THE SYNTHESIS AND PROPERTIES OF SOME NOVEL TELLURIUM-CONTAINING LIGANDS

by

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A thesis submitted for
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DECLARATION

The work described in this thesis was carried out between 1983 and 1986 at the University of Aston. It has been done independently and has not been submitted for any other academic award.

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Summary

The preparation of sodium 2-(4-ethoxyphenyltelluro)benzoate ligand is described. It can form complexes with some of the first row transition metal ions and some post-transition ions [Co(II), Ni(II), Cu(II), Fe(III), Cr(III), Tl(I), Ag(I)]. Only the thallium(I) complex shows a considerable conductivity in solution with thallium-ligand ion pairing. The other complexes are either monomeric or dimeric. Carboxylate groups are either chelating or bridging. Cu(II), Cr(III) and Fe(III) complexes show significant antiferromagnetism.

2-butyltellurobenzaldehyde reacts with diaminoethane to give 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (L), whose crystal structure shows a significant Te---N interaction. This ligand gives a 1:1 complex with $HgCl_2$. The crystal structure of this complex shows that it is monomeric with Hg(II) having a tetrahedral environment. The ligand is co-ordinating through two Te atoms and the Te---N interaction is maintained in the complex, but there is no Hg←N bonding, therefore,it has a 13-membered chelate ring structure.

The reaction of 2-butyltellurobenzaldehyde with hydrazine gives 1,4-bis-2-butyltellurophenyl-2,3-diazabuta-1,3-diene ligand (L'). Ligand (L) gives ionic complexes with Pd(II), Pt(II) and Rh(III), while ligand (L') gives non ionic compounds with them. $PdCl_2L.H_2O$ has trans Te atoms whereas $PtCl_2L.H_2O$ has cis tellurium ligands and undergoes Te-dealkylation with oxidation of Pt(II) to Pt(IV) in DMSO. $PdCl_2.L'$ and $PtCl_2.L'.H_2O$ have cis- Te ligands and the first isomerises in $CHCl_3$ into the trans complex. Rhodium(I) complex, RhClL, is monomeric and the ligand is tridentate (Te, N, Te). RhClL' is dimeric with bridging Cl and tellurium co-ordinating ligands.

2-Phenylpyridine and 2-phenylquinoline are mercurated by mercuric acetate. Transmetallation reactions of the mercurated derivatives with $TeBr_4$ and $4\text{-EtO-}C_6H_4TeCl_3$ have been studied. The diorganyltellurides and ditellurides and organotellurenyl bromides were prepared. Reduction of 2-(2-pyridyl)phenyltellurium(IV)tribromide with $NaBH_4$ gives the novel bis(2-(2-pyridyl)phenyl)tritelluride. The X-ray structure of this compound has shown a significant Te---N interaction, to which the stability of the compound has been attributed. Most of these compounds are potentially multidentate ligands, but only the dichloro-[bis(2-(2-pyridyl)phenyl)telluride] palladium(II) complex has been prepared.

KEY WORDS:

TELLURIUM LIGANDS, TRANSITION METAL TELLURIUM COMPLEXES, PYRIDINE, QUINOLINE

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LIST OF ABBREVIATIONS

πCp	πC_5H_5
Ph	C_6H_5-
p-Tolyl	p-CH_3-C_6H_4-
Me	CH_3-
Et	C_2H_5-
n-Bu	n-C_4H_9-
R	Alkyl
Ar	Aryl
DMSO	Dimethylsulphoxide
DMF	Dimethylforamide
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
Bipy	2,2'-bipyridyl
NaETB	Sodium 2-(4-ethoxyphenyltelluro)-benzoate
1,10-Phen	1,10-Phenanthroline
I.R.	Infra-red
U.V.	Ultra-violet
N.M.R.	Nuclear Magnetic Resonance
E.S.R.	Electron Spin Resonance
L	Ligand
COD	1,5-Cyclooctadiene
^{13}C [^1H] N.M.R.	Proton Decoupled Natural Abundance ^{13}C N.M.R.
dmdtc	Dimethyldithiocarbamato-

CHAPTER ONE

INTRODUCTION

1.1 General Introduction

Interest in ligands containing a heavier group 6A donor atom, sulphur, selenium or tellurium, and their co-ordination compounds has grown substantially in the last two decades, although their organic chemistry dates back to the last century(1-3). However, despite the extensive investigation of the co-ordination chemistry of ligands containing sulphur(4-10), and to some extent selenium ligands(4,6,11), the use of tellurium compounds as ligands with transition metals has been paid little attention and remained limited until recently; In fact, only about seven references to metal complexes with tellurium ligands were mentioned in the early review by Livingstone in 1965(4). After approximately ten years, Irgolic(1974) mentioned only about twenty more references in this area(12). And in the last ten years publications, dealing with co-ordination compounds of tellurium ligands, have increased dramatically(13,14), with more than one hundred and eighty new publications.

So, what was the reason for that limitation in the field of tellurium chemistry?. There were probably two reasons for this, firstly, a wide variety of organotellurium ligands are not commercially available, in contrast to, for example, organophosphines and organosulphurs. Secondly it was believed that organotellurium compounds, basically due to the early work by Chatt et al(15-18), dealing with dialkyltelluride complexes of Pd(II) and Pt(II), are air sensitive and extremely toxic compounds, but diorganyltellurides do not always have these properties, since the diaryl derivatives, with the exception of the liquid diphenyltelluride, are air stable with little or no smell. But what in fact has accelerated the trend of the co-ordination chemistry of organotellurium ligands is the increasing familiarity of organotellurium synthetic methodology to the practising co-ordination chemist, and also to extend the study of sulphur and selenium ligands to tellurium ligands in order to increase knowledge of the chemical behaviour of Group 6A elements in their complexes, as these have been somewhat neglected compared to those of Group 5 (nitrogen, phosphorus, arsenic, antimony). In addition, the advances in instrumentation and computational facilities have helped in solving structural problems and moved the field from a primarily synthetic exploratory stage to a more sophisticated stage. In this context some techniques like X-ray crystallography(19), ^{125}Te Mössbauer effect(20) and ^{125}Te NMR spectroscopy(21), have proven to be very useful probes in tellurium ligands chemistry and have provided valuable information about ligand-metal interaction.

Interest in this field has also been established within the tellurium group at Aston University, since the previous workers have contributed to the development of tellurium chemistry and the associated metal complexes. Rattanaphani(1973) found that diaryltellurides form quite stable complexes with metal ions like Cu(I), Rh(I) and Rh(III)$^{(22)}$. Chia$^{(23)}$ prepared a number of organotellurium complexes with Pd(II), Pt(II), Pd(0) and Rh(I), and she also came to the conclusion that the Lewis basicity of some tellurium ligands increases as follows:

$(4\text{-EtO-Ph})_2Te_2 < PhCN < Ph_2Te, (4\text{-EtO-Ph})_2Te$

according to their reaction with the $[Pd(PhCN)_2Cl_2]$ complex. Using ^{125}Te Mössbauer data, McWhinnie and coworkers$^{(24)}$ suggested an order of Lewis acidity for some metal ions relative to bis(4-ethoxyphenyl)telluride :

Hg(II) > Pt(II) > Pd(II) > Cu(I)

Later Al-Rubaie et al$^{(25)}$ using a mixture of diarylditellurides were able to isolate some complexes of copper(I) and mercury(II), which were postulated as $RR'Te_2.2MX_n$ (where R=phenyl, R'= 4-ethoxyphenyl; M=Cu(I), Hg(II); X=Cl, Br; n= 1, 2) based on infra-red spectra, mass spectra and Raman data which gave reasonable evidence for ν(Te-Te) and (Te-M), in constrast to the 1:1 complexes (e.g., $R_2Te_2.CuX$) prepared in the same laboratory but using a different solvent$^{(26)}$. More recently some new <u>bis</u>-telluride ligands have been prepared in our laboratory and their complexes of Pd(II), Pt(II) and Hg(II) have been investigated$^{(27)}$. Therefore,the work presented here is an extension of the effort of the previous workers within our tellurium group.

1.2 Technological and Scientific Interest

In the last few years, the great incitement for the development of co-ordination chemistry has been the application of such complexes in many useful fields, such as homogeneous catalysis (e.g., organophosphine stabilisation of low-valent noble metal species)(28), and the synthesis of materials described as one dimensional conductors (e.g., dithiolene complexes)(29). However, little attention has been paid to application oriented work of complexes incorporating tellurium ligands.

One of the major interests, in this respect, is the use of organotellurium compounds or their complexes as imaging systems in photography. An earlier review by Gysling(30a) described two kinds of processes. The first is the use of tellurium compounds in a conventional silver halide process, and the second is the use of various tellurium compounds in heat-processed imaging elements. In the first kind, silver(I) co-ordination complexes with organotellurium ligands could be used as components of so-called dry silver processes(31) (i.e., development is effected by heating the exposed film rather than by conventional solution development, (Scheme 1.1).

$$\mathrm{AgX} \xrightarrow{h\nu} \mathrm{Ag(0)} + \mathrm{AgX} \xrightarrow[\text{Agent}]{\text{Reducing}} \mathrm{Ag(0)} + \text{Oxidised reducing agent}$$

The Conventional Silver Halide Process

$$AgX(TeAr_2)_n + \text{Reducing agent} \xrightarrow[\text{heat}]{h\upsilon(AgX)} Ag(0)$$

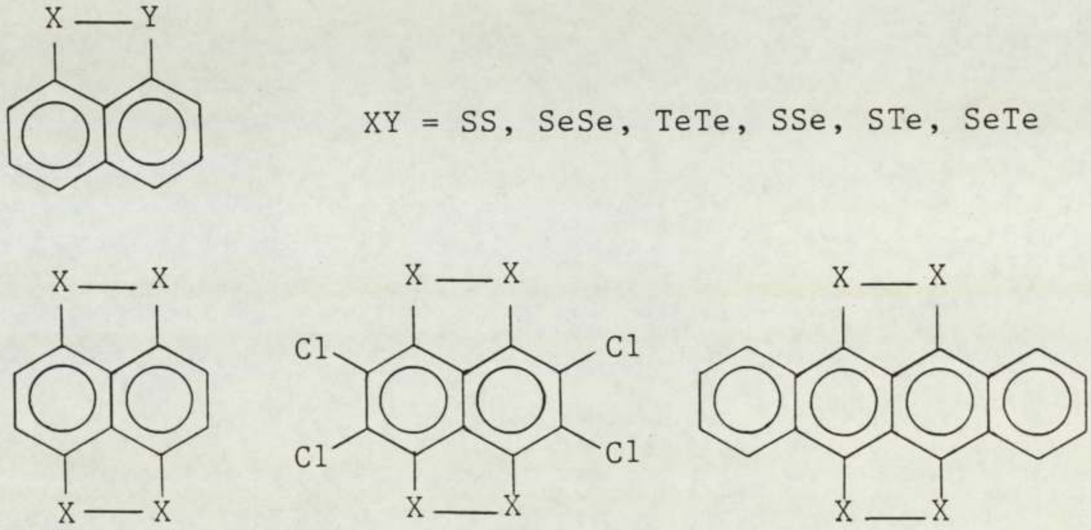
Dry Silver Process

Scheme 1.1

Therefore, the tellurium compounds were incorporated as addenda to facilitate the formation of neutral silver images. The second processing type is centered on the use of tellurium compounds as thermal precursors of Te(0) images. For this case several examples have been mentioned, and in one of them, complexes of organotellurium(II) ligands (e.g.,$PdCl_2L_2$, $L = Te[(CH_2)_3SiMe_3]_2$) are exposed then immersed in an aqueous solution of a reducing agent(e.g., N_2H_4) to give negative images(32). In some cases of dry non silver imaging processes an amplification factor of 10^8 is obtained compared with 10^9 of that of the conventional silver halide process.

Many metal complexes have been used as catalysts for organic synthesis, for example rhodium-phosphine complexes, like $Rh(PPh_3)_3Cl$, have been used as homogeneous catalysts(33) for hydrogenation of aromatic nitro compounds into the corresponding amines in benzene, xylene/methanol solutions. Some publications have also appeared describing the use of tellurium compounds or their complexes as reagents for organic synthesis, for example ditellurocuprate(III) has been used in oxidation of some aliphatic ketones which is followed spectrophotometrically by estimating the disappearance of the tellurium compound(34). Aryltellurium(IV) compounds have been reacted with alkenes(35) to give the corresponding arylated alkenes in moderate to quantitative yield in the presence of palladium(II) salts; trans-metalation of tellurium with palladium is thought to be a key step of the reaction.

A class of organochalcogen compounds containing one or two chalcogen-chalcogen bonds has been used as ligands with transition metal ions. These ligands are of the type illustrated in Fig.1.1, and they have been shown to have



XY = SS, SeSe, TeTe, SSe, STe, SeTe

TTN TTT TCTTC

X = S, Se and / or Te

Figure 1.1

significant conductivity in the solid state(36). A series of transition metal(M) containing complexes $[M(L)]_x$ (where L = TTN, TTT, TCTTC as illustrated in Fig.1.1) have also been used as active materials for battery electrodes(37).

1.3 Different Kinds of Tellurium Ligands

The simple tellurium ligands, dialkyltellurides and diaryltellurides have been used by Chia and McWhinnie(23) and Hieber et al(38). In addition, several other types of tellurium ligands have been mentioned and used by the above authors; but generally we can classify them into three main categories:

(a) terminal, of the type metal-TeR and TeR_2 (where R is either H, organic, organometallic or an organometalloid group). Baddley and co-workers(39) demonstrated that a terminal M-TeAr bond could be formed by the cleavage of Te-Te bond, as follows:-

$$[\pi CpFe(CO)_2]_2 + Te_2Ph_2 \xrightarrow[\text{reflux}]{C_6H_6} \pi CpFe(CO)_2TePh \quad (eq.1.1)$$

An interesting complex, incorporating both termimal and bridging aryltellurol ligands, was reported by Chia and McWhinnie(23) in a reaction involving the splitting of diarylditellurides. A mercuric phenyltellurol complex was also prepared(40a), and the structure of its tetraphenylphosphonium salt was reported(40b) as shown in (Fig.1.2). In a single crystal X-ray diffraction study(41), the complex $Pd[SCN]_2[Te(CH_2CH_2SiMe_3)_2]_2$ has been confirmed to be in a trans-form in agreement with other spectroscopic evidence (Fig. 1.3). Lappert et al(42) have reported, the first metal complex with a ligand incorpora-

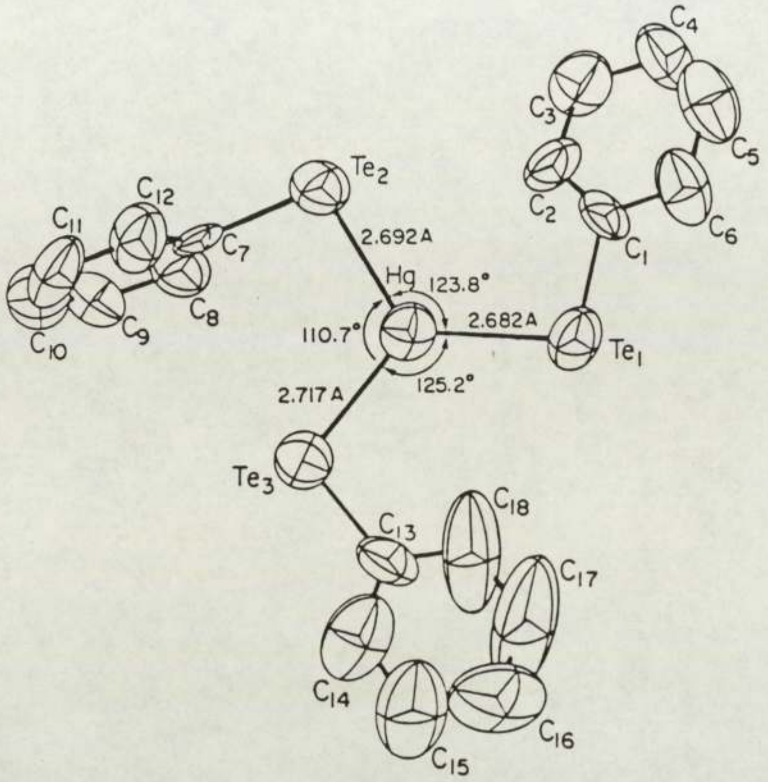


Figure 1.2: Molecular structure of $[Hg(TePh)_3]^-$

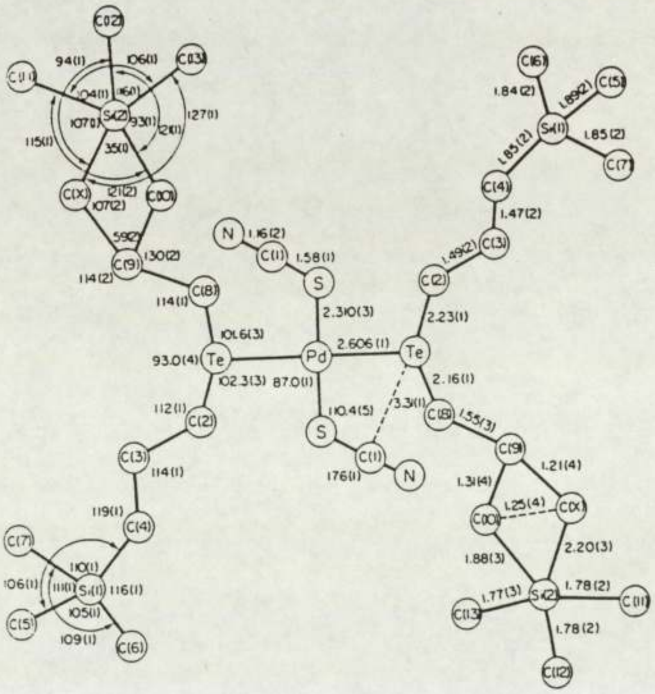


Figure 1.3: Molecular structure of $Pd[SCN]_2[Te(CH_2CH_2SiMe_3)_2]_2$

ting telluourea functioning as a terminal ligand also. The crystal structure of this chromium(0) complex is shown in (Fig. 1.4a). Recently, the first stable tellurophosphorane complexes $M(CO)_5(R_3PTe)$ (M=Cr, Mo, W; R= Bu^t) have been reported (43), in which the tellurophosphorane acts as a terminal tellurium ligand. These complexes have been formed by photolysis of $M(CO)_6$ in the presence of $R_3P{=}Te$ in THF. A representative molecular structure of W(0) complex is shown in (Fig. 1.4b). The first example of complexes with the terminal TeH^- ligand have recently been prepared by photochemical (eq. 1.2) and thermal (eq. 1.3) substitution reactions (44), but no crystal structure of such complexes has been reported.

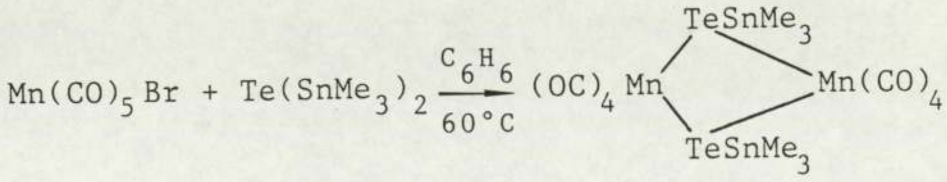
$$M(CO)_6 \xrightarrow[h\nu,-40°C]{THF} CO + M(CO)_5THF \xrightarrow[(2)\ C^+Cl^-]{(1)\ Na_2Te/EtOH,-60°C}$$

$$\overset{+}{C}[M(CO)_5TeH]^- \quad (C^+ = PPN^+;\ M = Cr) \qquad \text{eq.1.2}$$

$$[PPN][Cr(CO)_5Cl] + Na_2Te \xrightarrow[r.t.]{EtOH} [PPN][Cr(CO)_5TeH] \qquad \text{eq.1.3}$$

(b) Bridging, of the type metal-[$\mu(Te_nR_m)$]-metal (where R could be H, organic, organometallic, S, Se or Te; n=1,2; m=0,1,2). A variety of complexes containing bridging TeR group have been reported (26,45), where R= Ph(eq.1.4) or $SnMe_3$ (eq.1.5)

$$\overset{+}{Na}TePh^- \ + \ CuCl \xrightarrow{EtOH} [CuTePh]_n \qquad \text{eq.1.4}$$



$$Mn(CO)_5Br + Te(SnMe_3)_2 \xrightarrow[60°C]{C_6H_6} (OC)_4Mn(\mu\text{-}TeSnMe_3)_2Mn(CO)_4$$

eq.1.5

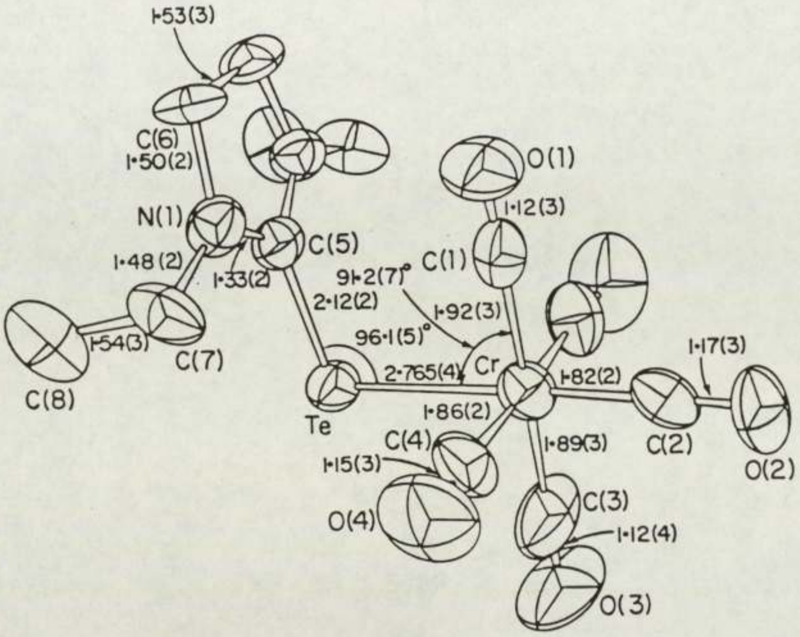


Figure 1.4a: Molecular structure of $Cr(CO)_5[Te{=}\overline{CNEtCH_2CH_2N}Et]$

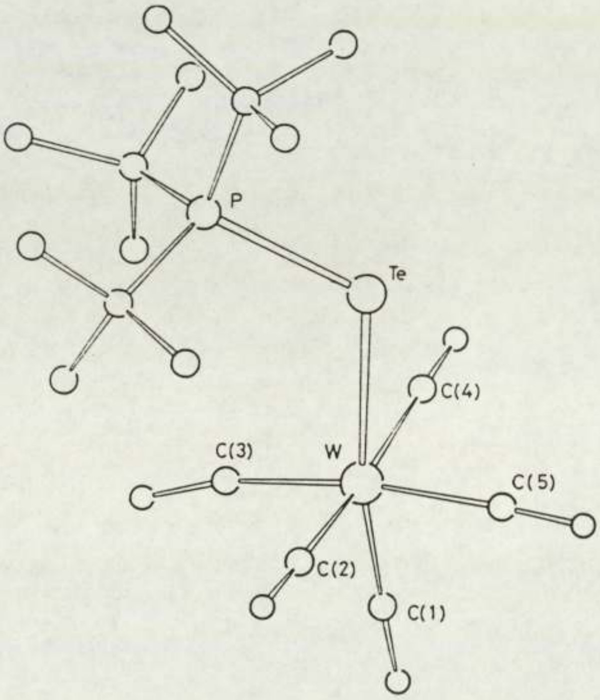


Figure 1.4b: The structure of $W(CO)_5(R_3PTe)$

Recently it has been reported that diethyltelluride reacts with copper(I) chloride to give polymeric chloro-(diethyltelluride)copper(I) (46), for which the X-ray analysis showed that its structure contains infinite sheets consisting of bridging Et_2Te ligands between two copper(I) cores (Fig. 1.5).

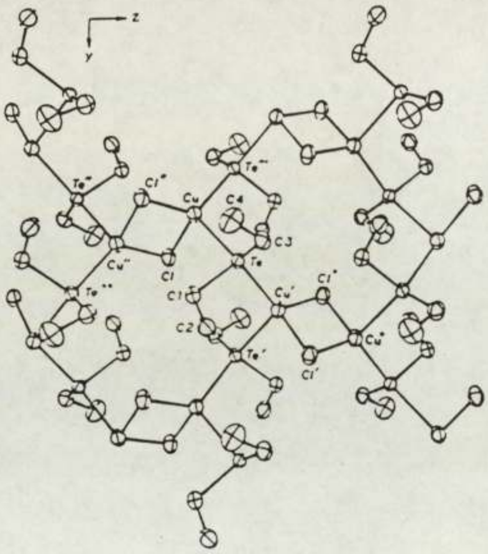


Figure 1.5: A polymeric sheet of $Et_2Te.CuCl$ down the X-axis

Bridging diorganylditellurides are also known with the Te-Te bond intact. The first crystal structure for a diarylditelluride rhenium(I) complex has been reported (47), which consists of pseudo-octahedral Re(I) centres joined by two bromides and Te_2Ph_2 bridges (Fig. 1.6). Tellurium(2-) ions can also form bridges or cage type structures. An ionic compound $(2,2,2\text{-crypt-}K^+)_2Tl_2Te_2.en$ has been reported (48). The interesting aspect of its structure is the butterfly-shaped configuration in which Te-Te separation of 4.414 Å is plausibly non-bonding separation (Fig.1.7).

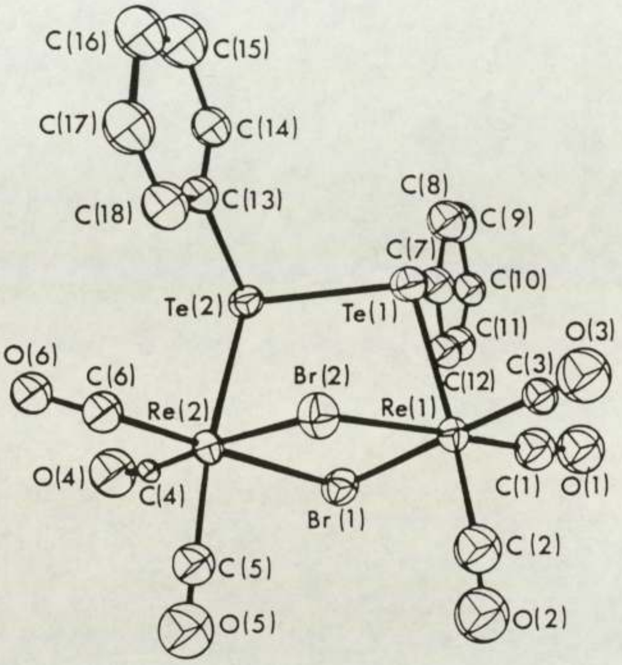


Figure 1.6: Molecular structure of $(OC)_3Re(\mu\text{-}Br)_2\text{-}(\mu\text{-}Ph_2Te_2)Re(CO)_3$

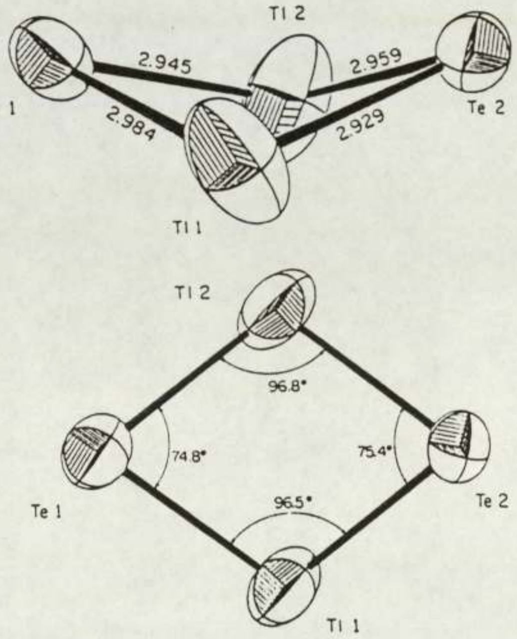


Figure 1.7: Two views of the $Tl_2Te_2^{2-}$ anion in $(2,2,2\text{-crypt-}K^+)_2Tl_2Te_2^{2-}$.en.

Many cage type complexes, or what are called cluster compounds, incorporating tellurium atoms as bridges between three transition metal atoms, have been reported together with their crystal structures$^{(49)}$. One example is the $Fe_3Te_2(CO)_9$ complex$^{(49b)}$, whose structure is shown in (Fig. 1.8).

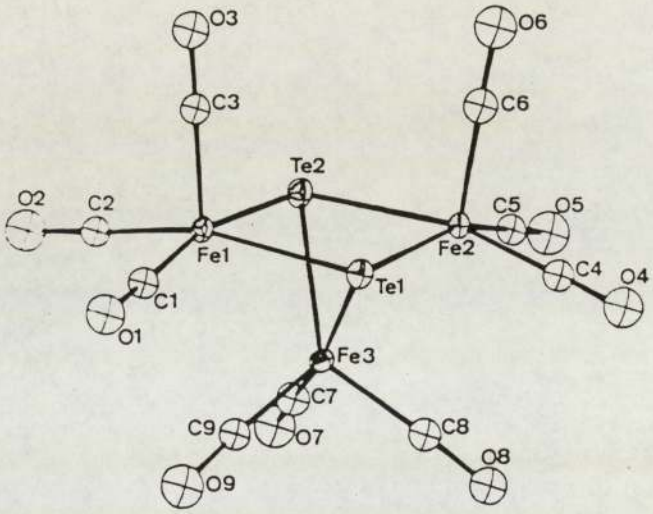
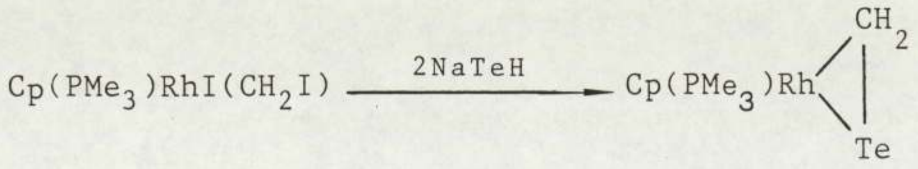


Figure. 1.8: The molecular structure of $Fe_3Te_2(CO)_9$.

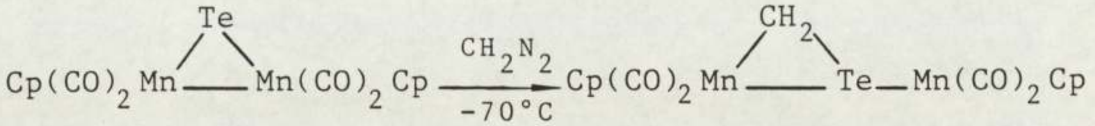
<u>(c)</u> Chelating or bidentate tellurium ligands:

Complexes containing terminal chelating telluroformaldehyde $[Cp(PMe_3)Rh(\eta^2\text{-}CH_2Te)]^{(50a)}$, and bridging telluroformaldehyde $[Cp(CO)_2Mn(\mu_2,\eta^2\text{-}CH_2Te)Mn(CO)_2Cp]^{(50b)}$ were prepared according to (eqs.1.6, 1.7).



$$Cp(PMe_3)RhI(CH_2I) \xrightarrow{2NaTeH} Cp(PMe_3)Rh\overset{CH_2}{\underset{Te}{<|}}$$

eq.1.6



$$Cp(CO)_2Mn(\mu\text{-}Te)Mn(CO)_2Cp \xrightarrow[-70^\circ C]{CH_2N_2} Cp(CO)_2Mn(\mu\text{-}CH_2)Te\text{—}Mn(CO)_2Cp$$

e.q. 1.7

The first examples of hybrid bidentate ligands have been prepared, incorporating tellurium as well as phosphorus atoms, and the X-ray structure of a Pt(II) complex, bis-[phenyl-o-(diphenylphosphino)phenyltelluro-P,Te]-platinum (II) tetra-thiosulphato-S-platinum(II) <u>bis</u>-dimethyl formamide, $[Pt(tep)_2][Pt(SCN)_4].2DMF$, has been reported$^{(51)}$, and is shown in (Fig. 1.9).

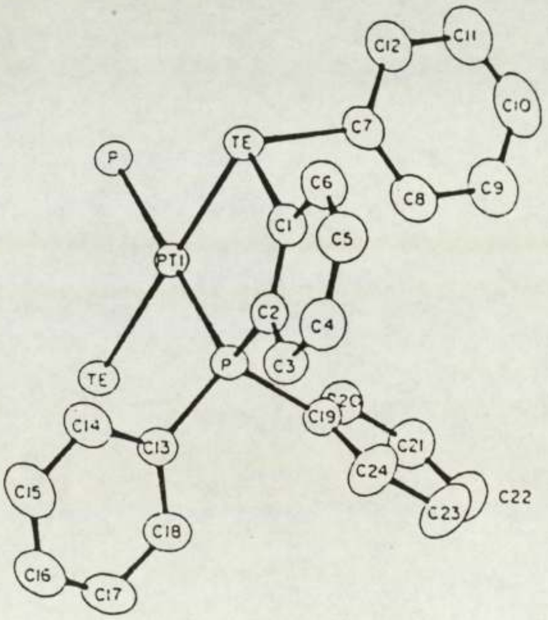
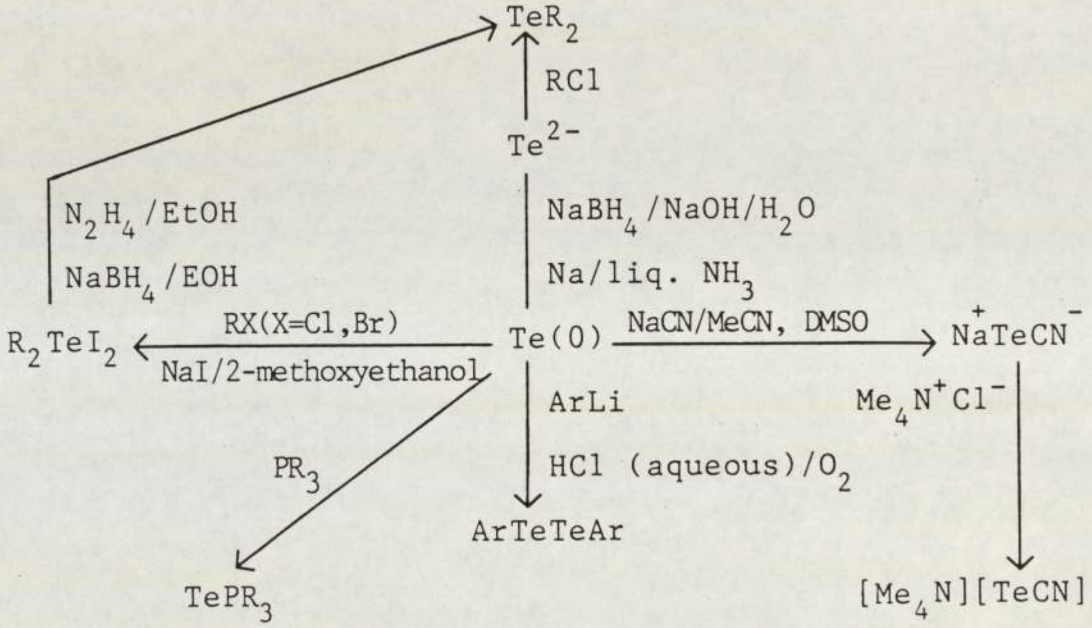


Figure 1.9: The structure of $[Pt(tep)_2]^{2+}$ ion of the complex $[Pt(tep)_2][Pt(SCN)_4].2DMF$.

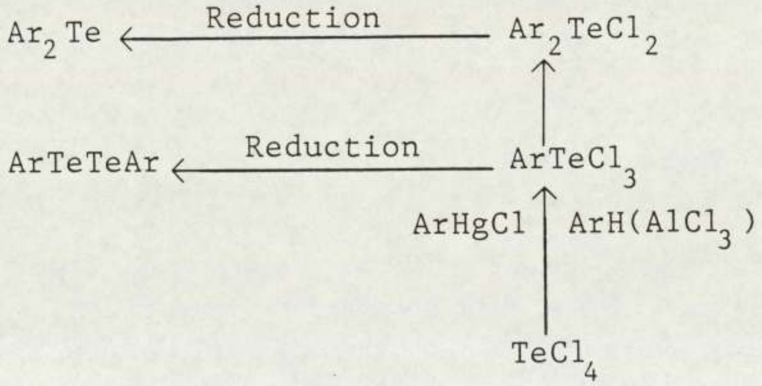
More details and examples of different kinds of tellurium ligand and their complexes are given in two recent reviews by Gysling$^{(14,52a)}$.

1.4 Synthesis of Organotellurium Ligands

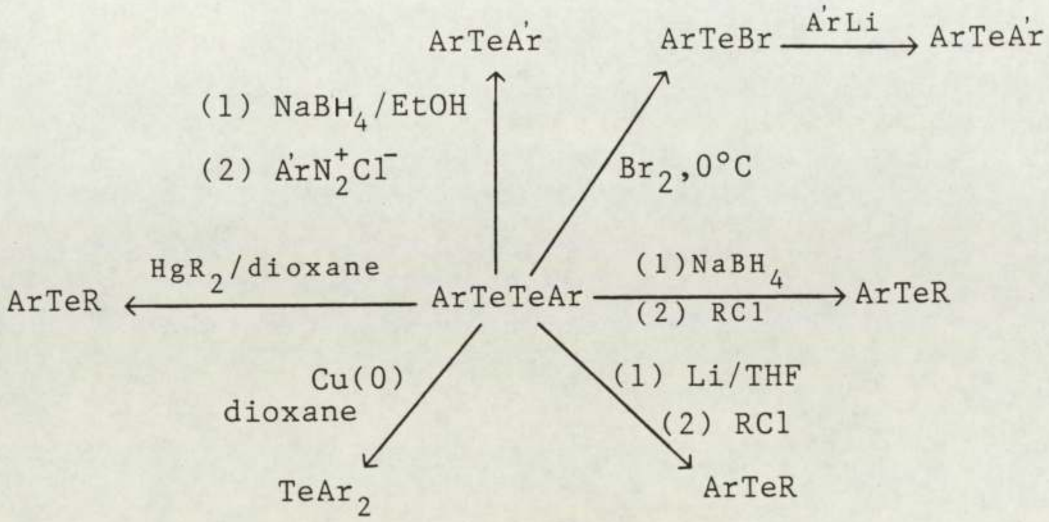
The synthetic aspects of organotellurium chemistry have received increasing attention, and different methods have been developed for the synthesis of symmetric and unsymmetric diorganyltellurides and diorganylditellurides. These aspects have been discussed in detail in several reviews (12,13,53,30c), and some examples are given in schemes 1.2-1.4.



Scheme 1.2. The use of Te(0) in organotellurium synthesis



Scheme 1.3. The use of TeCl$_4$ in organotellurium synthesis



Scheme 1.4. Synthesis of diorganotellurides from ditellurides

1.5 Hard and Soft Nature of Ligands

Tellurium ligands could form complexes with a variety of transition metal ions, but which of these metal ions are the more likely to co-ordinate with the tellurium donor atoms, i.e., which of the transition metal ions could easily form more stable co-ordination complexes with tellurium ligands?. In order to answer this question we have to discuss the basicity of the tellurium ligands.

In 1938 G.N. Lewis put forward a theory in which he called those substances capable of acting as ligands, bases, and the substances with which these react, acids. That means a Lewis acid is an acceptor of an electron pair, and it could be either a positive ion, like H^+, Ag^+, Cu^{2+}, a molecule like $BeCl_2$, BF_3 or a compound in which the central atom may use its d-orbitals like $SiCl_4$, $SnCl_4$, $TeCl_4$, and a Lewis base is a donor of an electron pair, which could be a negative ion (Cl^-, CN^-, OH^-, TeH^-,...etc.), molecules with one or two lone pairs of electrons (NH_3, PPh_3, H_2O, Me_2S, Ph_2Te,.....etc.) or molecules having carbon-carbon multiple bonds ($CH_2{=}CH_2$, $CH{\equiv}CH$, C_6H_6, ...etc.). This theory lacks quantitative aspects and enables only qualitative predictions to be made about complex formation. However, if it were possible to construct scales of Lewis acid and Lewis base strengths, the relative stabilities of all complexes could be predicted. If this is the case, a reference acid has to be chosen to quantify the strengths of different bases. Broadly speaking, for the proton (H^+) to be a reference acid, it is found that those bases containing nitrogen, oxygen or fluorine, as the donor atom, are stronger than those containing phosphorus, sulphur or chlorine. And therefore, acids such as Hg^+, Cu^+, and Pt^{2+} which form more stable complexes with phosphorus or sulphur ligands are weaker acids than those which form strong complexes with nitrogen ligands, Fe^{3+} and Cr^{3+} for example. These two classes of acids and bases are described as hard and soft acids and bases. For a better understanding, hard bases could be described as having high electronegativity, low polarisability and high resistance to oxidation, while soft bases are those which have low electronegativity, high polarisability and are readily oxidised. Soft metal ions are large, of low charge or have valence shell electrons which are easily distorted or removed, and they usually bond to soft ligands, while hard metal ions prefer hard ligands. However, it appears that many ions, transition metal ions in particular, cannot be classified as either hard or soft and they are regarded as borderline. The concept of symbiosis is very useful here. A cation which is classified as borderline is made softer by the co-ordination of a soft ligand or harder by the co-ordination of a hard ligand, and so more likely to add soft or hard ligands respectively. In Table 1.1 some metal ions and ligands are classified(54).

	Acids	Bases
Hard	H^+, Li^+, Na^+, K^+ Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{2+} Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+} Cr^{3+}, Co^{3+}, Fe^{3+}, Ce^{3+} Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+} VO_2^{2+}, VO^{2+}, MoO^{3+}	H_2O, R_2O, ROH, NH_3, RNH_2 OH^-, OR^-, Cl^-, ClO_4^-, NO_3^-, $CH_3CO_2^-$ SO_4^{2-}, CO_3^{2-} PO_4^{3-}
Soft	Cu^+, Ag^+, Au^+, Tl^+, Hg^+ Cd^{2+}, Hg^{2+}, Pd^{2+}, Pt^{2+} Tl^{3+} Pt^{4+}	R_2S, RSH, R_2Te, R_3P, R_3As RS^-, RTe^-, I^-, NCS^-, CN^-, H^-, R^- $S_2O_3^{2-}$
Border line	Zn^{2+}, Sn^{2+}, Pb^{2+} Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ru^{2+} Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}	Py Br^-, N_3^-, NO_2^- SO_3^{2-}

Table 1.1. Classification of some species as hard and soft acids and bases

The hardness of acid and bases is thus affected by size, oxidation state, electronic structure and the nature of attached groups already present.

Ahrland, Chatt and Davies introduced a different method of classification depending on the affinities of ligand atoms for metal ions and they concluded that metals could be divided into two classes:
Metals that form stable complexes with ligands containing (N, O, F) are considered as class (a), while class (b) metals are those that prefer ligands containing P, S, Cl donor atoms. Thus class (a) metal ions resemble the hard acid type and class (b) are comparable to the soft acid metal ions.

Since the tellurium atom has lower electronegativity (2.01) and higher single-bond covalent radius (1.37 Å) compared to the sulphur atom with an electronegativity of 2.44 and single-bond covalent radius of 1.04 Å, tellurium should be a softer donor than sulphur. Accordingly organotellurium ligands prefer to bond to metal ions having soft character. In fact, most of the complexes of tellurium ligands have been reported to be with metal ions which have soft acid character (14,60).

Laing and Pettit (55) have reported a comparative study of the donor properties of some dicarboxylic acids of sulphur, selenium and tellurium towards the silver(I) ion.

It was found that the general trend in the formation constant (Table 1.2) was Te > Se > S ≫ O, which is a typical behaviour of soft-acid interaction.

Ligand H_2L	Log $K_{Ag(H_2L)}$	Log $K_{Ag(HL)}$	Log K_{AgL}
$S(CH_2CH_2CO_2H)_2$	3.22	3.34	3.85
$Se(CH_2CH_2CO_2H)_2$	3.96	4.32	4.50
$Te(CH_2CH_2CO_2H)_2$	4.97	5.35	6.28(0.2M acetate buffer)

Table 1.2. Silver complex formation constants with chalcogenide ligands at 25°C and 0.1M KNO_3

However, complexes with metal ions having less soft-acid character than Ag(I) could be isolated. When pentacarbonyl manganese(I) halides were refluxed in diethyl ether with diphenyltelluride two carbonyl groups were replaced by diphenyltelluride(38a).

$$Mn(CO)_5X + 2Te(C_6H_5)_2 \longrightarrow Mn(CO)_3(TePh_2)_2X + 2CO \quad \text{eq. 1.8}$$

X= Cl, Br, I

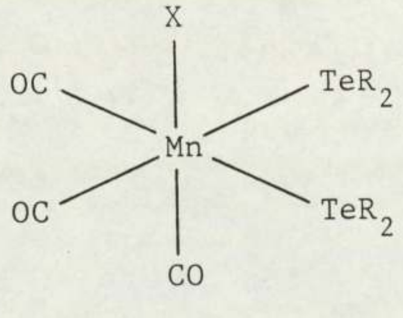
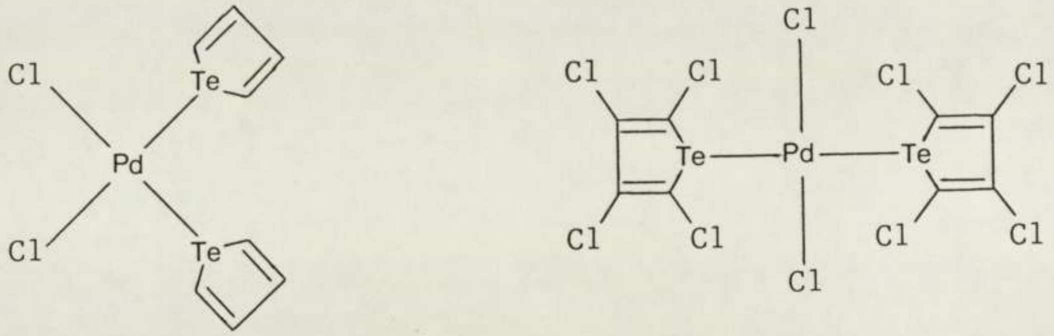


Figure 1.10. Configuration of $Mn(CO)_3(TePh_2)_2X$

The above complexes are thought to be stabilised by (Mn)d$\pi \longrightarrow$ (Te)dπ π-dative bond made possible by the electron-withdrawing phenyl groups. The analogous dibutyltelluride adduct could not be isolated due to the electron-donating groups in this dialkyltelluride, which increases the electron density on the tellurium atom and prevents dπ-dπ interaction, while $Re(CO)_5X$ (X = Cl, Br, I) reacts with dibutyltelluride to give the disubstituted products $Re(CO)_3(Te(n\text{-}Bu)_2)_2X$, in poor yields$^{(38b)}$ presumably because Re(I) is a softer ion than Mn(I). In more recent work$^{(56)}$, complexes of diphenyl-dichalcogenides with Mn(I) have been prepared with the formation of a bidentate dichalcogenide bridge. The ligand displacement reactions of CO and THF by E_2Ph_2 (E = S, Se, Te) were studied and equilibrium data were collected. The results established increased stability of these complexes in the sequence of increased softness, S<Se<Te.

The softness of the chalcogens (Te > Se > S) could be reflected on the other ligands attached to the metal ion. This is obvious from the highest energy of the carbonyl stretching frequencies in the complexes π-$CpMo(CO)_3EPh$ (E = S, Se, Te) when going from Te (CO_{str} = 2016cm^{-1}) <u>via</u> Se (CO_{str}= 2026cm^{-1}) to S (CO_{str}= 2033cm^{-1})$^{(57)}$, thus decreasing the bonding strength between Mo and CO in this sequence causes a higher thermal stablity for the tellurium complex than for the selenium and sulphur complexes.

The reaction of Na_2PdCl_4 with tellurophene in methanol gave mostly (70% yield) a monomeric cis-compound (A), while with tetrachlorotellurophene it gave a monomeric complex formulated as the trans- compound (B)$^{(58a)}$, the



(A) ν(Pd-Cl)=303,287cm^{-1} (B) ν(Pd-Cl)=354cm^{-1}

Figure 1.11. The trans-effect of withdrawing groups on the geometry of tellurium complexes.

larger trans-influence of the tetracholorotellurophene versus tellurophene has been rationalised on the basis of increased π-accepter properties of the chloro-substitued ligand. A comparison of the ν_{CO} bands of the complexes of the type $(OC)_3Fe(\mu\text{-}TeAr)_2Fe(CO)_3$ (Ar = C_6H_5, ν_{CO} = 2056, 1978, 1969cm^{-1}; Ar = C_6F_5 , ν_{CO} = 2070, 2041, 2007, 1997 cm^{-1})$^{(58b)}$also suggests an increased π-acceptor capacity of the TeC_6F_5- briged complex.

1.6 Accommodating Tellurium Ligands with Borderline and Soft Metal Ions by Using Chelate Ligands

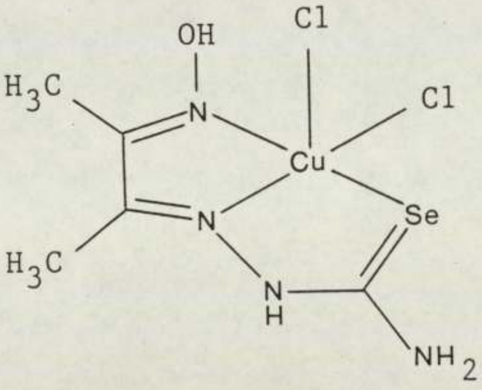
According to the above illustration of the softness of tellurium ligands and the stability of a certain tellurium complex, it seems that it is not easy to prepare and isolate complexes which incorporate hard or borderline metals with monodentate tellurium ligands, unless something is done to increase the stability of such complexes. Indeed, in a comprehensive review in 1981 of transition-metal co-ordination complexes of thio-, seleno- and telluroethers, Murray and Hartley(59) stated that it was difficult to prepare all but the simplest organotellurium ligands, and at that time only monodentate telluroethers and consequently their complexes were known.

1.6.1 Some Borderline and Hard Metal Complexes

(A) Copper(II)

Although Cu(I) tellurium complexes have been widely investigated, it seems that their analogues with Cu(II) were neglected. This might be due to various reasons, among them is that Cu(II) ion is reduced to Cu(I) when reacted with tellurium ligands(46), and also Cu(II) ion shows little tendency to co-ordinate to such soft ligands.

Nevertheless, copper(II) can form well characterised complexes with sulphur and selenium ligands. When solutions of copper(II) chloride and diacetylselenosemicarbazone oxime(H_2dseo) were mixed, the green crystalline $CuCl_2.H_2$dseo was separated without reduction of Cu(II) to Cu(I)(60a). This was confirmed by measurement of the effective magnetic moment, and it has been assumed that the (H_2dseo) behaves as a terdentate ligand (two nitrogen and one selenium donors).



(i)

The crystal and molecular structures of copper(II) diethyldiselenocarbamate [Cu(dsec)$_2$] have been reported(60b) in which the co-ordination geometry of the copper atom is closely related to a tetragonal pyramid (Fig. 1.12) with normal bonds to four Se atoms, and a fifth long bond to a selenium atom of the centrosymmetrically related molecule.

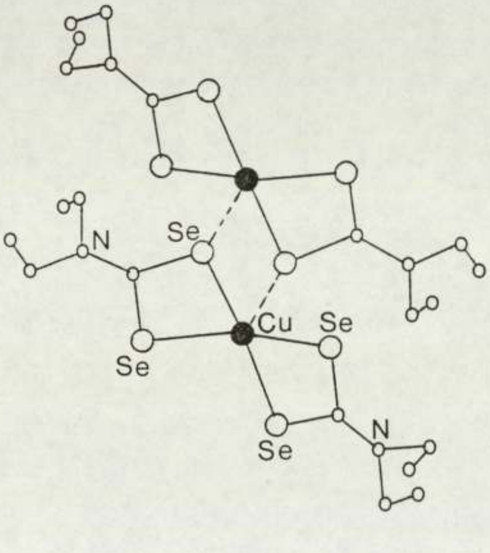


Figure 1.12. Bimolecular unit of Cu(dsec)$_2$.

Only one example of a Cu(II) complex with a tellurium ligand has been mentioned and it was postulated as $CuCl_2.[(o\text{-}NH_2\text{-}C_6H_4)_2Te_2]$ based only on the elemental analysis(61). Therefore, it is reasonable to further investigate Cu(II) complexes containing tellurium ligands.

(B) Nickel(II)

Like copper(II), nickel(II) has also been reported to form complexes with sulphur and selenium containing ligands(62a). The complex bis-(diethyldiselenocarbamato)-nickel(II) has been prepared, and its crystal structure been determined(60b,62b), in which each complex molecule is formed by the two ligands in planar co-ordination to a nickel atom through four selenium atoms (Fig. 1.13). Unlike the copper(II) analogue, Ni(II) atom in this complex shows no tendency to co-ordinate a fifth selenium atom.

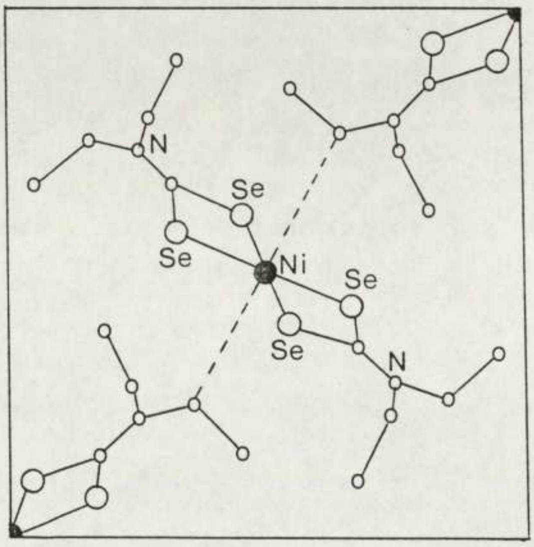


Figure 1.13. Crystal structure of $Ni(dsec)_2$

Although a nickel(II) complex of the type RNiTeR' has been proposed as an intermediate in Ni(II) phosphine complex catalysed carbon-carbon bond-forming reactions between diorganotellurides and Grignard reagents$^{(62c)}$, no Ni(II) complex with a tellurium ligand has been synthesised or separated. Therefore, it is interesting to extend the use of sulphur and selenium to tellurium ligands.

However, the softer nickel(II), on the basis of the symbiosis concept that borderline metal ions could be made softer by the co-ordination of certain soft ligands, has been reported to form well characterised compounds with aryl-tellurium ligands. The synthesis of nickel(II) compounds with, for example, the phenyltellurol ligand have been described$^{(62d)}$, in which the compound πCpNi-$(P(n\text{-}Bu)_3)(Te\text{-}C_6H_5)$ has been prepared by exchange reaction:

$$[\pi CpNi(P(n\text{-}Bu)_3)_2]^+Cl^- + NaTe\text{-}C_6H_5 \longrightarrow \pi CpNi(P(n\text{-}Bu)_3)(Te\text{-}C_6H_5) + NaCl + P(n\text{-}Bu)_3 \qquad \text{eq.1.9}$$

This complex, which is moderately stable in air, decomposes in CH_2Cl_2 and CCl_4 to give the complex $\pi CpNiP(n\text{-}Bu)_3Cl$.

(C) Cobalt(II) and Cobalt(III)

Complexes of these metal ions with sulphur and selenium ligands have been prepared and investigated. Most of these complexes are with chelating ligands such as $[Co^{II}(o\text{-}Ph_2P\text{-}C_6H_5\text{-}SeMe)_2Br]ClO_4$ (63a), $Co^{II}[Ph_2P(Se)\text{-}CH_2P(Se)Ph_2]_2$ (63b,d), $[Co^{III}(en)_2(SeCH_2COO)]ClO_4$ and $[Co^{III}\text{-}(en)_2(SeCH_2CH_2NH_2)](NO_3)_2$ (63c). The last complex has been investigated by X-ray crystallography (Fig. 1.14).

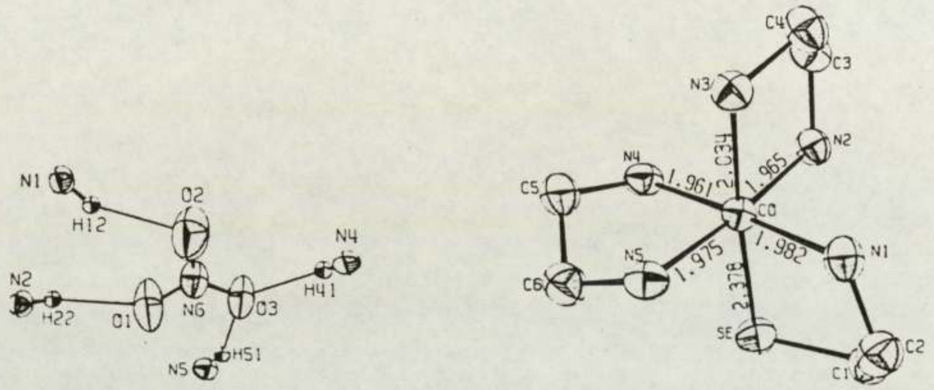
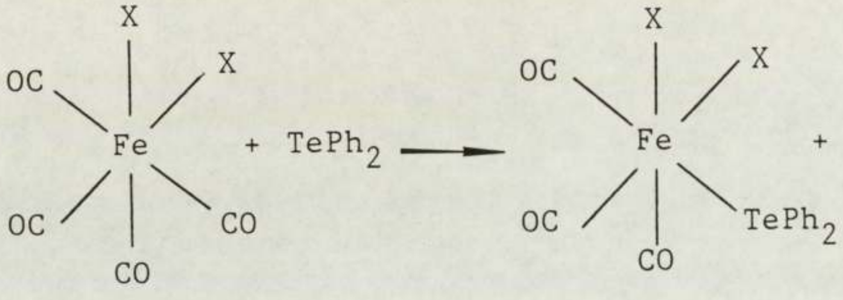


Figure 1.14. The structure of $[Co(en)_2(SeCH_2CH_2NH_2)][NO_3]_2$

An organotellurium complex with the softer ion Co(I) has been synthesised by the reaction of $\pi Cp_2Nb(TePh)_2$ with $Hg[Co(CO)_4]_2$ (63e) to give $[(\pi Cp)_2Nb(\mu\text{-}TePh)_2Co(CO)_2]$ which is stable under nitrogen, but its DMSO solution immediatly decomposes in air. Its diamagnetism suggests the presence of a Nb-Co bond, which might be the driving force for the formation of the complex. However, only one Co(II) complex with a tellurium ligand has been reported and studied by ESR (64), and it was not isolated. Therefore, it is feasible to further investigate Co(II) complexes with tellurium ligands.

(D) Iron(III) and Iron(II)

Many iron(III) complexes with sulphur and selenium ligands have been mentioned (65), but tellurium complexes have not been reported. This gives the impetus to investigate such complexes. The reaction of some iron(II) complexes with diphenyltelluride has been studied (38a), involving displacement of a cis CO group to the halides by a tellurium ligand (eq. 1.10).


eq. 1.10

X = Br, I

These tellurium derivatives show considerably enhanced stability to air and moisture compared with the original complex.

In contrast, the heavier borderline metal ions could form complexes with tellurium ligands without difficulty. Reaction of rhodium trichloride hydrate with excess $TePh_2$ in ethanol under reflux gave $(Ph_2Te)_3RhCl_3$ (66a). Rhodium(III) complexes comprising both terminal and bridging $TePh^-$ ligands have also been prepared (66a) by the following routes:

$$RhCl_3.3H_2O + TePh_2 \xrightarrow[EtOH/reflux]{aq.CH_2O} RhCl_2TePh(TePh_2)_2 \quad eq.1.11$$

$$RhCl_3.3H_2O + TePh_2 \xrightarrow[EtOH/reflux]{aq.CH_2O/KOH} Rh(TePh)_3 \qquad eq.1.12$$

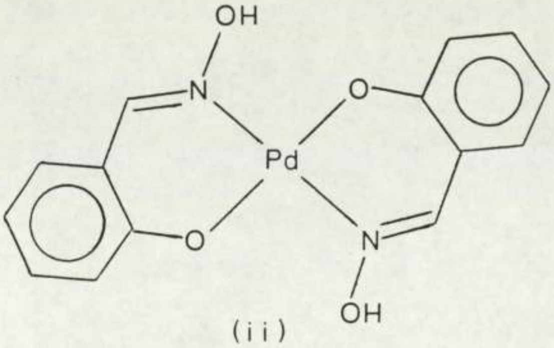
Reaction of an alcoholic CO- saturated solution of ruthenium trichloride hydrate with diphenyltelluride gave a mixture of di- and trisubstituted Ru(II) complexes, $[Ru(CO)_2(TePh_2)_2Cl_2].\frac{1}{2}CH_2Cl_2$ and $[Ru(CO)(TePh_2)_3Cl_2].\frac{1}{2}CH_2Cl_2$, which were separated by fractional crystallisation from CH_2Cl_2/pentane (66b).

The ruthenium(III) complex $[Ru(NH_3)_5TePh_2]^{3+}$ was generated in solution by electrochemical and chemical (e.g.,30% H_2O_2 in 0.2M HCl) oxidation of the Ru(II) analogue and was characterised by electronic spectroscopy in solution without isolating the complex (66c).

1.6.2 Soft Metal Ions Complexes

There are some metal ions which are regarded as class (b) or of soft character (e.g. Pd(II), Pt(II), Hg(II)), but in fact they can form well defined complexes with both hard and soft ligands.

Potassium tetrachloropalladate(II) reacts with salicylaldoxime to give bis(salicylaldoximato)palladium(II) dichloride in which the ligands are bidentate, coordinating through the hard nitrogen and oxygen atoms (67a).



(ii)

X-ray examination showed that the complex posesses a centre of symmetry, and therefore has a planar configuration. Also complexes of palladium containing both hard and soft ligands are known (67b,c). An example is the *cis*-*bis*[dimethyl(phenyl)phosphine]bis(5-methyltetrazolato)-palladium(II) (67b), which has approximately *cis*-square-planar configuration (Fig. 1.15).

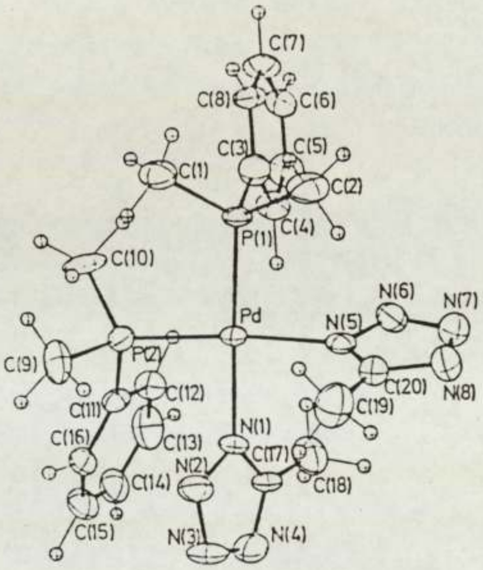
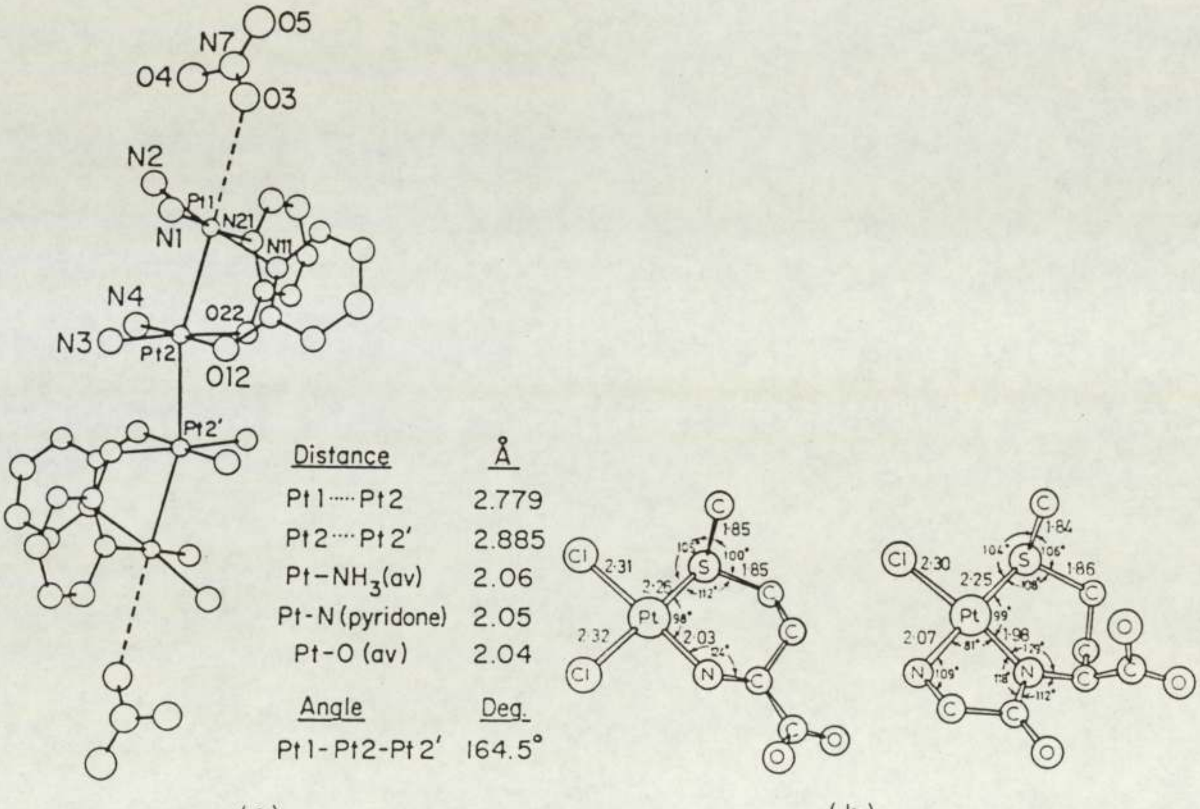


Figure 1.15. The molecular structure of a palladium complex with both hard and soft ligands.

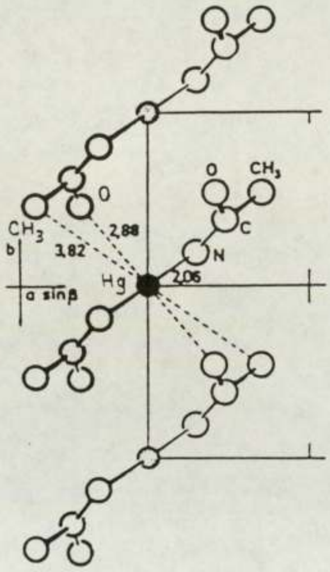
Some platinum compounds, known as Magnus salts, have well known structures. An example is the complex $Pt(NH_3)_4PtCl_4$, which has a tetragonal structure with the two planar $Pt(NH_3)^{2+}$ and $PtCl_4^{2-}$ ions stacked over one another and a Pt-Pt distance of 3.25 Å (68a). Another example of platinum(II) ion bonded to hard ligands is the *cis*-diamineplatinum α-pyridone complex (68b), in which some of the ligands act as bidentate ligands through nitrogen and oxygen atoms (Fig. 1.16a). Complexes of Pt(II) containing both hard and soft donor atoms are also known. The crystal structure of platinum(II) complexes with L-methionine and glycyl-L-methionine, prepared by the interaction of $PtCl_4^{2-}$ with the free ligands in aqueous solutions, were reported $^{(68c)}$, in which the ligands are either bidentate or tridentate, bonded through nitrogen and sulphur atoms (Fig.1.16b).



(a) (b)

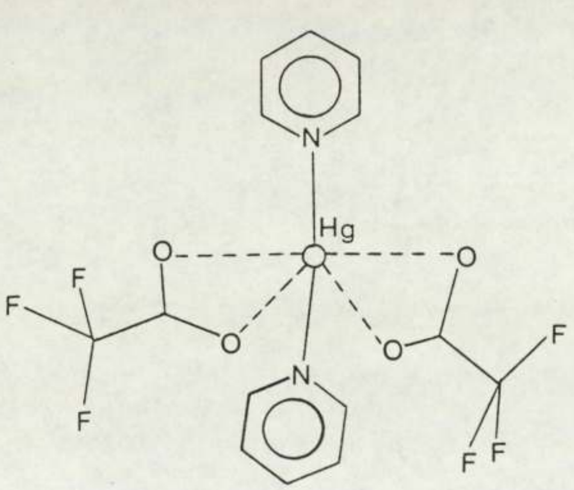
Figure 1.16: Platinum(II) complexes with hard ligands (a), and with hard and soft ligands (b)

Many mercury(II) compounds have been published in which the mercury ions show an affinity toward hard ligands as well as soft ligands. Mercury(II) oxide dissolved in molten acetamide, gave Hg(CH_3CONH_2) which could be isolated by dissolving the mixture in water. Crystallographic investigation showed that mercury is coordinated to the nitrogen and, to a lesser extent, the oxygen of the acetamide ligand$^{(69a)}$.



(iii)

Interaction of pyridine with mercuric trifluoroacetate brings the nitrogen of two pyridine groups into the coordination sphere of the mercury ion which is located in a distorted octahedral environment$^{(69b)}$.



(iv)

The reaction of mercury(II) chloride with bis(2-pyridyl)-disulphide gave the complex Hg(pySSpy)Cl_2 . The crystal structure of this complex showed that the mercury(II) ion is co-ordinated by two chloride ions and two pyridyl nitrogen atoms (69c). The infra-red spectrum of the complex revealed no change in the frequency ν(S-S), which occurs at 548cm^{-1}, that means the sulphur atoms are not co-ordinated to mercury and this is supported by X-ray crystallography, (Fig.1.17). This might be surprising because it is known that mercury(II) shows a good affinity to soft donor atoms like sulphur.

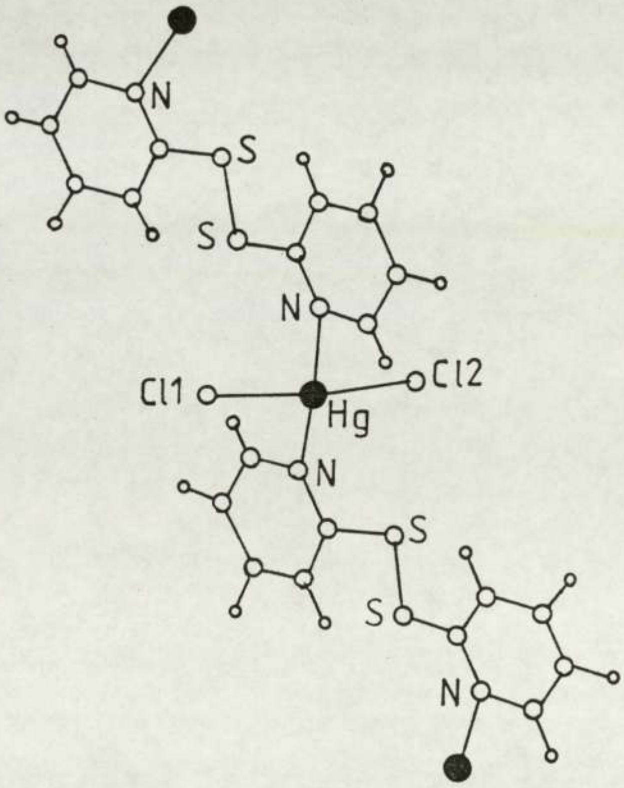


Figure 1.17: the structure of Hg(pySSpy)Cl_2

There are also many well defined complexes of Hg(II) with soft ligands. The complex diacetato-bis(tricyclohexylphosphine)mercury(II) dihydrate is an example of a complex with a phosphorus ligand, and its crystal structure has been solved$^{(69b)}$. Figure (1.18) shows the co-ordination of two phosphine ligands to Hg(II).

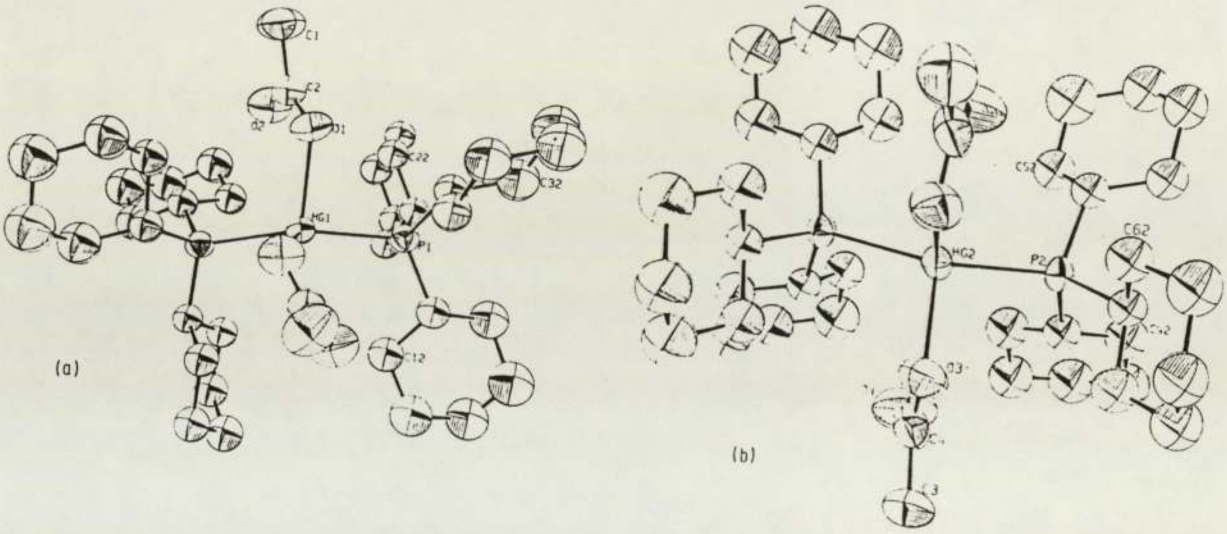


Figure 1.18. Views of independent molecules of $Hg(PCy_3)_2(OAc)_2$

Since the ions Pd(II), Pt(II) and Hg(II) are well known to form complexes with tellurium ligands$^{(14)}$, as well as being able to accommodate hard and soft donor atoms in their co-ordination sphere, it is very interesting to study their complexes with chelating ligands containing a hard donor and a tellurium donor atoms. Such complexes have not been widely studied, although the first example of a Pt(II) complex has been reported by Gysling$^{(52)}$.

1.6.3 The Present Work

The object of the present work is, therefore, to synthesise potentially bidentate or multidentate ligands containing both tellurium and donor atoms such as nitrogen or oxygen, and try to prepare a wide range of transition metal and post transition metal complexes with these ligands, and investigate their structure by the kinds of physical methods available including infra-red, visible-u.v., ESR, magnetic measurements, NMR, Mössbauer and X-ray crystallography.

CHAPTER TWO

GENERAL EXPERIMENTAL TECHNIQUES

The preparation and handling of organic tellurium compounds need care. Therefore, all the experiments involving such compounds have been done under an inert atmosphere, nitrogen gas or argon gas; these were bubbled into a chromium(II) solution and passed over calcium chloride and phosphorus pentoxide prior to use.

2.1 Chemicals

The starting materials used for many reactions were obtained either from British Drug Houses (BDH) or Aldrich Chemical Company and were used without further purification. Platinum, palladium and rhodium compounds, used in complex preparations, were obtained from Johnson and Matthey Ltd. The known tellurium compounds used in the present work, were prepared by literature methods starting from either Te powder 99.5% (BDH) or $TeCl_4$ (BDH) and they gave satisfactory melting points, I.R. and N.M.R. spectra.

2.2 Solvents

All the solvents were obtained from commercial sources. Analytically pure solvents were used without further purification. Other solvents were cautiously purified where necessary by distillation and were kept over molecular sieve type A4 (70), and stored in clean coloured containers.

2.3 Physical Measurements and Techniques

2.3.1 Melting Points

Melting points of all solid compounds were determined using a Gallenkamp electrically heated melting point apparatus provided with a mercury thermometer. All readings were uncorrected.

2.3.2 Conductivity Measurements

Molar conductance of dilute solution (10^{-3}M) 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.

2.3.3 Infra-red Spectra

Infra-red spectra were recorded on a Perkin-Elmer infra-red spectrophotometer model 599B in the range 4000-200cm^{-1} at a normal scan speed which took 12 minutes for each run. Spectra of solid samples were either taken as KBr pellets (-1%) or as nujol mulls between KBr discs, while liquid samples were spread as thin films between KBr discs.

2.3.4 Ultra-violet and Visible Spectra

U.V. and visible absorption spectra were taken for solution samples using 10mm path length quartz cells with the pure solvent being used in the reference beam. These spectra were recorded on Unicam visible U.V. instruments models SP800 B and SP8100.

2.3.5 Elemental Analyses

Micro-elemental analyses for carbon, hydrogen, nitrogen and halogen were carried out by the Analytical Services Unit of the Molecular Sciences Department of Aston University. Tellurium was analysed volumetrically by the following method (71):

A known weight of the compound was dissolved in, and oxidised with a mixture of concentrated nitric acid and perchloric acid (2:1). The volume of the mixture was then cautiously reduced in a fume cupboard to $10cm^3$ and another $10cm^3$ of conc.$HClO_4$ was added; heating was continued until the solution became effectively colourless, it was then cooled and diluted with distilled water to $250cm^3$ in a volumetric flask. To an aliquot of $50cm^3$ of the sample solution was added a known excess of standard 0.1N potassium dichromate solution, and the mixture was allowed to stand half an hour at room temperature. Then the solution was treated with an excess of 0.1N iron(II) ammonium sulphate solution. The unreacted iron(II) was back titrated with a standard 0.1N potassium dichromate solution using a few drops of diphenyl amine indicator (prepared by dissolving 2.7g of diphenyl amine in 100ml of conc.H_2SO_4) and about $2cm^3$ of conc. phosphoric acid as a complexing agent for iron(III)ions.

1ml 0.1N $K_2Cr_2O_7$ = 0.00638g Te

2.3.6 Mass Spectra

Mass spectra of some compounds were recorded on an AEl MS9 spectrometer at an ionising potential of 70 eV. Measurements were carried out on ^{130}Te isotope which is the isotope of largest mass number and highest relative abundance.

2.3.7 Magnetic Measurements

Magnetic susceptibility measurements of solid samples were taken with a Stanton Gouy balance model (SM 12) at 22°C using the Gouy method. Samples were ground and prepared according to the literature method using $HgCo(NCS)_4$ as a calibrant(72). Magnetic moments were calculated with correction for diamagnetism.

2.3.8 Mössbauer Measurement

One ^{57}Fe Mössbauer spectrum was measured at Birmingham University by Dr. F. J. Berry to whom many thanks are due.

2.3.9 Nuclear Magnetic Resonance Measurements

Some ^{1}H N.M.R. spectra were determined with a Perkin-Elmer R12B instrument (60Hz) using tetramethylsilane(TMS) as an internal standard. Other ^{1}H N.M.R. and proton decoupled natural abundance ^{13}C N.M.R. spectra were obtained on an FX-90Q(JEOL) multinuclear spectrometer at 90 and 22.5 MHz, respectively. The ^{125}Te N.M.R. spectra were also measured for solution samples at room temperature on the FX-90Q (JEOL) spectrometer at 28.2 MHz by M. Perry in the Molecular Sciences Department of Aston University. The instrument was first checked by using standard materials, like diphenyltelluride in dichloromethane and <u>bis</u>(diethyldithiocarbamato)tellurium(II), as 1M solution in deuterated chloroform, for which the chemical shifts (δ) were in agreement with literature values(63b), and within the experimental error of ±0.5 ppm. The data were referenced to the frequency of the standard dimethyltelluride for which δ is considered as zero(73).

2.3.10 Electron Paramagnetic Resonance Spectra Measurement (EPR)

EPR spectra of solid samples were obtained with a JEOL PE-1X spectrometer, using a manganese(II) standard to check the magnetic field and as g-marker. In general solid samples were packed inside a capillary glass tube (1mm diameter) up to about 1cm and put inside a quartz tube of 5mm diameter which is inserted in the resonant cavity between the magnetic poles.

2.3.11 X-ray Measurements

Crystals of the tellurium compounds were obtained by recrystallisation from suitable solvents. Preliminary examination of single crystals by photographic methods was used to check the quality of the crystals.

Accurate cell dimentions and reflection intensities were measured with graphite-monochromated Mo-K_α radiation on an Enraf-Nonius CAD-4 diffractometer operating in the mode ω-2θ. Two standard reflections were measured every two hours to check the stability of the system. For one of the crystals (refer to Chapter Four) absorption corrections were applied.

The structures were solved by Patterson and Fourier methods, using reflections having $I > 2.5\,\sigma(I)$. The refinements were by least-squares, using anisotropic temperature factors for the heavier atoms. Hydrogen atoms were either located from difference Fourier maps or placed in calculated positions (C-H = 1.08 Å) "riding" on their respective carbon atoms; their parameters were not refined. Refinement was terminated when all calculated shift/error ratios were < 0.1.

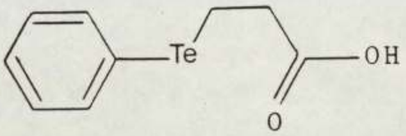
Computations were carried out on the University of Birmingham Honeywell computer with the SHELX program(74) and also on the University of Manchester Regional Computer Centre.

CHAPTER THREE

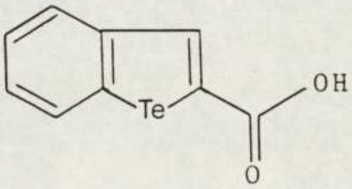
SODIUM 2-(4-ETHOXYPHENYLTELLURO)BENZOATE LIGAND PREPARATION AND CO-ORDINATION CHEMISTRY

3.1 Introduction

Building in a carboxylate functional group and a tellurium atom within the same molecule is not new. Many such compounds have been prepared, and some may chelate, but in others the tellurium atom and the carboxylate group may not be favourably placed for chelation. Piette and Renson(75a) could prepare phenyltelluro-3-propionic acid (i) by reacting sodium phenyltelluride (obtained by reduction of diphenylditelluride with sodium borohydride) with 3-chloropropionic acid sodium salt in an ethanol/benzene mixture. Later on, the same authors(75b) reported the preparation of benzo-(b)-tellurophene-2-carboxylic acid (ii) by three step cyclisation of 2-methyl-tellurobenzaldehyde with 2-bromoacetic acid.

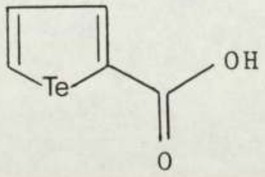


(i)



(ii)

Fringuelli et al(76), later, reported the preparation of tellurophene-2-carboxylic acid(iii), by reacting tellurophene and n-butyl-lithium to give the 2-lithio substituted tellurophene which was then poured on solid CO_2 and hydrolysed.



(iii)

In 1978 Piette et al (77) reported another series of ortho-substituted carboxylate compounds, the o-phenyltelluro-benzoic acid in particular, from the reaction of diazotised anthranilic acid and sodium phenyltelluride. More recently Engman (78a) tried to prepare the previously reported(78b) bis(2-carboxyphenyl)telluride by the reaction of potassium tellurocyanide and 2-carboxyphenyldiazonium tetrafluoroborate, but he obtained only 8% yield.

Nevertheless, only a few examples of complexes of such carboxy-tellurium compounds with metal ions are known. Laing and Pettit (55) reported the formation of some metal complexes with bis(3-carboxypropanyl)telluride. They measured the complex formation constants potentiometrically for some bivalent first-row transition metal ions and Ag(I) in solution without trying to isolate the complexes.

In order to establish, more firmly, the nature of the complexes, we tried to prepare and isolate such materials in the form of solid compounds, which could be studied by several physical techniques, and finally to ascertain if by co-ordinating a hard oxygen donor atom of the bidentate ligand to a hard or borderline metal ion, the tellurium atom would also co-ordinate.

3.2 Experimental

3.2.1 Synthesis of 2-(4-Ethoxyphenyltelluro)benzoic Acid

A method similar to that described by Piette et al(85) was used and is described below:

A solution of 2-aminobenzoic acid (27.5g,0.2 mole) in concentrated hydrochloric acid (25cm^3) and distilled water (100cm^3), was diazotised at 0-5°C with sodium nitrite (13.8g) dissolved in distilled water (25cm^3) *. Then the pH was rendered basic with the minimum of sodium bicarbonate solution. The cold solution, thus obtained, was shaken rapidly with a warm solution (at about 30°C) of sodium 4-ethoxyphenyltelluride obtained by reduction of a warm solution of bis(4-ethoxyphenyl)ditelluride(79) (25g, 0.05 mole) in a mixture of ethanol (50cm^3) and tetrahydrofuran (100cm^3) with minimum amount of a basic sodium borohydride solution (2.5g in 35cm^3 of 1N NaOH), while passing nitrogen gas. After the major evolution of N_2, the solution was again warmed, and then extracted with benzene, from which some of the starting ditelluride compound was recovered. The aqueous layer was chilled

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* The yield was noticed to be a few percent more when the diazotisation is performed under nitrogen gas.

with ice, and the precipitate, so formed, was filtered off, washed with benzene, then dissolved in acetone and reprecipitated by adding petroleum ether (60-80°C) to give an almost white crystalline sodium salt (yield, 19.1g = 49%), which, after drying over phosphorus pentoxide, melts at 257-260°C.

Found C = 40.1%, H = 4.50%; $C_{15}H_{13}NaO_3Te.3H_2O$
requires C = 40.4%, H = 4.29%

The acid form was prepared by adding hydrochloric acid (1M) to the sodium salt solution in 1:3 ethanol:water. The white precipitate was filtered, washed with water and dried over P_4O_{10}; it melts at 194-196°C.

Found C = 48.5%, H = 3.50%; $C_{15}H_{14}O_3Te$
requires C = 48.7 %, H = 3.81%

3.2.2 Synthesis of Complexes of 2-(4-Ethoxyphenyltelluro)benzoate

3.2.2.1 Thallium(I) Complex

The thallium(I) compound was prepared by reacting a hot solution of 2-(4-ethoxyphenyltelluro)benzoate (0.89g, 0.002 mole) in distilled water ($50cm^3$) with thallium(I) sulphate (0.3g, 0.001 mole) in water ($25cm^3$). The white precipitate was filtered, washed several times with water then ethanol, and vacuum dried to give almost quantitative yield. It was recrystallised from a 1:5 DMSO/CH_3CN mixture to give white crystals m.p 200-201°C.

Found C = 31.2%, H = 2.30%; $(C_{15}H_{13}O_3Te)Tl$
requires C = 31.4 %, H = 2.28%

3.2.2.2 Silver(I) Complex

A solution of sodium 2-(4-ethoxyphenyltelluro)benzoate (0.89g, 0.002 mole) in distilled water ($50cm^3$) was added with stirring to a solution of silver(I) perchlorate (0.415g, 0.002 mole) in distilled water ($25cm^3$) to get a gelatinous white precipitate, which was filtered, washed with water and dried in an oven at 60°C for three hours, then recrystallised from a 1:5 DMSO/CH_3CN mixture; the white compound decomposes at about 203°C.

Found C = 36.5%, H = 2.85%; $(C_{15}H_{13}O_3Te)Ag.H_2O$
requires C = 36.4%, H = 3.05%

3.2.2.3 Cobalt(II) Complex

An aqueous solution of cobalt(II) nitrate hexahydrate (0.873g, 0.003 mole) was added with stirring to a warm solution of sodium 2-(4-ethoxyphenyltelluro)benzoate (2.67g, 0.006 mole) in water ($75cm^3$). The pink precipitate, so formed, was filtered, washed with water and air dried, then recrystallised from chloroform and dried in a vacuum desiccator. The violet compound melts at 210°C with decomposition.

Found C = 43.3%, H = 3.30%, $Co(C_{15}H_{13}O_3Te)_2 \cdot 2H_2O$
requires C = 43.3%, H = 3.63%

3.2.2.4 Nickel(II) Complex

An aqueous solution of nickel nitrate hexahydrate (0.872g, 0.003 mole) was added slowly with stirring to a warm solution of the ligand (2.67g, 0.006 mole) in water (75cm^3). The light green precipitate was filtered, washed several times with water and air dried. It was recrystallised from chloroform to give an apple green compound with m.p 195-198°C

Found C = 44.2%, H = 3.30%, $Ni(C_{15}H_{13}O_3Te)_2 \cdot H_2O$
requires C = 44.2%, H = 3.47%

3.2.2.5 Copper(II) Complex

An aqueous solution of copper(II) nitrate trihydrate (2.46g, 0.006 mole) was added with stirring to a warm solution of the ligand (2.67g, 0.006 mole) in water (75cm^3). The precipitate was filtered, washed with water, then methanol and dried in vacuum to give a dark green complex, having a melting point 172-174°C.

Found   C = 44.1%, H = 3.50%, $Cu(C_{15}H_{13}O_3Te)_2.H_2O$
requires C = 44.0%, H = 3.44%..

3.2.2.6 Iron(III) Complex

An aqueous solution of $(NH_4)_2Fe_2(SO_4)_2.10H_2O$ (0.68g, 0.001 mole) was added slowly with stirring to a warm solution of the ligand (2.67g, 0.006 mole) in water (75cm^3). During the addition a violet-brown precipitate separated and was left at room temperature to settle, then filtered off, washed with water, alcohol and dried in a vacuum desiccator. The violet-brown compound melts at 165-168°C.

Found   C = 45.9%, H = 3.40%; $Fe(C_{15}H_{13}O_3Te)_3.H_2O$
requires C = 45.8%, H = 3.50%

3.2.2.7 Chromium(III) Complex

A solution of chromium(III) nitrate trihydrate (0.46g, 0.002 mole) in water (20cm^3) was added slowly to a warm solution of the carboxylate ligand (2.67g, 0.006 mole) in water (75cm^3), with stirring. During the addition a fine light green precipitate formed, which was allowed to settle, filtered and washed with water then with cold ethanol, and air dried. It was dissolved in a minimum amount of acetone and left to evaporate at room temperature, leaving a dark green solid, m.p = 163 - 165°C.

Found C = 45.8%, H = 3.20%; $Cr(C_{15}H_{13}O_3Te)_3.H_2O$ requires C = 45.9%, H = 3.51%

3.3 Results and Discussion

Generally, the reaction between sodium 2-(4-ethoxyphenyltelluro)benzoate (NaETB) and the metal salts involves an exchange between the cations and the anions leading to the precipitation of the less soluble complexes. All the prepared complexes gave good elemental analysis data after recrystallisation, however, only the thallium(I) compound afforded well defined crystals.

3.3.1 Infra-red Spectra of the Carboxylate Group

The i.r. spectra could be helpful in the structural discussion of the compounds which contain carboxylate groups. Extensive infra-red studies have been made on metal complexes of carboxylic acids. The carboxylate ion may have any of the following structures:

Ionic (I)

Unidentate (II)

Chelate (III)

Bridging (IV)

Figure 3.1

Compound	Found %		Calculated	
	C	H	C	H
$C_{15}H_{14}O_3Te$	48.5	3.50	48.7	3.81
$C_{15}H_{13}NaO_3Te.3H_2O$	40.1	4.50	40.4	4.29
$(C_{15}H_{13}O_3Te)Tl$	31.2	2.30	31.4	2.28
$(C_{15}H_{13}O_3Te)Ag.H_2O$	36.5	2.85	36.4	3.05
$(C_{15}H_{13}O_3Te)_2Co.2H_2O$	43.3	3.30	43.3	3.63
$(C_{15}H_{13}O_3Te)_2Ni.H_2O$	44.2	3.30	44.2	3.47
$(C_{15}H_{13}O_3Te)_2Cu.H_2O$	44.1	3.50	44.0	3.44
$(C_{15}H_{13}O_3Te)_3Cr.H_2O$	45.8	3.20	45.9	3.51
$(C_{15}H_{13}O_3Te)_3Fe.H_2O$	45.9	3.40	45.8	3.50

Table 3.1 The elemental analysis of the ligand 2-(4-ethoxyphenyltelluro)benzoate (ETB) and its complexes.

Compound	ν(OH)	ν_a(COO)	ν_s(COO)	Δ(COO)
Acid form(HETB)	3300-2500	1660(s)	1270(s)	390
Sodium salt	3650-3100	1572	1395(s)	177
Tl(I) complex	-	1512	1380	132
Ag(I) complex		1532	1388,1375	-150
Co(II) complex	3550-3200	?	1395(s)	
Ni(II) complex	3600-3200	1650,1525(sh)	1390(s)	
Cu(II) complex	3600-3300	1590	1395(s)	195
Cr(III) complex	3300-2500	1658,1525(sh)	1263,1410	
Fe(III) complex	3300-2500	1660,1515	1265,1410	

Table 3.2 Infra-red data of ETB^- ligand and its complexes (s) = strong; (sh) = shoulder

Compound	Wave length, λmax in nm(ϵ)*				
Co^{2+} complex	624 nm (93.75)	589 nm (110)	540 nm (88.75)	354 nm (13200)	324 nm(obscured) (10000)
Ni^{2+} complex	750 nm (5.57)	679 nm (6.17)			324 nm(broad) (7600)
Cu^{2+} complex	752 nm (58.1)			347 nm (5000)	320 nm(obscured) (8250)
Cr^{3+} complex	800 nm (26.25)	575 nm (61)		357 nm (14000)	324 nm(obscured) (6000)
Fe^{3+} complex	480 nm (770)			354 nm (14800)	315 nm(obscured) (10000)

* ϵ = Extinction coefficient (l $mole^{-1}$ cm^{-1})

Table 3.3 Electronic absorption spectra of the complexes of the ligand (ETB)

Compound	$\Lambda^{(a)}$	$\mu_{eff}^{(b)}$	Mössbauer data	
			$\delta^{(c)}$	$\Delta^{(d)}$
Co^{2+} complex	2.19(acetone)	5.52		
Ni^{2+} complex		2.83		
Cu^{2+} complex		1.55		
Cr^{3+} complex		2.48		
Fe^{3+} complex	7.6 (DMF)	2.80	0.37±0.03	0.61±0.05
Tl^{+} complex	15 (DMSO)	-		
Ag^{+} complex	3.5 (DMSO)	-		

(a) Molar conductivity ($ohm^{-1}cm^{2}mole^{-1}$) of 10^{-3}M solution at 22°C

(b) Magnetic susceptibility (B.M) at a current of 10 amps. at 22°C, 1 B.M = 9.27×10^{-25}kJ/gauss

(c) Chemical isomer shift (mm sec^{-1}) vs. Fe metal

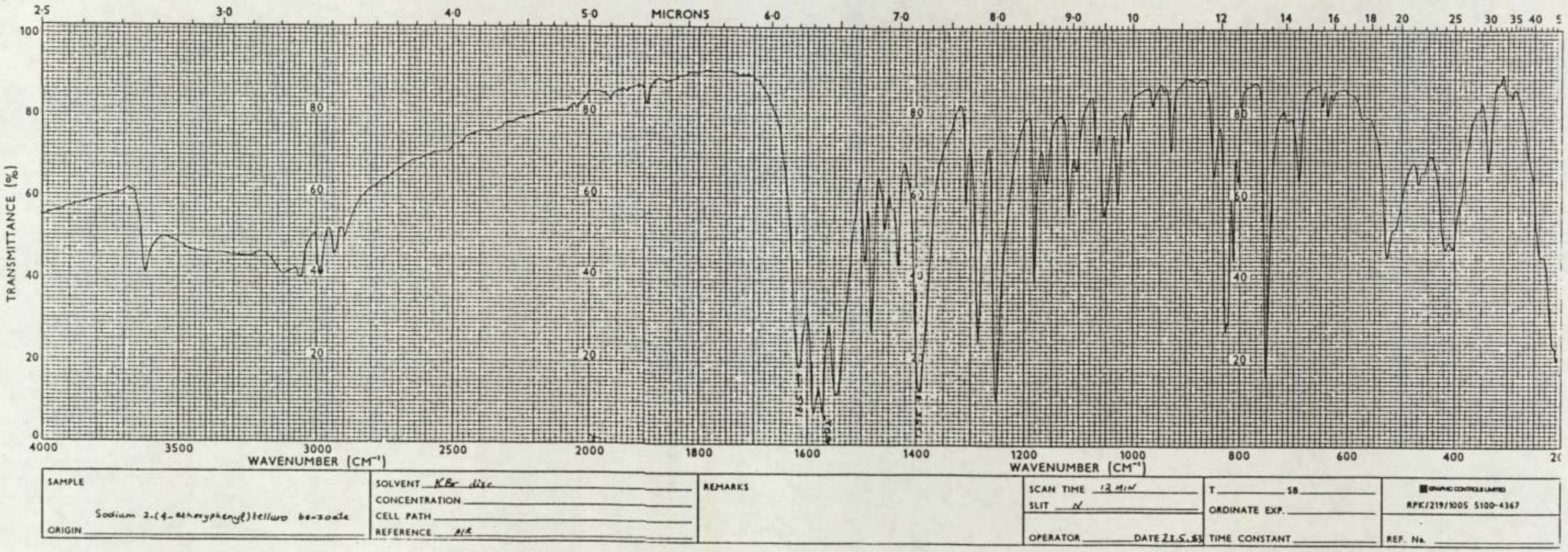
(d) Quadrupole splitting (mm sec^{-1})

Table 3.4 Magnetic, conductivity and Mossbauer data of the complexes of the ligand (ETB).

From a comparison of the infra-red spectra of the acetate ion in compounds of known structure, Curtis(80) has shown that it is possible to distinguish between the various types of acetate co-ordination on that basis. The asymmetrical stretching frequency $\nu_a(COO^-)$ and symmetrical stretching frequency $\nu_s(COO^-)$ of free acetate ion are $1578cm^{-1}$ and $1414cm^{-1}$ respectively, for sodium acetate(81), which resembles structure (I) (Fig. 3.1). In the unidentate complexes (structure (II)), $\nu(C=O)$ is higher than $\nu_a(COO^-)$ and $\nu(C-O)$ is lower than $\nu_s(COO^-)$. As a result the separation between the two $\nu(CO)$ is much larger in unidentate complexes than in the free ion. The opposite trend is observed in the bidentate (chelate) complex (structure III), the separation between the $\nu(CO)$ is smaller than that of the free ion. In the bridging complex (structure IV), however, the two $\nu(CO)$ are close to the free ion values(82).

3.3.2 2-(4-Ethoxyphenyltelluro)benzoic acid (HETB)

The i.r. spectrum of this compound (Table 3.2) revealed the characteristic bands for the hydroxyl group and the carboxylate group. The OH stretching absorption spread over a wide frequency range ($3300-2500cm^{-1}$) indicating a strong hydrogen bonding. For the carboxylate group, the band at $1660cm^{-1}$ could be attributed to $\nu(C=O)$ stretching vibration and a band at $1270cm^{-1}$ could be assigned as $\nu(C-O)$ stretching.



SAMPLE Sodium 2-(4-ethoxyphenyl)telluro benzoate

ORIGIN

SOLVENT KBr disc

REFERENCE air

SCAN TIME 12 MIN

SLIT N

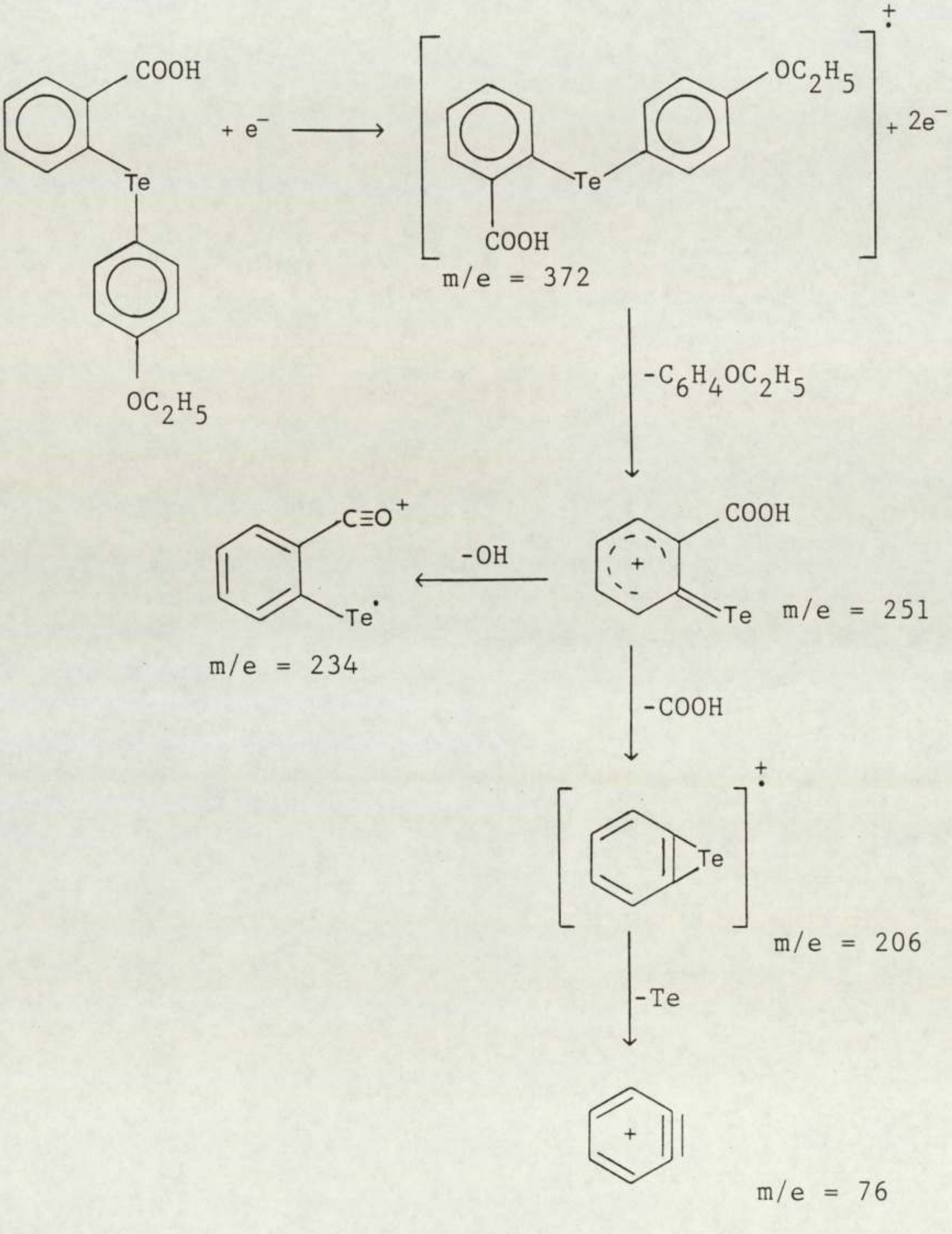
OPERATOR

DATE 21.5.85

Figure 3.2 : I.R. spectrum of sodium 2-(4-ethoxyphenyltelluro)benzoate

The sodium salt of this compound revealed a rather different i.r. spectrum (Fig. 3.2). A wide absorption between 3650-3100cm^{-1} could be due to ν(OH) stretching of water molecules in the crystal lattice, while the band at 1615cm^{-1} may be due to the δ(HOH) bending of water molecules. In the lower-frequency region, absorption between 530-400cm^{-1} could be due to rotational oscillation of the lattice water molecules$^{(83)}$. The carboxylate absorption appeared at 1572cm^{-1} and 1395cm^{-1} which correspond to $\nu_a(COO^-)$ and $\nu_s(COO^-)$ respectively, with a separation of 177cm^{-1}, thus it may have structure(I) (Fig.3.1)

The mass spectrum of the 2-(4-ethoxyphenyltelluro)benzoic acid at 70 eV revealed a peak at 372 which corresponds to the molecular ion ($M^{\bullet+}$). The molecular ion can lose ethoxyphenyl group (m/e = 121) giving another ion with a mass of 251, which can lose either a hydroxyl group, to give a new ion of mass (234), or a carboxyl group to give a radical ion with mass 206. The dissociation of the compound is shown in Scheme 3.1.



Scheme 3.1. The dissociation of 2-(4-ethoxyphenyltelluro)-benzoic acid in the mass spectrometer; all values of m/e are based on ^{130}Te, ^{16}O, ^{12}C.

3.3.3 2-(4-Ethoxyphenyltelluro)benzoato-Thallium(I)

The reaction between sodium 2-(4-ethoxyphenyltelluro)-benzoate (NaETB) and thallium(I) sulphate in stoichiometric amounts gave a 1:1 compound according to the elemental analysis. And since the thallium atom is comparatively large the compound could be isolated without water of crystallisation, this is confirmed by the i.r. spectrum, where no absorption due to H_2O appeared in the region above $3100cm^{-1}$ or at $1615-1620cm^{-1}$.

It is known that the thallium(I) ion can give stable derivatives with carboxylate ligands. For example, thallium-(I) compounds of 2-hydroxybenzoic acid and 2-aminobenzoic acid have been prepared as 1:1 derivatives(84a). The conductivity measurements of these derivatives showed much lower values than that of their potassium salts, implying at least a stronger Tl^+-ligand ion-pairing; however, their i.r. spectra have not been thoroughly discussed. The ion pairing was later confirmed by the X-ray crystal structure of salicylato-(1,10-phenanthroline)thallium(I), in which the compound was found dimeric in the crystal, and the carboxylate group of the salicylate ion forms asymmetrical bidentate co-ordination with the thallium ion. One of the oxygens, also, has a weaker interaction with a second thallium ion, but it has been stated that the nitrogen donor ligands (i.e., 1,10-phen.) approach the cation more closely than the oxygen donors(84b)

Potentially chelating ligands containing carboxylate groups were also reported to form complexes with the Tl(I) ion. For example, ligands like 2-mercaptobenzoic acid and cysteine have been shown, according to the i.r. spectra, to co-ordinate through both sulphur and the carboxylate group, thus indicating the ease with which thallium will form complexes with soft ligands, and moreover, the conductivity measurements in dimethylsulphoxide or acetone solution showed the compounds to be non-electrolytes(85a). The crystal structure of DL-cysteinatothallium(I) compound(85b) shows that the complex is a dimer and that the Tl atom is bonded to two O and two S atoms (Fig. 3.3), which confirms the tendency of Tl^+ to co-ordinate to sulphur atom rather than to the nitrogen atom of the ligand.

The infra-red spectrum of 2-(4-ethoxyphenyltelluro)benzoatothallium(I) (TlETB) revealed two bands in the absorption region of the carboxylate group (Fig. 3.4). The band at $1380cm^{-1}$ could be assigned as the symmetrical stretching of the carboxylate $\nu_s(COO^-)$, while the other band at $1512cm^{-1}$ could arise from the asymmetrical vibration, $\nu_a(COO^-)$. As seen, the difference between the two frequencies (Δ) is $132cm^{-1}$, which is fairly close to that of the sodium salt ($177cm^{-1}$), but obviously having a lower value. Therefore, the compound could have one of the three structures, the sodium salt structure (I),

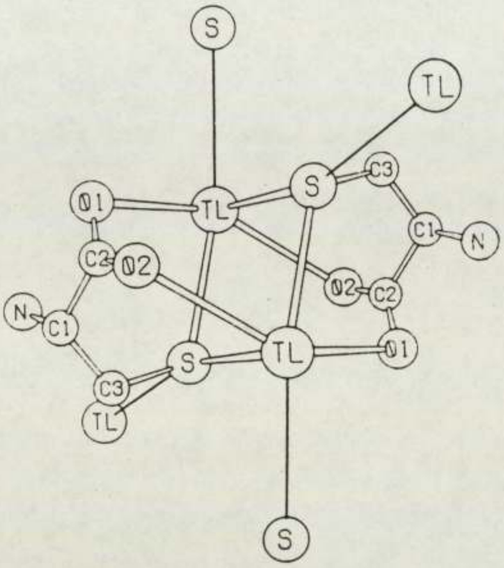
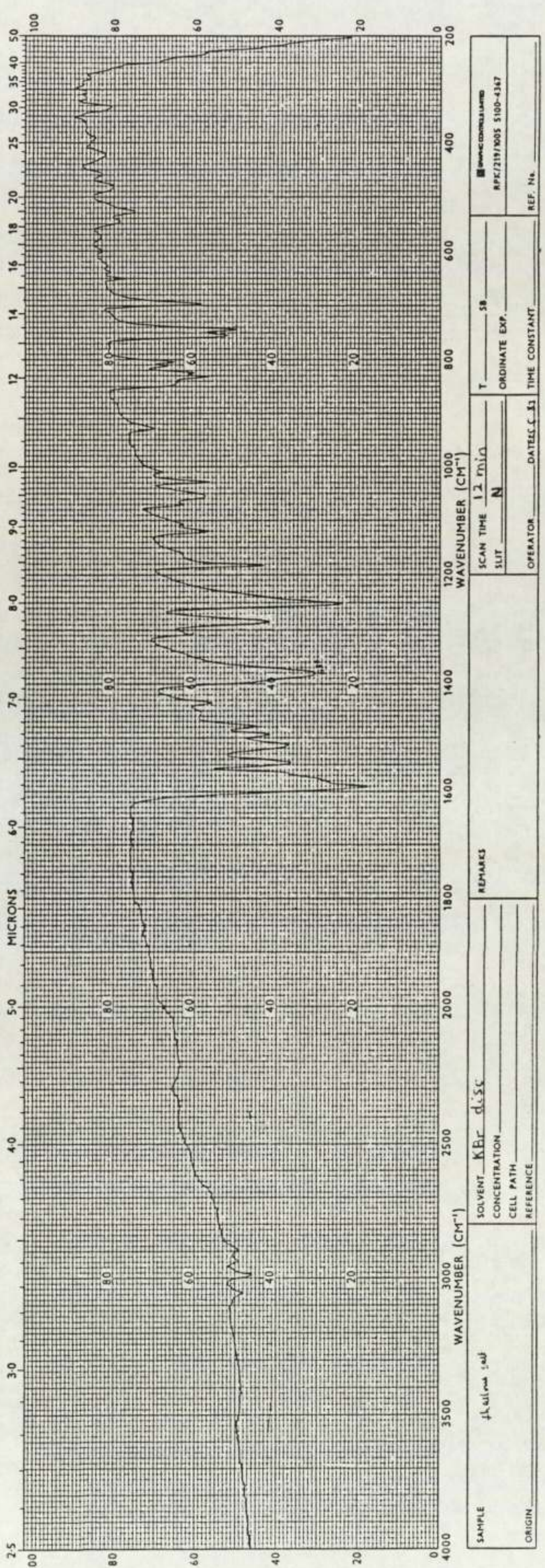


Figure 3.3. Molecular structure of Tl(DL-cysH). The long contacts between Tl and S atoms in different dimers are in thin bonds.

chelate structure(III) or bridging structure(IV) as shown in (Fig. 3.1).

Since the compound has a molar conductivity of 15 $ohm^{-1}cm^2$ $mole^{-1}$ in DMSO, which is unlikely to be due to the solvation of the compound in this solvent, one can conclude that it has some ionic character (a 1:1 electrolyte, 10^{-3} M in DMSO has a molar conductivity of 30 ohm^{-1} cm^2mole^{-1}), thus the possibility of bridging structure could be excluded. The compound could, therefore, have a structure which is an intermediate between the ionic structure (I) and the chelate structure (III). the low



SOLVENT KBr disc

SCAN TIME 12 min

SLIT N

Figure 3.4 : I.R. spectrum of Tl(ETB) complex

solubility of the compound in common solvents and its low conductivity value in DMSO could also, imply that the compound is dimeric in the solid state and in solution, with some strong thallium-ligand ion-pairing; these properties of thallium-carboxylate compounds are not unusual, and have been reported earlier(84).

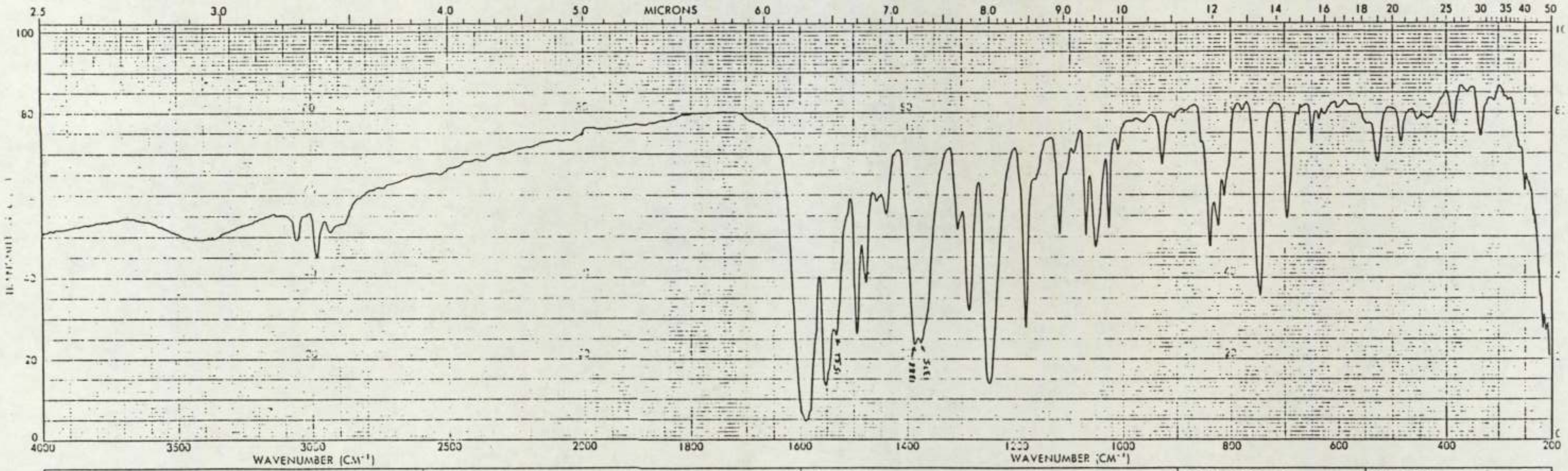
The ease, with which thallium can form complexes with soft ligands(85a), and the tedency of Tl(I) ion to co-ordinate to a tellurium atom (Fig. 1.17) may suggest that in this compound, (TlETB), there could be some kind of interaction between the tellurium atom of the ligand and the thallium ion of an adjacent molecule; bearing in mind that the chelating character of the carboxylate group would not allow an ortho-tellurium atom to interact with the same central metal ion (thallium(I) in this case). An attempt to get the crystal structure of the present Tl(I) compound was made, but was met with some difficulties at the early stage of data collection(199).

3.3.4 2-(4-Ethoxyphenyltelluro)benzoato-silver(I) hydrate

This compound has been prepared by the reaction of silver perchlorate with the ligand (Na-ETB). The elemental analysis data suggest a monohydrate, and its low solubility in many solvents may suggest that the compound is dimeric or polymeric. Many silver(I) carboxylates have been reported to have a dimeric structure. Silver perfluorobutyrate was confirmed by X-ray study (86) to be dimeric with an eight-membered ring and Ag-Ag distance of 2.90 Å, and the carboxyl groups are bridging between two silver atoms.

The title compound was found to be a non-electrolyte (Λ = 3.5 $ohm^{-1}cm^{2}mole^{-1}$ in DMSO), which suggests a strong silver-ligand interaction. Its i.r. spectrum (Fig. 3.5) revealed a broad band at $3400cm^{-1}$, which is due to the OH stretching vibration of the water molecules. The band at $1532cm^{-1}$ could be assigned as the asymmetric vibration of the carboxylate group ($\nu_a COO^-$), while the symmetrical vibration frequency is split into two very close bands at 1388 and $1375cm^{-1}$. The difference between the symmetrical and the asymmetrical bands shows that the carboxylate groups are bridging between two silver atoms, and the splitting of the symmetrical vibration band could indicate that one of the carboxylate oxygen is weakly bonded either to a hydrogen of H_2O or to a silver atom of another adjacent dimer.

In an extended study of silver(I) complexes with ligands containing carboxylate groups and chalcogenide atoms, Pettit et al (55,87) reported that the formation constants of such complexes increases with the increase of the chalcogenide atomic weight (i.e., form O to Te). This shows that chelation is increasing by going from oxygen to tellurium (a typical soft acid-base interaction). It



SAMPLE Ag(I) complex (28) ORIGIN	SOLVENT KBr disc CONCENTRATION CELL PATH REFERENCE	REMARKS	SCAN MODE 12 SLIT N TIME CONSTANT PART No. 5100-4367	OPERATOR N. ALSALIM DATE REF. No

Figure 3.5 : I.R. spectrum of $Ag(ETB).H_2O$

is, therefore, reasonable here to suspect that there might be an interaction between tellurium donor atoms and silver atoms within the present compound, but this remains unconfirmed until further evidence, ^{125}Te Mössbauer data for example.

3.3.5 Bis[2-(4-ethoxyphenyltelluro)benzoato]-cobalt(II) dihydrate

This violet compound is hygroscopic, and when left in air it turns pink after absorption of moisture. Therefore, this compound was carefully dealt with, especially during the infra-red and the magnetic measurements.

Cobalt(II) acetate tetrahydrate has been described as having unidentate carboxylate groups using one oxygen atom$^{(88)}$. A benzoate complex, $Co_2(PhCOO)_4L_2$ (L = quinoline), has been reported to be a dinuclear with bridging carboxylate groups, and a long Co-Co distance of 2.83 Å showing a very weak interaction with a magnetic moment of 4.11 B.M. at 293K$^{(89)}$.

The infra-red spectrum of the title compound revealed the characteristic band of water OH stretching at 3400cm^{-1}. The carboxylate symmetrical stretching band appeared at 1395cm^{-1}, while the band caused by the asymmetrical stretching vibration is not very clear, since it merged with the other ligand bands below 1600cm^{-1}. It is, then, clear that the carboxylate groups are not acting as unidentate ligands by using only one of the oxygen atoms, because unidentate carboxylate groups should show a band above 1600cm^{-1} (ν_a COO) with a difference between the symmetrical and asymmetrical stretchings of more than 200cm^{-1} (80). The structure, therefore, could be described as having chelate carboxylate groups (Fig. 3.1).

The visible spectrum of a chloroform solution (Fig. 3.6) exhibits an absorption band with complex envelopes, the most intense envelope being at 590 nm ($\epsilon = 110$); this could be caused by a number of transitions to doublet excited states which occur in the same region and aquire some intensity by means of spin-orbit coupling. Absorption in this region with such molar intensity is characteristic of $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ transition in octahedral Co(II) complexes, in contrast to tetrahedral complexes which are blue and absorb at longer wave length with intensities 10-100 fold greater.

Magnetically $Co^{2+}(d^7)$ in high spin octahedral complexes shows effective magnetic moments ranging between 4.7 to 5.2 B.M. at room temperature, i.e., higher than the theoretical value (3.88 B.M.) due to orbital contribution to the total angular momentum. Dimeric cobalt(II) compounds have been reported to have antiferromagnetic properties, due to the exchange mechanism which arises from Co-Co interaction (89a,90). The experimental μ_{eff}

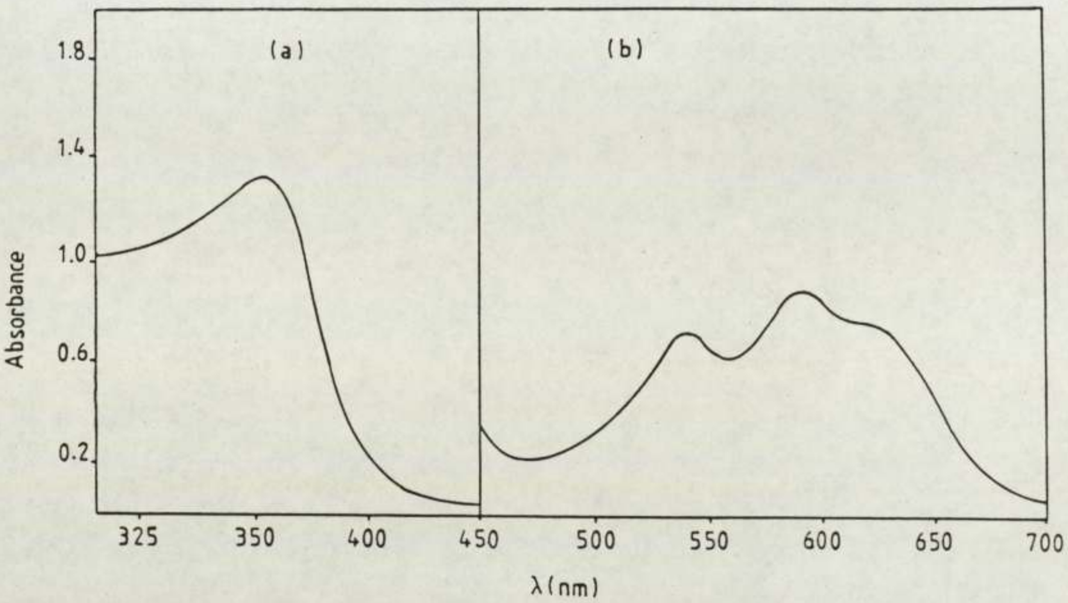


Figure 3.6 : The visible-U.V. spectrum of $Co(ETB)_2$.-$2H_2O$ in chloroform (a) 10^{-4}M, (b) 8 x 10^{-3}M

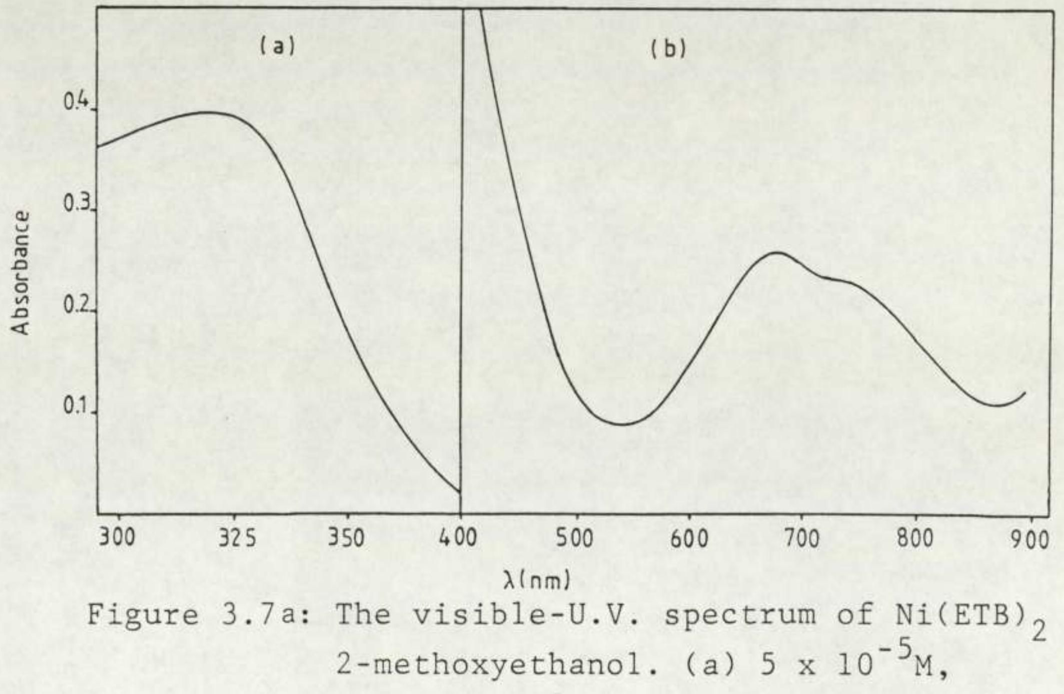


Figure 3.7a: The visible-U.V. spectrum of $Ni(ETB)_2$ in 2-methoxyethanol. (a) 5 x 10^{-5}M, (b) 4 x 10^{-2}M.

value of the title complex was found to be 5.52 B.M. at room temperature, which is consistent with the values of monomeric octahedral cobalt(II) complexes in a high spin state. Accordingly, it could be concluded that this compound is monomeric having two chelate carboxylate groups and two water molecules occuping the other sites of the octahedron.

3.3.6 Bis[2-(4-ethoxyphenyltelluro)benzoato]-nickel(II) hydrate

The elemental analysis of this compound confirms the presence of two ligand molecules per nickel atom, and the presence of water was also confirmed by the occurance of OH stretching at ca. 3400cm^{-1}. Many nickel-carboxylate compounds have been reported with differing kinds of structure. Nickel acetate tetrahydrate, for example, was given a structure of pseudo-octahedral co-ordination with the nickel atom being co-ordinated to one oxygen of each of the acetate ions and the oxygen atoms of the four water molecules(88). In another study a number of complexes of sulphur containing amino acid (DL-methionine) were isolated(91). From the spectral and magnetic data the authors concluded that the nickel(II) complex is octahedral and polymeric with carboxylato-bridges, so that the ligand co-ordinates to one nickel ion via the nitrogen atom and one oxygen atom of the carboxyl group and to a neighbouring nickel ion via the other oxygen

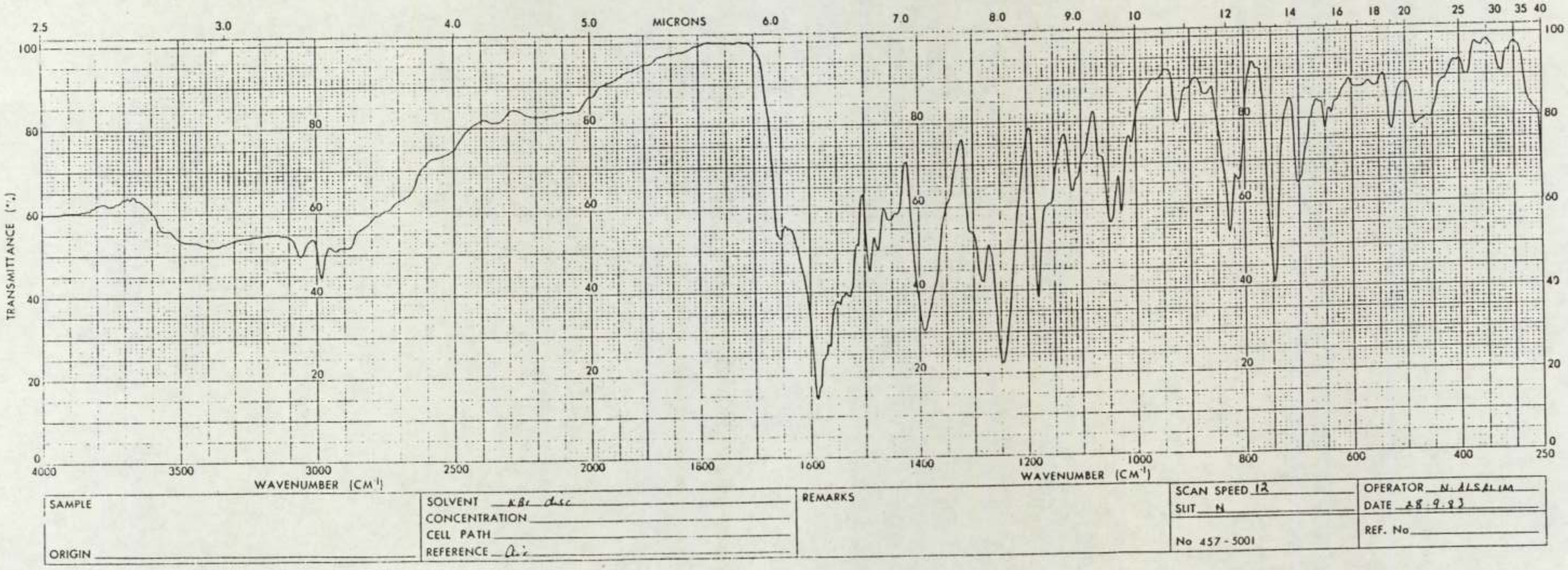


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Figure 3.7b : I.R. spectrum of $Ni(ETB)_2.H_2O$

atom of the carboxyl group, and they obtained bands at $1617cm^{-1}$ ($\nu_a COO^-$) and $1399cm^{-1}$ ($\nu_s COO^-$).

The infra-red spectrum of the title compound revealed a band at $1390cm^{-1}$, which could be assigned as $\nu_s(COO^-)$. Another complex shoulder at $1525cm^{-1}$ and a medium band at $1650cm^{-1}$ may lead to the conclusion that carboxylate groups, in this compound, exist in different environments. They could be bridging between two nickel ions, with one of the carboxylate oxygens is strongly interacting with one nickel atom, while the other oxygen is weakly bonded to the other nickel atom.

The visible spectrum of this complex (Fig. 3.7a) is consistent with an octahedral arrangement of ligands about the metal ion, and it is similar to the spectra of $Ni(H_2O)_6^{2+}$ and many other six-co-ordinated nickel complexes(92). The broad band between 800 nm and 600 nm could be assigned as electronic transition $^3A_{2g} \longrightarrow {}^3T_{1g}(F)$. This spilts into two bands at 750 nm ($\epsilon = 5.57$) and at 679 nm ($\epsilon = 6.17$) due to spin-orbit coupling that mixes the $^3T_{1g}$ (F) and ^1E_g states, which are very close in energy at the Δ_o value of such weak carboxylate environment. Another band, which is expected to appear around 400 nm [$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$], has not been resolved and might be obscured by the tail of the intense charge transfer band at 325 nm.

Magnetically, high spin octahedral nickel(II) complexes have experimental magnetic moments ranging from 2.9 to 3.4 B.M., depending on the magnitude of the orbital contribution. The μ_{eff} value obtained for the present nickel complex is 2.83 B.M., being similar to the previously reported experimental values, within experimental errors. This may imply a regular or a slightly distorted octahedral arrangement of the ligands around the Ni(II) ion. This leads to the same conclusion from the visible spectrum argument.

Pettit et al(55), in their study of chalcogenide dicarboxylic acid complexes, have reported that the formation constant of Ni(II) complexes increases from O to Te (i.e., Te > Se < S > O) (Table 3.5).

Ligand	Log K_{NiL}
$CH_2(CH_2CH_2COO)_2$	1.20
$O(CH_2CH_2COO)_2$	1.39
$S(CH_2CH_2COO)_2$	2.15
$Se(CH_2CH_2COO)_2$	1.83
$Te(CH_2CH_2COO)_2$	3.00

Table 3.5. Formation constants of Ni^{2+} complexes with carboxylate ligands(55)

The relatively high formation constant value for the tellurium complex , in table 3.5, could be due to a "stronger chelating effect" in the compound. According to this and to other suggested complexes comprising Ni(II) and a tellurium ligand (92c), it is reasonable to suggest that in the title compound, the tellurium atom may play a role in the co-ordination.

3.3.7. Bis[2-(4-ethoxyphenyltelluro)benzoto]-copper(II) hydrate

This green complex was confirmed by the elemental analysis to contain two ligand molecules per copper atom. Its colour indicates that the copper(II) ion has not been reduced to Cu(I) by the interaction with the tellurium ligand . The presence of Cu(II) ion in the complex was also confirmed by magnetic and electron spin resonance measurements at room temperature.

The infra-red spectra could be helpful in the elucidation of the nature of this copper complex. The presence of a broad band at about 3500cm^{-1} could be attributed to the OH stretching of water molecules. The band at 1395cm^{-1} may be assigned as $\nu_s(COO^-)$, while the band due to asymmetrical stretching of (COO) group is not very clear and combined with the more intense band at 1590cm^{-1}. Therefore, one may assume that the carboxylate groups are bridging between two copper ions, since bridging carboxylates are

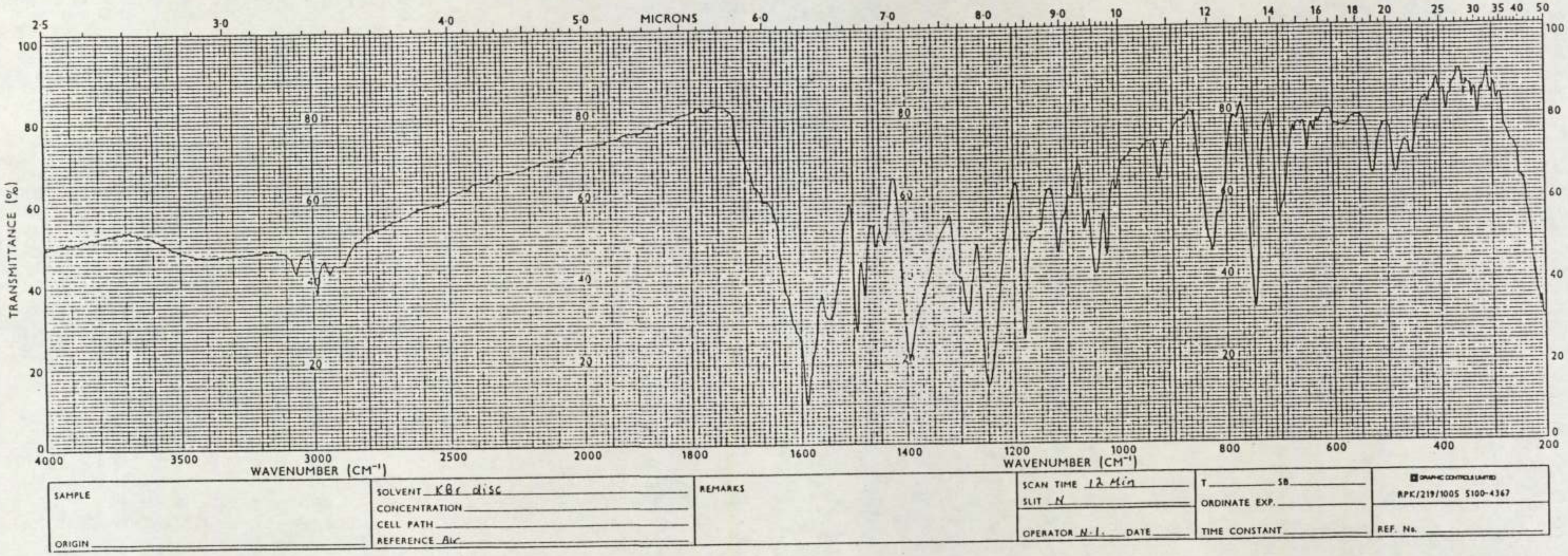


Figure 3.8 : I.R. spectrum of $Cu(ETB)_2.H_2O$

familiar in many copper(II) compounds. It has been shown, by X-ray crystal analysis, that in copper(II) acetate monohydrate (93a) copper atoms are bridged in pairs by four acetate groups to form dimer molecules in which the Cu-Cu distance is as short as 2.64 Å. Copper(II) benzoate has also been reported to contain bridge carboxyl groups (93b).

The visible spectrum of the copper(II) complex in chloroform exhibits a broad absorption with a maximum at 752 nm (ϵ = 58.1 l $mol^{-1}cm^{-1}$) (Fig. 3.10), which is characteristic of a d-d transition within the copper ion. Copper(II) ion has a d^9 electronic configuration, and the electronic energy levels will spilt into two main levels (E_g, T_{2g}) in an octahedral environment, these will further spilt, if there is a tetragonal distortion (Fig. 3.9).

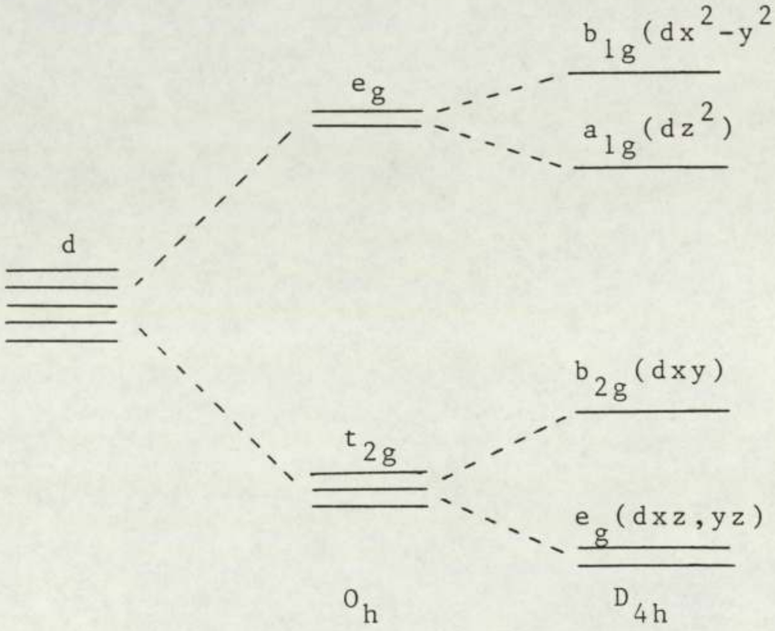


Figure 3.9. The energy level splittings for Cu^{2+} ion.

Since the absorption band in the visible region did not spilt, but only broadened, one may assume that the distortion from octahedral symmetry is not very large, and the maximum at 752 nm could be assinged as the $^2B_{1g} \longrightarrow {}^2E_g$ transition. The solid state spectrum, however, did not show a clear maximum in the visible region.

The magnetic measurement of this complex, at room temperature , resulted in a calculated μ_{eff} of 1.55 B.M. per copper atom (Table 3.4). This value is less than 1.73 B.M., the theoretical value of the spin-only moment. In most instances, copper(II) compounds, with subnormal magnetic moments, have non monomeric structures with bridging ligands. Dimeric copper(II) acetate monohydrate shows this unusual magnatic behaviour(93a), and this has been attributed to the short Cu-Cu distances, which allows coupling of the single electrons on each copper atom. The precise nature of such interaction has been disputed, however. The magnetic susceptibility measurement of copper(II) salicylate tetrahydrate gave a value of μ_{eff} = 1.44 B.M., while the results of a complete X-ray crystal analysis showed no pairs of copper atoms of close distance of approach in the crystal(94). Nevertheless, copper(II) benzoate trihydrate gave a normal magnetic moment (1.87 B.M.) per copper atom (95) , although a close distance of approach (3.15 Å) and bridging arrangement of copper atoms have been reported (93b) . Therefore, one can only

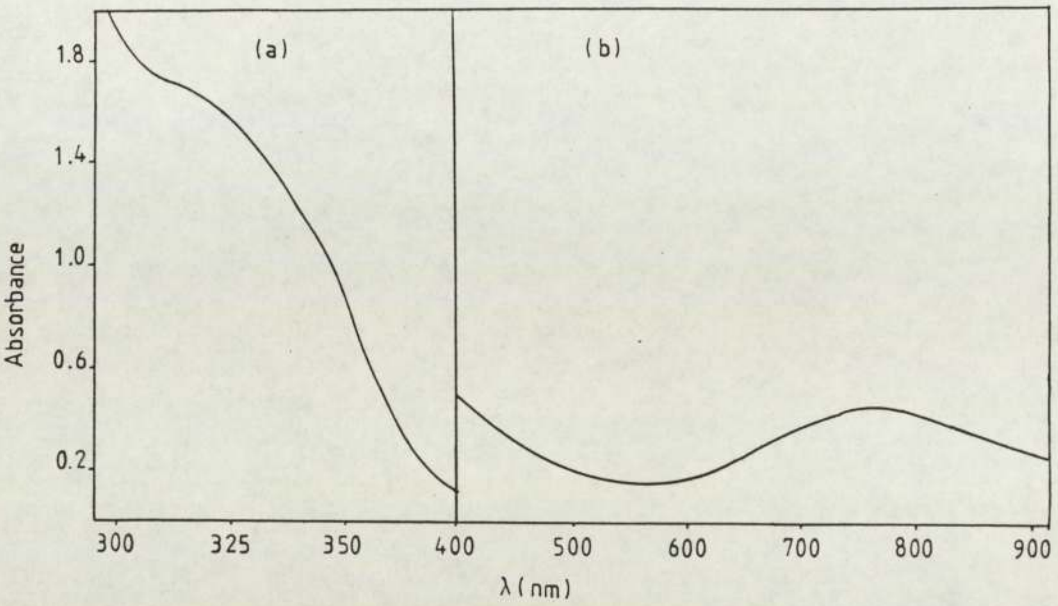


Figure 3.10 : The visible spectrum of $Cu(ETB)_2$ in chloroform. (a) $2 \times 10^{-4}M$ (b) $8 \times 10^{-3}M$

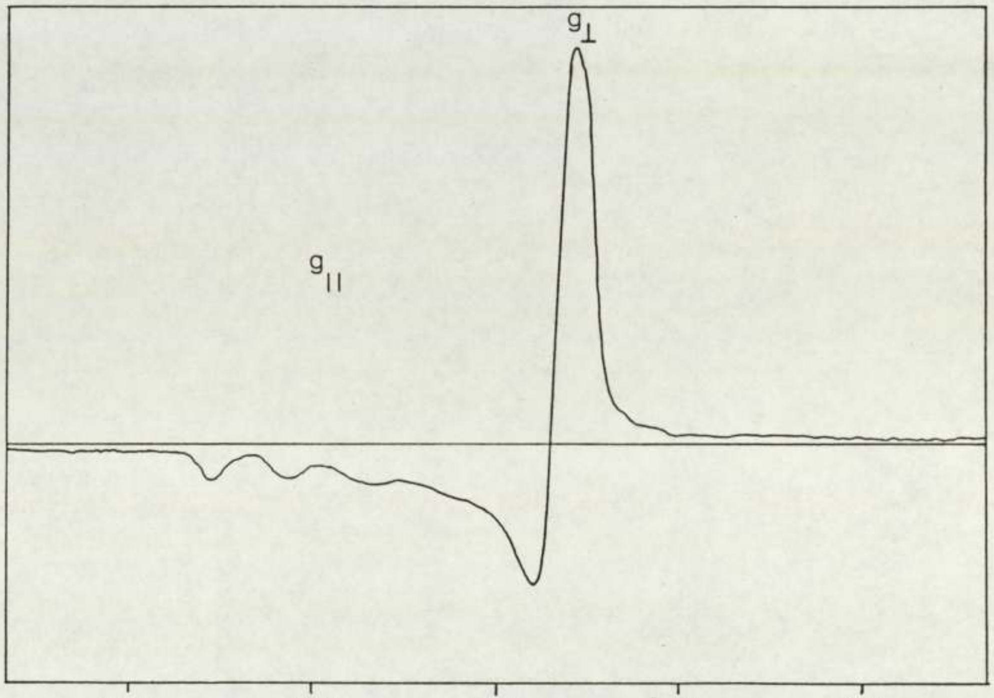


Figure 3.11 : The ESR spectrum of polycrystalline sample of $Cu(ETB)_2.H_2O$ at room temp.

imply that the observed magnetic moment of the title complex resulted from some sort of interaction, but not necessarily through divalent copper-copper interaction.

The ESR spectrum of a polycrystalline sample of the $Cu(ETB)_2.H_2O$ complex was recorded. The spectrum gave two g-values indicating a normal tetragonal copper(II) ion environment (D_{4h}) (Fig. 3.11), where $g_{||} = 2.254$ and $g_{\perp} = 2.069$. In D_{4h} symmetry the g-values for the copper(II) ion with a$^2B_{1g}$ ground state are given by the following expressions$^{(96)}$:

$$g_{||} = 2 - \frac{8K_{||}^2 \lambda}{E(^2B_{1g} \longrightarrow {}^2B_{2g})}$$

$$g_{\perp} = 2 - \frac{2K_{\perp}^2 \lambda}{E(^2B_{1g} \longrightarrow {}^2E_g)}$$

Where K is the orbital reduction factor and λ is the spin orbital coupling constant, which for the free Cu(II) ion equals $-829cm^{-1}$. These expressions yield an equation:

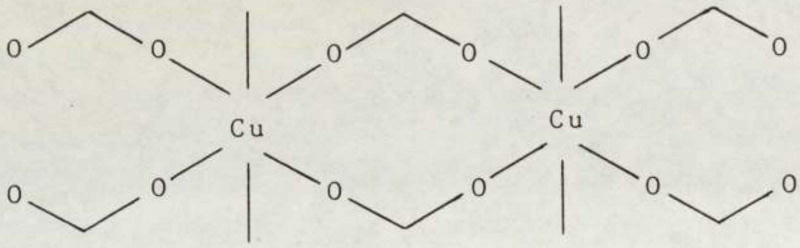
$$\frac{g_{||} - 2}{g_{\perp} - 2} = \frac{4K_{||}^2}{K_{\perp}^2} \cdot \frac{E(^2B_{1g} \longrightarrow {}^2E_g)}{E(^2B_{1g} \longrightarrow {}^2B_{2g})} = G$$

$$\frac{2.254 - 2}{2.069 - 2} = G = 3.681$$

By calculating G, it is possible to evaluate $\kappa_{\|}$ and $\kappa_{\perp}$, in the above expressions, if the energies of the electronic transitions are known. It has been established that the numerical value of G may be used as a criterion for estimating whether or not exchange coupling effects invalidate the use of the observed g-values to reflect the local Cu(II) ion environment (97). If the G value lies above 4.00, the criteria suggest that exchange coupling is not present or only very weak, and the g-values probably reflect the local copper(II) ion environment, and the Cu(II) ions are in crystallographically equivalent sites and there is good alignment of tetragonal axes. If the G value is, however, less than 4.00, which is the case for the present complex, the possibility of exchange coupling must be considered, and the alignment of the tetrahedral axes is poor. This is in agreement with the magnetic susceptibility measurement, which gave a magnetic moment of 1.55 B.M., that is lower than the spin value for uncoupled electrons in a d^9 copper ion.

The possibility of a copper-copper interaction was considered, and ESR measurements were done over a wide range of magnetic field (H) between zero and 5500 gauss. No signals other than that shown in Fig. 3.11 could be recorded. Wasson et al (98) reported the powder ESR spectra of the dimeric copper(II) cyanoacetate, in which many signals were recorded at room temperature and at 77K.

The line in both spectra at about 3200 gauss was attributed to the free, that is nondimeric, copper ions, which they estimated to be less than 2%, while the other line at 700, 4800 and 6300 gauss were considered as due to the triplet state of the dimeric Cu-Cu complex. From the above discussion one may conclude that the present complex has an essentially tetragonal environment but with exchange coupling and probably fairly long Cu----Cu distances in chain.



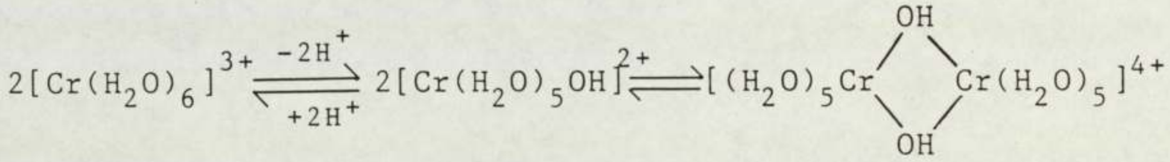
3.3.8 Chromium(III) Complex with ETB Ligand

The elemental analysis of the chromium(III) complex fits with several possible formulae:
$Cr(ETB)_3.H_2O$, $Cr_2(OH)_2(ETB)_4(HETB)_2$, $Cr_3(ETB)_8(OH)$, and $Cr_4O(ETB)_{10}$. There is also a possibility of a water molecule or a hydroxyl ion; however, the infra-red spectrum showed only a weak broad absorption at $3500cm^{-1}$ characteristic of OH stretching.

Metal triacetates should result only under absolutely anhydrous conditions. Since this preparation was carried out in an aqueous solution, one can, therefore, rule out the possibility of a monomeric complex containing three ligand molecules.

The infra-red spectrum (Fig. 3.12) revealed strong bands at 1658 and 1263cm^{-1}, which are very close to those of the acid form of the ligand, 1660 and 1270cm^{-1} respectively, and broad absorption bands between 3300-2500cm^{-1} which are probably due to a carboxyl OH. Other absorptions at 1525cm^{-1} (shoulder) and 1410cm^{-1} also appeared, which could be assigned as asymmetric and symmetric stretching of a chelate carboxylate group.

The aqua chromium(III) ion is, infact, basic (pK=4), and the hydroxo ion condenses to give a dimeric hydroxo bridge species:



$$2[\mathrm{Cr(H_2O)_6}]^{3+} \underset{+2\mathrm{H}^+}{\overset{-2\mathrm{H}^+}{\rightleftharpoons}} 2[\mathrm{Cr(H_2O)_5OH}]^{2+} \rightleftharpoons [\mathrm{(H_2O)_5Cr}\begin{matrix}\mathrm{OH}\\ \\ \mathrm{OH}\end{matrix}\mathrm{Cr(H_2O)_5}]^{4+}$$

These two hydrogen ions may react with the sodium salt of the ligand to give two (HETB). This could explain the appearance of bands, in the i.r. spectrum, for both the ionised and the acid form of the ligand. Another significant band, in the i.r. spectrum, is that of medium intensity at 520cm^{-1} which gained some intensity relative to the band at 552cm^{-1} originally present in the ligand spectrum. This could be attributed to the

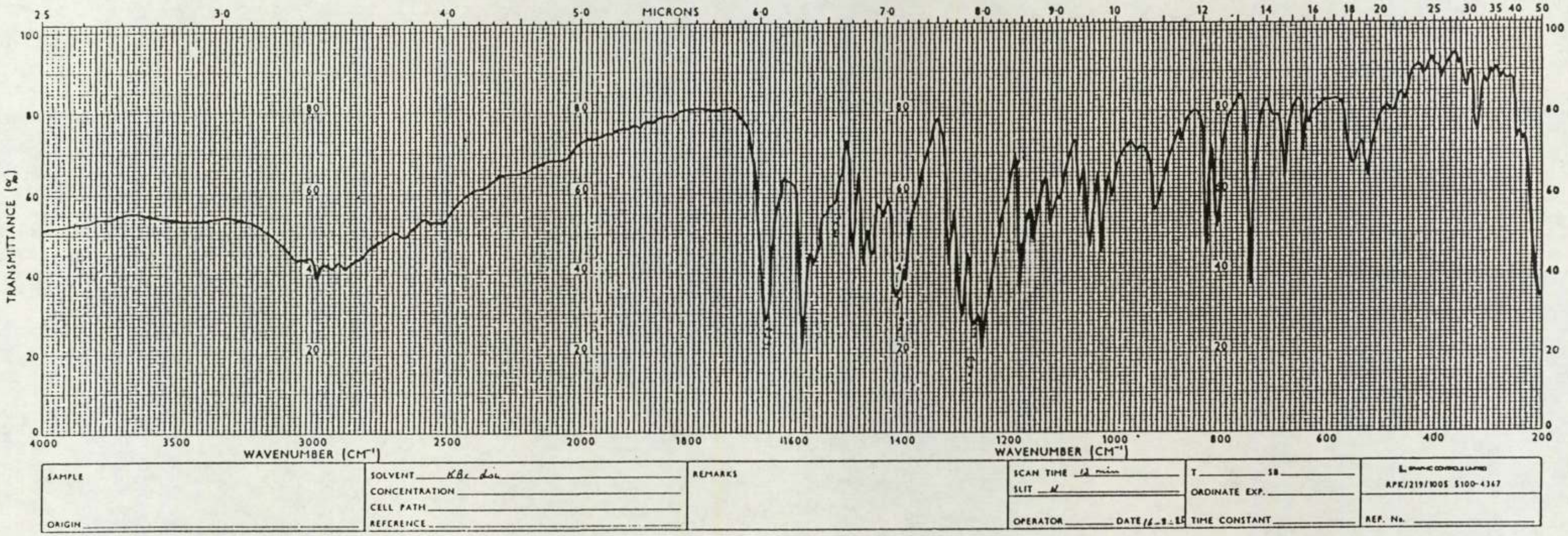


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Figure 3.12 : I.R. spectrum of Cr^{3+} complex of the ligand (ETB)

Cr-(OH)-Cr stretching, which has been reported to be around 550cm^{-1} (99).

Chromium(III) complexes in an octahedral environment usuallly have three spin allowed transitions, namely $^4A_{2g} \longrightarrow {}^4T_{2g}$, $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ and $^4A_{2g} \longrightarrow {}^4T_{1g}(P)$. The visible spectrum of the present complex revealed a weak band at about 800 nm (ϵ = 26.25 l mole^{-1} cm^{-1}) and another more intense band at 575 nm (ϵ = 61 l mole^{-1} cm^{-1}). The former absorption could be due to the transition $^4A_2 \longrightarrow {}^4T_2$ and the second band may be due to the transition $^4A_2 \longrightarrow {}^4T_1$ (F).

The magnetic measurement showed a significant magnetic interaction with μ=2.48 B.M. (theoretical μ is 3.88 B.M.) Many chromium(III) compounds containing bridged hydroxyl groups have significantly low magnetic moments, for example $[Cr_2(OH)(NH_3)_9OH]Cl_4$ has been reported to show a magnetic moment of 2.3 B.M.(100). Therefore, it is possible that the title complex has the formula $Cr_2(OH)_2$-$(ETB)_4(HETB)_2$.

3.3.9 Iron(III) Complex of (ETB)

Like the chromium(III) complex, the elemental analysis of the iron(III) complex could be fitted with several possible formulae:

$Fe(ETB)_3.H_2O$, $Fe_2O(ETB)_4(HETB)_2$, $Fe_2(OH)_2(ETB)_4(HETB)_2$,

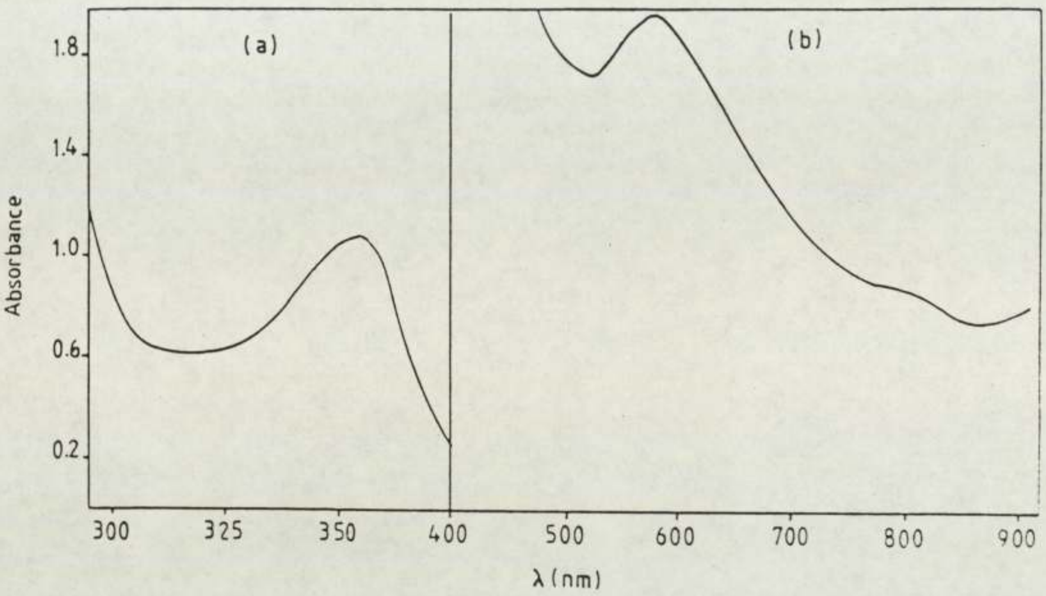


Figure 3.13 : The visible spectrum of Cr(III) complex with (ETB) ligand in $CHCl_3$

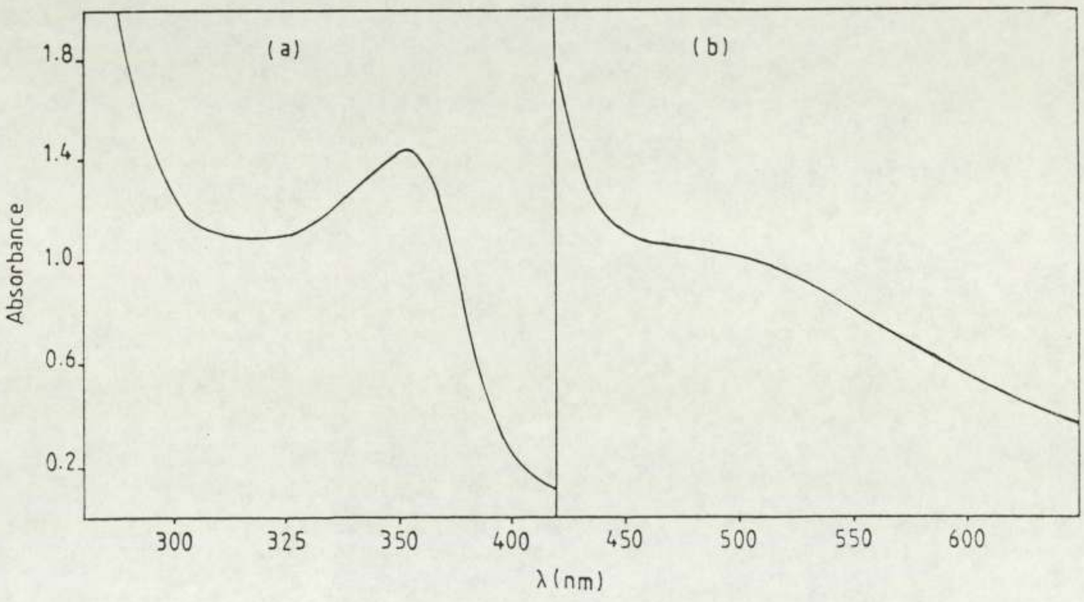


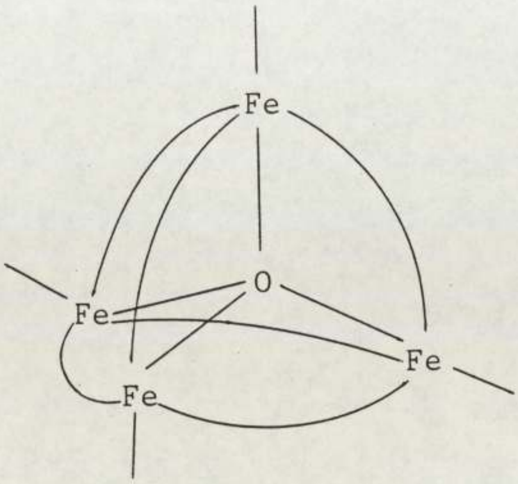
Figure 3.14 : The visible spectrum of Fe(III) complex with (ETB) ligand in $CHCl_3$

$Fe_3(OH)(ETB)_8$ and $Fe_4O(ETB)_{10}$. It is, therefore, difficult to suggest which formula is correct using the analytical data only.

The conductivity measurement of the title compound in solution gave a molar conductance of 7.6 $ohm^{-1}cm^2mole^{-1}$ in DMF indicating the non-ionic character of this complex.

Iron(III) forms basic carboxylates having a so called oxygen-centered structure, in which the oxide ion is either in the centre of a triangle, linking three iron atoms, or in the centre of a tetrahedron, linking four iron atoms, and the carboxylates are bridging between each two iron atoms (101).

The infra-red spectrum, in the COO stretching region suggests two different types of carboxylate co-ordination. Both the asymmetrical stretching (1660, 1515cm^{-1}) and the symmetrical stretching (1410, 1265cm^{-1}) are apparantly spilt. Such splitting was also observed in the complex $Fe_4O(O_2CMe)_{10}$, with $\nu_a(COO^-)$ at 1627, 1560cm^{-1} and $\nu_s(COO^-)$ at 1454, 1380cm^{-1} (101), but this splitting is rather different to our data. For the above iron(III) complex, a structure has been suggested in which a tetrahedron of iron atoms are linked by an oxygen atom located in the centre. The acetate groups are being chelating between two iron atoms along each edge of the tetrahedron, and a unidentate carboxylate group on each iron atom.



It has been reported also that such a complex has a magnetic moment of 6.4 B.M. at room temperature being higher than the spin-only value (5.92 B.M.), while the magnetic moment of the title complex based on $Fe_4O(ETB)_{10}$ formula is only 2.60 B.M. per iron atom.

Another possible structure is the binuclear structure with a bridging oxygen (Fe-O-Fe). An important feature of oxygen bridged binuclear complexes is their infra-red spectroscopy. The unit Fe-O-Fe may be considered as linear or bent three body system. For such system, there will be three fundamental vibrations: ν_1 (sym. str.). ν_2 (deformation mode) which is likely to be too low in frequency, and ν_3 (asym. str.); in either case ν_3 should have higher frequency than ν_1. A band in the region 800 -900cm^{-1} has been assigned as M-O-M asymmetric stretching (ν_3), and another band at 215-230cm^{-1} has been assigned as ν_1 in linear systems$^{(99)}$. Bent M-O-M systems, however, showed a lower ν_3 (770-830cm^{-1}), and a higher ν_1 value (450-560cm^{-1})$^{(102)}$. Since no new band, even weak, appeared in the i.r. spectrum of the present iron(III) complex in the range 700-900cm^{-1} , it is, therefore, unlikely that the title complex has a mono or a bridging oxygen structure.

The complex may be described as containing M-$(OH)_2$ -M unit, with two chelating carboxylate groups and one acid form of the ligand on each iron atom. The appearance of a new medium band at 500cm^{-1} in the i.r. spectrum could be attributed to the asymmetric stretching (ν_3) of Fe-$(OH)_2$-Fe.

The iron-57 Mössbauer spectrum of the title compound has been measured at room temperature. The isomer shift value, δ , is 0.37 (Fig. 3.11), which is of the magnitude expected for high spin iron(III) complexes, and the value of the quadrupole splitting, Δ , is 0.61, which is also expected for the high spin iron(III) complexes$^{(103)}$. The most interesting aspect of the Mössbauer spectrum is the asymmetry observed in the intensity of the quadrupole split lines. The component at the lower energy side is more intense than its companion. A similar feature has been attributed to the anisotropy of the recoil free fraction of the iron atoms in the reduced symmetry site, and is predicted to decrease with decreasing temperature$^{(103)}$.

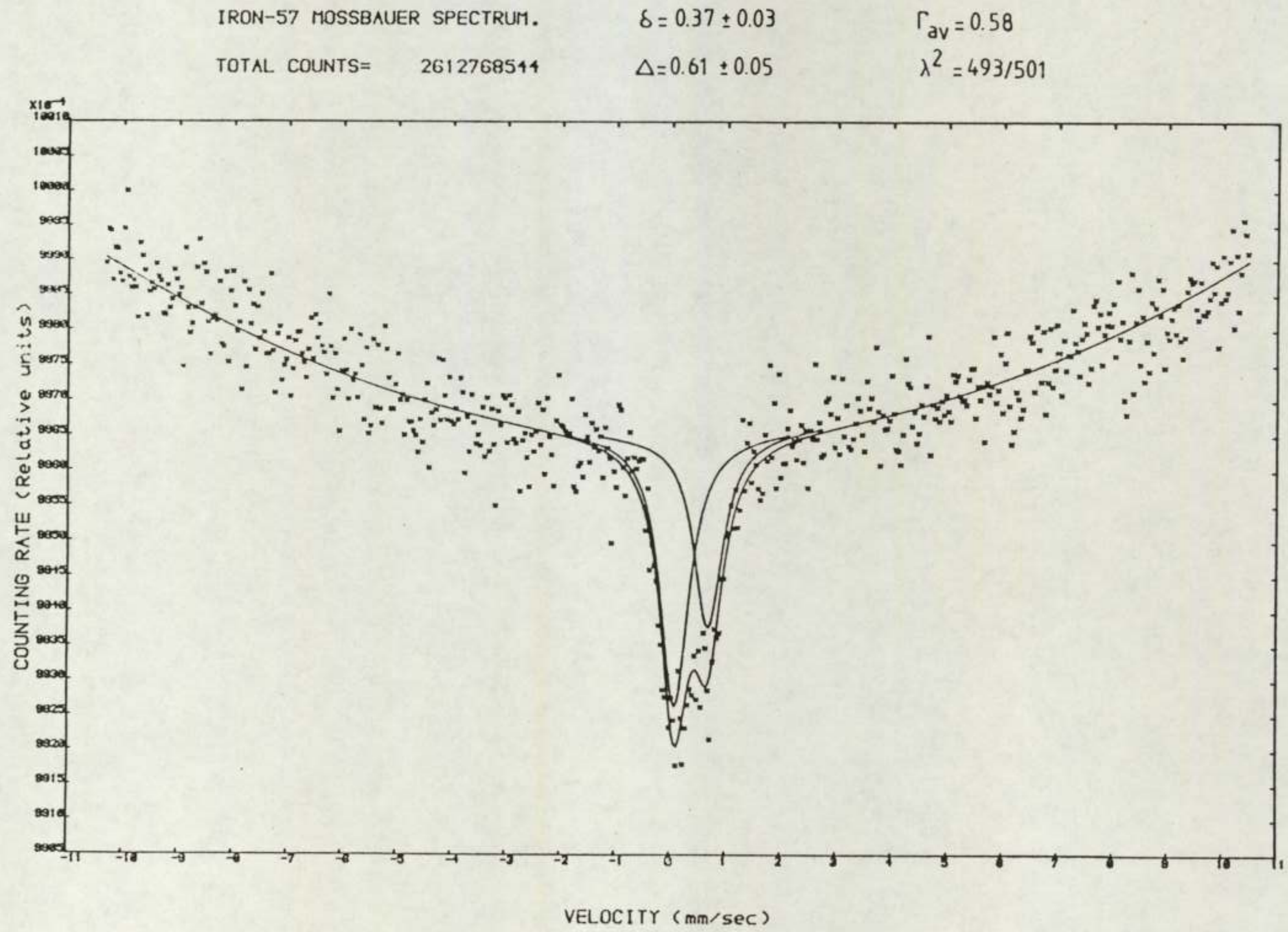


Figure 3.15 : ^{57}Fe spectrum of the solid iron(III) complex of the ligand (ETB)

The calculated μ_{eff}, based on the formula $Fe_2(\mu OH)_2(ETB)_4$-$(HETB)_2$, is 2.80 B.M., which is much lower than the spin-only value (5.92 B.M.) because of the antiferromagnetic behaviour of the complex due to Fe-Fe interaction, probably through the bridging hydroxyl groups, which allows coupling of the electrons on both iron atoms.

The powder X-ray diffraction spectra of the Cr(III) and Fe(III) complexes revealed very similar patterns, which may indicate that the two complexes are isostructural.

3.3.10 Summary

From the above discussions, it seems that the 2-(4-ethoxyphenyltelluro)benzoato-ligand can give many types of structure with metal ions. Only the thallium(I) complex showed a considerable conductivity in solution and its structure could be considered as having some strong thallium-ligand ion pairing with the possibility that two complex molecules are linked by a tellurium-thallium bonding. The silver(I) complex was described as dimeric with the carboxyl groups are bridging between two silver atoms, and the tellurium donor atoms might have the opportunity to interact with the silver atoms. The copper(II) complex was also described as having bridging carboxylate groups,and the compound could be dimeric or polymeric with significant magnetic interaction at room temperature due to exchange coupling. The local environment around Cu(II) ions is distorted octahedral. The cobalt(II) complex is considered to be monomeric with two chelating carboxylate groups and two water molecules occuping the other sites of the octahedron. Nickel(II) compound could contain bridging carboxylates, each carboxyl group is strongly interacting with one nickel atom through one oxygen and weakly bonded to another nickel through the other carboxylate oxygen. The complex, however, has an ordinary magnetic moment and the two nickel atoms could be quite appart from each other.

The chromium(III) and iron(III) complexes are believed to be isomorphous or isostructural, showing a significant antiferromagnetism. This could be due to electron pairing which may be induced through the two bridging hydroxyl groups linking two of the metal ions (Fe^{3+} or Cr^{3+}). The infra-red spectra of both compounds show the presence of the ionised and the acid forms of the ligand.

CHAPTER FOUR

CRYSTAL AND MOLECULAR STRUCTURES OF: 1,6-BIS-2-BUTYLTELLUROPHENYL-2,5-DIAZAHEXA-1,5-DIENE LIGAND AND ITS COMPLEX WITH MERCURY(II) CHLORIDE

4.1 Introduction

As stated in Chapter one, the interest in the ligand chemistry of tellurium has increased during the past few years (14,52a). Despite this, few bidentate or polydentate ligands containing the element are known, but such complexes based on Group 5A donor atoms, phosphorus(104) and arsenic (105) are well known. A number of crystallographically characterised examples exist, incorporating even macrocyclic ligands, for example [IrCl(CO)-$(Bu^t_2P(CH_2)_{10}PBu^t_2)$], [$PtCl_2(Bu^t_2P(CH_2)_{12}PBu^t_2)$] and [RhCl(CO) $(Bu^t_2P(CH_2)_{10}PBu^t_2)$] (106). Many structures of complexes incorporating bidentate selenium ligands, with various combinations of Group 5A and 6A donor atoms, have also been reported. The X-ray crystal structure of the compound $Ni[Se\text{-}o\text{-}Ph_2P.C_6H_4)]_2$, for example, which contains phosphorus and selenium donor atoms, has been determined(107). An example of the complexes containing bidentate tellurium ligands is the compound [Pt PhTe(o-$Ph_2P.C_6H_4)_2$][$Pt(SCN)_4$].2 DMF, which has recently been the subject of a structure determination (51). The complex was described as monomeric, in which tellurium and phosphorus are the donor atoms, and was shown to have the trans-configuration with a Pt-Te bond length of 2.575 Å.

Among other ligands, that contain two tellurium atoms, are the diarylditellurides which can act as bidentate ligands. The molecular structures of their binuclear complexes, for example $M_2Br_2(CO)_6Te_2Ph_2$ (M= Re, Mn), have been reported, in which the tellurium ligand is considered as bridging rather than chelating (47,56). Complexes that incorporate chelating tellurium ligands, of the type $ArTe(CH_2)_nTeAr$, n = 5-10, have been the subject of a recent investigation (108), but no X-ray crystal structures of such complexes are available.

Although polydentate ligands incorporating the heavier donor atoms of Group 5A have been reported, an illustrative example is tris-(o-dimethylarsinophenyl)bismuthine (bitas) and its nickel complex $[Ni(bitas)Cl]BPh_4$ (109), only sulphur and a few selenium polydentate ligands are known. The compounds $(o\text{-}CH_3Se.C_6H_4)_3P$(TSeP) and its nickel complex $[Ni(TSeP)_2](ClO_4)_2$, for example have been prepared (110). Polydentate tellurium ligands are, however, unprecedented, and therefore, such ligands will be of much interest in the future.

In this chapter, the preparation and the single crystal structure of one of the potentially polydentate tellurium ligands, 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (I), which contains two nitrogen and two tellurium donar atoms, are described. Its 1:1 mercury(II) chloride complex $HgCl_2$.(I) was also prepared and its X-ray crystal structure was determined.

Many organotellurium complexes of mercury(II) have been reported; these are either with simple monodentate or diorganylditelluride ligands. Only two Hg(II) complexes, however, are of ambiguously known structure: the tetrameric $(Ph_2Te)HgI_2$ (111) (Fig. 4.1) and $[PPh_4][Hg(TePh)_3]$ (Fig. 1.2) 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.

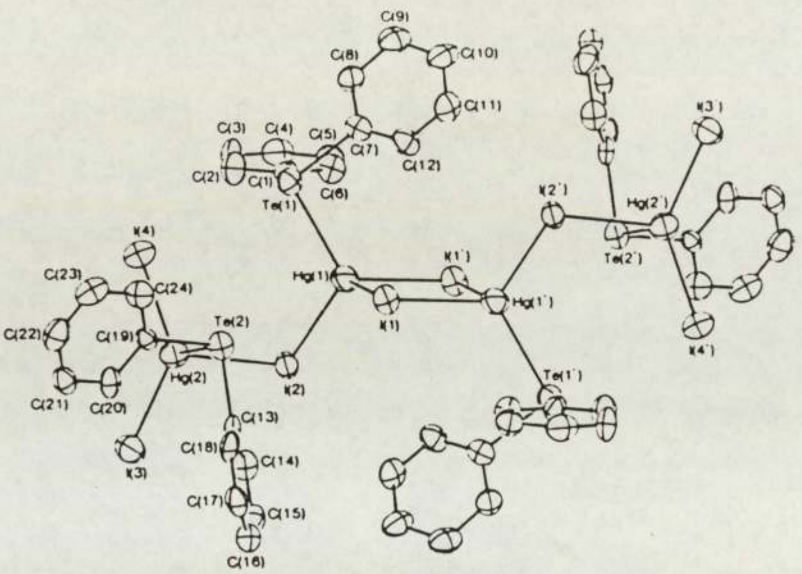


Figure 4.1. Molecular structure of $(Ph_2Te)HgI_2$

4.2 Experimental

4.2.1 The Preparation of the Ligand 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (Compound I)

This compound was prepared starting from 2-bromobenzaldehyde according to Scheme 4.1. Firstly, 2-bromobenzaldehyde (25g, 0.135 mole) was converted into 2-bromobenzaldehyde diethyl acetal, by reacting it with triethylorthoformate (20g, 0.135 mole) in refluxing ethanol ($16cm^3$) containing

0.5g of potassium hydrogen sulphate ($KHSO_4$). After stirring for three hours, ethanol was removed under vacuum, then water ($100cm^3$) and diethylether ($100cm^3$) were added and shaken. The organic layer was separated and dried over anhydrous Na_2SO_4 . After removal of the solvent, the yield of the resultant liquid diethyl acetal was 33.5g (yield 95.7%).

2-Bromobenzaldehyde diethyl acetal (13g, 0.05 mole) was then dissolved in dry diethylether ($50cm^3$), and n-butyl lithium (3.2g in $15cm^3$ether/cyclohexane solution) was added slowly under N_2 gas from a separating funnel during 15 minutes. The mixture, then, was allowed to cool to room temperature, and tellurium powder (6.5g, 0.05 mole) was added slowly, with stirring. After refluxing for 30 minutes, the mixture was cooled and poured on ice and extracted with ether. The mixture was dried over Na_2SO_4, and the solvent was removed in a rotary evaporator to give a yellow liquid (2-butyltellurobenzaldehyde diethyl acetal), with a boiling point of 148-150°C at 0.1mm Hg, and 9g yield (68%).

The above product (9g) was hydrolysed by heating it gently with concentrated hydrochloric acid ($10cm^3$). The cold mixture was then extrated with diethylether and dried over anhydrous $MgSO_4$. The solvent was eliminated under reduced pressure, and the product was distilled under vacuum at 141-143°C and 0.1mm Hg (lit.140-142°C(112)) to give 5.5g of the 2-butyltellurobenzaldehyde (80% yield.

Found $C = 43.2$ %, $H = 4.0\%$; $C_{11}H_{14}OTe$
requires $C = 43.49\%$, $H = 3.83\%$

Finally, the above product, 2-butyltellurobenzaldehyde, (5.2g, 0.018) in absolute ethanol (10cm^3) was reacted with a solution of dry ethylene diamine (1,2-diamino-ethane) (0.54g, 0.009 mole) in absolute ethanol (10cm^3), and the mixture was refluxed for 30 minutes. After cooling the mixture to room temperature, a yellow crystalline material was obtained, which was separated and recrystallised from ethanol to give shiny yellow needles (3.68g, 68%), m.p. 83-85°C.

Found $C = 47.4\%$, $H = 5.50\%$, $N = 4.60\%$; $C_{24}H_{32}N_2Te_2$
requires $C = 47.7\%$, $H = 5.3\%$, $N = 4.64\%$

The density of the above compound, (I), was experimentally obtained by flotation of suitable crystals in a mixture of tetrachloroethylene/ethanol and found to be 1.60 gcm^{-3}.

4.2.2 The Preparation of the Complex $HgCl_2$.(I), Compound(II)

The ligand (I) (0.604g, 0.001 mole) was dissolved in absolute ethanol (30cm^3) and heated. Then a solution of mercury(II) chloride (0.2715g, 0.001 mole) in ethanol (20cm^3) was added slowly to the refluxing ligand solution under nitrogen gas. During the addition a white precipitate formed, and the solution was heated for a further 30 minutes. The solid was filtered off, and washed with hot ehtanol then with diethylether. The white compound was recrystallised from hot nitromethane to give pale yellow crystals (0.65g, 74.2% yield) which melted at 172°C with decomposition.

Found C = 32.4%, H = 3.60%, N = 3.10%; $C_{24}H_{32}N_2Te_2.HgCl_2$ requires C = 32.9%, H = 3.66%, N = 3.20%

Conductivity (10^{-3}mole litre^{-1}) in nitromethane = 2.8 ohm^{-1}cm^{2}mole^{-1}.

The density of the above complex was experimentally obtained by flotation of suitable crystals in a mixture of bromoform/CCl_4 and found to be 2.08 gcm^{-3}.

4.2.3 X-ray Structure Analysis of Compound (I) and (II)

After preliminary examination by photographic methods, crystals with dimensions c.a. 0.2 x 0.4 x 0.6 mm of compound (I) and 0.1 x 0.13 x 0.38 mm of compound (II) were mounted on an Enraf-Nonius CAD-4 diffractometer. The final cell dimensions and reflection intensities were measured using monochromated Mo-K_α radiation in the $\omega/2\theta$ scan mode. Two standard reflections were measured every hour to check the stability of the system. A total of 1382 reflections (compound I) and 3912 reflections (compound II) were scanned in the range $2 < \theta < 25°$.

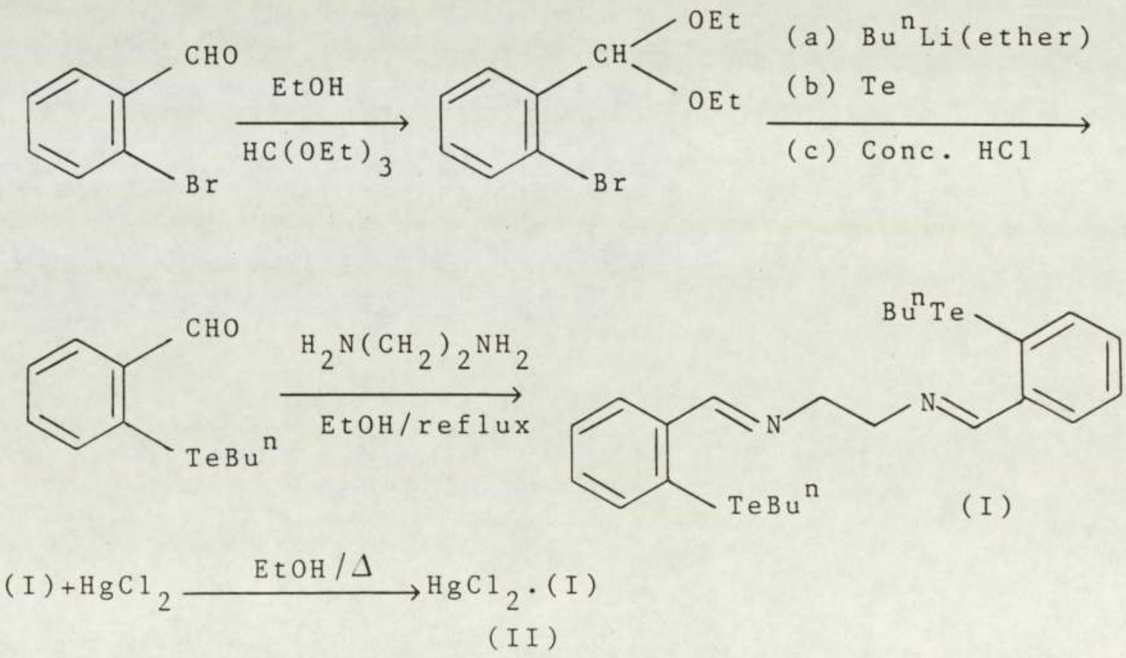
Reflections having $I > 2.5\sigma(I)$ were used in the analyses. The structures were solved by Patterson and Fourier methods and refined by least squares using anisotropic temperature factors for the heavier atoms [Te, N, C for (I) and Hg, Te, Cl for (II)]. Hydrogen atoms were either located from difference Fourier maps or placed in calculated positions "riding" on their respective carbon atoms. The weighing scheme used was:

$w = 1/[\sigma^2(F) + KF^2]$, with K = 0.0015 (compound I) and 0.005 (compound II).

The refinements were terminated when all calculated shift/error ratios were < 0.1. Final R values are 0.048 (compound I) and 0.054 (compound II). Absorption corrections were applied to compound (I), but made no significant difference. Computations were carried out on the Honeywell computer at the University of Birmingham and on the CDC 7600 at the University of Manchester regional computer centre with SHELX$^{(74)}$ and PLUTO$^{(113)}$.

4.3 Results and Discussion

The preparation of the ligand 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (I) is illustrated in Scheme (4.1).



Scheme 4.1

First of all, the aldehyde group was protected by conversion into acetal, which is insensitive to butyl-lithium and after complete telluration, the acetal group was acid hydrolysed into the original aldehyde. The ability of such group to react with primary amine groups and eliminate water was utilised. Ethylene diamine(1,2-diaminoethane) was used to link two tellurium compounds, giving finally the ligand which incorporates two tellurium and two nitrogen atoms.

The ligand (I) was found to be stable in air at room temperature. Passing a current of air through an ethanol solution of (I) for three days did not oxidise the compound or change its structure as confirmed by infrared spectroscopy and elemental analysis. Trying to reduce the carbon-nitrogen bond (C=N), by using an ethanol solution of sodium borohydride also failed.

The reaction of the ligand with mercury (II) chloride in a 1:1 ratio, always produces the complex (II), whether the reaction is performed under nitrogen gas or in the open atmosphere. The result was also the same when the reaction was carried out in different solvents (ethanol, methanol, nitromethane) or over a range of time between 15 min. and 2 hours.

4.3.1 Crystal Data

All the crystal parameters for compound (I) and (II) are included in Table 4.1. Final fractional atomic coordinates for (I) and (II) are in Tables 4.2 and 4.7.

The anisotropic temperature factors are shown in Table 4.4.

4.3.2 The Crystal and Molecular Structure of 1,6-bis-2-butyltellurophenyl-2,5-diaza-hexa-1,5-diene, and 1,6-bis-2-butyltellurophenyl-2,5-diaza-hexa-1,5-diene (Te,Te)-dichloromercury(II).

Pertinent distances and angles are given in Table 4.3 (Compound I) and 4.8 (Compound II). The structure and the stereoscopic packing arrangement are illustrated in Figures 4.2 and 4.3 (Compound I) and Figures 4.5 and 4.6 (Compound II). The torsion angles for both compounds are included in Table 4.6.

A-Compound(I)

In the crystal this compound is centrosymetric. Both Te-C bond lengths are within previously observed limits, with Te-C (alkyl) 2.181 Å and Te-C (phenyl) 2.111 Å. The longer Te-alkyl bond is not unexpected:the difference in radius between sp^2- and sp^3- hybridised carbon atom would only account for <u>ca</u>. 0.03 Å), but the fact that the tellurium atom is approached by the nitrogen <u>trans</u> to the alkyl carbon would account for the additional 0.04 Å. The Te---N distance of 2.773 Å is well within the Van der Waals distance (3.61 Å following Bondi(114) or 3.7 Å following Pauling (115)). The C(4)-Te-C(5) bond angle is

	(I)	(II)
Molecular formula	$C_{24}H_{32}N_2Te_2$	$C_{24}Cl_2H_{32}HgN_2Te_2$
Molecular weight	603.73	875.226
Crystal size (mm)	0.2x0.4x0.6	0.1x0.13x0.38
Cell constants (Å) a	13.239(5)	9.134(3)
b	5.985(2)	9.430(5)
c	16.198(6)	17.335(7)
(°) α	90	80.73(5)
β	107.23(5)	84.54(5)
γ	90	73.82(5)
Cell volume ($Å^3$)	1225.8	1413.41
Space group	$P2_1/n$(monoclinic)	$P\bar{1}$ (triclinic)
Density (g cm^{-3})calc.	1.64	2.06
Density (g cm^{-3})measur.	1.60	2.08
Absorption coeff.,μ(mm^{-1})	2.48	7.86
Data collection range		
λ = 0.71069(Å), 2θ(°)	4 - 50	4 - 50
Scan range (ω°)	$1.10+0.35\tan\theta$	$1.50+0.35\tan\theta$
Scan speed range(°min^{-1})	3.4 - 0.9	3.4 - 1.10
Total data measured	2157	4957
Significant data[$I>2.5\sigma(I)$]	1382	3912
Least-squares weights		
$W = 1/[\sigma^2(F) + KF^2]$	K = 0.0015	K = 0.005
Final R (%)	4.80	5.41
Final R_w(%)	4.74	5.88
Z	2	2
Residual electron density in final difference map (e $Å^{-3}$)	-1.35 to +1.47	-3.52 to + 3.54
F (000)	588	816

Table 4.1 Crystal and experimental parameters

Atom	x	y	z	U_{iso}
Te(1)	7238(1)	4748(1)	5262(1)	*
N(1)	6203(6)	1214(13)	5766(5)	*
C(1)	8232(10)	11607(20)	3311(8)	*
C(2)	8698(8)	10171(18)	4106(7)	*
C(3)	7919(7)	8524(15)	4265(7)	*
C(4)	8419(8)	7053(16)	5062(7)	*
C(5)	8287(7)	3094(14)	6325(5)	*
C(6)	9307(8)	3890(17)	6698(7)	*
C(7)	10009(8)	2797(20)	7374(7)	*
C(8)	9699(8)	861(21)	7697(7)	*
C(9)	8710(8)	53(16)	7362(6)	*
C(10)	7971(7)	1145(15)	6683(6)	*
C(11)	6912(7)	217(14)	6357(6)	*
C(12)	5150(8)	190(18)	5470(6)	*
H(A1)	7982(0)	10089(0)	2879(0)	43(23)
H(B1)	7624(0)	11820(0)	3387(0)	111(54)
H(C1)	8740(0)	12893(0)	3304(0)	94(38)
H(A2)	8848(0)	10820(0)	4610(0)	58(30)
H(B2)	9376(0)	9649(0)	4043(0)	47(24)
H(A3)	7270(0)	9544(0)	4472(0)	31(19)
H(B3)	7629(0)	7513(0)	3697(0)	204(89)
H(A4)	9000(0)	6125(0)	4860(0)	38(21)
H(B4)	8686(0)	7991(0)	5663(0)	281(90)
H(6)	9527(0)	5155(0)	6319(0)	131(57)
H(7)	10862(0)	3034(0)	7471(0)	126(49)
H(8)	10260(0)	-17(0)	8126(0)	57(27)
H(9)	8413(0)	-1336(0)	7645(0)	80(33)
H(11)	6724(0)	-1320(0)	6627(0)	136(53)
H(A12)	5121(0)	-1221(0)	5805(0)	43(23)
H(B12)	4606(0)	859(0)	5700(0)	67(30)

Table 4.2. Fractional atomic co-ordinates ($x10^4$) with e.s.d's in parentheses and isotropic temp. factors ($Å^2 x 10^3$) for compound (I)

* Atoms are anisotropically refined (Table 4.4)

Te(1) ---C(4)	2.181 (10)	C(5) ---C(10)	1.419 (12)
Te(1) ---C(5)	2.111 (8)	C(6) ---C(7)	1.373 (14)
N(1) ---C(11)	1.273 (11)	C(7) ---C(8)	1.383 (16)
N(1) ---C(12)	1.467 (12)	C(8) ---C(9)	1.350 (15)
C(1) ---C(2)	1.519 (14)	C(9) ---C(10)	1.398 (13)
C(2) ---C(3)	1.503 (13)	C(10) ---C(11)	1.455 (12)
C(3) ---C(4)	1.540 (14)	C(12) ---C(12)′	1.472 (20)
C(5) ---C(6)	1.390 (12)		
C(4) -Te(1) -C(5)	95.2 (4)	C(5) -C(6) -C(7)	121.6 (9)
C(11) -N(1) -C(12)	117.9 (8)	C(6) -C(7) -C(8)	119.6 (10)
C(1) -C(2) -C(3)	112.9 (8)	C(7) -C(8) -C(9)	120.6 (10)
C(2) -C(3) -C(4)	111.9 (8)	C(8) -C(9) -C(10)	121.2 (9)
Te(1) -C(4) -C(3)	109.7 (6)	C(5) -C(10) -C(9)	118.9 (8)
Te(1) -C(5) -C(6)	120.9 (7)	C(5) -C(10) -C(11)	122.3 (8)
Te(1) -C(5) -C(10)	121.1 (6)	C(9) -C(10) -C(11)	118.8 (8)
C(6) -C(5) -C(10)	118.0 (8)	N(1) -C(11) -C(10)	120.7 (8)

Table 4.3. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

Compound I	U11	U22	U33	U23	U13	U12
Te(1)	55(1)	30(1)	55(1)	2(1)	8(1)	0(1)
N(1)	54(4)	41(4)	60(5)	-7(4)	11(4)	-8(4)
C(1)	71(8)	63(8)	81(8)	24(6)	18(6)	-1(6)
C(2)	52(5)	71(7)	59(6)	7(6)	16(4)	1(5)
C(3)	59(6)	38(5)	61(6)	1(4)	17(5)	-5(4)
C(4)	63(6)	41(5)	70(7)	6(5)	19(5)	-2(4)
C(5)	53(5)	32(4)	41(5)	-3(4)	6(4)	1(4)
C(6)	52(5)	52(6)	59(6)	0(5)	11(5)	-4(4)
C(7)	54(6)	71(7)	70(7)	-3(6)	12(5)	3(5)
C(8)	59(6)	73(7)	61(6)	8(6)	4(5)	20(6)
C(9)	64(6)	50(6)	57(5)	7(5)	17(5)	7(5)
C(10)	53(5)	35(4)	46(5)	-5(4)	18(4)	7(4)
C(11)	59(5)	33(4)	45(4)	-1(4)	16(4)	-6(4)
C(12)	58(5)	63(7)	62(6)	-10(5)	22(5)	-23(5)
Compound II						
Hg	44(1)	45(1)	40(1)	-14(1)	2(1)	-12(1)
Te(1)	39(1)	52(1)	31(1)	-8(1)	1(1)	-9(1)
Te(2)	51(1)	41(1)	36(1)	-7(1)	-8(1)	-10(1)
Cl(1)	47(2)	57(2)	77(2)	-17(1)	-1(1)	-2(1)
Cl(2)	76(2)	49(2)	71(2)	-10(1)	-2(2)	-24(1)

Table 4.4 Anisotropic temperature factors (Å^2 x 10^3) with e.s.d.'s in parentheses

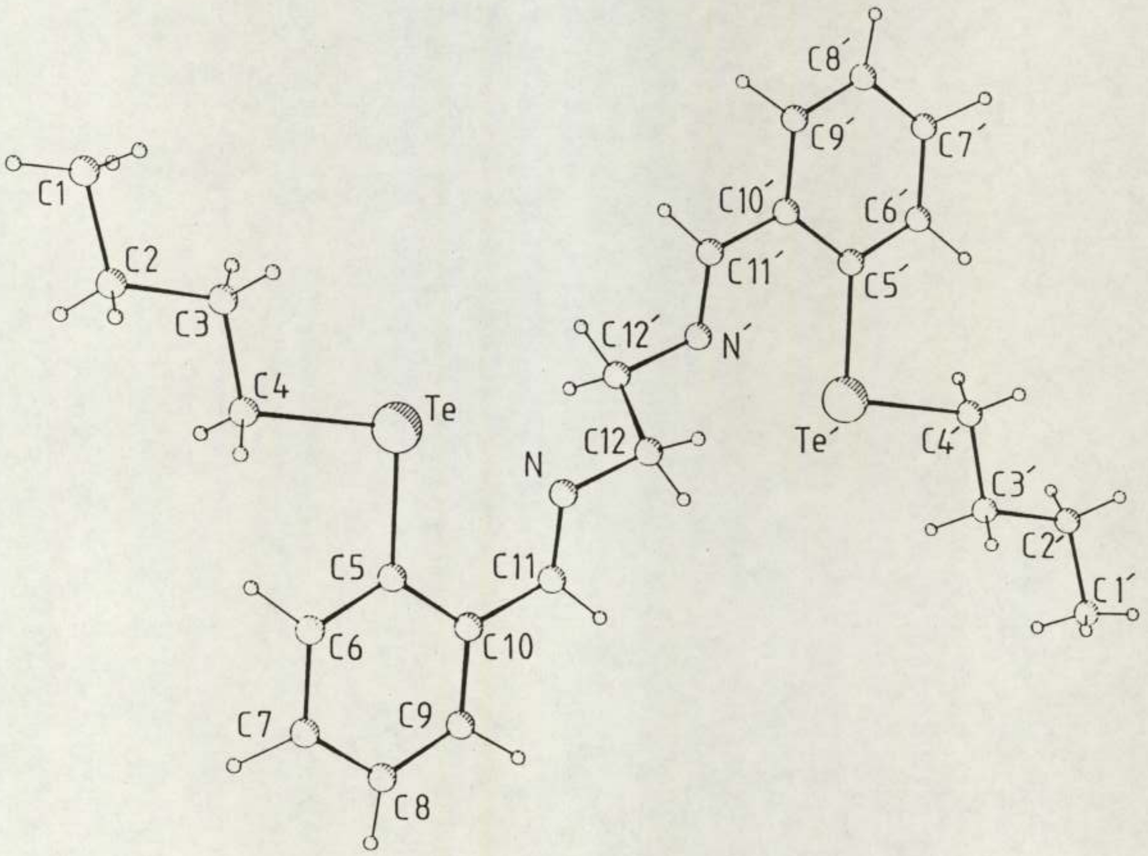


Figure 4.2 : The molecular structure of $C_{24}H_{32}N_2Te_2$

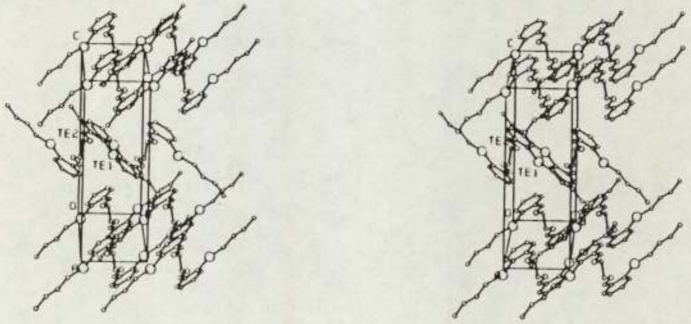


Figure 4.3 : A stereoscopic view of the unit cell of $C_{24}H_{32}N_2Te_2$

P_1 Plane defined by C(1), C(2), C(3), C(4), Te
$0.4601X - 0.6741Y - 0.5777Z + 3.3680 = 0$

P_2 Plane defined by Te, C(5), C(10), C(11), N
$0.4916X - 0.5832Y - 0.6465Z + 3.4760 = 0$

P_3 Plane defined by C(5), C(6), C(7), C(8), C(9), C(10)
$0.5263X - 0.5491Y - 0.6492Z + 3.2065 = 0$

P_4 Plane defined by Te, C(5), C(6), C(7), C(8), C(9), C(10), C(11)
$0.5229X - 0.5632Y - 0.6397Z + 3.1480 = 0$

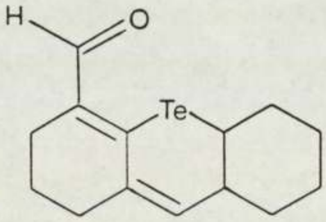
P_5 Plane defined by C(1), C(2), C(3), C(4), Te, C(5), C(6), C(7), C(8), C(9), C(10), C(11), N, C(12)
$0.4853X - 0.6381Y - 0.5976Z + 3.0987 = 0$

Atoms	P_1	P_2	P_3	P_4	P_5
Te	0.0026	-0.0251	-0.0760	-0.0310	0.1540
N	-0.2291	0.0399	0.1192	0.1215	0.0547
C(1)	-0.0082	-0.6879	-0.9650	-0.8258	-0.1215
C(2)	0.0123	-0.5120	-0.7647	-0.6485	-0.0515
C(3)	0.0037	-0.3789	-0.5589	-0.4627	0.0083
C(4)	-0.0105	-0.2373	-0.3936	-0.3207	0.0431
C(5)	-0.1190	0.0285	-0.0146	0.0037	0.0786
C(6)	-0.0043	0.1026	0.0041	0.0276	0.1581
C(7)	-0.1185	0.1011	0.0066	0.0130	0.0731
C(8)	-0.3497	0.0274	-0.0065	-0.0231	-0.0920
C(9)	-0.4471	-0.0255	-0.0045	-0.0269	-0.1534
C(10)	-0.3141	-0.0036	0.0149	0.0095	-0.0484
C(11)	-0.4050	-0.0397	0.0395	0.0270	-0.0980
C(12)	-0.3333	0.0008	0.1415	0.1354	-0.0050
C(12)′	-1.3495	-1.0984	0.9539	-0.9493	-1.0434

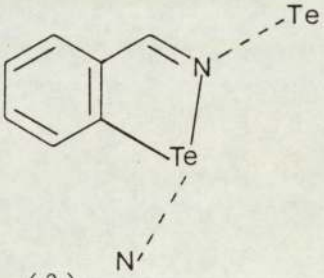
Table 4.5. Equations of least-squares planes and deviations (Å) of atoms from the planes, for compound I.

95.2° which is close to the previously reported values(116).

The co-ordination about tellurium is approximately trigonal bipyramidal with the phenyl carbon atom C(5) and the two lone pairs in the equatorial positions, and the alkyl carbon C(4) and the nitrogen atom in the axial positions. Thus, the position trans to C(5) is unoccupied. Consequently, tellurium(II) in this compound exhibits Lewis acid character with the imine nitrogen being the donor atom. This is generally more pronounced for organotellurenyl compounds, RTeX (e.g., 2-phenylazophenyl.(C,N)tellurium(II) chloride)(117), but it is not without precedent for R_2Te ; e.g., compound (1)(118) has a Te---O distance of 2.574 Å (cf. Van der Waals distances of 3.58(114) or 3.6 Å(115).



(1)



(2)

However, compound (I) could be considered as the first example of three co-ordinate R_2Te---X, involving nitrogen with a T-shaped structure. This feature is significant, and may be not incidental, since the nitrogen of an imine group ortho- to a carbon atom would not necessarily be directed toward that carbon. In a single crystal X-ray study(119), it was found that in the compound 1-(o-methylbenzylideneamino)pyridinium iodide (Fig. 4.4.), for example, the imine nitrogen is pointing away from the ortho-carbon atom.

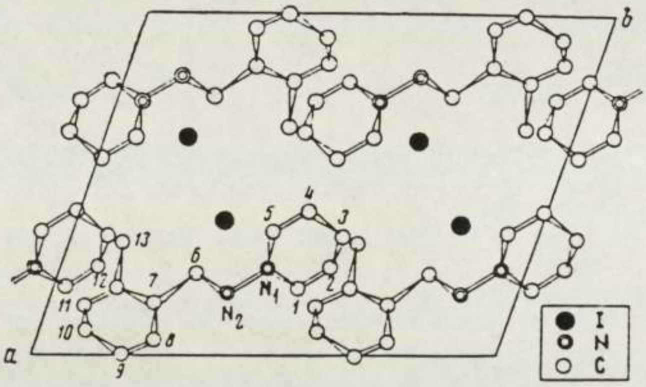


Figure 4.4. The crystal structure of $[C_{13}H_{13}N_2]^+I^-$

The Te---N interaction, in compound (I), could account for its stability against air oxidation and the chemical reduction, which has been pointed out earlier. The yellow colour of this compound may be also due to Te---N interaction and to the resonance in the moiety Te-C(5)-C(10)-C(11)-N, which is coplanar to within ± 0.030 Å. The C(11)-N double bond has a length of 1.273 Å which is very close to the C=N distance (1.27 Å) previously reported for 1,2-benzisotellurazole(2), which has a covalent Te-N bond and an intermolecular Te---N interaction of 2.47 Å. This intermolecular interaction was considered to account for the "anomalous" physical properties of compound (2)$^{(120)}$

No other significant secondary bonding or interaction between adjacent molecules occurs in the crystal structure of compound (I).

The molecule is centrosymmetric, and the centre of the C(12)-C(12)' bond is coinciding with the crystallographic inversion centre (1/2, 0, 1/2). The two tellurium atoms are, therefore, situated on opposite sides of the ethylenediimine chain, preventing any interaction between them (Fig. 4.2) with the Te---Te distance 5.740 Å (sum of Van der Waals radii 4.40 Å).

In general terms, the geometry of the molecule can be described as consisting of two main planes, each plane contains half of the molecule (i.e., butyl, Te, phenyl and imine groups), with the atoms coplanar to within ±0.095 Å. Only the phenyl group, in fact, is slightly off the plane due to a twist around the Te-C(5) bond of ca. 8°. These two planes are linked by C(12)-C(12)' of the ethylene diimine group.

B-Compound (II)

The reaction of compound (I) with mercury(II) chloride in ethanol gave a 1:1 complex according to the elemental analyses. After recrystallisation from hot nitromethane it afforded light yellow crystals, which proved to be suitable for X-ray study. The conductivity of a solution of this complex (10^{-3}mol 1^{-1}) in nitromethane is 2.8 ohm^{-1}

Ligand Atoms				Angles	Complex Atoms				Angles
C(10)	C(11)	N	C(12)	-179.90	C(10)	C(11)	N	C(12)	176.59
C(11)	N	C(12)	C(12)′	-123.45	C(11)	N(1)	C(12)	C(13)	-127.16
N	C(12)	C(12)′	N′	180.00	N(1)	C(12)	C(13)	N(2)	61.34
C(12)	C(12)′	N′	C(11)′	123.45	C(12)	C(13)	N(2)	C(14)	156.49
C(4)	Te	C(5)	C(10)	-172.12	C(13)	N(2)	C(14)	C(15)	173.16
C(4)	Te	C(5)	C(6)	8.16	N(2)	C(14)	C(15)	C(20)	-4.66
N	C(11)	C(10)	C(5)	- 4.40	N(1)	C(11)	C(10)	C(5)	1.12
N	C(11)	C(10)	C(9)	176.77	Te(1)	C(5)	C(10)	C(11)	-1.47
C(1)	C(2)	C(3)	C(4)	178.57	Te(2)	C(20)	C(15)	C(14)	4.81
C(2)	C(3)	C(4)	Te	179.30	Cl(1)	Hg	Te(1)	C(4)	-98.02
C(3)	C(4)	Te	C(5)	177.34	Cl(1)	Hg	Te(1)	C(5)	165.23
					Cl(1)	Hg	Te(2)	C(20)	25.12
					Cl(1)	Hg	Te(2)	C(21)	122.71
					Cl(2)	Hg	Te(1)	C(4)	19.48
					Cl(2)	Hg	Te(1)	C(5)	-77.25
					Cl(2)	Hg	Te(2)	C(20)	-96.68
					Cl(2)	Hg	Te(2)	C(21)	0.90

Table 4.6. The torsion angles (°) for the ligand (compound I) and the complex (compound II)

Atom	x	y	z	U_{iso}
Hg	-2524(1)	-462(1)	2498(1)	*
Te(1)	-1135(1)	-435(1)	975(1)	*
Te(2)	-485(1)	-206(1)	3519(1)	*
Cl(1)	-5029(3)	1382(3)	2485(2)	*
Cl(2)	-2888(4)	-3013(3)	2870(2)	*
N(1)	234(11)	1495(10)	1508(5)	47(2)
N(2)	-1797(10)	2649(10)	2822(5)	46(2)
C(1)	-5223(17)	-2697(16)	-288(9)	74(4)
C(2)	-3680(17)	-3148(16)	57(9)	69(4)
C(3)	-3295(16)	-1820(15)	332(8)	65(3)
C(4)	-1721(14)	-2305(14)	633(7)	56(3)
C(5)	1078(13)	-1673(12)	1374(7)	46(2)
C(6)	1560(14)	-3181(13)	1359(7)	56(3)
C(7)	3000(15)	-4001(14)	1641(8)	61(3)
C(8)	3902(16)	-3318(15)	1943(8)	63(3)
C(9)	3396(15)	-1782(14)	1958(8)	58(3)
C(10)	1974(12)	-954(12)	1677(6)	45(2)
C(11)	1523(14)	651(13)	1732(8)	55(3)
C(12)	-204(15)	3021(14)	1606(8)	60(3)
C(13)	-1765(15)	3474(14)	2031(8)	59(3)
C(14)	-2780(14)	3198(13)	3335(7)	52(3)
C(15)	-2971(13)	2379(13)	4087(7)	50(3)
C(16)	-4089(17)	3070(16)	4606(9)	72(4)
C(17)	-4406(22)	2336(21)	5346(11)	93(5)
C(18)	-3580(18)	913(17)	5564(9)	73(4)
C(19)	-2436(15)	150(14)	5040(8)	61(3)
C(20)	-2173(13)	886(12)	4295(7)	49(3)
C(21)	-105(14)	-2400(14)	4174(8)	57(3)
C(22)	983(16)	-3477(15)	3673(9)	68(3)
C(23)	1224(23)	-5128(22)	4075(12)	105(6)
C(24)	1971(29)	-6229(28)	3520(15)	135(8)

Table 4.7. Fractional atomic co-ordinates (x 10^4) with e.s.d.'s in parentheses isotropic temperature factors (Å^{2}x 10^3) for compound (II)

* Atoms are anisotropically refined (Table 4.4)

Atom	x	y	z	Uiso
H(A1)	-5308(0)	-1758(0)	-737(0)	70(0)
H(B1)	-6109(0)	-2382(0)	176(0)	70(0)
H(C1)	-5444(0)	-3611(0)	-525(0)	70(0)
H(A3)	-3367(0)	-907(0)	-173(0)	70(0)
H(B3)	-4170(0)	-1352(0)	771(0)	70(0)
H(A4)	-1659(0)	-3177(0)	1160(0)	70(0)
H(B4)	-851(0)	-2808(0)	209(0)	70(0)
H(6)	829(0)	-3739(0)	1130(0)	70(0)
H(8)	5017(0)	-3965(0)	2143(0)	70(0)
H(11)	2305(0)	1150(0)	1983(0)	70(0)
H(A12)	620(0)	3234(0)	1979(0)	70(0)
H(B12)	-189(0)	3749(0)	1057(0)	70(0)
H(A13)	-2579(0)	3185(0)	1685(0)	70(0)
H(B13)	-2135(0)	4646(0)	2052(0)	70(0)
H(14)	-3492(0)	4334(0)	3172(0)	70(0)
H(16)	-4788(0)	4259(0)	4444(0)	70(0)
H(17)	-5244(0)	2884(0)	5774(0)	70(0)
H(18)	-3881(0)	301(0)	6127(0)	70(0)
H(19)	-1941(0)	-1016(0)	5199(0)	70(0)
H(A21)	-1187(0)	-2710(0)	4292(0)	70(0)
H(B21)	363(0)	-2444(0)	4731(0)	70(0)
H(A22)	2117(0)	-3249(0)	3608(0)	70(0)
H(B22)	583(0)	-3344(0)	3090(0)	70(0)
H(A23)	56(0)	-5280(0)	4220(0)	70(0)
H(B23)	1790(0)	-5303(0)	4598(0)	70(0)
H(A24)	1259(0)	-6752(0)	3372(0)	70(0)
H(B24)	2931(0)	-7008(0)	3861(0)	70(0)
H(C24)	2488(0)	-5616(0)	3044(0)	70(0)
H(A2)	-2844(0)	-3626(0)	-341(0)	70(0)
H(B2)	-3616(0)	-3957(0)	430(0)	70(0)
H(7)	3296(0)	-5151(0)	1601(0)	70(0)
H(9)	4056(0)	-1158(0)	2188(0)	70(0)

(Table 4.7 continued)

Hg ---Te(1)	2.819(1)	C(6) ---C(7)	1.415(17)
Hg ---Te(2)	2.769(1)	C(7) ---C(8)	1.361(18)
Hg ---Cl(1)	2.457(3)	C(8) ---C(9)	1.396(18)
Hg ---Cl(2)	2.494(3)	C(9) ---C(10)	1.403(16)
Te(1) ---C(4)	2.161(12)	C(10) ---C(11)	1.470(15)
Te(1) ---C(5)	2.149(11)	C(12) ---C(13)	1.523(18)
Te(2) ---C(20)	2.101(12)	C(14) ---C(15)	1.427(17)
Te(2) ---C(21)	2.146(12)	C(15) ---C(16)	1.385(19)
N(1) ---C(11)	1.279(15)	C(15) ---C(20)	1.399(15)
N(1) ---C(12)	1.416(15)	C(16) ---C(17)	1.401(23)
N(2) ---C(13)	1.465(16)	C(17) ---C(18)	1.356(23)
N(2) ---C(14)	1.266(15)	C(18) ---C(19)	1.429(20)
C(1) ---C(2)	1.506(20)	C(19) ---C(20)	1.398(18)
C(2) ---C(3)	1.546(19)	C(21) ---C(22)	1.527(19)
C(3) ---C(4)	1.498(18)	C(22) ---C(23)	1.567(23)
C(5) ---C(6)	1.371(15)	C(23) ---C(24)	1.508(30)
C(5) ---C(10)	1.382(15)		

Table 4.8. Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses.

Te(1) -Hg -Te(2)	109.1(0)	C(7) -C(8) -C(9)	118.9(12)
Te(1) -Hg -Cl(1)	110.0(1)	C(8) -C(9) -C(10)	120.8(12)
Te(2) -Hg -Cl(1)	116.4(1)	C(5) -C(10) -C(9)	119.2(12)
Te(1) -Hg -Cl(2)	105.3(1)	C(5) -C(10) -C(11)	123.8(10)
Te(2) -Hg -Cl(2)	106.2(1)	C(9) -C(10) -C(11)	116.9(10)
Cl(1) -Hg -Cl(2)	109.2(1)	N(1) -C(11) -C(10)	121.7(11)
Hg -Te(1) -C(4)	99.7(3)	N(1) -C(12) -C(13)	112.4(10)
Hg -Te(1) -C(5)	93.6(3)	N(2) -C(13) -C(12)	112.1(10)
C(4) -Te(1) -C(5)	96.0(4)	N(2) -C(14) -C(15)	122.0(11)
Hg -Te(2) -C(20)	95.1(3)	C(14) -C(15) -C(16)	117.7(11)
Hg -Te(2) -C(21)	97.9(3)	C(14) -C(15) -C(20)	122.9(11)
C(20) -Te(2) -C(21)	96.8(5)	C(16) -C(15) -C(20)	119.2(12)
C(11) -N(1) -C(12)	120.4(10)	C(15) -C(16) -C(17)	121.9(14)
C(13) -N(2) -C(14)	119.6(10)	C(16) -C(17) -C(18)	118.9(17)
C(1) -C(2) -C(3)	111.9(12)	C(17) -C(18) -C(19)	120.9(15)
C(2) -C(3) -C(4)	110.0(11)	C(18) -C(19) -C(20)	119.3(12)
Te(1) -C(4) -C(3)	110.3(8)	Te(2) -C(20) -C(15)	120.2(9)
Te(1) -C(5) -C(6)	119.7(8)	Te(2) -C(20) -C(19)	120.0(8)
Te(1) -C(5) -C(10)	119.8(8)	C(15) -C(20) -C(19)	119.7(11)
C(6) -C(5) -C(10)	120.5(11)	Te(2) -C(21) -C(22)	107.3(9)
C(5) -C(6) -C(7)	119.6(12)	C(21) -C(22) -C(23)	110.9(13)
C(6) -C(7) -C(8)	120.9(12)	C(22) -C(23) -C(24)	112.1(18)

(Table 4.8 continued)

P_1 Plane defined by Te(1), C(5), C(10), C(11), N(1)
$0.3630X + 0.1667Y - 0.9167Z + 1.9242 = 0$

P_2 Plane defined by Te(2), C(20), C(15), C(14), N(2)
$-0.7119X - 0.5982Y - 0.3678Z + 2.5251 = 0$

P_3 Plane defined by C(1), C(2), C(3), C(4), Te(1)
$0.3663X + 0.1735Y - 0.9141Z + 1.9475 = 0$

P_4 Plane defined by C(24), C(23), C(22), C(21), Te(2)
$-0.8763X - 0.3843Y - 0.2902Z + 1.9458 = 0$

P_5 Plane defined by Te(1), C(5), C(10), C(11), N(1), C(12), C(13), N(2), C(14), C(15), C(20), Te(2)
$-0.8462X - 0.4229Y - 0.3240Z + 1.6856 = 0$

Atoms	P_1	P_2	P_3	P_4	P_5
Hg	2.7742	-2.5980	2.7491	-2.5954	-2.1457
Cl(1)	3.3692	-3.5151	3.3439	-4.1070	-3.5493
Cl(2)	3.8594	-3.9999	3.8500	-3.5814	-3.1940
C(1)	-0.0425	-8.3505	-0.0224	-7.6456	-7.4156
C(2)	-0.0158	-7.1106	-0.0022	-6.2372	-6.0267
C(3)	0.0454	-5.8252	0.0469	-5.2338	-4.9632
C(4)	0.0006	-4.6179	-0.0039	-3.8407	-3.5942
Te(1)	0.0033	-2.8140	-0.0182	-2.4220	-2.0946
C(5)	-0.0072	-1.4498	-0.0337	-0.6800	-0.4082
C(6)	0.0330	-1.9394	0.0140	-0.8194	-0.6116
C(7)	0.0622	-1.0406	0.0400	0.3239	0.4965
C(8)	0.0769	0.3049	0.0442	1.5595	1.7618
C(9)	0.0408	0.7910	0.0004	1.6878	1.9554
C(10)	0.0071	-0.0882	-0.0300	0.5634	0.8664
C(11)	-0.0014	0.5147	-0.0472	0.7924	1.1649

Table 4.9. Equations of least-squares planes and deviations (Å) of atoms from the planes for compound II

Atoms	P_1	P_2	P_3	P_4	P_5
N(1)	-0.0019	-0.2028	-0.0457	-0.1715	0.2385
C(12)	0.0622	0.4022	0.0099	0.0690	0.5484
C(13)	1.1862	-0.1896	1.1354	-0.8296	-0.2799
N(2)	2.5029	0.0004	2.4524	-0.6164	-0.0441
C(14)	3.5344	-0.0121	3.4815	-0.9190	-0.2766
C(15)	4.8510	0.0240	4.7992	-0.8681	-0.2029
C(16)	5.9164	-0.0090	5.8619	-1.2330	-0.4899
C(17)	7.2467	-0.0323	7.1935	-1.2680	-0.4977
C(18)	7.4958	-0.0060	7.4466	-0.9192	-0.2001
C(19)	6.4254	0.0017	6.3792	-0.5620	0.0758
C(20)	5.1063	-0.0198	5.0591	-0.5761	0.0351
Te(2)	3.5151	0.0074	3.4722	-0.0393	0.4530
C(21)	4.6962	-0.3714	4.6614	-0.0578	0.3913
C(22)	3.7285	-0.5647	3.6989	0.1527	0.5116
C(23)	4.4993	-0.9631	4.4765	0.0376	0.3588
C(24)	3.5772	-1.4817	3.5617	-0.0932	0.1389

(Table 4.9 continued)

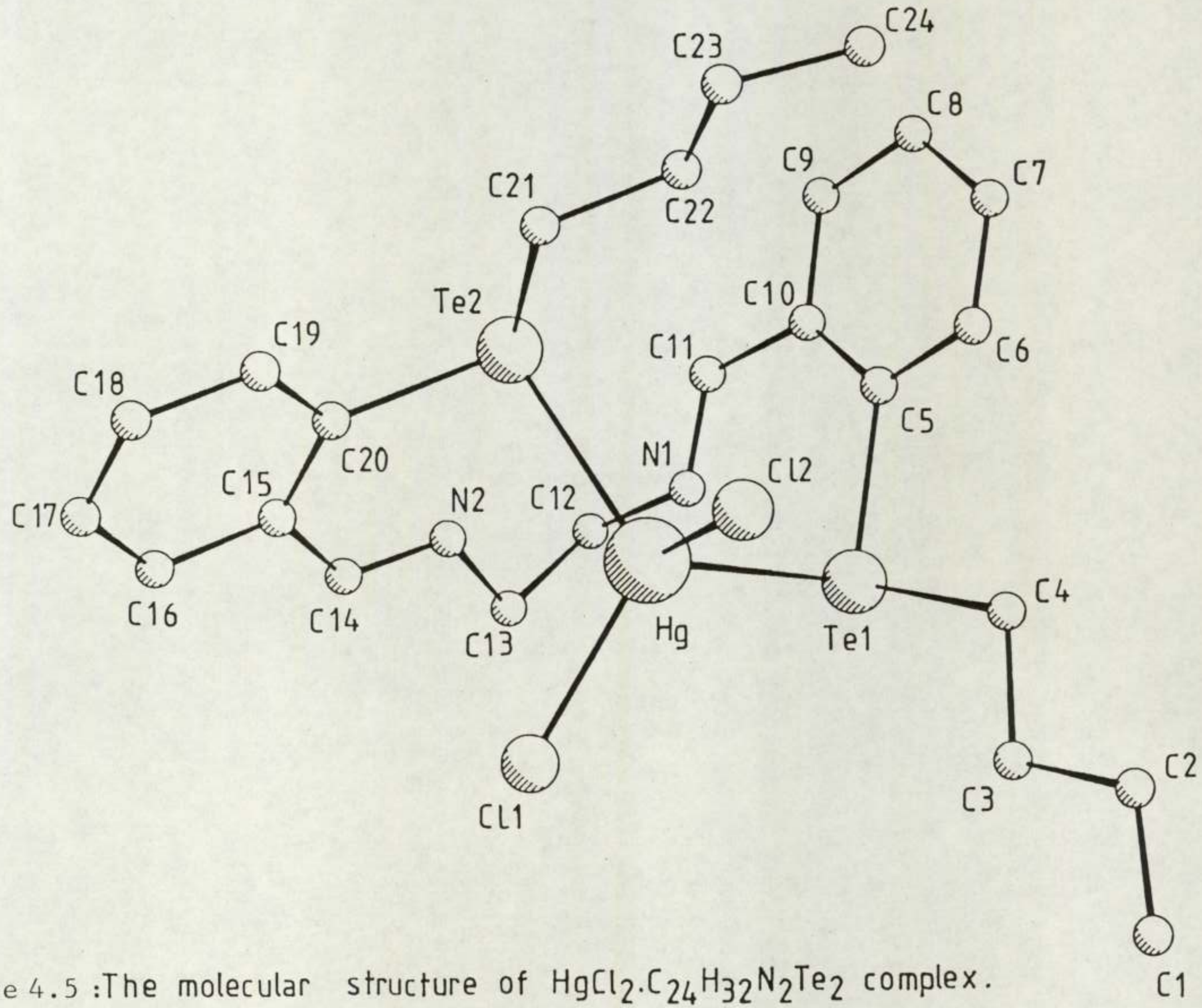


Figure 4.5 :The molecular structure of $HgCl_2.C_{24}H_{32}N_2Te_2$ complex.

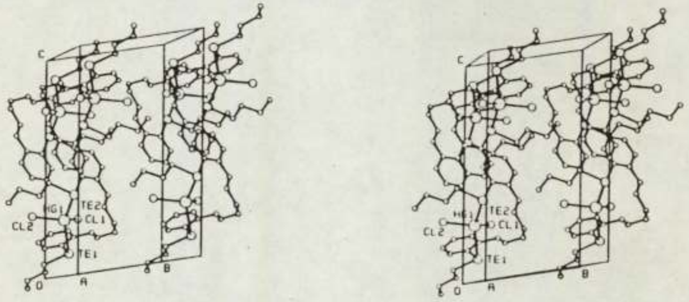
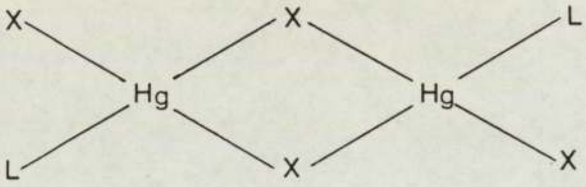


Figure 4.6 : A stereoscopic view of the unit cell of $HgCl_2.C_{24}H_{32}N_2Te_2$

cm^2mol^{-1} at room temperature. This value clearly implies the non ionic character of the compound.

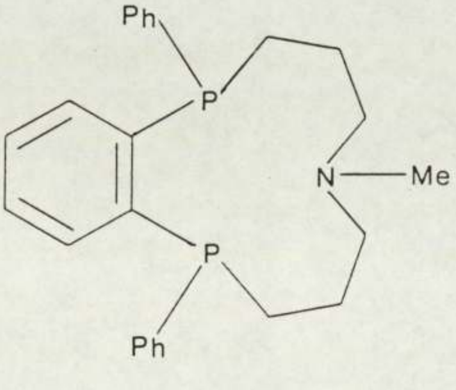
Most of the crystallographic data of mercury(II) complexes show that the solid state structure of these compounds is either dimeric or polymeric with halogen bridges, in which Hg atoms lie in a tetrahedral environment and donor ligands have mutually trans positions with respect to one another(111).



(3)

The crystallographic space group of this compound is triclinic, and the crystal analysis showed that the compound is monomeric. The mercury atom is situated in a roughly tetrahedral environment with bond angles in the range 105.3°-116.4° (Table 4.8), bonding to two chlorine and two tellurium atoms (Fig. 4.5).

The major points of interest are, first, the large (13-membered) chelate ring, which is the first example involving a main group element (i.e., Hg), and the first involving a tellurium ligand. The second point of interest is the fact that Hg---N distances (3.668 Å, 3.324 Å) are non-bonding. As is known, mercury(II) shows a strong preference for "soft" ligands, and this is illustrated quite dramatically by the present structure, since the option of tellurium and nitrogen co-ordination, to give a six membered chelate ring, clearly exists. The preference of soft acids for soft ligands has also been noted by many previous workers, although the option of hard and soft ligands also existed. In the molybdenum complex $[Mo(CO)_4(P,N,N,P)]^{(121)}$, where (P,N,N,P) is the macrocyclic ligand $(Ph_2PCH_2N(CH_3)CH_2-)_2$, it has been shown, by single crystal X-ray study, that only phosphorus atoms are ligated to the molybdenum atom. The structure $^{(122)}$ of the complex $[(Ph_2PCH_2CH_2)_2NEt]Cr(CO)_3$ has been described as a distorted octahedron with an "astonishingly" long Cr-N bond. Similarly, in a single crystal X-ray structure determination, it has been reported that the Mo-N bond, in the complex (4)-$Mo(CO)_3$, is very long (2.44 Å), which is "essentially" the same length as the Mo-P bonds in the complex $^{(123)}$.

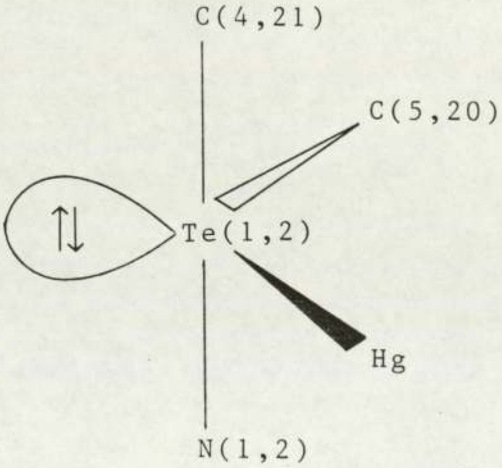


(4)

The very important feature of the present complex, which is quite different from that of the above mentioned complexes, is that although the Hg---N distances are inconsistent with Hg$\leftarrow$N co-ordination, the planarity of the Te-C-C-C-N moieties are again well maintained in the complex to within ± 0.007 Å and ± 0.024 Å (Table 4.9), and the Te---N interactions (the distances are 2.786, 2.752 Å) remain well within the Van der Waals distance (3.61 Å following Bondi(114) or 3.7 Å following Pauling(115)

The Hg-Te bond length in this complex are 2.769 and 2.819 Å, which are close to the distances 2.753 and 2.818 Å found for the tetrametric $(Ph_2Te)HgI_2$ (111), and $[PPh_4][Hg(TePh)_3]$ (40b) with Hg-Te distances of 2.682, 2.692 and 2.717 Å.

The tellurium(II) is then acting simultaneously as a Lewis acid (towards nitrogen) and a Lewis base (towards mercury), a feature which we think to be a very rare occurance and unique for R_2Te compounds. The geometry around tellurium is, therefore, achieving a trigonal bipyramid, with C(5), Hg and the lone pair in equatorial positions, and C(4) and N atoms in axial positions, as illustrated below:



(5)

The Hg-Te-C(5,20) angles are 93.6 and 95.1°, and C(4,21)-Te-C(5,20) 96.0 and 96.8° (Table 4.6). These values are not very different to C(4)-Te-C(5) bond angle found in the ligand (95.2°).

In mercury(II) complexes, it has been noted that when the ligands are bulky (e.g., Ph_3PSe) dimeric structures result, and the L-Hg-Cl bond angle is around ca. 136 Å (124). Although the ligand (compound I) is relatively bulky, the complex is monomeric and the Te-Hg-Cl bond angles, ranging between 105.3-116.4 Å, are small. Moreover, the Te(1)-Hg-Te(2) angle is only 109.1° which is ideal for a tetrahedral arrangement of the ligands, but when the ligand size is considered this value is certainly low. This could mean that the small electronegativity of tellurium helps to decrease the repulsion between these two atoms; however, the same bond angle value was found for Cl(1)-Hg-Cl(2) (109.2°), which involves the more electronegative chlorine ligands. The electronegativity approach is, therefore, void here, and this fact may alternatively indicate that the ligand is not very flexible although there are eleven bonds between the two tellurium donor atoms of the ligand. The inflexibility (i.e. the backbone rigidity) of the ligand might be caused by the Te---N interactions and the planarity of the Te-C-C-C-N moieties, which has been mentioned earlier.

The colour of the mercury complex is fainter relative to the colour of the ligand. This could be explained in terms of the decrease in the magnitude of the resonance in the $\overline{\text{Te-C=C-C=N}}$ ring, due to the removal of one of the tellurium electron pairs by co-ordination with the mercury ion.

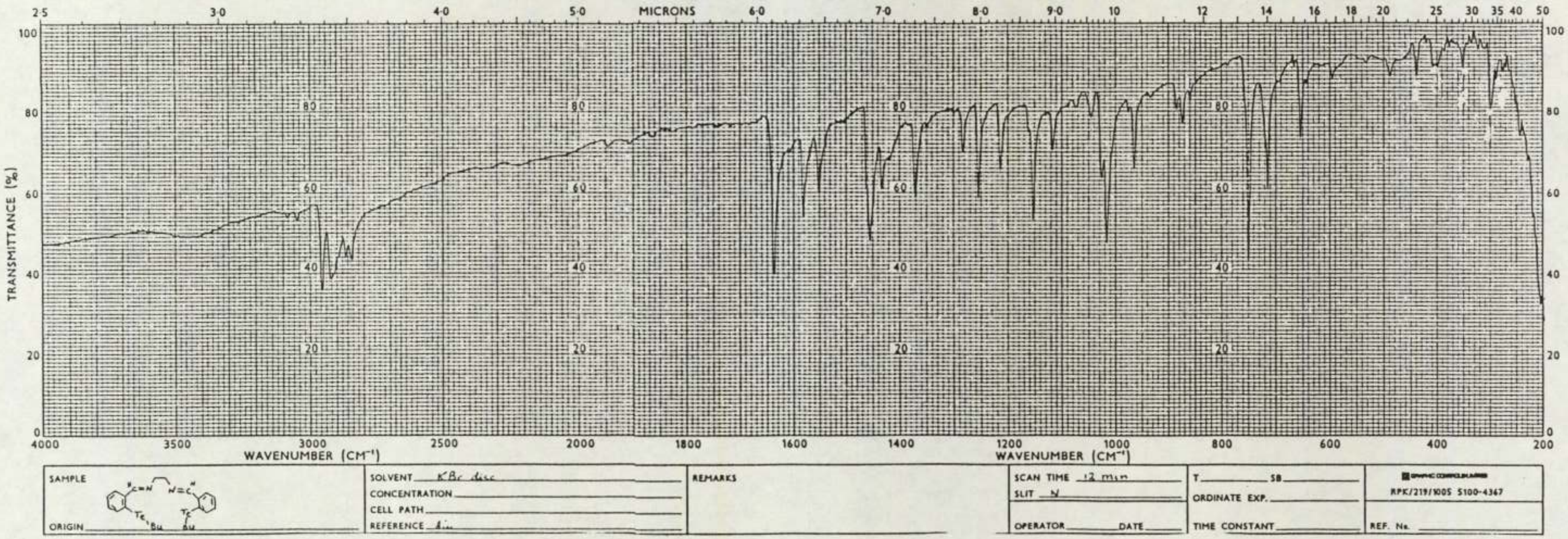
It is also noted that the smallest tellurium-mercury-chlorine angles are the ones which involve Cl(2); this is reflected by the longer Hg-Cl(2) bond (2.494 Å) relative to the Hg-Cl(1) bond distance (2.457 Å) (see Table 4.8).

In this complex, tellurium-carbon bond lengths are well within the previously reported values. The Te-C(alkyl) bonds are longer than the Te-C(phenyl) bonds by 0.012-0.045 Å. This difference is less than that observed in the structure of the unco-ordinated ligand, although the Te---N interaction, <u>trans</u> to the alkylcarbon, results in a distance for Te---N of 2.752 Å in the complex, which is shorter than that in the ligand. A possible reason for the decrease in the difference between Te-C(sp^3) and Te-C(sp^2) bond lengths in the complex is the removal of electron density from tellurium to mercury. The partial removal of the electron density from tellurium occurs in a direction almost perpendicular to the Te-C bonds (i.e. from an orbital which has mainly p-character), while donation of electron density from the nitrogen atom to tellurium is taking place in a direction which is almost in the C-Te-C plane. Therefore, one can conclude that the interaction taking place out of the plane is felt by the carbon atoms bonded to tellurium more than the interaction which takes place in the plane of these carbon atoms. This may lead us to conclude that the lone pair of the nitrogen is interacting with the tellurium empty d-orbital (which is not involved in bonding with carbon atoms) rather than with the tellurium p-orbitals, for which any change in the electron density will affect the strength of the Te-C bonds.

4.3.3 Infra-red Spectra

The infra-red spectrum of compound (I) in the solid state was measured in KBr disc, as shown in Fig. 4.7. The stretching vibration of the imine group, $\nu(C=N)$, appeared at $1636cm^{-1}$ as a sharp and strong band. This band is very slightly shifted to a higher energy ($1642cm^{-1}$) in the mercury complex, and becomes less sharp (Fig. 4.8). Among other changes in the i.r. spectrum of the ligand after complexation, is the appearance of new medium and weak bands in the fingerprint part of the spectrum. These changes are due to the rotation of half of the molecule along the alkyl carbon-carbon bond of the ethylene diimine group. This rotation, which is necessary to bring both tellurium atoms within bonding distance of the mercury atom, would cause a strain in that part of the ligand.

Another weak band, in the ligand spectrum, at 300cm^{-1} could be attributed to the Te---N intramolecular stretching vibration. The weak band, in the i.r. spectrum of the complex, at 312cm^{-1} could be assigned as ν(Hg-Cl).



SAMPLE
ORIGIN
SOLVENT KBr disc
CONCENTRATION
CELL PATH
REFERENCE Air
REMARKS
SCAN TIME 12 min
SLIT N
OPERATOR
DATE
T
SB
ORDINATE EXP.
TIME CONSTANT
RPK/219/100S S100-4367
REF. No.

Figure 4.7 : The I.R. spectrum of 1;6-bis-2-butyltellurophenyl-2,5-diaza-hexa-1,5-diene (compound I) in KBr disc

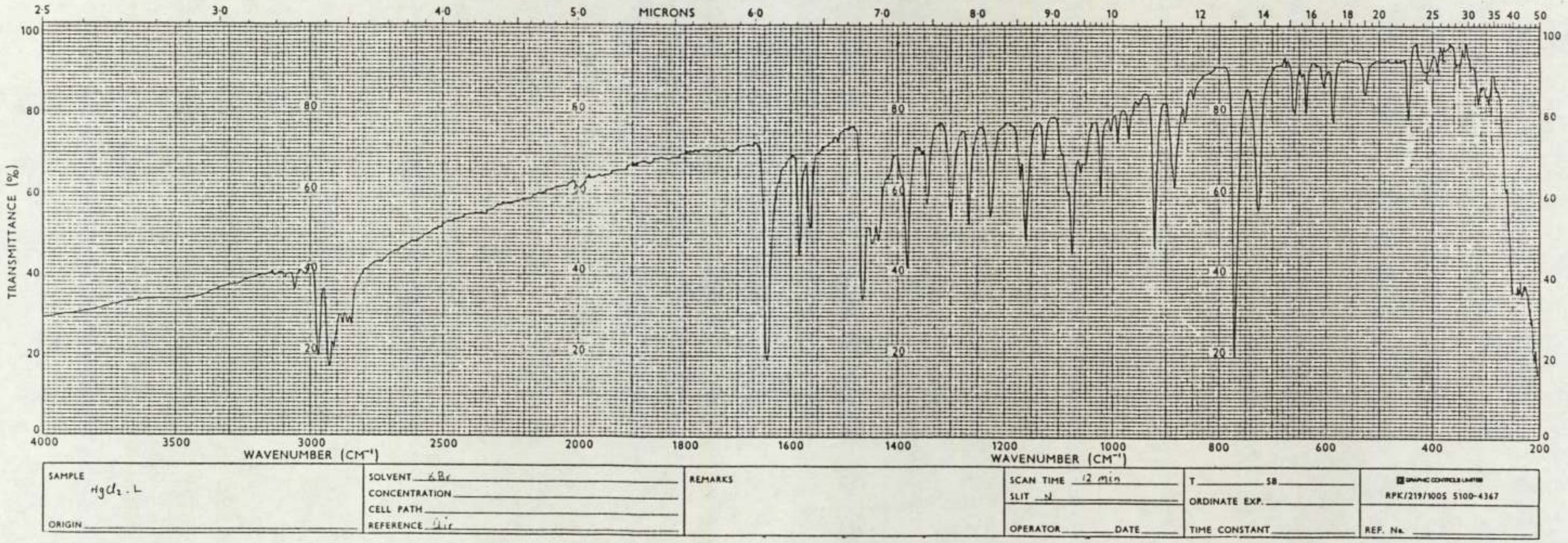


Figure 4.8 : The I.R. spectrum of the complex $HgCl_2$.(I) in KBr disc

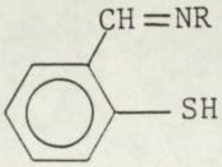
CHAPTER FIVE

COMPLEXES OF MULTIDENTATE TELLURIUM LIGANDS DERIVED FROM ETHYLENE DIAMINE AND HYDRAZINE

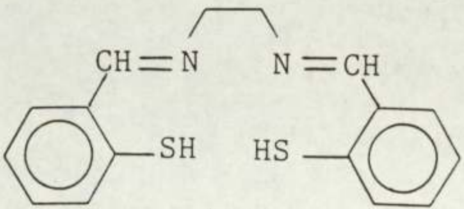
5.1 Introduction

Multidentate ligands, which contain mixed donor atoms of both groups 5A and 6A are known. The tetradentate ligand tris(o-methylselenophenyl)phosphine, for example, has been prepared together with some of its nickel(II) complexes [Ni(TSeP)X]ClO_4 (where X = Cl, Br, I, SCN). The structure of these complexes was described as trigonal-bipyramidal, in which the three selenium atoms are located at equatorial positions of the trigonal-bipyramidal structure.

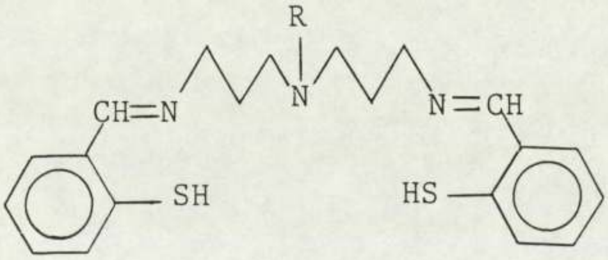
Bertini et al(125) reported the preparation of a series of Schiff base ligands having donor sets SN, S_2N_2 and S_2N_3. Such ligands have been obtained from o-mercaptobenzaldehyde and various amines as shown below:



(i)



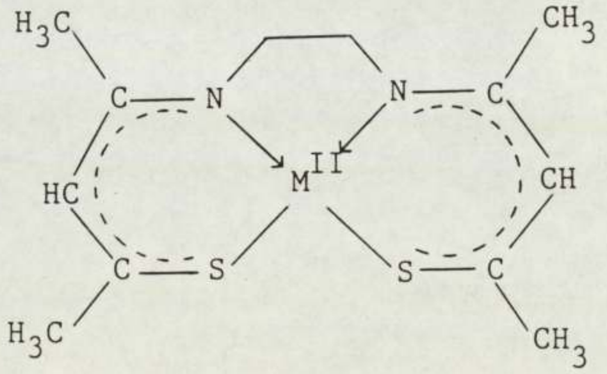
(ii)



(iii)

Some nickel(II) and cobalt(II) complexes with the above Schiff base ligands have also been prepared (125). The nickel complexes were described as planar both in the solid state and in solution, and this structure was believed to be stabilised by the presence of the sulphur atoms.

The interest in the "novel properties" of sulphur containing chelates and a search for oxygen-carrying metal complexes have led Blum and coworkers (126) to synthesise a series of metal complexes containing a tetradentate Schiff base ligand as shown below:

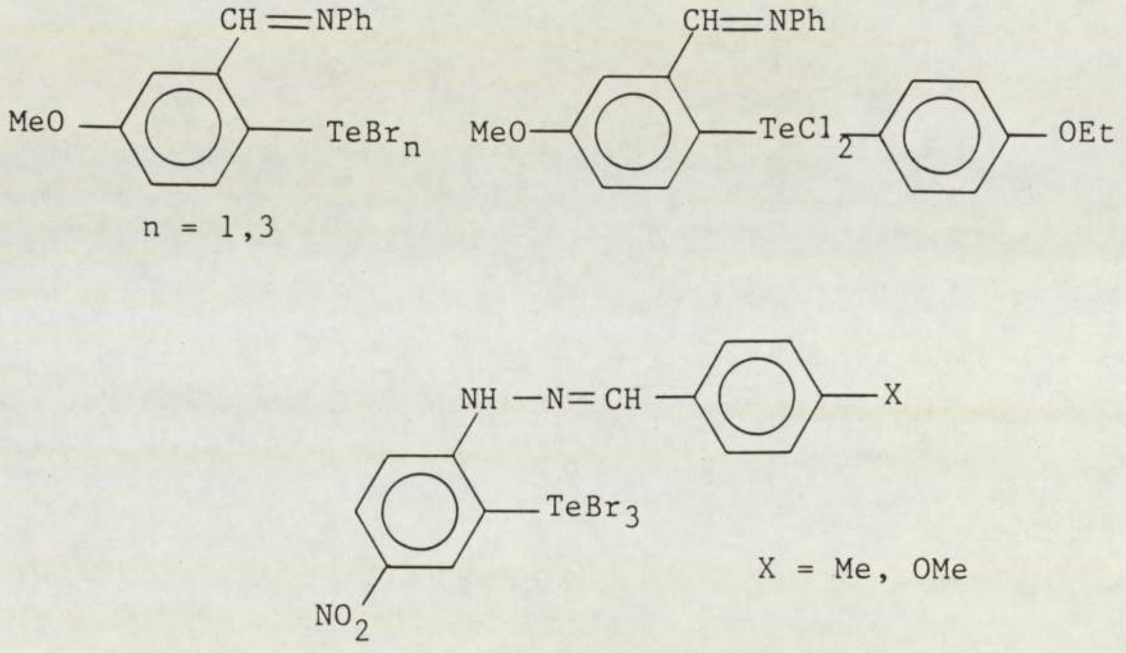


(iv) M(II) = Ni, Cu, Co, Pd, Zn, Cd

It was concluded that all of these complexes are square-planar monomeric species.

Later on, the selenium analogue of cobalt(II) complex (iv) was prepared and studied by ESR spectroscopy (127) to understand the effect of systematically varying an equatorial ligating atom (O ⟶ S ⟶ Se).

Some tellurated Schiff bases and hydrazones have been prepared in our laboratory by <u>trans</u>- metallation of the mercurated derivatives(128). These compounds are illustrated below (v):-



(v) Some tellurated Schiff bases

But, obviously, these compounds cannot be used as tellurium ligands unless the tellurium atoms in them are reduced to a lower oxidation state.

In this chapter the preparations of some transition metal complexes of the telluro-Schiff base, 1,6-<u>bis</u>-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (L), and the hydrazone 1,4-bis-2-butyltellurophenyl-2,3-diazabuta-1,3-diene (L') are described and discussed. This work can be considered as an extension of the study which has been described in chapter four as well as to extend the research which has been done on oxo-, thio-, and seleno-Schiff bases to include telluro-Schiff bases.

5.2 Experimental

The preparation of the ligand 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (L) was described in detail in chapter four. Its molecular and crystal structures were also discussed therein.

5.2.1 Synthesis of 1,4-Bis-2-butyltellurophenyl-2,3-diazabuta-1,3-diene (L')

This compound was prepared from the reaction of 2-butyltellurobenzaldehyde (5.90g, 0.02 mole) (see chapter four) with hydrazine hydrate (0.5g, 0.01 mole) in absolute ethanol (50 cm^3). The mixture was refluxed for 30 minutes, then allowed to cool slowly to room temperature. The orange crystalline compound, so formed, was filtered off, washed with ethanol then petroleum ether (40-60°C) and recrystallised from ethanol (yield ~70% based on hydrazine). It has a melting point 113-115°C.

Found C = 46.1%, H = 4.75%, N = 5.00%, $C_{22}H_{28}N_2Te_2$ requires C = 45.9%, H = 4.85%, N = 4.86%

5.2.2 Synthesis of a Rhodium(III) Complex of Ligand (L)

Dipotassium pentachloroaquo-rhodium(III) $[K_2RhCl_5H_2O]$ (0.3764g, 0.001 mole) was dissolved in a mixture of methanol (20 cm^3) and DMSO (10 cm^3), and reacted with a warm solution of ligand (L) (0.603g, 0.001 mole) in methanol (10 cm^3). The mixture was stirred for two hours under a nitrogen atmosphere, then the methanol was removed in *vacuo*, and the remaining solution was left to evaporate at room temperature. After complete dryness, dichloromethane (20 cm^3) was added to dissolve the compound, and the solution was filtered. The filtrate was left to evaporate at room temperature giving a brown compound, m.p. = 122°C.

Found C = 34.1%, H = 4.00%, N = 3.80%; $RhCl_3.C_{24}H_{32}N_2Te_2$-$2H_2O$ requires C = 34.0%, H = 4.27%, N = 3.30%

5.2.3 The Preparation of a Rhodium(III) Complex of Ligand (L')

$K_2RhCl_5H_2O$ (0.188g, 0.0005 mole) was dissolved in 20cm^3 of ethanol:DMSO mixture (1:1) and treated with a solution of ligand (L') (0.288g, 0.0005 mole) in ethanol (10cm^3). The mixture was stirred at 80°C under a nitrogen atmosphere for two hours. During that time the colour changed from orange to dark red-brown. The solution was then condensed to 5cm^3 in vacuo, and left to dry at room temperature. After drying, chloroform was added to dissolve the compound, and the solution was filtered. The solvent was removed in vacuo to leave a brown compound, which was washed with hot methanol, then diethyl ether and dried. It decomposes at about 160°C.

Found C = 32.8%, H = 3.40%, N = 3.50%; $RhCl_3.C_{22}H_{28}N_2Te_2$-$H_2O$ requires C = 32.9%, H = 3.73%, N = 3.50%

5.2.4 Preparation of Rhodium(I) Complexes of Ligand (L)

Method (A):

Di-μ-chloro-bis(η^4-1,5-cyclooctadiene)dirhodium(I) (0.148 g, 0.0003 mole) [this yellow complex was prepared according to the literature(129) by the reaction of rhodium(III) chloride hydrate with 1,5-cyclooctadiene in a refluxing ethanol-water mixture (5:1) for 18 hours and recrystallised from dichloromethane/diethyl ether] was dissolved in dichloromethane (10cm^3) and added slowly to a solution of the ligand (L) (0.362g, 0.0006 mole) in dichloromethane (15cm^3). The colour changed immediately into brown. After reflux for four hours the colour became red-brown with the formation of some precipitate. The solution was filtered to give a red-violet solid (product A), which was washed with dichloromethane and dried in air (yield

0.02g); it decomposes at 243°C. To the filtrate diethyl ether was added to precipitate a brown compound, which was separated by filtration and redissolved in cold ethanol and filtered. The filtrate was left to evaporate at room temperature giving a brown compound (product B, yield 0.26g), which decomposes at 185°C.

Method (B):

Di-μ-chloro-bis(η^4-1,5-cyclooctadiene)dirhodium(I) (0.148 g, 0.0003 mole) was dissolved in dichloromethane (10cm^3) and added to a dichloromethane solution (10cm^3) of ligand (L) (0.543g, 0.0009 mole) at room temperature. The mixture was then kept in the fridge for four hours. At the end of that period the solution was filtered to give a red-violet crystalline compound (product A), which was washed with dichloromethane (yield 0.1g); it decomposes at about 243°C. The filtrate was treated with diethyl ether to precipitate a brown compound, which was seperated by filtration, dried, and then dissolved in cold ethanol. The resulting solution was filtered and the filtrate was evaporated in vacuo to give a brown compound (product B), which was dried in air (yield 0.28g); it starts decomposition at about 186°C.

Product A in both methods:

Found C = 39.4%, H = 4.60%, N = 3.80%;

$RhCl(C_{24}H_{32}N_2Te_2)_{1.08}$ requires

C = 39.4%, H = 4.40%, N = 3.83%

Product B in both methods:

Found C = 38.5%, H = 4.40%, N = 3.50%; $RhCl.C_{24}H_{32}N_2Te_2$ requires C = 38.8%, H = 4.34%, N = 3.70%

5.2.5 Preparation of a Rhodium(I) Complex of Ligand (L^{10})

$[1,5\text{-COD-RhCl}]_2$ (0.0349g, 0.00007 mole) was dissolved in dichloromethane ($5cm^3$), and added to a solution of 1,10-bis(4-ethoxyphenyltelluro)decane (which has been borrowed)(27), in dichloromethane ($10cm^3$); no sudden change in colour was noticed. The mixture was refluxed for 24 hours, during which the colour changed into red. At the end, the solvent was evaporated to a minimum volume and petroleum ether was added. The brown precipitate formed was filtered off and washed several times with dichloromethane, to remove any unreacted materials, and air dried. The blackish-brown compound (yield 0.066g) decomposed at about 210°C, and it is insoluble in many organic solvents and water.

Found C = 40.3 %, H = 5.10%; $Rh_2Cl_2(C_{26}H_{38}O_2Te_2)_2$ requires C = 40.23%, H = 4.90%

5.2.6 Preparation of a Rhodium(I) Complex of Ligand (L')

The compound $[1,5\text{-COD-RhCl}]_2$ (0.246g, 0.0005 mole) was dissolved in dichloromethane ($15cm^3$) and added slowly to a solution of ligand (L') (0.576g, 0.001 mole). The resulting solution was stirred with reflux for seven hours under dinitrogen, and during that time the colour changed from orange to deep brown. The solution was, then, cooled and diethyl ether was added to precipitate a brown compound, which was filtered off and washed with hot ethanol then diethyl ether and dried (yield 0.51g); it decomposes at 220°C.

Found C = 36.7%, H = 3.90%, N = 3.80%

$[RhClC_{22}H_{28}N_2Te_2]_2$ requires

C = 37.0 %, H = 3.95%, N = 3.90%.

5.2.7 Preparation of a Palladium(II) Complex of Ligand (L)

Bis(benzonitrile)dichloro-palladium(II) $[Pd(PhCN)_2Cl_2]$ (0.383g, 0.001 mole) [this starting material was prepared according to the literature$^{(130)}$ by heating a solution of palladium dichloride in benzonitrile at 100°C for 20 min., then treating with pet. ether (80°C-100°C) to precipitate the yellow complex] was dissolved in acetonitrile ($15cm^3$). To this was added an acetonitrile solution ($15cm^3$) of ligand (L) (0.603g, 0.001 mole), and the mixture was stirred under dinitrogen for two hours at room temperature. The volume was then reduced to $5cm^3$ in a stream of nitrogen gas, and benzene was added to precipitate a brown compound, which was filtered off, washed with benzene, then diethyl ether, and left to dry in a vacuum desiccator giving a blackish-brown compound (yield 0.67g) which melts at 131-132°C with decomposition.

Found C = 35.8%, H = 4.30%, N = 3.40%;
$PdCl_2 \cdot C_{24}H_{32}N_2Te_2 \cdot H_2O$ requires
C = 36.1%, H = 4.28%, N = 3.50%

5.2.8 Preparation of a Palladium(II) Complex of Ligand (L')

Method (A):
$Pd(PhCN)_2Cl_2$ (0.378g, 0.001 mole) was dissolved in a 1:1 benzene/acetonitrile mixture ($15cm^3$). To this, a warm solution of ligand (L') (0.576g, 0.001 mole) in acetonitrile ($15cm^3$) was added. The mixture was stirred at 50°C under dinitrogen for five hours. At the end of that period, the brown precipitate formed was collected by filtration, and washed several times with benzene. Recrystallisation from toluene gave a brownish-red crystalline compound, which melts at 183-185°C with decomposition.

Found C = 35.4%, H = 3.80%, N = 3.70%; $PdCl_2 \cdot C_{22}H_{28}N_2Te_2$ requires C = 35.1%, H = 3.75%, N = 3.72%

Method (B):
A solution of $[AsPh_4]_2 PdCl_4$ (0.203g, 0.0002 mole) [this starting material was prepared by the reaction of aqueous solutions of Na_2PdCl_4 and $AsPh_4Cl$] in dichloromethane ($15cm^3$) was added slowly with stirring to a dichloro-

methane solution ($10cm^3$) of ligand (L') (0.115g, 0.0002 mole). The mixture was left standing for two hours, during which time a shiny orange-brown crystalline compound formed. The solution was filtered, and the precipitate was washed with dichloromethane and air dried (yield 0.136g); it melts with decomposition at 185°C.

Found C = 35.2%, H = 3.70%, N = 3.50%;
$PdCl_2.C_{22}H_{28}N_2Te_2$ requires
C = 35.1%, H = 3.75%, N = 3.72%

5.2.9 Preparation of Platinum(II) Complexes of Ligand (L)

$[AsPh_4]_2[PtCl_4]$ (1.103g, 0.001 mole) [prepared from K_2PtCl_4 and $AsPh_4Cl$] was dissolved in dichloromethane ($20cm^3$) and added to a dichloromethane solution ($15cm^3$) of ligand (L) (0.603g, 0.001 mole). The mixture was refluxed for one hour, during which time a light cream coloured suspension formed which was collected by filtration and washed with dichloromethane and air dried (product A), yield 0.3g. During the melting point measurement this compound darkened at about 80°C and finally became black, and did not melt at 310°C.

Product A:
Found C = 32.1%, H = 3.50%, N = 3.10%;
$PtCl_2.C_{24}H_{32}N_2Te_2.H_2O$ requires
C = 32.47%, H = 3.86%, N = 3.15%

When the same experiment was carried out in a refluxing acetonitrile solution, instead of dichloromethane, the cream coloured suspension appeared for the first 15 min. of the reaction, but when the reflux was continued beyond that, the solution became brownish. After two hours, the dark brown solution was filtered to get a dark brown solid (product B), which was washed with acetonitrile then pet. ether (60-80°C) and air dried. The compound does not melt at 310°C.

Product B:
Found C=24.7%, H = 2.30%, N = 3.30%;
$PtCl_2.C_{16}H_{14}N_2Te_2.2H_2O$ requires
C = 24.3%, H = 2.30%, N = 3.54%.

5.2.10 Preparation of a Platinum(II) Complex of Ligand (L')

$[AsPh_4]_2[PtCl_4]$ (0.22g, 0.0002 mole) was dissolved in dichloromethane (15cm^3), and added slowly with stirring to a solution of ligand (L') (0.115g, 0.0002 mole) in CH_2Cl_2 (10cm^3). The resulting mixture was stirred and refluxed for five hours. The orange precipitate, so formed, was filtered off, washed with dichloromethane and air dried (yield 0.1g). It melts with decomposition at 170°C.
Found C = 30.3%, H = 3.20%, N = 3.00%;
$PtCl_2.C_{22}H_{28}N_2Te_2.H_2O$ requires
C = 30.7%, H = 3.48%, N = 3.25%

Reactants		Products	Colour	M.Pt°C
L	$K_2RhCl_5.H_2O$	$RhCl_3.L.2H_2O$	Brown	122(dec.)
3L	$[RhCl.COD]_2$	RhCl.L	Brown	185(dec.)
		$RhCl(L)_{1.08}$	Red-violet	243(dec)
(a) 3L^{10}	$[RhCl.COD]_2$	$[RhCl.L^{10}]_n$	Blackish-brown	210-212(dec.)
L	(b) $PtCl_4^{2-}$	$PtCl_2.L.H_2O$	Light-cream	>80(dec.)
L	(c) $PtCl_4^{2-}$	(d) $PtCl_2.L^{2-}.2H_2O$	Dark-brown	>310
L	$PdCl_2(PhCN)_2$	$PdCl_2.L.H_2O$	Blackish-brown	131-132
L'	$K_2RhCl_5.H_2O$	$RhCl_3.L'.H_2O$	Brown	160(dec.)
L'	$[RhCl.COD]_2$	$[RhCl.L']_2$	Brown	220(dec.)
L'	(e) $PdCl_4^{2-}$	$PdCl_2.L'$	Orange-brown	185(dec.)
L'	$PdCl_2(PhCN)_2$	$PdCl_2.L'$	Red-brown	183-185(dec.)
L'	(b) $PtCl_4^{2-}$	$PtCl_2.L'.H_2O$	Orange	>170(dec.)

(a) $L^{10} = ArTe(CH_2)_{10}TeAr$ (ref.27)

(b) As $[AsPh_4]_2PtCl_4$ in CH_2Cl_2

(c) As $[AsPh_4]_2PtCl_4$ in refluxing CH_3CN

(d) L^{2-} is ligand L minus two butyl groups

(e) As $[AsPh_4]_2PdCl_4$ in CH_2Cl_2

Table 5.1. Colours and melting points of the various complexes of ligand(L), (L') and L^{10}.

Complex	Found %			Required %		
	C	H	N	C	H	N
$RhCl_3.L.2H_2O$	34.1	4.00	3.80	34.0	4.27	3.30
$RhCl.L$	38.5	4.40	3.50	38.8	4.34	3.70
$[RhL_{1.08}Cl$	39.4	4.60	3.80	39.4	4.40	3.83
$[RhCl.L^{10}]_n$	40.3	5.10	-	40.23	4.90	-
$^{(a)}PtCl_2.L.H_2O$	32.1	3.50	3.10	32.47	3.86	3.15
$^{(b)}PtCl_2L^{2-}.2H_2O$	24.7	2.30	3.30	24.3	2.30	3.54
$^{(c)}PdCl_2L.H_2O$	35.8	4.30	3.40	36.1	4.28	3.50
$RhCl_3.L'.H_2O$	32.8	3.40	3.50	32.9	3.73	3.50
$[RhCl.L']_2$	36.7	3.90	3.80	37.0	3.95	3.90
$^{(c)}PdCl_2.L'$	35.4	3.80	3.70	35.1	3.75	3.72
$^{(d)}PdCl_2.L'$	35.2	3.70	3.50	35.1	3.75	3.72
$PtCl_2.L'.H_2O$	30.3	3.20	3.00	30.7	3.48	3.25
Ligand(L)	47.4	5.50	4.60	47.7	5.30	4.64
Ligand(L')	46.1	4.75	5.00	45.9	4.85	4.86
$^{(e)}$Ligand L^{10}	49.4	6.10	-	49.0	6.00	-

(a) Complex precursor $[AsPh_4]_2PtCl_4$ in refluxing CH_2Cl_2

(b) Complex precursor $[AsPh_4]_2PtCl_4$ in refluxing CH_3CN

(c) Complex precursor $PdCl_2(PhCN)_2$ in CH_3CN

(d) Complex precursor $[AsPh_4]_2PdCl_4$ in CH_2Cl_2

(e) Ref. 27

Table 5.2. Elemental analysis of ligands L, L' , L^{10} and their complexes.

Complex	ν(C=N)cm^{-1}	Δ(C=N)cm^{-1}	ν(M-Cl)cm^{-1}	$\Lambda^{(a)}$
Ligand(L)	1637			
Ligand(L')	1616			
$RhCl_3$.L.$2H_2O$	1640	+3	322	20.44(DMSO)
RhCl.L	1632,1595	-5,-42	300	10.6 (CH_3CN)
RhCl$(L)_{1.08}$	1660,1595	+23,-42		
$HgCl_2$.L	1645	+8	312	
$PtCl_2$.L.H_2O	1625	-12	315	35.0 (DMSO)
$PtCl_2$.L^{2-}.$2H_2O$	1615	-22		11.5 (DMSO)
(b) $PdCl_2$.L. H_2O	1635	-2	345	35.0 (DMSO)
$RhCl_3$.L'.H_2O	1620	+4	340,365	6.6 (DMSO)
[RhCl.L'$]_2$	1610	-6	-	7.0 (CH_3CN)
(b) $PdCl_2$.L'	1622	+6	335,290	
(c) $PdCl_2$.L'	1622	+6	332,288	2.7(C_6H_5CN)
(d) $PdCl_2$.L'	1620	+4	332,289,345	
$PtCl_2$.L'.H_2O	1626	+10	325,295	2.0(C_6H_5CN)

(a) Molar conductivity ($ohm^{-1}cm^2mol^{-1}$) of 10^{-3}M solution

(b) Complex precursor $PdCl_2(PhCN)_2$ in CH_3CN

(c) Complex precursor $[Asph_4]_2PdCl_4$ in CH_2Cl_2

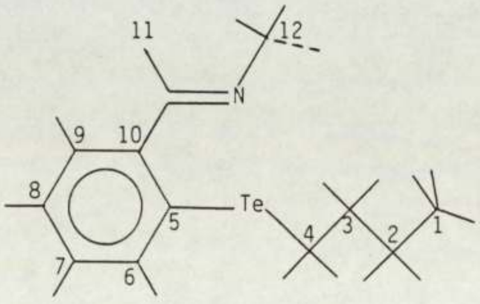
(d) The above complex after digestion in $CHCl_3$

Table 5.3. Selective infra-red bands and molar conductivities of the complexes of ligands (L) and (L').

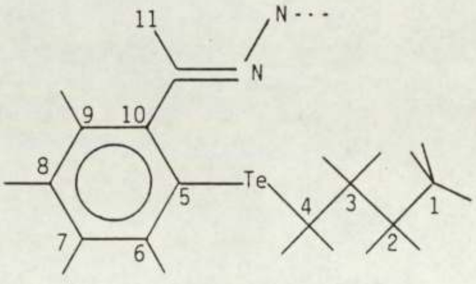
$^{(a)}\delta$, Ligand(L')	$^{(a)}\delta$, Ligand(L)
H_1 = 0.95(t), 6H; J= 6.88Hz	H_1 = 1.00(t), 6H; J= 7.03
$H_{2,3}$= 1.36 - 1.92(m), 8H	$H_{2,3}$= 1.46 -2.55(m), 8H
H_4 = 2.72(t), 4H; J= 7.32Hz	H_4 = 2.54(t), 4H
H_{Ar} = 7.20 - 7.70(m), 8H	H_{Ar} = 7.13 - 7.52(m), 8H
H_{11} = 8.38(s), 2H	H_{11} = 8.53(s), 2H
	H_{12} = 4.10(s), 4H

(a) Chemical shifts measured in ppm relative to Me_4Si

(t)- triplet, (m)- multiplet, (s)- singlet



Ligand(L)



Ligand(L')

Table 5.4. ^{1}H NMR data of ligands (L) and (L').

Compound	Chemical shift [(a)]						
	C-5	C-6	C-7	C-8	C-9	C-10	C-11
Ligand(L)	121.22	132.27	133.14	124.90	129.67	136.17	162.94
Ligand(L')	120.24	133.25	133.68	125.55	130.43	135.20	162.61

(a) In ppm relative to Me_4Si

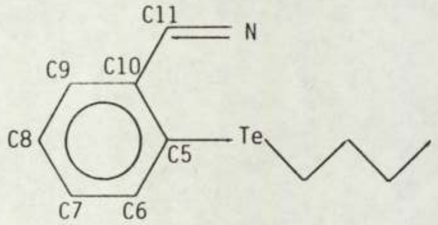


Table 5.5. ^{13}C NMR data (aromatic region) of ligands (L) and (L')

Compound	Chemical shift[(a)]				
	C-1	C-2	C-3	C-4	C-12
Ligand (L)	13.51	25.54	31.93	8.20	60.43
Ligand (L')	13.51	25.54	32.25	9.17	-

(a) In ppm relative to Me_4Si

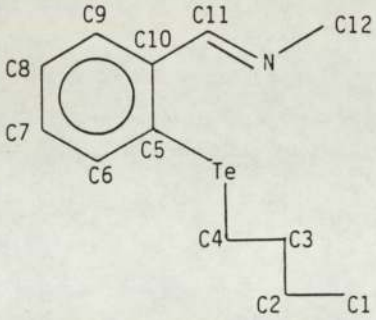


Table 5.6. ^{13}C NMR data (aliphatic region) of ligands (L) and (L')

Compounds	λ_{max}(nm)*	$\bar{\nu}_{max}$(cm^{-1})	ϵ#
Ligand L	366	27,322	6880
Ligand L'	410	24,390	5600
$RhCl_3.L.2H_2O$	395	25,310	15000
$RhCl(L)_{1.08}$	660;555;	15,151;18,018	50;575;4125
	390;315;295	25,641;31,746;33,898	5925;8125
$PtCl_2.L.H_2O$	430;465(s)	23,250;21,505	400;350
$PtCl_2.L^{2-}.H_2O$	400;470(s);560(s)	25,000;21,275;17,857	12000;6750;1500
$PdCl_2.L.H_2O$	464;384	21,550;26,040	1125;1875
$RhCl_3.L'.H_2O$	412	24,270	18000
$PdCl_2.L'$	435;320;355	22,988;31,250;28,169	1700;3125;2125
$PtCl_2.L'.H_2O$	360(s);425(s)	27,777;23,530	4000;250

* s = shoulder

ϵ in $cm^{-1}mole^{-1}l$

Table 5.7. Visible-u.v. spectral data of ligand (L) and (L') and their complexes

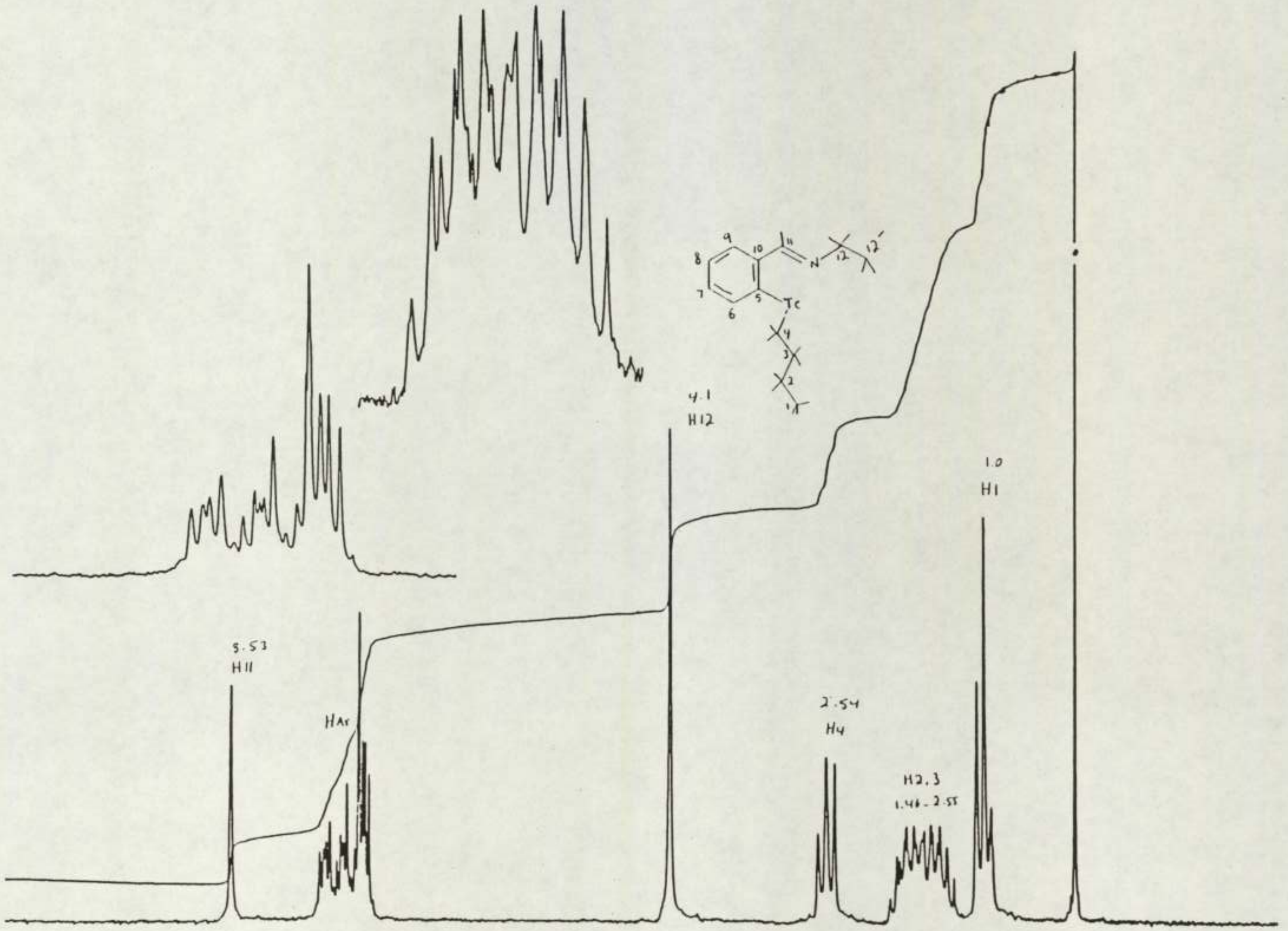


Figure 5.1 : ^{1}H N.M.R. spectrum of ligand (L) $C_{24}H_{32}N_2Te_2$ in $CDCl_3$

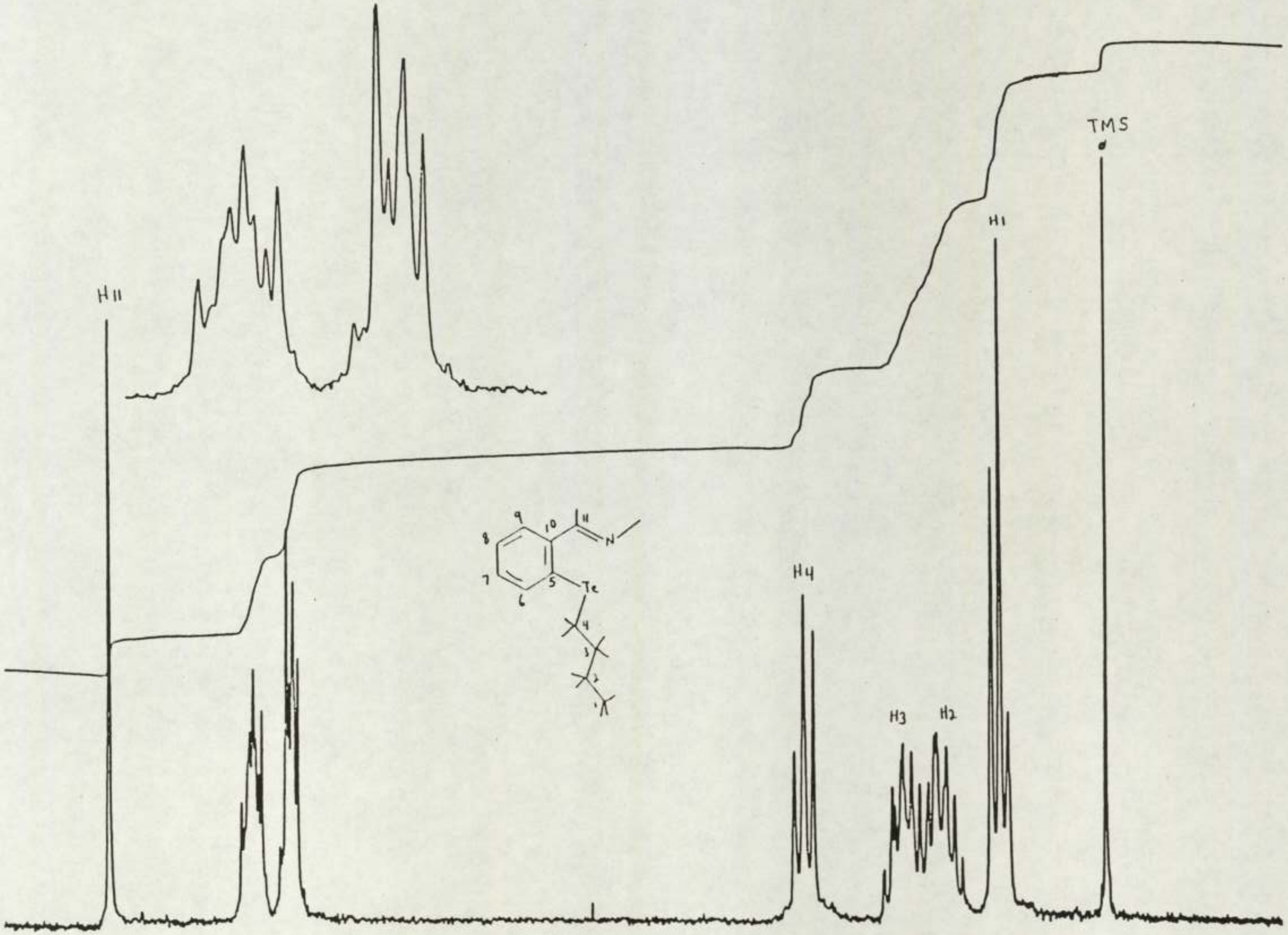


Figure 5.2 : ^{1}H N.M.R. spectrum of ligand (L') $C_{22}H_{28}N_2Te_2$ in $CDCl_3$

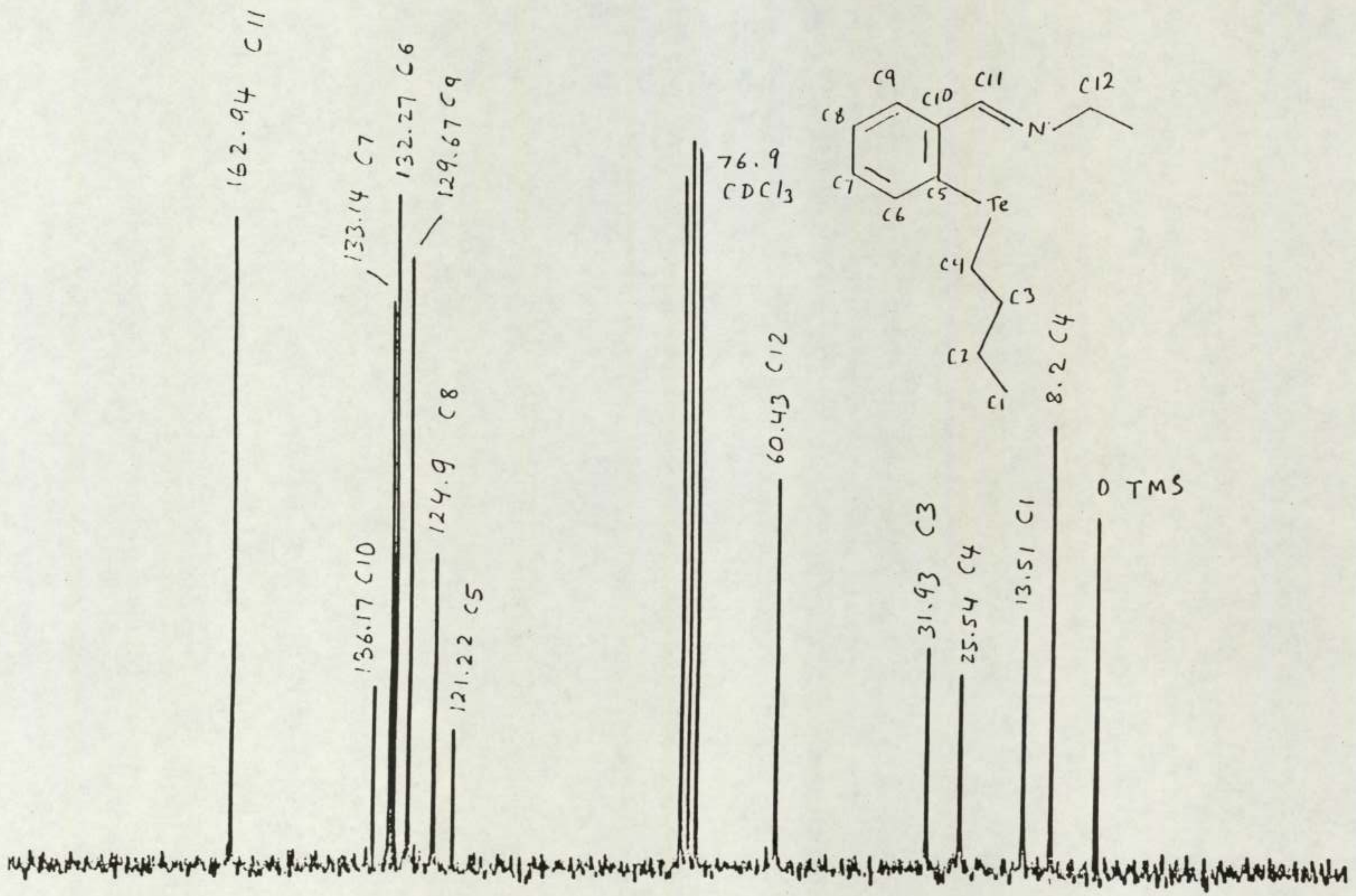


Figure 5.3 : $^{13}C[^{1}H]$ N.M.R. spectrum of ligand (L) in $CDCl_3$

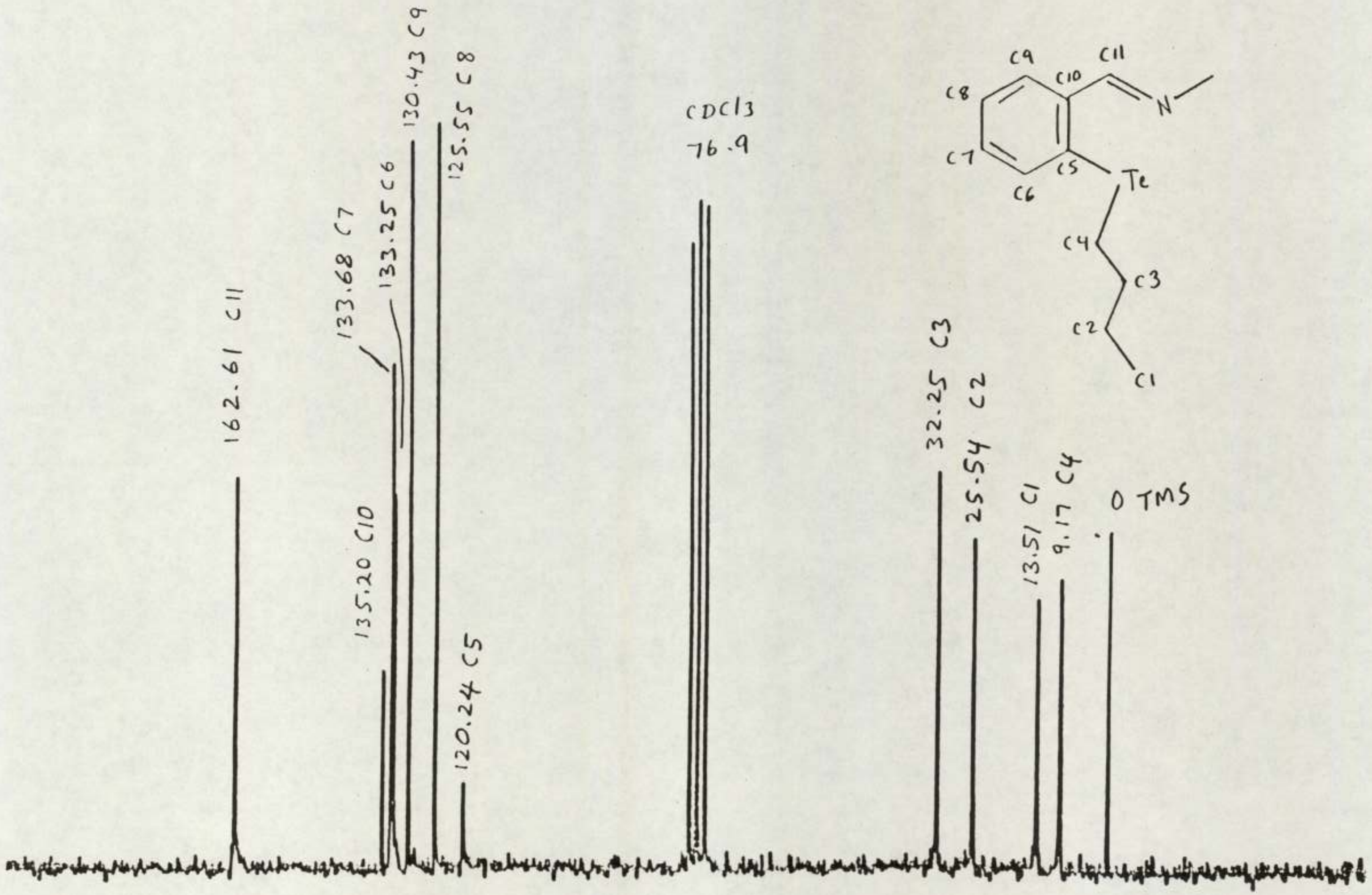


Figure 5.4 : $^{13}C[^1H]$ N.M.R. spectrum of ligand (L') in $CDCl_3$

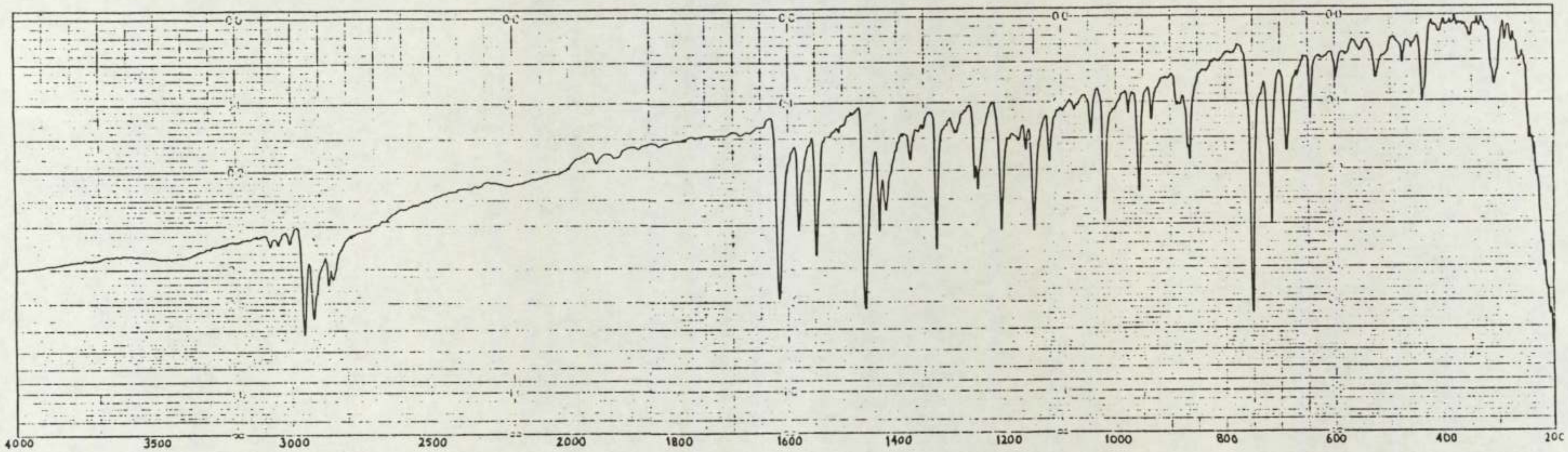
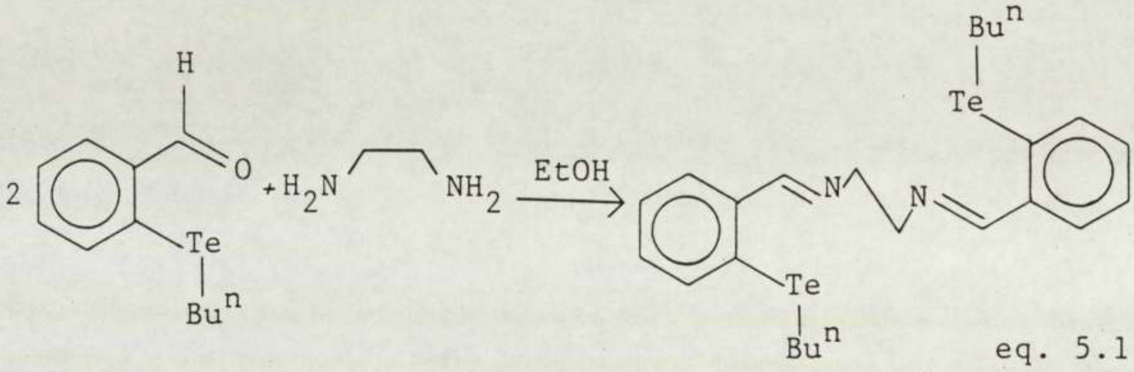


Figure 5.5 : I.R. spectrum of ligand (L') as KBr disc

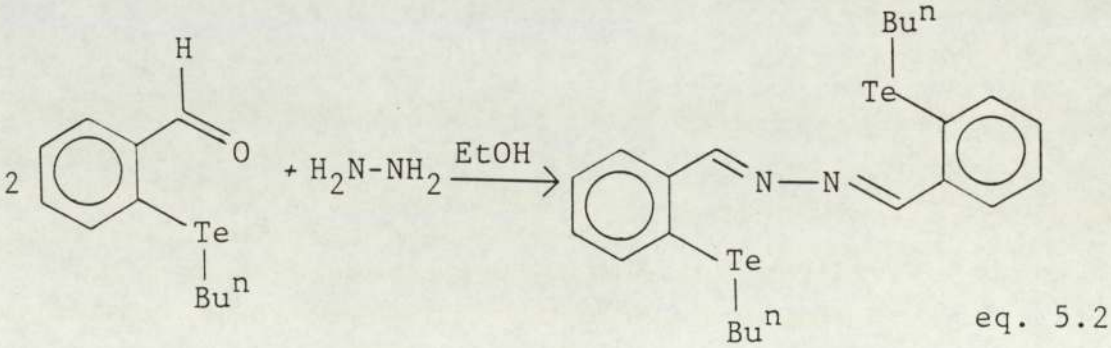
5.3 Results and Discussion

5.3.1 Characterisation of the New Tellurium-Schiff Base (L) and Tellurium-Hydrazone (L') Ligands (I.R. and N.M.R)

The reaction of two equivalents of 2-butyltellurobenzaldehyde with diaminoethane (en) or with hydrazine led to the condensation on both amino-groups of these compounds (eqs. 5.1, 5.2)



eq. 5.1



eq. 5.2

This was confirmed by the elemental analyses, the ^{13}C N.M.R. spectra and the X-ray structure determination of the Schiff base (L) (see chapter four). Each of the resulting compounds, therefore, contains two tellurium and two nitrogen donor atoms.

The infra-red spectra of both ligands confirm the absence of the aldehyde carbonyl group and the appearance of lower energy bands, at 1637cm^{-1} in the case of ligand (L) and 1616cm^{-1} in the spectrum of ligand (L'), which could be assigned as the stretching frequencies of the imine groups, ν(C=N), in both compounds (Figures 4.7, 5.5).

The orange colour of the hydrazone ligand (L') is not astonishing, since many hydrazone compounds are coloured, but this colour could be due to the higher degree of conjugation compared to ligand (L) as well as the possibility of a tellurium-nitrogen interaction, which has been confirmed crystallographically in the structure of ligand (L) (chapter four).

The ^{1}H N.M.R. spectra of both ligands (Table 5.4) were recorded using $CDCl_3$ as the solvent. The major difference between the two spectra is the presence of a peak at 4.10 ppm in the case of ligand (L). This peak is attributed to the resonance of the protons attached to the carbon atoms of the "en" chain. This peak appears as singlet instead of the expected triplet; nevertheless, its integrated intensity is in agreement with the presence of four protons.

The ^{13}C-[^{1}H] N.M.R. spectra of both ligands were also recorded in $CDCl_3$ (Tables 5.5, 5.6 and Figures 5.3, 5.4). These spectra can be divided into two distinct regions:-

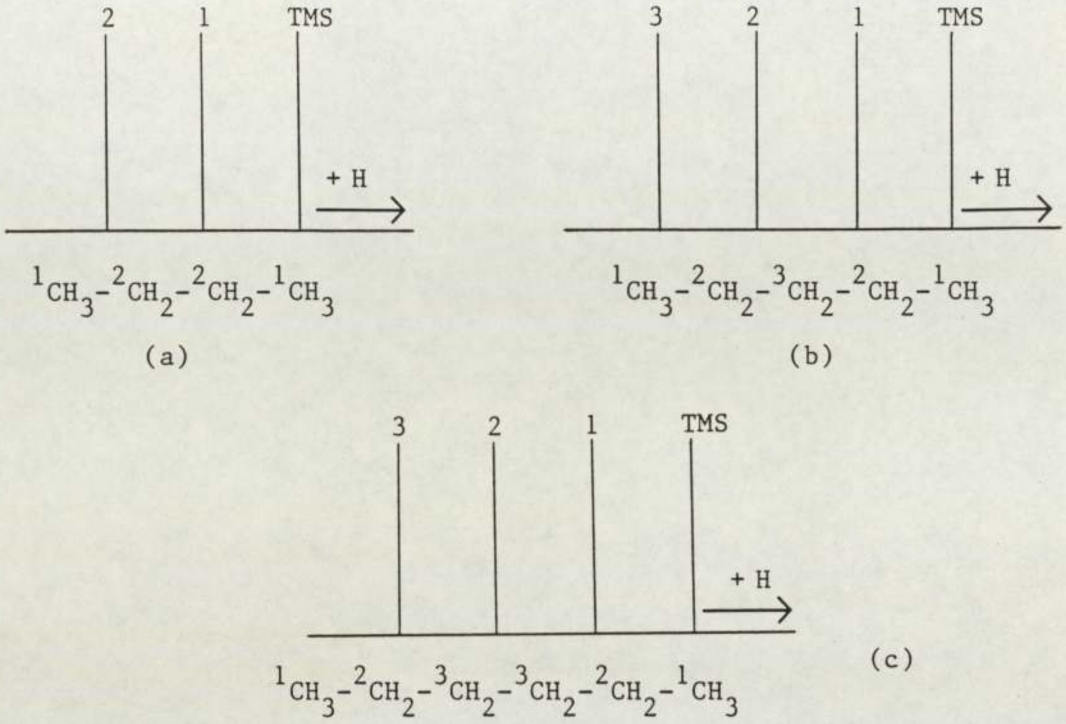
1. the aliphatic region
2. the aromatic region

The 7% natural abundance of ^{125}Te did not allow observation of C-Te coupling in the ^{13}C-[^{1}H] N.M.R. spectra of these ligands.

The assignments of the ^{13}C-[^{1}H] resonances have been made by comparison with the available literature data of alkyl phenyltellurides (131) and aromatic Schiff bases (132).

1. The aliphatic region:
The absence of ^{13}C - ^{125}Te coupling in the spectra of the Schiff base- and the hydrazone-tellurium ligands, and the lack of data in the literature about similar n-butyltellurium compounds make the assignment difficult. For comparison, the ^{13}C N.M.R. spectra of n-alkanes could be considered. The trend observed for linear alkanes up to and including n-hexane is simple. The schematic spectra of some of them are shown below (vi).

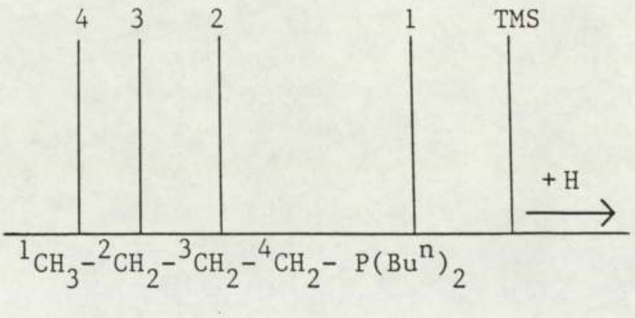
As seen from this schematic diagram, the terminal carbon has the lowest chemical shift (i.e. the highest field), and it has been assigned at 13 to 13.7 ppm (133,134). The next carbon, C2, resonates at a lower field than C 1, and the middle carbon, C3, still lower (31.5-34 ppm).



(a) (b) (c)

(vi) Schematic ^{13}C-[^{1}H] N.M.R. spectra of some n-alkanes

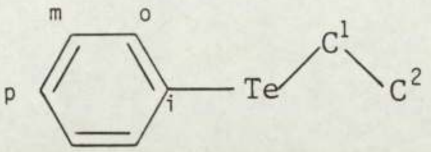
When a phosphorus atom is attached to one of the terminal carbon atoms, the symmetry of the alkane chain, and the trend in the chemical shift will change. In tri-n-butylphosphine (vii), for example, there are four resonances, with the carbon attached to the phosphorus atom having the highest chemical shift (δ 29.3 ppm.), and the terminal carbon having the lowest, δ 14.7 ppm (135).



(vii) Schematic $^{13}C[^{1}H]$ N.M.R. of tri-n-butylphosphine

Similar chemical shift values were reported for dibutylphenylphosphine (135). The relatively high chemical shift of the carbon directly attached to phosphorus has also been reported elsewhere (136,137). These values are close to that found for n-heptane and n-octane (134). The similarity between ^{13}C chemical shifts in the tertiary phosphines and linear alkanes, and the small influence of phosphorus on ^{13}C chemical shifts have been attributed to the similarity in the electronegativities of $-PMe_2$ (-2.28) and $-CHMe_2$ (-2.28) (135).

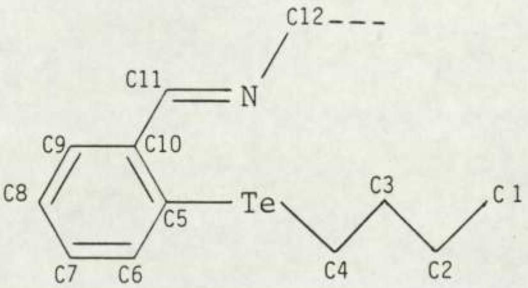
Although there is little ^{13}C N.M.R. work on alkyltellurium(II) compounds, it seems that the trend in the chemical shift is different than that of phosphines. It has been noted that the δC values of the methyl carbon relative to E in MeEPh (E = O, S, Se, Te) are linearly related to the electronegativity of E (137). Kalabin et al (131), in their ^{13}C N.M.R. study of some REPh compounds (R = Me, Et, Pr^i, Bu^t ; E = O, S, Se, Te), have pointed out that in going from ethers to tellurides $\delta C1$(alkyl) decreases by 50-70 ppm, while $\delta C2$(alkyl) increases by 2-5 ppm, and that these changes are in a trend similar to that observed in haloalkanes. However, the chemical shifts of the carbon attached to tellurium (c.a. δC 1 alkyl -15 ppm) in the above compounds (131) and in di-n-butyltelluride (δC 1 4.1 ppm) (138), were reported to be less than $\delta C2$(alkyl) (35.7 ppm in Bu_2Te, for example). A similar observation has been recently reported for some bis-



(viii)

tellurium(II) compounds ($ArTe(CH_2)_nTeAr$), when δC 1 was assigned at c.a. 9 ppm and δC2 around 30 ppm(27). This assignment has been made by comparison with the $^{13}C-[^1H]$ N.M.R. spectrum of a similar bis-tellurium(IV)tribromide compound ($Br_3Te(CH_2)_6TeBr_3$), where a downfield shift in the resonance of C 1 was observed (δC 1, 59.7 ppm).

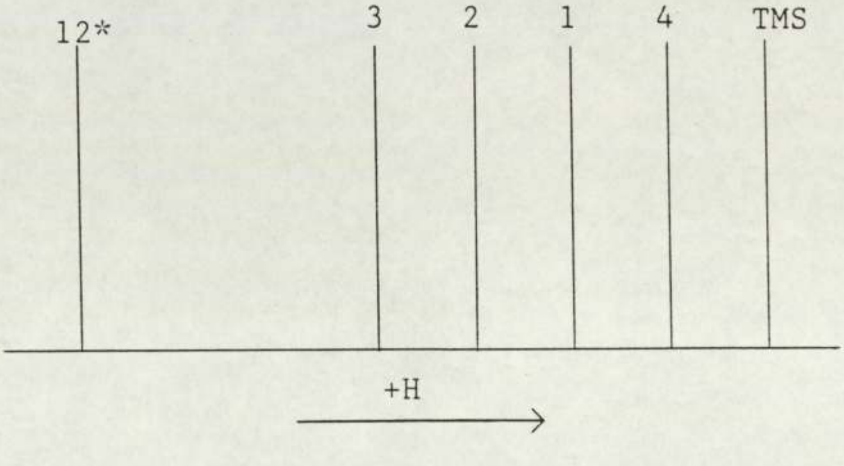
The $^{13}C-[^1H]$ N.M.R. spectra of the present Schiff base- and hydrazone-tellurium compounds in the aliphatic region (Table 5.6) are similar, except an additional signal in the spectrum of the former compound at a lower field (δC 60.43 ppm), which could be assigned to the "ethylene" carbons (C12) attached to the nitrogens, see below.



(ix)

The signals at δ 8.2 and 9.17 ppm in the spectrum of the Schiff base (L) and the hydrazone (L') are very close to that reported for bis-tellurium(II) compounds mentioned earlier (c.a. 9 ppm)(27). Therefore, they could be assigned to the butyl carbon (C4) attached to tellurium in both compounds respectively. These chemical shift values indicate that the nitrogen-tellurium interaction in (L) and (L') has no significant effect on δC4, although the nitrogen is trans to C4.

The remaining three ^{13}C signals, in this region, are very close to those reported for n-hexane (scheme vi)(133,134), thus they are assigned as C1, C2, and C3 at successively lower fields. A schematic representation of the spectra of ligands (L) and (L') is shown below (x):



(x) Schematic ^{13}C spectrum for ligands (L) and (L'), the numbering is as shown in (ix).

* this signal appears in the spectrum of (L)

This trend of chemical shift is similar to that reported for di-n-butyltelluride(138), although the chemical shift values are different. This is obviously different to the trend in the spectrum of tri-n-butylphosphine(135).

2. The aromatic region

The aromatic region in the $^{13}C-[^{1}H]$ N.M.R. spectra of ligand (L) and (L') showed seven resonances, six for the phenyl carbons and one for the imine carbon (Figures 5.3, 5.4). The signal at $\delta \approx 162.7$ ppm in both spectra could be assigned as C11, in agreement with the value previously reported for the imine carbon in N-methylphenylimine(139), which absorbs at δ 162.2 ppm. The carbon atoms, C5 and C10 (see compound ix) do not possess a directly bound hydrogen atom, and such carbons usually show signals of low intensity. Therefore, the low intensity peaks, in the spectra of ligand (L) and (L'), at δ 136.17 and 135.2 ppm could be asisgned as C10 respectively. A similar value (δ 137.3 ppm) has been assigned to the phenyl carbon attached to the imine group in N-methylphenylimine(139).

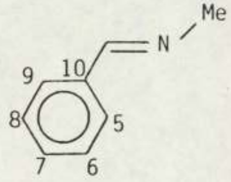
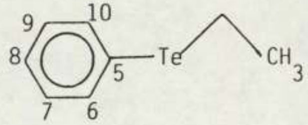
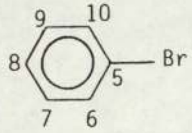
In a discussion of the effect of tellurium on the directly attached carbon of phenyl ring, it has been assumed(131), that the "heavy atom" effect is the major basis for the significant decrease in δC (c.a. 112 ppm in PhTeEt) relative to benzene (δ 128.7 ppm). A "large highfield" shift for the phenyl carbons attached to tellurium in diaryltellurides (e.g., 114.7 for Ph_2Te) relative to benzene, has been reported to result from shielding effects of the electropositive tellurium atom(140). A similar chemical shift value (137) and even lower values (c.a. 100 ppm)(27), have been reported for the ipso-carbon of some aromatic tellurium(II) compounds.

The signals with low intensity and lowest chemical shift, in the aromatic region of the $^{13}C-[^{1}H]$ N.M.R. spectrum of ligand (L) and (L'), were observed at δ 121.2 and 120.2 ppm respectively, and therefore could be assigned as C5 or the ipso-carbon. Such a chemical shift is the highest ever recorded for the ipso-carbon in organotellurium(II) compounds. This could be due to the influence of Te----N interaction, which is to be discussed later. However, these values are lower than δ C (ipso) reported for iso-propylphenylselenide (129.5 ppm)(131), higher than in iodobenzene (96.7 ppm), but not very far from that of the bromobenzene (123.3 ppm)(141).

Chadha and Miller (140), by examination of the deviations of the chemical shift values from the calculated values for a series of aromatic tellurium(II) compounds, have pointed out that the negative values of $\Delta\delta(^{13}C)$ for the carbon in a para-position to tellurium suggest that the tellurium atom in tellurides possesses π-donor properties. Therefore, the δC(para) values are mainly dependant on the tellurium π-electron effect which could be transfered to the para-carbon mesomerically. Consequently, the para-carbon will be shielded by the mesomerically transfered π-electrons, and therefore resonates at a higher field. The signals with the highest resonating field, apart from that assigned as C5 (ipso), in the aromatic region of the spectra of ligands (L) and (L') are those at δ 124.9 and 125.5 ppm respectively. These resonances could be assigned to the carbon atom in the para-position to tellurium (i.e., C8) in both compounds. However, these values are lower than any of that reported in the literature (131,137,138,140) for a para-carbon atom, for which δC ranges between 126.6 to 128.2 ppm depending on the other organic groups bonded to tellurium. This may imply that the tellurium atoms in these compounds (L and L') are possessing more π-donor properties than the simple phenyltellurium(II) compounds.

In order to assign the resonances of the remaining three carbon atoms of the phenyl rings, namely C6, C7 and C9, it would be better if we employ the additivity principle by using the carbon chemical shifts of similar compounds. For this purpose, it may be proper to adopt δC values, reported earlier, for ethylphenyltelluride (131), and N-methylphenylimine (139) and compare them to the values shown in (Table 5.5) for ligands (L) and (L').

As shown in (Table 5.8), the values obtained from compound (A) plus compound (B) are inconsistent with the

Compounds [(a)]	Chemical shifts (p.p.m.) relative to Me_4Si [(b)]						Reference
	C 5	C 6	C 7	C 8	C 9	C 10	
(A) 	129.0 (+0.3)	128.6 (-0.1)	130.8 (+2.1)	128.6 (-0.1)	129.0 (+0.3)	137.3 (+8.6)	139
(B) 	111.7 (-17)	138.9 (+10.2)	128.4 (-0.3)	127.2 (-1.5)	128.4 (-0.3)	138.9 (+10.2)	131
(C) 	123.3 (-5.4)	132.0 (+3.3)	130.9 (+2.2)	127.7 (-1)	130.9 (+2.2)	132.0 (+3.3)	142
(A + B)	112.0	138.8	130.5	127.1	128.7	147.5	
(A + C)	123.6	131.9	133.0	127.6	131.2	140.6	

(a) The numbering of the phenyl carbons is done to match that of the ligands (Table 5.5).

(b) Values between parentheses are the deviation $\Delta\delta C$ from δC(benzene) taken as 128.7 ppm.

Table 5.8. Applicatiom of the additivity principle to compounds which are related to ligands (L) and (L')

values obtained for ligands (L) and (L') (Table 5.5). The wildest calculated chemical shift value is for C5 (c.a. 121 ppm) which has an unexpected large deviation ($\Delta\delta$ = -9.2 ppm) from the calculated value. From (Table 5.8) also, the values obtained from compounds (A) and (C) are close to that recorded for (L) and (L'). This result, as well as it confirms the failure of the additivity principle for closely related aromatic compounds of Group 6, as noted but to a less extent by many authors (138,140), it may also show that the total effect of tellurium atoms in ligands (L) and (L') is as close as the effect of bromine on δC of the phenyl carbon atoms. According to this calculation, the remaining three signals at δ 132.27, 133.14 and 129.67 ppm in ligand (L) spectrum and at δ 133.25, 133.68 and 130.43 ppm in ligand (L') spectrum are assigned as C6, C7 and C9 respectively.

In order to explain the reason for different ranges in δC (ipso) in compounds having the formula $PhER_n$ (where E is Group 4A, 5A, 6A or 7A; n=3,2,1,0), Kalabin et al (131) assumed that these differences are related to different numbers of unshared electron pairs: zero for G4A, one for G5A, two for G6A and three for G7A, and they argued that the observed trends in these compounds are the result of nonbonded interactions of the substituents with the unshared electron pairs of the heteroatoms. This could well be the case in the present compounds, ligands (L) and (L'). Tellurium(II) has two unshared electron pairs, therefore, theoretically phenyltellurium(II) compounds should show similar chemical shifts for the ipso-carbon atom.

As seen from the structure determination of ligand (L) (chapter four), there is a weak but a considerable interaction between tellurium and nitrogen, in which the nitrogen pair of electrons is partially donated to the tellurium atom (acting as Lewis acid here). Consequently, the effective electron density on tellurium is more than two electron pairs. This will bring the behaviour of Te nearer to the halogens, thus will increase its π-donor property. That could be the reason for the consistency in the chemical shifts observed for ligand (L) and (L') and the calculated values from compound (A) and bromobenzene (Table 5.8). Therefore, this may provide an acceptable explanation for the high δC (ipso) (c.a. 121 ppm) and the low δC (para) (c.a. 125 ppm) in the present compounds.

^{125}Te N.M.R. spectra of ligands (L) and (L') were recorded in $CDCl_3$. The proton-decoupled spectra show one signal for each compound (Figures 5.6,5.7) at δ 464.4 ppm for ligand (L) and δ 464.1 ppm for ligand (L'). This is indicative of two things, first, the two tellurium atoms in the individual compounds are equivalent, and second that the tellurium atoms in both compounds are in similar environments. Since the two ligands have the same

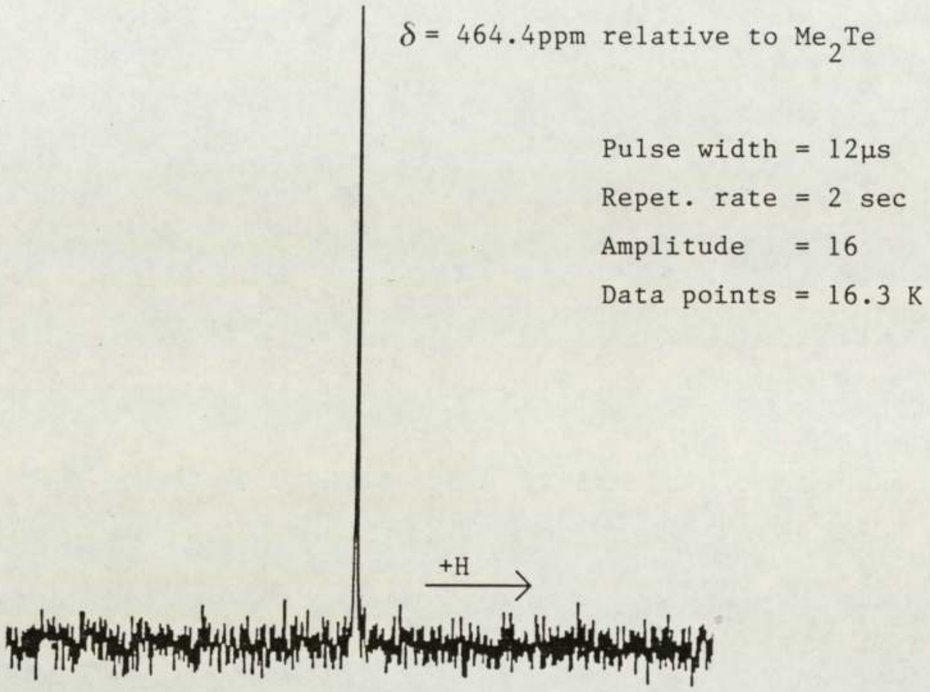


Figure 5.6 : $^{125}Te[^{1}H]$ N.M.R. spectrum of ligand (L) $C_{24}H_{32}N_2Te_2$ in $CDCl_3$

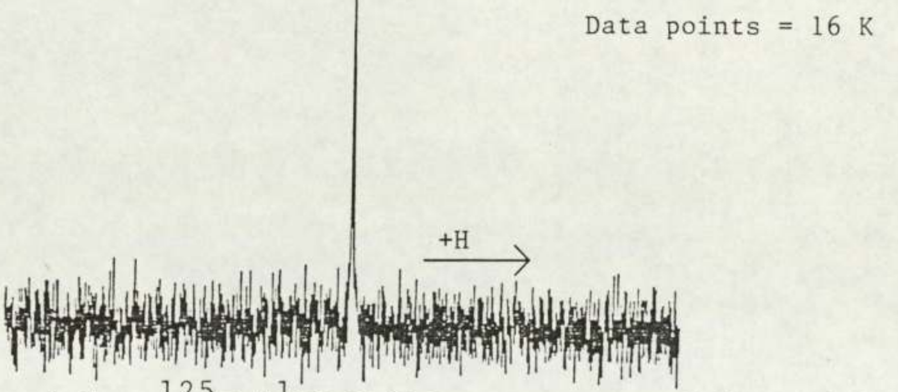


Figure 5.7 : $^{125}Te[^{1}H]$ N.M.R. spectrum of ligand (L') $C_{22}H_{28}N_2Te_2$ in $CDCl_3$

chemical shift within experimental error, Te---N interaction is also expected in ligand (L'), for which no crystal structure is available yet. These chemical shift values are similar to that reported for PhTeBu$^{(n)}$ (468 ppm)$^{(142)}$, but slightly different to that reported recently for ArTe$(CH_2)_n$TeAr compounds (454.7 ppm)$^{(108)}$.

5.3.2 Characterisation of the Complexes of Ligand (L) (Schiff Base) and Ligand (L') (Hydrazone)

The complexes prepared in this chapter can be discussed in terms of the metal ions used:

1. Palladium complexes
2. Platinum complexes
3. Rhodium complexes

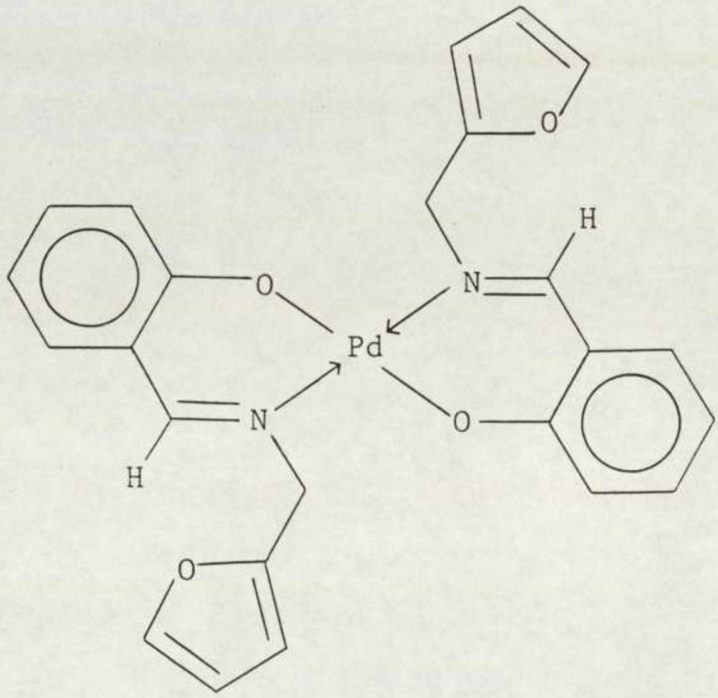
5.3.2.1 Palladium Complexes of Ligands (L) and (L')

The complex precursor bis(benzonitrile)dichloro-palladium(II) was used to prepare the complex of ligand (L), while the above precursor and tetrachloropalladate(II) as $[AsPh_4]^+$ salt were reacted with ligand (L'). These reactions were carried out in 1:1 molar ratios, and in the case of ligand (L'), identical products were obtained regardless of the complex precursor used (Table 5.2).

The complex of ligand (L) is soluble in methanol, CH_3CN, CH_2Cl_2 and DMSO. The conductivity measurements in CH_3CN

(Λ = 114 $ohm^{-1}cm^{2}mole^{-1}$) and DMSO (Λ=35.0 $ohm^{-1}cm^{2}mole^{-1}$) indicate a 1:1 electrolyte based on the formula $PdCl_2.L.H_2O$. The calculation based on the formula $Pd_2Cl_4.L_2.(H_2O)_2$ gives a value of Λ 227.8 (CH_3CN) and Λ 70 (DMSO), which indicates a 2:1 electrolyte.

The infra-red spectrum of $PdCl_2.L.H_2O$ shows a broad band at $3400cm^{-1}$, characteristic of OH stretching of water molecules. The imine stretching vibration, ν(C=N), at $1635cm^{-1}$, is almost unshifted from that of the free ligand ($1637cm^{-1}$). A lower energy shift of $48cm^{-1}$, in the frequency of the imine group, has been reported in the palladium(II) complex (xi)$^{(143)}$.



(xi)

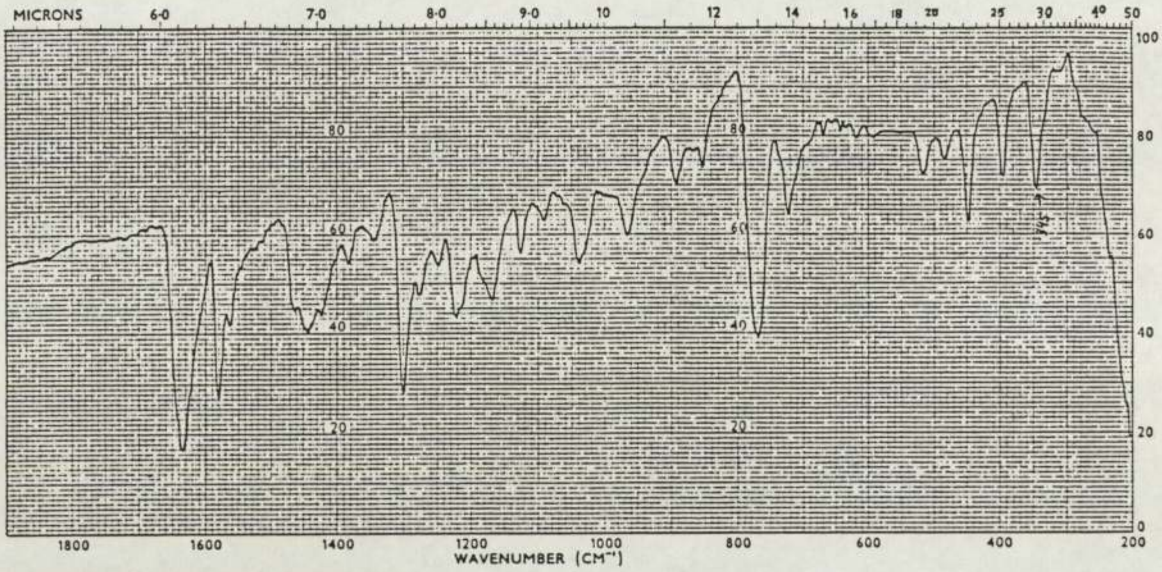


Figure 5.8 : I.R. spectrum of Pd(II) complex of ligand (L)

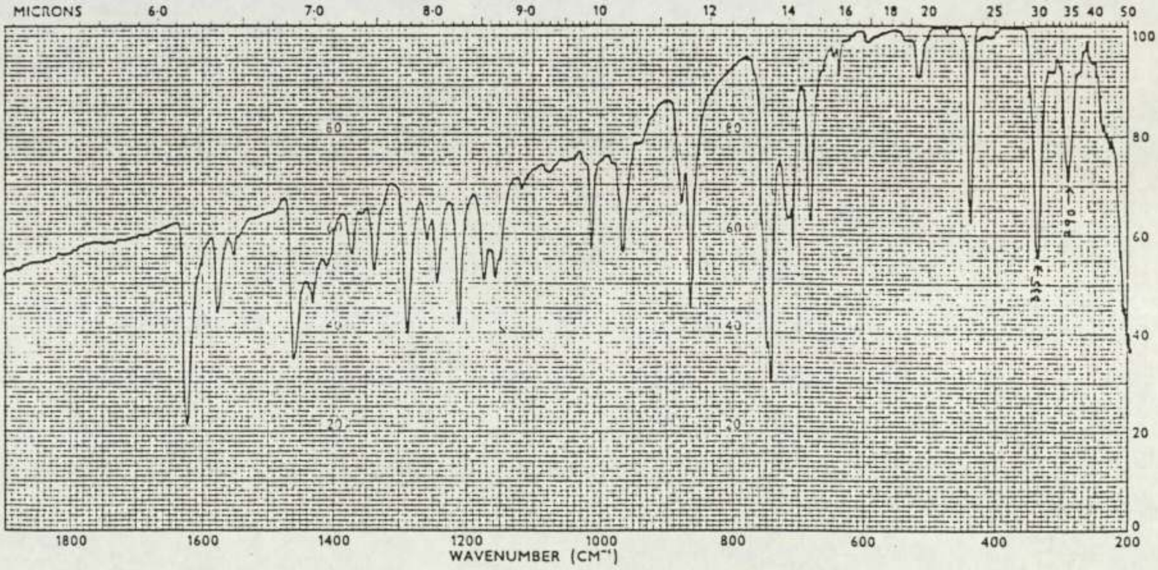
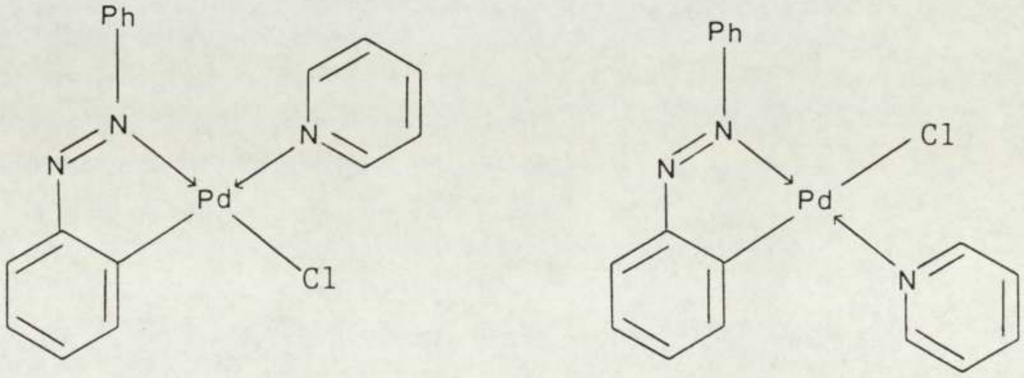


Figure 5.9 : I.R. spectrum of Pd(II) complex of ligand (L')

Therefore, in the complex $PdCl_2.L.H_2O$, it may be concluded that the nitrogen atoms of the ligand are non co-ordinating with the palladium atom. The low frequency infra-red spectrum of this complex shows a band at 345cm^{-1} which can be assigned as ν(Pd-Cl). Since the conductivity measurement indicates that the complex is an electrolyte, then one of the chlorides could be ionic while the other is co-ordinating to Pd. Hence, this band may be attributed to a terminal Pd-Cl vibration. On the basis of the <u>trans</u>- influence (that is the tendency of a ligand to weaken the bond <u>trans</u> to itself in a complex(144) and according to the infra-red data Crociani et al (145) assigned the complex [Pd(az)(Py)Cl] as isomeric having a chloride either <u>trans</u> to the azo nitrogen or to the phenyl carbon.



ν(Pd-Cl) = 352cm^{-1} (A)

ν(Pd-Cl) = 280cm^{-1} (B)

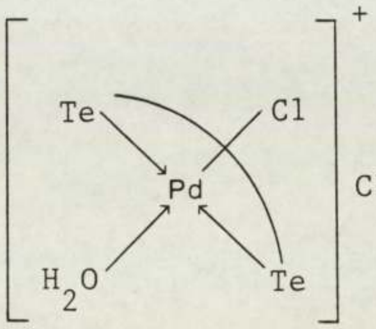
(xii) Isomers of [Pd(az)(Py)Cl]

It has been also noted(146) that the Pd-Cl stretching frequencies for the complexes $[PdClL'L_2]^+$, where L'= neutral ligand and L = phosphine, vary with changes in L'[ν(Pd-Cl), L'= 330cm^{-1}, CO; 312cm^{-1}, $P(OC_6H_5)_3$; 300cm^{-1}, $P(C_6H_5)_3$]. It is also mentioned that the trans influence decreases in the order C-donors ($sp^3 \simeq sp^2 > sp$) > P-donors $\geqslant$ As-donors > S-donors > N-donors > halide $\geqslant$ O-donors, and that Te-donors > Se-donors $\geqslant$ S-donors(147).

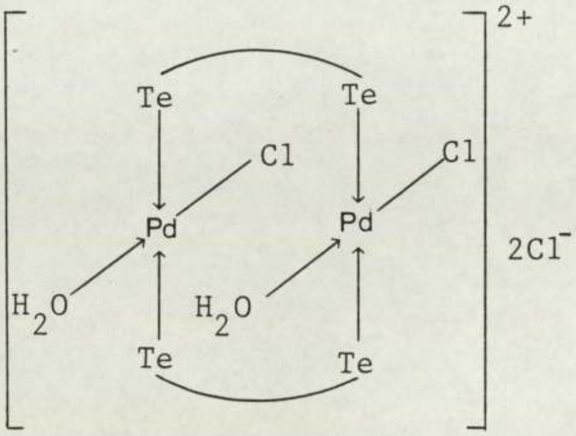
According to these arguements, one may conclude that the chloride ligand in the present $PdCl_2.L.H_2O$ complex is probably trans to the H_2O ligand, because if the chloride were trans to the tellurium, ν(Pd-Cl) would be at somewhat lower frequencies rather than being observed at 345 cm^{-1}, which is close to that reported (352cm^{-1}) for compound (xiiA)(145), and to the ν(Pd-Cl) 351cm^{-1} reported for trans-$Pd[(4\text{-}EtO\text{-}C_6H_4)_2Te]_2Cl_2$(148) and 348cm^{-1} reported for trans-$PdCl_2[Te(CH_2Si(CH_3)_3)_2]_2$(41).

^{13}C N.M.R. spectra of $PdCl_2.L.H_2O$ complex and of the other complexes mentioned in this chapter could not be recorded on the N.M.R. instrument at the Chemistry Department / Aston University, but samples have been sent elesewhere for investigation.

According to the above discussion, structures (A) and (B) can be suggested for $PdCl_2.L.H_2O$, but the dimeric structure (B) may be more favoured.

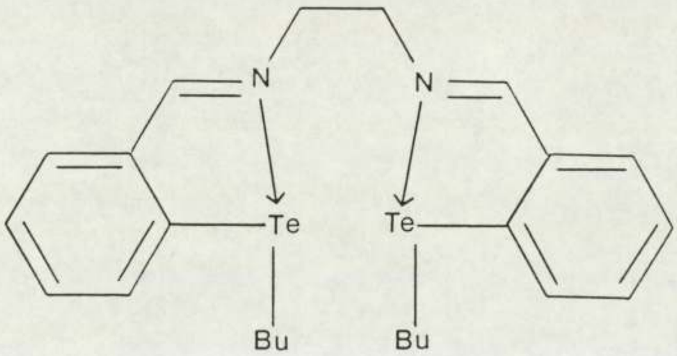


(A)



(B)

Although, in principle, structure (B) must allow two ν(Pd-Cl) but mechanical coupling between the two chlorides may be weak. If the Te---N interaction and the planarity of the moiety Te-C-C-C-N in the ligand (L) are considered, one may argue that the number of bonds between the tellurium atoms are pseudo-five instead of the real eleven bonds, see below.



Such a pseudo-five bond backbone probably does not enable the tellurium atoms of the same ligand molecule to span trans positions around the same central metal ion (Pd(II)). In chapter four, it has been argued that the Te-Hg-Te bond angle (109.1°) is smaller than expected, although it is typical for a tetrahedron. Moreover, it has been suggested that this probably indicates a rigid backbone. Simple calculation on that mercury complex shows that the bite of the two tellurium donor atoms is 4.552 Å. This is shorter than the 5.212 Å found between trans tellurium donor atoms in the palladium complex $Pd[Te(CH_2CH_2CH_2SiMe_3)_2]_2(SCN)_2$ (41), and shorter than the sum of covalent radii 5.26 Å (using 1.32 Å for tetrahedral Te and 1.31 Å for square planar Pd(II)(115)). This may emphesise the inability of ligand (L) to span trans around Pd. Space filling models suggest that, at least, a six bond backbone (i.e., five atoms) between the two tellurium atoms is needed to respond to the torsion demand of a chelating trans structure. However, ligands of the type $E(CH_2)_nE'$, where $n \geqslant 5$ and E and E' are donor groups, tend to bridge metal atoms in preference to forming a chelate ring. The addition of $Me_2N(CH_2)_nNMe_2$, where n = 5, 7, to a solution of $PdCl_2(PhCN)_2$ has been found to give the binuclear complexes trans- $Pd_2Cl_4[Me_2N(CH_2)_nNMe_2]_2$ confirmed by single-crystal X-ray determination, in which the ligands are bridging between Pd atoms (149). Phosphine ligands of the type $Bu^t_2P(CH_2)_nPBu^t$ (n = 5-7) where also reported to form binuclear complexes trans- $Pd_2Cl_4(Bu^tP(CH_2)_nPBu^t)_2$ (150). The molecular structure of the Pd(II) complex of the bis-sulphide ligand, $Bu^tS(CH_2)_5SBu^t$ has also been shown to be a trans-binucler with bridging ligands (151). The complex $PdCl_2L^5$ (L^5= Ar-$Te(CH_2)_5TeAr$) has been reported to be "probably polymeric" in the solid state with trans dichloro-ligands, but is monomeric probably with cis- stereochemistry in solution (108). The formation of bridging structures rather than chelates, in the above examples, has been attributed to the thermodynamic stability and some times to the effect of the bulky t-alkyl groups in stabilizing these binuclear complexes in terms of torsional effects.

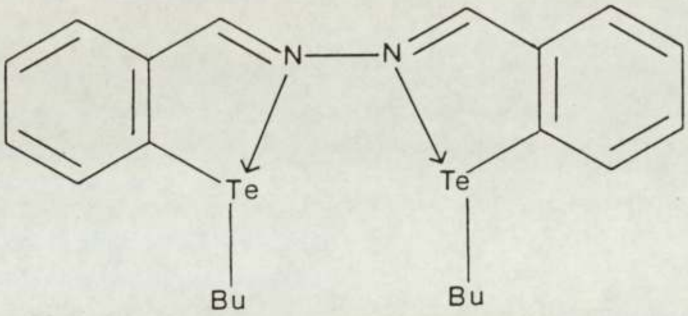
According to the above evidence, the present complex may have the binuclear structure (B), and therefore, will form a large-ring chelate complex (26-membered or a pseudo 14-membered ring, if palladium is included.

The palladium(II) complex of ligand (L') is soluble in hot benzene and chloroform but insoluble in ethanol, DMF and DMSO. The molar conductivity of this complex in benzonitrile indicates that the compound is nonionic (Table 5.3). The elemental analysis suggests a 1:1 Pd/L' structure ($PdCl_2.L'$), and there is no evidence for the presence of water in the infra-red spectrum of the compound.

The infra-red spectrum of this compound revealed a band at 1622cm^{-1} which is attributed to ν(C=N), and is slightly shifted from the position of the band in the free ligand (1616cm^{-1}). This could be an evidence that the nitrogen atoms of the ligand are not involved in coordination with palladium. In the low frequency region of the i.r. spectrum of $PdCl_2$.L', the presence of two bands at 332cm^{-1} and 288cm^{-1}, which are attributed to ν_{as}(Pd-Cl) and ν_s(Pd-Cl) respectively, is indicative of a cis- configuration in the solid state. However, the ν_{as}(Pd-Cl) in cis- palladium compounds was reported to be lower than our value (e.g., 305-312cm^{-1}), while ν_s(Pd-Cl) has been assigned at 285-292cm^{-1} (21a,152). Trying to recrystallise $PdCl_2$.L' from hot chloroform gave a compound which has the same elemental analysis, but its low frequency i.r. spectrum differs slightly from the original compound, where another band at about 345cm^{-1} appeared as well as the original bands at 322, 288cm^{-1}. The low solubility of this compound in chloroform at room temperature, which increases by warming the solution, and the appearance of the new band (345cm^{-1}) in the i.r. spectrum of the recrystallised compound may indicate that in solution a cis-trans equilibrium takes place (eq. 5.4), and therefore, the recrystallised compound could be a mixture of cis- and trans- isomers.

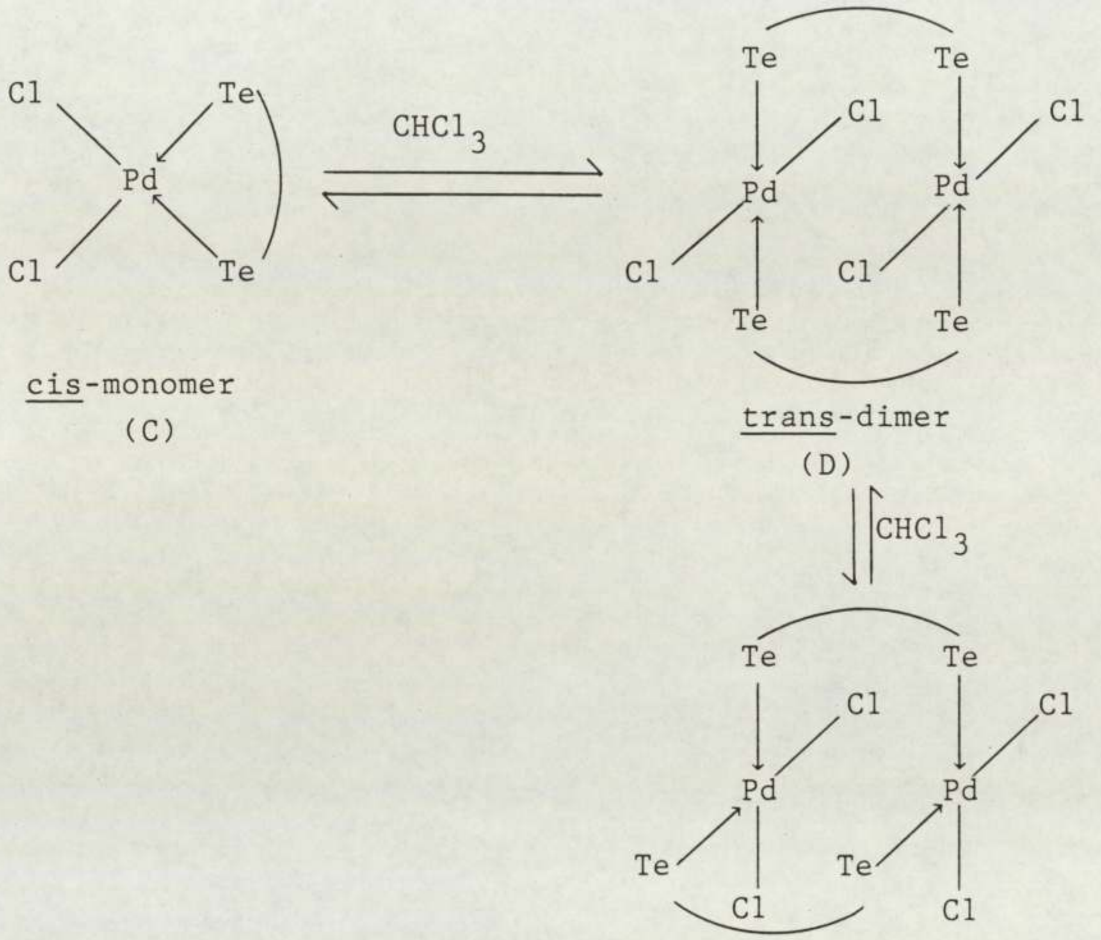
$$\text{cis-}PdCl_2.L' \xrightleftharpoons{CHCl_3/\text{Heat}} \text{cis- and trans-}PdCl_2.L' \qquad \text{eq. 5.4.}$$

In the hydrazone ligand (L'), the nine bond backbone between the two tellurium atoms, may be able to span trans- positions. However, similar to ligand (L), this backbone may be rigid due to the possible Te---N interaction and resonance in the compound, which could hold Te-C-C-C-N intact and planar. Therefore, the number of bonds between tellurium atoms, in the same molecule, will be pseudo-three, instead of the real nine bonds as shown below.



This pseudo-three bond backbone may, therefore, allow the formation of a Pd(II) complex having cis- configuration. $PdCl_2$ .L' complex could, also, be a dinuclear complex, and the ligands are bridging between two palladium atoms. These possible structures are shown in scheme 5.1.

Di-selenium compounds, of the type RSeR'SeR (R = CH_3, Ph; R'= CH_2CH_2, CH=CH, o-C_6H_4), which possess a three bond backbone, have been also reported to form chelate cis-palladium(II) complexes with ν(Pd-Cl) of c.a. 317 and 305 cm^{-1} (153). Chelate cis-palladium(II) compounds have been



Scheme 5.1

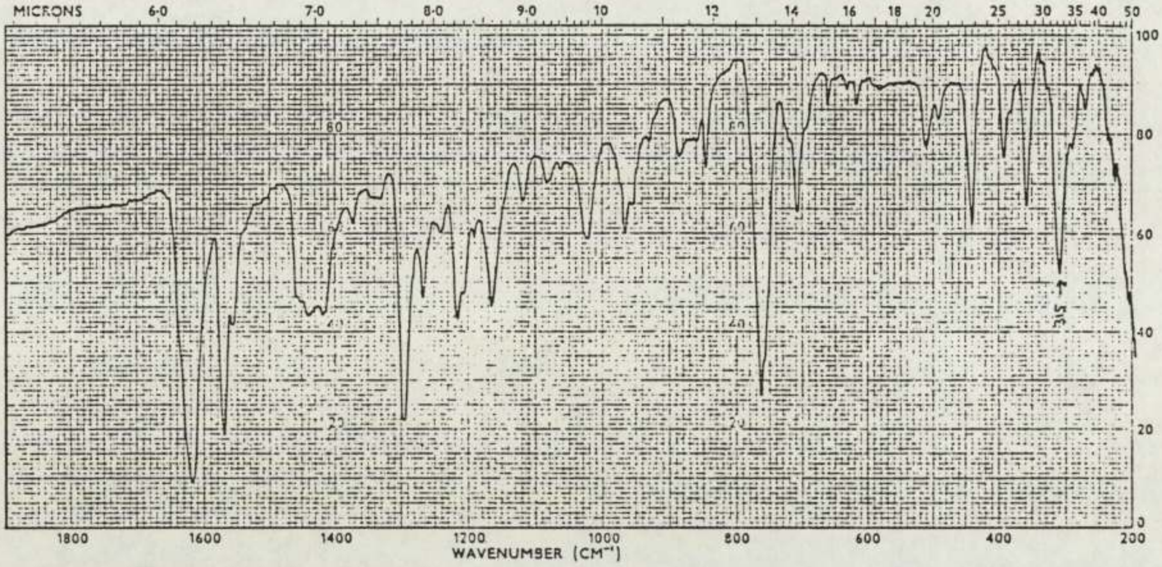
also obtained by reacting Na_2PdCl_4 with o-phenylenebisdiphenylphosphine(154).

The visible spectrum of $PdCl_2.L.H_2O$ compound in chloroform revealed bands at 21550cm^{-1} (ϵ = 1125)and 26040cm^{-1} (ϵ = 1875), while the spectrum of $PdCl_2.L'$ showed a band at 22988cm^{-1} (ϵ = 1700) (Table 5.7). These bands are characteristic of square-planar palladium(II) complexes, which have been reported to shown medium intensity bands around 26000cm^{-1} for di-stibine complexes $^{(155)}$, 27000cm^{-1} for di-arsine complexes $^{(156)}$, 25000cm^{-1} for di-selenium complexes $^{(153)}$, and 24000 for di-tellurium complexes $^{(108)}$.

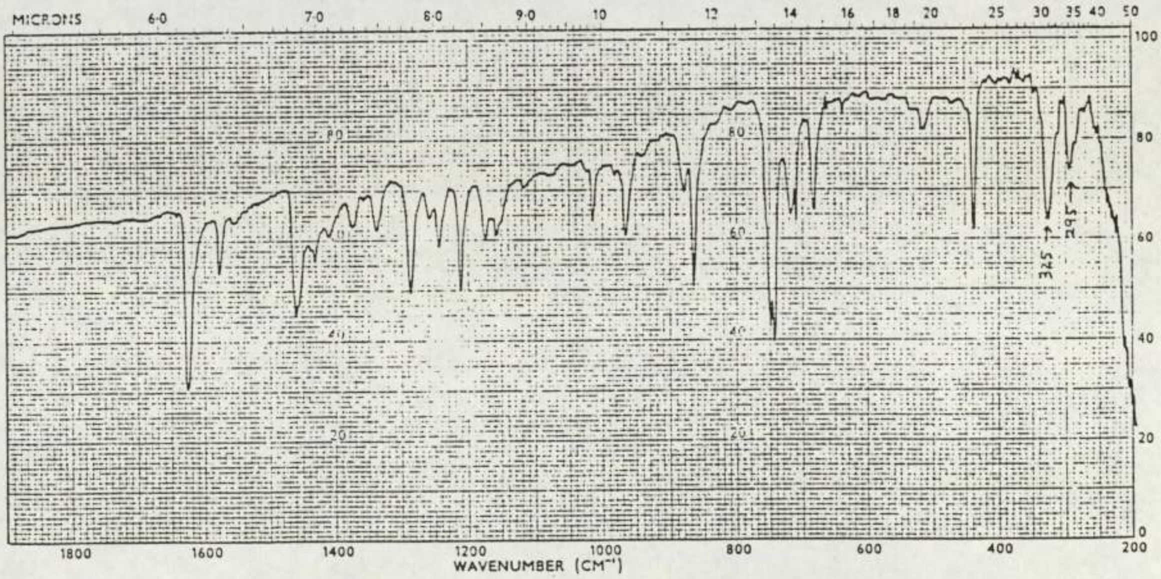
5.3.2.2 Platinum Complexes of Ligands (L) and (L')

The reaction of tetrachloroplatinate(II) [as tetraphenylarsonium salt] in dichloromethane with ligand (L) gave a light cream coloured compound, while with ligand (L') it gave a light orange compound. The elemental analyses suggest a 1:1 formula for both complexes, $PtCl_2.L.H_2O$ and $PtCl_2.L'.H_2O$.

The infra-red spectrum of $PtCl_2.L.H_2O$ showed a broad band at about 3400cm^{-1}, which is characteristic of OH stretching of water molecules. Another strong band at 1625cm^{-1}, which is assigned as ν(C=N), has not shifted very much from that of the free ligand (1637cm^{-1}). The 12cm^{-1} lower frequency shift could be as a result of a strong platinum-tellurium interaction. The low frequency region of the i.r. spectrum showed one band at 315cm^{-1} characteristic of Pt-Cl stretching. However, this frequency is lower than that reported for <u>trans</u>- $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$ (νPt-Cl=337cm^{-1}) $^{(21a)}$, <u>trans</u>-$PtCl_2(SeEt_2)_2$ (νPt-Cl=339cm^{-1} $^{(157)}$, <u>trans</u>- $PtCl_2[Bu^t_2P(CH_2)_nPBu^t_2]$ (n = 5-12, νPt-Cl <u>c.a.</u> 333cm^{-1}) $^{(150,158)}$ and <u>trans</u>- $PtCl_2(Sbcy_3)_2$ (cy = C_6H_{11}, νPt-Cl=333cm^{-1}) $^{(159)}$. The conductivity measurement in DMSO gave a value of Λ 35 ohm^{-1}cm^{2}mole^{-1}, based on the

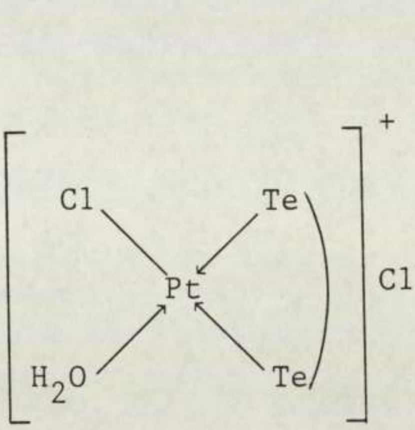


5.10 : I.R. spectrum of Pt(II) complex of ligand (L)

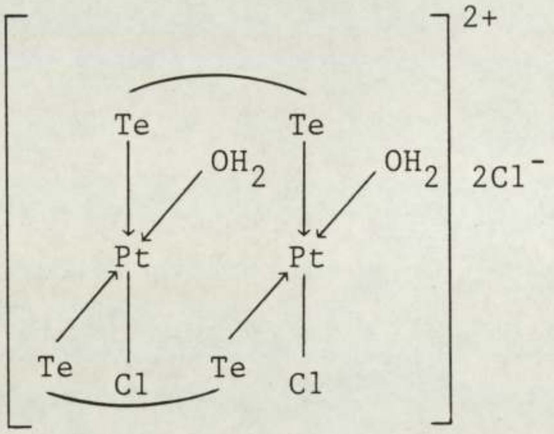


5:11 : I.R. spectrum of Pt(II) complex of ligand (L') formula $PtCl_2.L.H_2O$, which indicates a 1:1 electrolyte (but see later). Therefore, one of the chlorides could be ionic. Hence, the absorption frequency at $315cm^{-1}$ could not be due to the asymmetrical stretching of trans-[Cl-Pt-Cl], but probably due to the stretching of a terminal Pt-Cl. In this case, since the ligand's nitrogen atoms have been excluded from co-ordination with platinum, the chloride ligand is, therefore, co-ordinated trans to either a water ligand or a tellurium ligand. The ν(Pt-Cl) has been found to vary with changes in the ligand trans to Cl. These variations are interpreted in terms of the trans influence of the ligands, as mentioned earlier in the discussion (146). The values of ν(Pt-Cl) in a series of complexes trans-$[PtClL(PEt_3)_2]ClO_4$ where L is a neutral ligand, have been determined by infra-red spectroscopy (160). When L is $P(OMe)_3$, in this series, ν(Pt-Cl) was reported at $316cm^{-1}$, while if Cl is trans to a pyridine ligand ν(Pt-Cl) would be at 337 cm^{-1} (147).

It has been also reported that, in the compound $[Pt(bmsp)Cl]PF_6$ (bmsp = $(MeSeCH_2CH_2CH_2)_2Se$) in which Cl is trans to Se, the ν(Pt-Cl) appears at $320cm^{-1}$ (161). All this evidence, and the fact that Te ligands have higher trans-influence than H_2O (147), indicate that in the present compound, $PtCl_2.L.H_2O$, the chloride is located in a trans position to a tellurium atom rather than to H_2O ligand. Accordingly, we come to a conclusion that this complex may have a structure in which the tellurium donor atoms are in a cis position, as shown below:

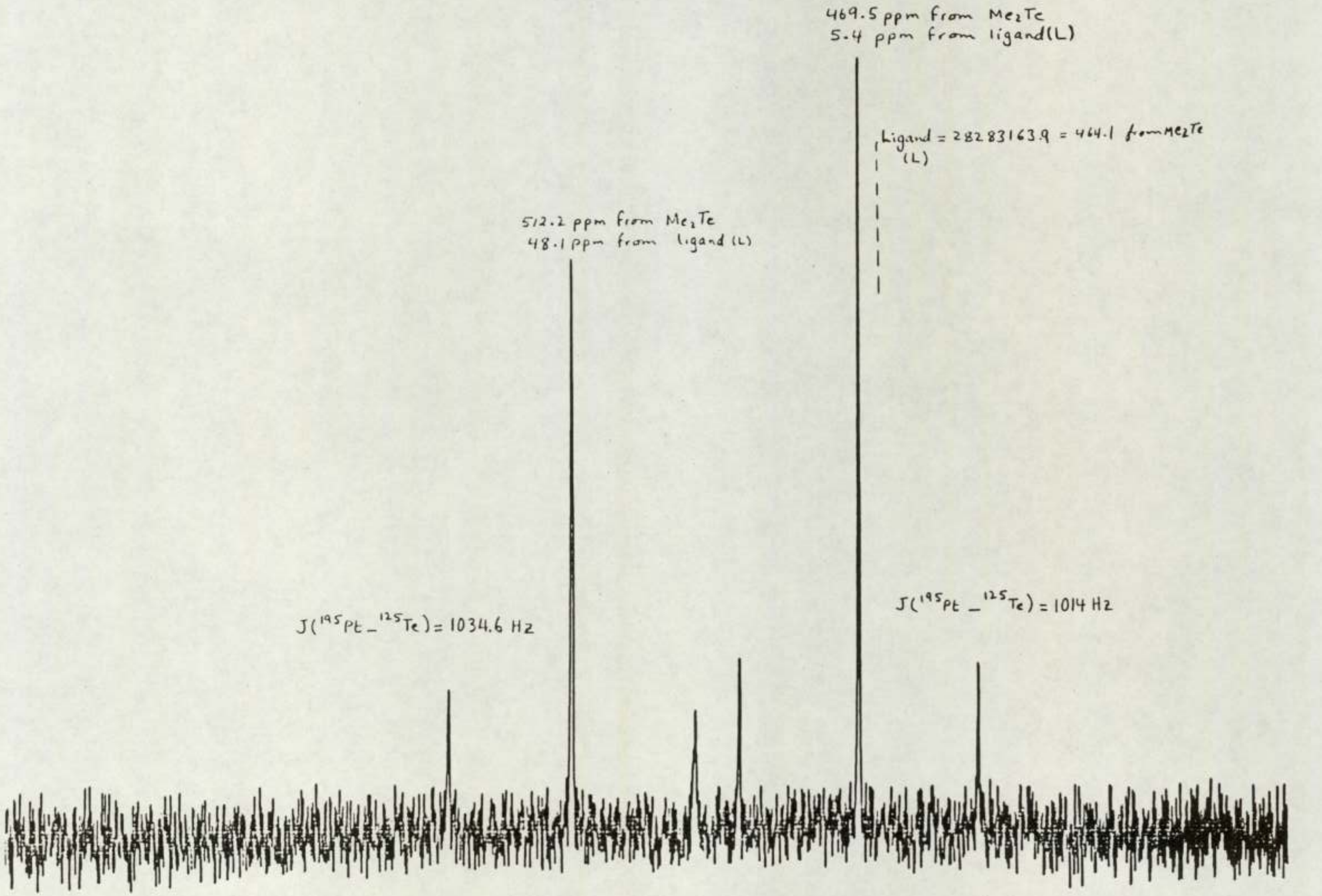


(F)



(G)

The ^{125}Te N.M.R. measurement of this complex was carried out in DMSO, but not without gentle heat to obtain the right concentration, in order to get a good resolution. The colour of the solution, however, became slightly brownish during the dissolution process. The spectrum shows two sets of signals centered at δ 469.5 and 512.2 ppm downfield from Me_2Te (Fig. 5.12). These resonances are at lower field compared to the ^{125}Te resonance of the unco-ordinated ligand (δ 464.4 ppm) (Fig. 5.6). A downfield shift is expected upon co-ordination of diorganyltelluride ligands to metal ions, which reflects a deshielding of the tellurium atoms, as previously reported$^{(21a,108)}$. Each of these sets comprises of a main peak with two satellites resulting from coupling of ^{125}Te with ^{195}Pt (nuclear spin 1/2, natural abundance



5.12 : ^{125}Te[^{1}H] N.M.R. spectrum of platinum(II) complex of ligand (L) in DMSO

33.7%). This indicates that both tellurium atoms of the ligand are bound to platinum. The appearance of two sets of signals may indicate two things, either there are two distinct species in solution or, if there is one compound, the two tellurium atoms of the ligand should be inequivalent.

The presence of two distinct species could arise from different possibilities:

(1) _cis_-_trans_ equilibrium
(2) meso-DL isomerism
(3) alkyl and dealkyl compounds

The presence of one species with inequivalent tellurium atoms may arise from the presence of alkyl and dealkyl tellurium atoms in the same compound.

In order to discuss these possibilities, two parameters should be considered, the ^{125}Te chemical shift and the coupling constant J(^{195}Pt-^{125}Te).

(1) _Cis_-_trans_ equilibrium

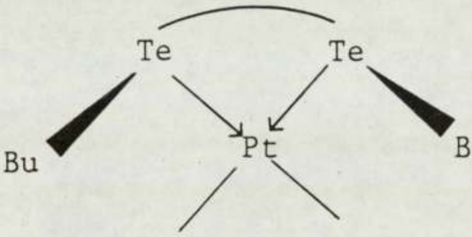
If there is a _cis_-_trans_ equilibrium, two sets of signals should be obtained downfield from the ligand signal. The _trans_- isomer is known to resonate at a lower field than the _cis_-isomer. Gysling et al $^{(21a)}$ have reported a downfield shift of 133 ppm for the _trans_ complex $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$, while 87.8 ppm downfield shift for the _cis_-

isomer was observed compared to the free ligand. McWhinnie et al (108) have recently reported a similar observation, where downfield shifts $\Delta\delta$(83-91 ppm) for the cis complexes $PtCl_2(ArTe(CH_2)_nTeAr)$ (n = 7, 9, 10) and downfield shifts $\Delta\delta$(114-124 ppm) for the trans isomers relative to the free ligands, were obtained. These results show that $\Delta\delta$ trans/ $\Delta\delta$ cis ratio is about 1.5. However, J(^{195}Pt-^{125}Te) for the cis complex was reported to be ~1.5 times that in the trans isomer (21a), a ratio which is similar to that reported for cis and trans $[PtCl_2(Bu_3P)_2]$ (144).

The lowest downfield shift in the spectrum of the present complex is for the signal at δ 512.2 ppm, which is 47.8 ppm downfield from the free ligand. The other signal, however, is only 5.1 ppm downfield from the ligand signal. Non of these relatively small shifts, which may indicate that ligand (L) is a harder ligand compared to simple tellurium ligands due to Te ⟵ N interaction, could be considered as due to a trans isomer. Moreover, the coupling constants J(^{195}Pt-^{125}Te) are 1034.6 and 1014 Hz respectively, which are comparable to the J value (900 Hz) obtained for the cis- $PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$ (21a). The difference between the reported coupling constant and our values may be due to solvent effect (162), since a different solvent has been used in each case. Therefore, the cis-trans isomerism could be disregarded here and, in fact, the similarity in J(^{195}Pt-^{125}Te) values for the two sets of signals may indicate that these signals are due to species in which the tellurium donors are occuping similar positions around platinum (i.e., cis- position); this is in agreement with the infra-red arguement mentioned earlier here.

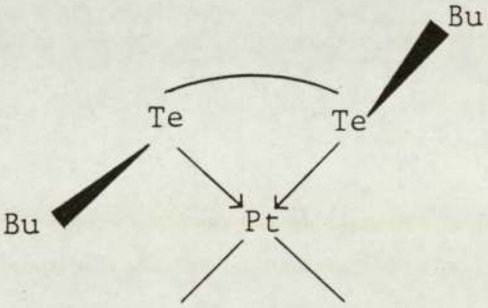
(2) Meso-DL

The presence of meso and DL invertomers, which arise from pyramidal inversion at tellurium, is also possible, as shown below:



meso

(xiii)



DL

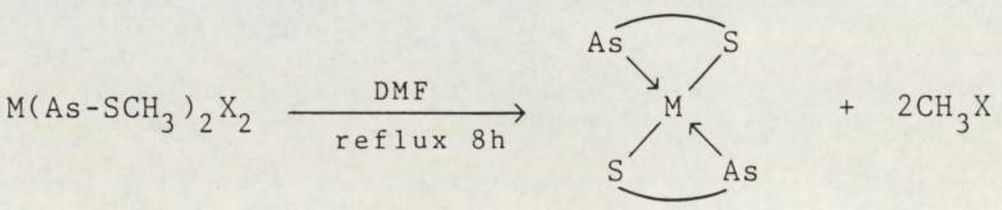
(xiv)

Previous studies (153,163) have shown that inversion at selenium is more difficult than at sulphur. Inversion at tellurium may be more difficult than at selenium, but no evidence for this is available however. In N.M.R. studies of di-selenium (153) and tri-selenium (164) complexes of Pt(II), two ^{77}Se signals were observed due to meso and DL isomers, for which the resonances of the different invertomers differ by c a. 3-12 ppm owing to the different orientation of the nonbonded selenium lone pairs in the two isomers.

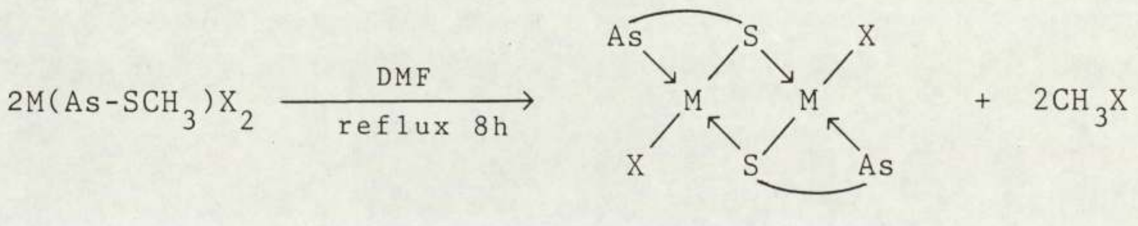
A difference of 42.7 ppm between the two signals in the ^{125}Te spectrum of the present complex is, therefore, very large to be considered as due to a meso-DL isomerism.

(3) Alkyl and dealkyl species

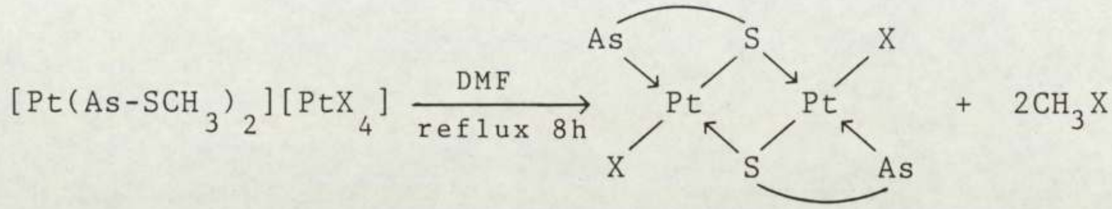
The possibility of alkyl and dealkyl compounds could be the more likely explanation. The idea of de-alkylation of chalcogenide compounds in their complexes is well established. Several examples of S-dealkylation of coordinated thioether ligands have been demonstrated(164). Examples are shown in scheme 5.2, where (As-SCH_3) is dimethyl-o-methylthiophenylarsine.



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



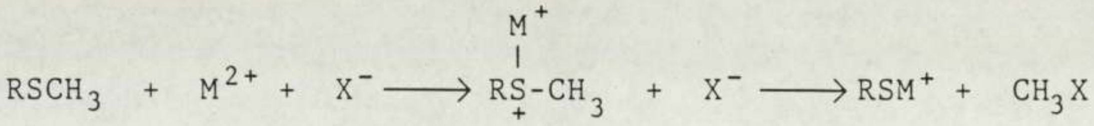
(B) M = Pd, Pt; X = I



(C) X = Cl, Br

Scheme 5.2

The presence of dimethylformamide which is known to react with alkyl halides was regarded to be a factor in the facile demethylation in the above scheme, and a nucleophilic attack mechanism was postulated for the S-demethylation reactions (162a), as shown in eq. 5.5.



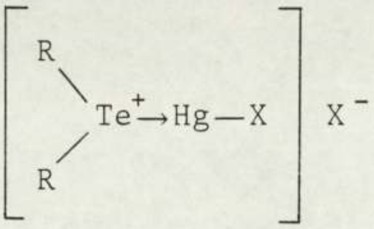
$$RSCH_3 + M^{2+} + X^- \longrightarrow R\overset{M^+}{\underset{+}{S}}\text{-}CH_3 + X^- \longrightarrow RSM^+ + CH_3X$$

eq 5.5

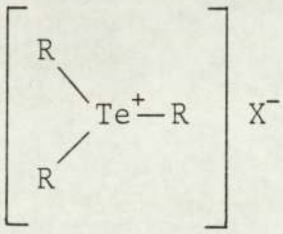
Demethylation of co-ordinated selenoethers has also been reported. When nickel(II) or palladium(II) complexes of diphenyl(o-methylselenophenyl)phosphine were heated in DMF or n-butanol, the ligand readily underwent demethylation within 5-15 min. The relatively easy demethylation of the selenoethers as compared to the thioether was attributed to the lower dissociation energy of Se-C bond (165). Preliminary studies on several [M(L-L)X_2] complexes (M = Pt, Pd; L-L = di-selenium ligand; X = Cl, Br) in $(CD_3)_2SO$, have been claimed to show that, on raising the temperature, some ^1H N.M.R. signals were identified as due to the alkyl halide and the solutions darkened during these studies, which indicates Se-dealkylation is occuring$^{(153)}$. These studies were, however, not pursued.

Te-dealkylation of the complexes of organotellurium ligands is unprecedented, although it may occur in a similar manner to sulphur and selenium complexes. Many ^{125}Te Mössbauer studies of organotellurium complexes, particularly of Pt(II) and Hg(II), showed that the ^{125}Te Mössbauer parameters, in all cases, were similar to those for tellurium atoms in triorganotellurium salts$^{(24-26)}$. As shown in Table 5.9, the quadrupole splitting parameter (Δ) for such complexes is around 6 mm s^{-1}, which is very close to Δ values of the corresponding telluronium salts.

According to such Mössbauer data and in view of the apparent presence of R_2Te^+ groups within complexes, it has been suggested$^{(25)}$ that the tellurium mercury complexes are of the type (xv) similar to sulphur complexes (eq. 5.5) and to $[R_3Te^+]X^-$ (xvi).



(xv)



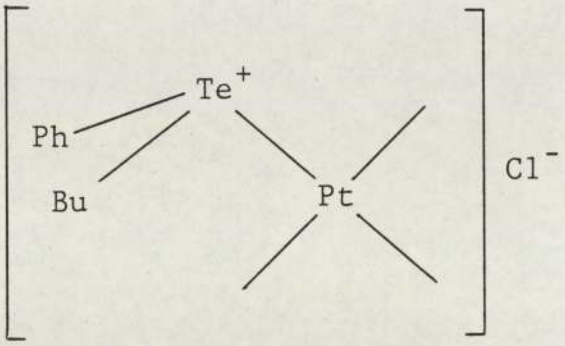
(xvi)

It is reasonable, therefore, to suggest that the tellurium ligand in the present platinum(II) complex may

Compound	δ(mm s^{-1})	Δ(mm s^{-1})	Ref.
$(p\text{-EtO-}C_6H_4)_2Te$	0.24	11.13	24
$[(p\text{-EtO-}C_6H_4)_2Te]_2PdCl_2$	0.31	7.61	24
$[(p\text{-EtO-}C_6H_4)_2Te]_2PtCl_2$(cis)	0.35	6.63	24
$[(p\text{-EtO-}C_6H_4)_2Te]_2HgCl_2$	0.32	5.96	24,25
$(p\text{-MeO-}C_6H_4)_2TeMe^+I^-$(DMSO)	0.29	5.7	26
($CDCl_3$)	0.32	5.6	26
(solid)	0.15	5.8	26
Ph_2Te	0.18	10.5	25
$Ph_2Te.HgI_2$	0.27	6.04	25
$Ph_3Te^+Cl^-$(solid)	0.35	5.8	26
$Ph_3Te^+Cl^-$(DMSO)	0.29	5.7	26

Table 5.9. Mössbauer data of some tellurium ligands, their complexes and salts

behave similarly to the telluronium salt (xvi) as shown below:



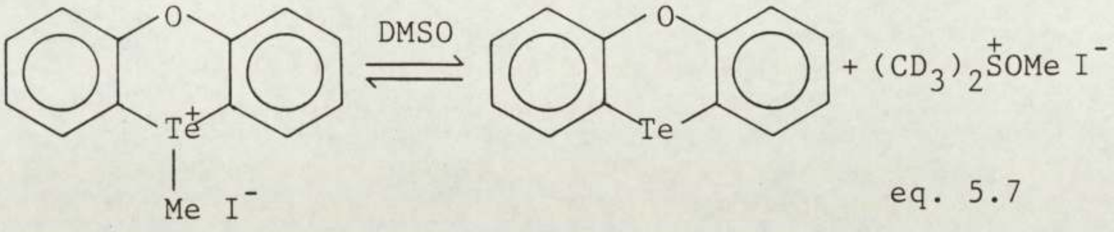
(xvii)

McWhinnie et al (166) stated that conductivity and ^1H N.M.R. data suggest that telluronium salts of the type $Ph_2(CH_3)TeX$ (X = Cl, Br, I, NCS) are covalent in $CHCl_3$, but more ionic in DMSO, and to a lesser extent, DMF (eq. 5.6).

$$Ph_2(CH_3)TeX \underset{CHCl_3}{\overset{DMSO}{\rightleftharpoons}} Ph_2(CH_3)Te^+X^- \qquad \text{eq.5.6}$$

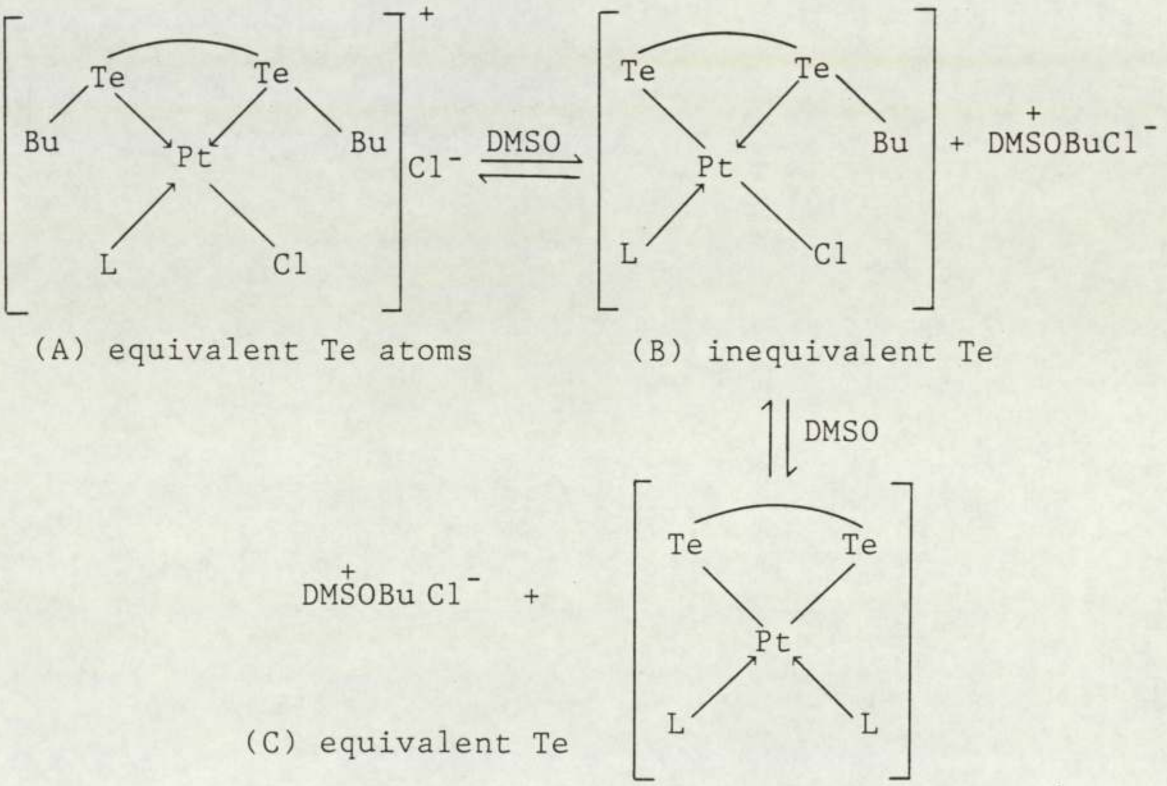
"covalent" "ionic"

In a recent study, Rainville and Zingaro (167) have reported that the difference in the methyl ^1H N.M.R. resonance of 10-methylphenoxatelluronium iodide in DMF-d_7 versus $(CD_3)_2SO$ is due to the formation of phenoxa-tellurine and $(CD_3)_2\overset{+}{S}OMeI^-$, and stated that this methylation and demethylation equilibrium in DMSO is reversible for methyltelluronium salts (eq. 5.7).



eq. 5.7

In view of the above Mössbauer, conductivity and ^1H N.M.R. investigations, one can imply that, since organotellurium ligands, in their complexes, behave like telluronium salts, Te-alkylation and Te-dealkylation equilibrium in DMSO solution of such complexes is also likely to occur. Therefore, it is possible that when the present platinum(II) complex was dissolved in $(CD_3)_2SO$ for ^{125}Te N.M.R. measurement, such equilibrium gave different species in the solution (scheme 5.3)



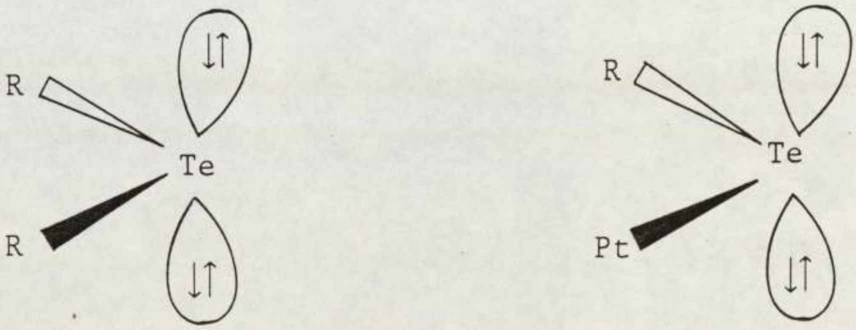
(A) equivalent Te atoms

(B) inequivalent Te

(C) equivalent Te

Scheme 5.3

The appearence of two sets of signals in the ^{125}Te N.M.R. spectrum indicates that there are only two kinds of tellurium atoms with a different environment. The signal centered at δ 512.2 ppm could be due to the alkylated co-ordinated tellurium atom, while the other signal centered at δ 469.5 ppm may be due to the dealkylated co-ordinated tellurium atoms. The idea of the presence of a dealkylated tellurium atom could well explain the very small chemical shift difference between the signal at δ 469.5 ppm and the signal of the unco-ordinated ligand (δ = 464.4 ppm), because virtually Te atoms in the two species of Figure 5.13 will have similar electronic environment, and thus a similar chemical shift.



Ligand

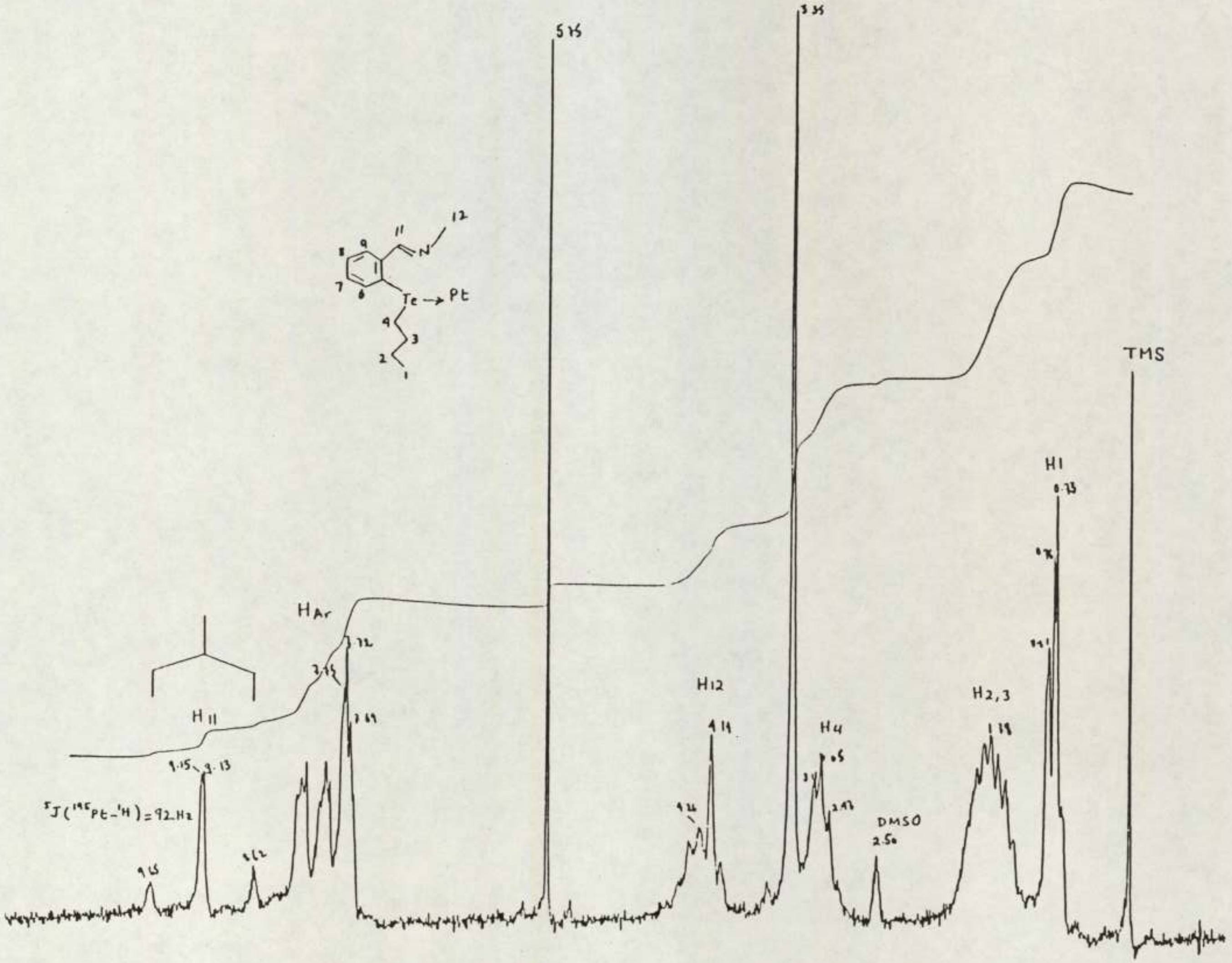
Te-dealkylated complex

Figure 5.13. The similarity between a tellurium ligand and a dealkylated complex.

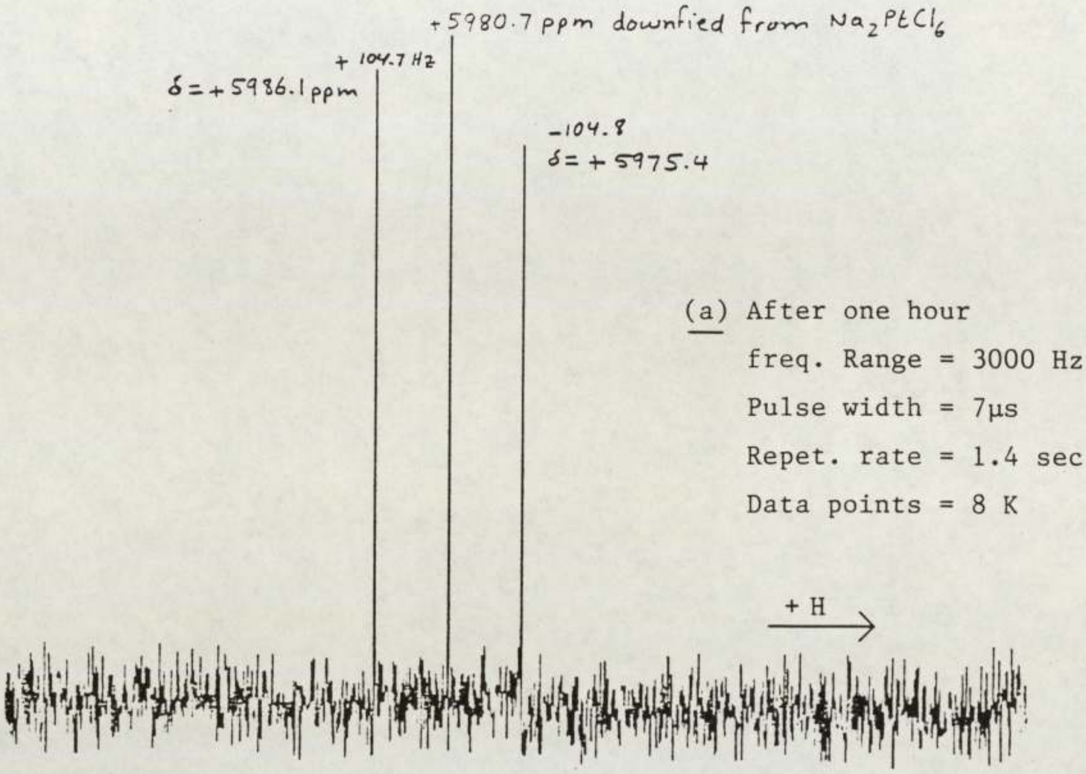
Conductivity measurement of this platinum(II) complex (Λ= 35 ohm^{-1}cm^{2}mole^{-1}) in DMSO indicates a 1:1 electrolyte. Therefore, only species (A) and (B) of scheme 5.3 could be present in solution at least in the early stages of the equilibrium (see later).

The similarity in the coupling constants $J(^{195}Pt-^{125}Te)$ of the two sets of signals may indicate that both of these signals arose from tellurium atoms located in a cis position. However, the signal, which is attributed to a dealkylated tellurium atom, has a lower J value than the signal attributed to the alkylated tellurium atom. This may indicate that a dealkylated tellurium atom is weakly co-ordinated to Pt as compared to an alkylated Te, since the RTe^- ligand is a harder base compared to R_2Te.

The ^1H N.M.R. spectrum of this Pt(II) complex in DMSO (Fig. 5.14), shows all the peaks of the unco-ordinated ligand. However, the signals centered at 3.05 ppm and 9.1 ppm, which are attributed to the protons of C4 (adjacent to Te) and the imine proton respectively, are shifted by more than 0.5 ppm to a lower field. This indicates deshielding of these protons due to the co-ordination of tellurium to platinum. However, the signal, due to the imine proton, is very clearly split into two peaks (δ 9.12 & 9.15 ppm), with the appearance of two satallites at δ 8.62 & 9.65 ppm, result from $^{195}Pt-^1H$ coupling. The $^5J(^{195}Pt-^1H)$ value of 92 Hz is higher than $^3J(Pt-H)$ reported for some organoseleniumplatinum(II) complexes (153,164) cf. 41 Hz. This may indicate two things, first the resonance in the moiety Te-C-C-C-N, and



5.14 : ^{1}H N.M.R. spectrum of platinum complex of ligand (L) in DMSO



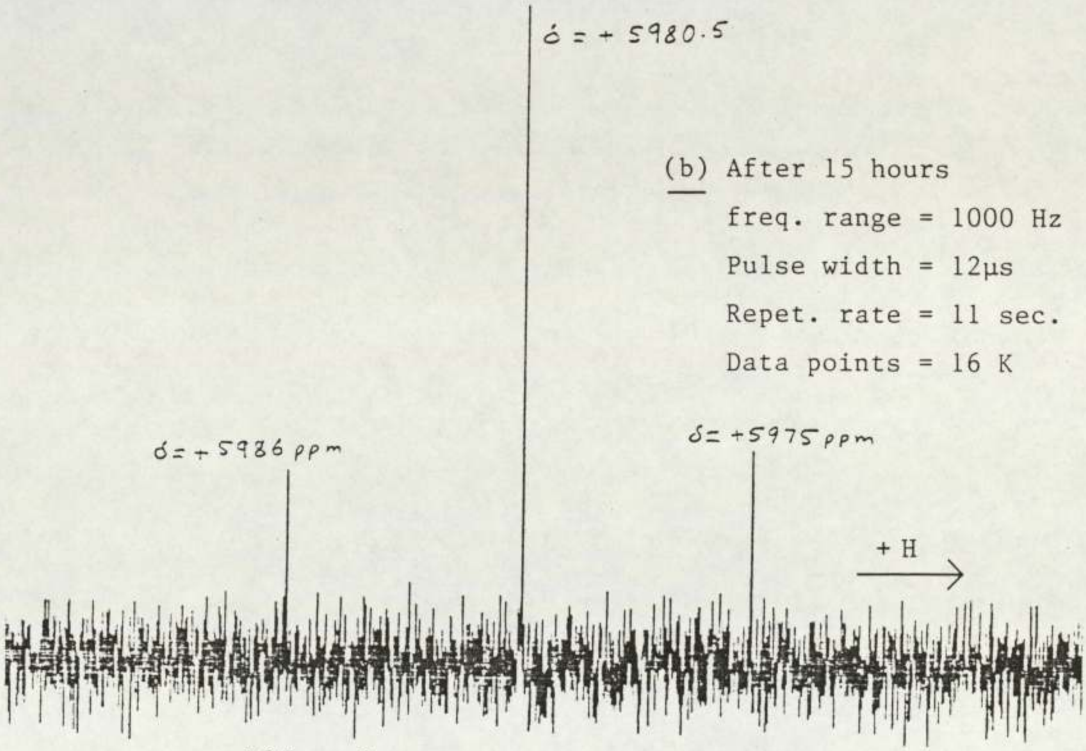
(a) After one hour

freq. Range = 3000 Hz

Pulse width = 7μs

Repet. rate = 1.4 sec

Data points = 8 K



(b) After 15 hours

freq. range = 1000 Hz

Pulse width = 12μs

Repet. rate = 11 sec.

Data points = 16 K

Figure 5.15 : $^{195}Pt[^{1}H]$ N.M.R. spectrum of platinum complex of ligand (L) in DMSO-d_6

therefore its planarity, is maintained in this complex (crystallographically observed for Hg complex in chapter four), which allowed a five-bond coupling with Pt. Second, platinum is interacting inequivalently with tellurium atoms of the ligand, which results in the splitting of the signal into two peaks. The apparent splitting in the other alkyl protons' signals and the appearance of a new multiplet, in the ^1H N.M.R. spectrum of the complex, centered at δ 4.26 ppm could be interpreted as due to the formation of butyl chloride as a result of dealkylation process.

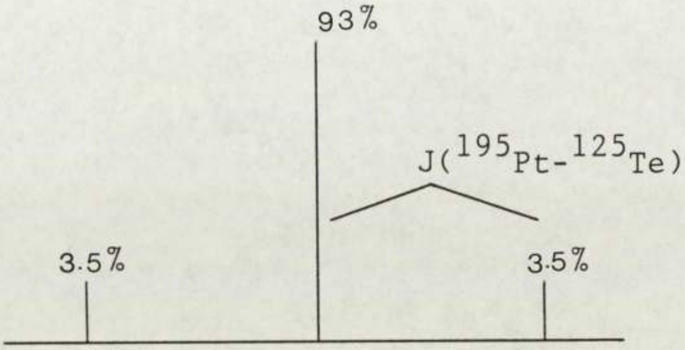
^{195}Pt N.M.R. spectrum of $PtCl_2.L.H_2O$ was recorded in DMSO. It is known that ^{195}Pt resonance covers a wide range of chemical shifts$^{(168)}$, and usually Pt(II) resonates at a higherfield than the reference Na_2PtCl_6 , while Pt(IV) could resonate at a higherfield or at a lowerfield. The search in the higherfield down to δ=- 6700 ppm, did not give a convincing signal, for this complex. The search in the lowerfield, however, gave first a set of signals of almost equal intensity at δ=+ 5986.1, + 5980.7 and 5975.4 ppm (interval frequency $\sim$104 Hz), which are characteristic of Pt(IV) rather than Pt(II), as shown in Fig. 5.15a.

During the period of N.M.R. measurement, the solution changed from light yellow to brownish. This change in colour may be accompanied by oxidation of Pt(II) to

Pt(IV) with intermediate Te-dealkylated species. This process was followed by conductivity measurements. A solution of $PtCl_2.L.H_2O$ (10^{-3}M) in DMSO has Λ 35 $ohm^{-1}cm^2 mole^{-1}$ (indicating a 1:1 electrolyte), but when heated it became brownish with a decrease in the molar conductivity. After heating for 30 min., the solution became completely brown and the conductivity dropped to 12 $ohm^{-1}cm^2mole^{-1}$ (indicating a non electrolyte solution).

As stated in the experimental section, that when the preparation of this compound was carried out in a refluxing acetonitrile, a brown compound was obtained. The elemental analysis showed a formula $PtCl_2.C_{16}H_{14}N_2Te_2{\cdot}2H_2O$ (i.e., a dealkylated platinum(IV) complex) which has a molar conductance of 11.5 $ohm^{-1}cm^2mole^{-1}$ in DMSO. This evidence together with ^{195}Pt N.M.R. study clearly support the formation of a Pt(IV) complex.

It is feasible then to see resonances due to Pt(IV) in the ^{195}Pt N.M.R. spectrum. If a ^{195}Pt nucleus is coupled with two ^{125}Te (I = 1/2, natural abundance 7%), the observed ^{195}Pt spectrum should appear as one intense line flanked by a doublet (relative intensity 1/2x 7%) whose interval is exactly J(^{195}Pt-^{125}Te)$^{(168)}$. Therefore, one would expect three signals of relative intensity 0.035 : 1 : 0.035, if this is within the spectrometer detection capability as shown in the schematic diagram (xviii) below:



(xviii) Schematic ^{195}Pt N.M.R. spectrum showing the coupling to ^{125}Te nuclei.

It has been stated that the ratio of the coupling constants J(Pt(IV)-L) / J(Pt(II)-L) should be close to 0.67, because the S-character of a bond formed by Pt(II) in a square planar complex $[PtX_2L_2]$ is approximately 1/4, as the metal atom makes use of dsp^2-hybrids, while in the corresponding octahedral complex of Pt(IV) $[PtX_4L_2]$ it is approximately 1/6, as the metal atom makes use of d^2sp^3-hybrids (169). It has been found experimentally, that this ratio is about 0.6 in tertiary phosphine complexes (144,170), and about 0.5 in selenium complexes(171). Thus it would be expected that J(Pt(IV)-Te) is about half J(Pt(II)-Te) (i.e., about 500 Hz). Since neither the intensity requirement nor the interval frequency between the three signals obtained in the ^{195}Pt N.M.R. spectrum are satisfying the above discussion, one can not regard these signals as due to ^{195}Pt-^{125}Te coupling. It is possible, then, that these three signals are due to three different species in solution. After overnight accumulation, the position of these signals did not change while the relative intensity became 0.28 : 1 : 0.38, which may mean that the equilibrium has shifted in favour of the central signal (Fig. 5.15b).

The structure of the present platinum complex appears to be more complicated than what was thought, but what seems almost certain is that the complex has cis tellurium atoms around platinum. The solution (DMSO) ^{125}Te N.M.R. spectrum showed that there are two kinds of tellurium, one is three co-ordinated (alkylated) and the other is two co-ordinated (dealkylated). The way in which dealkylation proceeded is unknown, probably by simple elemination or by platinum insertion between the tellurium atom and the butyl group, then finally settled on a DMSO molecule. The ^{195}Pt N.M.R. spectrum in DMSO showed the presence of Pt(IV) complex, which is believed to be the same complex that was separated when the reaction was carried out in acetonitrile, and having no butyl groups according to the elemental analysis.

The platinum(II) complex of ligand (L') was prepared using $PtCl_4^{2-}$, to give a 1:1 complex $PtCl_2.L'.H_2O$, which is soluble in hot $CHCl_3$ but not soluble in DMSO, CH_3CN, ethanol or nitromethane.

The infra-red spectrum of this complex showed a band at 1626cm^{-1} characteristic of ν(C=N), which is shifted to a higher energy by 10cm^{-1} as compared to the free ligand absorption. The low frequency region of the i.r. spectrum showed two bands at 325, 295cm^{-1} characteristic of ν_{as}(Pt-Cl) and ν_{s}(Pt-Cl) respectively, which indicate a cis configuration in the solid state. These are comparable to the values 320, 299cm^{-1} reported for cis-$PtCl_2[ArTe(CH_2)_7TeAr]_2$(108), and the values 315, 293cm^{-1} reported for some cis-diphosphine platinum(II) complexes(154). As stated earlier in the discussion, the number of bonds between the tellurium atoms in ligand (L') could be considered as pseudo-three instead of the real nine bonds. Such a three bond backbone would not allow a trans configuration unless the ligands are bridging. Accordingly this complex may have a structure similar to that of palladium (structure C or D).

The visible spectrum of $PtCl_2.L.H_2O$ in DMSO revealed a band at 23250cm^{-1}($\epsilon = 400$) and a shoulder at about 21505 cm^{-1} ($\epsilon = 350$), while the spectrum of $PtCl_2.L'.H_2O$ in chloroform showed a band at 27777cm^{-1} ($\epsilon = 4000$) and a shoulder at about 23530cm^{-1} ($\epsilon = 250$) (Table 5.7). These bands are characteristic of square-planar Pt(II) complexes. The electronic spectra of many square-planar platinum(II) complexes show a weak intensity band ($\epsilon \sim 250$) at the lower energy region, and an intense or a medium intensity band ($\epsilon \geqslant 1000$) at the higher energy side, but some times one of them does not show due to overlapping. These bands have been reported to occur at $\sim$25000cm^{-1} for di-arsine complexes (156), 27000 and $\sim 31500cm^{-1}$ for di-stibine complexes (155,159), ~ 25500 and $\sim 31100cm^{-1}$ for di-selenium complexes (153), and $\sim 29500cm^{-1}$ for di-tellurium complexes (108).

When a DMSO solution of $PtCl_2.L.H_2O$ is heated, its colour changes into brown and the electronic spectrum is gradually changed to give finally a band at $25000cm^{-1}$ (ϵ=12000) and shoulders at $21275cm^{-1}$ (ϵ = 6750) and $17855cm^{-1}$ (ϵ = 1500), which could be due to electronic transition in Pt(IV).

5.3.2.3 Rhodium complexes of ligands (L) and (L')

A-Rhodium(III) Complexes

The complex precursor $K_2RhCl_5(H_2O)$ was used in the preparation of Rh(III) complexes of (L) and (L'). Brown 1:1 complexes of the formula $RhCl_3.L.2H_2O$ and $RhCl_3.L'.H_2O$ were obtained, according to the elemental analyses (Table 5.2).

The complex $RhCl_3.L.2H_2O$ is soluble in methanol, $CHCl_3$, CH_2Cl_2 and DMSO. Conductivity measurement of this compound in DMSO ($10^{-3}M$) gave a value of Λ 20.4 $ohm^{-1}cm^2$ $mole^{-1}$, and 65 $ohm^{-1}cm^2mole^{-1}$ in acetonitrile, which are less than the value expected for 1:1 electrolytes. Thus the compound could be dimeric. The infra-red spectrum shows a band at $1640cm^{-1}$ assigned as ν(C=N) which has not shifted much from that of the free ligand. The low region of the i.r. spectrum showed bands at 322, 380cm^{-1} characteristic of $\nu(Rh^{3+}-Cl)$ vibrations.

The complex $RhCl_3.L'.H_2O$ is not soluble in methanol but soluble in benzene, $CHCl_3$ and DMSO. The conductivity measurement of this compound in DMSO (10^{-3}M) gave a value of Λ 6.6 $ohm^{-1}cm^2mole^{-1}$ indicative of the non-ionic behaviour in solution. The infra-red spectrum revealed a band at 1620cm^{-1} attributed to ν(C=N) stretching, which has not shifted much from its position in the free ligand (1616cm^{-1}). The low frequency region of the i.r. spectrum showed bands at 340 and 365cm^{-1} characteristic of $\nu(Rh^{3+}-Cl)$ vibrations.

B-Rhodium(I) Complexes

The complex precursor $[RhCl.COD]_2$ (COD is 1,5-cyclooctadiene) was used to prepare the rhodium(I) complexes of (L) and (L'). Brown 1:1 complexes of the formula RhCl.L and RhCl.L' were obtained (Table 5.2). They are both soluble in dichloromethane and slightly soluble in acetonitrile. Both of these complexes are non-ionic in CH_3CN (Table 5.3).

The infra-red spectrum of RhCl.L' showed a band at 1610 cm^{-1} assigned as ν(C=N), which has been slightly shifted to a lower energy as compared to the free ligand. The low frequency i.r. spectrum did not show any band above 200

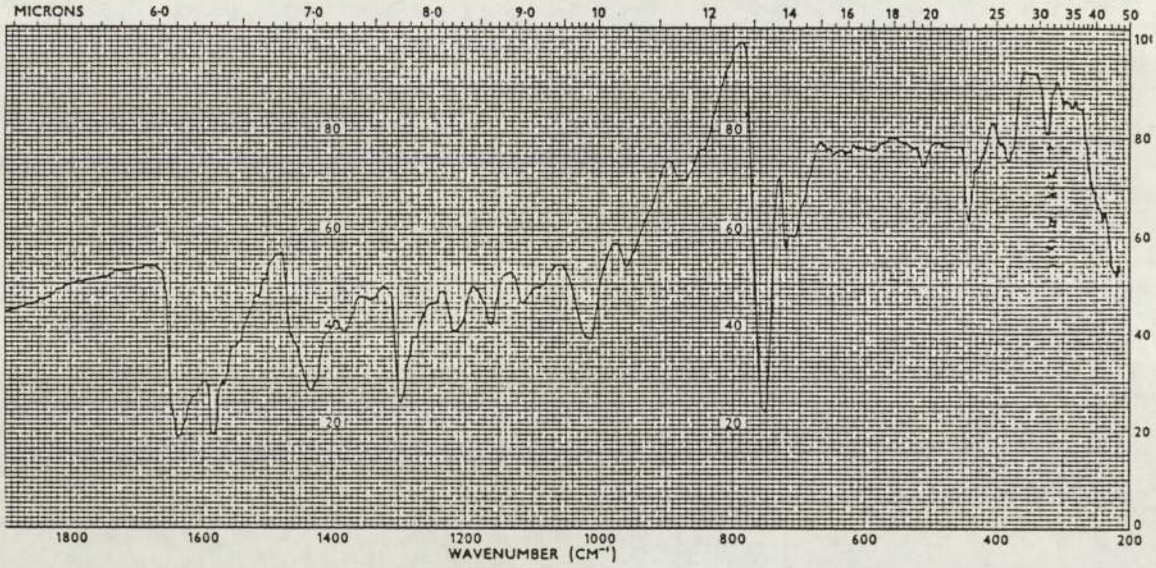


Figure 5.16 : I.R. spectrum of Rh(III) complex of ligand (L)

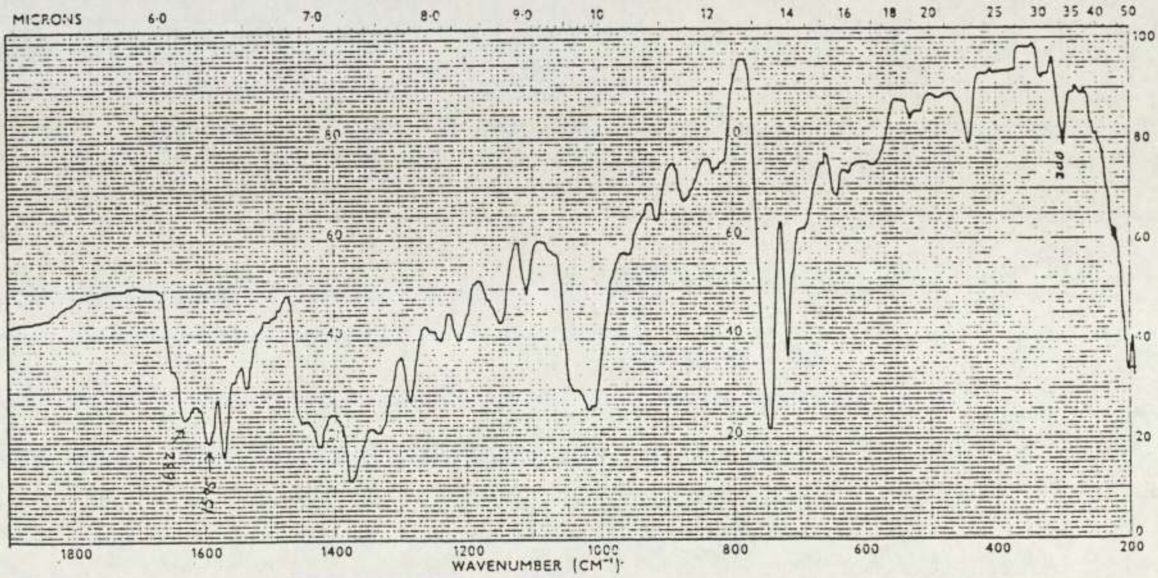
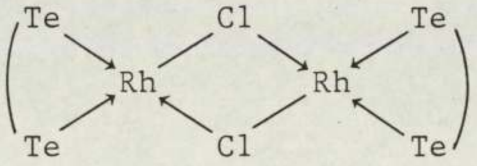


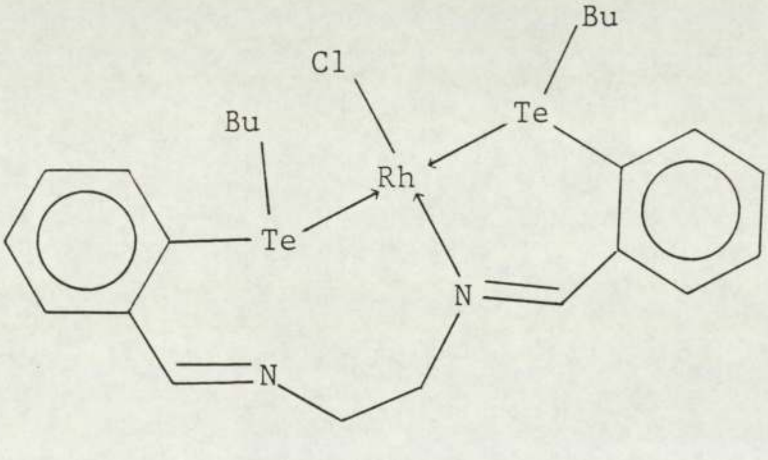
Figure 5.17 : I.R. spectrum of Rh(I) complex of ligand (L)

cm^{-1} which could be assigned to ν(Rh-Cl). This could mean that this complex is dimeric with bridging chlorides and chelating ligands as shown in structure (H).



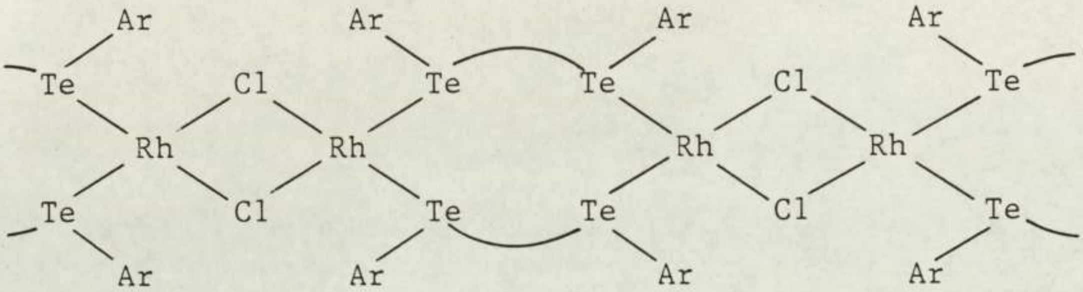
(H)

The infra-red spectrum of RhCl.L (Fig. 5.17) showed bands at 1632 and 1595cm^{-1} which could be assigned as ν(C=N) for unco-ordinated and co-ordinated imine groups respectively. The low frequency region of the i.r. spectrum showed a band at 300cm^{-1} assignable to ν(Rh$^+$-Cl). Therefore the compound could be monomeric with a terminal chloride, and having a structure shown below:



(J)

For comparison, the complex $[RhCl.L^{10}]_n$ was prepared by the reaction of $[RhCl.COD]_2$ with $L^{10}(ArTe(CH_2)_{10}TeAr)$(27). The resulting compound is insoluble in many organic solvents, and its low frequency i.r. spectrum did not reveal a band characteristic to ν(Rh-Cl) above $200cm^{-1}$. This could mean that the complex is polymeric with bridging tellurium ligands and bridging chlorides.



(K)

The visible spectra of $RhCl_3.L.H_2O$ and $RhCl_3.L'.H_2O$ exhibit bands at $25310cm^{-1}$ (ϵ= 15000) and $24270cm^{-1}$ (ϵ= 18000) respectively which are characteristic of absorptions in Rh(III) complexes. It has been reported that Rh(III) complexes show intense band ($\epsilon \geqslant 17000$) at $31000cm^{-1}$ for di-phosphine complexes(154), $30000cm^{-1}$ for diarsine complexes (156b), $27000cm^{-1}$ for di-stibine complexes(155) and $26500cm^{-1}$ for di-selenium complexes(164).

5.3.2.4 Summary

As a result of this study, it has been noted that generally the reaction of ligand (L) with Pd(II), Pt(II) and Rh(III) gives ionic compounds, while the reaction of these transition metal ions with ligand (L') gives non-ionic compounds. No reduction of these metal ions to a lower oxidation state has been noticed as a result of the reaction with such tellurium ligands, in contrast to some of the di-tellurium ligands [$ArTe(CH_2)_nTeAr$], which were reported to reduce Pt(II) to Pt(I) and Rh(III) to Rh(I)$^{(27)}$.

Ligand (L) could be considered as having a pseudo-five bond backbone between tellurium atoms instead of the real eleven bonds, and ligand (L') could be regarded as having a pseudo-three bond backbone between telurium atoms, instead of the real nine bonds. This was attributed to the significant tellurium-nitrogen interaction in both ligands.

The complexes could be described as follows:

(1) Palladium(II) Complexes

a-with ligand (L): it is ionic, dimeric with trans bridging tellurium ligands and chloride is trans to H_2O.

b-with ligand (L'): the complex has a cis configuration. It is non ionic and it could be monomeric or dimeric. It isomerises in $CHCl_3$ solution into trans.

(2) Platinum(II) Complexes

a-with ligand (L): it is ionic, monomeric or dimeric having cis tellurium ligands. It is not stable in DMSO solution, and undergoes Te-dealkylation with oxidation of Pt(II) to Pt(IV) and finally became non ionic.

b-with ligand (L'): the complex has a cis configuration. It could be monomeric or dimeric.

(3) Rhodium(III) Complexes

a-with ligand (L): the complex is ionic and it could be dimeric. Only tellurium atoms are co-ordinating.

b-with ligand (L'): the complex is non-ionic and only tellurium atoms are co-ordinating.

(4) Rhodium(I) complexes

a-with ligand (L): the complex may be monomeric with a terminal chloride and the ligand is acting as tridentate through Te, N and Te atoms.

b-with ligand (L'): the complex is dimeric with bridging chloride and only tellurium atoms are co-ordinating.

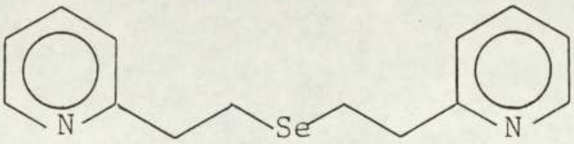
CHAPTER SIX

NEW ORGANOTELLURIUM COMPOUNDS DERIVED FROM PYRIDINE AND QUINOLINE

6.1 Introduction

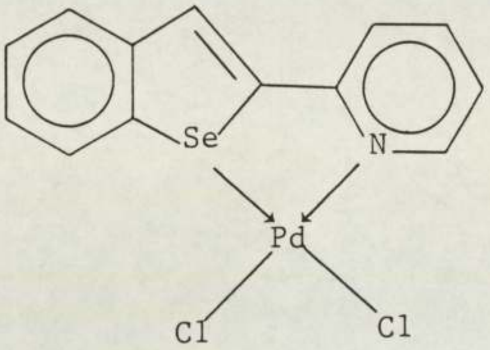
In the previous chapters, the preparation of some tellurium ligands, containing carboxylate or imine groups, have been described and some of their complexes have been discussed. As the aim of this work is to prepare and study tellurium ligands that incorporate hard donor atoms,pyridine and quinoline functionalised ligands may be good examples.

Some chalcogenide compounds which contain pyridine or quinoline groups and capable of acting as bi- or multidentate ligands have been reported in the literature. Bis(β-(2-pyridyl)-ethyl)selenide (DPSe) was prepared from 2-vinylpyridine and H_2Se in ethanol, its 1:1 complexes $Cu(DPSe)X_2$ ($X=Cl$, Br, NO_3, ClO_3) were also prepared in which the ligand was shown to be tridentate through two nitrogen atoms and one selenium atom$^{(172)}$.



(DPSe)

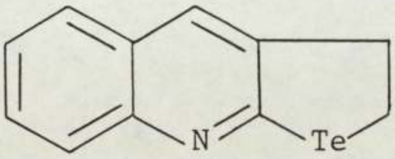
The preparation of 2-(2-pyridyl)benzo[b]selenophene (PBSe) has been also reported$^{(173)}$. This compound has been investigated as a possible reagent for palladium. It was postulated that this ligand might be highly selective for palladium, and it acts as a bidendate ligand involving a Pd-Se bond (174).



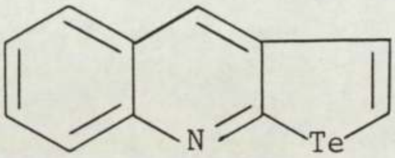
$Pd(PBSe)Cl_2$

Selenium compounds involving a quinoline group have also been prepared, and 8-methylselenoquinoline is one example (175). Some cadmium(II), zinc(II) and lead(II) 1:1 complexes of quinoline-8-selenol were investigated, and their formation constants were determined (176).

The only bidentate tellurium compounds of the above category, which have been reported to date, are [4,5-d]-quinolino-2,3-dihydrotellurophene (i) and [4,5-d]-quinolinotellurophene (ii), which were prepared in fair yield (30-50%). No complexes of these compounds have been reported however (200).



(i)



(ii)

In this chapter, the preparation of some tellurated pyridine and quinoline derivatives is described. Telluration of the starting organic compounds was performed via <u>trans</u>-metallation of the mercurated derivatives. Some of these tellurium compounds are potentially bi- or multidentate ligands, and one palladium complex was prepared. A novel tritelluride compound was isolated, and its molecular structure determined by a single crystal X-ray crystallographic study.*

6.2 Experimental

6.2.1 Synthesis of 2-(2-Pyridyl)phenylmercury(II)chloride

2-Phenylpyridine (7.81g, 0.05 mole) and mercury(II) acetate (15.93g, 0.05 mole) were mixed in absolute ethanol ($100cm^3$) and refluxed for 24 hours. At the end of this

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

period, lithium chloride (4.4g) in methanol ($100cm^3$) was added with vigorous stirring, and the thick mixture was heated for 15 minutes. It was then poured into distilled water ($300cm^3$) and filtered. The solid product was washed with water then methanol, dissolved in hot methanol and filtered. The filtrate was left to stand at room temperature whereupon a white crystalline compound formed, which was separated by filtration, washed with cold methanol and dried at 60°C in an oven, yield 35.5%, m.p. 138-140°C.

Found C = 33.7%, H = 2.00%, N = 3.50%; $C_{11}H_8ClNHg$ requires C = 33.8%, H = 2.05%, N = 3.58%

6.2.2 Synthesis of 2-(2-Pyridyl)phenyltellurium(IV)tribromide

A solution of 2-(2-pyridyl)phenylmercury(II)chloride (3.9g, 0.01 mole) in dry dioxane ($20cm^3$) was added to tellurium tetrabromide (4.47g, 0.01 mole) dissolved in dry dioxane ($15cm^3$). The mixture was refluxed under dinitrogen for two hours, during which time a yellow compound formed. At the end of this period, the hot solution was filtered and the yellow compound was washed several times with absolute ethanol. It was recrystallised from 1:1 acetonitrile/ethanol giving yellow crystals, yield ~77%, m.p. 283-285°C.

Found   C = 25.7%, H = 1.40%, N = 2.80%, Br = 46.3%

$C_{11}H_8NTeBr_3$ requires

C = 25.3%, H = 1.55%, N = 2.68%, Br = 46.0%

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

2-(2-Pyridyl)phenyltellurium(IV)tribromide (1.04g, 0.002 mole) was suspended in absolute ethanol (30cm^3). To this was added hydrazine hydrate (0.1g, 0.002 mole) in ethanol (10cm^3) under nitrogen gas with stirring. The solid dissolved after the completion of addition, and the clear solution was refluxed for 15 min., then left to cool to room temperature. The yellow crystalline compound, so formed, was filtered and washed with ethanol, yield 65%, m.p. 178-180°C.

Found   C = 37.0%, H = 2.20%, N = 3.80%, Br = 22.3%

$C_{11}H_8NTeBr$ requires

C = 36.5%, H = 2.22%, N = 3.87%, Br = 22.1%

6.2.4 Synthesis of Bis(2-(2-pyridyl)phenyl)ditelluride

2-(2-Pyridyl)phenyltellurium(IV)tribromide (1.04g, 0.002 mole) was dissolved in 2:1 acetonitrile/ethanol (30cm^3) and treated with excess hydrazine hydrate (0.6g, 0.012 mole) in ethanol (10cm^3), and the mixture was refluxed for 20 min. The precipitate, so formed, was filtered off and recrystallised from benzene to afford yellow-orange crystals, yield 60%, m.p. = 150-152°C.

Found C = 46.6%, H = 3.00%, N = 5.20%, Te = 45.3%

$C_{22}H_{16}N_2Te_2$ requires

C = 46.9%, H = 2.86%, N = 5.00%, Te = 46.0%

6.2.5 Synthesis of Bis(2-(2-pyridyl)phenyl)tritelluride

2-(2-Pyridyl)phenyltellurium(IV)tribromide (2.60g, 0.005 mole) was suspended in absolute ethanol (60cm^3) and treated dropwise with a solution of sodium borohydride (1.1g, 0.03 mole) in absolute ethanol (20cm^3). At the begining of the addition, the solid dissolved with evolution of gas, then black tellurium was noticed. After completion of $NaBH_4$ addition, when the solution had turned red, it was heated for 10 min., and filtered hot. Upon standing at room temperature a brown-red solid formed, which was filtered off, washed with water then ethanol. It was recrystallised from a benzene/toluene mixture, yield ~ 90% based on the tribromide, m.p. 165-166°C.

Found C = 39.0%, H = 2.30%, N = 3.90%, Te = 55.6%

$C_{22}H_{16}N_2Te_3$ requires

C = 38.2%, H = 2.33%, N = 4.0%, Te = 55.4%.

6.2.6 Reduction of Bis(2-(2-pyridyl)phenyl)tritelluride with Cu°.

Bis(2-(2-pyridyl)phenyl)tritelluride (1.38g, 0.002 mole) was dissolved in dioxane (15cm^3), and copper powder (0.38g. 0.006 mole) was added. The mixture was refluxed for 24 hours, then filtered, and the solution was evaporated in *vacuo*. The residue was recrystallised from ethanol giving a golden-yellow crystalline compound, yield ~75%, m.p. 146-147°C.

Found C = 46.6%, H = 2.60%, N = 4.80%; $C_{22}H_{16}N_2Te_2$
requries C = 46.9%, H = 2.86%, N = 5.00%

6.2.7 Synthesis of Bis(2-(2-pyridyl)phenyl)telluride

2-(2-Pyridyl)phenyltellurium(IV)tribromide (1.04g, 0.002 mole) and 2-(2-pyridyl)phenylmercury(II)chloride (0.78g, 0.002 mole) were dissolved in dry dioxane (20cm^3), and the mixture was refluxed for three hours. The white solid, so formed, was filtered off, washed with dry methanol and recrystallised from nitroethane, m.p. 235-238°C.

Found C = 29.3%, H = 1.80%, N = 3.10%;
$C_{22}H_{16}N_2TeHgClBr_3$ requires
C = 29.0%, H = 1.77%, N = 3.07%

The above white compound (0.91g,0.001 mole) was suspended in ethanol, stirred and treated dropwise with a solution of hydrazine hydrate (0.2g,≈0.005 mole) in ethanol ($5cm^3$), then heated. During that time elemental mercury deposited and the solution turned yellow. The solution was filtered, and water was added to precipitate a yellow compound, which was separated, washed with water and crystallised from ethanol, yield ~65%, m.p. 102 - 103°C.

Found C = 60.5%, H = 3.70%, N = 6.30%, Te = 28.5%

$C_{22}H_{16}N_2Te$ requires

C = 60.6%, H = 3.70%, N = 6.42%, Te = 29.2%

6.2.8 Preparation of Bis(2-(2-pyridinium)phenyl)tellurium Di-perchlorate.

Bis(2-(2-pyridyl)phenyl)telluride (0.44g, ~0.001 mole) was dissolved in hot methanol ($30cm^3$) and treated with an excess of perchloric acid. The solution was heated with stirring for 30 min., then filtered. The filtrate was set aside at room temperature, and over a period of time a yellow crystalline compound formed, which was filtered off, washed with methanol and air dried. It decomposed at about 270°C.

Found C = 41.6%, H = 2.60%, N = 4.10%; $C_{22}H_{18}Cl_2N_2O_8Te$ requires C = 41.5%, H = 2.53%, N = 4.40%

6.2.9 Synthesis of 2-(2-Pyridyl)-4-ethoxyphenyltelluride

2-(2-Pyridyl)phenylmercury(II)chloride (1.95g, 0.005 mole) and 4-ethoxyphenyltellurium(IV)trichloride (1.28g, 0.005 mole) were dissolved in dry dioxane (20cm^3) and refluxed for two hours. The white material, so formed, was filtered off while the solution was hot, washed with methanol and dried in an oven at 100°C.

Found C = 30.4%, H = 2.50%, N = 1.60%; $C_{19}H_{17}NOTeHgCl_4$ requires C = 30.6%, H = 2.30%, N = 1.87%

The above white compound (1.49g, 0.002 mole) was suspended in ethanol (30cm^3) and treated dropwise with an excess of hydrazine hydrate and stirred for 15 min. Water (50cm^3) was then added, and the solution was filtered. The solid ,obtained, was recrystallised from 1:1 ethanol/acetone to give a pale yellow crystalline compound, yield 67.4 %, m.p. 124-126°C.

Found C = 56.5%, H = 4.10%, N = 3.40%, Te = 31.1%
$C_{19}H_{17}NOTe$ requires
C = 56.6%, H = 4.25%, N = 3.47%, Te = 31.7%

6.2.10 Synthesis of Dimethyldithiocarbamato-2-(2-pyridyl)-phenyltellurium(II)

Method (A):

2-(2-Pyridyl)phenyltellurium(IV)tribromide (1.04g, 0.002 mole) in acetonitrile ($30cm^3$) was treated with acetonitrile solution ($20cm^3$) of sodium dimethyldithiocarbamate (1.08g, 0.006 mole) and the mixture was refluxed under dinitrogen for two hours. The solution was filtered, and the filtrate was left standing at room temperature. After one hour, the yellow crystalline compound, so formed, was filtered off, washed with acetonitrile and air dried, yield 70%, m.p. 165-166°C.

Method (B):

2-(2-Pyridyl)phenyltellurium(II)bromide (0.36g, 0.001 mole) in acetonitrile ($15cm^3$) was treated with an acetonitrile solution ($15cm^3$) of sodium dimethyldithiocarbamate (0.18g, 0.001 mole), and the mixture was heated for 30 min. The solution was then filtered and the filtrate was left to cool down giving rise to a yellow crystalline compound, yield 75%, m.p. 165-167°C. The compounds prepared by both methods gave identical analyses.

Found C = 42.0%, H = 3.50%, N = 7.00%, Br < 1%

$C_{14}H_{14}N_2S_2Te$ requires

C = 41.8%, H = 3.51%, N = 6.97%, Br = 0.0%

6.2.11 Synthesis of 2-Phenylquinoline(177)

A mixture of o-nitrobenzaldehyde (15.1g, 0.1 mole) and acetophenone (12g, 0.1 mole) was saturated with dry hydrogen chloride gas and left overnight. The brown crystalline product was kept molten and flushed with nitrogen until it became free of HCl. It was allowed to solidify then ground and recrystallised from an ethanol/ water mixture to get a cream like coloured platelets of o-nitrostyrylphenylketone, yield 21.1g (78%) m.p. 121°C (lit. 122-123°C).

A solution of o-nitrostyrylphenylketone (20g, 0.08 mole) in ethanol (600cm^3) and conc. HCl (20cm^3) was treated with iron powder (16g) during 30 min. The mixture was then refluxed for two hours, filtered and saturated with HCl gas. When the bulk of ethanol was evaporated and the solution was cooled, 2-phenylquinoline hydrochloride (20g) deposited. The crude hydrochloride was stirred with aqueous ammonia, then ethanol was added to dissolve the residue. A further quantity of ammonia solution (5cm^3) was added and the mixture was boiled, filtered, partly evaporated then cooled. The 2-phenylquinoline deposited, was separated and recrystallised from aqueous ethanol in white needles (65% yield) m.p. 84-85°C (lit. 85- 86°C).

Found C = 87.2%, H = 5.20%, N = 6.80%; $C_{15}H_{11}N$
requires C = 87.8%, H = 5.40%, N = 6.82%

6.2.12 Synthesis of 2-(2-Quinolinyl)phenylmercury(II)-chloride

2-Phenylquinoline (10.25g, 0.05 mole) and mercuric acetate (15.93g, 0.05 mole) were mixed and refluxed in absolute ethanol (100cm^3). After seven hours, lithium chloride (4.4g) in methanol (30cm^3) was added. The mixture was treated in a similar manner to that mentioned in section (6.2.1). The resultant white crystalline compound (yield 6g, 34%) melts at 180-182°C.

Found C = 40.9%, H = 2.10%, N = 2.90%; $C_{15}H_{10}ClNHg$
requires C = 40.9%, H = 2.30%, N = 3.18%

6.2.13 Synthesis of 2-(2-Quinolinyl)phenyltellurium(IV)-tribromide

2-(2-Quinolinyl)phenylmercury(II)chloride (4.4g, 0.01 mole) and $TeBr_4$ (4.47g, 0.01 mole) were refluxed in dioxane (20cm^3) for two hours. The rest is similar to section (6.2.2). The bright yellow crystalline compound (3.6g, 63%) melts at about 340°C.

Found C = 31.3%, H = 1.70%, N = 2.60%, Br = 41.9%
$C_{15}H_{10}NTeBr_3$ requires
C = 31.2%, H = 1.76%, N = 2.45%, Br = 41.9%

6.2.14 Synthesis of 2-(2-Quinolinyl)phenyltellurium(II)-bromide

2-(2-Quinolinyl)phenyltellurium(IV)tribromide (1.14g, 0.002 mole) was suspended in ethanol ($30cm^3$) and treated with hydrazine hydrate (0.002 mole) in ethanol ($10cm^3$). The mixture was refluxed for 15 min., and the yellow compound, so formed, was filtered off and recrystallised from benzene to give yellow needle-like crystals which decompose at about 150°C.

Found C = 43.9%, H = 2.30%, N = 3.20%, Br = 19.3%

$C_{15}H_{10}NTeBr$ requires

C = 43.8%, H = 2.45%, N = 3.40%, Br = 19.4%

6.2.15 Synthesis of Bis(2-(2-quinolinyl)phenyl)ditelluride

2-(2-Quinolinyl)phenyltellurium(IV)tribromide (1.14g, 0.002 mole) was suspended in ethanol ($30cm^3$) and treated with hydrazine hydrate (0.6g, 0.012 mole) in EtOH ($15cm^3$). The mixture was refluxed for 15 min., and the orange precipitate, so formed, was filtered off and recrystallised from benzene, yield ~90%, m.p. 220-222°C. Reduction by an ethanol solution of sodium borohydride also gave an orange compound m.p. 220-222°C. The products from the different reduction methods gave identical elemental analyses.

Found C = 54.1%, H = 2.90%, N = 3.90%, Te = 38.1%

$C_{30}H_{20}N_2Te_2$ requires

C = 54.3%, H = 3.04%, N = 4.20%, Te = 38.5%

6.2.16 Synthesis of Bis(2-(2-quinolinyl)phenyl)telluride

Bis(2-(2-quinolinyl)phenyl)ditelluride (1.33g, 0.002 mole) and copper powder (0.38g, 0.006 mole) were stirred and refluxed in dioxane (15cm^3) for 24 hours. The mixture was then filtered and the solvent was evaporated *in vacuo*. The residue was crystallised from ethanol giving a yellow crystalline compound (yield ~70%) m.p. 187-189°C.

Found C = 67.5%, H = 3.50%, N = 4.90%, Te = 23.6%

$C_{30}H_{20}N_2Te$ requires

C = 67.2%, H = 3.76%, N = 5.22%, Te = 23.8%

6.2.17 Synthesis of Bis(2-(2-quinolinyl)phenyl)tritelluride

2-(2-Quinolinyl)phenyltellurium(IV)tribromide (2.28g, 0.004 mole) was suspended in ethanol (25cm^3). Tellurium powder (0.26g, 0.002 mole) was added, and the mixture was stirred under argon gas. Sodium borohydride (1.1g) in ethanol (20cm^3) was then introduced slowly, until all tellurium powder disappeared. The resulting red solution was refluxed for 30 min., then allowed to cool to room temperature, whereupon an orange compound formed which was filtered off and recrystallised from benzene to give an orange-brown compound, m.p. 211-212°C, yield ~80%.

Found $C = 45.8\%$, $H = 2.30\%$, $N = 3.50\%$, $Te = 47.5\%$
$C_{30}H_{20}N_2Te_3$ requires:
$C = 45.5\%$, $H = 2.55\%$, $N = 3.54\%$, $Te = 48.4\%$

6.2.18 Synthesis of Dimethyldithiocarbamato-2-(2-quinolinyl)phenyltellurium(II)

2-(2-Quinolinyl)phenyltellurium(IV)tribromide (1.14g, 0.002 mole) was suspended in acetonitrile ($30cm^3$) and treated with an acetonitrile solution ($20cm^3$) of sodium dimethyldithiocarbamate (1.08g, 0.006 mole). The mixture was stirred and refluxed under dinitrogen for one hour, then filtered. The filtrate was left standing at room temperature. After two hours, the golden yellow crystalline compound, so formed, was filtered off, washed with acetonitrile and air dried, m.p. 206°C.

Found $C = 48.0\%$, $H = 3.30\%$, $N = 6.40\%$; $C_{18}H_{16}N_2S_2Te$
requires $C = 47.8\%$, $H = 3.56\%$, $N = 6.20\%$

6.2.19 Preparation of a Pd(II) Complex of Bis(2-(2-pyridyl)phenyl)telluride

Bis-(benzonitrile)chloro-palladium(II) (0.383g, 0.001 mole), in acetonitrile ($15cm^3$) was added to an acetonitrile solution (15cm^3) of bis(2-(2-pyridyl)phenyl)-telluride (0.13g, 0.001 mole) and stirred for one hour at room temperature. The yellowish-brown compound, so formed, was filtered off, washed with acetonitrile and dried in air; it decomposed at 230°C into black.

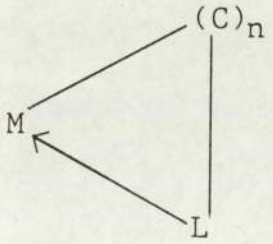
Found C = 43.1%, H = 2.50%, N = 4.60%; $C_{22}H_{16}Cl_2N_2PdTe$
requires C = 43.1%, H = 2.61%, N = 4.56%

6.3 Results and Discussion

The elemental analyses, melting points and yields, and ^{13}C N.M.R data of 2-phenylpyridine and 2-phenylquinoline derivatives are shown in Tables 6.1 - 6.5. Infrared spectra of some of these derivatives are shown in Figures 6.2 - 6.13.

6.3.1 Mercuration of 2-phenylpyridine and 2-phenylquinoline

Many organic compounds, bearing an atom or a group which can form an intramolecular co-ordination bond, have been reported to form ortho-metalated compounds$^{(178)}$.



M = metal
L = co-ordinating atom
$n \geqslant 1$

(iii)

Compound	Found %					Required %				
	C	H	N	Br	Te	C	H	N	Br	Te
$C_{11}H_8NHgCl$	33.7	2.0	3.50			33.8	2.05	3.58		
$C_{11}H_8NTeBr_3$	25.7	1.40	2.80	46.3		25.3	1.55	2.68	46.0	
$C_{11}H_8NTeBr$	37.0	2.20	3.80	22.3		36.5	2.22	3.87	22.1	
$C_{22}H_{16}N_2Te_2$	46.6	3.00	5.20		45.3	46.9	2.86	5.00		46.0
$C_{22}H_{16}N_2Te_3$	39.0	2.30	3.90		55.6	38.2	2.33	4.00		55.4
$C_{22}H_{16}N_2Te$	60.5	3.70	6.30		28.5	60.6	3.70	6.42		29.2
$C_{22}H_{16}N_2Te.2HClO_4$	41.6	2.60	4.10			41.5	2.53	4.40		
$C_{19}H_{17}NOTe$	56.5	4.10	3.40		31.1	56.6	4.25	3.47		31.7
$C_{14}H_{14}N_2S_2Te$	42.0	3.50	7.00	< 1		41.8	3.51	6.97	0.0	
$PdCl_2.C_{22}H_{16}N_2Te$	43.1	2.50	4.60			43.1	2.61	4.56		

Table 6.1. Elemental analyses of the pyridine derivatives.

Compound	Found %					Required %				
	C	H	N	Br	Te	C	H	N	Br	Te
$C_{15}H_{11}N$	87.2	5.20	6.80			87.8	5.40	6.82		
$C_{15}H_{10}NHgCl$	40.9	2.10	2.90			40.9	2.30	3.18		
$C_{15}H_{10}NTeBr_3$	31.3	1.70	2.60	41.9		31.2	1.76	2.45	41.94	
$C_{15}H_{10}NTeBr$	43.9	2.30	3.20	19.3		43.8	2.45	3.40	19.4	
$C_{30}H_{20}N_2Te_2$	54.1	2.90	3.90		38.1	54.3	3.04	4.20		38.5
$C_{30}H_{20}N_2Te$	67.5	3.50	4.90		23.6	67.2	3.76	5.22		23.8
$C_{30}H_{20}N_2Te_3$	45.8	2.30	3.50		47.5	45.5	2.55	3.54		48.4
$C_{18}H_{16}N_2S_2Te$	48.0	3.30	6.40	< 1		47.8	3.56	6.20	0.0	

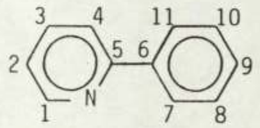
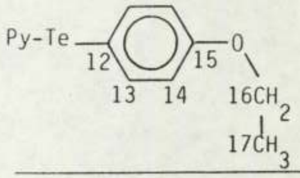
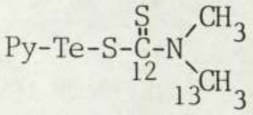
Table 6.2. Elemental analyses of the quinoline derivatives.

Compound	Colour	m.p.(°C)	Yield%	$\Lambda^{(a)}$
$C_{11}H_8NHgCl$	White	138-140	35.5	
$C_{11}H_8NTeBr_3$	Yellow	283-285	~77	
$C_{11}H_8NTeBr$	Yellow	178-180	65	
$C_{22}H_{16}N_2Te_2$	Yellow-orange	150-152	60	
$C_{22}H_{16}N_2Te_3$	Brown-red	165-166	~90	
$C_{22}H_{16}N_2Te$	Yellow	102-103	65	
$C_{22}H_{16}N_2Te.2HClO_4$	Dull yellow	270(dec.)	-	251 (CH_3CN)
$C_{22}H_{16}N_2TeHgClBr_3$	White	235-238	-	73.7 (CH_3NO_2)
$C_{19}H_{17}NOTeHgCl_4$	White		-	33.6 (DMSO)
$C_{19}H_{17}NOTe$	Pale yellow	124-126	67	
$C_{14}H_{14}N_2S_2Te^{(b)}$	Yellow	165-166	70	
$PdCl_2.C_{22}H_{16}N_2Te$	Yellow-brown	230(dec.)	-	2.0(DMSO)
$C_{15}H_{11}N$	White	84-85	65	
$C_{15}H_{10}NHgCl$	White	180-182	~34	
$C_{15}H_{10}NTeBr_3$	Bright yellow	~340	63	
$C_{15}H_{10}NTeBr$	Yellow	150(dec.)	-	
$C_{30}H_{20}N_2Te_2$	Orange	220-222	~90	
$C_{30}H_{20}N_2Te$	Yellow	187-189	~70	
$C_{30}H_{20}N_2Te_3$	Orange-brown	211-212	~80	
$C_{18}H_{16}N_2S_2Te^{(b)}$	Golden	206	65	

(a) Molar conductance ($ohm^{-1}cm^2mole^{-1}$) of $10^{-3}M$ solution

(b) Prepared from the corresponding tribromide compound.

Table 6.3. Some physical properties of the pyridine and quinoline derivatives

Compound$^{(a)}$	^{13}C Chemical shifts(ppm) relative to TMS											
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	
	149.1	119.9	136.2	121.5	156.7	138.8	126.3	-	128.1	-	126.3	
						139.6	127.1	128.7	129	128.7	127.1	(b)
Py-HgCl	149.5	120.9	138.3	123.4	155.9	141.3	147.9	137.8	128.2	129.2	127.1	
						136.5	151	136.5	127.9	127.6	127.9	(c)
Py-TeBr$_3$	145.1	122.7	133.6	126.4	151.5	-	144.3	132.2	129.3	131.1	127.9	
	145.7	119.9	134.4	121.7	-	142.1	115.3	136.8	128.9	133.2	127	
	C12	C13	C14	C15	C16	C17						
	109.7	142.3	115.7	159.1	63.2	14.7						
 $\text{Py-Te-S-}\underset{12}{\overset{\text{S}}{\overset{\Vert}{\text{C}}}}\text{-N}(\text{CH}_3)(^{13}\text{CH}_3)$	142.9	119.9	134.6	122.2	154.1	134.9	130.1	137.9	126.3	130.3	126.1	C13 44.7
(Py)$_2$Te$_3$	146	119	137.2	122.3	-	140.2	120.4	140.7	129.5	125.6	126.8	

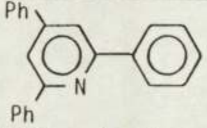
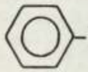
(a) Py = 2-(2-pyridyl)phenyl, (b) Data for  , (c) Data for  -HgCl (ref.132)

Table 6.4. ^{13}C NMR data of some 2-phenylpyridine derivatives.

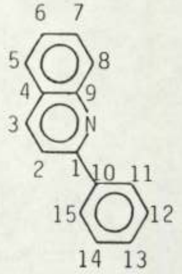
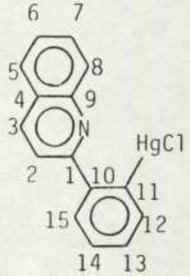
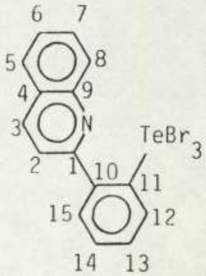
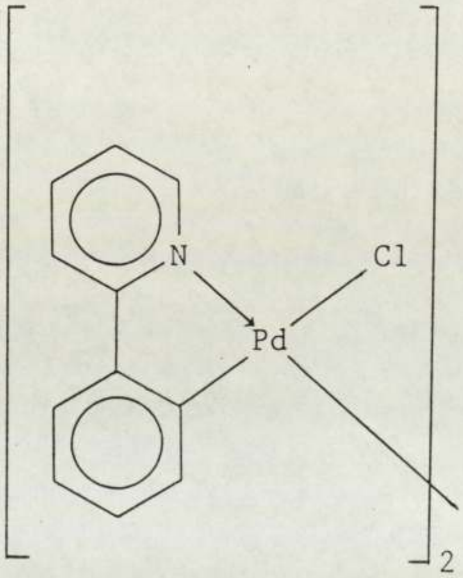
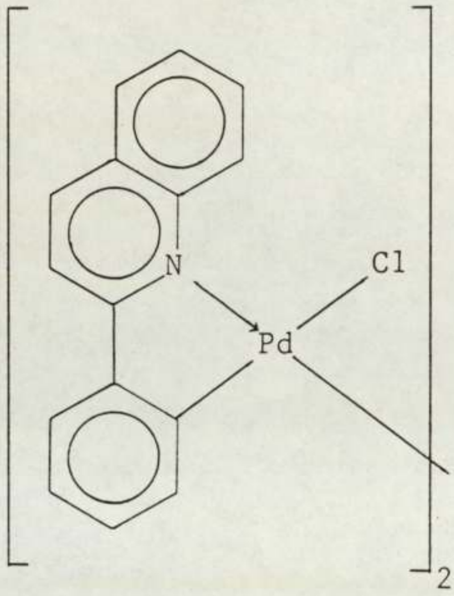
Compound	^{13}C Chemical shifts (ppm) relative to TMS														
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15
	156.2	118.8	137.2	127.8	127.2	126.5	129.6	129.9	147.6	138.7	127	128.9	129.1	128.9	127
	156	119.1	135	-	127.9	126.8	-	130.4	146.3	141.1	150	138.2	130.1	128.2	127.4
	150.9	118.9	132.7	-	128.5	124.5	129.6	131.8	144.7	140.8	-	134.4	131.8	-	127.8

Table 6.5. ^{13}C NMR data of some 2-phenylquinoline derivatives.

2-Phenylpyridine and 2-phenylquinoline were shown to be ortho-palladated when reacted with sodium tetrachloropalladate in alcohol. The resulting yellow compounds were believed to have the dimeric structure (iv) and (v), in which the co-ordination group comprises the σ-Pd-C bond and Pd←N.



(iv)



(v)

It has been pointed out that for ortho-metallation reactions to take place, the metal centre should be coordinatively unsaturated and highly electrophilic(179). These two properties of tellurium have been used to stabilise the rather unstable organotellurenyl compounds. As an example, azobenzene was orthometallated by using $TeCl_4$ in forcing conditions, to get the (2-phenylazophenyl-C,N')tellurium(IV)trichloride which could be reduced by hydrazine hydrate into the phenylazophenyl(C,N')-tellurium(II)chloride(117,180).

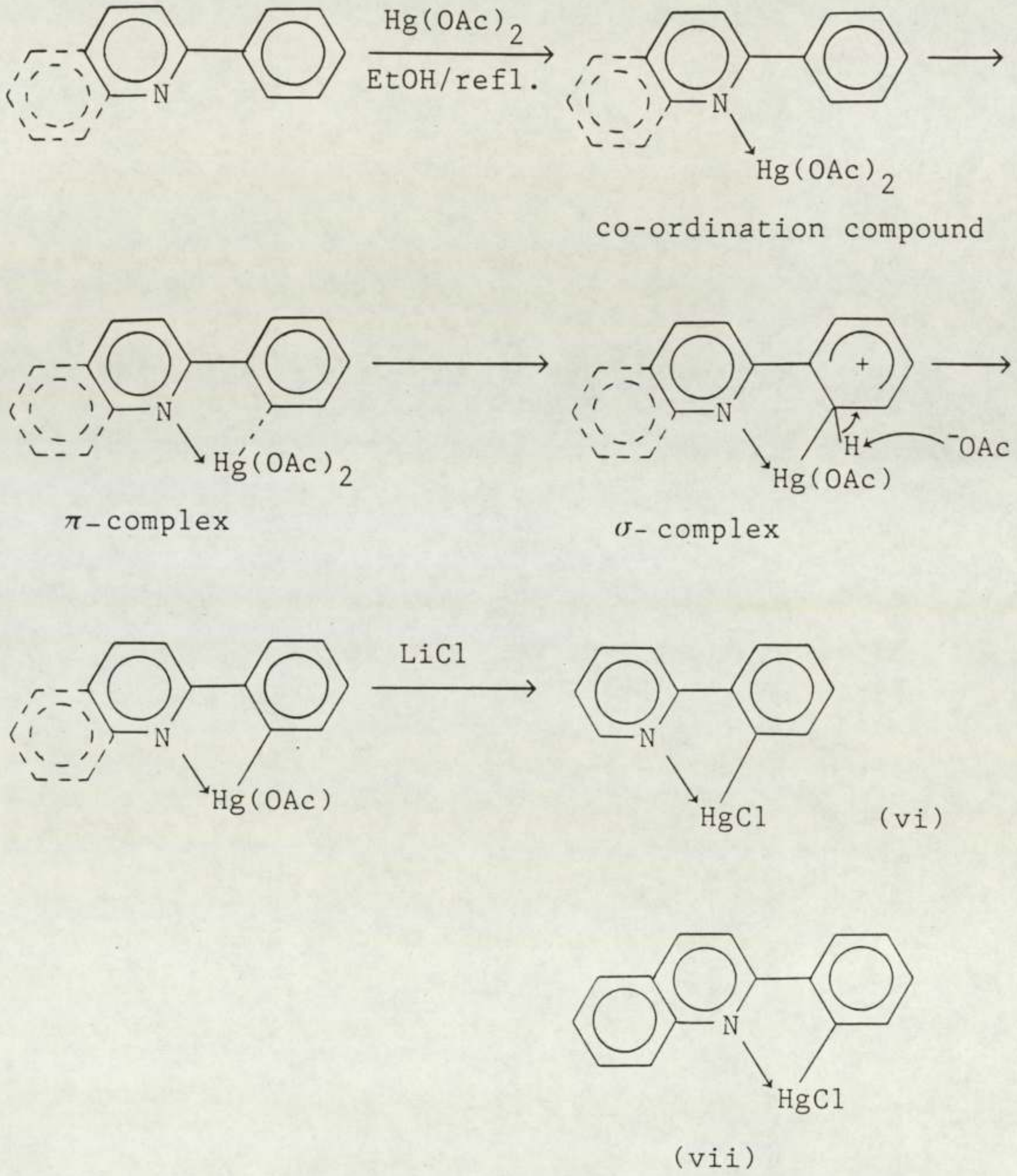
However, using tellurium tetrachloride for direct metallation is not always easy and successful. A previous worker in the laboratory attempted the direct metallation of some typical Schiff bases by tellurium tetrachloride and tetrabromide, and found that the reaction of tetrahalides gave only ionic compounds containing the protonated bases (181) . Direct telluration and trans-metallation of some Schiff bases and mercurated Schiff bases, using $TeCl_4$ were reported to give ionic products, despite taking precautions to dry solvents (128) . However trans-tellurations of some mercurated Schiff bases using $TeBr_4$ or (4-ethoxyphenyl)tellurium(IV)trichloride were successful (128).

Pyridine and quinoline compounds are, in fact, as susceptible as Schiff bases towards protonation. Therefore, the use of tellurium tetrachloride was avoided in the present work, and mercuration was done as a first step.

The weaker electrophile mercuric acetate ($Hg^{2+} + 2e \longrightarrow Hg^\circ$, $E^\circ = 0.85V$) (182) was used in mercuration since, in its reactions, the metal often remains in the Hg(II) state and affords stable mercurated products,whereas covalent mercuric chloride was reported to be a poor electrophile (183) .

A method similar to that reported for the mercuration of azobenzene (184) was adopted. When 2-phenylpyridine or

2-phenylquinoline was treated with mercury(II) acetate followed by addition of lithium chloride in methanol, compounds (vi), and (vii) were obtained resulting from attack at the phenyl ring

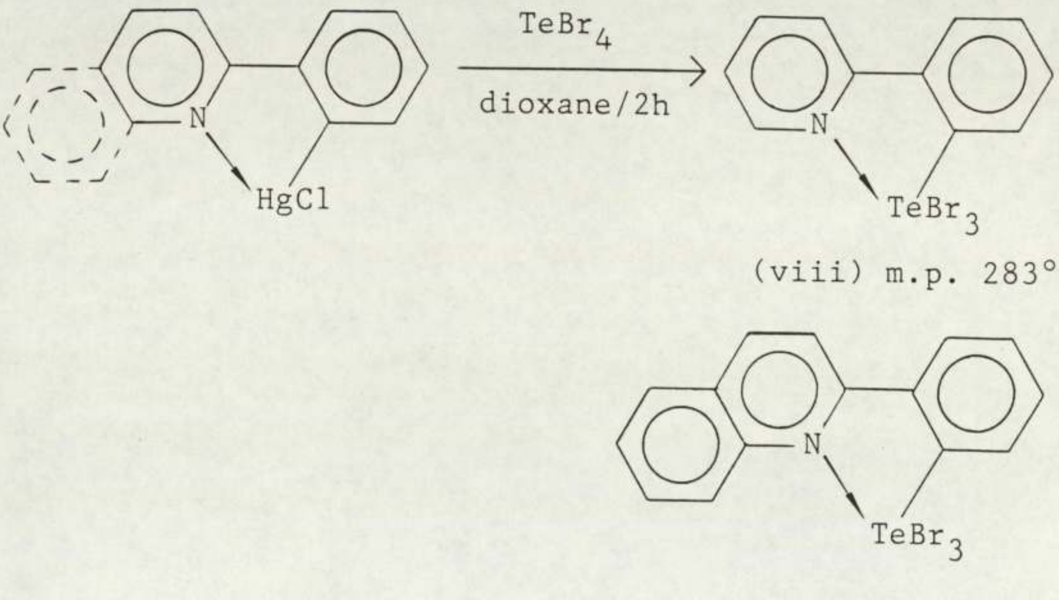


Scheme 6.1 A possible mechanism for the mercuration of 2-phenylpyridine and 2-phenylquinoline

6.3.2 Transmetallation

Arylmercury compounds have proved valuable for their trans-metallation properties, and this characteristic has been used in the present study for synthesis of the desired organotellurium compounds. In the trans-metallation of the mercurated derivatives (vi) and (vii) tellurium tetrachloride was not used, and instead $TeBr_4$ and 4-C_2H_5O-$C_6H_4TeCl_3$ were chosen to avoid protonation of the heterocylic ring as mentioned earlier.

The reaction of $TeBr_4$ with compound (vi) or (vii) in 1:1 molar ratios in refluxing dioxane afforded yellow compounds (viii) and (ix), which were separated from the warm solution by filtration. In this case the resulting mercury(II) chloride was washed out with the filtrate.

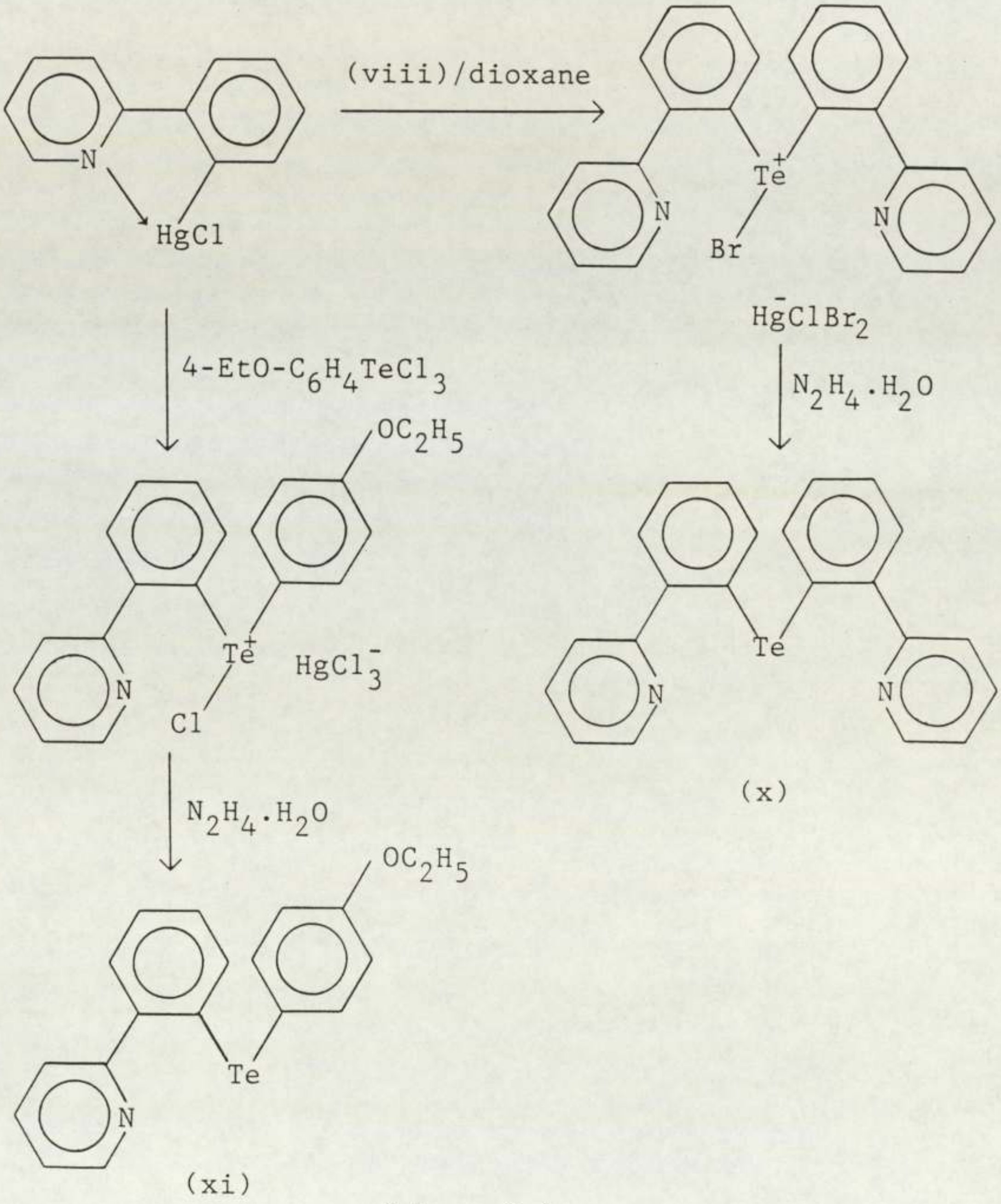


(viii) m.p. 283°C

(ix) m.p. 340°C

Scheme 6.2

The reaction of the mercurated compound (vi) with the tribromide (viii) or $4\text{-}C_2H_5O\text{-}C_6H_4TeCl_3$ should give the diorganyltellurium(IV) dihalides, but the elemental analysis suggests that mercury(II) halide was not released into the solution. Therefore, HgX_2 (X = Cl, Br) adducts of unknown structures were obtained, which were



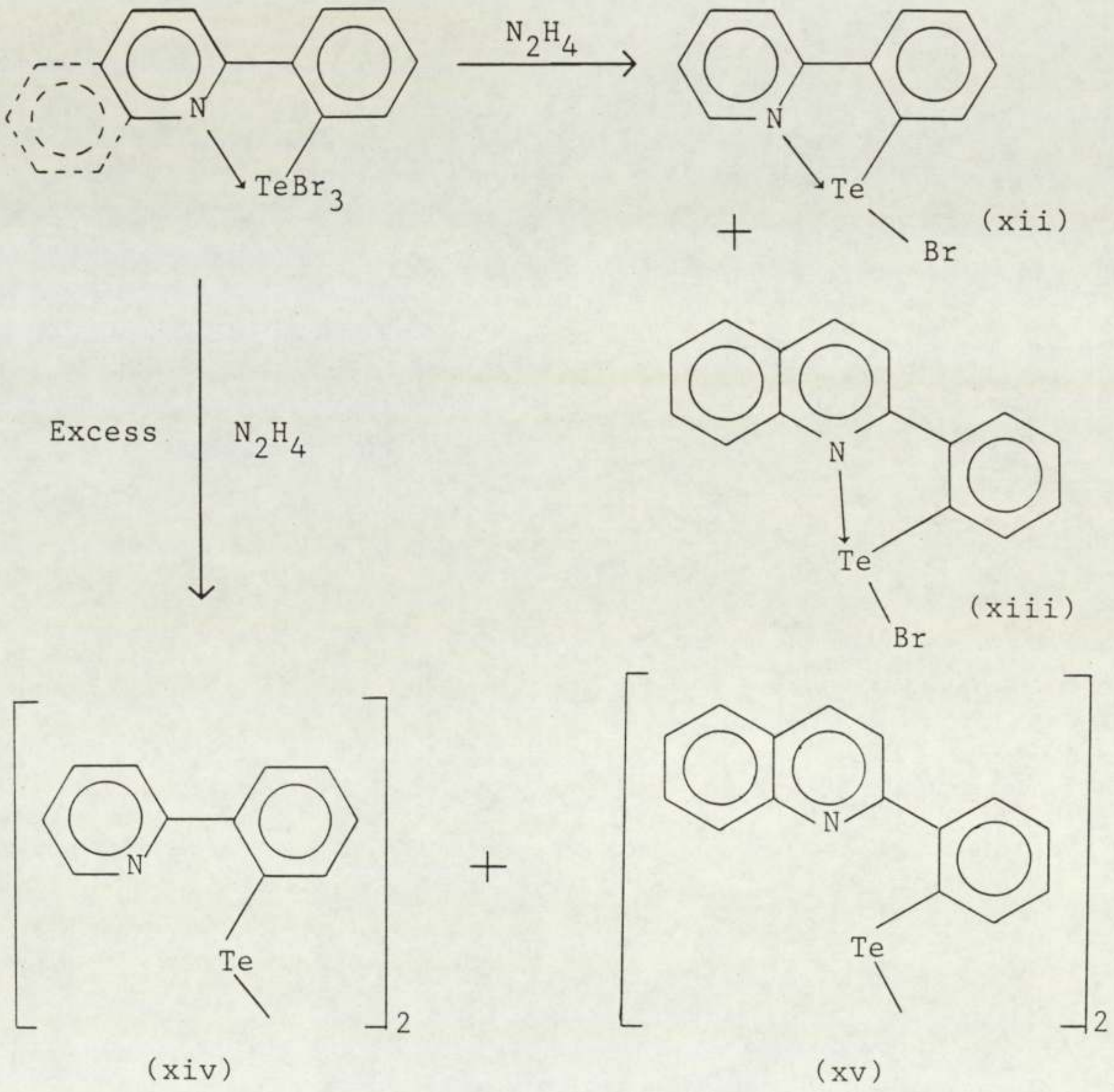
Scheme 6.3

shown by conductivity measurements to be 1:1 electrolytes (Table 6.3). However, reduction of these adducts with hydrazine caused the precipitation of elemental mercury and the formation of tridentate and bidentate ligands (x) and (xi). The above finding may indicate that these adducts could be in a form of telluronium cation and HgX_3^- anion, which upon reduction can give a Te(II) compound and Hg° (Scheme 6.3). This implies that the affinity of tellurium to nitrogen is more than mercury. Crystals of (xi) were obtained from ethanol solution, while compound (x) did not afford crystals, and it was converted to the crystalline perchlorate salt by reacting it with perchloric acid in methanol.

6.3.3 Reduction Reactions

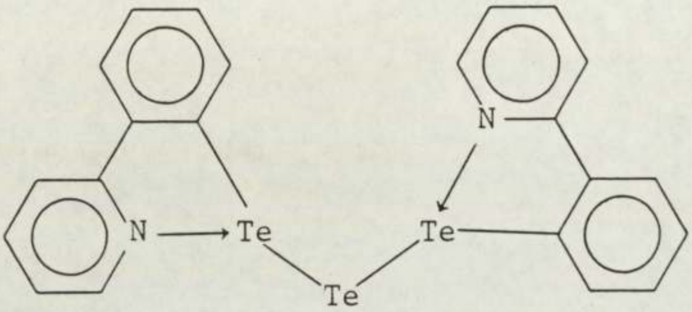
6.3.3.1 Reduction of 2-(2-pyridyl)- and 2-(2-quinolinyl)-phenyltellurium(IV)tribromide

Reduction of organotellurium(IV)trihalides, which have a donor group in the ortho-position, with N_2H_4 (180b,181b) or with sodium bisulphite (185) afforded organotellurenylhalides, which are stabilised by the intramolecular interaction. It has been reported also that reduction of such compounds with excess hydrazine could afford the corresponding ditelluride (180a). This phenomenon was applied, and the present tribromide compounds (viii) and (ix) were reduced with ethanolic hydrazine hydrate. By using 1:1 reactant ratios, yellow crystalline compounds were obtained, whose elemental analysis data (Tables 6.1 and 6.2) agree with the formation of the tellurenylbromides (xii) and (xiii). When an excess of hydrazine hydrate was reacted with the tribromides (viii) and (ix) a yellow-orange and an orange compounds were obtained respectively, whose elemental analyses showed that they are the ditellurides (xiv) and (xv).



Scheme 6.4

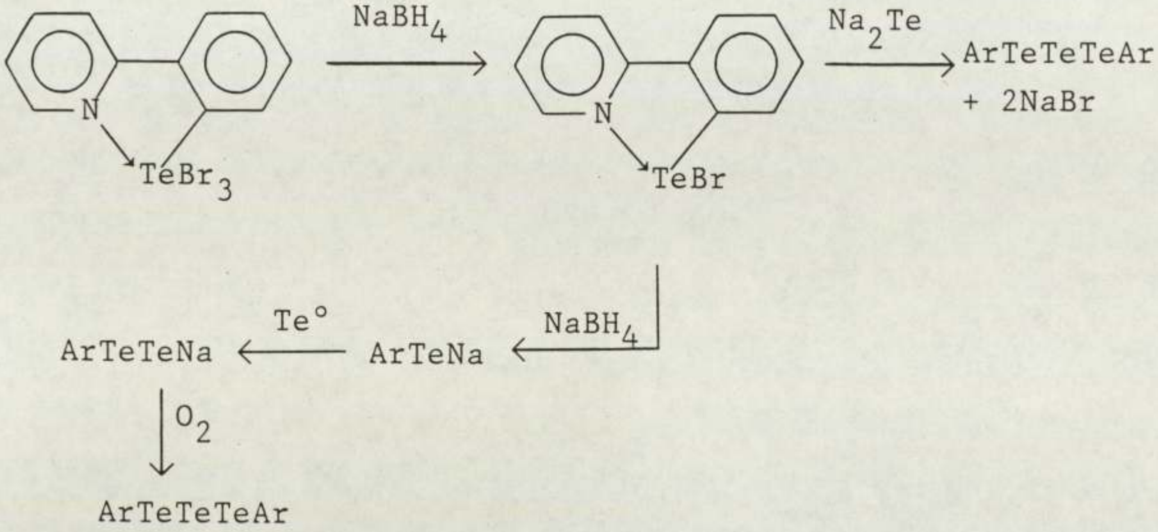
Whilst attempting to reduce the tribromides (viii) and (ix), by use of $NaBH_4$, to the sodium organyltelluride(-1), a brown-red and an orange compounds were obtained respectively. Elemental analysis data showed that the quinolinyl derivative was the ditelluride (xv), while the pyridyl derivative was a novel tritelluride compound (xvi).



(xvi)

6.3.3.2 The Formation of Bis(2-(2-pyridyl)phenyl)tritelluride

The deposition of tellurium metal during the reduction of 2-(2-pyridyl)phenyltellurium(IV)tribromide by $NaBH_4$ may provide a clue for the mechanism in which the bis(2-(2-pyridyl)phenyl)tritelluride has formed. During the first step of the reduction, 2-(2-pyridyl)phenyltellurium(II)-bromide may have formed. This could react with sodium telluride which is known to to be generated in solution by the reaction of $NaBH_4$ and tellurium. An alternative mechanism is that tellurium could insert into the tellurenyl salt to give the product according to scheme 6.5.

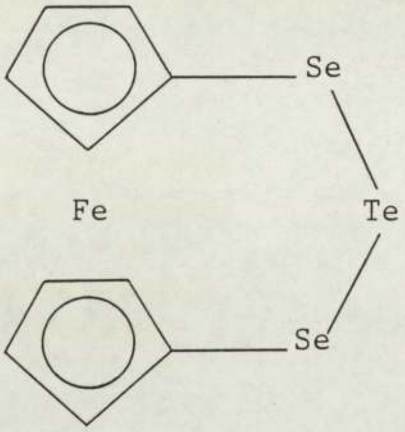


Scheme 6.5

However, no tellurium was noticed during the reduction of 2-(2-quinolinyl)phenyltellurium(IV)tribromide with $NaBH_4$, and therefore, the reduction process went through to the ditelluride. In a separate experiment tellurium metal was deliberately added to the mixture, and consequently, the corresponding tritelluride compound was obtained according to the elemental analysis data. This may confirm the above suggestion of the role of Te^{2-} in scheme 6.5. More mechanistic studies of this reaction are needed, however, before a satisfactory explanation may be given.

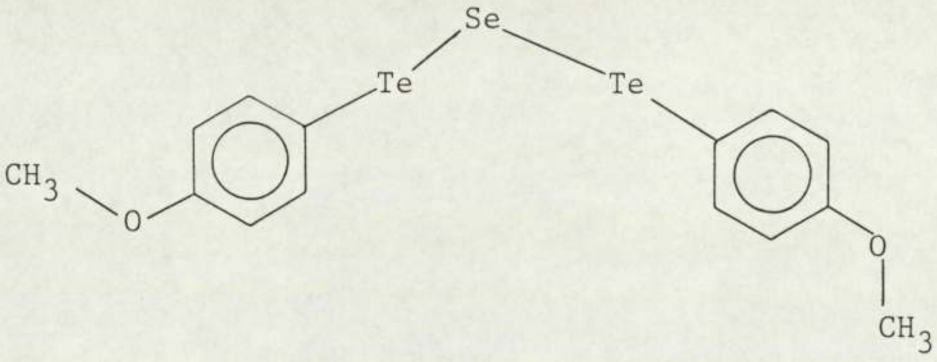
Organic triselenide have been reported to easily form, in contrast to the corresponding tritellurides. 1,2,3-triselena-[3]ferrocenophane and 1,3-diselena-2-tellura-[3]-

ferrocenophane (xvii), for examples, were reported with the absence of the tritellura-derivative(186). Compound (xvii) was prepared by the reaction of ferrocene 1,1'-diselenol with tellurium dichloride.

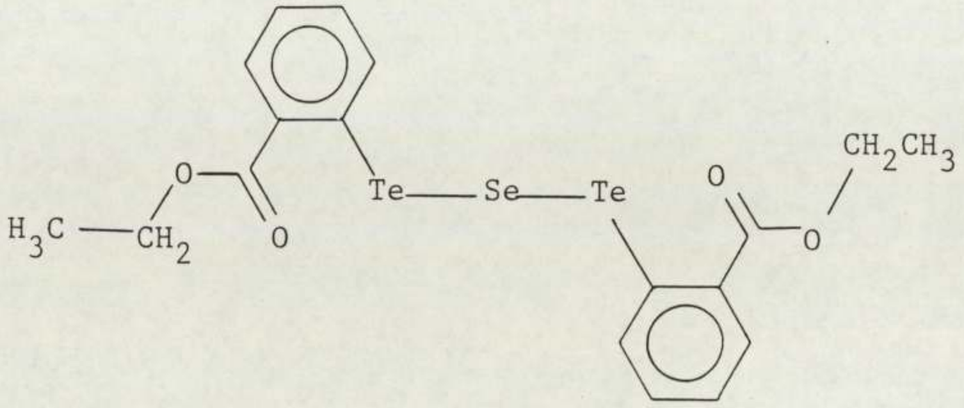


(xvii)

Zingaro et al (187) have reported the molecular structures of bis(4-methoxybenzenetellurenyl)selenide (xviii) and bis(2-ethylcarboxybenzenetellurenyl)selenide (xix), which involves a Te---O interaction (Te---O distance 2.658 Å).

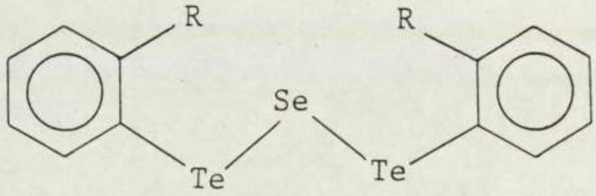


(xviii)



(xix)

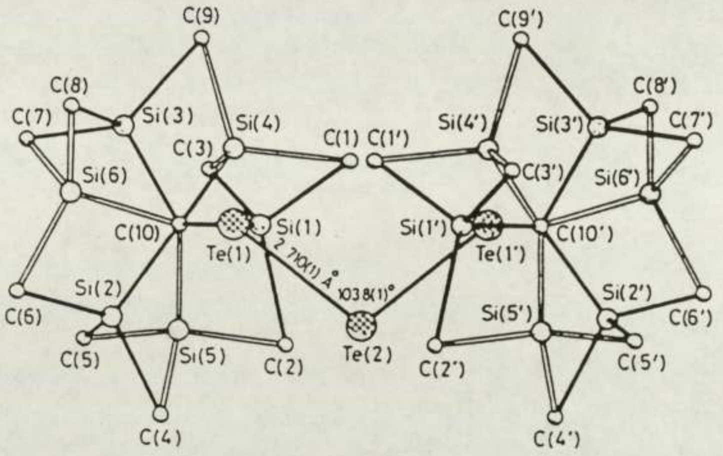
Later on Zingaro et al[(188)] reported the preparation and N.M.R. data of $(ArTe)_2Se$ compounds (xx), formed by reacting the ditellurides with SeO_2 in hot pyridine.



R = CHO, COOH

(xx)

Apart from the ionic tritelluride $[crypt\text{-}K^+]_2[Te_3^{2-}]$ (crypt = 4,7,13,16,21,24-hexa-1,10-diazabicyclo-[8.8.8]-hexacosane, $C_{18}H_{36}N_2O_6$)[(189)], the organic tritellurides remained unknown until recently, when in 1985, Sladky et al[(190)] reported the molecular structure of $[(Me_3Si)_3\text{-}C]_2Te_3$ (xxi) which involves a Te-C bond. The structure of the above tritelluride (xxi) was, in fact, reported while the structure of the present bis(2-(2-pyridyl)phenyl)tritelluride was being solved.



(xxi)

The tritelluride (xxi) was prepared by a rather different method to that used in the preparation of the present tritelluride. A lithiated compound was reacted with two equivalents of Te, then oxidised to give compound (xxi) as illustrated in scheme 6.6.

$$\mathrm{TsiLi} \xrightarrow{2\mathrm{Te}} \mathrm{TsiTeTeLi} \xrightarrow{H_2O/O_2} \mathrm{TsiTeTeTeTsi}$$

red-black crystals

(xxi)

Tsi=tris(trimethylsilyl)methyl-

Scheme 6.6

6.3.3.3 The Molecular Structure of Bis(2-(2-pridyl)phenyltritelluride*

Crystals of bis(2-(2-pyridyl)phenyltritelluride suitable for single crystal X-ray diffraction study were obtained from benzene/toluene mixture. The density was determined in EtOH/$CHBr_3$. The cell dimensions and reflection intensities were measured with an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-K_α radiation. 1634 reflections in the range $2 < \theta < 25$; $I > 2.5\sigma(I)$ were used in the analysis. The structure was solved by Patterson and Fourier methods and refined by least-squares with SHELX-76 (74), using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located from a difference map and included in fixed positions. The calculations were terminated when all shifts/error ratios were < 0.1, and R and R_w were 0.064 and 0.088, respectively. The weighing scheme used was $w = 1/(\sigma^2(F)+0.005F^2)$.

The structure was drawn with PLUTO (113) and is shown in Figure 6.1.

Crystal data:

$C_{22}H_{16}N_2Te_3$, $M_r = 691.2$

Monoclinic, space group I2/c

---

*T. A. Hamor, N. Al-Salim, A. A. West and W. R, McWhinnie, J. Organomet. Chem., 1986, 310, C5.

$a = 14.721(3)$, $b = 9.290(4)$, $C = 15.996(10)$

$\beta = 106.39(3)°$

$U = 2098.7\ \text{Å}^3$

$Z = 4$, $D_c = 2.188\text{gcm}^{-3}$, $D_{exp.} = 2.09\text{gcm}^{-3}$

$F(000) = 1272$

$\mu = 3.92\ \text{mm}^{-1}$

The atomic co-ordinates, anisotropic temperature factors, and bond lengths and bond angles are given in Tables 6.6, 6.7 and 6.8 respectively.

The compound exhibits two-fold symmetry with the central tellurium atom laying on a crystallograpic two-fold axis.

The Te(1)-C(1) bond length, 2.130 Å, found in this compound, is close to that in some aromatic ditellurides, e.g. bis(4-methylphenyl)ditelluride(191), and is longer by 0.007 Å than the corresponding length in bis(2-ethylcarboxybenzenetellurenyl)selenide (xix).

The Te(1)-Te(2) bond length, 2.776 Å, found in the present tritelluride is longer than Te-Te bond lengths found in aromatic ditelluride compounds(191,192). It is also longer than Te(1)-Te(2) bond length found in bis(tris-(trimethylsilyl)methyl)tritelluride(190) by 0.066 Å, a difference which may be a manifestation of somewhat stronger Te-C binding involving an aromatic carbon atom (Te-C shorter by 0.083) in our compound. It could be

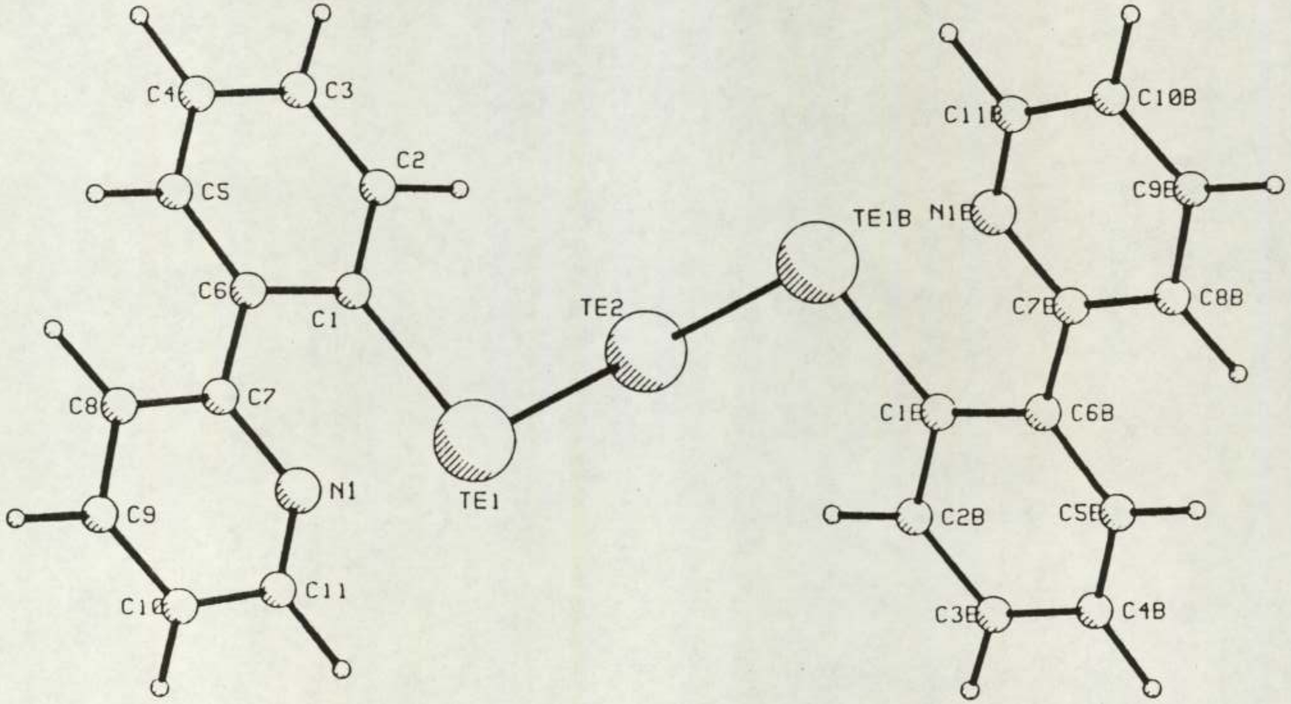


Figure 6.1 : The molecular structure of bis[2-(2-pyridyl)phenyl]tritelluride

Atom	x	y	z	U(iso)
Te1	706(1)	5097(1)	1505(1)	*
Te2	0	3184(1)	2500	*
N(1)	1619(5)	6771(8)	765(5)	*
C(1)	2154(6)	5107(8)	2254(6)	*
C(2)	2453(6)	4235(9)	3021(5)	*
C(3)	3403(7)	4236(10)	3511(6)	*
C(4)	4033(8)	5141(11)	3253(9)	*
C(5)	3747(6)	5970(10)	2531(6)	*
C(6)	2826(5)	5967(8)	2019(5)	*
C(7)	2536(7)	6856(8)	1230(6)	*
C(8)	3146(8)	7702(12)	937(8)	*
C(9)	2791(11)	8492(12)	155(9)	*
C(10)	1856(11)	8344(12)	-297(8)	*
C(11)	1302(8)	7486(10)	41(6)	*
H(2)	1921	3556	3190	80(11)
H(3)	3592	3598	4088	80(11)
H(4)	4754	5147	3660	80(11)
H(5)	4244	6656	2335	80(11)
H(8)	3909	7794	1313	80(11)
H(9)	3308	9154	-63	80(11)
H(10)	1620	8974	-902	80(11)
H(11)	532	7433	-366	80(11)

Table 6.6. Fractional atomic co-ordinates (Å x 10^4) with e.s.d.'s in parentheses, and isotropic temperature factors($Å^2$x 10^3)

* Atoms are anisotropically refined (Table 6.7)

	U11	U22	U33	U23	U13	U12
Te(1)	55(1)	46(0)	45(1)	1(0)	20(0)	-2(0)
Te(2)	65(1)	43(1)	57(1)	0(0)	33(0)	0(0)
C(2)	64(4)	52(5)	50(4)	7(4)	13(3)	11(4)
C(3)	68(5)	62(5)	58(5)	0(4)	14(4)	7(4)
C(4)	65(5)	71(7)	85(8)	-8(5)	5(6)	17(5)
C(5)	50(4)	57(5)	79(6)	-16(5)	29(4)	-6(4)
C(6)	62(4)	37(4)	53(4)	-19(3)	28(3)	-3(3)
C(1)	61(4)	38(4)	49(5)	-9(3)	22(4)	0(3)
C(8)	90(7)	64(5)	92(8)	-14(6)	52(6)	-27(5)
C(9)	127(10)	61(6)	90(9)	-1(6)	66(8)	-25(6)
C(10)	137(11)	62(6)	66(7)	-7(5)	46(7)	-21(7)
C(11)	106(7)	52(5)	53(5)	1(4)	31(5)	-13(5)
N(1)	68(4)	53(4)	48(4)	-2(3)	24(3)	-13(3)
C(7)	79(5)	40(4)	52(4)	-17(3)	42(4)	-14(3)

Table 6.7. Anisotropic temperature factors ($\mathring{A}^2 x\ 10^3$)
with e.s.d.'s in parentheses.

Te(1)---Te(2)	2.776(1)	C(7)---C(8)	1.371(12)
Te(1)---C(1)	2.130(9)	C(8)---C(9)	1.416(18)
Te(1)---N(1)	2.554(7)	C(9)---C(10)	1.369(21)
C(1)---C(2)	1.431(12)	C(10)---C(11)	1.357(15)
C(2)---C(3)	1.397(13)	C(11)---N(1)	1.302(12)
C(3)---C(4)	1.396(15)	N(1)---C(7)	1.348(13)
C(4)---C(5)	1.352(16)		
C(5)---C(6)	1.373(11)		
C(6)---C(1)	1.403(11)		
C(6)---C(7)	1.467(13)		
C(1)-Te(1)-Te(2)	99.1(2)	C(11)-N(1)-Te(1)	128.3(7)
N(1)-Te(1)-Te(2)	170.7(2)	C(7)-N(1)-Te(1)	110.9(5)
N(1)-Te(1)-C(1)	71.6(3)	C(8)-C(7)-C(6)	123.9(9)
Te(1)-Te(2)-Te(1)'	100.4(1)	N(1)-C(7)-C(6)	116.4(7)
N(1) C(7) C(6) C(5)	179.39	C(8) C(7) C(6) C(5)	1.79
N(1) C(7) C(6) C(1)	-0.76	C(8) C(7) C(6) C(1)	-178.36

Table 6.8. Bond lengths(Å), bond angles(°) and torsion angles(°) for bis(2-(2-pyridyl)phenyl)tritelluride. Other ring inner angles range between 118.4 - 123.3°.

P_1 Plane defined by C(1), C(2), C(3), C(4), C(5), C(6)

$0.3730X - 0.7463Y - 0.5512Z + 4.6427 = 0$

P_2 Plane defined by C(7), C(8), C(9), C(10), C(11), N(1)

$0.3750X - 0.7737Y - 0.5105Z + 4.6989 = 0$

P_3 Plane defined by Te(1), C(1), C(6), C(7), N(1)

$0.3620X - 0.7632Y - 0.5352Z + 4.7070 = 0$

Angles between planes 1 and 2 is 2.81°

Atoms	P_1	P_2	P_3
Te(2)	0.1007	-0.0280	0.0126
Te(1)	0.0294	0.0082	0.0119
C(1)	0.0016	-0.0698	-0.0144
C(2)	0.0102	-0.1314	-0.0372
C(3)	-0.0143	-0.1889	-0.0609
C(4)	0.0064	-0.1313	-0.0082
C(5)	0.0058	-0.0655	0.0208
C(6)	-0.0097	-0.0469	0.0054
C(7)	-0.0347	0.0001	0.0130
C(8)	-0.0798	-0.0072	-0.0003
C(9)	-0.1301	0.0116	-0.0209
C(10)	-0.1778	-0.0091	-0.0727
C(11)	-0.1259	0.0018	-0.0532
N(1)	-0.0614	0.0027	-0.0160

Table 6.9. Equations of least-squares planes and deviations(Å) of atoms from planes for bis(2-(2-pyridyl)phenyl)tritelluride.

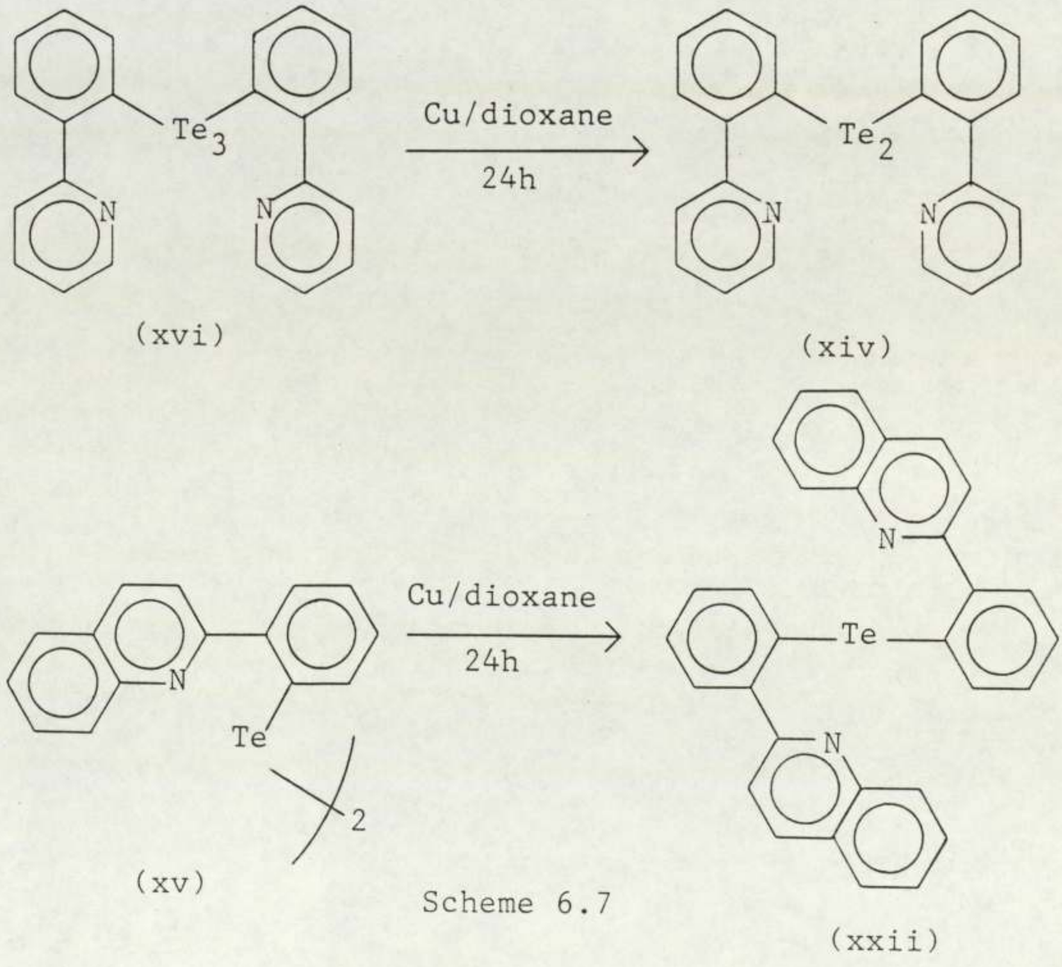
also due to the trans-influence of the co-ordinated pyridyl nitrogen, where non - bonded Te---N distance is 2.554 Å and N---Te(1)-Te(2) bond angle of 170.7(2)° is fairly close to 180°. This is absent in simple ditellurides and in the tritelluride compound (xxi).

The Te---N interaction appears to hold the ligand in an essentially planar geometry; the pyridyl and phenyl rings are, nevertheless, bent very slightly relative to one another to form shallow V shape, with internal angle 177.2(4)°. The co-ordination of Te(1) by Te(2), N and C(1) is accurately planar to within ±0.0127 Å (Table 6.9).

This tritelluride has a Te(1)-Te(2)-Te(1)' bond angle of 100.4(1)° and a torsion angle about the Te(1)-Te(2) bond of 97.3(3)° compared to 103.8(1)° and 105.2(2)°, respectively in $[(Me_3Si)_3C]_2Te_3$ (190) . The bulky $(Me_3Si)_3C$-groups are believed to contribute to the stability of the later compound. The present diorganyltritelluride, by contrast, appears to owe its stability to the significant Te---N interaction, suggesting that if the organic ligands have a suitably positioned donor atom, many more successful syntheses of tritellurides should be possible.

6.3.3.4 Reduction of Bis(2-(2-pyridyl)phenyl)tritelluride and Bis(2-(2-quinolinyl)phenyl)ditelluride

The reduction of these compounds was performed by heating a dioxane solution with copper powder. This is similar to the method used by Sadekov et al$^{(193)}$ when some diaryl-ditellurides were converted to symmetrical diaryl-tellurides with the formation of CuTe. The title tri-telluride and ditelluride were converted to the corresponding ditelluride and telluride compounds respectively. The tritelluride $[(Me_3Si)_3C]_2Te_3$ have been similarly converted to the corresponding ditelluride by shaking its pentane solution with mercury$^{(190)}$.



Scheme 6.7

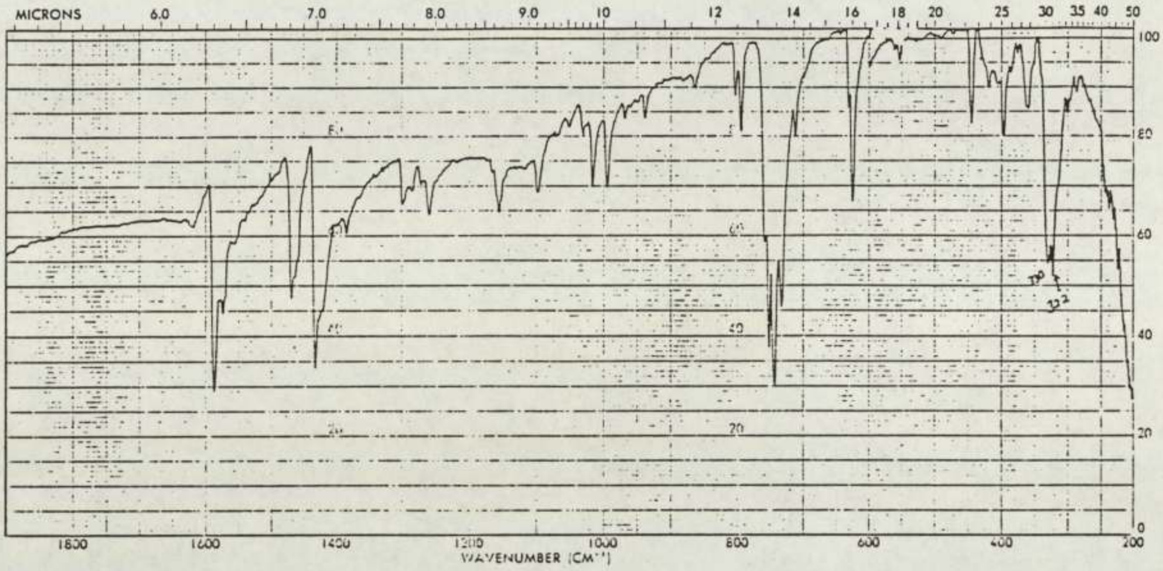


Figure 6.2 : I.R. spectrum of 2-(2-pyridyl)phenylmercury(II) chloride

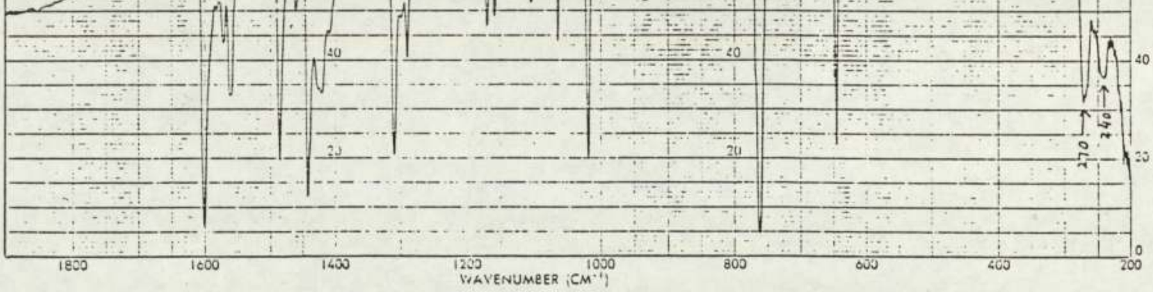


Figure 6.3 I.R. spectrum of 2-(2-pyridyl)phenyltellurium(IV) tribromide

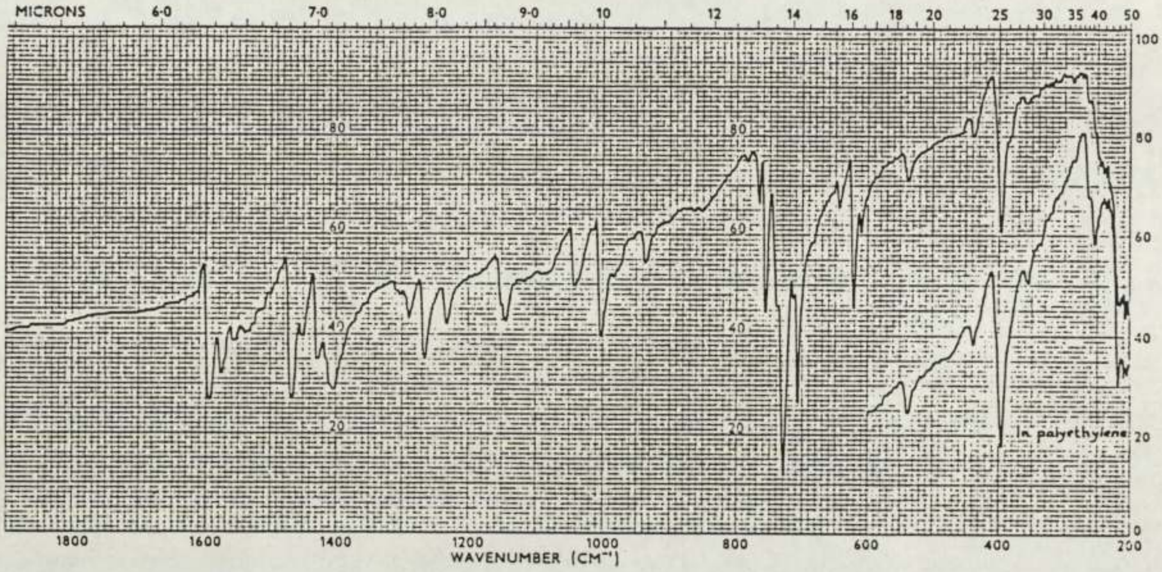


Figure 6.4 : I.R. spectrum of 2-(2-pyridyl)phenyltellurium(II)-bromide

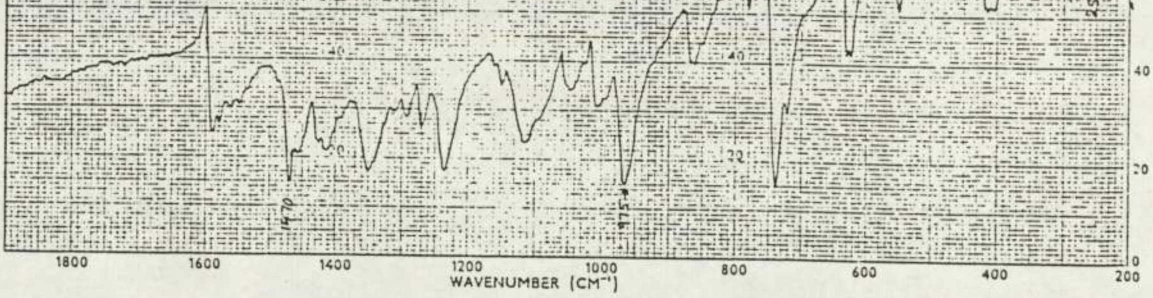


Figure 6.5 : I.R. spectrum of dimethyldithiocarbamato-2-(2-pyridyl)phenyltellurium(II)

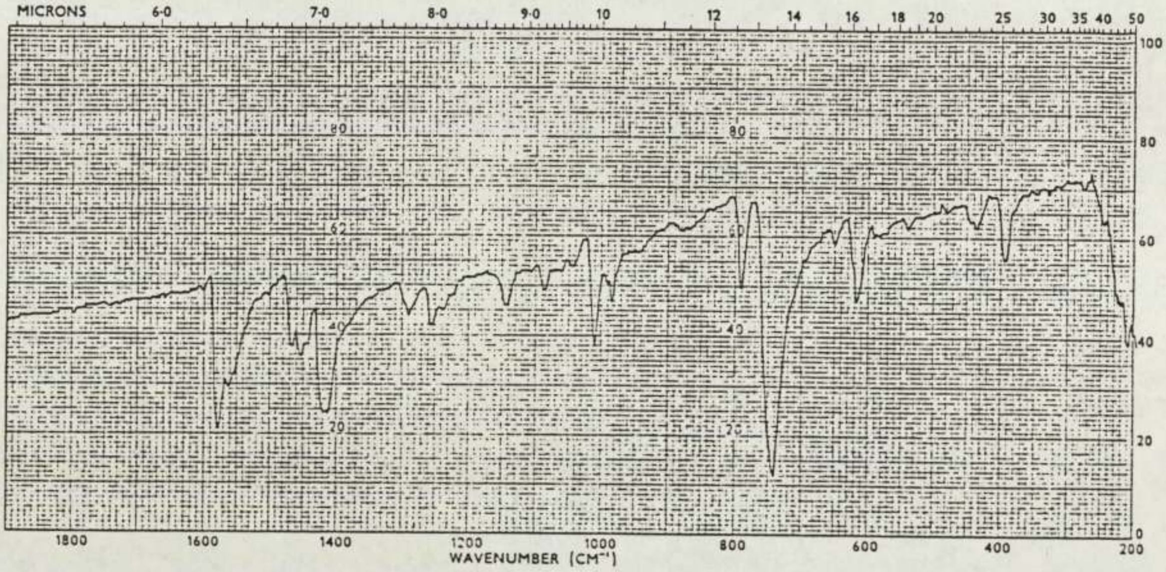


Figure 6.6 : I.R. spectrum of bis[2-(2-pyridyl)phenyl]-telluride

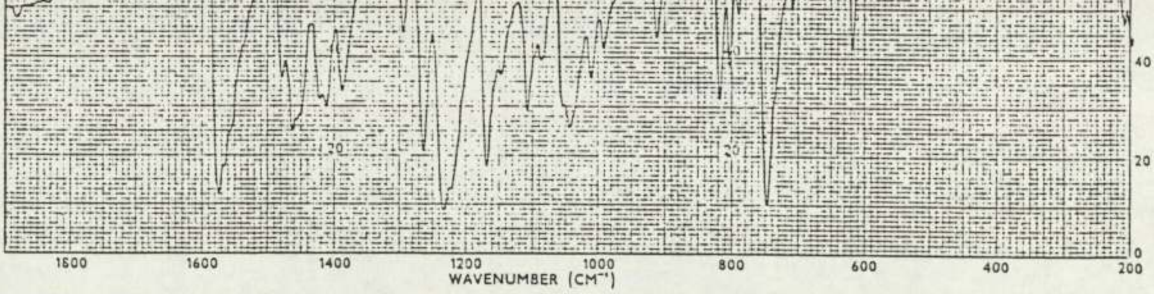


Figure 6.7 : I.R. spectrum of 4-ethoxyphenyl-2-(2-pyridyl)-phenyltelluride

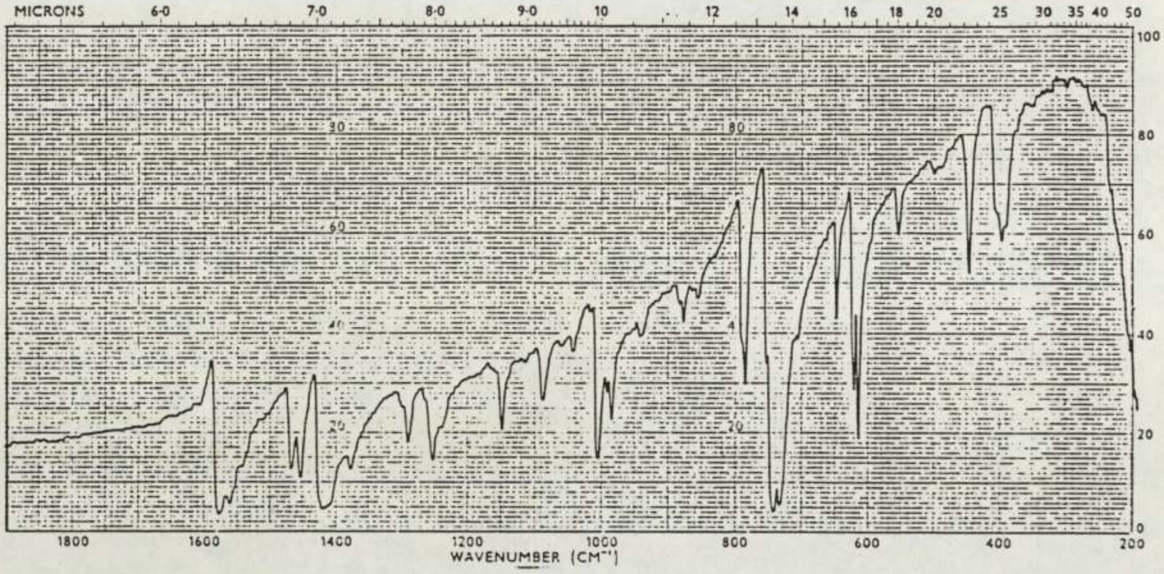


Figure 6.8 : I.R. spectrum of bis[2-(2-pyridyl)phenyl]-ditelluride

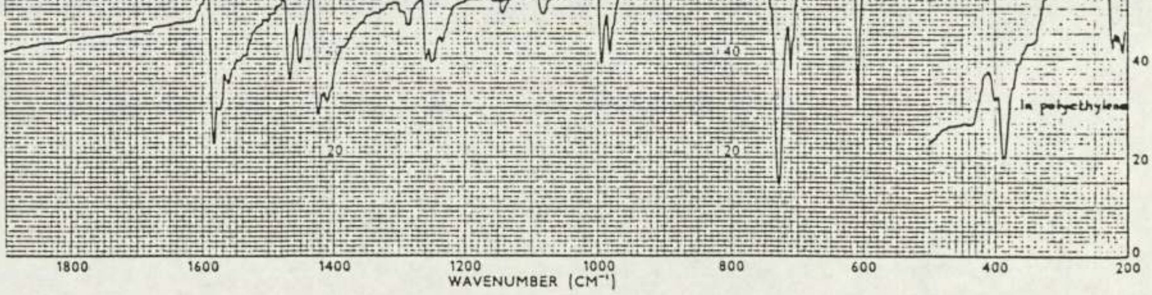


Figure 6.9 : I.R. spectrum of bis[2-(2-pyridyl)phenyl]-tritelluride

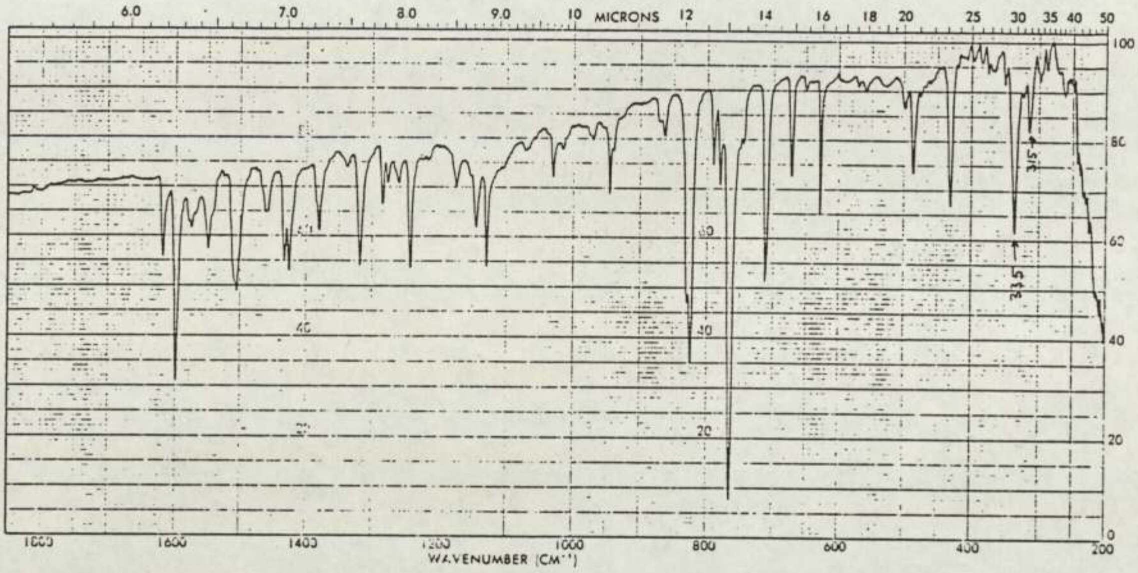


Figure 6.10 : I.R. spectrum of 2-(2-quinolinyl)phenylmercury(II)chloride

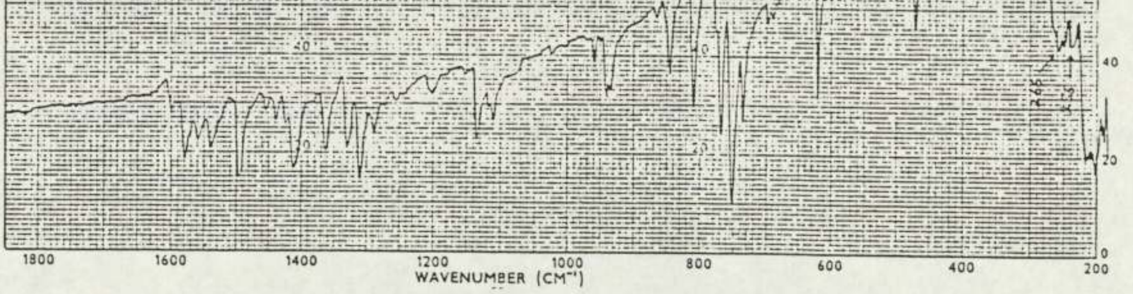


Figure 6.11 : I.R. spectrum of 2-(2-quinolinyl)phenyltellurium(IV)tribromide

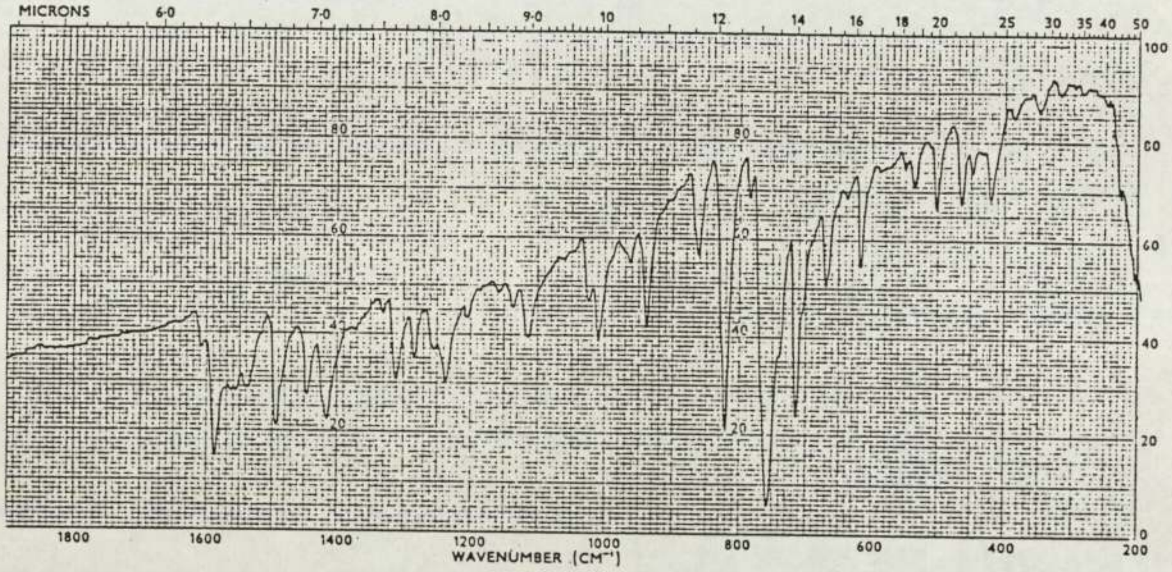


Figure 6.12 : I.R. spectrum of bis(2-(2-quinolinyl)phenyl)-telluride

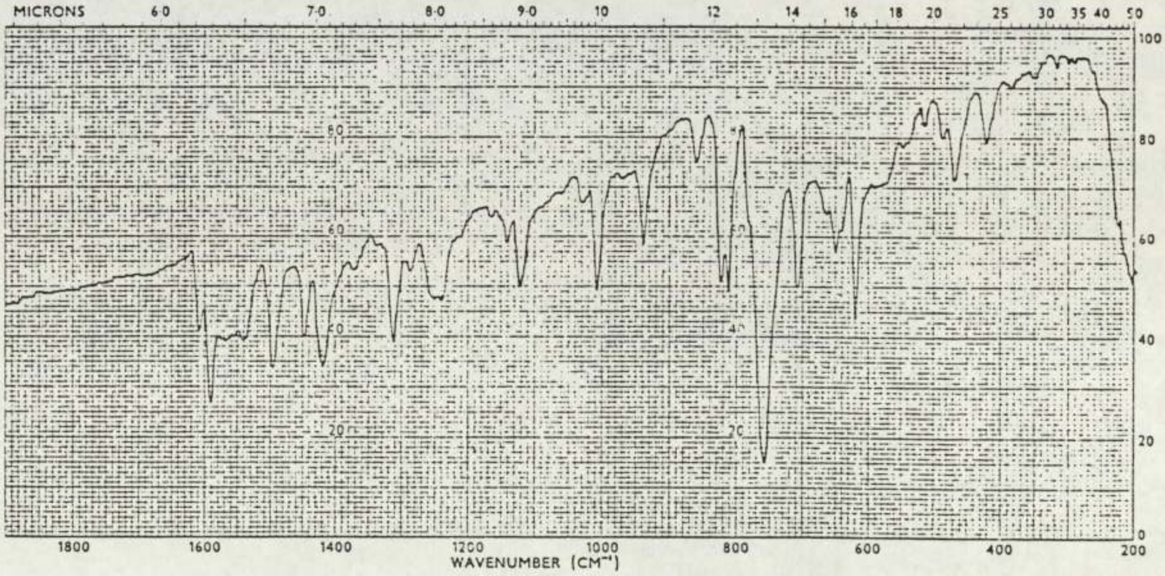


Figure 6.13 : I.R. spectrum of bis[2-(2-quinolinyl)phenyl]-ditelluride

6.3.4 Vibrational Spectroscopy

Some important infra-red absorptions of the pyridyl and quinolinyl derivatives are given in Table 6.10.

Mercuration of 2-phenylpyridine and 2-phenylquinoline should, in principle, produce compounds in which the mercury atom is three co-ordinated by carbon, halogen and nitrogen. Two ν_s(Hg-Cl) absorptions were found in the range 315-335cm^{-1} which are characteristic of a terminal Hg-Cl stretching, and the splitting may be due to a factor group splitting. For solid mercury(II) chloride, ν_s(Hg-Cl) has been assigned at 310, 330cm^{-1} (194), and therefore, it is reasonable to suggest that the two mercurated compounds (vi) and (vii) could be monomeric where C-Hg-X is linear and the hetrocyclic nitrogen is co-ordinating to mercury atom. The neutral chloro-complexes $HgCl_2$.L, where L is either 2-phenylpyridine or 2-phenylquinoline, do not show bands above 300cm^{-1} which could be assigned as ν(Hg-Cl). This is indicative of a structure with bridging chlorides in contrast to the mercurated compounds mentioned above.

The i.r. spectra of the tribromides (viii) and (ix) showed two bands in the lower frequency region between 240-270cm^{-1}, which may be a combination of ν(Te-C) and ν(Te-Br). Dance and McWhinnie(195) investigated the low frequency i.r. spectra of isotopically pure ^{126}Te- and

Compound (1)	δ Phenyl	δ Pyrid.,Quin.	Te-C + M-X(2)
2-phenylpyridine	690(s),744(vs)	610,620,638(s)	-
Py-HgCl	733,742,751(s)	625(m)	322,330(s)
Py-TeBr$_3$	762(s)	645(s)	270,240(s)
py-TeBr	710(s),730(vs)	610(m),620(s)	255(s)
Py$_2$Te$_2$	738,746(vs)	636(m),620(s)	-
Py$_2$Te$_3$	710(s),730(vs)	610(s)	-
ArPyTeHgCl$_3$	740(s),770(vs)	630(m),645(s)	322(m),287(vs)
ArPyTe	747(vs)	620(m)	-
Py$_2$Te.HClO$_4$	720,740(s)	600(s),630(m)	255(m)
Py$_2$Te	740(s)	618(m)	-
Py-Tedmdtc	720(s),740(vs)	625(m)	250(m)
	CS = 975(s)	CN = 1470(s)	
2-phenylquinoline	742,773(s)	684(s)	-
Q-HgCl	712(m),765(s)	630,671(m)	315m,335(s)
Q-TeBr$_3$	735,750,767(s)	636(s)	266,256(s)
Q-TeBr	725(s),760(s)	615(s)	260(w)
Q$_2$Te$_2$	710(m),760(s)	620(m)	-
Q$_2$Te$_3$	742(s)	605,660(s)	-
Q$_2$Te	715(s),760(vs)	620(m)	-
Q-Tedmdtc	CS = 945(s)	CN = 1470(s)	260(w)

(1) Py = 2-(2-pyridyl)phenyl- ;Q = 2-(2-quinolinyl)phenyl-

(2) M = Te, Hg; X = Cl, Br, S where applicable.

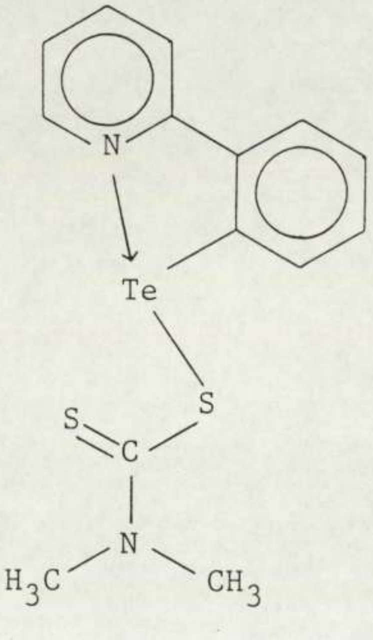
m = medium, s = strong, vs = very strong, w = weak.

Table 6.10. Some important i.r. absorptions of pyridyl and quinolinyl derivatives.

^{130}Te-$(C_6H_5)_2TeX_2$ (X = Cl, Br) and found that bands at 270 and 245cm^{-1} underwent shifts and therefore due to ν(Te-C). The ν(Te-Cl) modes at 286 and 245cm^{-1} were also shifted.

The i.r. spectra of the monobromides (xii) and (xiii) showed a single band at 255 and 260cm^{-1} respectively, which could be similarly due to ν(Te-C)$^{(195)}$.

The reaction of 2-(2-pyridyl)phenyltellurium(II)bromide or the corresponding tribromide with sodium dimethyldithiocarbamate afforded the mono-dithiocarbamato-2-(2-pyridyl)phenyltellurium(II), (xxiii), but not the <u>tris</u>-(dithiocarbamato) compound. Similarly the reaction of 2-(2-quinolinyl)phenyltellurium(IV)tribromide with sodium dimethyldithiocarbamate gave the mono-dithiocarbamato-derivative.



(xxiii)

The formation of some tris(dithiocarbamato)-compounds by the reaction of 2-phenylazophenyl(C,N')tellurium(IV)trichloride and sodium dialkyldithiocarbamate has been reported recently(196). However, these compounds which have been formulated as loose charge transfer complexes of the mono-dithiocarbamates [e.g., $Te(C_6H_4N_2C_6H_5)(CH_3)_2$-$NC(S)S$] and the disulphide $(CH_3)_2NC(S)S-SC(S)N(CH_3)_2$, readily dissociate in solution to give the mono-dithiocarbamate(196).

The i.r. spectrum of compound (xxiii) (Fig. 6.5) shows the characteristic bands of a co-ordinated dithiocarbamato-ligand. The ν(C-N) absorption is a strong band at 1470cm^{-1}, and the ν(C-S) band occured with a strong intensity at 975cm^{-1}. These correspond to the bands at 1485 and 980cm^{-1} which were reported for $Te(C_6H_4N_2C_6H_5)$-(dmdtc)(196). The observation of unsplit bands of ν(C-N) and ν(C-S) suggests the bidentate nature of dithiocarbamato-ligands(197), and the bidentate nature of the similar azo-derivative has been confirmed by X-ray study(196). The medium intensity band at 250cm^{-1} could be attributed to ν(Te-S). This occured at a lower frequency than that of the above mentioned azo compound which has been reported to be at 295cm^{-1}. The i.r. spectrum of dimethyldithiocarbamato-2-(2-quinolinyl)phenyltellurium(II) revealed strong bands at 1470 and 975cm^{-1} which could be assigned as ν(C-N) and ν(C-S) respectively.

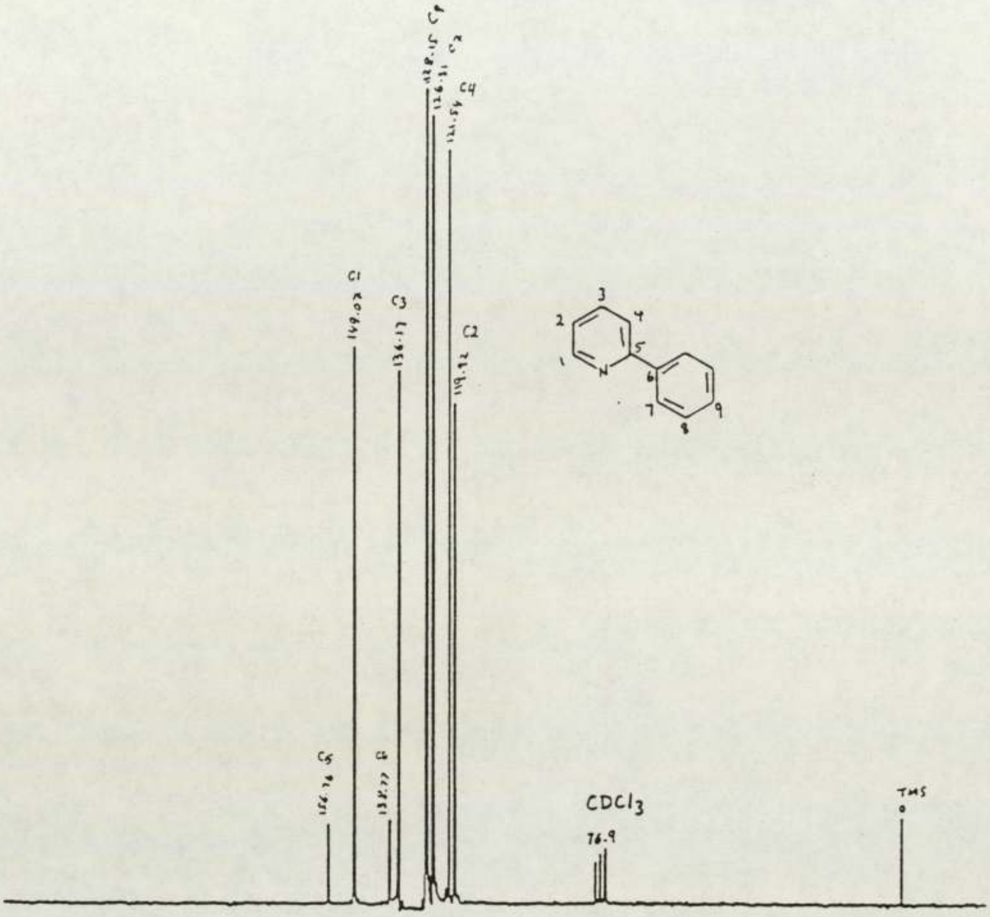


Figure 6.14 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{11}H_9N$ in $CDCl_3$

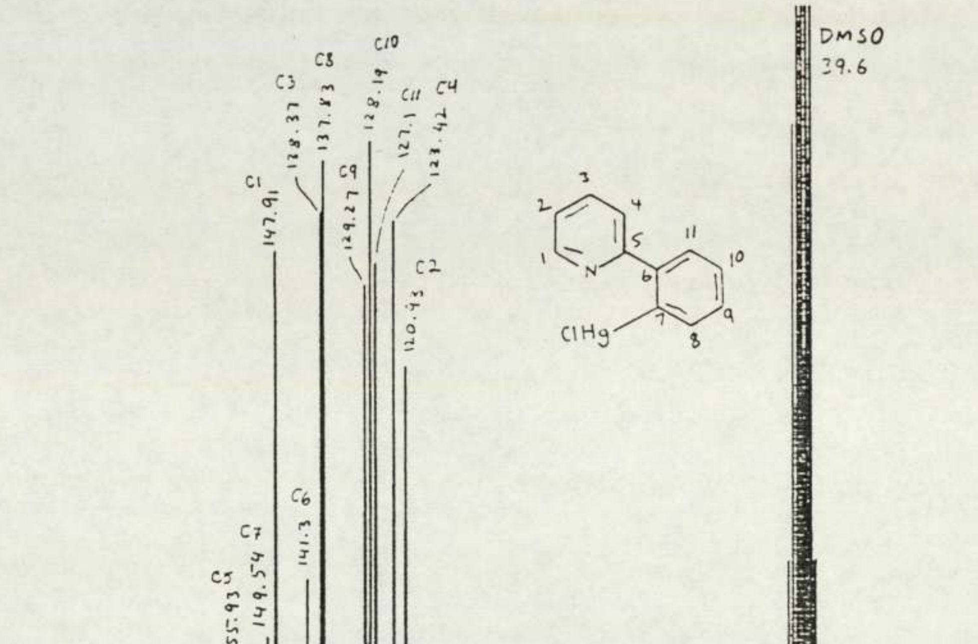


Figure 6.15 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{11}H_8NHgCl$

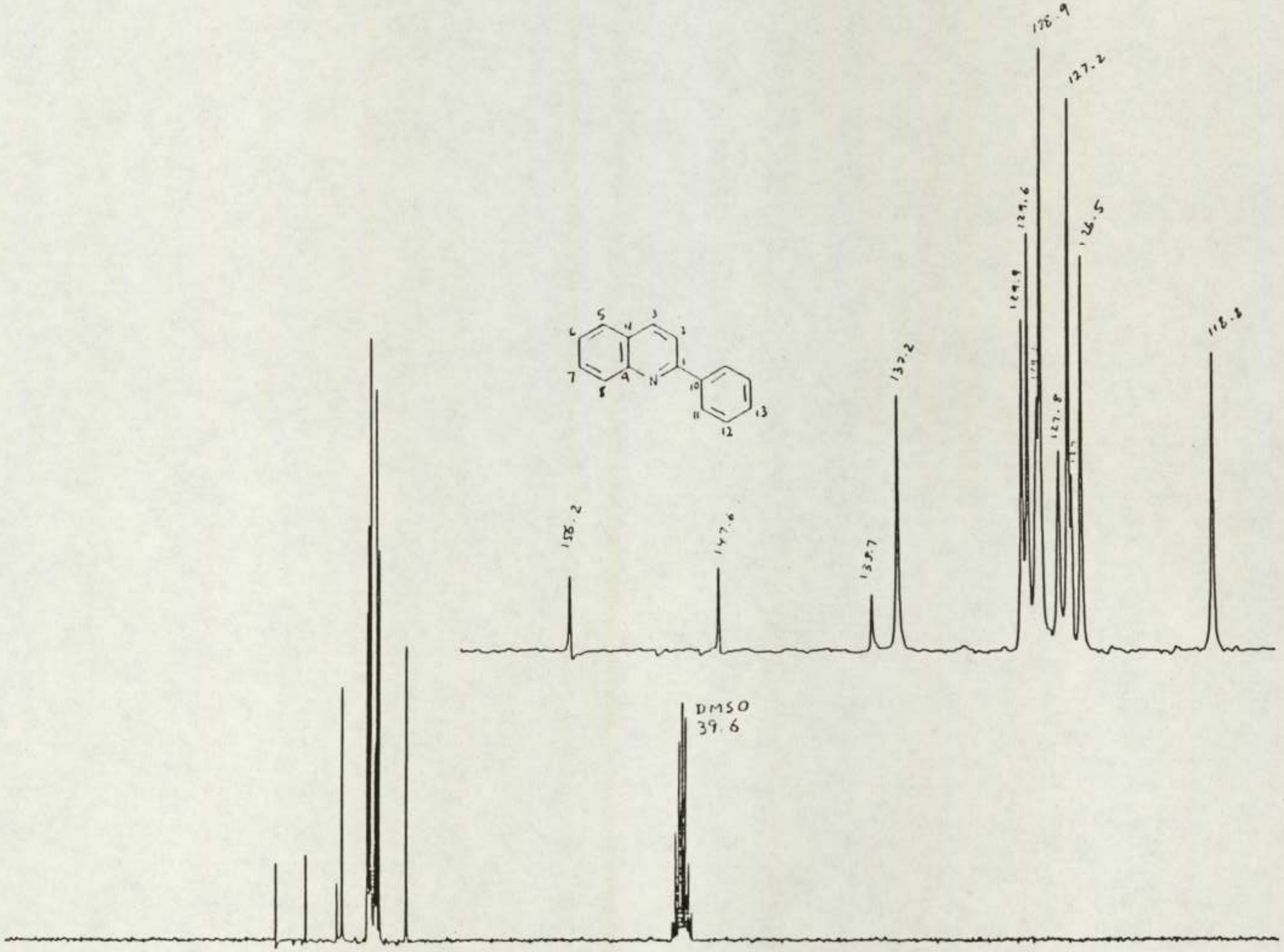


Figure 6.16 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{15}H_{11}N$ in DMSO

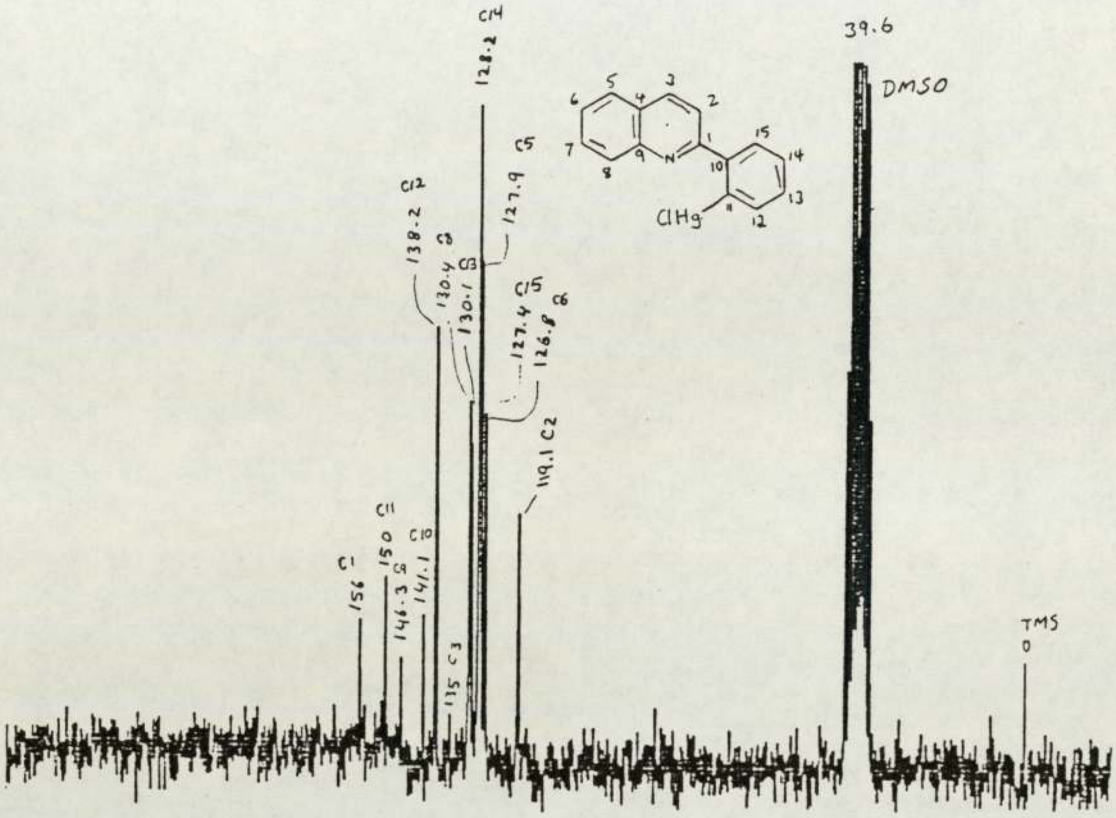


Figure 6.17 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{15}H_{10}NHgCl$

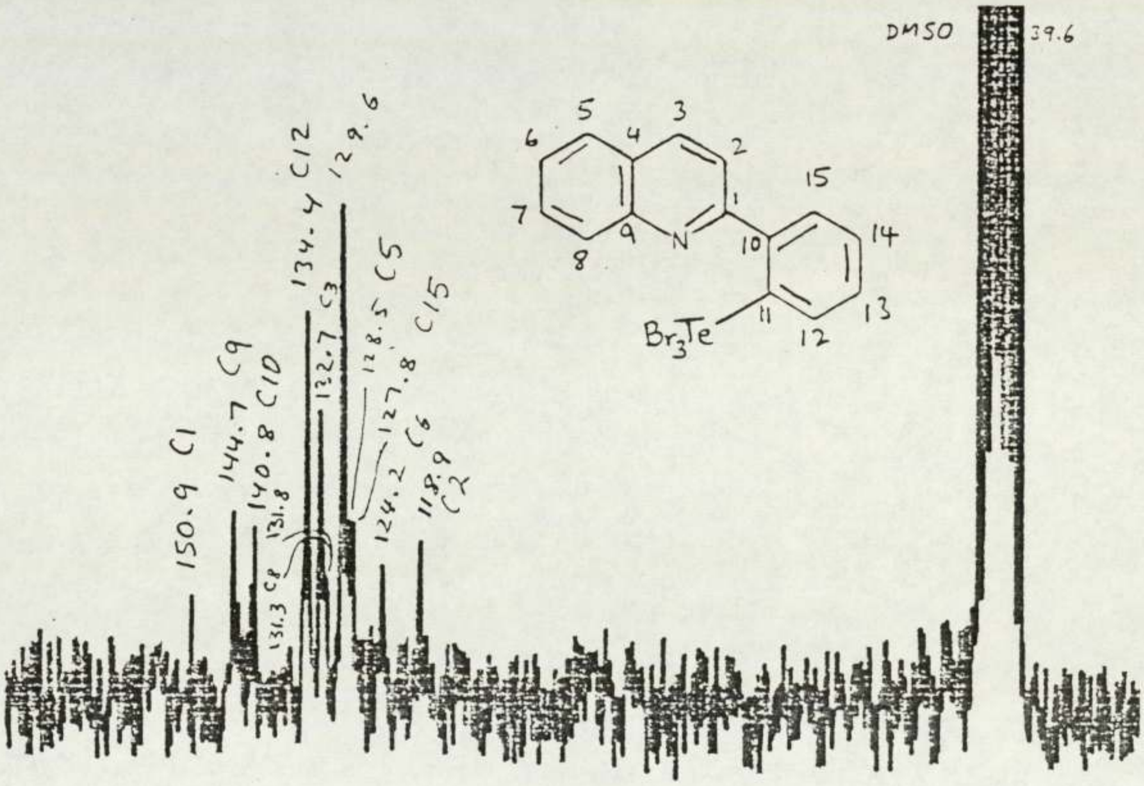


Figure 6.18 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{15}H_{10}NTeBr_3$

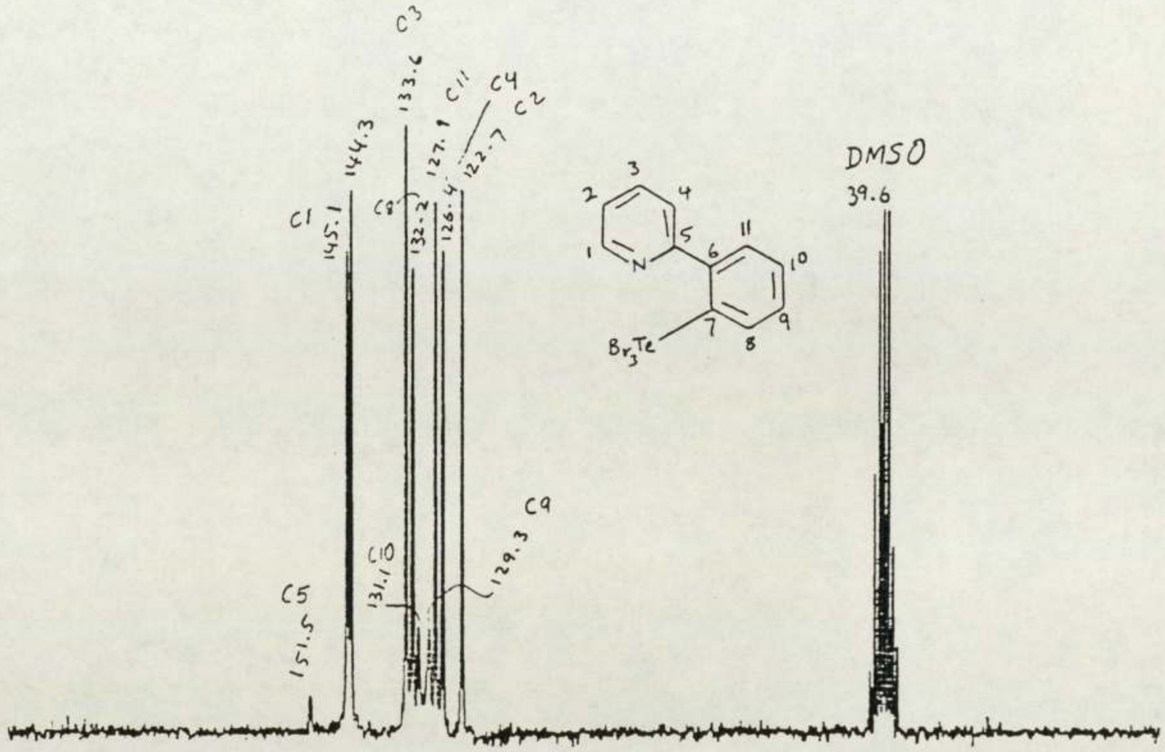


Figure 6.19 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{11}H_8NTeBr_3$

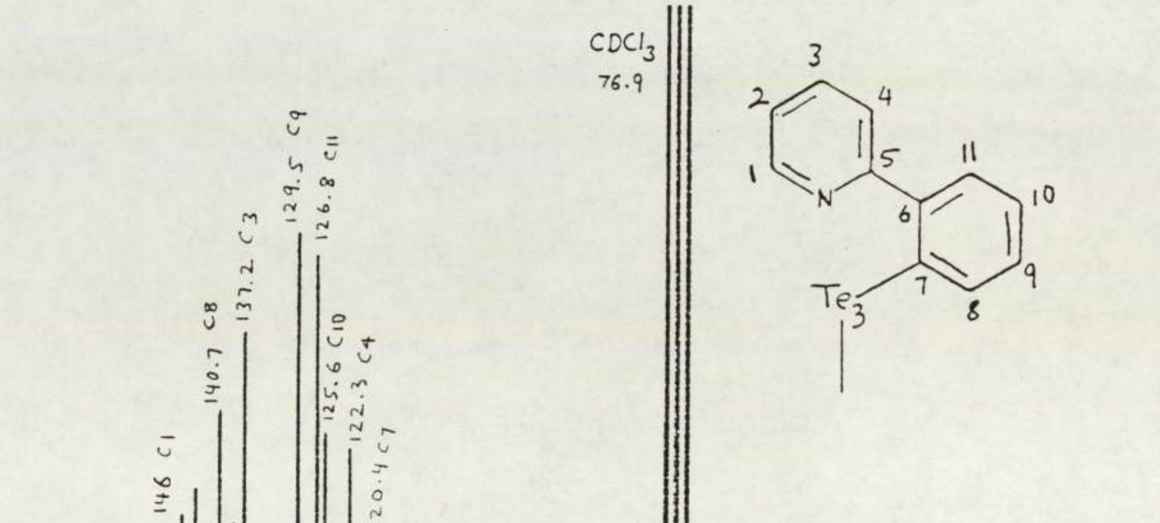


Figure 6.20 : $^{13}C[^{1}H]$ N.M.R. spectrum of $[C_{11}H_8N]_2Te_3$

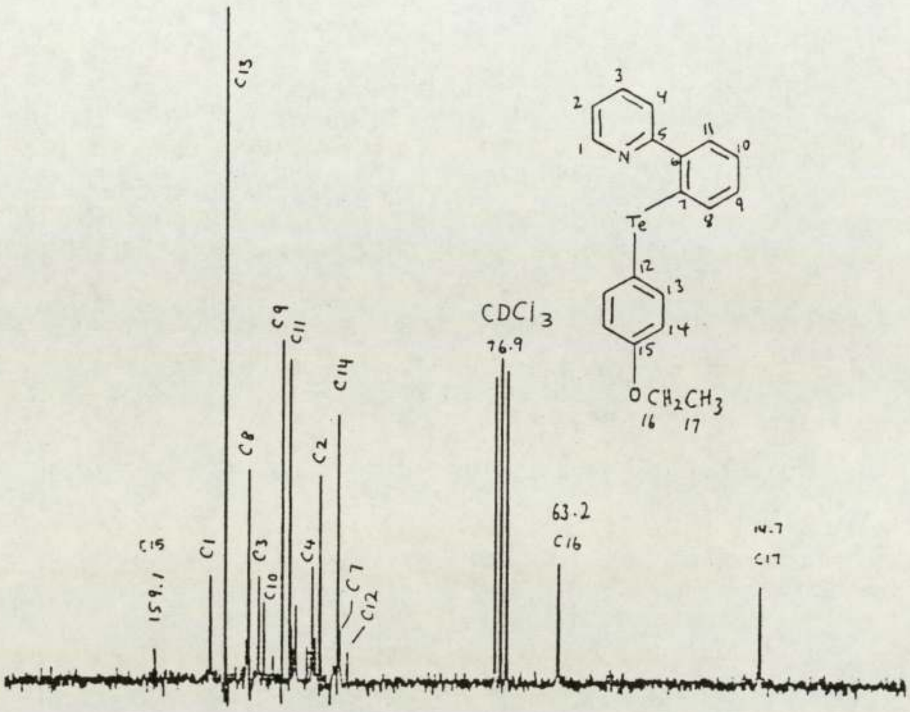


Figure 6.21 : $^{13}C[^{1}H]$ N.M.R spectrum of $C_{19}H_{17}NOTe$

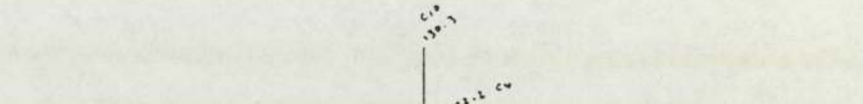


Figure 6.22 : $^{13}C[^{1}H]$ N.M.R. spectrum of $C_{14}H_{14}NS_2Te$

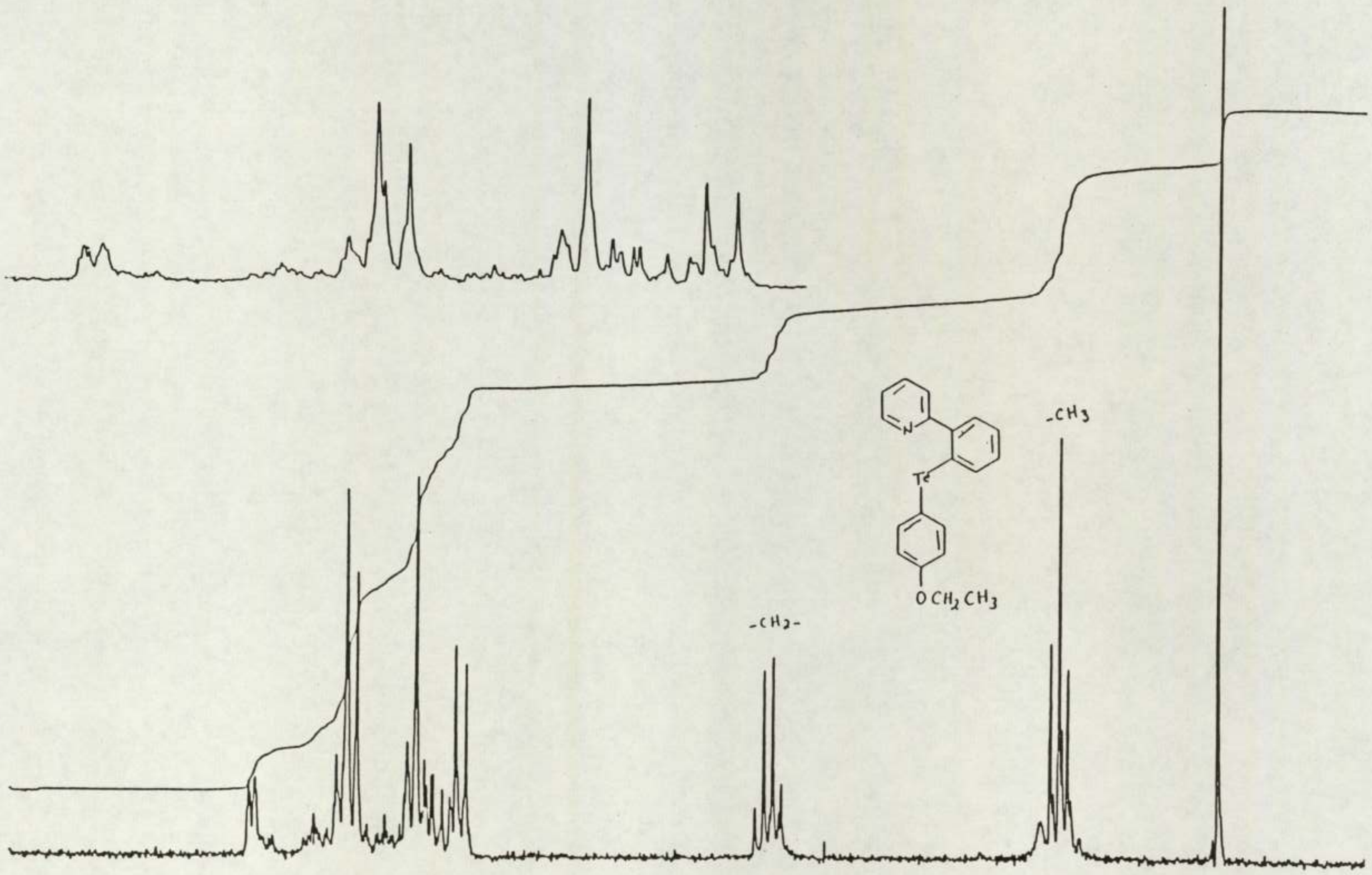


Figure 6.23 : ^{1}H N.M.R. spectrum of $C_{19}H_{17}NOTe$

6.3.5 N.M.R. Spectroscopy

$^{13}C[^{1}H]$ N.M.R. spectra were recorded using a JEOL FX-90Q Fourier transform multi-nuclear magnetic resonance spectrometer. ^{13}C resonances were observed at 22.5 MHz within a spectral width of 10 KHz. A tube and a probe of 5mm width were used at a normal operating temperature c.a. 300K. The pulse width was 6μs (60°) and a repetition rate of 1.5 seconds was used. Solvents were used as internal standards, but the ^{13}C chemical shifts were referenced to TMS.

The chemical shifts are presented in Tables 6.4 and 6.5 and some of the spectra are produced in Figures 6.14-6.22. ^{13}C Chemical shift assignments were based on comparison with suitable model compounds, as well as estimates of the effect of substituents on the aryl moiety of the starting materials using the simple additivity relationships, and on consideration of peak intensity.

^{1}H N.M.R. spectra were also recorded on the same instrument using 10 mm wide tube and probe. The chemical shifts were also referenced to TMS.

Mercuration of 2-phenylpyridine and 2-phenylquinoline was evident from the change in the ^{13}C N.M.R. spectra. These spectra were found useful in the assignment of the metallation site. The carbons bearing mercury experience a substantial downfield shift (c.a. 22 ppm). The unsubstituted ortho-carbons also resonate at a lower field by ~ 9 ppm compared with the starting materials, while the chemical shifts of meta-carbons are very similar to those of the parent bases. Similar observations were reported for some mercurated compounds (128,132,180a), where (^{199}Hg-^{13}C) couplings were obtained unlike our compounds, which are insufficiently soluble in DMSO to observe the coupling satellites.

The substituted carbon atoms including the mercurated ones showed signals of low intensities because of their long relaxation times. This helped in the assignments of the spectra.

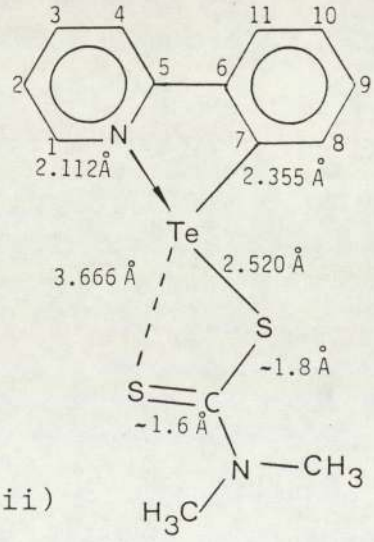
The trans-telluration of the mercurated compounds is also confirmed by the change in the position of some signals, although the spectra of the tribromides (viii) and (ix) are poorer than the corresponding mercurated derivatives due to solubility problems. In general, the resonances of tellurated carbons and of those in ortho- and para-positions to them have shifted a few ppm to a higherfield. The resonances of the carbons in ortho- and para- positions to the nitrogen atoms are clearly more sensitive to the presence of tellurium than of mercury, and they are higherfield shifted by about 4 ppm (Tables 6.4, 6.5). This may imply a stronger co-ordinate interaction of the nitrogen atoms with tellurium(IV) than with mercury(II).

The ^{13}C N.M.R. spectrum of <u>bis</u>(2-(2-pyridyl)phenyl)tritelluride (Fig. 6.20) also showes some points of interest. The most interesting features of the spectrum is the resonance of the tellurated carbon at 120.4 ppm, which has shifted to a higherfield by about 24 ppm compared to the corresponding tribromide and mercurated compounds. There is no comparable ^{13}C chemical shift value for a tritelluride compound in the literature, but Zingaro et al(188) have reported values 123-125 ppm for the <u>ipso</u>-carbons of some tellurenyl selenide compounds (xx) [-Te-Se-Te-]. A 3 ppm higherfield shift in the resonance of C 1 (adjacent to N) compared to the present base and its mercurated derivative indicates a Te---N interaction, which has been crystallographically confirmed (see earlier discussion).

The ^{13}C N.M.R. spectra of 2-(2-pyridyl)phenyl-4-ethoxyphenyltelluride (xi) (Figure 6.21) was assigned following the literature(140,198), and by comparison with the other pyridyl derivatives mentioned in this chapter. The aliphatic region contains ^{13}C resonances assignable to $-OCH_2$ (63.2 ppm) and $-CH_3$ (14.7 ppm) which are in good agreement with values found in the literature(198). The carbon atoms attached to tellurium (C7 and C12) have the lowest chemical shifts among the aryl carbons. This may result from shielding effects of the electropositive tellurium atom(140). A 4 ppm highfield shift of δC 1 (adjacent to N), relative to the mercurated derivative, may indicate a stronger Te---N interaction in this tellurium compound. The ^1H N.M.R. spectra of this compound (Fig. 6.23) revealed the proton signals of the ethoxy group. The triplet signal centered at 1.44 ppm is due to the resonance of $-CH_3$ protons (J = 7.03 Hz), and the quartet, centered at 4.07 ppm is due to OCH_2- protons (J = 7.03 Hz). The aromatic protons gave a multiplet between 6.8 and 8.7 ppm, with the integral ratio indicating the participation of twelve protons.

The ^1H N.M.R. spectrum of dimethyldithiocarbamato-(2-(2-pyridyl)phenyltellurium(II) showed a singlet at 3.63 ppm due to the resonance of $-N(CH_3)_2$ protons, which could be fluxional in solution. The integral ratio showed the presence of only one dimethyldithiocarbamato-ligand in the compound. The aromatic protons gave a multiplet between 7.19 and 8.75 ppm. The ^{13}C N.M.R. spectra of this dithiocarbamato-derivative (Fig. 6.22) shows a signal at 44.7 ppm assignable to $-N-CH_3$. The resonance of S-C(S)-N carbon could not be extracted from the spectrum, probably due to a very low intensity because of a long relaxation time. The resonances of all the aromatic carbon atoms have been observed. The interesting chemical shift value 130.1 ppm of C7 (the carbon attached to Te) shows that Te(II) in this compound is behaving as intermediate between Te(IV) of the corresponding tribromide (144.3 ppm) and Te(II) of the teluride (xi) (115.3 ppm) in terms of Te-C polarity and tellurium electropositivity. The highfield chemical shift (+6.6 ppm) of C 1(adjacent to N) compared to that of the corresponding mercurated derivative may indicate that Te(II)--N interaction in the dithiocarbamato-compound is stronger than Hg(II)---N interaction. This has been noted earlier in the discussion of the <u>trans</u>-metallation where it was found that tellurium prefered nitrogen over halogen while mercury prefered halogen over nitrogen.

We have been told(199) that crystallographic data of the present pyridyl compound (xxiii) revealed a Te---C(7) distance 2.355 Å, which may account for the peculiar δC7 mentioned above, and a Te---N distance of 2.112 Å which is significantly shorter than that found in the corresponding azo compound with Te---N distance of 2.340 Å (196). However, the crystallographer told us that SHELX program could not differentiate between pyridyl and phenyl groups, but thermal parameters for the dimethyldithiocarbamato-2-(2-pyridyl)phenyltellurium(II) compound were quite acceptable.



(xxiii)

In this context, we believe that a crystal structure investigation of dimethyldithiocarbamato-2-(2-quinolinyl)-phenyltellurium(II) compound would clarify the ambiguity in position of the nitrogen atom.

The high affinity of tellurium to the pyridyl nitrogen has been also noted in the X-ray structure of the previously mentioned tritelluride compound (section 6.3.3.3) with Te---N of 2.554 Å. This is shorter than Te---N (2.773 Å) found in the structure of the diene ligand, an interaction which is strong enough that it was maintained in the mercury complex of that ligand (chapter four).

6.3.6 Dichloro-[bis(2-(2-pyridyl)phenyl)telluride]palladium(II)

This palladium(II) complex of bis(2-(2-pyridyl)phenyl)-telluride is non electrolyte in solution (Λ 10.7 and 2.0 $ohm^{-1}cm^{2}mole^{-1}$ in 10^{-3}M CH_3CN and DMSO respectively). Therefore, one would expect that both chlorides are bonded to palladium. The infra-red spectrum of the solid revealed all the bands of the ligand, and the appearance of one medium intensity band at 340cm^{-1}, which is characteristic to ν(Pd-Cl), is indicative of a trans structure in organotellurium complexes(41,148).

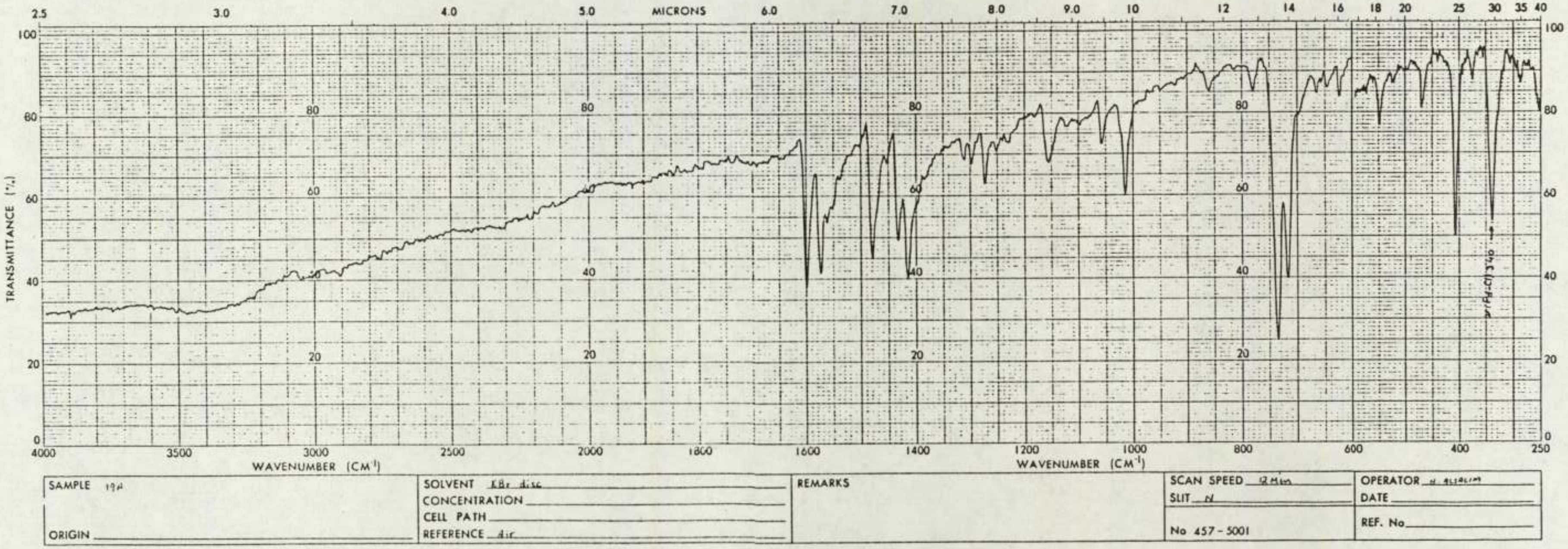


Figure 6.24 : I.R. spectrum of trans-$PdCl_2[C_{22}H_{16}N_2Te]$

Although it is known that diorganotelluride ligands can replace benzonitrile in $PdCl_2(PhCN)_2$ (23,27) , it is not clear from the i.r. spectrum whether tellurium, nitrogen or both are co-ordinating to palladium. This will need further investigations, which are lacked here due to time running out.

6.3.7 Summary

2-Phenylpyridine and 2-phenylquinoline were successfully mercurated using $Hg(OAc)_2$ in refluxed ethanol. The mercurated derivatives were trans tellurated using $TeBr_4$. Reduction of the resulting tribromides by hydrazine hydrate proceeded in two steps. In the first, monobromides were obtained, and further reduction gave the ditellurides. However, using the rather strong reducing agent $NaBH_4$ gave a novel tritelluride in the case of pyridyl derivative, and the ditelluride in the case of quinolinyl derivative. This was mainly attributed to the precipitated tellurium in the former case, which might be reduced to Te^{2-} ion by the borohydride, and react with the monobromide to form the tritelluride. Alternatively Te° may insert into the sodium tellurenyl compound giving a sodium ditellurenyl intermediate which when air oxidised can afford the tritelluride. The corresponding quinolinyl tritelluride derivative was prepared by deliberate addition of Te metal to the tribromide in the presence of $NaBH_4$. The X-ray molecular structure of bis-

(2-(2-pyridyl)phenyl)tritelluride was described in which the significant Te---N interaction is thought to be responsible for the stability of this compound, which could be reduced to the corresponding ditelluride by Cu° in dioxane. Other pyridyl and quinolinyl derivatives, which are potentially tridentate and bidentate ligands, were also prepared. Reaction of 2-(2-pyridyl)phenyltellurium(IV)tribromide with sodium dimethyldithiocarbamate resulted in the reduction of Te(IV) to Te(II) and formation of a mono-dithiocarbamato- compound. Elemental analyses, I.R., ^{1}H N.M.R., ^{13}C N.M.R. and X-ray crystallography were very helpful in confirming the progress of the reactions. The Te---N interaction is clearly reflected on the carbon atoms of the hetrocyclic ring as shown by their ^{13}C chemical shifts.

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Lewis Acid and Lewis Base Behaviour of a Tellurium(II) Compound: A Mercury(II) Complex of a Bis-telluride Ligand with a 13-Member Macrocyclic Chelate Ring

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The structure of 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (**1**) reveals a weak tellurium–nitrogen interaction giving the tellurium atom an effective co-ordination number of 3; with $HgCl_2$, (**1**) forms the complex [$HgCl_2$·(**1**)] which is monomeric with four-co-ordinate mercury(II) bonded to two chlorine and two tellurium atoms, (**1**) thus forming a 13-membered chelate ring.

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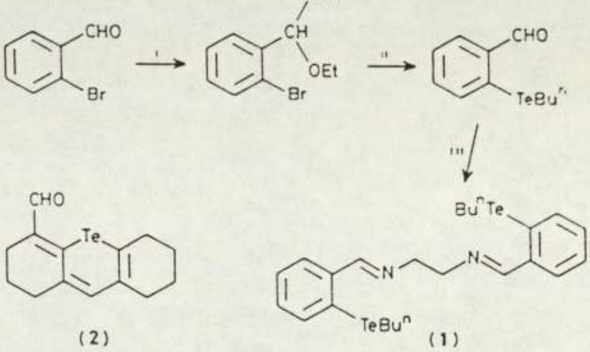
The structure of 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene (**1**) reveals a weak tellurium–nitrogen interaction giving the tellurium atom an effective co-ordination number of 3; with $HgCl_2$, (**1**) forms the complex $[HgCl_2{\cdot}(\mathbf{1})]$ which is monomeric with four-co-ordinate mercury(II) bonded to two chlorine and two tellurium atoms, (**1**) thus forming a 13-membered chelate ring.

Despite the recently developing interest in the ligand chemistry of tellurium,[1,2] few bidentate or polydentate ligands containing the element are known, although the compound $[Pt\{PhTe(o\text{-}Ph_2P{\cdot}C_6H_4)\}_2][Pt(SCN)_4]{\cdot}2DMF$ (DMF = dimethylformamide) was recently the subject of a structure determination.[3] We were interested to synthesise potentially multidentate ligands containing both tellurium and donor atoms such as N or O; thus compound (**1**) has been prepared following the reactions in Scheme 1.

Compound (**1**) was recrystallised from ethanol to give crystals suitable for *X*-ray structure determination. The structure is shown in Figure 1.† Both Te–C bond lengths are within previously observed limits. The Te · · · N distance of 2.773 Å is well within the Van der Waals distance (3.61 Å following Bondi[4] or 3.7 Å following Pauling[5]), and the planar nature of the Te–C–C–C–N moiety is noticeable. Thus tellurium(II) exhibits Lewis acid character in this molecule. This is generally more pronounced for organyltellurenyl compounds, RTeX, *e.g.* (2-phenylazophenyl-*C*,*N*')-tellurium(II) chloride,[6] but it is not without precedent for R_2Te, *e.g.* compound (**2**) has Te · · · O of 2.574 Å[7] (*cf.* Van der Waals distance of 3.58[4] or 3.6 Å[5]); we do, however believe this to be the first example of three-co-ordinate $R_2Te \cdots X$ involving nitrogen.



Scheme 1. Compound (**1**) and all intermediate compounds gave satisfactory elemental analyses, i.r. and n.m.r. spectra. *Reagents:* i, EtOH, $HC(OEt)_3$; ii, a Bu^nLi, Et_2O, b Te, c conc. HCl; iii, ethylenediamine, EtOH, reflux. (**1**), m.p. 83—85 °C, 68% yield.

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† *Crystal data:* Ligand (**1**): $C_{24}H_{32}N_2Te_2$, M_r = 603.7, monoclinic, space group $P2_1/n$, a = 13.239(5), b = 5.985(2), c = 16.198(6) Å, β = 107.23(5)°, U = 1226 Å^3, Z = 2, D_c = 1.64 g cm^{-3}. Mercury complex: $C_{24}H_{32}N_2Te_2HgCl_2$, M_r = 875.2, triclinic, space group $P\bar{1}$, a = 9.134(3), b = 9.430(3), c = 17.335(7) Å, α = 80.73(5), β = 84.54(5), γ = 73.82(5)°, U = 1413 Å^3, Z = 2, D_c = 2.06 g cm^{-3}. For both structures, intensities were measured with an Enraf-Nonius CAD-4 diffractometer using monochromated Mo-K_α radiation in the range $2 < \theta < 25°$. Reflections having $I > 2.5\,\sigma(I)$ were used in the analyses. The structures were solved by Patterson and Fourier methods and refined by least-squares with SHELX.[12] The weighting scheme was of the form $w = 1/[\sigma^2(F) + gF^2]$ where g = 0.0015 (ligand) and 0.005 (Hg complex). The ligand structure was refined with anisotropic thermal parameters for all non-hydrogen atoms. In the case of the mercury complex, only Hg, Te and Cl atoms were assigned anisotropic thermal parameters. Hydrogen atoms were included in calculated positions in both structures. Final R values are 0.048 for 1382 reflections (ligand) and 0.054 for 3912 reflections (Hg complex). The atomic co-ordinates for both structures are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

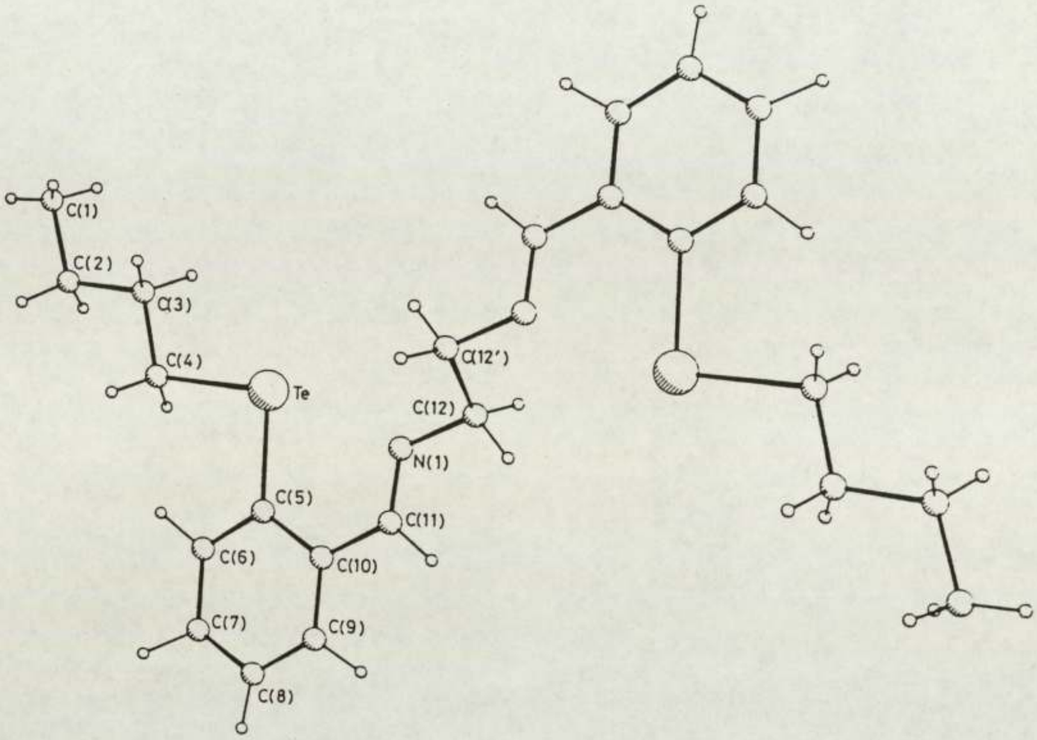

Figure 1. The structure of the ligand (**1**). The molecule is sited at a crystallographic inversion centre. Selected bond lengths (Å): Te–C(4) 2.181(10), Te–C(5) 2.111(8), N(1)–C(11) 1.273(11); <C(4)–Te–C(5) 95.2(4)°.

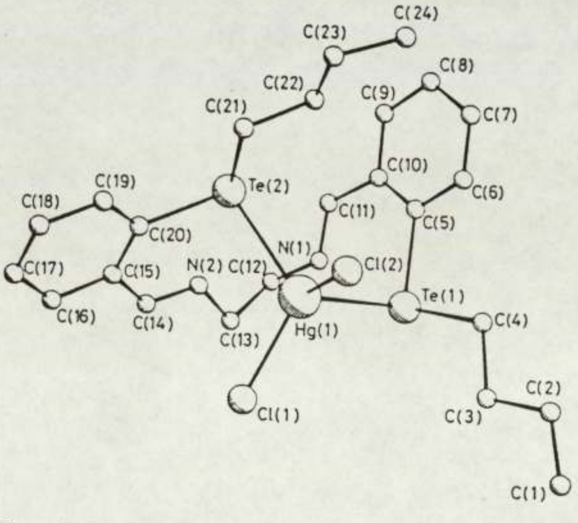

Figure 2. The structure of the mercury complex of (**1**). Hydrogen atoms have been omitted. Selected bond lengths (Å): Hg–Te(1) 2.819(1), Hg–Te(2) 2.769(1), Hg–Cl(1) 2.457(3), Hg–Cl(2) 2.494(3), Te(1)–C(4) 2.16(1), Te(1)–C(5) 2.15(1), Te(2)–C(20) 2.10(1), Te(2)–C(21) 2.15(1), N(1)–C(11) 1.28(2), N(2)–C(14) 1.27(2).

The ligand chemistry of (**1**) has been investigated and crystals of a mercury(II) chloride complex, $HgCl_2\cdot(1)$, proved suitable for *X*-ray crystallography. The structure is shown in Figure 2.† The co-ordination geometry at mercury is essentially tetrahedral with angles at the metal atom ranging from 105.3(1) to 116.4(1)°. Angles at tellurium are all in the range 93.6(3)—99.7(3)°. The major points of interest are the large (13-membered) chelate ring, and the fact that the Hg · · · N distances (3.668, 3.324 Å) are non-bonding. Tellurium ligands show a strong preference for 'soft' acids and this is illustrated quite dramatically by the present structure since the option of Te,N co-ordination to give a six-membered chelate ring clearly exists.

Macrocyclic chelates, usually based on phosphorus or arsenic, are well known and a number of crystallographically characterised examples exist, *e.g.* $[IrCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]$,[8] $[PtCl_2\{Bu^t_2P(CH_2)_{12}PBu^t_2\}]$,[8] $[RhCl(CO)\{Bu^t_2P(CH_2)_{10}PBu^t_2\}]$,[8] and $[Mo(CO)_4\{Ph_2PCH_2N(Me)(CH_2)_2N(Me)CH_2PPh_2\}]$;[9] this is the first example involving a main group element and the first involving a tellurium ligand.

Only two organotellurium complexes of mercury(II) are of unambiguously known structure: the tetrameric $(Ph_2Te)HgI_2$[10] which has Hg–Te 2.753 and 2.818 Å, comparable to the distances 2.769 and 2.819 Å seen here; and $[PPh_4][Hg(TePh)_3]$[11] with Hg–Te 2.682, 2.692, and 2.717 Å. Although in the present structure the Hg · · · N distances are inconsistent with Hg ← N co-ordination, the planarity of the

Te–C–C–C–N moiety is maintained in the complex and the Te · · · N interactions remain well within the Van der Waals distance (2.786, 2.752 Å); the tellurium(II) is then acting simultaneously as Lewis acid and Lewis base.

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Preliminary communication

BIS(2-(2-PYRIDYL)PHENYL)TRITELLURIDE – SYNTHESIS AND CRYSTAL STRUCTURE

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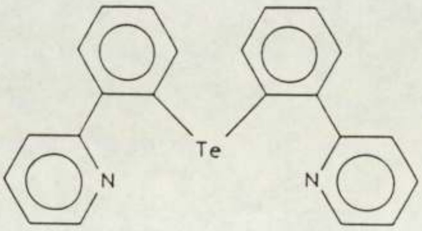
Summary

The synthesis and molecular structure of bis(2-(2-pyridyl)phenyl)tritelluride are described. There is a short Te · · · N non-bonded interaction of 2.554(7) Å, which may be responsible for the stability of the molecule. The tritelluride can be converted into the related ditelluride by treatment with copper in refluxing dioxane. The ditelluride may also be prepared by a route not involving the tritelluride.

Whilst attempting to prepare the functionalised tellurium-containing ligand (I), we tried, by use of $NaBH_4$, to reduce an organyltellurium tribromide (III) directly to the sodium organyltelluride(−1). Instead a novel tritelluride was isolated in good yield (see Scheme 1). The tritelluride was converted into the ditelluride (V) by treatment with copper powder in refluxing dioxane.



(I)

Crystals of IV suitable for single crystal X-ray diffraction studies were obtained from benzene/toluene:
Crystal data. $C_{22}H_{16}N_2Te_3$, $M_r = 691.2$, monoclinic, space group *I2/c*. *a* 14.721(3), *b* 9.290(4), *c* 15.996(10) Å, β 106.39(3)°, *U* 2098.7 Å^3, $Z = 4$, D_c 2.188 g cm^{-3}, $F(000) = 1272$.

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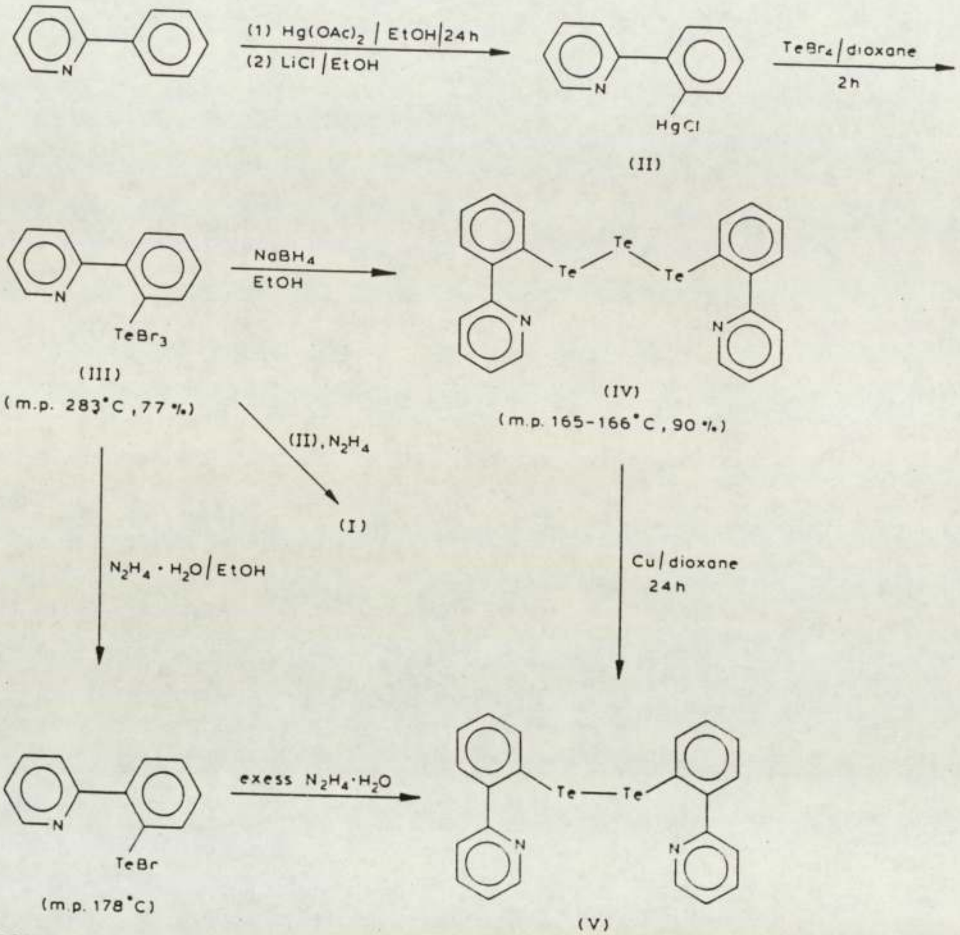

SCHEME 1

Cell dimensions and intensities were measured with an Enraf–Nonius CAD-4 diffractometer using monochromated Mo-K_α radiation. 1634 reflections in the range $2 < \theta < 25°$ having $I > 2.5\sigma(I)$ were used in the analysis. The structure was solved by Patterson and Fourier methods and refined by least-squares with SHELX [1], using anisotropic temperature factors for all non-hydrogen atoms. Hydrogen atoms were located from a difference map and included in fixed positions. The calculations were terminated when all shifts were < 0.1 and R and R_w were 0.064 and 0.088, respectively; $w = 1/(\sigma^2(F) + 0.005F^2)$.

A stereoscopic view of the structure of IV drawn with PLUTO [2] is shown in Fig. 1. The compound exhibits two-fold symmetry with the central tellurium atom lying on a crystallographic two fold axis *.

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* The atomic coordinates for this structure are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

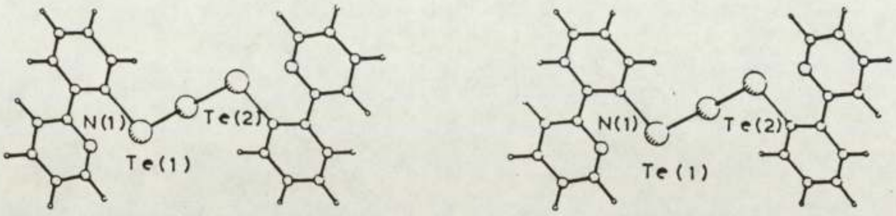

Fig. 1. Stereoscopic view of the molecule. Selected bond lengths (Å) and angles (°): Te(1)–Te(2), 2.776(1); Te(1)–C, 2.130(9); Te(1) ··· N, 2.554(7); Te(1)–Te(2)–Te(1)′, 100.4(1); C–Te(1)–Te(2), 99.1(2); N ··· Te(1)–Te(2), 170.7(2); N ··· Te(1)–C, 71.6(3).

Of particular note is the short Te ··· N non-bonded interaction of 2.554(7) Å, which appears to hold the ligand in an essentially planar geometry: the pyridyl and phenyl rings are, nevertheless, bent very slightly relative to one another to form a shallow V shape, with internal angle 177.2(4)°. The coordination of Te(1), by Te(2), N, and its bonded carbon atom is accurately planar. The torsion angle about the Te(1)–Te(2) bond is 97.3(3)°.

During the course of this work the structure of bis(tris(trimethylsilyl)methyl)tritelluride was reported [3]. The Te–Te bond length found in that compound (2.710(1) Å) is shorter by 0.066 Å than the corresponding length in our structure. This difference may be a manifestation of somewhat stronger Te–C binding involving an aromatic carbon atom (Te–C shorter by 0.083 Å) in our compound.

Apart from the tritelluride ion, $[Te_3]^{2-}$ [4], $(Me_3Si)_3C_2Te_3$ and the present compound are the only tritellurides reported to date. The bulky $(Me_3Si)_3C$ groups are believed to contribute to the stability of the former compound [3]. The diorganyltritelluride reported here, by contrast, appears to owe its stability to the significant Te ··· N interaction, suggesting that if the organic ligands have a suitably positioned donor atom, many more successful syntheses of tritellurides should be possible.

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