature, localised, regions occur due to the lack of a moderating solvent. The existence of these hot spots causes the thermal decomposition of the S/N species. Thus the reaction goes critical due to the rapid increase in temperature of the reaction, there being no solvent to dissipate any thermal energy.

From the results obtained from experiment 4.4b(i) (page 203) it is known that exchange does occur between $(\text{NSCl})_3$ and CsF. Thus a reaction system was devised so that a chain reaction, caused by localised heating effects within the solid phase reactants, could not occur.

It has been known for many years that trichlorotrithiatriazene decomposes on heating in \textit{vacuo} yielding the monomer thiazyl chloride.\textsuperscript{85} Hence in order to separate the cesium fluoride and trichlorotrithiatriazene it was decided to pass thiazyl chloride through a column of cesium fluoride (see figures 4.15, 4.16, pages 216, 217). Initially a relatively simple design was adopted in which the $(\text{NSCl})_3$ and CsF were heated to the same temperature (70°C). The exchange reaction was however inefficient under these conditions, thiazyl chloride passing through the cesium fluoride column unreacted. To improve the exchange efficiency it was found necessary to heat the column and $(\text{NSCl})_3$ independently. The most efficient exchange appeared to occur with the cesium fluoride column at 110°C and the trichlorotrithiatriazene container at 70°C. The products from the exchange reaction were monitored by expanding the volatiles, coming off the column, into a gas phase infra-red cell and identifying the products by their infra-red spectra. (Standard infra-red spectra are referenced in Appendix A, page 313). Initially
it was noted that approximately equal concentrations of
thiazyl fluoride and sulphur tetrafluoride were produced but
this ratio rapidly altered, there being no sulphur tetra-
fluoride formed after ca. 10 minutes. The presence of $\text{SF}_4$
in the volatiles initially produced, is suggested to be due
to the thermal decomposition of thiazyl chloride into nitrogen
and disulphur dichloride, the latter then reacting with cesium
fluoride forming $\text{SF}_4$ (*equation 4.5d).

\[
\begin{align*}
2/3 (\text{NSCl})_3 & \xrightarrow{\Delta} 2\text{NSCl} \xrightarrow{\Delta} \text{N}_2 + \text{S}_2\text{Cl}_2 \\
\text{S}_2\text{Cl}_2(l) + 4\text{CsF}(s) & \xrightarrow{} 4\text{CsCl}(s) + \text{SF}_4(g) + \frac{1}{8}\text{S}_8(s)
\end{align*}
\]

$\Delta H^o = -323 \text{ kJ mol}^{-1}$

The thermal decomposition of $(\text{NSCl})_3$ in to $\text{N}_2$
and $\text{S}_2\text{Cl}_2$ is likely to occur to a small extent throughout
the reaction but initially the rate of decomposition is likely
to be higher due to non-uniform heating of the $(\text{NSCl})_3$.

In the latter stages of the reaction exchange
efficiency drops significantly with thiazyl chloride passing
through the column unreacted. It is believed that the reason
for the gradual decrease in efficiency of the column with time,
is due to the surface coating of $\text{CsF}$ by $\text{CsCl}$. Hence the
effective exchange area presented by the cesium fluoride is
decreased and therefore eventually "saturation" of the column
occurs, there being little or no exchange area. Thiazyl
chloride is thus observed in the volatiles.

The exchange reaction using potassium fluoride
as the exchange reagent, and raising the column temperature
to $130^\circ\text{C}$ produced a low yield of thiazyl fluoride (experiment
4.4b(vi) page 206). It may therefore be suggested that, as
the heats of formation of potassium fluoride and potassium
chloride do not change significantly with temperature, then
the term $\Delta H^r_{f} \text{NSF}(g) - \Delta H^r_{f} \text{NSCl}(g)$ appears to become more
negative. With the increase in temperature it is also likely
that the entropy terms will start to play a significant role
in the calculation of the free energy of the reaction. Thus
the formation of thiazyld fluoride from thiazyld chloride using
potassium fluoride as the exchange reagent at high temperatures
may be due to the increased significance of the entropy terms
and/or the variation with temperature of the heat of formation
of the thiazyld halides.

4.5.c. Conclusion

The Exchange Reactions of Trichlorotrithiatriazene
with Cesium Fluoride

The exchange reactions of trichlorotrithiatriazene
with cesium fluoride yield, to a greater or lesser extent,
thiazyld fluoride and trifluorotrithiatriazene. At ambient
temperatures, using a solvent, a mixture of NSF and (NSF)$_3$
is produced whereas at elevated temperatures the majority of
the fluorinated product is NSF.

From the heats of reaction presented in table 4.21
it can be seen that if exchange occurs using cesium fluoride,
then it is likely that the rate of the conversion will be
higher with silver or thallium fluoride. It is believed
that (NSF)$_3$ would be readily produced in high yields on
reacting (NSCl)$_3$ with either AgF or TlF in perfluorobenzene
(C$_6$F$_6$), as under the same conditions CsF gave a 65\% yield
of NSF and its oligomers. The rate of conversion using a
column of AgF or TlF with thiazyld chloride is also likely to
be higher than in the case of a CsF column due to the conversion
per unit area of exchange fluoride being greater.
The efficiency of the column exchange method is however a function of both the conversion efficiency of the column and the generation of thiazyl chloride. Little work has been done using thiazyl chloride as a reactant (Chapter Five, page 227) and thus the techniques for its continuous generation without a significant impurity level are not well documented.\textsuperscript{85} Hence an improvement to the exchange procedure will almost certainly occur when a method for producing thiazyl chloride at a steady rate, over a period of hours, is found.

The efficiency of the column is a function of the exchange fluoride, the total surface area upon which exchange can occur and the temperature at which the column is maintained. In designing a column it is recommended that a long narrow bore column is used, so as to increase the path length of the thiazyl chloride through the exchange fluoride. The use of a non-participating dispersant within the column will probably increase the net surface area of the exchange reagent relative to the same mass of pure exchange fluoride. With the increased conversion rate per unit area of fluoride (AgF and TlF relative to CsF) it is likely that the column temperature can be lowered thus minimising any dissociation of thiazyl chloride in to nitrogen and disulphur dichloride (equation 4.5d) that may occur on the column.

Hence it is concluded that a high yield of thiazyl fluoride can be produced by the exchange reaction of thiazyl chloride with a suitable ionic fluoride on an efficient column.
Figure 4.15

- FEP tube
- CsF
- \( S_3N_3Cl_3 \)
- FEP chippings
- Vacuum line
- Oil bath
Figure 4.16

Monel vacuum line

Swagelock valve

to vacuum pump

to gas cell

-196°C

collection vessel

CsF column (110°C)

oil bath (70°C)
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CHAPTER FIVE

THE OXIDATION OF SULPHUR-NITROGEN SPECIES

AND SOME REACTIONS OF THIAZYL CHLORIDE

5.1 Introduction

The oxidation of sulphur-nitrogen compounds covers a considerable area of chemistry which, for the most part, falls into four main categories.

(i) The reactions of tetrasulphur tetranitride with halogens.

(ii) The reactions of tetrasulphur tetranitride with Lewis acids.

(iii) The reactions of trichlorotrithiatriazene with Lewis acids.

(iv) The reactions of thiazyl halides with Lewis acids.

5.1.1 The Reactions of Tetrasulphur Tetranitride with Halogens and Inter-halogens

A considerable study has been made of the reactions of halogens and inter-halogens with $S_4N_4$.

(a) Fluorination of $S_4N_4$

The fluorination of $S_4N_4$ has been discussed in Chapter Four and is, therefore, not commented on further in this section.

(b) The Chlorination of $S_4N_4$

The chlorination of $S_4N_4$ has been the subject of much study over the last two decades.\(^1\)\(^-\)\(^5\) The principal product formed in the reaction of $S_4N_4$ with chlorine is $(NSCl)_3$, although intermediate species and by-products have been isolated (e.g. $S_4N_4Cl_2$\(^3\) and $(NSCl)_4$\(^2\))
(c) The Bromination of $S_4N_4$

The reaction of $S_4N_4$ with bromine has been studied both in solution and in the vapour phase. Zborilova et al.6-8 investigated the bromination of $S_4N_4$ in solution, isolating S/N/Br compounds (e.g. $S_4N_2Br$, $S_3N_2Br_2$). However Street et al.9,10 have studied the reactions of $S_4N_4$ with bromine in the vapour phase, obtaining modified $(SN)_x$ ((SNBr$_0.4$)$_x$). Since 1977 there has been a considerable interest in the doping of $(SN)_x$ by halogens and inter-halogens11-16 and this field is an expanding area of research in sulphur-nitrogen halogen chemistry.

(d) The Iodination of $S_4N_4$

Little or no work has been reported on the iodination of $S_4N_4$ by iodine.9 However recent work by Banister and Smith17 has led to the synthesis of a series of compounds $(SNI_y)_x$ where $y$ is variable (cf. the doping of $(SN)_x$ by bromine).

5.1.2 The Reactions of Tetrasulphur Tetranitride with Lewis Acids

It is known that sulphur, selenium and tellurium can be oxidised by Lewis acids (AsF$_5$, SbF$_5$) to the homoatomic polycations ($M_x^+$, Chapter Six, page 260).

Many reactions have been reported in which $S_4N_4$ forms adducts with Lewis acidic species.18 The majority of reported adducts have the stoichiometry of 1:1 ($S_4N_4$: Lewis acid). Examples of adducts with stoichiometries of 1:$X$ ($X>1$) are not that common, there being only two examples of 1:$4$ adducts, that of $S_4N_4$:4SbF$_5$19 and $S_4N_4$:4TiF$_4$.18

The reaction of $S_4N_4$ with arsenic and antimony pentahalides has been studied by Gillespie et al. who have isolated
the species $S_2N_2^+AsF_6^-$ from the reaction of $S_4N_4$ with $\text{AsF}_5$ in $\text{SO}_2$ and in recent work (1977) the cation $S_4N_4^{2+}$ (equation 5.1.2).

$$S_4N_4 + 3\text{SbCl}_5 \rightarrow S_4N_4(\text{SbCl}_6)_2 + \text{SbCl}_3 \quad (5.1)$$

$$S_4N_4 + 4\text{SbF}_5 \rightarrow S_4N_4(\text{SbF}_6)(\text{SbF}_3) \quad (5.2)$$

The X-ray crystal structures of both the $S_3N_2^+$ (figure 3.2, page 107) and $S_4N_4^{2+}$ cations have been determined which indicate that they are essentially planar. The formation of these cations from the reactions of the strongly oxidising Lewis acids ($\text{AsF}_5$, $\text{SbF}_5$ and $\text{SbCl}_5$) with $S_4N_4$ represent the first reported examples of Lewis acids oxidising $S_4N_4$ rather than forming adducts.

5.1.3 The Reaction of Trihalotrithiatriazenes with Lewis acids

The reactions of trihalotrithiatriazene ($S_3N_3F_3$) with Lewis acids have been discussed in Chapter Four (page 161).

Trichlorotrithiatriazene is known to form adducts with Lewis acids (e.g. $\text{AlCl}_3$, $\text{FeCl}_3$, $\text{SbCl}_5$, $\text{SnCl}_4$, $\text{TiCl}_4$ and $\text{BCl}_3$) in a variety of solvents (thionyl chloride, sulphur dioxide and carbon tetrachloride) (equations 5.3-5).

$$(\text{NSCl})_3 + \text{TiCl}_4 \rightarrow (\text{NSCl})_3 \cdot \text{TiCl}_4 \quad (5.3)$$

$$2(\text{NSCl})_3 + \text{SnCl}_4 \rightarrow 2(\text{NSCl})_3 \cdot \text{SnCl}_4 \quad (5.4)$$

$$(\text{NSCl})_3 + \text{MCl}_3 \rightarrow (\text{NSCl})_3 \cdot \text{MCl}_3 \rightarrow (\text{NSCl})_3 \cdot 2\text{MCl}_3 \quad (\text{ref.} 23) \quad (5.5)$$

$(M = \text{Fe}, \text{Al})$

Special note is made of the reactions of $\text{BCl}_3$ and $\text{SbCl}_5$ with trichlorotrithiatriazene. The reaction of
(NSC\(_1\))\(_3\) with \(\text{BCl}_3\) in the presence of \(\text{SCl}_2\) produces the cation \(\text{N(SCl}_1)_2^+\) (equation 5.6).

\[
(\text{NSC}_1)_3 + 3\text{SCl}_2 + 3\text{BCl}_3 \rightarrow 3 \text{N(SCl}_1)_2^+ \text{BCl}_4^- \quad \text{(ref.25)}(5.6)
\]

The reaction of antimony pentachloride with trichlorotrithiatrizene has been reported on at least three different occasions, the products identified being different each time (equations 5.7-9).

\[
(\text{NSC}_1)_3 + 3\text{SbCl}_5 \rightarrow (\text{NSC}_1)_3 \cdot x\text{SbCl}_5 \quad (x=1-3) \quad \text{(ref.22)} \quad (5.7)
\]

\[
(\text{NSC}_1)_3 + \text{SbCl}_5 \rightarrow \text{S}_3\text{N}_2\text{Cl}_2^+\text{SbCl}_6^- \quad \text{(ref.24)} \quad (5.8)
\]

\[
(\text{NSC}_1)_3 + 3\text{SbCl}_5 \rightarrow \text{S}_4\text{N}_4^2+(\text{SbCl}_6^-)_2 + \text{SbCl}_3 \quad \text{(ref.21)} \quad (5.9)
\]

5.1.4 The Reactions of Thiazyl Halides with Lewis Acids

Although some areas of the chemistry of thiazyl fluoride (NSF) have been investigated (Chapter Four, page 159), little or no chemistry of thiazyl chloride has been reported. As no previous reference has been made, in this thesis, to the preparation, physical properties, structure or reactions of thiazyl chloride, the chemistry of this compound is reviewed briefly in section 5.1.4(iii).

(i) The Formation and Reactions of Thiazyl Fluoride

The formation and reactions of thiazyl fluoride have already been discussed in Chapter Four (page 151), but particular note is made here of the reactions of thiazyl fluoride with the Lewis acids \(\text{AsF}_5\) and \(\text{SbF}_5\) (equations 5.10,11).

\[
\text{NSF} + \text{AsF}_5 \xrightarrow{\text{SO}_2} \text{NS}^+\text{AsF}_6^- \quad \text{(ref.26)} \quad (5.10)
\]

\[
\text{NSF} + \text{SbF}_5 \xrightarrow{\text{SO}_2} \text{NS}^+\text{SbF}_6^- \quad \text{(ref.26)} \quad (5.11)
\]

The thionitrosyl salts \(\text{NS}^+\text{MF}_6^-\) sublime readily at 40°C (\(M=\text{As}\)) or 100°C (\(M=\text{Sb}\)) and dissolve in sulphur dioxide.27
The S-N stretching frequency of the cation varies depending on the anion; \( \text{NS}^+\text{SbF}_6^- \) (1448 cm\(^{-1}\)), \( \text{NS}^+\text{AsF}_6^- \) (1437 cm\(^{-1}\)).

(ii) The Chemistry of the Thionitrosyl Cation

The chemistry of the thionitrosyl cation has not been investigated in depth. However examples of three modes of reaction have been reported. (equations 5.12-14).

(a) Anion exchange.

\[
\text{NS}^+\text{AsF}_6^- + \text{NO}^+\text{CF}_3\text{SO}_3^- \xrightarrow{\text{SO}_2} \text{NS}^+\text{CF}_3\text{SO}_3^- 
\]

(ref.27) (5.12)

(b) Reactions with nucleophiles.

\[
\text{NS}^+\text{AsF}_6^- + \text{S}_4\text{N}_4 \xrightarrow{\text{SO}_2} (\text{S}_5\text{N}_5^+\text{AsF}_6^-)_x
\]

(ref.27) (5.13)

(c) Reactions with polar bonds.

\[
\text{NS}^+\text{AsF}_6^- + \text{SCl}_2 \xrightarrow{\text{SO}_2} \text{N(SCl)}_2^+\text{AsF}_6^-
\]

(ref.27) (5.14)

(iii) The Preparation, Structure, Physical Properties and Reactions of Thiazyl Chloride

(a) Preparation of Thiazyl Chloride

Thiazyl chloride can be produced by the dissociation of trichlorotrithiaatriazene, (NSCl\(_3\)), into monomeric thiazyl chloride units\(^{28-31}\) and by the thermal decomposition of thiotritiazyl chloride (S\(_4\)N\(_3\)Cl)\(_3\)\(^{32}\) and chlorothiodithiazyl chloride (S\(_3\)N\(_2\)Cl\(_2\)).\(^{33}\)

The vapour pressure of thiazyl chloride in equilibrium with solid trichlorotrithiaatriazene in the temperature range 30-60°C is given by the equation

\[
\log P_{\text{NSCl}}(\text{torr}) = 12.321 - 3360/T. \quad \text{(ref.29)}
\]

\[
\text{(NSCl)}_3(S) \rightarrow 3\text{NSCl}(g) \quad \Delta H^0 = 193 \pm 6 \text{ kJ mol}^{-1} \quad \text{(ref.29)}
\]

\[
\Delta S^0 = 524 \pm 20 \text{ J deg}^{-1}\text{mol}^{-1}
\]
(b) Structure and Vibrational Spectrum of Thiazyl Chloride

The structure of thiazyl chloride was elucidated by Beppu et al. (1970)\textsuperscript{34} from the microwave spectrum. The molecule is bent with a $N - S - Cl$ of 117.7° (Figure 5.1).

Figure 5.1 Structure of Thiazyl Chloride\textsuperscript{24}

\[ \text{Infra-red spectrum of Thiazyl Chloride } (N^{14} = S^{32} - Cl^{35}) \]

\[
\begin{align*}
\nu_1 &= 1327.3 \text{ cm}^{-1} \\
\nu_2 &= 403.75 \text{ cm}^{-1} \\
\nu_3 &= 267.4 \text{ cm}^{-1}
\end{align*}
\]

The photoelectron spectrum\textsuperscript{35,36} and molecular constants have been determined for the gas phase species but are not discussed in this thesis.

(c) Reactions of Thiazyl Chloride

There are no reported reactions in which gaseous thiazyl chloride is used as a reactant. The species has, however, been postulated as the reacting moiety in refluxing solutions of trichlorotriothiazene ($S_3N_3Cl_3$). There is however little or no evidence to substantiate whether the thiazyl chloride monomeric unit is the reactive species in the apple
green refluxing solutions of \((\text{NSCl})_3\) in carbon tetrachloride or benzene.

(iv) **Other Thiazyl Halides**

There is no reference made in the literature to the preparation, structure or reactions of thiazyl iodide. Thiazyl bromide has been synthesised and its infra-red spectrum analysed.\(^\text{13}\) There are however no references made to any reactions of the bromide.

**THE OXIDATION OF SULPHUR-NITROGEN SPECIES**

5.2 **Experimental**

5.2.1 The Oxidation of Tetrasulphur Tetranitride

(1) The Oxidation of \(S_4N_4\) by \((\text{XeF}^+)\)(\(\text{Sb}_2\text{F}_{11}^-\))

\(\text{XeF}_2\) (0.2615g, 1.545 mmole) was placed in a pre-dried, vacuum tight tube sealed with a Rotoflo valve and antimony pentafluoride (0.8345g, 3.856 mmole) condensed \((\text{in \text{vacuo}})\) in to the vessel. The reaction was warmed slowly to 90°C for 30 min. and then cooled to room temperature. A large quantity of colourless crystals in a pale green solution were formed. The excess \(\text{SbF}_5\) was removed \((\text{in \text{vacuo}})\) and the weight of the product recorded (0.7878g, 1.306 mmole of \(\text{XeF}^+\text{Sb}_2\text{F}_{11}^-\)).

To the \(\text{XeF}^+\text{Sb}_2\text{F}_{11}^-\) was added \(S_4N_4\) (0.0711g, 0.386 mmole). The system was evacuated and the reaction slowly warmed to 90°C for 4h. A vigorous reaction occurred at ca. 45°C in which a blue compound was seen to be produced. After 4h. at 90°C the solution appeared to lighten and colourless crystals were formed. The reaction was cooled to -196°C and the volatiles present (300 torr), tested by the colour of
their discharge. Nitrogen and xenon were identified but no evidence for the presence of fluorine was noted. The reaction was then warmed to room temperature and the volatiles present at this temperature removed. The system was pumped on for 6h. and the majority of the SbF$_5$ was removed, however, even after this time SbF$_5$ could still be detected in the discharge. The product was isolated in a dry-box but residual SbF$_5$ made the material virtually impossible to work with. The reaction was terminated at this point as excessive pumping on the material at room temperature or elevated temperatures is likely to sublime any NS$^+$SbF$_6^-$ out of the system (NS$^+$SbF$_6^-$ sublimes readily at 100°C in vacuo).

(ii) Reaction of Tetrasulphur Tetranitride with Antimony Pentfluoride

S$_4$N$_4$ (0.5532g, 3.007 mmole) was placed in a pre-dried, vacuum tight vessel sealed by a Rotoflo valve and SbF$_5$ (7.8212g, 36.01 mmole) condensed in. The reaction vessel was then evacuated. On warming the reaction slowly to room temperature a vigorous reaction occurred which was highly exothermic and could not be controlled by submerging the vessel in liq.N$_2$. A blue product was formed which was soluble in the excess antimony pentfluoride (possibly S$_8^{2+}$ (SbF$_6^-$)$_2$ or S$_4$N$_4^{2+}$ (SbF$_6^-$)(Sb$_3$F$_{16}^-$)) and a white crystalline product was observed which coated the walls of the vessel. After the reaction had subsided the system was cooled to -196°C and the volatiles at this temperature tested (250 torr). Nitrogen was identified by its discharge. The reaction mixture was then warmed to room temperature and the excess SbF$_5$ removed in vacuo. The white microcrystalline product was isolated and its Raman spectrum recorded.
Raman spectrum of the white microcrystalline material
(green line): 654s, 634s, 292w cm$^{-1}$.

(iii) The Reaction of Tetrasulphur Tetranitride
with Antimony Pentafluoride at Elevated Temperatures

$S_4N_4$ (0.3531g, 1.919 mmole) was placed in
a pre-dried, vacuum tight, pyrex vessel, sealed by a Rotoflo
valve and $SbF_5$ (9.6177g, 4.437 mmole) condensed in. The re-
action vessel was evacuated and then warmed very slowly, via
slush baths at -45$^\circ$C and -22$^\circ$C, to room temperature over a
period of 6h. The system was then stirred at room temper-
ature for 2h, and then the temperature was raised slowly
150$^\circ$C for 100h.

Colourless parallelepiped crystals were
produced (main face ca. 3mm by 3mm) in a pale yellow $SbF_5$
solution. The reaction was then cooled slowly to room
temperature. At ca. 120$^\circ$C a pale yellow solid started to
be deposited which coated the crystals. The reaction mixture
virtually solidified into a cream mass on cooling to room
temperature and the removal of excess antimony pentafluoride
proved difficult. A few colourless crystals were isolated
from the sticky mass and the Raman spectrum of these recorded.
Raman spectrum of the colourless crystals (green line): 654s,
634m, 292w cm$^{-1}$.

(iv) Reaction of Tetrasulphur Tetranitride
with Antimony Pentafluoride in Arsenic
Trifluoride

$S_4N_4$ (0.8414g, 4.57 mmole) was placed in a
pre-dried vacuum tight, pyrex vessel and $AsF_3$ (7.2219g) and
$SbF_5$ (4.0123g, 18.52 mmole) condensed in. The vessel was
evacuated and on warming to room temperature a very deeply
coloured solution was formed which did not change colour on heating to 125°C for 24h. After ca. 18h. colourless crystals were seen in the deep red solution. The reaction was slowly cooled to room temperature, the colourless crystals being coated with an orange-red precipitate. The solvent and excess antimony pentafluoride were removed under reduced pressure and the product isolated in a dry-box. The product was sorted by hand using a microscope fitted to the outside of the dry-box, the colourless crystals being loaded into a Raman tube for investigation.

Raman spectrum of the colourless crystals (green line):

686m, 664s, 644s, 626w, 607w, 292m cm⁻¹.

Infra-red spectrum of the colourless crystals (powder):

680m, 672m, 658s, 649s, 620m(sh), 475m, 450m,br; cm⁻¹.

Infra-red spectrum of the red non-crystalline material (powder):

1495m, 1220m, 1010w, 655vs,br, 475w,br, 436w, 378m cm⁻¹.

5.2.2 The Oxidation of Trichlorotrithiatriazene (\((\text{NSCl})_3\))

(i) Reaction of \((\text{NSCl})_3\) with SbF₅ in AsF₃.

\((\text{NSCl})_3\) (0.8389g, 3.431 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel and arsenic trifluoride (5.7879g, 43.874 mmole) and antimony pentafluoride (4.3836g, 20.224 mmole) were condensed in. The reaction vessel was evacuated and then warmed slowly to room temperature yielding a deep green solution which, on refluxing under sealed system conditions for 72h. changed to deep red. After refluxing for 72h. a yellow solid was precipitated and on cooling the reaction to room temperature more of the same precipitate was formed. The system was cooled to -196°C to test for N₂ or F₂. No pressure of volatiles was recorded. The gas phase
infra-red spectrum of the volatiles present at room temperature was recorded and the spectrum indicated the presence of SbF₅, AsF₃, SiF₄ and SOF₂ (Appendix A, page 313). Volatiles present at room temperature were completely removed and the product isolated under dry-box conditions. The product still contained some free SbF₅ and thus was recrystallised from sulphur dioxide (12.6341g). The product completely dissolved in the solvent forming a deep red solution. However on cooling the solution to ca. -63°C a creamy-white precipitate was noted. The solution was thus cooled to ca. -78°C and the precipitate isolated.

Raman spectrum of the precipitate (green line): 1208$s$, 692$vw$, 666$w$, 646$s$*, 620$w$, 564$w$*, 499$vs$, 296$w$(sh)*, 282$m$, 234$s$, 226$vs$, 142$s$ cm$^{-1}$ (*Denotes peaks assignable to SbF₆⁻)⁴². 

Infra-red spectrum of the precipitate (powder): 815$w$, 800$m$, 670$s$(sh), 658$vs$, 650$vs$, 640$(sh)$, 570$w$, 465$m$, 382$s$ cm$^{-1}$

Difficulty was found in drying the soluble red product (due to SbF₅) and thus an infra-red spectrum was not recorded.

(ii) Reaction of Trichlorotrithiatriazene and Arsenic Pentafluoride

\((\text{NSCl})₃\) (1.21g, 4.95 mmole) was placed in a pre-dried, vacuum tight, Monel vessel and arsenic pentafluoride (4.13g, 24.32 mmole) condensed in. The vessel was evacuated and the reaction warmed slowly to room temperature and then to 70°C for 24h. The system was then cooled to -196°C and tested for nitrogen (50 torr, 0.01g). The excess AsF₅ was removed by pumping on the products at room temperature. The residue (4.59g) was isolated in a dry-box and the
infra-red and Raman spectra recorded on the yellow solid.

Infra-red spectrum of the product (nujol mull): 700vs, 500s, 390vs cm\(^{-1}\).

Infra-red spectrum of the product (fluorolube): 1445s, 500s, 390vs cm\(^{-1}\).

No Raman spectrum could be obtained using the green line. The Raman spectrum recorded some two months after the experiment using a red laser is given below:

Raman spectrum (red line): 681m, 498m, 420vs, 396w, 371w, 185s, 154s cm\(^{-1}\) (c.f. AsCl\(_4^+\)AsF\(_6^-\)).

(iii) The Reaction of Trichlorotrithiatriazene with Aluminium Trichloride

Anhydrous AlCl\(_3\) (8.43g, 63.2 mmole) and \((NSCl)_3\) (3.24g, 13.75 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel. The system was evacuated, sealed under vacuum by a Rotoflo valve and the top of the vessel cooled with cold nitrogen gas, generated by placing a tube in a Dewar of liquid nitrogen. No product appeared to sublime. The reactants were then heated to 70°C resulting in the formation of a yellow sublimate which on warming became liquid then gaseous. On stabilising the whole vessel at room temperature the solid residue appeared to be "wet" with a yellow liquid. The volatiles were tested at various slush bath temperatures and identified from their infra-red and Raman spectra. At -196°C a low pressure of incondensable gas was noted which on removal from the system did not represent a great enough weight loss to be recorded on the balance (i.e. less than 0.01g). The volatiles present at -63°C did not give an infra-red spectrum but were identified as being predominantly chlorine from their Raman spectrum. The volatiles at -63°C were removed
prior to the volatiles at room temperature being tested). The volatiles present at room temperature are believed to be mainly disulphur dichloride from the infra-red spectrum recorded.

The reaction was terminated at this point as complete degradation of the sulphur-nitrogen system appeared to have occurred.

5.2.3 Reactions of Thiazyl Chloride

(i) The Reaction of Thiazyl Chloride (NSCl) with Boron Trichloride

Thiazyl chloride (NSCl), generated by heating (NSCl)\textsubscript{3} in vacuo,\textsuperscript{29} was expanded into a gas cell (figure 1.5 page 16). The pressure of NSCl in the gas cell was adjusted such that ca. 80% absorbance was recorded for the infra-red band at 1320 cm\textsuperscript{-1}. The complete gas phase infra-red spectrum of the volatiles within the cell was recorded between 4000 and 300 cm\textsuperscript{-1} (KBr windows). BCl\textsubscript{3} contained in a sealable side arm was then expanded into the gas cell. An immediate reaction occurred yielding a yellow solid which coated the gas cell.

Infra-red spectrum of the products: 1468m(sh), 1460m, 1422s, 1375m, 1252m, 1245m, 1010-920vs,br,(xsBCl\textsubscript{3}), 725m, 718m, 618m, 520m, 485m(sh), 475s, 462s, 454vs, 444s cm\textsuperscript{-1}.

The gas cell was pumped on for 10 min. and the spectrum re-run. No peaks were observed.

(ii) Reaction of Thiazyl Chloride with Tin(IV)Chloride

NSCl, generated by heating (NSCl)\textsubscript{3} in vacuo,\textsuperscript{29} was expanded into a gas cell (figure 1.5, page 16). The gas phase infra-red spectrum of the volatiles present in the
gas cell were recorded and tin (IV) chloride, contained in a sealable side arm, was then expanded into the cell. A series of infra-red spectra were recorded over a period of 16h, which indicated that a slow reaction was taking place, with the slow decrease in concentration of NSCl.

Gas phase infra-red spectrum recorded after 16h.: 1378s (sh)*, 1372s*, 1360vs*, 1350s*, 1342s*, 1260s (sh), 1255s, 1246s, 1165w*, 1135w*, 850m, 535w*, 505m*, 498m, 468s, 460s, 410vs cm⁻¹ (* Denotes bands assignable to SO₂).

(iii) Reaction of Thiazyl Chloride with Antimony Pentachloride

NSCl, generated by heating (NSCl)₃ in vacuo, was expanded into a gas cell and the gas phase infra-red spectrum of the species contained within the cell recorded. Antimony pentachloride, contained in a sealable side arm, was then expanded into the cell and the gas phase infra-red spectrum recorded. Due to coating of the gas cell windows by a white compound, a very low transmission of energy through the cell resulted, consequently no infra-red data of any significance were recorded.

(iv) Reaction of Thiazyl Chloride with Antimony Pentachloride (Preparative Scale)

The apparatus used for this experiment is shown in Figure 5.2 (page 253). Trichlorotrithiatriazene (0.98g, 4.01 mmole) was placed in bulb A and antimony pentachloride (7 cm³, 54.78 mmole) in bulb B. The apparatus was then completely evacuated and the inlet valve for the antimony pentachloride closed. The apparatus was then flamed out under dynamic vacuum, the (NSCl)₃ not being heated. The (NSCl)₃ was heated to 70°C under a dynamic vacuum and the
volatiles condensed at \(-196^\circ C\) in trap 2. After ca. 10 min. a green liquid was seen to condense in trap 2 (NSCl). Trap 1 was then cooled to \(-7^\circ C\) and the antimony pentachloride inlet valve opened. A colourless crystalline material was readily formed which was contaminated by a green non-crystalline material. The majority of the product was deposited just prior to the \(-7^\circ C\) trap (trap 1). After ca. 4h. the production of NSCl monomer appeared to have stopped and thus the reaction was terminated. The product was sublimed into trap 1 and traps 1 and 2 were sealed off under vacuum.

The product was isolated under dry-box conditions, loaded into a pre-dried vacuum tight vessel (figure 1.2 page 14) and washed with pre-cooled \(\text{SO}_2\) \((-63^\circ C\)). The sulphur dioxide was then removed and the dry (no \(\text{SbCl}_5\) present) pale yellow microcrystalline material isolated. The purified product was then placed in a pre-dried, sublimation tube and the product sublimed, \textit{in vacuo}, to the upper reaches of the tube \((80^\circ C, 10^{-2} \text{ torr})\).

The product was then removed from the sublimation tube in a dry-box and the Raman and mass spectra recorded.

Raman spectrum of the product (red line): 1402vs, 1389w, 330s, *284w, *178m* cm\(^{-1}\) (* Denotes band assignable to the \(\text{SbCl}_6^-\) anion)\(^{42}\)

Mass spectrum (m/e (abundance) assignment) (spectrum run up to mass 226 only): 226(25) \(\text{SbCl}_3\); 195(2) \(\text{SbCl}_2\); 193(100) \(\text{SbCl}_2\); 191(82) \(\text{SbCl}_2\); 160(3) \(\text{SbCl}\); 158(12) \(\text{SbCl}\); 156(9) \(\text{SbCl}\); 123(9) \(\text{Sb}^{123}\); 121(13) \(\text{Sb}^{121}\); 48(6) \(\text{S}\); 46(22) NS; 38(46) \(\text{HCl}^{38}\); 37(3) \(\text{Cl}^{37}\); 36(72) \(\text{HCl}^{35}\); 35(30) \(\text{Cl}^{35}\).
Analysis of the product.

Found: S, 8.04; N, 3.23; Cl, 57.0%

\[ \text{NS}^+\text{SbCl}_6^- \text{ requires: } S, 8.40; N, 3.68; Cl, 55.94\%

(v) Reaction of Thiazyl Chloride with Silver Metal (cf. experiment 3.2.3(c,v) page 123)

\[
\text{(\text{NSCl})}_3 \quad (0.34\text{g, 1.39 mmole}) \text{ contained in a break seal capsule, was placed in a pre-dried vacuum tight pyrex vessel (figure 5.3, page 254). Silver wool (0.9113g, 8.45 mmole) was also placed in the vessel, some 5 cm. from the (NSCl)}_3 \text{ capsule. The complete vessel was then evacuated (10}^{-6} \text{ torr) and flamed out (not the area containing the (NSCl)}_3 \text{ capsule). The (NSCl)}_3 \text{ capsule was then broken and the temperature in the vicinity of the (NSCl)}_3 \text{ slowly raised to ca. 60°C. The volatiles produced were passed over the pre-heated silver wool (200°C), in a dynamic vacuum of 10}^{-5} \text{ torr and the volatile species formed condensed in either the } -15^\circ\text{C trap or the -78°C trap. A deep blue film was rapidly formed, almost directly after the silver wool, which grew in intensity over a period of two hours. During this period of time evidence for the production of } S_2N_2 \text{ was noted in the upper section of the -15°C trap. It was noted that whereas the silver becomes black (Ag}_2\text{S) when cracking } S_4N_4 \text{ to yield } S_2N_2, \text{ the silver from its reaction with thiazyl chloride has a white appearance (AgCl).}

After ca. 2h. thiazyl chloride was noted in the -78°C trap, and from this point onwards a multitude of colours were seen in both the -78°C and -15°C traps. A red compound was also formed which coated the blue (suspected polymer) film. The reaction was continued for 60h. but no further reaction appeared to occur, the only products observed being thiazyl chloride and sulphur chlorides. After 60h. the vessel was
cooled to room temperature and the "U" tubes and tube containing the suspected polymer were sealed in vacuo. The infra-red spectrum of the yellow product isolated from the -78°C trap was consistent with the species being \((\text{NSCl})_3\).

The suspected "polymer" coating gradually turned deep red over a period of a month and the silver surface became black.

Infra-red spectrum of the suspected polymer: 964m, * 944s, * 928s, † 725m, † 715m (sh), * 708s, * 698vs, * 582m, * 552s, † 430m, * 347s † cm⁻¹.

* Denotes peaks assignable to \(\text{S}_2\text{N}_2\text{Cl}\). ⁴⁶
† Denotes peaks assignable to \(\text{S}_4\text{N}_4\). ⁴⁷

5.2.4 Reactions of Thionitrosyl Hexachloroantimonate(V)

(1) The Reaction of \(\text{NS}^+\text{SbCl}_6^-\) with liquid chlorine

\(\text{NS}^+\text{SbCl}_6^-\) (0.3264g, 0.86 mmole) was loaded into a pre-dried vacuum tight pyrex tube (2mm inside diameter, 4m outside diameter) fitted with a Rotoflo valve. The vessel was evacuated and pre-dried chlorine (1.6348g, 4.03 mmole) condensed in. The reaction was agitated at room temperature for 10h. and then the chlorine removed. The Raman spectrum of the resulting compound was identical to that recorded for \(\text{NS}^+\text{SbCl}_6^-\). Chlorine (1.2419g, 17.44 mmole) was again condensed into the vessel and the reaction heated to 80°C for 72h. The chlorine was removed and the Raman spectrum of the resulting yellow compound recorded.

Raman spectrum of the product (red line): 718vs, 654w, 508w, 333s, * 288w, * 220, * 202w, 176m, * cm⁻¹.

(* Denotes bands assignable to \(\text{SbCl}_6^-\)). ⁴²
Infra-red spectrum of the product (nujol mull): 1131m, 720m, 656m, 520vs, 495s, 340vs cm\(^{-1}\).

(cf. \((\text{SCl})_2^+\text{NSbCl}_6^-\): Infra-red spectrum 1130m, 735m(sh), 721m, 654s, 521s, 520s, 494s cm\(^{-1}\)).

Analysis of the product.

Found: N, 3.12; S, 12.2; Cl, 59.5%.

\(\text{NS}_2\text{SbCl}_6\) requires: N, 2.90; S, 13.23; Cl, 58.71%.

(i) Reaction of \(\text{SN}^+\text{SbCl}_6^-\) with excess Elemental Sulphur

Sulphur (1.30g, 5.08 mmole) was loaded into the non-sealable section of a pre-dried, vacuum tight pyrex vessel (figure 1.2, page 14) and pumped on in vacuo for 36h. to remove all traces of moisture. \(\text{NS}^+\text{SbCl}_6^-\) was then loaded into the sealable section of the vessel, whilst under dry-box conditions, and the whole system evacuated. Sulphur dioxide (13.41g) was then condensed in and the \(\text{NS}^+\text{SbCl}_6^-\) solution filtered onto the sulphur. An immediate reaction occurred forming a deep red solution. After agitating for 2h. at room temperature the system was filtered. The insolubles were washed with recondensed sulphur dioxide removing all possible traces of the solubles. It was noted that a brown insoluble compound had been produced. The solvent was slowly evaporated from the filtrate and an orange-red precipitate was deposited. The solvent was finally removed and the products dried in vacuo. The vessel was then placed in the port of the dry-box and left for 1h. On admitting the vessel to the box it was noted that the brown insolubles had changed, yielding a pale yellow species, presumed to be sulphur due to its lack of an infra-red spectrum. The solubles were isolated and the infra-red spectrum recorded.
Infra-red spectrum of the solubles (nujol mull): 1495 vs, *
1130 m, † 1058 m, 1020 w, 974 w, 942 vs, ‡ 805 w, 785 w, 775 w,
745 w, 718 m, † 692 w, 654 m, † 622 w, 570 s, 520 vs, † 498 s, †
470 s, 440 s, † 425 vs, † 374 s, *, ‡ 340 vs (SbCl$_6^-$) cm$^{-1}$.

(* Denotes bands assignable to S$_2$N$^+$SbCl$_6^-$.
† Denotes bands assignable to (SCl)$_2$N$^+$SbCl$_6^-$
‡ Denotes bands that may be assignable to S$_3$N$_2$Cl$^+$SbCl$_6^-$).
5.3 Discussion

The chemistry of thionitrosyl salts has not been developed significantly since their reported synthesis in 1970.\textsuperscript{26} The reason for this is thought to be due to the difficulty in preparing the basic starting material thiazyl fluoride (NSF). As noted previously, Chapter Four (page 159), the chemistry of thiazyl fluoride is itself largely unexplored, probably due to the problems of handling the gas and the related problems of synthesising the compound. No other route to thionitrosyl salts has been reported other than via NSF and thus investigations were carried out to determine whether various sulphur-nitrogen species, which were readily available, could be oxidised under vigorous conditions to yield thionitrosyl salts.

5.3.1 The Oxidation of Tetrasulphur Tetranitride and Trichlorotrithiatriazene

The oxidation of tetrasulphur tetranitride by $\text{XeF}^+$, $\text{SbF}_5$ and $\text{SbF}_5$ in $\text{AsF}_3$ solution were studied. In all cases the results were disappointing due to the problems of removing the excess, relatively involatile, $\text{SbF}_5$ at the end of the reaction. Although obvious signs of reaction were noted and reduced products were obtained ($\text{SbF}_3 \cdot \text{SbF}_5 \text{(Form A)}$\textsuperscript{50} colourless crystals, experiment 5.2.1(ii), page 231) no definite identification of the oxidised products was made.

The investigation of the reactions of trichlorotrithiatriazene with arsenic trifluoride and antimony pentafluoride were carried out at elevated temperatures for prolonged periods of time (72h.) (experiment 5.3.2(1), page 232).
The reaction was designed with the intention that the thiazyl chloride would exchange with either \( \text{AsF}_3 \) or \( \text{SbF}_5 \) to yield thiazyl fluoride, which would then react with the excess \( \text{SbF}_5 \) to form \( \text{NS}^+\text{SbF}_6^- \). Prolonged refluxing of the reaction did not decolorize the system, as would have occurred if the \( \text{NS}^+\text{SbF}_6^- \) salt had been produced. The product obtained, on removing the solvent and excess \( \text{SbF}_5 \), was deep red and still contained appreciable quantities of \( \text{SbF}_5 \), even after drying in \textit{vacuo} for 10h. In order to remove the excess \( \text{SbF}_5 \) the product was washed with sulphur dioxide. It was noted that on cooling the \( \text{SO}_2 \) to \(-63^\circ\text{C}\), a white compound was precipitated. The Raman spectrum of this species was remarkably simple consisting of bands assignable to \( \text{SbF}_6^- \) and three other bands at 1208, 499 and 266 cm\(^{-1}\). The simplicity of the Raman spectrum implies that the cation must be relatively small and probably of quite high symmetry. Comparison of the spectrum with known sulphur-nitrogen species led to the conclusion that the 1208 cm\(^{-1}\) band is consistent with a species containing an S-N band of high bond order (cf. \( \text{ClN}=\text{SF}_2 \) 1178 cm\(^{-1}\)). The observed band at 499 cm\(^{-1}\) is very similar to that observed in the \( \text{SCl}_3^+ \) cation (\( \text{SCl}_3^+ \) \( \nu_1 \) (\( A_1 \)): 498 cm\(^{-1}\) very strong). Hence from the vibrational data it would seem plausible to suggest that the cation could be \( (\text{N}=\text{SCl}_2^+) \). Such a cation would be isoelectronic and isostructural to \( \text{O}=\text{SCl}_2 \). Thus a similar vibrational spectrum would be expected (table 5.1).

**TABLE 5.1 The Raman Spectrum of Thionyl Chloride**

| \( \nu(S-O) \) \( \nu_s(\text{SCl}_2) \) \( \delta(\text{SOCl}) \) \( \delta(\text{SCL}_2) \) \( \nu_{as}(\text{SCl}_2) \) \( \delta \) |
|---|---|---|---|---|---|
| 1229 | 490 | 394 | 194 | 443 | 284 |
As seen from Table 5.1, \( v_1, v_2 \) and possibly \( v_6 \) correspond to the bands observed in the product at 1208, 499 and 266 cm\(^{-1}\). It is therefore suggested that the reaction of (NSCl)\(_3\) with SbF\(_5\) (molar ratio 1:4) produces \( \text{NS}^+\text{SbF}_6^- \) and \( \text{NSCl}_2^+\text{SbF}_6^- \) (equation 5.15).

\[
\frac{2}{3}(\text{NSCl})_3 + 3\text{SbF}_5 \rightarrow \text{NS}^+\text{SbF}_6^- + \text{NSCl}_2^+\text{SbF}_6^- + \text{SbF}_5
\]  (5.15)

The postulate was tested by reacting (NSCl)\(_3\) with AsF\(_5\) (molar ratio 1:4) (Experiment 5.2.2(iii), page 233) and observing the weight of residue at the end of the reaction. The weight of residue was found to be consistent with that expected from equation 5.15 when using AsF\(_5\) instead of SbF\(_5\). The infra-red spectrum of the product, from the reaction of (NSCl)\(_3\) with AsF\(_5\), contained a band assignable to the \( \text{NS}^+\text{AsF}_6^- \) salt (observed stretching frequency 1445 cm\(^{-1}\) reported 1437 cm\(^{-1}\)) and also contained a band at 500 cm\(^{-1}\), that could be assigned to the species \( \text{NSCl}_2^+\text{AsF}_6^- \). Hence it seems likely that the species \( \text{NSCl}_2^+\text{MF}_6^- \) could be formed in the reactions of (NSCl)\(_3\) with SbF\(_5\) or AsF\(_5\). Analysis of the product isolated from the reaction of SbF\(_5\) with (NSCl)\(_3\), using AsF\(_3\) as a solvent, was not however of any use in identifying the compound as more than one species appeared to be present. In an attempt to synthesise \( \text{NSCl}_2^+\text{SbF}_6^- \) and isolate the salt in a pure state \( \text{NS}^+\text{SbCl}_6^- \) was reacted with chlorine (see section 5.3.4, page 250), the product obtained did not however possess the same Raman spectrum as that of the supposed \( \text{NSCl}_2^+ \) cation.

5.3.2 The Reactions of Thiazyl Chloride with Lewis Acids

By direct analogy with the reactions of thiazyl fluoride with fluoro Lewis acids (BF\(_3\), SbF\(_5\) and AsF\(_5\)),\(^{26,27}\) the reactions of thiazyl chloride with chloro Lewis acids
(BCl₃, SbCl₅, SnCl₄ and AlCl₃) were investigated. All the initial investigative reactions, except that with AlCl₃, were carried out using a gas cell, in order to monitor the reaction of the Lewis acid with thiazyl chloride and hence identify the products by their infra-red spectra. The procedure was successful in the cases of SnCl₄ and BCl₃ but with SbCl₅, coating of the gas cell windows occurred which virtually stopped all transmission of energy through the cell (experiment 5.2.3(iii), page 236). The products from the slow reaction of tin(IV) chloride with thiazyl chloride were SO₂ and an unidentified gaseous product (experiment 5.2.3(ii), page 235). It was therefore concluded that tin(IV) chloride and thiazyl chloride do not in fact react, the products observed in the gas phase infra-red spectrum being hydrolysis products of NSCl. The reaction between thiazyl chloride and boron trichloride (experiment 5.2.3(i), page 235) was however very rapid forming a series of compounds (deduced from the complexity of the spectrum) one of which gave an infra-red band at 1422 cm⁻¹, which would be consistent with a species NS⁺BCl₄⁻. However on removing the excess boron trichloride all the products were lost from the cell thus implying that the thionitrosyl salt, if produced, sublimes very easily or readily dissociates into BCl₃ and NSCl, which are then removed.

In order to increase the stability of the thionitrosyl, the synthesis of salts with larger anions were investigated in preparative scale reactions. The reaction of aluminium trichloride with trichlorotrithiatriazene at elevated temperatures (70°C) (effectively AlCl₃ and NSCl) produced no oxidised sulphur-nitrogen species only chlorine
and disulphur dichloride, basically the thermal breakdown products of NSCl. However on reacting thiazyll chloride with gaseous SbCl$_5$ in a flow system, with pre-cooled traps, a virtually colourless crystalline material was formed which was contaminated by a deep green amorphous material (experiment 5.2.3(iv), page 236). The product readily sublimed and was found to trap out in a ca. -10°C trap. The main contaminant of the product, other than the aforementioned green material, was excess SbCl$_5$. Initially attempts were made to purify the product by sublimation but the vapour pressure, due to the SbCl$_5$, slowed the sublimation down. However SbCl$_5$ would have been a contaminant even if the sublimation were successful. Methods of removing the SbCl$_5$ as the first step in the purification procedure were therefore sought. The most convenient and effective method found was to wash the crude product with cold sulphur dioxide and a sealed system sublimation of the washed product, in vacuo, at 80°C yielded virtually colourless crystals of the product. The deep green impurity did not sublume but was noted to change in colour to yellow after 5-10h. Raman spectra of both the impurity and the product were recorded. The product gave an excellent spectrum with a strong band at 1402 cm$^{-1}$ and a very weak side band at 1389 cm$^{-1}$. The non-sublimed impurity did not give a Raman spectrum due to decomposition in the laser beam.

The Raman spectrum of the product is very simple, there being only the two bands at 1402 and 1389 cm$^{-1}$ and bands assignable to the SbCl$_6^-$ anion. The simplicity of the spectrum and the position of the main band at 1402 indicates that the product is almost certainly NS$^+\text{SbCl}_6^-$. Mass spectral and analytical data confirm that the species is NS$^+\text{SbCl}_6^-$. 
The main band at 1402 cm\(^{-1}\) is somewhat lower than that observed in NS\(^+\)SbF\(_6\)\(^-\) (1448 cm\(^{-1}\)),\(^{27}\) NS\(^+\)AsF\(_6\)\(^-\) (1437 cm\(^{-1}\))\(^{26}\) and NS\(^+\)CF\(_3\)SO\(_3\)\(^-\) (1443 cm\(^{-1}\)):\(^{27}\) It is suggested that greater cation-anion interactions occur in the NS\(^+\)SbCl\(_6\)\(^-\) salt than in the SbF\(_6\)\(^-\) and AsF\(_6\)\(^-\) salts due to the higher polarisability of the SbCl\(_6\)\(^-\) anion thus causing a drop in the observed stretching frequency of the N=S\(^+\) cation.

The side band at 1389 cm\(^{-1}\) is of the correct intensity for the (N=S\(^{34}\))\(^+\) cation, i.e. 5% of the intensity of the (N=S\(^{32}\))\(^+\) band (1402 cm\(^{-1}\)). The theoretical position of the (N=S\(^{34}\))\(^+\) band can be calculated knowing the reduced mass of each cation and the band position of (N=S\(^{32}\))\(^+\) (equation 5.16).

Equation 5.16
\[
\frac{v_{\text{spec}}}{v_{\text{spec}}} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}} \quad \text{(ref. 55)}
\]
(K = the force constant; \(\mu\) = the reduced mass; \(c\) = the velocity of light).

For comparison of the stretching frequencies of the cations (N=S\(^{32}\))\(^+\) and (N=S\(^{34}\))\(^+\) the above equation may be simplified

\[
\frac{v_{\text{spec}}}{v_{\text{spec}}} \propto \frac{1}{\sqrt{\mu}}
\]

Thus if the stretching frequency of the (N\(^{14}\)=S\(^{32}\))\(^+\) cation is known (x cm\(^{-1}\)) then the stretching frequency of the (N\(^{14}\)=S\(^{34}\))\(^+\) cation is given by

\[
v_{N=S^{34}} = x \cdot \sqrt{\frac{\mu_{(N=S^{34})^+}}{\mu_{(N=S^{32})^+}}} = 1402 \cdot \sqrt{\frac{0.1008}{0.1027}} = 1389 \text{ cm}^{-1}
\]
The calculated and observed positions of the \( (N = S^{3/4})^+ \) band are therefore coincident thus reinforcing the basic assumption that the \( 1402 \text{ cm}^{-1} \) band is assignable to the \( N = S^+ \) stretching vibration.

5.3.3 Further Reactions of Thiazyl Chloride

Several unsuccessful reactions were attempted in which thiazyl chloride was passed through columns of sodium hexafluorophosphate, sodium tetrafluoroborate and aluminium trichloride. In all cases the formation of the desired product, \( (NS^+ \text{ salts}) \) was not observed, thiazyl chloride passing through the column unreacted or being dissociated in to \( N_2 \) and sulphur chlorides. Attention is however drawn to the reactions of thiazyl chloride with cesium fluoride in which thiazyl fluoride is formed (Chapter Four, page 205).

As noted in Chapter Three (page 123), when trichlorotrithiatriazene is placed under vacuum in the presence of silver wool it appears to be reduced forming the blue precursor to \( (SN)_x \). It was suspected that the actual sulphur-nitrogen reactant in the above reaction was thiazyl chloride \( (NSCl) \), which when reduced yields \( [NS]^- \) radicals which form short open chain species which, in turn, slowly polymerise to give \( (SN)_x \). The reaction of thiazyl chloride with silver was therefore investigated.

Thiazyl chloride was passed over heated silver wool and the deep blue film of polymer precursor quickly formed (experiment 5.2.3(v), page 238). The film of polymer precursor grew rapidly over the first two hours virtually no thiazyl chloride passing through the silver unreacted. Evidence was seen in the first "U" tube trap \((-15^\circ C)\) of \( S_2N_2 \). However after two hours thiazyl chloride started to condense
in the \(-78^\circ\text{C}\) trap. It is believed that after ca. 2h. the surface of the silver wool had become coated with chloride and the transport of silver through the chloride coat was not rapid enough to cope with the flux of thiazyl chloride, hence thiazyl chloride was observed in the traps. The products finally isolated from the reaction proved to be \(S_3N_2\text{Cl}\) and \(S_4N_4\) (the suspected polymer coating) and \((\text{NSCl})_3\) from the \(-78^\circ\text{C}\) trap. The presence of \(S_4N_4\) and \(S_3N_2\text{Cl}\) can be explained by the cyclisation of the open chain polymer precursors and their reaction with thiazyl chloride.

It is therefore concluded that although the reaction of thiazyl chloride with silver reported in this chapter was not successful, with respect to the isolation of \((\text{SN})_x\), the basic principle of passing thiazyl chloride over a silver surface to produce "\(\text{SN}\)" fragments, which act as polymer precursors, is valid. If a sufficiently large surface area of silver is used, such that no thiazyl chloride passes through without reaction, then a useful, non-hazardous method of coating substrates (e.g. ZnS, ZnSe) with \((\text{SN})_x\) would be available for use under general laboratory conditions. (It should be noted that the silver can be easily regenerated by the passage of hydrogen over the heated surface thus removing the chlorine as hydrogen chloride).

One of the main problems encountered throughout the work with thiazyl chloride was its generation from trichlorotrithiatriazene. Although Patton and Jolly describe the method of production in detail, difficulty was found in practice when trying to produce large quantities at a steady rate. In an attempt to avoid this problem preliminary investigations into the possibilities of storing thiazyl
chloride on a molecular sieve (4A) were carried out. The NSCl was generated in a gas cell and then a valve opened to allow the volatiles to come in contact with activated 4A molecular sieve. By observing the main bands in the infrared spectrum of thiazyl chloride (1328 cm\(^{-1}\)) the concentration of the thiazyl chloride could be monitored with respect to time.

It was found that the concentration of thiazyl chloride quickly decreased on exposure to the molecular sieve. The above procedure was repeated many times until the molecular sieve appeared saturated. The section containing the molecular sieve was then left opened to the gas cell and heated to drive off the absorbed thiazyl chloride. No traces of thiazyl chloride were seen in the gas phase spectrum. Thus it is concluded that thiazyl chloride is strongly absorbed on to the substrate. No further work was carried out on this problem but it is believed that a more thorough investigation into the storing of thiazyl chloride on substrates, such as molecular sieves, may solve the problem of continuous, controllable production of thiazyl chloride for gas phase reactions. If such a production should be found then thiazyl chloride could, as indicated by some of its reactions in this thesis, become a useful synthetic reagent.

5.3.4 The Reactions of the Thionitrosyl Cation (Experiments 5.2.4(i,ii), pages 239,240)

(i) The Reaction of the Thionitrosyl Cation with Chlorine

As previously noted in this chapter (section 5.3.1, page 243), \((\text{NSCl})_3\) reacts with SbF\(_5\) forming a species, which from its Raman spectrum was deduced to be \(\text{NSCl}_2^+\text{SbF}_6^-\).
In order to gain evidence as to the nature of this compound, an attempt to synthesise it from $\text{NS}^+\text{SbCl}_6^-$ and $\text{Cl}_2$ was carried out. The Raman spectrum of the product from the reaction of $\text{NS}^+\text{SbCl}_6^-$ and $\text{Cl}_2$ was compared with that of the postulated $\text{NSCl}_2^+$. The spectra were not identical, the product from the $\text{NS}^+\text{SbCl}_6^-/\text{Cl}_2$ reaction being identified as $(\text{SCl}_2)^+\text{NSbCl}_6^-$. Hence no further evidence as to the exact nature of the product from the $(\text{NSCl})_2^+/\text{SbF}_5$ reaction was gained.

Mews has reported$^{27}$ that $\text{SCl}_2$ reacts with the thionitrosyl cation to form $(\text{SCl}_2)^+\text{N}^+$ salts. Therefore it would seem likely that during the reaction of $\text{NS}^+\text{SbCl}_6^-$ with chlorine at elevated temperatures, $\text{SCl}_2$ is formed as an intermediate which reacts with the thionitrosyl salt present, to form the observed $\text{N}(\text{SCl})_2^+\text{SbCl}_6^-$ salt.

(ii) The Reaction of the Thionitrosyl Cation with Elemental Sulphur

The reactions of $\text{S}_8^{2+}(\text{AsF}_6^-)_2$ with azides have been studied in this thesis (Chapter Six), in order to synthesise cations of the form $\text{S}_x\text{N}^+$ ($x = 1-7$). It was found that the only sulphur-nitrogen cation present in the product of the $\text{S}_8^{2+}/\text{N}_3^-$ reaction was $\text{S}_2\text{N}^+$. Hence in an attempt to prepare $\text{S}_x\text{N}^+$ cations from a different angle, the thionitrosyl cation was reacted with elemental sulphur. The products isolated were characterised, where possible, by their infra-red spectra. The main product from the reaction of $\text{SN}^+$ with sulphur was $\text{S}_2\text{N}^+$. Hence it appears as though all cations of the form $\text{S}_x\text{N}^+$ ($x > 2$) are unstable with respect to $\text{S}_2\text{N}^+$ and sulphur.
The other species identified in the products of the $\text{NS}^+\text{SbCl}_6^-/\text{S}_8$ reaction were $(\text{SCl})_2\text{N}^+\text{SbCl}_6^-$ and $\text{S}_2\text{N}_2\text{Cl}^+\text{SbCl}_6^-$. These cations are probably formed by the reaction of $\text{S}_2\text{N}^+\text{SbCl}_6^-$ with chlorine and thiazylic chloride respectively.
Figure 5.2

Vacuum line

Bulb B

Bulb A

Trap 1

70°C

Trap 2

196°C
Figure 5.3

vacuum line

"polymer" coating

silver wool
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CHAPTER SIX
THE REACTIONS OF GROUP VI POLYCATIONS
WITH NITROGEN CONTAINING SPECIES

6.1 Introduction

Neutral and anionic homonuclear polyatomic species (e.g. $\text{P}_4$, $\text{O}_3$, $\text{S}_8$, $\text{Br}_2$ and $\text{I}_3^-$, $\text{I}_5^-$, $\text{O}_2^-$ and $\text{S}_4^{2-}$) have been known for many years. Homonuclear aggregates of atoms are also present in cluster compounds such as $\text{B}_9\text{H}_9^{2-}$, $\text{Fe}_3\text{CO}_{12}$ and $\text{Ru}_6(\text{CO})_{18}$, in which the ligand donates electron density to the skeletal bonding. However, with the exception of $\text{Hg}_2^{2+}$, which has been known for many years, it is only within the past decade that other stable, cationic homonuclear aggregates - "polycations" - have been synthesised and characterised.

By analogy with the mercury cation, there is substantial evidence for the existence of polyatomic cations in the reactions of metals with their corresponding metal chloride melts (e.g. $\text{Cd}_2^{2+}$, $\text{Zn}_2^{2+}$, $\text{Pb}_2^{2+}$, $\text{Mg}_2^{2+}$, $\text{Ca}_2^{2+}$, $\text{Sr}_2^{2+}$ and $\text{Ba}_2^{2+}$). The first firm evidence for a polyatomic cation $\text{M}_{x}^ {\text{Y}^+}$ (where $x>2$) came in 1963 when Hershaft and Corbett proved, by X-ray crystallography the existence of $\text{Bi}_5^{3+}$, which was later followed by evidence for the existence of $\text{Bi}_8^{2+}$. Since 1963 there have been notable developments in anionic, cationic and neutral homonuclear catenates for the elements in Groups V, VI and VII.  

GROUP VI POLYCATIONS

6.1.1 Polycations of Oxygen

$\text{O}_2^+$ is the main example of the oxygen polycations.
although $O_3^+$ has been observed in atmospheric studies.$^{13,14}$ The polycations of oxygen are reviewed by Gillespie and Passmore$^{26}$ and are not discussed further in this thesis.

6.1.2 Synthetic Routes to Sulphur, Selenium and Tellurium Polycations

The existence of sulphur polycations has been known since 1804, when Bucholz$^{15}$ dissolved sulphur in oleum and obtained various coloured solutions, depending on the composition of the oleum and the relative concentration of the sulphur. Particular note was made of the intense blue colouration that could be produced and various possibilities were suggested as to the identity of the species responsible for this colouration, e.g. $S_2O_3$, $S_2$, $[X_2S-SX_2]^+$, and also a species $S_x$. It was not until 1969, when Gillespie and Passmore$^{20}$ isolated the first crystalline sulphur polycations ($S_8^{2+}$ (AsF$_6^-$)$_2$ and $S_{16}^{2+}$ (AsF$_6^-$)$_2$) that the intensely coloured solutions of $S_8$ in highly oxidising acid media were due to the presence of sulphur polycations. The oxidation of $S_8$ by arsenic or antimony pentafluorides (AsF$_5$, SbF$_5$) in the correct molar ratio, yields either the deep blue $S_8^{2+}$ polycation or the deep red polycation, $S_{16}^{2+}$ (equations 6.1-4).

$$2S_8 + 3\text{AsF}_5 \xrightarrow{\text{HF/So}_2} S_{16}^{2+} (\text{AsF}_6^-)_2 + \text{AsF}_3 (\text{ref.20,21}) \quad (6.1)$$

$$2S_8 + 3\text{SbF}_5 \xrightarrow{\text{HF/So}_2} S_{16}^{2+} (\text{AsF}_6^-)_2 + \text{SbF}_3 (\text{ref.21,22}) \quad (6.2)$$

$$S_8 + 3\text{AsF}_5 \xrightarrow{\text{HF/So}_2} S_{8}^{2+} (\text{AsF}_6^-)_2 + \text{AsF}_3 (\text{ref.20,21}) \quad (6.3)$$

$$S_8 + 3\text{SbF}_5 \xrightarrow{\text{So}_2} S_{8}^{2+} (\text{SbF}_6^-)_2 + \text{SbF}_3 (\text{ref.21,22}) \quad (6.4)$$

(sealed tube)
The cation $S_4^{2+}$ was first isolated as $S_4^{2+} (SO_2F)_2$ from the reaction of $S_8$ with $S_2O_6F_2$, using sulphur dioxide as a solvent at $-23^\circ C$. Then as $S_4^{2+} (Sb_{2F_{11}}^-)_2$ from the reaction of $S_8$ with SbF$_5$ at $140^\circ C$.  \(^{22}\)

(ii) Preparation of the Polycations of Selenium

As in the case of sulphur, highly coloured solutions had been observed (since the early eighteen hundreds (Magnus 1827)\(^{23}\) on dissolving selenium in oxidising acids. The nature of these solutions was not however elucidated until 1968 when Barr et al. presented evidence for the existence of the $Se_4^{2+}$ and $Se_8^{2+}$ polycations from photometric, conductiometric and cryoscopy studies. Salts containing the selenium polycations have been isolated from a variety of reactions (table 6.1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reaction</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Se_4(HS_2O_7)_2$</td>
<td>Se+$65%$ Oleum</td>
<td>$50^\circ-60^\circ$C. Soln. goes yellow-brown. Crystallisation on standing</td>
<td>25</td>
</tr>
<tr>
<td>$Se_4(AsF_6)_2$</td>
<td>$4Se+3AsF_5$</td>
<td>$SO_2$ solvent; $80^\circ$C for 8 days. Yellow solid from green solution</td>
<td>26</td>
</tr>
<tr>
<td>$Se_8(SeCl_4)_2$</td>
<td>$8Se+5SeCl_4$</td>
<td>Solvent $SO_2$: $-23^\circ$C; 3 days</td>
<td>27</td>
</tr>
<tr>
<td>$Se_8(AlCl_4)_2$</td>
<td>$Se/SeCl_4/4AlCl_3$</td>
<td>Obtained from melts</td>
<td>28, 29</td>
</tr>
<tr>
<td>$Se_8(AlCl_4)_2$</td>
<td>$Se/SeCl_4/2AlCl_3$</td>
<td>Fuse at $350^\circ$ for 3h.</td>
<td>28</td>
</tr>
</tbody>
</table>
(iii) Preparation of the Tellurium Polycations

It has been known for 150 years that tellurium dissolves in sulphuric acid to give a deep red colouration\(^\text{30}\) (cf. \(S_{2},Se\) in highly oxidising acids). Bjerrum\(^\text{31,32}\) postulated that the species responsible for the red colouration was of the form \(\text{Te}_{2n}^{2+}\). Investigation of the solutions of tellurium in various acid media by conductometric and cryoscopic methods\(^\text{33,34}\) supported the postulate made by Bjerrum and suggested that the species was in fact \(\text{Te}_{4}^{2+}\). During the past decade various crystalline compounds containing tellurium polycations have been synthesised (table 6.2) and their X-ray crystal structure determined.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Synthesis</th>
<th>Conditions</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Te}<em>{4}(\text{SbF}</em>{5})_{2})</td>
<td>(4\text{Te}+5\text{SbF}_{5})</td>
<td>(\text{SO}<em>{2}) solvent: stirred for several days at (-23^\circ\text{C}). (\text{SO}</em>{2}) soluble products isolated</td>
<td>34</td>
</tr>
<tr>
<td>(\text{Te}<em>{4}(\text{AsF}</em>{6})_{2})</td>
<td>(4\text{Te}+3\text{AsF}_{5})</td>
<td>(\text{Solvent SO}_{2}:) stirred 24h. at (25^\circ\text{C})</td>
<td>34</td>
</tr>
<tr>
<td>(\text{Te}<em>{6}(\text{AsF}</em>{6})_{2})</td>
<td>(6\text{Te}+3\text{AsF}_{5})</td>
<td>(\text{Solvent SO}_{2}:) stirred 24h. at (25^\circ\text{C})</td>
<td>34</td>
</tr>
<tr>
<td>(\text{Te}<em>{4}(\text{AlCl}</em>{3})_{2})</td>
<td>(\text{Te/TeCl}<em>{4}/4\text{AlCl}</em>{3})</td>
<td>Obtained from the melt</td>
<td>35</td>
</tr>
<tr>
<td>(\text{Te}<em>{x}(\text{SO}</em>{3} \cdot \text{F})_{x})</td>
<td>(4\text{Te}+8\text{SO}<em>{2} \cdot \text{F}</em>{2})</td>
<td>Yellow comp. Unstable above (-20^\circ\text{C})</td>
<td>34</td>
</tr>
<tr>
<td>(\text{Te}<em>{6}(\text{AsF}</em>{6})<em>{4} \cdot 2\text{AsF}</em>{3})</td>
<td>(6\text{Te}+6\text{AsF}_{5})</td>
<td>Solvent (\text{AsF}_{3})</td>
<td>36</td>
</tr>
</tbody>
</table>
6.1.3 The Structures of the Group VI Polycations

(i) Structures of the Cations containing Four Group VI Atoms

The X-ray crystal structures of both the Se$_4^{2+}$ and Te$_4^{2+}$ polyatomic cations have been determined and in both cases a close approximation to a square planar arrangement is found (figure 6.2, page 301). Knowing the structures of Se$_4^{2+}$ and Te$_4^{2+}$, it is possible to deduce from magnetic circular dichroism, visible U.V., and solution Raman data that a similar square planar arrangement is likely for S$_4^{2+}$.

(ii) Structures of the Cations containing Eight Group VI Atoms

Two homonuclear cations are known with the formulation $X_8^{2+}$ ($X = S, Se$). The X-ray crystal structures of both these species have been determined and similar structures have been deduced (figure 6.3, page 301). The average bond distance in the S$_8^{2+}$ ring is 204 pm, which is identical to that found in the S$_8^{4+}$ ring. However, the cross ring distances are significantly reduced with respect to elemental S$_8$, implying significant cross ring interactions. This is supported by the reduction in the bond angles found in S$_8$ (109.7°) to the range 91.5° to 104.3°, as found in S$_8^{2+}$. In the Se$_8^{2+}$ cation a similar skeletal arrangement is found. The Se(3) - Se(7) cross ring distance (284pm) is however relatively shorter than the S(3)-S(7) distance (286pm) in S$_8^{2+}$. Whereas the Se(4)-Se(6) (329pm) and Se(2)-Se(8) (335pm) cross ring distances are relatively longer than the corresponding distances in S$_8^{2+}$ (300 and 294pm respectively). Thus the canonical form shown in figure 6.3 (page 301) is more
significant in the valence bond description of Se$_8^{2+}$ than S$_8^{2+}$. The bond lengths in Se$_8^{2+}$ vary between 229pm and 236pm which are not that significantly different from those found in α or β selenium.$^{42,43}$ As in the case of S$_8^{2+}$ the bond angles in the selenium polycation decrease with respect to those in α or β selenium, being in the range 89.8-103.6°.

(iii) Crystal Structure of Te$_6^{4+}$(AsF$_6^{-}$)$_4$·2AsF$_3$.\[36$

The Te$_6^{4+}$ cation represents the first example of a hexa-atomic trigonal prism (figure 6.4, page 302) (cf. C$_6$(CH$_3$)$_6$, $^{44}$ Bi$_9^{5+}$ $^{45}$). The Te-Te bond lengths found within the triangles show significant multiple bond character being similar in length to those in Te$_4^{2+}$ which may be described as having 25% double bond character.$^{46}$

6.1.4 Reactions of the Group VI Polycations

There are very few reactions of the Group VI polycations reported in the literature. Those reactions published to date fall within three categories:

(i) The formation of heteronuclear Group VI polycations,
(ii) The reactions of Group VI polycations with Group VII elements.
(iii) The reaction of Group VI polycations with perfluorinated alkenes.

6.1.4 (i) The Formation of Heteronuclear Group VI Polycations

Since the isolation of the homonuclear polycations, in the early 1970s, there has been an interest in the preparation and structures of the inter-chalcogen (heteronuclear) analogues. No mixed sulphur-selenium cations have been reported to date but both tellurium-selenium and tellurium-sulphur cations have been prepared,$^{47,48}$ and their structures
determined.

(a) Preparation and Structure of Te$_2$S$_3^{2+}$

\[
\text{Te}_4^{2+}\left(\text{AsF}_6^-ight)_2 + \text{S}_8^{2+}\left(\text{AsF}_6^-ight)_2 \xrightarrow{\text{SO}_2} \text{Te}_2\text{S}_3^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 48)}
\]

\[
\text{Te/S alloy (1:1) + 3AsF}_5 \xrightarrow{\text{SO}_2} \text{Te}_2\text{S}_3^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 48)}
\]

\[
\frac{3}{8} \text{S}_8 + 3\text{Te} + 3\text{AsF}_5 \xrightarrow{\text{SO}_2} \text{Te}_2\text{S}_3^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 48)}
\]

The structure of Te$_2$S$_3^{2+}$ is given in figure 6.4 (page 302).

(b) Preparation and Structure of Te$_2$Se$_4^{2+}$

\[
\text{Te} + \text{Se} \xrightarrow{\text{SO}_2/\text{AsF}_5} \text{Te}_2\text{Se}_4^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 48)}
\]

The structure of Te$_2$Se$_4^{2+}$ is given in figure 6.4 (page 302).

(c) Preparation and Structure of Te$_2$Se$_8^{2+}$

\[
2\text{Te} + \text{Se}_8^{2+}\left(\text{AsF}_6^-ight) \xrightarrow{\text{SO}_2} \text{Te}_2\text{Se}_8^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 47)}
\]

The structure of Te$_2$Se$_8^{2+}$ is given in figure 6.4 (page 303).

(d) Preparation and Structure of Te$_{3.7}$Se$_{6.3}^{2+}$\left(\text{AsF}_6^-ight)_2

\[
\text{Se} + \text{Te} + 3\text{AsF}_5 \xrightarrow{\text{SO}_2} \text{Te}_{3.7}\text{Se}_{6.3}^{2+}\left(\text{AsF}_6^-ight)_2 \text{(ref. 47)}
\]

\[
\text{Te}_{3.7}\text{Se}_{6.3}^{2+}\left(\text{AsF}_6^-ight)_2 \xrightarrow{24\text{h.}} \text{Te}_{3.7}\text{Se}_{6.3}^{2+}\left(\text{AsF}_6^-ight)_2
\]

The crystal structure of the species (figure 6.4, page 303) indicates that there is a mixture of Te$_3$Se$_7^{2+}$ and Te$_4$Se$_6^{2+}$ in approximately equal concentrations.

6.1.4(ii) The Reactions of the Group VI Polycations with the Halogens

There has only been one paper published in this area of chemistry, that of Passmore et al.\textsuperscript{49} in which they prepared S$_3$$^+$MF\textsuperscript{6} isoelectronic to S$_8^{2+}$, S$_7^{50,51}$ and S$_8^{52,53}$. 
and determined its crystal structure. The $S_7I^+$ cation was the first binary sulphur iodide isolated to be stable at room temperature.

The species $S_7I^+$ was prepared by a variety of routes (figure 6.1).

FIGURE 6.1 Preparative Routes to the $S_7I^+$ Cation

\[
\begin{align*}
&\text{I}_3^+ \text{AsF}_6^- + S_8 \quad \text{(excess)} \xrightarrow{\text{AsF}_3} \quad S_7I^+_\text{MF}_6^- \\
&\text{I}_2^+\text{Sb}_2\text{F}_{11}^- + S_8 \quad \text{(excess)} \xrightarrow{\text{AsF}_3} \\
&S_8 + I_2 + \text{AsF}_5/\text{SbF}_5 \quad \text{(excess)} \xrightarrow{\text{AsF}_3} \\
&S_{16}^{2+}(\text{AsF}_6^-)_2 + I_2 \quad \text{(excess)} \xrightarrow{\text{AsF}_3}
\end{align*}
\]

The structure of $S_7I^+\text{SbF}_6^-$ is given in figure 6.5 (page 304).

Recent attempts by Passmore and Sutherland to prepare $S_8I^+$ have failed. However in an attempt to prepare $S_5I^+$ from the reaction of sulphur with iodine and antimony pentafluoride, in the appropriate ratio, the species $(S_7I)_2I^3+ (\text{SbF}_6^-)_3 \cdot 2\text{AsF}_3$ was isolated,$^{54}$ (equation 6.5).

$$28/8 \, S_8 + 3I_2 + 10\text{SbF}_5 \xrightarrow{\text{AsF}_6} 2 \,(S_7I)_2I^3+ \,(\text{SbF}_6^-)_3 \cdot 2\text{AsF}_3 \tag{6.5}$$

The structure of the $(S_7I)_2I^3+$ cation is given in figure 6.5, (page 304).

6.1.4(iii) The Reaction of the Group VI Polycations with Perfluoro-alkenes

Passmore et al.$^{55-58}$ have reported the reactions of all the Group VI polycations (except $\text{Te}_6^{4+}$) with
tetrafluoroethene \((C_2F_4)\). The products of these reactions vary in nature depending on whether a solvent (normally sulphur dioxide) is present or not. The products of the above reactions are presented in tables 6.3a,b.

The reactions of \(S_4^{2+}\) and \(S_8^{2+}\) with perfluoropropene \((C_3F_6)\) have also been studied by Passmore and Desjardins\(^5\) and are found to proceed by a similar mechanism, yielding analogous organo-Group VI species to those isolated from the reactions of sulphur polycations with \(C_2F_4\).

### Table 6.3a Reactions of Group VI Polycations with Perfluoroethene without Solvents

<table>
<thead>
<tr>
<th>Group VI Polycation</th>
<th>(S_8^{2+})</th>
<th>(S_4^{2+})</th>
<th>(Se_8^{2+})</th>
<th>(Se_4^{2+})</th>
<th>(Te_4^{2+})</th>
<th>(Te_6^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Classification</td>
<td>value of (x)</td>
<td>value of (x)</td>
<td>value of (x)</td>
<td>value of (x)</td>
<td>value of (x)</td>
<td></td>
</tr>
<tr>
<td>((C_2F_5)_2M_x)</td>
<td>2,655</td>
<td>2,58</td>
<td>2,356</td>
<td>1,358</td>
<td>1,257</td>
<td>1,257</td>
</tr>
<tr>
<td>((C_4F_9)_2M_x)</td>
<td>1,256</td>
<td>2,256</td>
<td></td>
<td></td>
<td>1,257</td>
<td>1,257</td>
</tr>
<tr>
<td>((C_4F_9)_2M_x)</td>
<td>1,258</td>
<td>2,256</td>
<td></td>
<td></td>
<td>1,257</td>
<td>1,257</td>
</tr>
<tr>
<td>((C_2F_5)M_xC_2F_6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((C_2F_5)_2M_x)_2Hg</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(C_2F_5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Group VI Polycation</td>
<td>$S_8^{2+}$</td>
<td>$Se_6^{2+}$</td>
<td>$Se_4^{2+}$</td>
<td>$Te_4^{2+}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------------------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Product Classification</td>
<td>value of $x$</td>
<td>value of $x$</td>
<td>value of $x$</td>
<td>value of $x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(CF_3)_2M_x$</td>
<td>358</td>
<td>256</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(C_2F_5)_2M_x$</td>
<td>2,355</td>
<td>2,658</td>
<td>2,342</td>
<td>157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(C_4F_9)_2M_x$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2F_5M_xCF_3$</td>
<td>2,355</td>
<td>3,558</td>
<td>256</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_4F_9M_xC_2F_5$</td>
<td>1,257</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(CF_3)M_xCF_2C(0)F$</td>
<td>3,458</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(C_2F_5)M_xC_3F_6C(0)F$</td>
<td>2,355</td>
<td>2,558</td>
<td>258</td>
<td>157</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(CF_2COF)_2M_x$</td>
<td>2,458</td>
<td>258</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.2 Experimental

6.2.1 Reactions of Group VI Polycations with Azides

(1) Reaction of $S_8^{2+}(AsF_6^-)_2$ with Sodium Azide using Sulphur Dioxide as a Solvent

$S_8^{2+}(AsF_6^-)_2$ (0.3945g, 0.622 mmole) and NaN$_3$ (0.0420g, 0.646 mmole) were placed in a pre-dried vacuum tight, pyrex vessel (figure 1.1, page 14) and SO$_2$ (4.5191g) condensed in. The reaction was allowed to warm slowly to room temperature. The initial deep blue coloration of the polycation solution gradually turned deep green then red. The reaction was agitated at room temperature for 12h. during which time precipitation of a pale yellow compound occurred. The product, soluble in sulphur dioxide, was filtered off leaving a pale yellow precipitate. The solvent was removed under reduced pressure and the weight due to the solvent and any other volatile species was recorded (4.5394g), corresponding to 4.5191g of SO$_2$ and 0.0203g of volatile product (nitrogen).

The infra-red and Raman spectra were recorded on both the soluble and insoluble products.

Infra-red spectrum of the insolubles (nujol mull): 695vs, br, 394vs cm$^{-1}$.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm$^{-1}$.

Infra-red spectrum of the solubles (nujol mull): 1498s, 695vs, br, 394vs cm$^{-1}$.

Raman spectrum of the solubles (red line): not obtained.
(ii) Reaction of $S_8^{2+}(AsF_6^-)_2$ with Sodium Azide using Arsenic Trifluoride as a Solvent

$S_8^{2+}(AsF_6^-)_2$ (2.8248g, 4.455 mmole) was loaded into an isolatable bulb of a pre-dried, vacuum tight, pyrex vessel (figure 1.2, page 14) and NaN$_3$ (0.2916g, 4.486 mmole) into the second bulb. The AsF$_3$ (17.4813g) was condensed on to the polycation and the deep blue solution was added to the azide, with the resulting formation of a green then deep red solution. The reaction was stirred at 0°C for 54h. An orange-red precipitate was formed in a deep red solution. The solution was filtered off and the insolubles were washed with recondensed solvent yielding an orange solution and a pale yellow precipitate.

Slow removal of the AsF$_3$ solvent from the solution did not yield crystals but gave an amorphous mass which "foamed" when pumped on at reduced pressure. The weight loss recorded after the removal of all the volatiles present at room temperature corresponded to a loss of the solvent and 0.1228g of volatile product (nitrogen). The vessel was broken under dry-box conditions and the soluble product (0.910g) and insoluble product (2.024g) isolated.

Infra-red spectrum of the insolubles (nujol mull): 695vs, 394vs cm$^{-1}$.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm$^{-1}$.

Infra-red spectrum of the solubles (nujol mull): 1495s, 695vs, 394vs cm$^{-1}$.
(iii) Reaction of $S_8^{2+}(\text{AsF}_6^-)_2$ with CsN$_3$ using SO$_2$ as a Solvent

$S_8^{2+}(\text{AsF}_6^-)_2$ (0.8886g, 1.402 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (Figure 1.2, page 14) and sealed. CsN$_3$ (0.2546g, 1.455 mmole) was loaded into the second bulb and SO$_2$ (15.1364g) condensed in. The cesium azide solution was then filtered on to the polycation solution. An immediate reaction occurred forming a deep red solution and a pale yellow precipitate. The reaction was agitated for 4h. at room temperature and then the soluble product filtered off. The solvent was slowly removed from the filtrate leaving an intensely coloured red oil which "foamed" when the vessel was pumped on under reduced pressure.

The weight loss recorded on removal of the volatiles at room temperature corresponded to the weight of solvent and 0.0529g of volatile product (nitrogen). The vessel was broken under dry-box conditions and the solubles and insolubles isolated. The Raman and infra-red spectra of the products were recorded.

Infra-red spectrum of the solubles (nujol mull): 1495m, 695vs,br, 395vs cm$^{-1}$.

Raman spectrum of the solubles (red line): not obtained.

Infra-red spectrum of the insolubles (nujol mull): 695vs,br, 392vs cm$^{-1}$.

Raman spectrum of the insolubles (red line): 152, 220, 243, 434, 472 cm$^{-1}$.

Analysis of the soluble product.

Found: S, 50.47; N, 1.65; As, 19.3%.

$S_{13}\text{Na}_2\text{As}_2\text{F}_{12}$ requires: S, 51.48; N, 1.73; As, 18.57%.
(iv) Reaction of $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$ with Cesium Azide ($\text{CsN}_3$)

Se$_4^{2+}(\text{AsF}_6^-)_2$ (0.8537g, 1.230 mmole) was loaded into the sealable section of a pre-dried, vacuum tight, pyrex vessel (Figure 1.2, page 14) and sealed. Cesium azide (0.2250g, 1.266 mmole) was placed in the second bulb and $\text{SO}_2$ (15.6314g) condensed into the vessel (approx. 50% of the $\text{SO}_2$ in each bulb). The yellow CsN$_3$ solution was then filtered on to the green selenium polycation solution. An immediate reaction occurred forming a deeply coloured solution and a brown precipitate. The reaction was agitated for 4h. and then the solubles were filtered off leaving a tan coloured insoluble residue. The solvent was slowly removed from the solution yielding a black precipitate. On complete removal of the solvent a weight loss corresponding to the weight of solvent and 0.0364g of volatile product (nitrogen) was recorded.

The solubles (0.1443g) and insolubles (0.8198g) were isolated under dry-box conditions and their infra-red spectra recorded.

- Infra-red spectrum of the insolubles (nujol mull): 695vs, br, 392vs cm$^{-1}$.

- Infra-red spectrum of the solubles (nujol mull): 720s(sh), 695vs, 395vs cm$^{-1}$.

Analysis of the insolubles.

Found: N, 0.38%.
(v) Reaction of Se$_8^{2+}$(AsF$_6^-$)$_2$ with Et$_4$N$^+$N$_3^-$

Se$_8^{2+}$(AsF$_6^-$)$_2$ (3.1009g, 3.071 mmole) was loaded into a pre-dried, vacuum tight, pyrex vessel and sealed off by a Rotoflo valve. Et$_4$NCl (0.5732g, 3.463 mmole) and NaN$_3$ (0.3071g, 4.725 mmole) were placed in a second sealable section and SO$_2$ (10.4834g) was condensed into both bulbs (similar to figure 1.2, page 14 but with three bulbs, two of which are sealable). The resulting deep yellow Et$_4$N$^+$N$_3^-$ solution was then filtered on to the deep green polycation solution forming a red-brown solution and an insoluble black precipitate. The reaction was stirred at room temperature for 15h. and then the soluble product filtered off. The solvent was then slowly evaporated off the solution leaving a deep brown microcrystalline material (3.064g) and a black insoluble product (0.289g).

Infra-red spectrum of the insolubles (nujol mull): 1080w, 1015w cm$^{-1}$.

Infra-red spectrum of the solubles (nujol mull): 1400m, 1305m, 1180s, 1145w, 1072w, 1028s, 1000s, 930m, 789s, 720-670vs, 630s(sh), 580m, 452m, 400-380vs cm$^{-1}$.

(The solubles contain an Et$_4$N$^+$X$^-$ salt, identified from the above infra-red spectrum).

(vi) Reaction of Te$_4^{2+}$(AsF$_6^-$)$_2$ with Sodium Azide

Te$_4^{2+}$(AsF$_6^-$)$_2$ (1.2595g, 1.418 mmole) was placed in a pre-dried, vacuum tight, pyrex vessel and sulphur dioxide (11.4386g) condensed in. To this deep cherry red solution was added anhydrous NaN$_3$ (0.1103g, 1.697 mmole). A rapid reaction occurred in which the cherry red coloration disappeared with the formation of a colourless solution and
a black precipitate. The solubles were filtered off and
the precipitate washed several times with sulphur dioxide
to remove all traces of the solubles. The solvent was then
slowly removed leaving a creamy-white "tar" which, when
pumped on under reduced pressure at room temperature, lost
solvent forming a white compound. The vessel was separated
in the dry-box and the insolubles (0.8833g) isolated. On
scraping out the soluble product an explosion occurred which
was forceful enough to break the containing glass bulb.
The experiment was terminated.

The weight of the insolubles corresponds to 1.418 mmoles of
NaAsF$_6$ and 3 x 1.418 mmoles of Te.

**(vii) Reaction of Te$_4^{2+}$ (AsF$_6^{-}$)$_2$ with Et$_4$N$^+$N$_3^-$**

Experiment 6.2.1(vi) was essentially repeated.

Te$_4^{2+}$ (AsF$_6^{-}$)$_2$ (3.7069g, 4.173 m mole) and Et$_4$N$^+$N$_3^-$ (4.380 mmoles)
(form ed in situ from Et$_4$N$^+$Cl$^-$ (0.7117g, 4.380 mmoles) and NaN$_3$
(0.3388g, 5.212 mmoles) cf. experiment 5.2.1(v)) were reacted
together in SO$_2$ (10.2233g). The cherry red coloration
rapidly disappeared with the formation of a colourless solution
and a black precipitate. The creamy-white solubles (1.622g)
and insolubles (2.775g) were isolated under dry-box conditions.

Analysis of the solubles:

**Found:** C, 23.71; H, 5.50; N, 3.65%

Et$_4$N$^+$AsF$_6^{-}$ requires: C, 30.1; H, 6.27; N, 4.39%
6.2.2 Reaction of Group VI Polycations with Tetrasulphur Tetranitride

(1) Reaction of $S_8^{2+}(\text{AsF}_6^-)_2$ with $S_4N_4$ (Ratio 2:1)

$S_8^{2+}(\text{AsF}_6^-)_2$ (0.6543g, 1.032 mmole) and $S_4N_4$ (0.0961g, 0.522 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14) and arsenic trifluoride (7.7088g) condensed on to the reactants. The reaction was warmed to room temperature, rapidly forming a red-brown solution. The system was agitated for 12h. at room temperature during which time a yellow precipitate was formed which floated on the surface of the solvent (indicative of sulphur). The reaction mixture was filtered and the insoluble product washed with recondensed solvent to remove all traces of the soluble product. The solvent was then slowly evaporated from the system yielding a red-orange microcrystalline product which, on close examination using a microscope, was seen to be a yellow crystalline material coated by a red amorphous material.

The solubles (0.927g) and insolubles (0.249g) were isolated and their infra-red and Raman spectra recorded.

Infra-red spectrum of the insolubles (nujol mull): Only peaks assignable to the mulling agent were observed.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm$^{-1}$.

The mass spectrum of the insolubles gave a break down pattern consistent with the species $S_8$.

Infra-red spectrum of the solubles (nujol mull): 1498s, 695vs,br, 394vs cm$^{-1}$.

Raman spectrum (red line): no bands observed.
(ii) Reaction of $S_8^{2+}(AsF_6^-)_2$ with $S_4N_4$ (Ratio 1:2)

$S_8^{2+}(AsF_6^-)_2$ (0.99g, 1.56 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1.2, page 14) and $S_4N_4$ (0.60g, 3.26 mmole) in the second bulb. $SO_2$ (8.36g) was condensed in (some into each bulb) and the resulting deep blue polycation solution filtered slowly into the $S_4N_4$ solution. An immediate reaction occurred forming a deep red solution and a finely divided, pale coloured precipitate. All the polycation was washed over on to the $S_4N_4$ solution and the reaction was agitated at room temperature for 4h. The solubles were filtered off and the insolubles were repeatedly washed to remove the soluble product. The solvent was then slowly evaporated from the solution yielding an orange-red micro-crystalline precipitate. The insoluble product (0.29g) and soluble product (1.28g) were isolated and the Raman and infra-red spectra recorded where applicable.

Infra-red spectrum of the solubles (nujol mull): 1329w, 1298w, 1280w, 1260w, 1215w, 1068w, 1036m, 1018m, 995ms, 970vw, 928m, 865vs, 750m, 740s, 700vs,br, 594w, 578m, 569m(sh), 560w(sh), 525vw, 495m, 395vs cm$^{-1}$.

Raman spectrum of the insolubles (green line): 152, 220, 243, 434, 472 cm$^{-1}$.

(iii) Reaction between $S_8$, $S_4N_4$ and $AsF_5$

$S_4N_4$ (0.2063g, 1.121 mmole) and $S_8$ (1.5830g, 6.184 mmole) were placed in a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14) and $SO_2$ (5.7452g) and $AsF_5$ (1.3357g, 7.857 mmole) condensed on to the reactants. The reaction was slowly warmed to room temperature. At ca. -60°C
a reaction occurred forming a deep blue solution which, on warming further, went first green then deep red. The reaction was stirred for 2h. at room temperature and then the soluble products were filtered off, the pale yellow residue being washed several times with recondensed solvent. Slow evaporation of the solvent from the solution did not yield a crystalline material but a red amorphous mass which, when pumped on under reduced pressure, "foamed" (cf. $S_{16}^{2+}$ when pumped on under reduced pressure). Recrystallisation of the product from a 1:5 mixture of $SO_2ClF:SO_2$ (by weight) did not produce crystalline material.

Infra-red spectrum of the solubles (nujol mull): $1495\text{m,}$ $1020\text{w,}$ $695\text{vs,br,}$ $394\text{vs cm}^{-1}$.

Raman spectrum of the solubles (red line): no spectrum observed.

Infra-red spectrum of the insolubles (nujol mull): peaks assignable to mulling agent only.

Raman spectrum of the insolubles (green line): $152$, $220$, $243$, $434$, $472\text{ cm}^{-1}$.

(iv) Reaction of $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$ with $\text{S}_4\text{N}_4$ (Ratio 2:1)

$\text{Se}_4^{2+}(\text{AsF}_6^-)_2$ (1.5800g, 2.277 mmole) and $\text{S}_4\text{N}_4$ (0.2160g, 1.174 mmole) were loaded into a pre-dried, vacuum tight, pyrex vessel (figure 1.1, page 14) and $SO_2$ (9.1483g) condensed on to the reactants. A rapid reaction occurred in which a black precipitate was formed in a deep green solution. The precipitate was washed, with the recondensed solvent, several times to remove all traces of the soluble product. The solvent was then slowly evaporated from the solution leaving a small quantity of orange crystalline product and a deep green mass ($\text{Se}_8^{2+}(\text{AsF}_6^-)_2$).
Infra-red spectrum of the orange crystalline product (nujol mull): 1035w, 995vw, 928w, 860m, 740m(sh), 700vs, 580vw, 500w, 400s cm\(^{-1}\). (cf. experiment 3.2.3(iii), page 122).

Infra-red spectrum of the insolubles (nujol mull): 998m, 954s, 715vs, 690s, 665s, 620s, 580w, 547m, 398vs, 354m cm\(^{-1}\).

\[(v)\] Reaction of \(\text{Se}_4^{2+}(\text{AsF}_6^{-})_2\) with \(\text{S}_4\text{N}_4\) (Ratio 1:2)

\[
\text{Se}_4^{2+}(\text{AsF}_6^{-})_2 (2.0689g, 2.982 \text{ mmole}) \quad \text{and} \quad \text{S}_4\text{N}_4 (1.1546g, 6.275 \text{ mmole}) \quad \text{were loaded into a pre-dried, vacation tight, pyrex vessel (figure 1.1, page 14) and sulphur dioxide (8.9321g) condensed in.} \quad \text{On warming to room temperature a rapid reaction occurred with the formation of a deep red solution and the deposition of a purplish precipitate. The reaction was stirred for 24h, and then the solubles were filtered off, the residue being washed several times to remove all traces of the solubles. The solvent was then slowly evaporated off from the solution yielding a deep orange crystalline material (0.843g).}
\]

The soluble and insoluble products (1.273g) were isolated under dry-box conditions and their vibrational spectra and analyses recorded.

Infra-red spectrum of the soluble product (nujol mull): 1036m, 995w, 927w, 864vs,br, 748m(sh), 738s, 700vs, 580m, 550w, 500m, 470w, 397vs, 380s cm\(^{-1}\) (cf. experiment 3.2.3(iii), page 122).

Raman spectrum of the solubles (red line): 1036w, 680m, 620m, 572w, 514vw, 372w, 350m, 268s, 242w, 222m, 182s, 162m, 62vs cm\(^{-1}\).
Infra-red spectrum of the insolubles (nujol mull): 996m, 952s, 924m, 610w, 688s, 670m(sh), 664s, 630w(sh), 620s, 550m, 404s(sh), 395vs cm⁻¹.

Analysis of the insolubles:
Found: S, 11.27; N, 6.44, Se, 43.9%.

Mass spectrum of the solubles (m/e,(abundance) assignment):
151(100) AsF₄⁻ ; 132(19) AsF₃⁻ , 113(27) AsF₂⁻ ; 94(13) AsF⁻ ;
92(75)S₂N₂⁻ ; 78(10) S₂N⁻ ; 65(26) NSF⁻ ; 46(44) NS⁻.

Mass spectrum of the insolubles (m/e (abundance) assignment):
158(8) S₂NSe₈₀⁻ ; 156(4) S₂NSe₇₈⁻ ; 151(11) AsF₄⁻ ; 138(25)
S₂N₃⁻ ; 132(5) AsF₃⁻ ; 113(6) AsF₂⁻ ; 94(9) AsF⁻ ; 92(100)
S₂N₂⁻ ; 80(4) Se₈₀⁻ ; 78(9) S₂N,Se₇₈⁻ ; 64(21) S₂,SO₂⁻ ;
48(11) SO⁻ ; 46(82) NS⁻; 32(12) S⁻ ; 28(67) N₂⁻.

A diagrammatic representation of the above mass spectra are given in figure 6.6(a) and (b) respectively, pages 305,306.

(vi) Reaction of Te₄²⁺(AsF₆⁻)₂ with S₄N₄ (Ratio 1:2)

Te₄²⁺(AsF₆⁻)₂ (0.8615g, 0.970 mmole) was placed in the sealable section of a pre-dried, vacuum tight, pyrex vessel (figure 1.2, page 14) and sealed off with the Rotoflo valve. S₄N₄ (0.3592g, 1.952 mmole) was placed in the second bulb and SO₂ (14.6439g) condensed in (approx. 75% on to the Te₄²⁺ and 25% on to the S₄N₄). The deep cherry red solution of the polycation was then filtered on to the S₄N₄ solution. An immediate reaction occurred forming a black precipitate in a deep orange solution. The tellurium polycation was completely dissolved and filtered over onto the S₄N₄ solution. The reaction was then agitated for 4h. at room temperature without any obvious signs of further reaction. The deep orange solution was then filtered off and the black precipitate washed with recondensed solvent. The
solvent was then slowly evaporated from the solution (using a 2°C temperature gradient across the vessel) yielding a bright orange crystalline material.

Infra-red spectrum of the insolubles (nujol mull): Only peaks assignable to the mulling agent were observed.

Infra-red spectrum of the solubles (nujol mull): 1329w, 1200vs, 1155w, 1068w, 1035s(sh), 1025s, 1010s, 948s, 935s, 838m, 705vs, 772s(sh), 582s, 532vw, 522vw(sh), 494m, 482m, 398vs, 375w, 368w, 332w, cm⁻¹

Analysis of the solubles:

Found: S, 26.7; N, 9.71; Te, 23.33; As, 15.05%.

Te₂S₈N₅As₂F₁₂ requires: S, 25.57; N, 11.18; Te, 25.48; As, 14.98%.

Te₂S₈N₇As₂F₁₂ requires: S, 25.93; N, 9.94; Te, 25.85; As, 15.19%.

Te₄S₇N₃AsF₆ requires: S, 26.31; N, 8.63; Te, 26.22; As, 15.41%.

Mass spectrum of the soluble product (m/e(abundance) assignment):

132(15) AsF₃; 113(16) AsF₂; 94(4) AsF; 92(33) S₂N₂;
78(5) NS₂; 76(2) CS₂; 64(100) S₂; 63(13) CSF;
48(33) S0; 47(3) NSH; 46(26) NS; 44(3) CS.

A diagrammatic representation of the above mass spectrum is given in figure 6.6c, page 307.
6.3 Discussion

6.3.1 The Reactions of Group VI Polycations with Azides

The use of azide intermediates as a route to main group - nitrogen heterocycles is well documented (equation 6.3.1(a-f)).

Boron-Nitrogen Heterocycles\(^{59,60}\)

\[
\begin{align*}
\text{Ph}_2\text{B} - \text{N} - \text{N} = \text{N} \quad &\xrightarrow{200^\circ \text{C}} [\begin{array}{c}
\text{Ph} \\
\text{B}
\end{array}] - \text{N} \quad \rightarrow \quad \frac{1}{3}(\text{PhB-NPh})_3 \\
\end{align*}
\]

Silicon-Nitrogen Heterocycles\(^{61}\)

\[
\begin{align*}
\text{Ph}_2\text{Si} - \text{N} - \text{N} = \text{N} \quad &\rightarrow [\text{Ph}_2\text{Si} - \text{N} - \text{Ph}] + \text{N}_2 \\
\text{Ph}_2\text{Si} &\rightarrow \text{NPh} \\
\text{PhN} &\rightarrow \text{SiPh}_2
\end{align*}
\]

Phosphorus-Nitrogen Heterocycles\(^{52,63}\)

\[
\begin{align*}
\text{R}_2\text{PCl} + \text{R}_3\text{SiN}_3 &\rightarrow \frac{1}{3}(\text{R}_2\text{PN})_3 + \text{R}_3\text{SiCl} \\
\text{R} &= \text{Me, Ph}^{62,63}
\end{align*}
\]

Sulphur-Nitrogen Heterocycles\(^{64-66}\)

\[
\begin{align*}
2\text{S}_2\text{Cl}_2 + 4\text{MN}_3 &\rightarrow \text{S}_4\text{N}_4 + 4\text{MCl} + 4\text{N}_2 \\
&\qquad (\text{M} = \text{Li, Al(N}_3\text{)}_3^{65}). \\
\text{PhS(O)Cl} + \text{NaN}_3 &\rightarrow \text{PhS(O)N}_3 \quad \xrightarrow{0^\circ \text{C}} (\text{Ph(O)SN})_3 \quad (\text{ref. 66}) \\
\text{S}_4\text{N}_3\text{Cl} + \text{MN}_3 &\rightarrow \text{S}_4\text{N}_4 + \text{N}_2 + \text{MCl} \quad (\text{ref. 65})
\end{align*}
\]

Hence by analogy with work done by Passmore and Sutherland, in which they have isolated a range of compounds from the reactions of \(\text{S}_8^{2+}\) with halides and pseudohalides.
(CNS\(^-\)) the reaction of \(S_8^{2+}\) with \(N_3^-\) was investigated. It was suggested that an intermediate of the form \(S_8N_3^+\) may exist which, on thermal decomposition, would yield a sulphur-nitrogen cation of the form \(S_xN^+\) (\(x = 1-7\)).

6.3.1(i) Reaction of Sulphur Polycations with Azides

The reactions of \(S_8^{2+}(\text{AsF}_6^-)_2\) with both \(\text{NaN}_3\) and \(\text{CsN}_3\), using sulphur dioxide and arsenic trifluoride as solvents, were studied. All the reactions proceeded in the same manner, forming deep red solutions which, on evaporation of the solvent deposited an orange-red material which "foamed" on pumping under reduced pressure. The foaming of the product is very reminiscent of the effect that pumping at reduced pressure has on \(S_{16}^{2+}(\text{AsF}_6^-)_2\).\(^{67}\) Therefore it is thought likely that some \(S_{16}^{2+}(\text{AsF}_6^-)_2\) is formed as a by-product in the reaction. The reaction was found to produce measurable quantities of nitrogen but a quantitative measure of nitrogen, from the weight loss on its removal, was not accurate enough to determine whether one mole of azide evolved one mole or \(3/2\) moles of nitrogen. The Raman spectrum of the insoluble product was consistent with that of sulphur, the infra-red spectrum indicating only the presence \(\text{Na}^+\text{AsF}_6^-\).

The analysis of the soluble product from the reaction of \(S_8^{2+}(\text{AsF}_6^-)_2\) with cesium azide in sulphur dioxide indicates that a compound or mixture of the overall formulation \(S_{15}^2\text{Na}_{2}\text{As}_2\text{F}_{12}\) is produced. From this analytical result and the assumption that \(S_{16}^{2+}(\text{AsF}_6^-)_2\) is present in the soluble product, it is suggested that the solubles are a mixture of \(S_xN^+(\text{AsF}_6^-)_2\) and \(S_{16}^{2+}(\text{AsF}_6^-)_2\). The presence of \(S_{16}^{2+}(\text{AsF}_6^-)_2\) can be readily explained by the reaction of \(S_8\) (formed in the initial reaction of \(S_8^{2+}\) with azide...
The presence of the $S_{16}^{2+}$ polycation in the product indicates that either the azide anion does not react with $S_{16}^{2+}$ or that the azide becomes deactivated during the reaction thus changing the apparent reaction ratio. The latter explanation is most likely to be correct because the solubility of both sodium azide and hexafluoroarsenate is low in sulphur dioxide and thus coating of the azide, by the virtually insoluble hexafluoroarsenate salt, inhibits further reaction. Consequently the $S_8^{2+}(\text{AsF}_6^-)_2$ reacts with the sulphur by-product (equation 6.3.1g), producing the observed $S_{16}^{2+}(\text{AsF}_6^-)_2$.

In an attempt to overcome the problem of the azide being coated, an azide of higher solubility (in SO$_2$ or AsF$_3$) was employed (CsN$_3$). It was, however, found that the solubility of cesium azide in SO$_2$ was not significantly better than that of sodium azide, and the same products were obtained (i.e. $S_8$, $M^{+}\text{AsF}_6^-$, $S_{16}^{2+}(\text{AsF}_6^-)_2$ and $S_{x}^{+}\text{AsF}_6^-$).

The nature of the species $S_{x}^{+}\text{AsF}_6^-$ was elucidated from its infra-red spectrum (1498s, 695vs, br, 394vs cm$^{-1}$). The infra-red spectrum of the cation is very simple consisting of only one observed band (1498 cm$^{-1}$), the other two observed bands being due to AsF$_6^-$ ($v_3$: 700 cm$^{-1}$, $v_4$: 400 cm$^{-1}$). Comparison of the observed S-N stretching frequency with those of other sulphur-nitrogen cations in the
literature (Table 6.4) indicates that the compound is not the AsF\(_6^-\) salt of a previously synthesised cation.

**TABLE 6.4** The Infra-red active stretching modes for some Sulphur-Nitrogen multiple bonds

<table>
<thead>
<tr>
<th>Species</th>
<th>S-N Stretching frequency (cm(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N} \equiv \text{SF}_3 )</td>
<td>1515</td>
<td>69</td>
</tr>
<tr>
<td>( \text{N} \equiv \text{S}^+ )</td>
<td>1447 (SbF(_6^-) salt)</td>
<td>70</td>
</tr>
<tr>
<td>( \text{N} \equiv \text{S} - \text{F} )</td>
<td>1372</td>
<td>69</td>
</tr>
<tr>
<td>( \text{ClN} = \text{SF}_2 )</td>
<td>1204</td>
<td>71</td>
</tr>
</tbody>
</table>

As noted in Table 6.4 the species has a stretching frequency higher than that recorded for NS\(^+\) and only slightly lower than that of NSF\(_3\). However, due to the preparative route, the formation of a sulphur-nitrogen cation containing S\(^{VI}\) is highly unlikely.

Comparison of the stretching frequencies of the species NO\(^+\) (2220 cm\(^{-1}\))\(^{68}\) with NO\(_2^+\) (\(v_3\): 2360 cm\(^{-1}\))\(^{68}\) and CO (2143 cm\(^{-1}\))\(^{68}\) with CO\(_2\) (2349 cm\(^{-1}\))\(^{68}\) indicates that the formation of a linear triatomic molecule (XY\(_2\)) increases the observed stretching frequency by up to ca. 10% relative to the diatomic (XY). Hence it was suggested that the most probable structure for the species S\(_x\)N\(^+\) based on vibrational frequency data, is S\(_2\)N\(^+\), a linear triatomic, isoelectronic and isostructural to CS\(_2\).

A linear triatomic of the form XY\(_2\) has three normal modes of vibration (Figure 6.7).
Figure 6.7 Normal modes of vibration of a linear triatomic \( (XY_2) \)

![Diagram](image)

\[ \text{\( v_1 \)} \]

\[ \text{\( v_2 \) (doubly degenerate)} \]

\[ \text{\( v_3 \)} \]

*(There are an infinite number of vibrations of the type \( v_2 \) which differ only in their directions perpendicular to the molecular axis. Any of these vibrations can be resolved into two mutually perpendicular base vibrations \( v_{2a} \) and \( v_{2b} \). Thus the \( v_2 \) mode in a linear triatomic is said to be "doubly degenerate").

The \( v_1 \) mode in the species \( XY_2 \) is infra-red inactive, there being no net change in dipole moment, but is Raman active. The modes \( v_2 \) and \( v_3 \) are infra-red active and hence, as a consequence of the mutual exclusion principle, are not Raman active. By comparison with the bands in \( \text{CS}_2 \), the band observed in the infra-red spectrum of \( S_XN^+ \) at 1498 cm\(^{-1}\) is probably comparable with the \( v_3 \) band in \( \text{CS}_2(1) \) (1510 cm\(^{-1}\)). Hence the \( v_2 \) band in \( S_XN^+ \) would be expected to occur at slightly lower frequencies than that in \( \text{CS}_2 \) (397 cm\(^{-1}\)), probably in the region of 370-390 cm\(^{-1}\).

The identity and the structure of the \( S_XN^+ \) cation was subsequently clarified by comparison of the vibrational spectrum of the above species with that reported by Faggiani et al\(^{71} \) for the cation \( S_2N^+ \) (figure 6.8 and table 6.5).
Figure 6.8 Structure of the $S_2N^+$ Cation

![Structure of $S_2N^+$ Cation](image)

<table>
<thead>
<tr>
<th>Infra-red Spectrum $S_xN^+(\text{cm}^{-1})$</th>
<th>Infra-red Spectrum $S_2N^+(\text{cm}^{-1})$</th>
<th>Raman Spectrum $S_2N^+(\text{cm}^{-1})$</th>
<th>Assignment of the band</th>
</tr>
</thead>
<tbody>
<tr>
<td>1498s</td>
<td>1498m</td>
<td></td>
<td>$v_3 S_2N^+$</td>
</tr>
<tr>
<td>766m</td>
<td></td>
<td>$2v_2 S_2N^+$</td>
<td></td>
</tr>
<tr>
<td>688m</td>
<td></td>
<td>$v_1 S_2N^+$</td>
<td></td>
</tr>
<tr>
<td>374m</td>
<td></td>
<td>$v_2 S_2N^+$</td>
<td></td>
</tr>
<tr>
<td>333vs</td>
<td></td>
<td>$v_1 SbCl_6^-$</td>
<td></td>
</tr>
<tr>
<td>320s</td>
<td></td>
<td></td>
<td>$v_3 SbCl_6^-$</td>
</tr>
<tr>
<td>293w</td>
<td></td>
<td></td>
<td>$v_2 SbCl_6^-$</td>
</tr>
<tr>
<td>283w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>180m</td>
<td></td>
<td></td>
<td>$v_5 SbCl_6^-$</td>
</tr>
<tr>
<td>167vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>778vs</td>
<td></td>
<td></td>
<td>lattice modes</td>
</tr>
<tr>
<td>67s</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hence it is concluded that the reaction between $S_8^{2+}$ and $N_3^-$ (molar ratio 1:1) yields the linear triatomic $S_2N^+AsF_6^-$ and $S_{16}^{2+}(AsF_6^-)_2$. (The latter compound prevents the Raman spectrum of the former being recorded).
The apparent stability of the $S_2N^+$ cation implies that it is highly unlikely that intermediates of the form $S_xN^+AsF_6^-$ ($x = 3-7$) will be isolated from the reaction of $S_8^{2+}$ with azide. If however intermediate cyclic species are to be isolated then it is believed essential that the reaction be between solutions of azide and polycation thus avoiding the coating problems associated with less soluble azides.

6.3.1(ii) Reaction of Selenium and Tellurium Polycations with Azides.

By analogy with the reactions of $S_8^{2+}$ with azides, in which $S_2N^+$ was formed, it was proposed that the species Se$_2N^+$ and Te$_2N^+$ may be synthesised by reaction of the appropriate polycation with an azide.

The reactions of Se$_4^{2+}(AsF_6^-)_2$ (experiment 6.2.1(iv), page 277), Se$_8^{2+}(AsF_6^-)_2$ (experiment 6.2.1(v), page 278) and Te$_4^{2+}(AsF_6^-)_2$ (experiment 6.2.1(vi), page 279) with azides were, therefore investigated. In all cases reaction occurred with the evolution of nitrogen and a noticeable change in colour of the solution. The reactions of selenium polycations with azides produced deep brown solutions and brown precipitates. Due to the infra-red spectrum of the solubles possessing only bands assignable to the mulling agent and AsF$_6^-$, it is suggested that the soluble product is likely to be a higher selenium polycation (e.g. Se$_{10}^{2+}(AsF_6^-)_2$ cf. $S_{16}^{2+}(AsF_6^-)_2$ in the reactions of $S_8^{2+}(AsF_6^-)_2$ with azides). The insoluble tan-brown precipitate also gives essentially no infra-red spectrum. Analysis of the insoluble product from the reaction of CsN$_3$ with Se$_4^{2+}(AsF_6^-)_2$ indicates that the compound, to all intents and purposes,
does not contain nitrogen. (Analysis of insoluble product
$\text{CsN}_3/\text{Se}_4^{2+}(\text{AsF}_6^-)_2$: N, 0.38%). It is, therefore, concluded
from the above evidence that the reaction between selenium
polycations and azides produces two ionic compounds neither
of which contain nitrogen and must therefore be homoatomic
selenium polycations with the $\text{AsF}_6^-$ anion.

The reactions of tellurium polycations
($\text{Te}_4^{2+}(\text{AsF}_6^-)_2$) with azides are very rapid, quickly de­
colouring the cherry red $\text{Te}_4^{2+}$ solutions yielding colourless
solutions with a black precipitate (elemental tellurium).
The product is highly soluble in sulphur dioxide and has a
great affinity for the solvent, forming creamy-white oils or
tars, from which it is very difficult to remove the remaining
sulphur dioxide. It was noted that the creamy-white product
tends to explode with friction. Hence although there is no
firm evidence for the formation of a tellurium nitrogen cation,
in the reaction of $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$ with azide, it is strongly
suspected, from the weights of residual elemental tellurium,
the affinity for sulphur dioxide, the colour of the compound
and the tendency to explode with friction, that a species of
the form ($\text{TeN}^+$)$_x$ has been produced.

Investigations into the reactions of selenium
and tellurium polycations with azides are being undertaken, at
the present time, by MacLean and Passmore at the University of
New Brunswick.

6.3.2 The Reactions of Group VI Polycations
with Tetrasulphur Tetranitride

(i) The Reactions of $\text{S}_8^{2+}(\text{AsF}_6^-)_2$
with Tetrasulphur Tetranitride

In the reaction of $\text{S}_8^{2+}(\text{AsF}_6^-)_2$ with tetra­
sulphur tetranitride (ratio 2:1) (experiment 6.2.2(i), page 275)
both the soluble and insoluble products are readily identified from their vibrational spectra as $S_8$ (insoluble) and $S_2N^+AsF_6^-$ (soluble product). There is also evidence for the formation of $S_{16}^{2+}(AsF_6^-)_2$ from the foaming of the soluble product when pumped on under reduced pressure.

In the reaction of $S_8^{2+}(AsF_6^-)_2$ with tetrasulphur tetranitride (ratio 1:2) (experiment 6.2.2(ii), page 275) the reaction appears to proceed in the same way as that of the 2:1 reaction, forming a deep red solution and a pale yellow insoluble material. The pale yellow insoluble material is identified from its Raman spectrum as $S_8$. The soluble product is not however $S_2N^+$. The infra-red spectrum of the soluble product has major peaks and 865, 740, 700 and 395 cm$^{-1}$. From this evidence it is readily concluded that an ionic species is present in the solubles containing the $AsF_6^-$ anion (700, 395 cm$^{-1}$). Comparison of the rest of the spectrum, particularly the 865 cm$^{-1}$ band, with other recorded infra-red spectra of sulphur-nitrogen cations leads to the conclusion that the compound produced in the reaction of $S_8^{2+}(AsF_6^-)_2$ with $S_4N_4$ (ratio 1:2), is identical to that formed in the reaction of Fe with $S_2N_2Cl_2$, using SO$_2$ as a solvent ($S_{10}N_8^{2+}$) (Chapter Three, experiment 3.2.3(iii), page 122).

Hence overall equations for the reactions of $S_8^{2+}(AsF_6^-)_2$ with $S_4N_4$ can be written (equations 6.3.2(a,b))

**Ratio 2:1**

$$S_8^{2+}(AsF_6^-)_2 + \frac{1}{2} S_4N_4 \rightarrow 2S_2N^+AsF_6^- + \frac{6}{8} S_8 \quad (6.3.2(a))$$

**Ratio 1:2**

$$S_8^{2+}(AsF_6^-)_2 + 2S_4N_4 \rightarrow (S_{10}N_8^{2+})(AsF_6^-)_2 + \frac{6}{8} S_8 \quad (6.3.2(b))$$
It has been found that the reaction of $S_8^{2+}(\text{AsF}_6^-)_2$ with tetrasulphur tetranitride in a ratio of 2:1 yields the cation $S_2^+$ and that in a ratio of 1:2 the species postulated to be $(S_{10}^8 S_{10}^{2+})(\text{AsF}_6^-)_2$ is formed. Hence by analogy with the reactions of $S_8^{2+}(\text{AsF}_6^-)_2$ with $S_4N_2$, the reactions of $Se_4^{2+}(\text{AsF}_6^-)_2$ with $S_4N_4$ were investigated with a view to preparing the previously unsynthesised $\text{SeNS}^+\text{AsF}_6^-$ salt and the selenium substituted analogue of $(S_{10}^{10} S_{10}^{2+})(\text{AsF}_6^-)_2$.

The reactions of $Se_4^{2+}(\text{AsF}_6^-)_2$ with $S_4N_4$ were therefore investigated using a molar ratio of 1:2 and 2:1 (experiments 6.2.2(iv,v), pages 277, 278).

It was found that the insoluble products in both the 2:1 and 1:2 reactions gave the same infra-red spectrum whereas the soluble products were not identical. The soluble product from the 2:1 reaction was identified as being mainly $Se_8^{2+}(\text{AsF}_6^-)_2$ but a few orange crystals were isolated which gave the same infra-red spectrum as the soluble component of the 1:2 reaction. The infra-red spectrum of the solubles formed in the 1:2 reaction was compared with infra-red spectra of known sulphur-nitrogen species and was found to be identical to that recorded for the cation $S_{10}^{10} S_{10}^{2+}$. From the analytical data obtained on the soluble product and the lack of any significant shifting in the infra-red bands, it is concluded that the soluble product, from the reaction of $Se_4^{2+}(\text{AsF}_6^-)_2$ with $S_4N_4$ (in a molar ratio of 1:2) is $(S_{10}^{10} S_{10}^{2+})(\text{AsF}_6^-)_2$, with a low percentage of a selenium substituted analogue.
The insoluble products of both the 2:1 and 1:2 reaction gave an infra-red spectrum consistent with the product being ionic and probably containing a selenium analogue of a cyclic sulphur-nitrogen cation. It was, therefore, surprising that the salt was not soluble to some extent in sulphur dioxide, as it has been found throughout this thesis that, in general, all sulphur-nitrogen salts, with the exception of $S_3N_2Cl$, dissolve readily in sulphur dioxide.

The colour of the compound is also noted, as virtually all sulphur-nitrogen salts are red, orange or yellow. The main exception to the above statement is $S_3N_2Cl$ which is green-black. Hence from purely physical evidence it would appear reasonable to suggest that the salt isolated in the insolubles could be an analogue of the $(S_3N_2^+)_2$ system. The infra-red spectrum of the insoluble product was compared with that of $S_3N_2Cl$, and the recently reported species $(SSe_2N_2^+)_2(X^-)_2$ ($X = Cl, Br$), (table 6.6).

It is observed that the antisymmetric S-N stretching frequencies, occurring in the 900-1000 cm$^{-1}$ region of the spectrum, are very similar in $S_3N_2Cl$, $SSe_2N_2Cl$ and the product. Two strong bands occur in this region which move to higher wave numbers in the order $S_3N_2Cl$ lower than $SSe_2N_2Cl$ lower than the insoluble product. The splitting in the two main bands in the 900-1000 cm$^{-1}$ region is also noted to increase in the same order as observed above, being greatest for the insoluble product (splitting of 44 cm$^{-1}$). It is suggested that the effects noted in the infra-red spectra when comparing $S_3N_2Cl$ with $SSe_2N_2Cl$ would be amplified when comparing $S_3N_2Cl$ with $SSe_2N_2^+AsF_6^-$. The $AsF_6^-$ anion is likely to interact much less strongly with the cation than
TABLE 6.6 Comparison of the Infra-red Spectra of $S_2N_2Cl$, $SSe_2NCl$ and that of the insoluble product from the reactions of $Se_4^{2+}(AsF_6^-)_2$ with $S_4N_4$.

<table>
<thead>
<tr>
<th>$S_2N_2Cl$ (cm$^{-1}$)</th>
<th>$SSe_2N_2Cl$ (cm$^{-1}$)</th>
<th>Insoluble Product (cm$^{-1}$)</th>
</tr>
</thead>
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<tr>
<td>964s</td>
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<td>998m</td>
</tr>
<tr>
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<td>941s</td>
<td>954s</td>
</tr>
<tr>
<td>745w</td>
<td></td>
<td>801w</td>
</tr>
<tr>
<td>716s(sh)</td>
<td></td>
<td>720s(sh)</td>
</tr>
<tr>
<td>708vs</td>
<td>720w</td>
<td>710vs, br $(AsF_6^-)$</td>
</tr>
<tr>
<td>699s(sh)</td>
<td></td>
<td>690s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>655s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>617s</td>
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<tr>
<td></td>
<td></td>
<td>588m</td>
</tr>
<tr>
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<td>548m</td>
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<tr>
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<td>569w</td>
</tr>
<tr>
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<td>472w</td>
</tr>
<tr>
<td>456w</td>
<td></td>
<td>356vs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>354s</td>
</tr>
</tbody>
</table>

The chloride anion and will therefore increase the effective positive charge on the ring, hence tending to move the observed antisymmetric ring modes to higher wave numbers. The effect of lowering the degree of anion-cation interaction is also likely to cause a greater splitting in the observed bands. ($SSe_2N_2Cl$ splitting 31 cm$^{-1}$, product splitting 44 cm$^{-1}$). Hence by comparison of the bands occurring in the region 900-1000 cm$^{-1}$ it appears that the product could be the $AsF_6^-$ salt of $SSe_2N_2^+$.

However on examination of the infra-red spectrum of the product in the region 650-750 cm$^{-1}$ it is noted that a large number of strong bands are observed, the main one of which (710 cm$^{-1}$) is assignable to the $AsF_6^-$ anion. The
bands occurring between 650 and 750 cm$^{-1}$ are not thought to be due to Se-N vibrations as the major bands in Se$_4$N$_4$ occur below 580 cm$^{-1}$.

Comparison of this area of the spectrum with that of S$_3$N$_2$Cl shows up certain similarities. However the bands observed below 700 cm$^{-1}$ occur at noticeably lower wave numbers than those in S$_3$N$_2$Cl, the band at 617 cm$^{-1}$ being similar to that observed in SSe$_2$N$_2$Cl. Hence from spectroscopic evidence it would seem likely that the product is either \((\text{SSe}_2\text{N}_2^+)\_2\ (\text{AsF}_6^-)\_2\) or \((\text{SSe}_2\text{N}_2^+)\ (\text{s}_3\text{N}_2^+)\ (\text{AsF}_6^-)\_2\).

The latter species could explain the number of bands observed in the region 650-750 cm$^{-1}$ and their similarity to those observed in the spectrum of S$_3$N$_2$Cl.

The analytical data on the insoluble species, although not giving an exact stoichiometry of the compound, indicates a sulphur:nitrogen ratio of 3:4. Hence as there are very few cationic species in which the ratio of sulphur: nitrogen is less than 1:1 \((\text{S}_4\text{N}_5^+)\)\textsuperscript{74}, it is thought likely that selenium is substituted into the ring in place of sulphur, therefore giving a Group VI to nitrogen ratio of greater than or equal to 1:1.

From the physical properties, infra-red spectrum and analytical data of the insoluble compound it is suggested that a selenium analogue of S$_3$N$_2$Cl has been produced. The exact nature of the compound is not known, as a pure sample has not been isolated and thus without accurate analytical data no firm conclusion as to the structure of the product is drawn. However it is thought that the two most likely structures for the product are \((\text{SSe}_2\text{N}_2^+)\ (\text{AsF}_6^-)\_2\) and \((\text{SSe}_2\text{N}_2^+)\ (\text{s}_3\text{N}_2^+)\ (\text{AsF}_6^-)\_2\) both of which will probably adopt a similar structure to \((\text{s}_3\text{N}_2^+)\_2\ (\text{AsF}_6^-)\_2\).\textsuperscript{75}
(iii) The Reaction of $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$ with $S_4N_4$
(Ratio 1:2) (experiment 6.2.2(vi), page 279)

By analogy with the reactions of $\text{Se}_4^{2+}(\text{AsF}_6^-)_2$
with $S_4N_4$, it was postulated that a tellurium analogue of
$S_2N_2^+$ may be synthesised by the reaction of $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$
with $S_4N_4$.

On reacting together $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$ and
$S_4N_4$ in a ratio of 1:2 a rapid reaction occurred forming
an orange-red solution and a black precipitate. Investigation
of the solubles and insolubles revealed that the insolubles
consisted of only elemental tellurium and sulphur. The
infra-red spectrum of the soluble species was compared with
the spectra of known sulphur-nitrogen species but was found
to be significantly different. A series of spectra were
run on different parts of the sample to discover whether the
product was a mixture or not. It was noted that significant
changes in the intensity of some bands occurred with differing
spectra thus implying that the product was indeed a mixture.

The band at $1338 \text{ cm}^{-1}$ was noted to vary in intensity from spectrum
to spectrum. A band at $1338 \text{ cm}^{-1}$ is generally regarded as
being high for a sulphur-nitrogen system (except for $\text{NS}^+$,
$S_2\text{N}^+$ and $\text{NSF}$) but the band could be in approximately the
correct position for $\text{TeSN}^+$. If the difference in the
position of the $v_3$ bands in $\text{CS}_2$ ($v_3 = 1510 \text{ cm}^{-1}$)\textsuperscript{68} and $S_2\text{N}^+$
($v_3 = 1498 \text{ cm}^{-1}$)\textsuperscript{71} is used as the basis on which to deduce
the $v_3$ band position of $\text{TeSN}^+$, from the $v_3$ band in $\text{TeSC}$
($v_3 = 1347 \text{ cm}^{-1}$)\textsuperscript{76}, then a shift to lower wave numbers, of
ca. 10-15 cm$^{-1}$ is expected. Therefore the $v_3$ band in $\text{TeSN}^+$
is postulated as occurring between 1337 and 1332 cm$^{-1}$ (c.f.
observed band 1338 cm$^{-1}$).
The majority of the other bands in the observed infra-red spectrum occur between 450 and 1250 cm\(^{-1}\). It is likely that these bands are assignable to S-N modes as Te-N and Te-S stretching vibrations will probably occur at wavenumbers lower than 450 cm\(^{-1}\). The main peak of interest, in the above region of the spectrum, is the 1200 cm\(^{-1}\) band, which is very strong. The position of this band is similar to, but slightly higher than that observed in ClN=SF\(_2\) (1176 cm\(^{-1}\)). Hence it is concluded that the structure of one compound in the product possesses a sulphur-nitrogen grouping with a high bond order. The remainder of the spectrum between 450 and 1050 cm\(^{-1}\) is similar to the spectrum expected for a cyclic sulphur-nitrogen cation. The analysis of the solubles although indicating that the overall stoichiometry is either Te\(_4\)N\(_3\)AsF\(_6\) or Te\(_2\)Se\(_8\)N\(_8\)As\(_2\)F\(_{12}\) does not help significantly in deducing the nature of the species present in the mixture. The experiment is regarded as an initial investigative reaction. The above results will hopefully be followed up either at the University of Durham (England) or at the University of New Brunswick (Canada).

6.3.3 SUGGESTED MECHANISM BY WHICH GROUP VI POLYCATIONS REACT WITH TETRASULPHUR TETRANITRIDE

In the reactions of Se\(_4\)\(^{2+}\)(AsF\(_6\))\(_2\) with S\(_4\)N\(_4\) (ratio 2:1 and 1:2) and S\(_8\)\(^{2+}\)(AsF\(_6\))\(_2\) with S\(_4\)N\(_4\) (ratio 1:2) the primary intermediate species, around which all the products appear to be built, is the X\(_3\)N\(_2\)\(^+\) unit (X = S and/or Se). The isolation of a product suspected of containing the Se\(_2\)SN\(_2\)\(^+\) cation (insolubles Se\(_4\)\(^{2+}\)(AsF\(_6\))\(_2\)/S\(_4\)N\(_4\)), indicates
that the polycation probably attacks the $S_4N_4$ cage across the nitrogens, producing the $SSe_2N_2^+$ which dimerises yielding $(S_2Se_4N_4^{2+})(AsF_6^-)_2$. In the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) reaction the soluble product was identified as basically $(S_{10}N_8^{2+})(AsF_6^-)_2$ with a low selenium substitution, i.e. $(S_2N_2\cdot S_4N_4\cdot Se_2SN_2)^{2+}(AsF_6^-)_2$. As mentioned briefly in Chapter Three (page 141) it is believed that $S_2^2N_2^+$ units will add to $S_4N_4$ more readily than $SSe_2N_2^+$ units, as in the former case a sulphur-sulphur inter-ring linkage is formed which is likely to be stronger, and therefore more thermodynamically favoured than the sulphur-selenium linkage if $SSe_2N_2^+$ bonds to the $S_4N_4$ ring. Hence an overall mechanism can be suggested to explain the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) reaction (equation 6.3.2(c)).

Equation 6.3.2(c)

$$2Se_4^{2+}(AsF_6^-)_2 + 2S_4N_4 \rightarrow 2Se_2SN_2^{2+}AsF_6^- + 2S_3N_2^{2+}AsF_6^- + 4Se^{1+}$$

If the above mechanism is correct then the insoluble product isolated from the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 2:1) must be $(Se_4S_2N_4^{2+})(AsF_6^-)_2$. It was noted in the reaction of $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ (ratio 1:2) (experiment 6.2.2(iv), page 277) that the $Se_4^{2+}(AsF_6^-)$ was in excess for the observed reaction. It is therefore suggested that the reaction stoichiometry to produce the proposed $(Se_4S_2N_4^{2+})(AsF_6^-)_2$ salt is in fact 1:1. Hence it is proposed that the $Se_4^{2+}(AsF_6^-)_2/S_4N_4$ reaction (ratio 1:1) proceeds via a transition state in which "$Se_4$" ring interacts with all four nitrogens of the $S_4N_4$ unit, which adopts a similar configuration to that in $S_4N_4^{2+}$.
The transition state then dissociates into two SSe$_2$N$_2^+$ units which dimerise yielding (S$_2$Se$_4$N$_4^{2+}$)(AsF$_6^-$)$_2$, the observed product, and 2/8 S$_8$ (equation 6.3.2(d)).

$$S_4N_4 + Se_4^{2+}(AsF_6^-)_2 \rightarrow (S_2Se_4N_4^{2+})(AsF_6^-)_2 + 2/8 S_8$$

Hence from a mechanistic point of view it is concluded that the insoluble product in the reactions of Se$_4^{2+}$(AsF$_6^-$)$_2$ with S$_4N_4$ (ratios 1:2 and 2:1) is (S$_2$Se$_4$N$_4^{2+}$)(AsF$_6^-$)$_2$.

The mechanism by which S$_8^{2+}$(AsF$_6^-$)$_2$ reacts with S$_4N_4$ (ratio 1:2) is almost certainly via the attack of the polycation on the nitrogens of the S$_4N_4$ unit, with the formation of two S$_3$N$_2^+$ units which subsequently attack an S$_4N_4$ unit producing (S$_{10}$N$_8^{2+}$)(AsF$_6^-$)$_2$, the observed product (cf. the proposed mechanism for the Se$_4^{2+}$(AsF$_6^-$)$_2$/S$_4N_4$ reaction (ratio 1:2) equation 6.3.2(c)).

In the reaction of S$_8^{2+}$(AsF$_6^-$)$_2$ with S$_4N_4$ (ratio 2:1) the S$_2N^+$ cation is produced. There is a possibility of at least two mechanisms by which S$_2N^+$AsF$_6^-$ could be formed. The first assumes that the initial reaction of S$_4N_4$ with S$_8^{2+}$(AsF$_6^-$)$_2$ produces two S$_3$N$_2^+$ units and elemental sulphur. Subsequent reaction of S$_3$N$_2^+$ with S$_8^{2+}$(AsF$_6^-$)$_2$ then yields two S$_2N^+$ units and S$_{16}^{2+}$(AsF$_6^-$)$_2$. The S$_{16}^{2+}$(AsF$_6^-$)$_2$ then attacks the S$_4N_4$ forming two S$_2N_2^+$ units and the cycle is continued. The second possibility is that in the initial attack of S$_8^{2+}$(AsF$_6^-$)$_2$ on the S$_4N_4$ cage, two S$_2N^+$ cations are produced along with an S$_2N_2$ unit and elemental sulphur. The S$_2N_2$ unit then reacts further with the S$_8^{2+}$(AsF$_6^-$)$_2$ forming S$_2N^+$ units and elemental sulphur.
The latter mechanism appears the most feasible as the former invokes the attack of a doubly charged cation on an $S_2N_2^+$ ring whereas in the latter case $S_8^{2+}(AsF_6^-)_2$ is postulated to attack only neutral entities (i.e. $S_2N_2$). It is also suggested that the $S_2N^+$ cation is thermodynamically highly favoured due to the delocalised linear configuration and thus, as seen from the reactions of azides with $S_8^{2+}(AsF_6^-)_2$ and $NS^+SbCl_6^-$ with $S_8$ (experiment 5.2.4(ii), page 240), the species is very readily produced. Hence it would seem likely that the $S_8^{2+}(AsF_6^-)/S_4N_4$ intermediate would dissociate forming the thermodynamically favoured $S_2N^+$ units.

6.4 Conclusion

The reactions of Group VI polycations with azides and tetrasulphur tetranitride provide useful inroads into the previously little explored area of homo-Group VI-nitrogen and hetero-Group VI-nitrogen cation chemistry.

The $S_2N^+$ cation as synthesised by Gillespie\(^7\)\(^8\) is not a viable synthetic reagent due to the difficulty of preparing the starting materials and also what are suspected to be rather poor yields of the product. However as an extension to the work described in this thesis, Maclean and Passmore\(^7\)\(^9\) reacted sulphur with tetrasulphur tetranitride and arsenic pentafluoride (in the correct stoichiometry) in the presence of catalytic quantities of bromine and isolated quantitative yields of $S_2N^+AsF_6^-$ (cf. experiment 6.2.2(iii), page 276). Hence using $S_8/S_4N_4/AsF_5/Br_2$ as the synthetic route to $S_2N^+AsF_6^-$, $S_2N^+$ is a viable and potentially useful sulphur-nitrogen reactant. MacLean\(^7\)\(^9\) has prepared the $N(SCl)_2^+AsF_6^-$ and $N(SBr)_2^+AsF_6^-$ salts by the reaction of $S_2N^+AsF_6^-$ with
the respective halogens and is presently investigating
the reactions of $S_2N^+AsF_6^-$ further.

From the reactions of $S_8^{2+}(AsF_6^-)_2$ and $Se_4^{2+}(AsF_6^-)_2$ with
$S_4N_4$ (ratio 1:2), the salt $(S_4^{10}N_8^{2+})(AsF_6^-)_2$ has been pro-
duced. The formation of this salt via the above routes
provides conclusive evidence that the compound that analysed
as $S_5N_4FeCl_4$ (experiment 3.2.3c(iii), page 122) is an ionic
species. The salt $(S_4^{10}N_8^{2+})(X)_2^-$ has not been reported
and thus from work in this Chapter and that in Chapter Three,
two completely independent synthetic routes have been found
to this postulated multi-cyclic system.

The reactions of $Se_4^{2+}(AsF_6^-)_2$ with $S_4N_4$ (ratio 1:2 and
2:1) produced the same insoluble product which is postulated
to be $(S_2Se_4N_4)(AsF_6^-)_2^+$. The $AsF_6^-$ salt of the $S_2Se_4N_4^{2+}$
cation can not be synthesised by the route described by
Wolmershäuser et al$^{72}$ and thus the reactions of selenium
polycations with $S_4N_4$ provide a useful route to the $Se_4S_2N_4^{2+}$
salts with anions such as $AsF_6^-$, $SbF_6^-$, $SbCl_6^-$ and $AlCl_4^-$. The potential of these salts could be great in the field of
modified sulphur-nitrogen polymers. If the $SSe_2N_2^{2+}$ cation
is reduced, as in Chapter Three (cf. reductions of the $S_3N_2^{2+}$
cation), mixed sulphur selenium nitrides of the form $X_4N_2$ and/or
$X_4N_4$ (X = S and or Se) could be formed. The cracking of
the $X_4N_4$ species on silver metal (cf. $S_4N_4$ splitting$^{80}$) may
well yield $(XN)_X$, a selenium doped sulphur-nitrogen polymer.

Gillespie is also believed to be working on the reactions
of selenium polycations with tetrasulphur tetranitride and
is thought to have isolated $(Se_4S_2N_4^{2+})(AsF_6^-)_2$.$^{81}$
Although the reactions of $\text{Te}_4^{2+}(\text{AsF}_6^-)_2$ with azides and tetrasulphur tetranitride did not yield products that were easily characterised, it is believed from these initial investigative reactions that tellurium-nitrogen and tellurium-sulphur-nitrogen cations should be isolatable. Maclean (University of New Brunswick) is, at present, investigating the $\text{Te}_4^{2+}/\text{N}_3^-$ reaction and has isolated crystals for X-ray structure determination.
A significant resonance canonical structure for the $\text{Se}_8^{2+}$ cation.
Figure 6.4

\[ \text{Te}^{4+} \quad (\text{AsF}_6^-)_2 \]

\[ \text{Te}_3\text{S}_3^{2+} \quad (\text{AsF}_6^-)_2 \]

\[ \text{Te}_2\text{Se}_4^{2+} \quad (\text{AsF}_6^-)_2 \]
Figure 6.4

\[ \text{Te}_2\text{Se}_8^{2+} \]

\[ \text{Te}_3\text{Se}_7^{2+} \]

\[ \text{Te}_4\text{Se}_6^{2+} \]
Figure 6.5

$S_7I^+$

$(S_7I)_2I^3+$
**Figure 6.6.a**  \( \text{Se}^{2+}(\text{AsF}_6^-)_2/2\text{S}_4\text{N}_4 \) (Solubles)

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Figure 6.6.b  $\text{Se}^{2+}(\text{AsF}_6^-)_2/2\text{S}_4\text{N}_6$  (Insolubles)

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Figure 6.6.c

$\text{Te}^{2+}[\text{AsF}_6^-]_2/2\text{S}_4\text{N}_4$ (Solubles)

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REFERENCES


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    (Durham) (1979)
### Table 1: Sulphur-Nitrogen Species

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Photographic representations of various infrared spectra referenced in this thesis.

$\text{S}_2\text{N}_2\text{Cl}_2/\text{Fe}/\text{SO}_2$

solubles
(Expt. 3.2.3c-ii)

$\text{S}_2\text{N}_2\text{Cl}_2/\text{Hg}/\text{SO}_2$

insolubles
(Expt. 3.2.3vi)
$S_2^2\left( AsF_6^{-}\right)_2 / 25_2 H_4$
Solubles
(Expt. 6.2.2.v)

$S_2^2\left( AsF_6^{-}\right)_2 / 25_2 H_4$
Insolubles.
(Expt. 6.2.2.v)

$T_2^2\left( AsF_6^{-}\right)_2 / 25_2 H_4$
Solubles
(Expt. 6.2.2.vi)

$T_2^2\left( AsF_6^{-}\right)_2 / 25_2 H_4$
Solubles
(Expt. 6.2.2.vi)
REFERENCES TO APPENDIX A


APPENDIX B

THERMODYNAMIC DATA RELEVANT TO THIS THESIS

\[ \Delta H^\circ_f (S_N^4) = +536 \text{ kJ mol}^{-1} \] (ref.1)

\[ \Delta H^\circ_{sub}(S_N^4) = + 89 \text{ kJ mol}^{-1} \] (ref.2)

\[ \Delta H^\circ_f (\text{ClF}) = -51 \text{ kJ mol}^{-1} \] (ref.3)

\[ \Delta H^\circ_f (\text{NSF}) = -21 \text{ kJ mol}^{-1} \] (ref.4)

\[ \Delta H^\circ_f (\text{SF}_4) = -775 \text{ kJ mol}^{-1} \] (ref.5)

The standard heats of formation of the metal chlorides and fluorides (Table 4.2, page 157) were referenced from the "G.R.C. Handbook Chemistry and Physics", 57th Ed. 1976-77.

(a) Calculation of the Heat of Formation of (NSCl)\(_g\)

The following assumptions were made in this calculation

(1) The \( D^0_{N=S} \) in \( N=S-F \) and \( N=S-Cl \) is the same.

(2) That \( D^0_{S-F} - D^0_{S-Cl} \) for NSCl and NSF respectively, is the same as \( D^0_{S-F} - D^0_{S-Cl} \) for SOF\(_2\) and SOCl\(_2\) respectively.

\[ D^0_{N=S} (\text{NSF}) = 526 \text{ kJ mol}^{-1} \] (ref.4)

\[ D^0_{S-Cl} (\text{SOCl}_2) = 265 \text{ kJ mol}^{-1} \] (ref.5)

\[ D^0_{S-F} (\text{SOF}_2) = 322 \text{ kJ mol}^{-1} \] (ref.6)

(Equ.A) \[ \Delta H^\circ_{disrupt.} (\text{NSF})_g = \Delta H^\circ_f (\frac{1}{2}N_2)_g + \Delta H^\circ_f (S)_s + \Delta H^\circ_f (\frac{1}{2}F)_g + \Delta H^\circ_f (\text{NS}F)_g \]

(Equ.B) \[ \Delta H^\circ_{disrupt.} (\text{NSCl})_g = \Delta H^\circ_f (\frac{1}{2}N_2)_g + \Delta H^\circ_f (S)_s + \Delta H^\circ_f (\frac{1}{2}Cl)_g - \Delta H^\circ_f (\text{NSCl})_g \]

(Equ.C) \[ \Delta H^\circ_{disrupt.} (\text{NSF})_g = D^0_{N=S} + D^0_{S-F} \]

(Equ.D) \[ \Delta H^\circ_{disrupt.} (\text{NSCl})_g = D^0_{N=S} + D^0_{S-Cl} \]
Equ. B-Equ. A = $\Delta H^0_{\text{disrupt.}}(\text{NSCl})_g - \Delta H^0_{\text{disrupt.}}(\text{NSF})_g$

= $\Delta H^0_f(\text{NSF})_g - \Delta H^0_f(\text{NSCl})_g$

Equ. D-Equ. C = $\Delta H^0_{\text{disrupt.}}(\text{NSCl})_g - \Delta H^0_{\text{disrupt.}}(\text{NSF})_g$

= $D^0_{\text{S-Cl}} - D^0_{\text{S-F}}$

\[ 265-322 = -21 - \Delta H^0_f(\text{NSCl})_g \]

\[ \Delta H^0_f(\text{NSCl})_g = +78 \text{ kJ mol}^{-1} \]

(b) Calculation of the Heat of Formation of (NSCl)$_3$

\[ (S_2N_2Cl_3)_{\text{s}} \rightarrow 3\text{NSCl}_g \quad \Delta H^0 = +193 \pm 6 \text{ kJ mol}^{-1} \]  
(ref. 7)

\[ \Delta H^0_f((S_2N_2Cl_3)_{\text{s}}) = 3(\Delta H^0_f(\text{NSCl})_g) - 193 \text{ kJ mol}^{-1} \]

\[ \Delta H^0_f((S_2N_2Cl_3)_{\text{s}}) = +41 \text{ kJ mol}^{-1} \]
REFERENCES TO APPENDIX B

1. G. Pilcher et al, CATCH Tables (Nitrogen Compounds), University of Sussex (1972)


3. J.D. Cox et al CATCH Tables (Halogen Compounds), University of Sussex (1972)


APPENDIX C

The Board of Studies in Chemistry requires that each postgraduate research thesis should contain an appendix listing all research colloquia, seminars and lectures (by external speakers) arranged by the Department of Chemistry during the period when research for the thesis was carried out.

Research Colloquia, Seminars and Lectures Arranged by the Department of Chemistry between October 1976 and September 1979

20 October 1976

Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur"

10 November 1976

Dr. J.S. Ogden (University of Southampton), "The Characterisation of High Temperature Species by Matrix Isolation"

17 November 1976

Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable Inorganic Solids"

24 November 1976

Dr. M.I. Page, (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions"

8 December 1976

Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals"

26 January 1977

Dr. A. Davis (E.R.D.R.), "The Weathering of Polymeric Materials"
2 February 1977
Dr. M. Falk (N.R.C. Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases"

9 February 1977
Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions"

23 February 1977
Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines"

25 February 1977
Professor H.T. Dieck (Frankfurt University), "Diazadienes - New Powerful Low-Valent Metal Ligands"

2 March 1977
Dr. F. Hibbert (Birkbeck College, University of London),
"Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids"

9 March 1977
Dr. I.O. Sutherland (University of Sheffield), "The Stevans' Rearrangement: Orbital Symmetry and Radical Pairs"

18 March 1977
Professor H. Bock (Frankfurt University), "Photo-electron Spectra and Molecular Properties: A Vademecum for the Chemist"

30 March 1977
Dr. J.R. MacCallum (University of St. Andrews),
"Photo-oxidation of Polymers"
20 April 1977

Dr. D.M.J. Lilley (Research Division, G.D. Searle),
"Tails of Chromatin Structure - Progress Towards a Working Model"

27 April 1977

Dr. M.P. Stevens (University of Hartford), "Photo-
cycloaddition Polymerisation"

4 May 1977

Dr. G.C. Tabisz (University of Manitoba), "Collision
Induced Light Scattering by Compressed Molecular Gases"

11 May 1977

Dr. R.E. Banks (U.M.I.S.T.), "The Reactions of Hexa-
fluoropropene with Heterocyclic N-Oxides"

18 May 1977

Dr. J. Atwood (University of Alabama), "Novel Solution
Behaviour of Anionic Organooaluminium Compounds: the Formation
of Liquid Clathrates"

25 May 1977

Professor M.M. Kreevoy (University of Minnesota),
"The Dynamics of Proton Transfer in Solution"

1 June 1977

Dr. J. McCleverty (University of Sheffield), "Consequences
of Deprivation and Overcrowding on the Chemistry of Molybdenum
and Tungsten"

6 July 1977

Professor J. Passmore (University of New Brunswick, Canada),
"Adducts Between Group V Pentahalides and a Postscript on S_I^+"
27 September 1977

Dr. T.J. Broxton (La Trobe University, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents"

19 October 1977

Dr. B. Heyn (University of Jena, D.D.R.), "σ-Organo-Molybdenum Complexes as Alkene Polymerisation Catalysts"

27 October 1977

Professor R.A. Filler (Illinois Institute of Technology), "Reactions of Organic Compounds with Xenon Fluorides"

2 November 1977

Dr. N. Boden (University of Leeds), "N.M.R. Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-½ Pairs"

9 November 1977

Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids"

14 December 1977

Dr. R.O. Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry"

25 January 1978

Dr. G. Richards (University of Oxford), "Quantum Pharmacology"

1 February 1978

Professor K.J. Ivln (Queens University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring-Opening Polymerisation of Cycloalkenes"
3 February 1978

Dr. A. Hartog (Free University, Amsterdam), "Some Surprising Recent Developments in Organo-Magnesium Chemistry"

22 February 1978

Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere"

1 March 1978

Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions"

3 March 1978

Dr. G. van Koten (University of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds"

15 March 1978

Professor G. Scott (University of Aston), "Fashioning Plastics to Match the Environment"

22 March 1978

Professor H. Vahrenkamp (University of Freiburg), "Metal-Metal Bonds in Organometallic Complexes"

19 April 1978

Dr. M. Barber (U.M.I.S.T.), "Secondary Ion Mass Spectra of Surfaces Adsorbed Species"

15 May 1978

Dr. M.I. Bruce (University of Adelaide), "New Reactions of Ruthenium Compounds with Alkynes"

16 May 1978

Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals"
18 May 1978

Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science"

22 May 1978

Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds"

24/25 May 1978

Professor P. von R. Schleyer (University of Erlangen, Nürnberg),
(i) "Planar Tetra-Coordinate Methanes, Perpendicular Ethylenes and Planar Allenes"
(ii) "Aromaticity in Three Dimensions"
(iii) "Non-Classical Carbocations"

21 June 1978

Dr. S.K. Tyrlik (Academy of Sciences, Warsaw), "Dimethylglyoxime-Cobalt Complexes - Catalytic Black Boxes"

23 June 1978

Professor W.B. Person (University of Florida), "Diode Laser Spectroscopy at 16 µm"

27 June 1978

Professor R.B. King (University of Georgia, Athens, Georgia, U.S.A.), "The Use of Carbonyl Anions in the Synthesis of Organometallic Compounds"

30 June 1978

Professor G. Mateescu (Cape Western Reserve University), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion Pairs: Facts, Plans and Dreams"
15 September 1978
Professor W. Siebert (University of Marburg, West Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry"

22 September 1978
Professor T. Fehlner (University of Notre Dame, U.S.A.), "Ferraboranes: Syntheses and Photochemistry"

12 December 1978
Professor C.J.M. Stirling (University of Bangor), "Parting is Such Sweet Sorrow - the Leaving Group in Organic Reactions"

14 February 1979
Professor B. Dunnell (University of British Columbia), "The Application of N.M.R. to the Study of Motions in Molecules"

16 February 1979
Dr. J. Tomkinson (Institute Laue-Langevin, Grenoble), "Studies of Adsorbed Species"

28 March 1979
Dr. A. Reiser (Kodak Ltd.), "Polymer Photography and the Mechanism of Cross-link Formation in Solid Polymer Matrices"

5 April 1979
Dr. S. Larsson (University of Uppsala), "Some Aspects of Photoionisation Phenomena in Inorganic Systems"
23 May 1979

Dr. B. Wakefield (University of Salford), "Electron Transfer in Reactions of Metals and Organometallic Compounds with Polychloropyridine Derivatives"

13 June 1979

Dr. G. Heath (University of Edinburgh), "Putting electrochemistry into mothballs - (Redox processes of metal porphyrins and phthalocyanines)"

14 June 1979

Professor I. Ugi (University of Munich), "Synthetic Uses of Super Nucleophiles"

20 June 1979

Professor J.D. Corbett (Iowa State University, Ames, Iowa, U.S.A.), "Zintl Ions: Synthesis and Structure of Homopolyatomic Anions of the Post-Transition Elements"

27 June 1979

Dr. H. Fuess (University of Frankfurt), "Study of Electron Distribution in Crystalline Solids by X-ray and Neutron Diffraction"