LIGAND CHEMISTRY OF TELLURIUM

BY

HEMA MALINIE KUMBALGODA KANKANAM PATHIRANA

A thesis submitted for
the Degree of Doctor of Philosophy
of the
University of Aston in Birmingham

October 1985

DECLARATION

The work described in this thesis was carried out between 1982 and 1985 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

....HMKKPathirana..........

H.M.K.K.Pathirana

To my mother and father
without whose unfailing efforts and guidance
I would not have had the opportunity to
accomplish a successful education

and

to Professor W. R. McWhinnie
who led the way and gave much light
in this study

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Summary

Potentially bidentate tellurium ligands having the molecular formula $ArTe(CH_2)_nTeAr$, (L^n), n=1, 5, 6, 7, 9, 10 and $o\text{-}C_6H_4(CH_2TeAr)_2$, (L) are prepared by reacting ArTeNa with 1,n-dibromoalkanes or with $o\text{-}C_6H_4(CH_2Br)_2$. Changing the reactant ratio from 2:1 to 1:2 resulted in a telluronium salt only in the case of 1,5-dibromopentane. The bromination of some of the bis-tellurides resulted in bis-tribromides due to the rupture of the tellurium-aryl bond. The ^{13}C N.M.R. spectra are particularly useful in characterisation of these ligands.

L^1 undergoes slow (16h) oxidation in solution with dioxygen, but in the presence of metal ions rapid (15min) oxidation occurs and complexes of the bis-telluroxide are formed e.g., $(ArTe(O)CH_2Te(O)Ar)HgCl_2$. Thus, all syntheses of complexes of this ligand and other ligands were carried out with the strict exclusion of dioxygen.

Three distinct classes of complexes are isolated from L^1. They are $L^1_2M_2X_2$ (M=Pd, Pt; X=Cl, Br); $L^1_2MCl_2$ (M=Pd) and L^1MCl_2 (M=Hg).

Palladium, Platinum, Mercury and Rhodium complexes of L^n(n=5-7, 9, 10) are prepared. They are trans-PdX_2L^n (X=Cl, Br; n=5-7, 9, 10), cis-PtX_2L^n (X=Cl, Br; n=6, 7, 9, 10), $Pt_2Cl_2L^5_2$, $HgCl_2L^n$ (n=5-7, 9, 10) and $RhClL^n$ (n=6, 7). Much interest was focused on palladium and platinum complexes. These metal ions form oligomeric or polymeric complexes with L^6. The rest are monomeric, except $Pt_2Cl_2L^5_2$. The ^{13}C N.M.R. data of these soluble complexes indicate the co-ordination of both tellurium atoms. Reduction of Rh(III) by Te(II) to Rh(I) occurs in the preparation of rhodium complexes. Thus, RhClL is obtained, the complex is believed to have a structure base on Rh_2Cl_2 units.

Complexes having the molecular formula $L_2M_2Cl_2$ (M=Pd, Pt) and $LMCl_2$ (M=Hg) are isolated from $o\text{-}C_6H_4(CH_2TeAr)_2$ ($L=o\text{-}C_6H_4(CH_2TeAr)_2$).

A potentially tetradentate ligand, $C(CH_2TeAr)_4$ is prepared by the nucleophilic attack of $ArTe^-$ with $C(CH_2Br)_4$. Preliminary experiments indicated the formation of complexes with soft metal ions.

Key Words:
TELLURIUM
DIORGANODITELLURIDES
TELLURIUM LIGANDS
BIS-ORGANYLTELLUROALKANES
SOFT LEWIS ACIDS

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CHAPTER ONE

INTRODUCTION

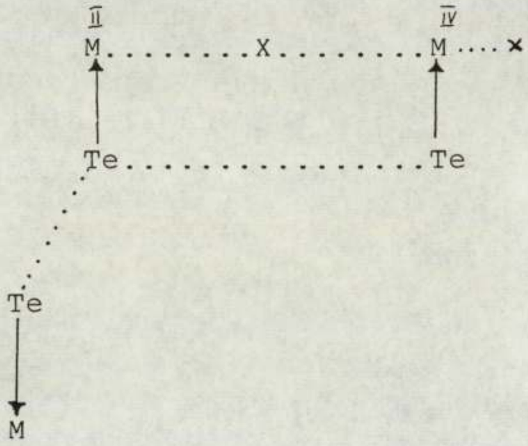
1.1 Introduction

The idea of coordination is related to acid-base neutralisation in the Lewis sense. In terms of coordinate bond formation, a metal ion is a Lewis acid and a ligand is a Lewis base. These Lewis acids and bases have been classified in terms of hardness and softness(1). For a given element, hardness increases with oxidation number. Softness is a quality which may be associated with π-back coordination on the part of the metal ion (or atom). Ligands associated with hard metal ions are those with σ-donor properties, while those associated with soft metal ions are those with π-acceptor properties. Hard metal ions prefer to coordinate with hard ligands, while soft metal ions prefer to coordinate with soft ligands. The term class 'A' and class 'B' are also used to define hard and soft metal ions(2). Class 'A' metals are those which form their most thermodynamically stable complexes with the first ligand atom of each group in the periodic table i.e., N, O and F. Class 'B' metals form their most stable complexes with the second or subsequent ligand atom of each group in the periodic table. The stabilities for complexes for class 'A' metals are O>>S>Se>Te and for class 'B' S>>O, but any sequence of S, Se, Te is possible(3).

Although this division into hard and soft can be useful regarding the interaction between some metal ions and ligands, there are many intermediate situations where it is difficult to make the classification rigid, and many metal ions fall between the two extremes. Since class 'B' or soft acid character increases with increasing number of d-electrons and also with decreasing charge on the metal, Pt(II), Pt(IV), Pd(II), Pt(0), Pd(0) and Hg(II) have been classified as class 'B'(4).

According to the above description, tellurium can be classified under soft ligands. Since soft ligands prefer to react with class 'B' metals, tellurium also reacts with class 'B' metals such as Pd(II), Pt(II), Hg(II) and Cu(I). In this study, interests were focused on Pd(II) and Pt(II) because of their ability to form square planar complexes. The reason for paying particular interest to the synthesis of square planar complexes is because of the possible useful applications of these in the future. For example, these complexes might be catalytically active, similar to complexes synthesised from analogous bidentate diphosphine ligands(5,6).

In addition to this, these complexes may be of use as organic semiconductors. The use of bis-telluride ligands with heavy metal ions which have an ability to form square planar complexes may result in a stacked structure with intermolecular interactions. For example, square planar complexes prepared from bis-tellurides may be convertible by partial oxidation to conducting systems, having 1-D or 2-D tellurium-tellurium interactions as illustrated below.



Therefore, use of bidentate tellurium ligands will be a useful new contribution.

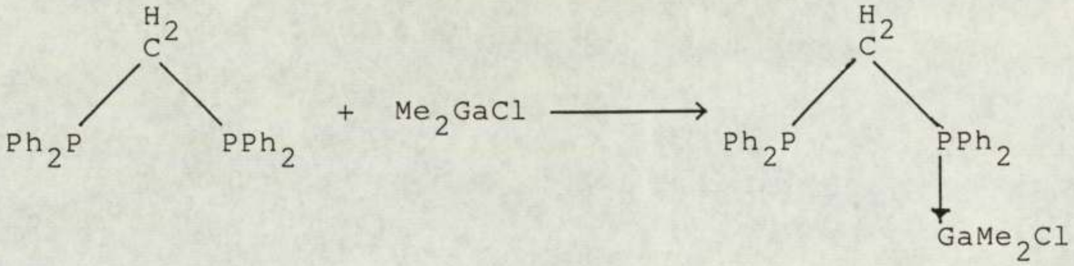
There are several modes of coordination open to a potentially bidentate ligand, some or all of which may be achieved in practice under appropriate synthetic conditions. Although this is an unexplored area in tellurium chemistry, examples for all the possible binding modes of bidentate ligands have been reported in phosphorus chemistry. These binding modes can appear when the bidentate ligand is acting in the following ways:-

1. as a monodentate ligand
2. as a chelating bidentate ligand
3. as a bridging bidentate ligand

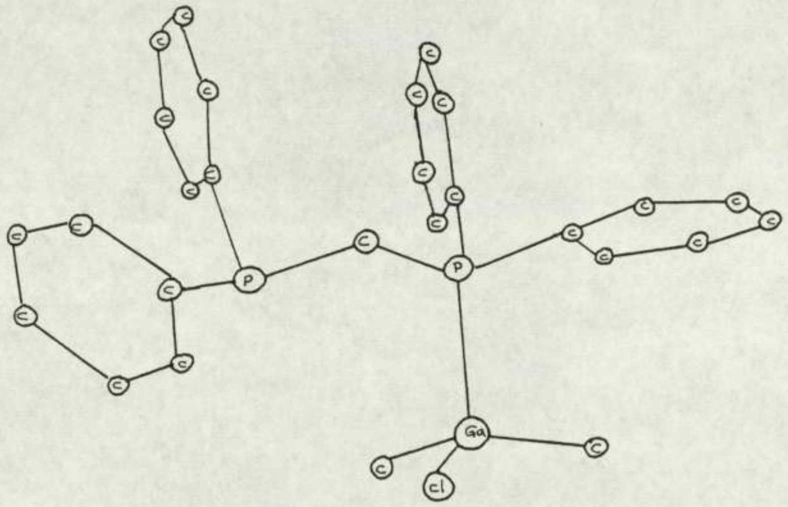
A brief description about these binding modes is given below with examples from phosphorus chemistry.

1. As a monodentate ligand

The formation of a complex in which L〰L (e.g., $Ph_2P(CH_2)_nPPh_2$) functions as a monodentate ligand has been achieved by reacting bis-(diphenylphosphino)methane with chlorodimethylgallium(7).



A single crystal X-ray diffraction study has given evidence supporting this structure(7).



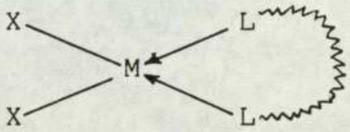
2. As a chelating bidentate ligand

The chelation of a bidentate ligand to a metal ion can result in the following types of complexes:-

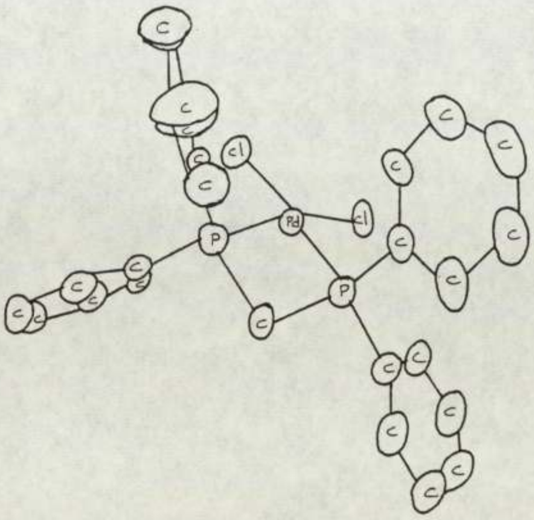
(a) cis-bonded monomeric chelates
(b) trans-bonded monomeric chelates
(c) complexes having more than one chelate ring
(d) cyclometallated complexes.

Much work has been reported by Shaw about ligands in this category(9,12).

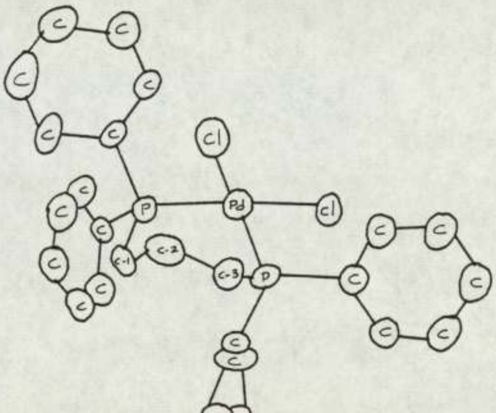
(a) cis-bonded monomeric chelates



Chelated cis-$PdLX_2$ has been obtained by reacting Na_2PdCl_4 with o-phenelenebis-(diphenylphosphine)(8) or with $Ph_2P(CH_2)_nPPh_2$, n=1, 2, 3(9). Single crystal X-ray diffraction studies have given evidence for chelated cis-$PdCl_2\{Ph_2PCH_2PPh_2\}$ and cis-$PdCl_2\{Ph_2P(CH_2)_3PPh_2\}$(91).

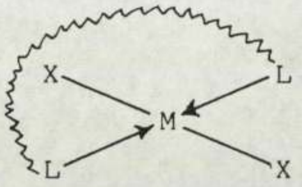


$\mathrm{PdCl_2\{Ph_2PCH_2PPh_2\}}$(91)



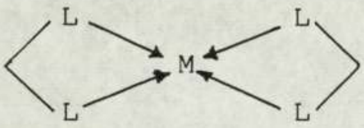
$\mathrm{PdCl_2\{Ph_2P(CH_2)_3PPh_2\}}$(91)

(b) trans-bonded monomeric chelate complexes



Trans-$PdLX_2$ has been obtained by reacting Na_2PdCl_4 with $Bu^t_2P(CH_2)_nPBu^t_2$ where n=10, 12(9).

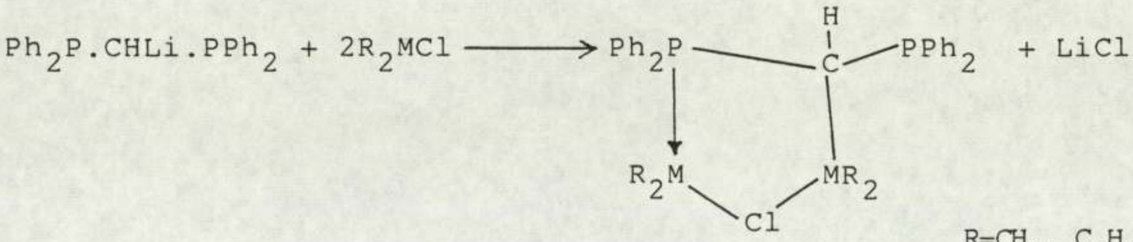
(c) Complexes having more than one chelate ring



e.g., $[Pd(Ph_2PCH_2PPh_2)_2]Cl_2$. This has been prepared by reacting Na_2PdCl_4 with $Ph_2PCH_2PPh_2$ in 1:2 molar ratio(88).

(d) Cyclometallation

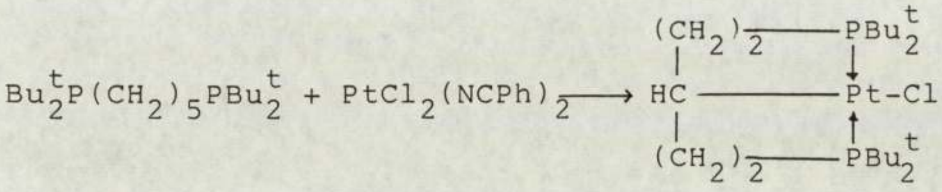
Another type of chelation, cyclometallation, has been achieved by reacting lithiated *bis*-(diphenylphosphino)methane with chlorodimethylgallium(11).



R=CH_3, C_2H_5

M=Ga, Al

Another example for a chelated cyclometallated complex has been achieved by reacting $[PtCl_2(NCPh)_2]$ with $Bu^t_2P(CH_2)_5PBu^t_2$ (12).



3. As a bridging bidentate ligand

Again a considerable amount of work has been reported by Shaw about this type of phosphorus ligand(13,14). The following types of binding modes can appear when the ligand acts as a bridging bidentate ligand:-

(a) as a bridging bidentate ligand forming a binuclear complex, but without any ring formation.

(b) As a cis-bonded bridging bidentate ligand forming a binuclear complex and a cyclic ring system.

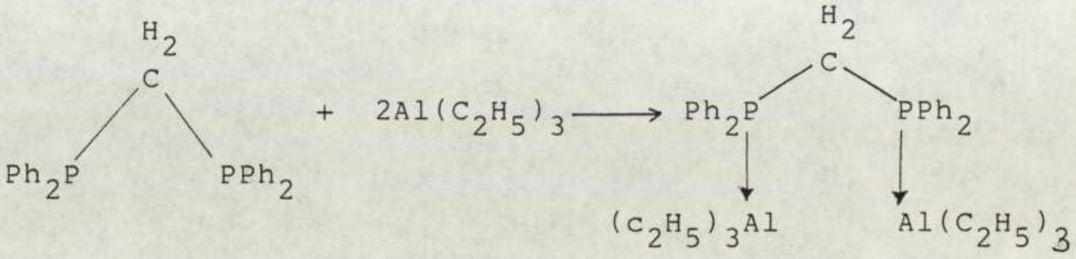
(c) As a trans-bonded bridging bidentate ligand forming a binuclear complex and a cyclic ring system.

(d) As a bridging bidentate ligand forming complexes with metal-metal bonds, but no other bridging groups.

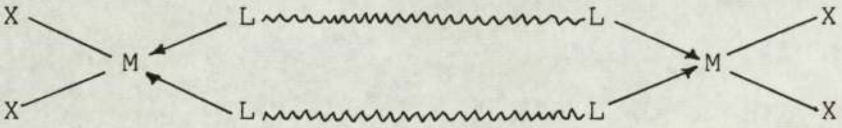
(e) As a bridging bidentate ligand forming complexes with other bridging groups.

(a) As a bridging bidentate ligand forming a binuclear complex but without any ring formation

e.g.,

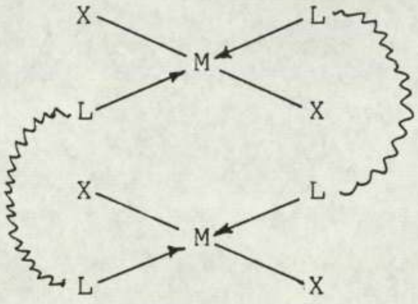


(b) As a *cis*-bonded bridging bidentate ligand forming a binuclear complex and a monocyclic ring system

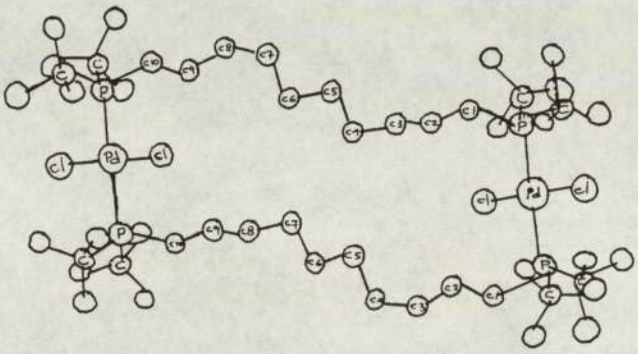


Complexes belonging to this category have been prepared by reacting K_2PtCl_4 with *bis*-(diphenylphosphino)alkanes$^{(10)}$.

(c) As a *trans*-bonded bridging bidentate ligand forming a binuclear complex and a cyclic ring system



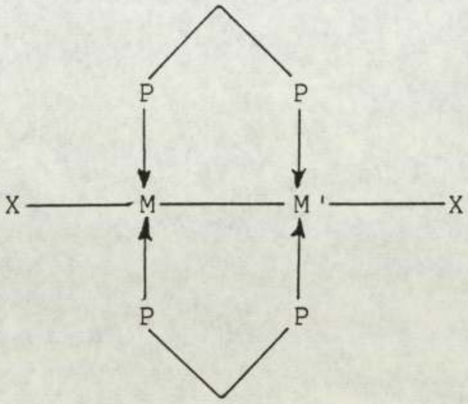
The reaction of Na_2PdCl_4 with $Bu^t_2P(CH_2)_nPBu^t_2$, n=10, 12 results in complexes belonging to this category(9). The crystal structure of $[PdCl_2\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]_2$ is given below.



<u>trans</u>-$[PdCl_2\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]_2$ (9)

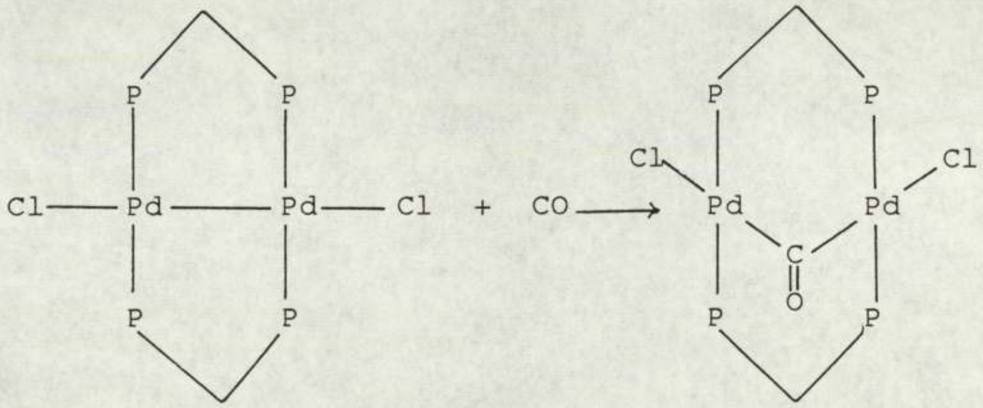
<u>(d) As a bridging bidentate ligand forming complexes with metal-metal bonds, but no other bridging groups</u>

The best studied complexes of this kind are the singly metal-metal bonded derivatives having the molecular formula of $[MM'X_2(\mu\text{-dpm})_2]$; M,M'=Pd, Pd or Pt, Pt or M,M' = Pd, Pt; dpm = diphenylphosphinomethane(13-15).



(e) As a bridging bidentate ligand forming complexes with other bridging groups

These complexes may or may not have a metal-metal bond(5,16,17).



(15)

Although the coordination chemistry of ligands containing heavier group V donor atoms(8-10,12) and S(18) ligands has been widely investigated, the analogous chemistry of tellurium ligands is relatively unexplored. One of the possible reasons for this is the supposed toxic effects of tellurium compounds, another, the belief of some that the M⟵Te bond is weak.

Tellurium is classified in Group VI of the periodic table and is located between Se and Po. It has the atomic number of 52 and an atomic weight of 127.6. The electronic structure of Te is [Kr], $4d^{10}$, $5s^2$, $5p^4$. As a member of Group VI, tellurium bears a resemblance to selenium and sulphur in many of its properties. Within this group, the metallic nature increases as the atomic weight increases in proceeding from oxygen to polonium, as seen by the fact that oxygen and sulphur are insulators, selenium and tellurium are semiconductors and polonium, a conductor.

Tellurium exhibits a wide variety of oxidation states. Its common oxidation states are Te^{-2}, Te^{-1}, Te^{+1}, Te^{+2}, Te^{+4} and Te^{+6}. The oxidation states important in ligand chemistry of tellurium are Te^{-2}, Te^{-1}, Te^{+1} and Te^{+2}.

Because of the outer vacant shell of tellurium, Te^{+2} and Te^{+4} can act as Lewis acids by accepting electrons from electron donors. Te^{+2} forms complexes of the type TeL_2X_2(19,20); $[TeL_4]X_2$(21) (L=thiourea or selenourea and X=halide, pseudohalide). Te^{+4} acts as a Lewis acid by forming complexes with amines(22), sulphides(23) and tetramethylthiourea(24).

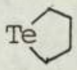
When reacting with transition metal ions, organotellurium compounds can act as Lewis bases because of the lone pair of electrons of the outer shell of tellurium.

The main objective of this work was to study the co-ordination chemistry of potentially bidentate tellurium ligands. A brief review of co-ordination chemistry of tellurium ligands is given below.

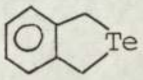
1.2 Monodentate Tellurium Ligands

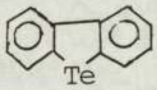
The first monodentate tellurium ligand, $TeEt_2$, was prepared in 1840 by Wöhler(25). After this work, the area remained dormant for a long period. Since 1960, there has been a steadily increasing interest in organotellurium chemistry.

Possible types of monodentate tellurium ligand are listed below. References for preparative methods are given in parentheses.

1. R_2Te (R=alkyl or aryl or alkyl.aryl)(26,27)
2. Tellurolates, RTe^- (R=alkyl or aryl)(28-30)
3. Tellurols, TeH^-(31)
4. Tellurium heterocycles
    (a) 

    (32)
    (b) 

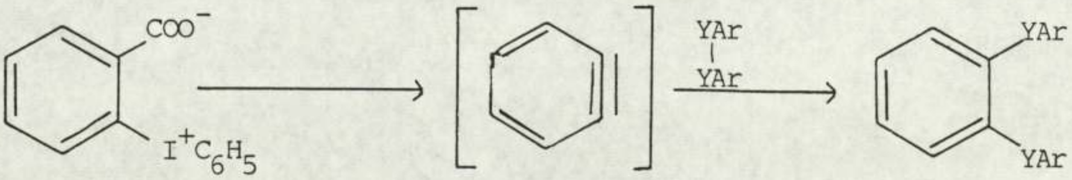
    (33)
    (c) 

    (34)
    (d) 

    (35)
5. Telluroesters, ArTeCOAr'(30)
6. TeO_2(36)
7. Te^{2-} (37)

1.3 Bidentate Tellurium Ligands

Petragnani *et al* have reported the synthesis of bidentate ligands of the type $ArY.C_6H_4.YAr$ by the reaction of benzyne which is an intermediate formed from the benzyne precursor (2-phenyliodonio)benzoate with ditelluride, diselenide or selenoditelluride(38,39)

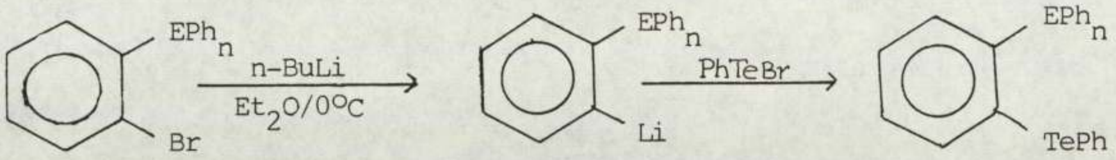


Y,Y = Te,Te ; Ar = $CH_3O.C_6H_4$

Se,Se ; Ar = $C_2H_5O.C_6H_4$

Te,Se ; Ar = $CH_3.C_6H_4$

Similar types of ligands have been synthesised in the following way(40a,40b):-



E = S, Se, Te ; n = 1

= N, P ; n = 2

Another class of bidentate ligands, bis-(phenyltelluro)-methane has been synthesised by the addition of diazomethane to diaryl ditellurides(41).

$$R.YY.R + CH_2N_2 \longrightarrow RY.CH_2.YR + N_2$$

R = p.$CH_3O.C_6H_4$; Y = Te

= p.$C_2H_5O.C_6H_4$; Y = Te

= C_6H_5 ; Y = Se

= $C_6H_5.CH_2$; Y = Se

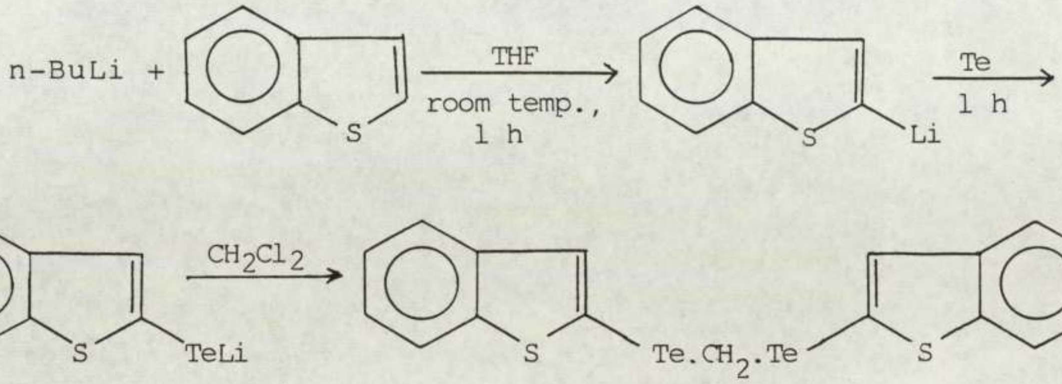
= p.$CH_3.C_6H_5$; Y = S

The alkylation of lithium benzene tellurolate with diiodomethane results in the same compound(42). However, the yield in this process is very low(42).

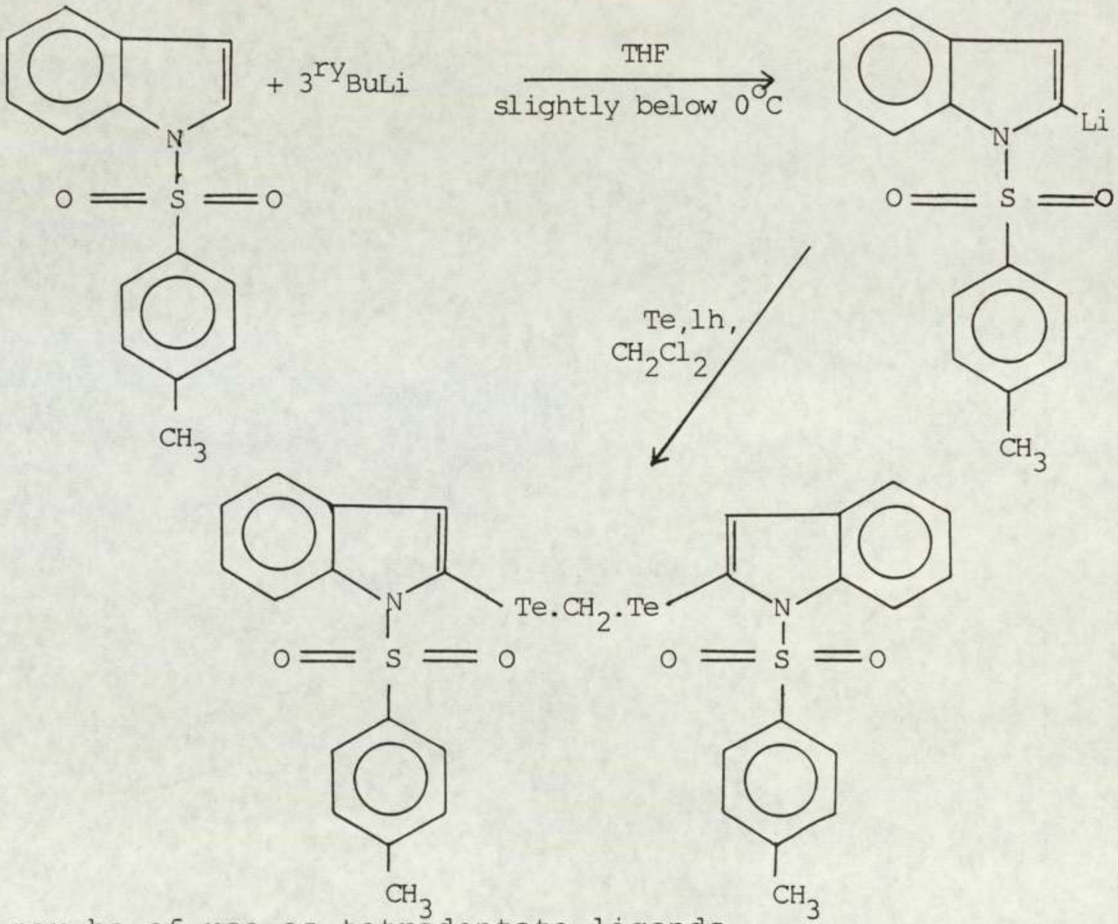
$$2C_6H_5Li + 2Te \xrightarrow{THF} 2(C_6H_5TeLi) \xrightarrow{CH_2I_2} C_6H_5TeCH_2TeC_6H_5$$

Higher yields of this type of compound have been obtained by reacting heterocyclic lithium tellurolates with dichloromethane(43).

(a)



(b)



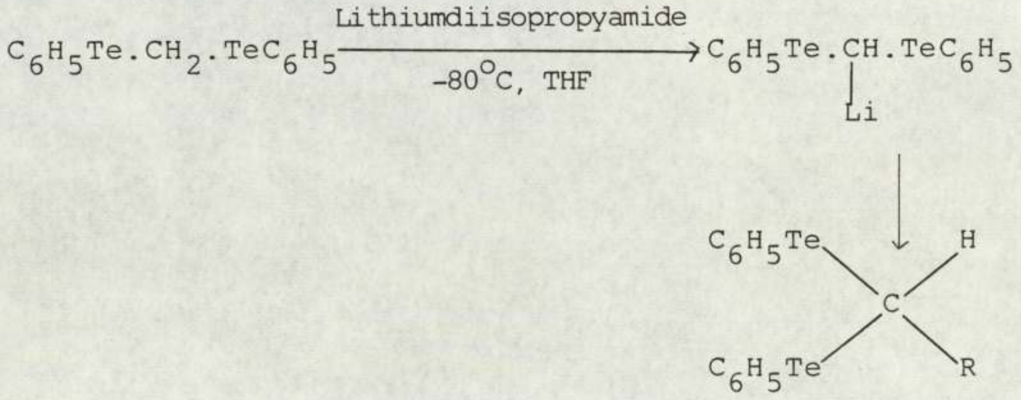
These may be of use as tetradentate ligands.

Usually, for ditellurides, during complex formation, first the Te-Te bond undergoes reductive cleavage, and then the RTe^- group acts as a monodentate ligand(44,45). Complexes with dialkylditellurides and diarylditellurides in which the Te-Te bond remains intact have also been reported(46,47). Therefore, ditellurides could also be used as bidentate ligands.

A bidentate ligand with an alkane chain backbone and having Te and P as the donor atoms, has been synthesised in the following way(40a):-

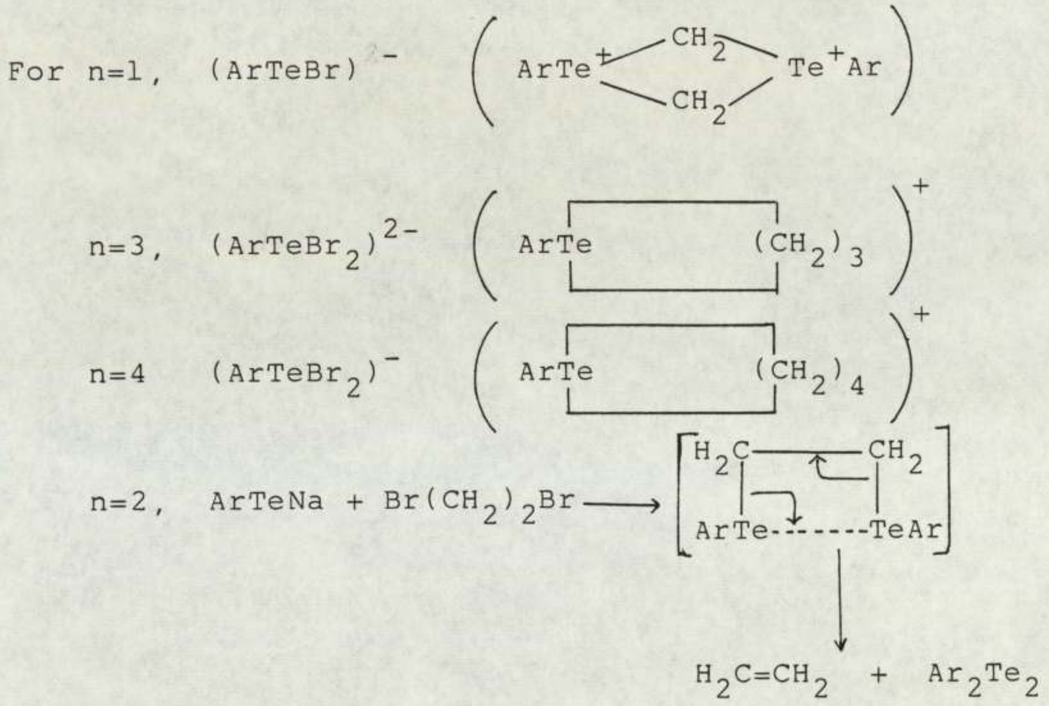
$$Cl.CH_2CH_2.Cl \xrightarrow{Ar_2PNa} Cl.CH_2CH_2.PAr_2 \xrightarrow{ArTeNa} ArTe.CH_2CH_2.PAr_2$$

By using bis-(phenyltelluro)methane as the starting material, Seeback and Beck have synthesised another bidentate ligand(42):-



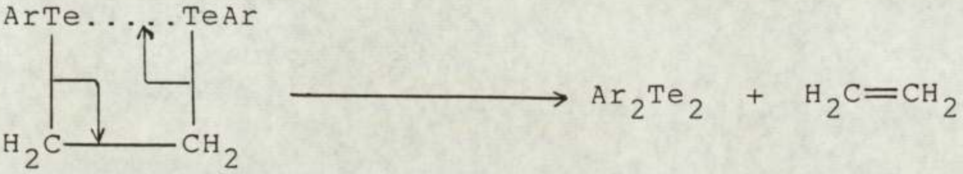
(42)

The synthesis of bistellurides having the molecular formula, $ArTe(CH_2)_nTeAr$, was attempted by some of the earlier workers in our laboratory(3,48,49). The reaction of ArTeNa with dihaloalkane of the type, $Br(CH_2)_nBr$, n=1, 2, 3, 4 was first carried out by Davies as an attempt to synthesise this type of bidentate ligand(3). A 2:1 ratio of ArTeNa and $Br(CH_2)_nBr$, where n=1,3 and 4, has resulted in a white precipitate, while ditellurides were recovered for n=2 state. The following formulations have been proposed, although they are not confirmed by physical data:-

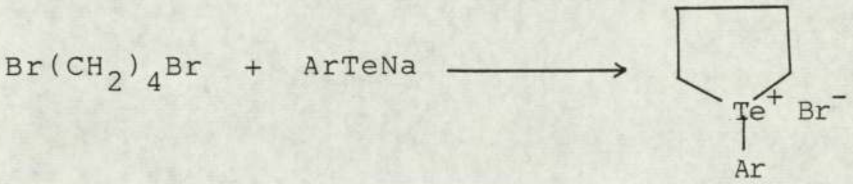


Later, McWhinnie and coworkers studied the reaction of ArTeNa with excess dihalomethane and have obtained the bis-telluride, $ArTeCH_2TeAr$, in the form of a charge transfer complex of the stoichiometry $ArTeCH_2TeAr.CH_2I_2$. This charge transfer complex has been identified by elemental analysis, I.R., N.M.R., mass, E.S.R. and Mössbauer spectroscopy(50).

The reaction of ArTeNa with other dihaloalkanes, $(CH_2)_nX_2$, where n=2,3 and 4, has followed different pathways⁽⁵⁰⁾. In the reaction of ArTeNa with dibromoethane, nucleophilic substitution occurs and ditelluride then is eliminated in a concerted process, as in the case of the arsenic analogue⁽⁵¹⁾.



In the reaction of ArTeNa with dibromopropane and dibromobutane, nucleophilic substitution of one halogen atom of the dihaloalkane occurs, but cyclisation then proceeds more rapidly than further attack by $ArTe^-$ at the second C-X bond, forming a telluronium salt, with a stoichiometry of $ArTe(CH_2)_nBr$, n=3, 4.



In this study, the reaction of ArTeNa with $Br(CH_2)_nBr$, n=5,6,7...10, was studied under slightly modified conditions, as an attempt to make new bis-tellurides.

1.4 Transition Metal Complexes Of Organotellurium Ligands

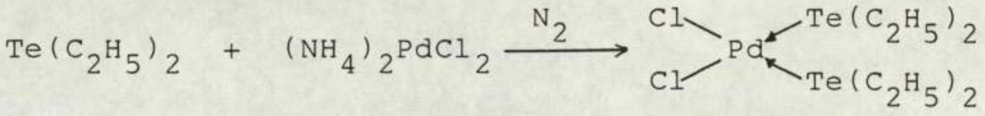
Transition metals form a variety of complexes with organotellurium ligands. These complexes have been prepared using metal halides of the type MX_n, (M=Ag, Hg, Cu) or K_2MX_n (M=Pd or Pt), metal carbonyls and metal carbonyl halides. Usually organotellurium ligands prefer to form complexes with soft or class 'B' metals, as mentioned earlier.

Complexes with monodentate tellurium ligands

Most of the studied monodentate tellurium ligands form both terminal M-TeR and bridging $M(\mu\text{-TeR})_2M$ linkages with transition metal ions.

R_2Te

Complexes with terminal dialkyl tellurides

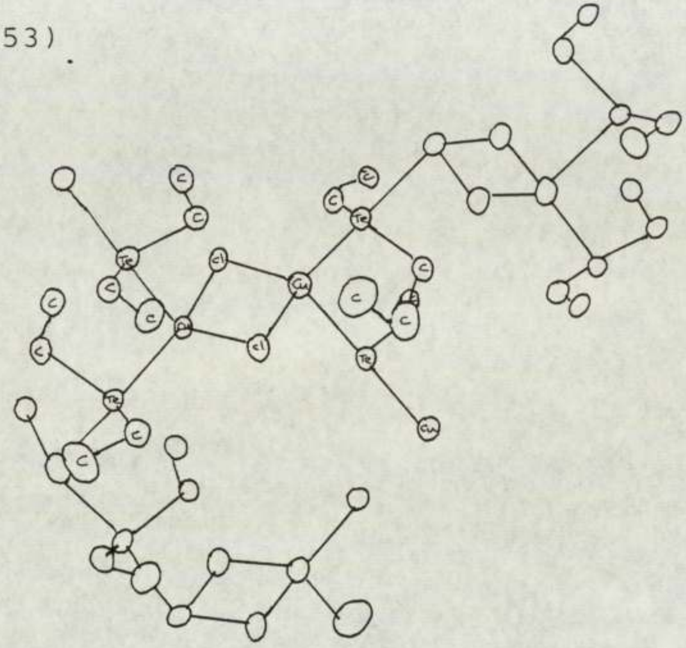


$$Te(C_2H_5)_2 + (NH_4)_2PdCl_2 \xrightarrow{N_2} Cl_2Pd \leftarrow [Te(C_2H_5)_2]_2 \quad (52)$$

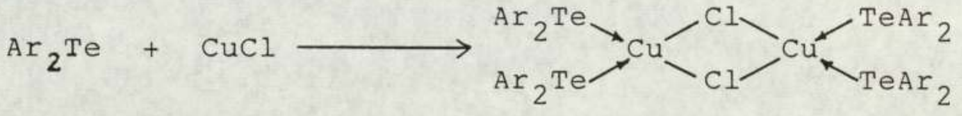
Complexes with bridging dialkyl tellurides

$$Te(C_2H_5)_2 + CuCl \longrightarrow [CuCl.Te(C_2H_5)_2]_n \quad (53)$$

X-ray analysis has shown that its structure contains infinite sheets in which two $Te(C_2H_5)_2$ ligands are bridged between two di-μ-chlorodicopper(I) cores. The geometry around both Cu and Te atoms is that of a distorted tetrahedron$^{(53)}$.



Complexes with terminal diaryl tellurides

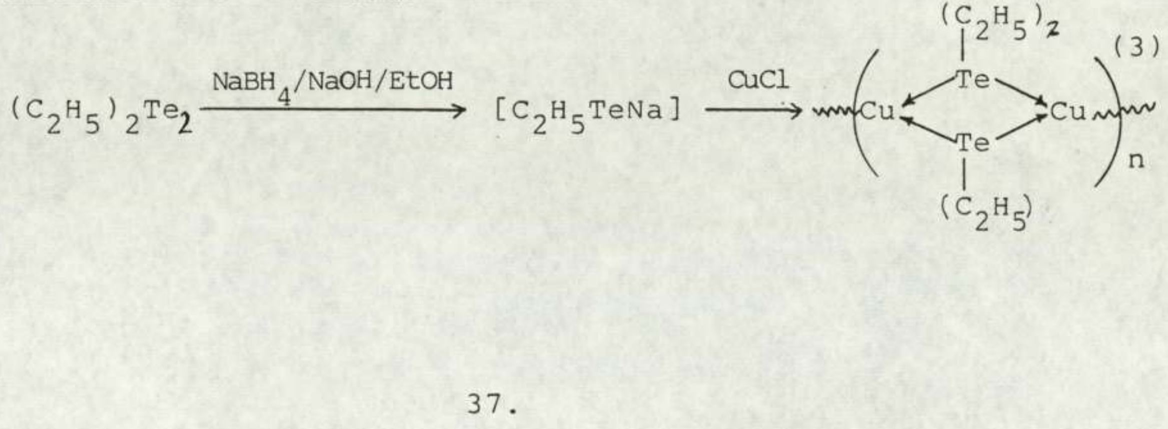


$$Ar_2Te \;+\; CuCl \longrightarrow \begin{matrix} Ar_2Te\searrow & & Cl & & \swarrow TeAr_2 \\ & Cu & & Cu & \\ Ar_2Te\nearrow & & Cl & & \nwarrow TeAr_2 \end{matrix} \qquad (54)$$

Ar=Ph, p-$OC_2H_5.C_6H_4$

RTe^-

Complexes with bridging Te(ALKYL)$^-$



$$(C_2H_5)_2Te_2 \xrightarrow{NaBH_4/NaOH/EtOH} [C_2H_5TeNa] \xrightarrow{CuCl} \left(\sim Cu \begin{matrix} (C_2H_5)_2 \\ | \\ \swarrow Te \searrow \\ \\ \nwarrow Te \nearrow \\ | \\ (C_2H_5) \end{matrix} Cu \sim \right)_n \qquad (3)$$

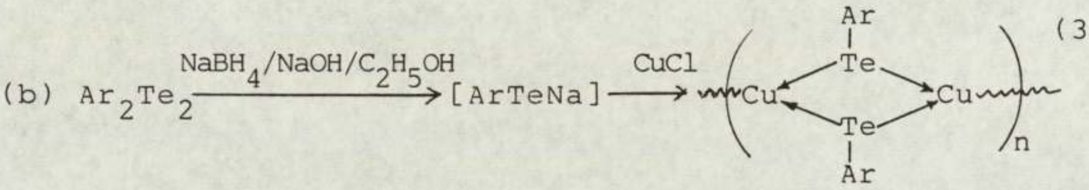
Complexes with terminal Te(ARYL)$^-$

$$[C_pMo(CO)_3]_2 + Ph_2Te_2 \xrightarrow[C_6H_6]{25^\circ C, h\nu} \pi.C_pMo(CO)_3.TePh \qquad (55)$$

Complexes with bridging Te(ARYL)$^-$

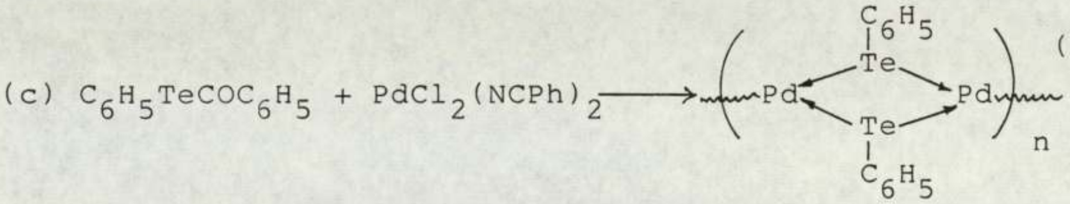
(a) $[C_pMo(CO)_3]_2 + Ph_2Te_2 \xrightarrow[C_6H_6]{reflux, 14h} \pi.C_p(CO)_2Mo(\mu\text{-}TePh)_2Mo(CO)_2\pi C$ (55)

(b) (3)

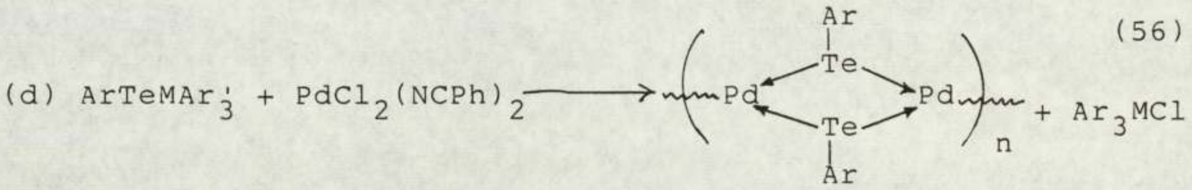


Ar=p-$C_2H_5O.C_6H_4$

(c) (30)

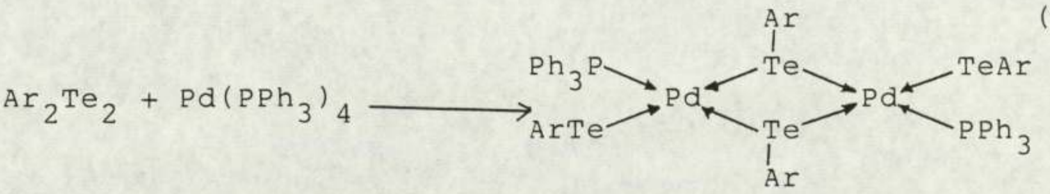


(d) (56)



Complexes containing both terminal and bridging Te(ARYL)$^-$

(44)



Ar=p-$C_2H_5O.C_6H_4$

TeH^-

Complexes with terminal $(TeH)^-$

$$Cr(CO)_6 \xrightarrow[h\nu\ -40^{\circ}C]{THF} Cr(CO)_5(THF) + CO \qquad (57)$$

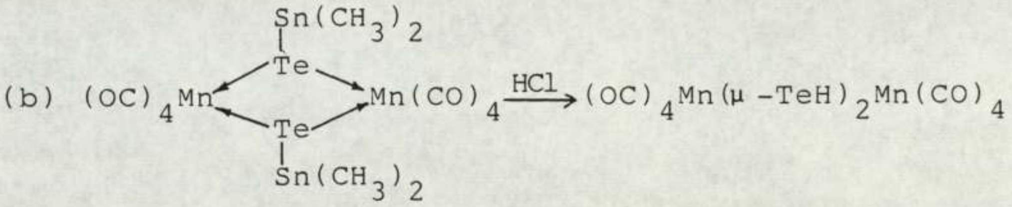
$$\begin{tikzcd}
Cr(CO)_5(THF) \arrow[r, "Na_2Te", "C_2H_5OH/-60^{\circ}C"'] & Na^+[Cr(CO)_5TeH]^- \arrow[d, "PPN^+Cl^-"] \\
 & PPN^+[Cr(CO)_5TeH]^-
\end{tikzcd} \qquad (58)$$

$PPN = [(Ph_3P)_2N]^+$

Complexes with bridging TeH^-

(58)

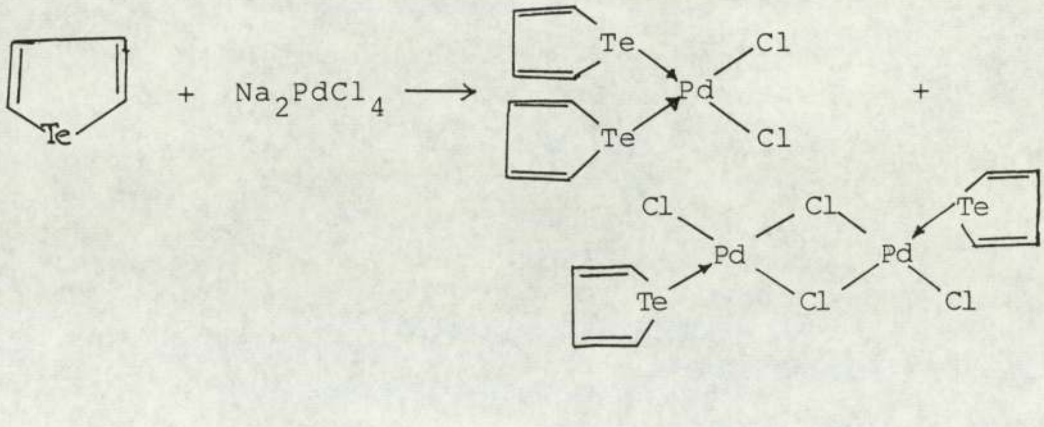
(a) $PPN^+[Cr(CO)_5TeH]^- + Cr(CO)_5(THF) \longrightarrow PPN^+[(OC)_5Cr(\mu\text{-}TeH)Cr(CO)_5]^-$

(b) 

(31)

Tellurium heterocycles

Only the complexes having terminal M-Tellurium heterocycle linkages have been reported.



(59)

Te^{2-}

An example of a Te atom that functions as a six electron donor* has been reported(36).

$$CpMn(CO)_3 \xrightarrow{THF/h\nu} CpMn(CO)_2(THF)$$

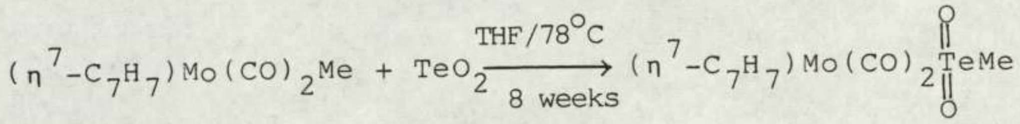
$$Al_2Te_3 \xrightarrow{HCl} H_2Te$$

$$CpMn(CO)_2(THF) + H_2Te \longrightarrow Te[Mn(CO)_2Cp]_3^* + Te_2[Mn(CO)_2Cp]_3$$

TeO_2

TeO_2 prepared in a metal-atom reactor inserts into the metal-methyl bond in $(\eta^7\text{-}C_7H_7)Mo(CO)_2Me$(37).

$$TeO_2 \xrightarrow[(C_2H_5)_2O/-196^\circ C]{\text{metal atom reactor}} TeO_2$$

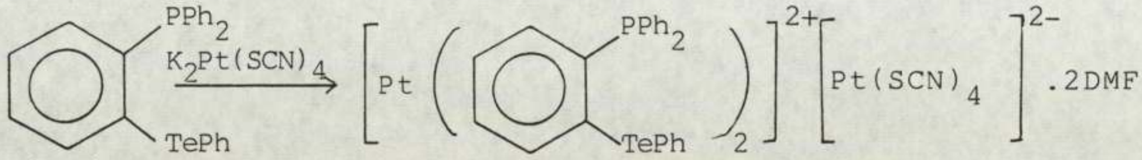


$$(\eta^7\text{-}C_7H_7)Mo(CO)_2Me + TeO_2 \xrightarrow[\text{8 weeks}]{THF/78^\circ C} (\eta^7\text{-}C_7H_7)Mo(CO)_2\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Te}}Me$$

Complexes of bidentate tellurium ligands

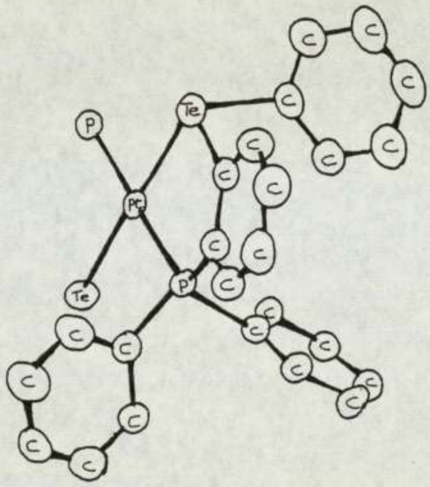
Although a few bidentate tellurium ligands have been reported in literature, very little work has been reported on the coordination chemistry of these bidentate ligands.

A metal complex containing a hybrid bidentate ligand has been synthesised by Gysling very recently$^{(40a,40b)}$.

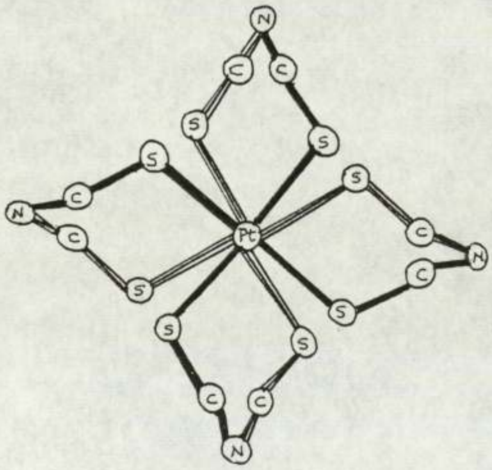


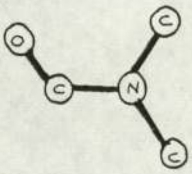
(tep)

X-ray analysis of this magnus-type salt has shown that the structure consists of discrete, centrosymmetric $Pt(tep)_2^{2+}$ and $Pt(SCN)_4^{2-}$ ions, and the coordination about both Pt atoms is square planar$^{(40b)}$.



$[Pt(tep)_2]^{2+}$ (40b)

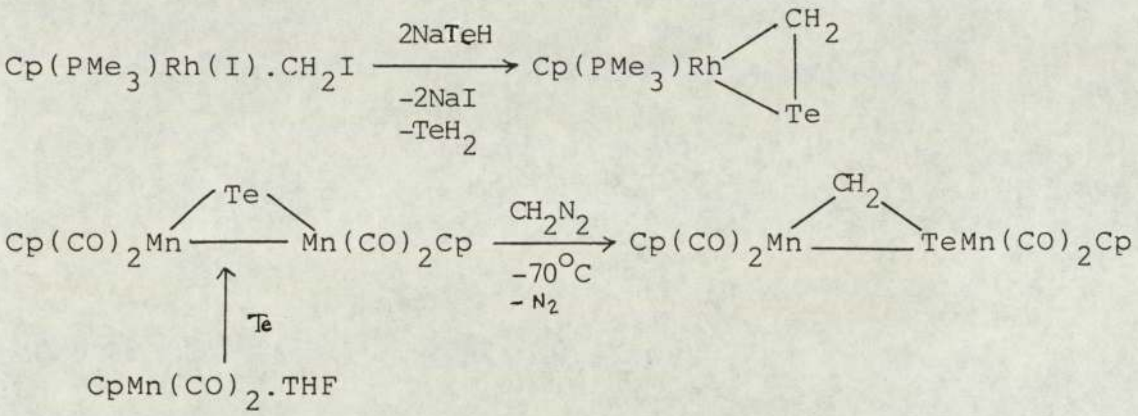




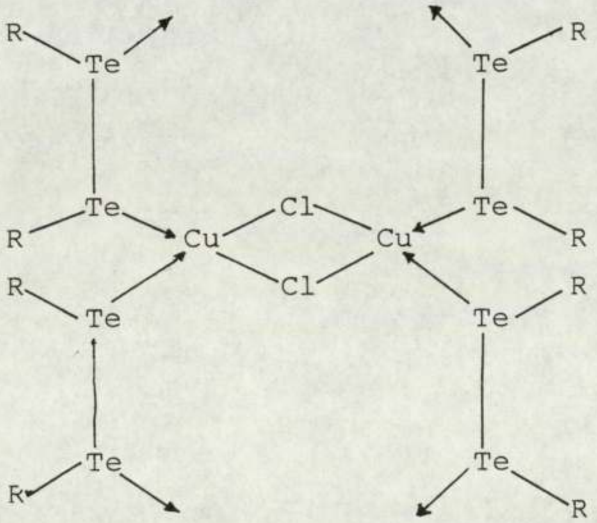
DMF (40b)

$[Pt(SCN)_4]^{2-}$ (40b)

Complexes containing terminal chelating telluroformaldehyde$^{(60)}$ and bridging telluroformaldehyde ($Cp(CO)_2Mn(\mu\text{-}\eta^2\text{-}CH_2Te)Mn(CO)_2Cp$) have been reported$^{(61)}$.



As mentioned earlier, ditellurides can form complexes in which the Te-Te bond remains intact. The reaction between equimolar amounts of Cu(I) halide and diarlyditellurides results in a complex belonging to this category$^{(46)}$.



Proposed structure for diorganoditelluride complexes with Cu(I) halides$^{(46)}$.

Coordination of both Te atoms of the ditelluride ligands in these complexes has been supported by their ^{125}Te Mössbauer spectra, by giving one quadrupole doublet. The chemical isomer shifts (δ) were similar to those of the free ditellurides, indicating that no significant change in hybridisation at Te has occurred on coordination. The quadrupole splitting values were lowered vs. the free ditellurides indicating coordination of the p-lone pair, resulting in a lowering of the p-orbital imbalance(46). Therefore, ditellurides could also be used as bidentate (catenating) ligands.

1.5 Present Work

In the present work, a study of the coordination chemistry of potentially bidentate tellurium ligands was undertaken to extend the knowledge on coordination chemistry of tellurium ligands.

This work involved:

1. the synthesis of potentially bidentate tellurium ligands,
2. the synthesis and characterisation of metal complexes of these ligands.

CHAPTER TWO

EXPERIMENTAL

2.1 Chemicals

All the known organotellurium compounds used in this study were prepared by literature methods, using tellurium tetrachloride or tellurium powder as starting materials. Tellurium powder was obtained from commercial sources.

2.2 Solvents

All the solvents were obtained from commercial sources and were purified where necessary by literature methods$^{(62,63)}$ and kept over molecular sieves.

2.3 Elemental Analysis

Analyses for C, H and Halogen were carried out by the Analytical Service Unit, University of Aston. Tellurium was analysed by atomic absorption spectroscopy. The atomic absorption spectrometer was the Perkin-Elmer model 460. Standard solutions containing 20μg Te/cm^3 were prepared by diluting B.D.H. atomic absorption spectroscopy grade solution of telluric acid. Samples for analysis were prepared by heating the sample (1-2mg) with conc. HNO_3 (10cm^3) and perchloric acid (10cm^3) to dryness and by dissolving it in warm distilled water containing conc. HCl (0.5cm^3) and diluting up to 100cm^3.

2.4 Melting Points

The melting points were determined using a Gallenkamp electrically heated melting point apparatus.

2.5 Conductivity Measurements

Molar conductivities were measured with a Mullard Conductivity bridge, using a standard conductivity cell type E7591/B with a cell constant of 1.36.

2.6 Infra-red Spectra (IR)

Spectra in the range 4000-200cm^{-1} were recorded on a Perkin-Elmer 599 B spectrophotometer. Solid state samples were examined as KBr discs or as mulls. Mulls were supported between NaCl plates. Nujol paraffin oil was used as the mulling agent. For the investigations of the range of 400-200cm^{-1}, the spectra were recorded using polyethene discs.

2.7 Mass Spectra

Mass spectra were recorded with an AEl MS9 spectrometer, generally at an ionisation potential of 70eV (1eV=1.60x10^{-17}J).

2.8 Nuclear Magnetic Resonance Spectra (NMR)

^{1}H NMR were obtained on a Perkin-Elmer R12 B instrument (60MHz) using tetramethylsilane as internal standard. Proton decoupled ^{13}C NMR were obtained on a Jeol FX 90Q spectrometer (22.5MHz). Proton decoupled and proton nondecoupled ^{125}Te NMR spectra were obtained using the same instrument at 28.3MHz.

2.9 Electronic Spectra

Electronic absorption spectra in ultra-violet and visible regions were performed with a Unicam sp8-100 spectrophotometer for chloroform solutions of samples.

2.10 Electron Spin Resonance Spectra (ESR)

ESR spectra at room temperature were obtained with a JEOL PE-1X spectrometer. Calibration was with a standard Manganese(II) sample diluted with Magnesium oxide.

2.11 ^{125}Te Mössbauer Measurements

These were obtained as previously reported using a $^{125}Sb/Cu$ source(64). Both source and absorber were at 4 K.

2.12 Molecular Weight Determinations

The use of a vapour pressure osmometer (65,66) is one of the most convenient ways to measure molecular weights. Unfortunately, inconsistent results were obtained using this method because of a fault which appeared in the instrument during the period of this study. Attempts to measure the molecular weights using Beckmann's (65) method gave disappointing results due to the large quantities of sample required and the low solubility of some of the samples in suitable solvents. However, acceptable results were obtained using Rast's method (65) although it is not an accurate way to determine molecular weights.

CHAPTER THREE

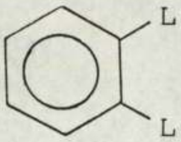
COORDINATION CHEMISTRY OF BIS-(p-ETHOXYPHENYLTELLURO)METHANE(eptm)

3.1 Introduction

Bidentate ligands considered in this thesis can be classified into three major types:-

(i) $L.CH_2.L$ - two donor groups attached to a methylene group.

(ii) $L(CH_2)_nL$ - two donor groups attached to a short, medium or long flexible alkane chain back bone.

(iii)  - two donor groups attached to a rigid back bone.

(L = group having the donor atoms).

The two donor atoms in these ligands are identical.

The coordination chemistry of a potentially bidentate ligand belonging to the first category, bis-(p-ethoxyphenyltelluro)methane, is described in this chapter. Ligands belonging to the second and third categories are discussed in the next three chapters.

As mentioned in Chapter One, very little information is available in the literature on the synthesis of bis-tellurides belonging to the first category. One method is the alkylation of lithium benzene tellurolate with diiodomethane(42).

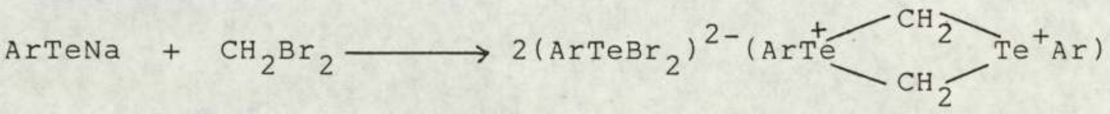
$$2C_6H_5Li \;+\; 2Te \xrightarrow{THF} 2(C_6H_5TeLi) \xrightarrow{CH_2I_2} C_6H_5TeCH_2TeC_6H_5 + LiI$$

Another method is to react diazomethane with diaryl ditellurides(41).

$$ArTeTeAr + CH_2N_2 \longrightarrow ArTeCH_2TeAr + N_2$$

$$Ar = p\text{-}C_2H_5O.C_6H_4$$
$$= p\text{-}CH_3O.C_6H_4$$

The use of ArTeNa to synthesise these type of bis-tellurides was first attempted by Davies who has explained the reaction in the following way(3):-



Later, McWhinnie and coworkers reported that the product obtained from the above reaction is a charge transfer complex of bis-(p-ethoxyphenyltelluro)methane with diiodomethane(50). In the present study, bis-(p-ethoxyphenyltelluro)methane was synthesised without the formation of a charge transfer complex, by carrying out the same reaction under modified conditions.

In the formation of transition metal complexes, bis-(p-ethoxyphenyltelluro)methane may act in some or all of the following ways:

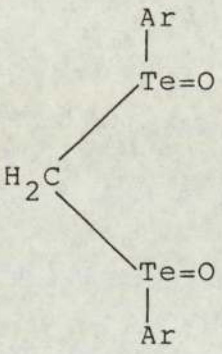
1. as a chelating ligand
2. as a monodentate ligand
3. as a bridging bidentate ligand

In forming chelate complexes, the optimum ring size for a metal having natural bond angles at 90° to one another is five(67). The chelation of bis-(p-ethoxyphenyltelluro)-methane with a transition metal ion should result in a four membered ring. But the four membered ring so formed is strained and the ligand may have a tendency to act either as a monodentate ligand or as a bridging bidentate ligand.

Although there is much interest in mono- and bi-metallic complexes of bis-(diphenylphosphino)methane, its tellurium analogue $ArTeCH_2TeAr$ has been very little studied. The aim of this chapter is to discuss the behaviour of bis-(p-ethoxyphenyltelluro)methane in the formation of complexes with transition metal ions.

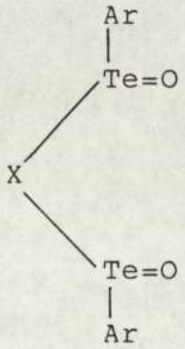
3.1.1 Insertion Of Dichlorocarbene Into Te-Te Bond In Diorganoditellurides

During the complex formation reactions bis-(p-ethoxyphenyltelluro)methane can oxidize to a telluroxide and this telluroxide can form complexes with transition metal ions.



(This is discussed in more detail later in this chapter).

This oxidation prompted us to synthesise some analogous ligands having the following molecular formula:



X = O, CCl_2, CO

3.I.I - (a)

The attempts carried out by Petragnani and Schill to insert dichlorocarbene into Te-Te bond have resulted in products of indefinite composition(41). However, Gross and Armbrecht successfully inserted dichlorocarbene into $Me_3SnSnMe_3$(68).

$$Me_3SnSnMe_3 + C_6H_5HgCCl_3 \longrightarrow Me_3SnCCl_2SnMe_3 + C_6H_5HgCl$$

The formation of a compound having the above molecular formula, 3.1.1-(a), where X=O, has been observed by Singh, during the oxidation of diaryl ditellurides in the presence of dichlorocarbene(69). Therefore, some further investigations of this reaction were also carried out during this study.

3.2 Experimental

In some instances tellurium tetrachloride was prepared according to the method mentioned by Elgy(70), (p-ethoxyphenyl) tellurium trichloride and bis-(p-ethoxyphenyl)ditelluride were prepared according to the literature method(28).

Preparation of Tellurium Tetrachloride

8g of finely powdered Te was heated with dried $CHCl_3$ in a dinitrogen atmosphere. When the refluxing commenced, Cl_2

gas was passed into the system for 10-11h. while refluxing continued. The reaction flask was covered with an aluminium foil to prevent the ingress of light. A schematic diagram for the apparatus is given in Figure 3.1.

Preparation of (p-Ethoxyphenyl) Tellurium Trichloride(28)

When all the tellurium powder had disappeared in the above reaction, the reaction was stopped and a calculated amount of phenatole was added to the reaction flask. This was refluxed for 2½h. in a dinitrogen atmosphere. After cooling the flask, the precipitate was filtered and washed with $CHCl_3$ and dried in vacuo.

Preparation of Bis-(p-Ethoxyphenyl)ditelluride(28)

This was prepared according to literature method(28).

3.2.1 Preparation Of Bis-(p-Ethoxyphenyltelluro)methane-diiodomethane Charge Transfer Complex

The literature method(49) was slightly modified during this study.

Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene (10cm^3) and ethanol(20cm^3) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in

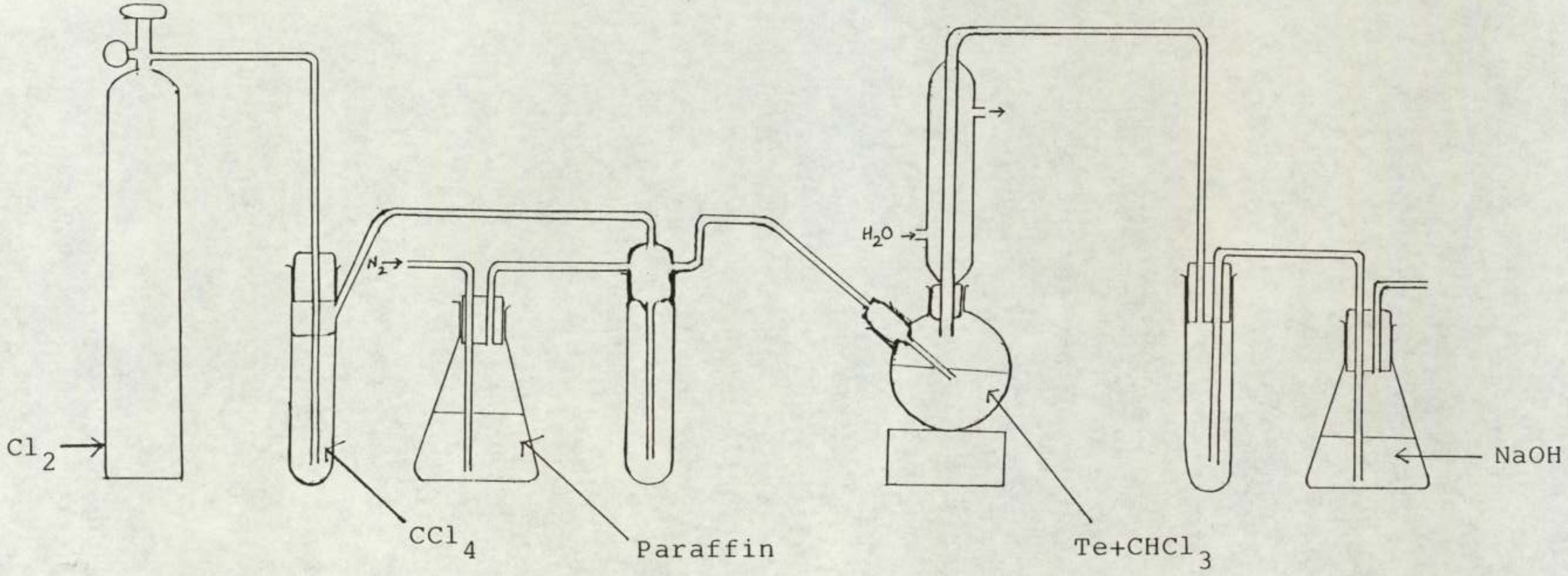


Figure 3.1

1mol dm^{-3} sodium hydroxide ($12cm^3$) was added dropwise to this solution. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, diiodomethane (12.3g, 46mmol) was added and stirred for 15 min. Then the reaction mixture was added to distilled water and stirred well. The organic layer was separated, washed with distilled water and added to diethyl ether to induce precipitation. The precipitate was separated and dried in vacuo. Recrystallisation from acetonitrile gave a yellow compound in 65% yield. M.p. 116-117°C (literature 118°C).

Found	C27.3	H2.90%
$C_{18}H_{22}O_2Te_2I_2$ requires	C27.7	H2.80%

3.2.2 New Synthesis Of <u>Bis</u>-(p-Ethoxyphenyltelluro)methane

<u>Bis</u>-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene ($10cm^3$) and ethanol($20cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1mol dm^{-3} sodium hydroxide($12cm^3$) solution was added dropwise. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage diiodomethane (2.68g, 10mmol) was added and the mixture was stirred for 1½-1¾h. at room temperature. During the stirring a bright yellow colour

appeared. Then the solution was poured into distilled water and stirred well. The organic layer was separated, washed with water and acetonitrile added. The mixture was stirred for 1-2h. while cooling in an ice bath. During the stirring a yellow precipitate was formed and the colour of the precipitate slowly changed to pale green. The precipitate was separated and dried in vacuo. Recrystallisation from acetonitrile or petroleum ether (60-80°C) gave ultimately a green precipitate via a yellow material as observed above.

Yield 52% m.p. 42-43°C.

Found	C39.6	H4.20%
$C_{17}H_{20}O_2Te_2$ requires	C39.9	H3.90%

3.2.3 Effect Of Dioxygen On *Bis*-(p-Ethoxyphenyltelluro)-methane

A stream of dioxygen was bubbled through a solution of *bis*-(p-ethoxyphenyltelluro)methane in $CHCl_3$ for 16h. Evaporation of the solvent resulted in a cream coloured precipitate.

Found	C36.8	H3.80%
$C_{17}H_{20}O_4Te_2$ requires	C37.6	H3.70%

3.2.4 Synthesis Of Transition Metal Complexes Of Bis-(p-Ethoxyphenyltelluro)methane In An Open Atmosphere

(a) A solution of $HgCl_2$ (0.81g, 3mmol) in acetone was added dropwise to a solution of the charge transfer complex of bis-(p-ethoxyphenyltelluro)methane (2.34g, 3mmol) in $CHCl_3$ and was stirred for 15-20min. The pale yellow precipitate was filtered and washed with $CHCl_3$ and acetone and dried in vacuo over P_4O_{10}.

Yield 64% m.p. 113-114°C.

Found	C24.5	H2.40	Cl 8.7	Te31.4%
$C_{17}H_{20}O_4Te_2HgCl_2$ requires	C25.0	H2.50	Cl 8.7	Te31.3%

(b) A solution of $HgBr_2$(1.08g, 3mmol) in ethanol was added dropwise to a solution of the charge transfer complex of bis-(p-ethoxyphenyltelluro)methane (2.34g, 3mmol) in $CHCl_3$ and was stirred for 15-20min. The yellow precipitate was filtered, washed with $CHCl_3$ and ethanol and dried in vacuo over P_4O_{10}.

Yield 58% m.p. 106-107°C.

Found	C21.8	H2.30	Te28.8%
$C_{17}H_{20}O_4Te_2HgBr_2$ requires	C22.6	H2.20	Te28.2%

(c) A solution of the charge transfer complex of bis-(p-ethoxyphenyltelluro)methane (2.34g, 3mmol) in $CHCl_3$ was added to a solution of $CuCl_2$(0.51g,3mmol) in acetone. The solution was warmed to 30-40°C and was stirred for 1h. The yellowish-brown precipitate was filtered, washed with $CHCl_3$ and acetone and dried in vacuo over P_4O_{10}.

Yield 59% m.p. 115-116°C.

Found	C24.5	H2.60	Te31.3	Cu 14.7	Cl 16.2%
$C_{17}H_{20}O_4Te_2.2CuCl_2$ requires	C25.1	H2.50	Te31.4	Cu 15.6	Cl 17.5%

3.2.5 Synthesis Of Transition Metal Complexes Of Bis-(p-Ethoxyphenyltelluro)methane In A Dinitrogen Atmosphere

All the following preparations were carried out under the passage of oxygen free dinitrogen.

(a) A solution of sodiumtetrachloropalladate(II) trihydrate (0.174g, 0.5mmol) in distilled water was added dropwise to a solution of bis-(p-ethoxyphenyltelluro)methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h. The reddish-brown precipitate was filtered, washed with distilled water and acetone and dried in vacuo over P_4O_{10}.

Yield 48% m.p. 156-158°C (dec).

Found	C31.3	H3.00%
$C_{34}H_{40}O_4Te_4Pd_2Cl_2$ requires	C31.2	H3.05%

(b) A solution of sodiumtetrachloropalladate(II) trihydrate (0.174g, 0.5mmol) in distilled water was stirred for 5-6h. with a five-fold excess of KBr. This solution was added dropwise to a solution of <u>bis</u>-(p-ethoxyphenyltelluro)-methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h. The dark brown precipitate was filtered, washed with distilled water and acetone and dried in vacuo over P_4O_{10}.

Yield 40% m.p. 164-165°C (dec).

Found	C28.8	H2.90%
$C_{34}H_{40}O_4Te_4Pd_2Br_2$ requires	C29.3	H2.90%

(c) A solution of sodiumtetrachloropalladate(II) trihydrate (0.174g, 0.5mmol) in distilled water was added dropwise to a solution of <u>bis</u>-(p-ethoxyphenyltelluro)methane (0.512g, 1mmol) in acetone in a dinitrogen atmosphere, and was stirred for 12h. The dark chocolate brown coloured precipitate was filtered, washed with distilled water and acetone and dried in vacuo over P_4O_{10}.

Yield 30% m.p. 114-115°C

Found	C34.6	H3.30%
$C_{34}H_{40}O_4Te_4PdCl_2$ requires	C34.0	H3.30%

(d) A solution of *bis*-(benzonitrile)palladium(II) chloride(71) (0.192g, 0.5mmol) in acetone was added dropwise to a solution of *bis*-(p-ethoxyphenyltelluro)methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h . The brown precipitate so formed was filtered, washed with acetone and dried in vacuo over P_4O_{10}.

Yield 46% m.p. 156-158°C (dec).

Found	C31.3	H3.00%
$C_{34}H_{40}O_4Te_4Pd_2Cl_2$ requires	C31.2	H3.05%

(e) A solution of potassiumtetrachloroplatinate(II) (0.208g, 0.5mmol) in distilled water was added dropwise to a solution of *bis*-(p-ethoxyphenyltelluro)methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h . The yellow precipitate so formed was filtered and washed with distilled water and acetone and dried in vacuo over P_4O_{10}. The colour of the precipitate changed to brown when it became dry.

Yield 40% m.p. 164-165°C (dec).

Found C28.4 H2.90%

$C_{34}H_{40}O_4Te_4Pt_2Cl_2$ requires C27.5 H2.70%

(f) A solution of potassiumtetrachloroplatinate(II) (0.208g, 0.5mmol) in distilled water was stirred with five-fold excess of KBr for 5-6h. This was added dropwise to a solution of bis-(p-ethoxyphenyltelluro)methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h. The yellow precipitate so formed was filtered, washed with distilled water and acetone and dried in vacuo over P_4O_{10}.

Yield 40% m.p. 158-159°C (dec).

Found C26.3 H2.50%

$C_{34}H_{40}O_4Te_4Pt_2Br_2$ requires C25.9 H2.50%

(g) A solution of $HgCl_2$ (0.136g, 0.5mmol) was added dropwise to a solution of bis-(p-ethoxyphenyltelluro)methane (0.256g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h.The yellow precipitate was filtered, washed with acetone and dried in vacuo over P_4O_{10}.

Yield 49% m.p. 152-154°C.

Found	C26.0	H2.00%
$C_{17}H_{20}O_2Te_2HgCl_2$ requires	C26.1	H2.60%

3.2.6 Attempted Reactions Of Charge Transfer Complex Of Bis-(p-Ethoxyphenyltelluro)methane With Molybdenum Hexacarbonyl

All the reactions were carried out in a dinitrogen atmosphere.

(a) A solution of the ligand (0.78g, 1mmol) in $CHCl_3$ was stirred with a solution of $Mo(CO)_6$ (0.26g, 1mmol) in hexane at room temperature for 2h . No reaction occurred.

(b) The above reaction mixture was refluxed for 3h . A yellowish precipitate appeared. The infra-red spectrum of this compound does not indicate any bands in the carbonyl region. Spot-test for molybdenum(72) indicates the absence of molybdenum.

(c) A solution of the ligand (0.78g, 1mmol) in $CHCl_3$ was refluxed with a solution of $Mo(CO)_6$ (0.26g, 1mmol) in xylene for ½h . The ash colour precipitate obtained did not show any bands in the carbonyl region of the infra-red spectrum. However, the spot-test for molybdenum was positive.

(d) A solution of the ligand (0.78g, 1mmol) in $CHCl_3$ was stirred with a solution of $Mo(CO)_6$ (0.26g, 1mmol) in hexane under U.V. irradiation for 4h . A brownish-yellow precipitate appeared. The infra-red spectrum of this compound does not contain any carbonyl bands.

(e) A solution of $Mo(CO)_6$ (0.26g, 1mmol) in tetrahydrofuran (THF) was stirred under U.V. irradiation. When a bright yellow solution appeared, a solution of the ligand (0.78g, 1mmol) in tetrahydrofuran was added and stirred for 2h . at 0°C. No reaction was observed.

Because of the disappointing results with the bidentate ligand, the reactivity of a monodentate tellurium ligand with $Mo(CO)_6$ was studied.

(f) 1,3-dihydro-2-telluraindene was prepared according to literature method(34).

A solution of the monodentate ligand 1,3-dihydro-2-telluraindene (0.06g, 0.25mmol) and $Mo(CO)_6$ (0.07g, 0.25mmol) in hexane was left under U.V. irradiation for 5h . The infra-red spectrum of the black precipitate obtained shows no bands in the carbonyl region.

3.2.7 Synthesis Of $(RTeO)_2CCl_2$ And $(RTe)_2CO$

Tributyl benzyl ammonium tetrafluoroborate was prepared using the literature method$^{(48)}$.

(a) Tributyl benzyl ammonium tetrafluoroborate (6g) and 50% NaOH ($120cm^3$) was added to a solution of bis-(p-ethoxyphenyl)ditelluride (6g, 12mmol) in benzene. The temperature was adjusted to 55-60°C and ethanol free distilled $CHCl_3$ was added dropwise. The vigorous stirring of the solution caused a change in the colour of the solution to colourless within 10-15min. Stirring was continued for 30min. to complete the reaction.

The aqueous and organic layers were separated and the organic layer was washed with distilled water and dried over anhydrous Na_2SO_4. A foul smelling product was obtained after evaporating the solvents in the organic layer. Yield 10%.

The aqueous phase of the reaction mixture on acidification with conc. HCl resulted in a white precipitate (at pH≈2) and was recrystallised from methanol. Yield 80%. M.p. 222-224°C.

Found	C33.2	H3.10	Cl 12.6%
$C_{17}H_{18}O_4Te_2Cl_2$ requires	C33.3	H2.90	Cl 11.6%

(b) The reaction of the foul smelling compound with phenyl hydrazine in ethanol yielded bis-(p-ethoxyphenyl)ditelluride. This was recrystallised from petroleum ether (B.p. 80-100°C).

Found	C38.6	H3.50%
$C_{16}H_{18}O_2Te_2$ requires	C38.6	H3.60%

(c) The white compound obtained from the aqueous phase was refluxed with a solution of thiourea in NaOH for $\frac{1}{2}$h . The precipitate of bis-(p-ethoxyphenyl)ditelluride was recrystallised from petroleum ether (B.p. 80-100°C).

Found	C38.6	H3.50%
$C_{16}H_{18}O_2Te_2$ requires	C38.6	H3.60%

(d) The white compound obtained from the aqueous phase was reacted with phenylhydrazine in ethanol in an ice bath. The precipitated bis-(p-ethoxyphenyl)ditelluride was recrystallised from petroleum ether (B.p. 80-100°C).

Found	C38.8	H3.60%
$C_{16}H_{18}O_2Te_2$ requires	C38.6	H3.60%

3.3 Results

3.3.1 Solubility

The charge transfer complex of bis-(p-ethoxyphenyltelluro)-methane has a poor solubility in common organic solvents. It is soluble in chloroform, dichloromethane, dimethylformamide (DMF) and dimethylsulfoxide (DMSO). Bis-(p-ethoxyphenyltelluro)methane is soluble in common organic solvents and is insoluble in acetonitrile, methanol, ethanol and petroleum ether.

The oxidised bis-(p-ethoxyphenyltelluro)methane is soluble in halocarbon solvents. Mercuric complexes of bis-(p-ethoxyphenyltelluro)methane which were prepared in open atmosphere are soluble in DMF and warm halocarbon solvents and slightly soluble in benzene. They are insoluble in other organic solvents. The Cu(II) complex prepared under similar conditions is soluble in DMF and is insoluble in other organic solvents.

The complexes prepared by reacting 1:1 molar ratio in a dinitrogen atmosphere are insoluble in common organic solvents. The Pd(II) complex prepared in 2:1 molar ratio is soluble in DMF and slightly soluble in halocarbon solvents and in benzene. It is insoluble in methanol, ethanol and petroleum ether.

$(RTeO)_2CCl_2$ is insoluble in common organic solvents.

3.3.2 Elemental Analysis

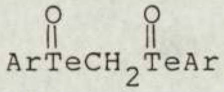
Compound	Found%		Required%	
	C	H	C	H
$ArTeCH_2TeAr$	39.6	4.20	39.9	3.90
$ArTeCH_2TeAr.CH_2I_2$	27.3	2.90	27.7	2.80
 $Ar\overset{\overset{O}{\|}}{Te}CH_2\overset{\overset{O}{\|}}{Te}Ar$	36.8	3.80	37.6	3.70

Table 3.1 The elemental analyses of *bis*-(p-ethoxyphenyltelluro)methane in different states

Complex	Found					Required				
	C	H	Te	Cu	Cl	C	H	Te	Cu	Cl
$(ArTe(O)CH_2Te(O)Ar)HgCl_2$	24.5	2.40	31.4		8.7	25.0	2.50	31.3		8.7
$(ArTe(O)CH_2Te(O)Ar)HgBr_2$	21.8	2.30	28.8			22.6	2.20	28.2		
$(ArTe(O)CH_2Te(O)Ar)2CuCl_2$	24.5	2.60	31.3	14.7	16.2	25.1	2.50	31.4	15.6	17.5

<u>Table 3.2</u> The elemental analyses of complexes of <u>bis</u>-(p-ethoxyphenyltelluro)methane which were prepared in open atmosphere

Complex	Found%		Required%	
	C	H	C	H
$(ArTeCH_2TeAr)_2Pd_2Cl_2$ (a)	31.3	3.00	31.2	3.05
$(ArTeCH_2TeAr)_2Pd_2Br_2$	28.8	2.90	29.3	2.90
$(ArTeCH_2TeAr)_2PdCl_2$	34.6	3.30	34.0	3.30
$(ArTeCH_2TeAr)_2Pd_2Cl_2$ (b)	31.3	3.00	31.2	3.10
$(ArTeCH_2TeAr)_2Pt_2Cl_2$	28.4	2.90	27.5	2.70
$(ArTeCH_2TeAr)_2Pt_2Br_2$	26.3	2.50	25.9	2.50
$ArTeCH_2TeAr.HgCl_2$	26.0	2.00	26.1	2.60

(a) - complex precursor - Na_2PdCl_4 (b) - complex precursor - $PdCl_2(PhCN)_2$

Table 3.3 The elemental analyses of complexes of bis-(p-ethoxyphenyltelluro)methane which were prepared in a dinitrogen atmosphere

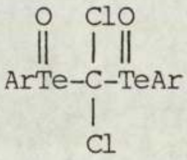
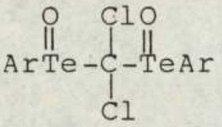
Compound	Found%			Required%		
	C	H	Cl	C	H	Cl
 $\mathrm{ArTe\overset{\overset{O}{\|}}{}-\underset{\underset{Cl}{\mid}}{\overset{\overset{Cl}{\mid}}{C}}-\overset{\overset{O}{\|}}{}TeAr}$	33.2	3.10	12.6	33.3	2.90	11.6

Table 3.4 The elemental analysis of  $\mathrm{ArTe\overset{\overset{O}{\|}}{}-\underset{\underset{Cl}{\mid}}{\overset{\overset{Cl}{\mid}}{C}}-\overset{\overset{O}{\|}}{}TeAr}$.

Compound	Chemical Shift$^{(a)}$			
	Aromatic Region	Aliphatic Region		
		$-CH_3$	$Te-CH_2$	$-OCH_2$
$\mathrm{ArTeCH_2TeAr}$	6.8(d) 7.7(d) (J(AB)=8.63Hz)	1.4(t)	3.8(s)	4.0(q)

(a) chemical shift measured in ppm relative to Me_4Si internal standard.

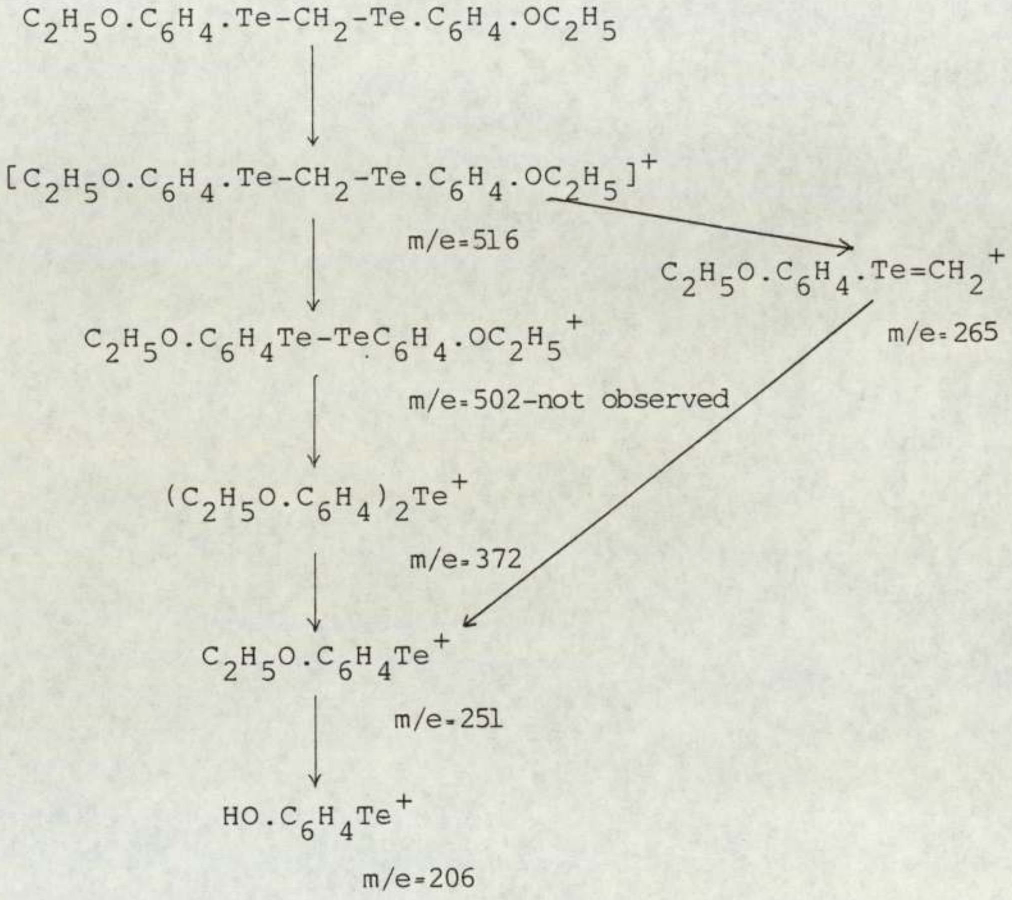
(d) doublet, (t) triplet, (s) singlet, (q) quadruplet.

Table 3.5 ^1H N.M.R. data for $\mathrm{ArTeCH_2TeAr}$

Compound	Chemical Shift(a)						
	Aromatic Region				Aliphatic Region		
	IPSO	ORTHO	META	PARA	Te-CH_2	$-OCH_2$	$-CH_3$
$ArTeCH_2TeAr$	96.3	141.0	115.9	159.6	?	63.6	14.8

(a) Chemical shift measured in ppm relative to Me_4Si internal standard.

Table 3.6 ^{13}C N.M.R. data for $ArTeCH_2TeAr$



Quoted m/e values are referenced to ^{130}Te , ^{1}H and ^{16}O.

Scheme 3.1 Mass fragmentation pattern of $ArTeCH_2TeAr$.

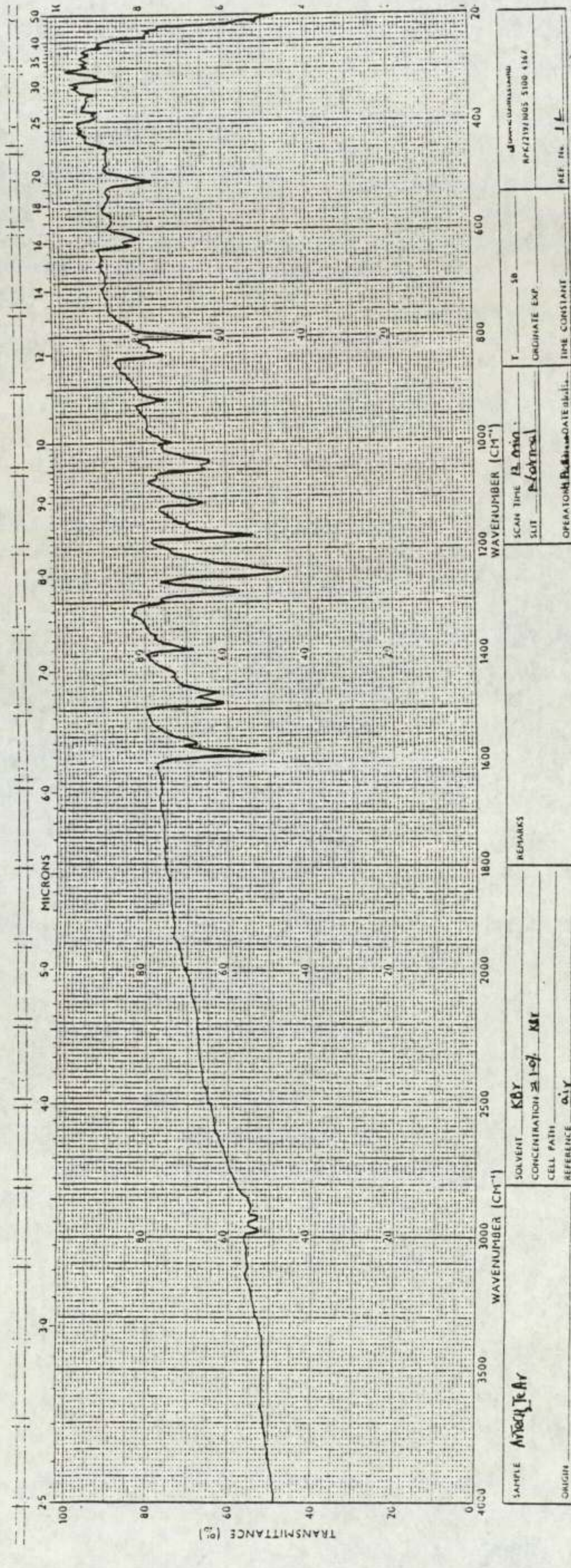


Figure 3.2 I.R. spectrum of $ArTeCH_2TeAr$

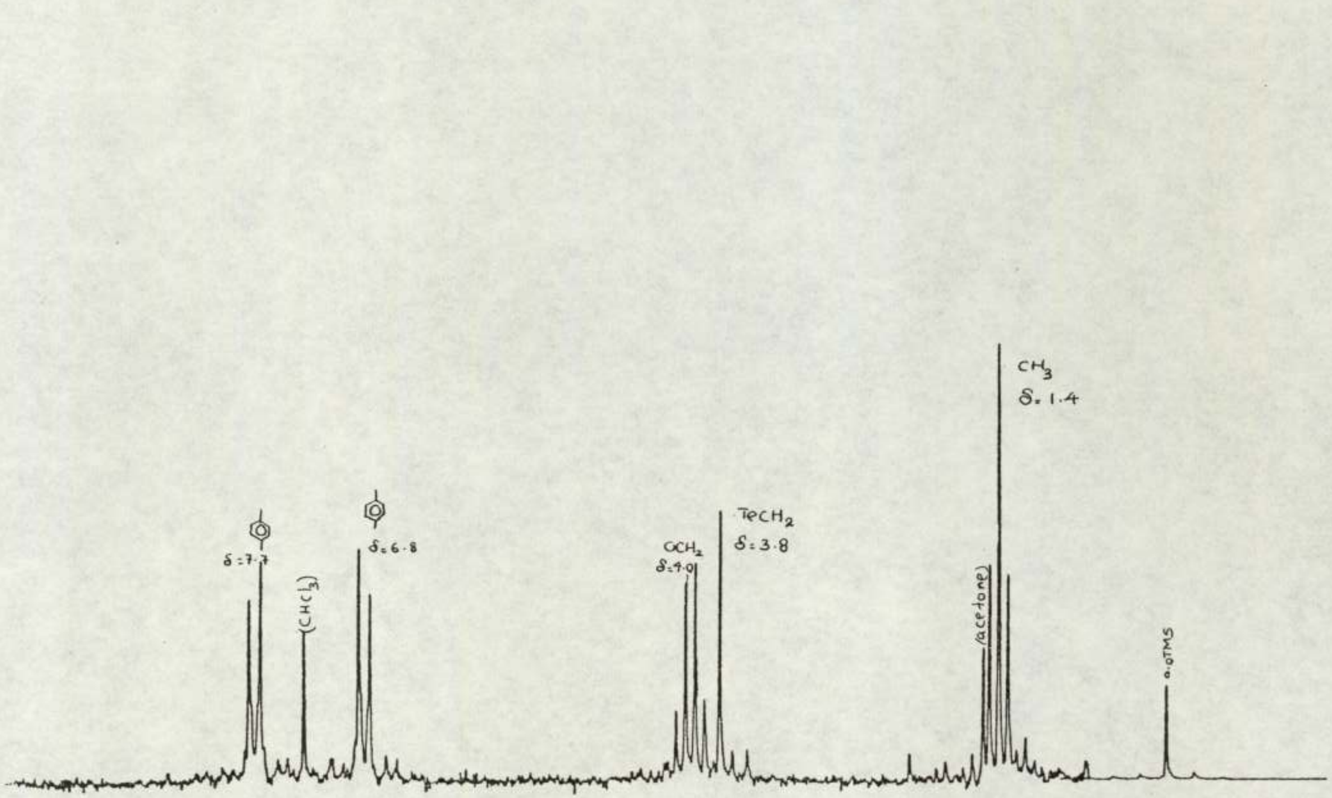


Figure 3.3 ^{1}H N.M.R. spectrum of $ArTeCH_2TeAr$

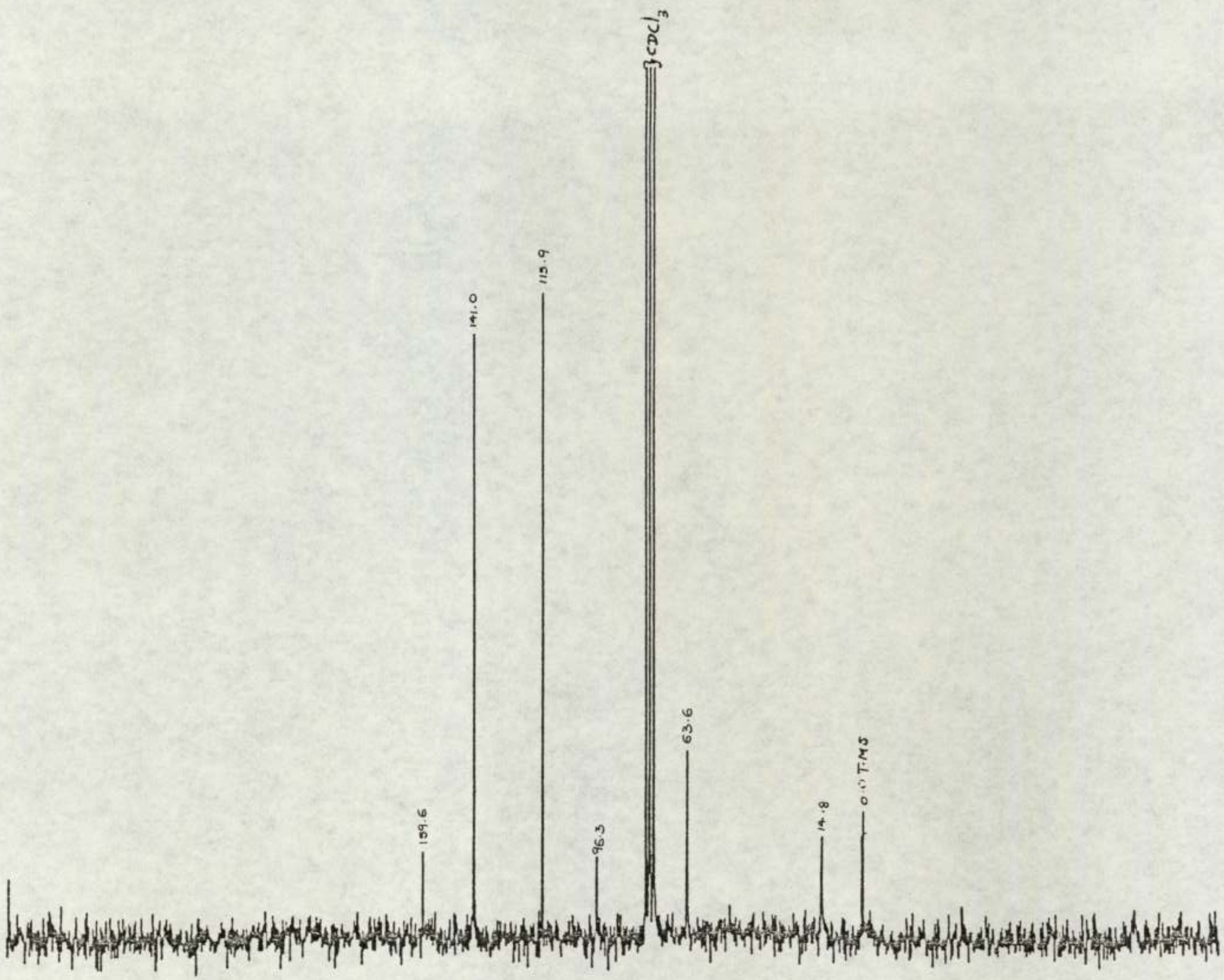
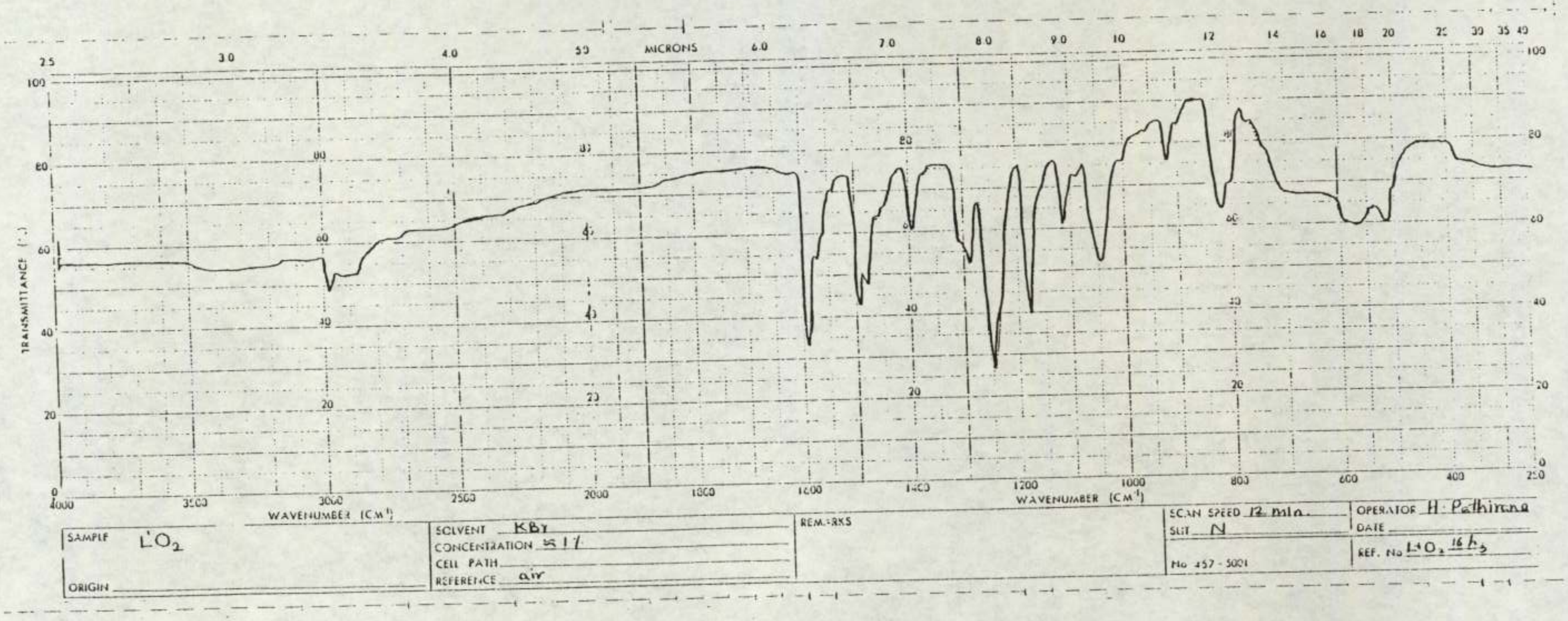


Figure 3.4 $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTeCH_2TeAr$



SAMPLE L'O_2
ORIGIN
SOLVENT KBr
CONCENTRATION ≈ 1%
CELL PATH
REFERENCE air
REMARKS
SCAN SPEED 12 min.
SLIT N
No 457-5001
OPERATOR H. Pathirana
DATE
REF. No L'O_2 16 hr

Figure 3.5 I.R. spectrum of $ArTe(O)CH_2Te(O)Ar$

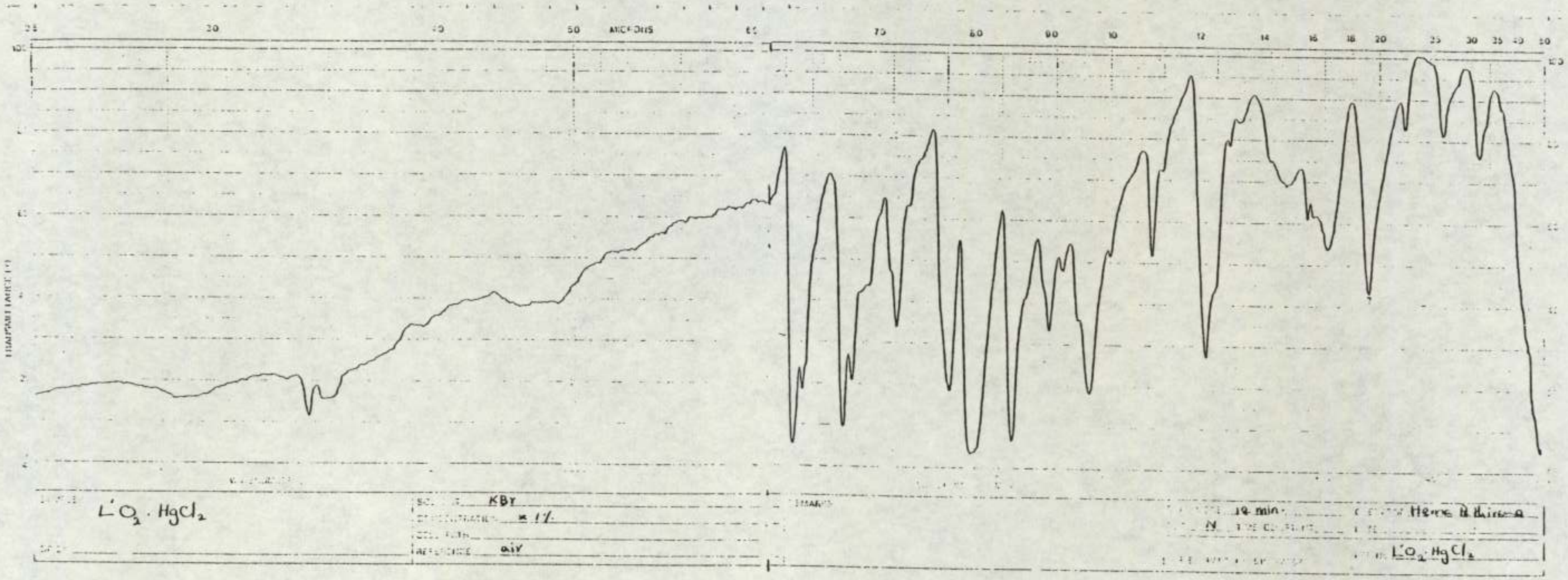
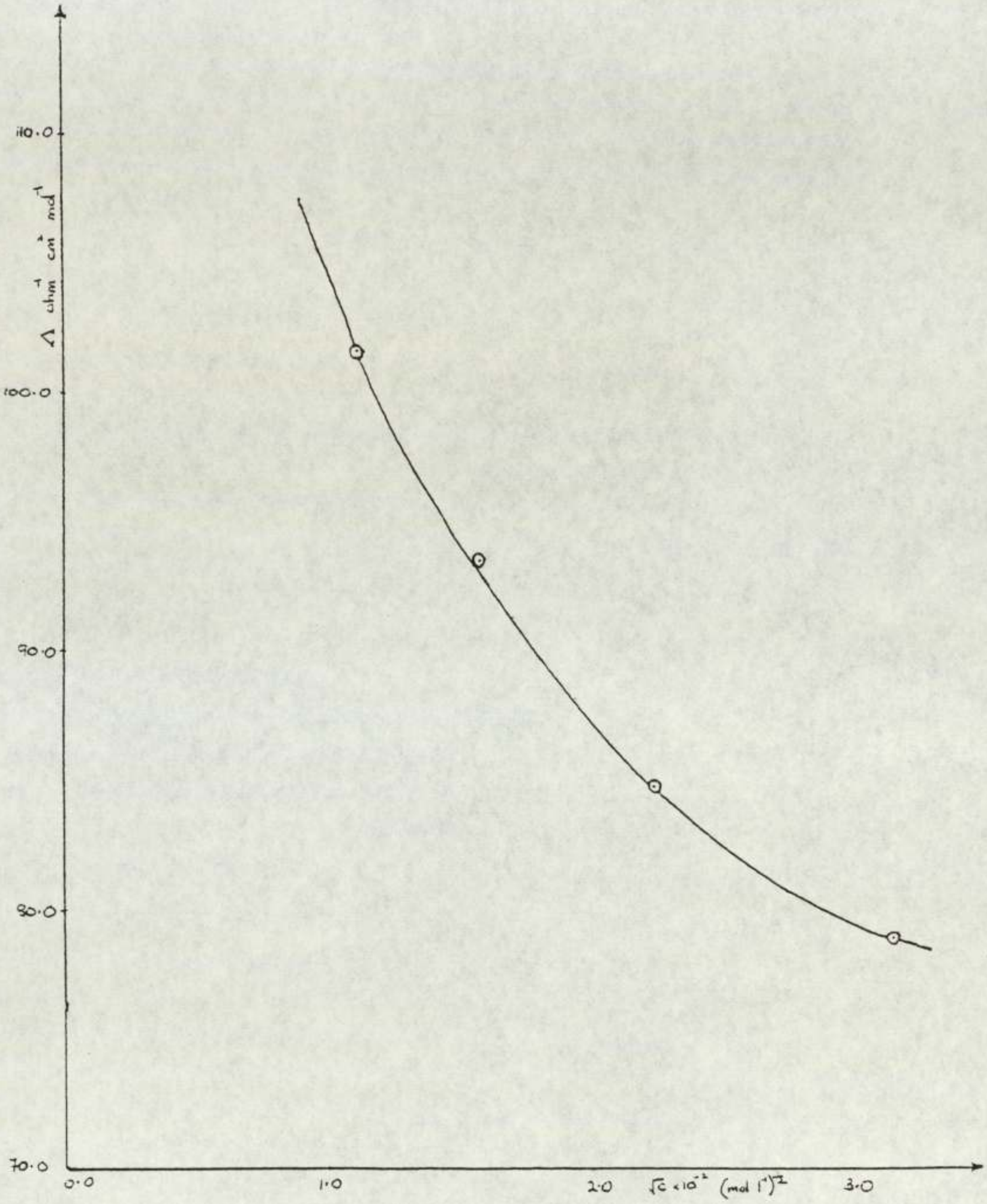


Figure 3.6 I.R. spectrum of $(ArTe(O)CH_2Te(O)Ar)HgCl_2$



<u>Figure 3.7(a)</u> Conductivity of ArTe(O)CH_2Te(O)Ar.$2CuCl_2$ in DMF

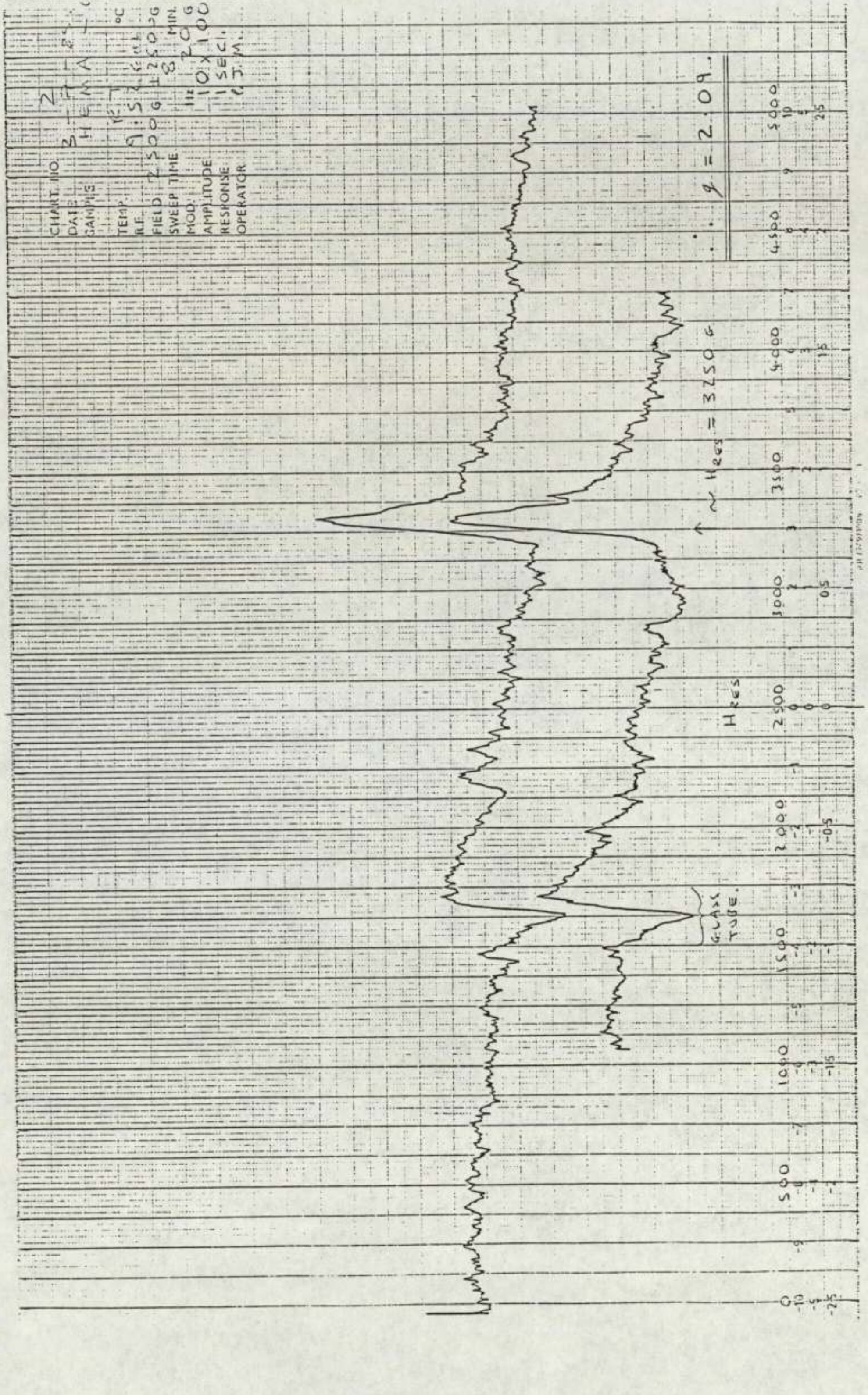


Figure 3.7(b) E.S.R. spectrum of ArTe(O)CH$_2$Te(O)Ar).2CuCl$_2$

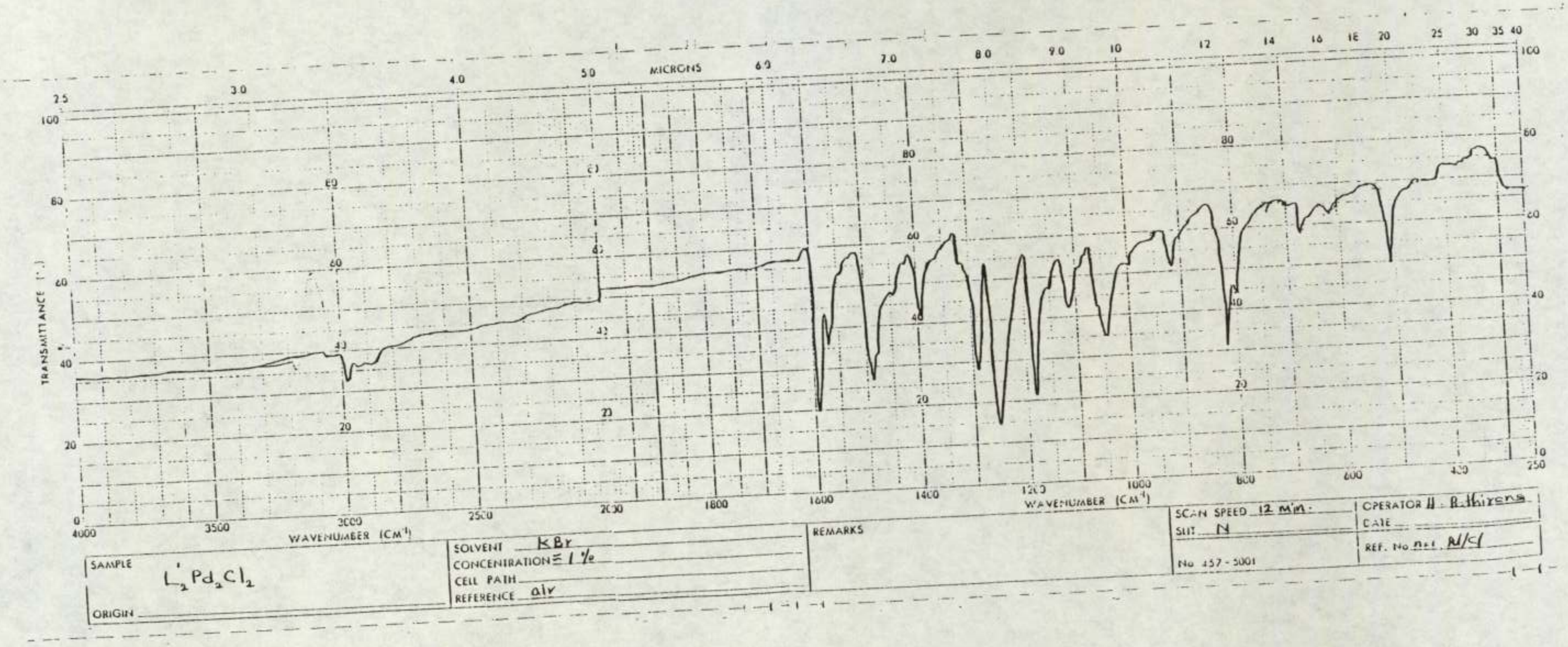


Figure 3.8 I.R. spectrum of $(ArTeCH_2TeAr)_2Pd_2Cl_2$

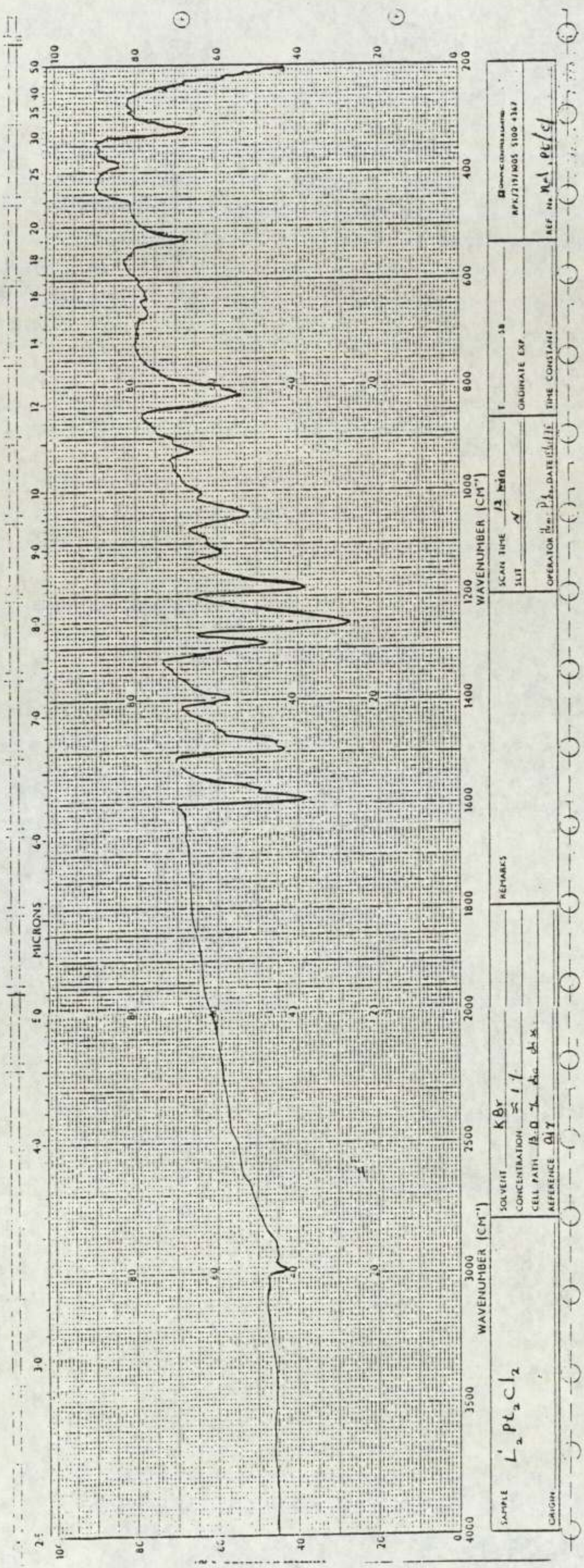


Figure 3.9 I.R. spectrum of $(ArTeCH_2TeAr)_2Pt_2Cl_2$

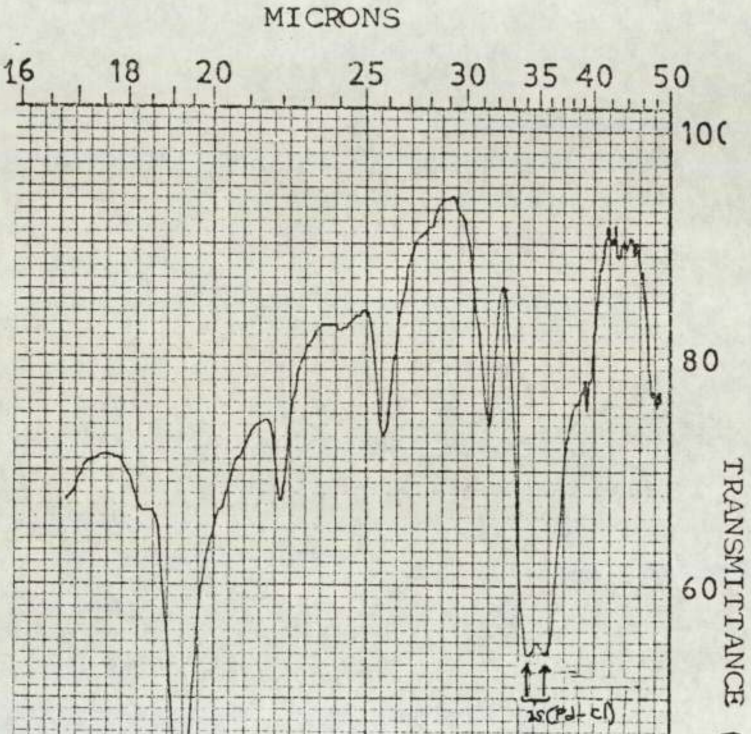


Figure 3.10 Far-infra-red spectrum of $(ArTeCH_2TeAr)_2Pd_2Cl_2$

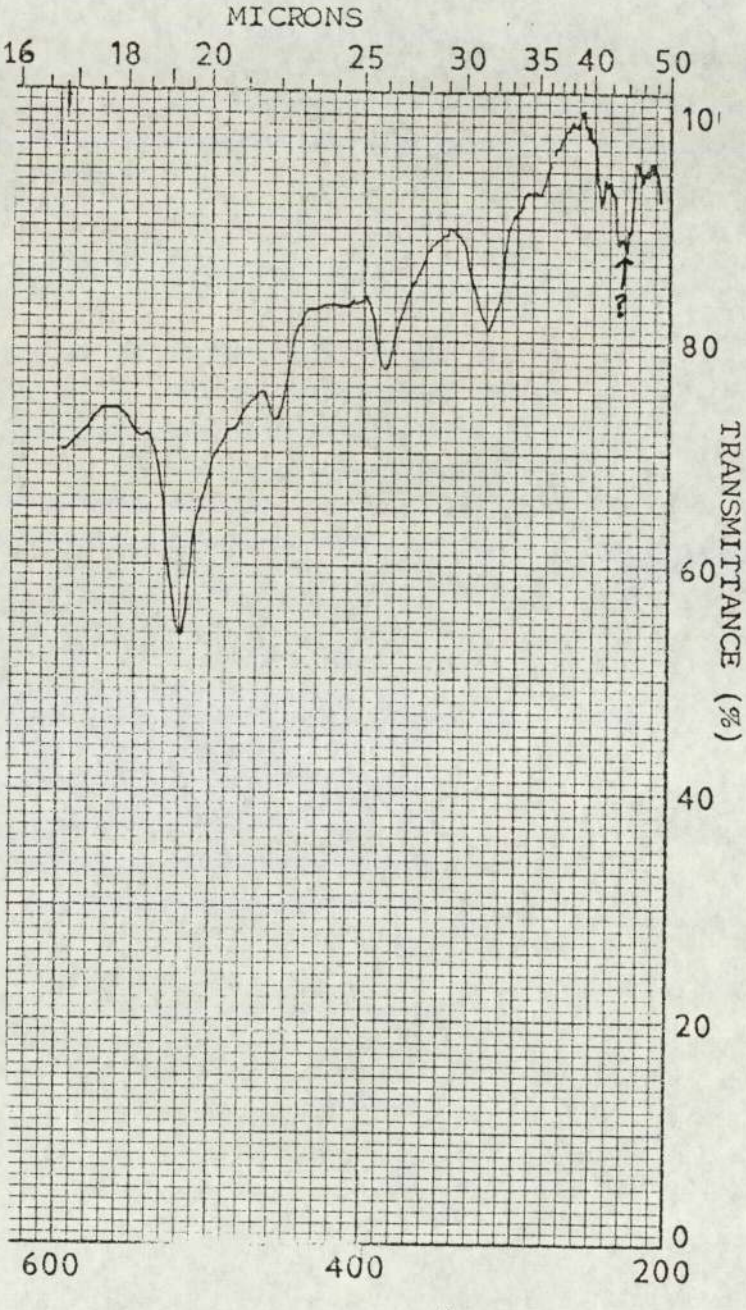


Figure 3.11 Far-infra-red spectrum of $(ArTeCH_2TeAr)_2Pd_2Br_2$

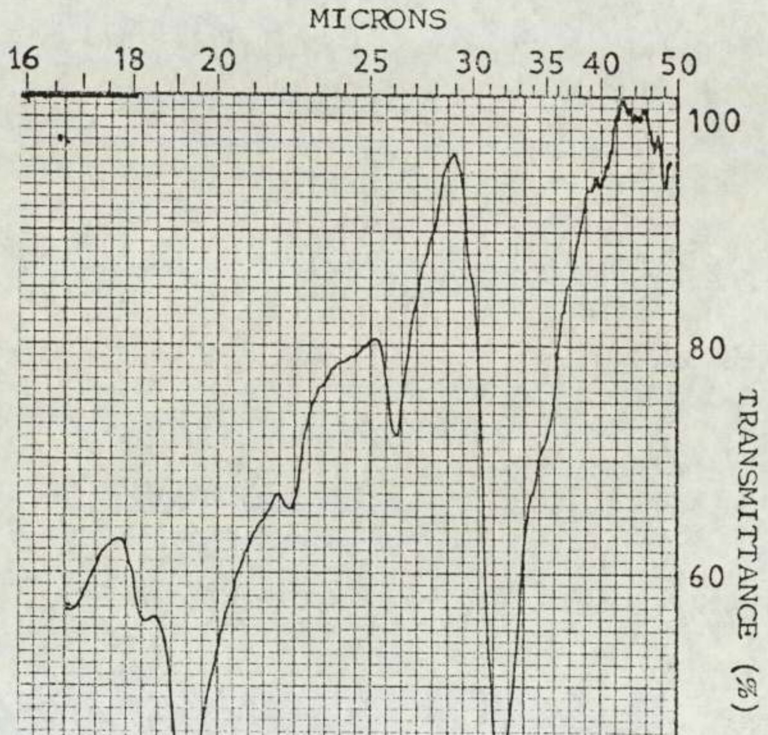


Figure 3.12 Far-infra-red spectrum of $(ArTeCH_2TeAr)_2Pt_2Cl_2$

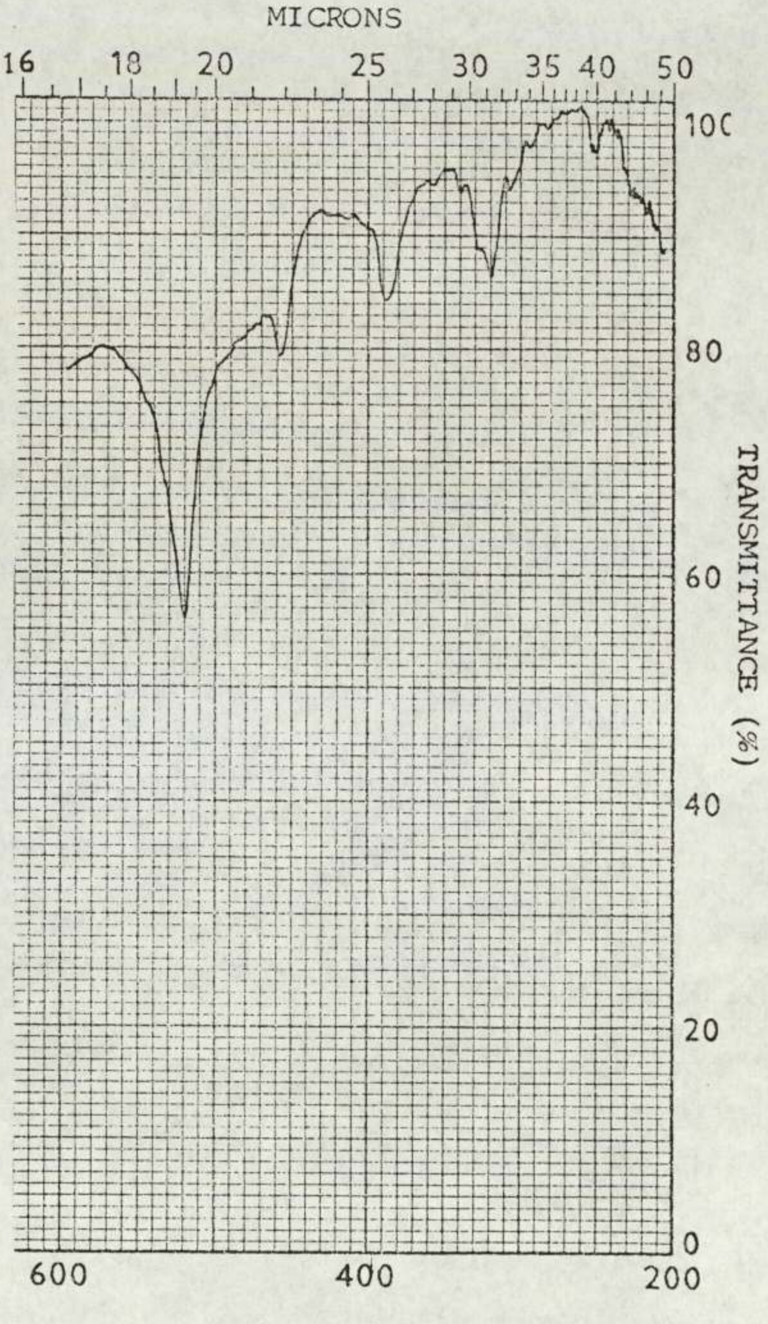


Figure 3.13 Far-infra-red spectrum of $(ArTeCH_2TeAr)_2Pt_2Br_2$

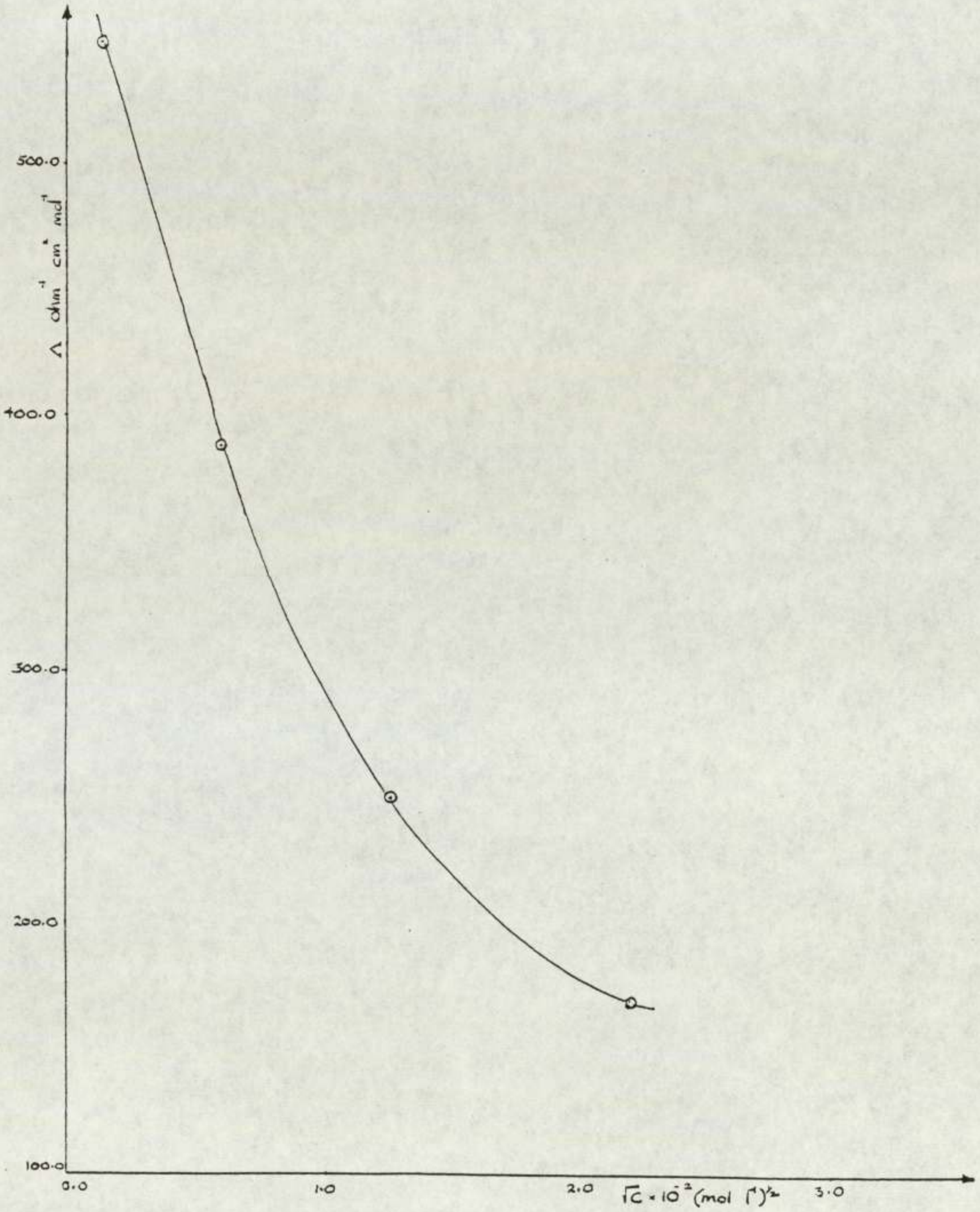


Figure 3.14 Conductivity of $PdCl_2(eptm)_2$ in DMF

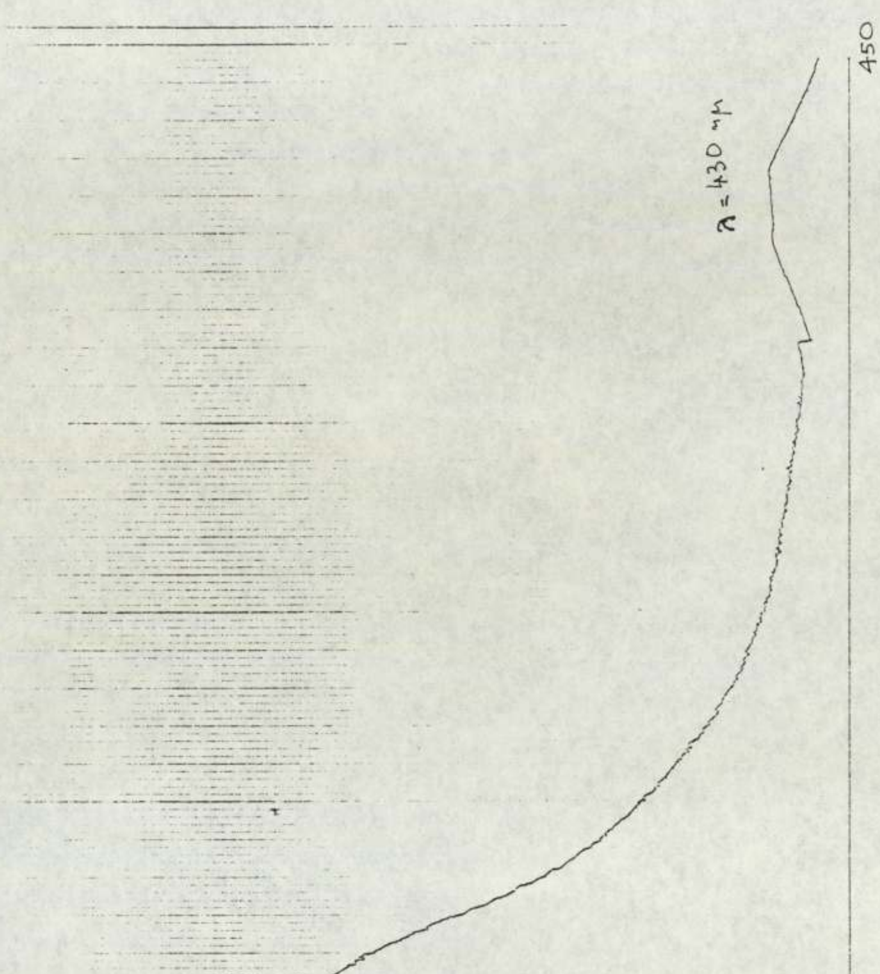


Figure 3.15 U.V. spectrum of $(ArTeCH_2TeAr)_2PdCl_2$

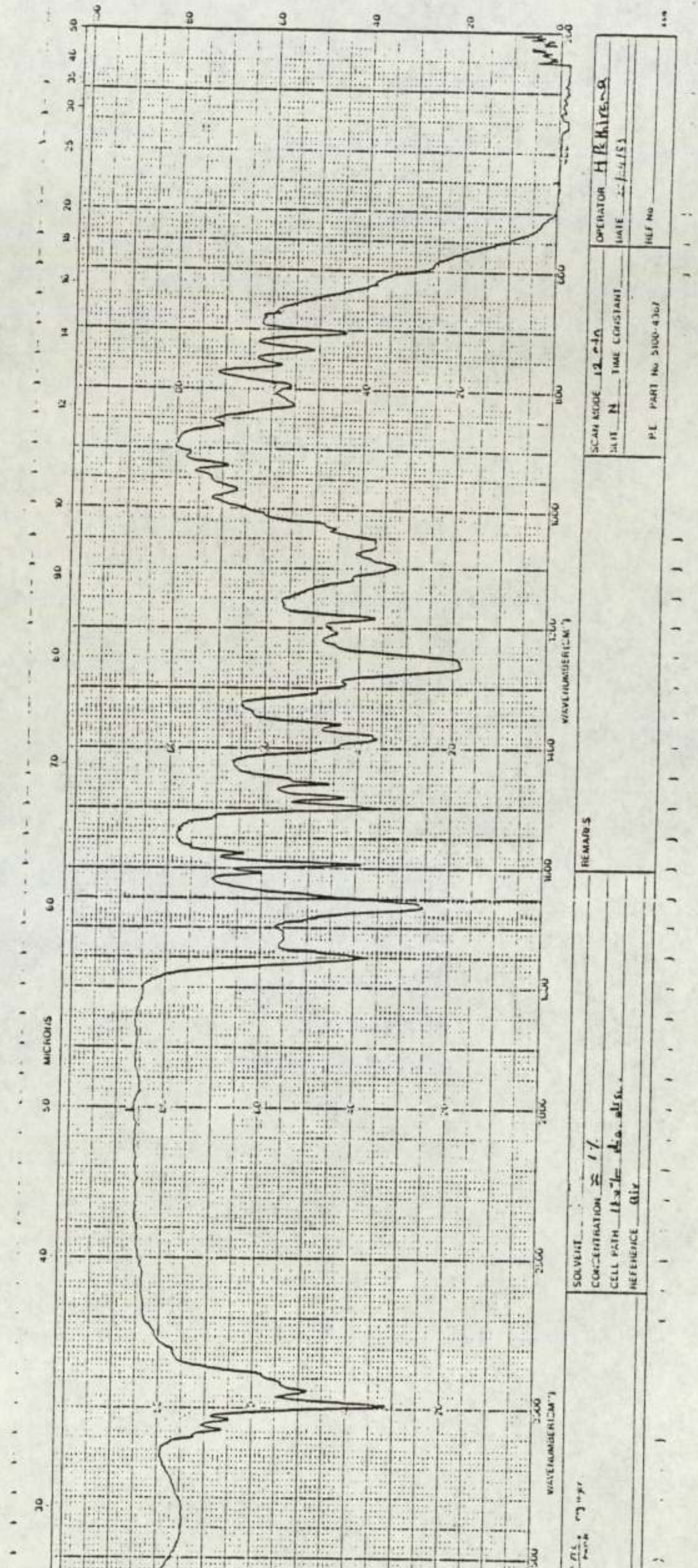
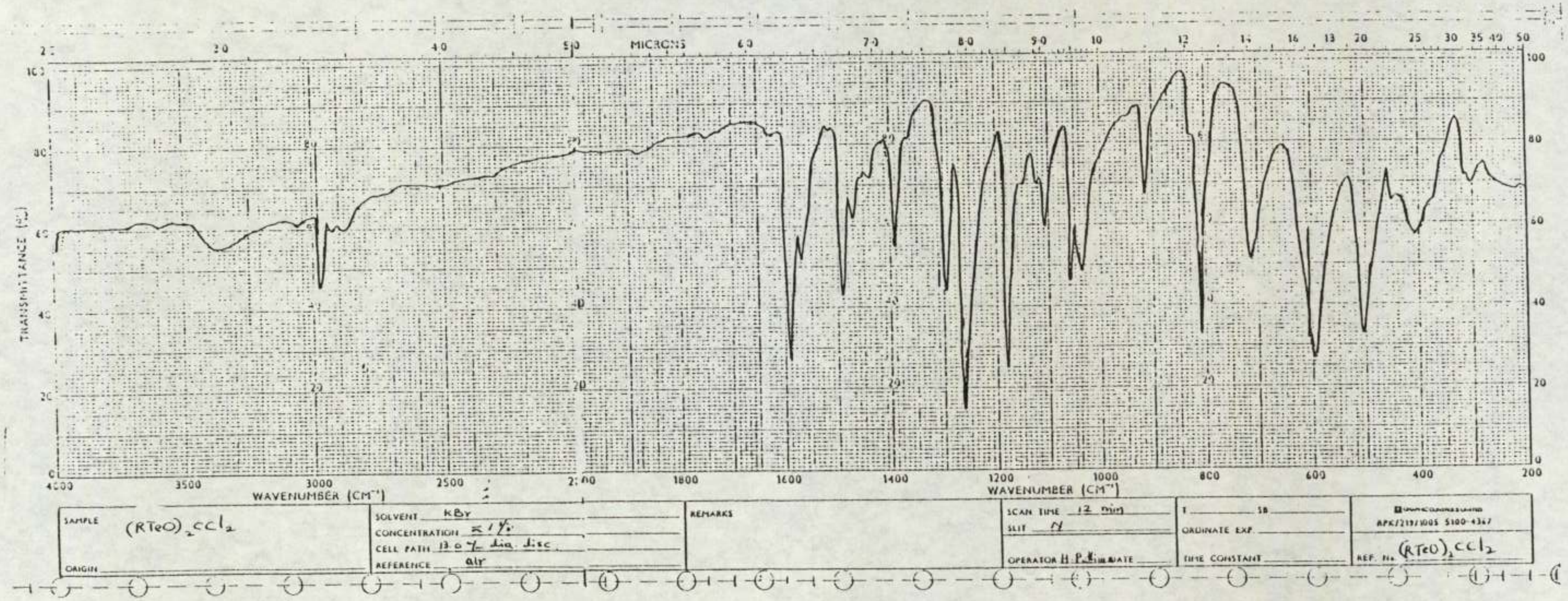


Figure 3.16 I.R. spectrum of $(ArTe)_2CO$



SAMPLE (RTeO)$_2$CCl$_2$

ORIGIN

SOLVENT KBr

CONCENTRATION ≈1%

CELL PATH 13.0 ½ dia. disc

REFERENCE air

REMARKS

SCAN TIME 12 min

SLIT N

OPERATOR H. P. Kim DATE

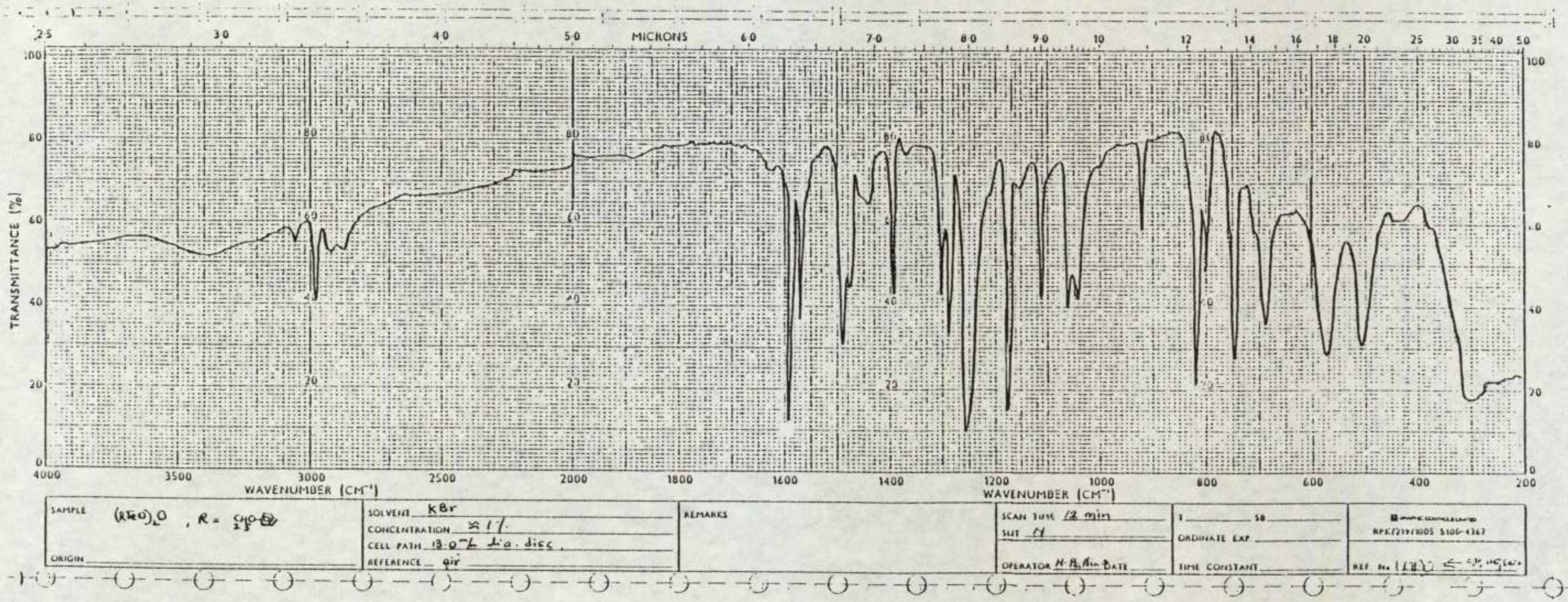
T SB

ORDINATE EXP.

TIME CONSTANT

REF. No. (RTeO)$_2$CCl$_2$

Figure 3.17 I.R. spectrum of (ArTeO)$_2$CCl$_2$



SAMPLE $(RTeO)_2O$, R = C_2H_5O-

ORIGIN

SOLVENT KBr

CONCENTRATION ≈ 1%

CELL PATH 13.0 mg in a disc.

REFERENCE air

REMARKS

SCAN TIME 12 min

SLIT N

OPERATOR H.A.Hin DATE

I SB

ORDINATE EXP.

TIME CONSTANT

RPK/2191/005 5106-4367

REF. No. (III) ≤ [illegible]

Figure 3.18 I.R. spectrum of $(ArTeO)_2O$

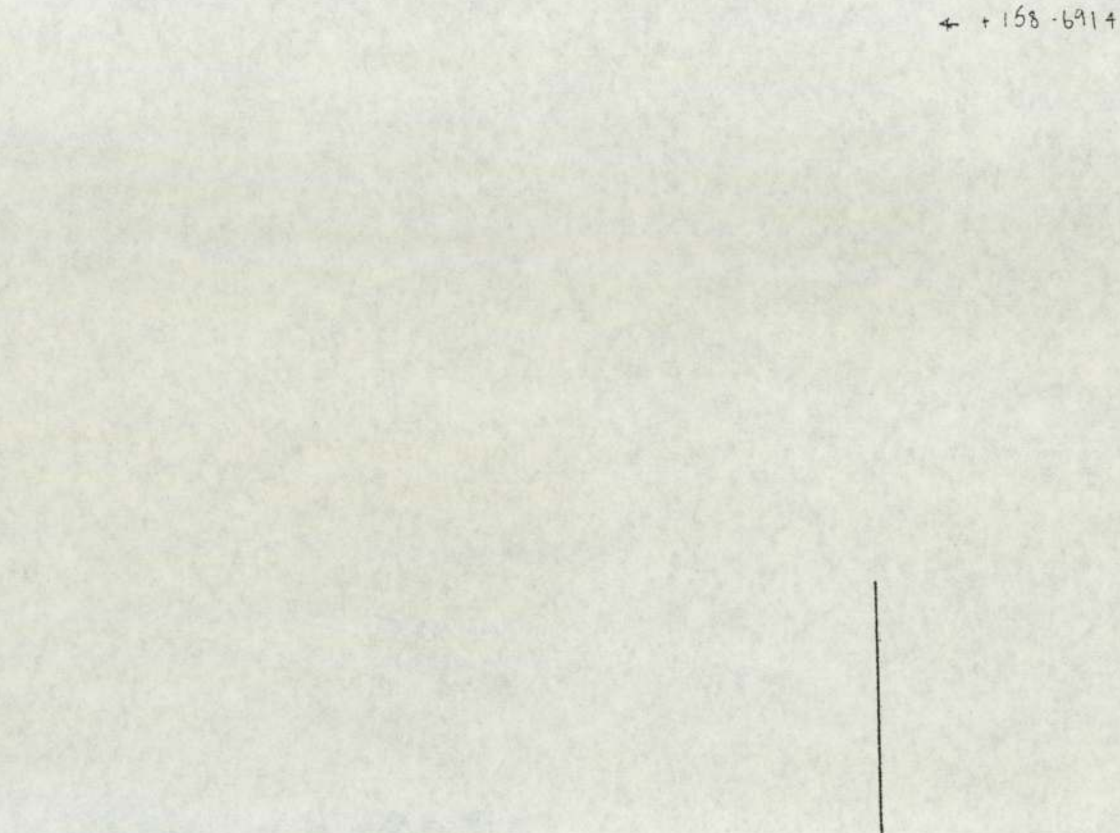
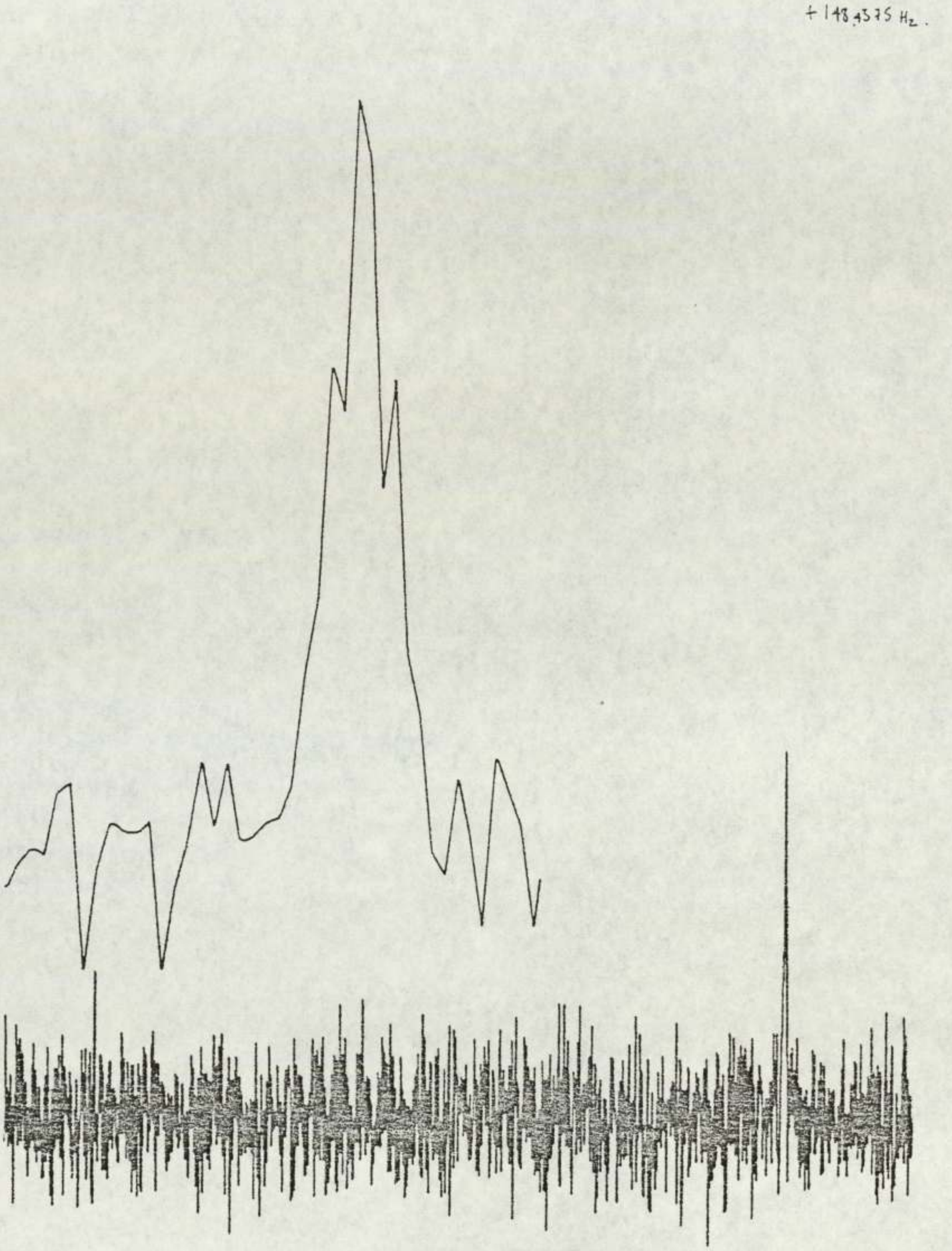


Figure 3.19 $\{^1H\}^{125}Te$ N.M.R. spectrum of $(ArTeO)_2CCl_2$



<u>Figure 3.20</u> ^{125}Te N.M.R. spectrum of $(ArTeO)_2CCl_2$

3.4 Discussion

3.4.1 The New Synthesis Of *Bis*-(p-ethoxyphenyltelluro) Methane (eptm)

The reaction of diorganoditellurides with alkaline sodium tetrahydroborate affords solutions with the chemical properties of NaTeAr(29).

$$\mathrm{ArTeTeAr} \xrightarrow[\mathrm{NaOH,\ C_2H_5OH}]{\mathrm{NaBH_4}} \mathrm{ArTeNa}$$

$$\mathrm{ArTeNa} \rightleftharpoons \mathrm{ArTe^-} + \mathrm{Na^+}$$

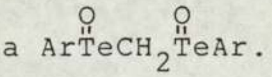
The method used for the synthesis of *bis*-(p-ethoxyphenyltelluro)methane (eptm) in this study was based on the nucleophilic substitution of both halogen atoms of dihalomethane by $\mathrm{ArTe^-}$. In the presence of excess dihalomethane, the product obtained was a charge transfer complex of eptm(50).

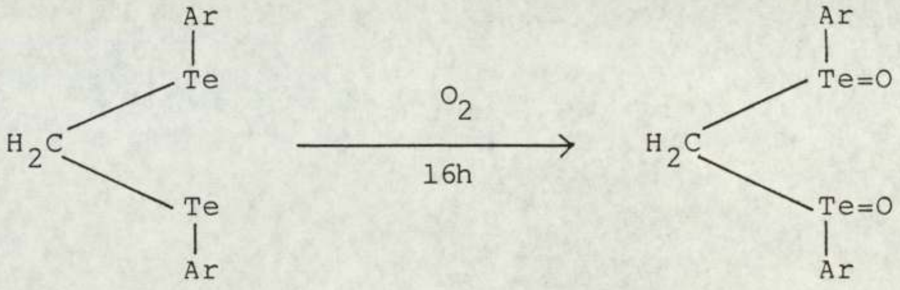
$$\mathrm{ArTeNa} + \text{excess } \mathrm{CH_2I_2} \longrightarrow \mathrm{ArTeCH_2TeAr.CH_2I_2}$$

The poor solubility of this charge transfer complex gave problems in the preparation of transition metal complexes. This inspired us to find a method of synthesis of the ligand without the formation of the charge transfer complex. Instead of using diiodomethane in excess, the use of exact stoichiometric amounts prevented the formation of a charge transfer complex and resulted in $ArTeCH_2TeAr$ as a green coloured compound. This was identified in the following way.

The elemental analyses of the green compound suggests the molecular formula $ArTeCH_2TeAr$. The conductivity measurement indicates that this green compound is a non-electrolyte. The bands due to CH_2I_2 appeared at 1114, 725 and 529cm^{-1} in the infra-red spectrum of $ArTe.CH_2.TeAr.CH_2I_2$(50). The disappearance of bands at 725, 529cm^{-1} and the decreased intensity of the band at 1114cm^{-1} in the infra-red spectrum of the green compound suggests the absence of CH_2I_2 in the new material (Figure 3.2). The broad signals appearing in the N.M.R. spectrum of $ArTeCH_2TeAr.CH_2I_2$ are replaced by sharp signals (Figure 3.3). $ArTeCH_2TeAr.CH_2I_2$ gave an E.S.R. spectrum(50). The line broadening in the N.M.R. spectrum was attributed to paramagnetism. The ^{13}C N.M.R. spectrum of eptm is presented in Figure 3.4. The ^{13}C resonances of the carbon nuclei of p-OEt.C_6H_4 group were assigned using the literature assignments(73,50) (Table 3.6). The observed values agree with the literature assignments. The ^{13}C resonance for CH_2-Te was not observed in the studied spectrum. The mass spectrum of the green compound indicates the parent ion at m/e=516.The fragmentation pattern is illustrated in Scheme 3.1.

Although the green compound was characterised by physical methods as $ArTeCH_2TeAr$, the puzzling thing was its green colour. Experience suggests tellurium compounds appear green when radical species are present. But no paramagnetism was detected by E.S.R. spectroscopy. This indicates the probable absence of tellurium radicals.

A stream of oxygen was bubbled through a solution of the green compound in an attempt to see whether the green colour was due to incomplete oxidation. The infra-red spectrum of the product obtained indicated a broad band at $580cm^{-1}$ showing the presence of Te=O group (Figure 3.5). The elemental analysis suggests the molecular formula  $Ar\overset{O}{\overset{\|}{Te}}CH_2\overset{O}{\overset{\|}{Te}}Ar$.



By using all this evidence, it can be concluded that the reaction of ArTeNa with CH_2I_2 in 2:1 molar ratio results in bis-(p-ethoxyphenyltelluro)methane.

$$2ArTeNa + CH_2I_2 \longrightarrow ArTeCH_2TeAr$$

3.4.2 Transition Metal Complexes of Bis-(p-ethoxyphenyltelluro)methane

Some complex formation reactions of bis-(p-ethoxyphenyltelluro)methane with transition metal ions were carried out under two different conditions:

(i) in an open atmosphere
(ii) in a dinitrogen atmosphere.

3.4.2.1 Complexes Synthesised In An Open Atmosphere

The complex formation reactions of eptm with Pd(II) gave ill defined products and with Cu(I) did not give any product. Surprisingly, eptm gave complexes with Cu(II). The poor results obtained from the elemental analyses of these complexes led us to examine their physical characterisations carefully. Similar difficulty was faced for the Hg(II) complexes.

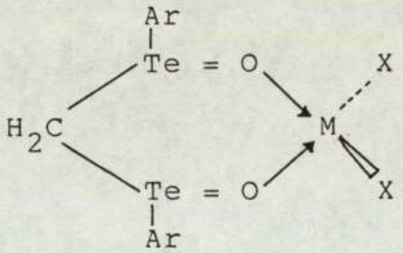
The paragraph 3.4.1 indicates a possible oxidation process of eptm to form telluroxide. Careful study of the elemental analyses of these Cu(II) and Hg(II) complexes suggests the molecular formulae $LO_2.HgX_2$; X=Cl, Br, and $LO_2.2CuCl_2$ (LO_2= $ArTe(O)CH_2Te(O)Ar$). The formation of these telluroxide complexes from eptm takes only about 15min. However, the formation of telluroxide by bubbling oxygen through a solution of eptm is a slow process and it needs about 16h.

This suggests that the oxidation of eptm to form telluroxide is a metal catalysed process. The telluroxide so formed has acted as a ligand and has formed complexes with transition metal ions. The absorption band at $600cm^{-1}$ in the infra-red spectra of the complexes strongly indicates the presence of the oxidised ligand (Figure 3.6). The peak at m/e 548 in the mass spectra of the complexes confirms the presence of the oxidised ligand. Therefore, it may be assumed that the telluroxide acts as the ligand in complex formation reactions when the reaction is carried out in air.

All these complexes displayed some common features.

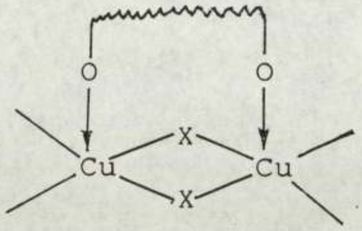
The absence of the CH_2I_2 group in the complexes formed by the ligand is confirmed by the comparison of infra-red and mass spectra of the free ligand and complexes. The presence of the oxidised ligand in the complexes is confirmed by the comparison of infra-red (band at $600cm^{-1}$) and mass spectra (peak at m/e 548 for $CH_2(Te(O)Ar)_2^+$) of the complexes and the free ligand.

All the Hg(II) complexes were yellow or brown in colour. They are soluble in DMF and hot $CHCl_3$. The elemental analyses of these complexes suggest a general formula of $LO_2.HgX_2$ where LO_2=ArTe(O)CH$_2$Te(O)Ar. The tellurium determinations of these Hg(II) complexes were carried out using two methods; namely the method reported by Clark and Althuraihi(74) and that reported by Thavornyutikarn$^{(75)}$. Low values resulting from Clark's method may probably be due to the incomplete oxidation of the organic content of tellurium compounds. The far-infra-red spectrum (400-200cm^{-1}) does not give any information about the ν(Hg-Cl). These vibrational bands may be obscured by the ligand vibrational bands. The conductivity measurements obtained using DMF indicated that these complexes are non-electrolytes. On the basis of this evidence, the following structure for the Hg(II) complexes is suggested:

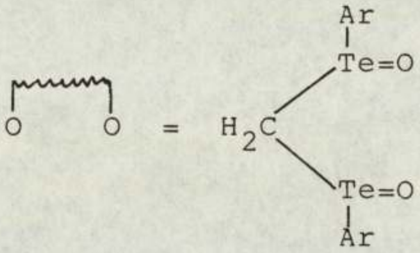


M=Hg(II)
X=Cl, Br

The complex formed from Cu(II) chloride was yellowish brown and was insoluble in organic solvents. The insolubility of this complex indicates the probable polymeric nature. The analytical data for this complex suggests the molecular formula $LO_2.2CuCl_2$ (LO_2=ArTe(O)CH$_2$Te(O)Ar). The far-infrared spectrum indicated the absence of terminal Cu-Cl bonds. The conductivity measurements for this complex in DMF could indicate that it is a 1:1 electrolyte (Λ_M=80ohm^{-1}cm^{2}mol^{-1}), however, the plot of Λ_M vs. (conc)$^{\frac{1}{2}}$ is non-linear (Figure 3.7(a)) This complex gives an E.S.R. signal in the solid state centered on g=2.09. The following structure is suggested on the basis of all this evidence:



where,



Therefore, it can be concluded that bis-(p-ethoxyphenyltelluro)methane oxidises to a telluroxide in the presence of dioxygen and transition metal ions, and the telluroxide so formed can act as a ligand in complex formation reactions. In the presence of dioxygen only, the oxidation of eptm to telluroxide is a very slow process. Therefore it can be suggested that the metal salts have a catalytic effect on the oxidation of eptm.

3.4.2.2 Complexes Synthesised In A Dinitrogen Atmosphere

The complexes listed in Table 3.3 fall into three groups on the basis of stoichiometry.

(a) $(ArTeCH_2TeAr)_2M_2X_2$; M=Pd, Pt ; X=Cl,Br

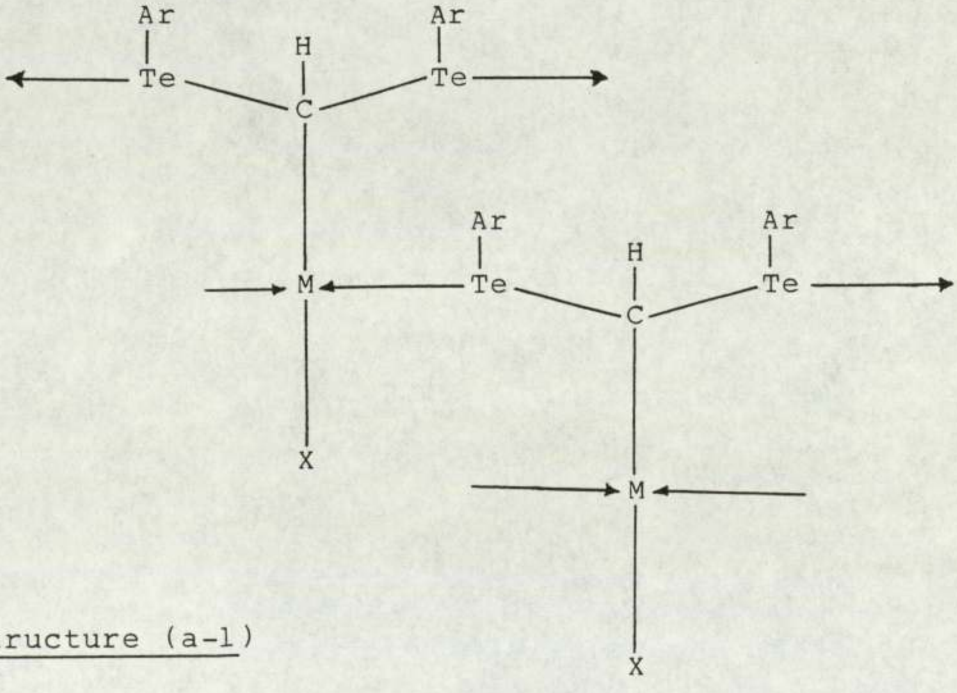
(b) $(ArTeCH_2TeAr)_2MX_2$; M=Pd ; X=Cl

(c) $(ArTeCH_2TeAr)MX_2$; M=Hg ; X=Cl

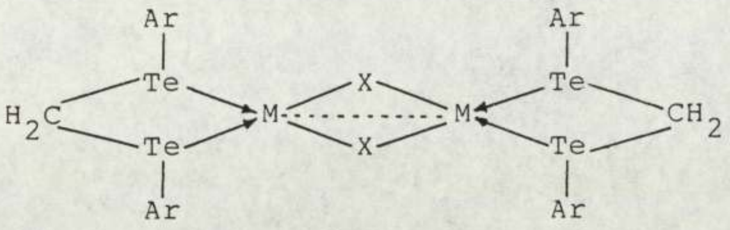
(a) Complexes having the stoichiometry $M_2(ArTeCH_2TeAr)_2X_2$

Complexes belonging to this category were prepared with Pd(II) and with Pt(II).

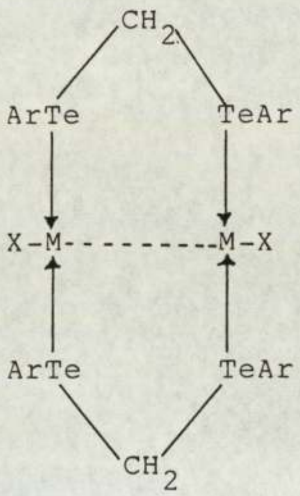
The reaction of Pd(II) or Pt(II) with bis-(p-ethoxyphenyltelluro)methane in a 1:1 molar ratio resulted in brown or yellow insoluble solids. The insoluble nature together with high melting points is probably indicative of magnus type salt $[ML_2][MX_4]$(8,18) or polymeric(8,18) structures. However, the elemental analyses suggest the stoichiometry $(ArTeCH_2TeAr).MX$; M=Pd, Pt, X=Cl, Br. Therefore these complexes can possess a C-metallated structure (a-1) or a halogen bridged structure (a-2) or a ligand bridged structure (a-3).



Structure (a-1)



Structure (a-2)



Structure (a-3)

The mass spectra (70eV, 1eV = 1.60×10^{-17}J), which were recorded as an attempt to provide information about the molecular weights, showed only fragments of low m/e values, probably arising from the thermal decomposition. The insolubility of these complexes prevents conductivity measurements, N.M.R. studies and molecular weight determinations.

The use of sodiumtetrachloropalladate(II) or bis-(benzonitrile)palladium(II)chloride as the complex precursor gave the same complex. The absence of a band due to ν(C≡N) and the presence of bands due to *bis*-(p-ethoxyphenyltelluro)-methane in the infra-red spectrum of the palladium complex obtained from PdCl$_2$(PhCN)$_2$ indicates the displacement of the benzonitrile group from the complex. All the palladium and platinum complexes show characteristic absorptions of eptm (Figures 3.8 and 3.9). The absence of a band at 600cm^{-1} indicates the presence of the unoxidised ligand or, in other words, it indicates the absence of Te=O group.

Careful examination of the far-infra-red spectra of palladium complexes indicates a very weak band as a shoulder at 549cm^{-1} which could be assigned as ν(C-Pd)(76) (Figure 3.10). The change in the metal atom from palladium to platinum should cause a shift of ν(M-C) frequency due to the larger atomic mass of platinum. However, this weak band appears in the infra-red spectrum of the platinum complex at the same frequency (Figure 3.12). Therefore, this weak shoulder cannot be assigned as the ν(M-C) and this precludes the structure (a-l). However, this weak band may be assigned as the ν(Te-aliphatic C) according to literature values(77).

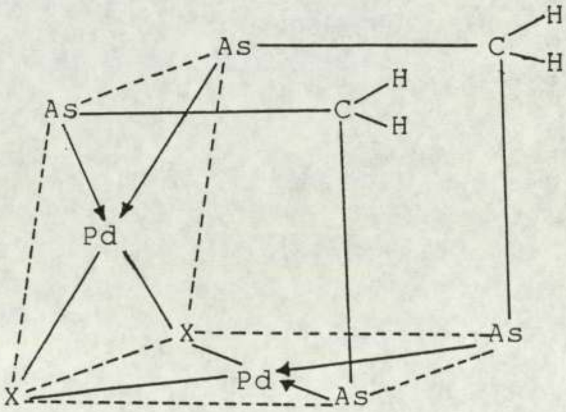
The metal-halogen stretching frequencies in the low frequency infra-red spectra are illustrated in Figures 3.10-3.13. The terminal *trans*-ν(Pd-Cl),*trans*-ν(Pd-Br),*cis*-ν(Pd-Cl) and bridging ν(Pd-Cl) frequencies for Pd(II) complexes of monodentate tellurium ligands have been assigned at~350cm^{-1}(78,80,81),~275 cm^{-1}(44,86)

~285, 305 cm^{-1} (79,81) and ~270, 298cm^{-1} (85) respectively. Therefore the band at 280, 292cm^{-1} in the far-infra-red spectrum of this new palladium complex (Figure 3.10) can be assigned as terminal ν(Pd-Cl). There is little doubt about the assignment of ν(Pd-Cl) frequency, since it gave an intense band in the spectrum and is not present in the spectrum of the corresponding bromo- complex (Figure 3.11). Therefore, the presence of terminal ν(Pd-Cl) band in the infra-red spectrum precludes the structure (a-2). The splitting of the band may be due to the non-planar structure of the complex. This may be due to the slightly bent planar structure of the complex. The low ν(Pd-Cl) obtained for this new complex indicates the high trans-influence of metal-metal bond in structure (a-3). Similar decreases in ν(Pd-Cl) have been obtained for analogous palladium(I) complexes of bis(diphenylphosphino)methane(249cm^{-1}).(14) This similarity strongly suggests that the present complex contains the linear ClPdPdCl units as required in structure (a-3).

The terminal trans-ν(Pt-Cl), trans-ν(Pt-Br) and terminal cis-ν(Pt-Cl) frequencies for Pt(II) complexes of monodentate tellurium ligands has been assigned at ~301cm^{-1} (44,78,84) ~245cm^{-1} (44) and ~303, 283cm^{-1} (82,83,85) respectively. Therefore, the band at 315cm^{-1} in the far-infra-red spectrum of this new platinum complex (Figure 3.12) can be assigned as terminal ν(Pt-Cl). As in the case of the analogous palladium complex, there is little doubt about the assignment of ν(Pt-Cl) frequency, since it gave an intense band in the spectrum and is not present in the spectrum of the corresponding bromo- complex (Figure 3.13). Therefore, the presence of the terminal ν(Pt-Cl) band in the far-infra-red spectrum precludes the structure (a-2) and suggests the structure (a-3).

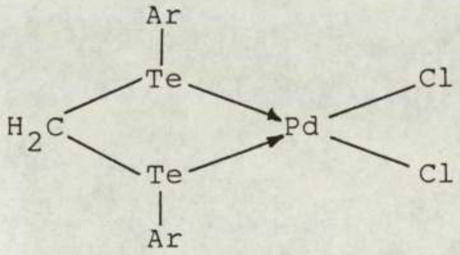
The ν(M-Br), M=Pd(I), Pt(I) stretching frequency of the bromo- complexes was not present in the observed far-infra-red region (400-200cm^{-1}) (Figures 3.11 and 3.13). However, on the basis of the structure of the chloro- complexes, structure (a-3) could be suggested for these bromo- complexes also.

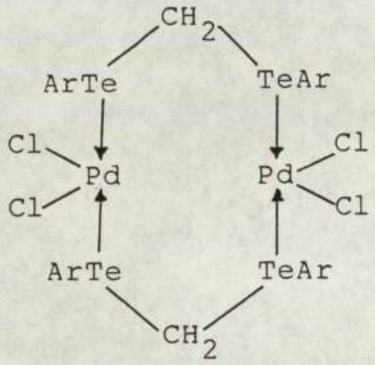
The following structure has been suggested for the analogous palladium complex of bis-(diphenylarsino)methane(87).



However, the observation of terminal M-Cl bands in the far-infra-red spectra of these new complexes also precludes this possibility.

The complex obtained from the reaction of $PdCl_2(PhCN)_2$ with bis-(p-ethoxyphenyltelluro)methane has previously been formulated by De Silva as $ArTeCH_2TeAr.PdCl_2$, who suggested the following structures(49).





The elemental analyses of all the palladium and platinum complexes studied in the present work agree with the molecular formula $(AtTeCH_2TeAr)_2M_2X_2$ and do not agree with the molecular formula suggested by De Silva. The far-infra-red spectrum of the platinum complex indicates the absence of cis-ν(Pt-Cl) (Figure 3.12). Therefore, although a splitting of the ν(Pd-Cl) band is observed in the far-infra-red spectrum of this new palladium complex (Figure 3.10), it is not justified to assign it as cis-ν(Pd-Cl). This splitting may be due to the non-planar structure as explained earlier in this discussion. Therefore, it would appear that De Silva based her proposal in an incorrect stoichiometry and an incorrect assignment of ν(Pd-Cl).

All this evidence suggests the molecular formula $(ArTeCH_2TeAr)_2$-M_2X_2 and structure (a-3) for this new class of complex.

The comparison of M-Cl stretching frequencies of $(ArTeCH_2TeAr)_2M_2Cl_2$ and $(Ph_2PCH_2PPh_2)_2M_2Cl_2$⁽¹⁴⁾ gives the following order.

$Pd_2(ArTeCH_2TeAr)_2Cl_2$ > $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$
$280, 292cm^{-1}$ $249cm^{-1}$

$Pt_2(ArTeCH_2TeAr)_2Cl_2$ > $Pt_2(Ph_2PCH_2PPh_2)_2Cl_2$
$315cm^{-1}$ $249cm^{-1}$

This may be due to the poorer σ-donor property of bis-(p-ethoxyphenyltelluro)methane compared with bis-(diphenylphosphino)methane.

The order of the metal-chlorine stretching frequency of Pd(I) and Pt(I) complexes of $M_2(ArTeCH_2TeAr)_2Cl_2$ is given below.

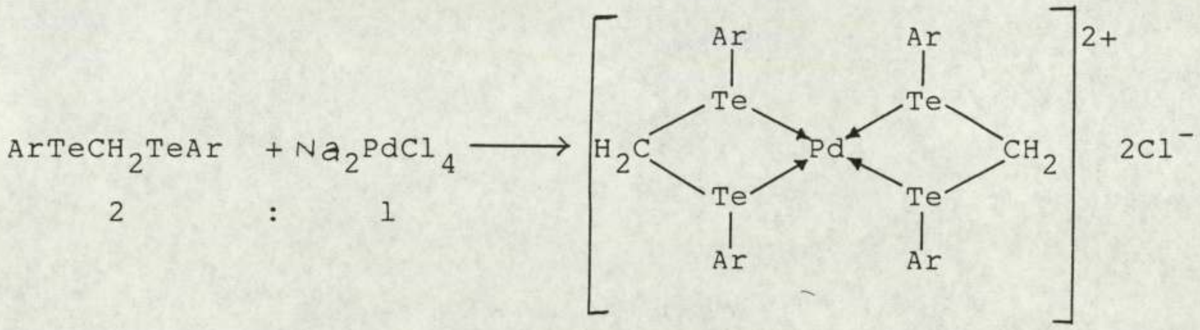
$Pt_2(ArTeCH_2TeAr)_2Cl_2$ > $Pd_2(ArTeCH_2TeAr)_2Cl_2$
$315cm^{-1}$ $280, 292cm^{-1}$

The implication is that there is some π-back donation in $Pt_2(ArTeCH_2TeAr)_2Cl_2$ thus increasing the Lewis acidity of the metal in the platinum complex so causing a higher ν(Pt-Cl) in the platinum complex than in the palladium complex. Therefore, the order of Lewis acidity towards eptm is Pt(I)>Pd(I). An alternative explanation is the weakness of the Pt....Pt bond which results in a higher ν(Pt-Cl) stretching frequency. This will be explained in more detail in Chapter Five.

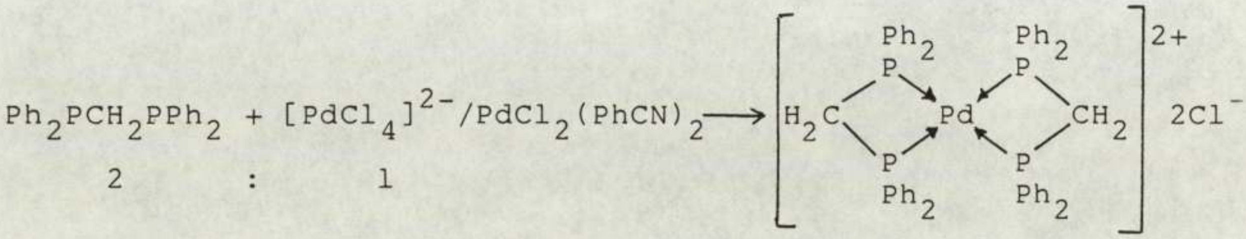
(b) Complexes having the stoichiometry $(ArTeCH_2TeAr)_2MX_2$

The reaction of eptm with sodiumtetrachloropalladate(II) in 2:1 molar ratio resulted in a brown complex which is partially soluble in benzene and halocarbon solvents. The elemental analysis of this compound suggests the stoichiometry $(ArTeCH_2TeAr)_2PdCl_2$. This complex is a 1:2 electrolyte in dimethylformamide (Λ_M=178ohm^{-1}cm^{2}mol^{-1} at 1x10^{-3}M) (Figure 3.14) and the electronic spectrum exhibited an absorption ≈ 24,000cm^{-1}, consistent with the presence of a planar $[ML_2]^{2+}$ cation (L=$ArTeCH_2TeAr$) (Figure 3.15). No ν(Pd-Cl) stretching frequencies were detected in the far-infra-red spectrum of the complex. The absence of Te=O bands in the infra-red spectrum suggests the presence of the unoxidised ligand.

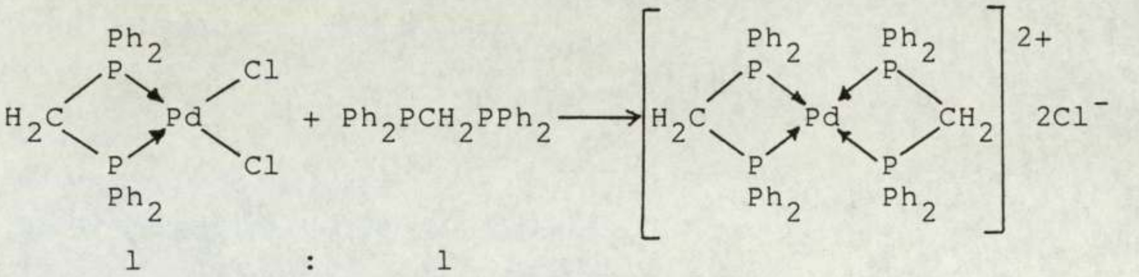
According to the above evidence, this complex could be formulated as $[(ArTeCH_2TeAr)_2Pd]^{2+}.2Cl^-$.



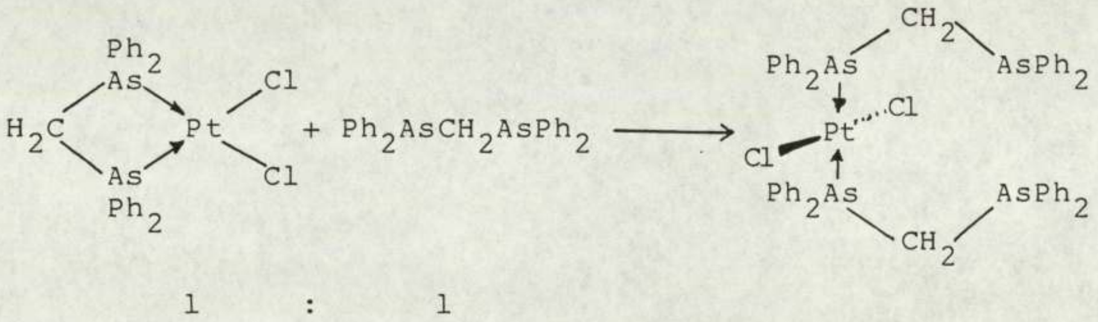
The reaction of bis-(diphenylphosphino)methane with either $[PdCl_4]^{2-}$ or $[PdCl_2(PhCN)_2]$ in 2:1 molar ratio gives a palladium complex which is analagous to that above (88,89).



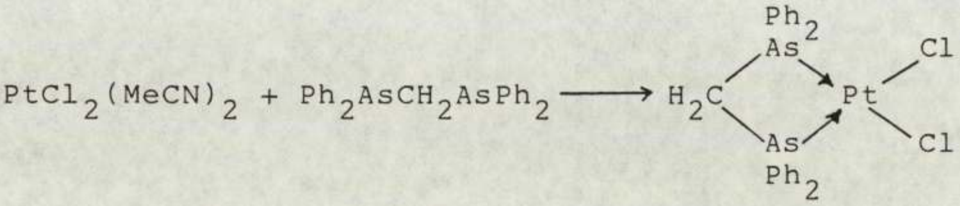
A similar type of product has been obtained by the reaction of chelated $(Ph_2PCH_2PPh_2)MCl_2$ with another mole of $Ph_2PCH_2PPh_2$ (88,89).



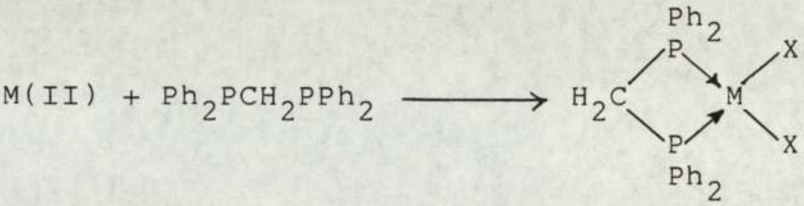
In contrast, the reaction of chelated $(Ph_2AsCH_2AsPh_2)PtCl_2$ with another mole of $Ph_2AsCH_2AsPh_2$ has resulted in the neutral complex $Pt(Ph_2AsCH_2AsPh_2)_2Cl_2$ (90).



However, chelated complexes having the formula $(Ph_2AsCH_2AsPh_2)PtCl_2$ have been prepared by reacting $Ph_2AsCH_2AsPh_2$ with $PtCl_2(MeCN)_2$ in 1:1 molar ratio$^{(90)}$.

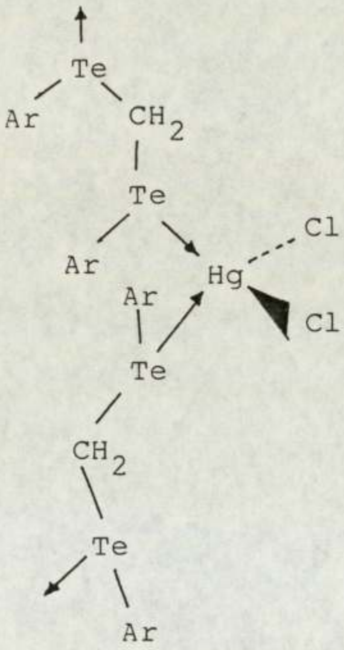


Chelated complexes having the molecular formula, $(Ph_2PCH_2PPh_2)MX_2$, M=Pd, Pt; X=Cl, Br, have been prepared by reacting $Ph_2PCH_2PPh_2$ with either $[MCl_4]^{2-}$ or $MCl_2(PhCN)_2$ in 1:1 molar ratio$^{(89,91)}$.



(c) Complexes having the molecular formula $(ArTeCH_2TeAr)MX_2$

The reaction of eptm with $HgCl_2$ in 1:1 molar ratio resulted in a yellow insoluble complex. Elemental analysis of this complex suggests the stoichiometry $(ArTeCH_2TeAr)HgCl_2$. The infra-red spectrum of this complex indicates the bands characteristic for $ArTe(CH_2)TeAr$. The far-infra-red spectrum does not give any information about Hg-Cl vibrations because these vibrational bands may be obscured by ligand vibrational bands or may not appear in the observed far-infra-red region (400-200cm^{-1}). The insolubility of these complexes prevents conductivity measurements and N.M.R. studies. The mass spectrum exhibited only fragments of low m/e value due to the thermal decomposition of the complex. The following structure is suggested for this complex.



It is impossible to confirm the structure without carrying out more work e.g., a comprehensive vibrational study.

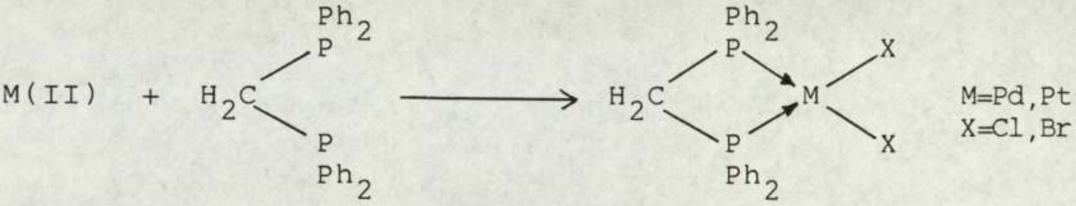
In summarising all this data, it can be concluded that the metal catalysed oxidation of eptm does not occur when the complex formation reactions are carried out in a dinitrogen atmosphere. The physical measurements on these complexes suggest:-

(1) complexes having molecular formula $L_2M_2X_2$ are formed when L is reacted with M(II) in 1:1 molar ratio (L= eptm).

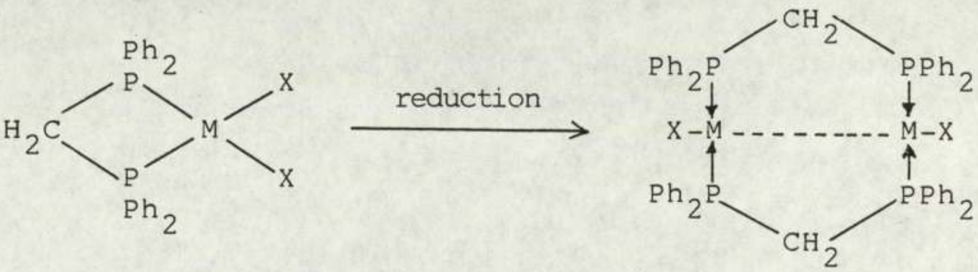
(2) complexes having molecular formula L_2PdCl_2 are formed when L is reacted with Pd(II) in 2:1 molar ratio (L= eptm).

(3) complexes having molecular formula $LHgCl_2$ are formed when L is reacted with Hg(II) in 1:1 molar ratio (L= eptm).

The reaction of bis-(diphenylphosphino)methane with M(II) in 1:1 molar ratio results in chelated complexes.M(II) = Pd(II), Pt(II)$^{(91)}$.



The reduction of these chelated complexes results in ligand bridged complexes$^{(14,15,92)}$.



The treatment of M(II) with a solution of M(0) and bis-(diphenylphosphino)methane has also resulted in the ligand bridged M(I) complexes(14).

In contrast, the reaction of bis-(p-ethoxyphenyltelluro)-methane with M(II), M=Pd, Pt, in 1:1 molar ratio directly resulted in ligand bridged M(I) complexes. The formation of M(I) complexes from M(II) complex precursors indicates that eptm is acting as a reducing agent in the complex formation reactions (M=Pd,Pt).

$$\mathrm{Te(II) + 2M(II) \longrightarrow Te(IV) + 2M(I)}$$

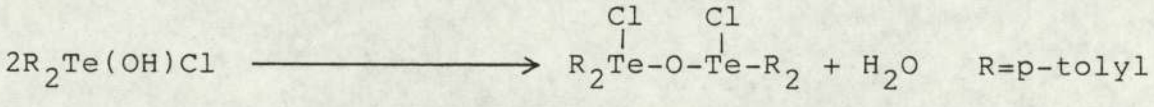
$$\mathrm{Te(II) + M(I) \longrightarrow complex}$$

It has been reported in literature that di-p-tolyl-telluride has reduced Fe(III), Cu(II) and Hg(II) chlorides to lower valent metal chlorides transforming the telluride into dichlorides(93).

$$\mathrm{2FeCl_3 + R_2Te \xrightarrow{\text{glacial HOAc}} R_2TeCl_2 + 2FeCl_2}$$

In the presence of moisture, the dichlorides will be hydrolysed to the hydroxide chloride or their anhydrides.

$$\mathrm{R_2TeCl_2 + H_2O \longrightarrow R_2Te(OH)Cl + HCl}$$



$$\mathrm{2R_2Te(OH)Cl \longrightarrow R_2\overset{Cl}{\overset{|}{Te}}\text{-}O\text{-}\overset{Cl}{\overset{|}{Te}}\text{-}R_2 + H_2O} \quad \mathrm{R{=}p\text{-}tolyl}$$

Therefore, the behaviour of eptm as a reducing agent is not a surprising or an unacceptable observation.

Although chelated complexes have been produced with bis-(diphenylphosphino)methane, bridged complexes were obtained with bis-(p-ethoxyphenyltelluro)methane. This suggests that the ring strain for chelated complexes of $Ph_2PCH_2PPh_2$ is much lower than that for $ArTeCH_2TeAr$. The greater ring strain for $ArTeCH_2TeAr$ may be due to the large atomic size of tellurium. The preference of $ArTeCH_2TeAr$ for making ligand bridged structures over the ligand chelated structures is probably in part due to the lower ring strain when $ArTeCH_2TeAr$ acts as a bridging ligand (giving a five membered ring), than when it chelates (giving a four membered ring).

Nevertheless, the formation of $\overset{1}{L}_2PdCl_2$ **indicates** the possible chelation of eptm (L'=eptm).

3.4.3 Attempted Reactions With $Mo(CO)_6$

The synthesis of carbonyl derivatives of $Mo(CO)_6$ with $ArTeCH_2TeAr$ was attempted to study the formation of π-bonding of $ArTeCH_2TeAr$. Unfortunately, the reactions carried out under the conditions used, failed to produce complexes containing both the ligand and CO. This may be due to the weakness of the Mo←Te bond compared with the Mo←CO or Mo←THF bond.

3.4.4 Insertion Of Dichlorocarbene Into Diorganoditellurides

The addition of $CHCl_3$ into an aqueous solution of conc. NaOH in the presence of a phase transfer catalyst, results in the formation of dichlorocarbene(94).

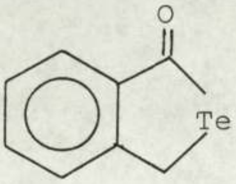
$$\mathrm{NaOHaq} + \mathrm{QBrorg} \longrightarrow \mathrm{QOHaq} + \mathrm{NaBraq}$$

$$\mathrm{QOHaq} \longrightarrow \mathrm{QOHorg}$$

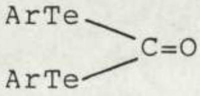
$$\mathrm{QOHorg} + \mathrm{CHCl_3org} \longrightarrow \mathrm{H_2O} + \mathrm{Q^+Cl_3C^-org}$$

$$\mathrm{Q^+Cl_3C^-} \longrightarrow \mathrm{QCl} + |\bar{\mathrm{C}}\mathrm{Cl_2}$$

The reaction of dichlorocarbene with diarylditelluride resulted in a colourless solution. After the reaction was complete, the phases were separated and the organic phase was dried and evaporated. A foul smelling unstable compound was obtained in a very low yield. Two strong bands were observed at $1670cm^{-1}$ and $1750cm^{-1}$ in the infra-red spectrum of this compound, which could be due to splitting of the carbonyl group frequency (Figure 3.16). A similar splitting of carbonyl band ($1690, 1740cm^{-1}$) has been reported for tellurophthalide(95).



The mass spectrum of this product indicated the parent ion at m/e=530. Therefore, the following structure is proposed.

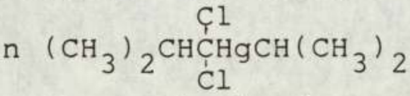


$$\mathrm{(ArTe)_2C{=}O}$$

This compound may be formed by the hydrolysis of the dichlorocarbene derivative of the ditelluride.

The reaction of this compound with hydrazine hydrate resulted in ditelluride and did not form any hydrazone derivative.

Similar observations have been reported by Singh$^{(69)}$.

Acidification of the aqueous phase with hydrochloric acid resulted in a white compound. Elemental analysis of this white compound suggests a molecular formula $(ArTeO)_2CCl_2$. The infra-red spectrum of this compound indicates the presence of ν(Te=O) at 600cm^{-1} (Figure 3.17). The vibrational frequency typical for ν(C-Cl) in  $(CH_3)_2CH\overset{Cl}{\underset{Cl}{C}}HgCH(CH_3)_2$ has been assigned at 692cm$^{-1(96)}$. Therefore, the band present at 710cm^{-1} is assigned as ν(C-Cl). This assignment is fairly confident since the band is not present in the infra-red spectrum of $(ArTeO)_2O$, Ar=p-$OC_2H_5.C_6H_4$ (Figure 3.18). The ^{125}Te N.M.R. spectrum of an aqueous NaOH solution of $(ArTeO)_2CCl_2$ (pH≈13) indicates that all tellurium atoms present in the molecule are equivalent (Figure 3.19). The triplet in the proton non-decoupled ^{125}Te N.M.R. is due to the coupling of tellurium with the <u>ortho</u>- hydrogens of the benzene ring (Figure 3.20).

The reaction of $(ArTeO)_2CCl_2$ with hydrazine hydrate or thiourea resulted in the ditelluride.

$$(ArTeO)_2CCl_2 + N_2H_2 \xrightarrow{\hspace{3em}} Ar_2Te_2$$
$$(ArTeO)_2CCl_2 + SC(NH_2)_2 \xrightarrow{\hspace{3em}} Ar_2Te_2$$

Earlier, this compound was identified as $(ArTeO)_2O$ by Singh(69). Therefore, $(ArTeO)_2O$ was prepared according to literature method(97) and the melting point, infra-red (Figure 3.18), ^{125}Te N.M.R. spectra of $(ArTeO)_2O$ were compared with those of $(ArTeO)_2CCl_2$.

The melting points and infra-red spectra of the two compounds were not identical. The presence of a band at $710cm^{-1}$ in the infra-red spectrum of $(ArTeO)_2CCl_2$ (Figure 3.17) and the absence of it in the infra-red spectrum of $(ArTeO)_2O$ (Figure 3.18) strongly suggests the presence of C-Cl in $(ArTeO)_2CCl_2$. The ^{125}Te N.M.R. of two compounds indicate the same chemical shift. This may reflect equal electronegativity effects caused by $O\overset{/}{\underset{\backslash}{}}$ and $Cl-\overset{/}{\underset{\backslash}{C}}-Cl$ groups.

Singh has observed the formation of $(ArTeO)_2CCl_2$ when phenyl(trichloromethyl)mercury was used for generating $|\bar{C}Cl_2$ for the reaction of $|\bar{C}Cl_2$ with diarylditellurides(69).

It has been reported earlier that the reaction of ditellurides in solution with dioxygen produces radical intermediates(98). Later, Miller et al reported the oxidation of solutions of ditelluride in the presence of alcohols, O_2 and light(97,99).

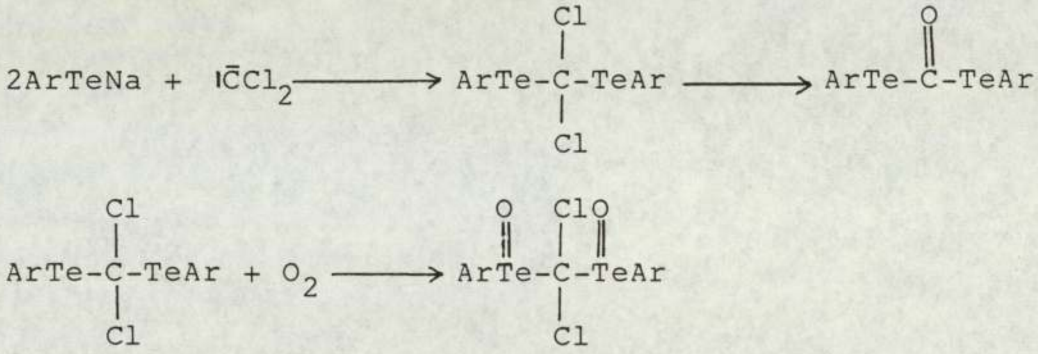
$$Ar_2Te_2 \xrightarrow{h\nu} Ar_2Te_2^*$$
$$Ar_2Te_2^* + O_2 \longrightarrow Ar_2Te_2O_2$$

Comasseto et al have reported the disproportionation of ditelluride under phase transfer conditions as follows:(100,101)

$$ArTeTeAr \xrightarrow[PTC, N_2, \text{room temp}]{50\%NaOH,\ THF} 3ArTeNa + ArTeO_2Na$$

Therefore, the reaction of Ar_2Te_2 with $|\bar{C}Cl_2$ could be represented as follows:-

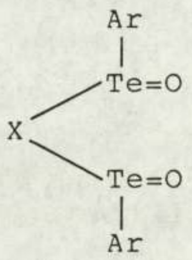
$$ArTeTeAr \xrightarrow[PTC, 55^{\circ}C]{50\%NaOH, benzene} ArTeNa + ArTeO_2Na$$



$$2ArTeNa + |\bar{C}Cl_2 \longrightarrow ArTe\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}TeAr \longrightarrow ArTe\text{-}\overset{O}{\overset{\|}{C}}\text{-}TeAr$$

$$ArTe\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}TeAr + O_2 \longrightarrow Ar\overset{O}{\overset{\|}{Te}}\text{-}\overset{Cl}{\underset{Cl}{C}}\text{-}\overset{O}{\overset{\|}{Te}}Ar$$

During this study, it was hoped to use $(ArTeO)_2CCl_2$ and $(ArTeO)_2O$ as ligands because of their similarity to the molecular formula of the telluroxide formed from eptm.



$X=CH_2, CCl_2, O$

Unfortunately, the insolubility of these two compounds prevented their use as ligands.

CHAPTER FOUR

SYNTHESIS OF BIDENTATE TELLURIUM LIGANDS HAVING ALKANE CHAIN BACKBONES, $ArTe(CH_2)_nTeAr$

4.1 Introduction

Synthesis of bidentate ligands having alkane chain backbones have been reported for Phosphorus, Arsenic, Antimony and Sulphur, but nothing has been reported for analogous Tellurium ligands. The aim of this study was to devise methods to synthesise this type of tellurium ligand, initially unsuccessfully attempted by Davies(3) and later by Monsef-Mirzai(48) in this laboratory. However, successful results were obtained in this work producing potentially bidentate tellurium ligands having short, medium and long alkane chain backbones. The following experimental section describes the synthesis and characterisation of these new bidentate ligands.

4.2 Experimental

4.2.1 Synthesis of 1-Bromo-1-p-ethoxyphenyltelluracyclohexane

Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene ($10cm^3$) and ethanol ($20cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in $1mol\ dm^{-3}$ solution of sodium hydroxide ($12cm^3$) was added dropwise to this solution. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, 1,5-dibromopentane (9.2g, 40mmol) was added and the warm mixture was stirred for 30min. During the stirring, a white precipitate was formed. The precipitate was then separated and dried in vacuo. Recrystallisation from acetonitrile gave a white compound in 50% yield. m.p. 203-204°C.

Found	C 40.0	H 4.70%
$C_{13}H_{19}OTeBr$ requires	C 39.1	H 4.80%

4.2.2 Synthesis of 1,5-Bis(p-Ethoxyphenyltelluro)pentane

Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene (10cm^3) and ethanol (20cm^3) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1mol dm^{-3} solution of sodium hydroxide (12cm^3) was added dropwise to this solution. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, 1,5-dibromopentane (2.3g, 10mmol) was added and the mixture was stirred for 1.75-2h, at room temperature. This was added to distilled water and stirred well. The organic layer was separated, washed with water and acetonitrile was added to induce precipitation. The precipitate was separated and dried in vacuo over P_4O_{10}. Recrystallisation from acetonitrile gave an orange-yellow product in 52% yield. m.p. 63-65°C.

Found	C 44.2	H 4.30%
$C_{21}H_{28}O_2Te_2$ requires	C 44.4	H 4.90%

The following 1,n-*bis*-(p-ethoxyphenyltelluro)alkanes were prepared by a similar reaction of the appropriate 1,n-dibromoalkane with *bis*-(p-ethoxyphenyl)ditelluride in 1:1 molar ratio.

4.2.3 Synthesis Of 1,6-*Bis*-(p-Ethoxyphenyltelluro)hexane

A cream coloured precipitate was obtained in 60% yield. m.p. 53-54°C.

Found	C 45.5	H 5.30%
$C_{22}H_{30}O_2Te_2$ requires	C 45.4	H 5.20%

4.2.4 Synthesis Of 1,7-*Bis*-(p-Ethoxyphenyltelluro)heptane

A cream coloured precipitate was obtained in 47% yield. m.p. 48-49°C.

Found	C 46.5	H 5.50%
$C_{23}H_{32}O_2Te_2$ requires	C 46.4	H 5.40%

4.2.5 Synthesis Of 1,9-*Bis*-(p-Ethoxyphenyltelluro)nonane

A white precipitate was obtained in 50% yield. m.p. 54-55°C.

Found	C 47.8	H 5.90%
$C_{25}H_{36}O_2Te_2$ requires	C 48.1	H 5.80%

4.2.6 Synthesis Of 1,10-*Bis*-(p-Ethoxyphenyltelluro)decane

By using a solution of 1,10-dibromodecane in benzene, a bright yellow precipitate was obtained in 55% yield. m.p. 55-56°C.

Found	C 49.4	H 6.10%
$C_{26}H_{38}O_2Te_2$ requires	C 49.0	H 6.00%

4.2.7 Reaction Of 1,6-*Bis*-(p-Ethoxyphenyltelluro)hexane With Bromine

A solution of excess bromine (in CCl_4) was added to a solution of 1,6-*bis*-(p-ethoxyphenyltelluro)hexane in benzene, and the mixture was shaken for three days. The yellow precipitate obtained was washed with CCl_4 and benzene and dried in vacuo. m.p. 151-153°C (dec). Yield 40%.

Found	C 9.1	H 1.30%
$C_6H_{12}Te_2Br_6$ requires	C 8.8	H 1.50%

4.2.8 Reaction Of 1,10-*Bis*-(p-Ethoxyphenyltelluro)decane With Bromine

A solution of excess bromine (in CCl_4) was added to a solution of 1,10-*bis*-(p-ethoxyphenyltelluro)decane in benzene, and the mixture was shaken for three days. The yellow precipitate was separated by filtering and was washed with CCl_4 and C_6H_6 and dried in vacuo. m.p. 157-159°C (dec). Yield 40%.

Found	C 13.3	H 1.50%
$C_{10}H_{20}Te_2Br_6$ requires	C 13.7	H 2.30%

4.3 Results

All the bis-telluride ligands considered in this Chapter are soluble in common organic solvents. They are insoluble in acetonitrile, methanol, ethanol and petroleum ether. The bromo-derivatives of the ligands are insoluble in chloroform, benzene, ethanol and ether. They are soluble in dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The telluronium salt is soluble in water, chloroform, ethanol, DMF and DMSO. The conductivity measurements indicate that 1-bromo-1-p-ethoxyphenyltelluracyclohexane is a weak electrolyte (Figure 4.1) in distilled water and all the bistellurides are non-electrolytes in DMF (Table 4.3).

Compound	Found%		Required%	
	C	H	C	H
AtTe.$(CH_2)_5$.Br	40.0	4.70	39.1	4.80
ArTe.$(CH_2)_5$.TeAr	44.2	4.30	44.4	4.90
ArTe.$(CH_2)_6$.TeAr	45.5	5.30	45.4	5.20
ArTe.$(CH_2)_7$.TeAr	46.5	5.50	46.4	5.40
ArTe.$(CH_2)_9$.TeAr	47.8	5.90	48.1	5.80
ArTe.$(CH_2)_{10}$.TeAr	49.4	6.10	49.0	6.00

Table 4.1 The elemental analyses of *bis*-tellurides and the telluronium salt

Compound	Found%		Required%	
	C	H	C	H
Br_3Te.$(CH_2)_6$.TeBr_3	9.1	1.30	8.8	1.50
Br_3Te.$(CH_2)_{10}$.TeBr_3	13.3	1.50	13.7	2.30

Table 4.2 The elemental analyses of bromo-derivatives of *bis*-tellurides

Compound	Molar Conductivity $ohm^{-1}cm^{2}mol^{-1}$	Solvent
$ArTe.(CH_2)_5.Br$	99.3)	(H_2O
	)	(
	61.2)	(DMF
$ArTe.(CH_2)_5.TeAr$	4.1	DMF
$ArTe.(CH_2)_6.TeAr$	1.7	DMF
$ArTe.(CH_2)_7.TeAr$	3.9	DMF
$ArTe.(CH_2)_9.TeAr$	3.2	DMF
$ArTe.(CH_2)_{10}.TeAr$	2.5	DMF

Table 4.3 Molar conductivities of new organotellurium compounds

Compound	Chemical shift[a]	
	aromatic region	aliphatic region
$ArTe.(CH_2)_5.Br$	6.75(d) ,7.7(d) ;J(AB)=8.66Hz	4.0 (q),2.8 (t),1.5(m)
$ArTe.(CH_2)_5.TeAr$	6.8 (d) ,7.7(d) ;J(AB)=8.66Hz	4.08(q),2.8 (t),1.5(m)
$ArTe.(CH_2)_6.TeAr$	6.75(d) ,7.7(d) ;J(AB)=8.66Hz	4.0 (q),2.8 (t),1.5(m)
$ArTe.(CH_2)_7.TeAr$	6.65(d) ,7.7(d) ;J(AB)=8.66Hz	4.0 (q),2.75(t),1.5(m)
$ArTe.(CH_2)_9.TeAr$	6.8 (d) ,7.7(d) ;J(AB)=8.66Hz	4.0 (q),2.85(t),1.5(m)
$ArTe.(CH_2)_{10}.TeAr$	6.8 (d) ,7.7(d) ;J(AB)=8.66Hz	4.0 (q),2.85(t),1.5(m)
$Br_3Te.(CH_2)_6.TeBr_3$	-	2.5 (s),2.1 (s).1.4(s)

a-chemical shifts measured in ppm relative to Me_4Si

(d)-doublet, (q)-quadruplet, (t)-triplet, (m)-multiplet, (s)-singlet

Table 4.4 ^1H N.M.R. spectra of new organotellurium compounds

Compound	Chemical shift			
	ipso	ortho	meta	para
$ArTe.(CH_2)_5.Br$	?	137.1	115.4	159.9
$ArTe.(CH_2)_5.TeAr$	96.1	141.0	115.6	159.1
$ArTe.(CH_2)_6.TeAr$	100.2	140.9	115.5	159.0
$ArTe.(CH_2)_7.TeAr$	100.6	141.1	115.8	159.3
$ArTe.(CH_2)_9.TeAr$	100.5	140.9	115.6	?
$ArTe.(CH_2)_{10}.TeAr$	100.3	140.8	115.5	159.0

Table 4.5 ^{13}C N.M.R. spectra of (aromatic region) new organotellurium compounds

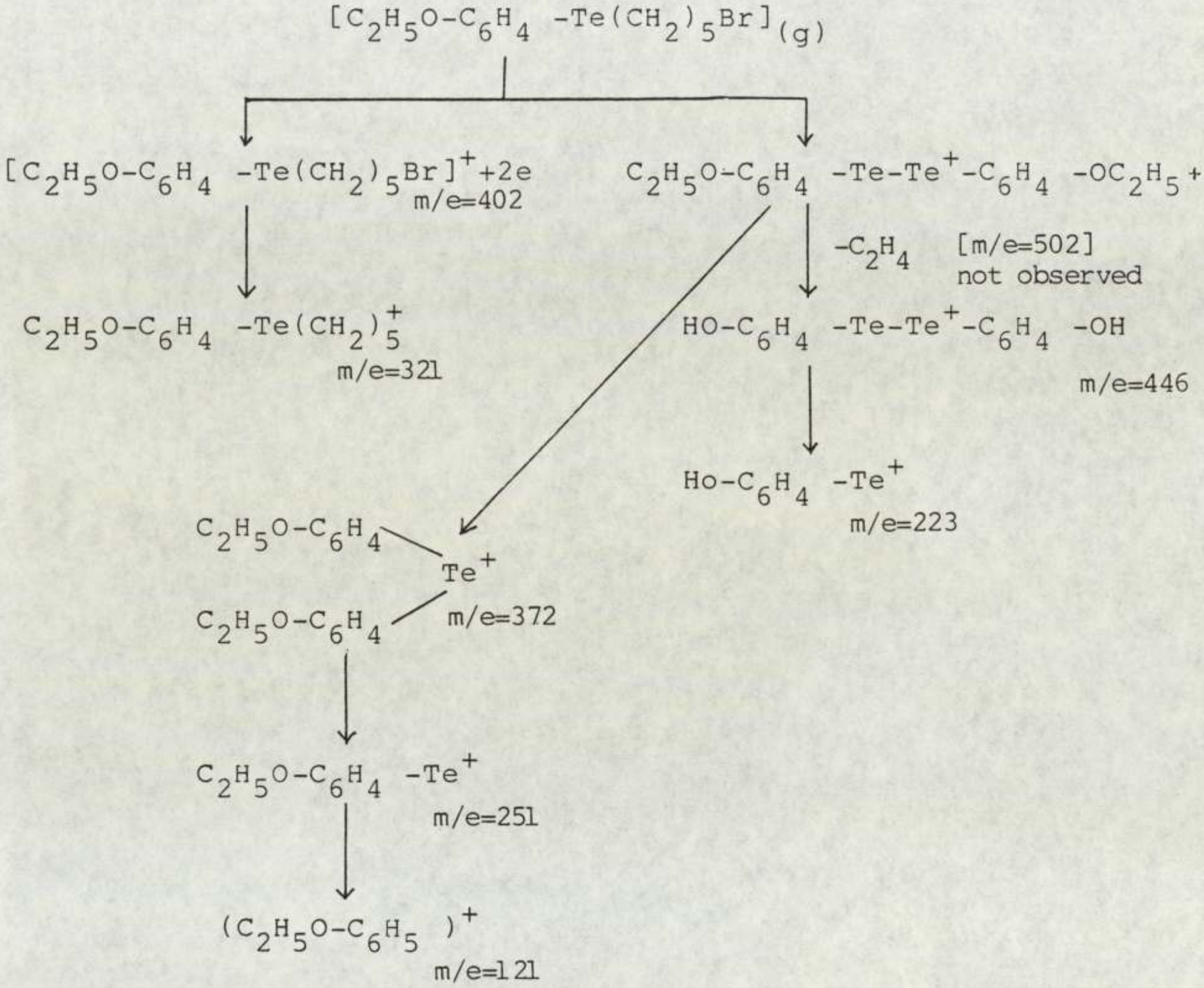
Compound	Chemical shift$^{a(b)}$						
	C-1	C-2	C-3	C-4	C-5	$-OCH_2$	$-CH_3$
$ArTe.(CH_2)_5.Br$	27.5	26.3	21.3			63.3	14.9
$Br_3Te.(CH_2)_6.TeBr_3$	59.7	29.8	27.0				
$ArTe.(CH_2)_5.TeAr$	8.7 (13.5)	31.0 (22.2)	34.0 (34.1)			63.4	14.9
$ArTe.(CH_2)_6.TeAr$	8.8 (13.7)	31.0 (22.7)	31.4 (31.7)			63.3	14.8
$ArTe.(CH_2)_7.TeAr$	9.1 (13.7)	29.1 (22.6)	31.9 (32.0)	29.7 (29.0)		63.6	14.9
$ArTe.(CH_2)_9.TeAr$	9.1 (13.8)	28.8 (22.7)	31.8 (32.0)	29.0 (29.4)	? (29.6)	63.4	14.8
$ArTe.(CH_2)_{10}.TeAr$	9.0 (13.9)	28.8 (22.8)	31.8 (32.3)	29.4 (29.7)	29.6 (30.1)	63.3	14.7

a-Chemical shifts measured in ppm relative to Me_4Si internal standard.
(b)- Chemical shifts (ppm) reported$^{(106-108)}$ for n-alkanes (relative to Me_4Si internal standard)

$$(ArTe-\underset{1}{CH_2}-\underset{2}{CH_2}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{CH_2})_2$$

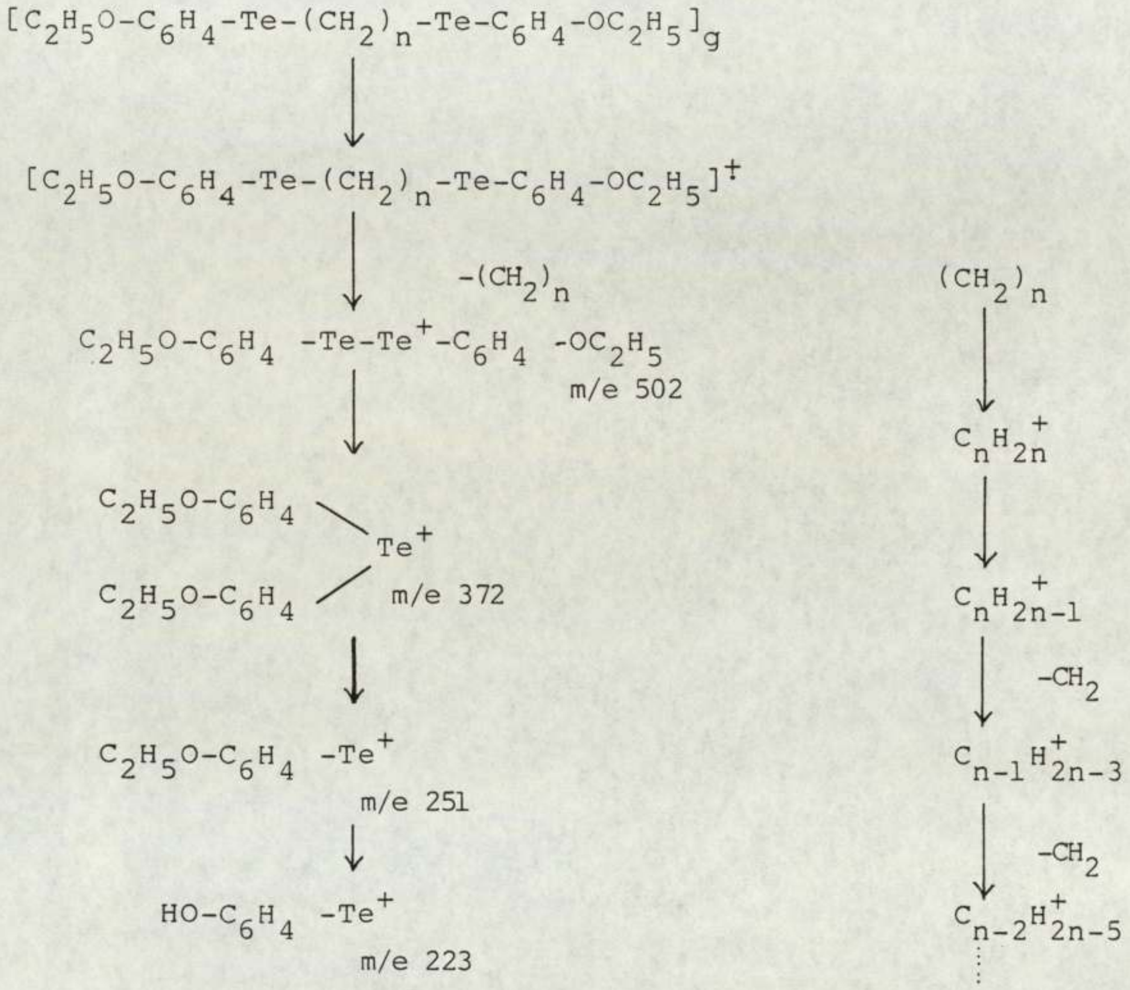
Number system used to designate individual carbon atoms in the methylene backbone of the ligands

Table 4.6 ^{13}C N.M.R. spectra of (aliphatic region) new organotellurium compounds



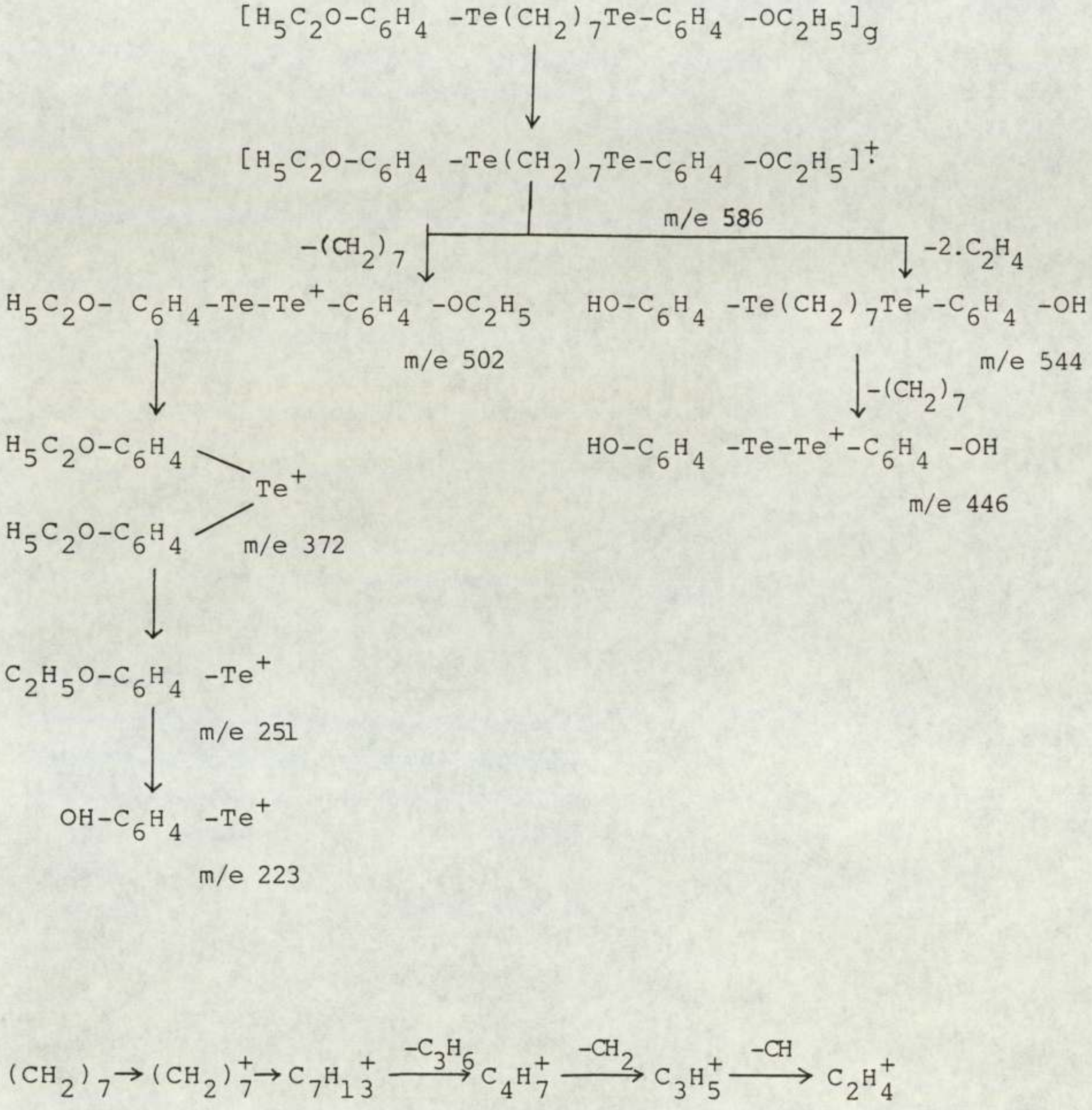
Scheme 4.1 Mass fragmentation pattern* of $\mathrm{Ar}\overline{\mathrm{Te(C}}\mathrm{H_2)_5Br}$

* Quoted m/e values are referenced to $^{130}\mathrm{Te}$, $^{81}\mathrm{Br}$, $^{12}\mathrm{C}$, $^{1}\mathrm{H}$ and $^{16}\mathrm{O}$.



Scheme 4.2 Typical mass fragmentation pattern* for $ArTe(CH_2)_nTeAr$, n=5,6,9,10

* Quoted m/e values are referenced to ^{130}Te, ^{12}C, ^{1}H and ^{16}O.



Scheme 4.3 Mass fragmentation pattern* for ArTe(CH$_2$)$_7$TeAr

* Quoted m/e values are referenced to ^{130}Te, ^{12}C, ^{1}H and ^{16}O.

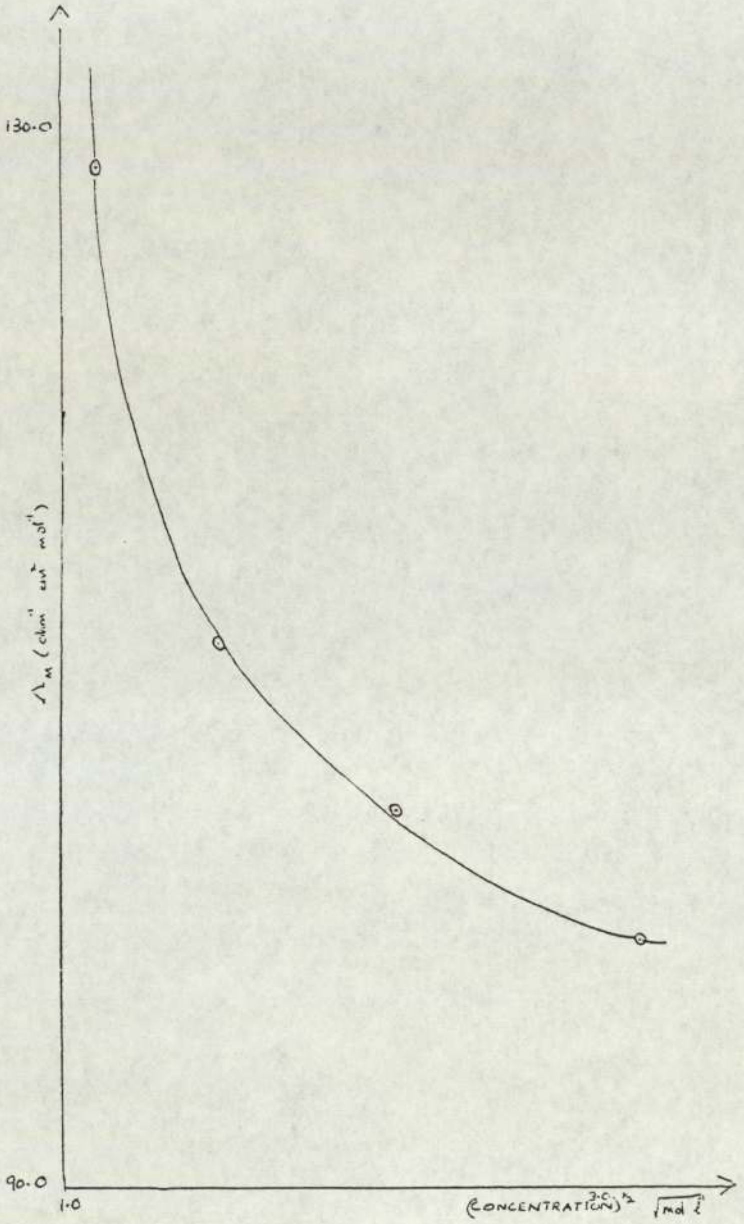


Figure 4.1 Conductivity of $\mathrm{Ar\overline{Te(CH}_2)_5Br}$ in DMF

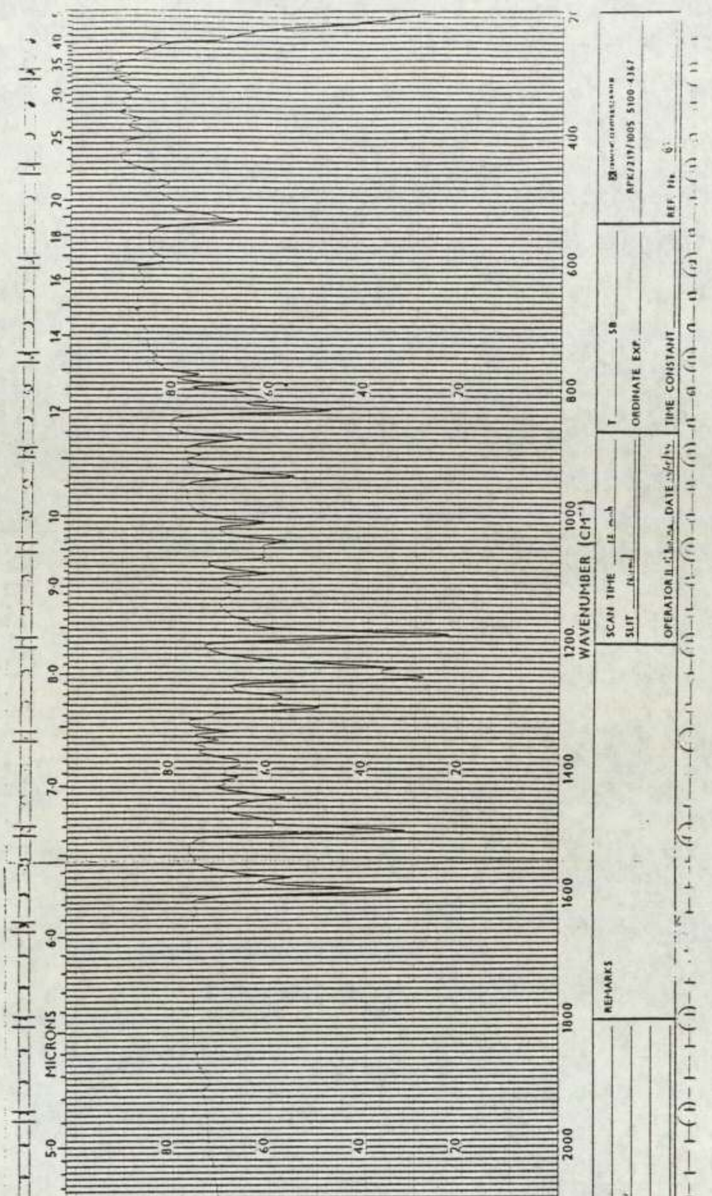
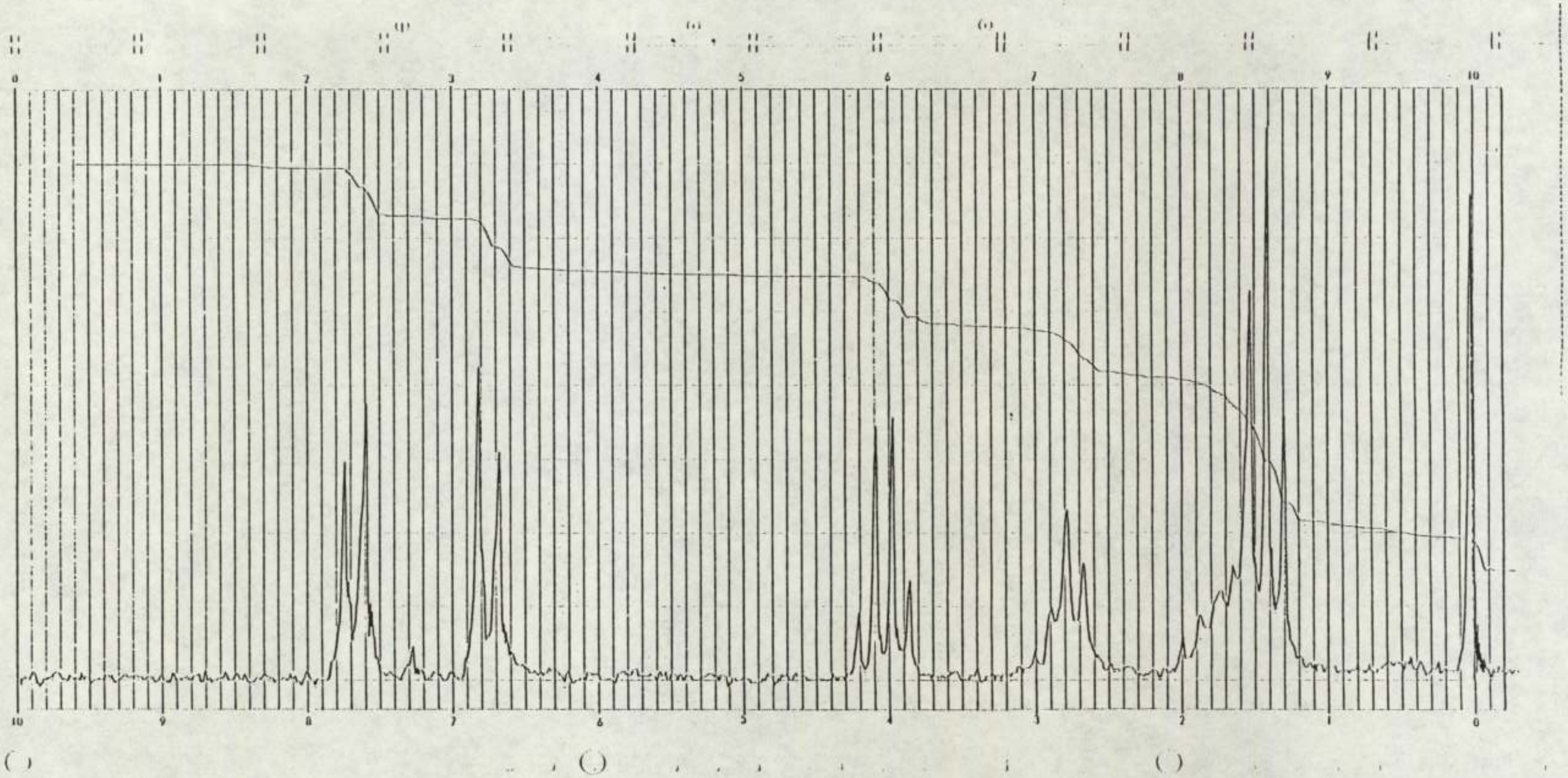


Figure 4.2 I.R. spectrum of $\mathrm{Ar\overline{Te(CH_2}})_5\mathrm{Br}$



<u>Figure 4.3</u> ^{1}H N.M.R. spectrum of $\mathrm{ArTe(CH_2)_5Br}$

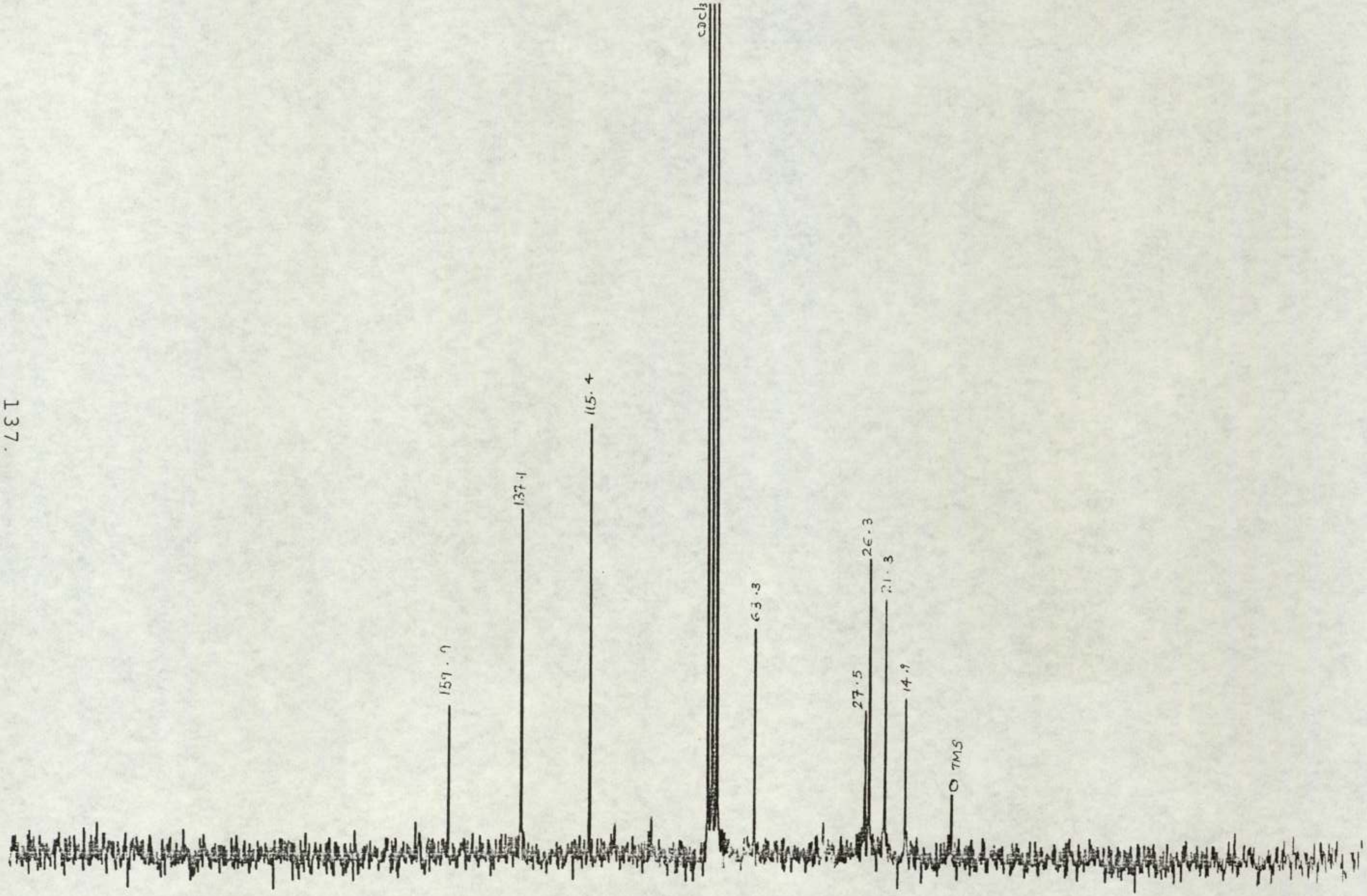


Figure 4.4 $\{^1H\}$ ^{13}C N.M.R. spectrum of $ArTe(CH_2)_5Br$

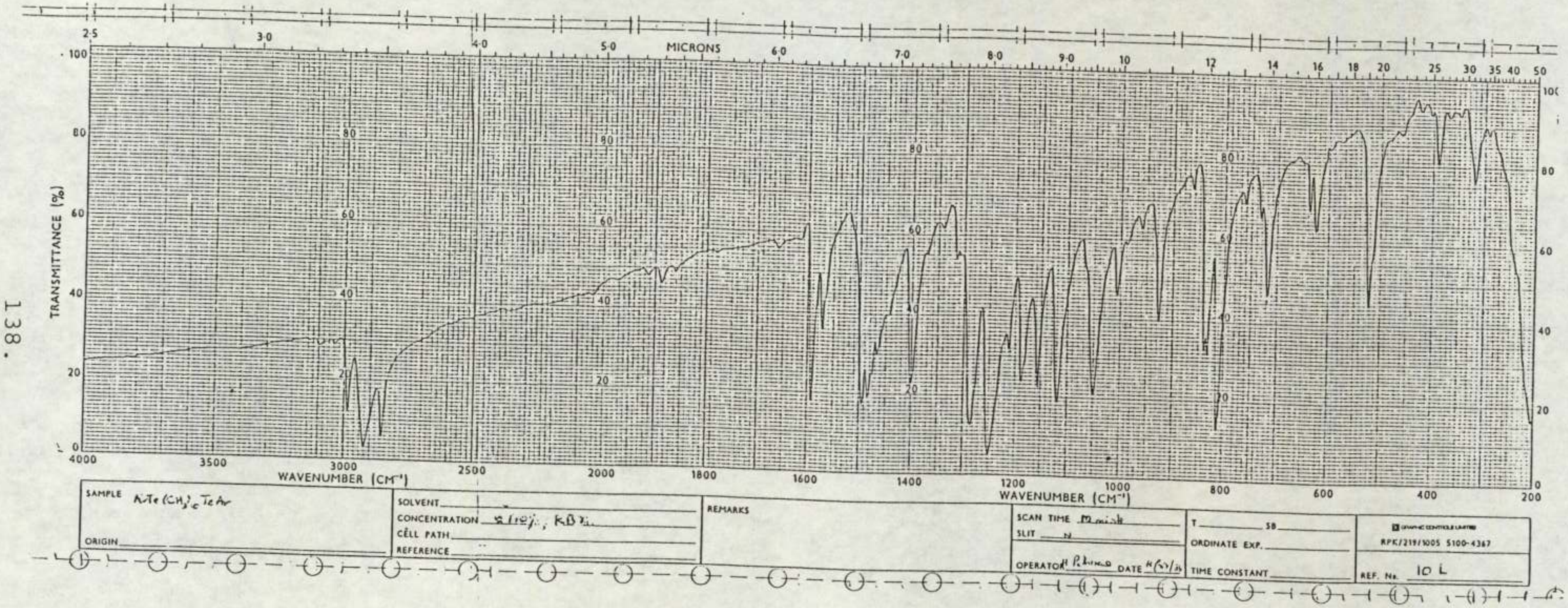


Figure 4.5 I.R. spectrum of $ArTe(CH_2)_{10}TeAr$

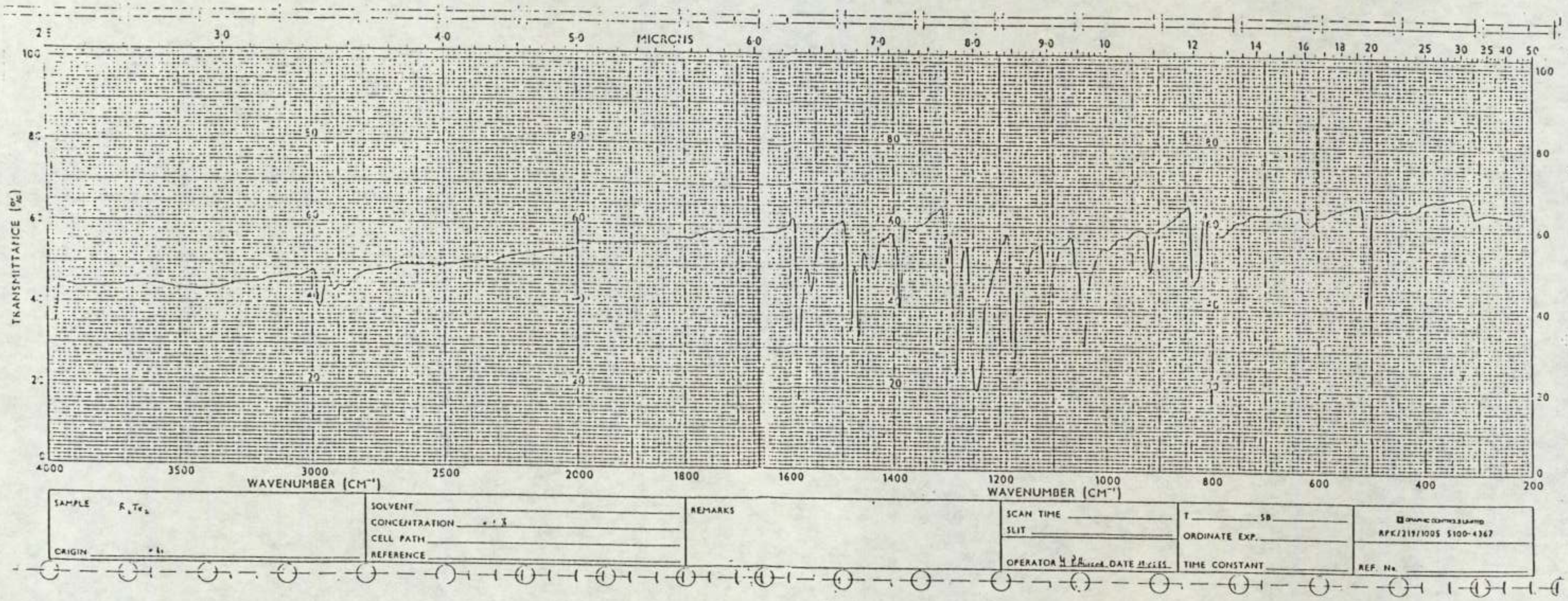


Figure 4.6 I.R. spectrum of Ar_2Te_2

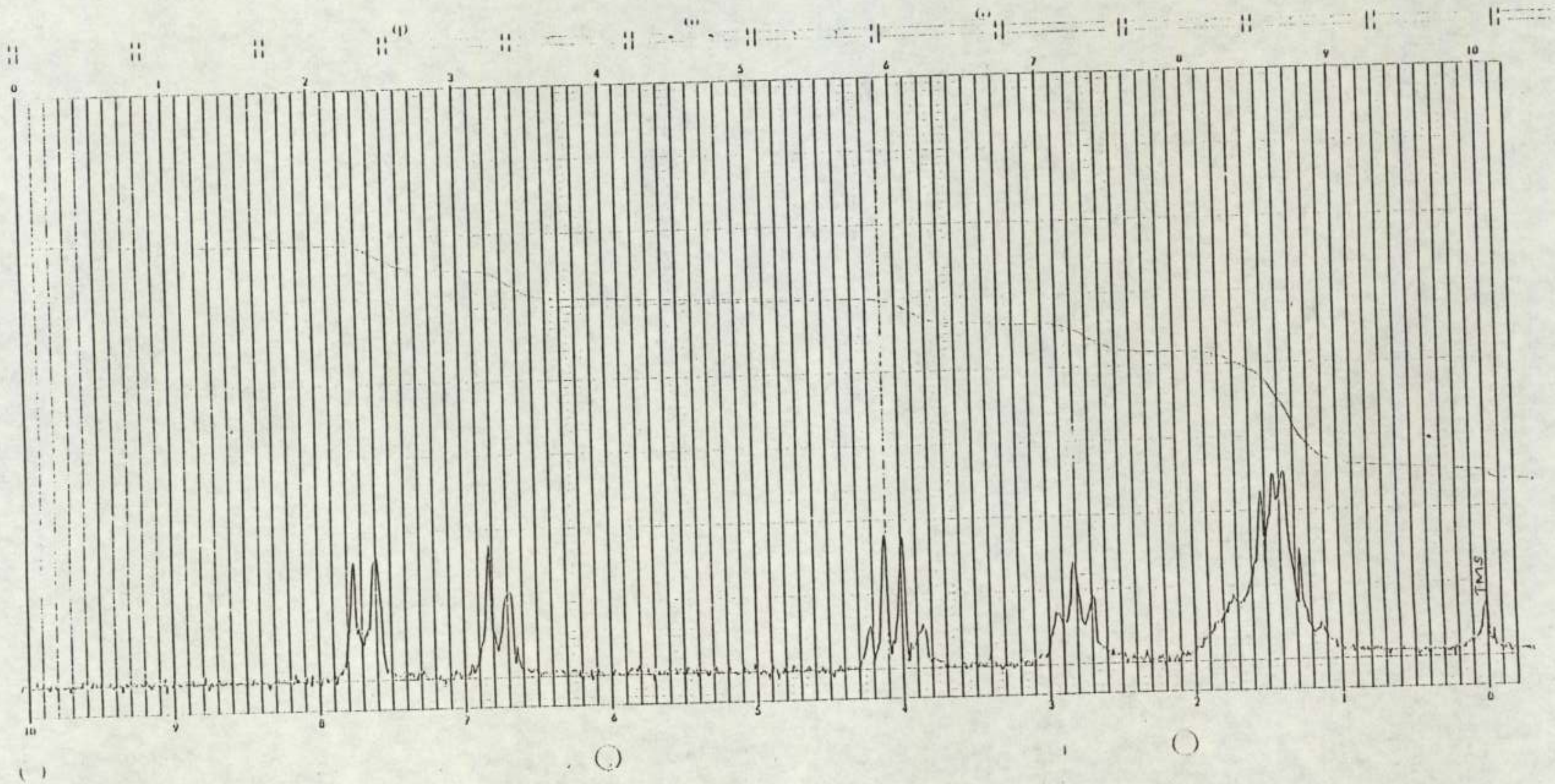


Figure 4.7 ^{1}H N.M.R. spectrum of $ArTe(CH_2)_6TeAr$

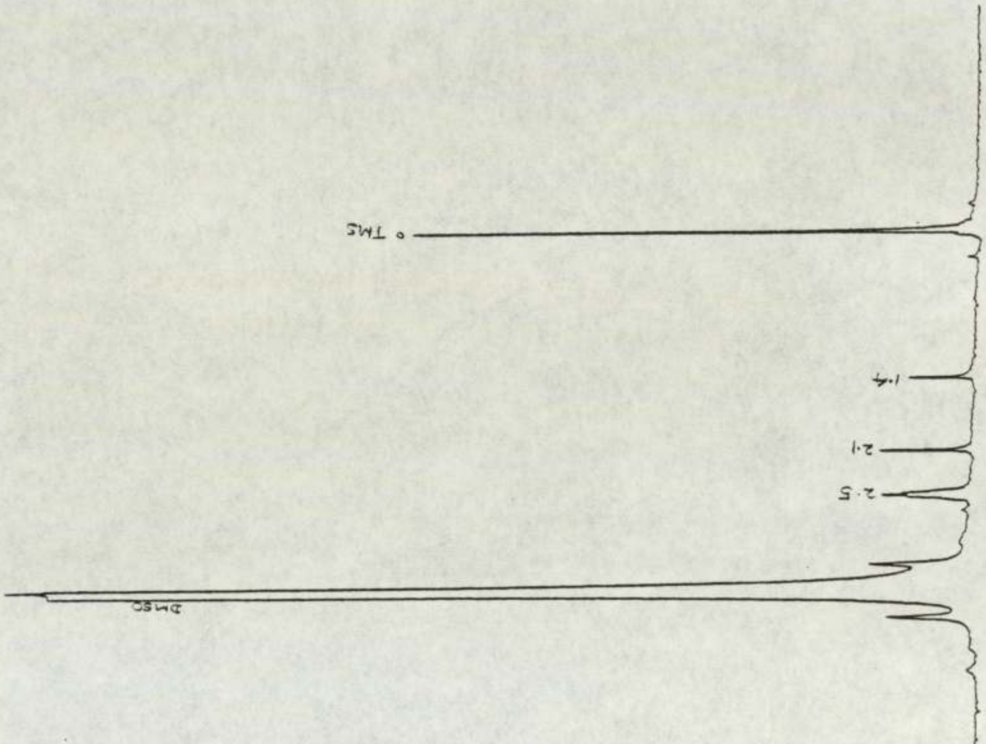
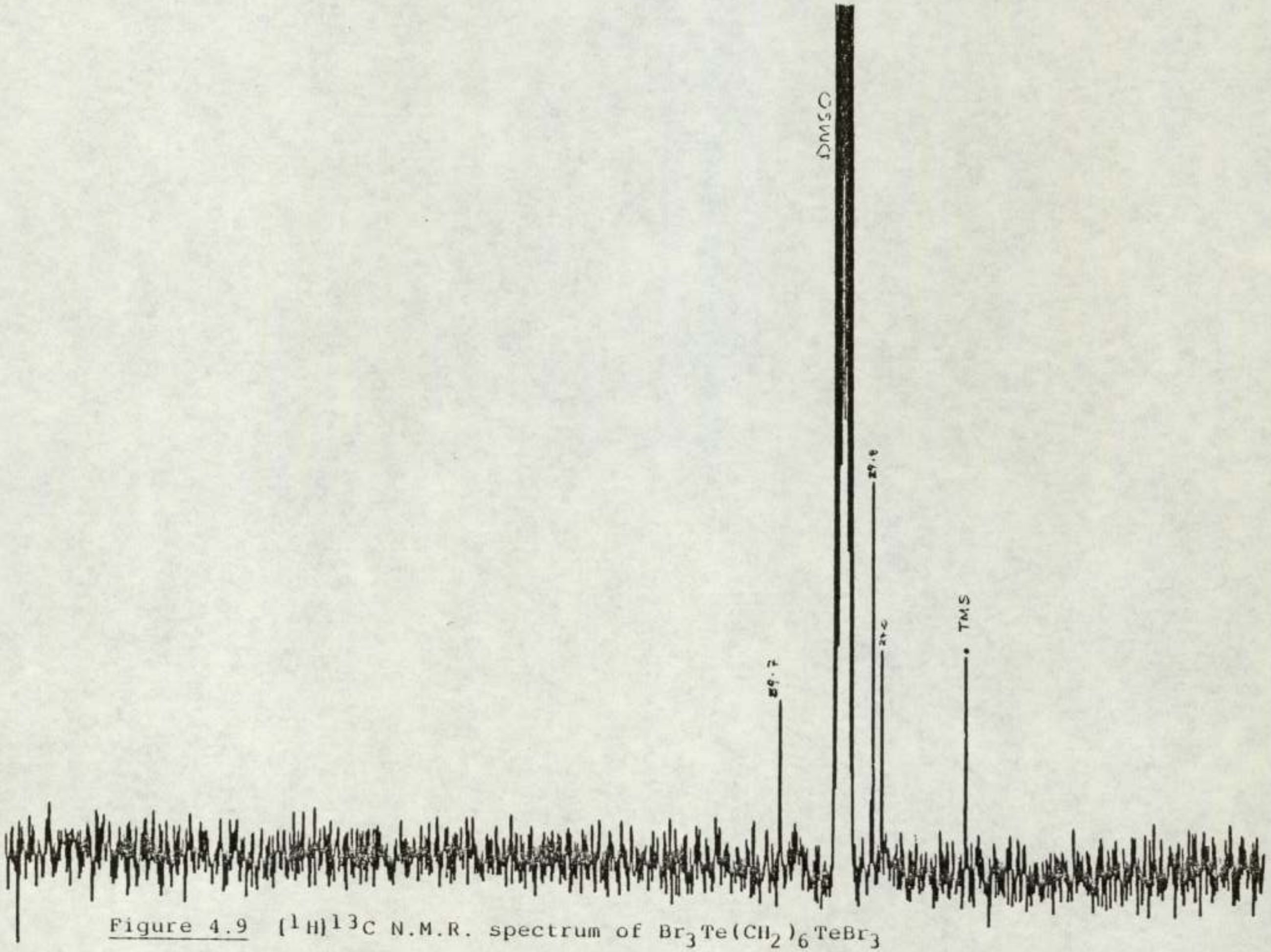
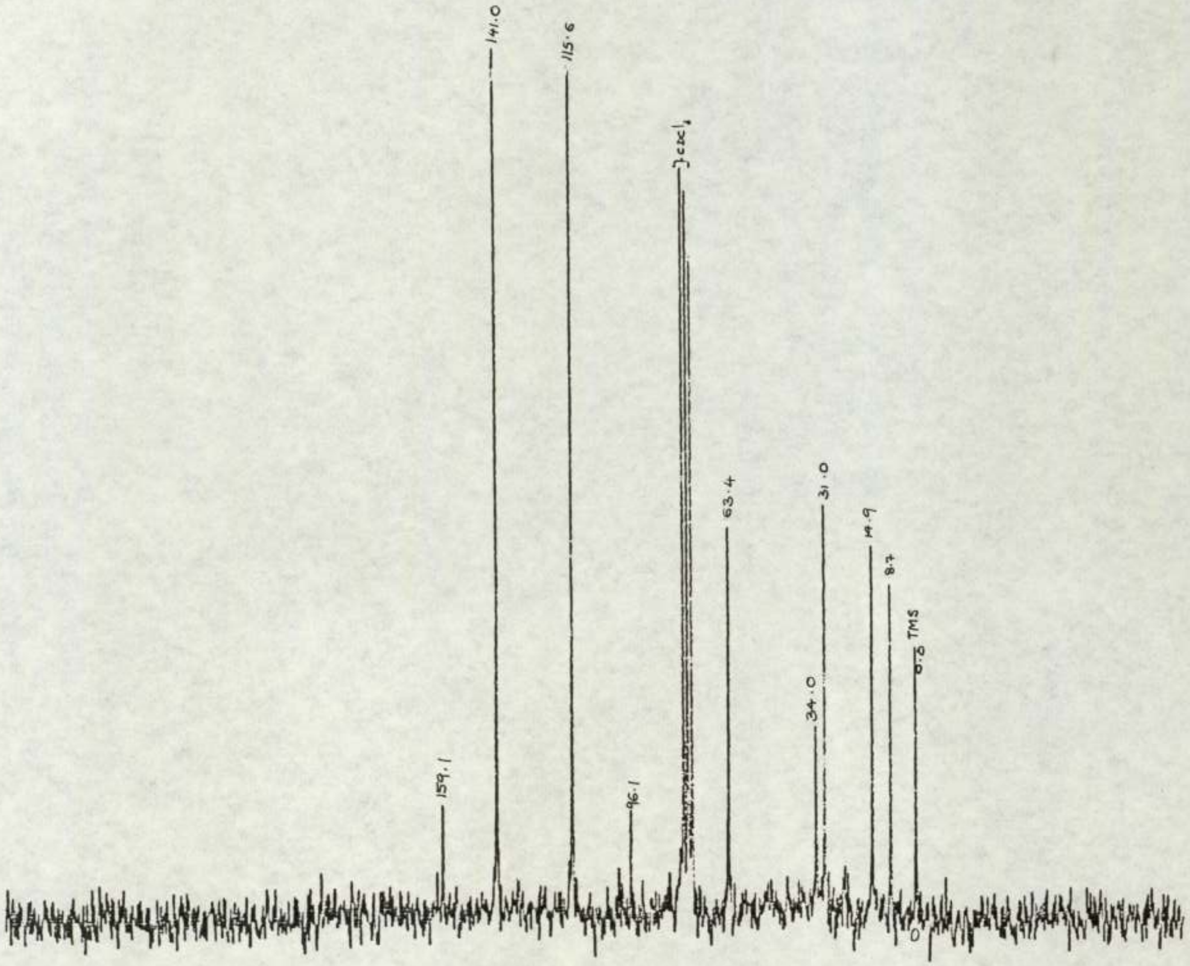


Figure 4.8 ^{1}H N.M.R. spectrum of $Br_3Te(CH_2)_6TeBr_3$



<u>Figure 4.9</u> $\{^{1}H\}^{13}C$ N.M.R. spectrum of $Br_3Te(CH_2)_6TeBr_3$



<u>Figure 4.10(a)</u> $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTe(CH_2)_5TeAr$

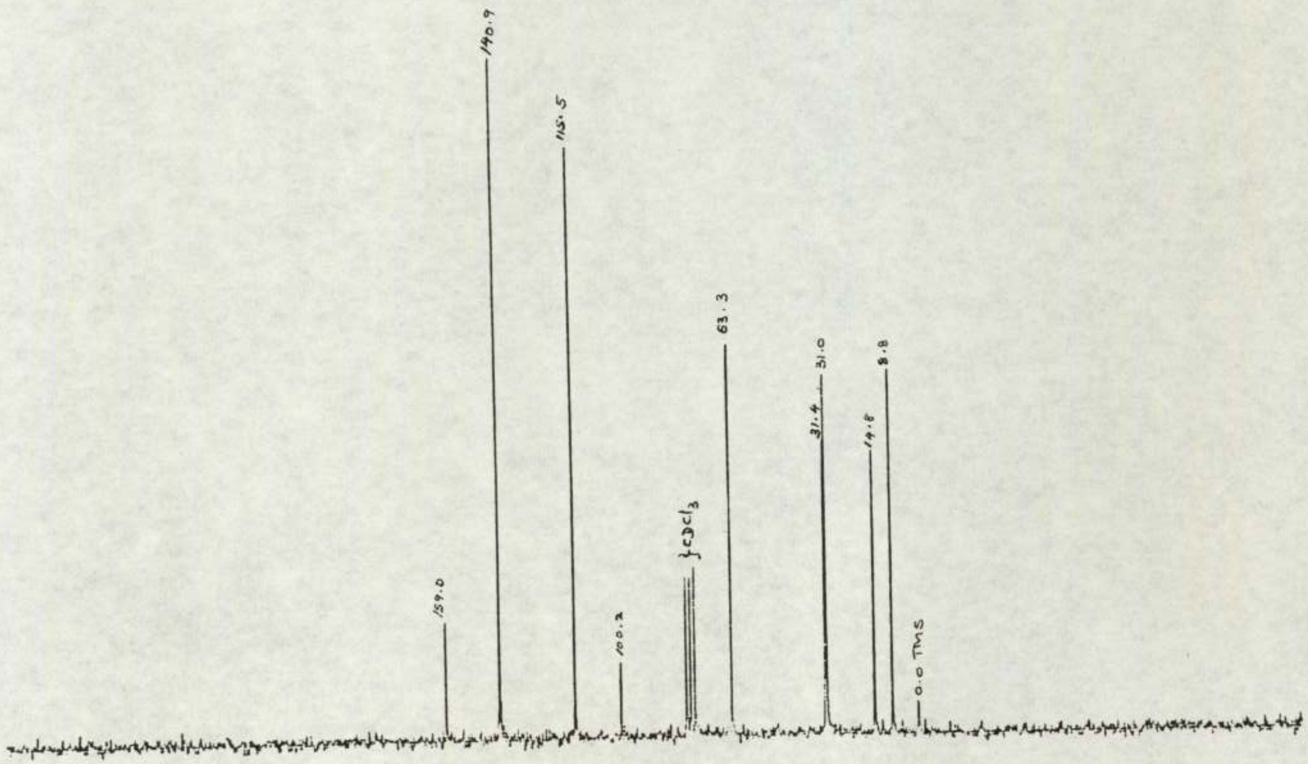


Figure 4.11(a) $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTe(CH_2)_6TeAr$

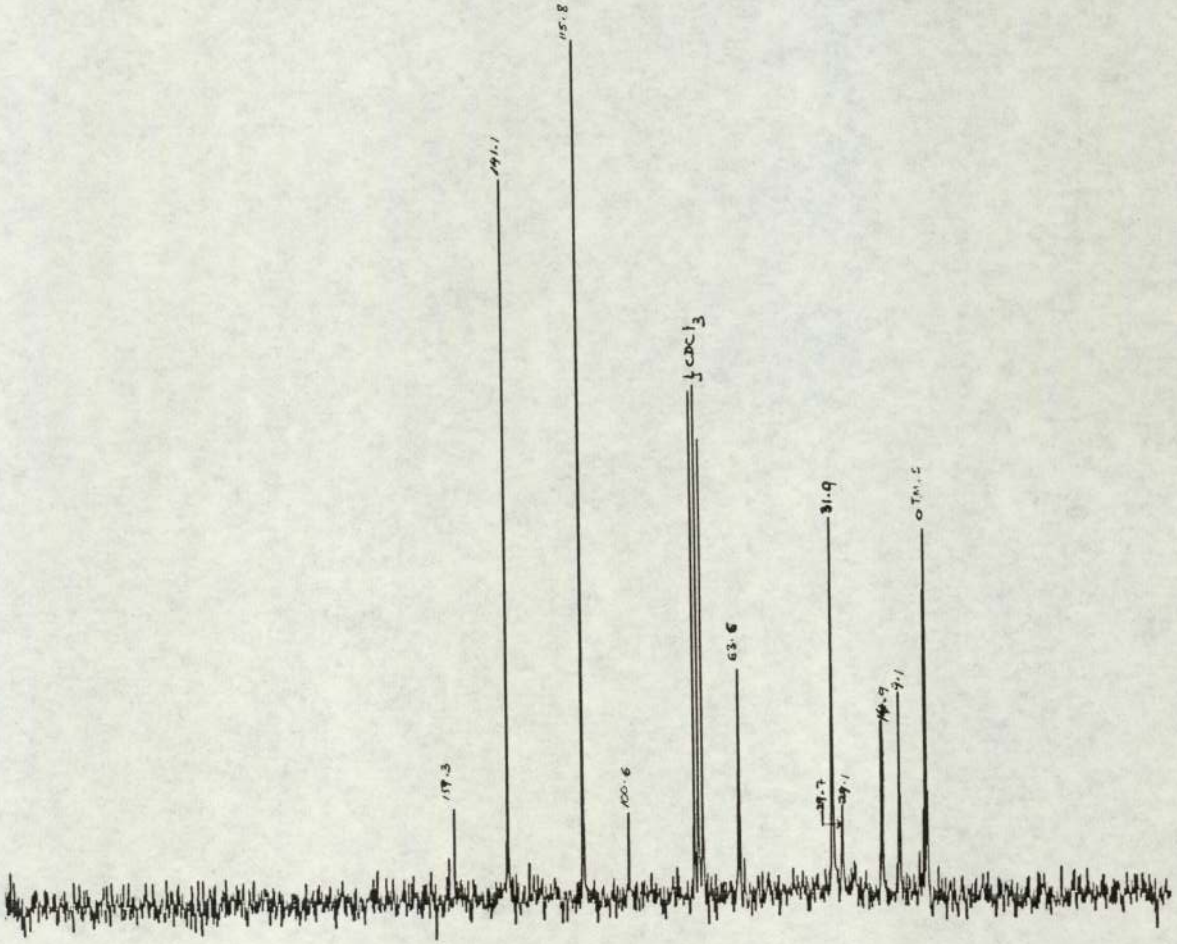


Figure 4.12(a) $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTe(CH_2)_7TeAr$

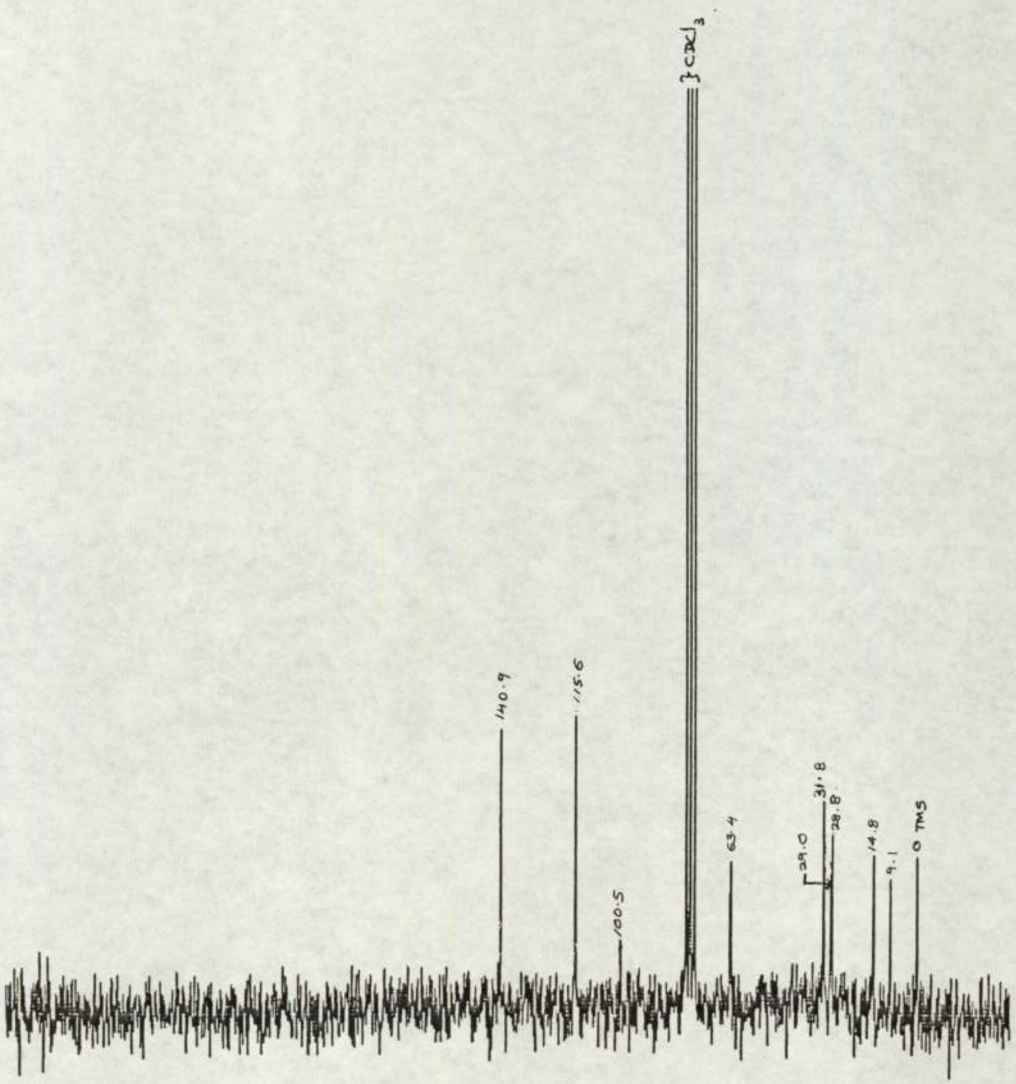


Figure 4.13 $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTe(CH_2)_9TeAr$

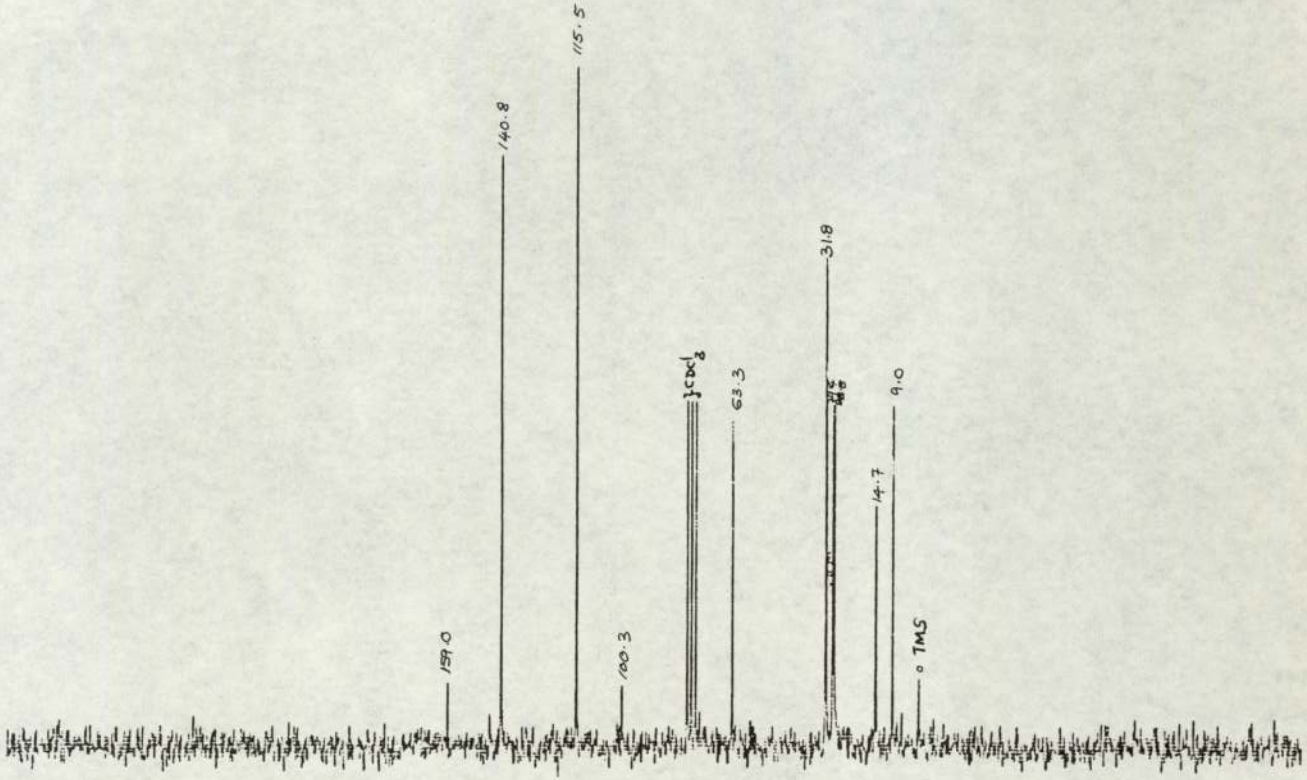
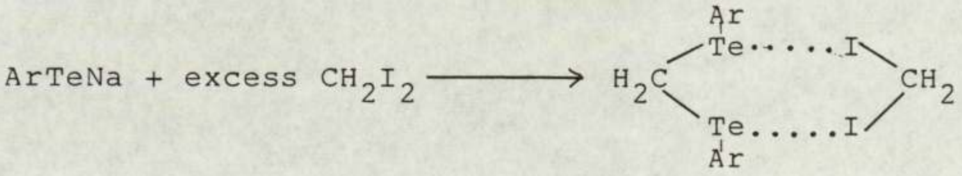


Figure 4.14 $\{^1H\}^{13}C$ N.M.R. spectrum of $ArTe(CH_2)_{10}TeAr$

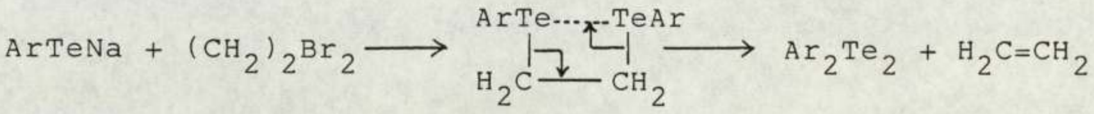
4.4 Discussion

The reaction product of ArTeNa with 1,n-dihaloalkanes depends on the length of the alkane chain. As explained in Chapter Three, bis-(p-ethoxyphenyltelluro)methane is formed in the reaction of ArTeNa with diiodomethane in 2:1 molar ratio. In the presence of excess diiodomethane, a charge transfer complex is formed and there is no possibility of internal quaternisation(50).

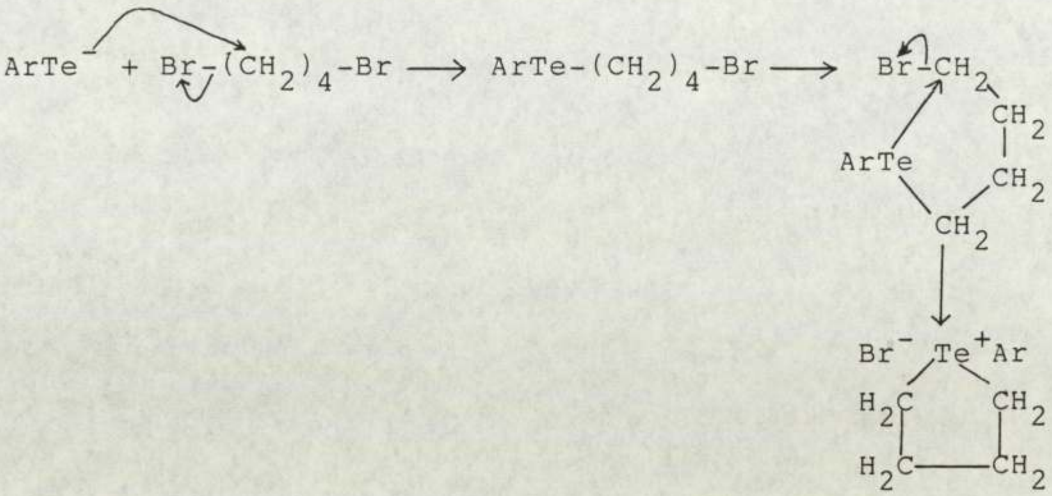
$$2ArTeNa + CH_2I_2 \longrightarrow ArTeCH_2TeAr$$



The reaction of ArTeNa with dibromoethane seems to proceed, but the product is unstable resulting in ditelluride elimination(50).

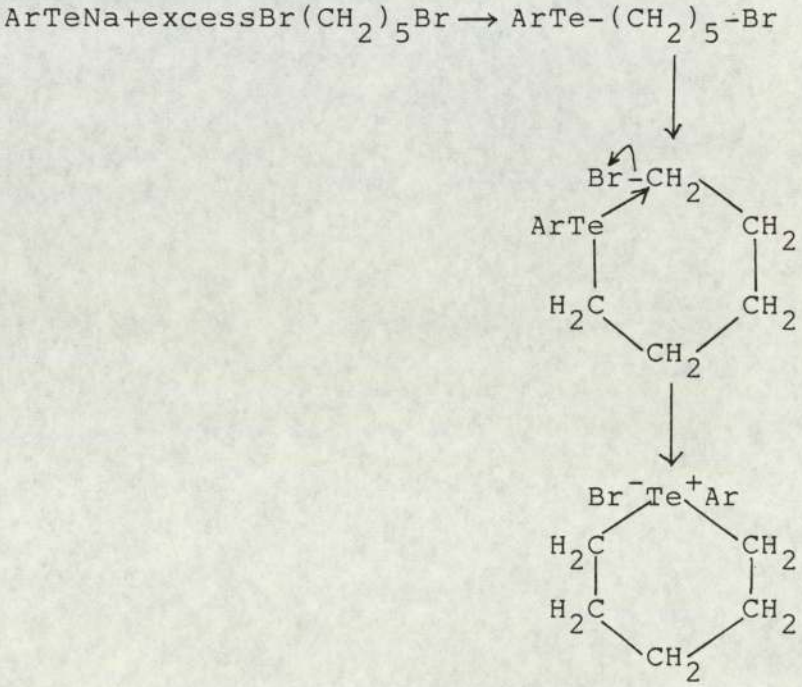


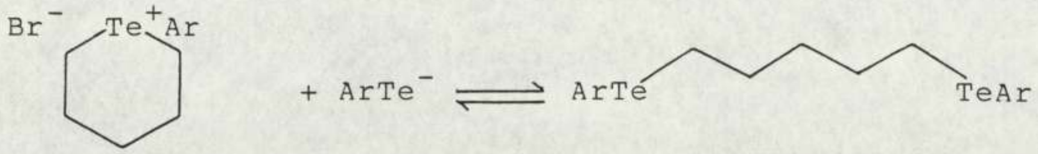
When n=3 or 4, in $Br(CH_2)_nBr$, the nucleophilic attack by $ArTe^-$ has taken place, but kinetically more favourable internal quaternisation then proceeds more rapidly than attack at the second C-Br bond by further $ArTe^-$. As a result, a polymer or a five-membered ring is formed for n=3 and n=4 respectively(50).



The phenomenon of internal quaternisation led us to examine this reaction with the increase of the alkane chain length of the dihaloalkane. In the one case of 1,5-dibromopentane both the formation of the telluronium salt and the bis-telluride are found to be possible and the product obtained depends on the experimental conditions.

(i)



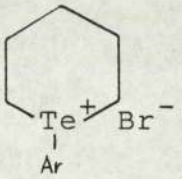
(ii) 

When the alkane chain contains 6, 7, ...etc., methylene groups, internal quaternisation is not kinetically favoured because of the unfavourable ring size. Therefore only the bis- telluride is formed.

These new bidentate tellurium ligands were characterised as follows.

4.4.1 Characterisation Of 1-Bromo-1-p-ethoxyphenyltelluracyclohexane

The elemental analysis suggests that the reaction of ArTeNa with excess 1,5-dibromopentane results in the formation of $ArTe(CH_2)_5Br$ (Table 4.1). The conductivity data in DMF and water show ionic character (Table 4.3), but the concentration dependence of the data indicate considerable ion pairing in DMF (Figure 4.1). The explanation for the conducting behaviour of $ArTe(CH_2)_5Br$ is its telluronium salt like structure.



The mass spectrum of the compound shows a parent ion at m/e=402, which indicates association in the gas phase. The fragmentation pattern is very similar to that earlier reported for $\mathrm{Ar\overline{Te(C}H_2)_4Br}$(50) (Scheme 4.1). The ^1H N.M.R. spectrum in $CDCl_3$ exhibits a quadruplet, a triplet and a multiplet centred at $\delta = 4.0$, 2.8 and 1.5ppm which are assignable to protons of $-OCH_2$ group, $-CH_3$ group and the $-CH_2$ backbone respectively. The aromatic protons give, as expected, an AB spectrum with $\delta = 6.85$ and 7.7ppm and $J(AB) = 8.66$Hz (Figure 4.3). The $\{^1H\}^{13}C$ N.M.R. spectrum is inconsistent with an open-chain structure, $ArTe(CH_2)_5Br$, for which extra carbon resonances would be expected, and is assigned following the literature(50,77) for $\mathrm{Ar\overline{Te(C}H_2)_4Br}$ (Tables 4.5 and 4.6, Figure 4.4). Al-Rubaie <u>et al</u> have synthesised $\mathrm{Ar\overline{Te(C}H_2)_4Br}$ very recently using a different method(77).

Thus, the most acceptable formulation of the product is as a telluronium salt derived from 1-telluracyclohexane. Therefore, nucleophilic attack on 1,5-dibromopentane by $ArTe^-$ has taken place, but quaternisation then has proceeded more rapidly than attack at the second C-Br bond by further $ArTe^-$.

4.4.2 Characterisation Of New *Bis*-telluride Ligands

The elemental analyses suggest that the reaction of ArTeNa with $Br(CH_2)_nBr$, n=5, 6, 7, 9, 10, in a 2:1 molar ratio results in the corresponding *bis*-tellurides having the molecular formula $ArTe(CH_2)_nTeAr$ (Table 4.1). This inference is supported by the electrical conductivity of $1 \times 10^{-3}M$

solutions in DMF (Table 4.3). All these bis-tellurides are non-electrolytes.

The infra-red spectra of all the bis-tellurides exhibit bands characteristic of the alkane chain and of the aryl groups. No bands were observed which could be assigned to ν(C-Br) (Figure 4.5). The mass spectra of all ligands were examined to see if the variation in backbone length exerted any marked effect upon the fragmentation patterns. A comparison of mass spectra of all $ArTe(CH_2)_nTeAr$ ligands reveals that the elimination of the alkane backbone is a characteristic of this type of ligand. This idea is supported by the presence of the series of ions found at low m/e corresponding to the normal fragments derived from the alkane backbone. The major tellurium peaks are as expected $(p\text{-}EtO.C_6H_4)_2Te^+$, $(p\text{-}EtO.C_6H_4)Te^+$ and $(p\text{-}HO.C_6H_4)Te^+$. There is no marked effect on the spectra with variation of the backbone length. The fragmentation pattern typical of a bis-telluride is illustrated in Scheme 4.2.

Instead of exhibiting this fragmentation pattern, $ArTe(CH_2)_7TeAr$ clearly exhibits another fragmentation route (Scheme 4.3). Here, the first step is the formation of $(p\text{-}HO.C_6H_4Te^+)_2(CH_2)_7$ due to the successive loss of two C_2H_4 molecules from the parent ion. Then, elimination of the alkane backbone results in $(p\text{-}HO.C_6H_4)_2Te_2^+$. The presence of the series of ions at low m/e corresponding to the fragments derived from the alkane backbone supports this idea also (Scheme 4.3).

These fragmentation patterns cannot be confirmed because of the absence of metastable ions in the mass spectra. However, the elimination of the backbone to give $Ph_2EEPh_2^+$ has been observed in the mass spectra of alkane backboned di-Group VB donor ligands (E=P, As, etc.)$^{(102,103)}$.

The ^1H N.M.R. spectra of all the *bis*-tellurides were recorded using $CDCl_3$ as the solvent and were assigned (Table 4.4) as described in the case of $\text{Ar}\overline{\text{Te(C}}\text{H}_2\text{)}_5\text{Br}$. A ^1H N.M.R. spectrum typical of a *bis*-telluride is given in Figure 4.7. The integrated intensities are in agreement with those expected for each ligand.

The reaction of the *bis*-aryltelluroalkanes with excess bromine led to rupture of the Te-aryl linkage and resulted in *bis*-tribromotelluroalkanes (Table 4.2). The infra-red, ^1H and $\{^1H\}^{13}C$ N.M.R. spectra of this product indicate the absence of the aromatic group. The ^1H and $\{^1H\}^{13}C$ N.M.R. spectra clearly give evidence for the presence of the alkane backbone in *bis*-tribromotelluroalkane (Figures 4.8 and 4.9)

i.e., $ArTe(CH_2)_6TeAr + \text{excess } Br_2 \longrightarrow Br_3Te(CH_2)_6TeBr_3$

The co-ordination requirements of the tellurium atoms may be satisfied by their mutual interaction via bromo-bridges as explained for $C_6H_{10}Te_2Br_2$ by Hazell(104).

The most useful data for the characterisation of these bis-telluroalkanes are the $\{^1H\}^{13}C$ N.M.R. spectra (Tables 4.5 and 4.6, Figures 4.10(a)-4.14) . These spectra can be divided into two distinct regions:-

1. the aromatic region,
2. the aliphatic region.

The aromatic region shows resonances for the ortho-, meta-, para-, and ipso- carbons of the phenyl group. The para- and ipso- carbons do not possess a directly bound hydrogen atom and the peaks are of low intensity. The $\{^1H\}^{13}C$ resonances in the aromatic region are assigned following the literature(50,73).

The aliphatic region contains $\{^1H\}^{13}C$ resonances assignable to $-OCH_2$, $-CH_3$ and -methylene backbone carbon nuclei. The chemical shifts observed for $-OCH_2$ and $-CH_3$ carbon atoms are in good agreement with values found in the literature(50).

The assignment of the $\{^1H\}^{13}C$ resonances of the alkane chain backbones of bis-(diphenylphosphino)alkanes have been made by using the values of C-P coupling constants and by comparing with the spectra of corresponding diarsines(105).

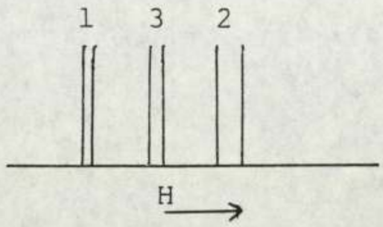


Figure (a): schematic representation of the aliphatic region of the $\{^1H\}^{13}C$ N.M.R. spectra of bis-(diphenylphosphino)hexane(105)

$Ph_2P\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2PPh_2$

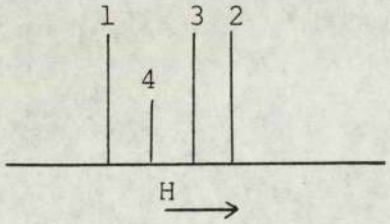


Figure (b): schematic spectrum for bis-(diphenylarsino) heptane(105)

$Ph_2As\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_2\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}H_2AsPh_2$

Although the 100% natural abundance of ^{31}P has resulted in ^{13}C-^{31}P coupling in $\{^1H\}^{13}C$ N.M.R. spectra of $Ph_2P(CH_2)_nPPh_2$, the 7% natural abundance of ^{125}Te did not allow observation of C-Te coupling in the $\{^1H\}^{13}C$ N.M.R. of these new bis-telluroalkanes. The absence of ^{13}C-^{125}Te coupling in spectra of these bis-tellurides, and the lack of data in the literature, gave difficulties in assigning the $\{^1H\}^{13}C$ resonances of alkane chain backbones. To overcome this problem, a comparison of $\{^1H\}^{13}C$ resonances of $ArTe(CH_2)_6TeAr$ with those of $Br_3Te(CH_2)_6TeBr_3$ was used. The $\{^1H\}^{13}C$ resonance which was observed at the highest field ($\delta \approx 8.7$ppm) in <u>bis</u>-tellurides (Table 4.6) have shifted down field ($\delta = 59.7$ppm) in $Br_3Te(CH_2)_6TeBr_3$ (Figure 4.9). The withdrawal of electron density from the tellurium atom by bromine may cause this down field shift. Therefore, the $\{^1H\}^{13}C$ resonance which is seen around $\delta = 8.7$ppm can be assigned to the carbon nuclei of the alkane chain directly attached to tellurium (C-1). The occurrence of the C-1 resonance at high field ($\delta \approx 8.7$ppm) may be due to the screening caused by the large atomic size of tellurium. In contrast to this, the C-1 resonance of <u>bis</u>-(diphenylphosphino)alkanes and <u>bis</u>-(diphenylarsino) alkanes occurs at lower field ($\delta \approx 31.1$ and 31.5ppm respectively)(105). However, the C-1 resonances in n-alkanes are assigned at the highest field ($\delta \approx 13.5$ppm)(106-108). Therefore the assignment of the rest of the $\{^1H\}^{13}C$ resonances of alkane chain backbones of the <u>bis</u>-tellurides was made by comparison with the assignments of corresponding n-alkanes(106-108).

The C-2 and C-3 resonances for n-pentane (107) and n-hexane are assigned at successively lower fields. A schematic spectrum of n-pentane is shown in Figure (c).

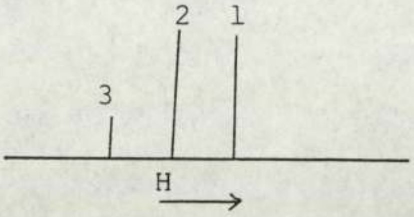


Figure (c) schematic spectrum of n-pentane

$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_3}$

The assignment of $\{^1H\}^{13}C$ resonances of n-alkanes having more than six methylene units is different to the above sequence. A schematic spectrum of n-decane is shown in Figure (d) and is typical for this class of alkanes.

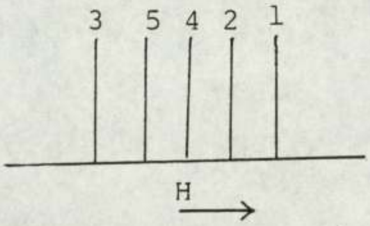


Figure (d) schematic spectrum of n-decane(105)

$\overset{1}{CH_3}\overset{2}{CH_2}\overset{3}{CH_2}\overset{4}{CH_2}\overset{5}{CH_2}\overset{5}{CH_2}\overset{4}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_3}$

No satisfactory explanation has been presented for this behaviour, although it has been suggested that the formation of pseudo-rings might be responsible for the anomalous position of the C-3 resonance (Figure (e))(105,107) e.g.,for n=10.

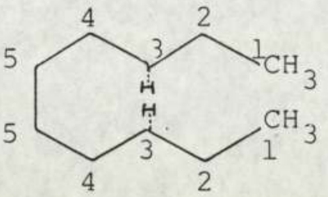


Figure (e)

The rest of the aliphatic resonances of bis-tellurides were found to parallel those of the n-alkanes rather than those of diphosphines or diarsines.

The C-2 and C-3 resonances of $ArTe(CH_2)_5TeAr$ can be assigned on the basis of intensities as reported for n-pentane$^{(107)}$. Therefore, the low intensity peak appeared at δ=34.0ppm is assigned as C-3 and then the remaining peak is assigned as C-2 (Figure 4.10(a)). A schematic representation of the spectrum of $ArTe(CH_2)_5TeAr$ is shown in Figure 4.10(b).

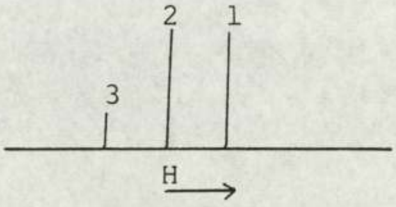


Figure 4.10(b) schematic spectrum for 1,5-bis-(p-ethoxyphenyltelluro)pentane .

$$\overset{1}{ArTeCH_2}\overset{2}{CH_2}\overset{3}{CH_2}\overset{2}{CH_2}\overset{1}{CH_2}TeAr$$

The spectrum of 1,6-bis-(p-ethoxyphenyltelluro)hexane appears as a three line system with all lines of nearly equal intensity (Figure 4.11(a)). It is reasonable to make the assignments of $\{^1H\}^{13}C$ resonances of this compound by comparison with 1,5-bis-(p-ethoxyphenyltelluro)pentane.

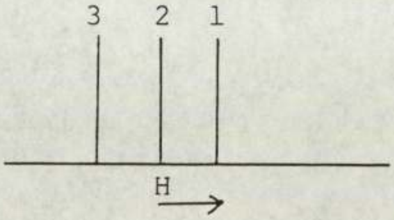
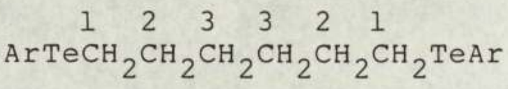


Figure 4.11(b) schematic spectrum for 1,6-bis-(p-ethoxyphenyltelluro)hexane



$\mathrm{ArTe}\overset{1}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}\mathrm{TeAr}$

It is difficult to observe a clear intensity difference in the $\{^1H\}^{13}C$ resonances in the relevant alkane region of the rest of the bis-tellurides. However, the comparison of the n-heptane spectrum with 1,7-bis-(p-ethoxyphenyltelluro)heptane allows us to assign C-3, C-4 and C-2 resonances.

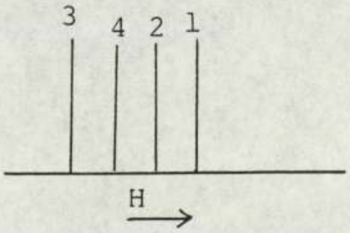
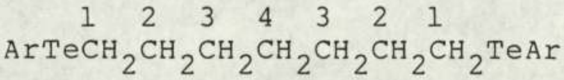


Figure 4.12(b) schematic spectrum for 1,7-bis-(p-ethoxyphenyltelluro)heptane



$\mathrm{ArTe}\overset{1}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{4}{\mathrm{CH_2}}\overset{3}{\mathrm{CH_2}}\overset{2}{\mathrm{CH_2}}\overset{1}{\mathrm{CH_2}}\mathrm{TeAr}$

The $\{^1H\}^{13}C$ resonances of C-2 to C-5 carbon nuclei of the rest of the bis-tellurides are assigned in a similar manner with considerable confidence i.e., by comparison of the corresponding n-alkane(106-108) and bis-telluride spectra. All the C-3, C-4 and C-5 resonances agree very well with the assignments reported for n-alkanes. The anomalous chemical shift values for C-3 resonances in these bis-tellurides may be due to the formation of pseudo- rings as suggested for n-alkanes(105-107).

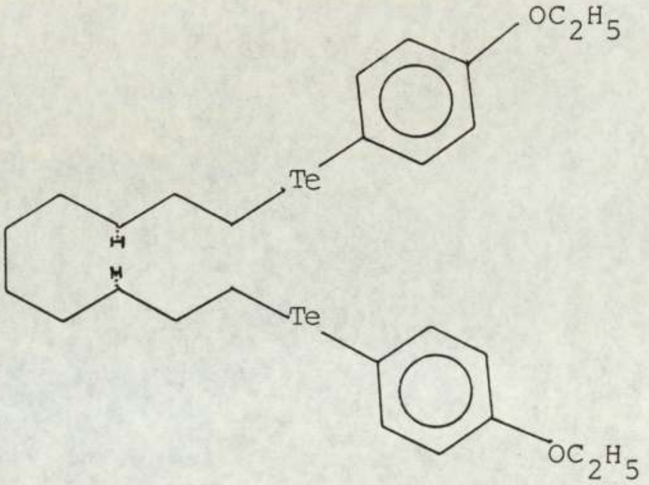
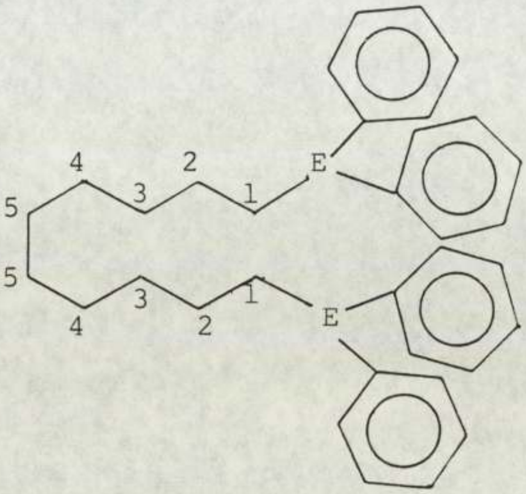


Figure (f) A diagram indicating the formation of pseudo-6-membered ring in 1,10-bis-(p-ethoxyphenyltelluro) decane

The presence of a single p-ethoxyphenyl group attached to tellurium may not provide any steric factors regarding the formation of pseudo- rings, but a steric effect may arise due to the presence of two phenyl groups attached to P or As in the diphenylphosphine- and diphenylarsine- derivatives.

e.g.,



E = P or As

Figure (g) A diagram indicating the inability of the formation of pseudo-six-membered ring due to bulky substituents

CHAPTER FIVE

COMPLEXES OF BIDENTATE TELLURIUM
LIGANDS HAVING
FLEXIBLE ALKANE CHAIN BACKBONES

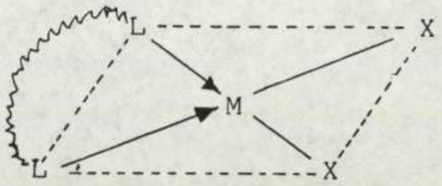
5.1 Introduction

The possible modes of co-ordination open to a potentially bidentate ligand having an alkane chain backbone are,

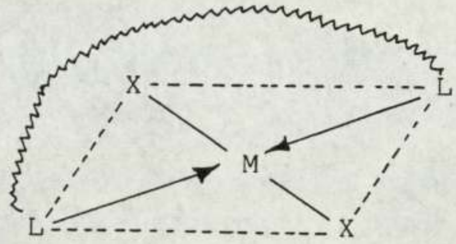
1. as a monodentate
2. as a chelate bidentate
3. as a bridging bidentate.

These co-ordination modes are described in more detail in Chapter One.

Until recently, it was thought that large chelate rings from long chain flexible bidentate ligands would not be stable with respect to open-chain polynuclear species(109,110). The investigations pioneered by Shaw and co-workers(9,12,109,111,112) helped to overcome the misunderstanding of this concept. Recently, there has been renewed interest in the synthesis of bidentate ligands with longer backbones in order to examine the effects of length and nature of the backbone on the determination of the stereochemistry of their complexes with transition metal ions. A vast majority of cis- and trans- chelated complexes have been synthesised from bidentate phosphine ligands. It has been established that when bidentate phosphine ligands possessing relatively short backbones, behave as chelates (i.e., ligands in which the carbon backbone linking the donor atoms consists of 2, 3 or 4 atoms), they necessarily co-ordinate cis- to the metal atom(113,114).



The stability of cis- chelate complexes varies with the chelate ring size and reaches a maximum for five membered, such as those formed by bidentate ligands with bimethylene or o-phenylene bridges between the two donor atoms(114,91). Shaw proposed that the internal entropy effects and chain length of less than five methylene units between the donor atoms would be strained to allow trans- co-ordination(9,12,114). The ligands which can overcome this difficulty form trans-chelated complexes.



Although Shaw proposed that the presence of bulky substituent groups (i.e., t-Bu) in the donor atoms promotes the trans- chelation(9,12,115), studies by McAuliffe(116-118) and others(119) have shown that ligands with methyl or phenyl substituents can form this type of complex providing the backbone length is correct.

Although the factors that govern the chelation in square planar transition metal complexes have been a topic for much discussion in the recent literature, no definitive postulate has yet appeared that explains the formation of *cis*- and *trans*- bidentate chelate complexes.

In this Chapter, complexes of potentially bidentate tellurium ligands having flexible alkane chain backbones i.e., $ArTe(CH_2)_nTeAr$, n=5, 6,....10, are discussed. In this study the first *trans*- chelates with tellurium donor ligands are prepared by reacting Pd(II) salts with these ligands. This can be considered as an extension of the work reported on *trans*- chelation of bidentate ligands having flexible alkane chain backbones.

5.2 Experimental

All the ligands were prepared as described in Chapter Four. All the complex formation reactions were carried out in an oxygen free dinitrogen atmosphere.

5.2.1 Synthesis Of Palladium Complexes

(a) Synthesis of dichloro{1,5-*bis*(p-ethoxyphenyltelluro)-pentane}palladium(II); $[PdCl_2L^5]$

A solution of sodium tetrachloropalladate(II) trihydrate (0.174g, 0.5mmol) in distilled water was added dropwise to a solution of bis(p-ethoxyphenyltelluro)pentane (0.283g,0.5mmol) in acetone in a dinitrogen atmosphere. A brown precipitate was instantaneously formed. This was stirred for 12 h. The precipitate was filtered off, washed with distilled water and dry acetone and dried over P_4O_{10} under vacuo. Yield 65%. m.p. 110-111°C.

Found C 33.8 H 3.45%
$C_{21}H_{28}O_2Te_2PdCl_2$ requries C 33.8 H 3.80%

The following reactions were carried out as above using the appropriate 1,n-bis(p-ethoxyphenyltelluro)alkane as the ligand.

(b) Synthesis of dichloro{1,6-bis(p-ethoxyphenyltelluro)-hexane}palladium(II); $[PdCl_2L^6]$

A yellow precipitate was obtained in 79% yield. m.p. 150-152°C(dec).

Found C 34.5 H 4.00%
$C_{22}H_{30}O_2Te_2PdCl_2$ requires C 34.8 H 4.00%

(c) Synthesis of dichloro{1,7-bis(p-ethoxyphenyltelluro)-heptane}palladium(II); $[PdCl_2L^7]$

An orangish-yellow precipitate was obtained in 70% yield. m.p. 108-109°C.

Found	C 35.1	H 4.05%
$C_{23}H_{32}O_2Te_2PdCl_2$ requires	C 35.7	H 4.10%

(d) Synthesis of dichloro{1,9-bis(p-ethoxyphenyltelluro)-nonane}palladium(II); [$PdCl_2L^9$]

A maroon-red coloured precipitate was obtained in 75% yield. m.p. 102-103°C.

Found	C 37.3	H 4.55%
$C_{25}H_{36}O_2Te_2PdCl_2$ requires	C 37.5	H 4.50%

(e) Synthesis of dichloro{1,10-bis(p-ethoxyphenyltelluro)-decane}palladium(II); [$PdCl_2L^{10}$]

An orangish-red coloured precipitate was obtained in 74% yield. m.p. 108-110°C.

Found	C 38.3	H 4.65%
$C_{26}H_{38}O_2Te_2PdCl_2$ requires	C 38.3	H 4.70%

(f) Synthesis of dibromo{1,6-bis(p-ethoxyphenyltelluro)-hexane}palladium(II); [$PdBr_2L^6$]

A solution of sodium tetrachloropalladate trihydrate(0.174g, 0.5mmol) in distilled water was stirred with a five-fold excess of a solution of KBr for 4-5h. The dark brownish coloured solution obtained was added dropwise to a solution of bis(p-ethoxyphenyltelluro)hexane (0.291g, 0.5mmol) in acetone in a dinitrogen atmosphere. A yellowish-brown precipitate instantaneously formed. This was stirred for 12h. The precipitate was filtered off, washed with distilled water and dry acetone,and dried over P_4O_{10} under vacuo. Yield 80%. m.p. 170-171°C(dec).

Found	C 31.0	H 3.30%
$C_{22}H_{30}O_2Te_2PdBr_2$ requires	C 31.2	H 3.50%

(g) Synthesis of dibromo{1,10-bis(p-ethoxyphenyltelluro)-decane}palladium(II); $[PdBr_2L^{10}]$

This reaction was carried out as in 5.2.1(f), except with bis-(p-ethoxyphenyltelluro)decane as the ligand. A maroonish-brown coloured precipitate was obtained in 84% yield. m.p. 120-121°C.

Found	C 34.9	H 4.90%
$C_{26}H_{38}O_2Te_2PdBr_2$ requries	C 34.5	H 4.20%

(h) Effect of complex precursor on complex formation

This reaction was carried out as for reaction 5.2.1(c) except bis(benzonitrile)palladium(II) chloride in acetone was used as the complex precursor. A maroonish-brown precipitate was obtained in 78% yield. m.p. 107-109°C.

Found	C 36.2	H 4.00%
$C_{23}H_{32}O_2Te_2PdCl_2$ requires	C 35.7	H 4.10%

(i) Effect of reactant ratio on complex formation

A solution of sodium tetrachloropalladate trihydrate (0.174g, 0.5mmol) in distilled water was added dropwise to a solution of bis(p-ethoxyphenyltelluro)decane (0.637g, 1mmol) in a dinitrogen atmosphere. An orange-red percipitate instantaneously formed. This was stirred for 12h. The precipitate was filtered off, washed with distilled water and dry acetone, and dried over P_4O_{10} under vacuo. Yield 44%. m.p. 108-110°C.

Found	C 38.2	H 4.90%
$C_{26}H_{38}O_2Te_2PdCl_2$ requires	C 38.3	H 4.70%

5.2.2 Synthesis Of Platinum Complexes

(a) Synthesis of bis-μ-{1,5-bis(p-ethoxyphenyltelluro)pentane}-bis(chloroplatinum)(Pt-Pt). [$Pt_2Cl_2L^5_2$]

A solution of potassium tetrachloroplatinate (0.208g, 0.5mmol) in distilled water was added dropwise to a solution of bis-(p-ethoxyphenyltelluro)pentane (0.284g, 0.5mmol) in acetone in a dinitrogen atmosphere. A yellow precipitate was instantaneously formed. This was stirred for 12h. The precipitate was filtered off, washed with distilled water and dry acetone, and dried over P_4O_{10} under vacuo. Yield 50%. m.p. 123-124°C.

Found	C 31.5	H 3.65%
$C_{42}H_{56}O_4Te_4Pt_2Cl_2$ requires	C 31.6	H 3.50%

Following reactions were carried out as above, except with the appropriate 1,n-bis(p-ethoxyphenyltelluro)alkane as the ligand.

(b) Synthesis of dichloro{1,6-bis(p-ethoxyphenyltelluro)-hexane}platinum(II); $[PtCl_2L^6]$

A yellow coloured precipitate was obtained in 66% yield. m.p. 135-136°C.

Found	C 31.4	H 3.65%
$C_{22}H_{30}O_2Te_2PtCl_2$ requires	C 31.2	H 3.50%

(c) Synthesis of dichloro{1,7-bis(p-ethoxyphenyltelluro) heptane}platinum(II); $[PtCl_2L^7]$

A yellow precipitate was obtained in 70% yield. m.p. 114-115°C.

Found	C 31.7	H 3.35%
$C_{23}H_{32}O_2Te_2PtCl_2$ requires	C 32.0	H 3.70%

(d) Synthesis of dichloro{1,9-*bis*(p-ethoxyphenyltelluro)-nonane}platinum(II); $[PtCl_2L^9]$

A yellow precipitate was obtained in 58% yield. m.p. 121-122°C.

Found	C 33.9	H 4.00%
$C_{25}H_{36}O_2Te_2PtCl_2$ requires	C 33.7	H 4.05%

(e) Synthesis of dichloro{1,10-*bis*(p-ethoxyphenyltelluro)-decane}platinum(II); $[PtCl_2L^{10}]$

A bright yellow precipitate was obtained in 64% yield. m.p. 118-120°C.

Found	C 34.5	H 4.25%
$C_{26}H_{38}O_2Te_2PtCl_2$ requires	C 34.5	H 4.20%

(f) Synthesis of dibromo{1,6-*bis*(p-ethoxyphenyltelluro)-hexane}platinum(II); $[PtBr_2L^6]$

A solution of potassium tetrachloroplatinate(II) (0.208g, 0.5mmol) in distilled water was stirred with five-fold excess of a solution of KBr in distilled water for 4-5h.

The yellow solution obtained was added dropwise to a solution of bis(p-ethoxyphenyltelluro)hexane (0.291g, 0.5mmol) in acetone in a dinitrogen atmosphere. A yellow precipitate was instantaneously formed. This was stirred for 12h. The precipitate was filtered off, washed with distilled water and dry acetone and dried over P_4O_{10} under vacuo. Yield 62%. m.p. 126-128°C.

Found	C 27.8	H 3.00	Br 17.6%
$C_{22}H_{30}O_2Te_2PtBr_2$ requires	C 28.2	H 3.20	Br 17.1%

(g) Synthesis of dibromo{1,6-bis(p-ethoxyphenyltelluro)-decane}platinum(II); $[PtBr_2L^{10}]$

The reaction was carried out as above, except with bis-(p-ethoxyphenyltelluro)decane as the ligand. A brownish-orange precipitate was obtained in 76% yield. m.p. 120-121°C.

Found	C 31.6	H 4.00%
$C_{26}H_{38}O_2Te_2PtBr_2$ requires	C 31.5	H 3.80%

5.2.3 Synthesis Of Mercury Complexes

(a) Synthesis of dichloro{1,5-bis(p-ethoxyphenyltelluro)-pentane}mercury(II); $[HgCl_2L^5]$

A solution of $HgCl_2$ (0.136g, 0.5mmol) in dry acetone was added dropwise to a solution of bis(p-ethoxyphenyltelluro)-pentane (0.284g, 0.5mmol) in dry acetone in a dinitrogen atmosphere. A pale yellow precipitate was formed. This was stirred for 4-5h. The precipitate was filtered off, washed with dry acetone and dried over P_4O_{10} under vacuo. Yield 40%. m.p. 66-68°C.

Found	C 30.3	H 3.40%
$C_{21}H_{28}O_2Te_2HgCl_2$ requires	C 30.0	H 3.30%

The following reactions were carried out as above, using appropriate 1,n-bis(p-ethoxyphenyltelluro)alkane.

(b) Synthesis of dichloro{1,6-bis(p-ethoxyphenyltelluro)-hexane}mercury(II); [$HgCl_2L^6$]

A pale yellow precipitate was obtained in 50% yield. m.p. 82-83°C.

Found	C 30.2	H 3.45%
$C_{22}H_{30}O_2Te_2HgCl_2$ requires	C 31.0	H 3.50%

(c) Synthesis of dichloro{1,7-bis(p-ethoxyphenyltelluro)-heptane}mercury(II); [$HgCl_2L^7$]

A pale yellow precipitate was obtained in 60% yield. m.p. 73-74°C.

Found	C 31.3	H 3.30%
$C_{23}H_{32}O_2Te_2HgCl_2$ requires	C 31.8	H 3.70%

(d) Synthesis of dichloro{1,9-*bis*(p-ethoxyphenyltelluro)-nonane}mercury(II); [$HgCl_2L^9$]

A pale yellow precipitate was obtained in 61% yield. m.p. 79-80°C.

Found	C 33.2	H 3.60%
$C_{25}H_{36}O_2Te_2HgCl_2$ requires	C 33.5	H 4.00%

(e) Synthesis of dichloro{1,10-*bis*(p-ethoxyphenyltelluro)-decane}mercury(II); [$HgCl_2L^{10}$]

A pale yellow precipitate was obtained in 65% yield. m.p. 74-75°C.

Found	C 33.6	H 4.00%
$C_{26}H_{38}O_2Te_2HgCl_2$ requires	C 34.3	H 4.20%

5.2.4 Synthesis of Rhodium(I) Complexes

(a) Synthesis of [$RhClL^6$]$_n$

A solution of $RhCl_3.3H_2O$ (0.132g, 0.5mmol) in distilled water was added dropwise to a solution of 1,6-*bis*(p-ethoxyphenyltelluro)hexane (0.291g, 0.5mmol) in acetone in a dinitrogen atmosphere. This was stirred for 12h. The brownish-yellow precipitate was filtered off, washed with distilled water and dry acetone,and dried over P_4O_{10} under vacuo. Yield 70%. m.p. 185-187°C(dec).

Found	C 37.2	H 4.10%
$C_{22}H_{30}O_2Te_2RhCl$ requires	C 36.7	H 4.20%

(b) Synthesis of $[RhClL^7]_n$

This was carried out as 5.2.3(a), using 1,7-bis(p-ethoxyphenyltelluro)heptane as the ligand. A chocolate-brown coloured precipitate was obtained in 74% yield. m.p. 196-198°C(dec).

Found	C 37.7	H 4.40%
$C_{23}H_{32}O_2Te_2RhCl$ requires	C 37.6	H 4.45%

5.3 Results

All the palladium, platinum and mercury complexes except MX_2L^6, (M=Pd, Pt, Hg; X=Cl, Br) are soluble in halocarbon solvents and DMF. Although PdX_2L^6 is extremely insoluble in halocarbon solvents, analogous platinum and mercury complexes are fairly soluble in warm halocarbon solvents. $RhClL^n$ (n=6, 7) are insoluble in common organic solvents . All the soluble complexes are non-electrolytes in DMF.

Complex	Found%		Required%	
	C	H	C	H
$PdCl_2L^5$	33.8	3.45	33.8	3.80
$PdCl_2L^6$	34.5	4.00	34.8	4.00
$^aPdCl_2L^7$	35.1	4.05	35.7	4.10
$PdCl_2L^9$	37.3	4.55	37.5	4.50
$^bPdCl_2L^{10}$	38.3	4.65	38.3	4.70
$PdBr_2L^6$	31.0	3.30	31.2	3.50
$PdBr_2L^{10}$	34.9	4.90	34.5	4.20
$^cPdCl_2L^7$	36.2	4.00	35.7	4.10
$^dPdCl_2L^{10}$	38.2	4.90	38.3	4.70

a- complex precursor K_2PdCl_4

b- reactant ratio 1:1 (L:M)

c- complex precursor $PdCl_2(PhCN)_2$

d- reactant ratio 2:1 (L:M)

Table 5.1 Elemental analyses of palladium complexes

Complex	Found%		Required%	
	C	H	C	H
$Pt_2Cl_2(L^5)_2$	31.5	3.65	31.6	3.50
$PtCl_2L^6$	31.4	3.65	31.2	3.50
$PtCl_2L^7$	31.7	3.35	32.0	3.70
$PtCl_2L^9$	33.9	4.00	33.7	4.05
$PtCl_2L^{10}$	34.5	4.25	34.5	4.20
$PtBr_2L^6$	27.8	3.00	28.2	3.20
$PtBr_2L^{10}$	31.6	4.00	31.5	3.80

Table 5.2 Elemental analyses of platinum complexes

Complex	Found%		Required%	
	C	H	C	H
$HgCl_2L^5$	30.3	3.40	30.0	3.30
$HgCl_2L^6$	30.2	3.45	31.0	3.50
$HgCl_2L^7$	31.3	3.30	31.8	3.70
$HgCl_2L^9$	33.2	3.60	33.5	4.00
$HgCl_2L^{10}$	33.6	4.00	34.3	4.20

Table 5.3 Elemental analyses of mercury complexes

Complex	Found%		Required%	
	C	H	C	H
$RhClL^6$	37.2	4.10	36.7	4.20
$RhClL^7$	37.7	4.40	37.6	4.45
(124) $RhClL^{10}$	40.3	5.10	40.2	4.90

Table 5.4 Elemental analyses of rhodium complexes

Complex	Colour	M.Pt^{o}C	Molar Cond. ohm^{-1}cm^{2}mol^{-1}
$PdCl_2L^5$	brown	110-111	21.9
$PdCl_2L^6$	yellow	150-152(dec)	
$^{a}PdCl_2L^7$	orangish-yellow	108-109	4.5
$PdCl_2L^9$	maroonish-red	102-103	4.2
$^{b}PdCl_2L^{10}$	orangish-red	108-110	4.8
$PdBr_2L^6$	yellowish-brown	170-171(dec)	
$PdBr_2L^{10}$	maroonish-brown	120-121	8.6
$^{c}PdCl_2L^7$	maroonish-brown	107-109	4.5
$^{d}PdCl_2L^{10}$	orangish-red	108-110	4.8

a- complex precursor K_2PdCl_4

b- reactant ratio 1:1 (L:M)

c- complex precursor $PdCl_2(PhCN)_2$

d- reactant ratio 2:1 (L:M)

Table 5.5 Colour, melting points and molar conductivities ($1x10^{-3}$M in DMF) of palladium complexes

Complex	Colour	M.Pt°C	Molar Cond. $ohm^{-1}cm^{2}mol^{-1}$
$Pt_2Cl_2(L^5)_2$	yellow	123-124	29.2
$PtCl_2L^6$	yellow	135-136	4.2
$PtCl_2L^7$	yellow	114-115	4.5
$PtCl_2L^9$	yellow	121-122	4.4
$PtCl_2L^{10}$	bright yellow	118-120	3.7
$PtBr_2L^6$	yellow	126-128	3.8
$PtBr_2L^{10}$	brownish-orange	120-121	14.6

Table 5.6 Colour, melting points and molar conductivities ($1x10^{-3}M$ in DMF) of platinum complexes

Complex	Colour	M.Pt°C	Molar Cond. $ohm^{-1}cm^{2}mol^{-1}$
$HgCl_2L^5$	pale yellow	66-68	48.2
$HgCl_2L^6$	pale yellow	82-83	6.3
$HgCl_2L^7$	pale yellow	73-74	8.0
$HgCl_2L^9$	pale yellow	79-80	8.3
$HgCl_2L^{10}$	pale yellow	74-75	12.0

Table 5.7 Colour, melting points and molar conductivities ($1x10^{-3}M$ in DMF) of mercury complexes

Complex	Colour	M.Pt. °C
$RhClL^6$	brownish-yellow	185-187(dec)
$RhClL^7$	chocolate brown	196-198(dec)
(124)$RhClL^{10}$	blackish-brown	210-212(dec)

Table 5.8 Colour and melting points of rhodium complexes

Complex	ν(M-Cl) cm^{-1}	ν(M-Br) cm^{-1}
$PdCl_2L^5$	352	
$PdCl_2L^6$	342	
$^aPdCl_2L^7$	350	
$PdCl_2L^9$	342	
$^bPdCl_2L^{10}$	342	
$PdBr_2L^6$		270
$PdBr_2L^{10}$		265
$^cPdCl_2L^7$	348	
$^dPdCl_2L^{10}$	341	
$Pt_2Cl_2(L^5)_2$	301,322	
$PtCl_2L^6$	299,315	
$PtCl_2L^7$	299,320	
$PtCl_2L^9$	298,315	
$PtCl_2L^{10}$	299,316	

a-complex precursor K_2PdCl_4 b-reactant ratio 1:1 (L:M)
c-complex precursor $PdCl_2(PhCN)_2$ d-reactant ratio 2:1 (L:M)

Table 5.9 Metal-halogen vibrations of some complexes (observed far-infra-red region 400-200cm^{-1})

Complex	Chemical shift[a]	
	aromatic region	aliphatic region
$PdCl_2L^5$	6.8, 7.3 (J(AB)=8.66Hz)	1.5(m), 3.1(t), 4.0(q)
$PdCl_2L^7$	6.9, 7.7 (J(AB)=8.66Hz)	1.4(m), 3.2(t), 4.1(q)
$PdCl_2L^9$	6.8, 7.6 (J(AB)=8.66Hz)	1.3(m), 3.1(t), 4.0(q)
$PdCl_2L^{10}$	6.8, 7.6 (J(AB)=8.66Hz)	1.3(m), 3.2(t), 4.0(q)
$PdBr_2L^{10}$	6.9, 7.8 (J(AB)=8.66Hz)	1.4(m), 3.3(t), 4.1(q)

a-chemical shifts in ppm relative to TMS as internal standard

Table 5.10 ^1H N.M.R. data of palladium complexes

Complex	Chemical shift$^{a(b)}$										
	Aromatic region				Aliphatic region						
	IPSO	ORTHO	META	PARA	C-1	C-2	C-3	C-4	C-5	OCH_2	CH_3
$PdCl_2L^5$	? (96.1)	138.6 (141.0)	115.9 (115.6)	160.4 (159.9)	28.2 (8.7)	33.5 (31.0)	34.0 (34.0)			63.5 (63.4)	14.7 (14.9)
$PdCl_2L^7$	105.1 (100.6)	138.5 (141.1)	116.1 (115.8)	160.5 (159.3)	26.1 (9.1)	27.3 (29.1)	29.5 (31.9)	30.3 (29.7)		63.6 (63.6)	14.7 (14.9)
$PdCl_2L^9$	96.1 (100.5)	138.5 (140.9)	115.8 (115.6)	? (?)	27.4 (9.1)	27.7 (28.8)	30.3 (31.8)	30.7 (29.0)	? (?)	63.5 (63.4)	14.7 (14.8)
$PdCl_2L^{10}$	103.2 (100.3)	138.8 (140.8)	115.8 (115.5)	160.3 (159.0)	27.1 (9.0)	28.0 (28.8)	28.9 (31.8)	31.5 (29.4)	? (29.6)	63.5 (63.3)	14.7 (14.7)
$PdBr_2L^{10}$	? (100.3)	138.6 (140.8)	115.8 (115.5)	160.3 (159.0)	28.1 (9.0)	29.0 (28.8)	30.4 (31.8)	31.8 (29.4)	? (29.6)	63.5 (63.3)	14.7 (14.7)

a-chemical shifts in ppm relative to TMS as internal standard
b-chemical shifts observed for the free ligand are given in parentheses

Table 5.11 $\{^1H\}^{13}C$ N.M.R. data of palladium complexes

Complex	Chemical shift[a]	
	aromatic region	aliphatic region
$Pt_2Cl_2(L^5)_2$	6.70(b), 7.40(b)	1.5(m), 3.0(b), 4.0(q)
$PtCl_2L^7$	6.75(b), 7.45(b)	1.4(m), 3.1(b), 4.0(q)
$PtCl_2L^9$	6.70(b), 7.40(b)	1.4(m), 3.2(b), 4.1(q)
$PtCl_2L^{10}$	6.72(b), 7.42(b)	1.3(m), 3.3(b), 4.0(q)
$PtBr_2L^{10}$	6.72(b), 7.42(b)	1.4(m), 3.3(b), 4.0(q)

a-chemical shifts observed in ppm relative to TMS as internal standard
b-broad, m-multiplet, q-quadriplet.

Table 5.12 ^1H N.M.R. data of platinum complexes

Complex	Chemical shift$^{a(b)}$										
	Aromatic region				Aliphatic region						
	IPSO	ORTHO	META	PARA	C-1	C-2	C-3	C-4	C-5	OCH_2	CH_3
$Pt_2Cl_2(L^5)_2$	100.7 (96.1)	138.1 (141.0)	115.7 (115.6)	160.6 (159.9)	20.5 (8.7)	27.3 (31.0)	32.7 (34.0)			63.6 (63.4)	14.7 (14.9)
$PtCl_2L^7$	96.1 (100.6)	137.2 (141.1)	115.8 (115.8)	160.9 (159.3)	27.7 (9.1)	28.1 (29.1)	30.0 (31.9)	30.4 (29.7)		63.6 (63.6)	14.7 (14.9)
$PtCl_2L^9$	? (100.5)	138.1 (140.9)	115.7 (115.6)	161.1 (?)	27.5 (9.1)	27.9 (28.8)	28.3 (31.8)	30.2 (29.0)	? (?)	63.6 (63.4)	14.7 (14.8)
$PtCl_2L^{10}$	? (100.3)	138.1 (140.8)	115.4 (115.5)	164.8 (159.0)	27.3 (9.0)	28.7 (28.8)	29.3 (31.8)	30.7 (29.4)	31.9 (29.6)	63.6 (63.3)	14.7 (14.7)
$PtBr_2L^{10}$	? (100.3)	138.1 (140.8)	115.7 (115.5)	160.6 (159.0)	26.2 (9.0)	27.6 (28.8)	28.3 (31.8)	29.6 (29.4)	30.5 (29.6)	63.6 (63.3)	14.7 (14.7)

a-chemical shifts in ppm relative to TMS as internal standard
b-chemical shifts observed for the free ligand are given in parentheses

Table 5.13 $\{^1H\}^{13}C$ N.M.R. data of platinum complexes

Complex	λmax mμ	νcm^{-1}	ε
$PdCl_2L^5$	412	24,272	11,000
$PdCl_2L^7$	420	23,810	13,000
$PdCl_2L^9$	414	24,155	19,000
$PdCl_2L^{10}$	417	23,981	27,000
$PdBr_2L^{10}$	428	23,650	15,000
$Pt_2Cl_2(L^5)_2$	320	31,250	13,000
$PtCl_2L^6$	335	29,851	16,000
$PtCl_2L^7$	340	29,412	13,000
$PtCl_2L^9$	344	29,070	17,000
$PtCl_2L^{10}$	330	30,303	14,000
$PtBr_2L^{10}$	340	29,412	14,000
$HgCl_2L^5$	310	32,258	25,000
$HgCl_2L^7$	317.5	31,496	18,000
$HgCl_2L^9$	317.5	31,496	17,000
$HgCl_2L^{10}$	317.5	31,496	17,000

Table 5.14 U.V. spectral data of palladium, platinum and mercury complexes

Complex	Chemical shift[a]	
	aromatic region	aliphatic region
$HgCl_2L^5$	6.8, 7.75 (J(AB)=8.66Hz)	1.5(m),3.25(t), 3.95(q)
$HgCl_2L^7$	6.8, 7.75 (J(AB)=8.66Hz)	1.5(m),3.25(t), 3.95(q)
$HgCl_2L^9$	6.8, 7.75 (J(AB)=8.66Hz)	1.4(m),3.25(t), 3.95(q)
$HgCl_2L^{10}$	6.8, 7.75 (J(AB)=8.66Hz)	1.4(m),3.25(t), 3.95(q)

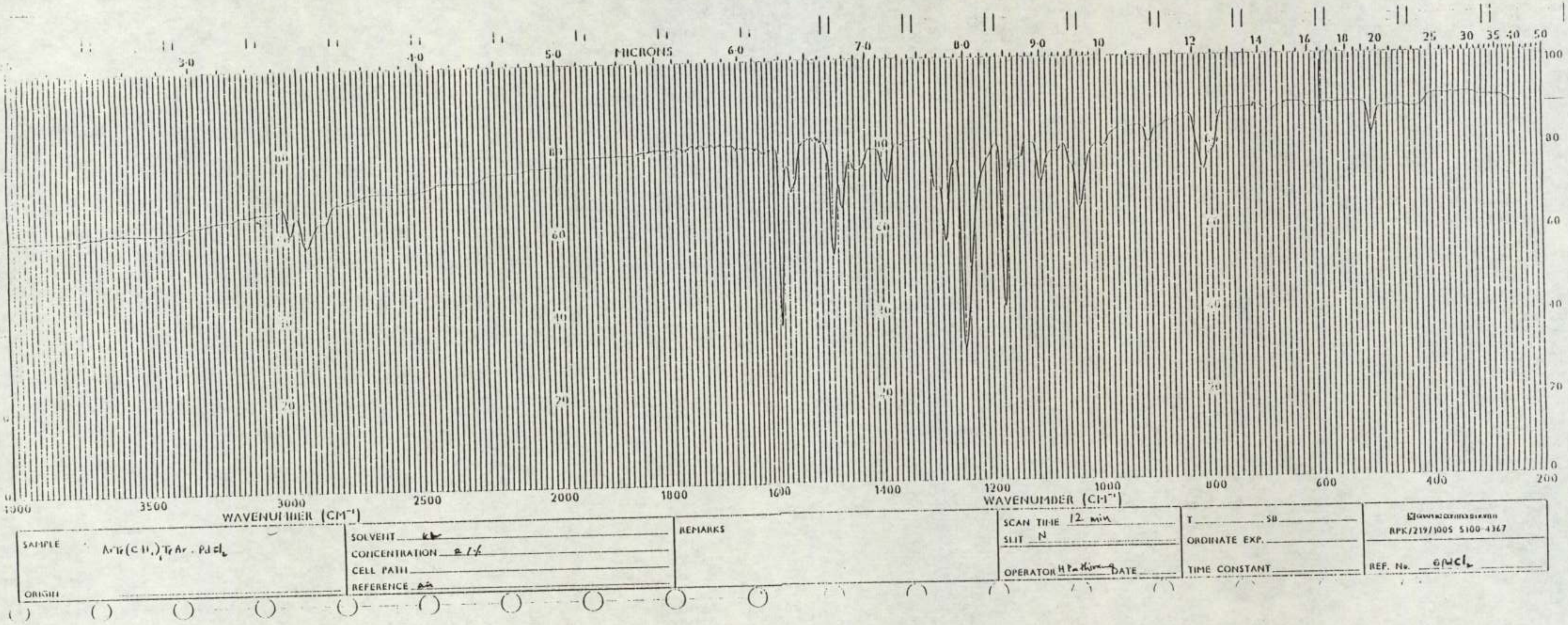
a-chemical shifts observed in ppm relative to TMS as internal standard

Table 5.15 ^{1}H N.M.R. data of mercury complexes

Complex	Molecular Weight[a]
$PdCl_2L^5$	705 (744)
$PdCl_2L^7$	829 (772)
$PdCl_2L^9$	835 (800)
$PdCl_2L^{10}$	726 (814)
$PdBr_2L^{10}$	917 (903)
$PtCl_2L^7$	858 (861)
$PtCl_2L^9$	860 (889)
$PtCl_2L^{10}$	870 (903)
$PtBr_2L^{10}$	800 (992)

a-calculated values are given in parentheses

Table 5.16 Molecular weight data of palladium and platinum complexes



SAMPLE ArTe(CH$_2$)$_4$TeAr . PdCl$_2$
ORIGIN
SOLVENT KBr
CONCENTRATION ≈ 1%
CELL PATH
REFERENCE air
REMARKS
SCAN TIME 12 min
SLIT N
OPERATOR H P[illegible] DATE
T SB
ORDINATE EXP.
TIME CONSTANT
RPK/219/1005 5100-4367
REF. No. 6PdCl$_2$

Figure 5.1 I.R. spectrum of $[PdCl_2L^6]_n$

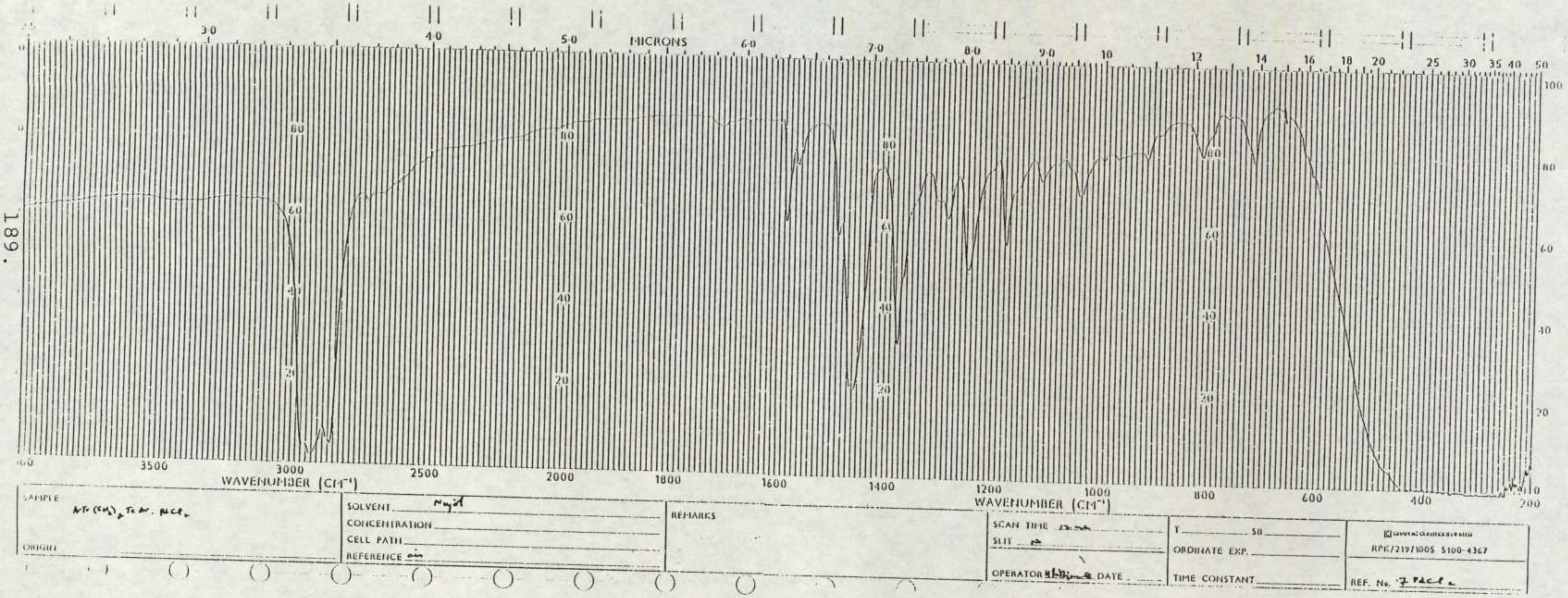


Figure 5.2 I.R. spectrum of $PdCl_2L^7$

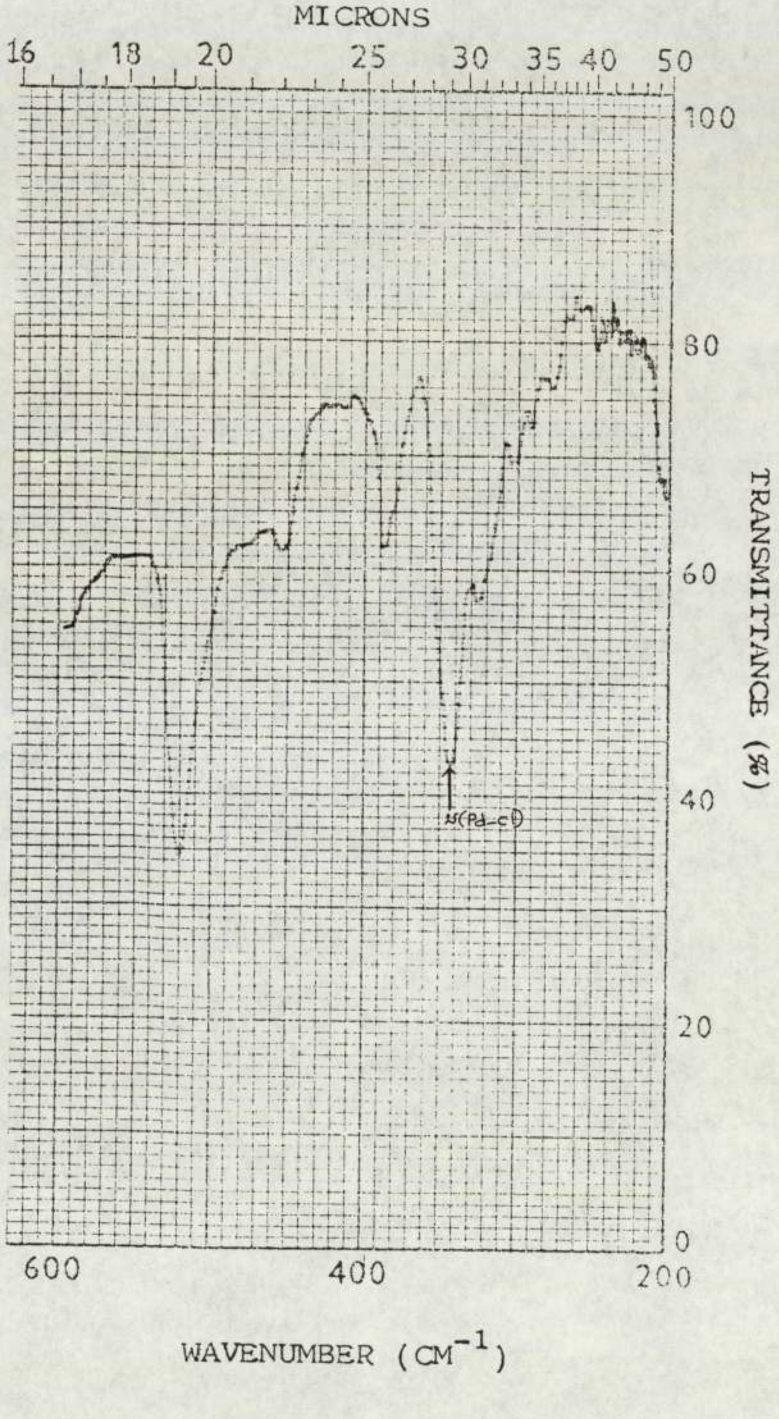


Figure 5.3 Far-infra-red spectrum of $PdCl_2L^{10}$

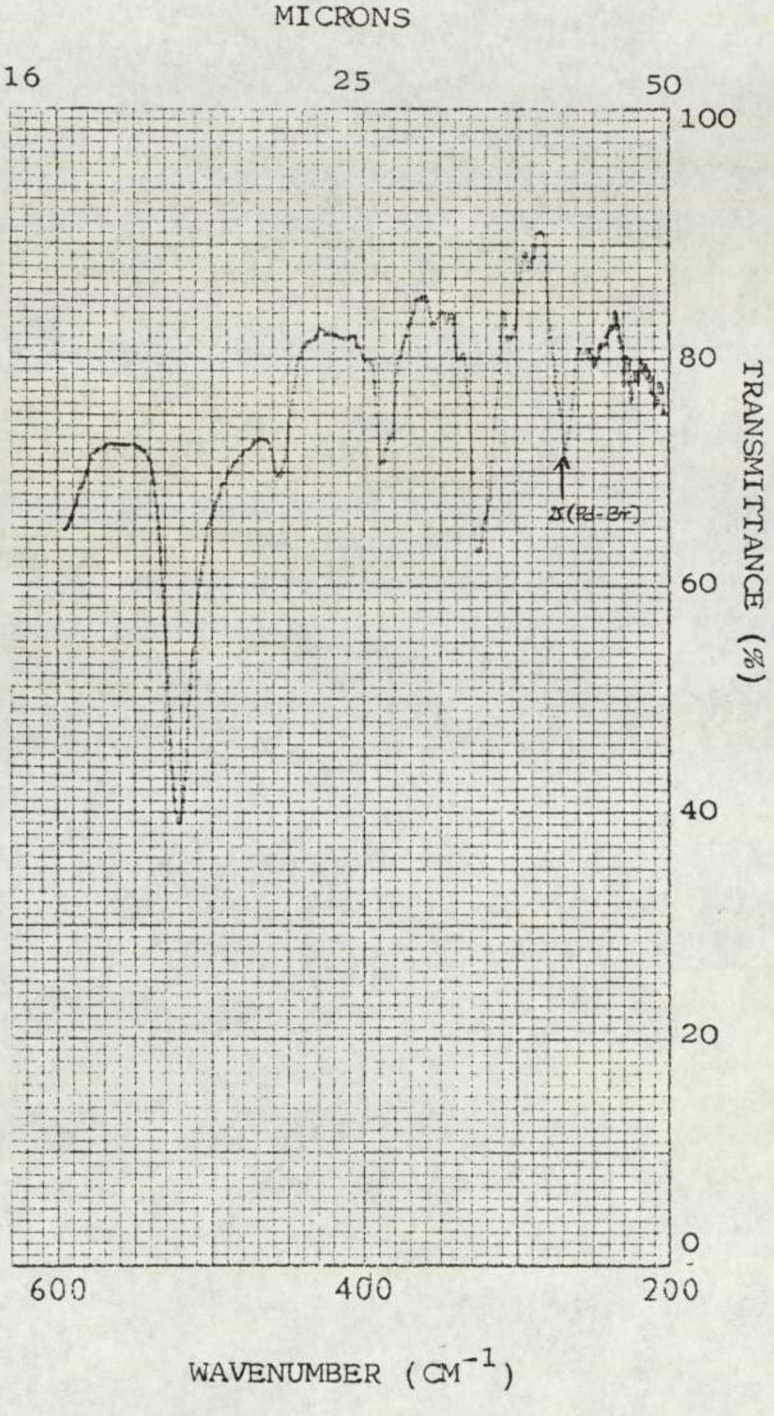


Figure 5.4 Far-infra-red spectrum of $[PdBr_2L^6]_n$

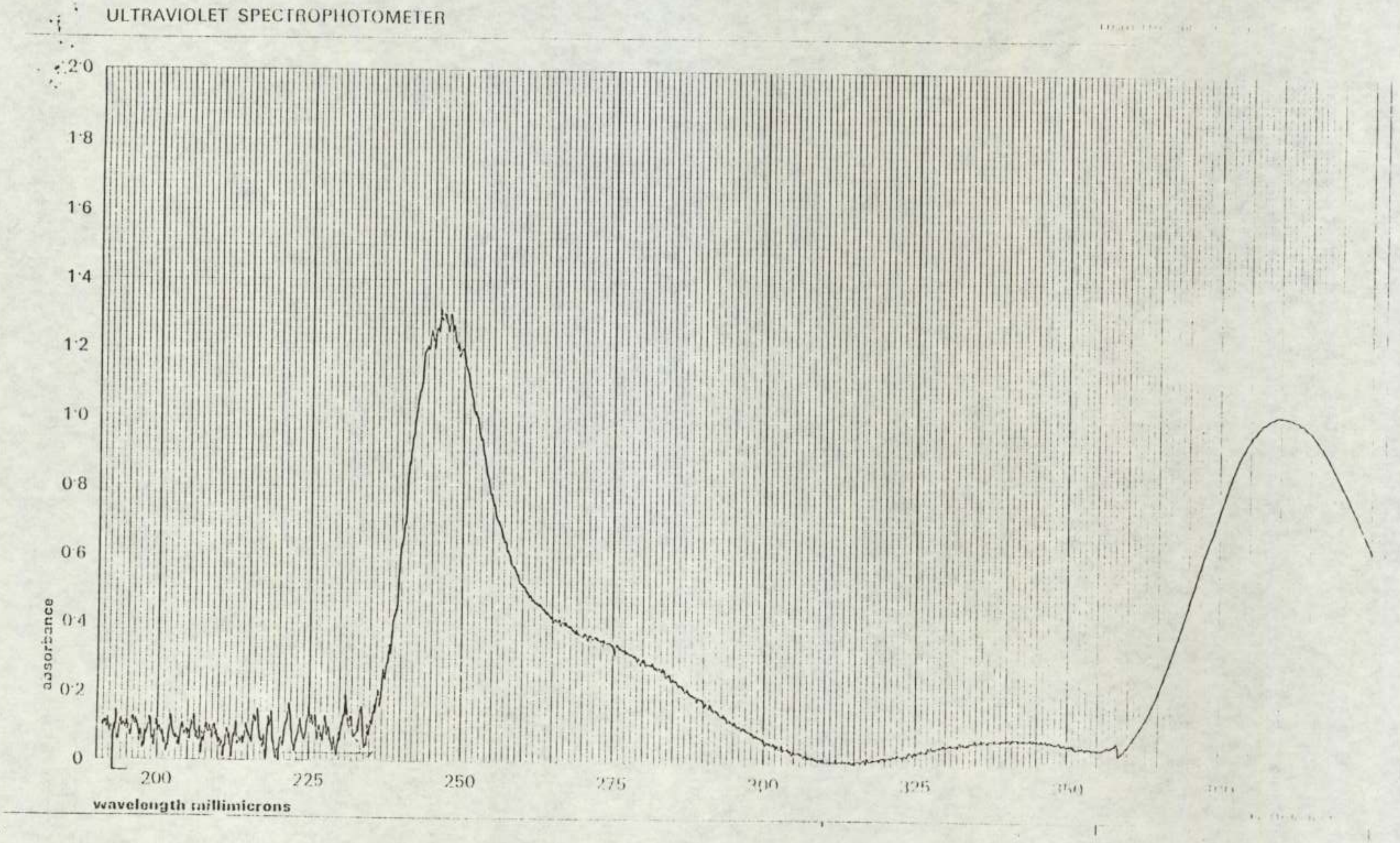


Figure 5.5 U.V. spectrum of $PdCl_2L^7$

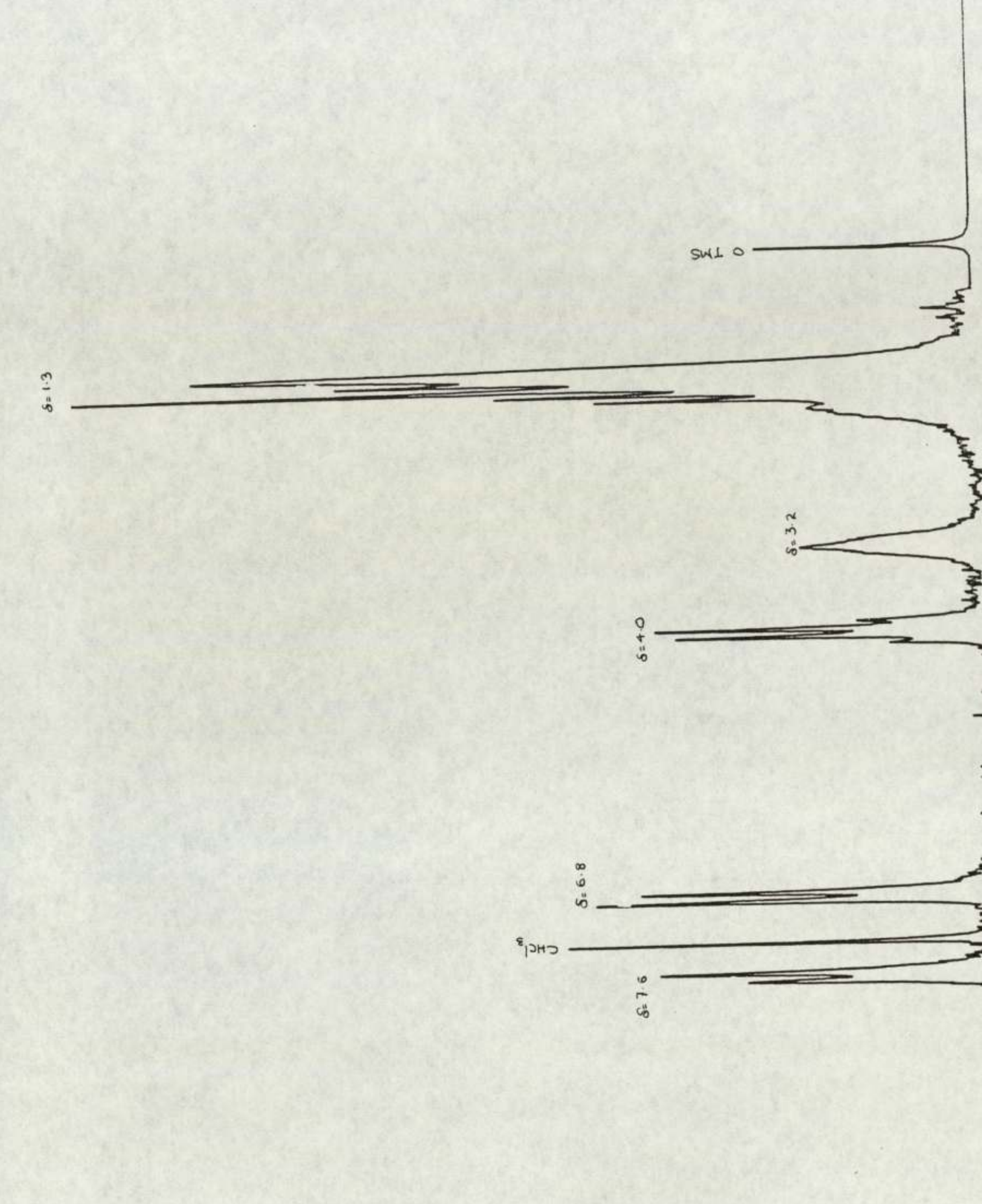


Figure 5.6 ^1H N.M.R. spectrum of $PdCl_2L^{10}$

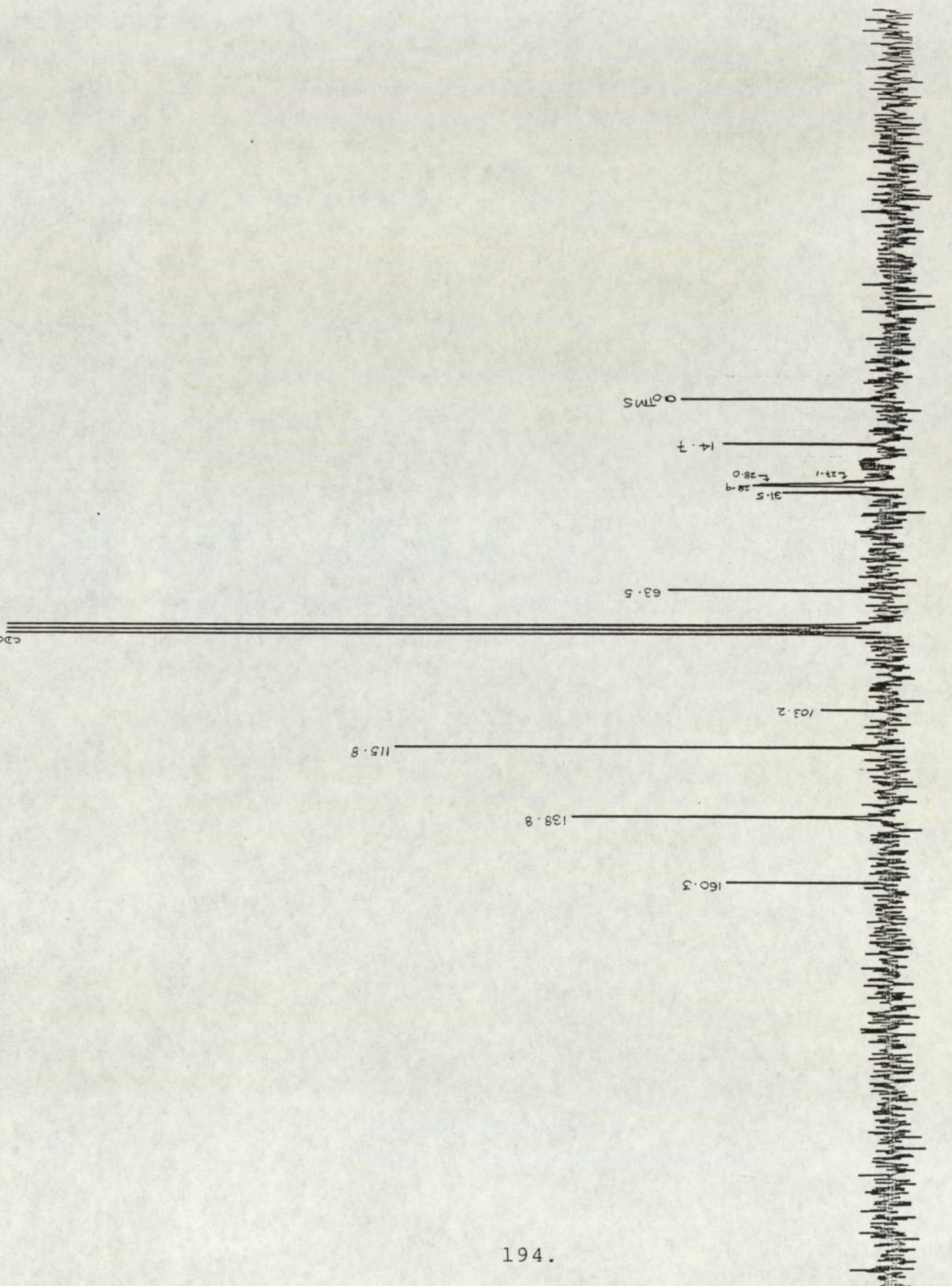


Figure 5.7 $\{^1H\}$ ^{13}C N.M.R. spectrum of $PdCl_2L^{10}$

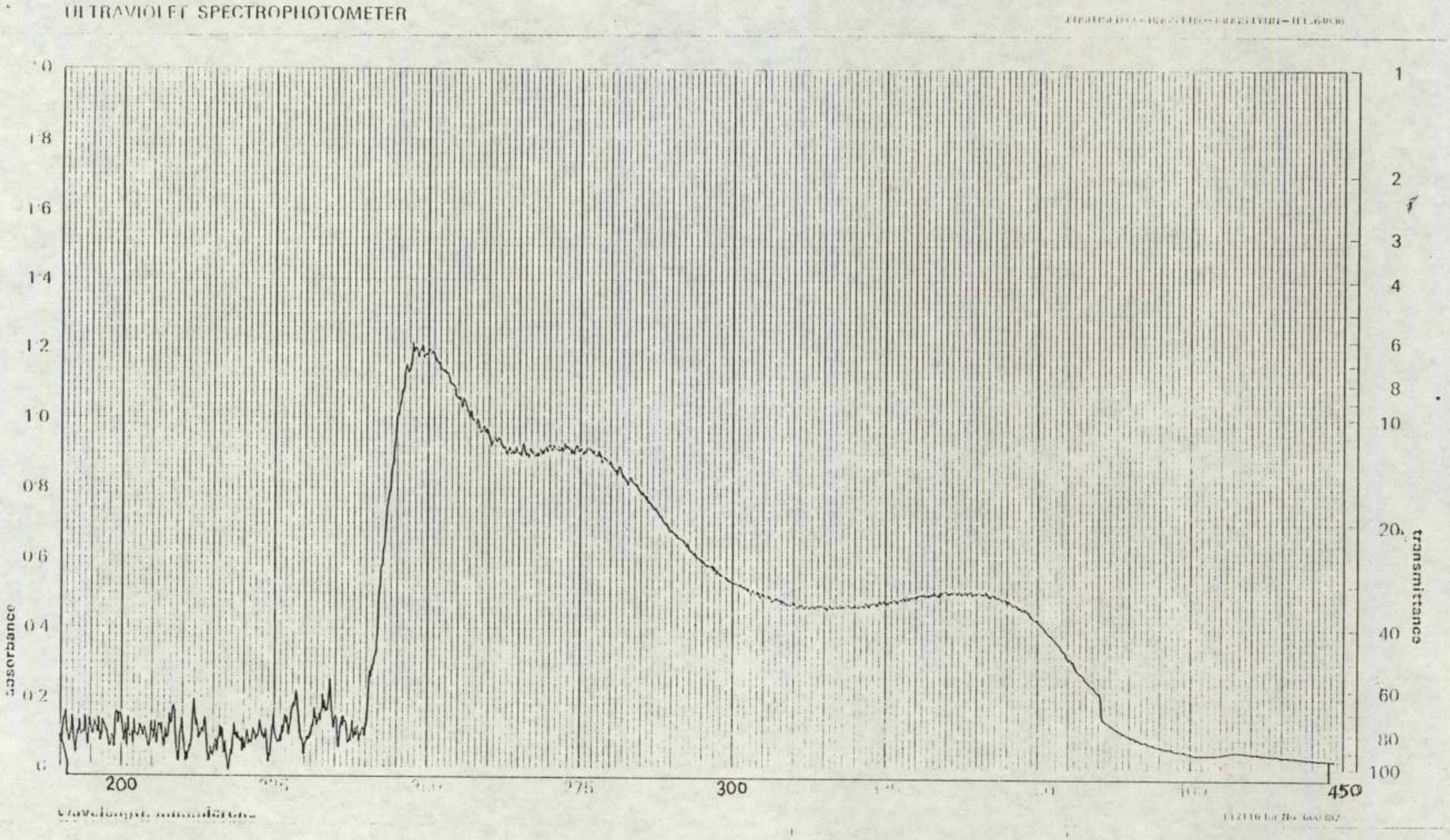


Figure 5.8 U.V. spectrum of $PtCl_2L^7$

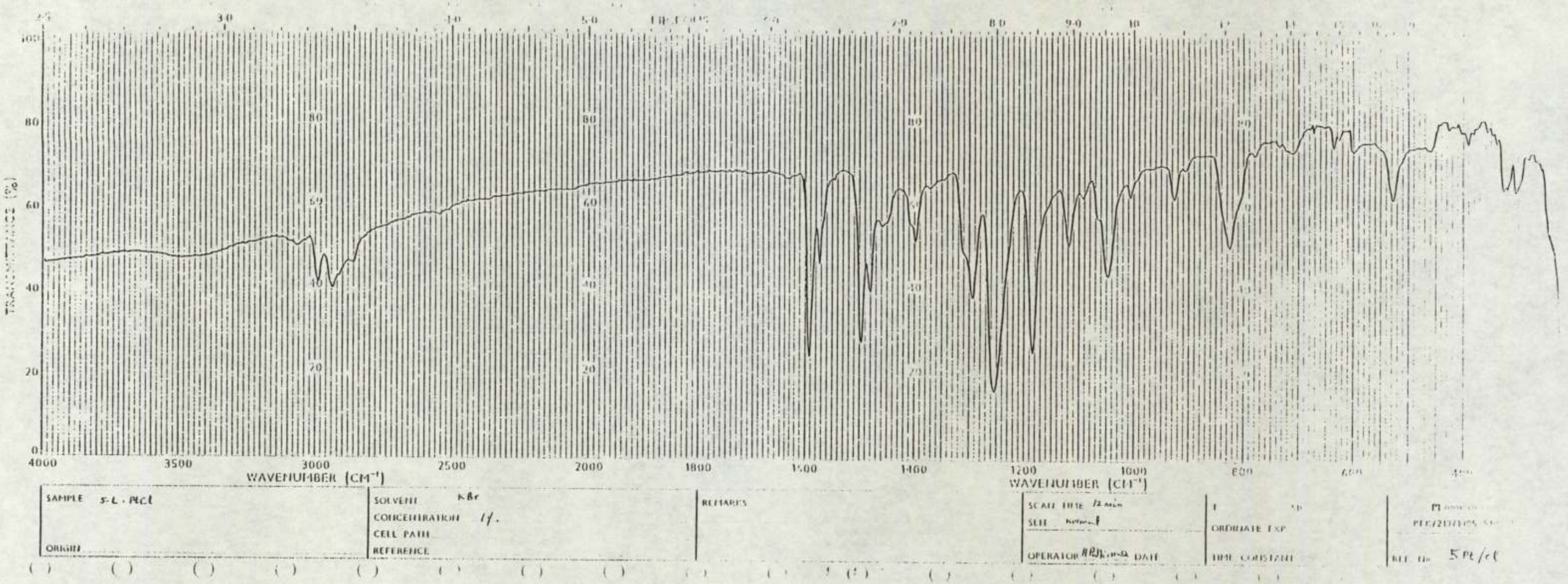


Figure 5.9 I.R. spectrum of $Pt_2Cl_2L^5_2$

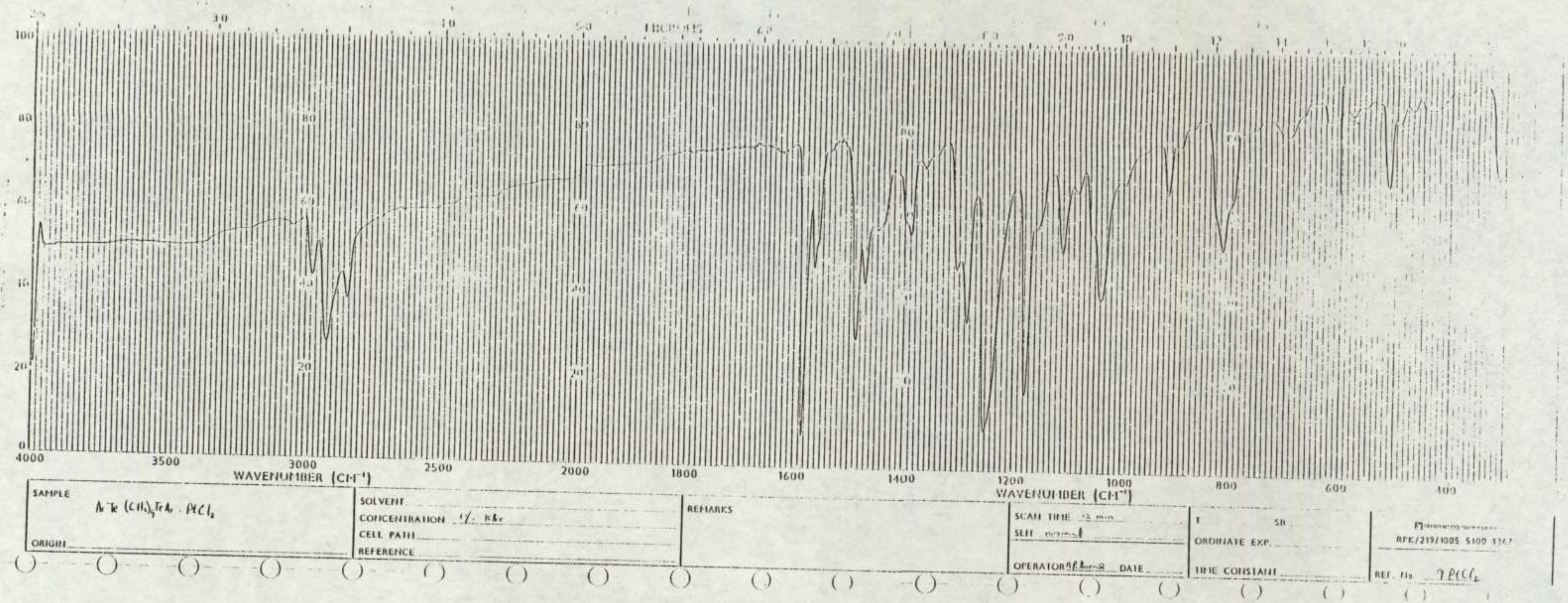
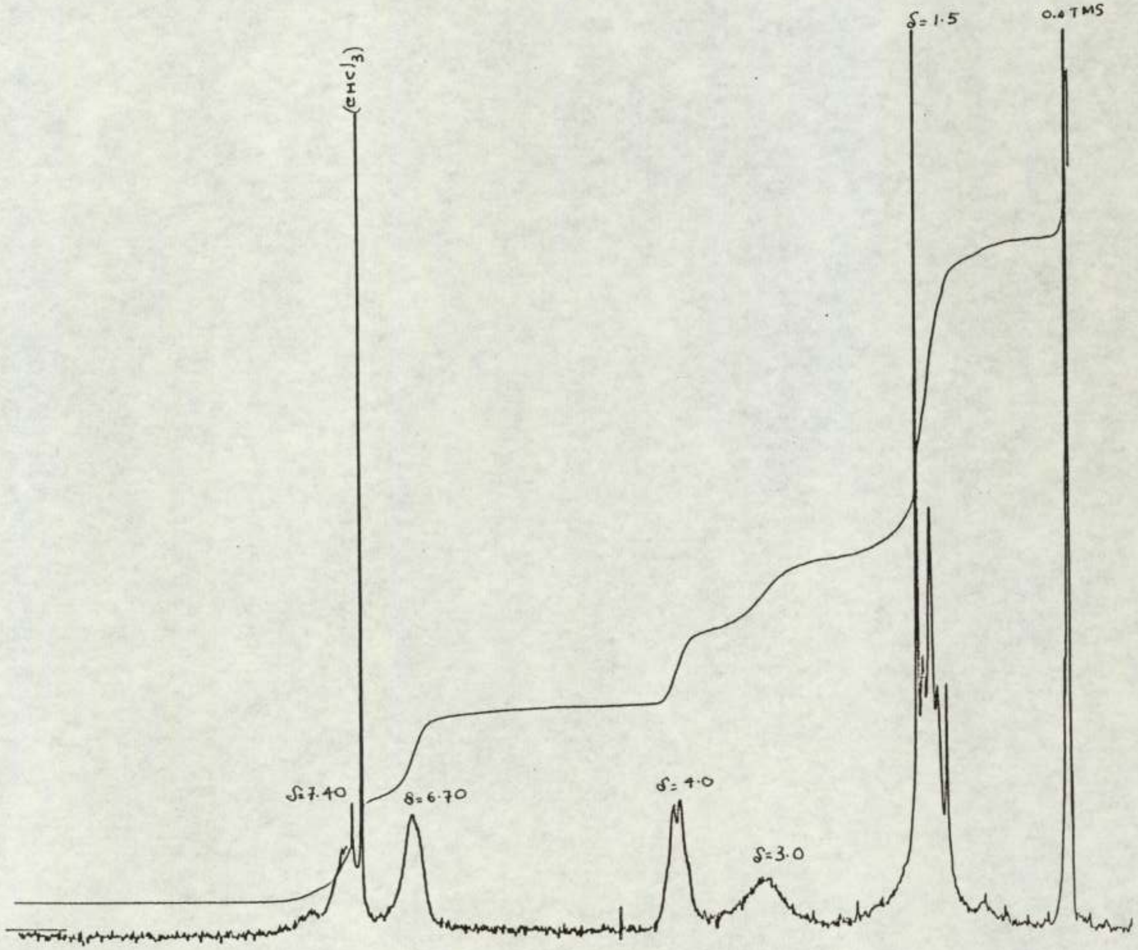


Figure 5.10 I.R. spectrum of $PtCl_2L^9$



<u>Figure 5.11</u> ^1H N.M.R. spectrum of $Pt_2Cl_2L^5_2$

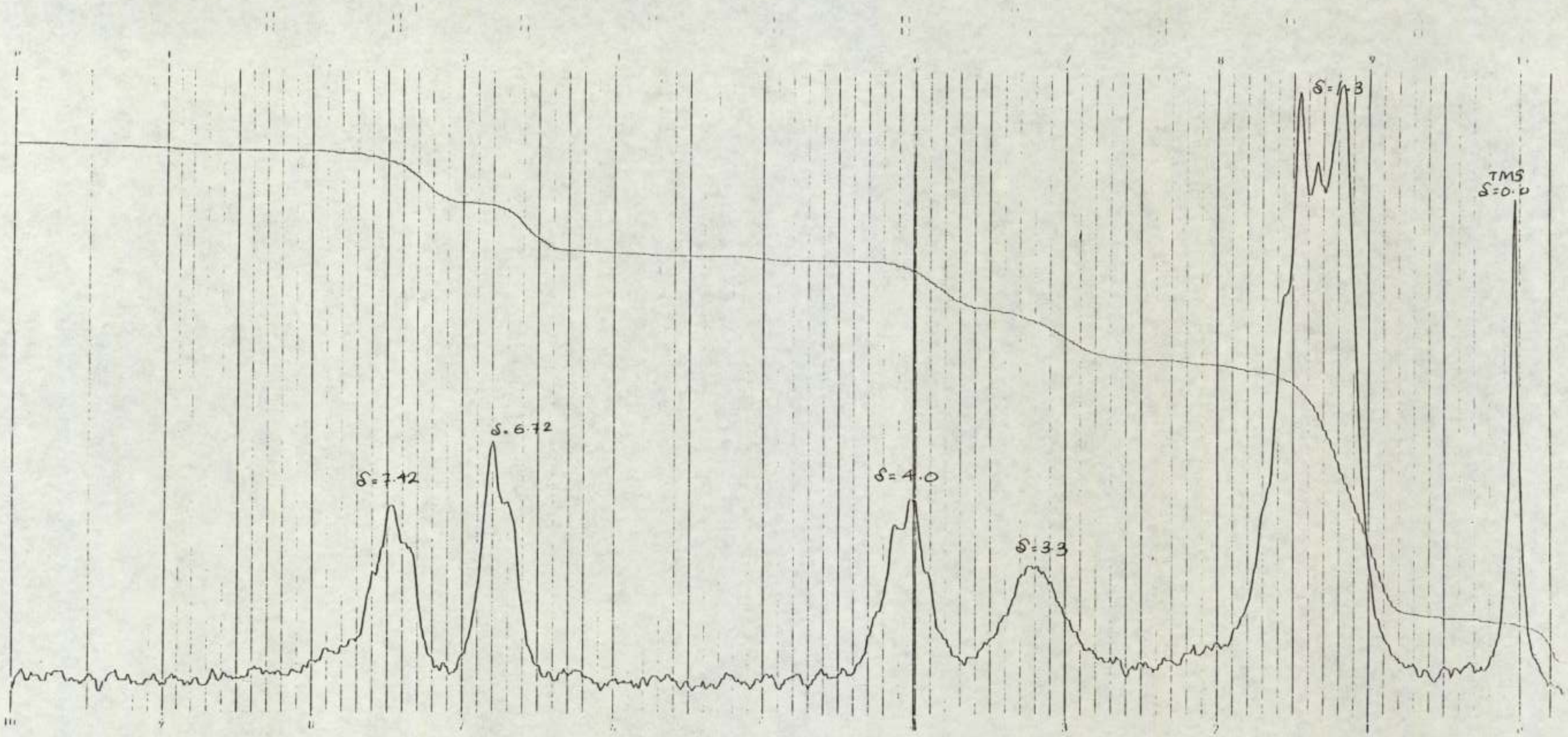
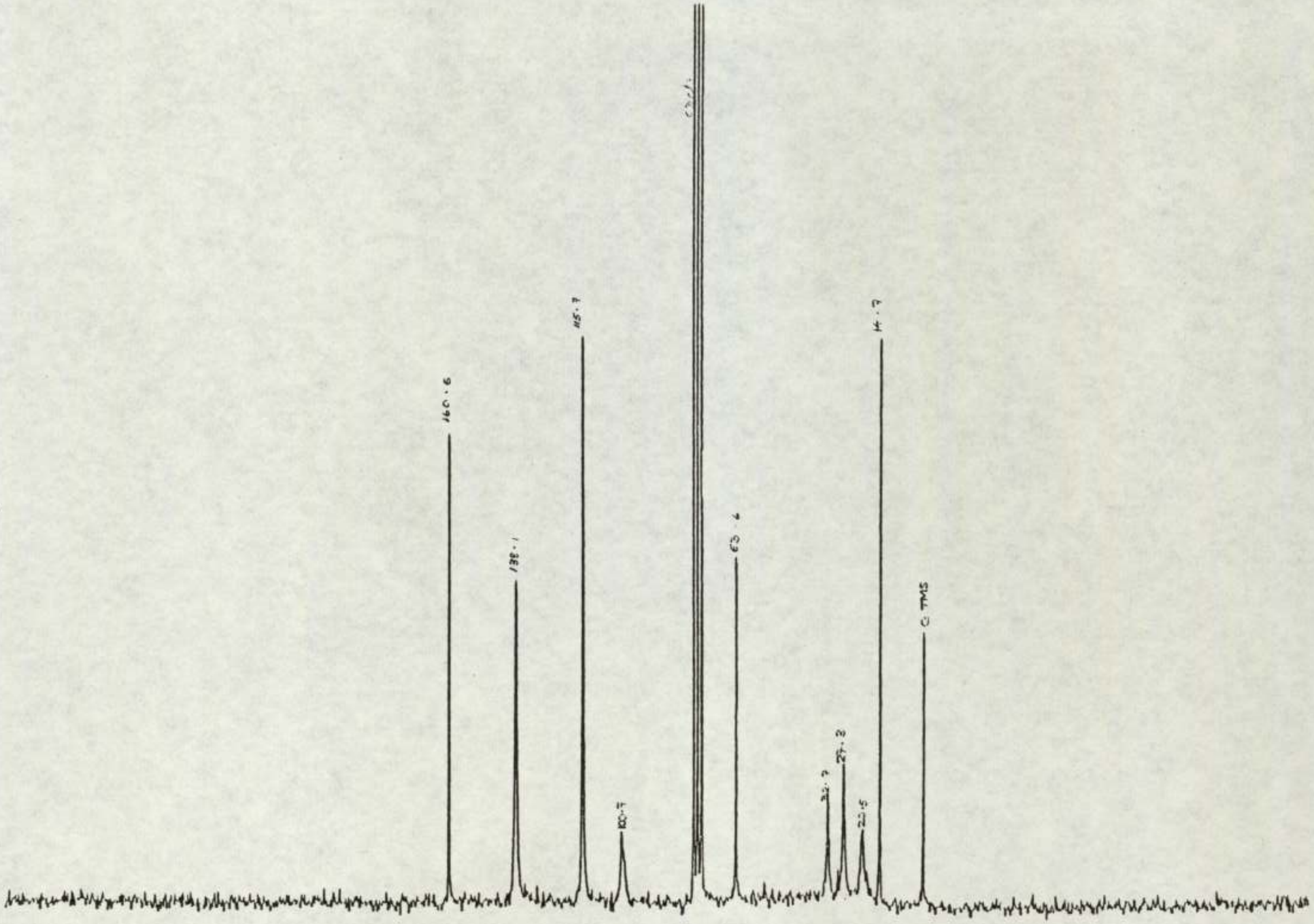


Figure 5.12 ^1H N.M.R. spectrum of $PtCl_2L^{10}$



<u>Figure 5.13</u> $\{^1H\}^{13}C$ N.M.R. spectrum of $Pt_2Cl_2L^5_2$

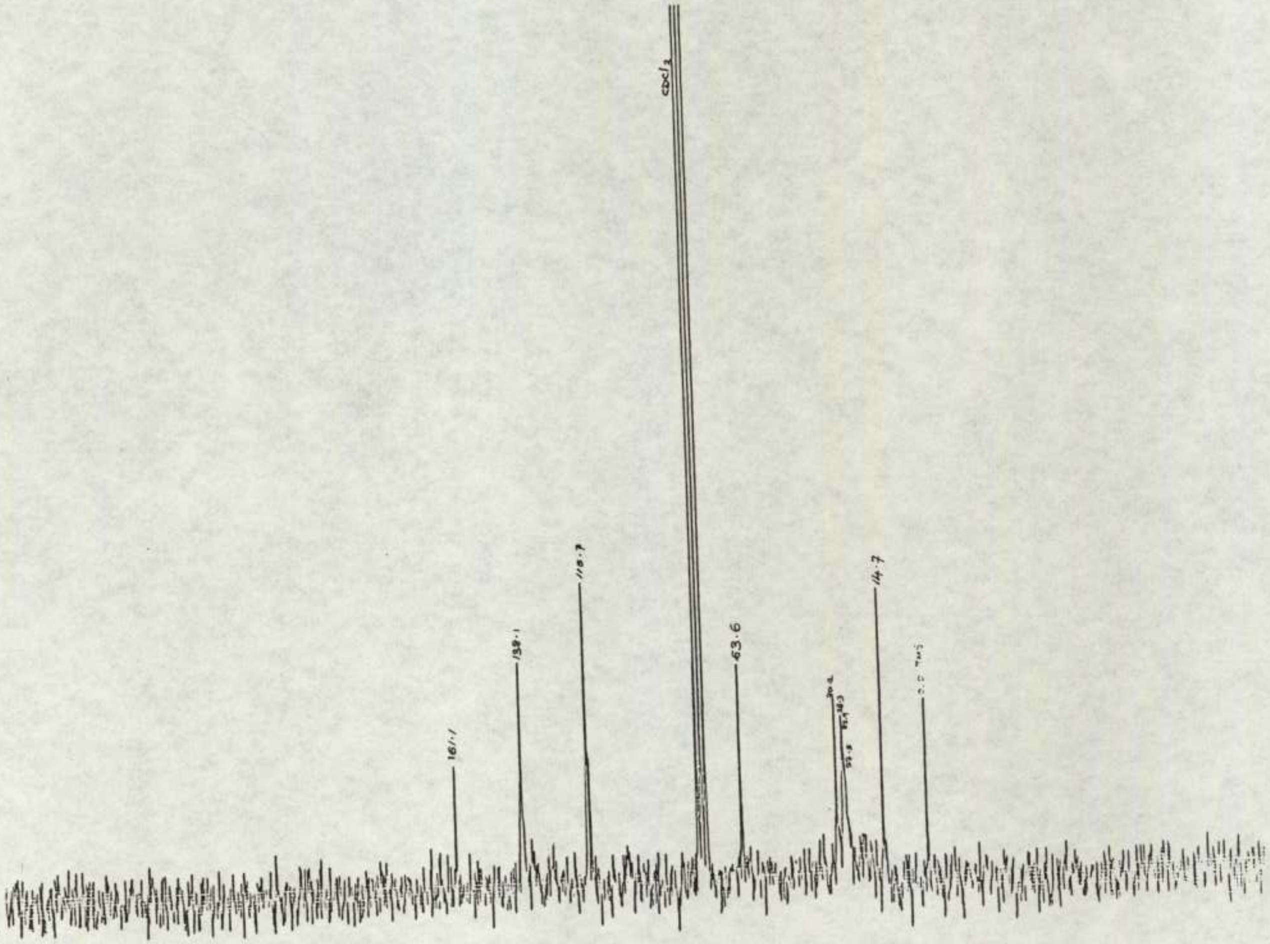
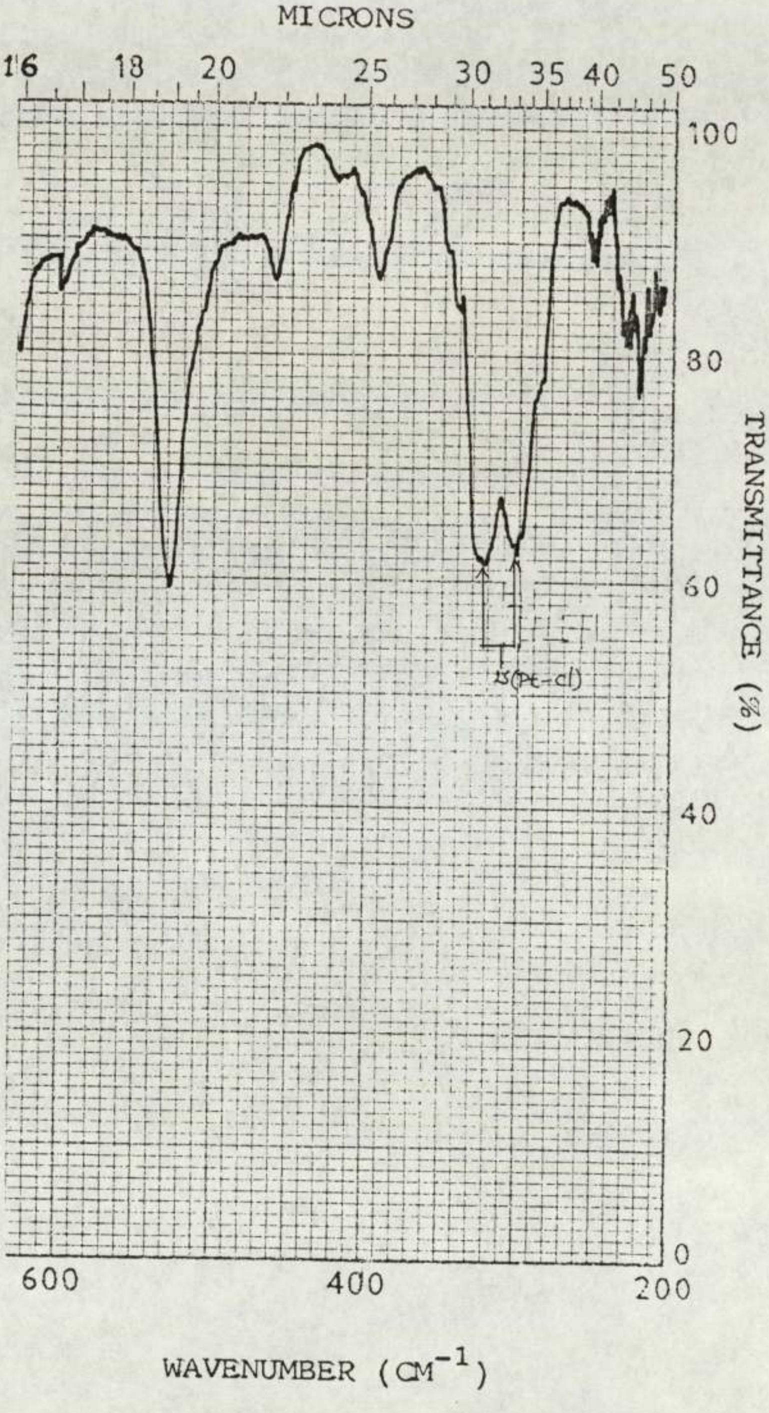


Figure 5.14 $\{^1H\}^{13}C$ N.M.R. spectrum of $PtCl_2L^9$



<u>Figure 5.15</u> Far-infra-red spectrum of $Pt_2Cl_2L_2^5$

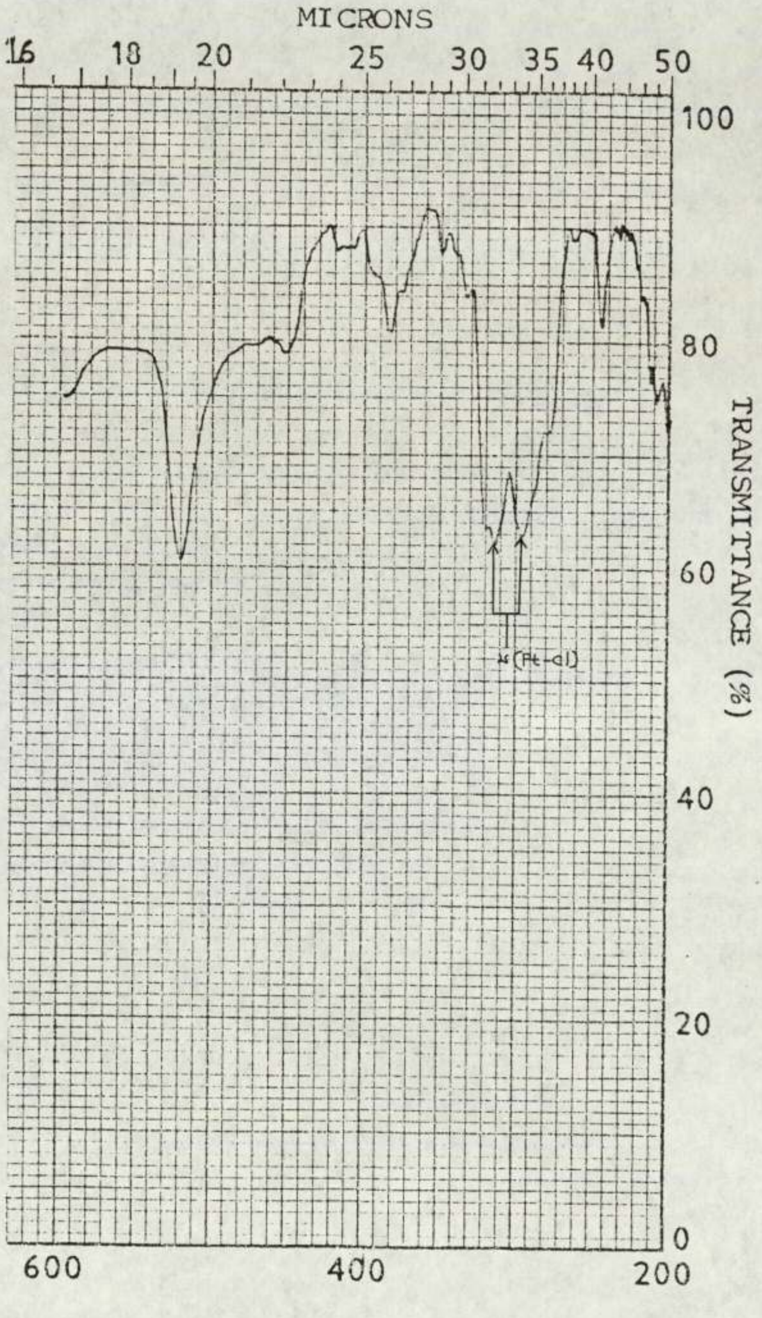


Figure 5.16(a) Far-infra-red spectrum of $PtCl_2L^9$

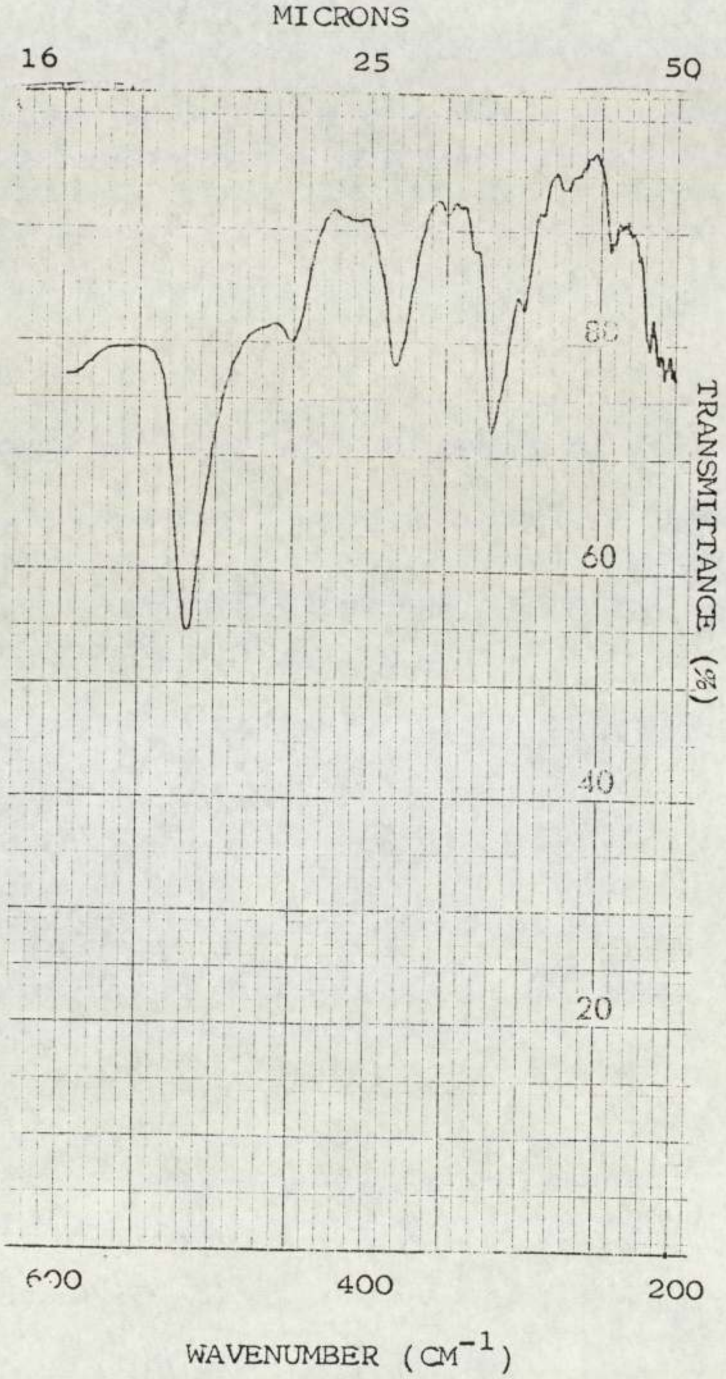


Figure 5.16(b) Far-infra-red spectrum of $PtBr_2L^6$

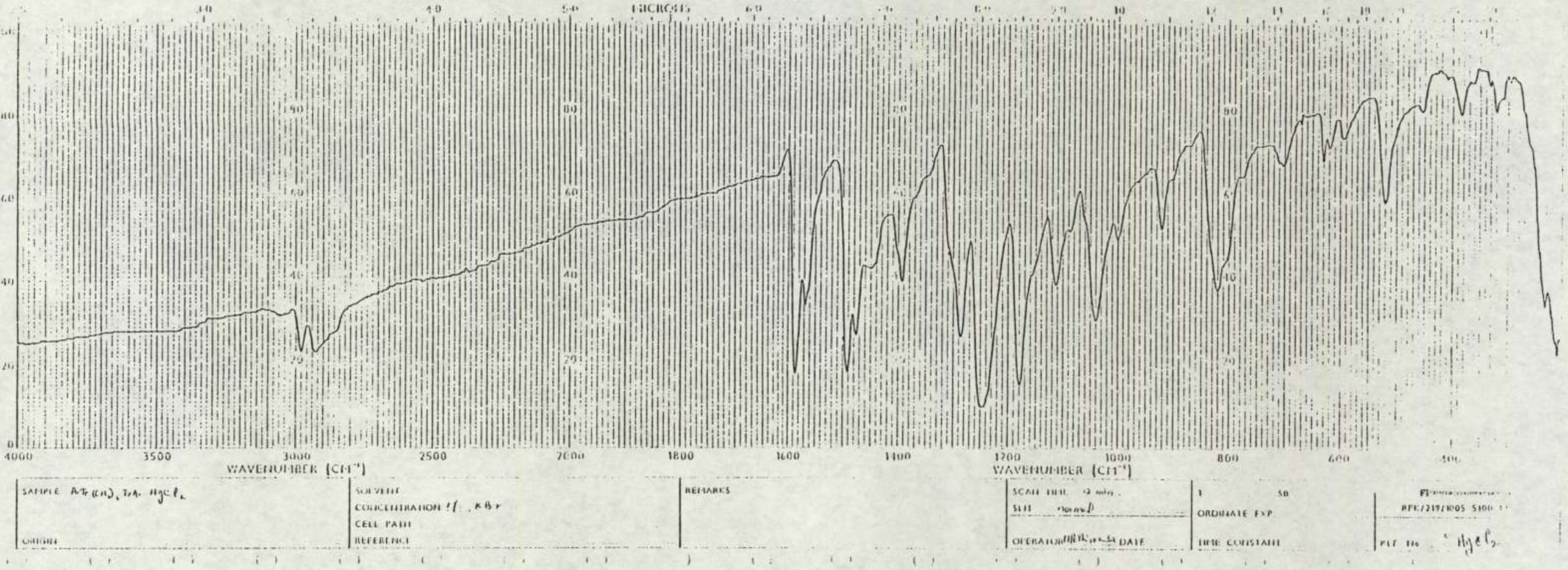


Figure 5.17 I.R. spectrum of $[HgCl_2L^6]_n$

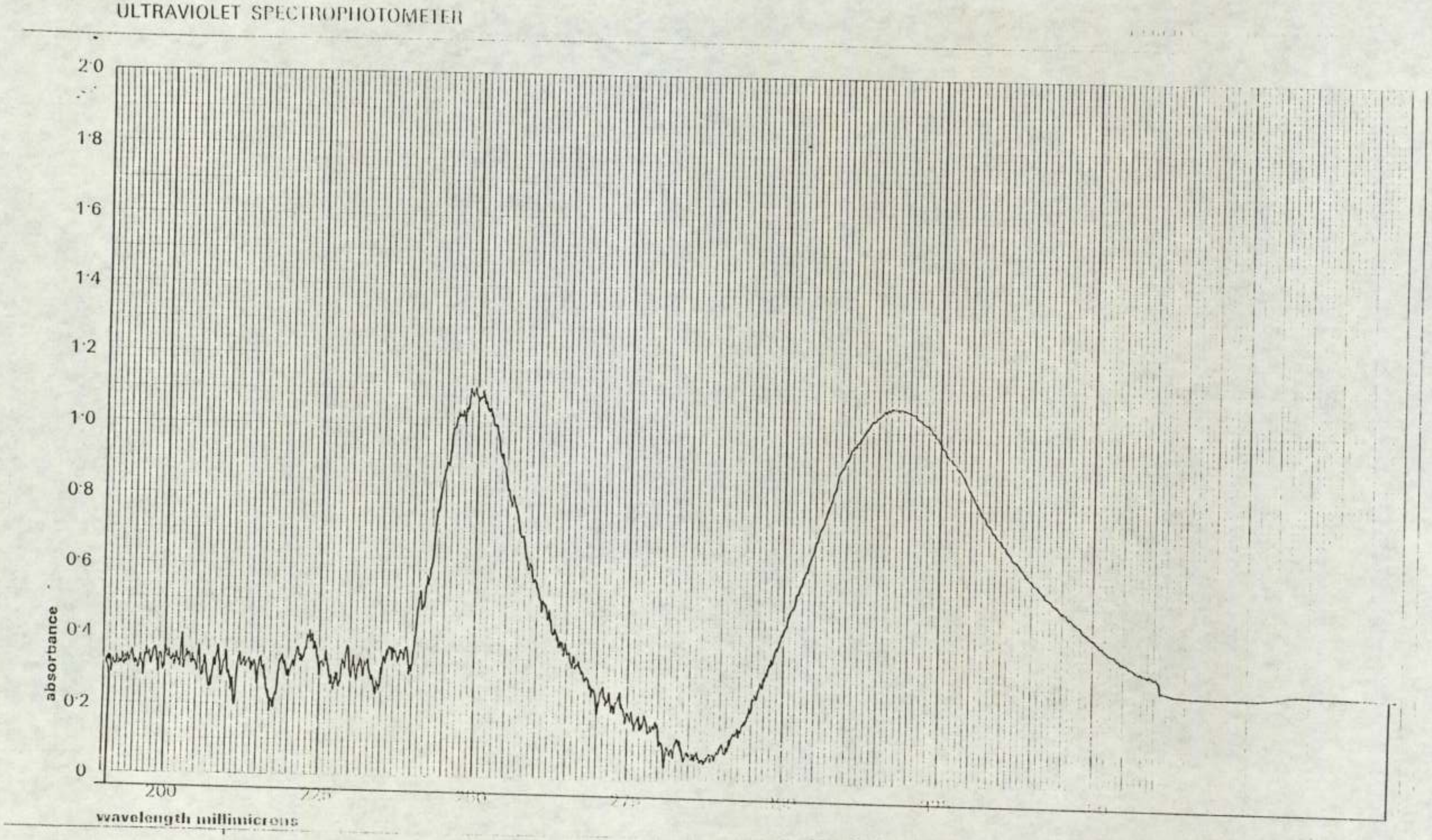


Figure 5.18 U.V. spectrum of $HgCl_2L^7$

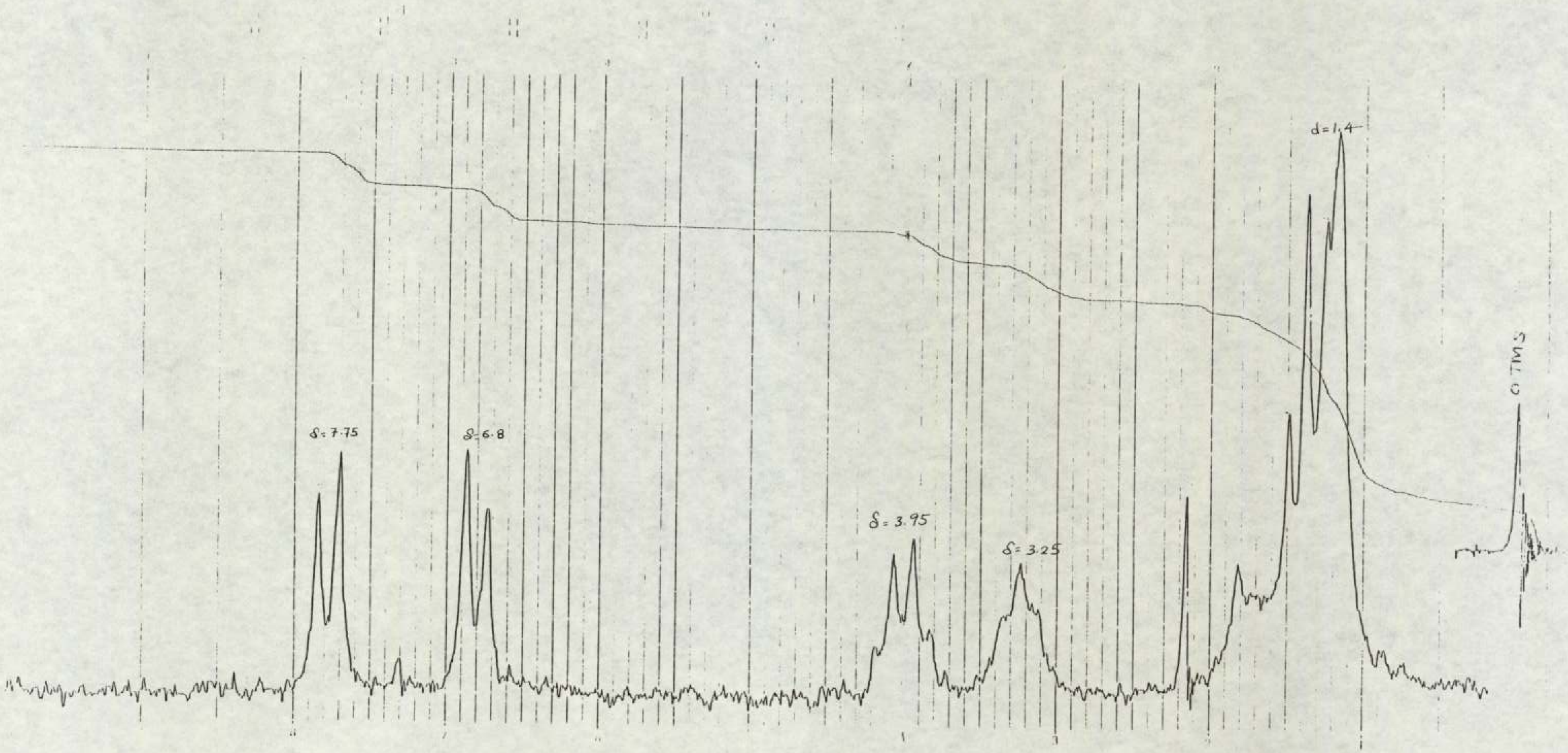


Figure 5.19 ^{1}H N.M.R. spectrum of $HgCl_2L^{10}$

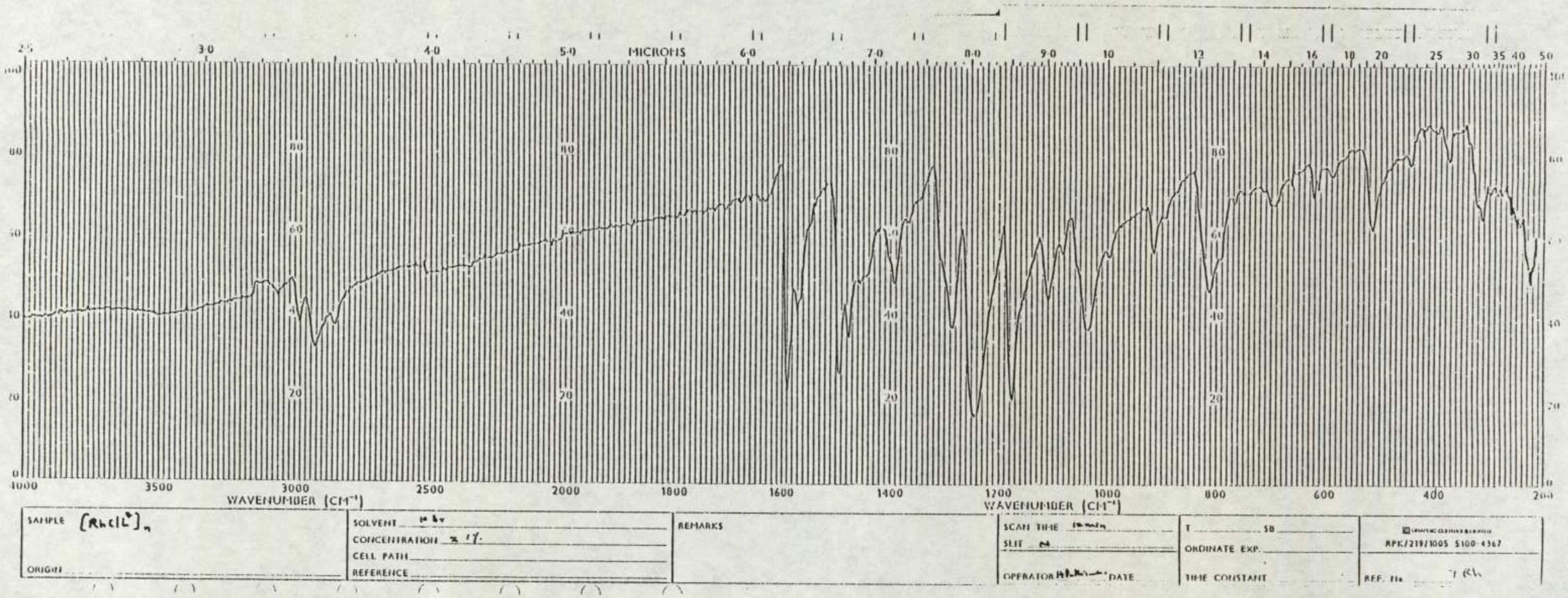


Figure 5.20 I.R. spectrum of $[RhClL^7]_n$

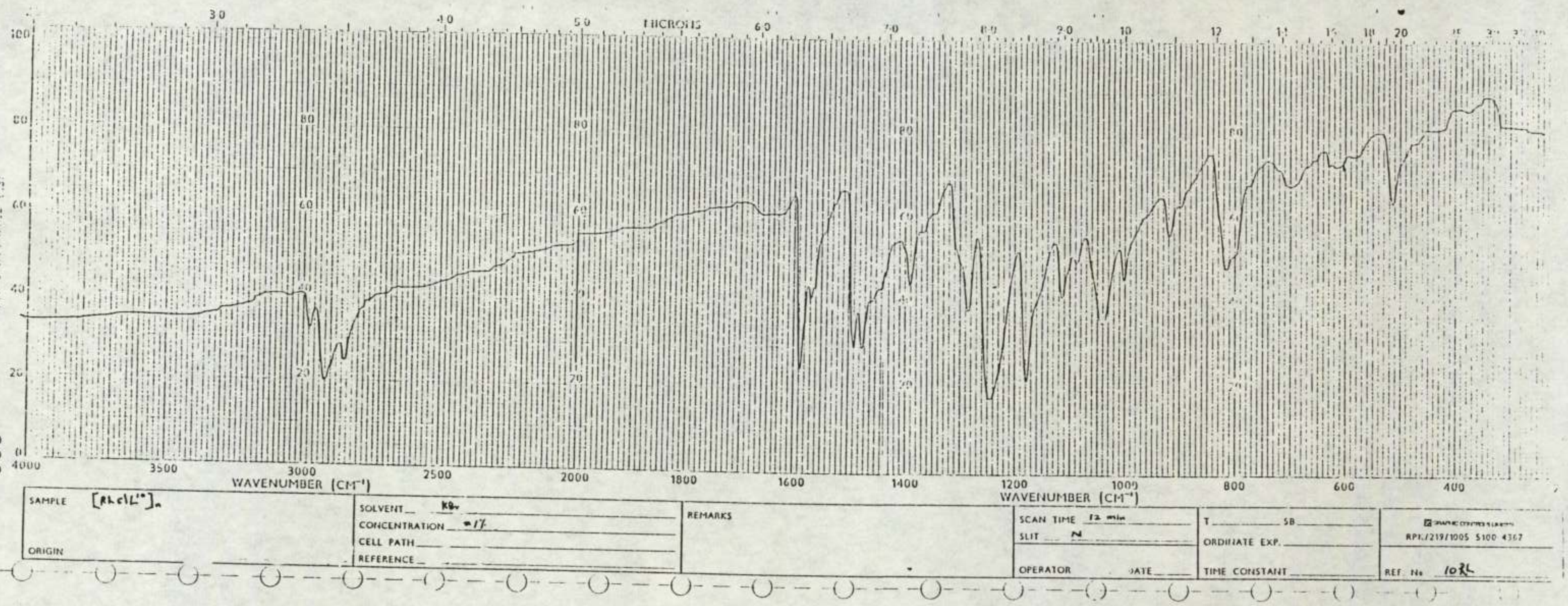


Figure 5.21 I.R. spectrum of $[RhClL^{10}]_n$

5.4 Discussion

The complexes of 1,n-bis-(p-ethoxyphenyltelluro)alkane prepared in this chapter can be divided into four groups on the basis of the co-ordinated metal ion.

1. palladium complexes
2. platinum complexes
3. mercury complexes
4. rhodium complexes

5.4.1 Palladium Complexes of 1,n-Bis-(p-ethoxyphenyltelluro)-alkanes, n=5, 6, 7, 9, 10

The reaction of sodium tetrachloropalladate(II) with 1,n-bis-(p-ethoxyphenyltelluro)alkane in 1:1 molar ratio resulted in complexes having the stoichiometry $PdCl_2L^n$, n=5, 6, 7, 9, 10. Analogous bromide derivatives could be obtained by treating sodium tetrachloropalladate(II) with a five-fold excess of potassium bromide, before reacting it with the ligand. Identical products were obtained by reacting Na_2PdCl_4 with $ArTe(CH_2)_{10}TeAr$ in 1:1 or 1:2 molar ratios. The use of sodium tetrachloropalladate(II) or bis-(benzonitrile)palladium(II) chloride as the complex precursor in the reaction of Pd(II) with $ArTe(CH_2)_7TeAr$ in 1:1 molar ratio resulted in identical products (Table 5.3.1).

All these complexes, except PdX_2L^6 (X=Cl, Br) are soluble in halocarbon solvents, benzene, DMF, DMSO and are non-electrolytes in DMF (at $1x10^{-3}M$) (Table 5.3.5). PdX_2L^6 is extremely insoluble in organic solvents. The insolubility, together with their high melting points (Table 5.3.5) indicate a polymeric structure for these complexes. The insolubility prevented molecular weight determinations on the $[PdX_2L^6]_n$ complexes. The molecular weight determinations by Rast's method indicate that all the other palladium complexes are monomeric (Table 5.3.16).

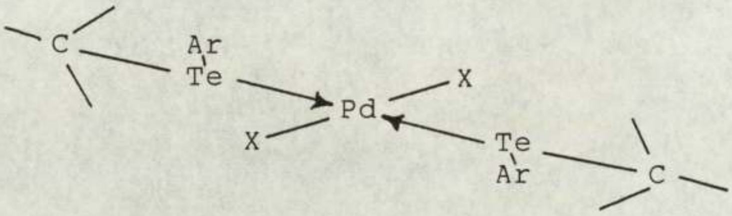
The infra-red spectra of all the palladium complexes indicate characteristic absorptions of the 1,n-bis-(p-ethoxyphenyltelluro)alkane. An infra-red spectrum typical of a soluble monomeric complex and a spectrum of the insoluble polymeric complex are illustrated in Figures 5.1 and 5.2 respectively. The low frequency infra-red spectra of these complexes indicate ν(Pd-Cl) around $342cm^{-1}$ and ν(Pd-Br) around $265cm^{-1}$ (Table 5.3.9). The assignment agrees with a trans-configuration since only one metal-halogen stretching frequency is observed. The Pd-X stretching frequency is in excellent agreement with the values reported for trans-palladium(II) complexes of monodentate tellurium ligands.(44,78,80,81) Far-infra-red spectra typical of a trans-(Pd(II)-Cl) complex and a trans-(Pd(II)-Br) complex are given in Figures 5.3 and 5.4 respectively.

The U.V. spectra of the soluble complexes were studied in $CHCl_3$ solutions (Table 5.3.14). The presence of a low intensity band around 24,000cm^{-1} indicates a square planar geometry(120,121) while the high extinction coefficient ($\varepsilon \approx 10^4$) indicates a charge transfer transition(120,121). A U.V. spectrum typical of a monomeric Pd(II) complex is illustrated in Figure 5.5.

The ^{1}H N.M.R. spectra of $CDCl_3$ solutions of the soluble complexes indicate that the proton resonances are not greatly affected by co-ordination (Table 5.3.10). The spectral pattern is similar to that of the unco-ordinated ligand, 1-n-bis-(p-ethoxyphenyltelluro)alkane. This indicates that the ligand retains its identity in the complexes. A ^{1}H N.M.R. spectrum typical of a monomeric Pd(II) complex is given in Figure 5.6.

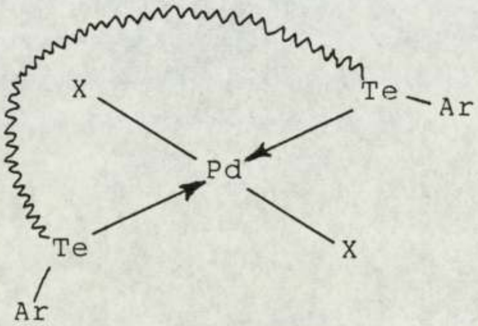
The $\{^1H\}^{13}C$ N.M.R. spectra of $CDCl_3$ solutions of these soluble complexes indicate that the C-1 resonance which was seen around $\delta \approx 8.7$ppm in the free ligand is shifted to $\delta \approx 27.4$ppm (Table 5.3.11). This down field shift arises as a result of the deshielding at C-1. This deshielding occurs because of the withdrawal of electron density from tellurium to palladium, during the formation of the co-ordinate bond. A $\{^1H\}^{13}C$ N.M.R. spectrum typical of a monomeric Pd(II) complex is given in Figure 5.7. The down field shift at both C-1 carbon nuclei indicates the co-ordination of both tellurium atoms of the bis-telluride in these complexes. The rest of the ^{13}C resonances were assigned in the order of increasing chemical shift. According to all the above evidence, the following structures can be suggested.

Possible structure for trans-$[PdX_2L^6]_n$



The long alkane chain may provide conformers of this structure.

Possible structure for trans-PdX_2L^n, n=5, 7, 9, 10



5.4.2 Platinum Complexes Of 1,n-Bis-(p-Ethoxyphenyltelluro)-alkanes

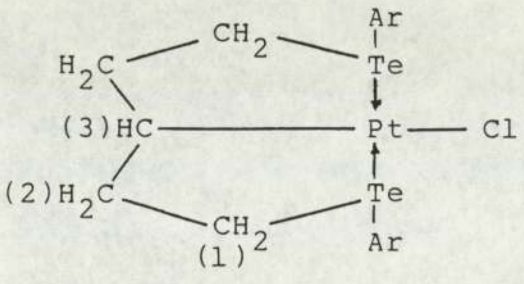
The reactions of potassium tetrachloroplatinate(II) with 1,n-bis-(p-ethxoyphenyltelluro)alkane are different to those of the palladium(II) analogues. Three different types of products were obtained according to the length of the alkane chain of the *bis*-telluride (Table 5.3.2). They are:-

1. $Pt_2Cl_2(L^5)_2$
2. *cis*-$[PtX_2L^6]_n$, X =Cl, Br
3. *cis*-PtX_2L^n, X=Cl, Br; n=7, 9, 10

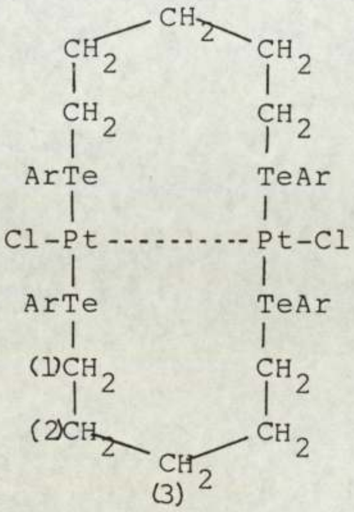
The reaction of potassium tetrachloroplatinate(II) with $ArTe(CH_2)_5TeAr$ in 1:1 molar ratio resulted in a yellow complex and the elemental analysis was compatible with the stoichiometry $PtClL^5$ or $PtCl\{ArTe(CH_2)_2CH(CH_2)_2TeAr\}$. The compound is soluble in benzene and halocarbon solvents and is a non-electrolyte in DMF (at $1x10^{-3}M$) (Table 5.3.6). However, under the same reaction conditions the rest of the ligands resulted in complexes having the stoichiometry PtX_2L^n, n=6, 7, 9, 10. Analogous bromo- complexes could be prepared by treating K_2PtCl_4 with a five-fold excess of KBr before reacting it with the ligand. All these platinum complexes are soluble in halocarbon solvents, benzene and DMF except PtX_2L^6, X=Cl, Br. The latter complex is soluble in hot halocarbon solvents and hot DMF. All these platinum complexes are non-electrolytes in DMF (at $1x10^{-3}M$) (Table 5.3.6). The insolubility of PtX_2L^6 prevented molecular weight determinations. However, the insolubility suggests an oligomeric or a polymeric structure. The molecular weight determinations carried out by Rast's method for the rest of the platinum complexes indicate monomeric species (Table 5.3.16).

As previously indicated for the Pd(II) complexes, the U.V. spectra of $CHCl_3$ solutions of all these platinum complexes (Table 5.3.14) indicate square planar configurations ($\nu \approx 29{,}000 cm^{-1}$)(120,121) and charge transfer transitions ($\varepsilon \approx 10^4$)(120,121). However, the lowest energy absorption arises as a shoulder and is higher in energy than the analogous palladium absorption (Figure 5.8).

The infra-red spectra of all the complexes indicate characteristic bands for 1,n-bis-(p-ethoxyphenyltelluro)alkane (Figures 5.9 and 5.10). The ^1H N.M.R. spectra are not much changed due to co-ordination (Table 5.3.12). The ^1H N.M.R. spectrum of the platinum complex of $ArTe(CH_2)_5TeAr$ and a spectrum typical of $PtCl_2L^n$, n=7, 9, 10, are shown in Figures 5.11 and 5.12 respectively. The integration of the spectrum in Figure 5.11 agrees with the formulation $PtClL^5$ (i.e., there is no evidence for loss of a proton). The $\{^1H\}^{13}C$ N.M.R. spectra are useful for the discussion of the structure of these complexes. The aromatic region and the resonances arising from p-CH_3CH_2O- group are readily assigned following the literature(50,73) (Table 5.3.13). The assignment of ^{13}C resonances of the alkane chain is more useful. On the basis of the stoichiometry alone, the following structures may be suggested for the platinum complex of $ArTe(CH_2)_5TeAr$.



structure (a)



structure (b)

Structure (a) contains Pt(II) and structure (b) contains Pt(I).

The $\{^1H\}^{13}C$ N.M.R. spectrum indicates that the C-1 resonance which is assigned at δ=8.7ppm in $ArTe(CH_2)_5)TeAr$ is shifted down field to δ=20.5ppm (Figure 5.13, Table 5.3.13). As explained for the Pd(II) complexes, this down field shift indicates the co-ordination of both tellurium atoms during the formation of co-ordinate bonds. The C-2 and C-3 resonances are assigned in the order of increasing chemical shift. Structure (a) suggests the phenomenon of cyclometallation. The C-3 resonance in a cyclometallated complex is expected to appear at a lower field than that in $ArTe(CH_2)_5TeAr$. The comparison of the $\{^1H\}^{13}C$ N.M.R. spectrum of this complex with that of $ArTe(CH_2)_5TeAr$ indicates the absence of such a down field shift at C-3. This precludes structure (a) (as does the ^1H N.M.R. spectrum). In the formation of the σ-bond between tellurium and platinum the withdrawal of electron density from tellurium to platinum should be higher in the case of Pt(II) than that of Pt(I). Therefore, the $\{^1H\}^{13}C$ resonance for C-1 is expected to move up field for a Pt(I) complex than in Pt(II) complexes. The comparison of the C-1 resonance of this complex (δ=20.5ppm) with the analogous resonance of the Pt(II) complexes of the rest of the ligands (δ=between 26.2 and 27.7ppm) supports the postulate of a lower oxidation state in the former complex. Thus, structure (b) is reasonable.

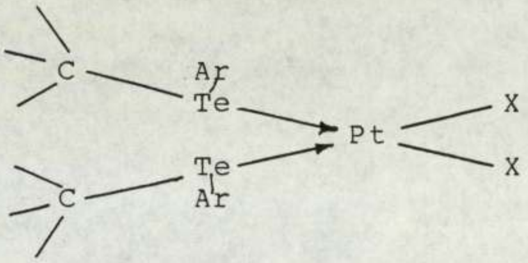
The low frequency infra-red spectrum indicates ν(Pt-Cl) at 301, 322cm^{-1} (Figure 5.15, Table 5.3.9). The Pt-Cl stretching frequency in Pt(I) is expected to appear at lower frequency than in Pt(II). However, no such shift to low frequency is observed for this complex. An explanation may be based on the probable weakness of the Pt.....Pt bond in structure (b). A similar higher frequency (315cm^{-1}) was observed for ν(Pt-Cl) of the Pt(I) complex of $ArTeCH_2TeAr$ (Chapter Three). The compound $Pt_2Cl_2(L^5)_2$ possesses local D_{2h} symmetry if it has structure (b). Group theory predicts that Pt-Cl stretching vibrations for this complex should give rise to one band. However, a splitting of the band is observed. The presence of the long alkane chain could and probably does, lower the ideallised D_{2h} symmetry. This is expected to result in a splitting of the Pt-Cl band to form two bands, however the symmetric vibration may be expected to be of lower intensity than the antisymmetric vibration. However, the splitting of the Pt-Cl band of this complex has resulted in two bands with nearly equal intensity. The reason for this is not clear at this time.

As mentioned earlier in this discussion, the platinum complexes of the rest of the ligands contain Pt(II). A low frequency infra-red spectrum typical of these is illustrated in Figure 5.16(a).The Pt-Cl stretching frequency in far-infra-red spectra of Pt(II) complexes (Table 5.3.9) was assigned by comparing with spectra of analogous bromo- complexes(Fig 5.16(b)). The splitting of the Pt-Cl band resulted in two bands with equal intensity. These Pt-Cl stretching frequencies agree well with the range established for <u>cis</u>-monodentate telluride complexes(82,83,85). As explained earlier, if the complex has a <u>trans</u>-configuration, the presence of the long alkane chain may effectively lower the ideallised D_{2h} symmetry for the <u>trans</u>-configuration. As a result, a sharp band and a weak shoulder should appear for ν(Pt-Cl). The equal intensity of the two bands observed renders this unlikely and suggests a <u>cis</u>-configuration. The ν(Pt-Br) is not observed in the available far-infra-red region (400-200cm^{-1}). However, on the basis of the evidence obtained from the chloro- complex, these could be assigned as <u>cis</u>-species.

A $\{^1H\}^{13}C$ N.M.R. spectrum typical of a Pt(II) complex is given in Figure 5.14. The down field shift of about 18.0ppm for the ^{13}C resonance of C-1 indicates that both the tellurium atoms are co-ordinated to Pt(II). The rest of the resonances are assigned in the order of increasing chemical shift (Table 5.3.13).

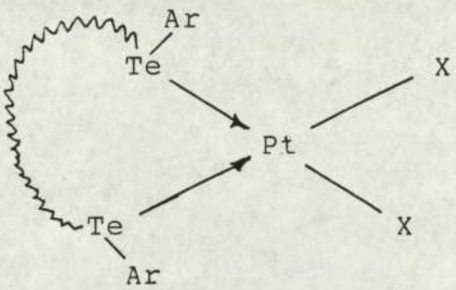
According to all the above evidence, the following structures could be suggested.

Possible structure for cis-$[PtX_2L^6]_n$



Conformers of this structure could form due to the presence of the alkane chain.

Possible structure for cis-PtX_2L^n, n=7, 9, 10



5.4.3 Mercuric(II) Complexes Of 1,n-Bis-(p-Ethoxyphenyltelluro)alkanes

The reaction of mercuric chloride with 1,n-bis-(p-ethoxyphenyltelluro)alkane in 1:1 molar ratio resulted in complexes having the stoichiometry $HgCl_2L^n$, n=5, 6, 7, 9, 10 (Table 5.3.3). All these complexes are soluble in halocarbon solvents, DMF and DMSO except $HgCl_2L^6$. The soluble complexes are non-electrolytes in DMF (at $1x10^{-3}M$) (Table 5.3.7). The insolubility of $HgCl_2L^6$ suggests an oligomeric or a polymeric structure. The infra-red spectra of all these complexes indicate bands characteristic for the bis-tellurides. An infra-red spectrum typical of an $HgCl_2L^n$ complex is shown in Figure 5.17. The far-infra-red spectrum in the region studied,does not give any information about the Hg-Cl stretching frequencies.

The U.V. spectra of $CHCl_3$ solutions of these complexes (Table 5.3.14) indicate charge transfer transitions ($\varepsilon \approx 10^4$). A U.V. spectrum typical of $HgCl_2L^n$, n=5, 7, 9, 10, is illustrated in Figure 5.18 .

The ^1H N.M.R. spectra are not much changed due to co-ordination (Table 5.3.15, Figure 5.19).

The limited data available make it unwise to propose definite structures.

5.4.4 Rhodium Complexes of 1,n-Bis-(p-Ethoxyphenyltelluro)-alkanes

The reaction of $RhCl_3.3H_2O$ with $ArTe(CH_2)_nTeAr$, n=6, 7, resulted in complexes having the molecular formula $RhCl(L^n)$ (Table 5.3.4). These complexes are very sparingly soluble in halocarbon solvents and DMF. The infra-red spectra indicate the characteristic bands for the ligand (Figure 5.20). The Rh-Cl stretching frequency is not observed in the low frequency infra-red region studied (400-200cm^{-1}). This suggests the absence of terminal Rh-Cl bonds(122,123a.123b). The insolubility and high melting point (Table 5.3.8) suggest a polymeric structure. The insolubility precluded N.M.R. studies. A colleague who is working with Rh(I) complexes synthesised a complex having the stoichiometry $RhClL^{10}$ by reacting $ArTe(CH_2)_{10}TeAr$ with $[Rh(COD)Cl]_2$ (COD=cyclooctadiene)(124). All the physical measurements on this complex indicate that it is the same as the product from $Rh(III)Cl_3$.

The behaviour of these bis-tellurides as reducing agents is not surprising. As mentioned earlier in this chapter, such reduction is observed in the reaction of Pt(II) with $ArTe(CH_2)_5TeAr$. The reduction of M(II) to M(I) is also observed in the reaction of M(II) with $ArTe(CH_2)TeAr$ (M(II)= Pd(II), Pt(II); Chapter Three). As mentioned in Chapter Three, this kind of reductive behaviour has been reported with monodentate tellurium ligands in the literature$^{(93)}$.

e.g., $2FeCl_3 + R_2Te \xrightarrow{\text{glacial HOAc}} R_2TeCl_2 + 2FeCl_2$

Therefore, it is reasonable to suggest that the <u>bis</u>-telluride is acting as a reducing agent in the above reactions.

Thus, $Te(II) + 2Pt(II) \longrightarrow Te(IV) + 2Pt(I)$

$Pt(I) + Te(II) \longrightarrow Pt_2\{ArTe(CH_2)_5TeAr\}_2Cl_2$

With Rh(III);

$Te(II) + Rh(III) \longrightarrow Te(IV) + Rh(I)$

$Rh(I) + Te(II) \longrightarrow [Rh\{ArTe(CH_2)_nTeAr\}Cl]_m$, n=6,7

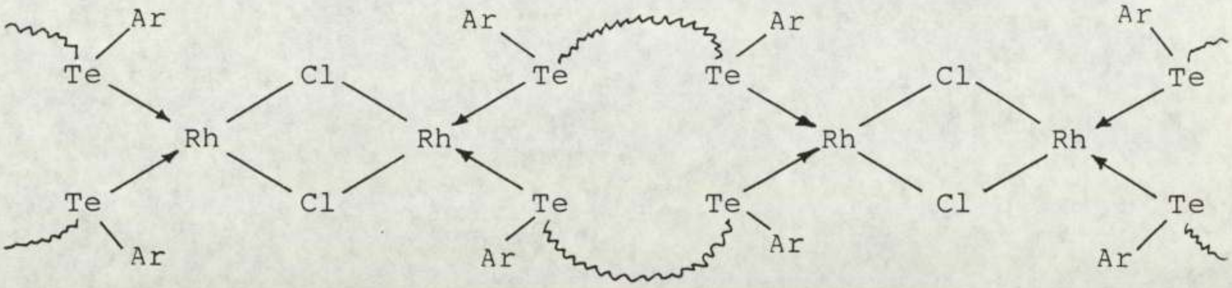
The reaction of Rh(III) with excess $TePh_2$ has resulted in $RhCl_3(TePh_2)_3$$^{(125)}$.

$$RhCl_3.3H_2O + TePh_2 \xrightarrow{EtOH} RhCl_3(TePh_2)_3$$

However, the reaction of Rh(III) with excess PPh_3 has resulted in Rh(I)$^{(126)}$.

$$RhCl_3.3H_2O + \text{excess } PPh_3 \xrightarrow[\text{or acetone}/H_2O]{EtOH} RhCl(PPh_3)_3$$

According to all the above evidence, the following structure could be suggested for these Rh(I) complexes:



In summarising, the following classes of complexes are prepared using bis-tellurides having alkane chain backbones.

(a) with palladium(II),

PdX_2L^n; n=5, 7, 9, 10; soluble, monomeric (X=Cl, Br)
PdX_2L^n; n=6; insoluble, polymeric (X=Cl, Br)

(b) with platinum(II),

$Pt_2Cl_2(L^5)_2$
PtX_2L^6; n=6; sparingly soluble, oligomeric or polymeric
PtX_2L^n; n=7, 9, 10; soluble, monomeric (X=Cl, Br)

(c) with mercury(II)

$HgCl_2L^n$; n=5, 7, 9, 10; soluble
$HgCl_2L^n$; n=6; insoluble, oligomeric or polymeric

(d) with rhodium(III) and rhodium(I)

$RhClL^n$; n=6, 7; insoluble, polymeric

where, $L^n = ArTe(CH_2)_nTeAr$

The nature of the complex precursor, co-ordinated anion and the reactant ratio do not appear to play any part in determining the stoichiometry and the stereochemistry of the resulting Pd(II) complex. The change in co-ordinated anion from chloride to bromide does not affect the stoichiometry of the Pt(II) complexes.

The formation of trans-bonded Pd(II) complexes and cis-bonded Pt(II) complexes with these ligands may be due to,

(1) size factors caused by the larger Pt(II) or,
(2) the greater π-basicity of Pd(II) than Pt(II) towards these bis-tellurides.

Considerable effort was expended in attempting to grow single crystals of these palladium and platinum complexes, suitable for a structural determination, from a variety of solvents, but unfortunately no satisfactory results were obtained. Although $HgCl_2L^{10}$ was formed as microcrystalline solids, no single crystals large enough for an X-ray examination were ever found.

5.4.5 Comparison Of Physical Properties Of Complexes With Published Data For Analogous Diphosphine And Diarsine Complexes

5.4.5.1 Far-infra-red Spectra

The comparison of far-infra-red data of palladium(II) complexes gives the following trend:-

$Pd(DPH)Cl_2 > Pd(DASH)Cl_2 > Pd(DSH)Cl_2 \approx PdCl_2L^6$

$357cm^{-1}$(127) $350cm^{-1}$(116) $343cm^{-1}$(18) $342cm^{-1}$

<u>Bis</u>-tellurides (L^n) are poorer σ-donors compared with diphosphines and diarsines. Therefore, we expect an increase in ν(Pd-Cl) stretching frequency in $PdCl_2L^6$. The above mentioned order indicates that the reverse is true. The reason is that there may be some π-back donation in $Pd(DPH)Cl_2$ and this will increase the Lewis acidity of the metal in the diphosphine complex. This will result in a higher ν(Pd-Cl) than in the other complexes. The order of ν(Pd-Cl) for the complexes corresponds to the order of the relative <u>trans</u>-effect. Thus, the strongest <u>trans</u>-effect of <u>bis</u>-tellurides is reflected in the weakest <u>trans</u>-(Pd-X) bond. Therefore, the order of the <u>trans</u>-effect can be given as follows:-

$P < As < S \approx Te$

A comparison of <u>cis</u>-ν(Pt-Cl) of these new Pt(II) complexes with published data(10) for analogous diphosphine complexes is given below.

$Pt(DPH)Cl_2$	$PtCl_2L^6$
295, $320cm^{-1}$	299, $315cm^{-1}$

5.4.5.2 U.V. Spectra

Comparison of the U.V. data of the palladium complexes is given below.

$\nu_{max}(cm^{-1})$ $Pd(DPD)Cl_2 \approx Pd(DAsD)Cl_2 > PdCl_2L^{10}$

$29,400cm^{-1}$(127) $29,400cm^{-1}$(116) $23,981cm^{-1}$

This indicates that $ArTe(CH_2)_nTeAr$ produces rather weak ligand fields and suggests the following spectrochemical series:

P ≈ As > Te

5.4.6 Comparison Of Lewis Basicity Of *Bis*-tellurides With Ditellurides

Although $ArTe(CH_2)_7TeAr$ replaces PhCN in $PdCl_2(PhCN)_2$ to form $Pd\{ArTe(CH_2)_7TeAr\}Cl_2$, it has been reported that $(p-OC_2H_5C_6H_4)_2Te_2$ could not form analogous complexes with $PdCl_2(PhCN)_2$(122). Therefore, on the basis of the reactivity with $PdCl_2(PhCN)_2$, the following trend in Lewis basicity is obtained.

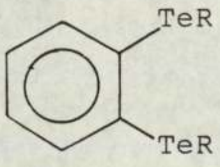
$ArTe(CH_2)_nTeAr > Ar_2Te_2$

CHAPTER SIX

CO-ORDINATION CHEMISTRY OF BIDENTATE TELLURIUM LIGANDS HAVING RIGID BACKBONES

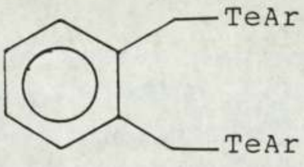
6.1 Introduction

This work was carried out to examine the effect of a rigid backbone on the co-ordination mode of the _bis_-telluride. Therefore, the interests were focused on 1,2-_bis_-(p-ethoxyphenyltelluro)benzene, 1,2-_bis_-(n-butyltelluro)benzene (i) and α,α'-_bis_-(p-ethoxyphenyltelluro)o-xylene (ii).



R=(p-$OC_2H_5.C_6H_4$ or n-Bu)

(i)



(ii)

Apart from this work, the synthesis of potentially tetradentate tellurium ligands was attempted, by the method used to prepare the bidentate tellurium ligands. Considerable difficulties were often experienced in attempts to synthesise and isolate a product in reasonable yield. However, the first potentially tetradentate tellurium ligand, the spirocyclic $C(CH_2TeAr)_4$, was successfully synthesised and characterised in this study. However, the yield was poor.

6.2 Experimental

6.2.1 Attempted Synthesis Of 1,2-*Bis*-(p-ethoxyphenyltelluro)-benzene

(a) This was carried out as reported by Petragnani(39). 2-(phenyliodonio)benzoate was recrystallised from a 0.02% solution of EDTA in water before using(39).

Bis-(p-ethoxyphenyl)ditelluride (0.5g, 1mmol) and 2-(phenyliodonio)benzoate (0.65g, 2mmol) in 1,2-dichlorobenzene (5cm^3) were heated at 180°C for 0.5h in an argon atmosphere. The removal of the solvent and iodobenzene resulted in a pale yellow, ill-defined product.

(b) Attempted synthesis of 1,2-*bis*-(n-butyltelluro)benzene

A solution of 1,2-dibromobenzene (2.36g, 10mmol) in dry ether was added dropwise to a solution of n-butyllithium (25mmol) in dry ether in an argon atmosphere. The reaction mixture was gently refluxed during the addition, and was stirred for 20-30min to complete the reaction. Finely ground tellurium powder (2.56g, 20mmol) was added to the reaction mixture, which was then refluxed for 2.5h, and then cooled to room temperature. n-BuBr was then added and the mixture stirred for 0.5h, after which the unreacted tellurium was filtered off. The organic layer was separated, washed with distilled water and dried over anhydrous Na_2SO_4. The evaporation of ether resulted in a pale yellowish-cream coloured precipitate. Recrystallisation from acetonitrile gave a cream coloured ill-defined product.

6.2.2 Synthesis of α,α'-Bis-(p-ethoxyphenyltelluro)o-xylene

This preparation was carried out in the dark.

Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene ($10cm^3$) and ethanol ($20cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in $1moldm^{-3}$ sodium hydroxide solution was added dropwise. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, a solution of α,α'-(dibromo)o-xylene (2.64g, 10mmol) in benzene was added, and was stirred for 2h at room temperature. The yellow solution obtained was added to distilled water and stirred well. The organic layer was separated, washed with distilled water, and then petroleum ether added (b.p. 40-60°C) and stirred well. The yellow precipitate was filtered and dried in vacuo over P_4O_{10}. Recrystallisation from petroleum ether (b.p. 40-60°C) resulted in a bright yellow precipitate in 50% yield. m.p. 69-70°C.

Found	C 47.9	H 4.00%
$C_{24}H_{26}O_2Te_2$ requires	C 47.9	H 4.30%

6.2.3 Synthesis Of Transition Metal Complexes Of α,α'-*Bis*-(p-ethoxyphenyltelluro)o-xylene

All the following preparations were carried out in the dark under the passage of oxygen free dinitrogen.

(a) A solution of potassiumtetrachloropalladate(II) (0.163g, 0.5mmol) in distilled water was added dropwise to a solution of α,α'-*bis*-(p-ethoxyphenyltelluro)o-xylene (0.301g, 0.5mmol) in acetone in a dinitrogen atmosphere, and was stirred for 12h. The orangish-yellow precipitate was filtered and dried in vacuo over P_4O_{10}. Yield 49%. m.p. 145-146°C(dec).

Found	C 38.6	H 3.20%
$C_{48}H_{52}O_4Te_4Pd_2Cl_2$ requires	C 38.8	H 3.50%

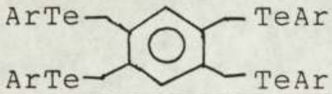
(b) A solution of potassiumtetrachloroplatinate(II) (0.208g, 0.5mmol) in distilled water was added dropwise to a solution of α,α'-*bis*-(p-ethoxyphenyltelluro)o-xylene (0.301g, 0.5mmol) in acetone in a dinitrogen atmosphere and was stirred for 12h. The yellow precipitate so formed was filtered, washed with distilled water and dry acetone, and then dried over P_4O_{10}. Yield 48%. m.p. 160-161°C(dec).

Found	C 34.6	H 2.65%
$C_{48}H_{52}O_4Te_4Pt_2Cl_2$ requires	C 34.6	H 3.10%

(c) A solution of mercuric chloride (0.136g, 0.5mmol) in acetone was added dropwise to a solution of α,α'-<u>bis</u>-(p-ethoxyphenyltelluro)o-xylene (0.301g, 0.5mmol) in a dinitrogen atmosphere, and was stirred for 12h. The yellow precipitate was filtered, washed with dry acetone, and dried in vacuo over P_4O_{10}. Yield 68%. m.p. 120-121°C.

Found	C 33.0	H 2.90%
$C_{24}H_{26}O_2Te_2HgCl_2$ requires	C 33.0	H 3.00%

6.2.4 Attempted Synthesis Of



The reaction was carried out in an oxygen free dinitrogen atmosphere.

Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene ($10cm^3$) and ethanol ($20cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1mol dm^{-3} NaOH solution was added dropwise. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, a solution of α,α'-tetrabromo-o-xylene (2.3g, 5mmol) in benzene was added. As soon as the tetrabromoxylene was added, the colour changed to orange and ditelluride was formed.

6.2.5 Synthesis Of Tetrakis-(p-ethoxyphenyltelluromethyl)-methane

The reaction was carried out in an oxygen free dinitrogen atmosphere.

(a) Bis-(p-ethoxyphenyl)ditelluride (4.97g, 10mmol) in benzene (10cm^3) and ethanol (20cm^3) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1mol dm^{-3} NaOH solution was added dropwise. The reaction mixture became colourless on completion of the addition. Immediately after the appearance of the colourless stage, a solution of $C(CH_2Br)_4$ (1.94g, 5mmol) in benzene (25cm^3) was added and stirred for 1.75h at room temperature. No visible change was observed in the reaction mixture. When the reaction mixture was opened to air, ditelluride was formed.

(b) The same reaction was carried out as in 6.2.4(a), using a solution of $C(CH_2Br)_4$ in tetrahydrofuran (25cm^3) instead of using benzene. After the addition of this $C(CH_2Br)_4$ solution,a reddish-brown colouration appeared which then immediately disappeared. The solution then changed to a very pale yellow. This was stirred for 1.75h at room temperature. The solution was then added to distilled water, after which the organic layer was separated, washed with distilled water, and then acetonitrile added and stirred well. A cream coloured precipitate was separated in a very low yield. This was filtered and dried in vacuo. Recrystallisation from acetonitrile resulted in a white precipitate in very poor yield.

(c) The reaction 6.2.4(b) was slightly modified in the following way, in order to obtain a pure compound and better yield.

After the addition of the solution of $C(CH_2Br)_4$ (1.94g, 5mmol) in tetrahydrofuran (25cm^3), another 145cm^3 of tetrahydrofuran was added to the reaction mixture and refluxed for 5h. This was then added to distilled water, stirred well and the precipitated Te filtered off. The organic layer was separated, washed with distilled water, and then acetonitrile added and stirred well. The white precipitate was filtered off and dried in vacuo. Recrystallisation from acetonitrile resulted in a white precipitate in 5% yield. m.p. 146-147°C.

Found	C 42.1	H 3.70%
$C_{37}H_{44}O_4Te_4$ requires	C 41.8	H 4.10%

6.3 Results

α,α'-bis-(p-ethoxyphenyltelluro)o-xylene is soluble in common organic solvents, i.e. halocarbon solvents, benzene, acetone, ether, DMF. It is insoluble in petroleum ether, hexane and cold ethanol. The conductivity measurement indicates that this is a non-electrolyte in DMF (at 1×10^{-3}M) (Table 6.3).

All the transition metal complexes prepared by reacting M(II), (M=Pd, Pt, Hg) with $o\text{-}C_6H_4(CH_2TeAr)_2$ in 1:1 molar ratio, are very sparingly soluble in common organic solvents. They are soluble in hot DMF. The conductivity measurements indicate that these are non-electrolytes in DMF (at 1×10^{-3}M) (Table 6.3).

Tetrakis-(p-ethoxyphenyltelluromethyl)methane is soluble in halocarbon solvents and in warm acetone.

Compound	Found%		Required%	
	C	H	C	H
$o\text{-}C_6H_4(CH_2TeAr)_2$	47.9	4.00	47.9	4.30
$Pd_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2Cl_2$	38.6	3.20	38.8	3.50
$Pt_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2Cl_2$	34.6	2.65	34.6	3.10
$[o\text{-}C_6H_4(CH_2TeAr)_2]HgCl_2$	33.0	2.90	33.0	3.00

Table 6.1 The elemental analysis of α,α'-bis-(p-ethoxyphenyltelluro)o-xylene and transition metal complexes of it.

Compound	Found%		Required%	
	C	H	C	H
$C(CH_2TeAr)_4$	42.1	3.70	41.8	4.10

Table 6.2 The elemental analysis of tetrakis-(p-ethoxyphenyltelluromethyl)methane.

Compound	Colour	M.P. °C	Λ (1×10^{-3}M in DMF) ($ohm^{-1}cm^2mol^{-1}$)
$o\text{-}C_6H_4(CH_2TeAr)_2$	bright yellow	69-70	8.03
$Pd_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2Cl_2$	orangish-yellow	145-146 (dec)	17.0
$Pt_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2Cl_2$	yellow	160-161 (dec)	21.9
$[o\text{-}C_6H_4(CH_2TeAr)_2]HgCl_2$	yellow	120-121	39.4

Table 6.3 Some physical properties of α,α'-bis-(p-ethoxyphenyltelluro)o-xylene and metal complexes of it.

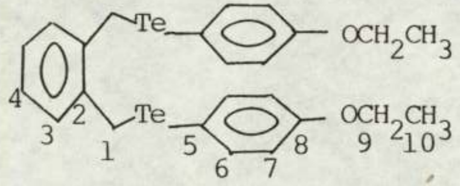
Compound	δ mm s^{-1}	Δ mm s^{-1}
$o\text{-}C_6H_4(CH_2TeAr)_2$	0-03(±0.08)	10.72(±0.1)

Table 6.4 Mössbauer data for α,α'-*bis*-(p-ethoxyphenyltelluro)o-xylene (relative to Sb/Cu)

Compound	Chemical shift$^{(a)}$									
	Aliphatic Region			Aromatic Region						
	C-1	C_9	C_{10}	2	3	4	6	7	8	5
L	10.1	68.4	14.7	137.8	129.8	126.5	115.6	142.0	159.3	102.4

(a)-chemical shift measured in ppm relative to Me_4Si internal standard

L =



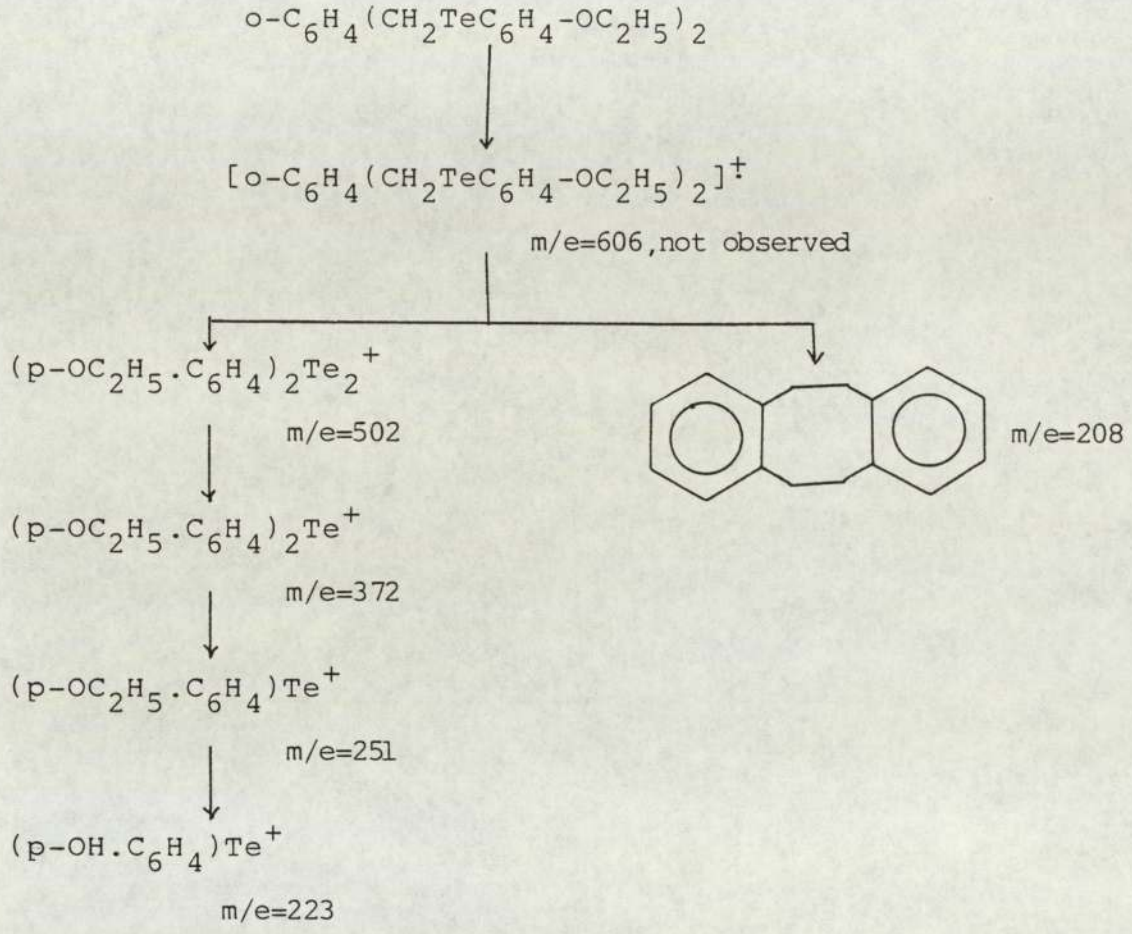
number system used to designate individual carbon atoms of o-$C_6H_4(CH_2TeAr)_2$

Table 6.5 ^{13}C N.M.R. data for o-$C_6H_4(CH_2TeAr)_2$

Compound	Chemical Shift[(a)]							
	Aliphatic Region				Aromatic Region			
	C	CH_2	OCH_2	CH_3	o-	m-	p-	i-
$C(CH_2TeAr)_4$	25.4	21.2	63.3	14.8	115.4	136.8	159.9	109.6

(a) - chemical shift measured in ppm relative to Me_4Si internal standard

<u>Table 6.6</u> ^{13}C N.M.R. data for $C(CH_2TeAr)_4$



Quoted m/e values are referenced to ^{130}Te, ^{12}C, ^{1}H and ^{16}O.

Scheme 6.1 Mass fragmentation pattern for α,α'-*bis*-(p-ethoxyphenyltelluro)o-xylene

$$\mathrm{C[CH_2Te(C_6H_4OC_2H_5)]_4}$$

$$\downarrow$$

$$\mathrm{C[CH_2Te(C_6H_4OC_2H_5)]_4^{+\cdot}}$$

m/e=1072 not observed

$$\downarrow$$

$$\mathrm{(p\text{-}OC_2H_5.C_6H_4)_2Te_2^{+}}$$

m/e=502

$$\downarrow$$

$$\mathrm{(p\text{-}OC_2H_5.C_6H_4)_2Te^{+}}$$

m/e=372

$$\downarrow$$

$$\mathrm{(p\text{-}OH.C_6H_4)_2Te^{+}}$$

m/e=316

Quoted m/e values are referenced to ^{130}Te, ^{12}C, ^{1}H and ^{16}O.

Scheme 6.2 Mass fragmentation pattern for $C(CH_2TeAr)_4$

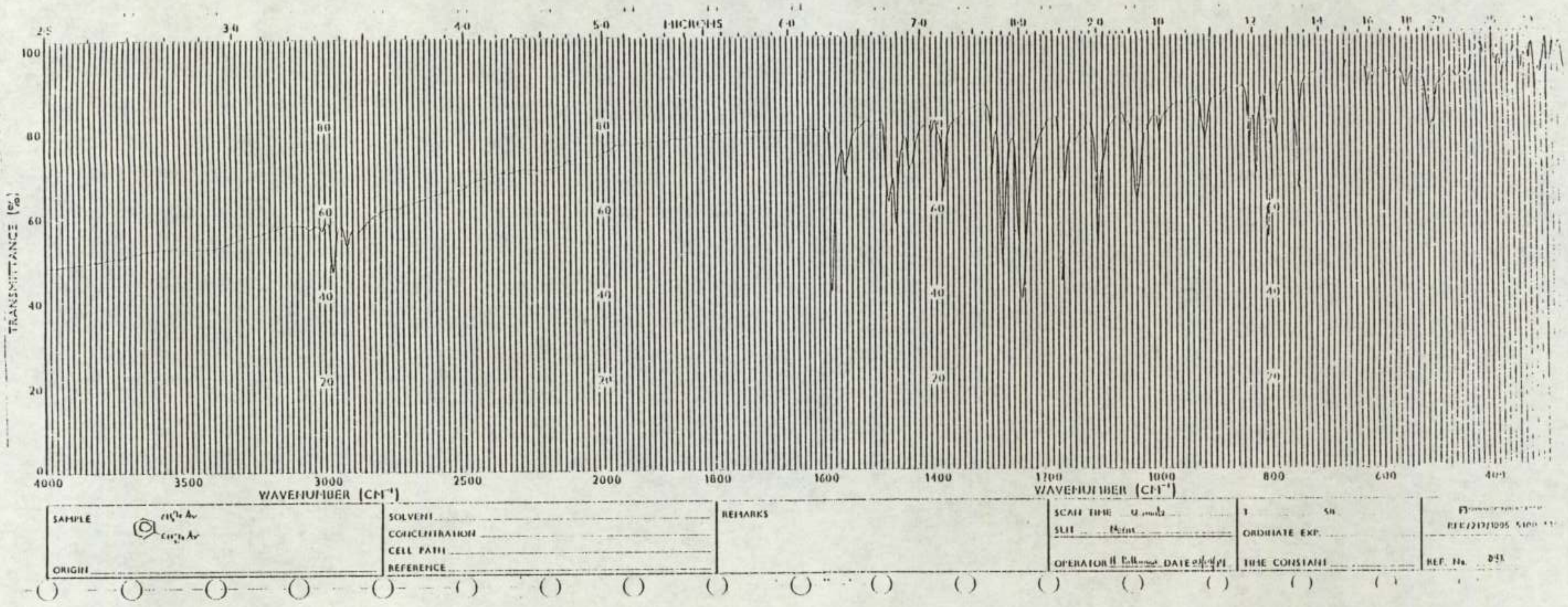


Figure 6.1 I.R. spectrum of o-$C_6H_4(CH_2TeAr)_2$

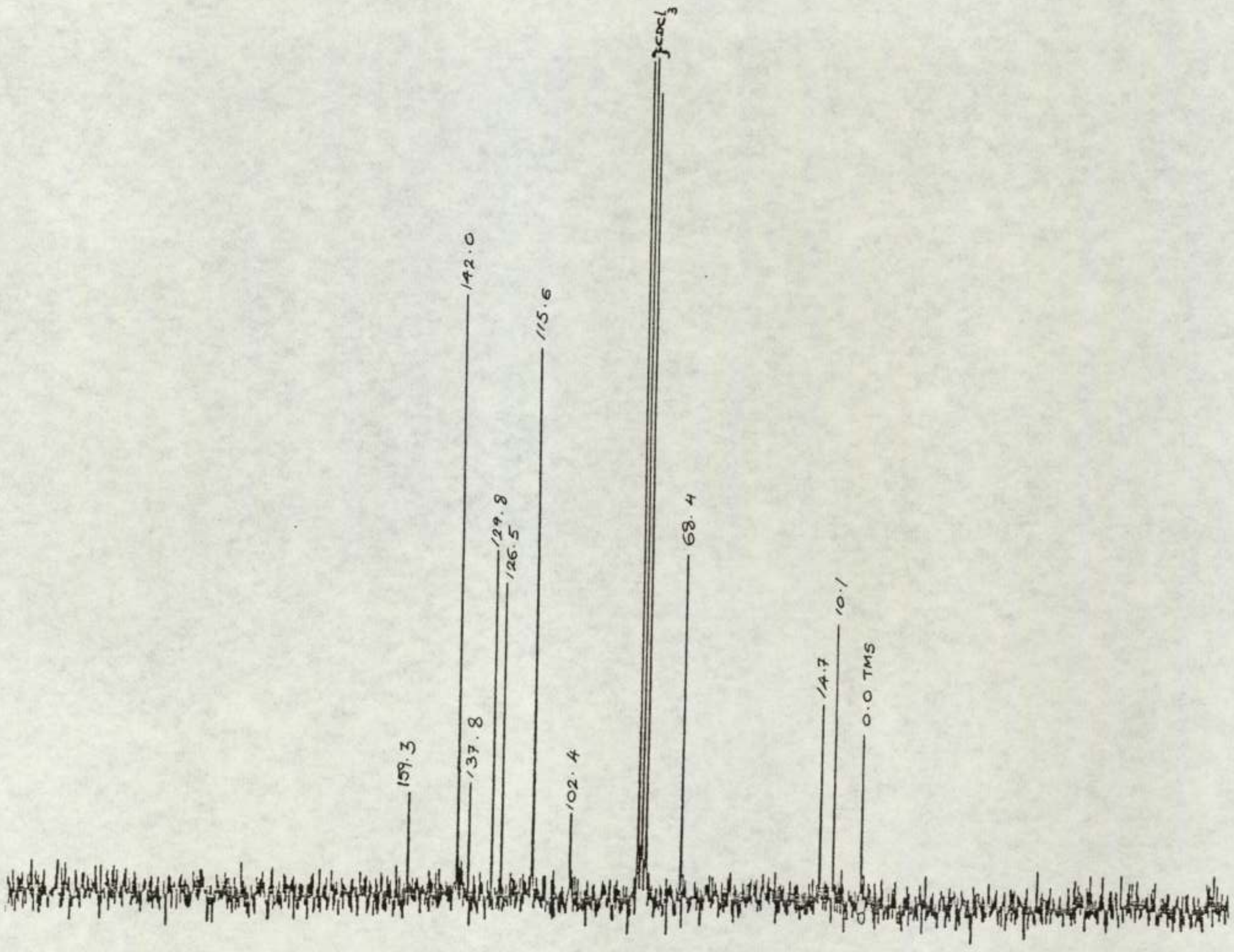


Figure 6.2 $\{^1H\}^{13}C$ N.M.R. spectrum of o-$C_6H_4(CH_2TeAr)_2$

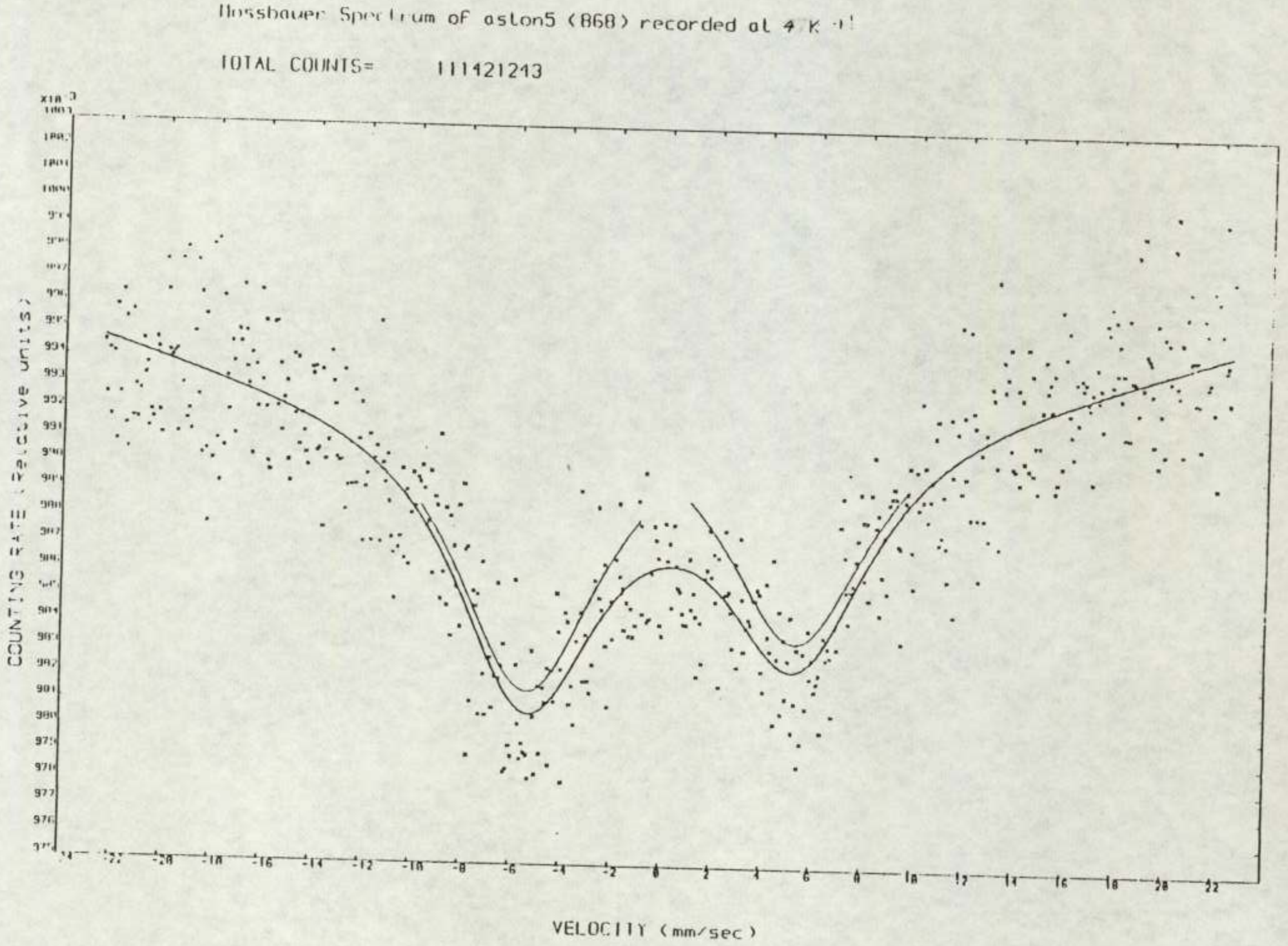


Figure 6.3 Mössbauer spectrum of o-$C_6H_4(CH_2TeAr)_2$

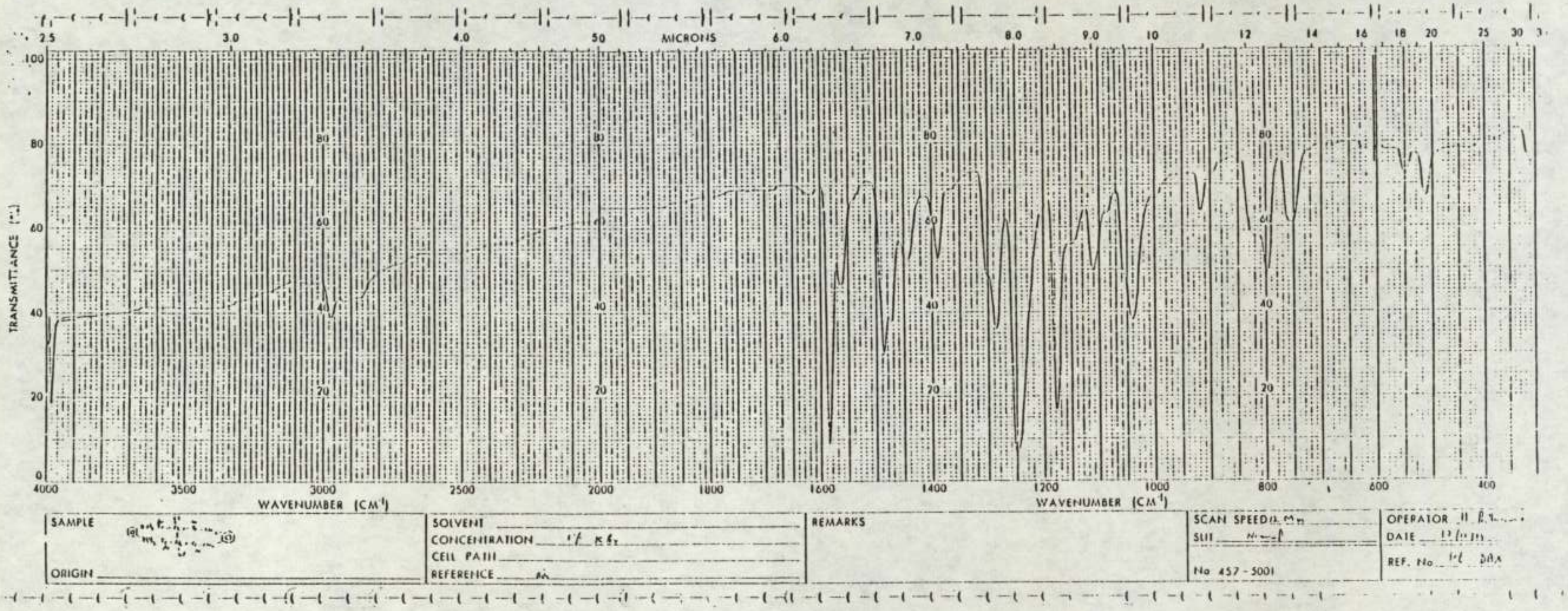


Figure 6.4 I.R. spectrum of $Pt_2Cl_2L_2$ ($L=o-C_6H_4(CH_2TeAr)_2$)

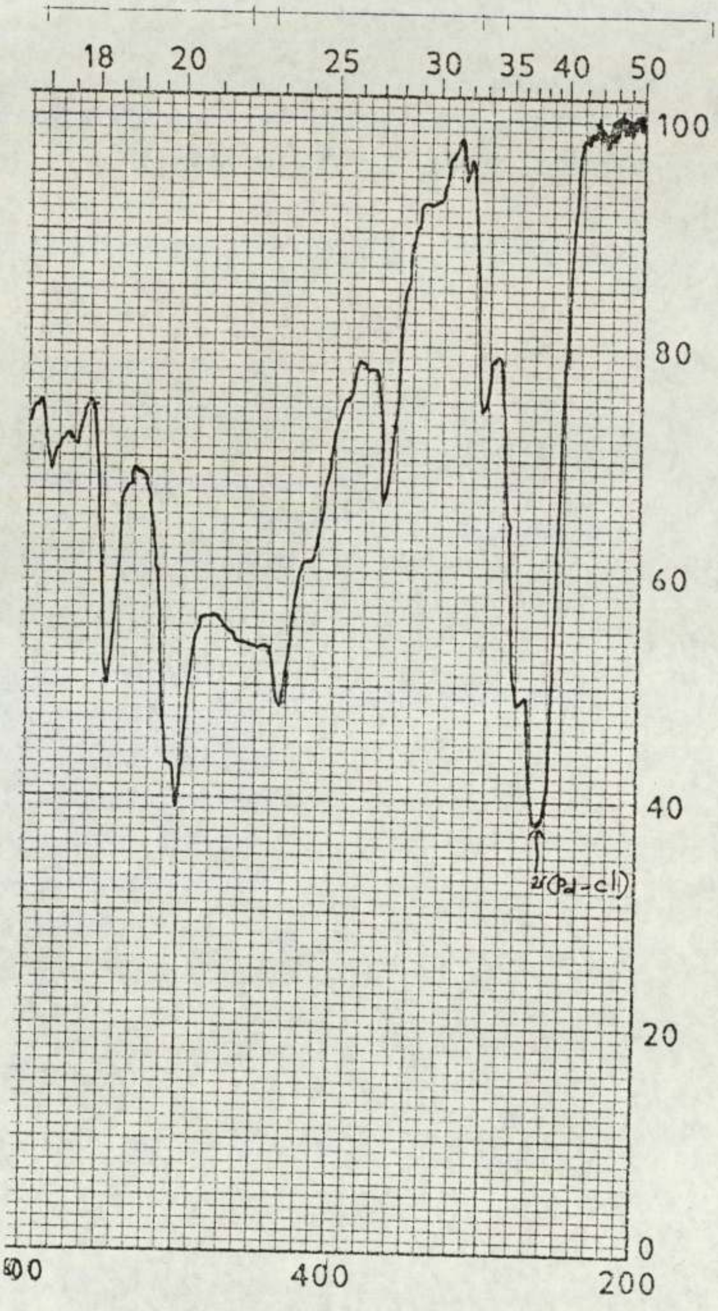


Figure 6.5 Far-infra-red spectrum of $Pd_2Cl_2L_2$ ($L=o-C_6H_4(CH_2TeAr)_2$)

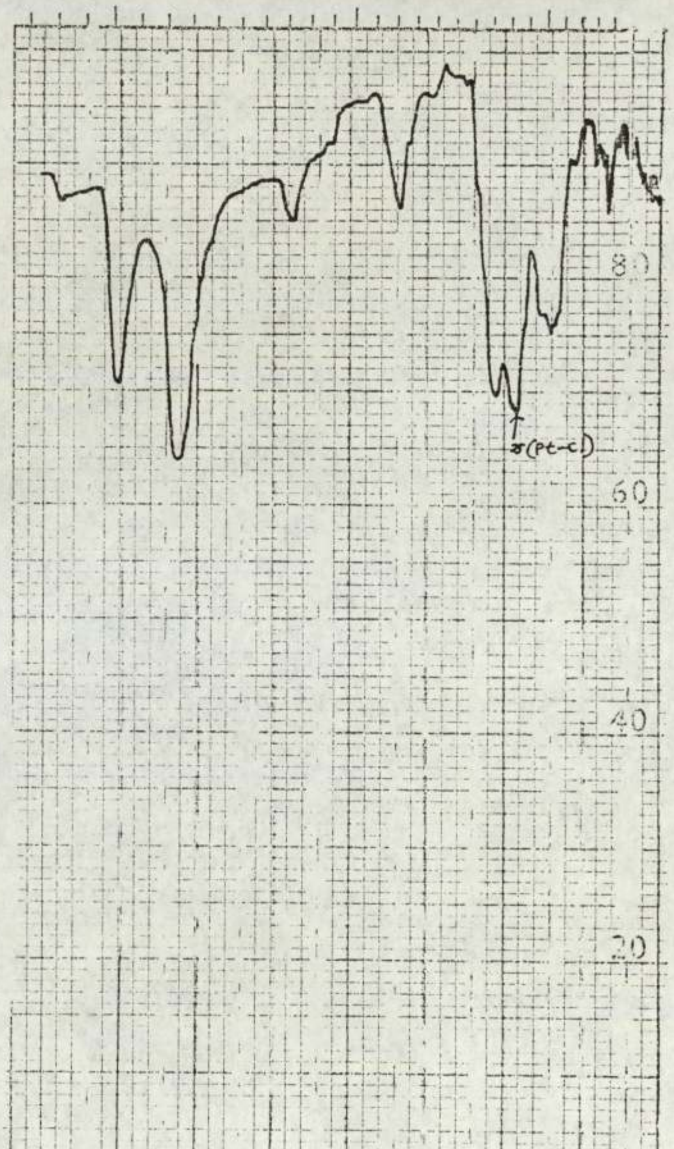


Figure 6.6 Far-infra-red spectrum of $Pt_2Cl_2L_2$ $(L=o\text{-}C_6H_4(CH_2TeAr)_2)$

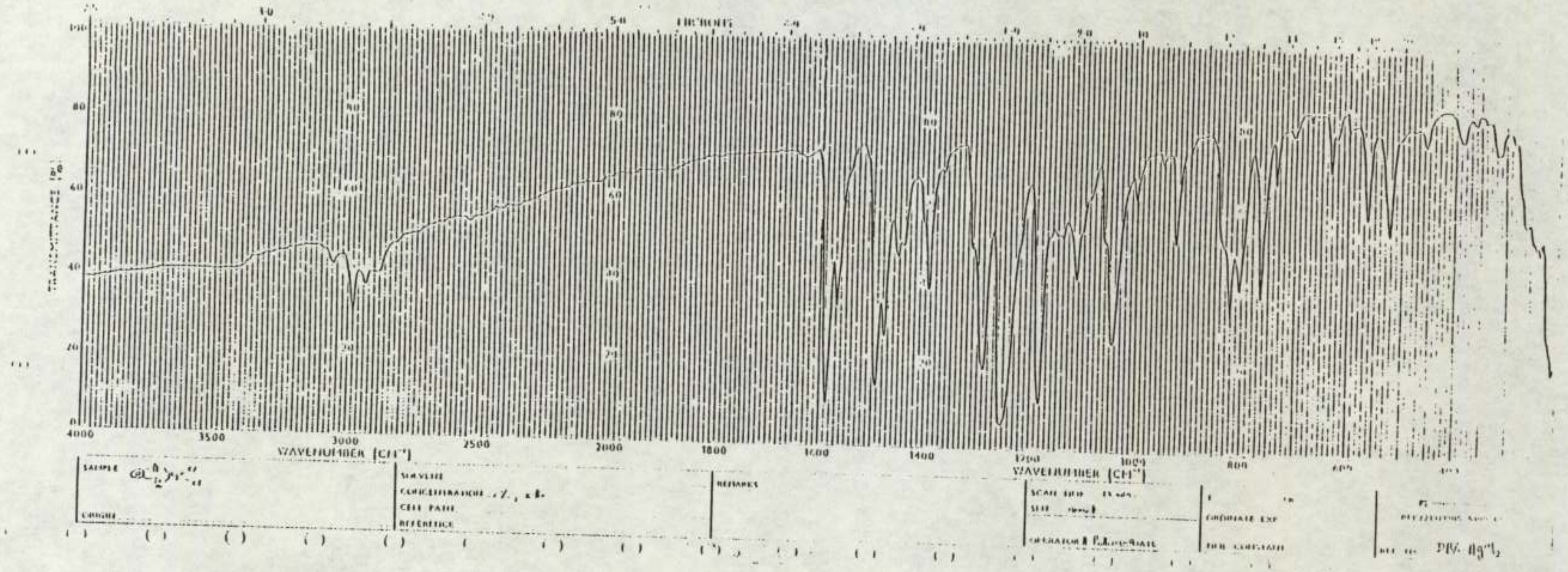


Figure 6.7 I.R. spectrum of $HgCl_2L$ ($L=o-C_6H_4(CH_2TeAr)_2$)

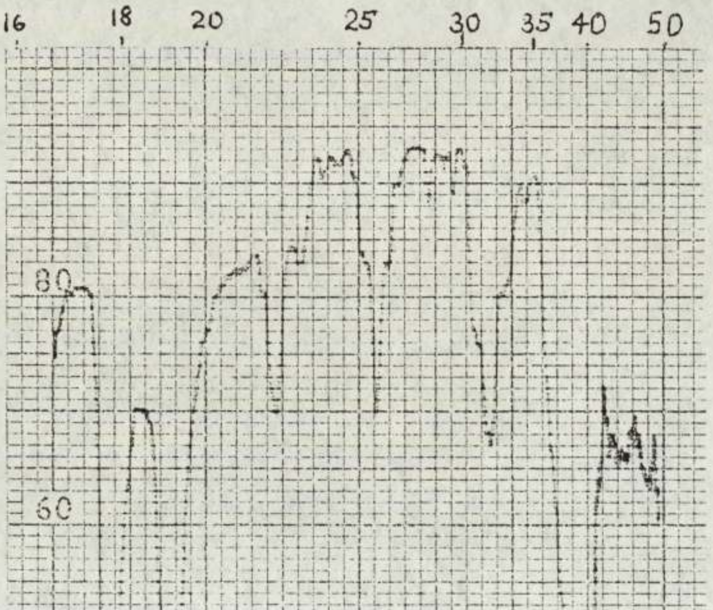


Figure 6.8 Far infra-red spectrum of $HgCl_2L$

($L=o\text{-}C_6H_4(CH_2TeAr)_2$)

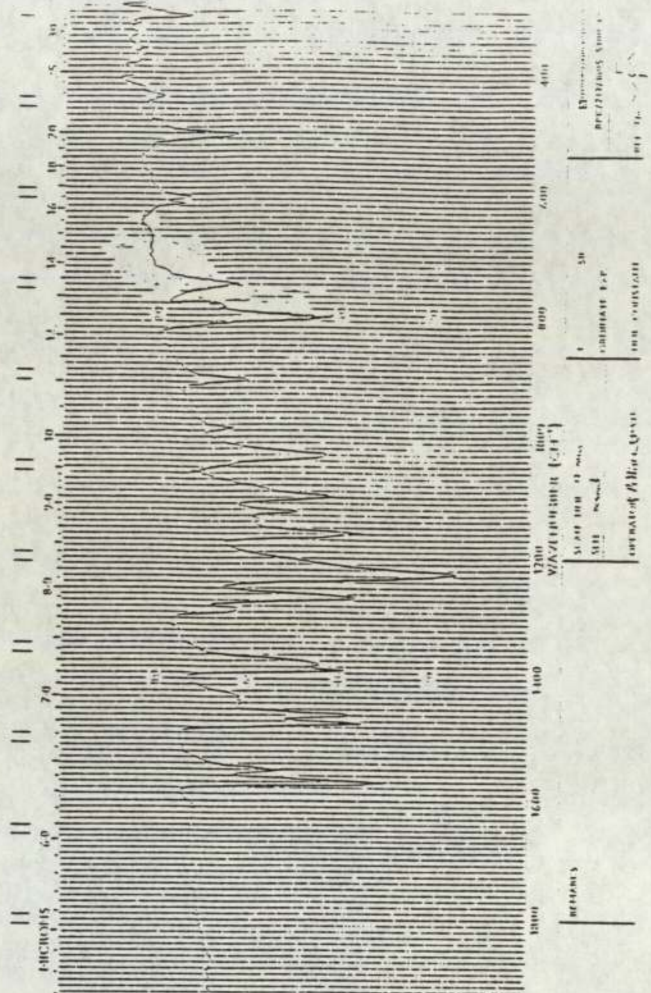


Figure 6.9 Infra-red spectrum of $C(CH_2TeAr)_4$

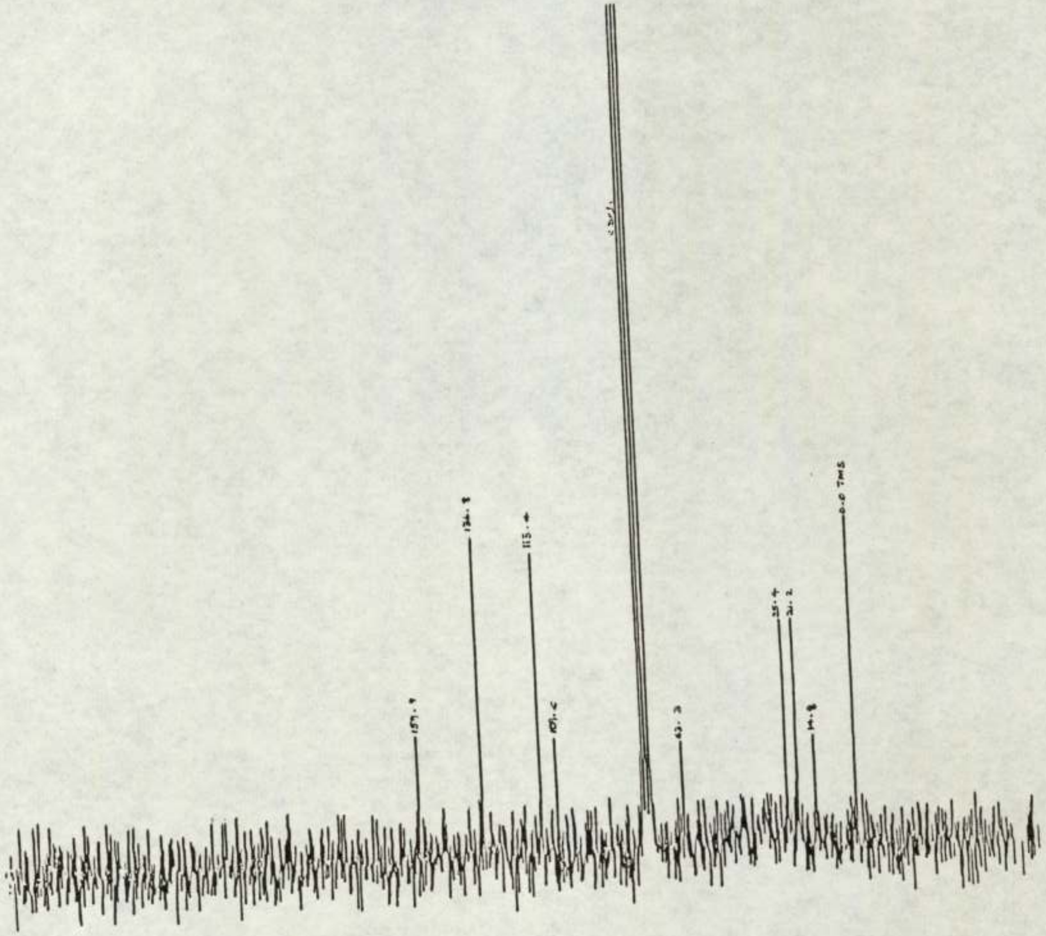


Figure 6.10 $\{^1H\}$ ^{13}C N.M.R. spectrum of $C(CH_2TeAr)_4$

6.4 Discussion

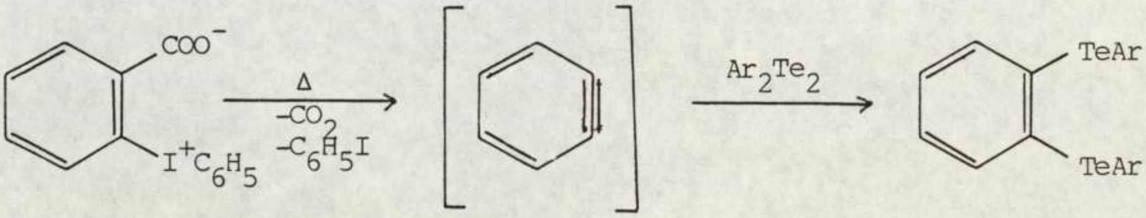
6.4.1 Attempted Reactions To Synthesise 1,2-Bis-[(Aryl/alkyl)telluro]benzene

Two methods of synthesis for 1,2-bis-[(aryl/alkyl)telluro]benzene were evaluated:

(a) the use of benzyne as intermediate
(b) the use of n-butyllithium

(a) The use of benzyne intermediate

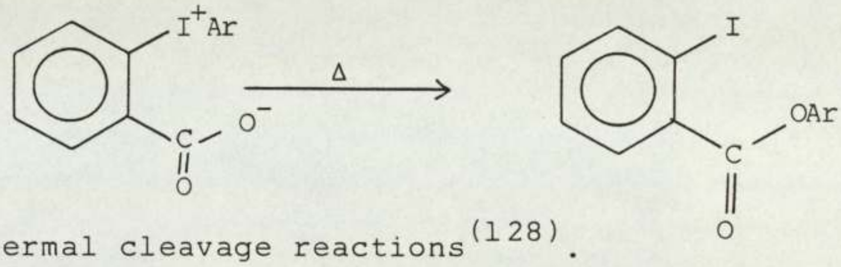
The method reported by Petragnani et al was used for this reaction(39).



The mechanism of this reaction involved the concerted insertion of singlet benzyne(39). They have also reported that the reaction is not entirely reproducible, frequently leading to ill-defined products unless a purified iodonium salt obtained by recrystallisation from a dilute solution of EDTA in water is used. The inconsistent results obtained in their earlier work has been reported to be due to the presence of heavy metal ions as impurities(39). The implication is that the decomposition of iodonium salts are markedly influenced by the presence of heavy metals(128-130).

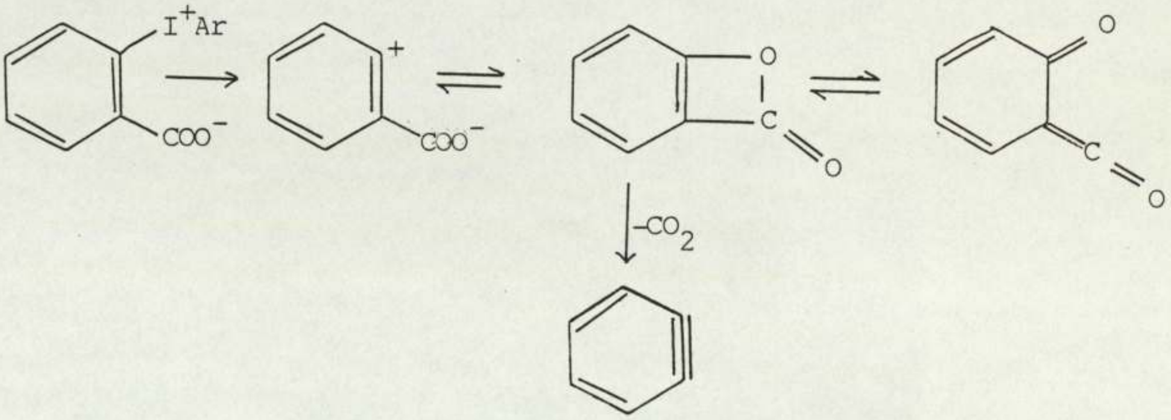
In the present study an ill-defined product was obtained by following Petragnani's method(39). The presence of certain heavy metal ions, inhibits certain reactions involving benzyne(128-130). Therefore, even after re-crystallising from EDTA, traces of metal ions may have remained in the iodonium salt. The following unwanted reactions may have occurred in the system.

1. Rearrangement at low temperature(128).

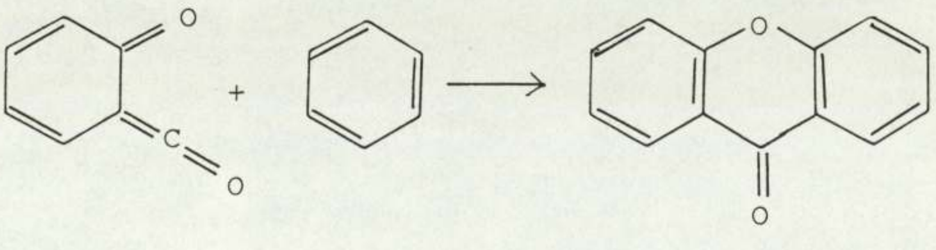


2. Thermal cleavage reactions(128).

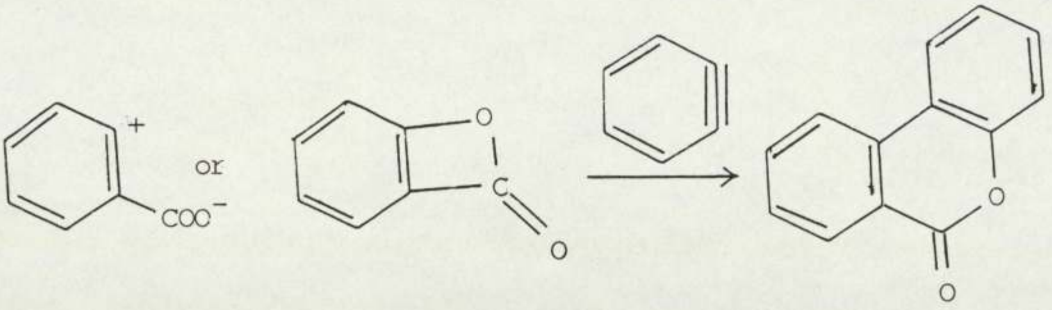
(i)



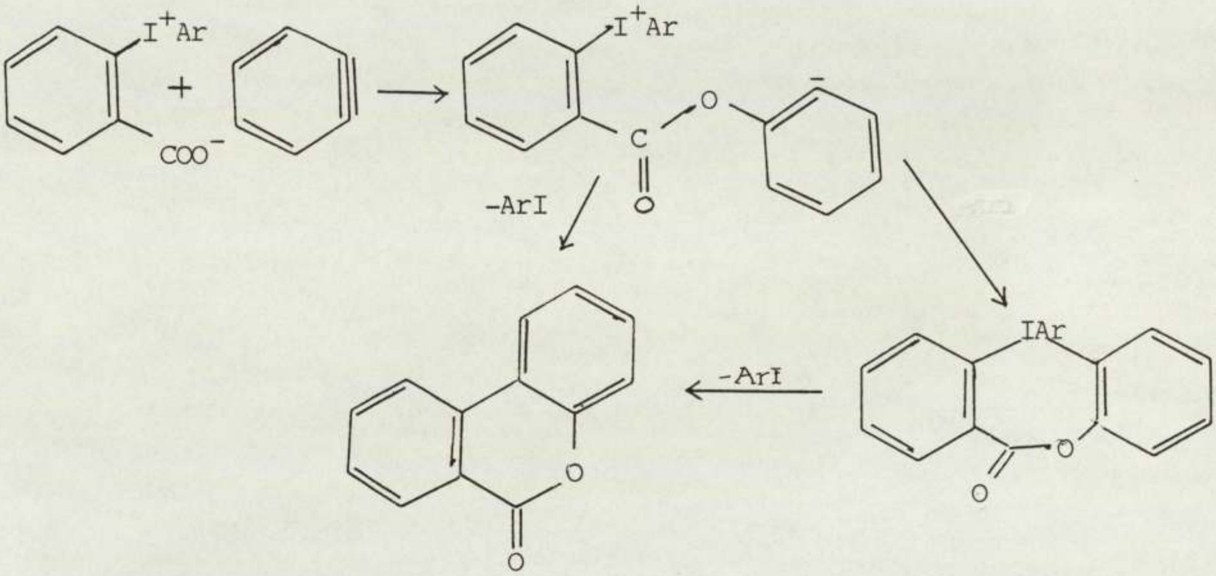
(ii)



(iii)

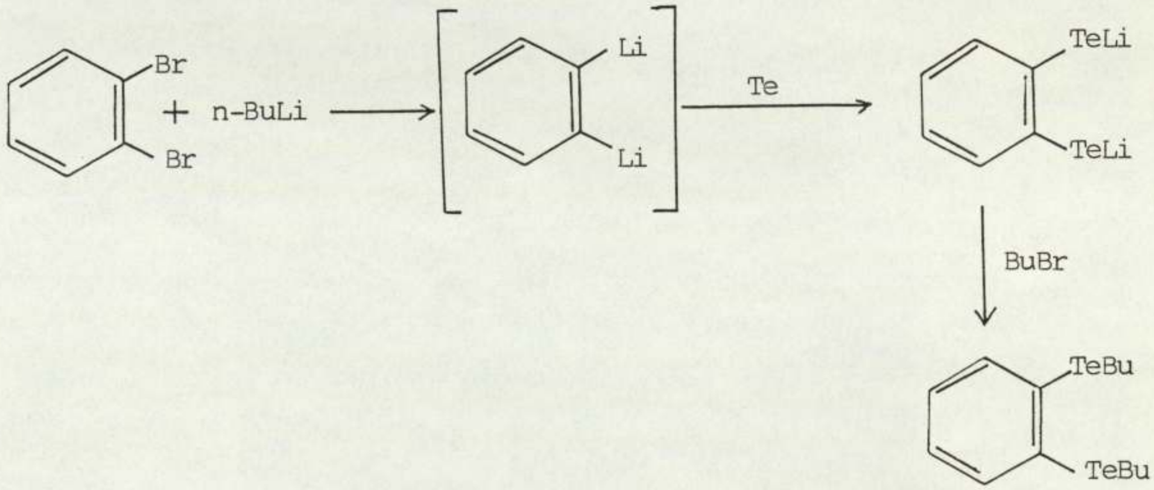


(iv)



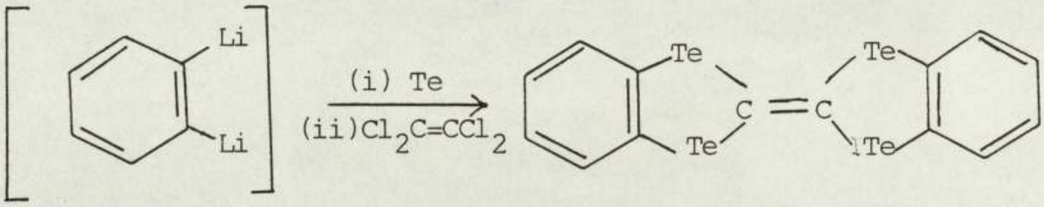
(b) The use of n-butyllithium

The unsuccessful results obtained from the above synthesis prompted the use of n-butyllithium, the following reaction being expected.



Unfortunately, this reaction also resulted in ill-defined products.

In the synthesis of dibenzotetratellurofulvalene, the insertion of tellurium into dilithiobenzene has been carried out in THF at -10°C by Bloch and co-workers(131).



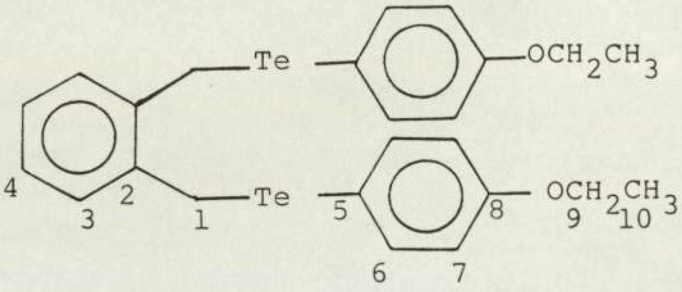
The unsuccessful results obtained in the present study may be due to the use of ether instead of THF and refluxing the reaction mixture instead of using low temperature.

6.4.2 Synthesis of α,α'-Bis-(p-Ethoxyphenyltelluro)o-xylene

The new ligand α,α'-bis-(p-ethoxyphenyltelluro)o-xylene was characterised using elemental analysis, mass (Scheme 6.1), infrared (Fig 6.1), ^{13}C N.M.R. (Fig 6.2) and ^{125}Te Mössbauer spectroscopy (Fig 6.3).

The elemental analysis suggests the formation of α,α'-bis-(p-ethoxyphenyltelluro)o-xylene from the reaction of ArTeNa with α,α'-(dibromo)o-xylene in 2:1 molar ratio. The mass fragmentation pattern of this compound is illustrated in Scheme 6.1. The elimination of the backbone occurs to give $(p\text{-}OC_2H_5.C_6H_4)_2Te_2^+$, similar to that of the bis-tellurides with alkane chain backbones. In contrast, the elimination of the backbone to give $Ph_2EE'Ph_2^+$ is unimportant in o-$C_6H_4(EPh_2)(E'Ph_2)$ E=E'=P, As; E=P, E'=As; E=P, E'=Sb; E=As, E'=Sb(102).

The $\{^1H\}^{13}C$ resonances of the aliphatic and the aromatic regions are assigned as follows (Figure 6.2, Table 6.5).



Number systems used to designate individual carbon atoms in the ligand.

The ^{13}C resonances of the p-ethoxyphenyl group (carbon atoms C_5-C_{10}) were assigned following the literature(50,73). The ^{13}C resonance at δ=10.1ppm was assigned as C-1 and it agrees with the assignment for C-1 in <u>bis</u>-tellurides with alkane chain backbones[($ArTe^1CH_2{}^2CH_2$.....TeAr) Chapter Four]. The C-2 resonance is distinguished by its low intensity. The C-3 and C-4 resonances were assigned in the order of increase in the chemical shift.

The Mössbauer data indicates a small chemical isomer shift($\delta = 0.03 \pm 0.08 mms^{-1}$) and a large quadrupole splitting constant ($\Delta = 10.72 \pm 0.1 mms^{-1}$) (Figure 6.3, Table 6.4). The small positive chemical isomer shift indicates the small s-electron density at the tellurium nucleus. Such a low value (δ=0.06(±0.08) mms^{-1}) has been observed for $(CH_3)_2Te$(64). The comparison of the isomer shift with published data for ditellurides gives the following trend:

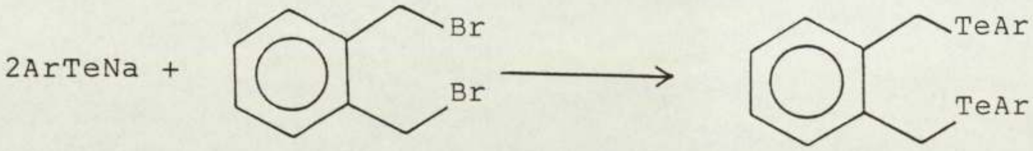
$o\text{-}C_6H_4(CH_2Te.C_6H_4OC_2H_5) < (p\text{-}C_2H_5OC_6H_4)_2Te_2$

0.03(±0.08)mms^{-1} 0.28(±0.08)mms^{-1}(64)

This corresponds to an increase in s-electron density at the tellurium nucleus in ditelluride rather than in the bis-telluride.

A large quadrupole splitting arises from a considerable imbalance in the 5p- orbital population on the tellurium atom. This indicates considerable covalent character in the Te-C bonds. Such large values for quadrupole splitting have been reported for dialkyl (Δ=10.5(±0.1)mms^{-1}) and diaryl (Δ=10.5(±0.1)mms^{-1}) tellurides,(64) and for ditellurides (Δ=10.6(±0.1)mms^{-1})(132). The small chemical isomer shift (0.03±0.08mms^{-1}) and large quadrupole splitting (10.72±0.1mms^{-1}) of this new compound suggest that the Te-C bonds possess some s- character and that the bonding is intermediate between p^3 and sp^3. The absence of splitting of the bands indicates that both the tellurium atoms are equivalent.

The formation of $o\text{-}C_6H_4(CH_2Te.C_6H_4OC_2H_5)_2$ suggests that, although the quaternisation is more favoured for 1,4-dibromobutane, it is not so for o-dibromoxylene. The benzene ring provides a rigidity to the four carbon atom chain and it may prevent the quaternisation. Therefore, the nucleophilic substitution of both bromine atoms in o-$C_6H_4(CH_2Br)_2$, by $ArTe^-$, occurs in the reaction of ArTeNa with o-$C_6H_4(CH_2Br)_2$, under the conditions used.



6.4.3 Transition Metal Complexes Of α,α'-*Bis*-(p-Ethoxyphenyltelluro)o-xylene

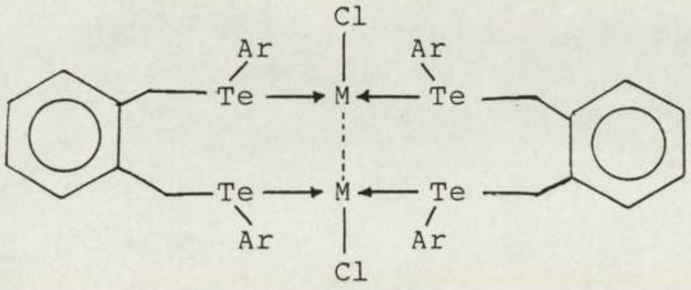
The complexes prepared using o-$C_6H_4(CH_2TeAr)_2$ fall into two categories according to the stoichiometry (Table 6.1).

1. $M_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2X_2$; M=Pd. Pt, X=Cl
2. $[o\text{-}C_6H_4(CH_2TeAr)_2]MX_2$; M=Hg, X=Cl

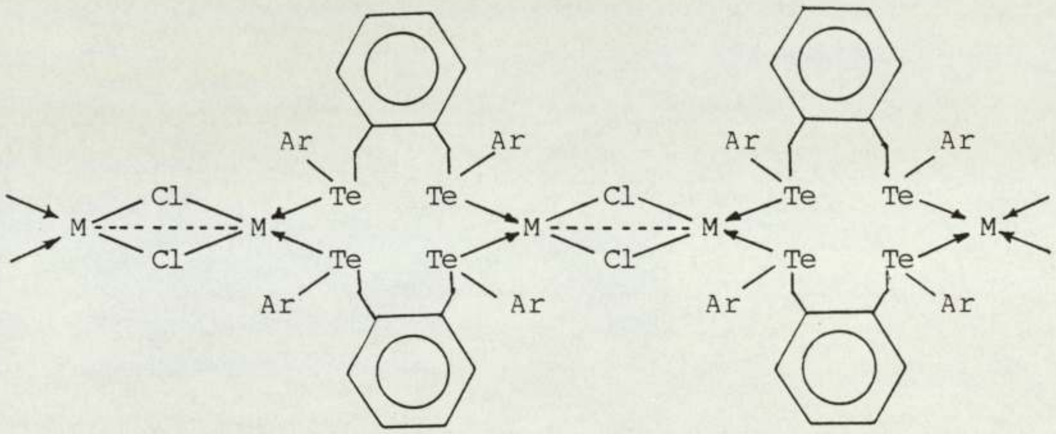
6.4.3.1 Complexes Having The Stoichiometry $M_2[o\text{-}C_6H_4(CH_2TeAr)_2]_2X_2$

The reaction of K_2MX_4, (M=Pd(II), Pt(II)) with o-$C_6H_4(CH_2TeAr)_2$ in 1:1 molar ratio resulted in orangish-yellow or yellow complexes with the stoichiometry $M[o\text{-}C_6H_4(CH_2TeAr)_2]X$. The insolubility and high melting points (Table 6.3) of these complexes suggest a polymeric(8,18) or a magnus type salt(8,18) structure. The conductivity measurements indicate that these compounds are non-electrolytes in DMF (at $1x10^{-3}M$).

The infra-red spectra indicate all the bands characteristic for the ligand (Figure 6.4). All this evidence suggests the following structures:



structure (a)



structure (b)

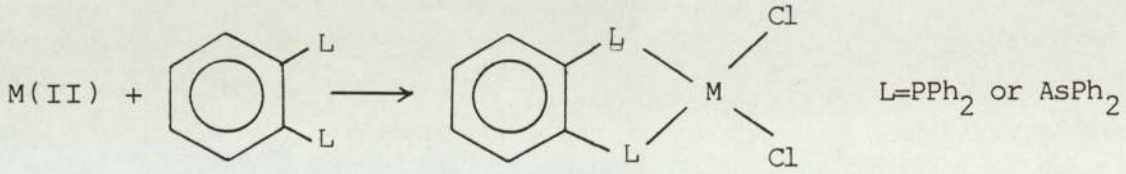
The band at $266cm^{-1}$ in the far-infra-red spectrum of the palladium complex is (Figure 6.5) assigned as terminal ν(Pd-Cl), consistent with literature assignments (44,78). The presence of the terminal ν(Pd-Cl) in the far-infra-red spectrum ruled out structure (b). The terminal trans-Pd-Cl stretching frequency of palladium(II) complexes of mono-dentate tellurium ligands has been assigned around $350cm^{-1}$ (78,80,81). The low ν(Pd-Cl) observed for this new complex indicates the high trans-effect of the Pd-Pd bond in structure (a). A similar low Pd-Cl stretching frequency was observed for $Pd_2(ArTeCH_2TeAr)_2Cl_2$ (ν=280, 292cm^{-1}); Chapter Three). Analogous low ν(Pd-Cl) values have been reported for the $Pd_2(Ph_2PCH_2PPh_2)_2Cl_2$ (ν=249cm^{-1})(14). Therefore, it is reasonable to suggest structure (a). The insolubility of this complex prevented the N.M.R. studies and the molecular weight determinations. The mass spectrum gave only fragments of low m/e.

The far-infra-red spectrum of the platinum complex is given in Figure 6.6. The terminal trans-(Pt-Cl) stretching frequency for platinum(II) complexes of monodentate tellurium ligands have been assigned around 301cm^{-1}(44,78,84). The Pt-Cl stretching frequency of this complex is assigned at 292cm^{-1}. The ν(Pt-Cl) of $Pt_2(ArTeCH_2TeAr)_2Cl_2$ was assigned at 315cm^{-1} (Chapter Three) and that of $Pt_2(Ph_2PCH_2PPh_2)_2Cl_2$ has been assigned at 249cm^{-1}(14). Therefore, it is reasonable to suggest the structure (a). The high ν(Pt-Cl) indicates the probable weakness of the Pt......Pt bond. Another possible reason is the π-back donation in $Pt_2[o-C_6H_4(CH_2TeAr)_2]_2Cl_2$. This increases the Lewis acidity of Pt(I) and increases the ν(Pt-Cl). The mass spectrum resulted in only fragments of low m/e. The insolubility prevented the N.M.R. and molecular weight studies.

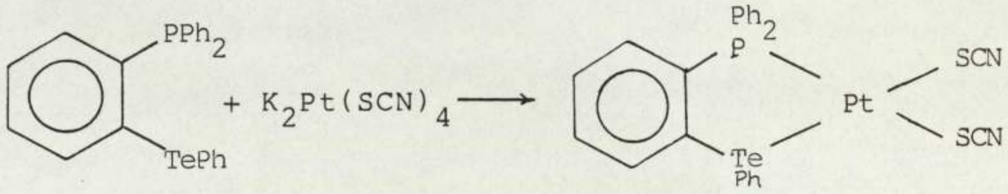
The formation of these M(I) complexes suggests that $o-C_6H_4(CH_2TeAr)_2$ has acted as a reducing agent in the complex formation reactions. The low yield (≈48%) of the complexes formed suggests that some of the ligand has been used for the reduction of M(II).

$$\mathrm{Te(II)} + 2\mathrm{M(II)} \xrightarrow{\qquad} \mathrm{Te(IV)} + 2\mathrm{M(I)}$$
$$\mathrm{Te(II)} + \mathrm{M(I)} \xrightarrow{\qquad} \text{Complex}$$

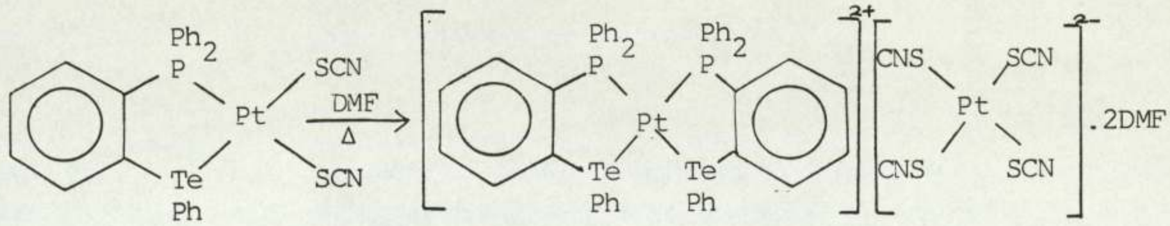
In contrast, o-$C_6H_4(PPh_2)_2$ and o-$C_6H_4(AsPh_2)_2$ which are examples for the bidentate ligands having a rigid backbone, have formed <u>cis</u>- chelated M(II) complexes when the ligand was reacted with M(II), M=Pd, Pt(8,120).



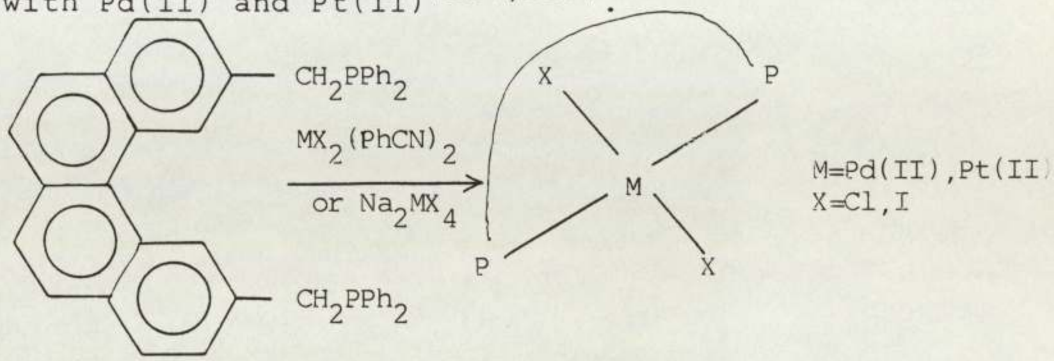
The reaction of $K_2Pt(SCN)_4$ with a hybrid bidentate ligand having a rigid backbone has resulted in a monomeric <u>cis</u>-complex with S-bonded thiocyanate(40a,b).



The recrystallisation of this complex from DMF has resulted in a magnus-salt type complex(40a,b).



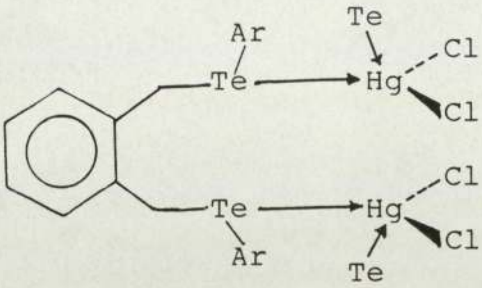
2,11-bis-(diphenylphosphinomethyl)benzo(c)phenanthrene, which has a rigid backbone has formed monomeric, trans-complexes with Pd(II) and Pt(II)(127,133).



Therefore, the reductive property of the ligand in the complex formation reactions is not found in bidentate diphosphines, diarsines, distibines or hybrid tellurium ligands having rigid backbones, and is limited only to the analogous bis-tellurides.

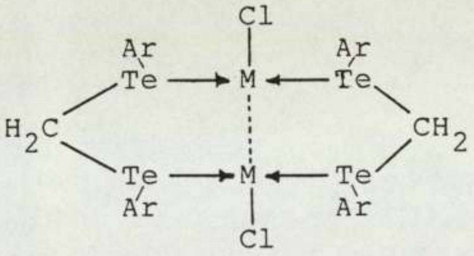
6.4.3.2 Complex Having The Stoichiometry o-$C_6H_4(CH_2TeAr)_2HgCl_2$

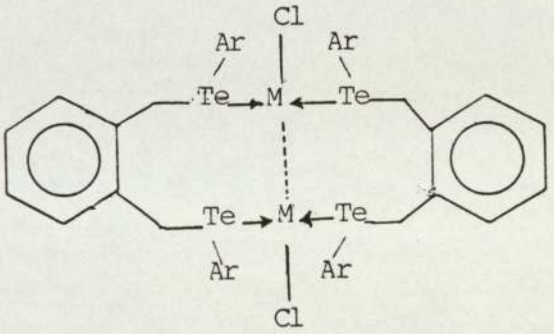
A complex having this stoichiometry is prepared by reacting $HgCl_2$ with o-$C_6H_4(CH_2TeAr)_2$ in 1:1 molar ratio. The insolubility of this complex suggests a polymeric nature. The infra-red spectrum indicates the bands characteristic of the ligand (Figure 6.7). The conductivity measurement indicates that this is a non-electrolyte in DMF (at 1×10^{-3}M). The bands due to ν(Hg-Cl) are difficult to identify in the far-infra-red region (400-200cm^{-1}) (Figure 6.8). The insolubility prevented the molecular weight determinations. The mass spectrum gave only fragments of low m/e. All this evidence suggests this material to be:



The comparison of the complex formation reactions of $o\text{-}C_6H_4(CH_2TeAr)_2$ with those of $ArTeCH_2TeAr$ indicates a similar behaviour.

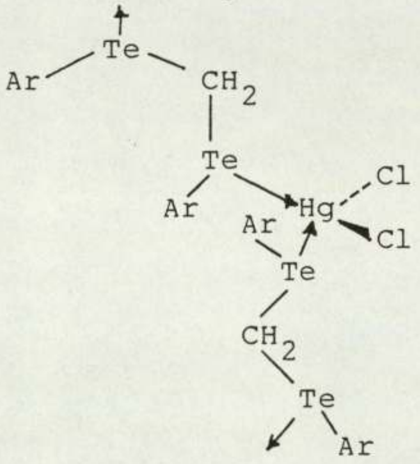
(a) with Pd(II) and Pt(II)

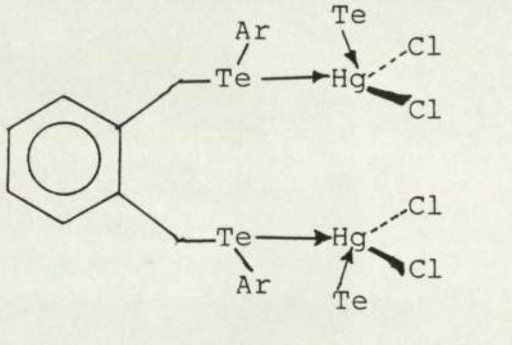




M=Pd, Pt

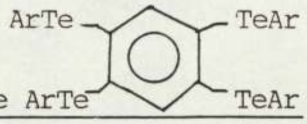
(b) with Hg(II):





6.4.4 Synthesis Of Multidentate Tellurium Ligands

6.4.4.1 Attempted Reaction To Synthesise

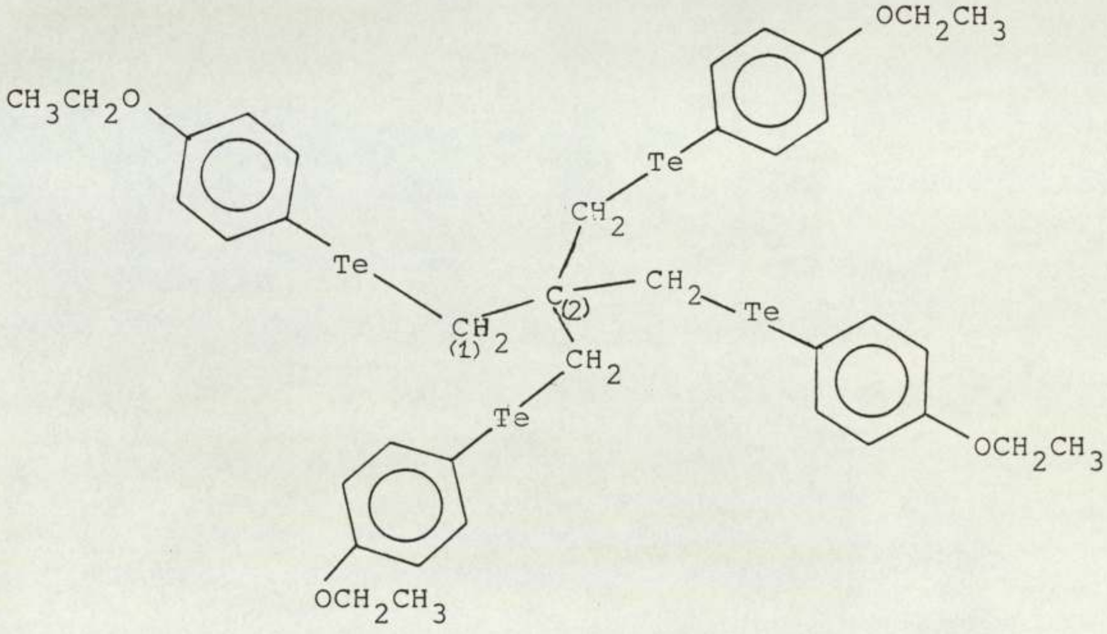


As soon as tetrabromoxylene was added to ArTeNa, ditelluride formed. The reason for this is uncertain.

6.4.4.2 Synthesis Of Tetrakis-(p-Ethoxyphenyltelluromethyl)-methane

There was no reaction between ArTeNa and $C(CH_2Br)_4$ in benzene. When the solvent was changed from benzene to tetrahydrofuran, a product was formed; but the yield was very poor. The addition of excess tetrahydrofuran and refluxing the reaction mixture for 5h resulted in a better yield, but it was still only 5%. The elemental analysis of this product suggests the molecular formula $C(CH_2TeAr)_4$. The infra-red spectrum of the compound is illustrated in Figure 6.9. The bands due to the $\nu(C-(CH_2)_4)$ are difficult to distinguish from the vibrational bands of the p-ethoxybenzene group. The mass fragmentation pattern for $C(CH_2TeAr)_4$ is shown in Scheme 6.2. The elimination of $Ar_2Te_2^+$ and the usual fragmentation pattern for $Ar_2Te_2^+$ was observed in the mass spectrum.

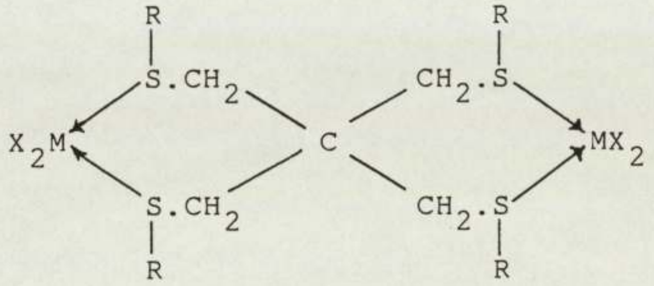
The $\{^1H\}^{13}C$ N.M.R. spectrum of this new compound is given in Figure 6.10. The ^{13}C resonances for ortho-, meta-, para-and ipso- carbon atoms of the benzene ring are assigned according to literature assignments(50,73). They are in good agreement with the published data. The aliphatic region contains ^{13}C resonances for $-OCH_2$, $-CH_3$, $-CH_2$ and C- groups. The resonances arising from CH_3- and CH_2O- groups are readily assigned at δ=14.8 and 63.3ppm respectively(50,73). The remaining two resonances appearing in the aliphatic region are assigned in the following way. The C-1 carbon atom which is directly attached to the tellurium atom should resonate more up field than the C-2. Therefore the resonances at δ=21.1ppm and δ=25.4ppm are assigned as C-1 and C-2 respectively.



Preliminary experiments indicated that this material forms complexes with soft metal centres such as Pd(II) and Pt(II).

Analogous quadridentate ligands containing P, As and S donor atoms have been reported in literature(134-136). It has been found that these ligands behave as doubly bidentate chelates(135,137,138).

i.e.,



; M=Pd,Pt,Hg (135)
X=Cl,Br,I

6.5 Suggestions For Future Work

The aim of this study was to synthesise new bis-tellurides and to investigate whether it is possible to synthesise complexes of such ligands with soft metal ions. Analysis of the experimental results indicate that the work carried out has successfully helped to achieve this aim. However, in view of the co-ordination chemistry of new bis-telluride ligands, the work reported in this thesis is merely an introduction. This work can be extended in the following ways to obtain more detailed information on the co-ordination chemistry of bis-tellurides.

1. Studies on the reactions of these complexes.
2. Studies on the structures of these complexes.
3. Studies on the modifications of the ligand structure.
4. Studies on the reactions of bis-tellurides with other metal ions (preliminary experiments indicating that these ligands form complexes with iridium and cadmium ions).

REFERENCES

1. R.G.Pearson,J.Am.Chem.Soc.,1963,85,3533.
2. S.Arhland,J.Chatt and N.R.Davies,Quart.Rev.Chem.Soc., 1958,12,265.
3. I.Davies,Ph.D.Thesis,University of Aston in Birmingham, 1977.
4. N.G.Albano,P.L.Bellon and V.Scatturn,Chem.Commun.,1966, 507.
5. C.L.Lee,C.T.Hunt and A.L.Balch,Inorg.Chem.,1981,20, 2498.
6. J.Bakos,I.Toth,B.Heil and L.Marko,J.Organomet.Chem., 1985,279,23.
7. H.Schmidbaur,S.Lauteschläger and G.Müller,J.Organomet. Chem.,1985,281,25.
8. W.Levason and C.A.McAuliffe,Inorg.Chim.Acta.,1976,16, 167.
9. A.Pryde,B.L.Shaw and B.Weeks,J.Chem.Soc.(Dalton Trans.), 1976,322.
10. W.E.Hill,D.M.A.Minham,T.C.Taylar and C.A.Mcauliffe,J. Am.Chem.Soc.,1982,104,6001.
11. H.Schmidbaur,S.Lauteschläger and G.Müller,J.Organomet. Chem.,1985,281,33.
12. N.A.Al Salem,H.D.Empsall,R.Markham,B.L.Shaw and B.Weel, J.Chem.Soc.(Dalton Trans.),1972,1979.
13. P.G.Pringle and B.L.Shaw,J.Chem.Soc.(Chem.Commun),1982, 81.
14. P.G.Pringle and B.L.Shaw,J.Chem.Soc.(Dalton Trans.), 1983,889.
15. M.P.Brown,R.J.Puddephatt,M.Rashidi and K.R.Seddon,J. Chem.Soc.(Dalton Trans.),1977,951.

16. L.S.Benner and A.L.Balch,J.Am.Chem.Soc.,1978,100,6099.

17. D.M.Hoffman and R.Hoffman,Inorg.Chem.,1981,20,3543.

18. F.Hartley,S.G.Murray,W.Levason,H.E.Soutter and C.A. McAuliffe,Inorg.Chim.Acta,1979,35,265.

19. O.Foss,Pure and Applied Chem.,1970,24,31.

20. K.S.Fredin,K.Maroy and S.Slogwik,Acta Chem.Scand.Ser. A,1975,29,212.

21. S.Husebye,Acta Chem.Scand.,1967,21,42.

22. G.T.Morgan and H.Burgess,J.Chem.Soc.,1929,1103.

23. I.P.Gołdshtein,E.N.Guryanova,A.F.Volkov and M.E. Peisakhova,Zh.Ohsch.Khim.,1973,43,1669.

24. N.Katsaros and J.W.George,J.Inorg.Nucl.Chem.,1969,31, 3503.

25. F.Wöhler,Ann.Chem.,1840,35,111.

26. N.Petragnani and J.V.Comasseto,Proc.of the 4th Int. Conf.on Org.Chem.of Selenium and Tellurium,Eds.F.J. Berry and W.R.McWhinnie,1983,p.98.

27. K.Bowden and A.E.Braude,J.Chem.Soc.,1952,1068.

28. G.T.Morgan and H.D.K.Drew,J.Chem.Soc.,1925,127,2307.

29. J.L.Peitte and M.Renson,Bull.Soc.Chem.Belg.,1970,79,353.

30. S.A.Gardner and H.J.Gysling,J.Organomet.Chem.,1980, 197,111.

31. V.Küllmer and H.Vahrenkamp,Chem.Ber.,1977,110,228.

32. G.T.Morgan and F.H.Burstall,J.Chem.Soc.,1931,180.

33. W.Lohner and K.Praefcke,Chem.Ber.,1978,111,3745.

34. R.F.Zioło and W.H.H.Günther,J.Organomet.Chem.,1978, 146,245.

35. J.D.McCullough,Inorg.Chem.,1975,14,2285.

36. W.Dell and M.L.Ziegler,Angew.Chem.Int.Engl.,1981,20, 471.

37. W.Dell and M.L.Ziegler,Angew.Chem.Int.Ed.Engl.,1982,37, 1.

38. N.Petragnani and V.G.Toscano,Chem.Ber.,1970,103,1652.

39. J.B.S.Bonilha,N.Petragnani and V.G.Toscano,Chem.Ber., 1978,111,2510.

40(a).H.J.Gysling,4th International Conference on the Organic Chemistry of Selenium and Tellurium-1983,July.

40(b).H.J.Gysling and H.R.Luss,Organometallics.,1984,3,596.

41. N.Petragnani and G.Schill,Chem.Ber.,1970,103,2271.

42. D.Seebach and A.K.Beck,Chem.Ber.,1975,108,314.

43. L.Engman and M.P.Cava,orgnaometallics.,1982,1,470.

44. L.Y.Chia,W.R.McWhinnie,J.Organomet.Chem.,1978,148,165.

45. I.Davies and W.R.McWhinnie,Inorg.Nucl.Chem.Lett.,1976, 12,763.

46. H.J.Gysling,Co-ord.Chem.Rev.,1982,42,133.

47. I.Davies,W.R.McWhinnie,N.S.Dance and C.H.W.Jones, Inorg.Chim.Acta.,1978,29,L217.

48. Z.M.Mirzai,Ph.D.Thesis,University of Aston in Birmingham,1982.

49. K.de Silva,Ph.D.Thesis,University of Aston in Birmingham,1984.

50. K.de Silva,Z.M.Mirzai and W.R.McWhinnie, J.Chem.Soc. (Dalton Trans.),1983,2143.

51. A.Tzschach and W.Lange,Chem.Ber.,1962,95,1360.

52. J.Chatt and L.M.Venanzi,J.Chem.Soc.,1957,2351.

53. R.K.Chadha and J.E.Drake,J.Organomet.Chem.,1985,286,121.

54. W.R.McWhinnie and V.Rattanaphani,Inorg.Chim.Acta.,1974, 9,153.

55. E.W.Tillay,E.D.Schermer and W.H.Baddley,Inorg.Chem., 1968,7,1925.

56. S.A.Gardner,A.J.Trotter and H.J.Gysling.,J.Organomet. Chem.,1981,212,35.

57. H.Schumann,R.Mohtachemi,H.J.Kroth and U.Frank,Chem.Ber., 1973,106,2049.

58. H.Hausmann,M.Höfler,T.Kruck and H.W.Zimmermann,Chem. Ber.,1981,114,975.

59. K.Ofele and E.Dötzauer,J.Organomet.Chem.,1972,42,C87.

60. W.Paul and H.Werner,Angew.Chem.Int.Ed.Engl.,1983,22, 316.

61. W.A.Herrmann,J.Weichmann,R.Serrano,K.Blechschmitt, H.Pfisterer and M.L.Zeigler,Angew.Chem.Int.Ed.Engl., 1983,22,314.

62. A.I.Vogel,A text book of practical organic chemistry, 4th edition,Longman,London, 1978.

63. D.D.Perrin,W.F.L.Armarego,D.R.Perria,Purification of laboratory chemicals,2nd edition,Fergman Press,1980.

64. C.H.W.Jones,R.Schults,W.R.McWhinnie and N.S.Dance, Can.J.Chem.,1976,54,3234.

65. B.P.Levitt,Findlay's practical physical chemistry, Longman Group Limited,1973.

66. S.Glasstone,Textbook of Physical Chemistry,2nd edition, Macmillan and Co.Ltd.,1960.

67. R.J.Puddephatt,Chem.Soc.Rev.,1983,99.

68. E.Gross and F.M.Armbrecht,J.Am.Chem.Soc.,1967,89,2790.

69. H.B.Singh,Ph.D. Thesis,University of Aston in Birmingham, 1983.

70. C.Elgy,Personal communication.

71. J.R.Doyle,P.E.Slade and H.B.Jonassen,Inorg.Synth.,1960, 6,216.

72. A.I.Vogel,Macro and Semimicro Qualitative Inorganic Analysis,4th Edition,Longmans,Green and Co.Ltd.,1978.

73. R.K.Chadha and J.M.Miller,J.Chem.Soc.(Dalton Trans.), 1982,117.

74. E.R.Clark and M.A.Al Turaihi,J.Organomet.Chem.,1976, 118,55.

75. P.Thavonyutikarn,J.Organomet.Chem.,1973,51,237.

76. F.R.Hartley,The Chemistry of Platinum and Palladium, Applied Science Publishers Ltd.,1973.

77. A.Z.Al Rubaie,H.A.Y.Al Shirayda,P.Granger and S. Chapelle,J.organomet.Chem.,1985,321.

78. The Organic Chemistry of Tellurium,K.J.Irgolic,Gordon and Breach Science Publishers,1974.

79. R.J.Cross,T.H.Green and R.Keat,J.Chem.Soc.(Dalton Trans.),1976,382.

80. H.J.Gysling,H.R.Luss and D.L.Smith,Inorg.Chem.,1979, 18,2696.

81. H.J.Gysling,N.Zumbulyadis and J.A.Robertson,J.Organomet.Chem.,1981,209,C41.

82. D.M.Adams,J.Chatt,J.Gerratt and A.D.Westland,J.Chem. Soc.,1964,734.

83. H.J.Gysling,Proc.of the 3rd Int.Symp.on organic chemistry of Selenium and Tellurium compounds,July 1979.

84. F.Faraone,L.Silvestro,S.Sergi and R.Pietropaolo,J. Organomet.Chem.,1972,34,C55.

85. J.R.Alkins and P.J.Hendra,J.Chem.Soc.A.1967,1325.

86. J.E.Fergusson and K.S.Loh,Austral.J.Chem.,1973,26,2615.

87. R.Colton,R.H.Farthing and M.J.McCormick,Austral.J.Chem., 1973,26,2607.

88. F.S.M.Hassan,D.P.Markham,P.G.Pringle and B.L.Shaw,J. Chem.Soc.(Dalton Trans.),1985,279.

89. C.R.Langrick,D.M.McEwan,P.G.Pringle and B.L.Shaw,J. Chem.Soc.(Dalton Trans.),1983,2487.

90. G.B.Jacobsen and B.L.Shaw,J.Chem.Soc.(Chem.Commun.), 1985,692.

91. W.L.Steffen and G.T.Palenik,Inorg.Chem.,1976,15,2432.

92. M.P.Brown,R.J.Puddaphatt and M.Rashidi,Inorg.Chim. Acta.,1976,19,L33.

93. M.M.Campos,E,L.Suranyi,H.de Andrade and N.Petragnani, Tetrahedron,1964,20,2797.

94. W.P.Weber and G.W.Gokel,Phase transfer catalysis in organic synthesis (vol.4),Springer-verlay,1977.

95. L.Engman and M.P.Cava,J.Org.Chem.,1981,46,4194.

96. J.A.Landgrebe and R.D.Mathis,J.Am.Chem.Soc.,1966, 88,3545.

97. R.T.Mehdi,J.D.Miller and T.A.Tahir,Inorg.Chim.Acta., 1984,90,85.

98. A.Z.Al-Rubaie,Ph.D.Thesis,University of Aston in Birmingham,1981.

99. R.T.Mehdi and J.D.Miller,J.Chem.Soc.(Dalton Trans.), 1983,1071.

100. J.V.Comasseto,J.T.B.Ferreira,J.A.Fontanillas-Val and A.R. M.de Oliveira,"Synthesis of aryl alkyl tellurides under phase transfer conditions"-4th International Conference on the Organic Chemistry of Selenium and Tellurium,1983,July.

101. J.V.Comasseto,J.T.B.Ferreira and J.A.Fontanillas-Val, J.Organomet.Chem.,1984,277,261.

102. W.Levason,C.A.McAuliffe and R.D.Sedgwick,J.Organomet. Chem.,1975,84,239.

103. W.Levason,C.A.McAuliffe,I.E.Niven,R.V.Parish and P.D.Randall,J.Organomet.Chem.,1977,125,209.

104. A.C.Hazell,Acta.Chem.Scand.,1972,26,1510.

105. W.E.Hill,D.M.A.Minahan,J.G.Taylor and C.A.McAuliffe, J.Chem.Soc.(Perkin Trans.II),1982,327.

106. E.G.Paul and D.M.Grant,J.Am.Chem.Soc.,1963,85,1701.

107. D.M.Grant and E.G.Paul,J.Am.Chem.Soc.,1964,86,2984.

108. L.P.Lindeman and J.Q.Adams,Anal.Chem.,1971,43,1245.

109. B.L.Shaw,J.Am.Chem.Soc.,1975,97,3856.

110. D.Munro,Chem.Brit.,1977,13,100.

111. A.J.Pryde,B.L.Shaw and B.Weeks,J.Chem.Soc.(Chem. Commun.),1973,947.

112. A.Constable,W.S.McDonald and B.L.Shaw,J.Chem.Soc. (Dalton Trans.),1979,496.

113. W.Levason,C.A.McAuliffe and S.G.Murray,Inorg.Chim. Acta.,1977,24,63.

114. D.M.A.Minahan,W.E.Hill and C.A.McAuliffe,Co-ord.Chem. Rev.,1984,55,31.

115. Phosphine,Arsine and Stibine complexes of the Transition elements,C.A.McAuliffe and W.Levason,Elsevier Scientific Publishing Co.,1979.

116. W.E.Hill,D.M.A.Minaham and C.A.McAuliffe,Inorg.Chem., 1983,22,3383.

117. W.Levason,C.A.McAuliffe and S.G.Murray,J.Organomet. Chem.,1976,110,C25.

118. C.A.McAuliffe,H.E.Soutter,W.Levason,F.R.Hartley and S.G.Murray,J.Organomet.Chem.,1978,159,C25.

119. N.W.Alcock,J.M.Brown and J.C.Jeffery ,J.Chem.Soc. (Dalton Trans.),1977,888.

120. W.Levason and C.A.McAuliffe,J.Chem.Soc.(Dalton Trans.), 1974,2238.

121. W.Levason,C.A.McAuliffe and S.G.Murray,J.Chem.Soc. (Dalton Trans.),1976,2321.

122. L.Y.Chia,Ph.D. Thesis,University of Aston in Birmingham, 1976.

123(a).F.Faraone,R.Pietropaolo and S.Sergi,J.Organomet. Chem.,1970,24,797.

123(b).C.Crocker,R.J.Errington,R.Markham,C.J.Moulton,K.J. Odell and B.L.Shaw,J.Am.Chem.Soc.,1980,102,4373.

124. W.R.McWhinnie and N.Al Salem,Personal communication.

125. S.A.Gardner,J.Organomet.Chem.,1980,190,289.

126. J.A.Osborn,F.H.Jardine,J.F.Young and G.Wilkinson,J. Chem.Soc.A,1966,1711.

127. W.E.Hill,C.A.McAuliffe,I.E.Niven and R.V.Parish, Inorg.Chim.Acta.,1980,38,273.

128. F.M.Beringer and S.J.Huang,J.Org.Chem.,1964,29,445.

129. M.C.Caserio,D.L.Glusker and J.D.Roberts,J.Am.Chem. Soc.,1959,81,336.

130. R.G.Miller and M.Stiles,J.Am.Chem.Soc.,1963,85,1798.

131. K.Lerstrup,D.Talham,A.Bloch,T.Poehler and D.Cowan, J.Chem.Soc.(Chem.Commun.),1982,336.

132. F.J.Berry,E.H.Kustan and B.C.Smith,J.Chem.Soc.(Dalton Trans.),1975,1323.

133. N.J.De Stefano,D.K.Johnson and L.M.Venanzi,Angew.Chem. Int.Ed.Engl.,1974,13,133.

134. J.Ellermann and K.Dorn,Chem.Ber.,1966,99,653.

135. D.C.Goodall,J.Chem.Soc.A.,1967,1387.

136. J.Ellermann and K.Dorn,Chem.Ber.,1967,100,1230.

137. J.Ellermann and K.Dorn,J.Organomet.Chem.,1966,6,157.

138. J.Ellermann and K.Dorn,Angew.Chem.Int.Ed.Engl.,1966, 5,516.