Some reactions of tetrasulphur tetranitride and trithiazyl trichloride

Alange, G. G.

SOME REACTIONS OF TETRASULPHUR TETRANITRIDE

AND TRITHIAZYL TRICHLORIDE

by

G.G. ALANGE

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SUMMARY

The thesis can be conveniently divided into two parts (a) the reactions of tetrasulphur tetranitride and (b) the reactions of trithiazyl trichloride.

(a) Reactions of tetrasulphur tetranitride

The reactions of tetrasulphur tetranitride with many Lewis acids in inert organic solvents have been studied. Adducts of 2:1, 1:1, 1:2, 1:4 (S_4N_4: Lewis acid) stoichiometry have been prepared; it is likely that in most of these compounds the nitrogen of S_4N_4 is coordinated to the Lewis acid. The following new compounds have been prepared: $2S_4N_4.SnBr_4$, $S_4N_4.TiBr_4$, $S_4N_4.4TiF_4$, $S_4N_4.TiI_4$, $S_4N_4.ZrCl_4$, $S_4N_4.HfCl_4$, $S_4N_4.SeCl_4$, $S_4N_4.TeCl_4$, $S_4N_4.TeF_4$, $S_4N_4.NbCl_5$, $S_4N_4.NbF_5$, $S_4N_4.TaCl_5$, $S_4N_4.TaF_5$, $S_4N_4.2AlCl_3$, $S_4N_4.2AlBr_3$, $S_4N_4.2GaCl_3$, $S_4N_4.2InCl_3$, $S_4N_4.2TlCl_3$(?), $S_4N_4.PhBCl_2$, $S_4N_4.WBr_4$, $S_4N_4.WOCl_4$(?). Silicon tetrachloride, germanium tetrachloride and tin tetraiodide do not react under the conditions studied; p-tolytin trichloride gives $2S_4N_4.SnCl_4$ due to disproportion into tin tetrachloride and tetra-p-tolytin.

The infrared spectra of the new adducts and some of the previously reported adducts are recorded and their structures have been discussed. These compounds can be roughly divided into two types (i) adducts with infrared spectra similar to the infrared

of compounds of known structure ($S_4N_4.SbCl_5$, $S_4N_4.BF_3$) and (ii) the infrared spectra of products whose spectra differ from the infrared spectra of $S_4N_4.SbCl_5$ and $S_4N_4.BF_3$. Compounds of type (i) are considered to contain monodentate S_4N_4; in other cases possible structures have been discussed by analogy with other adducts described in the literature.

A study of the reactions between S_4N_4 and (a) sulphuryl chloride and (b) chlorine led to (a) a new convenient synthesis for trithiazyl trichloride and (b) a new compound thought to be $S_6N_6Cl_4$.

(b) Reactions of trithiazyl trichloride

The second part of the thesis deals with trithiazyl trichloride reactions. Apart from conversion to the trifluoride no other reactions of this compound are known. Trithiazyl trichloride reacts with epoxides to give the following esters (i) $(NSO.C_3H_5Cl_2)_3$ (ii) $(NSOC_3H_5BrCl)_3$, (iii) $(NSOC_2H_4Cl)_3$, (iv) $(NSOC_4H_8O)_3$. Trithiazyl trichloride reactions with nitriles yielded a variety of products and possible structures are discussed.

ACKNOWLEDGEMENTS

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INTRODUCTION

The chemistry of sulphur nitrogen compounds has been a topic of interest since the first synthesis of tetrasulphur tetranitride.[1] Today many sulphur nitrogen compounds are known which are derived from this nitride and their chemistry has been thoroughly investigated. It shows hardly any analogy with that of nitrogen oxygen compounds. This observation may be ascribed to the facts that (a) nitrogen is the less electronegative partner in binary oxygen nitrogen compounds[2], (b) many of the characteristic properties of oxygen are related to its small size, thus its ionization potential is appreciably higher than for sulphur, (c) the non-availability to oxygen of d-orbitals limits the covalency maximum to four. The chemistry of sulphur-nitrogen compounds has several interesting and important features, namely, stability of the sulphur-nitrogen bond, tendency to form six and eight membered rings, ring contraction, polymerisation and ion formation. Compounds with six or eight membered rings of alternating sulphur-nitrogen atoms have aroused considerable interest in connection with the bonding properties of their π-electrons[3,4,5].

The sulphur nitrides

Monomeric sulphur nitride or 'thiazyl', SN is the thio-analogue of nitric oxide, and like nitric oxide, is a radical[5].

Nitric oxide exhibits a tendency to lose electrons to form the positively charged nitrosonium ion which is isoelectronic with elemental nitrogen and the cyanide ion. Because of the lower electronegativity of sulphur compared with O, there would appear to be a greater tendency to form a cation but no definite $NS^{\oplus}$ compounds have been isolated. There is some evidence however, that a positive S≡N species does exist as an intermediate, especially since trithiazyl trichloride, $(NSCl)_3$, is obtained by the direct chlorination of S_4N_4.[7] It has only actually been detected (from its emission spectrum) in a mixture of nitrogen and sulphur vapour subjected to an electric discharge[8]. It has also been prepared by the reaction of H_2S with atomic nitrogen,[9] and its presence as an intermediate in reactions of some sulphur-nitrogen compounds has been invoked.[10] Since many reactions of trithiazyl trichloride, $(NSCl)_3$, in solution proceed by way of thiazyl chloride, NSCl[11], several reactions of tetrasulphur tetranitride may proceed via monomeric sulphur nitride NS.[11]

The structure of monomeric thionitrosyl can be represented by a typical 3-electron bond configuration, as in the case of nitric oxide. In principle a stable ion can be achieved by loss of an electron to give $N\equiv\overset{+}{S}$, or by electron addition to give $\bar{N}=S$.

The monomer, NS can be represented either by a V.B. representation involving a three electron bond, :N≡S: or more precisely by a M.O. picture similar to that for NO.

The probable analogy between an S≡N and the C≡N groups in the monomeric thiazyl and cyanogen compounds appears worthy of consideration. Such triple bonds to nitrogen are stable among the carbon compounds R-C≡N; they are apparently not stable in phosphorus chemistry ($N{\equiv}PX_3$) and are only known in sulphur chemistry for NSF_3, NSF and NSCl.

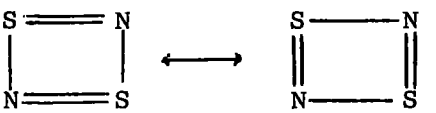
Disulphur dinitride

When tetrasulphur tetranitride is sublimed in vacuo and the vapour led through a zone filled with silver wool and heated to 300°C thermal fission of the molecule occurs. Although (SN) and a little sulphur (as Ag_2S) and nitrogen are formed, the predominant product (60% yield) consists of a white volatile substance which can be condensed in a trap cooled to -196° - 80°C.[12,17] This compound is soluble in benzene, ether, carbon tetrachloride, acetone, tetrahydrofuran, dioxane and can be recrystallised from them, but insoluble in water[13,14]. The colourless product obtained in this way contains equal numbers of sulphur and nitrogen atoms and has the formula S_2N_2[15]. It sublimes at room temperature at 0.01mm Hg and has a strong unpleasant odour. It has been reported[12] to decompose explosively above 30°C or on impact.

In more recent investigations S_2N_2 vapour was unaffected by glass wool at 300° and on heating above 30°, rapid polymerisation not detonation was observed[17].

Disulphur dinitride rapidly dimerises to tetrasulphur tetranitride when an alkali metal or an alkali carbonate or cyanide is added to its benzene solution[16]. Spontaneous polymerisation occurs when the compound is stored at below 30°C. A compound with the composition $(SN)_x$ is formed as well as the tetrasulphur tetranitride. The polymeric sulphur nitride $(SN)_x$ is the sole product if moisture is rigorously excluded.[13]

The infrared spectrum and chemical properties of S_2N_2 have led to its formulation as a four-membered planar ring with alternating S and N atoms.[14a]



This is supported by X-ray examination of the adduct $S_2N_2.SbCl_5$[17].

Reactions of disulphur dinitride with antimony pentachloride and boron halides have been studied recently[17] and the effect of donation on the stability and structure of the S_2N_2 ring have been investigated.

Solutions of S_2N_2 in dichloromethane react with antimony pentachloride (in excess) and form a diadduct $S_2N_2(SbCl_5)_2$ which can further react with S_2N_2 to form a monoadduct $S_2N_2SbCl_5$. The

monoadduct can be reconverted to the diadduct by treatment with $SbCl_5$. The physical and chemical properties of these compounds indicate that the S_2N_2 ring structure is maintained intact. The monoadduct $S_2N_2.SbCl_5$ reacts irreversibly with S_2N_2 to form both the previously characterised $S_4N_4.SbCl_5$ and, in lower yields, a less reactive material $(S_4N_4.SbCl_5)_x$. Antimony pentachloride acts as a catalyst for the dimerisation of S_2N_2.[17]

Disulphur dinitride reacts with boron trichloride in dichloromethane to form the following compounds:[17] $S_4N_4BCl_3$, $S_2N_2(BCl_3)_2$ and $(S_2N_2BCl_3)_2$. At 0^oC $S_2N_2(BCl_3)_2$ loses BCl_3 to form the adduct $S_2N_2BCl_3$ which can be reconverted to the diadduct by treatment with BCl_3 at -78^oC. Antimony pentachloride $SbCl_5$ displaces boron trichloride; BCl_3 from $S_2N_2BCl_3$ to form $S_2N_2(SbCl_5)_2$, the polymeric compound, $(S_2N_2BCl_3)_x$ is inert toward both BCl_3 and $SbCl_5$. The properties of S_2N_2 BCl_3 and $S_2N_2(BCl_3)_2$ indicate that the S_2N_2 ring structure remains intact. Reaction of S_2N_2 with BF_3 yields only $S_4N_4BF_3$.[17]

Tetrasulphur tetranitride

The earliest known nitride of sulphur is tetrasulphur tetranitride. The compound is formed when disulphur dichloride and ammonia are reacted together and was first discovered by Gregory[15]. Tetrasulphur tetranitride can be formed in a variety of reactions[8]. It can also be obtained from several other sulphur-

nitrogen compounds. S_4N_4 is usually prepared by passing gaseous ammonia into a solution of sulphur dichloride, SCl_2 in an inert solvent such as CCl_4[16,18] ($S_2Cl_2 + Cl_2 \rightleftharpoons 2SCl_2$; $6SCl_2 + 16NH_3 \longrightarrow S_4N_4 + 2S + 12NH_4Cl$). This preparation is typical for non-metal- nitrogen compounds (viz: non-metal halide and NH_3 or NH_4^+ salt). In organic solvents of low dielectric constant yields of S_4N_4 from disulphur dichloride and ammonia are higher than in solvents of high dielectric constants.[6] Insufficient is known about the course of the sulphur-chloride ammonia reaction to be able to explain these yield variations. It is however, thought that the tetrasulphur tetranitride may be formed via thiodithiazyl dichloride, $S_3N_2Cl_2$, containing a five-membered S-N ring and thiotrithiazyl chloride S_4N_3Cl, which contains a seven membered ring.[6,21,22] A convenient laboratory preparation for small amounts of the tetranitride makes use of the reaction between disulphur dichloride vapour and dry pellets of ammonium chloride at 160° ($6S_2Cl_2 + 4NH_4Cl \longrightarrow S_4N_4 + 8S + 16HCl$).[23]

Tetrasulphur tetranitride can also be prepared by the folbwing methods:-

(a) Reaction between elemental sulphur and liquid ammonia at room temperature under pressure. While crystalline sulphur is insoluble in this medium below 11·5°C, blue solutions are formed at higher temperatures which remain stable at room temperature ($10S + 4NH_3 \longrightarrow$

$6H_2S + S_4N_4$). If H_2S is removed from the equilibrium system, tetrasulphur tetranitride can be isolated from the solid residue after evaporating the ammonia[12].

(b) It is prepared by the reaction between disulphur dichloride and lithium azide in an inert solvent at 0^oC ($4LiN_3 + 2S_2Cl_2 \longrightarrow 2S_2(N_3)_2 + 4LiCl$; $2S_2(N_3)_2 \longrightarrow S_4N_4 + 4N_2$)[24]

(c) It is formed when active nitrogen is allowed to react with sulphur or sulphur compounds (S_2(vapour) $\xrightarrow{(N)}$ $S_4N_4 + (NS)_x$)[25]

(d) It is obtained by the ammonolysis of sulphur tetrafluoride ($SF_4 \xrightarrow{NH_3} S_4N_4$)[19]

Tetrasulphur tetranitride is a pale orange crystalline solid, m.p. 178^oC[26]. It dissolves in many organic solvents but is insoluble in water. It has the following solubilities[27] (moles per 1000 g. solvent): dioxane at 18^oC, 0.20, at 60^oC., 0.23; carbon disulphide at 0^oC., 0.0155, at 30^oC., 0.0573; benzene at 0^oC., 0.0137, at 60^oC., 0.121; ethanol at 0^oC., 0.0043, at 20^oC., 0.0072.

The molecular structure of tetrasulphur tetranitride, which has been a subject of controversy for a long period of time is now established. Electron diffraction[28] and X-ray analyses[29,30], show that the S_4N_4 molecule is an eight membered ring (Fig.1). In the vapour[28] and in the solid state,[29,30] the tetramer is in the form of

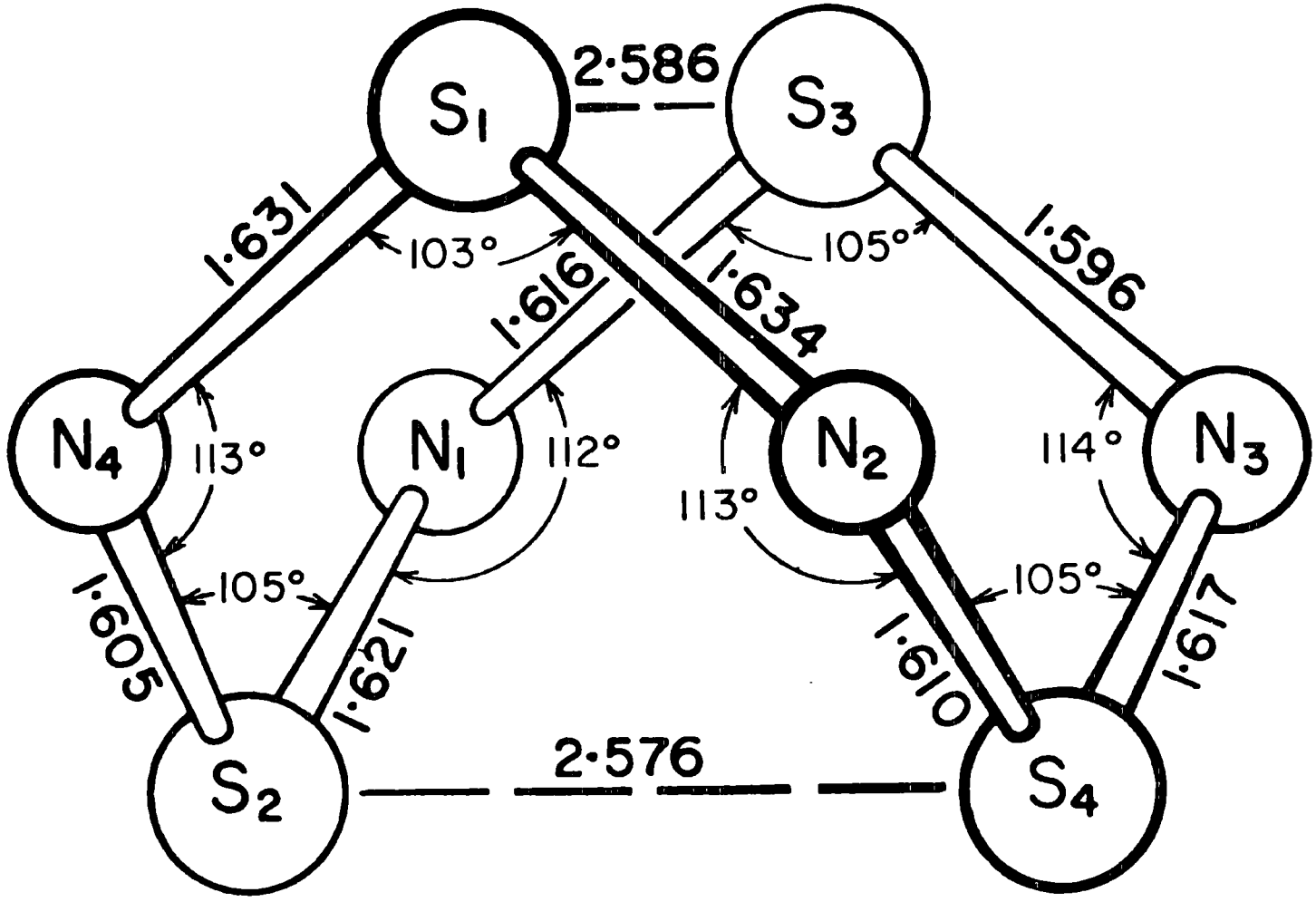


Fig. Bond distances and angles.

of a cradle-type puckered ring with all four nitrogen atoms in the same plane. All the sulphur atoms are chemically and physically identical[31]. Evidence for pi-bonding in the tetramer is provided by the fact that the equal bond length of 1.62Å [28,29] are shorter than the theoretical value of 1.74Å for S-N single bonds, and longer than the calculated value of 1.54Å for S=N double bonds. According to the relationship between S-N bond order and the S-N bond length[32], a bond length of 1.62Å corresponds to a bond order of 1.5. This is most plausibly explained by the existence of a pi-electron system in the molecule due to overlap between the p-pi orbital of nitrogen and the d-pi orbital of sulphur[3,5]. Self-consistent field molecular orbital calculations suggested that considerable pi electron delocalization takes place in the $(SN)_4$ system[33]. The calculations also indicate that bonds are polarised as $\overset{\ominus}{N} - \overset{\oplus}{S}$ units and that some sulphur-sulphur bonding occurs mostly by overlap of p orbitals, but one-third by overlap of sulphur d_{xy} orbitals.

Electron spin resonance spectra have been observed with $(SN)_4$ and the spectrum of the anion, $(SN)_4^-$, was consistent with a structure in which delocalization occurred over the ring and involved all four nitrogen atoms.[34]

The visible and ultraviolet spectra of $(S-N)_4$ have been interpreted in terms of a structure in which weak S-S bonding was present[35].

(a) Reduction and oxidation of S_4N_4

The hydrogenation of tetrasulphur tetranitride with stannous chloride[36] or with dithionite, $S_2O_4^{2-}$ produces tetrasulphur tetraimide[26]. This has not been detected among the products of the sulphur chloride/ammonia reaction but may well be there in very minute quantities. Tetrasulphur tetraimide was discovered by Wolbling[6]. It is colourless and crystallises in the orthorhombohedral system[38].

The structure of $S_4N_4H_4$ has been elucidated[39,40]. The arrangement of the nitrogen and sulphur atoms in the ring is of crown shape like that in the S_8 sulphur ring[40,41]. The sulphur nitrogen bonds in tetrasulphur tetraimide are equal in length and are in the range 1.65 - 1.67Å[39,40]. This implies that there is an appreciable amount of pi-character in the skeletal bonds, and that some delocalization occurs[42]. The fact that the ring structure is puckered suggests that sulphur d orbitals are involved, and pi-bonding probably takes place by donation of nitrogen lone pair electrons to vacant sulphur d orbitals[42]. The diamagnetic susceptibility, however gives no evidence of any ring current arising from delocalized multiple

bonding[6, 43], probably because[6(a)] the nitrogen lone pairs will donate into sulphur d orbitals, the symmetry of which (two nodal planes) prevents the formation of uninterrupted molecular orbitals enclosing the whole molecule (cf. chlorophosphazenes[42]).

The hydrogen in tetrasulphur tetraimide can be replaced by metals. Becke-Goehring and Schwarz[44] studied the reaction of S_4N_4 with triphenymethyl sodium and obtained orange-red solid, $Na_4S_4N_4$. Another sodium salt is $Na_2(H_2S_4N_4)$, which has been obtained as a lemon yellow precipitate[44]. Stepwise replacement by lithium has been observed[51] in the reaction between $S_4N_4H_4$ and ^nBuLi and the various colour changes are red, yellow, blue, yellow. The $S_4N_4^{4-}$ ion contained in the sodium salts can be obtained, reducing S_4N_4 by other methods. The reaction of tetrasulphur tetranitride with sodium in dimethoxyethane shows colour changes, red, deep blue, green and yellow green[46]. When S_4N_4 is treated with vacuum-distilled potassium in scrupulously dry dimethoxyethane, various colour changes are exhibited[46], a scarlet red solution is first observed, on further shaking a green solution is produced. The colour changes have been interpreted as indicating the formation of the following sequence of ions[46]:

$S_4N_4^- \longrightarrow$	$S_4N_4^{2-} \longrightarrow$	$S_4N_4^{3-} \longrightarrow$	$S_4N_4^{4-}$
red	yellow	blue or blue-green	yellow or yellow-green

Tetrasulphur tetraimide forms adducts, e.g. $S_4N_4H_4 \cdot TeBr_4$[47]. A tetrameric thionylimide, ($O_4S_4N_4H_4$) is produced from the air oxidation of $S_4N_4H_4$[48]. Further work on $S_4N_4H_4$ is in progress in this department.

(b) Tetrasulphur tetranitride adducts

In inert organic solvents tetrasulphur tetranitride forms coloured stable adducts with many Lewis acids. The following adducts have been prepared in the past : $S_4N_4SbCl_5$[52,53] $S_4N_4 \cdot BF_3$[54], $4S_4N_4 \cdot BF_3$[50] (this unusual stoichiometry is probably due to incomplete reaction[54]) $2S_4N_4 \cdot SnCl_4$[52, 53], $S_4N_4 \cdot TiCl_4$[52,53] $S_4N_4 \cdot 2SO_3$[49], $S_4N_4 \cdot 4SO_3$[49], $S_4N_4TeBr_4$[47], $S_4N_4 \cdot 2SbF_5$[6,57], $S_4N_4 \cdot 4SbF_5$[55] $S_4N_4 \cdot WCl_4$[52,53], $S_4N_4 \cdot MoCl_5$(?)[52,53], $S_4N_4 \cdot VCl_4$[56], $S_4N_4 \cdot BCl_3$[54], $S_4N_4 \cdot BBr_3$[54], $S_4N_4 \cdot BCl_3 \cdot SbCl_5$[54], $S_4N_4 \cdot 2SbBr_3$[57,6], $S_4N_4 \cdot 2SbI_3$[57,6] $S_4N_4 \cdot Se_2Cl_2$(?)[53,6], $S_4N_4 \cdot 2TiCl_3$(?)[53,6]. Adducts queried are not unambiguously established. Further adducts with many other metal halides are discussed in the experimental section.

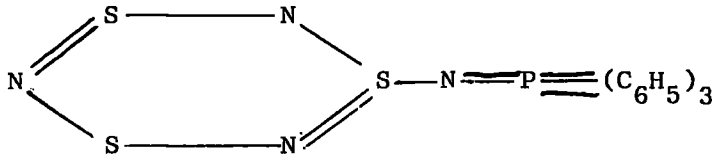
X-ray studies on two of these adducts ($S_4N_4 \cdot SbCl_5$, $S_4N_4 \cdot BF_3$) have been published[58,59]. The structures consist of an eight membered sulphur-nitrogen ring, with one of the nitrogen atoms, bonded to the antimony or boron atom. In adducts the sulphur atoms form a square and the nitrogen atoms a tetrahedron. This conformation differs from that of S_4N_4 in which the nitrogen atoms are square planar and the sulphur atoms (two above and two

below) form a slightly elongated tetrahedron. Infrared spectra and structure of many new S_4N_4 adducts with Lewis acids are considered in the discussion.

Lewis-acid behaviour of S_4N_4 is usually followed by ring contraction or degradation[2]. The observations suggest that nucleophiles invariably attack the more electropositive atoms, viz: sulphur atoms as would be expected. All forms of nucleophilic attack on S_4N_4 break down the ring[6]. The only one which may have the ring preserved is the thiazyl fluoride adduct (it is not well characterized[2]) which can be made by reaction of various fluorinating agents, on S_4N_4[19] ($S_4N_4 \xrightarrow{IF_5} I_2 + S_4N_4(NSF)_4$).

Ruff and Geisel[60] showed that S_4N_4 and ammonia give an ammoniate of the composition $S_4N_4.2NH_3$. In a similar reaction S_2N_2 gives an ammoniate $S_2N_2.NH_3$[1]. However according to X-ray patterns and the absorption spectra, the two compounds appear to be identical and since S_2N_2 can be sublimed from these ammoniates even at room temperature, it is assumed that S_4N_4 is cleaved during the reaction with ammonia.

Ring contraction appears to result from the reaction of triphenyl phosphine and S_4N_4 ($S_4N_4 + 2P(C_6H_5)_3 \longrightarrow SP(C_6H_5)_3 + (C_6H_5)_3PN_4S_3$)[61] The following structure has been proposed for $(C_6H_5)_3PN_4S_3$.



Reactions with Grignard reagents cause ring degradation[62,129(a)] ($C_6H_5MgBr \xrightarrow{S_4N_4} C_6H_5SN{=}S{=}NSC_6H_5$). Complete degradation has been observed in the reaction of S_4N_4 with $C_6H_5PCl_2$[63].

(c) Reactions of S_4N_4 in polar solvents

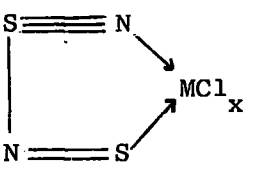
In polar solvents more involved reactions of S_4N_4 with Lewis acids have been found to occur[10]. X-ray diffraction[64-68] and spectroscopic[69], and chromatographic investigations[70] have established that products of three main structural types may be obtained, containing: (i) MN_2S_2 five membered rings (PbN_2S_2,NH_3[64], $Ni(MeN_2S_2)$[66,67] and $Pt(HN_2S_2)$[65]); (ii) MNS_3 five membered rings ($Pd(NS_3)_2$)[68,70]; and (iii) both MN_2S_2 and MNS_3 rings (Co, Ni and Pd compounds[69, 70]). In dimethylformamide, copper (II) chloride and bromide give low yields of $S_2N_2.CuCl_2$ and $S_2N_2.CuBr_2$[71]. In methyl or ethyl alcohol, cobalt, nickel and palladium[70, 73,74] halides react to give mixtures which include compounds of all three types. In organic solvents S_4N_4 reacts with selenium dichloride to give thiotrithiazyl chloride, S_4N_3Cl and elemental selenium, whereas in thionyl chloride the same reaction may give selenotrithiazyl hexachloroselenate, $Se_2S_6N_6.SeCl_6$, containing a three-element pi-delocalized cation[75]. Reactions of S_4N_4

with several metal halides in thionyl chloride have been studied and products of variety of sulphur-nitrogen-metal ratios have been obtained[10,76] e.g. $SNMnCl_2$, $SNCoCl_2$.,$S_2N_2ZrCl_4$, $S_2N_2CrCl_3$. The compounds contain rings or chains involving metal atoms and $(SN)_n$ units; vibrational spectra suggest 2,3 and 4 as the most likely values for n[10].

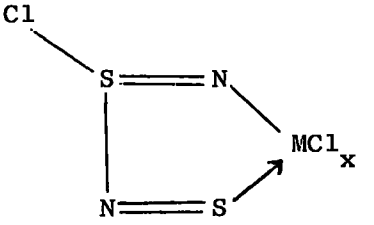
The structures of these compounds involve units of the type 1-3[10].

(i) $Cl_xM.S.N:S:N.MCl_x$

(ii)



(iii)



(d) Some other important reactions of S_4N_4

An important group of reactions illustrating the basic function of the tetranitride is with hydrogen halides. These reactions may well begin with protonation of a nitrogen atom in the ring; in the case of hydrogen chloride, the first product of reaction in carbon tetrachloride is a dark red precipitate which is thought to be $S_4N_4.HCl$. Especially in the presence of water, this changes

to thiotrithiazyl chloride[6]. The overall reaction is consistent with a process proceeding by the following steps[85],

$$S_4N_4 + HCl \longrightarrow S_4N_4.HCl \text{ (red precipitate)}$$

$$S_4N_4.HCl + 3HCl \xrightarrow{H^+} S_4N_3Cl + NH_4Cl + Cl_2$$

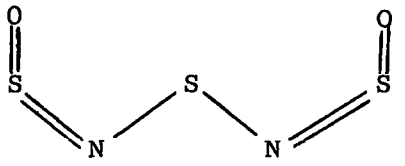
With HBr or HI in CCl_4, S_4N_3Br or S_4N_3I is believed to be formed at once[6]. With excess HI in anhydrous formic acid, S_4N_4 is completely broken down ($S_4N_4 + 12HI \longrightarrow 4S + 6I_2 + 4NH_3$)[6].

Tetrasulphur tetranitride readily undergoes base hydrolysis ($2S_4N_4 + 6\ OH^- + 9\ H_2O \longrightarrow 2S_3O_6^{2-} + S_2O_3^{2-} + 8NH_3$)[86] This result is typical for a substance with sulphur in the plus three oxidation state, since it can readily undergo disproportionation to sulphur (II) and sulphur (IV). Formation of ammonia (rather than hydrazine) and products containing S-S bonds is consistent with the structure of S_4N_4; the molecule contains S-S bonds rather than N-N bonds. Tetrasulphur tetranitride also undergoes acid hydrolysis[87].

When S_4N_4 is reacted with $SOCl_2$ in the presence of SO_2, arsenic trichloride or nitric oxide, the compound $S_3N_2O_2$ is obtained[80,81]. It is also obtained by the reaction between ammonia and $SOCl_2$[82]. Recently it has been shown that $S_3N_2O_2$ is formed in small yields in the reaction between S_4N_4 and $SOCl_2$.[75,83] It is also obtained by the reaction between S_4N_4 and certain metal

halides in $SOCl_2$[83].

The crystal structure of $S_3N_2O_2$ shows that the molecule consists of a planar zig-zag chain of sulphur and nitrogen atoms, as shown below:



Thiodithiazyl dioxide reacts with $SbCl_5$ and $TiCl_4$ to give $S_4N_4.SbCl_5$ and $S_4N_4.2TiCl_4$, respectively[84].

Tetrasulphur tetranitride reacts with cyclopentadiene in an inert solvent at 135-136°C and gives $S_4N_4.4C_5H_6$. In a similar way compounds $S_4N_4.2C_7H_{10}$ and $S_4N_4.2C_7H_8$ have been prepared by the reaction of the nitride with bicycloheptene (norbornene) and bicyclopentadiene, respectively.[79]

Polymeric sulphur nitride, $(SN)_x$

This compound is produced by the polymerisation of disulphur dinitride in the absence of moisture. The polymerisation is best effected by leaving disulphur dinitride in an evacuated desiccator for 30 days at 20° - 25°C.[6] The product is stable and forms fibrous crystals up to 3mm long with a shiny, brass-like appearance.[6]

The polymer shows evidence of delocalization. It is diamagnetic and conducts electricity[42]. The polymer is more stable than S_4N_4[1]. The infrared spectrum showed a strong band at 1225 cm^{-1} which was attributed to an S=N stretching vibration for a bond length of 1.48Å. A band at 1015 cm^{-1} was suggestive of an S-N mode with a more single bond character[42]. The optical spectrum showed a strong absorption near 7000Å which might indicate the presence of a pi-electron delocalised system[77]. The conductance of the polymer increased with rising temperature and also with rising pressure. The semiconductance behaviour might be explained in terms of pi-electron delocalization along the polymer chain in a similar manner to the delocalization of the cyclic tetramer[42]. Each nitrogen atom can contribute one p-pi electron to the pi system and each sulphur can contribute two 3p-pi lone-pair electrons or one or two 3d-pi electrons. However the physical data could be rationalised in terms of a structure which contained alternating sequence of greater and less pi character[77].

Tetrasulphur dinitride

S_4N_2 can be prepared by the following methods:-

(a) Tetrasulphur tetranitride is heated with carbon disulphide in an autoclave at 120°C, (poor yield)[6].

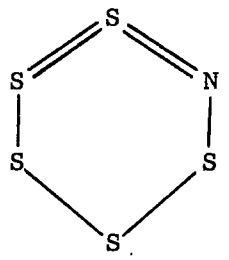
(b) It is prepared in 42% yield by the reaction between

disulphur dichloride and a sulphur-nitrogen-mercury compound

$$(Hg_5(NS)_8 + 4S_2Cl_2 \xrightarrow{CS_2} 4S_4N_2 + 3HgCl_2 + Hg_2Cl_2)^{6}.$$

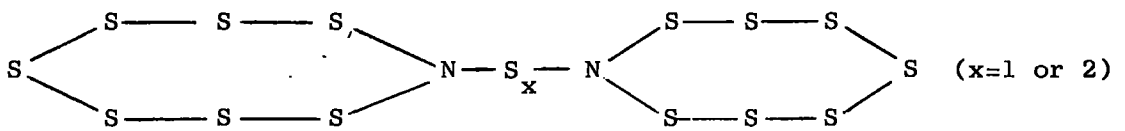
(c) Heating to 80°C, the reaction products from sulphur dioxide and ammonia[6]. Tetrasulphur dinitride has an unpleasant odour and melts at 23°C.[78]

No physical structure determination has been reported and the following unsymmetrical cyclic formula has been proposed[6].



Polymeric sulphur nitrides

The nitrides $S_{15}N_2$ and $S_{16}N_2$ are derived from the eight-membered ring system of heptasulphur imide. They are made by condensing this imide in carbon disulphide solutions with sulphur dichloride or disulphur dichloride respectively[6]. Their infrared spectra are featureless except broad bands in the S-N stretching region[6]. They have the following structures,



(x=1 or 2)

Sulphur-nitrogen-halogen compounds

These compounds have interesting chemical (see below) and structural properties. They can contain single, double and triple bonds as well as localized and delocalized pi-bonds in rings. Rings with delocalized double bonds may be considered as inorganic aromatic compounds[88].

(i) Monomeric thiazyl halides

The thionitrosyl halides S=N-F, S=N-Cl, and nitrosyl halides, O=N-F, O=N-Cl are isomeric with N≡S-F and N≡S-Cl and $\bar{N}{=}\overset{+}{O}$-F, $\bar{N}{=}\overset{+}{O}$-Cl, respectively. In reality only nitrosyl halides ONF, ONCl and thiazyl halides NSF, NSCl are known. The monomeric nitrosyl bromide, BrNO is known but monomeric NSBr has not yet been prepared. In the nitrosyl halides the halogen is attached to nitrogen, whereas in the thiazyl halides it is attached to ~~nitrogen~~ Sulphur. This has been ascribed to the fact that the halogen atom would join itself for preference to the atom of lowest electronegativity in these compounds[6].

(a) Thiazyl chloride

NSCl is prepared by the depolymerisation of trithiazyl trichloride[90,91]. In a continually evacuated sublimation apparatus, $S_3N_3Cl_3$ sublimed very slowly at 55°C, to a water cooled cold-finger giving yellow $S_3N_3Cl_3$ on the cold-finger while only traces of NSCl were pumped out. However, when 40 mm pressure of nitrogen

or helium was present during closed sublimation at 70-80°C, to a liquid nitrogen cold-finger a yellow-white film, and later white to purple crystals, collected, which virtually all pumped out when warmed to 20°C and proved to be NSCl with less than 5% of the material remaining as $S_3N_3Cl_3$.[91] The experiments involving depolymerisation of $S_3N_3Cl_3$ indicated that the depolymerisation is a reversible process, and the following reaction sequence is proposed on the basis of the known species involved during the depolymerisation[91].

$$S_3N_3Cl_3(s) \rightleftharpoons S_3N_3Cl_3(g) \qquad \text{(i)}$$

$$S_3N_3Cl_3(g) \rightleftharpoons 3NSCl(g) \qquad \text{(ii)}$$

$$2NSCl(g) \rightleftharpoons N_2(g) + S_2Cl_2(g) \qquad \text{(iii)}$$

$$S_2Cl_2(g) + S_3N_3Cl_3(s) \longrightarrow S_3N_2Cl_2(s) + NSCl(g) + SCl_2 \qquad \text{(iv)}$$

$$2SCl_2(g) \rightleftharpoons S_2Cl_2(g) + Cl_2(g) \qquad \text{(v)}$$

$$Cl_2(g) + S_3N_2Cl_2 \longrightarrow 2NSCl(g) + SCl_2(g) \qquad \text{(vi)}$$

$$S_2Cl_2(g) + S_3N_3Cl_3(s) \longrightarrow S_3N_2Cl_2(s) + NSCl(g) + SCl_2(g) \qquad \text{(vii)}$$

The process explains the observed autocatalytic behaviour by the enhanced occurrance of step 3 with build up of NSCl(g).

The following methods also have been used to prepare NSCl[89,92].

(i) When a stream of ~~active~~ disulphur dichloride was passed into a stream of active nitrogen, NSCl is formed ($2N + S_2Cl_2 \longrightarrow 2NSCl$).

(ii) It is prepared by heating under reflux a suspension of ammonium chloride in excess of disulphur dichloride ($NH_4Cl + 2S_2Cl_2 \longrightarrow 3S + NSCl + 4HCl$).

(iii) It is an intermediate in the preparation of $S_3N_3Cl_3$ from $S_3N_2Cl_2$ and chlorine, and can be isolated ($S_3N_2Cl_2 + Cl_2 \longrightarrow 2NSCl + SCl_2$).

(iv) When $S_3N_2Cl_2$ is heated in vacuo to 80-90°C., NSCl and SCl_2 are evolved ($3S_3N_2Cl_2 \longrightarrow S_3N_2Cl + 2NSCl + SCl_2$).

(v) NSCl can be obtained by the action of chlorine on gaseous NSF.

Thiazyl chloride is a greenish-yellow gas. It reacts with water to give ammonia, sulphur dioxide and hydrochloric acid ($NSCl + H_2O \longrightarrow HNSO + HCl$; $NHSO + H_2O \longrightarrow NH_3 + SO_2$).

It is possible that NSCl has the structure with chlorine attached to nitrogen, but the very high value of force constant (10.02 m dynes/Å) and the NS bond order,[95,96] 2.3 show that only the structure in which chlorine is attached to sulphur is likely, since in the case of SNCl no expansion of the valency shell of the

nitrogen is possible to give a bond order N_{NS} 2.[93] According to the Walsh rule[94], NSCl should be non-linear. A non-linear assymetric molecule gives rise (according to the relevant symmetry considerations and selection rules) to three vibrational degrees of freedom, constituting three fundamental frequencies, namely ν_1(NS stretching), ν_2(SCl stretching) and ν_3(the NSCl bending vibration). The infrared spectrum of NSCl (from 300 to 4000cm^{-1}) showed two fundamental frequencies, ν_1(1325 cm^{-1}), ν_2(414 cm^{-1}), and ν_3(273 cm^{-1}) was calculated from the overtone and combination bands[93]. It was confirmed that NSCl has the structure NSCl with C_s symmetry and is not SNCl.

(b) Thiazyl fluoride

NSF is an unstable colourless gas (m.p. -89°C., b.p. 0.4°C). It can be prepared by several methods given below, (minor products shown in brackets).

(i) $NH_3 + S + 4AgF_2 \xrightarrow{CCl_4} NSF + 3HF + 4AgF\ (NSF_3)$

(ii) $NH_3 + SF_4 \longrightarrow NSF + 3HF$

(iii) $F_2S{=}N{-}COF \xrightarrow{190^\circ C} NSF + COF_2$

(iv) $NF_3 + S \xrightarrow{400^\circ C} NSF\ (S_2F_2, SF_4)$

(v) $S_4N_4 \xrightarrow{F_2(-75^\circ C)} NSF\ (NSF_3, SF_4)$

(vi) $S_4N_4 \xrightarrow{SeF4(-10^oC)} NSF\ (SOF_2, SiF_4, Se)$

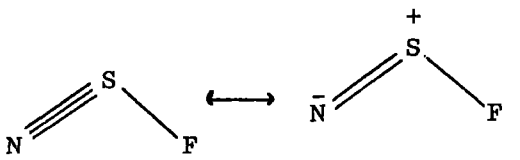
(vii) $S_4N_4.4SbF_5 \xrightarrow{145^oC} NSF$

(viii) $S_4N_4 \xrightarrow[CCl_4]{AgF_2, HgF_2} NSF$

(ix) $S_4N_4 \xrightarrow[SF_4]{} NSF$

The fluorination of S_4N_4 using AgF_2 or HgF_2 in boiling CCl_4 is a suitable method. In the case of HgF_2, the fluorination proceeds under milder conditions and better yields are obtained.

NSF is a bent triatomic molecule with sulphur in the middle and a fluorine atom attached to sulphur[97,98]. After NSF_3, thiazyl fluoride has the highest SN bond order of all the sulphur-nitrogen halides[32]. The bond order of more than two would correspond to resonance structures shown below,



The NSF molecule can be thought of as being derived from SF_4 with three of the fluorine atoms replaced by a triply bonded nitrogen atom. The SF distance in NSF is the same as the SF distance in SF_4 and the SN distance of NSF is only slightly greater than the SN distance in NSF_3.[98]

NSF is highly reactive and undergoes hydrolysis with water vapour yielding thionyl imide, HNSO, as an intermediate[97,98]. The final hydrolysis products are sulphite, fluoride and ammonia, the course of this reaction has not yet been elucidated. In copper or teflon vessels, NSF can be stored for a short time without decomposition, but it trimerises to $S_3N_3F_3$ on standing. It decomposes slowly in glass vessels. The reaction with glass proceeds rapidly at about 200°C and gives S_4N_4, SOF_2, SO_2 SiF_4 and N_2 at [32]. NSF polymerises to give $S_3N_3F_3$ at high pressures, whereas/low pressures, green-yellow crystals of $S_3N_2F_2$ separate out on the walls of the container. NSF forms a colourless crystalline adduct with boron trifluoride[90,100]. This compound $NSF.BF_3$ or $NS^+BF_4^-$ is stable for a short time at low temperatures and dissociates into its components in the gas phase[6].

(ii) Polymeric thiazyl halides

(a) Polythiazyl bromide

When bromine is allowed to react with S_4N_4 in CS_2, deep-red brown compound of composition $(NSBr)_x$ is obtained[26,101]. The infrared spectrum of this compound is given in the experimental section. It is stable in dry air, but hydrolysed in moist air. It is thought to be a bromine derivative of $(SN)_x$ and the following structure has been proposed.[6]

$$-(S = N)_x^-$$
$$\quad\quad |$$
$$\quad\quad Br$$

It reacts with ammonia at $-40^{o}C$ to give a red solution (probably $(NS\text{-}NH_2)_x$) and ammonium bromide[6].

(b) Trithiazyl trichloride and trithiazyl trifluoride

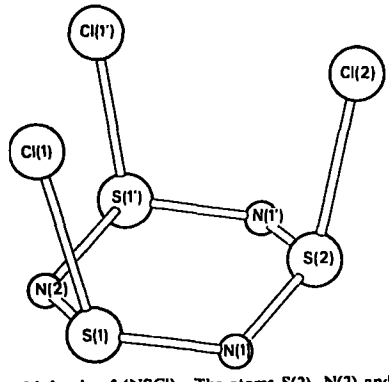
(i) $S_3N_3Cl_3$

Trithiazyl trichloride may be prepared by the method originally described by Demarcay[127] and Meuwsen[102] and most recently revised by Schroeder and Glemser[117] on passing chlorine through a suspension of S_4N_4 in an inert solvent ($3S_4N_4 + 6Cl_2 \longrightarrow 4S_3N_3Cl_3$). A more convenient method recently described by Jolly and Maguire[104] utilising the reaction:

$$3S_3N_2Cl_2 + 3Cl_2 \longrightarrow 2S_3N_3Cl_3 + 3SCl_2.$$

This method, but with CCl_4 solvent, was first described by Meuwsen[118]. The preparation of $S_3N_3Cl_3$ from S_4N_4 using sulphuryl chloride as the chlorinating agent is described in this thesis.

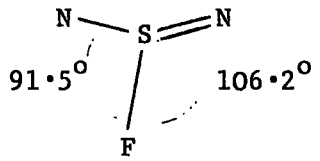
In the structure of $S_3N_3Cl_3$ shown below



Molecule of $(NSCl)_3$. The atoms S(2), N(2) and Cl(2) are on the mirror plane.

the molecule consists of a six-membered ring compound of alternating sulphur and nitrogen atoms in a chair configuration with the three nitrogen atoms below the sulphur atoms and one chlorine bonded to each sulphur in an axial position above the ring.[107,108] One chlorine atom (marked Cl(2) on the previous diagram) differs from the other two - compare $(NSOCl)_3$.[110,190] In this structure both sulphur and nitrogen atoms contribute one electron each to the π system. These bonds have been proposed to consist of nitrogen p_π-sulphur d_π overlap delocalized either over the entire ring[3] as in benzene or over separate three-centre S-N-S bonds.[4] The SN bonds are all short and equal (1·605Å), which indicates the presence of π bonds.[107,108] The aromatic ring of $S_3N_3Cl_3$ is in contrast to the alternating single and double bonds of $S_3N_3F_3$ and $S_4N_4F_4$. The presence of localised double bonds in $S_3N_3F_3$ is deduced from ^{19}F n.m.r. data (the trimer and tetramer fluoride show similar shifts);[88] the sulphur-nitrogen distances in $S_4N_4F_4$ are known from an X-ray structure determination.[115] Glemser[88] explains the different ring bonding in the chloride and fluorides as follows (cf. Allen[2]): "Each fluorine atom polarizes the sulphur, by drawing off electrons, to such an extent that, in comparison to S_4N_4, a weaker repulsion between the lone electron pair on the S and that on the N results. In this way, the bond length can be decreased and the tendency towards formation of a double bond is enhanced. Alternating shorter and longer S-N distances may frequently be more favourable than two proportionately shorter, but equal distances, such as occur in

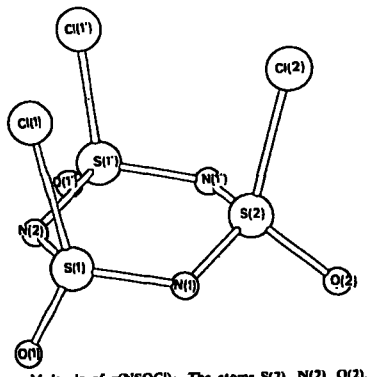
delocalized bonds. That is to say, the attraction term of the bond energy increases exponentially with decreasing distance, so that, in the case of alternating distances, the gain in double bond energy may exceed the delocalisation energy for equal distances. This effect is intensified by the position of the fluorine, which tends to form an N=S-F angle as wide as possible, as is evidenced by the structure of $N_4S_4F_4$:



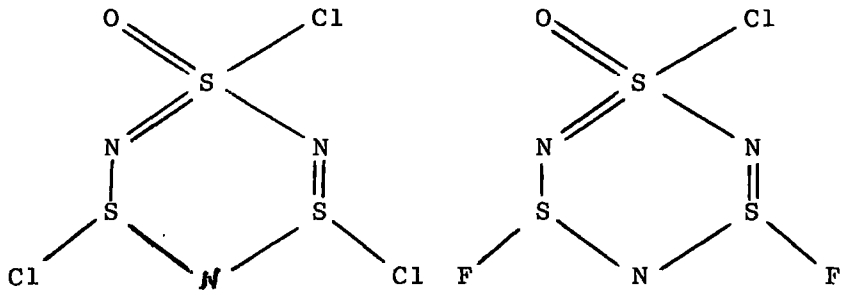
The same assumptions must be valid for $N_3S_3F_3$. In $N_3S_3Cl_3$, however, the chlorine cannot polarize the sulphur as strongly as flurdne can in $N_3S_3F_3$. Therefore, no preponderance is given localized double bonds and S-N distances are longer, i.e. the symmetrical arrangement of chlorine and the gain in delocalizing energy are more favoured."

Trithiazyl trichloride reacts with sulphur trioxide and gives a pale-yellow adduct $S_3N_3Cl_3.3SO_3$ and then the olive-coloured $S_3N_3Cl_3.6SO_3$.[6] When these adducts are heated to 140-160°C, β α-sulphanuric chloride $S_3N_3Cl_3O_3$ is formed. The structure of α-sulphanuric chloride has been determined.[108,109,110] The results show that α-sulphanuric chloride is trimeric with an S_3N_3 ring (like $S_3N_3Cl_3$ but with oxygen atoms taking the place of lone pairs

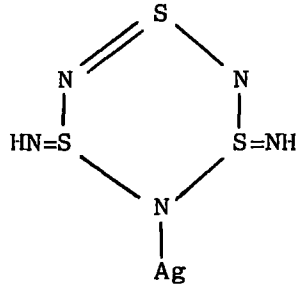
on sulphur). The molecule exists as the chair form with the chlorine atoms in axial positions and with all S-N distances equal (1·571Å)[110] as in $S_3N_3Cl_3$ there are two types of axial chlorine atoms.[110,190] The shortness and equality of the skeletal bonds probably denotes appreciable p_π-d_π overlap; it also seems likely that there is donation of the nitrogen lone-pair to sulphur, to form a co-ordinate π-bond[42] especially since the sulphur atoms in $(NSOCl)_3$ have considerable Lewis acidity [sulphanuric chloride forms an adduct $(py.NSOCl)_3$ with pyridine].[128] Two new sulphur and nitrogen containing six-membered ring compounds ($S_3N_3Cl_3O$ and $S_3N_3F_2ClO$) have recently been reported.[111] Chlorination of $S_3N_2O_2$, by means of liquid chlorine yields the crystalline colourless mixed thiazyl-sulphanuric ring compound, $S_3N_3Cl_3O$; with silver difluoride $S_3N_3Cl_3O$ gives another colourless crystalline ring compound $S_3N_3F_2ClO$. The following structures have been proposed for these compounds.[111] Conformations similar to $(NSCl)_3$ (p.25) and $(NSOCl)_3$ (below) are to be expected, i.e. axial halogen atoms.



Molecule of α(NSOCl)$_3$. The atoms S(2), N(2), O(2), and Cl(2) are on the mirror plane.



The thermal depolymerisation of $S_3N_3Cl_3$ to form thiazyl chloride has already been described (page 20). $S_3N_3Cl_3$ is easily hydrolysed by water, acqueous acid or alkali, presumably by nucleophilic attack on sulphur[6], giving ammonia and chloride. Ammonolysis of trithiazyl trichloride produces the amide $(H_2N\text{-}SN)_3$[12]. If the freshly prepared amide is dissolved in acqueous ammonia and then rapidly precipiated with silver nitrate a very explosive yellow silver salt can be isolated after removing ammonia under vacuum[112]. The following probable structure has been proposed for the silver compound[12].



$S_3N_3Cl_3$ reacts with dimethyl sulphoxide giving new type of sulphur-nitrogen cation ($S_3N_3Cl_3 + 6(CH_3)_2SO \longrightarrow 3\,[(CH_3)_2S{=}\overset{+}{N}{=}S(CH_3)_2]\,Cl^- + 3SO_2$)[6]. When trithiazyl trichloride is allowed to react with tetrasulphur tetraimide or heptasulphur imide in the presence of pyridine, tetrasulphur tetranitride is formed, suggesting the formation of both the $N{\equiv}S^+$ and $\bar{N}{=}S$ ions in these reactions[88] ($4S_3N_3Cl_3 + 3S_4N_4H_4 \longrightarrow 6S_4N_4 + 12HCl$; $4S_3N_3Cl_3 + 12S_7NH \longrightarrow 6S_4N_4 + 12HCl + 72S$). If the reaction is carried out in the absence of pyridine, which is intended to capture HCl, a brown red adduct is formed, which reacts with traces of water to give S_4N_3Cl ($S_4N_4.4HCl \longrightarrow S_4N_3Cl + NH_4Cl + Cl_2$)[88].

Molybdenum hexacarbonyl reacts with trithiazyl trichloride in dichloromethane to give microcrystalline brown solid, $MoS_3N_3Cl_3$ ($S_3N_2Cl_3 + Mo(CO)_6 \longrightarrow MoS_3N_3Cl_3 + 6CO$)[113] A polymeric structure involving metal-metal bonding was thought, on the basis of its being insoluble in non-polar solvents and the observed low ratio of $S_3N_3Cl_3$ to Mo.

(ii) $S_3N_3F_3$

When NSF is allowed to stand in a sealed glass container for three days, a mixture of crystals is formed from which $S_3N_3F_3$ can be sublimed[97]. $S_3N_3F_3$ is more conveniently prepared by

fluorinating $S_3N_3Cl_3$ in CCl_4 using AgF_2[97].

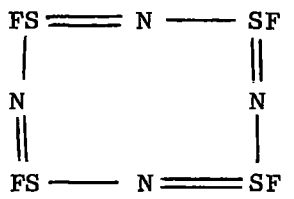
$S_3N_3F_3$ is a colourless, volatile, crystalline compound (m.p. 74.2°C., b.p. 92.5°C) and soluble in inert solvents such as benzene, CCl_4[97]. No X-ray structure determation has been reported, but the cyclic formula can be inferred from the fact that there is only one nuclear magnetic resonance line for fluorine, showing that all three fluorine atoms are in equivalent environments[6]. The infrared spectrum of $S_3N_3F_3$ shows absorption peaks at 1085, 720 and 650 cm^{-1}[97]. It is more moisture sensitive than $S_3N_3Cl_3$ and $S_4N_4F_4$. It is stable in dry air and turns black in moist air with decomposition[6]. In cold diluted sodium hydroxide solution $S_3N_3F_3$ is hydrolysed by the following reaction[32],

$$S_3N_3F_3 + 9H_2O \longrightarrow 3NH_4F + 3H_2SO_4.$$

(c) Tetrathiazyl tetrafluoride

$S_4N_4F_4$ is prepared from the reaction of AgF_2 on S_4N_4 in CCl_4 (the reaction of elementary fluorine with solid S_4N_4 is too violent and gives sulphur fluorides and nitrogen)[88] but attempts to obtain this compound by the polymerisation of NSF have been unsuccessful[32]. It is therefore considered that the formation of $S_4N_4F_4$ from S_4N_4 and AgF_2 does not involve intermediate SN radicals but that the fluorine atoms add directly to the sulphur atoms of the S_4N_4 ring.

$S_4N_4F_4$ molecule, has a puckered eight-membered ring type of molecular structure, with the plane of the nitrogen atoms above the plane of the sulphur atoms[2]. X-ray diffraction measurements indicate that in the tetrameric fluoride, $S_4N_4F_4$, there is an alternation of double and single bonds[114,115]. Delocalization of π electrons, therefore is minimal. This is in part due to the fact that the π bonding itself is weak, due to a repulsion of the nitrogen lone-pair, by the sulphur-lone-pair[5] and also because the non-bonded interactions (lone-pair, polar and steric repulsions) force the ring to assume a tub configuration. This reduces the possibility that delocalized $p_\pi - p_\pi$ bonding can occur. An additional factor which limits $d_\pi - p_\pi$ bonding to alternate skeletal bonds is that although there is a large overlap between a sulphur d_π orbital and one nitrogen p_π orbital, the $d_{x^2-y^2}$ orbital, which is directed towards the p_π orbital of the other neighbouring nitrogen is not polarized sufficiently to form a strong π bond[5]. Thus the aromatic character of the ring is lost and the puckered eight-membered ring has a different shape from that of S_4N_4[6]. Infrared bands[97] that can be used for the identification of $S_4N_4F_4$ lie at 1117, 786, 760, 709, 645 and 520cm^{-1}. The structure of $S_4N_4F_4$ is shown below:



$S_4N_4F_4$ is a white crystalline compound (m.p. 153°C (decomp.)). It is soluble in CCl_4 (3.44g. per litre at 2°C)[6]. It forms a green adduct $F_4S_4N_4 \longrightarrow BF_3$ the thermal decomposition of which yields NSF[32]. The compound hydrolyses completely in warm sodium hydroxide ($S_4N_4F_4 + 12H_2O \longrightarrow NH_4F + 4H_2SN_3$).

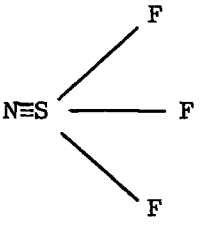
(iii) Sulphur-nitrogen halides derived from sulphur hexafluoride

Thiazyl trifluoride

NSF_3 is a derivative of SF_6 in which three fluorine atoms are replaced by nitrogen atoms and it resembles the hexafluoride to some degree in its stability and lack of reactivity[6]. It is formed when ammonia is passed into a suspension of sulphur and AgF_2 in CCl_4[32] ($NH_3 + S + 6AgF_2 \xrightarrow{CCl_4} NSF_3 + 3HF + 6AgF$). NSF_3 is also formed in all fluorinations of S_4N_4 with AgF_2 in CCl_4[32] ($S_4N_4 + 12AgF_2 \xrightarrow{CCl_4} 4NSF_3 + 12AgF$).

NSF_3 is a colourless, pugently smelling gas (m.p. -72.6°C, b.p. -27.1°C)[6]. Its molecular structure has been established from studies of the microwave spectrum, infrared spectrum and fluorine nuclear magnetic resonance[6]. NSF_3 is isoelectronic with OPF_3

(tetrahedral, having the symmetry C_{3v}) which gives a very similar infrared spectrum to that of $FClO_3$[6,32]. The calculated force constants corresponds to a bond order of 2.7 for the SN bond[32]. Infrared spectrum[97] of NSF_3 shows peaks at 1515, 811, 775, 521, 429 and 342 cm^{-1}. Its structure is shown below:



The chemical properties also seem to indicate that it is reasonable to compare NSF_3 with SF_6. However, whereas the 3s, 3p and 3d electrons in SF_6 are hybridised to the octahedral sp^3d^2 state, the orbitals in NSF_3 are sp^3 hybridised[32]. There are two $p_\pi - d_\pi$ overlaps between nitrogen and the sulphur in NSF_3. The fact that the F-N-F angle in NSF_3 (94^oA) is smaller than the ideal tetrahedral angle indicates some contribution of d and p states in sulphur[32].

Thiazyl fluoride does not react at room temperature with ammonia gas[6]. It reacts slowly with water at room temperature, but it is hydrolysed by sulphuric acid and fluoride ion when boiled with sodium hydroxide solution[6]. It is stable towards metallic sodium and reacts only at about 400^oC to form Na_2S,

nitrogen and sodium fluoride[97].

NSF_3 reacts with BF_3 to form colourless $NSF_3.BF_3$,[88] which can be purified by sublimation. Infrared measurements and molecular weight determinations indicate that the gaseous phase consists of an equimolar mixture of NSF_3 and BF_3. The spectrum of the solid but not the liquid compound in the near infrared resembles those of the alkali metal tetrafluoroborates. The compound is therefore assumed to have the formula 1 in the liquid state and formula 2 in the solid state[32] as shown below

$F_3S{\equiv}N \longrightarrow BF_3$ (1) $[NSF_2]^+ [BF_4^-]$ (2)

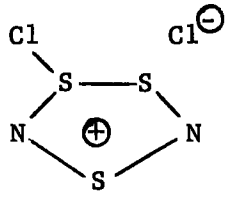
The instability of these adducts indicate that the donor power of nitrogen is considerably weakened by the N≡S bond. In addition to NSF_3, compounds of the type, F_2NSF_5, F_5SNH_2, $CF_3N{=}SF_4$ and $SF_5N{=}SF_2$ have been prepared[32].

(iv) Thiodithiazyl monochloride, dichloride and difluoride

(i) Thiodithiazyl chloride, S_3N_2Cl, was first prepared by Demarcay[128], from the reaction between S_4N_4 and S_2Cl_2. It can be obtained by the vacuum sublimation of $S_3N_2Cl_2$ at 80-90°C ($3S_3N_2Cl_2 \xrightarrow{80\text{-}90^\circ C} 2S_3N_2Cl + 2NSCl + SCl_2$)[123]. It is also formed in the reaction of NOCl with S_4N_4 or when $S_3N_3Cl_3$ reacts with NO in nitromethane.[32]

(ii) Thiodithiazyl dichloride, $S_3N_2Cl_2$ was reported by Meuwsen[103] in the chlorination of $S_3N_3Cl_3$ in CCl_4. It can be prepared by refluxing a mixture of S_2Cl_2 and ammonium chloride ($2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2$)[123]. $S_3N_2Cl_2$ was first identified by Demarcay[124], who prepared it by allowing SCl_2 or S_2Cl_2 to react with S_4N_4. It may also be prepared by the reaction of tetrachloro ethylene (or trichloro ethylene) with $S_3N_3Cl_3$[125].

An X-ray crystal structure analysis on $S_3N_2Cl_2$ shows that the compound is a salt consisting of a chloride anion, and $S_3N_2Cl^+$ cation, the sulphur and nitrogen atoms form a puckered five membered ring as shown below



The chemistry of $S_3N_2Cl_2$ has been reviewed[129(a)].

(iii) Thiodithiazyl difluoride, $S_3N_2F_2$ is prepared by the decomposition of NSF in a six litre glass flask at pressures of about 600 mm Hg[88]. After one week greenish-yellow crystals are obtained. $S_3N_2F_2$ sublimes at 40°C and 55°C giving yellowish-green and bright-green crystals respectively[88].

Both the compounds are soluble in CCl_4 and have the same molecular weights and ultraviolet spectra (the two compounds are thought to be polymorphic modifications of the same compound). Since $S_3N_2F_2$ is soluble in CCl_4, an ionic structure similar to $S_3N_2Cl_2$ is less probable, and a structure, which is given below is proposed on the basis of the qualitative conversion of its nitrogen to ammonia by alkaline hydrolysis[6]

F-S-N=S=N-S-F

(v) Thiotrithiazyl halides

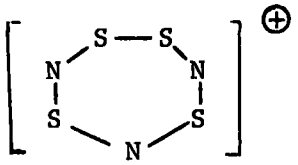
Thiotrithiazyl halides contain the cationic seven-membered ring $S_4N_3^+$. The relatively stable chloride serves as the starting material for these compounds. All the four halides have been reported by Padley[129]. Later attempts to repeat the preparation of the pure iodide were unsuccessful[125].

S_4N_3Cl was first prepared by Demarcay[127] by heating together S_4N_4 and S_2Cl_2 in CCl_4 ($3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$). It can be prepared by the action of $SOCl_2$ or acetyl chloride on S_4N_4[129] or by the reaction of S_4N_4 with diselenium dichloride in CCl_4[129]. All other sulphur chlorides as well as the adduct $S_4N_4.4HCl$ can be converted to S_4N_3Cl. When $S_3N_3Cl_3$ or $S_3N_2Cl_2$ is heated with S_2Cl_2 in CCl_4, S_4N_3Cl is formed. Reaction of

$S_3N_3Cl_3$ with diphenyl acetylene or carbon monoxide at about 40°C in CCl_4 gives S_4N_3Cl (this thesis p. 82). It can also be prepared by the reaction between S_2Cl_2 and lithium azide in CCl_4[32]. Since the same reaction gives S_4N_4 at 0°C, it is assumed that S_4N_4 is the initial product which reacts with S_2Cl_2 to form S_4N_3Cl ($4LiN_3 + 2S_2Cl_2 \longrightarrow S_4N_4 + 4LiCl + 4N_2$; $3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$).

S_4N_3Cl is a yellow crystalline solid, stable in dry air. It decomposes at 170°C in vacuo to give S_4N_4[129]. It is insoluble in solvents of low dielectric constants, but soluble in $SOCl_2$ and formic acid[6]. It can be recrystallised from $SOCl_2$ in red needles[129]. S_4N_3Cl decomposes slowly in benzene, $CHCl_3$, acetone, and acetic acid by development of a red colour[129]. The course of hydrolysis of S_4N_3Cl depends on the reaction conditions. With ice-cold sodium acetate solution, the initial product at 0°C is the black S_4N_3OH, whereas black $(S_3N_3OH)_2$ is formed at room temperature[129]. The hydroxides are probably polymeric and unstable giving S_4N_4 on standing.

The S_4N_3 cation is a planar seven membered ring with three alternating S-N bonds and one S-S bond[130,131].



The evidence for pseudoaromaticity in the ring is provided by structural and spectral studies. There is however disagreement in the literature over the extent of π delocalization. Johnson et al[132] reports that, the planar structure and short, equal, S-N bond lengths (1.55Å compared with 1.62Å for $(S-N)_4$) of the thiotrithiazyl ($S_4N_3^+$) cation suggest that considerable π bonding occurs in this ring system and the electronic spectrum is consistent with a delocalized, ten electron π system in which sulphur d orbitals are used. Whereas Bailey et al[133] proposed a six or eight π electron system and their results indicate that delocalization does not occur over the whole ring, the delocalized system and the disulphide group are best considered separately, however the existence of a certain amount of delocalization across the disulphide group is quite likely.

S_4N_3F is obtained by the replacement of the chloride ion in S_4N_3Cl, when anhydrous HF gas is allowed to react with S_4N_3Cl in a polyethylene or teflon tube[88] ($S_4N_3Cl + HF \longrightarrow S_4N_3F + HCl$). A convenient general method for the preparation of thiotrithiazyl compounds consists in the metathesis of solutions of the chloride in anhydrous formic acid. An orange-yellow bromide, bronze coloured S_4N_3SCN, red-brown tetraphenyl borate, $S_4N_3.B(C_6H_5)_4$ and $S_4N_3.SbCl_6$ have been made in this way[6]. With nitric

acid and sulphuric acid, S_4N_3Cl gives $S_4N_3.NO_3$ and $S_4N_3.HSO_4$ respectively[6]. A novel preparation of the bromide is by the reaction of bromine on $(HNS)_4$ ($S_4N_4H_4 + Br_2$ $S_4N_3Br + NH_4Br$)[51].

Ring expansion of $S_4N_3^+$ can be achieved by reaction of S_4N_3Cl with aluminium azide or ammonia[6].

$$3S_4N_3Cl + Al(N_3)_3 \longrightarrow 3S_4N_4 + 3N + 3N_2 + AlCl_3,$$

$$S_4N_3Cl + NH_3 \longrightarrow S_4N_3NH_3Cl + S_4N_4NH_2 + S_4N_4.$$

EXPERIMENTAL

PREPARATIONS

Tetrasulphur tetranitride:-[14,15,16,18,19,23,26]

A three-necked round-bottomed was used as the reaction vessel. This was fitted with a paddle stirrer through the main neck and a gas inlet tube through one of the side necks.

700 ml of carbon tetrachloride (dried over P_4O_{10}) and 25 ml of disulphur dichloride (sulphur monochloride) were added to a one-litre reaction vessel. While stirring briskly dry chlorine gas was passed through the solution until a distinctly green layer of chlorine gas was observed over the solution. After about three quarters of an hour, the apparatus was immersed in an ice-bath and a fast stream of ammonia from a cylinder was passed through the solution as rapidly as possible without causing material to splash from the flask.

Initially copious white fumes were formed which soon disappeared and a thick yellow brown suspension was formed in the flask. The colour then changed to a grey green, brown and finally after about three hours to a reddish brown or yellowish brown suspension. The flow of ammonia was then stopped. During the passage of ammonia the liquid in the flask was maintained to a constant volume by occasionally adding carbon tetrachloride through the third neck of the flask using a funnel.

The reaction mixture was filtered on a sintered-glass funnel and the solid material was slurried with about 500 ml of water for 10-15 minutes. The precipitate was separated by filteration and thoroughly air-dried for a day or two.

To remove S_7NH, the dried residue was shaken with 150 ml of ether for ten minutes in a wide necked reagent bottle. The solution was decanted off and the process was repeated. (This process removes so little material, there is some doubt if it is necessary). The yellow or yellowish green dry residue was extracted with dry benzene. Either a Soxhlet extractor or an extraction tube was used for this. The extraction was continued until the eluate was colourless or faintly orange yellow. When all the S_4N_4 was extracted, the extraction pot was cooled and pure tetrasulphur tetranitride crystallised from the solution as orange-red or orange-yellow needles. Yields of 12-14 g. of S_4N_4 (m.p. 178-179^{o}) were obtained. Further purification if necessary may be effected by sublimation in high vacuum with a bath temperature of about 100^{o}C.

Precautions for working with S_4N_4 are as follows[14(b)]. S_4N_4 itself can only become dangerous in a dry state, but one should take note of the following:

Do not work with more than 10g of dry S_4N_4. Do not touch it with a metal spatula, and do not store the dry substance in bottles

with ground glass stoppers in order to save the crystals from being ground between the two surfaces, which usually causes an explosion. While working with S_4N_4 in dry state normal precautions are sufficient, e.g. a plate of safety-glass.

Phenylboron dichloride ($PhBCl_2$) [54(a),(b),191]

Boron trichloride (5.214g., 0.453 mol.) was added to a suspension of tetraphenyl tin (4.205g.,) in dry methylene dichloride (10 ml) at -80°C. The mixture was allowed to warm gradually to between 0°C and 5°C when a violent reaction occurred. The volatile material (methylene dichloride containing some boron trichloride) was removed and trapped at -80°C. The residue gave a mixture of phenylboron dichloride (b.p. 65-70°C) and phenyltin trichloride (b.p. 129-130°C). Phenylboron dichloride was purified by several distillations under vacuo (Yield 4.2 g., 90% based on the equation, $Ph_4Sn + 3BCl_3 \longrightarrow 3PhBCl_2 + PhSnCl_3$).

Diphenyl mercury:

B.D.H. laboratory reagent was purified by recrystallisation from hot chloroform.

p-Tolytin trichloride: ($C_7H_7SnCl_3$) [52(a),(b)]

p-Bromotoluene (171 g, 1 mole) in ether (100 ml) was added to magnesium (24.3 g., 1 g atom) in ether (500 ml) during one and a half hours. The reaction mixture was refluxed for 30 minutes

and then allowed to cool to room temperature. Stannic bromide (76·5 g., 0·175 moles) in benzene was added to the reaction mixture during 40 minutes and then the reaction mixture was refluxed for two and a quarter hours. The reaction mixture was cooled to room temperature and hydrolysed by the addition of ice-water (500 ml) and ice-cold 5% hydrochloric acid (200 ml.) After filtration the organic layer was separated, dried over $MgSO_4$, and solvent was removed under vacuum to give tetra-p-tolytin (71 g., 85%), which was recrystallised from benzene.

p-Tolytin trichloride was prepared by the redistribution reaction of tetra-p-tolytin with stannic chloride. The two components in 1:1 ratio were mixed at room temperature and allowed to stand for 2-3 hours.

Stannic chloride (B.D.H. standard laboratory reagent) was purified by distillation under dry nitrogen atmosphere or under vacuo.

Stannic bromide (B.D.H.) was purified by sublimation under vacuum at room temperature.

Stannic iodide (B.D.H.) was purified by recrystallisation from hot chloroform.

Stannic fluoride (Alfa Inorganics Inc.) was used directly without further purification.

Titanium tetrachloride (B.D.H.) was purified by distillation under vacuo.

Titanium tetrabromide (Alfa Inorganics Inc.) purified by sublimation under vacuum at 30-40°C.

Titanium tetraiodide (Alfa Inorganics Inc.) was purified by sublimation under vacuum at 140-160°C.

Titanium tetrafluoride (Alfa Inorganics Inc.) was used without further purification.

Zirconium tetrachloride (B.D.H.) was first refluxed with $SOCl_2$ to remove any traces of moisture and then purified by recrystallisation from $SOCl_2$.

Zirconium tetrafluoride (Alfa Inorganics Inc.) was used without further purification.

Hafnium tetrachloride (Alfa Inorganics Inc.) was used without further purification.

Aluminium trichloride was purified by sublimation in a dry nitrogen atmosphere.

Aluminium tribromide (Hopkin and Williams) was purified by sublimation under vacuo.

Gallium trichloride was purchased from Koch-Light Ltd., and used without further purification.

Indium trichloride, $InCl_3.H_2O$ was purchased from B.D.H. and water was removed by refluxing with thionyl chloride.

Thallium trichloride was prepared from thallous chloride (Alfa (Inorganics Inc.) and chlorine in dry acetonitrile, (pp.67-68).

Selenium tetrachloride was prepared by the reaction between selenium and chlorine in dry CCl_4[36]. Pure selenium was suspended in CCl_4 in a two-necked round-bottomed flask and dry chlorine was then introduced. The Se soon dissolved and the solution turned brown (formation of Se_2Cl_2); after some time $SeCl_4$ separated as a yellow-white powder. $SeCl_4$ was filtered in absence of moisture and dried by suction. $SeCl_4$ was purified by sublimation at 196°C in the atmosphere of dry chlorine gas.

Selenium tetrafluoride was prepared by the reaction between ClF_3 and Se_2Cl_2 by analogy with the published preparation viz from fluorine and diselenium dichloride ($Se_2Cl_2 + 5F_2 \longrightarrow SeF_4 + 2FCl$)[47(a)] The apparatus used was constructed from Pyrex, and employed cone and socket and ball socket joints. It consisted of a 250 ml three-necked round-bottomed flask for mixing dry nitrogen and chlorine-trifluoride and a 100 ml two-necked reaction flask followed by a train of traps at -196°C for purification. Each section of the apparatus was capable of isolation by means of stopcocks. All joints were greased with Fluorolube 'W' grease.

Diselenium dichloride (10 g.) was cooled in an ice salt bath. This was found to be necessary to prevent ignition at the commencement of fluorination. The apparatus was flushed with dry nitrogen for about an hour. Chlorine trifluoride from the

cylinder diluted with dry nitrogen was passed slowly for half an hour and then the rate of chlorine trifluoride supply was increased until only a colourless liquid remained in the reaction vessel. The chlorine trifluoride was switched off and the apparatus was flushed with dry nitrogen for about an hour. The product was then purified by trap to trap distillation in vacuo.

Tellurium tetrafluoride[47(b)]

The reaction employed for the preparation of tellurium tetrafluoride was that of selenium tetrafluoride and tellurium dioxide (TeO_2 + $2SeF_4 \longrightarrow TeF_4 + 2SeOF_2$). Selenium tetrafluoride was distilled from a storage bulb into a carefully dried, evacuated train of bulbs, the first of which carried the dry tellurium dioxide. The mixture was slowly heated by means of a water-bath. As the temperature approached 80°C there was a vigorous reaction and the tellurium dioxide dissolved. The temperature was raised until the liquid began to reflux under its own vapour pressure and was kept at that temperature for about 15 minutes, after which the selenium tetrafluoride and selenium oxyfluoride were distilled into another bulb. The last traces being removed from the residue by keeping it at 100°C in vacuo. TeF_4 was purified by sublimation in vacuo.

Tellurium tetraiodide[36]: TeI_4 was prepared by the reaction between telluric acid and hydrogen iodide ($Te(OH)_6 + 6HI \rightarrow TeI_4 + I_2 + 6H_2O$).

A very concentrated telluric acid solution is mixed with slightly more than the stoichiometric quantity of fuming hydriodic acid. A heavy, grey precipitate of TeI_4 immediately separated. It was suction filtered on a fritted glass filter and washed several times with pure CCl_4 to remove iodine. The product was analytically pure (Found: I = 80·3%; theory I = 79·93).

Niobium pentachloride was purchased from Alfa Inorganics Inc. and purified by sublimation in vacuo.

Niobium pentafluoride (Koch-Light standard laboratory reagent) was used without further purification.

Tantalum pentachloride and Tantalum pentafluoride (Koch-Light standard laboratory reagents) were used without further purification.

Vanadium oxytrichloride and $WOCl_4$ were prepared by the methods described by Brauer.[36]

Tungsten hexachloride was purhcased from Koch-Light and used without further purification.

Tungsten hexabromide[120]

$WCl_6 + 2BBr_3 \longrightarrow WBr_6 + 2BCl_3$ 2·1 g. of WCl_6 was placed in a two-necked round-bottomed flask and excess of boron tribromide (B.D.H.) was condensed on it at -196°C. The reaction flask slowly warmed to 0°C when a vigorous reaction occurred. The flask was allowed to stand in a bath of cold water (10°C) for about an hour and the excess of boron halides were removed by condensing at -196°C. The tungsten hexabromide

was obtained as a black powder (Found: Br = 72.18; theory: Br = 72.30).

Trithiazyl trichloride ($S_3N_3Cl_3$)[11]

The preparation was carried out in the absence of moisture. A Schlenk or a two-necked round bottomed flask was used as the apparatus for the preparation. Tetrasulphur tetranitride (5 g.) was placed in a Schlenk and freshly purified (p. 50) sulphuryl chloride (25 ml) was added to the S_4N_4. The reaction mixture was stirred at room temperature using a teflon stirrer. The colour of the reaction mixture slowly changed to red after 1-2 hours, and the stirring was continued for 16-24 hours, until the evolution of sulphur dioxide ceased (the exit gas was led away through rubber (decomposes with SO_2Cl_2) or plastic tubing into a fuming chamber).

The pale-yellow-white powdery $S_3N_3Cl_3$ which settled out was filtered from the supernatent red liquid, washed with sulphuryl chloride (5-10 ml) dried in vacuo, and if necessary purified by recrystallisation from dry CCl_4. The red liquid was evaporated by pumping and further yellow-white $S_3N_3Cl_3$ was obtained and recrystallised from dry CCl_4. The total yield before crystallisation was quantitative.

The trithiazyl trichloride when freshly crystallised was a pale-yellow-white crystalline solid, which changed to yellow after standing for several days. The m.p. of the first batch of $S_3N_3Cl_3$

was 90-91°C, whereas the $S_3N_3Cl_3$ recrystallised from SO_2Cl_2 melted at 93-94°C.

$S_3N_3Cl_3$ is soluble in carbon tetrachloride (1 g in 25 ml CCl_4), benzene, chloroform, carbon disulphide, thionyl chloride, and sulphuryl chloride. When recrystallised from hot benzene it crystallises as yellow-white flakes. $S_3N_3Cl_3$ should be stored in glass containers with air-tight polyethylene stoppers or glass stoppers with teflon sleeves.

Drying and purification of solvents and other liquid materials

Most of the solvents were dried and purified by the methods described by A.Weissberger[36(a)]. Non-halogenated solvents were dried over sodium wire, redistilled if necessary from sodium and stored in a three-necked flask over clean sodium wire, in a nitrogen atmosphere. Quantities of solvents were removed by using a long needled syringe whilst dry nitrogen was flushed through the vessel.

Carbon tetrachloride[104] CCl_4 (AnalaR grade) was dried on standing over P_2O_5 for a day or two and then if necessary purified by distillation under dry nitrogen atmosphere.

Carbon disulphide[36(a)] Commercial carbon disulphide was agitated with mercury for 4-6 hours, dried with phosphorus pentoxide and fractionally distilled in vacuum avoiding all greased joints.

Methylene dichloride[54] CH_2Cl_2 was refluxed for 3-4 hours over phosphorus pentoxide, distilled, and stored in a dry nitrogen atmosphere.

Sulphuryl Chloride[36] SO_2Cl_2 (B.D.H. standard laboratory reagent) was fractionally distilled through a twelve inch column packed with glass helices, connected to a reflux distillation head equipped with a calcium chloride drying tube. The middle colourless fraction boiling between 69-70°C was pure SO_2Cl_2.

Thionyl chloride[119] Triphenyl phosphite (160 ml) was added to the thionyl chloride (1 litre) with vigorous stirring for 30 minutes. The mixture was fractionated and the 'water white' middle fraction was collected and stored.

Nitriles[36(a)] Acetonitrile, propionitrile, isobutyronitrile and tetertiarybutyl cyanide were dried over phosphorus pentoxide and purified by fractional distillation.

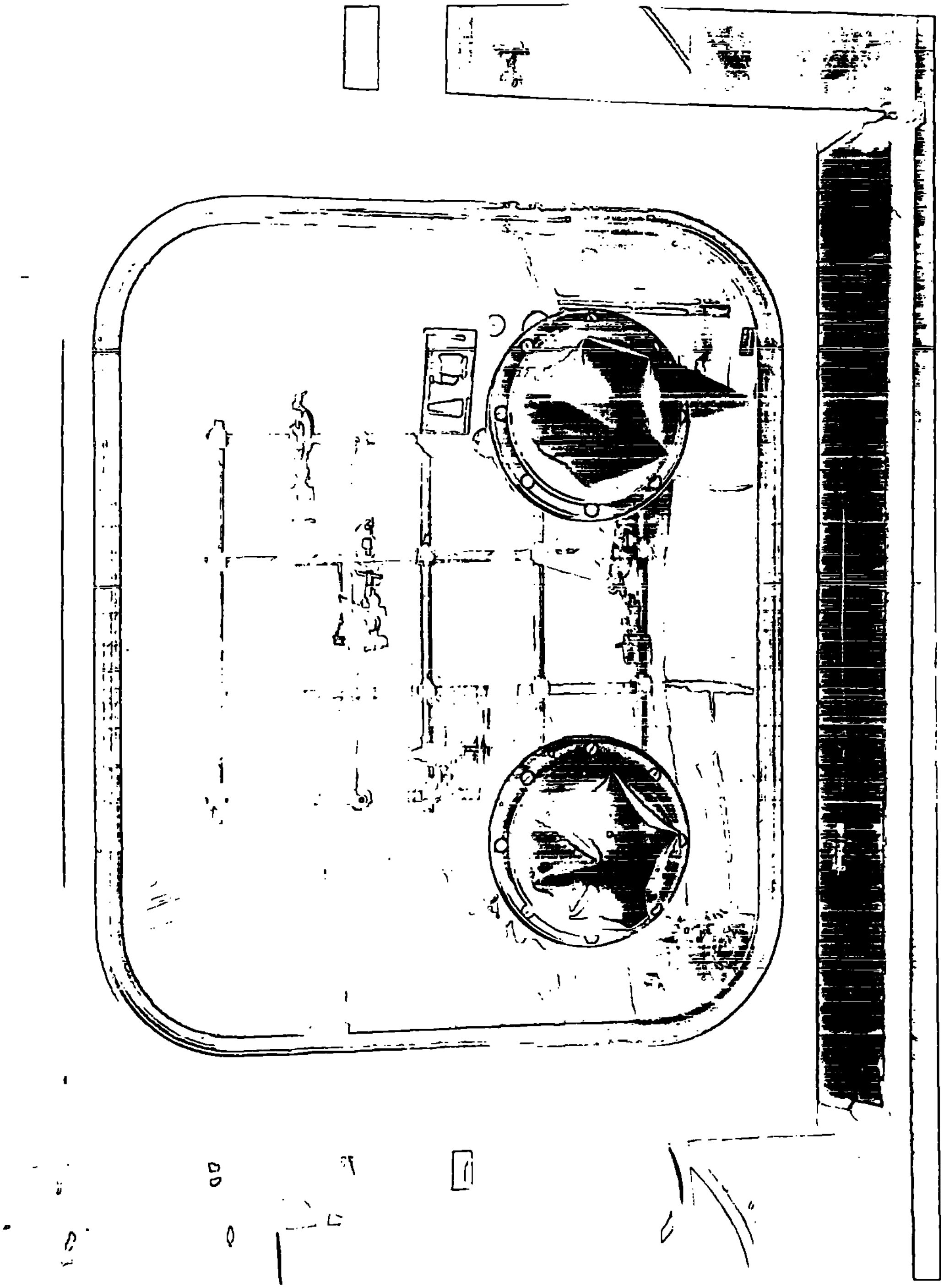
Epoxides[36(a)] Epichlorohydrin was purified by fractional distillation (b.p. 116°C.) Ethylene oxide and epibromohydrin were vacuum distilled.

Experimental Techniques

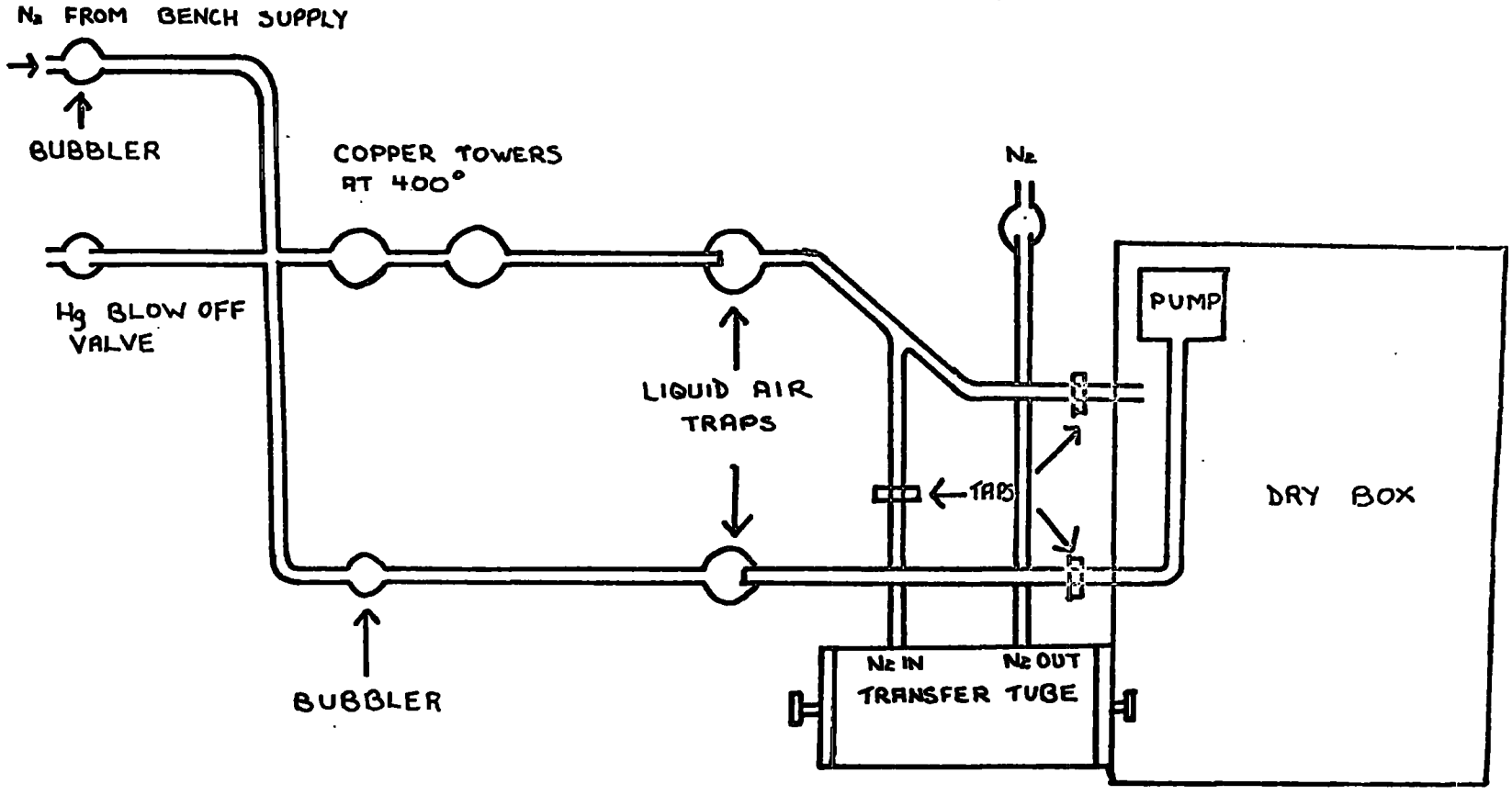
All manipulations of air and moisture sensitive compounds were carried out in the glovebox shown in figure overleaf.

The Drybox

This consisted of a steel box 39 inches long, 29 inches high and 24 inches deep with a perspex roof and front, and with two front



PLAN VIEW OF FLOW



ports used for armholes. It was obtained from Lintott Engineering Ltd., Horsham, Sussex (MK XI Glovebox). The perspex windows were fitted with rubber airtight seals; 'Charco, Buta-sol, 5B 3032' (or neoprene) arm-length gloves were used on the front parts. At one side of the box was a cylindrical transfer tube ('posting port') 18 inches long and 9 inches diameter, which opened into the drybox by means of a screw-in part and which similarly opened to the air at the other end. A strip-light was mounted outside the perspex roof and electricity was carried into the box which contained a recirculating pump. Behind the transfer tube were four 1 cm. diameter tubes leading through the side of the apparatus and closed inside and out by 4 mm. glass high vacuum taps, whilst the floor was covered with a sheet of black plastic material or aluminium kitchen foil.

The nitrogen atmosphere in the dry box was kept free from oxygen and moisture in the following way. The pump which could completely recycle the atmosphere in the box in ten hours, passed nitrogen out through a 4 mm. tap, through a trap 18 inches deep cooled in liquid air, over copper wire packed in two silica towers at 400^{o}C, through a second trap similarly cooled, and back through another 4 mm. tap into the box. This circulation was maintained whenever the dry box was not being used for experiments.

Copper towers and liquid air traps were connected to the drybox by P.V.C. and silicone tubing and normally the pressure in the box was maintained slightly above atmospheric. Nitrogen from the bench supply could be introduced into the system via the copper towers and liquid air cooled traps as shown in the figure.

All the apparatus introduced into the drybox was first placed in the transfer tube which had an inlet connected to the nitrogen system of the drybox,and nitrogen from the bench supply was flushed through via the copper towers and liquid air traps and passed out of the transfer chamber via a gas bubbler into the air. When the transfer tube had been purged for at least one hour the apparatus could be moved into the drybox.

Analyses:

Analyses were performed by Messrs. R.Coult and T.Holmes of this department and by Drs. Weiler and Strauss of the Micro-analytical laboratory, Oxford.

Molecular Weights:

Mol. wt. determinations were carried out either using a Mechrolab vapour pressure Osmometer, model 301A or the cryoscopic technique usually in benzene adapted to facilitate the use of air and moisture sensitive compounds.

Mass spectra:

Mass spectra were obtained with an A.E.I. (MS9) mass spectrometer on samples mounted on an inert ceramic and introduced on a direct insertion probe.

Infrared Spectra:

Infrared spectra under nitrogen were recorded on Grubb-Parsons GS2A or Spectromaster (4000-400 cm^{-1}) and DM2/DB3(475-200 cm^{-1}) prism grating spectrophotometers.

Spectra in the potassium bromide region were obtained either as thin liquid films (in the case of low melting compounds) or as Nujol mulls, between KBr plates.

For spectra in the caesium iodide region, the thin liquid films or mulls were supported between two sheets of one tenth mm. thick polyethylene clamped in a cell (Nujol cell) to give an air-tight seal.

Reactions

Most of the reactions were carried out in a Schlenk or in a two-necked round-bottomed flask in an atmosphere of dry nitrogen.

Reaction between tetrasulphur tetranitride and metal halides:

Tin tetrabromide

$SnBr_4$ (1.2 g.) was dissolved in dry hexane or heptane (40 ml) at room temperature and S_4N_4 (1.0 g.) was added to the solution.

The reaction mixture was stirred for 48-60 hours. The reaction was slow and no immediate colour change was observed. After ~12-14 hours, the colour of the solution turned reddish brown, finally a deep brown precipitate was obtained, and no further change in the colour of the product was observed after about 48 hours. The precipitate was filtered, washed in hexane (20 ml) and dried in vacuo. The adduct is insoluble in CCl_4, CH_2Cl_2, Et_2O, CS_2. Found: S = 31.8; N = 13.65; Br = 39.0. $SnBr_4.2S_4N_4$ requires: S = 31.73; N = 13.65; Br = 39.61%. M.P. 198-200°C (decomposition). The compound gradually changed to a yellow product upon exposure to air. The infrared spectrum of the sample exposed to air after several days (30-40) was similar to the i.r. spectrum of S_4N_4, with additional peaks at 1400 cm^{-1}, 3194 cm^{-1} probably due to the hydrolysis product of the halide.

Tin tetrachloride[52,53]

Tetrasulphur tetranitride (0.92 g) was dissolved in CCl_4 (50 ml) and tin tetrachloride (1.3 g) added dropwise at room temperature. A deep red precipitate of $SnCl_4.2S_4N_4$ was formed immediately. The compound was filtered, and purified by washing in CCl_4 and pumped dry at room temperature. M.P. 200°C (decomp.) The adduct is insoluble in CCl_4, CH_2Cl_2, Et_2O, CS_2. Found, Cl = 22.54; $SnCl_4.2S_4N_4$ requires: Cl = 22.57.

Tin tetrafluoride:

Attempts were made to prepare the adduct of SnF_4. In one experiment tin tetrafluoride (1.0 g) was suspended in 30 ml of acetonitrile and S_4N_4 (1.0 g) was added, the solution was refluxed for 24 hours, while in an another experiment, SnF_4 (0.7 g) was held in 40 ml of dry T.H.F. and S_4N_4 (0.7 g) was added, the mixture was refluxed for 14 hours. No colour change or other change in appearance was noted. The i.r. spectra of the products showed only unchanged starting materials.

Tin tetraiodide:

(a) SnI_4 (1.9 g) was dissolved in dry chloroform (40 ml) and S_4N_4 (1.1 g) in 25 ml of hot dry chloroform was added in portions, no immediate reaction was observed. The solution was stirred for 24 hours. No change in appearance was observed; the spectrum of the evaporated solution showed only S_4N_4.

(b) SnI_4 (1.5 g) was dissolved in CS_2 (30 ml) and S_4N_4 (0.9 g) in CS_2 (40 ml) was added at room temperature. The solution was stirred for 24 hours and concentrated to a small volume. No reaction was found to take place.

Stannous chloride

Tetrasulphur tetranitride (1.0 g) was suspended in ether (40 ml) and $SnCl_2$ (1.0 g) added at room temperature. The reaction mixture was stirred for 48 hours. No obvious reaction was observed.

Germanium tetrachloride

Following attempts were made to study the reaction between $GeCl_4$ and S_4N_4.

(a) Tetrasulphur tetranitride (1.2 g) was suspended in CCl_4 and $GeCl_4$ (2 ml) added at room temperature. The solution was stirred for 24 hours. No reaction was found to take place.

(b) $GeCl_4$ (10 ml) was added to S_4N_4 (1.0 g) at room temperature and the reaction mixture was stirred for 30 hours. Since there was no obvious reaction, the reaction temperature was raised to 75°C and stirring was continued for 4 hours. No colour change or other change in appearance was noted. The infrared spectrum of the evaporated solution showed only unchanged starting materials.

Silicon tetrachloride

Tetrasulphur tetranitride (1.0 g) was taken in a Schlenk and $SiCl_4$ (10 ml) added at room temperature. The reaction mixture was stirred for 48 hours. The infrared spectrum of the evaporated solution showed only unchanged starting materials.

Selenium tetrachloride

$SeCl_4$ (1.1 g) was suspended in benzene or toluene (20 ml) and tetrasulphur tetranitride added to the solution at 0°C. The solution was stirred for 24 hours. The reaction was vigorous initially and a bright yellow precipitate was obtained at the end of the reaction after 24 hours. The precipitate was filtered,

washed in benzene (15 ml) and dried in vacuo. Found: Se=20.60, S=28.71, N=13.88, Cl=34.61; $SeCl_4.S_4N_4$ requires; Se=19.54; S=31.60, N=13.83, Cl=34.99. M.P. 127-129°C. The compound is insoluble in CCl_4, $CHCl_3$. It turns red upon exposure to air.

Tellurium tetrachloride

Tetrasulphur tetranitride (0.46 g) was dissolved in toluene (20 ml) and tellurium tetrachloride (0.73 g) in toluene (10 ml) added at room temperature. An immediate deep red precipitate was formed and filtered off. The compound was washed in toluene and dried by pumping at room temperature. Found: S= 28.75, N =12.45; Cl = 31.60; $TeCl_4.S_4N_4$ requires: S= 28.26; N= 12.35; Cl= 31.25. M.P. 140°C. The compound is insoluble in CCl_4, CH_2Cl_2, CS_2, Et_2O. The adduct changes to a yellow product giving probably tetrasulphur tetranitride and the hydrolysis product of the halide.

Tellurium tetrafluoride

The reaction was carried out in a two-necked 100 ml round-bottomed flask. Tellurium tetrafluoride (0.4 g) was dissolved in dry acetonitrile (45 ml) at room temperature and tetrasulphur tetranitride (0.36 g) added to the above solution. No immediate colour change was observed. The solution was refluxed for 72 hours and a deep red solution was obtained. The solution was concentrated to a small volume (10 ml) and a bright deep red precipitate was

obtained. The precipitate was filtered, washed in acetonitrile and dried in vacuo. When dry the compound was brownish-orange in colour. Found: N=15.24, $TeF_4.S_4N_4$ requires, N=14.44. M.P. 92°C. There was insufficient sample for further analysis. The adduct changes to a yellow compound upon exposure to air.

Tellurium tetraiodide

TeI_4 (1.0 g) and tetrasulphur tetranitride (0.29 g) in ether (40 ml) were shaken together for about a week. No reaction was found to take place, probably due to the insolubility of tellurium tetraiodide in ether. Methylene dichloride was also used as a solvent to study the reaction, but no reaction was observed.

Titanium tetrabromide

$TiBr_4$ (2.0 g) was dissolved in 30 ml of dry methylene dichloride (or o-dichlorobenzene or ether) and tetrasulphur tetranitride (0.67 g) added at room temperature. Immediately a reddish brown precipitate was formed. The solution was stirred for 10 hours. The deep brown precipitate was filtered, washed in methylene dichloride and pumped dry at room temperature. Found: S=22.1, N=10.34, Br=59.1; $TiBr_4.S_4N_4$ requires; S=23.2, N=10.15, Br=57.34. M.P. 138°C. It is insoluble in CCl_4, CH_2Cl_2. When exposed to air, it turns yellow giving probably tetrasulphur tetranitride and the hydrolysis product of the halide.

Titanium tetrachloride[52,53]

Tetrasulphur tetranitride (0.92 g) was dissolved in carbon tetrachloride (40 ml) and titanium tetrachloride (0.81 g) added at room temperature. An immediate yellow-orange precipitate of $S_4N_4.TiCl_4$ was obtained and filtered from the solution. The product was washed in CCl_4 and pumped dry. M.P. 135° (decomp.) It is insoluble in CCl_4, CH_2Cl_2.

Titanium tetrafluoride

Attempts to prepare the adduct of TiF_4 using the solvents acetonitrile, T.H.F., CH_2Cl_2 were unsuccessful. Methylene dichloride was found to be the most suitable solvent. (i) TiF_4 (1.0 g) was refluxed with 30 ml of dry acetonitrile for 24 hours and filtered, to the filtrate was added tetrasulphur tetranitride (0.2 g) in acetonitrile (20 ml) at room temperature. The solution was stirred for 12 hours. The infrared spectrum of the evaporated product showed only unchanged starting materials. (ii) TiF_4 (1.0 g) was suspended in acetonitrile and S_4N_4 (0.2 g) added to the solution. The reaction mixture was refluxed for 48 hours at 92°C. No obvious reaction was observed. (iii) TiF_4 (1.1 g) was refluxed with T.H.F. (70 ml) and tetrasulphur tetranitride (0.2 g) added at room temperature. The solution was stirred for 12 hours. No reaction was found to take place.

(iv) TiF_4 (1.5 g) was suspended in methylene dichloride and tetrasulphur tetranitride (0.75 g) added at room temperature. No immediate reaction was observed. The reaction mixture was stirred for 48 hours. A deep red precipitate was slowly formed. The compound was filtered, washed in CH_2Cl_2 and pumped dry at room temperature. When dry the adduct was orange in colour. Found: S=17.90, N=7.81, F=46.60; $S_4N_4TiF_4$ requires: S=18.83, N=8.24, F=44.70, M.P. decomposed above 120°C. It is insoluble in CH_2Cl_2, CS_2. The adduct changes to a yellow product upon exposure to air.

Titanium tetraiodide

TiI_4 (1.0 g) was dissolved in 40 ml of dry CCl_4 (or CH_2Cl_2 or CS_2) and tetrasulphur tetranitride (0.25 g) added at room temperature. The solution was stirred for 48 hours and a black precipitate was obtained. The compound was filtered, washed in CCl_4 and dried in vacuo. Found: S=17.05, N=8.74, I=68.70, $TiI_4 \cdot S_4N_4$ requires, S=17.30, N=7.58, I=68.61. M.P. decomposition above 100°C. The compound is insoluble in CCl_4, CH_2Cl_2, CS_2. It changed to a yellow product when exposed to air.

Zirconium tetrachloride

$ZrCl_4$ (0.8 g) was suspended in CCl_4 (30 ml) and tetrasulphur tetranitride (0.63 g) added at room temperature. Immediately the solution turned red. The solution was stirred for 12 hours and a deep reddish-orange precipitate was obtained. The compound was

filtered, washed in CCl_4 and dried in vacuo. Found: S=29.55, N=12.80, Cl=33.10, $ZrCl_4.S_4N_4$ requires: S=30.67, N=13.42, Cl=33.99. M.P. 260°C (decomp.) It is insoluble in CH_2Cl_2, CS_2. The adduct changed to a yellow product when exposed to air.

Zirconium tetrafluoride

ZrF_4 (0.5 g) was suspended in dry methylene dichloride (or o-dichlorobenzene) at room temperature and S_4N_4 (0.54 g) added to the solution. The solution was stirred for 48 hours. No reaction was found to take place.

Hafnium tetrachloride

$HfCl_4$ (1.9 g) was suspended in CCl_4 (25 ml) and tetrasulphur tetranitride added at room temperature. The reaction mixture was stirred for 24 hours and a bright deep red compound was obtained. The precipitate was filtered, washed in CCl_4 and dried in vacuo. Found: S=25.41, N=10.35, Cl=29.90; $S_4N_4.HfCl_4$ requires: S=25.37, N=11.10, Cl=28.14. M.P. decomposition above 140°C. It is insoluble in CH_2Cl_2. The adduct gave a yellow product when exposed to air.

Antimony pentachloride

Antimony pentachloride (1.0 ml) was dissolved in CCl_4 (20 ml) and a solution of S_4N_4 (0.92 g) in CCl_4 (40 ml) added at room temperature. The solution was stirred for 14 hours. A deep red precipitate was obtained. The precipitate was filtered, washed in

CCl_4 and pumped dry at room temperature. (Obtained for spectrum only; no analyses)

Antimony pentafluoride

SbF_5 (1.9 g) was suspended in 25 ml of CH_2Cl_2 and S_4N_4 (0.4 g) added at room temperature. The solution was stirred for 14 hours and a green precipitate was obtained. The precipitate was filtered, washed in CH_2Cl_2 and dried in vacuo. Found: F, 38.15, N, 5.14; S=11.87; $S_4N_4.4SbF_5$ requires: F, 36.16; N, 5.33; S=12.18. M.P. 145°C (decomp.)

Niobium pentachloride

$NbCl_5$ (2.2 g) was suspended in CCl_4 or CH_2Cl_2 (35 ml) and S_4N_4 (1.4 g) added at room temperature. The solution was stirred for 12 hours and a reddish-brown precipitate was formed. The precipitate was filtered, washed in CCl_4 and dried in vacuo. The adduct was recrystallised from methylene dichloride. Found: S=27.15, N=12.68, Cl=39.50; $S_4N_4.NbCl_5$ requires: S=28.17, N=12.32, Cl=39.06. M.P. 106°C. The adduct is soluble in CH_2Cl_2, CS_2. It changed to a yellow product in air.

Niobium pentafluoride

NbF_5 (1.35 g) was suspended in 40 ml of dry methylene dichloride and S_4N_4 (0.2 g) was added at room temperature. Immediately a deep red solution and a pinkish-white precipitate was obtained. The solution was stirred for 24 hours. The deep red solution was filtered and evaporated to a small volume (10 ml). A deep red-orange

precipitate was filtered, washed in CH_2Cl_2 (5 ml) and vacuum dried. Found: N = 14.35; $S_4N_4.NbF_5$ requires: N = 15.04. M.P. decomp. above 60°C. The adduct changed to a yellow product in moist air. The infrared spectrum of the pinkish-white precipitate showed peaks (at 3030 and 1612 cm^{-1}) due to -OH indicating presence of partially hydrolysed NbF_5.

Tantalum pentachloride

$TaCl_5$ (2.5 g) was suspended in CCl_4 or CH_2Cl_2 (40 ml) and tetrasulphur tetranitride (1.2 g) added at room temperature. Immediately a red precipitate was formed. The solution was stirred for 14 hours and a deep red compound was obtained. The compound was filtered and dried in vacuo and recrystallised from dry methylene dichloride. Found: S=23.40, N=10.88, Cl=33.20; $S_4N_4TaCl_5$ requires: S=23.59, N=10.32, Cl=32.72. M.P. 132°C (decomp). It changes to a yellow product in air. The adduct is soluble in CCl_4, CH_2Cl_2, CS_2. The solubility of $S_4N_4.TaCl_5$ in CH_2Cl_2 is Ca. 0. 8g/100 ml.

Tantalum pentafluoride

TaF_5 (1.0 g) was suspended in 70 ml of dry CH_2Cl_2 and tetrasulphur tetranitride (0.15 g) added at room temperature. The solution was stirred for 48 hours, a deep red solution and a white precipitate was obtained. The solution was filtered, the filtrate was evaporated to a small volume (10 ml) and a deep

bright red precipitate was obtained. The precipitate was filtered and washed in CH_2Cl_2 (5 ml) and pumped dry at room temperature. Found: S=26.59, N=12.24; $S_4N_4.TaF_5$ requires: S=27.81, N=12.17. The compound changed to a yellow product when exposed to air.

Tungsten hexachloride

WCl_6 (2.0 g) was suspended in CCl_4 (40 ml) and S_4N_4 (0.72 g) added at room temperature. Immediately a dark-brown precipitate was formed. The solution was stirred for 24 hours. The precipitate was filtered, washed in CCl_4 and pumped dry at room temperature. (Obtained for spectum only; no analyses).

Tungsten hexabromide

WBr_6 (1.2 g) was dissolved in carbon disulphide at room temperature and S_4N_4 (0.4 g) added to the solution. Immediately a dark-brown precipitate was formed. The solution was stirred for 48 hours. The dark-brown precipitate was filtered, washed in CS_2 and dried in vacuo at room temperature. Found: S=17.85, N=8.08, Br=44.5. $S_4N_4.WBr_4$ requires, S, 18.61, N=8.14, Br, 46.48. M.P. 251^{o}C.

Tungsten oxytetrachloride

$WOCl_4$ (0.2 g) was dissolved in dry benzene (20 ml) and S_4N_4 (0.1 g) added at room temperature. A dark-brown precipitate was immediately formed. The solution was stirred for 10 hours. The precipitate was filtered, washed in benzene and pumped dry.

Since the infrared spectrum of the compound was similar to that of $WBr_4.S_4N_4$, this compound is probably $WOCl_4.S_4N_4$. There was insufficient compound for analyses and other investigations.

Vanadium oxytrichloride

1 ml of $VOCl_3$ was dissolved in 20 ml of dry ether and S_4N_4 (1.8 g) added at room temperature. Immediately a dark brown precipitate was formed. The solution was stirred for 14 hours and the precipitate was filtered, washed in ether and dried in vacuo. Since the infrared spectrum of the product showed some hydrolysis of the compound, the compound was not investigated further.

Vanadium trichloride

VCl_3 (1.0 g) and tetrasulphur tetranitride in 40 ml of dry ether were shaken together for several hours at room temperature. No reaction was observed.

Aluminium tribromide

The reaction was studied in CCl_4, toluene, CS_2 and $CHBr_3$. Carbon disulphide and bromoform were found to be suitable solvents.

(i) $AlBr_3$ (1.2 g) was dissolved in CCl_4 or toluene (25 ml) and tetrasulphur tetranitride (0.4 g) added at room temperature. Immediately a dark-red solution was obtained. The solution was stirred for 14 hours and a black sticky mass was obtained. The reaction was not studied further.

(ii) $AlBr_3$ (1.5 g) was dissolved in carbon disulphide or bromoform (20 ml) and tetrasulphur tetranitride (0.51 g) added at room temperature. Immediately a red solution was obtained. The solution was stirred for 24 hours and an orange-brown compound was obtained. The compound was filtered, washed in CS_2 and vacuum dried at room temperature. Found: S=16.04, N=6.97, Br=68.74, $S_4N_4.2AlBr_3$ requires; S=17.83, N=7.80, Br=66.81. M.P. 144°C. The compound is slightly soluble in CS_2. It changed to a yellow product upon exposure to air.

Aluminium trichloride

$AlCl_3$ (1.9 g) was dissolved in 35 ml of carbon disulphide (or CCl_4) and tetrasulphur tetranitride (1.3 g) added at room temperature. A deep red solution was formed immediately. The solution was stirred for 14 hours and a deep red precipitate was obtained. The compound was filtered, washed in CS_2 and dried in vacuo. The adduct was recrystallised from CH_2Cl_2. Found: S, 29.45, N, 12.41; $S_4N_4.2AlCl_3$ requires: S=28.38, N=12.41, Cl=48.60; Cl=47.25. M.P. 89°C (decomp.) It changed to a yellow product in air.

Gallium trichloride

(i) $GaCl_3$ (1.05 g) was dissolved in CCl_4 or pentane (20 ml) and tetrasulphur tetranitride (0.55 g) added at room temperature. A sticky dark-red precipitate was immediately obtained. The solution was stirred for 10 hours and filtered. The product

was pumped dry. The reaction was not studied further since the oily product was difficult to handle.

(ii) $GaCl_3$ (1.0 g) was dissolved in carbon disulphide (15 ml) and tetrasulphur tetranitride (0.5 g) added at room temperature. Immediately a deep red precipitate was obtained. The solution was stirred for 24 hours. The deep red precipitate was filtered, washed in CS_2 and vacuum dried at room temperature. Found: S=23.48, N=11.22, Cl=37.89, $S_4N_4.2GaCl_3$ requires, S=23.87, N=10.44, Cl=39.71. M.P. 100°C (decomp.) It is soluble in CS_2. It changes to a yellow compound in air.

Indium trichloride

$InCl_3$ (0.8 g) was suspended in methylene dichloride (20 ml) and tetrasulphur tetranitride (0.33 g) added at room temperature. No immediate reaction was observed. The solution was stirred for 48 hours. A deep reddish-brown precipitate was slowly formed. The compound was filtered, wa shed in CH_2Cl_2 and dried in vacuo at room temperature. Found: S=20.30, N=9.33, Cl=34.99; $S_4N_4.2InCl_3$ requires; S=20.42, N=8.94, Cl=33.99. M.P. decomp. above 100°C. It changed to a yellow product when exposed to air. It is slightly soluble in methylene dichloride.

Thallium trichloride

$TlCl_3$ (0.4 g) was suspended in dry acetonitrile (25 ml) and chlorine gas (dried over P_2O_5) was passed through the solution till

all the thallous chloride was dissolved and a clear solution was obtained. Excess of chlorine was removed by flushing out with dry nitrogen and by condensing it at -196°C. Tetrasulphur tetranitride (0.15 g) was then added to the above solution at room temperature. After about 10-15 minutes an orange-yellow solution was obtained. The solution was stirred for 14 hours and a pale yellow solution was formed. The acetonitrile was removed by pumping at room temperature and a red oily compound was obtained. Since the infrared spectrum of the compound was similar to the I.R. spectra of $S_4N_4.2InCl_3$, $S_4N_4.2GaCl_3$ this compound may well be $S_4N_4.2TlCl_3$. The compound was soluble in CH_2Cl_2. There was not enough material for further investigations.

Iron (III) chloride

$FeCl_3$ (2.2 g) was suspended in 40 ml of dry CCl_4 and tetrasulphur tetranitride (1.2 g) added at room temperature. There was no immediate reaction. The solution was stirred for 48 hours. A brown-black precipitate was obtained. The precipitate was filtered, washed in CCl_4 and pumped dry at room temperature. The compound is soluble in CS_2 and CH_2Cl_2 and recrystallised from CH_2Cl_2 and a deep red-brown adduct was obtained. Found: S,24.31, N,10.5; Cl,43.72; $S_4N_4.2FeCl_3$ requires: S=25.16, N=11.01, Cl=41.87. M.P. 80°C (decomp.) It changes to a yellow product in air.

Reaction between tetrasulphur tetranitride and phenylboron dichloride

Tetrasulphur tetranitride (0.4 g) was dissolved in dry CCl_4 (20 ml) and phenylboron dichloride (0.3 ml) added at room temperature. Immediately an orange-red precipitate was obtained. The solution was stirred for 6 hours and a brownish-orange precipitate was obtained. The precipitate was filtered, washed in CCl_4 and pumped dry at room temperature. Found: S=35.10, N=15.75, C=19.92, Cl=21.30, H=1.33; $S_4N_4.PhBCl_2$ requires, S=37.30, N=16.32, C=20.98, H=1.46, Cl=20.69. M.P. 99-102°C. The compound changed to a yellow product when exposed to air. The i.r. spectrum of the product exposed to air for 48 hours indicated the presence of S_4N_4 and probably phenylboron dichloride hydrolysis products.

Reaction between tetrasulphur tetranitride and p-tolytin trichloride

0.7 ml (1.2 g) of p-tolytin trichloride was dissolved in dry CCl_4 (30 ml) and tetrasulphur tetranitride (0.4 g) added at room temperature. No immediate colour change was observed. The solution was stirred for 60 hours. A deep red precipitate was slowly formed and filtered. The precipitate was washed in CCl_4 and dried in vacuo. The infrared spectrum of the compound was identical to the infrared spectrum of $S_nCl_4.2S_4N_4$. Found: S=38.60, N=17.90, Cl=12.75, $SnCl_4.2S_4N_4$ requires; S=40.73, N=17.80, Cl=22.57. The p-Tolytin trichloride had undergone disproportionation in the presence of S_4N_4 giving $SnCl_4.2S_4N_4$ and tetra-p-tolyltin.

Reaction between trimethyl aluminium and tetrasulphur tetranitride

The reaction was carried out in dry hexane. Tetrasulphur tetranitride (1.9 g) was suspended in 25 ml of dry CCl_4 and the solution was cooled to -196°C. Trimethyl aluminium (1 ml, 0.75 g) added to the above solution. The solution was slowly warmed to room temperature and stirred for 24 hours. No visible change occurred and the unreacted yellow precipitate of S_4N_4 was recovered by filtration.

Reaction between phenylmercuric chloride and tetrasulphur tetranitride

Phenylmercuric chloride (1.0 g) and S_4N_4 (0.58 g) were shaken together in 40 ml of dry ether for 14 hours. No reaction was observed.

Reaction between tetrasulphur tetranitride and sulphuryl chloride

Tetrasulphur tetranitride (0.49 g) was suspended in 30 ml of dry toluene at -196°C. Sulphuryl chloride (1.0 ml) added under a current of dry nitrogen gas. The reaction mixture was slowly warmed to room temperature, but no obvious reaction was observed. The solution was stirred for 16 hours, the infrared spectrum of the evaporated product showed the unchanged starting material.

In another experiment the reaction was carried out in the absence of the solvent at room temperature (see page 48), and trithiazyl trichloride was obtained. Found: S = 39.4; N=17.60;

Cl= 43.40; mol.wt (cryoscopic in benzene) 244; $S_3N_3Cl_3$ requires S=39.31; N=17.16; Cl=43.45; mol.wt. = 244.57. $S_3N_3Cl_3$ probably gives NSCl on pumping, since the $S_3N_3Cl_3$ in the flask turned slightly green under vacuum. It forms ammonium chloride and SO_2 in moist air ($2S_3N_3Cl_3 + 12H_2O \rightarrow 6NH_4Cl + 6\ SO_2$)

Reaction between tetrasulphur tetranitride and chlorine

(a) 1.5 g of finely powdered tetrasulphur tetranitride was suspended in dry CCl_4 (20 ml) and chlorine gas (dried over P_2O_5) was carefully passed through the solution at room temperature for about 5 minutes until all the S_4N_4 was dissolved and a clear red solution was obtained. Excess of chlorine gas was removed by flushing out with dry nitrogen gas and condensing it at -196°C. The red solution was cooled to -16°C using cold refrigerator and bright red crystals were obtained. The precipitate was filtered and pumped dry at room temperature. The compound was recrystallised from dry CCl_4. Found: S=37.54, N=17.82, Cl=43.30; $S_3N_3Cl_3$ requires, S=39.36, N=17.16, Cl=43.45. M.P. 89-91°C. The compound turns white in moist air (cf. S_4N_4/SO_2Cl_2 product but contrast product obtained with a fast flow of chlorine (see (b) below). The filtrate was evaporated to dryness and more $S_3N_3Cl_3$ was obtained.

(b) Tetrasulphur tetranitride (1.5 g) was suspended in CCl_4 (20 ml) at room temperature and dry chlorine gas was passed at a very fast

rate through the solution. First after 2-3 minutes a red solution was obtained, the bubbling of chlorine gas was continued and a yellow precipitate came out of the solution after 10 minutes. The flow of chlorine gas was stopped after 4½ hours. The yellow precipitate was filtered and vacuum dried at room temperature. The compound was recrystallised from dry CCl_4. Found: (before recrystallisation), S=36.80, N=21.90, Cl=27.60 (2nd. 29.46); (recrystallised compound), S=45.70, N=23.60, Cl=26.90. M.P.58-64°C(decomp.) (repeat preparation), S=43.79, N=19.59, Cl=36.90. $S_6N_6Cl_3$ requires: S=50.19, N=21.90, Cl=27.84; $S_6N_6Cl_4$ requires: S=45.93, N=20.10, Cl=33.91. The compound changed to a yellow-black compound in moist air. I.R. spectrum of the black yellow compound exposed to air for 48 hours exhibited peaks mainly due to S_4N_4 and -OH. The infrared spectrum of $S_6N_6Cl_4$ showed the following peaks: 1011 vs, 948 ms(sh), 899 (sh), 780 ms, 699 s(sh), 686 vs, 670 vw(sh), 662 vs, 627 vw(sh), 577 s, 546 vs, 517 w(sh), 504 ms, (452 s).

(c) Tetrasulphur tetranitride was dissolved in dry CCl_4 (50 ml) and dry chlorine gas was bubbled through the solution at a very slow rate at room temperature for about 3 hours and a red solution was obtained. The solution was evaporated to a small volume (20 ml) by pumping and cooled to -16°C. A bright yellow crystalline compound was obtained. Found: Cl=42.90, $S_3N_3Cl_3$ requires; Cl=43.45. M.P. 82-85°C.

Reaction between tetrasulphur tetranitride and bromine

The reaction was carried out in an atmosphere of dry nitrogen gas in a 50 ml two-necked round-bottomed flask. Bromine (20 ml) dried over phosphorus pentoxide was condensed on tetrasulphur tetranitride (1.0 g) at -196°C and the reaction flask was warmed to room temperature. Carbon disulphide (20 ml) was then added to the above solution and the liquid was stirred for 14 hours at room temperature. A deep reddish-brown precipitate was slowly formed. The excess of solvent and bromine was removed by pumping at room temperature and a deep red-brown precipitate was obtained. Found: S=26.40, N=11.50, Br=66.10; $(NSBr)_n$ requires: S=25.41, N=11.19, Br=63.45. Mol.Wt. The compound was insoluble in CS_2. It is moisture sensitive. M.P. 121°C. Infrared absorptions occur at: 1169 vs, 1010 vs, 675 vs, 609 w, 574 vw (sh), 562 s, 537 w, 492 vs.

Reaction between $S_3N_3Cl_3$ and bromine

Dry bromine 15 ml was condensed in 1.0 g of $S_3N_3Cl_3$ in a two-necked round-bottomed flask and the solution was stirred for 6 hours at room temperature. Excess of bromine was removed by pumping and a yellow compound was obtained. The compound was found to contain chlorine and bromine. The reaction was not investigated further. Infrared absorptions occur at: 1100 s, 1018 s, 959vw, 763 vw, 724 w, 621 vw, 534 vs, 515 vvw(sh).

Reactions of trithiazyl trichloride

In all the reactions studied, $S_3N_3Cl_3$ prepared from S_4N_4 and SO_2Cl_2 was used as the starting material.

Reaction between trithiazyl trichloride and chlorine

$S_3N_3Cl_3$ (0.7 g) was dissolved in CCl_4 (25 ml) at room temperature and dry chlorine gas passed for 2 hours through the solution. The solution was cooled to $-16^{o}C$ and a yellow-white precipitate was obtained, filtered and dried in vacuo. The infrared spectrum of the compound showed that $S_3N_3Cl_3$ had undergone no change.

Attempted preparation of S_3N_3Cl

$S_3N_3Cl_3$ (0.89 g) was dissolved in 20 ml of dry methylene dichloride at room temperature and tetrasulphur tetranitride (1.0 g) added to the solution. (No immediate reaction was observed). The solution was stirred for 12 hours and cooled to $-16^{o}C$. A yellow precipitate was obtained. The precipitate was filtered and dried in vacuo. I.R. spectrum showed that the compound was S_4N_4.

The filtrate was evaporated to dryness and the infrared spectrum of the yellow product indicating that it was a mixture of S_4N_4 and trithiazyl trichloride.

Attempted oxidation of trithiazyl trichloride

Attempts were made to prepare sulphanuric chloride ($S_3N_3O_3Cl_3$) by the oxidation of trithiazyl trichloride using selenium dioxide, iodine pentoxide and ozone as the oxidising agents.

(a) Attempted oxidation of $S_3N_3Cl_3$ using SeO_2

Trithiazyl trichloride (1.0 g) was dissolved in dry CCl_4 (30 ml) and selenium dioxide (0.79 g) added at room temperature. The solution was stirred for 1-2 hours. Since there was no obvious reaction, the solution was refluxed for 6 hours. A red solution and a pinkish-white precipitate was obtained. The solution was filtered and evaporated to dryness. A crude red product was obtained. I.R. spectra of the pinkish-white precipitate (SeO_2) and the crude red product indicated that no sulphanuric chloride was formed. The reaction was not studied further.

(b) Attempted oxidation of $S_3N_3Cl_3$ using I_2O_5

$S_3N_3Cl_3$ (0.5 g) was dissolved in 25 ml of dry CCl_4 and iodine pentoxide (0.5 g) added at room temperature. The solution was stirred for 1 hour but no reaction was seen to take place. The solution was refluxed for 24 hours and a pink-white precipitate and a brown-coloured solution were obtained. The solution was filtered and evaporated to dryness and a brown precipitate was obtained. The i.r. spectrum of the pink-white precipitate showed that the compound was a mixture of I_2O_5 and silicone grease, whereas the i.r. spectrum of the brown precipitate indicated that no sulphanuric chloride was formed. The product was not investigated further.

(c) Attempted oxidation of $S_3N_3Cl_3$ using Ozone

(i) Trithiazyl trichloride (2.0 g) was dissolved in dry CCl_4 (50 ml) and ozone-oxygen mixture (dried over P_2O_5) was bubbled through the solution at very slow rate at $-10^{o}C$. The flow of ozone was discontinued after 48 hours. The solution was evaporated to dryness and a white-yellow precipitate was obtained. I.R. spectrum of the compound showed that $S_3N_3Cl_3$ had undergone no change.

(ii) Trithiazyl trichloride (2.0 g) was dissolved in 50 ml of dry CCl_4 and ozone-oxygen mixture was passed through the solution at $60^{o}C$ at slow rate for 24 hours. The i.r. spectrum of product showed that $S_3N_3Cl_3$ had undergone no change.

(iii) The oxidation was also carried out in the presence of MoO_3 as a catalyst as above, but no $S_3N_3O_3Cl_3$ formation was noticed.

Reaction between trithiazyl trichloride and pyridine

Trithiazyl trichloride (0.90 g) was taken in a 100 ml two-necked, round-bottomed flask and pyridine (o.9 ml) added at $0^{o}C$. The flask was slowly warmed to room temperature. The colour of the solution turned green after about 10 minutes, then changed to a pale yellow and finally a red oily thick pasty mass was obtained. Dry pentane (25 ml) was added to the oily mass and the solution was stirred for 12÷14 hours at room temperature. A

yellow-brown precipitate was obtained, filtered, washed in pentane and dried in vacuo. Found: C=31.05, H=3.66, N=15.00, S=17.20, Cl=29.0, $S_3N_3Cl_3$.2py requires; C=29.81, H=2.46, N=17.39, S=23.85, Cl=26.46, ($S_3N_3Cl_3$.3py requires; C=37.38, H=3.12, N=17.45, S=19.94, Cl=22.12. Reaction probably needs to be repeated and stopped at pale yellow stage. Infrared spectrum showed peaks at: 1259 vw, 1226 vw, 1180 w, 1122 vvw (sh), 1104 w, 1068 ms, 1047 w(sh), 1022 ms, 1000 w, 961 vvw, (926 w) 841 vs, 779 vs, 758 vs, 743 vvw(sh), 722 vw(sh), 701 vvw, 679 vs, 666 vvw (sh), 660 vw(sh), 621 vs, 608 vw, 600 w, 560 vs, 542 s, 491 w, 454 vw.

Reaction between diphenyl mercury and trithiazyl trichloride

Trithiazyl trichloride (1.2 g) was dissolved in about 25 ml of dry benzene and diphenyl mercury (1.7 g) added at room temperature. Immediately a yellow-green precipitate came out of the solution, the solution turned green after about 5 minutes and after 3 hours a black precipitate was obtained. The solution was stirred for 12 hours. The black precipitate was filtered and the filtrate evaporated to dryness, no ppt was obtained. The black precipitate was washed in benzene and pumped dry at room temperature. Found: S 16.50, N=8.06, Cl=18.60, C=23.61, H=1.57; $S_3N_3Cl_3$.$(Ph)_2Hg$ requires; S=16.02, N=7.01, Cl=17.77, Cl=24.03, H=1.67. M.P. 170°C. It is insoluble

in methylene dichloride. Infrared absorptions occur at: 2198 ms, 1156 vw, 1064 vw(sh), 1047 vs, 1020 vvw, 990 vs, 916 vvw, 855 ms, 797 vvw, 646 vs, 722 vs, 685 vs, 660 ms(sh), 609 w, 571 ms, 531 vs, 508 vs, 465 w, 436 w, 431 vs, 408 ms(sh), 394 vs, 347 vs, 330 vw, (309 w, 279 s), (227 w, 211 w) cm^{-1}.

Reaction between trithiazyl trichloride and antimony trichloride in $SOCl_2$

$SbCl_3$ (0.7 g) was dissolved in thionyl chloride (20 ml) and trithiazyl trichloride (2.0 g) added at room temperature. Immediately a dark-brown solution was obtained. The solution was stirred for 12 hours and a dark-brown precipitate was obtained. The precipitate was filtered, the filtrate was evaporated to dryness and a crude dark oil product was obtained. The dark-brown precipitate was washed in $SOCl_2$ and a yellow-pale green precipitate was obtained. Found: S=23.10, N=6.76, Cl=48.70; $S_4N_3SbCl_9$ requires: S=22.25, N=7.3, Cl=49.30. Infrared absorptions occur at: 217 ms, 126 vw, 1193 w, 1149 vw, 1057 s, 1010 vs, 803 ms, 735 vvw(sh), 719 ms, 666 vvw, 626 ms, (450 ms) 418 w. cm^{-1}.

Reaction between trithiazyl trichloride and titanium tetrachloride in thionyl chloride.

Trithiazyl trichloride (0.5 g) was dissolved in thionyl-chloride (10 ml) and titanium tetrachloride (1 ml) added at room temperature. Immediately a deep red solution was obtained. The solution was stirred for 4 hours and a deep red precipitate was

obtained. The precipitate was filtered, washed in $SOCl_2$ and pumped dry at room temperature. Found: S=16.0, N=9.60, Cl=52.00, $Ti_2S_2N_3Cl_6$ requires, S=15.43, N=10.31, Cl=51.36. M.P. 70°C (decomp.) Infrared spectrum showed the following peaks: 1324 w, 1012 vs, 966 vs, 840 vs, 732 vs, 697 s, 662 s, 608 vs, (5000 vs) cm^{-1}.

Reaction between trithiazyl trichloride and antimony pentachloride in thionyl chloride

$S_3N_3Cl_3$ (0.2 g) was dissolved in 10 ml of $SOCl_2$ and $SbCl_5$ (1 ml) added at room temperature. Immediately a bright orange solution was obtained. The solution was stirred for 2-3 hours and excess of the liquid was removed by pumping at room temperature. The infrared spectrum of the compound was comparable to the infrared spectrum of $Ti_2S_2N_3Cl_6$. There was insufficient compound for further investigations. I.R. absorptions occur at: 1156 vw, 1117 ms, 1058 vs, 1017 vs, 866 ms, 722 ms, 687 s, 666 w, 619 w, 599 s, 555 w, 513 vs (454 s), 431 ms cm^{-1}.

Reaction between trithiazyl trichloride and epoxides

(i) Epichlorohydrin

Trithiazyl trichloride (2.0 g) was taken in a Schlenk and epichlorohydrin (15-16 ml) added at -196°C under a current of dry nitrogen gas. Vigorous reaction was observed and the reaction mixture was slowly warmed to room temperature. After 15-20 minutes a green solution was obtained which changed to a pale-yellow liquid after 1-2 hours. Finally a red liquid was obtained after 12-14 hours,

and there was no further colour change. Excess of epichlorohydrin was removed by pumping at room temperature and a red oil was obtained. The red oil changed to sticky mass after 2-3 days, dry hexane (10 ml) was added to it, and the solution was stirred for 12-14 hours. A reddish-brown solid was formed, the solid was washed in ethanol and fine powdery white compound was obtained. Found: S=18.68, N=8.3, C=20.70, H=2.78, Cl=40.60, $S_3N_3(O\text{-}CH_2\text{-}CH\text{-}Cl.CH_2.Cl)_3$ requires: S,18.65; N=8.26; C,20.3; H,2.87; Cl,40.90. Mol.wt. 521. M.P. 86-89°C. It is air stable. It is soluble in acetone, insoluble in EtOH,MeOH.

(ii) Epibromohydrin

Trithiazyl trichloride (0.90 g) was taken in a Schlenk and epibromohydrin (6 ml) added at room temperature. Immediately the solution turned green which slowly changed to a pale-yellow liquid after about an hour. The solution was stirred for 20-24 hours at room temperature and a red solution was obtained. Excess of epibromohydrin was removed by pumping, and a red oil was obtained. Dry pentane (10 ml) added to the above oil and the solution was stirred for an hour, pentane was removed by suction and a yellow-white precipitate was obtained. The precipitate was washed in ethanol and a fine powdery solid was formed and dried in vacuo at room temperature. Found: S=13.55, N=7.40, C=16.30, H=2.16, Br=38.30, Cl=14.96; S_3N_3 $(O\text{-}CH_2\text{-}CH\,Cl.CH_2Br)_3$ requires, S=14.65, N=6.41, C=16.48, H=2.23, Cl=16.25, Br=36.58. M.P.92-94°C, Mol.wt.in benzene 644; theory 655.34.
It is air stable.

Ethylene oxide

Trithiazyl trichloride (1.0 g) was placed in a Schlenk and ethylene oxide was condensed on it at -196°C. The reaction mixture was slowly warmed to room temperature. A green solution was obtained immediately which changed to a pale yellow liquid after 2 hours. The liquid was stirred and finally a red solution was obtained after 24 hours. The excess of ethylene oxide was removed by pumping at room temperature and a red oil was obtained. Dry hexane (10 ml) was added to the oil and the solution was stirred for 12 hours. Hexane was removed under suction and a red oil was left behind. Found: S=24.00, N=11.30, Cl=27.14, C=19.96, H=3.06, $(NSCl.O.CH_2CH_2)_3$ requires: S=25.48, N=11.15, Cl=28.27, C=19.2, H=3.18. Mol. wt. 376 in benzene. The red oil became dark red at 50-60°C, probably due to decomposition. It decomposed to a yellow product in air.

Butylene oxide

Trithiazyl trichloride (1.8 g) was placed in a Schlenk and about 10 ml of butylene oxide added at room temperature. Immediately the solution turned green and there was vigorous reaction after 5 minutes. The solution was stirred for 14 hours and a red liquid was obtained. The excess butylene oxide was removed by pumping and a red oily product was obtained. Found: S=20.2, N,9.55, Cl=22.70, C=31.33, H=5.11; $S_3N_3(O\text{-}CH_2\text{-}Cl.\text{-}CH_2\text{-}CH_3)_3$ requires, S,20.84, N,9.12, Cl=23.11, C=31.25 H=5.20. It decomposed to a yellow product in air.

Reaction between trithiazyl trichloride and phenyl acetylene

Trithiazyl trichloride (0.5 g) was cooled to -196°C and phenyl acetylene was condensed on it. The reaction flask was warmed to room temperature. There was a vigorous reaction initially and green, pale-yellow to red colour change was observed. A red oily sticky mass was obtained. The reaction was not investigated further.

Reaction between trithiazyl trichloride and diphenyl acetylene

Trithiazyl trichloride (1.45 g) was dissolved in dry CCl_4 (45 ml) and diphenyl acetylene (1.2 g) added at room temperature. The solution was stirred for 6 hours at room temperature, but no obvious reaction was observed. The solution was stirred for 18 hours at 42°C. The liquid was changed to a green colour and a yellow precipitate came out of the solution. The precipitate was filtered, evaporated to dryness and a mixture of a red oil and a yellow product was obtained. The precipitate was washed in methylene chloride and pumped dry at room temperature. The infrared spectrum of the compound was indentical with the i.r. of S_4N_3Cl. Found: Cl=17.38, S_4N_3Cl requires; Cl=17.24. The mixture of the red oil and the yellow compound was ignored.

Reaction between trithiazyl trichloride and carbon monoxide

Trithiazyl trichloride (2.0 g) was dissolved in dry CCl_4 (50 ml) at room temperature. Carbon monoxide was bubbled through the solution at a very slow rate at room temperature, for 48 hours. The solution was evaporated to dryness and a pale-yellow white precipitate was obtained. The i.r. spectrum indicated that $S_3N_3Cl_3$ had undergone no change.

In another experiment the reaction was carried out at higher temperature. Carbon monoxide was bubbled through a solution of trithiazyl trichloride (2.0 g) in 50 ml of dry CCl_4 at 40^oC for 60 hours. A yellow precipitate(2) came out of the solution and the colour of the solution was pale red. The precipitate(1) was filtered, the filtrate was evaporated to dryness and a yellow compound(2) was obtained. The i.r. spectrum of compound no.1 was similar to S_4N_3Cl while the i.r. spectrum of the compound no.2 was identical with the product obtained by passing chlorine vigorously through a solution of $S_3N_3Cl_3$ in CCl_4. (See page 72)

Reaction between trithiazyl trichloride and nitriles

Acetonitrile

$S_3N_3Cl_3$ (2.0 g) was placed in a Schlenk and 15 ml of dry acetonitrile added at room temperature. The solution was stirred for 12-14 hours at room temperature. The colour of the solution was changed to green, then to pale yellow and finally to red.

Excess of acetonitrile was removed by pumping at room temperature. A crude black mass was obtained. The reaction was not investigated further.

Propionitrile

Trithiazyl trichloride (2.5 g) was taken in a Schlenk and dry propionitrile (12-15 ml) added at room temperature. The solution was turned green after 5-10 minutes, which slowly changed to pale yellow. The solution was stirred for 12-14 hours and a red liquid was obtained. The liquid was pumped and a red sticky oil was obtained. The reaction was not studied further.

Isobutyronitrile

Dry isobutyronitrile (15 ml) was added to trithiazyl trichloride (1.8 g) in a Schlenk. There was no immediate reaction. The colour of the solution was changed to green, then to yellow and at the end, after 12-14 hours a red oil was obtained. The solution was pumped and a black crude mass was obtained. The reaction was not investigated further.

Tertiarybutyl cyanide

Dry tertiarybutyl cyanide (10 ml) was added to $S_3N_3Cl_3$ (1.8 g) at room temperature in a Schlenk. The solution was stirred for 24 hours and no obvious reaction was seen to take place. The reaction temperature was raised to 58°C and the solution was stirred for 10 hours. A very small amount of yellow precipitate (No.1) was formed and the colour of the solution was red.

The precipitate was filtered, filtrate was evaporated to dryness and golden yellow (No.2) precipitate was obtained (M.P. 240°C decomp.) The infrared spectrum of (No.1) precipitate was recorded, but there was insufficient sample of this compound for further investigations. The compound (No.2) was analysed twice. Found: 1st. analysis in this department. C = 28.90, H=3.79, Cl=33.10, S=31.85, N=11.37. 2nd. analysis (Weiler and Strauss). C=29.39, H=4.34, Cl=16.25, S=26.55, N=9.37. $S_2N_2Cl_2(CH_3)_3Cl$ requires, C=30.56, H=4.58, Cl=18.00, S=32.59, 14.26; $S_2N_2C_2(CH_3)_3Cl_2$ requires, C=25.86, H=3.88, Cl=30.60, S=27.58, N=12.04; $S_2N_3C_2(CH_3)_3Cl_2$ requires, C=24.39, H=3.66, Cl=28.86, S=26.02, N=17.07. The infrared spectrum of compound (No.1) showed the following peaks: 1227w, 1163 ms, 1000 s, 889 s, 858 s, 803 vw, (7335 s, 722 s), 680 s, 607 vw, 565 s, 554 s, 525 vw, 466 vs, 451 vw (sh). The infrared spectrum of compound (No.2) showed peaks at: 1667 w, 1399 vw (sh), 1368 vs (sh), 1274 w, 1222 s, 1087 w, 1019 w, 980 vw, 943 w, 909 w, 885 vs, 855 s, 803 ms, 733 s, 722 vvw (sh), 590 vvw, 551 vs, 522 vvw, 510 ms, 476 ms, 407 ms, 379 vw, 341 w, 308 w, 288 vw, 253 w, 226 w cm^{-1}.

Trichloroacetonitrile

$S_3N_3Cl_3$ (2.45 g) was placed in a Schlenk and dry trichloroacetonitrile (15 ml) added at room temperature. The reaction mixture was stirred for 24 hours at room temperature, and a yellow solution was

obtained. The liquid was evaporated to dryness and a pale yellow precipitate was obtained. The infrared spectrum of the precipitate indicated that $S_3N_3Cl_3$ had undergone no change.

In another experiment, trichloroacetonitrile (10 ml) was added to $S_3N_3Cl_3$ (2.5 g) at room temperature and the solution was stirred for 2-3 days at 60°C. The solution was changed to green after about 1 hour, then to pale yellow after about 2 hours, and finally a red solution and a yellow precipitate was obtained after 14 hours. The precipitate (No.1) was filtered, washed in trichloroacetonitrile (5 ml) and dried in vacuo. The filtrate was evaporated to dryness and a pale yellow precipitate (No.2) was obtained. The compound (No.1) was ignored because there was insufficient compound for further investigations. The compound (No.2) was analysed twice, in this department. Found: 1st analysis, C=9.59, Cl=55.89, S=24.75, N=11.60; 2nd. analysis, C=9.99, Cl=52.80, S=21.98, N=10.51. $S_2N_2C_2Cl_4$ requires; C=9.53, Cl=55.04, S=24.80, N=10.85; $S_2N_2C_2Cl_5$ requires, C=8.19, Cl=60.34, S=21.81, N=9.54; $S_2N_3C_2Cl_5$ requires, C=7.81, Cl=57.72, S=20.81, N=13.66.

The compound changed to a white product in moist air. M.P. decomp. above 110°C. Infrared absorptions occur at: 1299 vw, 1266 vw, 1047 vs, 930 ms, 909 vvw (sh), 855 vs, (813 w (sh), 794 vs), 760 s, 722 vvw, 676 vs, 543 vs, 535 ms (sh), 517 w, 495 vw (sh), 483 s, 471 w(sh), 406 ms, 376 vw, 347 ms, 246 s, 225 vw cm^{-1}.

Benzonitrile

Trithiazyl trichloride (3.0 g) was placed in a Schlenk and dry benzonitrile was (20 ml) added at room temperature. The solution was stirred, a green clear solution was obtained after 10-15 minutes, which slowly changed to a pale yellow liquid after 2 hours. The solution was concentrated to 10 ml and cooled to $0^{o}C$. A pale yellow precipitate was obtained. The infrared spectrum of the precipitate indicated that $S_3N_3Cl_3$ had undergone no change.

In another experiment the reaction was carried out in a Schlenk clamped in a slightly slanting position. Benzonitrile (25 ml) added to trithiazyl trichloride (3.0 g) at room temperature. The solution was stirred at $60^{o}C$. Immediately a green solution was formed, the solution turned yellow after 15 minutes. Stirring was continued and the solution was red after 4 hours. After 3-4 days a bright yellow precipitate (No.1) was settled down the red liquid and bright yellow-orange needles (No.2) collected near the frit of the Schlenk. The red solution was cooled to $-196^{o}C$ and the yellow-orange compound (No.2) pumped dry at room temperature. After removing the compound (No.2), the red solution was warmed to room temperature and the yellow precipitate was filtered, the red filtrate was chilled to $0^{o}C$ and fine yellow needles (No.3) came out of the solution. The

solution was transferred to a 50 ml two-necked round bottomed flask and precipitate (No.3) was filtered, the filtrate was vacuum evaporated to dryness and a dark yellow compound (No.4) was obtained. The compound (No.4) was recrystallised from dry CCl_4 or CH_2Cl_2. The compound (No.1) was dried under vacuo. Some of the compound (No.1) (about 0.5 g) was dissolved in about 20 ml of hot benzonitrile (60°C) and a red solution was obtained, filtered, chilled to 0°C and fine yellow needles (No.1 and same as No.3) were obtained. The infrared spectra of the compounds (No.1,2 and No.3) were identical and analyses showed that the two compounds are the same.

Compound (No.1)

Found: C=41.72, H=2.55, Cl=14.92, S=26.5, N=14.22;

$S_2N_2C_7H_5Cl$ requires: C=38.80, H=2.31, Cl=16.40, S=29.56, N=12.93.

Compound (No.2)

Found: C=32.10, H=1.58, Cl=20.48, S=30.56, N=14.68.

$S_2N_2Cl_2C_7H_5$ requires: C=31.6, H=1.89, Cl=26.64, S=24.09, N=15.79.

Compound (No.3)

Found: C=31.2, H=1.14, Cl=22.83, S=29.73, N=16.60.

Compound (No.4)

Found: C=23.42, H=1.12, Cl=28.10, S=24.15, N=16.33.

$S_3N_3Cl_3$.PhCN requires, C=24.18, H=1.45, Cl=30.59, S=27.67, N=16.11.

Infrared spectra showed the following peaks:

Compound (No.1) 1660 w, 1290 vw(sh), 1212 vw, 1170 vw, 1149 s, 1070 w, 1029 ms, 1000 vw, 935 vvw, 921 s, 892 vs, 834 vs, 794 s, 781 s, 767 s, 707 w(sh), 699 vs, 662 vw(sh), 548 vs, 515 ms. cm^{-1}.

Compound (No.2 and 3) 1600 w, 1350 vw (sh), 1299 vvw, 1266 vvw, 1212 vvw, 1176 vvw, 1155 s, 1074 w, 1031 ms, 1002 vw, 943 vvw, 926 s, 897 vs, 844 vs, 787 s, 699 vs, 664 vw, 549 vs. cm^{-1}.

Compound (No.4) 1590 ms, 1290 w (sh), 1179 s, 1093 w, 1065 w, 1022 ms, 998 vvw (sh), 910 vs, 870 vvw (sh), 842 vvw (sh), 791 vs, 662 ms, 615 vvw, 525 s, 493 vs, 473 s. cm^{-1}.

DISCUSSION

Tetrasulphur tetranitride adducts with Lewis acids

Tetrasulphur tetranitride reacts with many Lewis acids (e.g. metal halides and SO_3) to give compounds of a variety of empirical compositions. In inert organic solvents, adducts of 2:1, 1:1, 1:2, 1:4 (S_4N_4 : Lewis acid) stoichiometry have been prepared, in which the nitrogen of S_4N_4 is co-ordinated to the Lewis acid. In these adducts, the S_4N_4 ring undergoes a conformational change as a result of donation of electrons from nitrogen and consequent weakening of the sulphur-sulphur bond.

The aims of the research were, to further explore the reactions of S_4N_4 as a Lewis base, to study the effects of coordination upon the reactivity of the S_4N_4 ring and to gain more information about the structures of the products. It was also hoped to correlate the various properties previously noted of S_4N_4, and the structures of the adducts.

We found that tin tetrachloride and tetrabromide gave adducts in which S_4N_4 to metal halide ratio is 2:1; on the other hand, tin tetraiodide, silicon tetrachloride, germanium tetrachloride and stannous chloride, gave no adducts under the conditions studied. No suitable solvent was found (because of insolubility of SnF_4 in non-coordinating solvents) to study the reaction between S_4N_4 and tin tetrafluoride.

Titanium tetrabromide and tetraiodide, $ZrCl_4$, $HfCl_4$, $SeCl_4$, $TeCl_4$, TeF_4, $NbCl_5$, NbF_5, TaF_5 and $WOCl_4$ (?) gave adducts of 1:1 composition, whereas $AlCl_3$, $AlBr_3$, $GaCl_3$, $InCl_3$, $TlCl_3$ (?) and $FeCl_3$ gave products of 1:2 stoichiometry.

In the reaction of tungsten hexabromide with S_4N_4, the bromide was first reduced to WBr_4 and gave the adduct, S_4N_4. WBr_4 (analogous to the reaction of S_4N_4 and WCl_6 to give $S_4N_4.WCl_4$).

Phenylboron dichloride reacted with S_4N_4 to yield the adduct $S_4N_4.PhBCl_2$, whereas p-tolytin trichloride gave $SnCl_4.2S_4N_4$ due to the disproportion of the p-tolytin trichloride to $SnCl_4$ and tetra-p-tolytin. Further details are given in Table 1.

Tetrasulphur tetranitride adducts were generally prepared by mixing the solutions of S_4N_4 and Lewis acids in solvents of low polarity, usually under an atmosphere of dry nitrogen. The reaction mixtures were stirred and the coloured products were filtered and dried in vacuo. The reaction time was found to depend on the solubility of the Lewis acid. In those cases, where the Lewis acid was soluble in the solvent, the reaction time was from 1-10 hours (until there was no further change in the colour of the product), whereas, if the Lewis acid was only slightly soluble in the solvent, the procedure was to add S_4N_4 to the suspension of the Lewis acid in the solvent and stir the solution for 12-24 hours or longer.

TABLE 1 TETRASULPHUR TETRANITIDE ADDUCTS

Metal halide	Stochiometry (S_4N_4:m-halide)	Colour	M.P. ^oC.	Solubility	Remarks
$SnBr_4$	2:1	deep brown	198-200 (decomp)	insoluble in CCl_4, CS_2 CH_2Cl_2	slow decomp. in moist air
$SnCl_4$	2:1	deep red	200-202 (decomp.)	"	"
$TiBr_4$	1:1	deep brown	138 (decomp.)	"	rapid decomp. in moist air
$TiCl_4$	1:1	orange yellow	135 (decomp.)	"	"
TiF_4	1:4	orange	decomp. above 120	"	"
TiI_4	1:1	black	above 360 (decomp. above 100)	"	"
$ZrCl_4$	1:1	red orange	260 (decomp.)	"	"
$HfCl_4$	1:1	deep red	decomp. above 140	"	"
$SbCl_5$	1:1	deep red	160-162	"	slow decomp. in moist air

TABLE 1 (contd....)

Metal halide	Stochiometry (S_4N_4:m-halide)	Colour	M.P. ^{o}C.	Solubility	Remarks
SbF_5	1:4	green	145 (decomp.)	"	very rapid decomp.in moist air
$NbCl_5$	1:1	red orange	106	soluble in CH_2Cl_2	rapid decomp. in moist air
NbF_5	1:1	deep red orange	decomp. above 60	"	"
$TaCl_5$	1:1	deep red	132 (decomp)	"	"
TaF_5	1:1	bright red	-	"	"
BBr_3[54]	1:1	orange brown	-	-	-
BCl_3[54]	1:1	red orange	137-138	soluble in CH_2Cl_2	slow decomp. in moist air
BF_3[54]	1:1	dark burgundy	145-147 (decomp.)	"	rapid decomp. i moist air
$PhBCl_2$	1:1	brown orange	99-101	-	"
$AlCl_3$	1:2	deep red	89(decomp.)	soluble in CS_2,CH_2Cl_2	"
$AlBr_3$	1:2	orange brown	144	slightly soluble in CS_2	"
$GaCl_3$	1:2	deep red	100(decomp.)	soluble in CS_2,CH_2Cl_2	"
$FeCl_3$	1:2	deep red-brown	80(decomp.)	"	"

TABLE 1 (contd.....)

Metal halide	Stochiometry (S_4N_4:m-halide)	Colour	M.P. ^oC.	Solubility	Remarks
$InCl_3$	1:2	deep red brown	decomp.above 100^oC	slightly soluble in CH_2Cl_2	rapid decomp. in moist air
$SeCl_4$	1:1	yellow	127-129	insoluble in CH_2Cl_2,CS_2	changed to a re comp. in moist air (rapid)
$TeCl_4$	1:1	deep red	140	"	rapid decomp. in moist air
TeF_4	1:1	brown orange	92	soluble in CH_3CN	-
WBr_6	(S_4N_4 : WBr_4)	dark brown	251	-	rapid decomp. in moist air.

In some cases, choice of a suitable solvent was found to be the important factor e.g. it was possible to prepare the S_4N_4 adduct of aluminium tribromide using the solvents bromoform or carbon disulphide, but the reaction of S_4N_4 and $AlBr_3$ in CCl_4 or toluene gave an oily sticky product. Because of thermal instability of many tetrasulphur tetranitride adducts (e.g. $S_4N_4.BF_3$ decomposes above 90^oC[54]) most of the reactions were studied between 0^o-20^oC.

Many adducts were stable under dry nitrogen atmosphere for several days but decomposed in moist air usually giving S_4N_4 and the hydrolysis product of the Lewis acid.

The electronegativity difference between sulphur (2.44)[138] and nitrogen (3.07)[138] in tetrasulphur tetranitride would cause partial negative charge on nitrogen atoms and partial positive charge on sulphur atoms. Consequently the compound may act as either a Lewis base through the nitrogen atoms or as a Lewis acid through the sulphur atoms. Since we have only studied the reactions of S_4N_4 with Lewis acids, the Lewis base behaviour of S_4N_4 is considered below.

Recently [134, 135, 136] a rule concerning the stability of acid-base complexes has been suggested "The Principle of Hard and Soft Acids and Bases" or HSAB principle, which may be applied to understand the donor properties of S_4N_4.

According to this rule, bases in which the donor atom is, N, O, or F (i.e. of high electronegativity and small size) are classified as 'hard' bases, e.g. NH_3,H_2O,OH^-, F^-; and bases in which the donor atom is P,S,I,Br,Cl or C are called 'soft' bases, e.g. R_2S, R_3P, CN^-; whereas the borderline category takes into account such factors as, the presence of unsaturation in some nitrogen donors, which should loosen up the valency electrons, e.g. $C_6H_5NH_2$, C_5H_5N. From the above classification of hard and soft bases it can be seen that S_4N_4 (containing unsaturated nitrogen) may fall in the borderline category (i.e. intermediate between a hard and soft base).

In exactly the same way it is possible to classify hard (Class A) and soft (Class B) Lewis acids: the Class A Lewis acids, in which acceptor atoms are small in size of high positive charge and do not contain unsaturated pairs of electrons in their valency shell (e.g. H^+, Li^+, BF_3); the Class B Lewis acids generally have acceptor atoms large in size, of low positive charge and containing unshared pairs of electrons (p or d electrons) in their valency shell (e.g. Hg^+, Cu^+, Tl^+, RS^+). For Lewis acids the important properties that determine softness are size, charge or oxidation state, electronic structure and the nature of the attached groups[135] (for examples see S_4N_4 adducts later).

In view of the above principle it was interesting to study the various adducts of tetrasulphur tetranitride with Lewis acids. It was hoped that any radical differences in the structures of the adducts would be revealed by infrared spectra and chemical properties.

(a) Tetrasulphur tetranitride adducts of tin tetrabromide and tin tetrachloride

The formation of coordination complexes by the tetrahalides of silicon, germanium and tin with pyridine and acetonitrile (borderline bases according HSAB principle) may be compared to the reactions of S_4N_4 with tetrahalides.

The observed ratios of acceptor to donor in these addition compounds are most frequently 1:2 or 1:1, more rarely 1:4 and occasionally ratios other than these[137]. The tetrahalides of silicon, germanium and tin appears to follow the acceptor sequence Sn Ge Si and F Cl Br I. It can be seen from Table 1 that the ratio of S_4N_4 to $SnCl_4$ and $SnBr_4$ in these adducts is 2:1, whereas $SiCl_4$, $GeCl_4$ form no adducts with S_4N_4. From the above observations we may assign increasing softness in the order $CH_3CN > S_4N_4 > C_5H_5N$. This appears to be reasonable since pyridine forms adducts with $SiCl_4$, $GeCl_4$ and SnI_4, whereas in the case of CH_3CN and S_4N_4, no adduct formation has been reported or observed with these halides. Tetrasulphur tetranitride can be considered as a stronger base than acetonitrile, because tellurium tetrafluoride

and thallium trichloride form adducts with S_4N_4 in acetonitrile solution (e.g. consider the acid-base substitution reaction, $B' + A:B \longrightarrow AB' + B$, where B' and B are bases and A is an acid, if the reaction goes as indicated B' is a stronger base than B)[135]. The relative donor ability of nitrogen bases more simply be explained by considering the state of hybridisation of the donor atom. With regard to the donor strength of nitrogen atoms, $N(sp^3) > N(sp^2) > N(sp)$; $\hat{N}_{(sp^2)}$ pyridine = 116°[99] ; $\hat{N}_{(sp^2)}$ S_4N_4 = 113°[30] $\hat{N}_{(sp)}$ CH_3CN = 180°.

In tin tetrahalides the order of acid strength is SnF_4 $SnCl_4 > SnBr_4 > SnI_4$ (from size, charge or oxidation state and the nature of the attached groups), because the high electronegativity of fluorine (4.1)[138] leaves higher positive charge on Sn in SnF_4 than on Sn in other tetrahalides of tin (E.N. values, Cl=2.83, Br=2.74, I=2.21)[138] and other factors are equal. Therefore it is not surprising that SnI_4 gave no complex with S_4N_4. (This does not necessarily mean that S_4N_4 - tin tetraiodide adduct is not preparable. It may be that the reaction has not been examined over sufficiently wide range of experimental conditions). It is generally accepted that intermolecular bonds of the donor-acceptor type are formed as the result of charge transfer from a donor molecule to an acceptor molecule. Consequently the properties of donor bonds should be dependent upon the degree of charge transfer from donor to

acceptor[121]. This has been verified by establishing the relationship between the degree of charge transfer (from the value of the dipole moment of the intermolecular bonds) and the stability (from the heat of complex formation[122]). Strength of a metal-ligand bond is most satisfactorily defined as the enthalpy change, ΔH, accompanying the gas-phase dissociation of the complex[118]. Sometimes however, this information is not available and the strength of the donor acceptor bond is estimated from the magnitude of the stability constant, which is the equilibrium constant, Kp, for the reaction[118]:

$$D(g) + MX_3(g) \rightleftharpoons D.MX_3(g)$$

D=donor, M=metal, X=halogen

When equilibrium constants are used as a criterion of stability care has to be taken in interpreting the results. This is because equilibrium constants are a measure of a free energy change, not the required enthalpy change, $\Delta G^{o} = -RTln.Kp$. Therefore, if Kp for one addition compound is greater than for a second at a given temperature, it does not necessarily follow that the dissociation of the former is accompanied by the smaller enthalpy change. This is only true if the entropy of dissociation in both reactions is very similar. As indicated above, the most satisfactory method of investigating the stability of an adduct is by studying the gas phase dissociation of the compound into its component parts. A knowledge of how the degree of dissociation

varies with temperature permits the thermodynamic functions, ΔH, ΔG^{o} and ΔS to be calculated and this enables a quantitative measure of the strength of the metal-ligand bond to be obtained. The experimental techniques for studying gas-phase dissociation of molecular addition compounds have been developed by Brown, Taylor and Gerstein[118]. The gas-phase dissociation technique for the study of addition compounds has certain limitations. Thus it is difficult to study in the gas phase adducts which have already attained a high degree of dissociation a few degrees above saturation point. The dissociation method is also unsuitable for the study of complex compounds which do not give a measurable dissociation at a convenient temperature.

In many instances the relative stabilities of molecular addition compounds have been established by displacement reactions (e.g. $S_4N_4.BF_3 + BCl_3 \xrightarrow{CH_2Cl_2} S_4N_4.BCl_3 + BF_3$)[54]. It has long been customary to infer orders of relative stability from measurement of saturation pressure[118]. As a general rule for two addition compounds of closely similar type and molecular weight the less stable exhibits the higher saturation pressure (e.g. the order of stability, $(CH_3)_3N.BF_3 > (CH_3)_3N.BCCH_3)_3$; the order of saturation pressure $(CH_3)_3N.(BCH_3)_3 > (CH_3)_3.BF_3$)[118] For addition compounds differing in molecular weight it is to be expected that the lighter would be more volatile (e.g. $S_4N_4.BCl_3$ $S_4N_4.BF_3$). If however the heavier complex is found to be more

volatile, this is taken to indicate that it is also more highly dissociated.

It is possible to consider the existence of a coordination complex in terms of an energy cycle[138] and the cycle can be used qualitatively for discussion of real or possible compounds. It should be understood that every donor-acceptor reaction requires adjustment of energy levels in relation to each other to accord with the actual properties of the system. In some instances the adjustment energy (or reorganisation energy) may be greater than the energy released by dative-bond formation so that there is no combination, the gas-phase free energy of formation being positive instead of negative. This may well be true for some of those extreme cases where no reaction takes place between acceptors and donors having large alkyl groups attached to them. On the other hand, from the kinetics of coordinate bond formation in the vapour phase, the energy of readjustment for reactions between some classes of donor and acceptor can be quite small. This is true for complex compound formation between certain amines and boron halides. Alternatively, the Donor.MX_3 standard state may lie above the (MX_3 + D) standard states so that the adduct would not form. All these energy steps are complex. Thus with respect to the acid, adjustment for bonding involves energy of rehybridisation of the metal atom to give the required coordination number, e.g. in the case of $SnCl_4$ to give an

octahedral coordination (reduction in bond angles from $109^{o}28'$ to approximately 90^{o}). Sometimes the existence of bonding between M and X in MX_3 makes this step energetically more costly than in other situations where such bonding is less or absent, (e.g. $S_4N_4.BCl_3$ is more stable than $S_4N_4.BF_3$).

Rehybridisation considerations also apply to the molecules of base although usually the changes are not as drastic as in the case of acceptors. A further complication occurs if the acceptor molecule exists as a polymer. Then conversion of MX_3 (standard state) to $MX_3(g)$ requires energy for depolymerisation (e.g. complex formation by dimeric aluminium halides in solution or by solid halides polymerised through halogen bridges). Thus from this brief consideration of the energy steps in complex compound formation, it is readily seen that it is impossible to assign definite strengths to electron-pair donors and acceptors valid for every acid-base reaction[118].

Since many S_4N_4 adducts are insoluble or slightly soluble in inert organic solvents, any physical measurements such as vapour pressure, dipole moment etc. would be difficult. However, in those cases where the adducts are soluble in inert solvents, it may be possible to gain more knowledge about the properties of S_4N_4 adducts. The adduct $S_4N_4.4SbF_5$ appears to be less stable than $S_4N_4.SbCl_5$, because of the very rapid decomposition of $S_4N_4.4SbF_5$ in moist air. This behaviour may be explained in

terms of two effects (i) the donation of electrons from one of the nitrogens of S_4N_4 causes the weakening of the donor ability of the other nitrogen atoms. Consequently, the antimony pentafluoride molecules will be attached more weakly than in (hypothetical) $S_4N_4.SbF_5$ and probably more weakly than in $S_4N_4.SbCl_5$. Rapid hydrolysis of $S_4N_4.4SbF_5$ in moist air is therefore to be expected, (ii) Steric effect: as the adduct gets bigger it may become less stable.

The case with which the S_4N_4 adducts undergo hydrolysis in moist air can be considered in terms of HSAB principle and may in turn probably explain their stabilities. Thus since neither the S_4N_4 is a very strong donor, nor the $SnCl_4$ is a strong acceptor, in the adduct, $2S_4N_4.SnCl_4$ both S_4N_4 and $SnCl_4$ may be considered as nearly matching partners and consequently one would expect the adduct to be relatively stable. This is shown by the slow decomposition of $2S_4N_4.SnCl_4$ in moist air. Further the same argument can be applied to explain the stabilities of $S_4N_4.BCl_3$ and $S_4N_4.SbCl_5$ adducts where the latter appears to be more stable than $S_4N_4.BCl_3$, since $S_4N_4.SbCl_5$ can be obtained from the adduct, $S_4N_4.SbCl_5.BCl_3$ at 85-90°C.[54] Thus $SbCl_5$ would be a better matching partner or acceptor for S_4N_4 than BCl_3. However, it is still quite possible for a compound formed from a hard acid and a soft base to be more stable than one made from a better matched pair[135].

(b) Tetrasulphur tetranitride adducts of titanium, zirconium and hafnium tetrahalides

Titanium tetrachloride, tetrabromide, tetraiodide, zirconium tetrachloride and hafnium tetrachloride, form 1:1 adducts with S_4N_4. From electronegativity considerations $TiCl_4$ would be a better acceptor for S_4N_4 than $SnCl_4$ (the estimated ionic radii, Sn^{4+} = 0.71Å, Ti^{4+} = 0.68Å)[138] since neutral acids and bases will have strength proportional to the local dipoles at the acceptor or donor end. Silicon tetrachloride and $GeCl_4$ do not form addition compounds with S_4N_4, although $TiCl_4$ and $SnCl_4$ do so, a difference which may be attributed to ability of the halogen atoms to fill the coordination sphere of the smaller Si and Ge atoms.

Zirconium tetrachloride and $HfCl_4$ (the radii of the Zr^{4+} and Hf^{4+} ions are 0.74 and 0.75 respectively[138]) resemble $TiCl_4$ in their chemical properties[138]. Similar considerations can be applied to other halides of the group. Titanium tetrafluoride gave the adduct $S_4N_4.4TiF_4$, thus using all the four basic sites in S_4N_4.

(c) Tetrasulphur tetranitride adducts of boron, aluminium, gallium, indium, thallium and iron trihalides

As previously mentioned (see page 11,91), BCl_3, BBr_3, $PhBCl_2$, form 1:1 adducts with S_4N_4, whereas in the case of BF_3, two adducts, $S_4N_4.BF_3$ and $BF_3.4S_4N_4$ have been reported. However, the adduct

$BF_3.4S_4N_4$ appears to be unusual since the inability of boron to have coordination numbers exceeding four. Aluminium trichloride and tribromide $GaCl_3$, $InCl_3$, and $FeCl_3$ gave 1:2 adducts (S_4N_4: metal halide), while the stoichiometry in thallium trichloride adduct is not known.

In BX_3 compounds the boron octet is incomplete; boron has a low-lying unfilled orbital, consequently BX_3 (x=halogen) compounds behave as Lewis acids in which boron achieves its maximum coordination number with approximately sp^3 hybridisation. There is good evidence that the relative strengths of the boron halides as Lewis acids are in the order $BBr_3 > BCl_3 > BF_3$. This order is opposite of what would be expected both in steric grounds and from electronegativity considerations. It can be explained at least partially in terms of the boron halogen bonding. Acceptor atoms are less effective when the vacant orbital can be at least partly used in multiple bonding within the molecule[140]. In an addition compound this π bonding is largely or completely lost so that addition compounds of the boron trihalides with the strongest π bonding will be the most destabilised through loss of the π bonding energy[139]. Calculations[138] indicate that the π bonding energies of the trihalides are in the order $BF_3 > BCl_3 > BBr_3$. However certain properties[138] of the BX_3 adducts with donor molecules suggest that the donor to boron bonds may themselves increase in strength in the order $BF_3 < BCl_3 < BBr_3$. This may be

explained by the application of the mutual stabilising effect called symbiosis[141] (i.e. soft bases tend to group together on a given central atom and hard ligands tend to group together). In BX_3 halides boron is formally in a plus three oxidation state. The hard F^- ligands form a complex which is strongly ionic, the boron atom in BF_3 is appreciably positive and hard. Thus the presence of hard fluoride ion in BF_3 makes it easy to add other hard bases (e.g. $BF_3.OR_2$ is more stable than $BF_3.SF_2$). In the adducts $S_4N_4.BF_3$ and $S_4N_4.BCl_3$ the latter is more stable (since BCl_3 replaces BF_3 from $S_4N_4.BF_3$ in CH_2Cl_2 to give $S_4N_4.BCl_3$)[54] because S_4N_4 is a better matching partner for BCl_3 than for BF_3 or the better stability of $S_4N_4.BCl_3$ compared to $S_4N_4.BF_3$ can be explained by considering BCl_3 as a better acceptor than BF_3. Thus both the above explanations can be used to explain the relative stabilities of these adducts.

Aluminium and its congeners Ga, In, Tl are considerably larger than boron (atomic radii of Al and B being 1.26 and 0.88 Å respectively) and their trihalides behave as Lewis acids and can accept either neutral donor molecules or anions to give tetrahedral species, the acceptor ability generally decreases Al > Ga > In with the position of Tl uncertain. There are however notable distinctions from boron. These arise in part due to the reduced ability to form multiple bonds and to the ability of heavier elements to have coordinate numbers exceeding four.

Thallium (III) chloride is softer than Tl(I) chloride, because of the inert pair of electrons in the 6S orbitals. The presence of electrons in these orbitals decreases softness by a shielding affect on the outer d electrons and consequently $TlCl_3$ would be a better matching partner for S_4N_4.

(d) Tetrasulphur tetranitride adducts of antimony niobium and tantalum halides

The pentahalides of Sb, Nb and Ta form adducts with donors, such as oxygen, nitrogen exhibiting various stoichiometries (e.g. $SbCl_5.SeOCl_2$, $NbCl_5.POCl_3$, $NbF_5.2NH_3$, $TaF_5.2C_5H_5N$)[142] Antimony pentachloride has been more extensively studied than the other pentahalides of Sb, Nb and Ta and the majority of its adducts conform to 1:1 stochiometry. Comparison of the values of the heats of reaction of BBr_3, BCl_3 and $SbCl_5$ with pyridine yields the order of acid strengths toward pyridine: $BBr_3 > BCl_3 > SbCl_5$. In the boron halide series (as previously described), variations in degree of bonding have been used to explain the order; apparently the pentahalides may coordinate with little disturbance to the degree of bonding present. The physical properties of the adducts of pentahalides vary but the majority are solids at room temperature[142]. Antimony pentafluoride has some unusual chemical behaviour (e.g. it dissolves S, Se, Te and from the solutions crystalline substances such as $(SbF_5)_2S$ may be isolated)[144]. Antimony pentafluoride (electronegativity values, Sb=1.82, F=4.1[138]),

as would be expected because of the high affinity of antimony (in SbF_5) for electrons, functions as a strong Lewis acid. The acid strength of SbF_5 (with respect to S_4N_4) can be compared with that of sulphur trioxide, since both the acids give S_4N_4 adducts of 1:2 (S_4N_4 Lewis acids) and 1:4 stochiometry. When one of the nitrogen atoms of S_4N_4 is involved in the adduct formation, the donor ability of other N atoms is considerably weakened, but in the presence of strong acceptors, the other donor sites of S_4N_4, though weak can be used in the formation of coordinate bonds, although according to HSAB principle, such bonds would be weaker than the bonds formed from better matched partners. The pentafluorides of niobium and tantalium give adducts with various donor ligands (e.g. $NbF_5.OEt_2$, $TaF_5.SeEt_2$) and hexafluoride anions are known for these elements. Niobium and tantalum also exhibit a coordination number greater than six. A coordination number of seven has been formed for niobium in $(NbF_7)^{2-}$, whereas species up to $(TaF_8)^{3-}$ and possibly $(TaF_9)^{4-}$ exist in solution[138]. The acceptor strength of SbF_5, NbF_5 and TaF_5 toward S_4N_4 is probably in the order, $SbF_5 > NbF_5 > TaF_5$, since SbF_5 gives 1:4 and 1:2 adducts, whereas Nb and Ta form 1:1 (S_4N_4: metal fluoride) adducts. However it would be interesting to see whether SbF_5 displaces NbF_5 or TaF_5 from $S_4N_4.NbF_5$ or $S_4N_4.TaF_5$ to give S_4N_4 adducts of SbF_5, because it is not possible

to write down any universal order of acid strength (it varies with the reference donor)[135]. As noted above, adduct formation is observed for oxygen, nitrogen and sulphur donors with the pentachlorides and bromides of Nb and Ta, exhibiting the stoichiometry of 1:1 and 1:2 (e.g. $NbCl_5.2(CH_3)_3N$, $TaCl_5.(CH_3)_2S$)[142].

Tantalum pentaiodide and NbX_5 (X=Cl, Br, I) are readily reduced by pyridine to give MX_4py_2 complexes[138].

(e) Tetrasulphur tetranitride adducts of selenium (IV) tellurium (IV) and tungsten halides and oxyhalides

The halides of selenium (IV) and tellurium (IV) are generally more stable than those of sulphur and they also differ in showing Lewis acidity[138] (e.g. they form complex halides such as $K(SeF_5)$, $K_2(SeCl_6)$, $(C_5H_5NH)_2(TeI_6)$). Selenium tetrachloride forms addition compounds with ammonia, $SeCl_4.4NH_3$, ethylenediamine $SeCl_4(en)$, $SeCl_4.2en$, and with many amines[145]. The pyridine adduct $SeCl_4.py_2$ is not analogous to $SeCl_6^{2-}$ since in acetonitrile acts like a salt of the cation $(SeCl_3.py_2)^+$, this ion probably has a distorted octahedral structure, like the $SeOCl_2.py_2$[138]. Tellurium tetrachloride also gives $TeCl_4.4NH_3$ with dry ammonia and adducts of the type $TeCl_4.py$, $TeCl_4.2py$, $TeCl_4.POCl_3$ have been obtained[145]. Frpm HSAB principle, $SeCl_4$ and $TeCl_4$ may be classified as soft Lewis acids, since the soft Lewis acids generally have acceptor atoms large in size, of low positive charge and

containing unshared pairs of electrons (p or d electrons) in their valency shell. Thus in $SeCl_4$ and $TeCl_4$, from electronegativity considerations (e.n. values for Se=2.48, Cl=2.83, Te=2.01)[138] one would expect relatively small positive charge on Se and Te atoms, and since they contain unshared pairs of electrons in sp^3d hybrid orbitals and also they are relatively large in size (covalent radii, Se=1.71Å, Te=1.37Å) consequently $SeCl_4$ and $TeCl_4$ may form stable complexes with soft bases e.g. $TeCl_4$.py would probably be more stable than $TeCl_4.POCl_3$ and relatively less stable than $S_4N_4.TeCl_4$ (however HSAB principle is a qualitative rule based on experimental facts, the above order may be disturbed by other factors). Selenium tetrafluoride and tellurium tetrafluoride are highly reactive fluorinating agents though tellurium tetrafluoride appears to be less useful as a fluorinating agent. It forms 1:1 addition compound with pyridine in dry ether[145]; the tetrafluoride reacts exothermically with a number of bases, but secondary reactions occurred before the complexes could be isolated in pure form.[146]

Tungsten hexachloride, WCl_6 is reduced by primary amines to give amido complexes in lower oxidation states[138], which is in analogy to the S_4N_4 reactions with WCl_6 and WBr_6. The reaction of oxytetrahalides $WOCl_4$ and $WOBr_4$ with various unidentate and bidentate ligands containing group V and group VI donor atoms has been recently studied[147]. Alkyl cyanides, pyridine and cyclic ethers give 1:1 adducts and the alkyl cyanide complexes (e.g.

$WOCl_4.CH_3CN$, $WOCl_4.C_2H_5CN$) appear to be six-coordinate complexes. The infrared spectra of $WCl_4.S_4N_4$, $WBr_4.S_4N_4$ and $WOCl_4.S_4N_n$ are discussed later.

The Structures of S_4N_4 adducts

The positions of the infrared absorptions of the S_4N_4 adducts are given in Table 2. The formation of a coordinate bond by donation of a lone pair of electrons merely perturbs the donor molecule, no great changes in stereochemistry are commonly required and the effect on the spectrum appears as small shifts in frequency, with perhaps spitting of bands and altered intensity[137,142]. In the case of S_4N_4 more marked changes occur. Even without change in the geometry of S_4N_4, lowering of the molecular symmetry on coordination gives rise to more infrared-active bands. Since coordination by nitrogen atoms flattens out the S_4N_4 molecule with loss of S-S bonds and SN bond lengths no longer equal, further changes are inevitable. As a diagnostic tool infrared spectrum is invaluable and the spectra of coordinated ligands frequently show considerable similarities in a wide variety of compounds. Examination of the element-halogen vibrations as well as the ligand vibrations would appear to offer a tool to investigate the stereochemistry of the adducts. Recent studies have shown that metal-halogen absorption bands (MX) are often intense, and therefore readily identifiable and that the frequencies

TABLE 2 VIBRATIONAL FREQUENCIES OF S_4N_4 ADDUCTS WITH METAL HALIDES

The following symbols are used to denote the relative intensity of the infrared absorptions: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder.

$SnBr_4.2S_4N_4$	1156 vw, 1041 vs, 961 vs, 794 vs, 725 vw, 671 ms, 621 ms(Br), 563 w, 513 s, 422 vs, 355 vs, 298 ms, 259 w, 234 s, 219 ms (Br) cm^{-1}.
$SnCl_4.2S_4N_4$	1170 vw, 1047 vs, 966 vs, 814 vs, 787 w(sh), 722 vw, 683 w, 623 ms, 568 vw, 516 s, 413 s, 365 vs, 319 vw(sh), 309 vs, 279 ms, 260 vw, 252 w, 245 vw(sh), 236 s, 225 w, 212 vw, 207 vw, 201 vw cm^{-1}.
$TiBr_4.S_4N_4$	1156 vw, 1036 vs, 936 vs, 929 vs, 807 s, 775 vs, 746 ms (sh), 681 ms, 621 w, 565 ms(br), 508 s, 416 w, 365 w, (322 w, 312 w, 299 w)(br), 280 vw, 279 w, 266 w, 253 w, 245 ms, 226 w, 220 w, 217 vw, 212 w, 211 w(sh), 206 w cm^{-1}.
$TiCl_4.S_4N_4$	1156 vw, 1041 w, 990 vw, 963 s, 927 vs, 810 w, 760 ms, 728 s, 700 vs, 620 vw, 549 vs, 529 vw(sh), 515 vw, 389 vw (sh), 370 vs, 340 vs cm^{-1}.
$TiF_4.S_4N_4$	1149 vw, 1059 vs, 985 vs, 724 w(sh), 662 vs(br), 613 vw, 510 ms, 510 vw, 378 ms, 351 vw, 282 s (br), 247 vw cm^{-1}.
$TiI_4.S_4N_4$	1156 vw, 1098 vw, 1020 w, 934 w, 793 w, 722 vw, 279 s, 248 s (br) cm^{-1}.
$ZrCl_4.S_4N_4$	1157 vw, 1034 vs, 957 vs, 807 vs, 795 vw(sh), 762 vs, 740 vw, 722 vs, 699 vs, 668 vw(sh), 626 ms, 551 vs, 529 vw, 510 ms, 367 w(sh), 340 vs, 305 ms, 245 vw cm^{-1}.
$HfCl_4.S_4N_4$	1156 vw, 1037 vs, 991 vw, 958 vs, 800 vs, 724 vw(sh), 682 s, 666 vw, 639 vw(sh), 624 s, 561 vw, 553vw, 514 vs, 422 vw, 399 vw, 359 w(sh), 324 s(br), 303 vw, 290 vw, 279 w, 267 w, 253 ms(sh), 247 s, 226 w, 220 w, 217 vw, 212 w, 206 w.

TABLE 2 (contd...)

$SbCl_5.S_4N_4$	1156 vw, 1058 vs, 975 vs, 807 vs, 786 vs, 738 w(sh), 722 ms (br), 682 s, 666 vw, 651 w, 623 vs, 608 vw(sh), 563 w, 511 vs, 483 vw, 411 vs, 370 s(sh), 370 w(sh), 361 w(sh), 345 vs, 308 s, 275 vs, 245 s, 239 w(sh), 226 w cm^{-1}.
$4SbF_5.S_4N_4$	1143 vw, 1058 vs, 986 vs, 943 vs, 886 vw(sh), 790 ms, 741 ms, 719 vw(sh), 695 s, 625 s, 571 s(br), 429 vs, 357 s, 339 s(br), 291 ms, 268 vw, 259 w, 250 vw(sh), 234 w, 228 w, 223 w, 214 w, 208 w cm^{-1}.
$NbCl_5.S_4N_4$	1041 vs, 987 ms, 954 vs, 883 ms, 788 vs, 750 s, 719 vw, 680 ms, 666 vw, 618 s, 506 vs, 431 ms, 365 vs, 340 vs cm^{-1}.
$NbF_5.S_4N_4$	1065 vs, 992 vs, 929 w, 891 vw, 800 ms, 722 ms, 676 ms, 606 vs(br), 515 vs.
$TaCl_5.S_4N_4$	1153 vw, 1045 vs, 957 vs, 797 vs, 749 s, 721 vw(sh), 682 ms, 669 vw, 637 ms(sh), 619 s, 568 vw, 505 vs, 425 ms, 372 w(sh), 359 ms(sh), 322 vs(br), 265 w, 252 vw, 244 vw, 226 w cm^{-1}.
$TaF_5.S_4N_4$	1153 vw, 1071 vs, 996 vs, 927 vs, 873 vw(sh), 803 ms, 744 ms, 727 w, 700 vs, 678 ms, 667 vw, 581 vs(br), 516 w cm^{-1}.
$BF_3.S_4N_4$ [54]	1171 w, 1138 ms, 1117 s, 1070 s, 1040 vs, 1014 w, 949 s, 908 w, 888 s, 840 w, 724 vw, 697 vw, 682 vw, 658 ms, 623 ms, 567 w, 552 w, 527 s, 502 w, 490 w(sh), 420 ms cm^{-1}.
$BCl_3.S_4N_4$ [54]	1064 s, 1042 w, 982 s, 958 s, 864 w, 736 w, 720 w, 695 w, 678 w, 660 w, 625 w, 615 vw(sh), 552 vw, 518 w, 430 w, cm^{-1}.
$PhBCl_2.S_4N_4$	1310 vw, 1156 vw(sh), 1087 vw(sh), 1265 vw, 1194 vw(sh), 1186 vw(sh), 1174 vs, 1057 vs, 1029 w(sh), 1000 vw(sh), 971 w(sh), 948 vw(sh), 921 vs, 888 w(sh), 875 s, 857 vw(sh), 797 ms, 762 ms, 738 vw(sh), 725 vw(sh), 704 vs, 693 vw(sh), 659 vs, 628 ms, 615 vw(sh), 551 s, 521 s, 420 vs, 359 vs, 352 vw(sh), 335 vs, 314 vs, 304 vw(sh), 282 vs, 261 w, 250 vs, 241 w, 238 vw(sh), 233 vw(sh), 228 ms, 222 w, 218 vw, 213 vw, 208 w.

TABLE 2 (contd....)

$2AlBr_3.S_4N_4$	1157 vw, 1126 vs, 934 ms, 869 vs, 776 ms, 736 ms, 710 vw(sh), 694 vw, 667 w, 633 w, 585 ms, 565 w, 481 vw (sh), 473 vs, 457 w, 437 ms, 414 ms, 395 ms, 349 vs, 318 ms, 276 ms, 259 ms, 251 ms, 244 ms, 238 vw, 226 s, 221 w (sh), 212 ms, 206 ms cm^{-1}.
$2AlCl_3.S_4N_4$	1162 vw, 1046 vs, 998 w, 967 vs, 866 vs, 800 vw, 755 ms, 719 w, 680 ms, 623 s, 573 w, 561 w, 530 w(sh), 507 vw(br), 476 w, 454 ms, 403 vs, 355 vs, 324 vs, 238 s, 225 ms cm^{-1}.
$2GaCl_3.S_4N_4$	1147 vw, 1033 vs, 993 w, 961 vs, 844 vs, 756 ms, 722 vw(sh), 680 ms, 666 vw(sh), 680 ms, 623 s, 566 w, 516 vs, (420 s, 408 s, 389 s, 374 s)(Br), 297 vs, 267 vs, 228 s cm^{-1}.
$2InCl_3.S_4N_4$	1266 ms, 1152 vw, 1040 vs, 954 vs, 893 vw, 824 vs, 777 ms(sh), 730 vs, 704 ms, 681 s, 645 vw(sh), 621 vs, 565 ms, 551 vw(sh), 521 vs, 403 vs, 361 vs, 312 vs, 236 ms(br) cm^{-1}.
$2TlCl_3.S_4N_4$	1156 vw, 1059 vs, 971 vs, 803 w, 741 w(sh), 722 s, 702 w, 655 w, 619 ms, 597 s, 580 s, 558 w, 533 ms, 523 w cm^{-1}.
$2FeCl_3.S_4N_4$	1162 vw, 1033 vs, 995 w, 957 vs, 797 vs, 737 ms, 720 vw(sh), 679 s, 619 vs, 565 w, 516 vs, (384 vs, 370 vs)(br), 340 s, 308 s, 255 vw, 248 vw, 234 w, 228 vw cm^{-1}.
$SeCl_4.S_4N_4$	1190 w, 1124 vs, 1105 ms(sh), 1016 ms, 945 w, 919 ms, 800 vw, 729 vs, 702 vw, 670 ms, 622 vs, 559 s(sh), 546 vs, 403 s, 383 s, 336 s, 309 s cm^{-1}.
$TeCl_4.S_4N_4$	1156 vw, 1047 vs, 966 vs, 806 s, 760 vs, 727vw(sh), 671 ms, 635 ms, 613 ms, 563 w, 500 s(br), 360 vs(br), 251 s(br), 225 w cm^{-1}.

TABLE 2 (contd....)

$TeF_4.S_4N_4$	1282 w, 1162 vw, 1036 s, 981 vs, 926 vs, 926 vs, 865 vw, 821 w, 768 s, 745 vw, 727 s, 700 vs, 627 vw, 591 vw, 458 vs cm^{-1}.
$WOCl_4.S_4N_4$(?)	1164 vw, 1075 vw, 1000 vw(sh), 980 vs, 926 vw, 857 w, 837 w, 792 w, 778 w, (735 w, 723 w)(br), 697 w, 662 vs, 617 vw, 551 w, 543 w, 515 ms cm^{-1}.
$WCl_4.S_4N_4$	1162 vw, 1119 w, 1070 vw, 1041 w(sh), 1010 vs, 971 ms, 934 w, 851 ms, 800 vw(sh), 788 vs, 768 w(sh), 723 vw, 703 s, 697 vw(sh), (660 s, 647 s) (br), 576 vw, 554 s, 515 vs, 494 ms(sh), 472 vw, 406 ms, (350 w (sh), 331 vs, 312 w, 294 w(sh),(br), 276 vw, 263 ms, 251 ms, 244 ms cm^{-1}.
$WBr_4.S_4N_4$	1169 w, 1066 vw, 1005 vs, 921 vw, (857 s, 837 s) (br), 780 ms, 769 ms, 735 w(sh), 722 w, 689 ms, 673 vw, 660 vw(sh), 653 vs, 623 vw, 548 s, 527 ms, 514 ms, 501 vw(sh), 467 s, 405 vs, 330 vs, 312 ms, 291 s, 279 s, 263 ms, 254 w cm^{-1}.

of these vibrations are related to the oxidation state and coordination number of the metal and also to the stereochemistry of the complex[148]. Thus an increase in coordination number leads to a decrease in ν M-Cl[149], e.g.

$Sn^{IV}Cl_4$ $(Sn^{IV}Cl_6)^{2-}$

$\nu 1 = 368\ cm^{-1}$ $311\ cm^{-1}$

and an increase in oxidation state causes an increase in ν M-Cl[149], e.g. $(FeCl_4)^{2-}$, $(FeCl_4)^{-1}$

$286\ cm^{-1}$ $377\ cm^{-1}$

Also in using vibrational data, one should be aware of the importance of environmental effects such as field affects, solvent effects, and site symmetry effects. However, the spectra of several adducts containing supposedly chelate ligands, such as 1,10-phenanthroline and 2,2'-bipyridyl show that the assignments of stereochemistry can be made, in the absence of complicating factors such as crystal field affects[137]. For infrared spectroscopy because it involves the direct study of the metal-ligand bond is particularly useful in assigning M-X stretching frequencies.

From Table 2 it can be seen that the spectra of the adducts of S_4N_4 with metal halides may roughly be divided into four types. Since the X-ray structures of $S_4N_4.SbCl_5$ and $S_4N_4.BF_3$ are known, it is useful to compare the infrared spectra of these adducts with the other complexes.

(a) The adducts, $SnBr_4.2S_4N_4$, $SnCl_4.2S_4N_4$, $TiBr_4.S_4N_4$, $ZrCl_4.S_4N_4$, $HfCl_4.S_4N_4$, $4TiF_4.S_4N_4$, $4SbF_5.S_4N_4$, $SbCl_5.S_4N_4$, $NbCl_5.S_4N_4$, $TaCl_5.S_4N_4$, $TaF_5.S_4N_4$, $TeCl_4.S_4N_4$, $2AlCl_3.S_4N_4$, $2GaCl_3.S_4N_4$, $2InCl_3.S_4N_4$, $2TlCl_3.S_4N_4$(?) have roughly similar infrared spectra to those of $S_4N_4.SbCl_5$ and $S_4N_4.BF_3$ with characteristic strong peaks at 1040, 960, 510 and 360 cm^{-1}.

(b) The infrared spectra of $S_4N_4.WOCl_4$, $S_4N_4.WCl_4$ and $S_4N_4.WBr_4$ are different from $S_4N_4.SbCl_5$ and $S_4N_4.BF_3$, but show similarity to one another with characteristic very strong peak near 1000 cm^{-1}. The strong peaks at 1040 and 1060 in the above adduct are missing in these adducts, the strong peaks in S_4N_4 at 924, 727 and 698 cm^{-1} are also missing in these adducts.

(c)The infrared spectra of $2AlBr_3.S_4N_4$ and $SeCl_4.S_4N_4$ are different from the above and one another.

(d) The infrared spectrum of $TiI_4.S_4N_4$ is weak.

The Structures of $SnBr_4.2S_4N_4$ and $SnCl_4.2S_4N_4$

The structures to be expected of these adducts are that based on an octahedral distribution about the central metal atom. A single Sn-Cl band has been observed in tin(IV) chloride complexes with nitrogen donors, such as pyridine[151] (e.g. $SnCl_4.2py$, Sn-Cl, 324 cm^{-1}, but a plitting of this band has been observed in complexes such as $SnCl_4$.2,2'-bipyridyl (νSn-Cl, 327, 280 cm^{-1})[151]

From this it was concluded that the former complexes are trans octahedral, whereas the latter are cis octahedral[151]. The infrared spectra of $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$ in 400-4000 cm^{-1} region are very similar or virtually identical except that in the case of $SnCl_4.2S_4N_4$ the very strong peak at 813 cm^{-1} has a shoulder at 986 cm^{-1}. Hence it is reasonable to conclude that both the adducts have similar structures. The metal-nitrogen stretching frequency is of particular interest since it provides direct information about the coordinate bond. Because of the relatively heavy mass of the metal and low bond order of the coordinate bond, the M-N stretching vibrations may appear in the low frequency region[156]. The assignment of metal-nitrogen stretching frequency is carried out by calculating approximate metal nitrogen force constant from Gordys rule[157] and then calculating the approximate metal-nitrogen stretching frequency.

This method is similar to the method described by Poller[159] for calculating Sn-O stretching frequency from the approximate value of force constant, except that the metal-nitrogen bond lengths used were from the X-ray data of the adduct of S_4N_4 with $SbCl_5$ (Sb-N=2.17Å)[58] whereas Poller calculated the Sn-O bond length from the sum of the covalent radii corrected for the elctronegativity difference[160]. Since the infrared spectra of $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$ are very similar to the infrared

spectrum of $S_4N_4.SbCl_5$, it is useful to assign the metal-nitrogen stretching frequency first in $S_4N_4.SbCl_5$ and then assign the Sn-N stretching frequencies in $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$ by comparison. Thus taking electronegativity values of 3.07 for nitrogen (Allred-Rochow scale)[138] and 1.82 for antimony (Allred-Rochow scale)[138] and the N-Sb bond length of 2.17Å a force constant of 2.2×10^5 dyn./cm. was obtained (see Appendix 1) This gave a value of 545 cm^{-1} for the N-Sb stretching frequency. If the electronegativity values for nitrogen and antimony are 3.04 and 2.05 (Pauling-type values)[138] respectively, the calculations gave a stretching frequency of 565 cm^{-1}. These are probably upper limits to the anticipated metal-nitrogen stretching frequency, on account of the large mass of the other (halogens) atoms attached to the metal atom. If such types of calculations are correct as a first approximation, one may assign N-Sb stretching frequencies near the above values. Since tin and antimony are of comparable atomic weights and electronegativities (atomic weights, Sn=118.69, Sb=121.80, E.N. values, Sn=1.96, Sb=2.04)[138] and both have nearly the same covalent radii (Sn=1.40Å, Sb=1.41Å)[160] it is reasonable to expect the Sn-N stretching frequencies in the region of Sn-N.

The metal-chlorine vibrational frequencies lie in the broad range[149] 650-200 cm^{-1} and the octahedral Sn(IV) complexes show no Sn-Cl absorptions above 400 cm^{-1}. Therefore all the bands

above 700 cm^{-1} in these adducts are assigned to S-N vibrations. Thus the very strong bands at 1040, 940 and 800 are assigned to S-N (no Sn-halogen or Sn-N bands are to be expected in this region, because of the above limits for Sn-N and Sn-halogen frequencies), in these adducts. The very strong bands at 515 and 360 cm^{-1} are assigned to S-N vibrations, because S_4N_4 has a ring stretching mode at 531 cm^{-1} and a ring deformation mode at 347 cm^{-1}[161]. The very strong band at 410 cm^{-1} in these adducts may be (1) from the S-N ring system, as the lowering of symmetry of S_4N_4 gives rise to additional bands, or (2) Sn-N ($SnCl_4.2S_4N_4$ = 413 cm^{-1}, $SnBr_4.2S_4N_4$ = 420 cm^{-1}). Several papers have appeared in the past few years dealing with the low frequency spectra of some nitrile adducts of tin tetrachloride[150, 151, 152, 153, 154]. There has been controversy over the assignment of the bands below 500 cm^{-1} in the spectrum of $SnCl_4.2CH_3CN$. Brown and Kubota[153] originally assigned the bands around 400 cm^{-1} as Sn-Cl stretching modes, whereas those bands occurring between 350 and 300 cm^{-1} were assigned to the assymetric and symmetric Sn-N vibrations. Beattie[151] et al., however, showed that the assignments of Brown and Kubota were incorrect; they assigned the bands around 400 cm^{-1} as ligand vibrations (NCC bending modes) and lower frequency bands as Sn-Cl stretching vibrations. On the basis of simple valency force field calculations, Beattie and Rule[155] predicted that the Sn-N stretching

frequency for $SnCl_4.2CH_3CN$ would occur below 265 cm^{-1}.

Aggarwal and Singh on the basis of the low frequency spectra of some amide, urea and aminobenzoic acid adducts of tin tetrachloride, reversed the assignment of Beattie et al., and support those of Brown and Kubota[153]. They observed a strong band in tin(IV) chloride complexes with nitrogen donors at about 310 cm^{-1}, but no band is present in this region in the tin (IV) chloride complexes with oxygen donors; had this band been due to a Sn-Cl vibration, then it should have appeared in all the complexes of tin(IV) chloride with nitrogen as well as oxygen donors.

However, Fowles[150] et. al., and Farona[152] et al., support the assignment of Beattie et al. They assigned the bands appearing in the 300 - 370 cm^{-1} region, in the spectra of all the $SnCl_4$ adducts, but missing in the spectra of corresponding $SnBr_4$ and SnI_4 adducts, to Sn-Cl stretching modes.

In $SnCl_4.2S_4N_4$ there is a very strong broad band at 308 cm^{-1} with a very weak shoulder at 319 cm^{-1}. Since this band is missing in the infrared spectrum of $SnBr_4.2S_4N_4$, it is reasonable to assign the band at 308 cm^{-1} to Sn-Cl stretching vibration. The medium strong bands at 235 cm^{-1} which appear in both the infrared spectra of $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$, are assigned to Sn-N. The medium strong broad band at 219 cm^{-1} in $SnBr_4.2S_4N_4$ is assigned to Sn-Br vibration, since a medium strong band at 220 cm^{-1}

has been assigned to Sn-Br mode in the adduct $SnBr_4$.2,2'-bipyridyl[152]. It was found to be difficult to assign the other bands appearing in the infrared spectra of $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$.

Beattie et al., have[151] observed one Sn-Cl stretching frequency (324 cm^{-1}) in the far infrared spectrum of $SnCl_4$.2py and predicted a trans structure for $SnCl_4$.2py whereas in $SnCl_4$.2,2'-bipyridyl two bands (327 vs, br, 280 s, br) were assigned to Sn-Cl and a cis octahedral structure, was proposed. Because usually large ligands (or sterically hindered ligands) such as pyridine give trans octahedral structure, therefore since S_4N_4 is also a sterically hindered ligand, the structures of $SnCl_4.2S_4N_4$ and $SnBr_4.2S_4N_4$ may be trans octahedral. However there are other bands in the far infrared spectra of these adducts, which were found to be difficult to assign and some of these bands may be due to Sn-Cl vibrations, which would then favour a cis octahedral structure for these adducts. Thus the choice between cis and trans appears to be difficult.

The Structures of $S_4N_4.4TiF_4$, $S_4N_4.TiBr_4$, $S_4N_4.TiF_4$, $S_4N_4.ZrCl_4$ and $S_4N_4.HfCl_4$.

Titanium, zirconium and hafnium halides form a wide variety of adducts with many oxygen and nitrogen donors, e.g. ethers[170], nitriles[148], and amides[171]. These compounds are usually either 1:1 or 2:1 (base:acid) adducts, the latter are six coordinate monomers, but former may be either five coordinate monomers, or six coordinate

dimers as in the compound $(TiCl_4.POCl_3)_2$[162] Eight-coordination for titanium has been established for bidentate arsine complexes of titanium (IV) halides[163].

The structures of $S_4N_4.TiBr_4$, $S_4N_4.TiF_4$, $S_4N_4.ZrCl_4$ and $S_4N_4.HfCl_4$, adducts are expected to contain unidentate S_4N_4, since their spectra are similar to the infrared spectra of $S_4N_4.SbCl_5$ (major peaks at, 1058, 976, 511 and 370 cm^{-1}) and $S_4N_4.BF_3$ (major peaks at 1040, 949, 502 cm^{-1}) in which only one nitrogen of S_4N_4 is used in coordination. The corresponding characteristic peaks for the new adducts occur at $S_4N_4.TiBr_4$, 1036, 963, 508, 365 cm^{-1}; 957, $S_4N_4.4TiF_4$, 1059, 985, 510 351 cm^{-1}; $S_4N_4.ZrCl_4$, 1034, 957, 510, 368; $S_4N_4.HfCl_4$, 1037, 958, 515, 360 cm^{-1}. However, the infrared spectra of $ZrCl_4$, $HfCl_4$, 4Ti F_4, S_4N_4 are different from the infrared spectrum of $S_4N_4.SbCl_5$ in a number of respects, while the infrared spectrum of $HfCl_4.S_4N_4$ is most like the infrared spectrum of $S_4N_4.SbCl_5$. Absorption frequencies and the outstanding similarities and differences in the infrared spectra of these adducts and $S_4N_4.SbCl_5$ are given below:

$S_4N_4.SbCl_5$: 1058 vs, 976 vs, 808 vs, 786 vs, 722 ms, 682 s, 623 vs, 511 vs.

$S_4N_4.HfCl_4$: 1037 vs, 958 vs, 800 vs, 741 s, 682 s, 624 s, 415 vs cm^{-1}.

$S_4N_4.ZrCl_4$: 1034 vs, 957 vs, 807 vs, 762 vs, 722 vs, 699 vs, 626 ms, 551 vs, 510 ms cm^{-1}.

$S_4N_4.TiBr_4$: 1037, 963 vs, 829 vs, 807 s, 746 ms, 681 ms, 621 w, 565 ms, 508 cm^{-1}.

$S_4N_4.4TiF_4$: 1059 vs, 985 vs, 725 w, 662 vs(br), 510 ms.

Since M-X frequencies in the above metal halides lie in the broad range 650-200 cm^{-1} (with exception of TiF_4 highest, Ti-F = 880 w(v.br)[172] all the strong bands above 700 cm^{-1} (except in $4TiF_4.S_4N_4$) are likely to be S-N stretching frequencies. The common bands at 510 and 365 cm^{-1} in these adducts are assigned to S-N, since S_4N_4 has a bond stretching mode at 545 and a bond bending mode at 347 cm^{-1} respectively.

In the far infrared spectrum of $TiBr_4.S_4N_4$, the band at 416 cm^{-1} can be assigned to either ν S-N or ν Ti-N, by analogy with other S_4N_4 adducts, in which M-N frequencies are assigned in this region (e.g. $SnCl_4.2S_4N_4$, Sn-N=413 cm^{-1}).

There are a number of other peaks in the far infrared spectrum of $TiBr_4.S_4N_4$, which cannot be assigned with certainty.

In the far infrared spectrum of $ZrCl_4.S_4N_4$, the peaks at 340 vs(br) 304 ms cm^{-1} are assigned to ν Zr-Cl, since ν Zr-Cl frequencies are assigned in the region 299-354 cm^{-1} in the addition compounds of $ZrCl_4$[148]. The infrared spectrum of $S_4N_4.4TiF_4$ has two peaks at 1059 and 985 which are assigned to S-N stretching vibrations. This infrared spectrum differs from the infrared spectrum of $S_4N_4.SbCl_5$ in that there is no very strong peak at 800 cm^{-1}. This may be because in TiF_4 the highest metal-

fluorine frequency for TiF_4 at 880 cm^{-1} may couple with the S-N stretching frequencies in this region; all the peaks in this region are probably due to the combination of S-N and Ti-F vibrations. There is broad very strong band at 662 cm^{-1} which may be assigned to Ti-F vibrations, since Ti-F stretching frequencies have been assigned in the region 550-670 cm^{-1} in TiF_4.2,2'bipyridyl, TiF_4.2py[167]. However Ti-N vibrations may also occur in this region, and it seems likely that the absorptions in the region 728-615 may be due to combination of S-N, Ti-N and Ti-F modes rather than simple group absorptions. In the far infrared spectrum of S_4N_4.4TiF_4 the band at 283 (vs,br) is assigned to Ti-F bending vibration, since a mode at 280 s(br) is assigned to Ti-F bending vibration in the infrared spectrum of TiF_4[172] and also because Ti-F deformations occur at 254-311 cm^{-1} in TiF_4 complexes[167]. The medium strong band at 370 could be due to ν S-N or ν Ti-N.

In the infrared spectrum of S_4N_4.$HfCl_4$ the very strong broad band at 325 cm^{-1} (shoulder at 303 cm^{-1}) is assigned to Hf-Cl vibration, by analogy with other S_4N_4 adducts of metal halides (e.g. S_4N_4.$ZrCl_4$, Zr-Cl 340, 305 cm^{-1}.

The infrared spectrum of TiI_4.S_4N_4 is weak even though the mulls were strong; the reason for this is presumably due to reduced polarity of bonds compared with the S_4N_4 complexes of the other titanium halides. In the far infrared spectrum of this

there is a strong band at 279 cm^{-1} which can be assigned to Ti-I, because metal-iodine bands usually occur at lower frequencies. The commonly occurring bands at 245 cm^{-1} in all the titanium halides adducts are assigned to Ti-N (in $ZrCl_4.S_4N_4$, Zr-N=245 cm^{-1}).

None of the above adducts of S_4N_4 with $TiBr_4$, $TiCl_4$, TiF_4, $ZrCl_4$ and $HfCl_4$ has a sharp melting point, in fact for the most part they do not melt below 250°C although most of them show signs of decomposition below this temperature. These complexes have very little solubility in inert solvents, whereas solvents like water, alcohols decompose these adducts. These properties of the adducts probably indicate that they may not be pentacovalent substances but rather that they are polymeric complexes, at least some of these complexes may be polymeric.

The structures of $S_4N_4.SbCl_5$, $S_4N_4.4SbF_5$, $S_4N_4.NbCl_5$, $S_4N_4.NbF_5$ $S_4N_4.TaCl_5$ and $S_4N_4.TaF_5$

As already mentioned, the X-ray structure of $S_4N_4.SbCl_5$ is known in which S_4N_4 acts as monodentate ligand. All the above adducts of S_4N_4 with the pentahalides of Sb,Nb and Ta may have six coordinate structures since the infrared spectra of these adducts are similar to the infrared spectrum of $S_4N_4.SbCl_5$. Absorption frequencies showing the outstanding similarities and differences, in the infrared spectra of these adducts are given below:

$S_4N_4.SbCl_5$	1058 vs	975 vs			807 vs	786 vs	722 ms	682 s	623 vs	511 vs	cm^{-1}
$S_4N_4.NbCl_5$	1041 vs	987 ms	954 vs	888 ms		788 vs	750 s	680 ms	618 s	506 vs	cm^{-1}
$S_4N_4.TaCl_5$	1045 vs		957 vs			797 vs	749 s	682 ms	619 s	505 vs	cm^{-1}
Assignments	S-N	S-N	S-N	S-N	S-N	S-N	S-N			S-N	
$S_4N_4.4SbF_5$	1058 vs	986	943			790 ms	741 ms	695 s	621 vs (br)	512 ms	cm^{-1}
$S_4N_4.NbF_5$	1065 vs	992 vs	929 w			800 ms	722 ms	676 ms	606 vs (br)	515 s	cm^{-1}
$S_4N_4.TaF_5$	1071 vs	996 vs	927 vs			903 ms	744 ms 727 w	700 vs 678 ms	581 vs (br)	516 w	cm^{-1}
Assignments	S-N	S-N	S-N			S-N			M-F	S-N	

In $S_4N_4.SbCl_5$ the very strong bands above 700 cm^{-1} are assigned to S-N (highest Sb-N = 565 cm^{-1} (ca), highest Sb-Cl = 395 cm^{-1} [148]). The very strong band at 511 cm^{-1} is assigned to S-N vibration, because S_4N_4 has a S-N ring stretching mode at 545 cm^{-1}.

In the far infrared spectrum of $S_4N_4.SbCl_5$ the strong band at 411 cm^{-1} is either due to S-N or Sb-N vibration. The strong band at 311 cm^{-1} is assigned as S-N, because S_4N_4 has a ring deformation mode in this region (347 cm^{-1}). The strong band at 370 cm^{-1} is assigned to Sb-Cl since $SbCl_5$ has Sb-Cl absorption modes in this region (Sb-Cl = 395, 371 cm^{-1} in $SbCl_5$ [148]). However, the bands in this region may arise due to the coupling of S-N and Sb-Cl modes. The very strong broad band at 345 cm^{-1} in $S_4N_4.SbCl_5$ is assigned to Sb-Cl, by analogy with other S_4N_4 adducts, e.g. $S_4N_4.2SnCl_4$, Sn-Cl = 310 vbr (sh.319) cm^{-1}. The number of other bands appearing in the far infrared spectrum of $S_4N_4.SbCl_5$ cannot be assigned with certainty. However, it is likely that the relatively weak bands at 308 and 345 cm^{-1} may be due to Sb-N vibrations, since the polarity of the metal-halogen bonds is higher than the metal nitrogen bonds.

The infrared active bands appearing in the region 700-550 cm^{-1} in $S_4N_4.SbCl_5$ are difficult to assign, since they may be combination bands rather than simple group absorptions.

In $S_4N_4.NbCl_5$ and $S_4N_4.TaCl_5$ the strong bands above 700 cm^{-1} are assigned to ν S-N by analogy with $S_4N_4.SbCl_5$ (highest ν Nb-Cl in $NbCl_5$ is at 497 cm^{-1} [156]). The strong band at 340 cm^{-1} in $S_4N_4.NbCl_5$ is assigned to ν Nb-Cl, whereas the band at 363 cm^{-1} is assigned to S-N analogy $S_4N_4.SbCl_5$. Similarly in $S_4N_4.TaCl_5$ the very strong broad band at 322 cm^{-1} is assigned Ta-Cl whereas the band at 360 cm^{-1} may be due to ν S-N.

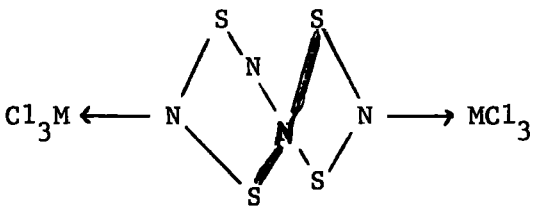
In a series of related molecules, variation of metal-halogen stretching frequency with metal may depend upon several factors. However, it is at least reasonable to expect that an increase in mass of the metal will cause a decrease in ν M-X (M= metal, X=halogen).

	$S_4N_4.SbCl_5$	$S_4N_4.NbCl_5$	$S_4N_4.TaCl_5$
M-X (cm^{-1})	345	340	322

In $S_4N_4.4SbF_5$, $S_4N_4.NbF_5$ and $S_4N_4.TaF_5$ the strong bands above 800 cm^{-1} are assigned to νS-N (highest Sb-F = 716 cm^{-1} [156]). In all these pentafluoride adducts there is a very strong broad band in the region 666-526 cm^{-1} ($S_4N_4.4SbF_5$=627 vs(br), $S_4N_4.NbF_5$= 606 vs(br), $S_4N_4.TaF_5$ = 581 vs(br) cm^{-1}, which may be either due to the combination of M-F, S-N and Sb-N modes or may be due to M-F mode only since M-F stretching frequencies in octahedral complexes lie in this region[148] (e.g. NbF_6^-, Nb-F = 585 cm^{-1}, TaF_6^-, Ta-F = 560 cm-1).

The Structures of $S_4N_4.2AlCl_3$, $S_4N_4.2AlBr_3$, $S_4N_4.2GaCl_3$, $S_4N_4.2InCl_3$ $S_4N_4.2TlCl_3$, $S_4N_4.2FeCl_3$ and $S_4N_4.PhBCl_2$

The infrared spectra of these adducts, with the exception of $S_4N_4.2AlBr_3$ and $S_4N_4.PhBCl_2$ are similar to the infrared spectrum of $S_4N_4.SbCl_5$. They all may have structures with monodentate S_4N_4 as shown below,



The infrared frequency assignments in the near infrared spectra of these complexes can be done in exactly the same way as for $S_4N_4.SbCl_5$. The far infrared spectra of all these adducts are described below.

In $S_4N_4.2AlCl_3$ the strong band at 403 is assigned to either S-N or Al-N, whereas the band at 354 is assigned to S-N by analogy with other S_4N_4 adducts. The very strong band at 324 is assigned Al-Cl, since metal-halogen frequencies in S_4N_4 adducts appear in this region. The relatively weak band at 225 cm^{-1} is assigned to Al-N vibration since this band also appears in $S_4N_4.2GaCl_3$, at 228 cm^{-1}, $S_4N_4.2InCl_3$ and $S_4N_4.2FeCl_3$ also absorb in this region (high background of spectrum prevents exact location of absorption maximum)

In $S_4N_4.2GaCl_3$, the bands in the broad envelope at 420, 408, 389 and 374 cm^{-1} are probably due to Ga-Cl and S-N combination modes, since gallium trichloride complexes show strong Ga-Cl bands in this region 340-400 cm^{-1} (ν sym.(Ga-Cl)= 348 $\pm$ 2 and ν asym (Ga-Cl) = 383 $\pm$ 3 cm^{-1})[167] The very strong bands at 297 and 267 are assigned to Ga-Cl vibrations, and the relatively weak band at 228 cm^{-1} to Ga-N vibration.

In $S_4N_4.2InCl_3$, the band at 361 cm^{-1} is assigned to ν S-N, whereas the band at 314 cm^{-1} to ν In-Cl. The strong band at 403 may be due to either the In-N or to S-N vibrations.

In $S_4N_4.2FeCl_3$ the very strong band (broad) with peaks at 384 and 370 cm^{-1} is probably a combination band due to the coupling of S-N and Fe-Cl modes (S-N = 354 cm^{-1}, Fe-Cl in $FeCl_4^-$ = 385 cm^{-1} [156]). The band at 308 cm^{-1} is assigned to Fe-Cl analogy with other S_4N_4 adducts. The adducts $S_4N_4.2AlCl_3$ $S_4N_4.2GaCl_3$, $S_4N_4.2InCl_3$, $S_4N_4.2TlCl_3$ and $S_4N_4.2FeCl_3$ are all soluble in inert organic solvents (e.g. CH_2Cl_2) indicating that they probably are covalent structures rather than ionic structures of the type $(S_4N_4.MX_2)^+MX_4^-$.

For $S_4N_4.PhBCl_2$, few assignments can be made on account of the large number of additional bands due to the phenyl group. However the far infrared spectrum of the adduct is relatively simple and similar in many respects to other S_4N_4 adducts of group III halides (e.g. $S_4N_4.2AlCl_3$). By analogy with other

adducts, it may have a structure with monodentate S_4N_4.
In the far infrared spectrum of $S_4N_4.PhBCl_2$ the strong band at 420 is either due to S-N or B-N vibration. The strong bands at 360 cm^{-1} is assigned to S-N as usual. The strong bands at 314 and 282 are assigned to B-Cl by analogy with other S_4N_4 adducts, (BCl_2 assym. deformation = 330 cm^{-1}, BCl_2 sym. deformation 230 cm^{-1})[47a].

The structure of $S_4N_4.2AlBr_3$ appears to be different from the above adducts, since the infrared spectrum is different (Table 2). The low solubility and relatively high melting point of this adduct indicates that it may have an ionic structure of the type $(S_4N_4.AlBr_2)^+.AlBr_4^-$. The near infrared spectrum shows three strong peaks at 1126, 869 and 473 in addition to other weak peaks. Since in the complex $AlBr_3.Et_2O$, the band at 445 cm^{-1} has been assigned to Al-Br stretching mode[171], the band at 438 in $S_4N_4.2AlBr_3$ is assigned to ν Al-Br. The very strong bands at 1126 and 869 cm^{-1} are assigned to S-N. In the far infrared spectrum of this adduct a strong band at 349 cm^{-1} can be assigned to Al-Br (cf. Al-Br in $BrCN \rightarrow AlBr_3$ absorbs at 341 and 445 cm^{-1}).

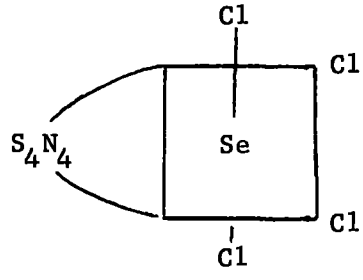
The structures of $S_4N_4.TeCl_4$ and $S_4N_4.SeCl_4$

The infrared spectrum of $S_4N_4.TeCl_4$ is similar to the infrared spectrum of $S_4N_4.SbCl_5$, as shown below:

$S_4N_4.SbCl_5$ 1058 vs, 975 vs, 807 vs, 786 vs, 722 ms, 682 s, 651 w, 623 vs, 563 w, 511 vs cm^{-1}.

$S_4N_4.TeCl_4$ 1047 vs, 966 vs, 806s, 760vs (SN), 727 vw, 671ms, 635ms, 613ms, 563 w, 500 vs, cm^{-1}.

In the far infrared spectrum of $S_4N_4.TeCl_4$, there are only three bands, two strong and broad bands at 360 and 251 cm^{-1} and a weak band at 225 cm^{-1}. The very strong broad band at 360 may be due to combination of S-N and Te-Cl modes since both $TeCl_4$ and S_4N_4 have strong absorption bands in this region ($TeCl_4$; 358 vs and 347 vs cm^{-1} [168,169]; S_4N_4, 347 s[161]) or it may only be due to S-N vibration. The broad band in the region 22-286 cm^{-1} centred at 251 cm^{-1} is probably caused by Te-Cl and Te-N vibrations. The assignment of frequencies in the near infrared spectrum of $S_4N_4.TeCl_4$ can be done in the same way as in the case of $S_4N_4.SbCl_5$. The structure of $S_4N_4.SeCl_4$ may be either six coordinate as in $SeCl_4$ ethylenediamine[145] or ionic as in $SeCl_4.2py$[138].



$[S_4N_4\text{-}SeCl_3]^+Cl^-$

or $[(S_4N_4)_2SeCl_2]^{2+}SeCl_6^{2-}$

Its insolubility in inert organic solvents may indicate an ionic structure. In their discussion of the infrared spectrum of $SeCl_4$,

George, Katsaros and Wynne[169] concluded that the available vibrational data are in accord with the presence of $SeCl_3^+$ spectra in solid $SeCl_4$ but are inconclusive regarding the nature of the anionic species. Since the far infrared spectrum of $((CH_3)_4N)_2.SeCl_6$ yields absorptions at 294 and 184 cm^{-1} which are absent in $S_4N_4.SeCl_4$, it seems more likely that $S_4N_4.SeCl_4$ has an ionic structure of the type $(S_4N_4.SeCl_3)^+Cl^-$. In the far infrared spectrum of $S_4N_4.SeCl_4$, the bands at 383 is assigned to an S-N vibration, because S_4N_4 has S-N bending mode at 347 cm^{-1} which may have shifted to 383 cm^{-1} on coordination, or it may be due to the coupling of Se-Cl and S-N modes. The band 403 cm^{-1} may be an additional S-N band due to coordination or it may be due to Se-N vibration. The solid $SeCl_4$ shows absorption bands at: 371 vs, 348 vs, 275 s, medium strong (broad) and 205 weak, therefore, the bands at 337 s, 309 s and medium strong bands broad in the region 260-217 cm^{-1} are assigned to Se-Cl vibrations.

The structures of $S_4N_4.WBr_4$, $S_4N_4.WCl_4$ and $S_4N_4.WOCl_4$(?)

The halides WX_4 (X= halogen) form a number of complexes of the type $WX_4.2L$ (L=monodentate: pyridine, RCN, dimethyl sulphoxide[173]) and $WX_4.L$(L= bidentate: 2,2'-bipyridyl)[173]. The complexes are obtained either from the tetrahalides or from higher halides.

The infrared spectra of $S_4N_4.WBr_4$ and $S_4N_4.WCl_4$ are different from the infrared spectrum of $S_4N_4.SbCl_5$. By virtue of the chelating nature of the ligand and on account of the tendency for WCl_4 and WBr_4 to achieve six coordination, the adducts $S_4N_4.WBr_4$ and $S_4N_4.WCl_4$ may have six coordinate structures, with bidentate S_4N_4 (cf. $MX_4.2,2'$-bipyridyl).

The infrared spectrum of the complex obtained from S_4N_4 and $WOCl_4$ shows some similarity with the infrared spectra of $S_4N_4.WBr_4$ and $S_4N_4.WCl_4$ (major peak at 1000 (vs) cm^{-1}).

This compound may be $S_4N_4.WOCl_4$ (but with structure different from $S_4N_4.SbCl_5$) or, since $WOCl_4$ is easily reduced, $S_4N_4.WOCl_3$. The structure of the latter may be similar to $WOX_3.2,2'$-bipyridyl complexes[147] (formed in reactions of the oxytetrahalides of tungsten with bipyridyl, and which contain six coordinate tungsten).

In the far infrared spectrum of $S_4N_4.WCl_4$, the band at 406 cm^{-1} may be due to either S-N or W-N vibration. The strong broad band in the region 286-385 is probably caused by W-N and S-N vibrations (S-N (deformation) = 347 cm^{-1} in S_4N_4[161], ν W-Cl (stretching) = 355 cm^{-1} Similarly in $S_4N_4.WBr_4$ the band at 405 cm^{-1} may be due to either S-N or W-N vibrations and the absorptions in the region 270-357 may be due to combinations of S-N and W-Br modes.

The preparation and reactions of trithiazyl trichloride

Baumgarten[174] has reported that pyridine reacts with sulphuryl chloride to give a complex oil product, which was thought to be $(C_5H_5NCl)SO_2Cl$ and $(C_5H_5NCl)_2SO_2$. This reaction has been repeated by Banister and Moore[128] and obtained an oily product of the formula $(C_5H_5N)_2SO_2Cl_2$, irrespective of the mole ratio of the reactants. By analogy with the above reaction, it was decided to study the Lewis acid behaviour of sulphuryl chloride towards tetrasulphur tetranitride. It was found that in this case, no adduct is formed but sulphuryl chloride slowly acts as a chlorinating agent to give trithiazyl trichloride (page 70). This is not surprising, because sulphuryl chloride is used as a chlorinating agent in a number of reactions, e.g. $Ph_3As+SO_2Cl_2 \rightarrow Ph_3AsCl_2$[175].

Trithiazyl trichloride may be prepared by the method described by Demarcay[127] and Meuwsen[103] and revised by Schroder and Glemser[117], of passing chlorine through a suspension of S_4N_4 in an inert solvent or by the method described by Meuwsen[103] and revised by Jolly and Maguire[104] involving the chlorination of the solid $S_3N_2Cl_2$. Jolly and Maguire prepared $S_3N_3Cl_3$, with a melting point of 91°C, from $S_3N_2Cl_2$ and chlorine, while Schroder and Glemser reported a melting point of 162.5°C for the $S_3N_3Cl_3$ prepared from S_4N_4 and chlorine. Trithiazyl trichloride obtained from the

reaction of sulphuryl chloride and S_4N_4 closely resembles that of Jolly and Maguire. This compound has a melting point of 89-91°C (decomp.) before recrystallisation, whereas the recrystallised $S_3N_3Cl_3$ melted at 93-94°C. It has been proposed[91] that this lowering of melting point is not principally due to depression of melting point by significant amounts of impurities, but is decomposition catalysed by small amounts of impurities.

We also prepared trithiazyl trichloride from S_4N_4 and chlorine by the method described previously[117], but observed that the infrared spectrum of the product varies remarkably with the experimental conditions. The simplest infrared spectrum (below) is obtained if the chlorination of S_4N_4 is carried out under the following conditions:

(i) large volume of the inert solvent in which S_4N_4 is suspended or dissolved.

(ii) slow rate of chlorination

(iii) short time or chlorination until all the S_4N_4 is dissolved; filter as soon as a clear red solution is obtained.

If the volume of the solvent in which S_4N_4 is suspended is small and the rate of chlorination is fast and for a longer time after the stage when a clear red solution is obtained, the reaction gives a product which even after recrystallisation from carbon tetrachloride has a much more complex infrared spectrum . (see section (ii) below)

The compound obtained by slow chlorination (of S_4N_4 suspension or dilute solution) melted at 89-91°C (recryst. CCl_4). The infrared spectrum of this compound was similar to the infrared spectrum of the trithiazyl trichloride prepared from S_4N_4 and SO_2Cl_2; though the peak 1015 cm^{-1} was broader than for the latter. This was almost certainly due to difference in particle size in the mull. The crystalline form is identical to the S_4N_4/Cl_2 product as studied by Wiegers and Vos[107,108].

Sample system	Wiegers monoclinic (from S_4N_4/Cl_2)	Hazell[176] monoclinic (S_4N_4/SO_2Cl_2)
a	5.55 Å ± .01	5.54 Å
b	11.23 Å ± .02	11.14 Å
c	6.13 Å ± .01	6.13 Å
α	90	90
β	99.2° ± .2	99.5
γ	90	90
Space group	$P2_1/m$	$P2/m$
or	$P2_1$	or $P2_1$
mols/cell	2	2

The infrared spectrum of $S_3N_3Cl_3$ obtained from $S_4N_4 + Cl_2$ (slow chlorination) or $S_4N_4 + SO_2Cl_2$ showed the following peaks: 1018 vs, 698 ms, 621 w(br), (514 ms, 488 ms) (br), 380 w, 320 w (br).

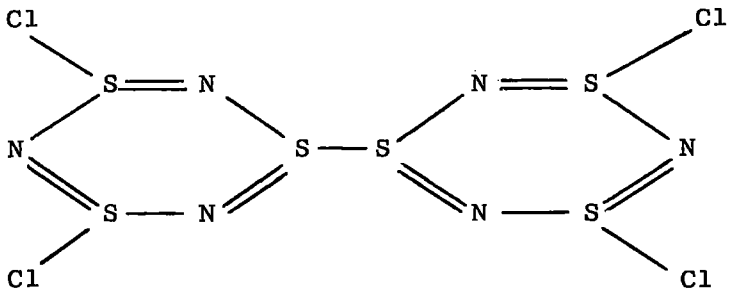
The highest frequency absorption at 1018 cm^{-1} is assigned to an S-N stretching frequency, the highest bands in other SN systems occur at: 1325 cm^{-1} (NSCl)[93], 1153 cm^{-1} (S_4N_3Cl)[133] 1085 cm^{-1} ($S_3N_3F_3$)[97], 925 cm^{-1} (S_4N_4)[161]. The higher S-N stretching frequency in $S_3N_3Cl_3$ compared with S_4N_4 is expected on account of the higher S-N bond order (sulphur-nitrogen bond) distances are: 1.60Å in $S_3N_3Cl_3$[107,108] and 1.62Å in S_4N_4[30]). The medium strong band at 698 cm^{-1} is probably a stretching rather than a bending mode (ν (stretching in S_4N_4 is at 696 cm^{-1}, the highest frequency bend ν (deformation) is at 347 cm^{-1}), whereas the weak (broad) band at 621 cm^{-1} cannot be assigned with certainty, because S-Cl and S-N modes appear in this region[156]. The medium strong broad band in the region 526-477 cm^{-1} with peaks at 514 and 488 cm^{-1} may be assigned to S-Cl stretching, because S-Cl stretching in NSCl is assigned at 414 cm^{-1}[93]. In the far infrared spectrum of $S_3N_3Cl_3$ (from S_4N_4 and SO_2Cl_2) the weak band at 380 cm^{-1} is assigned to S-N bending mode by analogy with S_4N_4 (S-N deformation) = 347 cm^{-1} whereas the weak broad band centred at 320 cm^{-1} is assigned to NSCl (ν NSCl (bending) = 273 cm^{-1})[93].

Mass spectrum of $S_3N_3Cl_3$

m/e	relative intensity	assignment
32	43	S
46	262	SN
64	100	S_2

m/e	relative intensity	assignment
78	240	S_2N
92	372	S_2N_2
138	242	S_3N_3
174	150	S_3N_3Cl
210	170	$S_3N_3Cl_2$

(ii) The rapid chlorination of S_4N_4 with chlorine gave a product which apparently contains a new compound. Chlorine gas was bubbled at a very fast rate through S_4N_4 suspension in carbon tetrachloride and at room temperature (page 72). This compound was prepared twice, but each time the analytical figures were different (page 72) and it was not possible to give definite formula for this compound. However it appears to consist of $S_3N_3Cl_3$ and a compound containing two cyclotrithiazyl rings as shown below (analytical figures correspond to a 2:3 mixture);



The outstanding difference in the isolation procedure is that this product precipitates out; (this is not just because the reaction solution is stronger; similar quantities of S_4N_4+CCl_4 solution were used as in the usual $(NSCl)_3$ preparation).

A relatively large number of extra peaks appear in the infrared spectrum and these are retained on crystallisation. The infrared spectrum is different from $S_3N_3Cl_3$, the comparison is given below,

$S_6N_6Cl_4$: 1011 vs, 943 w(sh), 893 ms(sh), 781 w(sh), 699 w(sh) 687 vs, 671 vw(sh), 662 vs, 625 vw(sh), 576 ms, 546 vs, 517 w(sh), 504 ms, 452 ms(br) cm^{-1}.

$S_3N_3Cl_3$ (from $S_4N_4/SOCl_2$) : 1018 vs, 698 ms, 621 w(br), (514 ms, 488 ms) (br) cm^{-1}.

All the bands above 680 cm^{-1} are assigned to S-N stretching vibrations, by analogy with $S_3N_3Cl_3$ and other sulphur nitrogen compounds (p.139). The medium strong broad band at 452 cm^{-1} may be assigned to νS-S because S-S modes appear in the region 400-500 cm^{-1}[177]. The strong band 546 is probably due to S-Cl stretching mode. The strong band at 662 cannot be assigned with certainty.

(iii) Trithiazyl trichloride and Cl_2 or CO:-

When trithiazyl trichloride obtained from S_4N_4 and SO_2Cl_2 was dissolved in a large volume of CCl_4 and chlorine gas was slowly bubbled through the solution, it was observed from the infrared spectrum of the evaporated product that $S_3N_3Cl_3$ does not undergo any further change. However, the compound tentatively proposed as $S_6N_6Cl_4$ is the major product in a reaction of $S_3N_3Cl_3$ (from S_4N_4/SO_2Cl_2) with carbon monoxide, giving a small amount of S_4N_3Cl.

The mechanism of the formation of $S_6N_6Cl_4$ appears to be complex, but may be as follows[178].

(1) $S_4N_4 + Cl_2 \longrightarrow S_3N_3Cl \xrightarrow{Cl_2} S_3N_3Cl_3$

(2) $S_3N_3Cl + S_3N_3Cl_3 \longrightarrow S_6N_6Cl_4$

the formation of $S_6N_6Cl_4$ may well depend upon a build up of concentration of S_3N_3Cl or some other incompletely chlorinated sulphur-nitrogen species as follows:

$$S_4N_4 \xrightarrow{\text{Fast}} \text{solution intermediate} \xrightarrow{\text{Fast}}$$

red S_3N_3Cl ⟷ (MED.) ⟷ yellow $S_6N_6Cl_4$

MED. yellow $S_3N_3Cl_3$ m.p.89-91°C

slower appreciably if solid $S_6N_6Cl_4$ precipitate out

m.p. 58-64°C (decomp.)

Reactions of trithiazyl trichloride (from S_4N_4 and $SOCl_2$):

(a) Attempted preparation of sulphanuric chloride from trithiazyl trichloride

The preparation of sulphanuric chloride involves the isolation and pyrolysis of the extremely hygroscopic trichlorophosphazosulphuryl chloride[179]. The trichlorophosphazosulphuryl chloride does not pyrolyse to give sulphanuric chloride if the sample is impure. Alternatively sulphanuric chloride can be obtained in a very poor yield by heating the pale yellow adduct of $S_3N_3Cl_3$ with sulphur trioxide.[6]

Since $(NSCl)_3$ is a relatively simple preparation the synthesis of sulphanuric chloride by the oxidation of trithiazyl trichloride was attempted. The use of SeO_2 and I_2O_5 as the oxidising agents were unsuccessful, because in each case the oxidising agent gave a new reaction product, which (from the i. r. spectrum) was not sulphanuric chloride. Trithiazyl trichloride did not undergo any oxidation, when a mixture of molecular oxygen and ozone was bubbled through a solution in CCl_4 at room temperature or at 60°C. Failure of trithiazyl trichloride to undergo direct oxidation with molecular oxygen is in contrast to the reaction that occurs with other sulphur nitrogen compounds

e.g. $S_4N_4H_4 \xrightarrow[110\text{-}120^oC]{O_2} (HNSO)_4$

(b) Reaction of trithiazyl trichloride with diphenyl mercury and pyridine

α-Sulphanuric chloride reacts with diphenylmercury to form diphenylsulphanuric chloride, $N_3S_3O_3Cl(C_6H_5)_2$[180]. It was though to prepare the analogous compound $S_3N_3Cl(Ph)_2$ by the reaction of trithiazyl trichloride with diphenyl mercury. However, it was found that diphenyl mercury gives an adduct with $S_3N_3Cl_3$ ($S_3N_3Cl_3 \longrightarrow Hg(Ph)_2$).

By analogy with the reaction of sulphanuric chloride with pyridine[128], it was decided to study the reaction between the trithiazyl trichloride and pyridine. Trithiazyl trichloride reacted with pyridine to give a pale yellow solid. The infrared

spectrum showed retention of the SN ring, shifts in the frequencies were slight. The exact stoichiometry is not established on account of variable analyses (p. 77)

The above two reactions exhibiting the donor and acceptor behaviour of trithiazyl trichloride.

(c) Reaction of trithiazyl trichloride with epibromohydrin, epichlorohydrin, ethylene oxide and butylene oxide

Peters and Kharasch[181] have studied the reaction between sulphuryl halides and epoxides e.g. ethylene oxide reacts with 2,4-dinitrobenzenesulphenyl chloride to give $Cl.CH_2.CH_2OSC_6H_5$. Since trithiazyl trichloride reacts vigorously with alcohols (not reported in experimental section) to give complex mixtures, it was hoped that epoxides would give trithiatriazene esters without ring cleavage. Epibromhydrin, epichlorohydrin, ethylene oxide, butylene oxide all apparently gave the required compounds. Epibromohydrin and epichlorohydrin gave white solid compounds whereas red oil products were obtained in the case of ethylene oxide and butylene oxide.

The infrared spectra of these compounds are given below,

$S_3N_3Cl_3(O.CH_2CHCH_2Br)_3$: 1429 vw, 1370 vs, 1299 vw, 1266 vw, 1235 vw, 1220 vw, 1205 vw, 1176 vw, 1104 vw, 1047 w(sh), 1036 vs, 1011 s, 990 vs, 962 s, 952 s(sh), 901 w(sh), 885 vs, 870 s, 855 vw(sh), 848 vw (sh), 826 vs, 781 ms, 769 vs, 746 s, 719 vs,

	694 s, 685 s, 667 s, 637 ms, 623 ms, 617 w (sh), 597 s, 564 ms, 532 vw, 526 vw, 516 vw, 504 ms, 489 ms, 435 ms, 423 s, 4000 vw(sh), 388 vs, 361 s, 348 w, 323 ms, 274 vw, 253 w, 240 ms cm^{-1}.
$S_3N_3Cl_3.(O.CH_2.CH.CH_2Cl)_3$	1342 vw, 1290 vw, 1258 vw, 1250 vw, 1212 vw, 1188 vw, 1149 vw, 1099 vw, 1053 vw(sh), 1036 vs, 1020 s, 990 vs, 962 vs, 901 vw(sh), 885 vs, 855 s(sh), 833 vs, 787 w(sh), 775 vs, 763 vw(sh) 730 vs, 709 vw, 699 ms, 676 s, 658 s, 570 s, 544 s, 521 vw(sh), 513 s, 495 ms, 442 ms, 428 s, 408 ms, 392 s, 377 s, 347 s, 331 ms, 276 s, 258 ms, 245 s, 227 ms(br), 216 vw, 213 vw cm^{-1}.
$S_3N_3Cl_3.(O.CH_2\text{-}CH_2)_3$	1453 vw(sh), 1430 w, 1379 vw, 1307 ms, 1258 vw (sh), 1198 vw, 1136 vw(sh), 1042 vs, 995 vs, 876 vs, 855 vs, 766 w(sh), 722 w(sh), 707 vs, 667 vs, 536 vw, 392 ms cm^{-1}.
$S_3N_3Cl_3.(O.CH_2\text{-}CH.CH_2.CH_3)_3$	1471 ms, 1439 vw(sh), 1372 vw(sh), 1370 w, 1312 w, 1252 vw, 1205 vw, 1042 vs, 980 vw(sh), 957 vs, 917 s, 866 s, 791 vs, 741 s(br), 694 vw(br), 673 vs(br), 556 vw, 420 ms, 402 vw, 395 vw, 387 vw cm^{-1}.

The assignment of the infrared active bands in these compounds cannot be done with certainty because S-N vibrational modes occur in the same region in which epoxides give absorption bands e.g. in ethylene oxide the bands at 1165, 1265 and 865 are associated with the epoxy group[182].

(d) Reaction of trithiazyl trichloride with nitriles

It was considered[125] that trithiazyl trichloride is likely to react in (at least) three ways: (i) as a sulphenyl chloride, RSCl, i.e. as an acid chloride of the hypothetical acid $(NS-OH)_3$ (see ref. 183 for a review of sulphenyl halide reactions). (ii) as a source of N≡S-Cl at temperatures sufficiently high to cause significant dissociation: $S_3N_3Cl_3$ 3NSCl. The thiazyl chloride monomer should then be able to copolymerise with other unsaturated systems containing CC,CN or CS multiple bonds, and (iii) reaction with X-H bonds (elimination of HCl).

Olefins can react in all three ways, chlorinated olefins as (i) and (ii); consequently the reaction between trithiazyl trichloride and tetrachloro ethylene was studied in some more detail by Banister[125]; a compound of empirical formula $S_2N_2C_2Cl_4$ was isolated.

The first reaction in the nitrile series, viz. the reaction between trithiazyl trichloride and trichloroacetonitrile was

initially performed to check if a reaction of the type (ii) above were possible. It was also hoped that the product(s) obtained from $S_3N_3Cl_3$ and trichloroacetonitrile might shed some light (e.g. by comparing infrared spectra) on the $S_3N_3Cl_3/C_2Cl_4$ reaction. A fully chlorinated nitrile was chosen because of the possibility of complications arising due to simultaneous reactions of type (iii), e.g.[184]

$$Cl_2CH - C\equiv N + PCl_5 \longrightarrow Cl_2C=C(Cl) - N=PCl_3 + HCl$$

$$\downarrow Cl_2 \text{ (from } PCl_5)$$

$$Cl_3C - CCl_2 - N = PCl_3.$$

(a) Reaction between $S_3N_3Cl_3$ and $Cl_3C.CN$.

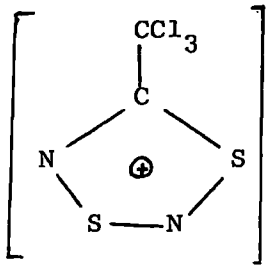
Trithiazyl trichloride (S_4N_4/SO_2Cl_2) was found not to react with $S_3N_3Cl_3$ at room temperature; a reaction temperature of 60°C was chosen by analogy with the reaction between $S_3N_3Cl_3$ and C_2Cl_4[125]. The reaction solution slowly undergoes colour changes from green to pale yellow to red and a yellow crystalline product was obtained which was found to be identical to the $S_2N_2C_2Cl_4$ obtained from $S_3N_3Cl_3/C_2Cl_4$ (page 85). The colour change which may be ascribed to the intermediate formation in solution of monomeric thiazyl trichloride does not seem very likely since (i) the bright green colour of the solution and (ii) perceptible dissociation in vacuum commences at 70-80°C[91].

This agrees with the proposal that monomeric thiazyl chloride does not form in solution unless at high temperatures (above 70°C)[91]. Analyses are given below (same batch of compound analysed at Durham).

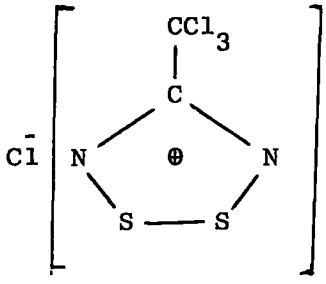
	Found		Calculated		
	anal.1	anal 2.	$S_2N_2C_2Cl_4$	$S_2N_2C_2Cl_5$	$S_2N_3C_2Cl_5$
C	9.59	9.99	9.53	8.19	7.81
Cl	55.89	52.80	55.04	60.34	57.72
N	11.60	10.85	10.85	9.54	13.66
S	24.75	21.98	24.80	21.81	20.81
Total	101.83	86.28			

Structure and the infrared spectrum of $S_2N_2C_2Cl_4$

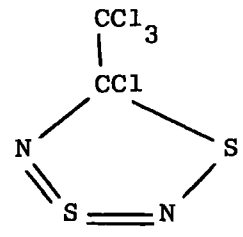
The m.p.(decomp. above 100°C) and the infrared spectrum of this compound is identical to the infrared spectrum of the product of the $S_3N_3Cl_3$ and C_2Cl_4 reaction (M.P. 205-208 decomp.) The following structures are proposed on the basis of the information discussed below:



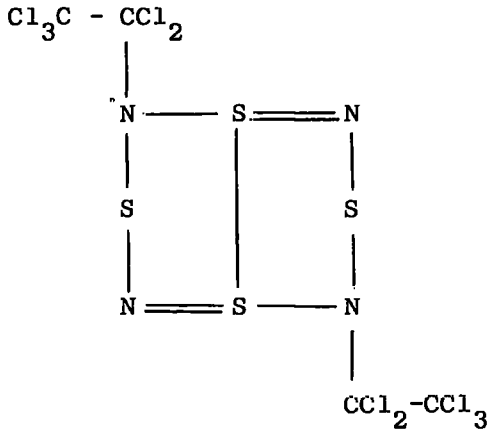
(I)



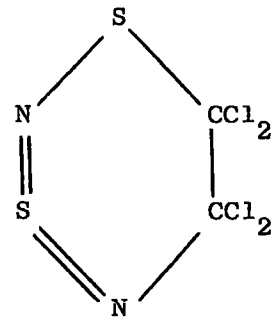
(II)



(III)



(IV)



(V)

Structure (IV) suffers from the disadvantage that it is difficult to see how it could arise from $S_3N_3Cl_3/C_2Cl_4$. Similarly it does not seem likely that structure (V) could arise from $S_3N_3Cl_3/Cl_3CCN$. The infrared spectrum shows no localized C=N (1630-1690 cm^{-1})[182] or C=C peaks (1620-1645 cm^{-1})[185] unless the absorptions happen to be very weak (C=N and C=C absorptions are often weak). The doublet at 1302 and 1270 cm^{-1} is intermediate in frequency between that expected for aC-N single bond (1100 cm^{-1}) and a C=N double bond (1600 to 1700 cm^{-1})[42] and so could be ring vibration(s) predominantly associated with CN stretching.

In view of the low solubility of $S_2N_2C_2Cl_4$ in non-polar (or low polarity) organic solvents and very low volatility (it cannot be sublimed in vacuum until 100°C and then decomposition occurs), the ionic structure appears to be more likely.

Such a structure is analogous with the structures of $S_3N_2Cl_2$[6] and 4-phenyl-1,2-dithiolium iodide, S_2C_3PhI.[187]

Further evidence for a structure containing a CCl_3 group comes from a study of the infrared spectrum of this compound. $\nu_{sym}CCl_3$ and $_{asym}CCl_3$ in $Cl_3C.CN$ occur at 787 and 491 cm^{-1} respectively[188] and peaks approximately in these positions (781 and 483 cm^{-1}) occur in $S_2N_2C_2Cl_4$. The strong band in the region 833-741 cm^{-1} is assigned to ν_{sym} CCl_3 by analogy with trichloroacetonitrile. Similarly the medium strong broad band in the region 500-465 centred at 483 with shoulders at 495 and 471 cm^{-1} is assigned to ν_{sym} CCl_3. The very strong band at 1052 cm^{-1} may be due to either S=N or C-N since trichloroacetonitrile absorbs in this region (ν C-C = 1000 cm^{-1})[189] The strong band at 543 cm^{-1} cannot be assigned with certainty.

(b) Reaction between $S_3N_3Cl_3$ and Bu^tCN

Trithiazyl trichloride was found not to react with tertiarybutyl cyanide at room temperature (for 24 hours). A 58°C reaction temperature was chosen by analogy with the Cl_3CCN reaction, a golden yellow precipitate was obtained (page 84). The analytical figures are given on page 151, (same batch of compounds).

	Found		Calculated		
	anal.1 (at Durham)	anal.2 (Weiler & Strauss)	$S_2N_2C_2(CH_3)_3Cl$,	$S_2N_2(CH_3)_3Cl_2$,	$S_2N_3C_2.(CH_3)_3Cl_2$
C	28.90	29.39	30.56	25.86	24.39
H	3.79	4.34	4.58	3.88	3.66
Cl	33.10	16.25	18.00	30.60	28.86
N	11.37	9.37	14.26	12.04	17.07
S	31.85	26.55	32.59	27.58	26.02
Total	109.01	85.90			

It is likely that this compound is $S_2N_2C_2(CH_3)_3Cl$, by analogy with $S_2N_2C_2Cl_4$ and similar structures can be considered for this compound. The infrared spectrum shows some similarity with the infrared spectrum of $S_2N_2C_2Cl_4$ (the peaks at 543, 676 and 855 cm^{-1} in $S_2N_2C_2Cl_4$ also appear in the presumed $S_2N_2C_2(CH_3)_3Cl$ at 551, 733 and 855 cm^{-1}). The peak at 733 cm^{-1} may be due to S-N, while the peak at 551 cm^{-1} cannot be assigned with certainty.

(c) The reaction between $S_3N_3Cl_3$ and benzonitrile

Trithiazyl trichloride was found not to react with benzonitrile at room temperature. The reaction at about 60°C gave four products two of which (products 2 and 3, page 88) proved to be the same. The first product settles down from the red solution during reaction and has an infrared spectrum similar to products 2 and 3 but with extra peaks in the region 794-767 cm^{-1}, which are lost on recrystallisation from PhCN or $SOCl_2$ (though the latter recrystallisation gives additional absorption at 510 cm^{-1}). Thus after recrystallisation from PhCN product 1 is the same as product 2 (the crystals that collect near the filter frit during reaction) and product 3 (the crystals that deposit on cooling the filtrate). Products 1 (recrystallised 1'), 2 and 3 do not give satisfactory analyses but i.r. similarities (two absorptions between 910 and 833 cm^{-1} one ~ 552 cm^{-1} and one near 700 cm^{-1}) to the Cl_3CCN and $(CH_3)_3CN$ products suggest similar structures for these three compounds.

Product 4 was obtained from the filtrate (left after filtering the product 3) by evaporation to dryness. A dark-yellow precipitate was obtained which was recrystallised from CCl_4 or CH_2Cl_2. After recrystallisation the compound was pale yellow and analyses (page 88) correspond to an empirical formula:

$$(NSCl)_3.PhCN$$

The infrared spectrum of this compound was different from other products (1 and 2). An 8-membered ring is proposed for this compound by analogy with $(NSF)_4$.

Numerous C-H absorptions occur between 1660-740 cm^{-1} as in PhCN, though the strong absorptions at 1342, 1179, 910 cm^{-1} may indicate superimposed CN and/or SN. The strong peaks at 701 and 790 are probably the characteristic peaks associated with mono-substituted benzene derivatives (usually at 694-701 cm^{-1} (CH deformation) and 758-747 cm^{-1} (CC stretching)[185,189]. The single absorption in the region 588-500 cm^{-1} is replaced by four: 525, 493, 473, 419 cm^{-1}. SCl may be responsible for one or more of these.

APPENDIX 1

Calculations of force constants[157]

Gordy's rule:- A relation of the form,

$$k = aN\,(X_A.X_B/d^2)^{\frac{3}{4}} + b$$

has been found to hold accurately for a large number of molecules in their ground states. Here k is the bond stretching force constant, d the bond length, N the bond order, and X_A and X_B are the electronegativities of the bonded atoms. k is measured in dynes/cm x 10^{-5} and d in Angstrom units, a and b have the values 1.67 and 0.30 respectively, for stable molecules exhibiting their normal covalencies, except those in which both bonded atoms have only one electron in their valency shell.

Thus since N-Sb = 2.17Å

X_A(N) = 3.07 (Allred-Rochow)

X_B(Sb) = 1.82 (Allred-Rochow)

and N = 1

Therefore, the (N-Sb) force constant =

$$1.67\,(3.07 \times 1.82/2.17^2)^{\frac{3}{4}} + 0.30$$

$$= 2.2 \times 10^5 \text{ dyne/cm.}$$

Now ν Sb-N = $1303.16\,(\lambda)^{\frac{1}{2}}$

Where $\lambda = \frac{\text{force constant}}{\text{reduced mass}} = \frac{k}{\mu}$

($\mu = \frac{m_1 m_2}{m_1 m_2}$, where m_1 and m_2 are atomic weights of N(14.007) and Sb(121.75) respectively).

$$\text{Sb-N} = 1303.16\ (2.2 \times 0.07959)$$

$$= \underline{545\ \text{cm}^{-1}}$$

Similarly using the values of electronegatives of 3.04 for nitrogen and 2.05 for antimony (Pauling-type values), a value of 565 cm^{-1} was obtained for the Sb-N stretching frequency.

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