SOME ASPECTS OF THE COMPLEX CHEMISTRY OF
TELLURIUM AND SELENIUM
WITH SULPHUR DONOR LIGANDS

by

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SUMMARY

The chemistry of some tellurium and selenium compounds have been studied with emphasis on their reaction with sulphur donor ligands.

The preparation of some tellurium compounds containing potentially bidentate ligands is described. These have formulae $ArTe^{IV}(tedto)X_3$, $Te^{IV}(tmdto)X_4$, $ArTe^{IV}(tmdto)X_3$ and $Te^{IV}(Me_2DH_2)X_4$, (where X = Cl or Br, Ar = C_6H_5, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-$C_6H_5OC_6H_4$, p-$C_6H_5SC_6H_4$ or p-BrC_6H_4, tedto = NNN'N' tetraethyldithio-oxamide, tmdto = NNN'N' tetramethyldithio-oxamide and Me_2DH_2 = NN' dimethyldithio-oxamide). Examination of vibrational spectra (infrared and Raman 400-40 cm^{-1}) indicates bands due to tellurium-sulphur and tellurium-halogen vibrational modes. Detailed or tentative assignments of the spectra for these complexes are suggested and in certain cases structures proposed.

Heterocyclic ligands containing both nitrogen and sulphur donors have been reacted with certain tellurium(II) and tellurium(IV) compounds. Complexes of type $Te^{IV}(ttz)_2X_4$, $Te^{IV}(ttz)_3Br_4$, $Te^{II}(ttz)_4Cl_2.H_2O$, $ArTe^{IV}(ttz)_xX_3$, $Te^{IV}(TBuL)_2X_4$, and $Te^{IV}(NMTBuL)_2X_4$ (where X = Cl, Br or I, x is integer, Ar = p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$ or p-$C_6H_5OC_6H_4$, ttz = thiazolidine-2-thione, TBuL = pyrrolidine-2-thione, and NMTBuL = N-methyl-pyrrolidine-2-thione) have been prepared. The infrared and Raman spectra of these complexes have also been examined and are reported here.

Spectroscopic evidence indicates that tellurium could be nitrogen and sulphur co-ordinated in the tellurium(II) and tellurium(IV) complexes with thiazolidine-2-thione, but only sulphur co-ordinated in the tellurium(IV) complexes of pyrrolidine-2-thione or N-methyl-pyrrolidine-2-thione.

Some tellurium(IV) compounds appear to be strong oxidising agents and react with some sulphur ligands to form diarylditellurides or diaryltellurides, the tellurium(IV) being reduced to tellurium(II) or free tellurium.

The preparation of diarylseleniumdichlorides have been investigated and two new synthetic routes are reported, both of which use selenium(IV) chloride as a starting material. The far infrared and Raman spectra of diarylseleniumdichloride are reported and certain assignments made.

The vibrational spectra and the structure of some arylseleniumtribromides have been investigated, and some proposals regarding their structure have been made.

The preparation, characterisation, infrared and Raman spectra of some new complexes of general formula $RSeLBr_3$ (where R = C_6H_5, p-ClC_6H_4, p-BrC_6H_4 or p-$CH_3C_6H_4$ and L = NNN′N′ tetramethyldithio-oxamide or NNN′N′ tetraethyldithio-oxamide) have been investigated. The far infrared and Raman spectra of these complexes indicates that co-ordination is through the sulphur atoms of thiocarbonyl group.

The reaction of o-nitrophenylselenocyanate and p-nitrophenylselenocyanate with some aromatic thiols in a non-aqueous media has been investigated. The main reaction products have been identified as the selenenyl sulphide or the diselenide (depending upon the reactants) and some infrared and Raman spectra of the products are reported.

In the course of all the investigations there was a need for a rapid micro-analytical method for the determination of tellurium in organotellurium compounds. An atomic absorption spectroscopic method was developed, which involves the decomposition of the compounds by oxygen flask combustion and the absorption of aqueous solutions formed in a solvent and subsequent admission into the flame of an atomic absorption spectrometer.

This work was carried out between 1973 and 1976 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

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ABBREVIATIONS

asym	Asymmetric
br	Broad
DMF	Dimethylformamide
dtc	dithio-carbonate
Et	Ethyl
etu	ethylenethiourea
Fig.	Figure
m	medium intensity
Me	Methyl
Me_2DH_2	NN′ dimethyldithio-oxamide
m.p.	Melting point
ms	medium-strong intensity
NMTBuL	N Methyl-pyrrolidine-2-thione
Ph	Phenyl
s	strong intensity
sh	shoulder intensity
sym.	symmetric
TBuL	Pyrrolidine-2-thione
tedto	NNN′N′ Tetraethyldithio-oxamide
tmdto	NNN′N′ Tetramethyldithio-oxamide
tmtu	Tetramethylthiourea
ttz	Thiazolidine-2-thione
tu	Thiourea
μg	Microgram
vs	very-strong intensity
vw	very-weak intensity
w	weak intensity
X	Halogen (Cl, Br or I)

SYMBOLS

Λ	conductivity
δ	deformation vibration
$\Delta\nu$	Raman frequency shift
ν	stretching vibration
τ	tau

CONTENTS:

1- E.Roy Clark and Mohammed A. Al-Turaihi, J. Organometal. Chem., 1975, 96, 251 .

2- E.Roy Clark and Mohammed A. Al-Turaihi, J. Inorg. Nucl., Chem., 1976, 38, 1443 .

CHAPTER I

Chemistry of tellurium compounds.

1.1 Chemistry of Tellurium.

Tellurium belongs to group VIB, the oxygen group of the periodic table. This element has the electronic configuration $ns^2 - np^4$ in the outermost orbitals. ($1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $5s^2$, $5p^4$) There are two electrons short of the noble gas xenon configuration. The element shows more non-metallic chemistry than metallic chemistry. The element has s, p and d orbitals available for use in bonding, so it can form more than four sigma bonds to other atoms. In addition to these s, p and d orbitals, sulphur and selenium have the ability to use $d\pi$ orbitals for hybridization, whilst the lower members of the group are more electronegative to form covalent compounds and acidic oxides. The two higher members of the group e.g. tellurium and polonium are less electronegative and have an increasing tendency to form compounds showing cationic properties. The increase in metallic character of the two higher members is shown by the increase in ionic and the basic character of the oxides tellurium dioxide and polonium dioxide. Tellurium has only weak cationic properties and the oxide tellurium dioxide is amphoteric.

The oxidation states of tellurium in compounds may be -2, 0, +2, +4 and +6 but +1 is possible in $TeSbF_6$ and a formal oxidation state of $+\frac{1}{2}$ has been noted in Te-$TeCl_4$ melts by Bjerrum and Smith.[1] Tellurium exhibits valencies of -2, +2, +4 and +6. Of these, four is the most stable. A coordination number of six is common in tellurium compounds.

Tellurium has a formal oxidation state of -2 in the tellurides Te^{2-} ion, which shows its tendency to complete the inert gas configuration.

Organotellurium compounds generally contain tellurium in oxidation states of either 2 or 4. The main types of compounds encountered are tellurols ($RTe^{II}H$), tellurides (R_2Te^{II}), ditelluride ($R_2Te^{II}{}_2$), organotelluriummonohalides $RTe^{II}X$, ($R_3Te^{IV}X$) organotelluriumdihalides ($R_2Te^{IV}X_2$) and organotelluriumtrihalides ($RTe^{IV}X_3$), and derivatives of these compounds.

The properties and stereochemistry of hydrogen telluride and its derivatives, tellurium oxides and oxyacids of tellurium, hexahalotellurates and organometallic compounds (i.e. those compounds which contain tellurium-carbon bonds) have been fully discussed in many of the standard inorganic chemistry text books.[2-11]

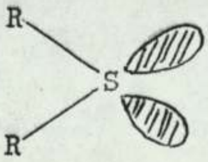
For an oxidation state of tellurium if +4, one lone pair and four bond pairs may be predicted. Thus from a total of five electron pairs a trigonal bipyramid shape is predicted as for Me_2TeCl_2. With the acceptance of another negative ligand, i.e. F^- as in TeF_5^-, a ψ octahedral structure for the ion is predicted, i.e. one lone pair and five bond pairs.

In the oxidation state of tellurium +6, tellurium will have six bonding pairs but no lone pair electrons. Thus for an isolated molecule an octahedral structure, i.e., $Te(OH)_6$, would be expected.

The stabilization of tellurium (II) and tellurium (IV) by sulphur containing ligands has received some attention. Tellurium(II) compounds would be expected to prefer sulphur donor ligands according to Pearson soft acid-soft base concept.

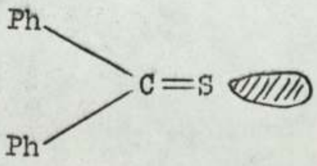
The types of sulphur ligand may be classified into the following groups :

(a) through lone pairs of sulphur from a thioether group, e.g. dimethylsulphide.



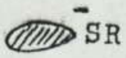
where R = CH_3

(b) through a lone pair of sulphur from a thiocarbonyl group, e.g. thioketones($C_6H_5-\overset{S}{\overset{\|}{C}}-C_6H_5$)



where Ph = C_6H_5

(c) through a lone pair from a thiol group e.g. Methanethiol (CH_3SH)



1.2 Thiourea and substituted thiourea complexes with tellurium (II) and tellurium (IV)

The reactions of sulphur donor ligands such as thiourea and substituted thioureas with tellurium (II) and (IV) have been extensively investigated.[12a] Typical examples of complexes of tellurium (II) and tellurium (IV) with thiourea and their derivatives $Te(Y)_n(X)_m$ are listed in table 1-1.

The crystal structure of a large number of compounds of this type have been determined by O. Foss et al.[12b]

These complexes may be obtained by reacting a mixture of tellurium dioxide in hydrochloric acid with thiourea or its derivatives in an aqueous methanol medium. Reduction of the tellurium (IV) often occurs giving rise to complex of tellurium (II) and the oxidation of the thiourea to formamidinium disulphide cations as indicated below :-

$$Te^{IV} + (n+2)S{=}C(NR_2)_2 + 2X^- \longrightarrow Te^{II}\left[S{=}C(NR_2)_2\right]_n X_2$$

$$\left[(R_2N)_2C\text{-}S\text{-}S\text{-}C(NR_2)_2\right]^{++}$$

where X = Cl, Br or F.

The corresponding iodides[13a, 13b] thiocyanates[13a, 13b] bromide[12] nitrates[13a] and perchlorates[13a, 13b] can be produced by ionic exchange reactions. An increase[13a] or decrease[13a, 13b] in the co-ordination number of the tellurium atom is possible, as can be seen from the following examples :-

TABLE 1-1

The complexes of Te^{+2} and Te^{+4} with thiourea and their derivatives $Te(Y)_n(X)_m$.

Where tu = thiourea, etu = ethylenethiourea, tmtu = tetramethylenethiourea, Prtu = propylenethiourea.

Y	X	n	m	References
tu	Cl, Br, I, SCN, or $CH_3S_2O_2$	2	2	13a, 13c, 14
tu	HF_2	3	2	13a
tu	Cl*, Br, SCN, F*, HF_2, NO_3, SO_4**, ClO_4, HC_2O_4**	4	2	13a, 14, 15
tu	Cl, Br	2	4	16
etu	Br, I, SCN, $CH_3S_2O_2$, $C_6H_5S_2O_2$	2	2	13b, 13c
etu	ClO_4	3	2	13a
etu	Cl*, Br*, ClO_4, $TeCl_6$***	4	2	13b
tmtu	Cl, Br	1	2	13c
tmtu	Cl, Br, I, $CH_3S_2O_2$, $C_6H_5S_2O_2$	2	2	13c
tmtu	Cl, Br	2	4	13c
Prtu	Cl**, ClO_4	4	2	13d
Prtu	ClO_4	3	2	13d
tu/tmdto	Cl, Br	2/2	2	13c

* crystallised in anhydrous from or with $2H_2O$

** crystallised with H_2O

*** obtained in the attempt to prepare $Te(etu)_2Cl_2$

$$Te(tu)_2Cl_2 + 2tu \longrightarrow Te(tu)_4Cl_2$$

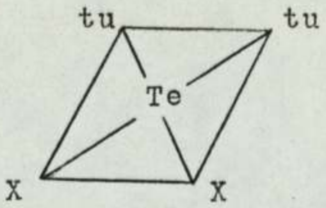
$$Te(etu)_4Cl_2.H_2O \xrightarrow[CH_3OH]{NaI} Te(etu)_2I_2$$

where tu = thiourea and etu = ethylenethiourea.

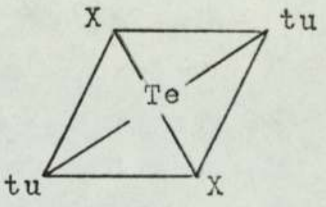
Sulphates [14] nitrates [13a,14] and oxalates [14] are also known.

In the well defined thiourea and substituted thiourea complexes,[12] the tellurium acceptor atom can cope with the charge from the lone pair electrons on the sulphur donor to form complexes of the types TeL_4X_2, TeL_2X_2 or Te(L)X; where L is thiourea or substituted thiourea and X is a halogen atom. When the ligand is tetramethylthiourea the electronegative nature of the lone pair is so great that the tellurium acceptor atom can only cope with the charge donated from one ligand, resulting in the formation of a 1:1 complex. The electronegativity of the lone pair electrons and presumably the size of the lone pair, is of great importance and is related to the nature of the rest of the ligand. The nature or electronegativity of the lone pair can then be altered, i.e., by the design of the ligand.

The stereochemistry of thiourea and substituted thiourea tellurium complexes (e.g. $Te^{II}(tu)_2Cl_2$) may have a cis or trans structure. Crystallographic study has shown that these compounds are basically of a square planar structure [17] as shown below :-



cis $Te(tu)_2X_2$



trans $Te(tu)_2X_2$

where X = halogen

Complex thioureaphenyltellurenylchloride was isolated by Foss [13a,13e] The equation for the reaction is shown and discussed in Chapter III (page 88).

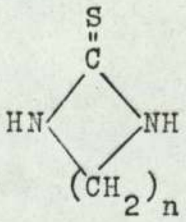
Tellurium(II) in the complex $C_6H_5Te(tu)Cl$ [18] is three coordinated. The structure is illustrated in Chapter III (page 140). There are three normal bonds and the fourth is very long. The Te---Cl bond opposite the phenyl group is virtually absent. The effect is probably due to the use of a single p orbital for bonding at 180°, so that one ligand is more strongly bound than the other.

Tellurium (IV) in the complex $CH_3TeSC(NMe_2)_2Cl_3$ is five coordinated.[19] The structure of this complex is illustrated and discussed later in Chapter III (page140).

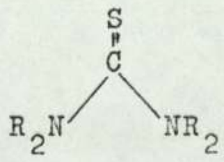
1.3 The reaction of some tellurium (IV) compounds with some sulphur donor ligands.

Clark et al[20] have studied the reaction of some tellurium (IV) compounds with NNN'N' tetraethyldithio-oxamide and suggest that the compounds formed may have a structure based on a coordination number of six for the tellurium atom, with one long Te-Cl bond or two long Te-Cl bonds.

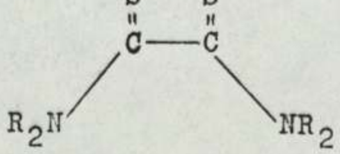
The ligand NNN'N' tetraalkyldithio-oxamide contains two $R-\overset{|}{N}-C=S$ groups and thus has the same essential groups as found in thiourea.



a heterocyclic thiourea
(where n = 2 or 3)



thiourea or substituted thiourea
(where R = H, CH_3, C_2H_5)



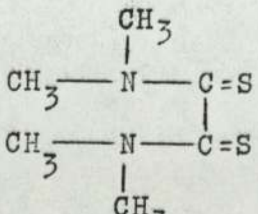
substituted dithio-oxamide
(where R = CH_3 or C_2H_5)

This thesis is concerned with the study of NNN'N' tetraalkyldithio-oxamide and their reaction with tellurium (IV) compounds. The reaction of related ligand such as dithiooxamide, heterocyclic (thiazolidine-2-thione, pyrrolidine-2-thione, N-methyl-pyrrolidine-2-thione), methyl-3-mercaptopropionate and 1,3di(2-pyridyl)-2-thiourea has also been investigated and the complexes formed, described and characterised.

Spectroscopic evidence indicates that co-ordination in these compounds is invariably through sulphur atoms but there are indications that nitrogen donor atoms are sometimes involved.

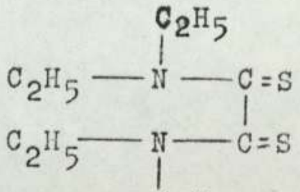
The reactions investigated and products produced are summarised in figures 1-1,1-2,1-3,1-4 and 1-5, overleaf.

The structural formulae of all the ligands used during the work described in this thesis are shown below ;-



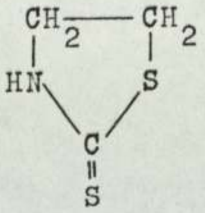
$$\begin{array}{lll} & CH_3 & \\ & | & \\ CH_3- & N- & C=S \\ & & | \\ CH_3- & N- & C=S \\ & | & \\ & CH_3 & \end{array}$$

Tetramethyldithio-
oxamide

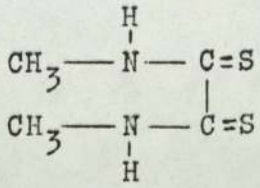


$$\begin{array}{lll} & C_2H_5 & \\ & | & \\ C_2H_5- & N- & C=S \\ & & | \\ C_2H_5- & N- & C=S \\ & | & \\ & C_2H_5 & \end{array}$$

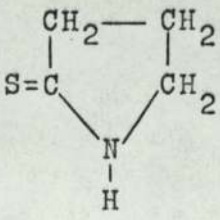
Tetraethyldithio-
oxamide



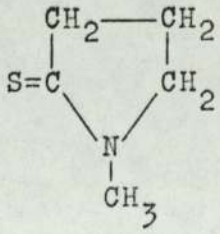
Thiazolidine-2-thione



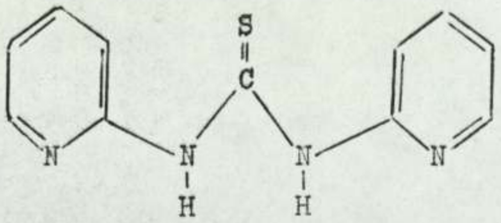
Dimethyldithio-oxamide



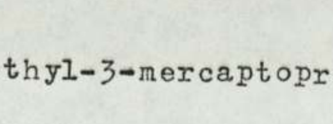
pyrrolidine-2-thione



N-methyl-pyrrolidine-2-thione



1,3di(2-pyridyl)-2-thiourea



$$H-S-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-CH_3$$

Methyl-3-mercaptopropionate

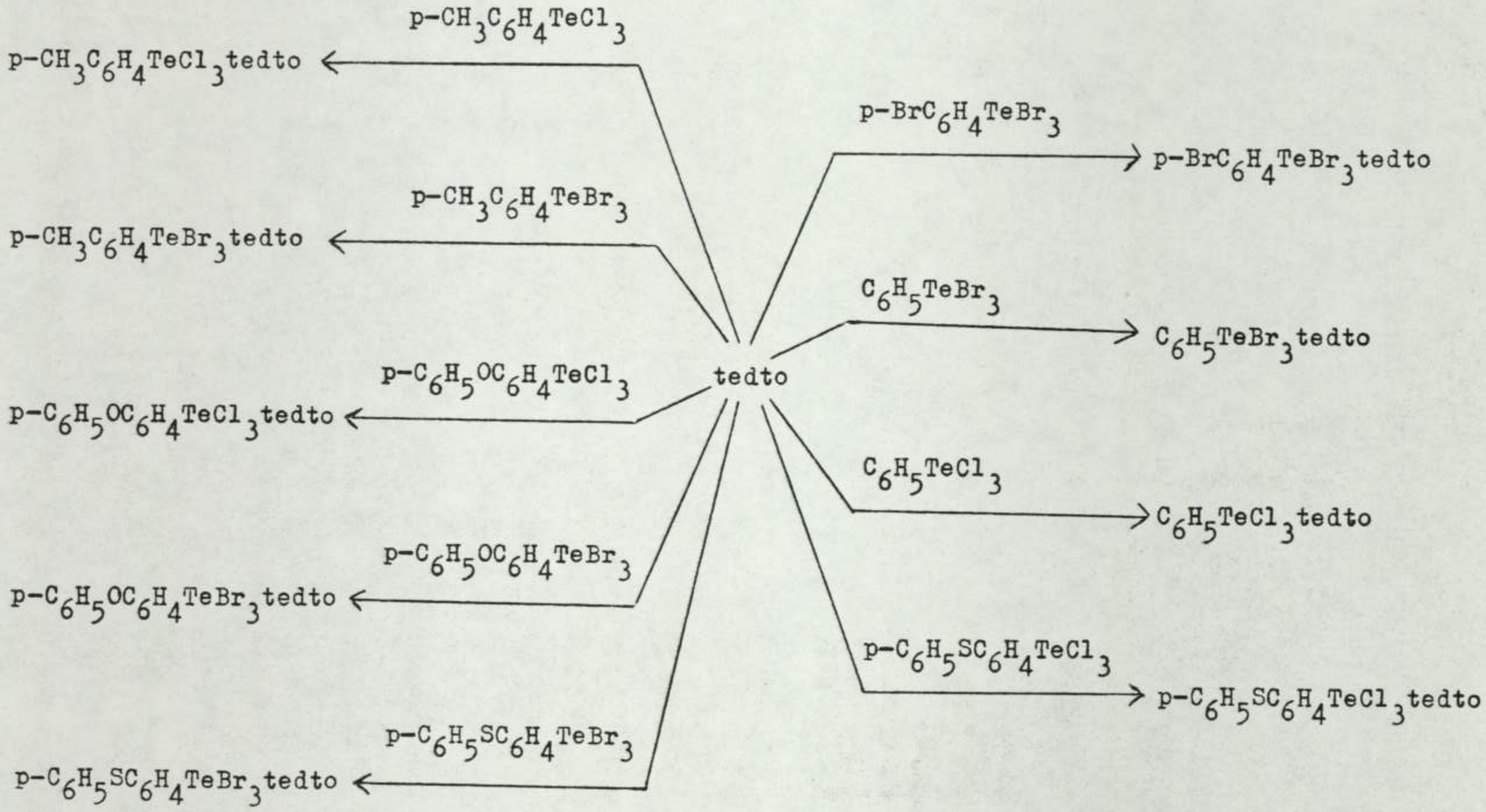


Fig. 1.1

where tedto is NNN'N' tetraethyldithio-oxamide.

The reactions of NNN'N' tetraethyldithio-oxamide with tellurium (IV) compounds.

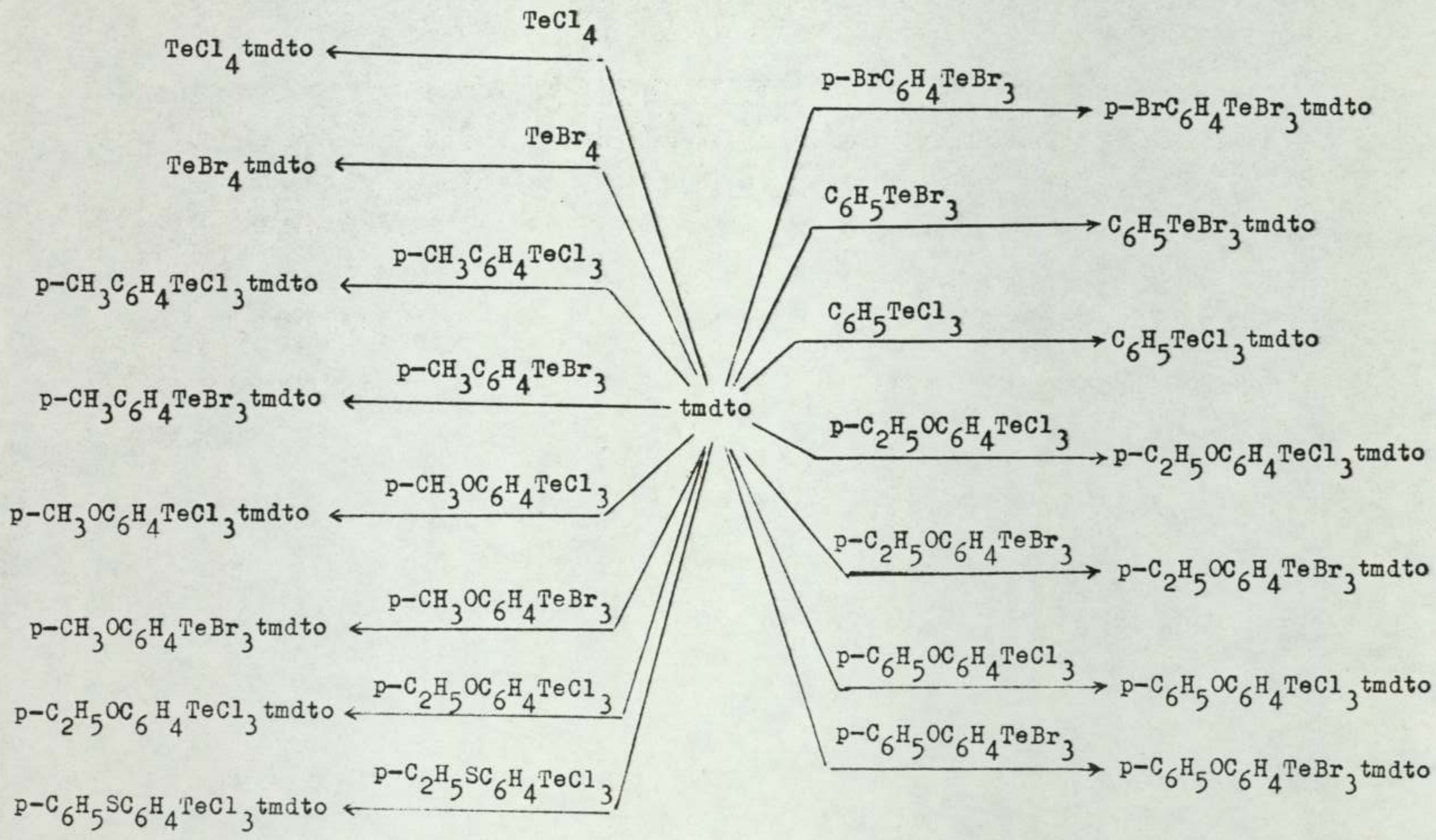


Fig. 1.2

where tmdto is NNN'N' tetramethyldithio-oxamide

The reactions of NNN'N' tetramethyldithio-oxamide with tellurium (IV) compounds.

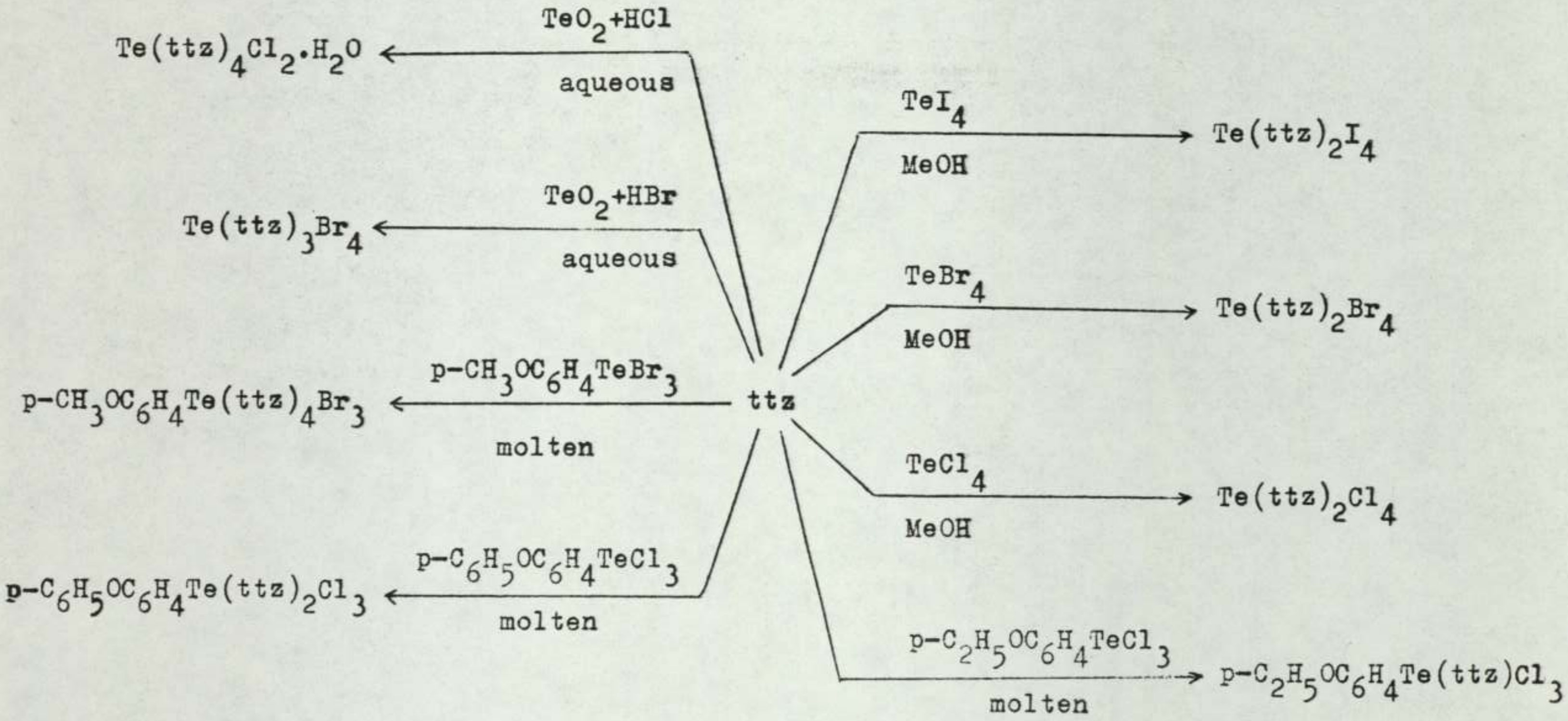


Fig. 1.3

where ttz is thiazolidine-2-thione

The reactions of thiazolidine-2-thione with tellurium (II) and tellurium (IV) compounds.

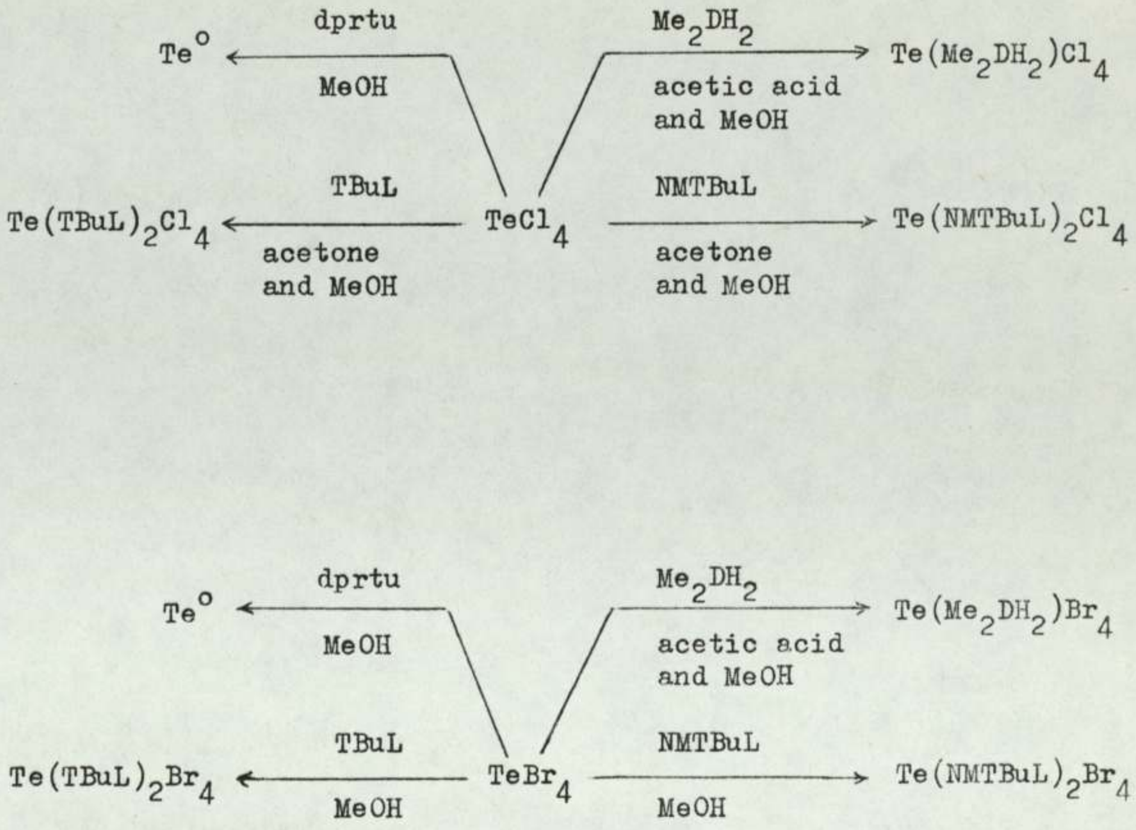


Fig. 1.4

Where: TBuL is pyrrolidine-2-thione

NMTBuL is N-methyl-pyrrolidine-2-thione

Me$_2$DH$_2$ is NN' dimethyldithio-oxamide

dprtu is 1, 3 di(2-pyridyl)-2-thiourea

The Reactions of Tellurium tetrahalide with some sulphur donor ligands.

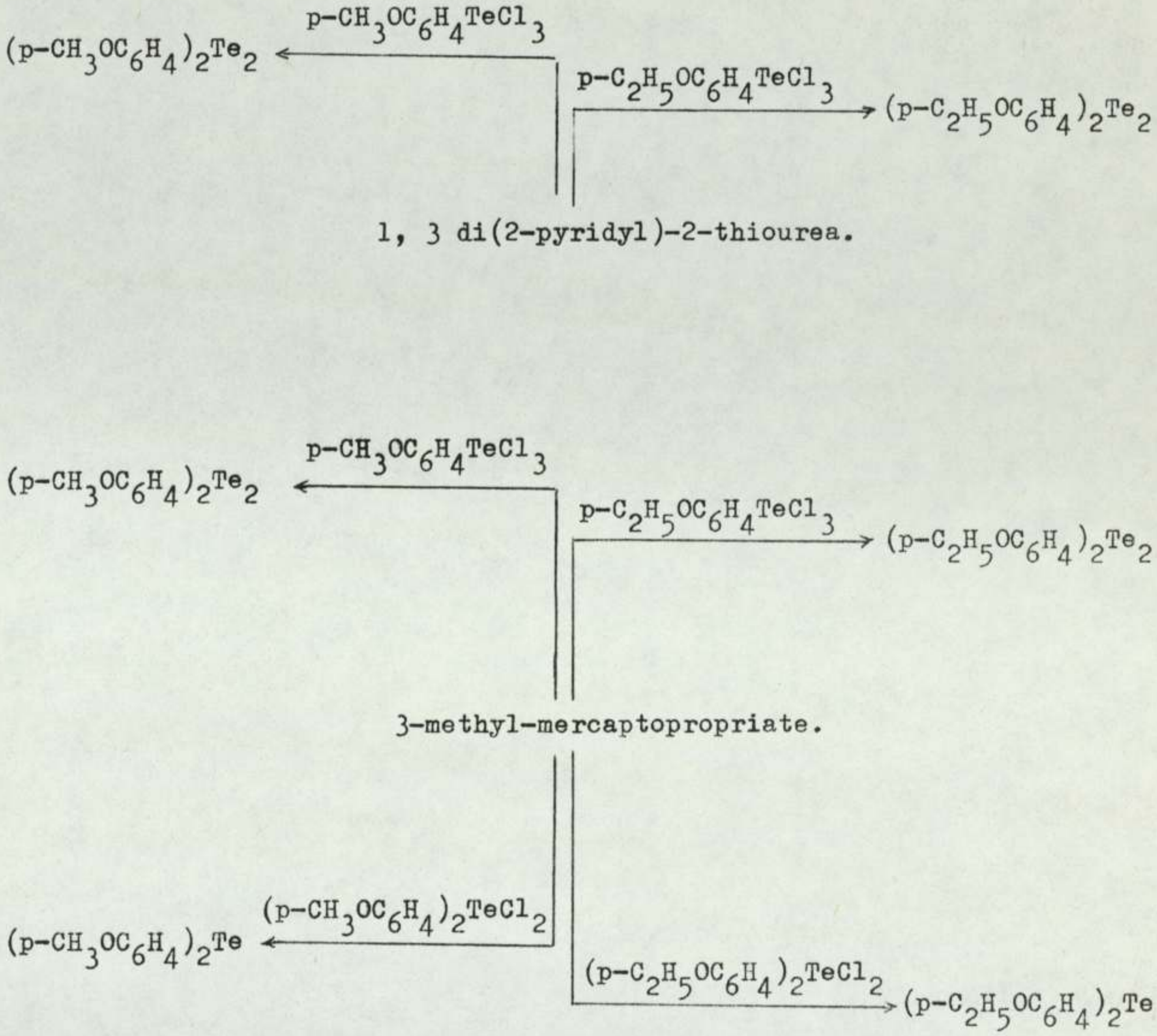


Fig. 1.5

The Reactions of some tellurium(IV) compounds with sulphur donor ligands.

1.4 Vibrational Analysis

The vibrational analysis of compounds containing tellurium-sulphur bonds have been limited to compounds where thiourea, mercapto acid and thiosulphide are ligands.

Aynsley et al[16] were the first workers to study the spectra of any compound containing a tellurium-sulphur bond. The complex examined was of the type Te(IV)$(tu)_2X_4$ (where X is chlorine or bromine and tu is thiourea). The tellurium atom was reported[16] to be the oxidation state (IV) but this compound was found to give a spectrum identical to that for Te(II)$(tu)_2Cl_2$ the preparation of which was published independently.[13a]

Hendra and Jovic[22] published the infrared and Raman spectra of $Te(tu)_4Cl_2$, $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ (where tu = thiourea). A band at 255 cm^{-1} was assigned to the tellurium-sulphur vibration, ν (Te-S).

Hendra and Jovic[23] examined spectroscopically the telluro complexes with substituted thioureas. These compounds had either cis or trans configuration. The ν (Te-S) symmetric stretching frequency was assigned to 230 cm^{-1} and the asymmetric ν (Te-S) to 210 cm^{-1}.

The preparation, infrared and Raman spectra of telluro-mercaptoacids (such as tellurobis-(3-mercaptopropionic acid), tellurobis-(2-mercaptoisobutyric acid), and tellurobis-(2-mercaptopropionic acid) were reported by Clark and Collett.[24]

These compounds were prepared by adding sodium tellurite in distilled water to the mercapto acids also dissolved in water. Tellurium-sulphur symmetric and asymmetric stretching vibrations in the Raman spectra to these compounds ranged from $\Delta\nu$ 247 and 234 cm^{-1} for telluro bis(2-mercaptoisobutyric acid) and to $\Delta\nu$ 212 and 197 cm^{-1} in the other two compounds.

Clark and Collett [25] also reported infrared and Raman spectra of seleno and telluro-pentathionates. These compounds contain anions of the formula $[M(S_2O_3)_2]^{2-}$ (where M = selenium or tellurium). It was suggested that the symmetric tellurium-sulphur stretching frequency in telluro-pentathionates was in the region 236-263 cm^{-1}.

The infrared and Raman spectra of all complexes, whose preparations are described in this thesis, were carried out, and the fundamental bands assigned where possible. As mentioned earlier, these are reported in more detail in Chapters II, III and IV.

It is suggested that the tellurium atom in these compounds are usually sulphur bonded but sometimes nitrogen bonded. From the vibrational data the possible stereochemistry of the tellurium atoms may be inferred but not imphatically proved.

The structure of some tellurium (IV) compounds with NNN′N′ tetramethyldithio-oxamide or NNN′N′ tetraethyldithio-oxamide suggest that the compounds formed may have a structure based on a coordination number of six for the tellurium atom with one long Te-Cl bond or two long Te-Cl bonds.

Also some tellurium (II) and tellurium (IV) compounds with thiazolidine-2-thione may have a cis or trans structure i.e., the tellurium atom in $Te(ttz)_2X_4$ probably has one sulphur donor, one nitrogen donor and the four halogen atoms occupy the four remaining positions.

Further aspects of the structure of the compounds are discussed in Chapters II and III.

1.5 Oxidation reactions of aryltellurium trihalide, diaryltellurium dihalide and tellurium tetrahalide.

These compounds are good oxidising agents and appear to vary in oxidising capacity. The reaction products are either diarylditelluride, diaryltelluride, or elemental tellurium as summarised in fig. 1-5 and discussed in greater detail in Chapter IV. These oxidation products were identified by infrared, elemental analysis and ^1H n.m.r. spectroscopy.

The reaction of tellurium (IV) compounds (such as $RTeCl_3$, R_2TeCl_2 or TeX_4, where X = Cl, or Br and R = $p\text{-}CH_3C_6H_4$ or $p\text{-}C_2H_5OC_6H_4$) with sulphur ligand donors (such as methyl-3-mercaptopropionate or 1,3di(2-pyridyl)-2-thiourea were investigated and the reactions occuring are summarised in Chapter IV.

1.6 Tellurium Analysis.

It was necessary to analyse the tellurium compounds and complexes for their tellurium content.

Consequently, the oxygen flask method was used to decompose the tellurium compounds and complexes and the tellurium, in the solutions produced, was determined by atomic absorption spectroscopy.

The full experimental details are given in Appendix II (page 266) and have recently been published.[212]

1.7 Stability of complexes.

The break-down of complexes in mass spectroscopy (tetramethyldithio-oxamide and tetramethyldithio-oxamide) was also investigated. A typical fragmentation pattern is shown and discussed in more detail in Chapter II (page 79).

CHAPTER II

NNN′N′ Tetraethyldithio-oxamide,
NNN′N′ Tetramethyldithio-oxamide
and NN′ Dimethyldithio-oxamide
complexes of Tellurium(IV).

2.1. INTRODUCTION

Fully substituted dithio-oxamides are potentially bidentate ligands in which co-ordination may occur through sulphur or/and nitrogen atoms. Insoluble complexes are formed with some metal ions by reaction with this type of ligand in a non-coordinating solvent such as acetone or n-butanol.[26,27,28]

Transition metal ions have received some attention. Maganese (II), iron (II), nickel (II), copper (II), form complexes[26] of the type $[M(tedto)_3][ClO_4]_2$ but second row transition metals form complexes of a different stoichiometry. For example, with tetraethyldithio-oxamide, $Pd(tedto)_2[ClO_4]_2$, a 1:2 electrolyte and $Pd(tedto)X_2$ a non-electrolyte have been reported.[27]

Tin (IV) chloride forms a complex $Sn(tedto)Cl_4$ [26] and more recently [29] the range of elements which form complexes with tetraethyldithio-oxamide has been extended to include zinc (II), cadmium (II) and mercury (II). Two classes of complexes are formed with these elements. The perchlorates of formula $[M(tedto)_3][ClO_4]_2$ are similar to those reported earlier for iron, nickel and copper but the 1:1 non-electrolytes of formula $M(tedto)X_2$ (where X = Cl, Br, or I) are analogous to the palladium compound referred to above. Co-ordination through sulphur is always involved for iron, nickel and copper. This is usually the case for other elements irrespective of the nature of the metal ion, i.e. whether it could be described as a soft or hard acid.

It is interesting to note that alternative donors are involved in NN′ disubstituted dithio-oxamide which are S,N coordinated for gold (III) but again S,S coordinated complexes (tedto AuX_4)(AuX_4) are formed with tetraethyldithio-oxamide .[30]

The reaction of fully substituted dithio-oxamide with non-transition elements has received little attention. Clark et.al.[20] reported the preparation of some tellurium(IV) complexes of the type Te(tedto)X_4 and RTe(tedto)X_3 where R = $CH_3OC_6H_4$, $C_2H_5OC_6H_4$ and X = Cl, Br, or I.

The only complexes of tetramethyldithio-oxamide, a potentially bidentate ligand, reported so far are those with zinc (II), cadmium (II), mercury (II)[29], silver[28], gold (III)[30] and palladium[27]. The first row transition elements for complexes of the type M(tmdto)X_2 where X = Cl, Br, or I (non-electrolytes) and others M$(tmdto)_3(ClO_4)_2$ which are 1:2 electrolytes. The second row transition metal tmdto complexes are of the formula $Ag_2(tmdto)_3(ClO_4)_2$; (tmdto)AuX_2(AuX_4); ionic Pd$(tmdto)_2(ClO_4)_2$ a 1:2 electrolyte; Pd(tmdto)X_2 a non-electrolyte.

Tetramethyldithio-oxamide should be a stronger donor than the ethyl analogue, because of the inductive effect of the four methyl groups, and should form stronger complexes.

In this chaper, the preparation of twenty-four new complexes are described. NNN′N′ tetramethyl or NNN′N′ tetraethyldithio-oxamide complexes were prepared by dissolving tetramethyldithio-oxamide or tetraethyldithio-oxamide (1 mmol.)

in a suitable dry solvent such as methanol or n-butanol and then adding this to the tellurium tetrahalides or aryltellurium trihalides (1 mmol.) dissolved in either methanol or n-butanol. The precipitates formed immediately after cooling at 10°C, or in an ice bath. Dimethyldithio-oxamide complexes were prepared by the addition of telluriumtetrahalides dissolved in acetic acid/methanol to a solution of dimethyldithio-oxamide in acetic acid/methanol. The precipitate formed after five minutes.

The starting materials (such as aryltellurium trihalides, **diarylditellurides, diaryltelluriumdichloride**, diaryltelluride, NNN'N' dimethyldithio-oxamide, NNN'N' tetramethyldithio-oxamide and NN' dimethyldithio-oxamide) which were used for the preparation of complexes with sulphur donor ligands, were prepared according to the literature procedures$^{31-44}$ and these are summarised in fig. 2-1, 2-2. Full experimental details of the preparation are given in appendix I (page 252). All compounds gave satisfactory analysis (see table A.2-5 page 289).

The complexes prepared were of the type Te(tmdto)X_4 ArTe(tmdto)X_3 and ArTe(tedto)X_3; where X = Cl, or Br, and Ar = phenyl; p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-$C_6H_5OC_6H_4$, p-$C_6H_5SC_6H_4$, p-BrC_6H_4, (tmdto is tetramethyldithio-oxamide and tedto is tetraethyldithio-oxamide). All compounds were analysed for carbon, hydrogen, nitrogen, and tellurium and were subjected to chemical and vibrational analysis. Assignments of the tellurium-halogen and tellurium-sulphur vibrational modes were also made. The reaction of; tellurium tetrachloride and tellurium tetrabromide with

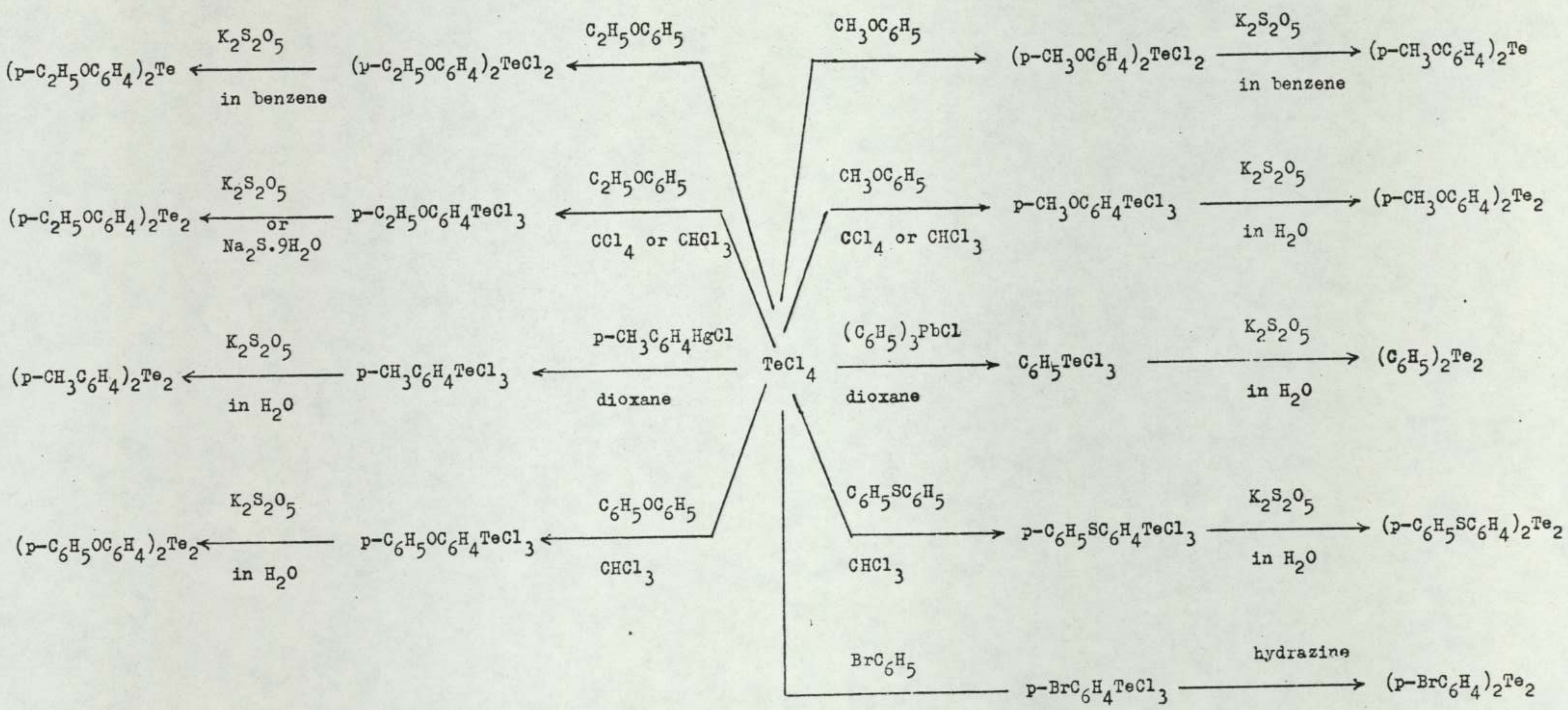


Fig. 2-1 Chemical reactions of the compounds of Tellurium(lV).

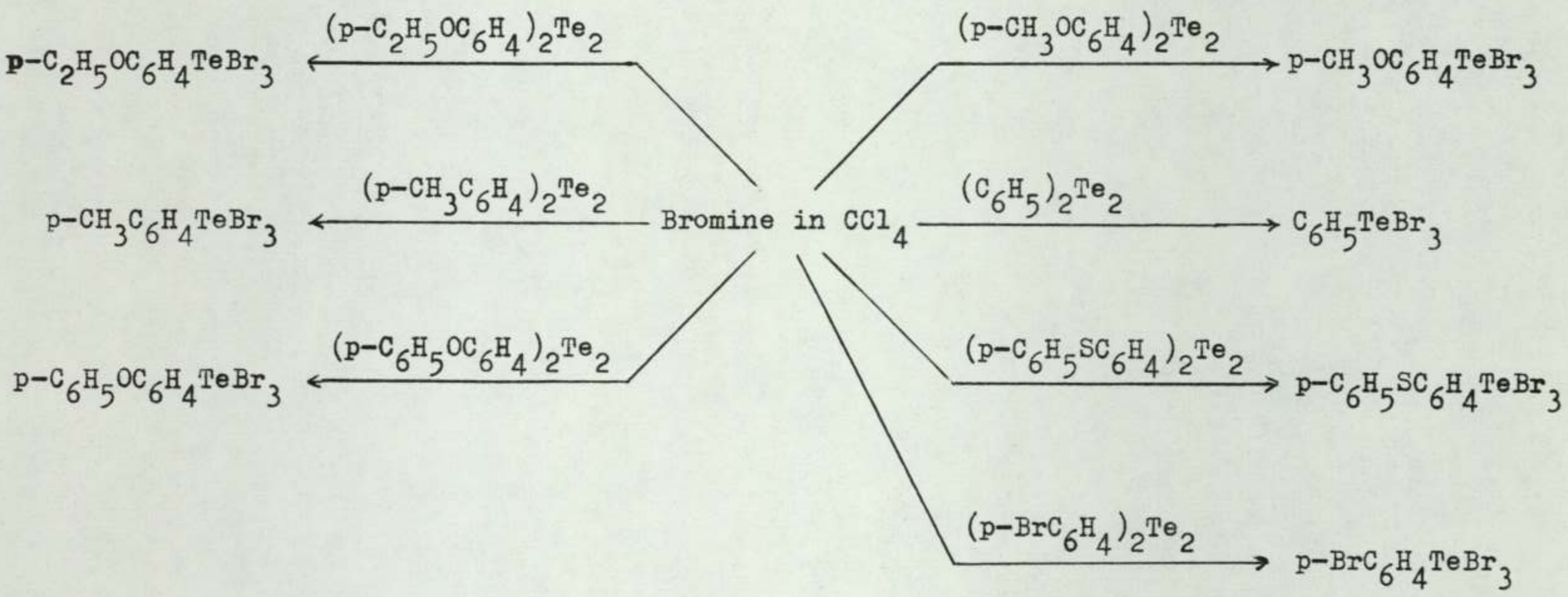


Fig. 2-2

Chemical reactions of the compounds of Tellurium (IV)

NN′ dimethyldithio-oxamide; and full substituted dialkyldithio-oxamides with aryltelluriumdichloride, was investigated and the possible structures of the compounds were discussed.

It is hoped that this study may contribute to a better understanding of the nature of the tellurium-sulphur bond and the factors involved with complex formation of sulphur donor ligands.

2.2 EXPERIMENTAL

2.2.1 Preparation of the NNN′N′ tetraethyldithio-oxamide complexes with Aryltelluriumtrihalides.

2.2.1.1 Phenyltelluriumtrichloride

A solution of 0.232 g. (1 mmol.) of tetraethyldithiooxamide in 5 cm^3 of dry methanol was added to a solution of 0.311 g. (1 mmol.) of phenyltelluriumtrichloride in 5 cm^3 of dry methanol. On stirring for 10 minutes a pale yellow precipitate formed immediately on cooling in an ice bath. The precipitate was filtered off, washed with dry methanol and dried in a vacuum desiccator. Yield 0.35 g. m.p. 125-130°C (decomp.)

[Found C, 35.58; H, 4.72; N, 5.35; Te, 23.32: $TeS_2C_{16}H_{25}N_2Cl_3$ requires C, 35.35; H, 4.64; N, 5.16; Te, 23.50 %]

2.2.1.2 Phenyltelluriumtribromide

Phenyltelluriumtribromide 0.444 g. (1 mmol.) in 7 cm^3 of dry methanol was added to a solution of 0.232 g. (1 mmol.) of tetraethyldithio-oxamide. On stirring for eight minutes a yellow-orange precipitate formed immediately on cooling in an ice bath. The product was filtered off and dried. Yield 0.46 g. m.p. 165-169°C (decomp.)

[Found C, 28.28; H, 3.91; N, 4.19; Te, 19.08; $TeS_2C_{16}H_{25}N_2Br_3$ requires C, 28.38; H, 3.73; N, 4.11; Te, 18.87 %]

2.2.1.3 Tolyltelluriumtrichloride

0.232 g. (1 mmol.) of tetraethyldithio-oxamide in 5 cm^3 of dry methanol was added to a solution of 0.325 g. (1 mmol.) of p-tolyltelluriumtrichloride in 7 cm^3 of dry methanol. On stirring for five minutes a pale yellow precipitate formed immediately on cooling. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.34g. m.p.165-168° C (decomp).

[Found C, 36.14; H, 4.89; N, 5.12; Te, 22.84: $TeS_2C_{17}H_{27}N_2Cl_3$ requires C, 36.62; H, 4.89; N, 5.01; Te, 22.91 %]

2.2.1.4 p-Tolyltelluriumtribromide

To a solution of 0.458 g. (1 mmol.) of p-tolyltelluriumtribromide in 7 cm^3 of dry methanol was added a solution of 0.232 g. (1 mmol.) of tetraethyldithio-oxamide in 5 cm^3 of dry methanol. A yellow-orange precipitate formed immediately after stirring and cooling in an ice bath. The product was filtered off and dried in a vacuum desiccator.
Yield 0.44 g. m.p. 175-178°C (decomp.)

[Found C, 29.86; H, 4.22; N, 4.19; Te, 18.35: $TeS_2C_{17}H_{27}N_2Br_3$ requires C, 29.55; H, 4.00; N, 4.06; Te, 18.48 %]

2.2.1.5 Phenoxyphenyltellurium trichloride

Tetraethyldithio-oxamide 0.580 g. (2.5 mmol.)in 15 cm^3 of dry n-butanol was added to a solution of 0.997 g. (2.5 mmol.) of p-phenoxyphenyltellurium trichloride in 15 cm^3 of dry n-butanol. On stirring a pale yellow precipitate formed immediately in an ice bath. The precipitate was filtered off and dried in a vacuum desiccator. Yield 1.25 g. m.p.180-184° C (decomp.)

[Found C, 41.86; H, 5.02; N, 4.46; Te, 20.09; $TeS_2C_{22}H_{29}ON_2Cl_3$ requires C, 47.17; H, 4.67; N, 4.47; Te, 20.03 %]

2.2.1.6 p-Phenoxyphenyltelluriumtribromide

A solution of 0.232 g. (1 mmol.) of tedto in 5 cm^3 of dry methanol was added to a solution of 0.536 g. (1 mmol.) of p-phenoxyphenyltelluriumtribromide in 5 cm^3 of dry methanol. On stirring a yellow precipitate formed immediately on cooling in an ice bath. The product was filtered off and dried in a vacuum desiccator. Yield 0.59 g. m.p.165-167° C (decomp.)

[Found C, 34.58; H, 3.70; N, 3.79; Te, 16.34; $TeS_2C_{22}H_{29}ON_2Br_3$ requires C, 34.36; H, 3.82; N, 3.79; Te, 16.61 %]

2.2.1.7 p-Thiophenoxyphenyltelluriumtrichloride

0.418 g. (1 mmol.) of p-thiophenoxyphenyltelluriumtrichloride in 7 cm^3 of dry methanol was added to a solution of 0.232 g. (1 mmol.) of tetraethyldithio-oxamide in 5 cm^3 of dry methanol. On stirring for ten minutes a pale yellow precipitate formed immediately on cooling in an ice bath. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.46 g. m.p. 165-170°C (decomp.)

[Found C, 40.84; H, 4.64; N, 4.41; Te, 19.91; $TeS_3C_{22}H_{29}N_2Cl_3$ requires C, 40.55; H, 4.49; N, 4.30; Te, 19.54 %]

2.2.1.8 p-Thiophenoxyphenyltelluriumtribromide

Tetraethyldithio-oxamide 0.232 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.542 g. (1 mmol.) of p-thiophenoxyphenyltelluriumtribromide in 6 cm^3 of dry methanol. A yellow-orange precipitate formed immediately on stirring for five minutes with cooling in an ice bath. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.51 g. m.p. 160-164°C (decomp.)
[Found C, 33.22; H, 3.70; N, 3.53; Te, 16.72:
$TeS_3C_{22}H_{29}N_2Br_3$ requires C, 33.66; H, 3.72; N, 3.57
Te, 16.27 %]

2.2.1.9 p-Bromophenyltelluriumtribromide

To a solution of 0.232 g. (1 mmol.) of tedto in 5 cm^3 of dry methanol was added a solution of 0.514 g. (1 mmol.) of p-bromophenyltelluriumtribromide in 6 cm^3 of dry methanol. On stirring for five minutes a yellow-orange precipitate formed immediately on cooling in an ice bath. The product was filtered off and dried in a vacuum desiccator.
Yield 0.53 g. m.p. 187-189°C (decomp.)
[Found C, 25.93; H, 3.51; N, 3.72; Te, 16.95:
$TeS_2C_{16}H_{24}N_2Br_4$ requires C, 25.42; H, 3.20; N, 3.71;
Te, 16.89 %]

2.2.2 Preparation of NNN´N´ tetramethyldithio-oxamide complexes with tellurium tetrahalides and aryltellurium trihalides.

2.2.2.1 Telluriumtetrachloride

Tetramethyldithio-oxamide 0.176 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.279 g. (1 mmol.) of telluriumtetrachloride in 4 cm^3 of dry methanol. On stirring a yellow-orange precipitate formed immediately after cooling at 10°C. The precipitate was filtered off, washed with dry methanol and dried in a vacuum desiccator.
Yield 0.35 g. m.p. 203°C (decomp.)
[Found C, 16.50; H, 2.80; N, 6.00; Te, 28.95: $TeS_2C_6H_{12}N_2Cl_4$ requires C, 16.17; H, 2.72; N, 6.29; Te, 28.65 %]

2.2.2.2 Telluriumtetrabromide

0.447 g. (1 mmol.) of telluriumtetrabromide in 5 cm^3 of dry methanol was added to a solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol. A red precipitate formed immediately on stirring and cooling to 10°C. The product was filtered off and dried in a vacuum desiccator.
Yield 0.52 g. m.p. 234°C (decomp.)
[Found C, 12.15; H, 2.11; N, 4.19; Te, 20.39; $TeS_2C_6H_{12}N_2Br_4$ requires C, 11.55; H, 1.94; N, 4.49; Te, 20.47 %]

2.2.2.3 Phenyltelluriumtrichloride.

0.176 g. (1 mmol.) of tetramethyldithio-oxamide in 5 cm^3 of dry methanol was added to a solution of 0.311 g. (1 mmol.)

of phenyltellurium trichloride in 5 cm^3 of dry methanol. On stirring a pale yellow precipitate formed immediately after cooling at 10°C. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.34 g. m.p. 147-151°C. (decomp.)
[Found C, 29.63; H, 4.22; N, 5.75; Te, 26.15: $TeS_2C_{12}H_{17}N_2Cl_3$ requires C, 29.57; H, 3.91; N, 5.75; Te, 26.20 %]

2.2.2.4 Phenyltelluriumtribromide.

A solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol was added to a solution of 0.444 g. (1 mmol.) of phenyltelluriumtribromide in 5 cm^3 of dry methanol. A yellow precipitate formed immediately after cooling and stirring to 10°C. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.46 g. m.p. 125-127°C. (decomp.)
[Found C, 23.89; H, 3.36; N, 4.60; Te, 20.01; $TeS_2C_{12}H_{17}N_2Br_3$ requires C, 23.21; H, 3.07; N, 4.51; Te, 20.57 %]

2.2.2.5 p-Tolyltelluriumtrichloride.

p-Tolyltelluriumtrichloride 0.325 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.176 g. (1 mmol.) of tetramethyldithio-oxamide in 5 cm^3 of dry methanol. On stirring a pale yellow precipitate formed immediately after cooling to 10°C. The product was filtered off and dried in a vacuum desiccator. Yield 0.35 g. m.p. 192-196°C (decomp.)
[Found C, 31.37; H, 4.22; N, 5.73; Te, 25.16: $TeS_2C_{13}H_{19}N_2Cl_3$ requires C, 31.14; H, 3.80; N, 5.59; Te, 25.47 %]

2.2.2.6 p-Tolyltelluriumtribromide.

To a solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol was added a solution of 0.458 g. (1 mmol.) of p-tolyltelluriumtribromide in 5 cm^3 of dry methanol. On stirring for five minutes a yellow precipitate formed after cooling to 10°C. The precipitate was then filtered off and dried in a vacuum desiccator. Yield 0.469 g. m.p. 186-190°C (decomp.)

[Found C, 25.28; H, 3.50; N, 4.37; Te, 20.03: $TeS_2C_{13}H_{19}N_2Br_3$ requires C, 24.60; H, 3.00; N, 4.41; Te, 20.12 %]

2.2.2.7 p-Methoxyphenyltelluriumtrichloride.

Tetramethyldithio-oxamide 0.176 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.341 g. (1 mmol.) of p-methoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. A yellow precipitate formed immediately after stirring and cooling at 10° C. The product was filtered off and dried in a vacuum desiccator. Yield 0.32 g. m.p.176-178°C (decomp.)

[Found C, 30.61; H, 3.70; N, 5.73; Te, 24.85: $TeS_2C_{13}H_{19}ON_2Cl_3$ requires C, 30.17; H, 3.70; N, 5.42; Te, 24.68 %]

2.2.2.8 p-Methoxyphenyltelluriumtribromide.

0.474 g. (1 mmol.) of p-methoxyphenyltelluriumtribromide in 5 cm^3 of dry methanol was added to a solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol. On stirring a yellow precipitate formed immediately after cooling to 10°C. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.55 g. m.p. 170-176°C (decomp.) [Found C, 24.10; H, 3.21; N, 3.91; Te, 19.69: $TeS_2C_{13}H_{19}ON_2Br_3$ requires C, 23.99; H, 2.96; N, 4.31; Te, 19.62 %]

2.2.2.9 p-Ethyoxyphenyltelluriumtrichloride.

A solution of 0.176 g. (1 mmol.) of tetramethyldithiooxamide in 5 cm^3 of dry methanol was added to a solution of 0.355 g. (1 mmol.) of p-ethoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. A pale yellow precipitate formed immediately after stirring and cooling at 10°C. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.39 g. m.p. 175-180°C (decomp.) [Found C, 32. 52; H, 4.31; N, 5.51; Te, 24.20: $TeS_2C_{14}H_{21}ON_2Cl_3$ requires C, 31.64; H, 3.94; N, 5.27; Te, 24.03 %]

2.2.2.10 p-Ethoxyphenyltelluriumtribromide.

p-Ethoxyphenyltelluriumtribromide 0.488 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol. On stirring a yellow precipitate formed immediately after cooling to 10° C. The product was filtered off and dried in a vacuum desiccator. Yield 0.42 g. m.p. 159-165°C (decomp.) [Found C, 26.07; H, 3.50; N, 4.14; Te, 19.02: $TeS_2C_{14}H_{21}ON_2Br_3$ requires C, 25.29; H, 3.19; N, 4.21; Te, 19.21 %]

2.2.2.11 p-Phenoxyphenyltelluriumtrichloride.

0.176 g. (1 mmol.) of tetramethyldithio-oxamide in 5 cm^3 of dry methanol was added to a solution of 0.403 g. (1 mmol.) of p-phenoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. A pale yellow precipitate formed immediately after cooling and stirring at 10°C. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.44 g. m.p. 164-166°C (decomp.)

[Found C, 37.87; H, 3.89; N, 4.41; Te, 22.16: $TeS_2C_{18}H_{21}ON_2Cl_3$ requires C, 37.31; H, 3.66; N, 4.84; Te, 22.04 %]

2.2.2.12 p-Phenoxyphenyltelluriumtribromide.

To a solution of 0.536 g. (1 mmol.) of p-phenoxyphenyltelluriumtribromide in 5 cm^3 of dry methanol was added a solution of 0.176 g. (1 mmol.) of tmdto in 5 cm^3 of dry methanol. On stirring a yellow precipitate formed immediately after cooling to 10°C. The product was filtered off and dried in a vacuum desiccator. Yield 0.55 g. m.p. 155-158°C (decomp.)

[Found C, 29.63; H, 3.07; N, 3.68; Te, 17.45: $TeS_2C_{18}H_{21}ON_2Br_3$ requires C, 30.32; H, 2.97; N, 3.94; Te, 17.91 %]

2.2.2.13 p-Thiophenoxyphenyltelluriumtrichloride.

Tetramethyldithio-oxamide 0.176 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.419 g. (1 mmol.) of p-thiophenoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. A pale yellow precipitate formed immediately after stirring and cooling to 10°C. The precipitate was

filtered off and dried in a vacuum desiccator. Yield 0.43 g. m.p. 161-163°C (decomp.)
[Found C, 36.34; H, 4.12; N, 4.41; Te, 21.10; $TeS_3C_{18}H_{21}N_2Cl_3$ requires C, 36.30; H, 3.87; N, 4.71; Te, 21.45 %]

2.2.3 Preparation of the NN′ dimethyldithio-oxamide complexes with Tellurium(IV) halide.

2.2.3.1 Telluriumtetrachloride

NN′ Dimethyldithio-oxamide 0.075 g. (0.5 mmol.) in a mixture of 2 cm^3 methanol and 3 cm^3 acetic acid was added to a solution of 0.27 g. (1 mmol.) of telluriumtetrachloride in a mixture of 3 cm^3 methanol and 2 cm^3 acetic acid. On stirring at room temperature the solution was changed from light yellow to violet, and a violet precipitate formed after ten minutes. The precipitate was filtered off and dried in a vacuum desiccator. Yield 0.2 g.
[Found C, 11.81; H, 2.18; N, 6.36; $TeS_2C_4H_8N_2Cl_4$ requires C, 11.51; H, 1.93; N, 6.70 %]

2.2.3.2 Telluriumtetrabromide.

A solution of 0.075 g. (0.5 mmol.) of Me_2DH_2 in a mixture of 2 cm^3 methanol and 3 cm^3 acetic acid was added to a solution of 0.447 g. (1 mmol.) of telluriumtetrabromide in a mixture of 3 cm^3 methanol and 2 cm^3 acetic acid. On stirring for ten minutes at room temperature the solution changed from yellow to dark red and a rust coloured precipitate formed. The product was filtered off and dried in

vacuum desiccator. Yield 0.24 g.
[Found C, 8.06; H, 1.36; N, 4.70: $TeS_2C_4H_8N_2Br_4$ requires C, 8.48; H, 1.60; N, 4.54 %]

2.2.4 Reaction of NNN'N' Tetraethyldithio-oxamide with diaryltelluriumdichloride.

All reactions failed to give crystalline precipitates.

2.2.4.1 Bis-p-methoxyphenyltelluriumdichloride.

0.232 g. (1 mmol.) of NNN'N' tetraethyldithio-oxamide in 5 cm^3 of dry methanol was added to a solution of 0.414 g. (1 mmol.) bis-p-methoxyphenyltelluriumdichloride in 5 cm^3 of dry methanol. A yellow colour is always produced by reaction of aryltelluriumtrihalide with NNN'N' tetraethyldithio-oxamide but after stirring this solution, the yellow colour was not produced, immediately, or after two weeks in a refrigerator. The solution was distilled under vacuum to give a white precipitate (m.p. 178°C) which was identified as bis-p-methoxyphenyltelluriumdichloride m.p. 180°C.[35]

2.2.4.2 Bis-p-ethoxyphenyltelluriumdichloride.

The reaction of bis-p-ethoxyphenyltelluriumdichloride with NNN'N' tetraethyldithio-oxamide failed to produce a complex which could be isolated.

2.3 RESULTS

2.3.1 Synthesis.

NNN'N' Tetraethyldithio-oxamide and NNN'N' Tetramethyldithio-oxamide complexes were prepared by dissolving tedto or tmdto in a suitable dry solvent such as methanol or n-butanol, and then adding this solution to the tellurium compounds dissolved in either methanol or n-butanol. NN' Dimethyldithio-oxamide complexes were prepared by dissolving Me_2DH_2 in a mixture of methanol and acetic acid and then adding this solution to the tellurium compounds dissolved in a mixture of methanol and acetic acid. The solvent used depended on the tellurium compound and those giving the best experimental conditions are recorded in the experimental section.

2.3.2 Conductivity Measurements.

The molar conductivity of tellurium (IV) complexes in DMF and nitromethane are shown in table 2-1 and 2-3.

2.3.3. U.V. and visible spectra.

The complexes are slightly soluble in dimethylformamide solution and all show strong absorptions at 35.7 kK and 36.36 kK.

2.3.4 Tellurium Analysis.

Samples were analysed for tellurium content by decomposition of the samples using the oxygen flask technique followed by atomic absorption of the solutions produced using a Perkin-Elmer 303 instrument (see Appendix II) The tellurium content of each complex is recorded in the experimental section.

2.3.5 ^{1}H n.m.r. spectra

There is no suitable solvent for tellurium (IV) complexes which would enable investigation of the compounds by ^{1}H n.m.r. However, the reactions of the two compounds, Bis-p-anisyl and Bis-p-penetyltelluriumdichloride, with NNN$'$N$'$ tetraethyldithio-oxamide were investigated and the reaction products examined by ^{1}H n.m.r.

2.3.6 Mass spectra

The mass spectra of tetraethyldithio-oxamide, tetramethyldithio-oxamide and its tellurium complexes are tabulated as follows :

Table 2-8 Tetraethyldithio-oxamide

Table 2-9 $C_6H_5TeX_3$tedto and p-$BrC_6H_4TeBr_3$tedto

Table 2-10 p-$CH_3C_6H_4TeCl_3$tedto and p-$CH_3C_6H_4TeBr_3$tedto

Table 2-11 p-$C_6H_5OC_6H_4TeCl_3$tedto and p-$C_6H_5SC_6H_4TeCl_3$tedto

Table 2-12 Tetramethyldithio-oxamide

Table 2-13 p-$CH_3OC_6H_4TeX_3$tmdto and p-$CH_3C_6H_4TeCl_3$tmdto

2.3.7 Vibrational spectra

The bands of the infrared spectra for tellurium (IV) complexes above 400 cm^{-1} are tabulated as follows;

Table 2-1	Tetraethyldithio-oxamide and its tellurium complexes.
Table 2-3	Tetramethyldithio-oxamide and its tellurium complexes.
Table 2-5	Dimethyldithio-oxamide and its tellurium complexes.
Table 2-7	Aryltelluriumtrihalides and its complexes.

The spectra are also reproduced in :

Fig. 2-3	$C_6H_5TeCl_3$, tedto and $C_6H_5TeCl_3$tedto
Fig. 2-4	$C_6H_5TeBr_3$, tmdto and $C_6H_5TeBr_3$tmdto
Fig. 2-5	tmdto, $TeCl_4$tmdto and $TeBr_4$tmdto
Fig. 2-6	Me_2DH_2, $Te(Me_2DH_2)Cl_4$ and $Te(Me_2DH_2)Br_4$

The bands of the i.r. and Raman spectra at low frequency (below 400 cm^{-1}) for all complexes are tabulated as follows;

Table 2-2	Tetraethyldithio-oxamide and its tellurium complexes.
Table 2-4	Tetramethyldithio-oxamide and its tellurium complexes.
Table 2-6	Dimethyldithio-oxamide and its tellurium complexes.

but the i.r. spectra of some complexes are reproduced in:

Fig. 2-7 Tetraethyldithio-oxamide and its tellurium complexes.
Fig. 2-8 Tetramethyldithio-oxamide and tellurium tetrahalides complexes.
Fig. 2-9 Tetramethyldithio-oxamide and its tellurium complexes.
Fig. 2-10 Dimethyldithio-oxamide and its tellurium complexes.

and also the Raman spectra of some complexes are reproduced in:

Fig. 2-11 $C_6H_5TeX_3$tedto
Fig. 2-12 TeX_4tmdto
Fig. 2-13 p-$C_2H_5OC_6H_4TeCl_3$tmdto

TABLE 2-1

I.r. spectra [a]

Compounds	ν(CN)	ν(CS)	Λ_{DMF} [b]	$\Lambda_{Nitromethane}$
Tetraethyldithio-oxamide	1500s	872m		
Phenyltelluriumtrichloride complex	1550s 1510s	863m	29	32
Phenyltelluriumtribromide complex	1540s 1510s	860m	42	48
p-Tolyltelluriumtrichloride complex	1546s 1510s	861m	26	35
p-Tolyltelluriumtribromide complex	1546s 1510s	862m	32	52
p-Phenoxyphenyltellurium-trichloride complex	1537s 1510s	862m	29	35
p-Phenoxyphenyltellurium-tribromide complex	1540s 1510s	860m 845m	48	43
p-Thiophenoxyphenyltelluriumtrichloride complex	1540s 1510s	859m	27	33
p-Thiophenoxyphenyltelluriumtribromide complex	1540s 1510s	858m	39	43
p-Bromophenyltelluriumtribromide complex	1548s 1515s	800m	38	45

a. The more important bands in cm^{-1}

b. $cm^2 . ohm^{-1} . mole^{-1} . 10^{-3}M$ solution at 20°C.

TABLE 2-2

Infrared and Raman spectra of tellurium tetraethyldithio-oxamide trihalo complexes below 410 cm^{-1}.

tedto		$C_6H_5TeCl_3$tedto		$C_6H_5TeBr_3$tedto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
405s		405w		402m		ligand vibration
365m						
344m	350w					
293m	297w			297w		
				276wsh		combination band
		289m	285s			ν (Te-Cl)
		260s	263m			
		237ssh	244msh	249vs	249w	ν (Te-S)
					237w	
		225vs	221w	217vs		
				203vs		
196s	185m	186msh	177wsh			ligand vibration
					189vs	ν (Te-Br)
				165vs	159vs	
154w	144w	155w	157vw			ligand vibration
				118w		δ (Te-Br) ?

Table 2-2....

Infrared and Raman spectra of tellurium tetraethyldithio-oxamide trihalo complexes below 410 cm^{-1}.

tedto		p-BrC$_5$H$_4$TeBr$_3$tedto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
405s		404w		ligand vibration
365m				
344m	350w			
		303m		Te-C bending mode*
293m	293w			ligand vibration
		280m	276vw	combination band
		252ssh		ν(Te-S)
		241m		
196s	185m			ligand vibration
		184vs	187s	ν(Te-Br)
		164vs	161s	
154w	144w			ligand vibration
		143m		δ(Te-S)
		108w		δ(Te-Br) ?

---

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-2....

Infrared and Raman spectra of tellurium tetraethyldithio-oxamide trihalo complexes below 410 cm^{-1}.

tedto		$p-CH_3C_6H_4TeCl_3$tedto		$p-CH_3C_6H_4TeBr_3$tedto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
405s		404w		402m		ligand vibration
365m		363vw		380m		
344m	350w					
		305w		302w		Te-C bending mode *
293m	293w					ligand vibration
				276w		combination band
		280s	276vs			ν (Te-Cl)
			260vs			
		242vs	237msh	246m		ν (Te-S)
				229ssh		
				220vs	217w	
		205vs				
196s	185m					ligand vibration
				186s	183s	ν (Te-Br)
				172s	173s	
					157vs	
154w	144w					ligand vibration
		142m		145msh		δ (Te-S)or δ (Te-Cl)
			133w			
				106w		δ (Te-Br)?

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-2....

Infrared and Raman spectra of tellurium tetraethyldithio-oxamide trihalo complexes below 410 cm^{-1}.

tedto		$p-C_6H_5OC_6H_4TeCl_3$tedto		$p-C_6H_5OC_6H_4TeBr_3$tedto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
405s		405w		403w		ligand vibration
365m						
344m	350w	353m		351w		
		313m		308w		Te-C bending mode*
293m	293w			286w	279vw	ligand vibration
		278vs	277vs			ν (Te-Cl)
		262msh	256s			
				252m		ν (Te-S)
		241vs	236msh	246w	243w	
				209s	207w	
196s	185m	198m				ligand vibration
			178w			
				178vs	173vs	ν (Te-Br)
				160msh	157vs	
154w	144w					ligand vibration
		142m		145msh		δ (Te-S) or δ (Te-Cl)
			133w		137wsh	

---

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-2....

Infrared and Raman spectra of tellurium tetraethyldithio-oxamide trihalo complexes below 410 cm^{-1}.

tedto		$p-C_6H_5SC_6H_4TeCl_3$tedto		$p-C_6H_5SC_6H_4TeBr_3$tedto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
405s		406w		405w		)ligand vibration
365m				382vw		
344m	350w					
		316s	317vw	313m		Te-C bending mode*
293m	293w		301w	287w		ligand vibration
					273vw	combination band
		276s	272vs			ν(Te-Cl)
		255ssh	253vs			
				252m		ν(Te-S)
		231vs	230ssh	246m	242w	
196s	185m	190m				)ligand vibration
		177m	179w			
				193s	194wsh	ν(Te-Br)
				185s	175s	
				155ssh	161s	
154w	144w					ligand vibration
		142m				δ(Te-S) or δ(Te-Cl)
			133w			

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* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

TABLE 2-3

I.r. spectra [a]

Compounds	ν(CN)	ν(CS)	Λ_{DMF} [b]	$\Lambda_{Nitromethane}$
Tetramethyldithio-oxamide	1528s	828m		
Tellurium(IV) chloride complex	1582s 1545s	821m	43	39
Tellurium(IV) bromide complex	1580s 1553s	810m	122	76
Phenyltelluriumtrichloride complex	1570s 1530s	817m	35	35
Phenyltelluriumtribromide complex	1565s 1530s	816m	48	45
p-Tolyltelluriumtrichloride complex	1570s 1530s	820m	32	33
p-Tolyltelluriumtribromide complex	1565s 1530s	818m	48	43
p-Methoxyphenyltellurium-trichloride complex	1575s 1535s	820m	33	34
p-Methoxyphenyltellurium-tribromide complex	1565s 1535s	818m	48	53
p-Ethoxyphenyltellurium-trichloride complex	1565s 1535s	814	31	34
p-Ethoxyphenyltellurium-tribromide complex	1565s 1530s	817	43	36
p-Phenoxyphenyltellurium-trichloride complex	1570s 1540s	820m	30	32
p-Phenoxyphenyltellurium-tribromide complex	1568s 1535s	820m	50	39
p-Thiophenoxyphenyltelluriumtrichloride complex	1566s 1530s	817m	27	26

a. The more important bands in cm^{-1}.

b. $cm^2 . ohm^{-1} . mole^{-1} . 10^{-3}M$ solution at 20°C

TABLE 2-4

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide tetrahalo complexes below 410 cm^{-1}.

tmdto		$TeCl_4$tmdto		$TeBr_4$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m	377w	380m	372w	378m		ligand vibration
346mw		345m		342m		
306s	311w					
		277s	273m			ν (Te-Cl)
		238vs	235w	254m	252w	ν (Te-S)
187m	179w	182m	180w			ligand vibration
				187vs	177s	ν (Te-Br)
				158m	153vs	
146w	133vw	145vw	133wsh	144msh		ligand vibration

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		$C_6H_5TeCl_3$tmdto		$C_6H_5TeBr_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m 346mw	377w	380m	377vw	380m	381vw	ligand vibration
				332w 320w		Te-C bending mode*
306s	311w					ligand vibration
		283s 264m	281s 267s			ν(Te-Cl)
		235m	232w	250m 215m	250m	ν(Te-S)
187m	179w	186m	178w			ligand vibration
				176vs 157msh	171s 159vs	ν(Te-Br)
146w	133vw	145vw	133w	145msh	132w	ligand vibration
				116w		δ(Te-Br) ?

*A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		$p-CH_3C_6H_4TeCl_3$tmdto		$p-CH_3C_6H_4TeBr_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m	377w	380m	377w	375w	374vw	ligand vibration
346mw						
		333m		320w		Te-C bending mode*
306s	311w	303wsh				ligand vibration
		276s	273m			ν(Te-Cl)
		262s	259m			
		234vs	235w	260w		ν(Te-S)
		208s	197w	223s	219w	
187m	179w	180w	177w			ligand vibration
				176s	177s	ν (Te-Br
				155vw	157vs	
		162w	159w			unassigned
146m	133vw	140vw	133w	143w	132w	ligand vibration

*A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoriodobenzene is said to involve C-I bending.[56]

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		p-$CH_3OC_6H_4TeCl_3$tmdto		p-$CH_3OC_6H_4TeBr_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m 346mw	377w	382m	378w	383m	377w	ligand vibration
		335w	339w	330m		Te-C bending mode*
306s	311w			303w		ligand vibration
		276m	277m			ν(Te-Cl)
		236vs	230w	221m	233w	ν(Te-S)
187m	179w	185m	179w			ligand vibration
				188vs 167m	185s	ν(Te-Br)
146w	133vw	143w	133vw	145w	132w	ligand vibration

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		$p-C_2H_5OC_6H_4TeCl_3$tmdto		$p-C_2H_5OC_6H_4TeBr_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m	377w	380m	375w	381m		ligand vibration
346mw						
		337m	337w			Te-C bending mode *
		327m	322w	329w		
306s	311w					ligand vibration
		273vs	276vs			ν(Te-Cl)
		255vs	255s			
		231vs	232m	251m	241w	ν(Te-S)
		210vs				
187m	179w	183w	178w			ligand vibration
				182vs	178s	ν(Te-Br)
		160w	157wsh			unassigned
146w	133vw	140w	133w	145w	133w	ligand vibration

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		$p-C_6H_5OC_6H_4TeCl_3$tmdto		$p-C_6H_5OC_6H_4TeBr_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m 346mw	377w	392m	384w	381m		ligand vibration
		335m	332w	331w 315w		Te-C bending mode *
306s	311w					ligand vibration
		278s 264s	272vs			ν(Te-Cl)
		235vs 205m	237w	240msh	240w	ν(Te-S)
187m	179w	181m	178w			ligand vibration
				180vs	178msh	ν(Te-Br)
146w	133vs	140w	133w	145w	132w	ligand vibration

* A strng band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

Table 2-4....

Infrared and Raman spectra of tellurium tetramethyldithio-oxamide trihalo complexes below 400 cm^{-1}.

tmdto		$p-C_6H_5SC_6H_4TeCl_3$tmdto		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
380m	377w	380m	371w	ligand vibration
346mw				
		330w		Te-C bending mode *
306s	311w			ligand vibration
		283m	273s	ν (Te-Cl)
		261m	259w	
		236vs	235w	ν (Te-S)
187m	179w	186m	180w	ligand vibration
146w	133vw	145w	133w	

* A strong band found at 312 cm^{-1} for p-iodoanisole and the band at 309 cm^{-1} in p-fluoroiodobenzene is said to involve C-I bending.[56]

TABLE 2-5

The infrared spectra of NN′ dimethyldithio-oxamide and its complexes with $TeCl_4$ and $TeBr_4$ between 500-3300 cm^{-1}, the more important bands.

Dimethyldithio-oxamide (Me_2DH_2)	$Te(Me_2DH_2)Cl_4$	$Te(Me_2DH_2)Br_4$	Assignment
690s	675m	690m	δ(NH)
868s	841vs	850m	ν(CS)
	905w	872vs	
		1005sh	
1020s	1010vs	1020vs	Thioamide III
	1060m	1090vs	
1160m	1155m	1160w	$\nu(C_RN)$
	1236m	1225w	
1350s	1350m	1355s	Thioamide II
	1395vs	1380s	
1530s	1548vs	1540vs	ν(CN)
	1570msh	1577ssh	
3180s	3200s	3180m	ν(NH)

TABLE 2-6

The infrared and Raman spectra of NN′ dimethyldithio-oxamide complexes of tellurium tetrahalides below 310 cm^{-1}.

Dimethyldithio-oxamide (Me_2DH_2)		$Te(Me_2DH_2)Cl_4$	$Te(Me_2DH_2)Br_4$	Assignment
i.r.	Raman Δν	i.r.	i.r.	
93s		98m	95m	ligand vibration
149w	157m	151msh	150m	
185m	175wsh	183m		
	193m			
			190vs	ν (Te-Br)
216m	209wsh		215msh	ligand vibration
		202s		ν (Te-S)
		235s	252m	
		270m		ν (Te-Cl)
290m	293w		280m	ligand vibration
		310m	302m	ν (Te-N)

TABLE 2-7

I.r. and Raman spectra of
Aryltelluriumtrihalides and its complexes.

	(Te-Cl)		(Te-Br)	
	i.r. cm^{-1}	Raman $\Delta\nu$	i.r. cm^{-1}	Raman $\Delta\nu$
$PhTeX_3$	337s	342s	213s	210s
	317sh	318m	198m	198vs
	306s	303m		
$PhTeX_3$tmdto	283s	281s	176vs	171s
	264m	267s	157msh	159vs
p-$MeC_6H_4TeX_3$	336s	341s	220ms	219m
	318sh	316w	204vs	199vs
	304s	303w		
p-$MeC_6H_4TeX_3$tmdto	276s	273m	176s	177s
	262s	259m	155vw	157vs
p-$MeOC_6H_4TeX_3$	323s	329s	213s	209m
		301m	192ms	
	295s	298m		
p-$MeOC_6H_4TeX_3$tmdto	276m	277m	188vs	185s
			167m	
p-$EtOC_6H_4TeX_3$	334s	330s	218s	216s
	326s	327s	206vs	
	318s		194vs	192wm
	298s	305m		
p-$EtOC_6H_4TeX_3$tmdto	273vs	276vs	182vs	178s
	255vs	255s		
p-$PhOC_6H_4TeX_3$	334s	339s	224m	224s
	320s	315ms	211s	204vs
	311s		194s	190s
p-$PhOC_6H_4TeX_3$tmdto	278s	272vs	180vs	178msh
	264s			

Where tmdto = tetramethyldithio-oxamide

TABLE 2-8

Mass spectrum of NNN′N′ Tetraethyldithio-oxamide.

m/e	Relative Abundance %	ions
232	35	$[(C_2H_5)_2\text{-N-}\overset{S}{\overset{\Vert}{C}}\text{-}\overset{S}{\overset{\Vert}{C}}\text{-N-}(C_2H_5)_2]^+$
203	54	$[(C_2H_5)_2\text{-N-}\overset{S}{\overset{\Vert}{C}}\text{-}\overset{S}{\overset{\Vert}{C}}\text{-N-}C_2H_5]^+$
177.6		metastable
168	5	$[(C_2H_5)_2\text{-N-}\overset{S}{\overset{\Vert}{C}}\text{-}\overset{S}{\overset{\Vert}{C}}]^+$
146	11	-
144	2	$[(C_2H_5)_2\text{-N-N-}(C_2H_5)_2]^+$
116	46	$[(C_2H_5)_2\text{-N-C=S}]^+$
115	4	$[(C_2H_5)_2\text{-N-N-}C_2H_5]^+$
114	41	-
113	19	-
98	29	-
88	49	$[\text{S=C-C=S}]^+$
86	14	-
74	14	-
72	57	$[(C_2H_5)_2\text{-N}]^+$
66.8		metastable
60	51	-
58	13	$[(C_2H_5)_2]^+$
56	60	-
56	22	-
44	17	$[\text{C=S}]^+$
43	22	-
42	24	-
32	7	S
29	100	$C_2H_5^+$
28	66	N_2
27	46	-

TABLE 2-9

Mass spectra of $C_6H_5TeX_3$tedto and $BrC_6H_4TeBr_3$tedto - Relative to ^{130}Te, ^{35}Cl, ^{79}Br.

$C_6H_5TeCl_3$tedto		$C_6H_5TeBr_3$tedto		p-$BrC_6H_4TeBr_3$tedto	
m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
412	1				
312	2			312	2
283	15	282	6	311	1
281	15	280	5	234	5
279	9				
232	65	232	64	232	60
218	29	205	7	204	7
203	75	203	71	203	75
200	13	200	12	200	14
186	31			188	2
177.6	metastable	177.6	metastable	177.6	metastable
168	14	168	14	168	12
160	7	160	6	160	6
154	49	154	19		
146	14	146	15	146	17
139	10	139	9	139	10
129	43	129	31	129	40
128	11	128	9	128	12
116	59	116	77	116	62
114	82	114	64	114	80
113	73	113	60	113	73
110	37	110	31	110	30

.../...

Table 2-9.....

$C_6H_5TeCl_3$tedto		$C_6H_5TeBr_3$tedto		p-$BrC_6H_4TeBr_3$tedto	
m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
98	100	98	84	98	100
88	55	88	62	88	59
86	19	86	22	86	23
84	15	84	4	84	27
77	51	77	29	77	20
72	90	72	100	72	80
66.8	metastable	66.8	metastable	66.8	metastable
60	49	60	62	60	57
56	90	56	89	56	93
44	14	44	17	44	17
42	35	42	36	42	39
36	45				
32	13	32	10	32	11
29	76	29	80	29	87
28	98	28	69	28	73
27	45	27	47	27	48

TABLE 2-10

Mass spectra of p-$CH_3C_6H_4TeX_3$ tedto - Relative to ^{130}Te, ^{35}Cl, ^{79}Br.

p-$CH_3C_6H_4TeCl_3$tedto		p-$CH_3C_6H_4TeBr_3$tedto	
m/e	R.A. (%)	m/e	R.A. (%)
		438	1
		343	1
312	3	312	9
310	3	310	9
246	2	246	13
232	33	232	59
214	12	214	63
203	33	203	62
200	24	200	15
183	6	182	27
177.6	metastable	177.6	metastable
168	12	168	12
160	3	167	10
146	7	146	13
139	8	139	6
129	40	129	32
128	8	128	9
124	10	124	40
123	8	123	29
116	34	116	57
114	78	114	63
113	72	113	57
98	100	98	79
92	40	92	13
		91	100
88	31	88	54
86	17	86	17
		79	13
		78	6
77	13	77	13
72	50	72	79
70	17	70	14

Table 2-10.....

$p\text{-}CH_3C_6H_4TeCl_3$tedto		$p\text{-}CH_3C_6H_4TeBr_3$tedto	
m/e	R.A. (%)	m/e	R.A. (%)
66.8	metastable	66.8	metastable
60	33	60	52
56	88	56	79
51	13	51	13
44	14	44	14
42	40	42	33
41	13	41	29
36	59		
35	8		
32	45	32	6
29	68	29	70
28	86	28	68
27	45	27	43

TABLE 2-11

Mass spectra of Aryltelluriumtrichloride tedto - Relative ^{130}Te, ^{35}Cl.

p-$C_6H_5OC_6H_4TeCl_3$tedto		p-$C_6H_5SC_6H_4TeCl_3$tedto	
m/e	R.A. (%)	m/e	R.A. (%)
232	28	232	24
203	30	203	25
		199	12
177.6	metastable	177.6	metastable
168	12	168	13
146	7	146	8
129	33	129	37
128	7	128	3
116	32	116	27
114	66	114	73
113	60	133	71
98	84	98	100
88	31	88	25
86	16	86	19
84	14	84	20
77	6	77	6
72	47	72	51
70	15	70	29
68	12	68	16
66.8	metastable	66.8	metastable
60	29	60	25
56	100	56	74
54	12	54	15
44	12	44	12
42	36	42	35
41	28	41	26
36	19	36	14
32	7	32	8
29	60	29	53
28	72	28	78
27	38	27	35

TABLE 2-12

Mass spectra of NNN′N′ Tetramethyldithio-oxamide.

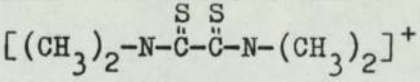
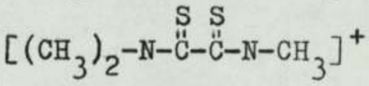
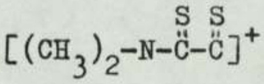
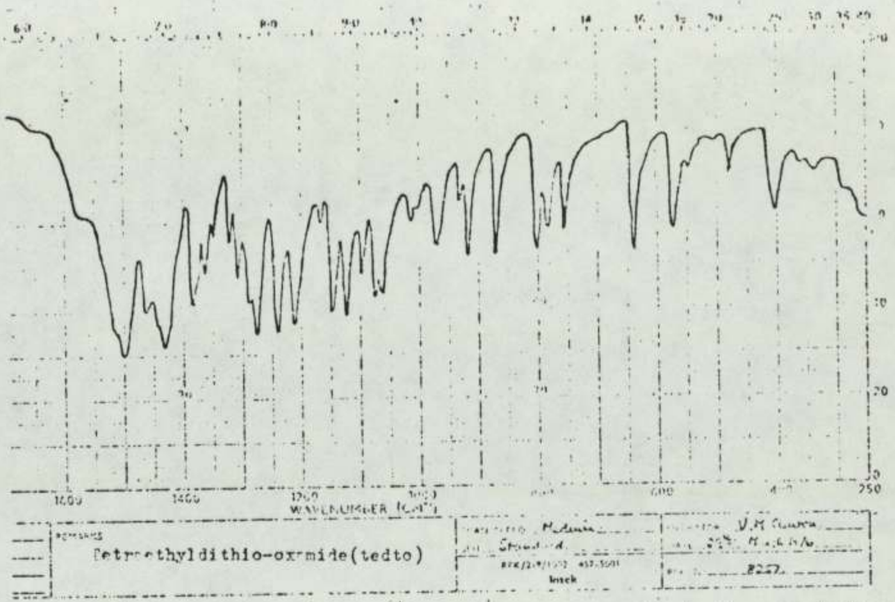
m/e	Relative Abundance %	ions
176	22	 $[(CH_3)_2\text{-}N\text{-}\overset{S}{\overset{\|}{C}}\text{-}\overset{S}{\overset{\|}{C}}\text{-}N\text{-}(CH_3)_2]^+$
161	39	 $[(CH_3)_2\text{-}N\text{-}\overset{S}{\overset{\|}{C}}\text{-}\overset{S}{\overset{\|}{C}}\text{-}N\text{-}CH_3]^+$
147.3		metastable
133	19	-
132	16	 $[(CH_3)_2\text{-}N\text{-}\overset{S}{\overset{\|}{C}}\text{-}\overset{S}{\overset{\|}{C}}]^+$
112	74	-
100	34	-
97	62	-
90	20	-
89	23	-
88	64	$[(CH_3)_2\text{-}N\text{-}C{=}S]^+$ or $[(CH_3)_2\text{-}N\text{-}N\text{-}(CH_3)_2]^+$
85	16	-
76	28	-
73	62	$[(CH_3)_2\text{-}N\text{-}N\text{-}CH_3]^+$
72	20	-
58	19	-
56	72	$[(CH_3)_2\text{-}N\text{-}C]^+$
44	13	$[(CH_3)_2\text{-}N]^+$
32	5	S
28	32	N_2
15	100	CH_3^+

TABLE 2-13

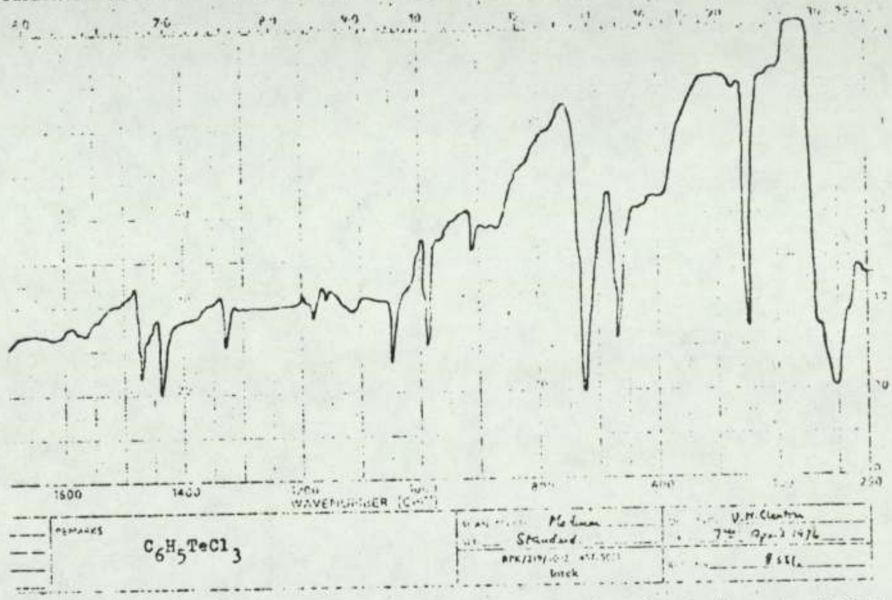
Mass spectra of Aryltelluriumtrihalide tmdto – Relative to ^{130}Te, ^{35}Cl, ^{79}Br.

$p-CH_3OC_6H_4TeCl_3$tmdto		$p-CH_3OC_6H_4TeBr_3$tmdto		$p-CH_3C_6H_4TeCl_3$tmdto	
m/e	R.A. (%)	m/e	R.A. (%)	m/e	R.A. (%)
345	3	345	1		
343	3	343	1		
				312	7
				310	6
246	4	246	5		
238	4	237	2		
234	3	235	4		
214	8	215	3	218	4
				214	10
200	9	199	4	199	2
				182	25
176	85	176	60	176	54
161	12	161	9	161	7
147.3	metastable	147.3	metastable	147.6	metastable
139	5	139	3		
133	5	133	4	133	4
132	5	132	4	132	3
129	12	129	11	129	13
122	7	125	2	124	5
112	7	112	8	112	13
107	3	107	2		
100	5	100	8	100	5
98	9	97	8	97	16
88	100	88	100	88	100
		80	3		
77	5	77	4	77	3
73	10	73	23	73	11
56	8	56	22	56	17
44	15	44	45	44	41
36	25			36	16
32	3	32	6	32	7
28	15	28	37	28	46
18	26	18	37		
15	9	15	39	15	24

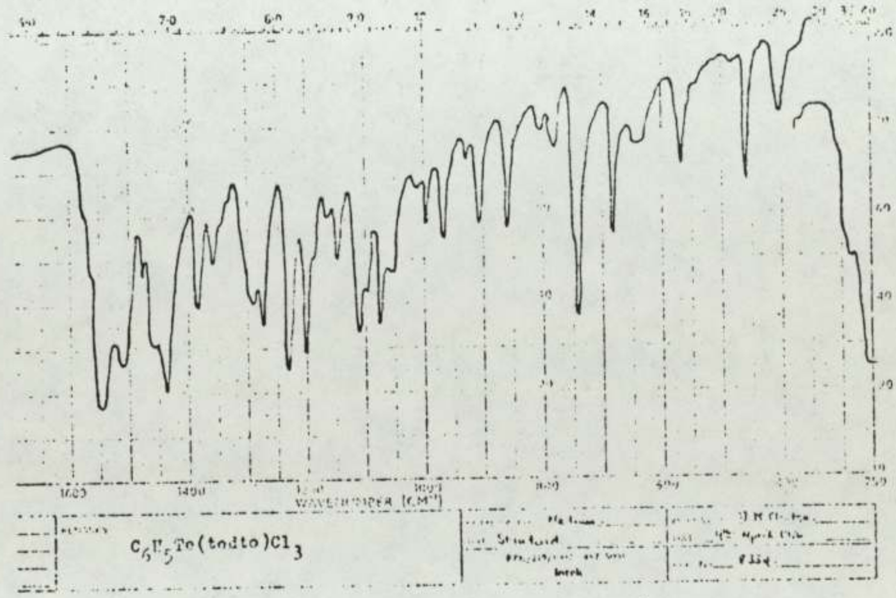
I.r. spectra of tedto and its tellurium complexes



Tetraethyldithio-oxamide(tedto)

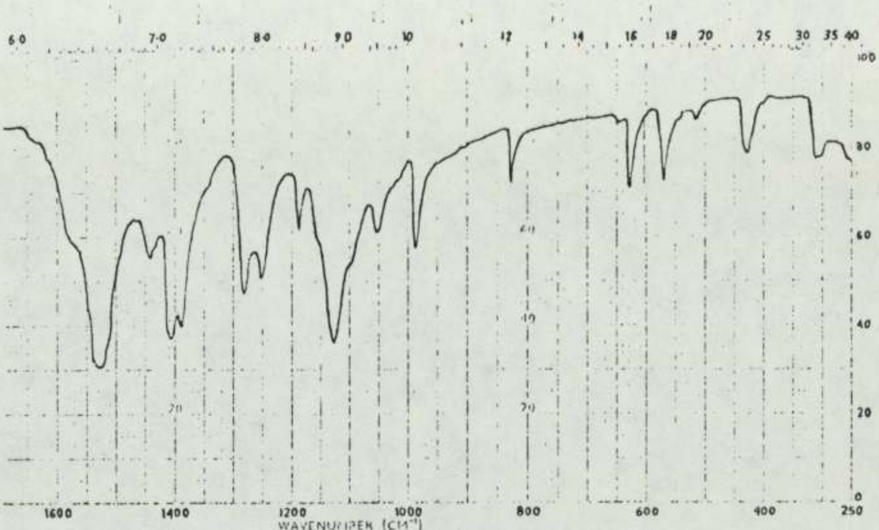


$C_6H_5TeCl_3$

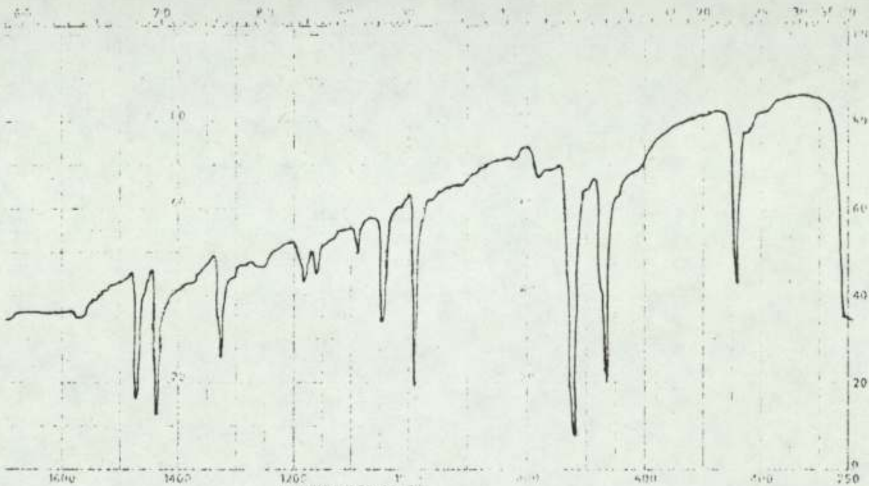


$C_6H_5Te(tedto)Cl_3$

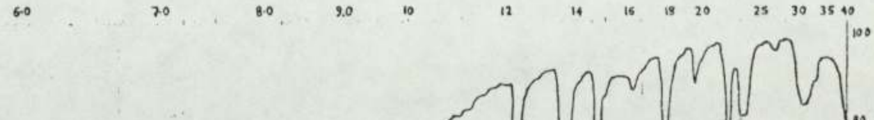
Fig. 2-3



REMARKS Tetramethyldithio-oxamide(tmdto)



REMARKS $C_6H_5TeBr_3$



$C_6H_5Te(tmdto)Br_3$

Fig. 2-4

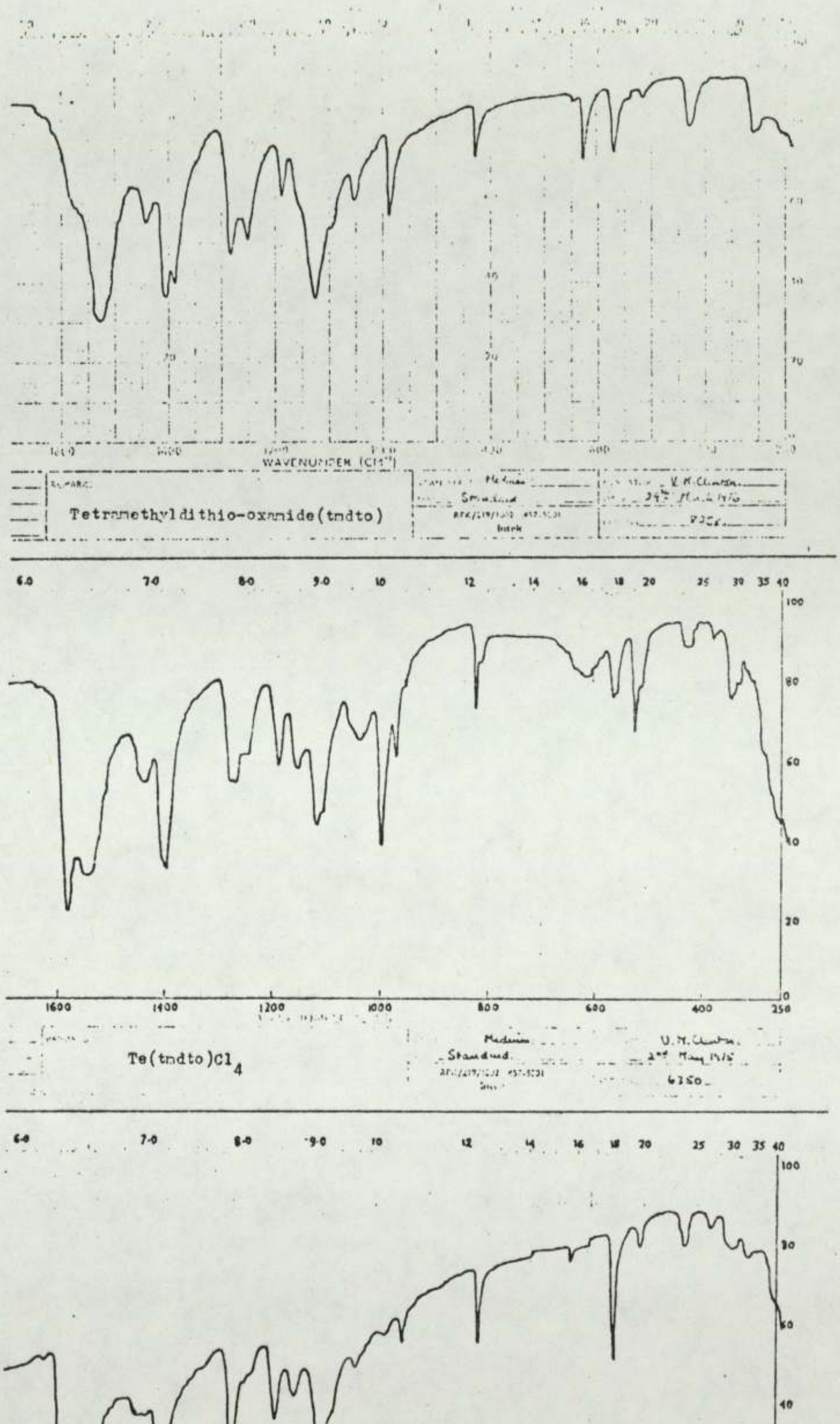
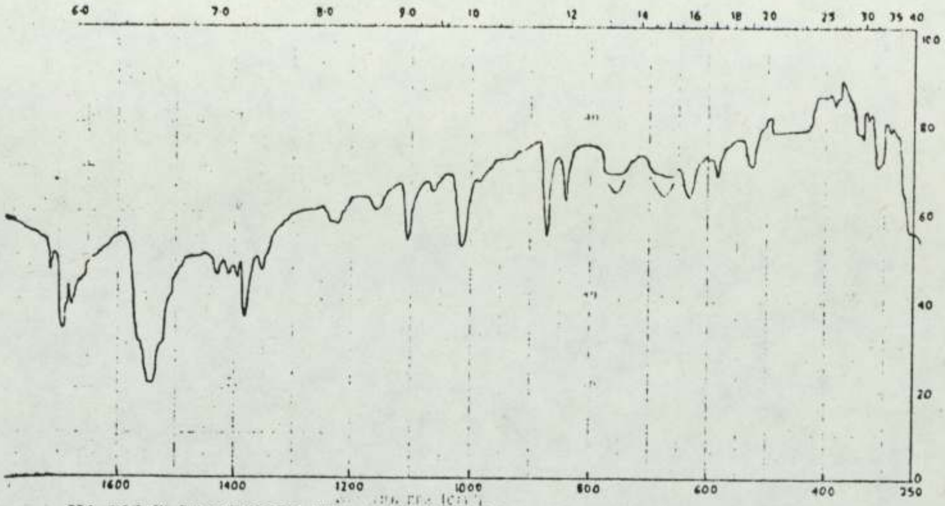
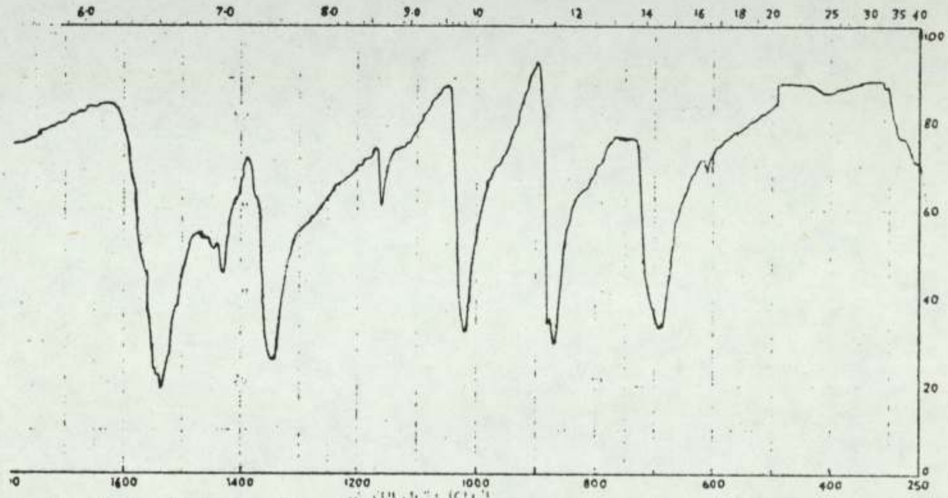

WAVENUMBER (CM⁻¹)
Tetramethyldithio-oxamide(tmdto)
Medium
Standard
V. H. Clunter
24th March 1976
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
100
80
60
40
20
0
1600
1400
1200
1000
800
600
400
250
Te(tmdto)Cl$_4$
Medium
Standard
V. H. Clunter
2nd May 1976
6350
Te(tmdto)Br$_4$
Medium
Standard
V. H. Clunter
2nd May 1976

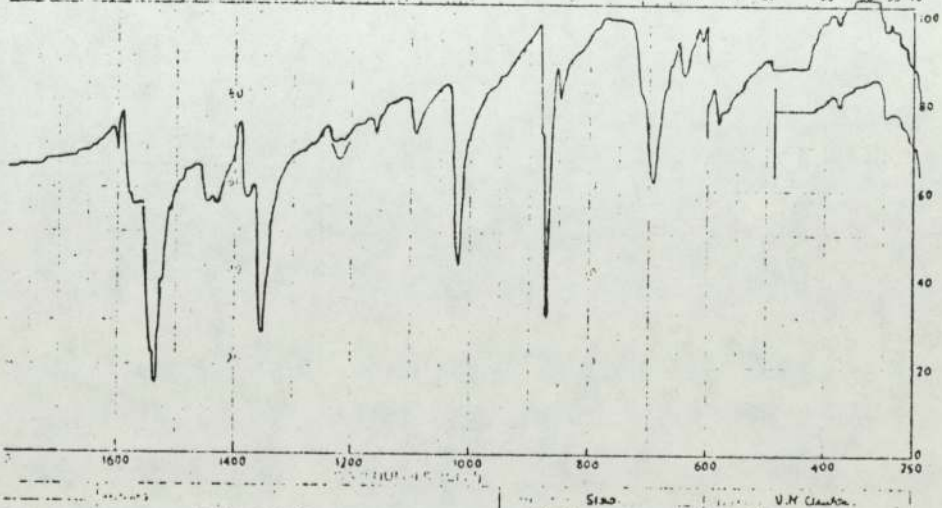
Fig. 2-5



Te(Me$_2$DH$_2$)Cl$_4$



Dimethyldithio-oxamide(Me$_2$DH$_2$)



Te(Me$_2$DH$_2$)Br$_4$

Fig. 2-6

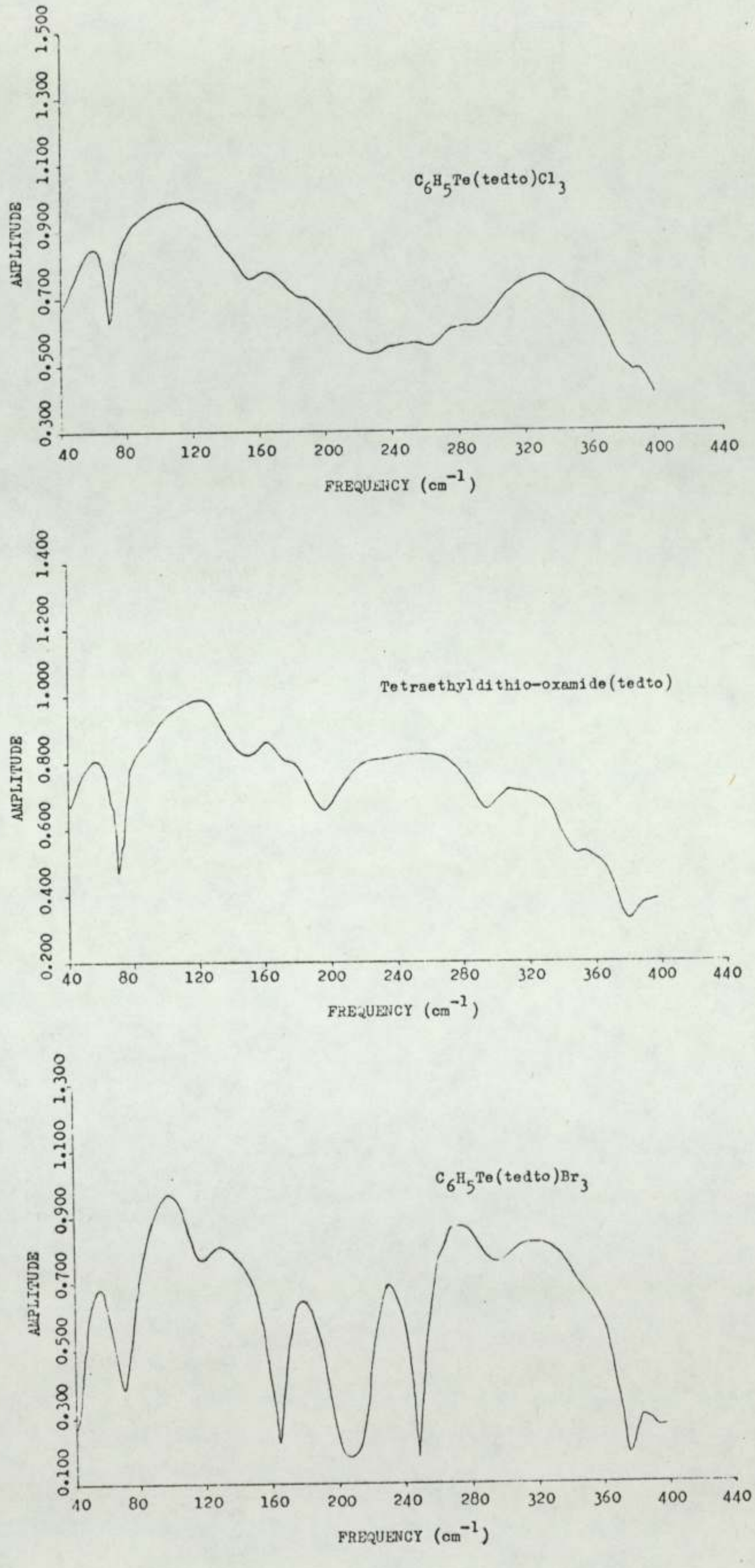

C6H5Te(tedto)Cl3
AMPLITUDE
0.300 0.500 0.700 0.900 1.100 1.300 1.500
40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm-1)
Tetraethyldithio-oxamide(tedto)
AMPLITUDE
0.200 0.400 0.600 0.800 1.000 1.200 1.400
40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm-1)
C6H5Te(tedto)Br3
AMPLITUDE
0.100 0.300 0.500 0.700 0.900 1.100 1.300
40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm-1)

Fig. 2-7

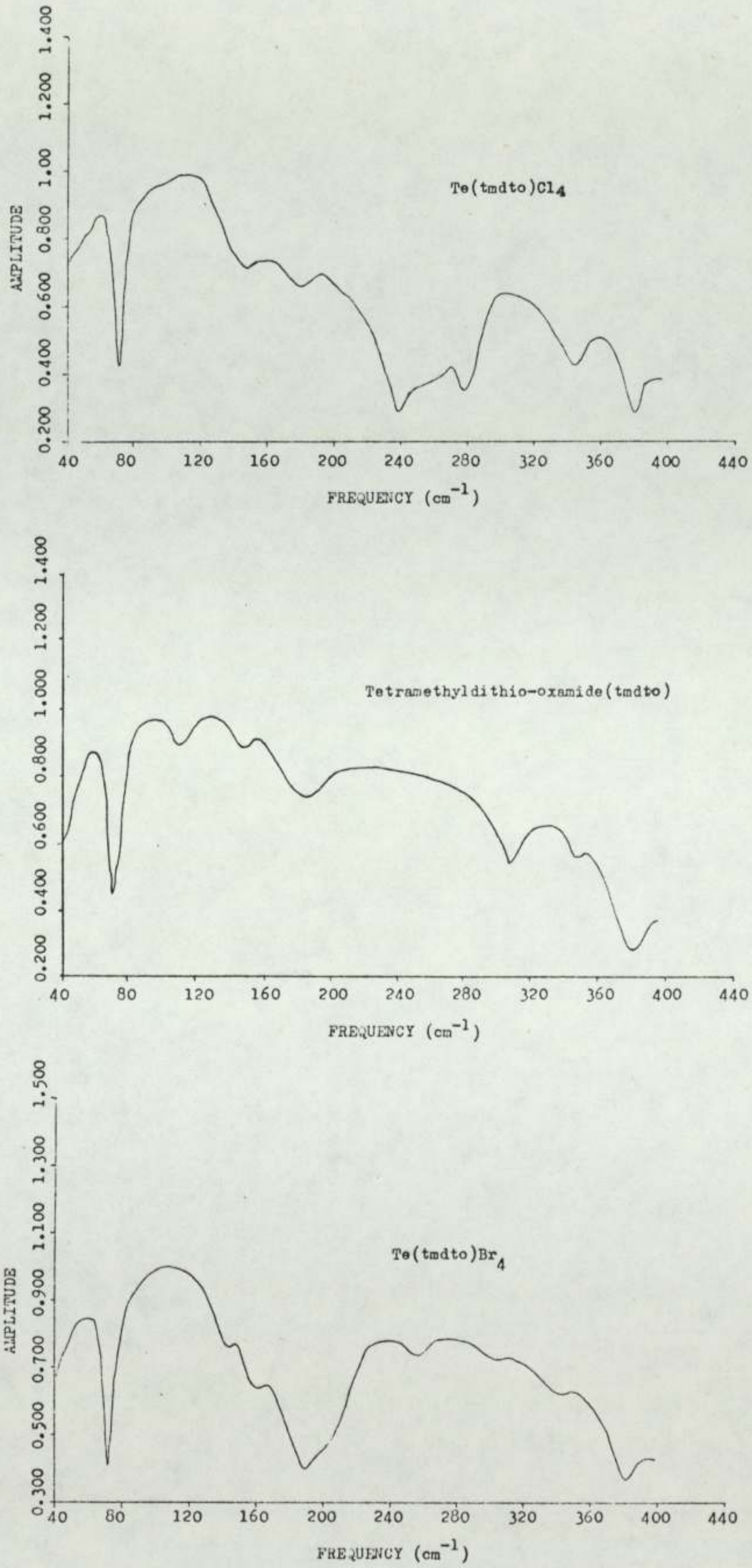

AMPLITUDE
0.200
0.400
0.600
0.800
1.00
1.200
1.400
Te(tmdto)Cl$_4$
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
0.200
0.400
0.600
0.800
1.000
1.200
1.400
Tetramethyldithio-oxamide(tmdto)
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.500
Te(tmdto)Br$_4$
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})

Fig. 2-8

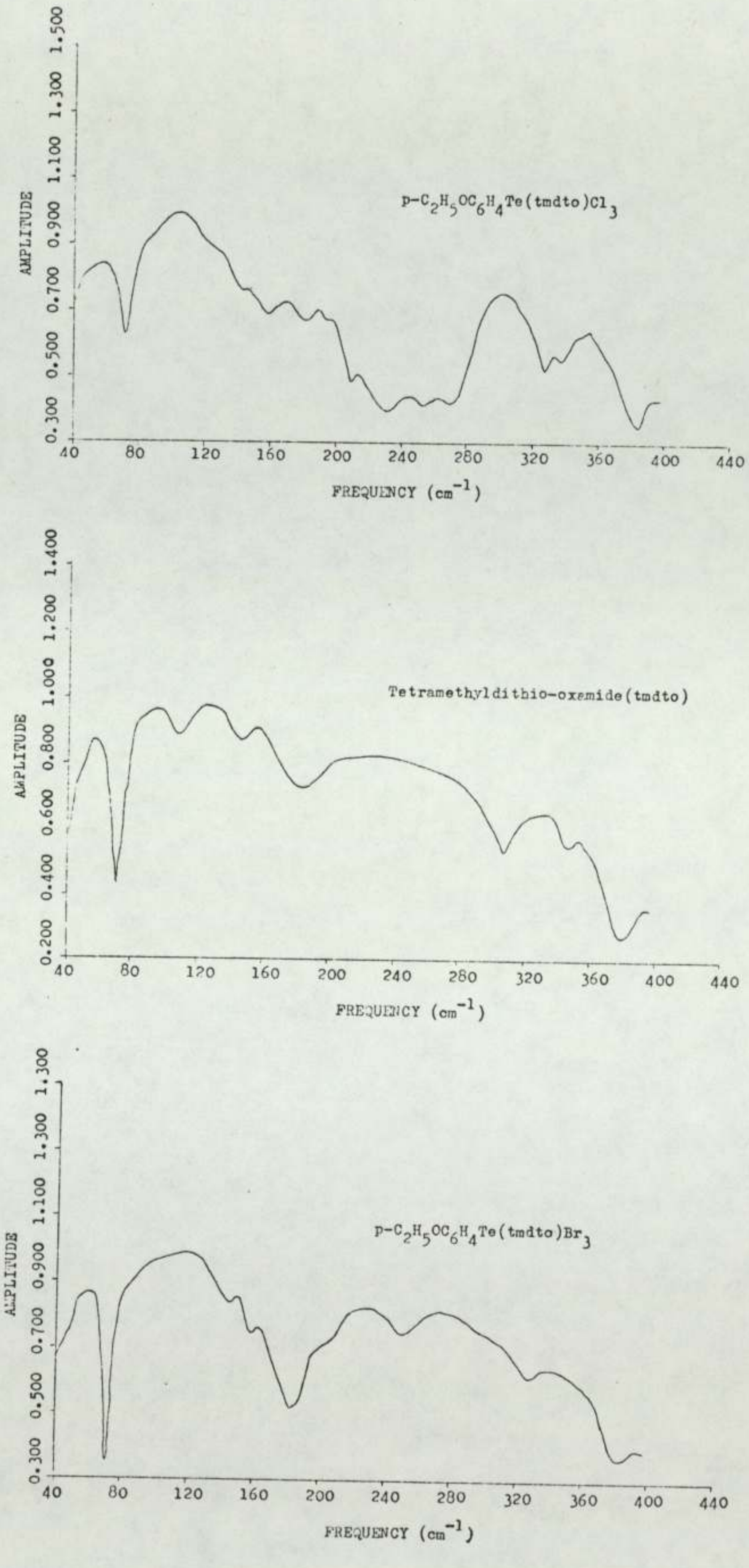

AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.500
p-$C_2H_5OC_6H_4Te(tmdto)Cl_3$
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
AMPLITUDE
0.200
0.400
0.600
0.800
1.000
1.200
1.400
Tetramethyldithio-oxamide(tmdto)
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.300
p-$C_2H_5OC_6H_4Te(tmdto)Br_3$
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})

Fig. 2-9

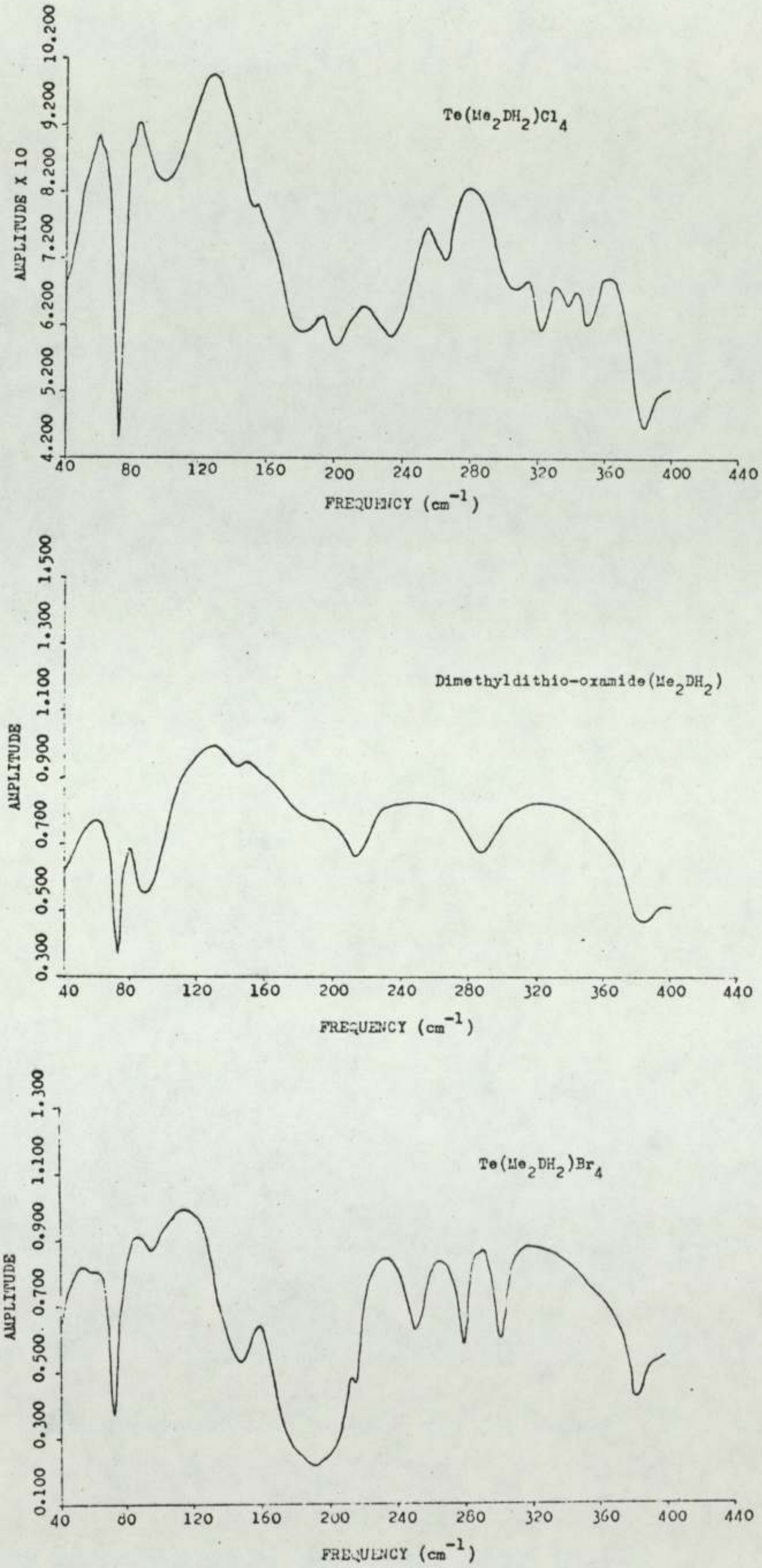
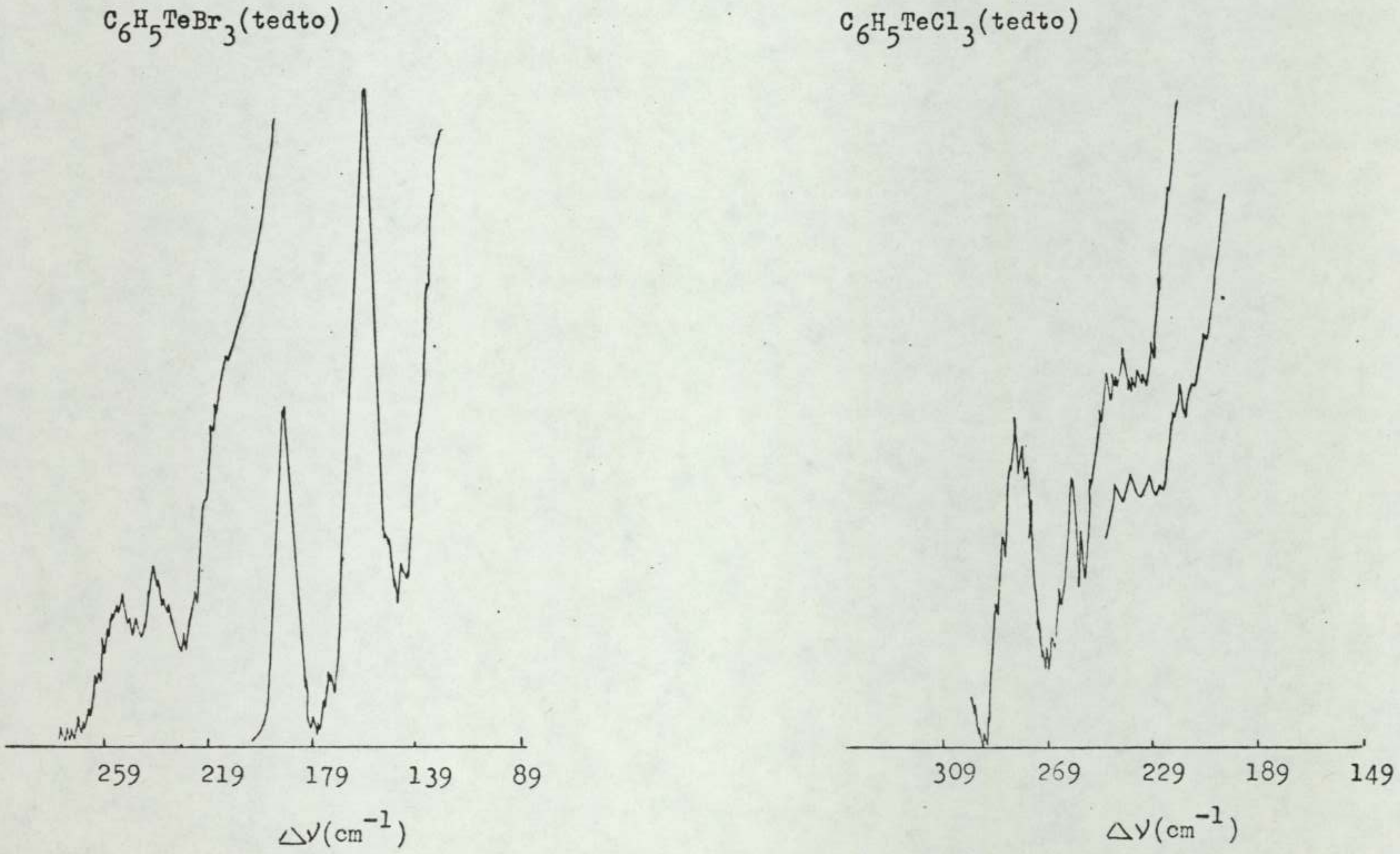

Te(Me$_2$DH$_2$)Cl$_4$
AMPLITUDE X 10
4.200
5.200
6.200
7.200
8.200
9.200
10.200
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
Dimethyldithio-oxamide(Me$_2$DH$_2$)
AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.500
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
Te(Me$_2$DH$_2$)Br$_4$
AMPLITUDE
0.100
0.300
0.500
0.700
0.900
1.100
1.300
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})

Fig. 2-10



$C_6H_5TeBr_3$(tedto)

$C_6H_5TeCl_3$(tedto)

Fig. 2-11

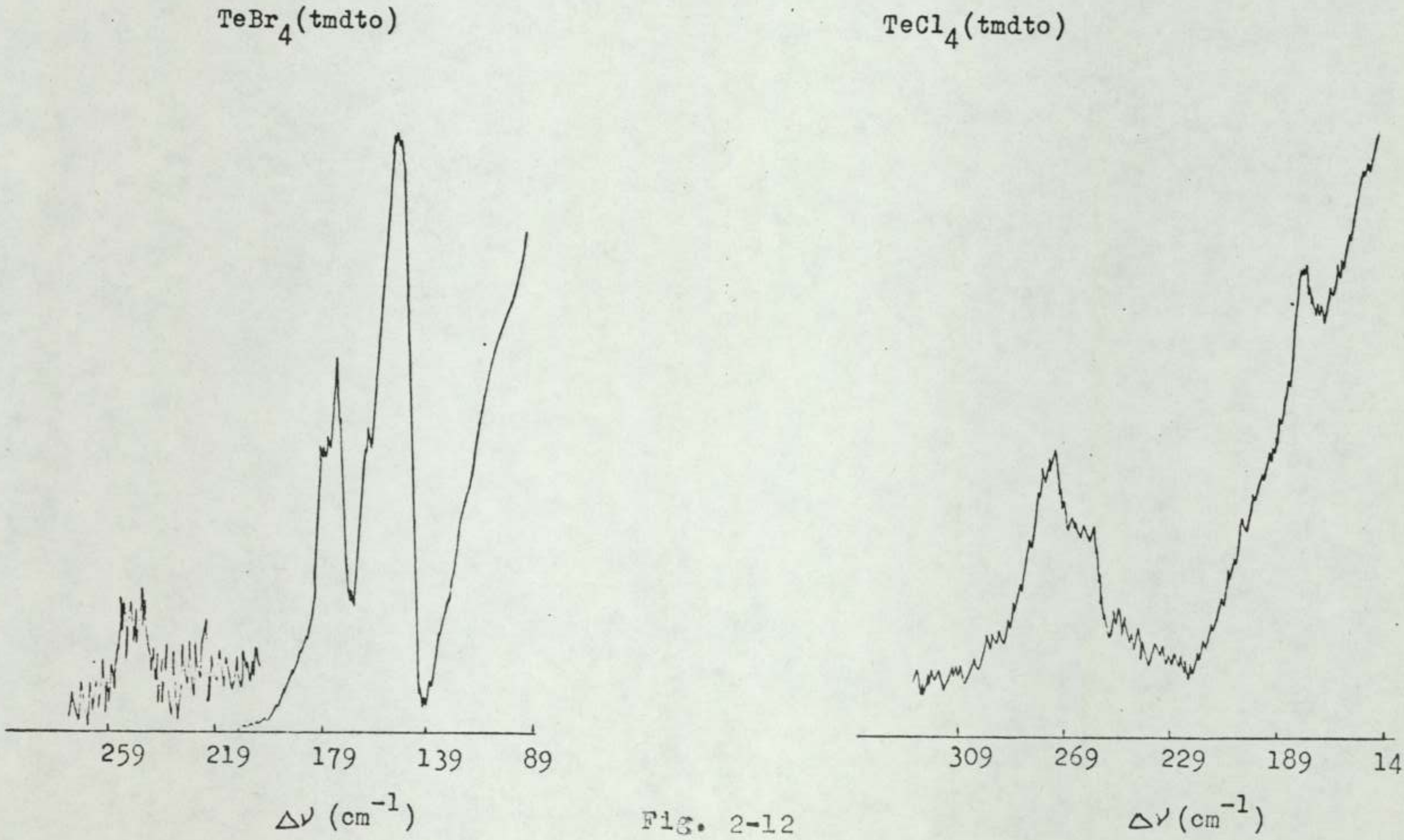
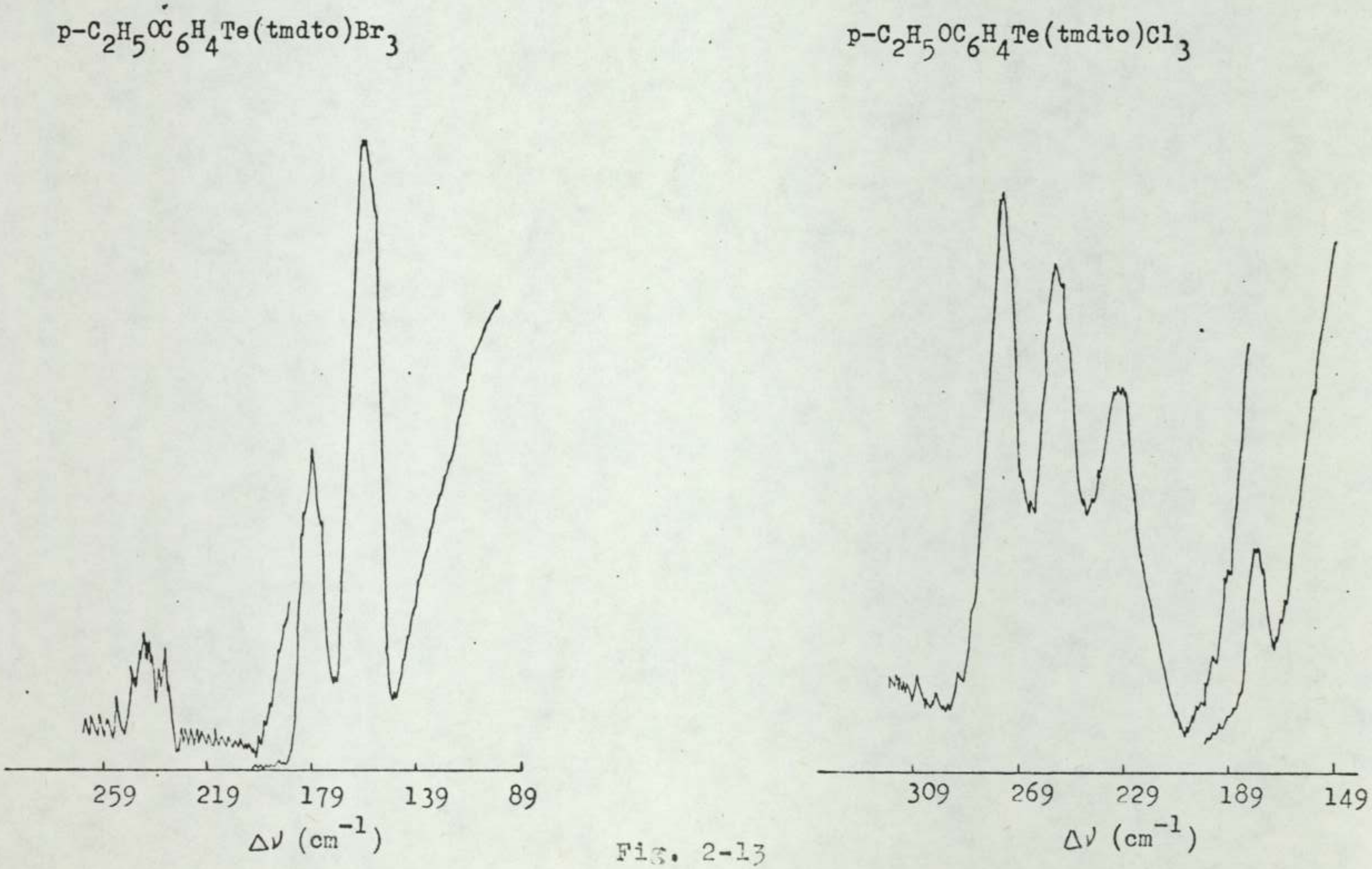

TeBr$_4$(tmdto)
259
219
179
139
89
$\Delta\nu$ (cm^{-1})
TeCl$_4$(tmdto)
309
269
229
189
149
$\Delta\nu$ (cm^{-1})

Fig. 2-12



p-$C_2H_5OC_6H_4Te(tmdto)Br_3$

p-$C_2H_5OC_6H_4Te(tmdto)Cl_3$

Fig. 2-13

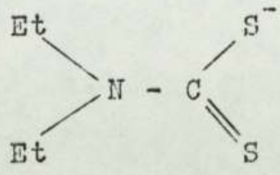
2.4 DISCUSSION

2.4.1 Synthesis.

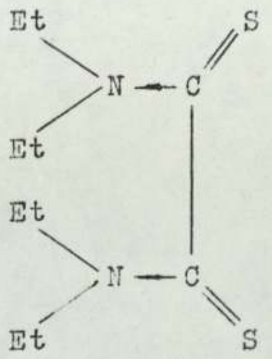
The pale yellow, yellow and yellow-orange chloro and bromo complexes were produced by the reaction of tellurium(IV) halides and aryltellurium trihalides with NNN'N' tetraethyldithio-oxamide or NNN'N' tetramethyldithio-oxamide are listed in tables 2-1, 2-3. All the complexes have a tellurium to ligand ratio of 1:1 and are of formula TeX_4tmdto, $ArTeX_3$tmdto and $ArTeX_3$tedto where tmdto = NNN'N' tetramethyldithio-oxamide, tedto = NNN'N' tetraethyldithio-oxamide, Ar = Ph, p-tolyl, p-$CH_3OC_6H_4$, p-$C_2H_5OC_6H_4$, p-$PhOC_6H_4$, p-$PhSC_6H_4$, p-BrC_6H_4 and X = Cl or Br. The violet and rusty red chloro and bromo complexes were produced by the reaction of tellurium(IV) halides with NN' dimethyldithio-oxamide are listed in the experimental part. These have a tellurium to ligand ratio of 1:1 and are of formula $Te(Me_2DH_2)X_4$ where X = Cl or Br and Me_2DH_2 = NN' dimethyldithio-oxamide.

2.4.2 U.V. and visible spectra

Dilute solution (5×10^{-4}M concentration) of tedto complexes and tmdto complexes in dimethylformamide solution all show one strong absorption at 35.7 kK and 36.36 kK respectively in contrast to those reported for diethyldithiocarbonate complexes of tellurium(II) and (IV) i.e. $Te(dtc)_2$ and $Te(dtc)_4$ [45] which are more complex in showing three bands but the main band position is in the same region of the spectra.



dtc.



TEDTO

2.4.3 Conductivity Measurements.

The conductivity of 10^{-3} Molar solution of tellurium(IV) complexes in dimethylformamide and nitromethane are shown in tables 2-1 and 2-3. Aryltelluriumtrihalides with tetramethyldithio-oxamide complexes had values of Λ at 20°C (26-48) $cm^2.ohm^{-1}.mole^{-1}$ and telluriumtetrahalides and aryltelluriumtrihalides with tetramethyldithio-oxamide had values of Λ at 20°C (27-122) $cm^2.ohm^{-1}.mole^{-1}$. In dimethylformamide and nitromethane solutions the compounds are ionised. Whilst the Λ values are lower than normally encountered for 1:1 electrolysis in those solvents[46] but too high to be assumed as non-electrolytes. These cationic species are presumably similar to telluronium cations $(R_3Te)^+$. The species $(ArTeX_2)^+$ will have one lone pair and three bond pairs. Two additional lone pairs from two sulphur donor atoms donated by one dithio-oxamide ligand will make up a total of one lone pair and five bond pairs. The basic shape of this cation will then be ψ octahedral, and thus a square pyramid shape for $(ArLTeX_2)^+$ (where L = NNN′N′ tetramethyldithio-oxamide or NNN′N′ tetraethyldithio-oxamide) may be predicted.

2.4.4 Mass spectra

The mass spectra of telluriumtetrahalide, and aryltelluriumtrihalide complexes are shown in tables 2-8 to 2-13. Most complexes give identical ionic mass charge ratios to tetraethyldithio-oxamide and tetramethyldithio-oxamide. In general the tetraethyldithio-oxamide and tetramethyldithio-oxamide ligands are decomposed more easily than the telluriumtetrahalide and aryltelluriumtrihalide complexes. This suggests that the tellurium-sulphur bond is weaker than tellurium-chloride and tellurium-bromide bonds.

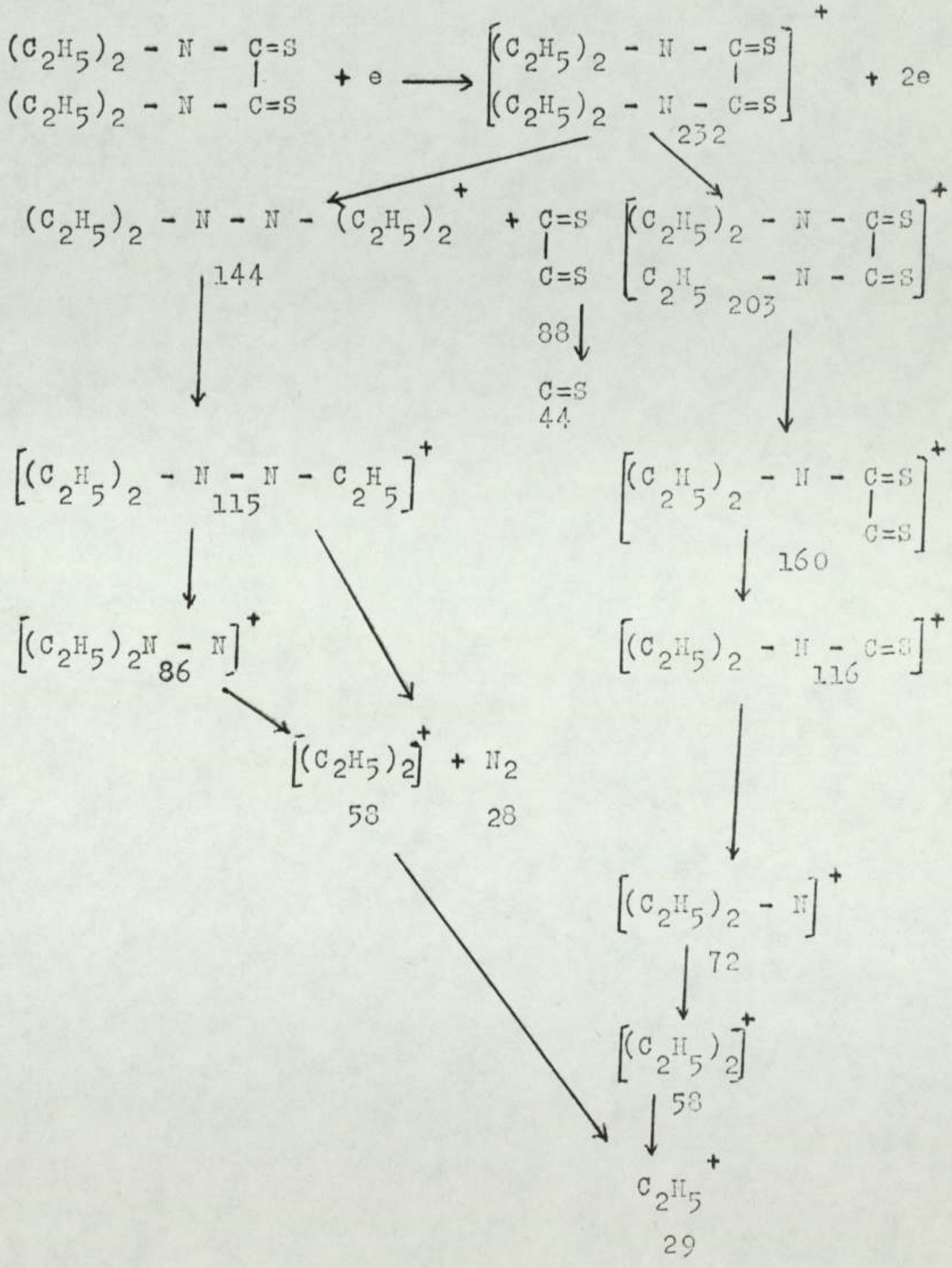
Fragmentation patterns of tetraethyldithio-oxamide, tetramethyldithio-oxamide, the complexes, $C_6H_5TeCl_3$tedto, and $CH_3OC_6H_4TeCl_3$tmdto are given here as examples.

McWhinnie and Thavornyutikarn[33] suggest that some aryltelluriumtrihalides must be dimers or trimers. There were two main reasons for this suggestion; the first was that the ions observed were at a higher mass charge ratio that the monomer molecule; and the second was the observation of ditelluride ions. These ions could only occur from the dimer or the trimer molecules (not from the monomer molecule) by breaking the tellurium-halogen bonds and forming tellurium-tellurium bonds.

2.4.5 Vibrational spectra

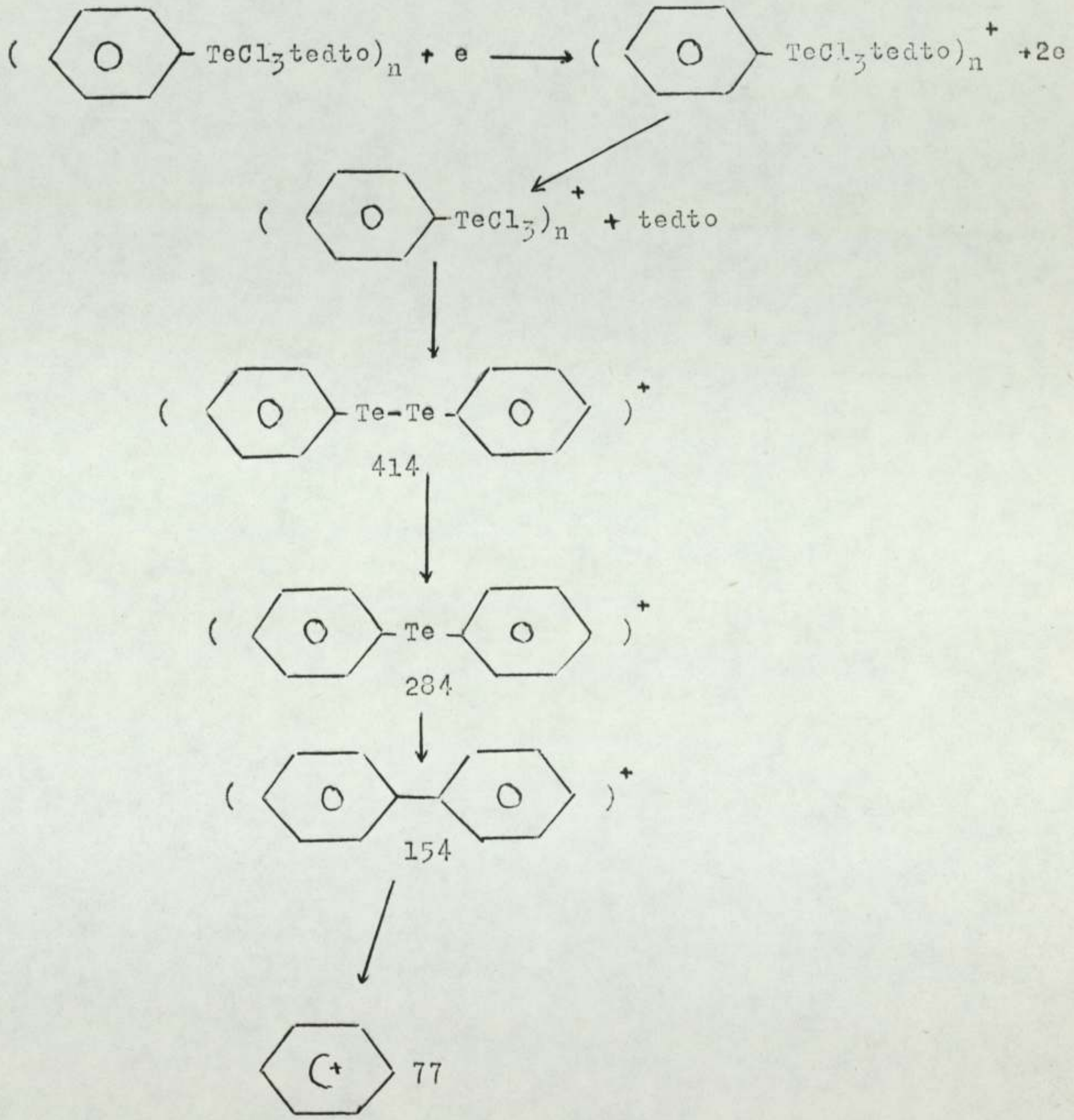
The infrared spectra of all complexes above 400 cm^{-1} are discussed below.

An illustrated example of the fragmentation pattern as shown by tetraethyldithio-oxamide (tedto).



The mass charge ratio ions observed from the spectra are indicated by the figures.

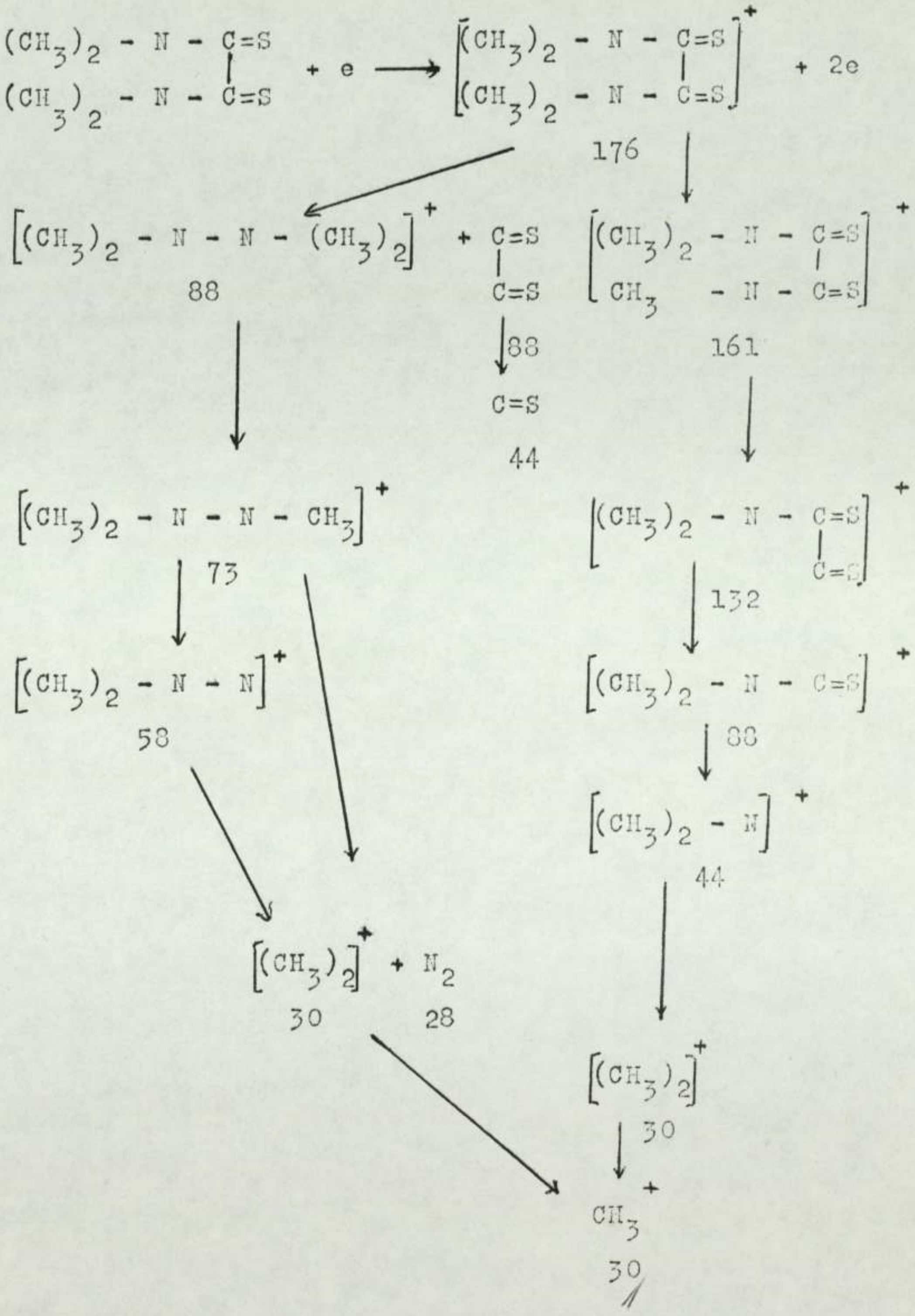
An illustrated example of the fragmentation pattern as shown by $C_6H_5TeCl_3$tedto



Where tedto = tetraethyldithio-oxamide

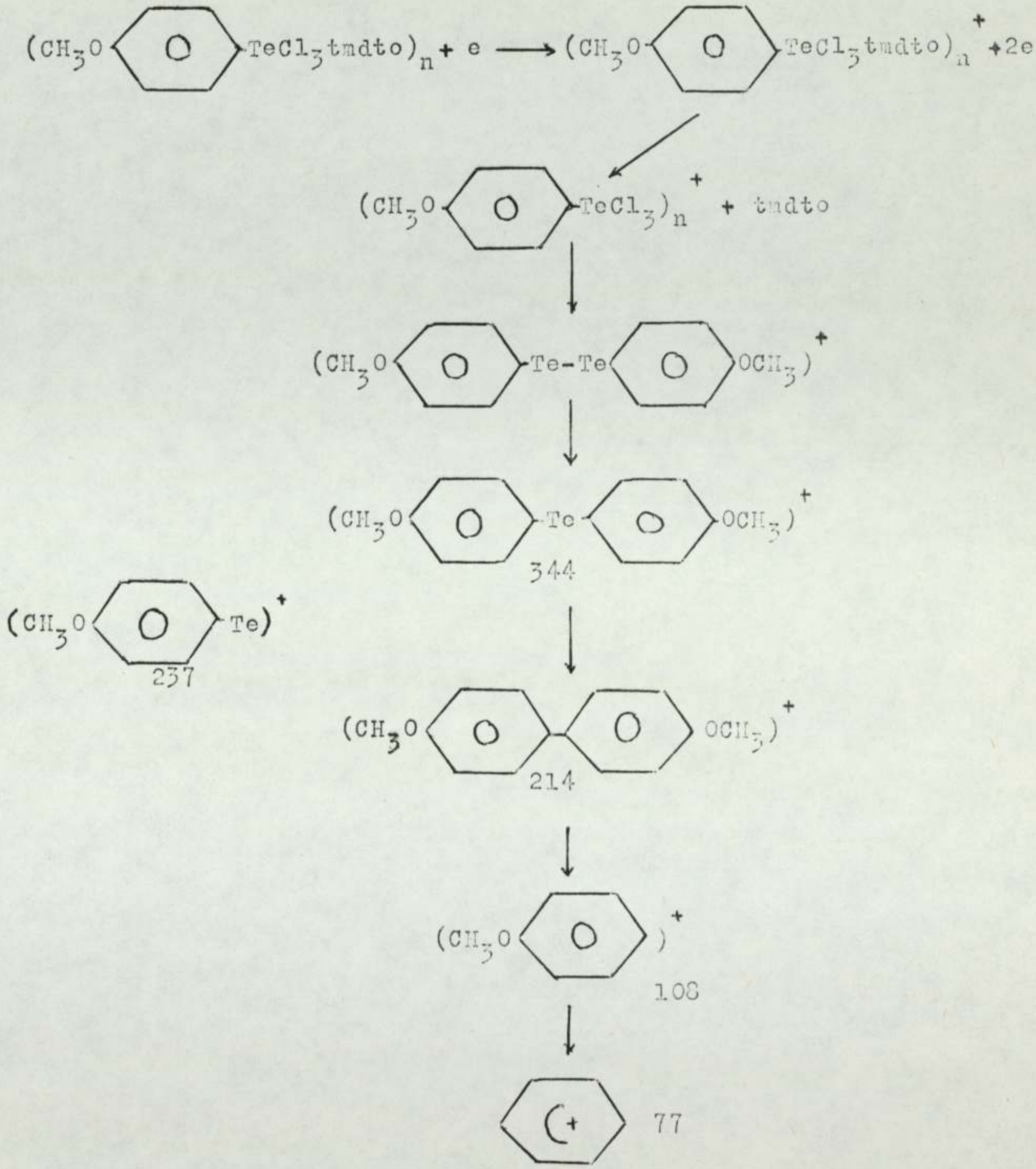
The mass charge ratio ions observed from the spectrum are indicated by the figures.

An illustrated example of the fragmentation pattern as shown by tetramethyldithio-oxamide (tmdto).



The mass charge ratio ions observed from the spectra are indicated by the figure.

An illustrated example of the fragmentation pattern as shown by p-$CH_3OC_6H_4TeCl_3$tmdto



Where tmdto = tetramethyldithio-oxamide

The mass charge ratio ions observed from the spectra are indicated by the figures.

2.4.5.1 NNN′N′ Tetraethyldithio-oxamide complexes of Tellurium(IV)

The most important bands in the infrared spectra above 400 cm^{-1} are listed in table 2-1. The i.r. spectrum of phenyltelluriumtrichloride, tetraethyldithio-oxamide and phenyltelluriumtrichloride complex, are shown in Fig. 2-3 Certain important differences between the spectra of ligand and the complex may be noted. For example, the bands at 1500 and 872 cm^{-1} in the ligand which have been assigned to ν(CN)and ν(CS) are shifted to higher and lower wavenumbers respectively on complex formation. The latter band is believed [29] to be due predominately to the C = S stretching mode and co-ordination through sulphur will produce such an effect. The band at 1500 cm^{-1} is shifted to 1550-1510 cm^{-1} and the band at 872 cm^{-1} is shifted to 863-800 cm^{-1} in the complexes. The band at 1500 cm^{-1} [47] is thought to be due mainly to a C-N stretching mode and its shift to a higher frequency would be expected if co-ordination is through the sulphur atoms of the thiocarbonyl groups.

2.4.5.2 NNN′N′ Tetramethyldithio-oxamide complexes of Tellurium(IV)

The infrared bands which arise from ν(CN) and ν(CS) in the ligand and complexes are listed in table 2-3 Fig. 2-4 shows the i.r. spectrum of phenyltelluriumtribromide, tetramethyldithio-oxamide and phenyltelluriumtribromide complex. The i.r. spectrum of tetramethyldithio-oxamide, telluriumtetrachloride complex and telluriumtetrabromide complex have been reproduced in Fig. 2-5.

The band at 1528 cm^{-1} assigned to ν(CN) is shifted to a higher wavenumber and is split on complex formation, and a band at 828 cm^{-1} assigned to ν(CS) is shifted to a lower wavenumber consistent with the proposal that co-ordination takes place through the sulphur atoms of the thiocarbonyl groups. The band at 1528 cm^{-1} is shifted to 1582-1530 cm^{-1} and the band at 828 cm^{-1} is shifted to 821-810 cm^{-1}. The shifts in these two bands are of the same order as in tetraethyldithio-oxamide.

2.4.5.3 Dimethyldithio-oxamide complexes of tellurium(IV)

As discussed in page 35 the tellurium(IV) halide NN′ dimethyldithio-oxamide complexes were prepared by addition of telluriumtetrachloride, or telluriumtetrabromide dissolved in a mixture of acetic acid and methanol to a solution of NN′ dimethyldithio-oxamide (Me_2DH_2) , also dissolved in a mixture of acetic acid and methanol. The rust coloured telluriumtetrabromide complex and the violet coloured telluriumtetrachloride complex formed after stirring for five minutes. The more important bands in the infrared spectra of the NN′ dimethyldithio-oxamide (Me_2DH_2) and its complexes now discussed, are listed in table 2-5 and are shown in Fig. 2-6.

The band at 1528 cm^{-1} assigned to ν(CN) is shifted to a higher frequency on complexation indicating a greater double band character and likely co-ordination through sulphur.

Thioamide bands III and IV are assigned to ν (CS). Thioamide band IV at 1020 cm^{-1} decreased to 1010 cm^{-1} in the $Te(Me_2DH_2)Cl_4$ and to 1005 cm^{-1} in the $Te(Me_2DH_2)Br_4$. The band at 868 cm^{-1} in the ligand assigned to ν (CS) is shifted to a lower frequency (841-850 cm^{-1}), in the tellurium tetrachloride complex and tellurium tetrabromide complex respectively (as expected for sulphur co-ordination) but is split to 872, 902 cm^{-1} in the $Te(Me_2DH_2)Cl_4$ and $Te(Me_2DH_2)Br_4$ respectively. The splitting and slight increase to ν (CS) suggests that some Te-N bonding may be involved.

Desseyn et. al.[48] reported the increase in intensity of the band at 1160 cm^{-1} ν (C_RN) mode, as an indication that in the complexes of disubstituted dithio-oxamide the metal-nitrogen bond is stronger than the metal-sulphur bond. The tellurium complexes show new bands at 1225-1236 cm^{-1} and at 1160 cm^{-1} but the band at 1160 cm^{-1} is not enhanced in intensity. These new bands may arise from vibrations of the ligands which are associated with tellurium-nitrogen bonding.

From table 2-6 it is seen that the bands in the complexes in the region 300-310 cm^{-1} are tentatively assigned to ν (Te-N), (also see fig. 2-10).

New bands were noted in the complexes at 270 cm^{-1}, 252-200 cm^{-1} and 190 cm^{-1} which are clearly attributed to ν (Te-Cl), ν (Te-S) and ν (Te-Br) respectively, after elimination of ligand bands.

The infrared and Raman spectra of all complexes at low frequency (below 400 cm^{-1}) are now discussed.

2.4.5.4 NNN' N' Tetramethyldithio-oxamide complexes of Tellurium (IV).

The bands in the far infrared and Raman spectra of the tetramethyldithio-oxamide complexes are given in table 2-4 The i.r. spectra of tmdto and its tellurium (IV) complexes are shown in Fig. 2-8 and 2-9 and the Raman spectra of tetramethyldithio-oxamide complexes are shown in Fig. 2-12 and 2-13.

In addition to bands found in the tmdto ligand and aryltelluriumtrihalides, new bands are noted in the complexes at 283-255 cm^{-1}, 254-205 cm^{-1} and 188-155 cm^{-1}.

Since the complexes are derived from tellurium-tetrahalides or aryltelluriumtrihalides and tmdto, it is convenient at this point to discuss the main features of the structure and spectra of these compounds.

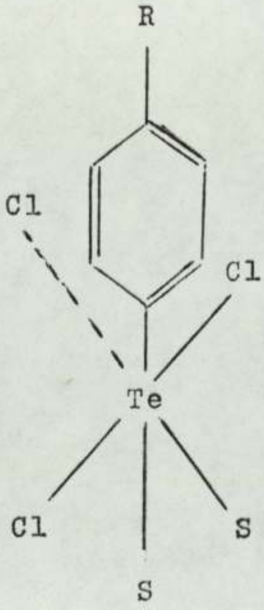
Recent studies by Buss and Kreks [49] using the X-ray analysis of $TeCl_4$, showed the crystal consisted of tetrameric units Te_4Cl_{16} i.e. a cubic like structure with short and long Te-Cl bonds giving essentially an array of $TeCl_3^+$ units (approx C_{3v}) and Cl^- ions. The possibility of Te-Te bonding was ruled out owing to the long Te-Te distance. The infrared and Raman spectra of $TeCl_4$ and $TeBr_4$ have been reported.[50-53]

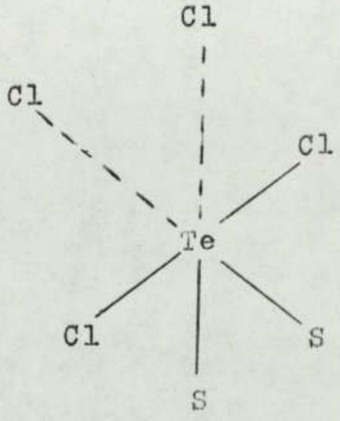
Hayward and Hendra reported the covalent structures of $TeX_4(C_{2v})$ to be ψ trigonal bipyramidal based. However, Greenwood and co-workers [53] after examining tellurium tetrahalide in the solid phase reported there was no evidence to suggest that the ionic structures of $TeX_3^+X^-$ (C_{3v}) is trigonal bipyramidal based. They suggested a pyramidal based structure from infra red data.[53]

The i.r. spectra below 400 cm^{-1} of tetramethyldithiooxamide is relatively simple (see table 2-4) and as expected the spectra of complexes of the formula TeX_4tmdto are simpler than those of formula p-$ArTeX_3$tmdto. Bands between 376-343 cm^{-1} reported for $TeCl_4$ [50] are absent in the complex $TeCl_4$tmdto, but new stronger to medium i.r. and Raman bands appear between 277-273 cm^{-1}. McWhinnie and Thavornyutikarn [33] have reported the infrared and Raman spectra (see table 2-7) of some aryltelluriumtrihalides and assign the bands at 342-298 cm^{-1} as being due to the ν(Te-Cl) terminal stretching modes whilst those terminal bromines ν(Te-Br) occur at 224-190 cm^{-1}. Further, they suggest that all aryltelluriumtrihalides may be regarded as complex structures, such as dimers or trimers built up from donor acceptor interactions of $ArTeX_2^+$ and X^- units. The strong bands in the region 342-298 cm^{-1} [33] for aryltellurium trichloride are absent in the corresponding tmdto complexes. All the complexes have strong to medium absorptions in the 283-255 cm^{-1} region which may be assigned to ν(Te-Cl) vibrations, whilst those at 188-155 cm^{-1} to ν(Te-Br). Thus, absorptions in the 254-205 cm^{-1} region are likely to be associated with ν(Te-S) vibrations. The ν(Te-Cl) assignment at 287-262 cm^{-1} is in agreement with those reported by McWhinnie et. al. in their studies on tetrachlorotellurates [54] and diaryltelluriumdihalides.[55]

The i.r. spectra of all the p-ArTeX_3tmdto complexes have one medium band in the region 339-315 cm^{-1}, a feature which is absent from the spectra of the TeX_4tmdto complexes and which therefore could be a band arising from the p-ArTe group. A strong band at 312 cm^{-1} is found for p-iodoanisole and the band at 309 cm^{-1} is p-fluoroiodobenzene is said to involve C-I bending.[56] The bands at 339-315 cm^{-1} in the ArTeX_3tmdto complexes could therefore involve C-Te bending[213].

Wynne and Pearson[19] have suggested that tellurium is pentaco-ordinate in methyltrichloro (tetramethyl-thiourea) tellurium (IV). The adducts they describe have the same stoichiometry as the tmdto derivatives of tellurium (IV) reported here and there are certain similarities in the spectra also. The high Te-Cl frequencies (said to be due to cis $TeCl_2$ groups) at 338 and 315 cm^{-1} in $MeTeCl_3$ are absent in $MeTeCl_3$(tmtu) adduct, and a band appears at 251 cm^{-1}. In the $TeCl_4$tmdto and $ArTeCl_3$tmdto complexes, the high Te-Cl frequencies are again absent and strong bands appear at 283-255 cm^{-1} i.e. close to the values found in Me_2TeCl_2 (251 cm^{-1})[56] in Ph_2TeCl_2 (287-262 cm^{-1}) and in $PhTeCl_3$tmdto (283-264 cm^{-1}). It is possible that in the tmdto complexes as in methyltrichloro(tetramethylthiourea)-tellurium (IV) the absorptions between 283-255 cm^{-1} are due to trans Cl-Te-Cl stretching and that the sulphur atoms of the dithio-oxamide ligand exert a strong trans bond lengthening effect than do the chlorine atoms. Six co-ordinate tellurium with one long Te-Cl bond is therefore likely in the $ArTeCl_3$tmdto complexes. A similar structure but with two long Te-Cl bonds is likely for $TeCl_4$tmdto.





TeCl$_4$tmdto

RC$_6$H$_4$TeCl$_3$tmdto

or RC$_6$H$_4$TeCl$_3$tedto

where R = H, Br, CH$_3$, CH$_3$O, C$_2$H$_5$O, PhO and PhS.

These structures with one or two long bonds are consistent with the proposal that one or two Cl$^-$ ions are removed from the co-ordination site in a suitable solvent. The conductivities of the complexes in DMF has already been discussed.

The far infrared data for the bromo tmdto complexes are similar to the chloro analogues. Tellurium-Bromine Raman bands at 250-200 cm^{-1} as found for TeBr$_4$ [51] or 215 cm^{-1} found for p-EtoC$_6$H$_4$TeBr$_3$ [47] are absent in the tmdto complexes but a new band appears at 192-158 cm^{-1} as found for (p-MeOC$_6$H$_4$)$_2$TeBr$_2$ [55] and may be assigned to ν (Te-Br).

2.4.5.5 NNN N Tetraethyldithio-oxamide complexes of Tellurium (IV).

Tetraethyldithio-oxamide complexes are similar to the tetramethyldithio-oxamide complexes and their analogues.

The far infrared and Raman bands for the tedto complexes are given in table 2-2. The i.r. and Raman spectra of complexes are shown in Fig.2-7 and 2-11 respectively.

There are six bands between 410-100 cm^{-1} for tedto and some are clearly altered by complex formation, but new bands due to ν(Te-S), ν(Te-Cl) and ν(Te-Br) may be clearly identified. Thus absorptions associated with ν(Te-S) occur at 252-203 cm^{-1} in the complexes and bands at 280-250 cm^{-1} and 194-155 cm^{-1} may be assigned to ν(Te-Cl) and ν(Te-Br) in agreement with those reported earlier by McWhinnie et. al.[54,55]

The bands at 145-133 cm^{-1} in table 2-2 and 118-106 cm^{-1} are tentatively assigned to δ(Te-S) or δ(Te-Cl) and δ(Te-Br) respectively. The values for δ(Te-Cl) are in agreement with those reported by McWhinnie.[55] The i.r. and Raman spectra of the tedto complexes p-thiophenoxyphenyltelluriumtrichloride and tribromide do not differ significantly from those of the other trihalides and there is no evidence to suggest that the sulphur atom of the thioether may take part in complex formation with the tellurium atom of another molecule.

CHAPTER III

Heterocyclic ligands containing nitrogen and sulphur and their reaction with Tellurium (II) and (IV) compounds.

3.1 INTRODUCTION

Foss and co-workers [12,13] have investigated the complexes of Tellurium (II) and Tellurium (IV) derivatives with thiourea. These complexes were obtained by reacting a mixture of tellurium dioxide dissolved in acids (such as hydrochloric acid) with thiourea or its derivatives. Tellurium (IV) is reduced and a complex of tellurium (II) is formed together with disulphide cation. The latter is obtained by oxidation of the thiourea :

$$Te^{+4} + (n+2)\ S{=}C(NR_2)_2 + 2X^- \longrightarrow Te\ S{=}C(NR_2)_2\ {}_nX_2 + \left[(R_2N)_2C\text{-}S\text{-}S\text{-}C(NR_2)_2\right]^{++}$$

where X = Cl, Br, F.

The complexes of tellurium (II) and (IV) with thiourea [78,79] and their derivatives $Te(Y)_n(X)_m$, are listed in table 1-1 Chapter 1, page 5.

Foss and co-workers [13a,13e] also isolated the thiourea-phenyl tellurerylchloride complex, which was formed according to the following reaction :

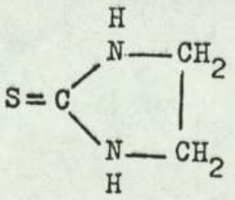
$$C_6H_5TeCl_3 + 3tu \longrightarrow C_6H_5Te(tu)Cl + \left[SC(NH_2)_2\right]_2^{++} + 2Cl^-$$

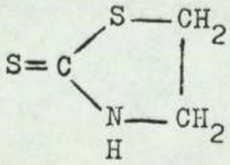
$$C_6H_5TeCl_3 + 4tu \longrightarrow C_6H_5Te(tu)_2Cl + \left[SC(NH_2)_2\right]_2^{++} + 2Cl^-$$

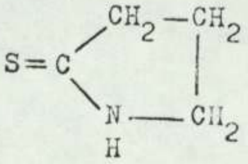
where tu = $S{=}C(NH_2)_2$

Thiourea and substituted thiourea complexes all contain the $-NR-\overset{|}{C}=S$ group, where R = hydrogen, alkyl, or aryl.

If the -NH- group in ethylenethiourea (A) is replaced by S or CH_2 a series of heterocyclic compounds are obtained. For example, when replaced by **S**, thiazolidine-2-thione (B) is formed, and with CH_2, pyrrolidine-2-thione (C) is obtained. These compounds with nitrogen and sulphur atoms could be potential ligands for co-ordination with tellurium (II) or tellurium (IV).


(A)


(B)


(C)

3.1.1 Thiazolidine-2-thione complexes

Some previous studies have been reported on thiazolidine-2-thione complexes. The preparation and characterisation of some chromium, molybdenum and tungsten complexes with thiazolidine-2-thione have been reported by Filippo and co-workers.[57] These complexes have the formula $M(CO)_5ttz$, where M = Cr, Mo, W; and ttz = thiazolidine-2-thione. All the compounds are diamagnetic and non-electrolytes in a chloroform solution. They were prepared using a deoxygenated toluene solution under nitrogen atmosphere using a metal hexacarbonyl and thiazolidine-2-thione in molar ratios from 1:1 to 1:4. After irradiation by u.v. source (about two hours) the solution changed to a yellow colour .The compounds separated after evaporation of the solvent. Spectroscopic studies on these complexes show that there is no co-ordination through the nitrogen atom but the ligand is bonded to the metal through the sulphur atom.

Fregni and co-workers [58] studied Iron (II) and (III) complexes of thiazolidine-2-thione and they reported complexes of the formula $Fe(ttz)_nX_3$ (where X = Cl, n = 2,4,6; X = Br, n = 3,6) and $Fe(ttz)_nI_2$ (where n = 2,3,4,6). These complexes were prepared from $FeX_3.2H_2O$ (X = Cl or Br) and $FeI_2.nH_2O$ by reaction in molten ligand media (at 105-110°C). The nitrogen atom of the ligand is the donor in the complexes as shown by the infrared spectra.

The preparation of nickel and cobalt complexes of thiazolidine-2-thione was investigated by D. de Filippo and C. Preti [59] P.P. Singh and R. Rivest [60b] and B. Singh and K. Thakur [60a].

Filippo and Preti reported the preparation of cobalt and nickel complexes of formula $M(ttz)_2X_2$ (where M = Co or Ni and X = Cl, Br or I). These complexes were obtained by reacting metal halides such as $CoX_2.nH_2O$ and $NiX_2.n\,H_2O$ (where X = Cl, Br or I) with an excess of molten thiazolidine-2-thione (at a temperature of 105-110°C). Cobalt complexes were obtained similarly from cobalt halides with thiazolidine-2-thione in refluxing ethanol. They believe that the metal ions are bonded through the sulphur atom.

Singh and Rivest reported a formula for cobalt complexes of $Co(ttz)_2X_2$ (where X = Cl, Br or I) and $Co(ttz)_4(ClO_4)_2$. The former complexes, $Co(ttz)_2X_2$ (where X = Cl, Br or I) were prepared by mixing the ligand and anhydrous cobalt halides (molar ratio 1:2) in chloroform, then refluxing for forty-eight hours. The perchlorate complex $Co(ttz)_4(ClO_4)_2$ was similarly prepared by refluxing $Co(ClO_4)_2.6H_2O$ and the ligand (ratio 1:4) in chloroform for forty-eight hours. They regard the metal ion to be nitrogen bonded.

Singh and Thakur [60b] reported the formula of cobalt and nickel complexes to be $Co(ttz)_2Cl_2$ and $Ni(ttz)_2I_2$. The preparation of these complexes were of the same method as D. de Filippo et.al. [59] They believe the metal ions are bonded through the sulphur atoms.

The preparation of thiazolidine-2-thione complexes of zinc, cadmium and mercury were reported by D. de Filippo and co-workers [61] and G. Colombini and C. Preti.[62]

Filippo and co-workers assign the formula $M(ttz)_2X_2$ (where M = Zn, Cd, or Hg and X = Cl, Br or I) to the complexes. These complexes were obtained by two methods. The metal halide was dissolved in excess of molten ligand (at 105°C) using a molar ratio of 1:2. Alternatively, a solution of metal halide in absolute ethanol was added to a solution of thiazolidine-2-thione using different ratios, which was then refluxed for four hours. The molar ratios used were 1:1, 1:2, 1:3 and 1:4.

Colonbini and Preti[62] have prepared complexes of formula $M(ttz)_2(NCS)_2$ (where M = Zn, or Cd and NCS = thiocyanate) $Zn(ttz)_2(BF_4)_2.2H_2O$, $CD(ttz)_2(BF_4)_2$ and $Hg(ttz)_4(BF_4)_2$ (where BF_4 = Fluoborate). The complex of $Zn(ttz)_2(NCS)_2$ was obtained by reaction of thiazolidine-2-thione and zinc thiocyanate under reflux for two hours in chlorobenzene, but the complex of $Cd(ttz)_2(NCS)_2$ was prepared by reacting the cadmium thiocyanate with the ligand in refluxing ethanol for one hour. The complexes $Zn(ttz)_2(BF_4)_2.2H_2O$ and $Cd(ttz)_2(BF_4)_2$ were prepared by reaction of zinc or cadmium fluoborate with the ligand in ethanol; but the complex of $Hg(ttz)_4(BF_4)_2$ was obtained by dissolving mercury(II) oxide in a cold solution of fluoboric acid with thiazolidine-2-thione.

It is noted that in both reports of the zinc, cadmium and mercury complexes, the metal ions are believed to be bonded through nitrogen. The evidence is again spectroscopic.

Stephen and Townshend[63] investigated silver complexes with thiazolidine-2-thione, but these authors did not present any spectroscopic evidence for the bonding.

3.1.2 Pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione complexes.

The nickel and cobalt complexes of pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione are the only ones which have been reported.

Madan and Sulich[64] found that the complexes had formula ML_2Cl_2, where L = TBuL or NMTBuL and M = Co, Ni.

3.1.3 Tellurium (IV) and its reaction with thiazolidine-2-thione, pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione.

The reaction of these three ligands with many metal ions has already been summarised above (p. 89). No reports of reaction of these ligands with tellurium (IV) or (II) has been reported.

In this chapter the preparation of some new complexes of tellurium (II) and (IV) with heterocyclic compounds are reported. The reaction of thiazolidine-2-thione, pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione and some tellurium compounds are also investigated.

3.1.3.1 Thiazolidine-2-thione complexes of tellurium (II) and tellurium (IV)

The complexes of thiazolidine-2-thione with tellurium (II) and (IV) reported in this thesis were prepared by several methods :-

1st method : A solution of tellurium tetrahalide in dry methanol was added to a solution of thiazolidine-2-thione in dry methanol. After stirring this solution at room temperature the precipitate formed immediately. The formula of these complexes was found to be $Te(ttz)_2X_4$ (where X = Cl, Br or I and ttz = thiazolidine-2-thione).

2nd method : A tellurium tetrachloride complex was prepared from tellurium dioxide and thiazolidine-2-thione each dissolved separately in hydrochloric acid and then mixing them together at room temperature. A yellow precipitate formed immediately. The formula of this complex was found to be $Te(ttz)_2Cl_4$.

3rd method : The complexes of aryltelluriumtrihalide with thiazolidine-2-thione were prepared by dissolving the tellurium compound in the molten ligand (at 105-110°C). After cooling at room temperature and adding dry methanol, the complexes were recrystallised.
(for the formula of these complexes see xperimental section)

4th method : $Te(ttz)_4Cl_2.H_2O$ and $Te(ttz)_3Br_4$ complexes were prepared by dissolving tellurium dioxide in a hydrochloric acid (or hydrobromic acid) aqueous media and then adding to a solution of thiazolidine-2-thione in water at 65°C. On cooling these solutions at room temperature the precipitates were formed.

The spectroscopic evidence indicates that in these complexes of tellurium (II) and (IV) with thiazolidine-2-thione the tellurium could be co-ordinated to nitrogen and sulphur donor atoms of the ligand (see Discussion page 136).

3.1.3.2 Pyrrolidine-2-thione complexes of tellurium (IV)

The tellurium tetrahalide complexes with pyrrolidine-2-thione were prepared by dissolving tellurium tetrahalide and pyrrolidine-2-thione separately in methanol and then mixing these solutions together. The precipitate formed immediately. The formula was found to be Te(TBuL)$_2$X$_4$ (where X = Cl or Br and TBuL = pyrrolidine-2-thione).

3.1.3.3 N-Methyl-pyrrolidine-2-thione complexes of tellurium (IV).

Tellurium tetrahalide complexes of N-methyl-pyrrolidine-2-thione were prepared using a similar method as with pyrrolidine-2-thione. The formula was found to be Te(NMTBuL)$_2$X$_4$ (where X = Cl or Br and NMTBuL = N-methyl-pyrrolidine-2-thione).

3.2 EXPERIMENTAL

3.2.1 Preparation of the Heterocyclic ligands.

Thiazolidine-2-thione (ttz) obtained from Fluka Laboratories was purified by double recrystallisation from hot distilled water. m.p. 106-107 °C (lit. 106-107 °C)[66] [Found C, 30.01; H, 4.45; N, 11.39; $C_3H_5NS_2$ requires C, 30.25; H, 4.24; N, 11.76 %]

3.2.1.1 Preparation of pyrrolidine-2-thione.

Pyrrolidine-2-thione was prepared from 2-pyrrolidine by addition of phosphorus pentasulphide. 6.5 g. (0.03 mol) of the latter was suspended in 50 cm^3 of xylene in a 500 cm^3 three-necked flask equipped with a mechanical stirrer. A dropping funnel contained 8.5 g. (0.1 mol) of 2-pyrrolidine in 50 cm^3 of dry xylene. The phosphorus pentasulphide solution was heated under reflux and then the amide was added dropwise. After the addition of all the amide the reaction mixture became so viscous that further stirring was impossible. The mixture was boiled under reflux for two hours. The hot reaction mixture was filtered off and the filtrate was allowed to cool at room temperature overnight when pale yellow crystals were obtained which were recrystallised twice from methanol. Yield 1.0 g. m.p. 110 °C (lit. 112-113 °C).[67] [Found C, 47.67; H, 6.82, N, 13.97; C_4H_7NS requires C, 47.50; H, 6.98; N, 13.85 %]

3.2.1.2 Preparation of N-methyl-pyrrolidine-2-thione.

20 g. of phosphorus pentasulphide was suspended in 40 cm^3 of carbon disulphide in a 500 cm^3 three necked flask equipped with a mechanical stirrer with a segment shaped paddle. N-methyl-2-pyrrolidine (18 g.) was added from a dropping funnel in small portions with vigorous stirring. The reaction mixture warmed up considerably and after addition of all the amide the reaction mixture became so viscous that further stirring was impossible. The yellow-brown mixture was boiled under reflux on a water bath for five hours. The carbon disulphide was decanted and 80 cm^3 of water was added to the contents of the flask. The aqueous solution was extracted several times with chloroform, and combined extracts were dried over anhydrous sodium sulphate. The chloroform solution of N-methyl-pyrrolidine-2-thione was evaporated under vacuum to give dark brown liquid residue which was distilled under reduced pressure to give a yellow liquid.[68]

3.2.1.3 Preparation of tellurium tetraiodide.

2.3 g. (1 mol.) of telluric acid in 5 cm^3 of distilled water was mixed at room temperature with 6.4 cm^3 (6 mol.) of fuming hydroiodic acid (d. 2.00). A heavy grey precipitate of tellurium tetraiodide formed immediately. The grey precipitate was filtered off. The crystals were washed several times with pure carbontetrachloride to remove the iodine, and then dried under vacuum.[69]

3.2.3 Preparation of thiazolidine-2-thione complexes

Thiazolidine-2-thione complexes were prepared by four different methods with tellurium (II) and (IV).

3.2.3.1 Preparation of $Te(ttz)_2Cl_4$ complex

Two different methods were employed for the preparation of $Te(ttz)_2Cl_4$: -

Method 1: From thiazolidine-2-thione in methanol with tellurium tetrachloride.

Thiazolidine-2-thione 0.24 g. (2 mmol.) in 5 cm^3 of dry methanol was added to 0.270 g. (1 mmol.) of tellurium tetrachloride in 5 cm^3 of dry methanol. The yellow precipitate , which formed on stirring at room temperature, was filtered off and dried in a vacuum desiccator.
Yield 0.25 g. m.p. 152-155°C decomp.
[Found C, 14.86; H, 2.26; N, 5.51; Te, 25.29; $TeS_4C_6H_{10}N_2Cl_4$ requires C, 14.19; H, 1.97; N, 5.51; Te, 25.16 %]

Method 2: From tellurium dioxide in aqueous acid with thiazolidine-2-thione.

Tellurium dioxide 1.6 g. (10 mmol.) dissolved in 4 cm^3 of concentrated hydrochloric acid was added at room temperature to 3.0 g. of thiazolidine-2-thione in 10 cm^3 of concentrated hydrochloric acid. The yellow precipitate which formed immediately, was filtered off, washed with dry diethylether, and finally dried in a vacuum desiccator. m.p. 152-155°C.

[Found C, 14.07; H, 2.16; N, 5.74; Te, 25.35; $TeS_4C_6H_{10}N_2Cl_4$ requires C, 14.19; H, 1.97; N, 5.51; Te, 25.16 %]

3.2.3.2 Preparation of $Te(ttz)_2Br_4$ complex.

A solution of 0.24 g. (2 mmol.) thiazolidine-2-thione in 5 cm^3 of dry methanol was added to a solution of 0.45 g. tellurium tetrabromide in dry methanol. The orange precipitate, which formed on stirring at room temperature, was filtered off and dried in a vacuum desiccator. Yield 0.35 g. m.p. 134-138°C. decomp.

[Found C, 11.47; H, 1.70; N, 3.97; Te, 18.48; $TeS_4C_6H_{10}N_2Br_4$ requires C, 11.47; H, 1.47; N, 4.08; Te, 18.62 %]

3.2.3.3 Preparation of $Te(ttz)_2I_4$ complex.

To a solution of 0.640 g. of tellurium tetraiodide in 200 cm^3 of dry methanol, 0.24 g. of thiazolidine-2-thione in 10 cm^3 of dry methanol was added. The solution was changed from dark red to brown. After standing in a vacuum desiccator for twenty-four hours, the volume of the solution was reduced to about one third of its original volume, when a brown crystalline product was obtained which was filtered off, washed with dry methanol and dried under vacuum. Yield 0.2 g. m.p. 162-166°C decomp.

[Found C, 11.51; H, 1.64; N, 4.01; Te, 14.76; $TeS_4C_6H_{10}N_2I_4$ requires C, 11.16; H, 1.55; N, 4.32; Te, 14.61 %]

3.2.3.4 Preparation of $Te(ttz)_4Cl_2{\cdot}H_2O$ complex.

Tellurium dioxide 0.8 g. (5 mmol.) was dissolved in a mixture of 10 cm^3 concentrated hydrochloric acid and 10 cm^3 of distilled water. After heating to 68 °C, 3.6 g. (30 mmol.) of thiazolidine-2-thione in 150 cm^3 of distilled water was added with rapid stirring. The liberated tellurium was filtered off and on standing at room temperature the complex formed slowly as a yellow precipitate. This precipitate was filtered off, washed many times with hot toluene in order to remove the excess of thiazolidine-2-thione and finally dried under vacuum. Yield 1.0 g. m.p. 82-84 °C decomp.
(This complex changed from yellow to green-yellow after being left overnight in a desiccator.)
[Found C, 20.96; H, 3.32; N, 8.16; Te, 18.22; $TeS_8C_{12}H_{22}N_4OCl_2$ C, 20.80; H, 3.20; N, 8.08; Te, 18.43 %]

3.2.3.5 Preparation of $Te(ttz)_3Br_4$ complex.

0.8 g. (5 mmol.) of tellurium dioxide was dissolved in a mixture of 10 cm^3 concentrated hydrobromic acid and 10 cm^3 of distilled water. After heating to 60 °C, 3.6 g. (30 mmol.) of thiazolidine-2-thione in 150 cm^3 of distilled water was added with rapid stirring. The liberated tellurium was filtered off and on standing at room temperature , the complex formed slowly as an orange-yellow precipitate. This precipitate was filtered off, washed many times with hot toluene in order to remove the excess ligand and finally dried under vacuum. Yield 1.8 g. m.p. 172-174 °C decomp.
[Found C, 13.26; H, 1.84; N, 5.09; Te, 16.20; $TeS_6C_9H_{15}N_3Br_4$ requires C, 13.30; H, 1.88; N, 5.22; Te, 15.87 %]

3.2.3.6 Preparation of p-$CH_3OC_6H_4Te(ttz)_4Br_3$ complex.

The starting materials i.e. arytelluriumtrihalides were obtained as described in Appendix II

p-Methoxyphenyltelluriumtribromide 0.474 g. (1 mmol.) was dissolved in fused thiazolidine-2-thione 1.2 g. (10 mmol.) at about 110°C, The solution of thiazolidine-2-thione changed from pale yellow to dark red in colour. The crude product formed on cooling at room temperature, then 5 cm^3 of dry methanol was added after standing for two days. The yellow-orange crystals formed were filtered off, washed with hot toluene in order to remove the excess of ligand, and dried under vacuum. Yield 0.42 g. m.p. 128-132°C decomp. [Found C, 19.80; H, 2.81; N, 5.95; Te, 13.38; $TeS_8C_{19}H_{27}N_4OBr_3$ requires C, 20.40; H, 2.85; N, 5.90; Te, 13.42 %]

3.2.3.7 Preparation of p-$C_2H_5OC_6H_4Te(ttz)Cl_3$ complex.

0.36 g. (1 mmol.) of p-ethoxyphenyltelluriumtrichloride was dissolved in fused thiazolidine-2-thione 1.2 g. (10 mmol.) at about 110°C. The solution of thiazolidine-2-thione changed from pale yellow to dark red. The crude product formed on cooling at room temperature. Dry methanol (5 cm^3) was added and the mixture allowed to stand overnight. The yellow crystals were filtered off, washed with hot toluene in order to remove the excess of ligand, and then dried under vacuum. Yield 0.20 g. m.p. 114-116°C decomp.

[Found C, 28.93; H, 3.42; N, 3.31; Te, 26.54; $TeS_2C_{11}H_{14}NOCl_3$ requires C, 28.00; H, 3.00; N, 3.00; Te, 26.92 %]

3.2.3.8 Preparation of $p-C_6H_5OC_6H_4Te(ttz)_2Cl_3$ complex.

p-Phenoxyphenyltelluriumtrichloride 0.41 g. (1 mmol.) was dissolved in fused thiazolidine-2-thione 1.2 g. (10 mmol.) at about 110 C. The solution of thiazolidine-2-thione changed from pale yellow to dark red. The crude product formed on cooling at room temperature and then 5 cm^3 of dry methanol was added and the mixture was allowed to stand overnight. The yellow crystals were filtered off, washed with hot toluene in order to remove the excess of ligand and dried under vacuum. Yield 0.31 g. m.p. 196-201°C decomp. [Found C, 33.14; H, 3.00; N, 4.14; Te, 19.50; $TeS_4C_{18}H_{19}N_2OCl_3$ requires C, 33.69; H, 2.99; N, 4.53; Te, 19.91 %]

3.2.3.9 Preparation of $Te(ttz)_2Br_2$ complex.

Tellurium dioxide 0.8 g. (5 mmol.) was dissolved in a mixture of 10 cm^3 concentrated hydrobromic acid and 10 cm^3 of distilled water. After heating to 60°C, 1.2 g. (10 mmol.) of thiazolidine-2-thione in 50 cm^3 of distilled water was added with rapid stirring. The liberated tellurium was filtered off and on standing at room temperature the complex formed slowly as an orange precipitate, which was filtered off, washed several times with hot toluene in order to remove the excess of thiazolidine-2-thione and then dried under vacuum. Yield 1.2 g. m.p. 146-148°C.
[Found C, 13.67; H, 1.84; N, 5.18; $TeS_4C_6H_{10}N_2Br_2$ requires C, 13.68; H, 1.91; N, 5.33 %]

3.2.3.10 Preparation of p-$CH_3OC_6H_4Te(ttz)_6Cl_3$ complex.

p-Methoxyphenyltelluriumtrichloride 0.34 g. (1 mmol.) was dissolved in fused thiazolidine-2-thione 1.2 g. (10 mmol.) at about 110°C. The solution of thiazolidine-2-thione changed from pale yellow to dark red. The crude product formed on cooling at room temperature . 5 cm^3 of dry methanol was added and the mixture was allowed to stand overnight. The yellow crystals were filtered off, washed with hot toluene in order to remove the excess of ligand and then dried under vacuum. Yield 0.15 g.

[Found C, 8.37; H, 29.30; N, 3.07; $TeS_{12}C_{25}H_{37}N_6OCl_3$ requires C, 7.94; H, 29.38; N, 3.32 %]

3.2.4 Preparation of pyrrolidine-2-thione complexes.

3.2.4.1 Preparation of $Te(TBuL)_2Cl_4.\frac{1}{2}\,CH_3COCH_3$ complex.

Pyrrolidine-2-thione (TBuL) 0.202 g. (2 mmol.) in 5 cm^3 of dry acetone was added to 0.27 g. (1 mmol.) tellurium tetrachloride in 5 cm^3 of dry acetone. The yellow precipitate which formed on stirring immediately, at room temperature was filtered off and dried in a vacuum desiccator. Yield 0.20 g. m.p. 141-147°C. This complex decomposed after two to three days.

[Analysis of freshly prepared material found C, 23.00; H, 3.50; N, 6.25; $TeS_2C_8H_{14}N_2Cl_4.\frac{1}{2}CH_3COCH_3$ requires C, 22.77; H, 3.42; N, 5.59 %]

3.2.4.2 Preparation of Te(TBuL)$_2$Br$_4$ complex.

0.45 g. (1 mmol.) of tellurium tetrabromide in 5 cm^3 of dry methanol was added to 0.202 g. (2 mmol.) in 5 cm^3 of dry methanol. The yellow-orange precipitate which formed on stirring at room temperature, was filtered off and dried under vacuum. Yield 0.25 g. m.p. 124-128°C decomp. [Found C, 15.40; H, 2.25; N, 4.30; $TeS_2C_8H_{14}N_2Br_4$ requires C, 14.78; H, 2.17; N, 4.31 %]

3.2.5 Preparation of N-methyl-pyrrolidine-2-thione complexes.

3.2.5.1 Preparation of Te(NMTBuL)$_2$Cl$_4$ complex.

0.23 g. (2 mmol.) of N-methyl-pyrrolidine-2-thione (NMTBuL) in 5 cm^3 of dry methanol was added to 0.27 g. (1 mmol.) of tellurium tetrachloride in 5 cm^3 of dry methanol. The yellow precipitate which formed on stirring immediately, at room temperature, was filtered off and dried under vacuum. Yield 0.18 g. m.p. 170-174°C decomp. [Found C, 24.80; H, 3.90; N, 5.50; $TeS_2C_{10}H_{18}N_2Cl_4$ requires C, 24.02; H, 3.63; N, 5.61 %]

3.2.5.2 Preparation of Te(NMTBuL)$_2$Br$_4$ complex.

Tellurium tetrabromide 0.45 g. (1 mmol.) in 5 cm^3 of dry methanol was added to a solution of 0.23 g. (2 mmol.) of N-methyl-pyrrolidine-2-thione in 5 cm^3 of dry methanol.

The yellow-orange precipitate which formed on stirring immediately, at room temperature, was filtered off and then dried under vacuum. Yield 0.20 g. m.p. 140-145°C decomp. [Found C, 16.60; H, 2.70; N, 3.80; $TeS_2C_{10}H_{18}N_2Br_4$ requires C, 17.72; H, 2.68; N, 4.13 %]

These complexes with N-methyl-pyrrolidine-2-thione decomposed after a few weeks.

3.3 RESULTS

3.3.1 Preparation

Tellurium(II) and (IV) complexes with thiazolidine-2-thione were prepared by four different procedures as summarised in page 93 of the Introduction, (also shown in Experimental Section).

3.3.2 Conductivity Measurements

The conductivity measurements were obtained by preparing 10^{-3}M of tellurium(II) and (IV) thiazolidine-2-thione complexes in dry NN′ dimethylformamide. The values of Λ are shown in table 3-1.

3.3.3 U.V. and Visible Spectra.

10^{-5}M solutions of the complexes dissolved in NN′ dimethylformamide were prepared. The absorptions were recorded on a Perkin-Elmer 137 spectrophotometer. A strong absorption in ultra violet at 35.7 kK was noted for each solution.

3.3.4 Tellurium analysis.

The method of analysis for tellurium content is reported in Appendix II.

3.3.5 I.r. and Raman Spectra.

The i.r. spectra of tellurium (II) and (IV) thiazolidine-2-thione, pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione complexes over the range 4000-250 cm^{-1} and 400-40 cm^{-1} are detailed below :-

3.3.5.1 Range 4000-250 cm^{-1}.

These were recorded as KBr discs on a Perkin-Elmer 457 i.r. spectrophotometer.

Fig. 3-1	i.r. spectra of thiazolidine-2-thione, $Te(ttz)_4Cl_2H_2O$ and $Te(ttz)_3Br_4$.
Fig. 3-2	i.r. spectra of thiazolidine-2-thione, $Te(ttz)_2Cl_4$, $Te(ttz)_2Br_4$ and $Te(ttz)_2I_4$.
Fig. 3-3	i.r. spectra of thiazolidine-2-thione, $p\text{-}CH_3OC_6H_4TeBr_3$ and $p\text{-}CH_3OC_6H_4Te(ttz)_4Br_3$.
Fig. 3-4	i.r. spectra of thiazolidine-2-thione, $p\text{-}C_2H_5OC_6H_4TeCl_3$ and $p\text{-}C_2H_5OC_6H_4Te(ttz)Cl_3$.
Fig. 3-5	i.r. spectra of thiazolidine-2-thione, $p\text{-}C_6H_5OC_6H_4TeCl_3$ and $p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$.
Fig. 3-6	i.r. spectra of pyrrolidine-2-thione, $Te(TBuL)_2Cl_4$ and $Te(TBuL)_2Br_4$.
Fig. 3-7	i.r. spectra of N-methyl-pyrrolidine-2-thione, $Te(NMTBuL)_2Cl_4$ and $Te(NMTBuL)_2Br_4$.

3.3.5.2 Range 400-40 cm^{-1}.

These were recorded as Nujol mulls between two polythene sheets using a Fourier spectrophotometer FS 720 (R.I.I.C.).

Fig. 3-8	i.r. spectra of thiazolidine-2-thione $Te(ttz)_4Cl_2.H_2O$ and $Te(ttz)_3Br_4$.
Fig. 3-9	i.r. spectra of thiazolidine-2-thione, $Te(ttz)_2Cl_4$, $Te(ttz)_2Br_4$ and $Te(ttz)_2I_4$.
Fig. 3-10	i.r. spectra of thiazolidine-2-thione $p-CH_3OC_6H_4Te(ttz)_4Br_3$, $p-C_2H_5OC_6H_4Te(ttz)Cl_3$ and $p-C_6H_5OC_6H_4Te(ttz)_2Cl_3$.
Fig. 3-11	i.r. spectra of pyrrolidine-2-thione $Te(TBuL)_2Cl_4$ and $Te(TBuL)_2Br_4$.
Fig. 3-12	i.r. spectra of N-methyl-pyrrolidine-2-thione $Te(NMTBuL)_2Cl_4$ and $Te(NMTBuL)_2Br_4$.

The Raman spectra of tellurium(II) and (IV) thiazolidine-2-thione, pyrrolidine-2-thione and N-methyl-pyrrolidine-2-thione complexes were recorded on a Cary 81 spectrometer with an exciting laser line at 6328 Å.

Table 3-1 shows some infrared bands of tellurium(II) and tellurium(IV) complexes with thiazolidine-2-thione e.g., $\nu(NH)$, thiamide 1 band, $\nu(CS) + \delta(NCS)$ and $\nu(C-S)$ (asym. and sym.)

Table 3-2 shows infrared and Raman spectra of tellurium(II) and tellurium(IV) complexes with thiazolidine-2-thione below 400 cm^{-1}.

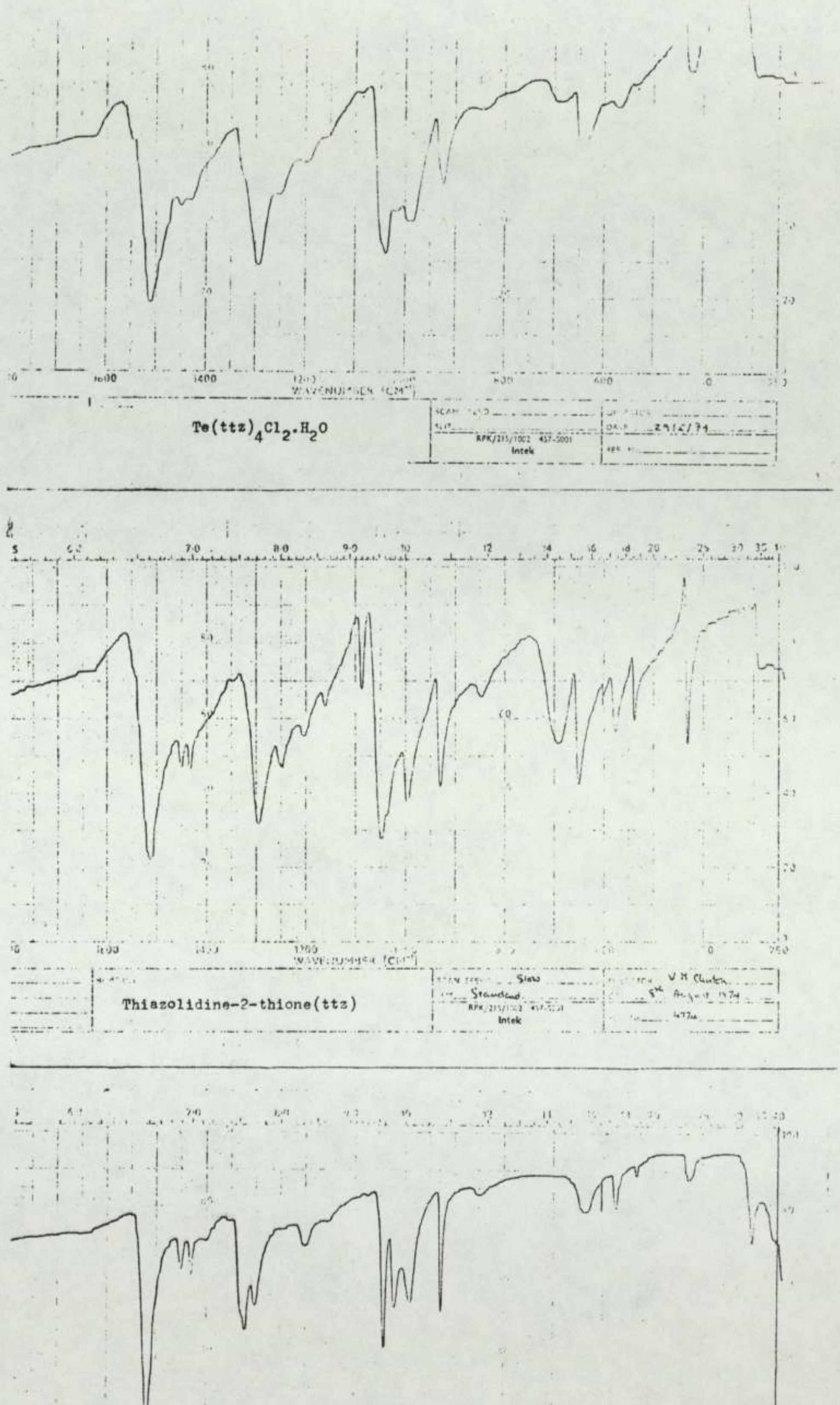
Table 3-3 shows the infrared spectra of pyrrolidine-2-thione(TBuL) and its complexes with $TeCl_4$ and $TeBr_4$ at 400-2000 cm^{-1}, (the more important bands).

Table 3-4 shows the infrared and Raman spectra of tellurium(IV) complexes with pyrrolidine-2-thione below 400 cm^{-1}.

Table 3-5 shows the infrared spectra of N-methyl-pyrrolidine-2-thione complexes with $TeCl_4$ and $TeBr_4$, at 400-2000 cm^{-1}, (the more important bands).

Table 3-6 shows the infrared and Raman spectra of N-methyl-pyrrolidine-2-thione complexes of tellurium tetrahalides below 310 cm^{-1}.

The complexes could not be recorded on the ^1H n.m.r. as there was no suitable solvent for dissolving them.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1400
1200
WAVENUMBER (CM⁻¹)
800
600
400
250
20
RPK/215/1002 457-5001
Intek
29/12/74
Te(ttz)$_4$Cl$_2$.H$_2$O
5
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
Slow
Standard
V M Clouton
5th August 1974
Thiazolidine-2-thione(ttz)
Medium
Standard
V M Clouton
5th August 1976
Te(ttz)$_3$Br$_4$

Fig. 3-1

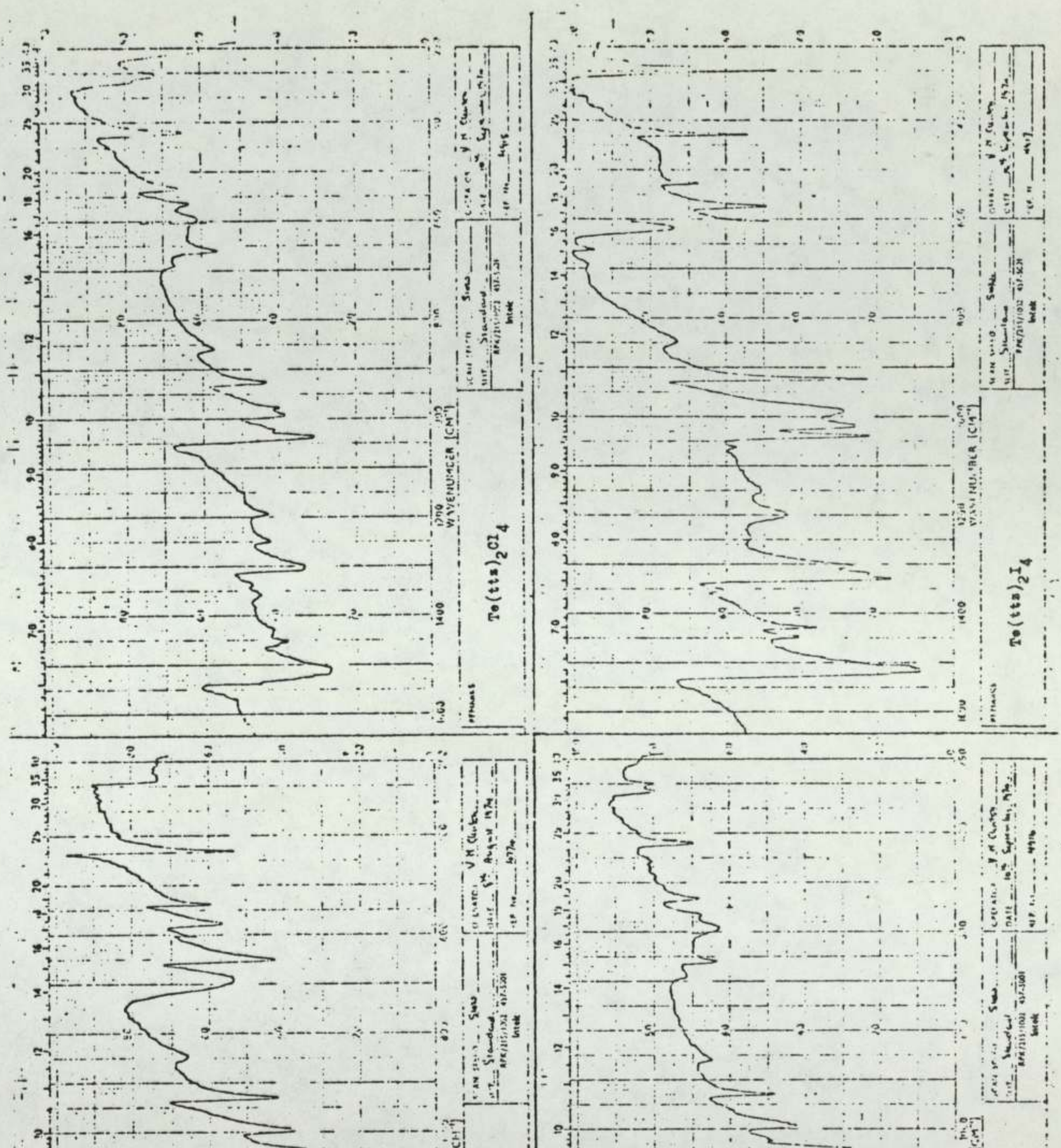

WAVENUMBER [CM⁻¹]
Thiazolidine-2-thione(tts)
Te(tts)$_2$Cl$_4$
Te(tts)$_2$Br$_4$
Te(tts)$_2$I$_4$

Fig. 3-2

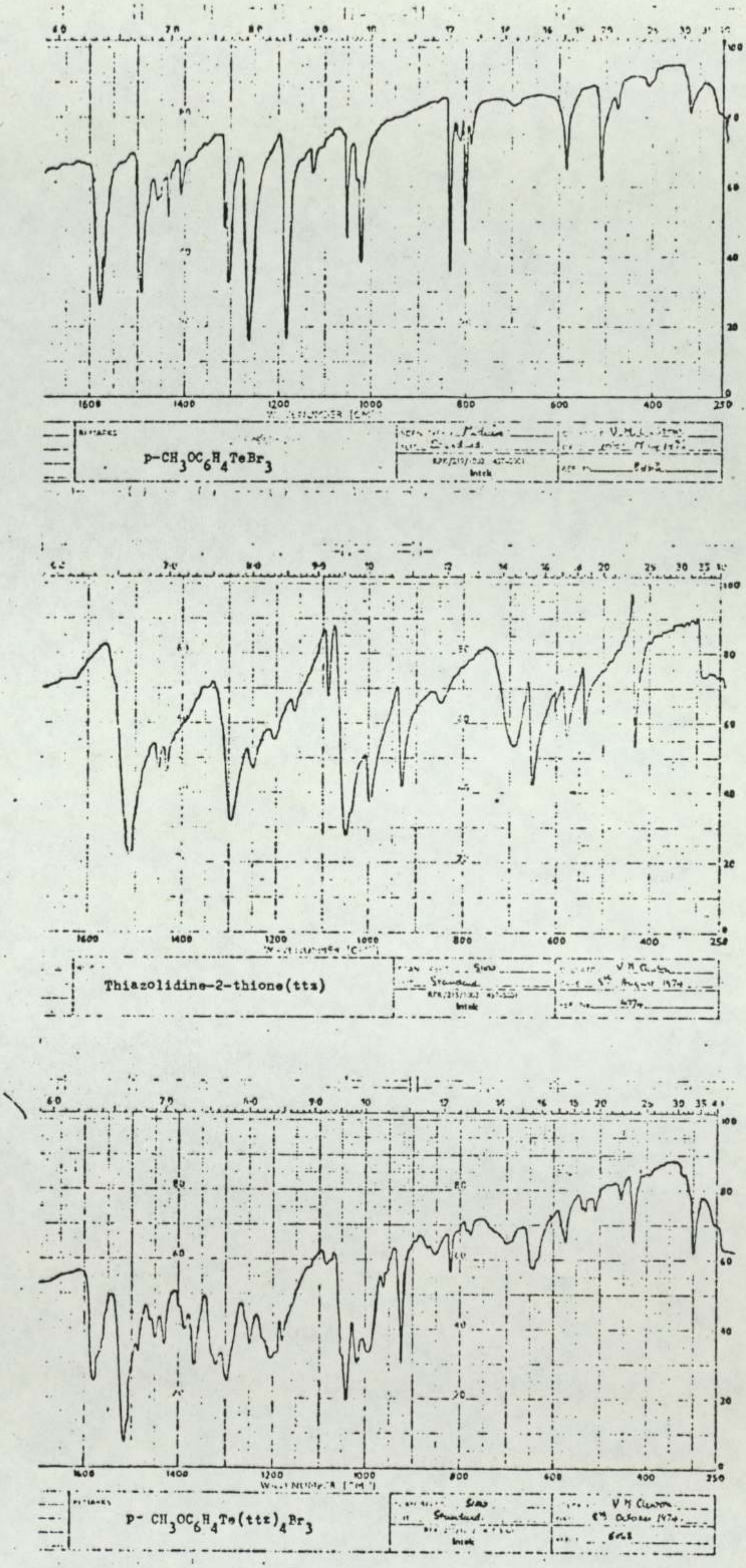
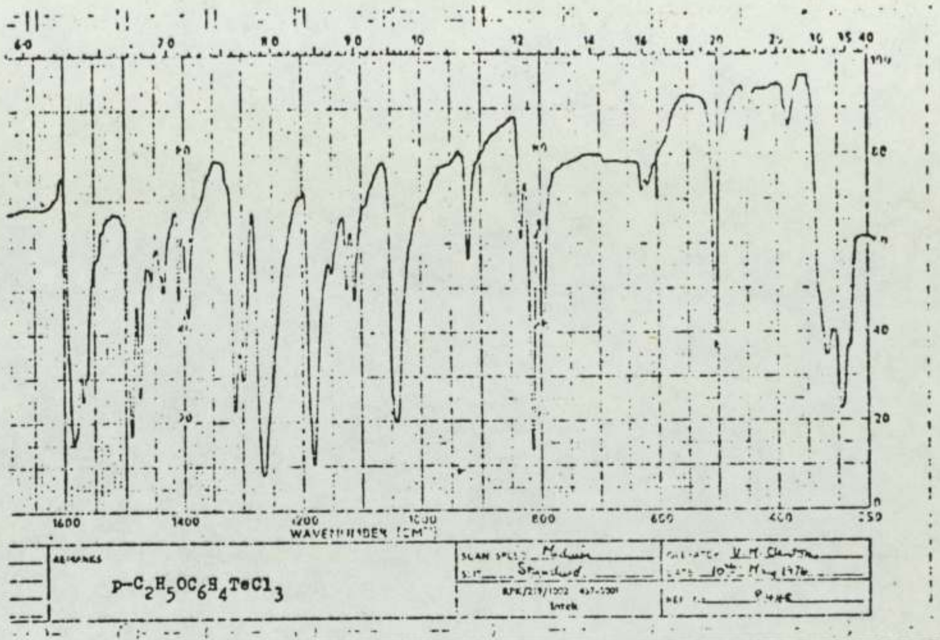
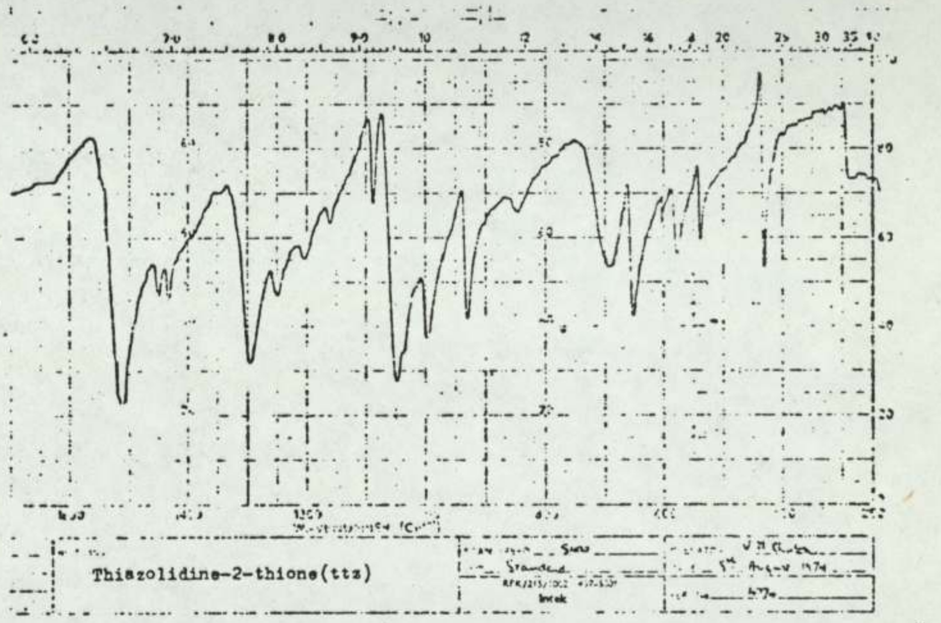

p-$CH_3OC_6H_4TeBr_3$
Thiazolidine-2-thione(ttz)
p- $CH_3OC_6H_4Te(ttz)_4Br_3$
1600
1400
1200
1000
800
600
400
250
100
80
60
40
20
0
Intek
V M Clarke
5th August 1974
6th October 1974

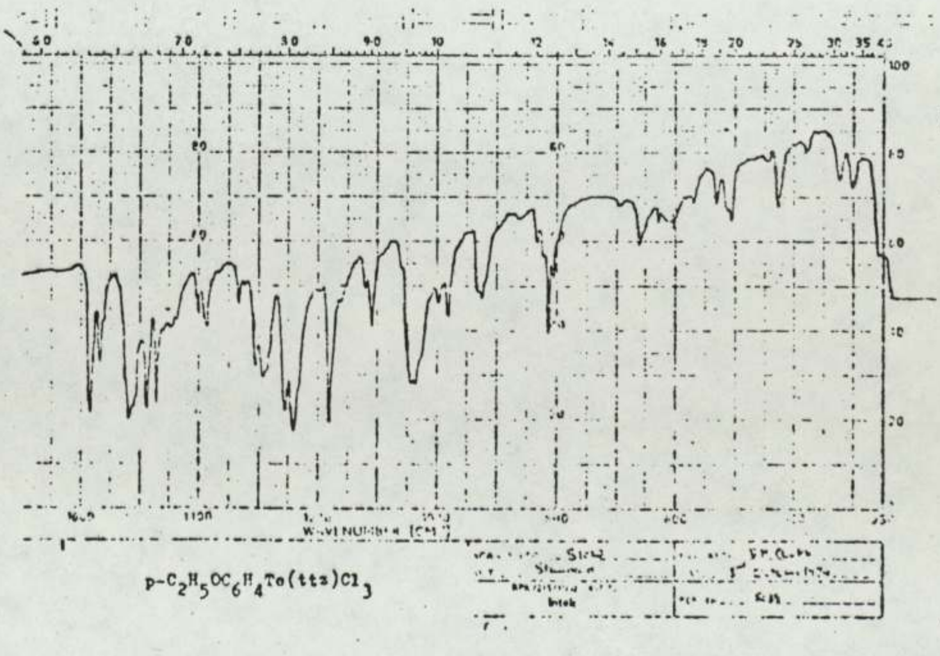
Fig. 3-3



p-$C_2H_5OC_6H_4TeCl_3$

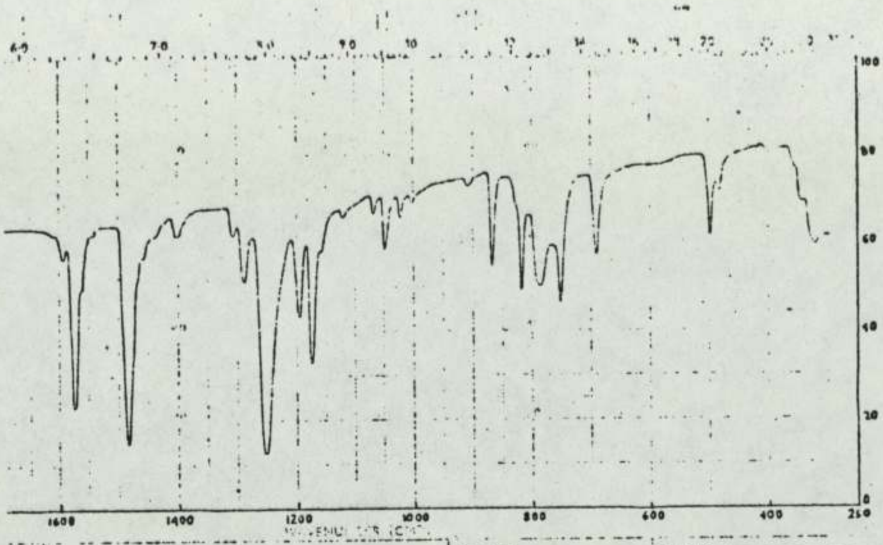


Thiazolidine-2-thione(ttz)

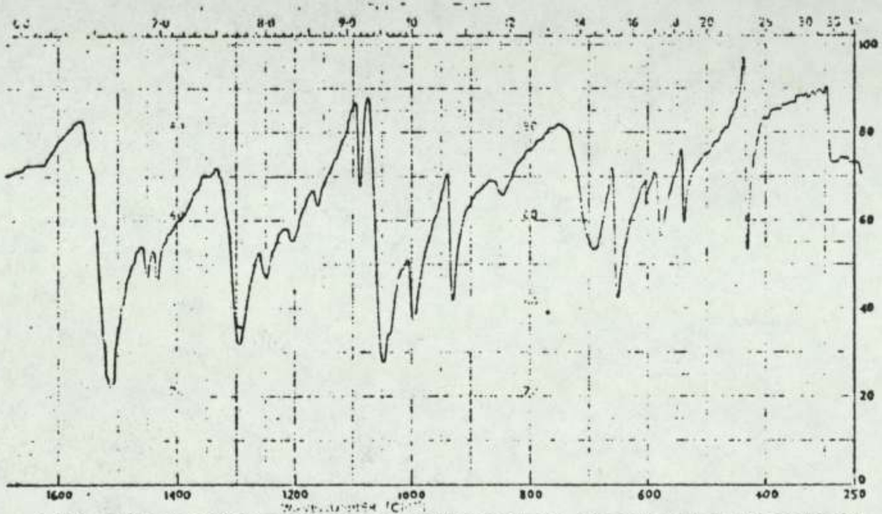


p-$C_2H_5OC_6H_4Te(ttz)Cl_3$

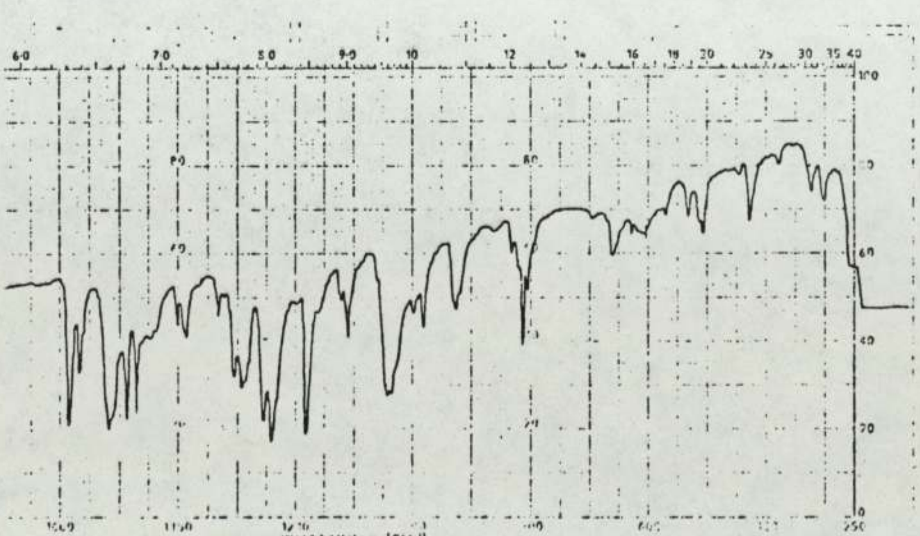
Fig. 3-4



$p\text{-}C_6H_5OC_6H_4TeCl_3$



Thiazolidine-2-thione(ttz)



$C_6H_5OC_6H_4(ttz)_2Cl_3$

Fig. 3-5

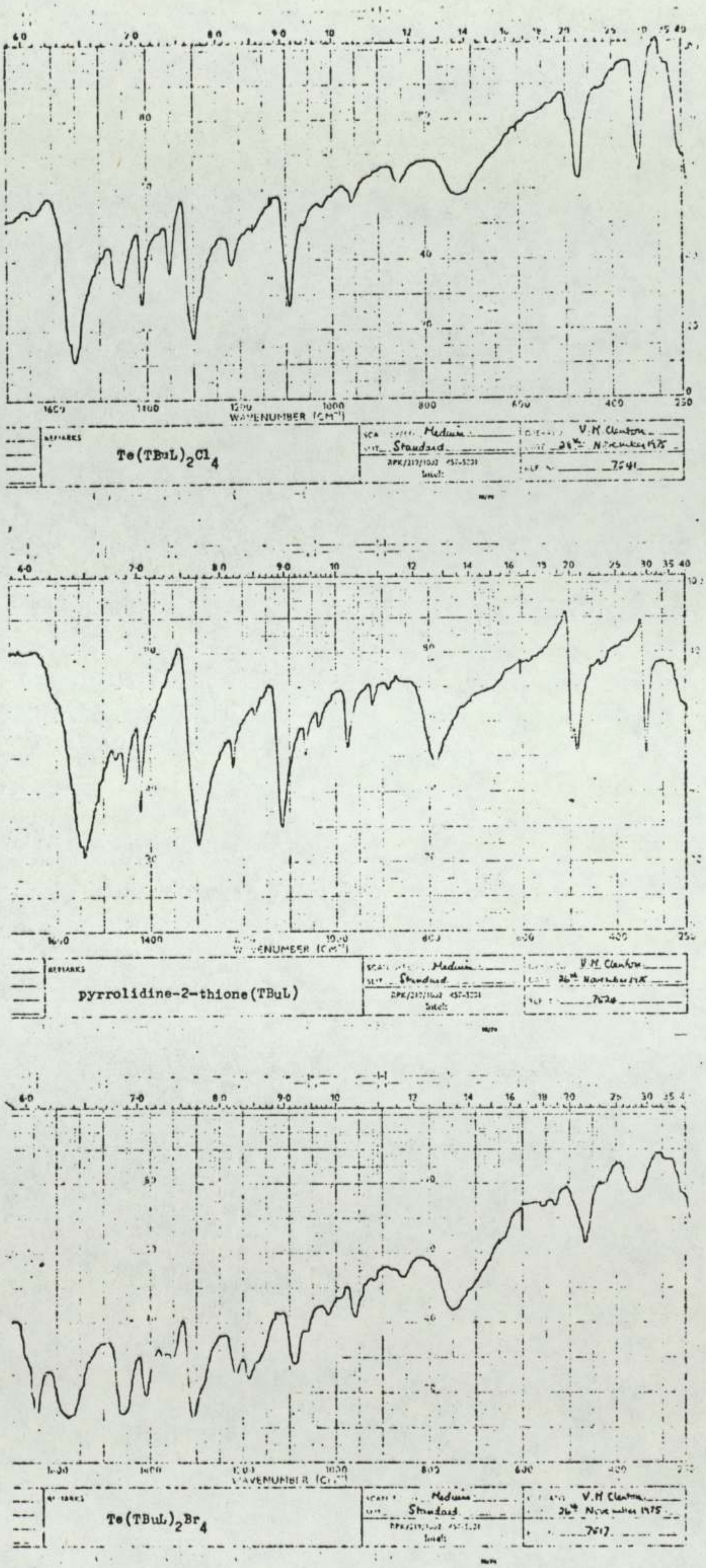
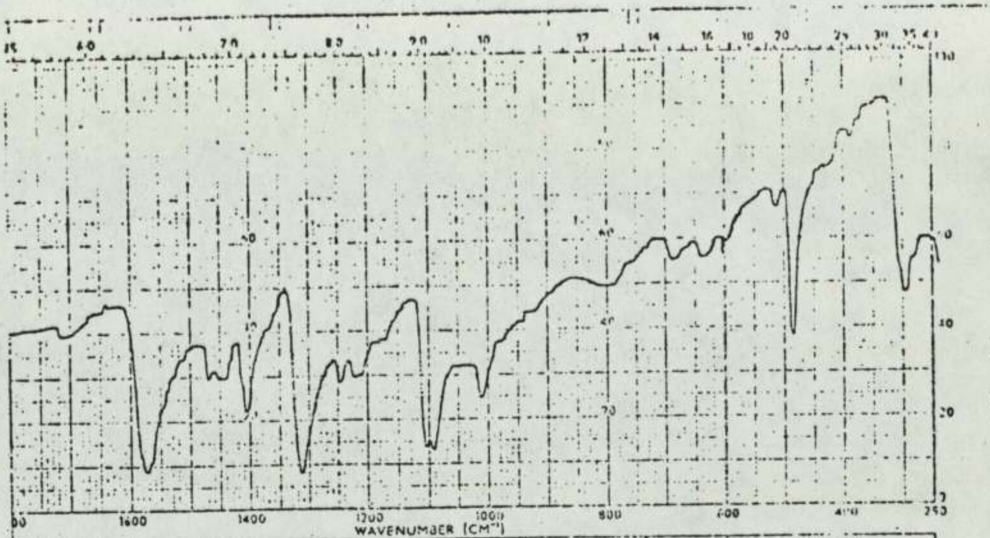
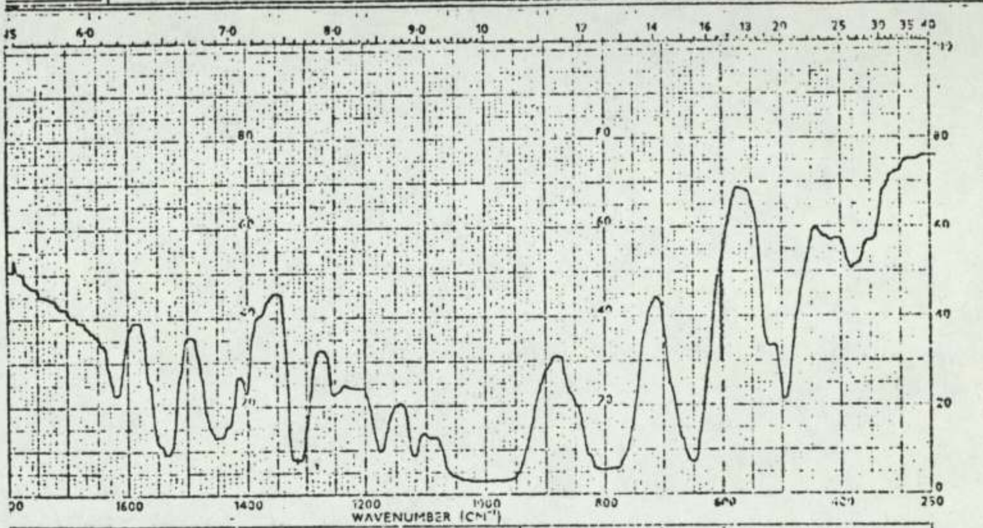

WAVENUMBER (CM⁻¹)
1600
1400
1200
1000
800
600
400
250
REMARKS
Te(TBuL)$_2$Cl$_4$
Medium
Standard
V.H. Clanton
26th November 1975
7541
pyrrolidine-2-thione(TBuL)
Medium
Standard
V.H. Clanton
26th November 1975
7526
Te(TBuL)$_2$Br$_4$
Medium
Standard
V.H. Clanton
26th November 1975
7517

Fig. 3-6



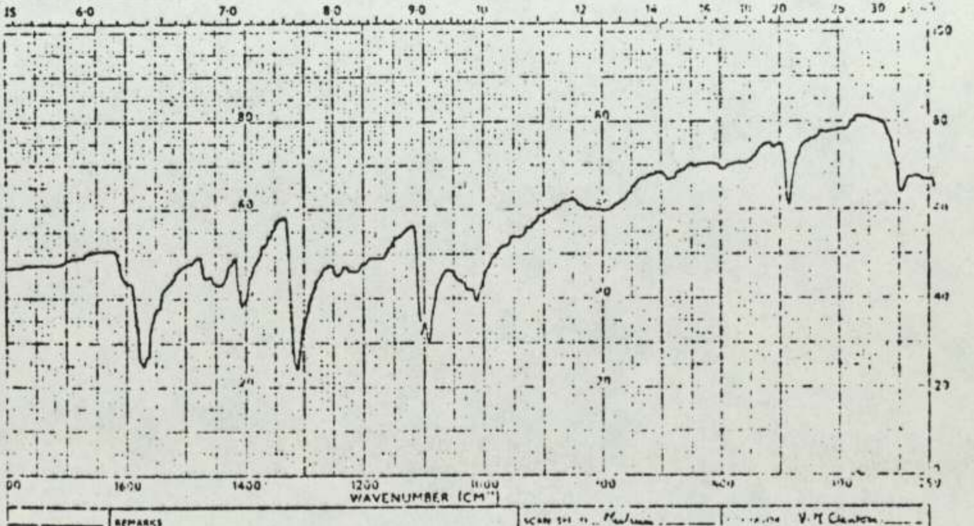
REMARKS

Te(NMTBuL)$_2$Cl$_4$



REMARKS

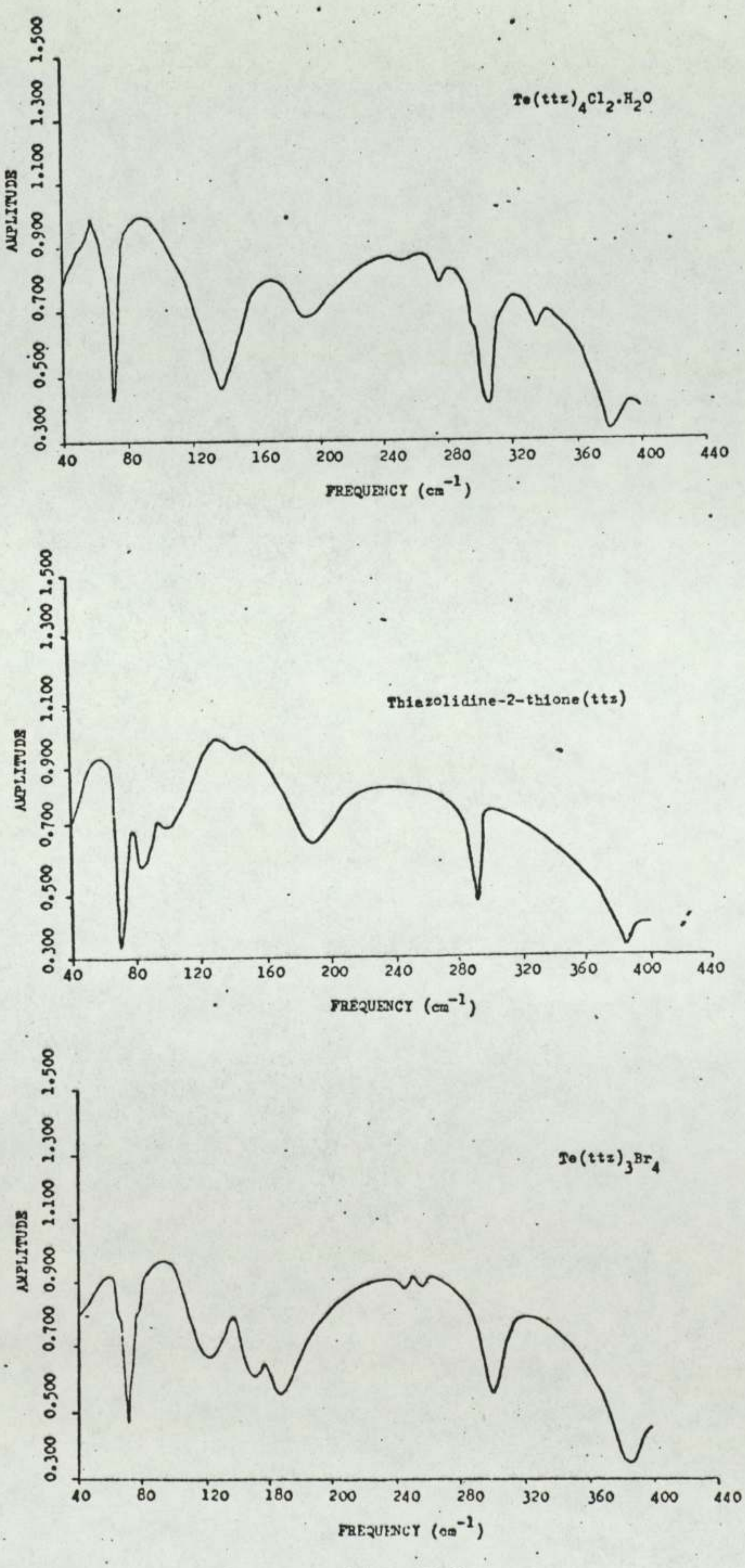
N-Methyl-2-pyrrolidine-thione
(NMTBuL)



REMARKS

Te(NMTBuL)$_2$Br$_4$

Fig. 3-7


Te(ttz)$_4$Cl$_2$.H$_2$O
AMPLITUDE
0.300 0.500 0.700 0.900 1.100 1.300 1.500
40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm^{-1})
Thiazolidine-2-thione(ttz)
AMPLITUDE
0.300 0.500 0.700 0.900 1.100 1.300 1.500
40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm^{-1})
Te(ttz)$_3$Br$_4$
AMPLITUDE
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40 80 120 160 200 240 280 320 360 400 440
FREQUENCY (cm^{-1})

Fig. 3-8

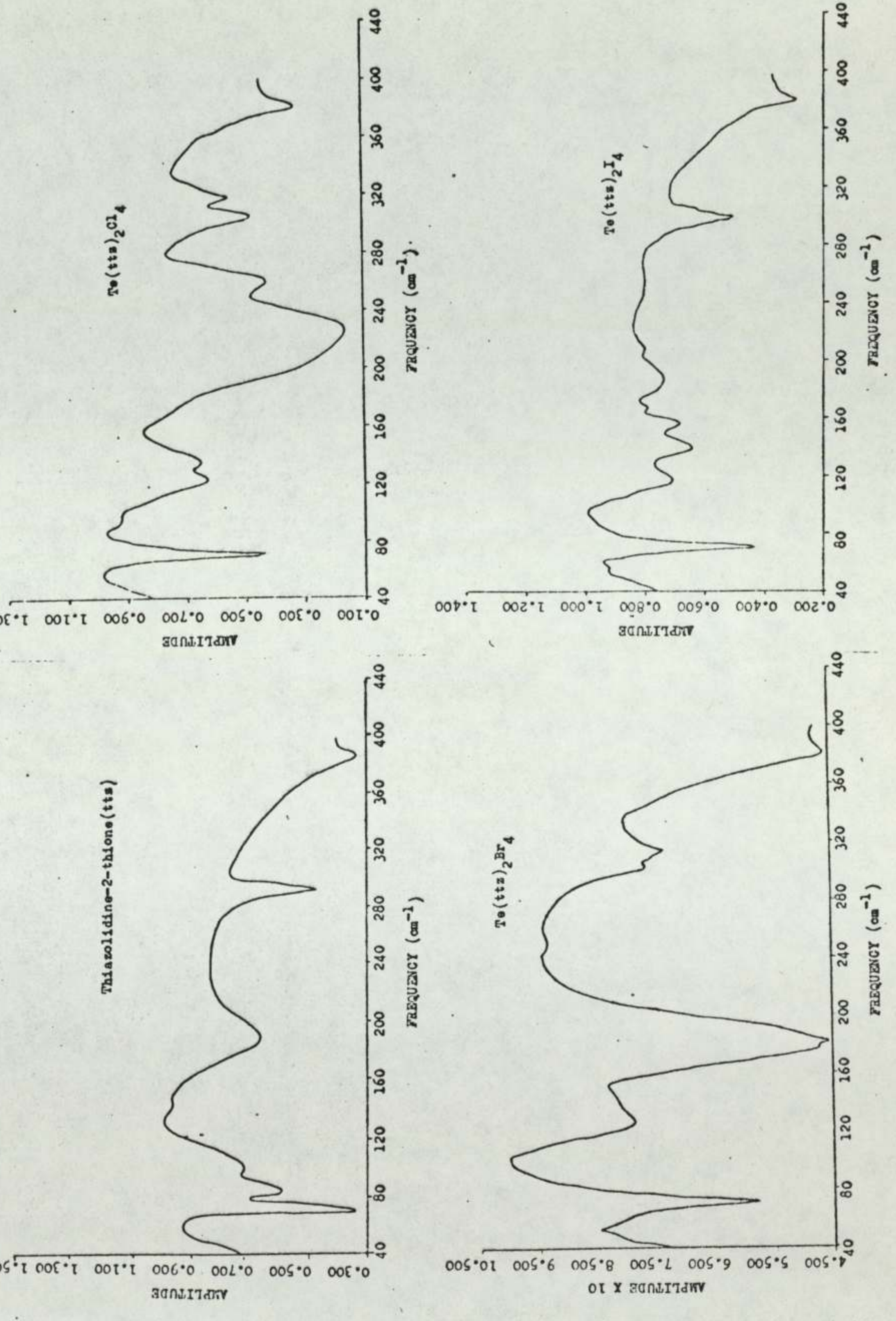

Thiazolidine-2-thione(tts)
AMPLITUDE
0.300 0.500 0.700 0.900 1.100 1.300 1.500
FREQUENCY (cm^{-1})
40 80 120 160 200 240 280 320 360 400 440
Te(tts)$_2$Cl$_4$
AMPLITUDE
0.100 0.300 0.500 0.700 0.900 1.100 1.300
FREQUENCY (cm^{-1})
40 80 120 160 200 240 280 320 360 400 440
Te(tts)$_2$Br$_4$
AMPLITUDE X 10
4.500 5.500 6.500 7.500 8.500 9.500 10.500
FREQUENCY (cm^{-1})
40 80 120 160 200 240 280 320 360 400 440
Te(tts)$_2$I$_4$
AMPLITUDE
0.200 0.400 0.600 0.800 1.000 1.200 1.400
FREQUENCY (cm^{-1})
40 80 120 160 200 240 280 320 360 400 440

Fig. 3-9

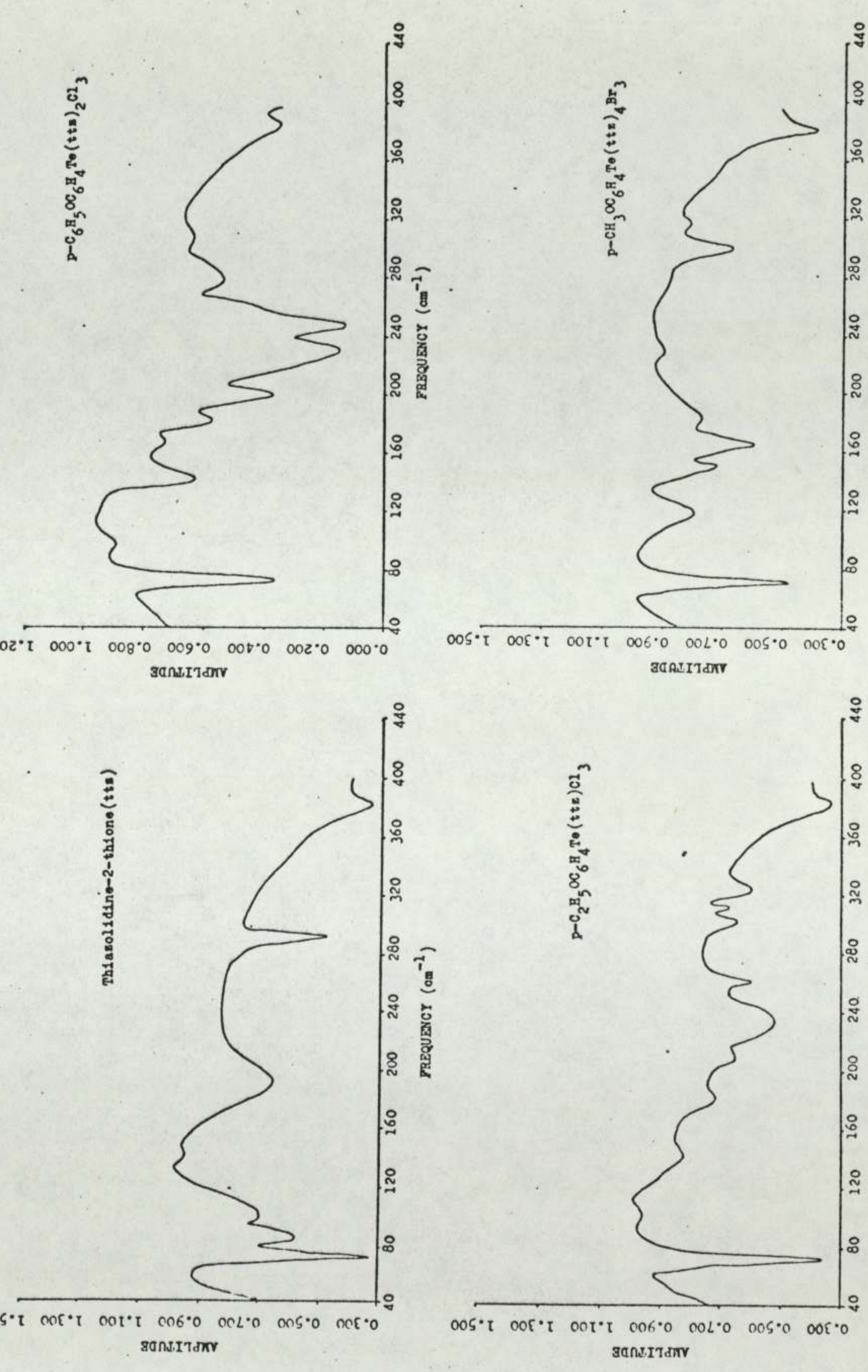

Thiazolidine-2-thione(tts)
p-$C_6H_5OC_6H_4Te(tts)_2Cl_3$
p-$C_2H_5OC_6H_4Te(ttz)Cl_3$
p-$CH_3OC_6H_4Te(ttz)_4Br_3$
AMPLITUDE
FREQUENCY (cm^{-1})
40
80
120
160
200
240
280
320
360
400
440
0.300
0.500
0.700
0.900
1.100
1.300
1.500
0.000
0.200
0.400
0.600
0.800
1.000
1.200

Fig. 3-10

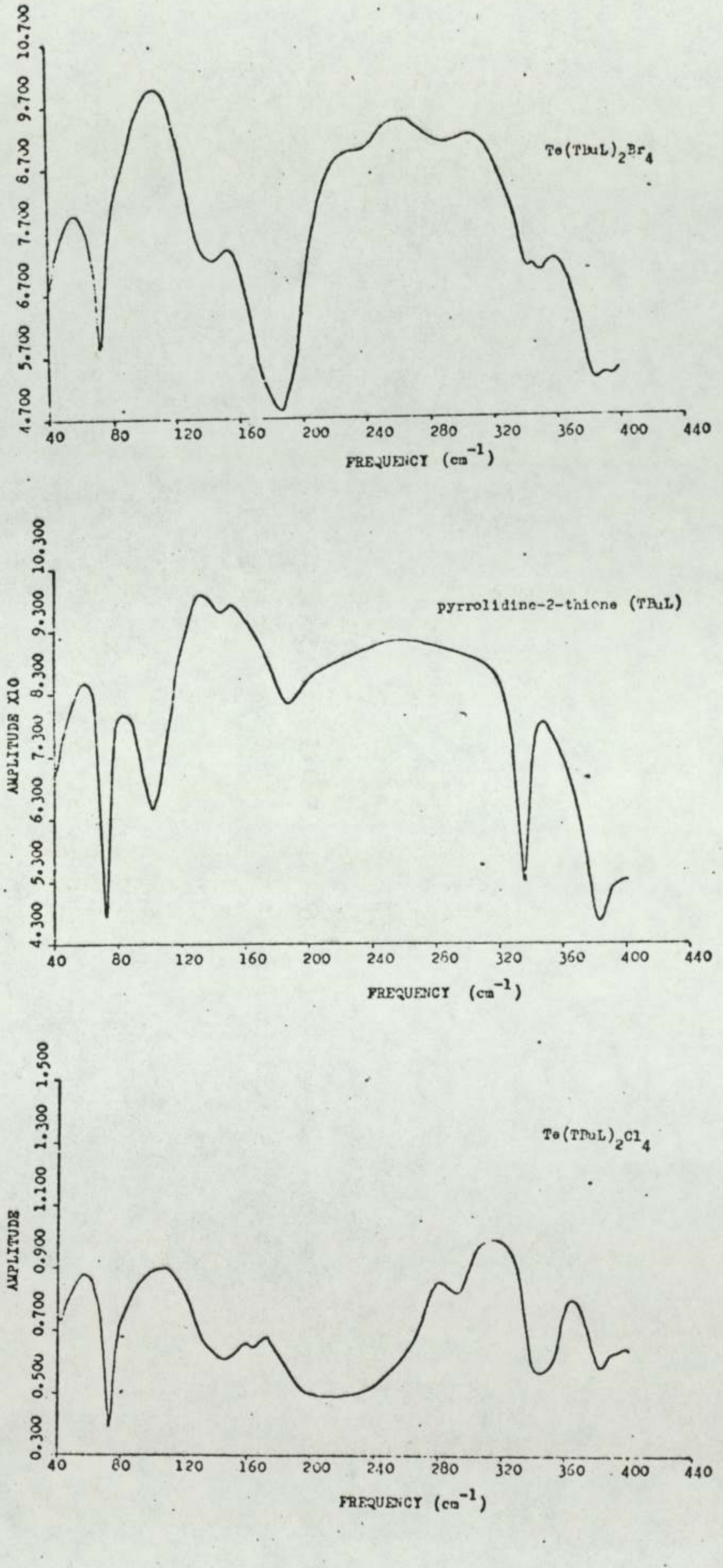

Te(TBuL)$_2$Br$_4$
AMPLITUDE X10
4.700
5.700
6.700
7.700
8.700
9.700
10.700
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
pyrrolidine-2-thione (TBuL)
AMPLITUDE X10
4.300
5.300
6.300
7.300
8.300
9.300
10.300
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
Te(TBuL)$_2$Cl$_4$
AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.500
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})

Fig. 3-11

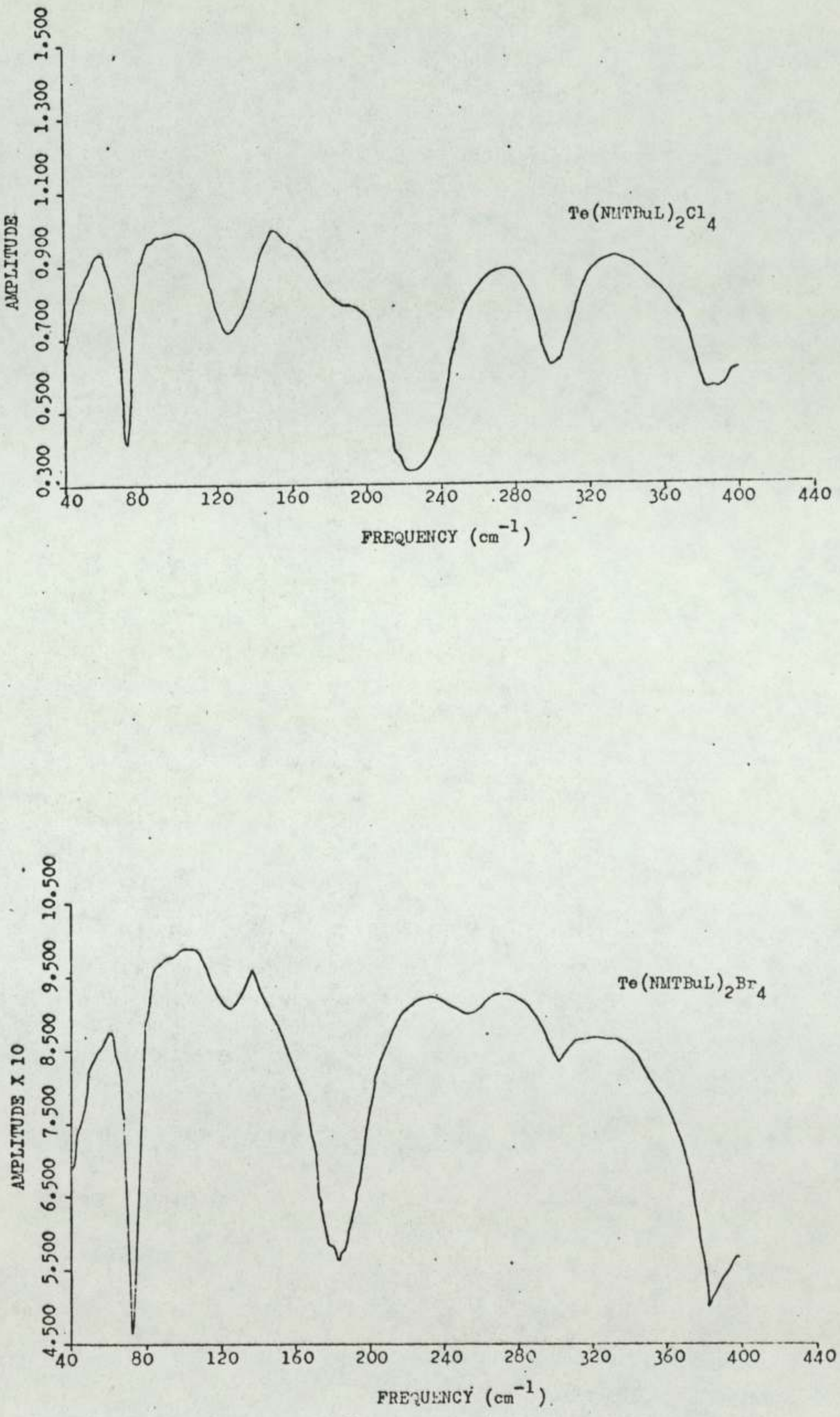

Te(NMTBuL)$_2$Cl$_4$
AMPLITUDE
0.300
0.500
0.700
0.900
1.100
1.300
1.500
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})
Te(NMTBuL)$_2$Br$_4$
AMPLITUDE X 10
4.500
5.500
6.500
7.500
8.500
9.500
10.500
40
80
120
160
200
240
280
320
360
400
440
FREQUENCY (cm^{-1})

Fig. 3-12

TABLE 3-1

Assignment of infrared bands.

Compounds	ν(N-H)	Thiamide 1	ν(C=S)+δ(NCS)	ν(C-S) asym.	sym.	DMF[a]
Thiazolidine-2-thione (ttz)	3400s[b]	1510vs	1290s	690s	650m	
$Te(ttz)_2Cl_4$	3200m	1515vs	1305s	690w	660m	52
$Te(ttz)_2Br_4$	3230m	1520) 1505) vs	1305s	690w	660m	124
$Te(ttz)_2I_4$	3230m	1517vs	1330) 1304) s	690w	662m	128
$Te(ttz)_4Cl_2 \cdot H_2O$	3130m	1510vs	1295s	685m	640m	42
$Te(ttz)_3Br_4$	3220) 3160) m	1510vs	1320) 1300) s		630m	85
$CH_3OC_6H_4Te(ttz)\ Br_3$	3230m 3120msh	1518vs	1322) 1297) s	700w	645m	108
$C_2H_5OC_6H_4Te(ttz)Cl_3$	3200m	1520vs	1305) 1294) s	695w	660w	29
$C_6H_5OC_6H_4Te(ttz)_2Cl_3$	3220m	1515m	1307s	691m	635m	49

a. cm^{2}.ohm^{-1}.mole^{-1} 10^{-3}M solution at 20°C.

b. Value in $CHCl_3$, 3140s cm^{-1} in KBr.

TABLE 3-2

Infrared and Raman spectra of Tellurium(II) and (IV) Thiazolidine-2-thione complexes below 400 cm^{-1}

Thiazolidine-2-thione(ttz)		$Te(ttz)_2Cl_4$		$Te(ttz)_2Br_4$		$Te(ttz)_2I_4$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
		318m	319s	316m	314m	325msh		ν (Te-N)
292m	292w	306m		303m		298m		ligand vibration
		260ssh	253s					ν (Te-Cl)
				254w				ν (Te-S)
		235vs	241s	236msh		212msh		
192s	180ssh					185m	178m	ligand vibration
				183vs				ν (Te-Br)
				178vs	176msh			
						155m	152s	ν (Te-I)
						139m	131s	
		134m			147w			δ (Te-Cl) or δ (Te-S)
		123m		128ssh		114w	109m	
103msh								ligand vibration
85msh								

Table 3-2 ....

Thiazolidine-2-thione(ttz)		$Te(ttz)_4Cl_2.H_2O$		$Te(ttz)_3Br_4$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
		336vw			318s	ν(Te-N)
		303s	300msh	302m		
292m	292w					ligand vibration
		276w	276w			ν(Te-Cl)
		252w		252w		ν(Te-S)
				243w		
192s	180ssh					ligand vibration
				165s	161msh	ν(Te-Br)
				147msh	139wsh	
		140vs				δ(Te-Cl) or δ(Te-S)
				124m		
103msh						ligand vibration
85msh						

Table 3-2 ....

Thiazolidine-2-thione(ttz)		$p\text{-}CH_3C_6H_4Te(ttz)_4Br_4$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
		316w	317s	ν (Te-N)*
292m	292m	298m		ligand vibration
			237m	ν (Te-S)
192s	180ssh			ligand vibration
		165s	160wsh	ν (Te-Br)
		151m	149wsh	
103msh				ligand vibration
85msh				

Thiazolidine-2-thione(ttz)		$p\text{-}C_6H_5OC_6H_4Te(ttz)Cl_3$		Assignment
i.r.	Raman	i.r.	Raman	
		324m	329m	ν (Te-N)*
		310w		
292m	292m	303m		ligand vibration
		263m	255m	ν (Te-Cl)
		235vs	229w	ν (Te-S)
		206msh		
192s	180ssh			ligand vibration
		140w		δ(Te-Cl) or δ(Te-S)
			133w	
103msh				ligand vibration
85msh				

A strong band found at 312 cm^{-1} for p-iodoanisole is said to be involve C-I bending mode occurs in this region.[32]

Table 3-2 ....

Thiazolidine-2-thione(ttz)		$p-C_6H_5OC_6H_4Te(ttz)_2Cl_3$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
		312w		ν(Te-N)*
292m	292m			ligand vibration
		286ssh	281m	ν(Te-Cl)
		230vs 203m	223w 201w	ν(Te-S)
192s	180ssh	183msh	175w	ligand vibration
		142w	133w	δ(Te-Cl) or δ(Te-S)
103msh 85msh				ligand vibration

* A strong band found at 312 cm^{-1} for p-iodoanisole is said to be involve C-I bending mode occurs in this region.[32]

TABLE 3-3

I.r. spectra of pyrrolidine-2-thione(TBuL) and its complexes with $TeCl_4$ and $TeBr_4$ at 400-2000 cm^{-1}, the more important bands.

Pyrrolidine-2-thione (TBuL)	$Te(TBuL)_2Cl_4$	$Te(TBuL)_2Br_4$	Assignment
482s	470s	465s	Thiamide V
790vs	730s	750s	δ(NH)
920w	960w	960m	
975s			
1038w	1025vs	1020w	
1065w	1060vw	1060w	
1113vw	1095vs	1090s	ν(CS)
1170w	1170vw	1185m	
1221w	1220w	1215m	
1295vs	1300vs	1305vs	
	1352s	1351m	
		1373m	
1421s	1410s	1410s	
1455m	1455m	1460s	
1473w	1470m		
1540vs	1555vs	1575s	ν(CN)
1620ssh	1640w	1645s	

TABLE 3-4

Infrared and Raman spectra of tellurium(IV) pyrrolidine-2-thione complexes below 400 cm^{-1}

Pyrrolidine-2-thione (TBuL)		$Te(TBuL)_2Cl_4$		$Te(TBuL)_2Br_4$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
336s	342w	345s	348m	346s	350m	ligand vibration
		292m	291w			ν(Te-Cl)
		220sbr	215w	230msh		ν(Te-S)
				186vs	185s	ν(Te-Br)
187m	179w					ligand vibration
		165msh				δ(Te-Cl)
					147vs	δ(Te-Br)
141msh 102s	130wsh	146m		145msh		ligand vibration

TABLE 3-5

I.r. spectra of N-methyl-pyrrolidine-2-thione complexes with $TeCl_4$ and $TeBr_4$, at 400-2000 cm^{-1}, the more important bands.

N-methyl-pyrrolidine-2-thione (NMTBuL)	$Te(NMTBuL)_2Cl_4$	$Te(NMTBuL)_2Br_4$	Assignment
495s	490s	486s	
650s	690w	690s	
800s			
1000sbr	1012m	1010w	ν(CS)
	1092vs	1092vs	
1120s	1105vs	1102vs	
1180m		1180vw	
1250m	1220m	1220vw	
	1275m		
1315s	1312vs	1310vs	
1400ssh	1408s	1400s	
1450vs	1445vs	1440m	
1535vs	1575vs	1570vs	ν(CN)
1620m	1680vw	1670w	

TABLE 3-6

The infrared and Raman spectra of N-methyl-pyrrolidine-2-thione complexes of tellurium tetrahalides below 310 cm^{-1}.

Te(NMTBuL)$_2$Cl$_4$		Te(NMTBuL)$_2$Br$_4$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
302s		303m		ligand vibration
281msh				ν (Te-Cl)
		256m		ν(Te-S)
			246wsh	
225vs	221wsh			
		185vs	180m	ν (Te-Br)
187msh				δ (Te-Cl)
130s	131w	130m	132w	ligand vibration

3.4 DISCUSSION

3.4.1 Preparation of thiazolidine-2-thione complexes of tellurium(II) and tellurium(IV).

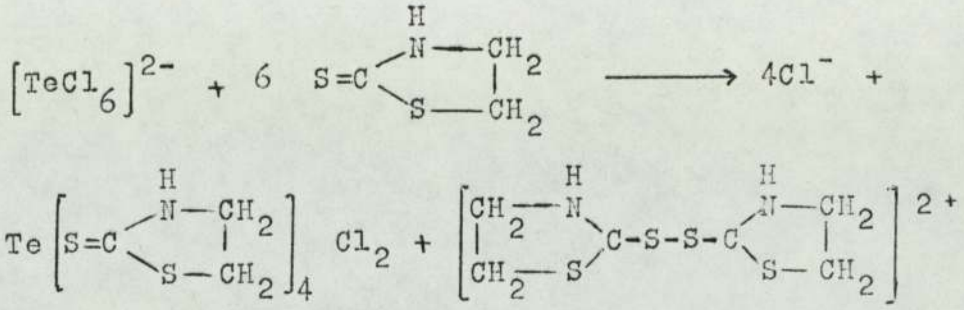
In the first preparative method of these tellurium(IV) complexes with thiazolidine-2-thione, tellurium tetrahalide was reacted with the ligand in methanol which gave general complexes formula of $Te(ttz)_2X_4$ (where X = Cl, Br or I).

The second preparative method, the tellurium tetrachloride complex was prepared by separately dissolving tellurium dioxide and thiazolidine-2-thione in hydrochloric acid and then mixing the solutions together at room temperature. The formula of this complex was found to be $Te(ttz)_2Cl_4$.

The third preparative method used to obtain the aryltelluriumtrihalide complexes, involved the dissolution of aryltelluriumtrihalide in molten thiazolidine-2-thione at 110°C.

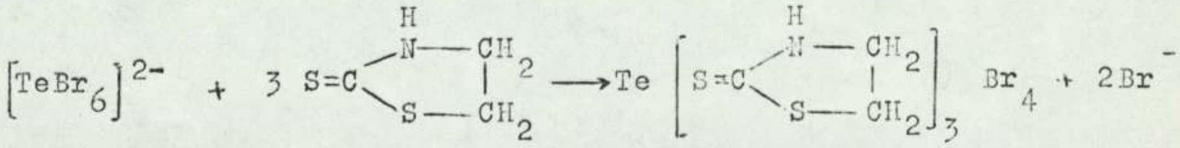
In the fourth method used for the preparation of the tellurium(II) complex with thiazolidine-2-thione; tellurium dioxide in aqueous hydrochloric acid was reacted with the ligand in distilled water at 65°C. This gave a complex formula of $Te(ttz)_4Cl_2.H_2O$, i.e., oxidation of the ligand occurs with reduction of tellurium(IV) to tellurium(II) as follows :-

$TeO_2 + 6HCl \longrightarrow [TeCl_6]^{2-} + 2H^+ + 2H_2O$



The $Te(ttz)_3Br_4$ complex was prepared by reaction of tellurium dioxide in aqueous hydrobromic acid with thiazolidine-2-thione in distilled water at 60°C. The reaction is shown below :-

$TeO_2 + 6HBr \longrightarrow [TeBr_6]^{2-} + 2H^+ + 2H_2O$



3.4.2 Vibrational analysis for thiazolidine-2-thione complexes for Tellurium(II) and Tellurium(IV).

Thiazolidine-2-thione contains a thioamide group (HNCS) and should ideally, give four i.r. bands[47,72-75]. These are known as "Thioamide bands" and arise from the following vibrational modes :-

Band I at $1510cm^{-1}$ has contributions from δ(NH) + δ(C-H) + ν(C N)

Band II at $1290cm^{-1}$ has contributions from ν(C=S) + δ(NCS)

Band III at 1000 cm^{-1} has contributions from $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ + $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$.

Band IV at 690 cm^{-1} has contributions from $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$

Fregni and co-workers [58] reported that $\nu(\mathrm{NH})$, thioamide 1 and $\nu(\mathrm{C{=}S}) + \delta(\mathrm{NCS})$ give rise to bands at 3400, 1490 and 1288 cm^{-1} respectively in thiazolidine-2-thione which are shifted to lower (-260 cm^{-1}) to higher (+40 cm^{-1}) and to higher (+21 cm^{-1}) wavenumbers respectively in the iron(II) and (III) complexes with thiazolidine-2-thione. Therefore, the iron in these complexes is co-ordinated through nitrogen. The far infrared spectra of the complexes shows bands to be present between 240-220 cm^{-1} which may be due to $\nu(\mathrm{Fe{-}N})$ and the band for $\nu(\mathrm{Fe{-}S})$ was absent.

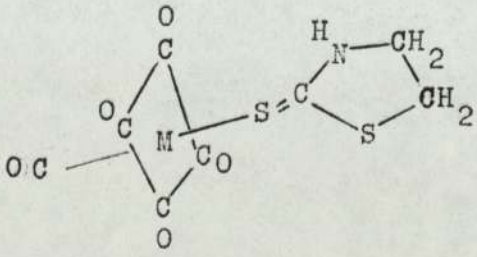
Zinc, cadmium and mercury complexes with thiazolidine-2-thione were prepared by Filippo and co-workers [61] and they report that the nitrogen in the ligand was co-ordinated with the metal atom. In the complexes $\mathrm{Zn(ttz)_2X_2}$, $\mathrm{Cd(ttz)_2X_2}$ and $\mathrm{Hg(ttz)_2X_2}$ (where X = Cl, Br, or I), the bands between (180-178 cm^{-1}), (176-167 cm^{-1}) and (158-147 cm^{-1}) were assigned as being due to $\nu(\mathrm{Zn{-}N})$, $\nu(\mathrm{Cd{-}N})$ and $\nu(\mathrm{Hg{-}N})$ respectively.

Colombini and Preti [62] also reported cadmium and zinc complexes, $\mathrm{Zn(ttz)_2(NCS)_2}$, $\mathrm{Cd(ttz)_2(NCS)_2}$, $\mathrm{Zn(ttz)_2Ac_2}$, $\mathrm{Cd(ttz)_2Ac_2}$, $\mathrm{Zn(ttz)_2(BF_4)_2{\cdot}H_2O}$, $\mathrm{Cd(ttz)_2(BF_4)_2}$ and $\mathrm{Hg(ttz)_4(BF_4)_2}$ and they found the nitrogen atom of the thiazolidine-2-thione to be the donor in the complexes. The bands in the complexes due to nitrogen metal stretching modes are as follows :-

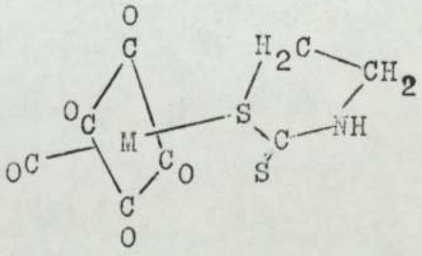
	M-N
$Zn(ttz)_2(NCS)_2$	192ms
$Cd(ttz)_2(NCS)_2$	170ms
$Zn(ttz)_2Ac_2$	176s
$Cd(ttz)_2Ac_2$	136s
$Zn(ttz)_2(BF_4)_2.2H_2O$	188ms
$Cd(ttz)_2(BF_4)_2$	168m
$Hg(ttz)_2(BF_4)_2$	147m

where NCS = thiocyanate, Ac = acetate,
BF_4 = fluoroborate and
ttz = thiazolidine-2-thione.

Filippo and co-workers [57] reported the preparation of complexes of chromium, molybdenum, and tungsten with thiazolidine-2-thione of formula $M(CO)_5ttz$ (where M = Cr, Mo, or W). They suggest that "the ligand should be bonded to the metal through one of the sulphur atoms", as shown below in A and B.



(A)



(B)

Silver forms complexes with thiazolidine-2-thione according to Stephen and Townshend [63] and they believe that the silver ion is sulphur bonded.

Cobalt and nickel complexes with thiazolidine-2-thione were reported by Filippo and Preti[59] B. Singh and K. Thakur[60b] and P. Singh and R. Rivest[60a] but the data available for the complexes is confusing.

Filippo and Preti[59] and B. Singh and K. Thakur[60b] believe that cobalt and nickel ions in the complexes are sulphur bonded but P. Singh and R. Rivest[60a] believe that cobalt ion is nitrogen bonded.

Filippo and Preti[59] reported from their i.r. spectra that the bandsat 1500 cm^{-1} and 1200-1000 cm^{-1} in the complexes do not change when compared with the free ligand but the band at 700-600 cm^{-1} due to ν(C-S) is shifted to lower frequencies by 40-50 cm^{-1}. Also they found new bands in the region 337-320 cm^{-1} for the complexes due to ν(Co-S). Therefore, they believe from these results that the ligand is co-ordinated via the sulphur atom.

P. Singh and R. Rivest[60a] observed that there are three positive shifts in the complexes when compared with the free ligand. The first concerns the thioamide 1 band; the second involves ν(C=S) + δ(NCS) and the third vibration is ν(C-S). The new band found between 341-325 cm^{-1} is assigned to ν (Co-N), (suggesting nitrogen bonding).

B. Singh and K. Thakur[60b] studied cobalt and nickel complexes with the ligands containing a thioamide group (such as 1-phenyltetrazoline-5-thione (PT5T), thiocarbohydrazide (Hteaz) and thiazolidine-2-thione).

These ligands contain a thiocarbonyl (CS) group and an adjacent imino group as potential donors. They have different co-ordination possibilities i.e., through sulphur only, through nitrogen only, or through both sulphur and nitrogen.

They believe the metals in the complexes $M(ttz)_2X_4$ $M(PT5T)_2$ and $M(Hteaz)_2X_2$ (where M = Co or Ni and X = Cl, Br, or I) are sulphur bonded, nitrogen and sulphur bonded, and nitrogen bonded respectively.

There is no coordination through the nitrogen atom in the thiazolidine-2-thione complexes of group VIB carbonyls as is shown by Filippo and co-workers[57] but only the sulphur atom of thioketonic group is involved in bonding to the metal.

Comparison of i.r. and Raman spectra of thiazolidine-2-thione complexes with tellurium (II) and (IV) and thiozolidine ligand from tables 3-1 & 3-2 and figures 3-1/2/3/-4/5/8/9/10 show the five most important bands. These bands are ν(NH), thioamide 1, ν(C=S) + δ(NCS), ν(Te-N), ν(Te-S) and ν(Te-X).

Thiazolidine-2-thione and $Te(ttz)_2X_4$ will first be discussed.

Table 3-1 and Fig.3-2 show that ν(NH), thioamide band 1 and ν(C=S) + δ(NCS) have bands 3400, 1510 and 1290 cm^{-1}

respectively in thiazolidine-2-thione which are shifted to lower (-200 cm^{-1}), to slightly higher (+10 cm^{-1}) and to higher (+40 cm^{-1}) wavenumbers respectively in the complexes. This therefore suggests that the tellurium in the complexes is nitrogen bonded. Although evidence from the shifts in ν(C-S) is less convincing. Fregni and co-workers[58] Singh and Rivest[60a] and Filippo and co-workers[61] stated that the slight shifts of the band due to ν(C=S) + δ(NCS) is indicative of co-ordination through nitrogen, but Filippo and co-workers[57] suggest that the positive shifts in the complexes are due to co-ordination through the sulphur atom of thioketonic group as mentioned before.

Table 3-2 and Fig.3-9 show new bands between (325-109 cm^{-1}) which are noted after elimination of ligand bands. Absorptions between (254-212 cm^{-1}) for the complexes were assigned to ν(Te-S) vibrations. These results agree with Clark and co-workers[20,76,77] whilst the ones at (260-255 cm^{-1}) are assigned to ν(Te-Cl), those at (183-176 cm^{-1}) to ν(Te-Br) and those at (155-131 cm^{-1}) to ν(Te-I).

Absorptions in the region (325-314 cm^{-1}) are shown in most of the complexes, and the absorption in this region can arise from Te-C bending mode but in these complexes the tellurium aryl linkage is absent, so the vibration observed could be due to ν(Te-N).

Therefore, the tellurium atom in these complexes could be co-ordinated with one nitrogen donor and one sulphur donor.

3.4.2.1 Comparison of the spectra of thiazolidine-2-thione and the complexes $Te(ttz)_4Cl_2 \cdot H_2O$ and $Te(ttz)_3Br_4$

The more important bands ν(NH), thioamide 1, ν(C=S) + δ(NCS), ν(Te-N), ν(Te-S) and ν(T-X) bands are shown in tables 3-1/2 and figures 3-1/8 for the complexes and ligand.

The negative shift of ν(NH), the slight positive shift of thioamide 1 and positive shift of ν(C=S) + δ(NCS) in the complexes as seem from table 3-2 and fig. 3-8 are similar to those of the $Te(ttz)_2X_4$ complexes.

The ν(Te-N), ν(Te-Cl), ν(Te-S) and ν(Te-Br) modes have bands in regions (336-302 cm^{-1}), 276 cm^{-1}, (252-243 cm^{-1}) and (165-139 cm^{-1}) respectively in the complexes (see table 3-2 and fig. 3-8.

Therefore the tellurium atom in these complexes could be co-ordinated with both nitrogen and sulphur donors.

3.4.2.2 Comparison of the spectra of thiazolidine-2-thione and complex $RTe(ttz)_xX_3$.

The complexes $p\text{-}CH_3OC_6H_4(ttz)_4Br_3$, $p\text{-}C_2H_5OC_6H_4(ttz)Cl_3$ and $p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$ have ν(NH), thioamide 1 and ν(C=S) + δ(NCS) bands are shown in table 3-1 and figures 3-3/4/5.

These bands are shifted to lower and to higher wavenumbers in the complexes and they are similar to the $Te(ttz)_2X_4$

complexes.

The band in regions (329-310 cm^{-1}), (286-255 cm^{-1}), (237-201 cm^{-1}) and (165-149 cm^{-1}) may be assigned to ν(Te-N), ν(Te-Cl), ν(Te-S) and ν(Te-Br) respectively.

Therefore it seems likely that nitrogen and sulphur atoms of thiazolidine-2-thione are donor atoms in these complexes (see table 3-2 and fig.3-10).

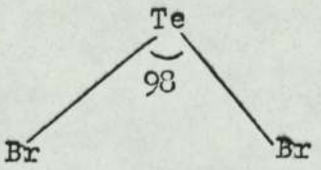
In the $p-C_2H_5OC_6H_4Te(ttz)_1Cl_3$ complex it is difficult to see how nitrogen and sulphur donor atoms from one ligand are involved. This complex has a tellurium-aryl linkage which could give rise to bands in the region (329-310 cm^{-1}) which are due to a Te-C bending mode but an absorption due to ν (Te-N) is also likely but cannot be proved.

Therefore, the tellurium atom in the complex is probably sulphur bonded and less likely but also possibly nitrogen bonded.

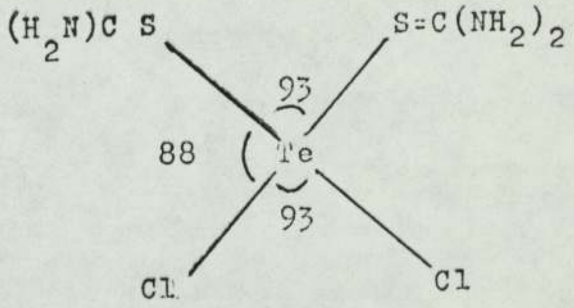
3.4.3 Structures.

The sterochemistry of the tellurium(II) atom in compounds such as $TeBr_2$ or Cis $Te(tu)_2Cl_2$ has been discussed and is believed to involve structures which are either two or four co-ordinated.

In $TeBr_2$ there are two bonds giving an angular shaped molecule (A) [70] but in Cis $Te(tu)_2Cl_2$ there are four bonds giving a square planar structure (B).

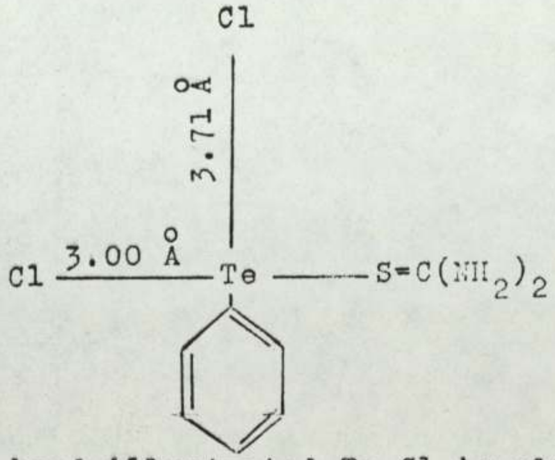


(A)



(B)

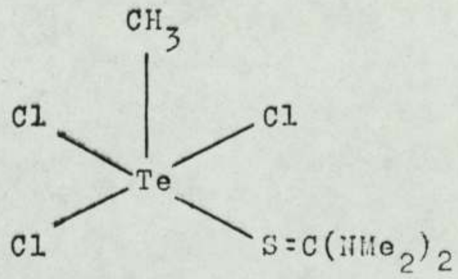
In the complex of $Te(tmtu)_2Cl_2$ there are four bonds to tellurium(II). Three of these are normal co-ordinate bonds which may be termed "planar", with a fourth which is a very long bond. This is called the "trans" effect and is exerted by one ligand in the complex. The structure of $C_6H_5Te(tu)Cl$ [71] also illustrates this effect :



(the bond illustrated Te-Cl is almost absent)

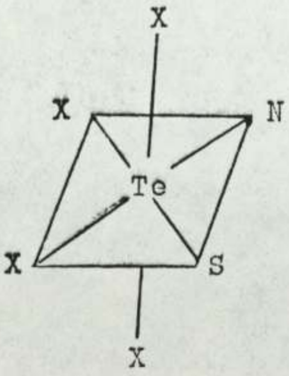
Buss and Krebs [49] showed that the co-ordination number of tellurium atoms in tellurium tetrachloride is six.

In the complex $CH_3TeSC(NMe_2)_2Cl_3$,[19] the tellurium(IV) atom is five co-ordinated and this compound is said to have a square pyramidal structure, as shown below :

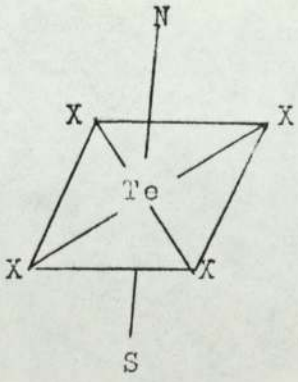


where $S=C(NMe_2)_2$ is Tetramethylthiourea

Assuming thiazolidine-2-thione to be a monodentate ligand in tellurium complexes, the co-ordination number of tellurium atom in $Te(ttz)_2X_4$ complexes could be six. This could arise from one sulphur donor and one nitrogen donor (occupying cis or trans positions) and four halogen atoms (in the four remaining positions), as follows :



'Cis' $Te(ttz)_2X_4$

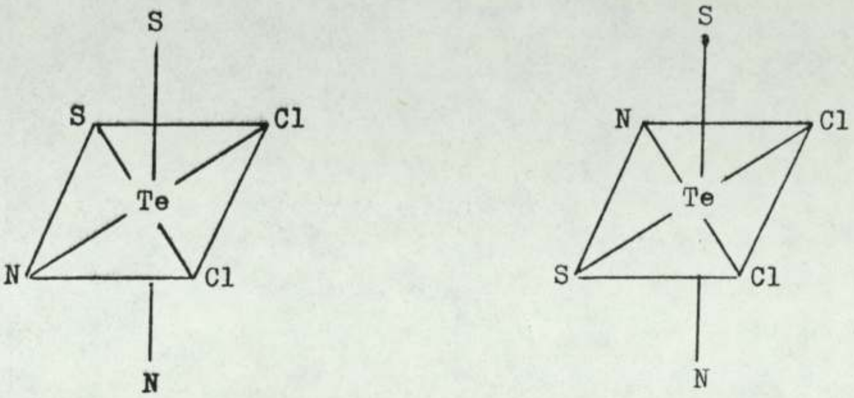


'trans' $Te(ttz)_2X_4$

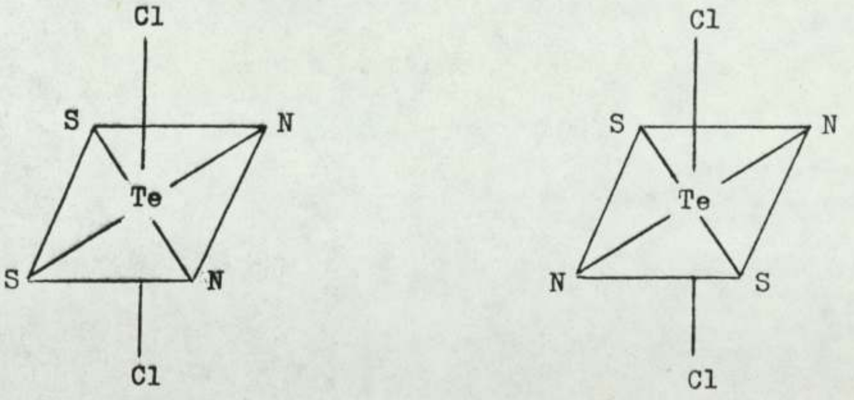
where X = Cl, Br or I and N & S are derived from two ligands.

One long Te-X bond may be involved. Conductivity measurements indicate a certain amount of ionisation.

It is also possible that the tellurium atom in $Te(ttz)_4Cl_2.H_2O$ could be six-coordinated i.e., two chlorine atoms (occupying cis or trans positions), and four atoms such as two sulphur and two nitrogen (in the remaining positions) as illustrated below :



Cis $Te(ttz)_4 Cl_2$

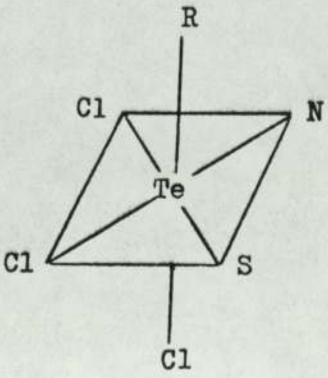


Trans $Te(ttz)_4 Cl_2$

where N & S are derived from four monodentate ligands.

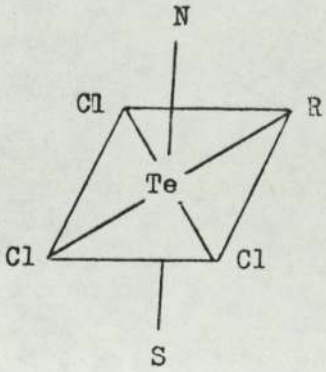
Coordination number six or seven for the tellurium atom could be envisaged for $Te(ttz)_3Br_4$. A high conductivity is indicated. One bromine atom in the complex could be present as Br^- giving coordination number of six.

p-Phenoxyphenyltelluriumtrichloride reacts with molten thiazolidine-2-thione to give a complex formula of $p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$. The co-ordination number of the tellurium atom in this complex could be six. This could arise as follows:



cis.

$p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$

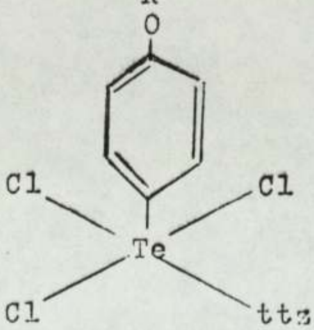


trans.

$p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$

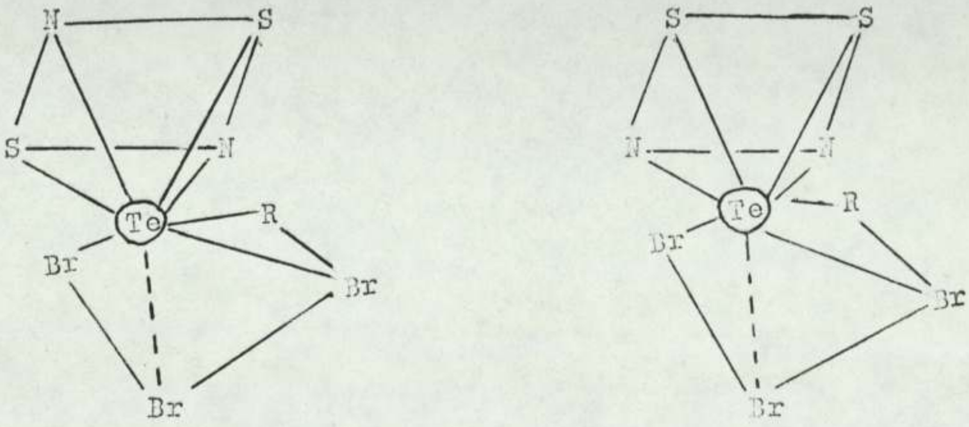
where $R = C_6H_5OC_6H_4$ and N & S are donors from two monodentate ligands.

When $p\text{-}C_2H_5OC_6H_4TeCl_3$ was reacted with thiazolidine-2-thione in the complex of formula $p\text{-}C_2H_5OC_6H_4Te(ttz)Cl_3$ was formed. In this complex, tellurium could have a coordination number of five and the structure of $p\text{-}C_2H_5OC_6H_4Te(ttz)Cl_3$ could thus be of a square pyramidal shape, i.e., the analogous to the structure of tetramethylthiourea methyl telluriumtrichloride



where ttz is thiazolidine-2-thione and $R = C_2H_5$

The $p\text{-}CH_3OC_6H_4Te(ttz)_4Br_3$ complex was prepared by the reaction of $p\text{-}CH_3OC_6H_4TeBr_3$ with molten thiazolidine-2-thione. In this complex tellurium could have coordination number of eight. A high conductivity value of 108 $cm^2.ohm^{-1}.mole^{-1}$ was indicated for this compound. One bromine atom could be present as Br^- in the complex thus leaving seven donors for coordination sites. Possible structures may be represented as follows :



$RTe(ttz)_4Br_3$

(where $R = p\text{-}CH_3OC_6H_4$)

3.4.4 Conductivity.

10^{-3} Molar solutions of tellurium(II) and (IV) complexes with thiazolidine-2-thione were dissolved in NN′ dimethylformamide and then the conductivity measurements were obtained at 20°C using a Mullar conductivity bridge Type E 7566/3. The values obtained are shown in table 3-1.

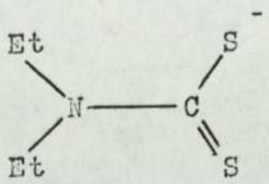
The complexes had values of conductivity of between 29-124 $cm^2.ohm^{-1}.mole^{-1}$ and these values could be expected for 1:1 electrolytes in this solvent.

The complexes of $Te(ttz)_3Br_4$ and $p\text{-}CH_3OC_6H_4Te(ttz)_4Br_3$ gave high conductivity values of 85 and 108 $cm^2.ohm^{-1}.mole^{-1}$ respectively. There could be one bromine atom present as Br^-, and therefore co-ordination numbers of six or seven for tellurium atom are possible.

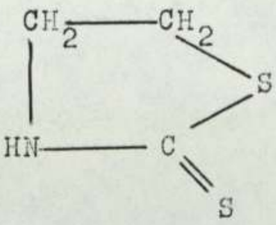
The conductivity values of $p\text{-}C_2H_5OC_6H_4Te(ttz)Cl_3$, $Te(ttz)_4Cl_2.H_2O$, $p\text{-}C_6H_5OC_6H_4Te(ttz)_2Cl_3$ and $Te(ttz)_2Cl_4$ are 29, 42, 49 and 52 $cm^2.ohm^{-1}.mole^{-1}$ respectively. The conductivity values of these complexes could arise from interaction between cationic and anionic species. Thus, the $Te(ttz)_2X_4$, $Te(ttz)_4Cl_2.H_2O$, $Te(ttz)_3Br_4$ and and $RTe(ttz)_xX_3$ complexes may be more conveniently written as $[Te(ttz)_2X_3]^+X^-$, $[Te(ttz)_4Cl]^+Cl^-.H_2O$, $[Te(ttz)_3Br_3]^+Br^-$ and $[RTe(ttz)_xX_2]^+X^-$ respectively.

3.4.5 U.V. and Visible Spectra.

The complexes (10^{-5} molar) were dissolved in dry NN' dimethylformamide and the u.v. and visible spectra of these solutions recorded on a Perkin-Elmer 137 spectrophotometer. All showed a strong single absorption at 35.7 kK. St.Nikolov and co-workers[45] reported that the U.V. and visible spectra of some tellurium complexes of diethyldithiocarbonate i.e., $Te(dtc)_2$ and $Te(dtc)_4$ have strong bands at 32.4 and 36.2 kK. The two ligands have similar arrangements of carbon, sulphur and nitrogen.



dtc.



ttz.

3.4.6 The reaction of other aryltelluriumtrihalides with thiazolidine-2-thione.

The organotellurium compounds of $C_6H_5TeCl_3$, $C_6H_5TeBr_3$, p-$CH_3C_6H_4TeCl_3$, p-$CH_3C_6H_4TeBr_3$, p-$C_2H_5OC_6H_4TeBr_3$ and p-$C_6H_5OC_6H_4TeBr_3$ all react with thiazolidine-2-thione. Most of them give yellow precipitates when the molten method [216] was used, but when they were reacted with thiazolidine-2-thione in dry methanol, sticky yellow compounds formed which could not be recrystallised. The i.r. spectra of these yellow compounds over the range 4000-250 cm^{-1} were examined and showed a negative shift of ν (NH), a slight positive shift of thioamide bond 1 and a positive shift of ν (C=S) + δ (NCS). The complexes also gave new bands on i.r. range 400-200 cm^{-1}. The analyses of these compounds were not satisfactory and the compounds could not be purified .

3.4.7 The reaction of thiazolidine-2-thione with thiourea.

The reaction of molten thiazolidine-2-thione with $Te(tu)_2Cl_2$ (where tu = thiourea) was also investigated.

The colour of the mixture changed from yellow to green on the addition of the two reactants. The formula of the compound produced could not be obtained because the product was impure.

3.4.8 Pyrrolidine-2-thione complexes of tellurium(IV).

The complexes of tellurium(IV) with pyrrolidine-2-thione (TBuL) were prepared by direct addition of tellurium tetrahalides with the ligand in dry methanol or acetone. The precipitate formed immediately.

The $Te(TBuL)_2Cl_4$ complex decomposes after two to three days. It is noted that the colour changes from yellow to brown and finally to black. Presumably elemental tellurium is precipitated. The $Te(TBuL)_2Br_4$ complex is stable however.

Conductivity measurements were obtained on 10^{-3}M solutions the complexes in dry NN′ dimethylformamide at 20°C using a Mullard conductivity bridge Type E 7566/3. The values of Λ were zero for these compounds.

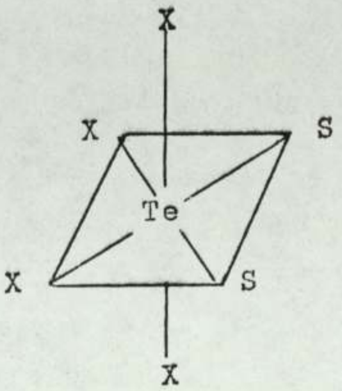
U.V. and visible spectra of the complexes were recorded on a Perkin-Elmer 137 spectrophotometer, after preparing more dilute solutions. Both solutions gave a strong absorption in U.V. at 36.7 kK, which agrees with the data found for other tellurium sulphur bonded complexes by St. Nikolov and co-workers[45] and other complexes reported in Chapter II of this thesis.

Comparisons of infrared and Raman spectra of pyrrolidine-2-thione complexes with tellurium(IV) with those of the pyrrolidine-2-thione ligand (tables 3-3/4 and fig. 3-6/11) have shown that ν(CN), ν(CS), thioamide V bands were shifted to higher and lower wavenumbers. Also new bands are obtained between 292-147 cm^{-1}.

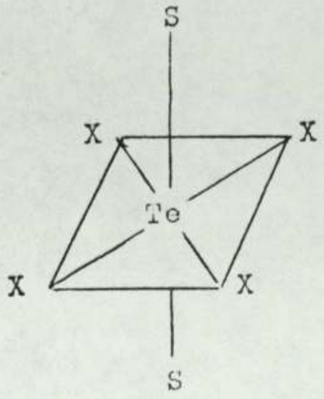
Table 3-3 and figure 3-6 show ν(CS) and ν(CN) have bands 1113 cm^{-1}, 1540 cm^{-1} respectively in pyrrolidine-2-thione, which are shifted to lower frequency, vis:- 1095 cm^{-1} in $Te(TBuL)_2Cl_4$ complex and 1090 cm^{-1} in $Te(TBuL)_2Br_4$ complex and to higher 1555 cm^{-1} in $Te(TBuL)_2Cl_4$ and 1575 cm^{-1} in $Te(TBuL)_2Br_4$ wavenumber respectively. Therefore, this indicates that the tellurium atom in the complexes is sulphur bonded through the thiocarbonyl group. New bands are shown in the complexes at 1352 and 1640 cm^{-1} and the band at 1421 cm^{-1} in the ligand is altered to 1410 cm^{-1} in the complexes. The band δ(NH) in the ligand at 790 cm^{-1} is lowered by 60 cm^{-1} in $Te(TBuL)_2Cl_4$ or 40 cm^{-1} in the $Te(TBuL)_2Br_4$ complex.

New bands between 292-147 cm^{-1} (shown in table 3-4 and fig. 3-11) are noted after elimination of ligand bands. The bands due to ν(Te-Cl), ν(Te-S) and ν(Te-Br) are clearly visible at 292 cm^{-1}, (230-215) cm^{-1} and 186 cm^{-1} respectively in infrared and Raman spectra. The ligand has a strong absorption at 335 cm^{-1} and that is the region where the ν(Te-N) stretching mode would appear, but there is no clear evidence of ν(Te-N) bonding in the complexes.

Conductivity data suggests a non-ionic species. The tellurium atom in $Te(TBuL)_2X_4$ complexes could be six co-ordinated with two sulphur donors occupying cis or trans positions, and the four halogen atoms using the remaining four sites. Possible structures are indicated below :-



$Te(TBuL)_2X_4$



$Te(TBuL)_2X_4$

where X - Cl, or Br and two sulphur atoms come from two pyrrolidine-2-thione (TBuL) ligands.

3.4.9 N-Methyl-pyrrolidine-2-thione complexes of tellurium(IV)

The tellurium(IV) complexes of N-methyl-pyrrolidine-2-thione were prepared by adding a solution of the ligand to a solution of tellurium tetrahalide in methanol. The precipitate was formed immediately. These compounds decomposed after a few weeks. Analyses and spectra were carried out as soon as possible.

The conductivity measurements were obtained by preparing 10^{-3}M of the complexes in dry NN′ dimethylformamide at 20°C The values of Λ obtained were zero.

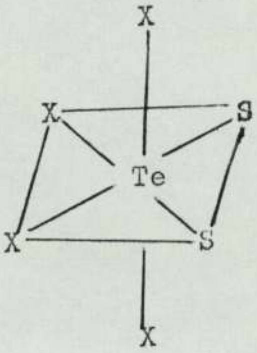
A dilute solution (10^{-5}M) of the complexes was used to record the U.V. and visible spectra and a strong absorption in the U.V. at 36.2 kK was found. St. Nikolov and co-workers[45] found that tellurium-sulphur bonded complexes had a similar range of absorption in U.V. Similar bands were obtained for the diethyldithiocarbamate complexes of tellurium(II) and (IV).

Comparison of i.r. and Raman spectra of N-methyl-pyrrolidine-2-thione complexes of tellurium(IV) with that of N-methyl-pyrrolidine-2-thione ligand (tables 3-5/6) shows that ν(CN) and ν(CS) are shifted to higher and to lower wavenumbers respectively. Also new bands appear between 281-185 cm^{-1}.

The band (see table 3-5) at 1120 cm^{-1} assigned to ν(CS) in the ligand is shifted to lower frequencies by 15-28 cm^{-1} in the complexes and also the band at 1535 cm^{-1} assigned to ν(CN) in the ligand is shifted to higher frequency 1570 cm^{-1} in the complexes. In the N-methyl-pyrrolidine-2-thione complexes the bands at 1352 and 1640 cm^{-1} could not be found but they were present in the spectra of the pyrrolidine-2-thione complexes.

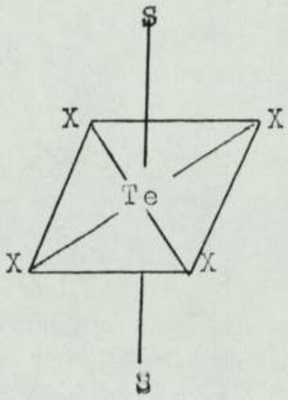
In table 3-6 the infrared and Raman spectra of N-methyl-pyrrolidine-2-thione complexes are shown. The bands due to ν(Te-Cl), ν(Te-S) and ν(Te-Br) are 281, (256-246) cm^{-1} and (185-180) cm^{-1} respectively. A band at 302 cm^{-1} could be attributed to ν(Te-N) or ligand vibration. It seems more likely that the tellurium in the complexes is co-ordinated through the sulphur atom of the thiocarbonyl group.

The structure of N-methyl-pyrrolidine-2-thione complexes is thus likely to be similar to that of the pyrrolidine-2-thione complexes.



Cis.

$Te(NMTBuL)_2X_4$



Trans.

$Te(NMTBuL)_2X_4$

where X = Cl or Br and two sulphur atoms from two N-methyl-pyrrolidine-2-thione (NMTBuL) ligands

CHAPTER IV

Investigation of the reactions of methyl-3-mercaptopropionate, and 1, 3 di(2-pyridyl)-2-thiourea with tellurium(IV) compounds.

4.1 INTRODUCTION

It has been pointed out in the introduction of Chapter I, II and III that tellurium compounds are often stabilised by sulphur donor ligands.

The preparation of a large number of compounds containing Te-S bonds have been published. These compounds were varied in their nature and consist of thiourea, substituted thiourea, disubstituted dithio-oxamides, tetrasubstituted dithio-oxamides, heterocyclic compounds, such as thiazolidine-2-thione, pyrrolidine-2-thione or N-methyl-2-pyrrolidine-thione. Clark and Collett[24] reported the preparation and vibrational spectra of some compounds of tellurium(II) such as tellurobis-(3-mercaptopropionic acid), tellurobis-(2-mercaptopropionic acid). In the latter reaction, the thioacid reacts with the tellurite ion, as follows :-

$$TeO_3{}^{2-} + 4H^+ + 2HSRCO_2H \longrightarrow Te^{2+} + 3H_2O + HO_2CRSSRCO_2H$$

but the reactions involved in the formation of the complex are, -

$$2HSRCO_2H \longrightarrow 2(SRCO_2H)^- + 2H^+$$

$$Te^{2+} + 2(SRCO_2H)^- \longrightarrow Te(SRCO_2H)_2$$

4.1.1 Preparation of starting materials.

Diaryltelluriumdihalides have been reduced to diaryltellurides by a variety of reagents using various procedures as follows:

Diphenyltelluride was the first member of the diaryltellurides and Kraff and Lyons [80] prepared this compound in 1894 by the reaction of elementary tellurium with diphenylmercury. The reaction was as follows:-

$$2Te + C_6H_5HgC_6H_5 \longrightarrow C_6H_5TeC_6H_5 + HgTe$$

Lederer [81] prepared ditolyltelluride by the reaction of aqueous $NaHSO_3$ or Na_2SO_3 with a solution of ditolyltelluriumdichloride dissolved in hot water or 10 per cent. aqueous sodium hydroxide.-

$$(CH_3C_6H_4)_2TeCl_2 + Na_2SO_3 + 2NaOH \longrightarrow 2NaX + H_2O + Na_2SO_4 + CH_3C_6H_4TeC_6H_4CH_3$$

Rohrbaech [82] used metallic zinc to reduce diaryltelluriumdihalides to diaryltellurides. In this method bis(p-methoxyphenyl)telluriumdichloride or bis(p-ethoxyphenyl)tellurium dichloride was refluxed with zinc dust in benzene and the di(p-methoxyphenyl)telluride or di(p-ethoxyphenyl)telluride were isolated respectively as crystalline solids.

Morgan and Kellet [35] obtained a 37 per cent. yield of the p-anisylderivative from the diaryltellurium dichloride using Rohrbaech's method, but Burstall and Suyden[83] reduced some compounds with zinc in glacial acetic acid to give a yield of 90 per cent. diaryltelluride.

Morgan and Burgess[84,85] obtained diaryltelluride from the reduction of diaryltelluriumdihalide with potassium metabisulphide in aqueous acetone. Also McWhinnie and Patel[55] reduced the bis(p-methoxyphenyl)tellurium dichloride or bis(p-ethoxyphenyl)tellurium dichloride to diaryltelluride. They added a saturated aqueous sodium-metabisulphide to a solution of diaryltelluriumdichloride in benzene and the mixture was stirred for four hours. The organic layer was separated and washed with distilled water. The benzene was removed by distillation under vacuum and the diaryltelluride was obtained.

Molten $Na_2S.9H_2O$ at 95 to 100°C reduces diaryltellurium dihalides (such as bis(p-methoxyphenyl)telluriumdichloride) to diaryltellurides and the molar ratio of halide to sulphide is kept at 1:15[86-88] The reduction is described by the following equation :-

$$(CH_3OC_6H_4)_2TeCl_2 + Na_2S \longrightarrow CH_3OC_6H_4TeC_6H_4OCH_3 + 2NaCl + S$$

Diphenyltelluriumdibromide was reduced to diphenyltelluride by lithium aluminium hydride in dioxane at room temperature[89] The reduction equation is as below :-

$$2(C_6H_5)_2TeBr_2 + LiAlH_4 \longrightarrow C_6H_5TeC_6H_5 + LiBr + AlBr_3 + 2H_2$$

Petragnani and Campos [90] obtained di(p-anisyl) or di(p-phenatyl)telluride by the reaction of bis(p-anisyl) or bis(p-phenatyl)tellurium ditelluride being refluxed for four and a half hours in toluene with di(p-anisyl) or di(p-phenetyl) tellurium dibromide respectively. They found that diarylditelluride did not decompose in boiling xylene (b.p. 137 to 140°C). The ditelluride was heated without solvent at 250°C and the formation of tellurium and diaryltelluride commenced at this temperature, but at or above 300°C a good yield of diaryltelluride was obtained.

Diphenyltelluride has been prepared by reducing triphenyltelluronium iodide with NaSH [86] according to the equation; -

$$(C_6H_5)_3TeI + NaSH \longrightarrow (C_6H_5)_2Te + C_6H_6 + NaI + S$$

Diarylditelluride was reduced by different methods.

Aryltelluriumtrihalides were reduced by $Na_2S.9H_2O$, $K_2S_2O_5$ or hydrogen sulphide to give diarylditelluride.

The reaction of Grignard reagents and telluriumdihalides gave ditelluride by-products.

The reduction of aryltelluriumtrihalides with potassium metabisulphite was used for the preparation of diaryltelluride. This method was employed by Morgan and co-workers [35, 40] Farrar [32] Drew [38] and Reichel and Kirschbaum [36]
This preparative method is commonly used for the synthesis of ditellurides. p-Methoxyphenyltelluriumtrichloride and p-ethoxyphenyltelluriumtrichloride have been reduced by aqueous potassium

metabisulphite in ice water to give a quantitative yield of di(p-methoxyphenyl)ditelluride and di(p-ethoxyphenyl)-ditelluride.

Also aryltelluriumtrichlorides (such as p-anisyltelluriumtrichloride or p-phenetyltelluriumtrichloride) may be reduced by molten sodium sulphide in a hydrate form ($Na_2S.9H_2O$) at 95 -100°C for fifteen minutes.[86, 37, 91]

In the reaction between tellurium dihalides and Grignard reagents, small amounts of ditelluride are detected, as by-products.[92,81]

Aryltelluriumtrichlorides are reduced to ditellurides by hydrazine in an ethanolic medium according to Bergman[39] Diaryltelluride is obtained by reducing diaryltelluriumdichloride in aqueous ethanol by adding a solution of hydrazine dissolved in ethanol and then refluxing.[39]

The reaction of some other potential ligands (e.g. methyl-3-mercaptopropionate or 1,3 di(2-pyridyl)-2-thiourea) with a number of tellurium(IV) compounds (such as, di(p-methoxyphenyl)telluriumdichloride, di(p-ethoxyphenyl)telluriumdichloride, p-methoxyphenyltelluriumtrichloride, p-ethoxyphenyltelluriumtrihalide, tellurium tetrachloride and tellurium tetrabromide) was also investigated under a variety of conditions in the course of the work for this thesis.

In the course of the reaction with the thio group, it was hoped that there would be a liberation of HCl. However, all the tellurium compounds used appeared to be strong oxidising agents, so the ligand was oxidised, giving a corresponding reduction of tellurium(IV) to tellurium(II), as reported for other sulphur containing ligands (i.e. thiourea).

Different products were obtained from the reaction of some tellurium(IV) compounds with 1,3 di(2-pyridyl)-2-thiourea.

The reduction products (i.e. $(p\text{-}CH_3OC_6H_4)_2Te$, $(p\text{-}CH_3OC_6H_4)_2Te_2$, $(p\text{-}C_2H_5OC_6H_4)_2Te$, and $(p\text{-}C_2H_5OC_6H_4)_2Te_2$) of the reactions were described and identified from their melting points, infrared spectra, and ^1H nmr spectra.

These tellurium compounds varied in their oxidising capacities. Some oxidised the ligand easily giving a precipitation of elemental tellurium. Others gave an ill-defined yellow precipitates, indicating that some reaction had occurred.

4.2 EXPERIMENTAL

4.2.1 Preparation of organotellurium compounds.

All organotellurium compounds (such as, p-methoxyphenyltellurium trichloride, p-ethoxyphenyltellurium trichloride, bis(p-methoxyphenyl)telluriumdichloride and bis(p-ethoxyphenyl)telluriumdichloride) were prepared by addition of tellurium tetrachloride to anisole or phenetole in chloroform or carbon tetrachloride. (Appendix I page 252)

4.2.2 Preparation of 1,3 di(2-pyridyl)-2-thiourea.

18.8 g. of 2-amino-pyridine was dissolved in 30 cm^3 of ethanol and then 30 cm^3 of carbondisulphide and 2 g. of potassium hydroxide was added. The mixture was refluxed for fifty-two hours and 100 cm^3 of water was added whilst the mixture was hot. The solution was cooled in an ice bath and a white precipitate was found. This precipitate was filtered off, washed with water, and then recrystallised by 60% ethanol and white needle crystals were obtained. Yield 7.5 g.
m.p. 160-161°C (lit. 161-162°C) [93]
[Found C, 57.30; H, 4.27; N, 23.67; $C_{11}H_{10}N_4S$ requires C, 57.36; H, 4.37; N, 24.33 %]

4.2.3 Reaction of methyl-3-mercaptopropionate with some tellurium(IV) compounds.

Methyl-3-mercaptopropionate was obtained from Aldrich Chemical Co. Inc.

4.2.3.1 Di(p-methoxyphenyl)telluriumdichloride.

0.48 g. (4 mmol.) of methyl-3-mercaptopropionate was added to 0.414 g. (1 mmol.) of di(p-methoxyphenyl)telluriumdichloride in a 25 cm^3 flask fitted with a drying tube. The diaryltelluriumdichloride was dissolved by the mercapto compound at room temperature. The reaction gave a strong evolution of hydrochloric acid gas and a light yellow solution was obtained. n-Butanol (5 cm^3) was added to this solution, which was then cooled to 0°C and white plate crystals were given. The crystals were filtered off and dried. Yield 0.30 g. m.p. 52-53°C (lit. 53-54°C) [35]

[Found C, 49.52; H, 4.25; Te, 37.14; $C_{14}H_{14}O_2Te$ requires C, 47.90; H, 4.13; Te, 37.35 %]

4.2.3.2 Di(p-ethoxyphenyl)telluriumdichloride.

Methyl-3-mercaptopropionate (0.48 g. : 4 mmol.) was added to di(p-ethoxyphenyl)telluriumdichloride (0.442 g. : 1 mmol.) in a 25 cm^3 flask fitted with a drying tube. The organotellurium compound was dissolved by thioaliphatic compound room temperature. The reaction gave a strong evolution of hydrochloric acid gas and a yellow solution was obtained. n-Butanol (5 cm^3) was added to this solution, which was cooled to 0°C and white needle crystals were found. The crystals were filtered off and dried. Yield 0.32 g. m.p. 64°C (lit. 64°C) [82]

[Found C, 52.21; H, 4.92; Te, 34.46; $C_{16}H_{18}O_2Te$ requires C, 51.95; H, 4.91; Te, 34.52 %]

4.2.3.3 p-Methoxyphenyltelluriumtrichloride.

To 0.682 g. (2 mmol.) of p-methoxyphenyltelluriumtrichloride, 0.72 g. (6 mmol.) of methyl-3-mercaptopropionate was added at room temperature. The mixture gave a strong evolution of hydrochloric acid and a brown precipitate was obtained. This precipitate was recrystallised in petroleum ether (30-40°C) under vacuum to give di(p-methoxyphenyl)ditelluride. Yield 0.25 g. m.p. 59°C (lit. 60°C) [86]

[Found C, 35.52; H, 3.12; $C_{14}H_{14}O_2Te_2$ requires C, 35.80; H, 3.01 %]

4.2.3.4 p-Ethoxyphenyltelluriumtrichloride.

0.72 g. (6 mmol.) of methyl-3-mercaptopropionate was added to 0.71 g. (2 mmol.) of p-ethoxyphenyltelluriumtrichloride. A strong evolution of hydrochloric gas was given off by the reaction and an orange precipitate was obtained. This precipitate was recrystallised in petroleum ether (80-100°C) by vacuum to obtain di(p-ethoxyphenyl)ditelluride. Yield 0.27 g. m.p. 108°C (lit. 109°C) [86]

[Found C, 38.73; H, 3.68; $C_{16}H_{18}O_2Te_2$ requires C, 38.61; H, 3.65 %]

4.2.4 Reaction of 1,3 di(2-pyridyl)-2-thiourea with some tellurium(IV) compounds.

4.2.4.1 p-Methoxyphenyltelluriumtrichloride.

A solution of 1.38 g. (6 mmol.) 1,3 di(2-pyridyl)-2-thiourea in 5 cm^3 of dry methanol was added to a solution of 0.682 g. (2 mmol.) p-methoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. A brown precipitate was obtained at room temperature and filtered off. This precipitate was recrystallised by petroleum ether (30-40°C) which gave a brown needle crystal. Yield 0.24 g. m.p. 58-59°C (lit. 60°C) [86] [Found C, 35.65; H, 3.15; $C_{14}H_{14}O_2Te_2$ requires C, 35.80; H, 3.01 %]

4.2.4.2 p-Ethoxyphenyltelluriumtrichloride.

1.38 g. (6 mmol.) of 1,3 di(2-pyridyl)-2-thiourea in 5 cm^3 of dry methanol was added to 0.71 g. (2 mmol.) of p-ethoxyphenyltelluriumtrichloride in 5 cm^3 of dry methanol. An orange precipitate was obtained at room temperature and filtered off. Petroleum ether (80-100°C) was used to recrystalise this precipitate and orange needle crystals were obtained. Yield 0.25 g. m.p. 108°C (lit. 109°C) [86] [Found C, 38.82; H, 3.72; $C_{16}H_{18}O_2Te_2$ requires C, 38.61; H, 3.65 %]

4.2.4.3 Tellurium tetrachloride.

Tellurium tetrachloride 0.27 g. (1 mmol.) in 5 cm^3 of dry methanol was added at room temperature to 0.92 g. (4 mmol.) of 1,3 di(2-pyridyl)-2-thiourea in 5 cm^3 of dry methanol. A black precipitate was obtained immediately.

For identification purposes the black precipitate was filtered off and dissolved in concentrated nitric acid. After heating to dryness, the residue obtained was dissolved in hydrochloric acid and finally diluted with distilled water. This solution was then run through the Atomic Absorption Spectrometer, which found a high percentage of tellurium present.

4.2.4.4 Tellurium tetrabromide.

0.92 g. (4 mmol.) of 1,3 di(2-pyridyl)-2-thiourea in 5 cm^3 of dry methanol was added at room temperature to 0.447 g. (1 mmol.) of tellurium tetrabromide in 5 cm^3 of dry methanol. A black precipitate was obtained immediately, which was identified by the same procedure as in tellurium tetrachloride reaction described.

4.2.4.5 Tellurium dioxide.

A solution of 0.92 g. (4 mmol.) of 1,3 di(2-pyridyl)-2-thiourea in a mixture of 3 cm^3 of concentrated hydrochloric acid and 3 cm^3 of distilled water, was added to a solution of tellurium dioxide 0.32 g. (2 mmol.) also dissolved in a mixture of 3 cm^3 of concentrated hydrochloric acid and 3 cm^3 of distilled water. A yellow precipitate formed immediately which was filtered off, washed with dry ether and dried under vacuum. The formula of the compound produced could not be obtained because the product was impure.

4.3 RESULTS AND DISCUSSION

The reduction products i.e. diaryltelluride or diarylditelluride were formed by the reaction of diaryltellurium dichlorides or aryltelluriumtrihalides with methyl-3-mercaptopropionate or 1,3 di(2-pyridyl)-2-thiourea. The melting points of the reduction products; di(p-methoxyphenyl)telluride, di(p-methoxyphenyl)ditelluride, di(p-ethoxyphenyl)telluride and di(p-ethoxyphenyl)ditelluride; agreed with literature values.[35,82,86] Also, the i.r. spectra agreed with published spectra.[33,55,94]

The proton nmr spectra of some tellurium compounds have been published[214,215] The spectra of the reduction products are shown in figures 4-1 to 4-7.

Methyl-3-mercaptopropionate and 1,3 di(2-pyridyl)-2-thiourea were reacted with some tellurium (IV) compounds. When reacting methyl-3-mercaptopropionate with diaryltelluriumdichloride or aryltelluriumtrichloride, tellurium(IV) was found to be reduced to tellurium(II) and diaryltelluride or diarylditelluride was obtained respectively.

The reaction gave a strong evolution of gas, and when tested with a solution of silver nitrate, a white precipitate was found, which proved the evolution to be hydrochloric acid gas.

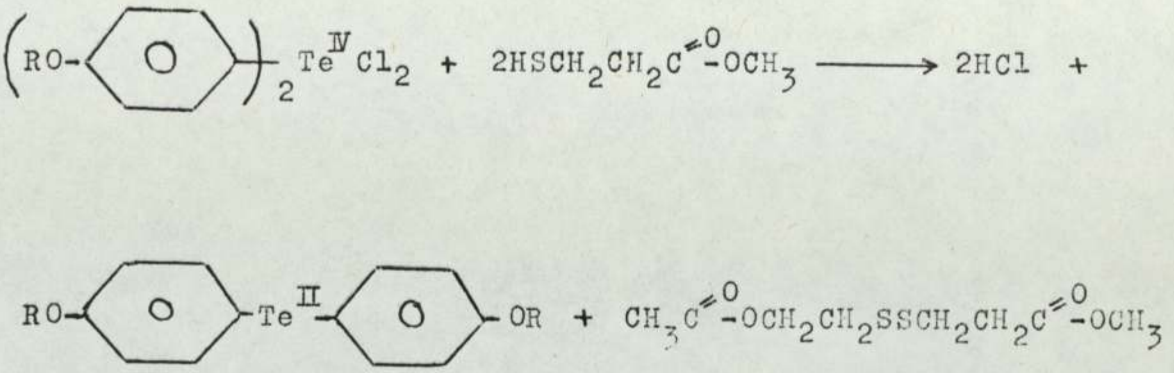
The yield of diaryltelluride was 87% and diarylditelluride 53%.

The reaction of 1,3 di(2-pyridyl)-2-thiourea with aryltelluriumtrichloride or tellurium tetrahalide produced diarylditelluride and elemental tellurium respectively. Tellurium(IV) was reduced to tellurium(II) or free tellurium (Te^o). The yield of diarylditelluride was 50%.

On comparing the method used (i.e. the reaction of methyl-3-mercaptopropionate with diaryltelluriumdichloride) for the preparation of diaryltelluride with those of Rohrbaech's[82], Morgan and co-workers[35,84,85] and the molten $Na_2S.9H_2O$ method[86-88]; the reaction was carried out at room temperature, no solvent was used, and less time was taken.

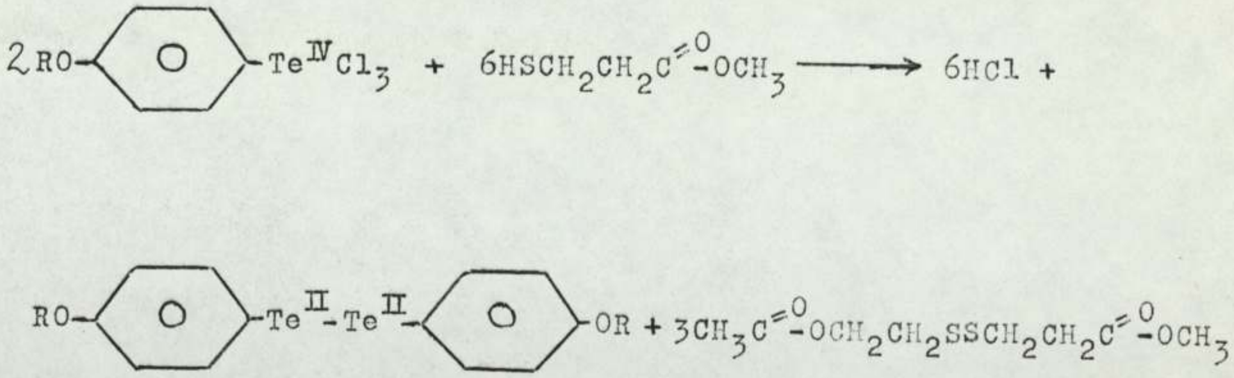
On comparing the method used (i.e. the reaction of methyl-3-mercaptopropionate with aryltelluriumtrichloride) for the preparation of diarylditelluride with those of Morgan and co-workers[35,40], Farar's[32], Drew's[38], Reichel and Kirschbaum's[36], Reichel's[86], Petragnani's[37] and Vicentini and co workers'[91]; the reaction was carried out at room temperature and again less time was required.

In the reaction of di(p-methoxyphenyl)telluriumdichloride or di(p-ethoxyphenyl)telluriumdichloride with methyl-3-mercaptopropionate, tellurium(IV) was again reduced to tellurium(II) and di(p-methoxyphenyl)telluride or di(p-ethoxyphenyl)telluride was formed. The reaction for the equation may be represented as follows :-



Where R = CH_3 or C_2H_5

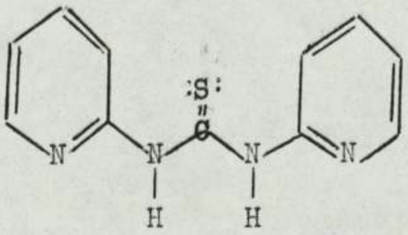
Di(p-methoxyphenyl)ditelluride or di(p-ethoxyphenyl)ditelluride was obtained by the reaction of p-methoxyphenyltelluriumtrichloride or p-ethoxyphenyltelluriumtrichloride with methyl-3-mercaptopropionate and tellurium(IV) was also reduced to tellurium(II). The reaction may be represented by the equation :-



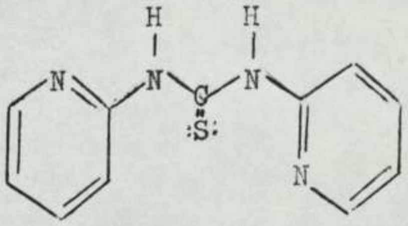
Where R = CH_3 or C_2H_5

Therefore, methyl-3-mercaptopropionate reduced tellurium(IV) to tellurium(II) and then became oxidised to formamidinium disulphide.

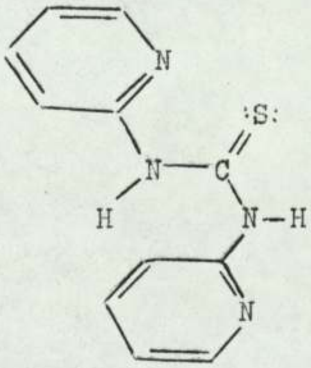
When using a 1,3 di(2-pyridyl)-2-thiourea model the following configurations were obtained :-



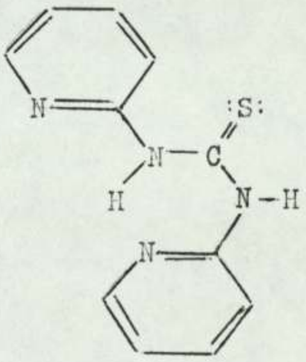
(A)



(B)

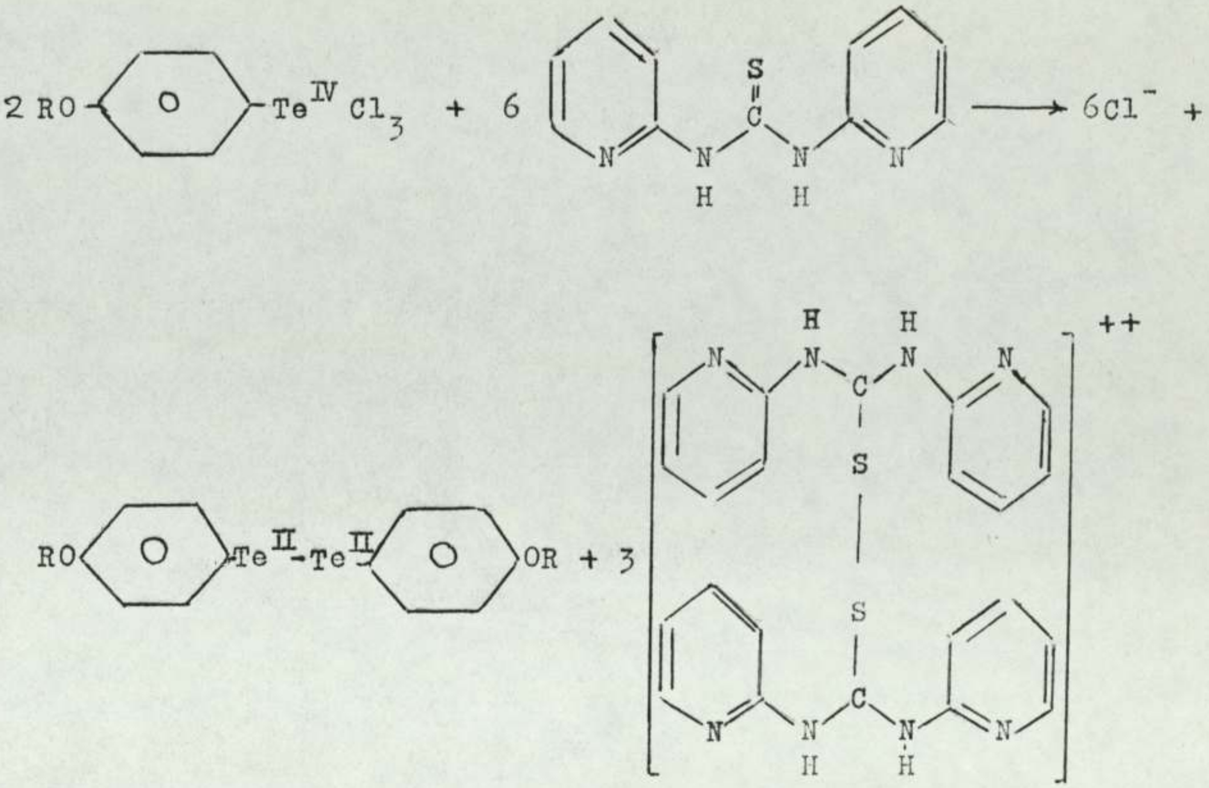


(C)



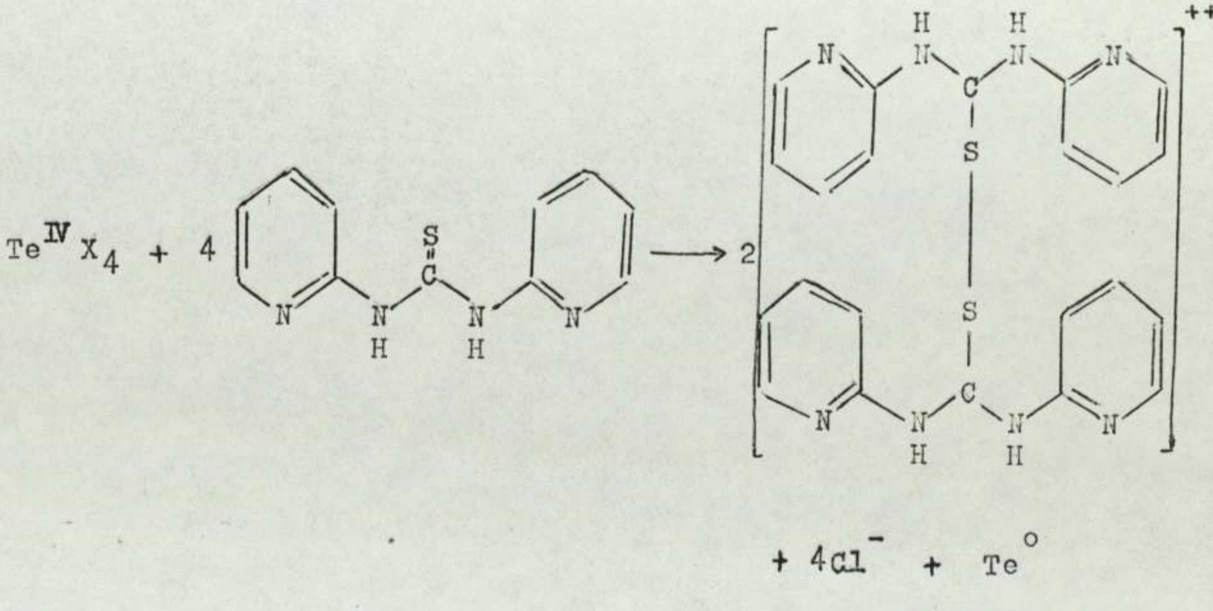
(D)

Di(p-methoxyphenyl)ditelluride or di(p-ethoxyphenyl)-ditelluride was obtained from the reaction of p-methoxyphenyl-telluriumtrichloride or p-ethoxyphenyltelluriumtrichloride with 1,3 di(2-pyridyl)-2-thiourea; and tellurium(IV) was subsequently reduced to tellurium(II). The reaction equation is as follows :-



Where R = CH_3 or C_2H_5

Free tellurium was obtained by reaction of tellurium tetrachloride or tellurium tetrabromide according to equation:-



Where X = Cl or Br

Diaryltellurides [di(p-methoxyphenyl)telluride and di(p-ethoxyphenyl)telluride] and diarylditellurides [di(p-methoxyphenyl)ditelluride and di(p-ethoxyphenyl)-ditelluride] were also characterised by their ^{1}H nmr and i.r. spectra.

Some low frequency bands of diaryltelluriumdichloride and diaryltelluride have been reported by McWhinnie and Patel [55] The range assigned in their paper for ν(Te-Cl) in di(p-methoxyphenyl)telluriumdichloride and di(p-ethoxyphenyl)-telluriumdichloride were 271-247 cm^{-1} and 274-263 cm^{-1} respectively.

On examination of di(p-methoxyphenyl)telluride and di(p-ethoxyphenyl)telluride (the products of diaryltelluride) on the i.r. spectrophotometer, the bands at 271-247 cm^{-1} and 274-263 cm^{-1} due to ν(Te-Cl) in di(p-methoxyphenyl)tellurium-dichloride and di(p-ethoxyphenyl)telluriumdichloride respectively were absent in diaryltelluride.

McWhinnie and Thavornyutikarn [33,94] reported the i.r. and Raman spectra of some aryltelluriumtrihalides and diaryldi-tellurides. The bands at 323-295 cm^{-1} and 334-298 cm^{-1} are due to ν(Te-Cl) in p-methoxyphenyltelluriumtrichloride and p-ethoxyphenyltelluriumtrichloride respectively. The bands at 184-156 cm^{-1} and 186 cm^{-1} are said to be due to ν(Te-Te) in di(p-methoxyphenyl)ditelluride and di(p-ethoxyphenyl)di-telluride respectively.

On examination of the suspected di(p-methoxyphenyl)ditelluride and di(p-ethoxyphenyl)ditelluride by vibrational analysis, new bands at 184-156 cm^{-1} and 186 cm^{-1} were shown respectively. These bands agree with the results obtained by McWhinnie and Thavornyutikarn[33,94] and are due to ν(Te-Te).

The ^{1}H nmr spectra were measured at 100 MHZ and 60 MHZ for the $CDCl_3$ or CCl_4 solution with a Varian R10 instrument (tetramethyl silane (TMS) internal standard).

The ^{1}H nmr spectra of methyl-3-mercaptopropionate was measured at 60 MHZ for the CCl_4 solution, and this is shown in figure 4-1. This spectra shows a triplet for the HS group at 8.2 τ, a quartet for the CH_2 group at 7.30 τ and a singlet for the CH_3 group at 6.37 τ

Figures 4-2/3/4 show the proton nmr spectra of di(p-methoxyphenyl)telluride, di(p-methoxyphenyl)ditelluride and di(p-methoxyphenyl)telluriumdichloride in CCl_4 or $CDCl_3$. The proton nmr spectra of these compounds show the centre of resonance for the singlet from the methyl group, the doublet for two orthoprotons, and the doublet for two meta-protons as indicated by the following :-

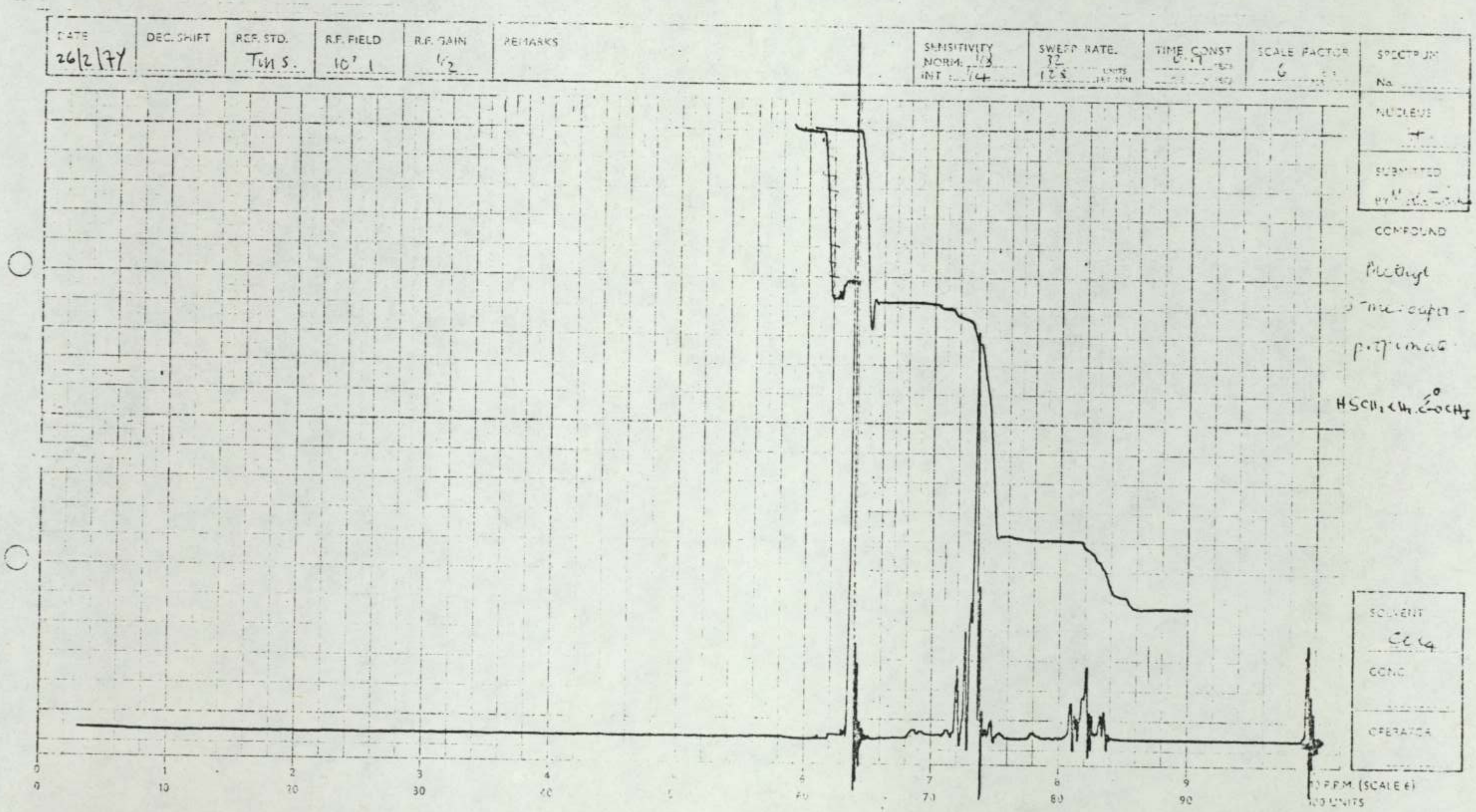


Fig. 4-1 ^{1}H nmr spectra of methyl-3-mercaptopropionate

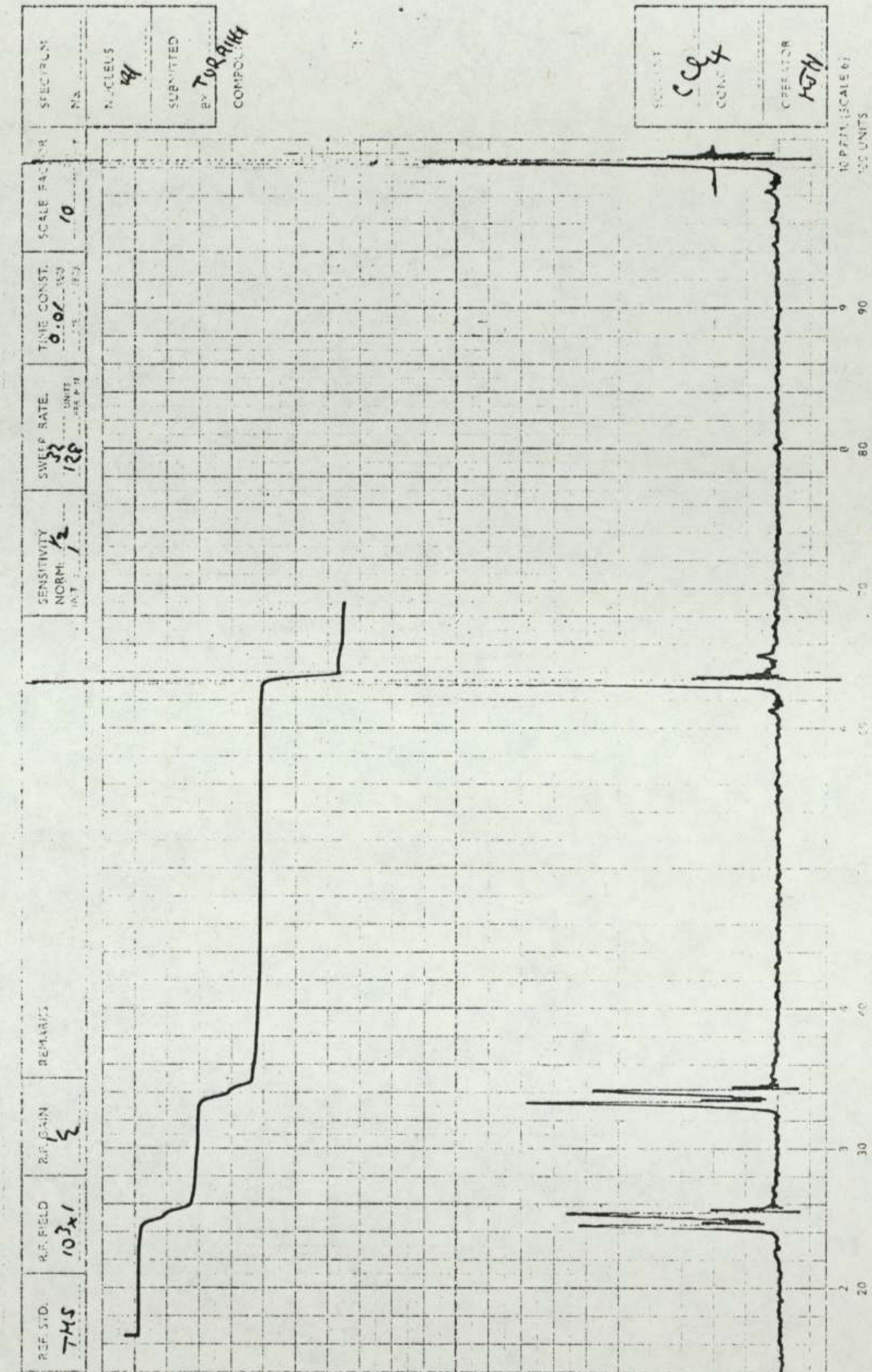


Fig. 4-2 ¹H nmr spectra of bis(p-methoxyphenyl)telluride

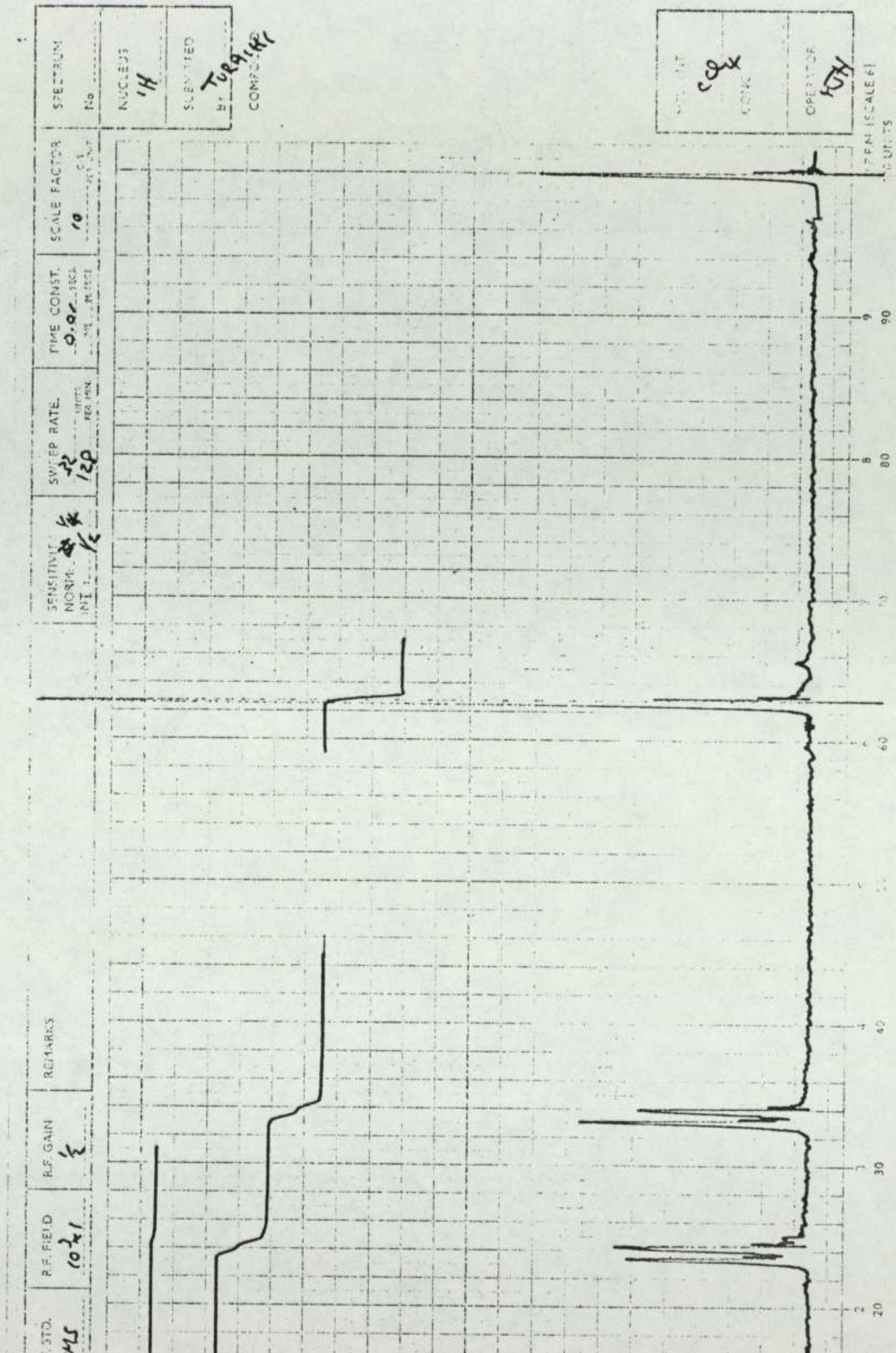


Fig. 4-3 ^{1}H nmr spectra of bis(p-methoxyphenyl)ditelluride

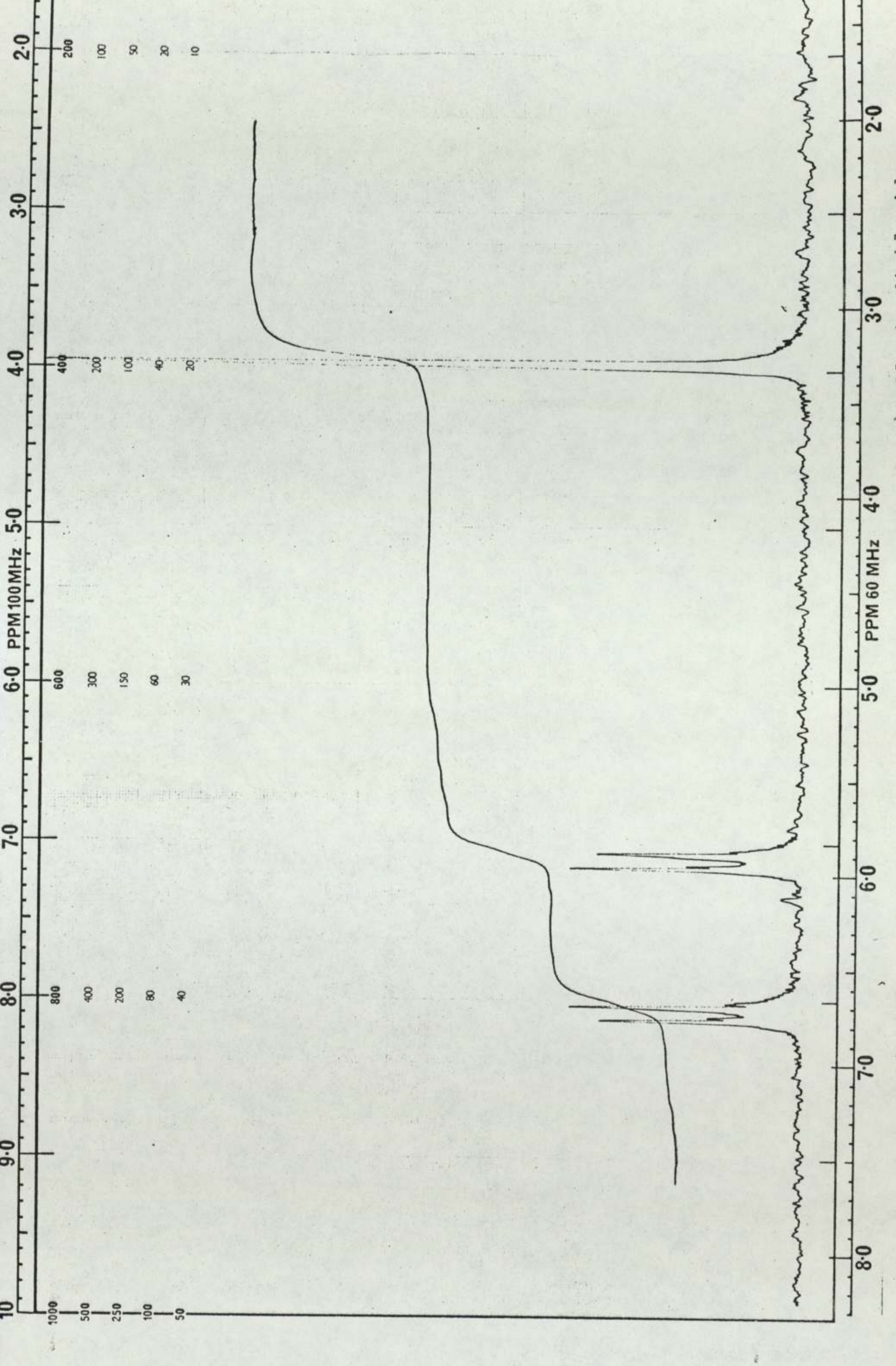


Fig. 4-4 'H nmr spectra of bis(p-methoxyphenyl)telluriumdichloride

Compounds	A.τ	B.τ	C.τ
di(p-methoxyphenyl)telluride	6.22	3.35	2.35
di(p-methoxyphenyl)ditelluride	6.27	3.35	2.45
di(p-methoxyphenyl)tellurium-dichloride	6.70	4.06	3.25

Where A - singlet of the methyl group
B - doublet of the orthoprotons
C - doublet for two metaprotons

The proton nmr spectra of di(p-ethoxyphenyl)telluride, di(p-ethoxyphenyl)ditelluride and di(p-ethoxyphenyl)tellurium dichloride are shown in figures 4-5/6/7 also the centre of resonance for the triplet from the methyl group (ratio 1:2:1) the quartet from the methylene (ratio 1:2:2:1), the doublet for the two protons at the ortho positions (relative to the ethoxy group ratio 1:1) and the doublet for the two meta protons (ratio 1:1) are as follows :-

Compounds	A.τ	B.τ	C.τ	D.τ
di(p-ethoxyphenyl)telluride	8.45	5.95	3.25	2.35
di(p-ethoxyphenyl)ditelluride	8.55	5.95	3.25	2.35
di(p-ethoxyphenyl)tellurium-dichloride	8.73	6.58	4.12	3.30

Where A - the triplet from the methyl group
B - the quartet from the methylene
C - the doublet from the two protons
D - the doublet for the two meta protons

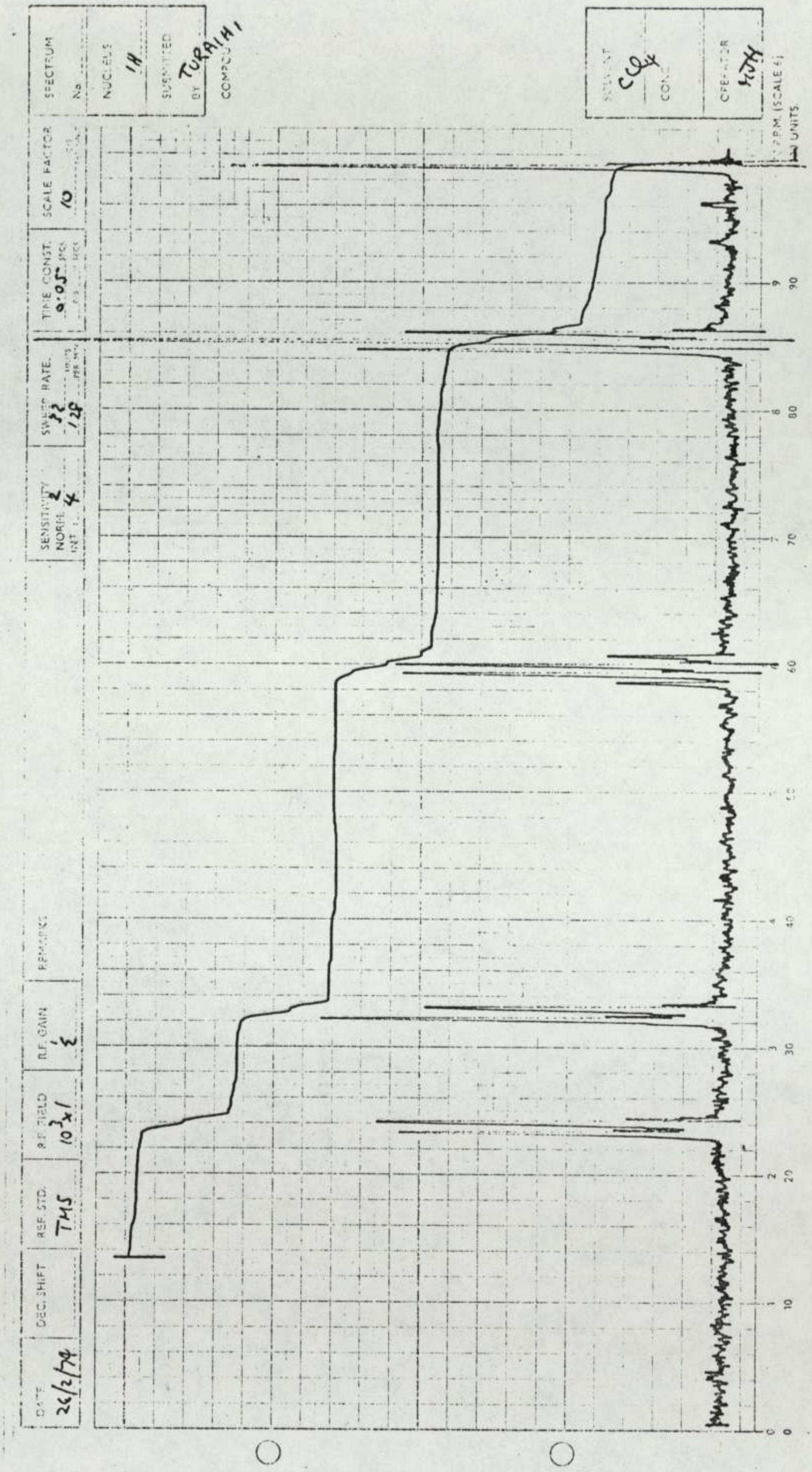


Fig. 4-5 ^{1}H nmr spectra of bis(p-ethoxyphenyl)telluride

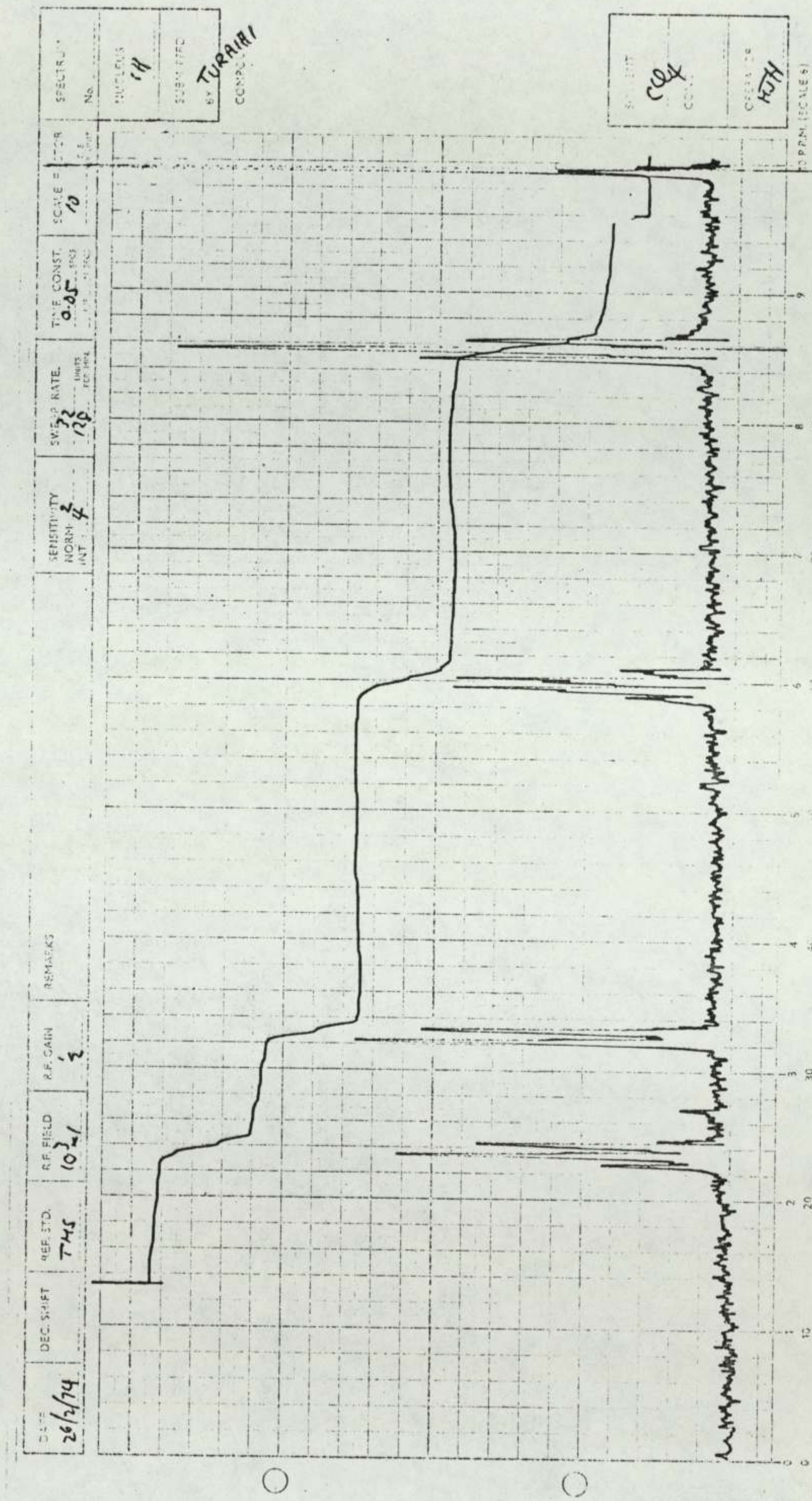


Fig. 4-6 'H nmr spectra of bis(p-ethoxyphenyl)ditelluride

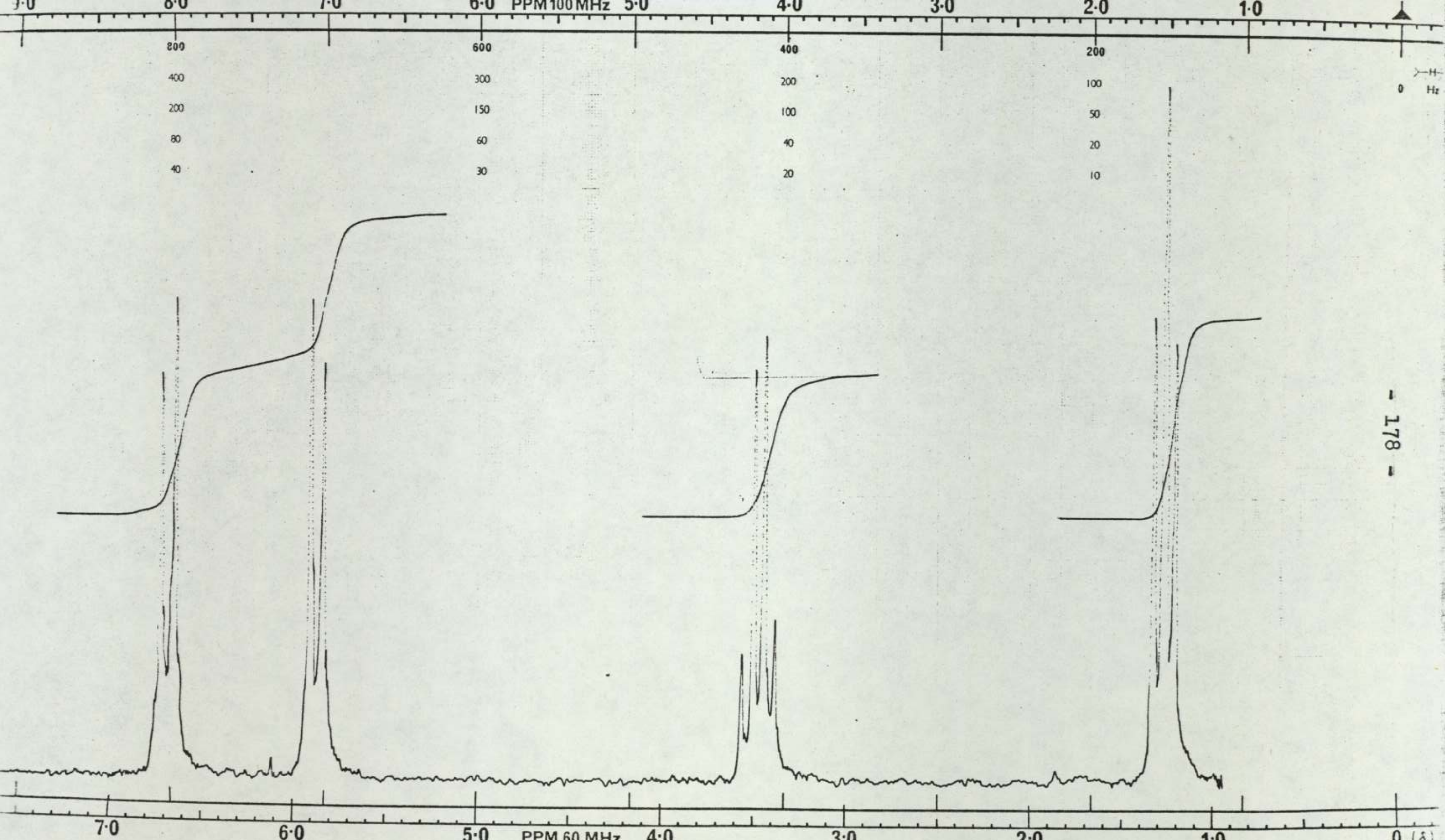


Fig. 4-7 'H nmr spectra of bis(p-ethoxyphenyl)telluriumdichloride

The melting points, infrared and proton nmr spectra all indicate that the products from the reaction of methyl-3-mercaptopropionate with diaryltelluriumdichloride or aryltelluriumtrichloride were diaryltelluride or diarylditelluride respectively and from the reaction of 1,3 di(2-pyridyl)-2-thiourea with aryltelluriumtrichloride was diarylditelluride.

CHAPTER V

Chemistry of selenium compounds.

5.1 INTRODUCTION

5.1.1 Chemistry of Selenium

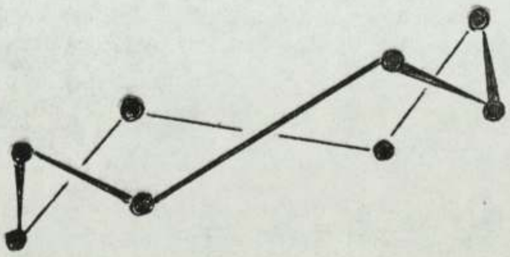
Selenium belongs to groups VIB of the Periodic Table and is located between sulphur and tellurium. Selenium has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^4$ and the outer electron shell is $4s^2\ 4p^4$. It has six electrons in the valency shell, and only needs two more to form the noble gas octet structure. Also accordingly it is hardly surprising that its chemistry shows a marked non-metallic chemistry. Chemically selenium is similar to sulphur and also to some extent tellurium and exhibits both metallic and predominatly non-metallic characteristics.

Selenium may be found in several allotropic forms[95] (ring-chain equilibrium, amorphous selenium (α-selenium), and crystalline selenium), and has a ring-chain equilibrium similar to that of sulphur. All of these are stable at room temperature. Selenium can also form on a molecular level, Se, Se_2, Se_4, Se_6, Se_8 and Se_n aggregates[96]. Only Se_8 and Se_n polymeric chains are known to exist at room temperature[97] At high temperatures the equilibrium shifts towards chains of up to 10,000 selenium atoms, and it is possible to extract Se_8 rings with carbon disulphide from these large polymeric chains. Briegleb[98] has shown that at 120°C, 55% soluble selenium (Se_8 rings) was extracted, whilst at 650°C only 14% was extracted, proving that at higher temperature less selenium is obtained.

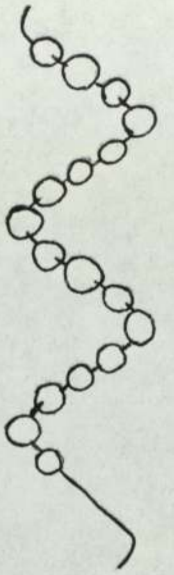
Amorphous selenium's (α-selenium) behavior is very similar to that of organic glasses. Selenium is a free-flowing liquid at above 230°C. Eisenberg[99] shows amorphous selenium rings change to a hard brittle glass below 31°C. However, above 31°C and below 230°C, selenium had a vitreous form, and above 230°C a liquid form.

Colloidal selenium (a particulate form of amorphous selenium) can be prepared by reducing cold aqueous solution of selenious acid with hydrazine, sulphur dioxide, hydrogen selenide etc. Colloidal hexagonal selenium crystals[100] were found after heating the colloidal amorphous selenium above 60°C.

Crystalline selenium has three forms α-monoclinic, β-monoclinic and hexagonal (trigonal). The α-monoclinic and β-monoclinic forms of selenium are red and dark red respectively, and are composed of Se_8 rings. The hexagonal form consists of helical Se_n chains, and are referred to as β-selenium or grey selenium.



the structure of Se_8 rings



long helical chains of selenium atoms in Se_n

Primary oxidation states of selenium are -2, 0, + 2, + 4, and + 6 as shown below :-

Oxidation State:	Example:	Structure:
6	SeF_6	Regular Octahedron (O_h)
+4	$SeCl_4$	Distorted tetrahdron due to inert pair effect probably producing trigonal bi-pyramid.
+2	$Se(SO_2CH_3)_2$	Few simple bivalent selenium
-2	H_2Se	Expect linear shape (bond angle 91°)

The chemistry of organoselenium compounds has been reviewed in several text books[2,3,8,95,115] The most important compounds are discussed here and in Chapter VI.

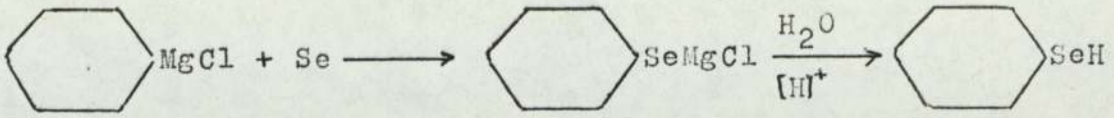
Organoselenium compounds generally contain selenium in the oxidation state 2 or 4 and the main types are selenols ($RSe^{II}H$), selenocyanates ($RSe^{II}CN$), selenides ($RSe^{II}R$), diselenides (RSeSeR), and organoselenium-halides (organoselenium mono-halides ($RSe^{II}X$), organoselenium dihalides ($R_2Se^{IV}X_2$) and organoselenium trihalides ($RSe^{IV}X_3$). There are also large numbers of selenium analogues of compounds such as aldehydes, ketones, and carboxylic acids.

5.1.2 Selenols.

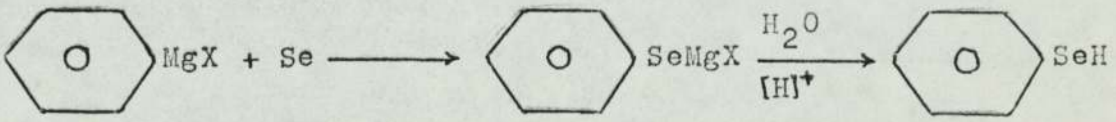
Aliphatic selenols which are known by the name of selenomercaptans are selenium analogs of alcohols and thiols. Siemens[101] reported the first synthesis of a selenol in 1847 by distilling a mixture of potassium selenide and potassium ethyl sulphate to give ethaneselenol. Wöhler and Dean[102] prepared methaneselenol by reacting dimethylsulphate and potassium selenide as shown in the equation below, -

$$(CH_3)_2OSO_3 + 2KHSe \longrightarrow 2CH_3SeH + K_2SO_4$$

Selenols may also be prepared by the use of a Grignard reagent but this method is more satisfactory for the production of aromatic selenols than that of aliphatic selenols. Kraff and Lyons[103] prepared the first aromatic selenols (benzeneselenol and phenylselenol) in 1894. Mailhe and Murat[104] reported that the cyclohexylmagnesium chloride reacts with selenium in anhydrous ether to yield an intermediate containing-selenium which on hydrolysis gave cyclohexaneselenol, as indicated by following equation :-

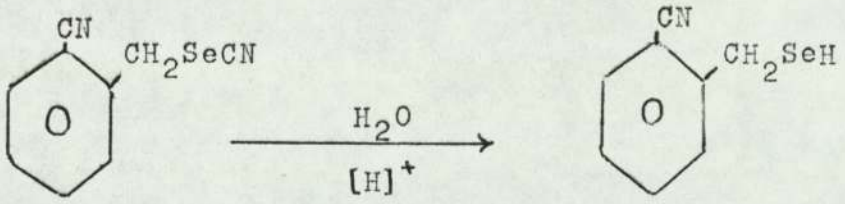


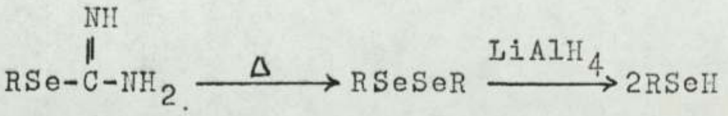
Tabourg[105] and Wuyts & Cosyns[106] discovered the reaction of elemental selenium with aromatic Grignard reagents, as in the following equation :-



Also aliphatic selenols can be prepared from alkyl halides[107], selenocyanates[108], selenopseudourea[109] and by the reduction of diselenide[110], as shown in the equations :-

$$RX + HSe^- \longrightarrow RSeH + X^-$$





$$RSe\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2 \xrightarrow{\Delta} RSeSeR \xrightarrow{LiAlH_4} 2RSeH$$

$$(RSe\text{-})_2 \xrightarrow[Liq.NH_3]{2Na} 2RSeNa \xrightarrow{[H]^+} 2RSeH$$

Aromatic selenols can also be prepared from aryllithium compounds[111] by reduction of diselenides[103] and selenocyanates as follows,-

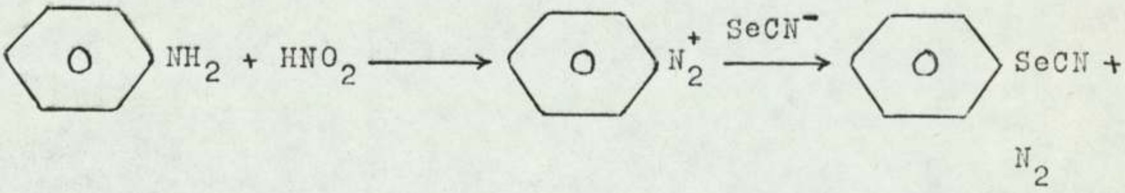
$$ArLi + Se \xrightarrow{Et_2O} ArSeLi \xrightarrow{H_2O} ArSeH + LiOH$$

$$(C_6H_5Se-)_2 \xrightarrow[\substack{C_2H_5OH \\ (2)\,[H]^+}]{(1)\ Na} 2C_6H_5SeH$$

$$ArSeCN \xrightarrow[[H]^+]{Zn} ArSeH$$

5.1.3 Arylselenocyanates

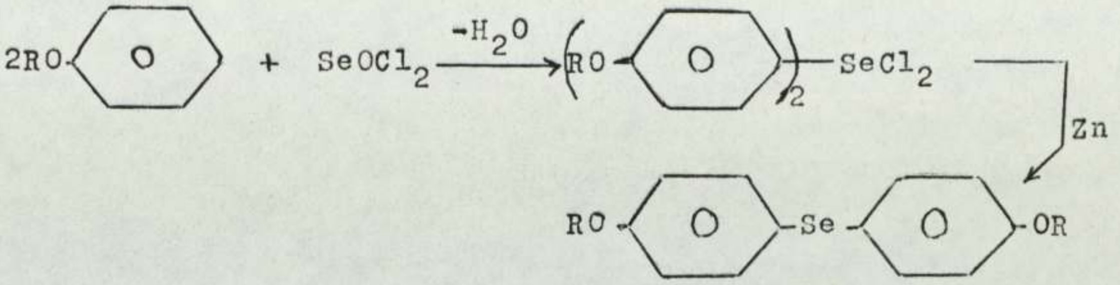
Bauer[112] in 1913 reported the first method for the preparation of phenylselenocyanate and substituted phenylselenocyanate by using a Sandmeyer type reaction in which selenocyanate ion is added to a diazolised arylamine:-



Selenocyanates provide a convenient starting material from which trihalide may be obtained.

5.1.4 Diarylselenide

Diarylselenides may be prepared by the reaction of aromatic ethers with selenium oxychloride in anhydrous ether, forming first the diarylselenium dichloride[113] which may then be reduced by powdered zinc to give the corresponding selenide :-



5.1.5 Diaryldiselenide

Generally, dialkyldiselenides are yellow/orange oils, but diaryldiselenides are yellow solids. Diselenides can be prepared by, air oxidation of selenols, or from selenocyanates. The most important method of obtaining diselenide is by alkaline hydrolysis of selenocyanates. The mechanism for this reaction is not clear-cut but Challenger et al[114] suggested that selenols are possibly the initial products of the hydrolysis, -

$$2ArSeCN + H_2O \longrightarrow 2ArSeH + 2HCNO$$

$$2ArSeH \xrightarrow{[O]} (ArSe-)_2 + H_2O$$

Another likely mechanism for the preparation of diselenide by alkaline hydrolysis of selenocyanate is one in which a selenenic acid is the intermediate product, as shown in the scheme below :-[115]

$$RSeCN + H_2O \longrightarrow RSeOH + HCN$$

$$RSeOH + RSeCN \longrightarrow (RSe-)_2 + HCNO$$

5.1.6 Arylselenium monohalides

The organoselenium monohalides (organoseleneyl halides) are generally solids and the chlorides are colourless/yellow but bromides are yellow to intense red. These compounds may be prepared by addition of halogen to a diselenide using chloroform as a solvent[116-120] as indicated below :-

$$(RSe-)_2 + Br_2 \longrightarrow 2RSeBr$$

When organoselenium trihalides are heated or reduced under pressure, seleneyl halides and halogen were found[121-125]

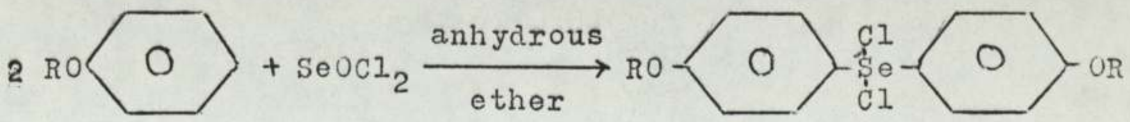
$$RSeX_3 \rightleftharpoons RSeX + X_2$$

Seleneyl halide was obtained when treating aromatic selenocyanates with bromine in dry chloroform.[126]

$$ArSeCN + Br_2 \longrightarrow ArSeBr + BrCN$$

5.1.7 Diarylselenium dihalides

Organoselenium dihalides as mentioned previously may be prepared by reacting selenium oxychloride with an aromatic compound in diethylether at room temperature for five days.[113,127,128]



5.1.8 Arylselenium trihalides

Organoselenium trihalides are obtained by the reaction of a selenol, diselenide or arylselenocyanate with halogen. This reaction can also produce monohalides depending upon the ratios of the reactants employed.[123,126]

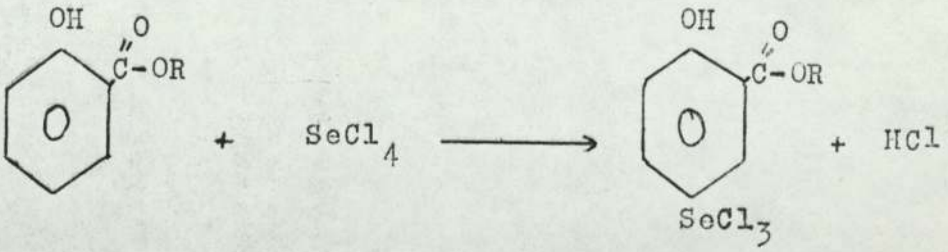
$$2\ C_6H_5SeH + 2Br_2 \longrightarrow 2C_6H_5SeBr + 2HBr$$

$$C_6H_5SeSeC_6H_5 + Br_2 \longrightarrow 2C_6H_5SeBr$$

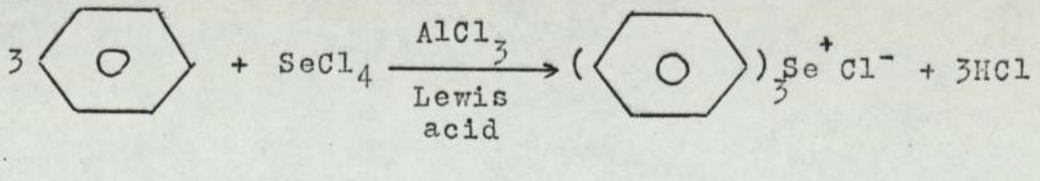
$$C_6H_5SeCN + Br_2 \longrightarrow C_6H_5SeBr + BrCN$$

$$C_6H_5SeBr + Br_2 \longrightarrow C_6H_5SeBr_3$$

Nelson et al[132] found that selenium tetrachloride reacts with ethers of salicylic acid in the absence of any solvent, to form arylseleniumtrichloride. This reaction involves the hydrogen para from the hydroxyl group .[132]



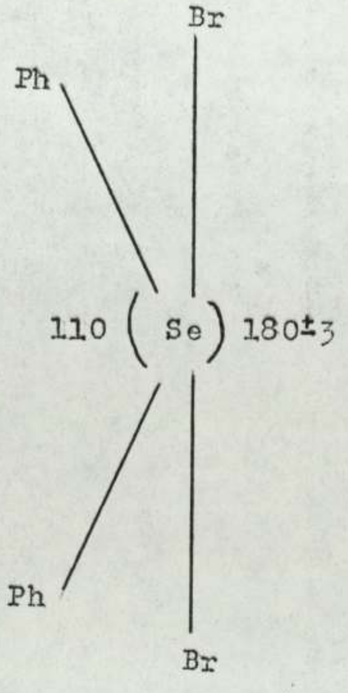
Although in the presence of anhydrous aluminium trichloride, benzene reacts with selenium tetrachloride and gives a moderate yield of diphenylselenide[133] a higher molecular ratio of benzene results in triphenylselenonium chloride.[134,135]

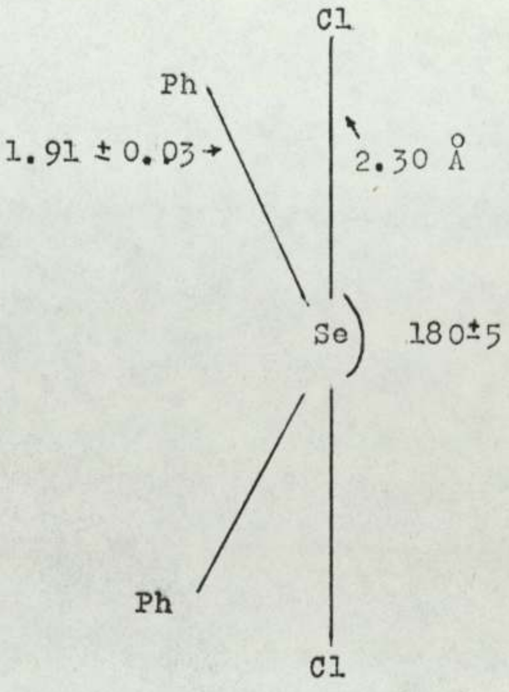


5.1.9 The structure of some organoselenium compounds.

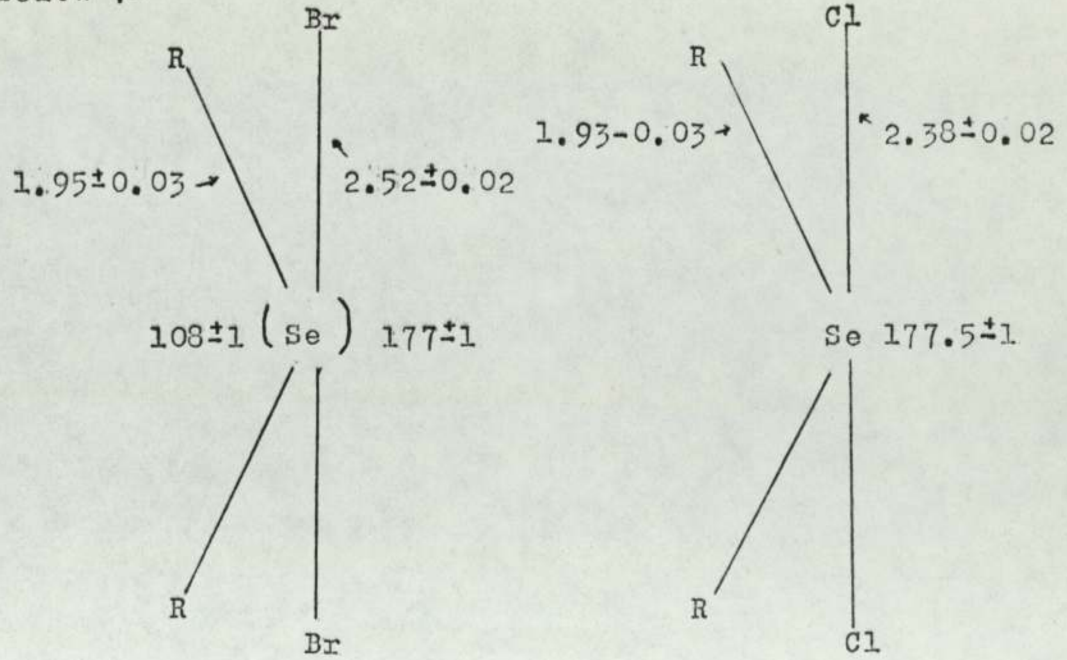
The crystal structures of diphenylseleniumdichloride, diphenylseleniumdibromide, di-p-tolylseleniumdichloride and di-p-tolylseleniumdibromide were investigated by McCullough and co-workers[129,130,153] The structure of diphenylseleniumdibromide has been shown to be orthorhombic bipyramidal. The dichloride has eight molecules per unit, whilst the dibromide has only four. The crystal structure of the di-p-tolylseleniumdichloride shows that there are two molecules per unit cell[153] The molecular structure of all these diarylselenium dihalides is a slightly distorted trigonal bipyramid, with a selenium atom at the centre, halogen atoms at the apices and two phenyl or p-tolyl groups plus an unshared pair of electrons in the equatorial positions.

The structures of diphenylseleniumdihalide, are shown below :-



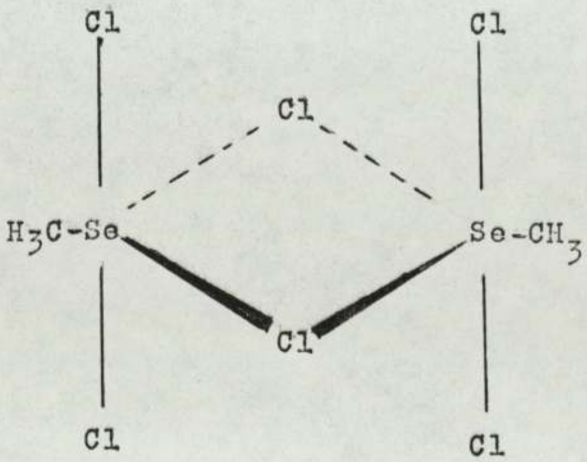


The structures of di-p-tolylseleniumdihalide, are shown below :-



The bond distances found in diphenylseleniumdihalide and di-p-tolylseleniumdihalide were Se-Br and Se-Cl which are larger than the sum of the covalent radii and the molecular symmetry is C_{2v}.

Wynne and George[131] have reported the structure of arylseleniumtrihalide and suggested that methylseleniumtrichloride is dimeric (see below) in methylene chloride.



5.1.10 Stereochemistry.

A few organoselenium compounds have been examined by 'X' ray analyses[129,153,157,172.171] and the stereochemistries of the donor atom reported.

Considering the number of lone pairs and number of bond pairs it is possible that the stereochemistry of selenium(II) and selenium(IV) may be predicted. The symmetry of molecules for selenium(II) (two lone pairs, two bond pairs) or selenium(IV) (one lone pair and four bond pairs) may be postulated as C_2 or C_{2v}. Hendra and Park[168] interpreted the spectroscopic data for Se_2Cl_2 and Se_2Br_2 based on assignments for C_2 symmetry, but Hayward and Hendra[50] suggested that selenium tetrachloride and selenium tetrabromide have a C_{2v} covalent structure. Wynne and co-workers[157] reported dibromo(tetramethylthiourea) selenium(II) to have a C_{2v} symmetry. Greenwood & Strugham[169] and Hendra & Jović[170] suggested that $(SeBr_6)^{2-}$ anion is octahedral but they do not agree fully on the assignments.

5.1.11 Vibrational spectra.

Horn and Paetzold[154] have discussed the infrared and Raman spectra of some organoselenium compounds such as $(C_6H_5)_2\,Se(NO_3)_2$, $(C_6H_5)_2Se(CH_3CO_2)_2$, $(C_6H_5)_2Se(CF_3CO_2)_2$ and $(C_6H_5)_2Se(CH_3SO_3)_2$. All of these compounds also possess a distorted ψ trigonal bipyramidal structure (molecular symmetry C_{2v}). The bands which are associated with the vibrations of the phenyl groups were also assigned.

Wynne & George [156] have reported the infrared and Raman spectra of dimethylseleniumdihalides and bands at 293 and 270 cm^{-1} for $(CH_3)_2SeCl_2$ were assigned to ν(Se-Cl).

The infrared and Raman spectra of some dialkyl and diaryldiselenides, [162-164] alkyl and arylselenocyanate, [165,166] diaryl and dialkylseleniumdihalides [152,154,156] seleno bis-(2-mercaptoisobutyric acid), [167] dichloro and dibromo (tetramethylthiourea)selenium(II) [157] selenium tetrabromide, selenium tetrachloride [50] Se_2Cl_2, Se_2Br_2 [168] and anions $(SeBr_6)^{2-}$ [169,170] have been reported.

It is not surprising that Raman spectra of compounds containing Se-Br bonds are particularly intense as the most abundant isotopes of selenium are 78(25.52%) and 80(49.82%) and bromine 79(50.53%) and 81(49.47%) and therefore the fundamental vibrations are associated with atoms of nearly equal mass. The red colour of arylseleniumtribromide is presumed to originate from elemental bromine as the colour is similar.

In this chapter, the far infrared and Raman spectra of diarylseleniumdichlorides (such as diphenylseleniumdichloride, di(p-methoxyphenyl)seleniumdichloride and di(p-ethoxyphenyl)-seleniumdichloride) which have not previously been reported in detail has been investigated. The spectra were examined during the course of this work and are given in table 5-4 The assignments are based on the published data for the analogous tin and tellurium compounds, such as $(C_6H_5)_2SnCl_2$[155] and $(C_6H_5)_2TeCl_2$[55] which are said to have similar structures.

McWhinnie and Thavornyutikarn[33] have reported the infrared and Raman spectra of phenyltelluriumtrihalides and suggest that the compounds are associated to some degree.

The infrared and Raman spectra of data for the corresponding arylseleniumtrihalides has not been reported. Vibrational analysis of arylseleniumtribromide (such as phenylselenium-tribromide, p-chlorophenylseleniumtribromide, p-bromophenyl-seleniumtribromide and p-tolylseleniumtribromide) was investigated during the course of this work, and is reported in this Chapter.

These compounds were found to decompose by the beam of an infrared spectrophotometer range 4000-250 cm^{-1}, but when using an interferometer, satisfactory spectra were obtained. Arylseleniumtribromides, were ultimately decomposed by long exposure to the laser beam of the Raman spectrometer but good spectra were obtained initially. Since arylselenium-tribromides decompose on storing, the infrared spectra were recorded immediately and the Raman spectra were carried out within twenty-four hours.

Analytical data for freshly prepared arylseleniumtri-bromides were obtained and gave satisfactory results (see table 5-6).

5.2 EXPERIMENTAL

5.2.1 Preparation of tetraphenyllead $(C_6H_5)_4Pb$

Tetraphenyllead was prepared using the method due to Setzer et al[136] To a stirred solution of phenylmagnesium bromide (0.5 mol.) in 150 cm^3 of dry diethylether, 150 cm^3 of dry toluene was added followed by 60 g. (0.22 mol.) of finely ground lead dichloride added in small portions. The mixture was refluxed for six hours and hydrolysed with a crushed ice-hydrochloric acid mixture. The organic layer was separated and the aqueous layer separated off. The latter was extracted with chloroform in a soxhlet extractor and then the solution obtained evaporated under vacuum which gave 11.5 g. of tetraphenyllead when recrystallised from chloroform. m.p. 225-226°C (lit. 225-226°C) [136,137] [Found C, 55.10; H, 3.78; $C_{24}H_{20}Pb$ requires C, 55.9; H, 3.88 %]

5.2.2 Preparation of triphenylleadchloride $(C_6H_5)_3PbCl$

To a boiling solution of 12 g. tetraphenyllead in 130 cm^3 of chloroform, dry hydrogen chloride (in vapour form) was passed for fifty-five minutes. A small amount of diphenylleaddichloride which formed was filtered off. The filtrate was evaporated to dryness and the residue obtained was then crystallised from absolute alcohol. Triphenylleadchloride (9.0 g.) was obtained. m.p. 204-205°C (lit. 205°C) [138] [Found C, 45.82; H, 3.27; $C_{18}H_{15}PbCl$ requires C, 46.56 H, 3.39 %]

5.2.3 Preparation of organoselenium compounds.

5.2.3.1 Preparation of diphenylseleniumdichloride $(C_6H_4)_2SeCl_2$

Diphenylseleniumdichloride was prepared by two methods as described below :-

1st Method : Reaction of seleniumtetrachloride and tetraphenyllead.

4.4 g. (0.02 mol.) selenium-tetrachloride and 10.3 g. (0.02 mol.) tetraphenyllead in a total volume of 80 cm^3 toluene or benzene were heated under reflux for six hours. The hot reaction mixture and the filtrate evaporated under vacuum to about 15 cm^3. This red coloured solution was allowed to cool in a refrigerator for two days when yellow crystals were obtained which were then recrystallised twice from benzene. Yield 35% . Improved yields of 50% were subsequently obtained, by reaction in the cold over fourteen hours, followed by evaporation after removal of the diphenylleaddichloride. m.p. 177°C. (lit. 178°C)[139]

[Found C, 47.95; H, 3.42; Se, 26.07; $C_{12}H_{10}SeCl_2$ requires C, 47.72; H, 3.28; Se, 25.98 %]

2nd Method : Reaction of seleniumtetrachloride and triphenylleadchloride.

4.4 g. (0.02 mol.) seleniumtetrachloride and 9.4 g. (0.02 mol.) triphenylleadchloride in a total volume of 100 cm^3 toluene were heated under reflux for six hours. The precipitated diphenylleaddichloride was filtered off from the hot reaction mixture and the filtrate was evaporated under vacuum to about 15 cm^3. After two days in a refrigerator yellow crystals formed which were recrystallised from benzene Yield 20% m.p. 178 °C (lit. 178 °C) [139]

[Found C, 48.33; H, 3.50; Se, 26.09; $C_{12}H_{10}SeCl_2$ requires C, 47.72; H, 3.28; Se, 25.98 %]

5.2.3.2. Preparation of di(p-methoxyphenyl)selenium dichloride $(p\text{-}CH_3OC_6H_4)_2SeCl_2$.

Selenium tetrachloride 11.25 g. (0.1 mol.) was added to 21.6 g. (0.2 mol.) of anisole contained in a 100 cm^3 flask fitted with a drying tube. Owing to the exothermic nature of the reaction, and strong evolution of hydrochloric acid gas, the contents were cooled in an ice bath for forty-five minutes and finally left at room temperature overnight or for twenty-six hours. The yellow-orange crystals which formed in the dark-red coloured liquid were filtered off and washed with a little dry diethylether. The dried crystals were dissolved in the smallest possible volume of dry chloroform, reprecipitated by addition of dry diethylether, filtered off and dried in a vacuum dessicator. Yield 45% m.p. 163 °C (lit. 163 °C) [128]

[Found C, 46.19; H, 4.03; Se, 21.86; $C_{14}H_{14}O_2SeCl_2$ requires C, 46.30; H, 3.87; Se, 21.70 %]

5.2.3.3 Preparation of di(p-ethoxyphenyl)seleniumdichloride $(p\text{-}C_2H_5OC_6H_4)_2SeCl_2$.

Selenium tetrachloride 11.25 g. (0.1 mol.) was added to 24.4 g. (0.2 mol.) of phenetole contained in a 100 cm^3 flask fitted with a drying tube. Using the same procedure as for the preparation of di(p-methoxyphenyl)seleniumdichloride di(p-ethoxyphenyl)seleniumdichloride was obtained.

Yield 67% m.p. 139°C (lit. 139°C)[128]

[Found C, 48.84; H, 4.64; Se, 20.18; $C_{16}H_{18}O_2SeCl_2$ requires C, 49.00; H, 4.60; Se, 20.16 %]

5.2.4 Determination of selenium by titration method.

All selenium compounds were analysed for their selenium content. 100-130 mg. of each compound was dissolved in dry methanol and 2 g. of potassium iodide and 2 cm^3 of 4M H_2SO_4 were added. The liberated iodine was treated with a standard solution of sodium thiosulphate.[145,146]

The reactions involved are :-

$$\begin{array}{l} (C_6H_5)_2SeCl_2 + 2\varepsilon^- \longrightarrow (C_6H_5)_2Se + 2Cl^- \\ \qquad 2I^- - 2\varepsilon^- \longrightarrow I_2 \\ \hline (C_6H_5)_2SeCl_2 + 2I^- \longrightarrow (C_6H_5)_2Se + I_2 + 2Cl^- \end{array}$$

$$2I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

$$\therefore \quad (C_6H_5)_2SeCl_2 = 2Na_2S_2O_3$$

here: 2 litres 1M $Na_2S_2O_3$ reacts with 1Se

2 litres 1M $Na_2S_2O_3$ reacts with 78.96 g.Se

1 litre 1M $Na_2S_2O_3$ reacts with $\frac{78.96}{2}$ g.Se

1 cm^3 of 1M $Na_2S_2O_3$ reacts with $\frac{78.96}{2000}$ g.Se

1 cm^3 of 0.1M $Na_2S_2O_3$ reacts with $\frac{78.96}{20000}$ g.Se

hence 1.0 cm^3 of 0.1M $Na_2S_2O_3$ reacts with 3.948 mg.Se. The selenium content in diarylseleniumdichlorides are shown in table 5-1

The same procedure may be used for determining the selenium content in arylseleniumtribromides. The reactions involved are :-

$$2RSeBr_3 + 6I^- \longrightarrow RSeSeR + 6Br^- + 3I_2$$

where R = C_6H_5, p-BrC_6H_4, p-ClC_6H_4 or p-$CH_3C_6H_4$

also,-

$$2C_6H_5SeBr_3 + 6\varepsilon^- \text{———} C_6H_5SeSeC_6H_5 + 6Br^-$$

$$6I^- - 6\varepsilon^- \text{———} 3I_2$$

$$2C_6H_5SeBr_3 + 6I^- \text{———} C_6H_5SeSeC_6H_5 + 6Br^- + 3I_2$$

$$3I_2 + 6Na_2S_2O_3 \text{———} 6NaI + 3Na_2S_4O_6$$

$$\therefore\ 2C_6H_5SeBr_3 = 6Na_2S_2O_3$$

$$1C_6H_5SeBr_3 = 3Na_2S_2O_3$$

here 3 litres 1M $Na_2S_2O_3$ reacts with 1Se

3 litres 1M $Na_2S_2O_3$ reacts with 78.96 g.Se

1 litre 1M $Na_2S_2O_3$ reacts with $\frac{78.96}{3}$ g.Se

1 cm^3 of 1M $Na_2S_2O_3$ reacts with $\frac{78.96}{3000}$ g.Se

1 cm^3 of 0.1M $Na_2S_2O_3$ reacts with $\frac{78.96}{30000}$ g.Se

hence 0.1 cm^3 of 0.1M $Na_2S_2O_3$ reacts with 2.632 mg.Se. The selenium content in arylseleniumtribromides are shown in table 5-2.

The 0.1M sodium thiosulphate was standardised by $\frac{M}{60}$ "Analar" potassium iodate.

TABLE 5-1

Determination of selenium content in diarylseleniumdichloride by titration method.

Compounds	Vol. of 0.1M $Na_2S_2O_3$ needs (cm^3)	wt. of sample in mg.	Se % found	Se % calc.
$(C_6H_5)_2SeCl_2$ [a]	7.0 *	106.0	26.07	25.98
$(C_6H_5)_2SeCl_2$ [b]	7.60	115.0	26.09	25.98
$(C_6H_5)_2SeCl_2$ [c]	7.30	110.4	26.11	25.98
$(CH_3OC_6H_4)_2SeCl_2$ [d]	5.80	104.7	21.86	21.70
$(CH_3OC_6H_4)_2SeCl_2$ [e]	5.90	106.3	21.91	21.70
$(C_2H_5OC_6H_4)_2SeCl_2$ [f]	6.10	119.5	20.18	20.16
$(C_2H_5OC_6H_4)_2SeCl_2$ [g]	5.90	115.2	20.22	20.16

a. Reaction of $(C_6H_5)_4Pb$ + $SeCl_4$

b. Reaction of $(C_6H_5)_3PbCl$ + $SeCl_4$

c. Reaction of $(C_6H_5)_2Se$ + nitric acid and hydrochloric .

d. Reaction of anisole + $SeCl_4$

e. Reaction of anisole + $SeOCl_2$

f. Reaction of phenetole + $SeCl_4$

g. Reaction of phenetole + $SeOCl_2$

* Each 1 cm^3 0.1M of $Na_2S_2O_3$ reacts with 3.948 mg. Se.

TABLE 5-2

Determination of selenium content in arylseleniumtribromide by titration method.

Compounds	Vol. of 0.1M $Na_2S_2O_3$ cm^3.	wt. of sample in mg.	Se % found	Se % calc.
$C_6H_5SeBr_3$	1.68 *	22.10	20.09	19.96
p-$BrC_6H_4SeBr_3$	1.61	25.10	16.84	16.67
p-$ClC_6H_4SeBr_3$	1.87	26.30	18.73	18.36
p-$CH_3C_6H_4SeBr_3$	1.89	26.30	18.91	19.27

*each 1 cm^3 0.1M of $Na_2S_2O_3$ reacts with 2.632 mg. Se.

5.3 DISCUSSION

5.3.1 Diarylseleniumdichloride.

Similar synthetic routes for the preparation of diarylselenium and diaryltellurium compounds are known.[10,95,115,146,147] The routes to diarylseleniumdihalide are reviewed here.

Benzene is known to react with $SeCl_4$ in the presence of anhydrous aluminium(III)chloride giving a moderate yield of diphenylselenide [133], but using a Lewis acid such as $AlCl_3$ and higher ratios of benzene results in the formation of triphenylselenoniumchloride $(C_6H_5)_3Se^+Cl^-$

$$C_6H_6 + SeCl_4 \xrightarrow{AlCl_3} (C_6H_5)_3Se^+Cl^- + 3HCl$$

A yield of 60% $(C_6H_5)_3TeCl$ was given by a molecular ratio of 3/1 $AlCl_3/TeCl_4$ using an analoguous method by Güther and co-workers [148] Diphenyltelluriumdichloride (45%) and phenyltelluriumtrichloride (17%) were isolated when a lower ratio of 2/1, $AlCl_3/TeCl_4$ was used.

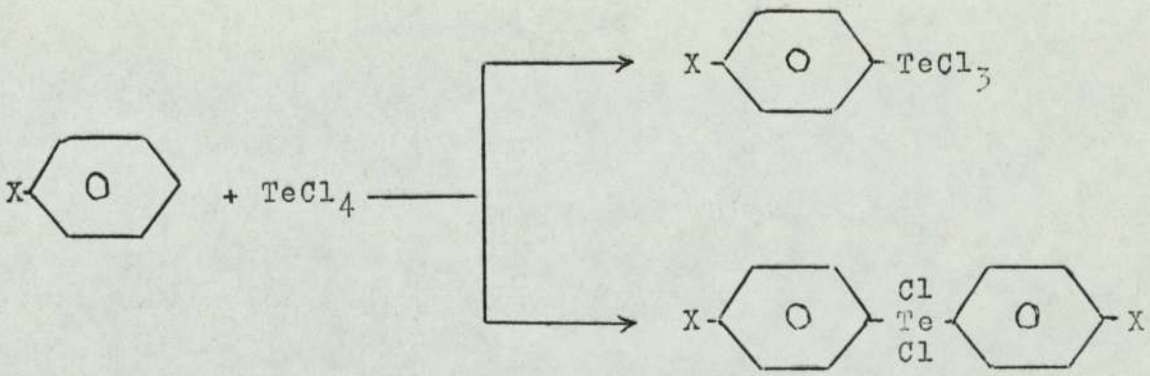
$$C_6H_6 + TeCl_4 \xrightarrow{AlCl_3} C_6H_5TeCl_3 + HCl$$

$$C_6H_6 + C_6H_5TeCl_3 \xrightarrow{AlCl_3} (C_6H_5)_2TeCl_2 + HCl$$

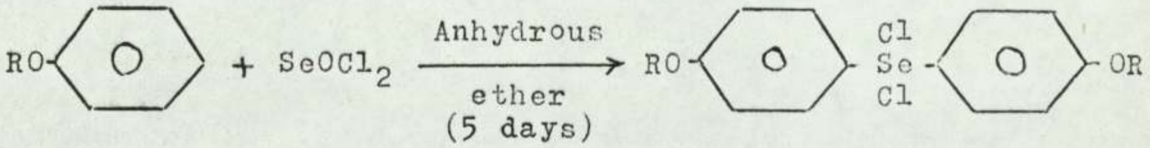
$$C_6H_6 + (C_6H_5)\ TeCl_2 \xrightarrow{AlCl_3} (C_6H_5)_3Te^+Cl^- + HCl$$

The presence of Lewis acids are essential when reacting C_6H_6 and $TeCl_4$ except when certain activating substituents X (where X = RO, HO, R_2N, RS) are present.[39,148,150] Thus $TeCl_4$

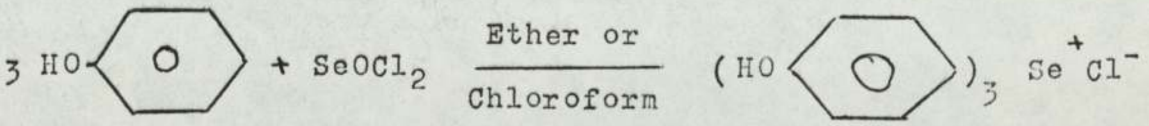
with C_6H_5X gives a mixture of products.



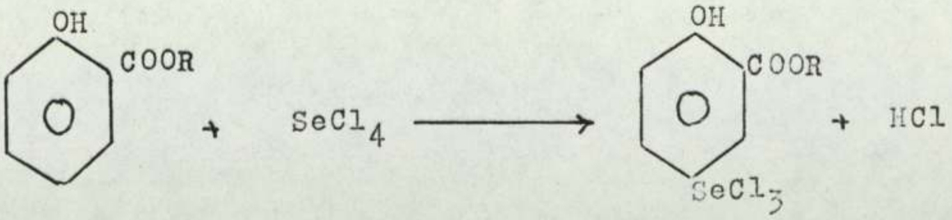
In the reaction of selenium oxychloride with an aromatic compound using anhydrous ether media, at room temperature, a para activating substituent must be present in the aromatic compounds.[127,128]



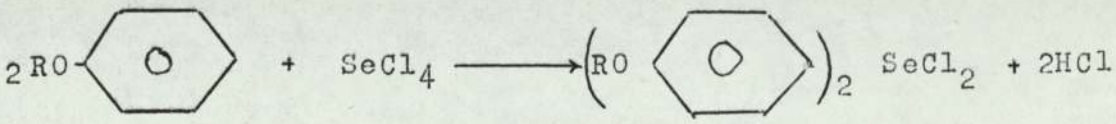
Morgan and Burstall[151] reported that the reaction of selenium oxychloride with an aromatic compound (such as phenol) in anhydrous ether or chloroform gives triarylselenoniumchloride.



Nelson and co-workers[132] found that selenium tetrachloride reacts with esters of salicylic acid (in the absence of solvent) and forms arylseleniumtrichloride.



The possible reaction of selenium tetrachloride with aromatic ethers has not previously been reported. However, it has been found in the work reported here that anisole and phenetole will react over twenty-six hours with selenium tetrachloride (in the absence of solvent) and gives good yields of bis(p-methoxyphenyl)seleniumdichloride and bis(p-ethoxyphenyl)-seleniumdichloride under controlled conditions.[152]



Pant [31] described the reaction of aryllead compounds with tellurium tetrachloride, as in the equation below:-

$$(C_6H_5)_4Pb + TeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2PbCl_2$$

In the analoguous reaction of selenium tetrachloride with an aryllead compound, the product obtained was diarylseleniumdichloride:-

$$(C_6H_5)_4Pb + SeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2SeCl_2 + (C_6H_5)_2PbCl_2$$

A 90% yield of phenyltelluriumtrichloride was obtained by reacting triphenylleadchloride with tellurium tetrachloride in dioxane [31] but when using selenium tetrachloride a lower yield (20%) of diphenylseleniumdichloride was obtained.

TABLE 5-3

Reactants	Main Product	m.p. °C Found (lit.)	Yield	Analytical data				
					C%	H%	Se%	Cl%
$(C_6H_5)_4Pb + SeCl_4$	$(p\text{-}C_6H_5)_2SeCl_2$	177	50%	Found	47.95	3.42	26.07	23.40
		(178)		Calc.	47.72	3.28	25.98	23.33
$(C_6H_5)_3PbCl + SeCl_4$	$(p\text{-}C_6H_5)_2SeCl_2$	178	20%	Found	48.33	3.50	26.09	23.53
		(178)		Calc.	47.72	3.28	25.98	23.33
$CH_3OC_6H_5 + SeCl_4$	$(p\text{-}CH_3OC_6H_4)_2SeCl_2$	163	45%	Found	46.19	4.03	21.86	19.68
		(163)		Calc.	46.30	3.87	21.70	19.48
$C_2H_5OC_6H_5 + SeCl_4$	$(p\text{-}C_2H_5OC_6H_4)_2SeCl_2$	139	67%	Found	48.84	4.64	20.18	18.31
		(139)		Calc.	49.00	4.60	20.16	18.09
$CH_3OC_6H_5 + SeOCl_2$	$(p\text{-}CH_3OC_6H_4)_2SeCl_2$	162	75%	Found	46.05	3.87	21.91	19.70
		(163)		Calc.	46.30	3.87	21.70	19.48
$C_2H_5OC_6H_4 + SeOCl_2$	$(p\text{-}C_2H_5OC_6H_4)_2SeCl_2$	138	71%	Found	49.47	4.84	20.22	18.23
		(139)		Calc.	49.00	4.60	20.16	18.09
$C_6H_5NH_2 \xrightarrow[KOH/Se]{NaNO_2/HCl} (C_6H_5)_2Se \xrightarrow[HCl]{HNO_3}$	$(p\text{-}C_6H_5)_2SeCl_2$	176	65%	Found	47.93	3.45	26.11	23.42
		(178)		Calc.	47.72	3.28	25.48	23.33

$$(C_6H_5)_3PbCl \; + \; SeCl_4 \xrightarrow{\text{toluene}} (C_6H_5)_2SeCl_2 \; + \; 2(C_6H_5)_2PbCl_2$$

Characterisation of the products obtained from the reaction of selenium tetrachloride with anisole, phenetole, tetraphenyllead, and triphenylleadchloride was made by the chemical analyses, infrared and Raman spectra and melting points.

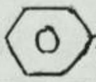
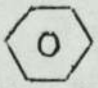
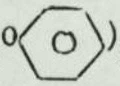
Analytical data for diarylseleniumdichlorides are given in table 5-3.

5.3.2 Vibrational spectra.

The infrared and Raman spectra of diarylseleniumdichlorides, (such as diphenylseleniumdichloride, di(p-methoxyphenyl)seleniumdichloride and di(p-ethoxyphenyl)seleniumdichloride are reported in table 5-4. The bands at 250-275 cm^{-1} and 245-255 cm^{-1} were assigned to $\nu_{sym.}$(Se-Cl) and $\nu_{asym.}$(Se-Cl) respectively. This proposal is consistent with the long bond length Se-Cl reported for diphenylseleniumdichloride.[130] Wynne and co-workers[157] assigned weak Raman bands at $\Delta\nu$ = 138 cm^{-1} to the Cl-Se-Cl deformation mode, for dichloro-(tetramethylthiourea)selenium(II). Therefore, the Raman bands at $\Delta\nu$ = 120-140 cm^{-1} for the diarylseleniumdichloride are tentatively assigned to δ(Se-Cl_2). The band assignments associated with vibrations of the phenyl groups were made in comparison with the published data for diphenyltindichloride[155] diphenyltelluriumdichloride[55] diphenylselenide, bromobenzene and p-bromoanisole. McWhinnie and Patel[55] reported the

TABLE 5-4

The i.r. and Raman spectra of some diarylseleniumdichloride 360-100 cm^{-1}.

( $)_2SeCl_2$		$(CH_3O$  $)_2SeCl_2$		$(C_2H_5O$  $)_2SeCl_2$		Assignment
i.r.	Raman	i.r.	Raman	i.r.	Raman	
329s	335vw	344s	345vw	356m	355vw	t)) or ν (Se-Ph) t')
307s	310vw	310w	310vw	336vs	338vw	
275vs	267vs	255s	250vs	272s	263vs	ν_s (Se-Cl)
	248s	245s		253m		ν_{as} (Se-Cl)
225vs	225w	245s		253m		Phenyl u
203vs		235s	235msh	225s	225w	Phenyl u'
173w		190m		186w	180vw	Phenyl x
151m						Phenyl x'
140m	132m	135s		134s	135s	δ $(Se-Cl_2)$
	120w		127mw			
105vw	107ms		112ms	110w	110m	unassigned

wavenumbers of the phenyl t and u modes for the diphenyltelluriumdichloride which are 249-272 cm^{-1} and 198-230 cm^{-1} respectively, but the bands found for the diarylseleniumdichlorides are 307-356 cm^{-1} and 203-253 cm^{-1}. So as expected the phenyl t and u modes all occur at slighlly higher wavenumbers than for the corresponding diphenyltelluriumdichloride.[55] The main Raman bands for $(C_6H_5)_2SeBr_2$ at $\Delta\nu = 157\ cm^{-1}$, ν(Se-Br) are well clear of the phenyl u band at $\Delta\nu = 249\ cm^{-1}$ [158] but the phenyl u modes for diarylseleniumdichlorides appear as shoulders or are hidden under the main Raman bands.

5.3.3 Arylseleniumtrihalides.

Organoseleniumtrihalides may be obtained by the reaction of a selenol, diselenide or arylselenocyanate with halogen and the methods used have been summarised by several authors.[123,126,159-161]

The infrared and Raman spectra of phenylseleniumtribromide, p-chlorophenylseleniumtribromide, p-bromophenylseleniumtribromide, and p-tolylseleniumtribromide, was carried out. Analysis of these spectra seems to suggest a more symmetrical environment for the selenium atoms than for the tellurium atoms in the corresponding phenyltelluriumtrihalides [33] as there are fewer coincidences of bands in the region 250-120 cm^{-1}.

Allun and co-workers [164] reported a strong Raman line at 293 cm^{-1} for di-n-butyldiselenide (c.p. 317 cm^{-1} for Br-Br in elemental bromine). Hayward and Hendra [164] reported

TABLE 5-5

The far infrared and Raman spectra of arylseleniumtribromide between 50-330 cm^{-1}

$C_6H_5SeBr_3$		p-$BrC_6H_4SeBr_3$		Tentative Assignments
i.r.	Raman	i.r.	Raman	
55s				
105m		103ssh		δ(Se-Br)
110ssh	120msh	120vs	116ssh	
	142w	137s		
	170m		170s	Phenyl x mode and δ(Se-Br)
179s		177s		
202vs	198vs	203vs		ν(Se-Br)
	214vs		211s	
220vs		220vs		
	242vs		233s	Phenyl u (Se) mode
254vs		250vs		
278s	280s	274msh	282vs	ν(Se-Br)
298s		295s	300vs	
305s				
330s		327s	322vw	Phenyl t (Se) mode

Table 5-5 ...

The far infrared and Raman spectra of arylseleniumtribromide between 50–330 cm^{-1}.

$p\text{-}ClC_6H_4SeBr_3$		$p\text{-}CH_3C_6H_4SeBr_3$		Tentative Assignments
i.r.	Raman	i.r.	Raman	
100s		94m		δ(Se-Br)
121wsh		120s		
134ssh	132s	140m	136ssh	
152vs				
	158w	161msh	159vs	Phenyl x mode and δ(Se-Br)
167vw				
203vs	196s	196vs		ν(Se-Br)
		207vs	208m	
210vs		217vs		
			231m	Phenyl u (Se) mode
	250w		248w	
258s			262w	
	267s			
280vw		284s		ν(Se-Br)
302s				
	310m	309s		
		316s	316vw	Phenyl t (Se) mode
330s		330s		

the frequency of the infrared bands for selenium tetrabromide at 266, 247, and 236 cm^{-1} as being due to selenium-bromine stretching, but it is suggested that the bands observed between 200-310 cm^{-1} for the arylseleniumtribromides described in this thesis are associated with selenium-bromine stretching modes. The bands of the infrared and Raman spectra of $SeBr_2$ have been assigned by Hendra and Park[168] The bands at 260 cm^{-1} due to ν(Se-Br); 286 cm^{-1} due to ν(Se-Se), and those between 110-150 cm^{-1} are said to be due to deformation modes. The strong bands at 184 and 150 cm^{-1} for dibromo-(tetramethylthiourea)selenium(II) [157] were assigned to asymmetric Br-Se-Br and symmetric stretching modes respectively but the lower frequency bands at 100-112 cm^{-1} were assigned to Br-Se-Br deformation modes. The infrared bands at 164 and 196 cm^{-1} observed for dimethylseleniumdibromide were associated with Se-Br stretching modes [21] but the Raman spectra of diphenylseleniumdibromide is said to show only two bands, one strong band at 157 cm^{-1} and a weaker one at 249 cm^{-1} [158] Other bands could have been missed due to poor sample preparation. The absorptions between 100-316 cm^{-1} are thus associated by the selenium-bromine stretching and deformation vibrations depending upon the environment of the selenium atom.

The infrared and Raman bands for arylseleniumtribromide are given in table 5-5 and the far-infrared spectra are shown in fig. 5-1/2/3/4.

Arylseleniumtribromides have bands in the region 100-220 cm^{-1} i.e., at frequencies similar or the same as found for $(SeBr_6)^{2-}$ [169,170] However, it is interesting to note that the Raman active bands in $(SeBr_6)^{2-}$ are infrared and/or Raman

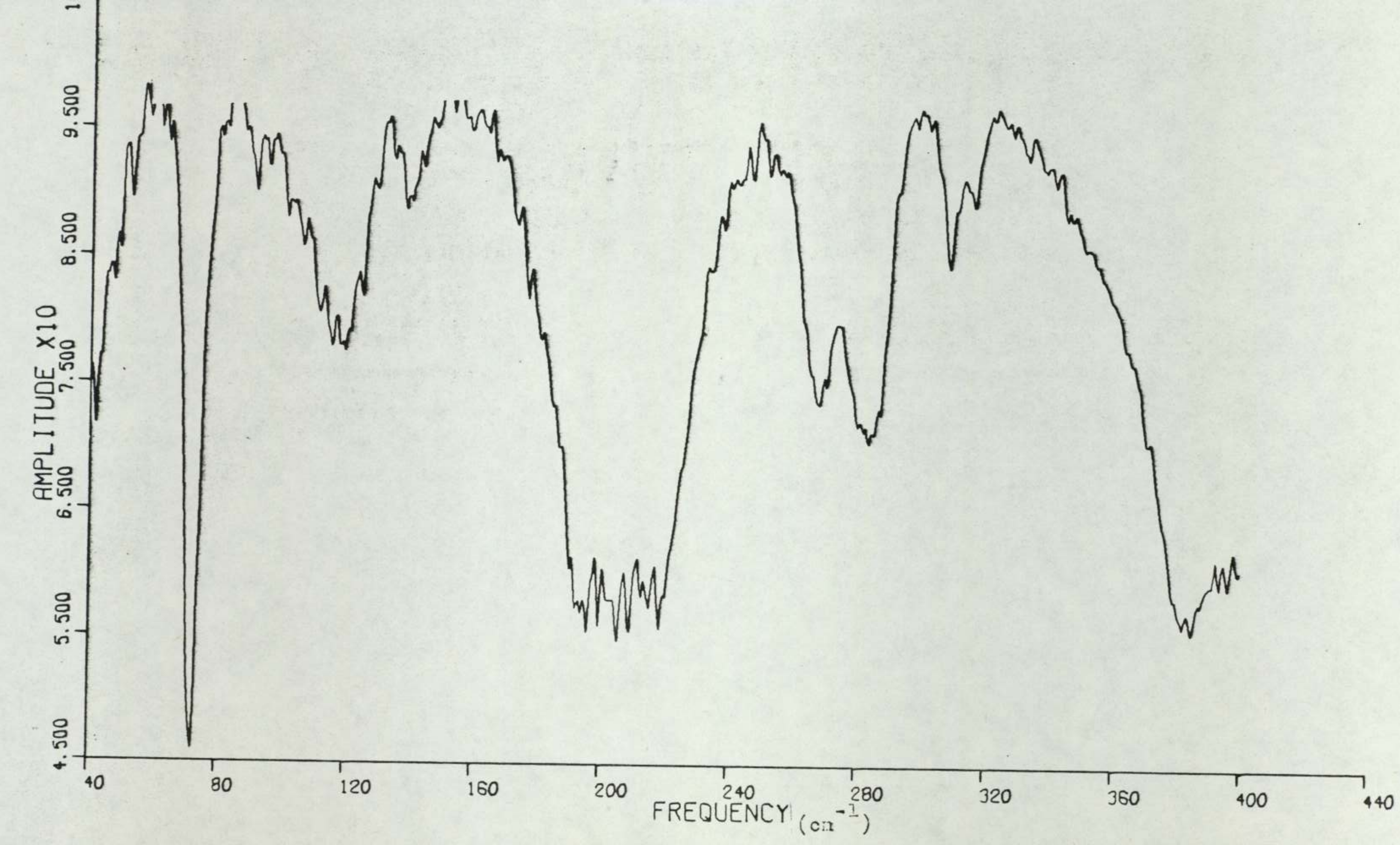


Fig. 5-1 Far infrared spectra of p-tolylseleniumtribromide

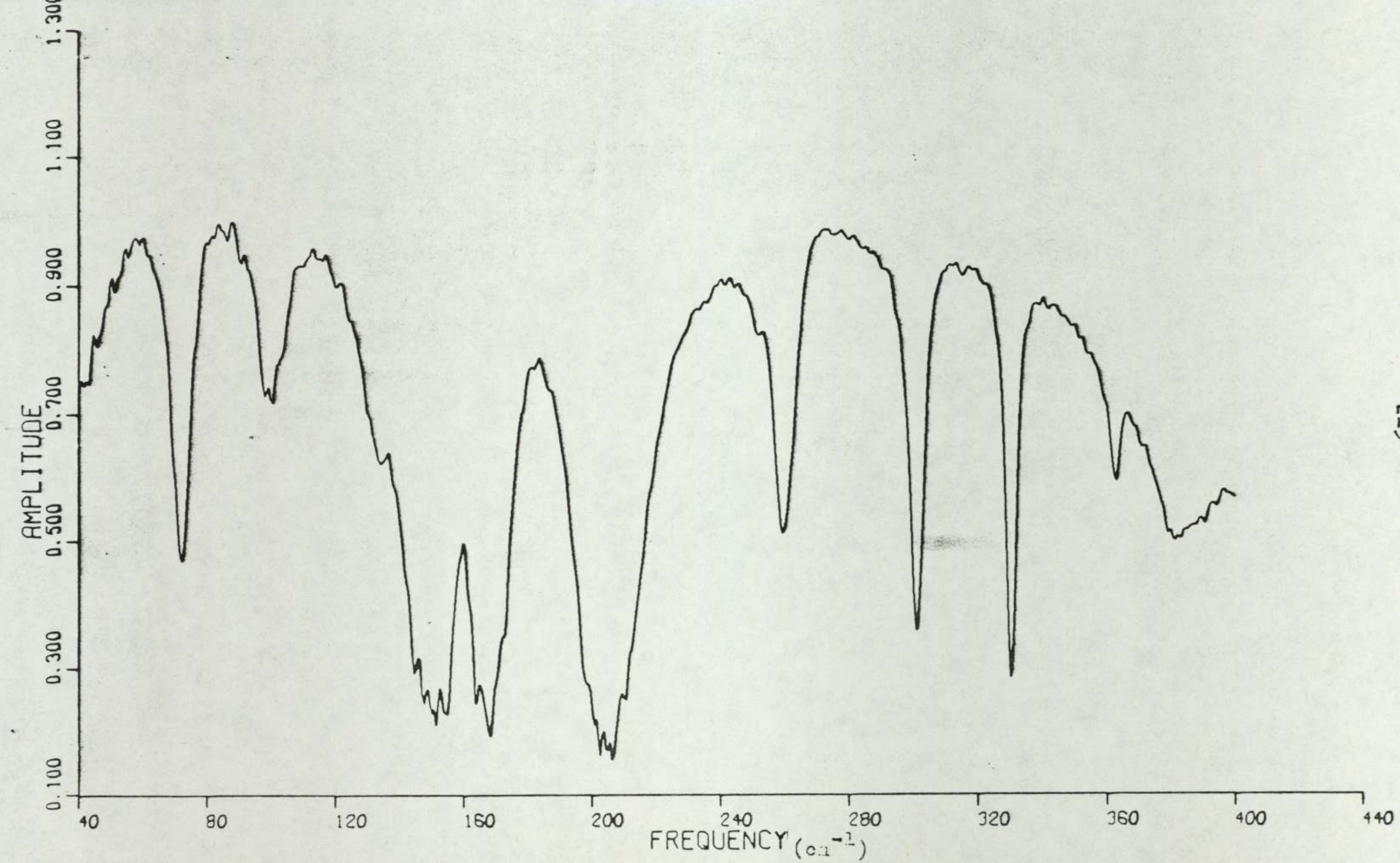


Fig. 5-2 Far infrared spectra of p-chlorophenylselniumtribromide

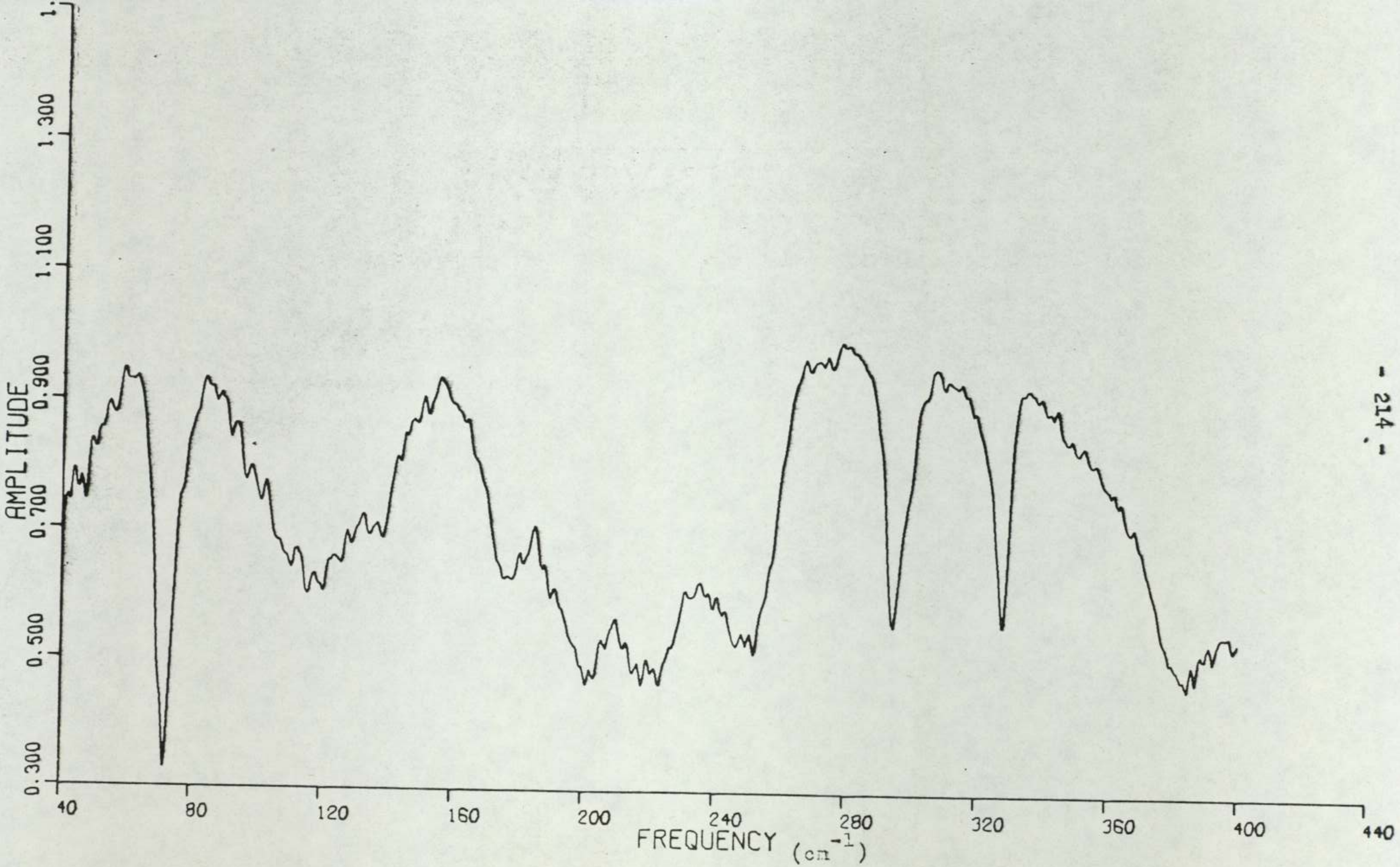


Fig. 5-3 Far infrared spectra of p-bromophenylseleniumtribromide

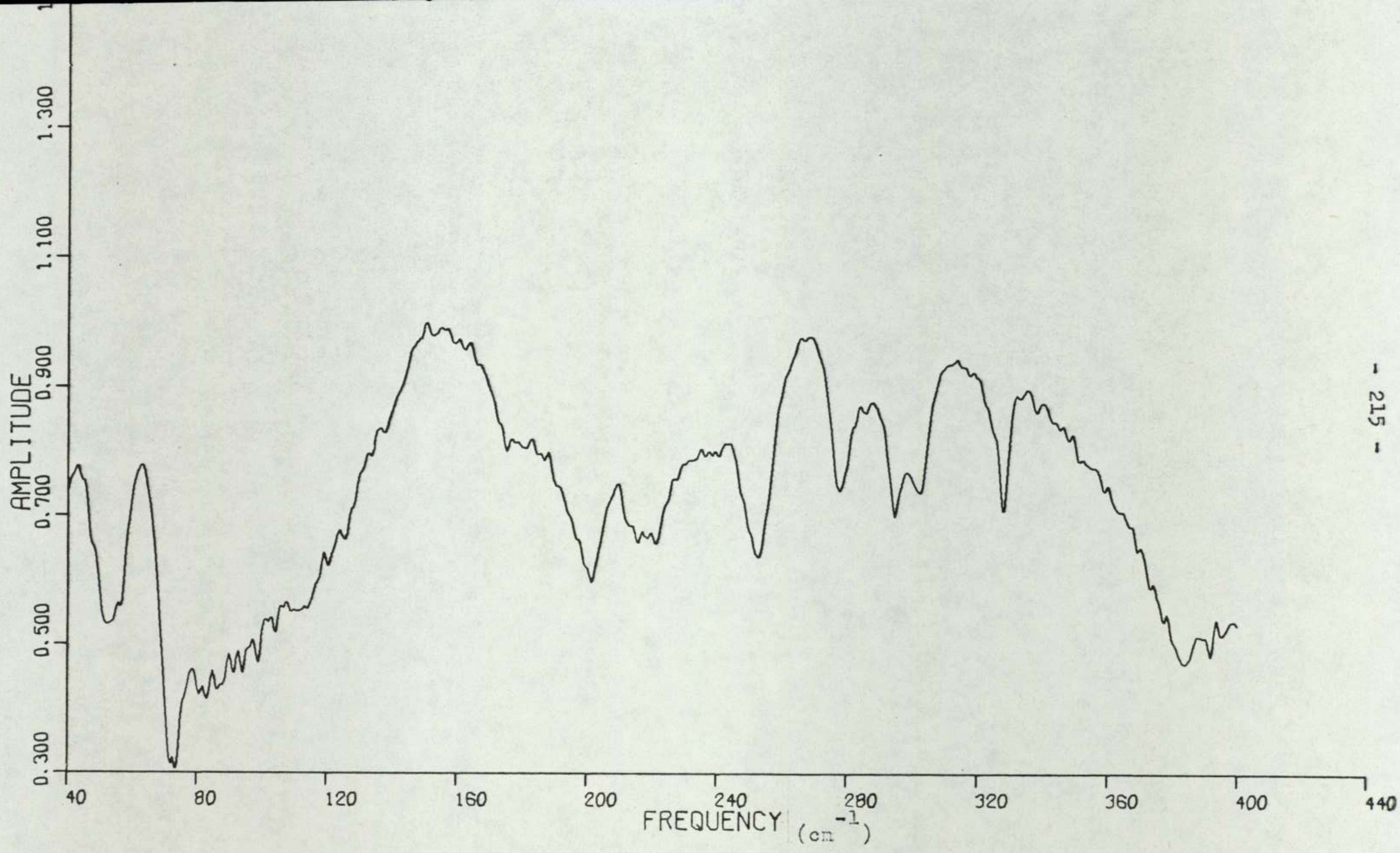


Fig. 5-4 Far infrared spectra of phenylseleniumtribromide

active in arylseleniumtribromides, whilst the infrared active bands in $(SeBr_6)^{2-}$ are infrared and Raman active in arylseleniumtribromides. A distorted octahedral environment for the selenium atoms seems likely as there is evidence of splitting of the bands. Bands between 230-316 cm^{-1} were found for $C_6H_5SeBr_3$ which are in the region noted for $SeBr_4$ [50] Se_2Br_2 [80], $(C_6H_5)_2SeBr_2$ [158] (and Br_2 itself). Absorptions arising in this region are probably due to the "stronger" selenium-bromine and selenium-phenyl vibrations.

5.3.4. Conductivity measurements and possible structures.

The conductivities of 10^{-3} Molar solutions of arylseleniumtribromides in dry NN′ dimethylformamide were measured using a Mullar conductivity bridge Type E 7566/3. Arylseleniumtribromides had values of Λ_m at 20°C between 40-50 $ohm^{-1}.cm^2.mole^{-1}$ (see table 5-6) which suggest that these are weak ionised in this solvent. A distorted octahedral environment for selenium of three long (selenium-bromine) bonds and three short (two selenium-bromine and one selenium-carbon) bonds could be envisaged in the tetramer unit, if this donor-acceptor interaction between $RSeBr_2$ and Br^- units persists in the solid state as shown in fig. 5-5.

The tetramer unit for phenylseleniumtribromide does not necessarily have to be based on a cube. A distorted cube arrangement also gives rise to Br^- ions which lie on a three fold axis. Tetramer units of a similar type have been proposed for thallium(II) methoxide [173] and basic beryllium acetate.[216]

TABLE 5-6

Analytical data for the arylseleniumtribromide.

	C	H	Se	m.p.	DMF*
$C_6H_5SeBr_3$	18.10 (18.20)	1.15 (1.27)	20.09 (19.86)	103°C (lit.105)	49
p-$BrC_6H_4SeBr_3$	15.30 (15.30)	0.70 (0.70)	16.84 (16.67)	132°C (lit.132)	50
p-$ClC_6H_4SeBr_3$	17.00 (16.89)	0.70 (0.95)	18.73 (18.36)	122°C (lit.123-4)	40
p-$CH_3C_6H_4SeBr_3$	20.50 (20.71)	1.60 (1.74)	18.91 (19.27)	115°C (lit.115-6)	50

Required values in parenthesis

*ohm^{-1} cm^2 $mole^{-1}$ $10^{-3}M$ solution at 20°C

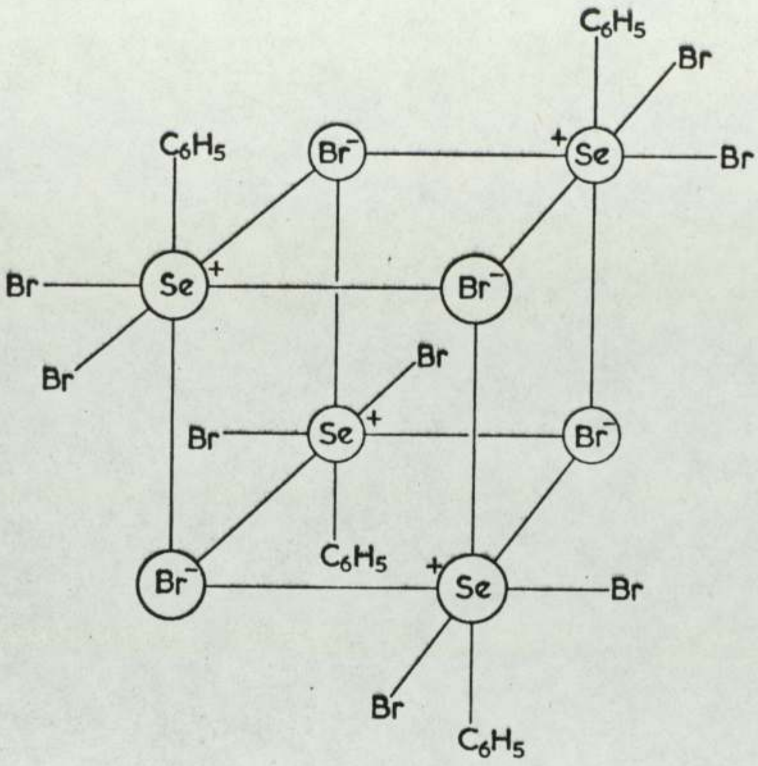


Fig. 5-5

Selenium atoms could be found in a tetramer unit which would give each acceptor atom an approximate C_{3v} environment.

Fig. 5-6 shows such a tetramer unit based on selenium-selenium bonds which could also give a local environment of C_{3v} for each selenium atom. The masses of selenium and bromine are similar, therefore bands of a similar frequency could arise. There is no way to distinguish between the two structures proposed (fig. 5-5 and 5-6).

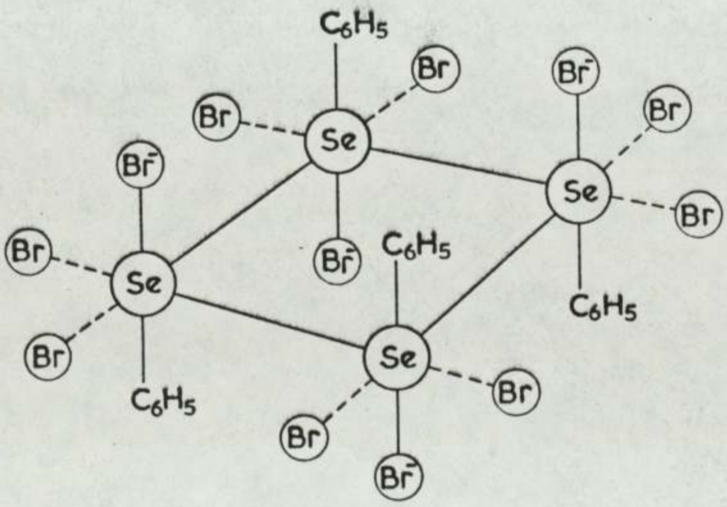


Fig. 5-6

The local symmetry of selenium atoms within the tetramer unit proposed for $C_6H_5SeBr_3$ can be regarded as of a MA_3B_3 type of unit. Each selenium atom (masses 78 or 80) is surrounded by three bromine atoms (masses 79 or 81) and more closely by two bromine atoms (masses 79 or 80) and one phenyl group (mass 77).

The fundamental vibrations for this molecule of point group C_{3v} are as follows, -

$$\Gamma = 4A_1\ (R.I.) \ + \ A_2(R) \ + \ 5E(R.I.)$$

Twelve to fifteen bands are in fact observed and these are listed together with tentative assignments in table 5-5.

5.3.5 Determination of the number and activity of a molecular MA_3B_3 belonging to the point group C_{3v}.

Number of fundamental vibrations is given by formula :

$$N_i = \frac{1}{N_G} \sum n_e \xi(R) X_i(R)$$

where N_G is the number of elements in the group

n_e is the number of elements in each class

$X_i(R)$ is the character of the vibration species.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{3N}	15	0	3

$$N_{A_1} = \frac{1}{6}\left[(1 \times 15 \times 1) + (2 \times 0 \times 1) - (3 \times 3 \times 1)\right] = 4$$

$$N_{A_2} = \frac{1}{6}\left[(1 \times 15 \times 1) + (2 \times 0 \times 1) + (3 \times 3 \times -1)\right] = 1$$

$$N_{E} = \frac{1}{6}\left[(1 \times 15 \times 2) + (2 \times 0 \times -1) + (3 \times 3 \times 0)\right] = 5$$

$$\Gamma_{3N} = 4A_1 + A_2 + 5E$$

$$\therefore \quad \Gamma_{3N} = 4A_1(\text{R.I.}) + A_2(\text{R}) + 5E(\text{R.I.})$$

Character table for the point group C_{3v}.

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	$X_i(R)$
E	2	-1	0	
θ	0°	120°	0°	
2 cos	2	-1	2	
$\pm 1 + 2\cos\theta$	3	0	1	$X_M(R)$
2	0°	240°	0°	
2 cos	2	-1	2	
$2 \pm 2\cos\theta + 2\cos 2\theta$	6	0	2	$X_a(R)$
u_R	4	1	2	
	proper rotations		improper rotations	

CHAPTER VI

NNN' N' Tetraalkylsubstituted dithiooxamide and some other sulphur bonded complexes of selenium(IV) & (II).

6.1 INTRODUCTION

6.1.1 Tetraalkyldithio-oxamide complexes.

NNN′N′ tetramethyldithio-oxamide and NNN′N′ tetraethyldithio-oxamide are known to react with certain metal ions in non-coordinating solvents.[20,26-30,76] Most of the tetramethyl or tetraethyldithio-oxamide complexes previously reported have involved transition and non-transition metal ions, and these have been summarised in Chapter II.

It has already been pointed out that many metal ions react with these potentially bidentate ligands to form stable complexes. Typical examples and the spectroscopic evidence for S-S or S-N coordination have been summarised in Chapter II.

In this chapter the preparation, characterisation, infrared and Raman spectra of complexes of the type $RSeLBr_3$ (where R = C_6H_5, p-ClC_6H_4, p-BrC_6H_4 or p-$CH_3C_6H_4$ and L = tetramethyldithio-oxamide or tetraethyldithio-oxamide) is described.

The complexes were prepared by dissolving the ligand (1 mmol.) in dry methanol or dry benzene and adding this to arylseleniumtribromide (1 mmol.) dissolved in either dry methanol or dry benzene. Yellow to orange precipitates formed immediately after cooling to 10°C, which were filtered off and stored in a vacuum desiccator.

Since aryltelluriumtribromides and tellurium tetrabromide are known to form stable complexes with NNN′N′ tetraalkyl-substituted dithio-oxamide [20,76] it was decided to investigate the corresponding reactions with the analogous selenium compounds. It was found however, that the tetraethyl and tetramethyldithio-oxamide complexes of selenium(IV) compounds are not as stable as the tellurium analogues.

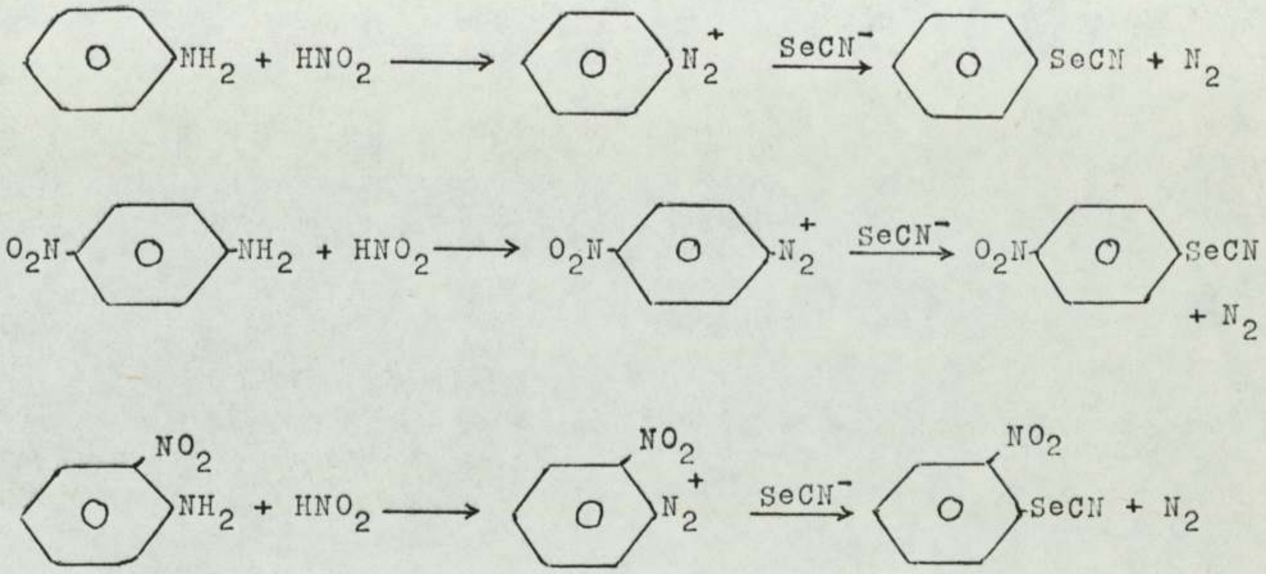
6.1.2 Vibrational spectra.

Bergson and Biezais [175] have suggested that a band found at 345 cm^{-1} in 1.2-thiaselenolane-4-carboxylic acid is due to the selenium-sulphur stretching mode. Bands between 100-305 cm^{-1} are said to be due to selenium-bromine stretching and deformation modes.[50,157,168,158,176]

Examination of the infrared and Raman spectra of the freshly prepared arylseleniumtribromide complexes indicate that co-ordination is through the sulphur atoms of thiocarbonyl groups. Assignments for the stretching mode of the selenium-halogen bond and selenium-sulphur bond are given, and the possible structure for the complexes are described.

6.1.3 Selenenyl sulphide.

A method for the preparation of phenylselenocyanate and substituted phenylselenocyanate was first reported by Bauer in 1913 [112] using a Sandmeyer type reaction in which selenocyanate ion is added to a diazolised arylamine.



Nakazaki[177] reported that the selenonyl sulphide compounds were obtained from the reaction of arylselenocyanates with thioaromatic compounds (e.g. thiophenol or o-nitrothiophenol) at room temperature. The reaction is exothermic and hydrogen cyanide is evolved.

$$RSeCN + R^{-}SH \longrightarrow RSeSR^{-} + HCN$$

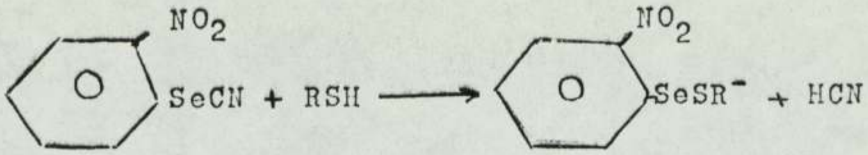
where $R = C_6H_5$ or $O\text{-}NO_2C_6H_4$

also $R^{-} = C_6H_5$ or $O\text{-}NO_2C_6H_4$

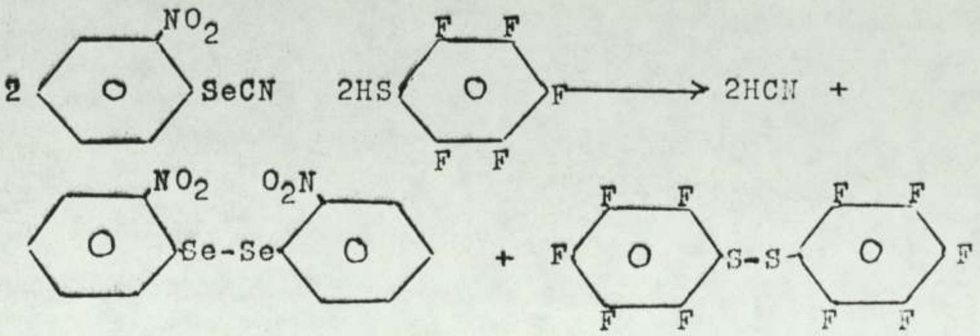
In this chapter, the reaction of o-nitrophenylselenocyanate and p-nitrophenylselenocyanate with several aromatic thiols (such as p-thiocresol, p-chlorothiophenol, p-bromothiophenol, o-mercaptobenzoic acid and pentafluorothiophenol) in a non-aqueous media is reported.

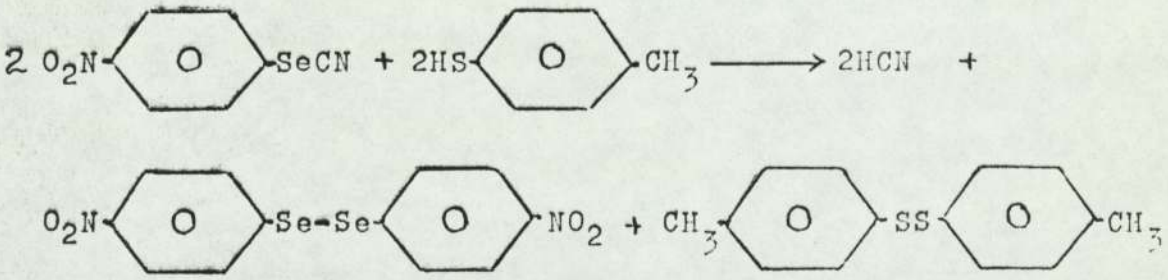
The main reaction products have been identified as selenenyl sulphide or diselenide depending upon the reactants.

Hydrogen cyanide and not cyanogen is given off from all reactions. The reactions involved as shown below:-



where R = p-$CH_3C_6H_4$, p-ClC_6H_4, p-BrC_6H_4, or O-$HOOC.C_6H_4$





Thus, the production of the selenenyl sulphide is favoured in most cases when o-nitrophenylselenocyanate is involved but the diselenide is produced when p-nitrophenylselenocyanate is used.

The infrared and Raman spectra of the selenenyl sulphide and diselenides were reported and assignments made. Also hydrogen cyanide was identified by infrared spectra.

6.2 EXPERIMENTAL

6.2.1 Preparation of NNN′N′ tetramethyl and NNN′N′ tetraethyldithio-oxamide.

Fully substituted dithio-oxamides (such as tetramethyl and tetraethyldithio-oxamide) were prepared by the reaction of phosphorus pentasulphide with tetramethyloxamide and tetraethyloxamide respectively using a procedure previously described by Hurd[41] (see appendix one page 262)

6.2.2 Preparation of arylseleniumtribromide.

Phenylseleniumtribromide, p-chlorophenylseleniumtribromide, p-bromophenylseleniumtribromide and p-tolylseleniumtribromide were prepared by the reaction of the appropriate arylselenocyanates or diaryldiselenides dissolved in dry chloroform with excess of bromine also dissolved in dry chloroform using methods which have previously been described.[123,126,114,122] (see appendix three page

6.2.3 Preparation of NNN′N′ tetramethyl and NNN′N′ tetraethyldithio-oxamide complexes of the arylseleniumtribromides.

The complexes were prepared by dissolving the ligand (1 mmol.) in methanol or benzene and adding the solution obtained to arylseleniumtribromide (1 mmol.) also dissolved in methanol or benzene. Yellow to orange precipitates formed immediately after cooling to 10°C, and were then filtered off at the pump and stored in a desiccator.

6.2.3.1 Purity of the complexes.

The arylseleniumtribromide complexes of tetramethyl or tetraethyldithio-oxamide were assayed immediately for selenium content by dissolving a weighed amount (20-50 mg.) in dry methanol. On addition of 2 g. KI and 2 cm^3 of 4M H_2SO_4 the liberated iodine was titrated with 0.1M $Na_2S_2O_3$ solution using starch as indicator [144,145] The reaction involved is shown as below :-

$$2RSeBr_3L + 6I^- \rightleftharpoons RSeSeR + 2L + 6Br^- + 3I_2$$

where L = tetraethyldithio-oxamide or tetramethyldithio-oxamide.

$R = C_6H_5$, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$ or $p\text{-}CH_3C_6H_4$

$$3I_2 + 6Na_2S_2O_3 \longrightarrow 6NaI + 3Na_2S_4O_6$$

$$\text{hence } 2RSeBr_3L \simeq 6Na_2S_2O_3$$
$$1RSeBr_3L \simeq 3Na_2S_2O_3$$

$\therefore$ 3 litres M $Na_2S_2O_3$ reacts with 1Se

1 litre M $Na_2S_2O_3$ reacts with $\frac{78.96}{3}$ Se

1 cm^3 of 0.1M $Na_2S_2O_3$ reacts with $\frac{78.96}{3 \times 10 \times 1000}$ Se

hence 1.0 cm^3 of 0.1M $Na_2S_2O_3$ reacts with 2.632 mg. Se

TABLE 6-4

Determination of selenium content in arylseleniumtribromide complexes, by titration methods.

Compounds	Vol. of 0.1M $Na_2S_2O_3$ needs cm^3	wt. of sample in mg.	Se % found	Se % calc.
$C_6H_5SeBr_3$ tedto*	2.25	45.80	12.93	12.58
p-$BrC_6H_4SeBr_3$tedto	1.05	26.20	10.55	11.04
p-$BrC_6H_4SeBr_3$tmdto**	1.05	23.20	11.91	12.14
p-$ClC_6H_4SeBr_3$tedto	1.12	25.90	11.38	11.93
p-$ClC_6H_4SeBr_3$tmdto	1.15	24.00	12.61	13.03
p-$CH_3C_6H_4SeBr_3$tedto	1.53	33.00	12.20	12.31
p-$CH_3C_6H_4SeBr_3$tmdto	1.03	20.40	13.29	13.48

*tedto = tetraethyldithio-oxamide

**tmdto = tetramethyldithio-oxamide

The percentage of selenium found in the complexes is shown in table 6-4.

6.2.4 Preparation of o-nitrophenylselenocyanate.

Bauer's [112] method was used, o-nitroaniline (13.8 g. 0.1 mol.) was dissolved in a hot mixture of 30 cm^3 of concentrated hydrochloric acid and 30 cm^3 of water. The solution was then cooled below 5°C and 7 g. of sodium nitrite in 20 cm^3 of water was added gradually so that the temperature did not rise above 5°C. The precipitate of o-nitroaniline hydrochloride appears and then dissolves to give a clear reddish liquid. Sodium acetate was added until the congo red paper gave a neutral colour. A solution of 15 g. of potassium selenocyanate in 40 cm^3 of water was gradually added keeping the temperature below 5°C. Immediately a yellow precipitate of o-nitrophenylselenocyanate was formed accompanied by a vigorous evolution of nitrogen. The precipitate was filtered off, washed with water several times and then recrystallised from ethanol and animal charcoal. m.p. 142°C (lit. 142°C) [112]

[Found C, 37.00; H, 2.00; N, 12.30; Se, 34.86; $C_7H_4N_2O_2Se$ requires C, 37.05; H, 1.76; N, 12.32; Se, 34.80 %]

6.2.5 Preparation of p-nitrophenylselenocyanate.

13.8 g. (0.1 mol.) of p-nitroaniline was treated with concentrated hydrochloric acid (20 cm^3) and ice (60 g.). After the mixture had been cooled to 0°C, sodium nitrite (8 g.) in 20 cm^3 of water was added slowly ensuring that the temperature did not rise above 0°C. The acidic solution produced was neutralised with a previously cooled solution of saturated sodium acetate until the congo red paper turned blue. Potassium selenocyanate (15 g. in 70 cm^3 of water) was then added drop-wise and with constant stirring and maintaining the temperature at 0°C, a dark brown solid was obtained, after all the nitrogen had been evolved. The solid was filtered off, washed with water several times and recrystallised three times from ethanol using decolourising charcoal, to give yellow crystalline plates. m.p. 136-138°C. (lit. 137-138°C) 112

[Found C, 37.15; H, 1.85; N, 12.16; Se, 34.60; $C_7H_4N_2O_2Se$ requires C, 37.05; H, 1.76; N, 12.32; Se, 34.80 %]

6.2.6 Reaction of o-nitrophenylselenocyanate with thioaromatic compounds.

6.2.6.1 p-Thiocresol.

O-nitrophenylselenocyanate (0.674 g. 3 mmol.) and p-thiocresol (0.372 g. 3 mmol.) in 10 cm^3 of dry benzene were heated under reflux for one hour in a three-necked flask equipped with a drying tube. A few drops of dry methanol was added to the dark red coloured solution which was formed. This solution was then cooled in an ice bath, when yellow crystals were obtained, which were filtered off and dried under vacuum. Yield 0.49 g.

[Found C, 48.20; H, 3.40; N, 4.28; Se, 24.83; $C_{13}H_{11}NO_2SSe$ requires C, 48.15; H, 3.39; N, 4.32; Se, 24.37 %]

6.2.6.2 p-Bromothiophenol.

A mixture of o-nitrophenylselenocyanate (0.674 g. 3 mmol.) and p-bromothiophenol (0.567 g. 3 mmol.) in 10 cm^3 of dry benzene was refluxed for one hour. The dark red coloured solution formed and was cooled. On addition of a few drops of dry methanol, yellow crystals were produced. These crystals were filtered off and dried under vacuum. Yield 0.37 g. m.p.85-88°C. [Found C, 37.75; H, 2.10; N, 3.65; Se, 21.01; $C_{12}H_8NO_2BrSSe$ requires C, 37.04; H, 2.07; N, 3.60; Se, 20.30 %]

6.2.6.3 p-Chlorothiophenol.

A mixture of o-nitrophenylselenocyanate 0.674 g. (3 mmol.) and p-chlorothiophenol 0.433 g. (3 mmol.) in 10 cm^3 of dry benzene was refluxed for one hour. The same procedure was used as for the reaction of o-nitrophenylselenocyanate and p-bromothiophenol. The yellow crystals obtained were filtered off and dried under vacuum. Yield 0.49 g. m.p. 95-98°C. [Found C, 41.80; H, 2.40; N, 4.40; Se, 22.39; $C_{12}H_8O_2NClSSe$ requires C, 41.82; H, 2.34; N, 4.07; Se, 22.92 %]

6.2.6.4 O-Mercaptobenzoic acid (thiosalicylic acid).

A mixture of 0.674 g. (3 mmol.) o-nitrophenylselenocyanate, 0.463 g. (3 mmol.) o-mercaptobenzoic acid, 10 cm^3 of dry methanol and 5 cm^3 of dry benzene were refluxed for fifteen minutes in a three necked flask equipped with a drying tube. Yellow crystals were formed, which were

filtered off when the solution was hot and then dried under vacuum. Yield 0.87 g. m.p. 225-230°C.
[Found C, 44.40; H, 2.60; N, 4.10; Se, 22.21; $C_{13}H_9O_4NSSe$ requires C, 44.07; H, 2.56; N, 3.96; Se, 22.31 %]

6.2.6.5 Pentafluorothiophenol.

O-nitrophenylselenocyanate 0.674 g. (3 mmol.), pentafluorothiophenol 0.6 g. (3 mmol.), 10 cm^3 of dry methanol and 5 cm^3 of dry benzene were mixed and then refluxed for one hour. Yellow crystals were formed, which were filtered off and dried under vacuum. Yield 0.30 g. m.p. 205-206°C. (lit. 209°C) [112]
[Found C, 35.90; H, 2.05; N, 6.75; Se, 39.51; $C_{12}H_8O_4N_2Se_2$ (di(o-nitrophenyl)diselenide) requires C, 35.83; H, 2.01; N, 6.94; Se, 39.28 %]

6.2.7 Reaction of p-nitrophenylselenocyanate with p-thiocresol.

A mixture of 0.456 g. (2 mmol.) p-nitrophenylselenocyanate, 0.249 g. (2 mmol.) p-thiocresol in 10 cm^3 of dry benzene was refluxed for one hour. Yellow crystals were formed which filtered off from the hot solution and dried under vacuum. Yield 0.20 g. m.p. 176-177°C (lit. 180°C) [178]
[Found C, 35.50; H, 2.30; N, 6.85; $C_{12}H_8O_4N_2Se_2$ (di(p-nitrophenyl)diselenide) requires C, 35.82; H, 2.01; N, 6.96 %]

6.2.8 Identification of the gaseous products evolved.

The gaseous products were collected in an absorption tube cooled at-180°C. The liquid products were then vaporised into an infrared gaseous absorption cell and the spectrum obtained over the ranges 800-670 cm^{-1} and 3350-3250 cm^{-1}. The fundamental bands obtained were compared with the published data for wavenumbers for the calibration of spectrometers.[179] Hydrogen cyanide was evolved from all reactions investigated. There was no evidence of any cyanogen being present.

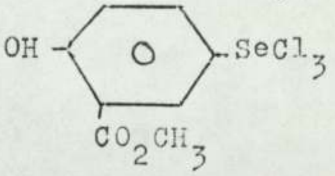
6.2.9 Identification of the products in the solutions.

The presence of thiocyanate in the solutions after the reaction was tested by using a modification of the standard qualitative tests using iron(III) and cobalt(II) solutions as recommended by Vogel.[180] Aqueous solutions of these reagents were shaken with the organic solvent in a separating funnel. The colours characteristic of $(CNS)^-$ were not produced.

6.3 DISCUSSION.

6.3.1 Arylseleniumtribromide complexes of tetramethyl and tetraethyldithio-oxamide.

Arylseleniumtribromides $RSeBr_3$ (where R = C_6H_5, p-BrC_6H_4, p-ClC_6H_4 or p-$CH_3C_6H_4$) have been found to react with sulphur donor ligands (such as tetraethyldithio-oxamide or tetramethyldithio-oxamide) in dry methanol or dry benzene to form yellow to orange precipitates which were filtered off and assayed immediately for their selenium content. The complexes produced all have a stoichemistry Se:ligand of 1:1. These arylseleniumtribromide complexes are not so stable as the corresponding tellurium compounds, but are stable enough to permit spectroscopic examination by an interferometer and are not immediately decomposed by the beam of a laser Raman instrument.

The reaction of selenium tetrachloride and arylseleniumtrichlorides (such as $C_6H_5SeCl_3$ or  with tetraethyldithio-oxamide or tetramethyldithio-oxamide in dry methanol or dry benzene were investigated but no precipitates were formed.

6.3.2 Vibrational spectra.

As mentioned in a previous chapter, fully substituted dithio-oxamide are known to give complexes with many metal ions, and co-ordination takes place through both sulphur atoms of the ligand.[20,26-30,76]

The more important bands in the ligands (tetramethyl or tetraethyldithio-oxamide) are ν(CN) and ν(CS) stretching vibrations and these bands are increased or decreased in the arylseleniumtribromide complexes respectively. The infrared and Raman spectra show new bands in the complexes which may be assigned to selenium-sulphur stretching.

The spectroscopic data for arylseleniumtribromide complexes with tetraethyl or tetramethyldithio-oxamide have features in common with the corresponding aryltellurium-tribromide complexes, and the more important bands are now discussed.

6.3.2.1 Tetramethyl and tetraethyldithio-oxamide complexes with selenium(IV).

The bands at 1528 cm^{-1} and 1500 cm^{-1} assigned to ν(CN) for tetramethyl and tetraethyldithio-oxamide respectively are shifted to higher wavenumbers and are split in the arylselenium-tribromide complexes (see table 6-1). The ν(CS) bands at 828 cm^{-1} and 872 cm^{-1} for each respective ligand, are shifted to lower wavenumbers in the complexes (see table 6-1). This is consistent with the proposal that co-ordination takes place through the sulphur atoms of the thiocarbonyl groups.

The bands in the far-infrared and Raman spectra for tetramethyl and tetraethyldithio-oxamide are reported in tables 6-2 and 6-3 and are worth further comment. There are seven bands between 352-117 cm^{-1} for the complexes. Some are clearly altered by complex formation, but new bands due to

TABLE 6-1

Infrared spectra of NNN′N′ tetramethyl and NNN′N′ tetraethyldithio-oxamide complexes of arylseleniumtribromides.

Compounds	ν (CN)	ν(CS)
Tetramethyldithio-oxamide (tmdto)	1528s	828m
Phenylseleniumtribromide complex	1593s 1540s	817m
p-Chlorophenylseleniumtribromide complex	1593s 1540s	818m
p-Bromophenylseleniumtribromide complex	1592s 1540s	818m
p-Tolylseleniumtribromide complex	1592s 1540s	818m
Tetraethyldithio-oxamide (tedto)	1500s	872m
Phenylseleniumtribromide complex	1555s 1520s	858m
p-Chlorophenylseleniumtribromide complex	1550s 1520s	857m
p-Bromophenylseleniumtribromide complex	1553s 1520s	857m
p-Tolylseleniumtribromide complex	1550s 1520s	857m

TABLE 6-2

Infrared and Raman spectra of selenium tetraethyldithio-oxamide complexes below 360 cm^{-1}

Tetraethyldithio-oxamide (tedto)		$C_6H_5SeBr_3$tedto		p-$BrC_6H_4SeBr_3$tedto		Tentative Assignments
i.r.	Raman Δν	i.r.	Raman Δν	i.r.	Raman Δν	
			118vw		117vw	δ(Se-Br) and ligand vibration
		136s		135s	130vw	
154w	144w					
196s	185m	184m				ligand vibration
		244vw	233w			Phenyl u mode and ν (Se-Br)
		252vw	257w	252vw	257w	
		280w				
293m	293w					ligand vibration
		338s	337m	335s	334vs	ν(Se-S) and ligand vibration
		349ssh	345m	350msh	345w	
344m	350w				352w	

Table 6-2 ...

Infrared and Raman spectra of selenium tetraethyldithio-oxamide complexes below 360 cm^{-1}.

tedto		p-$ClC_6H_4SeBr_3$tedto		p-$CH_3C_6H_4SeBr_3$tedto		Tentative Assignments
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
					119vw	δ(Se-Br) and ligand vibration
		135s	129vw	134vs		
154w	144w					
196s	185m	183w		184m		ligand vibration
			245w	251vw	259w	Phenyl u mode and ν(Se-Br)
		281m				
293m	293w	305m				ligand vibration
		324msh				ν(Se-S) and ligand vibration
		334s	333m	335s	336s	
344m	350m			349ssh		

TABLE 6-3

Infrared and Raman spectra of selenium tetramethyldithio-oxamide complexes below 360 cm^{-1}.

Tetramethyldithio-oxamide (tmdto)		$C_6H_5SeBr_3$tmdto		p-Br$C_6H_4SeBr_3$tmdto		Tentative Assignments
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
			132w	135s	132w	δ(Se-Br) and ligand vibration
146w	133w					
187m	179w			182w		ligand vibration
				227wsh	228wsh	Phenyl u mode and ν(Se-Br)
			259s	252msh	256s	
					298w	
306s	311w					ligand vibration
				312vw	316w	Phenyl (Se) t mode
			327msh		324wsh	
			344vw	345s	342vw	ν(Se-S)

Table 6-3...

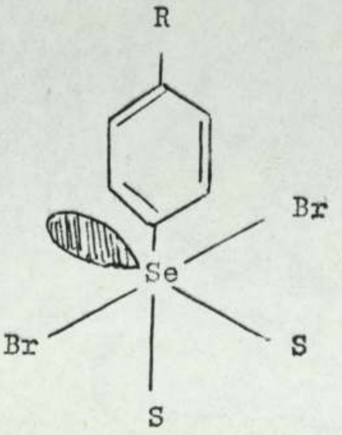
Infrared and Raman spectra of selenium tetramethyldithio-oxamide complexes below 360 cm^{-1}

tmdto		p-$ClC_6H_4SeBr_3$tmdto		p-$CH_3C_6H_4SeBr_3$tmdto		Tentative Assignments
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
		118m			120vw	δ(Se-Br) and ligand vibration
		140m	133m	134w	132m	
146w	133w					
187m	179w			184m	174w	ligand vibration
			242wsh			Phenyl u mode and ν(Se-Br)
		250msh	256vs	251vw	257m	
			266wsh			
				280vw	282w	
306s	311w					ligand vibration
		320msh	328wsh	320ssh	321w	Phenyl(Se) t mode
		345s	341vs	344s	342s	ν(Se-S)

ν(Se-S), ν(Se-Br) and δ(Se-Br) may be clearly identified. Thus, absorptions associated with ν(Se-S) occur at 345-333 cm^{-1} in the complexes. This proposal agrees with the observation of Bergson and Biezais [175] who assigned the absorption band at 345 cm^{-1} in 1.2-thiaselenolane-4-carboxylic acid as being due to a selenium-sulphur stretching mode. Wynne et al [157] suggest that the bands at 233-240 cm^{-1} may be tentatively assigned to a Se-S stretching mode for dibromo(tetramethylthiourea)selenium(II) and dichloro(tetramethylthiourea)-selenium(II), but it is noted that the bands are weak and that other bands are given at 320-370 cm^{-1} which do not occur in the ligand. The bands at 298-227 cm^{-1} and 140-118 cm^{-1} may be assigned to ν(Se-Br) and δ(Se-Br) respectively. This proposal agrees with suggestions that selenium-bromine stretching and deformation modes give rise to bands between 100-305 cm^{-1} [50,157,158,168,176]

6.3.3. Structure.

Arylseleniumtribromides are probably tetrameric structures formed by donor-acceptor interactions between Br^- and $RSeBr_2^+$ units (see Chapter V). The environment of each selenium atom is approximately of C_{3v} symmetry. The local symmetry of selenium atoms is higher than would be expected, because of the similar masses of the attached ligands i.e. C_6H_5 and Br. Arylseleniumtribromides give very rich Raman spectra but the bands in the same region for the arylseleniumtribromide complexes are less intense and all coincide with those found in the infrared spectra. The profiles of the spectra of the complexes have many similar features and a common structure of low symmetry seems likely. This could be a structure based on units $(RSeBr_2tedto)^+ Br^-$ and $(RSeBr_2tmdto)^+ Br^-$. Five co-ordinated selenium seems likely for these cations. This structure is inconsistent with a ψ octahedral structure with one lone pair and five bond pairs, as may be predicted for selenium(IV).



The possible structure of the $RC_6H_4SeLBr_2$ cation
where R = H, Cl, Br, or CH_3
L = tedto or tmdto.

6.3.4 Selenenyl sulphide and diselenide.

Diaryldiselenide may be obtained by air oxidation of selenols, or from selenocyanates[114,115] Challenger et al[114] believe that a selenol is the initial hydrolysis product:-

$$ArSeCN + H_2O \longrightarrow 2ArSeH + 2HCNO$$
$$2ArSeH \xrightarrow{[O]} ArSeSeAr + H_2O$$

Rheinboldt[115] suggests that another likely mechanism for the preparation of diselenide is by the alkaline hydrolysis of selenocyanate to give selenenic acid as an intermediate :-

$$RSeCN + H_2O \longrightarrow RSeOH + HCN$$

$$RSeOH + RSeCN \longrightarrow RSeSeR + HCNO$$

Behagel and Seibert[123] believe that $(CN)_2$ is formed as a byproduct and then HCN or HCNO is produced by reacting with water present.

$$2ArSeCN \longrightarrow ArSeSeAr + (CN)_2$$

$$(CN)_2 + H_2O \longrightarrow HOCN + HCN$$

The hydrolysis of arylseleniummonohalides appears to proceed by disproportionation via selenic acid.[123]

$$C_6H_5SeBr + H_2O \longrightarrow C_6H_5SeOH + HBr$$

$$2C_6H_5SeOH \longrightarrow C_6H_5SeO_2H + C_6H_5SeH$$

$$C_6H_5SeH + C_6H_5SeOH \longrightarrow C_6H_5SeSeC_6H_5 + H_2O$$

If a similar reaction occurred for arylselenocyanates the products of the reaction would be phenylselenic acid and diphenyldiselenide.

$$3ArSeCN + 2H_2O \longrightarrow ArSeO_2H + ArSeSeAr + 3HCN$$

Selenol formation seems likely in the presence of alklating agents since under these conditions selenides are formed which may be air oxidised to diselenides.[181-186]

Rheinboldt[115] type mechanism for the reaction with HSR seems possible, -

$$ArSeCN + HSR \longrightarrow ArSeSR + HCN$$

$$ArSeCN + ArSeSR \longrightarrow ArSeSeAr + RCNS$$

or more likely direct formation of diselenide and disulphide, -

$$2ArSeCN + 2RSH \longrightarrow ArSeSeAr + RSSR + 2HCN$$

The base of hydrolysis for selenocyanates always gives diselenides and hydrolysis under mineral acids also appears to proceed via selenol intermediates but again air oxidation is needed to proceed to the diselenide stage.

Nakasaki[177] described the preparation of diphenyldiselenide by the reaction of phenylselenocyanates with phenylselenol. It is not clear whether oxygen was absent or if the reactants were scrupulously dry.

In the work described in this thesis, the preparation of selenenyl sulphide was carried out by refluxing a mixture of the thioaromatic compounds with o-nitrophenylselenocyanate in dry benzene for one hour under an atmosphere of dry nitrogen gas. On addition of a few drops of dry methanol, yellow crystals were obtained.

Under the same conditions o-nitrophenylselenocyanate was reacted with pentafluorothiophenol and p-nitrophenylselenocyanate with thiocresol giving di(o-nitrophenyl)diselenide and di(p-nitrophenyl)diselenide, respectively. (see equation page 224)

In all of these experiments the reactants were thoroughly dry and care was taken to eliminate oxygen. The presence of hydrogen cyanide in the gas evolved was determined by analysis of the infrared spectra.

6.3.5 Vibrational spectra of diaryldiselenide.

Allun et al[164] have reported their investigations of the infrared and Raman spectra of dibutyldiselenide and suggest the Raman line at 293 cm^{-1} to be due to a Se-Se stretching mode. On comparing this to that for ν(Br-Br) (317 cm^{-1}) it is found to be quite close. Green and Harvey[162] have reported the infrared and Raman spectra of dimethyldiselenide and the vibration ν(Se-Se) was observed at 286 cm^{-1}.

The bands between 286-265 cm^{-1} for di(p-nitrophenyl)-diselenide and di(o-nitrophenyl)diselenide were assigned to selenium-selenium stretching modes. (see table 6-5)

6.3.6 Vibrational spectra of selenenyl sulphides.

The selenium-sulphur stretching mode of 1.2-thioselenolane-4-carboxylic acid has been tentatively assigned to an absorption band at 345 cm^{-1}.[175]

The far infrared and Raman spectra of tetraethyl and tetramethyldithio-oxamide complexes of selenium(IV) have been reported in this thesis and it has been suggested that the bands between 335-345 cm^{-1} may be assigned to selenium-sulphur stretching modes.

In the far infrared and Raman spectra (table 6-5) new bands at 318-351 cm^{-1} for the selenenyl sulphides are shown, which may be assigned to selenium-sulphur stretching modes.

TABLE 6-5

Infrared and Raman spectra of the selenocyanates and the products of reaction with thioaromatics.

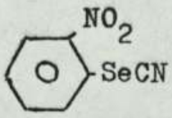
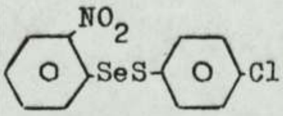
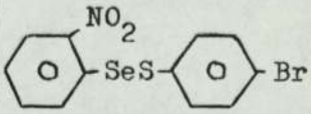
						Assignments
i.r.	Raman	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
120m						
142m		148m		147msh		
171msh		170s		170ssh		substituent sensitive vibration x
185s		182s		183s		
		188s				
		218s	211w			substituent sensitive vibration u
256w	261w			255m	250s	vibration associated with NO_2 group.
282	275s	283m	279w	282m	278m	
			293s			
	307w	302w	303m	302m	299w	substituent sensitive vibration t
318w	315m	311m				
		317m				
		335m		328m	322w	ν (Se-S)
		342msh		350msh		
361m	357w	357ssh	351m		359m	out-of-plane Se-C≡N bend
		387m				
393m						In-plane Se-C≡N bend

Table 6-5...

Infrared and Raman spectra of the selenocyanates and the products of reaction with thioaromatics.

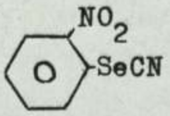
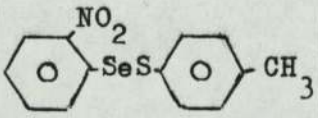
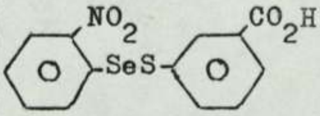
						Assignment
i.r.	Raman Δν	i.r.	Raman Δν	i.r.	Raman Δν	
120m						
142m		147msh	144ssh	146msh		
171msh		167msh		170ssh		substituent sensitive vibration x
185s		182s	176m	182ssh		
		189s				
				203vs		substituent sensitive vibration u
				224wsh	226w	
256w	261w					vibration associated with NO_2 group
282m	275m	283m	280w	281m	279m	
	307w	303w				substituent-sensitive vibration t
318w	315m			314m		
		322m	327m	334s	331m	ν (Se-S)
				346m		
361m	357m				368m	out-of-plane Se-C ≡ N bend
		378m	378w			
393m		393m				In-plane Se-C ≡ N bend

Table 6-5 ...

Infrared and Raman spectra of the selenocyanates and the products of reaction with thioaromatics.

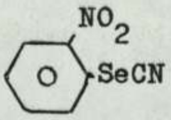
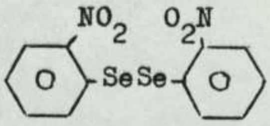
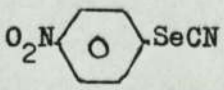
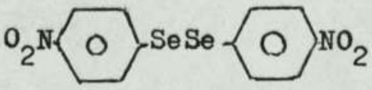
				Assignment
i.r.	Raman Δν	i.r.	Raman Δν	
120m				substituent-sensitive vibration x
142m		142m		
171msh		168msh	172w	
185s		181s		
256w	261w			vibration associated with NO_2 group
		269msh	265vs	ν(Se-Se)
		281s		
282m	275s			substituent-sensitive vibration t
	307w			
318w	315m	318w		
361m	357w			out-of-plane Se-C≡N bend
393m				In-plane Se-C≡N bend

Table 6-5 ...

Infrared and Raman spectra of the selenocyanates and the products of reaction with thioaromatics.

				Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
117m			110sh	substituent-sensitive vibration x
			158ssh	
186s			194sh	
235s		237m	234m	substituent-sensitive vibration u
263s		266s		vibration associated with NO_2 group
		266s		ν (Se-Se)
		273m	272m	
		286w	288s	
301s			305s	substituent-sensitive vibration t
		320w	329w	
353s				out-of-plane Se-C≡N bend
400w				In-plane Se-C≡N bend

APPENDIX 1

Preparation of aryltellurium compounds and sulphur containing ligands.

Most of the intermediate aryltellurium compounds and sulphur containing ligands are known and the preparation methods were carried out according to the procedures given by various literature surveys. All solvents such as methanol, ethanol, n-butanol, benzene, carbon tetrachloride, chloroform, toluene, xylene, and diethylether were dried according to recommended procedures.[217]

A.1.1 PREPARATION OF ARYLTELLURIUMTRIHALIDES AND DIARYLDITELLURIDES.

A.1.1.1 Phenyltelluriumtrichloride. $C_6H_5TeCl_3$

Pant's method for the preparation of phenyltelluriumtrichloride was used.[31]

A mixture of telluriumtetrachloride (3.4 g.) in triphenylleadchloride (5.7 g.) in dioxane (50 cm^3) was stirred at room temperature for four hours. The precipitated diphenylleaddichloride was filtered and the solvent removed under vacuum. The white solid obtained was recrystallized, from boiling a mixture of benzene/hexane to give phenyltelluriumtrichloride (3.65 g.). m.p. 214-17°C. (lit. 215-18° C) [32]
[Found C, 22.75; H, 1.55; Te, 41.15 : $C_6H_5TeCl_3$ requires C, 23.15; H, 1.62; Te, 41.04 %]

A.1.1.2 Phenyltelluriumtribromine. $C_6H_5TeBr_3$

To a cold solution of diphenylditelluride (0.81 g.) in carbontetrachloride at 10° C, bromine in carbontetrachloride was slowly added. The solution of diphenylditelluride changed from brown to yellow and a yellow precipitate separated out, at which point excess bromine solution was added. The mixture was continuously stirred for another thirty minutes, filtered off and dried under vacuum. The product was recrystallized from glacial acetic acid. Yellow crystals (0.76 g.) were obtained. m.p. 227-29° C. (lit. 227-29°C) [33]
[Found C, 16.15; H, 1.15; Te, 28.72 : $C_6H_5TeBr_3$ requires C, 16.21; H, 1.14; Te, 28.72 %]

A.1.1.3 Diphenylditelluride. $(C_6H_5)_2Te_2$

Morgan and Drew's [34] method was used for the preparation of diphenylditelluride.

Crude phenyltelluriumtrichloride (2.9 g.) was suspended in water (20 cm^3). The mixture was reduced by a solution of potassium metabisulphite (5.3 g.) in water (10 cm^3) which was slowly added at 0°C and with continuous stirring until an orange precipitate appeared. After the solution was used up, stirring was continued for another hour. The product was filtered off and dried over P_4O_{10} in a vacuum dessicator. The ditelluride was then recrystallized from petroleum ether (30/40) and orange needle crystals (0.75 g.), which melted at 64-65°C (lit. 66-67°C)[32,34] were obtained.
[Found C, 35.80; H, 2.42 : $C_{12}H_{10}Te_2$ requires C, 35.19; H, 2.46 %]

A.1.1.4 p-Tolyltelluriumtrichloride. $p\text{-}CH_3C_6H_4TeCl_3$

p-Tolyltelluriumtrichloride was prepared from p-tolylmercuricchloride (3.2 g.), tellurium tetrachloride (2.7 g.) and dioxane 20 cm^3 refluxed for one and a half hours.
The solution was cooled, the $HgCl_2$ .dioxane crystals filtered off, and the filtrate then evaporated under vacuum to dryness.
The crude product was first recrystallized from sym-tetrachloroethane and finally recrystallized from dry benzene. Colourless crystals were obtained (1.3 g.) m.p. 180-181°C (lit. 181-182°C).[32]
[Found C, 25.80; H, 2.06; Te, 39.02 : $C_7H_7Cl_3Te$ requires C, 25.85; H, 2.17; Te, 39.27 %]

A.1.1.5 p-Tolyltelluriumtribromide. $p\text{-}CH_3C_6H_4TeBr_3$

Bromine in carbontetrachloride was slowly added to a solution of bis-p-tolylditelluride (1.24 g.) in carbontetrachloride which had been cooled to about 5° C and magnetically stirred. The solution of bis-p-tolylditelluride changed from red brown to yellow with the precipitation of a yellow compound, at which point excess bromine solution was added. The mixture was continuously stirred for another thirty minutes. The precipitate was filtered off, dried and recrystallized from glacial acetic acid to yield yellow plate-like crystals (0.90 g.) which melted at 214-215°C dec. (lit. 215-216°C)[33]

[Found C, 18.60; H, 1.70; Te, 27.97: $C_7H_7Br_3Te$ requires C, 18.33; H, 1.54; Te, 27.84 %]

A.1.1.6 Bis-p-tolylditelluride. $(p\text{-}CH_3C_6H_4)_2Te_2$

A similar procedure as that used in the preparation of diphenylditelluride was employed.

p-Tolyltelluriumtrichloride (2.3 g.) was reduced by potassium metabisulphite (5.6 g.) to give orange crystals which were recrystallized from petroleum ether (30/40). m.p. 51-52° C (lit. 52.5°C)[32]

[Found C, 38.20; H, 3.27: $C_{14}H_{14}Te_2$ requires C, 38.43; H, 3.23 %]

A.1.1.7 p-Anisyltelluriumtrichloride. $p\text{-}CH_3OC_6H_4TeCl_3$

A mixture of anisole(10.4 g.), tellurium tetrachloride (13.5 g.) and dry chloroform or dry carbon tetrachloride (100 cm^3) was refluxed in a water bath for two hours. The yellow plate crystals obtained (10.5 g.) were recrystallized from dry chloroform to obtain yellow plates which melted at 190°C. (lit. 190°C) [35,36]

[Found C, 24.4; H, 2.10: $C_7H_7Cl_3OTe$ requires C, 24.64; H, 2.07 %]

A.1.1.8 p-Anisyltelluriumtribromide. $p\text{-}CH_3OC_6H_4TeBr_3$

p-Anisyltelluriumtribromide was prepared as follows: Bromine in carbontetrachloride was slowly added to an ice-cold solution of bis-p-anisylditelluride (1.4 g.) also dissolved in carbon tetrachloride and the excess of bromine solution was added. The solution was continuously stirred for another hour, after which time the yellow product was filtered and dried. The crude product was recrystallized from glacial acetic acid and yielded yellow crystals (1.16 g.) m.p. 187-88°C (lit. 188-89°C) [37]

[Found C, 17.65; H, 1.32: $C_7H_7Br_3OTe$ requires C, 17.71; H, 1.49 %]

A.1.1.9 Bis-p-anisylditelluride. $(p\text{-}CH_3OC_6H_4)_2Te_2$

p-Anisyltelluriumtrichloride (5.0 g.) was reduced by potassium metabisulphite (4.0 g.) at 0°C. The deep brown needle crystals of the ditelluride (1.5 g.) were obtained after recrystallization from petroleum ether (40/60°C). The bis-p-anisylditelluride has a m.p. 58-59°C.(lit. 60°C) [35,36] [Found C, 35.56; H, 3.10 : $C_{14}H_{14}O_2Te_2$ requires C, 35.81; H, 3.01 %]

A.1.1.10 p-Phenetyltelluriumtrichloride. $p\text{-}C_2H_5OC_6H_4TeCl_3$

Phenetole(17.0 g.), telluriumtetrachloride (12.0 g.) and dry chloroform or dry carbontetrachloride (100 cm^3) were mixed together and refluxed in a water bath for two hours. Yellow crystals (14.5 g.) were obtained which melted at 181-182°C. (lit. 182-183°C) [35,36]
[Found C, 26.95; H, 2.54: $C_8H_9Br_3OTe$ requires C, 27.05; H, 2.56 %]

A.1.1.11 p-Phenetyltelluriumtribromide. $p\text{-}C_2H_5OC_6H_4TeBr_3$

Bis-p-phenetylditelluride (2.0 g.) was reacted with excess bromine in carbontetrachloride. The tribromide product was recrystallized from glazial acetic acid and yellow crystals were obtained. m.p. 198-204°C (lit. 195-205°C) [37]
[Found C, 19.4; H, 1.92; Te, 26.10: $C_8H_9Br_3OTe$ requires C, 19.66; H, 1.86; Te, 26.13 %]

A.1.1.12 Bis-p-phenetylditelluride. $(p\text{-}C_2H_5OC_6H_4)_2Te_2$

A similar procedure as that used in the preparation of Bis-p-anisylditelluride was employed.

p-Phenetyltelluriumtrichloride (6.0 g.) was reduced by potassium metabisulphite (11.3 g.). The golden crystalline

ditelluride (2.4 g.) obtained had a melting point 106-107° C (lit. 107-108°C) [35,36]
[Found C, 38.70; H, 3.70: $C_{16}H_{18}O_2Te_2$ requires C, 38.62; H, 3.65 %]

A.1.1.13 p-Phenoxyphenyltelluriumtrichloride. p-$C_6H_5OC_6H_4TeCl_3$

A mixture of diphenylether (18.7 g.), telluriumtetrachloride (23.8 g.) and dry chloroform (15 cm^3) was heated under reflux for twenty-six hours. One hour after the reaction was started a pink precipitate was observed, which changed colour. The yellow crystals subsequently obtained were recrystallized from carbon tetrachloride and were found to melt at 155-156° C (lit. 156-157° C) [38]
[Found C, 36.10; H, 2.20; Te, 31.46: $C_{12}H_9Cl_3OTe$ requires C, 35.74; H, 2.25; Te, 31.65 %]

A.1.1.14 p-Phenoxyphenyltelluriumtribromide. p-$C_6H_5OC_6H_4TeBr_3$

Bis-p-phenoxyphenylditelluride (0.68 g.) was reacted with excess bromine in carbon tetrachloride. The tribromide (1.25 g.) was recrystallized from glacial acetic acid to yield yellow crystals which melted at 205-206° C (lit. 206-207° C) [37]
[Found C, 26.55; H, 1.66; Te, 23.72: $C_{12}H_9Br_3OTe$ requires C, 26.85; H, 1.69; Te, 23.78 %]

A.1.1.15 Bis-p-phenoxyphenylditelluride. $(p\text{-}C_6H_5OC_6H_4)_2Te_2$

p-Phenoxyphenyltelluriumtrichloride (4.0 g.) was reduced by potassium metabisulphite (6.6 g.) to yield deep violet

crystals (3.0 g.) which melted at 85-87° C (lit. 87-88° C) [37]
[Found C, 49.10; H, 3.05: $C_{24}H_{18}O_2Te_2$ requires C, 48.55; H, 3.06 %]

A.1.1.16 p-Thiophenoxyphenyltelluriumtrichloride. $p\text{-}C_6H_5SC_6H_4TeCl_3$

A solution of 9.3 g. diphenylsulphide and 13.5 g. telluriumtetrachloride in 20 cm^3 dry chloroform was refluxed for forty hours, during which time hydrogen chloride was evolved. The dark crystalline product obtained was dissolved in benzene and precipitated with petroleum ether (40/60). The crude trichloride (8.9 g.) was purified by recrystallisation from glacial acetic acid or from a mixture of benzene and petroleum ether (40/60) as dark yellow needles m.p. 164-165° C (lit 164.5-165.5° C) [37]
[Found C, 34.25; H, 2.13: $C_{12}H_9Cl_3Te$ requires C, 34.37; H, 2.17 %]

A.1.1.17 p-Thiophenoxyphenyltelluriumtribromide. $p\text{-}C_6H_5SC_6H_4TeBr_3$

To a cold solution of 0.63 g. di-p-thiophenoxyphenylditelluride was added dropwise with stirring excess bromine in carbon tetrachloride. The product (0.84 g.) was recrystallized from glacial acetic acid to yield yellow-orange plates which melted at 205-206° C (lit. 206-207° C) [37]
[Found C, 26.15; H, 1.67: $C_{12}H_9Br_3STe$ requires C, 26.07; H, 1.64 %]

A.1.1.18 Bis-p-thiophenoxyphenylditelluride. $(p\text{-}C_6H_5SC_6H_4)_2Te_2$

p-Thiophenoxyphenyltrichloride (4.2 g.) was added to hydrated sodium sulphide ($Na_2S.9H_2O$) and heated at 95-100°C for fifteen minutes. The reaction was exothermic and the bis-p-thiophenoxyphenylditelluride separated as a red oil. The mixture was then diluted with water, and on cooling the ditelluride separated and was recrystallised from petroleum ether (40/60°C) to yield red needles which melted at 88-90°C (lit. 89-90°C) [37]

[Found C, 45.90; H, 2.80: $C_{24}H_{18}S_2Te$ requires C, 46.07; H, 2.90 %]

A.1.1.19 p-Bromophenyltelluriumtrichloride. $p\text{-}BrC_6H_4TeCl_3$

Tellurium tetrachloride (27.0 g.) and bromobenzene (150 cm^3) were refluxed for twelve hours. The mixture was allowed to cool and the crystals formed were collected, washed with benzene and dried in a vacuum desiccator m.p. 209°C dec. (lit. 210°C) [39]

[Found C, 18.30; H, 0.97: $C_6H_4Br_4Te$ requires C, 18.48; H, 1.04 %]

A.1.1.20 p-Bromophenyltribromide. $p\text{-}BrC_6H_4TeBr_3$

Bromine in carbontetrachloride was slowly added to a cold solution of di-p-bromophenylditelluride (0.57 g.) in carbon-tetrachloride. The yellow precipitate was recrystallized from glacial acetic acid m.p. 223-5° C.

[Found C, 13.62; H, 0.70: $C_6H_4Br_4Te$ requires C, 13.76; H, 0.77 %]

A.1.1.21 Bis-p-bromophenylditelluride. $(p\text{-}BrC_6H_4)_2Te_2$

p-Bromophenyltelluriumtrichloride 3.90 g. (0.01 mol.) in 150 cm^3 of ethanol was slowly added to a refluxing mixture of hydrazine 3.2 g. (0.1 mol.) in 20 cm^3 of ethanol. In the beginning every addition resulted in a vigorous evolution of N_2 . When this evolution had ceased the mixture was filtered whilst still hot. On cooling (finally to -25° C) ditelluride crystals separated m.p. 161-162°C (lit. 162-163° C) [39]
[Found C, 25.15; H, 1.30: $C_{12}H_8Br_2Te_2$ requires C, 25.40; H, 1.42 %]

A.1.2 PREPARATION OF DIARYLTELLURIUMDICHLORIDE AND DIARYLDITELLURIDE.

A.1.2.1 Di-(p-methoxyphenyl)telluriumdichloride. $(p\text{-}CH_3OC_6H_4)_2TeCl_2$

Di-p-methoxyphenyltelluriumdichloride was prepared from the reaction of anisole and telluriumtetrachloride using the method described by Kellett [35] Telluriumtetrachloride (15 g.) and anisole (30 g.) were heated for twenty-four hours at 150-180°C. The solution was then allowed to solidify in vacuum. The crystalline product which separated was recrystallized from benzene/petroleum ether (40/60) to give colourless prisms. Yield 12.0 g. m.p. 181°C (lit. m.p. 181-182°C) [35]
[Found C, 40.81; H, 3.48; Te, 30.91: $C_{14}H_{14}Cl_2O_2Te$ requires C, 40.73; H, 3.42; Te, 30.93 %]

A.1.2.2. Di(p-methoxyphenyl)telluride. $(p\text{-}CH_3OC_6H_4)_2Te$

The di(p-methoxyphenyl)telluriumdichloride (10 g.) was dissolved in benzene (50 cm^3) and a saturated solution of potassium metabisulphite (60 cm^3) was added to it and then the mixture was stirred for four hours at room temperature. The organic layer was separated and washed with distilled water. The benzene solution was separated and the solvent evaporated under vacuum to leave behind light yellow solids when then recrystallized from aqueous alcohol, yield 6.7 g. m.p. 54°C. (lit. 53-54°C) [40]

[Found C, 49.30; H, 4.3; Te, 37.14: $C_{14}H_{14}O_2Te$ requires C, 49.18; H, 4.13; Te, 37.35 %]

A.1.2.3. Di(p-ethoxyphenyl)tellurium dichloride. $(p\text{-}C_2H_5OC_6H_4)_2TeCl_2$

The di(p-ethoxyphenyl)telluriumdichloride was prepared following the method of Morgan & Drew. [34] Tellurium tetrachloride (22 g.) was mixed with phenetole (95 g.) and the mixture was refluxed for eight hours at 180-190°C in an oil bath. Hydrogen chloride was evolved and the addition of petroleum ether to the mixture when cold caused the deposition of bis-p-phenetyltelluriumdichloride; which was purified by recrystallization from methanol. The dichloride formed colourless, glistening, prismatic needles. Yield 20 g. m.p. 108°C (lit. 108°C) [40]

[Found C, 43.20; H, 4.16; Te, 28.89: $C_{16}H_{18}Cl_2O_2Te$ requires C, 43.59; H, 4.12; Te, 28.89 %]

A.1.2.4. Di(p-ethoxyphenyl)telluride. $(p\text{-}C_2H_5OC_6H_4)_2Te$

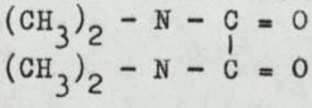
The di(p-ethoxyphenyl) telluride (15 g.) was dissolved in benzene (80 cm^3) and to this solution a saturated solution of potassium metabisulphite (60 cm^3) was added and the mixture was stirred for six hours at room temperature. The organic layer was separated and washed three times with distilled water. The organic layer was evaporated under vacuum and the residue was crystallized from aqueous methanol. Yield(10 g.) m.p. 64°C (lit. 64°C) [40]

[Found C, 52.25; H, 4.98; Te, 34.46: $C_{16}H_{18}O_2Te$ requires C, 51.95; H, 4.91; Te, 34.52 %]

A.1.3. PREPARATION OF SULPHUR CONTAINING LIGANDS

NNN'N' Tetramethyldithio-oxamide was prepared by reaction of NNN'N' tetramethyl-oxamide with phosphorus pentasulphide using an analogus preparation to that described by Hurd [41] for the preparation of NNN'N' tetraethyldithio-oxamide.

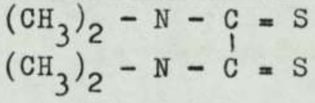
A.1.3.1. Preparation of NNN'N' Tetramethyl-oxamide



$$\begin{array}{l}(CH_3)_2 - N - C = O \\ \qquad\qquad\quad | \\ (CH_3)_2 - N - C = O\end{array}$$

A solution of 250 cm^3 (4.0 mol.) of dimethylamine in 3400 cm^3 of dry benzene was prepared. [42] 75 cm^3 (1 mol.) of oxalylchloride in 1500 cm^3 of dry benzene was added to this solution with stirring, the mixture then being cooled in an ice-bath. After standing for sixteen hours the dimethylaminehydrochloride was filtered off and the benzene solution of tetramethyloxamide evaporated under vacuum to give 82.0 g. of crude product. Recrystallisation from dry diethylether gave white needles m.p. 79°C (lit. 80°C)[42] [Found C, 49.65; H, 8.10; N, 19.20: $C_6H_{12}N_2O_2$ requires C, 49.97; H, 8.40; N, 19.44 %]

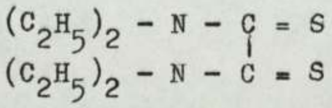
A.1.3.2 Preparation of NNN'N' Tetramethyldithio-oxamide.



$$\begin{array}{l}(CH_3)_2 - N - \underset{|}{C} = S \\ (CH_3)_2 - N - C = S\end{array}$$

NNN'N' Tetramethyloxamide (10 g.) in 150 cm^3 of dry xylene was heated to reflux and phosphorus pentasulphide 6.2 g. (0.4 mol.) added in small increments. The mixture was refluxed for four hours then filtered off hot and finally the solution was allowed to cool overnight. The yellow solid which crystallized out was filtered off, and washed with a little dry xylene to give 5.2 g. of crude product. Recrystallisation from dry ethanol gave yellow needles. m.p. 137°C (lit. 137°C)[42]
[Found C, 40.55; H, 7.36; N, 15.89: $C_6H_{12}N_2S_2$ requires C, 40.91; H, 6.87; N, 15.91 %]

A.1.3.3. Preparation of NNN'N' Tetraethyldithio-oxamide.

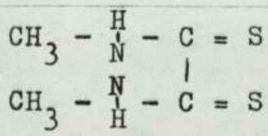


$$\begin{array}{l}(C_2H_5)_2 - N - \underset{|}{C} = S \\ (C_2H_5)_2 - N - C = S\end{array}$$

Tetraethyloxamide[43] was first prepared from diethylamine and oxalylchloride and the product reacted with phosphorus pentasulphide to form tetraethyldithiooxamide as described by Hart et. al.[26] a modification of the method first described by Hurd et. al.[41]

Tetraethyloxamide was prepared by the slow addition of oxalylchloride 100 g. (0.8 mol.) to a xylene solution (790 cm^3) of diethylamine 324 cm^3 (3.2 mol.). The mixture was cooled in an ice bath during the addition. After standing for sixteen hours the diethylamine hydrochloride was filtered off, and the xylene solution of tetraethyloxamide transferred to a two-necked boiling flask and brought to reflux. To the refluxing solution was added 71.3 g. (0.32 mol.) of phorphorus pentasulphide in small increments. The mixture was then refluxed for a further four hours, cooled and filtered. The xylene solution of NNN′N′ tetraethyldithiooxamide evaporated under vacuum to give 140 g. of an oily brown solid. This product was purified by treatment in a hot ethanolic solution with charcoal and recrystallization from ethanol gave 106 g. of a white solid. m.p. 88-89°C (lit. 88-90°C)[41] [Found C, 52.05; H, 8.65; N, 12.05: $C_{10}H_{20}N_2S_2$ requires C, 51.72; H, 8.70; N, 12.07 %]

A.1.3.4. Preparation of NN′ dimethyldithio-oxamide



$$\begin{array}{l} CH_3-\overset{H}{N}-C=S \\ \qquad\qquad\quad | \\ CH_3-\underset{H}{N}-C=S \end{array}$$

NN′ dimethyldithio-oxamide was prepared by reaction of dithio-oxamide 12 g. (0.1 mol.) with 6.2 g. (0.2 mol.) of methylamine in 60 cm^3 of ethanol. The solution was stirred at room temperature for four hours, then left to stand overnight. The solid which was obtained was filtered off and purified by recrystallization using ethanol and charcoal to give yellow crystals. m.p. 138°C (lit. 140°C) [41,44]

[Found C, 32.63; H, 5.52; N, 18.82; $C_4H_8N_2S_2$ requires C, 32.42; H, 5.44; N, 18.91 %]

APPENDIX 2

A new rapid procedure for the determination of tellurium content in organotellurium compounds by using Atomic absorption spectroscopy.

A.2.1 INTRODUCTION

Since a large number of organotellurium compounds were being prepared during the course of practical work; a new rapid procedure for the determination of the tellurium content was desired. Broadly there are three types of analytical methods available for the determination of tellurium; gravimetric, titrimetric and spectrophotometric.

A gravimetric method for the analysis of tellurium in organotellurium compounds was developed by Drew and Porter.[187] This method is applicable to alkyltellurium compounds only. Also a new gravimetric method was developed by Tsao[188] which involves fusion of the organotellurium compounds with sodium peroxide in a Parr bomb. The product obtained was finally reduced to tellurium metal and weighed. This method applied to all types of organotellurium compounds. The only disadvantage is that it involves a very tedious procedure. The particles of tellurium oxidise leading to high results.

A titrimetric method was developed by Kruse et al.[189] The sample was decomposed, first by heating with 70% nitric acid and then with a mixture of 30% nitric acid and 70% perchloric acid. To this final solution a known excess of iron (II) ammonium sulphate solution was added, and using standard potassium dichromate, back titration was performed. The Kruse et al method is less tedious than Tsao's method but it is subject to more errors and requires more samples for each analysis.[190]

A spectrophotometric method for analysis of tellurium in alloys by using atomic absorption spectroscopy, has been reported [191,192]. None of these methods for the preparation of sample solutions can be used to prepare a suitable solution of organotellurium compounds. Adaptation of this method for aryltelluriumtrihalides was described by Thavornyutikarn[190]. A 15-50 mg. sample was decomposed with a mixture of 3-4 cm^3 of nitric acid and 3-4 cm^3 of perchloric acid which was carefully heated on a hot plate. The acids were allowed to evaporate slowly to dryness in a very efficient fume-cupboard, for one and a half hours. The white residue obtained was dissolved in warm distilled water and 0.5 cm^3 of hydrochloric acid and the solution was then made up to an exact volume in a volumetric flask (50 cm^3). The absorption of this solution was recorded by atomic absorption spectrophotometry.

In the modification described here[212] the oxygen flask technique is used to decompose the organotellurium compounds and then the tellurium solution produced is submitted to atomic absorption spectrophotometry. Various organotellurium compounds such as diaryltellurides, diaryltelluriumdichlorides, aryltelluriumtrihalides, aryltelluriumtrihalide complexes and telluriumtetrahalide complex with sulphur donor ligands were used in order to evaluate this method.

The oxygen flask method[193-207] is a well known procedure for the decomposition of organic materials.

In 1892, Hempel[194] introduced the method of oxygen flask combustion of organic materials for the determination of sulphur in coals and other materials. The sample was ignited electrically in a platinum gauze basket suspended from the stopper of a 10 litre bottle which had been filled with oxygen. Meslans[195] in 1893 suggested a method for the determination of fluorine in gaseous alkylfluorides whereby the gas would be fed into a partially evacuated flask containing oxygen. Graefe[196] in 1904 recommended the use of cotton thread or filter paper as a fuse instead of electrical ignition, and provided oxygen from the sodium peroxide in the absorbing solution. Using this method the determination of halogens was first developed by Marcusson and Döscher[197]. A large separating funnel, as a combustion vessel, was used by Votocek[198] in 1922 so that the absorbent could be more readily transferred to a convenient flask for titration. The determination of chlorine was obtained this way. Roth[199] in 1950 determined traces of sulphur by ignition of samples. Schöniger[200,201] proved the oxygen flask method was versatile and how accurate the procedure could be for micro work for organic materials. Virtually all later investigations have been carried out from Schöniger's papers.

The oxygen flask method is a well known procedure for the fast decomposition of organic materials for the determination of halogen and sulphur[199,200], phosphorus[202], arsenic, boron, zinc, cadmium and magnesium complexes[203], calcium, cobalt and barium complexes[204], copper[205], manganese and nickel[206], and selenium[207] but the latter element is said to attack the platinum gauze and this leads to inaccurate results.

Organic tellurium compounds can be determined by a very simple procedure based on the titration, gravimetric or spectrophotometric method[187-190]. The oxygen flask technique is an extremely fast means of decomposing organic materials for the determination of various elements and so it was decided to investigate its applicability to a wide range of organotellurium compounds. Various aryltelluriumtrihalides, diaryltelluriumdichlorides, diaryltelluride, aryltellurium-trihalides complexes with sulphur donor ligands and tellurium-tetrahalide complexes such as $RTeX_3$, R_2TeCl_2, R_2Te, $RTeX_3$tedto $RTeX_3$tmdto, $RTe(ttz)_xX_3$ and TeX_4tmdto where X = Cl, Br or I, R = Phenyl, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$, $p\text{-}C_2H_5OC_6H_4$, $p\text{-}C_6H_5OC_6H_4$, $p\text{-}C_6H_5SC_6H_4$, $p\text{-}BrC_6H_4$, tedto is $NNN'N'$ tetraethyldithiooxamide, tmdto is $NNN'N'$ tetramethyldithiooxamide and ttz is thiazolidine-2-thione were studied in order to evaluate the method.

A.2.2 EXPERIMENTAL

A.2.2.1 The instrument

The Perkin-Elmer Model 303 Atomic Absorption spectrophotometer (Fig.A2-1/2) equipped with a Perkin-Elmer recorder Model no. 56 and a Fischer-Porter Burner regulator (Fig. A2-3) [air flow rate 9 acetylene 7-8] was used for the analysis of the tellurium content in the organotellurium compounds. This instrument is a double-beam ac system type. The instrument is represented in diagramatic form in figs. A2-2/4.[208-210]

By a rotating sector mirror, the emission from the spectral source (a tellurium hollow-cathode lamp) is split into two beams. One beam is directed through the sampling flame and the other bypasses it. The two beams are recombined by a semi-transparent mirror, and then they pass through a monochromotor to a photomultiplier detector. After this the signal is separated into sample and reference channels by a vibrating-reed chopper. The reference voltage is then attenuated by a slide-wire and recombined with the sample voltage, in such a way that the difference is taken between them. This different voltage is amplified, rectified and fed to a microammeter. The operator turns the slide-wire until the meter reads a null meter. A counter geared directly to the slide-wire is made to read out in percentage absorption. Alternatively, this nulling process can be accomplished automatically, by the use of a servomotor to drive the slide-wire.

A.2.2.2 The procedure for the determination of the Absorbance in atomic absorption spectrophotometer Model 303.

The operating procedure and the problems encountered arising from the use of the instrument, are given in the manual. Also a general procedure used to run the analysed solutions was provided.

The Activion tellurium hollow-cathode lamp was fitted into its holder, the power was switched on. The source knob was slowly turned clock-wise until the operating current of the lamp was 10 mA. After warming up the lamp and the instrument for thirty minutes, a wavelength of 214.2 nm, slit 4, range U.V. and the appropriate filter were set according to the manual.

The gain control was adjusted to bring the needle on the energy meter to the black portion of the scale, and the fine wavelength control was adjusted to maximum detection (to the right on the energy meter).

The flowmeter was adjusted to air and acetylene at 9 and 7-8 respectively. After lighting the flame, distilled water was aspirated and the zero control was adjusted to bring the meter to zero detection at 0.00 absorption reading. The scale of expansion and noise suppression were selected on a Perkin-Elmer recorder (Model No.56).

The standard and sample solutions of tellurium were analysed by the instrument. The absorptions were obtained either from the absorption scale, by bringing the needle of the zero meter to zero or from the chart paper of the readout unit. In order to verify base line stability, distilled water was run between each standard or sample solution. To obtain the base result each solution must run for at least thirty seconds.

The calibration curve was obtained by the dilution of 1000 µg. Te/ml. solution to give seven standards within the range 5-50 µg. Te/ml. For every six samples the run of the standard solutions were reported.

The percentage of absorption in the sample and in the standard solutions were converted to absorbance by using table A.2-1.

A.2.2.3 Apparatus for the oxygen flask method.

A conical flask($500\ cm^3$) with a B24 ground glass joint was used for this method which was suitable for the combustion of 3-10 mg. of organotellurium compounds. A short platinum wire (1 mm. diam.) was sealed into an airleak as shown in fig.A2-5 and a $1.5 \times 2.0\ cm^3$ oblong platinum gauze (36 mesh) was spot welded to the wire. The length of the wire should be about 5 cm so that the gauze was positioned just below the centre of the flask. The edge of the gauze should be turned over or welded in order to hold the paper securely.

The standard (Analar telluric acid) was weighed by using a"Stanton" balance but the samples (organotellurium compounds) were weighed by using an " oertling micro balance Model 147".

Analar telluric acid (purity 99.5%), as standard, was obtained from Hopkins and Williams Ltd. Hydrochloric acid (Analar) and hydrogen peroxide (50%) were obtained from Fisons Ltd.

A.2.2.4 Preparation of the standard tellurium solution.

The stock solution of 1000 µg Te/ml. was prepared by dissolving telluric acid 1.7951 g. with distilled water in a one litre volumetric flask containing concentrated hydrochloric acid ($10\ cm^3$). This stock solution was stored in a polythene bottle in order to avoid alteration of the concentration. From the stock solution seven different concentrations were prepared between 5-50 µg 1 ml. and a typical calibration curve is shown in figure A.2-6

A.2.2.5 The procedure for the decomposition of organotellurium compounds by the oxygen flask method.

Samples were weighed between (3-10 mg.) in a weighing tube, from a 3 x 3 cm square of Whatman No. 42 filter paper which has a 3 cm fuse protruding (fig.A2-5). The paper was wrapped up carefully and secured in the platinum hinge which had previously been heated to redness and cooled. 15 cm^3 of distilled water, 1 cm^3 of (50%) hydrogen peroxide and 1 cm^3 of hydrochloric acid was added to the flask and a fast flow of oxygen was passed through it for about 1 minute. [SAFETY GLASSES MUST BE WORN DURING THE NEXT OPERATION]. The filter paper and sample were ignited and the stopper was inserted quickly and the flask was inverted, turning it so that the solution formed a seal. The stopper and flask were held very firmly together during the combustion. The flask was shaken intermittently for about 10-15 minutes, until all the combustion products appeared to have been dissolved and then they were transferred to a volumetric flask (50 cm^3). The stopper and gauze were washed with 5 cm^3 of distilled water three times in order to make sure no solutions were left undissolved. The volume was made up to 50 cm^3 with distilled water.

The solutions of the standard and the unknown 4.602 mg. (p-$C_6H_5OC_6H_4TeCl_3$tedto) were analysed by an atomic absorption spectrophotometer to determine the absorption, and the results are shown in table A.2-2.

A calibration graph was obtained by plotting standard concentrations versus their absorbance as shown in Fig. A2-6. The unknown concentration read off from the graph is shown in fig. A.2-6.

$$\text{The Te percentage} = \frac{18.5\ \mu g/ml. \times 50\ ml. \times 100}{0.004602 \times 10^6\ \mu g}$$

The Te percentage = 20.10

The other samples were analysed using the same procedure as above and the results are shown in tables A.3-3/4/5.

A.2.3 DISCUSSION

In general to decompose aryltellurium compounds, a mixture of concentrated nitric and sulphuric acids or concentrated nitric and perchloric acids may be used, a time consuming process which is usually two to three hours.[188,189] It is difficult to evaporate sulphuric acid at a low temperature in a short time because it has a high boiling point 338°C. The mixture evaporates at a high temperature, when the rate of evaporation is increased it may cause the loss of the sample.

Organotellurium compounds have been decomposed by a mixture of concentrated nitric and perchloric acids The weight of the samples used were between 15-50 mg. and the time taken to decompose about one and a half hours.[190]

The disadvantage of the acid method of decomposition for the analysis of tellurium is that the decomposition of the compounds by a mixture of concentrated nitric and perchloric acids is potentially dangerous due to the explosive nature of perchloric acid.

"Analar" telluric acid (H_6TeO_6) was used for the preparation of the standard solution which was more convenient than the recommended method, of using tellurium metal.[211]

When following the recommended method, the tellurium metal has primarily to be dissolved in concentrated nitric acid, and then this acid has to be expelled by addition of hydrochloric acid and further heating which can easily introduce errors in the preparation of the standard solution.

The two methods of decomposing the organotellurium compounds were compared. The first method takes one and a half hours using concentrated nitric and concentrated perchloric acids (sample weight 15-50 mg.), and the oxygen flask method takes only thirty minutes using a sample weight of 3-10 mg. and a lower concentration of acid.

The determination of the tellurium content of organotellurium compounds by their decomposition using the oxygen flask technique followed by atomic absorption spectrophotometry has found to be successful as shown in tables A.2-3/5. A wide variety of tellurium compounds containing between 13-42%Te. were analysed by this method. Diarylditelluride (such as di-p-anisylditelluride) were not completely oxidised however. Presumably, they were not decomposed.

Nine analyses of tetraethyldithio-oxamide complex with p-phenoxyphenyltelluriumtrichloride were obtained. The standard deviation and coefficient of variation are 0.11 and 0.553 respectively as equation 1 and 2 (see table A.2-6).

$$S = \sqrt{\frac{\sum(\bar{x} - x)^2}{n - 1}} \qquad \ldots\ldots \qquad (1)$$

$$c = \frac{100\ S}{\bar{x}} \qquad \ldots\ldots \qquad (2)$$

where S = standard deviation

$\bar{x}$ = the mean value ($= \frac{\sum x}{n}$)

x = the true value

n = number of determination

c = coefficient of variation

From table A.2-7 and equation 1, standard deviation of 0.23 for forty-one other samples (such as aryltelluriumtrihalides, diaryltellurides, diaryltelluriumdichloride, aryltellurium-trichloride complexes with sulphur donor ligands and tellurium tetrahalide complexes) was obtained.

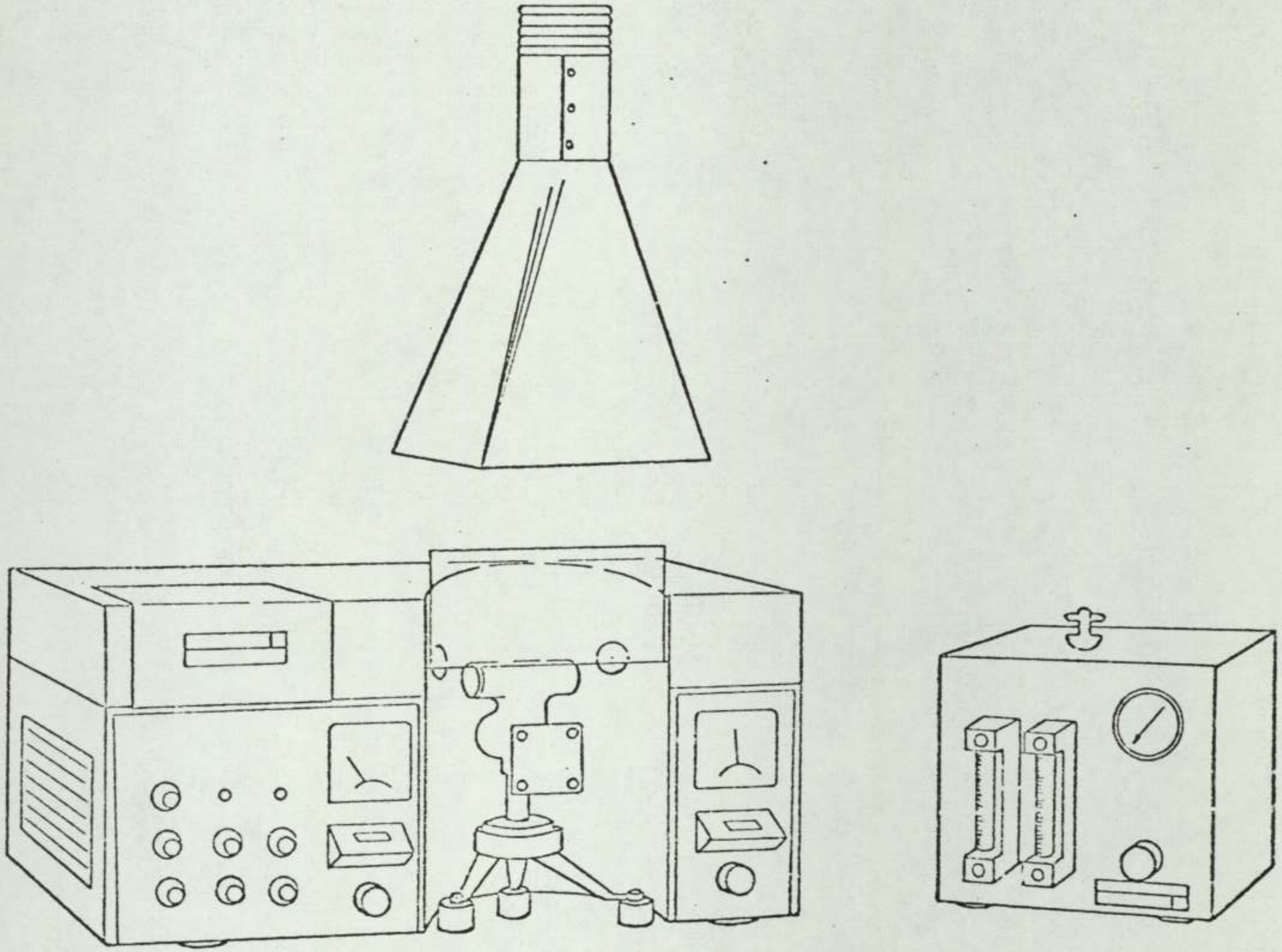


Fig. A.2-1 The double beam of Perkin-Elmer model 303

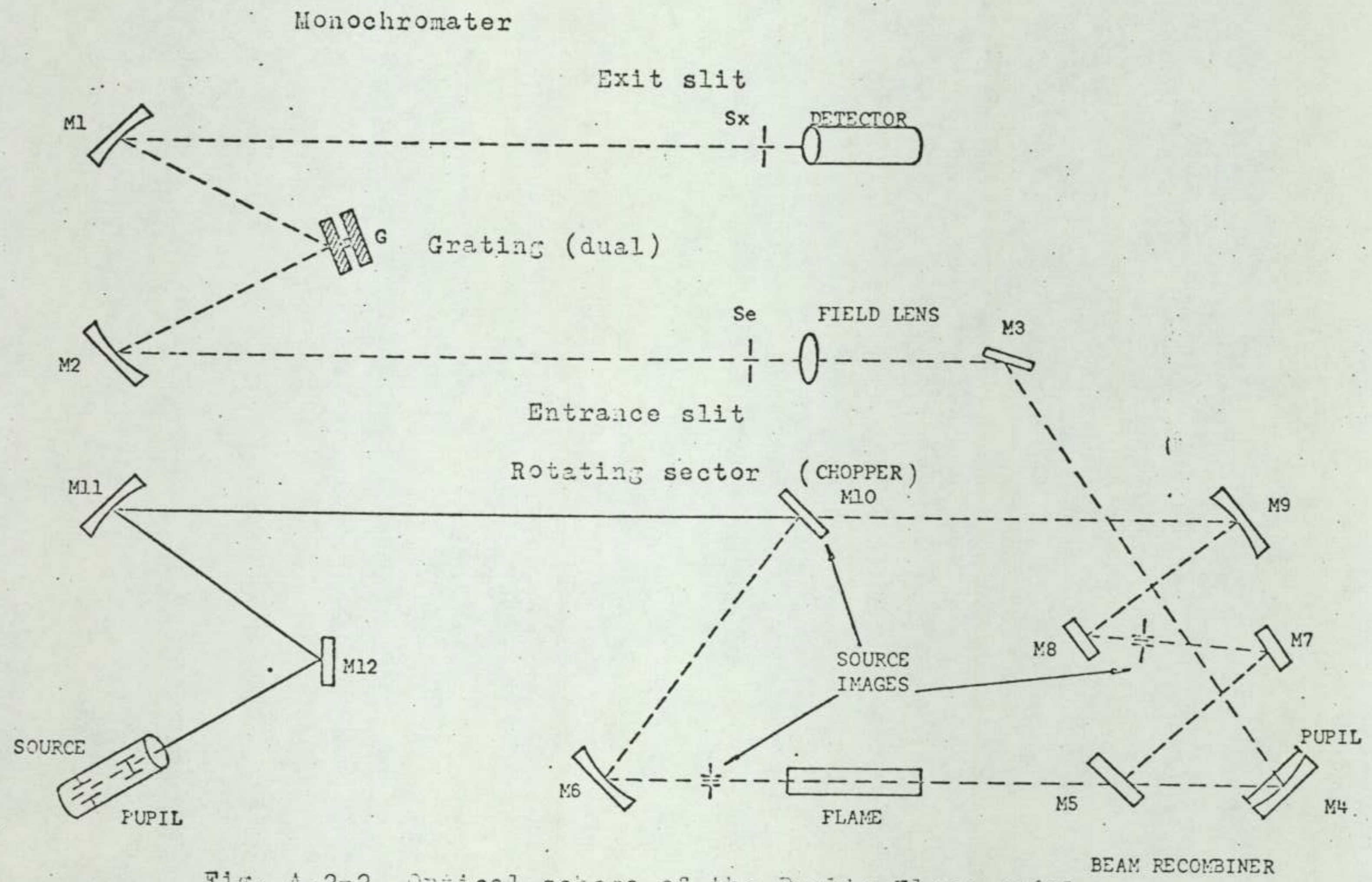


Fig. A.2-2 Optical scheme of the Perkin-Elmer model 303 double-beam spectrophotometer.

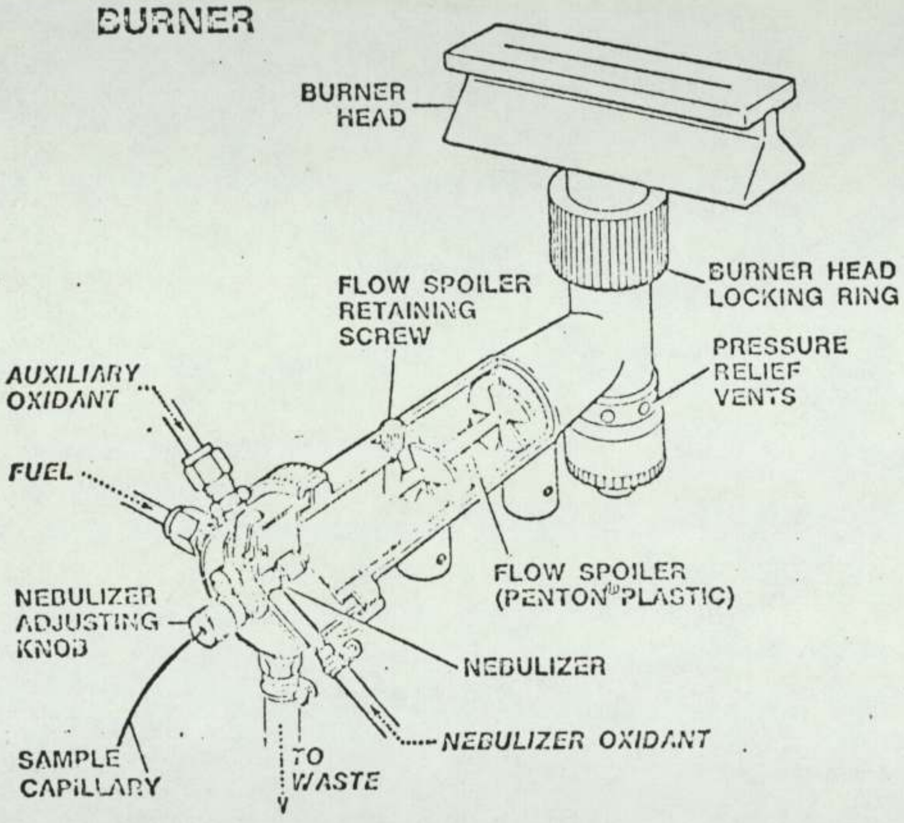


Fig. A.2-3

Fischer-Porter Burner for the Perkin-Elmer Model 303 double beam spectrophotometer.

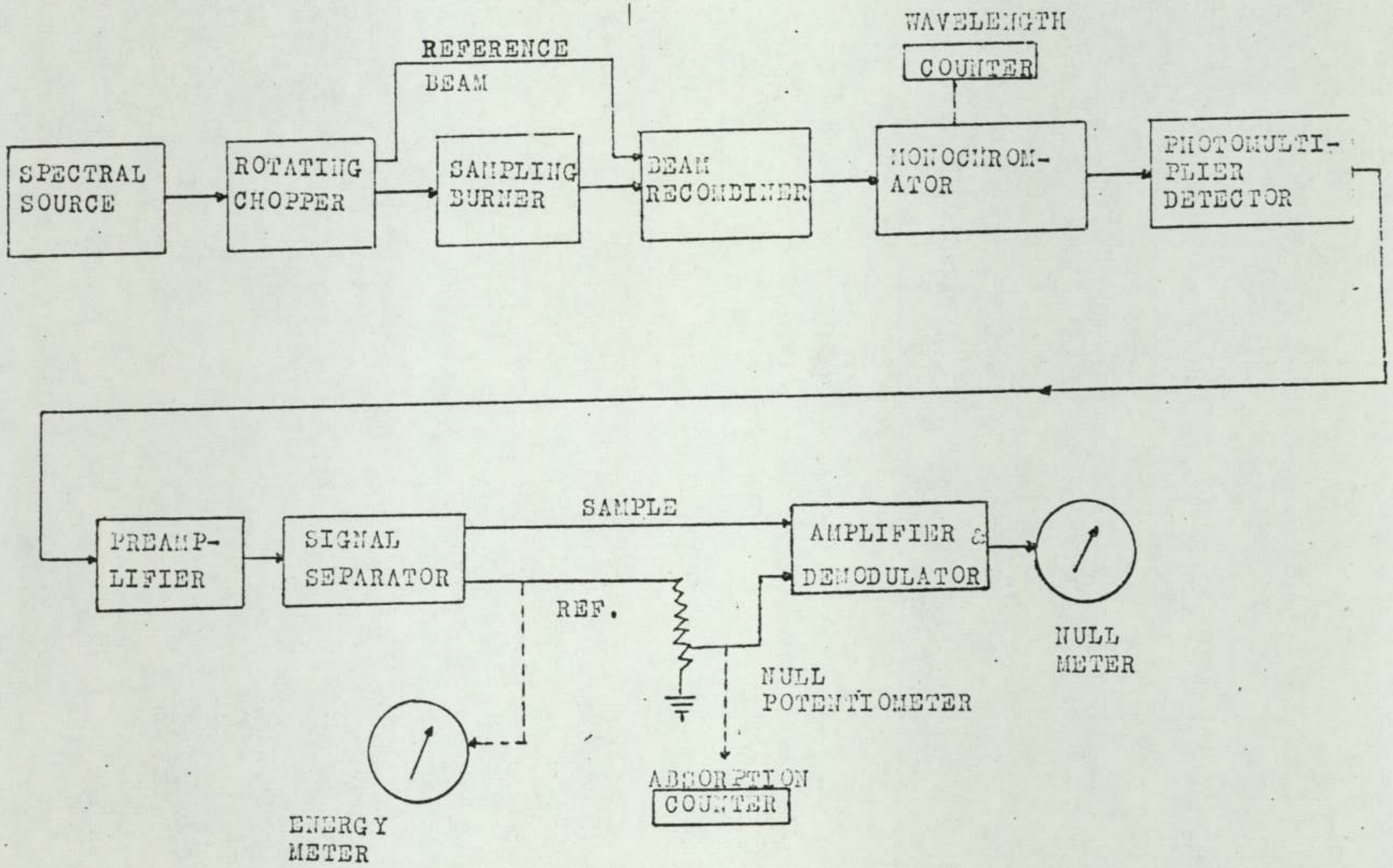


Fig. A2-4 Block diagram of the instrument

COMBUSTION OXYGEN FLASK APPARATUS:

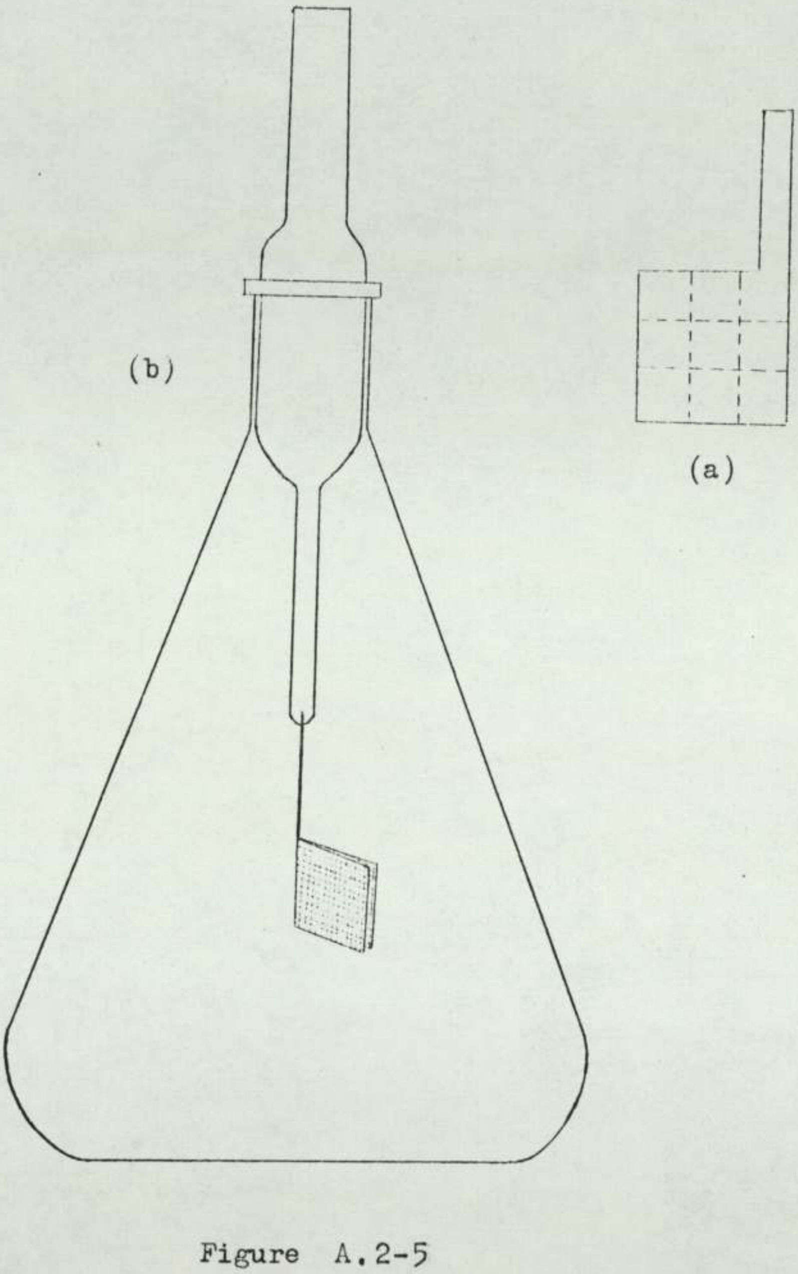


Figure A.2-5

(a) Ashless filter paper used for wrapping sample with fold lines indicated.

(b) Conical flask with platinum sample holder.

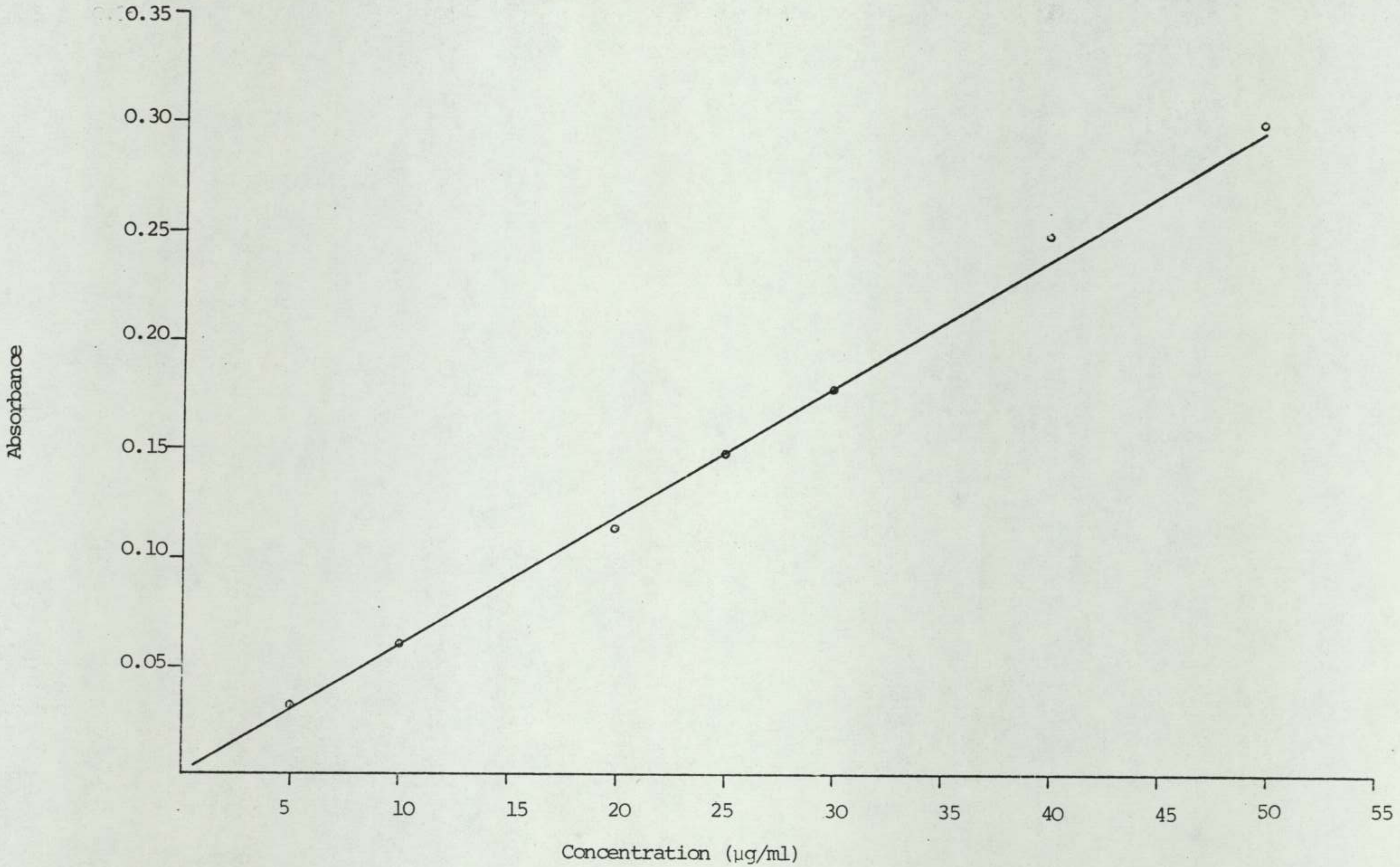

Absorbance
0.35
0.30
0.25
0.20
0.15
0.10
0.05
5
10
15
20
25
30
35
40
45
50
55
Concentration (µg/ml)

Fig. A. 2-6

Table A 2-1VALUES OF ABSORBANCE FOR PER CENT ABSORPTION

convert per cent absorption (%A) to absorbance, find the per cent absorption to the nearest whole digit the left-hand column; read across to the column located under the tenth of a per cent desired, and read value of absorbance. The value of absorbance corresponding to 26.8% absorption is thus 0.1355.

.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
.0000	.0004	.0009	.0013	.0017	.0022	.0026	.0031	.0035	.0039
.0044	.0048	.0052	.0057	.0061	.0066	.0070	.0074	.0079	.0083
.0088	.0092	.0097	.0101	.0106	.0110	.0114	.0119	.0123	.0128
.0132	.0137	.0141	.0146	.0150	.0155	.0159	.0164	.0168	.0173
.0177	.0182	.0186	.0191	.0195	.0200	.0205	.0209	.0214	.0218
.0223	.0227	.0232	.0236	.0241	.0246	.0250	.0255	.0259	.0264
.0269	.0273	.0278	.0283	.0287	.0292	.0297	.0301	.0306	.0311
.0315	.0320	.0325	.0329	.0334	.0339	.0343	.0348	.0353	.0357
.0362	.0367	.0372	.0376	.0381	.0386	.0391	.0395	.0400	.0405
.0410	.0414	.0419	.0424	.0429	.0434	.0438	.0443	.0448	.0453
.0458	.0462	.0467	.0472	.0477	.0482	.0487	.0491	.0496	.0501
.0506	.0511	.0516	.0521	.0526	.0531	.0535	.0540	.0545	.0550
.0555	.0560	.0565	.0570	.0575	.0580	.0585	.0590	.0595	.0600
.0605	.0610	.0615	.0620	.0625	.0630	.0635	.0640	.0645	.0650
.0655	.0660	.0665	.0670	.0675	.0680	.0685	.0691	.0696	.0701
.0706	.0711	.0716	.0721	.0726	.0731	.0737	.0742	.0747	.0752
.0757	.0762	.0768	.0773	.0778	.0783	.0788	.0794	.0799	.0804
.0809	.0814	.0820	.0825	.0830	.0835	.0841	.0846	.0851	.0857
.0862	.0867	.0872	.0878	.0883	.0888	.0894	.0899	.0904	.0910
.0915	.0921	.0926	.0931	.0937	.0942	.0947	.0953	.0958	.0964
.0969	.0975	.0980	.0985	.0991	.0996	.1002	.1007	.1013	.1018
.1024	.1029	.1035	.1040	.1046	.1051	.1057	.1062	.1068	.1073
.1079	.1085	.1090	.1096	.1101	.1107	.1113	.1118	.1124	.1129
.1135	.1141	.1146	.1152	.1158	.1163	.1169	.1175	.1180	.1186
.1192	.1198	.1203	.1209	.1215	.1221	.1226	.1232	.1238	.1244
.1249	.1255	.1261	.1267	.1273	.1278	.1284	.1290	.1296	.1302
.1308	.1314	.1319	.1325	.1331	.1337	.1343	.1349	.1355	.1361
.1367	.1373	.1379	.1385	.1391	.1397	.1403	.1409	.1415	.1421
.1427	.1433	.1439	.1445	.1451	.1457	.1463	.1469	.1475	.1481
.1487	.1494	.1500	.1506	.1512	.1518	.1524	.1530	.1537	.1543
.1549	.1555	.1561	.1568	.1574	.1580	.1586	.1593	.1599	.1605
.1612	.1618	.1624	.1630	.1637	.1643	.1649	.1656	.1662	.1669
.1675	.1681	.1688	.1694	.1701	.1707	.1713	.1720	.1726	.1733
.1739	.1746	.1752	.1759	.1765	.1772	.1778	.1785	.1791	.1798
.1805	.1811	.1818	.1824	.1831	.1838	.1844	.1851	.1858	.1864
.1871	.1878	.1884	.1891	.1898	.1904	.1911	.1918	.1925	.1931
.1938	.1945	.1952	.1959	.1965	.1972	.1979	.1986	.1993	.2000
.2007	.2013	.2020	.2027	.2034	.2041	.2048	.2055	.2062	.2069
.2076	.2083	.2090	.2097	.2104	.2111	.2118	.2125	.2132	.2140
.2147	.2154	.2161	.2168	.2175	.2182	.2190	.2197	.2204	.2211
.2218	.2226	.2233	.2240	.2248	.2255	.2262	.2269	.2277	.2284
.2291	.2299	.2306	.2314	.2321	.2328	.2336	.2343	.2351	.2358

Table A2-1 CONTINUED

%\	.0	.1	.2	.3	.4	.5	.6	.7	.8	.9
2.0	.2366	.2373	.2381	.2388	.2396	.2403	.2411	.2418	.2426	.2434
3.0	.2441	.2449	.2457	.2464	.2472	.2480	.2487	.2495	.2503	.2510
4.0	.2518	.2526	.2534	.2541	.2549	.2557	.2565	.2573	.2581	.2588
5.0	.2596	.2604	.2612	.2620	.2628	.2636	.2644	.2652	.2660	.2668
6.0	.2676	.2684	.2692	.2700	.2708	.2716	.2725	.2733	.2741	.2749
7.0	.2757	.2765	.2774	.2782	.2790	.2798	.2807	.2815	.2823	.2832
8.0	.2840	.2848	.2857	.2865	.2874	.2882	.2890	.2899	.2907	.2916
9.0	.2924	.2933	.2941	.2950	.2958	.2967	.2976	.2984	.2993	.3002
0.0	.3010	.3019	.3028	.3036	.3045	.3054	.3063	.3072	.3080	.3089
1.0	.3098	.3107	.3116	.3125	.3134	.3143	.3152	.3161	.3170	.3179
2.0	.3188	.3197	.3206	.3215	.3224	.3233	.3242	.3251	.3261	.3270
3.0	.3279	.3288	.3298	.3307	.3316	.3325	.3335	.3344	.3354	.3363
4.0	.3372	.3382	.3391	.3401	.3410	.3420	.3429	.3439	.3449	.3458
5.0	.3468	.3478	.3487	.3497	.3507	.3516	.3526	.3536	.3546	.3556
6.0	.3565	.3575	.3585	.3595	.3605	.3615	.3625	.3635	.3645	.3655
7.0	.3665	.3675	.3686	.3696	.3706	.3716	.3726	.3737	.3747	.3757
8.0	.3768	.3778	.3788	.3799	.3809	.3820	.3830	.3840	.3851	.3862
9.0	.3872	.3883	.3893	.3904	.3915	.3925	.3936	.3947	.3958	.3969
0.0	.3979	.3990	.4001	.4012	.4023	.4034	.4045	.4056	.4067	.4078
1.0	.4089	.4101	.4112	.4123	.4134	.4145	.4157	.4168	.4179	.4191
2.0	.4202	.4214	.4225	.4237	.4248	.4260	.4271	.4283	.4295	.4306
3.0	.4318	.4330	.4342	.4353	.4365	.4377	.4389	.4401	.4413	.4425
4.0	.4437	.4449	.4461	.4473	.4485	.4498	.4510	.4522	.4535	.4547
5.0	.4559	.4572	.4584	.4597	.4609	.4622	.4634	.4647	.4660	.4672
6.0	.4685	.4698	.4711	.4724	.4737	.4750	.4763	.4776	.4789	.4802
7.0	.4815	.4828	.4841	.4855	.4868	.4881	.4895	.4908	.4921	.4935
8.0	.4948	.4962	.4976	.4989	.5003	.5017	.5031	.5045	.5058	.5072
9.0	.5086	.5100	.5114	.5129	.5143	.5157	.5171	.5186	.5200	.5214
0.0	.5229	.5243	.5258	.5272	.5287	.5302	.5317	.5331	.5346	.5361
1.0	.5376	.5391	.5406	.5421	.5436	.5452	.5467	.5482	.5498	.5513
2.0	.5528	.5544	.5560	.5575	.5591	.5607	.5622	.5638	.5654	.5670
3.0	.5686	.5702	.5719	.5735	.5751	.5768	.5784	.5800	.5817	.5834
4.0	.5850	.5867	.5884	.5901	.5918	.5935	.5952	.5969	.5986	.6003
5.0	.6021	.6038	.6055	.6073	.6091	.6108	.6126	.6144	.6162	.6180
6.0	.6198	.6216	.6234	.6253	.6271	.6289	.6308	.6326	.6345	.6364
7.0	.6383	.6402	.6421	.6440	.6459	.6478	.6498	.6517	.6536	.6556
8.0	.6576	.6596	.6615	.6635	.6655	.6676	.6696	.6716	.6737	.6757
9.0	.6778	.6799	.6819	.6840	.6861	.6882	.6904	.6925	.6946	.6968
0.0	.6990	.7011	.7033	.7055	.7077	.7100	.7122	.7144	.7167	.7190
1.0	.7212	.7235	.7258	.7282	.7305	.7328	.7352	.7375	.7399	.7423
2.0	.7447	.7471	.7496	.7520	.7545	.7570	.7595	.7620	.7645	.7670
3.0	.7696	.7721	.7747	.7773	.7799	.7825	.7852	.7878	.7905	.7932
4.0	.7959	.7986	.8013	.8041	.8069	.8097	.8125	.8153	.8182	.8210
5.0	.8239	.8268	.8297	.8327	.8356	.8386	.8416	.8447	.8477	.8508
6.0	.8539	.8570	.8601	.8633	.8665	.8697	.8729	.8761	.8794	.8827
7.0	.8861	.8894	.8928	.8962	.8996	.9031	.9066	.9101	.9136	.9172
8.0	.9208	.9245	.9281	.9318	.9355	.9393	.9431	.9469	.9508	.9547
9.0	.9586	.9626	.9666	.9706	.9747	.9788	.9830	.9872	.9914	.9957

TABLE A.2-2

Analytical data for $p\text{-}C_6H_5OC_6H_4TeCl_3$tedto

Solutions	% Absorption			Absorbance	% Absorption reading from the graph	wt. of sample in mg.
	1st. Reading	2nd. Reading	Average			
standard 5 ug/ml	7.0	8.0	7.5	0.0339		
standard 10 ug/ml	13.0	14.0	13.5	0.0635		
standard 20 ug/ml	24.0	24.0	24.0	0.1192		
standard 25 ug/ml	29.0	29.0	29.0	0.1487		
standard 30 ug/ml	33.0	33.0	33.0	0.1739		
standard 40 ug/ml	43.0	43.0	43.0	0.2480		
standard 50 ug/ml	49.0	50.0	49.5	0.2967		
sample No.1	22.0	22.0	22.0	0.1079	18.5	4.602
sample No.2	22.0	22.0	22.0	0.1079	18.5	4.652
sample No.3	20.0	20.0	20.0	0.0969	16.5	4.150
sample No.4	22.5	22.5	22.5	0.1107	19.0	4.756
sample No.5	23.0	23.0	23.0	0.1135	19.5	4.902
sample No.6	21.0	21.0	21.0	0.1024	17.5	4.412
sample No.7	18.0	18.0	18.0	0.0862	15.0	3.808
sample No.8	21.0	21.0	21.0	0.1024	17.5	4.404
sample No.9	22.5	22.5	22.5	0.1107	19.0	4.760

TABLE A.2-3

Determination of tellurium in NNN′N′ tetraethyldithio-oxamide complexes with p-phenoxyphenyltelluriumtrichloride ($p-C_6H_5OC_6H_4TeCl_3$tedto)

Compound	Te% obtained	Te% calculated
Sample No.1	20.10	20.03
Sample No.2	19.88	20.03
Sample No.3	19.88	20.03
Sample No.4	19.98	20.03
Sample No.5	19.89	20.03
Sample No.6	19.83	20.03
Sample No.7	19.70	20.03
Sample No.8	19.87	20.03
Sample No.9	19.96	20.03

The p-phenoxyphenyltelluriumtrichloride complex gave satisfactory carbon, hydrogen, and nitrogen analyses as shown in table A. 2-5.

TABLE A.2-4

Analytical data for organotellurium compounds

Solutions	% Absorption			Absorbance	% Absorption reading from the graph	wt. of sample in mg.
	1st. Reading	2nd. Reading	Average			
$C_6H_5TeCl_3$	37.0	37.0	37.0	0.2007	33.2	4.034
$C_6H_5TeBr_3$	42.0	42.0	42.0	0.2366	39.6	6.896
p-$CH_3C_6H_4TeCl_3$	42.5	41.5	42.0	0.2366	39.6	5.074
p-$CH_3C_6H_4TeBr_3$	43.5	42.5	43.0	0.2441	40.5	7.240
p-$C_2H_5OC_6H_4TeBr_3$	43.0	43.0	43.0	0.2441	40.5	7.758
p-$C_6H_5OC_6H_4TeCl_3$	43.0	43.0	43.0	0.2441	40.5	6.436
p-$C_6H_5OC_6H_4TeBr_3$	42.5	41.5	42.0	0.2366	39.6	8.348
$(p\text{-}CH_3OC_6H_4\text{-})_2TeCl_2$	42.0	41.6	41.8	0.2351	39.5	6.388
$(p\text{-}C_2H_5OC_6H_4\text{-})_2TeCl_2$	40.0	40.0	40.0	0.2218	37.0	6.404
$(p\text{-}CH_3OC_6H_4\text{-})_2Te$	41.0	42.0	41.5	0.2328	39.0	5.250
$C_6H_5TeCl_3$tedto*	16.0	16.0	16.0	0.0757	14.0	3.002
$C_6H_5TeBr_3$tedto	25.0	25.0	25.0	0.1249	21.0	5.504
p-$CH_3C_6H_4TeCl_3$tedto	27.0	27.0	27.0	0.1367	23.75	5.198
p-$CH_3C_6H_4TeBr_3$tedto	29.0	28.0	28.5	0.1457	24.0	6.540
p-$C_6H_5OC_6H_4TeCl_3$tedto	23.0	23.0	23.0	0.1135	19.5	4.852
p-$C_6H_5OC_6H_4TeBr_3$tedto	21.0	21.0	21.0	0.1024	17.5	5.378
p-$C_6H_5SC_6H_4TeCl_3$tedto	25.0	25.0	25.0	0.1249	21.0	5.273
p-$C_6H_5SC_6H_4TeBr_3$tedto	24.0	24.0	24.0	0.1192	20.25	6.056
p-$BrC_6H_4TeBr_3$tedto	20.0	20.0	20.0	0.0969	16.5	4.868
$TeCl_4$tmdto**	27.0	27.0	27.0	0.1367	23.75	4.102
$TeBr_4$tmdto	23.0	24.0	23.5	0.1163	19.5	4.782
$C_6H_5TeCl_3$tmdto	24.0	23.0	23.5	0.1163	19.5	3.730
$C_6H_5TeBr_3$tmdto	28.0	27.0	27.5	0.1397	24.0	5.996

Table A2-4...

Solutions	% Absorption			Absorbance	% Absorption reading from the graph	wt. of sample in mg.
	1st. Reading	2nd. Reading	Average			
p-$CH_3C_6H_4TeCl_3$tmdto	27.0	27.0	27.0	0.1367	23.75	4.720
p-$CH_3C_6H_4TeBr_3$tmdto	29.0	29.0	29.0	0.1487	25.0	6.240
p-$CH_3OC_6H_4TeCl_3$tmdto	25.0	26.0	25.5	0.1278	21.5	4.326
p-$CH_3OC_6H_4TeBr_3$tmdto	27.0	27.0	27.0	0.1367	23.75	6.032
p-$C_2H_5OC_6H_4TeCl_3$tmdto	24.0	24.0	24.0	0.1192	20.25	4.184
p-$C_2H_5OC_6H_4TeBr_3$tmdto	26.0	27.0	26.5	0.1337	22.75	5.980
p-$C_6H_5OC_6H_4TeCl_3$tmdto	26.0	25.0	25.5	0.1278	21.5	4.850
p-$C_6H_5OC_6H_4TeBr_3$tmdto	24.0	24.0	24.0	0.1192	20.25	5.802
p-$C_6H_5SC_6H_4TeCl_3$tmdto	23.0	23.0	23.0	0.1135	19.5	4.620
$Te(ttz)_2Cl_4$ ***	24.0	24.0	24.0	0.1192	20.25	4.004
$Te(ttz)_2Br_4$	23.0	23.0	23.0	0.1135	19.5	5.276
$Te(ttz)_2I_4$	32.0	31.0	31.5	0.1643	27.25	9.226
$Te(ttz)_4Cl_2.H_2O$	24.0	24.0	24.0	0.1192	20.25	5.558
$Te(ttz)_3Br_4$	26.0	26.0	26.0	0.1308	23.5	7.254
p-$CH_3OC_6H_4Te(ttz)_4Br_3$	20.0	20.0	20.0	0.0969	16.5	6.166
p-$C_2H_5OC_6H_4Te(ttz)Cl_3$	24.0	24.0	24.0	0.1192	20.25	3.816
p-$C_6H_5OC_6H_4Te(ttz)_2Cl_3$	29.0	30.0	29.5	0.1518	25.25	6.474

* tedto is $NNN'N'$ tetraethyldithiooxamide

* * tmdto is $NNN'N'$ tetramethyldithiooxamide

* * * ttz is thiazolidine-2-thione

TABLE A.2-5

Determination of tellurium in organotellurium compounds.

Compounds	% Te	% C	% H	% N
$C_6H_5TeCl_3$	41.15 (41.04)	22.75 (23.20)	1.55 (1.60)	
$C_6H_5TeBr_3$	28.72 (28.72)	16.21 (16.20)	1.17 (1.15)	
p-$CH_3C_6H_4TeCl_3$	39.02 (39.27)	25.85 (25.90)	2.05 (2.10)	
p-$CH_3C_6H_4TeBr_3$	27.97 (27.84)	18.65 (18.30)	1.65 (1.55)	
p-$C_2H_5OC_6H_4TeBr_3$	26.10 (26.13)	26.95 (27.10)	2.56 (2.55)	
p-$C_6H_5OC_6H_4TeCl_3$	31.46 (31.65)	36.05 (35.80)	2.20 (2.25)	
p-$C_6H_5OC_6H_4TeBr_3$	23.72 (23.78)	26.55 (26.50)	1.67 (1.70)	
(p-$CH_3OC_6H_4$-$)_2TeCl_2$	30.91 (30.93)	40.81 (40.73)	3.48 (3.42)	
(p-$CH_3OC_6H_4$-$)_2Te$	37.14 (37.35)	49.30 (49.18)	4.30 (4.13)	
(p-$C_2H_5OC_6H_4$-$)_2TeCl_2$	28.91 (28.96)	43.20 (43.59)	4.16 (4.12)	
(p-$C_2H_5OC_6H_4$-$)_2Te$	34.46 (34.52)	52.21 (51.55)	4.92 (4.91)	
$C_6H_5TeCl_3$tedto	23.32 (23.50)	35.58 (35.35)	4.72 (4.64)	5.35 (5.16)
$C_6H_5TeBr_3$tedto	19.08 (18.87)	28.28 (28.38)	3.91 (3.73)	4.19 (4.11)

Table A.2-5...

Compounds	% Te	% C	% H	% N
$p-CH_3C_6H_4TeCl_3$tedto	22.84 (22.91)	36.14 (36.62)	4.89 (4.89)	5.12 (5.01)
$p-CH_3C_6H_4TeBr_3$tedto	18.35 (18.48)	29.86 (29.55)	4.22 (4.00)	4.19 (4.06)
$p-C_6H_5OC_6H_4TeCl_3$tedto	20.10 (20.03)	41.86 (42.17)	5.02 (4.67)	4.46 (4.47)
$p-C_6H_5OC_6H_4TeBr_3$tedto	16.34 (16.61)	34.58 (34.36)	3.70 (3.82)	3.79 (3.79)
$p-C_6H_5SC_6H_4TeCl_3$tedto	19.91 (19.54)	40.84 (40.55)	4.64 (4.49)	4.41 (4.30)
$p-C_6H_5SC_6H_4TeBr_3$tedto	16.72 (16.27)	33.22 (33.66)	3.70 (3.72)	3.53 (3.57)
$p-BrC_6H_4TeBr_3$tedto	16.95 (16.89)	25.93 (25.42)	3.51 (3.20)	3.72 (3.71)
$TeCl_4$tmdto	28.95 (28.65)	16.50 (16.17)	2.80 (2.72)	6.00 (6.29)
$TeBr_4$tmdto	20.39 (20.47)	12.15 (11.55)	2.11 (1.94)	4.19 (4.49)
$C_6H_5TeCl_3$tmdto	26.15 (26.20)	29.63 (29.57)	4.22 (3.91)	5.75 (5.75)
$C_6H_5TeBr_3$tmdto	20.01 (20.57)	23.89 (23.21)	3.36 (3.07)	4.60 (4.51)
$p-CH_3C_6H_4TeCl_3$tmdto	25.16 (25.47)	31.37 (31.14)	4.22 (3.80)	5.73 (5.59)
$p-CH_3C_6H_4TeBr_3$tmdto	20.03 (20.12)	25.28 (24.60)	3.50 (3.00)	4.37 (4.41)
$p-CH_3OC_6H_4TeCl_3$tmdto	24.85 (24.68)	30.61 (30.17)	3.70 (3.70)	5.73 (5.42)
$p-CH_3OC_6H_4TeBr_3$tmdto	19.69 (19.62)	24.10 (23.99)	3.21 (2.95)	3.91 (4.31)

Table A.2-5...

Compounds	% Te	% C	% H	% N
p-$C_2H_5OC_6H_4TeCl_3$tmdto	24.20	32.52	4.31	5.51
	(24.03)	(31.64)	(3.94)	(5.27)
p-$C_2H_5OC_6H_4TeBr_3$tmdto	19.02	26.07	3.50	4.14
	(19.21)	(25.29)	(3.19)	(4.21)
p-$C_6H_5OC_6H_4TeCl_3$tmdto	22.16	37.87	3.89	4.41
	(22.04)	(37.31)	(3.66)	(4.84)
p-$C_6H_5OC_6H_4TeBr_3$tmdto	17.45	29.63	3.07	3.68
	(17.91)	(30.32)	(2.97)	(3.94)
p-$C_6H_5SC_6H_4TeCl_3$tmdto	21.10	36.34	4.12	4.41
	(21.45)	(36.30)	(3.87)	(4.71)
Te(ttz)$_2$$Cl_4$	25.29	14.86	2.26	5.40
	(25.16)	(14.19)	(1.97)	(5.51)
Te(ttz)$_2$$Br_4$	18.48	11.47	1.70	3.97
	(18.62)	(11.47)	(1.47)	(4.08)
Te(ttz)$_2$$I_4$	14.76	11.51	1.64	4.01
	(14.61)	(11.16)	(1.55)	(4.32)
Te(ttz)$_4$$Cl_2 \cdot H_2O$	18.22	20.96	3.32	8.16
	(18.43)	(20.80)	(3.20)	(8.08)
Te(ttz)$_3$$Br_4$	16.20	13.26	1.84	5.09
	(15.87)	(13.30)	(1.88)	(5.22)
p-$CH_3OC_6H_4Te$(ttz)$_4$$Br_3$	13.38	19.80	2.81	5.95
	(13.42)	(20.40)	(2.85)	(5.90)
p-$C_2H_5OC_6H_4Te$(ttz)Cl_3	26.54	28.92	3.42	3.31
	(26.92)	(28.00)	(3.00)	(3.00)
p-$C_6H_5OC_6H_4Te$(ttz)$_2$$Cl_3$	19.50	33.14	3.00	4.14
	(19.91)	(33.69)	(2.99)	(4.53)

Required values in parenthesis

tedto is $NNN'N'$ tetraethyldithio-oxamide

tmdto is $NNN'N'$ tetramethyldithio-oxamide

ttz is thiazolidine-2-thione

TABLE A.2-6

Data for the standard deviation of $p\text{-}C_6H_5OC_6H_4TeCl_3$tedto

x	x^{-}	$(x^{-} - x)$	$(x^{-} - x)^2$
20.10	19.90	− 0.20	0.0400
19.88	19.90	+ 0.02	0.0004
19.88	19.90	+ 0.02	0.0004
19.98	19.90	− 0.08	0.0064
19.89	19.90	+ 0.01	0.0001
19.83	19.90	+ 0.07	0.0049
19.70	19.90	+ 0.20	0.0400
19.87	19.90	+ 0.03	0.0009
19.96	19.90	− 0.06	0.0036

where x = the true value

x^{-} = the mean value $\left(= \frac{\Sigma x}{n}\right)$

TABLE A.2-7

Data for the standard deviation of organotellurium compounds.

x	x^{-}	$(x^{-} - x)$	$(x^{-} - x)^2$
41.15	41.04	- 0.11	0.0121
28.72	28.72	0.00	0.0000
39.02	39.27	+ 0.25	0.0625
27.97	27.84	- 0.13	0.0169
26.10	26.13	+ 0.03	0.0009
31.46	31.65	+ 0.19	0.0361
23.72	23.78	+ 0.06	0.0036
30.91	30.93	+ 0.02	0.0004
37.14	37.35	+ 0.21	0.0441
28.91	28.96	+ 0.05	0.0025
34.46	34.52	+ 0.06	0.0036
23.32	23.50	+ 0.18	0.0324
19.08	18.87	- 0.21	0.0441
22.84	22.91	+ 0.07	0.0049
18.35	18.48	+ 0.13	0.0169
20.10	20.03	- 0.07	0.0049
16.34	16.61	+ 0.27	0.0729
19.91	19.54	- 0.37	0.1369
16.72	16.27	- 0.45	0.2025
16.95	16.89	- 0.06	0.0036
28.95	28.65	- 0.30	0.0900
20.39	20.47	+ 0.08	0.0064

Table A.2-7 ...

x	$\bar{x}$	$(\bar{x} - x)$	$(\bar{x} - x)^2$
26.15	26.20	+ 0.05	0.0025
25.16	25.47	+ 0.31	0.0961
20.03	20.12	+ 0.09	0.0081
24.85	24.68	- 0.17	0.0289
19.69	19.62	- 0.07	0.0049
24.20	24.03	+ 0.17	0.0289
19.02	19.21	- 0.19	0.0361
22.16	22.04	- 0.12	0.0144
17.45	17.91	+ 0.46	0.2116
21.10	21.45	+ 0.35	0.1225
25.29	25.16	- 0.13	0.0169
18.48	18.62	+ 0.14	0.0196
14.76	14.61	- 0.15	0.0225
18.22	18.43	+ 0.21	0.0441
16.20	15.87	- 0.33	0.1089
13.38	13.42	+ 0.04	0.0016
26.54	26.92	+ 0.38	0.1444
19.50	19.91	+ 0.41	0.1681

APPENDIX III

Preparation of arylselenium compounds.

The preparative methods for arylselenium compounds are known and were carried out according to published procedures.

A.3.1 PREPARATION OF DIARYLSELENIUMDICHLORIDE.

A.3.1.1 Preparation of diphenylseleniumdichloride.

Diphenylselenide was prepared by the reaction of 36.0 g. of powdered potassium hydroxide and 24 g. of black powdered selenium which had been thoroughly mixed and heated in an oil bath to 140°C, at which temperature they fused together. To a solution of the fused mass in 40 cm^3 of ice water, an ice cold solution of diazotised aniline hydrochloride (prepared from 13.8 g. aniline, 37 cm^3 hydrochloric acid, 20 g. ice and 10.4 g. sodium nitrite) was added slowly in small portions at a time. This solution was then added in a slow stream from a dropping funnel to a solution of potassium selenide, and then vigorously stirred with a mechanical stirrer. When all the diazotised solution had been added, the red aqueous solution obtained from the dark oil which formed, was decanted and then heated to boiling point. Whilst still hot this was poured back upon the viscous black mass, and then stirred. 30 cm^3 of chloroform was then added and the elemental selenium was collected on a filter and washed with a little more chloroform. After separating the chloroform layer, the aqueous layer was again extracted with 30 cm^3 of chloroform. The combined extract was then distilled, and diphenylselenide was collected at 300-315°C. Yield 12 g.

Diphenylseleniumdichloride was prepared by the reaction of 12 g. of diphenylselenide dissolved in 25 cm^3 of concentrated nitric acid with 17 cm^3 of concentrated hydrochloric acid. The dense yellow precipitate which formed was filtered off, washed with water and crystallised twice from benzene. m.p. 176°C (lit. 178°C) [140]

[Found C, 47.93; H, 3.45; Se, 26.11; $C_{12}H_{10}SeCl_2$ requires C, 47.72; H, 3.28; Se, 25.98 %]

A.3.1.2 Preparation of di(p-methoxyphenyl)seleniumdichloride.

Di(p-methoxyphenyl)seleniumdichloride was obtained by the reaction of 6.24 g. (0.04 mol.) selenium oxychloride with 4.32 g. (0.04 mol.) of anisole dissolved in 30 cm^3 of anhydrous diethylether. The mixture was stirred and then allowed to stand for five days at room temperature. The yellow crystals which formed were filtered off and recrystallised by dissolving in dry chloroform and reprecipitated by adding dry diethylether. The precipitate was filtered off and dried in a vacuum desiccator. m.p. 162°C (lit. 163°C) [128]

[Found C, 46.05; H, 3.87; Se, 21.91; $C_{14}H_{14}OSeCl_2$ requires C, 46.30; H, 3.87; Se, 21.70 %]

A.3.1.3 Preparation of di(p-ethoxyphenyl)seleniumdichloride.

Di(p-ethoxyphenyl)seleniumdichloride was prepared by the same procedure as used for di(p-methoxyphenyl)seleniumdichloride. Starting materials were 6.24 g. (0.04 mol.) of selenium oxychloride and 4.88 g. of phenetole. Di(p-ethoxyphenyl)seleniumdichloride produced had m.p. 138°C (lit. 139°C) [128]

Found C, 49.47; H, 4.84; Se, 20.22; $C_{16}H_{18}OSeCl_2$ requires C, 49.00; H, 4.60; Se, 20.16 %

A.3.2 PREPARATION OF ARYLSELENOCYANATE.

A.3.2.1 Preparation of phenylselenocyanate.

A mixture of 9.3 g. (0.1 mol.) of aniline in 60 g. ice and 20 cm^3 of concentrated hydrochloric acid was diazotised at 0°C with 8 g. sodium nitrite (20% solution). The acid was neutralised with sodium acetate using congo red paper and then a solution of 15 g. potassium selenocyanate in 70 cm^3 of water was added dropwise. With continuous stirring and keeping the temperature below 5°C, nitrogen was evolved and a dark brown oil was formed which formed as a layer on the surface of the reaction vessel. The brown oil was extracted from the diethylether. The diethylether was removed by distillation under vacuum to give a yellow oil which had a b.p. of 117-118°C. (lit. 117-118°C) [123,141].

A.3.2.2 Preparation of p-bromophenylselenocyanate.

The procedure for the preparation of p-bromophenylselenocyanate was similar to that used for the preparation of phenylselenocyanate. p-Bromoaniline 15 g. in 20 cm^3 of concentrated hydrochloric acid, 60 cm^3 water, sodium nitrite 7 g. in 20 cm^3 of water, sodium acetate and potassium selenocyanate 21 g. in 135 cm^3 of water at 0°C were used. After sixteen hours, the solid product was formed and then separated by distillation with steam. The compound was crystallised from eight petroleum ether (30-40°C) and gave white needles. m.p. 70-71°C (lit. 70.5-71.5°C).[114]

[Found C, 32.26; H, 1.52; N, 5.48; C_7H_4NBrSe requires C, 32.19; H, 1.55; N, 5.36 %]

A.3.2.3 Preparation of p-chlorophenylselenocyanate.

p-Chloroaniline 12.75 g. (0.1 mol.) in 20 cm^3 of concentrated hydrochloric acid and 60 g. of ice was diazotised at 0°C with 8 g. of sodium nitrite in 20 cm^3 of water. A solution of sodium acetate was added to neutralise the acid (congo red paper was used). Potassium selenocyanate 15 g. in 70 cm^3 of water was gradually added and with constant stirring, keeping the temperature below 5°C. A pale yellow precipitate of p-chlorophenylselenocyanate formed immediately, along with a vigorous evolution of nitrogen. After fifteen hours the precipitate was filtered off, washed with water several times, and dried in a vacuum desiccator. The precipitate was then recrystallised from light petroleum ether using charcoal, which gave colourless needles. m.p. 53-54°C (lit. 53.5-54.5°C)[114]

[Found C, 38.96; H, 1.96; N, 6.56; C_7H_4NClSe requires C, 38.82; H, 1.86; N, 6.47 %]

A.3.2.4 Preparation of p-tolylselenocyanate.

A solution of 10.7 g. (0.1 mol.) of p-toluidine in 60 cm^3 of sulphuric acid (1:5) was diazotised at 0°C with 8 g. of sodium nitrite in 20 cm^3 of water. The solution was neutralised with sodium acetate using congo red paper. A solution of 18 g. potassium selenocyanate in 110 cm^3 of water was added slowly with stirring and ensuring that the temperature did not rise above 5°C to this mixture, and was then left for sixteen hours. A dark solid with some selenium was obtained which was filtered off and washed with distilled water several times and dried under vacuum. The precipitate was extracted by adding light petroleum ether in the presence of charcoal which gave white crystals. m.p. 55-56°C (lit. 55-56°C) [114] [Found C, 49.23; H, 3.65; N, 7.22; C_8H_7NSe requires C, 48.99; H, 3.60; N, 7.14 %]

A.3.3 PREPARATION OF ARYLSELENIUMTRIBROMIDE AND DIARYLDISELENIDE.

A.3.3.1 Preparation of phenylseleniumtribromide.

Phenylseleniumtribromide was prepared by two methods, -

Method 1: 0.5 g. of lithium was cut into very small pieces and placed into a 250 cm^3 three necked flask; 25 cm^3 of dry diethylether was added and the mixture was refluxed. To this solution 5 g. bromobenzene in 50 cm^3 of dry diethylether was added drop by drop and then the mixture refluxed for one hour. The mixture was cooled at room temperature and 3 g. of selenium powder was added in small portions with stirring. The selenium was found to have dissolved and yellow precipitate was found. After refluxing for two hours, the mixture was hydrolysed carefully with cold water/hydrochloric acid mixture and extracted with ether. The solvent was removed by distillation under vacuum leaving a red oil which was dissolved in carbon tetrachloride. Then an excess of bromine in carbon tetrachloride was added dropwise. A vigorous reaction resulted. The solution became a very deep red colour and a red orange precipitate was formed. The precipitate was filtered off and dried quickly under vacuum to give 12 g. of phenylseleniumtribromide. m.p. 103°C (lit. 105°C).[123]

[Found C, 18.15; H, 1.20; Se, 20.09; $C_6H_5SeBr_3$ requires C, 18.20; H, 1.27; Se, 19.96 %]

Method 2: Phenylselenocyanate 1.82 g. (0.01 mol.) in 5 cm^3 of dry chloroform was treated with an excess of bromine in dry chloroform and a red orange precipitate was formed, filtered off and dried quickly under vacuum. A red orange precipitate was phenylseleniumtribromide which had a m.p. 105°C (lit. 105°C) [123]

[Found C, 18.10; H, 1.15; Se, 20.09; $C_6H_5SeBr_3$ requires C, 18.20; H, 1.27; Se, 19.96 %]

A.3.3.2 Preparation of bis(p-bromophenyl)diselenide.

p-Bromophenylselenocyanate 1.80 g. (0.01 mol.) was treated with alcoholic potassium hydroxide, bis(p-bromophenyl)diselenide was formed. m.p. 106-107°C (lit. 107-108°C) [142]
[Found C, 30.76; H, 1.70; $C_{12}H_8Br_2Se_2$ requires C, 30.64; H, 1.72 %]

A.3.3.3 Preparation of p-bromophenylseleniumtribromide.

p-Bromophenylseleniumtribromide was prepared by dissolving

0.471 g. (0.01 mol.) bis(p-bromophenyl)diselenide in 5 cm^3 of dry chloroform and then an excess of bromine in dry chloroform was added. A reddish precipitate formed which had a m.p. 132°C (lit. 132°C) [133]

[Found C, 15.30; H, 0.70; Se, 16.84; $C_6H_5SeBr_4$ requires C, 15.30; H, 0.90; Se, 16.67 %]

A.3.3.4 p-Chlorophenylseleniumtribromide.

p-Chlorophenylseleniumtribromide was prepared by dissolving 2.16 g. (0.01 mol.) p-chlorophenylselenocyanate in 5 cm^3 of dry chloroform and then treating this solution with an excess of bromine in dry chloroform. The red orange precipitate which formed was filtered off and dried in a vacuum desiccator. m.p. 122°C (lit. 123-124°C) [126]

[Found C, 17.00; H, 0.70; Se, 18.73; $C_6H_5ClBr_3Se$ requires C, 16.89; H, 0.95; Se, 18.36 %]

A.3.3.5 Preparation of p-tolyseleniumtribromide.

p-Tolylseleniumtribromide was prepared by dissolving 1.96 g. (0.01 mol.) of p-tolylselenocyanate in 5 cm^3 of dry chloroform and then treating this solution with an excess of bromine in dry chloroform. A red orange precipitate was obtained immediately which was filtered off and dried under vacuum. m.p. 115°C (lit. 115-116°C) [126]

[Found C, 20.50; H, 1.60; Se, 18.91; $C_7H_7Br_3Se$ requires C, 20.71; H, 1.74; Se, 19.27 %]

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A RAPID PROCEDURE FOR THE DETERMINATION OF THE TELLURIUM CONTENT OF ORGANOTELLURIUM COMPOUNDS

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Summary

A rapid micro-analytical procedure for the analysis of tellurium in organotellurium compounds is described. The compounds are decomposed using the conventional oxygen flask method followed by treatment with aqueous hydrogen peroxide/hydrochloric acid solution. The tellurium content of the resulting solution is determined by atomic absorption spectrophotometry. If the analyses are carried out batch wise i.e. 6—8 samples with each standardisation of the instrument, the total analysis time is about $\frac{1}{2}$ hour per sample.

Thavornyutikarn [1] has reviewed some of the methods which have been published for the determination of the tellurium content of organotellurium compounds. These gravimetric and titrimetric methods [2—4,] are time-consuming and invariably need large sample weights. Thavornyutikarn [1] also described a new procedure applicable to aryltellurium halides in which smaller sample weights (15—50 mg) were decomposed with a mixture of 3—4 ml of nitric acid and 3—4 ml of perchloric acid. The decomposition procedure takes about one and a half hours and an efficient fume cupboard is required. The white residue obtained is subsequently dissolved in hydrochloric acid, the solution made up to a convenient volume in a volumetric flask and the absorption of this solution measured by atomic absorption spectrophotometry.

A large number of tellurium compounds are prepared in our laboratory and there is a need for a reliable, reproducible method which is not time consuming. The oxygen flask method [5—10] is a well known procedure for the fast decomposition of organic materials and so it was decided to investigate its applicability to a wide range of organotellurium compounds. The aqueous solutions so obtained would be free from high concentrations of mineral acid and would give an ideal matrix for subsequent examination by atomic absorption spectro-

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* On study leave from the National Iraqi Minerals Company, Baghdad (Iraq):

photometry. The decomposition of organoselenium compounds by oxygen flask followed by analysis by the molecular emission cavity technique (MECA) has been recommended by Belcher et al. and the results compared with those obtained by atomic absorption [11]. Gubser [12] however states that selenium attacks the platinum gauze and this leads to inaccurate results.

For our study on application of the oxygen flask technique to tellurium containing compounds a wide range of organotellurium compounds were prepared. The list of selected compounds consisted of diaryl tellurides, diaryltellurium dihalides, aryltellurium trihalides, aryltellurium trihalide complexes with sulphur donor ligands and tellurium tetrahalide complexes. The analytical results obtained are given in the experimental section.

Experimental

Reagents. "Analar" telluric acid (purity 99.5%) used as a standard was obtained from Hopkins and Williams Ltd, and hydrogen peroxide (50%) was obtained from Fisons Ltd.

All tellurium compounds were also analysed for carbon and hydrogen and gave satisfactory analyses.

Standard Te solution. The stock solution of 1000 μg Te ml^{-1} was prepared by dissolving telluric acid 1.7951 g in distilled water containing conc.hydrochloric acid (10.0 ml). The calibration curve was obtained by dilution of this solution to give standards within the range 5—50 μg Te ml^{-1}.

Procedure. The accurately weighed sample (5—10 mg) contained in a wrapped filter paper is fixed into a hinge of a platinum gauze and then ignited in a 500 ml flask which has previously been flushed with oxygen, and which contains 15.0 ml of water, and 1.0 ml of hydrogen peroxide and 1.0 ml of hydrochloric acid. After ignition, the flask is shaken until the decomposition products are absorbed in the aqueous peroxide/hydrochloric acid solution which is transferred to a volumetric flask and the volume made up to 50.0 ml with distilled water. The percentage absorption of this solution or a suitable further dilution is determined by atomic absorption. We used a Perkin—Elmer 303 instrument equipped with a Perkin—Elmer recorder (Model No. 56), and a Fischer—Porter Burner regulator (air flow rate 9, acetylene 7—8). The absorptions were measured at 214.2 nm using an Activion tellurium hollow cathode lamp operated at 10 mA.

The platinum gauze may be used for about 10 combustions but then becomes brittle.

Results

Required values are in parentheses: $C_6H_5TeCl_3$ 41.15 (41.04); $C_6H_5TeBr_3$ 28.72 (28.72); p-$CH_3C_6H_4TeCl_3$ 39.02 (39.27); p-$CH_3C_6H_4TeBr_3$ 29.97 (27.84); p-$C_2H_5OC_6H_4TeBr_3$ 26.10 (26.13); p-$C_6H_5OC_6H_4TeCl_3$ 31.46 (31.65); p-$C_6H_5OC_6H_4TeBr_3$ 23.72 (23.78); $(CH_3OC_6H_4)_2TeCl_2$ 30.91 (30.93); $(C_2H_5OC_6H_4)_2TeCl_2$ 28.89 (28.96); $(CH_3OC_6H_4)_2Te$ 37.14 (37.35); $(C_2H_5OC_6H_4)_2Te$ 34.46

(34.52); $TeCl_4$tmdto * 28.95 (28.65); $TeBr_4$tmdto 20.39 (20.47); $C_6H_5TeCl_3$-tmdto 26.15 (26.20); $C_6H_5TeBr_3$tmdto 20.01 (20.57); p-$CH_3C_6H_4TeCl_3$tmdto 25.16 (25.47); p-$CH_3C_6H_4TeBr_3$tmdto 20.03 (20.12); p-$CH_3OC_6H_4TeCl_3$tmdto 24.85 (24.68); p-$CH_3OC_6H_4TeBr_3$tmdto 19.69 (19.62); p-$C_2H_5OC_6H_4TeCl_3$-tmdto 24.20 (24.03); p-$C_2H_5OC_6H_4TeBr_3$tmdto 19.02 (19.21); p-$C_6H_5OC_6H_4$-$TeCl_3$tmdto 22.16 (22.04); p-$C_6H_5OC_6H_4TeBr_3$tmdto 17.45 (17.91); p-C_6H_5-$SC_6H_4TeCl_3$tmdto 21.10 (21.45); $C_6H_5TeCl_3$tedto ** 23.32 (23.50); $C_6H_5TeBr_3$-tedto 19.08 (18.87); p-$CH_3C_6H_4TeCl_3$tedto 22.84 (22.91); p-$CH_3C_6H_4TeBr_3$-tedto 18.35 (18.48); p-$C_6H_5OC_6H_4TeCl_3$tedto 20.09 (20.03); p-$C_6H_5OC_6H_4$-$TeBr_3$tedto 16.34 (16.61); p-$C_6H_5SC_6H_4TeCl_3$tedto 19.91 (19.54); p-$C_6H_5SC_6$-H_4TeBr_3tedto 16.72 (16.27); p-$BrC_6H_4TeBr_3$tedto 16.95 (16.89); $Te(ttz)_2Cl_4$ *** 25.29 (25.16); $Te(ttz)_2Br_4$ 18.48 (18.62); $Te(ttz)_2I_4$ 14.76 (14.61); $Te(ttz)_4Cl_2$ H_2O 18.22 (18.43); $Te(ttz)_3Br_4$ 16.20 (15.87); p-$CH_3OC_6H_4Te(ttz)_4Br_3$ 13.38 (13.42); p-$C_2H_5OC_6H_4Te(ttz)Cl_3$ 26.54 (26.92); p-$C_6H_5OC_6H_4Te(ttz)_2Cl_3$ 19.50 (19.91).

Standard deviation was calculated from results for p-$C_6H_5OC_6H_4TeCl_3$tedto: C, 41.86; H, 5.02; N, 4.46%. Analysis found: Te, 20.10, 19.88, 19.88, 19.98, 19.89, 19.83, 19.70, 19.87, 19.96%. $C_{28}H_{29}Cl_3N_2S_2Te$ calcd.: C, 42.17; H, 4.67; N, 4.47; Te, 20.03%.

Discussion and conclusions

The analysis of the tellurium content of organotellurium compounds by their decomposition using the oxygen flask technique followed by atomic absorption spectrophotometry has been found to be successful for a wide variety of tellurium compounds containing from between 13—40% Te. The only class of compound not completely oxidised by the method was diaryl ditelluride.

A standard deviation of 0.11, coefficient of variation of 0.0055 and confidence limit for 95% of 19.90 ± 0.07 was obtained for $C_6H_5OC_6H_4TeCl_3$tedto analysed nine times. For the 41 other samples a standard deviation of 0.23 was obtained.

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* tmdto = *N,N,N',N'*-Tetramethyldithiooxamide

** tedto = *N,N,N',N'*- Tetraethyldithiooxamide

*** ttz = Thiazolidine-2-thione

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THE USE OF SELENIUM(IV) CHLORIDE FOR THE PREPARATION OF DIARYLSELENIUM DICHLORIDES

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(Received March 10th, 1975)

Summary

Two new synthetic routes for the preparation of diarylselenium dichlorides are reported both of which use selenium(IV) chloride as a starting meterial. In the first method, bis(*p*-methoxyphenyl) and bis(*p*-ethoxyphenyl)-selenium dichlorides are prepared by the reaction of $SeCl_4$ with anisole and phenetole respectively. In the second, diphenylselenium dichloride is prepared by the reaction of $SeCl_4$ with tetraphenyllead, a reaction in which the lead—carbon bond is cleaved.

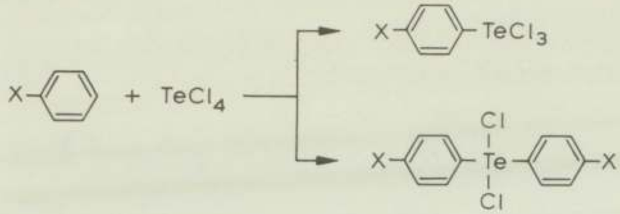
The far infrared and Raman spectra of the diarylselenium dichlorides are reported.

The synthetic routes to diarylselenium dihalides [1-3] and diaryltellurium dihalides [1,4,5] have been reviewed. There are certain similarities in the available routes for the selenium and tellurium compounds. Whilst benzene reacts with $SeCl_4$ in the presence of anhydrous aluminium(III) chloride to give a moderate yield of diphenyl selenide [6], a higher molecular ratio of benzene again using the Lewis acid $AlCl_3$, results in triphenylselenonium chloride $(C_6H_5)_3Se^+Cl^-$ [7,8]:

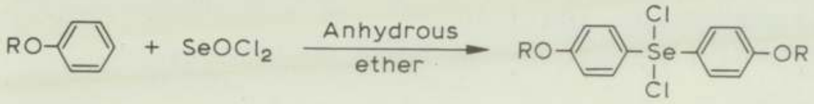
$$SeCl_4 + 3C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3Se^+Cl^- + 3HCl$$

An analogous method [9] using a molecular ratio of $AlCl_3/TeCl_4$ of 3/1 gave a 60% yield of $(C_6H_5)_3TeCl$. Products isolated at lower $AlCl_3/TeCl_4$ ratios, by quenching the reaction products when lower equivalents of hydrochloric acid were evolved, were diphenyltellurium dichloride and phenyltellurium trichloride.

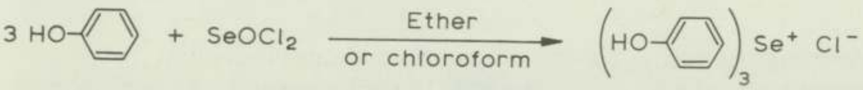
Whilst the presence of $AlCl_3$ is essential for the reaction of C_6H_6 and $TeCl_4$, no Lewis acid need be used when certain activating sustituents X (where X = RO, HO, R_2N, RS) are present [9—12]. Thus $TeCl_4$ with C_6H_5X gives a mixture of products:



These activating substituents also have to be present for the reaction between selenium oxychloride and an aromatic compound to take place [13,14]:

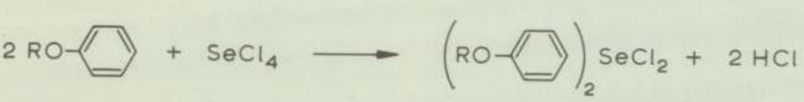


Under certain conditions this reaction can be modified to give triarylselenonium chloride as the main product [15].



Selenium(IV) chloride has been found to react with esters of salicylic acid, in the absence of any solvent, to form the arylselenium trichloride, a reaction in which the hydrogen *para* to the hydroxyl group is involved [16]:

The reaction of $SeCl_4$ with aromatic ethers does not appear to have been reported however. We find that anisole and phenetole will also react with $SeCl_4$ in the absence of any solvent and under controlled conditions to give good yields of bis(*p*-methoxyphenyl)selenium dichloride and bis(*p*-ethoxyphenyl)selenium dichloride respectively.



The synthesis of aryltellurium chlorides by treatment of various aryllead compounds with tellurium(IV) chloride or aryltellurium trichlorides has been described [17].

$$(C_6H_5)_4Pb + TeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2TeCl_2 + (C_6H_5)_2PbCl_2$$

The analogous reaction with $SeCl_4$ has been investigated:

$$(C_6H_5)_4Pb + SeCl_4 \xrightarrow{\text{Toluene}} (C_6H_5)_2SeCl_2 + (C_6H_5)_2PbCl_2$$

The reaction of triphenyllead chloride with tellurium(IV) chloride in dioxane gives a 90% yield of phenyltellurium trichloride but the analogous reaction with selenium(IV) chloride gives a low yield of diphenylselenium dichloride:

$$2(C_6H_5)_3PbCl + SeCl_4 \rightarrow (C_6H_5)_2SeCl_2 + 2(C_6H_5)_2PbCl_2$$

The products from the reactions of $SeCl_4$ with anisole, phenetole, $(C_6H_5)_4Pb$, and $(C_6H_5)_3PbCl$ were characterised by their melting points, chemical analyses, infrared and Raman spectra.

The crystal structure of diphenylselenium dichloride has been investigated [18], and has been shown to be orthorhombic D_{2h}^{15}-*Pbca* space group with 8 molecules per unit cell. The crystal structures of the di(*p*-tolyl)selenium dichloride and di(*p*-tolyl)selenium dibromide belong to space group $P2_12_12$-D_2^3 with two molecules per unit cell [19], but the molecular structure of all these diarylselenium dihalides is basically that of a slightly distorted trigonal bipyramid with the selenium atom at the centre, halogens at the apices and two phenyl or *p*-tolyl groups plus the unshared pair of electrons in the equatorial positions. The bond distances Se—Br and Se—Cl in all these diarylselenium dihalides are larger than the sum of the covalent radii and the molecular symmetry is C_{2v}.

The infrared spectra of selenium compounds of the type $(C_6H_5)_2SeX_2$ where X = NO_3, CH_3CO_2, CH_3SO_3 and NCO have been discussed [20]. These compounds also possess a distorted trigonal bipyramid structure (molecular symmetry C_{2v}), and some of the bands associated with the vibrations of the phenyl groups have been assigned [20]. The far infrared and Raman spectra of diarylselenium dichlorides have not previously been reported in detail and are given in Table 1. The assignments given here are based on the published data for the analogous tin and tellurium compounds $(C_6H_5)_2SnCl_2$ [21] and $(C_6H_5)_2TeCl_2$ [22] which have similar structures.

The infrared and Raman spectra of dimethylselenium dihalides and dimethyltellurium have been reported [23,24] and bands at 293 and 270 cm^{-1} assigned to ν(Se—Cl). For the diarylselenium dichlorides the values are ν_s(Se—Cl) 250-275 cm^{-1} and ν_{as}(Se—Cl) 245-255 cm^{-1}. This is consistent with

TABLE 1

THE IR AND RAMAN OF SOME DIARYLSELENIUM DICHLORIDE 360-100 cm^{-1}

$(C_6H_5)_2SeCl_2$		Bis(*p*-methoxyphenyl)-selenium dichloride		Bis(*p*-ethoxyphenyl)-selenium dichloride		Assignment
IR	Raman	IR	Raman	IR	Raman	
329s	335vw	344s	345vw	356m	355vw	t or ν(Se—Ph)
307s	310vw	310w	310vw	336vs	338vw	t'
275vs	267vs	255s	250vs	272s	263vs	ν_s(Se—Cl)
	248s	245s		253m		ν_{as}(Se—Cl)
225vs	225w	245s		253m		Phenyl *u*
203vs		235s	235m(sh)	225s	225w	Phenyl *u'*
173w		190m		186w	180vw	Phenyl *x*
151m						Phenyl *x'*
140m	132m	135s		134s	135m	$\delta(SeCl_2)$
	120w		127mw			
105vw	107ms		112ms	110w	110m	Unassigned

the long bond length Se—Cl reported for diphenylselenium dichloride [18]. The weak Raman bands at $\Delta\nu$ 120-135 cm^{-1} may be assigned to the Cl—Se—Cl deformation mode [25]. The assignments of bands associated with vibrations of the phenyl groups were made in comparison with the published data for diphenyltin dichloride [21], diphenyltellurium dichloride [22], diphenyl selenide, bromobenzene, and *p*-bromoanisole. As expected the phenyl *t*, and *u* modes all occur at slightly higher wave numbers than those for the corresponding diaryltellurium dichlorides [22]. The phenyl *u* modes appear as shoulders or are hidden under the main Raman bands but for $(C_6H_5)_2SeBr_2$ the main Raman bands but for $(C_6H_5)_2SeBr_2$ the main Raman band at $\Delta\nu$ 157 cm^{-1}, ν(Se—Br) is well clear of the phenyl *u* band at $\Delta\nu$ 249 cm^{-1} [26].

Experimental

Tetraphenyllead and triphenyllead chloride were prepared by conventional methods [27-29]. Selenium(IV) chloride was obtained from B.D.H. Limited. Toluene, benzene, diethyl ether and chloroform were dried as recommended by Vogel [30].

Reaction between selenium(IV) chloride and tetraphenyllead

$SeCl_4$ (4.4 g; 0.02 mol) and 10.3 g (0.02 mol) of tetraphenyllead in a total volume of 80 ml toluene or benzene were heated under reflux for 6 h. The precipitated diphenyllead dichloride was filtered off from the hot reaction mixture and the filtrate evaporated under vacuum to about 15 ml. This red coloured solution was allowed to cool in a refrigerator for two days when yellow crystals were obtained which were recrystallised twice from benzene. Yield 35%. Improved yields (50%) were obtained by reaction in the cold over 14 h, followed by evaporation after removal of the diphenyllead dichloride. M.p. 177°C (lit. [31] m.p. 178°). (Found: C, 47.95; H, 3.42; Se, 26.06. $C_{12}H_{10}SeCl_2$ calcd.: C, 47.72; H, 3.28; Se, 25.98%.)

Reaction between selenium(IV) chloride and triphenyllead chloride

$SeCl_4$ (4.4 g; 0.02 mol) and 9.4 g (0.02 mol) of triphenyllead chloride in a total volume of 100 ml toluene were heated under reflux for 6 h. The precipitated diphenyllead dichloride was filtered off from the hot reaction mixture and the filtrate evaporated under vacuum to about 15 ml. After two days in a refrigerator yellow crystals formed which were recrystallised from benzene. Yield 20%; m.p. 178°C (lit. [31] m.p. 178°). (Found: C, 48.33; H, 3.50; Se, 26.17. $C_{12}H_{10}SeCl_2$ calcd.: C, 47.72; H, 3.28; Se, 25.98%.)

Reaction of selenium(IV) chloride with anisole and phenetole

Selenium(IV) chloride (11.25 g; 0.1 mol) was added to 0.2 mol of anisole or phenetole contained in a 100 ml flask fitted with a drying tube. Owing to the exothermic nature of the reaction and strong evolution of hydrochloric acid gas the contents of the flask were cooled in an ice bath for 45 min and finally left at room temperature overnight for 26 h. The yellow-orange crystals which formed in the dark-red coloured liquid were filtered off and washed with a little dry diethyl ether. The dried crystals were dissolved in the smallest possible volume of dry chloroform; reprecipitated by addition of dry diethyl ether, filtered off and dried in a vacuum dessicator. Bis(*p*-methoxyphenyl)selenium dichloride, yield 45% m.p. 163°C (lit. [14] m.p. 163°). (Found: C, 46.19; H, 4.03; Se, 21.86. $C_{14}H_{14}O_2SeCl_2$ calcd.: C, 46.30; H, 3.87; Se, 21.70%.) Bis(*p*-ethoxyphenyl)selenium dichloride, yield 67%, m.p. 139°C (lit. [14] m.p. 139°). (Found: C, 48.84; H, 4.64; Se, 20.18. $C_{16}H_{18}O_2SeCl_2$ calcd.: C, 49.00; H, 4.60; Se, 20.16%.)

Diphenylselenium dichloride, bis(*p*-methoxyphenyl)- and bis(*p*-ethoxyphenyl)-selenium dichlorides were prepared by conventional methods [14,32] and gave satisfactory elemental analyses. The IR and Raman spectra and meltings points of these compounds were identical with those prepared by the new methods described above.

Raman spectra

These were recorded on a Cary 81 Laser Raman spectrometer (exciting line 6328 Å) and a Coderg Raman spectrometer (exciting line 4880 Å).

IR spectra

All compounds were examined as KBr disc on *a*) a Perkin—Elmer 457 infrared spectrophotometer (4000-250 cm^{-1}), *b*) a Perkin—Elmer 225 grating infrared spectrophotometer or *c*) on a Fourier spectrophotometer FS. 620 (Research and Industrial Instruments Co) over the range 250-20 cm^{-1}.

Chemical analyses

Carbon and hydrogen were determined by the usual combustion method. The selenium content was determined by addition of KI and titration with standard thiosulphate solution [33].

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THIAZOLIDINE-2-THIONE COMPLEXES OF TELLURIUM(II) AND (IV)

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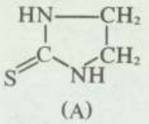
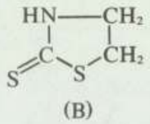
Abstract—Tellurium(IV) complexes of thiazolidine-2-thione(ttz) of formula $Te(ttz)_2X_4$ where X = Cl, Br or I and others of formula $RTe(ttz)_xX_3$ where X = Cl or Br and R = $CH_3OC_6H_4$-, $C_2H_5OC_6H_4$- and $PhOC_6H_4$-, x is an integer have been prepared and characterised. Using acid aqueous reaction media and varying the ratio of Te: ligand it is possible to effect oxidation to the ligand and to form tellurium(II) complexes such as $Te(ttz)_4Cl_2 \cdot H_2O$. The IR and Raman spectra of the complexes are reported and assignments made. Conductivity measurements in NN'dimethylformamide are also reported.

INTRODUCTION

TELLURIUM(II) and tellurium(IV) form a large number of well defined complexes with thiourea, substituted thioureas and substituted dithiooxamides. All these complexes contain the $-NR-\overset{|}{C}=S$ group where R = alkyl, aryl or hydrogen. For example, fully substituted dithiooxamides containing two such groups form 1:1 complexes, $Te(L)X_4$ and $RTe(L)X_3$, where R is an aryl group; X a halogen and L is NNN'N'tetraethyldithio-oxamide or NNN'N'tetramethyldithio-oximide[1, 2, 3]. Cyclic thioureas such as ethylene and propylene thiourea react with TeO_2 dissolved in acids to give a variety of crystalline compounds[4].

Replacement of a -NH- group in ethylenethiourea(A) by CH_2 or S gives a series of heterocyclic compounds which should be potential ligands for co-ordination to tellurium(II) or (IV). Thus, replacement of one -NH- group of ethylenethiourea by S gives thiazolidine-2-thione(B) and by CH_2 gives pyrrolidine-2-thione(C).


(A)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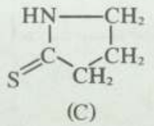
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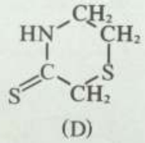
(D)

The ligand properties of thiazolidine-2-thione have been investigated and complexes are known to be formed with many elements such as zinc, cadmium and mercury[5, 6]; nickel[7, 8]; cobalt[7–9]; chromium, molybdenum, tungsten[10]; iron[11] and silver[12]. Thus the reactions of the ligand with transition elements only has been reported so far.

This paper deals with the investigation of reaction of tellurium(IV) compounds with thiazolidine-2-thione and the characterisation of the compounds formed. The ligand properties of pyrrolidine-2-thione(C) and thiomorpholine-3-thione(D), a six membered heterocyclic compound containing the same groups are discussed in subsequent papers.

EXPERIMENTAL

Tellurium(IV) oxide, tellurium(IV)chloride, tellurium(IV) bromide were obtained from B.D.H. Ltd or K and K Laboratories. Tellurium(IV)iodide was prepared by the reaction of telluric acid with hydriodic acid[13]. Methanol and carbon tetrachloride were dried as recommended by Vogel[14].

Thiazolidine-2-thione obtained from Fluka Laboratories was purified by double recrystallisation from hot water m.p. 106–7°C lit. 106–7°[15].

Preparation of aryltelluriumtrihalides. *p* - methoxyphenyltelluriumtrichloride, *p* - ethoxyphenyltelluriumtrichloride and *p* - phenoxyphenyltelluriumtrichloride were prepared by direct addition of tellurium(IV)chloride to anisole, phenetole and diphenylether respectively in carbon tetrachloride or chloroform[16–20]. The trichlorides were reduced with sodium sulphide or potassium metabisulphite to give the corresponding diarylditellurides[21] which were then treated with bromine in carbon tetrachloride to give the tribromides.

Thiazolidine-2-thione complexes. These were prepared by 4 different methods.

Method(A). Thiazolidine-2-thione (2 mmol) in dry methanol was added to the tellurium compound (1 mmol) also dissolved in dry methanol. The precipitates which formed on stirring at room temperature were filtered off and dried in a vacuum desiccator.

Method (B). The tellurium(IV) compound (1 mmol) was dissolved in fused thiazolidine-2-thione (10 mmol) at about 110°C. The crude product which formed on cooling was recrystallised from dry methanol, filtered off and washed with hot toluene in order to remove the excess of ligand.

Method(C). Tellurium(IV)oxide 0.8 g (5 mmol) was dissolved in a mixture of either 10 ml concentrated hydrochloric acid or hydrobromic acid and 10 ml of distilled water. After heating to 60°C, 3.6 g (30 mmol) of thiazolidine-2-thione in 150 ml of distilled water was added with rapid stirring. The liberated tellurium was filtered off and on standing at room temperature the complex formed slowly as an orange yellow precipitate.

Method (D). Tellurium(IV)oxide, 1.6 (10 mmol) dissolved in 4 ml of concentrated hydrochloric acid was added at room temperature to 3.0 g of thiazolidine-2-thione in 10 ml concentrated hydrochloric acid. The precipitate which formed immediately was filtered off washed with dry diethylether, and finally dried in a vacuum desiccator.

IR and Raman spectra. The spectra of the compounds were recorded as Nujol mulls or KBr discs on a Perkin–Elmer 457 IR spectrophotometer over the range 4000–250 cm^{-1}; as Nujol mulls on a Perkin–Elmer 225 grating IR spectrophotometer; as Nujol mulls between polythene sheets using a Fourier spectrophotometer F.S. 720 (R.I.I.C.) over the range 400–40 cm^{-1}.

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†On study leave from the National Iraqi Minerals Company, Baghdad, Iraq.

Raman spectra. These were recorded on a Cary 81 spectrometer with an exciting laser line at 6328 Å.

Conductivity measurements. Were made on 10^{-3} M solutions of the complexes in dry NN'dimethylformamide at 20°C using a Mullard conductivity bridge Type E 7566/3.

UV and visible spectra. Were carried out on a Perkin–Elmer 137 spectrophotometer. Dilute solutions of the complexes in NN'dimethylformamide solution all show strong absorptions at 35.7 kK.

Tellurium analysis. Samples were analysed for tellurium content by decomposition of the samples using the oxygen flask technique followed by atomic absorption of the solutions produced using a Perkin–Elmer 303 instrument.

DISCUSSION

The compounds prepared and preparative methods used are summarised in Table 1 together with decomposition temperatures and colours. The use of preparative method(A) results in compounds of the formula $Te(ttz)_2X_4$ but in aqueous hydrochloric acid conditions (Method C), oxidation of the ligand occurs with reduction of Te(IV) to Te(II);

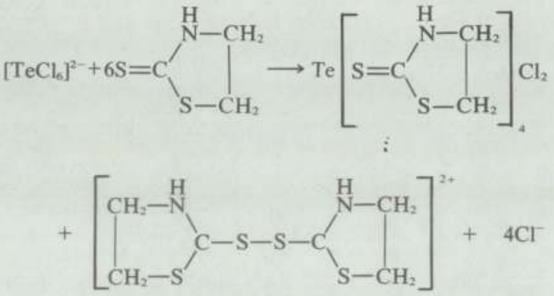

Table 1. Analytical data and some physical properties

Compounds	preparative method	colour	m.p.°C[b]	Analyses[a] C	H	N	Te
Thiazolidine-2-thione (ttz)		white	106- 107	30.01 (30.25)	4.45 (4.24)	11.39 (11.76)	
$Te(ttz)_2Cl_4$	A,D	yellow	152- 155	14.86 (14.19)	2.26 (1.97)	5.40 (5.51)	25.29 (25.16)
$Te(ttz)_2Br_4$	A	orange	134- 138	11.47 (11.47)	1.70 (1.47)	3.97 (4.08)	18.48 (18.62)
$Te(ttz)_2I_4$	A	brown	162- 166	11.51 (11.16)	1.64 (1.55)	4.01 (4.32)	14.76 (14.61)
$Te(ttz)_4Cl_2H_2O$	C	green- yellow	82- 84	20.96 (20.80)	3.32 (3.20)	8.16 (8.08)	18.22 (18.43)
$Te(ttz)_3Br_4$	C	yellow- orange	172- 174	13.26 (13.30)	1.84 (1.88)	5.09 (5.22)	16.20 (15.87)
$CH_3OC_6H_4Te(ttz)_4Br_3$	B	yellow- orange	128- 132	19.80 (20.40)	2.81 (2.85)	5.95 (5.90)	13.38 (13.42)
$C_2H_5OC_6H_4Te(ttz)_1Cl_3$	B	yellow	114- 116	28.92 (28.00)	3.42 (3.00)	3.31 (3.00)	26.54 (26.92)
$C_6H_5OC_6H_4Te(ttz)_2Cl_3$	B	yellow	196- 201	33.14 (33.69)	3.00 (2.99)	4.14 (4.53)	19.50 (19.91)

a. Required values in parentheses. b. With decomposition.

Table 2. Assignment of IR bands

Compounds	ν(N-H)	Thioamide 1	ν(C=S)+δ(NCS)	ν(C-S) asym.	sym.	Λ DMF[a]
Thiazolidine-2-thione (ttz)	3400s †	1510vs	1290 s	690 s	650m	
$Te(ttz)_2Cl_4$	3200m	1515vs	1305 s	690w	660m	52
$Te(ttz)_2Br_4$	3230m	1520 1505 } vs	1305 s	690w	660m	124
$Te(ttz)_2I_4$	3230m	1517vs	1330 1304 } s	690w	662m	128
$Te(ttz)_4Cl_2.H_2O$	3130 m	1510vs	1295 s	685m	640m	42
$Te(ttz)_3Br_4$	3220 3160 } m	1510vs	1320 1300 } s		630m	85
$CH_3OC_6H_4Te(ttz)_4Br_3$	3230m 3120msh	1518vs	1322 1297 } s	700w	645m	108
$C_2H_5OC_6H_4Te(ttz)_1Cl_3$	3200m	1520vs	1305 1294 } s	695w	660m	29
$C_6H_5OC_6H_4Te(ttz)_2Cl_3$	3220m	1515m	1307 s	691m	635m	49

† { Value in $CHCl_3$
3140s cm^{-1} in KBr }

a. $cm^2.ohm^{-1}.mole^{-1}$ 10^{-3} M solutions at 20°C.

Table 3. IR and Raman spectra of tellurium thiazolidine-2-thione complexes below 400 cm^{-1}

Thiazolidine-2-thione(ttz)		$Te(ttz)_2Cl_4$		$Te(ttz)_2Br_4$		$Te(ttz)_2I_4$		$Te(ttz)_4Cl_2 \cdot H_2O$		$Te(ttz)_3Br_4$		$p\text{-}CH_3OC_6H_4Te(ttz)_4Br_3$		$p\text{-}C_2H_5OC_6H_4Te(ttz)_1Cl_3$		$p\text{-}PhOC_6H_4Te(ttz)_2Cl_3$		Assignment
i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	i.r.	Raman $\Delta\nu$	
								336vw			318s			324m	329m			ν(Te-N) *
		318m	319s	316m	314m	325msh		303s	300msh	302m		316w	317s	310w		312w		
292m	292w	306m		303m		298m						298m		303m				ttz ligand
		260ssh	253s					276w	276w					263m	255m	286sh	281m	ν(Te-Cl)
				254w				252w		252w 243w			237m	235vs	229w	230vs	223w	ν(Te-S)
		235vs	241s	236msh		212msh								206msh		203m	201w	
192s	180ssh					185m	178m									183msh	175w	ttz ligand
				183vs						165s	161msh	165s	160wsh					ν(Te-Br)
				178vs	176msh					147msh	139wsh	151m	149wsh					
						155m	152s											ν(Te-I)
						139m	131s											
		134m			147w			140vs						140w		142w		δ(Te-Cl) or
		123m		128ssh		114w	109m			124m		120w			133w		133w	δ(Te-S)
103msh																		
85msh																		

* A strong band found at 312 cm^{-1} for p-iodoanisole is said to involve C—I bending and the Te—C bending mode occurs in this region (see text).

Method (B) results in the production of compounds of a more unexpected stoichiometry. The latter phenomenon has however been noted previously for iron(II) and (III) thiazolidine-2-thione complexes[11].

The large negative shifts of ν(NH) and the positive shift of the thioamide band (I) in these iron thiazolidine-2-thione complexes is indicative of co-ordination through nitrogen. The presence of iron-nitrogen bonds is supported by examination of the far IR spectra where bands due to ν(Fe–N) may be found (240–220 cm^{-1}) and the absence of bands which would be expected for ν(Fe–S). Sulphur bonded thiazolidine-2-thione is proposed for silver(I)[12] and chromium, molybdenum and tungsten[10] but zinc(II), cadmium (II) and mercury(II) are all nitrogen bonded[5, 6].

The position with cobalt(II) is confusing. De Filippo and Preti[7] believe this metal ion is S-bonded but Singh and Rivest[9] favour nitrogen. Examination of the far IR spectra does not always help. ν(M–N) and ν(M–S) may well lie in the same region for some metals.

Ligands containing a thiocarbonyl group adjacent to an imino group offer interesting alternative modes of co-ordination, i.e. through nitrogen only, through sulphur only or through both nitrogen and sulphur. These 3 possibilities may be distinguished, it is claimed, by an analysis of the positions and intensities of the thioamide bands[8]. The situation is clear in some cases. For instance, spectroscopic studies on the thiazolidine-2-thione complexes of groups VI B carbonyls[10] show that there is no co-ordination through the nitrogen atom, only the less sterically hindered sulphur atom of the thioketonic group is involved in bonding to the metal.

For the tellurium complexes of the types $Te(ttz)_2X_4$ and $RTe(ttz)_xX_3$ the far IR and Raman spectra [Table 3] clearly show the presence of bands in the range expected for ν(Te–S)[1, 2, 3] 254–201 cm^{-1}; the tellurium-halogen stretching frequencies are also retained, i.e. ν(Te–Cl) 286–253 cm^{-1}, ν(Te–Br) 183–161 cm^{-1}, ν(Te–I) 154–135 cm^{-1}. Most of the compounds show absorptions in the region 340–290 cm^{-1}. The Te–C bending mode gives rise to an absorption in this region but since tellurium-aryl linkages are absent in many of the complexes the bands observed could be attributed to ν(Te–N) vibrations.

The negative shift of ν(NH) and the slight positive shift of the thiomide I band in the spectra of the thiazolidine-2-thione complexes [Table 2] suggests that nitrogen in the donor atom. Evidence from the shifts in ν(C=S) is less convincing. Slight positive shifts of the band due to $\nu(C{=}S) + \delta(NCS)$ are said to be indicative of co-ordination through nitrogen[5, 9, 11] but de Filippo *et al.*[10] suggest that the positive shifts in $M(CO)_5ttz$ complexes are due to co-ordination through the sulphur atom of the thioketonic group.

The appearance of new bands in the far IR spectra of the tellurium complexes seems to indicate that nitrogen and sulphur are involved in co-ordination in all cases. A possible exception is p-$C_2H_5OC_6H_4Te(ttz)Cl_3$. It is difficult to see how 2 donor atoms are involved from 1 ligand.

Assuming that thiazolidine-2-thione is behaving as a monodentate ligand in the tellurium complexes, the tellurium atom in $Te(ttz)_2X_4$ type complexes could be 6 co-ordinate with 1 nitrogen donor 1 sulphur donor occupying *cis* or *trans* positions, the 4 halogen atoms using the remaining 4 sites. Six co-ordinate tellurium is also possibly involved in $Te(ttz)_4Cl_2H_2O$. The structures of the other complexes are more difficult to envisage. Five co-ordinate tellurium is possible for p-$C_2H_5OC_6H_4Te(ttz)Cl_3$ and 6 for p-$PhOC_6H_4Te(ttz)_2Cl_3$ but if all the thiazolidine-2-thione ligands are involved in co-ordination in p-$CH_3OC_6H_4Te(ttz)_4Br_3$ and $Te(ttz)_3Br_4$ a co-ordination number of 7 or 8 would have to be postulated. The high Λ values for the bromo complexes indicate that 1 bromine atom could be present as Br^- thus giving a co-ordination number of 6 or 7 in the cation.

Conductivity measurements [Table 2] show that there is considerable variation in the magnitude of Λ. Most of the complexes have values expected for 1 : 1 electrolytes but in some cases there is interaction between cationic and anionic species leading to low values of Λ. Thus, $Te(ttz)_2X_4$ complexes may be written as $[Te\,ttz_2X_3]^+X^-$ and those of the type $RTe(ttz)_xX_3$ as $[RTe\,ttz_xX_2]^+X^-$.

The UV and visible spectra in NN′dimethylformamide consist of 1 single absorption band for all complexes at 35.7 kK in agreement with the data found for other tellurium-sulphur bonded complexes[22].

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