THE CO-ORDINATION CHEMISTRY OF TELLURIUM AND RELATED SELENIUM LIGANDS

by

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SUMMARY

2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II), (RR^1Te) reacts with $HgCl_2$ at room temperature to give white $HgCl_2.RR^1Te$. On setting aside, or on warming the reaction mixture a yellow material, $[R^1HgCl.(RTeCl)_2]$ is formed. Multinuclear NMR(^{125}Te, ^{199}Hg, ^1H) and mass spectroscopy confirm the formulation, and confirm the ease of transfer of the p-ethoxyphenyl group (R^1) between the metal centres. The crystal structure of the yellow material consists of two discrete RTeCl molecules together with a R^1HgCl molecule. There is no dative bond formation between these species, hence the preferred description of the formation of an inclusion complex.

The reaction of RR^1Te with Copper(I) chloride in the cold gives an air sensitive yellow product $Cu_3Cl_3(RR^1Te)_2(0.5CH_3CN)$; under reflux in air changes to the green $Cu_2Cl(RR^1Te)(0.5\ EtOH)$. By contrast, the reaction of RR^1Te with acetonitrile solutions of Copper(II) salts under mild conditions affords the white materials $CuCl(RR^1Te)$ and $CuBr(RR^1Te)H_2O$.

RR^1Te reacts with $PdCl_2$ and $PtCl_2$ to give materials albeit not well defined, can be seen as intermediates to the synthesis of inorganic phase of the type $M_{3X}Te_{2X}Cl_{2X}$. Paramagnetism is associated with some of the palladium and platinum products. The ^{195}Pt NMR measurement in DMSO establishes the presence of six platinum species, which are assigned to Pt(IV), Pt(III) or Pt(II). The reactions show that in the presence of $PdCl_2$ or $PtCl_2$ both R and R^1 are very labile.

The reaction of RHgCl(R=2-(2-pyridyl)phenyl) with SeX_4(X= Cl, Br) gives compounds which suggest that both trans-metallation and redox processes are involved. By varying reaction conditions materials which appear to be intermediates in the trans-metallation process are isolated.

Potentially bidentate tellurium ligands having molecular formula $RTe(CH_2)_n$-TeR,L^n, (R=Ph,(t-Bu). C_6H_4, n = 5,10) are prepared. Palladium and Platinum complexes containing these ligands are prepared. Also complex Ph_3SnClL(L = p-EtO.C_6H_4) is prepared.

KEY WORDS TELLURIUM LIGANDS, TRANSITION METAL TELLURIUM COMPLEXES, PYRIDINE, ORGANOSELENIUM.

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LIST OF ABBREVIATIONS

Cp	C_5H_5
Ph	C_6H_5-
p-tolyl	p-CH_3- C_6H_4-
t-Bu	t-C_4H_9
DMSO	Dimethylsulphoxide
DMF	Dimethylformamide
THF	Tetrahydrofuran
PPN	$[N(PPh_3)_2]^+$
2,2,2-Crypt	4,7,13,16,21,24-hexa-oxa-1, 10-diaza-bicyclo[8.8.8]hexacosane.
$^{13}C[^1H]$ NMR	Proton Decoupled Natural Abundance ^{13}C NMR

CHAPTER ONE

INTRODUCTION

1.1 GENERAL INTRODUCTION

During recent years the field of co-ordination chemistry of organo-chalcogen (Te,Se) compounds has expanded tremendously as evidenced by the number of books(1-3), review articles and annual surveys(4-6), and the proceedings of three relevant international conferences in this area(7-9). Still the number of papers published per year dealing with this class of compounds is growing. Co-ordination compounds containing organochalcogen ligands can now be prepared by a variety of synthetic methods.

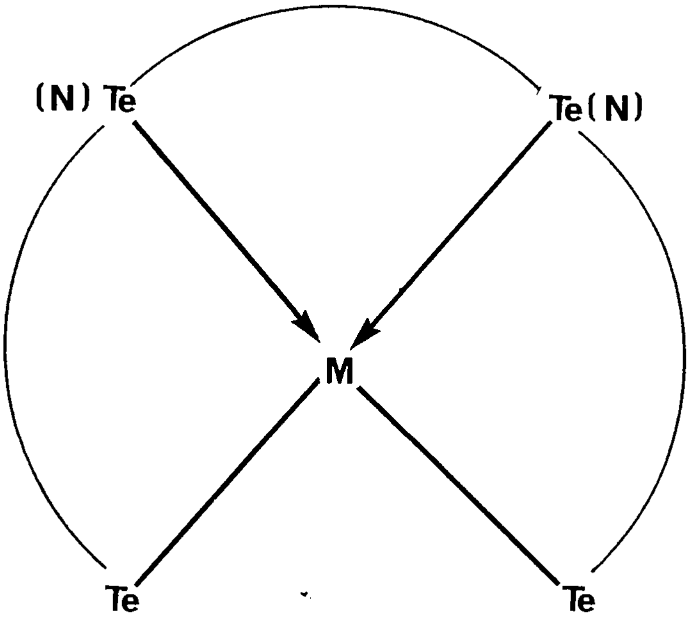
The fact that interest in these co-ordination compounds has been steadily growing is reflected by their growing importance in organic synthesis(10), photography(11) and in the synthesis of materials of high electrical conductivity(12). In addition the interest in these complexes still centres around the ability of these ligands to coordinate to a metal in a variety of different ways.

The ready availability of a wide range of physical techniques like Mössbauer(13) and NMR spectroscopy(14), and the possibility of determining molecular structures relatively easily by X-ray methods, has meant that a considerable body of information can be gathered not only on the way in which the ligand is bound to the metal, but also on factors which apparently influence the method of co-ordination adopted and the nature of the metal-chalcogen bond. From the point of view of physical investigation of co-ordination compounds tellurium ligands are most attractive. ^{125}Te is 6.99% abundant, has spin ½ and is suitable for use in both NMR and Mössbauer experiments. As an NMR nucleus, the receptivity(12.5) is considerably more favourable than for ^{13}C.

Although the first diorgano telluride Et_2Te was made as long ago as 1840$^{(15)}$, the use of such materials as ligands with transition metals has been paid little attention and remained limited until recently. Studies were hindered by the low stability of many compounds that were often light and air sensitive and frequently extremely malodorous.

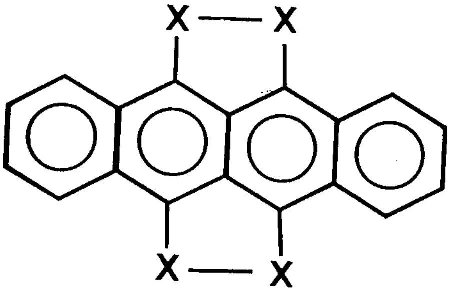
The idea of co-ordination is related to acid-base interaction in the Lewis sense. In terms of co-ordinate bond formation, a metal ion is a Lewis acid and a ligand is a Lewis base. These Lewis acids and bases have been classified in terms of "hardness" and "softness"$^{(16)}$. Tellurium and selenium ligands show very pronounced class B$^{(17)}$ or "soft" character, forming complexes with metals of strong class B character such as Pd(II), Pt(II), Hg(II) and Cu(I).

In this study interest was focussed on the synthesis of co-ordination compounds in particular those of nd^8 metal ions, because of their ability to form square planar complexes which might be catalytically active similar to complexes synthesised from analogous diphosphine ligands(18). Also that it is expected that these complexes may result in a stacked structure (A) with intermolecular Te--Te (or Se--Se) contacts since these constitute a common feature of

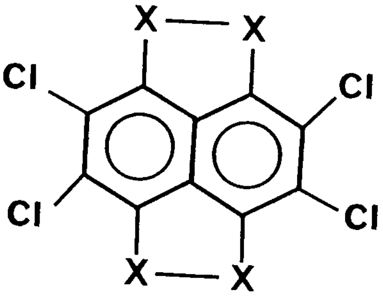


(A)

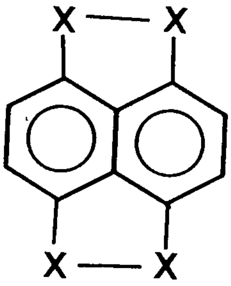
structural tellurium (selenium) chemistry, and if present may influence the solid state properties such as conductivity similar to complexes, $[M(L)]_x$ (where L = TTN, TTT, TCTTC) (B) which have shown to have significant conductivity in the solid state and used as active materials for battery electrodes(19).



TCTTC



TTT



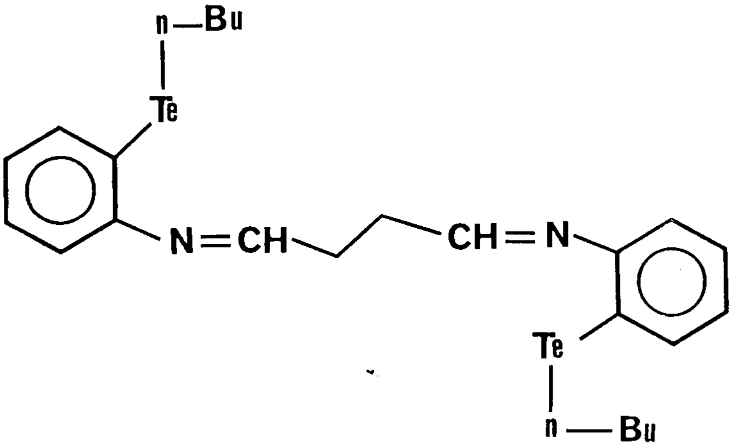
TTN

X= S, Se, and/or Te

(B)

It is worth pointing out that the interest in this field has also been established within the Aston Group and the experience of this group in synthetic particularly of organyltellurium chemistry is enormous. The Aston contribution in this field may be seen in the more general context in the recent review(20) in which it features the chemistry of tellurides and ditellurides, together with the co-ordination chemistry of the compounds.

Recently in our laboratory there has been a good deal of interest in the synthesis and complex formation of bidentate (Te,Te) ligands, and ligands containing both tellurium and nitrogen (Te,N) as potential donor atoms; the presence of nitrogen atom is designed to increase the affinity of the ligands for harder acids: Complexes $[ML^nX_2]$, (M = Pt, Pd, Hg, L = $(p\text{-EtO.}C_6H_4)Te(CH_2)_nTe(C_6H_4\text{.OEt-p})$, n = 5-10, x = Cl,Br) have been synthesised by Pathirana(21) and co-ordination has been established using IR and NMR spectroscopies. Also complexes of the ligand 1,6 - bis - 2 - butyltellurophenyl-2,5-diazahexa-1,5-diene(C) with palladium, platinum and mercury, have been prepared in our laboratory and their co-ordination chemistry investigated(22,23).



(C)

The work presented here is an extension of a recently initiated programme in our tellurium group of synthesis of the range of bi- and multi-dentate ligands including investigations of the co-ordination chemistry of these materials.

1.2 CO-ORDINATION MODES OF ORGANOCHALCOGEN COMPOUNDS.

Organochalcogen (Te,Se) compounds when reacting with transition metal ions can act as Lewis bases because of the lone pair of electrons of the outer shell of tellurium or selenium. Different modes of co-ordination have been identified. These include:

(a) terminal of the type M-ER, $M-ER_2$ (R = H, organic, or organometallic, E = Se,Te).

(b) bridging of the type $M-[\mu(E_n R_m)]-M$ (R = H, organic or organometallic, E = Se,Te).

(c) chelating or bidentate tellurium or selenium ligands.

For diorganyl chalcogenide ligands two modes (a, b) of co-ordination have been established. Complexes falling under this category include,

trans-$PdCl_2(EEt_2)_2$ (E=Se,Te),(24)
trans Pd $[SCN]_2$ $[Te(CH_2CH_2SiMe_3)_2]$(25)

in which the X-ray crystal structures (Fig 1.1 and 1.2) confirm the trans-formation. Other complexes are

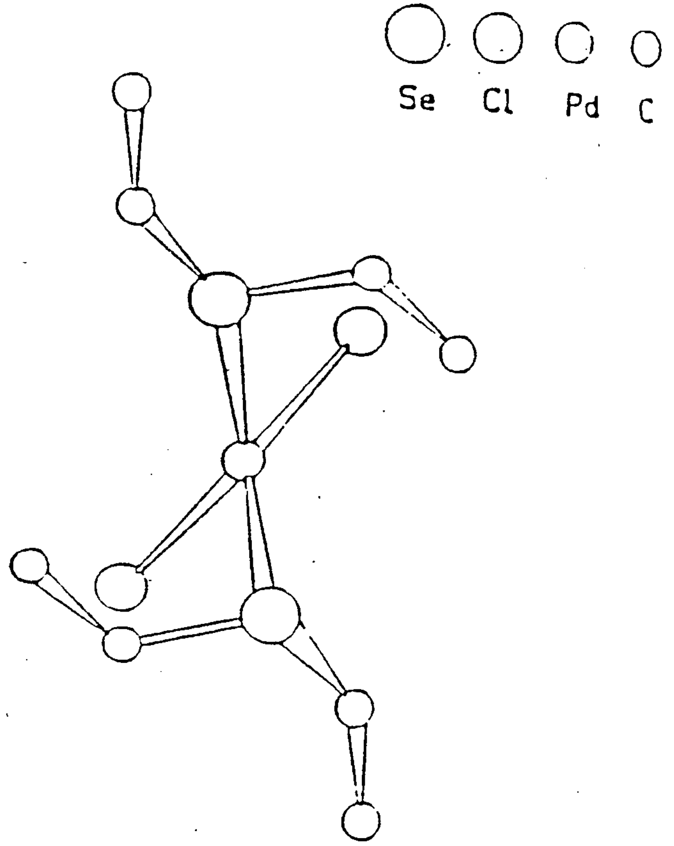


Fig 1.1: Molecular structure of $Pd(Et_2Se)_2Cl_2$

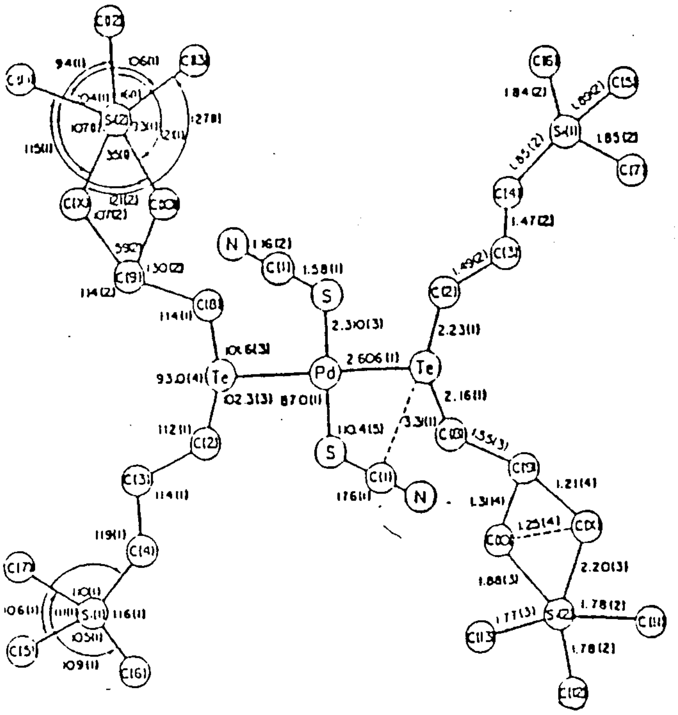


Fig 1.2: Molecular structure of $Pd[SCN]_2[Te(CH_2CH_2SiMe_3)_2]_2$

$[Mo(CO)_3(phen)(SePh2)]$(26)
$[RhCl\ (TePh_2)_3]$(27), and
<u>trans</u> $[RhCl(CO)(EEt_2)_2](E=Se,Te)$(28)

Complexes containing bridging TeR_2 group include,

$[IAg\ (\mu\text{-}TePh_2)\ AgI]$(29) and $[CuCl(TeEt_2)]$(30)

From X-ray analysis, the latter complex has a structure (Fig 1.3) based on layers of CuCl bridged by $TeEt_2$ with Cu-Te bond length of 2.625 and 2.535°A.

The anionic ligand RE^- and EH^- (E = Se, Te) can be coordinated on the metal in the terminal fashion mode (a) as in complex

$Cp(OC)_2\ FeEPh\ (E=Se,Te)$(31), $Pt(PPh_3)H(SeH)$(32),
$[PPN]\ [Cr(CO)_5TeH]$(33) and $[Ph_4P]\ [Hg(TePh)_3]$(34)

The X-ray crystal structure of the latter complex is shown in (Fig 1.4). Also complexes containing the RE^- or EH^- in the bridging mode are known. Examples are:

$[CuTePh]_n$(35), $Cp(OC)_2\ Fe(\mu\text{-}TePh)_2\ Fe(CO)_2\ Cp$(36)
$(ON)_2\ Fe\ (\mu\text{-}\ SeEt)_2\ Fe(NO)_2$(37),
$(OC)_4Mn(\mu\text{-}TeH)_2Mn(CO)_4$(38),
$[CpCo(\mu\text{-}PMe_2)_2(\mu\text{-}SeH)CoCp]PF_6$(39)

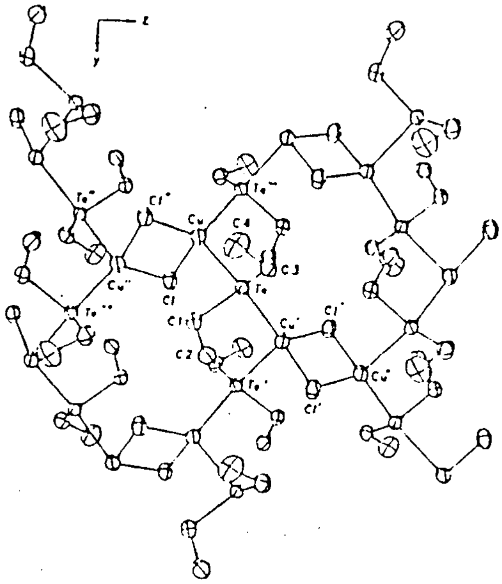


Fig 1.3: A polymeric sheet of $Et_2Te.CuCl$ down the X-axis.

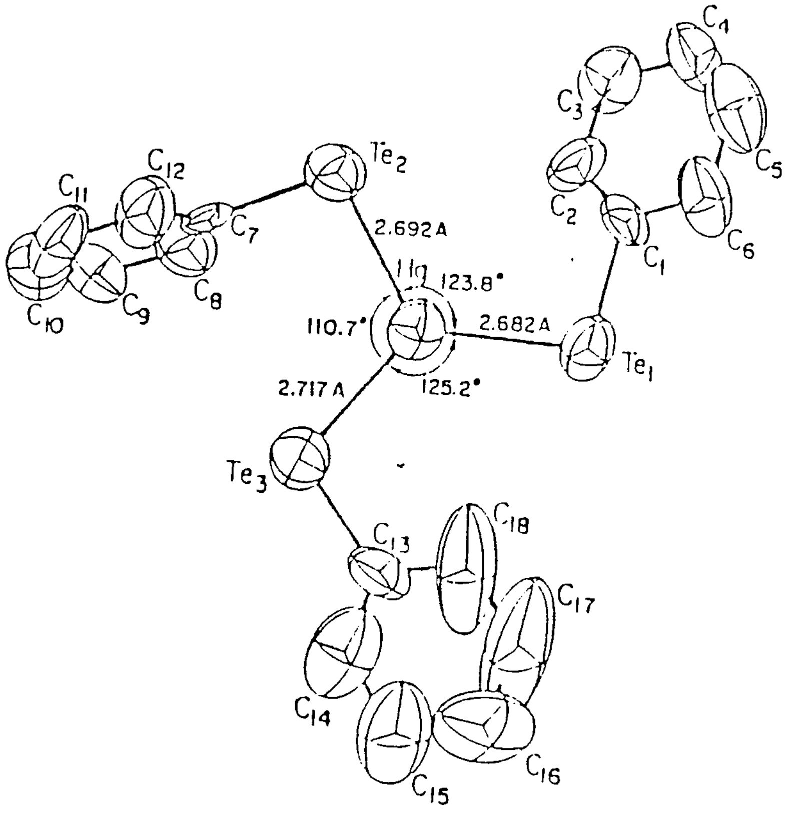
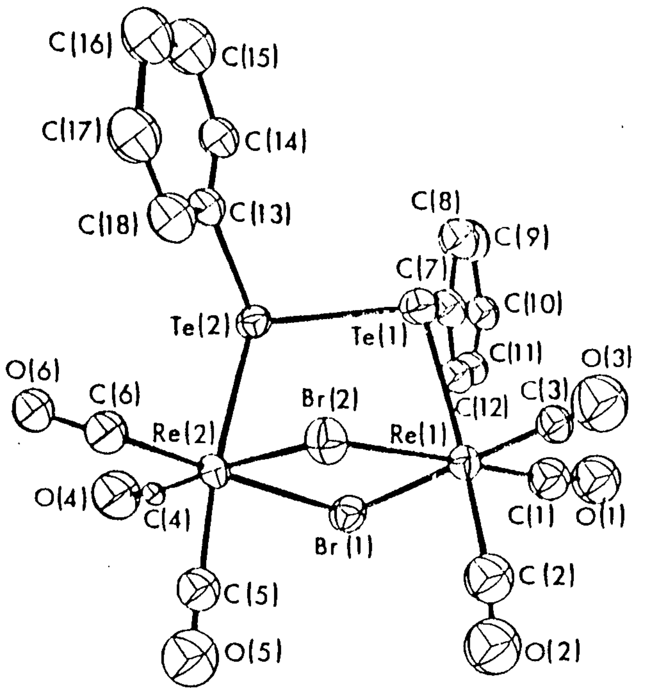


Fig 1.4: Molecular structure of $[Hg(TePh)_3]^-$

Although diorganyl dichalcogenides frequently undergo oxidative addition to a metal centre resulting in complexes of RE^- (E=Se,Te), they also function as bridging ligands in which the Se-Se or Te-Te bond of R_2E_2 remains intact. Dimeric Re(1) complexes with bridging diorganodichalcogenide ligands have been observed, $[(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}E_2Ph_2)\text{-}Re(CO)_3]$ (E=Se(40), Te(41)). The crystal structure for the complex (E = Te) consists of pseudo-octahedral Re(1) centres joined by two bromides and Te_2Ph_2 bridges (Fig 1.5). Also an ionic compound $(2,2,2\text{-Crypt-}K^+)_2Tl_2\text{-}Te_2.en$ has been reported(42). The interesting aspect of its structure is the butterfly-shaped configuration in which Te-Te separation of 4.414.4A is plausibly a non-bonding separation (Fig 1.6). Copper(1) complex $[CuCl.R_2Te_2](R=p\text{-}EtOC_6H_4)$ have been reported and are probably polymeric(36).

For bidentate chalcogen ligands, different co-ordination modes have been established. Complexes containing terminal chelating telluroformaldehyde $[Cp(PMe_3)Rh(\eta^2\text{-}CH_2)E]$ (E=Se, Te)(43), and bridging formaldehyde $[Cp(CO)_2Mn(\mu_2,\eta^2\text{-}CH_2E)\,Mn(CO)_2C_p]$ (E=Se,Te)(44) have been prepared.

A detailed discussion on this topic (particularly on diorganyl chalcogenides and diorganyl dichalcogen and their complexes) is given in two reviews by Gysling(45,46). More examples of bi or polydentate chalcogen ligands are given in section 1.4.



ig 1.5: Molecular structure of $(OC)_3Re(\mu\text{-}Br)_2(\mu\text{-}Ph_2Te_2)Re(CO)_3$

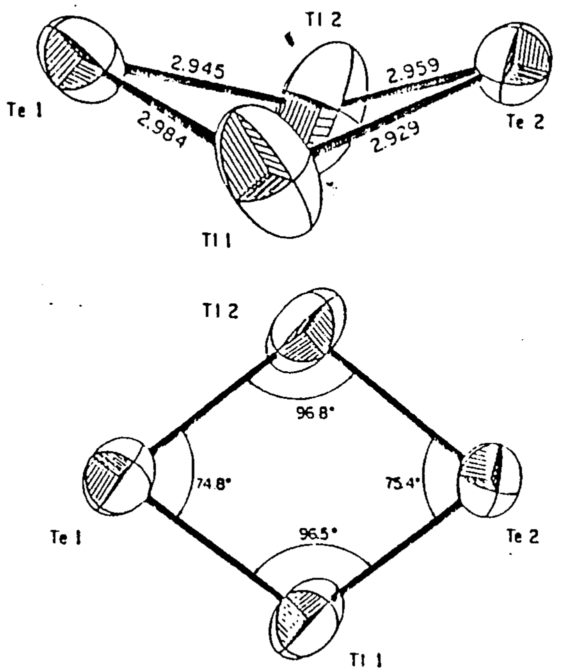


Fig 1.6: Two views of the $Tl_2Te_2^{2-}$ anion in $(2,2,2\text{-crypt-}K^+)_2Tl_2Te_2^{2-}$.en.

1.3 "HARD AND SOFT" NATURE OF LIGANDS

The concepts of acidity and basicity are so pervasive in chemistry that acids and bases have been defined many times and in various ways.

One of the most general and useful of all definitions was proposed by G.N. Lewis who defined an acid as an electron-pair acceptor and a base as an electron-pair donor. In the Lewis sense, all of the usual ligands can be regarded as bases and all metal ions can be regarded as acids. The degree of affinity of a metal ion for ligands can be termed its Lewis acidity, and the tendency of a ligand to become bound to a metal ion can be regarded as a measure of its Lewis basicity.

"Hardness and softness"(16) have also been used to classify Lewis acids and bases. Soft bases are those which have low electro-negativity, high polarisability and are readily oxidised; while hard bases could be described as having high electronegativity, low polarisability and high resistance to oxidation. The hardness of acids and bases is then affected by size, oxidation state, electronic structure and the nature of attached groups present. The hard metal ions (acids) prefer to co-ordinate with hard ligands (bases), while soft metal ions (acids) prefer to co-ordinate with soft ligands (bases).

A different method of classification of metals basing on affinities of ligand atoms for metal ions have been introduced by S. Arhland, H. Chatt and U.R. Davies(17). They used the term class (A) and class (B) to define hard and soft ions. Class (A) metals, complexes are most stable with the lightest ligands and less stable as each group is descended. For the type (B) elements the trend is just the opposite as summarised in the table below.

Complex of type (A) Metal.	Ligands			Complexes of type (B) metal
Strongest	R_3N	R_2O	F^-	Weakest
↑	R_3P	R_2S	Cl^-	↓
	R_3As	R_2Se	Br^-	
Weakest	R_3Sb	R_2Te	I^-	Strongest

Type (A) metal ions include those of alkali metals, alkaline earth metals and lighter transition metals in higher oxidation states such as Ti(IV), Cr(III), Fe(III) and CO(III). Class (B) metal ions include those of heavier transition metals, and those in lower oxidation states such as Cu(I), Ag(I), Hg(II), Pd(II) and Pt(II). According to their preferences towards with class (A) or (B) metal ions, ligands may be classified as type (A) or (B) respectively.

The terms "hard" and "soft" are relative referring to the special stability of hard-hard and soft-soft interaction and should be carefully distinguished from inherent acid-base strength: For example both OH^- and F^- are hard bases. Yet the Brønsted basicity of the hydroxide ion is about 10^{13} times that of the fluoride ion. Hence in considering acid-base interaction, it is necessary to consider both strength and hardness-softness.

Also there is no sharp dividing line between hardness and softness. This is illustrated in part by the third category (borderline) for both acids and bases. But even within a group of hard or soft, not all will have equivalent hardness or softness.

According to the above description, tellurium and selenium can be classified under soft ligands. Since soft ligands prefer to react with class (B) metals, organotellurium and selenium ligands form many complexes with metal ions which have soft acid character. The softness of the chalcogen increased in the order Te>Se>S as evidenced by the difference in energy of the carbonyl stretching frequencies in the complex $CpMo(CO)_3$ EPh (E = S, Se, Te), where the CO_{str} for these elements in the complex are as follows:

Te ($2016 cm^{-1}$) < Se ($2026 cm^{-1}$) < S ($2033 cm^{-1}$)(47)

This trend can be rationalized by comparing the Lewis basicity of the organochalcogen ligands which lies in the order SPh^- < $SePh^-$ < $TePh^-$. The electron density supplied to M0 increases in this order. The metal has increasing electron density to back-donate to CO. Thus CO_{str} decreases in the observed order.

It should be emphasised that the overall hardness and softness of both the metals and the ligand must be considered in the experimental design, i.e. the classification of the metals may be modified by the nature of the other ligands bonded to the metal. For example, an electron withdrawing group tends to make the metal harder, thus favouring bonding to the hardest ligand atom site, this type of behaviour being exemplified by the complex $[Pd(phen)(SCN)_2]$.(48) Similar alterations of electron density at the metal were originally suggested to account for the compounds $[Pd(NH_3)_2(SCN)_2]$ and $[Pd(PEt_3)_2(NCS)_2]$.(49) It was suggested that π- acceptor ligands such as PEt_3 favours bonding through the thiocynate N by making the metal harder.

In this connection, Jørgensen(50) has suggested that the formation of $[Co(NH_3)_5NCS]$ and $[Co(CN)_5SCN]^{3-}$ may be regarded as a "symbiosis"or a flocking together of like ligands.

Pearson(16) has noted that "antisymbiotic" effects are also known and he offers an explanation based on the trans effect or trans influence.

> "Two soft ligands in mutual trans position will have a destabilising effect on each other when attached to class (B) metal atoms."

This approach explains why, for example, in Pd(1-diphenylphosphino-3-dimethylaminopropane) (NCS)(SCN)[$Pd(C_6H_5)_2PCH_2CH_2N(CH_3)_2](SCN)(NCS)$](51) the N-bonded thiocynate is trans to P and the S-bonded thiocynate is trans to N. Thus a change from S to N bonding for thiocynate occurs when the thiocynate ligand binds trans to a soft ligand.

Although, the hard-soft rule is basically a pragmatic one allowing the prediction of chemical properties, there is no unanimity among chemists as to the detailed nature of "hardness and softness". Great problems arise because the acid-base pair can rarely be considered free of their environment in practice, so lattice or solvation factors could become dominant.

But clearly coulombic attraction will be of importance for hard-hard interaction while covalence will be quite significant for soft-soft interaction.

In an attempt to account quantitatively for the enthalpies ΔH_{AB} of combining a Lewis acid (A) with a Lewis base (B), R.S. Drago(52) proposed the following type of equation(1.1) based on the notion that for each acid-base interaction there will be both electrostatic and covalent components.

$$-\Delta H_{AB} = E_A E_B + C_A C_B, \qquad \text{(eq.1.1)}$$

ΔH_{AB} = the enthalpy of formation of a Lewis acid-base adduct.

E_A and C_A = parameters characteristic of the acid.

E_B and C_B = parameters characteristic of the base.

E = susceptibility of the species to undergo electrostatic interaction.

C = susceptibility of the species to form covalent bonds

This is a crude idea, and an arbitrary one, since there is no mathematically unique set of E and C values, no matter how many $-\Delta H_{AB}$'s are known. One of the problems of attempting to set up scales of Lewis acidity and basicity is that the equilibrium constant of a given complex forming reaction may be primarily determined by solvation or lattice energy terms, and not by the strength of a given co-ordinate bond. For organotellurium ligands it has been suggested(53) that, since ^{125}Te Mössbauer parameters are mainly sensitive to only the nearest neighbour environment, the variation of the quadrupole splitting as a given ligand, R_2Te, co-ordinates with a metal salt, MX_n, may indeed accurately reflect variation in the $Te \longrightarrow M$ bond strength. By assuming the quadrupole interaction is dominated by an imbalance in the tellurium p- orbital population the quadrupole splitting data (from Mössbauer spectroscopy) of complexes of bis (p-ethoxyphenyl) telluride, $(p\text{-EtOC}_6H_4)_2Te$, with various metal halides were interpreted in terms of the donor-acceptor interaction of the telluride with the metal halides and used to show that the order of Lewis acidity towards the ligand was Hg(II) > Pt(II) > Pd(II) > Cu(1)(53). Recently this postulate of assumption of p orbital bonding from Mössbauer spectroscopy has proved inadequate as more crystallographic data become available. For example $[CuCl(TeEt_2)]$(30) has a structure showing telluride bridging metal centres with bond angles about co-ordinated tellurium ranging from 95.6 to 130.5° indicating involvement of the participation orbitals other than p orbitals.

In summary, acid-base chemistry is conceptually rather simple, but the multiplicity of factors involved makes its treatment somewhat involved. Until more unifying concepts are developed, it will be necessary to apply each problem that is encountered the ideas, rules and the parameters available to it. Not surprisingly Cotton and Wilkinson(54) had this to say,

> "There have been those who have wondered, often to themselves and occasionally out loud, just where these various attempts to be precise and quantitative about the nature of acidity and basicity become too quixotic to be valuable."

1.4 LEWIS BASICITY OF ORGANOCHALCOGEN LIGANDS.

As mentioned earlier, organochalcogen (Te,Se) components form many complexes although the ligands show a strong preference for class (B) metals in the Arhland, Chatt, Davies classification(17). Thus the majority of complexes reported are either with metals of strong class (B) character, eg Hg(II), with metals in low oxidation states or with those such as Pd(II), Pt(II) and Rh(III) which may be considered borderline A/B in their behaviour. Despite current interest in organotellurium compounds, the studies of the ligand properties of organotellurium species still lag well behind that of the selenium analogues(55) and are mainly restricted to R_2Te or RTe^- species. Indeed the co-ordination chemistry of these species together with that of selenium analogues has been most comprehensively reviewed by Gysling.(45,46)

Very few bi- or poly- dentate tellurium ligands have been reported, although many complexes incorporating bidentate selenium ligands are known. $MeSe(CH_2)_2SeMe$ and $o\text{-}C_6H_4(SeMe)_2$ are examples of a bidentate selenium ligand used to complex Pt(IV)(56). Also complexes incorporating bidentate selenium ligands with various combinations of Group 5A and 6A donor atoms have been reported. The X-ray crystal structure of the compound $Ni[(Se\text{-}o\text{-}Ph_2P.C_6H_4)]_2$(57) which contains phosphorus and selenium donor atoms has been determined (Fig 1.7). The co-ordination geometry about the nickel atom is square planar with a trans arrangement of donor atoms. The Ni-P bond strength of 2.177A° is significantly shorter than the sum of the covalent radii 2.28A(58) and can be taken as evidence of significant metal-ligand Π bonding in this d^8 complex. The Ni-Se bond distance of 2.280A° is significantly , but not drastically shorter than the 2.35A° sum of the covalent radii.(58)

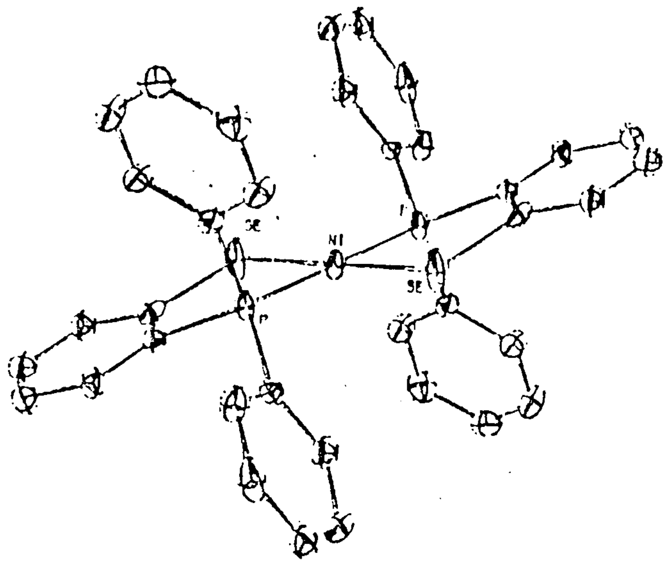


Fig 1.7: A stereoscopic view of the $Ni(Sep)_2$ molecule.

Another example of the multidentate ligand incorporating mixed donor atoms of Group 5A and 6A is the tetradentate ligand, tris(o-methylselenophenyl)phosphine $(o\text{-}CH_3Se.C_6H_4)_3P$ (TSeP). The complex $[Ni(TSep)_2](ClO_4)_2$ which contains octahedral nickel has been prepared.(59) A tetradentate selenoether ligand, 1, 3 bis(2-methylselenoethylseleno) propane $MeSe(CH_2)_2Se(CH2)_2SeMe$ (bsep) has been prepared. The ligand reacts with appropriate sodium tetrahalogen palladate(II)in ethanol to yield $[Pd_2(bsep)X_4]$ (X = Cl, Br or I) in which the ligand is bidentate to each palladium atom.(60)

A multidentate ligand which contains both a soft donor atom (Se) and a hard donor atom (N) has been reported. Bis [2-(2-pyridyl)ethyl] selenide, (L),(61) forms complexes $[Cu(L)X_2]$ (X = Cl, Br, NO_3 or ClO_4).

In comparison to selenium, only a few bidentate or polydentate tellurium ligands are known. An example of the complexes containing bidentate tellurium ligands is the compound $[PtL_2]$ $[Pt(SCN)_4].2DMF$ $(L{=}Ph_2P(o\text{-}C_6H_4TePh))$. The structure of this complex has been determined,(62) (Fig 1.8). It has been described as monomeric in which tellurium and phosphorous are the donor atoms, and have shown to have the trans- configuration with Pt-Te bond length of 2.575A^o (shorter than the sum of the Pauling covalent radii 2.63A^o)(58). The bond angles about the Te are all less than the tetrahedral angle as predicted by Valence Shell Electron Pair Repulsion theory.(63)

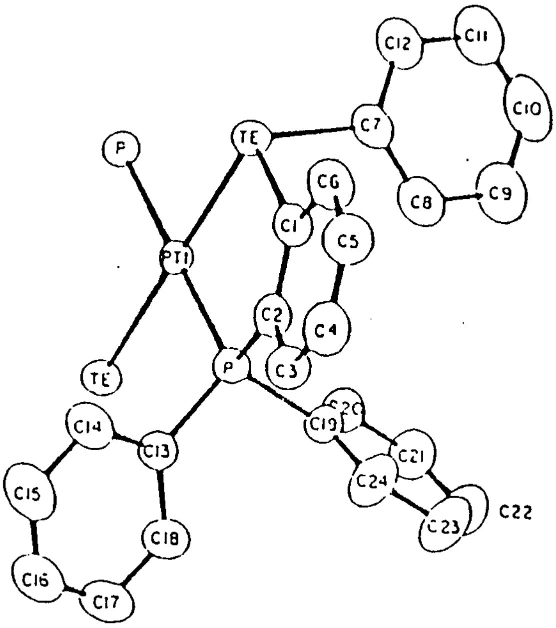


Fig 1.8: The structure of $[Pt(tep)_2]^{2+}$ ion of the complex $[Pt(tep)_2][Pt(SCN)_4].2DMF$

Complexes that incorporate chelating bidentate tellurium ligands of the type ML^nX_2 [M=Pd,Pt, L=(p-EtOC$_6$H$_4$Te(CH$_2$)$_n$Te C$_6$H$_4$OEt-p), n = 5-10, X = Cl, Br] are known. They appear to be in the solid state trans [PdL^nX_2] and cis [PtL^nX_2] but ^{125}Te NMR data reveal complex cis$\rightleftharpoons$trans equilibria.(21) Further studies were limited as the complexes were poorly crystalline and tended to have a limited range of thermal stability.

A multidentate ligand containing both tellurium (soft) and harder donor atoms nitrogen compound (C) has been successfully prepared in our laboratory. The crystal structure of compound (C) has been reported together with that of the complex $HgCl_2(C)$ (Fig 1.9) in which only the two tellurium atoms co-ordinate mercury (II).(23) The ligand in this case behaves as a bidentate (Te,Te) ligand, and an intraligand Te---N interaction seems responsible for the general non-availability of the nitrogen atom for co-ordination. In fact the nitrogen-tellurium interaction seen in unco-ordinated ligand (C) is retained in the complex (Te---N, 2.773A^o free ligand, 2.752, 2786A^o complex). Thus tellurium is simultaneously acting as a Lewis acid and a Lewis base.

The reaction of ligand (C) with Pt(II), Pd(II) and Rh(III) has also been described.(22) Some novel reactivity was observed for the platinum complex. The complex $[Pt(C)(H_2O)Cl]Cl$ in DMSO show labile alkyl group. The lability of alkyl group can be followed by ^{125}Te and ^{195}Pt NMR.

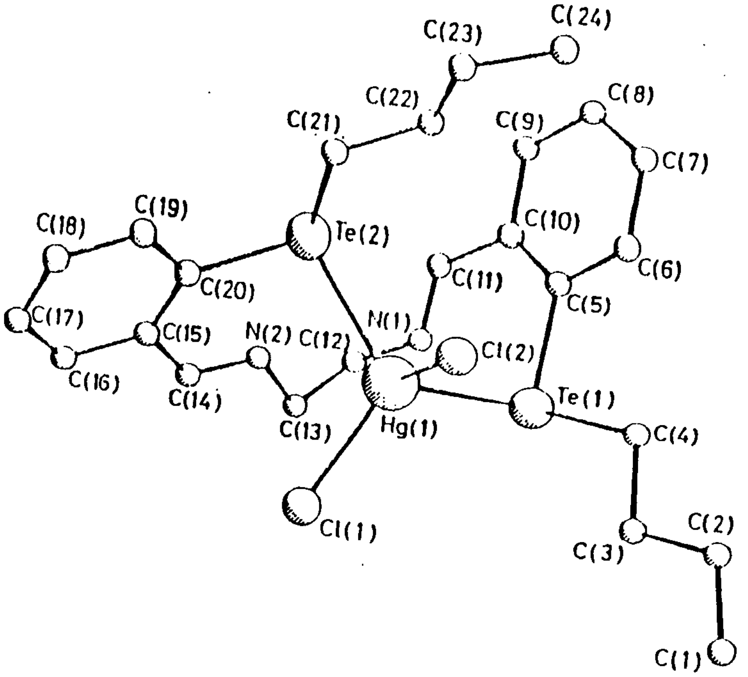
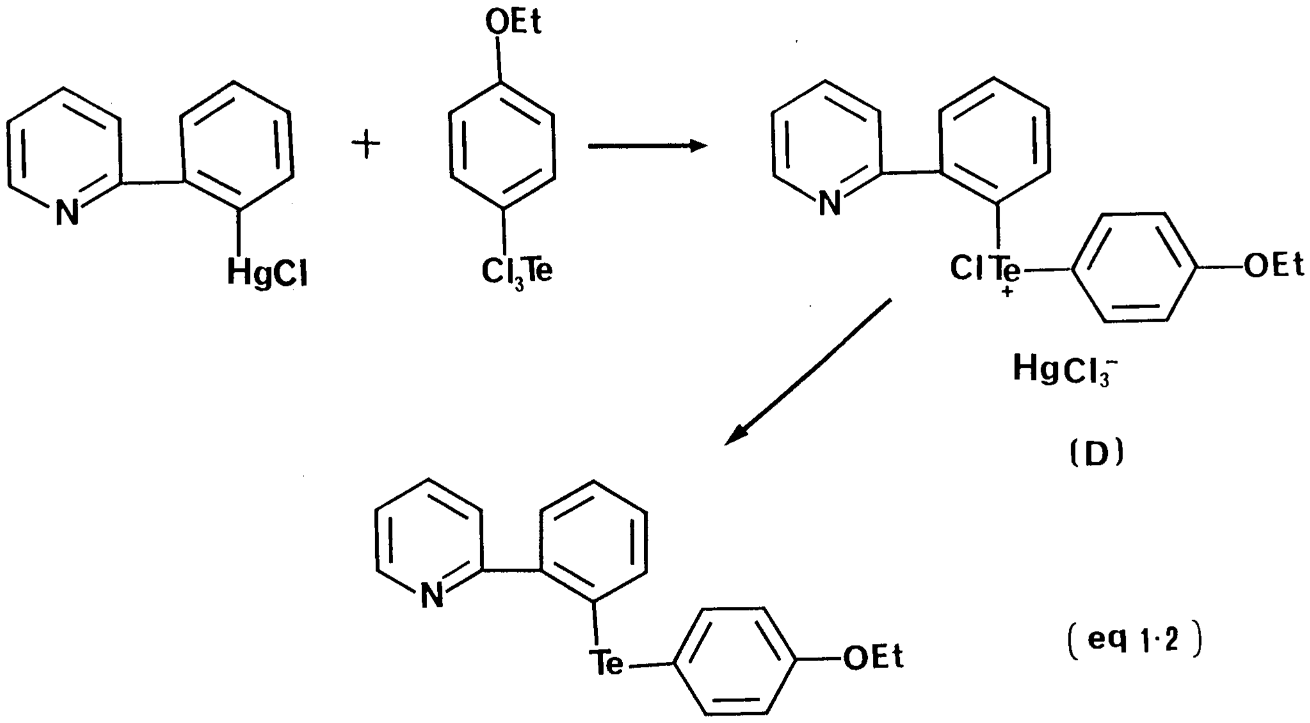


Fig 1.9: The molecular structure of mercury complex HgL(C).

The synthesis and crystal structure of the ligand 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II)(compound (E))having two centres of Lewis basicity (Te, N) have been reported.$^{(64)}$ It has been prepared from the reaction of 2-(2-pyridyl)phenylmercury(II)chloride with p- ethoxyphenyltellurium(IV) trichloride (eq. 1.2).



(D)

(eq 1·2)

(E)

The interesting observation from this reaction was the formation of the product (D) that contained both tellurium and mercury, in which it showed that the tellurium atom preferred bonding to one pyridyl nitrogen than to the second halogen. Normally diorganyltellurium(IV) dihalide would be formed. The conductivity and stoichiometry of compound (D) strongly suggested an ionic structure. Indeed this proposed formulation of a new type of telluronium ion stabilized by intra-molecular co-ordination to the pyridyl- nitrogen atom has been recently confirmed from the crystal and molecular structure of the compound (see Chapter Six). The geometry about tellurium has been described as ψ-trigonal bipyiramidal with N, Cl, axial and two Te-C bonds, together with the lone pair of electrons constituting the equatorial plane.

Only few bidentate tellurium ligands(21,65,66,67) and ligands which contain hard nitrogen donor and a tellurium or selenium donor atoms have been described,(22,23,61) and the data on these are very limited. Therefore it will be interesting to explore more about the co-ordination chemistry of these materials.

1.5 THE PRESENT WORK.

1. Objectives.

(i) The synthesis of new bidentate (Te,Te) ligands, and ligands having two centres of basicity (Te,N) or (Se,N).

(ii) The synthesis of a wide range of transition metal complexes with these ligands.

(iii) To study the coordination chemistry of these complexes using infra-red, visible- u.v., ESR, NMR and X-ray crystallography.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

2. GENERAL EXPERIMENTAL TECHNIQUES.

2.1 Chemicals

The starting materials used for many reactions were obtained either from British Drug Houses (BDH) or the Aldrich Chemical Company. Platinum, and palladium compounds, were obtained from Johnson and Matthey Ltd. The known tellurium and selenium compounds used in this study were prepared by literature methods using tellurium or selenium powder as starting materials obtained from commercial sources.

2.2 Solvents

All solvents were obtained from commercial sources and were purified where necessary by literature methods,(68) and kept over molecular sieves.

2.3 Elemental Analysis

The elemental analyses for carbon, hydrogen and nitrogen were carried out either by the Analytical Service Unit, University of Aston, using a Carlo Erba 1106 Elemental Analyser, or at Elemental Micro Analysis Ltd, Exeter Road, Okehampton, Devon, EX20 12A.

2.4 Melting Points

The melting points (uncorrected) were determined using a Gallenkamp electrically heated apparatus.

2.5 Conductivity Measurements

Molar conductance of dilute solution (10^{-3}) was measured at room temperature using a standard Mullard Conductivity bridge and immersion type bright platinum electrodes (type E 7591/B) with a cell constant of 1.46.

2.6 Infra-red Spectra

Spectra in the range 4000-200cm^{-1} were recorded on a Perkin-Elmer infra-red spectrophotometer model FT-IR 1710 instrument. Spectra of solid samples were either taken as KBr pellets or as Nujol mulls between CSI discs. Nujol paraffin oil was used as mulling agents.

2.7 Nuclear Magnetic Resonance Measurements

^{1}H, ^{13}C, ^{125}Te and ^{199}Hg N.M.R. spectra were determined with a Bruker AC 300 MHZ specification spectrometer at 300, 75.4, 94.7 and 53.7 MHz frequencies respectively. Tetramethylsilane (TMS) was used as internal reference for ^{1}H and ^{13}C. Other references were: bis (p-ethoxyphenyl) ditelluride (external) in $CDCl_3$ for ^{125}Te NMR (which has δ = 456 ppm relative to Me_2Te with respect to which all ^{125}Te shifts are cited) and mercury(II)chloride ($HgCl_2$) in water for ^{199}Hg.

2.8 Electron Spin Resonance and Ultra-violet and Visible Spectra.

The ESR and U.V. and visible absorption spectra were obtained with a JEOL JES-FE3XG spectrometer (field range 3000-25000 gauss) and a shimdazu UV-VIS recording spectrophotometer SP-3000 respectively; Dr T.S. Lobana of Guru Nanak Dev University, Amritsar - 143005, India is thanked for undertaking these measurements.

2.9 Mass Spectra

Mass spectra of some compounds using both low resolution EI-MS and Fast Atom Bombardment techniques were obtained from Birmingham University and SERC MASS SPECTROMETRY SERVICE CENTRE, Chemistry Department, University College of Swansea.

2.10 Microwave oven heating

The heating was carried out using a Sharp Carousel II R-84801 domestic microwave oven. It was performed in $100cm^3$ Teflon bottles with screw tops supplied by the Savillex Corporation, Minnetoka, Minnesota. 55345, U.S.A.

CHAPTER THREE

THE REACTION OF 2-(2-PYRIDYL)PHENYL (P-ETHOXYPHENYL)TELLURIUM(II) WITH MERCURY(II) CHLORIDE

3.1 INTRODUCTION

As stated in chapter one, recent years have seen a significant growth of interest in the ligand chemistry of organotellurium(II) compounds.(1,6,7,9) A major impetus for the study of organotellurium complexes containing mercury is the hope that some may be potential for the development of sensors for environmental Hg based on thin films of polymer supported tellurium ligands. This is indeed expected given the liking of tellurium ligands for "soft" metal ions and the evidence of reasonably strong co-ordinate bonds to, particularly mercury from Mössbauer studies.(35)

Many organotellurium complexes of mercury(II) have been reported. These include complexes with unique structures like a tetrameric $(Ph_2Te)HgI_2$(69) (Fig 3.1) and $[PPh_4]$-$[Hg(TePh)_3]$ (Fig 1.4) complexes in which the tellurium ligands are monodentate and the mercury atoms are either in the centre of a tetrahedron or in the centre of a triangle. The complex $(HgCl_2.L)$ $L=(Bu^nTe)C_6H_4CHN(CH_2)_2NCHC_6H_4(TeBu^n)$ (Fig 1.9) which is monomeric with four co-ordinated mercury(II) bonded to two chlorine and two tellurium atoms, thus forming a 13-membered chelate ring has also been reported.(23) It represents the only known type of ligands having two centres of Lewis basicity (Te,N). Therefore,

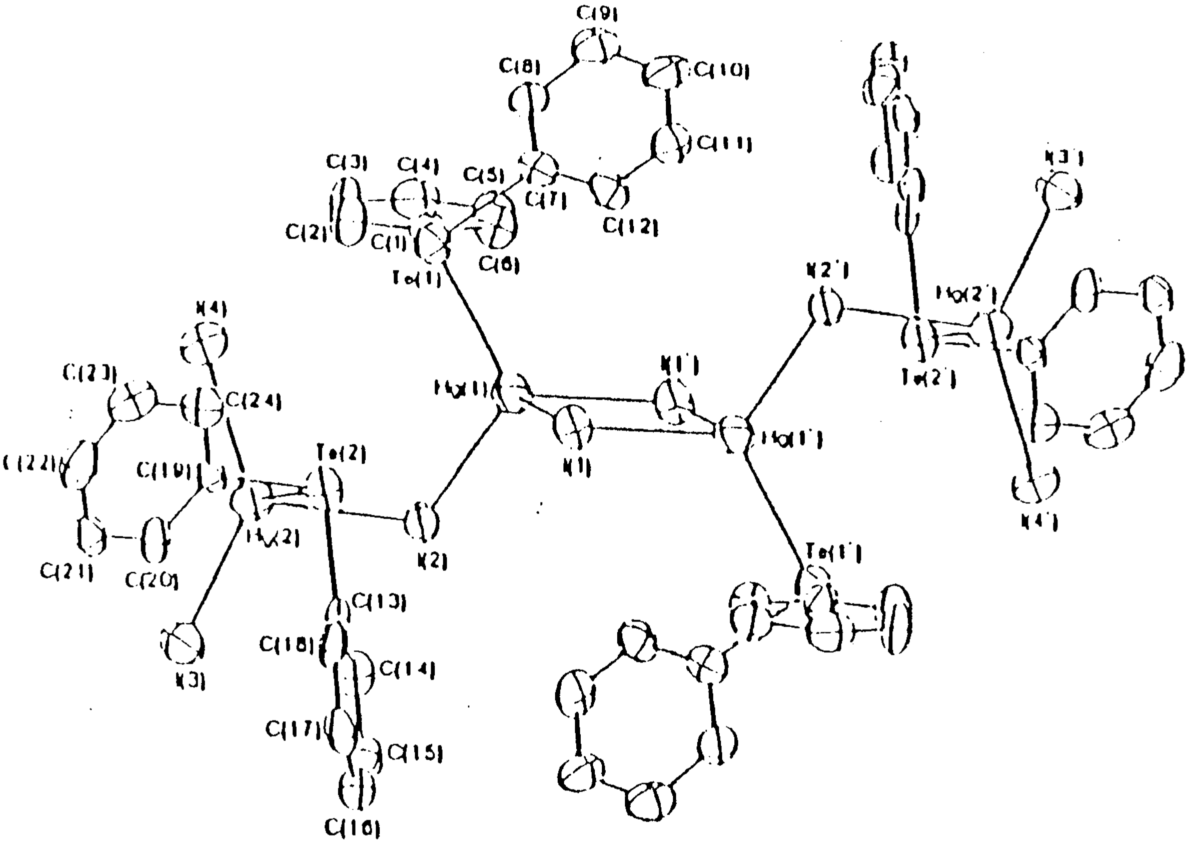


Fig 3.1: Molecular structure of $(Ph_2Te)HgI_2$.

investigations of the co-ordination chemistry of such ligands will be of much interest in the future.

In this chapter, the reaction of 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II) with mercury(II)chloride is discussed in which labilisation of organic groups from tellurium is observed.

3.2 EXPERIMENTAL

3.2.1 Preparation of the ligand 2-(2-Pyridyl)phenyl-(p-ethoxyphenyl)tellurium(II)

This was prepared according to the literature.(64)

3.2.2 Preparation of the mercury Complexes

2-(2-Pyridyl)phenyl(p-ethoxyphenyl)tellurium(II) (0.404g, 1 mmol) in acetonitrile or ethanol ($10cm^3$) was added to a solution of mercury(II)chloride (0.272g, 1mmol) in acetonitrile or ethanol ($10cm^3$). The solution was warmed very slightly and a white product formed which was filtered, washed with fresh solvent, and dried in *vacuo*. Yield 64% mp 145-147°C.

Found $C = 33.7\%$, $H = 2.42\%$, $N = 1.99\%$

$C_{19}H_{17}Cl_2HgNOTe$ requires

$C = 33.8\%$, $H = 2.52\%$, $N = 2.08\%$

If the above solution was set aside to evaporate slowly, or refluxed for 45 minutes, a yellow product was obtained. It was recrystallised from 1:1 acetonitrile/ethanol. Yield 62%, m.p. 150-152°C.

Found $C = 36.5\%$, $H = 2.40\%$, $N = 2.78\%$

$C_{30}H_{25}Cl_3HgN_2OTe_2$ requires

$C = 36.3\%$, $H = 2.52\%$, $N = 2.82\%$

3.2.3 Effect of complex precursor on complex formation

In order to ascertain the formation of the above mercury(II) complex (yellow) a different reaction was designed, the direct reaction of 2-(p-ethoxyphenyl) mercury(II)chloride with 2-(2-pyridyl) phenyl tellurium(II) bromide.

(i) Synthesis of 2-(p-Ethoxyphenyl) mercury(II) chloride

Phenetole (6.10g, 0.05 mole) and mercury(II) acetate (15.93g, 0.05 mole) were mixed in absolute ethanol (100 cm^3) and refluxed for 24 hours. Lithium chloride (4.42) in warm methanol (100 cm^3) was added and the resulting mixture was warmed for a further 30 minutes.

It was then poured into distilled water (300 cm^3) and filtered. Recrystallisation from chloroform gave a colourless solid of m.p in 70% yield.

Found $C = 26.8\%$ $H = 2.48\%$

C_8H_9ClHgO $C = 26.9\%$ $H = 2.51\%$

(ii) Synthesis of 2-(2-Pyridyl) phenyltellurium(II) bromide

This was carried out according to the literature.(64)

(iii) The reaction of 2-(p-Ethoxyphenyl)mercury(II)chloride with 2-(2-Pyridyl)phenyltellurium(II)bromide.

2-(p-Ethoxyphenyl)mercury(II)chloride (3.58g,0.01 mole) in warm ethanol (15cm^3) was added to a refluxing solution of 2-(2-pyridyl) phenyl tellurium(II) bromide (3.61g, 0.01 mole) in acetonitrile (15cm^3), and the mixture was refluxed for one hour. The solution was then filtered and the filtrate was left to cool down giving rise to a yellow compound. Recrystallisation from a mixture of acetonitrile/ethanol gave yellow crystals which melted at 128°-130°C. Yield 52%.

Found $C = 33.1\%$, $H = 2.45\%$, $N = 2.51\%$

$C_{30}H_{25}Br_2ClHgN_2OTe_2$ requires

$C = 33.3\%$, $H = 2.34\%$, $N = 2.59\%$

When the above reaction was carried out using different reactant ratio, 2:1 (RTeBr:R^1HgCl), a yellow crystalline compound was formed having the same melting point but different stoichiometry.

Found C = 32.3%, H = 2.14%, N = 2.28%

$C_{49}H_{42}Br_3Cl_2N_3OTe_3$ requires

C = 32.6%, H = 2.33%, N = 2.34%

3.3 RESULTS AND DISCUSSION

The reaction of 2-(2-pyridyl)phenyl(p-ethoxyphenyl) tellurium(II)(RR^1Te), with mercury(II)chloride in 1:1 ratio produces two types of complex under different conditions (equations 3.1 and 3.2).

(a) $$RR^1Te + HgCl_2 \xrightarrow[\text{mild condition}]{\text{EtOH}} \underset{\text{White (1)}}{HgCl_2.RR^1Te} \qquad \text{(eq 3.1)}$$

(b) $$RR^1Te + HgCl_2 \xrightarrow[\text{reflux, 45 min}]{\text{EtOH}} \underset{\text{Yellow (II)}}{R^1HgCl.(RTeCl)_2} \qquad \text{(eq 3.2)}$$

This was confirmed by the elemental analysis, the ^1H, ^{125}Te, and ^{199}HgNMR and mass spectroscopy.

An analogous bromide derivative of complex (**II**) (eq. 3.2) was prepared by reacting directly (p-ethoxyphenyl) mercury(II) chloride (R^1HgCl) and 2-(2-pyridyl) phenyl tellurium(II) bromide (RTeBr) (eq. 3.3).

(c) $$R^1HgCl + RTeBr \xrightarrow[\text{reflux, 45 min}]{\text{EtOH}} \underset{\text{Yellow (III)}}{R^1HgCl(RTeBr)_2} \qquad \text{(eq 3.3)}$$

In the above reaction RTeBr was used instead of RTeCl because it was readily available at the required time. Using different reactant ratio in the above reaction (c), produced products having different stoichiometries but with the same

Compound	%C (required)	%H (required)	%N (required)	C:N	MP(^oC)	Colour
$HgCl_2(RR^1Te)$ **(I)**	33.7 (33.8)	2.42 (2.52)	1.99 (2.08)	19:1	145-7	White
$R^1HgCl(RTeCl)_2$ **(II)**	36.5 (36.3)	2.40 (2.52)	2.78 (2.82)	15:1	150-2	Yellow
$R^1HgCl(RTeBr)_2{}^a$ **(III)**	33.1 (33.3)	2.45 (2.32)	2.51 (2.59)	15:1	128-130	Yellow
$(R^1HgCl)_2(RTeBr)_3{}^b$ **(IV)**	32.3 (32.6)	2.14 (2.33)	2.28 (2.34)	16.5:1	127-130	Yellow

a = reactant ratio 1:1 ($RTeBr:R^1HgCl$)
b = reactant ratio 2:1 ($RTeBr:R^1HgCl$)
R_1 = 2-(2-pyridyl) phenyl
R^1 = p-ethoxyphenyl

Table 3.1: Analytical data for mercury complexes.

Table 3.2: ^{1}H NMR data for some 2-phenyl pyridine derivatives and mercury complexes.

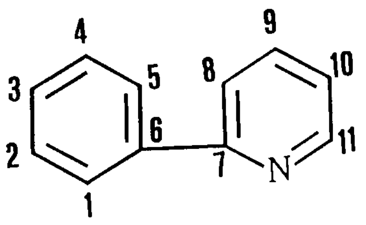
Compound (solvent)	δ(ppm vs TMS)^{a}
RTeBr	7.35 (t, C3), 7.51 (t, C4), 8.01 (t, C9), 8.11 (d, C5), 8.19 (d, C8), 8.56 (d, C2), 8.73 (d, C11).
RR^{1}Te (dmso-D_6)	1.45 (t, C17), 4.08 (q, C16), 6.85 (d, C14), 7.05 (t, C3), 7.25 (m, C4, C5, C8), 7.78 (d, C2), 7.85 (d, C13), 7.95 (2t, C9, C10), 8.74 (d, C11)
$HgCl_2$.RR^{1}Te (dmso-D_6)	Set 1: 1.40 (t, C17), 4.10 (q, C16), 6.95 (d, C14), 7.10 (d, C5), 7.25 (t, C3), 7.45 (m, C4, C8), 7.85 (d, C13), 8.30 (m, C9, C10), 8.70 (d, C2)
$HgCl_2$.RR^{1}Te (dmso-D_6)	Set 2: 1.30 (t, C17), 3.95 (q, C16), 6.85 (d, C14), 7.35 (d, C13), 7.65 (m, C3, C4, C10), 8.05 (t, C9), 8.35 (d, C5), 8.55 (d, C8), 8.75 (d, C2), 9.25 (d, C11).

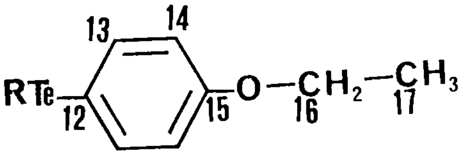
Table 3.2: ^{1}H NMR data for some 2-phenyl pyridine derivatives and mercury complexes. (continued)

Compound (solvent)	δ(ppm vs TMS)[a]
$R^1HgCl(RTeCl)_2$ ($CDCl_3$)	1.40 (t, C17), 4.04 (q, C16), 6.95 (d, C14), 7.18 (d, C13), 7.35 (t, C3), 7.50 (t, C4), 7.60 (t, C10), 8.00 (t, C9), 8.20 (d, C5), 8.25 (d, C8), 8.60 (d, C2), 8.80 (d, C11).
(dmso-D_6)	1.30 (t, C17), 3.95 (q, C16), 6.85 (d, C14), 7.35 (d, C13), 7.65 (m, C3, C4, C10), 8.25 (t, C9), 8.40 (d, C5), 8.55 (d, C8), 8.70 (d, C2), 9.25 (d, C11).

d = doublet, t = triplet, q = quartet, m = multiplet

a = carbon numbers in parenthesis refer to the protons attached to the numbered carbon atoms shown below.





Compound	^{13}C Chemical shifts (ppm)^{a} relative to TMS					
	C1	C2	C3	C4	C5	C6
	C7	C8	C9	C10	C11	C12
	C13	C14	C15	C16	C17	
(RTeBr)	128.4	138.5	126.7	133.7	126.7	133.2
	153.6	121.0	138.5	122.8	142.3	
(RR^1Te)	126.3	-	128.10	-	126.3	138.8
	156.7	121.5	136.2	114.9	149.3	109.7
	141.3	115.7	159.7	63.2	14.7	
$HgCl_2.RR^1Te$	133.1	130.9	123.7	132.0	127.3	137.9
	153.7	127.8	136.5	122.7	138.4	-
	134.2	115.9	158.3	62.7	14.6	
$[R^1HgCl.(RTeCl)_2]$	134.2	138.5	123.8	130.9	127.4	142.0
	153.7	127.7	139.9	120.5	143.6	-
	137.8	114.4	158.4	62.7	14.9	

a = Number system used to designate carbon atoms in the pyridine ring and ethoxyphenyl group is shown below the table 3.2

Table 3.3: ^{13}C N.M.R. data of some 2-phenylpyridine derivatives and mercury complexes.

Compound	Solvent	δ(Te)(ppm)(*vs*(p-OC$_6$H$_4$)$_2$Te$_2$)	δ(Te)(ppm)(*vs* Me$_2$Te)	δ(Hg)^a(ppm)
RR^{1}Te	CDCl$_3$	194.1	649.1	
HgCl$_2$.RR^{1}Te	dmso-D$_6$	186.5	641.5	
[R^{1}HgCl(RTeCl)$_2$]	CDCl$_3$	868.9	1323.9	469.7
RTeBr	dmso-D$_6$	842.0	1297.0	
[R^{1}HgCl(RTeBr)$_2$]	dmso-D$_6$	851.0	1306.0	

a = Hg Chemical shift relative to aqueous HgCl$_2$

Table 3.4: ^{125}Te and ^{199}Hg NMR data.

melting points. Indeed the C:N ratios fit exactly with the formulation of the complexes as shown in table 3.1, which were found to be different from that of the ligand (19:1). The similarity in melting points may indicate weak bonding between tellurium and mercury atom.

The complex (I) which is obtained under mild conditions is sparingly soluble in solvents of low polarity, while complexes (II) and (III) and (IV) are more soluble in less polar solvents.

3.3.1 Infra-red Spectroscopy

The infra-red spectra of complexes (I) and (II) in the solid state were measured in KBr discs, as shown in Fig 3.2 and 3.3. The infra-red spectra of both the mercury complexes indicate characteristic absorptions of both the 2-(2-pyridyl) phenyl- and p-ethoxyphenyl- groups. The low frequency infra-red spectrum of the white mercury complex (1) showed a weak band at 322 cm^{-1} which could be assigned as υ(Hg-Cl). For solid mercury(II) chloride, υ(Hg-Cl) has been assigned at 310, 330cm^{-1}.(70) The infra-red spectrum of the yellow mercury complex showed two bands in the lower frequency region 311-321 cm^{-1}, which could be assigned to υ(Hg-Cl). The freshly prepared (p-ethoxyphenyl)mercury(II)chloride showed a strong peak at 332cm^{-1} assigned as υ(Hg-Cl). This supports the assignment of υ(Hg-Cl) for the yellow complex,

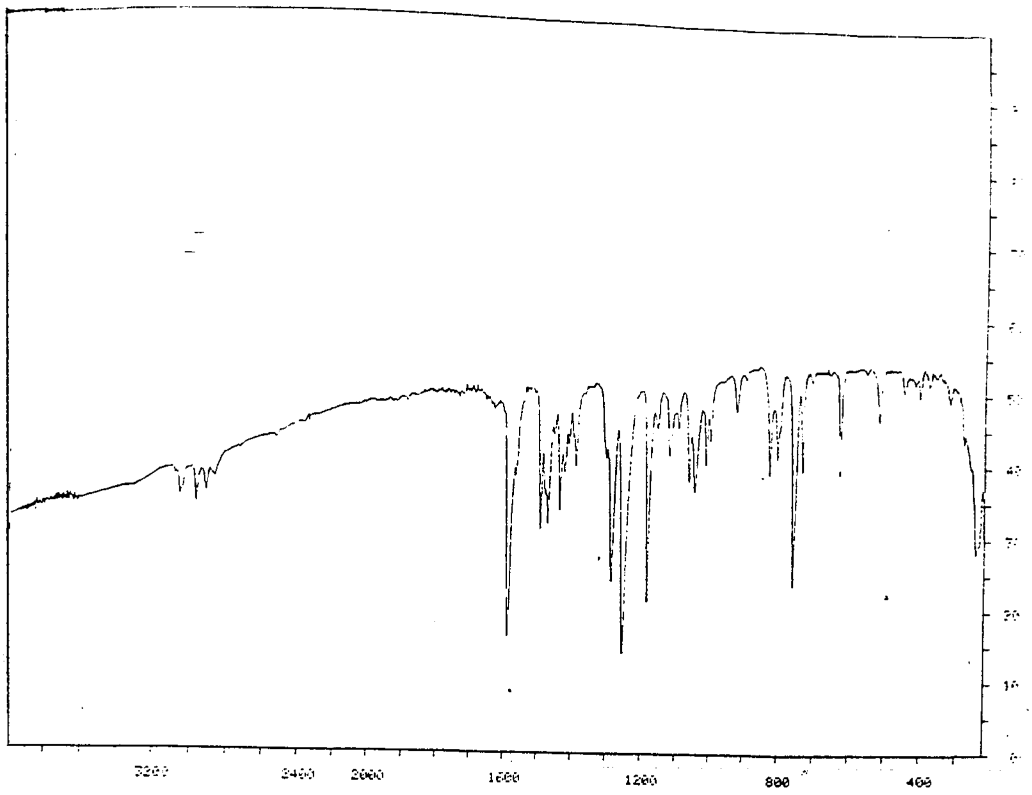


Fig 3.2: I.R. Spectrum of $(RR^1Te)(HgCl_2)$.

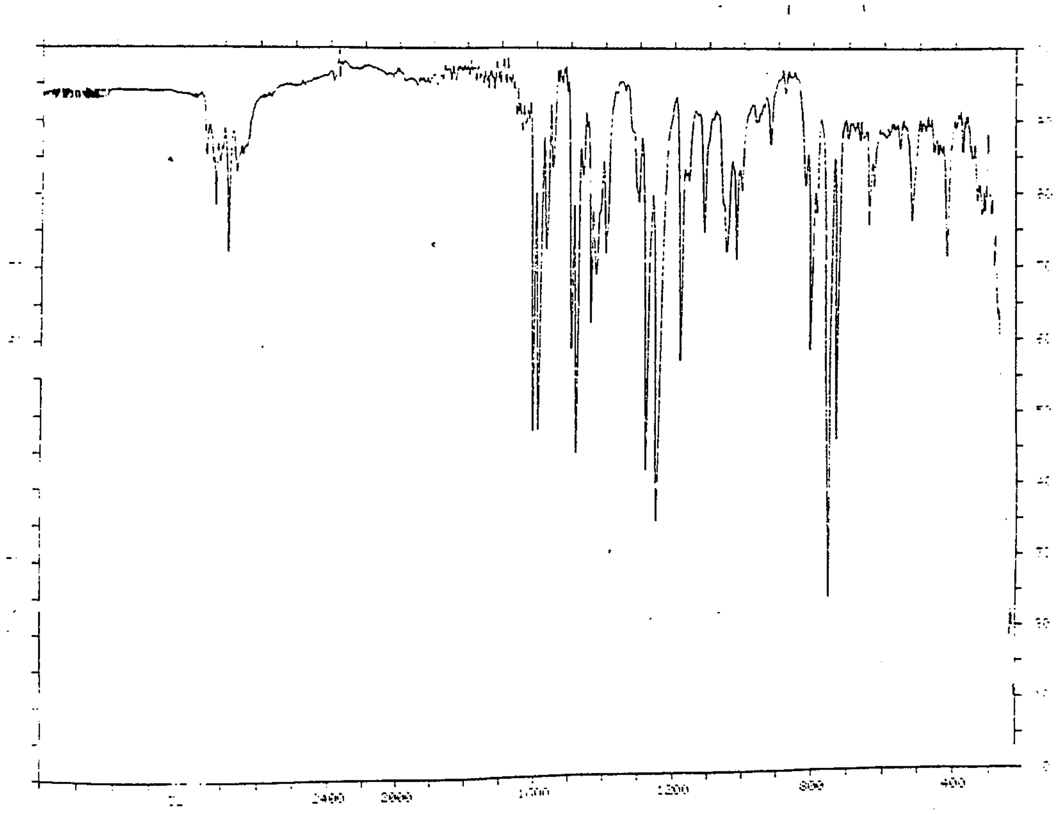


Fig 3.3: I.R. Spectrum of $(R^1HgCl).2(RTeCl)$.

since we expect when R^1HgCl is co-ordinated to RTeCl donation of electrons from tellurium to mercury would affect the degree of positive charge at the mercury atom, and thus Hg-Cl bond strength. The i.r spectrum for the yellow complex also showed two bands at 283 and 238cm^{-1}, which may be assigned to either υ(Te-C) or υ(Te-Cl). If compared with the i.r. spectrum of the ligand and white mercury complex (I), it is clear that the band at 283cm^{-1} which is not seen on the spectrum of the ligand or the white complex (I), could be attributed to υ(Te-Cl), and the band at 238cm^{-1} which is present in both the ligand (230cm^{-1}) and the white complex (I) (244cm^{-1}) could be assigned to υ(Te-C). The low frequency i.r spectra of isotopically pure ^{126}Te- and ^{130}Te-$(C_6H_5)_2TeX_2$(X = Cl,Br) have been investigated by Dance and McWhinnie,(71) and found that bands at 270 and 245cm^{-1} underwent shifts and were therefore due to υ(Te-C).

It is significant to note in the region of 1600cm^{-1}, various peaks are clearly resolved in the yellow complex (II), unlike that in the white complex (I) or free ligand. The structural change of the ligand from RR^1Te to RTeCl and R^1HgCl in the yellow compound appears to be responsible for higher resolution of peaks in the region mentioned above.

3.3.2 N.M.R. Spectroscopy

Table 3.2 contains ^{1}H NMR data of the ligand (RR^1Te), RTeBr and the mercury complexes. The ^{1}H NMR spectrum of RTeBr was assigned according to the literature.(64) This spectrum was found useful in assignment of other compounds as it distinguishes the chemical shifts of protons that belong to 2(2-pyridyl)phenyl and that of p-ethoxyphenyl group. The ^{1}H NMR spectrum of the yellow mercury complex (II) (Fig 3.4) was the most informative. It showed a clearly resolved spectrum consisting of triplets, doublets and a quartet unlike in the free ligand where various doublets and triplets do overlap in the aromatic region (Fig 3.5).

In the free ligand, the aromatic protons of p-ethoxyphenyl ring shows a pair of doublets at 6.85 and 7.85 ppm which are assigned to protons attached to C14 and C13 respectively. (C14 is the proton attached to the numbered carbon atom). The assignment is in good agreement with the values found in the literature.(66) The chemical shifts for these doublets in the yellow complex (II) are shifted to 6.95 and 7.18 ppm respectively. It is evident that the ortho-protons of the p-ethoxyphenyl group which showed a doublet at 7.85 ppm in the free ligand have been shifted to a higher field, 7.18 ppm. The shielding effect of the ortho-protons in the yellow complex (II) as compared to the ligand could only be explained to the increase in electropositive character on the

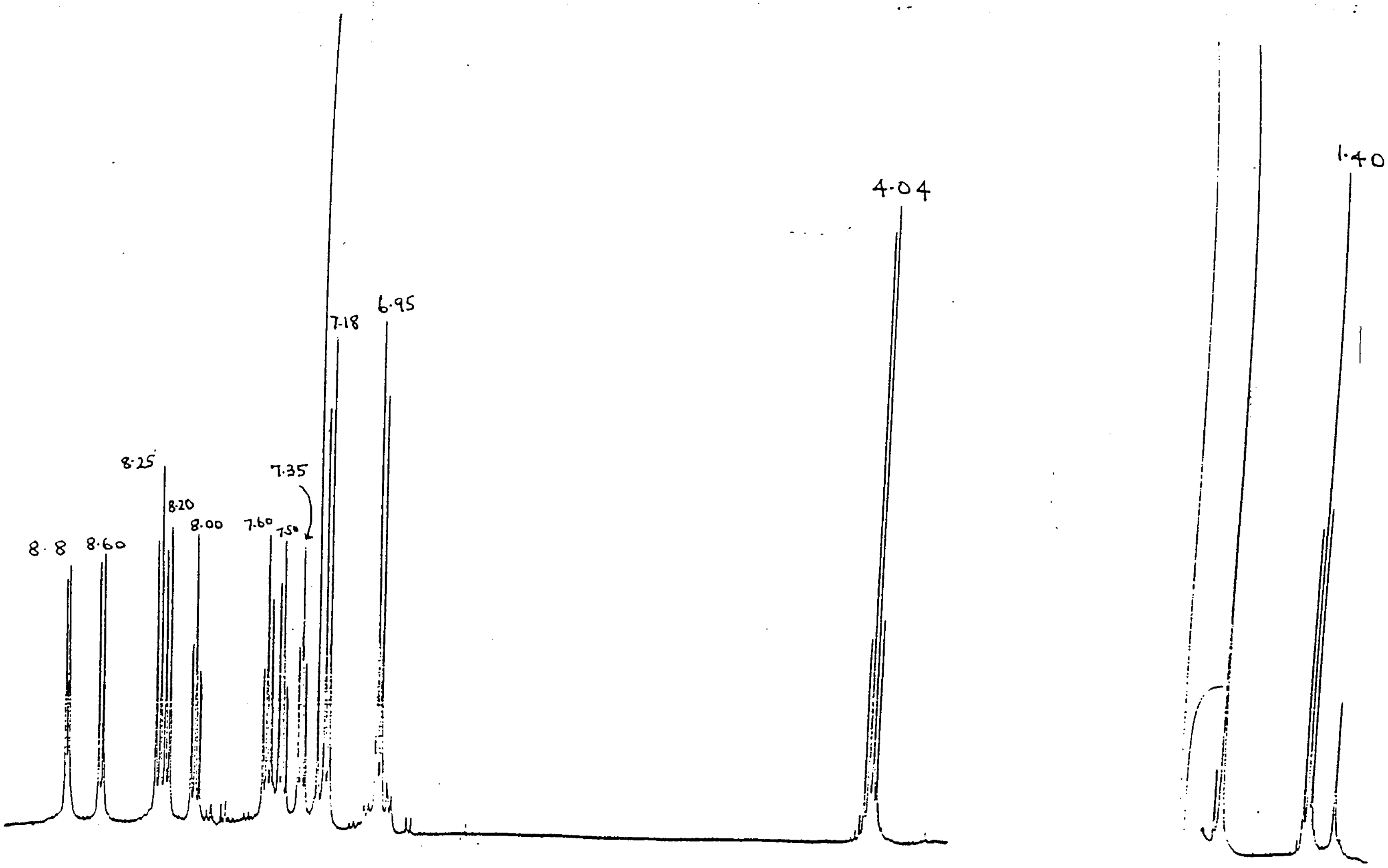


Fig 3.4: ^{1}H NMR spectrum of (R^1HgCl).2(RTeCl).

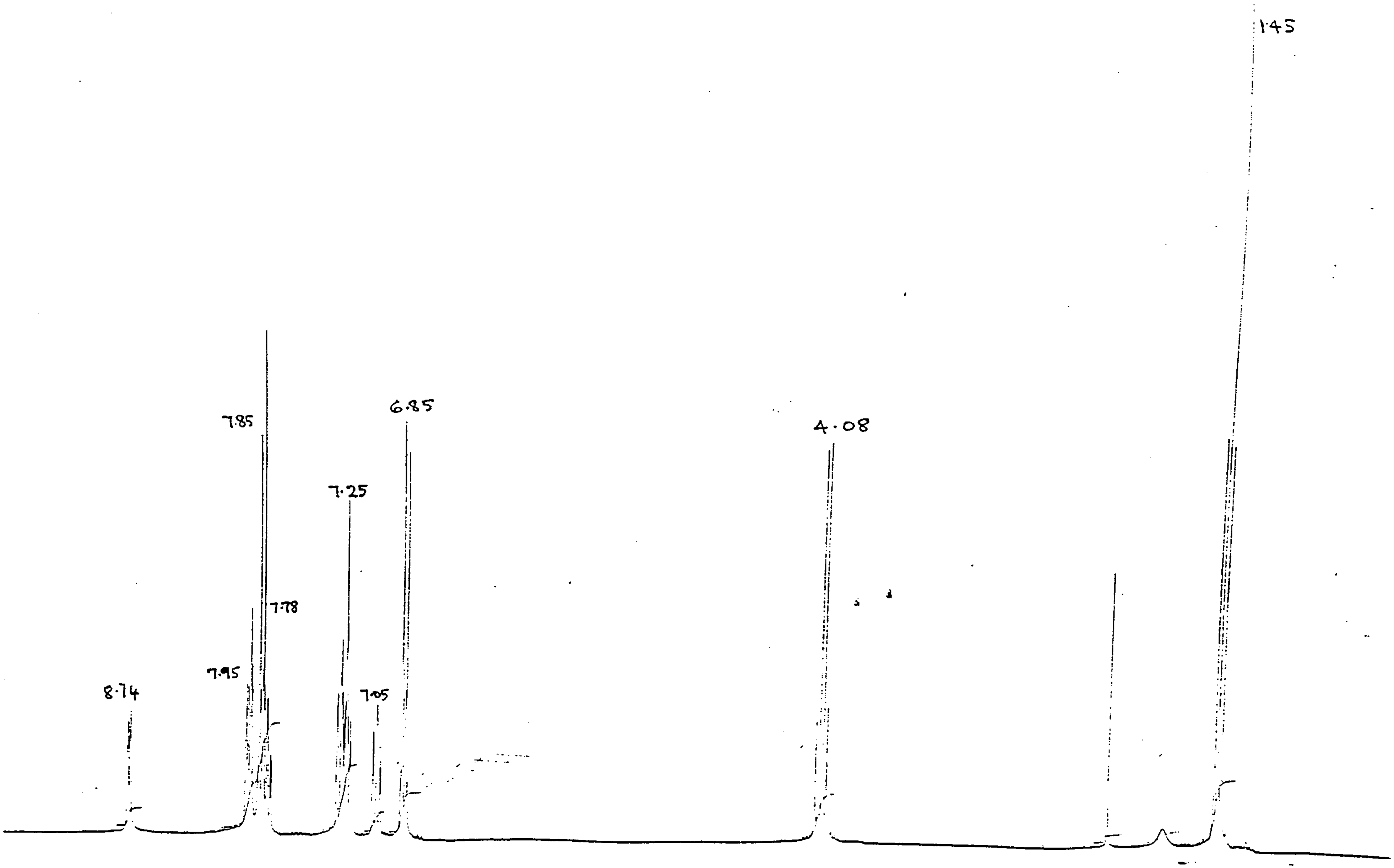


Fig 3.5: ^{1}H NMR spectrum of ligand (RR^{1}Te).

atom attached to C12. This could be attributed to the redistribution of RR^1 between tellurium and mercury, i.e. the migration of p-ethoxyphenyl group from tellurium to mercury. Mercury being more electropositive than tellurium causes the ortho-protons to be shifted to a higher field as compared to the ligand. The ^1H NMR spectrum of the white mercury complex (I) in dmso-D_6 was similar to that of the free ligand in $CDCl_3$, however on standing a second set of resonances developed which was identical to that of the yellow mercury complex (II) in the same solvent (Fig 3.6). The ratio of the intergrals of the R and R^1 was found to be 1.87 which is in good agreement with the value of 1.77 calculated from the formula $R^1HgCl\ (RTeCl)_2$ thus supporting the migration of R^1 (p-ethoxyphenyl) group from tellurium to mercury.

The ^{13}C NMR spectra (Table 3.3) of both mercury complexes (I) and (II) (Fig 3.7) were assigned following the literature(72,73,74) and by comparison with that of 2-(2-pyridyl)phenyltellurium(II) bromide and the ligand.

The quartenary carbon atoms showed signals of low intensities because of their long relaxation times. This helped the assignments of the spectra. In the white and yellow mercury complexes, all resonances of carbon atoms have been observed except that of C12. This may be probably due to a very low intensity because of a long relaxation time. The ^{13}C NMR spectrum of the ligand shows a signal at 141.3 ppm assignable

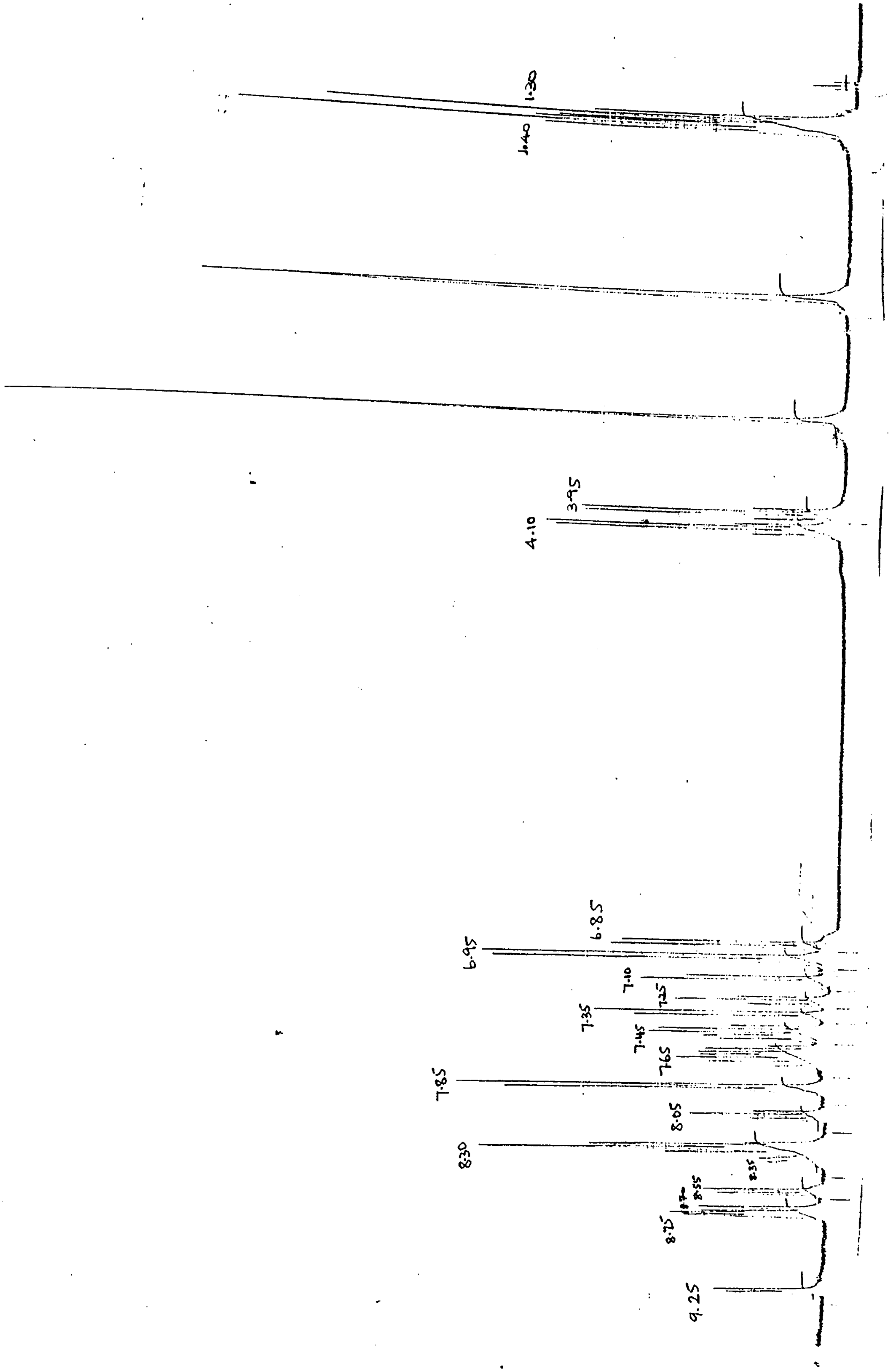


Fig 3.6: ^{1}H NMR spectrum of $(RR^1Te).(HgCl_2)$.

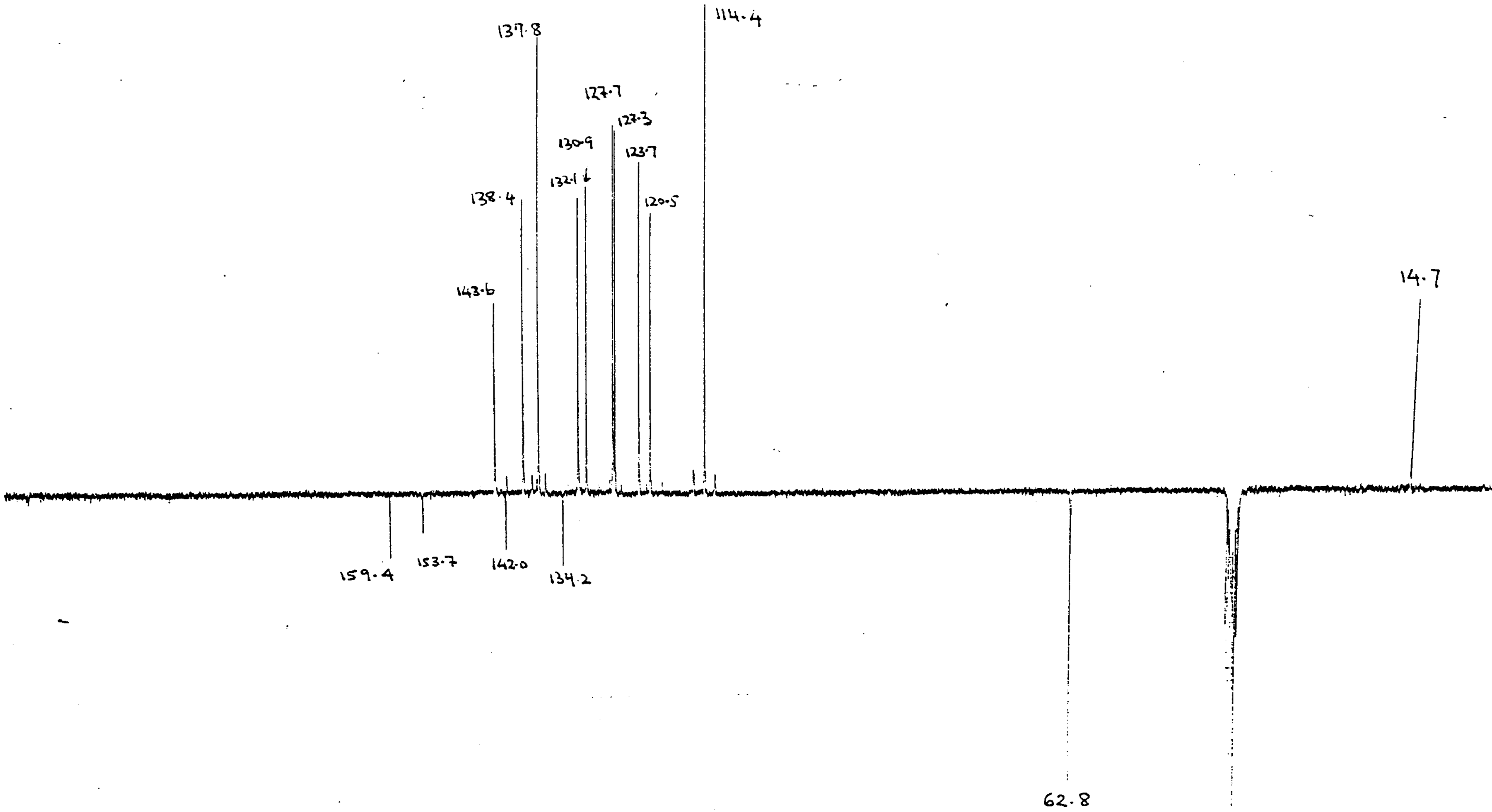


Fig 3.7: $^{13}C[^{1}H]$ NMR spectrum of (RHgCl).2(RTeCl).

to C13, which shifted to 137.8 ppm in the yellow mercury complex(II). A 4ppm high field shift of C13 relative to the ligand supports further the argument put earlier of the shielding effect of mercury atom as compared to tellurium atom when migration of p-ethoxyphenyl group from tellurium to mercury occurred.

The ^{125}Te NMR spectra of the ligand, 2-(pyridyl)phenyltellurium(II) bromide, and the mercury complexes were recorded in $CDCl_3$ and dmso-D_6 (Table 3.4)

The ^{125}Te NMR spectrum of the yellow complex (II) in $CDCl_3$ (Fig 3.8) showed a single resonance at 868.9 ppm (vs (p-$EtOC_6H_4)_2Te_2$).

This chemical shift is equivalent to 1323.9 ppm (vs Me_2Te), since ^{125}Te chemical shift of (p-$EtOC_6H_4)_2Te_2$ is 455 ppm (relative to Me_2Te). This chemical shift is at lower field compared to the ^{125}Te chemical shift of the unco-ordinated ligand in $CDCl_3$ ($\delta = 649.1$ ppm (vs Me_2Te)). A downfield shift is expected upon co-ordination of organotellurium(II) ligands to metal ions, which reflects deshielding of the tellurium atom as reported.(14a,21) The figure recorded for the yellow complex(II) is well outside the range normally associated with tellurides(75), but one well within the range associated with the related phenylazophenyl - C, N tellurium(II) halides, e.g. $(C_{12}H_9N_2)TeCl$, $\delta = 1486.5$ ppm (vs Me_2Te

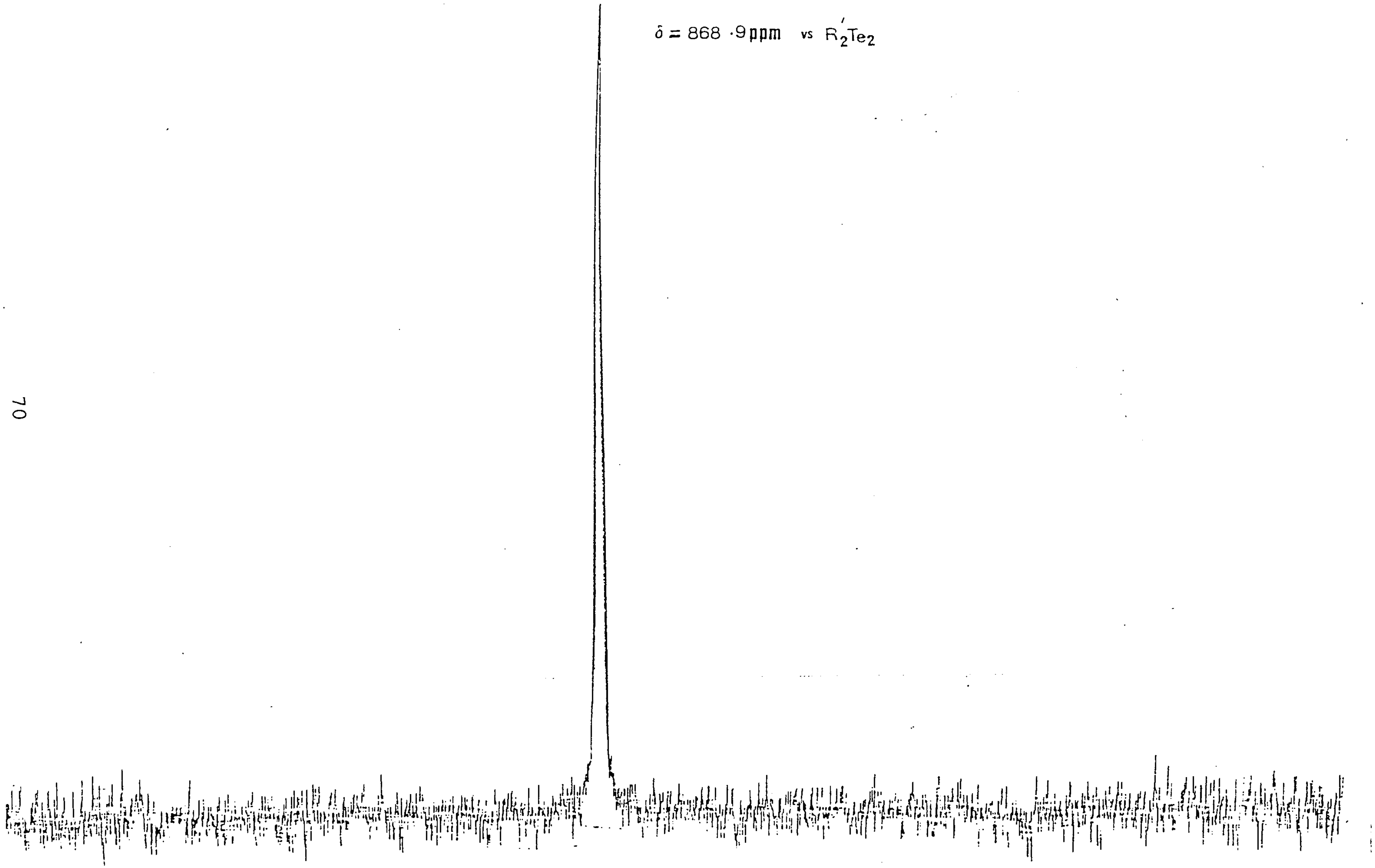


Fig 3.8: $^{125}Te[^1H]$ NMR spectrum of $(R^1HgCl).2(RTeCl)$.

in $CDCl_3$)(76). Sample of 2-(2-pyridyl)phenyl tellurium(II) bromide measured in this work (dmso-D_6, vs Me_2Te) gave δ= 1297 ppm. The only explanation of the drastic low energy shift in the yellow mercury complex(II) relative to the ligand is the structural change in the free ligand leading to the redistribution of R, R^1 and Cl between tellurium and mercury indicating that RR^1Te has been changed to RTeCl and that R^1 has migrated to mercury forming R^1HgCl; RTeCl may then co-ordinate to R^1HgCl. A solution of the product in $CDCl_3$ formed by reacting R^1HgCl and RTeBr (eq. 3.3) gave a ^{125}Te resonance at 1306 ppm. The shift ($\Delta\delta = \delta$(complex) - δ_{ligand} (RTeBr) is 9 ppm. This shows that the ^{125}Te chemical shift of the complex $(R^1HgCl)(RTeBr)_2$ is not significantly different from that of the ligand (RTeBr), though donation of electrons from tellurium to mercury in the adduct formation might be expected to cause deshielding of the tellurium atom. This may be either because of back donation of $d\pi$ electrons from mercury to tellurium or to weak bonding between the two atoms. The ^{125}Te NMR spectrum of the white mercury complex showed a single resonance at 641.5 ppm (vs Me_2Te) close to that of the free ligand at 649.1 ppm in $CDCl_3$.

Indeed the small difference in chemical shift is almost certainly a solvent effect and not a co-ordination shift, since co-ordination shifts are generally much greater (around

50 ppm) and in the opposite direction(21) thus the strongly co-ordinating dmso-D_6 has displaced RR^1Te from the co-ordination sphere of mercury.

The ^{199}Hg NMR measurement of the yellow complex was carried out in $CDCl_3$ solution (Fig 3.9). After three days accumulation, the spectrum consisted of a 1:2:1 triplet of 1:2:1 triplets with a central line at δ = 469.9 ppm. The relative intensities of the spectral components are inconsistent with coupling to ^{125}Te (7% abundance). It has been established that if a ^{199}Hg nucleus is coupled with two ^{125}Te ($I = \frac{1}{2}$, natural abundance, 7%) the observed ^{199}Hg spectrum should appear as one intense line with two doublets (relative intensity $\frac{1}{2} \times 7\%$) = 0.035. The distance between one doublet and the central peak is given as J (^{199}Hg - ^{125}Te). Therefore if coupling to ^{125}Te would occur, one would expect three signals of relative intensity 0.035:1:0.035 (0.07:2:0.07). The relative intensities of the ^{199}Hg spectra components of the yellow complex(II) is consistent with a major coupling to the equivalent <u>ortho</u>-protons of the p-ethoxyphenyl group (J_{HgH} = 370 Hz) and a minor coupling to the equivalent <u>meta</u>-protons (J_{HgH} = 50Hz) indicating a clear evidence of the transfer of p-ethoxyphenyl-group from tellurium to mercury. Even in the measurement of ^{125}Te NMR of the product $(R^1HgCl)(RTeBr)_2$ formed by reacting R^1HgCl and RTeBr, no Hg-Te coupling was

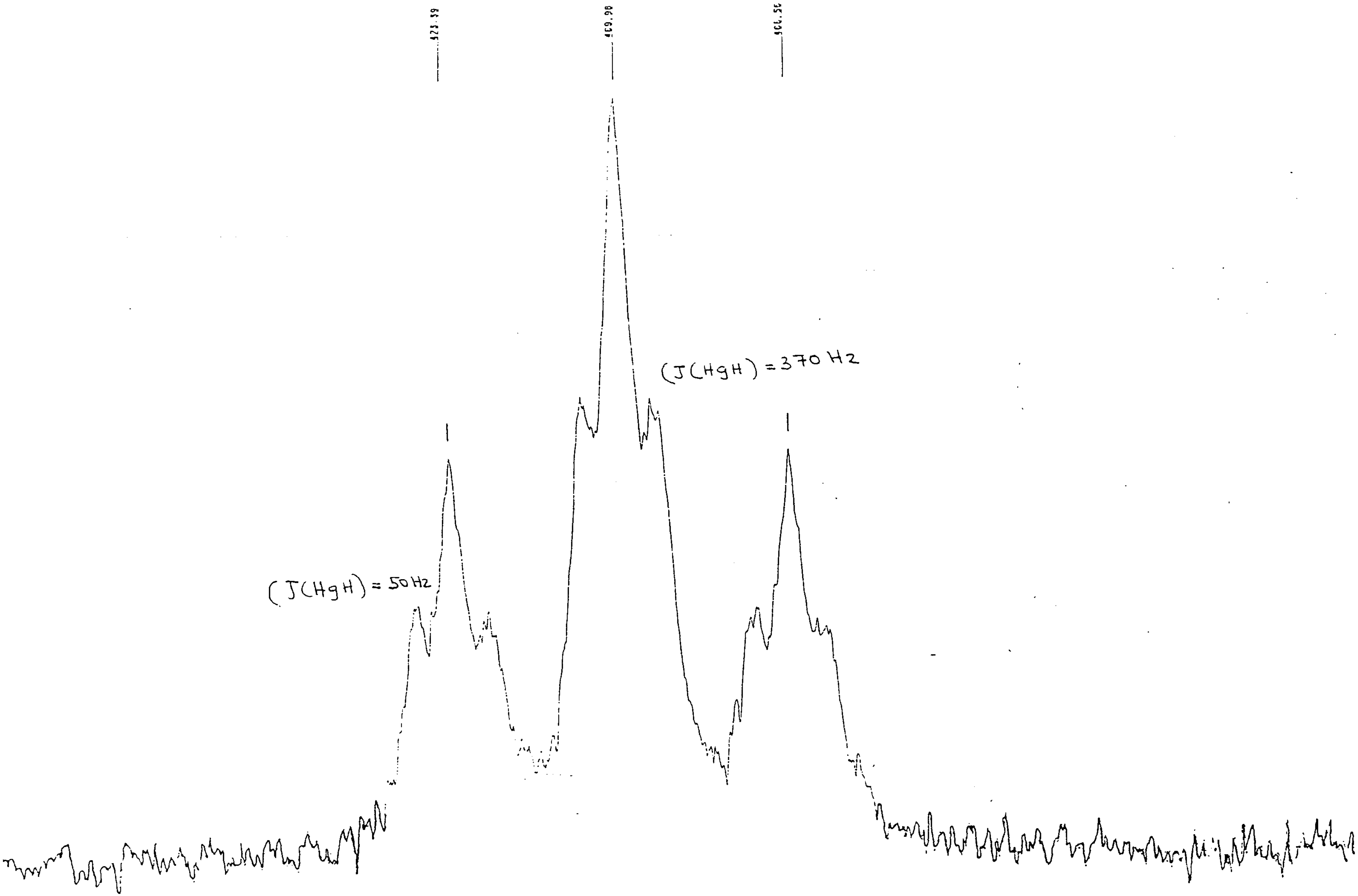


Fig 3.9: ^{199}Hg NMR spectrum of $(R^1HgCl).2(RTeCl)$.

observed implying that any interaction between the components in solution must be at best weak.

The electron impact mass spectrum of the yellow complex(II) was particularly interesting. All fragments were identified by computation of the isotopic patterns. The mass spectra of a number of organotellurium compounds have been described in the literature,(77,78) many compounds are sufficiently volatile at low probe temperatures and produce peaks due to the molecular ion and subsequent ion-decomposition products. However in complexes where ligand ions are often dominant, useful information can be obtained. The mass spectrum*a of the yellow complex revealed strong evidence for the presence of RTeCl in which the most abundant ions were RTe^+ and $RTeCl^+$ as shown from the following sequence:

$$\mathrm{RTeCl} + e^- \longrightarrow \mathrm{RTeCl}^+ + 2e$$

(m/e 100% = 319)

$$\Big\downarrow \; -\mathrm{Cl}$$

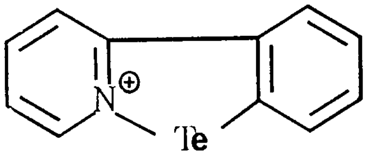
$$\mathrm{RTe}^+$$

(m/e 100% = 282)

N.B. *a = all values of m/e are based on ^{130}Te

Weak features were also noted for $R_2{}^1Te^+$ (m/e 100% = 372), RR^1Te (m/e 100% = 405), $[R_2Te_2Cl]^+$ (m/e 100% = 601) and $[R_2Te_2Cl_2]^+$ (m/e 100% = 636).

The dominance of the cluster at m/e = 282 (^{130}Te) may be due to the fact that the ion RTe^+ is isoelectronic with dibenzotellurophene, a stable known molecule as shown in the structure (i).

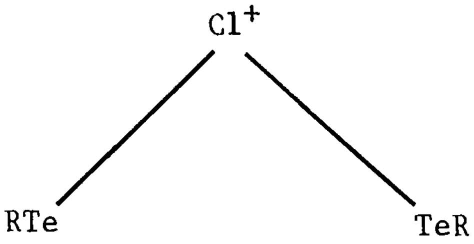


(i)

However, the mass spectrum of the yellow complex has not only revealed the presence of $RTeCl^+$, but also the dimer of the species is detectable in the gas phase. It has been noted that phenylazophenyl-C,N tellurium(II) chloride is a weak dimer in the solid state, and that the mass spectrum contained a significant cluster corresponding to $[(azo)HgClHg(azo)]^+$.(79)

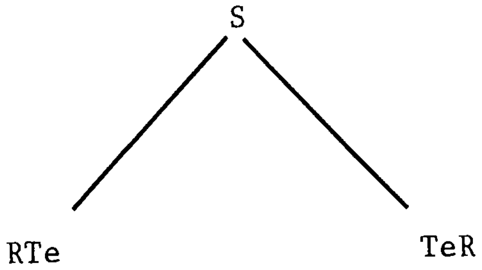
It is noted that "Cl^+" is isoelectronic with "S". Given the affinity of "soft" atoms such as mercury and tellurium for sulphur, such dimeric species should not be surprising.

e.g.



(ii)

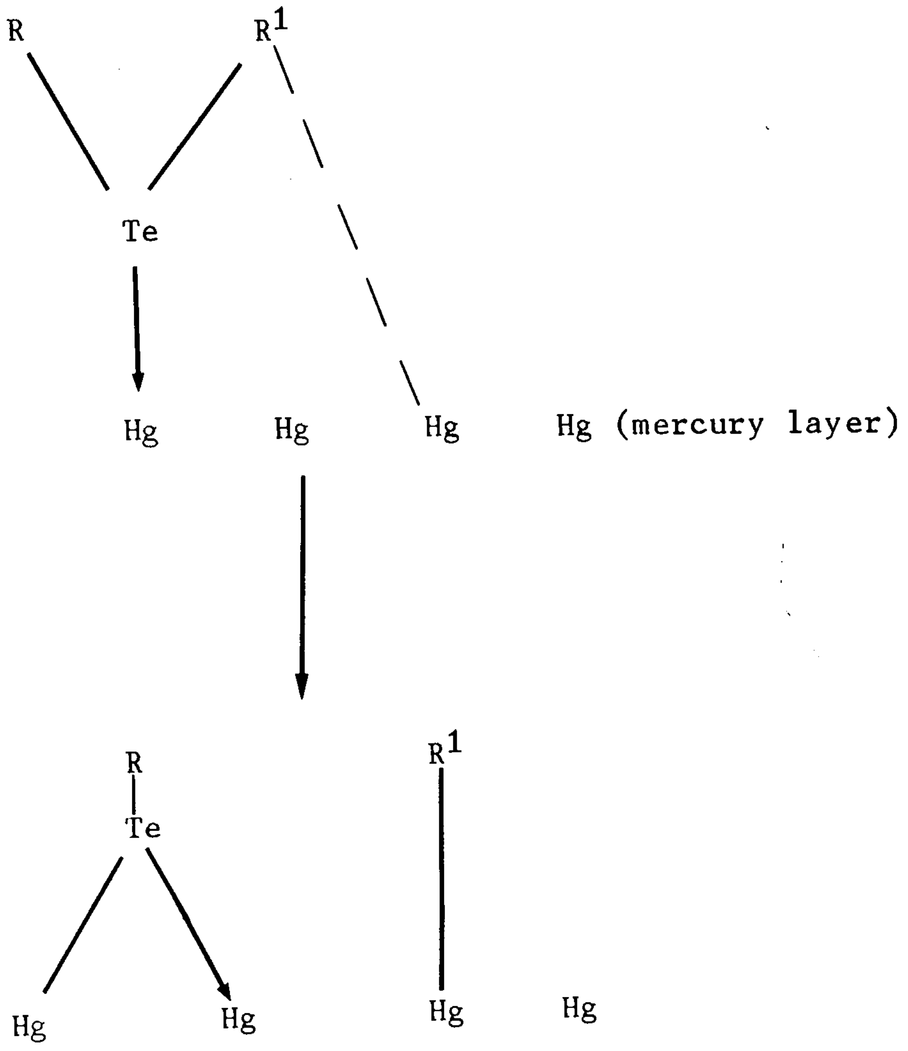
isoelectronic with



(iii)

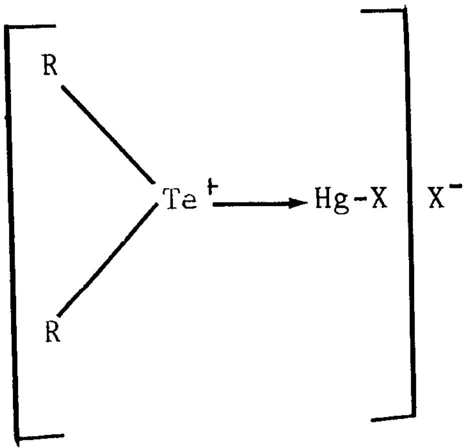
The migration of p-ethoxyphenyl group from tellurium to mercury (eq. 3.2) is quite a new phenomenon only observed recently in our laboratory. For many years organomercury compounds have shown to be effective trans-metallation reagents in the presence of inorganic tellurium compounds(80) thus the observed phenomenon is the opposite process and have been termed "reverse" trans-metallation. Since there is growing interest in developing precursors to semi-conductors consisting of Te-Hg, Te-Cd, and Te-Cd-Hg, the phenomenon may have significance in the context of the mechanistic aspects of the metal-organic vapour phase epitaxy (MOVPE) of telluride semi-conductors.(81)

For example, if a telluride were to co-ordinate to a mercury atom in a surface layer during an MOVPE experiment, an organic group might migrate from tellurium to mercury thus producing a thermally labile bond, as shown below (iv):

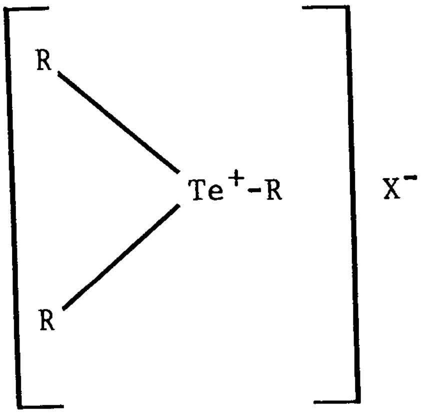


(iv)

^{125}Te Mössbauer studies have shown that tellurides assume an electronic environment not dissimilar to that in a telluronium salt when co-ordinated to "soft" metal centres.(53) McWhinnie et al(82) have suggested that, according to Mössbauer data and in view of the apparent presence of R_2Te^+ groups within complexes, the tellurium mercury complexes can be represented as shown below (v) similar to the telluronium salt (vi).



(v)



(vi)

Since it is known that triorganotelluronium salts are often labile with respect to the reductive elimination of an organic halide(83) (eq. 3.4),

$$Ph_2(CH_3)TeX \longrightarrow Ph_2Te + CH_3X \qquad \text{(eq. 3.4)}$$

it is reasonable, therefore to suggest that if lability is a characteristic of the salts, it might be observed in the complex too, due to the similarity in electronic environment of tellurium in the two cases. In view of the potential relevance of this observation to MOVPE status, it was desirable to explore the generality of "reverse" <u>trans</u>-metallation.

3.3.3 The Crystal and Molecular structure of mercury complex, $2(RTeCl).R^1HgCl$* [R = 2-(2-pyridyl)phenyl, R^1 = p-ethoxyphenyl]

Pertinent distances and angles are given in Tables 3.5 and 3.6 respectively.

The unit cell contains two discrete RTeCl molecules together with a R^1HgCl molecule (Fig. 3.10).

The major points of interest are first, the existence of RTeCl and R^1HgCl species, which confirms the correctness of the spectroscopic data supporting the migration of a p-ethoxyphenyl group from tellurium to mercury. The second point of interest is the fact that there is no bond between the R^1HgCl and RTeCl molecules. Thus the absence of dative bond formation between these species leads to the preferred description of the formation of an inclusion complex.

In this complex, tellurium-carbon bond lengths 2.105 and 2.005A° are in good agreement with the sum of the Pauling(58)

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* X-ray data collection was done in co-operation with Dr D Povey and Dr B Howlin, Dept. of Chemistry, University of Surrey

single bond covalent radii of Te(1.37A^o) and sp^{2}hybridised carbon (0.77A^o) and with the values in the crystal structures of the analogous compounds R^{1}RTe (2.138A^o)(64) and RTe (dmdtc)(64)(2.111A^o) (where dmdtc = dimethyl dithiocarbamato)

The Te-N distances of 2.231A^o and 2.242A^o are longer than the sum of the covalent raddi (2.07A^o),(58) but shorter than that reported for RTeBr$_3$(2.244A^o)(64), RTe(dmdtc)(2.354A^o), and for RR^{1}Te(2695A^o)(64) indicating a stronger interaction in this case. The interaction between Te and pyridyl nitrogen atom holds the organic ligand (RTeCl) in an essentially planar geometry.

The Hg-C distance of 2.044A^o is shorter by some 0.2A^o than the sum of the Pauling(58) single bond covalent radii of Hg(1.50A^o) and sp^2 hybridised carbon (0.74A^o) and as compared with the values in the cyrstal structures of analogous compounds, Ph$_2$Hg(dmp)$_2$ [dmp = 1,10-phenanthroline, 2,9-dimethyl-1, 10-phenanthroline], and Ph$_2$Hg(tmp)$_2$ [tmp = 2, 4,7,9-tetramethyl 1-1, 10-phenanthroline] which lie in the range 2.10-2.13A^o.(84)

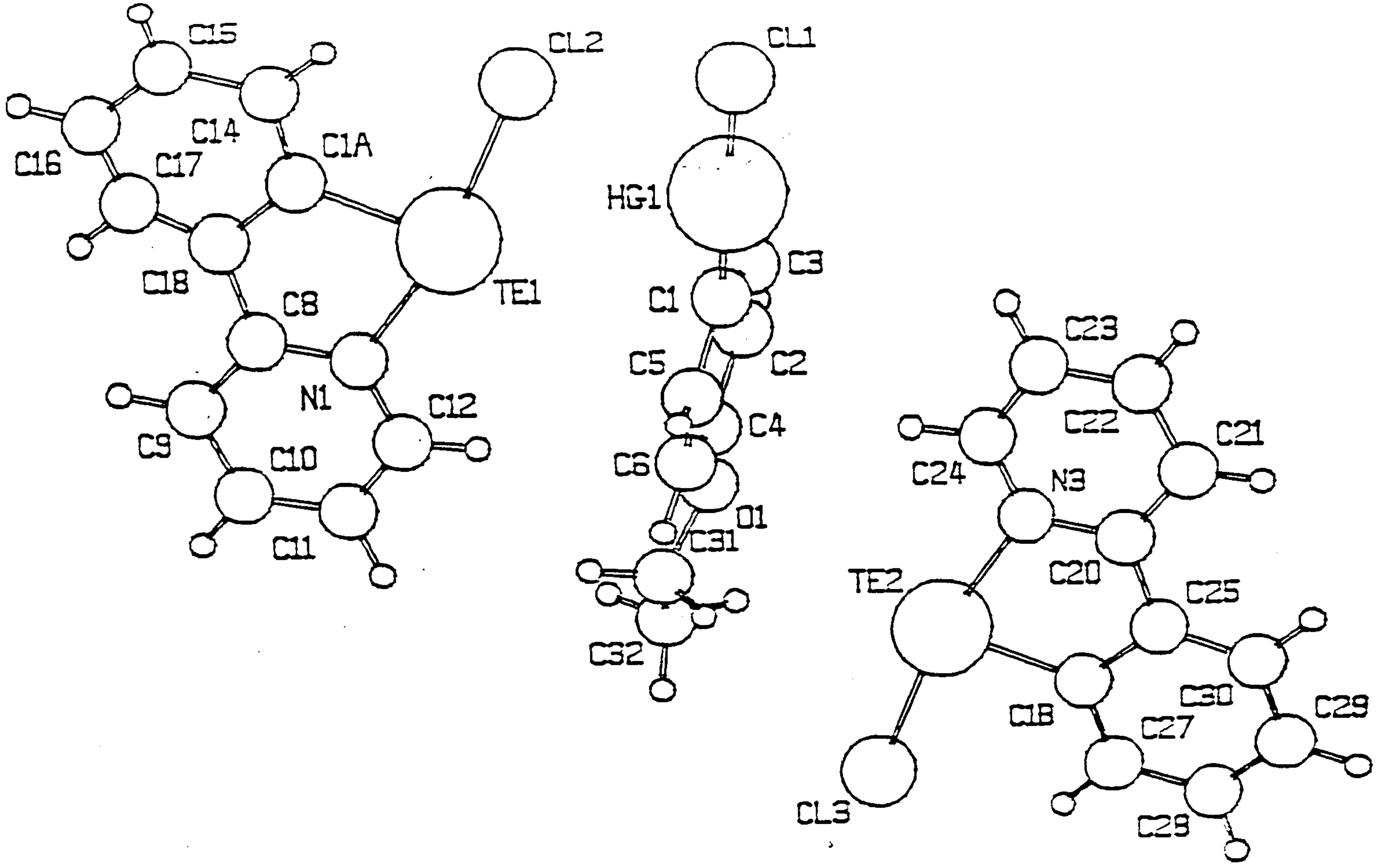


Fig 3.10: The molecular structure of $(R^1HgCl).2(RTeCl)$.

Atom1	Atom2	Distance	Atom1	Atom2	Distance	Atom1	Atom2	Distance
HG1	CL1	2.328(4)	C1B	C27	1.38(2)	C14	C15	1.44(2)
HG1	C1	2.044(14)	C1	C3	1.41(2)	C15	C16	1.39(2)
TE1	CL2	2.559(4)	C1	C5	1.36(2)	C16	C17	1.26(2)
TE1	N1	2.231(11)	C2	C3	1.35(2)	C17	C18	1.27(2)
TE1	C1A	2.105(14)	C2	C4	1.37(2)	C20	C21	1.40(2)
TE2	CL3	2.557(4)	C4	C6	1.39(2)	C20	C25	1.45(2)
TE2	N3	2.422(11)	C4	01	1.39(2)	C21	C22	1.40(3)
TE2	C1B	2.055(14)	C5	C6	1.36(2)	C22	C23	1.39(3)
N1	C8	1.34(2)	01	C31	1.40(2)	C23	C24	1.35(2)
N1	C12	1.31(2)	C31	C32	1.50(2)	C25	C30	1.38(2)
C1A	C14	1.38(2)	C8	C9	1.38(2)	C27	C28	1.39(2)
C1A	C18	1.41(2)	C8	C18	1.49(2)	C28	C29	1.36(2)
N3	C20	1.36(2)	C9	C10	1.39(2)	C29	C30	1.36(3)
N3	C24	1.29(2)	C10	C11	1.37(2)			
C1B	C25	1.45(2)	C11	C12	1.35(2)			

Table 3.5: Bond Distances (A^o)

Numbers in parenthesis are estimated standard deviations in the least significant digits.

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
CL1	HG1	C1	179.2(4)	C1	C5	C6	125.(2)	C8	C18	C17	129.(1)
CL2	TE1	N1	168.0(3)	C4	C6	C5	118.(2)	N3	C20	C21	118.(1)
CL2	TE1	C1A	92.1(4)	C4	O1	C31	118.(1)	N3	C20	C25	116.(1)
N1	TE1	C1A	76.0(5)	O1	C31	C32	108.(1)	C21	C20	C25	125.(1)
CL3	TE2	N3	168.8(3)	N1	C8	C9	120.(1)	C20	C21	C22	118.(2)
CL3	TE2	C1B	91.3(4)	N1	C8	C18	115.(1)	C21	C22	C23	121.(2)
N3	TE2	C1B	77.5(5)	C9	C8	C18	125.(1)	C22	C23	C24	117.(2)
C8	N1	C12	121.(1)	C8	C9	C10	117.(1)	N3	C24	C23	124.(1)
C14	C1A	C18	120.(1)	C9	C10	C11	121.(1)	C1B	C25	C20	116.(1)
C20	N3	C24	122.(1)	C10	C11	C12	118.(2)	C1B	C25	C30	118.(1)
C25	C1B	C27	117.(1)	N1	C12	C11	122.(1)	C20	C25	C30	126.(1)
C3	C1	C5	115.(1)	C1A	C14	C15	117.(1)	C1B	C27	C28	121.(1)
C3	C2	C4	120.(1)	C14	C15	C16	120.(2)	C27	C28	C29	122.(2)
C1	C3	C2	122.(1)	C15	C16	C17	113.(2)	C28	C29	C30	118.(1)
C2	C4	C6	120.(1)	C16	C17	C18	135.(1)	C25	C30	C29	124.(1)
C2	C4	O1	116.(1)	C1A	C18	C8	116.(1)				
C6	C4	O1	124.(1)	C1A	C18	C17	115.(1)				

Table 3.6: Bond Angles (°)

Numbers in parentheses are estimated standard deviations in the least significant digits.

CHAPTER FOUR

THE REACTIVITY OF 2-(2-PYRIDYL)PHENYL (P-ETHOXYPHENYL)TELLURIUM (II) TOWARDS COPPER (I) AND COPPER (II) HALIDES

4.1 INTRODUCTION.

Tellurium being a "soft" ligand atom readily forms complexes with copper (I), and many complexes which have been reported are either with simple monodentate or diorganyltelluride ligands. But only few complexes of copper (II) containing element are known: $CuCl_2.[(o-NH_2-C_6H_4)Te_2]$(85) and $Cu(ETB)_2.H_2O$(ETB= 2-(4-ethoxyphenyltelluro) benzoate)(86) are examples. This might be due to various reasons; among them is that Cu(II) ion is reduced to Cu(I) when reacted with tellurium ligands, and also Cu(II) ion shows little tendency to co-ordinate to such a soft ligand. However copper(II) complexes containing sulphur and selenium are well established: Bis(2-pyridylethyl)selenide forms complexes with copper (II) halides.(61) It is often the case that the presence of a nitrogen donor atom will increase the affinity of the ligands for "harder" acids. The crystal and molecular structure of copper (II) diethyl diselenocarbarmate [$Cu(dsec)_2$)] have been reported,(87). One cause of recent interest in the study of the co-ordination chemistry of organotellurium compounds is the fact that co-ordination may have a role in the mechanism of metal-organic vapour phase epitaxy (MOVPE) of telluride semi-conductors.(81)

In this chapter the reaction of 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II)(RR^1Te)with copper(I) both directly and produced in situ by reduction of copper (II) is described. This work can be considered as an extension of the work in chapter three to explore the generality of the behaviour of RR^1Te with other metal centres. In chapter three it was noted that labilisation of the p-ethoxyphenyl-group from tellurium to mercury occurred and the phenomenon was termed "reverse trans-metallation".

4.2 EXPERIMENTAL.

4.2.1. Synthesis of 2-(2-Pyridyl) phenyl (p-ethoxyphenyl)-tellurium(II), (RR^1Te).

This was done according to the literature method.(64)

4.2.2. Preparation of the complexes

Complex (1) (see table 4.1 for numbering scheme)

To a cold solution of RR^1Te (100mg, 0.0002mole) in ethanol ($10cm^3$) was added a solution of copper (I) chloride (23mg, 0.0002 mole) in a diethyl ether-acetonitrile (1:1 v/v) mixture ($10cm^3$) whilst passing argon. The contents of the flask were stirred at room temperature for 2h. The removal of excess solvent wih a flow of dry argon gave a pale yellow product which was filtered, washed with small amounts of ethanol or acetonitrile and dried in vacuo.

Complex (2)

To a solution of copper (I) chloride (23mg, 0.0002 mole) in an acetonitrile - ethanol mixture (1:1 v/v) ($10cm^3$) was added a solution of RR^1Te (100mg, 0.0002 mole) in ethanol ($10cm^3$). The reactants were refluxed for 1.5h when a green coloured solution was obtained, slow evaporation of which gave a green solid which was dried _in vacuo_.

Complex (3)

To a solution of copper (II) chloride (16mg, 0.00012 mole) in acetonitrile ($10cm^3$) was added a solution of RR^1Te (48mg, 0.00012 mole) in acetonitrile ($10cm^3$). The mixture was gently warmed following which the excess solvent was removed under a stream of dinitrogen to afford a white product which was filtered, carefully washed with acetonitrile and dried _in vacuo_.

Complex (4)

To a solution of copper (II) bromide (28mg, 0.00012 mole) in acetonitrile ($10cm^3$) was added a solution of RR^1Te (50mg, 0.00012 mile) in acetonitrile ($10cm^3$). The mixture was gently warmed under dinitrogen and a white compound separated out: The product was filtered, washed with acetonitrile and dried _in vacuo._

Complexes (5) and (6)

Ethanolic solutions ($10cm^3$) of copper (II) chloride (16mg, 0.00012 mole) and RR^1Te (48mg, 0.00012 mole) were mixed to give an initially colourless solution which, on refluxing for 2h, became yellowish-green. Slow evaporation gave a green product at the bottom of the container and a brown product on the walls: Mechanical separation followed by recrystallisation from ethanol gave green (5) and brown (6) complexes.

4.3 **RESULTS AND DISCUSSION.**

Generally the reaction of 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II) with copper(I) and copper(II) halides under mild conditions produces copper (I) complexes. However under forcing conditions copper (II) complexes are formed. Table 4.1 presents analytical data for the complexes (1) - (6), together with ESR data where appropriate. Table 4.2 and 4.3 show ^1H NMR and ^{13}C NMR data for copper(I) complexes with those of the free ligand, (RR^1Te) and the recently reported, $R^1HgCl.2RTeCl$ (Chapter three)respectively. The yellow complex (I) has limited stability in air, particularly when in solution. The CH_3CN content required to give a good analytical fit is confirmed by IR analysis.
($\upsilon(C\equiv N) = 2250$ cm^{-1})

No.	Formula	C	H	N	MP(^oC)	g
(1)	$Cu_3Cl_3(RR^1Te)_2$ (0.5 MeCN)	41.2	3.04	3.07	120-8(d)	-
	(yellow)	(41.7)	(3.16)	(3.11)		
(2)	$Cu_2Cl(RR^1Te)$(0.5EtOH)	40.8	3.50	2.45	170-2(d)	2.06
	(green)	(40.8)	(3.40)	(2.38)		
(3)	$CuCl(RR^1Te)$	47.5	3.47	2.86	240-2(d)	-
	(white)	(45.5)	(3.39)	(2.79)		
(4)	$CuBr(RR^1Te)$	40.3	3.03	2.94	203-5	-
	(white)	(41.7)	(3.11)	(2.56)		
(5)	$Cu_3Cl_3(RR^1Te)(H_2O)$	31.6	2.69	1.94	>270	2.15
	(yellow-green)	(31.8)	(2.77)	(1.95)		
(6)	$Cu_2Cl_2(RR^1Te)$(0.5 MeCN)	38.4	3.09	2.22	190-2(d)	2.15
	(brown)	(38.5)	(3.20)	(2.24)		

RR^1Te =2-(2-pyridyl) phenyl(p-ethoxyphenyl)tellurium(II)

Table 4.1 Analytical and ESR data for Copper Complexes

Compound (solvent)	δ Values (ppm, vs TMS)*			
RR^1Te	1.45 (t,C17)	4.08 (q,C16)	6.85 (d,C14)	
($CDCl_3$)	7.05 (t,C3)	7.25 (m,C4,C5,C8)	7.78 (d,C2)	
	7.85(d, C13)	7.95 (2t,C9,C10)	8.74 (d,C11)	
(1) $Cu_3Cl_3(RR^1Te)_2$	1.40 (t,C17)	4.00 (q,C16)	6.75 (d,C14)	
($CDCl_3$)	7.05 (t,C4)		7.25 (m,C2,C3,C9)	
	7.45 (d,C5)	7.55 (d,C8)	7.65 (d,C13)	
	7.70 (t,C10)	8.80 (d,C11)		
(3) $CuCl(RR^1Te)$	1.25 (t,C17)	3.95 (q,C16)	6.95 (d,C14)	
(dmso-D_6)		7.65 (d,C13)	7.85 (t,C3)	8.00 (t,C9)
	8.25 (t,C9)	8.35 (d,C5)	8.45 (t,C10)	8.55 (d,C8)
	8.65 (m,C4,C5,C8)	8.95 (d,C2)	9.55 (d,C11)	
(4) $CuBr(RR^1Te)$	1.25 (t,C17)	3.95 (q,C16)	6.95 (d,C14)	
(dmso -D_6)	7.55 (d)	7.65 (d,C13)	7.90 (t,C3)	8.05 (t,C9)
	8.25 (t,C9)	8.35 (d.C5)	8.50 (t,C10)	8.44 (d,C8)
	8.65 (m,C4,C5,C8)	8.75 (d,C2)	9.00 (d,C2)	9.45 (d,C11)
$(R^1HgCl)(RTeCl)$[a]	1.40 (t,C17)	4.04 (q,C16)	6.95 (d,C14)	
($CDCl_3$)	7.18 (d,C13)	7.35 (t,C3)	7.50 (t,C4)	
	7.60 (t,C10)	8.00 (t,C9)	8.20 (d,C5)	
	8.25 (d,C8)	8.60 (d,C2)	8.8 (d,C11)	

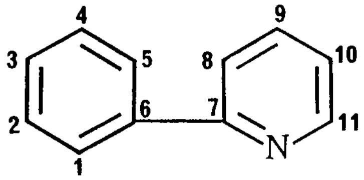
a see Chapter three

* see Table 4.3 for atom numbering.

Table 4.2 ^1H NMR data for Copper(I) complexes.

Compound (solvent)	Chemical Shift Values (δ)					
	C1 C7 C13	C2 C8 C14	C3 C9 C15	C4 C10 C16	C5 C11 C17	C6 C12
RR^{1}Te	126.30	-	128.10	-	126.30	138.80
(CDCl$_3$)	156.70	121.50	136.20	119.90	149.10	109.70
	141.30	115.70	159.70	63.20	14.70	
(3) CuClCRR^{1}Te	-	132.17-	128.19	132.17	126.30	133.60
(dmso-D$_6$)		133.15(m)		-133.15(m)		
	152.55	121.11	132.17	132.17-	145.57	-
			133.15(m)	133.15(m)		
	143.94	115.91	160.66	63.40	14.44	
(4) CuBr(RR^{1}Te)	126.48	(132.17-133.15m)	128.18	123.17-	126.51	134.32
(dmso-D$_6$)	151.95	122.53	132.17-	132.17	145.20	126.54
			(133.15)m	133.15(m)		
	144.02	115.96	160.70	63.42	14.35	
(R^{1}HgCl(RTeCl)$_2$^{a}	134.24	138.45	123.88	130.97	127.47	142.02
(CDCl$_3$)	153.72	127.77	139.88	120.47	143.64	-
	137.81	114.42	158.37	62.76	14.88	

[a] see Chapter three



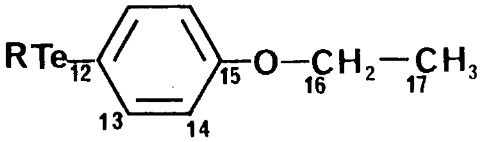


Table 4.3 ^{13}C NMR data (ppm) for Copper(I) Complexes.

The infra-red spectra of all copper complexes were measured in KBr disc and nujol mulls in CsI supports. The i.r. data support the presence of both R and R^1 groups, (Fig. 4.1-4.3). The infra-red spectrum of complex (5) shows a broad band at 3426 cm^{-1}, characteristic of OH stretching. The υ(C=N) of the ligand has been assigned at 1582, and 1562 cm^{-1} and on complexing copper atom there is a positive shift ca.20cm^{-1} in υ(C=N). Normally, if there were to be co-ordination through nitrogen, it would result in negative shift in υ(C=N).(88) It has been noted by Al-Salim(23) that the change in the ligand υ(C=N) frequency of (Bu^nTe) C_6H_4CHN $(CH_2)_2$ $NCHC_6H_4(TeBu^n)$ on complexing mercury (II) is + 5cm^{-1}, the crystal structure of the complex showed the absence of N$\longrightarrow$Hg bonds in the present case it is implied that the very weak Te---N interaction in the co-ordinated ligand remained intact.

Therefore it is not unreasonable to conclude the same in the case of copper complexes that nitrogen atom of the 2-(2-pyridyl) phenyl is non-co-ordinating with copper atom.

The ^1H NMR spectra of compound (3) and (4) (in dmso-D_6) were similar, and show doubling of resonances compared with the spectrum of RR^1Te (Fig 4.4), which is consistent with some dissociation of the complexes in solution, a phenomenon expected of copper (I) complex in a co-ordinating solvent.

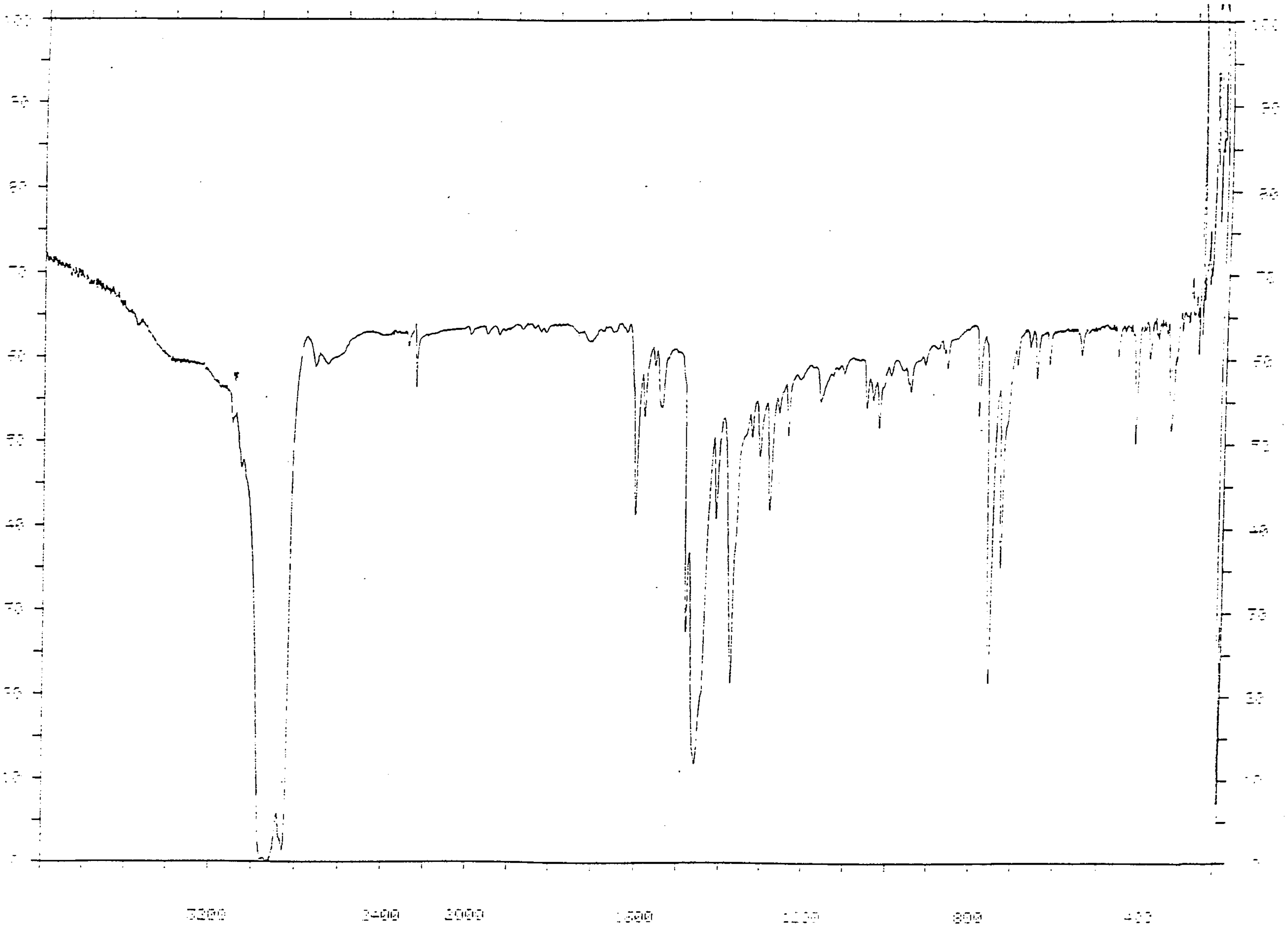


Fig 4.1: I.R. spectrum of complex (1).

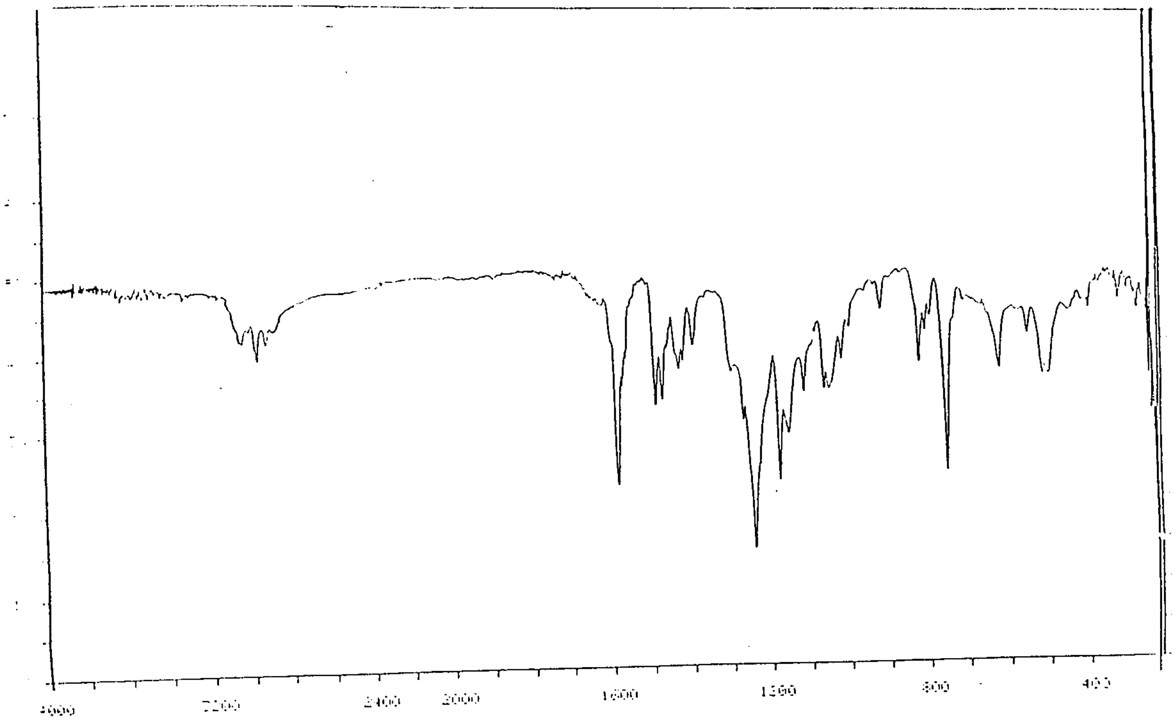


Fig 4.2: I.R. spectrum of complex (3).

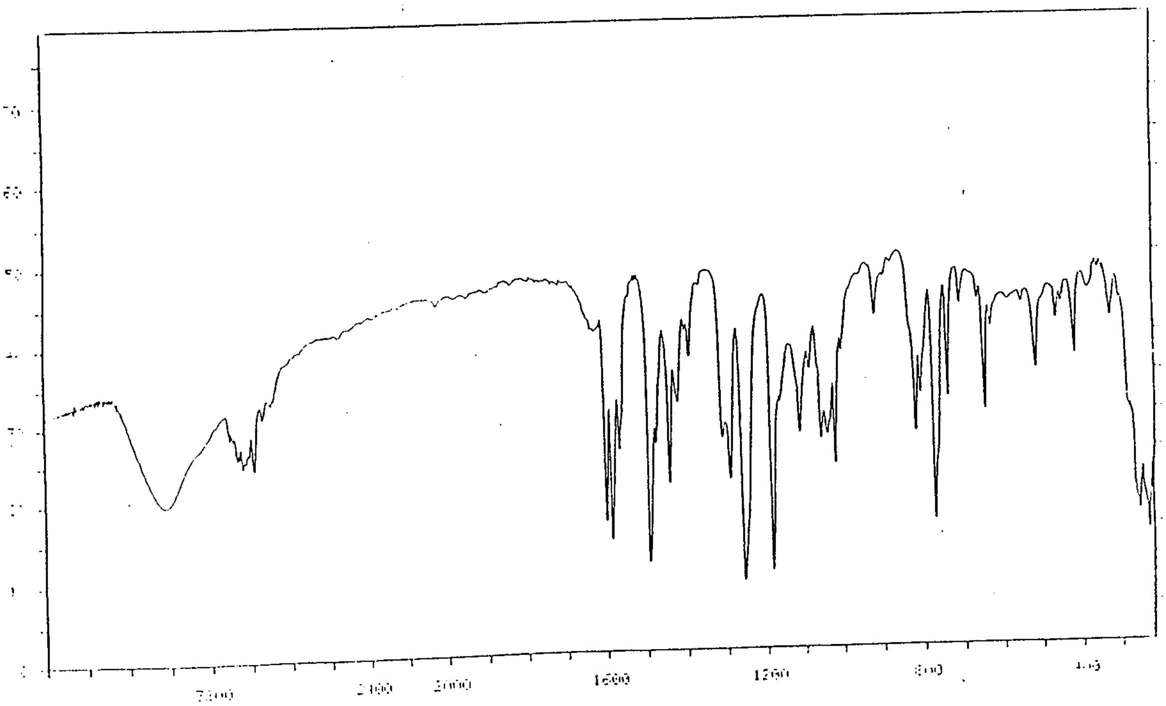


Fig 4.3: I.R. spectrum of complex (5).

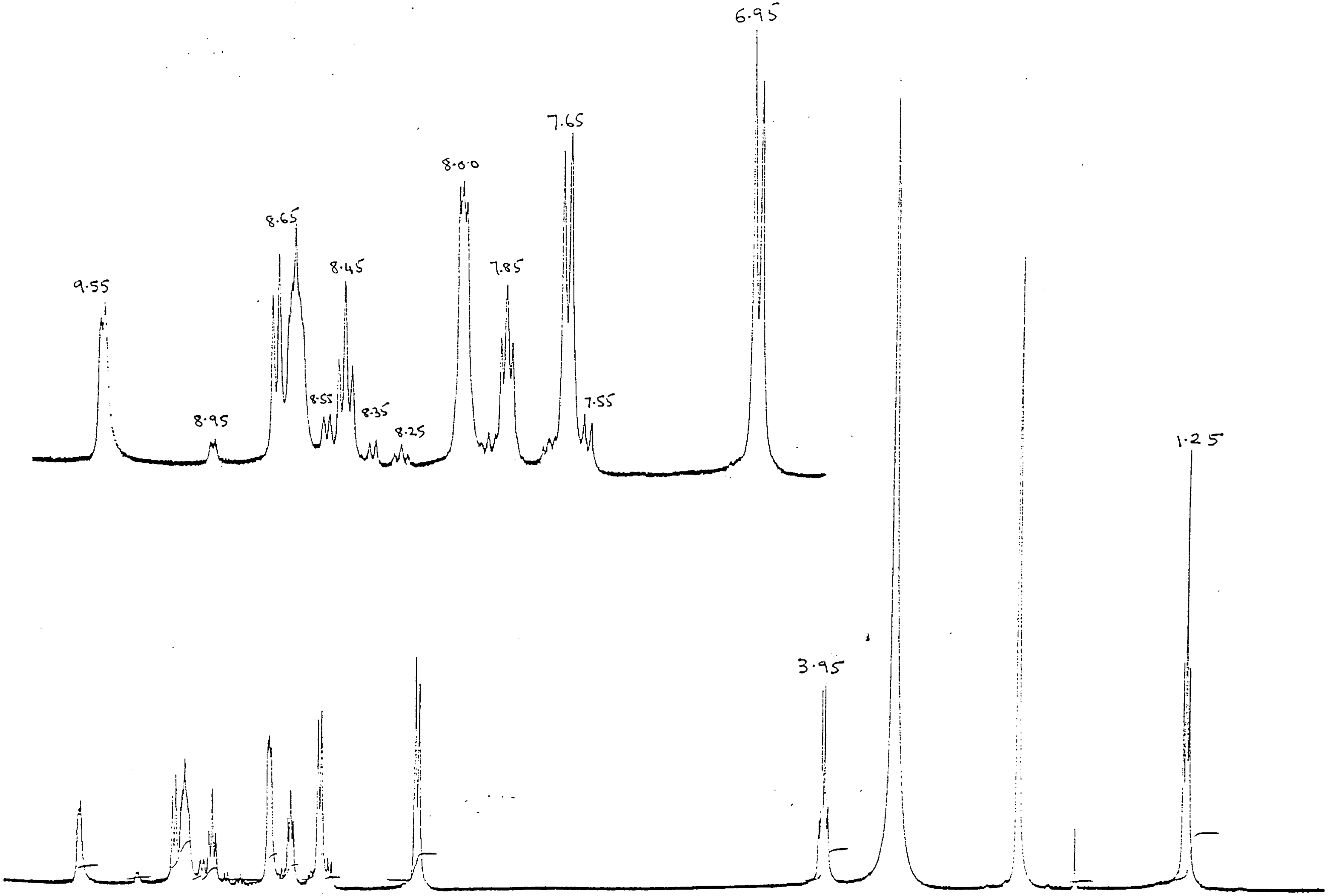


Fig 4.4: ^1H NMR spectrum of complex (3).

$$CuX.RR^1Te + dmso\text{-}D_6 = CuX.dmso - D_6 + RR^1Te \qquad \text{(eq. 4.1)}$$

The ^1H NMR spectrum of compound (**1**) (Fig 4.5) was well resolved and revealed similarity with that of $R^1HgCl.2RTeCl$ (Chapter three), and was different from that of the ligand (RR^1Te). Furthermore, the signal of the proton at C11 in the compound (**1**) (δ = 8.80ppm) is similar to that of the mercury compound (δ = 8.80ppm). It is known that the reaction of RR^1Te with $HgCl_2$ leads to a redistribution of organic groups between the metal centres and isolation of $R^1HgCl.2RTeCl$. The similarity of the ^1H NMR data and the colour of compound (**1**) and that of "mercury complex" (Chapter three) points to the following similar reactions.

$$CuCl + RR^1Te \longrightarrow R^1Cu + RTeCl \qquad \text{(eq.4.2)}$$

$$HgCl_2 + RR^1Te \longrightarrow R^1HgCl + RTeCl \qquad \text{(eq.4.3)}$$

The yellow colour of both the "mercury complex" and copper compound (**1**) being explained by the yellow colour of RTeCl. The compound (**1**) could therefore be formulated as $(R^1Cu)_2(RTeCl)_2(CuCl)$, suggesting labilisation of groups from tellurium to, particulary d^{10} ions may be general.

Thus a novel synthesis of organo copper (I) complexes is indicated; and could become the subject of further investigation. In the previous chapter it was noted that the compound $2RTeCl.R^1HgCl$ was effectively an inclusion compound.

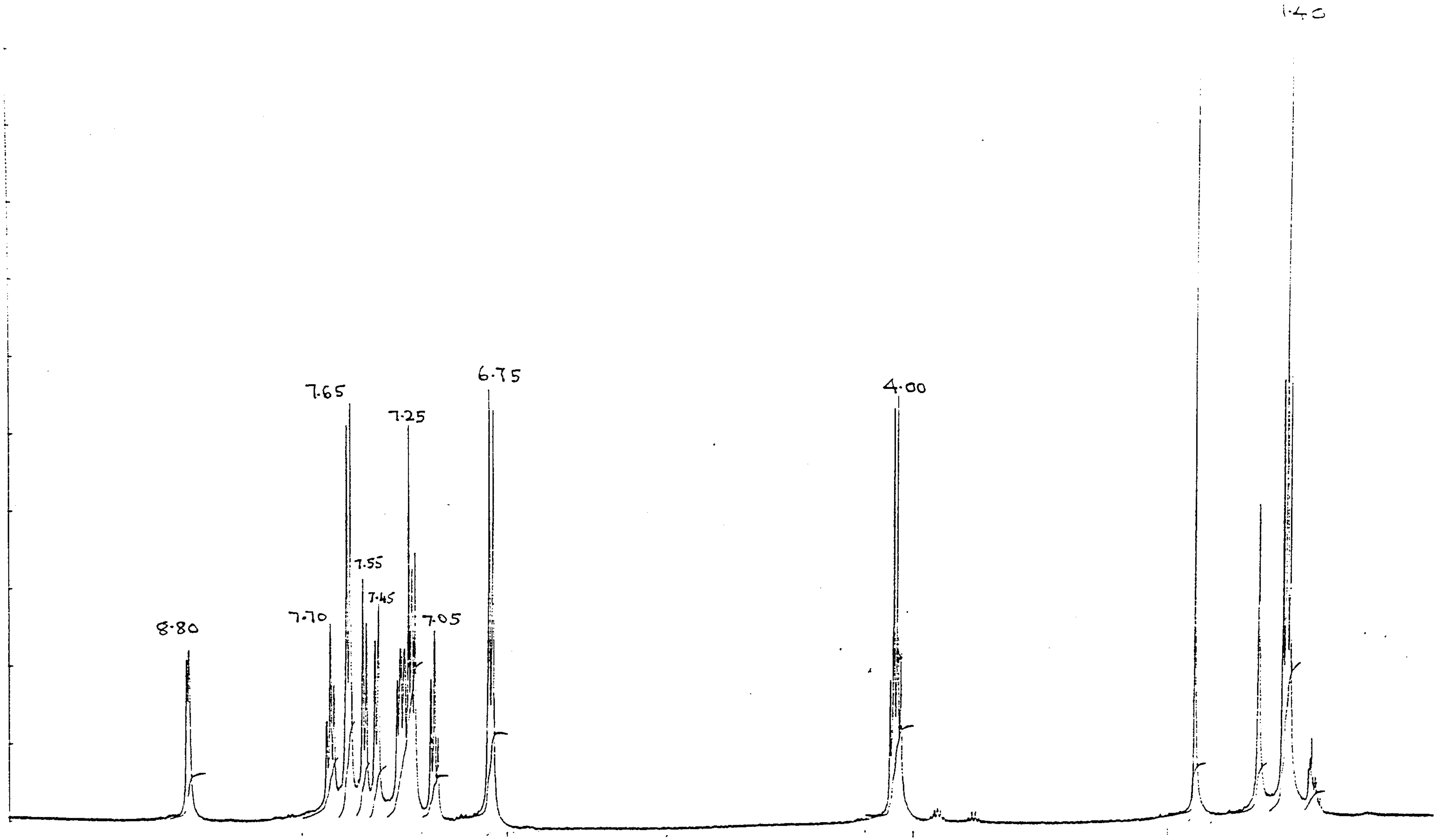


Fig 4.5: ^{1}H NMR spectrum of complex (1).

It is probable that the present material may be similarly described.

The ^{13}C NMR spectra of compound (3) and (4) show an enhanced number of peaks, particularly in the aromatic region, which support the presence of co-ordinated and free ligand (RR^1Te) in dmso-D_6 solution (Fig 4.6). The ^{13}C chemical shift assignments were done according to the literature(72,74) on comparisons with suitable model compounds 2-(2-pyridyl)phenyl and 2-(2-pyridyl)phenyl mercury (II) chloride.(64)

The U.V. spectra (qualitative) of the ligand and its copper (II) complexes were studied in chloroform solution (Fig. 4.7). The spectra provided limited information but did indicate that the major peak at 225mm for the ligand was unshifted in the copper (II) complexes, a shoulder at 270mm for ligand was not discernable in the complex spectra; and the ligand band at 360mm underwent a significant blue shift to 308mm in the complex spectra. Thus U.V. spectra of (2), (5) and (6) gave identical spectra which differ significantly from that of free ligand.

It has been pointed out that a better criterion of the stereo chemistry of the copper (II) ion in a complex is its electronic spectrum as this is determined by the relative

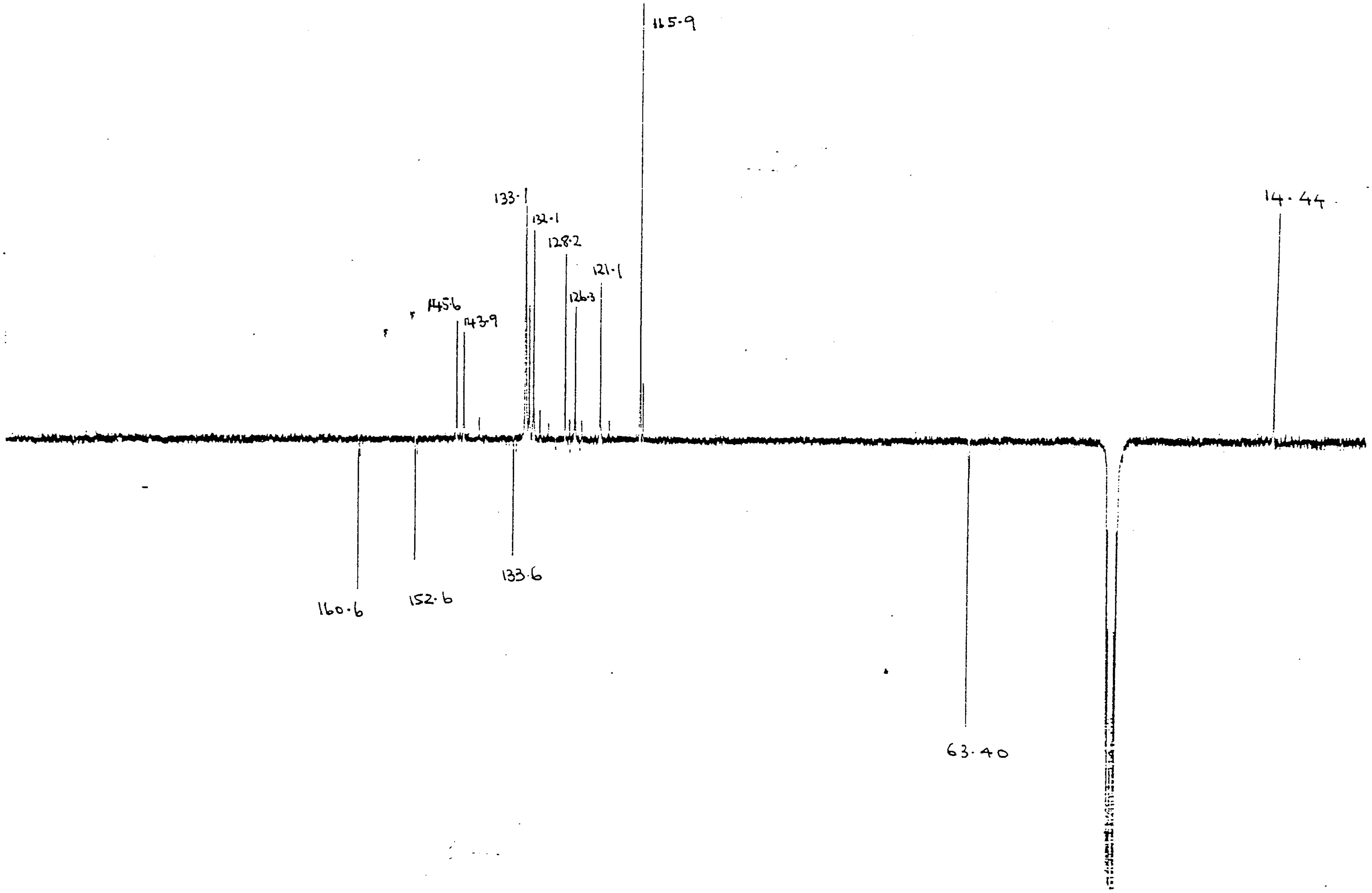


Fig 4.6: $^{13}C[^{1}H]$ NMR spectrum of complex (3).

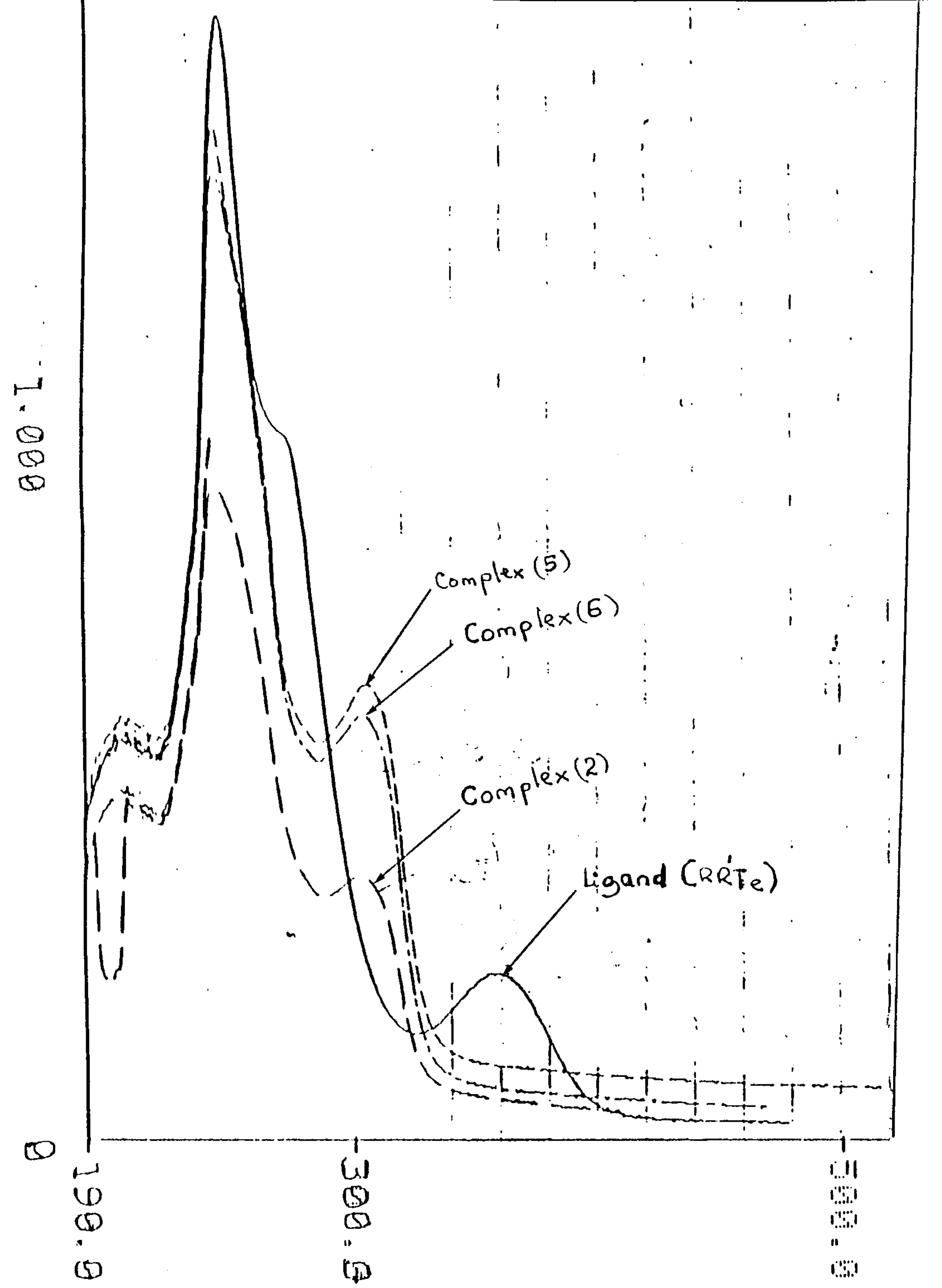


Fig 4.7: The visible spectrum of complex 2, 5 and 6 in chloroform.

ordering and energies of the one-electron energy levels (Fig 4.8). The copper (II) ion has a d^9 electronic configuration, and the electronic energy levels will be split into two main states (e_g t_{2g}) in an octahedral environment, these will further split, if there is a tetragonal distortion. Therefore d-d transitions should give absorption bands in the visible region. Unfortunately the complexes were unsufficiently soluble to give reliable visible spectra.

The ESR spectra of polycrystalline samples of copper (II) complexes were recorded at room temperature (Fig 4.9 - 4.10). The ESR spectra of (5) and (6) were identical and broad, so broad that no g-anisotropy could be resolved. The ESR of complex (2) suggests the presence of g-anisotropy (g - value for a centroid of the spectrum is 2.062).

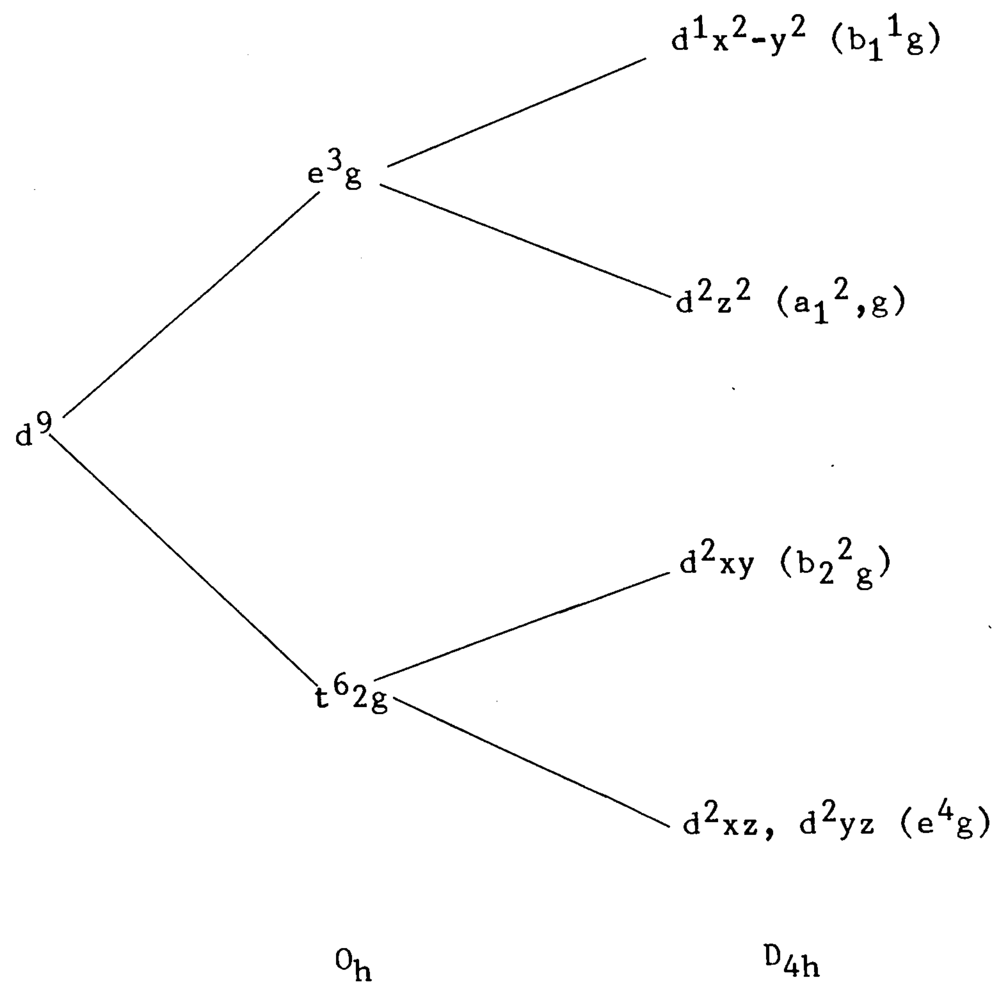


Fig 4.8 The relationship between the spectroscopic terms and the one electron energy configuration of a copper (II) ion in an elongated tetragonal octahedral ligand field.

The copper (II) ion with a d^9 configuration has an effective spin $S = \frac{1}{2}$ and associated spin angular momentum of $M_s = \pm\frac{1}{2}$ leading to a doubly degenerate spin energy that in the absence of a magnetic field. On application of a magnetic

Fig 4.9: ESR spectrum of polycrystalline sample of complex (2).

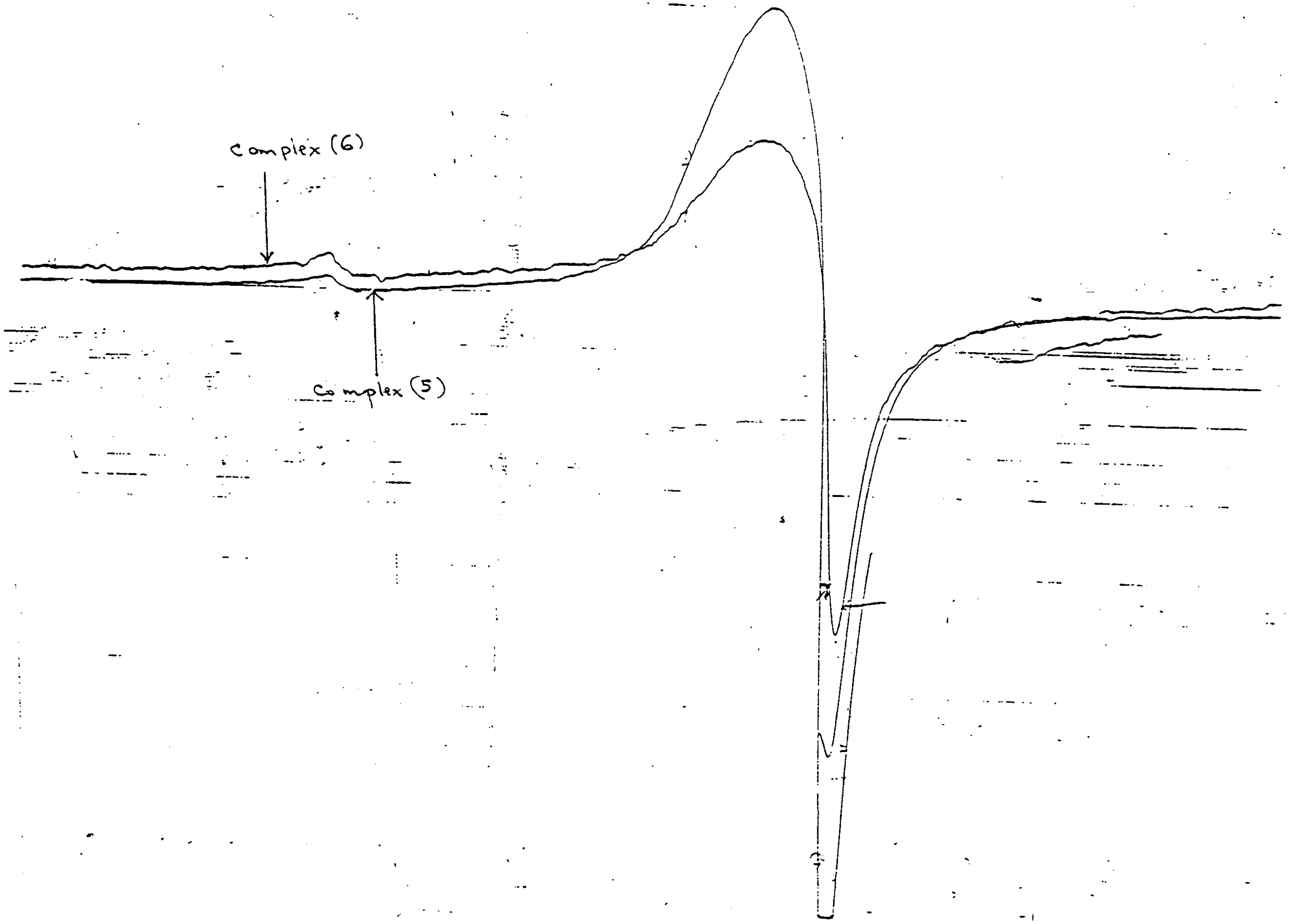


Fig 4.10: ESR spectrum of polycrystalline sample of complex (5) and (6).

field this degeneracy is removed and the transition occurs between two levels given by the relation $h\upsilon = gBH_A$

where h = Planck's constant

υ = Kystron frequency

B = Bohr magneton

H_A = average value of the parallel field components.

For a free electron "g" has the value 2.0023, whilst for an electron in a crystal field the value can differ from 2.0023. "g" is only isotropic in a cubic environment, in axial and rhombic crystal fields two or three different g - values are obtained respectively. Copper (II) ion is well known for its reluctance to take up a regular octhedral, or tetrahedral stereochemistry.(89) The $3d^9$ outer electron configuration of the copper (II) ion lacks cubic symmetry, and hence yields distorted forms of the basic stereochemistry.

The technique used to measure ESR spectra by polycrystalline powder method yields only "crystal-g" values and not necessarily related to the g-values of the local copper (II) ion environment.(90) it is possible for spin-spin relaxation effects to give very broad powder spectra which appear "isotropic". Unfortunately, this appears to be the case for the compounds considered in this chapter and consequently further analysis of the ESR data is not possible. The data do at least confirm the presence of paramagetic copper (II).

The broadly similar UV and ESR data for complexes (5) and (6) suggest similar chromophores may be present. This would be met by formulations:

(CuCl) (R^1CuCl) (RTeCuCl) ie "$Cu_3Cl_3RR^1Te$" (5) and
(R^1CuCl) (RTeCuCl) ie "$Cu_2Cl_2RR^1Te$" (6).

4.4 SUMMARY.

As a result of this study, it has been established that the reaction of 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II), (RR^1Te) with copper (I) chloride in the cold gives an ESR silent yellow complex, $Cu_3Cl_3(RR^1Te)_2(0.5\ CH_3CN)$. The great similarity of the ^1H NMR data for this complex and that of mercury complex reported in chapter three, suggests that libilisation of groups from tellurium to, particularly d^{10} ions, may be general. While the reaction of 2-(2-pyridyl) phenyl(p-ethoxyphenyl)tellurium(II) with copper (II) chloride or bromide under mild conditions gives colourless simple copper (I) complexes, $CuX(RR^1Te)$ (X = Cl, Br); which are also ESR silent.

CHAPTER FIVE

THE REACTION OF 2-(2-PYRIDYL)PHENYL (P-ETHOXYPHENYL)TELLURIUM(II) WITH PALLADIUM(II) AND PLATINUM(II) CHLORIDE

5.1 INTRODUCTION.

The literature contains few reports of transition metal complexes of bidentate (Te, Te) or (Te,N) ligands, although the reactions of $(Bu^nTe)C_6H_4CHN(CH_2)_nNCHC_6H_4(TeBu^n)$ (n = 0,1) with palladium(II), platinum(II), mercury(II) and rhodium(I) and rhodium(III) have been described.(22,23). Also preparation of a palladium(II) complex of bis(2(2-pyridyl)phenyl)telluride have been reported.(91) Due to the significance of the recently observed phenomenon of "reverse trans-metallation in relation to the metal-organic vapour phase epitaxy (MOVPE), from the study of the reactions of 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II) with mercury-(II)chloride and copper(I)chloride, it was decided to investigate further the reactivity of the 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II) towards other transition metal centres.

In this chapter, the reactions with palladium(II) and platinum(II) chlorides are described. Also included in this chapter is the reaction of 2-(2-pyridyl)phenyltellurium(II) bromide with palladium(II) and platinum(II) chlorides.

5.2 EXPERIMENTAL.

The preparation of the ligand 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II)(RR^1Te) and 2-(2-pyridyl)phenyl tellurium(II)bromide (RTeBr) were done according to the literature.(64)

5.2.1 Preparation of Palladium Complexes

(A) With ligand, 2-(2-Pyridyl)phenyl (p-ethoxyphenyl)tellurium(II) (RR^1Te)

Complex(**1**)

Palladium dichloride (0.09g, 0.5mmol) in a mixture of ethanol ($10cm^3$) and conc HCl($1cm^3$) was heated to reflux under dinitrogen atmosphere. RR^1Te(0.20g, 0.5mmol) in ethanol ($10cm^3$) was added. A dark brown precipitate formed and the reaction mixture was refluxed for 15 minutes. The solid was separated, washed with ethanol and dried *in vacuo*, m.p. 180°(dec).

Complex (**2**)

The same experiment was carried out as in complex (**1**), except that refluxing time was extended to 1½ hours. The solid formed was filtered, washed with ethanol and dried *in vacuo*, m.p. 254°C(dec).

Complex (3)

Palladium dichloride (0.09, 0.5mmol) in acetonitrile ($10cm^3$) was heated to reflux under a dinitrogen atmosphere. RR^1Te (0.20g, 0.5mmol) in acetonitrile ($10cm^3$) was added. A dark brown precipitate formed and the reaction mixture was stirred at room temperature for 15 min, after which the solid was separated, washed with ethanol and dried *in vacuo*, m.p. 197°C(dec).

Complex (4)

The same experiment was carried out as in complex (3), except refluxed for 1 hour. The dark brown precipitate formed was separated, washed with ethanol and dried *in vacuo*, m.p. 285°C(dec).

Complex (5)

The same experiment was carried out as in complex (3), except refluxing time was extended to 6 hours. The black precipitate formed was separated, washed with ethanol and dried *in vacuo*, to give a black compound (5),m.p. > 300°C. The filtrate was evaporated to dryness and the solid formed recrystallised from chloroform to give greenish-yellow complex, m.p. 245°C(dec) in which the analysis showed C=44.3%, H=2.82%, N= 4.16%.

(B) With ligand 2-(2-Pyridyl)phenyltellurium(II) bromide (RTeBr)

Complex (6)

2-(2-pyridyl)phenyltellurium(II)bromide (0.18g, 0.5mmol) in acetonitrile (10cm^3) was added to a refluxing solution of palladium dichloride (0.09g, 0.5mmol)in acetonitrile under dinitrogen. The reaction mixture was refluxed for 1 hour. The brown precipitate formed was filtered, washed with acetonitrile and dried *in vacuo*, m.p. 210°C(dec).

5.2.2 Preparation of Platinum Complexes.

(A) With ligand, 2-(2-Pyridyl)phenyl (p-ethoxyphenyl)tellurium(II) (RR^{1}Te)

Complex (7)

RR^{1}Te (0.20g, 0.5mmol) in acetonitrile (10cm^3) was added to a refluxing solution of platinum dichloride (0.13g, 0.5mmol) in acetonitrile under dinitrogen. The colour changed immediately to red. The mixture was stirred at room temperature for 30 minutes and filtered. Ethanol was added to the filtrate to give a red powder compound, m.p. 210°C(dec).

Complex (**8**)

The same procedure as for complex (7), except in this case the mixture was refluxed for 3 hours. the brown solid formed, was separated, washed with ethanol, and dried *in vacuo*, m.p. 265°C.

Complex (**9**)

RR^1Te (0.20g, 0.5mmol) in ethanol (10cm^3) was added to a refluxing solution of platinum dichloride (0.13g, 0.5mmol) in ethanol (10cm^3) and conc HCl(1.6cm^3) under dinitrogen. The mixture was refluxed for 1½ hours to give a red precipitate which was filtered, washed with ethanol and dried *in vacuo*, m.p. 212°C(dec).

(B) With ligand, 2-(2-Pyridyl)phenyltellurium(II) bromide, (RTeBr)

Complex (**10**)

Platinum dichloride (0.13g, 0.5mmol) in acetonitrile (10cm^3) was heated to reflux in a dinitrogen atmosphere. RTeBr (0.18g, 0.5mmol) in acetonitrile (10cm^3) was added and the resulting mixture was refluxed for 1 hour to give a yellow material which was filtered and washed with acetonitrile, m.p. 260°C(dec).

5.3 **RESULTS AND DISCUSSION.**

The reaction of the ligand RR^1Te (R= 2-(2-pyridyl)phenyl, R^1 = (p-ethoxyphenyl) with palladium(II) and platinum(II) halides gave compounds with stoichiometries as shown in table 5.1 The palladium complexes have high melting points and are sparingly soluble in a wide range of solvents as compared with platinum complexes which are soluble in many organic solvents. In the same table, complexes formed from the reaction of RTeBr (R=2(2-pyridyl)phenyl) with palladium(II) and platinum(II) halides are presented; to provide some comparative data for the complexes formed from the reaction of RR^1Te with $PdCl_2$ and $PtCl_2$ in the context of the previous observations (chapter three).

^1H and ^{125}Te NMR data have been used to infer labilisation of RR^1 groups from tellurium by comparing with previous data where this phenomenon was observed.

Complex		Colour	Found (%)			Calculated (%)		
			C	H	N	C	H	N
$(R^1TePdCl)(R)_x$ $(x = 0.016)$	**(1)**	dark brown	25.5	2.19	0.06	25.0	2.32	0.06
$(R^1TePdCl)(RTePdCl)_x(PdTeCl)_y$ $(x = 0.08, y = 0.25)$	**(2)**	dark brown	22.1	1.93	0.26	21.7	1.96	0.24
$(R^1TePdCl)$	**(3)**	dark brown	24.6	2.19	0.00	24.6	2.30	0.00
$(R^1TePdCl)(R)_x$ $(x = 0.57)$	**(4)**	dark brown	35.3	2.68	1.65	35.8	28.3	1.67
$(RTePdCl)(R^1TePdCl)_x(PdTeCl)_y$ $(x = 0.5, y = 2)$	**(5)**	black	14.3	0.95	1.32	14.5	0.94	1.34
$PdCl_2(RTeBr)_2.0.5\ CH_3CN$	**(6)**	brown	28.9	1.95	3.68	29.4	1.89	3.79
$(R^1TeCl)(RPtCl_2)_2$	**(7)**	red	32.0	2.70	2.42	32.0	2.23	2.49
$(R^1TePtCl)_7(RTePtCl)_2R_2$	**(8)**	brown	26.3	1.68	1.23	25.6	2.02	1.20
$(R_1TePtCl)_{28}(RTePtCl)_7R_{18}$	**(9)**	red brown	30.6	2.17	1.79	30.3	2.28	1.77
$PtCl_2\ (RTeBr)_2$	**(10)**	yellow	26.8	1.55	2.90	26.7	1.60	2.82

Table 5.1 Analytical Data and Colour for New Complexes.

5.3.1 Palladium Complexes

Table 5.1 shows that depending on experimental conditions, the reaction of palladium dichloride with RR^1Te gives different types of complex. Under mild conditions in either acetonitrile or conc HCl as solvent, co-ordination compounds are formed (complex (**1**) and (**3**) with almost complete loss of the R(2-(2-pyridyl)phenyl) group from tellurium as represented by the equation (5.1) below.

$$RR^1Te + PdCl_2 \longrightarrow R^1TePdCl + RCl \qquad \text{(eq. 5.1)}$$

The IR and ^1H NMR (Fig 5.1) both support the formulation in which the amount of R in these complexes is quite negligible as indicated also by the %N in the complexes. Indeed complex (**1**) is almost identical to (**3**) with only a little amount of R present. this may suggest that under controlled experimental conditions the final product is likely to be $R^1TePdCl$ similar to that of complex (**3**). Under forcing conditions (reflux), in HCl solvent (complex (**2**)), the 2-(2-pyridyl)phenyl groups tend to be labile. However, the general trend from complex (**2**), (**4**) and (**5**) observations suggest that, when the reaction is performed under reflux for a longer time this can lead to the formation of inorganic material as evidenced by the low %C in Complex(5). A scheme below (5.1) shows possible pathways leading to the eventual formation of inorganic materials.

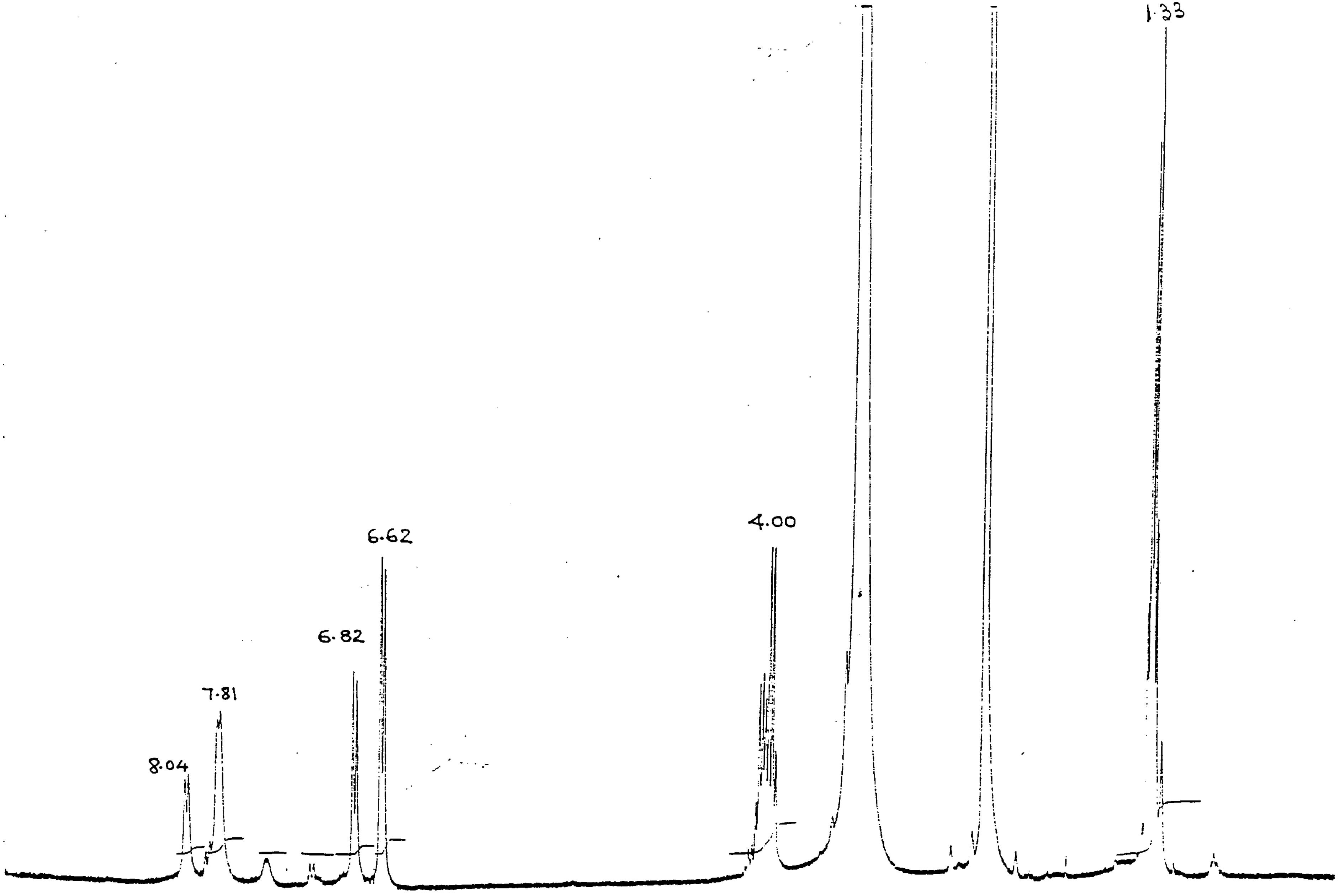
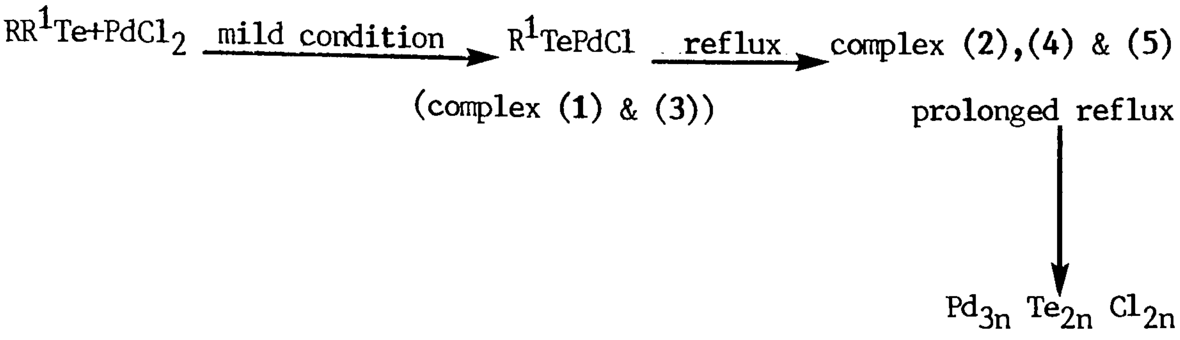


Fig. 5.1: ^{1}H NMR spectrum of complex (3).



Scheme 5.1

This implies that prolonged refluxing may eventually lead to the formation of inorganic materials of the type $Pd_{3n}Te_{2n}Cl_{2n}$ in which complexes (**1**,**2**,**3**,**4** and **5**) would be considered as intermediates. This is also supported by analysis of the filtrate complex (5) which has been refluxed for 6 hours, showing higher %C - i.e. carbon containing materials concentrates in the solvent (see experimental section).

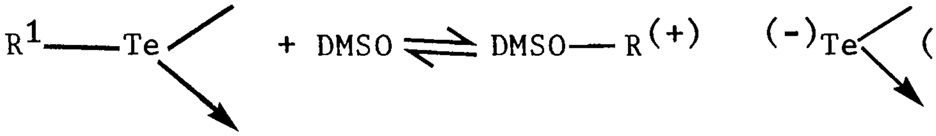
Complex (**3**) is particularly interesting as its analysis shows the %N to be "nil", hence it is formulated as $R^1TePdCl$, with no R groups (Table 5.1).

The ^1H NMR spectrum of this complex (Fig 5.1) shows two environments for R^1 groups. The formulation of the compound as $R^1TePdCl$ would imply only one environment for R^1. The appearance of two sets of signals for the R^1 group could arise from three possibilities.

(a) the dissociation of the complex in solution:

$$2R^1TePdCl \rightleftharpoons (R^1Te)_2\ Pd + PdCl_2 \qquad \text{(eq. 5.2)}$$

(b) the reaction of DMSO with the complex:



$$R^1\text{—}Te\langle + DMSO \rightleftharpoons DMSO\text{—}R^{(+)} \quad {}^{(-)}Te\langle \qquad \text{(eq. 5.3)}$$

(c) two distinct species i.e. "$R^1TePdCl$" may not be pure:

$$R^1TePdCl + R^1PdCl.\ 0.8PdCl_2 \qquad \text{(eq. 5.4)}$$

The ^{125}Te NMR spectrum (Fig 5.2) shows a single resonance at δ = 1057.9 ppm (cf free ligand (RR^1Te), 649.1ppm). This chemical shift is well outside the range reported in tellurides.(75) In the compound $(R^1HgCl)(RTeCl)_2$ reported earlier in chapter three, it was found that ^{125}Te NMR spectrum showed a single resonance at δ = 1323.9 ppm, a figure supporting the presence of RTeCl species (R = 2-(2-pyridyl)phenyl). Thus the NMR data suggest that complex (3) does not contain an RTeCl species as did the mercury compound reported earlier. Interestingly the ^{125}Te NMR spectrum of complex (6), a product formed from the reaction of RTeBr (R=2-(2-pyridyl)phenyl) with $PdCl_2$ giving a simple palladium complex, gave two resonances a major at δ = 1315.7ppm and a minor at δ = 1297.7 (Fig 5.3). The formation

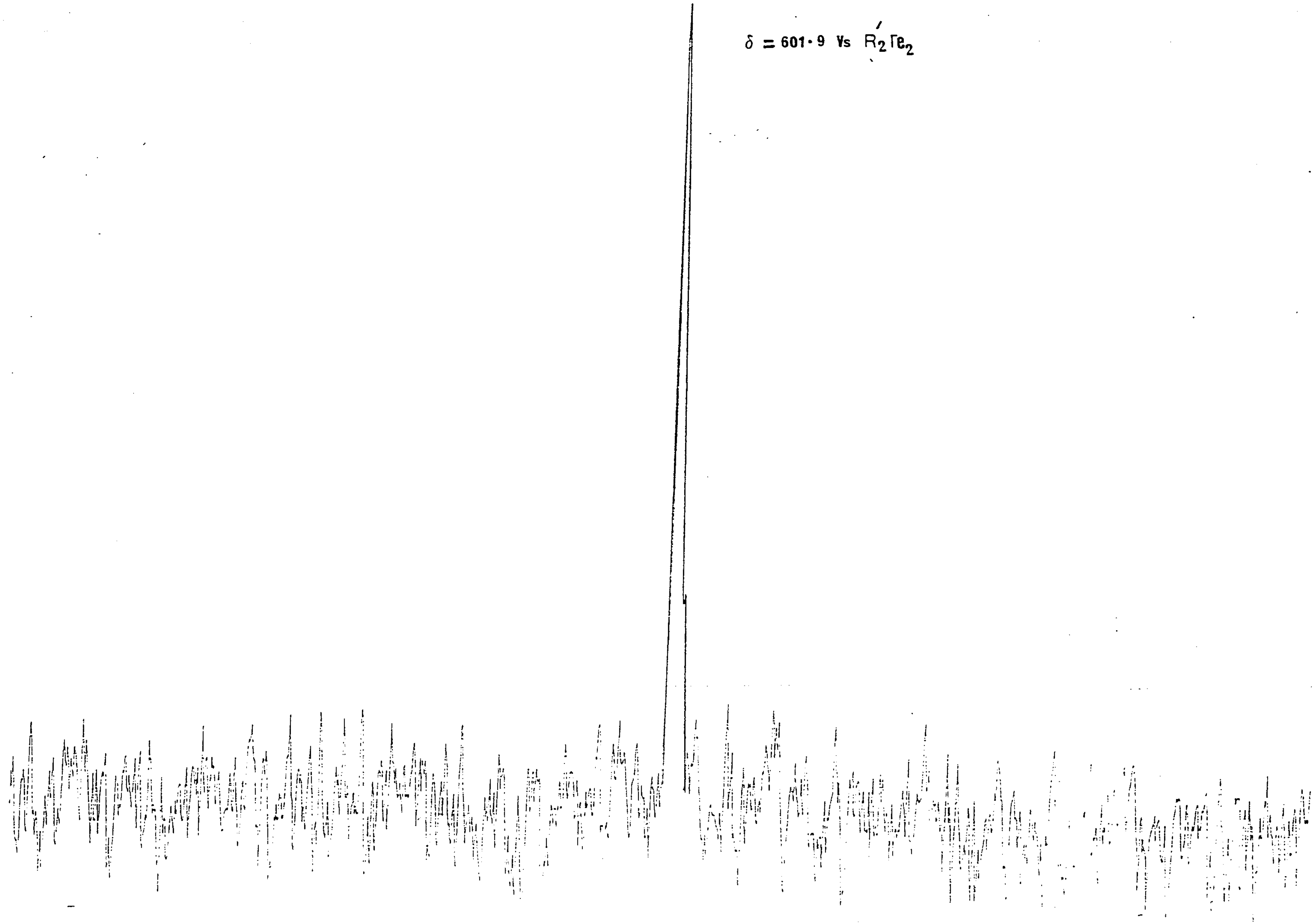


Fig 5:2: $^{125}Te[^{1}H]$ NMR spectrum of palladium complex (3) in DMSO.

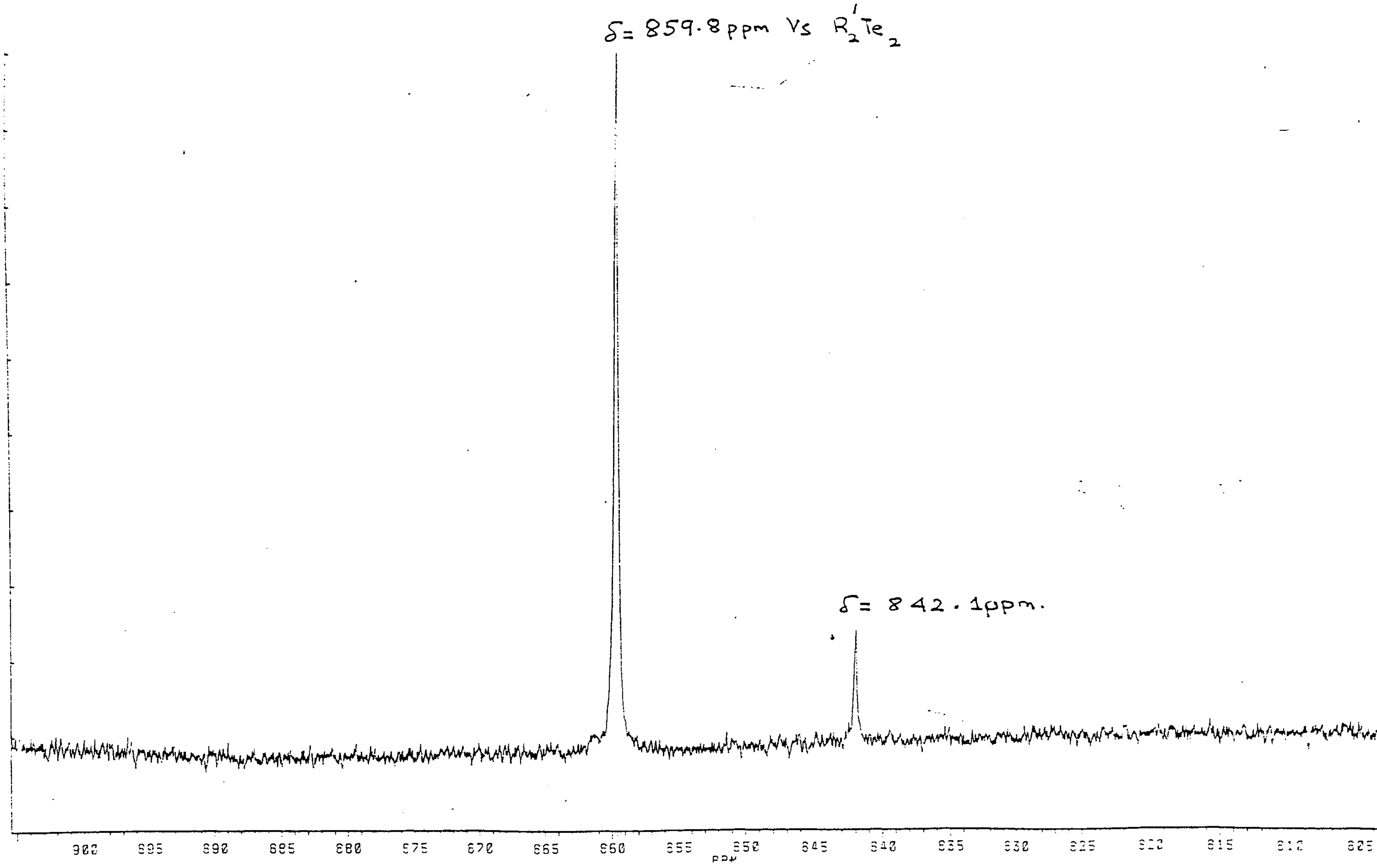


Fig 5.3: ^{125}Te[^{1}H] NMR spectrum of palladium complex (6) in DMSO.

of two peaks is believed to be due to co-ordination by DMSO (eq 5.5).

(eq. 5.5)

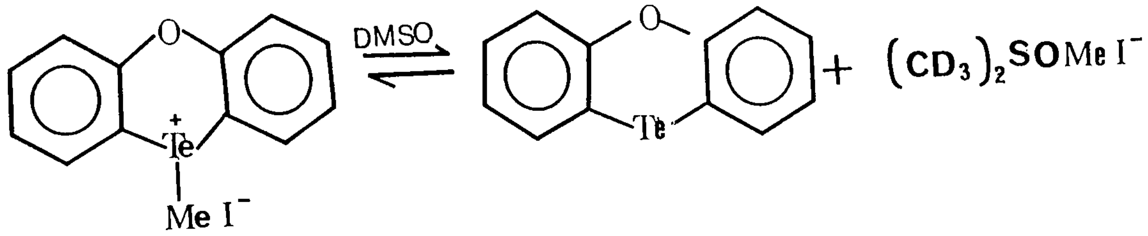
The chemical shift for the major peak further supports the argument that, for the formation of the species RTeX(R=2-(2-pyridyl)phenyl, X = Cl, Br), the ^{125}Te chemical shift would be ca.1300 ppm. The appearance of one signal in the ^{125}Te NMR spectrum implies the presence of only one tellurium environment in the complex.

In summary, viewing all the data relating to ^1H and ^{125}Te resonances, the following remarks can be made.

First the two environments for R^1 groups could indicate

(i) two distinct species in solution (eq. 5.4)

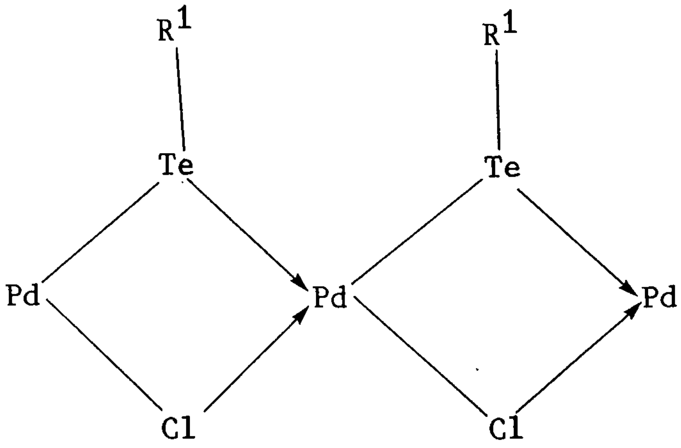
(ii) if there is one compound, then eq. 5.2 and 5.3 can account for the presence of two sets of signals in the ^1H NMR spectrum. Rainville and Zingaro(92) have reported similar observations, that 10-methylphenoxatelluronium iodide readily forms $[(CD_3)_2SO(Me)]^+I^-$ in $(CD_3)_2SO$ (eq 5.6).



(eq. 5.6)

The ^{125}Te NMR spectra for case (ii) (eq. 5.2 and 5.3) should however indicate two kinds of tellurium environment, however only one signal is observed. Thus an explanation based on (i) in which only one R^1 group is co-ordinated to tellurium and the other R^1 group co-ordinated directly to the palladium atom (eq. 5.4) is more probable. However (ii) could be allowed if, due to the low concentration of the product species in the equilibrium reaction (eq. 5.2 and 5.3), the observation of the second resonance could be difficult.

The high deshielding of the tellurium atom could be due to the species R^1TePdCl existing as a polymer in which tellurium atom is three-coordinated as shown overleaf, (a).



(a)

The electron withdrawal via the co-ordination linkage provides an explanation for the considerable deshielding of the tellurium atom.

The ^{1}H NMR spectra of complex (**2**, **4** and **5**) show doubling of resonances particularly at the alphatic region compared to that of the free ligand due to the reasons already explained. The spectrum for complex (**5**), formed on refluxing the reactants for 6h, shows broadening of resonances in the aromatic region of R(2-(2-pyridyl)phenyl) (Fig 5.4) implying the presence of a free radical. Indeed this is not surprising as it has been reported(93) that an intermediate Ni(III) species produced from the reaction of nickel(II)macrocyclic complex ions with OH and dihalogen radical anions was described as nickel(II) complexes containing a nitrogen-based ligand radical. The amine nitrogen radical site was considered to have lost a proton

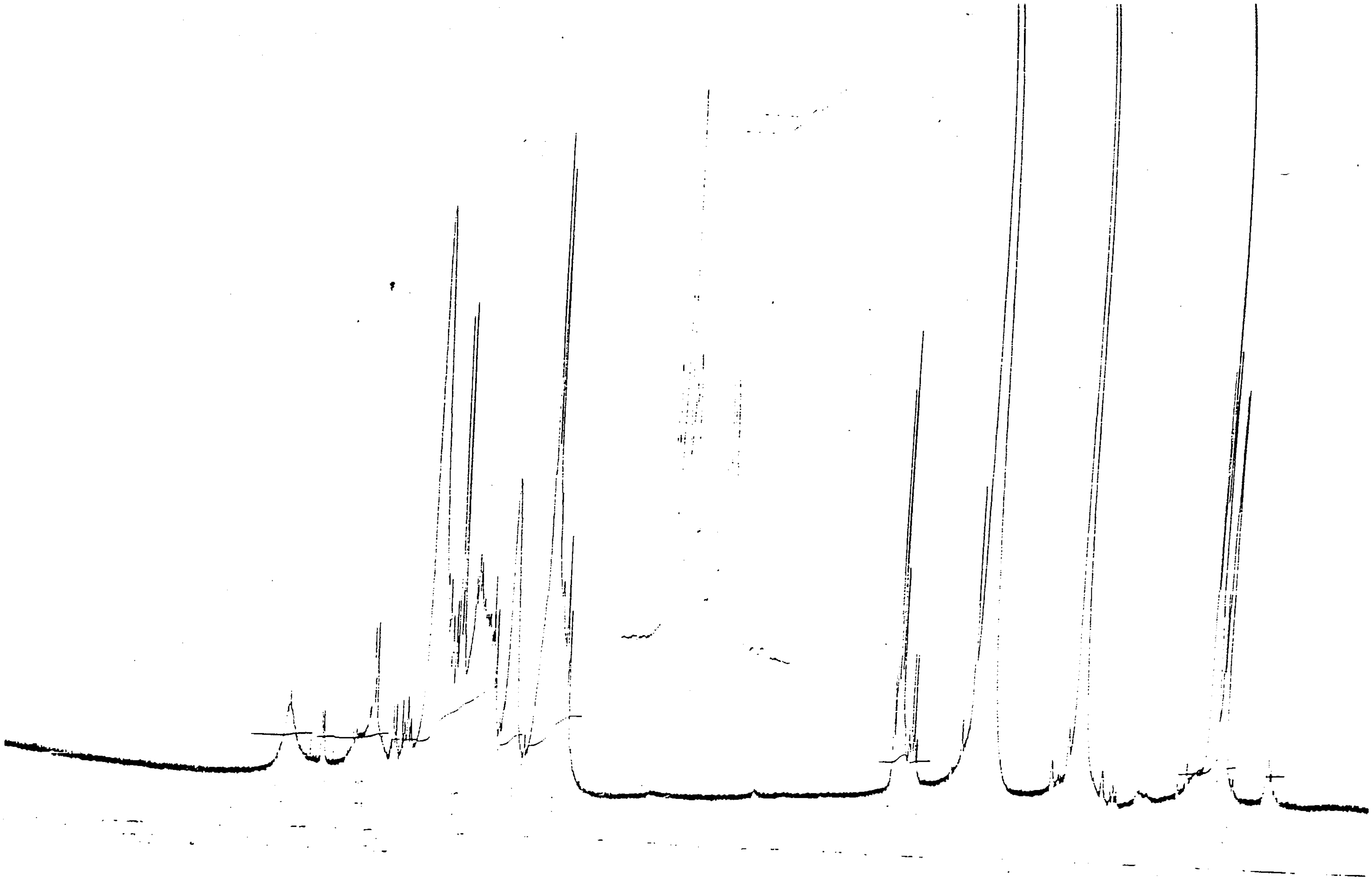
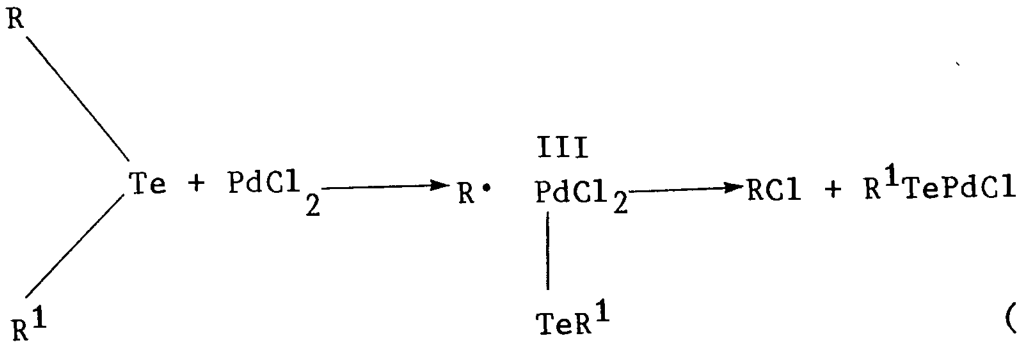


Fig 5.4: ^{1}H NMR spectrum of palladium complex (5) in DMSO.

in its formation. Using the same argument, it can be suggested that the free radical behaviour observed in complex (5) may imply the existence of Pd(III) species which may arise via an oxidative addition process (eq 5.7).



$$\begin{matrix} R \\ \quad\diagdown \\ \quad\;\; Te \\ \quad\diagup \\ R^1 \end{matrix} + PdCl_2 \longrightarrow R\cdot \; \begin{matrix} \text{III} \\ PdCl_2 \\ | \\ TeR^1 \end{matrix} \longrightarrow RCl + R^1TePdCl$$

(eq 5.7)

where R• may enjoy some degree of resonance stabilisation (b).

(b)

The existence of different intermediates in the reaction of $PdCl_2$ with RR^1Te may be reflected to the findings in the literature that radical cations are known to be important intermediates in various oxidation reactions. For example, The ^1H NMR spectrum of the complex in $CHCl_3$ (Fig 5.5) shows broadening of the peaks in the aromatic region whereas the peaks in the aliphatic region are well resolved and sharp. Careful analysis of the aromatic region shows two resolved peaks of equal intensity at $\delta = 6.89$ and 7.58 ppm which are assigned to protons C13 and C14 of the p-ethoxyphenyl group. This taken together with the fact that the aliphatic region shows resolved peaks, a triplet signal centred at 1.40ppm for $-CH_3$ protons and the $-CH_2$ quartet centred at 3.88ppm indicates that the broadening of the peaks in the aromatic region, which could imply the presence of a free radical or paramagnetism, is a function of the R(2-(2-pyridyl)phenyl group.

This can be interpreted in two ways:

(1) formation of a free radical R• similar to that discussed for the palladium compounds;

(2) formation of a stable platinum (III) species of currently unknown structure which contain R^1TeCl as a potential ligand e.g. $(R^1TeCl)(RPt^{(III)}Cl_2)_2$.

Case (1) seems unlikely as the equation 5.8 indicates that both R groups are involved in the formation of the complex as opposed to the palladium case where the R group was lost. Case (2) therefore, seems to be a possible alternative.

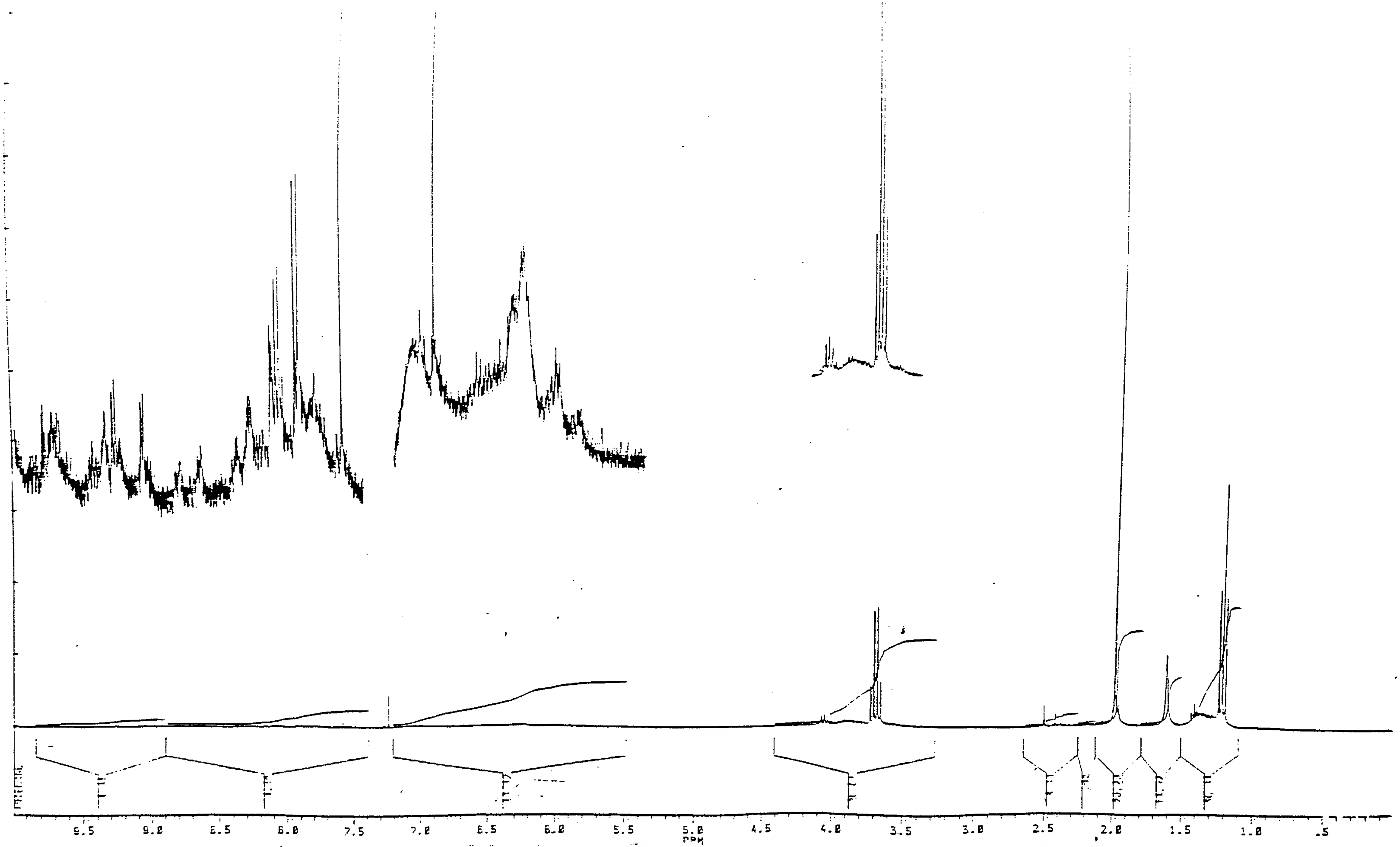


Fig 5.5: ^{1}H NMR spectrum of platinum complex (7) in $CDCl_3$.

The formulation of complex (7) as $(R^1TeCl)(R\overset{(III)}{Pt}Cl_2)_2$ would explain the ^1H NMR spectrum (Fig 5.5), in which the R^1 group (p-ethoxyphenyl) being not co-ordinated to the platinum centre would not be affected by the paramagnetic effect resulting from the presence of Pt(III) species.

Attempts to get ^{125}Te and ^{195}PtNMR measurement in $CHCl_3$ were unsuccessful, even when the measurements were carried for three days. But, by contrast, it did prove possible to obtain ^{195}PtNMR spectra in DMSO (see below).

When the ^1H NMR measurement was carried out in DMSO, the spectrum (Fig 5.6) shows some of peaks in the aromatic region to be resolved. The spectrum also shows the appearance of two doublets of different intensity at $\delta = 9.51$ and 9.98 ppm which are assigned to the proton <u>ortho</u> to the nitrogen in the pyridine ring. The two doublets may arise due to the introduction of solvent molecule (DMSO) in the co-ordination sphere (eq 5.9).

(eq 5.9)

However, the spectra are now so complex that it seems certain that many species co-exist in DMSO solution.

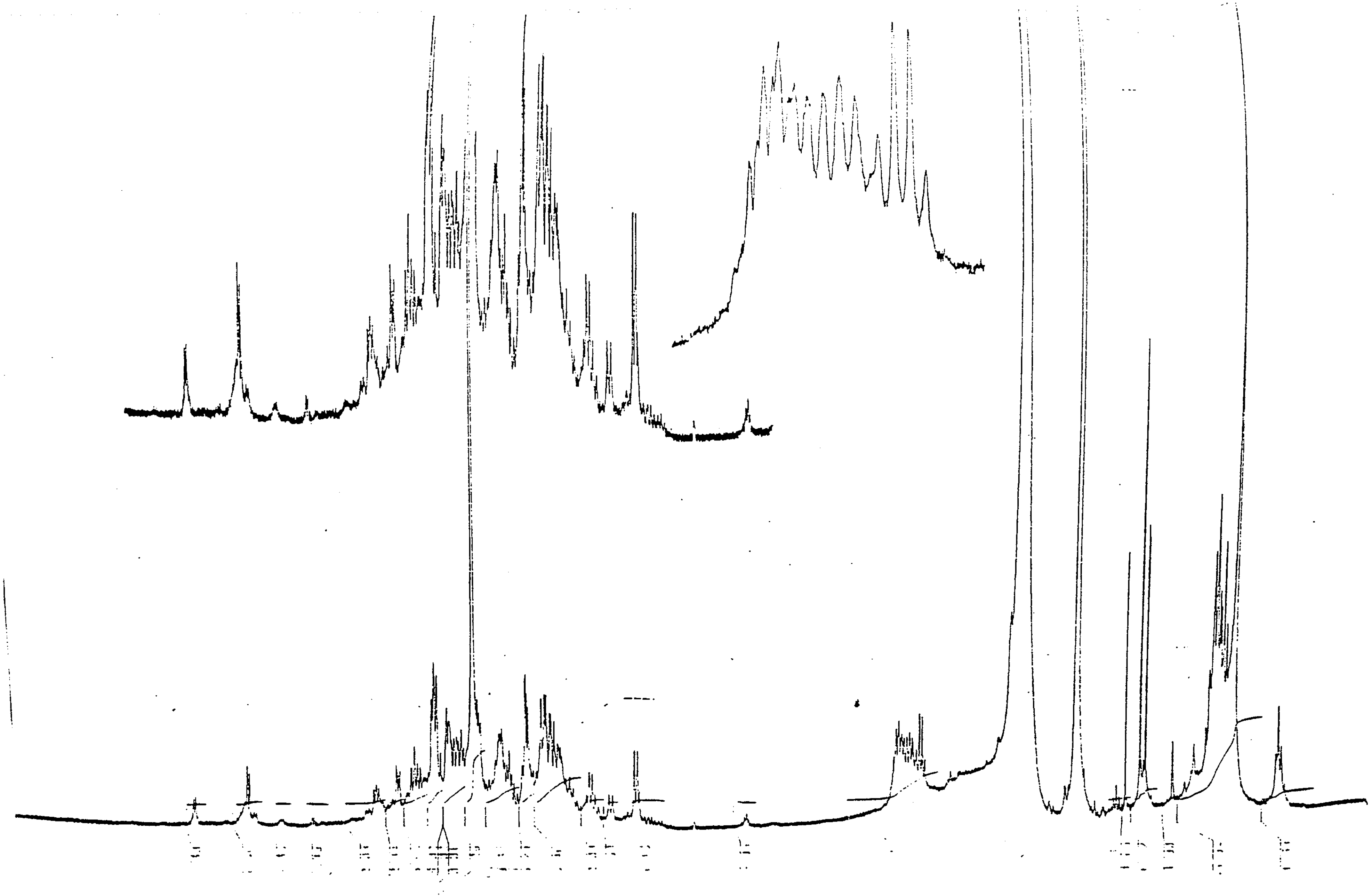
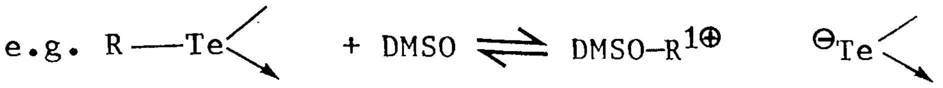


Fig 5.6: ^{1}H NMR spectrum of platinum complex (7) in DMSO.

It is even possible that DMSO could capture an organic group (eq 5.10)



eq.5.10

This is not without precedent since Rainville and Zingaro(92) observed similar behaviour with a telluronium salt as discussed earlier (eq 5.6).

Also, Mössbauer data show that co-ordination of tellurium to platinum produces an electronic environment about Te not dissimilar to that in a telluronium salt.(35,53) During the period of the NMR measurement in DMSO, the solution changed from red to reddish-brown, thus supporting the view that this solvent (DMSO) was not inert. Such changes will further complicate the spectra.

The ^{195}Pt NMR spectrum of this complex was recorded in DMSO. These spectra were monitored over 24 hours. After 3 hours, three signals were seen at 2612, 2954, and 2957 ppm upfield from $Na_2[PtCl_6]$ (Figure 5.7). Also on the same spectrum a weak signal was observed at 2798ppm. After 24 hours, the signal at 2612ppm had shifted slightly to 2611ppm and two new weak signals at 2597 and 2650ppm were observed (Fig 5.8a). The previously weak signal seen at 2798ppm had now become strong with two satellites arising from spin-spin coupling to ^{125}Te, J(PtTe) = 748Hz (Fig 5.8b). This

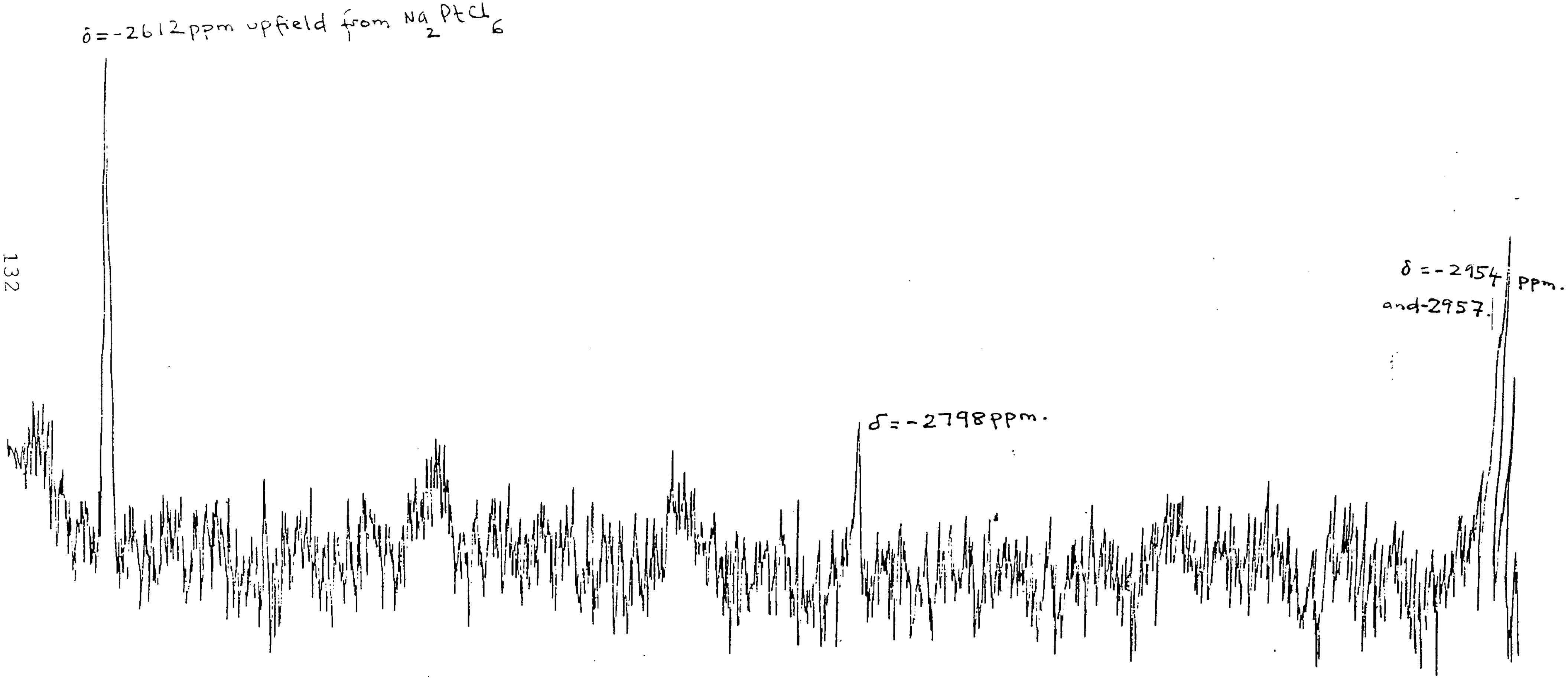


Fig 5.7: ^{195}Pt spectrum of complex (7) in DMSO (after 3h).

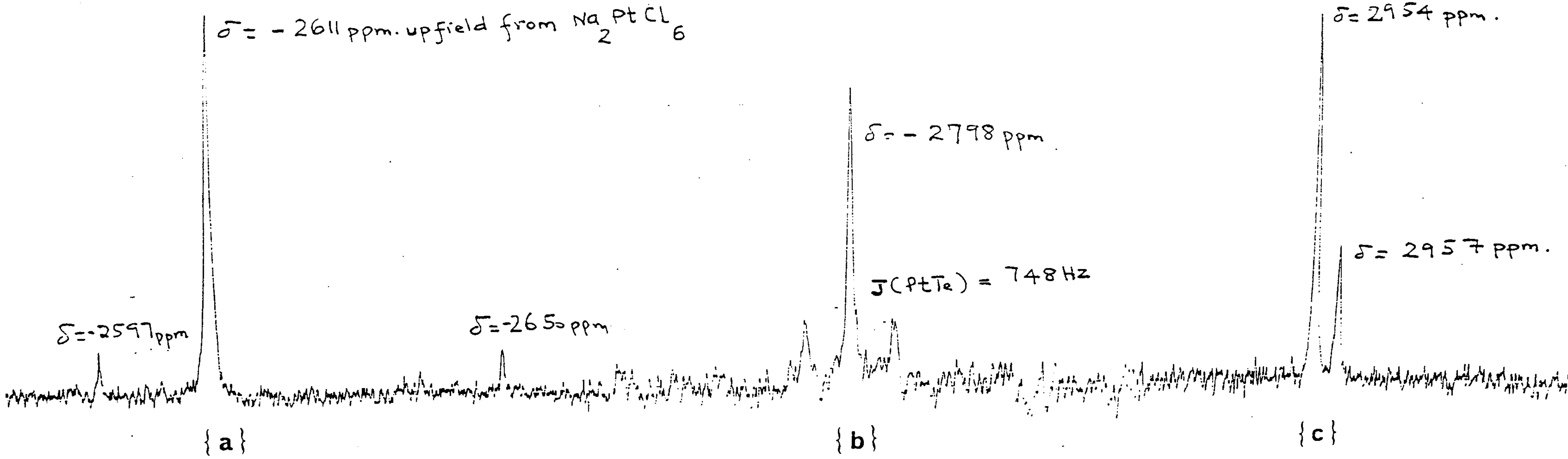


Fig 5.8: ^{195}Pt NMR spectra of complex (7) in DMSO (after 24h).

indicates that only one tellurium atom is co-ordinated to platinum which agrees with the formulation. After the same period, i.e. 24 hours, the position of two signals at 2954 and 2957 ppm did not change while the relative intensity changed in favour of the 2954 peak (Fig 5.8c). All the peaks show broadening consistent with the presence of a paramagnetic species.

The ^{195}Pt resonance covers a wide range of chemical shifts.(95) Pt(IV) can resonate at a higher field or at a lower field than the reference Na_2PtCl_6. The literature contains no data for the Pt(III) chemical shifts. The ^{195}Pt NMR spectrum (Fig 5.7) measured after 3 hours, suggests that at an early stage of the equilibrium a mixture of two major species and one minor species is detectable. It was suggested that this compound may be formulated as Pt(III) species $(R^1TeCl(R\overset{(III)}{Pt}Cl_2)_2)$, thus the signals at 2612, 2954 and 2957 ppm (major species) at an early stage of equilibrium may belong to platinum (III) species. A closeness of the two signals at 2954 and 2957 may indicate different solvation states as suggested in eq 5.9.

The weak signal at 2798ppm (minor species) in the early stages of the equilibrium is probably that due to a Pt(IV) species (see below).

After 24 hours, this weak signal had become strong with satellites indicating ^{195}Pt- ^{125}Te coupling. It has been reported that the ratio of the coupling constant J(Pt(IV)-L)/J(Pt(II)-L) is close to 0.67 because the S- character of bond formed by Pt(II) in a square planar complex $[PtX_2L_2)$ is approximately 1/4, as the metal atom make use of dsp^2-hybrids, while in the corresponding octahedral complex of Pt(IV) $[Pt\ X_4L_2]$ it is approximately 1/6, as the metal atom makes use of d^2sp^3 - hybrids.(96) In a similar compound containing both nitrogen and tellurium as donor atoms, Al-Salim(22) has reported J(Pt(II)-Te) = 1014Hz. Thus J(Pt (IV)-Te) would be expected to be close to 680Hz. Therefore the ^{195}Pt- ^{125}Te coupling constant (748Hz) in the present compound probably is due to the Pt(IV) species.

The signal seen at 2612ppm at the early stage of the equilibrium (Fig 5.7), after 24 hours, had shifted slightly to 2611ppm with formation of two new weak resonances at 2597 and 2650ppm (Fig 5.8a). A possible explanation to the appearance of these two weak signals would be the disproportionation reaction of Pt(III) intermediates to yield Pt(II) and Pt(IV) species. Indeed it has been suggested by Waltz et al(97) on the basis of kinetic results that, the ultimate disappearance of Pt(III) intermediates proceeds by disproportionation reaction to yield Pt(II) and Pt(IV) products.

Thus, after 24 hours, the experimental solution contains at least six detectable platinum species. One of these may be assigned to Pt(IV), the other may be Pt(II), Pt(III) and Pt(IV). Only in one case is tellurium co-ordinated. This extremely complex behaviour undoubtedly arises as a result of the lability of the organic groups of RR^1Te on initial reaction with platinum(II). Platinum(III) intermediates can be involved which, on disproportion, could give Pt(II) and Pt(IV).

Attempts to get ESR measurement for this complex were unsuccessful. This has been interpreted by Wright and Lawrence,(98) who were also unsuccessful in obtaining ESR data in their study of Pt(III) intermediates, to indicate a low-spin d^7 species, and they proposed that the species may be of square-planar form with two highly labile apical positions in a distorted octahedral system.

Complex **(8)** and **(9)** formed on reflux illustrate further the complicated behaviour of the reaction of platinum dichloride with the ligand RR^1Te. It indicates probably that the product formed in eq 5.8 is reacting with the starting materials.

Complex **(10)** like complex **(6)** demonstrates two things.

(1) platinum complex can be formed consisting of RTeBr as a ligand.

(2) Unlike the mercury complex in chapter three in which RTeCl (R= 2(2-pyridyl)phenyl) was formed and the complex formulated as $(RTeCl)_2.R^1HgCl$, there is a strong evidence in contrary for the present case to suggest the presence of R^1TeCl (R^1=p-ethoxyphenyl) species in the platinum complexes, e.g. complex (7). The yellow colour of the complex (**10**) may explain the absence of RTeCl (yellow)species in complex (7) which is red in colour.

5.3.3 Summary

The present study of the reaction of RR^1Te with $PdCl_2$ or $PtCl_2$ suggests that the materials isolated, albeit not well defined, can be seen as intermediates to the synthesis of inorganic phases of the type $M_{3x}Te_{2x}Cl_{2x}$. This observation highlights the potential usefulness of tellurides with particularly labile organic groups as precursors for the metal organic chemical vapour deposition (MOCVD) of both main group and transition metal chalcogenides.

In this context the recent report by Steigerwald et al is of interest.(99) Organometallic precursors were used to produce NiTe but intermediates $Ni_{20}Te_{18}(PEt_3)_{12}$ and

$Ni_9Te_6(PEt_3)_8$ were isolated. These compounds are better characterised than the solid phases reported in this chapter, but the parallel is striking.

CHAPTER SIX

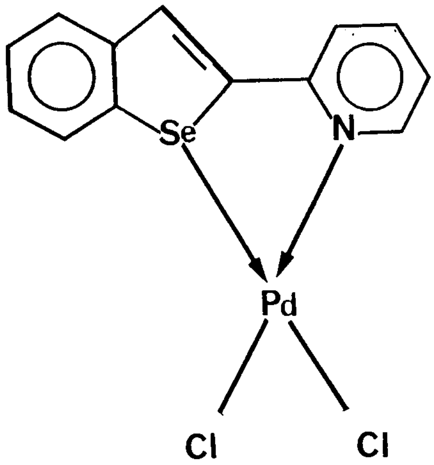
THE SYNTHESIS AND PROPERTIES OF NEW 2-(2-PYRIDYL) PHENYL SELENIUM COMPOUNDS

6.1 INTRODUCTION.

Recent synthetic work in our group has targeted ligands containing both tellurium and nitrogen as potential donor atoms. Thus, for example, organotellurium compounds functionalised with a 2-pyridyl group have been reported.(64) These compounds were prepared by reaction of appropriate tellurium compounds with 2-(2-pyridyl)phenylmercury(II) chloride which a recent structural determination has shown to be tetrameric.(100)

Selenium compounds which contain pyridine groups have also been reported in the literature. Bis[2-(2-pyridyl)ethyl] selenide (DPSe) as mentioned earlier was prepared from 2-vinylpyridine and H_2Se in ethanol.(61)

The preparation of 2-(2-pyridyl)benzo[b] selenophene (PBSe) has been reported together with the palladium(II) complex in which the ligand acts as a bidentate ligand involving a Pd-Se bond.(101) Also the preparation of *bis*(2-(2-pyridyl)phenyl) diselenide has been described. It has been prepared from the acid hydrolysis of 2(2-pyridyl)phenyl selenocyanate.(102)



Pd(PBSe)Cl$_2$

In the previous chapters, the study of the reaction of the ligand p-ethoxyphenyl 2-(2-pyridyl)phenyltelluride with Lewis acids particularly mercury(II) and Copper(I), or palladium(II) and platinum(II) salts revealed that there was considerable lability of the organic groups between metal centres. As part of the continuation on recent studies of the co-ordination chemistry of the bidentate and multidentate ligands containing tellurium together with a harder donor atom, particularly that of p-ethoxyphenyl 2-(2-pyridyl)phenyl telluride, it was decided to extend these studies to selenium anologue to explore further the phenomenon of "reverse *trans*-metallation". However, during the course of the preparative work using the same basic methodology,significant differences in the synthetic pathways for selenium and tellurium were noted.

In this chapter the new selenium compounds are reported, differences from the tellurium series noted, and the crystal structures of 2-(2-pyridyl)phenylselenium(II)tribromomercurate, and p-ethoxyphenyl 2(2-pyridyl)phenylselenide reported. Also included in this chapter is the study of analogous intermediate tellurium compound and its crystal structure for comparison purposes.

6.2 EXPERIMENTAL

Preparations

6.2.1 The reaction of $SeBr_4$ and $SeCl_4$ with 2(2-pyridyl)phenyl mercury(II) chloride.

A solution of 2-(2-pyridyl)phenylmercury(II) chloride$^{(64)}$ (0.78g, 0.0002 mol) in dry 1,4-dioxane (15 cm^3) was added to a solution of selenium tetrabromide (0.8g, 0.0002 mol) in dry dioxane (10 cm^3). The mixture was stirred under reflux for 2 hours during which time a yellow compound **1** precipitated. The solid was filtered and then dried in vacuo. Yield 64%, m.p. 181-182°C. Found: C, 21.5%, H, 1.71%, N, 1.95%

$C_{13}H_{12}Br_3HgNOSe$ (i.e. $C_{11}H_8Br_3HgNSe.\frac{1}{2}$dioxane) requires: C, 21.7%, H, 1.67% N, 1.95%.

Treatment of compound **1** with ethanol affords an orange product **2** which on washing with ethanol and drying *in vacuo*, gives m.p. 214-216°C. Found: C, 19.6%, H, 1.2%, N, 1.99%, $C_{11}H_8Br_3HgNSe$ requires: C, 19.6%, H, 1.19%, N, 2.08%.

A product **3**, shown to be identical to **2**, is obtained directly if the initial reaction with the organo-mercury is carried out in chloroform in place of 1,4-dioxane: found C, 19.9%, H, 1.23%, N, 2.09%.

If selenium tetrachloride (0.44g, 0.002 mol) in dry 1,4-dioxane is substituted for the solution of $SeBr_4$, and the mixture stirred under reflux for 4 hours, a solid was formed which was filtered and recrystallised from acetonitrile/ethanol (1:1 v/v) to give pale yellow crystals, **4**, in 72% yield with m.p. 175-178°C. Found: C, 26.1% H, 1.40% N, 4.15%, $C_{37}H_{30}Cl_9Hg_3N_5Se_3$ (i.e. $3(C_{11}H_8Cl_3HgNSe).2CH_3CN$) requires: C, 26.1%, H, 1.76%, N, 4.11%

Use of Chloroform as a solvent for the above reaction gives, directly, a solvent free yellow product, **5** in 60% yield with m.p. 159-161°C. Found: C, 23.9%, H, 1.51%, N, 2.50%, $C_{11}H_8Cl_3HgNSe$ requires: C, 24.4%, H, 1.48%, N, 2.60%.

6.2.2. The reaction of p-ethoxyphenyl selenium tribromide (prepared in situ) with 2-(2-pyridyl)phenyl mercury chloride.

A solution of bis (p-ethoxyphenyl) diselenide (2.0g, 0.005 mol), prepared by a literature method(103), in carbon tetrachloride was treated with a six fold molar excess of bromine at 0°C under dinitrogen. To this solution was added a chloroform ($25cm^3$) solution of 2-(2-pyridyl)phenyl mercury chloride, and the mixture was stirred for 2 hours at room temperature. A white compound, **6**, of m.p. 126-128°C was formed. Found C, 20.0%, H, 1.13%, N, 1.98%. $C_{11}H_8Br_3HgNSe$ requires C, 19.6%, H, 1.19%, N, 2.08%.

6.2.3. Treatment of products 2, 3 and 6 with hydrazine hydrate.

Treatment of compounds **2**, **3** or **6** as suspensions in ethanol with an excess of hydrazine hydrate gives the same pale yellow compound **7** m.p. 178-180°C. Found C, 26.2%, H, 1.55%, N, 2.67%, $C_{11}H_8Br_3HgNSe$ requires: C, 27.9%, H, 1.69%, N, 2.95%.

6.2.4. Preparation of p-ethoxyphenyl 2-(2-pyridyl) phenyl selenide.

A solution of 2-(2-pyridyl)phenylmercurychloride (4.0g, 0.01 mol) in chloroform (25cm^3) was added to a solution of p-ethoxyphenyl selenium tribromide prepared in situ by treatment of bis(p-ethoxyphenyl) diselenide (2.0g, 0.05 mol) and bromine (0.8g, 0.005 mol) at 0°C in carbon tetrachloride solution under dinitrogen. The mixture was stirred for 2 hours at room temperature when an ill defined white material, 8, m.p. 228-230°C was formed. 8 was suspended in ethanol (30cm^3) and treated dropwise with an excess of hydrazine hydrate. The mixture was stirred for 15 min; treated with water (50cm^3) and the solid product, 9, filtered. The product was recrystallised from ethanol/acetone (1:1 v/v) to give a 50% yield of pale yellow crystals having m.p. 102-104°C. Found C, 64.9%, H, 4.83%, N, 4.05%. $C_{19}H_{17}NOSe$ requires: C, 64.3%, H, 4.79%, N, 3.94%.

The preparative sequence is summarised in the scheme, figure 6.1.

6.3 RESULTS AND DISCUSSION.

Table 6.1 and 6.2 gives the stoichiometries and ^{13}C NMR of the new selenium compounds. Fig 6.1 shows the preparative scheme of these new compounds.

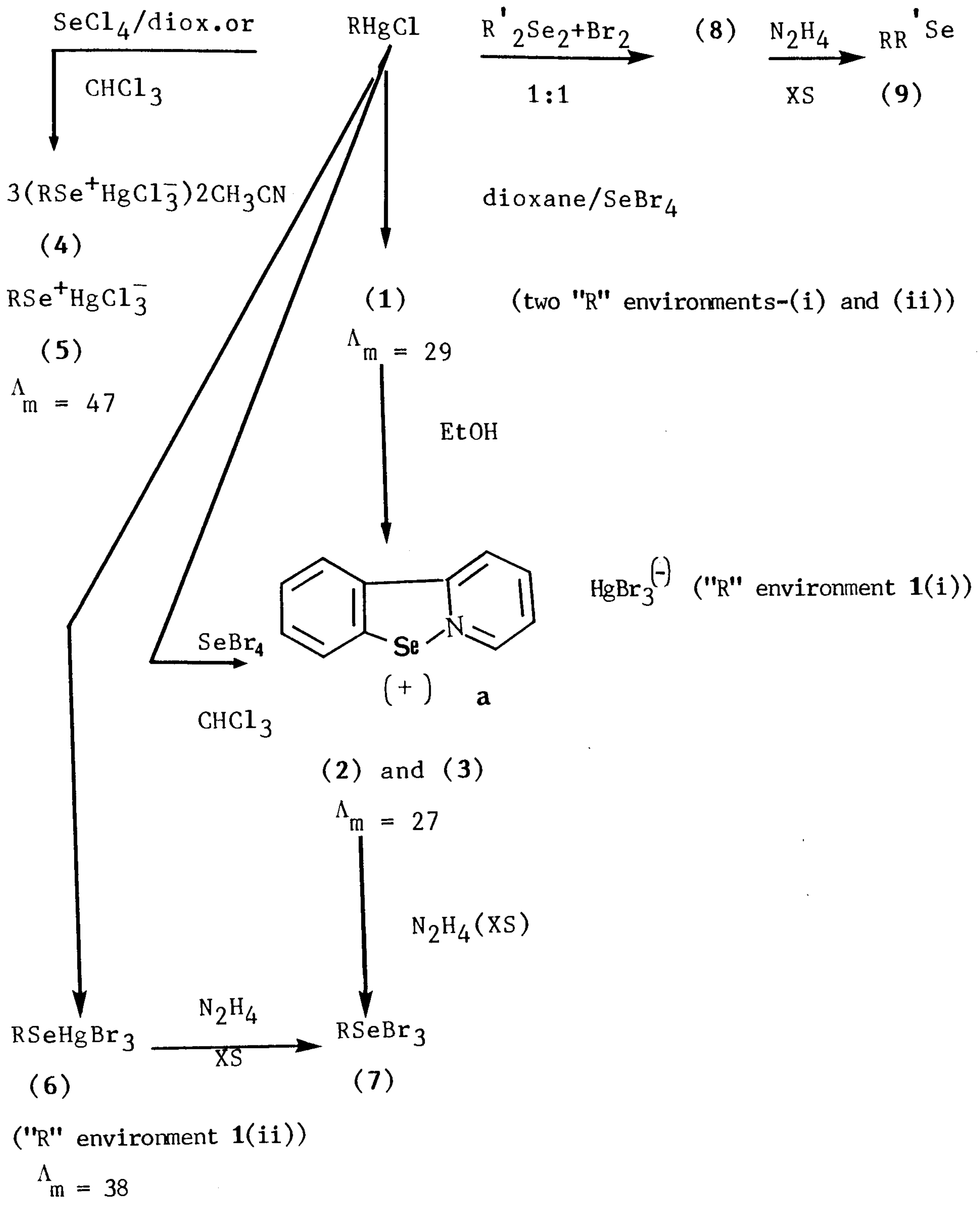


Figure 6.1 Preparative Scheme.

(R=2-(2-pyridyl)phenyl-, R' = p-ethoxyphenyl-. Molar conductivity data (m) for DMSO solutions (10^{-3}M), units are ohm^{-1} mol^{-1}1).

	Found %			Required %				Λ_M (DMSO)
	C	H	N	C	H	N	Colour	($ohm^{-1}cm^2mol^{-1}$)
$RSeHgBr_3 \cdot \frac{1}{2}$ dioxane (**1**)	21.6	1.71	1.95	21.7	1.67	1.95	Yellow	29
$[RSe][HgBr_3]$ (**2**)	19.6	1.12	1.99	19.6	1.19	2.08	Orange	
$[RSe][HgBr_3]$ (**3**)	19.9	1.23	2.09	19.6	1.19	2.08	Bright Yellow	27
$3([Rse][HgCl_3])2CH_3CN$ (**4**)	26.1	1.40	4.15	26.1	1.76	4.11	Pale Yellow	
$[RSe][HgCl_3]$ (**5**)	23.9	1.51	2.50	24.4	1.48	2.60	Yellow	47
$RSeHgBr_3$ (**6**)	20.0	1.13	1.98	19.6	1.19	2.08	White	38
$RSeBr_3$ (**7**)	26.2	1.55	2.67	27.9	1.79	2.95	Pale Yellow	
RR^1Se (**9**)	64.9	4.83	4.05	64.3	4.79	3.94	Pale Yellow	
$[RR^1TeCl][HgCl_3]$	30.5	2.20	1.80	30.6	2.30	1.85	White	34

Table 6.1: Elemental analyses colour and molar conductivities of new organoselenium compounds.

R = 2-(2-pyridyl)phenyl- R1 = p-ethoxyphenyl

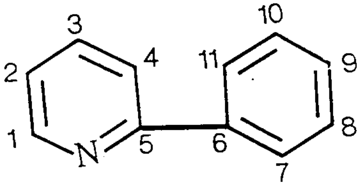
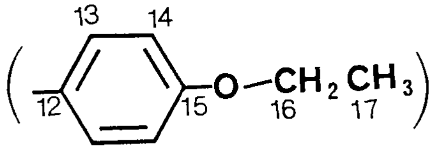
Compound	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}
	149.1	119.1	136.2	121.5	156.7	138.8	127.1	128.9	128.1	128.8	126.3
RHgCl	149.7	120.8	138.6	123.4	155.9	141.3	147.6	137.6	128.1	129.4	127.0
1	(141.8	122.9	140.4	124.0	151.8	128.2	142.0	132.3	126.3	127.3	-
	(144.5	125.5	143.5	126.3	153.0	121.4	133.2	132.2	129.3	131.9	127.4
2 and **3**	141.8	122.7	140.4	124.0	151.9	129.3	142.0	132.4	126.3	127.3	-
6	144.3	125.9	143.9	127.8	152.5	121.4	134.6	133.2	132.0	132.6	128.2
5	141.4	121.9	139.9	123.9	151.3	130.5	142.3	132.1	126.9	127.8	129.8
9	147.8	122.3	137.2	122.5	157.4	138.2	135.2	129.6	128.9	129.1	125.6
	120.8 (C^{12})	138.0 (C^{13})	115.8 (C^{14})	159.1 (C^{15})	63.1 (C^{16})	14.6 (C^{17})					

Table 6.2: ^{13}CNMR data for 2-(2-pyridyl)phenyl Selenium Compounds (ppm*vs*TMS)

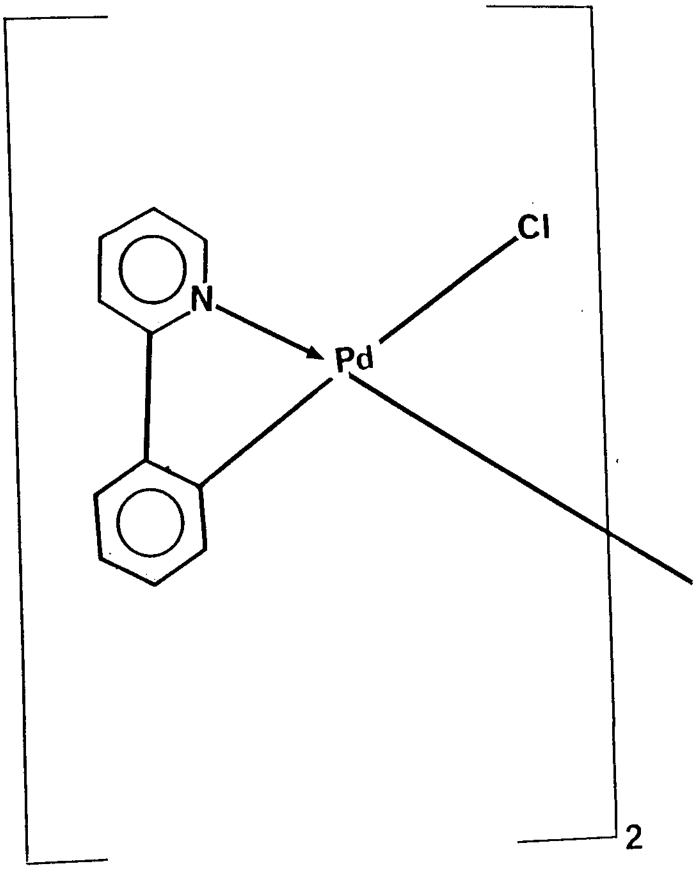
Compound	Solvent	δ(Hg)(ppm)[a]
[RSe][$HgBr_3$]	DMSO	-274.3
[RSe][$HgCl_3$]	DMSO	347.6

a = Hg chemical shift relative to aqueous $HgCl_2$

Table 6.3 ^{199}Hg NMR data

6.3.1 Transmetallation.

2-Phenylpyridine has been directly ortho-palladated when treated with $Na_2[PdCl_4]$ in ethanol,(104) as shown below.



Introduction of built in donors such as oxygen, nitrogen, into the ortho-position of the aryl group in organometallic compounds has been shown to be a useful method of stabilising organometallic compounds. The ortho-metallated complexes generally form strain-free five-membered ring structures.

It has been pointed out that although the direct metallation of azobenzene with tellurium tetrachloride could proceed under forcing conditions,(105) generally a trans-metallation route must be used for the synthesis of ortho-tellurated bases.(106). Arylmercury compounds have proved valuable for their trans-metallation properties. This characteristic was used by a previous worker for the synthesis of some 2-pyridyl-functionalised organotellurium ligands.(64) A similar method was adopted for the trans-metallation of mercurated 2-phenylpyridine with selenium tetrahalides (Cl,Br).

The reaction of selenium tetrahalides (Cl,Br) with 2-(2-pyridyl)phenylmercury(II)chloride in 1:1 molar ratio in refluxing dioxane or chloroform followed a different path to the well established reactions with tellurium tetrabromide.(64) For example, when reactions of selenium tetrahalides (Cl,Br) with 2-(2-pyridyl)phenylmercury chloride were carried out, it was anticipated that diorganyl selenium(IV) trihalide would be formed (eq. 6.1),

$$RHgCl + SeX_4 \xrightarrow{\text{dioxane}} RSeX_3 + HgClX \quad (X = Cl,Br) \qquad \text{(eq. 6.1)}$$

but the elemental analysis (Table 6.1) suggests that the product contained both selenium and mercury. The reaction of selenium tetrabromide with 2-(2-pyridyl)phenyl mercury chloride in refluxing dioxane afforded a yellow compound **(1)** which analyses as $RSeHgBr_3 \cdot \frac{1}{2}$ dioxane (eq. 6.2)

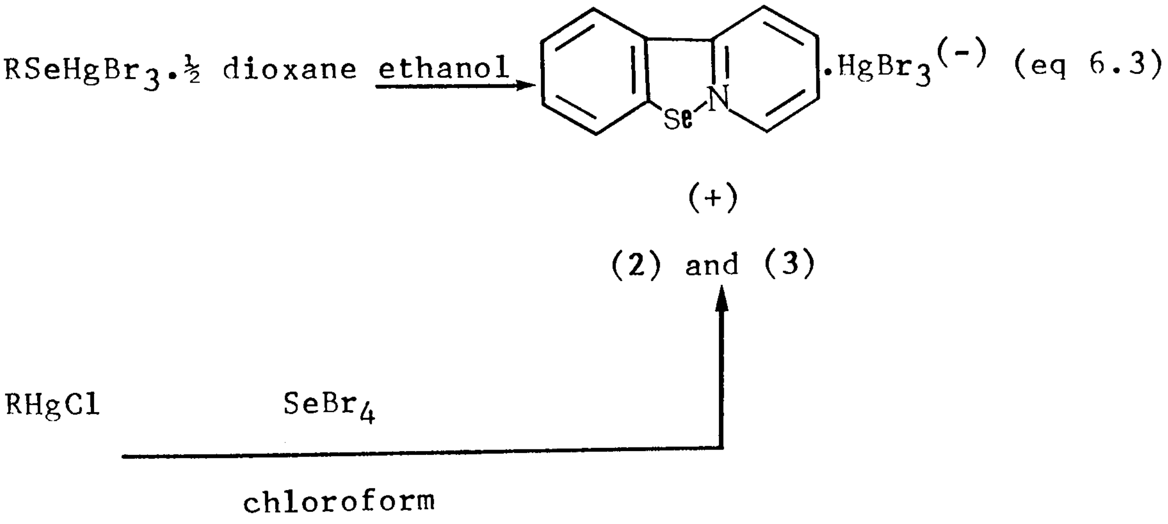
$$RHgCl + SeBr_3 \xrightarrow{dioxane} RSeHgBr_3 \cdot \tfrac{1}{2}\ dioxane \qquad (eq.\ 6.2)$$

(1)

The presence of dioxane is confirmed by IR and NMR spectroscopies (Section 6.3.3.). Of particular interest is that both the ^1H and ^{13}C NMR (Fig 6.2 and 6.3) show <u>two</u> environments for R (1:1), denoted as (**i**) and (**ii**) (Table 6.2)

Treatment of (**1**) with ethanol removed dioxane and gave compund (**2**) which contains a single environment, (**i**), for R.

When the initial reaction was carried out in chloroform, compound (**3**) identical to (**2**) was formed.



The structure of (**2**) was determined by the single crystal X-ray method, and shown to be an ionic compound. The

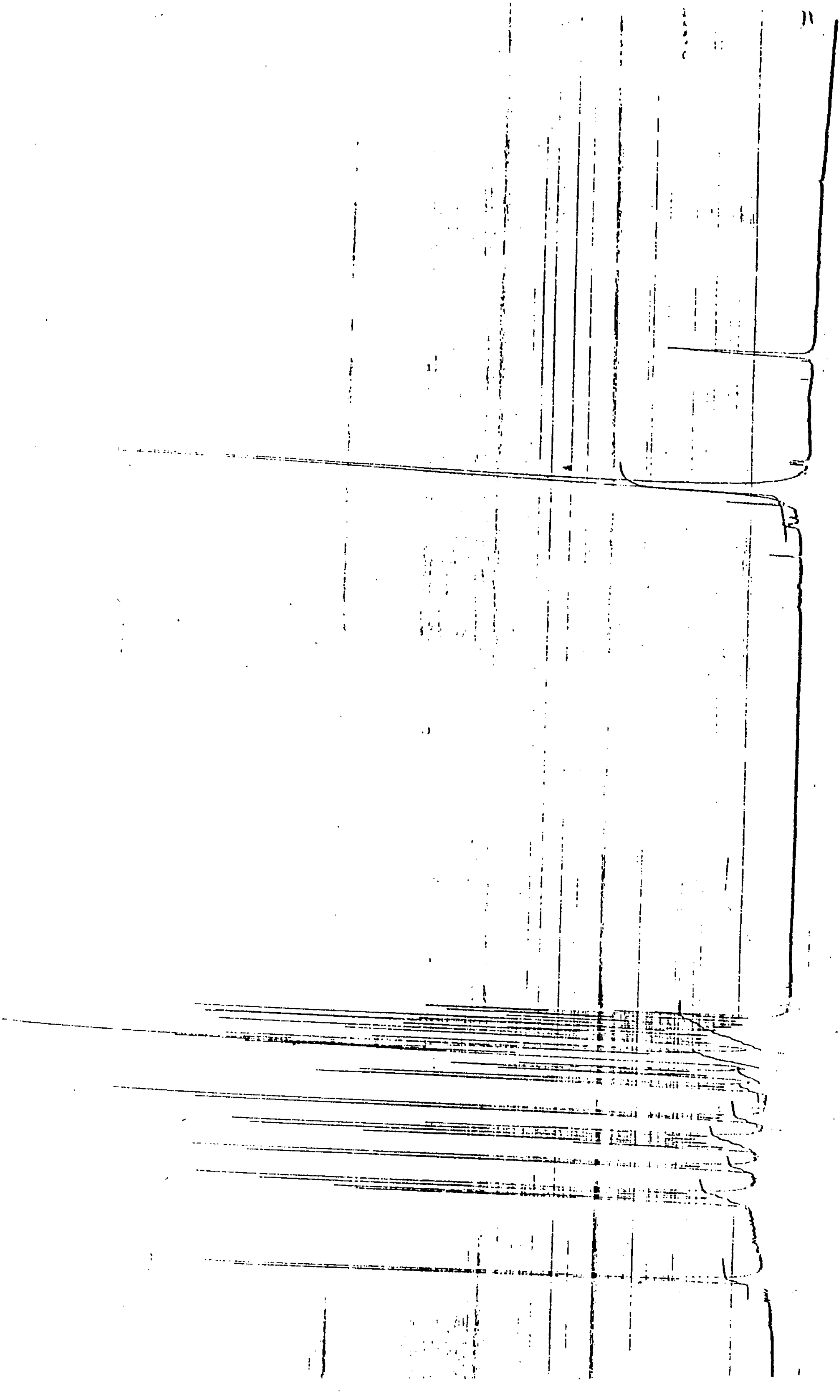


Fig 6.2: ^{1}H NMR spectrum of compound (1).

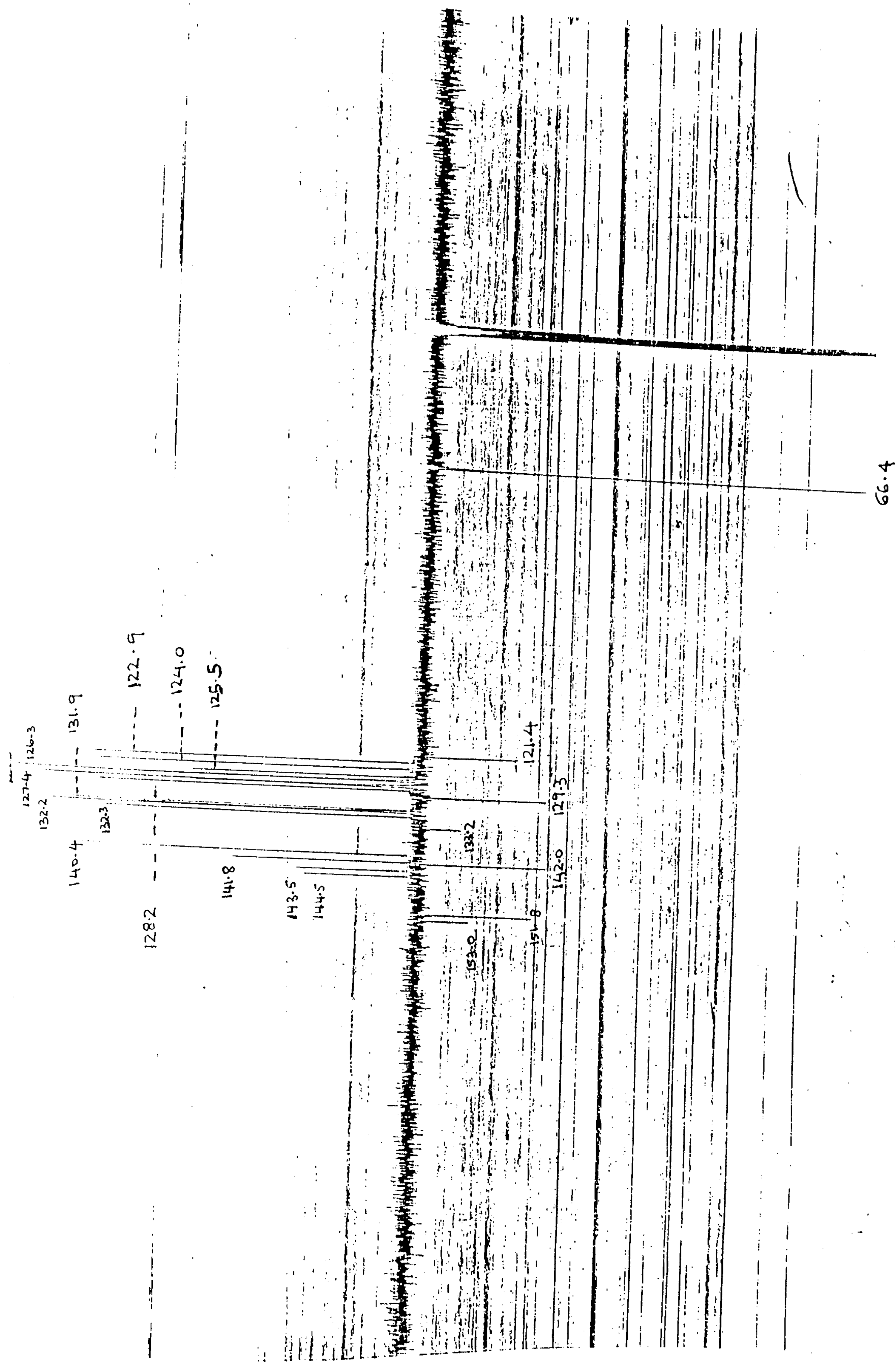


Fig 6.3: $^{13}C[^{1}H]$ NMR spectrum of compound(1).

conductivity of the compound in DMSO (Table 6.1) is indeed close to the value expected for a 1:1 electrolyte.

The reaction of selenium tetrachloride with 2-(2-pyridyl)phenylmercury(II)chloride in either dioxane or chloroform followed a similar pattern except that no intermediates comparable to (1) or (6) were isolated, (eq. 6.4 and 6.5).

$$\mathrm{RHgCl} \xrightarrow[\text{dioxane}]{\mathrm{SeCl_4}} 3\ (\mathrm{RSe^+\ HgCl_3^-})\ 2\ \mathrm{CH_3CN} \qquad \text{(eq. 6.4)}$$

(4)

$$\mathrm{RHgCl} \xrightarrow[\text{chloroform}]{\mathrm{SeCl_4}} \mathrm{RSe^+\ HgCl_3^-} \qquad \text{(eq. 6.5)}$$

(5)

Compound (4) and (5) are considered as the trichloromercurate (II) analogous of compound (2) and (3). This implies that compound (5) is a 1:1 electrolyte in DMSO.

All these products (2, 3, 4 and 5) contain selenium (II), indicating that a redox process is involved in addition to the trans-metallation reaction.

Treatment of compounds (2) and (3) with hydrazine hydrate at room temperature gave selenium (IV) products, but no precipitate of either selenium or mercury was noted. This obversation led to the following proposal for the mechanism for the formation of the selenium (IV) product. The reduction of $HgBr_3^-$ to mercury (I) species occurs first with the release of halogen which then oxidises selenium (IV) (compound 7) as shown below.

$$RSe^+ \; HgBr_3^- \xrightarrow{NH_2NH_2} RSe^+ + \tfrac{1}{2}Hg_2Br_2 + Br_2 \qquad \text{(1st step)}$$

$$RSe^+ \xrightarrow{\frac{3}{2}\,Br_2} \underset{(7)}{RSeBr_3} \qquad \text{(2nd step)}$$

The initial synthetic objective was the preparation of p-ethoxyphenyl 2-(2-pyridyl)phenyl selenide, RR^1Se, the analogy of RR^1Te. A different synthetic approach was persued as opposed to the previous one used by Al-Salim,(64), since the reaction of phenetole with $SeCl_4$ gives $R_2^1SeCl_2$ (R^1 = p-ethoxyphenyl-) even when performed at 0°C. In an attempt to prepare RR^1Se by the reaction of R^1SeBr_3 (produced <u>in situ</u> from the reaction of $R_2^1Se_2$ and Br_2) with 2-(2-pyridyl)phenyl mercury(II) chloride, (RHgCl) it was discovered that when R_2Se_2 is treated with a six molar excess of bromine, rupture of the R^1Se bond occurs. The subsequent reaction with RHgCl gave a white compound (6) for which NMR showed the absence of the R^1 group.

Interestingly, both ^{1}H and ^{13}C (Table 6.2) NMR spectra of this compound are identical with set (**ii**) of compound (**1**) (Fig 6.4). A conductivity measurement in DMSO indicates a 1:1 electrolyte (Table 6.1). Treatment with an excess of hydrazine gave compound (**7**) from which elemental analysis also showed to be $RSeBr_3$.

The FAB mass spectrum of the compound (**6**) shows RSe^+ as the dominant fragment. The spectrum is also identical to that of compound (**2**). Some of the selected peaks from the compound (**2**) and (**6**) are given below.

Compound (**2**)

m/e = 460 R_3^+
m/e = 389 R_2Se^+
m/e = 355 RHg^+
m/e = 308 R_2^+
m/e = 234 RSe^+
m/e = 154 R^+

Compound (**6**)

m/e = 389 R_2Se^+
m/e = 307 R_2^+
m/e = 234 RSe^+
m/e = 154 R^+

$[^{204}Hg, Se^{80}]$

From this data it clearly shows that under the conditions of the FABMS experiment, compound (**6**) is converted to compound (**2**).

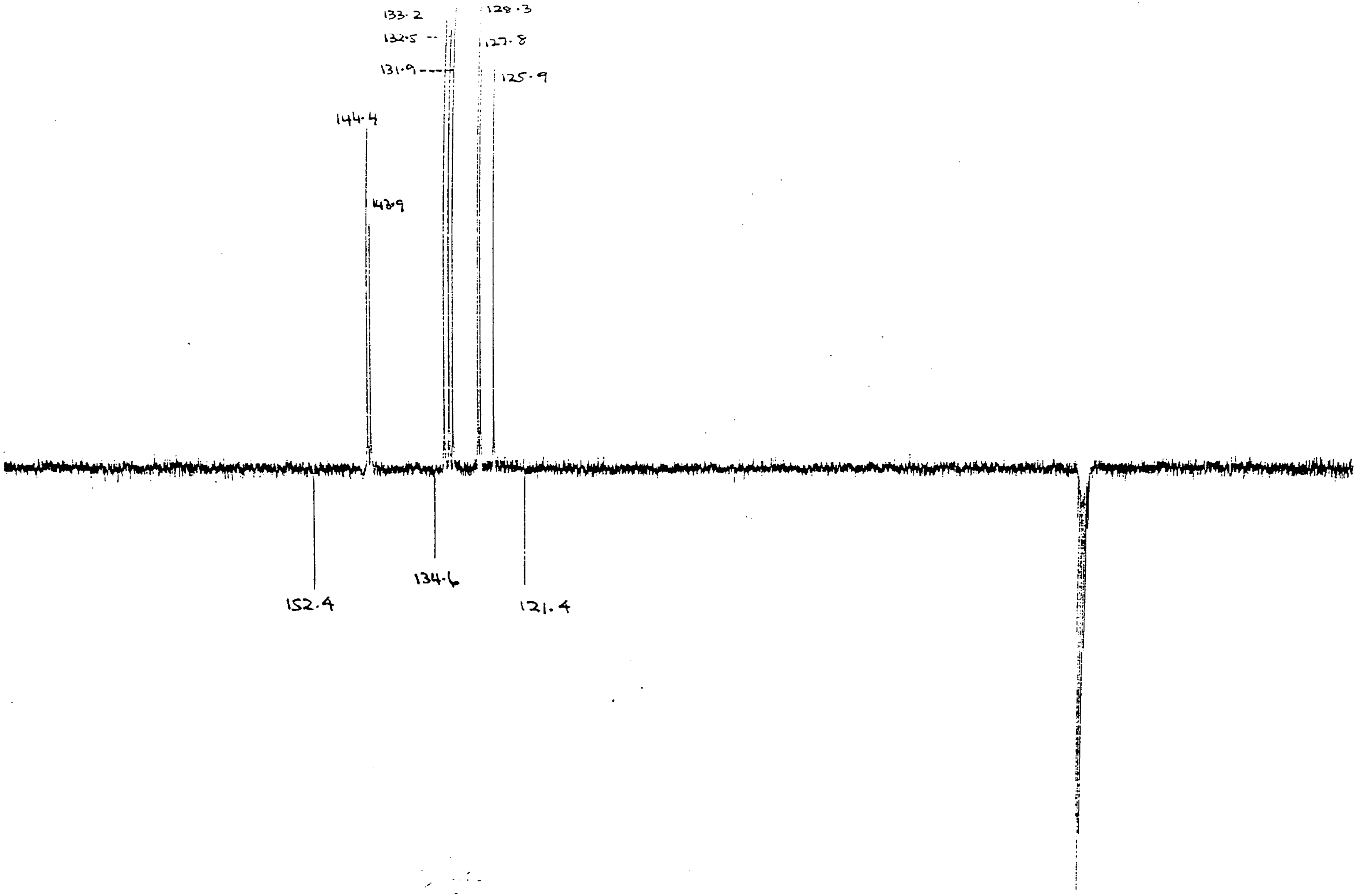
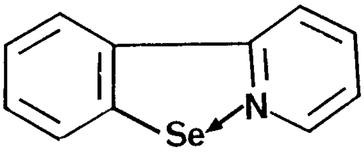


Fig 6.4: $^{13}C[^{1}H]$ NMR spectrum of compound(6).

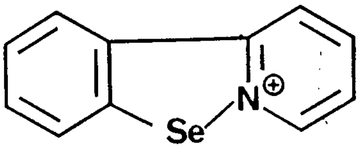
Since the NMR measurements and conductivity measurements for the compound (6) were both made in DMSO solutions, it is reasonable to assume that the data may relate to the same species. The conductivity measurement in DMSO showed a 1:1 electrolyte, therefore ionic model for compound (6) would be required. Two possible models are suggested:

(a) $RSe^+ HgBr_3^-$ (b) $RHg^+ SeBr_3^-$

Model (a) in which cannonical form (ii) is dominant would not be favoured to exist in equilibrium with the more thermodynamically stable form (iii) of compound (2) in solution, hence model (b) an extremely labile species is preferred.



(ii)



(iii)

According to these arguments, one may conclude that compound (1) can be formulated as a 1:1 mixture or inclusion compound of (2) and (6) in which some stability is conferred on the compound (6) component by dioxane - mercury co-ordination.

The synthesis of p-ethoxyphenyl 2-(2-pyridyl)phenyl selenide, RR^1Se was achieved by reacting "$RSeBr_3$" (produced in situ from the reaction of $R^1{}_2Se_2$ and Br_2 in exactly 1:1 ratio) with RHgCl. The ill defined white compound (8) on treatment with hydrazine hydrate gave compound (9) which analyses as RR^1Se.

6.3.2 Formation of chloro-p-ethoxyphenyl2-(2-pyridyl)phenyl tellurium(IV) trichloro-mercurate(II).

Reaction of p-ethoxyphenyltellurium (IV) trichloride (R^1TeCl_3) with 2-(2-pyridyl)phenylmercury(II)chloride(RHgCl) gave a compound from which elemental analysis, i.r. spectroscopy and m.p. agreed with that reported earlier.(64)

$$RHgCl + R^1TeCl_3 \longrightarrow [RR^1TeCl]\,[HgCl_3] \qquad (eq.\ 6.6)$$

Conductivity measurements (Table 6.1) showed the compound to be a 1:1 electrolyte.

The solution chemistry of this material via NMR studies showed interesting features: The ^{125}Te NMR spectrum (Fig 6.5) showed two peaks, the major one at δ = 1.056.4 ppm and the minor at 1059.1 ppm. It is known that tellurium chemical shifts of R_2TeXY species are sensitive to the electronegativity of X and Y;(75) the great similarity of

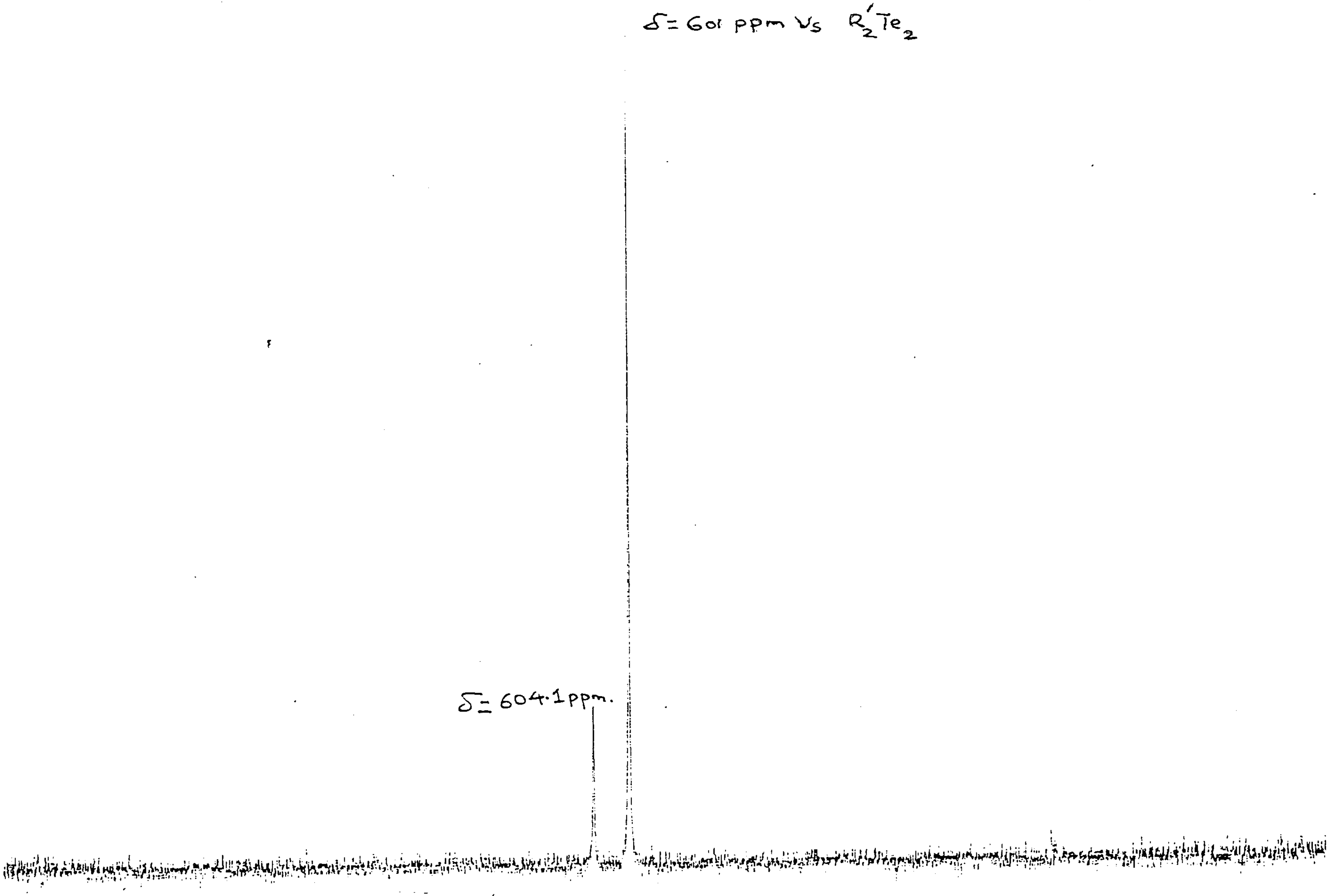


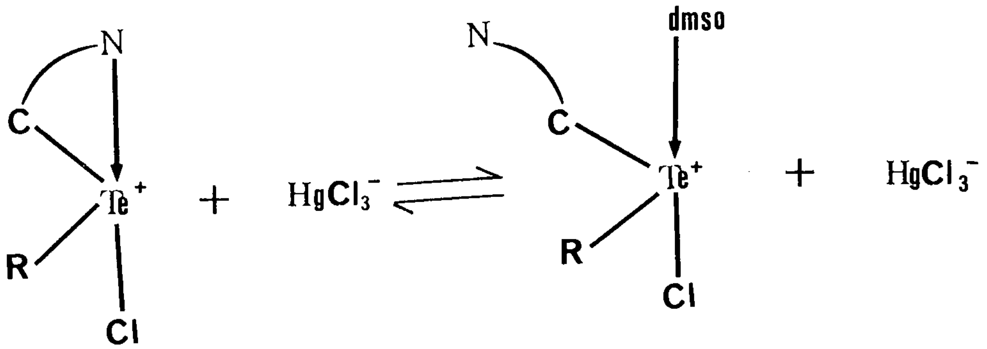
Fig 6.5: $^{125}Te[^1H]$ NMR of $[RR^1TeCl]^+[HgCl_3]^-$.

the values for the major and minor species imply therefore that the co-ordinated-nitrogen atom of the major species must be replaced by a ligand atom of similar electronegativity.

The ^1H NMR spectrum showed two environments for the 2-pyridyl-group, the major species showed the ortho-proton at $\delta = 9.133$ the minor at 8.968 ppm. The fact that proton ortho to nitrogen in the pyridine ring is more deshielded in the major solution species suggest this to be the ion with a co-ordinate Te $\longrightarrow$ N bond.

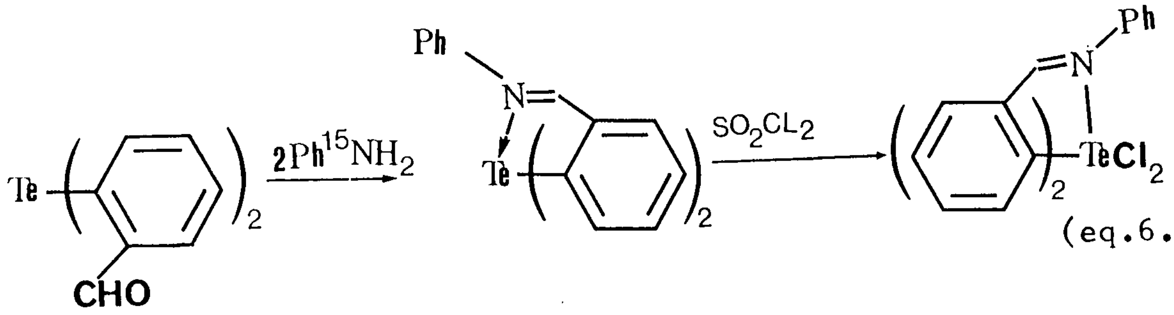
The ^{199}Hg NMR spectrum showed a single resonance at $\delta = 371$ ppm indicating the presence of a single chloromercurate(II) species.

According to all this evidence, the NMR data are consistent with the following equilibrium in DMSO solution (eq.6.7)



(eq.6.7)

The observation of a telluronium compound stabilized by intra-molecular co-ordination of nitrogen has also been described by Minkin et al(107) in the reaction (eq. 6.8)



(eq.6.8)

(iv) (v)

in which intra-molecular co-ordination of nitrogen in both (iv) and (v) was demonstrated by the observation of ^{125}Te - ^{15}N spin-spin coupling (61Hz for (iv), 122 Hz for (v))

6.3.3 Vibrational Spectroscopy.

Infra-red spectra for KBr discs and nujol mulls in CsI supports were obtained with a Perkin Elmer FTIR 1710 instrument.

The i.r. spectrum of compound (**1**) is shown in Figure 6.6. By comparing the i.r. spectrum of compound (**1**) with that of compound (**2**) (Figure 6.7) without dioxane, the bands in the region between 2766-2992cm^{-1} are characteristic of CH stretching arising from dioxane. The strong bands at 1112 and 868cm^{-1} could be attributed to C-O-C asymmetric and symmetric stretching. The i.r. of free dioxane has been investigated by Malherbe and Bernstein(108) and who assigned CH stretching in the region 2855-2966cm^{-1} and C-O-C asymmetric and symmetric stretching at 874 and 1127cm^{-1} respectively. The lowering of frequencies of some absorption bands particularly that of C-O-C stretching vibration in the compound (**1**) provide good evidence for the absence of free dioxane. It has been mentioned earlier that compound (**1**) could be an inclusion compound of (**2**) and (**6**) in which component (**6**) is possibly stabilised by dioxane-mercury co-ordination. The i.r. spectrum of compound (**1**) shows only a small change in C-O-C frequencies from that of free dioxane, indicating that the dioxane-mercury interaction to be very weak. Indeed the X-ray structure determination on Hg(dioxane)Cl_2 has shown the $HgCl_2$ and

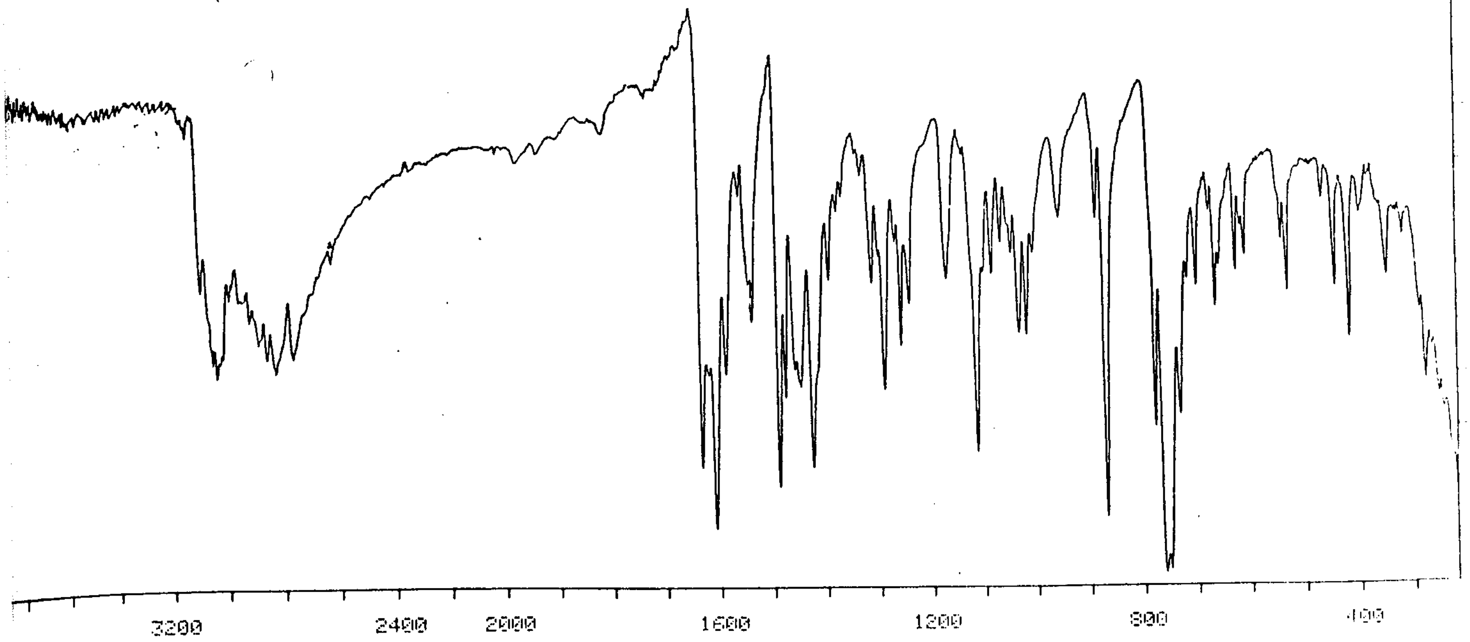


Fig 6.6: I.R. spectrum of compound (1).

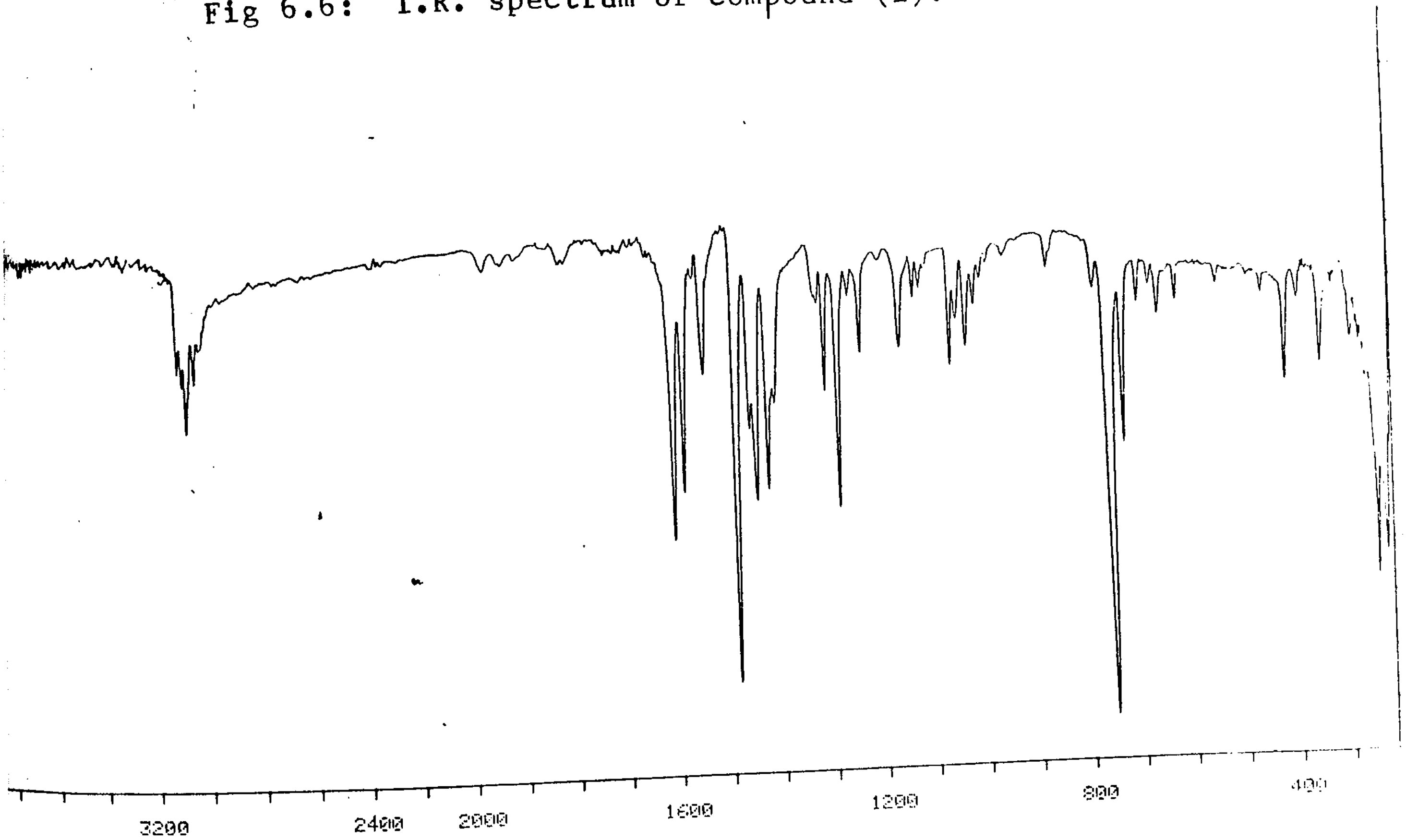


Fig 6.7: I.R. spectrum of compound (2).

dioxane molecules to be linked together by weak O-Hg-O bands to make a planar chain and that mercury(II) chloride and dioxane molecules retain a similar configuration to those in the free molecules even in the crystalline state.(109)

The i.r. spectrum of compound (4) showed a band at 2252cm^{-1} characteristic of the $-C{\equiv}N$ stretching which is compatible with the elemental analysis showing the presence of acetonitrile. With regard to the question whether Se-N coordination occurs as evidenced by the X-ray structure for compound (2), the i.r. data are not very informative. The ν(C=N) band at 1587cm^{-1} found in the 2-(2-pyridyl)phenyl mercury(II) chloride is almost unchanged in the compound (2), and the rest of selenium compounds discussed in this chapter.

6.3.4 N.M.R. Spectroscopy.

The ^{13}C NMR data of the new selenium compounds are presented in Table 6.2. Some of the spectra observed are shown in Figures 6.8-6.12. ^{13}C chemical shift assignments were based on comparison with suitable model compounds,(64,72,74) as well as on consideration of peak intensity.

The trans-selenation of mercurated compound was confirmed by the change in the position of some signals from that of the mercurated compound. Mercuration of the 2-phenylpyridine

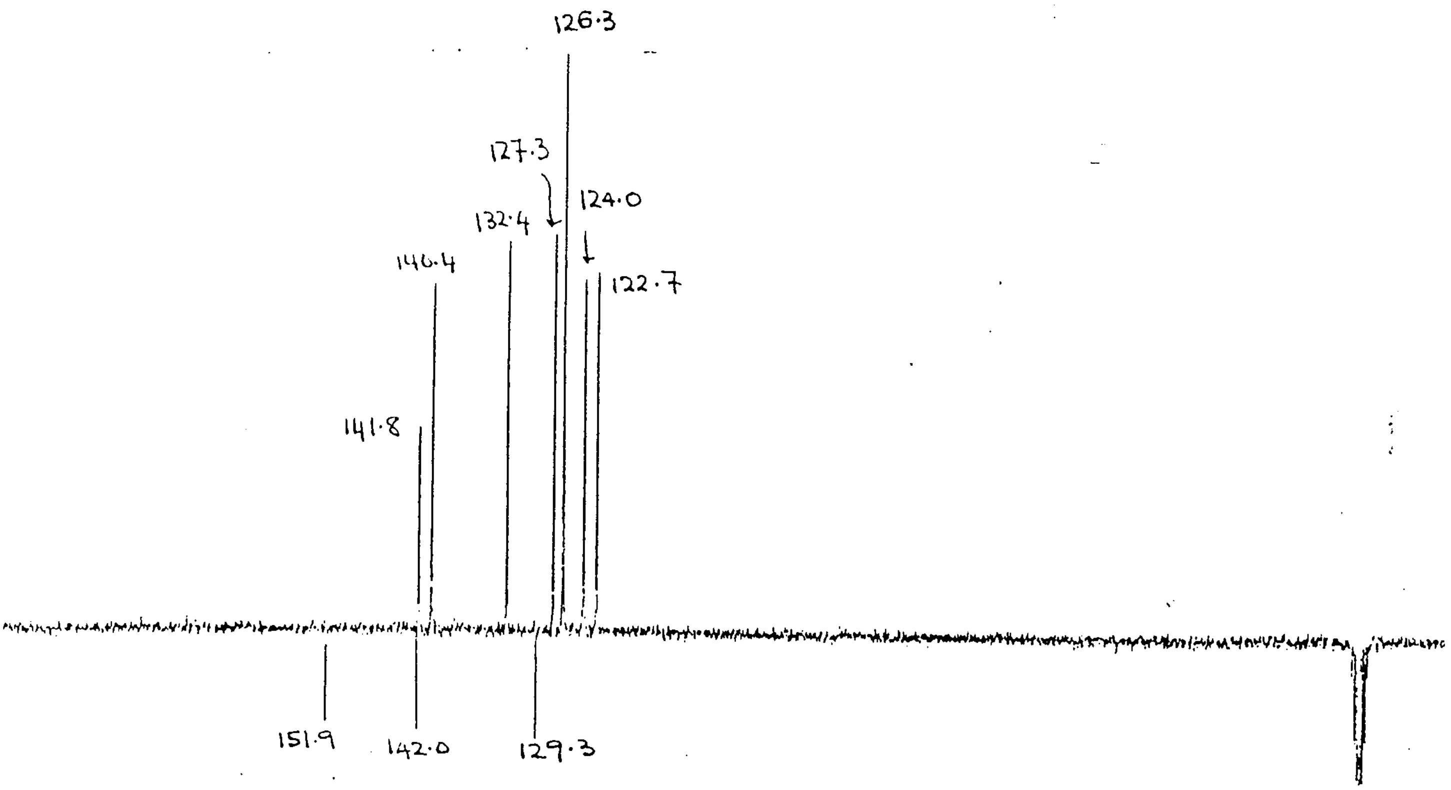


Fig 6.8: $^{13}C[^1H]$ NMR spectrum of compound (2).

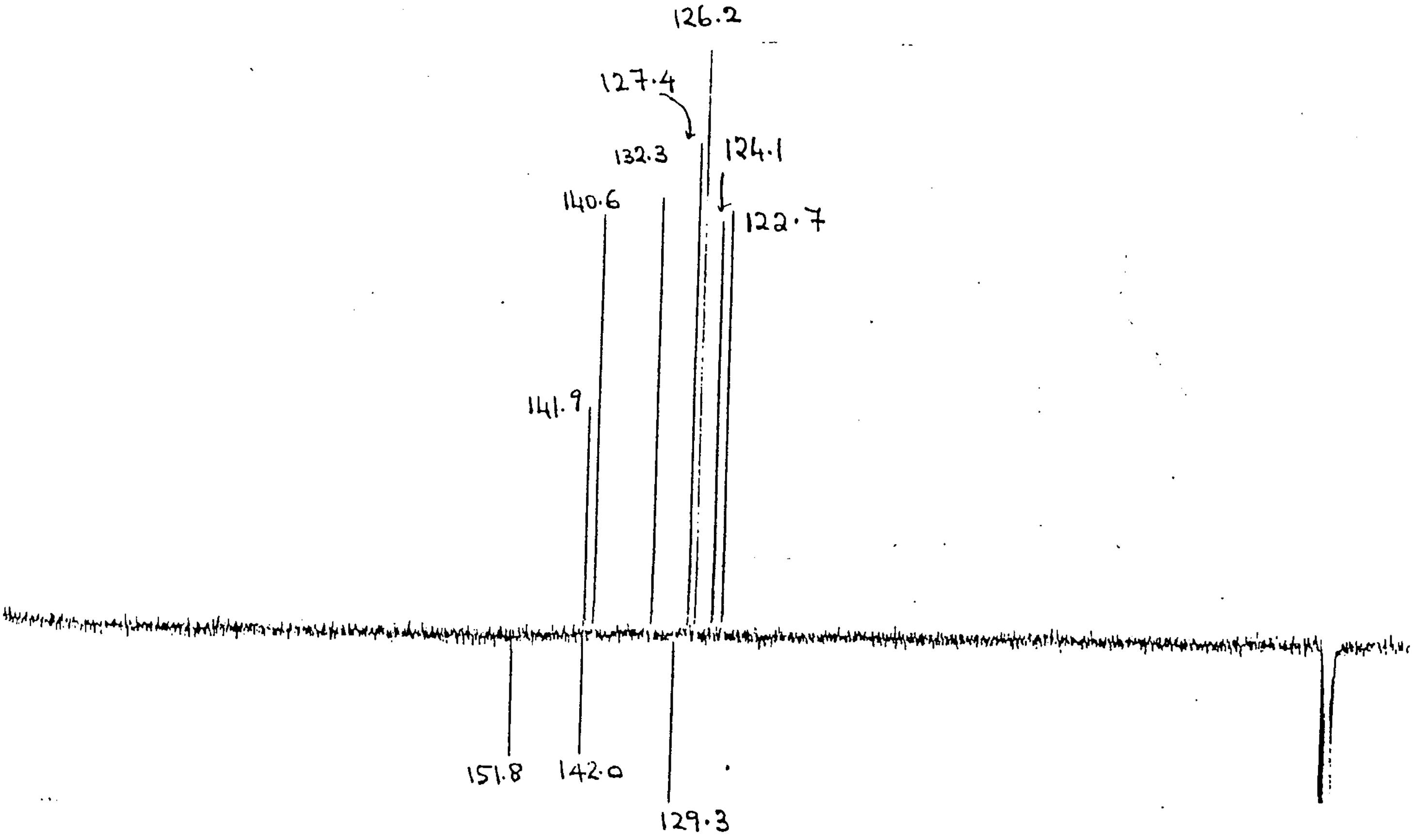


Fig 6.9: $^{13}C[^1H]$ NMR spectrum of compound (3).

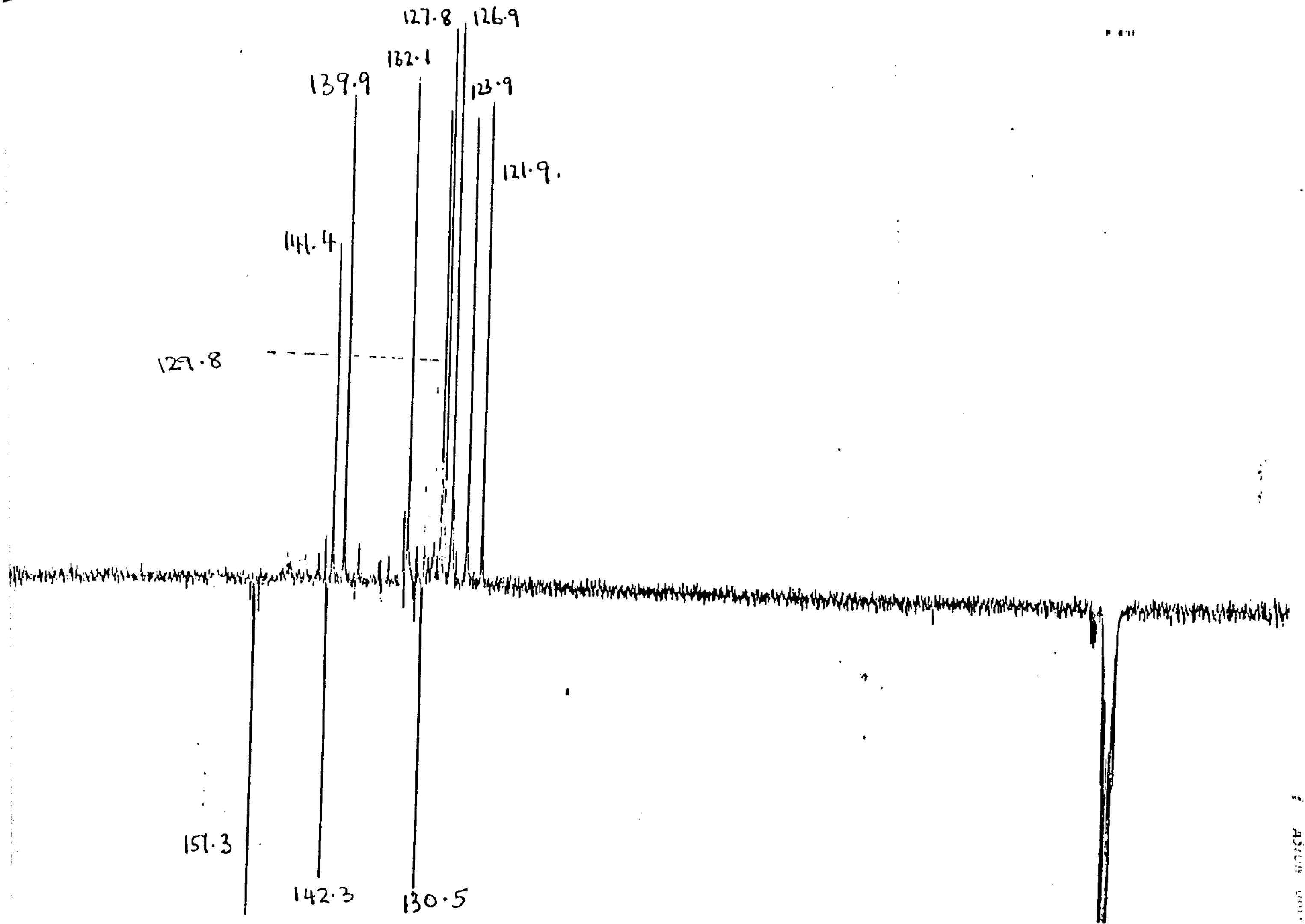


Fig 6.10: $^{13}C[^{1}H]$ NMR spectrum of compound (5).

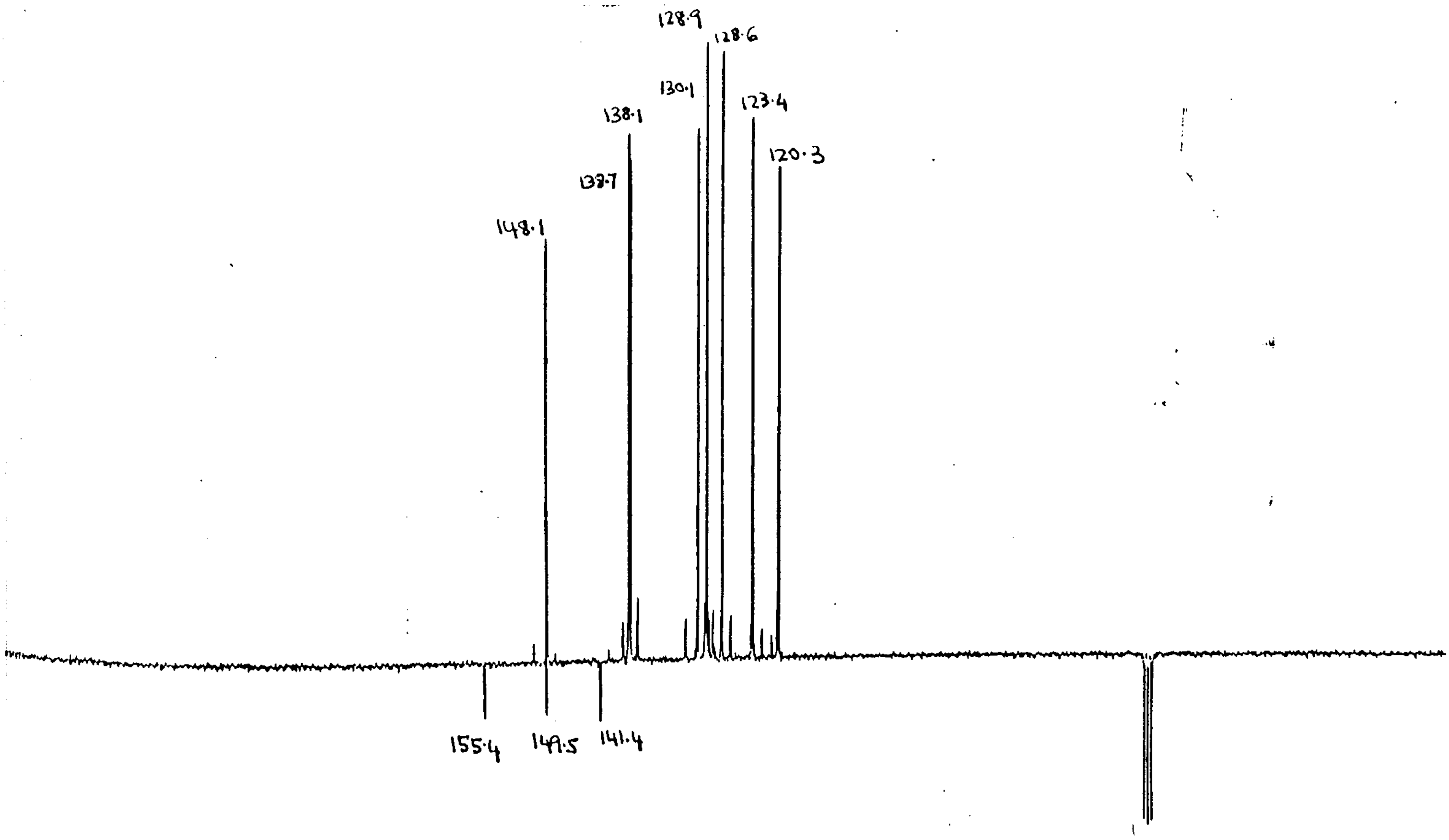


Fig 6.11: $^{13}C[^{1}H]$ NMR spectrum of compound (4).

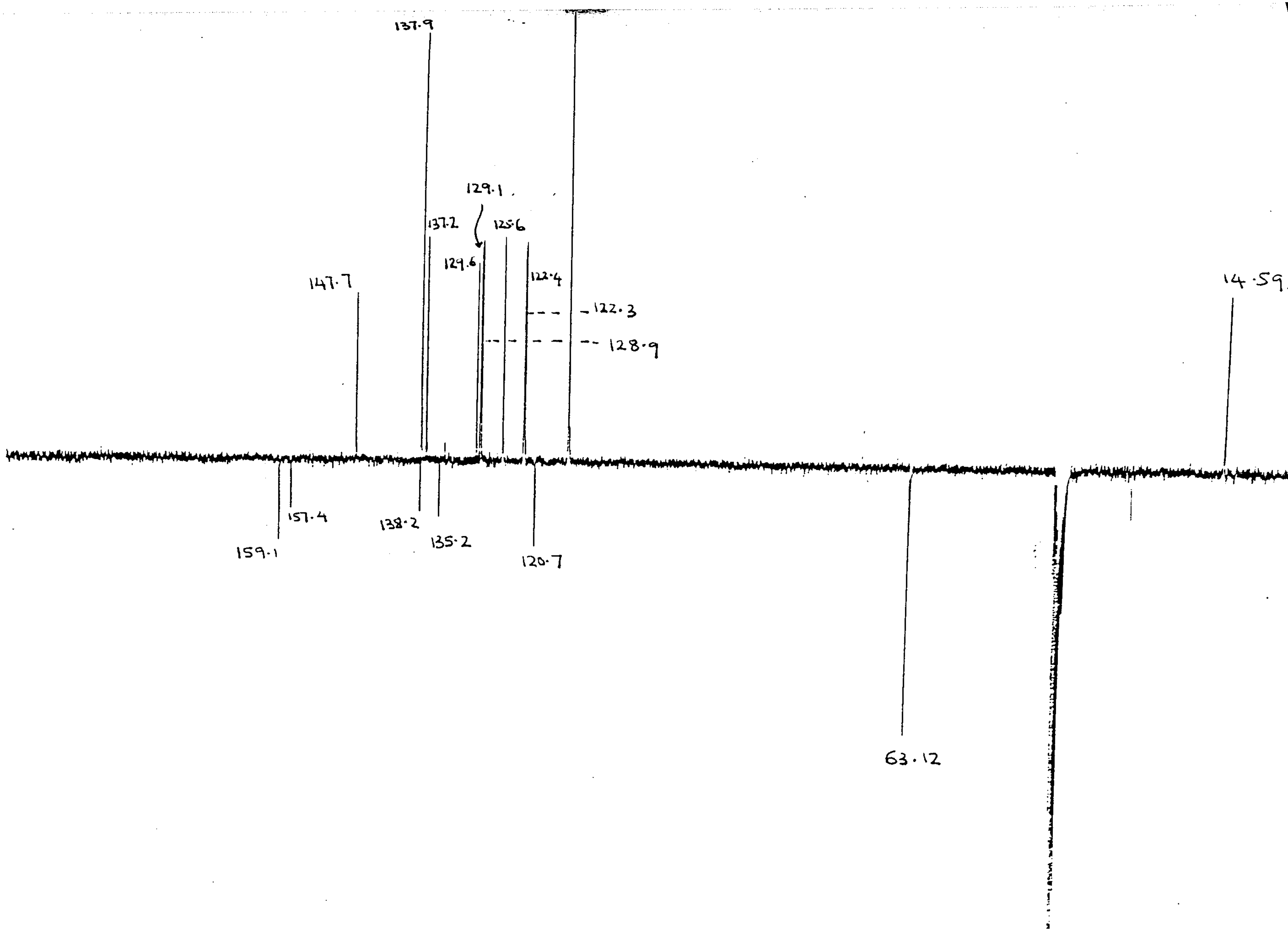


Fig 6.12: $^{13}C[^{1}H]$ NMR spectrum of compound (9).

shows a downfield (ca. 22 ppm) for the carbon atom bonded to mercury. Similar observations have been reported by Al-Salim.(64)

In general, the resonance of selenated carbon and those in ortho and para positions experience a small highfield shift while the chemical shift of meta-carbons are very similar to those of mercurated compounds.

The resonances of the carbons ortho and para to nitrogen in the pyridine ring are more sensitive to the presence of selenium than mercury, reflecting a stronger N-Se than N-Hg interaction in these new selenium compounds.

The ^{13}C NMR spectrum of compound (**1**) (Figure 6.3) shows some points of interest. It shows two environments for R (1:1) denoted as (**i**) and (**ii**) (Table 6.2). The alphatic region contains ^{13}C resonances assignable to $-CH_2$ (66.2 ppm) confirming the presence of dioxane in the structure as indicated in the molecular formula (Table 6.1).

An initial thought was that, since RHgCl (R=2-phenylpyridine) is a tetramer,(100) there was a possibility of one molecule of RHgCl being trans-metallated and another molecule still left attached in the system. This would result in having 2"R" of different environments. Comparison of the ^{13}C of the two species (**i**) and (**ii**) (Table 6.2) with that of RHgCl showed no similarities. Interestingly, the ^{13}C NMR of one species (**ii**) of compound (**1**) was similar to that of compound (**6**), making it necessary to formulate compound (**1**) as a mixture (or an inclusion compound) of (**6**) and species (**i**) which is the same as compound (**2**).

The ^{1}H NMR spectrum of compound (**1**) (Figure 6.2) revealed a singlet at 3.53 ppm due to the resonance of $-OCH_2$ protons of the dioxane. The integral ratio showed R: dioxane of 1:0.5 compatible with the formulation (Table 6.1).

The ^{13}C NMR data of compounds, (**2**) and (**3**) (Table 6.2) showed similarities with that of species (**i**) in compound (**1**). The carbon ortho to nitrogen in the pyridine ring shifted some 8 ppm to higher field compared to the corresponding base. If compared with the similar carbon atom in the selenide compound (**9**) in which a shift of only 1 ppm to higher field was indicated, it clearly demonstrated the stronger Se-N interaction in compound (**2**) than compound (**9**). Indeed this observation is supported by the crystal and molecular structure of these compounds where the Se-N bond length in compound (**2**) can be interpeted as a strong co-ordinate interaction, whilst that in compound (**9**) show to be a weak interaction.

The ^{13}C NMR spectrum of p-ethoxyphenyl 2-(2-pyridyl)phenyl selenide (Figure 6.12) was assigned following the

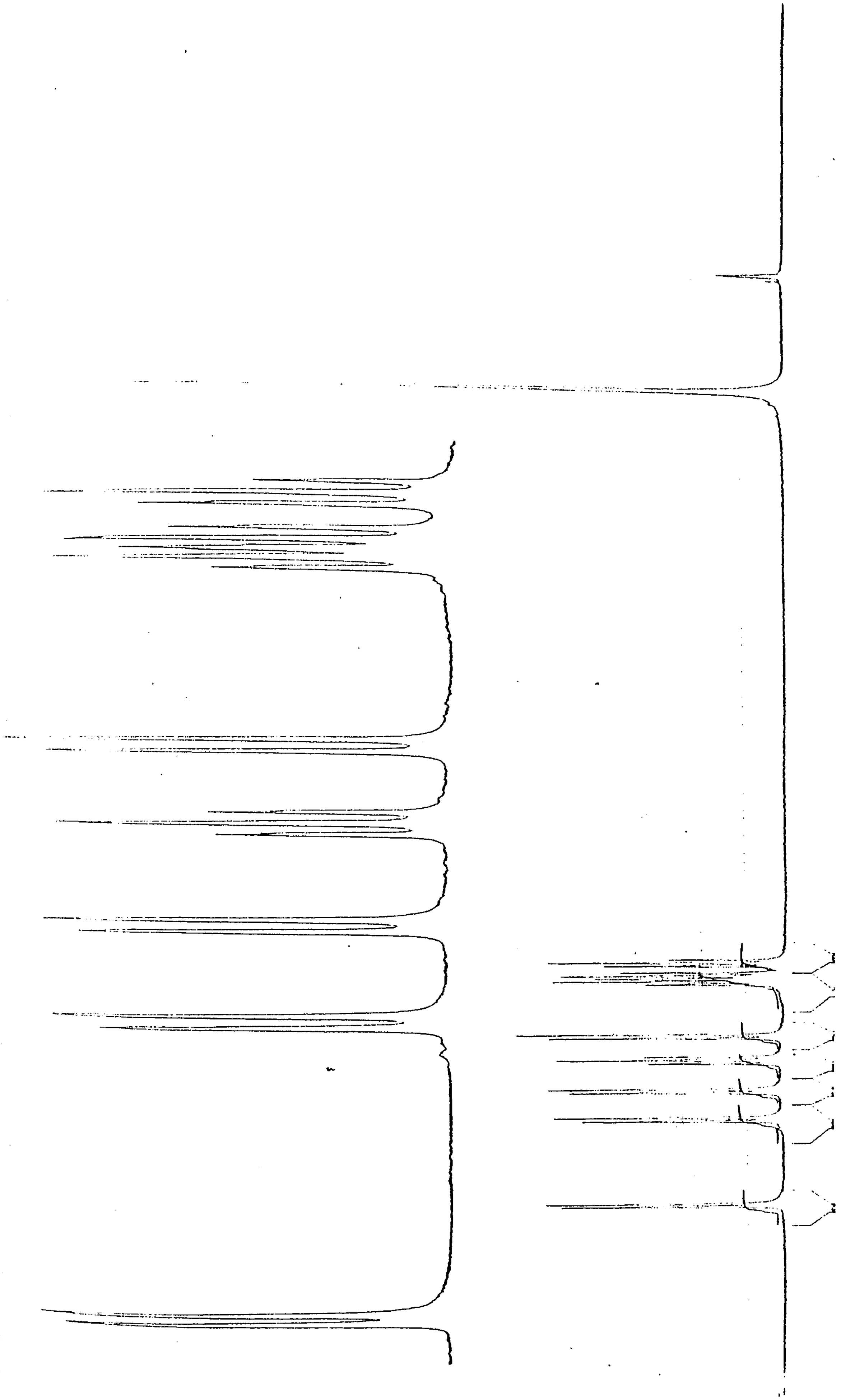


Fig 6.13: ^{1}H NMR spectrum of compound (3).

literature,(21,72) and by comparison with the other pyridyl derivatives.(64) The aliphatic region at 63.1 ppm is assigned to $-OCH_2$ and 14.6 ppm assigned to $-CH_3$ which are in good agreement with values found in the literature.(66) The ^1H NMR spectrum (Figure 6.14) revealed proton signals of the ethoxy group. The triplet signal centred at 1.33 ppm is assigned to the resonance of $-CH_3$ protons and the quartet, centred at 4.03 ppm is assigned to OCH_2-protons.

The spectra of other compounds in Table 6.2 were assigned according to the literature and by comparison with other pyridyl derivatives.(64,72)

The ^{199}Hg NMR spectra were recorded in DMSO (Table 6.3) using mercury(II) chloride as an external standard. The ^{199}Hg NMR spectra of compounds (2) and (5) (Figure 6.15 and 6.16) both showed single resonance at $\delta = -274.3$ ppm and 347.6 ppm respectively, implying the presence of single mercury(II) species in these compounds. The highfield chemical shift for Hg in compound (2) compared to (5) demonstrates the strong shielding effect of the larger bromine atom than chlorine, together with the electronegativity difference between these two atoms in which chlorine being more electronegative than bromine withdraws more electrons than bromine.

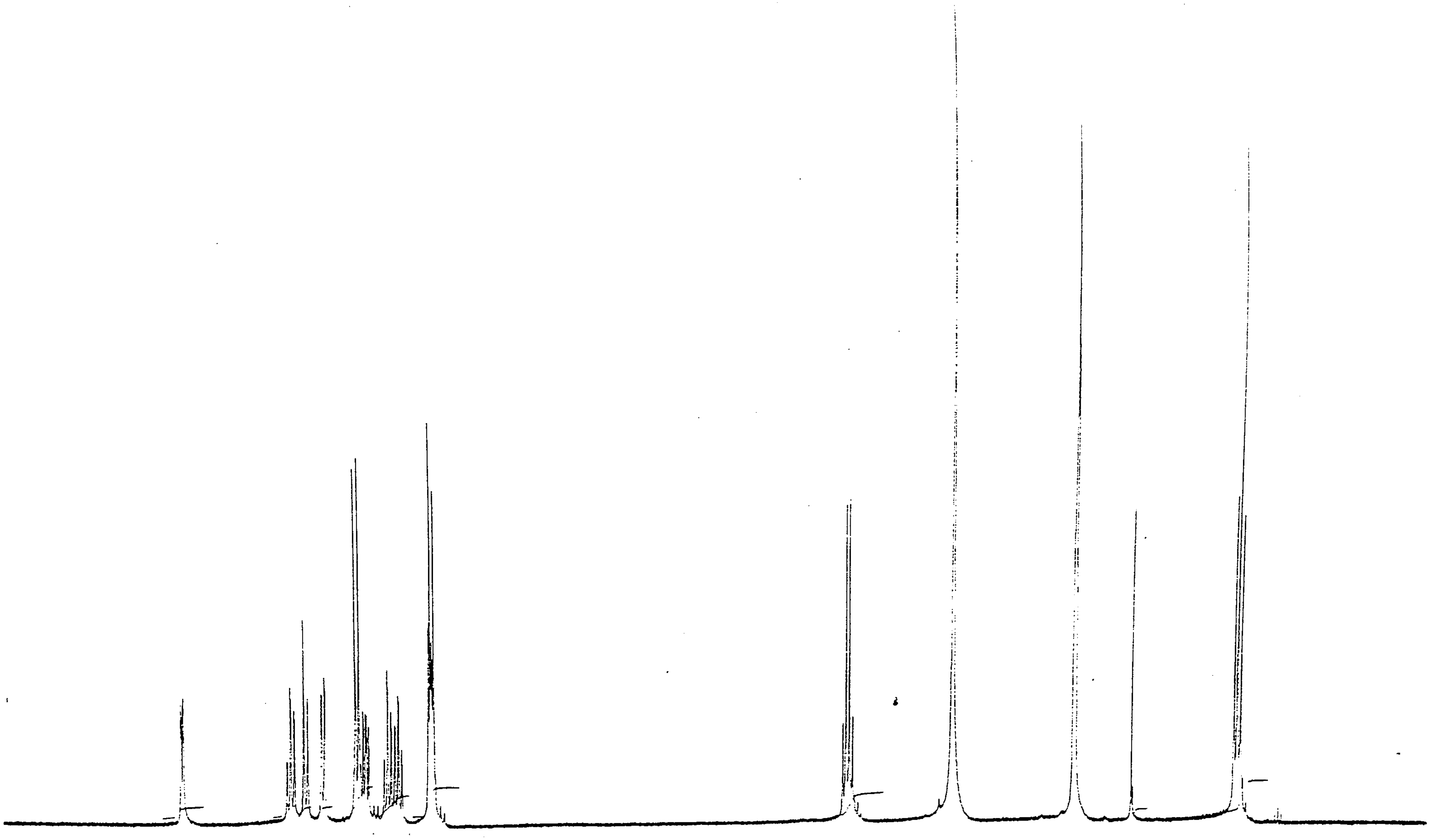


Fig 6.14: ^{1}H NMR spectrum of compound (9).

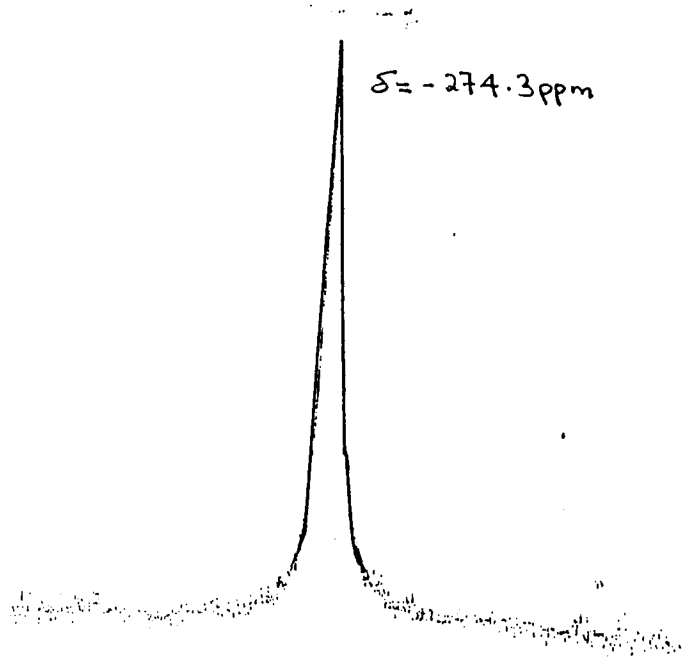


Fig 6.15: ^{199}Hg[^{1}H] NMR spectrum of compound (3).

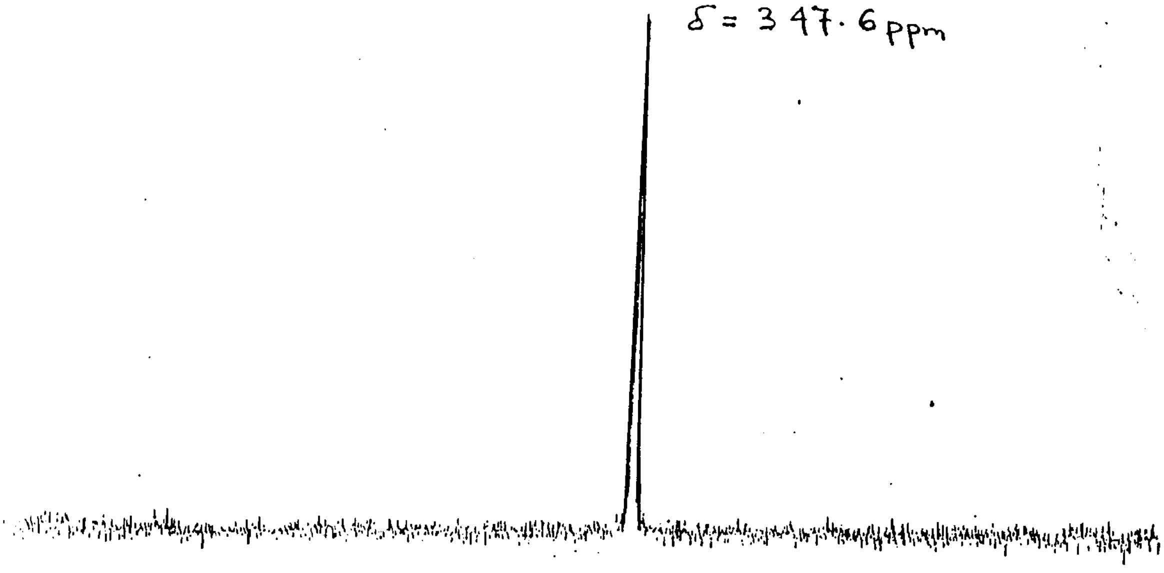


Fig 6.16: ^{199}Hg[^{1}H] NMR spectrum of compound (5).

6.3.5 The Crystal and Molecular Structure of 2-(2-Pyridyl) phenyl selenium(II) Tribromomercurate(II).*

The structure of the compound (Figure 6.17) consists of discreet cations and bromomercurate anions. The bond length and angles are listed in Table 6.4. Stereoscopic packing diagram showing the co-ordination about mercury(II) is given in Fig 6.18. The co-ordination about selenium is essentially distorted tetrahedral. The small value of the angle NC(1)-Se(1)-NC(1) [84(2)°] is due to the constraint of the five-membered chelate ring. Due to disorder within the structure, it was not possible to distinguish between the nitrogen atom and the carbon atom bonded to selenium, hence the NC-Se distances are equivalent (1.91(3)A°). The distance Se-C (1.91(3)A°) is in close agremeent with the sum of the Pauling(58) single bond covalent radii of Se (1.14A°) and sp^2 hybridised carbon (0.74A°) and with values in the structure of 9,10 diselenoanthracene(110) in which Se-C is in the range 1.897(5)-1.908(5)A°. The Se-N distance of 1.91(3)A° is longer than the sum of covalent radii (1.86A°)(58) but shorter than that reported for non-

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* Single crystal X-ray crystallography was done in co-operation with M. Greaves of our group at Aston University

Hg(1) --- Br(1)	2.518 (6)	C(2) --- C(3)	1.53 (6)
Hg(1) --- Br(2)	2.492 (8)	C(3) --- C(4)	1.22 (6)
Se(1) --- NC(1)	1.91 (3)	C(4) --- C(5)	1.39 (7)
NC(1) --- C(2)	1.33 (5)	C(5) --- C(6)	1.37 (6)
NC(1) --- C(6)	1.29 (5)	C(2) --- C(2')	1.41 (7)
Br(1) -Hg(1) -Br(2)	121.9 (2)	NC(1) -C(2) -C(2')	115 (4)
Br(1) -Hg(1) -Br(1')	116.2 (3)	C(3) -C(2) -C(2')	131 (4)
NC(1) -Se(1) -NC(1')	84 (2)	C(2) -C(3) -C(4)	123 (5)
Se(1) -NC(1) -C(2)	113 (2)	C(3) -C(4) -C(5)	121 (5)
Se(1) -NC(1) -C(6)	126 (3)	C(4) -C(5) -C(6)	117 (6)
C(2) -NC(1) -C(6)	121 (3)	NC(1) -C(6) -C(5)	124 (4)
NC(1) -C(2) -C(3)	114 (3)		

Table 6.4: Bond lengths (A^{o}) and bond angles (^{o}) with e.s.d.'s in parentheses.

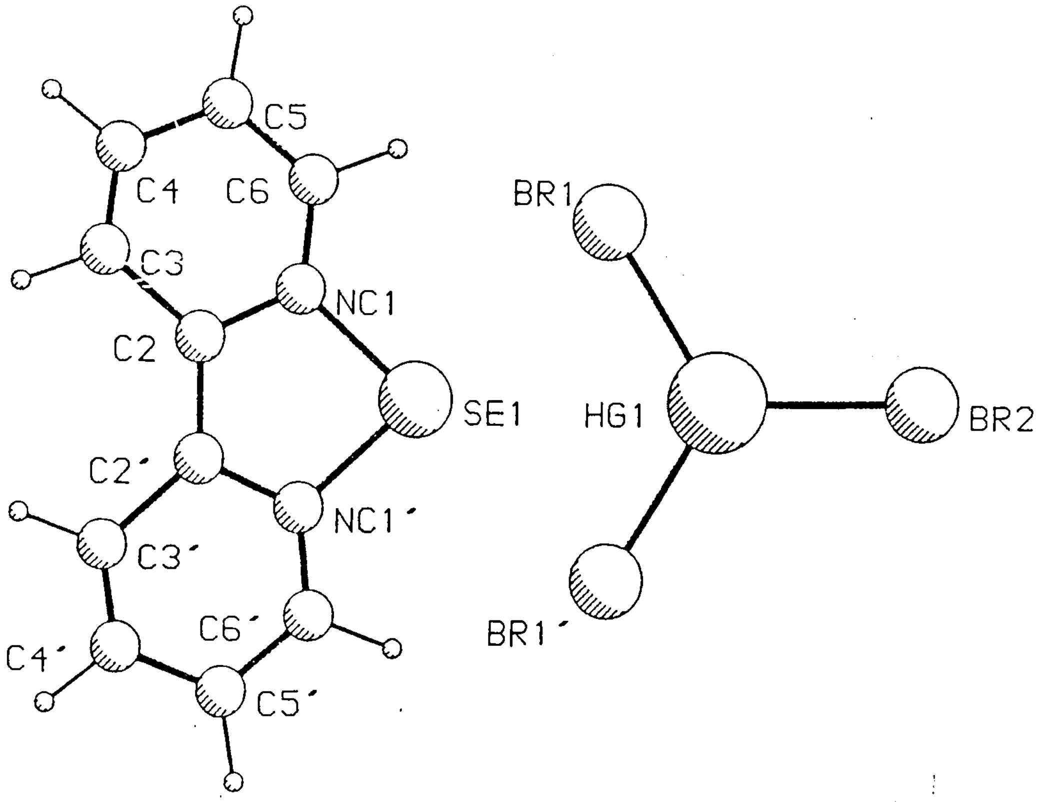


Fig 6.17: The molecular structure of 2-(2-pyridyl)phenyl selenium(II)tribromomercurate(II).

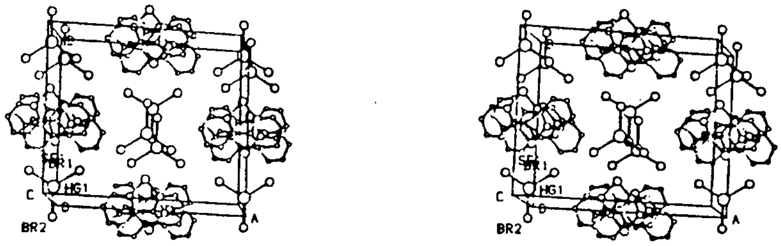
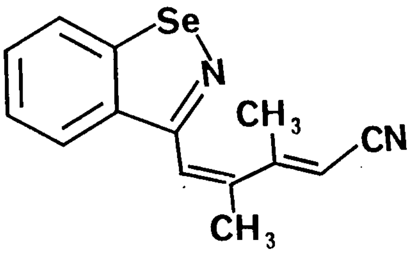


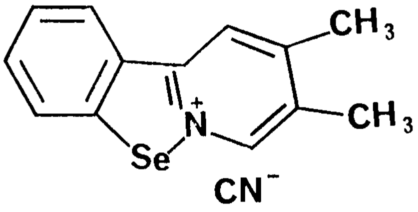
Fig 6.18: Stereoscopic packing diagram showing the co-ordination about mercury(II).

bonded Se——N interaction $SeOCl_2.2C_5H_5N$ (2.196 and 2.206A°)(111) and p-ethoxyphenyl2-(2-pyridyl)phenyl selenide (2.813(6)A°) (see section 6.3.6.) indicating a stronger interaction in this case. In the analogous compound,5-(1-2 benzoselenazo(-3-yl)-3,4-dimethylpenta-dienonitrile, the Se-N bond distance is 1.8333(7)A°.(102) The interaction betwen selenium and the pyridyl nitrogen atom holds the organic ligand in a planar geometry.

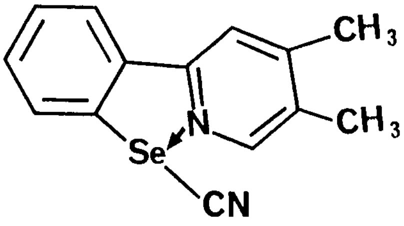
The Hg-Br distances (2.518(6) and 2.492(8)A) are in agreement with analogous Hg-Br in tetramethylammonium mercury(II)tribromide (2.48-2.56A°) and bis(tetramethylammonium)tetrabromo-mercury(II)(112)[2.585(3)-2.587(3)A°]. The co-ordination geometry about Hg is trigonal bypyramidal. There is a secondary intermolecular interaction between Se----Br(1) of 3.21A°, which is longer than the sum of covalent radii (2.31A°) but shorter than the Van der Waals distance of 3.75A°(58) implying a moderately strong secondary interaction. An intermediate (VIII) has also been postulated in the conversion of (VII) to (IX).(102)



(vii)



(viii)



(ix)

6.3.6 The Crystal and Molecular structure of p-Ethoxyphenyl 2-(2-pyridyl)phenyl selenide.

Crystallographic data obtained by standard methods(113) were obtained from Dr Edward R.T. Tiekink, Jordan Laboratories, Departmental of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia, 5001 (Australia).

Crystal data.

$C_{19}H_{17}NOSe$, M.W. = 354.3

Monoclinics, space group $\underline{PZ_i}/\underline{C}$ = 10.3

$\underline{a}$ = 9.268(1) $\underline{b}$ = 19.083(2)

β = 114.59(1)^{o} $\underline{V}$ = 1666.1A^{o3}

Z = 4 D_c = 1.413gcm^{-3}

F (000) = 1272 μ = 22.03

The bond lengths and bond angles are given in Tables 6.5

The crystal structure of this compound (Figure 6.19) comprised discrete diorganoselenium molecules with the selenium atom coordinated by two different organo groups: The Se-C(1) 1.932(4) and Se-C(12) 1.929(4) bond distances found in this compound are similar to the Se-C (Ph) bond distances found in the structure of [Ph_2Se_2] [acac], (acac is the dinegative MeC (=O) CC (=O)Me anion) which lie in the range 1.910(6)-1.927(5)A° but shorter than the Se-C (methine) bonds of 1.961(5)-1.991(5)A° in this compound and 1.965(3) and 1.981(3)A° found in [$Se(acac)]_2$.(114) The C(1)-Se-C(12) bond angle is 98.2(20) which is greater than that found (94.8(2)) in the analogous tellurium compound p-ethoxyphenyl 2-(2-pyridyl)phenyl telluride(64)(RR^1Te). This agrees well with the trend in electronegativity on the Periodic table, i.e. the electronegatvity decreases down the group. The co-ordination geometry about selenium is consistent with the presence of two stereochemically active lone-pairs of electrons.

The Se----N distance is 2.813(0)A° which is much greater than the sum the covalent radii (1.87°A) but is well within the sum of Van der Waals radii of 3.5A°(58) for these atoms.

The important feature of the present ligand is that although the Se----N distance is within the Van der Waals distance

Se-C(1)	1.932(4)	Se-C(12)	1.929(4)
C(1)-C(2)	1.391(5)	C(2)-C(3)	1.385(6)
C(3)-C(4)	1.373(6)	C(4)-C(5)	1.370(6)
C(5)-C(6)	1.385(5)	C(1)-C(6)	1.402(5)
C(6)-C(7)	1.474(5)	N(1)-C(7)	1.331(5)
C(7)-C(8)	1.396(5)	C(8)-C(9)	1.369(7)
C(9)-C(10)	1.358(7)	N(1)-C(11)	1.344(5)
C(10)-C(11)	1.367(6)	C(12)-C(13)	1.386(5)
C(13)-C(14)	1.368(5)	C(14)-C(15)	1.385(5)
C(15)-C(16)	1.383(5)	C(16)-C(17)	1.379(6)
C(12)-C(17)	1.376(5)	O(1)-C(15)	1.365(4)
O(1)-C(18)	1.429(4)	C(18)-C(19)	1.477(6)
C(1)-Se-C(12)	98.2(2)	Se-C(1)-C(2)	119.7(3)
Se-C(1)-C(6)	120.7(3)	C(1)-C(6)-C(7)	122.3(3)
N(1)-C(7)-C(6)	116.3(3)	C(6)-C(7)-C(8)	122.6(4)
C(7)-N(1)-C(11)	118.3(4)	Se-C(12)-C(13)	120.6(3)
Se-C(12)-C(17)	121.7(3)		

Table 6.5. Selected bond distances (A^{o}) and angles(^{o}) for p-ethoxyphenyl 2-(2-pyridyl) selenide.

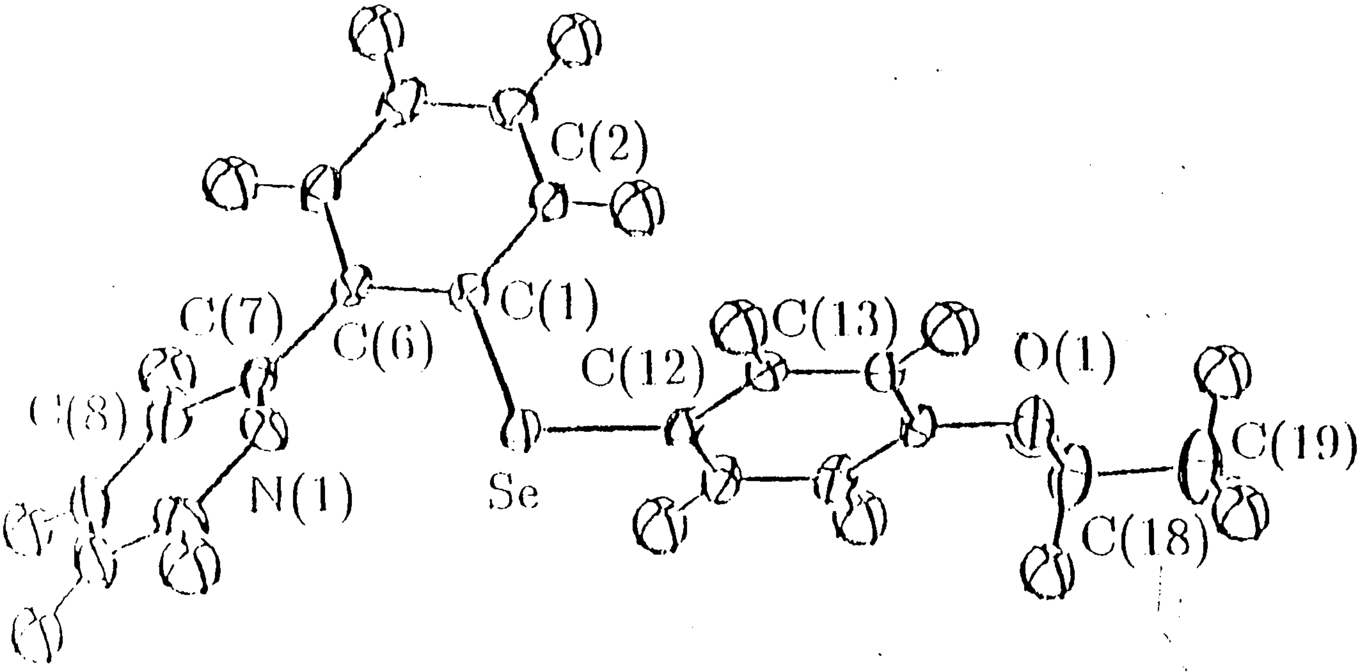


Fig 6.19: The molecular structure of p-ethoxyphenyl2-(2-pyridyl)phenyl selenide.

indicating a weak interaction between the two atoms, the structure shows there is a twist about the C(6)-C(7) bond such that the nitrogen atom is directed away from the selenium atom.

This may imply that the Se----N separation is not indicative of a significant interaction between these atoms as compared to the structure (Figure 6.20) of RR^{1}Te where Te----N was

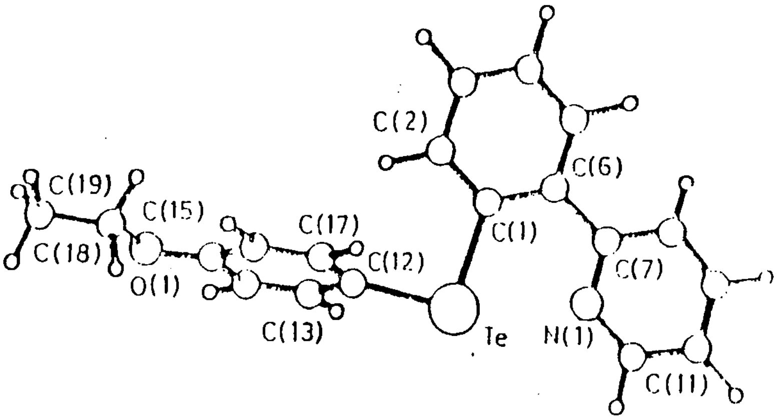


Fig 6.20: The molecular structure of p-ethoxyphenyl2-(2-pyridyl)phenyltelluride.

considered to constitute a three-co-ordinate RR^{1}Te----X involving nitrogen. This observation may be interpreted in terms of the Lewis acidity of the central atom (Te, or Se) in these two ligands RR^{1}Te and RR^{1}Se where the former will show greater Lewis acidity than the latter. Tellurium being more electropositive (metallic) than selenium will tend to attract electrons more readily than selenium. Indeed recently(section 6.3.7.) it has been noted that the Te----N separation in 2-(2-pyridyl)phenyl tellurium compound is sensitive to the group attached to the tellurium atom.

The p-ethoxyphenyl ligand is planar within experimental errors and forms a dihedral angle of 83.7° with the least-squares plane through C(1)-(C(6)

6.3.7 The Crystal and Molecular structure of Chloro-p-ethoxyphenyl-2-(2-pyridyl)phenyltelluronium(IV) trichloromercurate(II).

The structure determination was carried out using standard methods(115) at the University of Western Australia, Nedlands, Perth, Western Australia, 6009 in collaboration with Dr. Allan H. White.

Crystal data

$[C_{19}H_{17}ClNOTe]^{+}[HgCl_3]^{-}$, $\underline{M}$ = 745.4

Orthorhombic, space group Pbca (D_{2h}^{15} NO.61)

$\underline{a}$ = 28.098(8) $\underline{b}$ = 20.694(4) $\underline{C}$ = 7.598(5)A°
$\underline{U}$ = 4418A^3 $\underline{D}_c$ ($\underline{Z}$ = 8) = 2.24gcm^{-3}
$\underline{F}$ (000) = 2768 μ_{MO} 84cm^{-1}, specimen: 0.02 x 0.06 x 0.44mm
$\underline{A}$* min, max = 1.18, 1.64.

Pertinent distances and angles are given in Table 6.6. The structure is given in Figure 6.21 showing unit cell contents and the cation and anion respectively.

The structure of this compound consists of discrete cations and chloromercurate anions. The co-ordination about tellurium can be considered as ψ-trigonal bipyramidal with N,Cl, axial and two Te-C bonds with the lone pair of electrons constituting the equatorial plane.

The Te-C(7) bond length is in agreement with the sum of the Pauling(58) covalent radii for Te(1.37A°) and sp^{2}C(0.74A°), but Te-C(1) is some 0.06A° shorter than the Pauling estimate. Short Te-C bonds have also been noted in phenoxatellurium 10, 10-bis(trifluoroacetate)(116) (2.07A°),

Distances (Å)		Angles (degrees)	
(i) The cation			
Te-Cl(4)	2.43(1)	Cl(4)-Te-C(1)	88.7(9)
Te-C(1)	2.05(3)	Cl(4)-Te-C(7)	91.5(8)
Te-C(7)	2.11(3)	Cl(4)-Te-N(18)	166.6(6)
Te-N(18)	2.31(2)	C(1)-Te-C(7)	101(2)
		C(1)-Te-N(18)	85(2)
		C(7)-Te-N(18)	78(1)
(ii) The anion			
Hg-Cl(1)	2.406(10)	Cl(1)-Hg-Cl(2)	124.9(3)
Hg-Cl(2)	2.400(8)	Cl(1)-Hg-Cl(3)	120.5(3)
Hg-Cl(3)	2.434(10)	Cl(2)-Hg-Cl(3)	114.2(3)

Table 6.6 Metal atom environments.

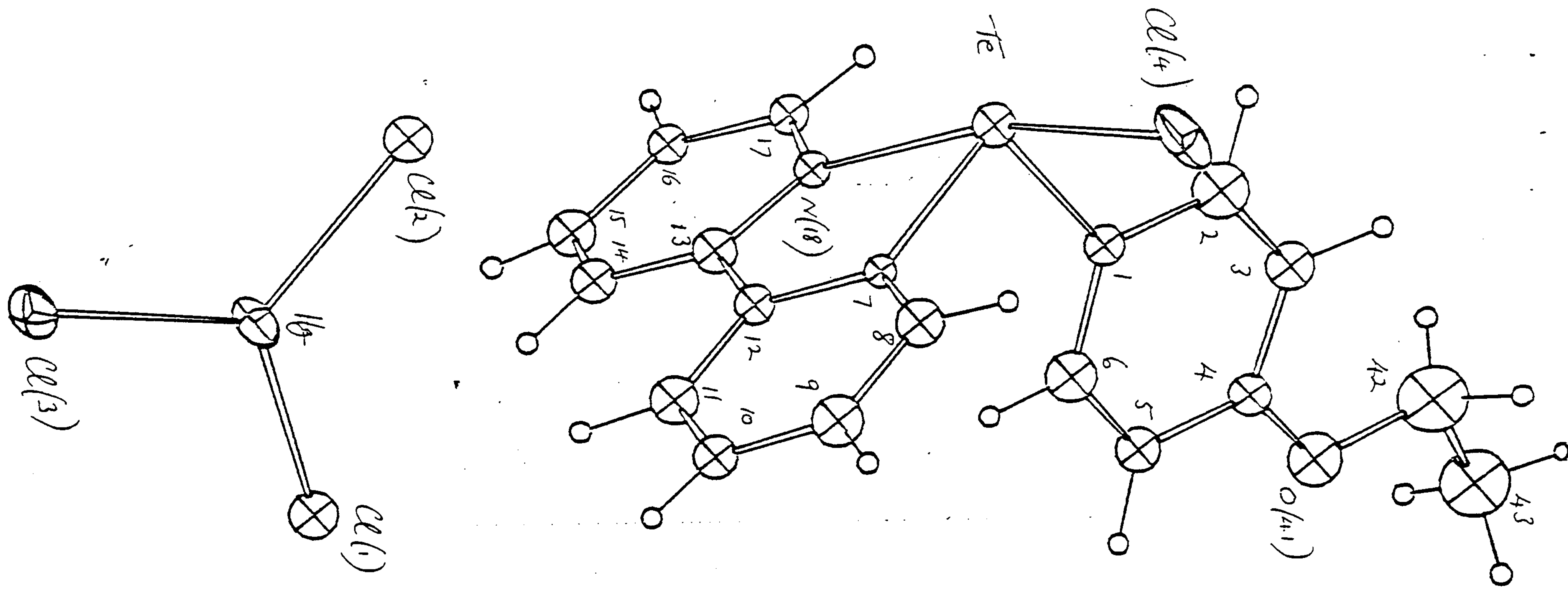


Fig 6.21: The molecular structure of chloro-p-ethoxyphenyl-2-(2-pyridyl)phenyltelluronium(IV)trichlromercurate(II).

and p-tolyl-linkage in p-tolyl-2-chlorohexyltellurium dichloride(117) (2.08A°).

The C(1)-Te-C(7) angle falls within the range observed for R_2TeX_2 compounds, e.g. bis-cis-2chlorocyclohexyl dichloride(118) 103° and α -dimethyltellurium dichloride(119) 96.8°

It has been noted that for R_2TeCl_2 compounds there is often one Te-Cl bond slightly shorter than the other, typical range being 2.42-2.49A° for the shorter bond and 2.50-2.57A° for the longer bond. The Te-Cl(4) bond length, 2.43A° found in the present structure, is at the lower end of the above ranges.

McWhinnie et al(120) have argued that for ψ -trigonal bipyramidal R_2TeXY it is sensible to view the central atom as ellipsoidal rather than spherical and proposed the use of Pauling radius(58) for equatorial (1.37A°) and estimated the axial radius to be 1.53A° for Te(IV). When the Pauling radii for Cl(0.99A°) and N(0.70A°) are considered, the predicted Te-Cl (axial) would be 2.52A° and Te-N (axial) 2.23A°. The observed values in (Table 6.6) are respectively, shorter and longer than estimates, suggesting a telluronium cation $R(R^1)TeCl^+$ stabilized by weak intramolecular co-ordination.

A significant amount of data has now been gathered for Te-N interactions in 2-(2-pyridyl)phenyltellurium compounds. If the length of the Te-N co-ordinate bond can be taken as a measure of the Lewis acidity of the central tellurium atom, then the following order of Lewis acidity is observed (Te-N in parenthesis)

$RTeBr_3$ (2.244A°)(64) > $R(R^1)TeCl^+$ (2.31A°) > RTe(dmdtc) (2.354°)(64) >R_2Te_3 (2.554A°)(121) > $R(R^1)Te$ (2.695A°)(64)

(R = 2-(2-pyridyl)phenyl- R^1 = p-ethoxyphenyl

dmdtc = dimethyldithiocarbamate).

6.4 Summary

As a result of this study, it has been established that the reaction of RHgCl (R=2-(2-pyridyl)phenyl-) with SeX_4 (X = Cl, Br) involves both trans-metallation and redox processes, the final product being 2-(2-pyridyl)phenyl selenium(II) tribromomercurate(II). The crystal structure of this compound shows to be isoelectronic with dibenzoselenophene. The study also shows that by varying reaction conditions materials which appear to be intermediates in the trans-metallation process are isolated.

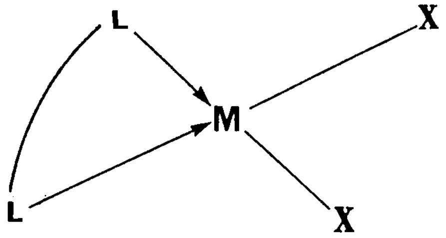
CHAPTER SEVEN

"SYNTHESIS AND CHARACTERISATION OF NEW BIDENDATE TELLURIUM LIGANDS AND THEIR COMPLEXES"

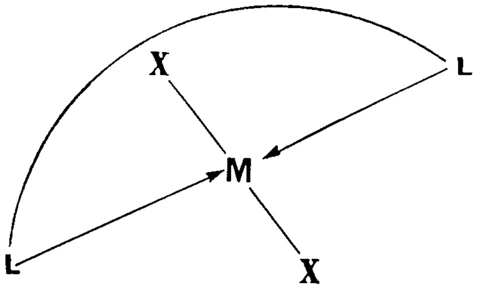
7.1 INTRODUCTION.

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. But the work reported by Shaw and his co-workers(122,123) in which they prepared <u>trans</u> $[MCl_2.Bu^t(CH_2)_nPBu_2{}^t]$ (n=10, or 12) meant that the generally held belief needed revision. Shaw(124) suggested that the formation of large chelate rings was a function of the bulk of substituents (i.e. t-Bu) on the ligand atom. However studies by McAuliffe(125) and others(126,127) in which they prepared complexes such as $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$ (with Rh(I)), $MeAs(CH_2)_{12}AsMe_2$ (with Pd(II)) and $Ph_2As(CH_2)_nAsPh2$ (n= 6-12,16) (with Pd (II)) showed that ligands with methyl or phenyl substituents can form this type of complex providing the backbone length is correct.

Recently, there has been growing interest in the synthesis of bidentate ligands with longer backbones in order to examine the effects of the length and nature of the backbone on the determination of stereochemistry of their complexes with transitional metal ions. Although many of the complexes which have been isolated with ligands containing long chain backbones have shown to have the ligand spanning <u>trans</u> positions (i) in the square planar environment <u>cis</u> complexes are also known (ii).(127) Recently, structures of cis $[PdLCl_2]$ and trans $[PdLI_2]$ ((L) = 1,8-bis(diphenylphosphino) 3,6-dioxaoctane) have been reported.(128)



(ii)



(i)

Although large chelate rings containing Group 5B donor atoms have been widely investigated,(129) the tellurium analogues have been very little studied, and only a few sulphur(130) and selenium(131) ligands with chelate rings have been reported. Pathirana(21) recently reported the preparation of complexes containing bidentate (Te,Te) ligands of the type $RTe(CH_2)_nTeR$ as mentioned in chapter one; also, the structure of the complex $[Pd(meso\text{-}PhTe(CH_2)_3TePh)Br_2]$(132) is known. It shows planar geometry about the palladium and confirms the presence of a six-membered chelate ring. In contrast to the phosphine complexes the materials prepared by Pathirana were sparingly soluble thus limiting the NMR data available. Also the complexes had limited thermal stability. A fresh synthetic approach was therefore required to produce more soluble complexes in order to obtain more information about the co-ordination chemistry of these materials. In this chapter, the synthesis and characterisation of some new bidentate ligands $RTe(CH_2)_nTeR$ (R=phenyl, $(t\text{-}Bu)C_6H_4$), and their complexes formed by reacting Pd(II) and Pt(II) and Hg(II) halides with these ligands is described. Also included in this chapter is the behaviour of both bidentate (Te,Te) and monodentate tellurium ligands toward organotin(IV) halides.

7.2 EXPERIMENTAL

7.2.1 Preparation of diphenylditelluride.

This was prepared according to a literature method.(103)

7.2.2 Preparation of Bis(p-tertiarybutylphenyl) ditelluride.

(6g, 0.25mole) of magnesium was placed in the flask and covered with 20ml THF, p-tertiarybutylbromobenzene (54g, 0.25 mole) in THF (30ml) was added through a dropping funnel at a rate sufficient to maintain gentle boiling. When the reaction was complete the mixture was refluxed for 1 hour, then poured into a 500ml flask at room temperature kept open to the atmosphere. Tellurium powder (33g, 0.26mole) was stirred into Grignard solution. As soon as ditelluride had formed as indicated by the appearance of a red colour, the solution was cooled to 0°C. The flask was then closed with a rubber stopper into which a glass tube provided with a stopcock and connected to an O_2 cylinder had been inserted. Oxygen was passed slowly for about 3 hours, the mixture was then warmed to room temperature and stirred for an additional 1.5 hours, then poured into a large beaker and allowed to stand overnight. To the red solid formed, ammonium chloride solution was added. From this heterogeneous mixture the ditelluride was extracted with diethyl ether. Orange-red crystals of ditelluride were obtained upon evaporation of the solvent. Recrystallisation from petroleum ether gave the orange-red ditelluride in 80% yield, m.p. 64°-66°C.

Found	C = 49.4%	H = 5.10%
$C_{20}H_{26}Te_2$ requires	C = 46.0%	H = 4.98%

N.B. The analysis was carried out after 4 weeks (see section 7.3.3.1.(b)) for details.

7.2.3 Synthesis of 1,5-Bis(phenyltelluro) pentane.

Diphenylditelluride (4.09g,10mmol) in benzene ($10cm^2$) and ethanol ($20cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1 mol^-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, dibromopentane (2.3g,10mmol) was added and the mixture stirred for 2 hours 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 dried ($MgSO_4$). The solvent was removed in vacuo to leave a pale yellow orange oil, product yield 62%.

7.2.4 Synthesis of 1,10 Bis(phenyltelluro) decane.

The same reaction as in 7.2.3 except by using 1,10 dibromodecane with diphenylditelluride in 1:1 molar ratio. After the organic layer was separated it was washed with distilled water and acetonitrile was added to induce precipitation. The mixture was stirred for 1½h while cooling on an ice bath. The precipitate was separated and dried in vacuo. Recrystallisation from acetonitrile gave an orange-yellow product in 51% yield, m.p. 33^{o}-34^{o}C.

Found	C = 47.9%	H = 5.40%
$C_{22}H_{30}Te_2$ requires	C = 48.1%	H = 5.60%

7.2.5 Synthesis of 1-bromo-phenyltellurocyclohexane.

Diphenyl ditelluride (4.09g, 10mmol) in benzene ($10Cm^3$) and ethanol ($20Cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1 $mol^{-}dm^{-3}$ 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 stirred for 2 hours 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 dried ($MgSO_4$). The solvent was removed <u>in vacuo</u> to leave a pale yellow orange oil, product yield 62%.

7.2.4 Synthesis of 1,10 Bis(phenyltelluro) decane.

The same reaction as in 7.2.3 except by using 1,10 dibromodecane with diphenylditelluride in 1:1 molar ratio. After the organic layer was separated it was washed with distilled water and acetonitrile was added to induce precipitation. The mixture was stirred for 1½h while cooling on an ice bath. The precipitate was separated and dried <u>in vacuo</u>. Recrystallisation from acetonitrile gave an orange-yellow product in 51% yield, m.p. 33^o-34^oC.

Found	C = 47.9%	H = 5.40%
$C_{22}H_{30}Te_2$ requires	C = 48.1%	H = 5.60%

7.2.5 Synthesis of 1-bromo-phenyltellurocyclohexane.

Diphenyl ditelluride (4.09g, 10mmol) in benzene ($10Cm^3$) and ethanol ($20Cm^3$) was heated to reflux in a dinitrogen atmosphere. Sodium tetrahydroborate (0.6g) in 1 $mol^- dm^{-3}$ 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 (9.2, 40mmol) was added and the warm mixture was stirred for 30 minutes. A white precipitate was formed which was then separated and dried in vacuo. Recrystallisation from acetonitrile gave a white compound in 55% yield, m.p. 196°-198°C.

Found	C = 37.5%	H = 4.00%
$C_{11}H_{15}BrTe$ requires	C = 37.7%	H = 4.20%

7.2.6 Synthesis of 1,10 Bis(p-tertiarybutylphenyltelluro) decane.

The experiment was carried out as in section 7.2.4 except bis(p-tertiarybutylphenyl) ditelluride was used in this case. Modifications were made to stir the mixture for about 6 hours after dibromodecane had been added. The separated organic layer was dried using $MgSO_4$ and solvent removed in vacuo to give an orange-yellow oil product in yield 58% which was used at once in complex formation. The experiment was carried out in darkness as mentioned earlier.

7.2.7 Synthesis of metal complexes of bidentate-tellurium ligands of alkane chain backbones.

(a) Synthesis of bis-μ-{1,5-bis(phenyltelluro)pentane}-bis(chloroplatinum)(Pt-Pt); [$Pt_2Cl_2L_2^5$]

A solution of potassium tetrachloroplatinate (0.208g) 0.5mmol) in distilled water was added dropwise to a solution of $PhTe(CH_2)_5TePh$ (0.249, 0.5mmol) in acetone in a dinitrogen atmosphere. A yellow precipitate was instantaneously formed. This was stirred for 12 hours. The precipitate was filtered off, washed with distilled and dry acetone and dried over P_4O_{10} *in vacuo*: Yield 50%, m.p. 122-126 (decompose)

Found C = 28.4% H = 2.50%

$C_{34}H_{40}Cl_2Pt_2Te_2$ requires C = 28.7% H = 2.50%

(b) Synthesis of Dichloro [1,10-bis(phenyltelluro)decane] platinum(II); [$PtCl_2L^{10}$]

The same reaction was carried out as above, except with $PhTe(CH_2)_{10}TePh$ as the ligand.

A pale yellow precipitate was obtained in 60% yield, m.p. 115°-117°C.

Found C = 32.4% H = 3.60%

$C_{22}H_{30}Cl_2PtTe_2$ requires C = 32.1% H = 3.68%

(c) Attempted synthesis of Dichloro [1,10 bis(p-tertiary-butylphenyltelluro)decane] platinum(II); ($PtCl_2L^{10}$)

The same reaction was carried out as in (a), except with $RTe(CH_2)_{10}TeR$ (R = (t-Bu).C_6H_4) as the ligand.

A pale yellow precipitate was obtained in 70% yield, m.p. 118-120°C.

	Found C = 41.5%	H = 4.60%
$C_{30}H_{46}Cl_2PtTe_2$	requires C = 38.8%	H = 4.96%
$C_{50}H_{72}Cl_2PtTe_4$	requires C = 41.3%	H = 4.28%

(d) Synthesis of Dibromo {1,10-bis(phenyltelluro)decane} platinum(II) [$PtBr_2L^{10}$].

A solution of potassium tetrachloroplatinate(II) (0.208g, 0.5mmol) in distilled water was stirred with a five-fold excess of a solution of KBr in distilled water for 4-5 hours. The yellow solution obtained was added dropwise to a solution of $PhTe(CH_2)TePh$(0.275g, 0.5mmol) in acetone in a dinitrogen atmosphere.

A brownish-orange precipitate instantaneously formed. This was stirred for 12 hours. The precipitate was filtered off, washed with distilled water and dry acetone and dried over P_4O_{10} *in vacuo*. Yield 70%, m.p. 122°-124°C.

Found C = 29.2%   H = 3.10%

$C_{22}H_{30}Br_2PtTe_2$ requires C = 29.2%   H = 3.31%

(e) Attempted synthesis of Dibromo {1,10 bis(p-tertiarybutylphenyltelluro)decane} platinum(II); [$PtBr_2L^{10}$]

The reaction was carried out as above, except with $RTe(CH_2)_{10}TeR$, R = [(t-Bu).C_6H_4] as the ligand. A chocolate brown precipitate was formed in 60% yield, m.p. 124°-126°C.

Found C = 40.5%   H = 5.20%

$C_{30}H_{46}Br_2PtTe_2$ requires C = 36.0%   H = 4.52%

$C_{50}H_{72}Br_2PtTe_4$ requires C = 38.9%   H = 4.61%

(f) Synthesis of Dichloro {1,10-bis(phenyltelluro)decane} palladium(II) [$PdCl_2L^{10}$]

A solution of sodium tetracholoropalladate(II)trihydrate (0.174g, 0.5mmol) in distilled water was added dropwise to a solution of $PhTe(CH_2)TePh$ (0.275g 0.5mmol) in acetone in a dinitrogen atmosphere. A maroon-red precipitate was instantaneously formed. This was stirred for 12 hours. The precipitate was filtered off, washed with distilled water and dry acetone and dried over P_4O_{10} *in vacuo*. Yield 68%, m.p. 94°-96°C.

Found C = 36.3% H = 3.70%

$C_{22}H_{30}Cl_2PdTe_2$ requires C = 36.3% H = 4.10%

(g) Synthesis of Dibromo {1,10 bis (phenyltelluro)decane} palladium(II); $[PdBr_2L^{10}]$.

A solution of sodium tetrachloropalladate trihydrate (0.174g, 0.5mmol) in distilled water was stirred with a five-fold excess of solution of KBr for 4-5 hours. The dark brownish coloured solution obtained was added dropwise to a solution of $PhTe(CH_2)_{10}TePh$ (0.275g, 0.5mmol) in acetone in a dinitrogen atmosphere. A yellowish-brown precipitate instantaneously formed. This was stirred for 12 hours. The precipitate was filtered off, washed with distilled water and dry acetone and dried over P_4O_{10} *in vacuo*. Yield 61%, m.p. 128°-130°C.

Found C = 33.2% H = 3.75%

$C_{22}H_{30}Br_2PdTe_2$ requires C = 32.4% H = 3.68%

(h) Synthesis of Dichloro {1,5 bis(phenyltelluro)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 $PhTe(CH_2)_5TePh$ (0.24g, 0.5mmol) in dry acetone in a dinitrogen atmosphere. A pale yellow precipitate was formed. This was stirred for 4-5 hours. The precipitate was filtered off, washed with dry acetone and dried over P_4O_{10} in vacuo yield 66%, m.p. 126°-128°C.

Found C = 26.9% H = 2.10%

$C_{17}H_{20}Cl_2HgTe_2$ requires C = 27.1% H = 2.66%

(i) Synthesis of Dichloro {1,10 bis(p-tertiarybutylphenyltelluro)decane} palladium(II), [$PdCl_2L^{10}$]

The same reaction was done as in (f), except with $RTe(CH_2)_{10}TeR$ (R=(t-Bu).C_6H_4) as the ligand. An orange-red precipitate immediately formed in 62% yield, m.p. 108°-110°C.

Found C = 40.22% H = 5.09%

$C_{30}H_{46}Cl_2PdTe_2$ requires C = 42.95% H = 5.48%

$C_{50}H_{72}Cl_2PdTe_4$ requires C = 44.2% H = 5.30%

7.2.8 Attempted reactions of 1,8 Bis(p-Ethoxyphenyltelluro) octane with organotin halide: (Ph_3SnCl, Ph_2SnCl, $PhSnCl_3$)

(a) A solution of the ligand 1,8 bis(p-ethoxyphenyltelluro) octane (prepared according to the literature method.(66,133) (0.305g, 0.5 mmol) in benzene(20cm^3) was stirred with a solution of the organotin halide (Ph_3SnCl, Ph_2SnCl or PhSnCl)(0.5mmol) in ethanol (30cm^3)

at room temperature for 12 hours. No reaction occurred. Using different reactant ratio i.e. 2:1 (salt:ligand) had no effect on the reaction process.

(b) A solution of the ligand (0.305g, 0.5mmol) in benzene was refluxed with a solution of Ph_2SnCl_2 (0.172g, 0.5mmol) in ethanol for 4 hours. The solution was evaporated in vacuo. The residue was recrystallised from iso-propanol giving a pale yellow compound. The elemental analysis, and m.p. suggested this product to be the ligand. Because of the disappointing results with the bidentate ligand, the reactivity of a monodentate tellurium ligand with organotin halides was studied.

7.2.9 Attempted reaction of Bis-(p-ethoxyphenyl)telluride with triphenyltin(IV) chloride.

A solution of the monodentate ligand bis(p-ethoxyphenyl) telluride (prepared according to the literature method(134)) (0.184g, 0.5mmol) in benzene was stirred with a solution of triphenyltin(IV) chloride (0.184g, 0.5mmol) in ethanol at room temperature for 24 hours. The product formed was recrystallised from benzene to give a white compound. Yield 48% m.p.

Found C = 54.09% H = 4.52%

$C_{34}H_{33}ClSnO_2Te$ requires C = 54.1% H = 4.52%

7.3 RESULTS AND DISCUSSION.

7.3.1 The synthesis of New Bis-telluride ligands $RTe(CH_2)_nTeR$ (R = Ph, t-Bu.C_6H_4) n = 5,10.

The reaction of diorgano ditellurides with alkaline sodium tetrahydroborate gives solutions with chemical properties of NaTeR.(136)

$$\mathrm{RTeTeR} \xrightarrow[\mathrm{NaOH/EtOH}]{\mathrm{NaBH_4}} \mathrm{RTeNa} \qquad \text{(eq.7.1)}$$

$$\mathrm{RTeNa} \qquad \mathrm{RTe^-} + \mathrm{Na^+} \qquad \text{(eq.7.2)}$$

The formation of bis-telluride ligands in the reaction of RTeNa with dibromoalkanes in 2:1 molar ratio is based on nucleophilic substitution of both halogen atoms of the dibromoalkane by RTe^-.

$$\mathrm{2RTeNa} + \mathrm{Br(CH_2)_nBr} \longrightarrow \mathrm{RTe(CH_2)_nTeR} \qquad \text{(eq.7.3)}$$

Compound	Found %		Required %	
	C	H	C	H
Ph_2Te_2	35.3	2.60	35.1	2.44
$R_2Te_2{}^{(b)}$	49.6	5.1	46.0	4.98
$PhTe(CH_2)_{10}TePh$	47.9	5.40	48.1	5.60
$PhTe(CH_2)_5Br$	37.5	4.00	37.7	4.20
$Pt_2Cl_2(L^5)_2{}^{(a)}$	28.4	2.50	28.7	2.80
$PtCl_2L^{10(a)}$	32.4	3.60	32.1	3.68
$PtCl_2(CH_2)_{10}(RTe)_4{}^{(b)}$	41.5	4.60	41.3	4.28
$PtBr_2L^{10(a)}$	29.2	3.10	29.2	3.31
$PtBr_2(CH_2)_{10}(RTe)_4{}^{(b)}$	40.5	5.20	38.9	4.61
$PdCl_2L^{10(a)}$	36.1	3.70	36.3	4.10
$PdBr_2L^{10(a)}$	33.2	3.75	32.8	3.68
$PdCl_2(CH_2)_{10}(RTe)_4{}^{(b)}$	40.3	5.10	44.2	5.30
$HgCl_2L^{5(a)}$	26.9	2.48	27.1	2.66
$Ph_3SnClL^{(c)}$	53.9	4.36	54.1	4.52

(a) $L^n = PhTe(CH_2)_nTePh$ (n = 5,10)

(b) $R = (t\text{-}Bu).C_6H_4$

(c) $L = R_2Te$ ($R = p\text{-}EtO.C_6H_4$)

Table 7.1 The elemental analysis of organotellurium ligands and their complexes.

Compound	Colour	m.p.(^{o}C)	Λ (M)
$Pt_2Cl_2(L^5)_2^{(a)}$	yellow	122-126(dec)	20 (DMSO)
$PtCl_2L^{10(a)}$	bright yellow	115-117	20 (DMF)
$PtCl_2(CH_2)_{10}(RTe)_4$	yellow	118-120	10 (DMF)
$PdCl_2L^{10(a)}$	maroon-red	94-96	16 (DMF)
$PdCl_2L^{10(b)}$	orange-red	108-110	15 (DMF)
$PtBr_2L^{10(a)}$	brownish-orange	122-124	26 (DMF)
$PtBr_2(CH_2)_{10}(RTe)_4$	brown	126-128	11 (DMF)
$PdBr_2L^{10(a)}$	yellowish-brown	128-130	20 (DMF)
$HgCl_2L^{5(a)}$	pale yellow	126-128	7.3 (DMSO)
$PhTe(CH_2)_5Br$	white	196-198	102.2 (water)

Table 7.2 Colour, melting points and the molar conductivities of new organotellurium compounds.

M = Molar conductance (ohm^{-1} Cm^2 mol^{-1} of 10^{-3}M solution)

Compound	Chemical shift*										
	Aromatic region				Alphatic region						
	IPSO	ORTHO	META	PARA	C-1	C-2	C-3	C-4	C-5	-C-	$-CH_3$
R_2Te_2(b)	104.2	137.7	126.5	151.5						34.62	31.34
$PhTe(CH_2)_{10}TePh$	111.8	129.1	127.4	138.2	8.76	28.80	31.86	29.36	31.72		
$PhTe(CH_2)_5Br$	118.7	129.6	129.2	135.8	27.47	26.40	21.36				
$PtCl_2L^{10}$(a)	112.5	129.9	133.2	138.0	25.23	26.76	28.77	29.21	30.94		
$PdCl_2L^{10}$(a)	-	129.5	132.3	137.1	25.27	26.81	28.42	29.79	31.54		
$PtCl_2L^{10}$(b)	-	136.0	126.5	153.4	28.04	28.57	29.05	-	-	34.74	31.15

Table 7.3 ^{13}C NMR data of some new organotellurium compounds:

1 2 3 4 5
$(RTe-CH_2-CH_2-CH_2-CH_2-CH_2)_2$ number system used to designate individual carbon atom in the methylene backbone of the ligands.

* Chemical shift in ppm relative to Me_4Si internal standard.

Compound	Aromatic Region								Alphatic region	
	C1	C2	C3	C4	C5	C6	C7	C8	OCH_2	CH3
$Ph_3SnCl.R_2Te$	104.1	139.6	115.9	158.9	137.2	128.7	129.5	136.4	63.29	14.82

Table 7.4 ^{13}C NMR data of tin complex.

Complex	υ(M-Cl)cm^{-1}	υ(M-Br)cm^{-1}
$Pt_2Cl_2(L^5)_2(a)$	316, 297	
$PtCl_2L^{10}(a)$	315, 300	
$PtCl_2(CH_2)_{10}(RTe)_4$	318, 301	
$PtBr_2L^{10}(a)$		255, 241
$PtBr_2(CH_2)_{10}(RTe)_4$		237, 232
$PdCl_2L^{10}(a)$	343	
$PdCl_2L^{10}(b)$	308	
$PdBr_2L^{10}(a)$		257

Table 7.5 Metal-halogen vibrations of some organotellurium complexes.
(observed from infra-red region 400-200cm^{-1})

The reaction of RTeNa with 1,n-dihaloalkane depends on the length of the alkane chain. It has been found that in the equation 7.3, when n = 3 or 4 for $Br(CH_2)_nBr$, materials of stoichiometry $RTe(CH_2)_nX$ are formed.(73) The ^{125}Te Mössbauer data of these materials showed typical of tellurium(IV) compound, and " Δ " in expected range for a telluronium salt. This formulation suggests a polymer or five membered ring is formed. It indicates that the nucleophilic attack by RTe has taken place, but kinetically more favourable internal quaternisation then proceeds more rapidly than the attack at the second C-X bond by further RTe^-. The phenomenon of internal quaternisation is not kinetically favoured when = 6,7 etc. due to unfavourable ring size. _bis_-telluride is the only product formed.

7.3.2 Characterisation of New Bis-telluride ligands.

The elemental analysis (Table 7.1) suggests that the reaction of RTeNa with $Br(CH_2)_nBr$ in a 2:1 molar ratio gives products of molecular formula $RTe(CH_2)_nTeR$.

The electrical conductivity of 10^{-3}M solution (Table 7.2) showed that these _bis_-tellurides are non-electrolytes.

The infra-red spectra of these ligands exhibit bands characteristic of the alkane chain and of the aryl group.

The ^1H NMR spectra of the ligands were recorded using $CDCl_3$ as the solvent. The integrated intensities are in agreement with that expected of the ligand.

The ^{13}C NMR (Table 7.3, Fig 7.1) of $RTe(CH_2)_{10}TeR$ (R = Ph) was assigned following the literature.(66,72) The aromatic region shows resonances for the ortho-,meta-, para-, and ipso-carbons of the phenyl. The assignment of the resonances of the alkane chain backbone was made by comparison with the assignments of corresponding n-alkanes.(66,136) The ^{13}C resonances which is seen around $\delta = 8.76$ ppm could be assigned to carbon nuclei of the alkane chain directly attached to tellurium, C-1. The occurrence of the C-1 resonance at high field may be due to the screening effect caused by the large atomic size of tellurium.

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

The ^{13}C resonances of C-2 to C-5 carbons of the ligand were assigned following the literature at successively lower fields.

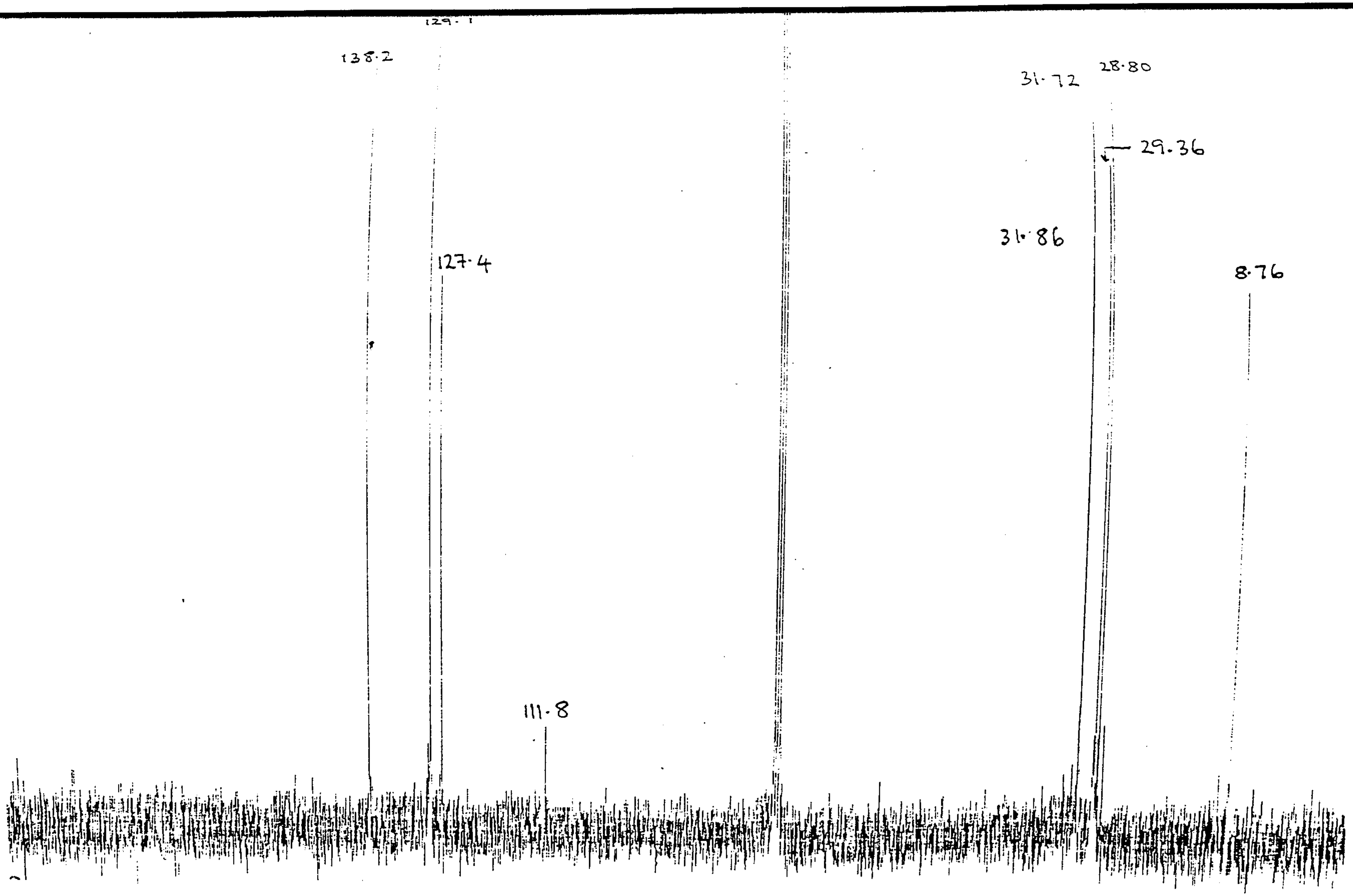


Fig 7.1: $^{13}C[^1H]$ NMR spectrum of $PhTe(CH_2)_{10}TePh$.

The reaction of the RTeNa with excess $Br(CH_2)_5Br$ gave a product whose elemental analysis suggests the formation of $RTe(CH_2)_5Br$ (Table 7.1). The conductivity data in water show ionic character (Table 7.2).

The ^{13}C NMR spectrum in $CDCl_3$ is inconsistent with an open-chain structure $RTe(CH_2)_5Br$ for which extra carbon resonances would be expected and was assigned following the literature.(66,73).

By using all this evidence, it can be concluded that a cyclic compound $[(C_6H_5)Te(CH_2)_5]Br$ is formed similar to that reported ealier.(66)

Therefore nucleophilic attack on 1,5 dibromopentane by RTe^- has taken place, but kinetically more favourable internal quaternisation then has proceeded rapidly than the attack at the second C-Br bond by further RTe^-.

7.3.3 Characterisation of the Complexes of Bidentate tellurium ligands having flexible alkane chain backbones.

The complexes prepared in this chapter are considered in two groups.

1: Platinum complexes

2: Palladium complexes.

7.3.3.1 (a) Platinum complexes of 1,n Bis(phenyltelluro) alkanes, n = 5,10.

The reaction of potassium tetracholoroplatinate(II) with $PhTe(CH_2)_5TePh$ in 1:1 molar ratio gave a yellow solid complex. The elemental analysis is compatible with the stoichiometry $Pt_2Cl_2(L^5)_2$. A similar formulation has been arrived by a previous worker in this laboratory by using a different ligand.(137) The formulation suggests that bis-telluride is acting as a reducing agent in this reaction.

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

$$Pt(I) + Te(II) \longrightarrow Pt_2\ RTe(CH_2)_5TeR\ {}_2Cl_2$$

For the platinum complexes of $PhTe(CH_2)_{10}TePh$, the elemental analysis agrees with the molecular formula PtX_2L^{10}(X = Cl, Br) (Table 7.1). The complexes are sparingly soluble in halocarbon solvents, benzene, DMF and DMSO. The conductivity measurements of these complexes show they are non-electrolytes.

The infra-red of all complexes indicate characteristic bands for the ligand, and the low frequency infra-red spectrum typical of these complexes is shown in Fig 7.2. The Pt-Cl stretching frequencies of Pt(II) complexes (Table 7.5) were assigned by comparing with

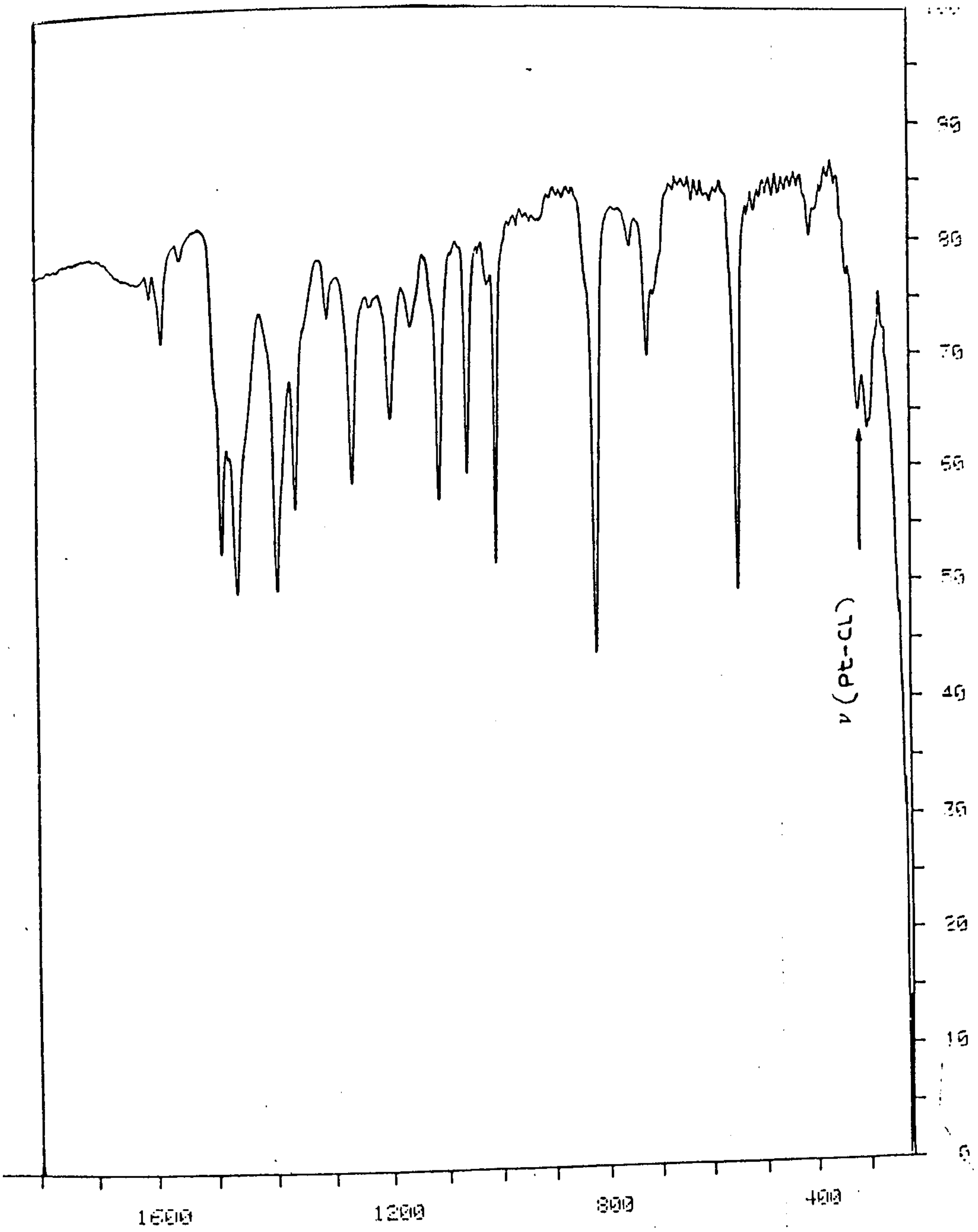


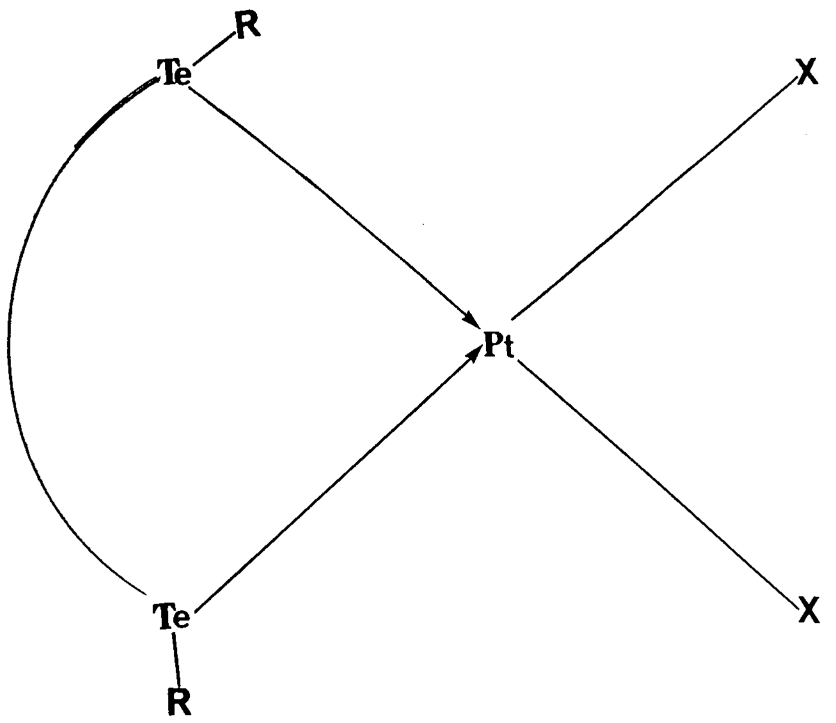
Fig 7.2: I.R. spectrum of $PtCl_2L^a$.

the spectra of analogous bromo-complexes. The change in the halogen atom from chlorine to bromine should cause a shift of υ(M-X) due to the larger atomic mass of bromine. The splitting of the Pt-Cl band resulted in two bands with equal intensity (Table 7.5) consistent with a cis dichloro configuration.(129,138)

Due to the poor solubility of these complexes, both ^{13}C and ^{1}H NMR data were of poor quality. Despite the limited solubility of the material; it was possible to note from the ^{13}C NMR spectrum that the C-1 resonance assigned at $\delta = 8.76$ ppm in the ligand $PhTe(CH_2)_{10}TePh$ has been shifted downfield to $\delta = 25.23$ ppm (Table 7.3). This downfield shift indicates deshielding at C-1 due to the withdrawal of electron density from tellurium to platinum during the formation of the co-ordinate bonds (a shift of C-1 to lower field of ca: 20 ppm on co-ordination of similar ligands has been reported).(21).

The ^{1}H NMR spectra of both platinum complexes of $PhTe(CH_2)_nTePh(n=5,10)$ showed the same aromatic:alphatic ratio as for the ligand.

According to the above evidence, the following structure could be suggested for the cis-PtX_2L^n, n=10, X = Cl, Br.



Proposed structure of cis-PtX_2L^n.

The limited data available for the complex of ligand $PhTe(CH_2)_5TePh$ make it unwise to propose a definite structure.

The poor solubility especially of the platinum complex of $PhTe(CH_2)_5TePh$, led us to investigate more reactions of this ligand with other metal ions.

Therefore, the reaction of mercuric chloride with the ligand was attempted. A pale yellow complex having stoichiometry $HgCl_2L^5$ was formed. The complex was insoluble in halocarbon solvents, DMF and DMSO. The insolubility precluded NMR studies.

(b) Platinum complexes of 1,10 Bis(p-tertiarybutylphenyltelluro)decane.

The reaction of bis(p-tertiarybutyltelluro)decane with potassium tetrachloroplatinate(II) in 1:1 molar ratio resulted in a pale yellow complex. The analogous bromide complex was prepared as mentioned in the experimental section. The elemental analysis suggest a formula $PtX_2(CH_2)_{10}(RTe)_4$ ($R=(t\text{-}Bu.C_6H_4)$, $X = Cl$, Br). Conductivity measurements (Table 7.2) show both complexes are non-electrolytes.

The infra-red spectra of the complexes exhibited characteristic absorptions of alkane-chain and of the aryl group. The low frequency region of the i.r. spectra showed ν(Pt-X) (Table 7.5) that are consistent with cis-PtX_2 arrangements.(129,138)

The ^1H NMR spectra of both complexes were recorded in $CDCl_3$ solution (Fig 7.3). The integrated intensities show lower alphatic:aromatic ratio (3.45) than that expected for the ligand (4.75), but agree well with the formulation suggested.

The ^{13}C NMR spectrum typical of the complexes is given in Fig 7.4. The downfield chemical shift at 28.04 ppm is characteristic of a ^{13}C resonance of C-1 in the

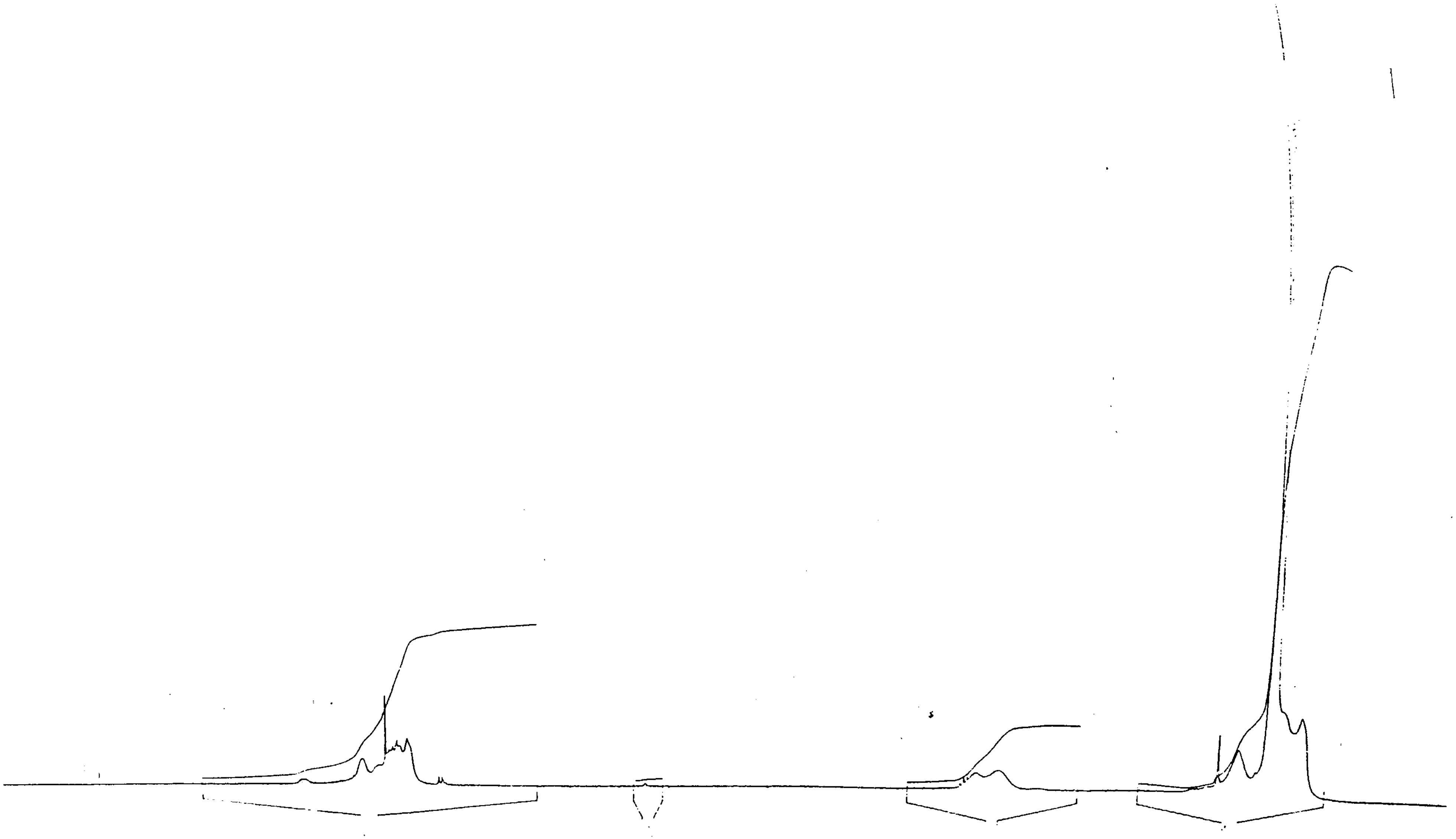


Fig 7.3: ^{1}H NMR spectrum of $PtCl_2L^b$.

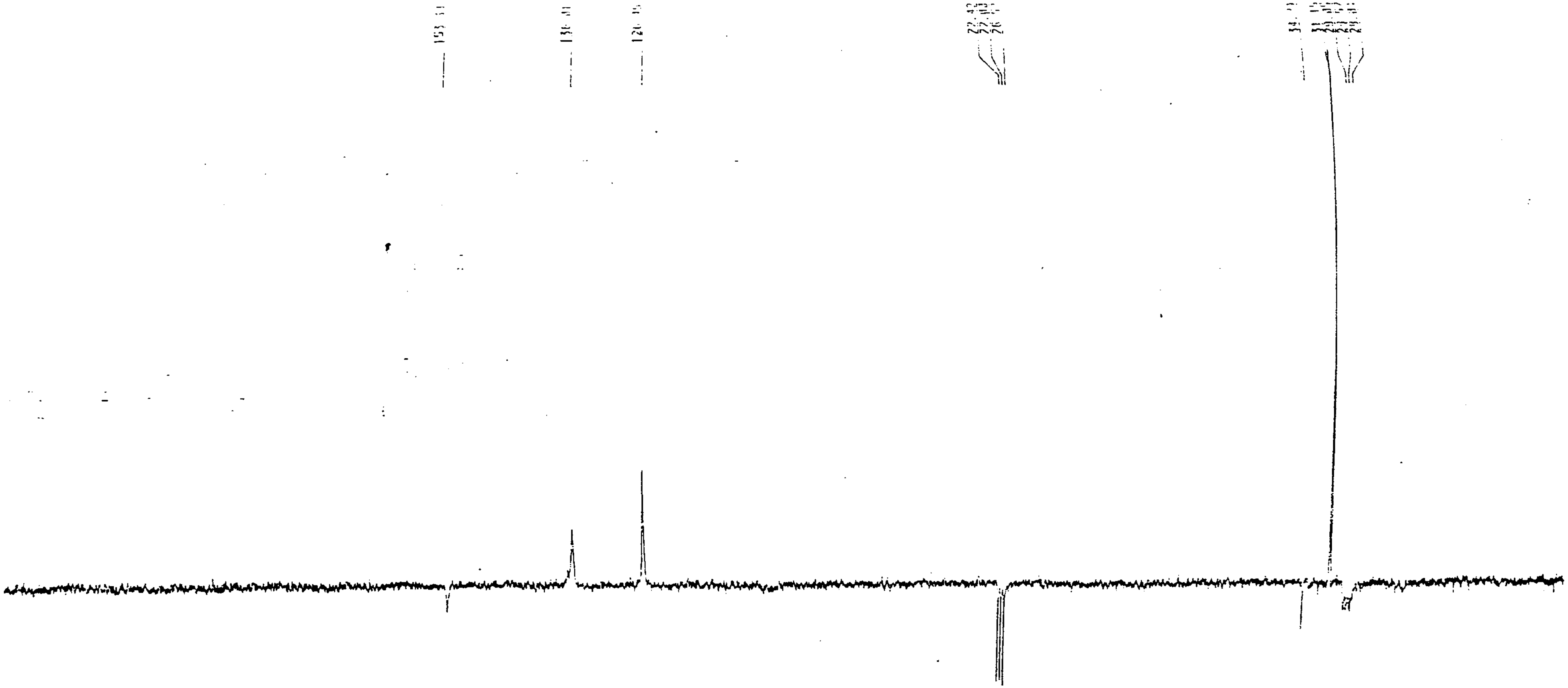


Fig 7.4: $^{13}C[^{1}H]$ NMR spectrum $PtCl_2L^b$.

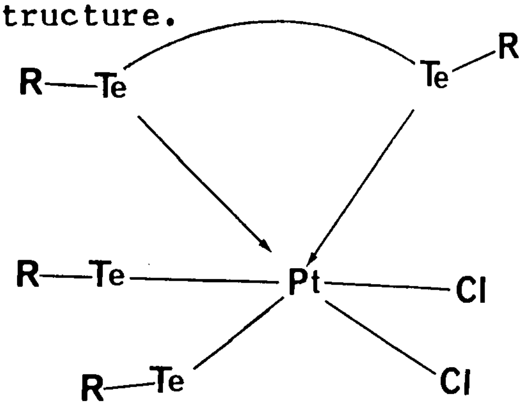
complexes of bidentate tellurium ligands mentioned earlier and that reported by Pathirana.(21) This suggests therefore, both tellurium atoms are co-ordinated to platinum.

Thus it can be concluded from this data that lower alphatic:aromatic ratio as compared to that of the ligand, may imply that these complexes are thermo and photosensitive. Based on comparison with the platinum complexes of other ligands $RTe(CH_2)_{10}TeR$(R=Ph,p-$EtOC_6H_4$) which did not show this behaviour, it may be suggested that the thermo and photosensitivity of these complexes is caused by the ligand ($RTe(CH_2)_{10}TeR$ R = t-Bu.C_6H_4. Unfortunately, there is not enough data for the ligands to justify this assumption. But the C,H analysis for the ditelluride also shows higher percentage of carbon than that expected (Table 7.1), whereas the ^1H NMR spectra shows integrated intensity to be exactly the same (2.25) as that expected for the ditelluride (NMR experiment was done after 2 days). This may suggest that this phenomenon of thermal and photosensitivity is actually exhibited by the ditelluride, (p-t-Bu.$C_6H_4)_2Te_2$, which some would decompose when exposed to light or heat to produce the corresponding telluride and elemental tellurium according to equation 7.4.

$$\mathrm{RTeTeR} \xrightarrow[\text{or light}]{} \mathrm{R_2Te + Te} \qquad \text{(eq.7.4)}$$

This would in turn account for the higher percentage of carbon in the ditelluride and consequently in the complexes. The fact that C,H analysis was done after 4 weeks and ^{1}H NMR just after two days may support this argument.

Indeed this is not surprising, as it has also been established that dibenzyl ditelluride(139) and some alkyl ditellurides(140) behave similarly when exposed to light. Thus the available data suggest the following structure.



Possible structure for cis-$PtX_2(CH_2)_{10}$ $(RTe)_4$

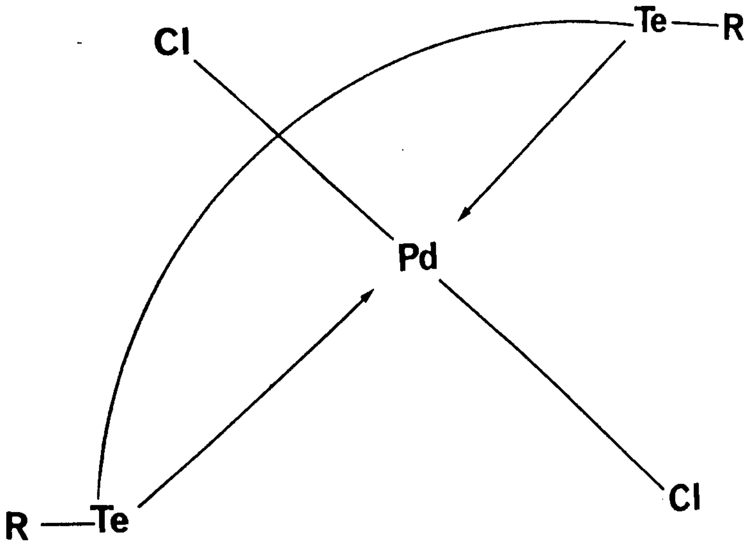
Attempts to get more information to confirm about this structure from ^{125}Te and ^{195}Pt NMR were unsuccessful due to the poor solubility of the complex. Comparison of the ν(Pt-Cl) for the proposed cis-platinum(IV) complex (301, 318 cm^{-1}) with the cis-platinum(II) complexes like $PtCl_2(RTe(CH_2)_{10}TeR)$ (R = p-$EtOC_6H_4$)(21) in which ʋ(Pt-Cl) were assigned at 299, $316cm^{-1}$, indicates very little change in the ʋ(Pt-Cl) on going from Pt(II) compound to Pt(IV) compound, despite the contribution made by the donation of electrons from tellurium to platinum in the complex formation which might be expected to modify the Pt-Cl frequency. The contribution is greater for the platinum(IV) complexes than for the platinum (II) complexes.

7.3.3.2 (a) Palladium complexes of 1,10 Bis(phenyltelluro) decane.

The reaction of sodium tetrachloropalladate(II) with 1,10 bis(phenyltelluro) decane in 1:1 molar ratio led to immediate precipitation of complex (Table 7.1). Analogous bromide derivative was obtained by treating sodium tetrachloropalladate(II) with a five-fold excess of potassium bromide before reacting with the ligand. The complexes are only slightly soluble in common organic solvents, and non-electrolytes in DMF (Table 7.2).

The far i.r. spectra (400-200Cm^{-1}) (Fig. 7.5) show a single υ(Pd-X) (X = Cl,Br) bond consistent with a <u>trans</u> - PdX_2 set.(129,138)

The ^{13}C NMR (Table 7.3) show that the C-1 resonance which was seen at δ = 8.76 ppm in the free ligand has shifted to δ = 25.27 ppm in the complex. This downfield shift of about 17 ppm for the ^{13}C resonance of C-1 indicates clearly that both the tellurium atoms are co-ordinated to Pd(II). The above interpretation suggests the following structure,



Possible structure for trans-PdX_2L^{10}

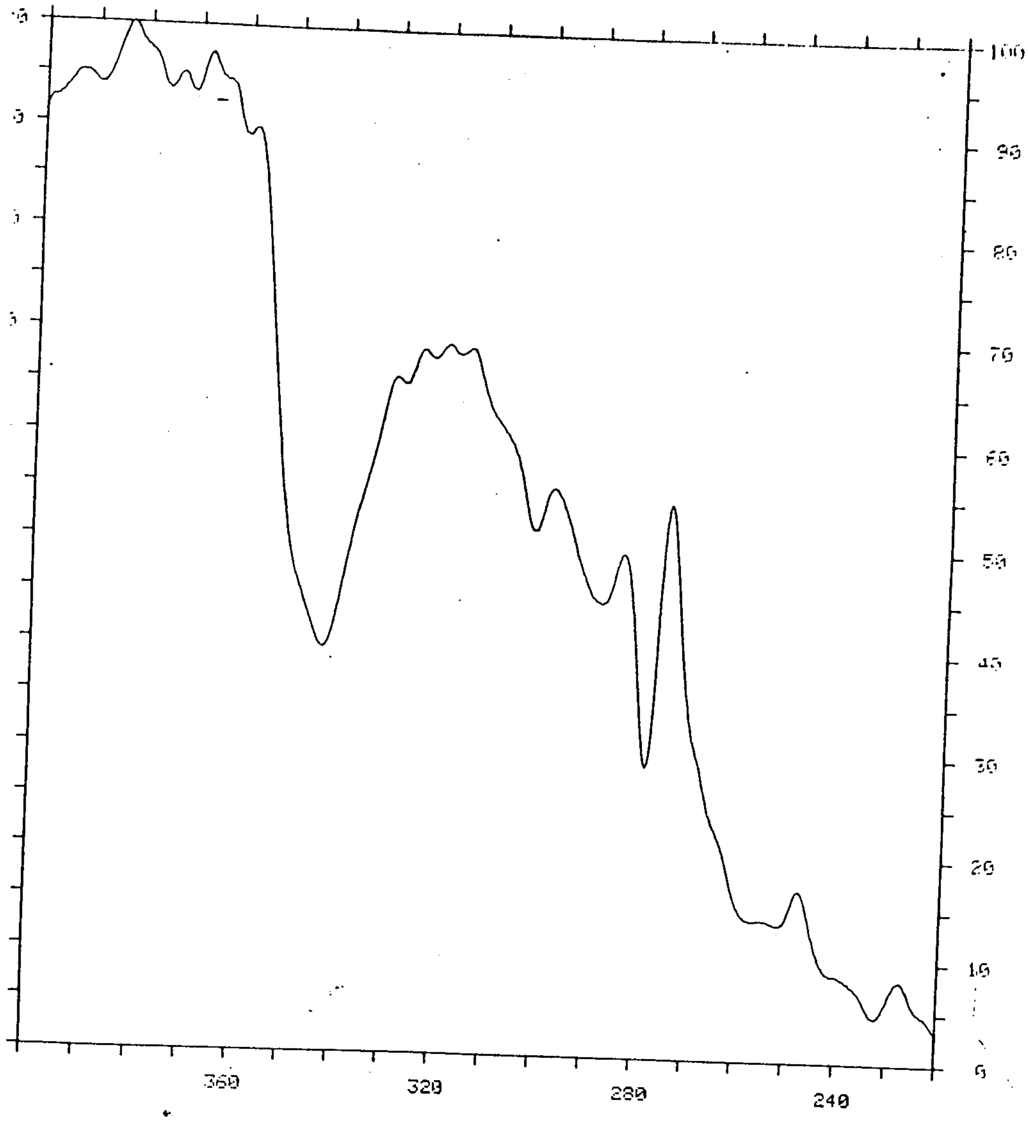


Fig 7.5: I.R. spectrum of $PdCl_2L^a$.

(b) Palladium complexes of 1,10 Bis(p-t-butylphenyltelluro) decane.

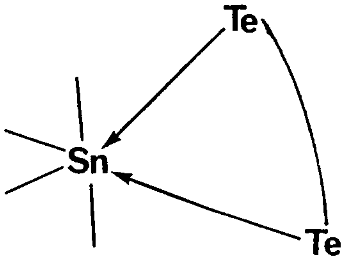
The elemental analysis for this complex indicates lower carbon percentage than that expected either for the formulation as $PdLX_2$ or $PdX_2(CH_2)_{10}(RTe)_4$ as found in the case of the analogous platinum complexes. This may be attributed to the presence of impurities such as tellurium as shown in eq. 7.3. Due to the poor solubility of the complex in many organic solvents, recrystallisation of the product was not possible.

The far i.r. spectrum showed a single υ(Pd-Cl) at $308cm^{-1}$ consistent with trans dichloro complex.(129, 138) Unfortunately attempts to get ^{13}C NMR data were unsuccessful. Hence the data available do not justify proposing definite structure.

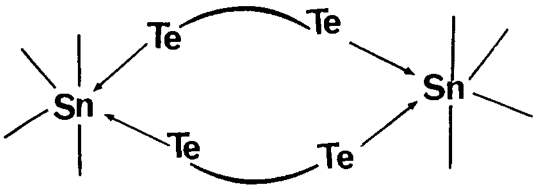
7.3.4 Attempted reactions of ligand 1,8 Bis(p-Ethoxyphenyltelluro) octane and Bis(p-Ethoxyphenyl)telluride with organotin(IV) halides.

The synthesis of organotin complexes of bidentate and monodentate tellurium ligands was attempted to study the influence of variation in Lewis acidity of the metal on these ligands. The Lewis acidity of tin increases in the order $Ph_3SnCl<Ph_2SnCl_2<PhSnCl_3$. This is explained by the

simultaneous action of the inductive effect and the mesomeric effect of the phenyl group. Therefore it might be expected that the reaction of Ph_3SnCl with bidentate ligand $RTe(CH_2)_8TeR$ = (L), (R = p-EtO.C_6H_4) would lead to complexes with stoichiometry $Ph_3SnCl.L$, in which "L" functions as a bridging monodentate ligand and tin assuming a co-ordination number of five. Whereas Ph_2SnCl_2 and $PhSnCl_3$ would be expected to form chelated complexes in which the co-ordination number of tin is increased from four to six as shown below (iii) and (iv)



(iii)



(iv)

This would indeed be interesting as it would give an opportunity to study both ^{125}Te and ^{119}Sn NMR and Mössbauer spectroscopy and compare with other compounds of organotellurium containing tin element to find out the effects if any of the length of the backbone on these parameters.

Unfortunately, attempts to prepare such compounds with the bidentate tellurium ligand under different conditions including extended reflux were unsuccessful. Elemental analysis and i.r. of the materials isolated only indicated them to be starting materials. This was somewhat surprising since it was supposed that tin would have a good affinity for tellurium. In contrast, the reaction of bis (p-ethoxyphenyl) telluride with triphenyltin(IV) chloride produced a white compound of molecular formula $Ph_3SnCl.R_2Te$ ($R = p\text{-}EtO.C_6H_4$) (Table 7.1).

The infra-red spectrum of this compound showed characteristic bands associated with the ligand and triphenyl tin halide. The far i.r. spectrum (Fig 7.6) showed a band at 330 cm^{-1} assignable to $\upsilon(Sn\text{-}Cl)$. $\upsilon(Sn\text{-}Cl)$ for Ph_3SnCl has been assigned at $329cm^{-1}$. The practically unchanged Sn-Cl stretching frequency on complex formation may imply weak bonding between tellurium and tin atoms, or even the formation of an inclusion compound.

The ^1H NMR spectrum of the complex $Ph_3SnCl.R_2Te$ in $CDCl_3$ is shown in (Fig 7.7). The integral ratio agrees well with the molecular formula.

The ^{13}C NMR spectrum of this complex (Fig. 7.8) was assigned following the literature.(21,66,72) The C-1. C-4 and C-7 resonances (Table 7.4) are distinguished by their low

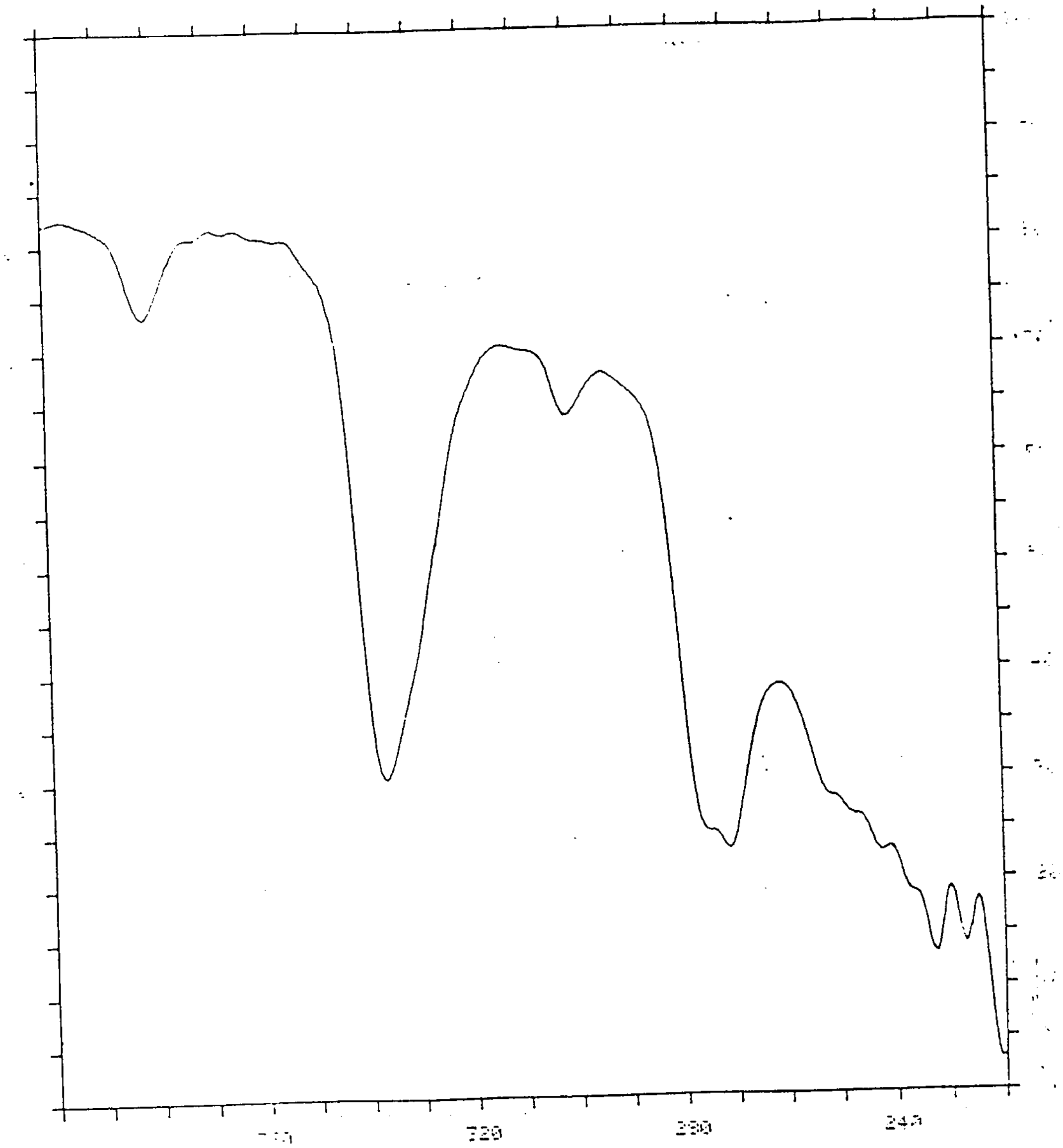


Fig 7.6: I.R. spectrum of Ph_3SnL^c.

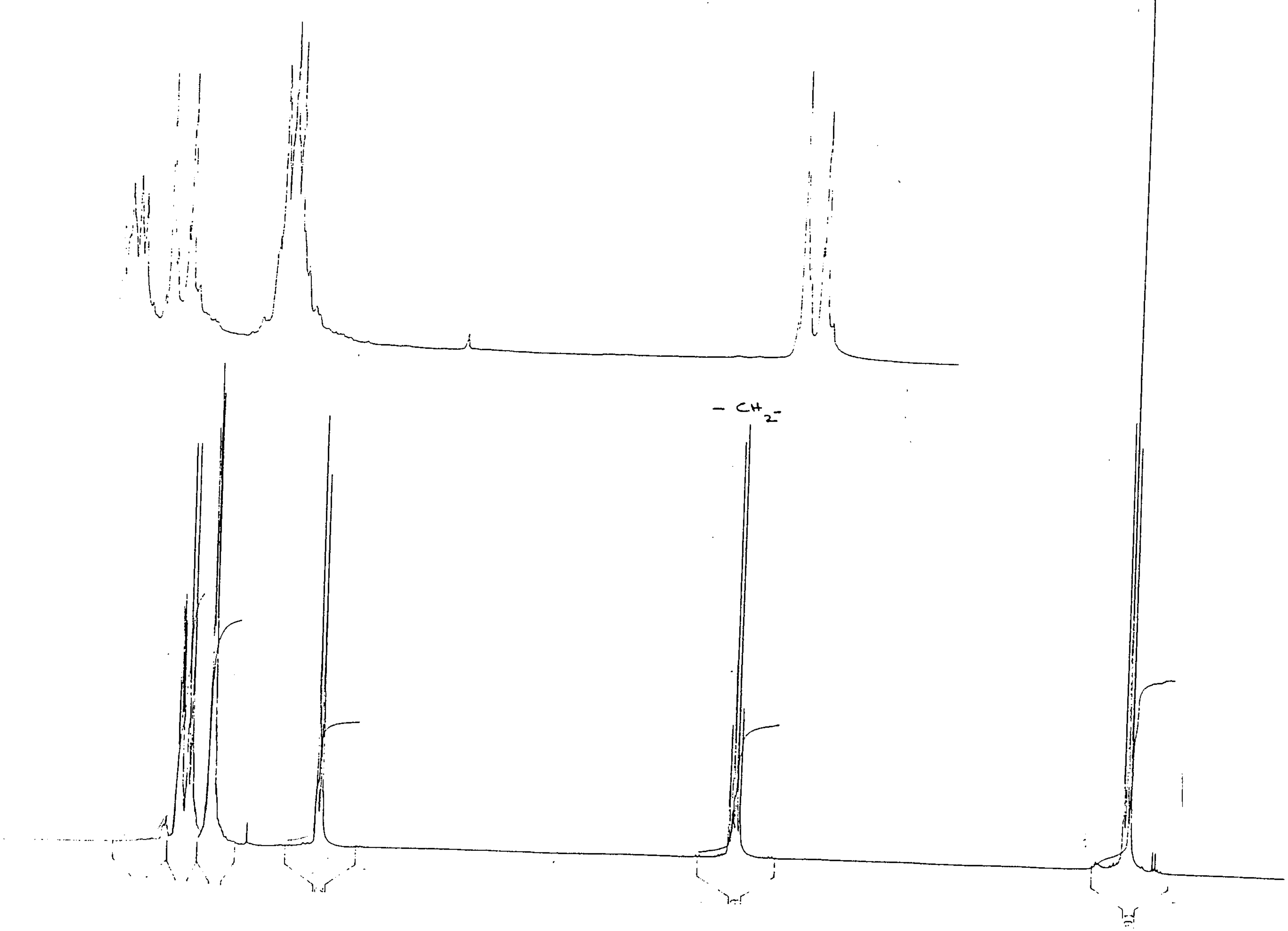


Fig 7.7: ^1H NMR spectrum of Ph_3SnL^c.

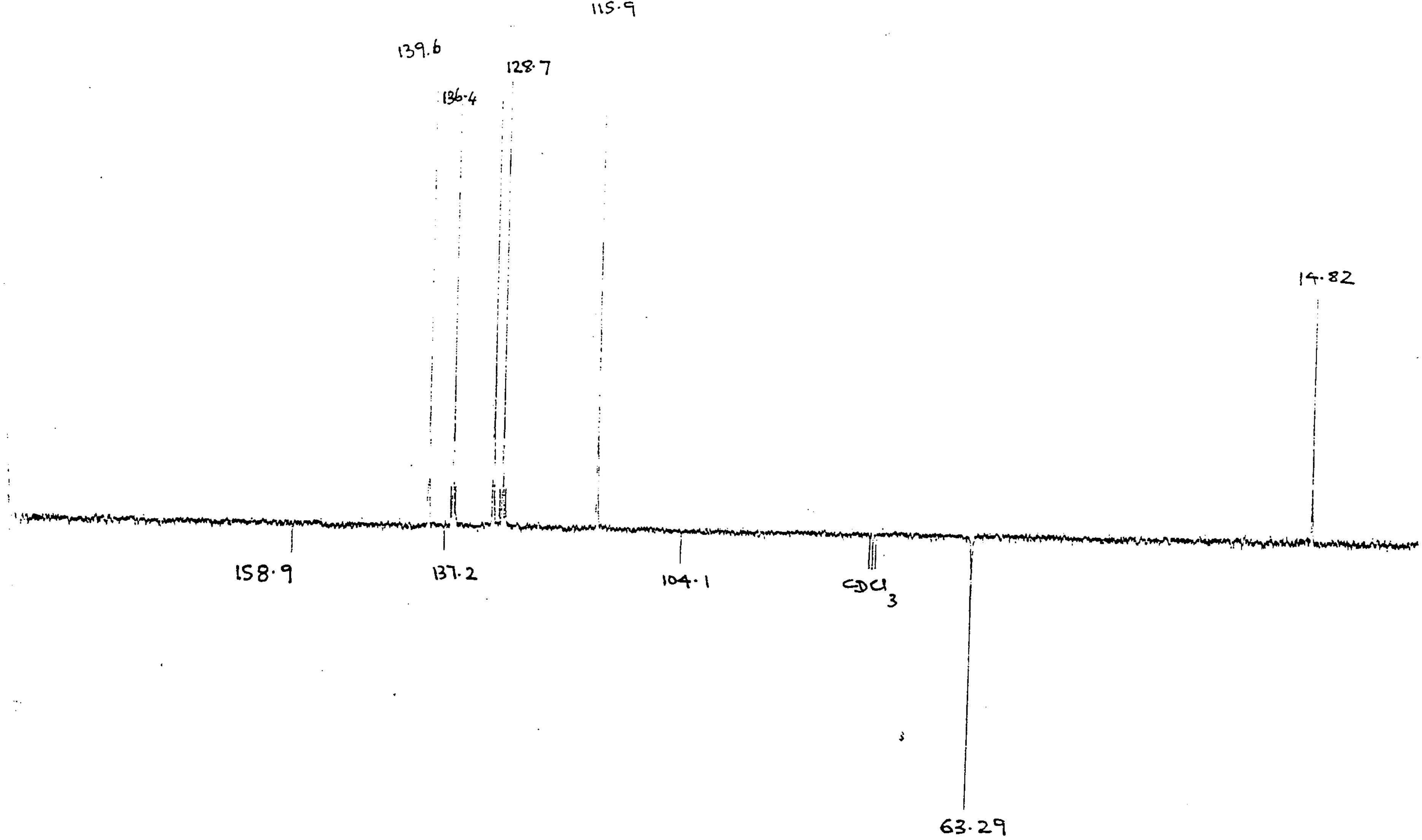


Fig 7.8: $^{13}C[^{1}H]$ NMR spectrum of Ph_3SnL^c.

intensity. The alphatic region contains ^{13}C resonances assignable to $-OCH_2$ (63.29ppm) and $-CH_3$ (14.82ppm) which are in good agreement with that from the literature.(66,73)

The failure of the bidentate ligand $RTe(CH_2)_8TeR$ to react with triphenyltin chloride may not be surprising. Chia(141) basing her conclusions on the reactivity of some tellurium ligands with $[Pd(PhCN)_2Cl_2]$, concluded that the Lewis basicity of tellurium ligands increases as follows $(p\text{-}EtO\text{-}Ph)_2Te_2 < PhCN < Ph_2Te$, $(4\text{-}EtO\text{-}Ph)_2Te$. Using the same criteria, Pathirana(137) concluded that the trend in Lewis basicity was $RTe(CH_2)_nTeR > R_2Te_2$. This scale is not conclusive, but one can reasonably assume that on the basis of these observations by Chia and Pathirana the Lewis basicity will increase as follows.

$$RTe(CH_2)_nTeR < R_2Te$$

This may explain why monodentate tellurium ligand (R_2Te) would form complexes with organotin halides as compared to the bidentate tellurium ligand ($RTe(CH_2)_8TeR$).

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