X-RAY DIFFRACTION STUDIES OF SOME POLYATOMIC CATIONS IN THE SOLID AND LIQUID STATE.

There are some things which cannot be learned quickly, and time, which is all we have, must be paid heavily for their acquiring. They are the very simplest things, and because it takes a man's life to know them the little new that each man gets from life is very costly and the only heritage he has to leave.

> E. Hemingway Death in the Afternoon

X-RAY DIFFRACTION STUDIES OF SOME POLYATOMIC CATIONS IN THE SOLID AND LIQUID STATE

by

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DOCTOR OF PHILOSOPHY (1971) (Chemistry) TITLE: X-Ray Diffraction Studies of some Polyatomic Cations in the Solid and Liquid State AUTHOR: David B. Crump B.Sc. (University of London) SUPERVISOR: Professor R. J. Gillespie NUMBER OF PAGES: x, 153. SCOPE AND CONTENTS:

In a study of the structures of some polyatomic cations of Group VI and VII, the compound $Se_4(HS_2O_7)_2$ has been prepared and its structure determined by single crystal X-ray diffraction. The bonding in the square planar cation has been discussed in terms of molecular orbital and valence bond theory. The anion geometry has been discussed and simple rules proposed to predict the changes which occur in bond length and bond angle when one or more oxygen in an SO₄ tetrahedron is bonded to another atom or group.

A θ/θ vertical diffractometer has been constructed, and computer programmes written, so that cation structures could be determined in solution. The structures of the Se₄²⁺ and Te₄²⁺ cations have been determined in fluorosulphuric acid, and are shown to be square planar.

Liquid diffraction studies of 3:1, $I_2/S_2O_6F_2$ solutions have shown the presence of a cation containing a linear chain of three iodine atoms.

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CHAPTER 1

Introduction

1. The Polyatomic Cations of the Group VI and VII Elements

The intensely coloured solutions, which are formed when the Group VI elements, S, Se, Te, are dissolved in oleum or 100% sulphuric acid, were first observed over 150 years ago (1,2). Since the reaction of SO_3 with these elements yielded coloured compounds, which analysed as XSO_3 (X = S, Se, Te) (3-9) the coloured solutions were commonly attributed to the formation of isolated, or polymeric, forms of XSO_3 .

In 1968 Gillespie et al (10) showed that the green and yellow solutions formed when selenium dissolves in fluorosulphuric, sulphuric, and disulphuric acids were due to the formation of the polyatomic cations $Se_8^{2^+}$ and $Se_4^{2^+}$. The formation of polyatomic cations would therefore seem to be a reasonable explanation for the coloured solutions produced by S and Te. The behaviour of both of these elements in strong acids has been reinvestigated, and the cations $S_{16}^{2^+}$, $S_8^{2^+}$, $S_4^{2^+}$ and $Te_4^{2^+}$ have been positively identified in solution (11,12,13).

Several polyatomic cations of iodine had been established prior to the work on the Group VI elements. Masson (14), in 1938, was the first to postulate the existence of the cations I_3^+ and I_5^+ as stable species in concentrated sulphuric acid, and their formation in sulphuric and fluorosulphuric acid was confirmed, in 1966, by Gillespie and coworkers (15,16). The I⁺ cation was commonly invoked as the reaction intermediate in electrophilic substitution reactions. The blue coloured solutions

obtained when iodine is dissolved in oleum were thought to be due to the formation of I^+ (17). It was subsequently shown that this blue species is the I_2^+ cation, and there is no evidence remaining for the existence of I^+ (18) as a stable species in solution.

The formation of cations is a property normally associated with the metallic elements. However, these results suggest that it may be a fairly common occurrence amongst the non-metals as well. Polyatomic cations of the non-metals are highly electrophilic species, and they can only exist in the presence of molecules and anions of very low basicity. This explains why they are stable in weakly basic solvents like fluorosulphuric and disulphuric acid. The recent development of the chemistry of strong acid systems provided an impetus to extend the search for cations formed by the Group VI and VII elements. The results of these investigations are the topics of two recent review articles, one considering the Group VI cations (19), the other the halogen and interhalogen cations (20).

The majority of the early chemistry of the cations was performed in solution, but more recently solid derivatives of the cations have been prepared with weakly basic anions, i.e., HS_2O_7 , SO_3F , SbF_6 , AsF_6 . Some new cations which had not been observed in solution, were isolated in the solid state. The solid state chemistry of the cations is also discussed in the review articles (19,20).

2. Purpose of This Work

The purpose of the work described in this thesis was to determine the structures of some polyatomic cations of the Group VI and VII elements. The structures of the cations were potentially interesting since they

appear to be comparatively simple molecules, analogous perhaps to the cluster compounds formed by the transition metals.

The initial approach to the problem was to prepare solid derivatives of the cations, in order to determine their structures by single crystal X-ray diffraction. All the solid derivatives which have been prepared are extremely hygroscopic, and readily decompose when exposed to the air. These properties introduce considerable practical difficulties to the preparative chemistry and to the X-ray experiment. However, this thesis describes both the preparation of the first crystalline derivative of a Group VI or VII polyatomic cation, and the determination of its structure by single crystal X-ray diffraction. During the course of this work the structures of the $S_8^{2^+}$, $Se_8^{2^+}$, $Te_4^{2^+}$, and Br_2^+ cations were determined by other workers, and these structures will be discussed in the concluding chapter.

The fact that very concentrated solutions of most of the cations can be prepared quite easily suggested a second approach to the problem of determining the cation structures, namely liquid X-ray diffraction. The atoms in the cations have high atomic numbers compared to the atoms in the solvent; therefore the cation atoms should make a major contribution to the scattered intensity. If the cations are analogous to metal clusters, the atoms will be arranged in a rigid group, and the structure can be determined on the basis of just a few inter atomic distances. This method would also allow for some interesting comparisons to be made between the structures of the cations in the solid and liquid state.

This thesis describes the development of an experimental technique

for measuring the angularly dependant intensity of the X-rays scattered by some polyatomic cation solutions. The interpretation of the experimental measurements in terms of the structures of the cations is also discussed.

CHAPTER 2

Chemical Experiments

1. Preparation and Purification of Materials

Selenium and tellurium

The finely powdered elements were used directly (99.7%, K. & K. Labs.). Iodine

Shawinigan reagent grade iodine was used directly.

Mercury

Shawinigan triple distilled mercury was used directly.

Sulphur dioxide

Matheson anhydrous sulphur dioxide was used after being passed through a P_2O_5 drying train.

Sulphur trioxide

Sulphur trioxide was distilled from Baker and Adamson 'Sulphan' in a still protected from moisture by a magnesium perchlorate drying tube. Sulphuric acid

Baker and Adamson concentrated sulphuric acid was used.

Disulphuric acid

Disulphuric acid of known composition was prepared by distilling sulphur trioxide into a weighed amount of concentrated sulphuric acid. Fluorosulphuric acid

Doubly distilled technical grade fluorosulphuric acid was provided by Mr. T. E. Peel. The method of purification has been described by Barr (21).

Peroxydisulphuryl difluoride

Peroxydisulphuryl difluoride was prepared by the method of Dudley and Cady (22), by reaction of fluorine and sulphur trioxide at 130°C over a silver catalyst. The catalyst was supported on copper mesh which had been coated in a silver cyanide complex bath. The flow rates of each reactant, diluted with nitrogen, were monitored with fluorolube oil bubblers. A small excess of fluorine was achieved by adjusting flow rates until solid sulphur trioxide ceased to form at the top of the collection trap, which was cooled in dry ice.

The product was distilled at -76°C into storage traps fitted with teflon-glass valves (Fischer and Porter). Prior to use the compound was doubly distilled from dry ice on a vacuum line fitted with teflon taps.

2. The Preparation of Tetraselenium bis-Hydrogen Disulphate

Powdered selenium was added to a weighed amount of 65% disulphuric acid, to make the solution about 6M with respect to selenium. The solution immediately turned the characteristic dark green colour of $\mathrm{Se_8}^{2^+}$, and was then maintained at 60-65°C for two hours. As further oxidation took place the solution became a very dark yellow, and orange needle crystals of $\mathrm{Se_4}(\mathrm{HS_2O_7})_2$ separated as the solution was allowed to cool. These crystals were recrystallized by reheating the solution, and allowing it to cool under more controlled conditions.

The compound, wet with mother liquor, was transferred in a dry box to the coarse sinter (C) of the apparatus shown in Figure 2.1i. The cap (B) was replaced; the apparatus was removed from the dry box and connected to a pump at the side arm (D). The majority of the mother liquor was removed by pumping at (D) for about 1 hour. Twenty per cent oleum was slowly added from the side-arm (A), in order to wash the crystals and remove any remaining mother liquor. As much of the oleum as possible was then removed by further pumping at (D).

The crystals were transferred, in a dry box, to the sinter (C) of the apparatus shown in Figure 2.1ii. The apparatus was removed from the dry box and an SO₂ cylinder connected to the B19 joint A. Taps 1 and 2 were opened, and the whole system was evacuated by means of the pump connected to the side arm (E). The dewar (B) was filled with liquid nitrogen, and with all the taps closed, SO₂ was allowed to condense in the vicinity of (B). Trap (D) was put in a -10°C salt-ice slush bath, before the liquid nitrogen was blown out of the dewar, allowing the SO₂ to liquefy and flow onto the crystals. A small magnetic stirring bar, which had been placed on the sinter initially, was activated with a magnetic stirrer held close to the sinter. The vapour pressure of the SO₂ increased as the liquid warmed up and liquid SO₂ began to flow through the sinter into trap (D). At this point the -10°C slush bath was quickly replaced by a liquid nitrogen dewar, so that all the SO₂ would condense in trap (D).

Dewar (B) was refilled with liquid nitrogen, tap 3 was opened, and the dewar around trap (D) was removed. In this way the SO_2 could be recondensed in the upper part of the apparatus, and any oleum which had been washed from the crystals remained in trap (D).

The whole procedure was repeated several times until the crystals



appeared to be free from oleum. All the SO_2 was then pumped away, and the crystals transferred, in a dry box, to a trap which was attached to a vacuum line. The sample was pumped for a few hours at 50°C to remove the last traces of SO_2 , and stored in the trap under vacuum.

3. Analysis

Selenium

Samples of the compound were weighed out in a dry box which was equipped with an analytical balance. The samples were decomposed with water, and the precipitated selenium dissolved in the minimum volume of warm nitric acid. The solutions were diluted and warmed with an excess of hydrazine hydrochloride for 1 hour. The precipitated selenium was filtered, dried, and weighed.

Sulphur

Samples were weighed out into conical flasks in the dry box. A small volume of water was added to the flasks, which were quickly stoppered and left for some time to allow any SO_3 evolved in the hydrolysis to dissolve. An excess of water was then added, and the solutions filtered to remove the precipitated selenium. The filtrate was collected and the sulphur content determined gravimetrically as $BaSO_4$.

The results are given in the Table 2.1, and are the averages of three determinations for each element (23).

Table 2.1

Analysis of $Se_4(HS_2O_7)_2$

	Found	Required for $Se_4(HS_2O_7)_2$
Selenium	46.61%	47.13%
Sulphur	19.26%	19.14%

4. Mounting Crystals for X-ray Experiments

The crystals, free from oleum, were extremely hygroscopic and had to be handled in a good dry box (HiVac, Vacuum Atmospheres Corporation).

The crystals were mounted in thin-walled quartz capillary tubes¹, which were carefully dried before use by heating for several days at 300°C, then pumping the hot tubes for an hour in the vacuum port of the dry box. Several crystals were added to each tube, which was immediately sealed with teflon tape. As soon as the tubes were removed from the dry box, they were sealed off in a flame.

The crystals were examined under a polarising microscope so that a well-formed single crystal could be selected for X-ray examination.

5. The Preparation of Polyatomic Cation Solutions

I₃⁺/HSO₃F

A solution of I_3^+ in HSO₃F of known concentration was prepared by the reaction of iodine with peroxydisulphuryl difluoride, $S_2O_6F_2$ (24).

 $3I_2 + S_2O_6F_2 \rightarrow 2I_3^+ + 2SO_3F^-$

A weighed amount of iodine was added to a known quantity of HSO_3F in a flask, which was then attached to an all-glass vacuum line fitted with teflon taps. $S_2O_6F_2$ was transferred by trap to trap distillation, to a trap of known weight. This trap, fitted with a teflon tap, could be removed and reweighed at intervals until it contained the stoichiometric quantity of the oxidising agent. The $S_2O_6F_2$ was then distilled into the reaction flask, which was cooled in liquid nitrogen. The flask

1

0.3 mm diameter tubes were obtained from the Pantax Company.

was allowed to warm up slowly to room temperature, and the reaction readily proceeded to give a deep brown solution of I_3^+ .

 Te_4^{2+}/HSO_3F

A solution of Te_4^{2+} in HSO_3F was prepared directly by the reaction of tellurium with HSO_3F (13).

 $4\text{Te} + 4\text{HSO}_3\text{F} \rightarrow \text{Te}_4^{2+} + \text{SO}_2 + \text{HF} + \text{H}_3\text{O}^+ + 3\text{SO}_3\text{F}^-$

 Se_4^{2+}/HSO_3F

A weighed quantity of $Se_4(HS_2O_7)_2$ was dissolved in the minimum quantity of fluorosulphuric acid.

CHAPTER 3

The Theory of X-Ray Diffraction

Introduction

met 202 X-rays are scattered by electrons which, in molecules in any physical state, are concentrated in the vicinity of the atomic nuclei. The diffraction patterns which result from this scattering were classified by Debye as a combination of two phenomena:

1. Internal interference effects - interference between the X-rays scattered by electrons on the same molecule;

2. External interference effects - interference between X-rays scattered by electrons on different molecules.

Internal interference is the major component of gas diffraction, and external interference the principal effect in a single crystal. A liquid shows a combination of both effects, a fact which caused the early workers considerable problems in interpreting the scattering patterns.

In this chapter a general expression for the X-ray scattering from a molecule is developed. This is applied to the random distribution of molecules in a liquid, and then to molecules which are ordered in a periodic lattice.

Derivation of the Atomic Scattering Factor.

In Diagram 1, Q is the origin of a beam of X-rays, which are scattered in the direction P by the electrons distributed about an atom centred at O,



Diagram 1

where \vec{S}_0 is the vector defining the direction of the incident X-ray beam, and \vec{S}_1 defines the direction of the scattered radiation. Let $|\vec{S}_0| = |\vec{S}_1| = 1/\lambda$,

where λ is the wavelength of the radiation,

then from Diagram 1,

 $|\vec{s}| = |\vec{s}_1 - \vec{s}_0| = 2\sin\theta/\lambda$ [3.1]

Let the total number of electrons of an atom per unit volume at a distance \vec{r} from the nucleus be $\sigma(\vec{r})$, then the atomic scattering factor, f_0 , can be defined as,

$$f_0 = \int \sigma(\vec{r}) e^{2\pi i \vec{S} \cdot \vec{r}} dv . \qquad [3.2]$$

The exponential term in Equation [3.2] describes the phase difference between the electron density at 0, and at a distance \vec{r} from 0. Values of f_0 can be calculated from the Fourier transform of the electron density $\sigma(|\vec{r}|)$, which is normally assumed to have spherical symmetry. This has been done for all atoms using either the self-consistent field or Hartree methods to evaluate $\sigma(|\vec{r}|)$.

There are two correction terms which may be applied to f_0 .

(i) Temperature factor T.

The electron density of an atom relative to the nucleus is largely independent of temperature. However, the nucleus has a finite amplitude of oscillation, which is temperature dependent. The temperature factor accounts for the spread of the electron density associated with the mean displacement of the nucleus from its equilibrium position.

For an isotropic motion of the nucleus,

$$T = e^{\left(-B \frac{\sin^2 \theta}{\lambda^2}\right)}$$
 [3.3]

where

B is the Debye-Waller temperature factor = $8\pi^2\bar{\mu}^2$,

and $\bar{\mu}^2$ is the mean square amplitude of vibration of the nucleus.

The corrected atomic scattering factor is written,

$$\mathbf{f}_{\mathrm{T}} = \mathbf{f}_{0} \cdot \mathbf{T} \, . \tag{3.4}$$

(ii) Dispersion correction.

The values of f_0 are independent of the X-ray frequency, except when this approaches an absorption frequency of the atomic electrons. In this case a dispersion correction must be applied, and f_0 is replaced by,

$$\mathbf{f} = \mathbf{f}_0 + \Delta \mathbf{f}' + \mathbf{i} \Delta \mathbf{f}'' . \qquad [3.5]$$

The values of $\Delta f'$ and $\Delta f''$ are approximately independent of the scattering angle, and have been tabulated for all atoms (25).

The Coherent Scattering from a Molecule F mol

The scattering factor of a molecule, F_{mol} , is defined as,

$$F_{mo1} = \int \sigma(\vec{r}) e^{2\pi i \vec{S} \cdot \vec{r}} dv . \qquad [3.6]$$

The integration is performed over the whole molecule, and $\sigma(\vec{r})$ is the electron density at any point \vec{r} from an arbitrary origin. Let it be assumed that the electron density of the molecule, $\sigma(\vec{r})$, can be separated into a sum of electron densities of the j atoms in the molecule.





In Diagram 2 the nucleus of atom A is \vec{r}_j from the origin 0, and the electron density about A can be defined in terms of the vector \vec{R} as $\sigma(\vec{R})$. From Diagram 2,

$$\vec{R} = \vec{r} - \vec{r}_{j}$$

$$\vec{r} = \vec{R} + \vec{r}_{j}$$
[3.7]

therefore,

$$\sigma(\vec{r}) = \Sigma_j \sigma_j (\vec{r} - \vec{r}_j) . \qquad [3.8]$$

Substituting [3.8] in [3.6], and using the conditions [3.7], gives

$$F_{mol} = \int \Sigma_j \sigma_j (\vec{r} - \vec{r}_j) e^{2\pi i \vec{S} \cdot (\vec{R} + \vec{r}_j)} dv . \qquad [3.9]$$

Equation [3.9] may be written,

$$F_{mo1} = \int \Sigma_{j} \sigma_{j}(\vec{R}) e^{2\pi i \vec{S} \cdot (\vec{R} + \vec{r}_{j})} dv_{\vec{R}}$$
$$= \Sigma_{j} \left[\int \sigma_{j}(\vec{R}) e^{2\pi i \vec{S} \cdot \vec{R}} dv_{\vec{R}} \right] e^{2\pi i \vec{S} \cdot \vec{r}_{j}} . \qquad [3.10]$$

The term in the square brackets in Equation [3.10] is identical with Equation [3.2] and represents the atomic scattering factor of the jth atom. Therefore,

$$F_{mol} = \Sigma_j f_j T_j e^{2\pi i \vec{S} \cdot \vec{r}_j} . \qquad [3.11]$$

In any X-ray experiment, it is the scattered intensity, I, which is recorded,

$$I \propto F_{mol} F_{mol}^*$$
 [3.12]

where F_{mol}^* is the complex conjugate of F_{mol} . It is important to note that only the magnitude of F_{mol} can be determined experimentally.

Equation [3.12] can be written,

$$I \propto (\Sigma_{j}f_{j}T_{j} e^{2\pi i \vec{S} \cdot \vec{r}_{j}}) \cdot (\Sigma_{k}f_{k}^{*}T_{k}^{*} e^{-2\pi i \vec{S} \cdot \vec{r}_{k}})$$

$$[3.13]$$

all atoms

$$I \propto \sum_{\substack{j,k}} f_j T_j f_k^* T_k^* e^{2\pi i \vec{S} \cdot (\vec{r}_j - \vec{r}_k)}.$$
[3.14]

Equation [3.14] is the fundamental equation relating the intensity of the scattered radiation to the separation of the atoms in a molecule. It will be shown in the following sections that the difference between the scattering from a liquid, and a periodic structure, is that in the latter case Equation [3.14] has only non-zero values at discrete values of \vec{S} .

1. Diffraction of X-Rays by a Liquid

Introduction

Debye and Scherrer (26), in 1916, recorded the diffraction haloes produced by liquid benzene in the hope of determining the molecular structure. They showed that the angular radii of the rings depended on wavelength in the manner expected for diffraction, but the external interference effects masked the internal structural details.

In 1922, Keesom and de Smedt (27) published the first internuclear distances for simple monatomic liquids derived from diffraction data. Zernike and Prins (28) provided the modern theoretical basis for the diffraction of X-rays by liquids by applying the Fourier integral theorem. This permits the calculation of a probability, or radial distribution function, of molecules around each individual molecule. The first quantitative application of this method was carried out by Debye and Menke (29) in 1930 for liquid mercury.

In this section the general intensity equation [3.14] is applied to a system of randomly distributed atoms or molecules, and the essential equations for determining the short range liquid structure are developed. (i) The general scattering equation for a random orientation

The general equation for the intensity of radiation scattered by an assembly of atoms is given by Equation [3.14]. This equation can be written in terms of a fixed atom separation, $(\vec{r}_j - \vec{r}_k)$, excluding the temperature factor as,

$$I = \sum_{\substack{j \\ k}} \sum_{k} f_{j} f_{k}^{*} e^{2\pi i \vec{S} \cdot (\vec{r}_{j} - \vec{r}_{k})} . \qquad [3.15]$$

It is convenient to let $(\vec{r}_j - \vec{r}_k) = \vec{r}_{jk}$.

In a liquid all orientations of the vector \vec{r}_{jk} are equally probable; therefore its terminal point can take all positions on the surface of a sphere of radius $|\vec{r}_{jk}|$, as shown in Diagram 3.



Diagram 3

From Diagram 3,

$$\vec{r}_{jk} \cdot \vec{S} = |\vec{r}_{jk}| |\vec{S}| \cos\phi \qquad [3.16]$$

where ϕ is the angle between the vectors \vec{r}_{jk} and \vec{s} . Substituting [3.16] in [3.15]

$$I = \sum_{\substack{\Sigma \ j \ k}} f_{j} f_{k}^{*} e^{(2\pi i |\vec{S}| |\vec{r}_{jk}| \cos \phi)}$$

$$[3.17]$$

and since $|\vec{S}| = 2\sin\theta/\lambda$ (Equation [3.1]), let $s = 4\pi \sin\theta/\lambda$, and Equation [3.17] can be written,

$$I = \sum_{\substack{j \\ k}} \sum_{k} f_{j} f_{k}^{*} e^{(is|\vec{r}_{jk}|\cos\phi)} . \qquad [3.18]$$

The average value for each exponential term in [3.18] is,

$$\langle e^{is|\vec{r}_{jk}|\cos\phi} \rangle = 1/(4\pi|\vec{r}_{jk}|^2) \int_{\phi=0}^{\pi} e^{(is|\vec{r}_{jk}|\cos\phi)} 2\pi|\vec{r}_{jk}|^2 \sin\phi d\phi$$

$$= \frac{\sin s |\vec{r}_{jk}|}{s |\vec{r}_{jk}|} .$$
[3.19]

The scattering factors, f, are functions of s, and if it is assumed that they are spherically symmetric, Equation [3.19] can be substituted in [3.18], and

$$I = \sum_{\substack{j \ k}} \sum_{k} f_{j}(s) f_{k}^{*}(s) \frac{\sin s |\vec{r}_{jk}|}{s |\vec{r}_{jk}|}.$$
 [3.20]

Equation [3.20] is Debye's equation for the total unmodified scattered intensity, and involves only the magnitudes of the atomic separations $|\vec{r}_{ik}|$.

(ii) Application of the general scattering equation to a liquid sample containing more than one kind of atom

In a polyatomic liquid, a certain group representing the bulk sample and containing m atoms may be chosen as the stoichiometric unit. From Equation [3.18] the total intensity scattered from this group is given by,

$$I = \sum_{j=1}^{m} f_{j}(s)f_{j}^{*}(s) + \sum_{j=1}^{m} f_{j}(s) \sum_{k=1}^{m} f_{k}^{*}(s) e^{(is|\vec{r}_{jk}|\cos\phi)}.$$
 [3.21]

An average scattering factor per electron is defined as,

$$\mathbf{f}_{e} = \begin{pmatrix} \mathbf{\Sigma} & \mathbf{f}_{j} \end{pmatrix} / \begin{pmatrix} \mathbf{\Sigma} & \mathbf{Z}_{j} \end{pmatrix}$$
[3.22]

where Z_j is the atomic number of the jth atom. The scattering factors, f_j , can be expressed in terms of the scattering factor for a single electron,

$$f_j = k_j f_e$$
 [3.23]

where k_j is the effective electron number for each type of atom, and will be approximately equal to Z_j . k_j will vary slowly with sin θ/λ , but in the following derivation it is treated as a constant. This discrepancy will be resolved by introducing a modification function M(s) at a later stage.

Equation [3.21] can be written,

$$I = \sum_{j=1}^{m} f_{j}(s) f_{j}^{*}(s) + f_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \sum_{k=1}^{m} k_{k} e^{(is|\hat{r}_{jk}|\cos\phi)} . \quad [3.24]$$

Let $\rho_j(\vec{r}_{jk})dv_k$ be the number of atom centres, each multiplied by its appropriate k_k , in the volume element dV_k at displacement \vec{r}_{jk} from atom j. The sum over k can now be replaced by an integral over the volume of the sample,

$$I = \sum_{j=1}^{m} f_{j}(s) f_{j}^{*}(s) + f_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \int \rho_{j}(\vec{r}_{jk}) e^{(is|\vec{r}_{jk}|\cos\phi)} dV_{k}.$$
 [3.25]

The average number of electrons/unit volume in the sample ρ_0 , is now separated out, so that the Fourier integral will converge.

$$I = \sum_{j=1}^{m} f_{j}(s) f_{j}^{*}(s) + f_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \int [\rho_{j}(\vec{r}_{jk}) - \rho_{o}] e^{(is|\vec{r}_{jk}|\cos\phi)} dV_{k}$$

+
$$f_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \rho_{o} \int e^{(is|\vec{r}_{jk}|\cos\phi)} dV_{k} . \qquad [3.26]$$

The third term in Equation [3.26] represents the contribution to the intensity at very small angles, since the integral will only have a significant value when s is very small, and can be ignored. If it is assumed that the sample has spherical symmetry, for a fixed displacement $\vec{r}_{jk} = |\vec{r}|$, let $\rho_{jk}(|\vec{r}|) = \langle \rho_j(\vec{r}_{jk}) \rangle_v$, where the average is over all the

atoms j. In an amorphous sample, $[\rho_{jk}(|\vec{r}|) - \rho_0]$ approaches zero for displacements $|\vec{r}|$ greater than a few atomic dimensions. Equation [3.26] can be multiplied by n, which is the total number of stoichiometric units in the sample. Thus,

$$I' = n \sum_{j=1}^{m} f_{j}(s) f_{j}^{*}(s) + n f_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \int [\rho_{jk}(|\vec{r}|) - \rho_{o}] e^{(is|\vec{r}|\cos\phi)} dV. \quad [3.27]$$

For an amorphous sample without any preferred orientations $[\rho_{jk}(|\vec{r}|) - \rho_{o}]$ will have spherical symmetry. It can be replaced by $[\rho_{jk}(r) - \rho_{o}]$ and the integration with respect to d ϕ performed in the same manner as for Equation [3.18]. The second term in [3.27] becomes,

$$nf_{e}(s) \sum_{j=1}^{m} k_{j} \int_{0}^{\pi} \int_{0}^{\pi} [\rho_{jk}(r) - \rho_{0}] e^{(isrcos\phi)} 2\pi r^{2}\phi d\phi dr$$
$$= nf_{e}^{2}(s) \sum_{j=1}^{m} k_{j} \int_{0}^{\pi} 4\pi r^{2} [\rho_{jk}(r) - \rho_{0}] \frac{\sin sr}{sr} dr . \qquad [3.28]$$

The reduced intensity i(s) may be defined as,

$$i(s) = [I'/N - \sum_{j=1}^{m} f_{j}(s)f_{j}^{*}(s)] / f_{e}^{2}(s)$$
[3.29]

where I'/N represents the measured intensity as a function of s, normalized to one stoichiometric unit of the sample. Subtracting the term $\sum_{j=1}^{m} f_{j}(s) f_{j}^{*}(s)$ removes the internal interference effects of the atoms in the stoichiometric unit, leaving the structure sensitive part of the expression. Substituting Equation [3.28], and the definition of the reduced intensity, Equation [3.29], in Equation [3.27] gives,

$$si(s) = 4\pi \int_{0}^{\infty} \sum_{j=1}^{m} k_{j} r \left[\rho_{jk}(r) - \rho_{0}\right] sin sr dr.$$
 [3.30]

Inverting the Fourier integral in Equation [3.30] gives,

$$\sum_{j=1}^{m} k_{j} 4\pi r^{2} \rho_{jk}(r) = 4\pi r^{2} \rho_{0} \sum_{j=1}^{m} k_{j} + \frac{2r}{\pi} \int_{0}^{\pi} si(s) \sin sr \, ds \, . \quad [3.30]$$

At this point a modification function M(s) is introduced, which is chosen to make the factors $[\Sigma f_j(s)f_k^*(s)]M(s)$ approximately independent of s. Two forms for M(s) have been suggested,

(i)
$$M(s) = [\sum_{j=1}^{m} f_{j}(s)]^{-2}$$
 (30)

(ii)
$$M(s) = \begin{bmatrix} \Sigma^m f_j(0) / \Sigma^m f_j(s) \end{bmatrix}^2$$
 (30)
 $j=1$

where $\sum_{j=1}^{m} f_{j}(s)$ is the value of the total scattering factor for the stoichiometric unit at s > 0, and $\sum_{j=1}^{m} f_{j}(0)$ is the value at s = 0. The units of the radial distribution function are dependent on the form of M(s) that is chosen, and therefore the units of ρ_{0} must be selected correctly. The function derived by the use of M(s) (i) has been classified by Harris (30) as a molecular radial distribution function in units of molecules/Å. Using M(s) (ii) an electronic radial distribution function in units of electrons²/Å is obtained.

These modification functions have the advantage of sharpening the peaks in the final distribution function. The intensity is corrected to that expected for point scatterers (cf. unitary structure factors), and the breadth due to the distribution of the electron density about the atoms is removed.

The use of modification functions has been criticized because it tends to emphasize the contribution of the intensities recorded at the larger values of s, where the experimental measurement is less precise. However, a weighting factor of the form e^{-as^2} can be introduced to offset this effect. It is obvious that the integration in Equation [3.31] cannot be performed to infinity and a damping factor of this type may be justified in order to correct for series termination errors.

Equation [3.31] can now be written in a form which can be solved knowing the reduced intensity i(s).

$$D(\mathbf{r}) = D_{o}(\mathbf{r}) + \frac{2\mathbf{r}}{\pi} \int_{s_{min}}^{s_{max}} \sin(s) \cdot M(s) \sin sr \, ds \qquad [3.32]$$

where $D_{\rho}(r) = 4\pi r^2 \rho_{\rho}$

$$D(\mathbf{r}) = \sum_{j=1}^{m} \sum_{k=1}^{m} D_{jk}(\mathbf{r}) = \sum_{j=1}^{m} 4\pi r^{2} \rho_{jk}(\mathbf{r})$$

and s_{max} = maximum recorded value of s

s_{min} = minimum recorded value of s.

The lower integration limit s_{min} has to be introduced since it is not possible to measure the intensity to s = 0. Harris (30) has shown that this initiation error does not seriously effect the radial distribution function, and in general it is quite satisfactory to extrapolate the observed intensity curve back to zero.

The experimentally observed intensity I(s), must be corrected for several angularly dependent effects in order to obtain the reduced coherent intensity i(s).

(i) Polarization correction P.

The polarization correction has been given (31) as,

$$P = \frac{(1 + \cos^2 2\theta' \cos^2 2\theta)}{(1 + \cos^2 2\theta')}$$
[3.33]

where θ is the diffraction angle at the sample surface, and θ' is the Bragg angle for the reflecting plane of the monochromator crystal.

The polarization correction takes this form since both the liquid sample and the monochromator crystal will scatter the different directions of polarization in the X-ray beam with variable efficiency.

(ii) Absorption correction A.

For the parafocusing geometry used in the experiment, the absorption correction should be independent of angle. This is true only if the sample is highly absorbing, and Levy (32) has calculated the form of the correction for a flat sample, where penetration is important, as,

$$A = [1 - (1 - e^{-x})/x]$$
 [3.34]

where $x = 2\alpha\mu/\sin 2\theta$

 μ = linear absorption coefficient of the sample

 α = the width of the incident beam at the sample surface. It can be seen that as x increases, A approaches unity. These two corrections are combined to give:

$$I'(s) = I(s)/P \cdot A$$
 [3.35]

I'(s) is in arbitrary units, and is scaled to the units of $\sum_{j=1}^{m} f_{j}^{2}(s)$. The scaling depends on the fact that at large values of s j=1 j (s) curve and the $\sum_{j=1}^{m} f_{j}^{2}(s)$ curve have almost the same gradient. It would be more exact to scale I'(s) to $[\sum_{j=1}^{m} f_{j}^{2}(s) + I_{inc}(s)]$, where $I_{inc}(s)$ is the incoherent scattering of the atoms in the stoichiometric unit. However, because of the geometry of the diffractometer, which has the monochromator in the scattered beam, the incoherent scattering
curve does not follow the theoretically predicted curve. This has been clearly demonstrated by Levy (33) and Warren (34), who have shown that the incoherent scattering diminishes rapidly from the theoretically expected value at high angles, thus the error introduced by neglecting the contribution of $I_{inc}(s)$ in the scaling is negligible.

The normalized intensity $I'_n(s)$ may have to be corrected for the contribution of $I_{inc}(s)$ at lower angles. Let it be assumed that the incoherent scattering in this region follows the curve predicted by Compton's expression (35),

$$I_{inc}(s) = Z[1 - \{\sum_{j=1}^{m} f_{j}(s)\}^{2}/Z]$$
[3.36]

where Z is the atomic number for the stoichiometric unit. If Z is very large, e.g., Hg, $I_{inc}(s)$ will represent only a few per cent of $\sum_{j=1}^{m} f_{j}^{2}(s)$, and can be ignored.

For the cases where $I_{inc}(s)$ does make a significant contribution to $I'_n(s)$, a semi-empirical method is used to calculate the correction curve. $I_{inc}(s)$ is a slowly undulating function of s, and its transform will be a rapidly undulating function at small distances in D(r). The region of D(r) between 0 and the first main peak should be essentially smooth, and follow the $D_o(r)$ curve. Any peaks occurring in this region must be due either to errors in the normalization, or the contribution of $I_{inc}(s)$. A curve to correct for these effects can be calculated by reinverting any undulations which occur below the first main peak in D(r). Equation [3.32] can be rearranged to give,

$$\frac{\left[D(\mathbf{r}) - D_{\mathbf{o}}(\mathbf{r})\right]}{\mathbf{r}} = \frac{2}{\pi} \int_{s_{\min}}^{s_{\max}} \operatorname{si}(s) \sin s\mathbf{r} \cdot M(s) \, ds \,. \qquad [3.37]$$

Inverting the Fourier integral in Equation [3.37] gives,

$$s \int_{r=0}^{r=r_1} \frac{[D(r) - D_o(r)]}{r} \sin sr M(s) dr = s[si'(s)]$$

and therefore,

$$i'(s) = \int_{r=0}^{r=r_1} [D(r) - D_o(r)] \frac{\sin sr}{sr} M(s) dr \qquad [3.38]$$

where r_1 is the chosen cut off point below the first main peak. The correction curve i'(s) can be applied to the reduced intensity i(s) and a new radial distribution function calculated, D'(r). The region below r_1 in D'(r) can be reinverted in the same way, and the procedure repeated until the curve below r_1 is essentially smooth.

The interpretation of D(r) is not a straightforward procedure for a polyatomic solution. From Equation [3.32] it can be seen that D(r)is a linear combination of all the radial pair distributions in the sample. In order to unfold D(r) uniquely for a liquid containing m different types of atoms, m(m + 1)/2 independent diffraction experiments, using different values of f would have to be performed. A single D(r)function must be analysed by comparison with a reasonable model for the short range structure in the sample. Each feature of D(r) can then be interpreted in terms of the peak shape associated with a particular jk pair distribution, $T_{ik}(r)$.

The distance, r_{jk} , separating each atom pair is not rigidly maintained, and a Gaussian distribution, G(s), of distances would be expected given by,

$$G(s) = (4b_{jk}\pi)^{-1/2} e^{[-(r - r_{jk})/4b_{jk}]}$$
 [3.39]

where $(r - r_{ik})$ is the difference between any value of r_{ik} and its

average, r. The transform of this Gaussian is another Gaussian, G(r),

$$G(r) = e^{(-b_{jk}s^2)}$$
 [3.40]

It is possible to identify Equation [3.40] with Equation [3.3] for the isotropic temperature factor. Equation [3.40] can be written,

$$G(r) = e^{\left[-b_{jk}\left(\frac{16\pi^{2}\sin^{2}\theta}{\lambda^{2}}\right)\right]}$$
 [3.41]

Equation [3.3], substituting the value for the Debye-Waller temperature factor, is,

$$T = e^{\left[-8\pi^{2}\bar{\mu}^{2}\left(\frac{\sin^{2}\theta}{\lambda^{2}}\right)\right]}.$$
 [3.42]

Equation [3.41] is equivalent to equation [3.42] when the coefficient b_{ik} equals $\bar{\mu}^2/2$.

If only interactions of the type jk are considered, the Debye Equation [3.20] can be written,

$$[I - f_{j}(s)f_{j}^{*}(s)] = f_{j}(s)f_{k}^{*}(s) e^{(-bjks^{2})} \frac{\sin s|\dot{r}_{jk}|}{s|\dot{r}_{jk}|}.$$
 [3.43]

Therefore,

$$si(s) = f_{j}(s)f_{k}^{*}(s)e^{(-b_{j}ks^{2})} \frac{sin \ s|\dot{r}_{jk}|}{|\dot{\vec{r}}_{jk}|}.$$
 [3.44]

Substituting [3.44] in [3.32],

$$D_{jk}(r) = D_{0}(r) + \frac{2r}{\pi} \int_{s_{min}}^{s_{max}} f_{j}(s) f_{k}^{*}(s) M(s) e^{(-bjks^{2})}$$

$$\frac{\sin s |\vec{r}_{jk}|}{|\vec{r}_{jk}|} \sin sr \, ds \, . \qquad [3.45]$$

Using the appropriate trigonometric identity [3.45] becomes,

$$T_{jk}(r) = D_{jk}(r) - D_{o}(r) = \frac{r}{\pi r_{jk}} \int_{s_{min}}^{s_{max}} f_{j}(s) f_{k}^{*}(s) M(s) e^{(-bjks^{2})}$$

$$[\cos(r - |\vec{r}_{jk}|)s - \cos(r + |\vec{r}_{jk}|)s]ds . \qquad [3.46]$$

Equation [3.46] represents the theoretical peak shape for the interaction between atoms j and k. In order to use this equation in interpreting D(r) for a polyatomic solution, two constants must be included.

(i) C_{jk} , which is the number of identical interactions between atoms of type j and k.

(ii) χ_j , which is the mole percentage of atom j in the solution. Equation [3.46] becomes,

$$T_{jk}(r) = \frac{\chi_{j} C_{jk} r}{\pi r_{jk}} \int_{s_{min}}^{s_{max}} f_{j}(s) f_{k}^{*}(s) M(s) e^{(-bjks^{2})}$$

$$[\cos(r - |\vec{r}_{jk}|)s - \cos(r + |\vec{r}_{jk}|)s]ds . \qquad [3.47]$$

2. Crystal Structure Determination

Crystals are composed of atoms or molecules, which are ordered in a three-dimensional periodic array. The theory of X-ray diffraction by a crystal can be given in terms of the translational periodicity of points, which represent identical groups of atoms or molecules, called lattice points. The array of lattice points forms the crystal lattice.

A parallelopiped, called the unit cell, can be chosen, and this,

when stacked side by side in three dimensions, produces the macroscopic crystal. The unit cell is defined by three translational vectors, \vec{a} , \vec{b} , \vec{c} . The angles between the vectors are α , β , γ , such that,

$$\vec{a} \cdot \vec{b} = |\vec{a}| |\vec{b}| \cos \gamma$$
 $\vec{a} \cdot \vec{c} = |\vec{a}| |\vec{c}| \cos \beta$ $\vec{b} \cdot \vec{c} = |\vec{b}| |\vec{c}| \cos \alpha$

and the volume of the unit cell v is $\vec{a} \cdot (\vec{b} \times \vec{c})$.

The information concerning the separations of the atoms in the crystal is contained in the structure factor expression F_{cryst} . If the crystal is regarded as a giant molecule, then Equation [3.6] can be used and written in the form,

$$F_{\text{cryst}} = \int_{\substack{\text{whole} \\ \text{crystal}}} \sigma(\vec{r}) e^{2\pi i \vec{S} \cdot \vec{r}} dv . \qquad [3.49]$$

The periodic nature of a crystal can now be introduced by imposing the condition that,

$$\sigma(\vec{r}) = \sigma(\vec{r} + m\vec{a} + n\vec{b} + o\vec{c})$$
 [3.50]

where m, n, o are any integers, and $\sigma(\vec{r})$ is the electron density \vec{r} from a unit cell origin, and $\sigma(\vec{r} + m\vec{a} + n\vec{b} + o\vec{c})$ is the electron density \vec{r} from another unit cell origin. Substituting Equation [3.50] in [3.49]

$$F_{\text{cryst}} = \sum_{mno} \int \sigma(\vec{r} + m\vec{a} + n\vec{b} + o\vec{c}) e^{[2\pi i(\vec{r} + m\vec{a} + n\vec{b} + o\vec{c})\cdot\vec{S}]} dv. \quad [3.51]$$

Equation [3.51] can be written,

$$F_{\text{cryst}} = \sum_{\substack{mno\\ vit\\ cell}} \int \sigma(\vec{r}) e^{\left[2\pi i(\vec{r} + m\vec{a} + n\vec{b} + o\vec{c})\cdot\vec{S}\right]} dv . \qquad [3.52]$$

Therefore,

$$F_{\text{cryst}} = \left[\int_{\substack{\sigma(\vec{r}) \\ \text{unit} \\ \text{cell}}} \sigma(\vec{r}) e^{2\pi i \vec{r} \cdot \vec{S}} dv \right] \sum_{\substack{\Sigma \ \Sigma \ \Sigma \ e}} 2\pi i (m\vec{a} + n\vec{b} + o\vec{c}) \cdot \vec{S} . \quad [3.53]$$

Equation [3.53] is the product of the structure factor for a unit cell and a term describing the interference due to all unit cells in the whole crystal. By comparison with Equation [3.2], the term in square brackets may be written in terms of the atomic structure factors of the N atoms in the unit cell, and Equation [3.53] can be written,

$$F_{\text{cryst}} = \sum_{j=1}^{N} f_j T_j e^{2\pi i \vec{r}_j \cdot \vec{S}} \sum_{\substack{\Sigma\Sigma\Sigma\\mno}} e^{2\pi i (m\vec{a} + n\vec{b} + o\vec{c}) \cdot \vec{S}}.$$
 [3.54]

For a very large number of unit cells, Equation [3.54] yields non-zero only if,

$$\vec{S} \cdot (\vec{ma} + \vec{nb} + \vec{oc}) = integer$$
. [3.55]

Let

$$\vec{S} = \vec{ha^*} + \vec{kb^*} + \vec{lc^*}.$$

If \vec{a}^* , \vec{b}^* , \vec{c}^* are chosen so that,

(i)
$$\vec{a} \cdot \vec{a}^* = \vec{b} \cdot \vec{b}^* = \vec{c} \cdot \vec{c}^* = 1$$

and

(ii)
$$\overrightarrow{a} \cdot \overrightarrow{b}^* = \overrightarrow{a} \cdot \overrightarrow{c}^* = \overrightarrow{b} \cdot \overrightarrow{a}^* = \overrightarrow{b} \cdot \overrightarrow{c}^* = \overrightarrow{c} \cdot \overrightarrow{a}^* = \overrightarrow{c} \cdot \overrightarrow{b}^* = 0$$

then equation [3.55] will be satisfied if,

hm + kn + lo = integer.

Since m, n, o are integers, h, k, & must also be integers.

The expression $(\vec{ma} + \vec{nb} + \vec{oc})$ describes the crystal lattice, and \vec{s} can also be described in terms of a lattice, called the reciprocal lattice. The reciprocal lattice is related to the crystal lattice by the conditions (i) and (ii), and \vec{a}^* , \vec{b}^* , \vec{c}^* define the reciprocal unit

cell. The reciprocal lattice is an important concept since it allows one to treat the scattering in terms of simple constructs. Thus F_{cryst} will only be non-zero when \vec{S} is equal to a vector between the origin of the reciprocal lattice, and the reciprocal lattice point h, k, ℓ . When this condition is satisfied, Equation [3.54] can be written:

$$F_{cryst} = \eta \sum_{j=1}^{N} f_j T_j e^{2\pi i \vec{S} \cdot \vec{r}_j} . \qquad [3.56]$$

where η is the total number of unit cells in the crystal. η is usually eliminated from Equation [3.56] and the structure factor is written in terms of a single unit cell, F,

$$F = \sum_{j=1}^{N} f_{j} e^{2\pi i \vec{S} \cdot \vec{r}_{j}} \cdot T_{j} . \qquad [3.57]$$

Writing,

$$\vec{r}_j = x_j \vec{a} + y_j \vec{b} + z_j \vec{c}$$
 [3.58]

where x_j , y_j , z_j , are the fractional coordinates of the jth atom, and substituting Equation [3.58] in [3.57],

$$F(h,k,\ell) = \sum_{j=1}^{N} f_j e^{2\pi i (x_j \vec{a} + y_j \vec{b} + z_j \vec{c}) \cdot \vec{S}} \cdot T_j$$
$$= \sum_{j=1}^{N} f_j e^{2\pi i (hx_j + ky_j + \ell z_j)} \cdot T_j . \qquad [3.59]$$

Equation [3.59] can be expressed in a trigonometric form,

$$F(h,k,l) = \sum_{j=1}^{N} f_{j}T_{j}[\cos 2\pi (hx_{j} + ky_{j} + lz_{j}) + i\sin 2\pi (hx_{j} + ky_{j} + lz_{j})]. [3.60]$$

If the structure is centrosymmetric for every atom at x_j , y_j , z_j ,

there is an equivalent atom at \bar{x}_j , \bar{y}_j , \bar{z}_j , and Equation [3.60] simplifies to,

$$F(h,k,l) = 2 \sum_{j=1}^{N/2} f_{j}T_{j} \cos 2\pi (hx_{j} + ky_{j} + lz_{j}) .$$
[3.61]

Representation of a Crystal by a Fourier Series

A crystal is periodic in three dimensions, and the periodic electron density $\sigma(x,y,z)$ can be represented by a three-dimensional Fourier series,

$$\sigma(\mathbf{x},\mathbf{y},\mathbf{z}) = \sum \sum \sum^{+\infty} C(\mathbf{h}'\mathbf{k}'\boldsymbol{l}') e^{2\pi \mathbf{i}(\mathbf{h}'\mathbf{x} + \mathbf{k}'\mathbf{y} + \boldsymbol{l}'\mathbf{z})}$$

$$\mathbf{h}'\mathbf{k}'\boldsymbol{l}'=-\alpha$$
[3.62]

where C(h'k'l') are the Fourier coefficients. Let the amount of scattering matter, i.e., electron density, in the volume element Vdxdydz be σ Vdxdydz, and the structure factor expression [3.59] can be written,

$$F(hkl) = \int_{x=0}^{1} \int_{y=0}^{1} \int_{z=0}^{1} V\sigma(x,y,z) e^{2\pi i (hx + ky + lz)} dx dy dz .$$
 [3.63]

Combining Equations [3.63] and [3.62],

$$F(hk\ell) = \iiint_{000}^{111} \Sigma\Sigma\Sigma_{-\alpha}^{\alpha}C(h'k'\ell') e^{2\pi i(h'x + k'y + \ell'z)} e^{2\pi i(hx + ky + \ell z)}$$

Equation [3.64] is non-zero only when,

$$h = -h' \qquad k = -k' \qquad \ell = -\ell'$$

and under these conditions,

$$F(hk\ell) = \iiint_{000}^{111} C(h'k'\ell')Vdxdydz$$
$$F(hk\ell) = C(\bar{h} \ \bar{k} \ \bar{\ell})V.$$

[3.65]

Substituting [3.65] in [3.62],

$$\sigma(\mathbf{x},\mathbf{y},\mathbf{z}) = \frac{1}{V} \sum_{\mathbf{k}} \sum_{\mathbf{k}} \sum_{\mathbf{k}} F(\mathbf{k}\mathbf{k}) e^{\left[-2\pi \mathbf{i}(\mathbf{k}\mathbf{x} + \mathbf{k}\mathbf{y} + \mathbf{k}\mathbf{z})\right]} . \quad [3.66]$$

Equation [3.66] can be simplified by defining an electron density projection down an axis of the unit cell, e.g., down \vec{b} ,

$$\sigma(\mathbf{x},\mathbf{z}) = \int_0^1 \sigma(\mathbf{x},\mathbf{y},\mathbf{z}) \, \overrightarrow{b} \, d\mathbf{y} \, . \qquad [3.67]$$

Substituting [3.67] in [3.66]

$$\sigma(\mathbf{x}, z) = \frac{1}{V} \int_{0}^{1} \Sigma \Sigma F(\mathbf{h} k \ell) e^{\left[-2\pi \mathbf{i} (\mathbf{h} \mathbf{x} + k \mathbf{y} + \ell z)\right]} d\mathbf{y}$$
$$= \frac{1}{A_{b}} \Sigma \Sigma F(\mathbf{h} k \ell) e^{\left[-2\pi \mathbf{i} (\mathbf{h} \mathbf{x} + \ell z)\right]} \int_{0}^{1} e^{\left(-2\pi \mathbf{i} k \mathbf{y}\right)} d\mathbf{y} \qquad [3.68]$$

where A_{b} is the area of the projection. Since the integral is 0 except when k = 0,

$$\sigma(\mathbf{x}, \mathbf{z}) = \frac{1}{A_b} \sum_{h \ \ell} F(h0\ell) e^{\left[-2\pi \mathbf{i} \left(h\mathbf{x} + \ell \mathbf{z}\right)\right]} .$$
 [3.69]

Equations [3.69] and [3.66] could be solved completely if the magnitudes and phases of the structure factors F(hkl) could be measured. The scattered intensity is proportional to the product of the structure factor and its complex conjugate (see Equation [3.14]), and consequently only the magnitude of F(hkl) can be determined experimentally. However, it has been shown in the section 1 that the magnitudes of the atomic separations in a liquid can be found from the measured intensity. Patterson (36) introduced a method of deriving the interatomic vectors in a crystal, using only the intensities of the Bragg peaks. The periodicity of the crystal is included in the Patterson function, which is analogous to an oriented radial distribution function, and the directions of the interatomic vectors can be found in addition to their magnitudes.

Patterson proposed the function,

$$P(u,v,w) = V \iiint_{000}^{111} \sigma(x,y,z) \cdot \sigma(x+u, y+v, z+w) dx dy dz .$$
 [3.70]

Substituting the values for the electron density from [3.66] in [3.70]

$$P(u,v,w) = \frac{1}{V} \iiint_{000}^{111} \sum_{hk\ell} \sum_{h'k'\ell'} F(hk\ell) e^{\left[-2\pi i(hx + ky + \ell z)\right]} \cdot F(h'k'\ell')$$
$$e^{\left[-2\pi i(h'x + k'y + \ell'z)\right]} e^{\left[-2\pi i(h'u + k'v + \ell'w)\right]} dxdydz. [3.71]$$

The right hand side of Equation [3.71] equals zero except when h = -h', k = -k', $\ell = -\ell'$, then

$$P(u,v,w) = \frac{1}{V} \sum_{h \neq l} \sum_{h \neq l} F(hkl) \cdot F(hkl) e^{[2\pi i (hu + kv + lw)]}.$$
 [3.72]

In Equation [3.72] F(hkl) and F(hkl) are complex conjugates; therefore,

$$P(u,v,w) = \frac{1}{V} \sum_{h \neq l} F(hkl) \cdot F^{*}(hkl) e^{2\pi i (hu + kv + lw)} . \qquad [3.73]$$

Equation [3.73] involves the product, $F(hkl) \cdot F^*(hkl)$, which is exactly the experimentally observed quantity. P(u, v, w) will only have large values at positions ($\vec{ua} + v\vec{b} + w\vec{c}$) corresponding to vectors in the unit cell connecting regions of high electron density. The techniques for interpreting this function have been well reviewed [(37), Chapter 14].

The usual method for finding the phase of F(hkl) is to calculate a set of structure factors, $F_c(hkl)$, for a reasonable model structure derived from a Patterson function, with atoms at x_i , y_i , z_i ,

$$F_{c}(hkl) = k \sum_{j=1}^{N} f_{j}(hkl)T_{j}(hkl) e^{[2\pi i(hx_{j} + ky_{j} + lz_{j})]} [3.74]$$

where k is a scale factor. T_j has been defined in Equation [3.3] for the isotropic motion of the nuclei. In a crystal it is possible to have anisotropic motion, in which case Equation [3.3] can be written,

$$T_{j} = e^{\left[-\frac{B_{j}}{4} \left(\frac{2\sin\theta}{\lambda}\right)^{2}\right]} = e^{\left[-\frac{B_{j}}{4} \left(|\vec{S}|^{2}\right)\right]}.$$
[3.75]

Substituting the value of B_i in Equation [3.75] gives,

$$T_{j} = e^{\left[-2\pi^{2}\bar{\mu}_{j}(|\vec{s}|^{2})\right]} = e^{\left[-2\pi^{2}(|\vec{s}|\cdot\bar{\mu}_{j}\cdot|\vec{s}|)\right]}$$
[3.76]

where $\bar{\bar{\mu}}_{j}$ is a dyad describing the mean displacement of the nucleus of the jth atom.

The model can be tested by calculating an agreement index, R, which compares the $|F_{c}(hkl)|$ with $|F_{o}(hkl)|$. Two values of R are quoted in this thesis,

$$R_{1} = \frac{\Sigma[|F_{o}(hk\ell)| - |F_{c}(hk\ell)|]}{\Sigma|F_{o}(hk\ell)|}$$
[3.77]

and

$$R_{2} = \left[\frac{\Sigma w [|F_{0}(hk\ell)| - |F_{c}(hk\ell)|]^{2}}{\Sigma w |F_{0}(hk\ell)|^{2}}\right]^{1/2}$$
[3.78]

where w in Equation [3.78] is a weighting factor. When changes are made to a model a decreasing value of R_1 , or R_2 , for a fixed number of variables, is indicative of a better fit between $|F_0(hkl)|$ and $|F_c(hkl)|$. R_1 is quoted in the preliminary stages of refining a model structure, and R_2 is used when the refinement is almost complete. R_2 has the advantage of including a weighting factor, which is calculated to reflect the precision of each intensity measurement. Since each intensity is measured only once, a number of weighting schemes have been proposed which depend on $|F_0(hkl)|$ alone. The one used in this study was introduced by Cruickshank (38),

$$w = (A + B|F_0| + C|F_0|^2)^{-1}$$
[3.79]

where A, B, C are constants, which are chosen so that for groups of structure factors of the same order of magnitude, the average value of $w[|F_0(hk\ell)| - |F_c(hk\ell)|]^2$ is approximately constant.

A three-dimensional electron density, or one of its projections, can be calculated using the structure factors of those reflections for which $|F_0(hkl)|$ agrees reasonably well with $|F_c(hkl)|$. The calculated phase is applied to the observed magnitude. These functions may suggest improvements in the model, and the whole procedure can be repeated.

An extremely useful method for improving a promising model structure is to calculate a difference electron density. The coefficients in Equation [3.66] are set equal to $[|F_0(hkl)| - |F_c(hkl)|]$, where the phase of $F_0(hkl)$ is assumed to be the same as $F_c(hkl)$. The contributions to the electron density of all the atoms in the original model are removed in the $(F_0 - F_c)$ function. This function also has the advantage of eliminating series termination error. The features observed in a difference electron density may indicate either coordinate shifts for atoms in the original model or the positions of new atoms to be included in the model.

A very powerful method for refining the parameters of model structures is based on least squares analysis. The basic principle of the method involves systematically varying the atomic parameters in the calculated structure factor expression, Equation [3.74], in order to minimize the function,

$$A = \sum_{hk\ell} w_{hk\ell} (|F_0| - |kF_c|)^2$$
[3.80]

where w is the weight assigned to an observation, and k is a scaling factor. F_c is a function of n independent parameters p_1 , p_2 , p_3 ,..., p_n , and A is minimized by differentiation with respect to each of these parameters in turn, and by setting the derivatives equal to zero,

 $\sum_{hkl} w_{hkl} [|F_0| - |kF_c(p_1, p_2, p_3, \dots, p_n)|] \frac{\partial |kF_c(p_1 \dots p_n)|}{\partial p_j} = 0 [3.81]$ where j = 1, n.

 $|F_c|$ is expanded as a Taylor series neglecting the second and higher terms so that,

$$|\mathbf{kF}_{c}(\mathbf{p}_{1}\ldots\mathbf{p}_{n})| = |\mathbf{kF}_{c}(\mathbf{a}_{1}\ldots\mathbf{a}_{n})| + \frac{\partial|\mathbf{kF}_{c}|}{\partial \mathbf{p}_{1}}\Delta \mathbf{p}_{1} + \ldots + \frac{\partial|\mathbf{kF}_{c}|}{\partial \mathbf{p}_{n}}\Delta \mathbf{p}_{n}$$
 [3.82]

where $a_1...a_n$ are the approximate values of $p_1...p_n$, and $p_j = p_j - a_j$. Substituting Equation [3.82] into [3.81] gives,

$$\sum_{hk\ell} w_{hk\ell} [|F_0| - |kF_c(a_1...a_n)| - \frac{\partial |kF_c|}{\partial p_1} \Delta p_1... - \frac{\partial |kF_c|}{\partial p_n} \Delta p_n] \frac{\partial |kF_c|}{\partial p_j}$$

= 0 [3.83]

where j = 1, n, or

$$\sum_{hk\ell} w_{hk\ell} \left[\Delta F - \frac{\partial |kF_c|}{\partial p_1} \Delta p_1 - \dots - \frac{\partial |kF_c|}{\partial p_n} \Delta p_n \right] \frac{\partial |kF_c|}{\partial p_j} = 0 \quad [3.84]$$

where j = 1, n, and ΔF is the difference $(|F_0| - |kF_c|)$.

If Equation [3.84] is expanded and rearranged a set of n equations in

n unknowns are obtained of the type,

$$\sum_{hk\ell}^{\Sigma} w_{hk\ell} \left(\frac{\partial |kF_c|}{\partial p_1} \right)^2 \Delta p_1 + \sum_{hk\ell}^{\Sigma} w_{hk\ell} \frac{\partial |kF_c|}{\partial p_1} \cdot \frac{\partial |kF_c|}{\partial p_2} \Delta p_2 \dots$$

$$+ \sum_{hk\ell}^{\Sigma} w_{hk\ell} \frac{\partial |kF_c|}{\partial p_1} \frac{\partial |kF_c|}{\partial p_n} \Delta p_n = \sum_{hk\ell}^{\Sigma} w_{hk\ell} \Delta F \frac{\partial |kF_c|}{\partial p_1}$$
[3.85]

These equations may be solved, and the calculations can be repeated until the changes in Δp_j , between successive calculations, are small compared to the value of p_j .

Experimental Methods

The diffraction patterns, produced by the interaction of a beam of X-rays with a crystal, can be recorded on photographic film. Special cameras, which are designed to photograph selected reciprocal lattice planes, are used. The Weissenburg camera photographs planes parallel to the incident X-ray beam, and the precession camera photographs the planes which are perpendicular to the incident beam. The dimensions, and many of the symmetry properties, of the unit cell can be found directly from the geometry of the diffraction patterns.

In order to obtain values for $|F_0(hkl)|$ the observed intensities I(hkl) have to be corrected for certain instrumental effects.

(i) Lorentz correction L.

L compensates for the variable time required for different reciprocal lattice points to move through their reflecting position, and is dependent on the camera geometry [(37), Chapter 7].

(ii) Polarization correction P.

P corrects for the fact that not all directions of polarization

of the X-rays in the incident beam are scattered from the crystal with equal efficiency. P is independent of the camera geometry, and has the form, $1/P = 2/(1 + \cos^2 2\theta)$.

These two corrections are usually combined for a particular camera geometry,

 $I_{c}(hkl) = I(hkl) / L.P.$ [3.86]

Systematic errors such as absorption and primary and secondary extinction, cannot always be treated in a straight-forward manner; therefore the experimental conditions are chosen to minimise their effects. If the linear absorption coefficient is calculated for the molecule being studied, it is possible to select a crystal of such a size that the absorption correction can be ignored. The effects of primary and secondary extinction can be minimised by choosing a small crystal which has a reasonable mosaic spread.

CHAPTER 4

The Crystal Structure of Tetraselenium Bis-Hydrogen Disulphate

Introduction

This chapter describes the procedures followed to solve and refine the crystal structure of tetraselenium bis-hydrogen disulphate. The basic cation structure was determined from intensities measured photographically. However, in order to refine the structure completely, a set of intensities had to be obtained with a diffractometer.

Experiments

The diffraction patterns of several crystals of Se₄(HS₂O₇)₂, which were wet with mother liquor and mounted in thin-walled capillary tubes, were recorded photographically. Weissenburg photographs of the hOl, hll and h2l planes, using Mo K_a radiation and precession photographs of the Okl and hkO planes, using Cu K_a radiation, were sufficient to give the crystal symmetry, and unit cell dimensions.

The density of the compound was measured with a pycnometer, using Fluorolube M0.10 oil as the displaced liquid.

These results are summarised in Table 4.1.

Photographic Measurement of Intensities

Integrated equi-inclination Weissenburg photographs of the hOl, hll and h2l planes of a crystal wet with mother liquor, and mounted with its needle (\vec{b}) axis parallel to the goniometer axis, were taken using Cu K_a

Table 4.1

Crystal Data for Se4 (HS207)2

Formula Weight	670.1
System	Monoclinic
Systematic Absences	hOl lodd
	0k0 k odd
Space group	$P2_1/c$ (no. 14, C_{2h}^5)
Density Measured	3.1(1) g/cm^3
Number of formula units/unit cell	2
Mo K_{α} Wavelength	0.70926 Å
Cu K _a Wavelength	1.54184 Å

Ce11	Constants	Preliminary Parameters	Accurate Parameters
	→ a	7.66 ± 0.05 Å	7.721 ± 0.002 Å
	Ď	5.90 ± 0.05 Å	5.606 ± 0.002 Å
	č	17.10 ± 0.08 Å	17.202 ± 0.007 Å
	β	108.8 ± 0.05°	109.78 ± 0.02°
Ce11	Volume	731.6 Å ³	700.64 Å ³
Calcu	lated Density	3.05 g/cm^3	3.17 g/cm^3

radiation. Three films were loaded simultaneously into the cassette, and the exposure times were selected to be integral numbers of the integration cycle. All the films were developed under identical conditions.

The intensities of the Bragg peaks were measured using a Joyce-Loebel double beam micro-densitometer. The intensities of about ten of the more reliable reflections for each film of a given layer were compared, so that all the intensities could be put on a common scale.

When the intensities of equivalent reflections were compared, sizeable absorption effects were noticed. An attempt was made to explain this effect by absorption in the capillary tube. The correction factors which were computed did not compensate for the difference in the intensities. Therefore, the intensities were only recorded from the half of the film showing the least absorption, and averaging equivalent reflections was not attempted. The measurements were corrected for Lorentz and polarisation effects using the programme WEILPC 6400.

Solution of the Structure

An (010) Patterson projection was calculated using the intensities of the 102 hOl reflections which had been measured. This was used to give the x and z coordinates of two selenium and two sulphur atoms. Since the space group is $P2_1/c$ and there are two molecules in the unit cell, the Se_4^{2+} ion must either be centred on a centre of symmetry, and be square planar, or be in the form of a spiral about a 2_1 axis.

The y coordinates for the two possible models were calculated imposing the conditions that the diagonals of a square are equal, and all Se-Se bonds are the same length in the spiral structure. The calculated y coordinates are given in Table 4.2.

Table 4.2

Calculated y Coordinates for the Se_4^{2+} Cation

	^y square	^y spiral
Se(1)	0.290	0.0
Se(2)	0.524	0.27
Bond lengths		
Se(1) - Se(2)	2.26 Å	2.42 Å
Se(1) - Se'(2)*	2.38 Å	2.42 Å

Se'(2) is the selenium atom related by the centre of symmetry in the square planar model, and the atom translated by half the y unit cell coordinate for the spiral model.

The square planar model was selected as being the more reasonable one on the basis of the bond lengths, since the Se bond length in the element is 2.34 Å. (39)

Estimates of the sulphur y coordinates were calculated by considering the overall packing of the molecular units in the cell. An (010) electron density projection was calculated using the phases calculated from these approximate Se and S coordinates. From this, reasonable positions for five oxygen atoms were obtained. Least squares refinement of the positional and isotropic temperature factors for these nine atoms gave an agreement index $R_1 = 0.19$.

Any attempts to refine the structure with the upper layer data failed. A complete refinement of the structure did not prove possible, due to the small number and unreliable nature of the intensity measurements.

The final coordinates of the selenium atoms found from this photographic study are given in Table 4.3. (40)

Table 4.3

Coordinates for the Se_4^{2+} Cation

	x	У	Z
Se(1)	0.072	0.280	0.062
Se(2)	0.202	0.52	-0.01
lengths			

Bond

Se(1) - Se(2)	2.24 Å
Se(1) - Se(2)	2.38 Å

2.32 Å Average Se-Se bond length

Diffractometer Measurement of Intensities

A cylindrical crystal 0.3 mm in length and 0.07 mm in diameter, free from mother liquor and sealed in a capillary tube, was mounted on a G.E. XRD-6 diffractometer, such that the needle axis (\vec{b}) was coincident with the ϕ axis of the quarter-circle goniometer. Accurate angular setting parameters were found for 24 of the more intense reflections with 5 < 20 < 40°, using Mo K_{α} radiation. These settings were used to refine the approximate cell dimensions by least-squares, and the values obtained, which are listed in Table 4.1, were used to calculate the angular settings for all the reflections with $2\theta \leq 45.0^{\circ}$. All the calculations were performed on a CDC 6400 computer, using the

components of the XRAY67 system.

The reflections in the range $2.5 \le 20 \le 30.0^{\circ}$ were recorded with a symmetric 0/20 scan of 2.25° at a scan rate of 2° /minute, while those in the range $30.0 \le 20 \le 45.0^{\circ}$ were recorded in a similar manner at 1° /minute. Stationary 40 second background counts were taken at the extremes of the 20 scan for each reflection. Zirconium filtered Mo K_{α} radiation was used for all the intensity measurements. Five standard reflections, chosen to be randomly distributed in the sphere of reflection with $20 \le 40.0^{\circ}$, were recorded after every 100 measurements to monitor the stability of the crystal and the generator. Since no time dependent trend was observed, the maximum intensity variation being of the order of 3° , all intensity measurements were put on a common scale. The linear absorption coefficient for $Se_4(HS_2O_7)_2$ for Mo K_{α} radiation is 11.2 mm^{-1} . Since the crystal was very small ($\mu r = 0.4$), and mounted with its needle axis perpendicular to the X-ray beam, no absorption correction was deemed necessary.

A total of 1967 reflections with $\sin\theta/\lambda < 0.54$ were measured and the recorded intensities corrected for background, Lorentz and polarization effects. A standard deviation (σ) was calculated for each intensity from the formula,

$$\sigma = [I - K(B_1 + B_2)(1 - K)]^{1/2}$$

where I = total integrated intensity

 B_1 and B_2 = the two background counts

K = counting time for I/counting time for $(B_1 + B_2)$.

Equivalent reflections were then combined to give a total of 985

reflections of which the 552 that had I > 3σ were used in the structure determination and refinement.

Solution and Refinement of the Structure

The positions and estimated temperature factors of the selenium atoms found in the photographic determination were refined by three cycles of full matrix least squares to give $R_1 = 0.33$. A threedimensional Fourier map then revealed the positions of the sulphur atoms. A further three cycles of refinement reduced R_1 to 0.20. Seven peaks in the vicinity of the sulphur atoms found in the subsequent threedimensional Fourier maps were assigned to oxygen atoms. Three cycles of least-squares refinement allowing the positional coordinates and isotropic temperature factors of all atoms to vary, reduced R_1 to 0.072.

At this point the structure was allowed to refine with anisotropic temperature factors to give $R_1 = 0.066$. Although the anisotropic temperature factors do not represent a significant improvement over the isotropic ones, according to Hamilton's significance test (41), they can be interpreted in terms of a physically reasonable model, and are included in Table 4.5. A final refinement was performed with the weighting scheme introduced by Cruickshank (38),

$$w = [6.00 - 0.08F_0 + 0.001 F_0^2]^{-1}$$

to give $R_2 = 0.060$. The final value of R_1 including all 985 reflections was 0.097.

The atomic scattering curves for Se, S, and O were taken from the International Tables for X-ray Crystallography (25) and the values for Se and S were corrected for the imaginary dispersion term. All computations were performed on a CDC 6400 computer using the least squares programme ORFLS and the Fourier programme FOURR-A of the XRAY 67 system.

A final difference Fourier map was calculated in an attempt to find the hydrogen atom. The map was essentially featureless, the highest peaks having values of the order of $0.2 - 0.3 \text{ e/A}^3$, but none of these were in a position that could be interpreted chemically as a hydrogen atom.

The observed structure amplitudes, $|F_0|$, and final calculated structure factors, F_c , are listed in Table 4.4. The final positional and thermal parameters for all atoms are listed in Table 4.5.

TABLE 4.4

Observed and Calculated Structure Factors in $Se_4(HS_2O_7)_2$.

FORS FCALC	FORS FCALC	FORS FEALC	FORS FCALC	FORS FCALC	FORS FCALC	FORST FCALC	FORS PEALS

Reflections for which I < 3σ *

\$

0000

Estimated Standard deviations in the final figures quoted are given in parentheses. The expression used to calculate the temperature effects is

 $\exp[-2\pi^{2}(U_{11}h^{2}a^{*2} + U_{22}k^{2}b^{*2} + U_{33}\ell^{2}c^{*2} + 2U_{12}hka^{*}b^{*}\cos\gamma^{*} + 2U_{13}h\ell a^{*}c^{*}\cos\beta^{*} + 2U_{23}k\ell b^{*}c^{*}\cos\alpha^{*})]$

Atom	x	у	Z	$U_{11}(Å^2)$	U ₂₂ (Å ²)	U ₃₃ (Å ²)	U ₁₂ (Å ²)	U ₁₃ (Å ²)	U ₂₃ (Å ²)
Se(1)	0.0730(4)	0.2777(5)	0.0620(2)	0.0309(15)	0.0307(15)	0.0320(14)	0.0036(18)	0.0080(12)	0.0076(14)
Se(2)	0.2013(4)	0.5258(5)	-0.0085(2)	0.0280(15)	0.0366(15)	0.0335(14)	0.0003(18)	0.0122(12)	0.0060(12)
S(1)	0.6031(8)	0.0404(11)	0.1158(4)	0.021(3)	0.026(3)	0.020(3)	0.000(3)	0.002(3)	0.001(4)
S(2)	0.7924(8)	0.3398(11)	0.2529(4)	0.027(3)	0.022(3)	0.028(3)	-0.002(3)	0.010(2)	0.000(3)
0(1)	0.748(2)	0.068(3)	0.082(1)	0.049(9)	0.039(10)	0.040(8)	-0.013(14)	0.020(8)	-0.005(14)
0(2)	0.536(2)	-0.198(3)	0.119(1)	0.053(9)	0.032(10)	0.036(8)	-0.010(12)	0.015(7)	0.005(10)
0(3)	0.466(2)	0.221(3)	0.090(1)	0.033(9)	0.031(9)	0.048(8)	0.019(5)	-0.014(12)	0.001(12)
0(4)	0.701(2)	0.091(3)	0.217(1)	0.036(8)	0.031(7)	0.030(12)	-0.004(15)	0.008(14)	-0.002(15)
0(5)	0.902(3)	0.430(3)	0.209(1)	0.048(9)	0.047(12)	0.037(8)	-0.022(15)	0.017(8)	0.001(12)
0(6)	0.874(2)	0.298(3)	0.342(1)	0.052(12)	0.039(10)	0.024(12)	-0.009(15)	0.012(15)	-0.014(8)
0(7)	0.629(3)	0.516(3)	0.244(1)	0.056(9)	0.028(11)	0.044(9)	0.014(5)	0.027(10)	0.004(8)

TABLE 4.5

Atomic Positional and Temperature Parameters for $Se_4(HS_2O_7)_2$.

CHAPTER 5

Description of the Structure of Tetraselenium Bis-Hydrogen Disulphate

1. General Description

The bond lengths and angles for $Se_4(HS_2O_7)_2$ are given in Tables 5.1 and 5.3. The four selenium atoms lie close to each other at the corners of a square centred on a centre of symmetry, as shown in Figure 5.1. This square is surrounded by a rectangle of four oxygen atoms from four different $HS_2O_7^-$ groups in such a way that all eight atoms lie in a single plane whose equation determined by least squares is given in Table 5.2. Each of these oxygen atoms has two selenium neighbours at distances of about 2.72 Å and 2.91 Å. These comparatively long Se-0 distances are very much longer than those of 1.635 Å found in $SeO_4^{2^-}(42)$, suggesting that the bonding between the selenium and oxygen atoms is primarily ionic, and that the compound should be formulated $Se_4^{2^+}(HS_2O_7)_2^{-}$.

2. The Se_4^{2+} Ion

The Se₄²⁺ ion has mean Se-Se bonds of length 2.283 (4) Å, and is, within experimental error, a square of D_{4h} symmetry, even though the only symmetry required by the crystal is C_i . The tensors describing the thermal motions of the selenium atoms have their maximum values, corresponding to an r.m.s. displacement of 0.20 Å, along the normal to the square and their minimum values (0.16 Å) along the lines from the selenium atoms to the centre of the square. One model which can account for these observations assumes that the square is rigid with its three

Table 5.1

Bond Distances and Angles around the Selenium Atoms in $Se_4(HS_2O_7)_2$

The primed atoms are related to the unprimed ones by inversion through the centre of symmetry at the centre of the Se_4^{2+} ion.

Bond (Å)	Uncorrected	Corrected	Bond angle (degrees)	
Se(1)-Se(2)	2.280(4)	2.287	Se(2)-Se(1)-Se(2)'	90.1(2)°
Se(1)-Se(2)'	2.286(4)	2.294	Se(1)-Se(2)-Se(1)'	89.9(2)°

Bond (Å)	
Se(1)-0(1)	2.89(2)
Se(1)-0(3)	2.93(2)
Se(1)-0(5)	3.33(2)
Se(2)-0(1)'	2.69(2)
Se(2)-0(3)	2.75(2)
Se(2)-0(2)	3.17(2)
Se(2) - 0(5)	3.27(2)

Table 5.2

Equation of the Plane of the Se_4^{2+} Ion

Equation of the plane of the Se₄²⁺ ion referred to orthogonal axes with \vec{x} (in Å) parallel to \vec{a} , \vec{y} (in Å) parallel to \vec{b} and the origin at the centre of the ion.

$$0.010\vec{x} + 0.629\vec{y} + 0.779\vec{z} = 0$$

Distances in Å of atoms from the plane

 Se (1)
 0
 0(1)
 -0.521

 Se (2)
 0
 0(3)
 +0.176



Figure 5.1. The Se_4^{2+} ion and its Environment.

translational components of thermal motion equal (0.16 Å). It is librating in its own plane with an r.m.s. amplitude of 3.2° and is also librating around its diagonals with an r.m.s. amplitude of 4.5° . In an alternative model the translational component of the thermal motion normal to the square is assumed to be larger than that in the plane, and the amplitude of libration around the diagonals is correspondingly reduced. Depending on the particular model chosen, a correction for thermal motion of between 0.004 Å and 0.011 Å must be made to the Se-Se bond length, resulting in the true Se-Se distance lying between 2.287 and 2.294 Å. This length is significantly less than that of 2.34 (2) Å found in the Se₈ molecule (39), indicating some degree of multiple bonding. This result is predicted by a valence bond description of the bonding, which would involve resonance structures of the type,



giving a net bond order of 1.25 for each Se-Se bond.

Alternatively the structure can be described in terms of a simplified molecular orbital theory. The principal assumptions in this method are:

(i) the presence of a closed-shell electron configuration is a

necessary condition for stability;

(ii) the characters of the occupied molecular orbitals can be determined by the s and p orbitals alone. The d atomic orbital contribution may be significant, but probably plays a secondary role in determining the geometry.

The three most symmetrical geometries for an X_4 molecule are linear $(D_{\alpha h})$, square planar (D_{4h}) , and tetrahedral (T_d) . The characters of the occupied molecular orbitals can be derived in the following manner, e.g. square planar geometry.



Diagram 1 shows the coordinate system used in the calculations and defines the three C_2 axes.

The four selenium atoms each contribute four atomic orbitals, the 3s, $3p_x$, $3p_y$, $3p_z$, making a total of 16 atomic orbitals.

The character table for the D_{4h} symmetry group is given below.

	E	2C4	C ₂	2C2	2C''	i	2S ₄	$^{\sigma}h$	$2\sigma_{\rm v}$	$2\sigma_{d}$
A _{lg}	1	1	1	1	1	1	1	1	1	1
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B _{1g}	. 1	-1	1	1	-1	1	-1	1	1	-1
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1
Eg	2	0	-2	0	0	2	0	-2	0	0
A _{lu}	1	1	1	1	1	-1	-1	-1	-1	-1
A _{2u}	. 1	1	1	-1	-1	-1	-1	-1	1	1
B _{lu}	1	-1	1	1	-1	-1	1	-1	-1	1
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
Eu	2	0	-2	0	0	-2	0	2	0	0

The characters of the reducible representations of the 16 molecular orbitals, Γ_{MO} , can be derived by assuming that 3 orbitals on each atom are in the xy plane, and the fourth orbital is perpendicular to this plane (π orbital). The in-plane orbitals consist of 2 σ bonding orbitals, directed along the internuclear axes, and a lone pair orbital directed along either the x or y axis. The reducible representation of the in plane orbitals, Γ_{MO}^{I} , and the out of plane orbitals, Γ_{MO}^{O} , can be found by summing the number of orbitals which remain unshifted when each of the symmetry elements of the D_{4h} group are applied to the molecule. The results are summarised below.

	Е	2C4	C ₂	2C2	2C2	i	$2S_4$	$^{\sigma}h$	$2\sigma_v$	$2\sigma_{d}$
г <mark>I</mark> MO	12	0	0	2	0	0	0	12	2	0
г <mark>0</mark> MO	4	0	0	-2	0	0	0	-4	2	0

The number of times each irreducible representation (a_i) of the D_{4h} group occurs in the reducible representations can be found from the relationship,

$$a_{i} = \frac{1}{h} \sum_{R} \chi(R) \chi_{i}(R)$$
[5.1]

where h = order of the group;

 $\chi(R)$ = character of the Rth reducible representation; and

 $\chi_i(R)$ = character of the Rth irreducible representation. The irreducible representations of the in plane orbitals, Γ_{MO}^{I} , are derived below,

 $A_{1g} = \frac{1}{16} (12 + 4 + 12 + 4) = 2$ $A_{2g} = \frac{1}{16} (12 - 4 + 12 - 4) = 1$ $B_{1g} = \frac{1}{16} (12 - 4 + 12 - 4) = 2$ $B_{2g} = \frac{1}{16} (12 - 4 + 12 - 4) = 1$ $E_{u} = \frac{1}{16} (24 + 24) = 3$

therefore,

$$\Gamma_{MO}^{1} = 2A_{1g} + A_{2g} + 2B_{1g} + B_{2g} + 3E_{u}$$

By similar reasoning it can be shown that the irreducible representations of the out of plane orbitals, $\Gamma^0_{MO},$ are,

$$\Gamma_{MO}^{0} = A_{2u} + B_{2u} + E_{g}$$
.

If it is assumed that the σ and lone pair orbitals are largely localised, the reducible representations of the σ orbitals, Γ_{σ} , and lone pair orbitals, Γ_{lp} , can be found as before,

	Е	2C4	C ₂	2C2	2C2	i	2S ₄	σ _h	$2\sigma_v$	$2\sigma_{d}$
Гlр	4	0	0	2	0	0	0	4	2	0
Γσ	4	0	0	0	2	0	0	4	0	2

The irreducible representations are therefore,

$$\Gamma_{\sigma} = A_{1g} + B_{2g} + E_{u}$$

$$\Gamma_{1p} = A_{1g} + B_{1g} + E_{u}$$

The σ and lone pair orbitals can accommodate 16 electrons; any remaining electrons will fill the π type orbitals. The relative energies of these orbitals can be calculated using simple Hückel theory.

The energy, ε_i , of a π molecular orbital ψ_i , is given by the expression,

$$\varepsilon_{i} = \int \psi_{i} H \psi_{i} d\tau \qquad [5.2]$$

Since a molecular orbital can be expressed as a linear combination of atomic orbitals ϕ_i , Equation [5.2] can be written

$$\varepsilon_{i} = \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} \int \phi_{\mu} H \phi_{\nu} d\tau \qquad [5.3]$$

where $C_{\mu i}^{}$, $C_{\nu i}^{}$ are the coefficients of the atomic orbitals $\phi_{\mu}^{}$ and $\phi_{\nu}^{}$. Equation [5.3] can be separated into two terms,

$$\varepsilon_{i} = \sum_{\mu} C_{\mu i}^{2} \int \phi_{\mu} H \phi_{\mu} d\tau + \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} \int \phi_{\mu} H \phi_{\nu} d\tau \qquad [5.4]$$

The first term in Equation [5.4] represents the energy of the individual atomic orbitals. If all of these are identical, as in Se_4^{2+} , this contribution to the energy is represented by the constant α . The second term

represents the interaction energy of orbitals on different atoms, and according to the Hückel approximation, this term only has a finite value when ϕ_{μ} and ϕ_{ν} are on adjacent atoms. If all the atoms are identical the integral is represented by the constant β . Therefore Equation [5.4] can be written,

$$\varepsilon_{i} = \alpha + \sum_{\mu} \sum_{\nu} C_{\mu i} C_{\nu i} \beta.$$
 [5.5]

The coefficients in Equation [5.5] can be found directly because of the high symmetry of the molecule. The relative energies of the π molecular orbitals are shown in Diagram 2.





In the same way it can be shown that the characters of the σ , π , and lone pair orbitals for T_d and D_{α h} symmetry are,

$$T_{d} \qquad D_{\alpha h}$$

$$\Gamma_{\sigma} = A_{1} + E + T_{2} \qquad \Gamma_{\sigma} = 2\sigma_{g} + \sigma_{u}$$

$$\Gamma_{1p} = A_{1} + T_{2} \qquad \Gamma_{\pi} = \pi_{g} + \pi_{u}$$

$$\Gamma_{1p} = \sigma_{u} + \sigma_{g}$$

The application of the closed shell criteria predicts that a stable tetrahedral molecule, e.g., P₄, would have 20 valence electrons, and a stable linear molecule 18 valence electrons. A stable square planar molecule could have 18, 22, or possibly 24 valence electrons. Corbett (43) has calculated the energies of the π molecular orbitals for D_{4h} symmetry as a function of an overlap parameter. The results indicate that the E_g orbitals are essentially non-bonding in the region of high overlap, while the B_{2u} orbitals are quite strongly anti-bonding suggesting that the 24 electron configuration would in fact be unstable.

According to this theory $Se_4^{2^+}$ with 22 electrons is expected to be square planar, with 6π type electrons occupying the A_{2u} and E_g levels, giving the molecule an additional stabilization, or resonance, energy of 4β (assuming $\alpha = 0$). These six electrons, according to simple Hückel theory, constitute an aromatic sextet, and provide a M.O., π bond order of 0.5. The M.O. bond order between two atoms is defined as the sum of the products of the coefficients of the atomic orbitals of the two atoms in each of the occupied M.O.'s, each product being weighted with the number of electrons occupying the M.O.

The intense yellow-orange colour of the Se_4^{2+} ion ($\lambda_{max} = 410$ nm, $\varepsilon = 8000$ moles/litre) is to be expected from the dipole allowed excitation of an electron from the highest filled π orbital, which is of symmetry E_g and almost non-bonding, to the lowest empty π orbital (B_{2u}). The results of magnetic circular dichroism experiments on solutions of selenium in disulphuric acid are consistent with this interpretation of the U.V. spectrum (44).

The infra-red and Raman spectra of the Se_4^{2+} ion have been studied,

both in crystalline solids and in solution (45). A force constant of 2.2 mdyn/Å was calculated for the Se-Se bond using a Urey-Bradley force field. This compares to a value of 3.498 mdyn/Å for the Se₂ molecule which contains an Se-Se double bond (bond length 2.1661 Å (46)), and 1.674 mdyn/Å for (CF_3)₂Se₂ which is an example of an Se-Se single bond (bond length 2.33(3) Å (47)). The intermediate value for the Se₄²⁺ ion is consistent with some degree of double bonding.

3. The HS_2O_7 Ion

The dimensions of the $HS_2O_7^-$ anion are listed in Table 5.3, and are shown in Figure 5.2. The long S(2)-O(7) bond (1.56 Å) and the short intermolecular distance between O(7)-O(2) (2.57 Å) suggest that the anions are hydrogen bonded into chains along the \vec{b} axis, with the hydrogen atom attached to O(7), as shown in Figures 5.3 and 5.4.

The tensors describing the thermal motion of the HS_2O_7 ion in Se₄(HS_2O_7)₂ are consistent with a rigid ion librating with an r.m.s. amplitude of 3 to 4° around the axes perpendicular to the S—S vector and about 8° around the axis parallel to this vector (each axis passing through the centres of mass), together with an isotropic translational motion with r.m.s. displacements of 0.14 Å. This results in corrections to the bond lengths between 0.006 and 0.026 Å (see Table 5.3).

With the exception of S(2) = O(7), the terminal S=0 bonds have an average uncorrected bond length of 1.43 Å. S(1) = O(1) and S(1) = O(3) are not significantly lengthened by coordination to the Se₄²⁺ ion.

Two interesting features of the anion structure are the significant difference in the lengths of the two bridging bonds (1.59(2) Å and)
Table 5.3

Bond Distances and Angles for the HS_2O_7 Ion in $Se_4(HS_2O_7)_2$

The twist angle is defined as the average of the three smallest angles occurring between the projections of opposite S-0 bonds onto the plane perpendicular to S(1)-S(2).

Bond	(Å)	Uncorrected	Corrected	Bond Angle	(degrees)
S(1)-	-0(1)	1.44(2)	1.45	0(4) - S(1) - 0(1)) 105(1)
S(1)-	-0(2)	1.44(2)	1.46	0(4) - S(1) - 0(2)) 99(1)
S(1)-	-0(3)	1.42(2)	1.45	0(4) - S(1) - 0(3)) 104(1)
S(1)-	-0(4)	1.67(2)	1.67	0(2) - S(1) - 0(3)) 116(1)
S(2)-	-0(4)	1.59(2)	1.60	0(2) - S(1) - 0(1)) 117(1)
S(2)-	-0(5)	1.41(2)	1.42	0(1)-S(1)-0(3) 113(1)
S(2)-	-0(6)	1.46(2)	1.47	0(4)-S(2)-0(5) 112(1)
S(2)-	-0(7)	1.56(2)	1.58	0(4)-S(2)-0(6) 104(1)
				0(4)-S(2)-0(7) 106(1)
0(1)-	-0(2)	2.46(4)		0(5)-S(2)-0(6) 120(1)
0(1)-	-0(3)	2.37(4)		0(5)-S(2)-0(7) 109(1)
0(1)-	-0(4)	2.48(4)		0(6)-S(2)-0(7) 105(1)
0(2)-	-0(3)	2.43(4)			
0(2)-	-0(4)	2.39(4)		S(1)-0(4)-S(2) 123(1)
0(3)-	-0(4)	2.46(4)			
0(5)-	-0(4)	2.49(4)		Twist Angle	14(2)
0(5)-	-0(6)	2.48(4)			
0(5)-	-0(7)	2.44(4)			
0(6)-	-0(4)	2.38(4)			
0(6)-	-0(7)	2.40(4)			
0(4)-	-0(7)	2.48(4)			
S(1)-	-S(2)	2.86(2)			
0(1)-	-0(5)	2.90(2)			
0(3)-	-0(7)	2.99(2)			
0(7)-	-H0	(2) 2.57(2)			





Figure 5.3. Projection of $Se_4(HS_2O_7)_2$ down \vec{c} .



1.67(2) Å), the shorter bond being associated with the sulphur atom which has the long S-O(H) bond, and the fact that most of the O-S-O bond angles deviate significantly from 109°. These structural features are also evident in the anion in $NO_2^+HS_2O_7^-$, which is the only other compound whose structure has been determined that contains the $HS_2O_7^$ anion. This compound was originally studied by Steeman and MacGillavry (48), but the anion geometry which they reported has rather large standard errors, and therefore a refinement of their intensity data using least squares was undertaken to try and reduce these errors.

Since the intensities measured by Steeman (49) were already on the same relative scale only one scale factor was refined. The reflections designated as unobserved or unreliable by the original author were omitted, reducing the number of measurements from about 500 to 360. The positional parameters quoted in the original paper, and isotropic temperature factors for all atoms, (except S for which anisotropic temperature factors were used) were refined using the full matrix least squares programme CUDLS. Scattering factors for all the atoms were taken from International Tables for X-ray Crystallography (25). As the results were not sensitive to the weighting scheme, unit weights were used throughout. R_1 dropped from 0.16 to 0.125.

The refined atomic parameters are given in Table 5.4, and the dimensions of the anion are listed in Table 5.5, and shown in Figure 5.5. By the same reasoning applied in the case of the $Se_4(HS_2O_7)_2$ structure, the hydrogen atoms would appear to be bonded to O(7) as shown in Figure 5.6. In fact the hydrogen bonding scheme is identical in two structures,

Estimated Standard deviations in the final figures quoted are given in parentheses. The expression used to calculate the temperature effects is

 $\exp[-2\pi^{2}(U_{11}h^{2}\dot{a}^{*2} + U_{22}k^{2}\dot{b}^{*2} + U_{33}k^{2}\dot{c}^{*2} + 2U_{12}h\dot{ka}^{*}\dot{b}^{*}\cos\gamma^{*} + 2U_{13}h\dot{ka}^{*}\dot{c}^{*}\cos\beta^{*} + 2U_{23}k\ell\dot{b}^{*}\dot{c}^{*}\cos\alpha^{*})]$

Atom		x	у	Z	U(Å ²)	$U_{11}(Å^2)$	$U_{22}(Å^2)$	U ₃₃ (Å ²)	U ₁₂ (Å ²)	$U_{13}(\text{\AA}^2)$	U ₂₃ (Å ²)
a	b	· · · · · · · · · · · · · · · · · · ·	₩-9 <u>00</u> -1-16-20-18-20-18-19-19-1-		. <u> </u>						
S(1)	S(1)	0.1559(8)	0.1752(7)	0.7698(14)		0.005(3)	0.014(3)	0.009(2)	-0.003(3)	0.008(4)	-0.010(4)
S(2)	S(2)	0.2970(8)	0.4264(7)	0.3359(15)		0.019(3)	0.013(3)	0.008(3)	-0.004(2)	-0.002(4)	-0.006(4)
0(1)	0(1)	0.320(2)	0.065(2)	0.742(5)	0.028(5)						
0(2)	0(5)	0.079(2)	0.204(2)	1.009(4)	0.026(5)						
0(3)	0(4)	0.028(3)	0.153(3)	0.633(6)	0.041(6)			· · · · · · · · · · · · · · · · · · ·	· · · ·		
0(4)	0(6)	0.222(2)	0,368(2)	0.625(5)	0.020(5)						
0(5)	0(2)	0.417(2)	0.293(2)	0.291(5)	0.022(5)	a. Atom n	ame corres	ponding to 1	the conventi	on used in	Table 4.5.
0(6)	0(3)	0.351(2)	0.595(2)	0.321(5)	0,029(6)	b. Atom n	ame given b	by Steeman a	nd McGillav	ry (48).	
0(7)	0(7)	0.129(2)	0.447(2)	0.186(4)	0.016(4)						
0(8)		0.680(3)	0.093(3)	0.609(6)	0.047(7)						
0(9)		0.773(3)	0.257(3)	0.294(6)	0.032(6)						
N(1)		0.726(3)	0.171(3)	0.465(6)	0.029(6)						

Table 5.4

Atomic Positional and Temperature Parameters for $NO_2(HS_2O_7)$.

Table 5.5

Bond Distances and Angles for the $\mathrm{HS}_2\mathrm{O}_7^-$ Ion in NO_2 ($\mathrm{HS}_2\mathrm{O}_7\mathrm{)}$.

See Table 5.3 for explanation of twist angle.

Bond (Å)		Bond Angle (deg	rees)
S(1)-0(1)	1.53(2)	0(4) - S(1) - 0(1)	100(1)
S(1) - 0(2)	1.47(2)	0(4) - S(1) - 0(2)	98(1)
S(1) - O(3)	1.43(3)	0(4) - S(1) - 0(3)	109(1)
S(1) - 0(4)	1.70(2)	0(2) - S(1) - 0(3)	109(1)
S(2) - 0(4)	1.59(3)	0(2) - S(1) - 0(1)	125(2)
S(2) - 0(5)	1.44(2)	0(1) - S(1) - 0(3)	113(2)
S(2) - 0(6)	1.52(2)	0(4) - S(2) - 0(5)	108(1)
S(2) - 0(7)	1.57(2)	0(4) - S(2) - 0(6)	100(2)
		0(4) - S(2) - 0(7)	103(1)
0(1)-0(2)	2.64	0(5) - S(2) - 0(6)	121(1)
0(1) - 0(3)	2.47	0(5) - S(2) - 0(7)	110(2)
0(1)-0(4)	2.48	0(6) - S(2) - 0(7)	112(1)
0(2)-0(3)	2.36		
0(2)-0(4)	2.36	S(1) - O(4) - S(2)	123(2)
0(3)-0(4)	2.44		
0(5)-0(4)	2.46	Twist Angle	16(3)
0(5)-0(6)	2.58		
0(5)-0(7)	2.46		
0(6)-0(4)	2.38		
0(6)-0(7)	2.55		
0(4)-0(7)	2.48		
S(1) - S(2)	2.87(1)		
0(1) - 0(5)	2.73(3)		
0(3)-0(7)	3.04 (3)		
0(7)-H0(2)	2.66(3)		



Figure 5.5. The $HS_2O_7^-$ anion in NO_2 (HS_2O_7).



Figure 5.6. Projection of NO2 (HS207) down \overrightarrow{a} .

the translation vector between the hydrogen bonded ions being $\vec{b} = 5.606$ Å in the Se₄²⁺ crystals and $\vec{c} = 5.55$ Å in the NO₂⁺ crystals.

The standard errors quoted are those based on the final cycle of least squares refinement and are possibly rather low. For example the difference in the two N-0 bonds [0.96(4) Å and 1.06(4) Å] is not significant, and the 0-N-0 angle $[178(7)^{\circ}]$ does not differ significantly from 180° but the error is large and the conformation of the ion is consistent with the bent model for NO₂⁺ proposed by Cruickshank for $(NO_2^{+})_2S_3O_{10}^{2-}$ (50).

The principal interest in the structure is the anion configuration. The difference in the lengths of the bridging bonds, 1.59(3) and 1.70(2) Å is significant, and the shorter bond is again associated with the sulphur atom which has the long S-O(H) bond. The O-S-O bond angles deviate from 109° in a similar manner to the angles in Se₄ (HS₂O₇)₂.

The geometries of the anions in these structures can be understood in terms of some simple quantitative rules, which can be developed by analysing the structural features of these and other anions containing SO_4 tetrahedra. It is convenient to divide the discussion into two sections, which deal with the following questions:

(i) What effect does the bonding of other atoms or groups to one or more of the oxygen atoms in an SO_4 tetrahedron have on the S-0 bond lengths?

(ii) What effect does the bonding of other atoms or groups to one or more of the oxygen atoms in an SO₄ tetrahedron have on the 0-S-0 bond angles?

Gillespie (51) introduced the "duodecet" rule, in which he suggests that the second row elements from silicon to chlorine tend to have twelve electrons in their valence shells. This infers that the total bond order about a sulphur atom in any environment should be six. Therefore, if one or more of the oxygen atoms in an SO_4 tetrahedron are bonded to other atoms, the bond lengths in the SO_4 group should change, so that the total bond order about the sulphur atom is still six.

Both Cruickshank (52) and Gillespie (53) have suggested a correlation expression between bond length and bond order for S-0 bonds. However, in the range of bond lengths of interest both these functions show approximately a linear relationship between bond order and bond length. In the following discussion only the sum of the bond lengths will be referred to, since a constancy of bond length implies a constancy of bond order.

Table 5.6 lists the sum of the bond lengths about the sulphur atom in various SO_4 tetrahedra in which one or more of the oxygen atoms is bonded to other atoms or groups. It can be seen that in all cases the sum of the bond-lengths about each sulphur atom is close to the mean value of 5.97 Å.

The comparatively large deviations in the cases of the two nitronium salts are still within experimental error. The bond lengths for $(NO_2)_2S_3O_{10}$ are the averaged values quoted by Cruickshank in his refinement of the original intensity measurements of Eriks and MacGillavry (54). The errors for $NO_2HS_2O_7$, although improved by the refinement discussed earlier compared to the original published parameters (48), are still high.

The inequality of the bridging bond lengths in the two HS_2O_7 salts is predicted if it is assumed that the sum of the bond lengths about both sulphur atoms must be close to 6.0 Å. The long bond S(2)-O(7), raises

Table 5.6

Sum of S-0 Bond Lengths in Some SO₄ Tetrahedra

		Total Bond Length About S(1) in Å	Total Bond Length About S(2) in A	Total Bond Length About S(3) in Å
NaHSO ₄ •H ₂ O	(55)	5.96(2)		
NH4 HSO4	(56)	5.84(4)		
KHSO4	(57)	5.95		
RbHSO ₄	(58)	5.91(4)		
K ₂ S ₂ 0 ₇	(59)	5,94(2)		
Se ₄ (HS ₂ 0 ₂) ₇		5.97(4)	6.02(4)	
$NO_2HS_2O_7$		6.13(5)	6.12(5)	
(NO ₂) ₂ S ₃ O ₁₀ *	(50)	5.84	5.98	
K ₂ S ₅ O ₁₆ *	(60)	5.98(2)	6.03(2)	6.08(2) [†]

^{*}Molecule has C_{2v} symmetry about S(1).

[†]The S(3)-0 bridging bond is very long, 1.83 Å, and is beyond the range of the linear relationship between bond order and bond length. Thus the sum of the bond lengths about S(3) is not such a reliable index of the sum of the bond orders. The authors regard the molecule as an $S_3O_{10}^{2^-}$ chain with an SO₃ molecule weakly bonded to each end. the total bond length of the terminal S-0 bonds about S(2) compared to S(1); therefore S(2)-O(4) must be shorter than S(1)-O(4) to equalise the sum of all the bond lengths about S(1) and S(2).

A similar inequality in the bridging bond lengths in $(NO_2)_2S_3O_{10}$ and $K_2S_5O_{16}$ would also be expected. The bond lengths in these two anions are given below.





In both of these structures S(1) has two short terminal S-0 bonds, and two longer bridging bonds. Taking a typical terminal S-0 bond

length as 1.43 Å, predicts that the bridging bond lengths about S(1) will be 1.54 Å. In $(NO_2)_2S_3O_{10}$, S(2) has three terminal S—0 bonds, and therefore the predicted S—0 bridging bond length would be 1.71 Å. In $K_2S_5O_{16}$, S(2)—0(2) is slightly lengthened by the coordination of O(2) to an SO₃ molecule. This results in a decrease in the S(2)—0(1) bond length compared to the values predicted for the $S_3O_{10}^{2-}$ ion.

The sum of the bond lengths about a bridging oxygen in polysulphate anions is also constant within experimental error, as shown in Table 5.7.

Table 5.7

Sum of Bond Lengths About Bridging Oxygens in Polysulphate Anions

		Total Bond Length About O(1) in Å	Total Bond Length About O(2) in Å
K ₂ S ₂ 0 ₇	(59)	3.29(2)	
$Se_4 (HS_2 0_7)_2$:	3.26(3)	
$NO_2HS_2O_7$		3.29(4)	
$(NO_2)_2S_3O_{10}$	(50)	3.26	
K ₂ S ₅ O ₁₆	(60)	3.26(2)	3.34(2)

The constancy of the sum of bond lengths about both the sulphur atom and the bridging oxygen atom in polysulphate anions provides a method of predicting both the presence of asymmetric S-0-S bridges, and the lengths of the S-0 bridging bonds.

Cruickshank (52) showed that the e_g set of d orbitals on atom X, where X = Si, P, S, Cl, in X-0-X bridging systems are suitably orientated for $d_{\pi} - p_{\pi}$ overlap with an unhybridised p orbital on the oxygen atom. This suggests a feasible mechanism by which the S—0 bridging bond length can be shortened to compensate for a lengthening of one or more of the terminal S—0 bonds.

The bond angles in an SO_4 tetrahedron are altered considerably when another group or atom bonds to one or more of the oxygen atoms. The bond angles can be predicted with reasonable accuracy by applying the following two rules:

 0^{0}_{1}

1.

When an atom or group X bonds to O(1), the sulphur atom moves away from O(1), down the three-fold axis which includes O(1) and S. The angles between O(1), S, and all the other oxygen atoms decrease, while all the other angles increase. The extent of the change is approximately linear between a 3° change for an S-0 bond of 1.51 Å and 7° for a bond of 1.72 Å. 2. If the atom or group X lies approximately in the same plane as O(1), S, and O(4) for example, then angle, O(1)-S-O(4) is reduced by an additional 3°, and the two other O(1)-S-O angles are increased by approximately 3°.

Table 5.8 lists the geometries of some anions containing SO_4 tetrahedra which have additional atoms or groups bonded to one of the oxygen atoms. The angles predicted by applying the two rules above are also given, and show remarkably good agreement with the experimental values. The agreement for KHSO₄ is not too good, but since the parameters quoted are based on a re-refinement of previous intensity measurements (61), the

Table 5.8

Geometries of Some SO4 Tetrahedra in Sulphate and Polysulphate Anions

$NaHSO_4 \cdot H_2O$	(55)					
Bond	(Å)	Bond (A	R)	Bond Angle (d	degrees) (Calculated
S-0(1) -0(2) -0(3) -0(4)	1.43(1) 1.48(1) 1.61(1) 1.44(1)	0(1)-0(2) 0(1)-0(3) 0(1)-0(4) 0(2)-0(3) 0(2)-0(4) 0(3)-0(4)	2.43 2.48 2.38 2.38 2.42 2.47	0(1)-S-0(2) 0(1)-S-0(3) 0(1)-S-0(4) 0(2)-S-0(3) 0(2)-S-0(4) 0(3)-S-0(4)	113(1) 109(1) 113(1) 101(1) 112(1) 108(1)	114.0 107.5 114.0 101.5 114.0 107.5
NH4HSO4 (5	56)					
S-0(1) -0(2) -0(3) -0(4)	1.43(2) 1.42(2) 1.44(2) 1.55(2)	0(1)-0(2) 0(1)-0(3) 0(1)-0(4) 0(2)-0(3) 0(2)-0(4) 0(3)-0(4)	2.38 2.38 2.42 2.41 2.40 2.31	0(1)-S-0(2) 0(1)-S-0(3) 0(1)-S-0(4) 0(2)-S-0(3) 0(2)-S-0(4) 0(3)-S-0(4)	113(1) 112(1) 109(1) 115(1) 108(1) 101(1)	113.3 113.3 108.3 113.3 108.3 102.3
KHSO ₄ (57)					
S-0(1) -0(2) -0(3) -0(4)	1.55 1.48 1.47 1.45	0(1)-0(2) 0(1)-0(3) 0(1)-0(4) 0(2)-0(3) 0(2)-0(4) 0(3)-0(4)	2.39 2.46 2.48 2.42 2.34 2.43	0(1)-S-0(2) 0(1)-S-0(3) 0(1)-S-0(4) 0(2)-S-0(3) 0(2)-S-0(4) 0(3)-S-0(4)	104 110 112 110 106 113	102.3 108.3 108.3 113.3 113.3 113.3
RbHSO ₄ (58	3) (Average	values for	the two	independent H	SO ₄ groups	are given.)
S-0(1) -0(2) -0(3) -0(4)	1.46 1.57 1.44 1.44	0(1)-0(2) 0(1)-0(3) 0(1)-0(4) 0(2)-0(3) 0(2)-0(4) 0(3)-0(4)	2.43 2.40 2.40 2.43 2.34 2.43	0(1)-S-0(2) 0(1)-S-0(3) 0(1)-S-0(4) 0(2)-S-0(3) 0(2)-S-0(4) 0(3)-S-0(4)	107 112 114 107 103 115	108 113.6 113.6 108 102 113.6
$K_2S_2O_7$ (59))					
S-0(1) -0(2) -0(3) -0(4)	1.438 1.428 1.447 1.645	0(1)-0(2) 0(1)-0(3) 0(1)-0(4) 0(2)-0(3) 0(2)-0(4) 0(3)-0(4)	2.42 2.39 2.44 2.41 2.34 2.43	0(1)-S-0(2) 0(1)-S-0(3) 0(1)-S-0(4) 0(2)-S-0(3) 0(2)-S-0(4) 0(3)-S-0(4)	115.5(4) 112.8(4) 106.1(4) 113.6(4) 101.3(4) 106.2(4)	114.8 114.8 106.8 114.8 100.8 106.8

errors are likely to be high.

The angles are calculated by summing the angular changes predicted when each of the rules is applied in turn to the SO_4 tetrahedron. In the acid sulphates the S-O-H bond is bent so that the hydrogen atom is approximately eclipsed with respect to one of the other oxygen atoms. Therefore, Rule 2 is applicable to these anions as well as to the disulphate anion in which the terminal oxygen O(2) lies in approximately the same plane as the S-O-S bridge.

The bond angles for some acid disulphate and polysulphate anions are given in Table 5.9. The angles about S(1) in both of the $HS_2O_7^$ anions, and about S(2) in the $S_3O_{10}^{2-}$ anion can be treated in the same way as the examples considered earlier, i.e., Rules 1 and 2 are each applied once. However in each of the anions listed in Table 5.9, one or more of the SO₄ tetrahedra forms two bridges. S(2) in the $HS_2O_7^-$ anion forms an S-O-S and an S-O-H bridge, while in the polysulphates one or more of the sulphur atoms form two S-O-S bridges. The calculated angles about these sulphur atoms should be calculated by applying Rules 1 and 2 twice.

The angles about S(2) in the $HS_2O_7^-$ anion were calculated by applying Rule 1 twice but Rule 2 only once, since there is some ambiguity concerning the O-S-O plane in which the H atom lies. This may account for the apparent poor fit between the observed and calculated value for the angle O(6)-S(2)-O(7). Both rules were applied twice to S(1) in the $S_3O_{10}^{2^-}$ anion, since S(1) forms two S-O-S bridges, and O(5) lies in the plane of S(1), O(1') and S(2'), and O(5') lies in the plane of the other S-O-S bridge. The agreement between the observed and calculated values is quite

Table 5.9

Bond Angles in Some Acid Disulphate and Polysulphate Anions

	$Se_4(HS_20_7)_2$	$NO_{2}^{+}(HS_{2}O_{7})$	Calculated
	Observed	Observed	
0(1)-S(1)-0(2)	117.0(1)	125.0(2)	115.3
0(1) - S(1) - 0(3)	113.0(1)	113.0(2)	115.3
0(1) - S(1) - 0(4)	105.0(1)	100.0(1)	106.3
0(2)-S(1)-0(3)	116.0(1)	109.0(1)	115.3
0(2)-S(1)-0(4)	99.0(1)	98.0(1)	100.3
0(3)-S(1)-0(4)	104.0(1)	109.0(1)	106.3
0(4)-S(2)-0(5)	112.0(1)	108.0(1)	111.5
0(4)-S(2)-0(6)	104.0(1)	100.0(2)	105.5
0(4)-S(2)-0(7)	106.0(1)	103.0(1)	103.5
0(5)-S(2)-0(6)	120.0(1)	121.0(1)	118.0
0(5)-S(2)-0(7)	109.0(1)	110.0(2)	110.0
0(6)-S(2)-0(7)	105.0(1)	112.0(1)	110.0
$(NO_2^+)_2S_3O_{10}$ (50)	Observ	ed <u>Calcu</u>	ulated
0(1)-S(1)-0(5')	108	100	5.3
0(1)-S(1)-0(5)	108	112	2.3
0(1)-S(1)-0(1')	101	101	1.3
0(5)-S(1)-0(5')	122	123	3.3
0(1)-S(2)-0(2)	102	10	5.8
0(1) - S(2) - 0(3)	102	105	5.8
0(1) - S(2) - 0(4)	102	99	9.8
0(2) - S(2) - 0(3)	116	115	5.8
0(2) - S(2) - 0(4)	116	11	5.8
0(3)-S(2)-0(4)	116	.11	5.8
$K_2S_5O_{16}$ (60)			
0(1) - S(1) - 0(1')	104	.6(6) 10	1.3
0(1) - S(1) - 0(8)	110	.5(5) 11	2.3
0(1) - S(1) - 0(8')	104	.6(5) 10	5.3
0(8) - S(1) - 0(8')	121	.1(8) 12	3.3
		Model I	Model II
0(1)-S(2)-0(2)	101	.8(5) 100.3	100.3
0(1)-S(2)-0(6)	102	.0(5) 103.3	103.3
0(1)-S(2)-0(7)	107	.0(5) 109.3	103.3
0(2)-S(2)-0(6)	113	.0(5) 115.3	118.3
0(2)-S(2)-0(7)	109	.2(5) 109.3	118.3
0(6)-S(2)-0(7)	121	.6(5) 124.3	115.3

Table 5.9 (continued)

	Observed	Calculated
0(2)-S(3)-0(3)	101.5(5)	103.5
0(2) - S(3) - 0(4)	101.7(5)	103.5
0(2) - S(3) - 0(5)	97.5(6)	97.5
0(3) - S(3) - 0(4)	115.0(6)	117.8
0(3)-S(3)-0(5)	118.2(6)	117.8
0(4)-S(3)-0(5)	117.5(6)	117.8

good considering that the observed values are based on a re-refinement of previous intensity measurements (54), and the errors are likely to be high.

The $S_5 O_{16}^{2^-}$ anion is an interesting case since the original authors speculate that the anion perhaps should be considered as an $S_3 O_{10}^{2^-}$ group with a planar SO_3 molecule loosely bound to each end. The angles about S(1) were calculated by applying both rules twice, and agree very well with the observed values. The angles about S(2) were calculated in two ways:

Model I considers S(2)-O(2) as a bridging bond and therefore each rule must be applied twice. Model II considers S(2)-O(2) as a terminal oxygen atom and therefore each rule is only applied once.

The calculated values for both models are given in Table 5.9, and Model I seems to provide a better fit between the observed and calculated values. This model requires that S(3) be treated as a tetrahedrally coordinated sulphur atom, as opposed to a planar SO_3 molecule. The angles about S(3) were calculated by applying each rule once, and the good agreement between the observed and calculated values would suggest that the anion can be described quite satisfactorily as a chain of SO_4 tetrahedra.

There are no apparent reasons why these rules should apply and work so well. Rule 1 is the necessary result of the sulphur atom in a tetrahedral SO₄ group, moving away from the centre, while the oxygen atoms remain in the same relative positions. Bauer (62) proposed a method of calculating bond angles in SO₄ groups by assuming that all the oxygenoxygen distances remain constant, an assumption which is substantiated by the structural data reviewed in this chapter. This would suggest that there is an oxygen-oxygen interaction, which would be expected to diminish in importance as the oxygen-oxygen separation increases. In the dichromates, where the oxygen-oxygen distance is increased to 2.6 Å compared with 2.4 Å in SO₄ tetrahedra, the regular tetrahedral arrangement of the oxygen atoms about each chromium atom is not maintained (63). However, in the HASO₄ anion where the oxygen-oxygen separation is 2.75 Å, the tetrahedral arrangement of the four oxygen atoms is maintained (64,65,66).

An extended π -bonding mechanism could be invoked to explain Rule 2, since it only applies when four or more atoms lie in approximately the same plane. This would be an extension of Cruickshank's scheme (52) involving the unhybridised p orbitals on the bridging oxygen atom. In the structure of the CH₂(SO₃)₂²⁻ anion (67) in which the bridging oxygen has been replaced by a CH₂ group, there are no electrons available for π bonding, yet Rule 2 still applies. The O-S-O angle for the oxygen atom which lies approximately in the S-C-S plane is 102.4°, compared with about 108.0° for the remaining O-S-C angles.

An understanding of the reasons for the changes both in bond lengths and bond angles in SO_4 tetrahedra may become evident when a full molecular orbital description of these anions has been calculated.

CHAPTER 6

Liquid Diffraction Experiments

Introduction

The intensity of the X-rays scattered by a liquid show slow angularly dependent oscillations of low amplitudes, particularly at high angles, and consequently are difficult to measure precisely. The problem of resolving the structure-sensitive portion of the scattered intensity is increased because it is superimposed on a continuously changing background.

The interatomic distances for some monatomic liquids were derived from intensities which were measured photographically; however, reliable results for polyatomic liquids were not obtained until the method of directly counting the scattered photons was introduced. The liquids to be studied in this work were solutions of some polyatomic cations in fluorosulphuric acid.

Fluorosulphuric acid was selected as the best solvent since many of the cations are very soluble and quite stable in this acid. The acid is a comparatively simple molecule, containing atoms of low atomic number compared to the atoms in the cations. Fluorosulphuric acid is a very corrosive liquid and it must be handled in glass or teflon apparatus, working in a dry atmosphere. These properties introduce certain experimental difficulties, particularly in the design of a sample holder.

The initial experiments to record the intensity of the X-rays scattered from fluorosulphuric acid solutions were performed on a $\theta/2\theta$ horizontal goniometer. The sample holder had to stand in the vertical plane, and

considerable problems were encountered as a result of the sample being in contact with the cell window. These problems were overcome by building a θ/θ vertical goniometer, in which the sample lies in the horizontal plane, and the sample holder can be designed so that the Xrays are scattered by the free liquid surface.

This chapter describes the modifications which were made to the $\theta/2\theta$ diffractometer, and also a θ/θ diffractometer and sample holder designed to record the intensity of the X-rays scattered by very corrosive solutions.

1. The Modification of a $\theta/2\theta$ Horizontal Goniometer for Use with Liquid Samples

The principal modification which had to be made to the Philips PW 1380 horizontal goniometer was to increase the angular increments of the step-scanning unit. This was done by using the command pulses from the step-scanning control unit (PW 1364) to operate a stepping motor which was mounted on the X-ray generator and connected to the drive shaft of the goniometer through a pair of spur gears. The increment in θ , $\Delta\theta$, could be varied by changing the gear ratios, since the motor always turned one revolution during each step. Gear ratios of 4:1, 2:1, 1:1 were used which gave $\Delta\theta$ of 0.125°, 0.25°, 0.5° respectively.

A cell to hold the liquid was made from teflon as it had to be resistant to fluorosulphuric acid. A rectangular cavity, 2.0 cm x 1.5 cm x 0.5 cm was drilled into a teflon block which could be fitted exactly inside the sample chamber of the goniometer. The surface of the block around the edge of the cavity was milled away to leave a raised lip over which a piece of 0.003" teflon sheet was stretched and clamped in place with a stainless steel template. A hole was drilled and tapped through the top of the block into the cavity, so that the cell could be filled, then sealed with a teflon screw. The cell was filled, using a hypodermic syringe, and sealed in a dry box. The filled cell was clamped to the sample mount of the goniometer, which had been modified to allow the cell to be moved horizontally back and forth in order to focus the X-rays at the liquid surface. The intensity of the scattered Mo K_{α} X-rays was recorded from θ = 5 to 65°, as the time required to accumulate a fixed number of counts. The monochromator/detector, and the electrical components used to count the photons are discussed in detail in Section 2.

Intensity measurements for carbon tetrachloride and water were recorded and compared to those given by Narten (68,33) to test the reliability of the experimental system. Angularly dependent discrepancies, which could introduce errors in the radial distribution functions, were quite obvious. The origin of the problem seemed to be the cell window. Since the cell was in the vertical plane, the liquid was in contact with the teflon window, and it was very difficult to ensure that the X-rays were focused at the liquid surface, rather than at the teflon window. Teflon is an amorphous solid and has a characteristic scattering pattern which contributes to the total scattered intensity.

During the course of the experiment, the weight of the liquid in the cell caused the teflon to stretch, and therefore the planar liquid surface becomes curved with time. The liquid can move out of the focal plane of the X-rays, and at low angles where the depth of focus is very small, this can introduce serious errors in the intensity measurements. The contribution

of the scattering of the teflon to the total scattered intensity also changes as the window sags. Therefore it was not possible simply to subtract the scattered intensity of the empty cell from the intensity of the filled cell, to obtain the contribution to the scattered intensity of the liquid.

The collimation system of the goniometer provides a divergence slit, and a receiving slit which is the same distance from the sample as the focal spot of the X-ray tube. The area of the sample viewed by the receiving slit is not necessarily the same as that illuminated by the incident beam. It is not very easy to apply an absorption correction to this geometry, which may mean that an angularly dependent correction term is not properly applied.

For the reasons outlined above it was thought to be worthwhile to design and build a diffractometer, which overcomes these major disadvantages. However, the radial distribution functions for two different concentrations of I_3^+ in HSO₃F are included in Chapter 7, since the principal features of the functions agree quite well.

2. <u>A θ/θ Diffractometer to Record the Intensity of the X-rays</u> Scattered by a Liquid

The desirable features of a diffractometer which is to be used to record the intensity of the X-rays scattered by a liquid are:

(i) the liquid surface should be planar;

(ii) the mechanical and optical components of the diffractometer should provide the maximum possible angular resolution of the scattered X-rays; and (iii) the sample holder should be designed so that the X-rays are scattered by the free liquid surface, and the window of the cell should not contribute to the angularly dependent scattered intensity.

Requirement (i) can be satisfied by using a θ/θ diffractometer (moving tube/moving counter), which has the sample stationary in the horizontal plane. A parafocusing geometry, where the distance between X-ray source and the sample and the distance between the sample and the detector are equal, coupled with a collimation system which restricts the vertical and horizontal divergence of the X-rays, provide the angular resolution required by condition (ii). A sample holder designed to fulfill condition (iii) is described later.

Diagram 1 shows the basic geometry of a θ/θ diffractometer in which the X-ray tube and the detector move in a vertical plane in opposite directions, about a circle whose axis is coincident with the centre of the sample.

A diffractometer of this type was built in the McMaster University instrument machine shop by Mr. G. Hine under the supervision of Mr. S. Kocsis. The design was based on the diffractometer built for Dr. A. H. Narten at the Oak Ridge National Laboratory (33). The radius of the circle



Diagram 1

in Diagram 1 was chosen as 17.3 cm, so that the divergence slits and monochromator/detector unit supplied with the Philips $\theta/2\theta$ diffractometer (PW 1380) could be used.

The diffractometer is shown in Figures 6.1 and 6.2. The sample holder is shown without a window so that the teflon cup which holds the liquid can be seen.

The Mechanical System

The principal mechanical components of the diffractometer are shown in Figure 6.1, and listed in Table 6.1.

The arms which support the X-ray tube and the scintillation counter can be seen in Figure 6.2. The arms are fabricated from 3/4" aluminium, and are bolted to the faces of two independent rotary tables, which were



Figure 6.1. Mechanical Components of the θ/θ Diffractometer.

Table 6.1

Mechanical Components of the θ/θ Diffractometer

1. Nine-inch rotary tables (Troyke Model R-9) gear ratio 90:1.

2. Cables supporting counter-weights.

3. X-ray tube housing.

4. High voltage cable from Philips PW 1011 generator.

5. Water tubes from generator.

6. Counter weights.

7. Control switches.

8. Drive shaft.

9. 120-tooth worm gear and worm.

10. Sliding mount supporting Slo-Syn motor (model SS 150).

11. Bevel gear pair. Ratio 1:1 or 4:1.

12. Micro-switch and cam for step-scanning.

13. Pin to disengage gear from drive shaft, for manual setting.

carefully aligned to be vertical, and to turn about a common horizontal axis. The load on the tables is counterbalanced by the weights, which are attached to the steel cables set into the grooves cut into the arms. The base holding the tube housing was inclined at an angle of 4° from the horizontal to set the take-off angle of the X-rays.

A Slo-Syn synchronous motor turns the common drive shaft via a pair of bevel gears, whose ratios can be chosen as 1:1, or 4:1, to provide continuous drive speeds of $2.4^{\circ}/\text{min.}$, or $0.6^{\circ}/\text{min.}$, in θ respectively. The tables turn in opposite directions since they are connected to the drive shaft through worm gear/worm combinations of opposite pitch. The worm gears can be disengaged from the drive shafts of the tables so that they can be turned manually by removing the pins. The angular settings can be read to the nearest 2 minutes of arc by means of the verniers attached to the drive shafts of the tables.

One of the manual cranks can be replaced by a notched aluminium disc to operate the diffractometer in the step-scan mode. The cam opens the micro-switch, thus cutting one side of the A.C. supply to the motor, which is wired to stop instantaneously when this happens. The motor is restarted by a relay wired in parallel to the micro-switch. The relay closes the circuit for five seconds by which time the disc has moved on far enough to close the micro-switch again, and the tables continue to turn until the next notch is reached. The angular increments $\Delta\theta$ can be varied by using discs with different numbers of notches, cut at equal distances around the perimeter. Wheels with 16 and 8 notches were used, which gave $\Delta\theta$ of 0.25° and 0.5° respectively. It was found that there

was no observable accumulated error in the $\boldsymbol{\theta}$ setting after 50 steps had been completed.

The sample holder fits into a holder mounted on a dovetail slide. The height of the sample holder can be accurately adjusted by turning the fine pitch screw (48 threads to 1 inch), and locking it into position with the locking nut.

When in use, the entire collimation system receiving the scattered radiation is protected with a lead shield to prevent any stray background radiation from being recorded.

Diffractometer Slit System

The optical components of the diffractometer are shown in Figure 6.2, and are listed in Table 6.2. The essential slit geometry is shown in Diagram 2.



Diagram 2



Figure 6.2. Optical Components of the θ/θ Diffractometer.

Table 6.2

Optical Components of the θ/θ Diffractometer

- 1. Divergence and Soller slit assembly (Sl and SSl), with height and rotational adjustments.
- 2. Sample height adjustment, with locking nut.
- 3. Divergence slit (S2).
- 4. Convergence and Soller slit assembly (S3 and SS2).
- 5. Track containing receiving slit system, monochromator and detector, with height adjustment.
- 6. A.M.R. LiF monochromator and scintillation counter.
- 7. Sample holder.
- 8. Arm supporting X-ray tube.
- 9. Arm supporting the detector assembly.

SS1 and SS2 are Soller slits which limit the horizontal divergence of the X-ray beam to about 2°. Slits Sl and S2 are a matched pair of divergence slits, which ensure that the area illuminated by the primary beam is exactly the same as that viewed by the receiving slit S3. This geometry is convenient for applying an absorption correction which allows for sample penetration (see "Absorption Correction" in Chapter 3).

Slits SSl and Sl are on a common mounting which can be rotated about a horizontal axis and moved vertically for alignment purposes. Slits SS2 and S3 are also in a common unit which is mounted on the monochromator track. The slit holder for S2 slides on the monochromator track, and can be bolted in position at the same distance from the machine axis as Sl. The entire receiving slit assembly is mounted on a track which can be moved in the vertical plane by means of the adjusting screw, and bolted into position.

Detector and Electronic System

The monochromator/detector unit is manufactured by A.M.R. Industries (Model 7-202H). The curved crystal LiF monochromator focuses the scattered X-rays into a scintillation counter, producing pulses, which are then amplified. A pulse height analyser is used to discriminate against pulses of energy, other than those of Mo K_{α} radiation. Having set a base line voltage in the range of the Mo K_{α} radiation, the window voltage was closed down to accept 95% of the scattered radiation. The output from the amplifier/pulse height analyser (PW 4280), is coupled to a ratemeter (PW 1362) and a strip chart recorder which can be used when the spectrometer is operated in the continuous mode.

When the step scan mechanism is used, the intensity is measured as the time required to accumulate a given number of counts. The count and time required in seconds are printed out on a digital printer (PW 4202) controlled by a printer control unit (PW 4255). The stepping mechanism was activated by the command pulses produced by the stepscanning unit (PW 1364).

During the course of the experiments with the $\theta/2\theta$ horizontal goniometer, the stability of the X-ray intensity produced by the Mo tube was carefully checked. The main beam was monitored using a second scintillation counter and ratemeter for a period of 36 hours. The intensity was recorded on a strip chart recorder, and showed little variation in that time; therefore no correction for generator instability was applied to any of the intensity measurements.

Sample Holder

The sample holder can be seen in Figures 6.1 and 6.2 mounted on the diffractometer. Figure 6.3 is an actual size cross-section of the cell, and the essential components are listed in Table 6.3. The cell is constructed entirely from stainless steel (wide cross-hatching in Figure 6.3) and teflon (narrow cross-hatching in Figure 6.3), and must be airtight since the samples under investigation are extremely corrosive.

The sample holder has a 1" diameter stud (8), which fits into the dovetail slide on the diffractometer, welded to one end-face of the cylinder. A stainless steel block (7) is bolted to the other face of the cylinder with the pair of screws (13) fitted with teflon washers. This end plate can be bolted into position by means of the studs and


Table 6.3

Components of the Sample Holder

- 1. Piston.
- 2. Bolt to apply pressure to the teflon rings.
- 3. Locking screw.

4. Teflon rings.

5. Restoring spring, with retaining collar.

6. Teflon cup.

7. Stainless steel cylinder block.

8. 1" diameter stud.

9. Teflon template.

10. Stainless steel templace.

11. 0.003" teflon sheet.

12. Teflon **O**-ring.

13. Stainless steel screw, with teflon washer.

14. Stainless steel studs and bolts (3 are used 120° apart).

bolts (14), and an air-tight seal is obtained by the teflon O-ring (12).

The teflon cup (6) slides smoothly inside the cylinder cut into the block (7), and the height of the cup can be varied by means of the piston (1), which drives against the force of the restoring spring (5). The piston is threaded inside the larger bolt (2), which can be tightened to compress the teflon rings (4) and locked into position by the locking screw (3). The pressure of these rings on the piston provide an airtight seal.

The teflon window (11) is stretched over the entire length of the cylinder, and clamped into position by the templates (9) and (10). By carefully tightening the sixteen screws around the edge of the templates, the window can be stretched tightly over the cavity in the cylinder, and a good air-tight seal is obtained.

Alignment of the diffractometer

 The height of the machine axis was located by aligning the crosshairs of a cathetometer with the centre mark on a steel rod, which had been fitted through the centre holes of the rotary tables. A clearance hole for the rod had been cut in the aluminium plate which supports the sample mount, so that the end of the rod could be lined up with the centre line defined by the optical components of the diffractometer.
 Using the centre mark of the rod as a reference, the mounting for slit S2 was fixed to be the same distance from the machine axis as S1.
 The rod was removed, and the sample holder was fitted on its mounting. A fluorescent screen was attached to the central steel block of the sample holder, which was then rotated about the machine axis until the screen was in the vertical plane. The rotary table which carries the arm supporting the tube housing was set to 0.0° . In this position the focal spot of the tube is horizontal with the machine axis, and 17.3 cm from the axis. The tube housing is tilted away from the vertical, defined through the machine axis, at an angle of 4°, to set the take-off angle of the X-rays.

With the tube zeroed, the slit unit containing SSI and SI was rotated about a horizontal axis, and moved vertically until the fluorescent screen was illuminated symmetrically.

4. The arm holding the monochromator/detector was zeroed to first order with a precision level. The track supporting the entire receiving slit system was moved vertically, using the adjusting screw (No. 5 in Figure 6.2), until the centre line of the track was horizontal with the machine axis. This position was determined by alignment with the cross hairs of the cathetometer. The track was levelled using the precision level, and bolted in position.

5. The sample holder was removed, and the fluorescent screen placed between slit S3 and the monochromator. The alignment of all the slits was checked using $1/2^{\circ}$ divergence slits and 0.1° receiving slits. 6. A silicon disk was mounted horizontally on the machine axis, and the two arms were moved to locate the 311 reflection. The angle of incidence was set at 12.5°, and using the $1/2^{\circ}$ divergence and receiving slits, the peak was scanned manually moving only the monochromator arm. The angular settings were recorded at half the peak height, on each side of the maximum, and the values averaged to give the exact setting for the Bragg peak. The vernier on the drive shaft of the table supporting the monochromator arm was set to read 12.5°, and the pins were inserted to couple

the worm gears to the drive shafts of the tables.

7. The drive shaft was raised to engage the worm gears and worms, and bolted into position. The diffraction pattern for the silicon standard was then recorded over the range of θ from 5.0° to 65.0°.

Experimental Procedures

The sample holder was attached to the machine and rotated until the central block was horizontal. This position could be determined since a scribe mark, which could be aligned with the cross hairs of the cathetometer, had been drawn across the diameter of the cover plate parallel to the block. The cell was locked into position and a polyethene glove bag was fitted over the cell and sealed off about the cell mounting.

The cell cover was pulled back about 1/4" on the 3 studs, and the solution under investigation and an eye-dropper were put in the glove bag, along with a dish of P_2O_5 . The bag was flushed with dry nitrogen for about 20 minutes then sealed. After about 1 hour the cup, which was in the lowered position, was filled to the brim with the solution using the eye-dropper. The three nuts were tightened in turn to push the cover evenly back into position, and finally the cover was bolted tight.

The glove bag was removed and both arms were set in the zero position. The direct beam intensity was recorded on the strip chart recorder using the $1/2^{\circ}$ slits, and the cell was raised vertically until the central block halved the measured intensity. The cell was lowered until the maximum intensity was again just recorded, and the locking nut was tightened in this position. The piston was now turned to drive the teflon cup upwards until the measured intensity was again halved. This procedure ensures that the liquid lies horizontally along the machine axis and is in the X-ray beam. The intensity was recorded for about one hour to make sure that the liquid level did not change.

The arms were driven to the minimum angle for data collection, usually $\theta = 5^{\circ}$. The intensity was measured out to 65° , and was recorded in the form of the time required to accumulate a given number of counts. The number of counts was chosen so that the statistical error in counting would be small.

The number varied from 40,000 at low angles to 200,000 at high angles where the scattered intensity is very weak.

The intensity data are collected in ranges using different sizes of divergence slits. Smaller slits must be used at low angles to restrict the illuminated length of the sample, but the slit divergence can be increased at the higher angles. Half degree, 1° , 2° , and 4° slits were used over the ranges 5° - 10° , 8° - 25° , 24° - 45° , 44° - 65° respectively. The ranges overlap so that the intensity measurements can be put on a common scale. The stepping increment was 0.25° for the two smaller slits, and 0.5° for the larger slits. All the intensity measurements were recorded using Zr filtered Mo radiation. At the completion of each range, the first few readings were re-recorded to monitor the generator stability and changes in the liquid level.

When all the intensity measurements had been made, the teflon cup could be lowered, and the cell removed in order to dispose of the liquid.

CHAPTER 7

Results of Liquid Diffraction Experiments

Introduction

The radial distribution functions, R.D.F's., for the liquids studied were all calculated in a similar manner. In this chapter the general method for treating the intensity measurements is discussed, before a detailed analysis for each liquid is given.

Mercury was chosen as a convenient standard to establish the reliability of the θ/θ diffractometer, and also to test the computer programmes, because of the extensive literature on this system. The results obtained for mercury are included in this Chapter, along with those for HSO₃F, Se₄²⁺/HSO₃F, Te₄²⁺/HSO₃F and I₃⁺/HSO₃F.

The experimental measurements, i.e., the angular settings and corresponding time to record the chosen number of counts, for all these liquids can be found in the Appendix.

1. Calculation of the Radial Distribution Function

The experimental measurements are the intensity of the X-rays scattered by a liquid sample as a function of the angle of diffraction. The intensities, which are recorded in a number of ranges characterised by the sizes of the divergence and scatter slits, are measured as the time (seconds) required to count a chosen number of scattered photons. A computer programme was written to convert the intensity measurements to counts/minute, apply the polarisation and absorption corrections (Equations [3.33] and [3.34]) and

to convert the constant grid in θ to a constant grid in §.

Scale factors were calculated, by comparing the regions of overlap between the separate ranges, to normalise all the measurements to the range characterised by the 1° divergence slit. A second computer programme multiplies each of the ranges of the corrected intensities by the appropriate scale factor, then normalises the entire intensity curve to the $\sum_{j=1}^{m} f_j^2(s)$ curve. The normalisation constant is calculated using a linear least squares routine to compare the two curves at high angles (s > 13.0). The reduced intensity, i(s), is calculated, and the i(s) curve is summed to test the quality of the normalisation. The values of i(s) are then used to calculate the R.D.F. (Equation [3.32])

$$D(\mathbf{r}) = D_{0}(\mathbf{r}) + \frac{2\mathbf{r}}{\pi} \int_{s}^{s} \sup_{s \in i(s) \cdot M(s)} \sin s\mathbf{r} \, ds$$

where
$$D_o(r) = \frac{\text{Density of solution x 0.602}}{\text{Molecular weight of the stoichiometric unit}}$$

$$M(s) = \begin{bmatrix} x \\ z \\ j=1 \end{bmatrix}^{m} f_{j}(s) = \frac{1}{2}$$

The R.D.F. will be in units of molecules/Å using these definitions of M(s) and $D_{r}(r)$.

The programme had an option to include an exponential term, e^{-as^2} , in the integral to correct for the series termination error in the R.D.F. The R.D.F. could be calculated with and without the exponential term, and the two curves compared in order to determine the positions and amplitudes of termination ripples in the undamped R.D.F. The D(r) curve rapidly converged to the D_o(r) curve beyond 6 or 7 Å for all the liquids studied, and the ripples caused by the termination error did not produce any significant alterations to the principal peaks in the R.D.F's. Therefore the undamped R.D.F's are shown for each sample.

The R.D.F. programme also has the capability of reinverting the high frequency ripples below the first main peak using Equation [3.38],

$$i'(s) = \int_{r=0}^{r=r_1} [D(r) - D_0(r)] M(s) \cdot \frac{\sin sr}{sr} dr$$

where r_1 is the chosen cut-off point below the first main peak and i'(s) is the correction curve which can be applied to the original i(s) curve. A new R.D.F. D'(r) is calculated, and the calculation can be repeated until the R.D.F. is essentially smooth between r = 0 and $r = r_1$. The corrected i(s) curve is summed after each cycle of reinversion as a test of the normalisation of the curve. [$\sum_{max}^{smax} i(s) = 0$, indicates perfect normalses min

In practice it was found that the initial normalisation of the corrected intensity curve to the $\sum_{j=1}^{m} f_j^2(s)$ curve was unsatisfactory, particularly in the range 5.0 $\leq s \leq 10.0$. Therefore, the i(s) curve was usually normalised to first order by fitting the entire corrected intensity curve to the $\sum_{j=1}^{m} f_j^2(s)$ curve. This procedure will not prejudice the R.D.F. since it involves applying a low frequency term to the corrected intensities. The transform of this low frequency term will be a high frequency term at small distances in the R.D.F. The small distance region of the R.D.F. can then be reinverted, and it was found that the normalisation was almost perfect after two or three reinversion cycles. It is important to point out that the positions of the principal peaks in the R.D.F. did not change during these reinversion cycles; however, the amplitudes of the peaks did change.

The R.D.F. is a linear combination of all the pair interactions in the liquid, and the interpretation of the function depends upon proposing a reasonable model structure for the sample. Therefore, the R.D.F. for pure HSO_3F was calculated to establish the positions and amplitudes of the peaks which result from interactions in the pure solvent. Any new features which appear in the R.D.F. of the cation solutions in HSO_3F , must be associated either with cation-cation or cation-solvent interactions.

Both the positions and amplitudes of the additional peaks which occur in the R.D.F. of the cation solution must be rationalised in terms of a reasonable model structure for the cation. This task is simplified if the multiplicity of each of the intra cation interactions is known. A computer programme was written to calculate theoretical peak shapes using Equation [3.47].

$$T_{jk}(r) = \frac{\chi_j C_{jk} r}{\pi r_{jk}} \int_{s_{min}}^{s_{max}} f_j(s) f_k^*(s) M(s) e^{(-b_{jk} s^2)} [\cos(r - |r_{jk}|)s]$$

- $\cos(r + |r_{jk}|)s] ds.$

Since the concentrations of the solutions are known, the mole percentage of atom j, x_j , is known. The programme allows the multiplicity of the jk interaction, C_{jk} , and the associated temperature factor, b_{jk} , to vary in order to find the parameters giving the best agreement between the observed and theoretical peak.

2. The Radial Distribution Function for Mercury

Figure 7.1 shows the normalised, reduced intensity function, $M(s) \cdot i(s) \cdot s$, for mercury and the Fourier transform of this intensity curve expressed in



Figure 7.1. Reduced Intensity and Radial Distribution Function for Mercury

units of atoms/Å. The positions and amplitudes of the maxima and minima in the $M(s) \cdot i(s) \cdot s$ curve reported by Kaplow (69) are included for comparison. The fit between the two curves is extremely good beyond s = 5.0, but there are some small deviations in the magnitudes of the peaks below this point. The principal features of the R.D.F. are summarised in Table 7.1.

Table 7.1

Principal Features of the R.D.F. for Mercury

Peak Position (Å)		Amplitude (Atoms/Å)		
		$[D(\mathbf{r}) - D_{o}(\mathbf{r})]$		
This Work	Kaplow	This work	Kaplow	
3.05	3.03	8.6	10.0	
5.95	5.90	6.5	4.4	

It is apparent from Table 7.1 that the peak positions are not influenced by the discrepancies in the two reduced intensity curves; however, the amplitudes are influenced quite considerably. This comparison supports Zachariasen's prediction that the low angle peaks in the intensity function make the major contribution to the amplitudes of the peaks in the R.D.F. (70).

The two principal peaks in the R.D.F. are shown in Figure 7.2, along with the theoretical peak calculated for the peak at 3.05 Å. The multiplicity of the Hg - Hg interaction was chosen as 8, which is the value most commonly quoted by other authors (71). Good agreement between the practical and theoretical peaks is obtained with b_{jk} equal to 0.021 Å. This implies that the mean square amplitude of vibration for the Hg-Hg interaction is 0.042 Å.





The agreement between the experimental and calculated peaks is very good below the peak maxima, but the two curves diverge considerably above the maxima. Kaplow (69) has pointed out that the atoms in a liquid have an additional degree of freedom compared to the atoms in a solid. In the latter case the atoms have vibrational freedom, whereas the atoms in a liquid can also diffuse through the sample. The first coordination sphere around a Hg atom is not rigidly maintained, and the coordinated atoms can exchange with other atoms in the sample, i.e., diffusion away from the central atom. The experiment records the time average of all the atomic interactions in the sample, and so the diffusion of atoms will show up in the R.D.F. as a broadening of the peak above the maxima.

The theoretical peak only allows for thermal vibration, and should be compared to the experimental peak below the maxima where the contribution from diffusion is negligible. In a molecular liquid the diffusion effect would be expected for inter-molecular interactions, while the vibrational broadening of the peaks should represent the major contribution to the intra molecular interactions.

The intensity measurements listed in the Appendix were recorded with the sample holder fitted with a teflon window. A set of intensities were also recorded for mercury without the teflon window on the cell. The two intensity curves differed only by a scaling factor, demonstrating that the teflon window does not make an angularly dependent contribution to the intensity.

3) The Radial Distribution Function for HSO₃F.

The normalised, reduced intensity function, $M(s) \cdot i(s) \cdot s$, and its Fourier transform, for HSO_3F are shown in Figure 7.3. The principal features of the R.D.F. are summarised in Table 7.2

Table 7.2

Principal Features of the R.D.F.

for HSO₃F

Position of Peak	Amplitude $(D(r) - D_0(r))$	Multiplicity	bjk (Å)
r (Å)	Molecules/Å		
1.47	0.84	8.0	0.01
2.40	0.40	12.0	0.0125

The peak at 1.47 Å can be assigned to the S-O and S-F interactions. Thompson (72) determined the structure of the SO_3F^- anion in the potassium salt, and reports S-O and S-F bond lengths of 1.43 and 1.58 Å respectively. In HSO_3F , one of the S-O bonds will be approximately 1.55 Å, because one of the oxygen atoms is co-ordinated to a hydrogen atom. There is no evidence that these three different bond lengths are resolved in the R.D.F. The single peak occurs at a distance which is very close to the arithmetic mean of the bond lengths (approximately 1.49 Å), and this would suggest that the limit of resolution of the experiment is about 0.2 Å

The second peak in the R.D.F. at 2.40 Å can be assigned as the average of the 0-0 and 0-F interactions. The ratio of the distances of the first two peaks is almost $(8/3)^{\frac{1}{2}}$, which is the value expected for



Figure 7.3. Reduced Intensity and Radial Distribution Function for Fluorosulphuric Acid.





Figure 7.4. Experimental and Theoretical Peaks for Fluorosulphuric Acid

a tetrahedral molecule; therefore, the multiplicities of the first and second peaks must be 8 and 12 respectively. Theoretical peaks were calculated using these multiplicities and varying the values of the temperature factor, b_{jk} . The parameters providing the best fit between the observed and theoretical peaks are given in Table 7.2, and the peaks are shown in Figure 7.4.

The peak at 1.47 Å was calculated on the assumption that it represents 8 identical interactions, and it agrees very well with the observed peak. The theoretical peak centred at 2.40 Å is broader than the experimental peak, and only the peak heights could be matched successfully. The value of b_{jk} seems quite reasonable since the vibrational amplitude of a non-bonded interaction would be expected to be larger than that for a bonded interaction.

The only other feature of any significance in the R.D.F. is the peak at 3.65 Å, which may represent an inter-molecular interaction. However, the amplitude of this peak diminished during the course of the reinversion cycles, while the amplitudes of the two principle peaks increased. This would suggest that the peak may be the result of some error in the intensity function. The major purpose of this experiment was to establish the principle features of the solvent R.D.F., and it is not necessary to make a definite assignment for this peak in terms of a structural model for HSO_3F .

4. The Radial Distribution Function for $Se_{L}^{2+}/HSO_{3}F$.

The normalised, reduced intensity function, $M(s) \cdot i(s) \cdot s$, and its

Fourier transform, for a solution of the Se_4^{2+} cation in HSO_3F , are shown in Figure 7.5. The principal features of the R.D.F. are summarised in Table 7.3.

Table 7.3

Principal Features of the R.D.F. for $Se_{\mu}^{2+}/HSO_{3}F$. Multiplicity Assignment b_{ik} (Å) Position of Peak Amplitude $(D(r) - D_0(r))$ r(Å)Molecule/Å 1.47 0.69 S-0 J . 8 0.010 S-F 0-07 2.38 0.84 12 O-F Se-Se 2 0.013 0.44 Se-Se 3.25 1 0.010 Se-0 ?

By comparing the results summarised in Table 7.3 with those in Table 7.2, the following differences are apparent:

- The peak at 1.47 Å has diminished in amplitude by approximately
 20%, a value which agrees very well with that predicted by knowing
 the composition of the solution (22% Selenium)
- ii) There is an increase in the amplitude of the peak at 2.40 Å, and its position has moved to smaller r.
- iii) A new peak appears at 3.25 Å.



Figure 7.5. Reduced Intensity and Radial Distribution Function for Se_4^{2+}/HSO_3F .

The peak at 1.47 Å can be assigned to S-O and S-F interactions in the solvent and the anion $HS_2O_7^-$. The solution was prepared by dissolving a known weight of $Se_4(HS_2O_7)_2$ in the minimum volume of HSO_3F . The anion will introduce two additional interactions in the R.D.F., the S-O bridging bond length at approximately 1.65 Å, and the S-S interaction at approximately 2.85 Å. The concentration of the anion is small (11%), and there is no evidence for either interaction in the R.D.F.

All the principal peaks in the R.D.F. for the solution of Se_4^{2+}/HSO_3F are shown in Figure 7.6, along with the corresponding peaks for the pure solvent. The peak at 2.38 Å can be assigned to a combination of the solvent 0-0 and 0-F interactions, and an Se-Se interaction. To find the amplitude and position of the Se-Se interaction the contribution of the solvent interactions must be subtracted. The solvent peak at 1.47 Å in the solution shows a decrease in amplitude of approximately 20% compared to the pure solvent peak. Therefore, the amplitude of the pure solvent peak at 2.40 Å was scaled down by 20%, and the remainder subtracted from the solution peak at 2.38 Å. This difference peak is also shown in Figure 7.6.

Theoretical peaks were calculated and compared with the difference peak, and a good fit was obtained for a peak at 2.32 Å with a multiplicity of 2 and b_{jk} equal to 0.013 Å. The agreement between the peaks above the peak maxima is better than below the maxima. This suggests that a small error may be introduced in the peak position because of the subtraction of the pure solvent peak.

The position and mean square amplitude (0.026 Å) of the Se-Se interaction agree very well with the values determined in the single crystal study (Se-Se bond length 2.286(4) Å, and average isotropic temperature



Table 7.6. Experimental and Theoretical Peaks for Se_4^{2+}/HSO_3F .

factor 0.03 Å). The multiplicity of 2 for the Se-Se interaction indicates that the square planar geometry for the Se₄²⁺ persists in solution. This assumption is confirmed by the peak at 3.25 Å which is in excellent agreement with the length of the diagonal in the Se₄²⁺ ion in the solid state (3.24 Å).

Theoretical peaks were calculated for this interaction with a multiplicity of 1, and varying the value of b_{jk} . The amplitude of the calculated peak could not be matched to the experimental peak, even for very small values of b_{jk} (0.005 Å). This suggests that the peak at 3.25 Å may be a combination of an Se-Se interaction and the Se-O, cation solvent interaction. A theoretical peak is shown in Figure 7.6 for the Se-Se interaction with b_{jk} equal to 0.0125 Å, and the amplitude is 0.30 molecules/Å.

In the single crystal study of $Se_4(HS_2O_7)_2$ the Se-O interactions are divided into two groups; the oxygens in the plane of the $Se_4^{2^+}$ ring are about 2.8 Å from the nearest selenium atom, while the out of plane oxygens are about 3.25 Å from the nearest selenium atom. It would be reasonable to propose that in solution the $Se_4^{2^+}$ ion is tumbling around in a spherical hole in the solvent, so that the average distance between any selenium atom and any of the oxygen atoms in the first coordination sphere is 3.25 Å.

This study of the Se_4^{2+} ion shows that the square planar ring of selenium atoms found in the solid _{exists} in solution. An estimate of the errors in the Se-Se bond lengths found from the liquid diffraction experiment can be made by comparing the results of the two determinations.

This would suggest that the error which should be assigned to the bond lengths derived from the liquid diffraction experiment is about 0.02 Å.

5. The Radial Distribution Function for Te_4^{2+}/HSO_3F .

The normalised, reduced intensity function, $M(s) \cdot i(s) \cdot s$, and its Fourier transform, for a solution of $Te_4^{2+}/HSO_3 F$ are shown in Figure 7.7. The principal features of the R.D.F. are summarised in Table 7.4.

Table 7.4

Principal Features of the R.D.F. for Te_4^{2+}/HSO_3F .

Position of Peak	Amplitude $(D(r) - D_0(r))$	Assignment	Multiplicity	b _{jk} (Å)
r(Å)	Molecules/Å			
1.55	0.75	s-0]	8	0.010
		S-F		
2.68	0.74	Te-Te	2	0.015
3.45	0.40	Te-0		
3.85	0.48	Te-Te	1	0.0125

The results summarised in Table 7.4 can be compared with those given in Table 7.2 in order to assign the peaks which are indicative of intra cation, or cation solvent interactions.

The peak assigned to the solvent S-O and S-F interactions has moved to a slightly larger distance compared with the pure solvent peak. The amplitude of the peak is 11% less than the pure solvent peak, a value which agrees very well with the predicted value. (Solution composition:-12% Te).



Figure 7.7. Reduced Intensity and Radial Distribution Function for Te_4^2 +/HSO₃F.

The peak at 2.68 Å in the R.D.F. can be assigned to a Te-Te interaction since the Te bond length in the element is 2.864 Å (73). All the principle peaks in the R.D.F. are shown in Figure 7.8, along with the corresponding peaks for the pure solvent.

Theoretical peaks were calculated for the Te-Te interaction, and a perfect fit between the calculated and experimental peaks was found for a multiplicity of 2 and b_{jk} equal to 0.015 Å. The theoretical peak is also shown in Figure 7.8.

There is no evidence of the solvent peak at 2.40 Å in this R.D.F., although there is a small feature at about 2.1 Å. This peak decreased in amplitude during the reinversion cycles, while the amplitudes of the other peaks increased, suggesting that the peak is the result of an error in the reduced intensity curve.

If it is assumed that Te_4^{2+} is a square planar ring, and is isostructural with Se_4^{2+} , the peak at 3.85 Å can be assigned to the cross ring Te-Te interaction. The theoretical peak, shown in Figure 7.8, matches the amplitude of the experimental peak exactly but is slightly broader. The peak was calculated for a multiplicity of 1 and b_{jk} equal to 0.0125 Å.

The other main feature in the R.D.F., the peak at 3.45 Å, can be assigned to the cation-solvent interaction. The bond length is longer than that proposed for the Se-O interaction, because of the greater radius of the Te atom compared with the Se atom.

During the course of this work the structure of the Te_4^{2+} ion was determined in the solid state by Corbett (74). He showed that the cation







is square planar, with an average Te-Te bond length of 2.665 Å, which is in good agreement with the value found in this liquid diffraction study. The shortening of the bond compared with elemental tellurium can be described in a similar manner to the shortening observed in the Se_4^{2+} ion (see Chapter 5).

6. The Radial Distribution Function for I_3^+/HSO_3F .

Intensity measurements were recorded on the $\theta/2\theta$ horizontal goniometer for two solutions containing $I_2/S_2O_6F_2$ in the ratio 3:1 with different I_2 concentrations. The normalised, reduced intensity function, $M(s) \cdot i(s) \cdot s$, and its Fourier transform for Run 1 (I_2 concentration 30 mole %) is given in Figure 7.9, and for Run 2 (I_2 concentrations 12 mole %) in Figure 7.10. The absolute amplitudes of the peaks in the two R.D.F.'s are probably not meaningful since the solvent peak at about 1.50 Å is virtually non-existent in both functions. However, the positions of the peaks are interesting, and a comparision of the relative amplitudes of the peaks in the two functions probably is valid.

The principle peaks for the two R.D.F.'s are shown in Figure 7.11. The peak centred at 2.65 Å can be assigned to an I-I interaction since the bond length for I_2 is 2.66 Å. The ratio of the intensity of this peak for the two solutions is about 3:1, which is quite close to the known ratio of the concentrations of I_2 in the two solutions.

The other main feature of the R.D.F.'s are the peaks at approximately 5.0 Å. In both R.D.F.'s there is a peak near to 5.40 Å or double the I-I separation. The ratio of the areas of the peaks at



Figure 7.9. Reduced Intensity and Radial Distribution Function for $_{I_3^{}+/HSO_3\,F}$ RUN 1



2.70 Å and 5.40 Å for Run 1 is close to 2:1, indicating that three iodine atoms must be in a linear chain. The R.D.F. for Run 2 has two peaks in the region of 5.40 Å, one at 5.20 Å the other at 5.60 Å.

The important feature of both of these R.D.F.'s is the absence of a peak in the vicinity of 3.80 Å. This is the value predicted for the long I-I distance in a bent I_3^+ structure which has a bond angle of 90°. Such a model would appear to be quite reasonable for I_3^+ since the isoelectronic cation ICl_2^+ has a bond angle of about 94° (75).

The results from these experiments, while not as reliable as those obtained with the θ/θ diffractometer, have to be interpreted in terms of three iodine atoms in a linear chain which seems a very unlikely structure for I_3^+ . The concentrations of the solutions studied are at least twenty times greater than those studied by Gillespie and Milne (18), and it is possible that the I_3^+ cation may polymerise at such high concentrations to give some new cation e.g. $I_6^{2^+}$. The system $I_2/S_2O_6F_2/HSO_3F$ will have to be studied as a function of the concentration of the oxidising agent, and the concentration of I_2 , in order to make a reliable interpretation of the structures of the cationic species which are formed.



Figure 7.11. Experimental Peaks for I_3^+/HSO_3F RUN 1 and RUN 2

CHAPTER 8

Conclusions

1) Introduction

This thesis describes some of the first structural studies of the Group VI and VII polyatomic cations. The structure of the $\mathrm{Se_4}^{2+}$ cation has been determined from a single crystal X-ray diffraction study of the compound $\mathrm{Se_4}(\mathrm{HS_2O_7})_2$. The cation was found to be square planar, with an average Se-Se bond length of 2.283(4) Å.

A reliable experimental technique for recording the intensity of the X-rays scattered from very corrosive liquids has been developed. This has allowed the structure of the Se_4^{2+} cation to be determined in solution, and a similar square planar structure was found. The similarity of the structures in the solid and liquid state suggests that the cation is a discreet molecular unit and its structure is not determined by crystal packing forces. A liquid diffraction study of the isoelectronic Te_4^{2+} cation has shown that this ion is also square planar.

The R.D.F.'s obtained from the $3:1 I_2/S_2O_6F_2$ solutions suggest that more work is necessary to completely understand the behaviour of this system. Liquid diffraction studies should be carried out on solutions in which the concentrations of the oxidising agent is varied, as well as the concentration of the cation. The u.v. spectra of the solutions would also be useful, since they should provide a clear indication of the formation of different cations.

2) The Structures of Polyatomic Cations of Group VI and VII.

The Group VI elements S, Se, and Te, all form a cation of the general formula X_4^{2+} . The structures of two of these, Se_4^{2+} and Te_4^{2+} , have been determined both in the solid and liquid state (76, 74), and have regular square planar structures. The results of Raman (77) and magnetic circular dichroism (44) studies indicate that the isoelectronic S_4^{2+} ion is also square planar.

The discussion of the bonding for the Se_4^{2+} cation given in Chapter 5 is equally applicable to S_4^{2+} and Te_4^{2+} . The shortening of the interatomic bonds, because of the double bond character introduced by the delocalisation of the 6π electrons, decreases as one goes up the group. The bond length in the Te_4^{2+} cation is about 7% less than the bond length in elemental Te, while the difference between the two for the Se_4^{2+} ion is about 2%. The bond shortening decreases going up the group, suggesting that the bond length in S_4^{2+} will be very close to that in elemental S.

Homonuclear square planar rings are comparatively rare in inorganic chemistry. Corbett (45) has interpreted the square Hg₄ rings in Na₃Hg₂ (78) in terms of an Hg₄⁶⁻ ion having a similar valence configuration to that proposed for Se₄²⁺, but it seems likely that there is some delocalisation of electrons from the Hg₄ ring onto the neighbouring Na atoms. The bond lengths reported for the Hg₄ ring, are 2.96 and 3.01 Å, values which are very close to the bond length of 3.0 Å reported for solid mercury at -46°C (69). The comparison of these bond lengths does not show the shortening, which would be expected for a Hg₄⁶⁻ ion. A similar situation is evident in the skutteridite type structures, which contain square As_4 and Sb_4 units (79, 80). Magnetic measurements on IrAs₃ and IrSb₃ indicate that the delocalisation of the charge away from the ring is so extensive that it is no longer possible to treat the ringsas isolated ions. The structure of S_2N_2 , which is isoelectronic with the Group VI X_4^{2+} cations, has been determined in the compound $S_2N_2(SbCl_5)_2$ (81). The S_2N_2 fragment is square planar with S-N bond lengths of 1.619 (5) Å. According to a correlation of bond order with bond lengths in S-N compounds (82), this corresponds to a valence bond order of approximately 1.3.

The structures of S_8^{2+} and Se_8^{2+} have been determined (83, 84), and are shown in Figure 8.1. The conformations of the rings in the two structures are essentially the same, however, there are some interesting differences in the lengths of the cross ring bond lengths. In S_8^{2+} the bonds S(3) - S(7), S(2) - S(8) and S(6) - S(4), are all somewhat shorter than the van der Waals contact distance. Thus the molecule may be described by valence bond structures of the following type.





 $<S_2S_1S_8 = <S_4S_5S_6 = 93^{\circ}$ all other angles = 102°

 $S_8^{2^+}(AsF_{\bar{6}})_2$



 $Se_8^{2+}(A1C1\bar{4})_2$

Figure 8.1. The structures of the S_8^{2+} and Se_8^{2+} cations.

In contrast, the Se_8^{2+} cation has one very short cross-ring interaction, Se(3) - Se(7), of 2.84 Å, compared with about 3.4 Å for Se(2) - Se(8) and Se(6) - Se(4). Resonance Structure 1 must dominate the structure of the Se_8^{2+} cation, while the other two forms play a less significant role than in S_8^{2+} .

There have been very few structural studies of the halogen cations. The Br_2^+ cation has a bond length of 2.13 Å (85), which is consistent with an increase in bond order over that for bromine resulting from the loss of an antibonding electron. The structures of the interhalogen cations ClF_2^+ , BrF_2^+ and ICl_2^+ , have been determined in the solid state (86, 87, 75). These cations are all angular, with bond angles close to 90°, the value expected for simple p orbital bonding $(ClF_2^+ 95.9^\circ, BrF_2^+ 93.5^\circ, ICl_2^+ average of two determinations 94.6^\circ).$

3) Predictions of Bond Lengths and Bond Angles in XO₄ Tetrahedra

The structural chemistry of the oxy-anions of many of the elements in the periodic table is based on isolated or linked XO_4 tetrahedra. Therefore it would be very useful if the changes in the tetrahedral geometry, that occur when one of the oxygen atoms is bonded to another atom or group could be understood in terms of some simple rules. The structural data for the sulphate and polysulphate systems reviewed in this thesis would indicate that this is possible.

The changes in bond lengths can be predicted by the rule that the sum of the X-O bond lengths is constant. The structures of several pyrophosphates have been determined at this university, and all of them
obey the rule very well. Table 8.1 reviews the pertinent bond lengths in various $M_2P_2O_7$ systems. The sum of the bond lengths about each phosphorus atom is very close to the mean value of 6.158 Å. An interesting feature of these structures is that O(3) is coordinated to only one cation, while the remaining five terminal oxygens are coordinated to two cations. Consequently P(1) - O(3) is shorter than the other P-O terminal bonds, and to maintain a constant sum of bond lengths about each phosphorus atom P(1) - O(4) must be, and is, longer than P(2) - O(4). (See Table 8.1). These pyrophosphates provide further examples of compounds which have an asymmetric X-O-X bridge.

The rules proposed for predicting the bond angles in SO_4 tetrahedra, where one of the oxygen atoms is bonded to another atom or group, seem to be generally applicable to other main group elements. It has been shown that Rule 1 does not apply to the transition elements chromium and vanadium (see Chapter 5). The difference in the behaviour of the main group and transition metal XO_4 tetrahedra cannot be accounted for in terms of the oxygen-oxygen contact distances. However, tetrahedral co-ordination in the transition metals implies sd³ hybridisation, compared with sp³ hybridisation for the main group elements, and perhaps this is the fundamental difference which accounts for the behaviour of the tetrahedral groups.

Rule 2 probably is the result of an extended π -bonding system which will only contribute in other structures where four or more atoms lie almost in the same plane. The evidence against a π -bonding mechanism provided by the structure of the $(CH_2(SO_3)_2)^{2^-}$ anion (67) is not necessarily overwhelming because the S-C-S angle is much greater than 109° (119.7°), which implies that there may be donation of

T	A1	ΒL	E	8		1
-			_	-	•	_

Comparison of Pertinent Bond Lengths in Various $M_2 P_2 O_7\ Systems$

		Bond Leng	gths in Å		
	Mg(88)	Co(89)	Zn (90)	Ni(91)	Cd (9 2)
P(1) - O(1) P(1) - O(2) P(1) - O(3) P(1) - O(4)	1.533 1.507 1.472 1.612	1.535 1.519 1.499 1.600	1.518 1.528 1.489 1.599	1.535 1.558 1.516 1.598	1.558 1.516 1.449 1.645
SUM	6.124	6.153	6.134	6.207	6.168
P(2) - 0(4) P(2) - 0(5) P(2) - 0(6) P(2) - 0(7)	1.569 1.539 1.527 1.521	1.566 1.527 1.510 1.514	1.566 1.520 1.518 1.531	1.606 1.541 1.545 1.527	1.605 1.530 1.548 1.488
SUM	6.156	6.117	6.135	6.219	6.171



electron density from the C-H bonds to the C-S bonds. A better understanding of Rule 2 may be gained by looking at the additional decrease in bond angle predicted by the rule as a function of the twist angle.

4. Suggestions for Further Work

During the course of this work a large number of new cations have been prepared by other members of this research group, and in certain cases only the oxidation state of the element has been found e.g. Te_n^{n+} (93). X-ray studies of this cation may be the only method for determining the value of n. The search for cations has been extended to Group V, and to certain of the transition elements. Mercury appears to form a large number of cationic species, and one of these. Hg_3^{2+} , has been positively identified and shown to be linear (94). Research in these laboratories suggests that mercury may form several more linear cations which may have to be identified by X-ray studies in the solid or liquid state.

Liquid X-ray diffraction represents a very useful, new experimental method for studying cation structures. Work is in progress to adapt a variable temperature cell, which has a temperature range from -100°C to 1600°C, to the θ/θ diffractometer. This should allow the structure of the I_4^{2+} cation to be determined, since the only method for preparing this cation reported to date is by the dimerisation of I_2^+ in fluorosulphuric acid at -80°C (95).

This thesis demonstrates the feasability of determining reliable

structural information from quite complex solutions by liquid X-ray diffraction. Since so much chemistry is performed in the liquid state, this technique may be expected to play an increasingly important role in inorganic chemistry.

APPENDIX

1. Intensity Measurements for Mercury

1/2° SLIT, 20,000 COUNTS

θ	Time	θ	Time	θ	Time
5.00	1210.8	14.00	809.28	24.75	1704.95
5.25	1696.12	14.25	695.73	25.00	1749.07
5.50	2485.92	14.50	704.57	25.25	1792.52
5.75	4044.7	14.75	733.43	25.50	1857.89
6.00	3406.98	15.00	730.83	25.75	1973.27
6.25	2379.47	15.25	788.8	26.00	1980.09
6.50	1879.31	15.50	811.88	26.25	1961.58
6.75	1627.34	15.75	869.6	26.50	1964.03
7.00	1269.5	16.00	909.46	26.75	2017.79
7.25	889.15	16.25	972.84	27.00	2082.39
7.50	890.71	16.50	1055.31	27.25	2079.44
7.75	972.82	16.75	1114.41	27.50	2094.89
8.00	1073.52	17.00	1159.21	27.75	2110.49
8.25	1212.9	17.25	1131.31	28.00	2071.72
8.50	1121.27	17.50	1205.91	28.25	2092.05
8.75	1500.23	17.75	1254.	28.50	2087.44
9.00	1681.18	18.00	1244.46	28,75	2141.1
9.25	1921.69	18.25	1300.71		
9.50	2184.75	18.50	1263.35	2° SLIT, 20	,000 COUNTS
9.75	2269.4	18.75	1180.16	-	
		19.00	1256.33	25.00	715.38
1° SLIT,	20,000 COUNTS	19.25	1249.29	25.50	743.76
		19.50	1282.21	26.00	778.38
9.00	570.66	19.75	1213.58	26.50	773.19
9.25	629.34	20.00	1296.36	27.00	842.21
9.50	701.63	20.25	1253.33	27.50	837.7
9.75	772.48	20.50	1275.17	28.00	848.9
10.00	869.24	20.75	1284.21	28.50	847.14
10.25	950.6	21.00	1271.5	29.00	860.22
10.50	995.09	21.25	1240.24	29.50	860.99
10.75	1058.64	21.50	1241.97	30.00	888.66
11.00	1093.79	21.75	1242.07	30.50	915.81
11.25	996.51	22.00	1258.57	31.00	955.9
11.50	1089.	22.25	1247.82	31.50	989.59
11.75	1098.3	22.50	1321.12	32.00	1023.96
12.00	1125.14	22.75	1326.	32.50	1079.95
12.25	1033.63	23.00	1358.23	33.00	1085.74
12.50	810.83	23.25	1411.17	33.50	1119.52
12.75	965.95	23.50	1460.7	34.00	1168.48
13.00	984.51	23.75	1533.31	34.50	1200.05
13.25	941.36	24.00	1600.89	35.00	1226.1
13.50	892.92	24.25	1647.58	35.50	1272.57
13.75	743.99	24.50	1694.22	36.00	1271.92

Intensity Measurements for Mercury (continued)

	θ	Time	θ	Time
	36.50	1276.54	53.00	2060.29
	37.00	1277.21	53.50	2050.44
	37.50	1321.17	54.00	2090.03
	38.00	1310.01	54.50	2060.17
	38.50	1370.46	55.00	2110.08
	39.00	1372.57	55.50	2109.16
	39.50	1440.69	56.00	2089.69
	40.00	1436.64	56.50	2096.43
	40.50	1518.13	57.00	2103.36
	41.00	1591.36	57.50	2077 25
	41.50	1617.95	58 00	2098 55
	42.00	1673 87	58 50	2124 8
	42.50	1699 76	59.00	2074 81
	43.00	1701.45	59.50	2088 17
	43 50	1738 02	60 00	2000.17
	44 00	1746 04	60.50	2076.87
	44.50	1832 42	61 00	2070.07
	45 00	1840 26	61 50	2000.52
	45 50	1836 88	62 00	2059.00
	46 00	1835 4	62.00	2055.10
	46.50	1876 16	63 00	2055.45
	47 00	1870.75	63 50	2037.00
	47.00	1807 02	64 00	2071.1
	48 00	10/0 05	64.00	2057 50
	18 50	1077 76	04.30	2037.39
	40.00	1050 74		
	49.00	1959.34		
	49.50	1975.1		
	50.00	19/0.43		
	50.50	2033.09		
4°	SLIT,	40,000 COUNTS		24
	45.00	1846.73		
	45.50	1855.22		
	46.00	1873.34		
	46.50	1878.15		
	47.00	1890.27		
	47.50	1906.33		
	48.00	1957.53		
	48.50	1950.49		
	49.00	1946.14		
	49.50	2001.88		
	50.00	1975.14		
	50.50	1975.76		

51.00

51.50 52.00 52.50 2005.43

2034.85 2050.24 2067.09

2. Intensity Measurements for Fluorosulphuric Acid

1° SLIT, 40,000 COUNTS

2° SLIT, 40,000 COUNTS

θ	Time	θ	Time	θ	Time
8.00	554.34	19.00	681 79	25 00	498 31
8.25	533.89	19.25	694 66	25.00	500 51
8.50	517 58	19.20	734 42	25.50	500.31
8.75	506 29	19.30	753 62	26.50	501.72
9 00	488 04	20.00	706 72	20.30	517 64
9.00	170 13	20.00	200.72 202 A2	27.00	515.04
9.50	477 27	20.23	844 19	27.30	570 61
9.50	477.27	20.30	044.10	28.00	530.01
10 00	479.	20.75	0/0./4	20.30	544.55
10.00	476.55	21.00	903.96	29.00	542.05
10.23	4/0.05	21.25	945.10	29.50	549.50
10.30	400.90	21.50	950.55	30.00	504.31
10.75	400.70	21.75	1010.92	30.50	569.44
11.00	403.39	22.00	1059.29	31.00	580.46
11.25	4/1./5	22.25	1107.44	31.50	595.32
11.50	4/7.06	22.50	1108.22	32.00	613.42
11.75	487.79	22.75	1159.09	32.50	625.74
12.00	495.23	23.00	1184.69	33.00	642.51
12.25	496.53	23.25	1254.65	33.50	658.12
12.50	502.3	23.50	1287.	34.00	673.
12.75	515.81	23.75	1297.89	34.50	704.77
13.00	528.41	24.00	1329.57	35.00	702.79
13.25	539.03	24.25	1368.16	35.50	735.03
13.50	538.12	24.50	1407.04	36.00	767.37
13.75	548.21	24.75	1424.64	36.50	779.69
14.00	548.02	25.00	1439.99	37.00	797.5
14.25	558.01	25.25	1478.69	37.50	829.8
14.50	550.91	25.50	1493.33	38.00	829.
14.75	553.03	25.75	1517.62	38.50	847.58
15.00	558.8	26.00	1531.88	39.00	866.02
15.25	561.28	26.25	1553.7	39.50	887.33
15.50	566.15	26.50	1573.08	40.00	930.34
15.75	570.64	26.75	1570.88	40.50	927.84
16.00	569.28	27.00	1603.97	41.00	954.27
16.25	581.84	27.25	1627.18	41.50	980.24
16.50	592.3	27.50	1641.61	42.00	999.86
16.75	594.2	27.75	1652.4	42.50	1011.93
17.00	602.81	28.00	1709.24	43.00	1021.88
17.25	606.17	28.25	1754.95	43.50	1028.33
17.50	607.13	28.50	1759.91	44.00	1028.1
17.75	613.35	28.75	1824.9	44.50	1041.91
18.00	620.27	29.00	1854.88	45.00	1045.22
18.25	634.61	29.25	1896.49	45.50	1066.08
18.50	655.29	29.50	1950.19	46.00	1053.16
18.75	668.54	29.75	1996.49	46.50	1077.85

2° SLIT, 40,000 COUNTS

θ	Time	θ	Time
47.00	1081.11	45.00	2422.62
47.50	1113.95	45.50	2431.36
48.00	1063.59	46.00	2439.47
48.50	1066.94	46.50	2457.02
49.00	1067.31	47.00	2450.21
49.50	1063.37	47.50	2455.42
50.00	1072.52	48.00	2489.16
50.50	1059.18	48.50	2477.41
51.00	1069.19	49.00	2454.43
51.50	1075.02	49.50	2452.7
52.00	1077.24	50.00	2454.98
52.50	1076.25	50.50	2476.17
53.00	1081.03	51.00	2493.68
53.50	1085.98	51.50	2468.14
54.00	1080.43	52.00	2457.13
54.50	1087.52	52 .5 0	2469.7
55.00	1086.87	53.00	2484.8
55.50	1081.82	53.50	2444.63
56.00	1092.85	54.00	2452 .26
56.50	1089.95	54.50	2465.02
57.00	1072.71	55.00	2451.17
57.50	1101.1	55.50	2433.78
58.00	1086.82	56.00	2426.04
58.50	1075.39	56.50	2450.7
59.00	1074.58	57.00	2439.5
59.50	1068.95	57.50	2431.29
60.00	1068.62	58.00	2437.83
60.50	1067.12	58.50	2435.46
61.00	1059.23	59.00	2407.24
61.50	1059.93	59.50	2404.47
62.00	1039.69	60.00	2390.27
62.50	1041.74	60.50	2370.49
63.00	1035.66	61.00	2358.51
63.50	1019.56	61.50	2320.81
64.00	1010.55	62.00	2285.
64.50	1011.01	62.50	2263.93

4° SLIT, 200,000 COUNTS

41.00	2219.44
41.50	2253.82
42.00	2294.42
42.50	2315.99
43.00	2359.29
43.50	2370.21
44.00	2412.3
44.50	2445.63

3. Intensity Measurements for $Se_4^{2^+}$ in Fluorosulphuric Acid

1/2° SLIT, 20,000 COUNTS

θ	Time	θ	Time	θ	Time
6.00	774.47	14.00	591.90	24.75	1285.8
6.25	831.12	14.25	596.15	25.00	1288.5
6.50	930.27	14.50	601.76	25.25	1319.2
6.75	1018.7	14.75	611.55	25.50	1353.5
7.00	1091.4	15.00	617.13	25.75	1364.7
7.25	1126.8	15.25	621.50		
7.50	1160.6	15.50	634.24	2° SLIT,	40,000 COUNTS
7.75	1160.3	15.75	641.33		
8.00	1138.7	16.00	645.90	23.00	829.61
8.25	1147.2	16.25	659.06	23.50	899.89
8.50	1132.5	16.50	673.81	24.00	927.36
8.75	1128.9	16.75	672.96	24.50	964.52
9.00	1126.8	17.00	672.57	25.00	989.86
9.25	1147.5	17.25	674.50	25.50	994.43
9.50	1166.1	17.50	682.03	26.00	1003.2
9.75	1198.1	17.75	671.00	26.50	1032.4
		18.00	669.20	27.00	1032.3
1° SLIT,	20,000 COUNTS	18.25	679.01	27.50	1032.9
		18.50	694.28	28.00	1054.0
8.00	433.75	18.75	694.06	28.50	1082.0
8.25	424.54	19.00	694.52	29.00	1098.1
8.50	417.30	19.25	719.90	29.50	1097.9
8.75	413.50	19.50	746.62	30.00	1127.2
9.00	420.95	19.75	753.70	30.50	1156.8
9.25	422.49	20.00	800.11	31.00	1197.6
9.50	427.29	20.25	810.56	31.50	1224.6
9.75	433.99	20.50	838.79	32.00	1259.1
10.00	440.36	20.75	853.57	32.50	1304.8
10.25	442.82	21.00	864.57	33.00	1356.6
10.50	455.17	21.25	901.58	33.50	1373.0
10.75	468.15	21.50	928.98	34.00	1431.9
11.00	471.27	21.75	957.25	34.50	1459.7
11.25	492.21	22.00	978.72	35.00	1512.0
11.50	495.50	22.25	1011.7	35.50	1542.4
11.75	512.58	22.50	1049.8	36.00	1585.6
12.00	528.73	22.75	1075.1	36.50	1646.7
12.25	536.99	23.00	1108.0	37.00	1680.0
12.50	545.88	23.25	1136.1	37 .5 0	1719.7
12.75	549.03	23.50	1175.6	38.00	1773.5
13.00	549.39	23.75	1186.4	38.50	1813.9
13.25	566.98	24.00	1234.7	39.00	1879.3
13.50	577.06	24.25	1276.7	39.50	1912.5
13.75	580.24	24.50	1305.3	40.00	1941.5

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2° SLIT, 40,000 COUNTS

	θ	Time	θ	Time
	40.50	1997.7	54.00	2875.1
	41.00	2035.2	54.50	2851.7
	41.50	2064.7	55.00	2831.0
	42.00	2098.9	55.50	2887.5
	42.50	2143.4	56.00	2863.3
	43.00	2173.8	56.50	2860.9
	43.50	2237.7	57.00	2850.1
	44.00	2279.1	57.50	2837.9
	44.50	2278.1	58 00	2820 2
	45.00	2351 8	58 50	2850 6
	45 50	2363 7	59.00	2827 1
	46 00	2351 0	59.00	2805 5
	46 50	2381.6	60.00	2805.5
	40.50	2362 7	60.50	2803.0
	47.50	2302.7	61 00	2012.1
	18 00	2/20 0	61 50	2740 0
	40.00	2420.0	62.00	2749.0
	40.50	2440.	62.50	2753.2
4°	SLIT,	100,000 COUNTS	63.00	2747.8
	41 00	2408 0	64 00	2705.3
	41.00	2430.0	64 50	2703.8
	41.00	2520.5	04.30	2/10.3
	42.00	2502.0		
	42.50	2009.5		
	43.00	2052.2		
	43.50	20/1.1		
	44.00	2/04./		
	44.50	2/3/.1		
	45.00	2705.0		
	45.50	2/8/.5		
	40.00	2808.3		
	40.50	2833.3		
	47.00	2861.7		
	47.50	2906.8		
	48.00	28/6.6		
	48.50	2857.3		
	49.00	2861.2		
	49.50	2886.6		
	50.00	2933.1		4 .
	50.50	2926.7		
	51.00	2910.9		
	51.50	2888.9		
	52.00	2928.6		
	52.50	2870.4		
	53.00	2844.5		
	53.50	2895.7		

4. Intensity Measurements for Te_4^{2+} in Fluorosulphuric Acid

θ	Time	θ	Time	θ	Time
6.00	384.62	13.25	374.81	24.25	744.68
6.25	417.12	13.50	382.51	24.50	747.19
6.50	469.38	13.75	389.59	24.75	760.27
6.75	509.79	14.00	393.70	25.00	760.81
7.00	543.43	14.25	396.39	25.25	780.9
7.25	565.82	14.50	402.68	25.50	782.70
7.50	581.27	14.75	404.16	25.75	798.80
7.75	573.32	15.00	397.80	26.00	808.71
8.00	566.18	15.25	402.16	26.25	825.01
8.25	552.35	15.50	396.65	26.50	845.73
8.50	552.2	15.75	392.33	26.75	849.89
8.75	548.06	16.00	402.39	27.00	865.13
9.00	562.43	16.25	397.97	27.25	879.33
9.25	577.06	16.50	396.03	27.50	867.59
9.50	590.35	16.75	404.62	27.75	898.44
9.75	600.57	17.00	404.35	28.00	891.59
10.00	619.9	17.25	409.86	28.25	927.57
10.25	635.28	17.50	414.08	28.50	935.38
10.50	657.63	17.75	417.04	28.75	956.20
10.75	677.26	18.00	427.73	29.00	951.39
		18.25	433.10	29.25	974.72
1° SLIT,	20,000 COUNTS	18.50	439.87	29.50	1004.77
		18.75	457.12	29.75	996.63
8.00	269.61	19.00	473.54		
8.25	259.8	19.25	484.78	2° SLIT,	40,000 COUNTS
8.50	255.00	19.50	505.13		
8.75	258.14	19.75	524.87	25.00	536.86
9.00	256.89	20.00	541.59	25.50	552.25
9.25	259.77	20.25	561.40	26.00	574.02
9.50	266.59	20.50	577.76	26.50	578.37
9.75	276.06	20.75	595.90	27.00	595.89
10.00	280.71	21.00	614.69	27.50	610.24
10.25	282.69	21.25	629.84	28.00	623.48
10.50	285.44	21.50	646.05	28.50	641.16
10.75	295.33	21.75	657.13	29.00	650.73
11.00	298.57	22.00	666.52	29,50	678.54
11.25	308.30	22.25	677.43	30.00	680.35
11.50	316.38	22.50	692.35	30.50	705.58
11.75	319.52	22.75	695.10	31.00	734.14
12.00	327.97	23.00	695.20	31.50	742.30
12.25	337.82	23.25	706.33	32.00	764.71
12.50	342.62	23.50	726.54	32.50	762.45
12.75	352.98	23.75	719.61	33.00	768.32
13.00	365.16	24.00	734.26	33.50	788.55

2° SLIT, 40,000 COUNTS

θ	Time
34.00	808.43
34.50	821.65
35.00	826.12
35.50	858.85
36.00	872.9
36.50	893.61
37.00	901.42
37.50	930.54
38.00	965.84
38.50	984.46
39.00	989.86
39.50	1004.26
40.00	991.63
40.50	997.19
41.00	1025.06
41.50	1048.52
42.00	1024.83
42.50	1072.85
43.00	1075.30
43.50	1071.63
44.00	1081.11
44.50	1104.77
45.00	1099.68
45.50	1115.23
46.00	1121.64
46.50	1148.76
47.00	1140.00
47.50	1146.28
48.00	1155.26
48.50	1162.74
49.00	1162.35
49.50	1169.62
50.00	1163.44
50.50	1172.26
51.00	1168.74
51.50	1175.30
52.00	1202.36
52.50	1224.24
53.00	1256.26
53.50	1206.80
54.00	1208.12
54.50	1208.

5. Intensity Measurements for I_3^+ in Fluorosulphuric Acid

Run 1

1/2° SLIT, 100,000 COUNTS

	θ	Time	θ	Time	θ	Time
	5.00	245.10	14.25	235.50	24.00	190.53
	5.25	261.53	14.50	233.35	24.50	196.68
	5.50	282.93	14.75	231 47	25.00	201 51
	5.75	304.70	15.00	230.25	25.50	206.37
	6 00	321 18	15.25	228 50	26.00	215 62
	6 25	341 67	15.50	236.72	26.50	222 30
	6 50	351 01	15.50	230.72	20.50	222.30
	6 75	365 83	16 00	233.30	27.00	242 60
	7 00	303.03	16.00	222.07	27.30	242.00
	7 25	071 30	16.23	223.30	28.00	250.40
	7.25	271.52	16.30	242.00	20,50	200.28
	7.50	204.01	17.00		29.00	2/4.99
	0 00	200.19	17.00	245.03	29.30	200.00
	0.00	204.10	17.20		30.00	204.15
	0.45	220.30	17.50	250.55	30.50	292.40
	8.50	118.9/	1/./5	264.00	31.00	299.63
	8.75	203.95	18.00	265.26	31.50	308.04
	9.00	204.85	18,25	271.50	32.00	313.13
	9.25	196.91	18.50	280.92	32.50	314.54
	9.50	164.03	18.75	291.80	33.00	320.33
	9.75	238.38	19.00	301.04	33.50	329.02
	10.00	260.37	19.25	317.50	34.00	343.77
	10.25	274.93	19.50	325.38	34.50	371.10
	10.50	295.07	19.75	336.50	35.50	380.74
	10.75	318.47	20.00	345.68	35.50	392.09
	11.00	336.38	20,25	356.50	36.00	404.33
	11.25	348.16	20.50	358.12	36.50	413.84
	11.50	377.36	20.75	374.10	37.00	426.57
	11.75	400.53	21.00	382.95	37.50	436.98
			21,25	393.30	38.00	446.30
1°	SLIT,	100,000 COUNTS	21.50	401.16	38.50	454.40
	•	•	21.75	413.25	39.00	476.92
	11.00	144.50	22.00	416.90	39,50	484.25
	11.25	149.50	22.25	419.00	40.00	492.62
	11.50	154.44	22.50	416.31	40.50	504.76
	11.75	171.50	22.75	414.90	41.00	504.50
	12.00	182.79	23.00	422.71	41.50	511.35
	12.25	191.20	23.25	424.00	42.00	523.61
	12.50	195.22	23.50	437.40	42.50	533.23
	12 75	200 12	23.75	444 50	43.00	540 21
	13.00	214,16			43.50	542 64
	13 25	221 50	2° SLTT	100 000 COUNTS	40.00	544 80
	13 50	221.00	2 Ouri,	100,000 000010	44.00 11 50	547 54
	13.30	220.20	23 00	176.00	44.50	07/.04
	1/ 00	231.00	23.00	197 20		
	14.00	443.04	23.30	102.00		

4° SLIT, 100,000 COUNTS

θ	Time
θ 43.00 43.50 44.00 44.50 45.00 45.50 46.00 45.50 46.00 47.00 47.50 48.00 49.00 49.50 50.00 50.50 51.00 51.50 52.00 52.50 53.00 53.50 54.00 54.50 55.00	Time 280.0 286.00 292.92 299.52 301.05 302.06 306.89 308.44 310.16 314.61 315.45 315.61 317.48 317.96 318.78 318.39 318.25 315.84 313.62 314.41 313.53 315.38 297.69 309.52 310.99
54.50	309.52
55.00	310.99
55.50	309.89
56.00	312.05
56.50	310.06
57.00	307.88
57.50	308.56
58.00	305.66
58.50	303.56
59.00	304.28
59.50	304.61
60.00	301.76
60.50	301.83
61.00	298.84
61.50	300.92
62.00	299.17
62.50	297.63
63.00	294.71
63.50	290.51
64.00	280.91
64.50	279.45

6. Intensity Measurements for I_3^+ in Fluorosulphuric Acid

Run 2

1/2° SLIT, 100,000 COUNTS

θ Time θ Time θ	Time
5.00 185.58	
5,25 203.01 14.50 216.70 24.50	205.50
5.50 227.63 14.75 212.50 25.00	211.50
5,75 257,26 15.00 215.66 25.50	218.44
6.00 288.29 15.25 218.60 26.00	222.35
6.25 315.33 15.50 224.68 26.50	228 78
6.50 335 75 15 75 219 50 27 00	244 26
6 75 333 18 16 00 200 28 27 50	250 57
7 00 329 93 16 25 218 00 28 00	250.57
7 25 271 88 16 50 214 03 28 50	255.70
7 50 301 68 16 75 227 00 20 00	260 56
7 75 282 22 17 00 272 26 20 50	209.50
8 00 256 04 17 25 277 00 70 00	201.57
8.00 250.94 17.25 255.99 50.00	209.31
0.25 209.97 17.50 238.92 50.50 0.60 117.77 17.75 247.7 71.00	299.43
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	304.46
8.75 195.16 18.00 247.46 51.50 0.00 107.07 10.05 250.5 50.00	305.25
9.00 193.03 18.25 252.5 32.00	324.52
9.25 1/9.89 18.50 261.50 32.50	328.82
9.50 121.39 18.75 271.28 33.00	326.88
9.75 218.29 19.00 282.18 33.50	341.12
10.00 251.75 19.25 289.20 34.00	350.93
10.25 273.23 19.50 288.67 34.50	352.50
10.50 283.75 19.75 298.72 35.00	367.83
10.75 314.6 20.00 311.85 35.50	375.45
11.00 327.84 20.25 319.00 36.00	380.55
11.25 327.56 20.50 327.98 36.50	395.74
11.50 371.97 20.75 342.33 37.00	410.07
11.75 391.75 21.00 350.37 37.50	420.59
21.25 361.50 38.00	425.20
1° SLIT, 100,000 COUNTS 21.50 371.13 38.50	431.74
21.75 381.46 39.00	447.75
11.00 142. 22.00 395.22 39.50	457.18
11.25 148. 22.25 396.33 40.00	461.21
11.50 156.88 22.50 403.92 40.50	460.39
11.75 166.3 22.75 418.55 41.00	483.26
12.00 173.45 23.00 430.00 41.50	486.12
12.25 181.60 23.25 444.28 42.00	509.10
12.50 187.19 23.50 445.61 42.50	514.49
12.75 187.9 23.75 452.30 43.00	514.33
13.00 205.29 43.50	506.78
13.25 209.10 2° SLITS, 100.000 COUNTS 44.00	507.52
13.50 214.57 44.50	514.34
13.75 217.52 23.00 194.00	
14 00 214 31 23 50 196 23	

4° SLIT, 100,000 COUNTS

θ	Time
43.00	274.00
43,50	276.00
44.00	277.52
44.50	278.20
45.00	281.75
45.50	292.23
46.00	292.77
46.50	295.37
47.00	301.17
47.50	299,93
48.00	302.85
48.50	303.31
49.00	304.36
49.50	304.87
50.00	305.38
50.50	306.76
51.00	307.45
51.50	307.67
52.00	308.19
52.50	307.24
53.00	306.37
53.50	306.89
54.00	304.67
54.50	304.18

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