ORGANOTELLURIUM COMPOUNDS FOR METAL ORGANIC VAPOUR PHASE EPITAXY

by

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A thesis submitted for the
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at

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DECLARATION

The work described herein was carried out at the University of Aston in Birmingham between October 1988 and October 1991. It has been done independently and submitted for no other degree.

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October 1991

Professor W. R. McWhinnie

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SUMMARY

The infra-red detector material cadmium mercury telluride can be grown by the technique of Metal Organic Vapour Phase Epitaxy using simple alkyl telluride compounds as the source of tellurium. New tellurium precursors are required in order to overcome handling and toxicity problems and to reduce the growth temperature in preparing the material.

A range of diaryltellurium(IV) dicarboxylates and some 2-(2'-pyridyl)phenyltellurium(II) and tellurium(IV) monocarboxylates have been synthesised and characterised by infra-red, ^{13}C N.M.R. and mass spectroscopy. Infra-red spectroscopy has been used to determine the mode of bonding of the carboxylate ligand to tellurium.

Synthetic methods have been devised for the preparation of diorganotritellurides (R_2Te_3) and mixed diorganotetrachalcogenides (RTeSeSeTeR). A mechanism for the formation of the tritellurides based on aerobic conditions is proposed.

The reaction of ArTe- with $(ClCH_2CH_2)_3N$ leads to tripod-like multidentate ligands $(ArTeCH_2CH_2)_3N$ which form complexes with the ions Hg(II), Cd(II), Cu(I), Pt(II) and Pd(II). Synthetic routes to aryltelluroalkylamines and arylselenoalkylamines are also reported.

The crystal structure of 2-(2'-pyridyl)phenyltellurium(II) bromide has been solved in which there are six molecules present within the unit cell. There are no close intermolecular Te---Te interactions and the molecules are stabilised by short Te---N intramolecular contacts. The crystal structure of 2-(2'-pyridyl)phenylselenium(II)-tribromomercurate(II) is also presented.

A study of the Raman vibrational spectra of some tellurated azobenzenes and 2-phenyl pyridines shows spectra of remarkably far superior quality to those obtained using infra-red spectroscopy.

Key Words:-

Metal Organic Vapour Phase Epitaxy
Organotellurium
Carboxylates
Polytellurides
Raman

To My Family

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Chapter One

INTRODUCTION

1.1 General Introduction

For many years silicon semiconductor technology dominated solid state material science. A whole range of devices based on silicon have been developed and are now used worldwide. It is possible by combining elements from groups III and V or from groups II and VI to produce isoelectronic materials having a variety of semiconductor and optoelectronic qualities, similar but in a number of ways far superior to those produced with silicon. For example the use of gallium arsenide to produce integrated circuits or discrete devices in place of silicon gives two significant advantages. Firstly they operate at eight times the speed and secondly they are more resistant to radiation. The disadvantage at present is the very high cost compared to silicon and hence uses in these areas have concentrated on space and military applications. Optoelectronic devices based on III-V and II-VI materials have generated the most commercial interest. As alloy semiconductors have a direct band gap, they are much more efficient emitters of photons than silicon which has an indirect band structure. If the composition of the alloys is varied, the wavelength emission can be varied. There are many applications illustrating this property, for example:-

(i) Photocathodes for night vision (AlGaAs)

(ii) Solar cells for space applications (AlGaAs)

(iii) Solid state lasers for compact disc reading (AlGaAs)

(iv) Emitters and detectors for optical fibre reading (InGaAsP)

(v) Infra-red detectors (CdHgTe)

The recognition of the potential of III-V and II-VI materials as electronic and optoelectronic devices has resulted in a change in direction and thrust in semiconductor growth technology.

1.2 Cadmium Mercury Telluride

In 1958, W.D.Lawson and co-workers at the Royal Signals and Radar Establishment, Malvern, discovered that $Hg_xCd_{1-x}Te$ alloys were semiconductors with band gaps that could be varied from 0.0 to 1.605eV as x increased from 0.17 to 1.0. The demonstration of longwavelength photoconductivity in these alloys led the way for subsequent development of infra-red detectors. By 1965, cadmium mercury telluride (CMT) photoconductive infra-red technology had advanced sufficiently so that prototype detectors could be made for thermal imaging systems. During the past two decades CMT alloys have found applications as infra-red detectors which are vital in a number of military, space and industrial applications. Civilian applications of CMT thermal imaging systems are also being explored including thermography for early detection of breast cancer. Today CMT ranks as one of the most thoroughly studied semiconductors and from an investment point of view is only out-ranked by silicon and gallium arsenide.

1.3 Metal Organic Vapour Phase Epitaxy

Traditionally the method of forming thin layers of semiconductor material in the silicon industry is by Chemical Vapour Deposition. This enables large areas to be produced and is the basis for low cost integrated circuits. Simplistically, the method requires the decomposition of silane at high temperatures generating silicon films and hydrogen.

$$SiH_4 \xrightarrow{1100^\circ C} Si + 2H_2 \qquad (1)$$

This crude bulk fabrication technology in which high growth temperatures are required can not be employed in the growth of CMT and related materials. Modern semiconductor technology requires the growth of high quality epitaxial layers of material. Epitaxial quality is a particular concern for high performance infra-red detectors. This is often achieved by the co-decomposition of organometallic compounds in the gas phase over a suitable substrate on which the film is to develop. If the deposited material is amorphous or polycrystalline the process is generally referred to as Metal Organic Chemical Vapour Deposition (MOCVD), whereas a process producing single crystalline material is Metal Organic Vapour Phase Epitaxy (MOVPE). In MOVPE a substrate crystal is used to orientate the growing layer so that it adopts the same structure as the substrate. The material grown may contain up to fifty different layers.

The use of organometallics and hydrides in chemical vapour deposition processes for the production of single crystal layers of III-V semiconductor compounds was first demonstrated in 1968 by Manasevit(1,2). Gallium arsenide was formed on gallium arsenide and germanium substrates by reacting triethylgallium or trimethylgallium and arsine in a carrier gas of hydrogen.

$$(C_2H_5)_3Ga + AsH_3 \xrightarrow{700^\circ C} GaAs + 3C_2H_6 \qquad (2)$$

In 1971, the first epitaxial layers of a II-VI compound ZnSe(3) were grown. Since then the use of the technique has been extended to many other II-VI compounds including $Cd_xHg_{1-x}Te$, HgTe, CdTe, CdSe, ZnTe, ZnS, ZnS_xSe_{1-x}, ZnO and CdS. This information has been reviewed relatively recently(4-6).

1.4 Reactor Design

The status of the II-VI materials is not as mature as that of the III-V's and reactor designs for II-VI compounds have followed closely developments in III-V compound growth. Two basic reactor designs have been used. A vertical type originated by Manasevit and Simpson(3) and a horizontal version described by Irvine and Mullin(7). Schematic representations of the horizontal design are shown in schemes 1.1 and figure 1.1. The main advantage of the horizontal version is considered to be the slightly angled susceptor (10°) which leads to uniform deposition as the reactants are depleted from the gas stream. The reactor shown in scheme 1.1 consists of a water cooled silica vessel containing a SiC coated graphite substrate pedestal which is heated by high frequency induction. Prior to use, the reactor is evacuated to normal rotary pump pressures and the graphite is baked at high temperatures (~1100°C). This baking process removes any unwanted organic impurities within the reactor. The reactant gases are controlled by mass flow controllers and conveyed to the reactor through the system manufactured entirely from stainless steel. Carrier gases of hydrogen and helium are purified by Pd/Ag membranes and molecular sieves respectively. Substrates are polished prior to use and etched in acid before loading into the reactor. The most important feature in the growth of II-VI compounds is the arrangement for mixing the gases in order to inhibit any prereaction between the constituent gas streams. Most reactor designs have concentrated on introducing the gases to the reactor separately usually by admitting the group VI source at the end of the reactor and the metal alkyl through a delivery tube much closer to the heated substrate(8). The use of some group VI sources which eliminate the pre-reaction(9) enables good mixing to take place and allows efficient gas mixer designed for GaAs growth to be utilised.

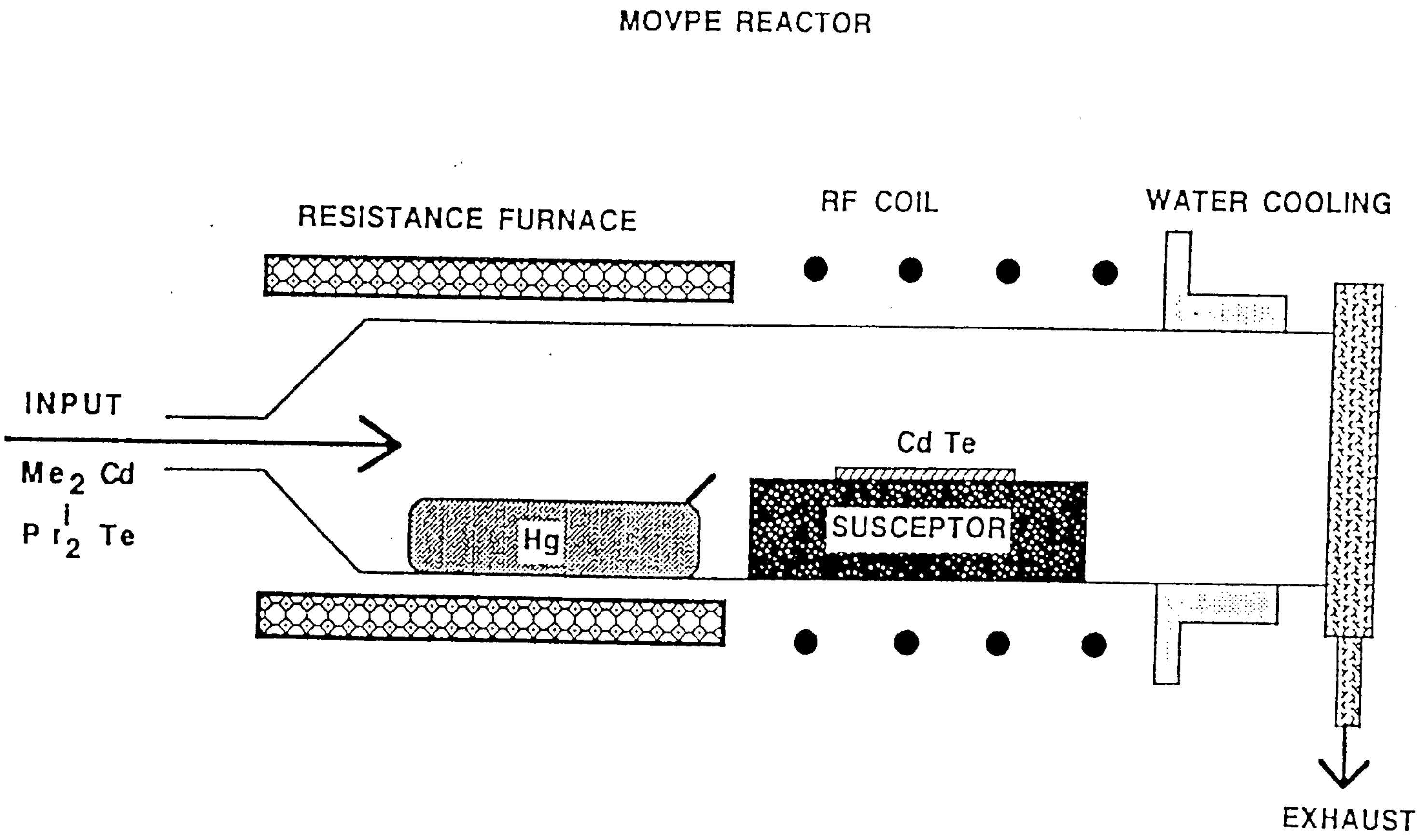
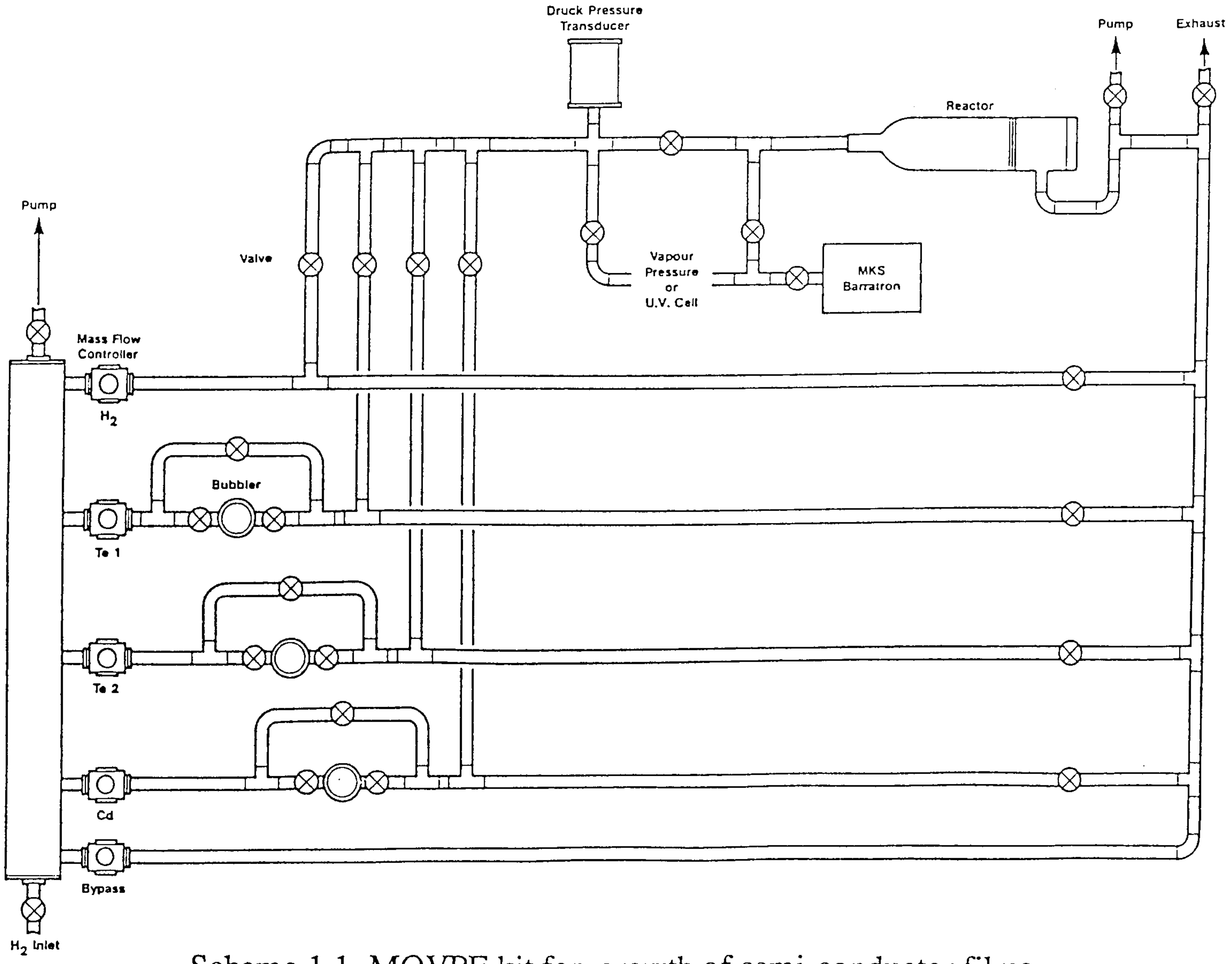


Figure 1.1 Typical reactor cell for pyrolytic growth of CMT.



Scheme 1.1 MOVPE kit for growth of semi-conductor films

1.5 Growth of HgTe, CdTe and $Cd_xHg_{1-x}Te$ by Thermal MOVPE

The first reported growth of HgTe was by Kuech and McCaldin(10) who reacted $(CH_3)_2Te$ and Hg vapour (from a liquid source) in H_2. They found that growth rates of the epitaxial layers in the temperature range 325-350°C to be very low ie. 0.3-0.6 μmh^{-1} . In contrast Irvine *et al* (11) and Bhat and Ghandi(12) used $(C_2H_5)_2Te$. Under similar conditions Irvine recorded growth rates of ~25μmh^{-1} at 410°C and Bhat and Ghandi noted growth rates of ~10μmh^{-1} at a temperature of 440°C. The use of diethyl- rather than dimethyltelluride and higher substrate temperatures clearly resulted in more efficient pyrolysis of the alkyls and was responsible for significantly higher growth rates than those found by Kuech and McCaldin.

Temperature understandably plays a crucial role in these pyrolysis processes. Mullin showed that the decomposition of Et_2Te(4) in H_2 requires a temperature of ~450°C to achieve 100% yield of Te, using a flow rate of ~20cms^{-1}. At 400°C the molecule is 50% decomposed and at 350°C the yield of Te is only 0.1%. However dimethyltelluride is much more stable; the corresponding temperatures for 100% and 50% decomposition being 510 and 475°C - an increase in stability of 60-75°C. Czerniak and Easton(13) in a mass spectroscopic study have shown that the pyrolysis of $(C_2H_5)_2Te$ began abruptly in a clean system at 410°C and was complete by 510°C. Additionally and more importantly the decomposition was autocatalytic. Thus the onset of pyrolysis could occur at 350°C in the presence of Te. The pyrolysis of $(CH_3)_2Cd$ has been studied extensively in the literature$^{(14)}$ and has been shown to be less stable than $(C_2H_5)_2Te$ by ~60°C under similar flow conditions.

The effect of these decomposition constraints can be seen in the epitaxial growth of HgTe, CdTe and $Cd_xHg_{1-x}Te$. In the case of HgTe grown on CdTe substrates, by reacting $(C_2H_5)_2Te$ and mercury vapour in a suitable MOVPE reactor, the growth rate is found to fall off dramatically below 410°C. This contrasts with the epitaxial growth of CdTe which is achieved by replacing Me_2Cd with Hg in the above system. Here deposition temperatures can be reduced to as low as 350°C for similar epitaxial film growth rates. Evidently, the reaction between Me_2Cd and Et_2Te is a cooperative one and does not require separate decomposition of Et_2Te. Mullin$^{(4)}$ originally suggested that adduct formation (ie $Me_2Cd{<}\!\!-\!\!-TeEt_2$) may provide an easier activation route for thermal decomposition (see later).

The growth of $Cd_xHg_{1-x}Te$ exhibits the characteristics of both HgTe and CdTe growth. Thus when the substrate temperature is below 380°C, CdTe and not $Cd_xHg_{1-x}Te$ is grown$^{(15)}$. This indicates not only the cooperative interaction of Me_2Cd and Et_2Te in the low temperature formation of CdTe, but also the need for separate decomposition of Et_2Te in the formation of HgTe. The problem that results is of finding matching growth conditions for the formation of HgTe and CdTe since the value of x that results in the growth of $Cd_xHg_{1-x}Te$ is very sensitive to temperature and flow conditions. By using compromise conditions growth rates of 3-4μmh^{-1} can be obtained using a substrate temperature of 415°C.

CMT films are adversely affected by the relatively high growth temperatures of 400-450°C using Et_2Te, Me_2Cd and Hg as precursor sources. At these high temperatures, diffusional processes broaden heterojunction interfaces (CdTe/CMT) . Furthermore, the equilibrium density of mercury vacancies increases with temperature and these act as sites for impurities (the equilibrium mercury vacancy concentration can only be controlled at <400°C). This results in a poor performance in the films electrical properties.

Attempts to grow superior films by modifying the growth conditions are the subject of worldwide interest. The thrust is towards lower temperature technologies. In conventional thermal MOVPE of CMT, using Et_2Te, Me_2Cd and Hg precursors, the growth temperature is controlled by the more stable organotellurium compound. Efforts have been directed to finding more suitable less stable organotellurium sources.

There are several important factors to consider when selecting an alternative precursor source. Firstly it must be stable at room temperature under an inert atmosphere if necessary, for at least several months or preferably indefinitely. Secondly it must also be sufficietly volatile ideally with a vapour pressure >1 torr at room temperature enabling it to be transported around the system "freely". Furthermore, and alternative organometallic source should not undergo any undesirable reactions such as premature vapour phase reactions and polymerisations. Finally it must be obtainable chemically pure.

An alternative to Et_2Te in CMT growth is i-Pr_2Te(16-18) whereby the growth temperature has been reduced to 350°C. To date i-Pr_2Te is still the most popular organotellurium precursor in CMT growth.

Table 1.1 lists the organotellurium precursors which have been used to grow films of CdTe, HgTe and $Cd_xHg_{1-x}Te$. As well as Me_2Te, Et_2Te and i-Pr_2Te other tellurium precursors have been successfully used. Ditertiarybutyltelluride(28,31,38) and diallyltelluride(37) have been used to grow HgTe and CdTe at low temperatures (250-350°C). A disadvantage of these compounds are the low vapour pressures, which necessitates the use of heated bubblers and lines to transport sufficient amounts of the organotellurium source to the reactor. Recently, methylallyltelluride(34) has been used to grow HgTe at about 320°C using dimethylmercury . This organotellurium source has a relatively high vapour pressure (6.2 Torr at 20°C) so that it can be transported readily to the reactor zone. Ghandi *et al* (35-36) have used it to grow epitaxial layers of HgTe and $Cd_xHg_{1-x}Te$ at 320°C. The superior morphology of the layers grown using methylallyltelluride rather than

Table 1.1 Organotellurium sources used in II-VI growth.

Precursor	Material Grown	Substrate Temp °C	Grown Method	Ref
Me_2Te	CMT			10
Me_2Te	CMT	150	Photolytic (parallel)	19
Et_2Te	CdTe HgTe	165 165	Photolytic (parallel)	20
Et_2Te	CdTe	100-150	Photolytic (parallel)	21
Et_2Te	CMT	200-300	Photolytic (perpendicular)	22
Et_2Te	CdTe	250-300	Photolytic (perpendicular)	23
Et_2Te	CMT	410	Conventional	24
Et_2Te	HgTe		Conventional	11
Et_2Te	HgTe CdTe CMT	250 250 250	Photolytic	25
Et_2Te	CMT	250	Photolytic (perpendicular)	26
Et_2Te	HgTe	200-300	Photolytic (perpendicular)	27
n -Pr_2Te	HgTe	390-410	Conventional	28

i-Pr_2Te	CMT	350	Conventional (IMP)	29
i-Pr_2Te	CMT	350	Conventional	16
i- Pr_2Te	CdTe	350	Conventional	16
t-Bu_2Te	HgTe	230	Conventional	30
	CdTe	230		
t-Bu_2Te	CdTe	220	Conventional	31
	HgTe	230		
Me_2Te_2	CdTe	250-500	Conventional	32
C_4H_6	CdTe	250	Conventional	33
allylTeMe	CdTe	290	Conventional	34
	HgTe	325		
allylTeMe	HgTe	250-320	Conventional	35
	CMT	250-320		
allylTeMe	HgTe	240-320	Conventional	36
	CMT	250-320		
$(allyl)_2Te$	HgTe	180	Conventional	37
	CdTe	180		

Table 1.1

di-isopropyltelluride is due to the lower growth temperatures used.

One can rationalise the low growth temperatures in terms of an alkyl stability model. The stability of organotellurium compounds is determined by the strength of the weakest bonds which are the carbon-tellurium bonds. The breaking of the first carbon-tellurium bond forming two free radicals is the rate determining step for pyrolysis. Consequently the activation energy for free radical formation will determine the stability of the molecule. An important mechanism for reducing the activation energy is delocalisation of the free radical unpaired electronic charge by neighbouring organic groups. Simplistically, the greater the delocalisation of charge, the lower the activation energy for carbon-tellurium bond dissociation and therefore the less stable the molecule. Table 1.2 shows the effect of delocalisation on activation energy using methane as a reference. As illustrated the stability order for alkyl hydrocarbon radicals is :-

tertiary > secondary > primary > methyl.

Using this model and referring to the growth temperatures in table 1.1 , the same stability order is seen for the organotellurium compounds,

$$Me_2Te > Et_2Te > n\text{-}Pr_2Te > i\text{-}Pr_2Te > t\text{-}Bu_2Te$$

Compounds of stability lower than tertiary molecules can be obtained if the free radical electron is delocalised in certain double bonded systems. Such a configuration exists in the allyl radical where

Radical Order	Radical Name	Chemical Equation	EACT (Kcal/mole)	Reduction in EACT by Delocalisation
0	Methyl	$CH_4 \longrightarrow CH_3^{\cdot} + H\cdot$	104	0
1°	Ethyl	$CH_3CH_3 \longrightarrow C_2H_5\cdot + H\cdot$	98	6
1°	n-propyl	$C_3H_8 \longrightarrow C_3H_7\cdot + H\cdot$	98	6
1°	n-butyl	$C_4H_{10} \longrightarrow C_4H_9\cdot + H\cdot$	98	6
2°	i-propyl	$(CH_3)_2CH_2 \longrightarrow (CH_3)_2CH\cdot + H\cdot$	95	9
3°	t-butyl	$(CH_3)_3CH \longrightarrow (CH_3)_3C\cdot + H\cdot$	92	12
	allyl	$CH_2CHCH_3 \longrightarrow CH_2CHCH_2\cdot + H\cdot$	87	17

Table 1.2 **Activation Energies for alkyl radical formation.**

two equal stability configurations can be represented :-

$$CH_2{=}CH{-}CH_2^{\cdot} \longleftrightarrow {}^{\cdot}CH_2{-}CH{=}CH_2$$

Using the stability model diallyltelluride should be even less stable than ditertiarybutyltelluride. Indeed for comparable growth rates of HgTe a lower growth temperature of 180°C is required for diallyltelluride compared to 230°C for ditertiarybutyltelluride(37). Hence one can expand the stability order model as follows :-

$$0^o > 1^o > 2^o > 3^o > \text{allyl}.$$

1.6 Mechanisms of pyrolytic film growth.

It is well known that many group II alkyls are Lewis acids (electron acceptors) where the acceptor strength follows the series Zn > Cd > Hg. Conversely the group VI alkyls can act as Lewis bases (electron pair donors) where the donor strength is O > S > Se > Te. There are many examples illustrating the reaction between strong donor and acceptor alkyls, for example $(CH_3)_2Zn \leftarrow O(CH_3)_2$(38).

In the formation of CdTe in the system $(CH_3)_2Cd/(C_2H_5)_2Te/H_2$ (discussed in section 1.5), Mullin(4) explained the low temperature growth in terms of an adduct formation, $(CH_3)_2Cd \leftarrow Te(C_2H_5)_2$ that would decompose efficiently down to 350°C. At this temperature $(C_2H_5)_2Te$ alone shows no significant decomposition. Mullin(4) obtained evidence to support his idea by the pyrolysis of $(C_2H_5)_2Te$ and $(CH_3)_2Cd$

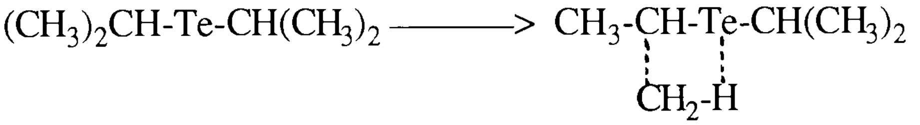
in a flow of H_2 in a heated silica tube in the absence of substrate. The atomic proportion of Cd:Te were found to be 1:1 in the deposits down to 310°C, the minimum temperature investigated. This is some 80°C below which $(C_2H_5)_2Te$ will decompose alone in the absence of $(CH_3)_2Cd$ under equivalent conditions. One would not have expected such a close 1:1 correlation without a unique reaction between the alkyls.

Mass spectroscopic studies by Czerniak and Easton(13) could also support Mullin's theory. They investigated the thermal decomposition of dimethylcadmium in the presence of diethyltelluride by *in-situ* gas sampling in a MOVPE growth reactor. Spectral peaks were identified from the reaction products as being $CH_3CdC_2H_5^+$ and $CH_3TeC_2H_5^+$. There are two possible explanations for this result. Firstly an adduct may form which dissociates and/or that exchange reactions are occuring between the alkyls. Both of these explanations would be expected to include reactions of the kind

$$(CH_3)_2Cd + (C_2H_5)_2Te \rightleftharpoons CH_3TeC_2H_5 + CH_3CdC_2H_5$$

Studies by Sritharan and Jones(39,40) on the MOVCD growth of ZnSe using a mixture of Me_2Zn, Et_2Se and H_2Se in H_2, cast doubt on the formation of an adduct $Me_2Zn.SeEt_2$ between the alkyls in their reactor. They showed that the infra-red spectra of the individual alkyls are similar to the spectra of a mixture of the alkyls. Since $Me_2Cd.TeEt_2$ is likely to be a weaker adduct than $Me_2Zn.SeEt_2$, its' existence must also be questioned too.

Hails *et al* have recently used G.C. mass spectroscopy to study "exhaust" gases in an MOVPE process⁽⁴¹⁾. In one experiment, isopropyltelluride was passed over a mercury source (heated to 170°C) and the vapours passed over a graphite susceptor heated to 370°C. The products detected were propene and propane together with unreacted isopropyltelluride. This decomposition arises without any interaction with mercury and could be explained by β-hydride elimination to yield propene followed by reductive elimination of propane to yield a deposit of tellurium.



$$(CH_3)_2CH\text{-}Te\text{-}CH(CH_3)_2 \longrightarrow \begin{array}{l} CH_3\text{-}CH\text{-}Te\text{-}CH(CH_3)_2 \\ \qquad\; CH_2\text{-}H \end{array} \quad (A)$$

$$A \longrightarrow CH_3CHCH_2 + HTeCH(CH_3)_2 \longrightarrow CH_3CH_2CH_3 + Te$$

Under the same experimental conditions but substituting isopropyl telluride for dimethylcadmium, methane, ethane and dimethylmercury were observed as mass spectral peaks. No dimethylcadmium was observed. There must therefore be some interaction of mercury with dimethycadmium. This reaction is known⁽⁴²⁾

$$R_2Cd + Hg \rightleftharpoons R_2Hg + Cd \qquad (3)$$

Dimethylcadmium has successfully been used to grow CdTe on GaAs substrates at 250°C using a purely thermal process. Here Steigerwald *et al* have suggested a more complicated mechanism than

Mullin's adduct theory. Based on the intrinsic reactivity of ditellurides(43), two mechanisms were proposed. It is well known that dimethylcadmium decomposes to give elemental cadmium(13,34). Steigerwald suggests that the ditelluride reacts with the dispersed cadmium to give an intermediate (A) in equation (4).

$$\text{RTe-TeR} + \text{Cd} \longrightarrow \text{RTeCdTeR (A)} \longrightarrow \text{CdTe} + R_2\text{Te} \quad (4)$$

Subsequent decomposition of (A) gives CdTe and an alkyl telluride as a volatile by-product. The vital step in the proposed mechanism is the insertion of cadmium into the Te-Te bond. Similar insertion reactions are known to occur at low temperatures(44). Another possible mechanism is related to the direct pyrolysis of dimethylditelluride. Such decomposition reactions of ditellurides have been the subject of some study(45,46); however the mechanism has not been unambigously established. Based on the related decomposition of disulphides(47) the route shown in equation (5) is proposed. It is suggested that (B) is a

$$\text{RTe-TeR} \longrightarrow R_2\text{Te=Te (B)} \longrightarrow R_2\text{Te} + \text{Te} \qquad (5)$$

very reactive species which can react with the organocadmium compound as in (6) or with the pyrolytically generated cadmium atoms as in (7).

$$R_2\text{Te=Te} + \text{Me}_2\text{Cd} \longrightarrow R_2\text{Te} + \text{MeTeCdMe} \longrightarrow \text{CdTe} + 2\text{CH}_3 \ (6)$$

$$R_2\text{Te=Te} + \text{Cd} \longrightarrow \text{CdTe} + R_2\text{Te} \qquad (7)$$

1.7 The Inter diffused Multilayer process (IMP).

Conventional thermal MOVPE of cadmium mercury telluride suffers from poor compositional uniformity throughout the layers. For the fabrication of arrays of infra-red detectors the lateral composition uniformity x in $Cd_xHg_{1-x}Te$ must not vary by more than 0.5% over 1cm. Typically thermal growth techniques produce $Cd_xHg_{1-x}Te$ layers with x varying by more than 5% over 1cm:- an order of magnitude worse than the required specification. The Interdiffused Multilayer Process (IMP)⁽⁴⁸⁾ developed by Irvine *et al* overcomes problems with compositional uniformity.

In the thermal MOVPE of $Cd_x\ Hg_{1-x}\ Te$ using $Et_2Te/Me_2Cd/Hg$ in a stream of H_2 gas, the breakdown characteristics of Et_2Te and Me_2Cd are different. A basic problem with designing an MOVPE technique is finding anion and cation precursors having similar or compatable characteristics. For example CdTe is quite a stable compound (ΔH_f°= -102.6kJ/mole) whereas HgTe is much less stable (ΔH_f°= -33.9kJ/mole). (N.B. ΔH_f°= standard molar heat of formation). This stability disparity, coupled with the greater reactivity of Et_2Te with Me_2Cd compared to with mercury, means that the optimum growth conditions of CdTe are different to that of HgTe. Experimentally, HgTe formation requires the individual breakdown of Et_2Te (~410°C) whereas CdTe formation which can occur at ~350°C is promoted by the presence of Me_2Cd either through adduct formation or alternatively as a breakdown characteristic of Me_2Cd. The control of the reactor wall temperature and also the mercury temperature is also critical. If the reactor wall temperature is too low, mercury vapour condenses out. But a high reactor wall temperature results in premature pyrolysis of the $Me_2Cd.TeEt_2$ adduct depositing CdTe and hence altering the concentration of adduct reaching the substrate. A compromise temperature is required which also maintains a high enough mercury vapour pressure over the substrate to avoid mercury depletion from the growing layer.

The IMP technique overcomes these problems by growing successive individual layers of CdTe and HgTe each under its own optimum conditions of growth. Very thin layers of HgTe and CdTe (combined thickness of ~0.2μm) are grown by switching the Me_2Cd and dilution flows on and off for predetermined times (usually less than 1 min). Most of the layers will completely interdiffuse during the period of growth (~30 mins). An additional anneal of a few minutes is used to homogenise the last layers of growth. The anneal is immediately after the growth period and is carried out at the growth temperature with a flow of H_2 and Hg vapour over the layer.

The technique relies on the fast interdiffusion between the main components but because the layers are very thin, good interfaces can be maintained between the substrate and the film. The IMP is shown diagrammatically in figure 1.2 with the individual layer thicknesses for HgTe and CdTe shown as t_1 and t_2 respectively. As the lattice parameters for HgTe and CdTe are similar, the composition of the CMT layer is

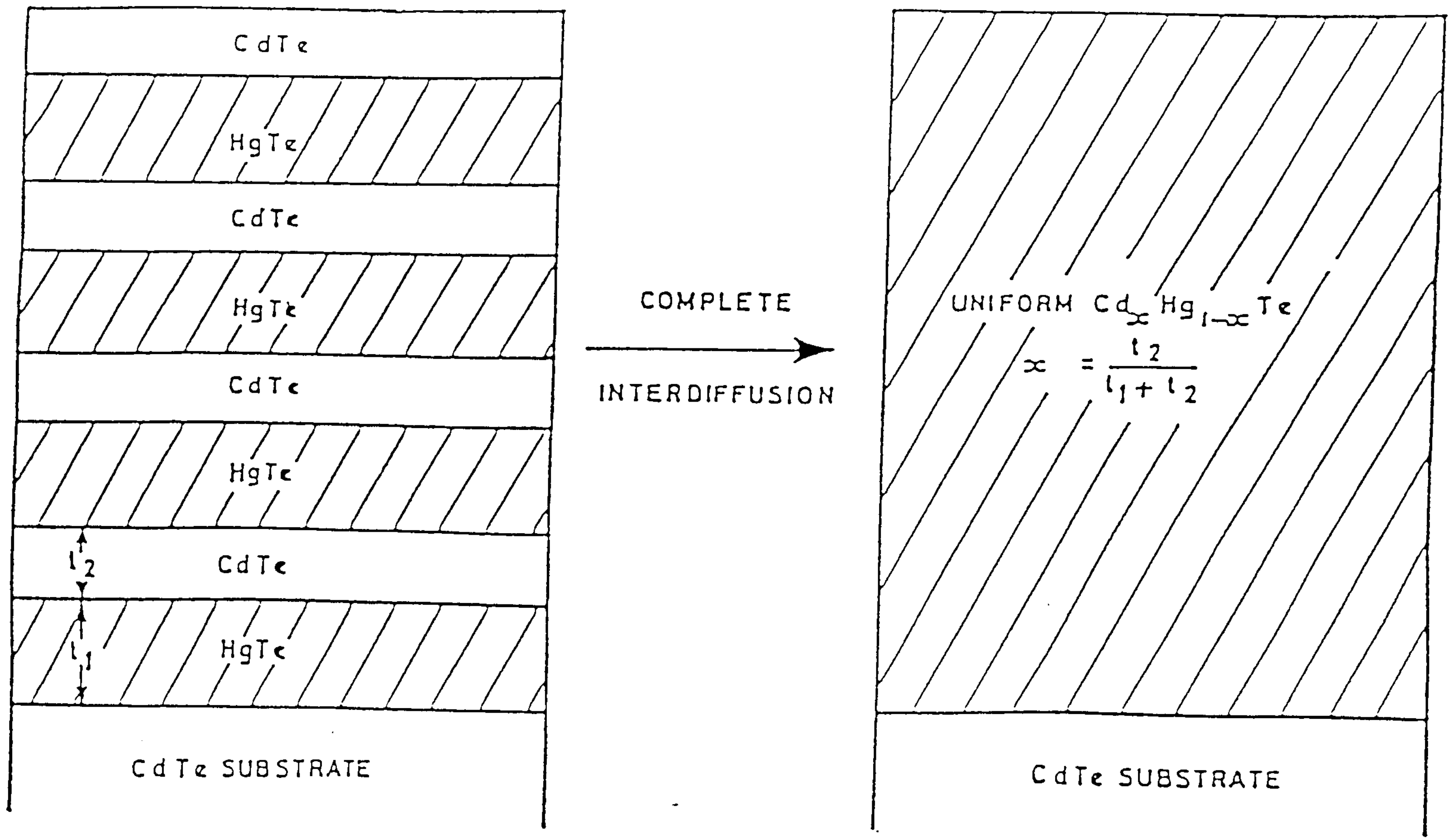


Figure 1.2 The Interlayer Multidiffusion Process.

given by the expression,

$$x = \frac{t_2}{t_1 + t_2}$$

Hence the CMT composition can be controlled by changing the growth times of the HgTe and CdTe layers. The IMP technique could have applications in the growth of other ternaries or complex multicomponent systems where cation and anion precursors have different stability and breakdown characteristics.

1.8 PHOTO-MOVPE

Epitaxial growth of thin films of the II-VI semi-conductor compounds CdTe, HgTe, and $Cd_xHg_{1-x}Te$ suffer from the relatively high growth temperatures needed. In conventional thermal MOVPE, the thrust has been directed to lower temperature growth by using less stable organotellurium sources. The reasons for reducing the epitaxial growth temperature are

a) to reduce defect concentrations

b) to reduce mercury vacancy concentrations

c) to reduce heterostructure abruptness.

Photo-MOVPE has been used for depositing a range of II-VI compounds and alloys at low temperatures. Some examples are listed in table 1.1 whereby u.v. radiation has been used to decompose the precursors at temperatures below the normal pyrolysis temperature. Cadmium mercury telluride has been grown down to below 200°C with significant improvement in the quality of the materials grown.

Two basic requirements must be met for photochemical decomposition. Firstly the incident radiation must be sufficiently energetic to effect decomposition; secondly the compound in question must have a sufficiently high absorption coefficient at the incident radiation for significant decomposition to occur. Typically a metal-carbon bond energy in dimethylcadmium and dimethyltelluride is ~250kJ/mole which corresponds to an incident wavelength of 480nm. Since these compounds have absorption maxima in the region 200-250nm, photolysis is most efficient for incident radiation near these wavelengths. Whilst conceptually simple and elegant, the use of photons eliminates the activation energy constraints imposed by thermal processes.

Epitaxial growth experiments have been carried out in a horizontal flow system, similar to the thermal apparatus, operating at one atmosphere pressure. A reactor cell is shown diagrammatically in figure 1.3 for HgTe growth. The u.v. source is generally placed perpendicular to the reactor wall with the beam centered on the substrate. The ultra-violet window is kept clear of deposits by maintaining a flow of hydrogen or helium gas in the top half of the reactor. In the bottom half, the metal-organics flow over the mercury reservoir and are mixed with the mercury vapour before passing over the substrate. There are potential hazards with photo-MOVPE. The use of photons to disintegrate organometallic molecules although elegant is a potential recipe for unwanted dust and non-epitaxial growth. Attempts

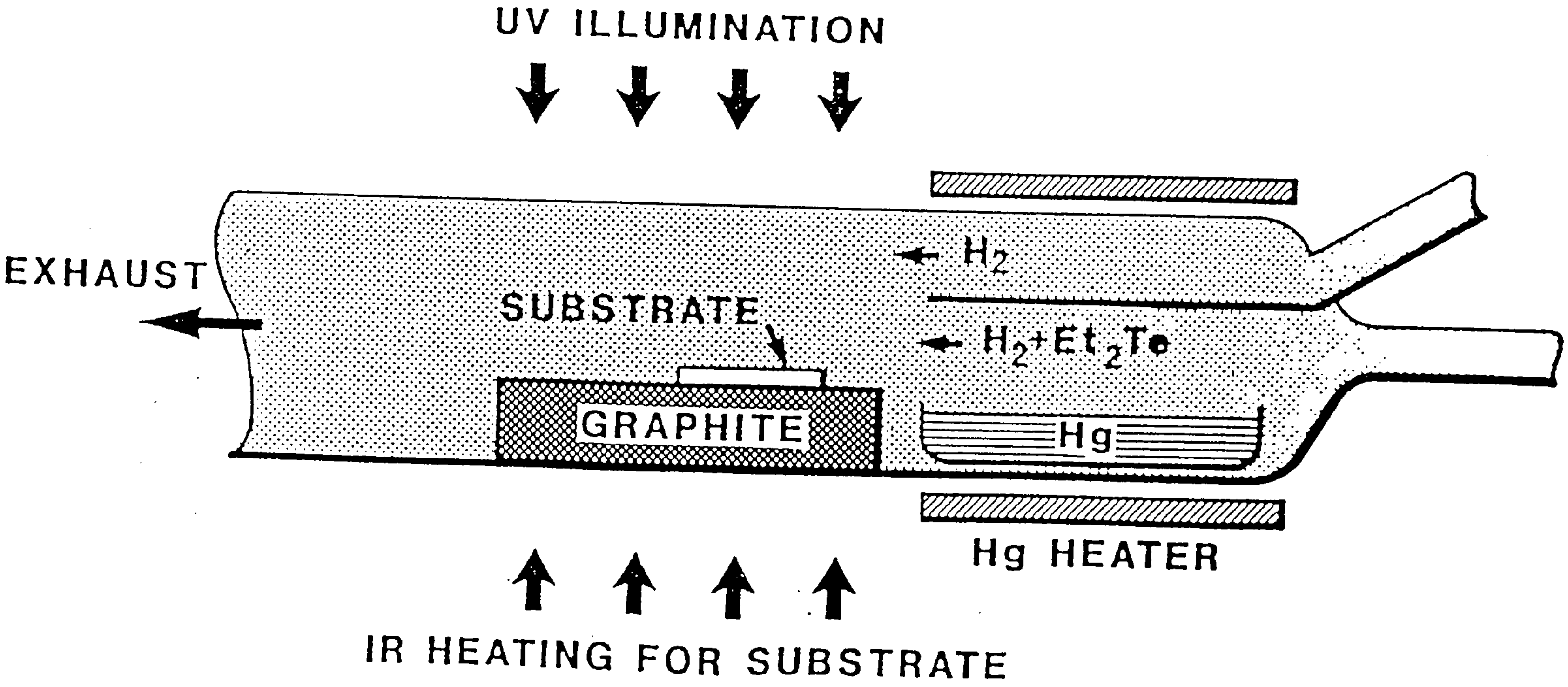


Figure 1.3 Typical reactor cell for photolytic growth of HgTe.

to bring about surface controlled reactions are important.

1.9 Photo-MOVPE of HgTe, CdTe and CMT.

The chemistries of the growth of the above semiconductor compounds and the reaction processes involved will be discussed in the next section. Significant aspects of the growth processes of the individual materials will be briefly discussed here.

The first reported photo-epitaxial growth of a II-VI compound was that of HgTe by Irvine(27,49) in 1984, using a mercury arc lamp source. High quality epitaxial films were grown onto GaAs and InSb substrates(49). Since then a number of reports using both arc lamps and more recently u.v. lasers have been made50-54). In HgTe growth studied by Irvine(27), vapours of Et_2Te in H_2 in the presence of mercury vapour at a pressure of ~0.05 atmosphere were passed over a CdTe substrate illuminated by u.v. photons from a 3kw mercury high pressure lamp. The high quality of the films was remarkable as well as the achievement of growing the film at 200°C. The previous lower limit using Et_2Te being 400°C(4). It was found that the growth rate became insignificant below a critical cut off pressure of 0.01 atmosphere mercury. The mechanism of this growth, which requires breakdown of Et_2Te (thermally stable at 200°C) has not been established unequivocably. However the proposed mechanism considers that a photosensitisation process is involved (to be discussed).

Whilst the photolysis of Et_2Te in the presence of mercury and hydrogen leads to epitaxial deposition of HgTe on CdTe substrates, the introduction of Me_2Cd into the system, additionally or as an alternative to mercury brings about the decomposition of Me_2Cd as the premature deposition of CdTe or $Cd_xHg_{1-x}Te$ as a dust. By substituting helium for hydrogen as the carrier gas Irvine *et al* (51,52) has overcome the problem of premature reaction. The high quality epitaxial films were free from dust in the region of high u.v. intensity. This discovery has enabled CdTe and $Cd_xHg_{1-x}Te$ to be grown epitaxially on CdTe by surface controlled processes. Kisker and Feldman(50) using a similar system but choosing a low pressure mercury lamp as their source of u.v. radiation were able to grow epitaxial quality CdTe dust free using hydrogen as the carrier gas. No mechanistic information can be given for this phenomenon.

1.10 REACTION MECHANISMS OF PHOTO-MOVPE

A) Photolysis of Me_2Cd and Et_2Te

The u.v. absorption spectrum of Et_2Te shows bands centered at ~218 and ~246nm whereas Me_2Cd shows a simple absorption peak at 215nm. Both compounds can be photolytically decomposed at room temperature in a flow of hydrogen using a high pressure mercury lamp. Both yield fine powders of the elements. Unexpectedly Et_2Te did not deposit tellurium in the region of high u.v. intensity but deposits were found downstream, following absorption of radiation at lower intensity. Thus the decomposition of Et_2Te to yield tellurium is more than a simple one step process. Mullin and Irvine(25) have calculated the mean bond dissociation enthalpy D(Te-Et) to be 235kJ/mole.

$$(C_2H_5)_2Te \longrightarrow Te + 2C_2H_5^{\cdot} \qquad (8)$$

Since the photon energy available from the 253.7nm line (470kJ/mole) is identical to the enthalpy of dissociation for the above reaction (ΔH°_{dis}), then thermodynamically it is possible for complete dissociation of Et_2Te by absorption of a single photon of energy. There is no evidence to support this in the literature although the photolysis of the closely related Me_2Te (ΔH°_{dis}= 483kJ/mole) suggests the chemistry is not simple(55). Flash photoysis revealed the presence of $CH_3Te^{\cdot}$ radicals and tellurium atoms. Furthermore the reaction between tellurium atoms and Me_2Te gave Te_2 species and two methyl radicals at virtually every collision. If comparisons can be made between the photolysis of Me_2Te and Et_2Te it is not unreasonable to predict that Et_2Te would yield $EtTe^{\cdot}$ radicals together with a smaller concentration of Te_2 and $Te^{\cdot}$

The photolysis of Me_2Cd is chemically simpler. It has been shown that absorption of a u.v. photon brings about the loss of one methyl radical(56), followed almost immediately by a second (eqns. 9 and 10).

$$(CH_3)_2Cd \longrightarrow CH_3Cd^{\cdot} + CH_3^{\cdot} \qquad (9)$$

$$CH_3Cd^{\cdot} \longrightarrow CH_3^{\cdot} + Cd \qquad (10)$$

The mean bond dissociation energy D[$Cd-CH_3$] was calculated to be

144kJ/mole from the enthalpy of dissociation for the reaction (ΔH°_{dis}= 288kJ/mole).

1.11 Mechanism to epitaxial growth of HgTe in the system $Et_2Te/Hg/H_2$

The epitaxial growth of HgTe can be achieved by photo-MOVPE at temperatures as low as 200°C. Since thermal decomposition of Et_2Te does not occur at these temperatures, u.v. absorption of the organometallic must be bringing about decomposition of the molecules. The proposed mechanism by Irvine and Mullin(25,27,51) considers that photosensitisation reactions are occuring. Initially, ground state $^1S_0$ Hg atoms absorb u.v. radiation generating 6^3P_1 Hg atoms. These excited atoms provide a well known route to energy transfer to other atoms and molecules.

$$Hg6^1S_0 + h\nu(253.7nm) \longrightarrow Hg6^3P_1 \qquad (11)$$

$$Hg6^3P_1 \longrightarrow Hg6^3P_0 \text{ (or Hg*)} \qquad (12)$$

Equation (12) occurs by spin-orbit relaxation : Hg* is metastable.

Assuming that Et_2Te and Hg species are present on the surface, the following reactions may occur.

$$Hg^*_{ad} + (C_2H_5)_2Te_{ad} \longrightarrow C_2H_5\text{-}TeHg_{ad} + C_2H_5^{\cdot} \qquad (13)$$

$$C_2H_5\text{-}TeHg_{ad} \longrightarrow HgTe_{ad} + C_2H_5^{\cdot} \qquad (14)$$

$$C_2H_5\text{-}TeHg_{ad} + H^{\cdot} \longrightarrow C_2H_6 + HgTe_{ad} \qquad (15)$$

Hydrogen atoms in equation (15) can be generated from (16)

$$Hg^* + H_2 \longrightarrow Hg + 2H\cdot \qquad (16)$$

Furthermore, hydrogen atoms could be effective in bringing about decomposition of Et_2Te as indicated in (17) and (18).

$$(C_2H_5)_2Te + H\cdot \longrightarrow C_2H_6 + C_2H_5Te\cdot \qquad (17)$$

$$C_2H_5Te\cdot + H_2 \longrightarrow Te + C_2H_6 + H\cdot \qquad (18)$$

The production of hydrogen atoms and ethyl radicals is capable of triggering a propagation reaction. However this likelihood diminishes in the region of the surface due to ease of deactivation and recombination processes here.

An alternative model for a surface selected reaction is one involving surface absorbed mercury reacting with Te or Te radicals, generated in the vapour by u.v. absorption of Et_2Te discussed earlier. Even though these reactions are thermodynamically favourable, the competing reaction would be a premature vapour phase reaction, thus precipitating HgTe on the surface as a dust. Dust formation, however is not observed in HgTe growth.

A potential problem with the surface controlled model involves the absorption of the 253.7nm mercury radiation. Theoretically, most of the photon energy will be absorbed within a millimetre of entering the mercury vapour. However since the emission line from the mercury lamp is broadened, wavelengths of $\pm$2nm of 253.7nm will reach the substrate. Mercury atoms chemisorped onto the surface could absorb this perturbed wavelength at a lower energy than 253.7nm due to the bonding energy of absorption. Therefore there is opportunity for photosensitisation to occur on the surface.

1.12 Mechanisms to the epitaxial growth of CdTe and $Cd_xHg_{1-x}Te$ in the system $Me_2Cd/Et_2Te/Hg/(H_2$ or He).

In section 1.10 it was interesting to note that epitaxial films of CdTe and $Cd_xHg_{1-x}Te$ could not be grown by using hydrogen as a carrier gas. Problems with CdTe and CMT precipitating out of the vapour as a dust were apparent. However substituting helium for hydrogen resulted in good quality epitaxial films. The chemistry of the two processes were therefore different. One important difference between CdTe and HgTe is the strength of the metal-tellurium bond. The bond dissociation energy for CdTe is 405.5kJmole^{-1} compared to 299kJmole^{-1} for HgTe. Hence the scope for u.v. bond dissociation is much less for CdTe than it is for HgTe. As a consequence of the strong bond energy between cadmium and tellurium, there is great difficulty in maximising high concentrations of Cd, Te and Te_2 vapours as a homogeneous mixture without precipitation of CdTe as a dust.

Both helium and hydrogen vapour must play roles in the surface and vapour phase reactions involved. Two arguements can be forwarded to explain the avoidance of premature reaction; (a) the decomposition of one or both organometallic compounds is surface controlled; (b) The Cd and Te atoms liberated in the vapour are not free to react due to thermodynamic constraints. Comparison between helium and hydrogen experiments suggests hydrogen is an active species in the reaction.

In the decomposition of Me_2Cd, two methyl radicals are generated.

$$(CH_3)_2Cd + hv \longrightarrow 2CH_3^{\cdot} + Cd \qquad (19)$$

The active methyl radicals can interact with hydrogen molecules generating hydrogen atoms which further react with more Me_2Cd molecules with release of a further methyl radical

$$CH_3^{\cdot} + H_2 \longrightarrow CH_4 + H^{\cdot} \qquad (20)$$

$$(CH_3)_2Cd + H^{\cdot} \longrightarrow CH_4 + CH_3^{\cdot} + Cd \qquad (21)$$

Equations (19)-(21) represent a chain reaction in which one u.v. photon can result in the decomposition of more than one Me_2Cd molecule. This chain reaction is clearly a recipe for generating a supersaturation of cadmium atoms. Moreover, H_2, through the formation of hydrogen atoms can bring about the decomposition of Et_2Te (equations 22 -24) with the formation of Te_2 and Te atoms.

$$(C_2H_5)_2Te + H^{\cdot} \longrightarrow Te + C_2H_6 + C_2H_5^{\cdot} \qquad (22)$$

$$C_2H_5^{\cdot} + H_2 \longrightarrow C_2H_6 + H^{\cdot} \qquad (23)$$

$$(C_2H_5)_2Te + Te \longrightarrow Te_2 + 2C_2H_5^{\cdot} \qquad (24)$$

It is not surprising from, the above network of reactions, why premature dust formation of CdTe occurs. Under conditions of CMT growth, the u.v. absorption of mercury atoms causes photosensitisation to Hg^* (equations 11-12), which on reaction with hydrogen is a further

$$Hg^* + H_2 \longrightarrow Hg + 2H\cdot \qquad (25)$$

route to hydrogen atoms (25). This further enhances the problem of supersaturation of Cd and Te atoms and leads to precipitation of CMT dust.

It is immediately evident then why substituting helium for hydrogen can suppress premature reaction. Helium is effectively inert to radicals and hence would prevent the chain reaction and limit the supersaturation conditions. Helium could thus create a thermodynamic constraint noted earlier. Using these ideas, Mullin and Irvine postulated a free radical model(25) which avoids premature reaction. Initially u.v. radiation is absorbed by the organometallic creating an atom radical atmosphere (equations 26-29).

$$Me_2Cd \rightleftharpoons MeCd\cdot + Me\cdot \qquad (26)$$

$$MeCd\cdot \rightleftharpoons Cd + Me\cdot \qquad (27)$$

$$(C_2H_5)_2Te \rightleftharpoons C_2H_5Te. + C_2H_5. \qquad (28)$$

$$C_2H_5Te\cdot \rightleftharpoons Te + C_2H_5\cdot \qquad (29)$$

A pseudoequilibrium would be set up with Cd and Te atoms formed at a rate dependent on the radical lifetimes. Radical recombination could occur at the substrate or walls of the reaction vessel (equations 30-32)

$$CH_3^{\cdot} + S + CH_3^{\cdot} \longrightarrow CH_3SCH_3 \longrightarrow C_2H_6 + S \qquad (30)$$

$$C_2H_5^{\cdot} + S + CH_3^{\cdot} \longrightarrow C_2H_5SCH_3 \longrightarrow C_3H_8 + S \qquad (31)$$

$$C_2H_5^{\cdot} + S + C_2H_5 \longrightarrow C_2H_5SC_2H_5 \longrightarrow C_4H_{10} + S \qquad (32)$$

Paneth *et al*(58) have recorded half lives of 0.1 seconds for methyl radicals. This order of magnitude would probably be adequate to account for the lack of premature reaction in the epitaxial deposition using helium. Using a linear velocity of helium carrier gas of $10cms^{-1}$ would enable radicals to be removed from the region of high u.v. intensity before they could recombine in the vapour. A surface controlled reaction can then be postulated where the deposition process is rate controlled by surface deactivation and recombination of radicals. Therefore it is probable that Et_2Te with its lone pairs of electrons, can chemisorb onto the substrate surface. Methyl radicals generated from the decomposition of Me_2Cd could readily bring about the formation of epitaxial CdTe or $Cd_xHg_{1-x}Te$ by the reactions below (equations 33-39)

$$(CH_3)_2Cd \longrightarrow CdCH_3^{\cdot} + CH_3^{\cdot} \qquad (33)$$

$$CH_3Cd^{\cdot} \longrightarrow Cd + CH_3^{\cdot} \qquad (34)$$

$$(C_2H_5)_2Te_{ad} \longrightarrow C_3H_8 + C_2H_5Te_{ad} \qquad (35)$$

$$C_2H_5Te_{ad} + CH_3^{\cdot} \longrightarrow C_3H_8 + Te_{ad} \qquad (36)$$

$$Cd(v) + Te_{ad} \longrightarrow CdTe \qquad (37)$$

$$Hg_{(c)} + Te_{ad} \longrightarrow HgTe \qquad (38)$$

CdTe would form preferentially because of its stronger bond. Excess Te in the region depleted of Cd would then be able to recombine with Hg which is present in excess. Using these ideas, it is not difficult to see why epitaxial growth of CdTe and $Cd_xHg_{1-x}Te$ can occur in helium and not in hydrogen. These propositions, although speculative, do provide a framework for discussion.

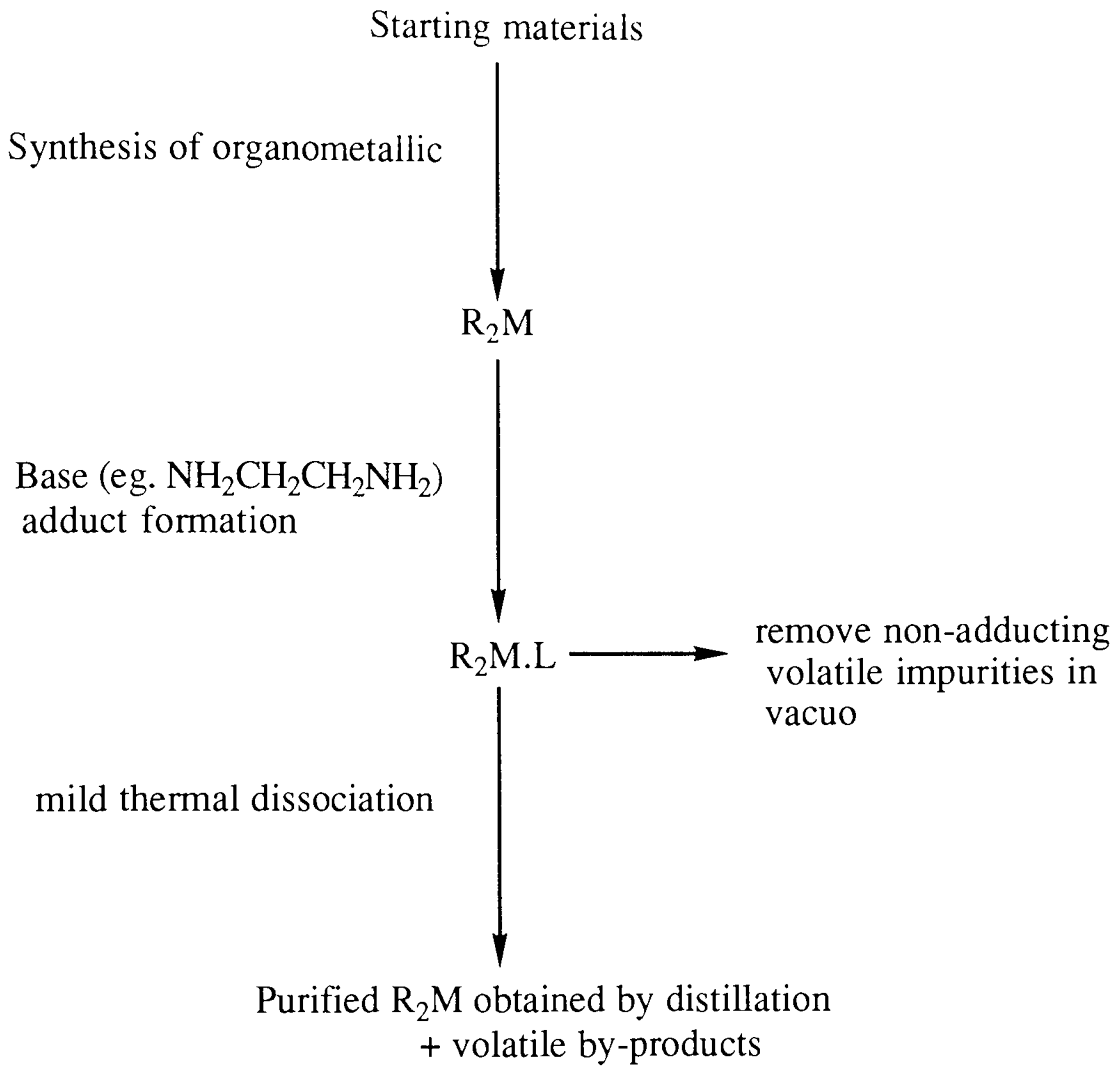
1.13 Synthesis and Purification of Organometallics for MOVPE of II-VI compounds

The growth of CdTe, HgTe and $Cd_xHg_{1-x}Te$ has generally featured the group II and VI alkyl compounds. The compounds have been known for a long time and although they are often pyrophoric, explosive and toxic, they can be synthesised in high yield from readily available starting materials. The main problem to the synthetic organometallic chemist is not the synthesis but obtaining high purity compounds to the required degree of purity. Generally, for organometallic compounds, purity of about 99% is acceptable. However this is not sufficient in semiconductor technology. The electrical properties of the layer can be completely destroyed if levels of undesirable impurity are greater than one part in 10^7. Extensive studies have shown that the purity of a semiconductor layer is often determined by the purity of the precursors.

Most metal alkyls required for MOVPE are volatile liquids for which the classical methods of purification are fractional distillation and low temperature crystallisation. One problem with these classical methods is that for metal alkyls which are highly reactive, large amounts often have to be discarded to obtain the highest purity. Since metal alkyls attract high commercial prices, it is clearly wise to maximise their recovery after purification. Chemical purification methods have overcome these problems and metal alkyls can now be synthesised to a high degree of purity.

The basic method used is adduct purification which was developed independently at two U.K. centres, Liverpool University(53) and Queen Mary College(54). The basic process is illustrated in scheme 1.2 below.

Since group II alkyls behave as Lewis acids, adducts can be formed by careful selection and reaction with Lewis bases. The lewis base and adduct must have well defined properties to be effective for the purification process. Neither must be volatile, but the adduct must dissociate to give the free metal alkyl and the lewis base at temperatures of ~50-150°C. Often the adduct is crystalline and hence crystallisation techniques can be removed to remove gross impurities. Volatile impurities and solvents can be removed by placing the adduct in a



Scheme 1.2

dynamic vacuum. Once the volatile impurities are removed, the adduct is heated to above its dissociation temperature where the metal alkyl distils and is collected in a cold trap. Involatile impurities, including the lewis base are left behind.

Table 1.3 lists some adducts that have been used to purify the group II metal alkyls [the zinc analogues have been included for comparison since these are useful for the epitaxial growth of ZnSe, ZnTe and ZnS_xSe_{1-x}]. As a result of the weaker electron acceptor

Metal alkyl (M)	Lewis base (L)	Adduct :L ratio
Dimethylcadmium	1,2-bis(dimethylamino)ethane	1:1
	4-dimethylaminopyridine	1:1
	3,3'-bipyridyl	1:1
	4.4'-bipyridyl	1:1
	1,4-bis(dimethylamino)benzene	3:2
Dimethylzinc	3,3'-bipyridyl	1:1
	4,4'-bipyridyl	1:1
	4-dimethylaminopyridine	1:1

Table 1.3

character of cadmium alkyls very few coordinate complexes between R_2Cd and donor ligands are known. Dimethylcadmium does form a series of complexes with chelating diamine and diethers. For example, dimethylcadmium can readily be prepared from $CdCl_2$ and MeMgI in diethylether(55) and addition of 2,2'-bipyridyl forms a 1:1 adduct from which Me_2Cd can be released on heating. This has been known for some time. The adduct (Me_2Cd).dioxane has been synthesised by simply adding Me_2Cd to 1,4-dioxane. It is likely to possess a chelate structure shown in figure 1.4.

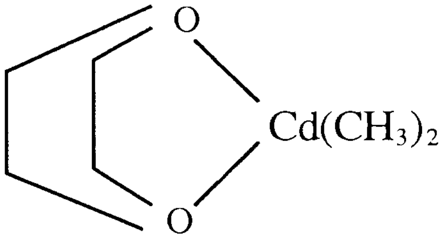


Figure 1.4

Cole-Hamilton *et al* have shown that adducts containing nitrogen can be prepared with zinc and cadmium alkyls. If an unstrained chelate ring is formed eg. 1,2-bis[dimethylamino]ethane the adduct sublimes without dissociation. However if two nitrogen atoms can not bind to the same metal for geometrical reasons, they bridge metal atoms and involatile dissociable adducts are formed. In most cases, eg. 3,3'-bipyridyl or 4-dimethylaminopyridine, the adduct has the stoichiometry, $Me_2Cd.L$ and are believed to be polymeric with a structure shown in figure 1.5

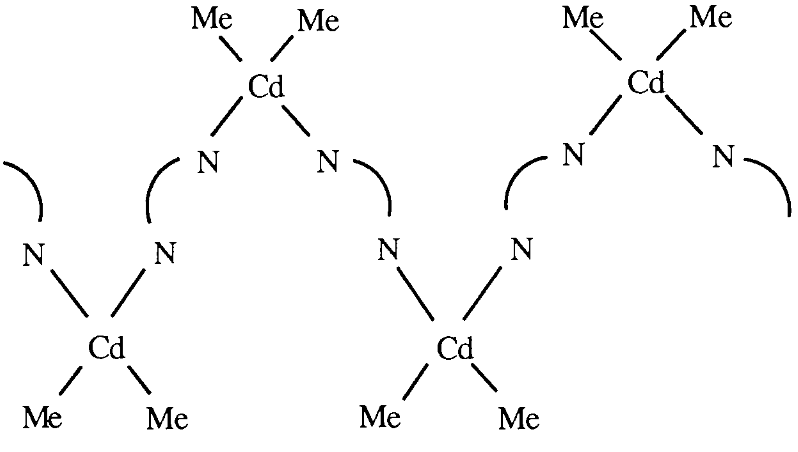


Figure 1.5

On the other hand for L= 1,4-bis(dimethylamino)benzene an adduct of stoichiometry $(Me_2Cd)_2.L_3$ is formed which may have the structure shown in figure 1.6. All these adducts dissociate on heating yielding Me_2Cd

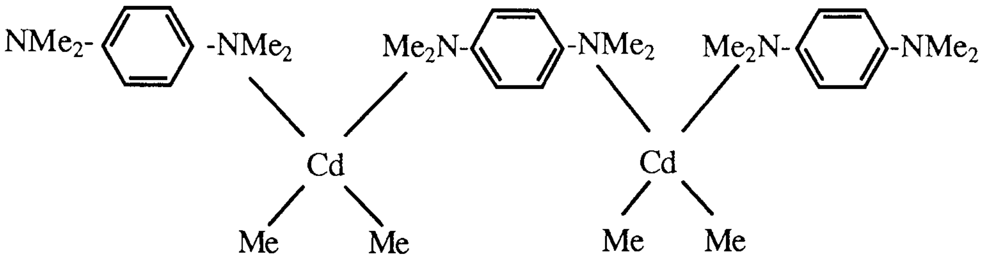


Figure 1.6

and so may be suitable for purification of Me_2Cd. The adducts are considerably safer to handle than the parent alkyl, being only mildly air sensitive and not pyrophoric

Synthetic methods can now be outlined for the group VI sources used in MOVPE. The main literature route to dialkyltellurides involves the reaction of sodium telluride with a bromoalkane. For example Cole-Hamilton *et al*(62) has recently used this reaction to synthesise diethyltelluride and diisopropyltelluride.

$$C_2H_5Br + Na_2Te \longrightarrow (C_2H_5)_2Te + 2NaBr \qquad (40)$$

The same research group obtained good yields of high purity mixed alkyl tellurides (RR'Te)(63) by reaction of R_2Te with R'_2Te_2 (R,R'= alkyl, allyl)

$$R_2Te + R'_2Te_2 \rightleftharpoons RTeR' + RTeTeR' \qquad (41)$$

The reaction relies on selecting a ditelluride with shorter chain alkyl groups than the alkyl telluride. The most most volatile component of the mixture RTeR' can be distilled from the mixture at reduced pressure. The equilibrium is then shifted to the right and on heating, RTeTeR' breaks down to yield tellurium and more RTeR'. Mixed ditellurides have been

$$RTeTeR' \longrightarrow RTeR' + Te \tag{42}$$

observed before(64) although their existence in the solid state is unknown.

Harris and Higa have synthesised diallyltelluride(65) in a reaction similar to (40) above.

$$2CH_2{=}CHCH_2Br + Na_2Te \longrightarrow (CH_2{=}CHCH_2)_2Te + 2NaBr \tag{43}$$

Using a Grignard method they have also been successful in synthesising allylmethyltelluride for example,

$$CH_2{=}CHCH_2Br + Mg \longrightarrow CH_2{=}CHCH_2MgBr \xrightarrow{Te}$$

$$CH_2CHCH_2TeMgBr \xrightarrow{CH_3I} CH_2{=}CHCH_2TeCH_3 + MgBrI \tag{44}$$

In section 1.5, emphasis was placed on reducing CMT growth temperature by careful selection of the organotellurium source. Using diisopropyltelluride currently the most popular tellurium source, growth temperatures of ~ 370°C are employed. High quality films were possible since Me_2Cd and $i\text{-}Pr_2Te$ both were compatable (similar decomposition temperatures). In all the growth systems highlighted,

Me_2Cd was used as the cadmium source. However if lower growth temperatures are sought, for example using diallyltelluride, then new organocadmium compounds having similar compatabilities to the tellurium source are required. Recently Et_2Cd has been formed, by the reaction of a Grignard reagent with $CdCl_2$.

$$2C_2H_5MgX + CdCl_2 \longrightarrow (C_2H_5)_2Cd + 2MgXCl \qquad (45)$$

The crude product which is extremely light sensitive was stabilised by the formation of a bis-amine adduct. Trial runs in the system $Et_2Cd/Pr_2Te/Hg$ have shown that Et_2Cd is a viable alternative to Me_2Cd for the lower temperature growth of CdTe and $Cd_xHg_{1-x}Te$(66).

Chapter Two

GENERAL EXPERIMENTAL

PHYSICAL MEASUREMENTS / CHEMICAL TECHNIQUES

2.1 Chemicals and Solvents

Most chemicals used were obtained from either the Aldrich Chemical Company, British Drug Houses (BDH) or Fluka Chemicals. Tellurium powder and tellurium tetrachloride were used as sources of tellurium. Platinum and palladium compounds were obtained from Johnson and Matthey. Common solvents were supplied by the Chemistry Department and were dried where necessary and stored over molecular sieves. Analytically pure solvents were used without further purification.

2.2 Elemental Analysis

Micro-elemental analysis for carbon, hydrogen and nitrogen were carried out either by Elemental Micro-Analysis Ltd, Okehampton, Devon or Medac Ltd, Department of Chemistry, Brunel University.

2.3 Melting points

A Gallenkamp electrically heated melting point apparatus with a mercury thermometer was used to determine all melting points.

2.4 Conductivity Measurements

Molar conductivity measurements were carried out on dilute solutions (10^{-3}M) of the compounds using a standard Mullard conductivity bridge and immersion type bright platinum electrodes (type E 7591/B) with a cell constant of 1.46.

2.5 Infra-red spectroscopy

Infra-red spectra were recorded on a Perkin-Elmer FTIR 1710 spectrophotometer equipped with a D.6300 data station. Spectra for the range 4000-220cm^{-1} were recorded using KBr discs. For some compounds the low wavenumber region (400-220cm^{-1}) was recorded using polyethylene discs.

2.6 Nuclear Magnetic Resonance Spectroscopy

N.M.R spectra (^{13}C and ^{1}H solution) were recorded within the Chemistry Department using a Bruker AC-300 MHz instrument. Tetramethylsilane was used as the internal reference. Tellurium (125) solution data were collected using bis(p-ethoxyphenyl)ditelluride as the reference.

2.7 Mass Spectroscopy

The electron impact, chemical ionisation and fast atom bombardment mass spectra of some compounds were recorded at Birmingham University and *via* the SERC mass spectroscopy service, University College, Swansea.

2.8 Ultra-violet, visible and near infra-red spectroscopy

Ultra-violet and visible measurements were carried out on a Unicam SP800 spectrophotometer using 1cm quartz cells. Near infra-red spectra were recorded on a Lamda 9 UV/VIS/NIR instrument at Brunel University.

2.9 X-ray Crystallography

Suitable crystals for the X-ray crystallography technique were obtained by recrystallisation from high purity solvents. Accurate cell dimensions and reflection intensities were measured with a graphite-monochromated Mo-Kα radiation on a Enraf-Nonius CAD-4 diffractometer operating in the ω-2θ scan mode. The structures were solved by Patterson and Fourier difference synthesis methods. Structure refinement was carried out by the least squares method. Computations were performed on the University of Birmingham Honeywell Multics computer with SHELX76 and SHELX86 suite of programs. Diagrams were drawn using PLUTO at the University of Manchester Regional Computer Centre.

2.10 Raman Spectroscopy

Raman spectra were recorded at Brunel University using a Perkin-Elmer FT-Raman 1700 instrument and using a NdYag laser operating at 1064nm. For colourless compounds, laser powers of 300mW were used. Coloured compounds required lower power outputs down to 50mW.

Chapter Three

ORGANOTELLURIUM CARBOXYLATES

3.1 Introduction

Diaryltellurium dicarboxylates are a well known class of compound and their synthesis and chemistry are well documented in the literature(66-68). However the tricarboxylates have often proved to be difficult synthetic targets and very few compounds are known. One recently reported example is p-methoxyphenyltrifluoroacetate(69). Apart from their uses as intermediates in synthetic chemistry, organotellurium carboxylate compounds have found very few applications.

One attraction may be as precursors in the MOVPE process. Conceptually, one may suggest that the thermal breakdown characteristics of the carboxylates under MOVPE conditions proceeds *via* loss of a stable carbon dioxide molecule releasing the organotellurium moiety as a volatile species. Thus for example, if a diaryltellurium dicarboxylate were to be heated, it may decompose with the loss of carbon dioxide *via* an unstable telluride intermediate according to the reaction scheme below.

$$R_2Te(OOCR')_2 \xrightarrow{\Delta} [R_2TeR'_2] \longrightarrow R_2Te + R'_2$$

Indeed related organometallics, for example dimethylgold(III) acetylacetone(70) and copper hexafluoroacetylacetone(71) have been used as volatile sources of gold and copper in chemical vapour deposition systems. Although their decomposition products have not been studied, they may breakdown *via* the loss of carbon monoxide as a stable species.

In this chapter we decided to synthesise a range of diaryltellurium(IV) dicarboxylates and study their decomposition by mass spectroscopy. Since organotellurenyl compounds RTeX [eg. X= Cl, Br and $(CH_3)_2NCS_2$] are now easily accesible and are stable solids at room temperature, we decided to synthesise some organotellurium(II) carboxylates and also study their decomposition by mass spectroscopy.

3.2 Experimental

The preparations of organotellurium(IV)trichlorides $(ArTeX_3)$(72), organotellurium(IV) dichlorides(Ar_2TeCl_2)(73) and (2-phpy)TeX(74) [2-Phpy = 2-(2'-pyridyl)phenyl and X= Cl, Br] were carried out according to the literature. Silver picolinate was prepared by the reaction of silver carbonate with picolinic acid (2-pyridine carboxylic acid). Potassium picolinate, potassium (2-chlorobenzoate) and sodium (4-iodobenzoate) were prepared by the alkaline addition of potassium hydroxide or sodium hydroxide to picolinic acid, 2-chlorobenzoic acid and 4-iodobenzoic acid.

3.2.1 Synthesis of Bis(p-methoxyphenyl)tellurium dibenzoate

Silver benzoate (3.44g, 0.015 mole) was suspended in warm 1,4-dioxane (80 cm^3). To this suspension was added a solution of bis(p-methoxyphenyl)tellurium(IV) dichloride (3.09g, 0.0075 mole) in 1,4-dioxane (40 cm^3). The mixture was refluxed for twelve hours, allowed to cool to room temperature and filtered. The residue consisted of a purple coloured solid (from mass balance calculations it is suggested this compound is AgCl; the purple colour probably arises from the tendency of silver salts to be light sensitive). The filtrate was concentrated using a rotary evaporator whereupon a white solid separated out, which on recrystallisation from ethanol yielded a white crystalline material. Yield 95%.

3.2.2 Synthesis of Bis(p-ethoxyphenyl)tellurium dibenzoate

Silver benzoate (2.29g, 0.01 mole) was suspended in warm 1,4-dioxane (60 cm^3). To this suspension was added a mixture of bis(p-ethoxyphenyl)tellurium(IV) dichloride (2.20g, 0.005 mole) in 1,4-dioxane (20 cm^3). The mixture was refluxed for twelve hours, allowed to cool to room temperature and filtered. The residue consisted of a purple coloured solid (AgCl). The filtrate was concentrated using a rotary evaporator whereupon a white solid separated out, which on recrystallisation from methanol yielded a white crystalline material. Yield 100%.

3.2.3 Synthesis of Bis(p-methoxyphenyl)tellurium dipicolinate

Silver picolinate (2.30g, 0.01 mole) was suspended in 1,4-dioxane (80 cm^3). To this suspension was added a solution of bis(p-methoxyphenyl)tellurium(IV) dichloride (2.06g, 0.005 mole) in 1,4-dioxane (20 cm^3). The mixture was refluxed for eighteen hours, allowed to cool to room temperature and filtered. The residue consisted of a purple coloured solid (AgCl). The filtrate was concentrated using a rotary evaporator whereupon a white solid separated out which on recrystallisation from benzene yielded a white crystalline material. Yield 90%.

3.2.4 Synthesis of Bis(p-ethoxyphenyl)tellurium dipicolinate

Silver picolinate (2.30g, 0.01 mole) was suspended in warm 1,4-dioxane (80 cm^3). To this suspension was added a solution of bis(p-ethoxyphenyl)tellurium(IV) dichloride in 1,4-dioxane (20 cm^3). The mixture was refluxed for 18 hours, allowed to cool to room temperature and filtered. The residue consisted of a purple coloured solid (AgCl). The filtrate was concentrated using a rotary evaporator whereupon an off-white solid formed. Recrystallisation from benzene using decolourising charcoal yielded a white crystalline material. Yield 85%.

3.2.5 Synthesis of Diphenyltellurium(IV) di(p-iodobenzoate)

Sodium (4-iodobenzoate) (2.70g, 0.01 mole) in hot methanol (20 cm^3) was added to a solution of diphenyltellurium(IV) dichloride (1.76g, 0.005 mole) in hot methanol (60 cm^3). The mixture was refluxed for six hours and allowed to cool to room temperature. The yellow solution was concentrated on a rotary evaporator yielding a pale yellow solid. On recrystallisation from nitromethane, a pale yellow crystalline material formed. Yield 90%.

3.2.6 Synthesis of diphenyltellurium(IV) di(2-chlorobenzoate)

Potassium (2-chlorobenzoate) (1.95g, 0.01 mole) in hot methanol (20 cm^3) was added to a solution of diphenyltellurium(IV) dichloride (1.76g, 0.005 mole) in hot methanol (60 cm^3). The mixture was refluxed for six hours and allowed to cool to room temperature. The colourless solution was concentrated using a rotary evaporator yielding a white solid. On recrystallisation from nitromethane a white crystalline material formed. Yield 80%.

3.2.7 Synthesis of Bis(3,4-dimethoxyphenyl)tellurium(IV) dibenzoate.

Silver benzoate (2.29g, 0.01 mole) was suspended in 1,4-dioxane (80 cm^3). To this suspension was added (3,4-dimethoxyphenyl)tellurium dichloride (2.37g, 0.005 mole) in 1,4-dioxane (20 cm^3). The mixture was refluxed for twelve hours, allowed to cool to room temperature and filtered. A purple residue was separated off (AgCl). The filtrate was concentrated using a rotary evaporator yielding a pale brown solid. Recrysallisation from benzene gave a brown crystalline material. Yield 70%.

3.2.8 Synthesis of Diphenylhydroxytellurium(IV) picolinate 0.5 1,4-dioxane

A solution of diphenyltellurium(IV) dichloride (1.76g, 0.005 mole) in 1,4-dioxane (20 cm^3) was added to a suspension of silver picolinate (2.30g, 0.01 mole) in 1,4-dioxane (80 cm^3). The mixture was refluxed for six hours, allowed to cool to room temperature and filtered. A purple residue was separated off (AgCl). The filtrate was concentrated using a rotary evaporator yielding a white crystalline solid which was recrystallised from ethanol. Yield 70%.

3.2.9 Synthesis of p-ethoxyphenyl-hydroxy-methoxytellurium picolinate

A solution of p-ethoxyphenyltellurium(IV) trichloride (1.775, 0.005 mole) in methanol (50 cm^3) was added to a solution of potassium picolinate (2.42g, 0.015 mole) in methanol (100 cm^3). The mixture was refluxed for eight hours and allowed to cool to room temperature. A white solid separated out which on filtration was recrystallised from chloroform. Yield 60%.

3.2.10 Reaction of p-ethoxyphenyltellurium(IV) trichloride and potassium picolinate

A solution of p-ethoxyphenyltellurium(IV) trichloride (1.42g, 0.004 mole) in 1,4-dioxane (40 cm^3) was added to a suspension of silver picolinate (2.77g, 0.012 mole) in 1,4-dioxane (40 cm^3). The reaction was carried out under dinitrogen (oxygen free atmosphere). The mixture was refluxed for six hours and allowed to cool to room temperature whereupon it was filtered. From the filtrate a white crystalline material formed which was recrystallised from methanol. Analytical data:- C= 48.68%, N= 3.43%, H= 6.62%.

3.2.11 Synthesis of p-ethoxyphenyl-dihyroxy-tellurium(IV) benzoate

A solution of p-ethoxyphenyltellurium(IV) trichloride (1.42g, 0.004 mole) in 1,4-dioxane (20 cm^3) was added to a suspension of silver benzoate (2.75g, 0.012 mole) in 1,4-dioxane (80 cm^3). The mixture was refluxed for six hours and allowed to cool to room temperature. On filtration a purple residue was isolated (AgCl) and a colourless solution retained. From the filtrate a white solid separated out which was washed in absolute ethanol. This material was found to be insoluble in common organic solvents. Yield 65%.

3.2.12 Synthesis of 2-(2-pyridyl)phenyltellurium(II) benzoate

2-(2'-pyridyl)phenyltellurium(II) chloride (1.59g, 0.005 mole) in 1,4-dioxane (30 cm^3) was added to a suspension of silver benzoate (1.15g, 0.005 mole) in 1,4-dioxane (70 cm^3). The mixture was refluxed for six hours, allowed to cool to room temperature and filtered. A purple residue was collected (AgCl). The filtrate was concentrated on a rotary evaporator whereupon a yellow solid separated out. On recrystallisation from benzene a pale yellow solid formed. Yield 50%.

3.2.13 Synthesis of 2-(2'-pyridyl)phenyltellurium(II) picolinate.

2-(2'-pyridyl)phenyltellurium(II) chloride (1.59g, 0.005 mole) in 1,4-dioxane (30 cm^3) was added to a suspension of silver picolinate (1.14g, 0.005 mole) in 1,4-dioxane (70 cm^3). The mixture was refluxed for six hours allowed to cool to room temperature and filtered. A purple residue was collected (AgCl). From the filtrate a yellow solid separated out which was recrystallised from nitromethane. Yield 60%.

3.2.14 Synthesis of 2-(2'-pyridyl)phenyldichlorotellurium(IV) picolinate

To a solution of 2-(2'-pyridyl)phenyltellurium(IV) trichloride (0.78g, 0.002 mole) in methanol (50 cm^3) was added to a solution of potassium picolinate (0.97g, 0.006 mole) in methanol (80 cm^3). The mixture was refluxed for twenty four hours and allowed to cool to room temperature. The pale yellow solution was concentrated on a rotary evaporator whereupon a yellow solid formed. This was recrystallised from toluene yielding a pale yellow solid. Yield 60%.

3.2.15 Synthesis of 2-(2'-pyridyl)phenyldibromotellurium(IV) benzoate.

A solution of 2-(2'-pyridyl)phenyltellurium(IV) tribromide (1.04g, 0.002 mole) in hot acetonitrile (40 cm^3) was added to a suspension of silver benzoate (0.46g, 0.002 mole) in 1,4-dioxane (50 cm^3). The mixture was refluxed for twelve hours under nitrogen, allowed to cool to room temperature and filtered. From the filtrate a yellow solid separated out which was recrystallised from nitromethane. Yield 55%.

3.2.16 Synthesis of 2-(2'-pyridyl)bromohydroxytellurium(IV) picolinate

To a solution of 2-(2'-pyridyl)phenyltellurium(II) bromide (0.36g, 0.001 mole) in hot acetonitrile (30 cm^3) was added a solution of potassium picolinate (0.16g, 0.001 mole) in hot methanol (20 cm^3). The mixture was refluxed for six hours under dinitrogen and allowed to cool to room temperature, whereupon a yellow solid formed. This was filtered off and recrystallised from nitromethane. Yield 60%.

3.2.17. Reaction of 1,3-dimethoxybenzene and $TeCl_4$

A) Tellurium tetrachloride (21.55g, 0.008 mole) in 1,4-dioxane (70 cm^3) was added to 1,3-dimethoxybenzene (11.05g, 0.08 mole). The mixture was stirred at room temperature and after 15 mins turned deep red. It was then refluxed for six hours and allowed to cool to room temperature. The deep red solution was concentrated on a rotary evaporator yielding a deep red coloured viscous oil. Addition of a 1:1 mixture of acetonitrile and ethanol to the oil produced a dark precipitate in a red solution. On filtration a green residue X was isolated which was found to be insoluble in common organic solvents. On evaporation of the filtrate a red solid formed Y which was recrystallised from acetonitrile. Yield 70%.

B) Tellurium tetrachloride (21.55g, 0.008 mole) in 1,4-dioxane (70 cm^3) was added to a solution of 1,3-dimethoxybenzene (22.10g, 0.16 mole). The reaction was worked up as in (A). A deep red viscous oil formed which on addition of a 1:1 mix of ethanol and acetonitrile gave a red solution. On evaporation, a red solid formed (Z) which was recrystallised from nitromethane. Yield 80%.

3.2.18 Synthesis of Bis(2,4-dimethoxy)phenyltellurium(IV) dibromide

To a solution of compound Y (0.5g) in acetonitrile was added dropwise an excess of bromine. The solution was stirred for two hours and allowed to evaporate in air yielding a pale orange solid. Recrystallisation from cyclohexane gave a white crystalline material.

3.2.19 Synthesis of Bis(p-methoxyphenyl)tellurium dibromide

To a solution of compound Z (0.5g) in acetonitrile was added dropwise an excess of bromine. The solution was stirred for two hours and allowed to evaporate in air yielding a pale orange solid. Recrystallisation from cyclohexane gave a white crystalline material.

RESULTS AND DISCUSSION

3.1 Characterisation of Diaryltellurium(IV) dicarboxylates

Diaryltellurium(IV) dicarboxylates can be prepared routinely by the stoichiometric addition of diaryltellurium(IV) dihalides to either silver carboxylate or sodium and potassium carboxylate salts in refluxing dioxane or alcoholic solvents.

$$R_2TeCl_2 + 2AgOOCPh \longrightarrow R_2Te(OOCPh)_2 + 2AgCl$$

Reactions of this type are not new and other synthetic pathways to diaryltellurium(IV) dicarboxylates have been studied one notable example being the reaction of lead tetraacetate with diaryltelluride.

$$R_2Te + Pb(OOCCH_3)_4 \longrightarrow R_2Te(OOCCH_3)_2 + Pb(OOCCH_3)_2$$

In the reactions involving the silver salts, purple residues were isolated which on mass balance calculations agree in all cases with the formation of silver chloride. The dicarboxylates formed here were found to be soluble in ethanol, methanol and benzene solvents.

Analytical, infra-red, N.M.R and mass spectroscopic data are collected in tables 1-4. In all cases the analytical data support the formation of diaryltellurium(IV) dicarboxylates with the exception of diphenyltellurium(IV) hydroxy-picolinate (0.5 dioxane), in which only one carboxylate group appears present (low % nitrogen value).

ANALYTICAL DATA

COMPOUND	M.Pt (^{0}C)	FOUND(REQUIRED) %C	%H	%N
R_2Te(benzoate)$_2$	209-210	56.8 (57.6)	3.92 (4.11)	
R'_2Te(benzoate)$_2$	195-196	58.6 (58.9)	4.55 (4.58)	
R_2Te(picolinate)$_2$	185-186	53.3 (53.3)	3.80 (3.76)	4.51 (4.78)
R'_2Te(picolinate)$_2$	150-152	54.4 (54.8)	4.20 (4.24)	4.00 (4.56)
Ph_2Te(4-iodobenzoate)$_2$	96-98	40.2 (40.2)	2.39 (2.34)	
Ph_2Te(2-chlorobenzoate)$_2$	95-97	52.4 (52.6)	3.02 (3.04)	
Ar_2Te(benzoate)$_2$	180-183	56.0 (55.9)	4.58 (4.35)	
Ph_2Te(OH)picolinate.0.5 diox	119-121	51.4 (51.4)	3.61 (3.57)	3.27 (3.33)
R'Te(OH)(OCH_3)picolinate	125-127	45.1 (44.7)	4.16 (4.22)	3.19 (3.32)
R'Te$(OH)_2$benzoate	241-243	44.6 (44.6)	3.35 (3.96)	
(2-phpy)Tebenzoate	170-172	53.1 (53.3)	3.28 (3.97)	3.39 (3.45)
(2-phpy)Tepicolinate	83-85	49.9 (50.5)	3.00 (2.97)	6.85 (6.94)

(2-phpy)$TeCl_2$.picolinate		257-259	42.8 (43.0)	2.60 (2.53)	5.54 (5.90)
(2-phpy)$TeBr_2$.benzoate		232-235	38.5 (38.4)	2.47 (2.33)	2.67 (2.49)
(2-phpy)Te(OH)(Br).picolinate		170-172	40.7 (40.8)	2.82 (2.60)	5.64 (5.59)
$(L_2TeCl^+)(LTeCl_2^-)$	(X green)	235-237	37.5 (37.3)	3.52 (3.49)	
$(L_2TeCl^+)(LTeCl_2^-)$	(Y red)	152(d)	37.3 (37.3)	3.41 (3.49)	
$L_2TeCl_2.2HCl$	(Z)	180(d)	35.2 (35.2)	3.47 (3.66)	
L_2TeBr_2			34.2 (34.2)	2.68 (3.21)	
R_2TeBr_2			33.4 (33.5)	2.81 (2.79)	

R = p-methoxyphenyl-

R'= p-ethoxyphenyl-

Ar = 3,4-dimethoxybenzene-

2-phpy = 2-(2'-pyridyl)phenyl-

L = 2,4-dimethoxybenzene-

Table 3.1 Analytical Data.

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv	δ(C-H)
Silver benzoate	1519	1387	132	836 718 678
Silver picolinate	1612	1391	221	839 751 743 699
Potassium (2-chlorobenzoate)	1576	1397	179	841 747 712 694 647
Sodium (4-iodobenzoate)	1539	1397	143	847 746 691 638

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv_{max}	**Te-O**	δ(C-H)
$R_2Te(OOCPh)_2$	1637	1321	317	552	825
	1621	1320			712
					678
$R'_2Te(OOCPh)_2$	1637	1319	319	551	833
	1625	1318			814
					716
					678
$R_2Te(OOCPy)_2$	1656	1350	332	553	827
	1630	1324			790
					747
					712
					697

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv	Te-O	δ(C-H)
$R'_2Te(OOCPy)_2$	1667 1638	1335 1320	347	553	834 820 806 752 710 696
$Ph_2Te(OOCC_6H_4I\text{-}p)_2$	1634	1305	329	561	843 739 687
$Ph_2Te(OOCC_6H_4Cl\text{-}2)_2$	1636	1311	325	565	848 744 722 687 649

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv	Te-O	δ(C-H)	Others
$Ar_2Te(OOCPh)_2$	1637	1298	339	548	855 842 808 783 766 711 678	
$Ph_2Te(OH)(OOCPy)$. 0.5 diox	1611	1376	235	570 525	872 851 832 739 697	3139 υ (OH)
$R'Te(OH)_2OOCPh$	1650	1320	320	627 558	824 799 710 681	

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv	Te-O	δ(C-H)	Others
R'Te(OH)(OCH$_3$)(OOCPy)	1625	1366	254	625	823 754 697	3431 υ(OH)
2-PhpyTeOOCPh	1624	1320	301	551	756 737 712 676	1605,1581 υ(C=N)
2-PhpyTeOOCPy	1630	1346	284	515	843 751 724 696	1604,1584 υ(C=N)
2-PhpyTeCl$_2$OOCPy	1561	1375	186	601 512	798 762 745 712 700	312 υ(Te-Cl) 1600,1580 υ(C=N)

COMPOUND	v_{as}(OCO)	v_{sym}(OCO)	Δv	Te-O	δ(C-H)	Others
2-PhpyTeBr_2(OOCPh)	1687	1326	361	631	753 708 685 668	1601,1580 υ(C=N)
2-PhpyTe(OH)Br(OOCPy)	1562	1366	194	597 519	845 763 749 700	3397 υ(OH) 1599,1580 υ(C=N)

R= p-methoxyphenyl-
R'= p-ethoxyphenyl-
Ar = 3,4-dimethoxybenzene-
2-Phpy = 2-(2'-pyridyl)phenyl-

Table 3.2 Infra-red Spectroscopic Data.

Mass Spectroscopy Data

Compound	Fragmentation Ion	m/e
$R_2Te(benzoate)_2$	Ph^+	78
	$CHO\text{-}C_6H_4^+$	105
Chemical Ionisation	$(PhCOOH)^+$	122
	RTe^+	237
	$RTe(OH)^+$	254
	$RTe(OH)_2^+$	271
	R_2Te^+	344
	$RTeOOCPh^+$	361
	$R_2TeOOCPh^+$	465
	$R_3Te_2^+$	577
$R'_2Te(benzoate)_2$	Ph^+	78
	$CHO\text{-}C_6H_4^+$	105
Chemical Ionisation	$(R'H)^+$	122
	$(Ph\text{-}COOH)^+$	122
	$R'Te^+$	251
	$RTe(OH)^+$	268
	$R'Te(OH)_2^+$	285
	$R'TeOOCPh^+$	372
	R'_2Te^+	372
	$R'_2TeOOCPh^+$	493
	$R'_3Te_2^+$	619
$R_2Te(OOCPy)_2$	$R_2TeOOCPy^+$	466
	R_2Te^+	344
Electron Impact	RTe^+	237
	$PyCOO^+$	124
	Py^+	79

Compound	**Fragmentation Ion**	**m/e**
$R'_2Te(OOCPy)_2$	Py^+	79
	$(PyCOOH)^+$	124
Electron Impact	$R'_2{}^+$	242
	R'_2Te^+	372
	$R'_2Te_2{}^+$	498
$Ar_2Te(OOCPh)_2$	Ph^+	78
	$CHO\text{-}C_6H_4{}^+$	122
Chemical Ionisation	$(PhCOOH)^+$	122
	R^+	105
	Ar^+	138
	$PhCOO^+$	244
	$ArTe^+$	267
	$Ar_2{}^+$	274
	Ar_2Te^+	404
	$Ar_2TeOOCPh^+$	525
$Ph_2Te(OH)(OOCPy).0.5$ diox	Ph^+	77
	Py^+	79
Electron Impact	$Ph_2{}^+$	154
	$PhTe^+$	207
	Ph_2Te^+	284
	$Ph_2Te(OH)^+$	301
$R'Te(OH)_2OOCPh$	Ph^+	77 EI
	R'^+	121 EI
Chemical Ionisation	$PhCOO^+$	121 EI
	$R'Te^+$	251
	$R'Te(OH)^+$	268
	$R'Te(OH)_2{}^+$	285
	$(R'_2Te + H)^+$	373

Compound	**Fragmentation Ion**	**m/e**
2-phpyTeOOCPh	$(Phpy)_2Te^+$	565
	$[(Phpy)_2Te + H]^+$	439
Chemical Ionisation	$[(Phpy)_2 + H]^+$	309
	RTe^+	284
	$(R + 2H)^+$	156
	$(Py - H)^+$	78
	$(PyCOO + H)^+$	124
2-phpyTeOOCPy	$(Phpy)_2Te_2^+$	565
	$(Phpy)_2Te^+$	438
Chemical Ionisation	$(Phpy)Te^+$	284
	$Phpy^+$	154
	$(PyCOO + H)^+$	124
	Py^+	79
$(L_2TeCl^+)(LTeCl_2^-)$ (X green)	$(L -2H)^+$	135
	LCl^+	171
Fast Atom Bombardment	L_2^+	274
	$LTeCl^+$	302
	L_2Te^+	404
	$L_2Te_2^+$	528
	$L_2Te_2Cl^+$	562

Compound	Fragmentation Ion	m/e
$(L_2TeCl^+)(LTeCl_2^-)$ (Y red)	$(L\text{-}H)^+$	136
	LTe^+	267
Chemical Ionisation	Ph_2Te_2	284
	$LTeCl^+$	303
	L_2Te^+	404
	L_2TeCl^+	439
	$L_2Te_2Cl^+$	565
	$L_3Te_2^+$	667
$L_2TeCl_2.2HCl$ (Z)	$(L\text{-}H)^+$	136
	L_2^+	274
Fast Atom Bombardment	$LTeCl^+$	302
	$LTeCl_2^+$	337
	L_2Te^+	404
	L_2TeCl^+	439
	$L_2TeCl_2^+$	473
	$L_2Te_2Cl^+$	561
	$L_2Te_3^+$	656
	$L_2Te_3Cl^+$	689

Based on ^1H, ^{12}C, ^{16}O, ^{35}Cl, ^{130}Te
(correct isotope patterns were observed for Te^{n+})

R = p-methoxyphenyl-

R'= p-ethoxyphenyl-

Ar = 3,4-dimethoxybenzene-

2-phpy = 2-(2'-pyridyl)phenyl-

L = 2,4-dimethoxybenzene-

Table 3.3 Mass Spectroscopic Data.

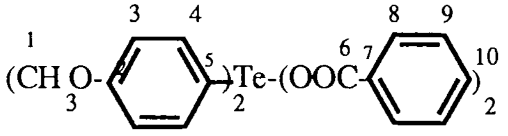
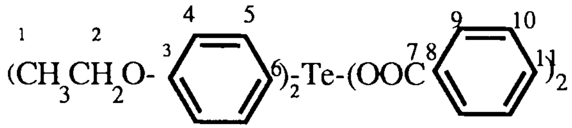
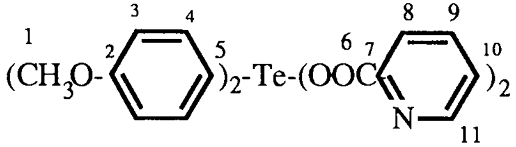
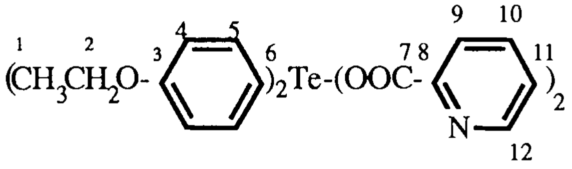
Compound	Solvent	C1	C2	C3	C4	C5	C6
		C7	C8	C9	C10	C11	C12
	$CDCl_3$	55.3	161.8	115.3	135.1	124.2	171.7
		132.0	128.1	129.8	132.2		
	$CDCl_3$	14.7	63.6	161.2	115.8	135.1	125.7
		171.1	132.1	128.0	129.8	132.2	
	$CDCl_3$	55.2	161.7	115.2	134.9	127.4	169.6
		149.3	137.1	126.2	125.1	149.1	
	$CDCl_3$	14.5	63.4	161.0	115.6	134.9	126.1
		169.5	149.3	125.5	136.8	125.1	149.1

Table 3.4 ^{13}C solution N.M.R

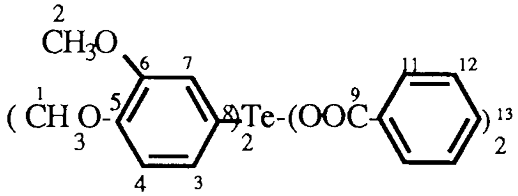
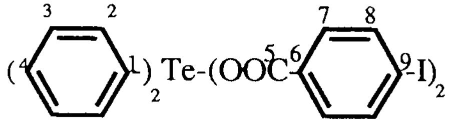
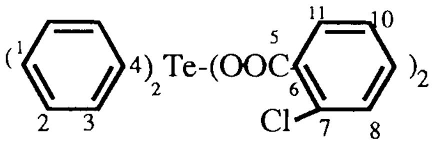
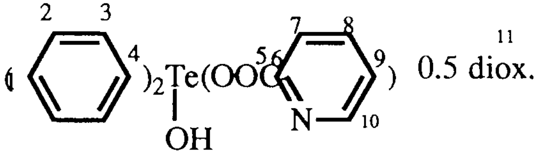
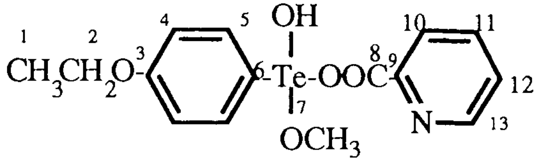
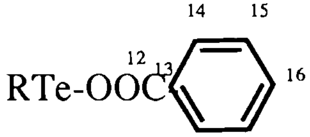
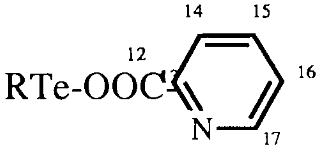
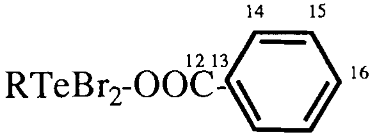
Compound	Solvent	C1 C8	C2 C9	C3 C10	C4 C11	C5 C12	C6 C13	C7 C14
	DMSO-D$_6$	55.1	55.6	111.8	116.3	149.6	151.4	132.4
		127.6	170.7	132.0	127.6	129.2	126.2	
	DMSO-D$_6$	129.6	128.1	128.6	136.4	171.8	137.8	133.3
		133.8	136.4					
	DMSO-D$_6$	129.8	126.4	129.7	131.8	171.3	133.1	135.0
		130.6	133.7	131.5	131.4			
	DMSO-D$_6$	129.6	133.1	128.6	140.7	169.8	152.5	124.1
		136.7	124.9	149.0	66.4			
	DMSO-D$_6$	14.6	63.3	---	115.7	137.0	---	52.7
		160.6	---	125.0	132.7	126.7	149.7	

Table 3.4 (continued) ^{13}C N.M.R data.

Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8	C9
		C10	C11	C12	C13	C14	C15	C16	C17	C18
	CDCl$_3$	133.1	132.9	128.0	131.3	130.7	134.3	155.0	120.7	137.9
		122.0	142.5	171.6	131.2	126.1	129.7	----		
	CDCl$_3$	133.0	137.9	120.2	138.1	124.8	133.5	150.3	121.0	142.1
		125.5	149.3	169.8	154.8	136.1	138.3	132.7	148.3	
	CDCl$_3$	130.7	139.6	128.5	133.4	124.0	134.2	153.0	121.0	143.7
		123.7	144.7	167.3	---	127.7	129.2	132.2		

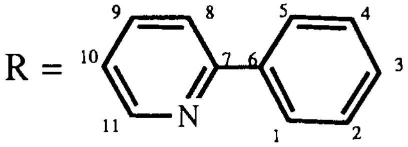
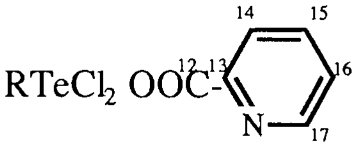
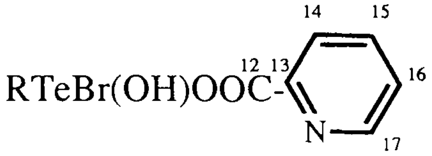


Table 3.4 (continued) ^{13}C N.M.R solution data.

Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8	C9
		C10	C11	C12	C13	C14	C15	C16	C17	C18
 RTeCl$_2$ OOC-	DMSO-D$_6$	---	---	120.4	137.0	124.8	135.2	---	124.1	140.8
		125.1	147.6	166.3	151.9	130.5	---	130.0	145.1	
 RTeBr(OH)OOC-	DMSO-D$_6$	---	137.1	129.9	---	124.7	135.1	146.5	120.4	140.8
		125.3	145.0	168.4	151.9	130.4	---	124.1	147.3	

R =

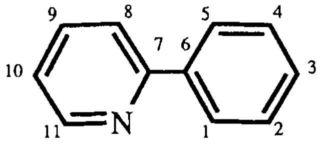


Table 3.4 (continued) ^{13}C solution N.M.R

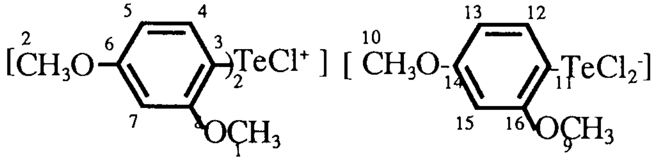
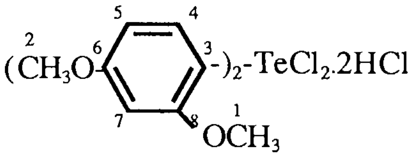
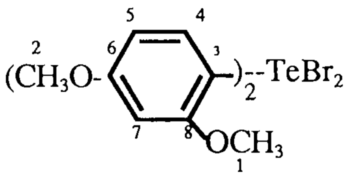
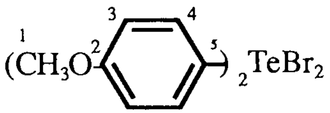
Compound	C1	C2	C3	C4	C5	C6	C7	C8
	C9	C10	C11	C12	C13	C14	C15	C16
 (Y)	57.2	55.9	115.7	134.6	108.7	164.0	99.4	160.0
	57.2	55.9	100.0	134.3	109.6	161.0	99.6	165.0
 (Z)	57.2	56.0	99.0	134.3	109.6	161.0	99.6	165.0
 (Y + Br$_2$)	56.5	56.5	101.2	134.7	132.1	155.4	98.8	156.0
 (Z + Br$_2$)	56.7	156.0	98.7	134.8	101.2			

Table 3.4 (continued) **^{13}C N.M.R data.**

From infra-red spectroscopic data solid state bonding features can be predicted. Carboxylate ligands may interact in a number of ways to metal centres (see Fig 3.1). Curtis(75) has shown that for acetato-complexes of tin, it is possible to distinguish ionic, unidentate, bidentate or bridging acetato-groups from the separation of the asymmetric and symmetric carboxylate (OCO) stretching vibrations. Thus Δv(OCO) will be greater for the monodentate group than for the free ion, whereas for the bidentate group, Δv(OCO) is generally less than for the free ion. For a bridging group the value of Δv(OCO) is comparable to that of the free ion. Although in our case we are not comparing "like with like", the model can help to predict important solid state structural features.

Examination of the infra-red spectra of the diorganyltellurium(IV) dibenzoates $R_2Te(OOCPh)_2$, $R'_2Te(OOCPh)_2$ and $Ar_2Te(OOCPh)_2$ [R= p-methoxyphenyl, R'= p-ethoxyphenyl- and Ar= 3,4-dimethoxyphenyl-] shows Δv separations of 317, 319 and 339cm^{-1} respectively. Comparing these values with that of the free ion (Δv = 132cm^{-1}) suggests that the carboxylate groups are bonding in a unidentate mode. On close inspection of the spectra of $R_2Te(OOCPh)_2$ and $R'_2Te(OOCPh)_2$, the asymmetric and symmetric vibrations actually exist as doublets. This detail either suggests there is coupling of the vibrations or their is a slight inequivalence of carboxylate ligands bonded to tellurium. An explanation of this may come from the packing of the molecules in the crystal lattice. If one regards the molecules as being four coordinate pseudo-trigonal bipyramidal, one carboxylate group may

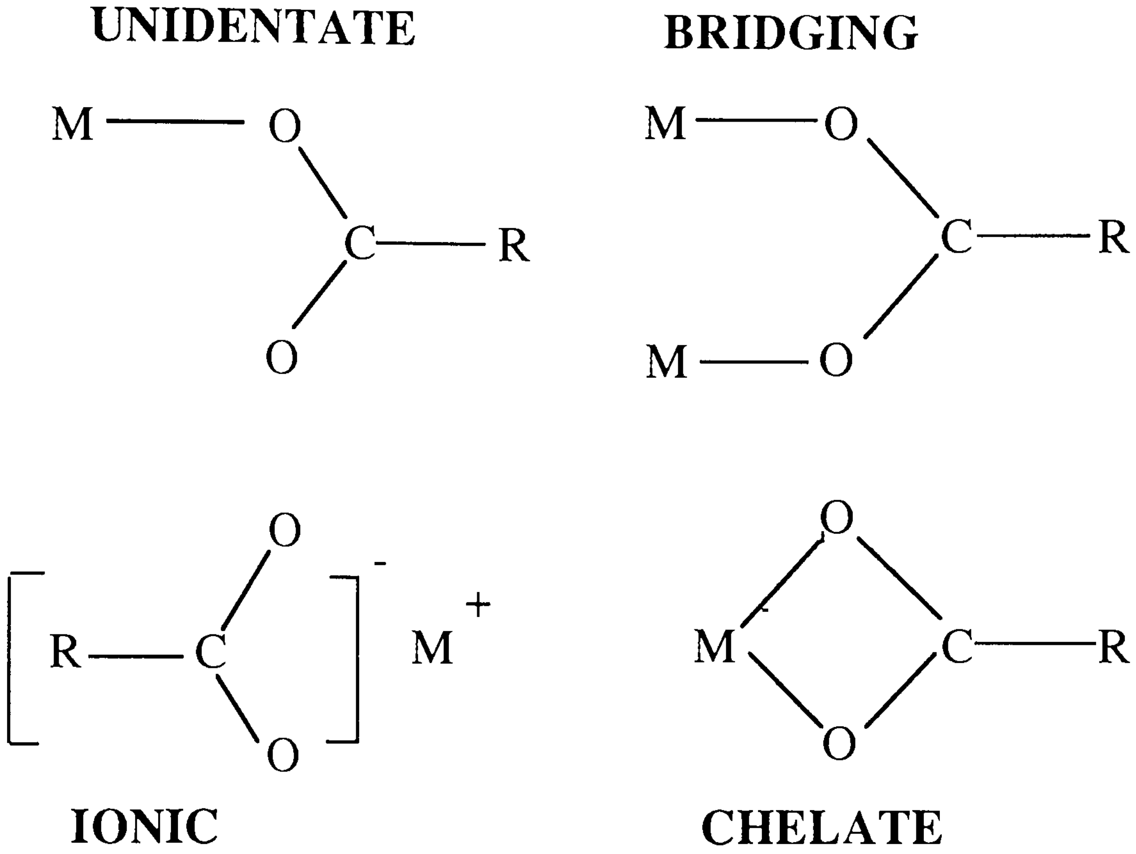


Figure 3.1 Types of structures the carboxylate ligand can adopt when interacting with a metal centre.

lie in the equatorial plane whilst the other lies in an axial position. Conversely and more likely, each ligand may have both equatorial and axial Te-O bonds. Using these models, axial Te-O bonds may be longer than equatorial Te-O bonds and hence their bonding to tellurium slightly weaker. Attempts to solve the crystal structure of $R_2Te(OOCPh)_2$ failed due to, we believe, a highly disordered packing arrangement of the molecules in the crystal lattice. Unit cell dimensions are quoted in chapter six.

In the case of the carboxylates formed from potassium and silver picolinate salts ($\Delta v = 221cm^{-1}$), the same pattern is observed. Thus $R_2Te(OOCPy)_2$ and $R'_2Te(OOCPy)_2$ ($\Delta v_{max} = 332$ and 347 cm^{-1} respectively) have inequivalent carboxylate groups bonding in a unidentate mode. Unidentate bonding of the carboxylate groups to tellurium is also found in Ph_2Te(4-iodobenzoate)$_2$ and Ph_2Te(2-chlorobenzoate)$_2$ but in these molecules no inequivalence of the ligands is observed.

In the reaction of diphenyltellurium(IV) dichloride and silver picolinate the dicarboxylate was not isolated. Instead, a white crystalline material, bearing only one picolinate group was formed (low % nitrogen). In the infra-red spectrum, the separation of the symmetric and asymmetic vibrations is $\Delta v=235cm^{-1}$. In this compound the carboxylate ligand probably interacts in an asymmetrical bidentate fashion. The broad band centered at $3139cm^{-1}$ is evidence for an O-H stretching vibration. This broad feature may imply hydrogen bonding. The occurence of broad bands centered at 570 and 525cm^{-1}, are assigned as Te-O vibrations and from this evidence it is likely that partial hydrolysis of the reactant has occurred at the tellurium site with the formation of a Te-OH bond. A common feature in the infra-red spectra of these compounds is the appearance of strong bands centered at around 500-600cm^{-1}. These bands are often broad in shape and are characteristic of Te-O vibrations in for example organotelluroximes(76).

Table 3.4 shows ^{13}C N.M.R data for the diaryltellurium(IV) dicarboxylate compounds. Assignments are based on comparison with model componds and in some cases by considering peak intensities (see later). Substituted carbons [e.g Te-C(aryl) and O-C(aryl)] also helped in the assignment. The most striking feature of each of the spectra is the appearance of a signal at ~170 ppm attributed to a carbonyl resonance. For comparison, the carbonyl signals in acetone and acetaldehyde are found at 203.8 and 199.3 ppm. In all the diaryltellurium(IV) dicarboxylate compounds, only one carbonyl signal is observed, implying equivalence of both carboxylate groups in solution under the conditions of the N.M.R experiment.

The chemical shift value for the signal from the *ipso*-carbon bonded to tellurium is unpredictable. In the compounds $R_2Te(OOCPh)_2$, $R'_2Te(OOCPh)_2$, $R_2Te(OOCPy)_2$, $R'_2Te(OOCPy)_2$ and $Ar_2Te(OOCPh)_2$ the signals are consistent at ~126 ppm. The small shift relative to benzene

(δ= 128.5 ppm) has been attributed to the "heavy atom effect" causing screening of the carbon nucleus. However downfield shifts to 131.8 ppm and 136.4 ppm are found in Ph_2Te(2-chlorobenzoate$)_2$ and Ph_2Te(iodobenzoate$)_2$.

Signals in the aliphatic region at ~15 ppm and ~63 ppm are assigned as methyl (CH_3) and methylene (CH_2) signals. The methylene carbon is deshielded somewhat due to the electron withdrawing effects of the electronegative oxygen atom deshielding the carbon nucleus.

The ^{13}C N.M.R spectrum of $Ph_2Te(OH)(OOCPy).0.5$ dioxane is useful in the characterisation of the compound. Assignment of the three quaternary carbon resonances is straight forward. Signals for the phenyl and the pyridyl groups could be distinguished from the 2:1 intensity differences. The signal at 66.4 ppm is assigned as 1,4-dioxane (all four carbons equivalent). This molecule could only have arisen from the solvent in the reaction. The proton N.M.R spectrum of this compound reveals a complex pattern in the aromatic region as expected. The dioxane signal is evident at 3.56 ppm. The presence of an O-H signal from the compound is not clear and may be masked in the aromatic region. Alternatively there may be rapid exchange with the small amount of water present in the N.M.R solvent.

Mass spectroscopic data for some of the diaryltellurium(IV) dicarboxylates are shown in table 3.4. As well as helping in the characterisation of these compounds, a number of important observations are made. Firstly the chemical ionisation spectra provide more information than the electron impact mass spectra. In no cases was the molecular ion observed. However the compounds fragment *via* the loss of one carboxylate ligand followed by a second loss and in all cases the R_2Te^+ ion was detected. It is therefore not surprising to find that the fragmentation ions RTe^+, $PhCOO^+$, $PyCOO^+$, Py^+ and Ph^+ are also noted. In the chemical ionisation spectra some of the ions often appear protonated. For example the compound $R_2Te(OOCPh)_2$ shows the ions $PhCOOH^+$, $RTe(OH)^+$ and $RTe(OH)_2{}^+$. Ions pertaining to tellurium clusters are also observed in some cases and probably arise from thermolysis of the sample.

In the context of MOVPE, the most important result from this work comes from the mass spectroscopic study. Clearly there is evidence from this work that diaryltellurium(IV) dicarboxylates decompose either thermally or *via* fragmentation with the initial loss of carboxylate groups. Although these compounds are non-volatile solids, their decomposition could release R_2Te or RTe species as volatile components within the MOVPE system. However the point must be made that the conditions of the mass spectroscopy experiment by no means match those used in MOVPE.

3.3.2 Attempts to form Aryltellurium(IV) tricarboxylates

Attempts to form aryltellurium(IV) tricarboxylates have been unsuccessful. Problems with alcolysis and hydrolysis were apparent despite efforts to dry solvents thoroughly.

In the reaction of p-ethoxyphenyltellurium(IV) trichloride and potassium picolinate a white solid was isolated. Analytical data support the presence of only one picolinate ligand in the molecule. The infra-red spectrum confirms the presence of picolinate with the separation of the asymmetric and symmetric (OCO) vibrations being 254cm^{-1} (c.f. Δv= 221cm^{-1} for potassium picolinate). Since the value is neither in the unidentate or bidentate regions, it is suggested that the bonding of the picolinate ligand to tellurium is almost certainly asymmetrical bidentate. A broad band at 3431cm^{-1} can be assigned to an O-H group.

On examination of the ^{13}C N.M.R spectrum the carbonyl signal is found at 160.6 ppm. Other signals are assigned similarly to those of the diaryltellurium(IV) dicarboxylate compounds. Interestingly, the signal at δ=52.7 ppm is assigned to a methoxy group and could only be explained by invoking methanolysis of the organometallic forming a Te-OCH$_3$ bond.

In a similar reaction but using an oxygen free atmosphere, a white unidentifiable crystalline material was formed. The high nitrogen value in the analytical data suggests three picolinate moieties are present. Close inspection of the infra-red spectrum confirmed the presence of a number of a number of carbonyl environments. Furthermore, a broad feature in the region 3000-2000cm^{-1}, implies the presence of free acid in the compound. The ^{13}C N.M.R. spectrum is not simple and although the paraethoxyphenyl group could be identified, along with at least one carbonyl resonance, the aromatic region was too complicated to confidently assign individual signals. Significant ions in the mass spectrum are Py^+ (m/e=79), Ph^+ (m/e=78), $R'_2{}^+$ (m/e=242) and R'_2Te^+ (m/e=372) [or $R'Te(OOCPh)^+$].

In the reaction of p-ethoxyphenyltelluruim(IV) trichloride with silver benzoate a white insoluble material was isolated. The analytical data, fits the formulation $R'Te(OH)_2(OOCPh)$. Evidence for the benzoate ligand comes from the infra-red spectrum in which $\Delta v=320cm^{-1}$ (c.f silver benzoate $\delta=132cm^{-1}$) implying unidentate bonding of the carboxylate ligand to tellurium. Whilst no N.M.R data could be obtained due to the compound's insolubility, mass spectroscopy data (table 3.3.) is helpful in the characterisation. No molecular ion is observed but the ions R'_2Te^+, $R'Te(OH)_2{}^+$, $R'Te(OH)^+$ and $R'Te^+$ are prominent. The presence of these ions suggests that fragmentation occurs by loss of the benzoate ligand. Since the compound is insoluble in a range of organic solvents, it is likely that it exists in a polymeric form, with propagation through Te-O bonds.

3.3.4 Characterisation of 2-(2’pyridyl)phenyltellurium(II) and tellurium(IV) carboxylates.

The reaction of equimolar solutions of 2-(2’-pyridyl)phenyltellurium(II) halide (2-phpyTeX) with either silver benzoate or silver picolinate affords both 2-(2’-pyridyl)phenyltellurium(II) benzoate and picolinate derivatives. The only other organotellurium(II)carboxylate reported is acetato(2-phenyl-C,N)tellurium(II) in which the crystal and molecular structure has been solved(77). In a similar reaction but using 2-(2’-pyridyl)phenyltellurium(IV)trihalide (2-phpyTeX_3), the related 2-(2’-pyridyl)phenyltellurium(IV)dihalocarboxylates are formed. Analytical, infra-red, N.M.R and some mass spectroscopic results are tabulated in tables 3.1-3.4. Some spectra are also included.

The analytical data fit the formulations $C_{18}H_{13}NO_2Te$ (ie. 2-PhpyTeOOCPh) and $C_{17}H_{12}N_2O_2Te$ (ie. 2-PhpyTeOOCPy). In the infra-red spectrum of 2-(2’-pyridyl)phenyltellurium(II)benzoate a doublet for both asymmetric and symmetric vibrations are observed. The separation $\Delta v=337cm^{-1}$ suggests that the ligands bond in a unidentate mode. The doublet for both vibrations is not unique and as described earlier may arise from coupling of carboxylate vibrations of different molecules within the crystal lattice. A similar observation is found in 2-(2’-pyridyl)phenyltellurium(II) picolinate where $\Delta v=310cm^{-1}$ and again unidentate bonding of the ligand to tellurium is invoked.

Structural bonding features can also be obtained for the organotellurium(IV)dihalocaboxylates. Thus 2-phpyTeBr_2(OOCPh) (Δv= 361cm^{-1}) shows unidentate bonding while 2-phpyTeCl_2(OOCPy) and 2-phpyTe(OH)Br(OOCPy) (Δv= 186 and 194cm^{-1} respectively) are likely to exist in bidentate co-ordination. In the latter compound a broad band at 3397cm^{-1} supports the view that an O-H functionality is present in the compound, bonded to tellurium.

On careful inspection of the C=N vibrations of the pyridyl ring, it is seen that the organotellurium(II) carboxylates bands appear at a slightly higher wavenumber (1604-1605cm^{-1}) than the organotellurium(IV) carboxylates (1599-1601cm^{-1}). If this difference is real then the tellurium-nitrogen contact is probably slighty stronger in the case of the tellurium(II) compounds. This observation can also be observed in the 2-(2'-pyridyl)phenyltellurium(II) and Te(IV) halides.

The ^{13}C N.M.R results are tabulated in table 3.4. Both the carboxylate and the 2-phenylpyridine signals are observed in all the compounds. The furthest downfield signals found are assigned to carbonyl carbons. These signals are found slightly further downfield in the tellurium(II) than those of the tellurium(IV) compounds. The ring carbons are assigned relative to model compounds particularly the useful bank of compounds based on 2-phenylpyridine characterised by Al-Salim(74).

There are similarities in the mass spectra of both the organotellurium(II) carboxylates. Both spectra show the ions $R_2Te_2^+$ as the highest m/e fragments, along with R_2Te^+ and RTe^+ species. The molecular ions are not observed. The carboxylate ions $PhCOO^+$ and $PyCOO^+$ are also prominent along with their fragmentation ions Ph^+ and Py^+. In the compound RTeOOCPh, the biaryl species R_2^+ is also noted.

The stability of organotellurenyl compounds involving 2-phenylpyridine has been attributed to the strong intra-molecular Te-N coordination(77). It is felt that the stability of these organotellurium(II) carboxylates are no exception. We may speculate that when these compounds are heated, they breakdown *via* the elimination of carbon dioxide releasing the unsymmetrical telluride. This in turn may be a volatile source of tellurium.

$$\text{RTeOOCR'} \xrightarrow{\Delta} \text{RTeR'} + CO_2$$

However mass spectroscopy does not detect any of the telluride species (RTeR') but nethertheless this does not mean it is not present. The experimental conditions here are more forceful that those used in the MOVPE process where the solids are simply heated and therefore we may not be seeing the real decomposition products (e.g RTeR')

A programme of work in which the benzoate and picolinate moieties are substituted with for example acetate, seems a worthy route for further investigations. The chances of forming solids at room temperature which may be a source of volatile compounds (eg. $RTeCH_3$), are likely to be in our favour. As mentioned earlier the compound acetato(2-(2'-pyridyl)phenyl-C,N)tellurium(II) has been reported and so other similar compounds should be realistic possibilities.

3.3.5 Attempts to characterise (L_2TeCl^+)($LTeCl_2^-$).

[Bis(2,4-dimethoxyphenyl)tellurium(IV) chloride][2,4-dimethoxytellurium(II) chloride.]

In an attempt to form bis(2,4-dimethoxyphenyl)tellurium(IV) dichloride (as a reactant for dicarboxylate synthesis), green (X) and red (Y) solids were isolated from the reaction of 1,3-dimethoxybenzene and tellurium tetrachloride in 1,4-dioxane. A fit for $L_3Te_2Cl_3$ can be obtained from the analytical figures for both compounds which may imply the formulation (L_2TeCl^+)($LTeCl_2^-$). The red (Y) solid was found to be a 1:1 electrolyte in acetonitrile (Λ= 92 ohm^{-1}cm^{2}mole^{-1}). The green solid (X) is insoluble in common organic solvents and hence its solution conductivity could not be recorded. The infra-red spectra of both compounds confirm the presence of the organic groups. The ^{13}C N.M.R. spectrum of Y (table 3.4) was recorded in DMSO and is complex. On first impression there appears to be two sets of signals with one set of double intensity relative to the other. The two signals at δ=108.2 and 100.0 ppm are assigned as Te-C(aryl) resonances. These carbons appear strongly shielded due to the "heavy atom effect" discussed earlier. This observation implies there are two positions on the ring which have been tellurated or two rings have been tellurated. Since there are fourteen signals present in the spectrum it is more likely that two rings have been tellurated. The position of telluration can be determined by considering electronic and steric effects (see figure 3.2).

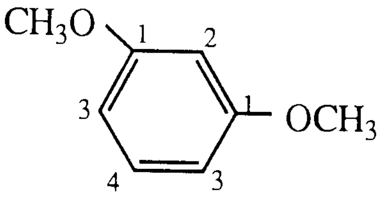


Figure 3.2

Electronically the positions likely to be tellurated are those ortho (or para) to the methoxy groups (eg. carbons 2 and 3). For steric reasons carbon (2) is an unlikely possibility. Carbon (4) which is sterically the most favourable position is electronically unlikely to be tellurated. Therefore the most likely position of telluration is at carbon (3). If this is so, six signals should be observed in the aromatic region. There are actually twelve and this leads us to the conclusion that there are two ortho-tellurated groups of different chemical constitution. Since the compound is an electrolyte in solution, it is likely to be dissociated in DMSO (the N.M.R solvent) and therefore a formulation based on $(L_2TeCl^+)(LTeCl_2^-)$ (L= 2,4-dimethoxybenzene) may be proposed. The set of signals of greater intensity belong to the ligand in the cationic moiety. Conversely the weaker set correspond to the ligand in the anionic moiety. This formulation suggests both Te(IV) and Te(II) species are present. The signal at δ= 100 ppm in the ^{13}C N.M.R spectrum lends support for the presence of the tellurium(II) species since the corresponding *ipso* signals in other tellurium(II) compounds have been observed in this region(78). The Te(IV)-C(aryl) signal is found further downfield as expected for organotellurium(IV) compounds. The red colour of the compound in the solid state and in solution may also be explained by the presence of tellurium(II) species. The visible absorption spectrum in acetonitrile showed a broad band at 515nm (e= 60 mole^{-1}dm^{3}cm^{-1}). An anomaly of the ^{13}C N.M.R spectrum lies in the aliphatic region. Whilst methoxy signals are present there are only two resonances. In theory and using the formulation $(L_2TeCl^+)(LTeCl_2^-)$, one might expect four signals since both ligand groups are in different chemical environments. One can only surmise that there are overlapping resonances in this region.

The chemical ionisation mass spectrum for Y shows ions for L_2TeCl^+, L_2Te^+, $LTeCl^+$ and LTe^+. Tellurium clusters are also noted at m/e=565 ($L_2Te_2Cl^+$) and m/e=667 ($L_3Te_2^+$). The fast atom bombardment mass spectrum of X shows the ions $LTeCl^+$, L_2Te^+ and tellurium clusters at m/e=528 ($L_2Te_2^+$) and m/e=562 ($L_2Te_2Cl^+$). Both X and Y are believed to be isomeric forms of the same compound.

The analytical figures for the green compound X are very similar to Y and we may have the same formulation $(L_2TeCl^+)(LTeCl^-)$. The insolubility of X suggests that it may exist in a polymeric form. For example the cation may be polymeric with propagation through Te-Cl bonds eg.

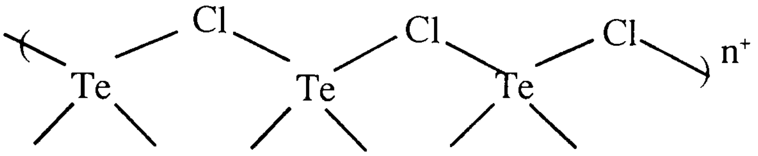


Figure 3.3

This type of species [ie. $(L_2Te_2Cl^+)_n$] is present in the mass spectrum and is isoelectronic to $(RTeSTeR)_n$.

On bromination of Y white crystals of bis(2,4-dimethoxyphenyl)-tellurium(IV) dibromide were obtained (characterised from analytical and ^{13}C N.M.R) as the only reaction product.

$$2(L_2TeCl^+)(LTeCl_2^-) \xrightarrow{\text{ex } Br_2,\ CH_3CN} 3L_2TeBr_2 + 6Cl^-$$

The tellurium chloride bonds are cleaved and replaced by tellurium bromide bond formation. The eight signals observed in the ^{13}C N.M.R spectrum supports the idea that telluration of 1,3-dimethoxybenzene occurs at the ortho position which is the least sterically hindered.

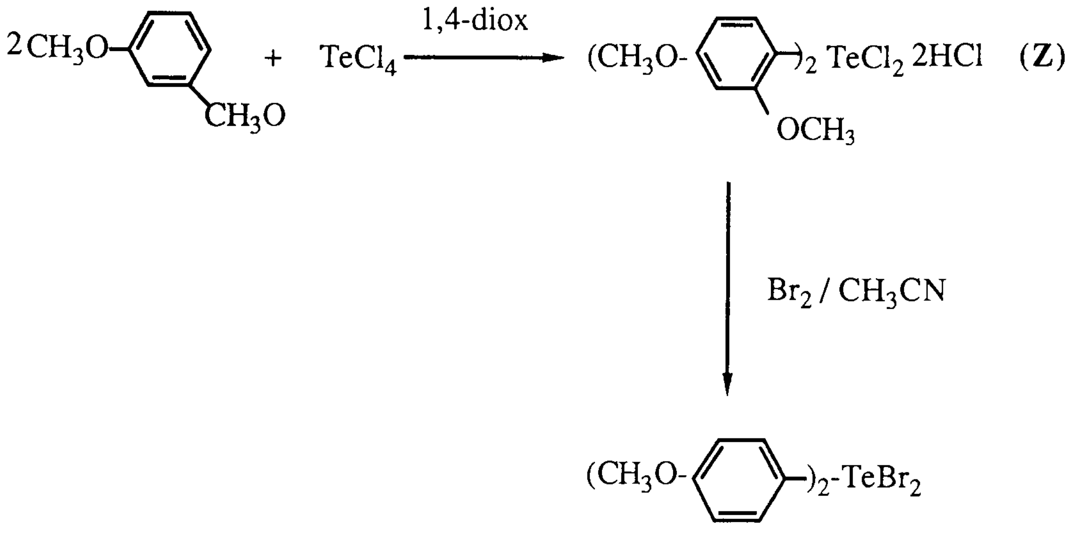
In conclusion, analytical, infra-red, conductivity, N.M.R and mass spectroscopy support the ionic formulation $(L_2TeCl^+)(LTeCl^-)$ for Y. Only limited data were collected for X and it's characterisation is more speculative. It is believed to be polymeric.

3.3.6 Attempts to characterise $L_2TeCl_2.2HCl$ (L= 2,4-dimethoxybenzene).

In a similar reaction to the above but using a two fold molar excess of 1,3-dimethoxybenzene, a red solid Z was isolated as the only reaction product. A fit for $L_2TeCl_2.2HCl$ was found from the analytical data. A broad feature in the infra-red spectrum at $3449cm^{-1}$ implies strong hydrogen bonding within the molecule attributed to either O-H or H-Cl bonding (the latter seems unlikely in view of the heavier mass of chlorine). The conductivity in acetonitrile (10^{-3}M solution) gave a value of $\Lambda = 115 ohm^{-1}cm^2mole^{-1}$ based on the formulation $L_2TeCl_2.2HCl$ slightly lower than expected for a 2:1 electrolyte. The ^{13}C N.M.R (table 3.4) shows eight signals. On comparison of these signals with those of the $RTeCl_2^-$ moiety (Y), it is found that both sets have almost identical chemical shifts. As concluded for compound Y, telluration occurs at the least hindered ortho position. An alternative formulation to $L_2TeCl_2.2HCl$ can be made; for example $(LH^+)_2TeCl_4^-$ in which protonation of a methoxy group is invoked. The broad band at $\upsilon=3449cm^{-1}$ in the infra-red spectrum would explain the presence of an O-H functionality. However the ^{13}C N.M.R data does not support this idea since there is no evidence for further deshielding of any of the methoxy carbons. Therefore the ^{13}C N.M.R and infra-red data are not consistent.

The fast atom bombardment mass spectrum of Z gives numerous tellurium cluster fragments for example, L_2Te^+, L_2TeCl^+ and $L_2TeCl_2^+$ (see table 3.3). Of particular interest is the fragment at m/e=656 ($L_2Te_3^+$) which is a rare example of a cluster containing three tellurium atoms. The spectrum only serves to confirm the presence of organic and tellurium moieties.

In an attempt to probe the formulation of Z further, its reaction with bromine was investigated. White crystals were isolated which from analytical, infra-red and ^{13}C N.M.R data, undoubtedly support the formation of bis(p-methoxyphenyl)tellurium(IV) dibromide. The interesting chemical point to note is the cleaving of the C-O bond with the loss of a methoxy group ortho to tellurium. The diagram below illustrates this.



No definitive mechanistic explanation can be given at this stage. However one may propose that Z exists in the form $L_2TeCl_2.2HCl$ and when brominated in acetonitrile, the acidic protons (H^+Cl^-) attack the site of the ortho-methoxy group yielding methanol and protonating the aromatic ring. The bromine appears only to attack the tellurium atom with Te-Cl bond cleavage and Te-Br bond formation.

In summary, the analytical data support the formulation $L_2TeCl_2.2HCl$. The compound is an electrolyte in solution. The ^{13}C N.M.R supports this formulation with telluration of the organic group occuring at the least sterically hindered ortho position. In contrast the infra-red spectrum supports the view that protonation of at least one of the methoxy groups has occured from the presence of a broad band at high wavenumber in the spectrum (O-H). Therefore infra-red supports the formulation $(LH)_2{}^+TeCl_4{}^{2-}$. Clearly more information is needed for complete characterisation.

3.4 Organotellurium carboxylates for MOVPE.

The compounds synthesised and characterised in this work are high molecular weight non-volatile solids. Conventional MOVPE requires compounds of vapour pressure >1 torr at room temperature and realistically our compounds are of little use in this respect. Nethertheless some important conclusions and suggestions can be made

An important observation from the mass spectroscopy study is that these compounds breakdown *via* Te-O bond cleavage and the loss of carboxylate ligands. In all cases either RTe^+ and/or R_2Te^+ are observed and in some cases the carboxylate ion (eg. $PhCOO^+$). This in turn decomposes with loss of carbon dioxide (not detected). Emphasis must be placed on the fact that the mass spectroscopy technique does not model the conditions in the MOVPE system but there are similarities. Along with tellurium and carboxylate species, biaryl ions are also prominent in some cases. From an MOVPE point of view, this is an important observation indicating that on breakdown of these compounds volatile by-products are produced which would be carried away in the MOVPE process and lead to less carbon contamination in the growing layer.

Whilst no efforts were made to optimise the design of this type of precursor, it is felt that by replacing the aromatic groups with alkyls say, therefore using lower molecular weight molecules, this class of compound must be worthy of further investigations.

CONCLUSIONS

Diaryltellurium(IV) dicarboxylates can be synthesised routinely and in high yield by the reaction of diaryltellurium(IV)dihalide with silver and potassium carboxylate salts. Attempts to form organotellurium(IV) tricarboxylates were unsuccessful. Problems with solvolysis were apparent leading to monocarboxylate compounds. Two organotellurium(II) carboxylates have been prepared and are believed to be stabilised by intra-molecular Te-N coordination.

In all the carboxylate compounds, structural bonding features of the carboxylate ligands to tellurium have been predicted using infra-red measurements. In the mass spectra of all of the compounds studied, fragmentation occurs with the loss of the carboxylate ligands releasing organotellurium ions (eg. RTe^+). Although the compounds are non-volatile high molecular weight solids they are stable in air and therefore easy to handle making them attractive for MOVPE purposes. They may decompose thermally *via* the loss of carbon dioxide to yield volatile telluride intermediates (eg. RTeR').

Chapter Four

ORGANOPOLYCHALCOGENIDE AND CYCLIC TELLURIUM COMPOUNDS

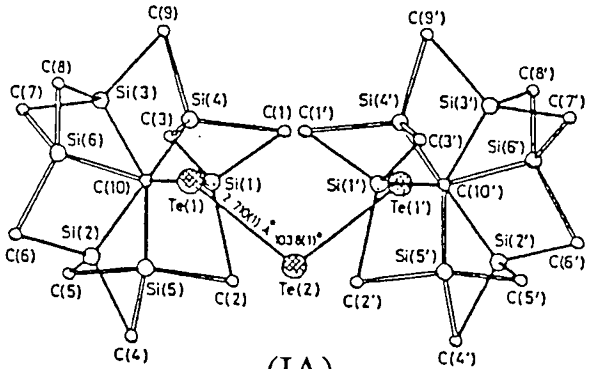
4.1 INTRODUCTION

Most tellurium sources explored to date for the growth of cadmium mercury telluride have featured the simple alkyl telluride precursors (eg. R_2Te). These are attractive compounds since they may be readily sythesised and offer suitable volatilities for film growth. However not only are these materials highly toxic and therefore present handling difficulties, they also require high temperatures for good quality film growth for reasons explained in chapter one.

We became interested in designing alternative tellurium precursors. There are many classes of organotellurium compounds which are worthy of investigation but for this programme of work we decided to select two types; organopolytellurides and cyclic tellurides. Cyclic tellurium compounds are a well known class of compound and there are numerous reports throughout the literature. On the contrary reports on organopolytellurides are rare. A major impetus for studying polytelluride compounds is the hope that they would be rich sources of tellurium. The prediction is that compounds of the type R_2Te_n decompose thermally *via* successive release of elemental tellurium, thus:-

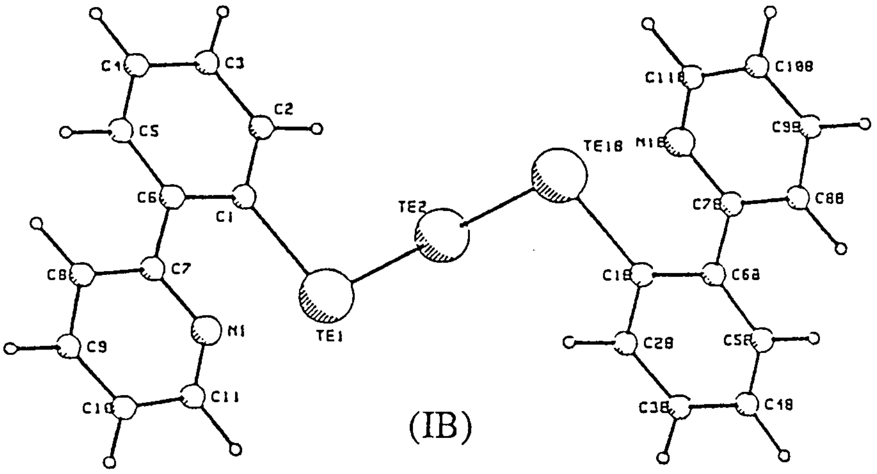
$$R_2Te_n \longrightarrow R_2Te_{n-1} \longrightarrow R_2Te_{n-2} \cdots\cdots\cdots> R_2Te$$

The propensity for catenation to form oligomeric E_n chains declines in the order S > Se >> Te. Organopolyselenium compounds, for example tri- and tetraselenium dimorpholide(79) are quite common. However it is not surprising to note that compounds involving chains of tellurium atoms are scarce. Diorganylditellurides are well known but only two diorganyltritellurides have been reported. The bulky ligand tris(trimethylsilyl)methyl has been used to stabilise the tritelluride (IA) below(80).



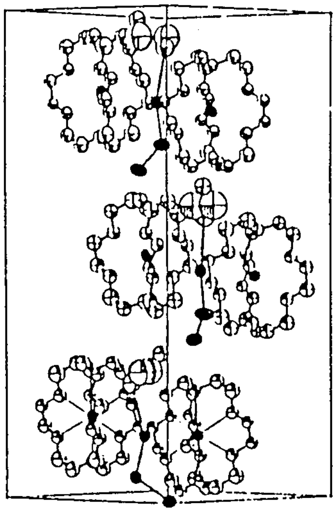
(IA)

Recently in our laboratory, bis(2-(2'pyridyl)phenyl)tritelluride (IB) was synthesised by the reduction of 2-(2'-pyridyl)phenyltellurium(IV) tribromide with sodium borohydride. The compound has been crystallographically characterised (Te-Te= 2.776(1) Å) and is believed to be stabilised by intra-molecular Te-N coordination(80).



(IB)

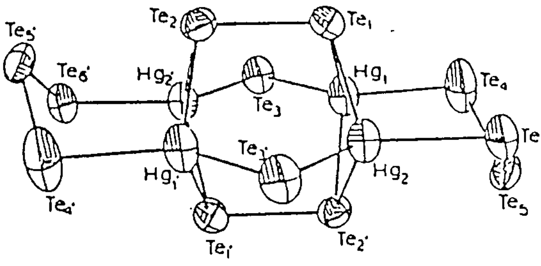
Despite only two diorganotritellurides being reported, there has been a handful of inorganic polytellurides reported in the last ten years. Very recently a comprehensive review by Ibers(81) highlights the progress made in synthesising inorganic polychalcogenide materials. A salt containing the tritelluride ion has been synthesised by using a crytand to sequester the alkali metal counterion(82). Thus (4,7,13,16,21,24-hexa-oxa-1,10diazobicyclo[8.8.8] hexacosane)-potassium tritelluride ethylenediamine (II) [$(KCrypt)_2Te_3$.en] contains a cryptate complexed potassium ion, ethylenediamine and the Te_3^{2-} anion (where Te-Te = 2.692 and 2.720 Å).



Tellurium and potassium atoms are darkened.

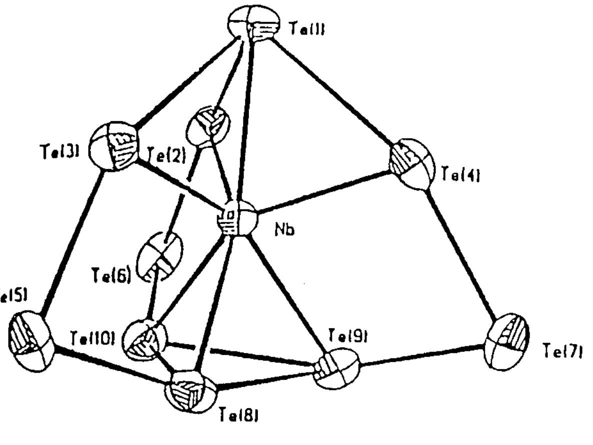
(II)

Polytelluride and polyselenide anions prepared from the elements and an alkali metal in liquid ammonia have been shown to be convenient reagents for the generation of a variety of metal polychalcogenides(83). Haushalter and co-workers found that the ethylenediamine extraction of certain ternary melts of composition $(M^1)_x(M^2)_yTe_2$ [M^1= alkali metal, M^2= Hg, Au,] provides a convenient preparative route to a variety of structurally diverse polytelluride clusters such as $[Hg_4Te_{12}^{4-}]$(84) (III) $[Hg_2Te_5^{4-}]$(84), $[KAu_9Te_7^{4-}]$(85) and $[Au_2Te_4^{2-}]$(85).



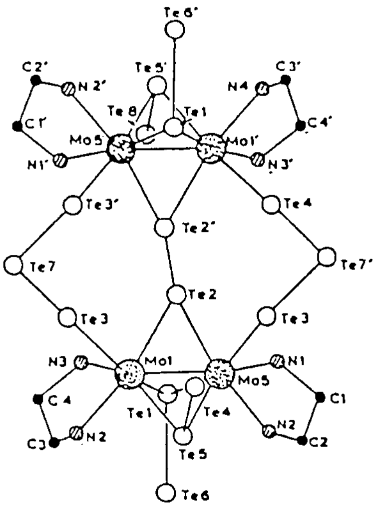
(III)

The solubility of polytelluride ions such as Te^{2-}, Te^{3-} and Te_4^{2-} in DMF and ethylenediamine has been used to form transition metal polytelluride clusters. Kolis and Flomer have reported the anion $NbTe_{10}^{3-}$ (86) in which the Nb atom is encapsulated by a bird-like sheath (IV).



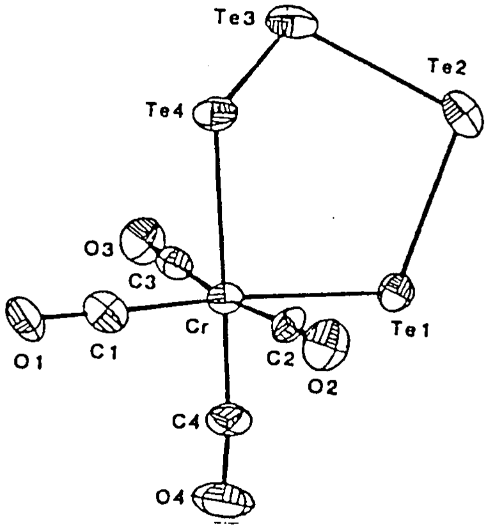
(IV)

The anion $Mo_4Te_{16}(en)_4^{2-}$(87) has also been reported and comprises of two d^3-d^3 Mo_2^{6+} units linked by a central Te_2^{2-} ligand and two Te_3^{2-} chains (V).



(V)

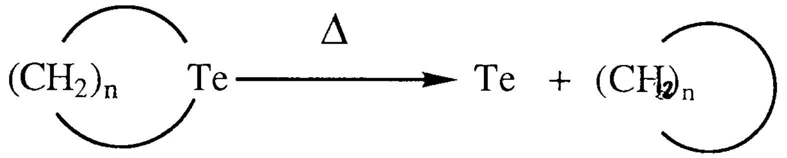
Anions containing chains of four tellurium atoms have also been reported eg. $Cr(CO)Te_4^{2-}$(83) (VI).



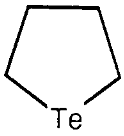
(VI)

These results inspired us to believe that organopolytelluride compounds should also be realistic possibilities. Due to constraints in our laboratory, the molecules targeted were based on high molecular weight aromatics (believed to be easier to handle). Recently in our laboratory, others have demonstrated that organotellurenyl halides (RTeX) (for example R= 2-phenylpyridine and 2-phenylquinoline) can be routinely synthesised(78) and are believed to be stable due to intra-molecular Te---N coordination. We believe that bis(2-(2'pyridyl)-phenyl)tritelluride can be considered as a bis(organotellurenyl)-telluride, ie. $(RTe)_2Te$ and that by reacting RTeX with polytelluride anions (Te_n^{2-}) other higher polytellurides $(RTe)_2Te_n$ should be viable compounds.

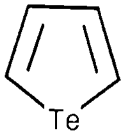
The choice of studying cyclic tellurium compounds as MOVPE precursors continues the theme of exploring molecules which readily release tellurium under thermal conditions. The key to decomposition lies in the ring strain effects in these organometallics.



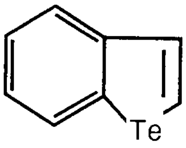
There are numerous reports in the literature of cyclic tellurium compounds stretching back to the beginning of the century(88). Examples are telluracyclopentane (VII), tellurophene (VIII) and benzotellurophene (IX).



(VII)

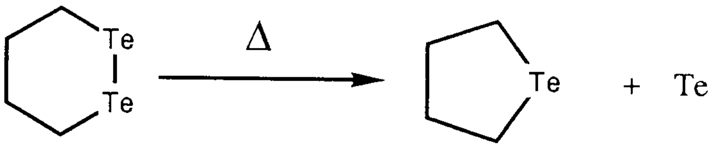


(VIII)

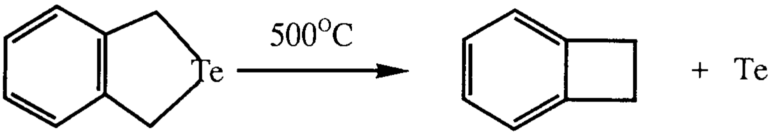


(IX)

1,2-Ditellurane has been synthesised by Singh and is an example of a six membered alicyclic ditelluride in which the Te-Te bond is believed to be highly reactive(89) due to ring strain effects. This type of precursor may be useful since on heating, tellurium extrusion may readily occur with the formation of telluracyclopentane (which in turn may yield a further source of tellurium).



Extrusion of tellurium does occur from some dihydrotellurophenes at temperatures of 500°C. This method has been used to synthesise cyclobutenes for example,



In the work reported here, some modified synthetic procedures are noted for some cyclic tellurium compounds. Their thermochemistry has not been studied as yet but may be the subject of future work.

4.2 EXPERIMENTAL

The compounds $RTeBr_3$, RTeBr (R= 2-(2'-pyridyl)phenyl-) $R'TeBr_3$ and R'TeBr (R'= 2-(2'-quinolinyl)phenyl-) were prepared according to the literature methods(78). The analogous chloride compounds were similarly prepared but substituting $TeCl_4$ for $TeBr_4$. The compounds (pap)$TeCl_3$(90) and (pap)TeCl(90) (pap= 2-phenylazobenzene) were also prepared by the literature methods.

4.2.1 Synthesis of Bis(2-(2'-pyridyl)phenyl)tritelluride

1) The same method was used here to that given by Al-Salim(74).

2-(2'-pyridyl)phenyltellurium(IV) tribromide (1.30g, 0.015 mole) was suspended in absolute ethanol (60 cm^3) and treated dropwise with a solution of sodium borohydride (0.55g, 0.015 mole) in absolute ethanol (10 cm^3). The solid dissolved with the evolution of a gas and black tellurium was noticed. After completion of addition, the tellurium redissolved and the solution appeared deep red. It was heated gently for 30 minutes and filtered whilst hot. On standing in air at room temperature a brown solid formed which partially decomposed to tellurium. The solid was filtered off, washed in ethanol (20 cm^3) and recrystallised from benzene. Yield 30%, m.p.= 166-167°C (lit. 165-166°C).

2) The same method was used as in (1) except the reaction was carried out under dinitrogen. The reaction proceeded smoothly until the

red solution was observed when almost immediately the solution decomposed to black tellurium and a colourless solution. The reaction was repeated several times with the same observation.

3) Tellurium powder (0.319g, 0.0025 mole) was suspended in DMF (40 cm^3) and the mixture stirred for one hour under argon gas. Sodium (0.115g, 0.005 mole) in small pieces was carefully added and the mixture stirred under gentle heat for one hour. The tellurium dissolved with the formation of a pale yellow solution. A solution of 2-(2'-pyridyl)phenyltellurium(II) bromide (1.085g, 0.005 mole) in DMF (20 cm^3) was added dropwise and the mixture heated at 60°C for three hours during which time the solution appeared pale orange. On cooling to room temperature, a black solid (tellurium) formed in an orange solution. The solution was filtered and the filtrate collected, concentrated to a small volume on a rotary evaporator, whereupon an orange solid formed. This solid was recrystallised from benzene. Yield 40%, m.p.= 166-167°C (lit.=165-166°C).

4) Rongalite (sodium formaldehyde sulfoxylate) (0.46g, 0.003 mole) was dissolved in an aqueous solution of sodium hydroxide (30 cm^3, 10%). To this solution was added tellurium powder (0.38g, 0.003 mole) and the mixture gently heated (~60°C) for three hours during which time the tellurium dissolved and a pale pink solution formed. A solution of 2-(2'-pyridyl)phenyltellurium(II) bromide (0.217g, 0.006 mole) in DMF (30 cm^3) was added dropwise whereupon a pale yellow coloured

solid formed. The mixture was gently heated for two hours and allowed to cool to room temperature. The yellow solid was filtered off and washed in DMF (50 cm^3). This solid was found to be insoluble in common organic solvents (characterised as RTe(O)Br - see later). Yield 80%, m.p.= 145°C(d).

4.2.2 Synthesis of Bis(2-(2'-Quinolinyl)phenyl)tritelluride.

Two methods were used. The first, method (A) was the same procedure as that used by Al-Salim(74).

A) 2-(2'-Quinolinyl)phenyltellurium(IV) tribromide (1.14g, 0.002 mole) was suspended in absolute ethanol (25 cm^3). Tellurium powder (0.13g, 0.001 mole) was added and the mixture stirred under argon gas. Sodium borohydride in ethanol (15 cm^3) was added dropwise until all the tellurium disappeared. During borohydride addition a red solution formed and a gas was evolved. The red solution was refluxed for 30 minutes and then allowed to cool to room temperature whereupon an orange solid formed which was filtered off and recrystallised from benzene. Yield 50%, m.p= 206-207°C (lit= 211-212°C).

B) Tellurium powder (0.319g, 0.0025 mole) was suspended in DMF (50 cm^3). Sodium (0.115g, 0.005 mole) was carefully added in small pieces and the mixture was heated to 60°C and stirred under argon for one hour during which time the tellurium redissolved and a pale orange coloured solution formed. A solution of 2-(2'-quinolinyl)phenyltellurium(II) bromide (2.07g, 0.005 mole) in DMF (10 cm^3) was added dropwise and the orange solution stirred at 60°C for three hours. On cooling to room temperature a black solid (tellurium) appeared in an orange solution. The solid was filtered off and from the filtrate an orange solid formed which was recrystallised from benzene. Yield 30%, m.p.= 208-209°C.

4.2.3 Generation of the ditelluride anion (Te_2^{2-})

In some of the following syntheses the ditelluride (Te_2^{2-}) anion is used. Three methods of generating this ion by reduction of tellurium have been devised and are given here.

(i) Rongalite ($HOHCH_2SO_2Na.2H_2O$) method.

Rongalite (0.92g, 0.006 mole) in aqueous solution (20 cm^3) was added to a solution of sodium hydroxide (30 cm^3, 10%) in which tellurium powder (1.52g, 0.012 mole) was suspended. The mixture was gently heated under dinitrogen for one hour. Most of the tellurium dissolved and a red solution developed (Na_2Te_2).

(ii) Super-hydride ($LiB(Et)_3H$) Method.

Tellurium powder (1.02g, 0.008 mole) was suspended in THF (40 cm^3) and stirred under dinitrogen at room temperature. Superhydride (8 cm^3, 0.008 mole of a 1M THF solution) was added dropwise *via* a syringe and septum. During the addition a gas was evolved. The mixture was gently heated for one hour. Most of the tellurium dissolved and a deep red solution developed (Li_2Te_2).

(iii) Sodium Method

Tellurium powder (0.638g, 0.005 mole) was suspended in DMF (40 cm^3) and stirred under argon gas for one hour at room temperature. Sodium (0.115g, 0.005 mole) was carefully added in small pieces. On completion of addition the mixture was gently heated whereupon most of the tellurium dissolved and a deep red solution developed (Na_2Te_2).

4.2.4 Attempted synthesis of Bis(2-(2'-Pyridyl)phenyl)-tetratelluride.

A) A solution of Na_2Te_2 (0.002 mole) was generated by the sodium reduction of tellurium using method (iii) above. To this solution was added a solution of 2-(2'-pyridyl)phenyltellurium(II) bromide (1.44g, 0.004 mole) in DMF (20 cm^3). The red solution was gently heated at ~60°C under argon for three hours. The solution was allowed to cool to room temperature and filtered. On filtration the red solution decomposed immediately to tellurium in 100% yield.

The reaction was also carried out using a five fold molar excess of Na_2Te_2 and the same observations noted. Also RTeCl (in 1,4-dioxane) was substituted for RTeBr but without success.

B) A solution of Li_2Te_2 was generated by the super-hydride reduction of tellurium in THF according to method (ii) above. To this solution was added a solution of 2-(2'-pyridyl)phenyltellurium(II) (2.88g, 0.008 mole) in THF (30 cm^3). The red coloured solution was gently refluxed for three hours and then allowed to cool to room temperature. On filtration in air the red solution decomposed immediately to yield tellurium in 100% yield.

The reaction was also carried out using a five fold molar excess of Li_2Te_2 and the same observations were noted. Also RTeCl (in 1,4-dioxane) was also substituted for RTeBr but without success.

4.2.5 Attempted synthesis of Bis(2-(2'-Quinolinyl)phenyl)-tetratelluride.

Two methods were used.

A) A solution of Na_2Te_2 (0.002 mole) was generated by the sodium reduction of tellurium in DMF solution using method (iii) above. To this solution was added a solution of 2-(2'-quinolinyl)phenyl tellurium(II) bromide (1.646g, 0.004 mole) in THF (20 cm^3). The deep red solution was heated at 60°C for two hours. It was allowed to cool to room temperature and then filtered. On filtration the red solution immediately decomposed to tellurium in 100% yield.

The reaction was also carried out using a five fold molar excess of Na_2Te_2. The same observations were noted.

B) A solution of Li_2Te_2 (0.002 mole) was generated by the super-hydride reduction of tellurium in THF using method (ii) above. To this solution was added a solution of 2-(2'-quinolinyl)phenyltellurium(II) bromide (1.646g, 0.004 mole) in THF (20 cm^3). The deep red solution was gently refluxed under dinitrogen for two hours. It was then allowed to cool to room temperature and then filtered. On filtration in air the red solution decomposed immediately to tellurium in 100% yield.

The reaction was also carried out using a five fold molar excess of Na_2Te_2. The same observations were noted.

4.2.6 Synthesis of Bis(2-(2'-Pyridyl)phenyltelluro)diselenide

Selenium powder (0.395g, 0.005 mole) was suspended in warm toluene (30 cm^3). Super-hydride (6 cm^3 of a 1M solution in THF) was added dropwise and the mixture stirred under dinitrogen for 1 hour. On completion of super-hydride addition, a red solution formed and then an orange coloured suspension. A solution of 2-(2'-pyridyl)phenyltellurium(II) chloride (1.59g, 0.005 mole) in warm toluene (30 cm^3) was added dropwise. The mixture was gently refluxed for three hours and then the orange coloured solution allowed to cool to room temperature whereupon it was filtered. From the filtrate a bright red coloured solid formed possessing an obnoxious odour. It was found to be insoluble in common organic solvents and decomposed in hot benzene and hot nitromethane. Yield 80%, m.p = 230°C(d).

4.2.7 Synthesis of Bis(2-(2'-Quinolinyl)phenyltelluro)-diselenide.

Selenium powder (0.395g, 0.005 mole) was suspended in warm 1,4-dioxane (30 cm^3). Super-hydride (6 cm^3 of a 1M solution in THF) was added dropwise and the mixture stirred under dinitrogen for one hour. On completion of super-hydide addition, a red solution formed. A solution of 2-(2'-quinolinyl)phenyltellurium(II) chloride (1.84g, 0.005 mole) in warm 1,4-dioxane (30 cm^3) was added dropwise. The mixture was gently heated for three hours and then allowed to cool to room temperature. The orange coloured solution was filtered and from the filtrate a red solid possessing an obnoxious odour formed. This solid was found to be insoluble in common organic solvents and decomposed in hot nitromethane. Yield 80%, m.p.= 150°C

4.2.8 Attempts to synthesise Bis(phenylazophenyl-C,N')-tetratelluride.

A solution of Na_2Te_2 (0.002 mole) was generated by the sodium reduction of tellurium in DMF according to method (iii) above. To this solution was added a solution of (2-Phenylazophenyl-C,N')tellurium(II) chloride (1.37g, 0.004 mole) in DMF (10 cm^3). The red coloured solution was gently heated at 60°C for two hours and allowed to cool to room temperature. On filtration the red solution decomposed immediately to tellurium in 100% yield.

4.2.9 Attempts to synthesise 1,2-Ditellurane Synthesis of 1,1'-Dibromo-1-telluracyclopentane

A solution of Na_2Te_2 (0.05 mole) was generated by the sodium reduction of tellurium in DMF according to method (iii) above.1,4-Dibromobutane (4.75 cm^3, 0.04 mole) was added dropwise and the red solution gently heated for four hours and stirred under argon. The solution was allowed to cool to room temperature and then filtered. On standing in air the filtrate gradually decomposed yielding tellurium and a cloudy solution. The tellurium was filtered off and the filtrate concentrated to small volume whereupon a colourless solid separated out. This solid was recrystallised from chloroform to give a colourless crystalline solid. Yield 70%, m.p.= 124-125°C.

4.2.10 Attempts to synthesise 1,2-Ditellurane. Synthesis of 1,1'-Diiodo-1-telluracyclopentane.

A solution of Na_2Te_2 (0.05 mole) was generated by the sodium reduction of tellurium in DMF solution according to method (iii) above. 1,4-Diiodobutane (0.04 mole) was added dropwise and the red solution was gently heated for 3 hours under argon. On cooling to room temperature a black solid in a red solution appeared. The solution was filtered and from the filtrate a red solid formed which was recrystallised from ethanol. Yield 75%, m.p = 149-150°C (lit= 149-150°C).

4.2.11 Attempted synthesis of Telluracyclopentane. Synthesis of Cyclotellurapentane-1-oxide.

1,1-Diiodo-1-telluracyclopentane (5g) was dissolved in hot ethanol (80 cm^3) and stirred under dinitrogen. Sodium borohydride in ethanol was added dropwise to the red solution. During the addition a gas was released and the solution gradually became colourless when the addition was stopped. The solution was allowed to cool to room temperature whereupon an oil separated out. On attempting to separate this oil a repulsive odour persisted. Therefore the solution was allowed to evaporate in air in a fume cupboard and a white coloured solid formed. The solid was filtered off and washed in water and ethanol. Yield 90%, m.p.= 180-182°C (lit.= 241°C(d)).

4.2.12 Synthesis of 3,4-benzo-1-telluracyclopentane.

1-1'-Diiodo-1-tellura-3,4-benzocyclopentane (1.0g) was dissolved in hot ethanol (80 cm^3) and the solution stirred under dinitrogen. To this red solution was added dropwise a solution of sodium borohydride in ethanol until the solution became colourless. During the addition a gas was evolved. The solution was allowed to cool to room temperature and filtered. The filtrate was concentrated using a rotary evaporator whereupon a yellow solid formed. The solid was filtered off and washed in water and ethanol. Yield 90%, m.p.= 130-132°C

4.3 RESULTS AND DISCUSSION

In this section the results of the attempts to form organopolytellurides and mixed organopolychalcogenide (Se,Te) compounds will be discussed.

4.3.1 Characterisation of Diorganotritellurides.

Attempts to form bis(2-(2'-pyridyl)phenyl)tritelluride *via* the literature method did not altogether proceed as expected. Two reactions were carried out. The first was carried out according to the literature method in which oxygen was not excluded in the reaction. In the second reaction oxygen was excluded using a nitrogen atmosphere. In the presence of nitrogen the reaction proceeded smoothly until the red solution (reported in the literature) formed which almost immediately decomposed to yield tellurium (100%). However using aerobic conditions the red solution persisted until it was filtered whereupon partial dissociation to tellurium occurred and the tritelluride was isolated in much lower yield (30%) than reported in the literature (90%). The analytical data support a fit for $C_{22}H_{18}N_2Te_3$. The melting point and infra-red data agree with the literature data. The electron impact mass spectrum did not show the molecular ion. The highest ion detected was R_2Te^+ (m/e= 438). The other major ions detected were RTe^+ (m/e= 284), R^+ (m/e= 154) and $(R\text{-}HCN)^+$ (m/e= 127). Nitrogen heterocyclic containing compounds often lose HCN as a stable molecule during fragmentation.

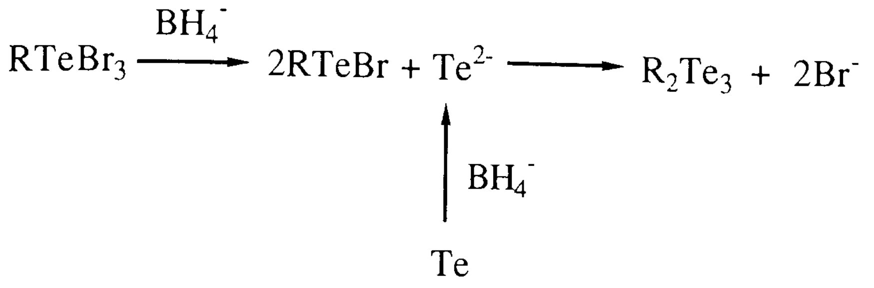
Table 4.1 ANALYTICAL DATA

COMPOUND	Found (Required) %C	%H	%N
$C_{22}H_{16}N_2Te_3$*	38.3 (38.2)	2.18 (2.33)	4.12 (4.05)
$C_{22}H_{16}N_2Te_3$**	38.4 (38.2)	2.56 (2.33)	3.86 (4.05)
$C_{30}H_{20}N_2Te_3$*	45.4 (45.5)	2.55 (2.53)	3.51 (3.54)
$C_{30}H_{20}N_2Te_3$**	45.2 (45.5)	2.67 (2.53)	3.43 (3.54)
$C_{11}H_8NOTeBr$	34.0 (35.0)	2.17 (2.12)	3.62 (3.17)
$C_{22}H_{16}N_2Se_2Te_2$	35.9 (36.6)	2.54 (2.24)	3.42 (3.88)
$C_{30}H_{20}N_2Se_2Te_2$	44.2 (43.9)	2.51 (2.45)	3.49 (3.41)
$C_4H_8TeBr_2$	14.2 (14.0)	2.12 (2.33)	
$C_4H_8TeI_2$	12.2 (11.0)	2.83 (2.53)	
C_4H_8OTe	25.0 (24.1)	4.32 (4.04)	
C_8H_8Te	40.8 (41.5)	3.54 (3.48)	

* Synthesised using the literature method.

** Synthesised by the reaction of RTeX (or R'TeX) with Te^{2-}.

The experimental observations noted may provide a clue to the mechanism for tritelluride formation. Al-Salim(74) proposed two mechanisms below:-

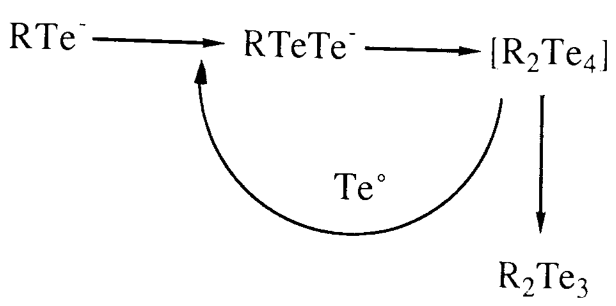


$$\begin{tikzcd} \mathrm{RTeBr_3} \arrow[r, "\mathrm{BH_4^-}"] & \mathrm{2RTeBr} + \mathrm{Te^{2-}} \arrow[r] & \mathrm{R_2Te_3} + \mathrm{2Br^-} \\ & \mathrm{Te} \arrow[u, "\mathrm{BH_4^-}"'] & \end{tikzcd}$$ (1)

$$\mathrm{RTeBr_3} \xrightarrow{\mathrm{BH_4^-}} \mathrm{RTe^-} + \mathrm{Te} \longrightarrow \mathrm{RTeTe^-} \xrightarrow{\mathrm{O_2}} \mathrm{R_2Te_3}$$ (2)

He noted in his experiments (as indeed is reported here) that during borohydride addition tellurium was released. In a similar reaction but using 2-(2'-quinolinyl)phenyl- as the organic moiety, Al-Salim noted no tellurium was released and the ditelluride formed. In a separate reaction but adding tellurium to the reactants, the tritelluride was obtained. On these findings Al-Salim proposed mechanism (1).

In the reaction carried out under nitrogen (absence of oxygen), the tritelluride failed to be isolated although it's existence in solution may be likely. On the contrary aerobic conditions lead to tritelluride formation. It appears that oxygen is responsible, in part, for tritelluride formation. In the light of these observations Al-Salim's initial proposal may have to be revised and mechanism (2) is now favoured. The last step in this proposal may occur *via* a tetratelluride intermediate for example:-



Using Al-Salim's method only small yields of this tritelluride could be obtained. For this reason new synthetic routes were devised in which the telluride anion (Te^{2-}) was reacted with an organotellurenyl halide (RTeX). Two methods were employed to generate Te^{2-} (polytelluride (Te_n^{2-}) anion formation is discussed furtheron). In the first, rongalite ($HOCH_2SO_2Na.2H_2O$) was used to reduce tellurium in an alkaline solution. Reaction with RTeBr did not lead to the expected tritelluride but an insoluble cream coloured solid. The analytical data supports a fit based on $C_{11}H_8BrNOTe$. The infra-red spectrum confirms the presence of the organic group. Bands in the range υ= 580-514cm^{-1} are evidence for Te-O vibrational modes. The N.M.R spectrum could not be recorded since the compound was insoluble in common organic solvents. Using this data it is proposed that the compound formed is the organotellurium(IV)oxybromide derivative (RTeOBr) whose insolubility may be due to a polymeric structure. It is not surprising that oxidation from Te(II) to Te(IV) has occurred since aqueous alkaline conditions were used.

The telluride anion can also be generated by reducing tellurium with sodium (in the ratio 1:2) in a DMF solution. On reacting with

RTeBr, the tritelluride compound is formed. Analytical, infra-red,

$$2RTeBr + Na_2Te \xrightarrow{N_2} R_2Te_3 + 2NaBr$$

melting point and mass spectroscopic data agree with that already reported and with the literature data. In this reaction in which oxygen was excluded, mechanism (1) is favoured. It appears that two separate mechanims are in operation in both types of reaction.

Bis(2-(2'quinolinyl)phenyl)tritelluride has been synthesised by two methods. In the first, the literature method was employed in which a suspension of $R'TeBr_3$ and tellurium were reduced and the reaction worked up accordingly. In the second, the reaction of R'TeBr with the telluride anion (Te^{2-}) was used. The reaction yields are smaller (50% and 30% respectively) than those obtained by Al-Salim (80%). The analytical data for both products support a fit for $C_{30}H_{20}N_2Te_3$. The melting point and infra-red are consistent with that reported in the literature. In the electron impact mass spectrum the molecular ion was not detected. The highest ion found was R'_2Te^+, (m/e= 538) with other ions found at $R'Te^+$ (m/e= 334) and R'^+ (m/e= 204). It is suggested that in both the mass spectra of R_2Te_3 and R'_2Te_3, it is the central tellurium which is released in the initial fragmentation step which might explain the absence of the molecular ions.

In summary, two methods can be used to synthesise the diorganotritellurides of 2-phenylpyridine and 2-phenylquinoline. One route is to reduce the organotellurium(IV) tribromides ($RTeBr_3$ and

R'TeBr$_3$) with sodium borohydride (in the case of R'TeBr$_3$, tellurium is also required as a reactant). Yields are lower than reported in the literature. The second method involves reacting an organotellurenyl halide (RTeX) with the telluride anion (Te^{2-}). It appears two different mechanisms lead to their formations involving aerobic and anaerobic conditions.

4.3.2 Attempt to form diorganotetratellurides (R$_2$Te$_4$)

No diorganotetratellurides have been reported to date. Given the knowledge that organotellurenyl halides (RTeX) can be stabilised by intra-molecular (Te-N) coordination, we attempted the synthesis of diorganyltetratellurides with the rationale that they exist as bis(organotellurenyl)ditellurides.

The ditelluride anion (Te$_2^{2-}$) was generated by reduction of tellurium using rongalite, elemental sodium and super-hydride reducing reagents. Deep red solutions formed in all cases. There are numerous examples in the literature of the reduction of tellurium using sodium in liquid ammonia. This method was not used in our reactions because other methods provided much simpler routes to Na$_2$Te and Na$_2$Te$_2$. Hugot in 1899 reported Na$_2$Te to be a colourless precipitate in liquid ammonia when he reacted sodium and tellurium in the molar ratio 2:1. A more comprehensive investigation by Kraus and Chiu(91) established the identities of the species sequentially formed in ammonia solution to be Na$_2$Te (yellow solution, white precipitate), Na$_2$Te$_2$ and

Na_2Te_4 (deep red solution). In 1931 Zintl, Goubeau and Dullenkopf(92) also investigated the sequential reactions of tellurium with sodium in liquid ammonia and reported the compounds formed to be Na_2Te (white precipitate, yellow solution), Na_2Te_2 (violet solution) and Na_2Te_3 (red solution). These authors questioned the formation of Na_2Te_4. Although there is general agreement as to the species formed in solution, there is still disagreement as to the identity of the highest sodium polytelluride. The reported products were based on reactant stoichiometries which is a questionable assumption. Very recently Schulz and Koehler(93) used U.V spectroscopy to study the species formed in solution. The species Na_2Te_2 (blue solution) and Na_2Te_3 (red solution) were found to be distinctive spectroscopically identifiable species. The proposed species Na_2Te_4 was found to be a 1:1 molar mixture of Na_2Te_3 and insoluble excess tellurium.

Super-hydride [$LiB(Et)_3H$] has recently become a popular reducing agent in organometallic chemistry. In the reaction of a 1:1 molar ratio of super-hydride and tellurium a dark red coloured solution formed characteristic of the ditelluride anion (Te_2^{2-}). The reaction may occur according to equation (1).

$$2LiB(Et)_3H + 2Te \longrightarrow Li_2Te_2 + H_2 + 2BEt_3 \quad (1)$$

Of the three methods used in this work to reduce tellurium, the super-hydride method was undoubtedly the most effective and efficient. However for precursor design it may be the least favoured since boron contamination might lead to purification problems.

Reduction of tellurium using rongalite (sodium formaldehyde sulfoxide) in aqueous alkali has been continuously employed over the years for the generation of Na_2Te and Na_2Te_2. By varying the ratio of rongalite to tellurium, the ditelluride ion (deep red solution) and the monotelluride (pale pink solution) can be formed. Bergson(94) found that tellurium with rongalite in a 2:1 molar ratio produces predominantly the ditelluride ion with the monotelluride and polytelluride species being present as impurities. Several reactions have been proposed for the formation of these species in solution. Thus:-

$$3Te + NaOH \longrightarrow 2Na_2Te + Na_2TeO_3\ 3H_2O \quad (2)$$

$$Na_2Te + Te \longrightarrow Na_2Te_2 \quad (3)$$

$$Na_2TeO_3 + 3HOCH_2SO_2Na + 3NaOH \longrightarrow Na_2Te + 3CH_2O + 3Na_2SO_3 + 3H_2O \quad (4)$$

$$Na_2Te_2 + HOCH_2SO_2Na + 3NaOH \longrightarrow 2Na_2Te + CH_2O + Na_2SO_3 + 2H_2O \quad (5)$$

Irgolic has suggested an alternative route thus:-

$$HOCH_2SO_2\text{-}Na \xrightarrow{Te} HOCH_2SO_2TeNa \xrightarrow{NaOH} Na_2Te + CH_2O + Na_2SO_3 \quad (6)$$

The ditelluride anion may be formed by the further insertion into a S-Te bond, for example,

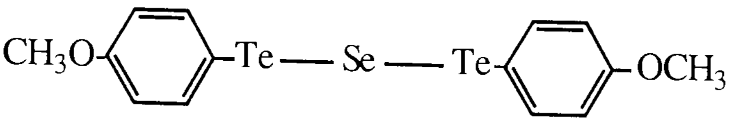
$$HOCH_2SO_2TeTeNa \xrightarrow{NaOH} Na_2Te_2 + CH_2O + Na_2SO_3 \quad (7)$$

Sandman(95) has shown that direct reduction of tellurium using sodium (in a DMF solution under an inert atmosphere) is a useful method of forming both Na_2Te and Na_2Te_2 ions. However Zingaro *et al* have shown that Na_2Te_2 reacts with the solvent under long reaction times and the compound bis(N,N-dimethylaminoformylditelluride) can be isolated whose crystal structure has been solved(96).

We believed diorganyltetratellurides could be synthesised by the reaction of an organotellurenyl halide (RTeX) and Te_2^{2-}. These reactions were attempted using R= 2-phenylpyridine, 2-phenylquinoline and 2-phenylazobenzene. In all these reactions a deep red coloured solution persisted throughout the reaction work-up until the solution was filtered in air whereupon decomposition to tellurium occurred. The existence of the tetratellurides under an inert atmosphere is a possibility but in air they may be unstable leading to decomposition.

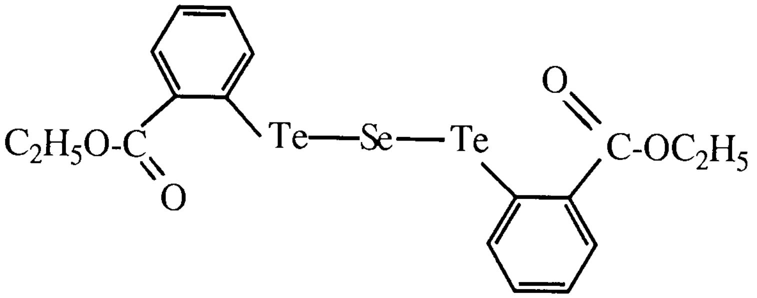
4.3.3 Characterisation of Bis(Organyltellurenyl)diselenides

Although no success was achieved in synthesising diorganotetratelluride compounds we were still driven by the belief that the organotellurenyl moiety could help stabilise similar compounds. Mixed organopolychalcogenide compounds are known. For example Zingaro(97)*et al* have reported the formation of bis(4-methoxyphenyltellurenyl)selenide (X).



(X)

The same authors also reported bis(2-ethylcarboxyphenyltellurenyl)-selenide (XI)⁽⁹⁷⁾ which involves intra-molecular Te---O coordination with a Te---O bond length of 2.658 Å.



(XI)

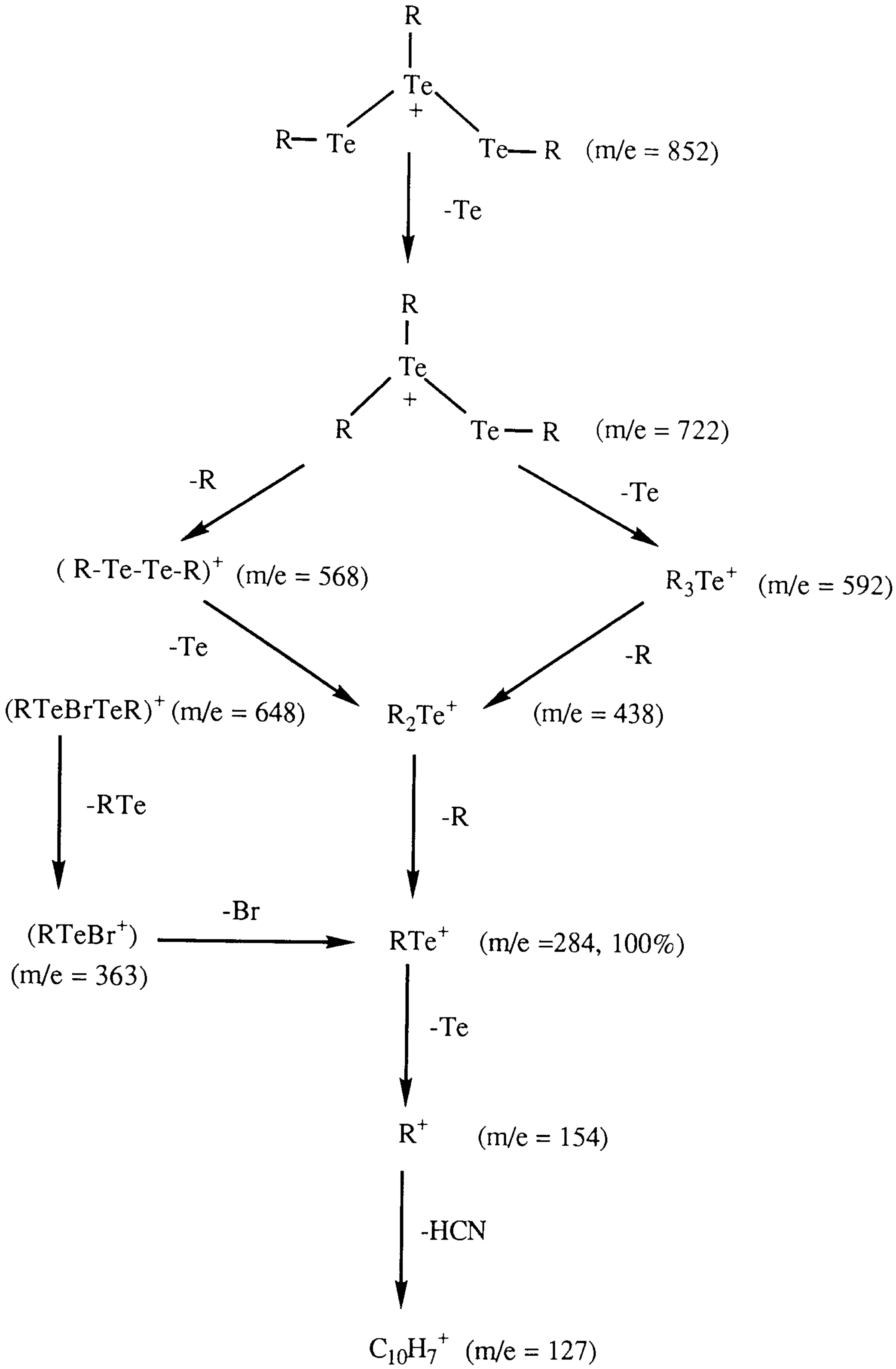
The compounds $(ArTe)_2Se$ (Ar= 2-C_6H_4CHO and 2-C_6H_4COOH) have also been reported in the literature(98) and are further examples mixed organopolychalcogenide compounds.

In the reactions of RTeCl and R'TeCl with Li_2Se_2 (generated by the super-hydride reduction of selenium), red solids were isolated in both cases possessing repulsive odours. The analytical data (table 4.1) support fits for $C_{22}H_{16}N_2Se_2Te_2$ (ie. $R_2Te_2Se_2$) and $C_{30}H_{20}N_2Se_2Te_2$ (ie. $R'_2Te_2Se_2$). The infra-red spectra confirm the presence of organic groups. In the fast atom bombardment mass spectrum of $R_2Te_2Se_2$, the only ions detected were RTe^+ (m/e= 284) and R^+ (m/e= 154). Similarly in the mass spectrum of $R'_2Te_2Se_2$ the only ions found were $R'Te^+$

(m/e= 334) and R'^+ (m/e= 204). Evidence for the presence of selenium in both compounds was obtained from the scanning electron microscopy technique in which selenium and tellurium were detected in a 1:1 ratio. Due to the insolubility of these compounds, the N.M.R spectra could not be recorded. Using these results it is plausible to assign the red solids as RTeSeSeTeR and R'TeSeSeTeR'.

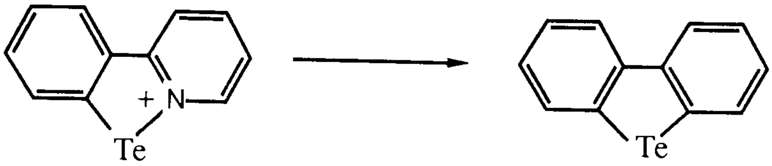
4.3.4 Mass Spectroscopy - The appearance of Polytelluride species.

During the routine examination of the mass spectrum of RTeBr (R= 2-(2'-pyridyl)phenyl-) (which was used as a precursor for polychalcogenide synthesis), species of higher m/e than the parent ion ($RTeBr^+$) were detected. The fragmentation process is illustrated in scheme 4.1. The most notable species is the ion at m/e= 848 which has been identified as $R_3Te_3^+$ (having the correct isotopic pattern for three telluriums). Species of this type are not common although a trace of $Ph_2Te_3^+$ has been identified in the mass spectrum of Ph_2Te_2(99). In the mass spectrum of $L_2TeCl_2.2HCl$ (L= 3,4-dimethoxybenzene) (see chapter three) a species identified as $L_2Te_3^+$ is also another rare example of an ion containing three telluriums. The mass spectrum of RTeBr also reveals an ion at m/e= 648, identified as $RTeBrTeR^+$. Interestingly this species happens to be isoelectronic with RTeSeTeR. Clusters of this type are common. On recording the mass spectrum of RTeCl, the related species $RTeClTeR^+$ was also identified. This species is isoelectronic with RTeSTeR.



Scheme 4.1 Major fragments in the Electron Impact Mass Spectrum of RTeBr (cited values of m/e based on ^{130}Te, ^{79}Br, ^{12}C, ^{1}H, ^{14}N. The observed isotope patterns were in exact agreement with those calculated for the indicated ions).

A common feature of both the spectra of RTeCl and RTeBr and indeed other 2-(2'-pyridyl)phenyltellurium compounds is the appearance of RTe^+ as the most abundant ion. The stability of this ion, which is isoelectronic with dibenzotellurophene, a well known stable compound, is probably due to resonance stabilisation of the positive charge.



4.3.5 Characterisation of 1,1'-dibromo-1-telluracyclopentane

In an attempt to form 1,2-ditellurane by the reaction of Na_2Te_2 and 1,4-dibromobutane, a white crystalline material was isolated. The analytical data fit the formulation $C_4H_8TeBr_2$. The compound was found to be a non-electrolyte in DMSO. In the electron impact mass spectrum the highest ion detected was $C_4H_8TeBr^+$ (m/e= 265). Other ions at m/e= 209 ($TeBr^+$) and m/e= 186 ($C_4H_8Te^+$) were also noted. The ^{13}C N.M.R spectrum was recorded in $CDCl_3$ and is shown in figure 4.1. Only two signals were observed. The resonance at δ= 32.3 ppm is assigned as the β-methylene carbon. The α methylene carbon signal is found at δ= 47.3 ppm. Interestingly this signal shows satelites due to carbon-tellurium coupling, with $J(^{125}Te-^{13}C)$= 79Hz and $J(^{123}Te-^{13}C)$= 69Hz. The ^1H N.M.R spectrum was recorded in DMSO-d^6 and two signals were observed. The protons on the β-carbons are found at

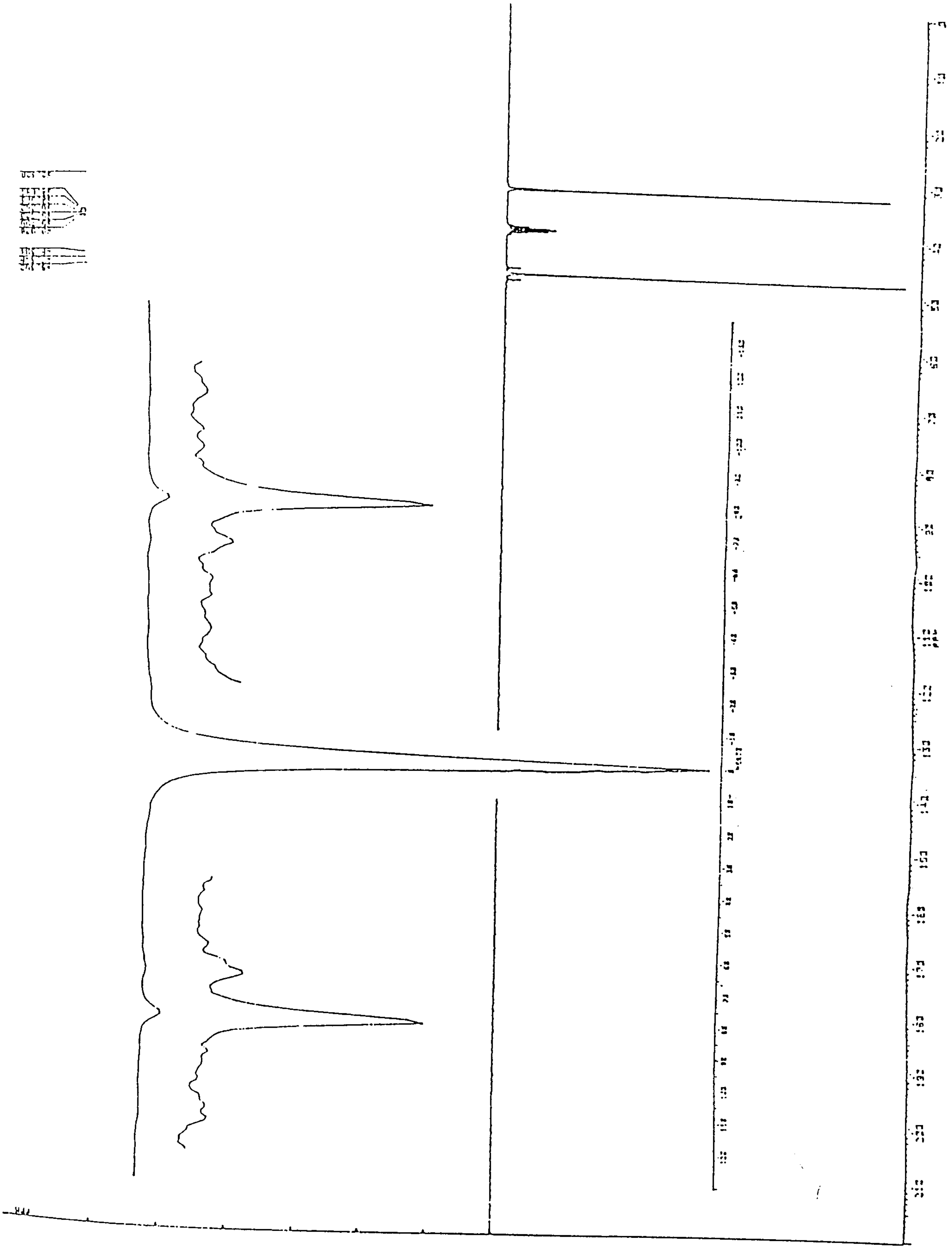
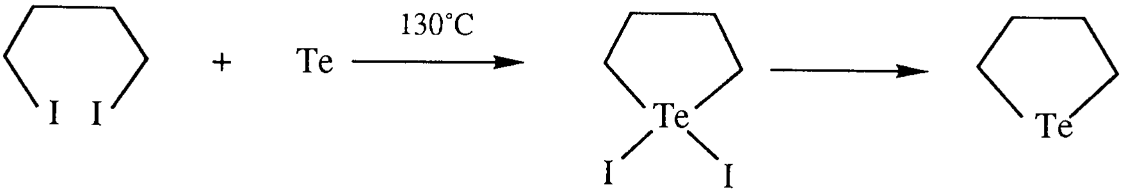


Figure 4.1 ^{13}C N. M. R. spectrum of $C_4H_8TeBr_2$.

$\delta = 3.43$ ppm. The α-carbon signals are seen at $\delta = 2.65$ ppm.. The infra-red spectrum confirmed the presence of the organic group but the Te-Br vibrations were not observed since the spectrum could only be recorded down to 220cm^{-1}. However the Raman spectrum was measured and was of outstanding quality (see fig 4.2) with Te-Br vibrations located at $\upsilon = 181$ and 167cm^{-1}.

4.3.6 Characterisation of 1-1'-Diiodo-1-telluracyclopentane.

In an attempt to form 1,2-Ditellurane by the reaction of Na_2Te_2 and 1,4-diiodobutane, a red solid was isolated. The analytical data fit the formulation $C_4H_8TeI_2$. The ^{13}C N.M.R spectrum shows only two signals with the α and β methylene carbons resonating at $\delta = 46.0$ and 31.2 ppm respectively. The compound has been synthesised by other methods and is an excellent source of tellurocyclopentane; for example,



4.2.7 Characterisation of cyclotellurapentane-1-oxide

The compound telluracyclopentane has been reported in the literature as a reddish-yellow oil(100). The synthesis of this material was attempted since we felt it would be a useful precursor to try on an MOVPE test kit. The reduction of 1-1'-diiodo-1-telluracyclopentane using sodium borohydride proceeded according to the literature with

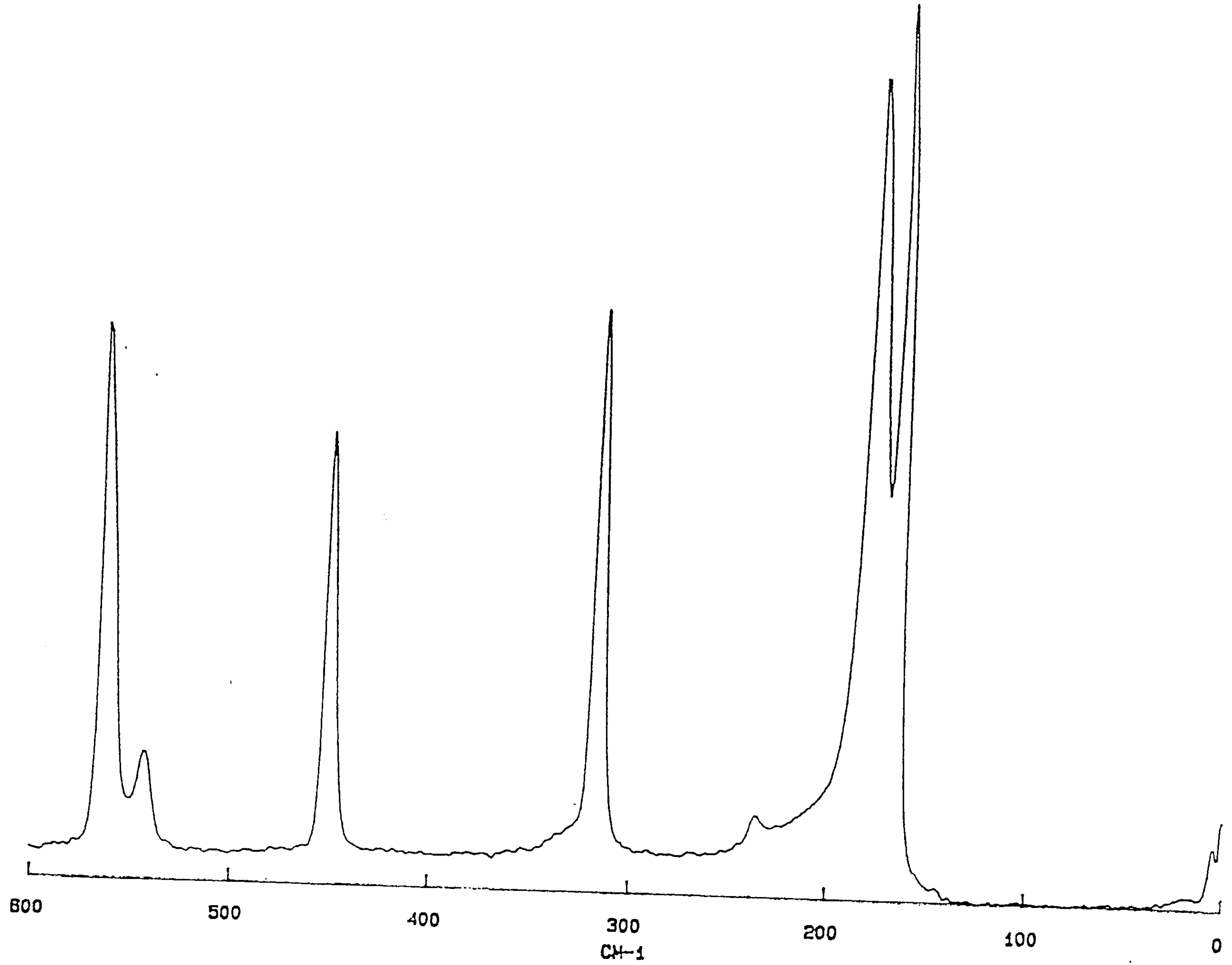
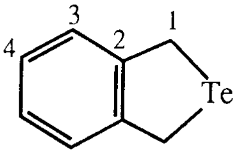


Figure 4.2 Raman spectrum of $C_4H_8TeBr_2$.

the formation of an oil. However the oil gave off an extremely strong and repulsive odour leading to handling difficulties and for this reason it was decided not to isolate this material. Instead the oil was left to stand in air whereupon oxidation occurred leading to the formation of a white crystalline material. The analytical data support a fit based on C_4H_8OTe (table 4.1). The infra-red spectrum confirms the presence of the organic group and bands at υ= 640 and 540cm^{-1} are assigned as a Te-O vibration modes. The ^1H N.M.R spectrum was recorded in DMSO-d^6. Partially resolved triplets are found at δ= 2.7 ppm and 3.1 ppm assigned as the α and β methylene signals respectively. The ^{13}C N.M.R spectrum shows signals at δ= 47.3 ppm (β-CH_2) and δ= 31.0 ppm (α-CH_2).

4.3.8 Characterisation of 3,4-benzo-1-telluracyclopentane

In the reaction of 1,1'-diiodo-1-tellura-3,4-benzocyclopentane with sodium borohydride a pale yellow solid was isolated. The analytical data fit the formulation C_8H_8Te. The infra-red spectrum confirms the presence of organic groups. The ^{13}C N.M.R spectrum was recorded in DMSO-d^6 and shows four signals as expected.



The α carbon (C1) is found at highest field (δ= 9.35 ppm) shielded by the large tellurium atom. The *ipso* carbon C(2) is found at δ= 139.5

ppm. Carbons C(3) and C(4) are located at δ= 130.1 and 127.1 ppm respectively. In the ^{1}H N.M.R spectrum a complex multiplet centered at δ= 7.2 ppm is assigned as the aromatic proton signals. The resonance at δ= 4.5 ppm is assigned as the methylene protons.

CONCLUSIONS

Two methods for the syntheses of the diorganyltritellurides R_2Te_3 and R'_2Te_3 (R= 2-phenylpyridine and 2-phenylquinoline) are presented. Reduction of $RTeBr_3$ with sodium borohydride leads directly to R_2Te_3. The related tritelluride R'_2Te_3 can be similarly prepared by reduction of $R'TeBr_3$ in the presence of tellurium. A mechanism has been proposed involving aerobic conditions which is contrary to the view of Al-Salim. The reaction of RTeX (and R'TeX) with the telluride ion (Te^{2-}) also leads to the tritelluride derivatives. An alternative mechanism involving anaerobic conditions is proposed. The compounds are stable in air and are non-volatile. Under mass spectroscopic conditions, the parent ions are not observed which may imply that the central tellurium is released as an initial step during the fragmentation process. This suggests that if other higher polytellurides can be synthesised they would be rich sources of tellurium and useful for MOVPE purposes.

Attempts to form diorganyltetratellurides (R_2Te_4) failed although their existence in solution is a possibility. However mixed diorganyltetra-chalcogenides (RTeSeSeTeR and R'TeSeSeTeR') can be synthesised by the reaction of RTeCl (and R'TeCl) with Li_2Se_2. In the mass spectra of RTeBr and RTeCl, the species $RTeBrTeR^+$ and $RTeClTeR^+$ are observed which happen to be isoelectronic with RTeSeTeR and RTeSTeR respectively.

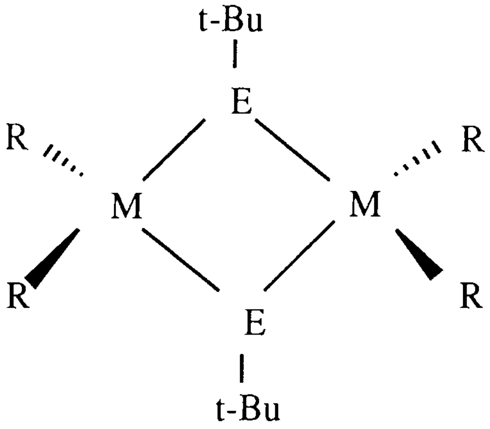
New synthetic methods have been devised for some cyclic organotellurium(IV) compounds. These materials are excellent sources of cyclic tellurides which, due to ring strain effects, may be useful sources of tellurium.

Chapter Five

NITROGEN CONTAINING ORGANOTELLURIUM COMPOUNDS AND THEIR COMPLEXES

5.1 Introduction

There are now many reports of complexes involving organotellurium ligands, particularly those of RTe^-, R_2Te and R_2Te_2. Notable examples are complexes formed with Hg(II), Pd(II) and Pt(II)(101-104). Mercuric(II) complexes are well known but those of cadmium(II) are rare. Since these complexes contain both groups II and VI atoms, we decided to explore related compounds which may be candidates as single source precursors in the MOVPE growth of cadmium mercury telluride. To date there are only a few examples of precursors of this type which have been used in II-VI semiconductor growth. For example the compound (t-butyl)HgTe(t-butyl) has been used to grow films of HgTe(105). Adducts of the type $Me_3In.PEt_3$ have been explored for InP film growth. They are easy to handle and purify and are relatively stable in air. Cowley and co-workers have found that compounds of the type (A) below are also excellent single source precursors for the preparation of III-V compounds(106).

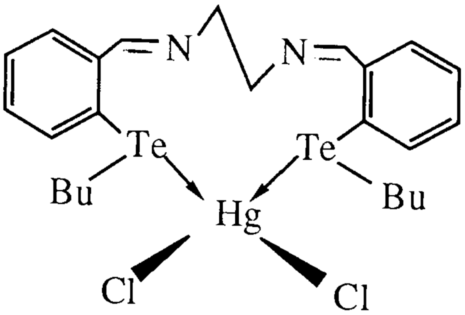


(A)

R= Me; M=Al, Ga, In; E= As, P

In the last ten years research within our laboratory has investigated the chemistry of nitrogen containing tellurium ligands. We decided to continue this theme since nitrogen containing organotellurium compounds could be useful as MOVPE precursors for at least two reasons. Firstly, decomposition of organometallic sources often leads to carbon contamination within the growing layer. Nitrogen contamination is less of a problem. Secondly incorporating nitrogen into organotellurium compounds can lead to bi- and multidentate ligands which offer more sites for coordination with metal ions. The challenge to the synthetic chemist is to design compounds whereby the II-VI bond is as strong or stronger than other bonds in the molecule, such that under film growth conditions, the II-VI bond remains intact while the other bonds are broken.

Very few bidentate and polydentate ligands containing tellurium (and hence their complexes) are known. It has been shown that among the nitrogen donors, azobenzene,(107) Schiff bases(108-109) and substituted pyridines,(110) can be tellurated. These ligands have two centres of lewis basicity (Te,N). McWhinnie *et al* have shown that the ligand 1,6-bis-2-butyltellurophenyl-2,5-diaza-hexa-1,5-diene forms a 1:1 complex with mercury(II) [see (B) below], whose crystal structure shows only the tellurium atoms are coordinating(111).The short Hg-Te distances (2.819 and 2.769 Å) indicate a strong interaction. Similar distances have also been observed in $(Ph_2Te)(HgI_2)$(112) (2.753 and 2.818 Å).

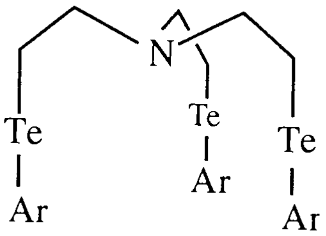


(B)

McWhinnie and co-workers(113) also investigated the reaction of 2-(2'-pyridyl)phenyl.p-ethoxyphenyltellurium(II) (RR'Te) with $HgCl_2$. At room temperature a white solid (RR'Te)($HgCl_2$) formed but on warming a new solid compound [R'HgCl.$(RTeCl)_2$] was isolated in which an organic group had migrated from tellurium to a mercury centre. The lability of organic groups has been observed before and in the context of MOVPE may have significant mechanistic implications.

Singh and Srivastava(114) have recently shown that 2-aryltelluroethylamines form complexes with mercury(II) in which both donor atoms (Te,N) are coordinated. This observation has led us in part, to synthesise a range of bidentate (Te,N) ligands along with some related (Se,N) ligands.

The same authors have reported novel potentially tripodal tetradentate (Te,N) ligands(115) such as (C). Interestingly, they have low melting points and although they have high molecular weights they may have the required volatility for MOVPE purposes.



(C)

Ar = $p\text{-}CH_3OC_6H_4\text{-}$ or $p\text{-}C_2H_5OC_6H_4\text{-}$

In their reaction with mercury(II) salts they form 1:1 complexes. We have decided to elaborate on this work and probe the ligands further by studying their complexes with other metal ions. Some selenium ligands are also noted.

Tripod-like tetradentate ligands generally favour five coordination in transition metal chemistry(116). However different geometries can be allowed depending on the nature of the metal centre and the ancillary ligand. For example palladium complexes of tris(2-diphenylphosphinoethyl)amine (tdpea) have been synthesised(117) and the phosphine in turn acts as a tetra-, ter or bidentate ligand. Apart from the work of Singh and Srivastava, there are no reports of tripod-like tellurium (Te,N) ligands in the literature and so their coordination with metal ions, if any, will be attractive from an MOVPE viewpoint and for studying a class of compound hitherto unresearched.

In this chapter the synthesis of a number of bidentate and tetradentate (Te,N) and (Se,N) ligands are reported. Some of the tetradentate ligands have been explored by complexing with the metal ions Hg(II), Cd(II), Cu(I), Pt(II) and Pd(II). The potential use of these ligands and their complexes with Hg(II) and Cd(II) as precursors for the MOVPE growth of cadmium mercury telluride is discussed.

5.2 EXPERIMENTAL.

Bis(p-methoxyphenyl)ditelluride, bis(p-ethoxyphenyl)ditelluride, diphenylditelluride and bis(p-tolyl)ditelluride were prepared by published methods(118). Diphenyldiselenide and bis(p-ethoxyphenyl)-diselenide were obtained from the Aldrich Chemical Company.

5.2.1 Generation of RTe^- and RSe^-

Diarylditelluride (0.002 mole) or diaryldiselenide (0.002 mole) was dissolved in warm ethanol (50 cm^3) under an oxygen free dinitrogen atmosphere. Sodium borohydride (~0.5g) dissolved in 1M sodium hydroxide was added dropwise *via* a syringe and septum. The generation of RTe^- was complete once the solution colour had changed from red to colourless. Similarly, the generation of RSe^- was complete once the solution had changed colour from yellow to colourless.

5.2.2 Synthesis of 2-(p-methoxyphenyltelluro)ethylamine.

To a solution of RTe^- (0.004 mole) in ethanol (50 cm^3) was added dropwise a solution of 2-chloroethylamine hydrochloride (0.463g, 0.004 mole) in 5 cm^3 distilled water. The colourless solution was refluxed for 5 hours under a brisk flow of dinitrogen. On cooling to room temperature, 10% sodium hydroxide solution was added to neutralise it whereupon a yellow oil separated out. This oil was extracted into chloroform and dried on sodium sulphate. On filtration the filtrate yielded a pale orange solid which was recrystallised from benzene. Yield 85%.

5.2.3 Synthesis of 3-(phenyltelluro)propylamine

To a solution of PhTe$^-$ (0.004 mole) in ethanol / benzene (70/5 cm^3) was added dropwise a solution of 3-chloropropylamine hydrochloride (0.520g, 0.004 mole) in water (5 cm^3). The mixture was refluxed for 6 hours under dinitrogen, allowed to cool to room temperature and then 10% sodium hydroxide solution added to neutralise the mixture. A pale yellow oil formed which was extracted into chloroform. The extract was dried on magnesium sulphate and filtered whereupon a pale orange solid formed which was recrystallised from ethanol. Yield 75%.

5.2.4 Synthesis of 3-(p-methoxyphenyltelluro)propylamine

A solution of RTe$^-$ (0.002 mole) in ethanol (50 cm^3) was added dropwise to a solution of 3-chloroethylamine hydrochloride (0.260g, 0.002 mole) in water (5 cm^3). During the addition the solution developed a pale yellow colour. The solution was refluxed for 4 hours under a brisk dinitrogen flow and then allowed to cool to room temperature. On filtration the filtrate was collected and allowed to evaporate in air. A brown solid formed which was washed in ethanol and dried in *vacuo*. Yield 60%.

5.2.5 Synthesis of 3-(p-ethoxyphenyltelluro)propylamine hydrochloride

To a solution of RTe^- (0.002 mole) in ethanol/benzene (50/5 cm^3) was added dropwise a solution of 3-chloropropylamine hydrochloride (0.260g, 0.002 mole) in water (5 cm^3). A yellow solution formed during the addition. The mixture was refluxed for 4 hours and then allowed to cool to room temperature. On filtration the filtrate was allowed to evaporate in air. A brown solid formed which was filtered off, washed in ethanol and dried in *vacuo*. Yield 70%.

5.2.6 Synthesis of 3-(p-tolyltelluro)propylamine hydrochloride

To a solution of RTe^- (0.002 mole) in ethanol (50 cm^3) was added dropwise a solution of 3-chloropropylamine hydrochloride (0.26g, 0.004 mole) in water (5 cm^3). The mixture was refluxed for 6 hours under dinitrogen and allowed to cool to room temperature whereupon it was filtered. From the filtrate a pale yellow solid formed which was washed in ethanol. Yield 50%.

5.2.7 Synthesis of 2-(phenylseleno)ethylamine.

To a solution of $PhSe^-$ (0.004 mole) in ethanol (50 cm^3) was added dropwise a solution of 2-chloroethylamine hydrochloride (0.463g, 0.004 mole) in water (5 cm^3). During the addition a pale yellow solution formed, which was refluxed for 5 hours and allowed to cool to room temperature. Sodium hydroxide (10%, 10 cm^3) was added to neutralise the solution whereupon an orange oil separated out. The oil was extracted into chloroform and dried on magnesium sulphate. On filtration the filtrate was collected from which a yellow solid formed. This was washed in diethylether and recrystallised from methanol. Yield 90%.

5.2.8 Synthesis of 3-(phenylseleno)propylaminehydrochloride

To a solution of $PhSe^-$ (0.004 mole) in ethanol (60 cm^3) was added a solution of 3-chloroethylamine hydrochloride (0.520g, 0.004 mole) in water (5 cm^3). The colourless solution was refluxed for 4 hours and allowed to cool to room temperature. The solution was filtered and from the filtrate pale yellow platelet crystals formed which were recrystallised from methanol. Yield 90%.

5.2.9 Synthesis of Tris[2-(phenyltelluro)ethyl]amine Ligand L^1

To a solution of $PhTe^-$ (0.004 mole) in ethanol (50 cm^3) was added dropwise a solution of tris(2-chloroethylamine) hydrochloride (0.321g, 0.00133 mole) dissolved in an equimolar concentration of NaOH solution (to liberate the free amine). The mixture was refluxed for 3 hours under dinitrogen and allowed to cool to room temperature where a colourless oil separated out. The oil was separated off and stirred with hot ethanol (10 cm^3) for 1 hour. On filtration colourless crystals formed. Yield 85%.

5.2.10 Synthesis of Tris[(p-methoxyphenyltelluro)ethyl]amine Ligand L^2

To a solution of RTe^- (0.004 mole) in ethanol (50 cm^3) was added a solution of tris(2-chloroethyl)amine hydrochloride (0.321g, 0.00133 mole) dissolved in a stoichiometric equivalent of 10% NaOH. The mixture was refluxed for 2 hours and allowed to cool to room temperature whereupon a colourless oil formed. The oil was separated off and stirred with hot ethanol (10 cm^3). On filtration a white solid formed. Yield 95%.

5.2.11 Synthesis of Tris[(p-ethoxyphenyltelluro)ethyl]amine Ligand L^3

To a solution of RTe^- (0.004 mole) in ethanol (50 cm^3) was added dropwise a solution of tris(2-chloroethylamine) hydrochloride (0.321g, 0.00133 mole) dissolved in a stoichiometric equivalence of NaOH. The mixture was refluxed for 2 hours under nitrogen and allowed to cool to room temperature. An oil formed which was separated off and stirred in 10 cm^3 of hot ethanol. On filtration a white solid formed. Yield 95%.

5.2.12 Synthesis of Tris[(phenylseleno)ethyl]amine Ligand L^4

To a solution of $PhSe^-$ (0.008 mole) in ethanol (50 cm^3) was added dropwise a solution of tris(2-chloroethyl)amine hydrochloride (0.642g, 0.00266 mole) dissolved in a stoichiometric equivalence of NaOH. The mixture was refluxed for 4 hours and allowed to cool to room temperature. An oil formed which was separated off and stirred in hot ethanol. On filtration a white solid formed. Yield 95%.

5.2.13 Synthesis of Tris[(p-ethoxyphenylseleno)ethyl]amine Ligand L^5

To a solution of RSe^- (0.008 mole) in ethanol (70 cm^3) was added dropwise a solution of tris(2-chloroethyl)amine hydrochloride (0.642g, 0.00266 mole) in a stoichiometric equivalence of 10% NaOH. The mixture was refluxed under dinitrogen for 4 hours and allowed to cool to room temperature. A colourless oil formed which was separated off and stirred in hot ethanol (20 cm^3). On filtration a white solid formed from the filtrate. Yield 95%.

5.2.14 Preparation of the Mercury(II) complex of L^2.

Mercuric chloride (0.136g, 0.0005 mole) was dissolved in acetone (5 cm^3) and added to a solution of L^2 (0.401g, 0.0005 mole) in chloroform (20 cm^3). The colourless solution was stirred at room temperature under dinitrogen for 1 hour. On addition of n-hexane (20 cm^3), a white solid separated out which was filtered off and washed in n-hexane and chloroform. Yield 90%.

5.2.15 Preparation of the Cadmium complex of L^2.

Cadmium iodide (0.183g, 0.0005 mole) in ethanol (10 cm^3) was added to a solution of L^2 (0.401g, 0.0005 mole) in chloroform (30 cm^3). The colourless solution was gently heated under dinitrogen for 3 hours and then allowed to cool to room temperature. On addition of n-hexane (30 cm^3) a cream solid formed which was filtered off and recrystallised from nitromethane from which a cream coloured crystalline solid formed. Yield 70%.

5.2.16 Preparation of the Platinum(II) complex of L^2.

A solution of potassium tetrachloroplatinate(II) (0.208g, 0.0005 mole) in water (5 cm^3) was added dropwise to a solution of L^2 in chloroform (20 cm^3). Initially the solution turned red but on completion of addition a brown solid formed. The mixture was stirred at room temperature under dinitrogen for 2 hours whereupon the precipitate turned yellow. The solid was filtered off, washed in water and chloroform and dried in *vacuo*. Yield 90%.

5.2.17 Preparation of the Palladium(II) complex of L^2.

A solution of sodium tetrachloropalladate (0.150g, 0.0005 mole) in water (5 cm^3) was added dropwise to a solution of L^2 (0.401g, 0.0005 mole) in chloroform (30 cm^3). An orange solid formed in the solution which was stirred at room temperature under dinitrogen for 5 hours. The solid was filtered off, washed in water and chloroform and dried in *vacuo*. Yield 90%.

5.2.18 Preparation of the Copper(I) complex of L^2.

A solution of copper(I) bromide (0.143g, 0.005 mole) in acetonitrile (10 cm^3) was added dropwise to a solution of L^2 (0.401g, 0.0005 mole) in chloroform (30 cm^3). The mixture was stirred under dinitrogen for 2 hours. The green solution was filtered and from the filtrate a green crystalline solid formed which was recrystallised from nitromethane. Yield 90%.

5.2.19 Preparation of the Mercury(II) complex of L^3.

A solution of mercuric chloride (0.136g, 0.0005 mole) in acetone was added to a solution of L^3 (0.422g, 0.0005 mole) in chloroform (20 cm^3). The pale yellow solution was stirred at room temperature under dinitrogen for 2 hours. On addition of n-hexane (25 cm^3) a white solid separated out which was filtered off, washed in chloroform and dried in *vacuo*. Yield 85%.

5.2.20 Preparation of the Cadmium(II) complex of L^3.

A solution of cadmium chloride (0.092g, 0.0005 mole) was added to a solution of L^3 (0.422g, 0.0005 mole) in chloroform (20 cm^3). The colourless solution was stirred under gentle heat and dinitrogen for 3 hours. On cooling to room temperature, n-hexane (20 cm^3) was added. A cream coloured solid separated which was filtered off and washed in ethanol. Recrystallisation from nitromethane gave a cream coloured crystalline material. Yield 60%.

5.2.21 Preparation of the Platinum(II) complex of L^3.

Potassium tetrachloroplatinate(II) (0.208g, 0.0005 mole) in water (5 cm^3) was added dropwise to a solution of L^3 (0.422g, 0.0005 mole) in chloroform (20 cm^3). Initially a red solution formed but on completion of addition a bright yellow coloured solution formed. The mixture was stirred at room temperature for 2 hours under dinitrogen. On addition of n-hexane (20 cm^3) a yellow solid separated out which was filtered off, washed in chloroform and water and recrystallised from benzene. Yield 70%.

5.2.22 Preparation of the Palladium(II) complex of L^3.

A solution of sodium tetrachloropalladate (0.150g, 0.0005 mole) in water (5 cm^3) was added dropwise to solution of L^3 (0.422g, 0.0005 mole) in chloroform (30 cm^3) whereupon an orange precipitate formed.

The mixture was stirred under dinitrogen for 2 hours at room temperature. It was then filtered off and washed in water and chloroform. Yield 90%.

5.2.23 Preparation of the Copper(I) complex of L^3.

Copper(I) bromide (0.058g, 0.0002 mole) in acetonitrile (10 cm^3) was added dropwise to a solution of L^3 (0.170g, 0.002 mole) in chloroform (20 cm^3). The mixture was gently heated for 4 hours under dinitrogen and allowed to cool to room temperature. On filtration a green coloured crystalline solid formed from the filtrate. Yield 85%.

5.2.24 Preparation of the Mercury(II) complex of L^4.

A solution of mercuric chloride (0.136g, 0.0005 mole) in acetone (5 cm^3) was added to a solution of L^4 (0.283g, 0.0005 mole) in chloroform (25 cm^3). The colourless solution was stirred at room temperature under dinitrogen for 3 hours and then n-hexane (20 cm^3) added whereupon a colourless precipitate separated. This was filtered off washed with ethanol and dried in *vacuo*. Yield 60%.

5.2.25 Preparation of the Mercury(II) complex of L^5.

A solution of mercuric chloride (0.136g, 0.0005 mole) in acetone (5 cm^3) was added to a solution of L^5 (0.349g, 0.0005 mole) in chloroform (20 cm^3). The colourless solution was stirred at room temperature for 2 hours and then n-hexane (20 cm^3) was added whereupon a white solid separated. This was filtered off. Yield 80% (based on Se).

5.2.26 Preparation of the Platinum(II) complex of L^5.

Potassium tetrachloroplatinate(II) (0.208g, 0.0005 mole) in water (5 cm^3) was added dropwise to a solution of L^5 (0.349g, 0.0005 mole) in chloroform (20 cm^3). The mixture was stirred for 4 hours at room temperature under dinitrogen. On addition of n-hexane and stirring for 30 mins a yellow solid separated which was filtered washed in water and dried in *vacuo*. Yield 80%.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterisation of Aryltelluroalkylamines and Arylselenoalkylamines or their hydrochloride derivatives

2-Aryltelluroethylamines, 3-aryltelluropropylamines (or their hydrochloride derivatives) can be prepared by the nucleophilic reaction of sodium aryltellurolate ($ArTe^-Na^+$) with 2-chloroethylamine or 3-chloropropylamine (or their hydrochloride derivatives). Initially the hydrochloride salts are formed but the free amines can be liberated by alkali addition.

$$\tfrac{1}{2}Ar_2Te_2 \xrightarrow{NaBH_4/NaOH/N_2} ArTe^-Na^+$$

$$ArTe^-Na^+ + Cl(CH_2)_nNH_2.HCl \longrightarrow ArTe(CH_2)_nNH_2.HCl$$

$$ArTe(CH_2)_nNH_2.HCl \xrightarrow{10\%\ NaOH} ArTe(CH_2)_nNH_2$$

The amines are soluble in common organic solvents whilst the amine salts are only soluble in highly polar solvents (eg DMSO). Arylselenoalkylamines can be synthesised in a similar fashion but using the nucleophile RSe^-. Singh and Srivastava(114) recently reported compounds of this type when they synthesised the ligands 2-aryltelluroethylamines (aryl = p-methoxyphenyl and p-ethoxyphenyl) and their complexes with $HgCl_2$.

Analytical, infra-red and N.M.R spectroscopic results are shown in tables 5.1-5.3. The results are discussed collectively rather than individual assignment of the compounds. The analytical data (table 5.1) support the formation of either the amine or the amine salt. Interpretation of the infra-red data (table 5.2) is straightforward and relevant infra-red absorptions are given. The C-N vibration in all the compounds is found at 1176-1183cm^{-1}. Absorptions in the range 700-1000cm^{-1} are assigned as out of plane (C-H) ring deformations along with weaker CH_2 rocking modes. In the high wavenumber region broad bands centered at ~3000cm^{-1} and tailing to 2400cm^{-1} have been assigned as H-Cl bands with strong hydrogen bonding present. For the amines, sharp bands at ~3240cm^{-1} are characteristic of N-H stretching modes.

The ^{13}C N.M.R spectra (table 5.3) are as expected with distinct signals in the aliphatic and aromatic regions. Of the methylene signals, it is the $Te-CH_2$ or the $Se-CH_2$ signals which are found furthest upfield. The chalcogen shields the neighbouring carbon with its lone pairs of electrons. The CH_2-NH_2 (or $CH_2-NH_3^+$) signals are found furthest downfield, deshielded by the electron withdrawing amine functionality.

The ^1H N.M.R spectra (table 5.3) again show separate features in the aromatic and aliphatic regions. Multiplicity and integration values are as expected. The NH_2 and NH_3^+ signals appear as broad signals. In the 2-aryltelluroethylamines and the 2-arylselenoethylamines, the $E-CH_2$ (E= Se,Te) and CH_2-NH_2 protons appear as triplets, except in the case of p-ethoxyphenyltelluroethylamine where a broad band at $\delta=3.6$ ppm is explained by the merging of both signals. The $E-CH_2$ protons are found

Analytical Data

Compound	m.pt.(^{0}C)	Found (Required)		
		%C	%N	%H
p-$CH_3OC_6H_4Te\ CH_2CH_2NH_2$	85-87	39.7	4.48	5.16
		(38.8)	(4.67)	(5.03)
p-$C_2H_5OC_6H_4TeCH_2CH_2NH_2$	90-92	41.1	4.80	4.53
		(41.0)	(5.13)	(4.78)
$PhTeCH_2CH_2CH_2NH_2$	78-80	41.3	4.69	4.50
		(41.1)	(4.39)	(4.62)
p-$CH_3OC_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$	75(d)	35.9	5.22	4.51
		(36.5)	(4.86)	(4.25)
p-$C_2H_5OC_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$	75(d)	38.3	4.95	3.85
		(38.5)	(5.24)	(4.08)
p-$CH_3C_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$	120(d)	38.3	5.07	4.29
		(38.3)	(5.15)	(4.47)
$PhSeCH_2CH_2NH_2$	50-51	48.5	4.70	6.85
		(48.0)	(5.54)	(7.00)
$PhSeCH_2CH_2CH_2NH_3^+Cl^-$	140-142	42.7	5.60	5.44
		(43.1)	(5.63)	(5.54)
$(PhTeCH_2CH_2)_3N$ L^1	65-66	39.9	3.74	1.91
		(40.5)	(3.79)	(1.97)
(p-$CH_3OC_6H_4TeCH_2CH_2)_3N$ L^2	58-59	40.2	4.06	1.68
		(40.4)	(4.12)	(1.75)
(p-$C_2H_5OC_6H_4TeCH_2CH_2)_3N$ L^3	66-67	42.6	4.65	1.74
		(42.7)	(4.62)	(1.66)

Analytical Data (continued)

Compound	m.pt (°C)	Found (Required) %C	%H	%N
$(PhSeCH_2CH_2)_3N$ L^4	46-47	50.3 (50.9)	4.72 (4.80)	2.35 (2.47)
$(p\text{-}C_2H_5OC_6H_4SeCH_2CH_2)_3N$ L^5	49-50	50.8 (51.6)	5.57 (5.63)	1.83 (2.01)
L^2HgCl_2	105-107	29.5 (30.2)	3.01 (3.07)	1.27 (1.30)
L^2CdI_2	86-87	28.1 (27.7)	2.97 (2.83)	1.30 (1.20)
$L^2PtCl_2.H_2O$	175(d)	29.3 (29.8)	3.09 (3.04)	1.07 (1.29)
$L^2PdCl_2.H_2O$	160-161	31.5 (32.5)	3.44 (3.51)	1.25 (1.40)
$L^2CuBr.H_2O$	110	31.6 (33.6)	3.40 (3.63)	1.36 (1.45)
L^3HgCl_2	103-105	31.8 (32.3)	3.41 (3.50)	1.21 (1.25)
$L^3Cd(OH)_2$	140(d)	36.4 (36.4)	3.99 (4.14)	1.95 (1.41)
$L^3PtCl_2.H_2O$	145-147	30.9 (31.9)	3.38 (3.63)	1.20 (1.24)

Analytical Data (continued)

Compound	m.pt. (°C)	Found (Required) %C	%H	%N
$L^3PdCl_2.H_2O$*	155-156	33.9 (34.6)	3.80 (3.95)	1.33 (1.35)
$L^3CuBr.H_2O$	100(d)	35.8 (35.8)	3.78 (4.08)	1.16 (1.39)
$L^4HgCl_2.\ 0.5CHCl_3$	45-46	32.5 (32.8)	3.13 (3.07)	1.43 (1.56)
$L^5.3HgCl_2$	80-81	23.5 (23.8)	2.69 (2.58)	1.04 (0.93)
$L^5PtCl_2.H_2O$	81-82	37.6 (36.7)	4.26 (4.17)	1.40 (1.43)

Table 5.1 Analytical Data

* %Cl = 7.44 (6.82)

Mass Spectroscopy Data

Compound	Fragmentation Ion	m/e
$PhSeCH_2CH_2CH_2NH_3{}^+Cl^-$	$PhSeCH_2CH_2CH_2NH_3{}^+$	215
	$PhSeCH_2CH_2CH_2{}^+$	199
Electron Impact	$PhSe^+$	157
	Ph^+	77
$(PhTeCH_2CH_2)_3N$	$(PhTeCH_2CH_2)_3N^+$	714
	$(PhTeCH_2CH_2)_2NCH_2CH_2{}^+$	508
Electron Impact	$(PhTeCH_2CH_2)_2{}^+$	466
	$Ph_2Te_2{}^+$	410
	Ph_2Te^+	284
	$PhTe^+$	207
	$Ph_2{}^+$	154
	Ph^+	77
$(p\text{-}CH_3OC_6H_4TeCH_2CH_2)_3N$	$(CH_3OC_6H_4TeCH_2CH_2)_3N^+$	802
	$(CH_3OC_6H_4TeCH_2CH_2)_2NCH_2CH_2{}^+$	570
Fast Atom Bombardment	$(CH_3OC_6H_4TeCH_2CH_2)_2N^+$	540
	$(CH_3OC_6H_4TeCH_2CH_2)_2{}^+$	526
	$(CH_3OC_6H_4TeCH_2CH_2N{=}CHCH_2)^+$	306
	$CH_3OC_6H_4TeCH_2CH_2{}^+$	265
	$CH_3OC_6H_4Te^+$	237
	CH_3OPh^+	108
	Ph^+	77

Compound	Fragmentation Ion	m/e
$L^2.PdCl_2H_20$	$(CH_3OC_6H_4TeCH_2CH_2)_3N.PdCl^+$	942
Fast Atom Bombardment		
$C_2H_5O\text{-}C_6H_4TeCH_2CH_2)_3N$	$(C_2H_5OC_6H_4TeCH_2CH_2)_3N^+$	845
	$(C_2H_5OC_6H_4TeCH_2CH_2)_2NCH_2CH_2^+$	598
Fast Atom Bombardment	$(C_2H_5OC_6H_4TeCH_2CH_2)_2N^+$	570
	$(C_2H_5OC_6H_4)_2Te^+$	372
	$(C_2H_5OC_6H_4Te + NH_3)^+$	268
	$C_2H_5O\text{-}C_6H_4Te^+$	251
	$C_2H_5O\text{-}Ph+$	122
$L^3.Cd(OH)_2$	$(C_2H_5OC_6H_4TeCH_2CH_2)_2NCH_2CH_2^+$	596
	$(C_2H_5OC_6H_4TeCH_2CH_2)_2N^+$	568
	$(C_2H_5OC_6H_4TeCH_2CH_2)_2^+$	555
	$C_2H_5OC_6H_4TeCH_2CH_2N(CH_2CH_2)_2^+$	346
	$C_2H_5OC_6H4TeCH_2CH_2NCH_2CH_2^+$	321
	$C_2H_5OC_6H_4TeCH_2CH_2^+$	279
	$C_2H_5OC_6H_4Te^+$	251
$L^3PdCl_2.H_2O$	$(C_2H_5OC_6H_4TeCH_2CH_2)_3N.PdCl^+$	986
	$(C_2H_5OC_6H_4TeCH_2CH_2)_2NCH_2CH_2^+$	598
	$C_2H_5OC_6H_4Te.PdCl^+$	357
	$C_2H_5OC_6H_4Te.PdCl^+$	485
	$C_2H_5OC_6H_4Te^+$	249

Compound	Fragmentation Ion	m/e
$(PhSeCH_2CH_2)_3N$	$(PhSeCH_2CH_2)_3N^+$	568
	$(PhSeCH_2CH_2)_2NCH_2CH_2^+$	410
Electron Impact	$(PhSeCH_2CH_2)_2N{=}CH_2^+$	398
	$PhSeCH_2CH_2^+$	185
	$PhSe^+$	157
	Ph^+	77
$(C_2H_5OC_6H_4SeCH_2CH_2)_3N$	$(C_2H_5OC_6H_4SeCH_2CH_2)_3N^+$	700
	$(C_2H_5OC_6H_4SeCH_2CH_2)_2NCH_2CH_2^+$	500
Chemical Ionisation	$(C_2H_5OC_6H_4SeCH_2CH_2)_2N{=}CH_2^+$	486
	$C_2H_5OC_6H_4Se^+$	77
L^5HgCl_2	$(C_2H_5OC_6H_4SeCH_2CH_2)_3N.HgCl^+$	935
	$(C_2H_5OC_6H_4SeCH_2CH_2)_3N^+$	701
Fast Atom Bombardment	$(C_2H_5OC_6H_4SeCH_2CH_2)_2NCH_2CH_2^+$	498
	$(CH_3CH_2OSeCH_2CH_2)_2N{=}CH_2+$	484
	$(C_2H_5OC_6H_4SeCH_2CH_2)_2N^+$	470
	$(PhSeCH_2CH_2)_2N^+$	378
	$C_2H_5OC_6H_4SeCH_2CH_2NCH_2CH_2^+$	271
	$C_2H_5OC_6H_4SeCH_2CH_2^+$	229

Table 5.2 Mass Spectroscopy Data

(based on ^1H, ^{12}C, ^{14}N, ^{16}O, ^{80}Se, ^{130}Te).

(correct isotopic patterns were observed for Te_n^+).

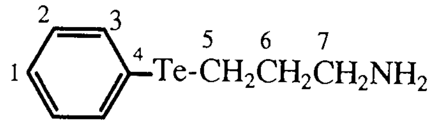
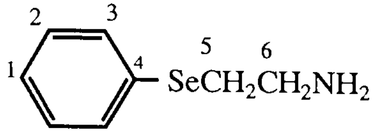
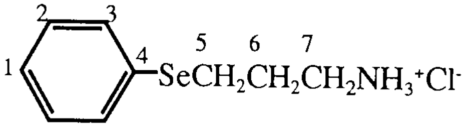
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7
	DMSO-D_6	127.4	137.0	129.4	112.3	2.9	4.3	40.4
	$CDCl_3$	126.1	132.7	130.0	---	31.8	41.3	
	DMSO-D_6	126.7	131.4	129.6	129.6	23.1	27.4	39.5

Table 5.3 ^{13}C N.M.R data.

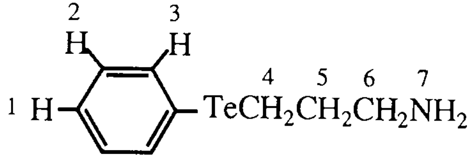
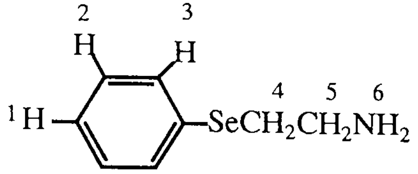
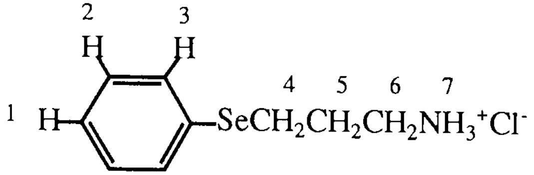
Compound	Solvent	H1	H2	H3	H4	H5	H6	H7
	DMSO-D_6	7.4 (s)	7.7 (m)	7.2 (m)	1.9 (t)	2.8 (m)	2.9 (m)	3.4 (b.s)
	DMSO-D_6	← 7.2--7.6 (m) →			2.8 (t)	3.0 (t)	2.6 (b.s)	
	DMSO-D6	7.3 (s)	7.5 (d)	7.2 (d)	1.9 (t)	2.8 (t)	3.0 (t)	8.2 (b.s)

Table 5.3 (continued) **s= singlet; b.s= broad singlet; d= doublet; t= triplet; m= multiplet.**

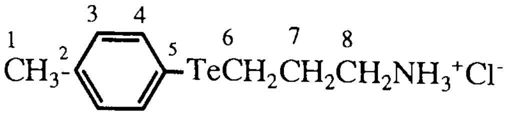
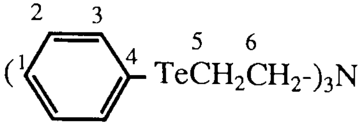
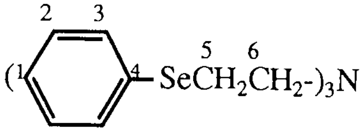
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8
	DMSO-D_6	20.7	136.9	130.2	137.6	107.8	4.3	28.9	40.3
	$CDCl_3$	112.6	127.4	138.1	129.1	7.9.	54.3		
	DMSO-D_6	127.4	132.2	130.1	121.4	25.9	53.7		

Table 5.3 (continued)

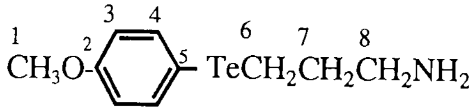
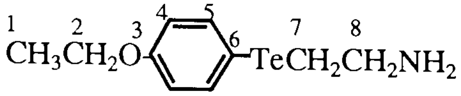
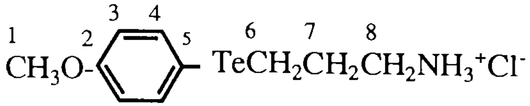
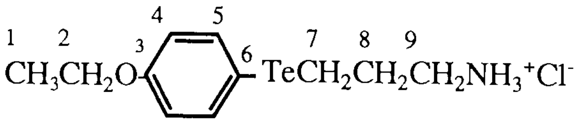
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8	C9
	$CDCl_3$	55.1	159.8	115.2	141.1	99.8	14.9	43.1		
	DMSO-D_6	14.6	63.0	158.5	131.6	139.9	100.3	12.5	43.1	
	DMSO-D_6	55.0	159.2	115.4	139.9	100.6	4.7	29.9	40.8	
	DMSO-D_6	14.6	62.9	158.5	139.8	115.8	100.7	4.9	31.2	41.4

Table 5.3 (continued).

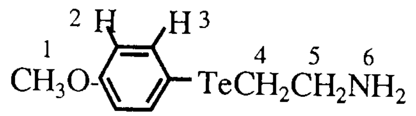
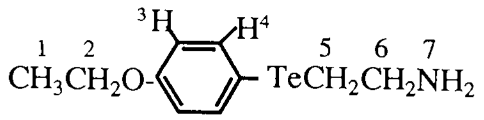
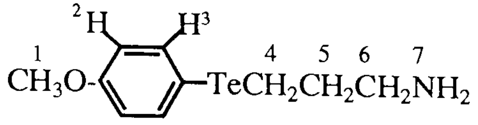
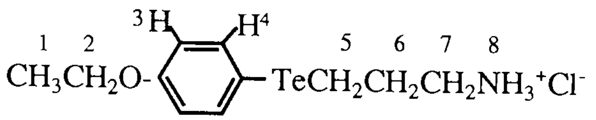
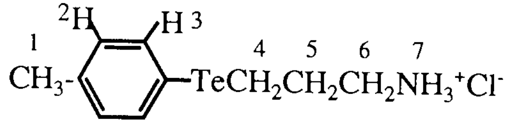
Compound	Solvent	H1	H2	H3	H4	H5	H6	H7	H8
	$CDCl_3$	3.8 (s)	6.7 (d)	7.6 (d)	2.8 (b.s)	3.0	1.9 (b.s)		
	DMSO-D_6	1.3 (t)	4.0 (q)	6.8 (d)	7.6 (d)	3.6 (b.s)		2.9 (b.s)	
	DMSO-D_6	1.4 (t)	6.8 (d)	7.6 (d)	1.9 (d)	1.9 (t)	2.7 (t)	2.9 (t)	5.0 (b.s)
	DMSO-D_6	1.3 (t)	4.0 (m)	6.8 (d)	7.6 (d)	1.8 (t)	2.7 (t)	2.8 (t)	4.0 (b.s)
	DMSO-D_6	2.3 (t)	7.1 (d)	7.5 (d)	2.0 (t)	2.8 (t)	2.9 (t)	3.7 (t)	

Table 5.3 (continued) **s= singlet; b.s= broad singlet; d= doublet; t= triplet; q=quartet; m= multiplet**

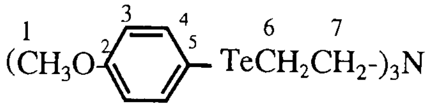
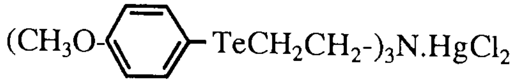
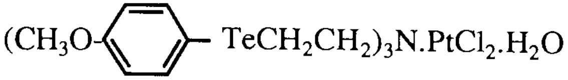
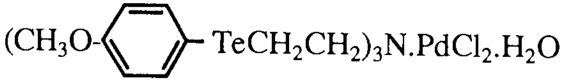
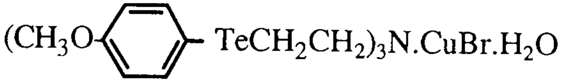
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7
	$CDCl_3$	55.1	159.6	115.1	140.6	101.1	8.0	54.2
	DMSO-D_6	56.2	161.3	116.7	139.9	103.3	18.3	52.0
	DMSO-D_6	55.0	159.1	115.2	139.6	101.4	9.2	53.3
	DMSO-D_6	55.2	160.3	115.7	139.5	---	---	---
	DMSO-D_6	55.2	160.2	115.7	139.5	---	---	---
	DMSO-D_6	55.2	159.9	115.7	137.8	100.5	16.4	51.9

Table 5.3 (continued) s= singlet; b.s= broad singlet; d=doublet; t= triplet; m= multiplet.

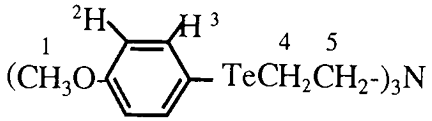
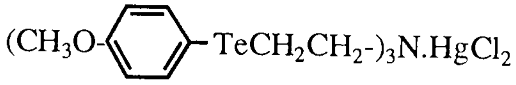
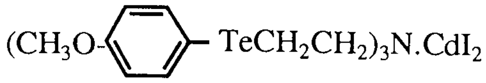
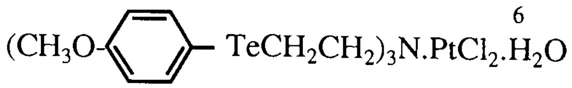
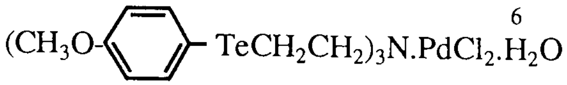
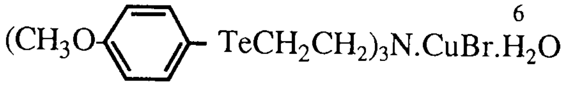
Compound	Solvent	H1	H2	H3	H4	H5	H6
	$CDCl_3$	3.7 (s)	6.8 (d)	7.6 (d)	← 2.8 (b.s) →		
	DMSO-D_6	3.7 (s)	6.9 (d)	7.8 (d)	2.8 (b.s)	3.2 (b.s)	
	DMSO-D_6	3.7 (s)	6.8 (d)	7.6 (d)	2.8 (b.s)	3.1 (b.s)	
	DMSO-D_6	3.8 (s)	6.9 (d)	7.8 (d)	2.8(b.s)	3.4*	3.5 (b.s)
	DMSO-D_6	3.8 (s)	6.9 (d)	7.8 (d)	2.9 (b.s)	4.1 (b.s)	3.4 (b.s)
	DMSO-D_6	3.7 (s)	6.9 (d)	7.6 (d)	2.8 (b.s)	2.9 (b.s)	3.5 (b.s)

Table 5.3 (continued) **s= singlet; b.s= broad singlet; d=doublet; t= triplet; m= multiplet.** * tentative assignment.

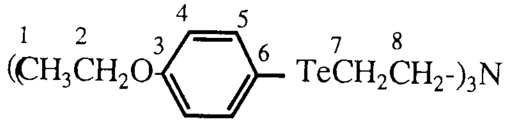
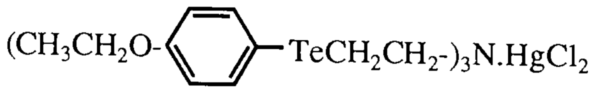
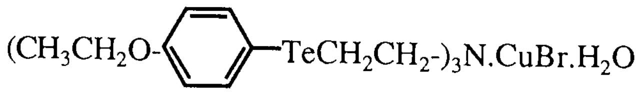
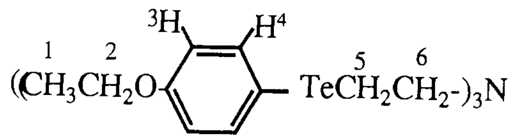
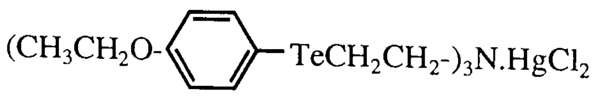
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8
	$CDCl_3$	14.8	63.3	159.0	115.7	140.7	101.0	7.9	54.2
	DMSO-D_6	15.5	64.1	160.9	117.0	140.3	102.9	---	52.8
	DMSO-D_6	14.5	63.2	---	116.0	134.9	---	---	---
	DMSO-D_6	14.6	63.2	159.4	116.1	138.6	---	---	---
	DMSO-D_6	14.6	63.1	159.2	116.0	139.2	100.9	16.0	51.9

Table 5.3 (continued)

Compound	Solvent	H1	H2	H3	H4	H5	H6	H7
	$CDCl_3$	1.4 (t)	4.0 (q)	6.7 (d)	7.6 (d)	←2.9 (b.s)→		
	DMSO-D_6	1.3 (t)	4.0 (q)	6.8 (q)	7.7 (d)	2.9 (b.s)	3.1 (b.s)	
	DMSO-D_6	1.3 (t)	4.0 (t)	6.9 (d)	7.8 (d)	2.9 (b.s)	4.0*	3.4 (b.s)
	DMSO-D_6	1.3 (t)	4.0 (d)	6.8 (d)	7.6 (d)	2.7 (b.s)	2.8 (b.s)	3.4 (b.s)

* tentative assignment

Table 5.3 (continued) **s= singlet; b.s= broad singlet; d= doublet; t=triplet; q= quartet; m=multiplet;**

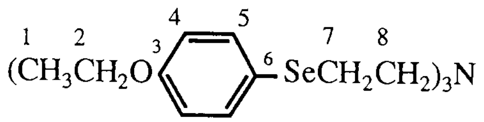
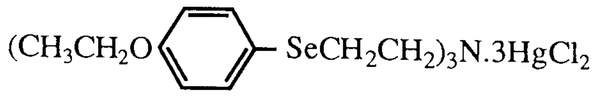
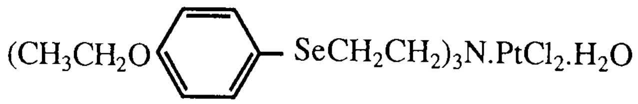
Compound	Solvent	C1	C2	C3	C4	C5	C6	C7	C8
 $(CH_3CH_2O$ $SeCH_2CH_2)_3N$	DMSO-D_6	14.6	63.1	157.9	115.3	134.4	119.5	25.9	52.9
 $(CH_3CH_2O$ $SeCH_2CH_2)_3N.3HgCl_2$	DMSO-D_6	14.6	63.3	158.9	115.8	134.4	116.6	27.8	50.7
 $(CH_3CH_2O$ $SeCH_2CH_2)_3N.PtCl_2.H_2O$	DMSO-D_6	14.5	63.4	159.7	115.8	134.7	117.4	25.9	52.8

Table 5.3 (continued).

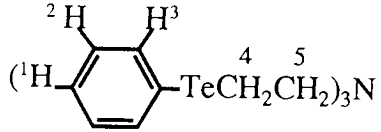
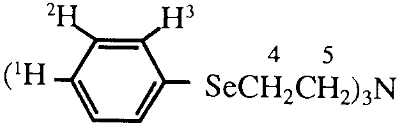
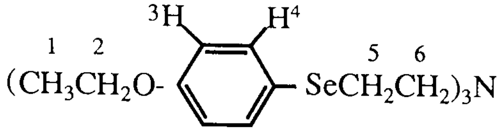
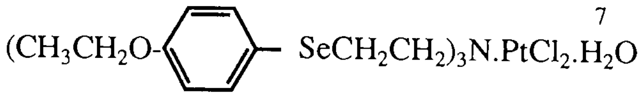
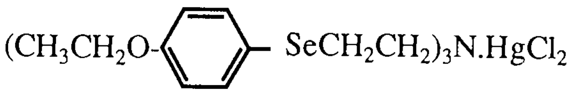
Compound	Solvent	H1	H2	H3	H4	H5	H6
	$CDCL_3$	← 7.1 - 7.8 →			← 2.9(m)→		
	DMSO-D_6	← 7.2 - 7.4 →			2.8 (t)	2.9 (t)	
	DMSO-D_6	1.3 (t)	4.0 (t)	6.8 (d)	7.3 (d)	2.6 (t)	2.8 (t)
	DMSO-D_6	1.3 (t)	4.0 (m)	6.9 (d)	7.8 (s)	3.2 (b.s)	3.6 (b.s)
	DMSO-D_6	1.3 (t)	4.0 (m)	6.9 (d)	7.5 (d)	2.8 (b.s)	3.1 (b.s)

Table 5.3 (continued) **s= singlet; b.s broad singlet; d= doublet ; t-=triplet; m= multiplet.**

Compound	υ(C-N)	δ(C-H)	δ(CH_2)	υ(M-X)	υ(Te-CH_2)	υ(Te-C_{arom})
$(CH_3CH_2OC_6H_4TeCH_2CH_2)_3N$ Ligand L^3	1175(s)	818(s)	919(m), 740(m) 697(m)		377(m), 354(m) 338(m)	315(w), 306(w) 291(w), 279(w) 265(w)
$L^3.HgCl_2$	1180(s)	819(s)	920(s)	317(m)	381(w), 358(w)	317(w), 284(w) 243(w), 255(w)
$L^3.Cd(OH)_2$	1179(s)	822(s)	922(m)	632(m) (Cd-O)	386(w), 371(w) 357(w), 337(w)	322(w), 306(w) 289(w), 279(w) 267(w)
$L^3.PtCl_2.H_2O$	1180(s)	818(s)	921(m) 695(m)	327(m)	353(w), 338(w)	281(w), 262(w) 254(w)
$L^3.PdCl_2.H_2O$	1179(s)	817(s)	921(m) 698(m)	321(m) 321(R)	381(w), 371(w) 357(w)	302(w), 276(w) 266(w)
$L^3.CuBr.H_2O$	1177(s)	817(s)	919(m) 696(m)		377(w), 370(w) 361(w), 346(w) 337(w)	317(w), 305(w) 293(w), 288(w) 281(w), 272(w)

Table 5.4 Infra-red Spectroscopic data w= weak; m= medium; s= strong R= Raman signal

Compound	υ(C-N)	δ(C-H)	δ(CH_2)	υ(M-X)	υ(Te-CH_2)	υ(Te-$C_{(arom)}$)
$(CH_3OC_6H_4TeCH_2CH_2)_3N$ L^2	1174(s)	817(vs), 786(vs)	852 698(m) 842(m)		350(w)	314(w), 296(w) 284(w), 263(w)
$L^2.HgCl_2$	1181(s)	823(s) 789(m)		322(m)	376(w), 355(w)	306(w), 300(w) 243(w), 255(w)
L^2CdI_2	1177(s)	822(s) 789(m)			362(w), 333(w)	309(w), 295(w) 285(w), 274(w) 250(w).
$L^2.PtCl_2.H_2O$.	1178(s)	823(m) 789(m)	712(m)	328(m)	387(w), 376(w) 358(m)	314(w), 295(w) 284(w)
$L^2.PdCl_2.H_2O$	1177(s)	822(s) 788(s)	711(m) 699(m)	321(m) 321(R)	392(w), 381(w) 376(w), 371(w) 365(w), 355(w) 342(w), 337(w)	317(w), 284(w)
$L^2.CuBr.H_2O$	1177(s)	821(s) 787(s)	747(m) 703(m)		391(w), 376(w) 354(w), 343(w) 343(w), 337(w)	316(w), 301(w) 291(w), 280(w) 268(w), 255(w)

Table 5.4 Infra-red spectroscopic data w= weak; m=medium; s=strong R= Raman signal

Compound	υ(C-N)	δ(C-H)	$\delta(CH_2)$	Others
$CH_3OC_6H_4TeCH_2CH_2NH_2$	1185(s)	817(m), 787(m)	724(m), 711(m)	3242(m) (N-H)
$C_2H_5OC_6H_4TeCH_2CH_2NH_2$	1177(s)	819(s), 806(s)	921(m), 754(m)	3244(w) (N-H)
$CH_3OC_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$	1177(s)	821(s), 810(s)	927(m),	2928(s) (H-Cl)
$C_2H_5OC_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$	1176(s)	819(s), 803(m)	944(m), 920(m) 743(w), 696(w)	2932(s) (H-Cl)
$PhTeCH_2CH_2CH_2NH_2$	1179(s)	820(s), 801(s)	940(m), 922(m)	3246(m) (N-H)
$CH_3C_6H_4TeCH_2CH_2CH_2NH_3^+Cl^-$		793(w),750(w) 728(w)	927(w)	3431(s) (H-Cl)
$PhSeCH_2CH_2NH_2$	1178(s)	738(s), 694(s)	792(m), 751(m)	3232(s) (N-H)
$PhSeCH_2CH_2CH_2NH_3^+Cl^-$	1183(s)	728(s), 688(s)	939(m), 897(m) 815(m), 784(m)	2884(s) (H-Cl)

Table 5.4 Infra-red Spectroscopic data. s= strong; m= medium; w= weak.

Compound	υ(C-N)	δ(C-H)	δ(CH_2)	υ(M-X)	υ(E-C_{Aryl})	υ(E-CH_2)
$(PhTeCH_2CH_2)_3N$	1175(w)	732(vs) 693(vs)	857(w) 797(w)		281(w),301(w)	397(w), 386(w) 381(w), 366(w) 357(w), 346(w) 337(w).
$(PhSeCH_2CH_2)_3N$	1181(m)	731(s)	840(m), 691(m)		316(w), 307 (w) 289(w)	381(w), 359(w) 338(w)
$(PhSeCH_2CH_2)_3N.HgCl_2$	1180(m)	730(s)	842(m) 690(m) 667(m)	322(m)	320(w), 309(w)	380(w), 360(m) 339(w)
$(C_2H_5OC_6H_4SeCH_2CH_2)_3N$ Ligand L^5	1174(s)	829(s) 810(s) 740(w)	920(m) 765(w)		304(m), 280(m) 255(w)	342(w), 327(w)
$L^5.HgCl_2$	1179(s)	822(s)	921(m)	322(m)	309(w), 302(w) 276(w)	357(w), 343(w) 338(w), 329(w)
$L^5.PtCl_2.H_2O$	1176(s)	821(s)	921(m) 730(m)	343(m) 333(m)	305(w), 277(w)	392(w)

Table 5.4 Infra-red spectroscopy data vs= very strong, s= strong, m= medium; w= weak. E= Se,Te

at higher field. The same trend is observed in the proton signals of the propyl groups in the aryltelluropropylamines where all three methylene signals appear as triplets.

Only the mass spectrum of phenylselenopropylamine hydrochloride was recorded. The highest mass fragment detected was at m/e = 215 pertaining to $PhSeCH_2CH_2CH_2^+$. The other fragments are shown in table 5.2.

5.3.2 Characterisation of Tris(2-aryltelluroethyl)amines, tris(2-arylselenoethyl)amines and their complexes.

Tris(2-aryltelluroethyl)amine ligands [aryl = phenyl (L^1), p-methoxyphenyl (L^2) and p-ethoxyphenyl (L^3) can be prepared by the reaction of a solution of sodium aryltellurolate with tris(2-chloroethyl)amine.

$$(ClCH_2CH_2)_3N.HCl \xrightarrow{10\% \ NaOH} (ClCH_2CH_2)_3N$$

$$(ClCH_2CH_2)_3N + 3Na^+TeAr^- \longrightarrow (ArTeCH_2CH_2)_3N$$

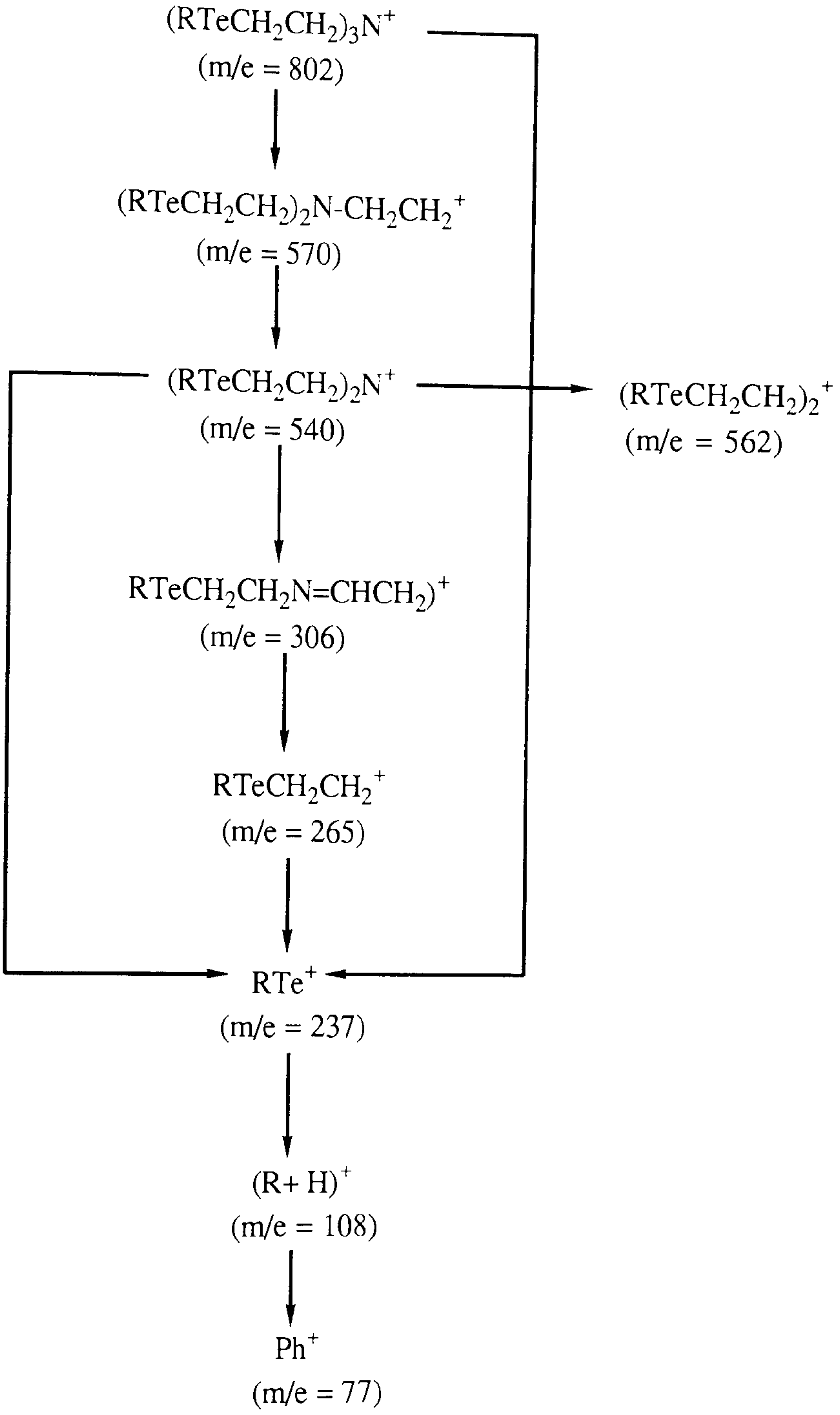
Ligands L^2 and L^3 were reported recently by Singh and Srivastava(115) along with their complexes with mercury(II). In a similar reaction, the analogous tris(2-arylselenoethyl)amines [Ar= phenyl (L^4) and p-ethoxyphenyl (L^5)] can be synthesised. These tetradentate ligands are found to be soluble in chloroform, benzene and hot alcoholic solvents. They are stable in air, have low melting points and are non-electrolytes in solution.

Analytical, infra-red, N.M.R and mass spectroscopic data are presented in tables 5.1-5.4. Some spectra are also illustrated.

The mass spectra of the free ligands (Te,N) and (Se,N) show the molecular ion in all cases. For the (Te,N) ligands, fragmentation occurs with loss of RTe^+ (R= Ph, p-$CH_3OC_6H_4$-, p-$C_2H_5OC_6H_4$) and the formation of $(RTeCH_2CH_2)_2NCH_2CH_2^+$. This ion undergoes further fragmentation. Detailed assignment of the ions for each compound are shown in table 5.2. As an illustration the fragmentation process of L^2 is shown in scheme 5.1.

The infra-red spectra of the ligands were recorded using KBr discs. Strong absorption bands at 1174-1183cm^{-1} are typical of C-N stretching vibrations. The Te-C(alkyl) and Te-C(aryl) vibrations are tentatively assigned in the regions 400-330cm^{-1} and 315-260cm^{-1} respectively. McWhinnie and coworkers(119) have shown from isotopic substitution experiments that bands in the latter region do undergo shifts and have been assigned as Te-C(aryl) vibrations. In the selenium ligands bands in the same regions have been assigned as Se-CH_2 and Se-C(aryl) vibrations.

The ^{13}C N.M.R spectra of the tellurium and selenium ligands



R = $CH_3OC_6H_4$- Based on ^{12}C, ^{1}H, ^{14}N, ^{16}O, ^{130}Te.

(correct isotopic patterns were observed for Te_n^+)

Scheme 5.1 **F.A.B Mass spectrum interpretation of Ligand L^2**

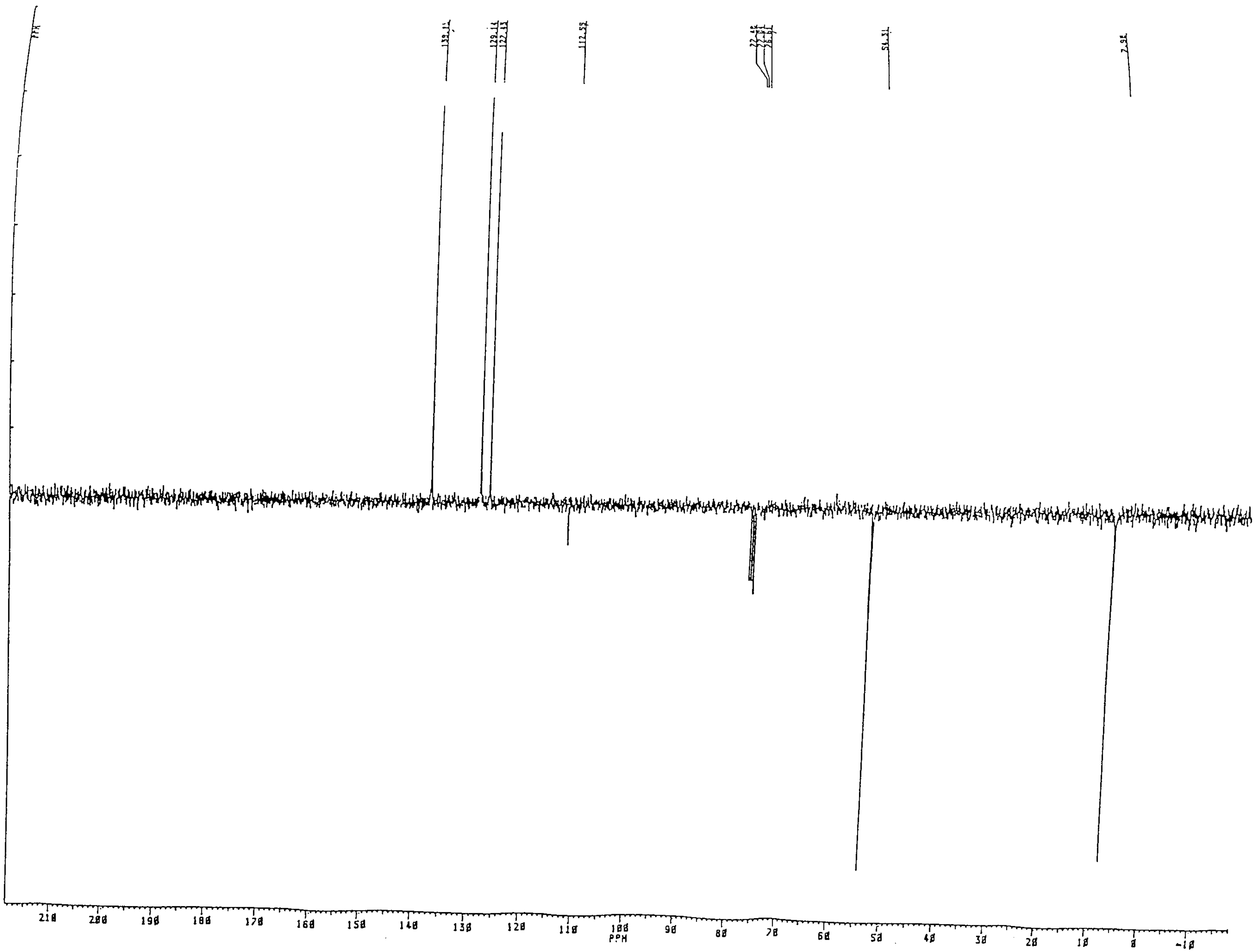


Figure 5.6 ^{13}C N.M.R. spectrum of Ligand L^1.

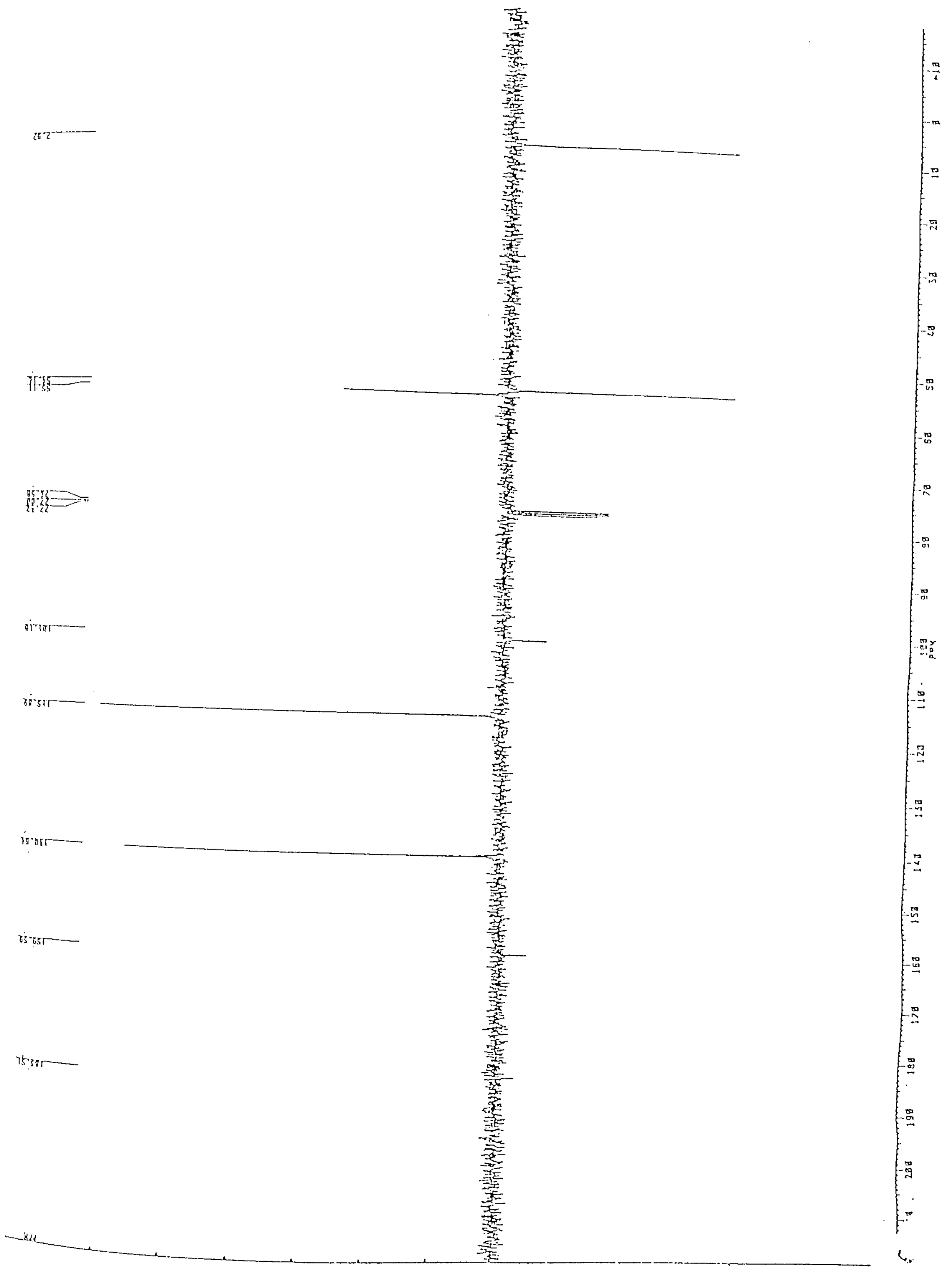


Figure 5.7 ^{13}C N.M.R. spectrum of Ligand L^2.

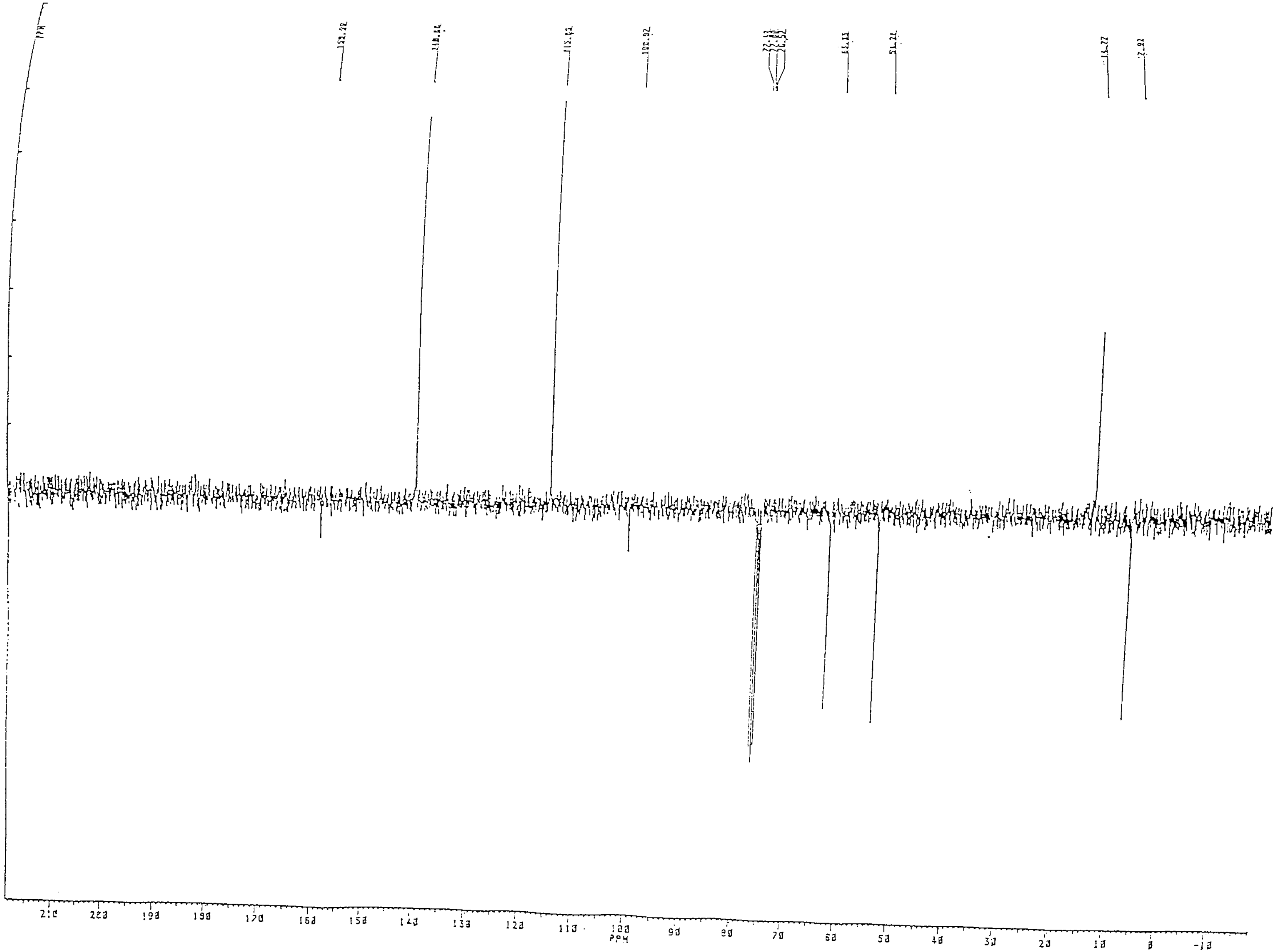


Figure 5.8 ^{13}C N.M.R. spectrum of Ligand L^3.

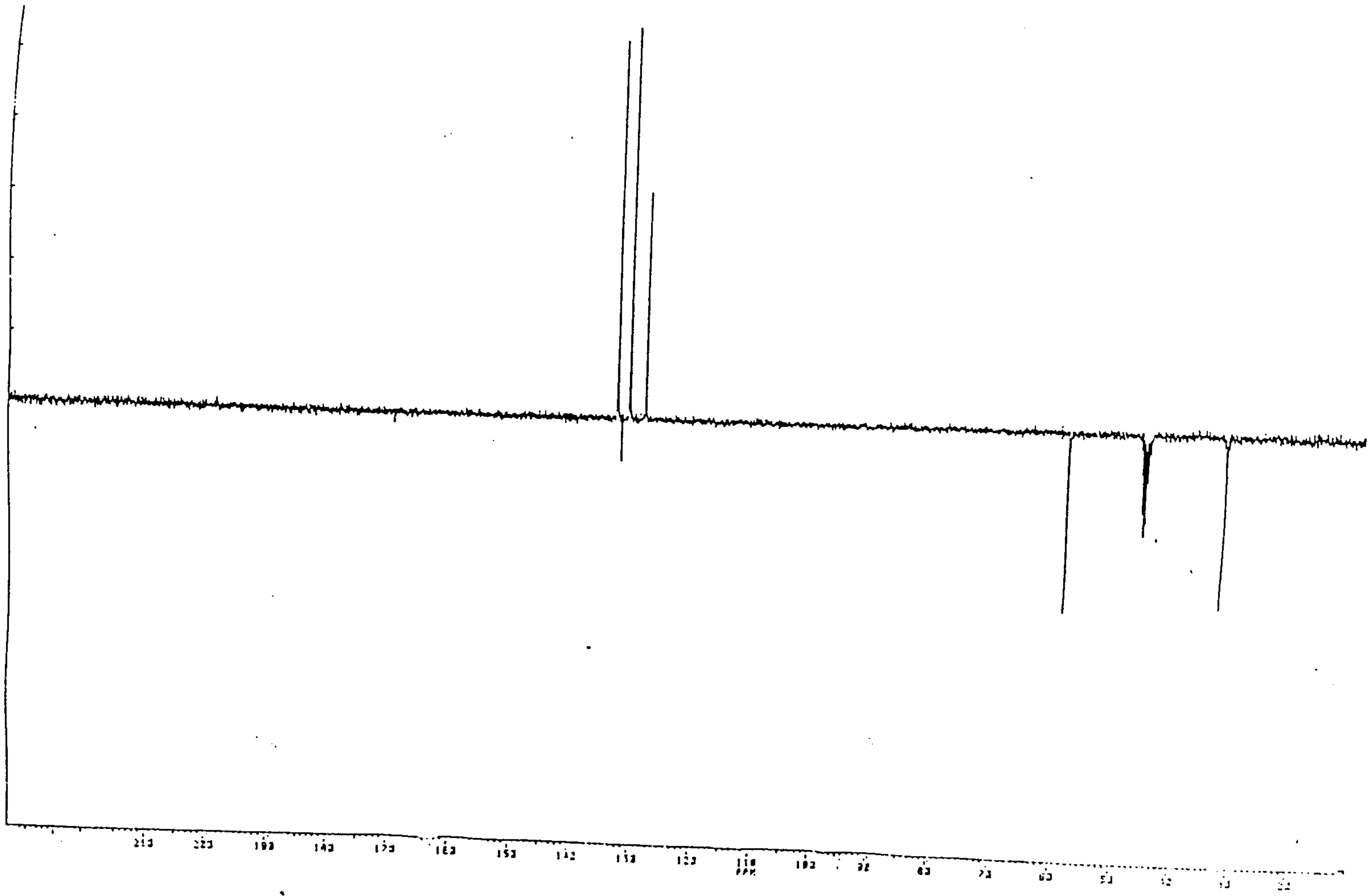


Figure 5.9 ^{13}C N.M.R. spectrum of Ligand L^{4}.

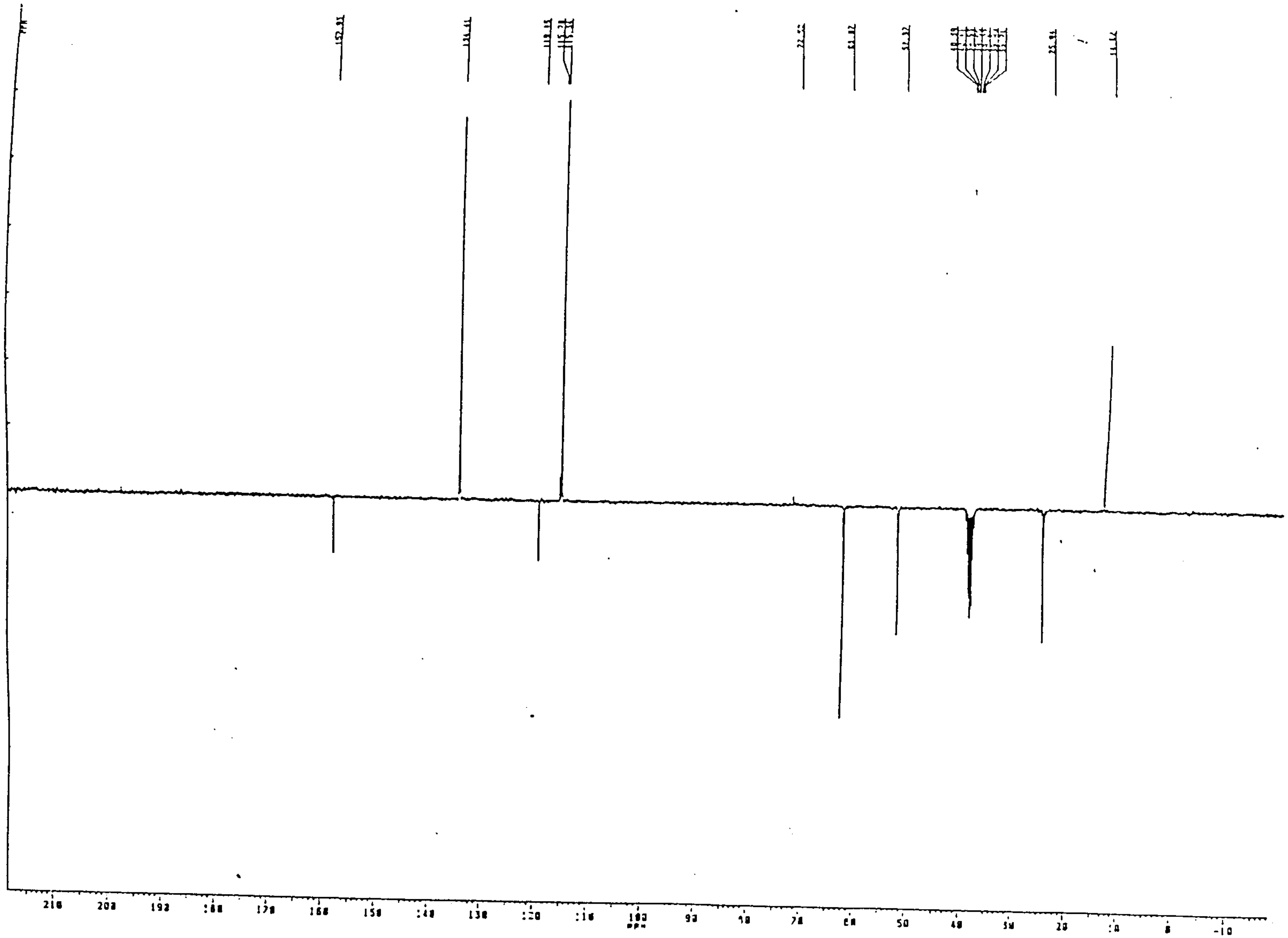


Figure 5.10 ^{13}C N.M.R. spectrum of Ligand L^5.

were recorded in chloroform and DMSO respectively and are illustrated in figures 5.6-5.10. There are no anomalies in any of the spectra with features in the aromatic and aliphatic regions as expected. The N-CH_2 signal is found further downfield than the neighbouring E-CH_2 signal. Furthermore the Te-CH_2 signal is found further upfield than the Se-CH_2 resonance and this can be explained by the larger screening effect of the tellurium atom(120). The same explanation can be applied to the lower chemical shift value found for the Te-C(aryl) signal (cf. δ= ~101 ppm) relative to that of the Se-C(aryl) resonance (cf δ= ~121 ppm). For comparison the *ipso* carbon for other aryltellurium(II) compounds(121) are found at δ= 100 ppm (cf. benzene 128.5 ppm).

The same trends are observed in the ^1H N.M.R, except that for the tellurium ligands the methylene signals can not be distinguished and are merged thus appearing as broad singlets at δ= ~2.8-2.9 ppm. However the methylene protons in the selenium ligands can be resolved and appear as triplets with the Se-CH_2 signals found at higher field.

Molecular weight measurements have not been carried out but Singh and Srivastava(115) have shown the ligands L^2 and L^3 to be monomeric.

5.3.3 Characterisation of the Hg(II) complexes of L^2 and L^3

The reaction of L^2 or L^3 with mercuric chloride in a 1:1 molar ratio produces adducts of stoichiometry $L.HgCl_2$. These compounds were recently reported by Singh and Srivastava(115). They are found to be moderately soluble in polar organic solvents and are non-electrolytes in DMSO. The spectroscopic data agree with that of Singh and Srivastava but in our case the ^{13}C and ^1H N.M.R of both compounds could be recorded (Singh and Srivastava had solubility problems with L^3HgCl_2).

The ^{13}C N.M.R spectra of both compounds are shown in figures 5.11-5.12. For the complex L^2HgCl_2, the Te-C(aryl) and Te-CH_2 signals resonate at 2 and 10 ppm downfield from the corresponding ligand signals. In the complex L^3HgCl_2 the *ipso* carbon is seen 2 ppm downfield but the Te-CH_2 resonance was not observed. [However Singh and Srivastava did observe this signal at 12 ppm downfield from the ligand]. From this evidence there appears to be a strong interaction between the lone pairs of electrons on tellurium and the mercury atom. Thus the mercury(II) centre appears to be behaving as a Lewis acid, withdrawing electrons from tellurium and hence deshielding the carbon nuclei. There is a slight shift in the N-CH_2 signals for both complexes and these shifts probably arise from the coordinaton of tellurium to mercury rather than any nitrogen-mercury interaction. Both spectra show only one set of signals implying equivalence of all three tellurium atoms. However on turning to the ^1H N.M.R spectra (see figures 5.13-5.14) there is evidence for non-equivalence of the telluriums in the complex L^3HgCl_2. On careful inspection of the aromatic region, not only are there strong signals characteristic of 1,4-disubstituted benzenes (AB splitting pattern) but two sets of weaker signals also emerge in the integration ratio 4:2:1. The implication is that each set perhaps corresponds to one, two and three coordinated telluriums. This detail probably arises from fluxionality of coordinated and uncoordinated tellurium atoms. Only one set of signals is seen in this region for L^2HgCl_2. For this compound it can be suggested that kinetically the fluxionality between coordinated and uncoordinated telluriums is much faster than the N.M.R time scale and hence the telluriums appear equivalent. In the aliphatic region of the spectra the Te-CH_2 and N-CH_2 protons appear as partially resolved triplets in both compounds with the former resonating furthest upfield.

In the solid state infra-red spectrum, the C-N stretching vibrations of both compounds are not shifted from the free ligand values, therefore supporting the N.M.R evidence that no mercury-nitrogen interaction is present. In the low frequency region bands at 322 and 317cm^{-1} for L^2HgCl_2 and L^3HgCl_2 respectively are assigned as Hg-Cl vibrations. For comparison $HgCl_2$ shows vibrations at 330 and 310cm^{-1} and υ_s(Hg-Cl) in the recently reported crystal structure 1,6-bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene(Te,Te)dichloro mercury(II)$^{(111)}$ is found at 312cm^{-1}. Bands in the regions assigned as

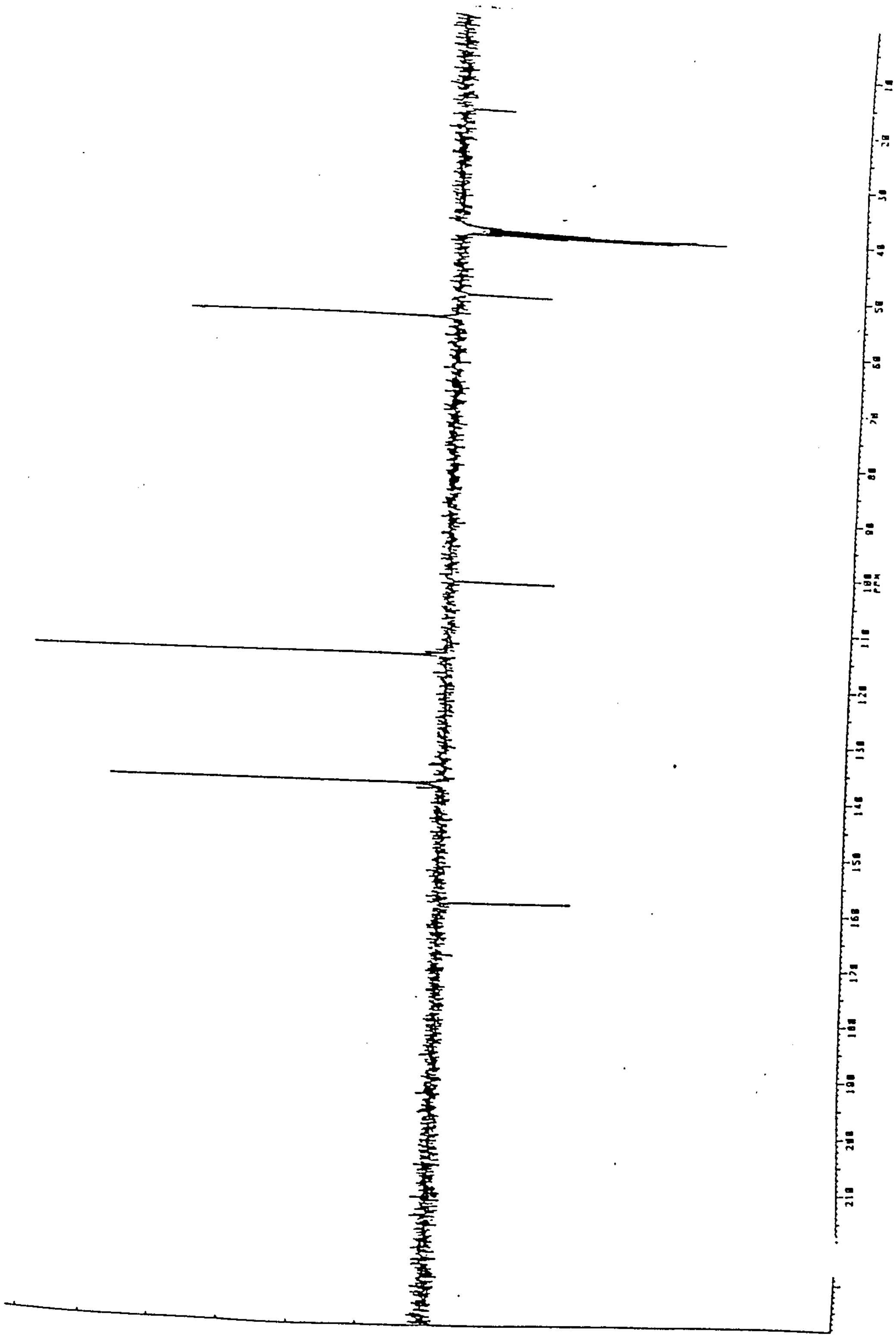


Figure 5.11 ^{13}C N.M.R. spectrum of L^2HgCl_2.

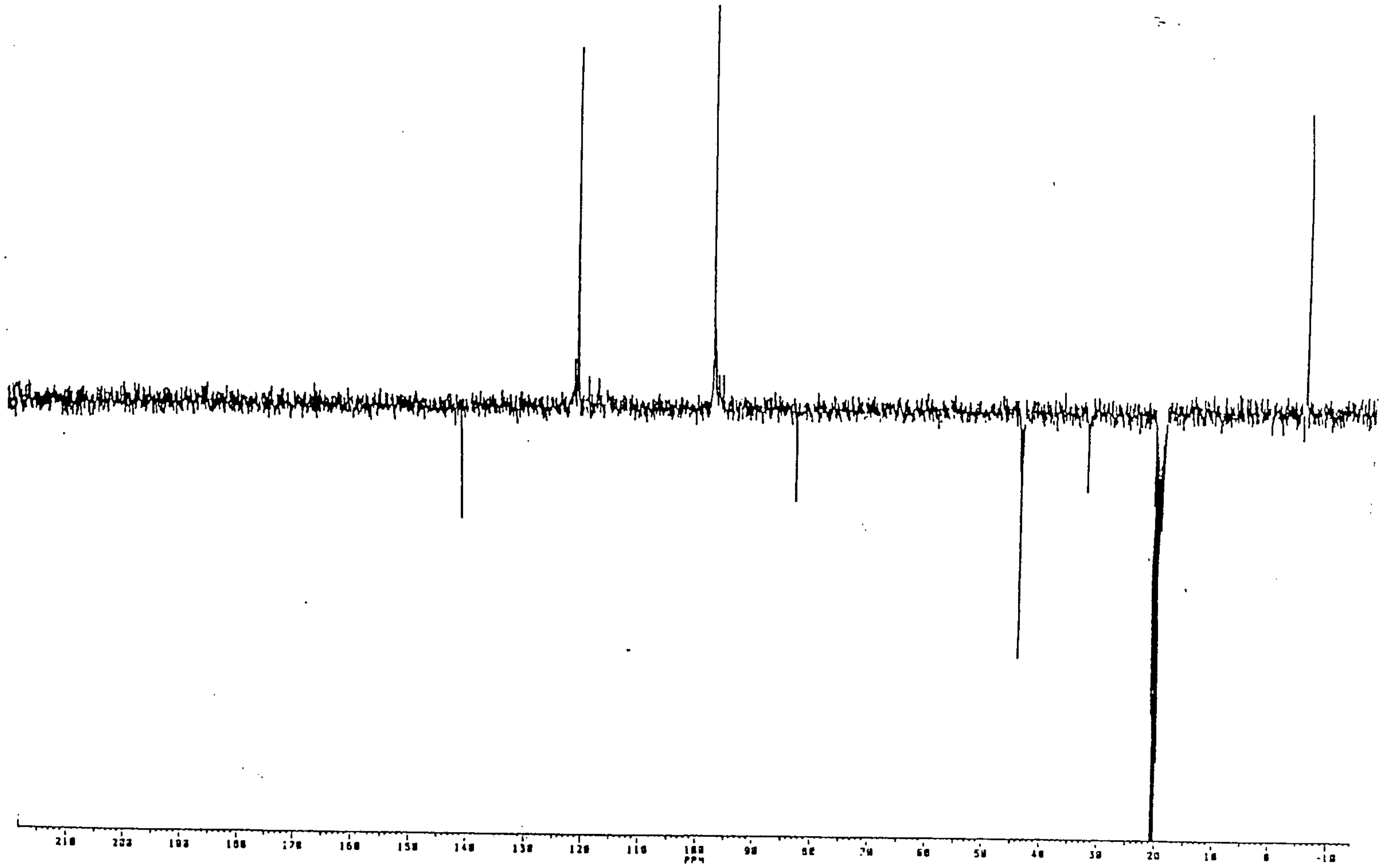


Figure 5.12 ^{13}C N.M.R. spectrum of L^3HgCl_2.

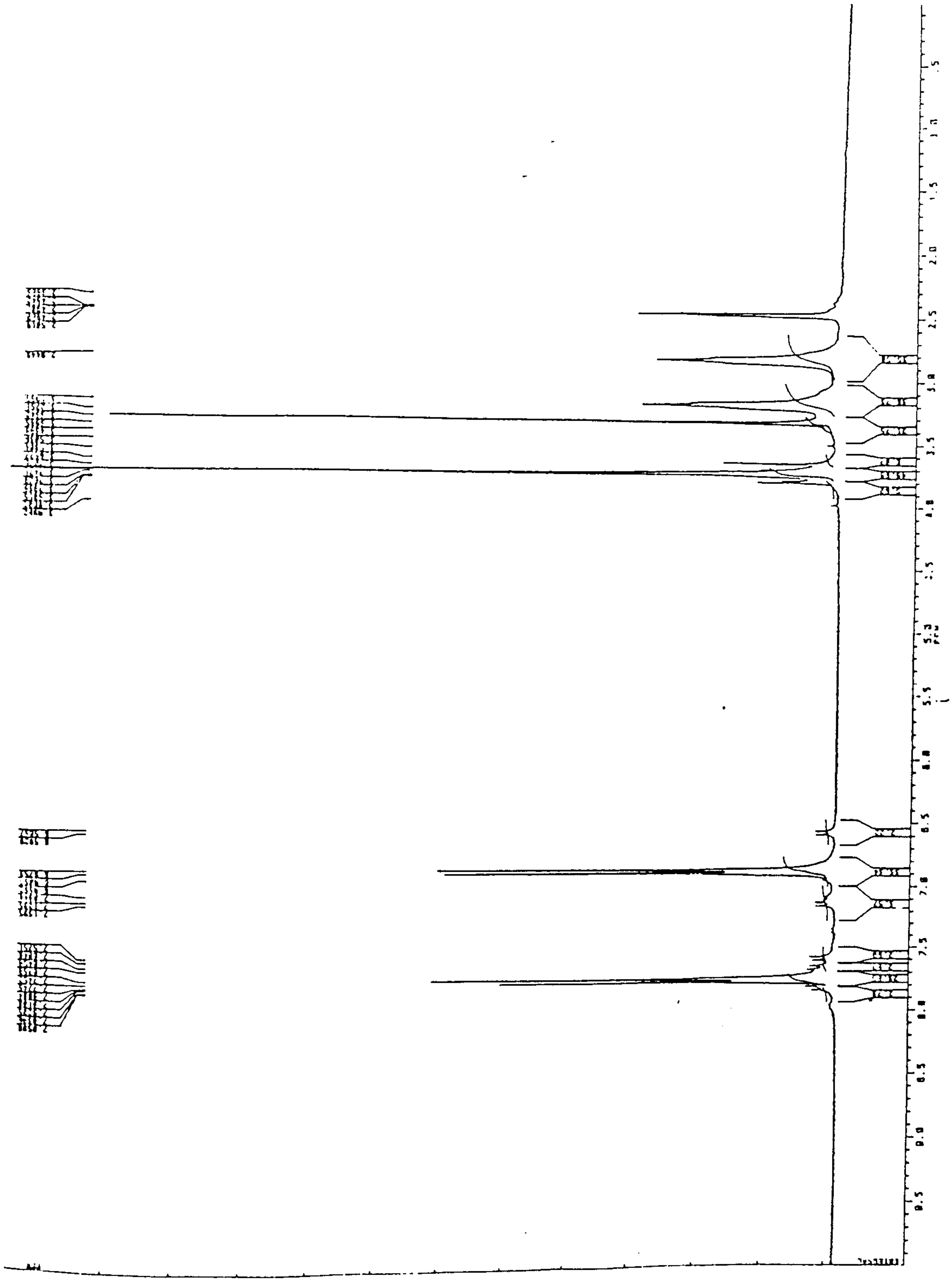


Figure 5.13 ^{1}H N.M.R. spectrum of L^2HgCl_2.

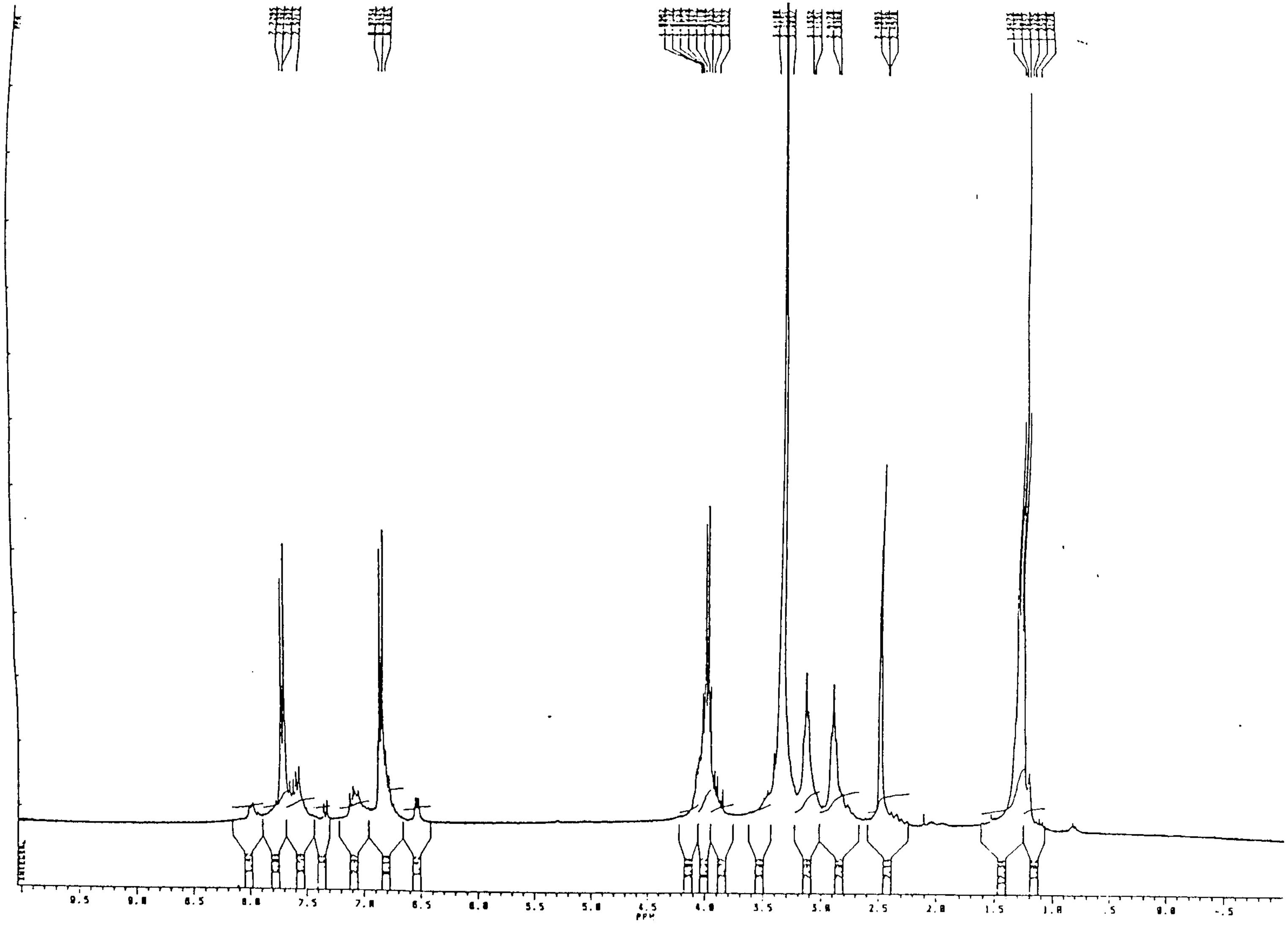


Figure 5.14 ^{1}H N.M.R. spectrum of L^3HgCl_2.

Te-CH_2 and Te-C(aryl) vibrations have undergone shifts in the complexes and new bands are also present. It is likely that these bands represent coordinated and uncoordinated telluriums.

If one assumes that the mercury atom adopts a four coordinate tetrahedral stereochemistry, two of the corners of the tetrahedron may be occupied by chlorine atoms whilst the other two positions may be occupied by two of the tellurium atoms of the ligand leaving one tellurium uncoordinated. Figure 5.1 illustrates the stereochemistry.

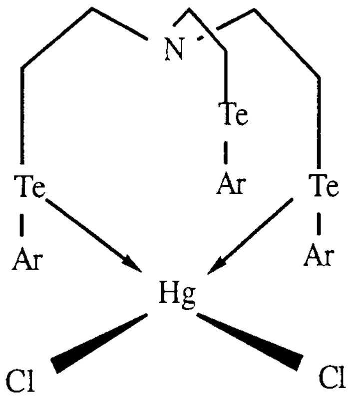


Figure 5.1

In summary, the solid state infra-red and ^{13}C N.M.R data do not appear to be consistent. The fact that all three telluriums appear equivalent in the ^{13}C spectra could be explained by the rapid exchange between coordinated and uncoordinated telluriums which at room temperature is faster than the N.M.R time-scale. However support for the inequivalence of the telluriums in at least one of the complexes is apparent from the ^{1}H N.M.R spectra.

5.3.4 Characterisation of the Cd(II) complexes of L^2 and L^3.

The reactions of CdI_2 with L^3 and of $CdCl_2$ with L^3 in a 1:1 molar ratio leads to products whose analytical data fit the formulae L^2CdI_2 and $L^3Cd(OH)_2$. The complex L^2CdI_2 was found to be soluble in polar organic solvents, for example, acetonitrile, nitromethane and DMSO. It was found to be a non-electrolyte in DMSO solution. The complex $L^3Cd(OH)_2$ was insoluble in all common organic solvents except hot nitromethane and hence its solution conductivity and N.M.R data could not be recorded. To help characterise this compound, a fast atom bombardment mass spectrum was obtained. The molecular ion was not observed but details of the fragments detected are given in table 5.2.

In the ^{13}C N.M.R spectrum of L^2CdI_2, (see figure 5.15), the Te-CH_2 signal is found 1 ppm downfield from the corresponding ligand signal. If this difference is real, then there is only a very weak interaction between the tellurium and cadmium atoms. Comparison of this shift with that of the Hg(II) complexes leads us to the conclusion that mercury(II) behaves as a stronger Lewis acid than cadmium(II) towards tellurium with this ligand. The N-CH_2 signal is shifted only very slightly from the analogous ligand resonance and this suggests there is no mercury-nitrogen interaction. The signals corresponding to the p-methoxyphenyl moiety do not appear as singlets. Instead a set of much weaker signals are found slightly off-set from the more intense resonances. Undoubtedly there are two environments for the p-methoxyphenyl moiety. The most likely explanation of this comes from the inequivalence of p-methoxyphenyl groups in which one set of signals corresponds to that of coordinated tellurium atoms, the other set to uncoordinated telluriums.

In the ^1H N.M.R spectrum (figure 5.16), this inequivalence of groups is even more pronounced. The methoxy protons appear as a doublet at $\delta = 3.7$ and 3.8 ppm of integration 4:3. Similarly in the aromatic region of the spectrum, the phenyl protons are characterised by the classic AB splitting pattern but with a second set of signals slightly off-set and further downfield. Again the integration ratio is consistent at 4:3. The favoured explanation is the inequivalence of p-methoxyphenyl groups due to coordination of at least one and more likely two of the telluriums. The Te-CH_2 and N-CH_2 resonances appear as broad bands at 2.8 and 3.1 ppm respectively.

In the solid state infra-red spectrum of $L^3Cd(OH)_2$ a broad band centered at $\upsilon=3424cm^{-1}$ can be assigned as an O-H vibration. The appearance of this band probably implies that hydrolysis of the Cd-Cl bond has occured in the reaction. From experience this has become a common feature when using $CdCl_2$ in synthetic reactions. A broad band at $\upsilon= 605cm^{-1}$ may be assigned as a Cd-O vibration although it is not unreasonable to assume that this band could conceivably be ascribed as a Te-O vibration; Te-O bands have been observed in this region in other compounds(76). The C-N vibrations in both complexes appears unshifted than for the free ligands therefore suggesting no interaction of cadmium

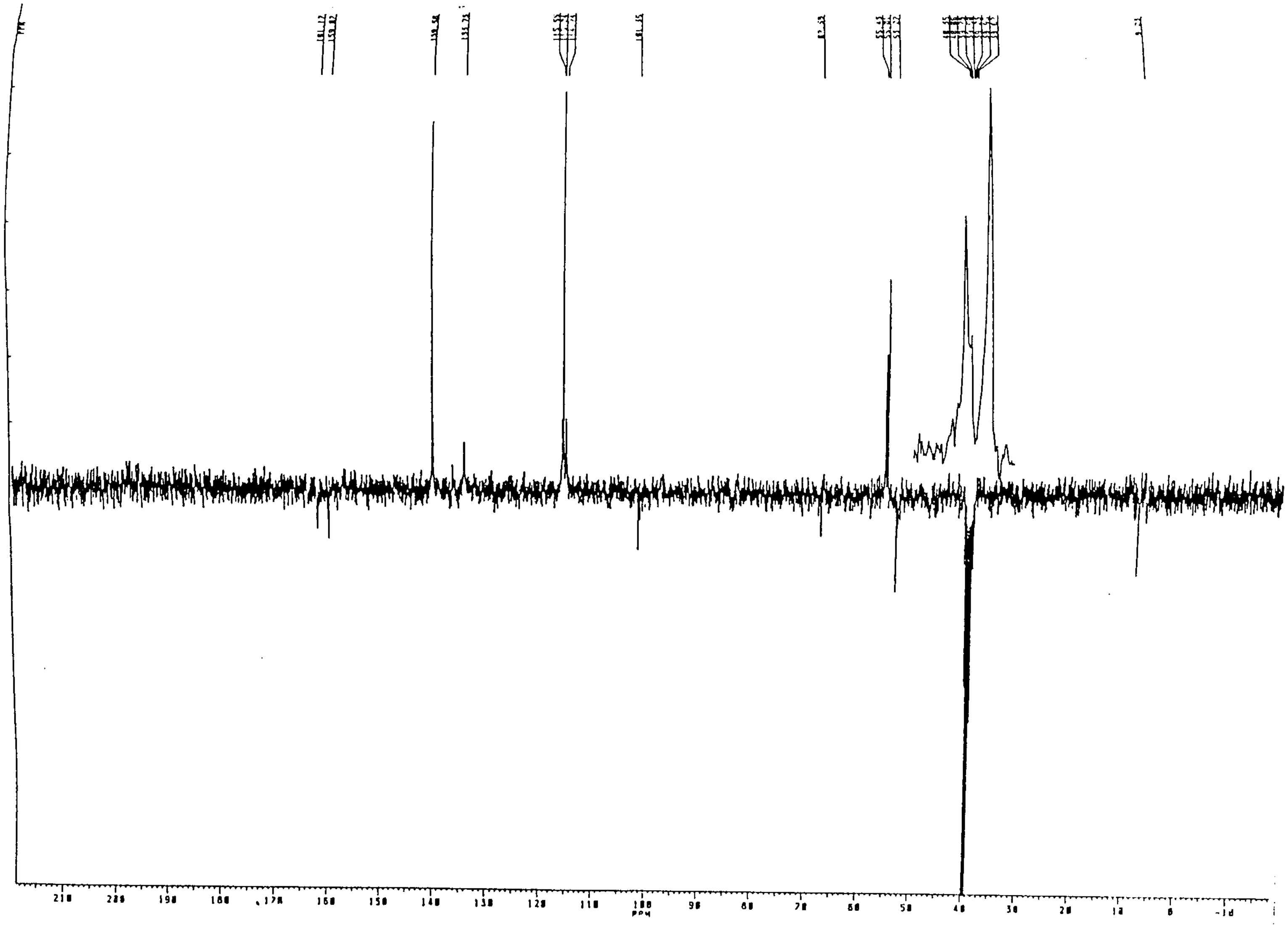


Figure 5.15 ^{13}C N.M.R. spectrum of L^2CdI_2.

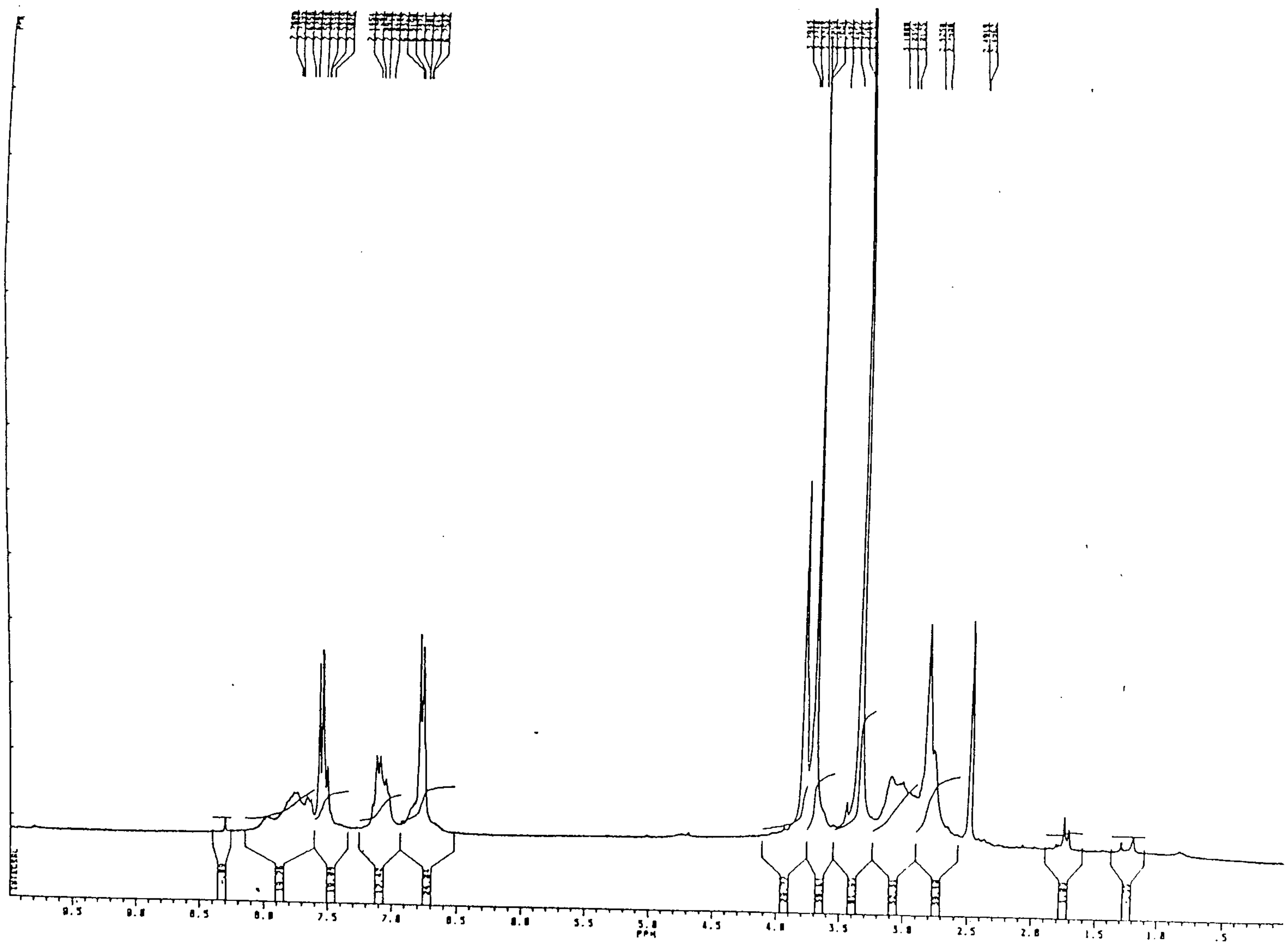


Figure 5.16 ^{1}H N.M.R. spectrum of L^2CdI_2.

with nitrogen, supporting the N.M.R. data. Bands attributed to Te-CH_2 and Te-C(aryl) vibrations are shifted slightly from the free ligand values and new bands are also seen in these regions. One can infer from this that there are probably coordinated and uncoordinated telluriums in the solid state.

Assuming the cadmium atom in both compounds adopts a four coordinate tetrahedral stereochemistry, it seems probable that two of the telluriums of the ligands are coordinating and in L^2CdI_2 the other positions are occupied by iodine atoms. The ^{13}C and ^1H N.M.R. data certainly support this claim. The remaining two positions in the complex $L^3Cd(OH)_2$ are likely to be occupied by hydroxyl groups. The insolubility of this compound might suggest that it is polymeric with propagation through Cd-O bonds. Unfortunately no comment can be made on the solution properties of this compound.

5.3.5 Characterisation of the Cu(I) complexes of L^2 and L^3.

In the reaction of equimolar amounts of solutions of CuBr and ligands L^2 and L^3, complexes of stoichiometry $L^2CuBr.H_2O$ and $L^3CuBr.H_2O$ were obtained according to the elemental analyses.

Both complexes are soluble in benzene, nitromethane and acetonitrile. Conductivity measurements in DMSO of 10^{-3}M solutions gave values of 33 and 32 ohm^{-1}cm^{2}mole^{-1} consistent with the values for

1:1 electrolytes.

The ^{13}C N.M.R spectra of both compounds are illustrated in figures 5.17-5.18. Since only one set of signals is observed in both spectra, then it appears that all the telluriums are in equivalent chemical environments. In both complexes the Te-CH_2 resonance is found 8 ppm downfield from the corresponding ligand chemical shifts implying interaction of tellurium with the metal centre. On comparing this shift with those of the mercury(II) and cadmium(II) compounds, a Lewis acidity series can be proposed. Hence mercury deshields the Te-CH_2 carbon the most and is therefore a stronger lewis acid, whilst cadmium deshields this carbon the least.

$$\mathrm{Cd(II)} < \mathrm{Cu(I)} < \mathrm{Hg(II)}$$

McWhinnie *et al*,(122) using Mossbauer spectroscopy, suggested an order of Lewis acidity for some metal ions relative to bis(p-ethoxyphenyl)telluride consistent with the results found here.

$$\mathrm{Cu(I)} < \mathrm{Pd(II)} < \mathrm{Pt(II)} < \mathrm{Hg(II)}$$

The N-CH_2 carbon resonance is shifted 3 ppm downfield in both the copper complexes. This results probably results from the coordinate interaction of tellurium with copper and not as a result of any copper-nitrogen contact. The ^1H N.M.R. spectra are illustrated in figures 5.19-5.20. The high quality of the spectra presents no interpretation problems. Only one set of signals is seen in both complexes. The appearance of peaks at δ= 3.35 ppm arise from the presence of water (inferred from the infra-red and elemental analysis). In both spectra the

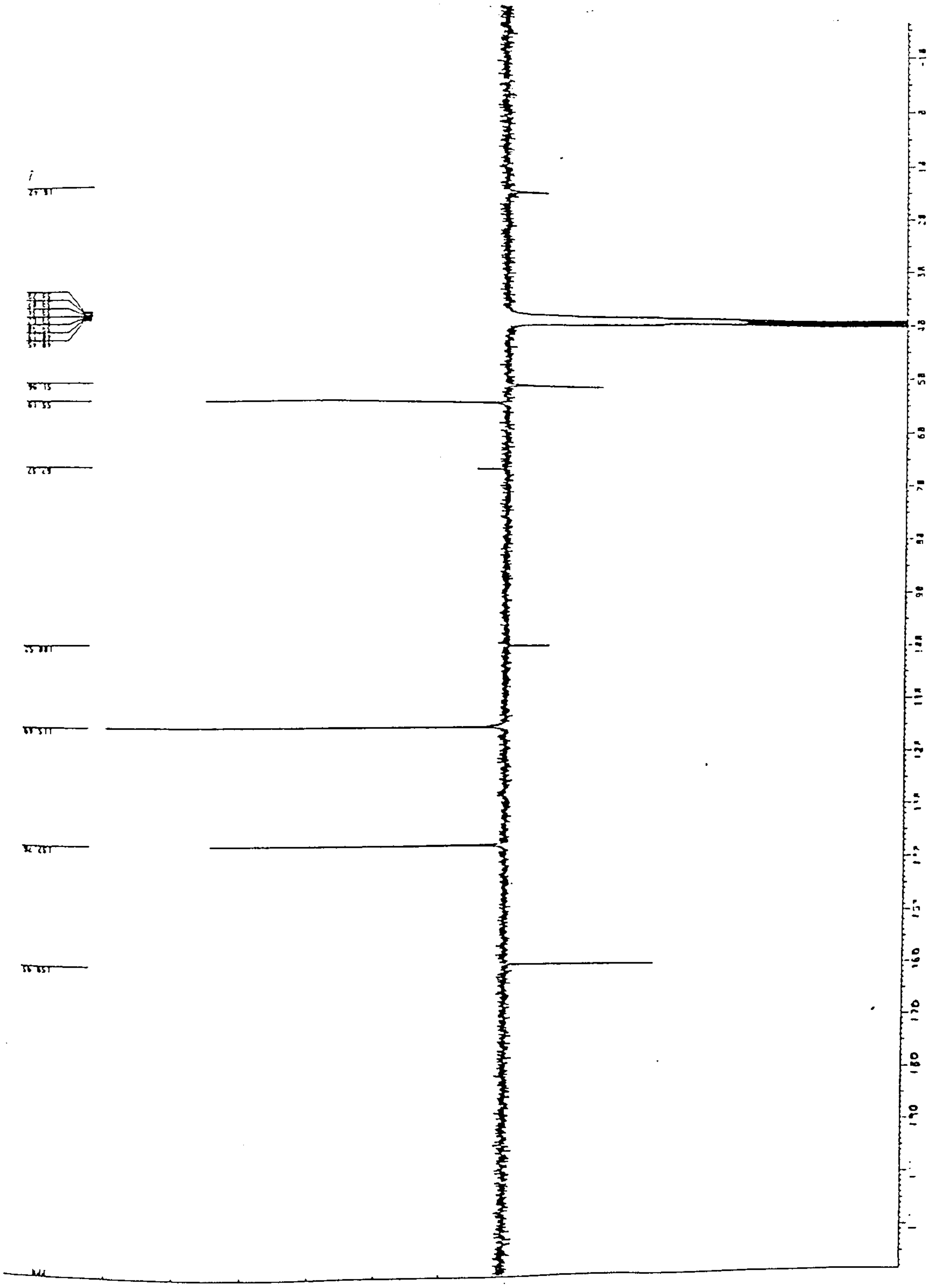


Figure 5.17 ^{13}C N.M.R. spectrum of $L^2CuBr.H_2O$.

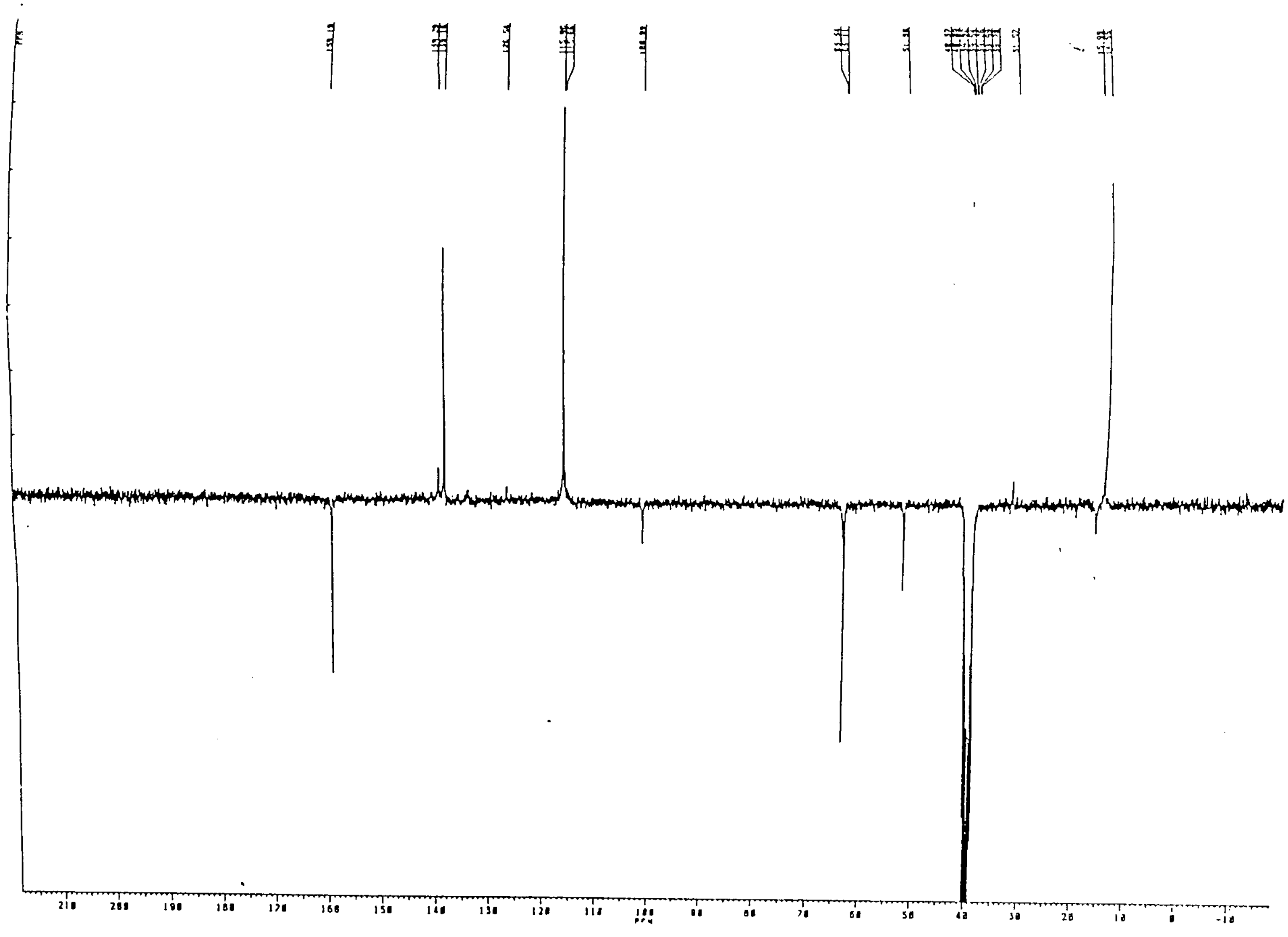


Figure 5.18 ^{13}C N.M.R. spectrum of $L^3CuBr.H_2O$.

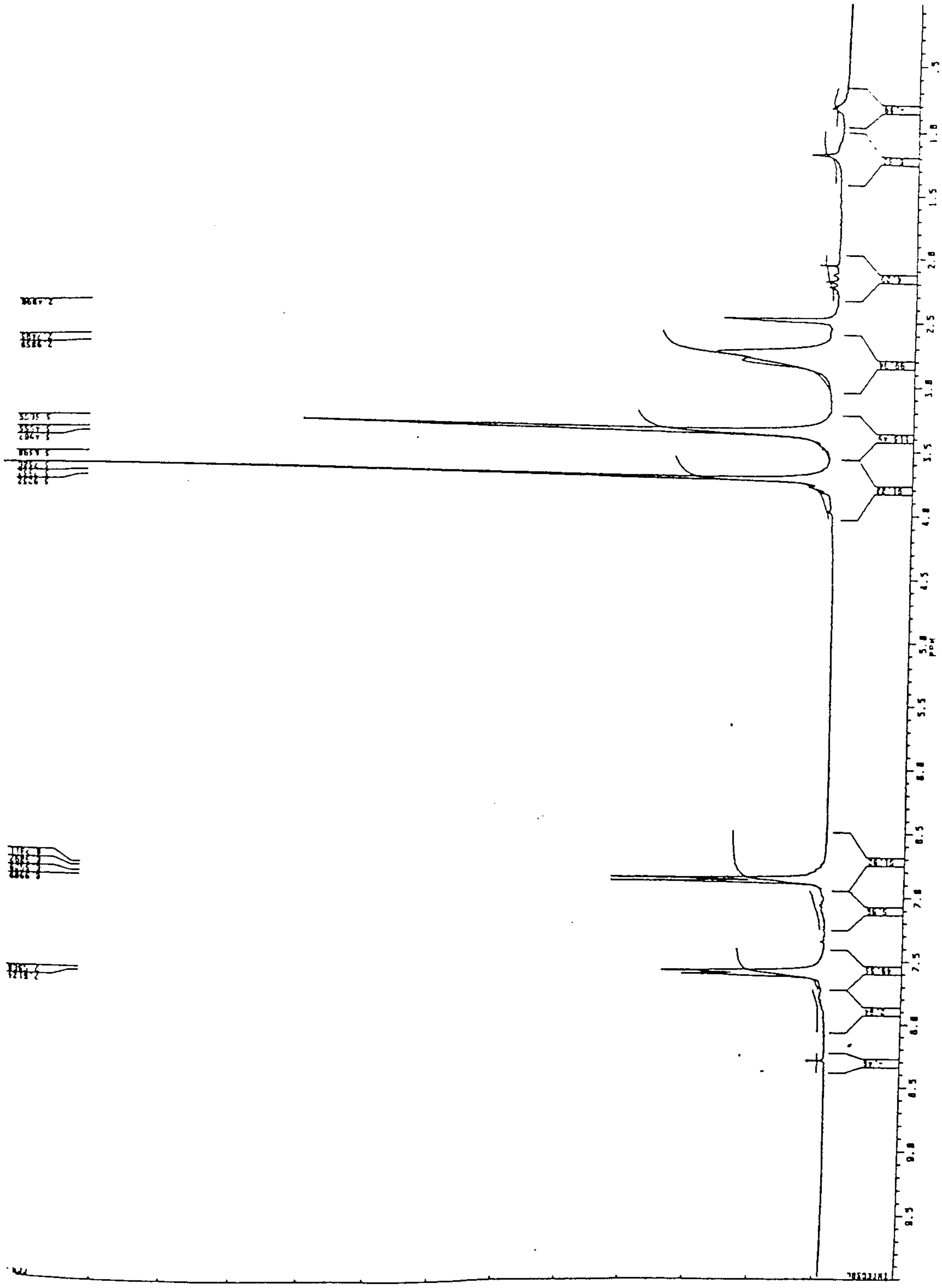


Figure 5.19 ^1H N.M.R. spectrum of $L^2CuBr.H_2O$.

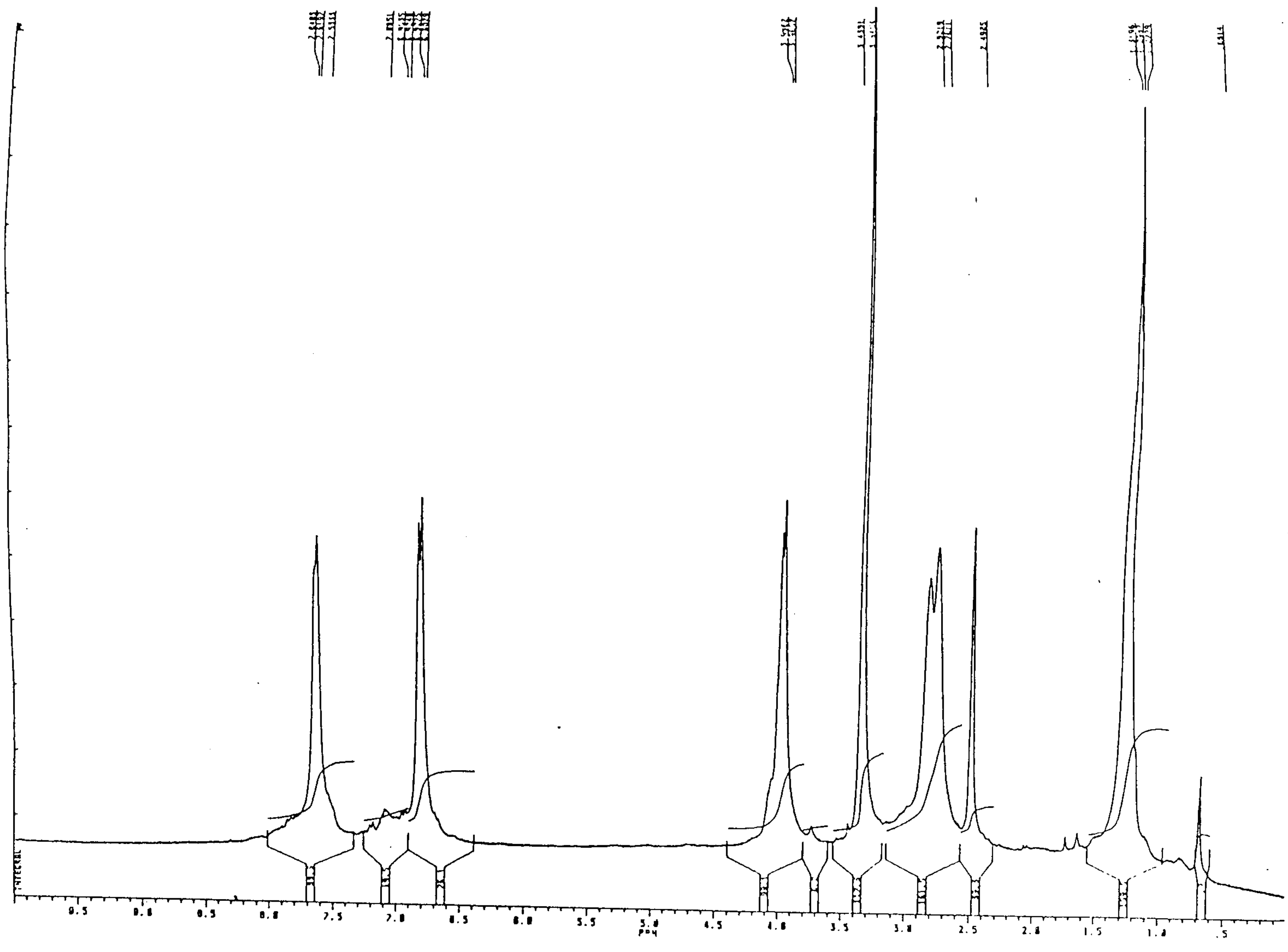


Figure 5.20 ^{1}H N.M.R. spectrum of $L^3CuBr.H_2O$.

two bands at δ= 2.8-2.9 ppm correspond to overlapping Te-CH_2 and N-CH_2 signals.

The solid state infra-red spectra of $L^2CuBr.H_2O$ and $L^3CuBr.H_2O$ show O-H bands at υ= 3436 and 3435cm^{-1} respectively. The C-N stretching vibration remains unchanged from the free ligand implying no copper-nitrogen interaction. The Te-C(alkyl) and Te-C(aryl) vibrations appear slightly shifted ($\Delta\upsilon$= 10cm^{-1}) from the free ligand values with new bands also present in this region. Although copper(I) compounds can adopt a linear geometry for lower coordination numbers (eg. $CuCl_2^-$), the usual stereochemistry is tetrahedral as in complexes such as $Cu(CN)_4^{3-}$, $Cu(py)_4^+$ and $Cu(L-L)_2^+$ (L= bipy, phen)(123). If one assumes a tetrahedral arrangement in our complexes (see figure 5.2), one may suggest that all three telluriums are coordinated to the metal centre, with the fourth position occupied by a water ligand. Since the complexes behave as 1:1 electrolytes in solution, the bromine atom is probably ionic in both compounds. As the ^{13}C and ^1H N.M.R spectra appear to show all three tellurium atoms as being equivalent, then it seems likely that all three telluriums in both complexes are coordinated to the metal centre.

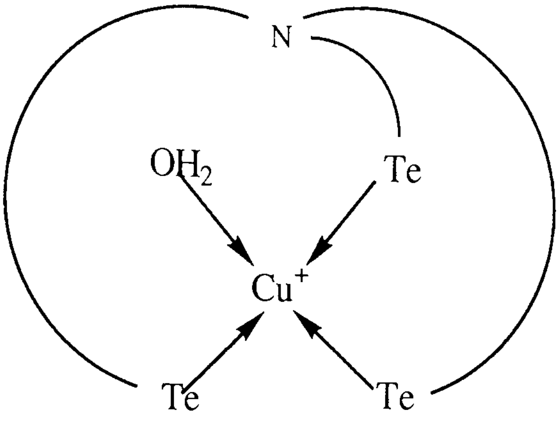


Figure 5.2

5.3.6 Characterisation of Pt(II) complexes of L^2 and L^3

The reaction of equimolar solutions of potassium tetrachloroplatinate(II) with L^2 and L^3 gives complexes whose analytical data suggest a 1:1 stoichiometry and fits for $L^2PtCl_2.H_2O$ and $L^3PtCl_2.H_2O$ can be derived. These complexes are moderately soluble in polar organic solvents. Their conductivities in 10^{-3}M DMSO solutions are 31 and 33 $ohm^{-1}cm^2mole^{-1}$ implying they are 1:1 electrolytes in solution.

In the solid state infra-red spectra recorded in KBr, both complexes show bands at υ= 3376cm^{-1} ($L^2PtCl_2.H_2O$) and 3387cm^{-1} ($L^3PtCl_2.H_2O$) characteristic of O-H stretching vibrations in water molecules. The C-N bands at 1178 and 1180cm^{-1} are unaltered from the free ligand values implying no platinum-nitrogen contact. The low wavenumber regions of both complexes show shifts in the Te-C vibrations along with new bands in this region supporting the view that both uncoordinated and coordinated telluriums are present in the solid state. Medium intensity bands at 328cm^{-1} ($L^2PtCl_2.H_2O$) and 327cm^{-1} ($L^3PtCl_2.H_2O$) are characteristic of Pt-Cl stretching vibrations(124). Since the complexes behave as 1:1 electrolytes in solution, it is likely that one of the chloride atoms in each complex is ionic and that the Pt-Cl absorption frequencies are due to terminal Pt-Cl vibrations and not asymmetric or symmetric Cl-Pt-Cl vibrations. If one assumes a square planar geometry of the ligands around platinum then two of the three telluriums may be coordinating along with chloride and water ligands. The molecules can adopt either a trans or cis configuration with the chloride atom either trans to a tellurium or a water ligand. In other complexes the Pt-Cl stretching frequency has found to change with the ligand coordinated trans to it. These variations can be interpreted in terms of the trans influence of the ligands(125) (which is the tendency of a ligand to weaken the bond trans to itself in a complex). It has been shown that the trans influence decreases in the order,(11)

Te-donor >Se-donor >S-donor > N-donor > halide-donor > O-donor

Therefore the stronger the Pt-Cl bond the higher the absorption frequency. In trans-$PtCl_2[Te(CH_2CH_2C_6H_5)_2]_2$(127), υ(Pt-Cl) = 337cm^{-1} and for trans-$PtCl_2.L.H_2O$ (L= 1,6-bis-2-butyltellurophenyl-2,5-diaza-1,5-diene) υ(Pt-Cl) = 315cm^{-1}. In cis-$PtCl_2[ArTe(CH_2)_7TeAr]_2$ the values of υ(Pt-Cl) were reported to be lower at 320 and 299cm^{-1}(103) in agreement with values of other cis-complexes of $PtCl_2$ with monodentate tellurium ligands.

Using this evidence and noting that water is a weaker donor than tellurium one can conclude that the values of 327 and 328cm^{-1} for the Pt-Cl stretching frequency probably indicates that the chloride ligand is trans to the water ligand in both complexes. This is shown diagrammatically in figure 5.3 below.

Since the complex $L^3PtCl_2.H_2O$ is only soluble in DMSO its ^1H N.M.R. spectrum only shows weak signals and its precise interpretation has been excluded here. Nethertheless there is little doubt that both p-ethoxyphenyl and methylene groups are present. Detailed examination of the ^1H N.M.R. spectrum of $L^2PtCl_2.H_2O$ (figure 5.21) shows two environments for the p-methoxyphenyl moiety in the aromatic region. The two sets of signals are in the ratio of approximately 2:1. This inequivalence of groups supports the infra-red data and therefore in solution there are probably both coordinated and uncoordinated telluriums. A sharp peak at δ= 3.45 ppm is assigned as signals from a water ligand. The N-CH_2 signal is broad at δ= 2.8 ppm. No confident

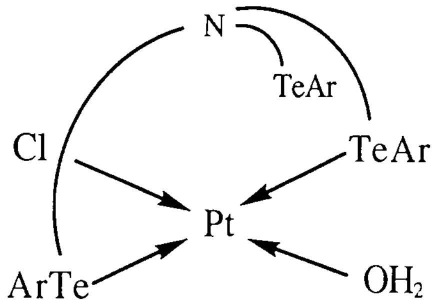


Figure 5.3

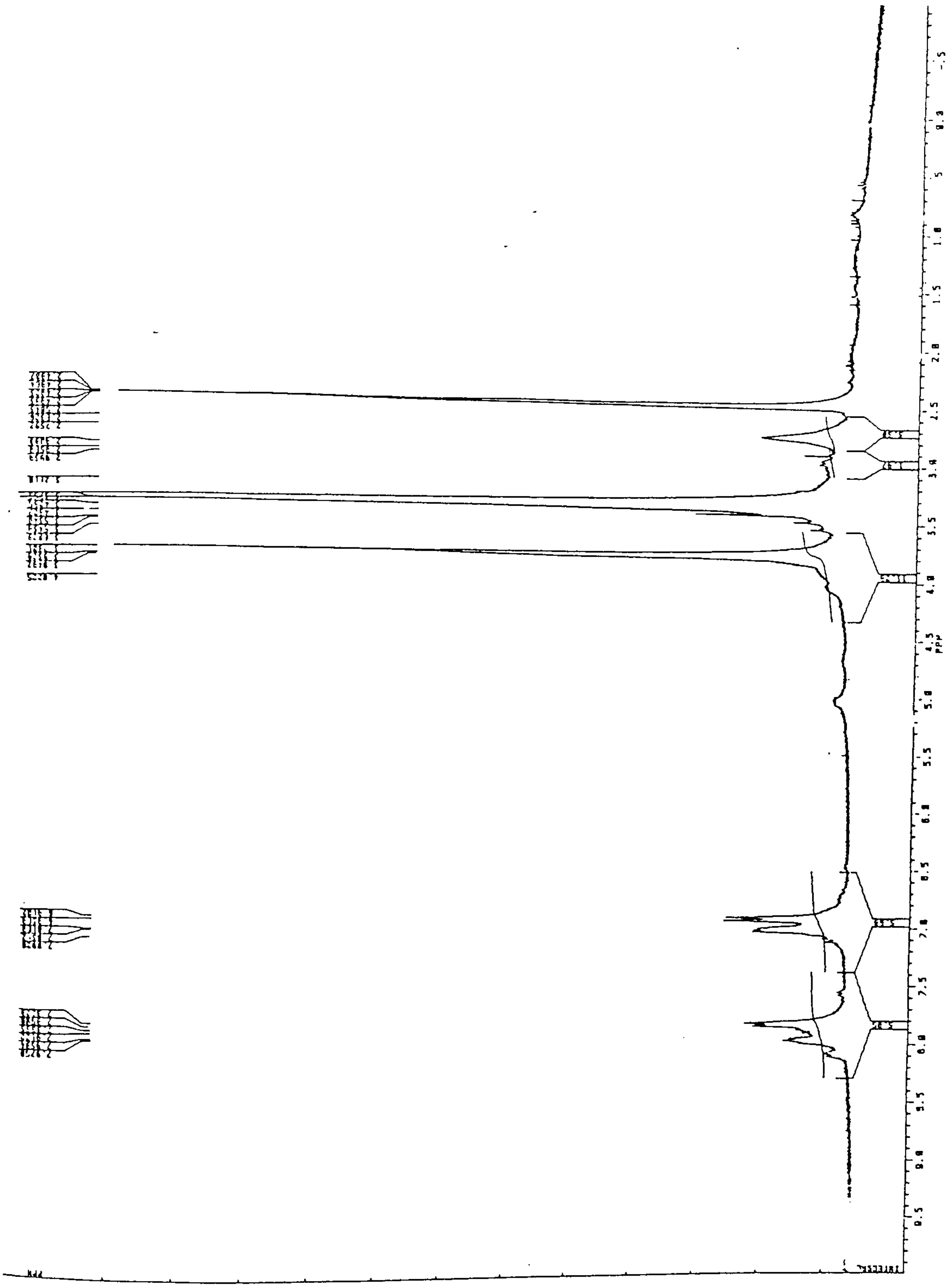


Figure 5.21 ^1H N.M.R. spectrum of $L^2PtCl_2.H_2O$.

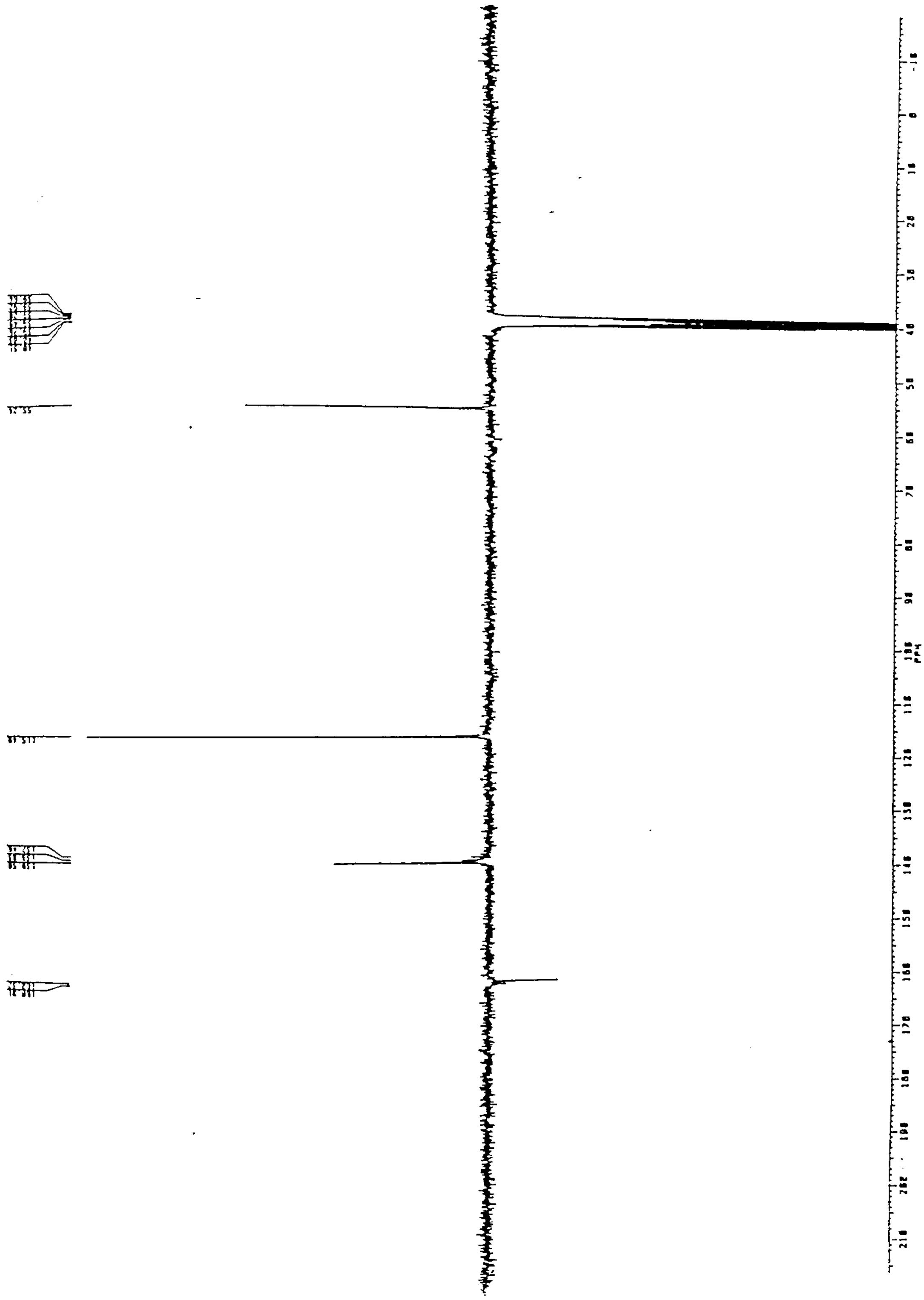


Figure 5.22 ^{13}C N.M.R. spectrum of $L^2PtCl_2.H_2O$.

assignment can be made of the Te-CH_2 proton signal, but it is believed to be masked in the broad signal at $\delta = 3.4$ ppm (due to moisture present in the DMSO solution). In the ^{13}C N.M.R. spectra of these complexes, surprisingly only the p-methoxyphenyl and p-ethoxyphenyl groups were observed. To illustrate this observation the spectrum of $L^2PtCl_2.H_2O$ is shown in figure 5.22. The *ipso* Te-C(aryl) signal was also absent. Two explanations for this anomaly can be given. Firstly the relaxation times of the *ipso* and the methylene carbons have increased dramatically on complexation. *Ipso* carbons are known to have longer relaxation times and sometimes do appear as weak signals or even not at all. It seems unlikely that the methylene carbons would also undergo long enough relaxation times to become absent. Secondly and more likely, the complexes may have undergone dealkylation with new species formed in solution. Indeed the ^{13}C N.M.R. spectra of these complexes were recorded several hours after the ^1H spectra. It therefore seems feasible to suggest that although the proton spectra do show methylene signals, on standing in solution for long periods the complexes decompose probably *via* Te-CH_2 bond cleavage.

5.3.7 Characterisation of the Pd(II) complexes of L^2 and L^3.

The reaction of sodium tetrachloropalladate(II) with L^2 and L^3 leads to orange coloured complexes in which analytical fits for $L^2PdCl_2.H_2O$ and $L^3PdCl_2.H_2O$ can be derived. These complexes are soluble in nitromethane but found to be insoluble in chloroform, ethanol and benzene. The conductivities of 10^{-3}M DMSO solutions are 30 $ohm^{-1}cm^2mole^{-1}$ and therefore behave as 1:1 electrolytes.

In the solid state infra-red spectra, a broad band at υ= 3408cm^{-1} for $L^2PdCl_2.H_2O$ is evidence for an O-H stretching vibration of water. The analogous band in $L^3PdCl_2.H_2O$ is much sharper and found at υ= 3410cm^{-1}. The C-N stretching frequency is unchanged from the free ligand values and thus the nitrogen atom remains uncoordinated to the metal centre. In the low frequency region, the Te-C bands appear slightly shifted from the free ligand values and new bands are also present. Medium intensity bands at υ= 321cm^{-1} in both complexes have been assigned as Pd-Cl vibrations. The Raman spectra of these complexes also show medium intensity bands at this wavenumber (see figure 5.23). Since the complexes were found to be 1:1 electrolytes in solution, then one of the chloride atoms in both compounds could be ionic with the other bonded to palladium. If this is so, then this band is likely to represent a terminal Pd-Cl vibration. Palladium complexes often adopt a square planar geometry. Assuming this to be the case here, the chloride ligand could lie trans to a water ligand, or, assuming two of the telluriums are coordinated, trans to a tellurium atom. As was described for the platinum complexes, the infra-red stretching frequency is representative of the strength of the Pd-Cl bond and this is reflected in the ligand trans to it. In the compound trans-$Pd[(p-C_2H_5OC_6H_4)_2Te]_2Cl_2$(128) υ(Pd-Cl)= 348cm^{-1}. Al-Salim has proposed a trans configuration for $LPdCl_2.H_2O$ (L= 1,6-bis-2-butyltellurophenyl-

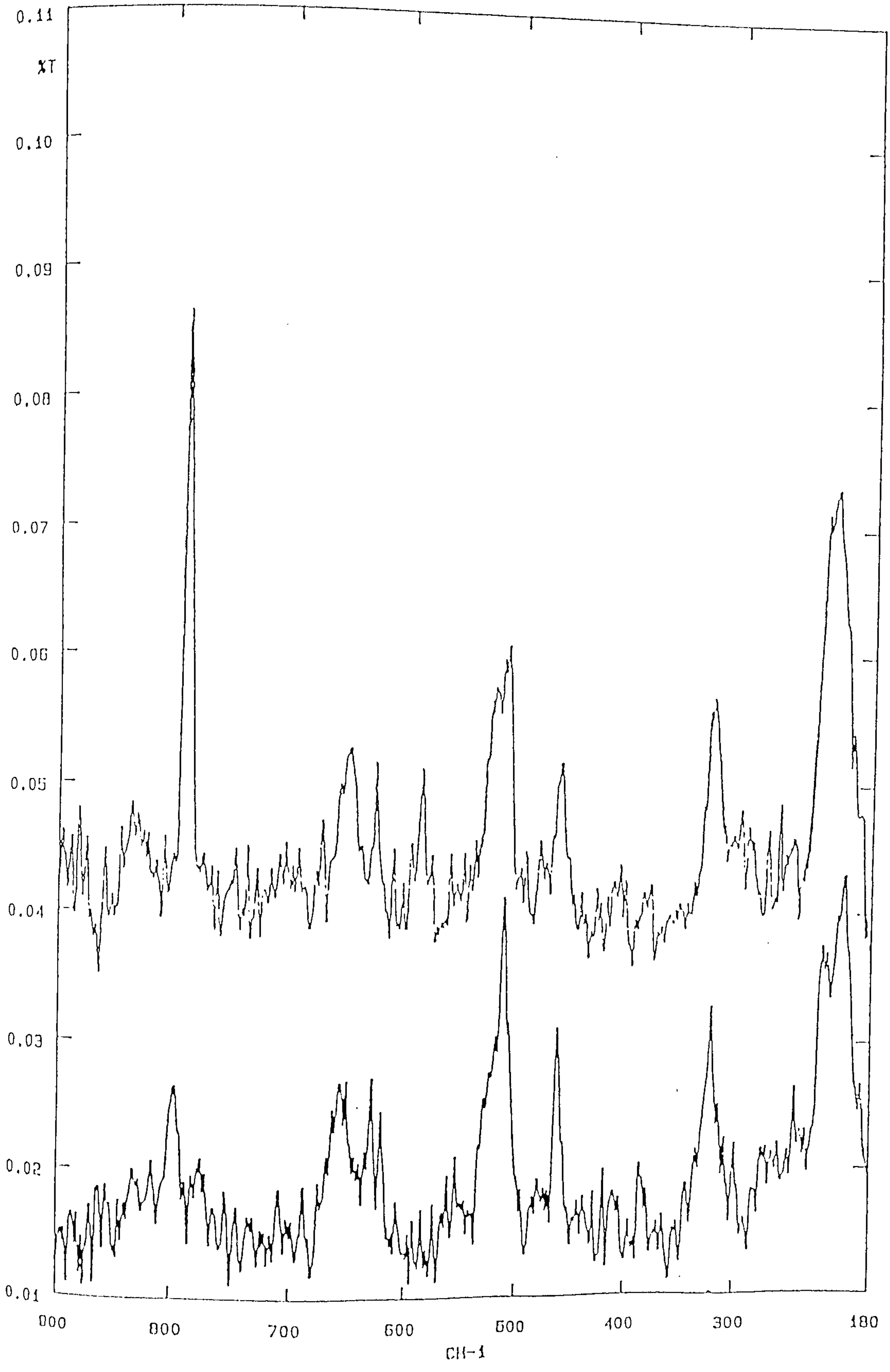
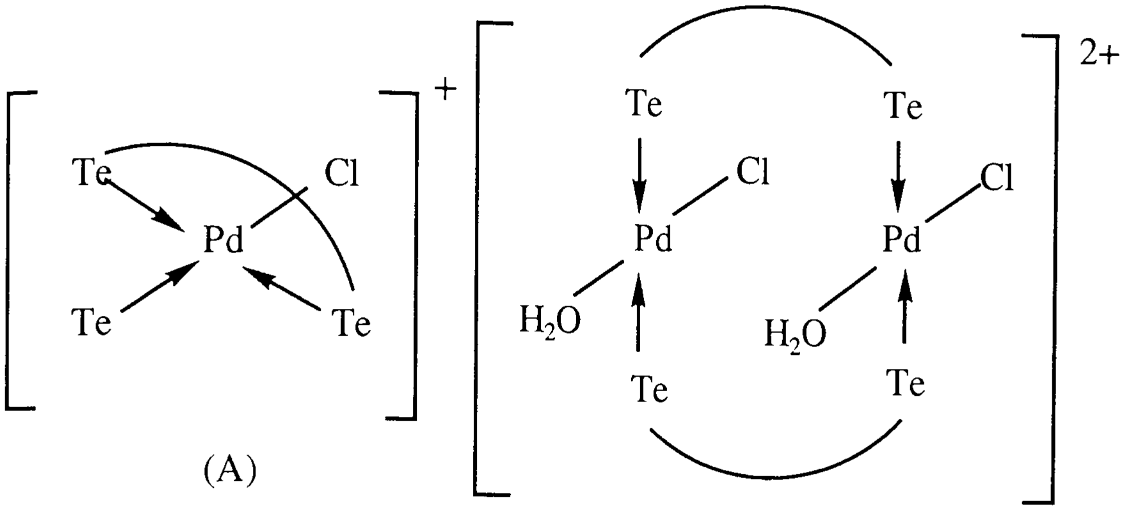


Figure 5.23 Raman spectrum of top:- $L^2PdCl_2.H_2O$.

bottom:- $L^3PdCl_2.H_2O$.

2,5-diaza-hexa-1,5-diene) in which the compound exists in a monomeric state (A) or is dimeric with bridging tellurium atoms (B) with υ(Pd-Cl)= 345cm^{-1}.

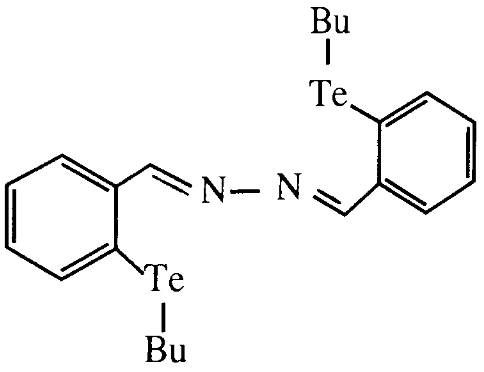


(A)

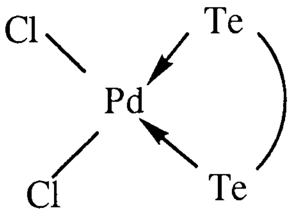
(B)

Figure 5.4

The same author proposes a cis configuration for $PdCl_2$.L' (L'= 1,4-bis-2-butyltellurophenyl-2,3-diazabuta-1,3-diene) where υ_{as}(Pd-Cl) =332cm^{-1} and υ_{s}(Pd-Cl)= 288cm^{-1}.



(L)



cis-monomer

Using this information the complexes $L^2PdCl_2.H_2O$ and

$L^3PdCl_2.H_2O$ (υ= 321cm^{-1}) are likely to adopt a cis configuration. If the chloride ligand was trans to the water ligand one may expect a higher frequency for the Pd-Cl vibration.

In the fast atom bombardment mass spectrum of $L^2PdCl_2.H_2O$ the only fragment detected was L^2PdCl^+ (m/e= 942). The highest m/e ion detected in $L^3PdCl_2.H_2O$ was also the analogous L^3PdCl^+ fragment but other ions were also detected (see table 5.2).

The ^1H and ^{13}C N.M.R spectra of both complexes show remarkable similarities to the platinum complexes. Thus in the ^1H N.M.R spectra close inspection of the aromatic region shows two sets of signals for the p-methoxyphenyl and the p-ethoxyphenyl groups in the integration ratio of ~2:1. This detail supports the theory that two of the three telluriums are coordinating to palladium as proposed from the solid state infra-red data. In both complexes the Te-CH_2 proton signals are found at δ= 2.9 ppm whilst the N-CH_2 resonance is believed to be merged within the broad band at δ= 3.4 ppm (due to the presence of H_2O). In the ^{13}C N.M.R. spectra only the p-methoxyphenyl and p-ethoxyphenyl signals are observed. As was described in the case of the platinum complexes, it is believed that on standing in solution for long periods, the complexes undergo dealkylation.

The visible absorption spectrum of $L^2PdCl_2.H_2O$ in DMSO revealed bands at 23600cm^{-1} (ε=5400) and 29400cm^{-1} (ε=5000), while

Table 5.5 U.V-Visible spectral data and conductivity data of the complexes of L^2 and L^3.

Compound	λmax (nm)	υmax(cm^{-1})	ε*	Λ**
$L^2\ HgCl_2$				2
$L^3\ HgCl_2$				2
$L^2\ CdI_2$				3
$L^3\ Cd(OH)_2$				ins
$L^2\ PtCl_2.H_2O$				31
$L^3\ PtCl_2.H_2O$				33
$L^2\ PdCl_2.H_2O$	424	23600	5400	30
	340	29400	5000	
$L^3\ PdCl_2.H_2O$	420	23800	4250	30
	340	29400	4300	
$L^2\ CuBr.H_2O$				33
$L^3\ CuBr.H_2O$				32

* ε in cm^{-1} mole^{-1}

** ohm^{-1} cm^2 mole^{-1} (of 10^{-3}M DMSO solutions)

ins = insoluble in common organic solvents

$L^3PdCl_2.H_2O$ showed bands at 23800cm^{-1} (ε=4250) and 29400cm^{-1} (ε=4300) (see table 5.5) implying the compounds adopt square planar geometries.

5.3.7 Characterisation of the Hg(II) complexes of the selenium ligands L^4 and L^5.

In the reactions of equimolar solutions of mercuric chloride and L^4 and L^5, colourless solids are formed whose analytical data fits the formulations $L^4HgCl_2.0.5CHCl_3$ and L^53HgCl_2. Due to the limited amount of L^4HgCl_2 prepared, only analytical and infra-red spectroscopic data were obtained. Unfortunately no conclusions can be derived about it's structural properties.

The complex L^53HgCl_2 was found to be a non-electrolyte in solution. In the infra-red spectrum the C-N stretching vibration appears unchanged from the free ligand and hence no mercury-nitrogen contact appears present. In the low wavenumber region a band at υ= 322cm^{-1} has been attributed to a Hg-Cl vibration. Bands in the region where Se-C vibrations are found are slightly shifted. This may imply coordination of selenium with mercury but this is only a tentative suggestion. In the ^{13}C N.M.R. (see figure 5.24) only one set of signals is observed with no pronounced shifts to those of the free ligand. The same observation is seen in the ^1H N.M.R. (figure 5.25). Therefore in solution there appears to be no coordination of mercury with the donor atoms selenium and nitrogen. This result is contrary to the infra-red data.

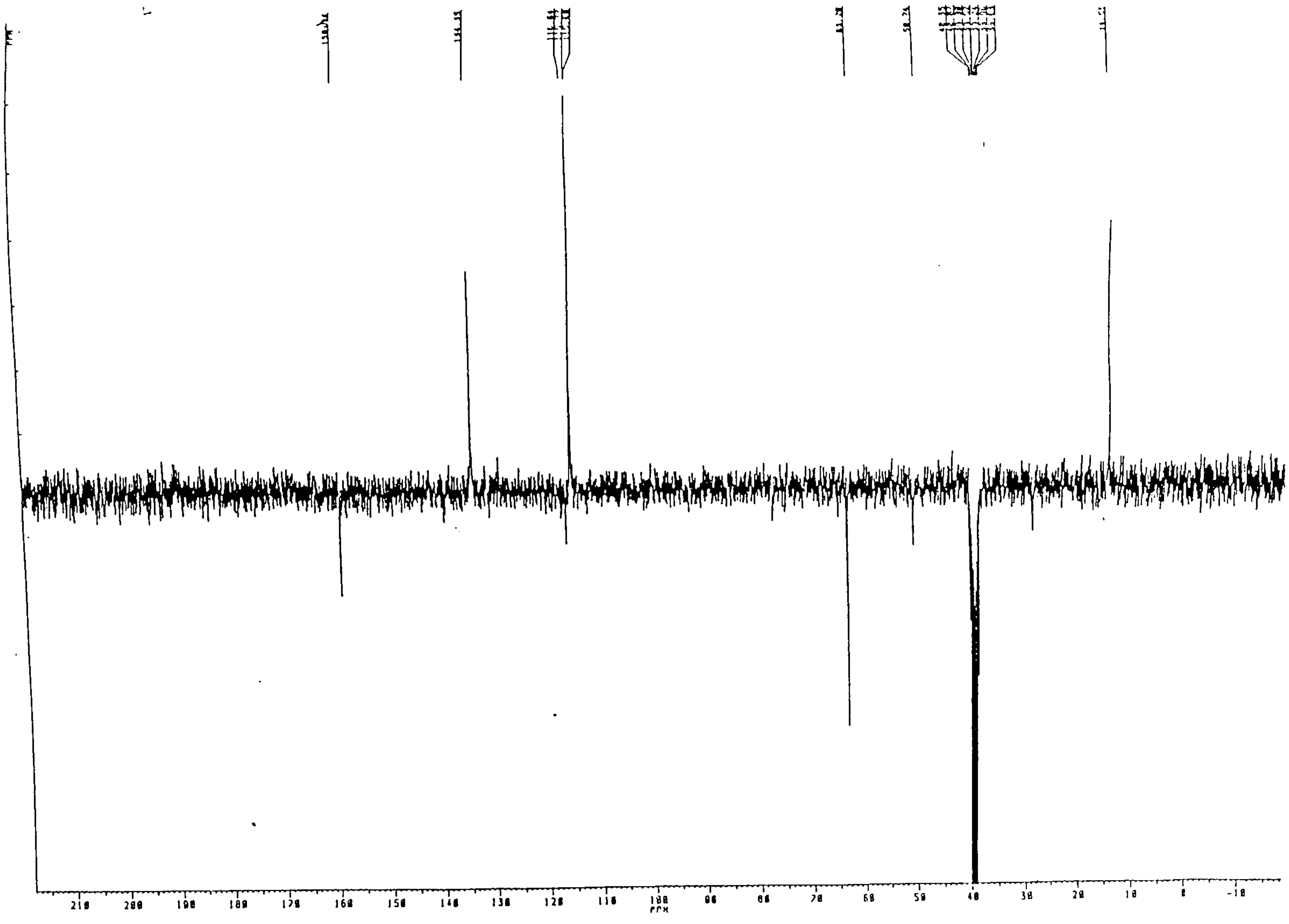


Figure 5.24 ^{13}C N.M.R. spectrum of $L^{5}3HgCl_2$.

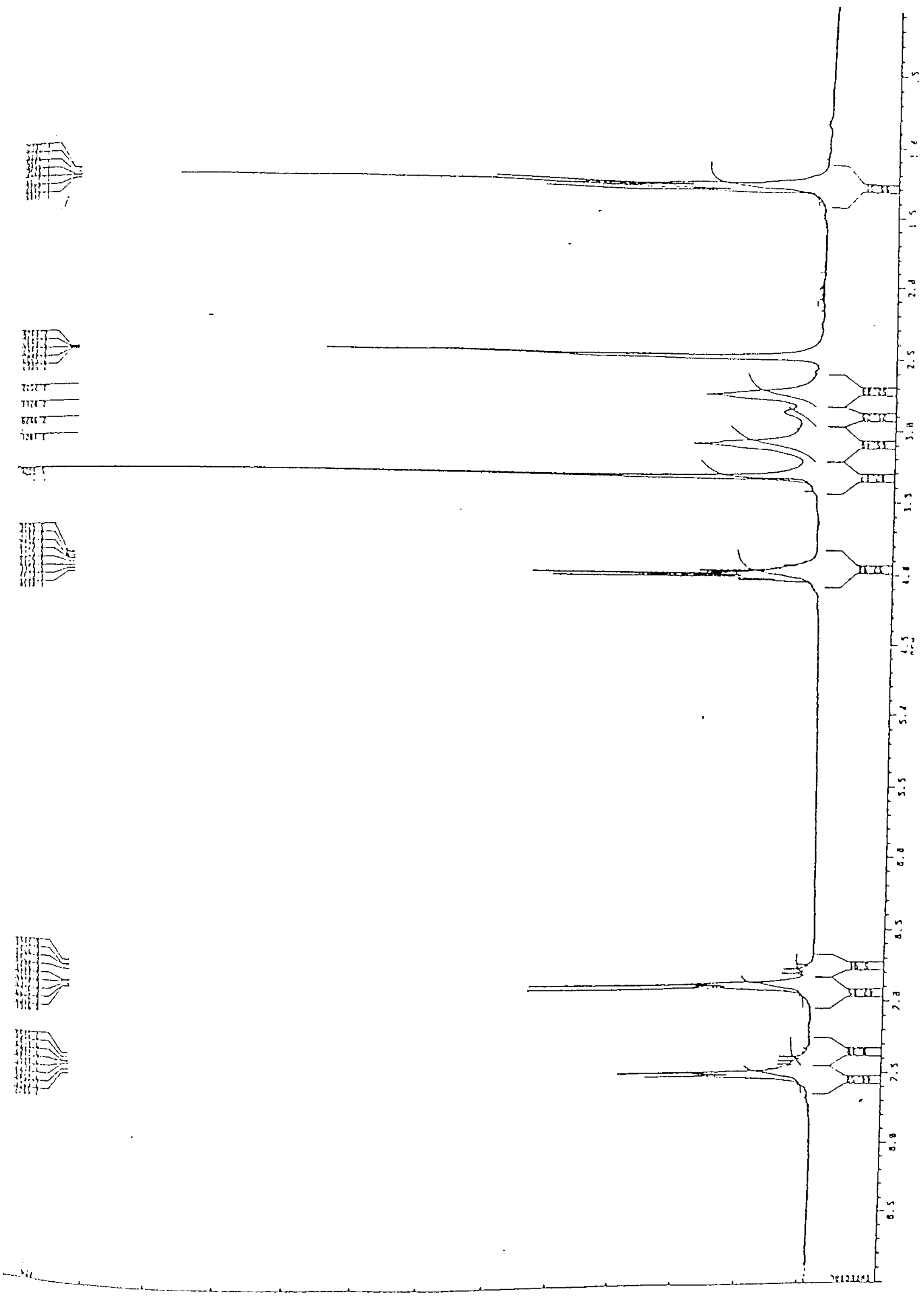


Figure 5.25 ^{1}H N.M.R. spectrum of $L^{53}HgCl_2$.

5.3.8 Characterisation of the Pt(II) complex of L^5.

In the reaction of L^5 with sodium tetrachloropalladate(II) a yellow solid formed which from analytical data fits the formulation $L^5PtCl_2.H_2O$. The compound is moderately soluble in chloroform, benzene and nitromethane. It is a non-electrolyte in solution.

In the infra-red spectrum a broad band at υ=3382cm^{-1} is characteristic of an O-H stretching vibration. The C-N band is unaltered from that of the free ligand. In the low frequency region bands at υ= 343 and 333cm^{-1} are characteristic of asymmetric and symmetric Pt-Cl vibrations. Bands at 392, 305 and 277cm^{-1} are assigned as Se-C vibrations. In the tellurium compounds the Te-C bands were used to show differences in the coordinated and the uncoordinated telluriums. No definitive assignments can be made here.

In the ^{1}H N.M.R. (see figure 5.26) there are two sets of signals for the p-ethoxyphenyl group of integration ratio 4:1. The weaker set of signals corresponds exactly with those of the free ligand. Furthermore, the Se-CH_2 and N-CH_2 resonances appear as broad bands further downfield from the free ligand. Therefore the ^{1}H N.M.R. supports the view that there is an interaction of selenium with platinum in which the methylene protons are deshielded. It seems feasible to assume that at least two of the seleniums are coordinating. However the ^{13}C spectrum is not so clear (see figure 5.27). There are two sets of signals for the p-

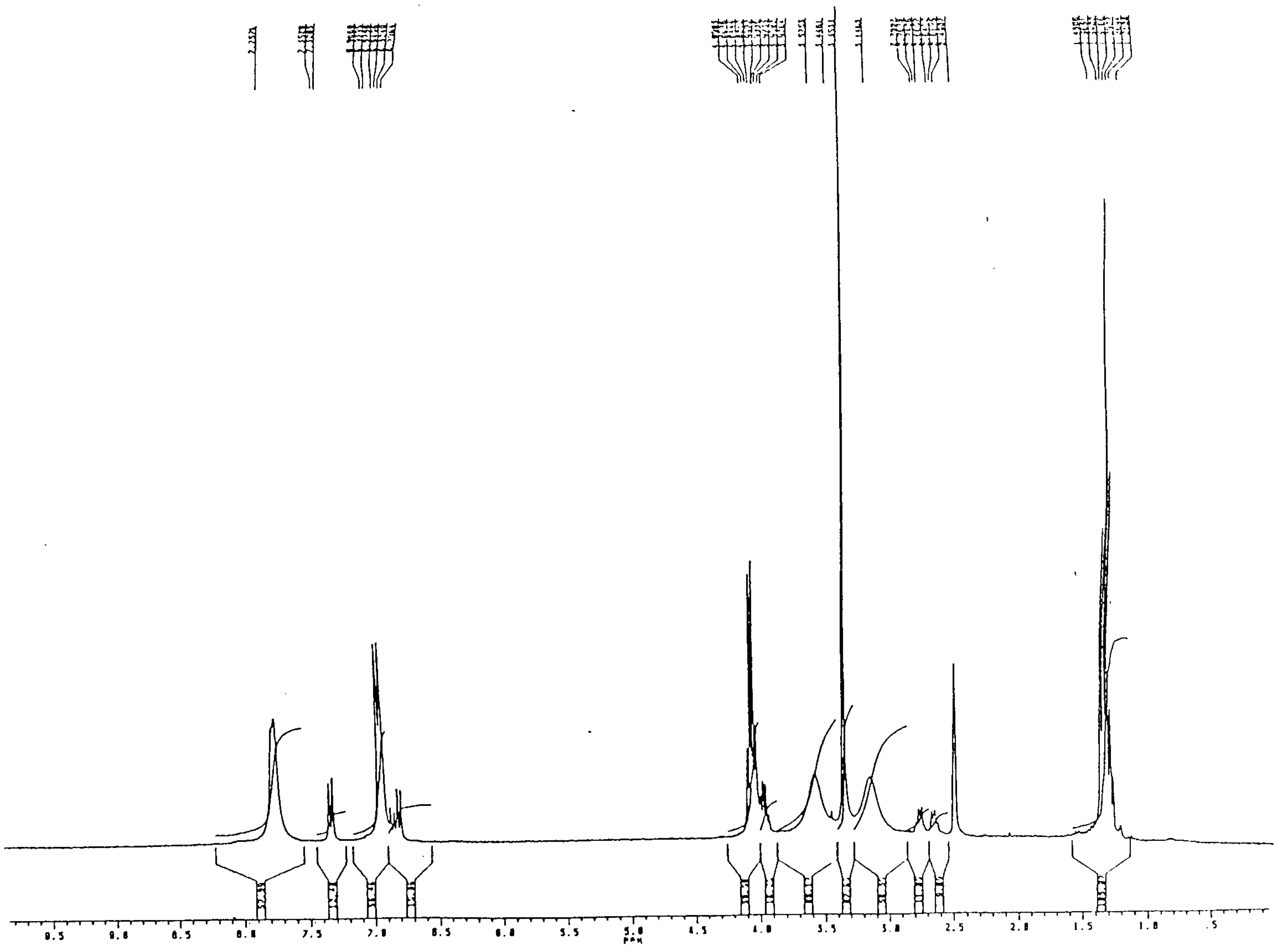


Figure 5.26 ^{1}H N.M.R. spectrum of $L^5PtCl_2.H_2O$.

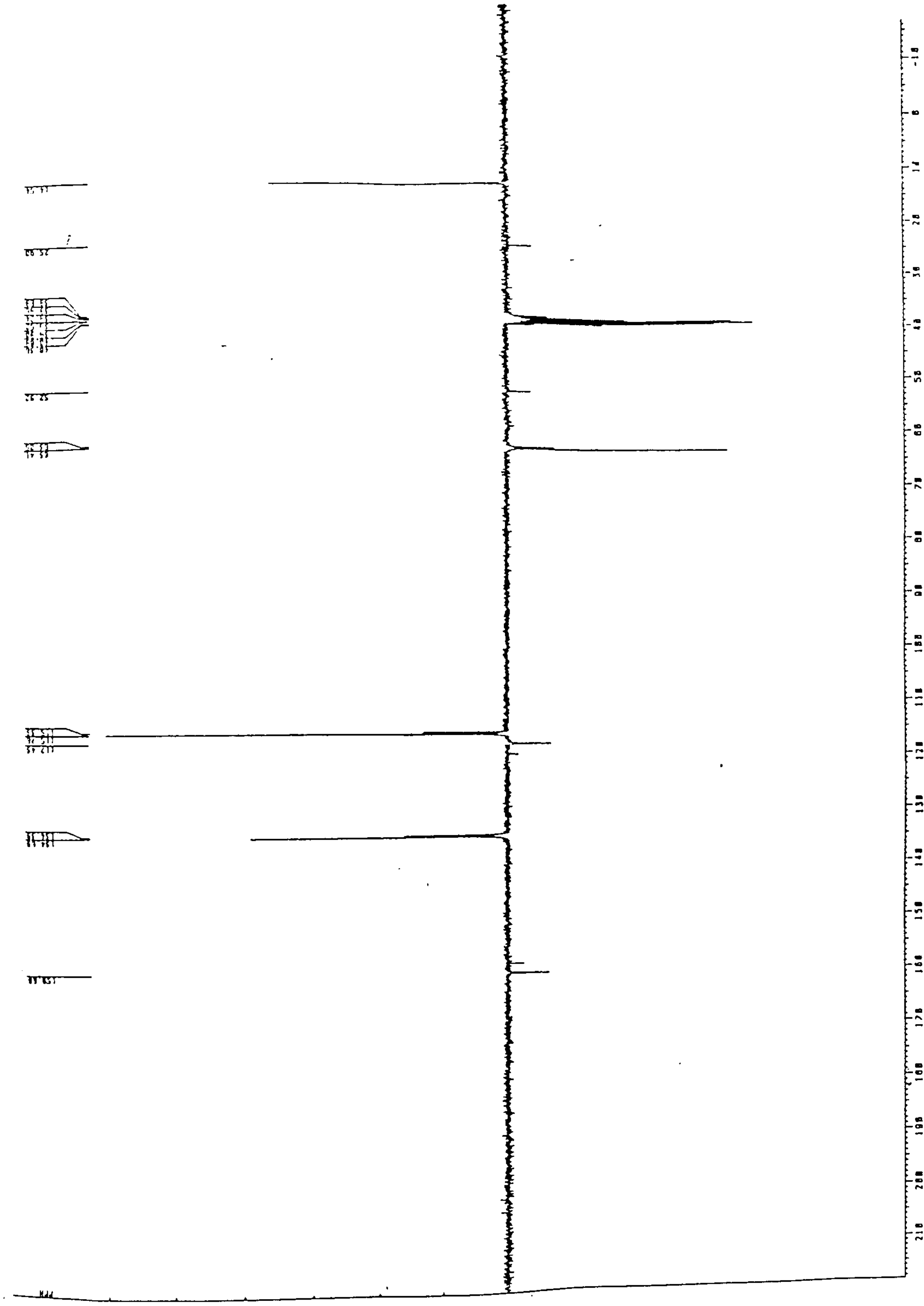


Figure 5.27 13C N.M.R. spectrum of $L^5PtCl_2.H_2O$.

ethoxyphenyl groups. Contrary to the ^1H N.M.R. data, the shifts in the signals are so small (~0.4 ppm) it is difficult to believe there is any interaction between the selenium and platinum centres. There are ambiguities in the N.M.R data and hence definitive characterisation has been avoided here.

5.4. Tellurium(125) N.M.R. Spectroscopy.

^{125}Te N.M.R. spectroscopy is now a powerful tool for the elucidation of structural detail in tellurium chemistry. The relative abundance of ^{125}Te (7%) and receptivity (12.5 times that of ^{13}C) has led to a steady increase in data for tellurium compounds and there are a number of articles illustrating this(129).

In order to probe these tetradentate ligands further, an examination of their chemistry in solution was undertaken by using this technique. The spectra of the ligands L^1, L^2 and L^3 are shown in figures 5.28-5.30 with δ= 22.11 ppm (L^1), δ= 7.34 ppm (L^2) and δ= 6.24 ppm (L^3).The chemical shift values reported here are relative to the standard bis(p-ethoxyphenyl)ditelluride. The signal for this ditelluride is found 455.0 ppm downfield of Me_2Te (the standard usually quoted) and so the new chemical shift values become δ=477.11 ppm (L^1), δ= 462.34 ppm (L^2) and δ= 461.24 ppm (L^3) respectively.

Despite vigorous efforts to obtain spectra of the complexes

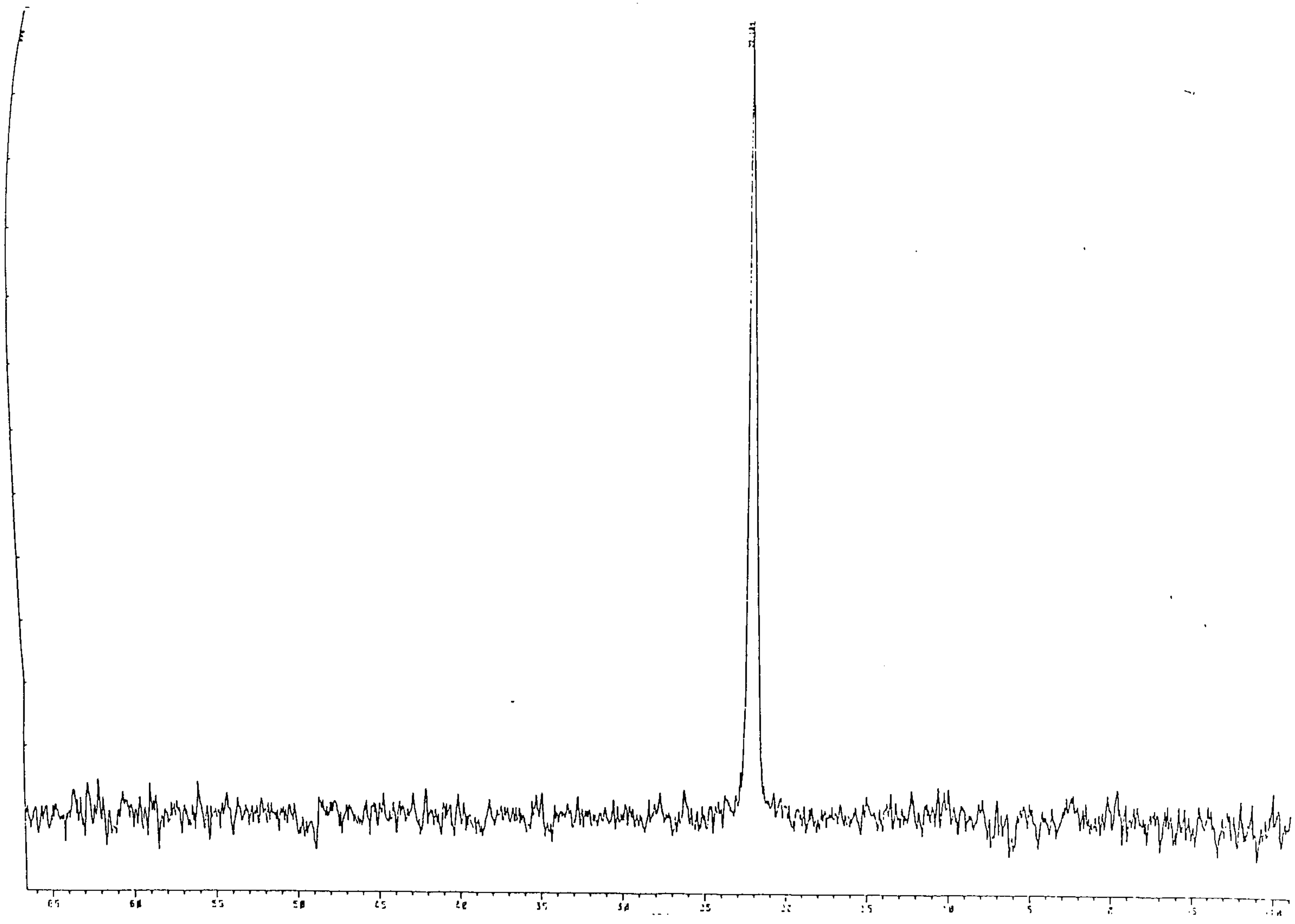


Figure 5.28 ^{125}Te N.M.R. spectrum of Ligand L^1.

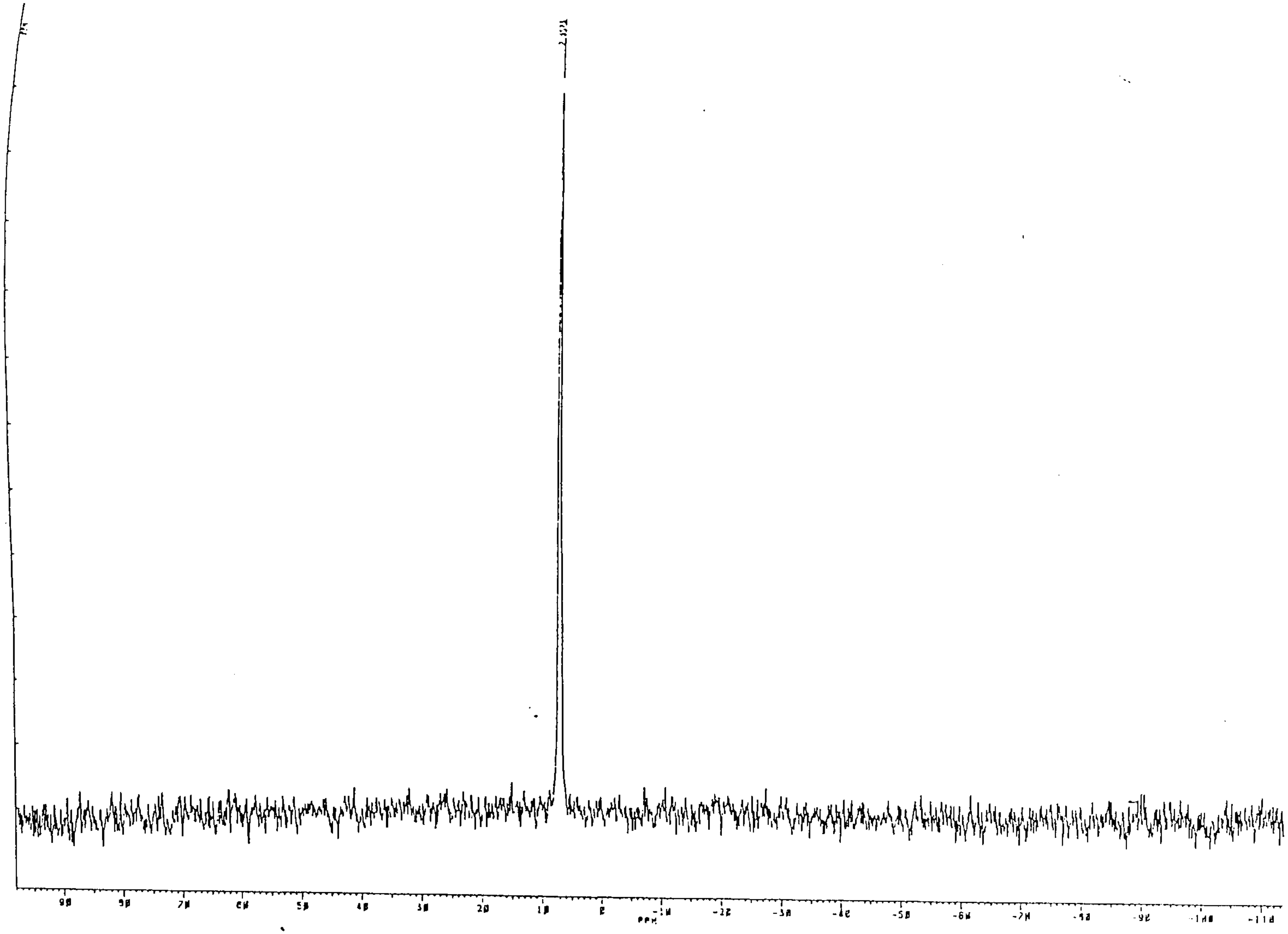


Figure 5.29 ^{125}Te N.M.R. spectrum of Ligand L^2.

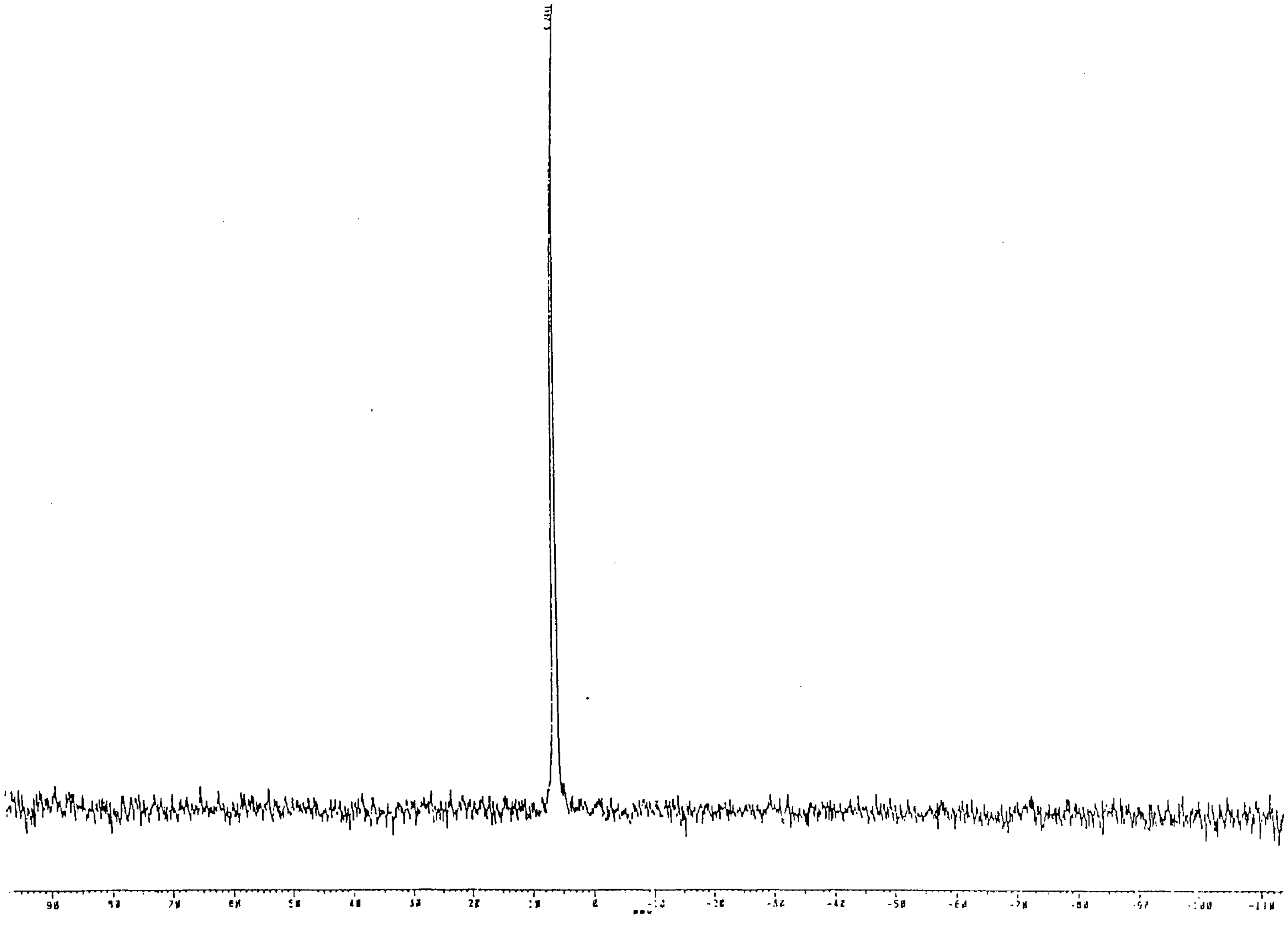


Figure 5.30 ^{125}Te N.M.R. spectrum of Ligand L^3.

[(Hg(II), Cd(II), Cu(I), Pt(II) and Pd(II)], no data were obtained. Based on the Lewis acidity of these metals, the tellurium signals ought to have resonated downfield from the ligands. During the experiments no hint of a signal was observed. The range scanned was 9000 ppm downfield to 5000 ppm upfield of the reference. The number of pulses used per window (each window being 500 ppm wide) was 5000. The pulse angle and relaxation time delay (T_1) was varied without success.

The solvent used in these experiments DMSO has been known to coordinate to tellurium in its complexes and has previously caused decomposition problems in other complexes studied in the research group. Whilst no decomposition of the complexes appeared subjectively, the possibility that DMSO could be screening the tellurium nucleus could not be discounted. Therefore the solvent was changed to 1,1,1-trichloroethane but without success. At this stage the only explanation that can be given for such disappointing results is that the concentration of the solution was too low for the detection of signals.

5.5 Precursors for MOVPE

Tris(aryltelluroethyl)amines and aryltelluroalkylamines are solids at room temperature and are stable in air for long periods. For this reason they are attractive as MOVPE precursors. They are high molecular weight low melting point solids. Although these solids are non-volatile, mild heat (to convert to the liquid form), may produce volatilities suitable for MOVPE purposes (>1torr) although these experiments were not carried out. In the mass spectroscopy experiments, the multidentate ligands fragment with loss of RTe^+ as a volatile ion. This in turn yields atomic tellurium under further fragmentation. Whilst no close comparisons should be made between the MOVPE and mass spectroscopy techniques, it is interesting to note that tellurium deposition does occur from these organometallics.

The tetradentate ligands do form complexes with metal ions such as Hg(II) and Cd(II) which are stable in air and have relatively low melting points. Unfortunately, from an MOVPE point of view, the Te:Cd and Te:Hg ratio is 3:1 and not 3:3 as we had hoped for. Nethertheless, there is evidence for a strong tellurium-mercury interaction in the mercury complexes and therefore this type of compound may be useful as a single source precursor containing groups II and VI atoms. None of these compounds have been tested on an MOVPE kit yet and so it is difficult to gain a measure as to their potential use as precursors. A programme of work in which the aryl substituents are replaced by alkyl groups must be worthy of further investigation.

5.5 SUMMARY

Some aryltelluroalkylamines and arylselenoalkylamines are reported and have been synthesised by the reaction of 2-chloroethylamine or 3-chloropropylamine with RE^- (E=Se,Te). They have been characterised by elemental analyses, infra-red and N.M.R. spectroscopy.

Some potentially tetradentate tripodal tris(aryltelluroethyl)amines and tris(arylselenoethyl)amines have been syntheised by the reaction of tris(2-chloroethyl)amine and RE^-. They have been characterised by elemental analyses, infra-red, N.M.R. and mass spectroscopy. The ligands tris(p-methoxyphenyltelluroethyl)amine (L^2) and tris(p-ethoxyphenyltelluroethyl)amine (L^3) form complexes with Hg(II), Cd(II), Cu(I), Pt(II) and Pd(II). In all cases the nitrogen donor atom is innocent in any coordination to the metal centre

For the Hg(II) complexes, formulae based on $LHgCl_2$ are proposed. Based on a tetrahedral geometry, the organic ligand coordinates in a bidentate (Te,Te) mode with the other two positions occupied by chloride atoms.

For the cadmium(II) complexes, formulae based on L^2CdI_2 and $L^3Cd(OH)_2$ are proposed. Based on a tetrahedral stereochemistry around cadmium, the organic ligand coordinates in a bidentate fashion (Te,Te) with the other two positions occupied by either iodine or hydroxy groups. $L^3Cd(OH)_2$ may be polymeric with propagation through Cd-O bonds.

Copper(I) forms complexes of stoichiometry $LCuBr.H_2O$. They behave as 1:1 electrolytes in solution with, it is believed, the bromide atom being ionic. Assuming a tetrahedral geometry around copper, the organic ligand appears to bond in a terdentate (Te,Te,Te) mode with the fourth position occupied by a water ligand.

Platinum(II) forms complexes of stoichiometry $LPtCl_2.H_2O$. They behave as 1:1 electrolytes in solution, with it is believed one of the chloride atoms being ionic. Based on a square planar stereochemistry around platinum, it is proposed that the organic ligand coordinates in a bidentate (Te,Te) mode with the other positions occupied by chloride and water ligands in trans positions.

Palladium(II) forms complexes of stoichiometry $LPdCl_2.H_2O$. In solution they behave as 1:1 electrolytes with, it is proposed one of the chloride atoms being ionic. Assuming a square planar geometry around the metal centre, it is suggested that the organic ligand coordinates in a bidentate (Te,Te) fashion with the other position occupied by chloride and water ligands. Infra-red data suggests the ligands adopt a cis-geometry around the metal centre.

Chapter Six

X-RAY CRYSTALLOGRAPHIC STUDIES

6.1 Introduction

The synthesis of 2-(2'-pyridyl)phenyltellurium(II) bromide (RTeBr) has been reported(78) and was one of the starting materials in this work for the synthesis of polychalcogenide compounds. During a routine examination of the mass spectrum of this compound (see scheme 4.1), not only was the parent ion observed but other ions of higher m/e were also seen pertaining to tellurium cluster species (eg. $R_3Te_3^+$). An X-ray crystal structure determination was undertaken to ascertain the presence or absence of intermolecular contacts in the solid state.

As part of other work being carried out in our research group, Mbogo studied the reaction of RHgCl with SeX_4(130) (X = Cl, Br) and isolated a range of products whose chemistries involved both trans metallation and redox processes. To help understand this complex chemistry, an X-ray structure determination of one of the materials, 2-(2'-pyridyl)phenylselenium(II) tribromomercurate(II) was carried out.

Finally, as part of the programme of work on the organotellurium carboxylate compounds, an attempt was made at solving the crystal structure of bis(p-methoxyphenyl)tellurium(IV) dibenzoate. There are remarkably few X-ray crystallographic reports in the literature of this class of compound despite the ease with which they form crystals. One example noted is phenoxatellurium(IV) bis(trifluoroacetate)(131). The results of this work are presented herein.

6.2 Experimental and Results.

Crystallographic Analysis of 2-(2-pyridyl)phenyltellurium(II) bromide (RTeBr).

Orange crystals of RTeBr were obtained from slow evaporation of a DMF solution at room temperature and a suitable crystal was mounted on an Enraf-Nonius CAD-4 diffractometer. Data were collected at room temperature using the ω-2θ scan technique. As a check on crystal stability three representative reflections were measured every two hours. Lattice parameters were obtained by least squares analysis from the setting angles of 24 reflections. Following unsuccessful attempts to solve the structure in space group P1 it was eventually solved by Patterson and Fourier methods in space group P1 and refined(132-133) by least squares. Details of the data collection are given in table 6.1. The tellurium and bromine atoms were refined anisotropically and all other non-hydrogen atoms isotropically. Hydrogen atoms were placed in calculated positions riding on their respective bonded atoms

Two of the molecules (labelled e and f), are affected by disorder corresponding to rotation of ca. 6% of the $C_{11}H_8NTe$ residues about the central bond so that the disordered telluriums, Te(e') and Te(f') make contacts of 3.02(3) and 2.78(2) Å with neighbouring bromine atoms.

Computations were carried out on the University of Birmingham

Crystallographic and Experimental Data. for RTeBr

Formula	$C_{11}H_8BrNTe$
Mol Wt.	361.7
Crystal Size mm,	0.35 x 0.13 x 0.23
Space Group	P1
System	triclinic
a, Å	11.217(2)
b, Å	12.026(2)
c, Å	13.346(4)
α, deg	77.87(2)
β, deg	77.17(2)
γ, deg	70.75(2)
V, Å^3	1639
Z	6
Dcalc, g/cm^3	2.20
μ/ mm^{-1}	6.65
λ(Mo-Kα), Å	0.71069
Temp, °C	25
No. of unique data	6520
Observed Data [$\|F>5\sigma F\|$]	4961
Scan Range, θ	2-25
Weighting Scheme	$w = 1/[\sigma^2(F) + 0.0003F^2]$
Absorption Correction	empirical (DIFABS)
R	0.050
Rw	0.058

Table 6.1

Honeywell computer. Figures 1 and 2 were drawn with PLUTO 88 at the Manchester Computer Centre.

6.3 DISCUSSION

The structure of RTeBr is shown in figures 6.1-6.2. Selected bond lengths and bond angles are tabulated in tables 6.2-6.3. Atomic coordinates, temperature factors and mean plane analyses are shown in tables 6.4-6.7.

In the structure of RTeBr six molecules are present in the unit cell. The coordination about tellurium can be considered as essentially pseudo-trigonal bipyramidal with the tellurated carbon and the two lone pairs making up the equatorial coordination and the bromine atom and pyridyl nitrogen atom the axial coordination. Since the position trans to the tellurated carbon is unoccupied, the molecule is essentially "T" shaped with the Te-C bond representing the stem.

The average Te-N distance is 2.24 Å. This value is in agreement with the postulated value for an axial Te-N(134) bond length and is comparable with the distances reported for (pap)Te(SCN) (2.243 Å)(135), (pap)TeCl (2.23 Å)(90b), (pap= 2-phenylazophenyl) and the recently reported structure of $(RTeCl)_2$.R'HgCl [R= 2-(2'-pyridyl)phenyl- and R'= p-ethoxyphenyl-] {2.236(6) Å}(136). The Te-N interaction holds the organic ligand in a planar geometry. The maximum angle between the phenyl and pyridyl planes is only 3.08° (range 0.85-3.08° over the six

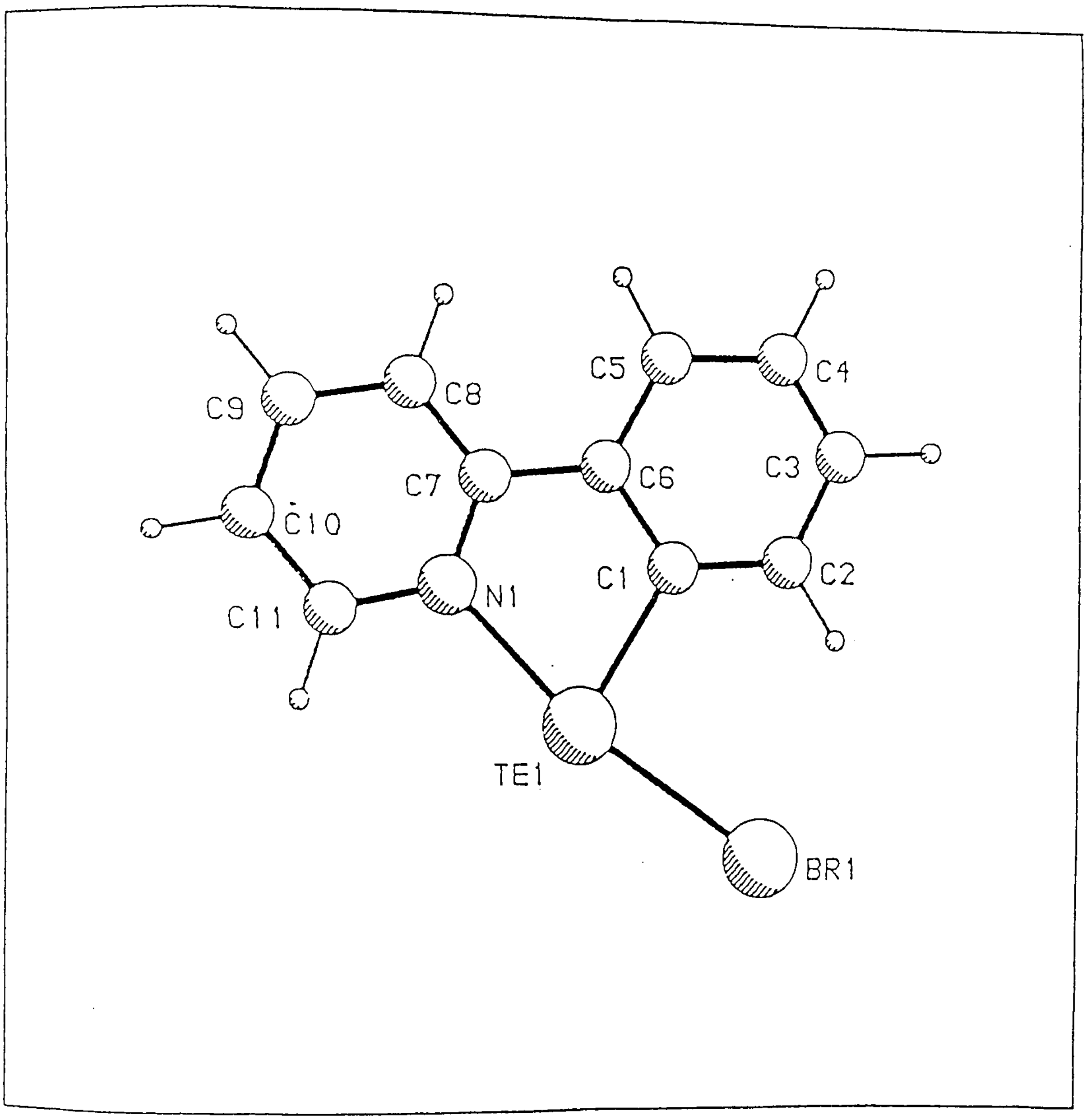


Figure 6.1 Structure of RTeBr.

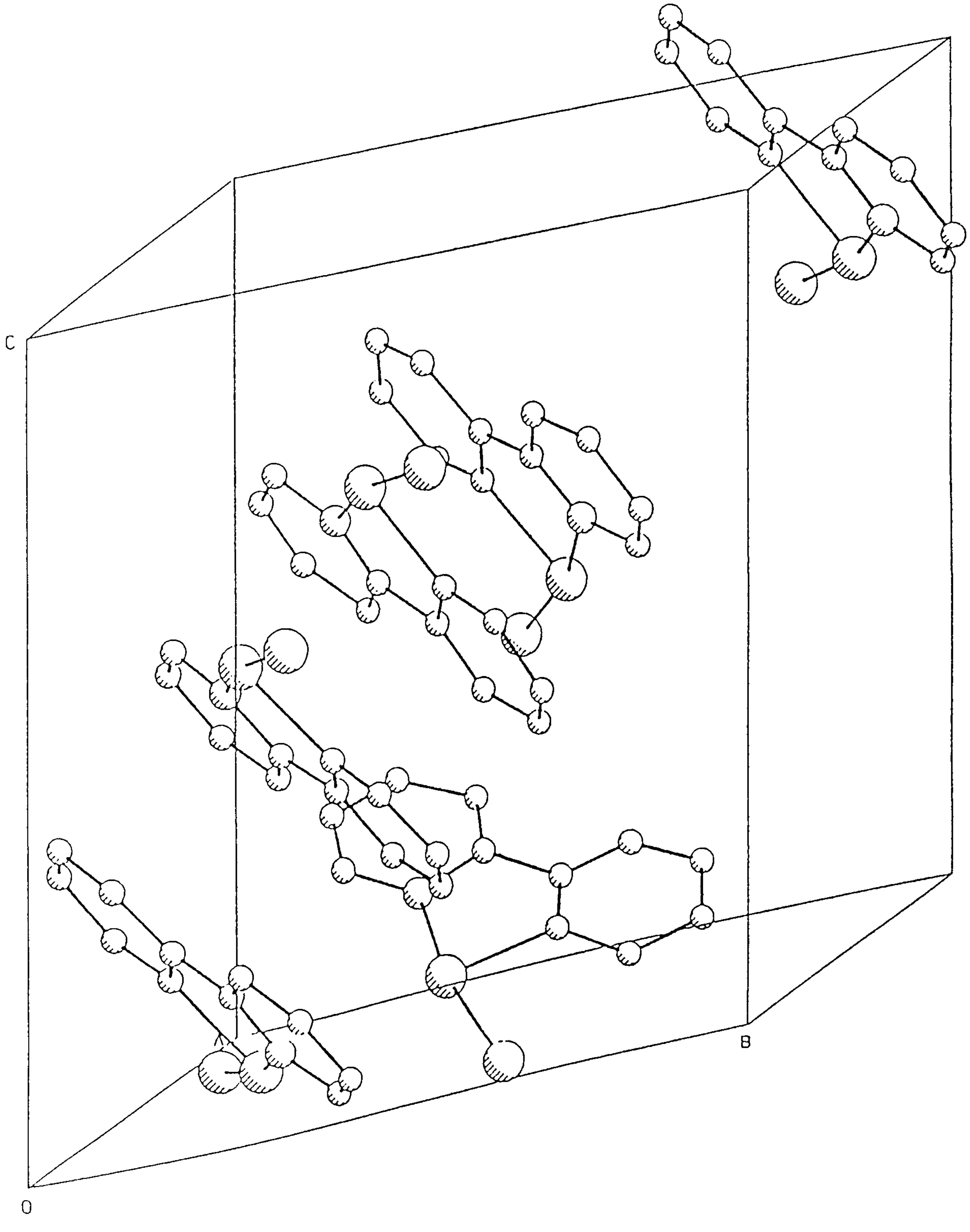


Figure 6.2 Packing diagram for RTeBr.

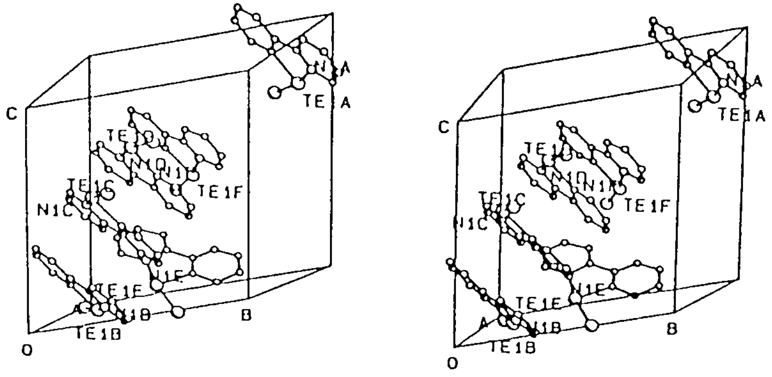


Figure 6.3 Stereoscopic view of RTeBr.

Table 6.2 Bond lengths (Å) and bond angles (°) with e.s.d's in parentheses for RTeBr.

Te(a) --- Br(a)	2.868(3)
Te(a) --- N(a)	2.243(16)
Te(a) --- C(1a)	2.108(22)
Te(b) --- N(b)	2.208(14)
Te(b) --- C(1b)	2.107(19)
Te(c) --- Br(c)	2.743(2)
Te(c) --- N(c)	2.214(16)
Te(c) ---C(1c)	2.110(17)
Te(d) --- Br(d)	2.666(6)
Te(d) --- N(d)	2.231(18)
Te(d) ---C(1d)	2.090(21)
Te(e) --- Br(e)	2.704(3)
Te(e) --- N(e)	2.281(16)
Te(e) --- C(1e)	2.139(18)
Te(f) --- Br(f)	2.724(3)
Te(f) --- N(f)	2.238(16)
Te(f) --- C(1f)	2.112(20)
N(a) --- C(7a)	1.306(24)
N(a) --- C(11a)	1.389(26)
N(b) --- C(7b)	1.306(22)
N(b) --- C(11b)	1.351(24)
N(c) --- C(7c)	1.383(24)
N(d) --- C(7d)	1.341(26)
N(d) --- C(11d)	1.340(28)
N(e) --- C(7e)	1.354(23)
N(e) --- C(11e)	1.435(26)
N(f) --- C(7f)	1.323(25)
N(f) --- C(11f)	1.394(25)
C(1a) --- C(2a)	1.419(27)
C(1a) --- C(6a)	1.369(27)
C(7b) --- C(8b)	1.404(28)
C(8b) --- C(9b)	1.429(30)
C(9b) --- C(10b)	1.333(30)
C(1c) --- C(2c)	1.330(23)
C(1c) --- C(6c)	1.403(23)
C(2c) --- C(3c)	1.391(27)
C(3c) --- C(4c)	1.447(26)
C(4c) --- C(5c)	1.355(27)
C(5c) --- C(6c)	1.386(27)
C(6c) --- C(7c)	1.486(25)
C(7c) --- C(8c)	1.387(26)
C(8c) --- C(9c)	1.319(28)
C(9c) --- C(10c)	1.378(29)
C(10c)--- C(11c)	1.351(30)
C(1d) --- C(2d)	1.361(27)
C(1d) --- C(6d)	1.414(27)
C(2d) --- C(3d)	1.382(33)
C(3d) --- C(4d)	1.397(34)
C(4d) --- C(5d)	1.390(31)
C(5d) --- C(6d)	1.344(30)
C(6d) --- C(7d)	1.475(27)
C(7d) --- C(8d)	1.351(33)
C(9d) --- C(10d)	1.313(35)
C(10d)--- C(11d)	1.405(34)
C(1e) --- C(2e)	1.419(25)
C(1e) --- C(6e)	1.326(25)
C(2e) --- C(3e)	1.377(28)
C(3e) --- C(4e)	1.382(30)
C(4e) --- C(5e)	1.353(28)
C(5e) --- C(6e)	1.339(25)

C(2a) --- C(3a)	1.383(30)
C(3a) --- C(4a)	1.324(32)
C(4a) --- C(5a)	1.411(31)
C(5a) --- C(6a)	1.449(30)
C(6a) --- C(7a)	1.479(27)
C(7a) --- C(8a)	1.387(28)
C(8a) --- C(9a)	1.441(32)
C(9a) --- C(10a)	1.326(32)
C(10a)--- C(11a)	1.439(31)
C(1b) --- C(2b)	1.445(26)
C(1b) --- C(6b)	1.391(26)
C(2b) --- C(3b)	1.372(29)
C(3b) --- C(4b)	1.354(33)
C(4b) --- C(5b)	1.411(34)
C(5b) --- C(6b)	1.387(29)
C(6b) --- C(7b)	1.446(26)
C(6e) --- C(7e)	1.509(22)
C(7e) --- C(8e)	1.376(25)
C(8e) --- C(9e)	1.399(26)
C(9e) --- C(10e)	1.334(28)
C(10e)--- C(11e)	1.404(29)
C(1f) --- C(2f)	1.392(26)
C(1f) --- C(6f)	1.366(26)
C(2f) --- C(3f)	1.390(30)
C(3f) --- C(4f)	1.410(32)
C(4f) --- C(5f)	1.284(32)
C(5f) --- C(6f)	1.460(31)
C(6f) --- C(7f)	1.475(23)
C(7f) --- C(8f)	1.339(27)
C(8f) --- C(9f)	1.399(31)
C(9f) --- C(10f)	1.371(33)
C(10f)--- C(11f)	1.391(28)

Table 6.2

Table 6.3 Bond Angles (°) with e.s.d's in parentheses for RTeBr.

Br(a) -Te(a) -N(a)	169.3(4)
Br(a) -Te(a) -C(1a)	94.2(6)
N(a) -Te(a) -C(1a)	75.2(7)
Br(b) -Te(b) -N(b)	169.9(4)
Br(b) -Te(b) -C(1b)	95.0(5)
N(b) -Te(b) -C(1b)	75.3(7)
Br(c) -Te(c) -N(c)	169.3(4)
Br(c) -Te(c) -C(1c)	91.7(4)
N(c) -Te(c) -C(1c)	77.9(6)
Br(d) -Te(d) -N(d)	169.2(5)
Br(d) -Te(d) -C(1d)	92.7(6)
N(d) -Te(d) -C(1d)	76.7(7)
Br(e) -Te(e) -N(e)	169.5(4)
Br(e) -Te(e) -N(e)	94.7(5)
N(e) -Te(e) -C(1e)	75.2(6)
Br(f) -Te(f) -N(f)	168.1(4)
Br(f) -Te(f) -C(1f)	93.4(5)
N(f) -Te(f) -C(1f)	75.1(7)
Te(a) -N(a) -C(7a)	116.2(13)
Te(a) -N(a) -C(11a)	122.4(14)
C(7a) -N(a) -C(11a)	121.1(17)
Te(b) -N(b) -C(7b)	115.6(12)
Te(b) -N(b) -C(11b)	121.0(13)
C(7b) -N(b) -C(11b)	123.3(16)
Te(c) -N(c) -C(7c)	115.2(13)
Te(c) -N(c) -C(11c)	125.6(14)
C(7c) -N(c) -C(11c)	119.2(17)
Te(d) -N(d) -C(7d)	115.4(14)
Te(d) -N(d) -C(11d)	121.6(16)
C(7d) -N(d) -C(11d)	123.0(20)
Te(e) -N(e) -C(7e)	113.7(12)
Te(e) -N(e) -C(11e)	123.5(13)
C(7e) -N(e) -C(11e)	122.4(17)
Te(f) -N(f) -C(7f)	118.1(13)
Te(f) -N(f) -C(11f)	122.5(14)
C(7f) -N(f) -C(11f)	119.4(17)
Te(a) -C(1a) -C(2a)	123.9(15)
N(b) -C(11b)-C(10b)	118.2(19)
Te(c) -C(1c) -C(2c)	123.4(13)
Te(c) -C(1c) -C(6c)	114.2(12)
C(2c) -C(1c) -C(1c)	122.2(17)
C(1c) -C(2c) -C(3c)	119.8(18)
C(2c) -C(3c) -C(4c)	119.5(19)
C(3c) -C(4c) -C(5c)	117.9(18)
C(4c) -C(5c) -C(6c)	122.1(18)
C(1c) -C(6c) -C(5c)	118.0(17)
C(1c) -C(6c) -C(7c)	119.6(16)
C(5c) -C(6c) -C(7c)	122.3(16)
N(c) -C(7c) -C(6c)	113.0(16)
N(c) -C(7c) -C(8c)	119.8(18)
C(6c) -C(7c) -C(8c)	127.2(18)
C(7c) -C(8c) -C(9c)	119.7(21)
C(8c) -C(9c) -C(10c)	120.6(21)
C(9c) -C(10c)-C(11c)	120.2(22)
N(c) -C(11c)-C(10c)	120.5(22)
Te(d) -C(1d) -C(2d)	124.4(16)
Te(d) -C(1d) -C(6d)	115.9(15)
C(2d) -C(1d) -C(6d)	119.7(20)
C(1d) -C(2d) -C(3d)	121.2(22)
C(2d) -C(3d) -C(4d)	118.3(26)
C(3d) -C(4d) -C(5d)	119.9(26)
C(4d) -C(5d) -C(6d)	120.6(24)
C(1d) -C(6d) -C(5d)	119.6(20)
C(1d) -C(6d) -C(7d)	117.3(18)
C(5d) -C(6d) -C(7d)	123.0(20)
N(d) -C(7d) -C(6d)	114.7(18)
N(d) -C(7d) -C(8d)	121.6(21)
C(6d) -C(7d) -C(8d)	123.8(20)
C(7d) -C(8d) -C(9d)	115.7(25)
C(8d) -C(9d) -C(10d)	122.2(28)
C(9d) -C(10d) -C(11d)	122.7(29)
N(d) -C(11d) -C(10d)	114.5(24)
Te(e) -C(1e) -C(2e)	120.9(14)
Te(e) -C(1e) -C(6e)	118.3(14)

Te(a) -C(1a) -C(6a)	116.2(16)
C(2a) -C(1a) -C(6a)	119.8(20)
C(1a) -C(2a) -C(3a)	121.1(20)
C(2a) -C(3a) -C(4a)	120.6(24)
C(3a) -C(4a) -C(5a)	120.5(26)
C(4a) -C(5a) -C(6a)	120.0(22)
C(1a) -C(6a) -C(5a)	117.6(20)
C(1a) -C(6a) -C(7a)	118.0(19)
C(5a) -C(6a) -C(7a)	124.3(19)
N(a) -C(7a) -C(6a)	114.1(17)
N(a) -C(7a) -C(8a)	122.8(20)
C(6a) -C(7a) -C(8a)	123.0(19)
C(7a) -C(8a) -C(9a)	118.0(23)
C(8a) -C(9a) -C(10a)	118.9(25)
C(9a) -C(10a)-C(11a)	121.5(25)
N(a) -C(11a)-C(10a)	117.6(21)
Te(b) -C(1b) -C(2b)	123.7(14)
Te(b) -C(1b) -C(6b)	116.6(14)
C(2b) -C(1b) -C(6b)	119.7(18)
C(1b) -C(2b) -C(3b)	118.4(19)
C(2b) -C(3b) -C(4b)	121.7(24)
C(3b) -C(4b) -C(5b)	120.9(28)
C(4b) -C(5b) -C(6b)	119.2(24)
C(1b) -C(6b) -C(5b)	120.0(20)
C(1b) -C(6b) -C(7b)	115.5(18)
C(5b) -C(6b) -C(7b)	124.5(19)
N(b) -C(7b) -C(6b)	116.9(16)
N(b) -C(7b) -C(8b)	120.8(19)
C(6b) -C(7b) -C(8b)	121.9(18)
C(7b) -C(8b) -C(9b)	116.7(21)
C(8b) -C(9b) -C(10b)	120.8(22)
C(9b) -C(10b)-C11b)	119.8(22)
C(2e) -C(1e) -C(6e)	120.7(18)
C(1e) -C(2e) -C(3e)	115.9(20)
C(2e) -C(3e) -C(4e)	123.2(23)
C(3e) -C(4e) -C(5e)	116.2(23)
C(4e) -C(5e) -C(6e)	123.3(21)
C(1e) -C(6e) -C(5e)	120.6(18)
C(1e) -C(6e) -C(7)	117.5(18)
C(5e) -C(6e) -C(7e)	121.9(18)
N(e) -C(7e) -C(6e)	115.3(16)
N(e) -C(7e) -C(8e)	119.6(17)
C(6e) -C(7e) -C(8e)	125.1(18)
C(7e) -C(8e) -C(9e)	118.5(18)
C(8e) -C(9e) -C(10e)	122.8(21)
C(9e) -C(10e)-C(11e)	120.6(22)
N(e) -C(11e -C(10e)	115.9(20)
Te(f) -C(1f) -C(2f)	123.3(14)
Te(f) -C(1f) -C(6f)	114.6(14)
C(2f) -C(1f) -C(6f)	122.0(19)
C(1f) -C(2f) -C(3f)	119.4(20)
C(2f) -C(3f) -C(4f)	119.3(24)
C(3f) -C(4f) -C(5f)	119.7(28)
C(4f) -C(5f) -C(6f)	124.0(24)
C(1f) -C(6f) -C(5f)	115.1(19)
C(1f) -C(6f) -C(7f)	121.6(18)
C(5f) -C(6f) -C(7f)	123.0(18)
N(f) -C(7f) -C(6f)	110.2(17)
N(f) -C(7f) -C(8f)	122.8(20)
C(6f) -C(7f) -C(8f)	126.7(19)
C(7f) -C(8f) -C(9f)	119.3(23)
C(8f) -C(9f) -C(10f)	119.8(25)
C(9f) -C(10f)-C(11f)	118.6(23)
N(f) -C(11f)-C(10f)	119.8(20)

Table 6.3 Bond Angles(°) for RTeBr.

Anisotropic Temperature Factors (Å^2 x 10^3) with e.s.d's in parentheses for RTeBr

	U11	U22	U33	U23	U13	U12
Te(e')	68(16)	56(15)	71(18)	8(13)	-38(14)	-15(12)
Te(f')	33(14)	32(15)	55(19)	0(13)	-23(12)	-5(11)
Te(a)	37(1)	56(1)	47(1)	-5(1)	-6(1)	-19(1)
Te(b)	41(1)	55(1)	50(1)	-9(1)	-3(1)	-16(1)
Te(c)	39(1)	55(1)	45(1)	5(1)	-8(1)	-16(1)
Te(d)	42(1)	58(1)	58(1)	1(1)	-9(1)	-18(1)
Te(e)	47(1)	45(1)	46(1)	-9(1)	-13(1)	-12(1)
Te(f)	43(1)	49(1)	42(1)	-2(1)	-8(1)	-14(1)
Br(a)	55(1)	137(1)	101(2)	-1(2)	-20(2)	-45(2)
Br(b)	49(1)	76(2)	121(2)	-18(2)	-9(2)	-20(1)
Br(c)	49(1)	86(2)	89(2)	11(2)	-18(1)	-24(1)
Br(d)	64(2)	150(3)	120(3)	10(2)	-33(2)	-51(2)
Br(e)	72(2)	88(2)	81(2)	-7(2)	-14(1)	-25(1)
Br(f)	59(1)	93(2)	108(2)	-18(2)	-23(2)	-21(1)

Table 6.4

Table 6.5. Fractional Atomic Coordinates (x 10^4) with e.s.d's in parentheses and isotropic temperature factors (Å^2 x 10^3) for RTeBr.

Ueq = 1/3 (trace of the orthoganised Uij tensor)

	x	y	z	Ueq/Uiso
Te(e')	1083(23)	7287(21)	3573(20)	64
Te(f')	14414(21)	4603(21)	8699(21)	39
Te(a)	8554	9095	7794	46
Te(b)	6159(2)	1392(2)	14(2)	49
Te(c)	9719(2)	142(2)	4362(1)	47
Te(d)	7116(1)	2568(1)	6506(1)	52
Te(e)	4540(2)	4428(2)	842(2)	45
Te(f)	11388(2)	7031(2)	5661(2)	45
Br(a)	6174(3)	8965(3)	7945(3)	96
Br(b)	3630(2)	1542(3)	460(3)	81
Br(c)	12243(2)	53(3)	4098(3)	75
Br(d)	9465(3)	2764(4)	6262(3)	109
Br(e)	6541(3)	4720(3)	-636(3)	80
Br(f)	9034(3)	7032(3)	5433(3)	84
N(a)	10570(15)	8925(14)	7917(13)	44(4)
N(b)	8225(14)	1103(13)	-69(13)	42(4)
N(c)	7645(15)	526(15)	4371(14)	50(4)
N(d)	5090(17)	2704(16)	6480(15)	62(5)
N(e)	2856(14)	4495(14)	2172(13)	52(4)
N(f)	13303(15)	6702(14)	6097(14)	49(4)
C(1a)	8920(20)	7880(18)	9159(18)	54(6)
C(2a)	8009(19)	7352(17)	9817(17)	49(5)
C(3a)	8319(22)	6536(20)	10689(19)	68(6)
C(4a)	9470(24)	6249(23)	10944(23)	82(8)
C(5a)	10436(23)	6688(20)	10282(20)	69(7)
C(6a)	10134(19)	7568(18)	9378(17)	52(5)

	x	y	z	Ueq/Uiso
C(7a)	11051(18)	8145(17)	8675(17)	47(5)
C(8a)	12295(21)	7919(20)	8834(20)	64(6)
C(9a)	13107(26)	8521(22)	8085(22)	81(8)
C(10a)	12619(23)	9301(21)	7308(20)	69(7)
C(11a)	11314(21)	9532(20)	7181(19)	63(6)
C(1b)	6665(18)	70(17)	1288(16)	48(5)
C(2b)	5770(20)	-466(18)	2011(17)	57(5)
C(3b)	6211(22)	-1307(20)	2820(20)	70(6)
C(4b)	7456(27)	-1660(26)	2937(26)	102(9)
C(5b)	8355(23)	-1176(20)	2224(19)	71(7)
C(6b)	7943(19)	-292(18)	1415(17)	54(5)
C7(b)	8767(17)	271(16)	634(15)	41(5)
C8(b)	10066(22)	35(21)	685(21)	72(7)
C9(b)	10774(21)	674(19)	-116(18)	62(6)
C(10b)	10208(21)	1464(20)	-860(19)	66(6)
C(11b)	8875(19)	1708(18)	-839(17)	52(5)
C(1c)	9410(15)	1476(14)	3058(14)	34(4)
C(2c)	10342(18)	1852(16)	2426(15)	47(5)
C(3c)	10056(19)	2749(17)	1590(17)	56(5)
C(4c)	8760(18)	3199(17)	1371(16)	51(5)
C(5c)	7872(19)	2712(17)	1992(17)	52(5)
C(6c)	8147(16)	1875(15)	2862(15)	41(5)
C(7c)	7165(17)	1368(16)	3565(15)	44(5)
C(8c)	5876(19)	1676(19)	3500(18)	60(6)
C(9c)	5120(20)	1158(18)	4204(18)	59(6)
C(10c)	5598(20)	321(19)	5009(18)	61(6)
C(11c)	6848(20)	27(20)	5087(19)	62(6)
C(1d)	6699(19)	3787(17)	5170(17)	51(5)
C(2d)	7541(21)	4317(18)	4520(18)	57(6)
C(3d)	7225(26)	5057(23)	3614(23)	84(8)
C(4d)	5969(24)	5356(23)	3435(22)	81(8)

	x	y	z	Ueq/Uiso
C(5d)	5127(23)	4777(20)	4077(20)	71(7)
C(6d)	5154(19)	4047(17)	4949(17)	51(5)
C(7d)	4581(19)	3443(18)	5678(17)	51(5)
C(8d)	3332(24)	3615(23)	5566(22)	76(7)
C(9d)	2691(26)	2949(23)	6283(22)	82(8)
C(10d)	3179(27)	2262(24)	7088(24)	87(8)
C(11d)	4444(23)	2074(22)	7215(21)	73(7)
C(1e)	3937(17)	6212(16)	1177(15)	47(5)
C(2e)	4566(18)	7053(17)	602(16)	51(5)
C(3e)	4104(21)	8172(20)	891(19)	66(6)
C(4e)	3098(21)	8479(21)	1692(19)	67(6)
C(5e)	2562(19)	7613(18)	2189(18)	56(5)
C(6e)	2961(16)	6514(15)	1936(14)	40(4)
C(7e)	2354(17)	5563(16)	2517(15)	47(5)
C(8e)	1340(16)	5720(16)	3325(14)	43(4)
C(9e)	896(20)	4745(18)	3801(18)	59(6)
C(10e)	1428(20)	3668(20)	3515(18)	62(6)
C(11e)	2455(21)	3471(21)	2686(19)	70(6)
C(1f)	11393(18)	5832(17)	7066(16)	47(5)
C(2f)	10340(19)	5450(18)	7576(17)	54(5)
C(3f)	10439(23)	4638(21)	8487(20)	72(7)
C(4f)	11571(25)	4282(24)	8916(24)	87(8)
C(5f)	12530(23)	4641(20)	8424(20)	70(7)
C(6f)	12495(19)	5505(18)	7473(17)	54(5)
C(7f)	13065(18)	5914(17)	6926(16)	48(5)
C(8f)	14737(21)	5633(20)	7239(20)	68(6)
C(9f)	15642(25)	6199(22)	6682(21)	83(8)
C(10f)	15386(21)	6995(20)	5800(18)	62(6)
C(11f)	14183(20)	7283(19)	5523(18)	55(6)

Table 6.5 Fractional atomic coordinates of non-hydrogen atoms

Fractional atomic coordinates (x 10^4) of the hydrogen atoms and isotropic temperature factors (Å^2 x 10^3) for RTeBr.

	x	y	z	Uiso
H(2a)	7055	7582	9640	70
H(3a)	7628	6125	11180	70
H(4a)	9671	5685	11669	70
H(5a)	11400	6349	10453	70
H(8a)	12640	7325	9505	70
H(9a)	14096	8326	8164	70
H(10a)	13213	9775	6756	70
H(11a)	10928	10147	6535	70
H(2b)	4773	-189	1930	70
H(3b)	5560	-1718	3373	70
H(4b)	7761	-2297	3602	70
H(5b)	9352	-1525	2307	70
H(8b)	10517	-612	1288	70
H(9b)	11783	494	-118	70
H(10b)	10746	1944	-1464	70
H(11b)	8386	2372	-1412	70
H(2c)	11325	1468	2547	70
H(3c)	10786	3118	1108	70
H(4c)	8506	3879	718	70
H(5c)	6913	3028	1813	70
H(8c)	5491	2349	2883	70
H(9c)	4123	1368	4143	70
H(10c)	4972	-102	5578	70
H(11c)	7206	-582	5747	70
H(2d)	8488	4105	4706	70
H(3d)	7932	5414	3080	70
H(4d)	5651	6028	2795	70

	x	y	z	Uiso
H(5d)	4184	4928	3908	70
H(8d)	2895	4223	4937	70
H(9d)	1716	3022	6246	70
H(10d)	2631	1770	7651	70
H(11d)	4884	1480	7848	70
H(2e)	5332	6829	-42	70
H(3e)	4567	8839	494	70
H(4e)	2743	9357	1918	70
H(5e)	1779	7817	2825	70
H(8e)	865	6581	3573	70
H(9e)	117	4842	4450	70
H(10e)	1070	2927	3892	70
H(11e)	2955	2599	2470	70
H(2f)	9450	5794	7274	70
H(3f)	9654	4285	8863	70
H(4f)	11648	3683	9642	70
H(5f)	13408	4303	8743	70
H(8f)	14926	4992	7929	70
H(9f)	16549	5991	6941	70
H(10f)	16102	7388	5330	70
H(11f)	13945	7932	4848	70

Table 6.6 **Atomic coordinates for the hydrogen atoms.**

	molecule / perpendicular distance from plane Å					
	a	b	c	d	e	f
C1	0.00407	-0.01678	-0.01930	0.02593	-0.01830	-0.02953
C2	-0.00510	0.00286	-0.03035	0.00174	-0.00943	0.02744
C3	-0.01559	-0.00105	0.01795	-0.03435	-0.00200	-0.01600
C4	0.03673	0.01417	0.00488	0.04061	0.00587	0.00765
C5	-0.03589	-0.02839	-0.01531	-0.01436	0.00223	-0.00953
C6	0.01579	0.02918	0.00353	-0.01958	-0.01496	0.01997
Mean Dev	0.01886	0.01540	0.01522	0.02276	0.00879	0.01835
R.M.S Dev	0.02299	0.01892	0.01773	0.02612	0.01073	0.02012

Table 6.7 Mean Plane Analysis for the Phenyl ring (C1-C6).

	molecule / perpendicular distance from plane Å					
	a	b	c	d	e	f
C7	-0.01985	-0.00146	0.00888	-0.00156	0.04082	-0.01593
C8	0.02146	0.00639	0.01091	0.01118	-0.01379	-0.00274
C9	-0.01338	-0.00474	-0.01402	-0.01226	-0.00189	0.02172
C10	0.00376	-0.00175	-0.00353	0.00328	0.01003	-0.02310
C11	0.00170	0.00679	0.02461	0.00731	0.03743	0.00581
N	0.00971	-0.00523	-0.02686	-0.00795	-0.05259	0.01425
Mean Dev	0.01165	0.00439	0.01480	0.00726	0.02610	0.01392
R.M.S Dev	0.01381	0.00487	-0.02686	0.00822	0.03197	0.01583

Table 6.7 (continued) **Mean Plane Analysis for the Pyridyl ring.**

	molecule / perpendicular distance from plane Å					
	a	b	c	d	e	f
Te	-0.01874	0.01352	-0.00250	-0.00458	0.01019	-0.00203
C1	0.01743	-0.02262	0.00781	0.01841	0.00138	-0.00541
C6	-0.00411	0.02151	-0.01064	-0.02602	-0.01773	0.02884
C7	-0.02220	-0.00299	0.00703	0.01987	0.03125	-0.04170
N	0.02762	-0.00942	-0.00169	-0.00768	-0.02508	0.02030
Mean Dev	0.01802	0.01401	0.00593	0.01531	0.01713	0.01965
R.M.S Dev	0.01964	0.01584	0.00682	0.01727	0.02013	0.02456

Table 6.7 (continued) **Mean Plane Analysis for the Te-C1-C6-C7-N ring.**

	molecule / perpendicular distance from plane Å					
	a	b	c	d	e	f
Te	-0.03871	0.01101	-0.01568	0.00867	-0.00392	-0.02294
C1	-0.00861	-0.03651	0.01935	0.03855	0.00444	-0.02720
C2	-0.00809	0.00454	-0.02301	0.00264	-0.00066	0.05819
C3	0.00883	0.01723	-0.02766	0.04911	-0.02519	0.02296
C4	0.04714	0.02887	0.00891	-0.02221	0.02900	0.02550
C5	-0.05163	0.03416	0.08142	0.02050	0.00332	0.01811
C6	-0.01261	-0.00556	-0.00206	-0.01054	0.03183	-0.00141
C7	-0.01108	-0.01316	-0.00335	0.02583	-0.01383	-0.05417
C8	0.00943	0.00280	-0.00127	0.03854	-0.04942	-0.06122
C9	-0.02663	0.00404	-0.01336	-0.01395	0.01458	-0.00465
C10	0.01087	0.01132	0.00972	-0.02147	0.03685	0.00383
C11	0.02674	0.01130	0.03757	-0.01654	0.06313	0.05067
N	0.03818	-0.01284	-0.02606	-0.00433	-0.07684	0.02574
Mean Dev	0.02296	0.01487	0.01587	0.02099	0.02715	0.02897
R.M.S Dev	0.02770	0.01844	0.01904	0.02470	0.03577	0.03520

Table 6.7 (continued) **Mean Plane Analysis for the RTe moiety.**

	molecule / perpendicular distance from plane Å					
	a	b	c	d	e	f
Te	0.02374	-0.02696	-0.04951	-0.02692	-0.06327	0.04989
Br	-0.09054	0.05452	0.04955	0.05265	0.08533	-0.17586
C1	0.02204	-0.05484	0.00232	0.02084	-0.02392	-0.01160
C2	0.04396	-0.01787	-0.4279	-0.01843	-0.03585	0.06870
C3	0.02235	0.00905	0.01955	-0.05776	0.01256	0.01678
C4	0.03412	0.03718	0.01635	0.03020	0.04259	0.00789
C5	-0.07125	-0.0225	-0.00820	-0.00956	0.02051	-0.03021
C6	-0.00994	0.00447	-0.00373	-0.01213	-0.03475	0.00604
C7	-0.01287	-0.01203	-0.00191	0.02729	-0.01156	-0.04341
C8	-0.01831	0.02014	0.01456	0.05535	-0.02248	-0.05992
C9	-0.05668	0.02228	0.00266	0.00236	0.04192	0.00397
C10	0.00537	0.01413	0.01270	-0.01831	0.04233	0.02971
C11	0.04787	-0.00163	0.02650	-0.02916	0.04421	0.08536
N	0.06016	-0.02619	-0.03805	-0.01641	-0.09763	0.05265
Mean Dev	0.03708	0.02311	0.02059	0.02696	0.04135	0.04585
R.M.S Dev	0.04446	0.02795	0.026735	0.031652	0.04811	0.06325

Table 6.7 (continued) **Mean Plane Analysis for the RTeBr molecules.**

independent molecules). With the help of the structure solved here and those reported elsewhere(74), a useful bank of information has been collected for molecules of the type RTeL [R= 2-(2'-pyridyl)phenyl-] illustrating the strength of the Te-N interaction relative to the group trans to the nitrogen atom. Relevant data are shown in table 6.8 below. Strong Te-N interactions are seen when L= Cl, Br. However the presence of a Te-C covalent bond trans to the Te-N vector significantly weakens the interaction. For these Te(II) compounds a trans influence series can be suggested

Compound	**Atom Trans to N**	**Te-N distance (Å)**
RTeBr	Br	2.24 (mean)
$(RTeCl)_2R'HgCl$	Cl	2.24 (mean)
RTe(dmdtc)	S	2.354(4)
RTeR'	C	2.695(4)

R= 2-(2'pyridyl)phenyl-
R'= p-ethoxyphenyl-
dmdtc = dimethyldithiocarbamate

Table 6.8. Trans influence on Te-N interactions.

$$Br{\sim}Cl < S < C$$

in agreement with results obtained previously from consideration of other tellurium compounds(137).

All six molecules have the RTeBr group planar to within ±0.08 Å with the bromine atom displacements from this plane in the range 0.10-0.23 Å. The small value for the C-Te-N bond angles [range 75.1-77.9°] is due to the constraint of the five membered chelate ring. It is this constraint that distorts the tellurium coordination from ideal pseudo trigonal bipyramidal values.

The Te-C distance (mean 2.11 Å) is in good agreement with the sum of the Pauling single bond covalent radii(138) and with the mean value given by Allen *et al* (12) for Te-C(aromatic) of 2.116 Å.

The bromine atom lies trans to nitrogen with N-Te-Br angles ranging from 168.1-169.9°. The mean Te-Br bond length of 2.71 Å may be compared with Te(IV)-Br distances of 2.59-2.67 Å in $RTeBr_3$ and 2.63-2.76 Å in [2-(dimethylaminomethyl)phenyl]tellurium(IV)-tribromide(139). However it is shorter than the distances in the Te(II) compounds PhTe(tu)Br (3.11 Å)(140), PhTe(etu)Br (2.83 Å)(141) and PhTe(esu)Br (3.05 Å)(142) where the bromine atom is trans to carbon.

Surprisingly there are no intermolecular contacts between the molecules and this result does not help explain the mass spectrum. Without further evidence one can only speculate that the high m/e ions in the mass spectrum arise as a result of thermolysis of the sample.

In collaboration with colleagues at Surrey University, the structure of (RTeCl)$_2$.(R'HgCl) [R= 2-(2'pyridyl)phenyl- and R'= p-ethoxyphenyl-] was determined as part of other work being carried out within the research group. A diagram of the structure is shown in figure 6.4 below. The link between this structure and that of RTeBr is greater than appears on first impression. Both compounds have the organotellurenyl halide (RTeX) molecules present. The molecular dimensions of RTeCl and RTeBr are very similar. Thus the geometry around tellurium in both structures is pseudo-trigonal bipyramidal with the lone pairs on tellurium occupying equatorial positions.

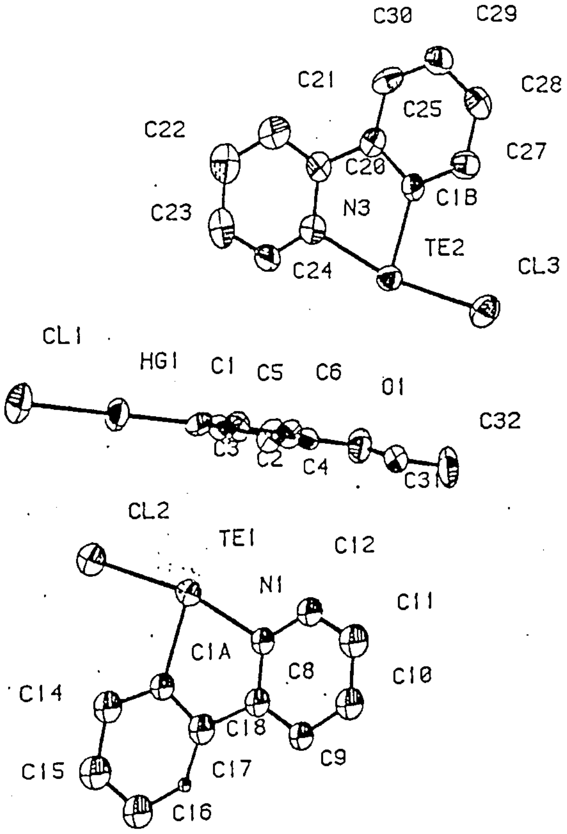


figure 6.4

The Te-N contact in RTeCl (2.24 Å) is similar to the value in RTeBr (mean = 2.24 Å). Both halogens lie trans to nitrogen. In $(RTeCl)_2.(R'HgCl)$ there are no intermolecular contacts between the RTeCl and R'HgCl molecules and the compound can be considered as an "inclusion compound". The interesting crystallographic point is that both compounds have six molecules in the unit cell. It is as if two molecules of RTeX have been replaced by two R'HgCl molecules to form $(RTeCl)_2.R'HgCl$. Based on this point of interest it may be possible to design similar inclusion compounds.

6.4 Experimental and Results

Crystallographic Analysis of 2-(2-pyridyl)phenylselenium(II) tribromomercurate(II).

In the past few years a whole range of organotellurium compounds based on 2-phenylpyridine have been synthesised and their chemistry is now well understood. On the contrary, the analogous selenium compounds were unknown until relatively recently when Mbogo at Aston University attempted some of their synthesis. During his work he encountered some differences in the synthetic pathways to those of the tellurium series(143). As part of this work the crystal structure of 2-(2'-pyridyl)phenylselenium(II) tribromomercurate(II) was solved.

An irregular shaped crystal of size $0.3mm^3$ was mounted on an Enraf Nonius CAD-4 diffractometer. Final cell dimensions and reflection intensities were measured with graphite monochromated Mo-$K\alpha$ radiation with the diffractometer operating in the ω-2θ scan mode. Three standard reflections were measured every three hours to monitor the stability of the system.

The structure was determined by Patterson and Fourier Methods and refined by least squares. Anisotropic thermal parameters were used for the heavier atoms Hg, Se and Br only. Carbon atoms were refined isotropically and hydrogen atoms were placed in calculated positions riding on their respective bonded atom. Details of the data collection are

Crystallographic and Experimental Data. for $RSe^+HgBr_3^-$

Formula	$C_{11}H_8Br_3HgNSe$
Mol Wt.	673.5
Crystal Size mm^{-3},	~0.3
Space Group	C2/c
System	monoclinic
a, Å	16.427(4)
b, Å	13.794(7)
c, Å	6.863(2)
β, deg	109.07(10)
V, $Å^3$	14.698
Z	4
Dcalc, g/cm^3	3.044
μ/ mm^{-1}	21.97
λ(Mo-Kα), Å	0.71069
Temp, °C	25
No. of unique data	1295
Observed Data [$\lvert F>5\sigma \lvert F\rvert$]	612
Scan Range, θ	2-25
Weighting Scheme	$w = 1/[\sigma^2(F) + 0.0001F^2]$
Absorption Correction	empirical (DIFABS)
R	0.093

Table 6.9

given in table 6.9. The molecule appears to be disordered about a two-fold axis, the carbon atom bonded to selenium and the pyridyl nitrogen atom becoming equivalent. Refinement in space group Cc without allowing for disorder did not converge satisfactorily

Computations were carried out on the University of Birmingham Honeywell computer with the SHELX(132-133) suite of programmes. An empirical absorption was applied using DIFABS(144) and the diagrams were drawn using PLUTO(145) at the University of Manchester Regional Computer Centre.

Bond lengths and bond angles are listed in table 6.12, and fractional atomic coordinates in table 6.11. Table 6.13 illustrates mean plane deviations of the atoms. The structure is shown in Figure 6.5 and the packing diagram in Fig 6.6.

6.5 Discussion

Owing to disorder in the structure it was not possible to distinguish between the nitrogen and the carbon atom bonded to selenium and hence the NC-Se bond distances are equivalent [1.91(3) Å]. This distance is close to the sum of the Pauling single bond covalent radii of selenium (1.14 Å) and sp^2 hybridised carbon (0.74 Å). Furthermore a search of the Cambridge structural database(146) for Se-C(sp^2) distances revealed 843 bond lengths with a mean distance of 1.898(2) Å which is in close agreement with the value found here; for

Table 6.10

Anisotropic temperature factors ($Å^2 \times 10^3$) with e.s.d's in parentheses.

	U11	U22	U33	U23	U13	U12
Hg(1)	76(2)	53(2)	110(3)	0	16(2)	0
Br(1)	88(4)	101(4)	111(5)	25(4)	34(4)	30(3)
Br(2)	195(11)	49(4)	65(5)	0	22(6)	0
Se(1)	72(4)	43(3)	3(2)	0	8(2)	0

Table 6.11

Fractional atomic coordinates (x10^4) with e.s.d's in parentheses and equivalent isotropic temperature factors (Å^2 x 10^3).

Ueq = 1/3 (trace of the U tensor)

	x	y	z	U
Hg(1)	0	955(2)	2500	83[a]
Br(1)	-1377(4)	1920(5)	1420(11)	100[a]
Br(2)	0	-851(5)	2500	108[a]
Se(1)	0	3660(4)	2500	40[a]
NC(1)	819(20)	4692(22)	3041(49)	40(8)**
C(2)	455(23)	5566(28)	2811(58)	44(9)
C(3)	1102(28)	6405(34)	3199(66)	61(11)
C(4)	1876(31)	6275(35)	3696(76)	70(13)
C(5)	2217(36)	5346(37)	3907(81)	81(15)
C(6)	1645(24)	4591(28)	3581(61)	47(10)

a Refined anisotropically.

** Due to disorder NC(1) represents 50% C and 50% N.

Fractional atomic coordinates (x10^3) of the hydrogen atoms with e.s.d's in parentheses and isotropic temperature factors (Å^2 x 10^3).

	x	y	z	Uiso
H(3)	903	7155	3072	70
H(4)	2322	6875	3965	70
H(5)	2902	5215	4380	70
H(6)	1897	3843	3636	70

Table 6.12 Bond lengths (Å) and bond angles (°) (e.s.d.'s in parentheses).

Hg(1) --- Br(1)	2.518(6)	C(2) --- C(3)	1.53(6)
Hg(1) --- Br(2)	2.492(8)	C(3) --- C(4)	1.22(6)
Se(1) --- NC(1)	1.91(3)	C(4) --- C(5)	1.39(7)
NC(1) --- C(2)	1.33(5)	C(5) --- C(6)	1.37(6)
NC(1) --- C(6)	1.29(5)	C(2) --- C(2')	1.41(7)

Br(1) -Hg(1) -Br(2)	121.9(2)	NC(1) -C(2) -(C2')	115(4)
Br(1) -Hg(1) -Br(1')	116.2(3)	C(3) -C(2) -C(2')	131(4)
NC(1) -Se(1) -NC(1')	84(2)	C(2) -C(3) -C(4)	123(5)
Se(1) -NC(1)-C(2)	113(2)	C(3) -C(4) -C(5)	121(5)
Se(1) -NC(1)-C(6)	126(3)	C(4) -C(5) -C(6)	117(6)
C(2) -NC(1)-C(6)	121(3)	NC(1) -C(6) -C(5)	124(4)
NC(1)- C(2) -C(3)	114(3)		

Table 6.13

Mean Plane Analysis for $(RSe^+)(HgBr_3^-)$.

Mean Plane Analysis for NC1-C2-C3-C4-C5-C6(Å)

NC1	-0.00568
C2	0.00749
C3	-0.00572
C4	0.00274
C5	-0.00103
C6	0.00220

Mean Plane Analysis for NC2-C7-C8-C9-C10-C11(Å)

NC2	0.00568
C7	-0.00749
C8	0.00572
C9	0.00274
C10	0.00103
C11	-0.00220

Mean Plane Analysis for Se1-NC1-C6-C11-NC2(Å)

Se1	0.00000
NC1	-0.00303
C6	0.00545
C11	-0.00545
NC2	0.00303

Mean Plane Analysis for Hg-Br(1)-Br(2)-Br(1')

Hg1	0.00000
Br1	0.00000
Br2	0.00000
Br1'	0.00000

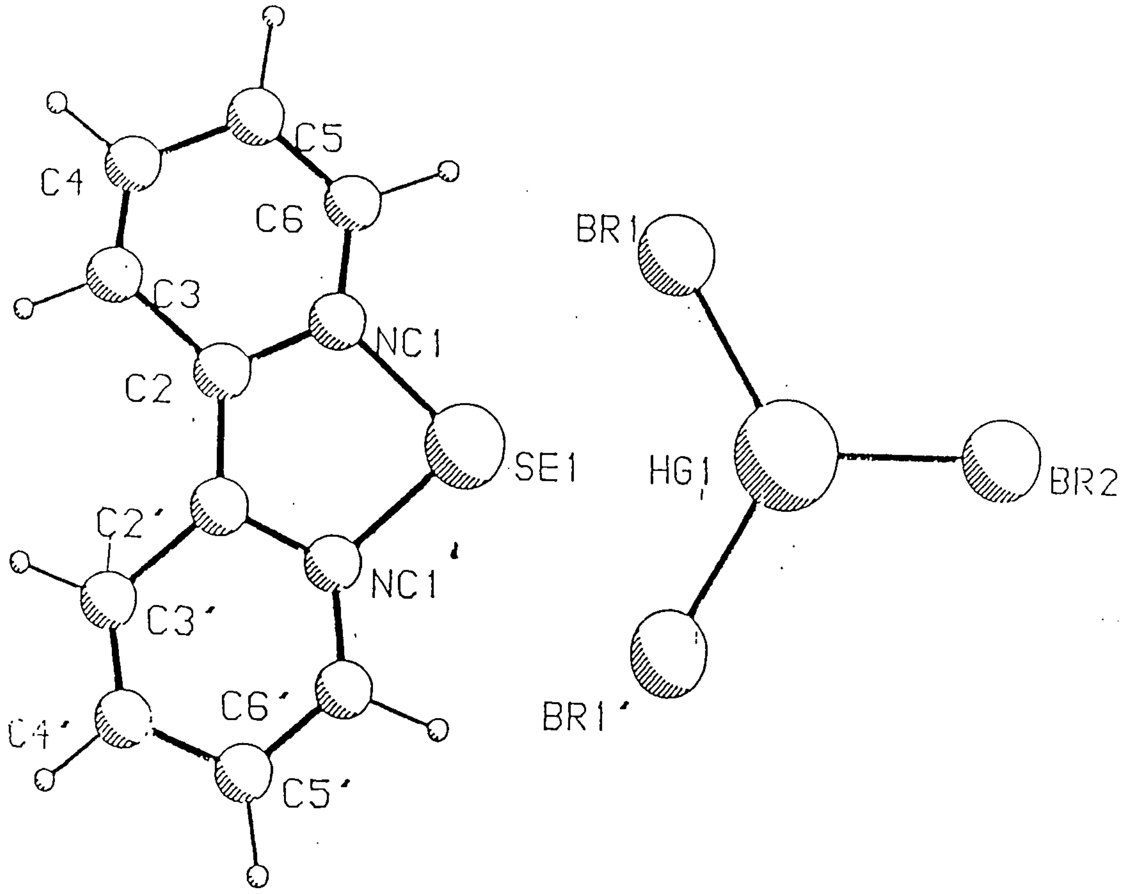


Figure 6.5 Structure of $RSe^{+}HgBr_3^{-}$.

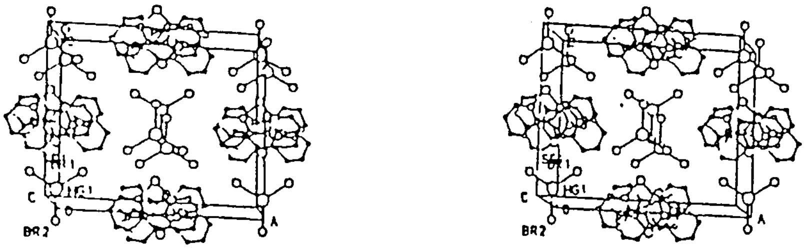


Figure 6.6 Stereoscopic view of $(RSe^{+})(HgBr_{3}^{-})$.

example in the structure of 9,10-diseleno-anthracene(147) the C-Se distances are in the range 1.89(5) to 1.908(5) Å.

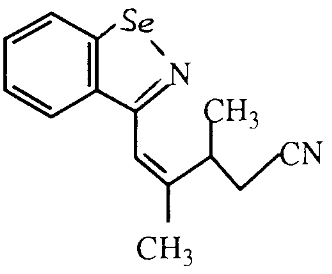
The sum of the Pauling covalent radii of Se (1.14 Å) and N (0.72 Å) is 1.86 Å(138). The Se-N distance is slightly longer, indicating that if this is not a formal bond then it is at least a strong coordinate interaction. This interaction holds the organic group in a planar geometry. The Cambridge structural database yielded 34 Se-N single bond distances, with a mean of 1.82 Å. In the analogous compound 5-(1,2-benzoselenazol-3-yl)-3,4-dimethyl-pentadienylnitrile, the Se-N bond distance is 1.833(7) Å(148). Values of 2.19(2) and 2.20(2) Å for a non-bonded Se-N interaction have also been reported for $SeOCl_2.C_5H_5N$(149).

The $HgBr_3^-$ anion is accurately planar and the RSe^+ cation is planar to within ±0.07 Å. The whole complex is planar to within ±0.02 Å. The Hg-Br distances of 2.518(6) and 2.492(8) Å are in agreement with analogous Hg-Br distances in tetramethylammonium tribromo mercurate(II)(150) (2.48-2.56 Å), bis(tetramethylammonium) tetrabromo mercurate(II)(151) [2.585(3) - 2.589(3) Å] and $HgBr_2$(152) (2.48 Å). A histogram of the Hg-Br distance in the literature peaks in the range 2.45-2.55 Å. The mercury atom has two additional Br atoms as close neighbours Br(2') and Br(2''), completing a trigonal bipyramidal coordination geometry about mercury (see Fig. 6.6) with Hg---Br(2') and Br(2'') 3.43(1) Å. These distances are close to those found in

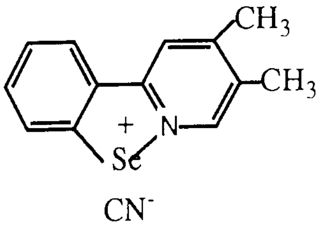
$HgBr_2$(152).

The value of 3.21(1) Å for the Se---Br(1) distance is outside the Pauling single bond length of 2.31 Å, but well within the van der Waals distance of 3.75 Å(138) implying a moderately strong secondary interaction. This interaction may be responsible for the slightly longer Hg---Br(1) bond length relative to the Hg---Br(2) value. The Br(1) atoms related by the two-fold axis lie almost exactly trans to the NC atoms with the NC1-Se-Br(1) angle 177.9°. Also noteworthy is the Hg---Se distance of 3.73(1) Å.

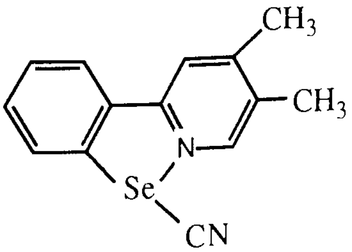
The demonstation of the existence of the 2-(2'pyridyl)phenyl selenium(II) cation, which is isoelectronic with dibenzoselenophene, in this structure is of interest in the context of earlier work. Thus Bryce *et al* (153) suggested that the compound 1(B) is an intermediate in the conversion of 1(A) to 1(C).



1A

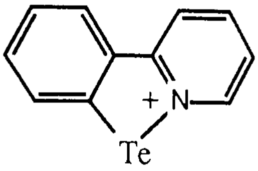


1B

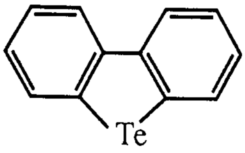


1C

There are similarities between this crystal structure and the 2-(2'-pyridyl)phenyltellurium compounds which have been studied in our laboratory. For example in the mass spectra of the tellurium compounds, the most dominant fragment is RTe^+ which happens to be isoelectronic to dibenzotellurophene, a well known stable compound.



RTe^+



dibenzotellurophene

This species is related to the selenium cation (RSe^+) in the crystal structure above. In the context of MOVPE, it is suggested that the thermal decomposition of compounds of the type RTeR' and RSeR' (R = 2-phenylpyridine and R' = alkyl) is determined by the stability of the these cations.

6.6 Crystallographic Analysis of bis(p-methoxyphenyl)-tellurium(IV) dibenzoate.

Colourless crystals of bis(p-methoxyphenyl)tellurium(IV) dibenzoate were obtained by recrystallisation from ethanol. Analytical, infra-red, N.M.R. and mass spectroscopic data have been used to characterise the compound (chapter 3). Since very little is known about the bonding of carboxylate ligands to tellurium, a crystal structure examination of this compound was undertaken.

A crystal of size 0.2 x 0.2 x 0.1 mm was selected from the batch of crystals and mounted on a CAD-4 diffractometer. The data collection proceeded smoothly but problems were encountered during the refinement. It became apparent that of the 4755 reflections collected (scanned in the range $2 < \theta < 25^0$) only 1473 of these could be used in the final analysis. It is believed that disorder within the structure led to poor data collection. However unit cell dimensions were obtained and are presented here.

Crystal data:-

Monoclinic:-

a = 10.976(2) Å, b = 15.274(3) Å, c = 15.733(3) Å, β =108.34(2)°.

Chapter Seven

RAMAN SPECTROSCOPY

7.1 INTRODUCTION

Raman spectroscopy is a useful technique for structural investigations of compounds. The technique relies on changes in bond polarisability and since tellurium is a large polarisable atom its compounds are attractive for Raman studies. Surprisingly reports on this class of compound in the literature are rare. On the contrary, there are many reports on the infra-red spectra of organotellurium compounds such that their spectra are well understood and have been used for detailed structural investigations. In general Raman spectroscopy has been used to supplement such infra-red data(154). With the emergence of X-ray crystallography as a powerful technique for crystal and molecular structure characterisation, infra-red is no longer the preferred technique for structural studies and has been relegated to the routine examination of tellurium compounds. In recent years our research group has reported a number of organotellurium halides, particularly those of azobenzene and 2-phenylpyridine, some of which have been crystallographically characterised. Since we had access to a FT-Raman spectrometer, we decided to take the opportunity of studying these compounds particularly in the light that tellurium-halogen vibrations should be highly polarisable.

7.2 EXPERIMENTAL

The following compounds were investigated and were prepared by the indicated literature methods; $RTeCl_3$, RTeCl, $RTeBr_3$(78) and RTeBr(78) [where R= 2-(2'-pyridyl)phenyl-]; (pap)$TeCl_3$(90), (pap)TeCl(90) and $(pap)_2Te_2$(90) (pap= 2-phenylazophenyl). $RTeCl_3$ was synthesised by the same method as $RTeBr_3$ but substituting $TeBr_4$ for $TeCl_4$. RTeCl was then obtained by reduction using conditions identical to those given for RTeBr. To extend the number of Te(II) compounds studied, R'TeCl and R'TeBr [R'= 2-(2'-quinolinyl)phenyl-] were prepared in a similar fashion to RTeCl and RTeBr above.

Raman spectra were obtained on a Perkin-Elmer FT-Raman 1700X spectrometer using a NdYag laser operating at 1064nm and a NIR detector cooled to 77K. Spectra were obtained from solids pressed to a powder and held with a cup sample holder. For colourless samples, data were collected using laser powers of 300-500mW. Coloured samples required lower laser power (100-300mW).

Electronic spectra were recorded on a Perkin-Elmer Lamda 9 UV/VIS/NIR spectrometer working in the absorbance mode. Spectra were measured on solutions in acetone contained in 1cm quartz cells. FT-IR spectra were recorded on a Perkin-Elmer 1710 instrument using KBr and polyethylene discs.

7.3 RESULTS

Raman spectra of outstanding quality were obtained for most of the compounds except azobenzene, (pap)TeCl and (pap)$_2$Te$_2$ which gave some problems with fluorescence. Some of the spectra are illustrated in figures 7.1-7.9. By contrast the FT-IR data showed weaker and broader bands, with the additional disadvantage that some analytically useful regions were masked by polyethylene vibrations (CsI could not be used due to its ready metathesis with these compounds). The low frequency Raman data are tabulated for the azobenzene derivatives (table 7.1), the 2-phenylpyridine derivatives (table 7.2) and the 2-phenylquinoline compounds (table 7.3)

Stuctural data are available for some of the compounds studied eg. (pap)TeCl$_3$ (P1, Z=2)(90a), (pap)TeCl (P1, Z=4)(90b), RTeBr$_3$ (P1, Z=2)(78) and RTeBr (P1, Z=6)(136). The compounds crystallising in space group P1, show coincidence of Raman and infra-red bands; the spectra are determined from molecular symmetry. RTeBr is more complex and is discussed further on.

In the high frequency region, bands assignable to υ(N=N) (azobenzene derivatives) and υ(C=N) (2-phenylpyridine and 2-phenylquinoline derivatives) showed enhanced Raman intensities. We therefore recorded the electronic spectra of all compounds but no near infra-red (NIR) bands coincident with or near to the laser frequency

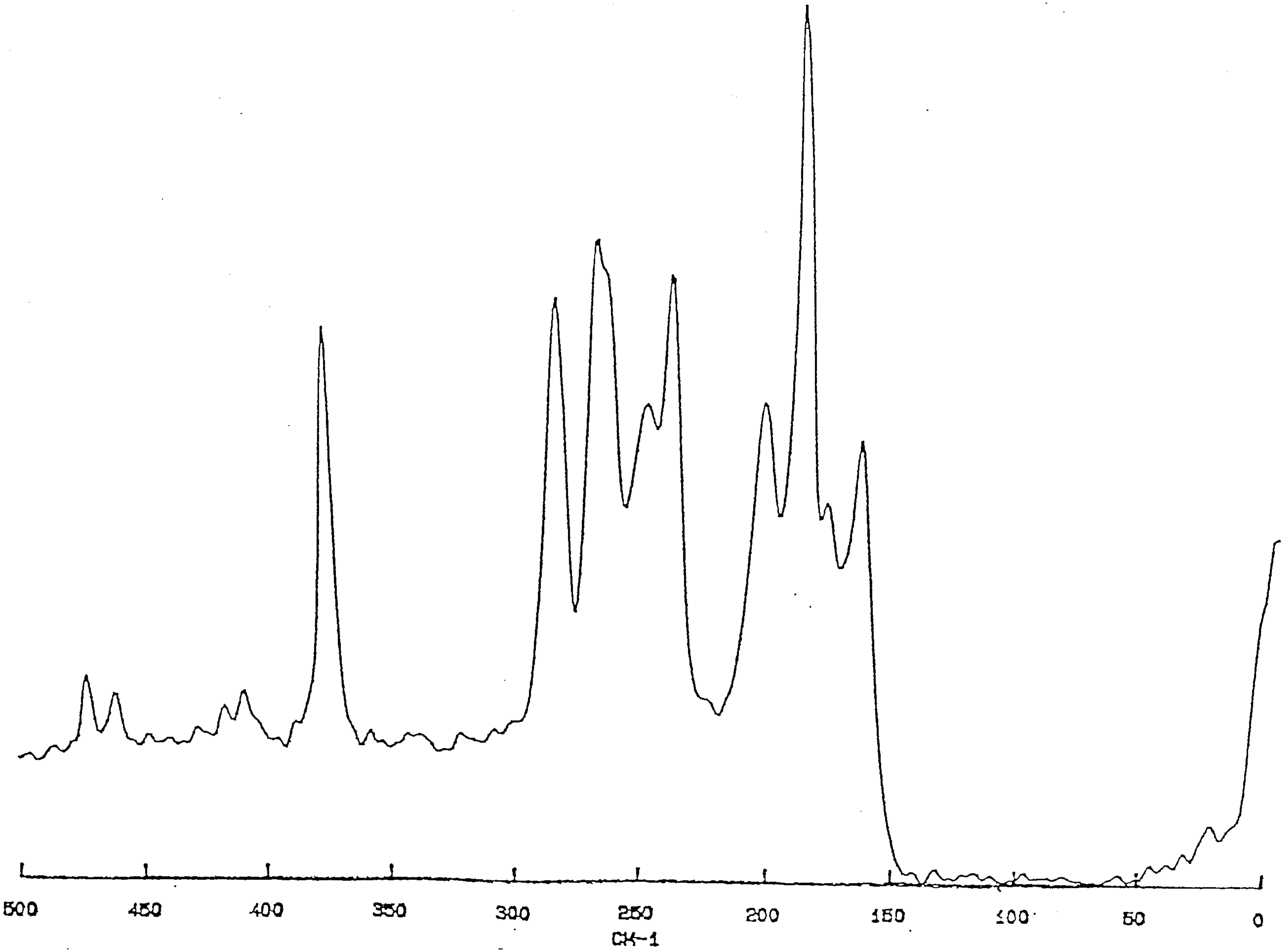


Figure 7.1 Low frequency Raman spectrum of $RTeBr_3$

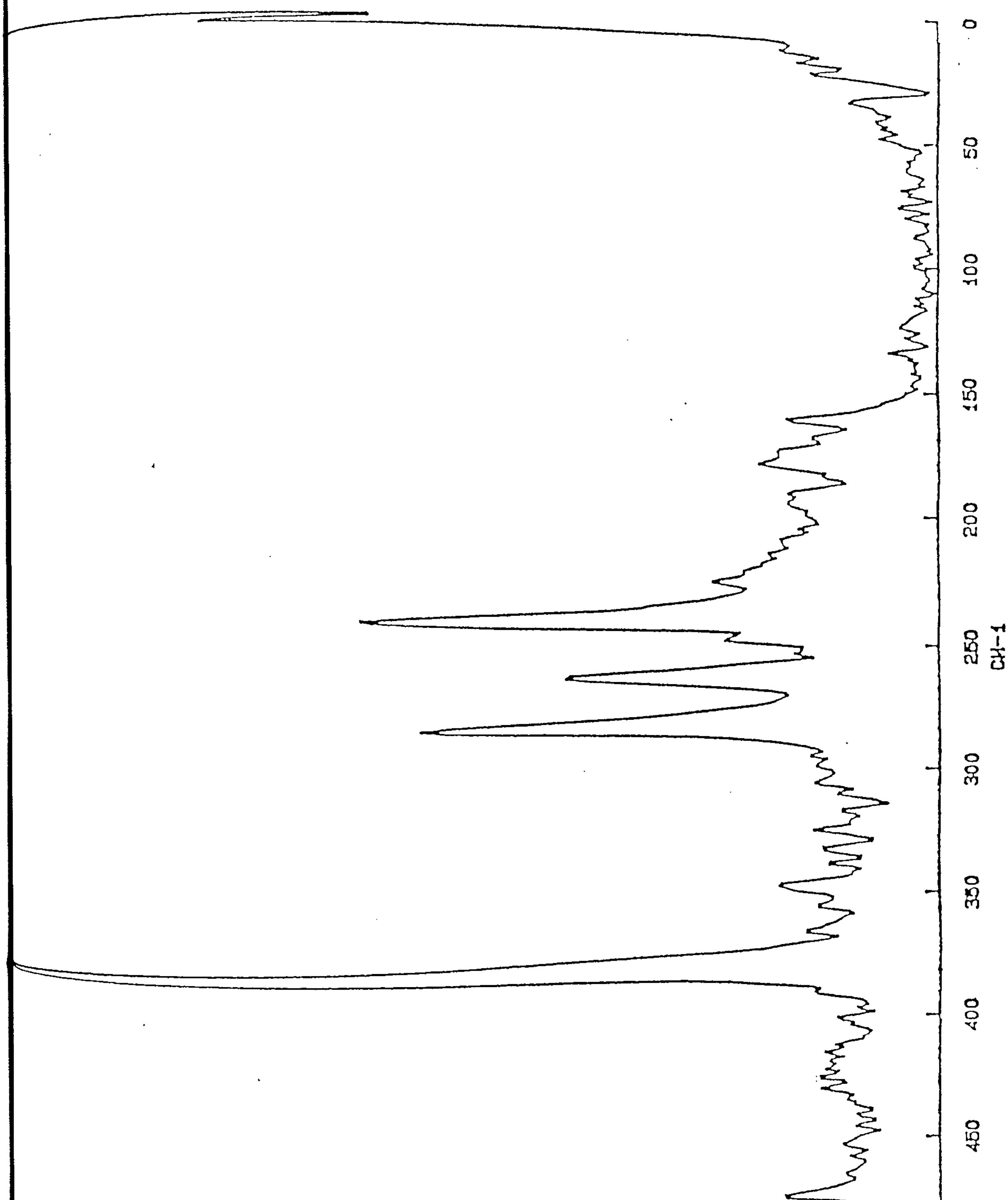


Figure 7.2 Low frequency Raman spectrum of RTeBr

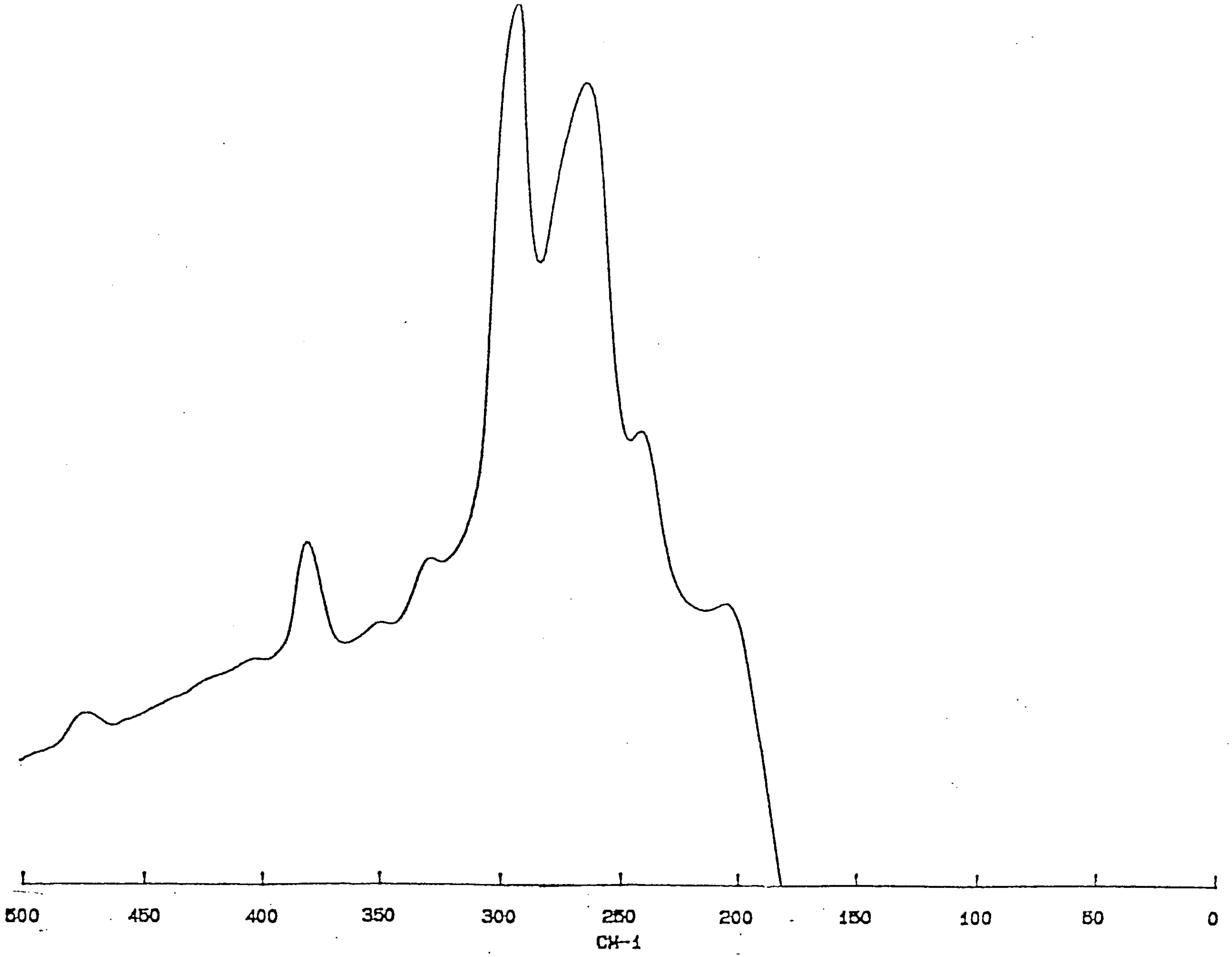


Figure 7.3 Low frequency Raman spectrum of $RTeCl_3$.

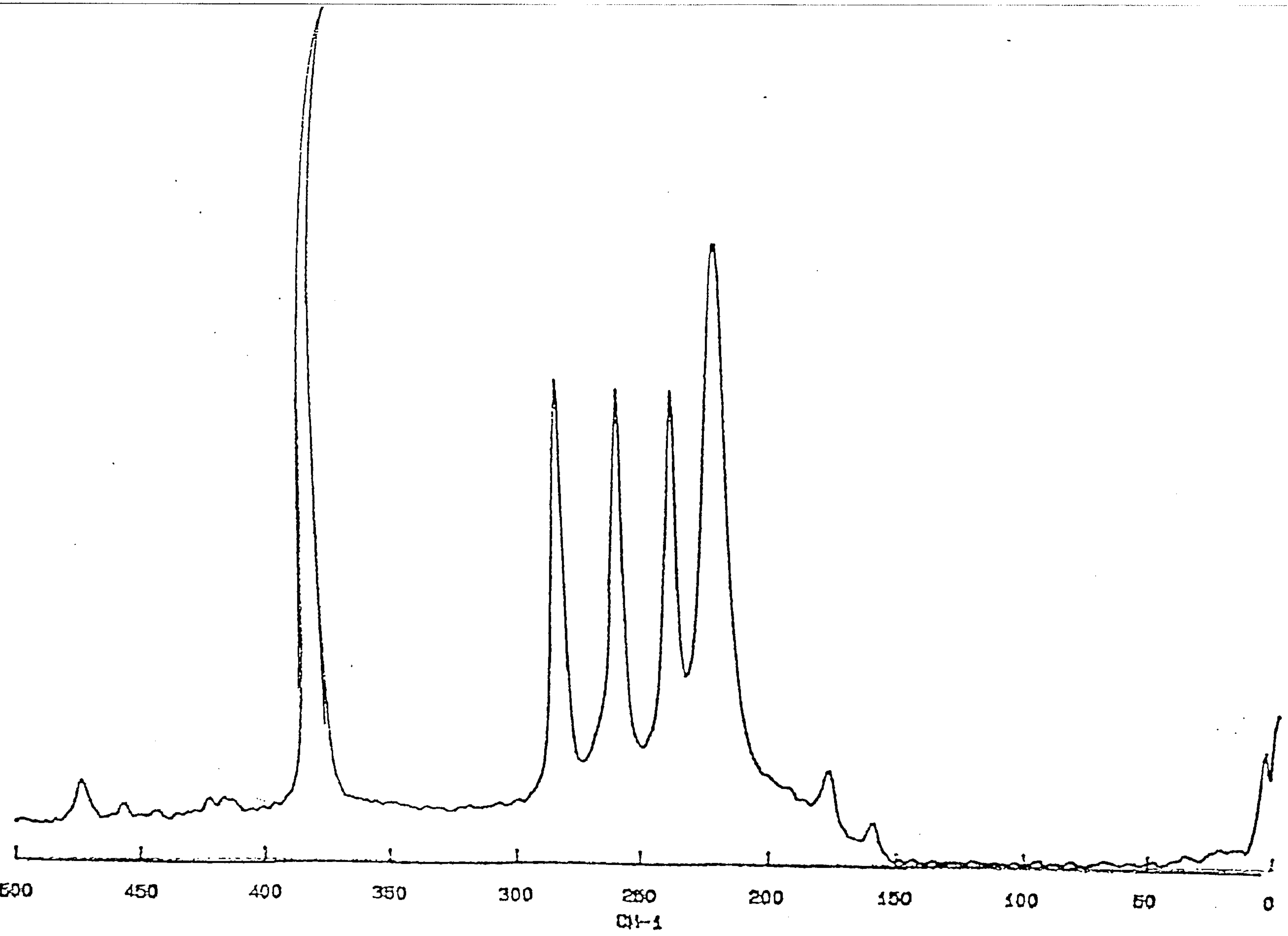


Figure 7.4 Low frequency Raman spectrum of RTeCl.

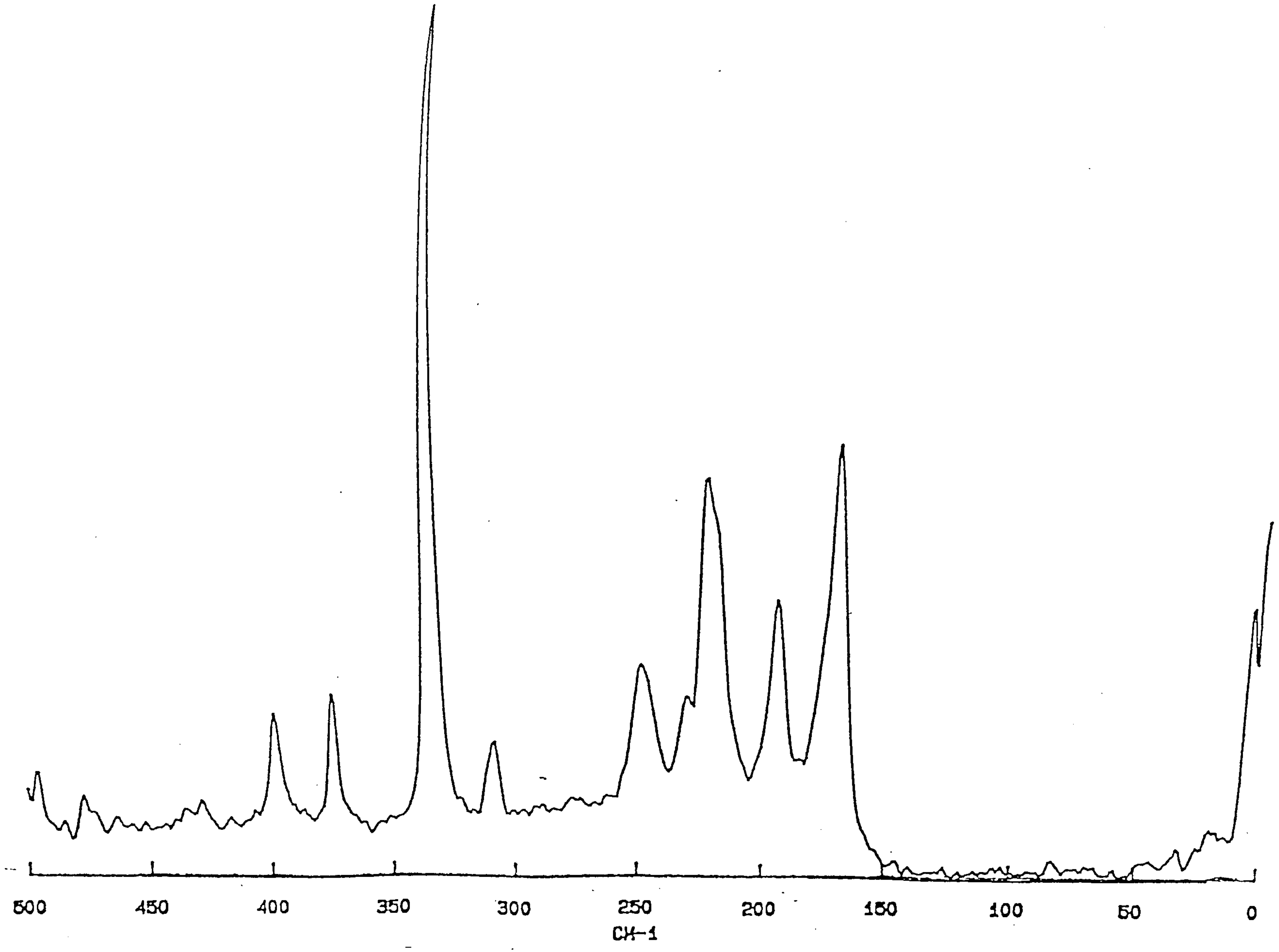


Figure 7.5 Low frequency Raman spectrum of R'TeBr.

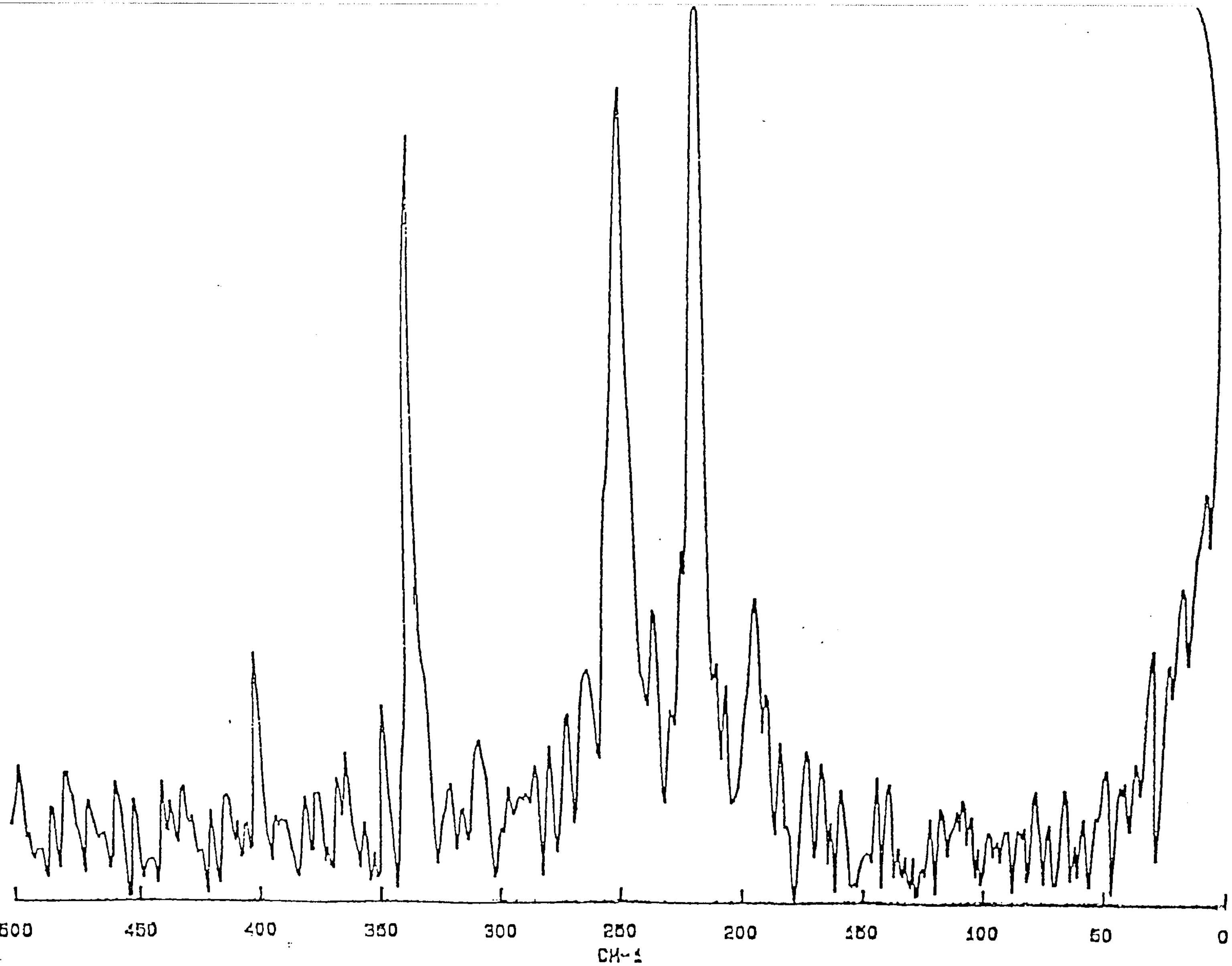


Figure 7.6 Low frequency Raman spectrum of R'TeCl.

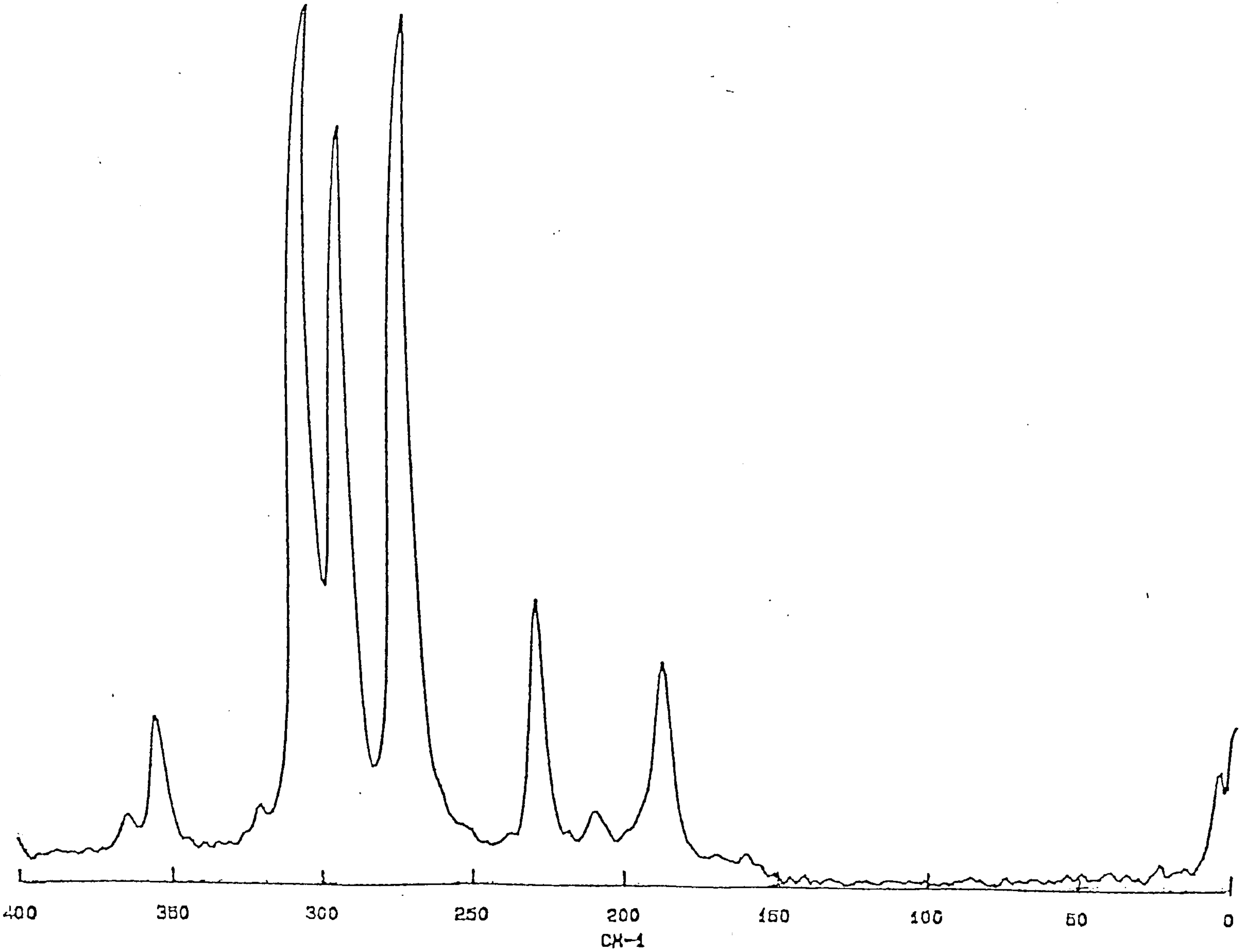


Figure 7.7 Low frequency Raman spectrum of (pap)TeCl$_3$.

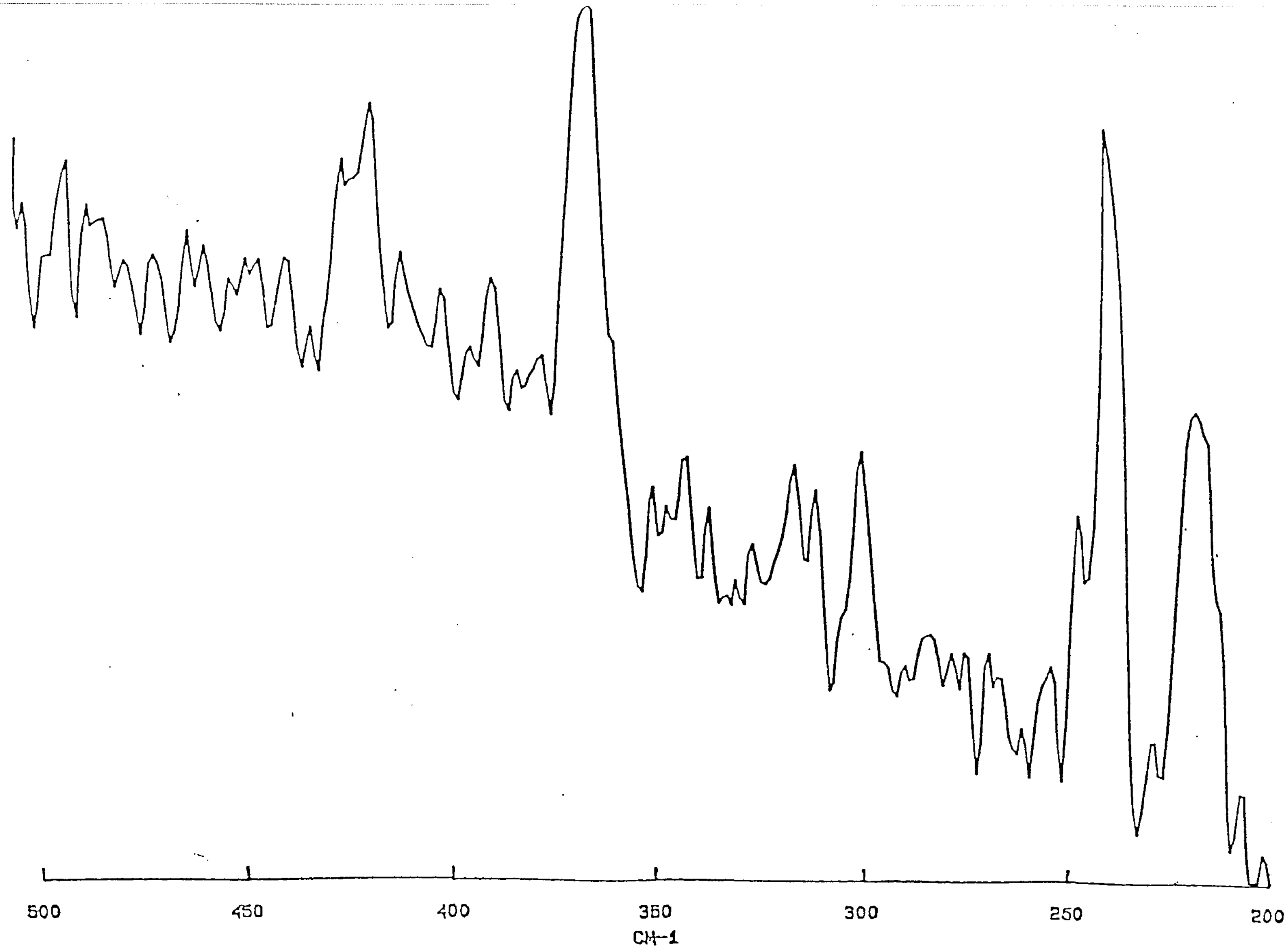


Figure 7.8 Low frequency Raman spectrum of (pap)TeCl.

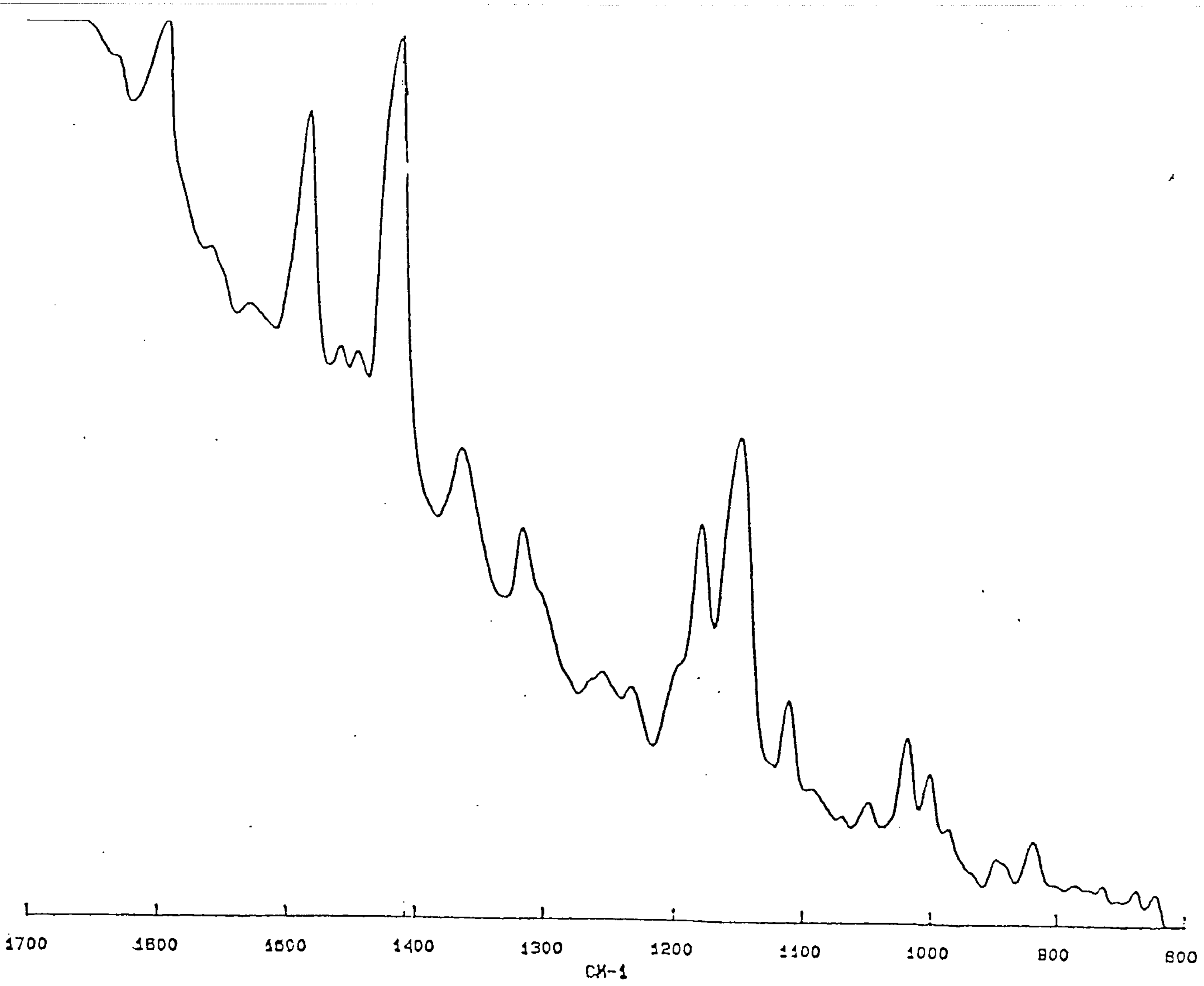


Figure 7.9 Raman spectrum of $(pap)_2Te_2$.

(1064nm) were observed. No resonance or pre-resonance enhancement need be considered.

7.4 DISCUSSION

The scarcity of Raman vibrational spectroscopic data for organotellurium compounds led us to probe a series of well characterised compounds featuring tellurium-halogen bonds. The quality of the Raman spectra was far more impressive than the infra-red traces and it is recommended that where available, Raman spectroscopy is the more useful of the two vibrational spectroscopic techniques.

In azobenzene υ(N=N) was located at 1433cm^{-1}. Telluration of this ligand to produce (pap)TeCl$_3$ and (pap)TeCl with consequent Te-N coordination leads to lowering of the υ(N=N) frequencies to 1410 and 1375cm^{-1} respectively. The lower frequency for the Te(II) compound reflects the stronger Te<-N interaction [N.B Te-N bond lengths are for (pap)TeCl {2.23(2) and 2.19(2) Å} and for (pap)TeCl$_3$ {2.417(4) Å}].

McWhinnie and coworkers studied the ^{125}Te Mossbauer spectroscopy of these compounds(155). The quadrupole splitting value (Δ) can be used to predict changes in p-electron density around tellurium. Compounds of the type RTeX$_3$ have been shown to have quadrupole splitting values of ~9.0 mms^{-1} and for RTeX of ~14 mms^{-1}. The value for (pap)TeCl$_3$ is 8.1 mms^{-1} is in accord with expectation. However (pap)TeCl shows $\Delta=11.8\mathrm{mms}^{-1}$ much lower than expected. One possibility is that the p-electron density is drained away from tellurium and is delocalised in the $\overline{\mathrm{C{=}C{-}N{=}N{\rightarrow}Te}}$ ring. This assumption is likely since the C-N and N=N bond lengths are longer than in azobenzene and there is a strong Te<-N interaction. Therefore the lowering of the Raman υ(N=N) vibrations in the azobenzene derivatives is consistent with the results obtained from the Mossbauer study.

The tellurium-halogen vibrations are readily assigned and are indicated in tables 7.1-7.3. The spectra of the azobenzene derivatives are "cleaner" in that the tellurium halogen vibrations overlap less with the X-sensitive modes of the organic ligand (ie. ligand bands (R) which shift on substitution with X groups in RX).

In a previous report by McWhinnie and coworkers the υ(Te-Cl) stretching vibration in (pap)TeCl has been assigned at 247cm^{-1} using infra-red data(70b). This assignment seemed reasonable since (pap)TeCl$_3$ showed no major bands in this region and υ(Te-Cl) was expected to be lower in Te(II) than Te(IV) compounds. In the Raman spectrum a further band at 220cm^{-1} is observed. This band is obscurred in the infra-red spectrum by strong polyethylene absorptions. Comparison of the spectra of RTeCl and RTeBr shows that υ(Te-Cl) is located at 218cm^{-1}. The molecular dimensions of RTeCl have been determined in the inclusion compound (RTeCl)$_2$(R'HgCl) (R'= p-ethoxyphenyl-)(136) in which the Te-Cl bond distance is 2.558 Å, similar to values reported in (pap)TeCl (ie. 2.552(8) and 2.549(8) Å). Therefore using this evidence it is suggested that the band at 220cm^{-1} is a Te-Cl vibration and the original assignment of 247cm^{-1} (IR) must be revised and may be a candidate for a Te-N vibrational mode. To support this observation, a strong band in the Raman spectrum of R'TeCl (R'= 2-(2'-quinolinyl)phenyl) at 218cm^{-1} is also asigned as υ(Te-Cl).

The crystal and molecular structure of RTeBr (R= 2-(2'-pyridyl)-phenyl) has been solved (see chapter six). The compound crystallises in space group P1 and there are six non-symmetry related molecules in the asymmetric unit. In the Raman spectrum the υ(Te-Br) region appears more complex than expected if only the molecular symmetry determined the selection rules. A weak band at υ= 168cm^{-1} is assigned as υ(Te-Br) which is similar to the value of υ= 165cm^{-1} observed in R'TeBr [R'= 2-(2'-quinolinyl)phenyl].

The low frequency Raman spectra of the 2-phenylpyridine and 2-phenylquinoline compounds are very rich (from X-sensitive contributions) and for this reason no Te-N assignment can be made.

In summary, the superior quality of the Raman spectra observed compared to the infra-red spectra, leads to the conclusion that where available, Raman spectroscopy is the technique of choice.

Table 7.1 Low frequency FT-Raman data for some tellurated 2-phenylpyridines.

$RTeCl_3$	$RTeBr_3$	RTeCl	RTeBr	RH	
377 m	375 m	379 s	377 s		
349 w					
329 w				322 w	
283 v.s	282 m	285 m	282 m		υ(TeCl)
266 s	266 m	260 m	259 m	261 sh	υ(TeCl)
	263 sh			256 sh	
241 m	247 m	240 m	238 m.s	246 s	
	236 m				
		218 s			υ(TeCl)
204 m	202 m				
	186 s				υ(TeBr)
	176 m	175 w	179 w.m		υ(TeBr)
	164 m		173 w.m		
		158 w	168 w.m		υ(TeBr)
			161 w.m		

R= 2-(2'pyridylphenyl)-

s= strong; m= medium; w= weak; sh= shoulder.

Table 7.2 Low frequency FT-Raman data for some tellurated azobenzene compounds.

(pap)$TeCl_3$	(pap)TeCl	
365 w	369 w	
354 w.m		
320 w		
303 v.s		υ(TeCl)
288 s		υ(TeCl)
272 v.s		υ(TeCl)
232 m	242 m	
	220 m.s	υ(TeCl)
210 w		
184		

pap= phenylazophenyl-

w= weak; m= medium; s= strong.

Table 7.3 **Low frequency FT-Raman data for some tellurated 2-phenylquinoline compounds.**

R'TeCl	R'TeBr	
399 w	395 w	
	372 w	
337 s		
335 sh	330 sh	
	307 w	
250 sh		
247 s	248 w.m	
	230 sh	
225 sh	222 m	
218 vs	220 sh	υ(TeCl)
193 w	193 w.m	
	165 m	υ(TeBr)

R'= 2-(2'-quinolinyl)phenyl-
w= weak; m= medium; s= strong

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APPENDIX

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                          PAGE  1

  H  K   L  10FO  10FC 10S      H  K   L  10FO  10FC 10S      H  K   L  10FO  10FC 10S      H  K   L  10FO  10FC 10S      H  K   L  10FO  10FC 10S

 -5-14  -1    77     5 -46      1-10  -1    13     0-334     -3 -7  -1    89     1 -20      5 -5  -1   305   306  10     10 -3  -1   209   175  19
 -4-14  -1   121     8 -29      2-10  -1    76     3 -55     -2 -7  -1   398   408  10      6 -5  -1   328   311  10     11 -3  -1    26     2-202
 -3-14  -1    15     1-336      3-10  -1   101     4 -29     -1 -7  -1   751   822  11      7 -5  -1   221   185  15    -12 -2  -1   281   302  16
 -8-13  -1    15     1-366      4-10  -1    14     1-358      0 -7  -1   859   833  11      8 -5  -1   290   286  14    -11 -2  -1   418   422  12
 -7-13  -1    15     1-355      5-10  -1    82     5 -63      1 -7  -1   933   924  12      9 -5  -1   176   170  23    -10 -2  -1   372   418  11
 -6-13  -1   227   240  19    -12 -9  -1   230   233  21      2 -7  -1    46     1 -45     10 -5  -1   320   330  15     -9 -2  -1   254   285  13
 -5-13  -1    70     4 -70    -11 -9  -1    14     1-360      3 -7  -1    76     2 -45    -13 -4  -1    91     6 -42     -8 -2  -1   573   592  11
 -4-13  -1    14     1-347    -10 -9  -1   172   220  23      4 -7  -1   774   739  12    -12 -4  -1   406   385  12     -7 -2  -1   389   416  10
 -3-13  -1   243   262  18     -9 -9  -1    73     3 -41      5 -7  -1   753   762  12    -11 -4  -1   286   284  14     -6 -2  -1   580   630   9
 -2-13  -1    14     1-333     -8 -9  -1     8     0-327      6 -7  -1   178   164  21    -10 -4  -1    12     0-319     -5 -2  -1   425   426   9
 -1-13  -1   179   215  24     -7 -9  -1   380   383  10      7 -7  -1   271   212  15     -9 -4  -1   734   750  12     -4 -2  -1   460   462   8
  0-13  -1   225   243  20     -6 -9  -1   179   171  17      8 -7  -1    72     4 -67     -8 -4  -1  1294  1329  15     -3 -2  -1  1924  1775  20
  1-13  -1   157   150  28     -5 -9  -1   898   916  12    -13 -6  -1   254   239  19     -7 -4  -1   411   385  11     -2 -2  -1   226   171   7
 -9-12  -1   356   371  14     -4 -9  -1   347   334  10    -12 -6  -1   322   310  14     -6 -4  -1   160   187  13     -1 -2  -1   321   346   8
 -8-12  -1   107     6 -33     -3 -9  -1   405   427  11    -11 -6  -1   217   240  18     -5 -4  -1   562   587   9      0 -2  -1   851   822   9
 -7-12  -1    78     4 -62     -2 -9  -1   218   224  14    -10 -6  -1   174   184  19     -4 -4  -1   352   335   9      1 -2  -1  1070   905  12
 -6-12  -1    14     1-334     -1 -9  -1   743   753  12     -9 -6  -1   405   345  11     -3 -4  -1   323   329   9      2 -2  -1   475   454   8
 -5-12  -1   400   398  11      0 -9  -1   502   511  13     -8 -6  -1   703   731  12     -2 -4  -1   288   266   7      3 -2  -1   517   518   9
 -4-12  -1   258   269  16      1 -9  -1    59     2 -43     -7 -6  -1   675   646  11     -1 -4  -1  1540  1604  16      4 -2  -1   975   996  11
 -3-12  -1   204   190  19      2 -9  -1    12     0-322     -6 -6  -1   938   922  12      0 -4  -1  1788  1790  18      5 -2  -1  1229  1260  14
 -2-12  -1    85     4 -35      3 -9  -1   402   386  10     -5 -6  -1   305   284   9      1 -4  -1   652   668   9      6 -2  -1   115   122  20
 -1-12  -1    65     3 -71      4 -9  -1   105     4 -28     -4 -6  -1  1234  1230  14      2 -4  -1   301   276   8      7 -2  -1   515   510  11
  0-12  -1   287   258  15      5 -9  -1    75     4 -61     -3 -6  -1   554   535   9      3 -4  -1  1335  1329  15      8 -2  -1   728   720  12
  1-12  -1   289   291  16      6 -9  -1    52     3 -94     -2 -6  -1   439   456  10      4 -4  -1  1113  1078  13      9 -2  -1   674   676  13
  2-12  -1    15     1-353    -12 -8  -1   256   270  19     -1 -6  -1   204   211  11      5 -4  -1   382   371  11     10 -2  -1    14     1-335
  3-12  -1    88     6 -61    -11 -8  -1    71     3 -67      0 -6  -1   362   382  10      6 -4  -1    11     0-300     11 -2  -1    86     5 -58
-10-11  -1   326   324  15    -10 -8  -1   179   174  21      1 -6  -1  1082  1038  13      7 -4  -1   176   199  17    -12 -1  -1   248   264  18
 -9-11  -1    69     3 -74     -9 -8  -1   462   456  12      2 -6  -1   633   635  10      8 -4  -1   219   212  16    -11 -1  -1   206   226  19
 -8-11  -1   481   477  12     -8 -8  -1   766   763  12      3 -6  -1   158   150  16      9 -4  -1    57     3 -54    -10 -1  -1   325   350  11
[illegible]-11  -1    37     1 -83     -7 -8  -1   195   209  16      4 -6  -1   249   262  11     10 -4  -1   125     7 -26     -9 -1  -1   983   988  13
 -6-11  -1   103     4 -26     -6 -8  -1    83     2 -25      5 -6  -1   176   178  17    -13 -3  -1   274   265  18     -8 -1  -1   612   635  11
 -5-11  -1    70     2 -60     -5 -8  -1   274   290  11      6 -6  -1   502   515  13    -12 -3  -1   396   402  12     -7 -1  -1   297   334   9
 -4-11  -1    46     2 -94     -4 -8  -1   976   977  12      7 -6  -1   213   183  17    -11 -3  -1   388   415  12     -6 -1  -1   421   468  10
 -3-11  -1   341   348  11     -3 -8  -1   594   634  11      8 -6  -1   206   198  20    -10 -3  -1   333   336  11     -5 -1  -1   222   245   9
 -2-11  -1   409   437  10     -2 -8  -1   229   205  12      9 -6  -1   358   332  14     -9 -3  -1   354   371  10     -4 -1  -1   346   340   8
 -1-11  -1   303   289  12     -1 -8  -1   259   300  11    -13 -5  -1   197   199  23     -8 -3  -1   692   740  11     -3 -1  -1   802   789   9
  0-11  -1   151   189  25      0 -8  -1    77     2 -45    -12 -5  -1    14     1-344     -7 -3  -1   272   325   9     -2 -1  -1  1279  1143  13
  1-11  -1    71     3 -63      1 -8  -1   687   695  11    -11 -5  -1   220   270  18     -6 -3  -1   389   397  10     -1 -1  -1  1175  1107  12
  2-11  -1   281   262  15      2 -8  -1   196   175  15    -10 -5  -1   197   157  16     -5 -3  -1   958   924  11      0 -1  -1   699   622   8
  3-11  -1   208   173  20      3 -8  -1   352   330  10     -9 -5  -1   747   772  12     -4 -3  -1  1710  1656  18      1 -1  -1   526   499   7
  4-11  -1    15     1-353      4 -8  -1   776   779  13     -8 -5  -1   312   306  10     -3 -3  -1  1437  1410  15      2 -1  -1     6     0-318
-11-10  -1   171   223  26      5 -8  -1    90     3 -33     -7 -5  -1   366   387  11     -2 -3  -1   257   296   7      3 -1  -1   241   234   8
-10-10  -1   175   200  24      6 -8  -1    34     2-133     -6 -5  -1   533   489  10     -1 -3  -1   440   455   8      4 -1  -1  1122  1132  13
 -9-10  -1   271   300  16      7 -8  -1   150   141  28     -5 -5  -1  2054  2009  21      0 -3  -1  3673  3619  39      5 -1  -1  1234  1241  14
 -8-10  -1    25     1-121    -12 -7  -1   260   266  18     -4 -5  -1   583   582   9      1 -3  -1   574   588   8      6 -1  -1   547   558  10
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

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9	12	-1	15	1	-372

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                    PAGE  3
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  2 13  -1   225   239  19      0-10   0   154   163  21     -3 -7   0   483   488  10      7 -5   0   435   438  13    -10 -2   0   377   412  11
  3 13  -1   113     7 -31      1-10   0   431   424  11     -2 -7   0   925   896  11      8 -5   0   295   284  13     -9 -2   0   592   610  12
  4 13  -1   275   276  17      2-10   0    60     2 -75     -1 -7   0   164   156  14      9 -5   0   163   162  24     -8 -2   0   168   167  16
  5 13  -1    10     1-354      3-10   0   314   295  13      0 -7   0  1196  1250  14     10 -5   0    56     4 -94     -7 -2   0   534   552  10
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  7 13  -1    62     4 -86      5-10   0   130     8 -26      2 -7   0    11     0-308    -11 -4   0   166   177  23     -5 -2   0  2077  2172  21
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                                            PAGE  4
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  -7   0   0   308   314   9       1   2   0   775   802   9       7   4   0  1244  1167  14      -6   7   0   398   383  10       8   9   0   266   271  13
  -6   0   0   543   538  10       2   2   0   583   580   8       8   4   0   434   418  11      -5   7   0   605   604  13       9   9   0   386   392  12
  -5   0   0   299   286   8       3   2   0     7     0-305       9   4   0   576   574  12      -4   7   0   303   289  11      10   9   0   244   247  17
  -4   0   0   962  1081  11       4   2   0   524   500   8      10   4   0   197   232  17      -3   7   0    11     0-314      11   9   0   192   219  23
  -3   0   0   739   819   9       5   2   0  2101  2176  22      11   4   0   210   207  18      -2   7   0   121   137  21      -5  10   0   150   153  28
  -2   0   0   195   194   8       6   2   0   473   485   9      12   4   0   154   234  29      -1   7   0   195   179  13      -4  10   0   170   166  24
   2   0   0   164   198   9       7   2   0   551   552  10     -10   5   0    10     1-352       0   7   0  1167  1241  13      -3  10   0   300   304  14
   3   0   0   734   812   9       8   2   0   144   163  18      -9   5   0   190   161  22       1   7   0   186   174  13      -2  10   0   140   158  25
   4   0   0   977  1075  11       9   2   0   597   602  12      -8   5   0   264   295  15       2   7   0   894   915  11      -1  10   0   428   415  11
   5   0   0   308   313   9      10   2   0   420   419  11      -7   5   0   400   439  14       3   7   0   481   490  11       0  10   0   150   176  22
   6   0   0   536   550   9      11   2   0   174   154  22      -6   5   0   151   140  19       4   7   0   911   871  12       1  10   0   480   533  12
   7   0   0   307   297   9      12   2   0   151   182  28      -5   5   0   415   403  10       5   7   0   418   403  10       2  10   0   176   217  18
   8   0   0   754   771  11     -11   3   0   255   258  18      -4   5   0   826   863  11       6   7   0   424   384  11       3  10   0   399   425  11
   9   0   0   189   181  16     -10   3   0    14     1-351      -3   5   0   757   758  10       7   7   0   181   149  16       4  10   0   161   159  20
  10   0   0   337   346  11      -9   3   0   441   435  13      -2   5   0   292   305   8       8   7   0   354   330  12       5  10   0    12     0-328
  11   0   0   283   272  15      -8   3   0   199   184  16      -1   5   0   706   751  10       9   7   0   549   534  13       6  10   0   289   325  12
  12   0   0   353   367  14      -7   3   0   429   454  12       0   5   0   692   740   9      10   7   0   316   286  13       7  10   0    34     1-123
 -12   1   0   178   185  26      -6   3   0   514   522  11       1   5   0   607   678   9      11   7   0   207   252  20       8  10   0   391   402  12
 -11   1   0   460   459  12      -5   3   0   827   806  11       2   5   0   301   306   8      12   7   0   423   404  13       9  10   0   292   306  15
 -10   1   0    59     2 -74      -4   3   0   473   501  10       3   5   0   401   388   9      -7   8   0    48     3-107      10  10   0    96     5 -52
  -9   1   0   244   233  14      -3   3   0   196   234  10       4   5   0  2043  1951  21      -6   8   0   147   209  27      11  10   0   166   202  28
  -8   1   0   326   342  10      -2   3   0   767   760   9       5   5   0  1095   987  13      -5   8   0   303   307  14      -4  11   0   258   254  18
  -7   1   0   134   122  18      -1   3   0  2327  2363  24       6   5   0   174   198  13      -4   8   0   279   265  13      -3  11   0   236   239  19
  -6   1   0   347   346   8       0   3   0   117    99  15       7   5   0   121   115  20      -3   8   0   510   517  13      -2  11   0   163   193  25
  -5   1   0   674   691  10       1   3   0   721   763   9       8   5   0   914   837  12      -2   8   0   425   443  12      -1  11   0   109     5 -29
  -4   1   0   717   702   9       2   3   0   416   344   8       9   5   0   694   612  12      -1   8   0   575   626  12       0  11   0   309   326  13
  -3   1   0  2135  2169  22       3   3   0  1182  1134  13      10   5   0   378   378  10       0   8   0   380   430  11       1  11   0   160   172  21
  -2   1   0   249   237   7       4   3   0  1351  1274  15      11   5   0    14     1-337       1   8   0   449   483  12       2  11   0   168   187  20
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   6   1   0   204   216  10      11   3   0   314   324  13      -4   6   0   128   112  21       8   8   0   661   622  12       9  11   0   348   333  14
   7   1   0   473   482  11      12   3   0   322   305  15      -3   6   0   360   359   9       9   8   0   634   582  13      10  11   0   103     6 -34
   8   1   0  1292  1327  15     -10   4   0   197   203  22      -2   6   0   260   272  10      10   8   0   367   343  12      -3  12   0   117     8 -31
   9   1   0   780   787  12      -9   4   0    52     2 -87      -1   6   0   429   434  11      11   8   0   285   305  16      -2  12   0   195   225  23
  10   1   0   137   165  24      -8   4   0   262   227  13       0   6   0   159   168  14      12   8   0   406   370  13      -1  12   0   165   175  25
  11   1   0   104     5 -29      -7   4   0   255   257  13       1   6   0  1233  1323  14      -6   9   0   151   162  27       0  12   0    54     3 -90
  12   1   0   281   246  16      -6   4   0   243   237  12       2   6   0   189   194  11      -5   9   0   324   310  13       1  12   0    55     3 -57
 -11   2   0   174   185  24      -5   4   0   751   757  11       3   6   0  1184  1128  13      -4   9   0   171   151  22       2  12   0     9     0-330
 -10   2   0   434   432  11      -4   4   0  1945  1929  20       4   6   0   312   287   8      -3   9   0   231   228  15       3  12   0    14     1-344
  -9   2   0   621   612  13      -3   4   0   260   252   8       5   6   0   996   935  12      -2   9   0   288   316  12       4  12   0   440   455  11
  -8   2   0   505   515  13      -2   4   0   347   337   9       6   6   0    25     0-121      -1   9   0   274   270  12       5  12   0   173   120  23
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  -6   2   0   237   270  10       0   4   0  1399  1484  15       8   6   0   328   324  10       1   9   0   261   277  12       7  12   0   396   124  42
  -5   2   0   559   558   9       1   4   0   843   864  10       9   6   0   336   305  11       2   9   0   175   220  17       8  12   0   389   371  12
  -4   2   0   646   654   9       2   4   0   106   113  17      10   6   0   175   125  19       3   9   0    11     0-334       9  12   0   173   130  26
  -3   2   0   817   804  10       3   4   0   967   836  11      11   6   0   274   263  15       4   9   0   756   791  12       0  13   0    73     5 -74
  -2   2   0   724   648   9       4   4   0  1639  1504  17      12   6   0   317   303  15       5   9   0   537   526  12       1  13   0   229   203  19
  -1   2   0    30     0 -66       5   4   0   346   310   9      -8   7   0    96     5 -36       6   9   0    70     2 -33       2  13   0    97     5 -51
   0   2   0   195   208   8       6   4   0   407   378  10      -7   7   0    76     3 -40       7   9   0   335   320  11       3  13   0    72     4 -70
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                   PAGE  5

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  4 13  0    72     4 -71     3-10  1   304   318  14     0 -7  1   207   213  12    10 -5  1    74     5 -46    -7 -2  1   307   315   9
  5 13  0   260   281  17     4-10  1   307   305  14     1 -7  1   742   767  11   -12 -4  1   472   467  14    -6 -2  1   135   142  15
  6 13  0    29     2-173     5-10  1    15     1-350     2 -7  1   320   326  10   -11 -4  1   213   216  18    -5 -2  1  1600  1591  17
  7 13  0    74     5 -76   -11 -9  1    15     1-373     3 -7  1   551   561  11   -10 -4  1   431   443  13    -4 -2  1  2412  2568  25
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  0-13  1   237   210  18    -3 -9  1   315   310  10   -10 -6  1   268   308  15    -2 -4  1   848   787  10     4 -2  1   395   389   9
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  0-11  1    13     1-326     1 -8  1   393   382  10    -9 -5  1   706   723  12    -2 -3  1   553   506   8     3 -1  1   870   883  10
  1-11  1   187   181  20     2 -8  1   376   364  10    -8 -5  1   420   463  11    -1 -3  1  1683  1666  17     4 -1  1  3074  3092  36
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

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-2	0	1	433	381	8	4	2	1	471	454	8	9	4	1	755	759	12	-7	7	1	247	212	16	7	9	1	390	385	11
-1	0	1	674	702	8	5	2	1	446	434	9	10	4	1	12	0	-318	-6	7	1	170	170	22	8	9	1	13	0	-333
1	0	1	1843	2064	21	6	2	1	607	648	9	11	4	1	281	282	15	-5	7	1	760	748	12	9	9	1	139	140	27
2	0	1	448	427	7	7	2	1	404	445	10	12	4	1	420	401	13	-4	7	1	772	728	12	10	9	1	189	217	22
3	0	1	340	348	9	8	2	1	589	586	11	13	4	1	48	3	-121	-3	7	1	64	1	-35	11	9	1	173	130	25
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8	0	1	84	2	-26	-11	3	1	10	1	-354	-6	5	1	308	318	11	2	7	1	404	412	10	-2	10	1	92	3	-47
9	0	1	321	303	10	-10	3	1	215	181	19	-5	5	1	325	313	10	3	7	1	48	1	-38	-1	10	1	13	0	-346
10	0	1	87	3	-48	-9	3	1	13	1	-330	-4	5	1	560	563	11	4	7	1	511	496	11	0	10	1	514	535	12
11	0	1	315	312	14	-8	3	1	811	800	13	-3	5	1	878	878	11	5	7	1	604	575	10	1	10	1	395	429	11
12	0	1	340	349	14	-7	3	1	51	1	-71	-2	5	1	410	418	10	6	7	1	74	1	-28	2	10	1	401	440	12
-11	1	1	41	2	-121	-6	3	1	299	291	10	-1	5	1	256	242	9	7	7	1	977	880	12	3	10	1	313	349	12
-10	1	1	336	373	13	-5	3	1	754	759	10	0	5	1	666	693	9	8	7	1	431	412	10	4	10	1	554	566	13
-9	1	1	18	1	-230	-4	3	1	428	410	10	1	5	1	292	337	8	9	7	1	69	2	-58	5	10	1	105	3	-24
-8	1	1	349	344	10	-3	3	1	488	497	9	2	5	1	433	378	9	10	7	1	313	290	12	6	10	1	267	264	13
-7	1	1	509	512	11	-2	3	1	148	161	12	3	5	1	334	282	9	11	7	1	248	211	17	7	10	1	101	3	-27
-6	1	1	561	539	10	-1	3	1	582	626	8	4	5	1	608	583	9	12	7	1	313	269	15	8	10	1	77	3	-57
-5	1	1	1237	1255	14	0	3	1	3637	3619	39	5	5	1	2142	2014	22	-7	8	1	125	7	-27	9	10	1	262	297	17
-4	1	1	1126	1131	12	1	3	1	439	465	8	6	5	1	561	515	10	-6	8	1	86	4	-55	10	10	1	228	204	18
-3	1	1	248	254	8	2	3	1	254	275	7	7	5	1	388	368	11	-5	8	1	72	3	-60	11	10	1	220	220	21
-2	1	1	6	0	-323	3	3	1	1478	1400	16	8	5	1	330	308	9	-4	8	1	782	781	13	-4	11	1	80	5	-66
-1	1	1	527	574	7	4	3	1	1737	1675	18	9	5	1	809	780	12	-3	8	1	326	327	11	-3	11	1	235	172	18
0	1	1	703	649	8	5	3	1	980	943	11	10	5	1	172	181	19	-2	8	1	161	179	19	-2	11	1	266	267	16
1	1	1	1196	1106	12	6	3	1	417	425	10	11	5	1	270	254	15	-1	8	1	673	695	11	-1	11	1	14	1	-357
2	1	1	1309	1096	14	7	3	1	314	242	9	12	5	1	98	5	-51	0	8	1	183	159	16	0	11	1	212	192	18
3	1	1	810	777	9	8	3	1	727	732	11	13	5	1	58	4	-99	1	8	1	263	279	11	1	11	1	261	293	14
4	1	1	336	314	9	9	3	1	375	390	9	-9	6	1	368	329	13	2	8	1	200	217	14	2	11	1	399	445	10
5	1	1	232	302	8	10	3	1	352	373	11	-8	6	1	173	203	24	3	8	1	600	627	11	3	11	1	343	350	11
6	1	1	429	407	10	11	3	1	402	407	11	-7	6	1	94	4	-48	4	8	1	1002	976	13	4	11	1	91	3	-47
7	1	1	302	302	9	12	3	1	398	398	12	-6	6	1	512	520	13	5	8	1	314	297	10	5	11	1	93	3	-29
8	1	1	600	620	11	13	3	1	279	268	17	-5	6	1	193	204	16	6	8	1	19	0	-176	6	11	1	161	131	21
9	1	1	985	1009	13	-10	4	1	65	4	-53	-4	6	1	238	256	12	7	8	1	230	208	13	7	11	1	112	5	-27
10	1	1	352	360	11	-9	4	1	94	4	-33	-3	6	1	167	146	16	8	8	1	850	765	12	8	11	1	486	480	13
11	1	1	217	211	18	-8	4	1	192	207	17	-2	6	1	629	631	10	9	8	1	514	466	14	9	11	1	192	149	23
12	1	1	287	251	16	-7	4	1	186	214	16	-1	6	1	1062	1044	12	10	8	1	219	189	17	10	11	1	318	322	16
-11	2	1	73	4	-46	-6	4	1	11	0	-300	0	6	1	362	384	8	11	8	1	42	2	-118	-3	12	1	101	7	-36
-10	2	1	14	1	-335	-5	4	1	370	365	11	1	6	1	184	178	12	12	8	1	300	268	16	-2	12	1	15	1	-361
-9	2	1	672	659	13	-4	4	1	1086	1068	13	2	6	1	450	459	10	-6	9	1	14	1	-352	-1	12	1	312	291	14
-8	2	1	737	717	12	-3	4	1	1333	1324	15	3	6	1	559	558	9	-5	9	1	92	4	-50	0	12	1	281	254	16
-7	2	1	500	522	12	-2	4	1	303	294	8	4	6	1	1294	1222	14	-4	9	1	158	166	24	1	12	1	113	5	-29
-6	2	1	134	135	18	-1	4	1	663	683	9	5	6	1	340	285	9	-3	9	1	371	397	11	2	12	1	77	3	-62
-5	2	1	1213	1264	14	0	4	1	1782	1794	26	6	6	1	1010	913	12	-2	9	1	12	0	-336	3	12	1	207	188	19
-4	2	1	976	1013	11	1	4	1	1514	1599	16	7	6	1	712	644	11	-1	9	1	87	2	-29	4	12	1	247	266	17
-3	2	1	528	519	8	2	4	1	279	274	7	8	6	1	758	746	12	0	9	1	495	496	13	5	12	1	382	394	12
-2	2	1	482	458	8	3	4	1	337	337	8	9	6	1	425	353	12	1	9	1	729	746	12	6	12	1	14	1	-349
-1	2	1	1069	917	11	4	4	1	364	332	9	10	6	1	202	167	16	2	9	1	235	232	13	7	12	1	109	5	-30
0	2	1	847	835	9	5	4	1	585	554	9	11	6	1	246	229	17	3	9	1	404	422	11	8	12	1	181	180	25
1	2	1	323	324	8	6	4	1	199	140	10	12	6	1	320	298	15	4	9	1	342	326	10	9	12	1	385	372	14
2	2	1	215	246	7	7	4	1	424	381	11	13	6	1	235	242	21	5	9	1	944	913	12	-1	13	1	114	8	-32

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
0	13	1	216	240	21
1	13	1	219	211	20
2	13	1	14	1	-345
3	13	1	268	263	16
4	13	1	14	1	-359
5	13	1	123	7	-27
6	13	1	213	244	20
7	13	1	15	1	-357
8	13	1	73	5	-74
3	14	1	15	1	-358
4	14	1	15	1	-357
5	14	1	172	149	26
-6	-13	2	174	172	25
-5	-13	2	107	7	-33
-4	-13	2	90	6	-39
-3	-13	2	156	109	27
-2	-13	2	15	1	-358
-1	-13	2	129	8	-27
-8	-12	2	15	1	-368
-7	-12	2	167	163	26
-6	-12	2	115	6	-28
-5	-12	2	75	4	-63
-4	-12	2	233	240	18
-3	-12	2	195	181	21
-2	-12	2	257	273	16
-1	-12	2	337	337	14
0	-12	2	173	121	23
1	-12	2	79	5	-42
2	-12	2	78	5	-45
-9	-11	2	324	341	15
-8	-11	2	204	181	21
-7	-11	2	113	5	-29
-6	-11	2	116	5	-27
-5	-11	2	99	4	-31
-4	-11	2	111	4	-26
-3	-11	2	277	281	14
-2	-11	2	93	4	-48
-1	-11	2	298	340	14
0	-11	2	446	430	12
1	-11	2	14	1	-333
2	-11	2	112	6	-27
3	-11	2	129	7	-26
4	-11	2	149	152	29
-10	-10	2	72	4	-49
-9	-10	2	210	213	20
-8	-10	2	444	421	11
-7	-10	2	9	0	-339
-6	-10	2	108	4	-25
-5	-10	2	239	249	15
-4	-10	2	301	313	12
-3	-10	2	205	186	16
-2	-10	2	190	238	17
-1	-10	2	185	172	17
0	-10	2	386	391	10
1	-10	2	306	341	12
2	-10	2	13	1	-315
3	-10	2	14	1	-337
4	-10	2	290	293	15
5	-10	2	105	6	-32
-11	-9	2	262	304	19
-10	-9	2	193	152	22
-9	-9	2	151	130	26
-8	-9	2	254	235	16
-7	-9	2	356	321	11
-6	-9	2	152	193	21
-5	-9	2	202	237	16
-4	-9	2	581	578	12
-3	-9	2	753	740	12
-2	-9	2	437	424	12
-1	-9	2	185	182	16
0	-9	2	488	495	13
1	-9	2	130	163	24
2	-9	2	225	261	15
3	-9	2	214	212	16
4	-9	2	85	4	-52
5	-9	2	407	390	12
6	-9	2	92	5	-54
-11	-8	2	95	6	-57
-10	-8	2	102	5	-32
-9	-8	2	204	169	19
-8	-8	2	57	2	-49
-7	-8	2	559	584	13
-6	-8	2	512	477	12
-5	-8	2	626	639	12
-4	-8	2	375	402	10
-3	-8	2	676	665	11
-2	-8	2	516	509	11
-1	-8	2	683	669	11
0	-8	2	174	161	16
1	-8	2	297	318	11
2	-8	2	273	280	11
3	-8	2	342	344	10
4	-8	2	8	0	-312
5	-8	2	111	4	-27
6	-8	2	186	211	21
7	-8	2	60	3	-56
-12	-7	2	208	186	23
-11	-7	2	83	4	-63
-10	-7	2	14	1	-345
-9	-7	2	328	329	12
-8	-7	2	465	474	13
-7	-7	2	254	261	13
-6	-7	2	344	319	9
-5	-7	2	728	732	11
-4	-7	2	787	810	11
-3	-7	2	425	433	10
-2	-7	2	428	403	10
-1	-7	2	464	457	11
0	-7	2	509	483	11
1	-7	2	268	284	10
2	-7	2	412	413	11
3	-7	2	647	672	11
4	-7	2	586	577	12
5	-7	2	12	0	-310
6	-7	2	72	3	-59
7	-7	2	343	297	13
8	-7	2	14	1	-353
-12	-6	2	292	285	17
-11	-6	2	93	5	-37
-10	-6	2	153	158	25
-9	-6	2	198	202	17
-8	-6	2	662	690	12
-7	-6	2	615	635	12
-6	-6	2	228	238	12
-5	-6	2	675	684	10
-4	-6	2	946	948	12
-3	-6	2	318	341	8
-2	-6	2	444	459	10
-1	-6	2	495	490	10
0	-6	2	727	743	10
1	-6	2	703	737	10
2	-6	2	292	301	9
3	-6	2	321	311	9
4	-6	2	1236	1206	14
5	-6	2	554	554	12
6	-6	2	327	322	11
7	-6	2	284	303	14
8	-6	2	278	234	15
9	-6	2	89	5	-59
-12	-5	2	246	184	19
-11	-5	2	280	293	16
-10	-5	2	263	272	15
-9	-5	2	284	254	12
-8	-5	2	780	844	12
-7	-5	2	989	989	13
-6	-5	2	299	288	9
-5	-5	2	288	282	9
-4	-5	2	1240	1272	14
-3	-5	2	755	734	10
-2	-5	2	366	360	9
-1	-5	2	646	660	9
0	-5	2	724	737	10
1	-5	2	1552	1567	16
2	-5	2	643	659	10
3	-5	2	445	447	10
4	-5	2	685	676	11
5	-5	2	469	491	12
6	-5	2	247	244	12
7	-5	2	166	167	19
8	-5	2	410	406	12
9	-5	2	312	316	14
10	-5	2	81	5	-65
-12	-4	2	217	151	21
-11	-4	2	342	364	13
-10	-4	2	284	258	14
-9	-4	2	564	570	12
-8	-4	2	240	270	13
-7	-4	2	708	716	11
-6	-4	2	370	385	10
-5	-4	2	1012	1054	12
-4	-4	2	570	581	9
-3	-4	2	813	834	10
-2	-4	2	562	510	9
-1	-4	2	512	511	9
0	-4	2	655	682	9
1	-4	2	1394	1418	15
2	-4	2	533	507	9
3	-4	2	726	724	10
4	-4	2	564	604	10
5	-4	2	393	366	10
6	-4	2	261	277	11
7	-4	2	269	276	12
8	-4	2	192	203	18
9	-4	2	558	539	13
10	-4	2	211	242	20
-12	-3	2	312	315	16
-11	-3	2	14	1	-345
-10	-3	2	262	296	14
-9	-3	2	479	480	12
-8	-3	2	718	785	11
-7	-3	2	394	422	10
-6	-3	2	249	222	9
-5	-3	2	955	967	11
-4	-3	2	103	107	18
-3	-3	2	896	920	10
-2	-3	2	931	920	11
-1	-3	2	871	842	10
0	-3	2	1514	1552	16
1	-3	2	942	1007	11
2	-3	2	519	528	9
3	-3	2	1027	1071	12
4	-3	2	319	321	8
5	-3	2	412	421	11
6	-3	2	354	363	10
7	-3	2	355	326	9
8	-3	2	471	465	12
9	-3	2	113	4	-25
10	-3	2	259	252	16
11	-3	2	229	226	19
-12	-2	2	311	296	16
-11	-2	2	344	387	13
-10	-2	2	291	304	13
-9	-2	2	770	759	12
-8	-2	2	639	692	11
-7	-2	2	205	167	13
-6	-2	2	251	251	9
-5	-2	2	513	548	9
-4	-2	2	988	1077	11
-3	-2	2	1589	1704	16
-2	-2	2	632	639	8
-1	-2	2	1042	1008	11
0	-2	2	3311	3396	36
1	-2	2	1263	1302	13
2	-2	2	772	796	9
3	-2	2	600	660	9
4	-2	2	649	658	9
5	-2	2	300	314	9
6	-2	2	276	290	9
7	-2	2	448	459	11
8	-2	2	728	738	12
9	-2	2	292	274	12
10	-2	2	224	173	17
11	-2	2	310	296	15
-12	-1	2	335	317	15
-11	-1	2	333	329	14
-10	-1	2	308	342	13
-9	-1	2	88	3	-45
-8	-1	2	817	828	12
-7	-1	2	503	533	11
-6	-1	2	203	221	11
-5	-1	2	395	381	9
-4	-1	2	977	1007	11
-3	-1	2	1947	1962	20
-2	-1	2	508	471	8
-1	-1	2	593	570	8
0	-1	2	1518	1509	16
1	-1	2	512	604	7
2	-1	2	636	634	8
3	-1	2	430	445	8
4	-1	2	972	1009	11
5	-1	2	1283	1384	14
6	-1	2	651	636	10
7	-1	2	211	208	12
8	-1	2	1151	1152	14
9	-1	2	565	563	13
10	-1	2	184	210	20
11	-1	2	178	181	22
12	-1	2	200	232	24
-12	0	2	15	1	-366
-11	0	2	302	314	15
-10	0	2	13	1	-326
-9	0	2	735	735	12
-8	0	2	396	403	9
-7	0	2	309	326	9
-6	0	2	383	407	10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
-5	0	2	280	339	8
-4	0	2	987	1005	11
-3	0	2	1133	1158	12
-2	0	2	142	111	11
-1	0	2	663	605	8
0	0	2	1155	1193	12
1	0	2	860	835	9
2	0	2	1777	1883	18
3	0	2	437	436	8
4	0	2	899	939	10
5	0	2	1455	1516	16
6	0	2	544	538	9
7	0	2	750	756	11
8	0	2	204	204	14
9	0	2	242	271	13
10	0	2	78	3	-54
11	0	2	153	158	26
12	0	2	297	328	16
-11	1	2	188	197	23
-10	1	2	86	4	-52
-9	1	2	226	246	15
-8	1	2	248	258	13
-7	1	2	251	212	11
-6	1	2	439	436	11
-5	1	2	1209	1200	14
-4	1	2	1350	1382	15
-3	1	2	985	1018	11
-2	1	2	1267	1199	13
-1	1	2	2291	2273	26
0	1	2	859	853	9
1	1	2	976	926	10
2	1	2	550	575	8
3	1	2	382	381	8
4	1	2	997	1002	11
5	1	2	452	417	9
6	1	2	243	276	9
7	1	2	673	684	10
8	1	2	625	649	11
9	1	2	403	414	12
10	1	2	311	301	11
11	1	2	162	189	24
12	1	2	229	229	19
-11	2	2	57	4	-61
-10	2	2	68	3	-71
-9	2	2	91	3	-48
-8	2	2	709	717	12
-7	2	2	436	428	11
-6	2	2	253	286	11
-5	2	2	697	705	10
-4	2	2	2307	2367	24
-3	2	2	669	664	9
-2	2	2	268	237	7
-1	2	2	697	629	9
0	2	2	555	561	8
1	2	2	1012	913	11
2	2	2	640	612	8
3	2	2	1037	913	11
4	2	2	2278	2166	23
5	2	2	1071	1038	12
6	2	2	334	345	9
7	2	2	823	825	11
8	2	2	630	645	11
9	2	2	472	519	13
10	2	2	128	162	24
11	2	2	137	140	27
12	2	2	327	345	14
13	2	2	249	232	19
-10	3	2	226	259	19
-9	3	2	67	3	-67
-8	3	2	242	249	14
-7	3	2	806	828	12
-6	3	2	167	194	16
-5	3	2	205	218	12
-4	3	2	1202	1201	13
-3	3	2	310	265	8
-2	3	2	250	264	8
-1	3	2	365	350	9
0	3	2	3846	3697	41
1	3	2	3281	2895	36
2	3	2	683	725	9
3	3	2	877	834	10
4	3	2	2172	2165	22
5	3	2	1702	1572	18
6	3	2	584	553	9
7	3	2	353	355	10
8	3	2	584	574	11
9	3	2	343	368	10
10	3	2	173	178	18
11	3	2	225	234	17
12	3	2	359	362	13
13	3	2	352	341	14
-10	4	2	181	205	25
-9	4	2	297	270	14
-8	4	2	172	135	19
-7	4	2	524	510	13
-6	4	2	444	468	11
-5	4	2	207	218	13
-4	4	2	539	536	10
-3	4	2	533	528	9
-2	4	2	282	270	8
-1	4	2	385	357	9
0	4	2	874	867	10
1	4	2	1935	1751	20
2	4	2	633	629	9
3	4	2	739	754	9
4	4	2	471	480	9
5	4	2	573	483	9
6	4	2	460	407	10
7	4	2	735	687	10
8	4	2	419	395	11
9	4	2	977	933	13
10	4	2	340	350	11
11	4	2	149	151	25
12	4	2	461	430	11
13	4	2	313	336	16
-9	5	2	365	360	13
-8	5	2	95	4	-50
-7	5	2	322	313	11
-6	5	2	236	235	14
-5	5	2	919	891	12
-4	5	2	212	173	13
-3	5	2	476	484	10
-2	5	2	514	495	10
-1	5	2	282	314	8
0	5	2	554	542	9
1	5	2	681	643	10
2	5	2	111	102	17
3	5	2	874	890	10
4	5	2	727	697	10
5	5	2	231	265	9
6	5	2	397	436	11
7	5	2	379	375	10
8	5	2	604	576	11
9	5	2	525	496	12
10	5	2	699	635	12
11	5	2	448	438	13
12	5	2	315	280	15
13	5	2	15	1	-379
-9	6	2	156	177	29
-8	6	2	554	517	15
-7	6	2	70	3	-64
-6	6	2	144	171	23
-5	6	2	307	326	11
-4	6	2	316	301	10
-3	6	2	325	324	9
-2	6	2	329	327	9
-1	6	2	956	928	12
0	6	2	1390	1339	15
1	6	2	550	582	10
2	6	2	608	637	10
3	6	2	1019	1054	12
4	6	2	841	849	11
5	6	2	1180	1150	13
6	6	2	144	97	16
7	6	2	176	130	15
8	6	2	881	834	12
9	6	2	492	450	13
10	6	2	83	3	-32
11	6	2	360	371	12
12	6	2	518	467	14
13	6	2	233	227	20
-8	7	2	187	186	24
-7	7	2	175	220	23
-6	7	2	80	3	-37
-5	7	2	103	3	-25
-4	7	2	590	573	12
-3	7	2	582	540	12
-2	7	2	76	2	-45
-1	7	2	280	264	10
0	7	2	1487	1465	16
1	7	2	802	805	11
2	7	2	346	362	9
3	7	2	442	441	11
4	7	2	178	211	14
5	7	2	554	523	10
6	7	2	298	308	10
7	7	2	278	253	11
8	7	2	629	605	12
9	7	2	560	530	13
10	7	2	76	3	-56
11	7	2	192	188	20
12	7	2	295	289	16
-7	8	2	14	1	-362
-6	8	2	159	191	26
-5	8	2	13	1	-338
-4	8	2	76	2	-57
-3	8	2	742	757	12
-2	8	2	304	318	11
-1	8	2	150	168	20
0	8	2	479	498	13
1	8	2	446	460	12
2	8	2	181	201	16
3	8	2	264	248	11
4	8	2	405	415	12
5	8	2	1110	1042	13
6	8	2	427	433	12
7	8	2	319	301	10
8	8	2	448	425	12
9	8	2	442	430	11
10	8	2	326	275	13
11	8	2	107	5	-30
12	8	2	90	5	-40
-6	9	2	260	248	17
-5	9	2	188	216	22
-4	9	2	171	194	23
-3	9	2	212	195	16
-2	9	2	463	487	13
-1	9	2	257	273	14
0	9	2	77	2	-54
1	9	2	384	402	10
2	9	2	150	156	21
3	9	2	11	0	-347
4	9	2	519	540	12
5	9	2	394	371	10
6	9	2	656	620	12
7	9	2	585	545	13
8	9	2	435	426	12
9	9	2	172	121	20
10	9	2	83	4	-56
11	9	2	322	274	15
12	9	2	60	4	-91
-5	10	2	385	372	13
-4	10	2	233	238	19
-3	10	2	14	1	-348
-2	10	2	75	3	-58
-1	10	2	408	385	11
0	10	2	75	2	-37
1	10	2	384	394	10
2	10	2	377	448	11
3	10	2	172	243	20
4	10	2	502	508	13
5	10	2	361	376	10
6	10	2	337	348	11
7	10	2	432	415	12
8	10	2	462	451	13
9	10	2	83	4	-57
10	10	2	28	1	-118
11	10	2	101	6	-54
-4	11	2	413	392	13
-3	11	2	154	75	27
-2	11	2	178	115	23
-1	11	2	290	285	15
0	11	2	192	210	21
1	11	2	233	212	16
2	11	2	76	3	-57
3	11	2	420	505	12
4	11	2	354	380	11
5	11	2	300	304	13
6	11	2	132	131	26
7	11	2	251	231	16
8	11	2	299	302	15
9	11	2	334	307	14
10	11	2	14	1	-357
11	11	2	15	1	-365
-3	12	2	201	204	23
-2	12	2	57	3	-93
-1	12	2	14	1	-369
0	12	2	278	285	16
1	12	2	248	198	17
2	12	2	155	166	26
3	12	2	13	1	-361
4	12	2	368	399	13
5	12	2	378	396	12
6	12	2	183	185	22
7	12	2	164	194	26

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
8	12	2	14	1	-369
9	12	2	40	2	-90
10	12	2	205	197	23
-1	13	2	102	7	-55
0	13	2	75	5	-73
1	13	2	297	289	16
2	13	2	166	217	27
3	13	2	89	5	-40
4	13	2	192	246	22
5	13	2	259	259	17
6	13	2	14	1	-357
7	13	2	10	1	-354
8	13	2	120	7	-31
3	14	2	15	1	-371
4	14	2	48	3	-112
5	14	2	30	2	-182
6	14	2	15	1	-366
-4	-13	3	113	8	-32
-3	-13	3	207	213	22
-2	-13	3	97	7	-53
-7	-12	3	81	5	-65
-6	-12	3	195	205	22
-5	-12	3	191	191	23
-4	-12	3	169	190	26
-3	-12	3	56	3	-88
-2	-12	3	114	6	-29
-1	-12	3	10	1	-351
0	-12	3	72	4	-76
1	-12	3	157	157	27
-9	-11	3	105	7	-35
-8	-11	3	339	328	14
-7	-11	3	339	368	14
-6	-11	3	51	2	-96
-5	-11	3	361	347	13
-4	-11	3	233	221	17
-3	-11	3	213	205	18
-2	-11	3	155	115	24
-1	-11	3	236	210	17
0	-11	3	236	219	17
1	-11	3	288	283	15
2	-11	3	122	7	-26
3	-11	3	15	1	-330
-10	-10	3	249	226	19
-9	-10	3	132	8	-26
-8	-10	3	380	366	13
-7	-10	3	316	320	14
-6	-10	3	323	350	13
-5	-10	3	174	174	20
-4	-10	3	278	268	13
-3	-10	3	311	311	12
-2	-10	3	176	224	19
-1	-10	3	153	158	21
0	-10	3	99	4	-27

H	K	L	10FO	10FC	10S
1	-10	3	325	308	13
2	-10	3	295	311	14
3	-10	3	95	5	-49
4	-10	3	221	187	18
5	-10	3	15	1	-353
-10	-9	3	95	6	-56
-9	-9	3	361	375	13
-8	-9	3	63	3	-74
-7	-9	3	178	207	21
-6	-9	3	128	112	25
-5	-9	3	385	389	10
-4	-9	3	140	126	22
-3	-9	3	294	311	12
-2	-9	3	617	627	12
-1	-9	3	389	411	10
0	-9	3	321	312	11
1	-9	3	341	346	11
2	-9	3	285	283	12
3	-9	3	393	396	12
4	-9	3	292	264	14
5	-9	3	14	1	-338
6	-9	3	175	174	24
-11	-8	3	15	1	-381
-10	-8	3	94	5	-37
-9	-8	3	375	381	12
-8	-8	3	457	486	12
-7	-8	3	78	3	-53
-6	-8	3	104	3	-24
-5	-8	3	190	207	16
-4	-8	3	298	307	11
-3	-8	3	214	250	14
-2	-8	3	225	233	13
-1	-8	3	877	899	12
0	-8	3	789	780	12
1	-8	3	180	184	16
2	-8	3	273	280	12
3	-8	3	278	263	12
4	-8	3	377	354	10
5	-3	3	137	132	26
6	-8	3	14	1	-345
7	-8	3	316	330	15
-11	-7	3	350	336	14
-10	-7	3	126	6	-25
-9	-7	3	383	379	12
-8	-7	3	576	574	13
-7	-7	3	112	3	-23
-6	-7	3	12	0	-305
-5	-7	3	451	436	11
-4	-7	3	932	955	12
-3	-7	3	632	630	11
-2	-7	3	205	210	13
-1	-7	3	195	209	14
0	-7	3	894	891	12

H	K	L	10FO	10FC	10S
1	-7	3	472	478	12
2	-7	3	153	151	17
3	-7	3	276	269	11
4	-7	3	358	359	10
5	-7	3	185	184	17
6	-7	3	13	1	-336
7	-7	3	142	98	26
8	-7	3	584	526	15
-11	-6	3	305	315	15
-10	-6	3	228	242	18
-9	-6	3	242	260	15
-8	-6	3	218	211	15
-7	-6	3	682	675	12
-6	-6	3	77	2	-28
-5	-6	3	156	176	16
-4	-6	3	663	660	10
-3	-6	3	1378	1418	15
-2	-6	3	267	267	9
-1	-6	3	533	527	10
0	-6	3	595	624	10
1	-6	3	208	222	12
2	-6	3	250	247	10
3	-6	3	651	649	11
4	-6	3	418	412	12
5	-6	3	889	880	12
6	-6	3	8	0	-300
7	-6	3	187	140	19
8	-6	3	240	222	17
9	-6	3	334	339	15
-12	-5	3	239	208	20
-11	-5	3	147	159	29
-10	-5	3	77	3	-60
-9	-5	3	387	379	10
-8	-5	3	249	293	14
-7	-5	3	690	652	11
-6	-5	3	974	952	12
-5	-5	3	459	460	11
-4	-5	3	368	382	10
-3	-5	3	1081	1086	12
-2	-5	3	939	909	11
-1	-5	3	905	886	11
0	-5	3	874	893	11
1	-5	3	597	609	9
2	-5	3	104	131	20
3	-5	3	405	380	11
4	-5	3	341	349	9
5	-5	3	764	775	11
6	-5	3	512	545	12
7	-5	3	217	241	15
8	-5	3	141	163	27
9	-5	3	178	165	23
10	-5	3	45	3	-117
-12	-4	3	238	259	21

H	K	L	10FO	10FC	10S
-11	-4	3	212	223	20
-10	-4	3	67	3	-66
-9	-4	3	343	328	11
-8	-4	3	559	573	12
-7	-4	3	68	1	-52
-6	-4	3	311	290	9
-5	-4	3	1141	1160	13
-4	-4	3	1031	1103	12
-3	-4	3	331	353	9
-2	-4	3	444	453	9
-1	-4	3	1104	1099	12
0	-4	3	604	629	9
1	-4	3	205	253	10
2	-4	3	800	814	10
3	-4	3	483	514	10
4	-4	3	481	498	10
5	-4	3	450	458	11
6	-4	3	364	383	9
7	-4	3	551	515	12
8	-4	3	260	250	14
9	-4	3	201	227	20
10	-4	3	286	259	15
-12	-3	3	240	232	20
-11	-3	3	168	126	25
-10	-3	3	172	157	22
-9	-3	3	157	97	20
-8	-3	3	611	655	12
-7	-3	3	666	668	11
-6	-3	3	132	128	17
-5	-3	3	515	521	10
-4	-3	3	1425	1488	15
-3	-3	3	335	346	9
-2	-3	3	499	499	9
-1	-3	3	493	464	8
0	-3	3	1193	1128	13
1	-3	3	1133	1160	12
2	-3	3	575	624	9
3	-3	3	1094	1088	12
4	-3	3	1898	1946	20
5	-3	3	157	168	15
6	-3	3	439	424	12
7	-3	3	413	399	11
8	-3	3	532	483	13
9	-3	3	253	217	15
10	-3	3	14	1	-324
11	-3	3	108	7	-32
-12	-2	3	34	2	-172
-11	-2	3	295	271	15
-10	-2	3	13	1	-335
-9	-2	3	431	415	12
-8	-2	3	474	519	13
-7	-2	3	1049	1042	13
-6	-2	3	227	199	11

H	K	L	10FO	10FC	10S
-5	-2	3	396	426	10
-4	-2	3	1484	1508	16
-3	-2	3	658	701	9
-2	-2	3	660	689	9
-1	-2	3	780	766	9
0	-2	3	1404	1378	15
1	-2	3	2302	2336	23
2	-2	3	619	612	9
3	-2	3	666	681	9
4	-2	3	1519	1524	16
5	-2	3	856	886	11
6	-2	3	137	141	17
7	-2	3	308	313	10
8	-2	3	315	304	10
9	-2	3	314	321	12
10	-2	3	223	205	17
11	-2	3	95	5	-36
-11	-1	3	301	251	15
-10	-1	3	356	339	12
-9	-1	3	165	171	20
-8	-1	3	301	312	11
-7	-1	3	744	730	11
-6	-1	3	602	590	10
-5	-1	3	844	887	11
-4	-1	3	294	283	8
-3	-1	3	788	812	10
-2	-1	3	360	321	9
-1	-1	3	198	231	9
0	-1	3	309	308	8
1	-1	3	2013	1943	20
2	-1	3	159	238	11
3	-1	3	390	389	9
4	-1	3	561	589	9
5	-1	3	118	130	16
6	-1	3	483	504	10
7	-1	3	467	461	11
8	-1	3	521	544	12
9	-1	3	988	951	13
10	-1	3	310	325	13
11	-1	3	352	355	13
12	-1	3	157	108	28
-11	0	3	63	4	-54
-10	0	3	337	366	13
-9	0	3	574	603	13
-8	0	3	789	803	12
-7	0	3	170	193	16
-6	0	3	18	0	-163
-5	0	3	981	1011	12
-4	0	3	597	631	9
-3	0	3	771	814	10
-2	0	3	1252	1201	13
-1	0	3	555	507	8
0	0	3	924	863	10

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
1	0	3	1140	1205	12
2	0	3	1553	1507	16
3	0	3	430	453	8
4	0	3	134	143	13
5	0	3	711	737	9
6	0	3	240	228	9
7	0	3	250	238	10
8	0	3	819	809	11
9	0	3	281	298	12
10	0	3	320	370	12
11	0	3	174	222	23
12	0	3	250	256	18
-11	1	3	183	203	25
-10	1	3	224	237	18
-9	1	3	455	466	13
-8	1	3	662	673	12
-7	1	3	380	391	10
-6	1	3	111	107	22
-5	1	3	299	258	8
-4	1	3	849	909	10
-3	1	3	1220	1257	13
-2	1	3	654	622	9
-1	1	3	1117	1052	12
0	1	3	3062	3019	34
1	1	3	654	636	8
2	1	3	1124	1097	12
3	1	3	1960	2015	20
4	1	3	1084	1146	12
5	1	3	651	675	9
6	1	3	384	400	9
7	1	3	170	160	14
8	1	3	511	524	11
9	1	3	561	582	12
10	1	3	155	131	20
11	1	3	370	362	12
12	1	3	56	3	-91
-11	2	3	306	299	16
-10	2	3	147	158	28
-9	2	3	230	215	17
-8	2	3	354	350	11
-7	2	3	310	344	11
-6	2	3	383	367	10
-5	2	3	140	147	16
-4	2	3	799	826	10
-3	2	3	1476	1528	16
-2	2	3	362	345	9
-1	2	3	212	223	9
0	2	3	3826	3558	41
1	2	3	1464	1213	15
2	2	3	533	542	8
3	2	3	790	724	9
4	2	3	940	873	11
5	2	3	1265	1294	14
6	2	3	509	505	9
7	2	3	744	787	10
8	2	3	1326	1358	15
9	2	3	423	450	12
10	2	3	269	287	13
11	2	3	227	224	17
12	2	3	406	390	12
13	2	3	228	228	21
-10	3	3	127	7	-27
-9	3	3	391	405	12
-8	3	3	70	2	-38
-7	3	3	201	205	16
-6	3	3	121	153	23
-5	3	3	638	656	11
-4	3	3	402	385	10
-3	3	3	1215	1210	13
-2	3	3	277	212	8
-1	3	3	264	257	8
0	3	3	462	439	9
1	3	3	2649	2183	31
2	3	3	730	744	9
3	3	3	282	266	7
4	3	3	1205	1172	13
5	3	3	2367	2225	24
6	3	3	874	815	11
7	3	3	751	698	10
8	3	3	790	770	11
9	3	3	651	652	11
10	3	3	232	213	14
11	3	3	307	293	13
12	3	3	213	192	20
13	3	3	161	159	29
-10	4	3	91	6	-59
-9	4	3	184	172	23
-8	4	3	393	393	11
-7	4	3	48	1	-54
-6	4	3	427	446	12
-5	4	3	575	605	11
-4	4	3	639	651	10
-3	4	3	781	786	10
-2	4	3	905	869	11
-1	4	3	926	905	11
0	4	3	8	0	-324
1	4	3	994	926	11
2	4	3	641	572	9
3	4	3	185	183	10
4	4	3	1084	1035	12
5	4	3	990	894	11
6	4	3	299	232	8
7	4	3	416	373	10
8	4	3	980	918	12
9	4	3	128	104	23
10	4	3	205	171	15
11	4	3	114	5	-26
12	4	3	339	336	14
13	4	3	379	362	14
-9	5	3	14	1	-358
-8	5	3	306	283	14
-7	5	3	267	243	14
-6	5	3	299	314	11
-5	5	3	541	537	12
-4	5	3	1284	1285	15
-3	5	3	223	210	12
-2	5	3	374	346	10
-1	5	3	552	535	10
0	5	3	530	523	10
1	5	3	403	427	11
2	5	3	662	613	9
3	5	3	357	324	8
4	5	3	1086	1119	12
5	5	3	759	737	10
6	5	3	628	579	10
7	5	3	649	603	11
8	5	3	396	388	11
9	5	3	600	559	12
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                                        PAGE 11

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 11   2   4   305   301  13     -7   5   4    13     0-343      2   7   4   375   323  10     -3  10   4   180   164  24      9  13   4   267   232  18
 12   2   4   416   406  12     -6   5   4   315   293  11      3   7   4   502   464  11     -2  10   4   231   239  18      3  14   4    89     6 -45
 13   2   4   376   361  14     -5   5   4   492   486  13      4   7   4   409   457  10     -1  10   4   239   250  16      4  14   4    81     5 -49
-10   3   4   345   351  14     -4   5   4   562   566  12      5   7   4   902   942  12      0  10   4   199   204  19      5  14   4   216   240  22
 -9   3   4   292   269  15     -3   5   4   885   886  12      6   7   4   320   314   9      1  10   4   489   462  13      6  14   4    10     1-366
 -8   3   4   387   371  11     -2   5   4   435   411  11      7   7   4   628   598  11      2  10   4   508   493  13     -4 -12   5    15     1-360
 -7   3   4   147   157  22     -1   5   4   224   216  10      8   7   4   616   545  12      3  10   4   225   165  17     -3 -12   5    64     4 -56
 -6   3   4   267   259  11      0   5   4  2014  1904  21      9   7   4   283   271  12      4  10   4   321   339  12     -2 -12   5   200   203  22
 -5   3   4   732   708  11      1   5   4   424   419  10     10   7   4   101     4 -27      5  10   4   317   349  11     -1 -12   5    91     6 -56
 -4   3   4   624   640  10      2   5   4   292   261   8     11   7   4    14     1-347      6  10   4   136   141  24     -7 -11   5   195   193  24
 -3   3   4   344   352   9      3   5   4   399   417  10     12   7   4   378   343  13      7  10   4   259   249  14     -6 -11   5    15     1-350
 -2   3   4   739   724  10      4   5   4   318   337   9     13   7   4   118     8 -33      8  10   4   341   322  12     -5 -11   5    46     3-112
 -1   3   4   429   444   9      5   5   4  1253  1205  14     -7   8   4   158   199  30      9  10   4   322   324  14     -4 -11   5    10     0-356
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
-3	-11	5	257	238	17
-2	-11	5	232	248	19
-1	-11	5	403	379	12
0	-11	5	10	1	-348
1	-11	5	365	351	13
2	-11	5	80	5	-44
-8	-10	5	111	7	-33
-7	-10	5	15	1	-352
-6	-10	5	14	1	-358
-5	-10	5	48	2	-101
-4	-10	5	472	466	12
-3	-10	5	213	195	19
-2	-10	5	228	265	18
-1	-10	5	243	288	16
0	-10	5	360	335	12
1	-10	5	9	0	-335
2	-10	5	174	228	24
3	-10	5	51	3	-100
4	-10	5	15	1	-349
-9	-9	5	269	309	18
-8	-9	5	207	173	21
-7	-9	5	196	196	21
-6	-9	5	316	306	13
-5	-9	5	34	1	-86
-4	-9	5	286	282	13
-3	-9	5	484	464	12
-2	-9	5	217	185	16
-1	-9	5	318	341	11
0	-9	5	173	141	20
1	-9	5	134	145	26
2	-9	5	114	5	-25
3	-9	5	276	236	15
4	-9	5	369	347	13
5	-9	5	161	157	25
-10	-8	5	87	6	-63
-9	-8	5	203	178	22
-8	-8	5	170	185	25
-7	-8	5	439	431	11
-6	-8	5	369	381	11
-5	-8	5	314	322	11
-4	-8	5	517	514	13
-3	-8	5	163	168	20
-2	-8	5	321	310	11
-1	-8	5	269	219	12
0	-8	5	639	635	12
1	-8	5	295	309	12
2	-8	5	13	0	-315
3	-8	5	48	2	-54
4	-8	5	218	193	18
5	-8	5	452	439	13
6	-8	5	225	211	19
7	-8	5	68	5	-77
-10	-7	5	118	7	-31
-9	-7	5	14	1	-350
-8	-7	5	198	205	20
-7	-7	5	274	261	13
-6	-7	5	511	516	13
-5	-7	5	589	599	12
-4	-7	5	337	310	10
-3	-7	5	630	634	12
-2	-7	5	82	2	-43
-1	-7	5	682	681	11
0	-7	5	303	319	11
1	-7	5	262	264	12
2	-7	5	489	479	13
3	-7	5	52	2	-46
4	-7	5	240	259	14
5	-7	5	340	307	12
6	-7	5	180	229	22
7	-7	5	116	6	-28
8	-7	5	275	270	17
-10	-6	5	92	5	-56
-9	-6	5	14	1	-349
-8	-6	5	317	323	13
-7	-6	5	369	384	10
-6	-6	5	212	195	15
-5	-6	5	555	547	12
-4	-6	5	911	906	12
-3	-6	5	353	325	9
-2	-6	5	123	135	22
-1	-6	5	147	176	17
0	-6	5	270	293	11
1	-6	5	471	434	10
2	-6	5	413	389	11
3	-6	5	784	786	11
4	-6	5	74	2	-34
5	-6	5	475	438	12
6	-6	5	52	2	-53
7	-6	5	236	197	17
8	-6	5	15	1	-338
9	-6	5	272	259	17
-11	-5	5	131	9	-29
-10	-5	5	234	193	19
-9	-5	5	14	1	-338
-8	-5	5	604	653	13
-7	-5	5	465	463	12
-6	-5	5	454	469	12
-5	-5	5	401	415	12
-4	-5	5	666	672	11
-3	-5	5	373	347	9
-2	-5	5	317	321	9
-1	-5	5	51	1	-57
0	-5	5	1071	1036	13
1	-5	5	443	438	11
2	-5	5	220	223	12
3	-5	5	279	282	10
4	-5	5	1265	1235	15
5	-5	5	323	300	10
6	-5	5	156	145	20
7	-5	5	176	146	20
8	-5	5	14	1	-329
9	-5	5	29	2	-171
-11	-4	5	413	403	13
-10	-4	5	101	5	-34
-9	-4	5	359	337	12
-8	-4	5	387	425	11
-7	-4	5	965	1003	13
-6	-4	5	226	199	13
-5	-4	5	667	661	11
-4	-4	5	682	656	10
-3	-4	5	651	653	10
-2	-4	5	247	241	9
-1	-4	5	600	601	10
0	-4	5	625	627	10
1	-4	5	1424	1438	16
2	-4	5	277	294	9
3	-4	5	90	2	-20
4	-4	5	455	441	11
5	-4	5	645	588	11
6	-4	5	262	273	12
7	-4	5	226	220	14
8	-4	5	424	418	11
9	-4	5	412	358	12
10	-4	5	78	5	-65
-11	-3	5	134	8	-28
-10	-3	5	404	438	13
-9	-3	5	174	178	22
-8	-3	5	365	406	11
-7	-3	5	183	212	17
-6	-3	5	238	238	12
-5	-3	5	789	794	11
-4	-3	5	507	507	10
-3	-3	5	1008	1001	12
-2	-3	5	1135	1081	13
-1	-3	5	783	774	10
0	-3	5	391	379	10
1	-3	5	1363	1328	15
2	-3	5	731	706	10
3	-3	5	346	336	9
4	-3	5	823	830	11
5	-3	5	414	443	10
6	-3	5	145	102	19
7	-3	5	12	0	-300
8	-3	5	490	492	12
9	-3	5	674	674	13
10	-3	5	340	333	14
11	-3	5	158	123	28
-11	-2	5	119	7	-32
-10	-2	5	210	154	20
-9	-2	5	542	533	14
-8	-2	5	483	491	12
-7	-2	5	425	446	12
-6	-2	5	502	514	12
-5	-2	5	146	140	17
-4	-2	5	441	454	11
-3	-2	5	147	150	14
-2	-2	5	1494	1418	16
-1	-2	5	1504	1375	16
0	-2	5	68	1	-35
1	-2	5	885	870	10
2	-2	5	491	449	9
3	-2	5	1149	1143	13
4	-2	5	419	422	10
5	-2	5	672	698	10
6	-2	5	733	732	11
7	-2	5	161	136	17
8	-2	5	218	231	15
9	-2	5	138	167	25
10	-2	5	201	275	20
11	-2	5	162	182	27
-11	-1	5	118	8	-32
-10	-1	5	293	317	16
-9	-1	5	238	216	17
-8	-1	5	561	578	13
-7	-1	5	82	2	-45
-6	-1	5	428	431	11
-5	-1	5	282	290	10
-4	-1	5	745	720	10
-3	-1	5	370	396	9
-2	-1	5	231	197	9
-1	-1	5	927	856	11
0	-1	5	2608	2598	26
1	-1	5	241	231	8
2	-1	5	105	156	18
3	-1	5	212	210	9
4	-1	5	803	822	10
5	-1	5	296	304	8
6	-1	5	299	304	9
7	-1	5	511	503	11
8	-1	5	371	407	11
9	-1	5	279	304	13
10	-1	5	121	5	-25
11	-1	5	200	241	22
12	-1	5	15	1	-363
-11	0	5	364	378	15
-10	0	5	32	2	-109
-9	0	5	347	331	12
-8	0	5	169	175	20
-7	0	5	261	234	12
-6	0	5	99	2	-22
-5	0	5	204	201	12
-4	0	5	841	848	11
-3	0	5	1472	1449	16
-2	0	5	777	738	10
-1	0	5	507	507	9
0	0	5	902	918	10
1	0	5	594	563	9
2	0	5	649	678	9
3	0	5	99	138	18
4	0	5	1707	1721	18
5	0	5	818	905	10
6	0	5	368	366	10
7	0	5	245	255	11
8	0	5	1224	1260	15
9	0	5	624	611	12
10	0	5	255	248	15
11	0	5	82	4	-58
12	0	5	243	195	19
-10	1	5	186	220	24
-9	1	5	254	235	17
-8	1	5	436	458	11
-7	1	5	702	658	12
-6	1	5	343	331	9
-5	1	5	472	474	11
-4	1	5	407	393	10
-3	1	5	1365	1345	15
-2	1	5	761	700	10
-1	1	5	836	830	10
0	1	5	319	347	9
1	1	5	592	593	8
2	1	5	476	511	9
3	1	5	459	492	9
4	1	5	443	490	9
5	1	5	2144	2252	22
6	1	5	567	568	10
7	1	5	278	299	10
8	1	5	222	206	13
9	1	5	530	554	13
10	1	5	137	137	24
11	1	5	87	4	-35
12	1	5	192	178	23
-10	2	5	173	151	26
-9	2	5	273	235	16
-8	2	5	171	164	21
-7	2	5	221	231	16
-6	2	5	961	958	12
-5	2	5	442	454	11
-4	2	5	204	216	12
-3	2	5	261	274	9
-2	2	5	660	614	9
-1	2	5	1260	1207	14
0	2	5	309	307	8
1	2	5	430	422	9
2	2	5	996	932	11
3	2	5	742	774	9

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
4	2	5	722	722	9
5	2	5	504	511	9
6	2	5	407	396	10
7	2	5	243	255	10
8	2	5	218	223	13
9	2	5	448	455	12
10	2	5	372	360	10
11	2	5	115	5	-27
12	2	5	390	379	13
-10	3	5	63	4	-90
-9	3	5	265	279	17
-8	3	5	215	216	18
-7	3	5	208	173	16
-6	3	5	133	150	23
-5	3	5	853	863	12
-4	3	5	1091	1086	13
-3	3	5	404	396	10
-2	3	5	468	461	10
-1	3	5	307	274	8
0	3	5	603	589	9
1	3	5	838	771	10
2	3	5	926	864	11
3	3	5	1228	1102	13
4	3	5	460	462	9
5	3	5	432	451	10
6	3	5	160	173	14
7	3	5	792	774	11
8	3	5	278	267	11
9	3	5	529	531	12
10	3	5	437	449	11
11	3	5	90	4	-51
12	3	5	275	290	16
13	3	5	261	225	19
-9	4	5	153	103	28
-8	4	5	497	502	12
-7	4	5	317	326	12
-6	4	5	234	233	15
-5	4	5	148	162	20
-4	4	5	918	907	12
-3	4	5	291	295	9
-2	4	5	652	643	10
-1	4	5	689	633	10
0	4	5	809	775	10
1	4	5	1155	1071	13
2	4	5	906	775	11
3	4	5	869	808	10
4	4	5	2428	2371	25
5	4	5	591	586	10
6	4	5	93	2	-19
7	4	5	125	104	20
8	4	5	756	732	11
9	4	5	472	471	12
10	4	5	260	237	13
11	4	5	291	296	14
12	4	5	232	284	19
13	4	5	226	236	22
-9	5	5	15	1	-362
-8	5	5	38	2	-132
-7	5	5	641	627	14
-6	5	5	13	0	-331
-5	5	5	12	0	-325
-4	5	5	7	0	-322
-3	5	5	254	284	11
-2	5	5	277	257	10
-1	5	5	512	500	10
0	5	5	1791	1649	19
1	5	5	2096	1937	22
2	5	5	85	1	-21
3	5	5	850	798	11
4	5	5	217	227	10
5	5	5	902	853	11
6	5	5	581	568	10
7	5	5	360	365	10
8	5	5	618	591	11
9	5	5	581	559	12
10	5	5	345	354	11
11	5	5	14	1	-338
12	5	5	570	532	15
13	5	5	280	266	18
-8	6	5	108	7	-33
-7	6	5	9	0	-350
-6	6	5	359	353	12
-5	6	5	324	343	11
-4	6	5	177	188	18
-3	6	5	312	309	11
-2	6	5	360	351	9
-1	6	5	250	239	11
0	6	5	697	693	10
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2	6	5	1122	978	13
3	6	5	456	417	11
4	6	5	522	540	10
5	6	5	436	396	11
6	6	5	181	198	15
7	6	5	506	494	12
8	6	5	303	304	11
9	6	5	873	825	12
10	6	5	213	216	16
11	6	5	275	255	16
12	6	5	225	203	20
13	6	5	329	295	16
-7	7	5	151	131	29
-6	7	5	84	4	-57
-5	7	5	231	176	17
-4	7	5	132	149	26
-3	7	5	401	396	11
-2	7	5	752	765	12
-1	7	5	447	444	12
0	7	5	326	319	10
1	7	5	327	331	10
2	7	5	638	543	11
3	7	5	633	576	11
4	7	5	207	217	13
5	7	5	208	253	14
6	7	5	332	341	9
7	7	5	265	266	11
8	7	5	755	727	12
9	7	5	417	409	10
10	7	5	505	477	13
11	7	5	175	160	23
12	7	5	342	301	14
13	7	5	296	239	17
-7	8	5	15	1	-364
-6	8	5	15	1	-364
-5	8	5	338	329	14
-4	8	5	176	164	21
-3	8	5	409	400	11
-2	8	5	182	156	18
-1	8	5	585	583	12
0	8	5	702	639	12
1	8	5	87	2	-48
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3	8	5	80	2	-50
4	8	5	454	449	11
5	8	5	755	822	11
6	8	5	207	208	15
7	8	5	586	575	12
8	8	5	406	389	10
9	8	5	453	450	12
10	8	5	79	3	-59
11	8	5	379	369	13
12	8	5	124	7	-30
-6	9	5	101	7	-55
-5	9	5	15	1	-359
-4	9	5	315	333	15
-3	9	5	267	267	16
-2	9	5	91	3	-31
-1	9	5	227	237	16
0	9	5	462	440	13
1	9	5	328	315	12
2	9	5	437	411	11
3	9	5	599	562	13
4	9	5	362	376	10
5	9	5	386	429	11
6	9	5	486	550	13
7	9	5	207	216	16
8	9	5	671	657	13
9	9	5	92	3	-51
10	9	5	210	199	20
11	9	5	72	4	-47
12	9	5	286	239	17
-5	10	5	105	7	-53
-4	10	5	65	4	-84
-3	10	5	425	406	12
-2	10	5	177	208	24
-1	10	5	13	0	-354
0	10	5	257	254	16
1	10	5	259	242	16
2	10	5	225	195	18
3	10	5	341	334	13
4	10	5	80	2	-59
5	10	5	491	538	12
6	10	5	339	366	11
7	10	5	338	393	11
8	10	5	143	95	25
9	10	5	237	222	17
10	10	5	306	279	15
11	10	5	15	1	-371
-3	11	5	10	1	-380
-2	11	5	358	321	14
-1	11	5	94	4	-55
0	11	5	116	5	-30
1	11	5	94	4	-55
2	11	5	35	1	-150
3	11	5	89	3	-38
4	11	5	587	535	14
5	11	5	13	0	-363
6	11	5	286	319	14
7	11	5	14	1	-348
8	11	5	314	348	15
9	11	5	14	1	-358
10	11	5	35	2	-100
11	11	5	225	227	22
-2	12	5	48	3	-122
-1	12	5	87	5	-43
0	12	5	30	2	-126
1	12	5	311	298	16
2	12	5	277	269	18
3	12	5	216	191	23
4	12	5	218	168	23
5	12	5	371	424	13
6	12	5	210	219	21
7	12	5	179	201	25
8	12	5	14	1	-376
9	12	5	99	6	-53
10	12	5	52	3	-72
0	13	5	15	1	-401
1	13	5	259	228	20
2	13	5	247	244	21
3	13	5	322	293	17
4	13	5	222	199	24
5	13	5	119	6	-29
6	13	5	174	165	26
7	13	5	10	1	-377
8	13	5	88	5	-44
9	13	5	216	235	24
3	14	5	114	8	-58
4	14	5	15	1	-448
5	14	5	95	6	-61
6	14	5	120	8	-32
-6	-11	6	251	241	19
-5	-11	6	216	193	21
-4	-11	6	26	2	-212
-3	-11	6	63	4	-80
-2	-11	6	157	97	27
-1	-11	6	10	1	-354
0	-11	6	299	260	16
1	-11	6	101	7	-52
-7	-10	6	168	184	27
-6	-10	6	51	3	-101
-5	-10	6	306	325	15
-4	-10	6	281	220	16
-3	-10	6	284	249	15
-2	-10	6	77	4	-41
-1	-10	6	61	3	-80
0	-10	6	242	257	18
1	-10	6	275	293	16
2	-10	6	72	4	-69
3	-10	6	10	1	-353
-8	-9	6	452	436	12
-7	-9	6	250	258	18
-6	-9	6	186	133	22
-5	-9	6	187	177	22
-4	-9	6	294	296	15
-3	-9	6	326	310	13
-2	-9	6	205	251	19
-1	-9	6	206	209	18
0	-9	6	325	318	13
1	-9	6	350	313	13
2	-9	6	62	3	-74
3	-9	6	14	1	-341
4	-9	6	283	286	16
5	-9	6	207	176	21
-9	-8	6	154	196	30
-8	-8	6	65	3	-82
-7	-8	6	302	305	15
-6	-8	6	170	168	24
-5	-8	6	13	0	-327
-4	-8	6	240	221	15
-3	-8	6	471	402	13
-2	-8	6	677	680	13
-1	-8	6	474	477	13
0	-8	6	325	319	12
1	-8	6	519	500	14
2	-8	6	271	204	13

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                                                      PAGE 15
   H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S

   3  -8   6   230   170  16       2  -5   6   195   182  14      -7  -2   6   222   214  15       2   0   6   860   805  10       9   2   6   213   151  15
   4  -8   6   247   230  16       3  -5   6   328   329  10      -6  -2   6   504   497  12       3   0   6   588   595   9      10   2   6    75     3 -54
   5  -8   6   222   221  19       4  -5   6   405   403  10      -5  -2   6   604   587  11       4   0   6   507   501  10      11   2   6   232   244  18
   6  -8   6   146   181  29       5  -5   6   757   748  12      -4  -2   6   989   999  12       5   0   6   555   575  10      12   2   6   101     6 -52
 -10  -7   6   225   256  23       6  -5   6   386   374  10      -3  -2   6   158   165  15       6   0   6   397   398  11      -9   3   6   119     7 -30
  -9  -7   6   131     7 -27       7  -5   6    90     4 -32      -2  -2   6   258   266   9       7   0   6   290   325  10      -8   3   6   182   158  23
  -8  -7   6   201   211  21       8  -5   6   388   342  12      -1  -2   6   542   534   9       8   0   6   497   508  12      -7   3   6    89     3 -49
  -7  -7   6    74     3 -63       9  -5   6   168   160  26       0  -2   6   675   673  10       9   0   6   997  1010  14      -6   3   6    89     3 -46
  -6  -7   6   115     4 -23     -10  -4   6   167   173  27       1  -2   6   359   382  10      10   0   6   463   455  12      -5   3   6   270   245  12
  -5  -7   6   137   136  24      -9  -4   6   233   215  18       2  -2   6   236   243   9      11   0   6   124     6 -26      -4   3   6   982   982  13
  -4  -7   6   472   447  13      -8  -4   6   223   231  18       3  -2   6   582   575  10      12   0   5   226   219  21      -3   3   6   899   883  12
  -3  -7   6   406   410  12      -7  -4   6   354   344  11       4  -2   6  1519  1539  16     -10   1   6   215   229  22      -2   3   6   343   341   9
  -2  -7   6   421   393  12      -6  -4   6   877   880  13       5  -2   6   610   604  11      -9   1   6   377   378  13      -1   3   6   731   741  10
  -1  -7   6   540   593  12      -5  -4   6    68     2 -54       6  -2   6   287   333  11      -8   1   6    14     1-348       0   3   6  1367  1324  15
   0  -7   6   626   609  12      -4  -4   6   671   644  11       7  -2   6   350   358  10      -7   1   6   148   181  23       1   3   6   501   480   9
   1  -7   6   353   338  10      -3  -4   6   873   894  12       8  -2   6   234   237  15      -6   1   6   329   356  11       2   3   6   537   499   9
   2  -7   6   125   133  25      -2  -4   6   409   394  10       9  -2   6   291   301  14      -5   1   6   543   554  11       3   3   6   720   716  10
   3  -7   6   181   151  18      -1  -4   6   606   599  10      10  -2   6   247   256  17      -4   1   6   392   385  10       4   3   6   557   540   9
   4  -7   6     8     0-325       0  -4   6   890   889  12      11  -2   6   123     8 -28      -3   1   6   112   101  20       5   3   6   815   824  11
   5  -7   6   251   234  16       1  -4   6   497   498  10     -10  -1   6    83     5 -44      -2   1   6  1255  1222  14       6   3   6   143   146  16
   6  -7   6   326   305  14       2  -4   6   637   606  10      -9  -1   6   305   273  15      -1   1   6   609   547   9       7   3   6   517   497  11
   7  -7   6   184   213  24       3  -4   6   327   360   9      -8  -1   6   301   313  13       0   1   6   566   557   9       8   3   6  1096  1100  14
 -10  -6   6    15     1-372       4  -4   6   399   408  12      -7  -1   6   857   858  13       1   1   6   549   556   9       9   3   6   561   560  12
  -9  -6   6   346   344  14       5  -4   6   720   691  12      -6  -1   6   250   248  13       2   1   6   465   455   9      10   3   6   313   314  12
  -8  -6   6   224   216  18       6  -4   6   152   187  20      -5  -1   6   593   577  11       3   1   6   483   478   9      11   3   6   193   179  20
  -7  -6   6   140   117  25       7  -4   6   167   161  19      -4  -1   6   392   411  10       4   1   6   867   914  11      12   3   6   286   277  16
  -6  -6   6   242   225  14       8  -4   6   243   216  16      -3  -1   6   345   335   9       5   1   6   350   401  10      -9   4   6    89     6 -60
  -5  -6   6   249   258  14       9  -4   6   160   112  26      -2  -1   6   259   261   9       6   1   6   945   971  12      -8   4   6    57     3 -59
  -4  -6   6   345   370  10      10  -4   6   123     8 -29      -1  -1   6   753   747  10       7   1   6   295   294  10      -7   4   6   367   384  12
  -3  -6   6   445   428  11     -10  -3   6    15     1-365       0  -1   6  1408  1293  15       8   1   6   524   564  13      -6   4   6   262   281  14
  -2  -6   6   346   348  11      -9  -3   6   114     5 -28       1  -1   6  2024  2000  21       9   1   6   428   457  12      -5   4   6   178   148  17
  -1  -6   6   467   474  12      -8  -3   6   164   135  21       2  -1   6   463   463   9      10   1   6   415   429  11      -4   4   6   365   370  11
   0  -6   6   619   600  12      -7  -3   6   410   418  12       3  -1   6   515   543   9      11   1   6   203   227  20      -3   4   6  1251  1235  15
   1  -6   6   209   221  14      -6  -3   6   426   403  12       4  -1   6  1000  1064  12      12   1   6    15     1-361      -2   4   6   382   402   9
   2  -6   6   315   294  10      -5  -3   6   846   851  12       5  -1   6   728   711  10     -10   2   6   110     7 -35      -1   4   6   447   438  11
   3  -6   6   174   196  17      -4  -3   6   719   726  11       6  -1   6   434   422  10      -9   2   6   285   267  16       0   4   6   504   502  10
   4  -6   6   535   507  13      -3  -3   6   609   586  10       7  -1   6   140   142  19      -8   2   6   586   551  14       1   4   6   123    98  18
   5  -6   6   148   163  23      -2  -3   6   475   464  10       8  -1   6   316   326  11      -7   2   6   162   174  21       2   4   6   393   394  10
   6  -6   6   255   253  15      -1  -3   6   204   215  11       9  -1   6   366   364  10      -6   2   6   148   138  21       3   4   6   604   581   9
   7  -6   6   352   342  13       0  -3   6   577   587  10      10  -1   6    14     1-335      -5   2   6   496   527  12       4   4   6   898   867  11
   8  -6   6   379   354  13       1  -3   6   610   610  10      11  -1   6   149   180  29      -4   2   6   236   245  12       5   4   6  1649  1639  17
 -10  -5   6   127     8 -30       2  -3   6   641   619  10     -10   0   6   366   351  14      -3   2   6   336   322   9       6   4   6   526   511  10
  -9  -5   6   217   158  20       3  -3   6   575   556  10      -9   0   6   150   131  27      -2   2   6   378   340  10       7   4   6   424   430  11
  -8  -5   6   329   312  13       4  -3   6   223   248  12      -8   0   6   169   193  21      -1   2   6  1334  1281  15       8   4   6   574   554  12
  -7  -5   6   499   496  13       5  -3   6   578   534  11      -7   0   6   232   238  14       0   2   6  1689  1625  18       9   4   6   710   683  12
  -6  -5   6   182   140  17       6  -3   6   406   426  10      -6   0   6   375   390  10       1   2   6   474   470   9      10   4   6   285   293  13
  -5  -5   6   347   343  10       7  -3   6   343   336  10      -5   0   6   284   272  10       2   2   6   210   194   9      11   4   6    39     2-116
  -4  -5   6   929   899  12       8  -3   6   287   276  13      -4   0   6   668   655  10       3   2   6   438   439   9      12   4   6    78     4 -65
  -3  -5   6   992   994  13       9  -3   6   375   370  13      -3   0   6   936   914  12       4   2   6   690   729  10      13   4   6   286   267  17
  -2  -5   6   164   134  16      10  -3   6   208   200  21      -2   0   6   789   771  10       5   2   6   657   682  10      -8   5   6    15     1-356
  -1  -5   6   625   574  11     -10  -2   6    15     1-365      -1   0   6   842   820  10       6   2   6   469   463  10      -7   5   6    92     4 -53
   0  -5   6   643   638  11      -9  -2   6   184   153  22       0   0   6   800   793  10       7   2   6   331   320  11      -6   5   6   638   646  13
   1  -5   6   503   485  12      -8  -2   6   606   613  13       1   0   6  2062  1960  21       8   2   6   378   407  10      -5   5   6    45     1 -92
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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
-4	5	6	63	2	-61
-3	5	6	173	188	17
-2	5	6	776	749	11
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0	5	6	383	386	9
1	5	6	333	307	8
2	5	6	254	244	10
3	5	6	469	461	10
4	5	6	998	1002	12
5	5	6	1146	1098	13
6	5	6	760	733	11
7	5	6	313	299	10
8	5	6	368	361	10
9	5	6	125	98	25
10	5	6	401	349	12
11	5	6	208	175	19
12	5	6	205	225	22
13	5	6	394	370	14
-8	6	6	15	1	-366
-7	6	6	10	0	-353
-6	6	6	237	218	17
-5	6	6	559	564	14
-4	6	6	354	333	10
-3	6	6	173	209	18
-2	6	6	275	283	11
-1	6	6	498	494	12
0	6	6	307	306	10
1	6	6	366	378	11
2	6	6	554	519	11
3	6	6	586	541	10
4	6	6	518	524	11
5	6	6	190	201	14
6	6	6	597	561	11
7	6	6	452	400	12
8	6	6	467	447	12
9	6	6	259	258	14
10	6	6	310	296	12
11	6	6	231	226	18
12	6	6	400	341	13
13	6	6	167	131	28
-7	7	6	41	3	-87
-6	7	6	14	1	-354
-5	7	6	168	150	24
-4	7	6	601	573	13
-3	7	6	64	2	-65
-2	7	6	252	226	13
-1	7	6	716	729	12
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1	7	6	648	636	11
2	7	6	170	148	17
3	7	6	1009	969	13
4	7	6	1024	1025	13
5	7	6	425	426	11
6	7	6	172	148	16
7	7	6	255	231	12
8	7	6	477	449	12
9	7	6	616	575	13
10	7	6	57	2	-53
11	7	6	173	176	24
12	7	6	324	310	15
-6	8	6	15	1	-364
-5	8	6	14	1	-356
-4	8	6	149	131	26
-3	8	6	205	226	18
-2	8	6	314	299	12
-1	8	6	198	184	17
0	8	6	788	763	13
1	8	6	705	689	12
2	8	6	181	174	18
3	8	6	432	420	12
4	8	6	572	546	12
5	8	6	482	492	13
6	8	6	378	397	10
7	8	6	421	428	10
8	8	6	288	239	12
9	8	6	322	289	12
10	8	6	351	352	13
11	8	6	49	2	-104
12	8	6	398	359	14
-5	9	6	49	3	-112
-4	9	6	9	0	-362
-3	9	6	216	224	19
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3	9	6	120	3	-24
4	9	6	465	458	11
5	9	6	111	3	-23
6	9	6	96	3	-27
7	9	6	220	250	16
8	9	6	171	193	20
9	9	6	683	633	14
10	9	6	326	310	14
11	9	6	245	230	19
12	9	6	43	3	-132
-4	10	6	103	6	-36
-3	10	6	103	5	-34
-2	10	6	403	388	12
-1	10	6	202	188	21
0	10	6	171	215	23
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3	10	6	206	195	20
4	10	6	192	208	20
5	10	6	153	201	23
6	10	6	68	2	-41
7	10	6	232	242	16
8	10	6	363	384	13
9	10	6	96	4	-34
10	10	6	441	400	12
11	10	6	263	240	18
-3	11	6	109	7	-36
-2	11	6	15	1	-384
-1	11	6	374	377	14
0	11	6	99	4	-56
1	11	6	93	4	-39
2	11	6	23	1	-229
3	11	6	224	219	20
4	11	6	56	2	-96
5	11	6	330	387	13
6	11	6	302	364	15
7	11	6	236	259	18
8	11	6	209	270	21
9	11	6	366	370	13
10	11	6	49	3	-112
11	11	6	207	140	23
-2	12	6	59	4	-100
-1	12	6	79	5	-74
0	12	6	300	305	17
1	12	6	59	3	-98
2	12	6	80	4	-48
3	12	6	336	325	16
4	12	6	14	1	-431
5	12	6	150	173	29
6	12	6	223	229	19
7	12	6	312	328	15
8	12	6	237	248	19
9	12	6	85	5	-64
10	12	6	83	5	-45
0	13	6	110	7	-56
1	13	6	238	189	22
2	13	6	124	7	-34
3	13	6	96	5	-66
4	13	6	111	6	-40
5	13	6	99	5	-61
6	13	6	194	171	24
7	13	6	164	184	28
8	13	6	156	147	31
5	14	6	74	5	-65
-3	-11	7	70	5	-79
-2	-11	7	15	1	-370
-1	-11	7	15	1	-365
-6	-10	7	166	151	27
-5	-10	7	15	1	-354
-4	-10	7	308	297	16
-3	-10	7	352	336	14
-2	-10	7	166	170	26
-1	-10	7	114	6	-30
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-5	-9	7	231	222	18
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3	-9	7	62	3	-82
4	-9	7	15	1	-330
-8	-8	7	205	172	22
-7	-8	7	208	192	21
-6	-8	7	267	287	16
-5	-8	7	409	385	11
-4	-8	7	14	1	-361
-3	-8	7	188	174	20
-2	-8	7	302	335	13
-1	-8	7	81	3	-52
0	-8	7	335	315	12
1	-8	7	203	177	19
2	-8	7	511	476	12
3	-8	7	443	457	11
4	-8	7	223	171	19
5	-8	7	92	5	-59
6	-8	7	92	6	-57
-9	-7	7	137	9	-28
-8	-7	7	394	413	13
-7	-7	7	219	212	19
-6	-7	7	88	4	-56
-5	-7	7	327	325	12
-4	-7	7	329	308	12
-3	-7	7	285	257	13
-2	-7	7	44	1	-59
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2	-7	7	247	268	15
3	-7	7	304	324	13
4	-7	7	486	495	12
5	-7	7	14	1	-346
6	-7	7	211	206	21
7	-7	7	103	7	-52
-9	-6	7	134	8	-27
-8	-6	7	446	438	12
-7	-6	7	436	426	13
-6	-6	7	148	167	24
-5	-6	7	97	3	-28
-4	-6	7	470	474	13
-3	-6	7	282	286	12
-2	-6	7	47	1	-81
-1	-6	7	208	199	15
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6	-6	7	78	4	-63
7	-6	7	36	2	-142
8	-6	7	283	271	17
-10	-5	7	232	231	21
-9	-5	7	216	209	21
-8	-5	7	280	242	16
-7	-5	7	258	260	16
-6	-5	7	221	201	16
-5	-5	7	329	329	11
-4	-5	7	178	184	18
-3	-5	7	473	484	13
-2	-5	7	416	411	11
-1	-5	7	12	0	-302
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3	-5	7	303	275	11
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5	-5	7	150	160	22
6	-5	7	314	316	13
7	-5	7	250	251	17
8	-5	7	199	224	22
9	-5	7	378	359	14
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-1	-4	7	739	697	11
0	-4	7	472	457	12
1	-4	7	737	714	11
2	-4	7	201	185	14
3	-4	7	305	277	10
4	-4	7	170	162	17
5	-4	7	599	604	12
6	-4	7	382	402	11
7	-4	7	179	173	21
8	-4	7	174	207	23
9	-4	7	197	194	22

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                     PAGE 17

   H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S

 -10  -3   7    45     3-132       0  -1   7   887   868  11       9   1   7   587   586  13      -3   4   7   227   253  14       9   6   7   499   483  13
  -9  -3   7   229   266  20       1  -1   7   154   144  15      10   1   7   185   233  21      -2   4   7   899   888  12      10   6   7   154   139  25
  -8  -3   7   332   318  14       2  -1   7   458   466  10      11   1   7    14     1-340      -1   4   7   591   571  11      11   6   7   116     5 -29
  -7  -3   7    48     2 -57       3  -1   7   305   315  10      12   1   7   247   257  19       0   4   7   177   181  15      -7   7   7   115     8 -32
  -6  -3   7   178   141  18       4  -1   7   971   997  12      -9   2   7   123     7 -30       1   4   7   813   789  11      -6   7   7   116     6 -30
  -5  -3   7   373   380  10       5  -1   7  1250  1237  14      -8   2   7   302   301  15       2   4   7   453   408  11      -5   7   7   110     5 -29
  -4  -3   7   681   682  12       6  -1   7   549   574  12      -7   2   7   528   514  13       3   4   7   220   219  11      -4   7   7   334   319  13
  -3  -3   7   433   413  10       7  -1   7   267   242  12      -6   2   7   363   359  11       4   4   7   673   663  10      -3   7   7   632   627  13
  -2  -3   7   410   412  11       8  -1   7   193   186  17      -5   2   7   356   376  12       5   4   7   140   149  17      -2   7   7   307   312  12
  -1  -3   7   901   868  12       9  -1   7   220   215  17      -4   2   7   633   630  11       6   4   7   756   749  11      -1   7   7    66     2 -61
   0  -3   7   883   857  12      10  -1   7   222   196  19      -3   2   7    19     0-176       7   4   7    30     1-482       0   7   7   530   519  13
   1  -3   7   240   246  11      11  -1   7   105     6 -33      -2   2   7   325   319   9       8   4   7   653   652  12       1   7   7   256   262  13
   2  -3   7   546   526  11     -10   0   7    90     6 -42      -1   2   7   366   377  10       9   4   7   529   551  13       2   7   7   488   433  13
   3  -3   7   259   247  11      -9   0   7   113     6 -30       0   2   7  1036  1025  12      10   4   7   413   434  11       3   7   7   202   208  16
   4  -3   7   230   206  12      -8   0   7   104     4 -30       1   2   7  1378  1362  15      11   4   7   333   349  14       4   7   7   712   703  12
   5  -3   7   188   252  16      -7   0   7   270   283  14       2   2   7   361   366   9      12   4   7    10     1-376       5   7   7  1004  1031  13
   6  -3   7   491   500  13      -6   0   7   596   606  13       3   2   7   720   746  10      -8   5   7   236   296  22       6   7   7   359   377  10
   7  -3   7   319   294  11      -5   0   7   606   604  12       4   2   7  1283  1324  14      -7   5   7   165   153  26       7   7   7   357   358  10
   8  -3   7   338   314  13      -4   0   7   262   246  11       5   2   7   557   571  10      -6   5   7   108     5 -31       8   7   7   539   511  13
   9  -3   7   230   254  19      -3   0   7   407   425  11       6   2   7   522   533  11      -5   5   7   274   297  14       9   7   7   466   443  12
  10  -3   7    57     3 -63      -2   0   7   330   331   9       7   2   7   252   289  12      -4   5   7   232   234  15      10   7   7   273   295  16
 -10  -2   7   195   183  25      -1   0   7   600   597  10       8   2   7    38     1 -96      -3   5   7   160   113  19      11   7   7   110     5 -31
  -9  -2   7    14     1-366       0   0   7   308   308   8       9   2   7   460   443  12      -2   5   7   432   437  12      12   7   7    10     1-424
  -8  -2   7   186   184  22       1   0   7  1095  1074  13      10   2   7   136   115  27      -1   5   7   896   876  12      -6   8   7   249   247  19
  -7  -2   7   379   370  11       2   0   7   763   743  10      11   2   7   151   196  26       0   5   7   680   660  11      -5   8   7   197   199  23
  -6  -2   7   314   305  12       3   0   7    10     0-272      12   2   7   229   217  20       1   5   7   404   417  11      -4   8   7    64     3 -78
  -5  -2   7   331   331  10       4   0   7   284   295   9      -9   3   7   254   219  19       2   5   7   223   229  12      -3   8   7   342   351  13
  -4  -2   7   991   975  13       5   0   7   955   976  12      -8   3   7   116     6 -30       3   5   7   401   421  10      -2   8   7   391   404  11
  -3  -2   7   988   972  12       6   0   7   327   370   9      -7   3   7   338   334  13       4   5   7   355   331  10      -1   8   7   231   237  16
  -2  -2   7   234   233  11       7   0   7   183   143  16      -6   3   7   223   260  16       5   5   7   746   735  11       0   8   7   387   399  14
  -1  -2   7   413   391  11       8   0   7   462   453  12      -5   3   7   101     3 -25       6   5   7   269   272  11       1   8   7   345   356  11
   0  -2   7  1018  1041  12       9   0   7   275   270  13      -4   3   7   250   247  13       7   5   7   249   215  12       2   8   7   402   393  11
   1  -2   7   360   351  10      10   0   7   304   284  14      -3   3   7   343   352  10       8   5   7   458   448  12       3   8   7   114     3 -23
   2  -2   7   335   342   8      11   0   7   360   326  13      -2   3   7   524   513  11       9   5   7    61     2 -48       4   8   7   495   490  13
   3  -2   7   512   503  10      12   0   7   219   236  22      -1   3   7   239   218  11      10   5   7    13     0-349       5   8   7   639   659  12
   4  -2   7   657   654  11      -9   1   7   166   185  27       0   3   7  1028   996  12      11   5   7    10     0-352       6   8   7   551   564  13
   5  -2   7   830   827  12      -8   1   7   356   395  13       1   3   7  1451  1392  16      12   5   7   331   335  15       7   8   7   253   239  14
   6  -2   7   490   472  12      -7   1   7     8     0-335       2   3   7   420   386  10      -7   6   7    10     1-391       8   8   7   350   346  12
   7  -2   7    80     2 -48      -6   1   7   445   442  13       3   3   7   203   197  11      -6   6   7   195   142  21       9   8   7   455    17-101
   8  -2   7   586   546  13      -5   1   7   543   557  13       4   3   7   655   673  10      -5   6   7   305   260  14      10   8   7    14     1-391
   9  -2   7   251   203  16      -4   1   7   840   844  12       5   3   7   139   139  17      -4   6   7   411   425  11      11   8   7    14     1-384
  10  -2   7   279   261  16      -3   1   7    86     2 -23       6   3   7   418   399  11      -3   6   7   429   400  10      12   8   7    71     4 -85
  11  -2   7    97     6 -55      -2   1   7   398   392  10       7   3   7   319   321  10      -2   6   7   223   246  15      -5   9   7    42     3-874
 -10  -1   7    34     2-161      -1   1   7   697   687  10       8   3   7   379   392  10      -1   6   7   541   541  13      -4   9   7    65     3 -87
  -9  -1   7   295   291  16       0   1   7   315   290   8       9   3   7   903   904  13       0   6   7   925   878  13      -3   9   7   209   150  21
  -8  -1   7    85     4 -36       1   1   7   211   211  11      10   3   7   533   523  14       1   6   7   352   336  10      -2   9   7   181   136  24
  -7  -1   7   549   559  13       2   1   7  1079  1056  13      11   3   7   239   213  17       2   6   7   222   222  14      -1   9   7   286   263  15
  -6  -1   7   597   605  13       3   1   7   858   849  11      12   3   7   373   361  14       3   6   7   517   546  13       0   9   7    63     2 -76
  -5  -1   7   301   298  11       4   1   7   795   824  11      -8   4   7    77     4 -70       4   6   7   371   366  12       1   9   7   144   201  28
  -4  -1   7   673   659  11       5   1   7   899   957  12      -7   4   7   218   225  19       5   6   7   526   493  12       2   9   7   560   537  14
  -3  -1   7   981   969  12       6   1   7   442   487  12      -6   4   7    87     3 -51       6   6   7    92     2 -29       3   9   7   457   445  14
  -2  -1   7   297   293   9       7   1   7   308   345  10      -5   4   7   481   490  13       7   6   7   331   371  11       4   9   7   200   230  19
  -1  -1   7   109    83  20       8   1   7   144   146  20      -4   4   7    53     1 -72       8   6   7   682   660  12       5   9   7   264   253  14
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
6	9	7	323	350	12
7	9	7	238	253	17
9	9	7	77	3	-62
11	9	7	106	6	-57
-4	10	7	137	9	-30
-3	10	7	15	1	-375
-2	10	7	28	1	-133
-1	10	7	286	255	17
0	10	7	129	5	-31
1	10	7	199	221	21
2	10	7	129	4	-26
3	10	7	53	2	-724
4	10	7	380	384	12
5	10	7	269	263	15
6	10	7	100	3	-31
7	10	7	254	244	16
8	10	7	14	1	-414
9	10	7	306	385	17
10	10	7	10	0	-411
11	10	7	10	1	-474
-3	11	7	10	1	-385
-2	11	7	98	6	-60
-1	11	7	14	1	-394
0	11	7	296	292	16
1	11	7	232	222	20
2	11	7	117	5	-31
3	11	7	158	134	29
4	11	7	401	379	13
5	11	7	185	207	23
6	11	7	182	191	22
7	11	7	273	269	16
8	11	7	171	202	26
9	11	7	232	218	20
10	11	7	177	154	26
-1	12	7	15	1	-407
0	12	7	39	2	-150
1	12	7	339	310	16
2	12	7	206	225	24
3	12	7	79	4	-75
4	12	7	191	210	26
5	12	7	170	138	27
6	12	7	70	3	-76
7	12	7	14	1	-360
8	12	7	121	7	-31
9	12	7	165	232	29
1	13	7	15	1	-417
2	13	7	254	234	21
3	13	7	114	7	-38
4	13	7	125	7	-34
5	13	7	179	136	29
6	13	7	113	7	-32
7	13	7	93	6	-41
8	13	7	114	7	-34

H	K	L	10FO	10FC	10S
-4	-10	8	100	7	-37
-3	-10	8	191	165	25
-2	-10	8	369	361	14
-1	-10	8	98	6	-37
0	-10	8	180	198	26
1	-10	8	116	8	-32
-6	-9	8	99	6	-37
-5	-9	8	209	232	22
-4	-9	8	220	171	20
-3	-9	8	181	177	24
-2	-9	8	59	3	-85
-1	-9	8	406	410	12
0	-9	8	174	128	24
1	-9	8	183	208	24
2	-9	8	119	7	-30
3	-9	8	15	1	-345
-7	-8	8	15	1	-371
-6	-8	8	91	5	-57
-5	-8	8	14	1	-346
-4	-8	8	462	516	14
-3	-8	8	14	1	-347
-2	-8	8	197	201	20
-1	-8	8	90	4	-51
0	-8	8	354	354	13
1	-8	8	180	160	23
2	-8	8	113	5	-28
3	-8	8	301	325	15
4	-8	8	260	210	17
5	-8	8	15	1	-359
-8	-7	8	94	6	-60
-7	-7	8	315	359	16
-6	-7	8	14	1	-349
-5	-7	8	165	155	24
-4	-7	8	472	444	13
-3	-7	8	741	714	13
-2	-7	8	8	0	-343
-1	-7	8	284	273	13
0	-7	8	277	264	14
1	-7	8	214	190	16
2	-7	8	169	150	22
3	-7	8	178	155	22
4	-7	8	406	431	13
5	-7	8	322	305	14
6	-7	8	101	6	-34
-8	-6	8	15	1	-370
-7	-6	8	388	397	13
-6	-6	8	571	551	14
-5	-6	8	250	207	16
-4	-6	8	305	283	13
-3	-6	8	263	281	14
-2	-6	8	217	185	16
-1	-6	8	148	158	22
0	-6	8	238	266	15

H	K	L	10FO	10FC	10S
1	-6	8	585	620	13
2	-6	8	179	178	18
3	-6	8	13	0	-313
4	-6	8	14	1	-324
5	-6	8	514	495	14
6	-6	8	236	224	18
7	-6	8	81	5	-43
-9	-5	8	65	4	-88
-8	-5	8	196	189	23
-7	-5	8	209	190	20
-6	-5	8	290	340	14
-5	-5	8	431	456	12
-4	-5	8	284	270	13
-3	-5	8	239	257	14
-2	-5	8	734	735	12
-1	-5	8	140	75	21
0	-5	8	75	2	-52
1	-5	8	215	198	15
2	-5	8	838	800	12
3	-5	8	269	293	13
4	-5	8	206	193	16
5	-5	8	333	311	12
6	-5	8	276	254	15
7	-5	8	215	196	19
8	-5	8	257	237	18
-9	-4	8	254	221	19
-8	-4	8	413	408	13
-7	-4	8	14	1	-349
-6	-4	8	169	184	21
-5	-4	8	416	419	10
-4	-4	8	557	549	13
-3	-4	8	105	3	-24
-2	-4	8	130	119	22
-1	-4	8	534	589	12
0	-4	8	417	421	12
1	-4	8	334	352	10
2	-4	8	225	235	14
3	-4	8	647	623	12
4	-4	8	555	567	13
5	-4	8	114	4	-23
6	-4	8	375	374	11
7	-4	8	14	1	-336
8	-4	8	82	4	-61
9	-4	8	154	184	30
-9	-3	8	205	220	24
-8	-3	8	422	444	12
-7	-3	8	481	517	14
-6	-3	8	235	229	15
-5	-3	8	80	2	-50
-4	-3	8	540	521	12
-3	-3	8	271	259	12
-2	-3	8	329	322	10
-1	-3	8	138	155	19

H	K	L	10FO	10FC	10S
0	-3	8	1108	1068	13
1	-3	8	599	594	11
2	-3	8	128	136	21
3	-3	8	154	168	18
4	-3	8	705	725	12
5	-3	8	258	266	13
6	-3	8	13	0	-323
7	-3	8	433	404	10
8	-3	8	267	284	16
9	-3	8	201	203	22
10	-3	8	116	8	-32
-9	-2	8	164	167	29
-8	-2	8	243	227	18
-7	-2	8	360	388	12
-6	-2	8	65	2	-66
-5	-2	8	429	416	11
-4	-2	8	145	154	21
-3	-2	8	896	887	12
-2	-2	8	315	295	10
-1	-2	8	256	260	11
0	-2	8	544	513	11
1	-2	8	1433	1392	16
2	-2	8	143	181	18
3	-2	8	247	240	11
4	-2	8	269	261	11
5	-2	8	172	170	17
6	-2	8	413	402	10
7	-2	8	404	410	12
8	-2	8	470	500	13
9	-2	8	554	538	15
10	-2	8	95	6	-54
-9	-1	8	57	3	-69
-8	-1	8	227	249	19
-7	-1	8	14	1	-346
-6	-1	8	238	211	15
-5	-1	8	218	195	15
-4	-1	8	298	332	11
-3	-1	8	524	533	12
-2	-1	8	1165	1157	14
-1	-1	8	355	364	11
0	-1	8	177	156	14
1	-1	8	747	729	11
2	-1	8	485	524	11
3	-1	8	202	222	13
4	-1	8	316	292	10
5	-1	8	802	803	12
6	-1	8	124	160	23
7	-1	8	49	1	-51
8	-1	8	316	315	12
9	-1	8	502	516	14
10	-1	8	223	227	20
11	-1	8	26	2	-200
-9	0	8	245	255	20

H	K	L	10FO	10FC	10S
-8	0	8	269	248	17
-7	0	8	94	4	-50
-6	0	8	259	260	14
-5	0	8	313	334	12
-4	0	8	412	418	10
-3	0	8	360	375	9
-2	0	8	605	600	11
-1	0	8	978	940	12
0	0	8	705	694	11
1	0	8	331	327	9
2	0	8	239	243	10
3	0	8	440	475	11
4	0	8	116	147	21
5	0	8	215	222	13
6	0	8	986	1041	13
7	0	8	79	2	-30
8	0	8	13	0	-321
9	0	8	258	247	16
10	0	8	255	274	17
11	0	8	49	3	-108
-9	1	8	15	1	-374
-8	1	8	14	1	-361
-7	1	8	77	3	-62
-6	1	8	235	302	16
-5	1	8	501	491	12
-4	1	8	791	778	12
-3	1	8	583	603	12
-2	1	8	261	251	11
-1	1	8	507	469	11
0	1	8	1389	1323	15
1	1	8	346	332	9
2	1	8	227	229	11
3	1	8	412	449	10
4	1	8	484	510	11
5	1	8	786	834	11
6	1	8	421	430	12
7	1	8	794	823	12
8	1	8	518	517	13
9	1	8	191	180	18
10	1	8	421	400	11
11	1	8	41	2	-127
12	1	8	185	135	26
-9	2	8	211	209	23
-8	2	8	79	4	-66
-7	2	8	318	322	14
-6	2	8	211	223	17
-5	2	8	381	406	13
-4	2	8	478	507	12
-3	2	8	801	786	12
-2	2	8	159	189	17
-1	2	8	328	327	9
0	2	8	267	259	10
1	2	8	396	383	10

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  H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S

  2   2   8   867   852  11     -7   5   8    84     5 -67      7   7   8   155   159  20     10  10   8   204   165  22     -3  -7   9   358   365  13
  3   2   8   213   207  12     -6   5   8   190   181  22      8   7   8   513   514  12     11  10   8   170   182  29     -2  -7   9   565   573  14
  4   2   8  1072  1136  13     -5   5   8   414   410  12      9   7   8   367   369  11     -2  11   8   124     8 -32     -1  -7   9    90     4 -35
  5   2   8  1013  1052  13     -4   5   8   342   313  12     10   7   8   400   419  12     -1  11   8    20     1-198      0  -7   9   314   276  14
  6   2   8   481   492  12     -3   5   8   168   176  19     11   7   8   225   200  19      0  11   8    87     4 -43      1  -7   9   254   225  16
  7   2   8   263   282  12     -2   5   8   142   118  21     12   7   8   244   232  20      1  11   8    94     4 -60      2  -7   9   359   347  13
  8   2   8   537   528  13     -1   5   8   296   298  11     -5   8   8    78     5 -70      2  11   8   207   221  22      3  -7   9    14     1-351
  9   2   8   175   227  19      0   5   8   591   600  12     -4   8   8   217   215  20      3  11   8   127     5 -29      4  -7   9   311   288  15
 10   2   8   224   234  17      1   5   8   842   834  12     -3   8   8    73     3 -67      4  11   8   183   146  24      5  -7   9   207   233  23
 11   2   8   224   205  19      2   5   8   284   270  10     -2   8   8   323   321  13      5  11   8   308   305  15     -8  -6   9    15     1-376
 12   2   8    99     6 -37      3   5   8   808   760  11     -1   8   8   290   350  14      6  11   8   342   387  14     -7  -6   9   165   192  29
 -8   3   8   189   192  24      4   5   8   606   598  11      0   8   8   525   507  13      7  11   8    14     1-357     -6  -6   9   230   242  19
 -7   3   8   119     6 -28      5   5   8   600   604  11      1   8   8   532   561  14      8  11   8   134     7 -27     -5  -6   9   249   234  17
 -6   3   8   419   451  12      6   5   8   346   338   9      2   8   8   561   570  14      9  11   8   106     6 -36     -4  -6   9   250   233  17
 -5   3   8   205   220  16      7   5   8   327   328  10      3   8   8    88     2 -50     10  11   8    98     6 -39     -3  -6   9   209   153  19
 -4   3   8   180   176  18      8   5   8   200   184  16      4   8   8   246   260  14      0  12   8    86     5 -48     -2  -6   9   448   447  13
 -3   3   8   328   364  11      9   5   8   342   317  11      5   8   8   397   419  11      1  12   8    53     3-113     -1  -6   9   656   672  13
 -2   3   8   245   250  12     10   5   8   257   250  16      6   8   8   302   291  12      2  12   8   217   199  23      0  -6   9    13     0-351
 -1   3   8   495   500  11     11   5   8    10     0-349      7   8   8   431   447  11      3  12   8   280   280  19      1  -6   9   264   269  15
  0   3   8   282   298  10     12   5   8   166   215  28      8   8   8   245   223  14      4  12   8    25     1-236      2  -6   9   295   316  14
  1   3   8   833   794  11     -7   6   8   240   258  20      9   8   8   300   303  15      5  12   8   138     7 -28      3  -6   9   199   151  20
  2   3   8   731   696  11     -6   6   8    83     4 -61     10   8   8    94     4 -54      6  12   8   179   187  25      4  -6   9    14     1-345
  3   3   8   474   463  11     -5   6   8   120     5 -27     11   8   8   159   135  27      7  12   8   161   263  30      5  -6   9   236   203  18
  4   3   8   150   150  16     -4   6   8    73     3 -64     12   8   8   234   251  21      8  12   8    33     2-112      6  -6   9   443   424  12
  5   3   8  1075  1091  13     -3   6   8    13     0-341     -4   9   8    15     1-366      9  12   8    15     1-390      7  -6   9   176   123  26
  6   3   8    77     2 -44     -2   6   8   342   357  11     -3   9   8   117     6 -30      2  13   8    65     4-103     -8  -5   9    83     5 -70
  7   3   8    12     0-303     -1   6   8   353   313  10     -2   9   8   191   231  22      3  13   8    88     6 -50     -7  -5   9    61     3 -90
  8   3   8   319   344  11      0   6   8   562   533  12     -1   9   8   290   273  15      4  13   8   250   245  22     -6  -5   9    14     1-354
  9   3   8    69     2 -39      1   6   8   741   724  12      0   9   8   330   337  13      5  13   8    15     1-410     -5  -5   9   348   342  13
 10   3   8   379   361  12      2   6   8   528   502  12      1   9   8   255   246  15      6  13   8   126     8 -31     -4  -5   9   519   504  13
 11   3   8   286   294  16      3   6   8   243   236  12      2   9   8   360   334  12      7  13   8    15     1-391     -3  -5   9   240   245  15
 12   3   8   287   287  17      4   6   8   801   765  12      3   9   8   196   195  19     -4  -9   9    15     1-360     -2  -5   9    83     3 -34
 -8   4   8    10     1-367      5   6   8   239   216  13      4   9   8   392   423  11     -3  -9   9   128     8 -28     -1  -5   9   261   288  14
 -7   4   8   148   165  29      6   6   8    58     1 -62      5   9   8    47     1 -93     -2  -9   9    89     5 -59      0  -5   9   634   608  12
 -6   4   8   417   405  12      7   6   8   329   317  10      6   9   8   276   296  13     -1  -9   9    15     1-370      1  -5   9   266   249  14
 -5   4   8   350   351  12      8   6   8   144   150  22      7   9   8   168   188  21      0  -9   9   333   347  15      2  -5   9   149   161  23
 -4   4   8   483   511  13      9   6   8   668   649  13      8   9   8   453   466  12      1  -9   9    88     5 -41      3  -5   9   523   561  14
 -3   4   8    84     2 -47     10   6   8   378   377  12      9   9   8   350   322  13      2  -9   9    96     6 -38      4  -5   9    13     0-335
 -2   4   8   175   175  17     11   6   8   320   329  15     10   9   8   258   254  18     -6  -8   9   155   139  30      5  -5   9   141   151  28
 -1   4   8   309   318  10     12   6   8   258   276  19     11   9   8    15     1-356     -5  -8   9   166   159  27      6  -5   9    62     3 -81
  0   4   8   522   534  11     -6   7   8    78     5 -69     -3  10   8   251   228  19     -4  -8   9    10     1-354      7  -5   9   425   434  13
  1   4   8    94     2 -22     -5   7   8   217   217  20     -2  10   8   153   149  29     -3  -8   9   326   330  15      8  -5   9   130     9 -30
  2   4   8   834   805  11     -4   7   8   181   184  22     -1  10   8   249   235  18     -2  -8   9   150   152  28     -8  -4   9    56     3-100
  3   4   8   355   344  10     -3   7   8   151   184  24      0  10   8    96     4 -54     -1  -8   9    99     5 -33     -7  -4   9   280   270  17
  4   4   8   677   629  11     -2   7   8   348   341  12      1  10   8    32     1-108      0  -8   9   254   221  17     -6  -4   9   111     5 -30
  5   4   8   494   499  11     -1   7   8   417   419  11      2  10   8   224   220  18      1  -8   9   450   463  13     -5  -4   9    13     0-348
  6   4   8   479   479  12      0   7   8   316   319  12      3  10   8   227   219  18      2  -8   9   159   148  28     -4  -4   9   568   573  13
  7   4   8    27     1 -84      1   7   8   719   677  12      4  10   8   299   295  14      3  -8   9   133     8 -27     -3  -4   9   605   583  13
  8   4   8    12     0-323      2   7   8   284   290  12      5  10   8   481   514  14      4  -8   9    15     1-355     -2  -4   9   389   366  11
  9   4   8   630   623  13      3   7   8   436   415  12      6  10   8    13     0-348     -7  -7   9    93     6 -61     -1  -4   9    12     0-326
 10   4   8   216   177  18      4   7   8   232   209  14      7  10   8   286   285  15     -6  -7   9    65     4 -83      0  -4   9   186   246  17
 11   4   8   149   189  28      5   7   8   280   280  12      8  10   8   300   284  15     -5  -7   9   109     6 -32      1  -4   9   345   317  10
 12   4   8   303   327  16      6   7   8   578   564  12      9  10   8   191   211  23     -4  -7   9    55     3 -91      2  -4   9   324   325  11
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 OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)                                                                                      PAGE 20

  H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S       H   K   L  10FO  10FC 10S

  3  -4   9   103     3 -25       1  -1   9   323   341  10      -5   2   9    75     3 -57       8   4   9   177   210  19       4   7   9   519   532  13
  4  -4   9   677   711  13       2  -1   9   561   573  12      -4   2   9   303   301  12       9   4   9   260   274  15       5   7   9   231   272  15
  5  -4   9   290   299  14       3  -1   9   865   850  12      -3   2   9   653   649  12      10   4   9   246   250  17       6   7   9   446   473  12
  6  -4   9    92     4 -50       4  -1   9   174   185  17      -2   2   9   755   749  12      11   4   9   222   257  20       7   7   9   221   263  16
  7  -4   9    94     5 -53       5  -1   9   225   234  14      -1   2   9    70     1 -51      12   4   9    82     5 -67       8   7   9   238   249  15
  8  -4   9   386   364  13       6  -1   9   278   266  13       0   2   9   276   261  11      -7   5   9   102     7 -37       9   7   9   338   320  13
 -8  -3   9   104     6 -35       7  -1   9   249   247  14       1   2   9   925   904  12      -6   5   9   101     5 -53      10   7   9    94     4 -53
 -7  -3   9   468   477  12       8  -1   9    14     1-355       2   2   9   787   799  11      -5   5   9   164   166  25      11   7   9   343   347  15
 -6  -3   9   386   402  12       9  -1   9   332   313  14       3   2   9   380   392  11      -4   5   9   583   592  14      12   7   9    38     2-162
 -5  -3   9   273   282  14      10  -1   9   344   361  15       4   2   9   344   360  10      -3   5   9   507   478  14      -5   8   9   305   290  16
 -4  -3   9   212   203  16      -8   0   9   453   464  13       5   2   9   696   694  11      -2   5   9    12     0-344      -4   8   9    51     3-103
 -3  -3   9   590   636  13      -7   0   9   335   324  14       6   2   9   409   449  11      -1   5   9   175   178  18      -3   8   9    14     1-362
 -2  -3   9   287   257  12      -6   0   9   259   259  16       7   2   9   310   332  11       0   5   9   371   369  10      -2   8   9     9     0-362
 -1  -3   9   324   277  11      -5   0   9    65     2 -68       8   2   9   387   389  10       1   5   9   285   281  11      -1   8   9   243   196  16
  0  -3   9   210   194  15      -4   0   9   371   395  11       9   2   9   699   758  13       2   5   9   715   704  12       0   8   9   182   207  20
  1  -3   9   607   610  12      -3   0   9   179   197  18      10   2   9   179   201  23       3   5   9   380   343   9       1   8   9   340   350  12
  2  -3   9    12     0-323      -2   0   9   455   425  12      11   2   9    15     1-359       4   5   9   739   724  12       2   8   9   248   260  15
  3  -3   9   144   162  21      -1   0   9   600   571  11      -8   3   9    15     1-375       5   5   9   544   567  12       3   8   9   289   321  13
  4  -3   9   320   343  11       0   0   9   906   861  12      -7   3   9    99     5 -52       6   5   9   601   575  12       4   8   9   179   192  19
  5  -3   9   862   873  13       1   0   9   383   414  12      -6   3   9   305   285  15       7   5   9   151   153  21       5   8   9   419   473  13
  6  -3   9   190   198  19       2   0   9   330   307  11      -5   3   9   148   148  25       8   5   9   670   634  13       6   8   9   352   353  11
  7  -3   9    83     3 -57       3   0   9   216   202  13      -4   3   9    76     2 -59       9   5   9     8     0-338       7   8   9   263   296  14
  8  -3   9    90     4 -37       4   0   9  1045  1050  13      -3   3   9   373   371  10      10   5   9   110     5 -29       8   8   9   251   247  16
  9  -3   9    78     5 -69       5   0   9   188   191  16      -2   3   9   710   725  12      11   5   9    67     3 -80       9   8   9   155   142  26
 -9  -2   9    90     6 -43       6   0   9    12     0-306      -1   3   9   592   602  12      12   5   9    46     3-121      10   8   9    90     4 -57
 -8  -2   9    15     1-375       7   0   9   373   358  10       0   3   9   318   306  10      -6   6   9   130     8 -29      11   8   9    15     1-365
 -7  -2   9    81     4 -63       8   0   9    89     3 -30       1   3   9   457   450  12      -5   6   9    14     1-364      -4   9   9   200   166  24
 -6  -2   9   481   506  14       9   0   9   263   273  16       2   3   9   234   241  12      -4   6   9    14     1-364      -3   9   9    70     4 -78
 -5  -2   9   263   296  14      10   0   9    80     4 -41       3   3   9   407   404  12      -3   6   9   489   516  12      -2   9   9    63     3 -85
 -4  -2   9   314   308  12      11   0   9   269   299  18       4   3   9   270   274  11      -2   6   9   140   180  25      -1   9   9   320   324  15
 -3  -2   9   176   207  18      -8   1   9    87     5 -41       5   3   9   276   305  11      -1   6   9   228   253  15       0   9   9   186   194  24
 -2  -2   9    89     2 -27      -7   1   9   357   394  14       6   3   9   853   925  12       0   6   9   499   495  13       1   9   9   361   376  12
 -1  -2   9   359   338  11      -6   1   9    61     2 -79       7   3   9   171   168  18       1   6   9   230   257  15       2   9   9   277   312  15
  0  -2   9   292   282  11      -5   1   9   284   296  13       8   3   9   290   315  12       2   6   9   321   315  11       3   9   9   321   326  13
  1  -2   9   546   537  12      -4   1   9   328   307  11       9   3   9    78     3 -36       3   6   9   421   410  11       4   9   9   307   321  13
  2  -2   9  1137  1137  14      -3   1   9   495   436  12      10   3   9   338   373  13       4   6   9   399   395  11       5   9   9    13     0-347
  3  -2   9   151   134  19      -2   1   9   223   199  14      11   3   9    14     1-363       5   6   9   761   760  12       6   9   9    77     3 -57
  4  -2   9    24     1-154      -1   1   9   200   211  14      12   3   9   154   129  31       6   6   9    12     0-314       7   9   9    67     3 -68
  5  -2   9   389   374  12       0   1   9   848   828  12      -7   4   9    97     6 -37       7   6   9   259   254  13       8   9   9    95     4 -50
  6  -2   9   352   359  11       1   1   9  1327  1305  15      -6   4   9    14     1-354       8   6   9   130   144  25       9   9   9   460   458  11
  7  -2   9     9     0-340       2   1   9   345   356   9      -5   4   9   495   463  11       9   6   9   147   143  26      10   9   9   157   132  28
  8  -2   9   366   346  13       3   1   9   157   170  16      -4   4   9   276   293  14      10   6   9   482   459  13      11   9   9   235   256  21
  9  -2   9   245   288  19       4   1   9    11     0-305      -3   4   9   311   297  12      11   6   9   119     6 -28      -3  10   9    58     4 -99
 10  -2   9   200   158  24       5   1   9   330   327  10      -2   4   9   108     3 -23      12   6   9   264   264  18      -2  10   9   213   214  23
 -8  -1   9   254   227  18       6   1   9   606   602  12      -1   4   9   651   628  12      -5   7   9    72     4 -76      -1  10   9    50     3-113
 -7  -1   9   121     6 -27       7   1   9   322   364  11       0   4   9   659   638  12      -4   7   9   116     6 -29       0  10   9   391   377  13
 -6  -1   9    91     4 -35       8   1   9   576   610  13       1   4   9   290   277  11      -3   7   9    48     2 -99       1  10   9   316   316  15
 -5  -1   9   576   546  13       9   1   9   464   478  11       2   4   9   261   277  12      -2   7   9   224   251  17       2  10   9   153   148  29
 -4  -1   9   497   452  13      10   1   9   282   260  16       3   4   9   422   421  11      -1   7   9    13     0-351       3  10   9   216   227  20
 -3  -1   9   332   334  11      11   1   9   108     6 -32       4   4   9   121   115  23       0   7   9   247   258  15       4  10   9   149   145  28
 -2  -1   9   399   375  12      -8   2   9    15     1-381       5   4   9   784   804  12       1   7   9   283   288  13       5  10   9    80     3 -41
 -1  -1   9   500   475  12      -7   2   9    14     1-348       6   4   9   288   320  12       2   7   9   368   363  11       6  10   9   341   394  13
  0  -1   9   231   235  13      -6   2   9    14     1-346       7   4   9   759   786  12       3   7   9   127   104  25       7  10   9    43     2 -77
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                                                                                                                                                PAGE 21
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  Compound (1)
  H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S      H   K   L  10FO  10FC 10S

  8  10   9   194   211  23      2  -6  10   169   167  24      9  -3  10   200   171  24      7   0  10    90     3 -48      4   3  10   656   674  12
  9  10   9    41     2-136      3  -6  10   195   210  22     -8  -2  10   205   196  24      8   0  10    48     2 -97      5   3  10   258   271  12
 10  10   9   312   335  16      4  -6  10   372   361  13     -7  -2  10    59     3 -90      9   0  10   157   155  27      6   3  10   212   233  15
 -1  11   9   133     8 -30      5  -6  10   105     6 -35     -6  -2  10   150   122  27     10   0  10   169   217  27      7   3  10   189   137  17
  0  11   9   245   274  21      6  -6  10    96     6 -57     -5  -2  10   406   416  13     -7   1  10    15     1-370      8   3  10   257   227  14
  1  11   9   239   201  20     -7  -5  10   273   285  18     -4  -2  10   266   257  14     -6   1  10   532   563  14      9   3  10   343   355  13
  2  11   9    14     1-391     -6  -5  10    15     1-360     -3  -2  10   269   259  13     -5   1  10    14     1-347     10   3  10    79     4 -66
  3  11   9    86     4 -65     -5  -5  10   160   185  27     -2  -2  10   103     3 -26     -4   1  10   203   200  18     11   3  10   272   293  17
  4  11   9   156   227  30     -4  -5  10    46     2 -71     -1  -2  10   287   277  12     -3   1  10    12     0-334     -7   4  10   288   283  17
  5  11   9    14     1-380     -3  -5  10   178   162  23      0  -2  10   531   507  13     -2   1  10   161   162  20     -6   4  10    63     4 -85
  6  11   9   123     6 -28     -2  -5  10    99     4 -32      1  -2  10   394   406  11     -1   1  10   181   159  16     -5   4  10    94     4 -35
  7  11   9   332   369  15     -1  -5  10   224   263  16      2  -2  10   295   282  12      0   1  10   133   186  23     -4   4  10   254   242  16
  8  11   9    71     4 -76      0  -5  10   451   436  11      3  -2  10   367   383  10      1   1  10   649   636  12     -3   4  10    13     0-346
  9  11   9   180   186  26      1  -5  10   495   497  13      4  -2  10    49     1 -83      2   1  10   795   803  12     -2   4  10   224   224  16
 10  11   9   116     8 -34      2  -5  10   414   386  11      5  -2  10   288   262  13      3   1  10   442   431  12     -1   4  10   151   148  22
  1  12   9    25     2-171      3  -5  10    36     1-126      6  -2  10   365   363  11      4   1  10   290   299  11      0   4  10   960   906  13
  2  12   9   162   152  32      4  -5  10   147   200  27      7  -2  10   499   518  14      5   1  10   681   672  12      1   4  10   685   673  12
  3  12   9    15     1-403      5  -5  10   119     6 -28      8  -2  10    14     1-348      6   1  10   361   394  10      2   4  10   243   258  13
  4  12   9   160   181  31      6  -5  10   236   223  19      9  -2  10   186   179  25      7   1  10   283   323  13      3   4  10   265   278  12
  5  12   9    98     5 -59      7  -5  10    59     4 -63     -8  -1  10   181   129  26      8   1  10    70     3 -64      4   4  10   377   366  10
  6  12   9    61     3 -90     -7  -4  10    15     1-378     -7  -1  10    99     5 -53      9   1  10   314   339  15      5   4  10    91     2 -27
  7  12   9    90     5 -62     -6  -4  10    14     1-349     -6  -1  10   105     5 -30     10   1  10   248   185  18      6   4  10   546   566  13
  8  12   9   286   322  18     -5  -4  10    88     4 -57     -5  -1  10   203   213  20     11   1  10    81     5 -71      7   4  10   285   273  13
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  5  13   9   236   266  23     -3  -4  10   831   761  13     -3  -1  10   517   467  13     -6   2  10   250   237  18      9   4  10   320   348  14
  6  13   9    18     1-222     -2  -4  10   409   381  12     -2  -1  10   456   462  13     -5   2  10   462   480  13     10   4  10   289   295  16
 -4  -8  10   290   243  17     -1  -4  10   310   310  12     -1  -1  10   244   212  13     -4   2  10    13     0-338     11   4  10    76     4 -47
 -3  -8  10   117     7 -32      0  -4  10   354   352  11      0  -1  10   502   515  13     -3   2  10   252   229  14     -6   5  10    79     5 -48
 -2  -8  10    72     4 -78      1  -4  10   491   450  13      1  -1  10   213   231  15     -2   2  10   495   508  12     -5   5  10   192   157  23
 -1  -8  10   174   153  26      2  -4  10   231   247  15      2  -1  10   496   506  13     -1   2  10    75     2 -53     -4   5  10    99     4 -33
  0  -8  10   107     6 -33      3  -4  10   316   335  12      3  -1  10   381   371  10      0   2  10    78     2 -30     -3   5  10   416   424  11
  1  -8  10   197   202  24      4  -4  10   174   174  22      4  -1  10   621   654  12      1   2  10   228   224  14     -2   5  10   220   205  16
  2  -8  10   229   262  21      5  -4  10   270   235  15      5  -1  10   239   276  15      2   2  10   761   792  12     -1   5  10   160   162  21
  3  -8  10   171   103  27      6  -4  10    14     1-348      6  -1  10    79     3 -53      3   2  10   491   483  12      0   5  10   233   221  15
 -6  -7  10   168   159  28      7  -4  10    15     1-345      7  -1  10   109     4 -28      4   2  10    39     1 -95      1   5  10   759   763  12
 -5  -7  10   184   189  25      8  -4  10   175   206  27      8  -1  10   518   473  14      5   2  10   163   127  18      2   5  10   273   293  13
 -4  -7  10    39     2-134     -8  -3  10    41     3-143      9  -1  10   153   184  29      6   2  10   332   339  11      3   5  10   481   463  12
 -3  -7  10   266   265  17     -7  -3  10    88     5 -65     10  -1  10   165   192  28      7   2  10   382   410  10      4   5  10   407   417  11
 -2  -7  10   227   204  20     -6  -3  10   393   379  13     -8   0  10    15     1-382      8   2  10   269   299  14      5   5  10   302   300  11
 -1  -7  10   196   204  22     -5  -3  10    14     1-343     -7   0  10   432   428  12      9   2  10   284   318  16      6   5  10   269   274  13
  0  -7  10    29     1-172     -4  -3  10   236   228  16     -6   0  10    53     2 -95     10   2  10   364   363  13      7   5  10   442   468  12
  1  -7  10   202   196  21     -3  -3  10    83     3 -34     -5   0  10   170   193  24     11   2  10   203   169  23      8   5  10   260   260  14
  2  -7  10   283   279  16     -2  -3  10   657   630  13     -4   0  10   302   284  13     -7   3  10    73     5 -78      9   5  10   611   607  14
  3  -7  10   329   329  15     -1  -3  10   369   390  10     -3   0  10   839   829  13     -6   3  10    50     3-102     10   5  10   153   193  28
  4  -7  10    73     5 -72      0  -3  10   311   320  11     -2   0  10    96     3 -26     -5   3  10    98     4 -49     11   5  10    78     4 -47
 -6  -6  10   269   269  18      1  -3  10   181   174  18     -1   0  10   431   410  11     -4   3  10   382   357  11     -5   6  10    86     5 -41
 -5  -6  10    59     3 -91      2  -3  10    12     0-321      0   0  10   103     2 -24     -3   3  10   161   163  22     -4   6  10    14     1-351
 -4  -6  10   123     6 -27      3  -3  10   323   301  11      1   0  10   403   374  10     -2   3  10   175   175  20     -3   6  10    50     2 -66
 -3  -6  10   123     6 -27      4  -3  10   322   265  11      2   0  10    70     2 -33     -1   3  10   725   715  12     -2   6  10   534   544  14
 -2  -6  10   217   239  20      5  -3  10   346   342  12      3   0  10   356   351  11      0   3  10   318   340  11     -1   6  10   157   204  23
 -1  -6  10   246   285  17      6  -3  10   493   529  13      4   0  10   579   611  12      1   3  10   351   345  10      0   6  10     8     0-341
  0  -6  10   474   432  11      7  -3  10   226   200  18      5   0  10   747   769  12      2   3  10   190   184  16      1   6  10   256   247  14
  1  -6  10    85     4 -58      8  -3  10    15     1-347      6   0  10   328   306  11      3   3  10   607   608  12      2   6  10   335   336  11
```

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
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4	6	10	217	224	15
5	6	10	393	399	10
6	6	10	519	557	14
7	6	10	225	210	16
8	6	10	364	361	11
9	6	10	46	2	-105
10	6	10	304	312	15
11	6	10	226	218	21
-5	7	10	258	270	19
-4	7	10	15	1	-354
-3	7	10	189	170	23
-2	7	10	86	4	-57
-1	7	10	486	497	13
0	7	10	88	3	-52
1	7	10	155	132	23
2	7	10	183	220	19
3	7	10	12	0	-328
4	7	10	159	146	21
5	7	10	354	363	11
6	7	10	346	370	11
7	7	10	363	377	11
8	7	10	248	235	16
9	7	10	291	266	15
10	7	10	185	190	24
11	7	10	100	6	-56
-4	8	10	347	331	15
-3	8	10	103	6	-36
-2	8	10	68	3	-74
-1	8	10	63	3	-78
0	8	10	332	310	14
1	8	10	88	3	-34
2	8	10	300	306	13
3	8	10	452	453	12
4	8	10	143	189	25
5	8	10	350	350	11
6	8	10	304	334	13
7	8	10	265	282	16
8	8	10	307	313	14
9	8	10	62	3	-82
10	8	10	15	1	-361
11	8	10	15	1	-372
-3	9	10	285	282	18
-2	9	10	15	1	-385
-1	9	10	10	0	-365
0	9	10	201	216	22
1	9	10	75	3	-68
2	9	10	265	254	16
3	9	10	166	220	26
4	9	10	471	458	13
5	9	10	334	354	13
6	9	10	83	3	-57
7	9	10	218	244	18
8	9	10	14	1	-351
9	9	10	14	1	-366
10	9	10	299	277	16
11	9	10	83	6	-46
-2	10	10	15	1	-393
-1	10	10	107	6	-36
0	10	10	79	4	-47
1	10	10	292	285	17
2	10	10	14	1	-397
3	10	10	217	246	21
4	10	10	236	243	19
5	10	10	303	318	15
6	10	10	226	261	19
7	10	10	200	190	22
8	10	10	197	222	23
9	10	10	84	5	-64
10	10	10	125	8	-31
0	11	10	143	9	-29
1	11	10	15	1	-392
2	11	10	406	411	13
3	11	10	50	3	-112
4	11	10	107	5	-35
5	11	10	253	239	19
6	11	10	233	224	19
7	11	10	15	1	-368
8	11	10	238	179	19
9	11	10	165	133	29
2	12	10	10	1	-419
3	12	10	275	269	19
4	12	10	15	1	-412
5	12	10	15	1	-391
6	12	10	170	128	28
7	12	10	34	2	-165
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-3	-7	11	15	1	-377
-2	-7	11	302	249	16
-1	-7	11	203	194	23
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1	-7	11	153	46	29
2	-7	11	204	234	24
3	-7	11	98	7	-58
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-4	-6	11	309	309	16
-3	-6	11	265	254	18
-2	-6	11	47	2	-77
-1	-6	11	221	219	20
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4	-6	11	224	234	21
5	-6	11	208	189	23
-6	-5	11	229	283	22
-5	-5	11	37	2	-150
-4	-5	11	264	261	18
-3	-5	11	267	250	16
-2	-5	11	76	3	-44
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0	-5	11	290	272	15
1	-5	11	368	349	13
2	-5	11	161	192	26
3	-5	11	187	170	23
4	-5	11	314	316	15
5	-5	11	298	300	16
6	-5	11	41	3	-133
-6	-4	11	280	258	17
-5	-4	11	199	207	22
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-3	-4	11	252	270	17
-2	-4	11	382	382	12
-1	-4	11	14	1	-339
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1	-4	11	407	409	12
2	-4	11	555	544	14
3	-4	11	261	247	16
4	-4	11	201	208	21
5	-4	11	291	249	15
6	-4	11	10	1	-354
7	-4	11	159	116	28
-7	-3	11	15	1	-389
-6	-3	11	194	213	24
-5	-3	11	243	233	19
-4	-3	11	204	179	21
-3	-3	11	122	5	-26
-2	-3	11	366	329	12
-1	-3	11	549	595	14
0	-3	11	269	237	14
1	-3	11	96	3	-29
2	-3	11	264	298	14
3	-3	11	225	230	16
4	-3	11	306	301	14
5	-3	11	329	339	13
6	-3	11	148	123	28
7	-3	11	15	1	-363
8	-3	11	95	6	-58
-7	-2	11	277	271	19
-6	-2	11	89	5	-63
-5	-2	11	70	3	-70
-4	-2	11	14	1	-354
-3	-2	11	13	0	-345
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-1	-2	11	516	512	14
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1	-2	11	373	358	11
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3	-2	11	325	302	12
4	-2	11	197	201	18
5	-2	11	14	1	-338
6	-2	11	308	348	14
7	-2	11	183	206	24
8	-2	11	280	242	16
9	-2	11	71	5	-82
-7	-1	11	113	7	-33
-6	-1	11	91	5	-39
-5	-1	11	91	4	-54
-4	-1	11	14	1	-348
-3	-1	11	470	462	14
-2	-1	11	278	254	14
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3	-1	11	396	408	12
4	-1	11	13	0	-335
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7	-1	11	248	250	17
8	-1	11	250	270	18
9	-1	11	330	340	16
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-6	0	11	179	231	26
-5	0	11	89	4	-38
-4	0	11	96	4	-50
-3	0	11	258	303	15
-2	0	11	610	611	13
-1	0	11	12	0	-335
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1	0	11	326	300	11
2	0	11	231	236	14
3	0	11	50	1	-81
4	0	11	426	410	12
5	0	11	368	340	12
6	0	11	537	550	14
7	0	11	308	296	14
8	0	11	369	327	13
9	0	11	285	294	16
10	0	11	15	1	-368
-7	1	11	15	1	-383
-6	1	11	15	1	-383
-5	1	11	281	332	16
-4	1	11	107	4	-30
-3	1	11	236	224	16
-2	1	11	441	455	13
-1	1	11	500	496	13
0	1	11	168	161	20
1	1	11	228	264	15
2	1	11	339	323	11
3	1	11	252	256	13
4	1	11	159	147	20
5	1	11	364	373	11
6	1	11	392	430	11
7	1	11	89	3	-52
8	1	11	329	339	14
9	1	11	185	195	24
10	1	11	10	1	-372
-6	2	11	10	1	-371
-5	2	11	347	328	14
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-3	2	11	161	211	24
-2	2	11	170	211	21
-1	2	11	418	395	11
0	2	11	427	417	12
1	2	11	148	176	21
2	2	11	280	288	12
3	2	11	556	577	13
4	2	11	273	316	13
5	2	11	298	317	12
6	2	11	62	2	-44
7	2	11	243	290	15
8	2	11	259	241	16
9	2	11	308	308	15
10	2	11	15	1	-353
-6	3	11	115	7	-32
-5	3	11	86	4	-61
-4	3	11	309	340	15
-3	3	11	548	550	15
-2	3	11	238	237	16
-1	3	11	74	2	-38
0	3	11	238	244	15
1	3	11	171	169	19
2	3	11	257	248	13
3	3	11	312	325	12
4	3	11	614	625	13
5	3	11	552	570	13
6	3	11	136	173	25
7	3	11	322	348	12
8	3	11	196	185	21
9	3	11	158	141	26
10	3	11	268	267	17
11	3	11	15	1	-385
-6	4	11	217	273	23
-5	4	11	78	4	-68
-4	4	11	94	4	-55
-3	4	11	14	1	-363
-2	4	11	233	259	16
-1	4	11	159	172	22
0	4	11	110	3	-25
1	4	11	529	533	14
2	4	11	461	471	13
3	4	11	177	201	19
4	4	11	409	419	11
5	4	11	641	663	13

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
6	4	11	323	341	11
7	4	11	378	399	11
8	4	11	74	3	-65
9	4	11	211	201	20
10	4	11	259	261	18
11	4	11	133	9	-28
-5	5	11	188	220	25
-4	5	11	96	5	-56
-3	5	11	14	1	-366
-2	5	11	270	292	16
-1	5	11	99	3	-29
0	5	11	43	1	-107
1	5	11	194	201	18
2	5	11	848	885	13
3	5	11	329	361	12
4	5	11	174	200	19
5	5	11	87	3	-49
6	5	11	250	272	15
7	5	11	13	0	-346
8	5	11	378	391	12
9	5	11	281	265	16
10	5	11	305	293	16
11	5	11	227	211	21
-5	6	11	72	5	-55
-4	6	11	224	218	21
-3	6	11	103	5	-34
-2	6	11	9	0	-360
-1	6	11	410	413	12
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1	6	11	84	3	-55
2	6	11	120	4	-24
3	6	11	571	583	14
4	6	11	255	255	14
5	6	11	166	154	20
6	6	11	101	3	-27
7	6	11	192	150	19
8	6	11	149	134	26
9	6	11	326	307	14
10	6	11	216	201	21
11	6	11	136	9	-29
-4	7	11	15	1	-386
-3	7	11	80	4	-70
-2	7	11	239	222	19
-1	7	11	204	204	21
0	7	11	471	454	11
1	7	11	234	274	17
2	7	11	25	1	-116
3	7	11	278	270	14
4	7	11	241	245	16
5	7	11	93	3	-47
6	7	11	236	256	16
7	7	11	361	347	12
8	7	11	243	256	18
9	7	11	257	252	18
10	7	11	107	6	-34
11	7	11	174	197	28
-3	8	11	186	218	27
-2	8	11	128	7	-29
-1	8	11	14	1	-378
0	8	11	151	146	29
1	8	11	466	448	12
2	8	11	216	237	20
3	8	11	13	0	-367
4	8	11	248	268	17
5	8	11	162	131	24
6	8	11	224	252	19
7	8	11	213	206	19
8	8	11	313	282	15
9	8	11	311	348	16
10	8	11	55	3	-70
-2	9	11	250	285	21
-1	9	11	15	1	-385
0	9	11	10	0	-380
1	9	11	14	1	-378
2	9	11	282	261	16
3	9	11	129	6	-28
4	9	11	96	4	-53
5	9	11	187	220	23
6	9	11	238	252	18
7	9	11	92	4	-55
8	9	11	228	217	20
9	9	11	211	159	22
10	9	11	195	158	25
-1	10	11	197	224	26
0	10	11	15	1	-387
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3	10	11	85	4	-43
4	10	11	25	1	-225
5	10	11	84	4	-63
6	10	11	244	299	19
7	10	11	135	7	-27
8	10	11	177	175	26
9	10	11	72	5	-80
1	11	11	99	6	-60
2	11	11	101	6	-40
3	11	11	238	195	21
4	11	11	15	1	-398
5	11	11	211	241	23
6	11	11	15	1	-374
7	11	11	238	295	21
8	11	11	15	1	-373
4	12	11	269	250	19
5	12	11	16	1	-390
-3	-6	12	350	346	15
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-1	-6	12	15	1	-361
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1	-6	12	301	311	16
2	-6	12	10	1	-359
3	-6	12	86	6	-63
-4	-5	12	16	1	-365
-3	-5	12	251	236	19
-2	-5	12	392	377	13
-1	-5	12	180	154	24
0	-5	12	153	127	29
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2	-5	12	47	3	-113
3	-5	12	15	1	-358
4	-5	12	10	1	-354
5	-5	12	329	318	16
-5	-4	12	292	280	17
-4	-4	12	130	8	-29
-3	-4	12	86	5	-41
-2	-4	12	241	241	19
-1	-4	12	338	306	13
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1	-4	12	181	156	24
2	-4	12	308	334	15
3	-4	12	176	212	24
4	-4	12	172	152	25
5	-4	12	15	1	-360
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-5	-3	12	270	249	18
-4	-3	12	442	416	12
-3	-3	12	182	214	25
-2	-3	12	260	213	17
-1	-3	12	179	174	23
0	-3	12	264	291	16
1	-3	12	14	1	-348
2	-3	12	103	4	-32
3	-3	12	446	462	12
4	-3	12	277	301	16
5	-3	12	173	191	25
6	-3	12	103	6	-52
7	-3	12	169	217	28
-6	-2	12	139	9	-29
-5	-2	12	15	1	-371
-4	-2	12	233	224	19
-3	-2	12	310	332	15
-2	-2	12	182	162	23
-1	-2	12	14	1	-349
0	-2	12	253	214	16
1	-2	12	256	258	16
2	-2	12	230	232	18
3	-2	12	28	1	-174
4	-2	12	609	628	14
5	-2	12	303	297	15
6	-2	12	14	1	-349
7	-2	12	191	196	24
8	-2	12	174	163	26
-6	-1	12	238	260	21
-5	-1	12	160	159	28
-4	-1	12	43	2	-124
-3	-1	12	14	1	-352
-2	-1	12	246	257	17
-1	-1	12	206	200	20
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1	-1	12	463	463	13
2	-1	12	387	393	11
3	-1	12	189	217	19
4	-1	12	14	1	-338
5	-1	12	452	498	13
6	-1	12	14	1	-345
7	-1	12	103	5	-34
8	-1	12	253	244	19
-6	0	12	99	7	-58
-5	0	12	187	173	25
-4	0	12	172	180	26
-3	0	12	179	205	24
-2	0	12	14	1	-360
-1	0	12	353	367	12
0	0	12	95	3	-30
1	0	12	176	151	20
2	0	12	484	504	13
3	0	12	278	296	13
4	0	12	111	4	-25
5	0	12	301	292	14
6	0	12	14	1	-335
7	0	12	185	133	23
8	0	12	26	1	-207
9	0	12	378	362	14
-6	1	12	106	7	-54
-5	1	12	15	1	-349
-4	1	12	89	4	-57
-3	1	12	14	1	-361
-2	1	12	187	200	22
-1	1	12	316	317	13
0	1	12	359	361	12
1	1	12	249	265	14
2	1	12	89	3	-50
3	1	12	441	463	14
4	1	12	82	3	-34
5	1	12	70	3	-64
6	1	12	322	342	13
7	1	12	276	264	16
8	1	12	199	210	22
9	1	12	163	204	29
-5	2	12	15	1	-359
-4	2	12	14	1	-357
-3	2	12	317	311	15
-2	2	12	309	296	14
-1	2	12	271	253	14
0	2	12	650	615	13
1	2	12	519	495	14
2	2	12	323	303	12
3	2	12	13	0	-344
4	2	12	366	362	11
5	2	12	242	246	15
6	2	12	55	2	-58
7	2	12	172	208	24
8	2	12	242	218	18
9	2	12	301	305	16
10	2	12	232	254	21
-5	3	12	15	1	-376
-4	3	12	10	1	-369
-3	3	12	313	321	15
-2	3	12	418	414	12
-1	3	12	294	276	13
0	3	12	182	212	20
1	3	12	319	343	13
2	3	12	181	207	19
3	3	12	208	226	17
4	3	12	323	318	12
5	3	12	82	3	-55
6	3	12	408	423	11
7	3	12	196	196	20
8	3	12	344	322	13
9	3	12	244	259	19
10	3	12	100	6	-38
-5	4	12	108	7	-36
-4	4	12	120	7	-30
-3	4	12	225	201	20
-2	4	12	307	328	15
-1	4	12	233	288	19
0	4	12	105	4	-28
1	4	12	104	4	-28
2	4	12	91	3	-32
3	4	12	288	311	13
4	4	12	29	1	-146
5	4	12	416	446	11
6	4	12	393	421	11
7	4	12	265	267	16
8	4	12	180	184	23
9	4	12	222	228	20
10	4	12	48	3	-120
-4	5	12	216	211	22
-3	5	12	88	5	-62
-2	5	12	230	220	19
-1	5	12	264	264	17
0	5	12	188	184	22
1	5	12	137	175	27
2	5	12	13	0	-354
3	5	12	396	399	11
4	5	12	276	296	14

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
5	5	12	111	4	-26
6	5	12	344	356	13
7	5	12	329	384	14
8	5	12	278	280	16
9	5	12	272	251	17
10	5	12	174	118	26
-4	6	12	215	213	24
-3	6	12	232	206	21
-2	6	12	202	226	23
-1	6	12	14	1	-374
0	6	12	108	4	-31
1	6	12	77	3	-64
2	6	12	222	231	18
3	6	12	218	205	17
4	6	12	375	395	11
5	6	12	387	433	12
6	6	12	119	5	-26
7	6	12	368	366	13
8	6	12	118	6	-29
9	6	12	15	1	-365
10	6	12	83	5	-71
-3	7	12	109	7	-36
-2	7	12	70	4	-52
-1	7	12	182	185	25
0	7	12	187	186	24
1	7	12	252	226	18
2	7	12	316	314	15
3	7	12	69	3	-71
4	7	12	353	349	13
5	7	12	348	346	13
6	7	12	212	275	20
7	7	12	14	1	-358
8	7	12	287	241	16
9	7	12	195	167	24
10	7	12	218	190	22
-2	8	12	85	6	-68
-1	8	12	42	2	-135
0	8	12	116	6	-31
1	8	12	80	4	-69
2	8	12	381	384	13
3	8	12	293	319	16
4	8	12	14	1	-365
5	8	12	161	136	26
6	8	12	103	5	-32
7	8	12	220	217	20
8	8	12	88	5	-62
9	8	12	76	5	-48
10	8	12	265	265	19
-1	9	12	105	7	-38
0	9	12	75	4	-76
1	9	12	33	2	-118
2	9	12	84	4	-43
3	9	12	238	252	19

H	K	L	10FO	10FC	10S
4	9	12	197	222	23
5	9	12	10	0	-359
6	9	12	51	3	-102
7	9	12	184	166	24
8	9	12	110	6	-32
9	9	12	123	8	-32
1	10	12	15	1	-398
2	10	12	15	1	-394
3	10	12	90	5	-42
4	10	12	91	5	-62
5	10	12	15	1	-366
6	10	12	15	1	-371
7	10	12	206	148	22
8	10	12	188	224	26
3	11	12	16	1	-395
4	11	12	101	7	-57
5	11	12	16	1	-383
6	11	12	173	183	28
-2	-5	13	170	192	30
-1	-5	13	254	246	19
0	-5	13	156	114	30
1	-5	13	34	2	-158
2	-5	13	10	1	-369
-3	-4	13	65	4	-87
-2	-4	13	15	1	-374
-1	-4	13	300	307	16
0	-4	13	412	363	13
1	-4	13	99	6	-54
2	-4	13	15	1	-372
3	-4	13	66	4	-81
4	-4	13	220	219	21
-4	-3	13	127	8	-31
-3	-3	13	294	304	17
-2	-3	13	39	2	-136
-1	-3	13	91	5	-61
0	-3	13	322	347	15
1	-3	13	425	415	12
2	-3	13	170	157	26
3	-3	13	85	5	-64
4	-3	13	166	164	26
5	-3	13	15	1	-360
6	-3	13	127	9	-30
-4	-2	13	85	5	-44
-3	-2	13	404	399	13
-2	-2	13	355	377	14
-1	-2	13	213	172	21
0	-2	13	48	2	-71
1	-2	13	166	120	25
2	-2	13	67	3	-50
3	-2	13	213	219	21
4	-2	13	15	1	-351
5	-2	13	425	414	13
6	-2	13	15	1	-367

H	K	L	10FO	10FC	10S
7	-2	13	16	1	-362
-4	-1	13	85	5	-67
-3	-1	13	15	1	-363
-2	-1	13	330	309	15
-1	-1	13	227	234	20
0	-1	13	187	214	23
1	-1	13	75	3	-65
2	-1	13	287	283	15
3	-1	13	117	5	-28
4	-1	13	211	200	20
5	-1	13	79	4	-66
6	-1	13	464	457	12
7	-1	13	15	1	-348
-5	0	13	287	335	19
-4	0	13	302	280	17
-3	0	13	47	2	-112
-2	0	13	260	234	18
-1	0	13	14	1	-356
0	0	13	181	198	23
1	0	13	202	230	20
2	0	13	235	240	17
3	0	13	355	340	13
4	0	13	94	4	-36
5	0	13	253	235	17
6	0	13	39	2	-133
7	0	13	326	341	15
8	0	13	46	3	-121
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-3	1	13	228	239	20
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0	1	13	44	2	-75
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3	1	13	197	188	20
4	1	13	586	577	13
5	1	13	154	149	26
6	1	13	158	162	26
7	1	13	15	1	-344
8	1	13	251	252	19
-4	2	13	80	5	-46
-3	2	13	229	243	20
-2	2	13	14	1	-369
-1	2	13	252	229	17
0	2	13	242	290	18
1	2	13	394	362	12
2	2	13	278	258	15
3	2	13	314	279	13
4	2	13	222	193	18
5	2	13	447	487	13
6	2	13	14	1	-346
7	2	13	161	189	27
8	2	13	196	182	23

H	K	L	10FO	10FC	10S
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-2	3	13	14	1	-368
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2	3	13	395	437	12
3	3	13	14	1	-349
4	3	13	217	230	19
5	3	13	159	167	25
6	3	13	32	1	-97
7	3	13	265	245	16
8	3	13	131	7	-27
9	3	13	350	365	15
-4	4	13	10	1	-383
-3	4	13	10	1	-365
-2	4	13	256	281	19
-1	4	13	232	251	19
0	4	13	202	195	21
1	4	13	166	191	25
2	4	13	288	266	15
3	4	13	262	255	16
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5	4	13	178	193	22
6	4	13	20	1	-245
7	4	13	85	4	-60
8	4	13	266	269	18
9	4	13	15	1	-382
-3	5	13	92	6	-63
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1	5	13	216	223	20
2	5	13	161	197	26
3	5	13	245	249	17
4	5	13	262	242	16
5	5	13	200	261	21
6	5	13	146	176	28
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-2	6	13	169	200	29
-1	6	13	155	143	29
0	6	13	322	342	15
1	6	13	231	244	20
2	6	13	9	0	-366
3	6	13	222	191	19
4	6	13	9	0	-359
5	6	13	62	3	-81
6	6	13	341	375	14
7	6	13	87	4	-59
8	6	13	298	283	16

H	K	L	10FO	10FC	10S
9	6	13	15	1	-371
-2	7	13	176	148	28
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1	7	13	48	2	-111
2	7	13	92	4	-56
3	7	13	260	263	17
4	7	13	147	179	29
5	7	13	252	240	18
6	7	13	249	260	18
7	7	13	288	303	16
8	7	13	92	5	-59
9	7	13	256	218	19
-1	8	13	16	1	-382
0	8	13	68	4	-83
1	8	13	85	5	-66
2	8	13	14	1	-268
3	8	13	94	5	-40
4	8	13	269	282	18
5	8	13	93	5	-58
6	8	13	167	199	27
7	8	13	15	1	-361
8	8	13	233	265	21
9	8	13	10	1	-382
1	9	13	15	1	-397
2	9	13	105	6	-37
3	9	13	89	5	-62
4	9	13	190	184	24
5	9	13	247	251	19
6	9	13	92	5	-40
7	9	13	117	7	-32
8	9	13	44	3	-130
3	10	13	132	9	-30
4	10	13	60	4	-98
5	10	13	90	6	-65
6	10	13	88	6	-65
-1	-3	14	16	1	-372
0	-3	14	15	1	-369
1	-3	14	334	367	16
2	-3	14	285	277	17
3	-3	14	103	7	-54
4	-3	14	16	1	-363
-2	-2	14	264	281	19
-1	-2	14	174	194	27
0	-2	14	132	8	-28
1	-2	14	45	3	-122
2	-2	14	311	326	16
3	-2	14	216	231	22
4	-2	14	130	8	-29
5	-2	14	10	1	-369
-3	-1	14	16	1	-376
-2	-1	14	101	6	-55
-1	-1	14	438	456	13

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR Compound (1)

H	K	L	10FO	10FC	10S
0	-1	14	301	292	16
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3	-1	14	91	5	-59
4	-1	14	132	7	-28
5	-1	14	236	268	21
6	-1	14	97	6	-39
-3	0	14	198	153	25
-2	0	14	15	1	-369
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0	0	14	465	487	13
1	0	14	319	307	15
2	0	14	248	236	18
3	0	14	202	207	22
4	0	14	15	1	-354
5	0	14	10	1	-359
6	0	14	286	286	17
7	0	14	27	2	-223
-3	1	14	368	373	15
-2	1	14	81	5	-69
-1	1	14	10	1	-366
0	1	14	90	5	-58
1	1	14	198	249	23
2	1	14	14	1	-350
3	1	14	195	226	23
4	1	14	237	280	19
5	1	14	329	338	15
6	1	14	82	5	-64
7	1	14	165	165	29
-3	2	14	96	6	-59
-2	2	14	288	308	18
-1	2	14	44	2	-123
0	2	14	15	1	-371
1	2	14	14	1	-357
2	2	14	14	1	-356
3	2	14	14	1	-353
4	2	14	184	191	24
5	2	14	279	301	16
6	2	14	399	423	13
7	2	14	15	1	-364
8	2	14	64	4	-89
-3	3	14	99	7	-57
-2	3	14	15	1	-368
-1	3	14	307	264	16
0	3	14	15	1	-368
1	3	14	163	181	27
2	3	14	220	272	21
3	3	14	123	6	-27
4	3	14	50	2	-68
5	3	14	191	202	23
6	3	14	196	222	23
7	3	14	201	250	23
8	3	14	16	1	-358
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-1	4	14	87	5	-65
0	4	14	103	5	-35
1	4	14	41	2	-130
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3	4	14	368	378	14
4	4	14	223	275	20
5	4	14	85	4	-61
6	4	14	108	6	-32
7	4	14	119	7	-30
8	4	14	15	1	-363
-2	5	14	94	6	-42
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1	5	14	205	151	22
2	5	14	184	177	25
3	5	14	164	191	27
4	5	14	384	378	13
5	5	14	211	234	21
6	5	14	15	1	-361
7	5	14	75	4	-72
8	5	14	15	1	-364
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0	6	14	15	1	-377
1	6	14	282	286	17
2	6	14	221	200	21
3	6	14	41	2	-129
4	6	14	250	271	19
5	6	14	260	256	18
6	6	14	59	3	-86
7	6	14	235	231	20
8	6	14	106	7	-53
0	7	14	10	1	-384
1	7	14	10	1	-376
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3	7	14	98	5	-57
4	7	14	15	1	-369
5	7	14	191	207	24
6	7	14	54	3	-67
7	7	14	15	1	-365
8	7	14	274	260	18
1	8	14	92	6	-65
2	8	14	15	1	-374
3	8	14	286	301	18
4	8	14	96	6	-58
5	8	14	133	8	-28
6	8	14	157	163	30
7	8	14	58	4	-99
4	9	14	16	1	-384
5	9	14	31	2	-186
0	-1	15	241	218	21
1	-1	15	64	4	-93
2	-1	15	16	1	-365
3	-1	15	110	7	-35
-1	0	15	16	1	-381
0	0	15	69	4	-85
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2	0	15	170	176	28
3	0	15	68	4	-83
4	0	15	16	1	-368
5	0	15	235	241	21
-1	1	15	16	1	-376
0	1	15	106	7	-53
1	1	15	117	7	-33
2	1	15	308	331	17
3	1	15	15	1	-363
4	1	15	39	2	-94
5	1	15	15	1	-375
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0	2	15	10	1	-380
1	2	15	50	3	-113
2	2	15	77	4	-47
3	2	15	157	163	29
4	2	15	15	1	-357
5	2	15	203	178	23
6	2	15	170	148	28
-1	3	15	10	1	-376
0	3	15	316	337	17
1	3	15	129	8	-29
2	3	15	154	122	30
3	3	15	89	5	-42
4	3	15	15	1	-372
5	3	15	68	4	-81
6	3	15	241	250	20
0	4	15	89	6	-66
1	4	15	271	266	18
2	4	15	88	5	-43
3	4	15	95	6	-39
4	4	15	192	252	25
5	4	15	223	190	21
6	4	15	53	3	-71
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1	5	15	15	1	-383
2	5	15	15	1	-376
3	5	15	96	6	-59
4	5	15	99	6	-57
5	5	15	262	296	19
6	5	15	184	235	27
1	6	15	16	1	-386
2	6	15	162	179	30
3	6	15	15	1	-372
4	6	15	75	5	-75
5	6	15	74	5	-78
6	6	15	210	241	24
3	7	15	93	6	-66
4	7	15	82	6	-72
5	7	15	62	4	-96

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  hgse                                                              PAGE  1

  H  K  L 10FO 10FC 10S      H  K  L 10FO 10FC 10S      H  K  L 10FO 10FC 10S      H  K  L 10FO 10FC 10S      H  K  L 10FO 10FC 10S

  2  0  0 4683 4694  11      9  7  0 1347-1315  10      0  2  1 2057-2111  10     -7  7  1  612  536  10    -18  0  2  248 -324   7
  4  0  0 2744 2301  10     11  7  0  721 -566  10      2  2  1  960  997  10     -5  7  1 2113 2214  10    -16  0  2  564 -750   7
  6  0  0 4701 4200  10      0  8  0  484 -460  11      6  2  1 1112-1123  10     -3  7  1 1666 1730  10    -14  0  2  556 -773   8
  8  0  0 3861 3331   9      2  8  0  470  512  11      8  2  1  488 -590  10     -1  7  1  333  295  11    -12  0  2  491 -738   8
 10  0  0 1519 1325   9      4  8  0 1217 1125  10     12  2  1  386 -156   9      1  7  1 1284 1309  11    -10  0  2 1445-2236   9
 12  0  0 1212  982   8      6  8  0  466   82  10     14  2  1  496 -326   8      3  7  1 2291 2419  10     -8  0  2 3502-3191  10
 14  0  0 1282 1100   8     10  8  0  802  801  10    -17  3  1  349 -256   8      5  7  1  839  819  10     -6  0  2 2872-2118   9
 16  0  0  629  534   8      1  9  0  919  918  11    -15  3  1  475 -451   9      7  7  1  676  603  10     -4  0  2 2524-2426   9
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