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# A SPECTROSCOPIC STUDY OF SOME HALOGENO- COMPLEXES OF TELLURIUM (IV)

by

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A thesis submitted in part fulfilment of the requirements
for the degree of Master of Science in the University of Durham.

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TO MY MOTHER

and

TO MY FATHER'S MEMORY

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# ABSTRACT

The aim of this work was to prepare and structurally characterise a series of halogeno- complexes of tellurium (IV). The principal technique used in the structural determination was to have been tellurium-125 nuclear magnetic resonance spectroscopy, used in conjunction with the method of pairwise interactions. Unfortunately, although this method has been used elsewhere with great success, the chemical shifts obtained in the present study did not yield any consistent results, and the presence of a pair of electrons, not formally involved in bonding, is presented as a possible cause of this behaviour.

Far-infrared and laser Raman spectroscopy were used in a qualitative manner to determine the configurations of the penta- and hexachlorobromo-complexes and the results obtained were found to agree with those predicted by a stereochemical model developed for complexes of tin. Assignments of new species were made, as far as possible, by analogy with published results for the corresponding complexes of selenium (IV) or antimony (V) and, in some cases, different assignments are given for previously reported species of tellurium (IV). Complexes containing iodine were found to give more complicated results but the new species $TeI_4X_2^{2-}$ (X=F,Cl,Br) were prepared and characterised as well as the $TeBr_4I^-$ anion. The attempted preparation of novel fluoro- species generally led to the isolation of the pentafluorotellurate anion, although the $TeBr_4F^-$ ion is reported for the first time.

The preparation of the unknown hexafluorotellurate anion was also attempted, and although it could not be isolated, some evidence was obtained for its presence in an excess of starting materials.

Finally, the behaviour of tellurium dioxide in anhydrous hydrogen chloride and hydrogen bromide has been studied. In both cases tellurium tetrahalide is formed and, for the chlorine compound, further reaction occurs to yield a chloroxo- species. A possible reaction pathway is proposed. The analagous aqueous systems were also investigated.

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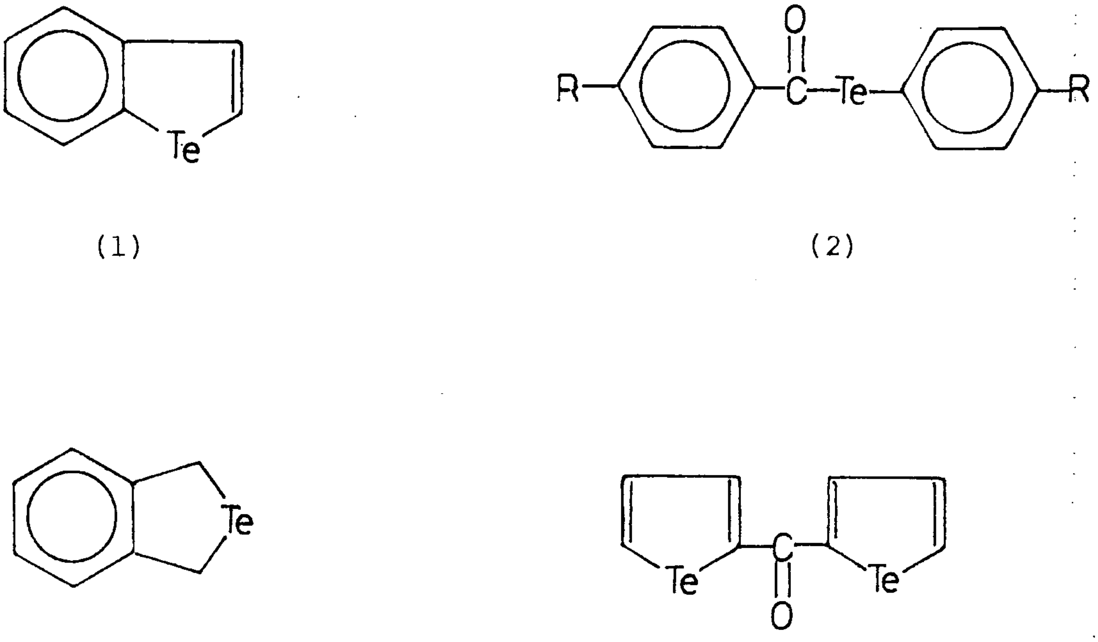
# CHAPTER ONE

## PREVIOUS STUDIES IN TELLURIUM-125 NUCLEAR MAGNETIC RESONANCE (N.M.R.) SPECTROSCOPY

Tellurium-125 ($I=\frac{1}{2}$; natural abundance 7.03%) has a receptivity of only $2.21 \times 10^{-3}$, relative to that of the proton, and this has delayed the direct observation of its chemical shift in systems of interest to the chemist until the advent of Fourier transform spectrometers, although measurements had been made on some solid state systems.[1] Prior to this, double resonance techniques were used in which the tellurium nucleus in question was coupled to a much more n.m.r.-receptive nucleus, usually a proton. If, when observing the proton spectrum, the sample is simultaneously irradiated at the tellurium resonance frequency, then the $^{125}$Te-$^{1}$H coupling will be destroyed. A knowledge of the exact frequency that gives optimum decoupling leads to the tellurium chemical shift. The results, obtained using this technique, for some organotellurium compounds, have been reviewed.[2]

The first high resolution Fourier transform study reported the effect of differing substituents on the chemical shifts of 2-substituted tellurophenes,[3] and since then a range of organic tellurium compounds has been investigated including benzotellurophene (Fig.1.1) and its derivatives,[4] tellurol esters[5] (Fig.1.2), 1,3-dihydrobenzotellurophene (Fig.1.3) and its dihalogeno- oxidation products,[6] cyclic and acyclic phenyltellurium compounds,[7(a)] di-2-tellurienylketone[7(b)] (Fig.1.4) and some trifluoromethyltellurium compounds.[8]

Phosphine tellurides ($R_3PTe$), tellurophosphines ($RTePR^1_2$) and their complexes,[9] tetraalkoxytelluranes,[10] diaryl ditellurides



(1) (2) (3) (4)

Figure 1

and diaryltellurium dichlorides and diacetates[11] have also been studied.

Very little work has been reported on exchange in tellurium compounds but diaryltellurides[12] and organic halogeno- compounds of tellurium (II) have been shown to exchange slowly whereas organotellurium (IV) halides exchanged rapidly even at 193K. The di- and tetrahalides themselves were found to undergo slow exchange at 213K. Chemical shifts ranged from 1743 to 3129 ppm. for tellurium (II) compounds and from 1508 to 2044 ppm. for those of tellurium (IV).[13]

The polyatomic cations[14,15] $Te_6^{4+}$, $Te_{4-n}Se_n^{2+}$, $Te_2Se_4^{2+}$ and $Te_3Se_3^{2+}$, exhibited chemical shifts between 152 and 3354 ppm., and use of $^{125}Te-^{125}Te$, $^{125}Te-^{123}Te$ and $^{125}Te-^{77}Se$ coupling constants was made in assignments.

The most comprehensive listing of chemical shifts for inorganic species has been presented by Goodfellow[16] and this is reproduced below:

TABLE 1.1

Reported Tellurium-125 N.M.R. Data for some Inorganic Tellurium Species

| SPECIES | CHEMICAL SHIFT (ppm.) | CONDITIONS |
|---|---|---|
| $TeCl_4$ | 1138 | 1M in $Me_2CO$ |
| $TeCl_4$ | 1725 | 1M in T.H.F. |
| $TeBr_4$ | 1442 | 1M in D.M.F. |
| $TeBr_4$ | 1962 | 1M in T.H.F. |
| $H_2TeCl_6$ | 1403 | 1M in $HCl/D_2O$ |
| $H_2TeBr_6$ | 1356 | 1M in $HBr/D_2O$ |
| $H_2TeI_6$ | 857 | 1M in $HI/D_2O$ |
| $(Bu_4N)_2TeCl_6$ | 1329 | 0.4M in $(CD_3)_2CO$ |
| $(Bu_4N)_2TeBr_6$ | 1341 | 0.3M in $(CD_3)_2CO$ |
| $H_6TeO_6$ | 712 | 1M in $D_2O$ |
| $K_2TeO_3$ | 1732 | 2M in $D_2O$ |

The tetrafluorotellurates (VI) cis and trans $(HO)_2TeF_4$, $HOTeF_4OMe$ and $(MeO)_2TeF_4$ have been prepared and their chemical shifts found to occur between 640 and 653 ppm.[17]. A study of the solvolysis of orthotelluric acid in anhydrous hydrogen fluoride yielded signals between 601 and 722 ppm., assignable to all possible intermediate species between $Te(OH)_6$ and $TeF_6$, although the signal for $TeF_6$ itself was not found.[18] Assignments were made on the basis of $^{125}$Te-$^{19}$F coupling constants which lay between 2754 and 3443 Hz. The chemical shift of $XeOTeF_5^+ SbF_6^-$ has also been reported at 576 ppm.[19]

Cis-trans isomerism has been observed in $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$[20] and the iron-tellurium cluster compounds $Fe_2(\mu\text{-}Te_2)(CO)_6$ and $Fe_3(\mu_3\text{-}Te)_2(CO)_9$[21] gave resonances at -733 and 1123 ppm. respectively.

Measurements of Larmor frequencies[22] and temperature effects on chemical shifts as well as a study of the relaxation mechanism for tellurium have been presented.[23]

# CHAPTER TWO

# THE HEXAHALOGENOTELLURATES

## INTRODUCTION

The species which form the subject of this chapter are discussed in two sections. The first section deals with the well known anions which contain only one halogen (excluding fluorine) whereas the second deals with mixed species, containing two halogens, some of which have not been previously reported.

## 2.1 The Hexachloro-, Hexabromo-, and Hexaiodotellurates

Although salts of these anions were known at the time of Berzelius,[24] they received only minor attention until the mid-1960's when far-infrared, laser Raman, Mössbauer and nuclear quadrupole resonance spectrometers became commercially available. This interest stemmed from the realisation, on the basis of early X-ray work, that the octahedral structure adopted by the anions, which possess fourteen valence electrons, did not conform to the distorted octahedral structure predicted by the valence shell electron pair repulsion theory of Gillespie and Nyholm.[25]

However, in spite of this new interest there are still only four recent reviews[26-29] and one monograph[30] which refer to these species.

### 2.1.1 X-Ray Diffraction Studies

This technique was first applied to the potassium rubidium, caesium, ammonium and thallium(1) hexachlorotellurates by Engel.[31] All, except potassium which was slightly distorted, were shown to be isostructural with $K_2PtCl_6$ and to crystallise with the fluorite lattice, and in each case the anions formed perfect octahedra. Subsequent investigations confirmed this for the ammonium[32] and rubidium[33] salts. Although further work reported noncubic symmetry in the unit cell, the anions in the dipyridinium,[34] hexa-aquo magnesium,[35] and tetrakis(ethylenethiourea)tellurium (II)[36] salts were also found to be octahedral. However, more recent work on the dipyridinium,[37] bis(N,N$^1$-dimethylformamidine)disulphide,[38] hydroxydimethylsulphonium-dimethylsulphoxide[39] and bis [(2,3-dihydro-3-hydroxy thiazolo[2,3-6] benzothiazolium]-dioxane[40] salts has shown some distortion in the anion to be present, this being ascribed to the cation, probably via hydrogen bonding.

A similar pattern emerged from the reported structures of the hexabromotellurates. The caesium,[41,42] ammonium[42,43] and hexa-aquo magnesium[35] salts were found to contain octahedral anions in a cubic structure. The symmetry of the unit cell in the potassium salt[44] was found to be distorted from that of $K_2PtCl_6$ although the anions were again octahedral. The distortion was attributed to the relative size of the cation and anion, the latter reorienting to lock the former in position and thereby achieving more efficient packing. The DL-α-ammonio-n-butyric acid[45(a)] and protonated discucinamide[45(b)] salts were found to be monoclinic and possess slightly distorted octahedral anions, the distortion being ascribed to hydrogen bonding. More extensive distortion was observed in the tetramethylammonium salt and the anion was found to define a slightly flattened trigonal antiprism.[46]

The hexaiodotellurates have been less extensively studied. The caesium,[47,48] and hexa-aquo magnesium[35] salts were shown to possess octahedral anions in a cubic unit cell, whereas an oxonium salt, $(H_7O_3^+)_2TeI_6.2H_2O$ [49] and the potassium salt[50] contain slightly distorted octahedral anions in an orthohombic and monoclinic unit cell respectively.

### 2.1.2 Nuclear Quadrupole Resonance (N.Q.R.) Spectroscopy

N.q.r. spectroscopy can provide information on chemical bonding and molecular structure in the solid state provided the nucleus under study possesses a quadrupole moment and is in sufficient natural abundance.[51] Chlorine, bromine and iodine satisfy the first condition and the technique has been successfully applied to a number of hexahalogenotellurates.

The earliest work presented results much in agreement with those obtained from X-ray diffraction[31,41,43,47,48,50] but ammonium hexaiodotellurate was assigned to a structure less regular than that of $K_2PtCl_6$.[52] Rubidium hexaiodotellurate[53] has been shown to have two kinds of crystallographically non-equivalent iodine atoms at room temperature, only adopting the fluorite lattice above 328K, whereas caesium-hexachlorotellurate displayed only one resonance at all temperatures studied, indicating the chlorine atoms to remain equivalent.

As mentioned above, n.q.r. can give information on chemical bonding. This can be achieved using the Townes-Dailey[55] procedure to assess the covalent character of the bond. As expected, the covalent character of the tellurium-halogen bond increased with decreasing difference between the electronegativities of the elements forming the bonds,[52] and was found to be lowest in caesium hexachlorotellurate.[54]

The effect of the cation on anion symmetry has been investigated for hexachlorotellurates.[56] The aim of the work was to try and distort the anion with a cation of low symmetry and compare the results with those obtained for hexachlorostannates and hexachloroplumbates. Any stereochemical effect of the lone pair (not present in $SnCl_6^{2-}$ or $PbCl_6^{2-}$) would be manifested in a decrease in ionic character (increase in n.q.r. frequency) as well as unequivalence in the chlorine atoms. However, no such results were observed, and the lone pair was presumed to remain "inert". The methylammonium salts of all three hexahalogenotellurates have also been shown to possess octahedral structures,[57] although there was some doubt about the space group for the hexachloro-salt ($CdI_2$ as opposed to $K_2PtCl_6$; the former being later confirmed by X-ray work.[58]).

Phase transitions[57-59] and molecular motion[60] have also been studied by n.q.r. in these species.

### 2.1.3 <u>Mössbauer Spectroscopy</u>

The Mössbauer Effect,[61] also known as nuclear $\gamma$-ray absorption or fluorescence, can be used to gain information on oxidation state and the nature of bonding by providing a measure of the s-electron density at the nucleus, in terms of the so-called isomer shift.

The early work of Shpinel *et al*[62-64] on hexahalogenotellurates demonstrated a linear dependence of isomer shift on the electronegativity of the attached halogen atom. An increase in halogen electronegativity caused a decrease in isomer shift reflecting the withdrawal of s-electrons from the nucleus and an increase in the ionic character of the bond.

This work was later refuted by Gibb *et al*[66] (see also [65]), who observed the reverse trend between halogen electronegativity and isomer shift. Their results were explained in terms of (i) direct removal of electron density through the bonds and (ii) radial expansion of the orbital involving the lone pair as the electronegativity of the halogen is decreased. Mechanism (i) will be effective for all elements and, in the absence of a lone pair, will lead to the trend observed by Shpinel *et al*. The effect of mechanism (ii) will depend upon the nature of the lone pair orbital and the reversal of the above trend indicates that this mechanism is dominant in the hexahalogenotellurates and that the lone pair must possess predominantly s-character. Later work has confirmed these results.[67]

The most recent work [68,69] has reported the absence of any effect due to alteration in the size or symmetry of the cation in agreement with the n.q.r. work of Brill and Walsh.[56] However, one interesting result obtained was a difference in isomer shift for tetraphenylarsonium hexachlorotellurate prepared from tellurium dioxide in concentrated hydrochloric acid when compared to that prepared from tellurium tetrachloride in dichloromethane. It was suggested that this may be due to some departure from octahedral symmetry in the former but this was not substantiated.

It may be noted here that nuclei in a non-cubic environment cause a quadrupole splitting due to hyperfine (non-coulombic) interactions between the nucleus and the surrounding electrons. Deviation from octahedral symmetry would cause such a splitting but it has never been observed.

### 2.1.4 Vibrational Spectroscopy

The metal halogen stretching frequencies for these complexes lie in the region 140-260 $cm^{-1}$, the deformation modes being even lower at 60-150 $cm^{-1}$, i.e. in the far infrared region of the spectrum. As mentioned previously, interest was aroused in these species since their structure did not appear to agree with that predicted by the electron-pair-repulsion theory of Gillespie and Nyholm. This interest was encouraged by a report of a distorted structure for the isoelectronic compound, xenon hexafluoride.[70(a),(b)]

For an octahedral species (point group $O_h$) the following internal vibrational modes are permitted:

| | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_6$ |
|---|---|---|---|---|---|---|
| Symmetry class | $a_{1g}$ | $e_g$ | $t_{1u}$ | $t_{1u}$ | $t_{2g}$ | $t_{2u}$ |
| Activity | R | R | i.r. | i.r. | R | inactive |

The earliest work[71] noted three broad bands in the infrared spectrum. The most intense band was always at much higher frequency than the other two and this was assigned to the antisymmetric metal-halogen stretching mode, $\nu_3$. The low frequency band was assigned to the bending mode $\nu_4$ while the remaining band was assigned to a lattice vibration, both assignments being made by comparison with spectra of compounds known to possess cubic structures in the solid state, e.g. potassium hexachlorostannate.

Deviations from either the regular octahedral structure of the ion or the cubic symmetry of the lattice would be expected to produce a splitting of the $t_{1u}$ fundamentals, and, if the distortions are appreciable, the selection rules for simple octahedral anions would break down completely. However, only deviations in the site symmetry of some iodotellurates were observed, where they had been predicted to be greatest.[44]

The effect of the lone pair of electrons on the positions of the vibrational modes was predicted qualitatively by comparison with the corresponding complexes of tin (IV). The increase in nuclear charge would perhaps cause the tellurium-halogen frequencies to be higher than the corresponding tin-halogen frequencies. In contrast, the extra pair of electrons on tellurium would cause an opposite shift and this effect would predominate, being greatest for the chloro-complexes where the covalent character of the bond is least.

Far-infrared spectra of the hexachlorotellurate species in solution[72] showed the $\nu_3$ band to possess a halfwidth, which although narrower than $\nu_3$ band in the solid state spectra of the corresponding lead (II), bismuth (III) and selenium (IV) compounds, was still broader than that for non-inert pair ions, e.g. tin (IV).

The intense colour of the compounds had made Raman investigations difficult until laser excitation became readily available, although some early work using mercury arc excitation had suggested hexachloro- and hexabromotelluric acids to be octahedral.[73] Subsequently, although the very dark iodo- compounds remained an obstacle, spectra were obtained from a variety of salts both in the solid state and in solution.[74,75] All showed three bands as expected, with no sign of splitting due to distortion. A summary of the results is given in Table 2.1.

TABLE 2.1 Summary of Reported Raman Spectra for the Hexachloro- and Hexabromotellurates

| SPECIES | $\nu_1$ | $\nu_2$ | $\nu_5$ |
|---|---|---|---|
| $TeCl_6^{2-}$ | 280-302 | 243-268 | 127-150 |
| $TeBr_6^{2-}$ | 167-180 | 144-160 | 79-91 |

Far-infrared results were also reported and a different interpretation was placed on the extreme width of the $\nu_3$ band when compared with the width of this band in the spectra of corresponding compounds of platinum, tin and lead. The spatial distribution of the lone pair was cited as the major reason and this is discussed more fully in the next section. Some doubt was also cast on the assignments of $\nu_4$ and the lattice mode due to vibrational coupling, especially in the bromo- and iodo- compounds where they are close in frequency. Interestingly, two hexachloro- complexes, the diphenyliodonium and the tetraphenylarsonium salts, showed a complex splitting in the far-infrared and this was taken as being indicative of distorted ($C_{3v}$) site symmetry for the anion (c.f. Mössbauer results[69]). Also, $\nu_1$ and $\nu_2$ were observed in the far-infrared spectrum of the tetraphenylarsonium salt. Calculated values of the inactive mode, $\nu_6$ were reported and placed between 80 and 125 $cm^{-1}$ for hexachloro- complexes and between 40 and 90 $cm^{-1}$ for hexabromo- species. A summary of these results is given below:

TABLE 2.2 Summary of Reported Far-Infrared Spectra for the Hexahalogenotellurates

| SPECIES | $\nu_3$ | $\nu_4$ | $\nu_L$ |
|---|---|---|---|
| $TeCl_6^{2-}$ | 210-251 | 96-146 | 62-100 |
| $TeBr_6^{2-}$ | 178-198 | ? | ? |
| $TeI_6^{2-}$ | 142-160 | ? | ? |

Later work [76,77] is in reasonable accordance with these results, although some splitting was observed in the Raman spectrum of potassium hexabromotellurate and ascribed to a lowering of anion site symmetry (c.f. X-ray work[44]). Raman spectra of hexaiodotellurates were reported for the first time and $\nu_1$ was found to be coincident with $\nu_2$ at 114 cm$^{-1}$. Again difficulty was experienced in the assignment of low frequency bands in the infrared spectra and in some cases a combination band, $\nu_4 + \nu_5$, was postulated, although splitting of $\nu_3$, in salts of unknown crystal structure, could not be ruled out.

Adams[78] has made an extensive vibrational study of halogeno- complexes of tellurium (IV) and the results for the hexacoordinate species were reported later.[79] Several differences were observed between the spectra of the tellurium complexes and those of the corresponding complexes of tin (IV) and antimony (V). These were:

(i) $\nu_4$ was not observed with any certainty above 60 cm$^{-1}$, either in the solid state or in solution,

(ii) $\nu_3$ occurred at much lower frequency,

(iii) $\nu_1$ and $\nu_2$ displayed comparable Raman intensities,

(iv) $\nu_3$ appeared in the Raman spectrum of hexabromotellurate in non-aqueous solution and hexaiodotellurate in hydriodic acid solution,

(v) $\nu_3$ for hexachlorotellurates both in the solid state and in non-aqueous solution was very broad with a halfwidth of 80 cm$^{-1}$ in the former and 40 cm$^{-1}$ in the latter.

These effects were explained in terms of dynamic pseudo Jahn-Teller distortion involving the octahedral ground state and a less symmetrical first excited state.

Adams has also provided a useful compilation of previous vibrational results.

Far infrared reflectance spectroscopy has been used to establish the true width of the $\nu_3$ band.[80] The results show that it is much broader than that of the corresponding compounds of tin or platinum.

Laser Raman studies of the hexachloro- and hexabromotellurates of potassium, rubidium, caesium and thallium (I) revealed no effect due to a distorted environment in the anion.[81]

The effect of pressure on the intensity of the $\nu_4$ band has been measured.[82] The gain in intensity with increase in pressure was explained in terms of dynamic rehybridisation whereby the lone pair acquired some directional character with a moment opposing that due to the change in nuclear positions during the $\nu_4$ mode. As the pressure increased the energy levels are altered and a permanent rehybridisation occurs which locks the inert pair in one orientation. The electric moments are no longer opposed and $\nu_4$ develops intensity.

An entirely different mechanism[83] has been proposed based upon relative intensity studies of $\nu_3$ and $\nu_4$ in the mixed phases $A_2[(Sn,Te)X_6]$ ($A=NH_4$,K,Rb or Cs; X=Cl or Br) and in the parent hexahalogenostannates and -tellurates. The low intensity of $\nu_4$ in the tellurium compounds, especially the bromo- species, was explained in terms of direct population of delocalised, solid state bands by the non-bonding electrons. In addition, force constant calculations led to the conclusion that, where both $\nu_4$ and $\nu_L$ are both observed, $\nu_4$ lies above $\nu_L$ for all compounds except ammonium hexabromotellurate.

Further work at high pressures[84] revealed two distinct modes of behaviour: (i) $\nu_4$ was very weak or absent at ambient but developed intensity at elevated pressure; (ii) $\nu_L$ was present at ambient pressure but rapidly vanished with applied stress. Also, in salts of organic cations, $\nu_4$ was either absent and failed to appear with applied pressure or was very weak and retained its intensity under pressure.

To explain these phenomena, antibonding halogen orbital- or $Te(d_\pi)-X(p_\pi)$ (X=halogen) overlap with cation s levels to form a conduction band was postulated. The extent of inert-pair delocalisation by these means would clearly vary with the relative energies of the orbitals, depending upon the particular cation-anion combination and since the effect of pressure is to decrease the energy gap between the various levels, the extent of inert-pair delocalisation would also be altered. The two modes of behaviour mentioned above can now be accounted for as follows: (i) there is little delocalisation at ambient pressure, but at high pressure the conduction band is lowered relative to the valence band thereby allowing greater delocalisation. Invoking the dynamic dehybridisation mechanism mentioned earlier the means of balancing the atom displacement dipole with an electronic one is removed and $\nu_4$ develops normal intensity. (ii) The reverse argument applies due to different relative orbital energies. Organic cations effectively envelop the anion in a hydrocarbon sheath and so $\nu_4$ will remain of low intensity.

A detailed Raman intensity and polarisibility study[85] revealed the orbital accommodating the inert pair to be significantly involved in bonding to the halogens. Also, the spectra of hexabromotellurates clearly exhibited a band due to $\nu_3$, but this breakdown of selection rules, observed previously,[79] did not occur in the chloro-species despite the prediction that the cause of the breakdown (*pseudo* Jahn-Teller distortion) would occur to a greater extent.[93]

Low temperature vibrational spectroscopy[86-89] has recently been applied to the hexahalogenotellurates and the chloro-compounds of rubidium, caesium, ammonium and thallium (I) yielded spectra very similar to those reported previously and were insensitive to cooling. The potassium[86,88] and tetramethylammonium salts[86,87] underwent phase transitions and no evidence of inert-pair stereo-chemical distortion could be detected. Hexabromotellurates[88,89] have also been studied and similar results obtained.

The vibrational results obtained since the compilation of Adams are tabulated below, (Tables, 2,3, 2,4 and 2.5).

### 2.1.5 Other Studies

Much thought has been expended to try and explain the regular octahedral geometry of these complexes. It was first suggested by Beach[90] that the configuration could be explained in terms of $5p^3 5d^2 6s$ hybridisation, with the lone pair in the 5s orbital. The use of the 6s orbital in bonding would then account for the fact that the octahedral radius for tellurium is 25% greater than the tetrahedral radius. Brown[44] had discussed the structure of potassium hexabromotellurate in terms of non-bonding Pauli repulsion between adjacent bromine atoms. If the anion formed a pentagonal bipyramid, the bromine-bromine distance would be 2.96Å or only about three-quarters of the Van der Waals distance (3.94Å). On the other

TABLE 2.3

Solid State Vibrational Data of Some Hexachlorotellurates

| Cation | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_L$ | Ref. |
|---|---|---|---|---|---|---|---|
| $K^+$ | | | 243 | 145 | | 111 | 80 |
| | 295 | 246 | | | 145 | | 81 |
| | 296 | 250 | 280,244, 216 | 158,148, 142 | 142 | 88,70 | 83 |
| | | | 197 | | | | 84 |
| | 297 | 251 | ∿255 | ∿140 | 142 | 87 | 86 |
| $Rb^+$ | 292 | 248 | | | 137 | | 81 |
| | | | 262 | 137 | | 65 | 82 |
| | 297 | 250 | 252 | | 140 | 64 | 83 |
| | | | 262 | | | 65 | 84 |
| | 298 | 250 | ∿250 | ∿136 | 140 | 66 | 86 |
| $Cs^+$ | 290 | 248 | | | 143 | | 81 |
| | | | 256 | 135 | | 66 | 82 |
| | 288 | 246 | 252 | | 141 | 66 | 83 |
| | | | 256 | 135 | | 66 | 84 |
| | 290 | 248 | ∿265 | | 141 | 64 | 86 |
| $Tl^+$ | 295 | 259 | | | 135 | | 81 |
| | 301 | 257 | ∿240 | | 132 | | 86 |
| $NH_4^+$ | | | 258 | 146 | | 108 | 80 |
| | 300 | 248 | 252 | 150 | 140 | 111 | 83 |
| | | | 255 | 151 | | 110 | 84 |
| | 300 | 248 | ∿245 | ∿140 | 142 | 106 | 86 |
| $Me_4N^+$ | | | 225 | | | 80 | 80 |
| | | | 236 | | | 78 | 84 |
| | 281 | 242 | ∿230 | | 136 | 75 | 86 |
| $Et_4N^+$ | | | 219 | | | 60 | 80 |
| $Bu_4N^+$ | | | 255 | | | | 84 |

## TABLE 2.4

### Solid State Vibrational Data of Some Hexabromotellurates

| Cation | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_L$ | Ref. |
|---|---|---|---|---|---|---|---|
| $K^+$ | 179 | 152 | | | 95 | | 81 |
| | 176 | 162 | 198 | 104 | 100,88 | 77 | 83 |
| | | | 200 | | | 77,53 | 84 |
| | 176 | 154 | $\sim$195 | 100 | 99,92 | 76 | 89 |
| $Rb^+$ | 184 | 148 | | | | 94 | 81 |
| | 178 | 153 | 202 | | 88 | 56 | 83 |
| | | | 201 | | | 54 | 84 |
| | 179 | 153 | $\sim$200 | | 89 | 55 | 89 |
| $Cs^+$ | 175 | 148 | | | 96 | | 81 |
| | 174 | 150 | 200 | | 90 | 57 | 83 |
| | | | 200 | | | 55 | 84 |
| | 174 | 150 | $\sim$200 | | 90 | 56 | 89 |
| $Tl^+$ | 183 | 152 | | | 89 | | 81 |
| $NH_4^+$ | 178 | 154 | 199 | 118 | 81 | 84 | 83 |
| | | | 195 | 125 | | 82 | 84 |
| | 178 | 153 | $\sim$200 | $\sim$118 | 79 | 84 | 89 |
| $Me_4N^+$ | 167 | 146 | $\sim$183 | 93 | 93 | 64 | 89 |
| $Et_4N^+$ | | | 176 | | | 63 | 84 |
| $PyH^+$ | | | 174 | | | 60 | 84 |

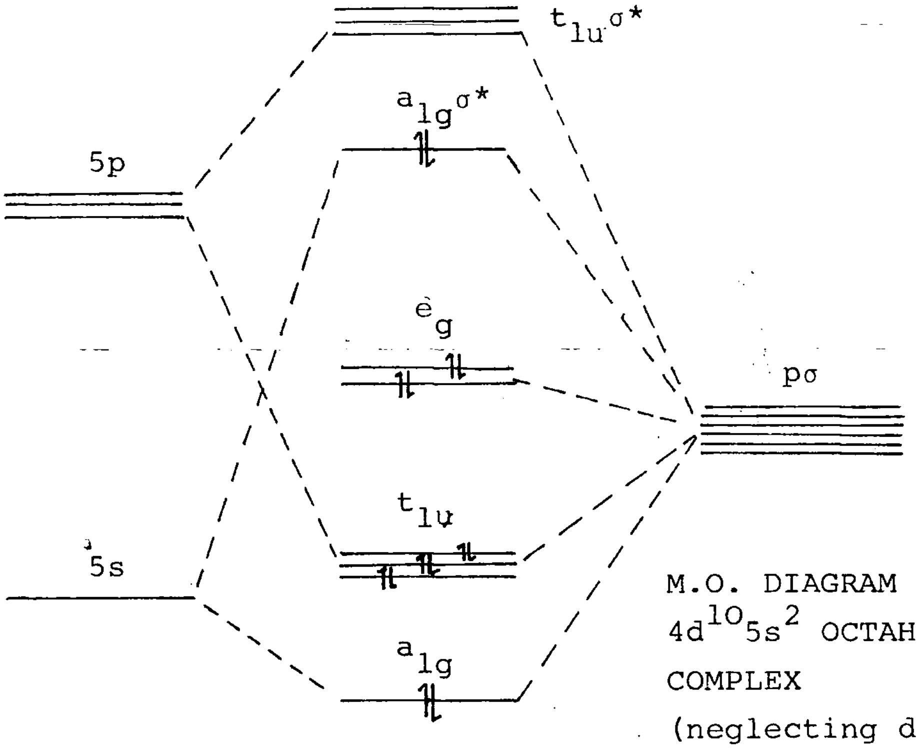
# TABLE 2.5

## Solid State Vibrational Data of Some Hexaiodotellurates

| Cation | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ | $\nu_L$ | Ref. |
|---|---|---|---|---|---|---|---|
| $K^+$ | | | 162 | 95 | | 64 | 83 |
| | | | 160 | | | 63 | 84 |
| $Rb^+$ | | | 167 | | | 50 | 83 |
| $Cs^+$ | | | 166 | | | 46 | 83 |
| | | | 159 | 88 | | 45 | 84 |
| $NH_4^+$ | | | 164 | | | 65 | 83 |
| | | | 158 | | | | 84 |
| $Et_4N^+$ | | | 157 | 100 | | 55 | 84 |
| $PyH^+$ | | | 147 | 103 | | 50 | 84 |

hand, an octahedral arrangement would bring the bromines only to within 3.82Å of each other with a consequent reduction in energy, since only coulombic repulsions are now in effect. However, as pointed out by Ware,[72] this argument loses much of its force in the case of the hexachloro- species.

Urch[91] had advanced a different explanation, based upon a qualitative molecular orbital approach. For a given set of ligand orbitals, the valence s orbital of the central atom will become less involved in bonding on descending and moving to the right of the periodic table. Therefore, the associated antibonding molecular orbital in an octahedral tellurium complex (see Figure 2.1), the antibonding character of which would be small, would be able to accommodate a pair of electrons without detracting from the stability or symmetry of the species.



M.O. DIAGRAM FOR A $4d^{10}5s^2$ OCTAHEDRAL COMPLEX (neglecting d orbitals)

Figure 2.1

If the 6s orbital of tellurium is involved as suggested by Beach, then this will become more tightly bound in the presence of highly electronegative ligands (e.g. fluoride ion). Even if this effect were small the energy gap between the ligand orbital and the tellurium 5s orbital will be greater than that involving the 6s orbital so that appreciable interaction might be expected. The antibonding orbital may then assume a slight bonding character, and enhance the stability of the complex.

Others have used Urch's descriptions to explain the low frequency and extreme width of the $\nu_3$ band in the infrared spectra of hexahalogentellurates.[75] The motion of the tellurium atom in this mode is said to produce an electrical asymmetry (i.e. the electron pair achieves a transient directional effect) which can lead to exchange of energy via the anharmonic terms of the potential function.

Molecular orbital calculations[92] have assigned the electron pair to an $a_{1g}{}^*$ orbital, largely of 5s character, whereas electronic spectra[93] have suggested that some delocalisation may occur. The presence of distorted excited states was also alluded to.

Other work[94,95] has interpreted similar results, as well as the unusual bandwidths in the infrared and intensities in the Raman spectra in terms of a dynamic Jahn-Teller effect in the excited state, thus supporting the conclusions of Adams and Downs.[79]

The intense colours, conducting properties and regular octahedral structures of these species have been accredited to the population of conduction bands in the solid state which arise from the mutual overlap of empty halogen d-orbitals.[96] The implications of this approach for the vibrational results have been discussed earlier.

Although the unusual Raman intensities have been ascribed to Jahn-Teller effects, attention has also been drawn to the possibility of a resonance Raman effect by which $\nu_2$ and $\nu_5$ are selectively enhanced relative to $\nu_1$.[78,94] Lack of data precluded any definite conclusions but an investigation using different exciting lines has since been reported and the intensity of the $\nu_2$ band was found to be dependent upon the exciting wavelength.[85]

## 2.2 Mixed Hexahalogenotellurates

Aynsley[97] prepared dipyridinium tetrachlorodibromotellurate by dissolving the dipyridine-tellurium dichloridebromide adduct in hot concentrated hydrochloric acid. Later,[98] dipyridinium dichlorodibromodiiodotellurate and tetrabromodiiodotellurate were prepared similarly.

More recently the tetra-ethylammonium salts of the dichlorotetrabromotellurate anion have been prepared and studied by vibrational spectroscopy,[99] and later this work was extended[100] to include the following anions:

$TeCl_4F_2^{2-}$
$TeCl_4Br_2^{2-}$
$TeCl_4I_2^{2-}$
$TeBr_4F_2^{2-}$
$TeBr_4Cl_2^{2-}$
$TeBr_4I_2^{2-}$
$TeF_2Cl_2Br_2^{2-}$
$TeCl_2Br_2I_2^{2-}$

The compounds were prepared by simply mixing stoichiometric amounts of the relevant tetrahalide and halide ion in dichloromethane or acetonitrile. Analysis of the spectra, involving force constant calculations, enabled the tetrachlorodibromo- and tetrabromodichlorotellurate anions to be assigned as the cis isomers. Since data was incomplete or of poorer quality for the remaining anions, normal coordinate analyses were not carried out and assignments were more speculative. However, the tetrachlorodifluoro and tetrabromodifluorotellurate species were also assigned as cis.

Petragnani *et al*[101] prepared salts of the tetraiododichloro and tetraiododibromo anions and assigned the former as trans, on infrared evidence.

Finally, some tetrachlorodihalogeno and tetrabromodihalogeno complexes have been studied using Mössbauer spectroscopy.[69] It was considered that removal of electron density by the more electronegative ligands would cause an increase in isomer shift; and that distortion from octahedral symmetry causing the 5s electrons to become stereochemically active would cause a decrease in isomer shift. However, the value of the isomer shift in this series appeared to be insensitive to the nature of the attached halogens, although fluorine did cause a slight decrease, implying the second effect to be dominant. Quadrupole splitting was not observed.

# RESULTS AND DISCUSSION

## 2.3 The Hexachloro-, Hexabromo- and Hexaiodotellurates

### 2.3.1 Raman Spectra

Spectra were recorded from the tetrabutylammonium salts in the solid state and also in acetonitrile and dichloromethane solutions, although solution spectra could not be obtained from the hexaiodo- species. The solid phase spectrum of tetrabutylammonium hexaiodotellurate displayed bands at 60m, 108s, 118s, 149w, 170w and 223vw $cm^{-1}$. The lowest frequency band is tentatively assigned to $\nu_5$, while the next two highest frequency bands are assigned to $\nu_1$ and $\nu_2$ respectively, the first time these have been observed separately. The bands at 149 and 170 $cm^{-1}$ could either be assigned to $\nu_3$, appearing in the Raman due to a lowering of site symmetry or a Jahn-Teller effect (Section 2.1.4). Since Adams[78] attributed a Raman band at 148 $cm^{-1}$ to $\nu_3$ in concentrated hydriodic acid solution, the latter explanation is preferred here. Finally, the feature at 223 $cm^{-1}$ is tenatively assigned to a combination band $\nu_1 + \nu_2$.

The results for the hexachloro- and hexabromo- species, together with assignments are given below:

TABLE 2.6

Raman Spectra of the Hexachloro- and Hexabromotellurate Species

| SAMPLE STATE | $(Bu_4N)_2\ TeCl_6$ | | | $(Bu_4N)_2\ TeBr_6$ | | |
|---|---|---|---|---|---|---|
| | ASSIGNMENTS | | | | | |
| | $\nu_1$ | $\nu_2$ | $\nu_5$ | $\nu_1$ | $\nu_2$ | $\nu_5$ |
| Solid | 285s | 245m | 129 | 171s | 150m | 82sh |
| Dichloromethane Solution | * | 252 | 137 | 171 | 151 | 82 |
| Acetonitrile Solution | 287 | 250 | 128 | 170 | 151 | 76 |

* obscured by solvent band.

The results compare well with those obtained by Adams.[78] A shoulder on the $\nu_1$ band of the hexabromo-tellurate ion in solution was also observed at 190 $cm^{-1}$ and assigned to $\nu_3$. Adams attributed this breakdown in selection rules as well as the unusual relative intensities to a dynamic Jahn-Teller effect as described earlier (Section 2.1.4), although the latter has now been explained in terms of a pre-resonance Raman effect (Section 2.1.5).

### 2.3.2 Far-Infrared Spectra

These are reported for the tetrabutylammonium salts in the solid state.

TABLE 2.7

Far-Infrared Spectra of the Hexachloro-, Hexabromo- and Hexaiodotellurate Species

| SPECIES | FREQUENCIES ($cm^{-1}$) |
|---|---|
| $TeCl_6^{2-}$ | 95vw, 132w, 144vw, 220vs, 245sh, 278sh |
| $TeBr_6^{2-}$ | 83w, 114vw,151m, 181vw |
| $TeI_6^{2-}$ | 88w, 116sh, 146s, 151s, 171m |

Since the crystal structures of these compounds have not been determined, spectral assignment is difficult and can only be tentative, especially for the hexachloro-compound. Adams[78] observed three bands in the spectrum of tetrabutyl-ammonium hexachlorotellurate at 111, 228 and 250 $cm^{-1}$. These were assigned to a lattice mode, $\nu_3$ and $\nu_2$ respectively, the latter usually being inactive in the infrared. The only other study[84] to include this salt reported a single band at 255 $cm^{-1}$, assigned to $\nu_3$. In this work the lowest frequency absorption was observed as a very weak, broad feature centred around 95 $cm^{-1}$, and is assigned to a lattice vibration. Two more very weak bands were observed at 132 and 144 $cm^{-1}$, the latter of which was also observed as a weak feature in the spectrum of tetrabutylammonium hexafluorophosphate and is thus assigned as a cation mode. The former is then assigned to $\nu_4$. The spectrum is dominated by a very intense, broad feature, seemingly split into two components centred around 220 $cm^{-1}$ and 245 $cm^{-1}$, and with a halfwidth of approximately 100 $cm^{-1}$. These values are in reasonable agreement with Adams[78] and are assigned accordingly. The highest frequency band is a shoulder at 278 $cm^{-1}$ and has previously been assigned to a combination band, $\nu_4 + \nu_5$, in Fermi resonance with $\nu_3$, in the caesium, ammonium, tetramethylammonium[77] and potassium[86] salts as well as the Raman active band $\nu_1$ in the tetraphenylarsonium, diphenyliodonium[75], caesium and tetraethylammonium[78] salts. The former studies assumed octahedral symmetry for the anion whereas the latter suggested a lowering of symmetry. Although tetraphenylarsonium and diphenyliodonium salts may well be distorted, there is no evidence for this in the caesium or tetraethylammonium salts and in the absence of any such data for the tetrabutylammonium salt, the shoulder is assigned to the combination band.

Adams[78] has reported bands at 109 and 183 $cm^{-1}$ for tetrabutylammonium hexabromotellurate and assigned them to $\nu_4$ and $\nu_3$ respectively. The bands at 114 and 183 $cm^{-1}$ observed in this work are thus assigned accordingly. The weak feature at 83 $cm^{-1}$ is then assigned to a lattice mode while the band at 151 $cm^{-1}$ is assigned to $\nu_2$, (c.f. $TeCl_6^{2-}$) tentatively assigned as such by Adams in the pyridinium and trisethylenediaminium salts.

Tetrabutylammonium hexaiodotellurate has been reported to show three bands at 115, 136 and 153 cm$^{-1}$, the first being tentatively assigned to $\nu_4$ and the remainder to $\nu_3$. In this work the band at 116 cm$^{-1}$ is assigned to $\nu_4$ while those at 146 and 151 cm$^{-1}$ are assigned to $\nu_3$. The feature at 88 cm$^{-1}$ is then assigned to a lattice mode while that at 171 cm$^{-1}$ is assigned to a further component of $\nu_3$ (c.f. Raman results).

### 2.3.3 Tellurium -125 N.M.R. Spectra

TABLE 2.8

Tellurium -125 N.M.R. Spectra of the Hexachloro-, Hexabromo- and Hexaiodotellurate Species

| SPECIES / SOLVENT | $TeCl_6^{2-}$ | $TeBr_6^{2-}$ | $TeI_6^{2-}$ |
|---|---|---|---|
| DICHLOROMETHANE | 1353 | 1330 | 1257 |
| ACETONITRILE | 1377 | 1358 | 1252 |
| ACETONE | 1334<br>1123 | 1342 | 1494 |

The results in dichloromethane solution exhibit a normal halogen dependence with shielding increasing with the decrease in electronegativity of the substituent halogen; in accordance with the results for hexahalogeno- complexes of phosphorus,[102] tin,[103] antimony,[104] platinum[105] and thallium.[106] In acetonitrile solution the same trend is observed, although the shifts for the chloro- and bromo- complexes are shifted to slightly lower field, perhaps due to partial solvolysis:

$$TeX_6^{2-} \xrightleftharpoons{CH_3CN} TeX_5.CH_3CN^-$$

That this does not occur for the iodo- compound is probably indicative of the greater strength of the tellurium-iodine bond. The order of shifts in acetone, however, is completely reversed, with the values for the chloro- and bromo-complexes agreeing well with those reported by Goodfellow.[16] An explanation for this effect of solvent on chemical shift is not at all clear cut but has been discussed elsewhere.[107] The extra line in the spectrum of the hexachloro- species is reasonably close to that reported for tellurium tetrachloride in acetone, at 1138 ppm.[16] This suggests the following equilibrium:

$$TeCl_6^{2-} \rightleftharpoons TeCl_4 + 2Cl^-$$

Although the pentachloro- species may well be an intermediate it can only be present transiently since when dissolved in acetone this complex exhibited only one resonance at 1128 ppm.

In all solvents under study, the hexaiodo- complex showed broader lines ($\Delta\nu_{\frac{1}{2}} \simeq 615$ Hz) when compared to those for the chloro- and bromo- complexes ($\Delta\nu_{\frac{1}{2}} \simeq 150$ Hz). This is most probably due to quadropole relaxation ($^{127}I$, $I = {}^{5}/_{2}$).

## 2.4 Mixed Hexahalogenotellurates

### 2.4.1 The Chlorobromotellurates

#### (a) Raman Spectra

These were recorded both in the solid state and in acetonitrile solution, as their tetrabutylammonium salts. Polarization studies were carried out on the solutions, where possible, and these results lie below those obtained in the solid state.

TABLE 2.9

Raman Spectra of the Hexachlorobromotellurates

| SPECIES | FREQUENCIES (cm$^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| $TeCl_5Br^{2-}$ (s) | 75vw | 128m | 151w | 180s | 243vs | 277s |
| (soln.) | | 125vw | 152w | 178m | 248s | 279vs |
| $TeCl_4Br_2^{2-}$ (s) | 78w | 125w | 158s | 178s | 244s | 270s |
| (soln.) | | | 154s | 173m,p | 250m | 272m,p |
| $TeCl_3Br_3^{2-}$ (s) | | | 154m | 179m | 248w | 270w |
| $TeBr_4Cl_2^{2-}$ (s) | 80w | 154s | 172m | 228w | 250w | |
| (soln.) | | 154s | 171m,p | | 258w,p | |
| $TeBr_5Cl^{2-}$ (s) | 81m | 151s | 172s | 196w | 222m | |
| (soln.) | | 154s | 171m | | | |

Only anions of general formula $TeX_4Y_2^{2-}$ have been previously discussed,[99,100] their spectra being recorded from solid samples of the caesium and tetraethylammonium salts. Although the tetrabutylammonium salts used in this work eventually decomposed in the laser beam, as did the tetraethylammonium salts used above, reasonable spectra were obtained, using low power and a defocussed beam. The results quoted for $(Et_4N)_2TeCl_4Br_2$[100] with bands at 124s, 175w, 252s and 282s are in fair agreement with the results presented here, although the strong band at 158 cm$^{-1}$ was not observed in the earlier work.

The bands at 272 and 173 cm$^{-1}$ are polarized and are therefore immediately assigned to totally symmetric stretching modes involving tellurium-chlorine and tellurium-bromine bonds respectively. These assignments are not in accord with those presented earlier for the caesium salt,[100] where bands at 276 and 175 cm$^{-1}$ were denoted as $b_2$ modes. The bands at 250 and

154 $cm^{-1}$ are again most probably associated with tellurium-chlorine and tellurium-bromine stretching vibrations while that observed at 125 $cm^{-1}$ in the solid sample may well be due to a deformation mode. The feature at 78 $cm^{-1}$ is assigned to a lattice vibration.

Earlier work[99] on $(Et_4N)_2TeBr_4Cl_2$ could not be repeated as the sample decomposed in the laser beam,[100] but results were quoted for the caesium salt (identical with the early results for the $Et_4N^+$ salt) and there is good agreement between the strong bands and the frequencies obtained in this work. The polarized bands at 258 and 171 $cm^{-1}$ are assigned to symmetric stretching vibrations involving tellurium-chlorine and tellurium-bromine bonds respectively. The weak feature at 228 $cm^{-1}$, observed only in the solid is assigned to a tellurium-chlorine stretching frequency while that at 154 $cm^{-1}$ is assigned to a tellurium-bromine stretching frequency. The band at 80 $cm^{-1}$ is most probably a lattice mode. Again there is some discrepancy between this and earlier work,[100] where the high frequency band was denoted as $b_2$ and that at 155 $cm^{-1}$ as $a_1$. The stereochemistry of the above anions is discussed in the section (d).

The assignment of the bands in the spectra of anions of general formula $TeX_5Y^{2-}$, which are likely to be of $C_{4v}$ symmetry, is made by analogy with that given for the corresponding antimony (V) species.[108] For the $TeCl_5Br^{2-}$ anion, the five highest frequency bands can be described as tellurium-chlorine stretching vibrations, while that at 128 $cm^{-1}$ is assignable to a tellurium-bromine mode. Similarly, the four low frequency bands in the spectrum of the $TeBr_5Cl^{2-}$ anion are assigned to tellurium-bromine stretching modes and that at 222 cm$^{-1}$ to a tellurium-chlorine mode.

Individual modes in the $TeCl_3Br_3^{2-}$ anion are not identified since mixing of Te-Cl and Te-Br modes make this unrealistic, as for the corresponding species of antimony (V).

Finally, the solution spectra suggest that the anions remain undissociated.

### (b) Far-Infrared Spectra

These were also obtained from the tetrabutylammonium salts but only in the solid state.

TABLE 2.10

Far-Infrared Spectra of the Hexachlorobromotellurates

| SPECIES | FREQUENCIES (cm$^{-1}$) | | | |
|---|---|---|---|---|
| $TeCl_5Br^{2-}$ | 90sh | 175s | 227s | 268m |
| $TeCl_4Br_2^{2-}$ | | 179vs | 225vs | 258sh |
| $TeCl_3Br_3^{2-}$ | | 185vs | 221vs | 259sh |
| $TeBr_4Cl_2^{2-}$ | 122w | 181vs | | 234vs |
| $TeBr_5Cl^{2-}$ | 118m | 179vs | 218sh | 236s |

There is good agreement between the above results and the literature values[99,100] for the anions of general formula $TeX_4Y_2^{2-}$. However, the broad nature of the bands makes assignment and comparison with Raman spectra very difficult, although the bands below 220 cm$^{-1}$ are probably due to tellurium-bromine stretching modes, whereas those above probably arise from tellurium-chlorine modes.

The number of tellurium halogen stretching modes can provide some assistance in assignment.

TABLE 2.11

Vibrational Spectroscopic Coincidences for Species of $C_{2v}$ and $D_{2h}$ Symmetry

| MODE | SYMMETRY | INFRARED | RAMAN | COINCIDENCES |
|---|---|---|---|---|
| νTeCl | $C_{2v}$ | 4 | 4 | 4 |
| νTeBr | $C_{2v}$ | 2 | 2 | 2 |
| νTeCl | $D_{4h}$ | 1 | 2 | 0 |
| νTeBr | $D_{4h}$ | 1 | 1 | 0 |

Consideration of the above table would indicate that the species in question adopt the cis ($C_{2v}$) arrangement in agreement with earlier work[100] although a different rationale is preferred here (Section (d)).

Although for species of $C_{4v}$ symmetry the eight possible infrared bands should also appear in the Raman, definite conclusions were again made difficult by the width of the infrared absorptions in the spectra of the $TeX_5Y^{2-}$ anions.

Again, vibrational mixing precludes definite assignment of bands to particular stretching modes for the $TeCl_3Br_3{}^{2-}$ ion. However, for the mer isomer ($C_{2v}$) six tellurium-halogen stretching modes, observed in both the infrared and Raman spectra, are expected, whereas for the fac isomer ($C_{3v}$), only four such modes are allowed. Since only four Raman bands and three infrared bands are observed here, the fac isomer seems preferable. Unfortunately, since failure to observe very weak bands or accidental degeneracy must also be taken into account when too few bands are observed, definite assignment cannot be made.

Consideration of the various frequencies observed would suggest that the species described in this section are unique and are not mixtures of the hexachloro- and hexabromotellurate anions.

### (c) Tellurium -125 N.M.R. Spectra

Vladimiroff and Malinowski[111] have provided theoretical justification for the interpretation of chemical shifts in terms of interactions between adjacent ligands, attached to a central atom, which act along the edges of the coordination polyhedron. The theory has been successfully applied to tetrahedral species of carbon-13,[112,114] aluminium-27,[113] boron-11,[114] germanium-73,[115] cadmium-111 and -113,[116] mercury-199,[116] gallium-71[117] and indium-115,[117] as well as to octahedral complexes of niobium-93,[118,119] phosphorus-31,[102,120] antimony-121[104] and tin-119.[103] The boron-11 and fluorine-19 chemical shifts of some boron trihalide adducts were also found to follow this relationship.[121]

The results of the application of the theory to the complexes under discussion, together with the observed chemical shifts are tabulated below in Table 2.12.

The Cl-Cl and Br-Br parameters were calculated from the hexahalogeno- shifts and were found to be 112.8 and 110.9 ppm. respectively. The Cl-Br parameter can be calculated from either the $TeBr_5Cl^{2-}$ or the $TeCl_5Br^-$ chemical shift but unfortunately these two species give different results; 115.9 and 107.7 ppm. respectively.

TABLE 2.12

Tellurium-125 N.M.R. Spectra of the Hexachlorobromotellurates

| SPECIES | INTERACTION COEFFICIENTS | | | CHEMICAL SHIFT (ppm) | | |
|---|---|---|---|---|---|---|
| | Cl-Cl | Cl-Br | Br-Br | Calc. | | Obs. |
| $TeCl_5Br^{2-}$ | 8 | 4 | 0 | 1366 | 1333 | 1333 |
| $TeCl_4Br_2^{2-}$ Cis | 5 | 6 | 1 | 1370 | 1321 | 1342(4)<br>1366(1) |
| Trans | 4 | 8 | 0 | 1378 | 1313 | |
| $TeCl_3Br_3^{2-}$ Fac | 2 | 8 | 2 | 1366 | 1309 | 1367 |
| Mer | 3 | 6 | 3 | 1374 | 1317 | |
| $TeBr_4Cl_2^{2-}$ Cis | 1 | 6 | 5 | 1362 | 1305 | 1390 |
| Trans | 0 | 8 | 4 | 1370 | 1313 | |
| $TeBr_5Cl^{2-}$ | 0 | 4 | 8 | 1350 | 1317 | 1350 |

As seen in the table above neither value leads to meaningful predictions of the chemical shifts and a possible reason for this is that the shielding of the tellurium nucleus is dominated by the lone pair of electrons which exhibits some p character. This is discussed further in the conclusion.

### (d) Stereochemistry

Although the previous discussion has indicated that the ions of general formula $TeX_4Y_2^{2-}$ very probably adopt the cis configuration, assignment of the $TeCl_3Br_3^{2-}$ species was less certain, on the basis of the vibrational results. In addition, the n.m.r. data was of no use since the pairwise interaction theory could not be applied with any success.

In this section a model which predicts that the cis configuration should be adopted by all species of general formula $MX_4Y_2$ (where X and Y are monoatomic) and that the fac configuration should be adopted by species of general formula $MX_3Y_3$ is presented.

Previously the cis arrangement of halogeno- complexes of tin (IV) and titanium (IV) of general formula $MX_4Y_2^{2-}$ was explained by postulating the π-donor ability of the halogens to the $t_{2g}$ orbitals of the metal to be the major factor in determining the geometry. In a trans complex the halogens would be competing for the same $t_{2g}$ orbital whereas in a cis complex they could π-donate into different orbitals.[109] While plausible for titanium, the mechanism is unlikely for complexes of tin and tellurium since the metal orbitals involved are of much higher energy. Instead, the approach of Zahrobsky is invoked here.[110] This is a stereochemical model based on intramolecular nonbonded interactions of atoms bonded to a central atom. Three basic assumptions are made:

1. The strongest non-bonded interactions occur in a region around a central atom that may be represented by a sphere which has a radius approximately equal to the average donor atom - central atom bond length and a centre that is coincident with the central atom.
2. The geometry of the molecule may be determined by balancing the forces acting about this sphere, and that the van der Waals surfaces of ligand atoms represent equipotential surfaces.
3. Nonbonded interactions may be minimised by arranging the donor atoms around the central atom such that the distances (or overlap) between the van der Waals surfaces of adjacent donor atoms are equalized.

The model approximates this condition by assigning to each donor atom a solid angle, the size of which is a function of the donor atom - central atom bond distance and the van der

Waals radius of the donor atom. These solid angles are then distributed around the central atom so that the distances between adjacent conic surfaces are equal. The solid angle representing a donor atom may be generated by considering the set of lines from a central atom, A, that are tangential to the van der Waals surface of a bonded ligand atom, B, as shown in Figure 2.2, where AB is the sum of the covalent radii and BC is the van der Waals radius of the donor atom.

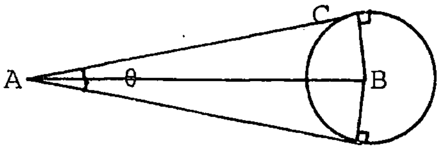


Figure 2.2

Then, the principal region of steric influence of a bonded ligand atom may be considered to lie within a "steric angle", θ, defined by θ = 2 arcsin (BC/AB).

Although three-dimensional distribution of different-sized cones with apices at a common point does not have an exact mathematical solution, approximate solutions for octahedral complexes may be readily obtained by separating the three dimensional problem into three two-dimensional analyses, represented by three mutually perpendicular planes, each of which cuts through the central atom and four donor atoms. Where more than one isomer is possible, the structure which possesses the greatest sum of steric angles in a particular plane may be assumed to have the greatest nonbonded repulsive interactions, and will not be the isomer which is predicted.

Application of this model to chlorobromo- complexes of tellurium (IV) of general formula $TeX_4Y_2^{2-}$ leads to the following sums for the steric angles which lie in the three mutually perpendicular planes that describe the octahedral geometry:

(i) $TeCl_4Br_2{}^{2-}$ : cis 405°, 402.5°, 402.5°
trans 405°, 405°, 400°

(ii) $TeBr_4Cl_2{}^{2-}$ : cis 407.5°, 407.5°, 405°
trans 410°, 405°, 405°

For $TeCl_4Br_2{}^{2-}$, the trans isomer contains two planes with angles of 405° whereas the cis isomer possesses only one. In the $TeBr_4Cl_2{}^{2-}$ species, the trans isomer contains a plane with an angle of 410°, which is greater than all others. Therefore, in both cases the cis isomer is preferred.

Similar arguments applied to the $TeCl_3Br_3{}^{2-}$ anion lead to the following angles:

(i) mer : 407.5°, 405°, 402.5°
(ii) fac : 405°, 405°, 405

Therefore, the fac isomer is preferred.

It should be noted that the relationship between configuration and steric angle is not linear; only the greatest angle is significant.

## 2.4.2 The Chloroiodotellurates

### (a) Raman Spectra

Raman spectra have not previously been reported for any of these systems but in this work spectra were obtained, from solid samples of the tetrabutylammonium salts, using a helium-neon laser.

The assignment of the spectra listed in Table 2.13 is complicated by their extreme similarity. The bands above 240 $cm^{-1}$ may be attributed with some confidence to vibrational modes involving tellurium-chlorine bonds whereas

TABLE 2.13

Raman Spectra of the Hexachloroiodo- Systems

| SYSTEM | FREQUENCIES (cm$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| *$TeCl_5I^{2-}$ | 53w | 112vs | 152w | 171vw | 228m | 245w | 278vw |
| $TeCl_4I_2^{2-}$ | 65vw | 112vs | 157w | | 223m | 248sh | |
| *$TeCl_3I_3^{2-}$ | | 111vs | 150sh | 171w | 225m | 245sh | |
| $TeI_4Cl_2^{2-}$ | 61w | 108vs | 142sh | | 222m | 250w | |
| *$TeI_5Cl^{2-}$ | 60w | 108vs | | | 225m | 245sh | |

*found to be mixtures.

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the remaining frequencies bear a clear resemblance to those obtained for the hexaiodo- species (Section 2.3.1). Consequently, X-ray powder photographs of the hexaiodo-, hexachloro- and all intermediate species were recorded, and these proved conclusively that mixtures of hexachloro- and hexaiodotellurates were not present (see Appendix, Table 1, for values of 4θ). However, the photographs of the $TeCl_5I^{2-}$, $TeCl_3I_3^{2-}$ and $TeI_5Cl^{2-}$ systems did all indicate more than one species to be present. The $TeCl_5I^{2-}$ system was shown to consist of a mixture of the $TeCl_6^{2-}$ and $TeCl_4I_2^{2-}$ anions, and the photograph of the $TeCl_3I_3^{2-}$ system exhibited lines due to the $TeCl_4I_2^{2-}$ species so that presumably a mixture of this and the $TeI_4Cl_2^{2-}$ ion was present. Similarly the $TeI_5Cl^{2-}$ system was found to consist of the $TeI_4Cl_2^{2-}$ and presumably the $TeI_6^{2-}$ species. The Raman spectra can now be interpreted in accordance with these results.

The data reported above suggest that only anions of general formula $TeX_4Y_2^{2-}$ are unique species and their configuration is discussed in the next section.

### (b) Far-Infrared Spectra

These were also recorded from the tetrabutylammonium salts in the solid state.

TABLE 2.14

Far-Infrared Spectra of the Hexachloroiodo- Systems

| SYSTEM | FREQUENCIES ($cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *$TeCl_5I^{2-}$ | | | 155m | 174m | 218sh | 233vs | 245sh | 271sh |
| $TeCl_4I_2^{2-}$ | 121m | | 153sh | 172m | 221vs | 232sh | | 268sh |
| *$TeCl_3I_3^{2-}$ | | 137sh | 154m | 170m | 220vs | | | |
| $TeI_4Cl_2^{2-}$ | 117w | 133w | 160s | | 221vs | | | |
| *$TeI_5Cl^{2-}$ | 115w | 134m | | | 216m | | | |

*found to be mixtures

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Of the above spectra, only that of $TeCl_4I_2^{2-}$ has been previously reported[100] and was stated to exhibit strong bands at 155, 170, 220 and 240 $cm^{-1}$ for the tetrabutylammonium salt, in good agreement with those presented here. The bands at 153 and 172 $cm^{-1}$ are thus assigned to tellurium-iodine stretching modes, while the remaining are assigned to tellurium-chlorine modes. In the case of the $TeI_4Cl_2^{2-}$ anion, the three low frequency bands are assigned to tellurium iodine stretching vibrations, while that at 221 $cm^{-1}$ is probably due to a tellurium-chlorine stretching mode.

For each of the species discussed above, the number of bands observed in both infrared and Raman spectra suggests that the cis configuration is adopted (Section 2.4.1 (d)).

The remaining spectra can be interpreted as mixtures, as discussed in the section on the Raman spectra (Section 2.4.2(a)).

### (c) Tellurium-125 N.M.R. Spectra

These are shown in Table 2.15 for the tetrabutylammonium salts in dichloromethane solution. Approximate relative intensities are given in parentheses.

TABLE 2.15

Tellurium-125 N.M.R. Spectra of the Hexachloroiodo- Systems

| SYSTEM | CHEMICAL SHIFT (ppm.) |
|---|---|
| $TeCl_5I^{2-}$ | 1446 (1) |
| | 1334 (5) |
| $TeCl_4I_2{}^{2-}$ | 1331 |
| $TeCl_3I_3{}^{2-}$ | 1447 (3) |
| | 1336 (2) |

The signal near 1330 ppm. is immediately assigned to the $TeCl_4I_2{}^{2-}$ anion, and its appearance in the spectra of the $TeCl_5I^{2-}$ and $TeCl_3I_3{}^{2-}$ systems is in agreement with the X-ray results. The origin of the signal at 1446 ppm. is less certain but it lies in the region between the signals obtained from six-coordinate species and those obtained from five-coordinate species and so could be due to an exchange resonance (the exchange signals for a 1:1 mixture of $TeCl_5{}^-$ and $TeCl_6{}^{2-}$ occurred at 1427 ppm.). However, the appearance of an exchange resonance at precisely the same position in two different systems is highly unlikely and so the presence of a chloroiodo- species of unknown composition is preferred here. The signal is also observed in the $TeCl_4I^-$ and $TeI_4Cl^-$ systems and this is discussed in Section 4.4.

Signals could not be observed for the $TeI_4Cl_2{}^{2-}$ and $TeI_5Cl^{2-}$ systems, presumably due to their extreme width.

### 2.4.3 The Bromoiodotellurates

#### (a) Raman Spectra

Raman spectra are reported for these systems for the first time. The solid phase spectra for the tetrabutylammonium salts are given in Table 2.16.

TABLE 2.16

Raman Spectra of the Hexabromoiodo- Systems

| SYSTEM | FREQUENCIES ($cm^{-1}$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *$TeBr_5I^{2-}$ | | 61w | 78w | 112m | 132s | 152w | 169m | |
| $TeBr_4I_2^{2-}$ | | 66w | 77w | 113s | 132m | | 169m | |
| *$TeBr_3I_3^{2-}$ | | 61w | | 110vs | | 159m | 174m | |
| $TeI_4Br_2^{2-}$ | 32w | 63w | | 112s | 132sh | | | 223w |

*found to be mixtures

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The spectrum of the $TeI_5Br^{2-}$ system is not reported since satisfactory analyses could not be obtained (Table 2.25).

Again, the spectra appear very similar and the presence of mixtures was verified by X-ray powder photography (see Appendix, Table 2, for values of 4θ). Thus, $TeBr_5I^{2-}$ was found to contain the $TeBr_4I_2^{2-}$, and presumably the $TeBr_6^{2-}$ species, and $TeBr_3I_3^{2-}$ to contain the $TeI_4Br_2^{2-}$ and $TeBr_4I_2^{2-}$ ions.

The bands above 150 $cm^{-1}$ are assigned to tellurium-bromine stretching vibrations while those below are assigned to tellurium-iodine modes. The weak feature at 223 $cm^{-1}$, observed in the spectrum of the $TeI_4Br_2^{2-}$ anion has been discussed in Section 2.3.1.

The configuration of these species is discussed in the next section.

### (b) Far-Infrared Spectra

These are reported for the tetrabutylammonium salts in the solid state in Table 2.17.

TABLE 2.17

Far-Infrared Spectra of the Hexabromoiodo- Systems

| SYSTEM | FREQUENCIES ($cm^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| [1,2] $TeBr_5I^{2-}$ | | | 151sh | | 175vs | |
| [2] $TeBr_4I_2^{2-}$ | | | 157s | 168s | | 183s |
| [1,2] $TeBr_3I_3^{2-}$ | | | 156m | 168sh | 172vs | 185sh |
| $TeI_4Br_2^{2-}$ | 117w | 135m | 156vs | 166vs | 178sh | |

(1) found to be mixtures

(2) recorded at 77K

---

The spectrum of the caesium salt of the $TeBr_4I_2^{2-}$ anion has been reported previously,[100] with bands at 90w, 163m and 196s $cm^{-1}$. The spectrum of $[Ph_3PCH_3][TeI_4Br_2]$ has also been reported and bands were observed at 141s and 194sh $cm^{-1}$. From this data the structure was assigned to the trans configuration.[101]

Although room temperature spectra of the $TeBr_5I^{2-}$, $TeBr_4I_2^{2-}$ and $TeBr_3I_3^{2-}$ systems displayed only single, broad bands around 174 $cm^{-1}$, splitting was observed in spectra recorded at 77K and these results are given in Table 2.17. The nature of the spectra at room temperature suggests that the bands are vibrationally coupled and so assignment to particular modes cannot be made with any degree of certainty. However, the frequencies observed below 175 $cm^{-1}$ most probably involve tellurium-iodine modes, while those above are assigned as predominantly tellurium-bromine modes.

Assignment of configuration for the $TeX_4Y_2^{2-}$ is more difficult but the number of bands observed both in this and previous work,[100] tends to suggest that the cis structure is adopted.

### (c) Tellurium-125 N.M.R. Spectra

These are reported for the tetrabutylammonium salts in dichloromethane solution in Table 2.18.

TABLE 2.18

Tellurium-125 N.M.R. Spectra of the Hexabromoiodo- Systems

| SYSTEM | CHEMICAL SHIFT (ppm) |
|---|---|
| $TeBr_5I^{2-}$ | 1353 |
| $TeBr_4I_2^{2-}$ | ∿ 1300 |
| $TeBr_3I_3^{2-}$ | ∿ 1300 |

The broad signals at 1300 ppm are immediately assigned to the $TeBr_4I_2^{2-}$ species. The signal at 1353 ppm is somewhat narrower, and, since $TeBr_5I^{2-}$ is known to contain $TeBr_4I_2^{2-}$ in the solid state, possibly arises from exchange between the latter species and a five-coordinate moiety, resonating at lower field (Chapter Four).

## 2.4.4 The Mixed Fluorotellurates

The attempted preparation of sodium (18-crown-6) ether pentachlorofluorotellurate failed due to the insolubility of sodium chloride (Section 2.6) and so no further reactions of pentahalogenotellurate with fluoride ion were carried out. The extreme unreactivity of the pentafluorotellurate species (Chapter Three) prevented the preparation of anions of general formula $TeF_5X^{2-}$ (X = Cl,Br,I) and since tellurium difluoride is unknown,[122] the species $TeF_3X_3^{2-}$ could not be synthesised. An exchange method for the latter ion was also prohibited since the hexafluorotellurate anion has not been prepared (Chapter Three). As a result, only species of general formula $TeF_4X_2^{2-}$ and $TeX_4F_2^{2-}$ are discussed further and, of these, only the bromo- and iodo- complexes could be isolated as solids.

### (a) Vibrational Spectra

TABLE 2.19 Vibrational Spectra of Some Mixed Fluorotellurate Systems

| SYSTEM | SPECTRUM | FREQUENCIES ($cm^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $TeBr_4F_2^{2-}$ | IR | 150w | 163sh | 170s | 182m | 583vw | | |
| | R | 30w | 61vw | 83m | 149vs | 167s | 178m | 193w |
| $TeI_4F_2^{2-}$ | IR | 132m | 138s | 145m | | | | |
| | R | 62m | 107vs | 213m | | | | |
| $TeF_4Br_2^{2-}$ | IR | 182s | 275s | 331s | 482s | 495s | 650m | |
| | R | 61w | 85m | 152s | 172m | | | |
| $TeF_4I_2^{2-}$ | IR | 118s | 129sh | 170w | 221w | 275w | 331s | 482s |
| | | | | | | | 495s | 650m |
| | R | 32w | 62vw | 112vs | 226w | | | |

Vibrational data has previously been reported for $Cs_2TeBr_4F_2$ [100] and there is moderate agreement with the data reported here. All of the above bands for species of general formula $TeX_4F_2^{2-}$ can be assigned to Te-X modes. The very weak band at 583$cm^{-1}$ observed in the normal infrared spectrum of the $TeBr_4F_2^{2-}$ anion is assigned to a tellurium-fluorine stretching vibration.

The above results are consistent with a cis structure for the anions (Section 2.4.1(d)).

The far-infrared spectra of the species of general formula $TeF_4Y_2^{2-}$ were found to be dominated by two strong bands at 275 and 331 $cm^{-1}$. These results indiate the presence of the pentafluorotellurate anion (Section 4.5.2). The remaining strong bands in the far-infrared can be assigned to the $TeY_6^{2-}$ species, although for the iodo- compound the $\nu_3$ band is absent (Table 2.7).

The Raman spectra also exhibit bands attributable to the hexahalogeno- species (Section 2.3.1), suggesting the following to have occurred:

$$5TeF_4 + 6X^- \longrightarrow 4TeF_5^- + TeX_6^{2-}$$

(b) N.M.R. Spectra

The fluorine-19 n.m.r. spectra for these species are entirely consistent with the above conclusions. The chemical shifts, measured downfield from hexafluorobenzene, are given in Table 2.20.

TABLE 2.20

Fluorine-19 N.M.R. Spectra of the $TeF_4Y_2^{2-}$ Systems

| SYSTEM | CHEMICAL SHIFT (ppm) | COUPLING CONSTANT (Hz) |
|---|---|---|
| $TeF_4Cl_2^{2-}$ | 122.5<br>131.2 | - |
| $TeF_4Br_2^{2-}$ | 123.7<br>133.2 | 50.3 |
| $TeF_4I_2^{2-}$ | 123.8<br>132.4 | 50.8 |

Although at room temperature, only two broad lines were observed in all the spectra, at 243K the signals near 123 and 132 ppm split into a doublet and quintet, respectively. These are the multiplets expected for axial fluorine-equatorial fluorine coupling in a square pyramidal species. The coupling constants are very close to that reported previously,[133] although the chemical shifts differ by over 100 ppm (Table 4.4).

Unfortunately, signals could not be obtained from species of general formula $TeX_4F_2^{2-}$.

The results obtained from tellurium-125 n.m.r. spectroscopy are reported in Table 2.21.

TABLE 2.21

Tellurium-125 N.M.R. Spectra of the Mixed Fluorotellurate Systems

| SYSTEM | CHEMICAL SHIFT (ppm) |
|---|---|
| $TeF_4Cl_2^{2-}$ | 1323 |
| $TeF_4Br_2^{2-}$ | 1347 (2) |
| | 1331 (1) |
| $TeF_4I_2^{2-}$ | 1139 |
| $TeCl_4F_2^{2-}$ | 1466 (3) |
| | 1577 (2) |
| | 1796 (1) |
| $TeBr_4F_2^{2-}$ | 1336 |
| $TeI_4F_2^{2-}$ | - |

These results are less conclusive than those obtained from fluorine-19 n.m.r. spectroscopy. The chemical shifts of the $TeF_4Cl_2^{2-}$ and $TeF_4Br_2^{2-}$ systems lie in the six-coordinate region and are tentatively assigned to intermediate species of unknown constitution with the peak at 1331 ppm in the spectrum of the $TeF_4Br_2^{2-}$ ion assigned to the $TeBr_6^{2-}$ species. The multiplet at 1139 in the spectrum of the $TeF_4I_2^{2-}$ ion is immediately assigned to the $TeF_5^-$ species (Section 4.5.2). The lack of correlation between the fluorine-19 and the tellurium-125 n.m.r. spectra for these chloro- and bromo- species is most probably a consequence of the differing temperatures at which the spectra were recorded, with exchange occurring at room temperature.

The spectra recorded from species of general formula $TeX_4F_2^{2-}$ are even more complicated especially for the chloro-compound. The signals at 1466 and 1577 ppm lie in the five-coordinate region and are assigned to unknown intermediate fluorochloro- species. The signal at 1796 ppm lies quite close to that observed for tellurium tetrachloride in acetonitrile, the solvent used in this study (1724 ppm), and so could be due to an unknown neutral fluorochloro- species. The signals at 1466 and 1796 ppm also appeared in the spectrum of the $TeCl_4F^-$ system. The signal at 1336 ppm for the bromo-compound is assigned to a six-coordinate intermediate fluorobromo- species, possibly $TeBr_4F_2^{2-}$. This further ionisation of the hexacoordinate species is probably due to the fairly good ionising properties of acetonitrile.

## CONCLUSION

The results for the hexachloro-, hexabromo- and hexaiodo-species show no evidence of distortion, neither in the solid state nor in solution. Although their colours, conductivity, and spectroscopic properties have been cited as evidence of population of solid state bands in these compounds, unusual spectroscopic behaviour can be adequately explained by second-order Jahn-Teller[78] or pre-resonance Raman effects.[85] The fact that the solutions are also coloured indicates a solid state mechanism to be invalid and the occurrence of $a_{1g}^{*} \longrightarrow t_{1u}^{*}$ transitions is a much more likely explanation. More work is necessary before the conductivity can be satisfactorily explained.[96]

The breakdown of the pairwise additivity rules for tellurium suggests that the lone pair of electrons is contributing to the shielding in an anisotropic manner, perhaps due to hybridisation with the tellurium p orbitals. There is some evidence that the s electrons are, indeed, involved in bonding.[85,93]

The presence of mixtures in the iodo- series may be a consequence of the strength of the tellurium-iodine bond; but further n.m.r. work at higher field and lower temperature may be enlightening. The appearance of a signal at 1446 ppm. in different chloroiodo- systems also merits further investigations.

The formation of the pentafluoro- anion in reactions of tellurium tetrafluoride with halide ion reflects the great stability of this species. The absence of Raman bands attributable to $TeF_5^-$ in these systems is probably due to the greater scattering power of the hexahalogeno- complexes.

## EXPERIMENTAL

### 2.5 The Hexachloro-, Hexabromo- and Hexaiodotellurates

These compounds were prepared by standard methods,[123] as their tetrabutylammonium salts, by mixing tellurium dioxide (B.D.H. laboratory reagent, 99%) and the appropriate halide (chloride and bromide supplied by Eastman Kodak, iodide supplied by B.D.H., 98%) in the corresponding hydrohalogenic acid (HCl, sq.gr. 1.18, 36% and HBr, sp.gr. 1.47, 47% were supplied by B.D.H. and HI, sq.gr. 1.70, 55% was supplied by Hopkin and Williams). The resulting hexachloro- (yellow), hexabromo- (orange) and hexaiodo- (black) complexes were filtered off on a sinter washed with the relevant hydrohalogenic acid and dried *in vacuo*. They were subsequently handled under nitrogen. All chemicals were used as supplied except the hydriodic acid which was distilled from red phosphorus at 400K to remove iodine.[124]

TABLE 2.22

Analytical Results for the Hexachloro-, Hexabromo- and Hexaiodotellurates

| SPECIES | C | H | N | Te | Halogen | |
|---|---|---|---|---|---|---|
| $(Bu_4N)_2TeCl_6$ | 46.4 | 8.8 | 3.4 | 15.5 | 25.8 | Calc. |
| | 44.6 | 8.5 | 3.3 | 15.6 | 25.6 | Obs. |
| $(Bu_4N)_2TeBr_6$ | 35.2 | 8.3 | 2.3 | 11.4 | 43.3 | Calc. |
| | 35.4 | 8.1 | 2.5 | 11.4 | 43.9 | Obs. |
| $(Bu_4N)_2TeI_6$ | 28.0 | 5.2 | 2.0 | 9.3 | 55.4 | Calc. |
| | 26.7 | 5.7 | 2.2 | 9.3 | 55.4 | Obs |

## 2.6 Mixed Hexahalogenotellurates

These complexes were prepared by mixing together the stoichiometric quantities of tellurium tetrahalide and tetrabutylammonium halide in dichloromethane under nitrogen. Although the tetrahalides were insoluble in dichloromethane, the complexes were freely soluble and total solution was achieved immediately on mixing. The solvent was then removed by pumping. Typically, 2-5 mmol of product were prepared. All the halides were dried by pumping except tetrabutylammonium chloride which was dried by removing water azeotropically, twice in methanol and finally in toluene.

TABLE 2.23

Analytical Results for the Mixed Chlorobromotellurates

| SPECIES | C | H | N | Te | Cl | Br | |
|---|---|---|---|---|---|---|---|
| $(Bu_4N)_2TeCl_5Br$ | 44.2 | 8.3 | 3.2 | 14.7 | 20.4 | 9.2 | Calc. |
| | 43.2 | 8.0 | 2.9 | 14.7 | 18.5 | 8.8 | Obs. |
| $(Bu_4N)_2TeCl_4Br_2$ | 42.1 | 7.9 | 3.1 | 13.9 | 17.5 | 15.5 | Calc. |
| | 42.7 | 8.1 | 3.4 | 13.8 | 33.0 | | Obs. |
| $(Bu_4N)_2TeCl_3Br_3$ | 40.1 | 7.5 | 2.9 | 13.3 | 11.1 | 25.0 | Calc. |
| | 38.3 | 8.0 | 2.8 | 13.3 | 36.1 | | Obs. |
| $(Bu_4N)_2TeCl_2Br_4$ | 38.3 | 7.2 | 2.8 | 12.7 | 7.1 | 31.9 | Calc. |
| | 36.8 | 7.2 | 2.5 | 12.6 | 6.9 | 32.5 | Obs |
| $(Bu_4N)_2TeClBr_5$ | 36.7 | 6.9 | 2.7 | 12.2 | 3.4 | 38.2 | Calc. |
| | 36.4 | 7.0 | 2.7 | 12.2 | 41.6 | | Obs |

In the chloroiodo- and bromoiodo- series, the systems of general formula $TeX_3Y_3{}^{2-}$ were prepared by mixing equimolar quantities of the hexachloro- and hexaiodo-, and hexabromo- and hexaiodotellurates, respectively.

### TABLE 2.24

### Analytical Results for the Hexachloriodo- Systems

| SYSTEM | C | H | N | Te | Cl | I | |
|---|---|---|---|---|---|---|---|
| $(Bu_4N)_2TeCl_5I$ | 41.9 | 7.9 | 3.1 | 13.9 | 19.3 | 13.9 | Calc. |
| | 41.2 | 8.8 | 2.8 | 14.1 | 19.5 | 14.3 | Obs. |
| $(Bu_4N)_2TeCl_4I_2$ | 38.2 | 7.1 | 2.8 | 12.7 | 14.1 | 25.2 | Calc. |
| | 39.1 | 7.5 | 2.7 | 12.7 | 13.2 | 24.9 | Obs. |
| $(Bu_4N)_2TeCl_3I_3$ | 34.9 | 6.5 | 2.5 | 11.6 | 9.7 | 34.6 | Calc. |
| | 34.6 | 7.3 | 2.3 | 11.6 | 9.5 | 34.6 | Obs. |
| $(Bu_4N)_2TeCl_2I_4$ | 32.3 | 6.0 | 2.4 | 10.7 | 6.0 | 42.6 | Calc. |
| | 32.6 | 6.8 | 2.2 | 10.1 | 6.0 | 39.0 | Obs. |
| $(Bu_4N)_2TeClI_5$ | 29.9 | 5.6 | 2.2 | 10.0 | 2.8 | 49.5 | Calc. |
| | 32.3 | 6.8 | 2.1 | 8.1 | 2.5 | 48.9 | Obs. |

### TABLE 2.25

### Analytical Results for the Hexabromoiodo- Systems

| SYSTEM | C | H | N | Te | Br | I | |
|---|---|---|---|---|---|---|---|
| $(Bu_4N)_2TeBr_5I$ | 32.8 | 6.3 | 2.5 | 11.2 | 35.1 | 11.1 | Calc. |
| | 33.5 | 6.4 | 2.4 | 11.0 | 34.5 | 11.0 | Obs. |
| $(Bu_4N)_2TeBr_4I_2$ | 32.4 | 6.1 | 2.4 | 10.8 | 27.0 | 21.4 | Calc. |
| | 32.1 | 6.3 | 2.3 | 10.7 | 26.8 | 21.4 | Obs. |
| $(Bu_4N)_2TeBr_3I_3$ | 31.1 | 5.8 | 2.3 | 10.3 | 19.4 | 30.9 | Calc. |
| | 31.3 | 6.2 | 3.0 | 9.9 | 19.5 | 20.8 | Obs. |
| $(Bu_4N)_2TeBr_2I_4$ | 30.0 | 5.6 | 2.2 | 9.9 | 12.5 | 39.7 | Calc. |
| | 30.2 | 5.9 | 2.1 | 9.9 | 12.5 | 40.2 | Obs. |
| $(Bu_4N)_2TeBrI_5$ | 28.9 | 5.4 | 2.1 | 9.6 | 6.0 | 47.8 | Calc. |
| | 35.9 | 6.9 | 2.2 | 5.9 | 7.3 | 39.6 | Obs. |

The species of general formula $TeI_5X^{2-}$ were found to give unsatisfactory analyses, especially where X is bromide. This problem could well be associated with the apparent greater stability of the $TeI_6^{2-}$ species.

As mentioned in Section 2.4.4, only species of general formula $TeF_4X_2^{2-}$ and $TeX_4F_2^{2-}$ could be prepared among the fluorotellurates and the chloro- compounds could not be isolated as solids. The analytical results are given in Table 2.26.

TABLE 2.26

Analytical Results for the Mixed Hexafluorotellurate Systems

| SYSTEM | C | H | N | Na | Te | F | Br | I | |
|---|---|---|---|---|---|---|---|---|---|
| $(Bu_4N)_2TeF_4Br_2$ | 45.3 | 8.5 | 3.3 | - | 14.9 | 9.0 | 18.8 | - | Calc. |
| | 44.9 | 11.9 | 3.4 | - | 15.0 | | 18.3 | - | Obs. |
| $(Na(18c6))_2TeBr_4F_2$ | 27.2 | 4.5 | - | 4.3 | 12.0 | 3.6 | 30.2 | - | Calc. |
| | 26.6 | 4.7 | - | 4.0 | 11.9 | | 30.8 | - | Obs. |
| $(Bu_4N)_2TeF_4I_2$ | 40.7 | 7.6 | 3.0 | - | 13.4 | 8.1 | - | 26.9 | Calc. |
| | 40.7 | 8.1 | 3.2 | - | 13.8 | | - | 26.8 | Obs. |
| $(Na(18c6))_2TeI_4F_2$ | 23.0 | 3.8 | - | 3.7 | 10.2 | 3.0 | - | 40.7 | Calc. |
| | | | - | 3.0 | 10.3 | | - | 40.9 | Obs. |

The tellurium tetrafluoride was prepared as described in Section 6.7.3. The species of general formula $TeX_4F_2^{2-}$ were prepared as their sodium (18-crown-6) ether (Na(18c6)) salts in order to confer solubility in organic solvents. The 18-crown-6 ether was supplied by Fluka A.G. and the sodium fluoride by B.D.H. Ltd. Acetononitrile was used as solvent. The difficulty encountered in isolating the fluorochloro-complexes as solids may have been due to the presence of fluoride ion, which has been found not to form a crystalline phase with the sodium (18-crown-6) ether cation.[184] In the case of the $TeCl_4F_2^{2-}$ system, the solvation of the fluoride ion by acetonitrile may decompose the $TeCl_4F_2^{2-}$ ion, generating fluoride ion from which the last traces of solvent cannot be removed. The situation is similar for the $TeF_4Cl_2^{2-}$ system with again the problem of removing the solvent, in this case dichloromethane, to obtain a solid phase.

The attempted preparation of the $TeCl_5F^{2-}$ species as its sodium (18-crown-6) ether salt failed since sodium chloride was found to be insoluble in a solution of the ether in acetonitrile. This may have been due to the low solvation energy of the chloride ion.

Addition of an equimolar quantity of chloride ion to a solution of tetrabutylammonium pentafluorotellurate in dichloromethane was found not to yield the $TeF_5Cl^-$ species. The tellurium-125 n.m.r. showed only the pentafluorotellurate ion to be present, with a chemical shift at 1141 p.p.m.

Finally, fluorine analyses were not determined on the solid compounds, since an insufficient quantity of sample was available.

# CHAPTER THREE

## THE HEXAFLUOROTELLURATE ANION

### INTRODUCTION

Although the hexafluorotellurate ion has been postulated several times, its existence has never been proved beyond doubt and, at the moment, it can be considered to be unknown. It is therefore considered separately.

The species was first reported[125] as the dipyridinium salt, prepared as buff-coloured, needle-shaped crystals from tellurium dioxide and pyridine in concentrated hydrofluoric acid. Later Seel and Massat[126] reported the reaction between tellurium tetrachloride and nitrosyl fluoride in liquid sulphur dioxide thus:

$$TeCl_4 + 6FSO_2NO \longrightarrow (NO)_2TeF_6 + 4NOCl + 6SO_2$$

The di-S-benzylthiuronium salt has also been described,[127] being prepared in a similar manner to the dipyridinium salt.

Edwards[128] reported three attempts at preparing the hexafluorotellurate ion:

(i) Heating of potassium pentafluorotellurate to 723K in a nickel tube under vacuum.

(ii) Fusion of potassium pentafluorotellurate with the stoichiometric quantity of potassium fluoride required to form the hexafluorotellurate.

(iii) Condensation of selenium tetrafluoride onto a mixture of potassium fluoride and tellurium dioxide in the molar proportions, 2:1, followed by warming.

However, in no case was the desired product obtained, methods (i) and (ii) yielding only starting materials and method (iii) yielding potassium pentafluorotellurate and potassium pentafluoroselenate; with selenium and tellurium also being formed.

Russian Mössbauer work[62-65] has alluded to the presence of the hexafluorotellurate species in solutions of tellurium dioxide in concentrated hydrofluoric acid, but has been severely criticised,[66] in favour of the pentafluorotellurate.

Sarma [129] has made numerous attempts to prepare hexafluorotellurate salts and these are summarised below:

(i) Reaction of tellurium dioxide with fluoride ion or an organic base in 40% hydrofluoric acid.

(ii) Fluorination of hexachlorotellurates with fluorine or iodine pentafluoride and of hexabromotellurates with fluorine, selenium tetrafluoride or potassium fluoride in liquid sulphur dioxide.

(iii) Fusion of tellurium tetrafluoride with caesium fluoride.

However, methods (i) and (iii) generally gave rise to pentafluorotellurates while method (ii) liberated tellurium hexafluoride.

Attempts to repeat the preparation of the dipyridinium[129,130] and di-S-benzylthiuronium[130] salts proved fruitless and only pentafluorotellurates were formed.

Adams and Downs[131] also failed to prepare the hexa-fluoro-species from solutions of tellurium dioxide in concentrated hydrofluoric acid and suggested that this anion must possess a significant positive free energy of formation with respect to the pentafluoro- species and fluoride ion. Milne and Moffett[130] likewise failed to produce hexafluorotellurates by mixing tetraalkylammonium fluorides with the corresponding pentafluorotellurates in concentrated hydrofluoric acid or acetonitrile.

More recently, the hexafluorotellurate ion has been reported as being present in solutions of tellurium tetrafluoride and dibutylammonium fluoride in dichloromethane.[132] The $^{19}F$ n.m.r. shift was found to be identical with that obtained from solutions of the pentafluorotellurate anion in dichloromethane although no actual values were given. The sharpening of the line assigned to $TeF_6^{2-}$ at low temperature was taken as due to exchange with fluoride ion. No splitting was observed in the spectrum of the pentafluorotellurate. This work was later questioned[133] and no evidence of $TeF_6^{2-}$ in solutions of $Bu_4NF$ and $Bu_4NTeF_5$ in dichloromethane at 303K was found.

Finally, Urch[91] has suggested that, if formed, the hexafluorotellurate ion may well be distorted since the fluorine 2p orbitals will be of comparable energy to the tellurium 5s orbitals and the resulting interaction will destabilise the $a_{1g}^*$ orbital (Section 2.1.5).

In this work four methods of preparation were attempted, all involving reaction of a pentafluorotellurate with fluoride ion.

## RESULTS AND DISCUSSION

### 3.1 Reaction between $Me_4NF$ and $Me_4NTeF_5$ in Liquid Sulphur Dioxide

The work of Seel and Massat[126] suggested liquid sulphur dioxide to be a suitable solvent for the preparation of the hexafluorotellurate anion. In the present work the tetramethylammonium rather than the nitrosonium cation was utilised, since a more favourable lattice energy change could be expected.

Accordingly, solutions of $Me_4NF$ and $Me_4NTeF_5$ were made up and mixed in a 1:1 molar ratio. Upon mixing a white solid was precipitated, presumably due to the high concentration of tetramethylammonium cation, and this was filtered off and its infrared spectrum recorded. However, only bands due to pentafluorotellurate[134] and fluorosulphite[135] were observed, the latter being known to be formed in solutions of fluoride ion in liquid sulphur dioxide.[136]

This experiment casts doubt on the earlier work and it is most probable that Seel and Massat obtained $NOTeF_5$.

### 3.2 Reaction between $Bu_4NF.nH_2O$ and $Bu_4NTeF_5$ in Dichloromethane

In this experiment tetrabutylammonium salts were used since their presence would not only lead to greater stabilisation of a large anion but would also confer solubility in inert, polar organic solvents, such as dichloromethane, enabling n.m.r. spectra to be recorded. Unfortunately, tetrabutylammonium fluoride cannot be prepared in an anhydrous state, it usually being associated with approximately 30 molecules of water. The compound was therefore dissolved in toluene and the toluene-water azeotrope distilled off leaving a gum-like substance. Due to its low solubility in toluene, the tetrabutylammonium pentafluorotellurate was added as a solution in dichloromethane. The gum dissolved but tellurium-125 n.m.r. of the solution showed the pentafluorotellurate (Section 4.5.2) ion to be the only tellurium containing species present.

### 3.3 Reaction between NaF and $NaTeF_5$ in the Presence of 18-Crown-6 Ether

As an alternative to decreasing the lattice energy using large organic cations, the fluorides of which are difficult to dry, sodium fluoride was dissolved in acetonitrile in the presence of 18-crown-6 ether. The crown-ether is known to define a cavity of sufficient size to envelope a sodium ion leaving "free" fluoride.[137] After the sodium pentafluorotellurate had been added and dissolved, the solution was evaporated to low volume and the white solid precipitated was filtered off in the dry box. The infrared spectrum of this solid showed only the pentafluorotellurate ion to be present.[134]

## 3.4 Reaction between $Bu_4NF.nH_2O$ and $Bu_4NTeF_5$ in the Fused State

In a final attempt to prepare the hexafluoro- species the starting materials were melted together as the tetrabutylammonium salts, the fluoride being first dried as much as possible by pumping under vacuum. The temperature was first increased to 343K, and infrared spectra of the produce showed pentafluorotellurate to be present as well as hydrogen bonded water and a new band at 250 $cm^{-1}$. Some idea of the nature of this band may be gained from a comparison of the spectra of the penta- and hexachlorotellurates. If the ratio between the $\nu_1$ mode for $Bu_4NTeCl_5$ (Table 4.5) and the bands assigned to $\nu_3$ and $\nu_4$ for $(Bu_4N)_2TeCl_6$ (Table 2.7) is used to determine $\nu_3$ and $\nu_4$ for $(Bu_4N)_2TeF_6$ from the $\nu_1$ band for $Bu_4NTeF_5$ (Table 4.10) then bands at 486, 434 and 261 $cm^{-1}$ are predicted. The two high frequency bands ($\nu_3$) would be obscured by these due to $\nu_2$ and $\nu_1$ of the pentafluoro- species, but the band at 261 $cm^{-1}$ ($\nu_4$) could correspond to that observed at 250 $cm^{-1}$.

Tellurium-125 n.m.r. spectra also exhibited new signals at 887, 817 and 718 ppm.

At higher temperatures, although the water band had disappeared, the new band was likewise no longer visible and control experiments established that tetrabutylammonium fluoride had decomposed at around 353K to give 1-butene and presumably tributylammonium fluoride.

The experiment was repeated with the tetramethylammonium salts, since the fluoride was available in an anhydrous state, but no advantage was gained and the compounds did not even melt at 483K, but only darkened and decomposed to give trimethylamine and presumably fluoromethane.

## CONCLUSION

It is obvious from this work that the pentafluorotellurate ion is extremely reluctant to accept a fluoride ion, perhaps due to repulsion by the tightly bound lone pair of electrons on tellurium. Even forcing conditions did not lead to any well-defined results but the following equilibrium can be postulated:

$$Bu_4NF.nH_2O + Bu_4NTeF_5 \rightleftharpoons (Bu_4N)_2TeF_6 + nH_2O$$

If the water can be quickly removed at 343K by using very high vacuum, then perhaps this illusive species can be finally isolated.

## EXPERIMENTAL

### 3.5 Reaction between $Me_4NF$ and $Me_4NTeF_5$ in Liquid Sulphur Dioxide

This experiment was performed in a Schlenk apparatus of the type depicted in Figure 7.21, of Schriver.[138] Dry tetramethylammonium fluoride, kindly donated by the late Professor T.C. Waddington, was dissolved in approximately 3cm$^3$ of sulphur dioxide, previously dried over phosphorus pentoxide. An equimolar quantity (3mmol.) of tetramethylammonium pentafluorotellurate, prepared as described in Section 6.7.2, was dissolved in about 5cm$^3$ of liquid sulphur dioxide in the other limb of the vessel. The solutions were then mixed and the resulting precipitate was filtered at the sinter by cooling one limb in a toluene slush bath at 178K. After the solvent had been pumped away, the apparatus was taken into the dry box where a nujol mull of the solid was made up. The infrared spectrum displayed bands at 273, 343, 480 and 632 cm$^{-1}$ assignable to the pentafluorotellurate ion[134] as well as bands at 590, 1095 and 1185 cm$^{-1}$ due to the fluorosulphite anion.[135]

## 3.6 Reaction between $Bu_4NF.nH_2O$ and $Bu_4NTeF_5$ in Dichloromethane

The hydrated fluoride (1mmol. n = 28.9 from analysis) prepared as described in Section 6.7.1 was dissolved in approximately 50 cm$^3$ of toluene contained in a 250 cm$^3$ two-necked, round-bottomed flask. In one neck of the flask was placed a distillation column, packed with glass helices and linked at the top to a receiver flask above which was a Liebig condenser, mounted vertically. A thermometer was also placed at the head of the distillation column.

The solution was heated using an isomantle and the toluene-water azeotrope distilled at 382K. Further aliquots of toluene were added until 300cm$^3$ had been added in all, whereupon the distillation was continued until only a gum-like substance remained in the flask. Final traces of toluene were removed by pumping under vacuum and the pentafluorotellurate (1mmol.), prepared as described in Section 6.7.2, was added as a solution in 2 cm$^3$ of dichloromethane, in the dry box. After 16 hours the volume of the resulting solution was reduced to 1 $cm^3$ on the vacuum line and an n.m.r. sample prepared in the dry box. The chemical shift measured, 1141 ppm, indicated that the pentafluorotellurate ion was present (Section 4.5.2).

## 3.7 Reaction between NaF and $NaTeF_5$ in the presence of 18-Crown-6-Ether

Sodium fluoride (1mmol.), previously dried under vacuum for 10 hours, was dissolved in approximately 5 $cm^3$ of dry acetonitrile containing 2mmol. of 18-crown-6 ether (Section 2.6) in solution in the dry box. Sodium pentafluorotellurate (1mmol.) was added to this and total dissolution achieved on shaking. The solvent was then removed on the vacuum line until a white solid was precipitated and this was filtered off on a sinter funnel in the dry box and a nujol mull made up for infrared analysis.

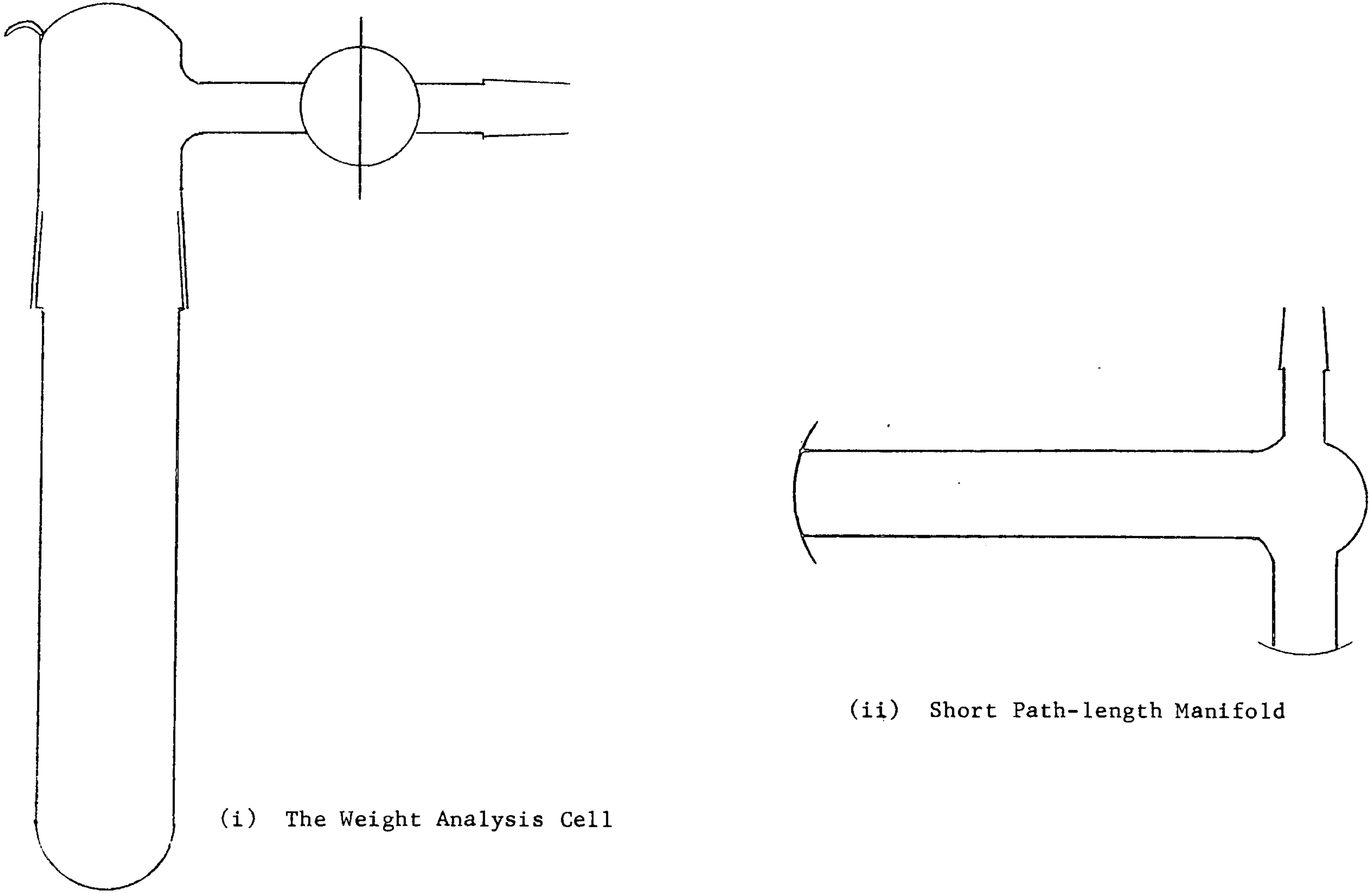
## 3.8 Reaction between $Bu_4NF.nH_2O$ and $Bu_4NTeF_5$ in the Fused State

The hydrated fluoride (0.5 mmol.), Section 6.7.1) was dried *in vacuo* for 24 hours during which time a loss in mass was observed which corresponded to the removal of 26mmol. of water (i.e. from n = 28.9 to n = 2.9). The pentafluorotellurate (0.5mmol.) was added in the dry box and the vessel (Figure 3.1) returned to the vacuum line. It was then heated to 343K by means of a silicone oil bath and maintained at this temperature for 2 days during which time the mixture partially liquified. The vessel was then allowed to cool to room temperature and taken into the dry box where samples of the sticky solid obtained were made up for infrared and tellurium-125 n.m.r. spectra, the results of which are discussed in Section 3.4.

The experiment was repeated but the temperature was this time raised to 363K. However, decomposition was observed to occur, as evidenced by a loss in mass. A similar procedure was followed using only the fluoride and decomposition was found to occur at around 353K. The contents of the trap on the vacuum line were condensed onto phosphorus pentoxide to remove any water present and then allowed to expand into an infrared gas cell. The spectrum exhibited bands at 900, 910, 920, 990, 1450, 1640 and 1835 $cm^{-1}$ all assignable to 1-butene.[139]

Since it was deemed necessary to remove the water quickly and efficiently, improvement of the vacuum system was attempted. An adaptor, shown in Figure 3.2, was constructed so that the reaction vessel could be attached directly to the pumping section. The tap shown in Figure 3.1 was replaced by a simple 8mm base tap with S35 and B24 sockets. Although some improvement was achieved and a vacuum of $6 \times 10^{-4}$ mm Hg attained, similar results were obtained.

The experiment with the tetramethylammonium salts was carried out in a manner similar to that described in the second paragraph, except that the fluoride provided by Professor T.C. Waddington, was assumed to be dry. The gas-phase infrared spectrum of the decomposition products showed bands at 823, 1030, 1055, 1182, 1270, 1440, 1458, 1472, 2780, 2820 and 2950 $cm^{-1}$ all assignable to trimethylamine by comparison with the spectrum of an authentic sample, kindly supplied by Dr. C.J. Ludman.



(i) The Weight Analysis Cell

(ii) Short Path-length Manifold

Fig. 3.

# CHAPTER FOUR

# THE PENTAHALOGENOTELLURATES

## INTRODUCTION

### 4.1 The Pentahalogenotellurates not Containing Fluorine

Unstable acids of the form $HTeX_5$ (where X=Cl, Br or I) were first postulated at the end of the nineteenth century,[24] but it was not until 1957 that the preparation of salts was reported. Aynsley and Campbell[140] presented preparations of uronium salts from mixtures of urea and tellurium dioxide in hydrochloric acid, followed by recrystallisation to form the pentachloro- complex, and then treatment with hydrobromic or hydriodic acids to form the pentabromo- and pentaiodo- compounds. Pyrimidinium and pyrazinium salts have also been reported.[140] Later, the crystal structure of uronium pentachlorotellurate[34] was interpreted as a random arrangement of square-pyramidal anions. However, the compound was subsequently shown to be ammonium hexachlorotellurate[141] ($NH_4^+$ formed by acid hydrolysis of urea).

Visible spectra of $TeX_4 - X^-$ systems (X = Cl, Br)[142,143] in dipolar organic solvents have been interpreted as containing pentahalogeno species at low concentrations, and ultraviolet spectra[74] of tellurium tetrachloride-pyridinium hexachlorotellurate solutions in acetonitrile have suggested the formation of the pentachloro species according to:

$$TeCl_4 + TeCl_6^{2-} \longrightarrow 2TeCl_5^-$$

Unfortunately, crystals could not be isolated and vibrational spectra proved inconclusive. Subsequent infrared investigations[77] of the tetraethylammonium salt implied the anion symmetry to be less than that of the expected square based pyramid.

Adams[78] has studied the vibrational spectra of the pentachloro- and pentabromotellurates both in the solid state and in solution. Assignments to $C_{4v}$ (square-based pyramid) were made largely on the basis of analogy with the pentafluorotellurates, which gave spectra of much higher quality - bands due to the corresponding hexahalogenotellurates caused difficulty by obscuring some of the pentahalogeno- fundamentals. A change in anion constitution between solid and solution was postulated for the tetraethylammonium salts, although it could not be decided whether the solids contained distorted but discrete anions or polymeric structures.

Electronic absorption spectra[94] have shown the pentachloro-anion to be present in very low concentrations of the hexachloro-species in dichloromethane solution.

A 1:1 compound formed between phosphorus pentachloride and tellurium tetrachloride has been reported and the crystal structure of the pentahalogeno-moiety was first solved in this species.[144] It was found to contain discrete tetrachlorophosphonium tetrahedra and polymeric chains of anions consisting of cis bridged octahedra. Later work confirmed this arrangement.[145]

An extensive vibrational analysis,[100] involving force constant calculations, has been reported for both the pentachloro- (Table 4.1) and pentabromo- (Table 4.2) compounds. In both cases $C_{4v}$ symmetry was assumed.

TABLE 4.1 Reported Vibrational Spectra of the Pentachlorotellurate Anion

| Infrared ($cm^{-1}$) | Raman ($cm^{-1}$) | Description of Mode |
|---|---|---|
| 320 sh | 336 s | ν TeCl ($a_1$) |
| 303 m | 295 ms | " ($b_1$) |
| 265 m | 266 ms | " ($a_1$) |
| 250 s | 244 w | " (e) |
| 221 w | 208 w,br | |
| 167 m | 143 m | δ TeCl ($b_2$) |
| | 115 | " (e) |

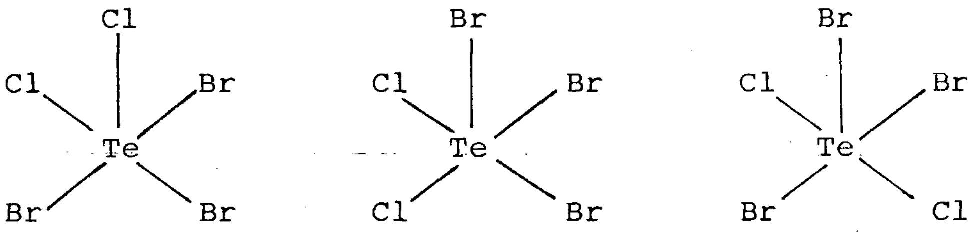
TABLE 4.2 Reported Vibrational Spectra of the Pentabromotellurate Anion

| Infrared | Raman | Description of Mode |
|---|---|---|
| 297 w | 300 vw | |
| 250 s | 240-245 br,w | ν TeBr (e) |
| 220 m | 220 s | " ($a_1$) |
| 207 mw | | |
| 188 s | 195 s | ν TeBr ($a_1$) |
| | 161 s | " ($b_1$) |
| | 147 m | δ TeBr (e) |
| | 134 m | " ($a_1$) |

These species have also been subjected to a Mössbauer study[69] and the lower isomer shifts, when compared to the hexahalogeno- species, were explained in terms of some stereochemical activity of the lone pair in a distorted octahedral structure. The absence of quadrupole splitting was attributed to the high coordination number and the presence of halogen bridges about the tellurium.

The pentachloro- species has been detected in $KCl - AlCl_3 - TeCl_4$[146,147] and $PCl_5 - TeCl_4$[148] melts. The pentabromo-anion has been prepared as the thiotrithiazyl salt,[149] and subsequently shown to dissolve in disulphuric and chlorosulphuric acids to form the tribromotellurium (IV) cation.[150]

The only mixed species to have been prepared in this series are the chlorobromotellurates. The tribromodichloro- anion has been prepared from tellurium dichloridedibromide and tetraethylammonium bromide in dichloromethane-benzene solution. However, the vibrational spectra[99] could not differentiate between the three possible isomers depicted in Figure 4.1



(A) (B) (C)

Figure 4.1

Later,[100] force constant calculations were used to assign the spectra to structure C with the trichlorodibromo- species adopting the corresponding structure.

The tetrachloromonobromo- compound may adopt one of the two possible structures, indicated in Figure 4.2:

(A) (B)

Figure 4.2

Force constant calculations showed the spectra to be in accordance with structure A and the spectra of the tetrabromomonochloro- anion indicated the formation of the corresponding structure.

The following reaction schemes were postulated:

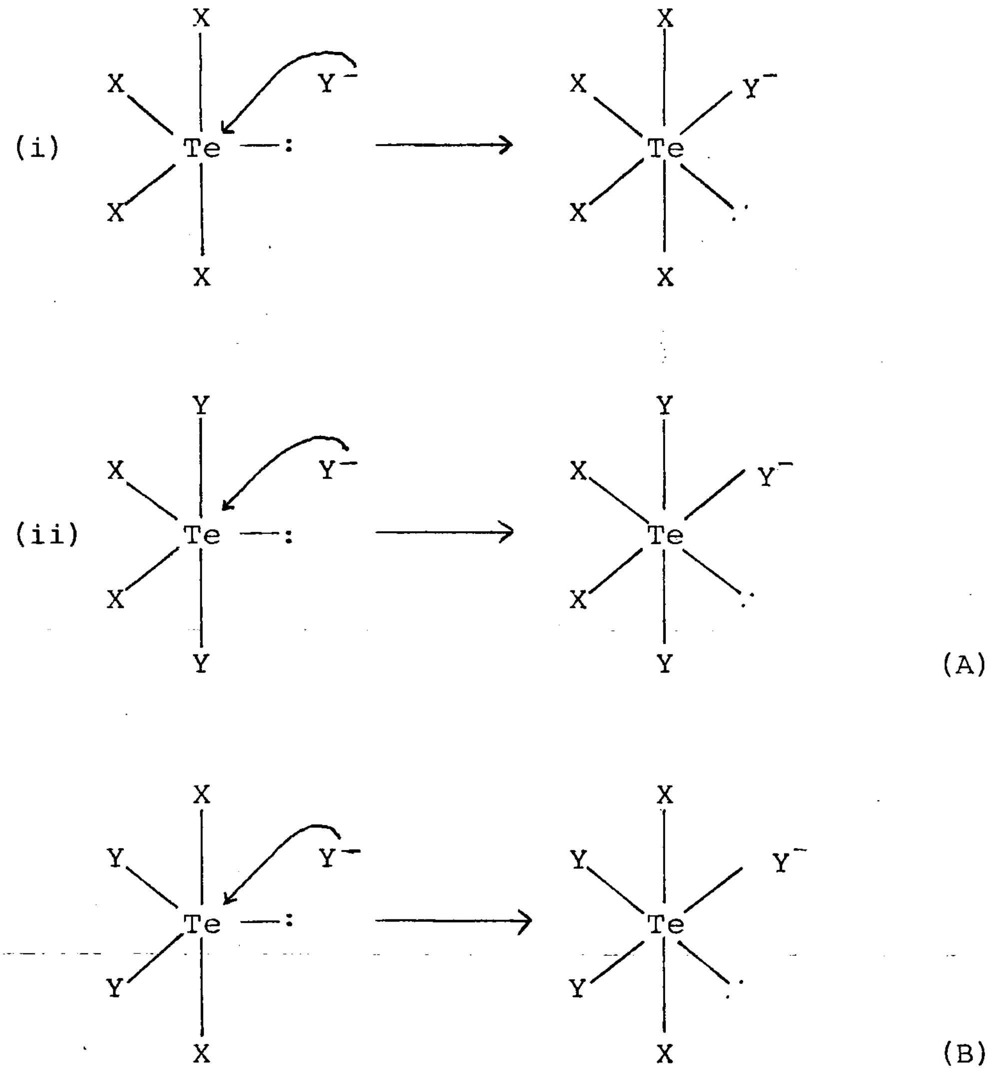


Figure 4.3

For scheme (i) it was argued that the entering halide ion would prefer to coordinate to the molecular tetrahalide in a position that was in the equatorial plane of the trigonal bipyramid and between the halogen and the non-bonding electron pair, rather than between the two halogen atoms already in the plane. Similarly, in scheme (ii) it was indicated that, for the two conformers of the mixed tetrahalide found to be present in solution,[151] the formation of anions A and B is to be expected.

## 4.2 The Pentafluorotellurates

The pentafluoro- species has been studied to a much greater extent than any other pentahalogenotellurate ion and can be simply prepared by dissolving tellurium dioxide and the appropriate fluoride in hydrofluoric acid.[24] The pyridinium compound can be made in the same solvent from tellurium tetrafluoride and pyridine,[125] and the nitryl compound, $(NO_2)TeF_5$ has been prepared by the action of nitryl fluoride on tellurium dioxide.[152] Later work[128] questioned the purity of the early preparations and obtained the potassium, rubidium and caesium salts from using the reactions:

$$TeO_2 + MF + 2SeF_4 \longrightarrow MTeF_5 + 2SeOF_2$$

However, Greenwood *et al*[134] vindicated the original preparations and reported vibrational spectra of several salts. Observations of the number of infrared and Raman active bands, together with the number of coincidences led to the conclusion that a square-based pyramid was the most likely structure, both in the solid state and in solution. The solid state results for the potassium salt, with assignments, are shown in Table 4.3. Later work, including a single crystal Raman study[153] and solution measurements,[131] agreed well with these results, although the location of $\nu_4$ remained in dispute.[131,133,154]

The crystal structure was first determined by Edwards and Mouty[155] for the potassium salt and they found isolated, square-pyramidal anions, with the tellurium atom lying slightly below the basal plane, the lone pair completing an approximately octahedral geometry. Later results[156,157] showed some distortion within the basal plane due to the effect of the lone pair on an adjacent

TABLE 4.3 Reported Vibrational Spectra of the Pentafluorotellurate Anion

| Infrared | Raman | Assignment |
|---|---|---|
| 616 ms | 616 vs | $\nu_1$ |
| 521 m | 511 s | $\nu_2$ |
| 293 m | 294 mw | $\nu_3$ |
| inact. | 570 mw | $\nu_4$ |
| " | unobs. | $\nu_5$ |
| " | 247 mw | $\nu_6$ |
| 472 vs | 484 s | $\nu_7$ |
| 347 m | 349 mw | $\nu_8$ |
| 119 )<br>)<br>130 )mw<br>)<br>140 ) | 132 vw | $\nu_9$ |

tellurium atom, and later vibrational work was interpreted in terms of $C_s$ symmetry.[133]

The Mössbauer spectrum[66] of the pentafluoro- species showed appreciable quadrupole splitting, as expected for square-pyramidal geometry, and also a less positive isomer shift than found for hexahalogeno- compounds, consistent with the more diffuse nature of the lone pair. This work was later substantiated.[158]

Fluorine-19 n.m.r. spectroscopy[132,133] has also been used to study this anion, but coupling was only observed in the more recent work for the tetrabutylammonium salt in dichloromethane solution at 223K. The result is shown in Table 4.4, the chemical shifts being measured downfield from hexafluorobenzene.

TABLE 4.4 Reported Fluorine-19 n.m.r. Spectra of the Pentafluorotellurate Anion

| Signal | Chemical Shift (ppm) | Coupling Constants (Hz) |
|---|---|---|
| a | 21.708 | $J(^{19}F_{ax.}-^{19}F_{eq})$ 50.9 |
| b | 31.717 | |
| c | 14.392 | $J(^{19}F_{ax.}-^{125}Te)$ 1375.7 |
| $c^1$ | 29.018 | |
| d | 15.651 | $J(^{19}F_{eq.}-^{123}Te)$ 1143.8 |
| $d^1$ | 27.786 | |
| e | 16.389 | $J(^{19}F_{ax.}-^{125}Te)$ 2883.3 |
| $e^1$ | 47.036 | |

Signals a and b are the expected doublet and quintet for a square-pyramidal anion, the distortion discussed earlier being removed in solution. The signals c, $c^1$ and e, $e^1$ are the result of $^{125}Te$ coupling with $^{19}F_{ax.}$ and $^{19}F_{eq.}$ respectively; being a doublet of doublets and a doublet of quintets. Peaks d, $d^1$, a doublet of doublets, are due to $^{19}F_{eq.}-^{123}Te$ coupling. The coupling of $^{19}F_{ax.}$ to $^{123}Te$ was not observed. The high values of the $^{125}Te-^{19}F_{ax.}$ coupling constants, when compared to those for $^{125}Te-^{19}F_{eq.}$ coupling were thought to be due to the high s character in the axial bond and the lone pair orbital, when compared to the s character of the bonds in the equatorial plane.

## RESULTS AND DISCUSSION

## 4.3 The Chlorobromotellurates

### 4.3.1 Raman Spectra

The Raman spectra were recorded for the tetrabutylammonium salts in the solid state and, when possible, in acetonitrile solution, and are reported in Table 4.5.

TABLE 4.5 Raman Spectra of the Pentachlorobromotellurates

| SPECIES | FREQUENCIES ($cm^{-1}$) |
|---|---|
| $TeCl_5^-$(s) | 134m 160w,sh 262s 284vs 354s,p |
| (soln.) | 133w 160vw,sh 260s 282vs,p 358s,p |
| $TeCl_4Br^-$(s) | 37s 138m 169m 191m 260s 280s 367m |
| (soln.) | 161w 187w 259sh 280s,p 360m,p |
| $TeCl_3Br_2^-$(s) | 87w 167s 191m 224m 255sh 272m 363w |
| $TeBr_3Cl_2^-$(s) | 28m 48m 86w 149m 154s 207vs 220s |
| | 255w 300m |
| $TeBr_4Cl^-$(s) | 29w 49vw 87m 142m 163w 198m 219vs |
| | 296m |
| $TeBr_5^-$(s) | 29vw 49w 82m 140m 163w 197s 219vs |

The frequencies obtained for the pentachloro- species in the solid state are only in fair agreement with those that have been reported previously for the tetraethylammonium salt.[78,100] The earlier work[78] reported a band at 358 $cm^{-1}$ in acetonitrile solution and suggested that the difference berween this frequency and the highest frequency solid state band at 336 $cm^{-1}$, may be due to the existence of a polymeric network in the solid. It is interesting that the band at 358 $cm^{-1}$ is in good agreement with the highest frequency band observed in the present study and this fact, when considered with the good agreement between solid state and solution data observed for the tetrabutylammonium salt, suggests that the pentachloro- anion may possess a different structure in the solid tetrabutylammonium salt from that in the solid tetraethylammonium salt, and may well be polymeric in the latter, as reiterated recently by LaHaie and Milne.[159]

The better agreement between the present work and the earlier reports[78,100] for the corresponding pentabromotellurate salts suggests that this anion possesses a similar structure with both cations. Unfortunately, solution spectra could not be obtained for this species, as indeed for any anion containing two or more bromine atoms. This was presumably due to their dark colour.

In order to explain the difference in the spectra of the tetraethylammonium and tetrabutylammonium salts when comparing the pentachloro- and pentabromo- species, it is suggested here that the smaller pentachloro- anion is bridged in the tetraethylammonium salt, but that in the presence of the larger tetrabutylammonium cation (or in solution) it exists as a discrete species. The pentabromo- anion, being somewhat larger may even adopt a bridged structure in the tetrabutylammonium salt and only exist as a discrete entity in solution.

The assignments preferred in this work differ from those given previously[100] and essentially follow those presented for the pentachloroselenate anion.[159] Thus, for the pentachloro- species, the two highest frequency bands at 284 and 354 $cm^{-1}$, which are polarised, are assigned to the in-phase tellurium-equatorial chlorine stretching vibration, $\nu_2$, and the tellurium-axial chlorine stretching vibration, $\nu_1$, respectively. The remaining $a_1$ mode, $\nu_3$, the umbrella deformation, is assigned to the weak feature at 133 $cm^{-1}$ (too weak for polarisation study). The remaining bands at 160 and 262 $cm^{-1}$ are assigned to the symmetric deformation and the out-out-phase symmetricstretching vibrations of the square-planar tellurium-equatorial chlorine moiety; $\nu_6$ ($b_2$) and $\nu_4$ ($b_1$), respectively. (In this work, $\nu_6$ is placed at higher frequency than $\nu_3$, contrary to previous assignment.[159] However, since $\nu_6$ is only active in the Raman and the lowest frequency band observed here is active in both the Raman and the infrared, it is felt that the new assignment is justified).

The bands due to the pentabromo- species are assigned similarly with the frequencies below 100 $cm^{-1}$ being due to deformation modes or lattice vibrations. The earlier work[100] is in better agreement for the pentabromo- species although the feature at 250 $cm^{-1}$ assigned to an e mode is most probably due to tellurium tetrabromide impurity. This compound may be present due to the equilibrium:

$$2TeBr_5^- \rightleftharpoons TeBr_4 + TeBr_6^{2-}$$

This reaction is known to occur for the pentachloro- species in acetonitrile and will be further to the right for the bromo- compound due to the greater stability of the hexabromo- species and the greater insolubility of tellurium tetrabromide. Earlier reports[78] of Raman spectra of the pentabromo- anion in solution in acetonitrile must therefore be viewed with some caution.

The two highest frequency bands are assigned to $a_1$ modes, the band at 197 $cm^{-1}$ being due to the in-phase tellurium-equatorial bromine symmetric stretching vibration, and that at 219 $cm^{-1}$ being due to the tellurium-axial bromine stretching vibration, while the features at 82, 140 and 163 $cm^{-1}$ are assigned to the $\nu_3$, $\nu_7$ and $\nu_4$ modes, respectively. The bands at 134 $cm^{-1}$, observed in the previous work,[100] was not observed here, but in any case its assignment as an $a_1$ mode is doubted since the corresponding mode of the pentachloro- species occurs at this frequency, consequently that of the pentabromo- compound would be expected at a somewhat lower frequency.

The results presented here for species of general formula $TeX_4Y^-$ are again only in moderate agreement with earlier work[100] involving the tetraethylammonium salts, and the explanation given previously for the pentachloro- and pentabromo- species is again invoked, being the absence of bridging in the tetrabutylammonium chloro- salts.

The presence of a band at 267 $cm^{-1}$, representing a tellurium-axial chlorine stretching frequency and the absence of any feature near 219 $cm^{-1}$ for the corresponding mode involving bromine, in the spectrum of the $TeCl_4Br^-$ species, indicates that the bromine atom occupies an equatorial position and that the symmetry of the anion is $C_s$ and not $C_{4v}$. It is difficult to assign bands to individual modes but it is probable that the bands at 260 and 280 $cm^{-1}$ involve predominantly tellurium-chlorine vibration whereas the feature at 190 $cm^{-1}$ will arise from tellurium-bromine motion. The lower frequency bands are probably deformation modes. Since the two highest frequency bands are polarised, they can be denoted as $A'$ modes, whereas the band at 260 $cm^{-1}$ can be denoted as an $A''$ mode. The low frequency bands were too weak for polarisation studies to be carried out.

A similar argument to the above can be used to assign the $TeBr_4Cl^-$ species to $C_s$ symmetry. There is no feature near 350 $cm^{-1}$ to indicate the presence of an axial chlorine atom and the very strong band at 219 $cm^{-1}$ is characteristic of tellurium-axial bromine stretching frequency. The highest frequency band can be assigned to a tellurium-chlorine stretching mode whereas the rest probably involve predominantly tellurium-bromine motion.

For the $TeBr_3Cl_2^-$ anion there is fair agreement between the results obtained in this work and those reported previously.[100]

This species was assigned to $C_{2v}$ symmetry, with a bromine atom occupying the axial position and the remaining two bromine atoms occupying trans positions in the equatorial plane. The assignment was made purely on the basis of the agreement between calculated and observed frequencies. In this work, the presence of a band at 220 $cm^{-1}$, coupled with the absence of a feature near 350 $cm^{-1}$, is invoked to rule out the configuration of $C_s$ symmetry in which a chlorine atom occupies the axial position. However, in the absence of any polarisation results it is not possible to establish which of the remaining isomers is present (Figure 4.1).

The spectrum presented here for the $TeCl_3Br_2^-$ species differs substantially from that reported earlier.[100] The band at 363 $cm^{-1}$ lends support to the presence of an axial chlorine atom but there is also a band at 220 $cm^{-1}$ characteristic of a tellurium-axial bromine stretching vibration. However, since there is no corresponding feature in the infrared spectrum (Table 4.6) assignment to one of the isomers containing an axial chlorine atom seems to be justified.

### 4.3.2 Far-Infrared Spectra

The far-infrared spectra are reported for the tetrabutylammonium salts in the solid state and are listed in Table 4.6.

There is fair agreement between the spectrum for the pentachloro-species and those reported previously for the tetra ethylammonium salt.[77,78,100] However, a band at 270 $cm^{-1}$, assigned in earlier work to a $b_1$ mode, $\nu_4$, active in the infrared due to crystal effects,[77] or to an $a_1$ mode, $\nu_2$,[100] was not observed in this work. Indeed, for a species of $C_{4v}$ symmetry, only those bands of a or e symmetry are allowed in the infrared

TABLE 4.6 Far-Infrared Spectra for the Pentachlorobromotellurates

| SPECIES | FREQUENCIES ($cm^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| $TeCl_5^-$ | 133m | 171m | 245vs | 289w | 367m | |
| $TeCl_4Br^-$ | 133w | 171sh | 186s | 199m | 248vs | 365s |
| $TeCl_3Br_2^-$ | 185m | 196sh | 247vs | 253sh | 362m | |
| $TeBr_3Cl_2^-$ | 122m | 189vs | 201sh | 218w | 248m | 293m |
| $TeBr_4Cl^-$ | 118m | 163w | 189vs | 215m | 293m | |
| $TeBr_5^-$ | 80sh | 116m | 139vw | 160w | 189vs | 211m |

spectrum, whilst all bands a, b and e are allowed in the Raman. Thus, the bands observed at 133, 289 and 367 $cm^{-1}$ are assigned to the $a_1$ modes, $\nu_3$, $\nu_2$ and $\nu_1$, respectively, the degree of coincidence being acceptable when the widths of the infrared bands are considered (∿10 $cm^{-1}$). The bands at 171 and 245 $cm^{-1}$ are assigned to the $\nu_8$ (e) and $\nu_7$ (e) modes respectively, which, although allowed in the Raman spectrum, are sometimes weak.[159] (Section 4.5.1).

Again, an analogous analysis is presented for the pentabromo-species with the bands at 80, 189 and 211 $cm^{-1}$ assigned to $a_1$ modes and those at 116, 139 and 160 $cm^{-1}$ assigned to $\nu_8$ (e), $\nu_7$ (e) and $\nu_4$ ($b_1$) modes respectively. The appearance of the last mode in the infrared may be due to a lifting of site symmetry, perhaps due to bridging. The agreement with earlier work[78,100] is fair, although the band observed previously[100] at 250 $cm^{-1}$ is probably due to tellurium tetrabromide.

The frequencies observed for the species of general formula $TeX_4Y^-$ are in fair agreement with those observed previously.[100] For a species of $C_s$ symmetry all vibrational modes should be active in both the infrared and Raman spectra and the agreement observed here supports assignment to this symmetry. Also, the presence of bands at 215 and 365 $cm^{-1}$ representing tellurium-axial bromine and tellurium-axial chlorine modes, in the spectra of the $TeBr_4Cl^-$ and $TeCl_4Br^-$ species, respectively, confirms the analysis.

Unfortunately, the infrared data for the species of general formula $TeX_3Y_2^-$ do not enable the $C_{2v}$ isomer to be distinguished from the $C_s$ isomer, in which an X atom occupies the axial position, since all vibrations are allowed in both the infrared and the Raman spectrum for these symmetries.

### 4.3.3 Tellurium-125 N.M.R. Spectra

These were recorded from the tetrabutylammonium salts in dichloromethane solution and are listed in Table 4.7.

TABLE 4.7 Tellurium-125 n.m.r. Spectra of the Pentachlorobromotellurates

| SPECIES | CHEMICAL SHIFT (ppm) |
|---|---|
| $TeCl_5^-$ | 1510 |
| $TeCl_4Br^-$ | 1515 |
| $TeCl_3Br_2^-$ | 1610 |
| $TeBr_3Cl_2^-$ | 1616 |
| $TeBr_4Cl^-$ | 1657 |
| $TeBr_5^-$ | 1645 |

The pairwise interaction theory (Section 2.3.3) would not be expected to be applicable to these species since the bond angles and bond lengths are not all equal, as assumed by the theory.

## 4.4 The Chloroiodo-, Bromoiodo- and Pentaiodotellurates

None of the anions of general formula $TeI_4X^-$ (where X = Cl, Br or I) could be prepared; this most probably is due to the very low solubility of tellurium tetraiodide in many solvents, as noted by Adams.[78] Thus, addition of an equimolar quantity of tetrabutyl-ammonium iodide in solution in dichloromethane to tellurium tetraiodide, yielded the hexaiodo-species as the only soluble product (Section 4.6).

Solid tellurium tetraiodide was also isolated from the reaction mixtures involving the other halide ions but the crystals recovered from the supernatant liquors proved more difficult to characterise. However, the vibrational spectra of the chloro- and bromo- systems, reported in Table 4.8, did suggest the presence of the hexacoordinate species (Tables 2.13, 2.14, 2.16 and 2.17).

Table 4.8 Vibrational Spectra of the $TeI_4X^-$ Systems (X=Cl,Br)

| System | Spectrum | Frequencies $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|---|
| $TeI_4Cl^-$ | IR | 94w | 146s | 174m | 220s | 273w | |
| | R | 32w | 108s | 114s | 149w | 169w | 222w |
| $TeI_4Br^-$ | IR | 90w | 160vs | 198w | | | |
| | R | 32w | 60w | 110s | 155w | 175w | 222w |

The tellurium-125 n.m.r. spectra of the above chloro- and bromo- systems exhibited single resonances at 1449 and 1423 ppm. respectively. Although the vibrational results suggest the presence of hexacoordinate species, these chemical shifts do not correspond to any of those reported for such species in Chapter Two, although the signal at 1449 ppm. did occur in the $TeCl_5I^{2-}$ and $TeCl_3I_3{}^{2-}$ systems (found to be mixtures). The composition of the $TeI_4X^-$ solutions therefore remains unknown.

Species of general formula $TeX_3Y_2{}^-$ could not be prepared since tellurium dichloridediiodide is unknown,[97] and although the preparation of tellurium dibromidediiodide has been reported,[98] it could not be repeated here (Section 6.7.5).

Addition of an equimolar quantity of tetrabutylammonium iodide in dichloromethane solution to tellurium tetrachloride also led to the recovery of tellurium tetraiodide. Vibrational spectra of the solid obtained from the supernatant liquor indicated a complicated mixture to be present. The infrared spectrum exhibited bands at 121w, 173m, 218vs and 270sh $cm^{-1}$, with those above 200 $cm^{-1}$ assignable to tellurium-chlorine modes and the remainder to tellurium-iodine modes (Section 2.3.1). The Raman spectrum displayed bands at 32w, 48w, 62w, 118s, 151m, 172m and 225w $cm^{-1}$, characteristic of six-coordinate iodo- species (Section 2.4.2(a)). Two tellurium-125 n.m.r. signals, at 1446 and 1500 ppm. were observed, the latter of which most probably represents a five-coordinate moiety. The latter signal was approximately 10 times more intense than the former. Unfortunately, no definite conclusions can be drawn on the basis of this information.

Addition of iodide ion to an equimolar quantity of tellurium tetrabromide yielded the $TeBr_4I^-$ anion. The vibrational spectra are reported in Table 4.9.

TABLE 4.9 Vibrational Spectra of the $TeBr_4I^-$ Anion

| FREQUENCIES ($cm^{-1}$) | |
|---|---|
| INFRARED | RAMAN |
| | 45w |
| | 62w |
| | 92w |
| 110m | 116vs |
| 160m | 167s |
| 189vs | 185m |
| 202m | 202m |
| 216m | 212m |

The presence of a band above $210cm^{-1}$, characteristic of a tellurium-axial bromine stretching vibration, indicates that the anion possesses $C_s$ symmetry. This assignment is further justified by the number of coincidences in the infrared and Raman spectra. The strong band at $116cm^{-1}$ is representative of a tellurium-iodine stretching vibration, whereas the remaining higher frequency bands probably involve tellurium-bromine motion.

The tellurium-125 n.m.r. spectrum showed a single resonance at 1658 ppm.

## 4.5 The Fluorotellurates

Since tellurium difluoride is unknown and the action of fluorine on tellurium dichloride[97] and tellurium dibromide[98] produces only tellurium tetrafluoride, none of the species of general formula $TeX_3Y_2^-$ were prepared.

### 4.5.1 Vibrational Spectra

The pentafluorotellurate ion has been reported previously (Section 4.2) and the vibrational results presented in Table 4.10 agree well with the earlier work.

TABLE 4.10 Solid State Vibrational Spectra and Assignments of $Bu_4NTeF_5$

| FREQUENCIES ($cm^{-1}$) | | Assignment |
|---|---|---|
| Infrared | Raman | |
| | 28vw | |
| | 58vw | |
| | 239vw | $\nu_6$ |
| 275m | 276w | $\nu_3$ |
| 332m | 339w | $\nu_8$ |
| 474s | | $\nu_7$ |
| 495s | 494m | |
| 518sh | 524s | $\nu_2$ |
| 647s | 649s | $\nu_1$ |

The assignments follow those of Adams and Downs[131] and assume the species to possess $C_{4v}$ symmetry. Although the caesium salt has been reported to adopt $C_s$ symmetry in the solid state,[157] this is thought to be unlikely in salts of the tetraalkylammonium cations and indeed, the spectra of tetraethylammonium pentafluorotellurate showed no significant change between those recorded in the solid state and in solution.[131] The splitting observed in the $\nu_7$ mode in this work could possibly be due to a lowering of site symmetry.

Since tellurium tetrafluoride was not observed to dissolve in dichloromethane, in the presence of an equimolar quantity of tetra-butylammonium chloride (Section 4.6) this reaction was not investigated further. However, solutions were obtained using bromide or iodide solutions and the vibrational results for these systems are reported in Table 4.11.

TABLE 4.11 Vibrational Spectra of the $TeF_4X^-$ Systems (X=Br, I)

| System | Spectrum | Frequencies ($cm^{-1}$) |
|---|---|---|
| $TeF_4Br^-$ | IR | 116m 161sh 187vs 212m 275s 332s 480s 495s 650m |
| | R | 62w 83m 112w 151m 164m 195s 220s |
| $TeF_4I^-$ | IR | 146m 170m 275s 330s 480s 495s 650m |
| | R | 65w 112vs 172w 223m |

The bands above $250cm^{-1}$ in the infrared spectra immediately identify the pentafluorotellurate ion as a reaction product (Table 4.10). For the bromo- species the remaining bands at 116, 161, 187 and $212cm^{-1}$ are assigned to the pentabromo- anion (Table 4.6 ) whereas the absorptions at 146 and 171 $cm^{-1}$ in the spectrum of the iodo- system can be assigned to the hexaiodo-complex (Table 2.7). The Raman data confirm these assignments (Section 2.3.1), suggesting the following reaction schemes:

$$5TeF_4 + 5Br^- \longrightarrow 4TeF_5^- + TeBr_5^-$$

$$5TeF_4 + 6I^- \longrightarrow 4TeF_5^- + TeI_6^{2-}$$

This latter equation is in agreement with previous work regarding the lack of formation of the pentaiodotellurate ion (Section 4.4).

For species of general formula $TeX_4F^-$, only reactions involving bromide or iodide ions yielded solids (c.f. hexahalogeno-systems) and since the iodo- system gave no meaningful analyses it was not investigated further. The vibrational data for the bromo- compound are given in Table 4.12.

TABLE 4.12 Vibrational Spectra of the $TeBr_4F^-$ Anion

| FREQUENCIES (cm$^{-1}$) | |
|---|---|
| Infrared | Raman |
| | 63vw |
| | 89w |
| 115m | |
| 140w | 143sh |
| 159sh | 150m |
| 173s | 166m |
| 190s | |
| 202sh | 202s |
| 217sh | 226vs |

The absence of a band near 650 cm$^{-1}$, characteristic of a tellurium-axial fluorine stretching vibration, together with the presence of a band near 220 cm$^{-1}$ indicates the species to be of $C_s$ symmetry. All of the remaining bands can be assigned to tellurium-bromine modes.

### 4.5.2 Tellurium-125 N.M.R. Spectra

The results are given in Table 4.13.

The spectrum of the pentafluorotellurate anion is shown in Figure 4.4 and consists of an overlapping doublet of quintets resulting from the spin-spin coupling between the tellurium nucleus and the axial and equatorial fluorines, where $J_{^{125}Te-^{19}F_{ax}} \simeq 2J_{^{125}Te-^{19}F_{eq.}}$, the former having a value of 2930 Hz and the latter 1465Hz, in fair agreement with results from $^{19}F$ n.m.r.[133]. The origin of the signal at 1237 ppm. is unknown.

FIGURE 4.4 Tellurium-125 N.M.R. Spectrum of $Bu_4NTeF_5$ in Dichloromethane

```
TE  BU4NTEF5 IN CH2CL2      18-OCT-81     31.25      -2000          28006
     1    -25867 -1366.37          0.1687     2     -24524 -1295.44          0.5971
     3    -23425 -1237.4           0.7411     4     -23059 -1218.06          1.0
     5    -21594 -1140.68          0.8985     6     -20129 -1063.31          0.8985
     7    -18787  -992.38          0.4569
```

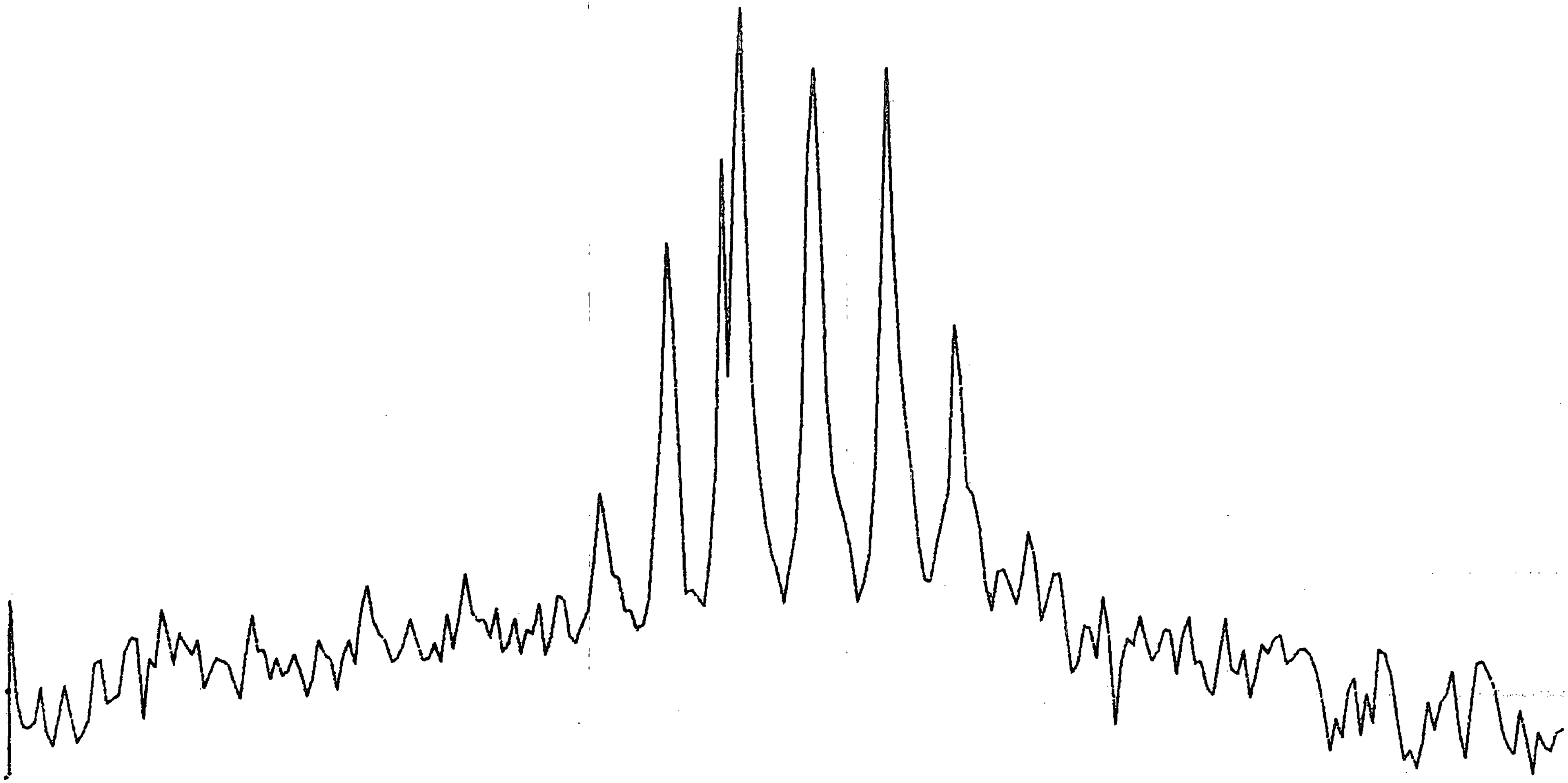


TABLE 4.13 Tellurium-125 N.M.R. Spectra of the Fluorotellurates

| SYSTEM | CHEMICAL SHIFT (ppm.) |
|---|---|
| $TeF_5^-$ | 1141 |
| $TeF_4Br^-$ | 1210 |
| $TeF_4I^-$ | 1146 |
| $(TeCl_4F^-)$ | 1815 (3) |
| | 1796 (1) |
| | 1672 (3) |
| | 1501 (5) |
| | 1470 (8) |
| $(TeBr_4F^-)$ | 1588 (3) |
| | 1534 (2) |

Relative intensities are given in parentheses.

---

The $TeF_4Br^-$ system gave rise to a broad resonance presumably due to exchange between $TeF_5^-$ and $TeBr_5^-$ (Section 4.5.1). However, the spectrum of the corresponding iodo- system showed only $TeF_5^-$ to be present indicating that exchange with $TeI_6^{2-}$ does not occur.

The spectrum of the $TeCl_4F^-$ system indicates a complicated mixture to be present. The signals at 1815 and 1796 ppm., the latter of which also occurred in the spectrum of the $TeCl_4F_2^{2-}$ system, are tentatively assigned to unknown neutral fluorochloro-species, whereas that at 1470 ppm., also observed in the spectrum of $TeCl_4F_2^{2-}$ is assigned to a five coordinate fluorochloro-anion. The signals at 1501 and 1672 ppm., are also assigned to pentacoordinate fluorochloro- anions. The signals observed in the spectrum of the $TeBr_4F^-$ anion are both assigned to five coordinate fluorobromo- species.

## CONCLUSION

The vibrational spectra of the chlorobromo- species enable their structures to be given with some confidence, without resort to force constant calculations[100] of doubtful validity.[159] Indeed, any model which assumes identical bond lengths and bond angles in corresponding square-pyramidal and octahedral species must be considered dubious.

The pentacoordinate systems involving tellurium-iodine bonds and tellurium-fluorine bonds resemble the corresponding hexacoordinate systems in that complicated iodine containing mixtures and the pentafluoro- anion are formed, again probably due to the strength of the tellurium-iodine bond and the great stability of the pentafluorotellurate species.

## EXPERIMENTAL

The species discussed in this chapter were prepared in an analogous manner to those discussed in Chapter Two. Analytical date are reported below, in Table 4.14.

Preparations involving tellurium tetraiodide always yielded solid tellurium tetraiodide, as well as a very dark coloured solution. The solid was filtered off on a sinter in the dry box and the solvent removed from the supernatant liquor on the vacuum line, leaving a black solid, the analytical results of which are given in Table 4.15. The $TeI_5^-$ system can be recognised to consist of the hexaiodo- complex (Table 2.2.2) but the remaining systems must contain mixtures.

TABLE 4.14 Analytical Results for the Pentachlorobromotellurates

| COMPOUND | C | H | N | Te | Cl | Br | |
|---|---|---|---|---|---|---|---|
| $Bu_4NTeCl_5$ | 35.1 | 6.6 | 2.5 | 23.3 | 32.4 | - | Calc. |
| | 32.6 | 6.7 | 2.3 | 24.1 | 32.3 | - | Obs. |
| $Bu_4NTeCl_4Br$ | 32.5 | 6.1 | 2.4 | 21.6 | 13.5 | 24.0 | Calc. |
| | 33.1 | 6.2 | 2.3 | 21.6 | 13.2 | 24.1 | Obs. |
| $Bu_4NTeCl_3Br_2$ | 30.2 | 5.7 | 2.2 | 20.1 | 16.7 | 25.1 | Calc. |
| | 30.4 | 7.0 | 2.2 | 20.3 | 16.7 | 24.8 | Obs. |
| $Bu_4NTeCl_2Br_3$ | 28.2 | 5.3 | 2.1 | 18.8 | 10.4 | 35.2 | Calc. |
| | 29.0 | 6.0 | 1.5 | 18.7 | 10.7 | 34.8 | Obs. |
| $Bu_4NTeClBr_4$ | 26.5 | 5.0 | 1.9 | 17.6 | 4.9 | 44.1 | Calc. |
| | 25.8 | 5.0 | 1.8 | 17.6 | 4.8 | 44.3 | Obs. |
| $Bu_4NTeBr_5$ | 24.9 | 4.7 | 1.8 | 16.6 | - | 51.9 | Calc. |
| | 25.3 | 5.6 | 1.9 | 15.9 | - | 51.1 | Obs. |

TABLE 4.15 Analytical Results for the $TeI_4X^-$ Systems (X=Cl,Br,I)

| SYSTEM | C | H | N | Te | I | X |
|---|---|---|---|---|---|---|
| $TeI_4Cl^-$ | 32.8 | 4.9 | 1.6 | 10.0 | 46.0 | 4.9 |
| $TeI_4Br^-$ | 29.2 | 5.8 | 1.6 | 10.3 | 45.7 | 2.5 |
| $TeI_5^-$ | 24.1 | 5.4 | 1.7 | 8.7 | 55.7 | - |

Tellurium tetraiodide was formed in the $TeCl_4I^-$ system, and, after filtration, the solid was analysed and again found to consist of a complicated mixture. However, homogeneity was obtained in the bromoiodo- system, and analysis did correspond to $Bu_4NTeBr_4I$, as shown in Table 4.16.

TABLE 4.16 Analytical Results for the $TeX_4I^-$ Systems (X=Cl,Br)

| SYSTEM | C | H | N | Te | X | I | |
|---|---|---|---|---|---|---|---|
| $TeCl_4I^-$ | 36.5 | 7.6 | 2.7 | 16.8 | 23.0 | 11.8 | |
| $TeBr_4I^-$ | 23.5 | 4.4 | 1.7 | 15.6 | 39.1 | 15.5 | Calc. |
| | 24.4 | 4.8 | 1.8 | 14.8 | 39.2 | 15.5 | Obs. |

The fluorotellurates were prepared by either mixing tellurium tetrafluoride (Section 6.7.3) with the appropriate tetrabutylammonium halide in dichloromethane and then pumping off the solvent from the resulting solution, or by mixing the appropriate tellurium tetrahalide with sodium fluoride and 18-crown-6 ether in acetonitrile. Tetrabutylammonium pentafluorotellurate was prepared as described in Section 6.7.2.

TABLE 4.17 Analytical Results for the Fluorotellurate Systems

| SYSTEM | C | H | N | Na | Te | Br | I | F | |
|---|---|---|---|---|---|---|---|---|---|
| $TeF_4Br^-$ | 36.5 | 6.8 | 2.7 | - | 24.3 | 15.2 | - | 14.5 | Calc. |
| | 36.5 | 8.6 | 2.7 | - | 24.3 | 15.0 | - | | Obs. |
| $TeF_4I^-$ | 33.5 | 6.7 | 2.4 | - | 22.2 | - | 22.1 | 13.3 | Calc. |
| | 34.6 | 8.4 | 2.6 | - | 22.5 | - | 22.0 | | Obs. |
| $TeBr_4F^-$ | 19.1 | 3.2 | - | 3.1 | 16.9 | 42.5 | - | 2.5 | Calc. |
| | 20.4 | 2.8 | - | 2.3 | 16.6 | 42.5 | - | | Obs. |
| $TeI_4F^-$ | 15.3 | 2.5 | - | 2.4 | 13.6 | - | 53.9 | 2.0 | Calc. |
| | | | - | | 7.7 | - | 10.2 | | Obs. |

Fluorine analyses were not obtained since an insufficient quantity of sample was available.

Addition of an equimolar quantity of tetrabutylammonium chloride dissolved in dichloromethane to a suspension of tellurium tetrafluoride in the same solvent produced no observable change. However, a white solid was recovered from the supernatant liquor and displayed infrared bands at 475s, 490s and 642m $cm^{-1}$, showing the pentafluorotellurate species to be present (Table 4.10). This suggests that the equilibrium:

$$5TeF_4 + 5Cl^- \rightleftharpoons 4TeF_5^- + TeCl_5^-$$

must lie well over to the left.

The reaction between tellurium tetrachloride and sodium fluoride (18-crown-6) ether in acetonitrile gave results very similar to those obtained for the corresponding $TeCl_4F_2^{2-}$ system in that a solid could not be isolated (Section 2.6), and again the solvation of the fluoride ion is invoked to explain this behaviour.

# CHAPTER FIVE

## REACTIONS OF TELLURIUM DIOXIDE WITH AQUEOUS AND ANHYDROUS HYDROGEN CHLORIDE AND HYDROGEN BROMIDE

### INTRODUCTION

### 5.1 Reaction of Tellurium Dioxide with Anhydrous Hydrogen Chloride

Early work[160] postulated an addition compound, $2TeO_2.3HCl$, formed by passing dry hydrogen chloride over tellurium dioxide at 263K. This compound dissociated at room temperature, yielding $TeO_2.2HCl$ (and presumably $TeO_2$), which lost water at 383K, and formed $TeOCl_2$ at 573K. Later[161] it was reported that tellurium dioxide and hydrogen chloride combine to form $TeO_2.3HCl$ at 273K and that this was successfully converted to $TeO_2.2HCl$ and tellurium tetrachloride on heating. No evidence was obtained for an oxychloride. Parker and Robinson[162] found hydrogen chloride to be absorbed in varying amounts at 273K, giving an inhomogenous product, which lost water continuously with rising temperature. They found no evidence for a definite addition compound in the temperature range 273 to 423K. Finally, Khodadad[163] described the reaction product as a yellow paste soluble in methanol and postulated the following:

$$TeO_2 + 4HCl \longrightarrow TeCl_4 + 2H_2O$$

He proposed $TeCl_4.2HCl.nH_2O$ or hexachlorotelluric acid to be the final product, similar to that obtained by dissolving tellurium dioxide in concentrated hydrochloric acid, although the evidence presented, viz. solubility in methanol can only be described as tenuous.

## 5.2 Reaction of Tellurium Dioxide with Aqueous Hydrogen Chloride

Chloro- complexes of tellurium (IV) in aqueous acidic media have been the subject of several conflicting reports in the literature. An early Raman study[164] of solutions of tellurium tetrachloride (1.5M) in hydrochloric acid gave the following results:

TABLE 5.1

Raman Spectra of Solutions of Tellurium Tetrachloride in Hydrochloric Acid

| Molarity of HCl | Frequencies (cm$^{-1}$) | | | | |
|---|---|---|---|---|---|
| 0 | | | 275w, br | | 668vw,br |
| 1.5 | | 136w | 263-286m | | 665vw,br |
| 3 | | 132w | 265-287m | | 665vw,br |
| 6 | 90vw | 138w | 256s, br | 297s, br | |
| 9.7 | 80vw | 133w | 263s, br | 308s, br | |
| 12.5 | 77vw | 138w | 264s, br | 311s, br | |

The strong polarised band near 300 cm$^{-1}$ was assigned to a tellurium-chloride symmetric stretch. Three other frequencies, 263, 135 and 80 cm$^{-1}$ were also thought to involve tellurium chlorine motion while that at 665 cm$^{-1}$ was assigned to a tellurium-oxygen stretching mode. Ether extracts of solutions at low acid concentrations were obtained and Raman spectra of the extracts showed that one complex, with bands at 134, 258, 289 and 668 cm$^{-1}$, was found to predominate. Analyses revealed the tellurium:chlorine ratio to be 1:4 and so the complex was identified as $TeCl_4.OH_2$ with the oxygen atom trans to the lone pair in an octahedral arrangement. Since the spectrum of this complex was very similar to that of the aqueous solution which yielded it, $TeCl_4.OH_2$ was assumed to be the dominant species at lower concentrations of hydrochloric acid. At higher concentrations, penta- and hexachloro- species were postulated.

The presence of $TeOCl_4^{2-}$ in concentrated hydrochloric acid was proposed[165] in an ion-exchange study. Later a similar study[166] identified $TeCl_3^+$, $TeCl_4$ and $TeCl_6^{2-}$ with hydrolysis products of the latter anion being present in very dilute solutions.

The species $TeCl_4(H_2O)_2$, $TeCl_5(H_2O)^-$ and $TeCl_4(OH)_2^{2-}$ or $TeCl_4(OH)(H_2O)^-$ were extracted into alcohols from solutions of tellurium (IV) in hydrochloric acid and identified by analogy with the known behaviour of tin (IV) and antimony (V).[167] Shikheeva[168] subsequently obtained formation constants for these species and proposed:

$$[Te(OH)_2Cl_4]^{2-} \rightleftharpoons [TeOCl_4]^{2-} + H_2O$$

A quantitative study,[169] using ultraviolet spectrophotometry, employed freshly precipitated tellurous acid in hydrochloric acid solutions. The species $TeO(OH)Cl$, $TeOCl_2$, $TeOCl_3^-$, $TeOCl_4^{2-}$ and $TeCl_6^{2-}$, were proposed as being progressively formed as the acid concentration was increased. Addition of lithium chloride to these solutions showed that with increase in acid concentration, the range in which chlorocomplexes predominate is displaced to lower chloride concentrations. Petkova and Vassilev[170] forwarded the following equilibrium, again on the basis of ultraviolet studies:

$$[Te(OH)_6]^{2-} + nHCl \rightleftharpoons [Te(OH)_{6-n}Cl_n]^{2-} + nH_2O$$

However, the composition of the complexes was not determined.

Raman spectra[76] of a solution of tellurium dioxide in hydrochloric acid showed only three bands at 130, 255 and 290 $cm^{-1}$. All were assigned to the hexachlorotellurate anion and no evidence of hydrolysis was observed.

Hexachlorotellurates have themselves been studied in hydrochloric acid solutions using ultraviolet and visible spectrophotometry and the following equilibrium put forward[171]:

$$TeCl_6^{2-} + iH_2O \rightleftharpoons TeCl_{6-i}(H_2O)_i^{i+(2-)} + iCl^-$$

## 5.3 Reaction of Tellurium Dioxide with Anhydrous Hydrogen Bromide

Ditte[173] found that tellurium dioxide and hydrogen bromide reacted at 258K to form $TeO_2.3HBr$, which decomposed, at 323K to give $TeO_2.2HBr$, at 343K to the oxybromide and above 343K to the tetrabromide. Parker and Robinson[173] also investigated the system but obtained no conclusive results.

## 5.4 Reaction of Tellurium Dioxide with Aqueous Hydrogen Bromide

Solutions of tellurium dioxide and lithium or sodium bromide in perchloric acid, and of the dioxide in a mixture of hydrobromic acid and perchloric acid, were studied using ultraviolet spectrophotometry.[174] In the latter system the hexabromotellurate anion was postulated whereas in the former, the cation $TeBr_3^+$ was proposed. The following equilibria were presented:

$$[Te_2O_3(OH)]^+ + 6Br^- + 7H_3O^+ \underset{ClO_4^-}{\overset{Li^+,Na^+,H_3O^+}{\rightleftharpoons}} 2TeBr_3^+ + 11H_2O$$

$$[Te_2O_3(OH)]^+ + 12Br^- + 7H_3O^+ \underset{ClO_4^-}{\overset{H_3O^+}{\rightleftharpoons}} 2TeBr_6^{2-} + 11H_2O$$

The nature of the product species was deduced from calculations of coordination number using equilibrium constants. Later[175] the hexabromotellurate anion was again postulated in solutions of tellurium (IV) in strong acids in the presence of bromide ions.

Solutions of tellurium dioxide in hydrobromic acid have also been studied using Raman spectroscopy[76] and the presence of the hexabromotellurate species inferred.

## RESULTS AND DISCUSSION

### 5.5 Reaction of Tellurium Dioxide with Anhydrous Hydrogen Chloride

Weight analysis experiments established $TeO_2.4HCl$ to be the stable product composition at room temperature and this composition, together with $TeO_2.2HCl$ and $TeO_2.6HCl$ were sealed up in 8mm. O.D. silica tubes. In each case, both a pale yellow solid and a dark yellow liquid were observed and for $TeO_2.6HCl$ an additional colourless, upper liquid phase. Raman spectroscopic data for the yellow liquid (Table 5.2) and the solid (Table 5.3) are given below:

TABLE 5.2

Raman Spectra of the Yellow Liquid Phase in the $TeO_2$-HCl Systems

| $TeO_2.2HCl$ | $TeO_2.4HCl$ | $TeO_2.6HCl$ |
|---|---|---|
| 92w | | |
| 144m | 142sh | 140sh |
| 290vs,p | 288m,p | 288sh,p |
| 356s,p | 362vs,p | 359vs,p |
| 650m | | |

## TABLE 5.3

Raman Spectra of the Solid Phase in the $TeO_2$-HCl Systems

| $TeO_2.2HCl$ | $TeO_2.4HCl$ | $TeO_2.6HCl$ |
|---|---|---|
| 27s | 61m | 60m |
| 39m | 88m | 85m |
| 41w | 152w | 149w |
| 81s | 344m | 342m |
| 87s | 350m | 349m |
| 95vs | 377vs | 376vs |
| 107sh | | |
| 138s | | |
| 152m | | |
| 182w | | |
| 200m | | |
| 260sh | | |
| 289s | | |
| 332vw | | |
| 363vs | | |
| 431s | | |
| 508m | | |
| 628m | | |
| 684m | | |

It is immediately apparent that $TeO_2.4HCl$ and $TeO_2.6HCl$ are very similar in nature. The above data indicate that the solid phase consists of tellurium tetrachloride[176] so that the following reaction may be proposed with some certainty:

$$TeO_2 + 4HCl \longrightarrow TeCl_4 + 2H_2O$$

This suggests that the yellow liquid phase could be a hydrolysis product of tellurium tetrachloride and in order to try and substantiate this, the latter was sealed up in 8mm.O.D. silica tubes along with water in varying relative amounts. The Raman spectra of the liquid phases are listed in Table 5.4.

TABLE 5.4

Raman Spectra of the Liquid Phase in the $TeCl_4$-$H_2O$ Systems

| $TeCl_4.1.5H_2O$ | $TeCl_4.3H_2O$ | $TeCl_4.6H_2O$ | $TeCl_4.10H_2O$ |
|---|---|---|---|
| 145m | 140m | 142m | 140m |
| 290vs, p | 290vs, p | 291vs, p | 289vs, p |
| 358s, p | 356s, p | | |
| 652m | 653m | 663m | 670m |

Again, the spectra are very similar, only differentiated by the appearance of a strong band at 356 $cm^{-1}$ in mixtures containing the least water. Indeed, these spectra appear almost identical to that of the liquid phase of $TeO_2.2HCl$ (Table 5.2). When more water is present, the band at 356 $cm^{-1}$ disappears but when more HCl is present, in the $TeO_2$-HCl systems, the bands at 144, 290 and 650 $cm^{-1}$ diminish, whereas the band at 356$cm^{-1}$ increases in intensity. These results indicate two species to be present in the $TeO_2$-HCl mixtures.

The band at 650$cm^{-1}$ is immediately assignable to a tellurium-oxygen single bond stretching vibration and the polarised band at 290 $cm^{-1}$ likewise assigned to a tellurium-chlorine symmetric stretching vibration. The low frequency feature is most probably a deformation mode. Unfortunately, these assignements give no information about the structure of the species in question. However, tellurium-125 n.m.r. spectra of $TeCl_4.6H_2O$ and $TeCl_4.10H_2O$ exhibited resonances at 1501 ppm and 1497ppm respectively and these values lie in the five coordinate region of the spectrum for chloro-complexes of tellurium (IV) (Section 4.3.3).

Taylor[164] has reported the species, $TeCl_4.OH_2$, to be present in solutions of tellurium tetrachloride in low concentrations of hydrochloric acid and Raman bands at 134m, 258m, 289s and 668w $cm^{-1}$ are quoted. The alternative formulation, $HTeCl_4OH$, was dismissed on the grounds that a hydroxyl group is unlikely to exist in acidic media.

Although not entirely analogous to the above, some comparison with Taylor's results can be made, and in this work it is preferred to invoke the presence of the complex acid for several reasons. Firstly, the band at 650 $cm^{-1}$ is at too high a frequency for a "solvate" bond and indeed the Raman spectrum of tellurium tetrachloride in diethyl ether, which forms a solvate,[177] exhibits bands at 154w, 168w, 281m, 355m, 369s and 443w $cm^{-1}$ (this work), with no band observed in the tellurium-oxygen single bond stretching region. The band at 443 $cm^{-1}$ probably represents the "solvate" bond. Secondly, as pointed out by Taylor himself, the tellurium-chlorine stretching vibrations in a solvate should be fairly close to those observed in tellurium tetrachloride itself (c.f. ether solvate, acetonitrile solvate[178]) but in the species under investigation here, the highest tellurium-chlorine stretching mode occurs at 290 $cm^{-1}$, approximately 90 $cm^{-1}$ lower. Thirdly, the corresponding fluoro- anion, $TeF_4(OH)^-$ has been reported to exhibit strong Raman bands at 460, 505 and 700 $cm^{-1}$.[179]

These were assigned to the out-of-phase and in-phase tellurium-fluorine symmetric stretches and the tellurium-oxygen stretch, respectively, and the bands observed here are assigned analogously. Failure to observe the out-of-phase mode in this work may be due to masking by the more intense, in-phase, stretch. Some support for this is supplied by the polarisation study of $TeCl_4.6H_2O$. When the analyser was perpendicular, the band at 290 $cm^{-1}$ appeared to come to a maximum at 270 $cm^{-1}$ and display a less intense shoulder at 290 $cm^{-1}$. Finally, the crystal structure of an aquotetrachlorohydroxotellurate has been reported.[180] The species was prepared from tellurium tetrachloride and tetraphenylarsonium chloride monohydrate in dichloromethane and although the data did not enable $TeCl_4(OH)^-.H_2O$ to be distinguished from $TeCl_4O^{2-}.H_3O^+$, the latter would give rise to a tellurium-oxygen double bond stretching frequency near 840 $cm^{-1}$, which we did not observe (c.f. $TeOF_4{}^{2-}$).[179]

The band at 356 $cm^{-1}$ was not observed by Taylor, but is tentatively assigned to the pentachlorotellurate anion, whose other strong bands at 260 and 282 $cm^{-1}$ are presumably masked (Section 4.3.1). This band is polarised and represents the tellurium-axial chlorine symmetric stretch.

The solid phase, present in the $TeCl_4.1.5H_2O$ and $TeCl_4.3H_2O$ systems, displayed Raman bands at 62m, 85m, 150w, 342m, 348s, 374vs and is thus characterized as tellurium tetrachloride. No solid phase was observed in $TeCl_4.6H_2O$ but in $TeCl_4.10H_2O$ a white solid was deposited over a period of several months. This displayed Raman bands at 60vs, 82s, 91w, 100s, 113w, 122w, 144m, 161m, 194w, 207s, 258m, 278m, br, 347w, 388w, 475m, 522w, 662s, $cm^{-1}$ and is most probably tellurous acid.

The nature of the solid phase in the $TeO_2.2HCl$ system is unknown but could possibly be $Te_6O_{11}Cl_2$.[163] (The tube was heated to 180°C to try and achieve homogeneity). Finally, the colourless liquid phase present in the $TeO_2.6HCl$ system, and which gradually disappeared at the expense of the yellow liquid phase, is probably a mixture of hydrogen chloride and water.[181]

On the basis of this evidence the following reaction scheme is proposed:

$$TeO_2 + 4HCl \rightleftharpoons TeCl_4 + 2H_2O$$

$$TeCl_4 + 2H_2O \rightleftharpoons TeCl_4(OH)^- + H_3O^+$$

$$TeCl_4(OH)^- + HCl \rightleftharpoons TeCl_5^- + H_2O$$

The presence of $TeCl_4(OH)^-.H_2O$ cannot be ruled out but in such acidic media, protonation is likely to occur. Also, the possible existence of hexachloro- species cannot be ignored where hydrogen chloride is present in excess; and an analogous situation has been described for chloro- complexes of selenium (IV).[182]

We suggest that $TeCl_4(OH)^-$ is a moderately strong acid (stronger than hydrogen chloride) to explain these results.

## 5.6 Reaction of Tellurium Dioxide with Aqueous Hydrogen Chloride

Solutions containing one mole of tellurium dioxide in varying concentrations of hydrochloric acid were made up and their tellurium-125 n.m.r. and Raman spectra recorded:

## TABLE 5.5

Raman and Tellurium-125 N.M.R. Spectra of $TeO_2$-$HCl_{(aq)}$ Systems

| Molarity of HCl | Raman Frequencies ($cm^{-1}$) | | | | | NMR Shift (ppm) |
|---|---|---|---|---|---|---|
| 11 | 128m | 272sh | 304vs | | 651m | 1390 |
| 10 | 135 | 265 | 295 | | 655 | 1432 |
| 9 | 133 | 265 | 289 | | 660 | 1465 |
| 8 | 136 | 267 | 288 | | 662 | 1484 |
| 7 | 132 | 265 | 288 | | 662 | 1502 |
| 6 | 131 | | 286 | | 670 | 1529 |
| 5 | | | 282 | 465vw | 672 | 1547 |
| 4 | | | 282 | 455vw | 672 | 1550 |

The three low frequency bands in solutions above 6M HCl can be immediately assigned to the hexachlorotellurate anion (Section 2.3.1), while that centred around 660 $cm^{-1}$ is due to a tellurium oxygen single bond stretch. When the band intensities, determined graphically and using the water bending mode at 1630 $cm^{-1}$ as the standard, were compared it was found that, whereas the hexachlorotellurate bands increased in intensity with increase in chloride ion concentration, the high frequency band decreased steadily over the same concentration range.

At lower concentrations, the shoulder at 265 $cm^{-1}$, the frequency of which became increasingly difficult to measure, finally disappeared and the most intense band moved to slightly lower frequency, while the tellurium-oxygen band moved to higher frequency. In addition, tellurium-125 chemical shift entered the five-coordinate region. In fact, the spectra closely resemble those obtained from the more dilute solutions of tellurium tetrachloride in water. Comparison can also be made with Taylor's[164] results since 1.5M tellurium tetrachloride in 1.5M hydrochloric acid is comparable to 1M tellurium dioxide in 5M hydrochloric acid.

The following equilibria are proposed to explain these results:

$$TeO_2 + 6HCl_{aq} \rightleftharpoons TeCl_6^{2-} + 2H_3O^+$$

$$TeCl_6^{2-} + H_2O \rightleftharpoons TeCl_4(OH)^- + HCl_2^-$$

The origin of the very weak bands at 460 $cm^{-1}$ remains unknown, but it could be due to a weak tellurium-oxygen "solvate"-type bond (Section 5.5).

## 5.7 Reaction of Tellurium Dioxide with Anhydrous Hydrogen Bromide

Tellurium dioxide was sealed up with hydrogen bromide in several ratios. In contrast to the chloro- analogues, these systems gave rise to only one product phase, a yellow-orange solid. The Raman data are listed in Table 5.6.

TABLE 5.6

Raman Spectra of the $TeO_2$-HBr Systems

| $TeO_2$.2HBr | $TeO_2$.3HBr | $TeO_2$.6HBr |
|---|---|---|
| 23w | | 23w |
| 50m | 50m | 49s |
| 63w | | 65sh |
| 77m | 78m | 75s |
| | | 105w |
| 124w | 124w | 125w |
| 133w | 133w | |
| | | 155w |
| 225s | 222sh | 225s |
| | 228s | 231m |
| 248s | 248s | 247s |

These results enable the solid to be characterized as tellurium tetrabromide.[176] The absence of a liquid phase, apart from liquid hydrogen bromide in $TeO_2.6HBr$, is surprising but it is clear that the species $TeBr_4(OH)^-$ is not obtained. This may well be due to the greater acidity of hydrogen bromide, when compared with hydrogen chloride, so that water is immediately protonated, forming $H_3O^+Br^-$. Some evidence for this is provided by the appearance of a weak, broad band at 3540 $cm^{-1}$, assignable to the hydroxonium cation,[183] in the Raman spectrum of $TeO_2.3HBr$. This suggests that $H_3O^+Br^-$ is a solid at room temperature but further work is necessary.

## 5.8 Reaction of Tellurium Dioxide with Aqueous Hydrogen Bromide

Solutions containing one mole of tellurium dioxide in varying concentrations of hydrobromic acid were prepared and their Raman and tellurium-125 n.m.r. spectra recorded:

TABLE 5.7

Raman Spectra of the $TeO_2$-$HBr_{(aq)}$ Systems

| Concentration of HBr(M) | Raman Frequencies ($cm^{-1}$) | | | | NMR Shift (ppm) |
|---|---|---|---|---|---|
| 9 | 74m | 155s | 173vs | 323w, br | 1339 |
| 8 | 74m | 158sh | 171vs | 328w, br | 1339 |
| 7 | 73m | 156sh | 172vs | 323w, br | 1343 |
| 6 | 73m | 152sh | 171vs | 632vw,br | 1354 |
| 5 | 72m | 155sh | 171vs | 645vw,br | 1408 |

The three low frequency bands can be immediately assigned to the hexabromotellurate anion (Section 2.3.1) and the n.m.r. results suggest this to be the most abundant species at all concentrations studied. The band at 645 $cm^{-1}$ indicates the presence of oxo- species but the origin of the feature at 323 $cm^{-1}$ remains uncertain. The absence of oxo- species in any significant quantity, in contrast to the chloro- system, may well be due to the greater stability of the hexabromotellurate anion.

## CONCLUSION

This work has established that tellurium dioxide reacts with anhydrous hydrogen chloride or hydrogen bromide to form the corresponding tellurium tetrahalide. The nature of the other products of the two reactions is less certain but they are clearly quite different. Further work is necessary in this area, including a study of the HBr-$H_2O$ system.

The aqueous acids react with tellurium dioxide to form the hexahalogenotellurate anions but only the chloro- species reacts further to any extent to form chloro-oxo- species, but again further work may yield more positive results.

## EXPERIMENTAL

### 5.9 Reaction of Tellurium Dioxide with Anhydrous Hydrogen Halide

In a typical experiment, tellurium dioxide (ca.4mmol.) was placed in an 8mm.O.D. silica tube approximately 18cm. in length, fitted with a B14 cone and with a construction approximately 4cm before the cone. The tube was then attached to the vacuum line via a tap and the whole was evacuated. The requisite amount of hydrogen halide was then condensed onto the dioxide at 77K from a bulb of accurately known volume. The tube was then sealed off at the construction and allowed to warm to room temperature in a fume cupboard.

## 5.10 Reaction of Tellurium Dioxide with Aqueous Hydrogen Halide

In this work, concentrated hydrochloric acid was assumed to be 11.3M and concentrated hydrobromic acid to be 9M. Aliquots of 2ml of concentrated acid were made up with the relevant amount of water to give the necessary concentrations. The solutions were made 1M in tellurium dioxide.

# CHAPTER SIX

# EXPERIMENTAL METHODS

## 6.1 The Dry Box

As many of the compounds used in this work were sensitive to moisture, their manipulation was carried out under an atmosphere of dry nitrogen. The box, of approximately 30 l. capacity, was manufactured in the Science Site workshop at Durham using a design originating from the University of Warwick. The nitrogen was provided from a central liquid nitrogen reservoir rated at less than 6 p.p.m. oxygen and 10 p.p.m. water. Deoxygenation was achieved before the gas entered the departmental line by passing over hot copper and was dried just before the box by means of a tower, about 1m. in length, containing phosphorus pentoxide, maintained in position by glass wool. Also, dishes of phosphorus pentoxide and sodium-potassium alloy were located around the box floor. The nitrogen in the box was periodically pumped through a trap, cooled to 87K with liquid air, to ensue the removal of any solvent vapour present. Entry to and exit from the box was effected by two ports. The main port was purged with nitrogen for at least 30 minutes before entry while the smaller "quick-entry" port could be purged much more quickly or evacuated. The rate of flow into the box was controlled using a needle valve. A water pump was connected to enable filtrations to be carried out.

## 6.2 The Vacuum Line

This is depicted in Figure 6.1 and consisted of three sections: a pumping section, a general working section and a fractionating section. The pumping section contained a Jencons mercury diffusion pump backed by an Edwards two-stage rotary oil pump. The capacity of the diffusion pump was better than 30 $l.s.^{-1}$ at $10^{-3}$ to $10^{-5}$ mm Hg. This pump was electrically heated using a 320W heating collar. The critical backing pressure of 0.2mm Hg was readily obtained using the oil pump, which provided a pumping speed of 22 $l. min.^{-1}$ and optimum vacuum better than $10^{-3}$mm Hg. The pumping section was protected by a cold trap maintained at 77K. After use, the diffusion pump was isolated via taps 1 and 2 and air was admitted to the rotary pump via tap 3 to prevent "suck-back" of pump oil. As a further precaution, the device shown in Figure 6.2 was inserted in the hose connection to the oil pump. The general working section contained five taps, four of which were fitted with B14 sockets, and the fifth (tap 4) fitted with an S19 socket. The three sockets below the manifold were used for the attachment of various pieces of apparatus while above the manifold the S19 socket was used to connect the manometer, the remaining tap being occupied by a Vacustat, a simple McLeod gauge capable of measuring pressure down to $10^{-5}$mm Hg. Sockets were found to be more convenient than cones on the vacuum line, since removal of grease from a detached piece of apparatus was easier if it terminated in a cone.

The fractionating section was used for the purification of hydrogen chloride and hydrogen bromide utilised in the reactions described in Chapter Five. The section comprised three isolatable traps of a diameter making a close fit with a standard "Thermos" dewar. The method of purification is described in Section 6.10.

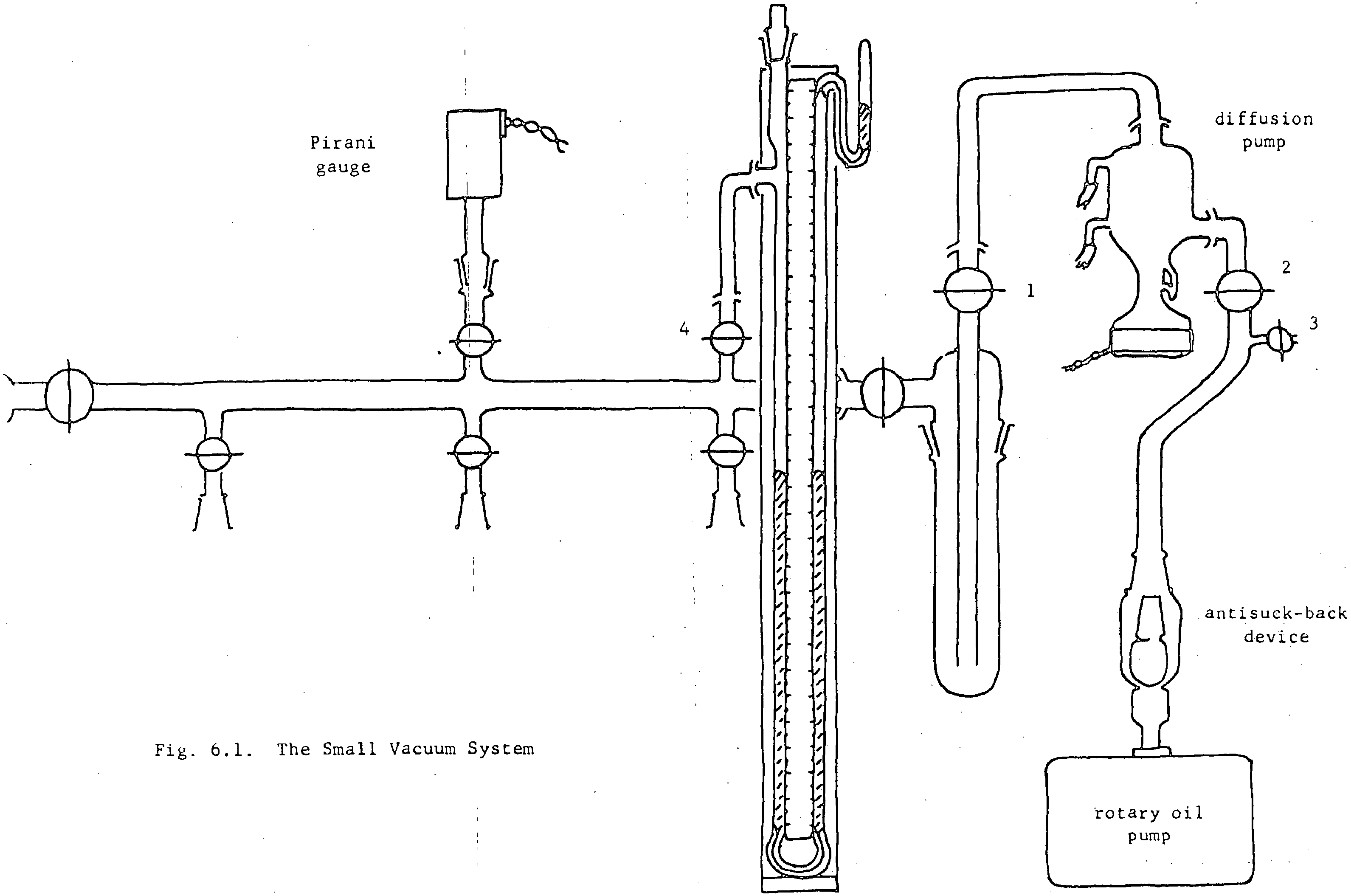


Fig. 6.1. The Small Vacuum System

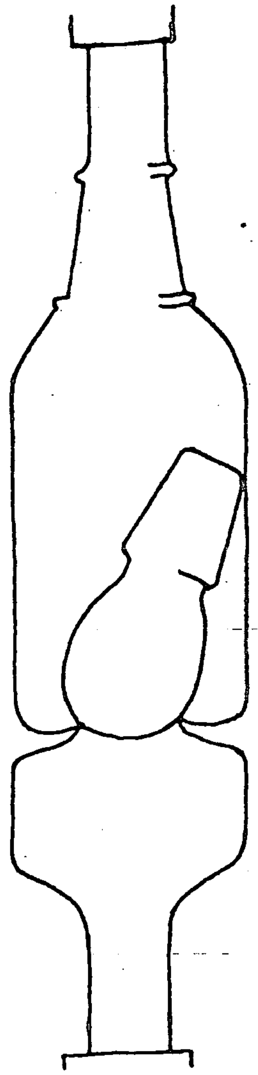


Fig. 6.2. The Antisuck-back Device

The pressure in the vacuum line was measured using a direct-reading, U-shaped mercury manometer. This was made from 10mm. bore tubing and was fastened to a meter rule which was itself attached to a vertical wooden board. The manometer was set up by evacuating it and then adding the mercury from a tap funnel in the top B14 socket. Air was then admitted and the tap funnel replaced by a stopper. A little mercury was then blown into the side reservoir thus removing any traces of volatile substances remaining. The pressure was measured by reading the difference in the mercury levels.

Saturated hydrocarbon grease (Apiezon L and M) was used in the vacuum system: (L grade being used for taps within the system since it remained more fluid at lower ambient temperature). Hydrocarbon wax (Picene) was employed on the tap connection to the diffusion pump since this would withstand the elevated temperature in this area.

## 6.3 X-Ray Power Diffraction Photography

Photographs were taken using a Philips PW1024 18cm. Debye Scherrer powder camera mounted on a Philips PW1009/80 X-ray generator, using copper $K_\alpha$ radiation. Samples were sealed in 0.5mm. glass capillary tubes.

## 6.4 Fluorine-19 N.M.R. Spectroscopy

Spectra were recorded at 84.675MHz on a Bruker HX90E spectrometer, modified for Fourier transform operation in this department using a Nicolet B-NC 12 computer. Samples were dissolved in dichloromethane-$d_2$ or acetonitrile-$d_3$ (the latter being a better solvent for species of general formula $TeX_4F_2^{2-}$ and

$TeX_4F^-$) at 298K. The solvent provided the deuterium lock at 13.811MHz. Sweep widths of 20KHz were used and chemical shifts were measured downfield from hexafluorobenzene, used as an internal reference.

## 6.5 The Tellurium-125 N.M.R. Spectrometer.

The system was based upon a 60MHz Perkin-Elmer R10 magnet linked to a PDP 11/34 computer. All spectral characteristics, i.e. sweep width, position of origin, number of spectral channels, pulse length and delay time, were set using the computer. The sweep width could be varied from 0.126KHz to 31.25KHz, the number of channels from $2^6$ to $2^{11}$, the pulse length from 1μs to 31μs and the delay from 0.1s to 25.5s. The base frequency for tellurium, 18.93487MHz, was applied to the relevant coil using a Racal frequency synthesiser also controlled by the computer. The system is shown schematically in Figure 6.3.

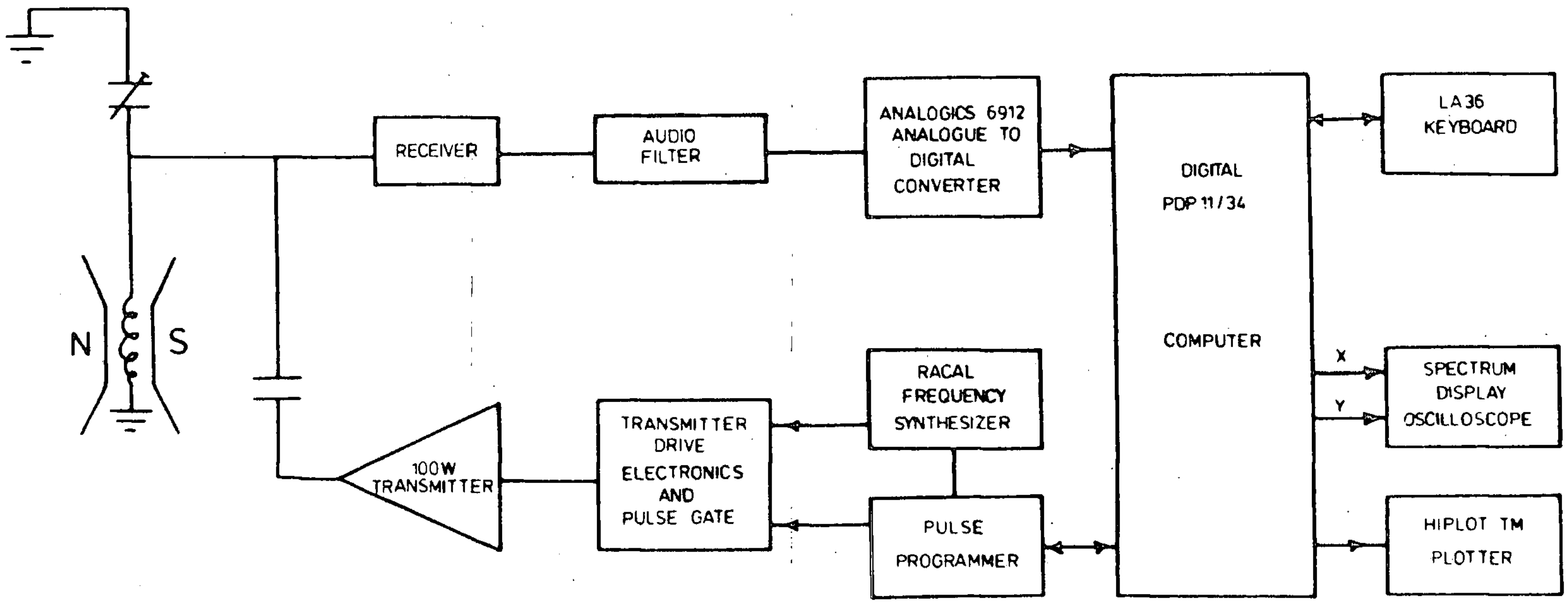
Spectra were recorded at 307.2K, as stationary samples contained in 8.4mm. external diameter n.m.r. tubes. The chemical shifts were measured relative to dimethyl tellurium as an external reference, the upfield direction being taken as negative. Typically, the spectrum of a sample was recorded as a saturated solution in dichloromethane, with a pulse length of 25μs and a delay of 2s. The sweep width was usually set at 20KHz, representing 1056 p.p.m., divided into 512 channels. Approximately 20,000 scans were normally accumulated.

## 6.6 Vibrational Spectroscopy

Infrared spectra were recorded as nujol nulls between caesium iodide plates on a Perkin-Elmer 577 infrared spectrophotometer. Far-infrared spectra were recorded as nujol mulls

Figure 6.3

Multinuclear n.m.r. Spectrometer.



between polythene plates on a Beckmann-R.I.I.C FS-720 Fourier transform spectrophotometer.

Raman spectra were recorded on a Cary 82 instrument, using either a Spectra Physics model 164 argon ion laser at 514.5nm or a model 125 helium-neon laser at 632.8nm. All samples were prepared under nitrogen.

## 6.7 Preparation of Starting Materials

### 6.7.1 Tetrabutylammonium Fluoride

This compound was prepared according to the method of Ludman,[181] converting the iodide to the fluoride in aqueous ammonia

$$Bu_4NI(aq.) + AgF(aq.) + NH_3(aq.) \longrightarrow Bu_4NF(aq.) + AgI.NH_3(s)$$

Typically, an excess of sodium hydroxide was dissolved in 50ml. water. Silver nitrate (20mmol) was then dissolved in 50ml. of water and the sodium hydroxide solution slowly added with stirring. The precipitated silver oxide was filtered off using a sinter washed with distilled water and washed into a beaker using distilled water. Ammonium fluoride (20mmol.) was added along with 60ml. of 0.88 ammonia and 60ml. of ethanol. The tetrabutylammonium iodide was dissolved in 50ml. of ethanol and 40ml. of 0.88 ammonia and this solution was slowly added to the silver fluoride solution, being washed in with 20ml. of ethanol. After standing for a few minutes the white precipitate of the silver iodide-ammonia complex was filtered off on a sinter and washed with ethanol. The filtrate was evaporated to a lower volume on a rotary evaporator and filtered to remove a further precipitate of $AgI.NH_3$. On allowing the solution to stand a considerable quantity of the fluoride clathrate crystallised and was filtered off (8.91mmol., 44.55%). A further batch of crystals were obtained by rotary evaporation of the filtrate (8.39mmol., 41.94%). Thus a total yield of 86.5% was obtained. This is presumably very approximate as the composition is known to vary considerably.[181]

Analysis: C,24.56; H,11.39; N, 1.86%. (This corresponds to $Bu_4NF. 28.9H_2O$).

### 6.7.2 The Pentafluorotellurates

In a typical experiment, tellurium dioxide (3mmol.) (B.D.H.Ltd., 99%) was dissolved in 2ml. of Aristar 40% hydrofluoric acid (B.D.H.Ltd.) contained in a small Teflon beaker. The tetrabutylammonium fluoride hydrate (taken to be $Bu_4NF.29H_2O$) was dissolved in 2ml. of concentrated hydrofluoric acid, although two layers were obtained. The first solution was added but two layers were still observed, even on standing overnight. More concentrated hydrofluoric acid was added until homogeneity was obtained, approximately 20ml. being required. The mixture was then heated on a steam bath in the fume cupboard for several hours until solid material was observed. The beaker was transferred to a plastic dessicator containing magnesium perchlorate and sodium hydroxide pellets for drying. When a white solid mass had formed, this was broken up with a spatula and pumped on for a further three hours. The final yield was 1.41g; 93.8%.

The sodium salt was prepared in an analogous manner. However, since tetramethylammonium fluoride was not available in sufficient quantity, the salt of this cation was obtained from the chloride using anhydrous hydrogen fluoride (B.D.H.Ltd.).

TABLE 6.1 Analytical Results for the Pentafluorotellurates

| CATION | C | H | N | Na | Te | F | |
|---|---|---|---|---|---|---|---|
| $Bu_4N^+$ | 41.3 | 7.8 | 3.0 | - | 27.4 | 20.4 | Calc. |
| | 41.6 | 8.1 | 3.0 | | | 20.2 | Obs. |
| $Me_4N^+$ | 16.2 | 4.0 | 4.7 | - | 43.0 | 32.0 | Calc. |
| | 16.3 | 4.4 | 5.0 | | 42.9 | 32.2 | Obs. |
| $Na^+$ | - | - | - | 9.4 | 52.0 | 38.7 | Calc. |
| | | | | 10.1 | 52.0 | 39.3 | Obs. |

### 6.7.3 Tellurium Tetrafluoride

This was prepared in a similar manner to the method of Seppelt[185]. Tellurium dioxide (8.2g., 0.05mmol.) (B.D.H.Ltd., 99%) was placed in a 160cm$^3$ stainless steel pressure vessel and sulphur tetrafluoride (22g., 0.2mmol), kindly provided by Professor R.D. Chambers, was condensed in at 77K. The vessel was then heated for 8 hours at 403K, after which it was cooled to room temperature and the gaseous products (excess $SF_4$, $SOF_2$) allowed to escape in a fume cupboard. The crystalline residue was sublimed at 379K and $10^{-2}$cm Hg. A yield of 7.87g representing 77% was obtained.

(Found: Te, 61.6; F, 37.3%. Calc. for $TeF_4$: Te, 62.7; F, 37.3%).

### 6.7.4 Tellurium Dichloridedibromide

Tellurium dichloride was prepared by a method similar to that of Aynsley.[97] Difluorodichloromethane (B.D.H. Ltd.), previously dried by passing through concentrated sulphuric acid and phosphorus pentoxide, was led over molten tellurium (Hopkin and Williams, technical grade) (∿4g) at 773K, and 100cm$^3$ min.$^{-1}$ contained in the second section of a 2.5cm O.D. Pyrex tube, constricted at intervals of $10cm^3$ to furnish six sections. A trap at 193K (solid carbon dioxide) was used to trap out excess difluorodichloromethane and this was protected by a calcium chloride drying tube. The black product was distilled forward in the gas stream into the last section which was then sealed off and taken into the glove box. The reaction proceeds according to:

$$2CF_2Cl_2 + Te \longrightarrow (CF_2Cl)_2 + TeCl_2$$

Tellurium dichloride (0.3g, 1.6mmol) was placed in a reaction vessel (simply a tube fitted with a B14 cone), which was then transferred to the vacuum line and evacuated and an excess of bromine (0.5ml, 9mmol) was condensed onto the dichloride at 77K. After having allowed the mixture to reach ambient temperature, excess bromine was pumped off yielding a yellow solid.

(Found: Te, 35.7; Cl, 19.6; Br, 44.4%. Calc. for $TeCl_2Br_2$; Te, 35.6; Cl, 19.8; Br, 44.6%).

### 6.7.5 Tellurium Dibromidediiodide

This preparation was attempted according to the method of Aynsley and Watson.[98] Bromotrifluoromethane (B.D.H.Ltd.) dried with concentrated sulphuric acid and then with phosphorus pentoxide was led over molten tellurium (∿4g) (Hopkin and Williams, technical grade) at about 773K, in an apparatus identical to that described in the previous section. The product, a black powder was sublimed forward in the gas stream and collected in the final section. This was then sealed off and taken into the glove where it was transferred to a sublimation apparatus. The black solid, a mixture of tellurium and its tetrabromide, was sublimed under vacuum at 473K on to a cold finger maintained at 89K (liquid air). The sublimate, a black solid together with the residue, also a black solid, were analysed and the results, together with the calculated values for tellurium dibromide, are given in Table 6.2.

TABLE 6.2 Analytical Results for $TeBr_2$ System

| | Te | Br |
|---|---|---|
| Sublimate | 44.7 | 54.4 |
| Residue | 91.1 | - |
| Calculated for $TeBr_2$ | 44.2 | 55.8 |

Although the sublimate gave results which appear promising it did not dissolve in ether and was recovered unchanged. It is therefore supposed that the product consists of a solid solution of tellurium in its tetrabromide.

## 6.8 Analyses

Carbon, hydrogen and nitrogen were determined by microcombustion using a Perkin-Elmer 240 elemental analyser, using the service provided in the Chemistry Department of the University of Durham.

Sodium and tellurium were determined by using a Perkin-Elmer 403 atomic absorption spectrophotometer.

Chlorine was determined potentiometrically against 0.01M silver nitrate solution using an Ag, AgCl electrode in an acetone medium, following Schoniger oxygen flask combustion. Bromine and iodine were determined, using iodometric methods,[186] also following Schoniger oxygen flask combustion. A total halogen content was first obtained for mixed chlorobromo- compounds using the potentiometric method, followed by iodometric determination of bromine only. For chloroiodo- species, treatment with hydrogen peroxide and fuming nitric acid was followed by potentiometric determination of chlorine. The iodine was then determined iodometrically. The halogens in bromoiodo- compounds were determined individually by iodometric titration.[186]

Fluorine was determined by dissolving the compound in water followed by passage down an ion-exchange column to yield hydrofluoric acid. This was then titrated against 0.02M sodium hydroxide.[187] The results obtained from the analytical service were found to be variable, especially those for mixed halogeno- species and in some cases only a total halogen content could be obtained (Table 2.23).

## 6.9 Solvents

Acetone and dichloromethane were dried over 4A mesh molecular sieve and stored under nitrogen. Acetonitrile was distilled from phosphorus pentoxide and then stored over molecular sieve under nitrogen.

## 6.10 Purification of Hydrogen Chloride and Hydrogen Bromide

Hydrogen chloride, electronic grade, was purchased from British Oxygen Chemicals Ltd., hydrogen bromide from B.D.H. Ltd. Hydrogen chloride was admitted to a 10 litre storage bulb, via the vacuum line, up to a pressure of 1 atmosphere. The hydrogen chloride was then cooled to 77K so that any air which may have leaked in could be removed by pumping. Subsequently, the gas was fractionated through traps at 189K (acetone/solid carbon dioxide slurry) and 178K (toluene slush bath) before being trapped at 77K. When all of the gas had been fractionated, it was returned to the storage bulb.

Hydrogen bromide was treated similarly, except that the traps in the fractionation section were maintained at 209K (chloroform slush bath) and 195K (ethanol/solid carbon dioxide slurry).

## APPENDIX

TABLE 1 Values of 4θ for the Chloroiodotellurate Systems

| $TeCl_6^{2-}$ | $TeCl_5I^{2-}$ | $TeCl_4I_2^{2-}$ | $TeCl_3I_3^{2-}$ | $TeI_4Cl_2^{2-}$ | $TeI_5Cl^-$ | $TeI_6^{2-}$ |
|---|---|---|---|---|---|---|
| 48.5(1) | 44.2(4) | 43.4(4) | 54.8(6) | 57.6(2) | 57.3(5) | 49.8(9) |
| 44.3(1) | 35.4(5) | 37.2(5) | 49.4(9) | 52.9(3) | 53.3(7) | 46.6(4) |
| 35.6(2) | 31.5(5) | 31.6(5) | 37.1(4) | 50.8(4) | 50.7(7) | 43.6(3) |
| 29.7(3) | 29.4(5) | 28.8(5) | 29.0(2) | 47.0(9) | 46.8(9) | 31.0(2) |
| 25.1(2) | 24.4(5) | 23.7(5) | 24.0(3) | 23.2(7) | 34.1(5) | 24.3(2) |
| 20.7(5) | 21.0(5) | 19.3(5) | 19.3(5) | 19.5(7) | 31.6(5) | 19.9(9) |
| 16.6(7) | 17.0(10) | 16.5(10) | 16.8(10) | 16.6(9) | 23.1(9) | 17.3(9) |

TABLE 2 Values of 4θ for the Bromoiodotellurate Systems

| $TeBr_6^{2-}$ | $TeBr_5I^{2-}$ | $TeBr_4I_2^{2-}$ | $TeBr_3I_3^{2-}$ | $TeI_4Br_2^{2-}$ |
|---|---|---|---|---|
| 49.9(6) | 51.6(4) | 51.1(3) | 54.6(5) | 54.5(9) |
| 47.0(6) | 46.3(3) | 45.7(2) | 52.1(4) | 49.1(10) |
| 45.4(6) | 39.1(2) | 38.7(2) | 49.2(10) | 22.7(6) |
| 36.1(6) | 34.9(3) | 29.6(2) | 19.3(10) | 19.4(8) |
| 29.0(6) | 29.9(4) | 19.4(10) | 16.4(10) | 15.5(8) |
| 24.1(6) | 26.2(4) | 17.0(10) | | |
| 19.6(8) | 22.7(4) | 15.7(6) | | |
| 16.5(10) | 20.0(10) | | | |
| | 17.1(10) | | | |
| | 15.7(10) | | | |

These values are the average of two readings. The relative intensities, shown in parentheses, were determined visually and are only very approximate, with the most intense lines assigned an intensity of 10.

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