

## The Coordination Chemistry of Bidentate Tellurium Ligands.

### I. Complexes of Palladium, Platinum, and Mercury with Large Chelate Rings

HEMA M. K. K. PATHIRANA, ALLAN W. DOWNS, WILLIAM R. McWHINNIE\*

Department of Molecular Sciences, Aston University, Aston Triangle, Birmingham B4 7ET, U.K.

and PIERRE GRANGER

Université Louis Pasteur de Strasbourg, Institut de Chimie, 1 Rue Blaise Pascal, 67008 Strasbourg Cédex, France

(Received June 1, 1987)

#### Abstract

Complexes formed from the reaction of palladium(II) and platinum(II) halides with (*p*-EtO·C<sub>6</sub>H<sub>4</sub>)Te-(CH<sub>2</sub>)<sub>n</sub>Te(C<sub>6</sub>H<sub>4</sub>OEt-*p*) (L<sup>n</sup>, *n* = 6, 7, 8, 9, 10) are reported together with data for some mercury(II) complexes, [HgL<sup>n</sup>Cl<sub>2</sub>] which are used for comparative purposes. The compounds [ML<sup>n</sup>X<sub>2</sub>] (M = Pd, Pt; *n* = 7, 8 (Pt only), 9, 10; X = Cl, Br) have molecular weights in molten naphthalene which fluctuate about the monomer value. [ML<sup>6</sup>X<sub>2</sub>] (M = Pd, Pt; X = Cl, Br) are totally insoluble and are believed to be polymeric. The palladium(II) complexes have *trans* dichloro groups whereas the platinum compounds show *cis* dichloro groups in the solid state.

<sup>13</sup>C NMR spectra are valuable to confirm the coordination of the ligand; the methylene resonance of the -Te-CH<sub>2</sub>- group undergoes a 19–20 ppm downfield shift on coordination. <sup>125</sup>Te NMR spectra of the Pd(II) and Pt(II) complexes show two broad resonances the chemical shifts of which imply the presence of *cis* and *trans* isomers in CDCl<sub>3</sub> solution. A more detailed variable temperature high field study of [PtL<sup>8</sup>Cl<sub>2</sub>] (<sup>125</sup>Te and <sup>195</sup>Pt NMR) reveals a complex solution chemistry involving at least two *cis* and two *trans* species. The temperature range over which the solution is stable (-10 to 70 °C) is insufficient to allow a totally unambiguous interpretation but a model based on monomer ⇌ dimer equilibria provides a self consistent interpretation.

#### Introduction

A generally held belief that large chelate rings should be unstable was shown to be in need of revision when Shaw and his co-workers [1, 2] reported *trans*[MCl<sub>2</sub>·Bu<sup>t</sup>P(CH<sub>2</sub>)<sub>n</sub>PBu<sub>2</sub><sup>t</sup>] (*n* = 10 or 12). Shaw [3] suggested that the bulky *t*-butyl groups on phosphorus induced restricted rotation about some P–C and C–C bonds on coordination of the first phos-

phorus atom to the metal and that, consequently, loss of internal entropy on cyclisation may be very small. However, others were able to prepare complexes of other phosphines (and arsines) such as Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>O(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub> (with Rh(I)) [4], MeAs(CH<sub>2</sub>)<sub>12</sub>-AsMe<sub>2</sub> (with Pd(II)) [5] and Ph<sub>2</sub>As(CH<sub>2</sub>)<sub>n</sub>AsPh<sub>2</sub> (*n* = 6–12, 16) (with Pd(II)) [6] which clearly showed that the formation of large chelate rings was not specifically a function of the bulk of substituents on the ligand atom. Although many complexes of Pd(II), Pt(II) and Rh(I) which have been isolated with ligands containing long chain backbones have been shown to have the ligand spanning *trans* positions in the square planar environment *cis* complexes are also known [6]. Indeed, very recently both *cis* and *trans* complexes of the ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (L) have been identified and structures are available for *cis*[PdLCl<sub>2</sub>] and for *trans*-[PdLi<sub>2</sub>] [7]. Furthermore the ability to form large chelate rings is not restricted to ligands containing group 5B (15) donor atoms, but ligands such as the poorer sulfur donor PhS(CH<sub>2</sub>)<sub>12</sub>SPh have been shown to give monomeric complexes such as [MCl<sub>2</sub>·PhS(CH<sub>2</sub>)<sub>12</sub>SPh] (M = Pd, Pt) [8].

Our long standing interest in organotellurium chemistry has led us to prepare a range of bis-tellurides, (*p*-EtO·C<sub>6</sub>H<sub>4</sub>)Te(CH<sub>2</sub>)<sub>n</sub>Te(C<sub>6</sub>H<sub>4</sub>OEt-*p*) (it is synthetically convenient to select the *p*-EtO·C<sub>6</sub>H<sub>4</sub> group which can also be helpful in NMR studies). Although we were able to synthesise the compound for which *n* = 1, those for which *n* = 2, 3, or 4 proved elusive for reasons which are well understood [9a]\*\*. Recently [10] we reported the synthesis of the series *n* = 5, 6, 7, 9, 10 (there is no significance in the omission of *n* = 8 which is described here) and we wish, in this paper, to report on complexes of these materials with Pd(II), Pt(II) and Hg(II) many of which are believed to contain large chelate rings.

\*\*Very recently the synthesis of RTe(CH<sub>2</sub>)<sub>3</sub>TeR (R = Me, Ph) by the reaction of RTeLi with X(CH<sub>2</sub>)<sub>3</sub>X (X = Cl, Br) in THF at low temperature was reported [9b].

\*Author to whom correspondence should be addressed.

TABLE I. Analytical Data, Yields and Melting Points

Complex (colour)	Melting point (°C)	Found (%)		Calculated (%)		$\Lambda_M$ (DMF) (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Molecular weight (calc.)
		C	H	C	H		
PtCl <sub>2</sub> L <sup>6</sup> (yellow)	150–152 (dec)	34.5	4.00	34.8	4.00	–	–
PdCl <sub>2</sub> L <sup>7</sup> (orange–yellow)	108–109	35.1	4.05	35.7	4.10	4.5	829 (772)
PdCl <sub>2</sub> L <sup>9</sup> (maroon–red)	102–103	37.3	4.55	37.5	4.50	4.2	835 (800)
PdCl <sub>2</sub> L <sup>10</sup> (orange–red)	108–110	38.3	4.65	38.3	4.70	4.8	726 (814)
PdBr <sub>2</sub> L <sup>6</sup> (yellow–brown)	170–171 (dec)	31.0	3.30	31.2	3.50	–	–
PdBr <sub>2</sub> L <sup>10</sup> (maroon–brown)	120–121	34.9	4.90	34.5	4.20	8.6	917 (903)
PtCl <sub>2</sub> L <sup>6</sup> (yellow)	135–136	31.4	3.65	31.2	3.50	4.2	–
PtCl <sub>2</sub> L <sup>8</sup> (yellow)	96	32.9	3.91	33.5	3.40	–	458 (875)
PtCl <sub>2</sub> L <sup>7</sup> (yellow)	114–115	31.7	3.35	32.0	3.70	4.5	858 (861)
PtCl <sub>2</sub> L <sup>9</sup> (yellow)	121–122	33.9	4.00	33.7	4.05	4.4	860 (889)
PtCl <sub>2</sub> L <sup>10</sup> (bright yellow)	118–120	34.5	4.25	34.5	4.20	3.7	870 (903)
PtBr <sub>2</sub> L <sup>6</sup> (yellow)	126–128	27.8	3.00	28.2	3.20	3.8	–
PtBr <sub>2</sub> L <sup>10</sup> (brown–orange)	120–121	31.6	4.00	31.6	3.80	15	800 (992)
HgCl <sub>2</sub> L <sup>6</sup> (pale yellow)	82–83	30.2	3.45	31.0	3.50	6.3	–
HgCl <sub>2</sub> L <sup>7</sup> (pale yellow)	73–74	31.3	3.30	31.8	3.70	8.0	–
HgCl <sub>2</sub> L <sup>9</sup> (pale yellow)	79–80	33.2	3.60	33.5	4.00	8.3	–
HgCl <sub>2</sub> L <sup>10</sup> (pale yellow)	74–75	33.6	4.00	34.3	4.20	12	–

## Experimental and Results

The synthesis of the ligands *p*-EtO·C<sub>6</sub>H<sub>4</sub>Te(CH<sub>2</sub>)<sub>*n*</sub>·Te(C<sub>6</sub>H<sub>4</sub>OEt-*p*) (denoted in this paper L<sup>*n*</sup>) for which *n* = 6, 7, 9 and 10 has been reported [10]. We have now prepared L<sup>8</sup> by an exactly similar method (Found: C, 47.2; H, 5.20. Calc. for C<sub>24</sub>H<sub>34</sub>O<sub>2</sub>Te<sub>2</sub>: C, 47.3; H, 5.62%. Melting point (m.p.) = 50 °C). All metal complex preparations were carried out in an oxygen free atmosphere of dinitrogen.

### Synthesis of Palladium Complexes

The same method was used for all complexes of PdCl<sub>2</sub>, typically:

#### *Dichloro(1,7-bis(p-ethoxyphenyltelluro)heptane)-palladium(II)*

A solution of Na<sub>2</sub>PdCl<sub>4</sub>·3H<sub>2</sub>O (0.17 g, 0.5 mmol) in distilled water was added dropwise to a solution of 1,7-bis(*p*-ethoxyphenyltelluro) heptane (0.3 g, 0.5 mmol) in acetone. A brown precipitate formed and the reaction mixture was stirred for 12 h. The solid was separated, washed with distilled water and acetone and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>.

Dibromo complexes were prepared by converting sodium tetrachloropalladate(II) to the tetrabromo complex by treating with a five-fold excess of potassium bromide. The preparation then followed the above procedure. Some preparations were repeated using a different precursor, [PdCl<sub>2</sub>(NCPH)<sub>2</sub>], however identical products were obtained. Also the reactant ratios were varied but now new products were formed.

### Synthesis of Platinum Complexes

The platinum complexes were synthesised from K<sub>2</sub>PtCl<sub>4</sub> or K<sub>2</sub>PtBr<sub>4</sub> following an identical procedure to that outlined for the palladium compounds. In the case of platinum a complex was also prepared with L<sup>8</sup> which has the same number of atoms linking to donor atoms as is the case for 1,8-bis(diphenylphosphino)-3,6-dioxaoctane [4, 7].

### Synthesis of Mercury Complexes

e.g. Dichloro-1,7-bis(*p*-ethoxyphenyltelluro)heptane mercury(II). A solution of HgCl<sub>2</sub> (0.14 g, 0.5 mmol) in dry acetone was added dropwise to a solution of L<sup>7</sup> (0.3 g, 0.05 mmol) in dry acetone. A pale yellow precipitate formed. The reaction mixture was stirred for 4–5 h after which the solid was separated, washed with dry acetone and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub>. Other mercury(II) complexes were prepared by an identical procedure.

Analytical data, yields and melting points are given in Table I.

### Physical Measurements

Infra-red spectra (4000–200 cm<sup>-1</sup>) were measured using a Perkin-Elmer 599B instrument (for the range 400–200 cm<sup>-1</sup> samples were examined as polythene discs). Mass spectra were recorded with an AE1 MS9 spectrometer (70 eV). <sup>1</sup>H NMR spectra were obtained with a Perkin-Elmer R12B instrument (60 MHz) and proton decoupled <sup>13</sup>C NMR spectra were recorded with a Jeol FX 90Q instrument and some were recorded with a Bruker AC300 instrument (TMS was internal standard for both <sup>1</sup>H and <sup>13</sup>C). <sup>125</sup>Te NMR

TABLE II. The UV (chloroform) and IR (metal-halogen) Spectra of Metal Complexes of Bis(organyltelluro)alkanes

Complex <sup>a</sup>	$\lambda_{\max}$ (nm)	$\lambda_{\max}$ (cm <sup>-1</sup> )	$\nu(\text{MCl})$ (cm <sup>-1</sup> )	$\nu(\text{MBr})$ (cm <sup>-1</sup> )
PdCl <sub>2</sub> L <sup>6</sup>			342	
PdCl <sub>2</sub> L <sup>7</sup>	420	23 810	350	
PdCl <sub>2</sub> L <sup>9</sup>	414	24 155	342	
PdCl <sub>2</sub> L <sup>10</sup>	417	23 981	342	
PdBr <sub>2</sub> L <sup>6</sup>				270
PdBr <sub>2</sub> L <sup>10</sup>	428	23 650		265
PtCl <sub>2</sub> L <sup>6</sup>	335	29 851	299, 315	
PtCl <sub>2</sub> L <sup>7</sup>	340	29 412	299, 320	
PtCl <sub>2</sub> L <sup>9</sup>	344	29 070	298, 315	
PtCl <sub>2</sub> L <sup>10</sup>	330	30 303	299, 316	
PtBr <sub>2</sub> L <sup>6</sup>				
PtBr <sub>2</sub> L <sup>10</sup>	340	29 412		
HgCl <sub>2</sub> L <sup>7</sup>	317.5	31 496		
HgCl <sub>2</sub> L <sup>9</sup>	317.5	31 496		
HgCl <sub>2</sub> L <sup>10</sup>	317.5	31 496		

<sup>a</sup>PtCl<sub>2</sub>L<sup>8</sup>:  $\nu(\text{PtCl}) = 299, 315 \text{ cm}^{-1}$ .

TABLE III. <sup>1</sup>H-<sup>13</sup>C NMR Data for Palladium and Platinum Complexes of Bis(organyltelluro)alkanes

Complex	Chemical shift (ppm vs. TMS)										
	Aromatic region				Aliphatic region						
	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>	C-1	C-2	C-3	C-4	C-5	OCH <sub>2</sub>	CH <sub>3</sub>
PdCl <sub>2</sub> L <sup>7</sup>	105.1	138.5	116.1	160.5	26.1	27.3	29.5	30.3		63.6	14.7
PdCl <sub>2</sub> L <sup>9</sup>	96.1	138.8	115.8	?	27.4	27.7	30.3	30.7	?	63.5	14.7
PdCl <sub>2</sub> L <sup>10</sup>	103.2	138.8	115.8	160.3	27.1	28.0	28.9	31.5	?	63.5	14.7
PdBr <sub>2</sub> L <sup>10</sup>	?	138.6	115.8	160.3	28.1	29.0	30.4	31.8	?	63.5	14.7
PtCl <sub>2</sub> L <sup>7</sup>	96.1	137.2	115.8	160.9	27.7	28.1	30.0	30.4		63.6	14.7
PtCl <sub>2</sub> L <sup>8</sup>	?	138.1	115.6	160.6	28.2	28.30	30.79	30.89		63.6	14.7
(L <sup>8</sup> )	(100.4)	(140.9)	(115.6)	(160.0)	(8.99) <sup>a</sup>	(28.71)	(31.64)	(31.73)		(63.3)	(14.7)
PtCl <sub>2</sub> L <sup>9</sup>	?	138.1	115.7	161.1	27.5	27.9	28.3	30.2	?	63.6	14.7
PtCl <sub>2</sub> L <sup>10</sup>	?	138.1	115.4	164.8	27.3	28.7	29.3	30.7	31.9	63.6	14.7
PtBr <sub>2</sub> L <sup>10</sup>	?	138.1	115.7	160.6	26.2	27.6	28.3	29.6	30.5	63.6	14.7

<sup>a</sup>J(TeC) = 75.5 Hz.

data were obtained mainly at the Université de Rouen (proton frequency 90 MHz) [11], but one compound PtL<sup>8</sup>Cl<sub>2</sub> has also been examined over a range of temperatures at the Université de Strasbourg (proton frequency 400 MHz); Bruker instruments were used in both cases and chemical shifts are referenced to dimethyltelluride. UV spectra for chloroform solutions were measured with a Pye-Unicam SP8-100 series instrument.

Molar conductivities were recorded with a Mullard bridge and dip cell (E 7591/B). Molecular weight determinations were generally frustrated by the limited solubility of the complexes, however they proved

more soluble in molten naphthalene and Rasts method was successfully employed [12].

UV and IR data are gathered into Table II, <sup>1</sup>H, <sup>13</sup>C NMR data constitute Table III and <sup>125</sup>Te NMR data are given in Tables IV and V.

## Discussion

The reaction of the ligand series RTe(CH<sub>2</sub>)<sub>n</sub>TeR (L<sup>n</sup>, where R = *p*-EtO·C<sub>6</sub>H<sub>4</sub>; n = 6, 7, 8, 9, 10) with palladium(II) or platinum(II) chloro-compounds gives complexes [MCl<sub>2</sub>L<sup>n</sup>] (Table I). Corresponding

TABLE IV. Some  $^{125}\text{Te}$  NMR Data for Palladium and Platinum Complexes of Bis(organyltelluro)alkanes<sup>a</sup>

Compound (scans)	$\delta$ (ppm) vs. $\text{Me}_2\text{Te}$ ( $\text{CDCl}_3$ solutions)	$\Delta\nu_{1/2}$ (Hz)
$\text{L}^7$ (19 500)	454.7	15
$\text{L}^9$ (40 500)	454.8	30
$\text{L}^{10}$ (30 000)	454.7	35
$\text{PdCl}_2\text{L}^9$ (338 000)	$\begin{cases} 559 \\ 617 \end{cases} \Delta\delta = 58$	$\begin{cases} 330 \\ 670 \end{cases}$
$\text{PdCl}_2\text{L}^{10}$ (254 000)	$\begin{cases} 529 \\ 560 \end{cases} \Delta\delta = 31$	$\begin{cases} 50 \\ 620 \end{cases}$
$\text{PtCl}_2\text{L}^7$ (150 000)	$\begin{cases} 546 \\ 569 \end{cases} \Delta\delta = 23$	$\begin{cases} 405 \\ 142 \end{cases}$
$\text{PtCl}_2\text{L}^9$ (250 000)	$\begin{cases} 546 \\ 573 \end{cases} \Delta\delta = 27$	$\begin{cases} 430 \\ 3000 \end{cases}$
$\text{PtCl}_2\text{L}^{10}$ (252 000)	$\begin{cases} 538 \\ 579 \end{cases} \Delta\delta = 41$	$\begin{cases} 940 \\ 610 \end{cases}$

<sup>a</sup> $J(\text{Te-Pt})$  could not be isolated from the spectrum.

bromides may be made and the complex stoichiometry is unaltered by change of metal:ligand ratio or of complex precursor (e.g.  $\text{MCl}_4^{2-}$  or  $\text{MCl}_2(\text{NCPH})_2$ ,  $\text{M} = \text{Pd}, \text{Pt}$ ). Mercury(II) chloride also forms 1:1 complexes with the ligands which, although they have low melting points, are sparingly soluble in a wide range of solvents and only those data (UV, conductivity) obtainable from dilute solutions are available. The main purpose of the rather intractable mercury complexes is to provide some comparative data for the palladium and platinum complexes.

The conductivity data (DMF) show the complexes to be non-electrolytes (Table I). It proved difficult to obtain molecular weight data (the complexes decompose in the mass spectrometer) however ultimately the reasonable solubility in molten naphthalene led to the application of Rasts' method. The method is subject to large errors (especially with naphthalene) thus the charge of over interpreting the difference between observed and calculated values must be avoided. The data in Table I scatter about the monomer value but warn that the solutions at this temperature (79 °C) may contain more than one species (see 'Discussion'  $^{125}\text{Te}$  NMR); however there is certainly no evidence for polymers. An exception may be the complexes of  $\text{L}^6$  which are totally insoluble in all solvents we have used; a likely explanation is that these materials are indeed polymeric. A similar conclusion has been reached in respect of  $[\text{Pd}(\text{MeSe}(\text{CH}_2)_6\text{SeMe})\text{Cl}_2]$  which, like  $[\text{PdL}^6\text{X}_2]$  here is considered to have *trans* dichloro groups [13]. By contrast,  $[\text{PtL}^6\text{Cl}_2]$  shows two  $\nu(\text{PtCl})$  at 315 and 299  $\text{cm}^{-1}$  which are in agreement with ranges characteristic of *cis* complexes of  $\text{PtCl}_2$  with monodentate tellurium ligands [14, 15].

The observations for  $\text{L}^6$  appear general. Thus for  $[\text{PdL}^n\text{Cl}_2]$  ( $n = 7, 9, 10$ ), a single  $\nu(\text{PdCl})$  is seen between 350 and 342  $\text{cm}^{-1}$  consistent with *trans* dihalogeno complexes [14–16]. The platinum(II) complexes,  $[\text{PtL}^n\text{Cl}_2]$  ( $n = 7, 8, 9, 10$ ), again show two  $\nu(\text{PtCl})$  in the range 320–299  $\text{cm}^{-1}$  consistent with a *cis* configuration (*i.e.*  $\text{Te trans to Cl}$ ) [14, 15]. The complex  $[\text{PtL}^8\text{Cl}_2]$  was subjected to more rigorous examination (*vide infra*) during which it was noted that evaporation of a dilute chloroform solution afforded a glass-like material (in contrast to cooling which led to precipitation of a solid). The IR of the glass showed  $\nu(\text{PtCl})$  at 296 and 306  $\text{cm}^{-1}$ . The slight frequency differences from the solid state values

TABLE V. Variable Temperature and Solvent Study of  $\text{PtL}^8\text{Cl}_2$  Using  $^{125}\text{Te}$  and  $^{195}\text{Pt}$  NMR

Resonance	$^{125}\text{Te}$ NMR ( $\text{CDCl}_3$ ) <sup>a</sup>				$^{125}\text{Te}$ NMR ( $\text{CHCl}_2\text{CHCl}_2$ ) <sup>a</sup>		$^{195}\text{Pt}$ NMR <sup>b</sup> 70 °C
	-10 °C	10 °C	27 °C	40 °C	40 °C	70 °C	
A	571 (broad)	570.5 (broad)	574 (broad)	573	582.6 ( $J = 1190$ ) <sup>c</sup>	580 ( $J = 1190$ ) <sup>c</sup> (narrow)	-2563
B	555 (broad)	552.5 (broad)	548.4 (broad)	545.5	533.6	535.1 ( $J = 1070$ ) <sup>c</sup> (narrow)	-2584
C	538 (broad)	539.5	541.5 ( $J = 727$ ) <sup>c</sup>	543.5	542.6	549.1 } 548.7 } ( $J = 659$ ) <sup>c</sup>	-2019.2 } -2020.4 }
D	519.5 (weak)	521.5	524.5 ( $J = 549$ ) <sup>c</sup>	527	525.1	528.5 ( $J = 549$ ) <sup>c</sup>	-1974

<sup>a</sup>Chemical shifts vs.  $\text{Me}_2\text{Te}$ .

<sup>b</sup>Chemical shifts vs.  $\text{PtCl}_6^{2-}$ .

<sup>c</sup> $J(\text{TePt})$  in Hz.

(Table II) probably reflect the solid–‘solution’ phase difference. Gysling *et al.* [17] have noted similar differences between solution and solid for Pt(Te(CH<sub>2</sub>CH<sub>2</sub>Ph)<sub>2</sub>)Cl<sub>2</sub>. (We note that attempts to form complexes of Pd(II) and Pt(II) with these related MeSe(CH<sub>2</sub>)<sub>12</sub>SeMe led to intractable oils [13].)

<sup>1</sup>H NMR data of the complexes show the same aromatic:aliphatic ratios as for the free ligands. <sup>13</sup>C NMR data are of more interest. Those for the free ligands have been reported and discussed [10]. The data for L<sup>B</sup> fit in well with the pattern seen for other ligands [10] and the use of the INEPT pulse sequence has confirmed the assignment of C-1, the methylene bonded to tellurium, at relatively high field (8.99 ppm; Table III); also <sup>1</sup>J(<sup>125</sup>Te–<sup>13</sup>C) has been resolved in this case and the value, 75.5 Hz, agrees well with observations by others [18] on di-organyltellurides. The most dramatic change in the <sup>13</sup>C NMR parameters on coordination of the ligand is the shift of the C-1 resonance some 20 ppm to lower field (Table III). The magnitude of this C-1 shift is much greater than for corresponding phosphine and arsine ligands [2, 6]; thus not only is the initial shielding by the tellurium atom greater than for phosphorus or arsenic, but the implication is that a significant transfer of charge occurs on coordination of the tellurium to Pd(II) or Pt(II), deshielding C-1 and implying a stronger M ← Te bond than is commonly supposed. The observation is analytically useful since the shift is a clear indicator for the coordination of tellurium. The data show, for the complexes under consideration, that the concentration of uncoordinated (or monodentate) ligand is below detectable limits.

<sup>125</sup>Te NMR is a powerful tool for the examination of coordination compounds of tellurium ligands. The ligand chemical shifts (relative to Me<sub>2</sub>Te) are relatively invariant and similar to the value (468 ppm) reported for Bu<sup>n</sup>TePh [19] (Tables IV and V). The complexes are rather sparingly soluble but long accumulation times did enable data to be produced (Table IV). In each case for ML<sup>n</sup>Cl<sub>2</sub> (M = Pd, Pt; n = 7, 9, 10) two broad resonances were observed downfield from the free ligand. The deshielding is an anticipated consequence of coordination and the chemical shifts of the two resonances correspond well with expectation [17] for *cis* (Δδ = 74–104 ppm (Pd) and 83–91 ppm (Pt)) and *trans* isomers (Δδ = 105–162 ppm (Pd) and 114–124 ppm (Pt)). Also the chemical shift difference for *cis*–*trans* pairs is in line with the literature [17].

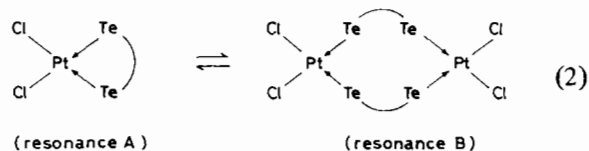
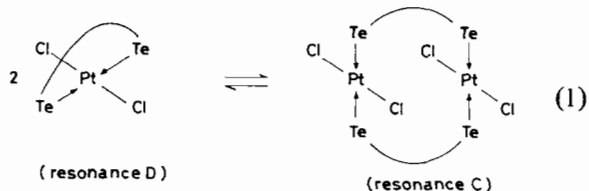
The above interpretation is not unambiguous. The broad resonances mask *J*(TePt) for the platinum(II) complexes thus denying access to more positive evidence for the combined presence of *cis* and *trans* isomers. The width of the resonance lines may suggest a *cis* ⇌ *trans* isomerisation occurring on a similar timescale to that of the NMR experiment; alternative-

ly the temperature of observation may be such that a second dynamic process is occurring on the NMR timescale. (Another complication is that the <sup>125</sup>Te NMR chemical shift shows a significant temperature dependence [20] and fluctuation of the probe temperature during accumulation of data may distort the line shape.) The most likely additional/alternative process to be considered must be inversion at coordinated tellurium and the presence of D, L and meso forms in equilibrium. Indeed, invertomers of [Pt(RSeCH<sub>2</sub>CH<sub>2</sub>SeR)Cl<sub>2</sub>] (R = Me, Ph) show <sup>77</sup>Se chemical shift differences of 5 (Ph) and 2 (Me) ppm [13] at room temperature and it is believed that inversion barriers increase in the order S < Se < Te [21]; thus even the two resonances observed may represent D, L and meso forms. However we were sceptical that such large differences in chemical shift as those observed would occur between such species.

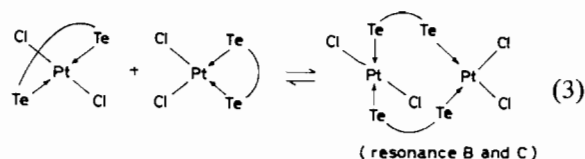
In view of the ambiguity of the above interpretation, one compound, [PtL<sup>B</sup>Cl<sub>2</sub>], was selected for more detailed study with a high field spectrometer using both <sup>125</sup>Te and <sup>195</sup>Pt NMR spectroscopy. The choice of L<sup>B</sup> represented the mid point of the series, L<sup>6</sup>–L<sup>10</sup>, under investigation. The room temperature tellurium spectrum revealed two broad (A, B; Table V) and two narrow resonances (C, close to B; D, weak), however it was noted that the CDCl<sub>3</sub> solution in the NMR tube, initially homogeneous, now consisted of two layers—a viscous lower layer from which A and B originated and a mobile upper layer. Cooling broadened all four resonances and below –10 °C precipitation occurred. It was therefore decided to warm the solution and at 40 °C a distinct narrowing of broad lines was observed encouraging continuation of the experiment. A change of solvent to CHCl<sub>2</sub>·CHCl<sub>2</sub> was required, this solvent gave a completely homogeneous solution with resonances A and B showing a significant solvent effect (Table V). The temperature was raised to 70 °C; all four lines were now narrow and coupling constants were readily resolved. These clearly indicate that two resonances (A and B) arise from *cis* species and two (C and D) from *trans* species (Table V). Also resonance C was now resolved into two lines (549.1, 548.7 ppm). The <sup>195</sup>Pt spectra at 70 °C and at room temperature are in good accord with the Te data. The <sup>195</sup>Pt chemical shifts for *cis*-Pt(Me<sub>2</sub>Se)<sub>2</sub>Cl<sub>2</sub> (–2089 ppm) and for *trans*-Pt(Me<sub>2</sub>Se)<sub>2</sub>Cl<sub>2</sub> (–1858 ppm) [22] are helpful, together with intensity and line width correlations, to enable the following pairings to be established for the 70 °C spectra: *cis* A: 580 ppm (Te), –2563 ppm (Pt), *J*(TePt) = 1190 Hz; B: 535.1 ppm (Te), –2584 ppm (Pt), *J*(TePt) = 1070 Hz. *trans* C: 549.1, 548.7 ppm (Te), –2019.2, –2020.4 ppm (Pt), *J*(TePt) = 659 Hz; D: 528.5 ppm (Te), –1974 ppm (Pt), *J*(TePt) = 549 Hz. Resonance D is weak and corresponds to the species of lowest concentration.

The 70 °C measurements represent the upper limits for total thermal stability of the solution of  $[\text{PtL}^8\text{Cl}]$  since the  $^{195}\text{Pt}$  spectra begin to give evidence of some decomposition (which may explain the low 79 °C molecular weight). The lower temperature limit (−10 °C) is determined by solubility limitations. Thus at low temperatures some process occurring on the NMR time scale is operative. The work of Cross *et al.* [21] makes it improbable that this is the interconversion of the D, L and meso invertomers since their study of simple tellurides coordinated to platinum(II) indicated that the inversion temperatures are quite high [21]. Indeed the resonances A, B, C and D must themselves be regarded as candidates for the two *cis* and the two *trans* invertomers, however we are sceptical that such large differences in  $^{125}\text{Te}$  chemical shifts would result from invertomer pairs (the resolution of resonance C into two bands at 70 °C may represent, for the species concerned, the D, L and meso forms). It may be that the low temperature process is based on ligand exchange.

Both  $^{13}\text{C}$  and  $^{125}\text{Te}$  NMR data are consistent in their elimination of the presence of uncoordinated tellurium, thus we may eliminate the presence of polymers (MW) and linear oligomers (since uncoordinated Te should be detectable). Cyclic oligomers may not be eliminated but the MW data makes it unlikely that molecules of greater complexity than dimers could exist. A possible explanation, which is self consistent as far as the data accessible are concerned, is based on monomer dimer equilibria:



There are good literature precedents for *cis* [23] and *trans* [4] dimers. The model predicts distinct resonances for the monomers and dimers. Resonance A is assigned to the *cis* monomer following values observed for monomeric complexes of unidentate ligands [17], leaving B as the *cis* dimer. Similar reasoning leads to the assignments of resonances C and D (see eqn. (1)). Each of the species postulated should show inversion at coordinated tellurium above the inversion temperature, thus, as stated above, the resolution of resonance C into two components may reflect the observation of invertomers, but an alternative explanation is represented by eqn. (3).



where the differences between the *cis*, *cis*; *cis*, *trans*; and *trans*, *trans* dimers are resolved for C and not B.

Unfortunately the data do not allow an unambiguous interpretation. We have attempted to synthesise other ligands with different aryl groups, e.g.  $\text{PhTe}(\text{CH}_2)_n\text{TePh}$  [23] but these offer no improvement in solubility for the complexes. More work with more simple ligands is now required; in the meantime we submit that the above interpretation offers a self consistent interpretation of the data which it is possible to obtain.

The mercury(II) complexes are rather intractable but they serve two useful purposes. Thus they helped in the assignments of (MX) and also assisted in a UV study. All the Pt(II) complexes were yellow, and yet many *cis* Pt(II) complexes are described as colourless. The UV spectra were similar to those of the pale yellow Hg(II) complexes (Table II) and hence the colour in both cases probably results from a ligand centered transition which tails into the visible.

The complexity of the NMR data throw into question the solid state structures of  $\text{ML}^n\text{X}_2$  (M = Pd, Pt;  $n = 6-10$ ; X = Cl, Br). If the complexes of  $\text{L}^6$  are *trans* polymeric (Pd) and *cis* polymeric (Pt), the others may be monomers or dimers. The IR spectra indicate the presence of only one species and the observed metal-halogen stretching frequencies happen to agree well with those reported for established monomers with large chelate rings. All crystals so far examined have proved to be twinned or to have other imperfections. Attempts are in progress to redesign the ligands in the hope that more soluble, better crystalline complexes may be obtained.

### Acknowledgements

H.M.K.K.P. thanks Ruhuna University (Sri Lanka) for study leave. We thank Johnson and Matthey Ltd., for a generous loan of palladium and platinum salts.

### References

- 1 A. J. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc., Chem. Commun.*, 947 (1973).
- 2 A. J. Pryde, B. L. Shaw and B. Weeks, *J. Chem. Soc., Dalton Trans.*, 322 (1976).
- 3 B. L. Shaw, *J. Am. Chem. Soc.*, 97, 3856 (1975).
- 4 N. W. Alcock, J. M. Brown and J. L. Jeffery, *J. Chem. Soc., Dalton Trans.*, 888 (1977).

- 5 W. Levason, C. A. McAuliffe and S. G. Murray, *J. Organomet. Chem.*, **110**, C25 (1976).
- 6 W. E. Hill, D. M. A. Minaham and C. A. McAuliffe, *Inorg. Chem.*, **22**, 3382 (1983).
- 7 W. E. Hill, J. G. Taylor, C. P. Falshaw, T. J. King, B. Beagley, D. M. Tonge, R. G. Prichard and C. A. McAuliffe, *J. Chem. Soc., Dalton Trans.*, 2289 (1986).
- 8 C. A. McAuliffe, H. E. Soutter, W. Levason, F. R. Hartley and S. G. Murray, *J. Organomet. Chem.*, **159**, C25 (1978).
- 9 (a) K. G. K. De Silva, Z. Monsef-Mirzai and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 2143 (1983); (b) E. G. Hope, T. Kemmitt and W. Levason, *Organometallics*, **6**, 206 (1987).
- 10 H. M. K. K. Pathirana and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, 2003 (1986).
- 11 P. Granger, S. Chapelle, W. R. McWhinnie and A. Z. Al Rubaie, *J. Organomet. Chem.*, **220**, I49 (1981).
- 12 B. P. Levitt, 'Findlays Practical Physical Chemistry', Longman, 1973.
- 13 D. J. Gulliver, E. G. Hope, W. Levason, S. G. Murray and G. L. Marshall, *J. Chem. Soc., Dalton Trans.*, 1265 (1985).
- 14 D. M. Adam, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, 734 (1964).
- 15 J. R. Atkins and P. J. Hendra, *J. Chem. Soc. A*, 1325 (1967).
- 16 A. Constable, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 496 (1977).
- 17 H. J. Gysling, N. Zumbulyadis and J. A. Robertson, *J. Organomet. Chem.*, **209**, C41 (1981).
- 18 R. K. Chadha and J. Miller, *J. Chem. Soc., Dalton Trans.*, 117 (1982).
- 19 D. H. O'Brien, K. J. Irgolic and C. K. Huang, in F. J. Berry and W. R. McWhinnie (eds.), 'Proceedings of the Fourth International Conference on the Organic Chemistry of Selenium and Tellurium', The University of Aston, Birmingham, 1983, pp. 468-491.
- 20 P. Granger and S. Chapelle, *J. Magn. Reson.*, **39**, 329 (1980).
- 21 R. J. Cross, T. G. Green and R. Keat, *J. Chem. Soc. Dalton Trans.*, 1150 (1976).
- 22 N. N. Greenwood and G. Hunter, *J. Chem. Soc. A*, 1520 (1967).
- 23 W. R. McWhinnie and S. Mbogo, unpublished data.