

NEW POLYATOMIC CATIONS OF SULPHUR, SELENIUM

TELLURIUM AND BISMUTH

NEW POLYATOMIC CATIONS OF SULPHUR, SELENIUM,

TELLURIUM AND BISMUTH

BY

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ABSTRACT

A number of new compounds containing polyatomic cations of the chalcogens have been prepared and their structures investigated. In particular methods for preparing heteroatomic cations containing two of the elements in the same cation have been extensively studied for the first time. Particular emphasis has been given to the preparation of crystalline samples suitable for the investigation of structure by x-ray crystallography. In addition some structural studies have been made by Raman spectroscopy.

The following compounds containing homopolyatomic cations have been prepared by the reaction of AsF_5 or SbF_5 with the appropriate element in solution in SO_2 and their structures investigated: $\text{S}_{16}(\text{AsF}_6)_2$, $\text{Se}_{10}(\text{AsF}_6)_2$, $\text{Te}_6(\text{SbF}_6)_2$, and TeAsF_6 . By reactions between two different homopolyatomic cations or by reactions of a single homopolyatomic cation with one of the elements sulphur, selenium or tellurium the following compounds of new heteropolyatomic cations were prepared and their structures studied: $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$, $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$, $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$, $\text{Te}_3\text{S}_3(\text{AsF}_6)_2$ and $\text{S}_2\text{Se}_8(\text{AsF}_6)_2$.

In a rather limited investigation of the reactions of bismuth with AsF_5 and SbF_5 the following compounds containing the Bi_5^{3+} cation have been prepared and characterized by Raman spectroscopy: $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$ and $\text{Bi}_5(\text{SbF}_6)_3$. A polymeric compound of composition $\text{BiF}_2 \cdot \text{AsF}_6$ was also prepared.

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CHAPTER I

Introduction

(1) Historical

During recent years a number of homopolyatomic cations (M_y^{x+} where $x \leq y$) have been prepared and characterized (1). These cations are important in terms of their bonding and stereochemistry and constitute a novel class of compounds of intrinsic interest. Homonuclear aggregates of atoms are well known among transitional metals in "cluster" compounds, such as $Mo_6Cl_8^{4+}$, and in the boron hydrides such as $B_{12}H_{12}^{2-}$. The description of the bonding in these compounds is somewhat complicated by the presence of the ligands. Therefore the structures of the homopolyatomic cations are of obvious interest particularly because of their simplicity in that they contain only one kind of atoms.

The most important and widely studied of these species are the homopolyatomic cations of S, Se, Te (and to a lesser extent Bi).

Sulphur Polyatomic Cations

The history of sulphur polyatomic cations can be traced back to 1804 when Bucholz (2) discovered that sulphur reacts with oleum to give brown, greenish blue and blue solutions. Then in 1812, Vogel (3) was able to isolate a deep blue liquid, a bluish-green solid, and a brown liquid which he considered to be definite compounds. Since then

a number of chemists have investigated these oleum solutions, with particular attention being given to the blue compound. The species responsible for the blue color has been identified by various workers as $S_2O_3(4)$, $S_2(5)$, the radical ion $(X_2S - SX_2^+)$ (6), and a species designated S_x (7).

The nature of solutions of sulphur in oleum was finally elucidated by Gillespie and his coworkers. The various colors produced by sulphur in oleum have been shown to be due to the cations S_{16}^{2+} , S_8^{2+} and S_4^{2+} (8-10). Solid compounds containing these cations can be conveniently prepared by the oxidation of sulphur with arsenic or antimony pentafluorides. The red compounds $S_{16}(AsF_6)_2$ and $S_{16}(SbF_6)_2$, the deep blue compounds $S_8(AsF_6)_2$ and $S_8(Sb_2F_{11})_2$ and the pale yellow compound $S_4(SbF_6)_2$ have all been prepared in this way (8,11). The structure of $S_8(AsF_6)_2$ has been determined by x-ray crystallography (10). Oxidation of sulphur by $S_2O_6F_2$ in fluorosulphuric acid at $0^\circ C$ (8) also produced red and blue solutions in which the presence of S_{16}^{2+} and S_8^{2+} were established by spectroscopic, conductometric and cryoscopic measurements. The pale yellow compound $S_4(SO_3F)_2$ has been prepared by carefully reacting $S_2O_6F_2$ with elemental sulphur in SO_2 at low temperature.

The reaction of sulphur with sulphuric acid and oleum has been studied by ultraviolet spectroscopy (12). In 95-100% H_2SO_4 sulphur forms a colloidal solution, but after 12 hours at 75° the element dissolves as S_8 molecules. In 5% oleum oxidation is observed and S_{16}^{2+} is formed. Increase in SO_3

concentration causes further oxidation to S_8^{2+} and to S_4^{2+} in oleum having more than 15% SO_3 . None of these solutions is completely stable, and oxidation continues slowly to give SO_2 as the final product. The presence of the radical ions S_4^+ and S_8^+ had been established in the oleum solutions by ESR studies (12).

Selenium Polyatomic Cations

In 1827, Magnus reported that fuming sulphuric acid dissolved selenium to yield a green solution (13), which deposits selenium when poured into water. Observing the evolution of SO_2 in the same reaction, Fisher (14) in 1828 first pointed out that selenium must have been oxidized. Then Weber (15) obtained a green compound by reacting selenium with SO_3 and he formulated this as $SeSO_3$ in the same way as he formulated the blue and red compounds obtained from the reactions of S and Te with SO_3 as S_2O_3 and $TeSO_3$ respectively. Divers and Shimose (16) agreed with Weber's finding and further observed that on heating the green $SeSO_3$ a bright yellow amorphous mass is obtained which they considered to be an allotropic form of the green compound. Since then various results (17) were reported on these species providing a substantial amount of data but little understanding of the system. Recently it has been shown that these compounds actually contain the yellow Se_4^{2+} and green Se_8^{2+} polyatomic cations (18).

The discovery of the nature of these species was due

to the studies of solutions of selenium in highly acidic media by Gillespie and his coworkers (18). In fluorosulphuric acid elemental selenium can be dissolved to form a green solution. In the presence of $S_2O_6F_2$, selenium has been shown to give green, yellow and finally colorless solutions as the quantity of $S_2O_6F_2$ is increased. The formation of Se_4^{2+} and Se_8^{2+} in these solutions was established by cryoscopic, conductometric and spectroscopic measurements. Since then a number of solid compounds containing Se_4^{2+} and Se_8^{2+} have been prepared by oxidizing selenium with sulphur trioxide, oleum, disulphuric acid, SbF_5 and AsF_5 (19,20,21). The presence of the cations was confirmed by comparison of the Raman spectra of the solid and the absorption spectra of their solutions in oleum or HSO_3F with those obtained previously for solutions of Se_4^{2+} and Se_8^{2+} in these solvents. From phase diagram studies on the systems $Se-(SeCl_4 \cdot 4AlCl_3)$, the compounds $Se_4(AlCl_4)_2$ and $Se_8(AlCl_4)_2$ have been identified, and the crystal structure of the latter compound has been reported (22).

Tellurium Polyatomic Cations

The red color produced when tellurium dissolves in concentrated sulphuric acid was first observed as long ago as 1798 (23), but the origin of this color has remained a mystery until recently. Bjerrum and Smith (24) and Bjerrum (25) have studied the reaction of tellurium tetrachloride with tellurium in molten $AlCl_3-NaCl$. A purple melt was formed,

which they concluded contained the species Te_{2n}^{n+} (probably Te_4^{2+}). At about the same time solutions of tellurium in various acids were investigated in detail by Gillespie and his coworkers (26,27). They found that red solutions are produced when tellurium is dissolved in sulphuric acid, fluorosulphuric acid, or oleum with the simultaneous production of SO_2 , indicating the tellurium is oxidized. The spectra of the solutions were found to be identical with those obtained by Bjerrum and Smith from their melts. Conductometric and cryoscopic measurements of the acidic solutions led to the conclusion that they contain a species Te_{2n}^{n+} which was certainly not Te_2^+ but probably Te_4^{2+} .

Reaction of tellurium with $\text{S}_2\text{O}_6\text{F}_2$, SbF_5 , and AsF_5 in SO_2 (27) gave the compounds $\text{Te}_4(\text{SO}_3\text{F}_2)$, $\text{Te}_4(\text{Sb}_2\text{F}_{11})_2$ and $\text{Te}_4(\text{AsF}_6)_2$, and from the $\text{Te}-(\text{TeCl}_4-\text{AlCl}_3)$ melts, the compounds $\text{Te}_4(\text{AlCl}_4)_2$ and $\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$ (28) were obtained. The formulation of the red species as Te_4^{2+} was finally confirmed by the determination of the crystal structures of the latter two compounds (29).

Tellurium can be oxidized by $\text{S}_2\text{O}_6\text{F}_2$ in fluorosulphuric acid to the yellow Te_n^{n+} (27). Solids of empirical formula TeSbF_6 , TeSO_3F , and $\text{Te}_2\text{S}_3\text{O}_{10}$ have been prepared (27,30,31). These compounds and concentrated solutions of Te_n^{n+} are diamagnetic, ruling out the possible formulas Te^+ , Te_3^{3+} etc. Cryoscopic measurements on Te_n^{n+} in fluorosulphuric acid showed that the cation is not Te_2^{2+} , but could not distinguish with

certainty between Te_4^{4+} , Te_6^{6+} and Te_8^{8+} (27). Paul and coworkers (32) have, however, concluded from absorption spectra and from cryoscopic and conductometric measurements that the yellow species is Te_2^{2+} . A similar conclusion was made by Bjerrum (33) from spectrometric measurements of TeCl_4 and elementary tellurium in KAlCl_4 melts buffered with KCl-ZnCl_2 . The possibility that there are various Te_n^{n+} species, depending on the nature of the solvent or accompanying ions obviously cannot be ruled out.

Attempts to obtain a tellurium analogue of the ions S_8^{2+} and Se_8^{2+} have not been successful although a diamagnetic compound, Te_3AsF_6 , containing tellurium in the +1/3 oxidation state, has been obtained (27). This compound presumably contains the Te_6^{2+} cation. The analogous compound, Te_3AlCl_4 , has been isolated in the course of phase diagram studies of the system $\text{Te-(TeCl}_4\text{-AlCl}_3)$; density and unit cell dimensions indicated that its molecular formula is $\text{Te}_6(\text{AlCl}_4)_2$ (28).

Bismuth Polyatomic Cations

The discovery of bismuth polyatomic cations arose out of an investigation into the nature of "BiCl", first prepared by reduction of bismuth trichloride by bismuth metal by Eggink (34) in 1908. Since then there has been a considerable amount of work on the compound but the real nature of the species remained uncertain due to its instability and the difficulty of purification from the melt solution until 1958. Corbett (35) was first able to isolate the compound in 98-99%

purity by sublimation or benzene extraction of the unreacted BiCl_3 from the Bi-BiCl_3 mixture. Though the compound was diamagnetic, he still thought it was BiCl in some polymeric form. The mystery of this compound was finally solved in 1963, when Corbett and Hershafit (36) obtained single crystals from the melt and by x-ray diffraction showed that the unit cell contained 4 Bi_9^{5+} , 8 BiCl_5^{2-} and $2 \text{ Bi}_2\text{Cl}_8^{2-}$, i.e., the stoichiometry is actually $\text{BiCl}_{1.167}$. More recently the cation Bi_5^{3+} was again identified in the compound $\text{Bi}_{10}\text{Hf}_3\text{Cl}_{18}$ which was shown to be $\text{Bi}^+ \text{Bi}_9^{5+} (\text{HfCl}_6^{2-})_3$ by x-ray crystallography(37).

Since the identification of Bi_9^{5+} , evidence has been obtained for other bismuth cations. Bjerrum and Smith have identified Bi^+ , Bi_5^{3+} (38,39) and Bi_8^{2+} (40) in fused salts. The formulas Bi^+ and Bi_5^{3+} were established by studying the equilibria involving these species in molten $\text{AlCl}_3\text{-NaCl}$ eutectic and $\text{ZnCl}_2\text{-KCl}$ eutectic using spectrophotometric measurements. The compounds $\text{Bi}_5(\text{AlCl}_4)_3$ and $\text{Bi}_8(\text{AlCl}_4)_2$ were later prepared by Corbett (41) and shown to be diamagnetic and to have absorption and reflectance spectra very similar to those of Bi_8^{2+} and Bi_5^{3+} in solution.

Reports of Bi_3^{3+} (42) and Bi_4^{4+} (43,44) have been shown to be incorrect (45,46).

(2) Preparation of Polyatomic Cations

Polyatomic cations of sulphur, selenium, tellurium and bismuth have generally been prepared in two ways.

1. Oxidation of the element with oxidizing agents such as AsF_5 or SbF_5 in highly acidic or weakly basic systems at room or low temperature.

2. Reduction of the corresponding chlorides by the element in the melt at high temperature.

Separation of products has usually been accomplished by solvent extraction in the first case and by vapor phase transport technique in the second.

The preparation of the known polycations of the elements S, Se, Te and Bi is summarized in Table 1.

(3) Structures of Polyatomic Cations

A number of very interesting structures have been found for the polycations of S, Se, Te and Bi. The known structures as determined by x-ray crystallography are summarized in Table 2.

No direct structural evidence is available for the other polycations, with the exception that S_4^{2+} is considered to be square planar since the ultraviolet and Raman spectra of S_4^{2+} (8) are very similar to those of Se_4^{2+} and Te_4^{2+} . The results of a study of the magnetic circular dichroism of solutions of S_4^{2+} , Se_4^{2+} and Te_4^{2+} also lead to the same conclusion (47).

(4) Purpose of this work

The main object of the present work was to continue the investigation of polyatomic cations of the elements sulphur, selenium, and tellurium with the following principal

aims;

- (a) to further investigate the structures of some previously prepared cations whose structures have remained uncertain.
- (b) to synthesise and investigate the structures of new cations containing two of the elements sulphur, selenium and tellurium.

Two main types of reaction were studied extensively in attempting to prepare such "mixed" cations.

- (i) The reaction between two different polyatomic cations.
- (ii) The reaction of a cation of a given element with the elemental form of another of the elements sulphur, selenium or tellurium.

Another objective of the work was to utilise the methods that have been successful for the preparation of the polyatomic cations of the chalcogens to attempt to prepare new compounds of the polyatomic cations of bismuth and to study their structures.

Table 1: Preparation of Compounds Containing Polyatomic Cations of S, Se, Te and Bi

<u>Cation</u>	<u>Compound</u>	<u>Reaction</u>	<u>Condition</u>	<u>Ref.</u>
S_{16}^{2+}	$S_{16}(SbF_6)_2$ $S_{16}(AsF_6)_2$	$2S_8 + 3SbF_5$ $2S_8 + 3AsF_5$	Solvent HF; 25° Solvent HF, slowly warmed from -78° to 0°	(8,48) (8,49)
S_8^{2+}	$S_8(Sb_2F_{11})_2$ $S_8(AsF_6)_2$	$S_8 + 5SbF_5$ $S_8 + 3AsF_5$	Solvent SO_2 ; 25° Solvent HF; 0°	(8,48) (8,49)
S_4^{2+}	$S_4(SbF_6)_2$ $S_4(SO_3F)_2$	$S_8 + \text{excess } SbF_5$ $S_8 + \text{excess } S_2O_6F_2$	Heated at 140° for few days Solvent SO_2 , slowly warmed from -63° to 25°	(8,48) (8,48)
Se_8^{2+}	$Se_8(Sb_2F_{11})_2$ $Se_8(AsF_6)_2$ $Se_8(AlCl_4)_2$	$8Se + 5SbF_5$ $8Se + 3AsF_5$ Obtained from $Se-SeCl_4-4AlCl_3$ melts	Solvent SO_2 , -23° for 3 days Solvent HF, warm up from -78° to 0° over 3 days	(21) (21) (22)

Table 1 (Cont.): Preparation of Compounds Containing Polyatomic

Cations of S, Se, Te and Bi

<u>Cation</u>	<u>Compound</u>	<u>Reaction</u>	<u>Condition</u>	<u>Ref.</u>
Se_4^{2+}	$\text{Se}_4(\text{HSO}_3)_2$	Se + 65% oleum	50-60°; left until yellow brown	(19)
	$\text{Se}_4\text{S}_4\text{O}_{13}$	Se + excess SO_3	0°; left 24 hr.	(19)
	$\text{Se}_4(\text{SO}_3\text{F})_2$	$4\text{Se} + \text{S}_2\text{O}_6\text{F}_2$	Solvent HSO_3F	(19)
	$\text{Se}_4(\text{Sb}_2\text{F}_{11})_2$	Se + excess SbF_5	Heat at 100-140° for 6 hr.	(19)
	$\text{Se}_4(\text{AsF}_6)_2$	$8\text{Se} + 6\text{AsF}_5$	Solvent SO_2 , 80° for 8 days	(20)
Te_6^{2+}	$\text{Te}_6(\text{AsF}_6)_2$	$6\text{Te} + 3\text{AsF}_5$	Solvent SO_2 , 25°	(27)
	$\text{Te}_6(\text{AlCl}_4)_2$	Obtained from $\text{Te}-(\text{TeCl}_4-4\text{AlCl}_3)$ melts		(28)
Te_4^{2+}	$\text{Te}_4(\text{Sb}_2\text{F}_{11})_2$	Te + SbF_5	Solvent SO_2 , -23°	(27)
	$\text{Te}_4(\text{AsF}_6)_2$	$4\text{Te} + 3\text{AsF}_5$	Solvent SO_2 , 25°	(27)
	$\text{Te}_4(\text{AlCl}_4)_2$	Obtained from $\text{Te}-(\text{TeCl}_4-4\text{AlCl}_3)$ melts		(28)
	$\text{Te}_4(\text{Al}_2\text{Cl}_7)_2$			

Table 1 (Cont.): Preparation of Compounds Containing Polyatomic Cations of S, Se, Te and Bi

<u>Cation</u>	<u>Compound</u>	<u>Reaction</u>	<u>Condition</u>	<u>Ref.</u>
Te_n^{n+}	$TeSbF_6$	$Te + SbF_5$	$TeSbF_6$ is insoluble in SO_2 , therefore readily separation from the SO_2 soluble $Te_4(Sb_2F_{11})_2$. SbF_3 is removed by vacuum sublimation	(27)
Bi_8^{2+}	$Bi_8(AlCl_4)_2$	Obtained in excess $Bi-BiCl_3-NaAlCl_4$ melts		(41)
Bi_9^{5+}	$Bi_6Cl_7 \cdot 167$	Obtained from excess $Bi-BiCl_3$ melt		(36)
	$Bi^+Bi_9^{5+}(HfCl_6)_3$	Obtained from $Bi-(2BiCl_3-3HfCl_4)$ melt		(37)
Bi_5^{3+}	$Bi_5(AlCl_4)_2$	Obtained from $4Bi-BiCl_3-3NaAlCl_4$ melt		(41)

Table 2: Structures of Polyatomic Cations of
S, Se, Te and Bi

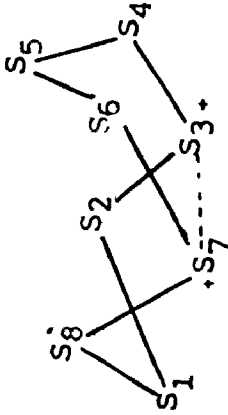
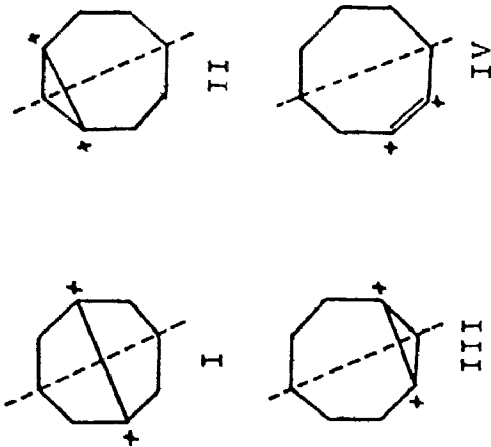
<u>Cation</u>	<u>Structure</u>	<u>Main Feature</u>
S_8^{2+}	 <p data-bbox="714 1113 773 1417">$(S_8^{2+}$ in S_8AsF_6)</p>	<p data-bbox="472 94 529 898">Consists a folded ring with approximately C_s symmetry and an endo-exo conformation. The average bond distance around the ring is 2.04Å. The average bond angle is 102° excluding the two end angles which have an average value of 93°. There is a relatively long bond of 2.83Å across the middle of the ring (S₃-S₇) and the other cross-ring distance (S₂-S₆ and S₄-S₈) are somewhat shorter than the Van der Waals distance. Thus the bonding may be described by the valence bond structure (I) and possibly others in addition, such as II, III and IV, where the dashed line indicates the plane of symmetry (10).</p>
		

Table 2 (Cont.): Structures of Polyatomic Cations of

S, Se, Te and Bi

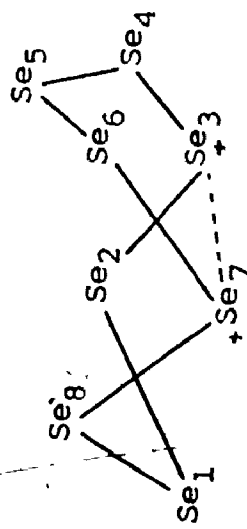
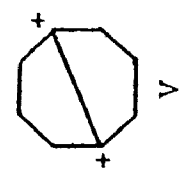
<u>Cation</u>	<u>Structure</u>	<u>Main Feature</u>
Se_8^{2+}	 <p>(Se_8^{2+} in $\text{Se}_8(\text{AlCl}_4)_2$)</p>  <p>(Se_4^{2+} in $\text{Se}_4(\text{HS}_2\text{O}_7)_2$)</p>	<p>Structure very similar to S_8^{2+} except that the cross ring distance $\text{Se}_3\text{-Se}_7$ is relatively shorter than that of S_8^{2+}, and the other cross ring distances $\text{S}_4\text{-Se}_6$ and $\text{Se}_2\text{-Se}_8$ are relatively long. The cation Se_8^{2+} is therefore reasonably well described by the valence bond structure V (22).</p> <p>Se_4^{2+} is shown to be square planar, with an Se-Se bond length of 2.28Å (Se-Se in Se_8 molecule: 2.34Å). The square planar structure is also consistent with the infrared and Raman spectra of several compounds containing Se_4^{2+}. The structure</p>

Table 2 (Cont.): Structures of Polyatomic Cations of

S, Se, Te and Bi

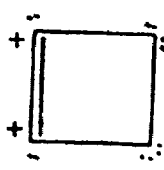
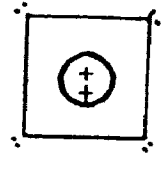
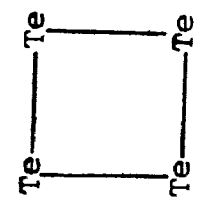
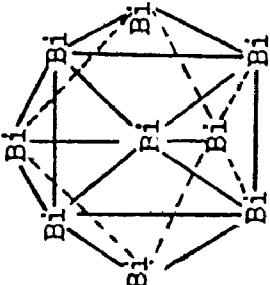
<u>Cation</u>	<u>Structure</u>	<u>Main Feature</u>
	 <p>VI</p>	<p>can be described by valence bond theory (4 structures equivalent to (VI)) or MO theory (VII) where the circle denotes a closed-shell six-π-electron system (47).</p>
	 <p>VII</p>	
Te_4^{2+}	 <p>(Te_4^{2+} in $\text{Te}_4(\text{AlCl}_4)_2$)</p>	<p>Te_4^{2+} is square planar and the Te-Te distance of 2.66Å is significantly shorter than the Te-Te distance of 2.864Å for the spiral chain in elemental Te. The bonding can be described in the same way as Se_4^{2+} (29).</p>

Table 2 (Cont.): Structures of Polyatomic Cations of S, Se, Te and Bi

<u>Cation</u>	<u>Structure</u>	<u>Main Feature</u>
Bi ₉ ⁵⁺		<p>The atomic arrangement in Bi₉⁵⁺ may be described as a trigonal prism plus three atoms outside the rectangular faces of the prism on each of the C₂ axes, or alternatively as three rectangular pyramids sharing opposite, basal edges. The average Bi-Bi bond distance is 3.13Å and most of the angles are within 2° of 60° (36,37).</p>

(Bi₉⁵⁺ in BiCl₃ 1.167)

CHAPTER II

Experimental

(1) Preparation and Purification of Starting Materials

Sulphur Dioxide

Anhydrous grade sulphur dioxide (Matheson of Canada) was distilled into a glass vessel containing P_2O_5 . The vessel was equipped with a Teflon stopcock which could stand the high pressure (up to 5 atmospheres pressure) generated by SO_2 at room temperature. SO_2 was stored at least 24 hours before use.

Arsenic Pentafluoride

Arsenic pentafluoride (Ozark Mahoning Co.) was used directly from the cylinder and was measured on a calibrated Pyrex vacuum line.

Antimony Pentafluoride

Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex glass still in an atmosphere of dry nitrogen. The fraction boiling between $142^{\circ}C$ and $143^{\circ}C$ was collected.

Fluorosulphuric Acid

Technical fluorosulphuric acid (Baker and Adamson) was purified by distillation as described by Barr (51).

Sulphur Trioxide

Sulphur trioxide (Eaker and Adamson) was distilled from 'Sulfan' in a still which was protected from moisture by a magnesium perchlorate drying tube.

Compounds Containing Polyatomic Cations of Group VI

The compounds $S_8(AsF_6)_2$, $Se_8(AsF_6)_2$, $Se_4(AsF_6)_2$, $Te_6(AsF_6)_2$, $Te_4(AsF_6)_2$ and $TeSbF_6$ etc. were prepared by the reaction of the respective element with the oxidizing agents AsF_5 or SbF_5 , as described previously (52). SO_2 was used as solvent in each case. The compounds were stored in sealed glass tubes before use.

It was found that the best way to prepare $Te_4(AsF_6)_2$ was to use a small excess over the stoichiometric amount of Te. The red product was extracted after stirring the reaction mixture for 2 days. A number of extractions were usually required. Using the stoichiometric amount of Te led to a product containing $Te_n(AsF_6)_n$ and $Te_6(AsF_6)_2$ due to the equilibrium between these ions in solution.

(2) General Experimental Techniques

Since all the compounds used in the reactions studied are extremely moisture sensitive, rigorous precautions were taken to exclude moisture in this work. All glassware was flamed under vacuum. All manual operations were carried out in a dry box (S. Blickman Inc.) containing a Mettler H6 balance. The dry box had an evacuable port which could be refilled with nitrogen. The atmosphere was circulated through an external circuit in which any volatile products were removed in liquid air traps.

The apparatus used in the preparations is shown in Fig. 1. The large reaction vessel was usually used when

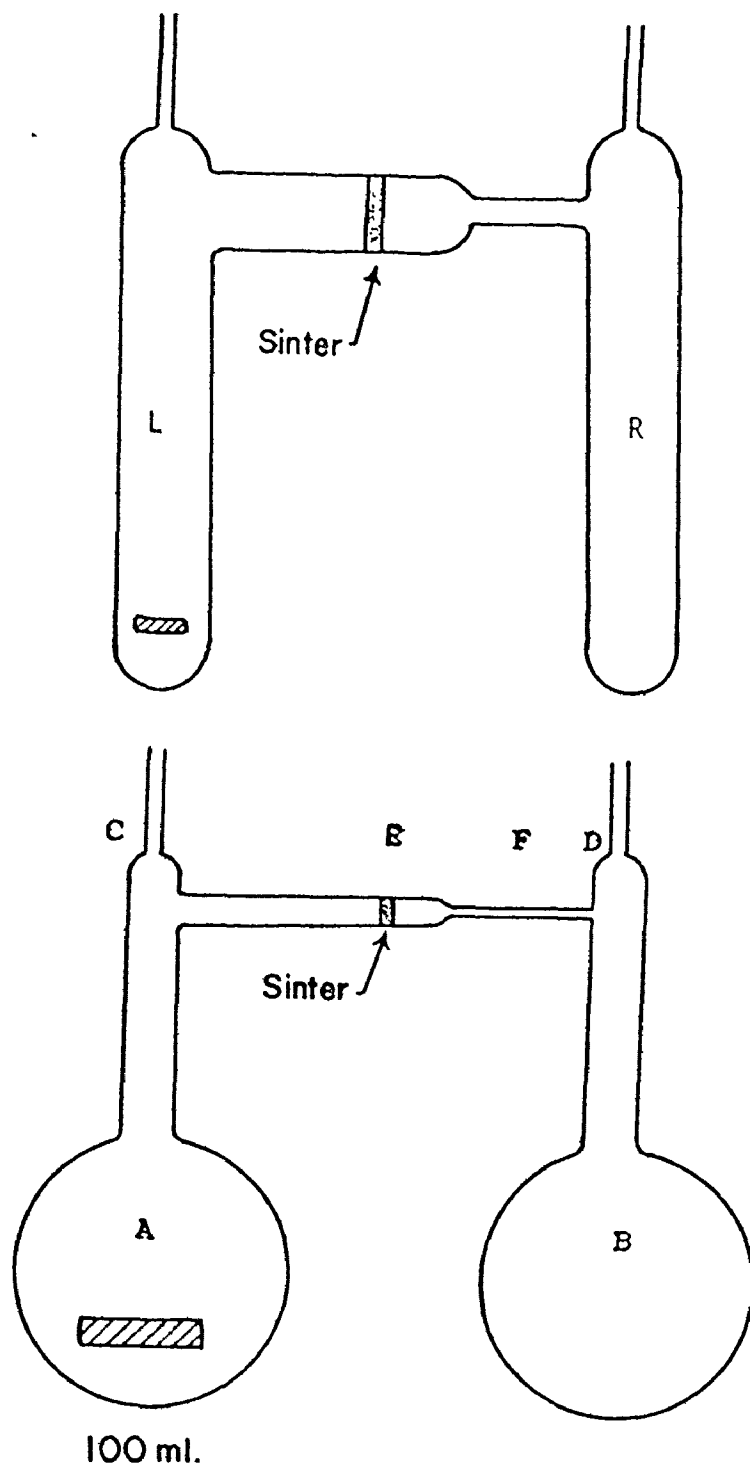


Figure 1. Reaction Vessels.

great amount of reaction product was required. It consists of two 100-ml flasks A and B, joined by a tube containing a fine or medium-grade sinter E and a constriction F. A has in it a 1-in Teflon-covered magnetic stirrer bar. The tubes C and D can be closed using Teflon valves or joined to the vacuum line with Teflon Swagelock fittings.

Some typical reaction procedures are described below.

Reactions with Arsenic Pentafluoride

Arsenic pentafluoride was handled on a calibrated Pyrex vacuum line equipped with a mercury manometer. The line was thoroughly flamed under vacuum before use. The stopcocks on the line were lubricated with Kel-F or halocarbon grease since AsF_5 attacks ordinary Apiezon grease. The mercury of the manometer is also attacked by AsF_5 but soon it is protected by a layer of product. An appropriate amount of the finely powdered element was introduced into flask A. The apparatus was flame sealed at D and connected to the vacuum line at C via a Teflon valve. It was evacuated and flamed at those parts where the element would not simultaneously be heated. About 40 ml of SO_2 was condensed into A which was cooled in liquid nitrogen. The valve was closed and AsF_5 was introduced into the vacuum line from the cylinder. The exact amount of AsF_5 was transferred into the cooled SO_2 by adjusting the valve while observing the reading of the manometer. The apparatus was flame sealed at C and allowed to warm to room temperature. The solution mixture was stirred until the reaction was

completed. To prevent transfer of SO_2 from A to B, the top of the flask A was wrapped with several turns of rubber tubing carrying cold tap water. Separation of the SO_2 -soluble product was achieved by extracting the contents of A with SO_2 into B through the sinter E. Finally volatiles were transferred to A by cooling A with cold tap water or a low temperature slush bath. Flask B was separated by sealing at F.

Reactions Between Elements and Polyatomic Cations

The element and the appropriate polyatomic cation compound were weighed in the dry box and introduced into flasks A and B respectively, C and D were closed using a Teflon valve and a Teflon Swagelock fitting with a glass blank. The apparatus was evacuated and heat sealed at C. SO_2 was distilled into A to give solution of the polyatomic cation compound and the apparatus was heat sealed at D. The solution was then transferred through the filter onto the sample of the element in flask B. The resulting mixture was then stirred until the reaction was complete.

Crystallization of Compounds for X-ray Diffraction Spectroscopy

It was a surprise to find out that most of the polyatomic cationic compounds of group VI e.g. Se_8^{++} , Te_4^{++} , Te_n^{n+} etc. are more soluble at low temperature. This property was used to grow single crystals of new polycationic compounds and proved to be a success. In a typical example the solution of $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$ was cooled at about -20°C and filtered to the other flask through the sinter. Crystals were formed on warming the solution to room temperature.

(3) Instrumentation

1. UV-Visible Absorption Spectroscopy

Absorption spectra were recorded from 200 to 700 nm on a Cary model 14 spectrophotometer. Custom made quartz cells (Helma Ltd.) with Teflon stoppers and 1 cm path length were used for acid solutions. Special quartz cells (Helma Ltd.) of 1 cm path length which had a Teflon stopcock (Fig.2) made to stand high pressure were used to obtain the spectra of SO₂ solution.

2. Infrared Spectroscopy

Infrared spectra were obtained on solid samples mixed either with KBr or Nujol oil between silver chloride plates using a Perkin-Elmer Model 227 spectrophotometer.

3. Laser Raman Spectroscopy

Raman spectra were recorded using a Spex Industries Model 1400 spectrometer employing a double monochromator and a phototube detector with an electrometer amplifier and recorder. Two types of exciting radiation, the green 5165-A Ar ion laser (Spectra-Physics Model 140) and the red 6328A He-Ne laser (Spectra-Physics Model 125) were available, which permitted the choice of a frequency not absorbed by the material under study. Samples were sealed in 2-mm-o.d. glass capillary tubes, or thin wall Pyrex NMR tubes. For low temperature spectra the sample tubes were mounted in a quartz tube with an evacuated jacket, silvered except for a 1-cm band around the centre. Nitrogen was boiled off at a variable rate

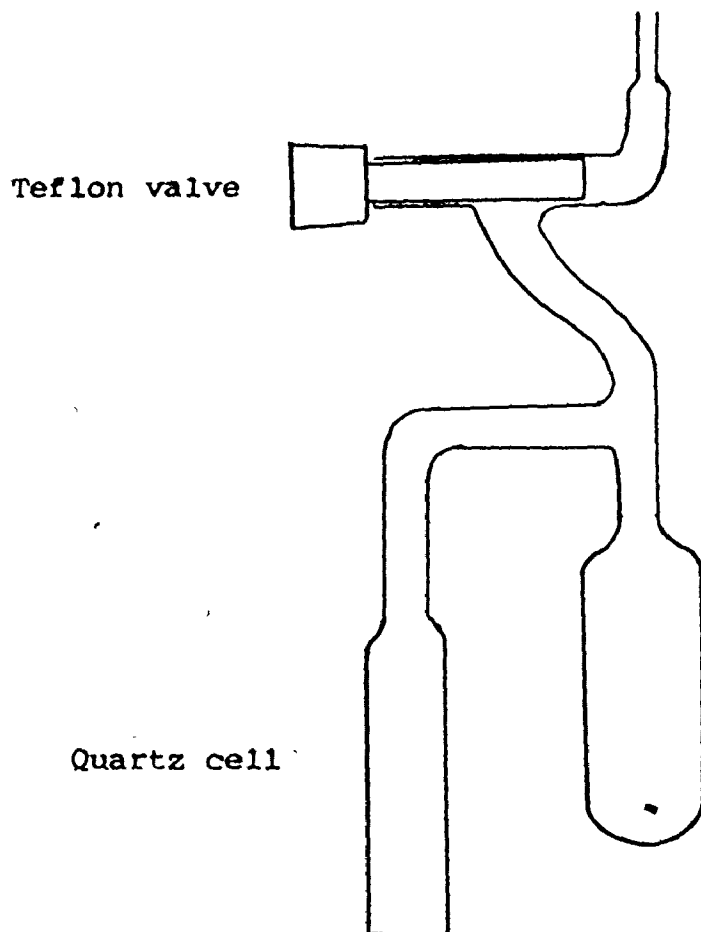


Fig. 2. Special quartz cell for measuring absorption spectra of samples in SO_2 solution

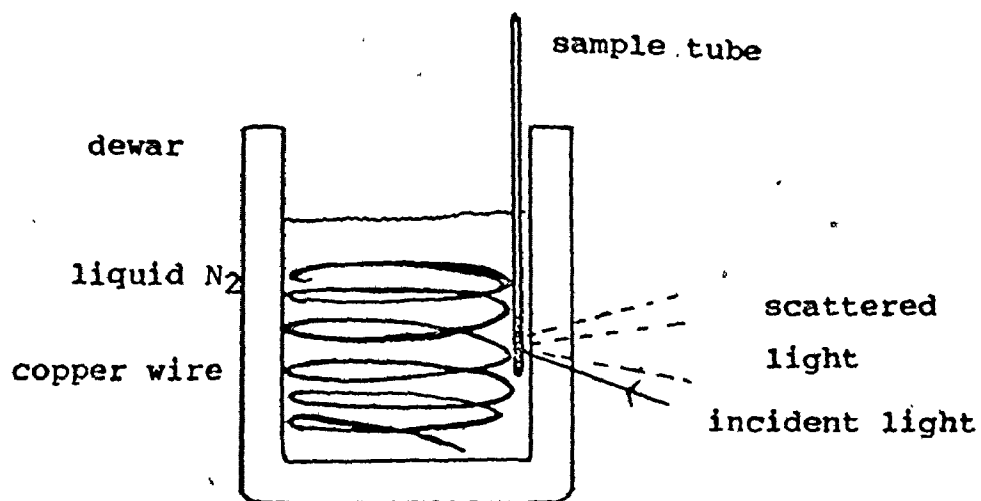


Fig. 3. Apparatus for measuring Raman spectrum at -196°C

from a dewar, and passed through the tube, and the temperature was recorded with a thermocouple. For spectra recorded at liquid nitrogen temperature, the samples were mounted in liquid nitrogen in a special vessel. (Fig. 3)

4. Reflectance Spectroscopy

The spectra were recorded on a Cary Recording Spectrophotometer Model 14R equipped with a Cary Model 1411 Diffuse Reflectance Accessory, operating within the visible region from 7500 - 3500Å. The solid samples were prepared by making a thin solid layer between two 1"x3" quartz plates which was then sealed with dried halocarbon grease and additionally with adhesive tape around the edge.

5. Nuclear Magnetic Resonance Spectroscopy

Fluorine nmr spectra were obtained using a Varian DA60 spectrometer operating at 56.4 MHz. Low temperature spectra were obtained using a Varian V-4540 temperature controller. Samples were prepared by placing the non-volatile components in an nmr tube in the dry box and then condensing the requisite amount of SO₂ into the tube in vacuo prior to sealing. Chemical shifts were measured relative to external CFCl₃.

6. X-ray Powder Diffraction Patterns

The solid compounds were finely ground and packed into dried 0.3-mm-o.d. quartz capillary tubes in the dry box. The sealed samples were exposed with a Philips PW 1024/10 camera using CuKα radiation of 1.5418Å wavelength.

7. X-ray Diffraction Spectroscopy

Single crystals were examined and placed in quartz capillaries (0.3-0.5mm o.d.) under a microscope (Bausch & Lomb) in a dry box. Since the crystals were extremely sensitive to moisture the capillaries were dried in an evacuated vessel heated at 250°C for at least two days before use. The sealed samples were finally mounted on a Syntex P1̄ diffractometer with Mo K α radiation after Weissenberg and precession photographs had been taken.

8. Density Measurement

The densities of the crystals were measured by the density bottle method using a fluorolube oil (Hooker Chemical Co.) which was fluorinated before use. About 0.5 g of crystalline material and 2 ml density bottles were used.

(4) Analysis

Microanalyses were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen Fritz-Pregl-Straße 14-16, West Germany, and Pascher Mikroanalytisches Laboratorium 53, Bonn, Buschstraße 54, West Germany.

Selenium analysis of the compound $\text{Se}_{10}(\text{AsF}_6)_2$ was determined gravimetrically. Weighed quantities of the compound were decomposed with water and dissolved in the minimum volume of warm nitric acid. The deluted solution was warmed with an excess of hydrazine hydrochloride for 1 hour, and the resulting grey selenium was filtered, dried and weighed.

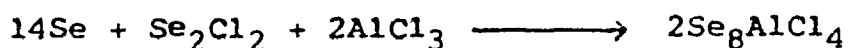
CHAPTER III

Selenium and Sulphur Cations

A. Selenium Cations(1) Introduction

It has been shown that selenium can be oxidized by various oxidizing agents to form compounds containing Se_8^{2+} and Se_4^{2+} cations (18). The structures of both cations have been determined by x-ray crystallography. Se_8^{2+} (22) is a folded eight-membered ring with an endo-exo configuration while Se_4^{2+} (52) is square planar.

Efforts to synthesize Se cations with oxidation states lower than $+1/4$ have been made by Gillespie's research group (53). A brown compound which has the composition Se_8AlCl_4 was prepared in SO_2 by the following reaction.



Another brown compound Se_5AlCl_4 was isolated from the decomposition products obtained by repeated washing of the compound $\text{Se}_8(\text{AlCl}_4)_2$ with SO_2 . These compounds are formulated as $\text{Se}_{16}(\text{AlCl}_4)_2$ and $\text{Se}_{10}(\text{AlCl}_4)_2$ and believed to contain Se_{16}^{2+} and Se_{10}^{2+} polycations. The proposal for the 'dimeric' formula seems not unreasonable since the existence of S_{16}^{2+} has been well established (19) and the presence of other 10 atom polyatomic cations ($\text{Te}_2\text{Se}_8^{2+}$, $\text{Te}_{3.7}\text{Se}_{6.3}^{2+}$) was found later in the investigation of mixed cations in this work.

This chapter reports the study of oxidation of Se using AsF_5 and $\text{Se}_8(\text{AsF}_6)_2$ as oxidizing agents, which had the objective of preparing new compounds of Se in the +1/5 and +1/8 oxidation states and establishing the existence of these oxidation states with more certainty. Particular effort was made to isolate the compounds as single crystals so that the structures of the cations could be studied by x-ray crystallography.

(2) Preparation of $\text{Se}_{10}(\text{AsF}_6)_2$ by Oxidation of Se with $\text{Se}_8(\text{AsF}_6)_2$

$\text{Se}_8(\text{AsF}_6)_2$ is very stable in SO_2 , therefore a reaction analogous to that by which $\text{Se}_{10}(\text{AlCl}_4)_2$ was prepared by decomposition of $\text{Se}_8(\text{AlCl}_4)_2$ with SO_2 could not be used. However, a brown compound which looked like $\text{Se}_{10}(\text{AlCl}_4)_2$ was obtained on treatment of 1 mole of $\text{Se}_8(\text{AsF}_6)_2$, with 2 moles of Se in SO_2 .

In a typical experiment 40 ml of anhydrous SO_2 was distilled onto a mixture of powdered Se (0.158 g, 0.002 mole) and $\text{Se}_8(\text{AsF}_6)_2$ (1.010 g, 0.001 mole) at -196°C . The reaction mixture was allowed to warm up to room temperature and stirred for 12 hours. A brown product with a brownish green supernatant solution was obtained. Since the solid was soluble in SO_2 giving a brownish green solution, the product could be extracted completely to the other side of the reaction vessel. No unreacted Se metal was found. A brown product was separated on removal of SO_2 .

The identification and separation of the product

proved to be very difficult in the early part of this work. It was thought that the brown compound was decomposed in SO_2 since it gave a dirty green coloration, the color being very close to that of Se_8^{2+} . It was natural to conclude that the brown compound was unstable in SO_2 and decomposed to give Se_8^{2+} and selenium. However, repeated preparations and careful observation proved that the brown product is stable in SO_2 and that the solution has a color rather similar to that of Se_8^{2+} . The solubility of the compound in SO_2 is much larger at low temperature. On warming up the cooled solution rapidly to room temperature large amount of brown powder was deposited. If the solution was warmed up extremely slowly dark crystals were formed.

The compound is very moisture sensitive and readily decomposed to red selenium when added to water. On heating in dry nitrogen, it melted at about 200°C with decomposition to black selenium. The infrared spectrum of the compound in Nujol mull showed a strong band at 700 cm^{-1} , the position expected for the ν_3 vibration of AsF_6^{-1} (54). Elemental analysis gave the following result: Found Se, 67.13%. Calculated for $\text{Se}_{10}(\text{AsF}_6)_2$, Se, 67.67%. (*See footnote on p.33.)

Single crystals were isolated for x-ray diffraction study. Since the crystals showed very large absorption of the x-ray radiation considerable efforts were made to find a crystal of suitable size. The larger crystals were found to absorb x-ray extensively and the smaller ones did not

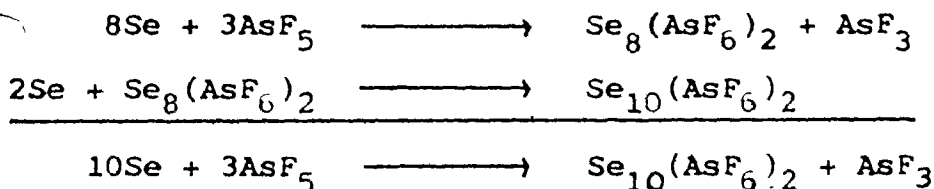
provide enough reflections. However, the problem was finally solved by cutting a large crystal to a suitable size (0.3x0.15x0.07 mm). The x-ray crystallographic determination of the structure on the compound is in progress. The crystals are orthorhombic, and the cell dimensions are $a=13.07$, $b=15.91$ and $c=18.36\text{\AA}$; $v=477.23\text{\AA}^3$. The cell volume indicates the molecule has 10 Se and 2 AsF_6^- if there are eight molecules in one unit cell and the volume of Se atoms and AsF_6^- ions are estimated to be 25\AA^3 and 110 to 120\AA^3 respectively. These approximate atomic volumes have been found to be quite reasonable for other compounds of polyatomic cations (67).

(3) Preparation of $\text{Se}_{10}(\text{AsF}_5)_2$ by Oxidation of Se with AsF_5

Only $\text{Se}_8(\text{AsF}_6)_2$ and $\text{Se}_4(\text{AsF}_6)_2$ were previously reported as products of the reaction of Se and AsF_5 . In the following preparation 10 moles of Se was reacted with 3 moles of AsF_5 in SO_2 and a brown compound was obtained.

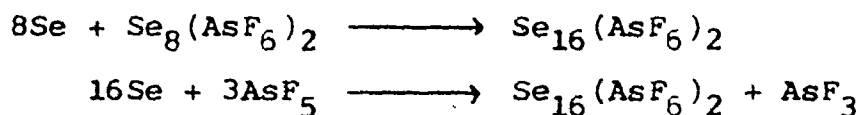
In a typical experiment AsF_5 (0.510 g, 0.003 mole) was condensed at -196°C onto the powdered Se (0.710 g, 0.01 mole) in liquid SO_2 . The mixture was warmed up and stirred. A green solution presumably due to $\text{Se}_8(\text{AsF}_6)_2$ with a small amount of unreacted Se was obtained almost immediately. The color of the solution turned a little brownish as the reaction proceeded. After 12 hours of stirring the reaction was stopped when all the Se was found to be completely reacted. The product was a brown precipitate in a brownish green solution. A powdery brown product was obtained on removal of solvent and volatiles.

The compound looked very similar to $\text{Se}_{10}(\text{AsF}_6)_2$ and was proved to be so by obtaining x-ray diffraction data on crystals grown from the brown powder in SO_2 . The formation of the compound might go through the following reactions.



(4) Attempted preparation of $\text{Se}_{16}(\text{AsF}_6)_2$ by Oxidation of Se with $\text{Se}_8(\text{AsF}_6)_2$ or AsF_5 .

Analogous reactions to the preparations of $\text{Se}_{10}(\text{AsF}_6)_2$ were attempted for the synthesis of $\text{Se}_{16}(\text{AsF}_6)_2$. The reactions between Se and $\text{Se}_8(\text{AsF}_6)_2$ or AsF_5 in SO_2 were expected to proceed according to the equations.



Stoichiometric amounts of reagents were added to SO_2 but unreacted Se was found in both reactions along with a brown product after several weeks of stirring. The brown product was identified as $\text{Se}_{10}(\text{AsF}_6)_2$. No evidence for the formation of the Se_{16}^{2+} species was obtained.

(5) Structure of Se_{10}^{2+}

Final conclusion on the structure of this cation still depends on the x-ray crystallographic studies on $\text{Se}_{10}(\text{AsF}_6)_2$ in progress. It seems reasonable to suppose that Se_{10}^{2+} is

isostructural with $\text{Te}_2\text{Se}_8^{2+}$ and $\text{Te}_{3.7}\text{Se}_{6.3}^{2+}$ which are described in chapter V of this thesis. They may be regarded as bicyclic clusters formed by a six-membered ring fused with an eight-membered ring (Fig.4).

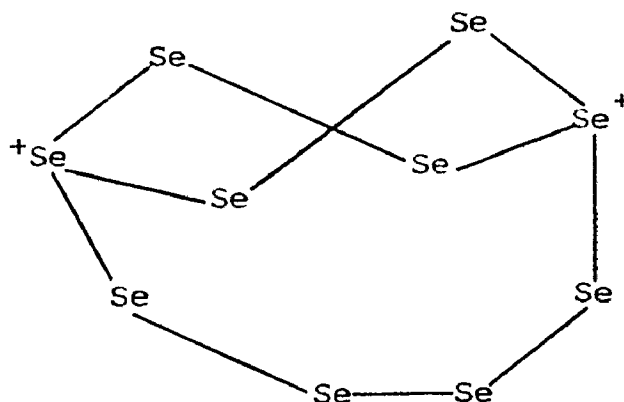


Fig. 4: Suggested Structure for Se_{10}^{2+}

B. Sulphur Cations

(1) Introduction

Of the three sulphur polyatomic cations, only the structure of S_{16}^{2+} is still uncertain. The structure of S_8^{2+} (10) has been shown by x-ray diffraction to be very similar to that of Se_8^{2+} , which is a folded eight-membered ring with an endo-exo configuration. The ultraviolet and Raman spectra of S_4^{2+} (8) are very similar to those of Se_4^{2+} and Te_4^{2+} (1) which have been shown to be square planar, suggesting that S_4^{2+} has the same geometry. The results of

a study of the magnetic circular dichroism of solutions of S_4^{2+} , Se_4^{2+} and Te_4^{2+} also lead to the same conclusion (47).

Magnetic susceptibility measurements on solid $S_{16}(AsF_6)_2$ and concentrated solutions of S_{16}^{2+} in fluorosulphuric acid showed it to have a very small paramagnetism (8). Esr studies of solutions of sulphur in oleum indicated that a signal at $g=2.027$ can be associated with a species that is always present together with the S_{16}^{2+} ion, and it is probable that this is the paramagnetic S_8^+ ion, existing in equilibrium with S_{16}^{2+} . The possible structures II and III (Fig.5) have been proposed for S_{16}^{2+} (8).

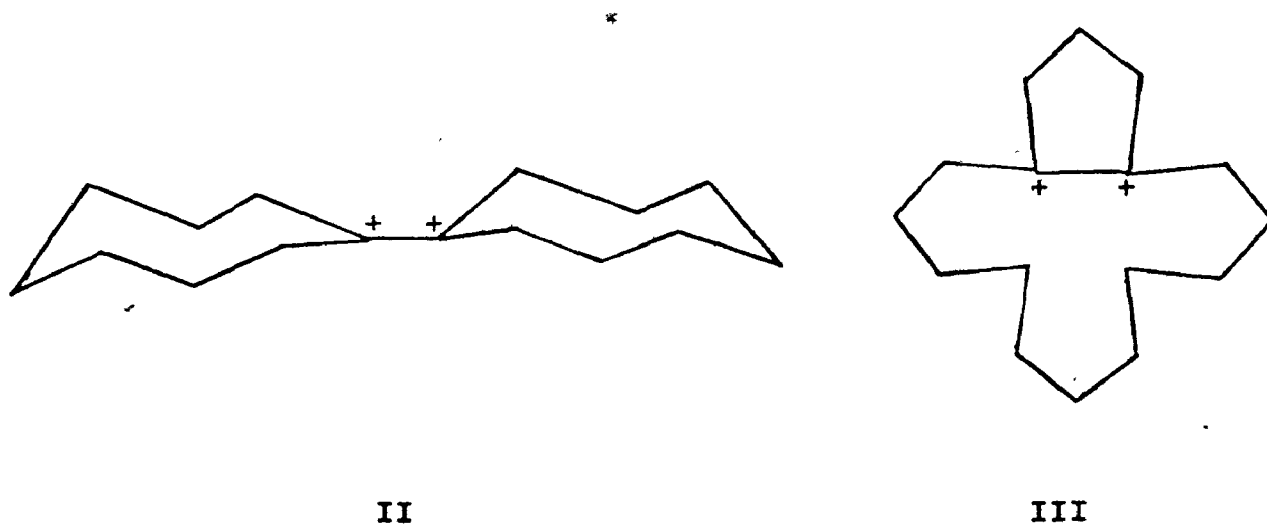
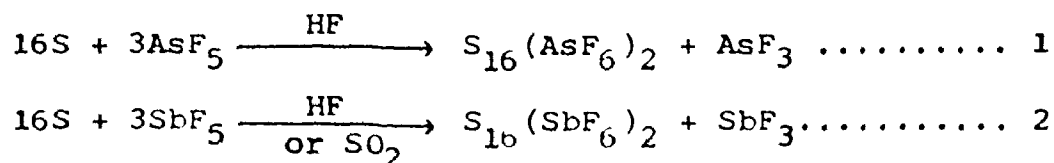


Fig. 5: Possible Structures of S_{16}^{2+}

(2) Preparation of Single Crystals of $S_{16}(AsF_6)_2$

Sulphur can be quantitatively oxidized by arsenic or antimony pentafluoride (8) to red compounds of composition $S_{16}(AsF_6)_2$ or $S_{16}(SbF_6)_2$ according to the equation 1 and 2.



both compounds were obtained as microcrystalline powders so that it was not possible to investigate the cation structure by x-ray crystallography. These compounds are so soluble in HF or SO_2 (e.g. at room temperature or low temperature 2g of $S_{16}(AsF_6)_2$ could be dissolved in less than 1 ml of SO_2 at $25^\circ C$) that it was not possible to grow any crystal from concentrated solutions by lowering the temperature or reducing the volume of the solutions. Later in this work it was found that most of the polycations increase their solubilities at low temperature. Thus the SO_2 solution of $S_{16}(AsF_6)_2$ was heated at $60^\circ C$ and single crystals were obtained.

In a typical experiment AsF_5 (0.402 g, 0.0024 mole) was distilled onto sulphur (0.400 g, 0.0126 mole) in 30 ml of liquid SO_2 at $-196^\circ C$. The reaction mixture was allowed to warm up to room temperature and stirred. The reaction was completed after 3 hours and an orange red solution was obtained. The solution was filtered to the other side of the vessel where it was heated slowly to $60^\circ C$ in an oil bath. The temperature

was kept constant for a few days until a large amount of dark red crystals were precipitated from a thick red solution. However, these crystals were stuck together in one large cluster and could not be well separated from each other. Since it took several hours to dissolve all the crystals it was possible to separate the crystals without dissolving by shaking the solid with a small amount of SO_2 and then rapidly filtering the solution back to its original side. On removing the solvent and volatiles, dark red crystals were obtained.

The crystals obtained were found to be triclinic. Determination of the structure of the compound by x-ray diffraction is still in progress.

*(From p.27)

The analytical result is based on the gravimetric determination of selenium in the compound (p.24). Microanalysis of the compound by Alfred Bernhardt Mikroanalytisches Laboratorium gave the following results. Calculated for $\text{Se}_{10}(\text{AsF}_6)_2$: Se, 67.67; As, 12.84; F, 19.54. Found: Se, 67.04; As, 10.69; F, 21.30. The As and F analyses are obviously not satisfactory. The anion has been shown to be AsF_6^- by infrared spectroscopy.

CHAPTER IV
Tellurium Cations

(1) Introduction

Gillespie and his coworkers have recently shown that elemental tellurium can be oxidized to the +1/3, +1/2 and +1 oxidation states by various oxidizing agents in highly acidic or weakly basic media. More than ten compounds (1) containing polyatomic cations of tellurium have been prepared. Among the three cationic species, the red Te_4^{2+} is most easily obtained and the structure has been unambiguously determined by single crystal x-ray diffraction (29). The ion has a center of symmetry and is almost exactly square planar.

Not too much structural information is available for the other two species Te_n^{n+} and Te_6^{2+} . X-ray crystallographic studies of Te_n^{n+} have not been made since the three compounds containing the cation, TeSbF_6 , TeSO_3F and $\text{Te}_2\text{S}_3\text{O}_{10}$ were only obtained previously in an amorphous powdered form. The solid compounds and their solutions are diamagnetic, suggesting that in Te_n^{n+} , n is an even number. Cryoscopic measurements (30) on Te_n^{n+} in HSO_3F showed that the cation is not Te_2^{2+} , but could not distinguish with certainty between Te_4^{4+} , Te_6^{6+} and Te_8^{8+} . Possible structures I, II, and III (Fig.6) for these cations have been postulated by Gillespie (30).

Only one peak was reported in the Raman spectra of Te_n^{n+} compounds and solutions (30). This does not give any

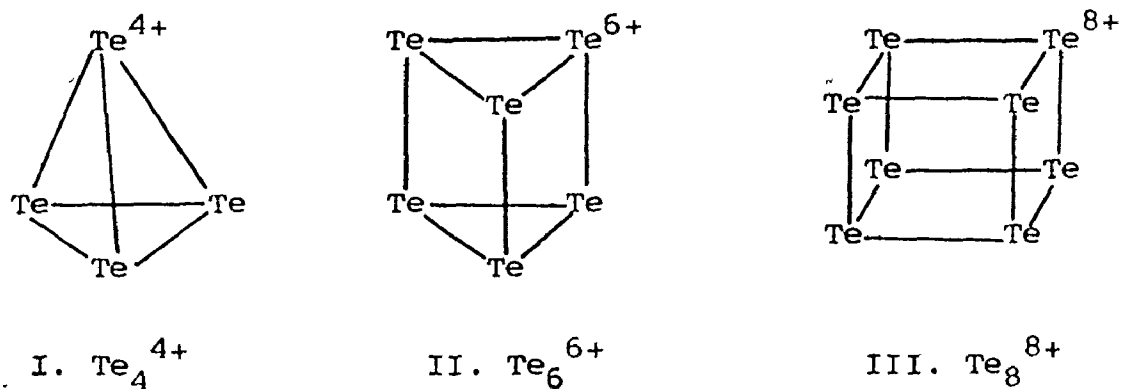


Fig. 6: Possible structures of Te_n^{n+}

evidence concerning the structure since all the structures suggested would have more than one Raman active vibration.

There was no evidence on the structure of Te_6^{2+} .

The Raman spectrum could not be obtained since the dark gray compound absorbed most of the incident light. No suitable solvent was found for the compound so that no crystals suitable for a x-ray crystallographic study could be obtained. Plausible structures IV, V (Fig.7) for Te_6^{2+} have been proposed (28).

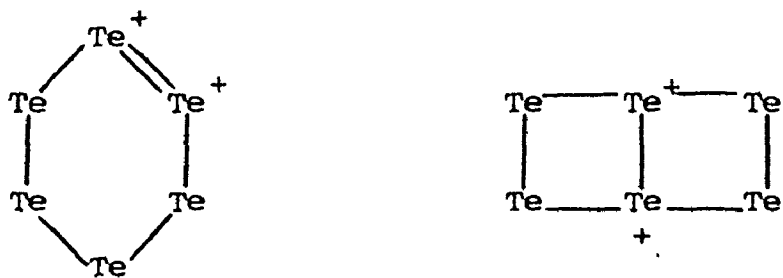


Fig. 7: Possible Structures of Te_6^{2+}

The structure IV also has other related resonance structure which are similar to that proposed for the isoelectronic S_4N_2 molecule. The structure V is a bicyclic structure which is reminiscent of bicyclo (2,2,0) hexane.

This chapter reports a further study of the polyatomic cations of tellurium by Raman spectroscopy. The preparation of new compounds containing the Te_n^{n+} and Te_6^{2+} ions was also attempted. Considerable efforts were also made to obtain the compounds in crystalline form suitable for the investigation of the structures by x-ray crystallography.

(2) Raman Spectra of Te_4^{2+}

Te_4^{2+} is square planar and has D_{4h} symmetry. Five fundamentals are predicted $A_{1g} + B_{1g} + B_{2g} + B_{2u} + E_u$. The mutual exclusion rule applies: A_{1g} , B_{1g} and B_{2g} are Raman active and E_u is infrared active while B_{2u} is both infrared and Raman inactive. Therefore 3 Raman peaks are expected in the Te_4^{2+} spectrum.

Only 2 Raman bands have been previously reported (20) for Te_4^{2+} in solid compounds and acid solution. The very intense 219 cm^{-1} peak is assigned to the A_{1g} mode and the weak 139 cm^{-1} to the B_{2g} mode. The missing B_{1g} mode was considered to be overshadowed by the strong 219 cm^{-1} band. In another report (57), resonance Raman spectra of Te_4^{2+} in concentrated sulphuric acid using 5145Å exciting radiation showed two fundamentals at 219 and 113 cm^{-1} , which were assigned to the

A_{1g} and B_{2g} respectively. The previously reported 139 cm^{-1} frequency was not observed.

In this work the Raman of Te_4^{2+} was reinvestigated. Spectra of different samples were recorded and the results are summarized in Table 3.

A typical spectrum of Te_4^{2+} (Fig.8) of tellurium in 95% H_2SO_4 shows 3 peaks, the frequencies of which are identical to those previously reported.

The vibrational assignments are shown in Table 4 where the isostructural Se_4^{2+} and S_4^{2+} assignments are also listed for comparison.

The very weak 139 cm^{-1} band is assigned to the Raman inactive mode E_u rather than the Raman active mode B_{1g} . The E_u mode of Se_4^{2+} and S_4^{2+} were also observed in the Raman spectra. This inactive mode of the centrosymmetric M_4^{2+} ions could become weakly allowed in the Raman if the symmetry of the cation is lowered by the site symmetry in the solid state. The missing B_{1g} mode was only observed in one spectrum in which there was a weak shoulder on ν_1 , at 210 cm^{-1} . However this was not reproducible in other samples and it appears that the band corresponding to ν_2 is very weak and is overshadowed by the intense 219 cm^{-1} band.

(3) Preparation of TeAsF_6 by Oxidation of Te with AsF_5 and the Raman Spectrum of Te_n^{n+}

The yellow compound TeAsF_6 is obtained by treating tellurium with excess AsF_5 in SO_2 . In a typical experiment

Table 3: Vibrational Frequencies of Te_4^{2+}

<u>Sample</u>	<u>Vibrational frequencies, cm^{-1}</u>		
Te in 95% H_2SO_4	219(s)	137(vw)	115(m)
$\text{Te}_4(\text{AsF}_6)_2$	219(s)	139(w)	113(m)
Te_4^{2+} in HSO_3F	219(s)	139(vw)	112(m)
$\text{Te}_4(\text{Sb}_2\text{F}_{11})_2$	219(s)	137(w)	113(m)

* Lines due to the overtones of Te_4^{2+} , the anion and the solvents are omitted for the convenience of comparison.

Table 4: Vibrational Frequencies of the Te_4^{2+} , Se_4^{2+} and S_4^{2+} ions, cm^{-1}

<u>Vibrational Mode</u>	Te_4^{2+}	Se_4^{2+}	S_4^{2+}
$\nu_1(\text{A}_{1g})$	219(100)*	327(100)	584(100)
$\nu_2(\text{B}_{1g})$	(210)**	319(30)	530(10)
$\nu_3(\text{E}_u)$	139(4)	306(1.6)	460(5)
$\nu_4(\text{B}_{2g})$	113(14)	192(7)	330(16)

* The intensity of A_{1g} Raman line is arbitrarily taken as 100. The measurements are from spectra of $\text{Te}_4(\text{AsF}_6)_2$, $\text{Se}_4(\text{SO}_3\text{F})_2$ (57), $\text{S}_4(\text{SO}_3\text{F})_2$ (20) respectively.

** Band shoulder not reproducible.

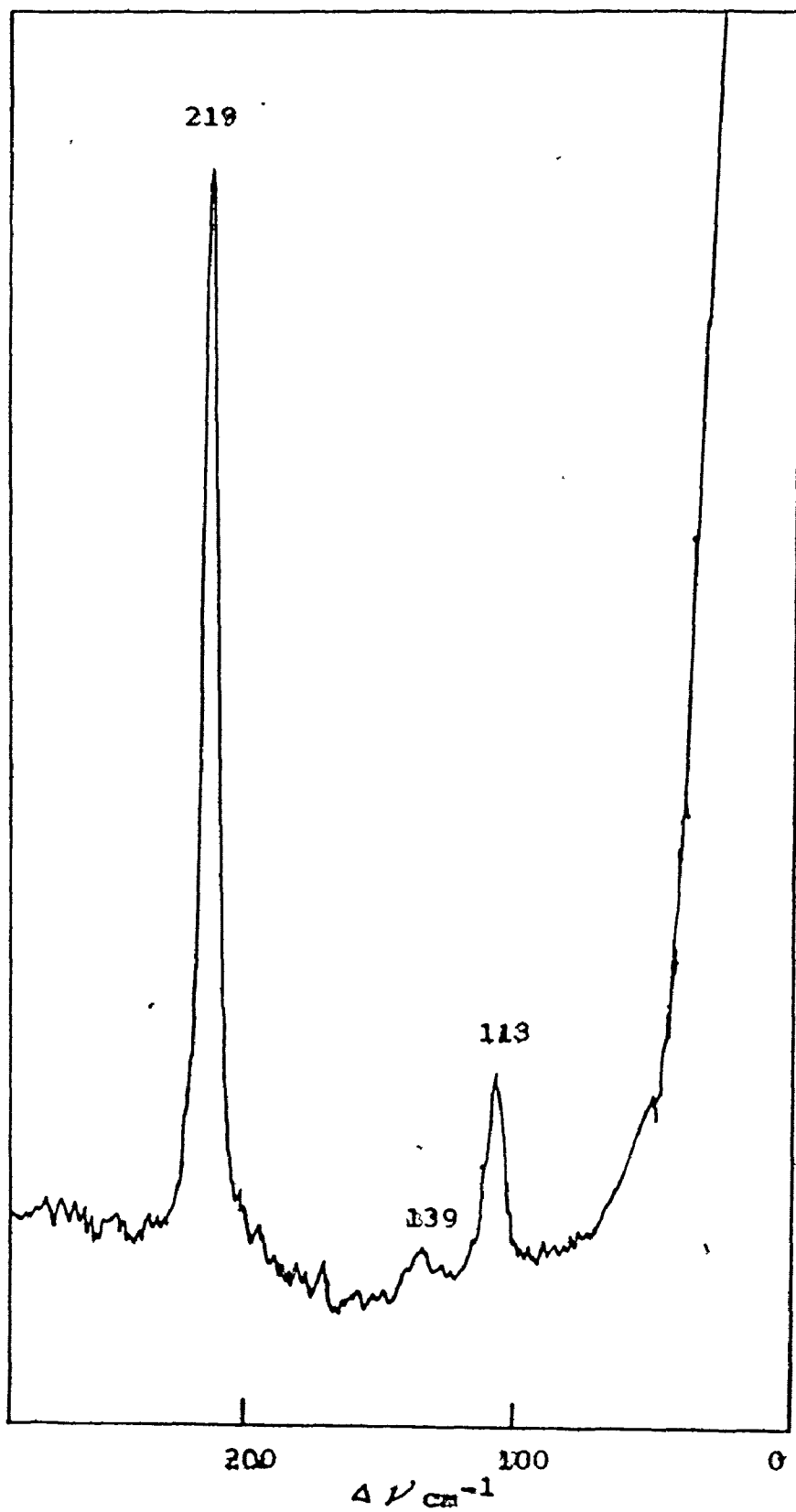


Fig.8. Raman spectrum of a 95% H_2SO_4 solution of Te

AsF₅ (1.698g, 0.015 mole) was condensed onto powdered tellurium (0.638g, 0.015 mole) in liquid SO₂ at -196°C and the mixture was warmed up and stirred at room temperature. A deep red solution containing a red solid, presumably Te₄(AsF₆)₂, was obtained in a few minutes. The reaction was allowed to proceed for a further few hours, when a yellow powder started to deposit from the red solution. More yellow product was formed after 12 hours of stirring. The red solution was filtered and the remaining yellow solid residue was washed repeatedly with SO₂ until no trace of red color appeared in the pale yellow solution in contact with the yellow solid. On removal of SO₂ and volatiles the product was a yellow powder.

The compound was extremely moisture sensitive and was readily decomposed to black tellurium when reacted with water. The infrared spectrum of the solid showed a strong absorption at 700 cm⁻¹, which may be assigned as the ν_3 vibration of the anion AsF₆⁻. (CsAsF₆, ν_3 at 699 cm⁻¹) (54). The color of the compound was very similar to that of TeSbF₆ and the absorption spectrum of the sample in HSO₃F gave the characteristic Te_nⁿ⁺ absorption bands. However this did not confirm the oxidation state of tellurium in the compound since HSO₃F is known to be strong enough to oxidize any tellurium species in a low oxidation state to +1. The compound is not soluble in HF or CH₂Cl₂, and is decomposed in most of the other solvents. It was found to be soluble in SO₂ but very rapidly decomposed to Te₄²⁺, even at low temperature.

A stable yellow solution was finally obtained when the compound was dissolved in SO_2 containing large amount of AsF_5 . The absorption spectrum of the solution showed two weak peaks at 350 and 430 nm, which are identical to those of Te_n^{n+} but it was not possible to observe the more characteristic intense 250 nm peak due to the strong SO_2 absorption at that region.

It was not possible to obtain the Raman spectrum of the yellow solid at room temperature or even at -90°C since it was immediately decomposed to Te_4^{2+} by the incident light. The Raman spectrum of the stable yellow SO_2 solution, containing excess AsF_5 at -80°C showed lines due to Te_4^{2+} , presumably as a consequence of decomposition, and a series of peaks due to the $\text{AsF}_5 \cdot \text{SO}_2$ complex. No peaks which could be attributed to the yellow species were observed.

A Raman line at 199 cm^{-1} has been previously assigned to the Te-Te stretching vibration of the yellow Te_n^{n+} cation from the spectra of a variety of samples in solids and solutions containing the species (20). A number of similar samples such as solid TeSbF_6 , a solution of TeSbF_6 in HSO_3F , a solution of $\text{Te}_2\text{S}_3\text{O}_{10}$ in oleum etc. were studied in the present work. However no peak at 199 cm^{-1} was observed under the same experimental conditions as were used previously. Instead the spectrum of Te_4^{2+} was obtained in every case, presumably due to the decomposition of Te_n^{n+} .

The yellow compound was found to have an increased

solubility at low temperatures. On warming the cooled solution rapidly to 60 or 70°C, many beautiful golden spots or golden plates would develop on the wall of the container. This was found to be an effective way to test for the presence of this species. On warming the cooled solution very slowly or leaving the AsF₅ rich solution at room temperature for one or two days, brown crystals were formed.

The crystals were isolated and studied by Raman spectroscopy. They behaved the same way as the yellow compound, decomposing to Te₄²⁺ rapidly when contacted with the laser radiation. However a small peak positioned at 240 cm⁻¹ was observed from a large size crystal. Another peak at 1130 cm⁻¹ which is the frequency of ν_1 of SO₂ was also seen in the spectrum. Unfortunately the result was not reproducible in other samples.

A new technique for measuring the Raman spectrum was finally developed. The solid sample was sealed in 2-mm-o.d. capillary tubes and mounted onto a special vessel containing liquid nitrogen. Therefore the spectra were actually measured at liquid nitrogen temperature at which the decomposition of the sample was found to be mostly stopped. Both the brown crystals and the yellow compound gave an identical spectrum which is shown on Fig.9. The Raman spectrum of TeSbF₆ was also recorded under similar experimental conditions. Aside from the anion frequencies, positions of the peaks in the spectrum were found to be coincident with those TeAsF₆ compound (Table 5). A small peak due to Te₄²⁺ was still

observed indicating a slight decomposition even at such a low temperature. At higher temperature the intensity of the 219 cm^{-1} peak of Te_4^{2+} went up rapidly while the intensities of the other peaks all decreased.

It is concluded that the yellow compound is TeAsF_6 , another compound containing Te_n^{n+} . The brown crystals, although they appeared to be physically different from the yellow compound, must be considered to be identical and this was also confirmed by the fact they gave identical x-ray powder patterns, (Table 6).

No vibrational assignments have been made for the five peaks ($240, 177, 126, 91, 73 \text{ cm}^{-1}$) of Te_n^{n+} as the structure of the species is still uncertain. However the multi-peak spectrum does rule out some of the suggested structures.

1. The value of n must be greater than 2 since no more than one vibration frequency is expected for a diatomic species. Te_2^{2+} was claimed to be prepared from $\text{Te}-\text{TeCl}_4-\text{KAlCl}_4$ melts (32). Though this might be true, Te_2^{2+} cannot be the tellurium cation present in the compounds TeAsF_6 and TeSbF_6 .

2. It also seems unlikely that n equals 4 as Te_4^{4+} would be expected to have a regular tetrahedron structure (30) and a tetrahedron (T_d symmetry) has only 3 Raman active modes (A_1, T_2 and E) whereas 5 bands were observed for Te_n^{n+} . Three bands have been observed in the Raman spectrum of white phosphorus (58). Very recently assignments have been made for the Ir_4 tetrahedron in $\text{Ir}_4(\text{CO})_{12}$ (59). Bands at $208, 164$ and 131 cm^{-1} were

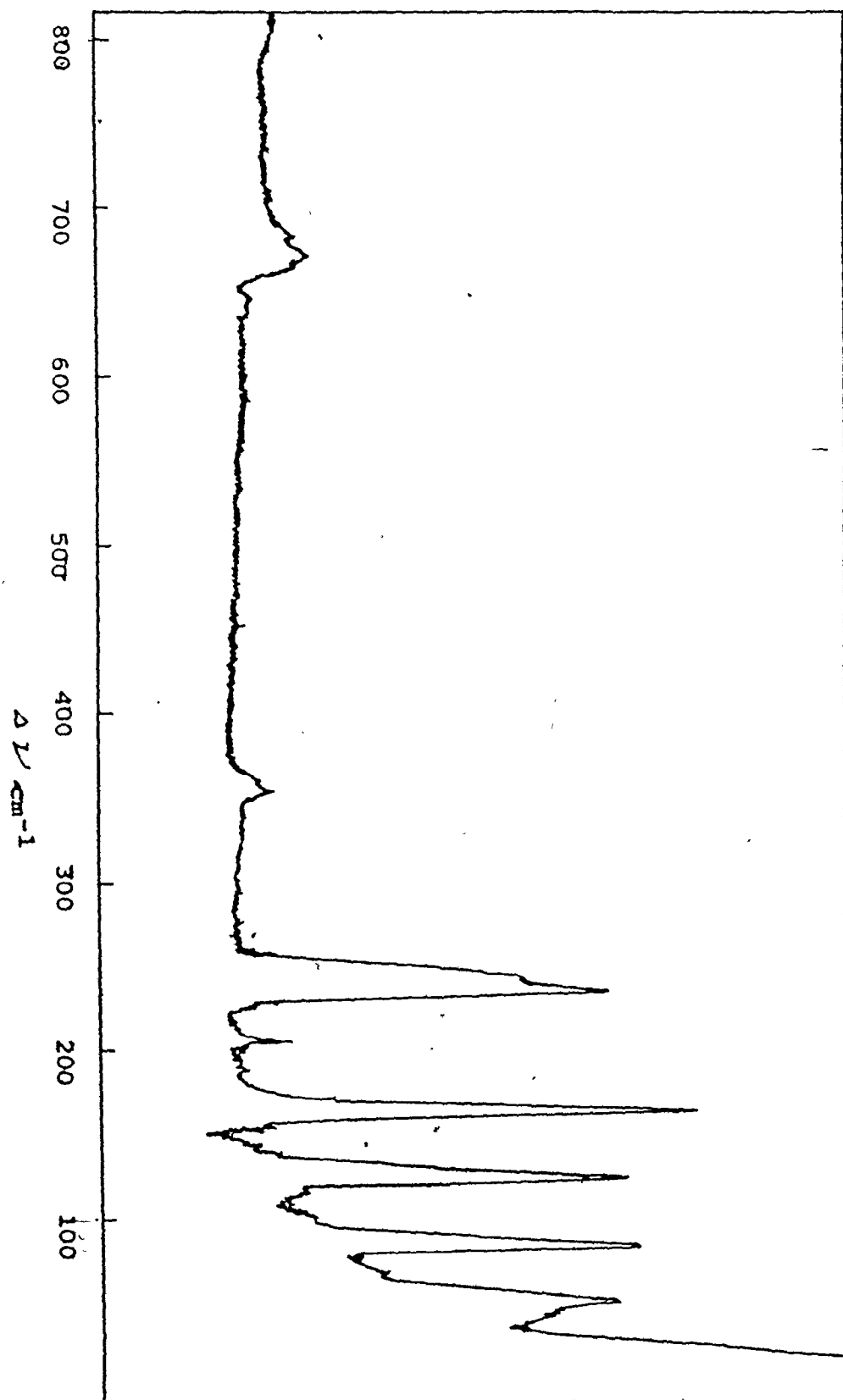


Fig. 9. Raman spectrum of TeAsF_6 at -196°C

Table 5

Vibrational Frequencies of TeAsF_6 and TeSbF_6

Vibrational Frequencies cm^{-1}	TeAsF_6	TeSbF_6
		73 (m)
	91 (s)	91 (m)
	126 (s)	126 (s)
	177 (s)	177 (s)
	219 ν_1 of Te_4^{2+}	219 ν_1 of Te_4^{2+}
	244 (s)	245 (s)
	370 ν_5 of AsF_6^{-*}	
		430 $2\nu_1$ of Te_4^{2+}
	680 ν_3 of AsF_6^-	640 ν_3 of SbF_6^{-**}

* CsAsF_6 372(ν_5), 685(ν_3)⁵⁴; ** KSbF_6 650(ν_3)⁵⁷

Table 6

X-ray powder diffraction data of TeAsF_6

1 ₁ d ₁ = 8.507 (m)	1 ₆ d ₆ = 3.466 (s)
1 ₂ d ₂ = 7.499 (s)	1 ₇ d ₇ = 3.243 (m)
1 ₃ d ₃ = 4.462 (s)	1 ₈ d ₈ = 2.992 (s)
1 ₄ d ₄ = 4.291 (m)	1 ₉ d ₉ = 2.538 (w)
1 ₅ d ₅ = 4.011 (w)	1 ₁₀ d ₁₀ = 2.186 (w)

assigned for the A_1 , T_2 and E modes respectively.

A considerable effort was made to investigate the structure of Te_n^{n+} by x-ray crystallography through the studies of the $TeAsF_6$ brown crystals. They have well-defined crystal faces and angles and appeared to be single crystals in various sizes. However no diffraction spots were ever obtained on the x-ray pictures. The fact that even x-ray powder lines were not observed on the pictures suggests they either are microcrystals or that they undergo a phase transformation from the crystalline state to an amorphous form. The latter explanation is preferred. Although the physical appearance of the crystals is excellent some slight change was found on the surface of the crystals when they were separated from the solvent. As mentioned previously an SO_2 peak was recorded on the Raman spectrum in one of the samples, it is highly probable that the crystals contain rather weakly held SO_2 which readily dissociate from the crystals and cause the phase transformation. The presence of SO_2 molecules in the crystals of a related compound ($Te_2Se_8AsF_6 \cdot SO_2$) has in fact been observed (see Chapter V).

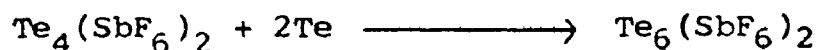
Crystals of $TeSbF_6$ were also successfully isolated by warming the cooled SO_2 solution very slowly. Unfortunately they also gave no x-ray diffraction pattern.

Attempts to seal the crystals in an SO_2 atmosphere for x-ray diffraction studies continue in order to obtain definite structural information on this novel cation.

(4) Raman Spectra of Te_6^{2+} and of Te Metal

$\text{Te}_6(\text{AsF}_6)_2$ was prepared by the reaction of tellurium with a stoichiometric amount of AsF_5 in SO_2 as described previously (28). The previously unobtainable Raman spectrum was successfully recorded at liquid nitrogen temperature (Fig.10). The spectrum is rather poor but has some quite characteristic features. The highest vibration frequencies 157 and 147 cm^{-1} are fairly reasonable for a Te-Te vibration compared to those of the highly charged Te_4^{2+} (219 cm^{-1}) and Te_n^{n+} ions (240 cm^{-1}). At high temperature the compound was decomposed by the incident light to Te metal. The Raman spectrum of Te metal at -196°C was obtained for reference (Fig. 11).

In order to confirm the vibration frequencies of Te_6^{2+} , $\text{Te}_6(\text{SbF}_6)_2$ was prepared. The preparation of this compound had been previously attempted by the reaction of Te with SbF_5 in SO_2 but the product could not be separated from SbF_3 , the other reaction product. A new synthetic route was therefore used. A stoichiometric amount of Te powder was mixed with $\text{Te}_4(\text{SbF}_6)_2$ in SO_2 .



A gray compound was obtained after stirring the reaction mixture for 12 hours. The product was separated and the Raman spectrum was recorded. The spectrum showed essentially the same peaks as that of $\text{Te}_6(\text{AsF}_6)_2$ except that the 157 and 148 cm^{-1} peaks were overlapped with each other. If excess

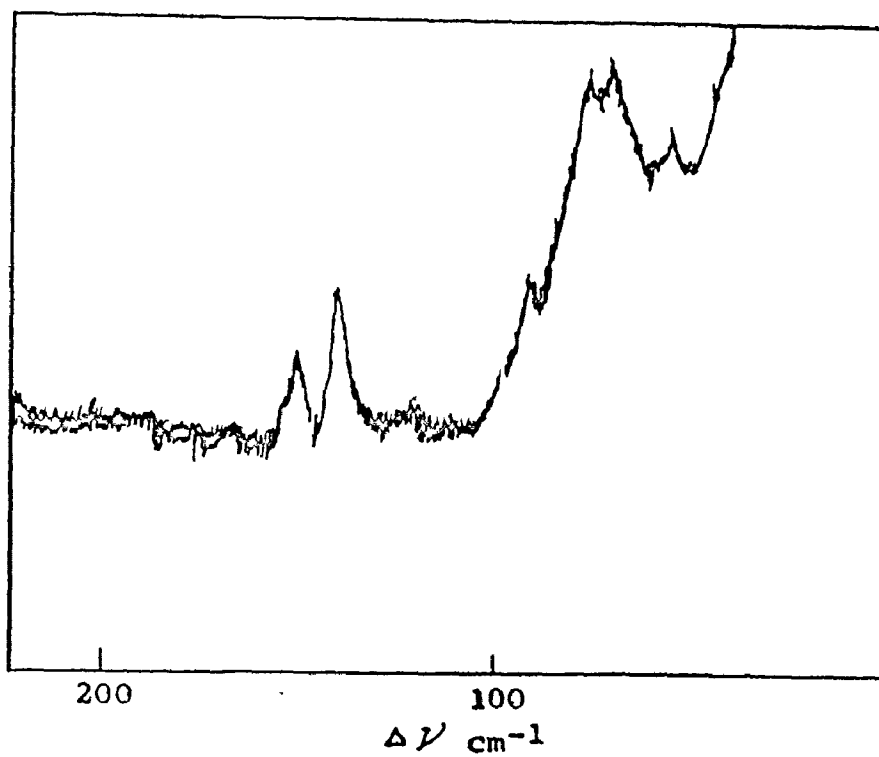


Fig. 10. Raman spectrum of $\text{Te}_6(\text{AsF}_6)_2$ at -196°C

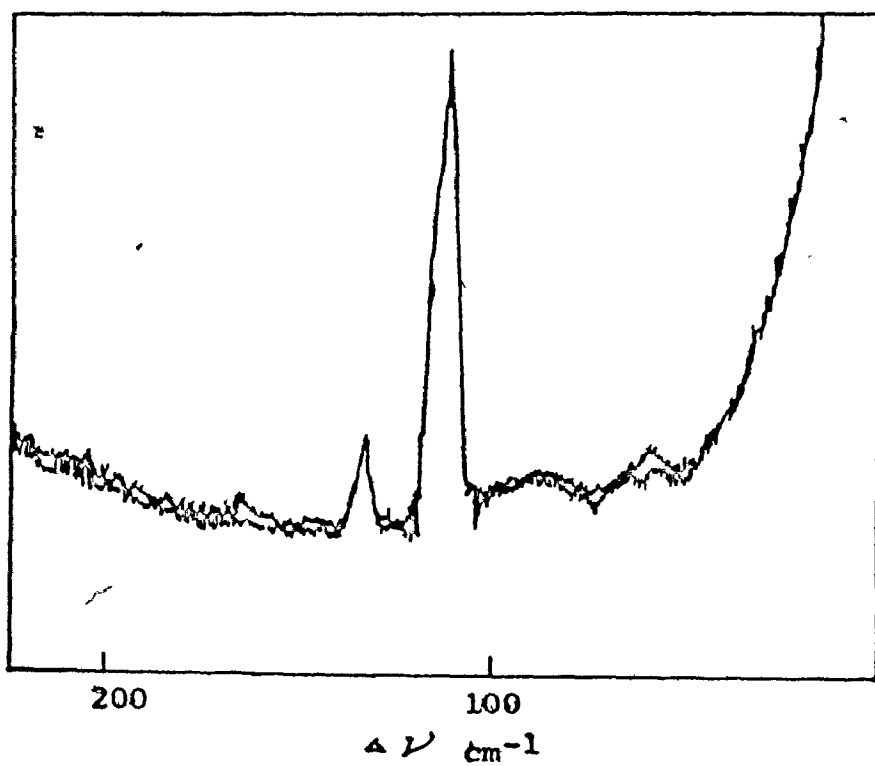


Fig. 11. Raman spectrum of Te metal at -196°C

Table 7: Vibration Frequencies of Te_6^{2+} and Te *

Compound	Te metal	$\text{Te}_6(\text{AsF}_6)_2$	$\text{Te}_6(\text{SbF}_6)_2$	Mixture of $\text{Te}_6(\text{SbF}_6)_2$ and Te	$\text{Te}_6(\text{AsF}_6)_2$ decom- position
Vibrational frequencies cm^{-1}		69	73	73	
		78			
		84	84	84	
		96	96	96	
	119			120(Te)	120(Te)
	141			140(Te)	141(Te)
	144	148	148		
	157	157(Sh)	157		

* Anion frequencies were not observed due to the high noise levels on all the spectra.

tellurium was used in the reaction the product mixture also showed peaks due to unreacted tellurium. The Raman results are summarized in Table 7.

(5) Vibration Frequencies of Tellurium Cations

Spiro (60) recently reviewed the studies on metal-metal bonds by vibrational spectroscopy and concluded that Raman spectroscopy should be the most helpful technique for the subject in the future. Polyatomic cations of tellurium certainly would serve a good example of this prediction.

No detailed assignment can be made of the vibrational frequencies of the tellurium cations due to lack of knowledge of their structures. The charge effect on these species, however, is noticeable (Table 8). The frequencies of iodine cations (61) are also given for comparison.

Table 8

Strongest Vibration Frequencies of Tellurium,
Iodine and Their Cation Species (61) cm^{-1}

Te metal	120	I_2	215
Te_6^{2+}	148	I_3^+	220
Te_4^{2+}	219	I_2^+	238
Te_n^{n+}	240		

CHAPTER V

Mixed Cations of Selenium and Tellurium

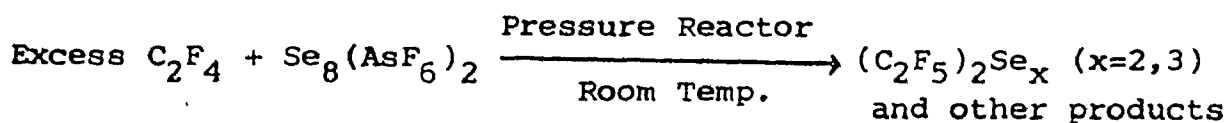
(1) Introduction

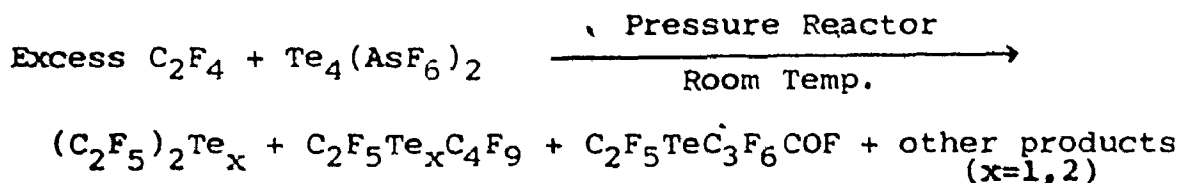
Polyatomic cations containing more than one element may be briefly called "mixed cations". A number of mixed triatomic cations are known for the elements of group VII in addition to the homopolyatomic halogen cations (61). These interhalogen cations were not prepared by oxidizing the elements but by the reaction of halides such as AsF_5 , SbF_5 or SbCl_5 with the interhalogens. For example, ICl_2^+ has been synthesized by the reaction (62).



In group VI mixed cations had not previously been prepared, and a similar method to that used for the interhalogen cations was not feasible.

It was proposed to prepare mixed cations of group VI by appropriate reactions of the known homopolyatomic cations of the group. The reactions of these cations, which are no doubt very interesting, had been almost completely uninvestigated. The only reaction that has been studied is that of tetrafluoroethylene with various polycations of group VI (63,64). Some of the typical reactions are





It appears that the products are complicated and it is believed radicals of C_2F_4 are involved in the reaction mechanism.

This chapter reports other types of reactions of polycations of tellurium and selenium with the principal aims of synthesizing and investigating new mixed cations of selenium and tellurium. Sulphur dioxide, a rather unreactive and very weakly basic substance, was chosen as solvent for these reactions.

(2) Preparation of $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$ by Oxidation of Te with $\text{Se}_8(\text{AsF}_6)_2$

In a typical experiment anhydrous SO_2 (40 ml) was distilled at -78°C onto a mixture of powdered Te (0.25g, 0.002 mole) and $\text{Se}_8(\text{AsF}_6)_2$ (1.009g, 0.001 mole) which was prepared from the reaction of Se and AsF_5 as described previously (21). The mixture was allowed to warm up to room temperature and stirred. The dark green color of the Se_8^{2+} species was found to diminish rapidly as the reaction proceeded. After stirring the mixture for 12 hours a light brown solution together with a dark brown solid was obtained. The solution was filtered at -20°C and allowed to stand at room temperature. Dark brown crystals were formed after one day. More product could be obtained by extracting the solid part of the original product with SO_2 .

As the solubility of the product in SO_2 is rather limited, a number of extractions were required in order to obtain a good yield of product.

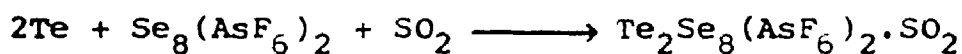
The compound was found to be very moisture-sensitive. It darkened very rapidly on exposure to moist air and instantly decomposed to the elements when added to water or basic organic solvents. With introduction of a trace amount of moisture into the SO_2 solution of the compound, the solution turned dark green and a small amount of metal deposited. The metal was filtered and dissolved in 100% H_2SO_4 . A red solution was obtained and the absorption spectrum of the solution indicated the Te_4^{2+} and Te_n^{n+} species were present. The dark green SO_2 solution had the characteristic color of Se_8^{2+} and this was further confirmed by its absorption spectrum. Thus the cation of the compound was shown to contain selenium and tellurium.

The infrared spectrum of the compound in Nujol mull had a strong absorption at 700 cm^{-1} , the position expected for the ν_3 vibration of AsF_6^- (CsAsF_6 , 699 cm^{-1}) (54). At room temperature, the ^{19}F NMR spectrum of solution obtained on decomposing the material with acetone showed, at 66.1 ppm, a partly collapsed 1:1:1:1 quartet which can clearly be assigned to AsF_6^- , thus confirming the nature of the anion present (65).

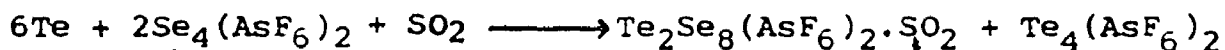
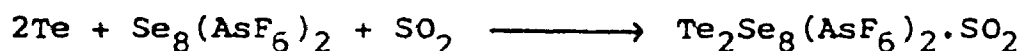
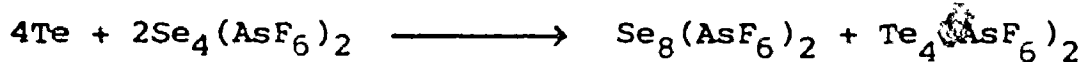
It was not possible to obtain a Raman spectrum, since the dark compound was readily decomposed by the laser light, even at low temperature. No suitable solvent for absorption

spectrum measurements was found as the compound is insoluble or decomposed in organic solvents, and oxidized rapidly to Te_4^{2+} and Se_8^{2+} in 100% H_2SO_4 and HSO_3F . In SO_2 , the complete UV region and part of the visible region was obscured by the strong absorption of the solvent at 280 nm. The visible spectrum also could not be obtained due to the low solubility of the compound.

Elemental analysis gave the following results. Calculated for $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$: Te, 19.20; Se, 47.54; As, 11.28; F, 17.15; SO_2 , 4.83. Found: Te, 19.31; Se, 48.03; As, 12.24; F, 17.14; SO_2 (by difference) 3.28. The analysis is obviously consistent with the formula $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$ which was later confirmed by single crystal x-ray diffraction studies. Therefore the formation of the compound can be represented by the equation



The same compound was also obtained by treating excess tellurium powder with $\text{Se}_4(\text{AsF}_6)_2$ in SO_2 . Te_4^{2+} was formed in the reaction. Very probably the reaction proceeded as follows.



(3) Preparation of $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$ by oxidation of Se with $\text{Te}_4(\text{AsF}_6)_2$

In a typical experiment anhydrous SO_2 (40 ml) was distilled at -78°C onto a mixture of powder Se (0.111g, 0.0014 mole) and $\text{Te}_4(\text{AsF}_6)_2$ (0.178g, 0.0002 mole) which had been prepared by the reaction of Te with AsF_5 (1). On warming to room temperature a red solution presumably due to Te_4^{2+} was obtained. The color of the solution was found to change gradually to dark brown when it was stirred. After 48 hours, a very dark brown solution together with a dark brown solid was obtained. The solution was filtered at -20°C and allowed to stand at room temperature. Dark colored crystals were formed after one day. More product could be collected by further extracting the solid part of the product residue with SO_2 .

The compound was found to be very sensitive to moisture, and was rapidly decomposed by water to give the elements. In 100% H_2SO_4 and HSO_3F it was oxidized to Te_4^{2+} and Se_8^{2+} . The infrared spectrum of the compound in Nujol mull showed a strong absorption at 700 cm^{-1} due to the anion AsF_6^- (54).

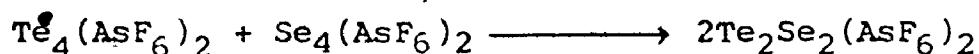
Single crystals were isolated for x-ray crystallographic studies. The crystals are orthohombic with $a=14.84$, $b=10.82$ and $c=13.35\text{\AA}$. These cell dimensions and x-ray diffraction patterns were found to be identical to those of the compound $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$ prepared by a reaction of 1:1 Se-Te "alloy" with AsF_5 in SO_2 (66).

(4) Preparation of $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$ by the Reaction of $\text{Te}_4(\text{AsF}_6)_2$ and $\text{Se}_4(\text{AsF}_6)_2$

A brown compound was obtained when equimolar amounts of $\text{Se}_4(\text{AsF}_6)_2$ and $\text{Te}_4(\text{AsF}_6)_2$ were mixed. SO_2 was distilled at -78°C onto $\text{Se}_4(\text{AsF}_6)_2$ (0.694g, 0.001 mole). The SO_2 was allowed to warm up to room temperature and the yellow $\text{Se}_4(\text{AsF}_6)_2$ solid was extracted to the other side of the reaction vessel which contained the red $\text{Te}_4(\text{AsF}_6)_2$ (0.888g, 0.001 mole). Several extractions were required to transfer all the $\text{Se}_4(\text{AsF}_6)_2$ to the reaction mixture. After a few minutes of stirring the yellow red solution turned dark and a brown solid appeared to deposit. The reaction was allowed to proceed for another 12 hours until a clear brown solution with a brown solid was obtained. The solid was found to be slightly soluble in SO_2 and could be extracted completely to the other side of the vessel. Then the solid was washed a few times with SO_2 before it was sealed in case trace amounts of the more SO_2 soluble Te_4^{2+} or Se_4^{2+} species was still left unreacted in the product.

Consistent with the general property of compounds of the Se-Te polycations, the product quickly blackened in moist air and readily decomposed to the metals when reacted with water. The infrared spectrum of the solid showed a strong band at 700 cm^{-1} , as expected for the anion AsF_6^- . The Raman spectrum of the solid was not obtainable due to its immediate decomposition by the laser radiation. However, the Raman

spectrum of the solution in SO_2 was obtained at room temperature with the 5165\AA Ar-ion laser. The spectrum showed two peaks (Fig.12) at 263 and 217 cm^{-1} . The 263 peak had a shoulder at 250 cm^{-1} . The low intensities of these peaks are very probably due to the limited solubility of the compound in solvent. These frequencies are reasonable for Se-Te stretching vibrations when compared with those of Se_4^{++} ($327, 306\text{ cm}^{-1}$) (57) and Te_4^{++} ($219, 139\text{ cm}^{-1}$) (see chapter IV of this thesis). This was confirmed when a compound $\text{Te}_2\text{Se}_2^{2+}(\text{Sb}_3\text{F}_{14}^-)$ (SbF_6^-) was later prepared in our laboratory (67). X-ray crystallography showed the cation is square planar and the Raman spectrum of SO_2 solution of the compound gave the same frequency pattern but with higher peak intensities. Therefore it is concluded the brown compound in this work can be formulated as $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$ and that it is formed according to the reaction.



(5) Preparation of $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$ by the reaction of $\text{Te}_6(\text{AsF}_6)_2$ and $\text{Se}_4(\text{AsF}_6)_2$

The $\text{Te}_2\text{Se}_2^{2+}$ species could also be prepared from the reaction of $\text{Te}_6(\text{AsF}_6)_2$ and excess $\text{Se}_4(\text{AsF}_6)_2$ in SO_2 . However, the preparation was complicated by the reduction of Se_4^{2+} by the Te_6^{2+} in the first place. (Presumably $2\text{Te}_6^{2+} + 2\text{Se}_4^{2+} \longrightarrow \text{Se}_8^{2+} + 3\text{Te}_4^{2+}$). Therefore the brown product was obtained in a dark green solution. The visible spectrum of solution showed that Se_8^{2+} was present as expected. The brown

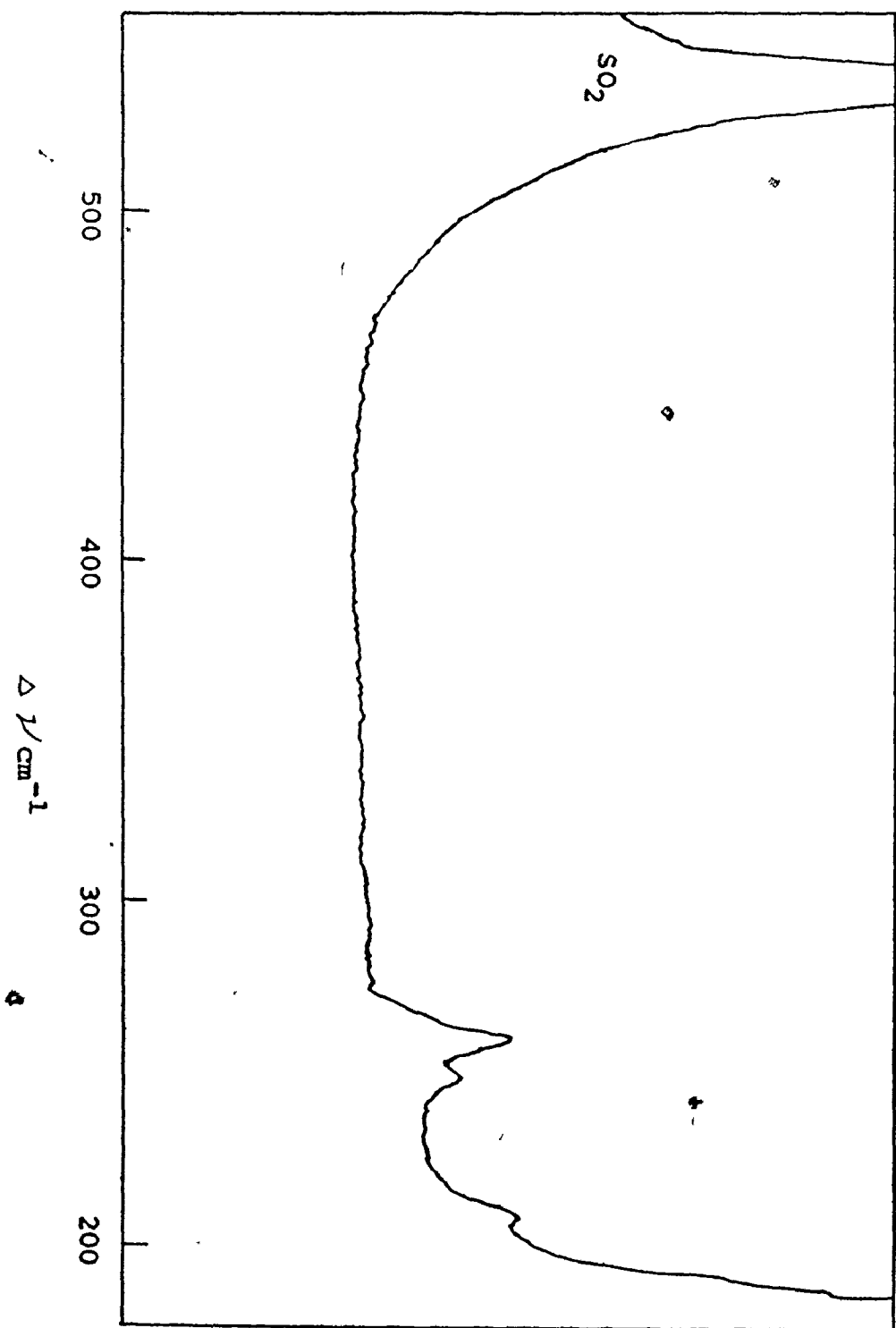
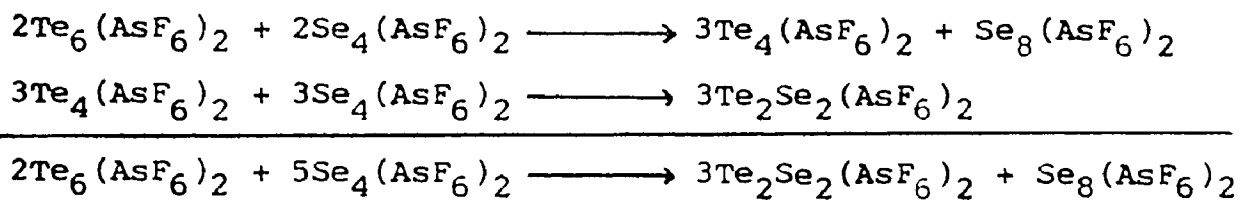


Fig. 12. Raman spectrum of a SO_2 solution of $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$

product was washed several time with SO_2 until a clear brown solution was obtained and then separated from the reaction mixture. It has the same properties as $\text{Te}_2\text{Se}_2(\text{AsF}_6)_2$ and the SO_2 solution gave an identical Raman spectrum. Very likely the following reactions took place in this preparation



(6) Structures

a. $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$ and $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$

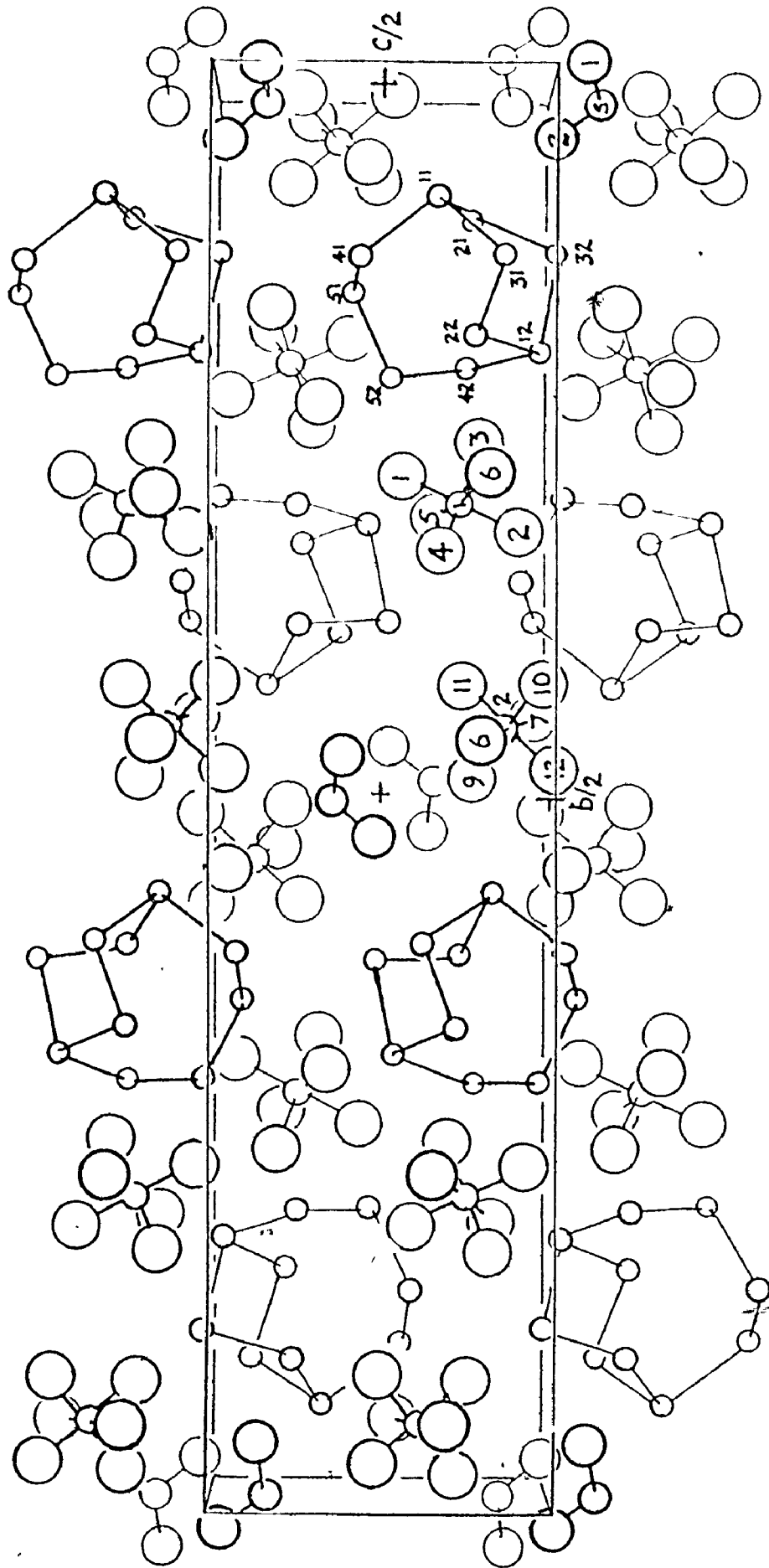
Single crystals of two compounds were obtained.

X-ray diffraction studies showed that both compounds contain interchalcogen cations with similar bicyclic structures but different compositions.

The $\text{Te}_2\text{Se}_8^{2+}$ ion is the best characterized. It consists a bicyclic ring which is very close to possessing a two-fold axis (Fig. 13). It can be thought of as a six membered ring linked across the middle by a chain of four Se atoms with two Te atoms in the three coordinate position.

Alternatively, it can be thought of as two fused 8 membered rings with the endo-exo conformation found in Se_8^{2+} (22) (Fig. 14a, 14b). As the two three-coordinate positions must carry a formal positive charge it is not surprising that they are occupied by the more electropositive Te atoms. The Se-Se bond lengths vary between 2.32 and 2.40 Å with a mean of 2.36 Å,

Fig. 13. Projection of the structure $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$ down $[100]$



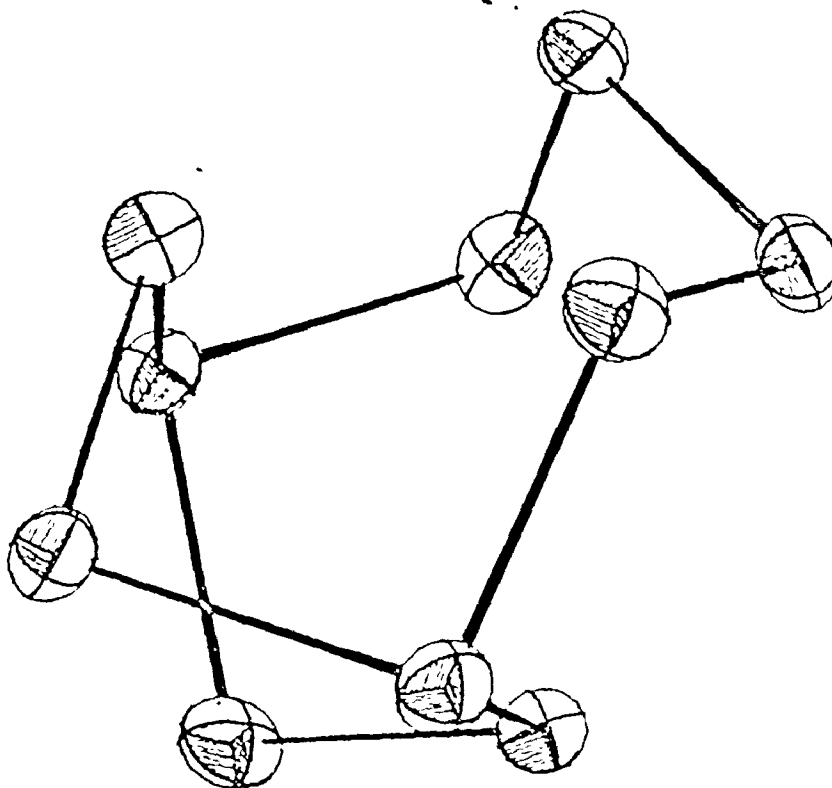


Fig. 14a Structure of $\text{Te}_2\text{Se}_8^{2+}$

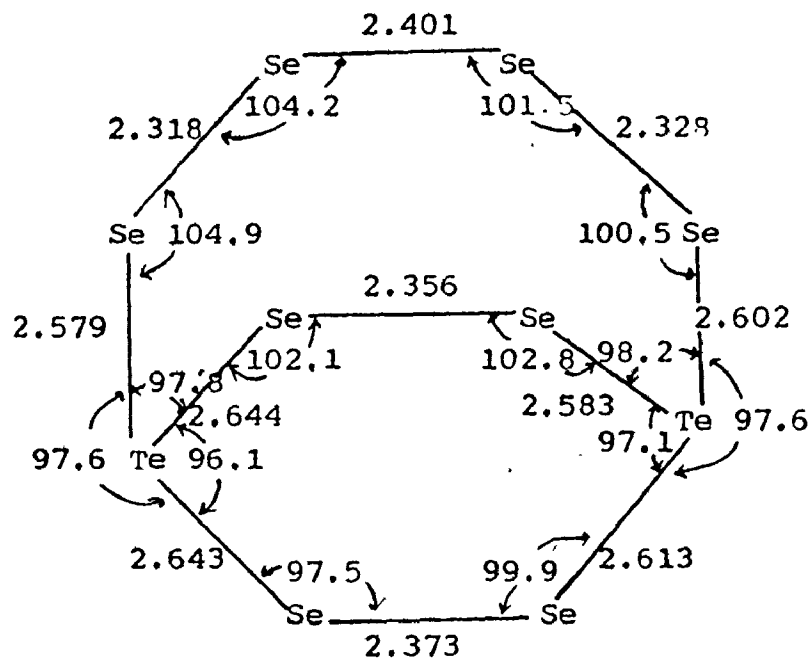


Fig. 14b Bond lengths and bond angles for the $\text{Te}_2\text{Se}_8^{2+}$ cation

close to the Se-Se bond lengths of 2.34Å in the Se_8 molecules and 2.37Å in hexagonal selenium (68). The central bond in the four atom Se chain is longer than the two outer ones an effect that has also been observed in chains of four or more sulphur atoms (69). The Te-Se distances vary from 2.58 to 2.64Å with a mean of 2.61Å close to the mean (2.58Å) of the Se-Se and Te-Te distances found in the elements (68). The angles subtended by Te are smaller (mean=97°) than those subtended by Se (mean=102°). The angular geometry of each atom in two cations is consistent with VSEPR theory (70). The Te atoms have an AX_3E configuration and all the other atoms have an AX_2E_2 configuration.

Each AsF_6^- ion is a regular octahedron with As-F averaging 1.67Å. The SO_2 molecule occupies a hole in the structure between the cations and anions. The dimensions of the SO_2 molecule are insignificantly different from those found in crystalline SO_2 (71). All the interionic and intermolecular distances are greater than 2.85Å and as expected any weak interionic bonding occurs from O or F to S, Se, or Te.

The density of the crystals was measured by the density bottle method using a fluorolube oil which had been fluorinated before use. In a single determination, the experimental value (3.88g cm^{-3}) agrees with the crystallographic density (3.90g cm^{-3}).

The compound $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$ was originally thought to be $\text{Te}_4\text{Se}_6(\text{AsF}_6)_2$ but the temperature factors of one of the

Te atoms suggested that it was partly Se. The Te-Se bond lengths involving this particular Te are also abnormally short (2.54Å) compared to the other Te-Se bond length (2.68Å) in the structure (Fig. 15). The refinement of the structure was greatly improved when Te was one third substituted by Se. This gives the formula of the compound to be $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$, with a structure which contains a random distribution of $\text{Te}_3\text{Se}_7^{2+}$ and $\text{Te}_4\text{Se}_6^{2+}$ cations (Fig. 16) in the proportion of 1:2. These cations are bicyclic clusters with structures similar to that of $\text{Te}_2\text{Se}_8^{2+}$. In a single determination, the density measured by the density bottle method gave a value of 4.16 g cm^{-3} corresponding to the density expected from a crystal of composition $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$ ($D_c=4.16$) rather than $\text{Te}_4\text{Se}_6(\text{AsF}_6)_2$ ($D_c=4.21$) or $\text{Te}_3\text{Se}_7(\text{AsF}_6)_2$ ($D_c=4.06$). However the accuracy of the density determination is not certain.

b. $\text{Te}_2\text{Se}_2^{2+}$

The $\text{Te}_2\text{Se}_2^{2+}$ cation has been found to be square planar by x-ray crystallographic studies on the compound (Fig.17). $\text{Te}_2\text{Se}_2^{2+}(\text{Sb}_3\text{F}_{14}^-)(\text{SbF}_6^-)$ (67). The average Se-Te bond length in the centrosymmetric square $\text{Te}_2\text{Se}_2^{2+}$ ion is 2.476Å, exactly midway between the Te-Te distance (2.664Å) in Te_4^{2+} and Se-Se distance (2.283Å) in Se_4^{2+} .

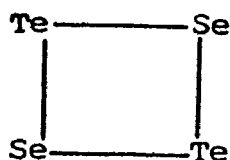


Fig.17: Structure of the $\text{Te}_2\text{Se}_2^{2+}$ cation

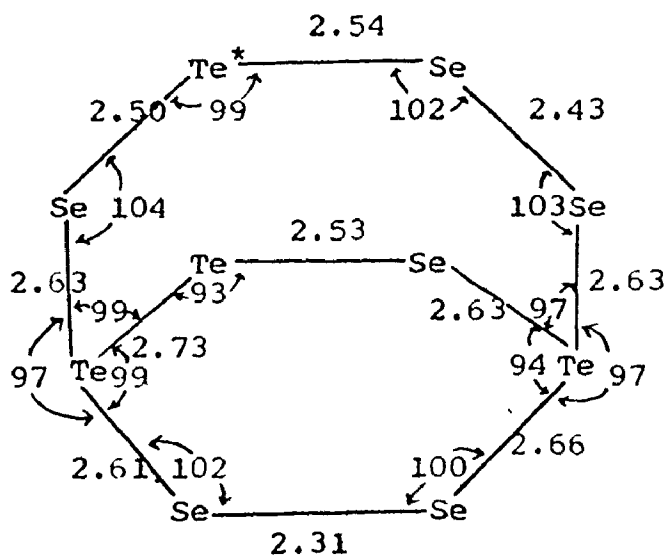


Fig. 15: Bond lengths and bond angles for $\text{Te}_{3.7}\text{Se}_{6.3}^{2+}$

* Te atom is 1/3 substituted by Se in the structure

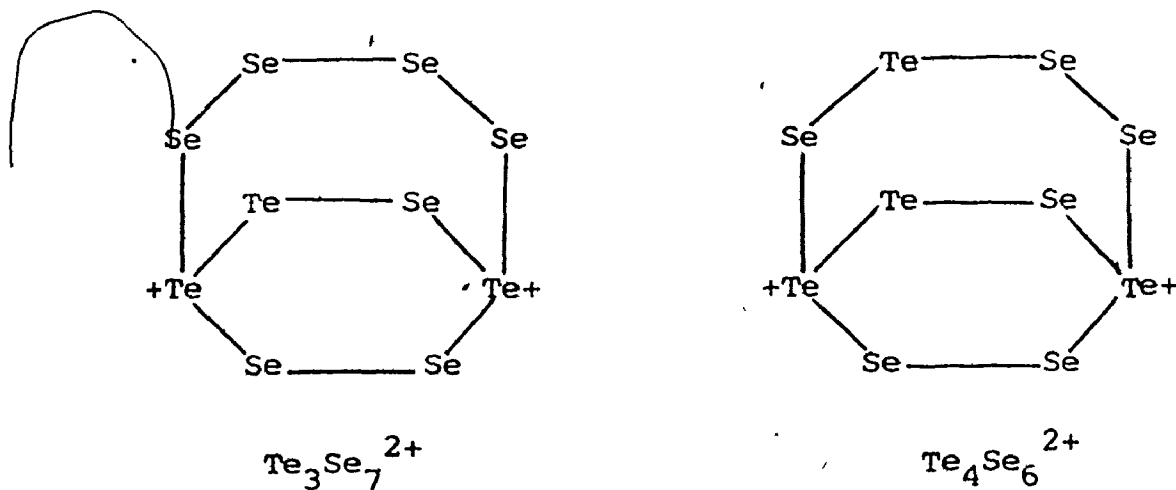


Fig. 16: $\text{Te}_3\text{Se}_7^{2+}$ and $\text{Te}_4\text{Se}_6^{2+}$ Cations in $\text{Te}_{3.7}\text{Se}_{6.3}(\text{AsF}_6)_2$

(7) Reactions of Polyatomic Cations of Selenium and Tellurium

It has been shown that various mixed cations can be prepared through different types of reactions of polycations. Basically these can be divided into two types of reactions:

a. The reaction of a cation of a given element with the elemental form of another element.

b. The reaction between two different polycations of different elements.

Some of the attempts to prepare new cations were not successful. For example the reaction between $\text{Se}_8(\text{AsF}_6)_2$ and $\text{Te}_4(\text{AsF}_6)_2$ was investigated in order to synthesize a new mixed cation species with oxidation state between 1/4 and 1/2, a brown product mixture was obtained but some of reactants were also found unreacted. Separation of products was difficult due to the similarity in solubilities of the species involved. Very recently E. Maharajh in our laboratory has prepared a new mixed cation species $\text{Te}_2\text{Se}_4^{2+}$, from the reaction of Te-Se "alloy" with AsF_5 (67). Possibly this cation was formed in the reaction of Se_8^{2+} with Te_4^{2+} . No reaction was found between Se and $\text{Te}_6(\text{AsF}_6)_2$, possibly due to the very limited solubility of the Te_6^{2+} in SO_2 . The results of all the reactions studied are summarized in Table 9.

Table 9

Reactions of Polycations of Se and Te in SO₂

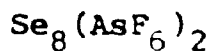
<u>Reaction</u>	<u>Product</u>
Te + Se ₈ (AsF ₆) ₂	Te ₂ Se ₈ (AsF ₆) ₂
6Te + 2Se ₄ (AsF ₆) ₂	Te ₂ Se ₈ (AsF ₆) ₂ + Te ₄ (AsF ₆) ₂
Se + Te ₆ (AsF ₆) ₂	no reaction
Se + Te ₄ (AsF ₆) ₂	Te _{3.7} Se _{6.3} (AsF ₆) ₂
Se ₄ (AsF ₆) ₂ + Te ₆ (AsF ₆) ₂	Te ₂ Se ₂ (AsF ₆) ₂ + Se ₈ (AsF ₆) ₂
Se ₄ (AsF ₆) ₂ + Te ₄ (AsF ₆) ₂	Te ₂ Se ₂ (AsF ₆) ₂
Se ₈ (AsF ₆) ₂ + Te ₄ (AsF ₆) ₂	Complicated
Se ₈ (AsF ₆) ₂ + TeAsF ₆	unidentified reaction products

CHAPTER VI

Mixed Cations of Sulphur and Selenium,
and of Sulphur and Tellurium(1) Introduction

Compounds formulated as $\text{Se}_4\text{SAlCl}_4$ and Se_4SAsF_6 were prepared in one of the previous studies of low oxidation state sulphur and selenium polyatomic cations in this laboratory (53). An excess of sulphur powder was reacted with $\text{Se}_8(\text{AlCl}_4)_2$ in a very small amount of SO_2 at room temperature. A brown compound $\text{Se}_4\text{SAlCl}_4$ was obtained after CS_2 extraction of the unreacted sulphur from the product mixture. In the preparation of Se_4SAsF_6 powdered $\text{Se}_8(\text{AsF}_6)_2$ and an excess of sulphur were heated together at 100°C with stirring for 2 hours. A brown product was obtained from the solid-solid reaction. Unreacted sulphur was extracted with CS_2 at -78°C to avoid decomposition of the Se_4SAsF_6 . No solvent was found for the two compounds. Studies of sulphur and tellurium mixed cations have not previously been reported.

This chapter reports attempts to prepare mixed cations of sulphur and selenium, and of sulphur and tellurium by the study of reactions of polycations with the elements S, Se and Te. Special efforts were made to obtain the products in a suitable crystalline form for the elucidation of the cation structures by x-ray crystallography.

(2) Preparation of Se_4SAsF_6 by Oxidation of Sulphur with

In a typical experiment, 30 ml of anhydrous SO_2 was distilled at -78°C onto a mixture of sulphur (0.064g, 0.002 mole) and an excess of $\text{Se}_8(\text{AsF}_6)_2$ (1.500g, 0.0015 mole). The SO_2 was allowed to warm up and the mixture was stirred for several days at room temperature. A large amount of a brown powder was formed in a dark green solution which presumably contained unreacted Se_8^{2+} . The solution was filtered at 0°C to the other side of the reaction vessel and warmed up slowly to room temperature. After several hours a small amount of brown product started to deposit. The supernatant green species is more soluble in SO_2 so that it could be filtered back to the original side of the vessel to extract more brown product. The product finally was washed with a dilute green SO_2 solution before being sealed. The brown product was found to be decomposed in pure SO_2 fairly rapidly to sulphur and Se_8^{2+} , as shown by the absorption spectrum of the solution. However, the decomposition was stopped when $\text{Se}_8(\text{AsF}_6)_2$ was added to the solution. In fact the compound was quite stable in SO_2 solution of $\text{Se}_8(\text{AsF}_6)_2$ over a period of a few weeks. The compound was fairly soluble in SO_2 , especially at lower temperature, as is in fact shown by its method of preparation. Dark crystals were grown and isolated for x-ray crystallography. The crystals are orthorhombic. Unfortunately, no satisfactory single crystal has been obtained up to the

present time.

The compound decomposed at 200°C when heated in a sealed tube, the same decomposition temperature as previously reported for Se_4SAsF_6 . The x-ray powder diffraction patterns also were identical (Table 10). Therefore it is concluded the compound is Se_4SAsF_6 and can be prepared according to the reaction.



Considering the existence of $\text{Te}_2\text{Se}_8^{2+}$, in the compound $\text{Te}_2\text{Se}_8(\text{AsF}_6)_2 \cdot \text{SO}_2$, the compound might be best formulated as $\text{Se}_8\text{S}_2(\text{AsF}_6)_2$.

Table 10: X-ray powder diffraction data of Se_4SAsF_6

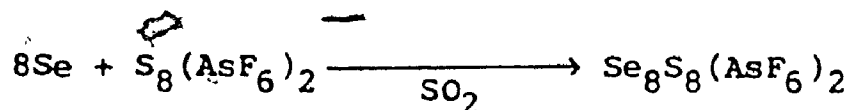
l_1	$d_1 = 7.4577$	(4.5)
l_2	$d_2 = 6.8276$	(7.0)
l_3	$d_3 = 5.1256$	(7.0)
l_4	$d_4 = 4.8305$	(3.7)
l_5	$d_5 = 4.3392$	(6.3)
l_6	$d_6 = 4.1393$	(3.7)
l_7	$d_7 = 3.7541$	(6.3)
l_8	$d_8 = 3.5900$	(10.0)
l_9	$d_9 = 3.2705$	(6.0)
l_{10}	$d_{10} = 3.1535$	(5.2)

(3) Attempted Preparation of S and Se Mixed Cations byOxidation of Se with $S_8(AsF_6)_2$

Several attempts were made to prepare S-Se mixed cations by studying the reactions of Se and $S_8(AsF_6)_2$ in SO_2 .

$S_8(AsF_6)_2$ was prepared as described previously (1).

a. Se with $S_8(AsF_6)_2$ (in mole ratio of 8 to 1). The mole ratio was chosen for the proposed reaction.



The blue S_8^{2+} solution very rapidly gave a dark green solid. The product was extracted with SO_2 leaving an insoluble pale yellow residue. The absorption spectrum of the green solution in SO_2 showed the presence of Se_8^{2+} and IR of the dark green solid showed the characteristic band of AsF_6^- at 700 cm^{-1} (54). The Raman spectrum of the yellow residue showed that it was elemental sulphur. Thus the reaction can be written as follows.



b. Se and excess $S_8(AsF_6)_2$ (in mole ratio of 8:3). In a typical experiment, Se powder (0.632g, 0.008 mole) was found to react readily with $S_8(AsF_6)_2$ (1.914g, 0.003 mole) in SO_2 . After stirring for 6 hours, a bright yellow compound was found to deposit from the dark greenish blue solution. The compound was soluble in SO_2 , but not as soluble as the unreacted S_8^{2+} in the solution. Therefore it was extracted with SO_2 to

the other side of the vessel and the blue solution was filtered back after the yellow compound was completely transferred. On removal of the solvent a bright yellow compound was obtained. A pale yellow residue not soluble in SO_2 was also found in the reaction mixture. No Se metal was left unreacted.

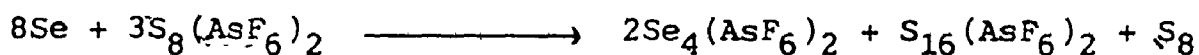
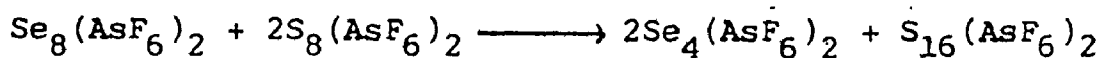
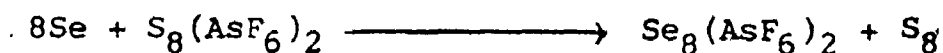
The IR of the yellow compound showed an intense band at 700 cm^{-1} indicating the anion is AsF_6^- . The Raman spectrum of the SO_2 solution and of the yellow solid have a sharp peak at 327 cm^{-1} , the characteristic frequency of the yellow Se_4^{2+} species (57). Red selenium, but no sulphur, was found on decomposing the compound in water. The SO_2 insoluble pale yellow product was separated in another reaction and identified to be elemental sulphur by its Raman spectrum.

c. $\text{Se}_8(\text{AsF}_6)_2$ and $\text{S}_8(\text{AsF}_6)_2$. The rapid formation of Se_4^{++} in the reaction of selenium and $\text{S}_8(\text{AsF}_6)_2$ in SO_2 indicates that $\text{S}_8(\text{AsF}_6)_2$ is a very strong oxidizing agent since Se_4^{2+} can be prepared only in a fairly drastic oxidation reaction (e.g. Se with excess AsF_5 , heat at 60°C for several days). In order to understand the mechanism of the formation of Se_4^{2+} , a reaction of $\text{Se}_8(\text{AsF}_6)_2$ with $\text{S}_8(\text{AsF}_6)_2$ in SO_2 was studied. On mixing the reactants in SO_2 , a yellow solid product was observed in a greenish blue solution. After several hours of stirring, the yellow product was separated as in the previous reaction and was shown to be $\text{Se}_4(\text{AsF}_6)_2$ by absorption and infrared spectroscopy. However, no sulphur was found in the

product mixture. The color of the solution was always greenish blue indicating incomplete reaction. The use of a larger than the stoichiometric amount of $S_8(AsF_6)_2$ did not change the pattern of the reaction. The following equation is suggested for the reaction.



Since the equilibrium is not completely to the right, a certain amount of the reactants are left unreacted in the reaction. As no elemental sulphur was found, it is assumed that S_8^{2+} is reduced to S_{16}^{2+} in the reaction, although no evidence for this was obtained. For the previous reaction in section b, the Se metal very probably was first oxidized by S_8^{2+} to Se_8^{2+} , which then readily reacted with the excess S_8^{2+} forming the Se_4^{2+} species. This can be expressed in the following reactions:

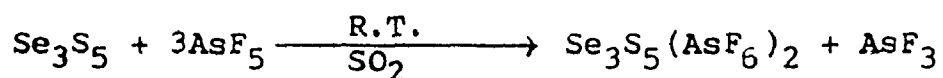


(4) Attempted Preparation of S and Se Mixed Cation by

Oxidation of Se_3S_5 with AsF_5

A different synthetic route was attempted to prepare a S and Se mixed cation. An orange compound formulated as Se_3S_5 was prepared by benzene extraction of the melt product of 1:1 Se-S mixture (67). The suggested reaction for the

compound with AsF_5 was studied in SO_2 .



The orange compound rapidly reacted to give a dark green solution when the reaction mixture was warmed up and stirred. A yellow product resulted after a few hours in a dark bluish green solution. It was found to be $\text{Se}_4(\text{AsF}_6)_2$ by Raman and infrared spectroscopy. Apparently the Se_3S_5 was oxidized to Se_8^{2+} and S_8^{2+} initially with AsF_5 and the two cations reacted with each other. The reaction was repeated at -63°C , but no significant differences were observed.

(5) Preparation of $\text{Te}_3\text{S}_3(\text{AsF}_6)_2$ by the reaction of $\text{Te}_4(\text{AsF}_6)_2$ and $\text{S}_8(\text{AsF}_6)_2$

In a typical experiment, 40 ml of anhydrous SO_2 was distilled onto the mixture of $\text{Te}_4(\text{AsF}_6)_2$ (0.900g, 0.001 mole) and $\text{S}_8(\text{AsF}_6)_2$ (0.325g, 0.0005 mole). After warming up the solution the blue color of the S_8^{2+} species soon diminished to give a orange red solution. The reaction mixture was stirred for several hours and filtered. Dark colored crystals were obtained on standing the filtrate at room temperature for a day. Other products were found to be present in the product mixture but it was impossible to separate them. Te_n^{n+} was obvious one of the products since on warming up the cooled solution rapidly to 60°C , many golden spots due to TeAsF_6 were formed around the reaction vessel, as described in the previous chapter.

The dark colored crystals were studied by x-ray crystallography and found to have identical cell dimensions and x-ray diffraction pictures to the recently identified $\text{Te}_3\text{S}_3(\text{AsF}_6)_2$ which was prepared by the reaction of AsF_5 with Se-Te "alloy" in SO_2 in our laboratory (67). The cation $\text{Te}_3\text{S}_3^{2+}$ has been shown by x-ray diffraction to be a six membered ring containing triangular Te_3 unit (Fig. 18).

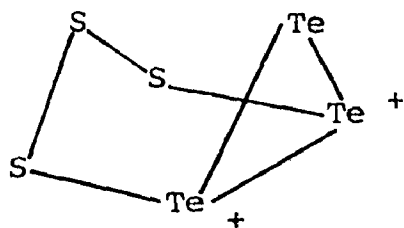
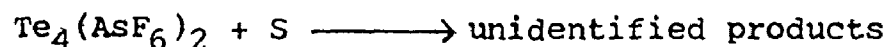
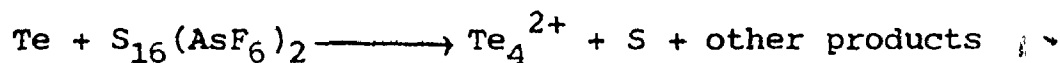
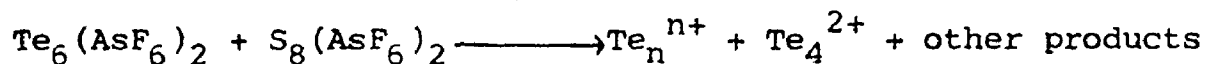
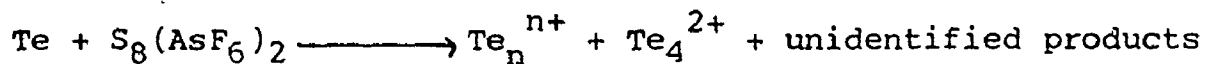


Fig. 18: Structure of $\text{Te}_3\text{S}_3^{2+}$

(6) Other Attempted Preparations of S and Te Mixed Cations

Other reactions of S and Te polyatomic cations were studied but no definite evidence for mixed cations was obtained. The product mixtures were complex and the somewhat similar solubilities of the species in SO_2 made the separation of products impossible. The reactions attempted and the results obtained were as follows.



The Te_4^{2+} was easily detected by means of its Raman

spectrum while the Te_n^{n+} was identified as previously mentioned (Chapter IV). The other products mostly had red-brown colors and were fairly unstable depositing S_8 when left in SO_2 for a long period of time.

(7) Reactions of Polycations of Sulphur and Selenium,
Sulphur and Tellurium

The results of all the attempted reactions of poly-atomic cations of sulphur and selenium, sulphur and tellurium are summarized in Table 11. It appears that $\text{S}_8(\text{AsF}_6)_2$ can be regarded as a very strong oxidizing agent since it can oxidize Te and Se respectively to Te_n^{n+} and Se_4^{2+} , both of which contain the highest oxidation state polycations known for each element. Compounds containing mixed cations of Te and S, and of Se and S are observed to be relatively unstable with respect to disproportionation in SO_2 when compared to the mixed cations of Te and Se.

Table 11
Reactions of Polyatomic Cations of S
and Se, S and Te in SO₂

<u>Reaction</u>	<u>Product</u>
$8\text{Se} + \text{S}_8(\text{AsF}_6)_2$	$\text{Se}_8(\text{AsF}_6)_2 + \text{S}_8$
$8\text{Se} + 3\text{S}_8(\text{AsF}_6)_2$	$\text{Se}_4(\text{AsF}_6)_2 + \text{S}_{16}(\text{AsF}_6)_2 + \text{S}_8$
$\text{Se}_8(\text{AsF}_6)_2 + 2\text{S}_8(\text{AsF}_6)_2$	$\text{Se}_4(\text{AsF}_6)_2 + \text{S}_{16}(\text{AsF}_6)_2$
$\text{Se}_8(\text{AsF}_6)_2 + \text{S}$	Se_4SAsF_6
$\text{Te}_4(\text{AsF}_6)_2 + \text{S}_8(\text{AsF}_6)_2$	$\text{Te}_3\text{Se}_3(\text{AsF}_6)_2 + \text{other products}$
$\text{Te}_6(\text{AsF}_6)_2 + \text{S}_8(\text{AsF}_6)_2$	$\text{Te}_n^{n+} + \text{Te}_4^{2+} + \text{other products}$
$\text{Te} + \text{S}_8(\text{AsF}_6)_2$	$\text{Te}_n^{n+} + \text{Te}_4^{2+} + \text{other products}$

CHAPTER VII

Bismuth Cations

(1) Introduction

The presence of the homopolyatomic cation Bi_9^{5+} was revealed by the determination of the crystal structure (36) of the compound "BiCl" (35). This cation was found together with two types of chlorobismuthate (III) anions in the proportions $(\text{Bi}_9^{5+})_2(\text{BiCl}_5^{2-})_4(\text{Bi}_2\text{Cl}_8^{2-})$ so that the stoichiometry is actually $\text{BiCl}_{1.167}$. Since then Bi^+ , Bi_5^{3+} (38,39) and Bi_8^{2+} (40) have been identified in fused salts. Generally the preparation and characterization of these cations have been carried out in fused salts melted at 200° to 400°C . Bismuth halides are reacted with appropriate amount of elemental Bi along with AlCl_3 which serves as a complexing agent for the halide ions liberated from the BiCl_3 on reduction.

The structure of the Bi_9^{5+} cation is a tricapped trigonal prism (see Chapter I) which ideally has D_{3h} symmetry. The bonding in this ion (72) has been treated using D_{3h} symmetry orbitals obtained from the 6p atomic orbitals in a linear combination. The stability and diamagnetism of the cation was explained by the closed-shell MO configuration of 22 p electrons in 11 bonding MO's.

No direct structural evidence on Bi_8^{2+} and Bi_5^{3+} has been obtained. Trigonal bipyramidal (D_{3h}) and square-

antiprismatic (D_{4d}) structures have been predicted for Bi_5^{3+} and Bi_8^{2+} on the basis of LCAO-MO calculations (41). The bonding in these cations was compared to that in the polyborane cages, specifically $\text{B}_3\text{C}_2\text{H}_5$, $\text{B}_8\text{H}_8^{2-}$.

The presence of Bi^+ has been shown in the structure of $\text{Bi}_{10}\text{Hf}_3\text{Cl}_{18}$ (37) which contains Bi_9^{5+} , Bi^+ and 3HfCl_6^{2-} ions.

This chapter reports attempts to prepare bismuth cations in solution at room temperature. Bismuth was oxidized by various oxidizing agents such as AsF_5 , SbF_5 etc. and the products were identified by Raman and NMR spectroscopy.

(2) Reactions of Bi with AsF_5 in SO_2

a. Preparation of $\text{Bi}_5(\text{AsF}_6)_2 \cdot 2\text{SO}_2$

A yellow compound was prepared by the reaction of Bi and AsF_5 in SO_2 at room temperature. In a typical experiment, AsF_5 (0.170g, 0.001 mole) was condensed at -196°C onto powdered Bi (0.209g, 0.001 mole) in 80 ml of liquid SO_2 in the reaction vessel. The reaction mixture was allowed to warm up to room temperature. A light yellow green color was first found in the solution after a few minutes of stirring. This solution was not stable, however, since the color soon disappeared and a greenish SO_2 insoluble compound started to deposit. While the solution remained colorless and the amount of green product increased the reaction was allowed to proceed for another 48 hours. The green product was gradually converted into a

bright yellow compound. The product was washed several times with solvent. On removal of SO_2 and volatiles, a yellow product was obtained. The green product which appeared earlier in the reaction was also separated in another preparation after 12 hours of reaction.

Consistent with the expected low oxidation states of bismuth, both the green and the yellow compound were very sensitive to moist air and decomposed to black bismuth instantly when added to water. At room temperature the ^{19}F NMR spectrum of the supernatant solution after the compound had been decomposed with acetone showed at $\delta_{\text{CFCl}_3} = 62$ ppm a partially collapsed 1:1:1:1 quartet with $J = 920\text{Hz}$ which can be assigned to AsF_6^- (54). The infrared spectrum of a Nujol mull of both solids had strong bands at 700cm^{-1} as expected for AsF_6^- (54), thus confirming the nature of anion present.

The identification of the cations in the two compounds was more difficult since no suitable solvent was found for them. They were not dissolved by SO_2 or HF ; they oxidized readily to Bi(III) when treated with HSO_3F and were decomposed to black bismuth by most organic solvents.

In a preliminary study in this laboratory (73) an analysis of the green compound had suggested that it should be formulated as $\text{Bi}_2(\text{AsF}_6)_2$. However no other supporting evidence was obtained. During the course of the present work, observation of the green material under a microscope showed that it contained unreacted bismuth and the yellow

compound. The reflectance spectra of the yellow and green compounds were also found to be completely identical. The spectrum of the yellow compound (Fig.19) has peaks at 365, 400, 430 and 700 cm^{-1} . The spectrum is quite similar to the previously reported spectrum of $\text{Bi}_5(\text{AlCl}_4)_3$ (41). Since the stoichiometry of the product was not certain an excess amount of AsF_5 was usually added in the earlier experiments in the preparations. This led to the formation of an additional white product which is soluble in SO_2 and could therefore be easily separated from the yellow product. However it was then found that this white product was slowly converted into an SO_2 insoluble material on standing in solution, sometimes even before all the bismuth was completely reacted. Obviously, this compound could not be separated from the yellow one since both are SO_2 insoluble.

In order to prepare the yellow compound in a pure state it was necessary to prevent the conversion of the SO_2 soluble white compound into the insoluble one. The soluble white compound was successfully prepared by adding excess AsF_5 to the yellow compound in SO_2 . On stirring the yellow compound was gradually dissolved giving a colorless solution. The solution was filtered. On removal of solvent and volatiles a white product was obtained. After careful observation of several reactions it was concluded that the conversion of the soluble compound to the insoluble one was not due to the reaction of AsF_5 but rather to some sort of polymerization

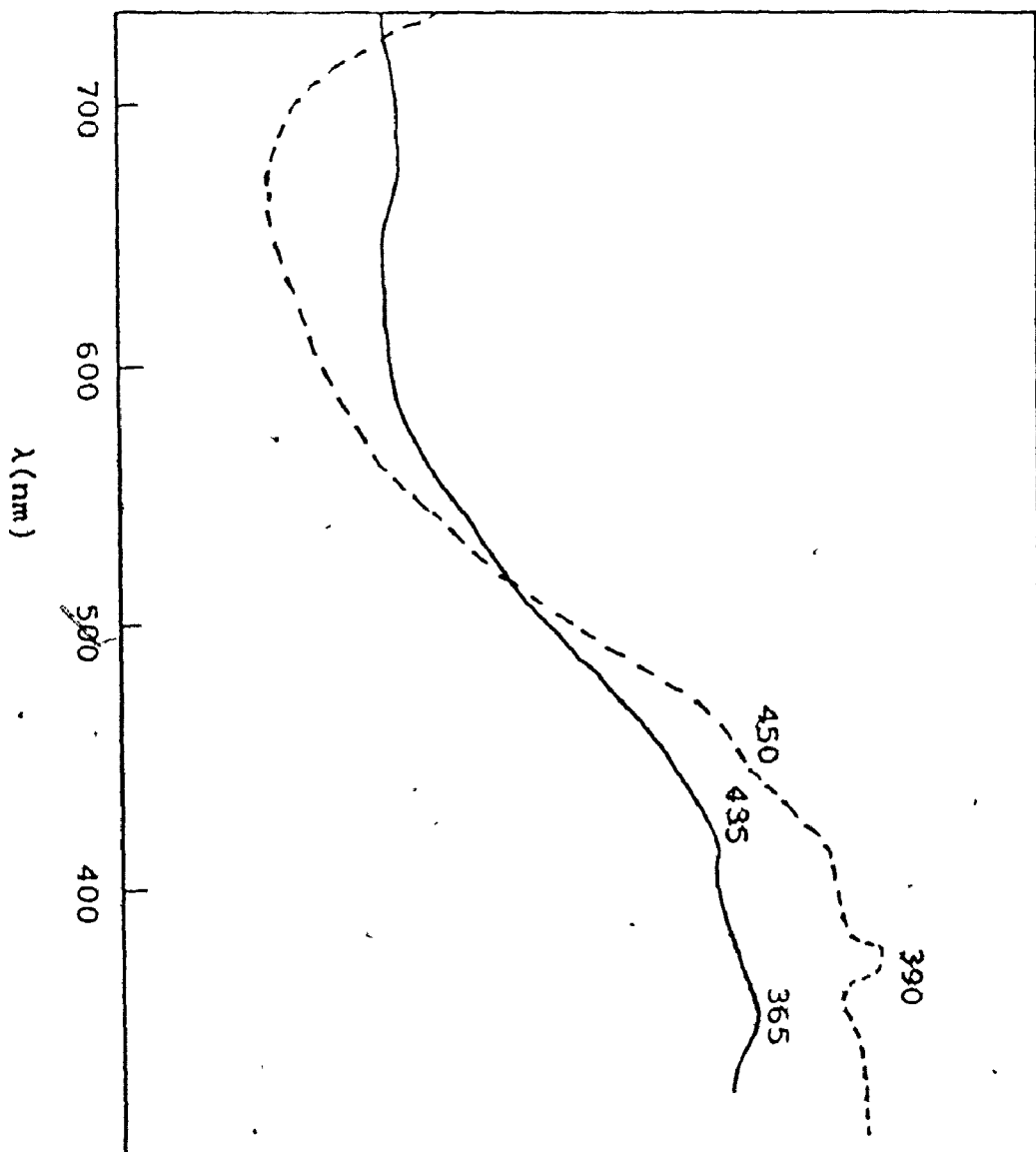
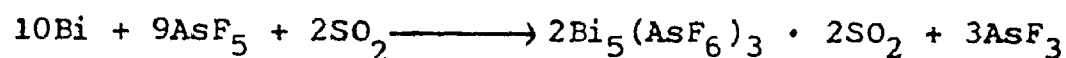


Fig. 19. Reflectance spectra of $\text{Bi}_5(\text{AlCl}_4)_3$ (dashed line) and of the yellow compound obtained from the reaction between Bi and AsF_5

in the solution. The factors leading to this polymerization are not completely clear but the process was certainly accelerated if the concentration of the compound in the SO₂ solution was high. The conversion was also found to be irreversible, i.e. the SO₂ insoluble product could not be transformed to the soluble compound. However, the most important discovery was that the polymerization did not occur if the concentration of the soluble compound in solution was not too high (less than 1 gram in 30 ml of SO₂) and the solution was not left too long at room temperature.

It was therefore possible to prepare the pure yellow compound by the following method. A small amount of reagents (0.02 mole of Bi and 0.02 mole of AsF₅) and a large amount of solvent (100 ml of SO₂) were used in each preparation. The SO₂ soluble white product was extracted from the yellow compound after 2 days of reaction. Careful titration of Bi with AsF₅ in SO₂ indicated that only a small amount of white compound was formed if the molar ratio of Bi/AsF₅ in the reaction was adjusted to be less than 1 to 1. The formation of the white compound could not be entirely avoided since the conversion of the yellow compound to the white compound had already started before all the Bi was reacted to the yellow product. The stoichiometry in this titration is found to be close to the formation of Bi₅(AsF₆)₂ according to the equation.



Elemental analysis gave the following result: Calculated for $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$, Bi, 60.06; As, 12.92; F, 19.62; SO_2 , 7.36. Found, Bi, 60.03, 59.90; As, 12.57, 12.65; F, 19.49, 19.68; SO_2 (by difference) 7.91, 7.77.

Early efforts to obtain the Raman spectrum of the yellow compound were not successful due to the immediate decomposition of the compound by the incident radiation. However the Raman spectrum was finally obtained at liquid nitrogen temperature using the technique as described in Chapter IV. As expected both the "green compound" and the yellow compound $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$ gave the identical spectrum shown in Fig. 20. The spectrum has 7 bands in which the weak 364 and 680 cm^{-1} lines can be assigned to the ν_5 and ν_3 vibration modes of AsF_6^- respectively. CsAsF_6 has bands at 372 and 685 cm^{-1} . The lines at low frequency are very intense with the strongest peak at 141 cm^{-1} . These frequencies are very reasonable for Bi-Bi vibrations when compared to 116 cm^{-1} for the Pb-Pb stretching vibration in Pb_2Me_6 (9) and 259 cm^{-1} for the Sb-Sb stretching vibration in $\text{Sb}_n(\text{SO}_3\text{F})_n$ (10).

No vibrational assignments are made for the peaks due to the Bi_5^{3+} cation as the structure of the species is still uncertain. A trigonal bipyramidal (D_{3h}) structure has been postulated (74) for this cation. Band assignments according to this geometry will be continued.

b. Identification of fluorobismuth complexes.

The white compounds isolated from the reactions of Bi

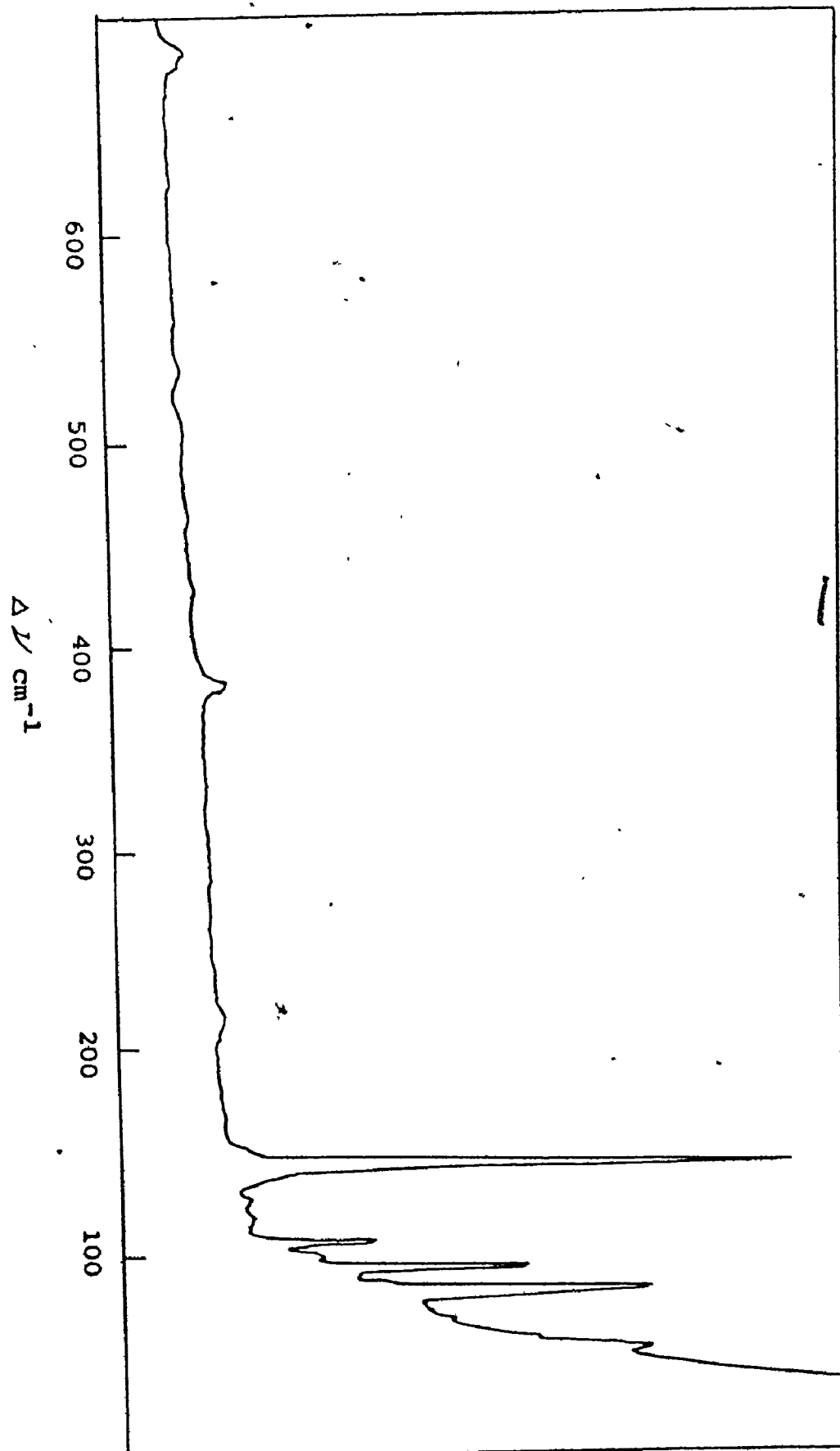
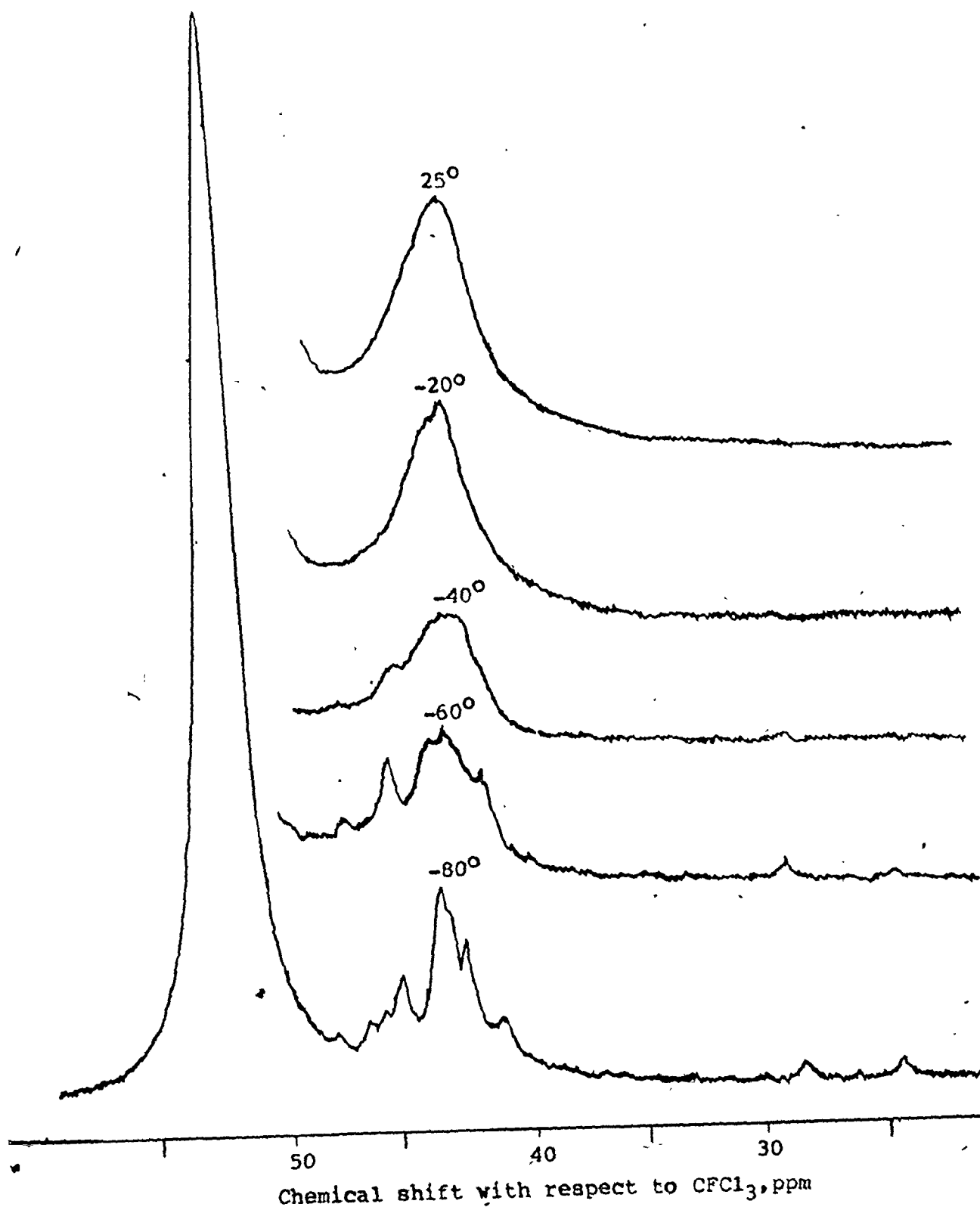


Fig. 20. Raman spectrum of $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$ at -196°C

and excess AsF_5 in SO_2 were presumably compounds of Bi(III) since they did not disproportionate to elemental bismuth when reacted with water. Information on the oxidation state of Bi was obtained when these compounds were prepared by a different type of reaction.

BiF_3 is polymeric (74) and very insoluble in almost all solvents. However, BiF_3 was gradually dissolved in a solution of AsF_5 in SO_2 to give a colorless solution. Equimolar amounts of BiF_3 and AsF_5 were needed to complete the reaction. On removal of solvent, a white product was obtained. Since no other product was found in the residual solution it is reasonable to formulate the compound as the adduct $\text{BiF}_3 \cdot \text{AsF}_5$. This compound behaved in an identical manner to the SO_2 solution compound obtained from Bi and AsF_5 in SO_2 , i.e. (a) it is transformed to a white insoluble compound on standing, (b) it gave an identical ^{19}F NMR spectrum to the SO_2 solution. The NMR spectrum (Fig.21) contains two peaks at room temperature, with chemical shifts of 54 and 46 ppm with respect to CFCl_3 and an area ratio of 3 to 1. The 54 ppm signal is in the region of fluorine on As (V). A solution of Bu_4NAsF_6 in SO_2 gave a signal at 60 ppm. With the addition of Bu_4NAsF_6 to the $\text{BiF}_3 \cdot \text{AsF}_5$ solution the 54 ppm signal was increased in intensity while the 46 ppm line remained unchanged. Therefore it is concluded that the 54 ppm peak is due to AsF_6^- . The shift of frequency from 60 ppm might be due to F exchange with the species responsible for the 46 ppm peak. At lower temperature

 ^{19}F NMR

of a

of

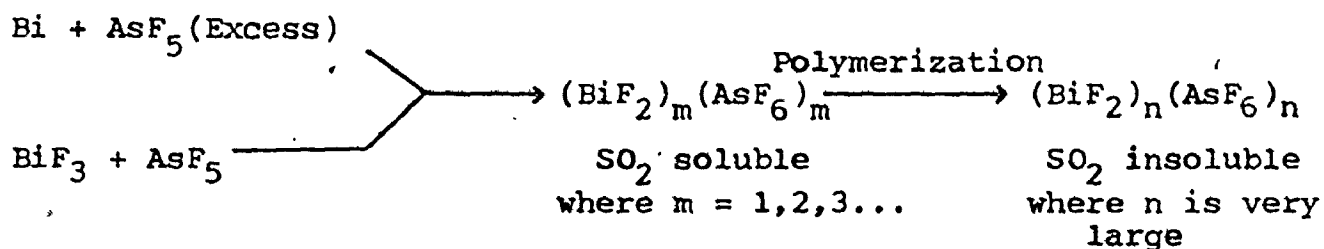
the 46 ppm signal was split into a multiplet. At least seven peaks were observed at this region and at -80°C together with another two peaks at 25 and 29 ppm (Fig.21). Since Bi has a nuclear spin of $9/2$ it is unlikely that these signals are due to Bi-F coupling in the expected cationic species BiF_2^+ as ten equal lines should be observed. Moreover rapid quadrupole relaxation and consequent collapse of the multiplet could be expected for BiF_2^+ . The total area of the small peaks at 25, 29 and complex signals around 46 ppm is $1/3$ of the area of the AsF_6^- signal at 54 ppm, suggesting that these peaks are due to the cation BiF_2^+ . This compound was shown to polymerize to a SO_2 insoluble compound on studying the concentrated SO_2 solution. Very probably there are several polymeric cationic species such as $\text{Bi}_2\text{F}_4^{++}$, $\text{Bi}_3\text{F}_6^{+++}$, etc. other than the expected BiF_2^+ present in the SO_2 solution and it is possible the F-F coupling in these species gives the complex spectrum at about 46 ppm. SO_2ClF was used as a solvent in an attempt to obtain the spectrum at a lower temperature (-115°C) but it was found there was interaction between the compound and the solvent.

The gelatin like appearance of the SO_2 insoluble white compound suggests that it is a polymer. The fact that no other product was detected after the polymerization occurred suggests this might be another form of $(\text{BiF}_2)_n \cdot (\text{AsF}_6)_n$ in which n is a very large number. The Raman spectrum of the solid is shown in Fig. 22 and the assignment of the vibrational frequencies

is summarized in Table 12. The spectrum of the polymeric BiF_3 (Fig.22) was also recorded for comparison. It can be shown that the general pattern due to the cation of $(\text{BiF}_2)_n(\text{AsF}_6)_n$ resembles that of BiF_3 . The peaks at 701, 688, 635, 520, 376 cm^{-1} are assigned to AsF_6^- . The rest of the bands are considered to be due to the polymeric cation.

A compound formulated as $\text{BiF}_3 \cdot \text{AsF}_5$ which was prepared from BiF_3 and excess AsF_5 in SO_2 has been reported previously (75). The assignment of the Raman vibrational frequency of this compound is also shown in Table 12 for comparison. The cation was suggested to be the polymeric $(\text{BiF}_2)_n^{n+}$. However except for a very broad band at 511 cm^{-1} no vibrational frequencies were assigned to this species. The lower frequencies are assigned to be ν_4, ν_5 of AsF_6^- and lattice vibration.

Thus the formation of $(\text{BiF}_2)_n(\text{AsF}_6)_n$ can be summarized by the following equations.



(3) Reactions of Bi with SbF_5 and PF_5 in SO_2

Attempts to prepare bismuth cations were made through the reactions of Bi with SbF_5 or PF_5 in SO_2 . Colored products were obtained in both cases but none of them could be isolated due to their insolubility in the solvent.

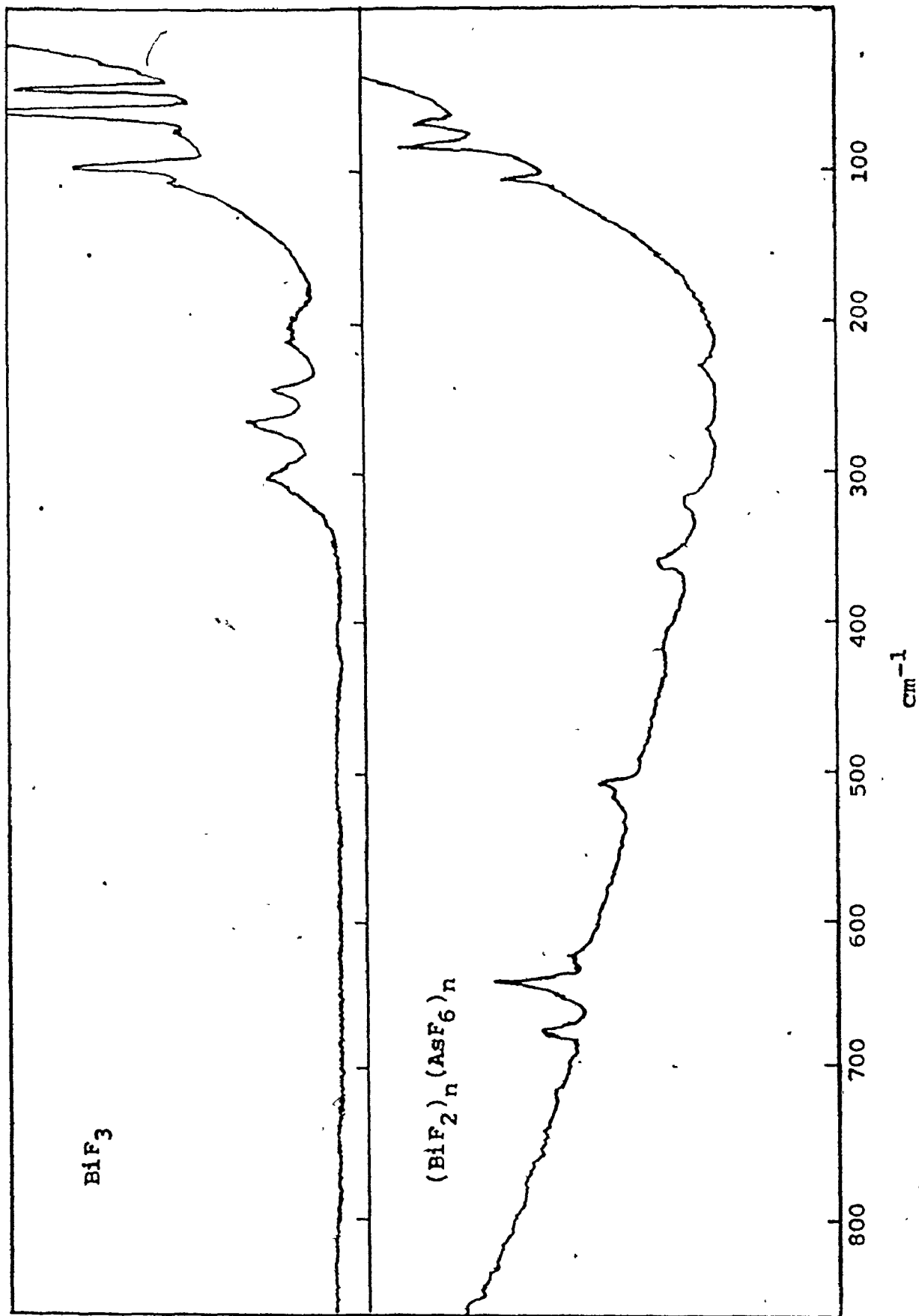


Fig. 22. Raman spectra of $(\text{BiF}_2)_n(\text{AsF}_6)_n$ and of BiF_3 at 25°C .

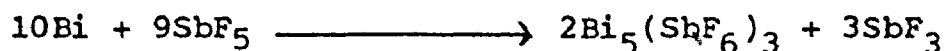
Table 12: Vibration Frequencies of $(\text{BiF}_2)_n(\text{AsF}_6)_n$ and Related Compounds in cm^{-1}

<u>$(\text{BiF}_2)_n(\text{AsF}_6)_n$</u>	<u>BiF_3</u>	<u>CsAsF_6</u>	<u>$\text{BiF}_3 \cdot \text{AsF}_5 (75)$</u>	<u>Assignment</u>
701				$\nu_3 \text{AsF}_6^-$
688		685	689 vs	
635			570 m	
520			546 m	
			511 m vbr	$\nu_2 \text{AsF}_6^-$ $\nu(F-\text{Bi}-F)$
376			391 sh 371 m 319 mwbr	ν_4, ν_5 AsF_6^-
333				
	307			
279	268			
237	241 210		241* 226	$\nu(F-\text{Bi}-F)$
113	111			
93	81			
75	67			

* frequencies assigned for lattice vibration

a. Reaction with SbF₅

The reaction proceeded generally in the same way as the reaction of Bi and AsF₅. However the yellow product was unable to be separated from the reduction product SbF₃ which is also SO₂ insoluble. Attempted separation by vacuum sublimation at +120°C led to the decomposition of yellow product to black bismuth. It was possible to record the Raman spectrum of the product mixture at -196°C. The spectrum was not so well resolved but clearly showed the peaks due to Bi₅³⁺. The vibrational frequencies are shown in Table 13. Thus the reaction of Bi and SbF₅ in SO₂ can be expressed by the equation.



b. Reaction with PF₅

A green product which later converted into a brown product was obtained by the reaction of Bi and excess PF₅ in SO₂ at room temperature. The products were not pure and unreacted Bi was present even after several weeks of reaction. This project was discontinued due to the difficulty of product separation.

(4) Reactions of Bi with HSO₃F, HSO₃Cl

Bismuth was immediately oxidized to white products presumably of Bi(III) in HSO₃F and HSO₃Cl. With small amounts of acid in SO₂, the results were generally the same except that an extra brown product could be obtained in the HSO₃Cl

reaction. However no evidence of formation of polyatomic cations of bismuth was obtained in any of these products.

Table 13: Vibrational Frequencies of Bi_5^{3+}

Vibrational Frequencies cm^{-1}	$\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$	Green product from reaction of Bi with SbF_5 in SO_2
	49 (m)	
	72 (s)	80 (w)
	88 (s)	90 (w)
	103 (s)	110 (w)
	141 (s)	141 (m)

CHAPTER VIII

Conclusions

Recently it has been shown that many elements especially those of group VII, VI, V and IIb can be obtained in the form of polyatomic cations in highly acidic or weakly basic media (1). The discovery of previously unsuspected cations of these elements has opened a new field of chemistry. Salts of homopolyatomic cationic clusters now constitute a well-established class of compound.

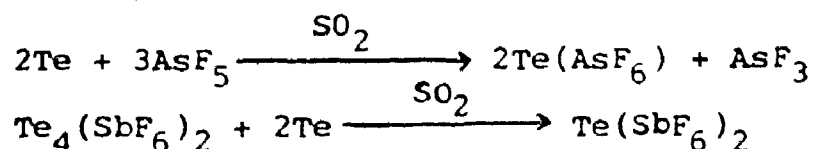
A list of the homopolycations of group VI that have been prepared is given in the following table.

Table 14: Homopolyatomic cations of group VI

oxidation state				
1+	1/2+	1/3+	1/4+	1/8+
	O_2^+			
	S_4^{2+}		S_8^{2+}	S_{16}^{2+}
	Se_4^{2+}		Se_8^{2+}	
Te_n^{n+}	Te_4^{2+}	Te_6^{2+}		

Among these cations, the structures of O_2^+ (76), Se_4^{2+} , Te_4^{2+} , S_8^{2+} and Se_8^{2+} (1) have been determined by single crystal x-ray diffraction. No structural information for the other ions had been obtained prior to the study of this work.

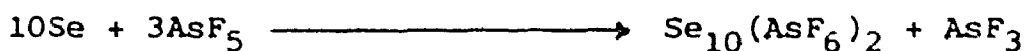
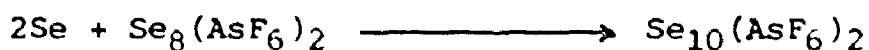
The current work has involved the use of Raman spectroscopy and x-ray crystallography to obtain structural information for Te_n^{n+} , Te_6^{2+} and S_{16}^{2+} . Two new compounds, TeAsF_6 and $\text{Te}_6(\text{SbF}_6)_2$, have been prepared by the reactions



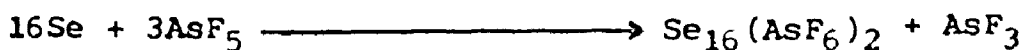
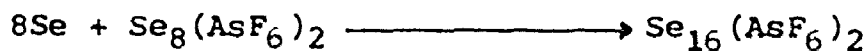
in order to obtain more information on cations. The previously unobtainable Raman spectra of Te_6^{2+} , Te_n^{n+} have been successfully recorded at a very low temperature (-196°C). Although the spectra yield no conclusive information they provide a method to identify Te_6^{2+} and indicate that Te_n^{n+} is not Te_2^{2+} and probably not Te_4^{4+} , leaving the possibility of the species to be either Te_6^{6+} or Te_8^{8+} . The Raman spectra of Te_4^{2+} have also been reinvestigated using different samples. The Raman bands obtained have been reassigned so as to remove discrepancies in the assignment of the vibrational modes given in previous reports (20,57).

Compounds containing polyatomic cations of group VI have been found to be more soluble at lower temperatures, noticeably those of Te_n^{n+} , Te_4^{2+} and Se_{10}^{2+} . This property was used to obtain compounds of Te_n^{n+} , and S_{16}^{2+} in suitable crystalline forms for single crystal x-ray diffraction studies. Although the structures of these cations are still uncertain their real nature should be unambiguously revealed after the completion of the crystallographic studies.

The compounds Se_5AlCl_4 and Se_8AlCl_4 had been prepared previously in this laboratory and were believed to contain Se_{10}^{2+} and Se_{16}^{2+} respectively. In this work studies of low oxidation state selenium polycations have been continued. The compound $\text{Se}_{10}(\text{AsF}_6)_2$ was obtained by the following reactions in SO_2 .



The properties of this compound were extensively studied and it proved possible to obtain the product in suitable crystalline form for single crystal x-ray diffraction studies. However the formation of the compound $\text{Se}_{16}(\text{AsF}_6)_2$ was not observed in the proposed reactions.



Reactions of polyatomic cations so far have been almost completely uninvestigated. In this work two types of reactions of polycations of S, Se and Te were extensively studied.

a. The reactions of a homopolyatomic cation with one of the elements S, Se and Te.

b. The reactions of two different homopolyatomic cations with each other.

The results are summarized in Table 15.

New "mixed cations" $\text{Te}_2\text{Se}_8^{2+}$, $\text{Te}_{3.7}\text{Se}_{6.3}^{2+}$ which consists of a mixture of $\text{Te}_3\text{Se}_7^{2+}$ and $\text{Te}_4\text{Se}_6^{2+}$ cations, $\text{Te}_2\text{Se}_2^{2+}$, $\text{Te}_3\text{S}_3^{2+}$ and $\text{S}_2\text{Se}_8^{2+}$ have been prepared by these reactions. From x-ray crystallographic studies, $\text{Te}_2\text{Se}_8^{2+}$ and $\text{Te}_{3.7}\text{Se}_{6.3}$ have been

Table 15: Reactions of Polycations of
S, Se and Te

<u>Reaction</u>	<u>Product</u>
$\frac{1}{4} S_8 + Se_8(AsF_6)_2$	$S_2Se_8(AsF_6)_2$
$8Se + S_8(AsF_6)_2$	$Se_8(AsF_6)_2 + S_8$
$8Se + 3S_8(AsF_6)_2$	$Se_4(AsF_6)_2 + S_{16}(AsF_6)_2 + S_8$
$Se + Te_6(AsF_6)_2$	no reaction
$Se + Te_4(AsF_6)_2$	$Te_{3.7}Se_{6.3}(AsF_6)_2$
$Te + S_8(AsF_6)_2$	$Te_n^{n+} + Te_4^{2+} + \text{other products}$
$2Te + Se_8(AsF_6)_2 + SO_2$	$Te_2Se_8(AsF_6)_2 \cdot SO_2$
$6Te + 2Se_4(AsF_6)_2 + SO_2$	$Te_2Se_8(AsF_6)_2 \cdot SO_2 + Te_4(AsF_6)_2$
$2Te + Te_4(SbF_6)_2$	$Te_6(SbF_6)_2$
$S_8(AsF_6)_2 + Se_8(AsF_6)_2$	$Se_4(AsF_6)_2 + S_{16}(AsF_6)_2$
$S_8(AsF_6)_2 + Te_4(AsF_6)_2$	$Te_3S_3(AsF_6)_2 + \text{other products}$
$S_8(AsF_6)_2 + Te_6(AsF_6)_2$	$Te_n^{n+} + Te_4^{2+} + \text{other products}$
$Se_4(AsF_6)_2 + Te_6(AsF_6)_2$	$Te_2Se_2(AsF_6)_2 + Se_8(AsF_6)_2$
$Se_4(AsF_6)_2 + Te_4(AsF_6)_2$	$Te_2Se_2(AsF_6)_2$
$Se_8(AsF_6)_2 + Te_4(AsF_6)_2$	complicated unidentified
$Se_8(AsF_6)_2 + TeAsF_6$	products

shown to be 10-membered bicyclic rings, while $\text{Te}_2\text{Se}_2^{2+}$ is square planar and $\text{Te}_3\text{S}_3^{2+}$ a six membered ring. $\text{S}_2\text{Se}_8^{2+}$ is expected to have a similar structure to $\text{Te}_2\text{Se}_8^{2+}$ but the direct evidence is still lacking.

S_8^{2+} was found to be much more oxidising than the polycations of Se and Te, as it oxidized Se to Se_4^{2+} and Te to Te_n^{n+} very readily in SO_2 solution. The oxidizing power of the other cations is more difficult to determine since mixed cations were usually produced in the reactions. For example, Se_4^{2+} is a better oxidizing agent than Te_6^{2+} since it can oxidize the latter to Te_4^{2+} . However, when Se_4^{2+} is reacted with Te_4^{2+} , a new species $\text{Te}_2\text{Se}_2^{++}$ is obtained and the reaction cannot be considered to be an oxidation reduction reaction.

Most of the compounds studied in this work contain AsF_6^- , one of the most common anions present in compounds of polycations. It is believed that if compounds of other anions such as $\text{Sb}_2\text{F}_{11}^-$, AlCl_4^- etc. are used, the pattern of reactions of the polycations might be somewhat different and this might lead to the formation of new products which it was not possible to obtain in the present work. New cations, e.g., $\text{S}_2\text{Se}_2^{2+}$, $\text{Te}_2\text{S}_8^{2+}$, $\text{Se}_8\text{S}_8^{2+}$ etc. may possibly be prepared in this way. The study of polycation reactions under different experimental conditions such as change of solvent or temperature, may also yield interesting results. The mixed cations of S, Se and Te so far been prepared are shown in Table 16.

Table 16: Mixed Cations of S, Se and Te

Oxidation States		
$\frac{+1/2}{\text{Te}_2\text{Se}_2^{2+}}$	$\frac{+1/3}{\text{Te}_2\text{Se}_4^{2+*}}$ $\text{Te}_3\text{S}_3^{2+}$	$\frac{+1/5}{\text{Te}_2\text{Se}_8^{2+}}$ $\text{Te}_{3.7}\text{Se}_{6.3}^{2+}$ $(\text{Te}_3\text{Se}_7^{2+}, \text{Te}_4\text{Se}_6^{2+})$

* Cation not prepared in the present work, see ref. (67).

The preparation of polyatomic cations of bismuth in SO_2 at room temperature was attempted in this work. Various oxidizing agents, e.g. AsF_5 , SbF_5 , PF_5 , HSO_3F and HSO_3Cl , were used. $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$ was isolated and characterized by Raman spectroscopy. Other polycations of bismuth, Bi_8^{2+} , Bi_9^{5+} and Bi^+ , have not been observed under our experimental conditions. A yellow green solution that appeared in the early stages of the reaction of Bi with AsF_5 may contain one of these species but unfortunately the compound could not be isolated due to its instability in the solution.

The reaction of $\text{Bi}_5(\text{AsF}_6)_3 \cdot 2\text{SO}_2$ with AsF_5 in SO_2 yielded a fluorobismuth complex formulated as $(\text{BiF}_2)_m(\text{AsF}_6)_m$ which was also obtained from the reaction of equimolar amounts of BiF_3 and AsF_5 in SO_2 . The ^{19}F NMR spectrum of the compound in SO_2 suggests the cation is present in several polymeric forms such as BiF_2^+ , $\text{Bi}_2\text{F}_4^{2+}$ and $\text{Bi}_3\text{F}_6^{3+}$ etc. This complex does not appear to be stable with respect to a more highly polymeric form $(\text{BiF}_2)_n(\text{AsF}_6)_n$ where n is very large and is

slowly transformed into this more extensively polymerised form which is insoluble in SO_2 .

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