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INVERSION AND PROCHIRALITY IN BIS-THIO- AND -SELENOETHER COMPLEXES OF TRIMETHYLPLATINUM(IV) HALIDES

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Summary

The ^1H NMR spectra of the complexes $[PtXMe_3(Me_2E)_2]$, X = Cl and Br, E = S and Se, show a non-equivalence of the Me_2E methyl groups at low temperatures arising from a lack of symmetry at the metal centre. Inversion at the E atoms equalises the environments, and activation energies for the process have been computed for three complexes.

Introduction

The tetrameric complexes $(PtXMe_3)_4$, X = Cl, Br and I, react with the bidentate ligands $MeE(CH_2)_nEMe$, E = S or Se, to give mononuclear complexes $[PtXMe_3\{MeE(CH_2)_nEMe\}]$ when n = 2 and 3, and binuclear complexes $[(PtXMe_3)_2MeE(CH_2)_nEMe]$ when n = 0 and 1 [1]. In both series the possibilities of inversion at both chalcogen atoms and of other internal dynamic processes render the complexes highly stereochemically non-rigid. This feature has been examined in detail by DNMR methods [2—4]. An unexpected feature of both series was their stability towards ligand dissociation. The compounds are indefinitely stable in the solid state, while DNMR solution studies show that dissociation does not occur below 100° C, and is fully reversed on cooling. By contrast the only trimethylplatinum(IV) complexes reported with the analogous monodentate ligands R_2S and R_2Se, namely $[PtMe_3(acac)Me_2S]$ [5] and $[PtIMe_3(Et_2S)]_2$ [6] both show evidence of slow ligand dissociation in the solid state and in $CHCl_3$ solution respectively. Since the latter complex was made by oxidative addition of MeI to $[PtMe_2(Et_2S)]_2$, it was of interest to see if the monodentate thio- and selenoethers Me_2E (E = S and Se) were sufficiently strong Lewis bases to break the halide bridges in $[PtXMe_3]_4$, and to examine the fluxional behaviour of the products.

Results and discussion

The complexes [$PtXMe_3(Me_2E)_2$], X = Cl and Br, E = S and Se, were made by adding an excess of Me_2S or Me_2Se to a solution of [$PtXMe_3$]$_4$ in chloroform or dichloromethane, and refluxing for ten minutes (Me_2S) or allowing to stand at room temperature for five hours (Me_2Se). On concentration and cooling to —20° C solid products were obtained as white, shining plates which were freely soluble in organic solvents. They melted with decomposition below 100° C, and all four had a pronounced odour of the ligand in the solid state. Decomposition leaves [$PtXMe_3$]$_4$ on prolonged standing at room temperature. It was not possible to obtain accurate analytical figures owing to this speed of decomposition at ambient temperature, and the complexes were characterised unequivocally by their ^1H NMR spectra at low temperatures (Table 1).

The spectra of all four compounds show the expected 2 : 1 pattern of methyl platinum signals, with ^2J(Pt—H) values in the usual ranges for methyls *trans* to terminal halide and chalcogen ligand atoms [1]. Assignments are based on the fact that in all complexes of the type [$PtXMe_3L_2$] the less intense signal for methyls *trans* to halide is invariably at higher field [1,7], and they confirm the bis stoichiometry of the complexes. The Σ^2J values for the platinum methyl groups are very close to those of the corresponding mononuclear complexes [$PtXMe_3\{MeE(CH_2)_3EMe\}$] with the six-membered chelate ring [1]. It is interesting to note that values of ^2J for methyls *trans* to sulphur are lower than the corresponding values in [$PtMe_3(acac)Me_2S$] (71.5 Hz) and [$PtIMe_3(Et_2S)$]$_2$ (72 Hz), reflecting somewhat stronger Pt—S bonds in [$PtXMe_3(Me_2S)_2$ [8].

Below —80° C (S complexes) and —30° C (Se complexes) two signals of equal intensity are seen in the region expected for the chalcogen methyl groups, both coupled to ^{195}Pt. This is an interesting contrast to the spectra of the *cis*- and *trans*- isomers of [$PtCl_2(Me_2S)_2$] [9] where only one methyl signal is observed. In this latter complex the two sulphur atoms are prochiral centres and the two methyl environments are distinct if a completely static structure is assumed. However, rotation about the Pt—S bonds is rapid on the NMR time scale, and this process averages the pairs of methyl environments. In the complexes [$PtXMe_3(Me_2E)_2$] the two E atoms are again prochiral, but rapid Pt—E bond rotation does not average the chemical shifts of the geminal methyl groups on each ligand because the Me_2PtE_2 plane is not a plane of symmetry (Fig. 1). The

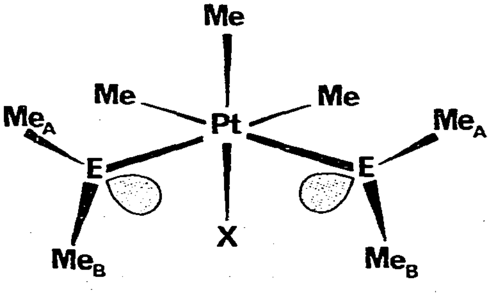

Fig. 1. Structure of the compounds [$PtXMe_3(Me_2E)_2$], X = Cl and Br, E = S and Se, showing the non-equivalence of the methyl groups on each Me_2E ligand.

signals are quite distinct in both coupling constant ^3J(Pt—H) and chemical shift. The ^3J values are lower for E = Se than for E = S, and are in the same range as, but usually slightly less than, those in the corresponding mononuclear chelate analogues (13.5—10.4 Hz).

As the temperature is raised, the ^{1}H NMR spectra of all four complexes show a platinum methyl region unchanged in general features. Small variations in ^2J and δ are seen, both parameters decreasing for methyls *trans* to halide and increasing for methyl *trans* to chalcogen, consistent with a weakening of the Pt—E bonds at higher temperatures. The ligand methyl region by contrast shows a marked alteration, the two signals broadening and then coalescing to a single signal as the methyl environments become equalised. Since coupling to ^{195}Pt is preserved throughout, the equalisation must result from an intramole-

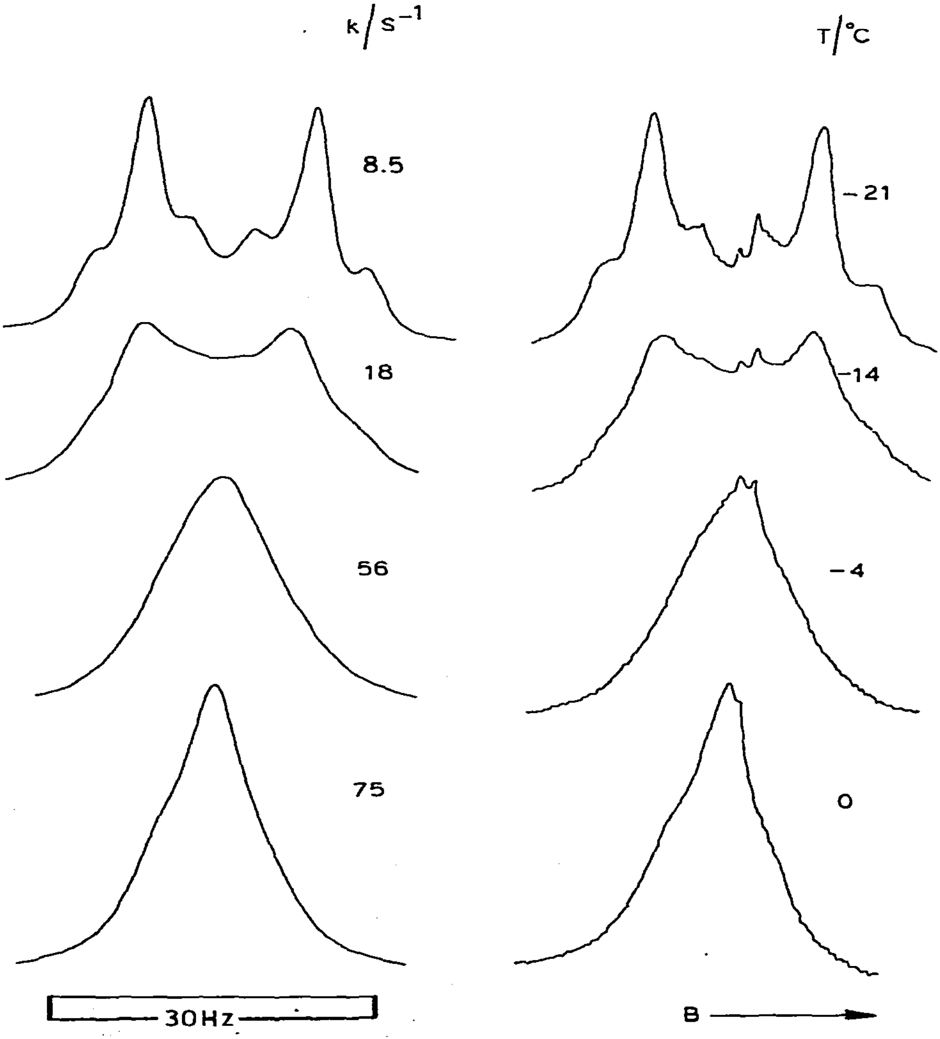

Fig. 2. Experimental and computer-simulated spectra of the Me_2Se ligand in the complex $[PtClMe_3(Me_2Se)_2]$ in the temperature range −21 to 0°C.

TABLE 1

^{1}H NMR PARAMETERS FOR THE COMPLEXES [$PtXMe_3(Me_2E)_2$]

X	E	T (°C)	PtMe *trans* to X [a]		PtMe *trans* to E [b]		Ligand signals [c]				
			δ (ppm)	^2J (Hz)	δ (ppm)	^2J(Hz)	δ_A (ppm)	^3J (Hz)	δ_B (ppm)	^3J (Hz)	t_2^* (s)
Cl	S	−88.1	0.66	72.6	1.03	68.4	2.24	13.4	2.40	11.0	—
Br	S	−90.0	0.79	71.9	1.12	68.5	2.26	13.6	2.46	11.4	0.250
Cl	Se	−58.5	0.67	72.9	1.09	69.1	2.11	11.0	2.27	9.3	0.305
Br	Se	−51.1	0.78	72.3	1.18	69.4	2.12	11.0	2.31	0.6	0.458

[a] Intensity 3H. [b] Intensity 6H. [c] Intensity 3H.

cular process (evidence for ligand dissociation is seen only at temperatures well above coalescence). The most likely such process is pyramidal inversion at the chalcogen atoms. It is assumed that rotation about the Pt—E bonds is fast even at the lowest temperatures, since slow rotation would require the presence of

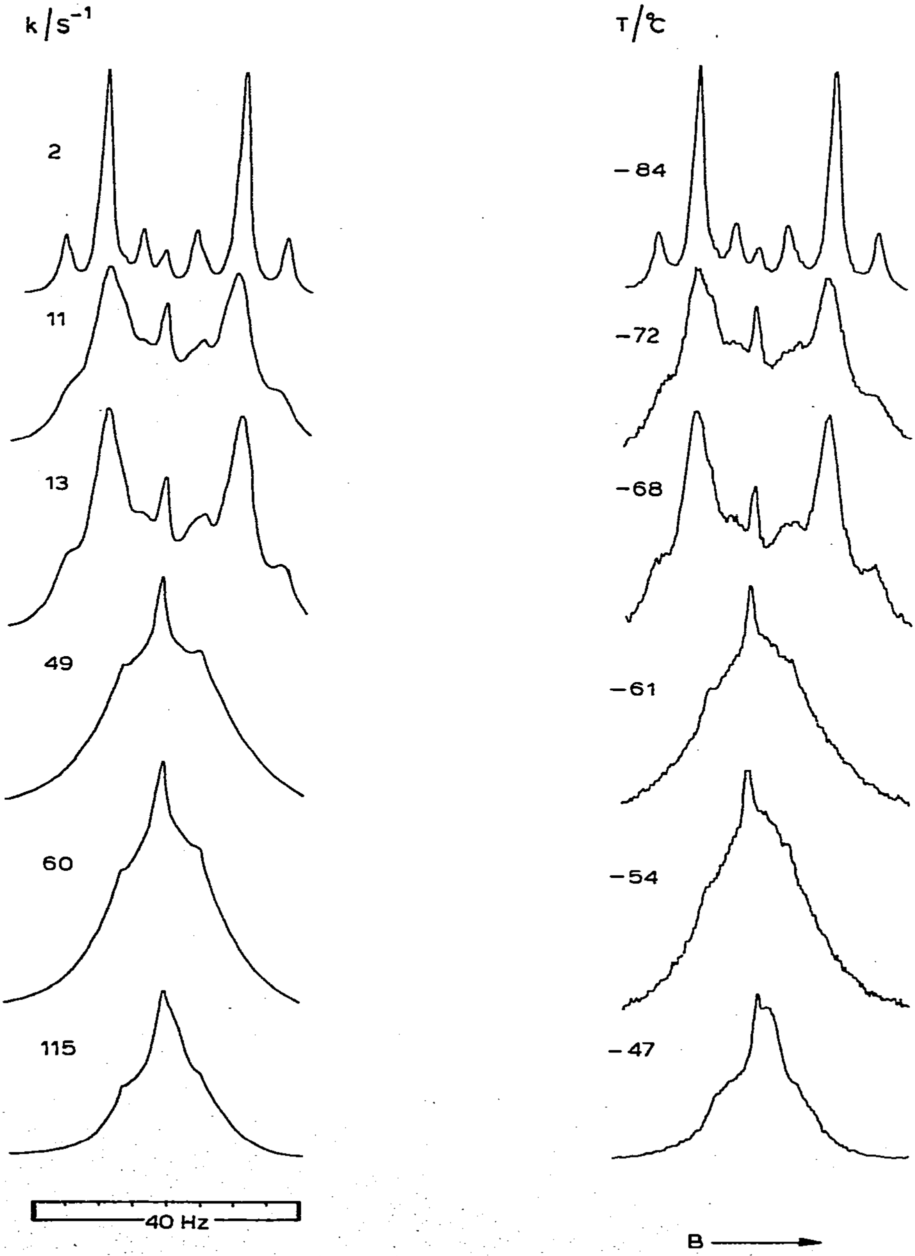

Fig. 3. Experimental and computer simulated spectra of the Me_2S ligand in the complex $[PtBrMe_3(Me_2S)_2]$ in the temperature range −84 to −47°C. The small additional signals are due to the presence of the dinuclear species $[(PtBrMe_3)_2(Me_2S)]_2$.

TABLE 2

ACTIVATION PARAMETERS FOR $[PtMe_3X(Me_2E)_2]$

X	E	E_a (kJ mol^{-1})	$\log_{10} A$	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
Br	S	40.5 ± 2.8	11.5 ± 0.7	38.7 ± 2.8	−30.5 ± 3.4	47.8 ± 6.8
Cl	Se	59.1 ± 2.7	13.2 ± 0.5	56.9 ± 2.7	−0.4 ± 10.1	56.8 ± 5.7
Br	Se	58.6 ± 2.4	13.0 ± 0.5	56.4 ± 2.4	−2.3 ± 8.9	57.0 ± 5.1

three distinct rotamers or conformers and therefore more complicated spectra than those found, except in the unlikely event of one conformer being of predominantly lower energy.

Computer simulation of the spectra of three complexes was done by superimposing two spectra of the systems $A \rightleftharpoons B$ (66.3%) and $AX \rightleftharpoons BX$ (33.7%), where A and B represent the chalcogen methyl groups and X is ^{195}Pt. Line shape fittings are based on the static parameters in Table 1 which are typical values from various low temperature spectra. The simulated and experimental spectra for $[PtClMe_3(Me_2Se)_2]$ and $[PtBrMe_3(Me_2S)_2]$ are shown in Figs. 2 and 3, and the activation parameters are listed in Table 2. The free energies of activation show the very small halide dependence found for the comparable inversion processes in the mononuclear complexes $[PtXMe_3\{MeE(CH_2)_nEMe\}]$, n = 2 and 3, and a slightly larger increase (19%) on replacing S by Se than in the 5-membered (15%) and 6-membered (17%) bidentate analogues (X = Br, n = 2 and 3) [2]. The $\Delta G^{\neq}$ values are markedly lower for the monodentate complexes than for either the 5-membered or 6-membered chelates. Comparison with related platinum(II) compounds, e.g. $[PtCl_2\{SMe(CH_2SiMe_3)\}_2]$ [10] and $[PtCl_2\{Se(CH_2SiMe_3)_2\}_2]$ [11], 61 and 78 kJ mol^{-1} respectively, shows that increase in the oxidation state of platinum also lowers the energy barrier.

The low temperature ^1H NMR spectra of the Me_2S complexes (Fig. 3) show additional signals attributable to small amounts of the dimeric species $[PtXMe_3(Me_2S)]_2$, X = Cl and Br. Comparison with the spectra of $[(PtXMe_3)_2MeSCH_2SMe]$ leaves little doubt that the dimers are halide- rather than sulphur-bridged (Table 3). The additional absorption for both compounds is a partially resolved

TABLE 3

^1H NMR PARAMETERS FOR $[PtXMe_3(Me_2S)]_2$

X	T (°C)	δ (ppm)	J (Hz)	
Cl	−68.3	0.83	76.0	PtMe *trans* to X
		0.84	76.0	
		1.45	69.0	PtMe *trans* to S
		2.31	^{a}	S—Me
		2.33	^{a}	
Br	−88.1	0.92	76.4	PtMe *trans* to X
		1.63	68.9	PtMe *trans* to S
		1.64	68.2	
		2.37	11.8	S—Me
		2.38	11.9	

[a] Not measurable.

doublet, which indicates that as in $[PtIMe_3py]_2$ [12] both *cis* and *trans* isomers are formed, in which the Me_2S ligands are related by a plane and a centre of symmetry respectively. Only three of the expected four platinum methyl signals are observed in each case, the 'missing peak' being most probably overlapped by stronger signals from the monomeric complexes. The line shape fittings for the Me_2S complexes took into account the presence of the dimeric species (Fig. 3), and the energies so obtained are therefore quite reliable. Only a very small amount of the dimeric species was detected in the spectra of the Me_2Se complexes.

Experimental

^1H NMR spectra were recorded at 100 MHz using a JEOL PS/PFT-100 spectrometer equipped with a standard variable temperature accessory. Temperature measurements were made with a calibrated copper-constantan thermocouple, and are considered accurate to $\leqslant 1°C$. Spectra were run in $CDCl_3$ or in CD_2Cl_2/CS_2 mixtures for above and below ambient temperatures respectively.

NMR band shape analyses were performed with the authors' modified version of the DNMR program of Kleier and Binsch [13,14].

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