Nuclear Magnetic Resonance Investigations of Configurational Non-rigidity in Dinuclear Platinum(IV) Complexes. Part 2.[1] Pyramidal Inversion and Novel Fluxional Rearrangements in [$(PtXMe_3)_2(MeEEMe)$] (E = S or Se) Complexes

By **Edward W. Abel, A. Rauf Khan, Kenneth Kite, Keith G. Orrell,* and Vladimir Šik**, Department of Chemistry, The University, Exeter EX4 4QD

New complexes of the type DL-[$(PtXMe_3)_2(MeEEMe)$] (E = S or Se; X = Cl, Br, or I) have been isolated and shown by both *X*-ray and ^1H n.m.r. data to possess dinuclear structures involving halogen-bridge bonds. Barrier energies for (*i*) pyramidal inversion of S or Se atoms, (*ii*) S or Se atom switching between Pt atom pairs, and (*iii*) scrambling of PtMe groups, have been separately evaluated by dynamic n.m.r. methods. The relative probabilities of simultaneous and non-simultaneous mechanisms for the inversion of pairs of chalcogen atoms are assessed.

WE have shown in Part 1 [1] of this series that reactions of [$(PtXMe_3)_4$] with sulphur or selenium ligands of type MeECHREMe lead to the isolation of stable complexes of stoicheiometry [$(PtXMe_3)_2(MeECHREMe)$]. Detailed ^1H n.m.r. studies revealed that in solution these complexes existed as dinuclear complexes of Pt^{IV} with halogen-bridge bonds between the pairs of Pt atoms. Furthermore, variable-temperature n.m.r. studies showed that at temperatures *ca.* −100 °C the complexes existed predominantly as the DL isomer with the E-methyls mutually *trans*. At higher temperatures the complexes undergo a remarkable variety of internal configurational and fluxional rearrangements.

This paper examines the n.m.r. and *X*-ray evidence for the structures of the complexes formed from [$(PtXMe_3)_4$] and dimethyl disulphide or dimethyl diselenide. The complexes possess the general stoicheiometry [$(PtXMe_3)_2(MeEEMe)$] (X = Cl, Br, or I; E = S or Se) and therefore appear analogous to the complexes of 2,4-dithia- and 2,4-diselena-pentanes discussed in Part 1.[1] However, if these new five-membered ring complexes do possess dinuclear structures with bridging halogens analogous to the six-membered ring complexes, considerable internal strain is to be expected since it is not possible in these new complexes for the four atoms of the Pt_2X_2 ring to remain co-planar while the Pt atoms retain an octahedral environment. However, dimethyl disulphide,[2] diphenyl diselenide,[2] and diphenyldiphosphine [3] have recently been shown to bridge metal atoms in [$\{ReBr(CO)_3\}_2(L\text{–}L)$].

We will provide evidence to show that the present platinum(IV) complexes are directly comparable to these rhenium(I) complexes. The paper will describe the solid-state and solution structures of these five-membered ring platinum(IV) complexes and then proceed to examine their dynamic stereochemistry using the d.n.m.r. methods previously described [1,4] for the other platinum(IV) complexes.

EXPERIMENTAL

The dinuclear complexes were prepared by the general method reported earlier.[5]

Crystal Data.†—$C_8H_{24}Br_2Pt_2Se_2$, Orthorhombic, a = 9.358(1), b = 12.425(2), c = 14.977(3) Å, space group $P2_12_12_1$, Z = 4, D_c = 3.158 g cm^{-3}, Mo-K_α radiation (λ = 0.710 69 Å), four-circle diffractometry, 1 581 independent observable reflections, of which 713 had $I > 3\sigma(I)$. The structure was solved by tangent and Fourier methods and refined by least squares. The conventional R is 0.04 with isotropic temperature factors on the carbon and hydrogen and anisotropic temperature factors on the heavier atoms. The structure was also refined in the opposite enantiomer to that given in Figure 1.

N.M.R.—The complexes were dissolved in CS_2–CD_2Cl_2 solvent mixtures for low-temperature studies and in $CDCl_3$ for above-ambient temperature studies. 100-MHz ^1H spectra were obtained using a JEOL PS/PFT-100 spectrometer equipped with a standard variable-temperature accessory. Temperature measurements were made with a precisely calibrated copper–constantan thermocouple and are considered accurate to ⩽1 °C. Band-shape analyses were performed with a modified version of the DNMR program of Kleier and Binsch.[6,7]

RESULTS

Nuclear magnetic resonance studies of the complexes at low temperatures (<*ca.* −80 °C for the S ligand complexes and <*ca.* −45 °C for the Se ligand complexes) yielded very similar spectra. The spectra were also quite similar, in respect of both the chemical shifts of the chalcogen and platinum methyl signals, and the spin–spin couplings ^2J(Pt–H) and ^3J(Pt–H), to the spectra of [$(PtXMe_3)_2(MeECH_2EMe)$] [1,5] for temperatures where the ring reversal in these complexes is rapid. This close resemblance in spectral patterns strongly suggests that the disulphide and diselenide complexes do possess dinuclear structures in solution analogous to those of the six-membered ring complexes. If we assume for the moment that this is the case, then the four observed bands in their low-temperature spectra may be assigned as follows. The band at lowest applied field is attributed to the EMe methyls, the single band at an intermediate field position is assigned to the platinum methyls *trans* to E (*i.e.* axial), and the two bands at highest field are then due to the platinum methyls *trans* to halogen (*i.e.* equatorial), with the more highly shielded equatorial Pt–Me groups being those directly above the E–Me bonds. The presence of a single band for the EMe methyls indicates that only a single geometrical isomer is

---

† The atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should include citation of the preliminary communication (ref. 10).

present, namely DL or *meso*. In accordance with our findings for $[(PtXMe_3)_2(MeECHREMe)]$,[1] the DL isomer with the EMe methyls mutually *trans* is expected to predominate. Similar *trans* dispositions of methyl,[2] phenyl,[8] and pentafluorophenyl [9] groups have been found in dinuclear complexes of types $[\{ReBr(CO)_3\}_2(RSSR)]$ (R = Me or Ph) and $[\{Co(CO)_3\}_2(C_6F_5SSC_6F_5)]$.

In order to establish unambiguously the dinuclear structure of the present complexes and the disposition of the E-methyls with respect to the E–E bond, a single-crystal *X*-ray crystallographic study was carried out on $[(PtBrMe_3)_2(MeSeSeMe)]$, results of which have already been briefly reported.[10]

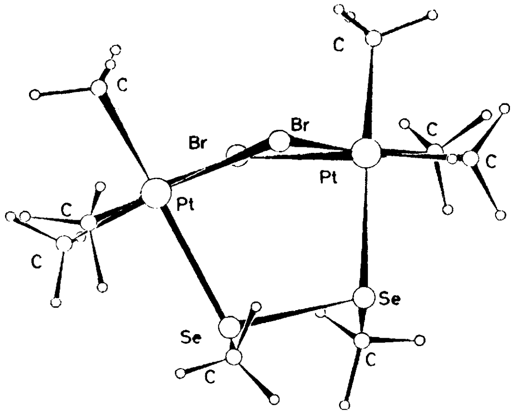


FIGURE 1 *X*-Ray crystal structure of $[(PtBrMe_3)_2(MeSeSeMe)]$

The *X*-ray data of $[(PtBrMe_3)_2(MeSeSeMe)]$ produced the structure shown in Figure 1. It can be seen that the two platinum atoms are held together by three bridging groups, two of these being conventional halogen bridges and the third a very unusual biselenium bridge. The Pt $\cdots$ Pt distance is 3.740(3) Å which compares [11] with 3.23 Å for the weak Pt $\cdots$ Pt interaction in Pt(dimethylglyoximate)$_2$. The Pt–Br bond lengths are all equivalent within 1 estimated standard deviation (± 0.007 Å), and have a mean value of 2.629 Å. The Pt–Br–Pt angles are both 90.7(2)°. These bond lengths are somewhat longer than those reported [12] for $Pt_2Br_6^{2-}$ (2.43 Å) where the Pt–Br–Pt angles are 94°, and the Pt $\cdots$ Pt contact is 3.55 Å. An Se–Se bond length of 2.36(1) Å is within, but near the higher limit of, the range of acceptable values.[13] The Pt–Se–Pt angles [mean 105.3(2)°], as well as the C–Se–X angles [mean 99(2)°], are equivalent. The configuration about each platinum atom is approximately octahedral, with the interbond angles in the ranges of 173—178° and 82—96°. Since the Se–Se bond length is 1.19 Å shorter than the Pt $\cdots$ Pt contact distance, it is not possible for the four atoms of the Pt_2Br_2 ring to be co-planar while the platinum atoms retain even an approximately octahedral environment. The Pt_2Br_2 unit therefore forms a bent system, with an angle of 29° between the normals to the planes of the two Br–Pt–Br fragments as shown in Figure 1.

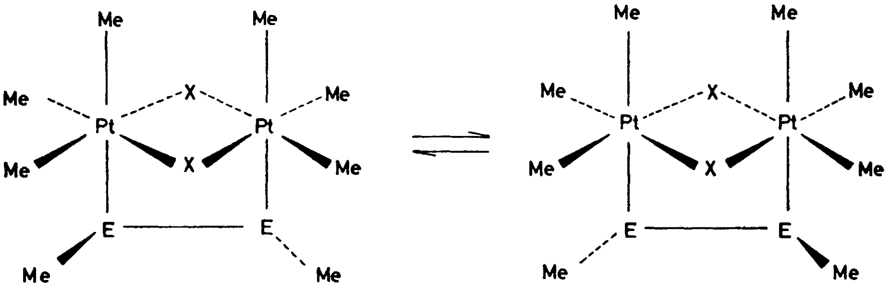


FIGURE 2 Structure of the complexes $[(PtXMe_3)_2(MeEEMe)]$ showing the effects of double E inversion on the environments of the equatorial platinum methyls

Dynamic N.M.R. Studies.—The low-temperature spectra of all the complexes in solution are perfectly compatible with the solid-state structure as found by the *X*-ray analysis. However, on warming the complexes (above *ca.* −80 °C for the S complexes and above *ca.* −45 °C for the Se complexes), they become configurationally non-rigid from the viewpoint of the n.m.r. technique since the equatorial PtMe absorption becomes very temperature dependent. The two bands steadily broaden with increasing temperature, merge into one broad band at the coalescence temperature, and finally sharpen to a single band with ^{195}Pt satellite signals. Such a sequence of changes is undoubtedly the result of inversion of the pair of E atoms which when sufficiently rapid causes chemical-shift equivalence of the equatorial methyl groups (A,B) (Figure 2). The line-shape changes for $[(PtClMe_3)_2(MeSeSeMe)]$ are illustrated in Figure 3.

Theoretical spectra were computed on the basis of a single two-site, equal population exchange (see below).

$$\underset{66\cdot3\%}{A \rightleftharpoons B} \text{ plus } \underset{33\cdot7\%}{AX \rightleftharpoons BX} \qquad X = {}^{195}Pt$$

This simple treatment is perfectly valid since no methyl–methyl spin interactions were detected. The method does *not* allow for any detectable amount of the *meso* isomer (in accordance with experimental findings) and is therefore applicable to either a simultaneous inversion of both E atoms or to a non-simultaneous inversion of individual E atoms leading to an undetectably low concentration of the *meso* isomer. We will discuss later which of these cases appears more likely.

The static parameters, namely chemical shifts, spin coupling constants, ^2J(Pt–H), and the effective transverse relaxation time T_2* used in the band-shape fittings are given in Table 1. The temperature dependences of the chemical shifts were measured over *ca.* 20—30 °C in the slow inversion temperature range. This enabled accurate extrapolations to be made into the temperature range of the band-shape fittings. This range was limited to only *ca.* 25 °C and so great care had to be exercised in deciding on the 'best fit' rate constants for each temperature. Energy parameters based on the Arrhenius and Eyring equations were computed and collected in Table 2.

Throughout the temperature ranges over which the sulphur or selenium inversions are affecting the appearance of the equatorial PtMe region of the spectra, the EMe signal remains a singlet plus satellite lines. In the case of the S ligand complexes the satellite spectrum consists of two lines due to ^{195}Pt–SMe coupling whereas in the Se ligand complexes it consists of four lines arising from both ^{77}Se–Me and ^{195}Pt–Se–Me couplings. On increasing the temperature of the complexes from *ca.* −10 to 20 °C in the case of the S ligand complexes and from *ca.* 0 to 40 °C in the case of the Se ligand complexes, the satellite spectra change in a manner analogous to that observed in [(PtXMe$_3$)$_2$(MeECH-REMe)] such that at the highest temperature referred to above, the total SMe signal of [(PtClMe$_3$)$_2$(MeSSMe)] becomes a quintet (1 : 7.8 : 17.5 : 7.8 : 1) and the SeMe signals of [(PtXMe$_3$)$_2$(MeSeSeMe)] (X = Cl or Br) become doublets of quintets (1 : 7.8 : 17.5 : 7.8 : 1). In both cases the magnitude of the coupling producing the quintet pattern is approximately half that responsible for the original doublet splitting. Such changes can only be reconciled by postulating some type of rapid commutation of the S or Se atoms between the two Pt atoms producing a ligand switching akin to that suggested for the analogous six-membered ring complexes.[1] Alternatively, the process can be visualised as an *inter*-atomic inversion of the E atom lone pairs rather than the conventional *intra*-atomic inversion.

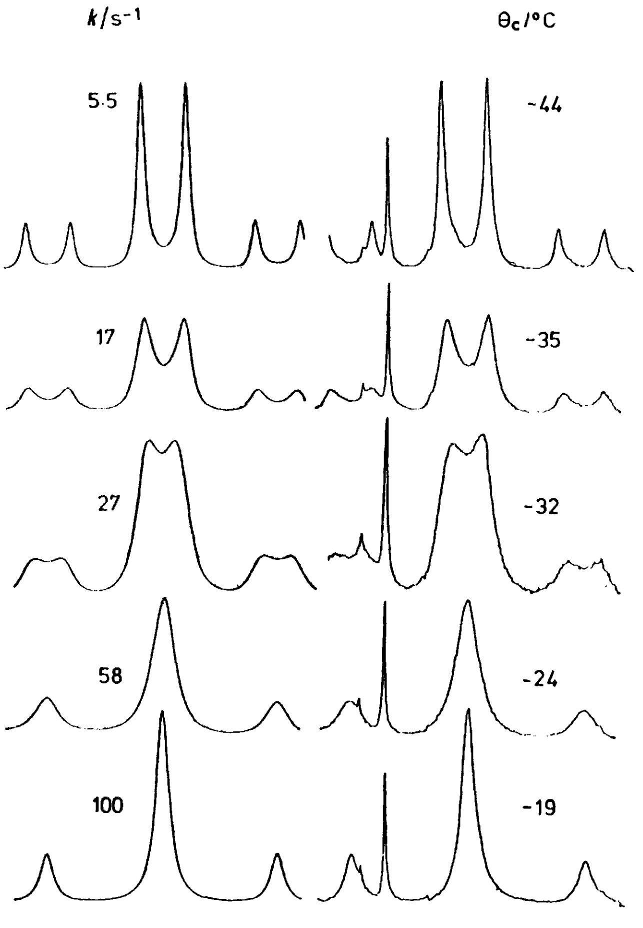


FIGURE 3 Low-temperature experimental spectra of the equatorial PtMe region of [(PtClMe$_3$)$_2$(MeSeSeMe)] and the ' best fit ' computer-simulated spectra. The additional band in the experimental spectra is a ^{195}Pt satellite line of the axial PtMe absorption

In order to estimate the energy of this novel process the experimental line shapes of the EMe region were carefully matched with computer-simulated spectra as described in Part 1. For the S ligand complex (1) (Table 1) this meant superimposing the line shapes of the three sub-spectra arising from the various combinations of spin-active and spin-inactive nuclei for the pairs of Pt atoms. In this computation the coupling ^3J(Pt–H) was 9.2 Hz and all other Pt–H, Pt–Pt, and H–H couplings were taken as zero. In the case of the Se ligand complexes (3) and (4) (Table 1), a fourth sub-spectrum had to be included to account for the ^{77}Se–Me coupling. In these computations the coupling ^3J(SeH) was 10.6 and 10.5 Hz for complexes (3) and (4) respectively and ^3J(Pt–H) was 7.6 Hz in both cases. All other couplings were taken as zero. This sub-spectrum represented the species having both Pt atoms spin inactive (I = 0) and *one* of the Se atoms spin active (^{77}Se, $I = \frac{1}{2}$). No attempt was made to simulate the sub-spectra of species with spin active selenium and one or two spin active platinums since such species would be in extremely low abundance. The experimental and computer-simulated spectra for [(PtClMe$_3$)$_2$(MeSeSeMe)] are given in Figure 4 and the resulting energy parameters in Table 3.

TABLE 1

Static parameters for the sulphur and selenium inversion energy calculations in [(PtXMe$_3$)$_2$(MeEEMe)]

	E	X	Equatorial Pt–Me						
			ν_A[a]/Hz	J_{AX}/Hz	p_A[b]	ν_B[a]/Hz	J_{BX}/Hz	p_B[b]	T_2*/s
(1)	S	Cl	105.7	77.2	0.5	91.6	77.1	0.5	0.183
(2)	S	Br	116.3	76.3	0.5	102.8	76.1	0.5	0.212
(3)	Se	Cl	112.5	77.5	0.5	96.6	77.5	0.5	0.229
(4)	Se	Br	121.6	76.4	0.5	106.4	76.6	0.5	0.199

[a] Shifts measured at low temperatures relative to SiMe$_4$. [b] Populations.

The ligand switching process postulated above totally fails to account for the spectral changes of the PtMe region. At low temperatures (<*ca.* −10 °C for S ligands and <*ca.* 0 °C for Se ligands) the axial and equatorial PtMe groups are revealed as two sharp signals with intensity ratio 1 : 2. On warming the complexes to *ca.* 30 °C above the coalescence temperatures for the S or Se inversion processes, the two bands broaden and eventually coalesce to a single band at a weighted mean chemical-shift position. On further heating, this band sharpens and ^{195}Pt satellite signals are observed. The case of [(PtClMe$_3$)$_2$(MeSeSeMe)] is illustrated in Figure 5. The change is very analogous to that observed in the six-membered ring complexes and we propose that the same mechanism is operating in these five-membered ring complexes, namely a random cleavage of individual halogen-bridge bonds to produce a short-lived five-co-ordinate species which then rapidly undergoes a type of trigonal twist or pseudorotation, [14] which in turn causes interconversion of the axial and equatorial PtMe environments. Line-shape fittings of the PtMe region as a function of temperature were performed in the usual way (Table 4) and the ' best fit ' spectra are shown in Figure 5.

TABLE 2

Chalcogen inversion energy parameters for $[(PtXMe_3)_2(MeEEMe)]$

E	X	E_a/kJ mol^{-1}	$\log_{10} A$	$\Delta G^\ddagger$/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
S	Cl	44.4 ± 2.5	13.3 ± 0.7	41.4 ± 6.2	42.8 ± 2.5	4.8 ± 12.7
S	Br	45.6 ± 3.4	13.6 ± 0.9	40.7 ± 8.5	43.9 ± 3.4	10.8 ± 17.4
Se	Cl	53.4 ± 1.4	13.0 ± 0.3	52.4 ± 3.2	51.4 ± 1.4	-3.3 ± 5.9
Se	Br	56.8 ± 1.7	13.4 ± 0.4	53.2 ± 3.7	54.8 ± 1.7	5.5 ± 6.7

Further heating of the complexes above the temperatures at which the two fluxional processes became rapid led to dissociation of the chalcogen ligands causing a loss of the ^{195}Pt satellite lines of the EMe signal. An approximate four-fold dilution of the n.m.r. solution caused the satellite spectrum to revert to its original quintet-like appearance, showing that the extent of dissociation–recombination had been substantially reduced. The PtMe region of the spectrum was quite unaffected by this procedure, which confirms the intramolecular nature of the methyl scrambling process. This was further proved in the case of $[(PtClMe_3)_2(MeSSMe)]$ {by adding $[(PtClMe_3)_4]$ to the n.m.r. sample at 30 °C} where its spectrum shows signs of ligand dissociation. No exchange between the bound and free trimethylplatinum(IV) chloride was seen in the spectrum.

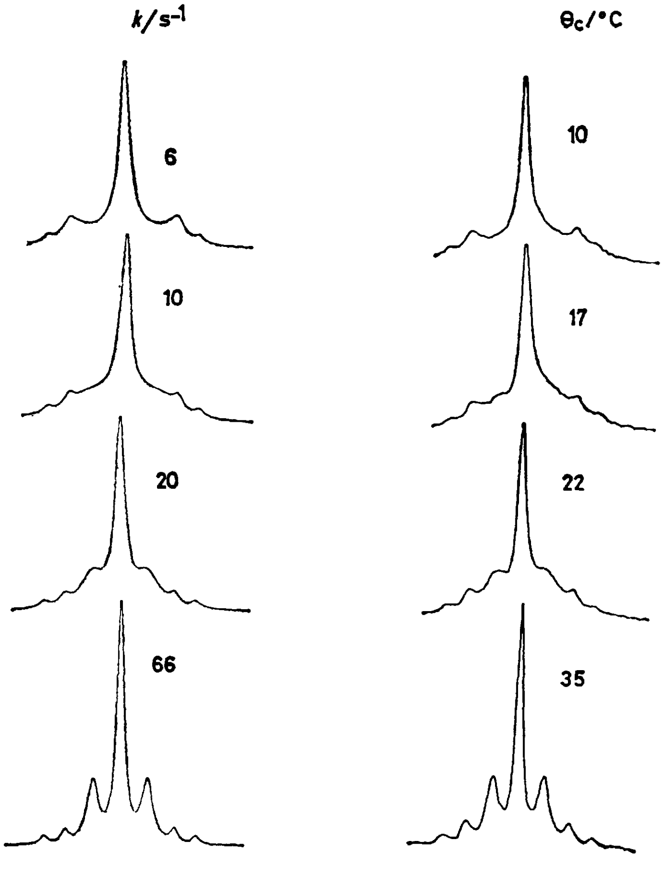


FIGURE 4 Experimental and computer-simulated spectra of the SeMe region of $[(PtClMe_3)_2(MeSeSeMe)]$ showing the effects of ligand switching

DISCUSSION

Energy Parameters.—First we will consider the energies of the two fluxional processes. Table 3 shows that both these processes have very similar energies, with the methyl scrambling process slightly the higher of the two if the $\Delta G^\ddagger$ values which are least prone to systematic

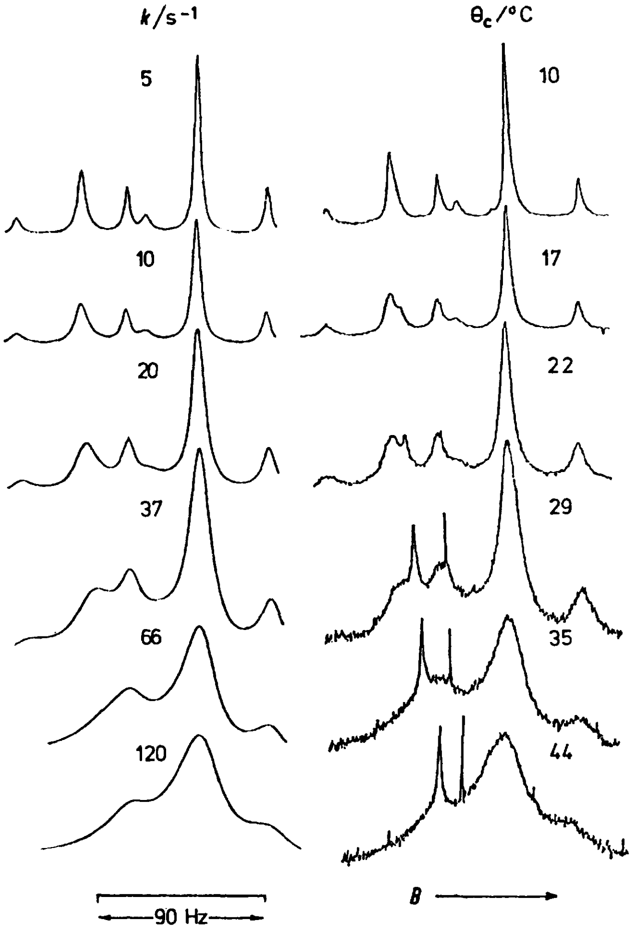


FIGURE 5 Experimental and computer-simulated spectra of the PtMe region of $[(PtClMe_3)(MeSeSeMe)]$ showing the effects of platinum methyl scrambling. The two additional bands in some of the experimental spectra are thought to arise from traces of water (broader band) and unreacted $[(PtClMe_3)_4]$ (sharper band)

error are considered. This is not unexpected if, as discussed in Part 1,[1] the two processes are to some extent correlated, with the ligand switching motion initiating the formation of the five-co-ordinate platinum(IV) species which then rapidly undergoes a pseudorotational rearrangement. Comparison of the energies with the corresponding six-membered ring complexes (Part 1, Table 5) reveals a decrease of 6—10 kJ mol^{-1} with decreasing ring size. This can be understood in terms of the appreciable ground-state strain which is clearly present in the five-membered ring complexes as revealed by *X*-ray data. This strain is likely to be more easily accommodated in the transition-state structure(s) for the switching process and thus the energy of this transition state relative to the ground-state energy will be lower than in the case of the six-membered ring complexes.

TABLE 3

Activation parameters for ligand switching and methyl scrambling in [$(PtXMe_3)_2(MeEEMe)$]

E	X	Process	E_a/kJ mol^{-1}	$\log_{10} A$	$\Delta G^\ddagger$/kJ mol^{-1}	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
S	Cl	Ligand switching	61.3 ± 3.9	12.8 ± 0.7	61.3 ± 8.2	59.0 ± 3.9	-7.8 ± 14.2
		Methyl scrambling	68.2 ± 2.0	13.8 ± 0.4	62.4 ± 4.0	65.8 ± 2.0	11.6 ± 7.2
Se	Cl	Ligand switching	70.9 ± 3.8	13.8 ± 3.8	65.1 ± 7.6	68.5 ± 3.8	11.6 ± 12.8
		Methyl scrambling	70.8 ± 2.4	13.8 ± 0.4	65.2 ± 4.8	68.3 ± 2.4	10.6 ± 8.0
Se	Br	Ligand switching	71.5 ± 3.0	14.0 ± 0.5	64.5 ± 6.2	69.1 ± 3.1	15.5 ± 10.5
		Methyl scrambling	67.0 ± 2.3	13.2 ± 0.4	64.6 ± 4.8	64.6 ± 2.4	0.1 ± 8.0

Table 3 shows the expected increase in energy on passing from sulphur to selenium complexes. The higher energy barrier may be accounted for both in terms of the heavier donor ligands involved and to the likelihood that there will be less strain in the ground-state structures of [$(PtXMe_3)_2(MeSeSeMe)$] compared to the corresponding S ligand complexes due to the longer E–E bond in the selenium complexes. This means that there will be less relative stabilisation of the transition-state structure compared to the ground state and thus a rather higher barrier energy.

TABLE 4

Static parameters for the Pt–Me scrambling process in [$(PtXMe_3)_2(MeEEMe)$]

		Equatorial Pt–Me			Axial Pt–Me			
E	X	$\nu_{A'}$*/Hz	$J_{A'X}$/Hz	p_A	ν_C*/Hz	J_{CX}/Hz	p_C	T_2*/s
S	Cl	104.1	77.1	0.667	162.8	72.0	0.333	0.275
Se	Cl	103.3	77.5	0.667	167.6	71.3	0.333	0.138
Se	Br	113.2	76.4	0.667	182.3	71.9	0.333	0.127

* Shifts measured relative to $SiMe_4$ in $CDCl_3$ solution. $\nu_{A'}$ represents the averaged shift of ν_A and ν_B (Table 1).

A comparison of the energy data for [$(PtXMe_3)_2$-$(MeSeSeMe)$] (X = Cl or Br) reveals no obvious halogen dependence for the ligand switching process. This is not surprising in view of the *cis* relationship of the halogens to the chalcogen atoms in these complexes. However, halogen dependence of the methyl scrambling process is expected since breaking and reforming of the halogen-bridge bonds occurs in the postulated mechanism. Table 3 shows that on going from X = Cl to X = Br there is a small but consistent decrease in the Arrhenius and Eyring parameters E_a, $\Delta G^\ddagger$, and $\Delta H^\ddagger$. While this change is within the experimental accuracies of these parameters, it may indeed represent a real effect. The trend is in the expected direction since increasing the size of the halogen will lead to weaker Pt–X bonds, which in turn will favour the formation of the five-co-ordinate intermediates. A similar halogen dependence of methyl scrambling has been observed in [$PtXMe_3(PMe_2Ph)_2$].[15]

Turning now to the pyramidal inversion energies of the S and Se atoms, a comparison of the values in Table 2 with those found for the corresponding dinuclear complexes [$(PtXMe_3)_2(MeECHREMe)$] (Table 2, Part 1) indicates that the $\Delta G^\ddagger$ values are 2—3 kJ mol^{-1} lower for the five-membered ring complexes. This small difference could again be the result of a higher ground-state energy of the strained five-membered ring complexes compared to the relatively unstrained six-membered ring complexes. It is, however, of greater importance to consider the very different magnitudes of inversion energies in the present dinuclear platinum(IV) complexes [1] compared to those of the corresponding mononuclear chelate complexes.[4] The barriers ($\Delta G^\ddagger$ values) in the dinuclear complexes are in the ranges 40—48 kJ mol^{-1} (S ligands) and 52—58 kJ mol^{-1} (Se ligands), whereas for the chelate complexes the ranges are 56—63 kJ mol^{-1} (S ligands) and 66—73 kJ mol^{-1} (Se ligands).

In Part 1 we suggested, albeit rather briefly, that these large differences may be explained in terms of the relative weakness of the Pt–E bonds in the dinuclear complexes. We will now present more detailed evidence to support this suggestion. This will be followed by an inquiry into the likely mechanisms of pyramidal inversion in these dinuclear complexes since it is possible that their lower inversion energies are due to an energetically favoured mechanistic pathway associated with the synchronous inversion of both E atoms, a process which we have already shown [4] is *not* dominant in the mononuclear chelate complexes.

Lambert *et al.*[16] found that in comparing 1,2-dimethyl-1,2-diphenyldiphosphine (T_c = 153 °C, $\Delta G^\ddagger$ = 98.7 kJ mol^{-1}) to monophosphines[17] ($\Delta G^{\ddagger} > 126$ kJ mol^{-1}) the large decrease in the phosphorus inversion barrier was due to p_{π}–d_{π} bonding between the P atoms. They confirmed this by studying the molecule PhMeP–PMe(S)Ph in which one P lone pair is replaced by sulphur. This led to a substantial increase in the energy barrier as its n.m.r. spectrum was temperature invariant up to 200 °C. The authors argued that since the S atom donates p electrons to the d orbital of the pentavalent P atom, any p_{π}–d_{π} bonding between the two P atoms would be correspondingly reduced. CNDO/2 semi-empirical molecular orbital calculations[18] on dimethyl sulphoxide and methyl silyl sulphoxide predict values of 166 and 78.6 kJ mol^{-1} respectively for the S inversion energies. This again points to a substantial lowering of the barrier due to p_{π}–d_{π} orbital overlap. We have already proposed[19-21] that there is considerable p_{π}–d_{π} overlap operating between the E atoms and Group 8 transition-metal atoms in order to account for the considerable lowering of the inversion energies in such transition-metal complexes compared to dimethyl sulphoxide and sulphonium ions.*

In the present dinuclear complexes it may not be unreasonable to consider that the magnitude of back donation experienced by either chalcogen atom is approximately twice that experienced by these atoms in the chelate complexes, since, in the former case each Pt atom back donates to one E atom as compared to the Pt atom sharing its back donation between two E atoms in the latter case. On this simplistic basis, the inversion barriers of the dinuclear compared to the mononuclear complexes can be rationalised.

The other major factor affecting the inversion energies of the chelate and dinuclear structures is likely to be the relative ground-state energies of these structures. These will be largely determined by the ground-state geometries of the complexes, particularly by the Pt–E bond lengths and the bond angles at the Pt and E centres. For example, a comparison of the Se inversion barriers in [$PdCl_2(SeEt_2)_2$][22] and [$PdCl_2(Pr^iSeC_2H_4SePr^i)$][23] shows that for the latter complex, which possesses the shorter Pd–Se bond length,[24,25] the energy is higher by *ca.* 11 kJ mol^{-1}. In the present dinuclear platinum(IV) complexes the Pt–E bonds are substantially longer than the sum of the covalent radii of the Pt and E atoms. *X*-Ray analysis of [$(PtBrMe_3)_2(MeSeSeMe)$] gives Pt–Se bond lengths of 255 pm, which are 11 pm greater than the sums of the covalent radii. Such increases in Pt–E bond lengths are also deducible from the magnitudes of the ^{195}Pt–axial methyl couplings,^2J(Pt–H), which are *ca.* 1.5 Hz higher in the dinuclear complexes compared to the chelate complexes. An increase in ^2J(Pt–H) indicates[26,27] a weakening of the Pt–E bond and/or a strengthening of the Pt–C bond *trans* to E. A parallel trend has been noted[28] in the case of the complexes [$PtIMe_3\{Ph_2P(CH_2)_nPPh_2\}$] ($n = 1$ or 2) where ^2J-[Pt–H(*trans* P)] decreases by 3 Hz on increasing the ring size. This has been attributed in part to an increase in *s* character, and a decrease in the length, of the Pt–P bond.

Thus, there is considerable evidence to suggest that the Pt–E bonds in these dinuclear complexes are appreciably weaker than in the chelated complexes. This will account, at least in part, for the relatively low inversion energies of pyramidal chalcogen atoms in these species regardless of the actual mechanism of this process.

Double Pyramidal Inversion Mechanisms.—There are basically three possible mechanisms for pyramidal inversion of pairs of identical atoms, namely (*i*) uncorrelated inversion of individual atoms, (*ii*) correlated non-simultaneous (*i.e.* consecutive) inversion of both atoms, and (*iii*) correlated simultaneous inversion of both atoms.†

In the case of the mononuclear complexes we have shown[4] that the line-shape changes of the EMe region can be fully explained on the basis of single E atom inversions. A dominant simultaneous double inversion process [mechanism (*iii*) above] will *not* account for the observed changes. However, the question of whether the inversions of the pair of E atoms are uncorrelated (*i.e.* independent) or correlated has not been discussed. If the inversions were totally uncorrelated then the DL and *meso* isomers should be present in statistical amounts since the pyramidal relationship of one E atom (in particular, the orientation of its lone-pair orbital and the attached Me group) would have no influence on that of the other E atom or on the rest of the molecule. This is obviously not the case in these mononuclear complexes where different magnitudes of EMe ··· EMe and EMe ··· PtMe non-bonded interactions result in very different populations of the DL and *meso* isomers. We therefore conclude that in these chelate complexes the inversion of the chalcogen atom pairs is a correlated, non-simultaneous process.

In the case of the dinuclear complexes we have shown that the line-shape changes are compatible both with a simultaneous double inversion mechanism and with a single-site non-simultaneous mechanism with the proviso that, in the latter case, the *meso* invertomer(s), which must inevitably be formed is(are) not present in an amount detectable by n.m.r. In the case of the non-simultaneous inversions we have again to consider whether they are correlated or not. However, since the *meso* invertomer(s) is(are) plainly energetically unfavoured this implies appreciable methyl–methyl non-bonded interactions which would cause the inversion of one E atom to influence the inversion of the other. We therefore conclude that in the dinuclear complexes, either the correlated non-simultaneous mechanism

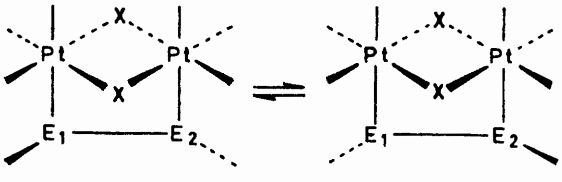
---

* More conclusive evidence of this would be obtained by studying inversion in the same ligands both when bound to transition metals and when unbound. Unfortunately, all suitable chalcogen donor ligands in the unbound state do not possess pairs of diastereotopic nuclei for monitoring the inversion process by n.m.r.

† In a previous study[29] of this type of problem the correlated inversion mechanisms (*ii*) and (*iii*) (above) have both been described as *synchronous* mechanisms. We feel this description is somewhat confusing and inaccurate since we would regard only the simultaneous inversion of both atoms as a truly synchronous process.

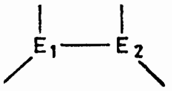
[mechanism (*ii*)] or the correlated simultaneous mechanism [mechanism (*iii*)] appear the most likely. Spectral observations alone cannot distinguish between them and one must resort to structural energy considerations.

Let us consider firstly the case of the complexes $[(PtXMe_3)_2(MeEEMe)]$. Nuclear magnetic resonance studies provide evidence of only the DL forms (1) and (1′) being present.



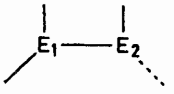
(1) (1′)

Simultaneous inversion of both E_1 and E_2 leads to the intermediate structure (2) in which both E atoms have planar configurations with sp^2 hybridisation and the E-methyls eclipsed. Consecutive inversion of E_1 and E_2 will lead to the transition-state structures (3) and (3′) and the *meso* invertomer (4).

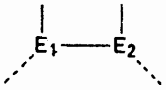


(2)

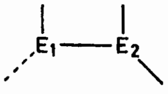
The two mechanisms may be summarised by Scheme 1. The potential energy profile of the simultaneous inversion process will possess a single maximum corresponding to structure (2) whereas the profile for the non-simultaneous or consecutive inversion will be more difficult to define precisely but will certainly contain at least two maxima corresponding to structures (3) and (3′).



(3)

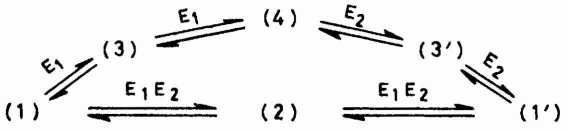


(4)



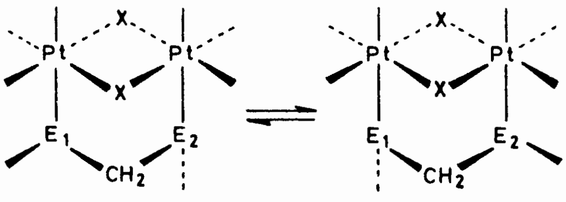
(3′)

The mechanism actually operating will depend on which of the transition-state structures (2) and (3)/(3′) has the lower energy. Anderson and Lehn [29] have considered this type of problem for double nitrogen inversion in some bicyclic systems. They assumed the potential energy profile depended essentially on two terms, a term E_{nb} arising from non-bonded interactions (particularly methyl–methyl interactions) and a term E_i due to the inversion process.



Scheme 1

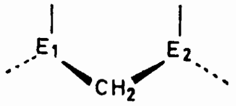
Extending this argument to our platinum(IV) complexes, the E_{nb} term will now include both PtMe · · · EMe and EMe · · · EMe methyl interactions, the E_i term will relate to S or Se inversion, and in addition a third term $E(p_\pi–d_\pi)$ needs to be included to represent the back donation between Pt and E atoms. This term will provide a negative contribution (*i.e.* stabilisation) to the total energy. Anderson and Lehn argued that in their nitrogen systems the E_i term exhibited a greater variation than the E_{nb} term during the inversion process and was the dominant term in determining the energy of the transition-state structures involving planar nitrogens. On this basis they considered the structure with *two* planar nitrogens (arising from the simultaneous process) to be *ca.* 40 kJ mol^{-1} less stable than the structures possessing single planar nitrogens which arise from the consecutive process. For this reason they favoured the latter mechanism. In our complexes it is impossible to estimate accurately the relative contributions (and variations in these contributions during the inversion process) of E_i, E_{nb}, and $E(p_\pi–d_\pi)$. The last term, in particular, could be very sizeable as we have suggested earlier. It is important to know how the $E(p_\pi–d_\pi)$ term varies when an E atom changes from a pyramidal to a planar configuration, and in particular the relative magnitudes of E_i and $E(p_\pi–d_\pi)$ in the structures (2) and (3)/(3′). If $|E_i| \gg |E(p_\pi–d_\pi)|$ then the argument of Anderson and Lehn should hold and the consecutive mechanism is favoured. However, if $|E_i| \not\gg |E(p_\pi–d_\pi)|$ in the transition state(s) the preferred mechanism remains uncertain. Considering only the E_{nb} term it would appear that both the EMe · · · EMe and PtMe · · · EMe methyl interactions would be rather less in the transition-state species (2) compared to (3)/(3′), thus favouring the simultaneous mechanism.



(1) (1′)

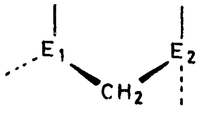
However, this E_{nb} term is unlikely to represent the dominant contribution to the total shape of the inversion energy profile. Therefore, in the absence of quantitative data for these three energy terms we cannot reach a definite conclusion about the inversion mechanism in the $[(PtXMe_3)_2(MeEEMe)]$ complexes.

The situation is even more complicated in the case of the six-membered ring complexes $[(PtXMe_3)_2(MeECH_2EMe)]$ where the double chalcogen inversion can proceed by three different routes, the simultaneous route and *two* different consecutive inversion routes (see below).

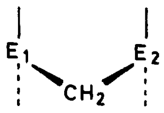


(2)

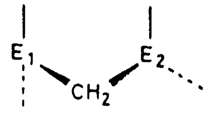
As in the five-membered ring series, no *meso* isomers were detected and so the basic interconversion is (1) $\rightleftharpoons$ (1′). Simultaneous inversion proceeds *via* the intermediate (2) with two planar E atoms. On the other hand consecutive inversion of E_1 and E_2 proceeds either *via* the transition-state structures (3) and (3′) and the *meso* invertomer (4) or *via* the transition-state structures (5) and (5′) and the other *meso* invertomer (6) depending on which (non-equivalent) E atom inverts first. This can be summarised by Scheme 2. Of the two consecutive inversion routes the one going through the *meso* invertometer (6) would seem to be more favoured if the EMe · · · EMe non-bonded interactions are the prime consideration. However, it is again uncertain whether this route or the simultaneous route is the more energetically favoured. A quantitative estimate of the extent of p_π–d_π stabilisation and how this stabilisation energy varies during the inversion process will be required before a clear preference for one inversion mechanism can be given.



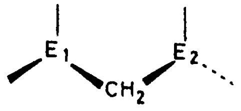
(3)



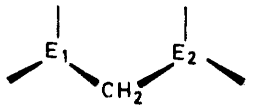
(4)



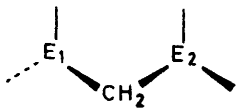
(3′)



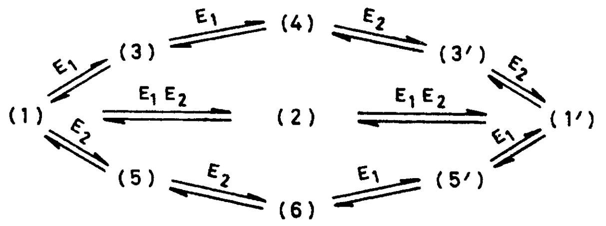
(5)



(6)



(5′)



SCHEME 2

[9/1919 *Received, 3rd December,* 1979]

REFERENCES

[1] Part 1, E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, preceding paper.

[2] I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Israel J. Chem.*, 1976—1977, **15**, 153; J. Korp, I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *J.C.S. Dalton*, 1979, 1492.

[3] J. L. Atwood, J. K. Newell, W. E. Hunter, I. Bernal, F. Calderazzo, I. P. Mavini, and D. Vitali, *J.C.S. Dalton*, 1978, 1189.

[4] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1980, 1175.

[5] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1980, 1169.

[6] D. A. Kleier and G. Binsch, *J. Magn. Reson.*, 1970, **3**, 146.

[7] D. A. Kleier and G. Binsch, DNMR3 Program 165, Quantum Chemistry Program Exchange, Indiana University, 1970.

[8] I. Bernal, J. L. Atwood, F. Calderazzo, and D. Vitali, *Gazzetta*, 1976, **106**, 971.

[9] G. Bor and G. Natile, *J. Organometallic Chem.*, 1971, **26**, C33.

[10] E. W. Abel, A. R. Khan, K. Kite, K. G. Orrell, V. Šik, T. S. Cameron, and R. Cordes, *J.C.S. Chem. Comm.*, 1979, 713.

[11] E. Frasson, C. Panattoni, and R. Zannetti, *Acta Cryst.*, 1959, **12**, 1027.

[12] N. C. Stephenson, *Acta Cryst.*, 1964, **17**, 587.

[13] A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, 1975, p. 593.

[14] E. L. Muetterties, *Accounts Chem. Res.*, 1970, **3**, 266; K. Mislow, *ibid.*, p. 321.

[15] M. P. Brown, R. J. Puddephatt, and C. E. E. Upton, *J.C.S. Dalton*, 1974, 2457.

[16] J. B. Lambert, G. F. Jackson III, and D. C. Mueller, *J. Amer. Chem. Soc.*, 1970, **92**, 3093.

[17] L. Horner and H. Winkler, *Tetrahedron Letters*, 1964, 461.

[18] A. Rauk, J. D. Andose, W. G. Frick, R. Tang, and K. Mislow, *J. Amer. Chem. Soc.*, 1971, **93**, 6507.

[19] E. W. Abel, G. W. Farrow, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1977, 42.

[20] E. W. Abel, A. K. S. Ahmed, G. W. Farrow, K. G. Orrell, and V. Šik, *J.C.S. Dalton*, 1977, 47.

[21] E. W. Abel, G. W. Farrow, and K. G. Orrell, *J.C.S. Dalton*, 1976, 1160.

[22] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1150.

[23] G. Hunter and R. C. Massey, *J.C.S. Dalton*, 1976, 2007.

[24] P. E. Skakke and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 2634.

[25] H. J. Whitfield, *J. Chem. Soc.* (*A*), 1970, 113.

[26] T. G. Appleton, H. C. Clark, and L. E. Manzer, *Co-ordination Chem. Rev.*, 1973, **10**, 335.

[27] D. E. Clegg, J. R. Hall, and G. A. Swile, *J. Organometallic Chem.*, 1972, **38**, 403.

[28] T. G. Appleton, M. A. Bennett, and I. B. Tomkins, *J.C.S. Dalton*, 1976, 439.

[29] J. E. Anderson and J. M. Lehn, *J. Amer. Chem. Soc.*, 1967, **89**, 81.