A Dynamic Nuclear Magnetic Resonance Study of Trimethylplatinum(IV) Halide Complexes of 1,1,2,2-Tetrakis(methylthio)ethane. Part 3.[1,2] Structure and Fluxionality of Dinuclear Complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$

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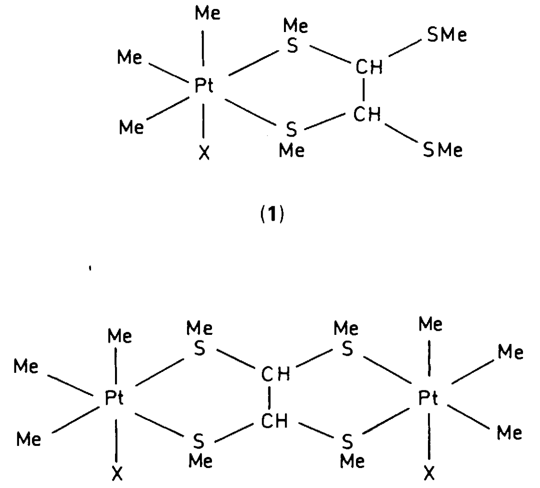
Dinuclear platinum(IV) complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ were prepared by treating the mononuclear chelate complexes $[PtXMe_3\{(MeS)_2CHCH(SMe)_2\}]$ with equimolar amounts of $[(PtXMe_3)_4]$ (X = Cl, Br, or I). In the new complexes the ligand acts as a double chelate towards the $PtXMe_3$ moieties. The most likely static solution structures of these complexes are deduced from n.m.r. evidence. Low-temperature ^1H n.m.r. bandshape analysis yielded pyramidal inversion energies of the co-ordinated S atoms [$\Delta G^‡(298.15\ K) = 57$—$59\ kJ\ mol^{-1}$] and high-temperature two-dimensional exchange spectroscopy n.m.r. spectra yielded energies associated with the Pt-methyl scrambling fluxion [$\Delta G^‡(298.15\ K) = 90$—$92\ kJ\ mol^{-1}$].

In the earlier parts[1,2] of this work the structures and fluxional properties of the chelate complexes of trimethylplatinum(IV) halides with the ligand 1,1,2,2-tetrakis(methylthio)ethane were examined in detail. This ligand readily uses two of its methylthio groups in forming five-membered ring chelate complexes (**1**) (Figure 1) when reacting with equimolar amounts of $[PtXMe_3]$. However, complex (**1**) has the potential to bind to another $PtXMe_3$ moiety, and indeed in its ^1H n.m.r. spectra there is evidence that small amounts of the dinuclear ligand-bridged complexes (**2**) are formed.[1,2] This paper is concerned with the isolation of pure samples of these dinuclear complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ and an n.m.r. investigation of their solution properties.

Many possible isomeric forms of (**2**) can be envisaged depending on the stereochemical relationship of the methine protons both with respect to each other and to the two $PtXMe_3$ groups, and the mutual relationship of the two $PtXMe_3$ moieties. The situation is further complicated at low solution temperatures where slow pyramidal sulphur inversion[3] can lead to numerous invertomers of each configurational isomer. However, it will be shown how the relatively simple n.m.r. spectra of these complexes and their changes with temperature point to only a single solution species being present.



(**1**)

(**2**)

Figure 1. The structure of the complexes $[PtXMe_3L]$ (**1**) and $[(PtXMe_3)_2L]$ (**2**) showing L, $(MeS)_2CHCH(SMe)_2$, acting as a chelate and bridging ligand

Experimental

Materials.—The ligand 1,1,2,2-tetrakis(methylthio)ethane, $(MeS)_2CHCH(SMe)_2$, was prepared as previously.[4] Syntheses of the mononuclear complexes $[PtXMe_3\{(MeS)_2CHCH(SMe)_2\}]$ were as reported in Part 1.[1]

The three halogen complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ were prepared in a similar fashion, the major difference in each case being the reaction time. The case of X = Cl is described fully, with the reaction times for the X = Br or I complexes given in parentheses.

Into a round-bottomed flask (50 cm^3) was placed $[PtClMe_3\{(MeS)_2CHCH(SMe)_2\}]$ (70 mg, 142 mmol), $[(PtClMe_3)_4]$ (40 mg, 145 mmol, based on the monomeric unit), and chloroform (20 cm^3). The solution was boiled under reflux for 3 h (X = Br, 5—7 h; X = I, 3 d), after which its volume was reduced to *ca.* 5 cm^3. To this was added hexane (*ca.* 30 cm^3) which caused precipitation of the dinuclear complex as fine white microcrystals, together with a small amount of the mononuclear complex. Recrystallisation of the crude product from chloroform–hexane (15:85) yielded an acceptably pure product. Yields, based on $[(PtXMe_3)_4]$, were: X = Cl, 23 mg (21%); Br, 50 mg (33%); and I, 99 mg (62%). Analytical data (Butterworth Laboratories, London) are as follows (calculated values in parentheses): $C_{12}H_{32}Cl_2Pt_2S_4$ C, 18.9 (18.8); H, 4.2 (4.2); $C_{12}H_{32}Br_2Pt_2S_4$ C, 16.6 (16.9); H, 3.6 (3.8); $C_{12}H_{32}I_2Pt_2S_4$ C, 15.3 (15.2); H, 3.3 (3.4)%.

N.M.R. Spectra.—Hydrogen-1 and platinum-195 spectra were recorded at 250.13 and 53.53 MHz, respectively, on a Bruker AM 250 F.T. spectrometer. A standard variable-temperature unit controlled the n.m.r. probe temperature which was checked periodically against a thermocouple to ensure temperature readings were within ±1 °C. All ^1H n.m.r. shifts are quoted relative to $SiMe_4$ and ^{195}Pt shifts relative to $\Xi(^{195}Pt) = 21.4$ MHz. The complexes were studied in $[^2H]$-chloroform up to temperatures of 333 K. Above this temperature, $[^2H_5]$nitrobenzene was used as solvent. The iodo

Table 1. Hydrogen-1 chemical shifts[a] and coupling constants for the complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ (X = Cl, Br, or I)

X	δ(CH)	^3J(Pt–H)/Hz	δ(SMe)	^3J(Pt–H)/Hz	δ(PtMe) *trans* to X	^2J(Pt–H)/Hz	δ(PtMe) *trans* to S	^2J(Pt–H)/Hz
(*a*) 293 K								
Cl	5.11	7.5	2.79	11.1	1.08	73.6	1.27	71.2
Br	5.16	7.6	2.87	11.7	1.17	72.6	1.36	71.5
I	5.16	7.7	2.99	12.5	1.30	69.9	1.53	72.2
(*b*) 213 K								
Cl	4.99	6.3[b]	2.79	11.0	1.11	73.9	1.24	70.3
			2.87	12.0			1.26	70.9
Br	4.97	6.5[b]	2.89	11.5	1.19	73.0	1.33	70.5
			2.93	12.6			1.35	71.2
I	4.89	7.4[b]	2.93	13.0	1.23	70.9	1.41	71.4
			2.97	12.1			1.44	72.0

[a] Relative to $SiMe_4$. [b] Quintet structure not well resolved. Value quoted may represent mean of marginally different pairs of values.

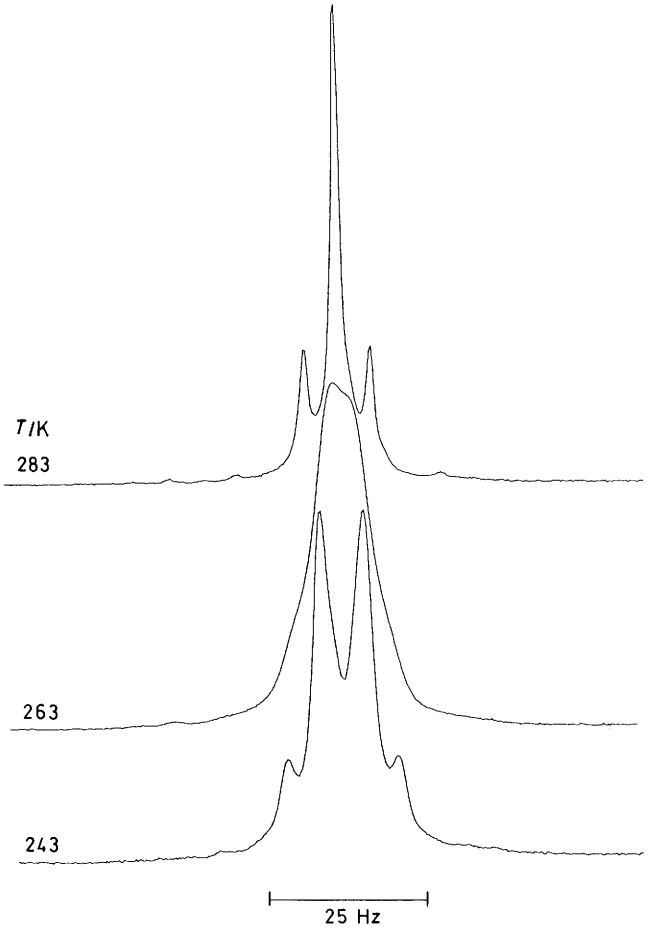


Figure 2. Variable-temperature ^{1}H n.m.r. spectra of the S-methyl signals of $[(PtBrMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$

complex was appreciably less soluble than the other complexes in either solvent. This led to somewhat higher uncertainties in the subsequent bandshape analyses.

Total bandshape analyses were carried out using the authors' version of the original DNMR3 program.[5] The ^{1}H two-dimensional exchange spectroscopy (EXSY) experiments on the platinum-methyl signals were performed with an F1 dimension of 64 words, zero-filled to 512 words, and an F2 dimension of 1 024 words. Sixteen scans per experiment were used giving a total experimental time of *ca.* 4 h. Magnitude-mode spectra were calculated, followed by symmetrisation about the diagonal. Optimum mixing times (*ca.* 1 s) were chosen to give greatest accuracy to the rate constants calculated from the D2DNMR program.[6] In these calculations, cross-relaxation effects were considered to be negligible as the platinum-methyl hydrogens exhibited no nuclear Overhauser enhancements.[7]

Results and Discussion

N.M.R. Spectra.—The proton n.m.r. spectra of all three dinuclear complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ (X = Cl, Br, or I) are remarkably simple at room temperature (293 K). Full details of spectral data are contained in Table 1. The methine region consists of a symmetrical 1:8:18:8:1 quintet signal, clearly due to the protons showing equal scalar coupling to pairs of platinum nuclei with spins 0 and $\frac{1}{2}$. The S-methyl region consists of a single line with a pair of ^{195}Pt satellites due to co-ordinated S-methyl protons. The Pt-methyl region contains two signals (intensity ratio 2:1) each with a pair of ^{195}Pt satellites, clearly assigned to axial and equatorial Pt-methyls.

On cooling to *ca.* 213 K, the following spectral changes were observed. The methine quintet first broadened slightly, with loss of multiplet structure, and then sharpened again but with the quintet structure less well defined. The S-methyl signal broadened and then split into two equal-intensity signals (Figure 2). The splitting was quite small and was greatest (≈20 Hz) for the chloro complex (Table 1). In the Pt-methyl region of the spectrum the equatorial signal split into two equal-intensity signals, while the axial signal remained a sharp singlet (Figure 3). Full proton n.m.r. data for the complexes measured at 293 and 213 K are given in Table 1. Platinum-195 spectra for the three complexes at 243 K were also measured and the shifts of the single ^{195}Pt signals are in Table 2. The values will be seen to display the usual halogen dependence, namely increasingly low frequency shifts with increasing halogen mass/size.[8]

The simplicities of the ^{1}H and ^{195}Pt n.m.r. spectra suggest that only a single solution species, out of the numerous possibilities, is present for all three complexes. Detailed arguments in support of the most likely structure will be deferred until later. From the variable-temperature ^{1}H n.m.r. spectra it is clear that pyramidal inversion of the co-ordinated S-methyls is occurring. The resulting changes in the Pt-methyl signals were too slight to yield quantitative rate data for the process. The changes in the S-methyl region were also not well suited to accurate bandshape analysis methods,[9] due to the small chemical shift difference of the signals. However, fittings

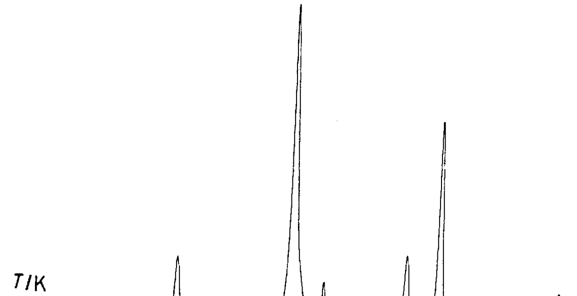


Figure 3. Variable-temperature ^1H n.m.r. spectra of the Pt-methyl signals of $[(PtBrMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$

Table 2. Platinum-195 chemical shifts for $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ at 243 K

X	δ*
Cl	1 360
Br	1 266
I	1 102

* Values ±1 p.p.m., relative to $\Xi(^{195}Pt) = 21.4$ MHz.

Table 3. Free energies of activation for pyramidal S inversion and Pt-methyl scrambling in the complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$

	$\Delta G^‡(298\ K)/kJ\ mol^{-1}$	$\Delta G^‡(353\ K)/kJ\ mol^{-1}$
X	S inversion	Pt-methyl scrambling
Cl	58.8 ± 0.4	92.3 ± 0.5
Br	57.8 ± 0.5	91.0 ± 0.5
I	57.5 ± 0.8	90.0 ± 0.5

were performed at 243, 253, 263, and 273 K, from which moderately accurate rate constants and $\Delta G^‡$(298 K) data were derived (Table 3).

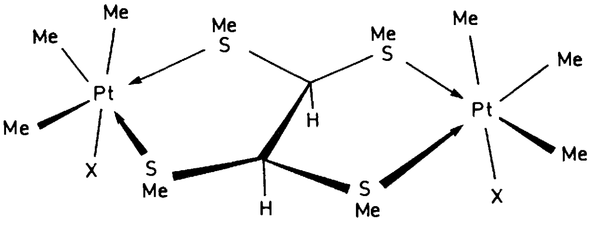
Trimethylplatinum(IV) halide complexes with chelate or bridging chalcogen ligands invariably exhibit high-temperature fluxionality which has previously been described in terms of ligand rotation or switching movements and concomitant fluxionality of the $PtMe_3$ moiety leading to a single averaged methyl environment. Such movements were not expected in the present dinuclear complexes where the ligand is effectively 'locked' between the two $PtXMe_3$ moieties. However, high-temperature ^1H n.m.r. studies did reveal a Pt-methyl fluxionality which may have been initiated by a ligand rotation, although such a movement is not detectable as it cannot produce any chemical shift averaging. A somewhat analogous 'loose-ball-joint' movement has been proposed for the complexes $[M(dppe)(\mu\text{-}SMe)_2PtXMe_3]$ [M = Pd or Pt, dppe = 1,2-bis(diphenylphosphino)ethane].[10] Irrespective of the lack of identification of the ligand fluxions, the activation energies of the subsequent Pt-methyl scrambling process were measured from proton two-dimensional EXSY experiments on the Pt-methyl signals in the temperature range 353—373 K. Cross-peaks between axial and equatorial Pt-methyl signals were clearly detected at these temperatures and yielded kinetic information.[6] Exchange broadening became significant at *ca.* 400 K with band coalescence only being achieved at the accessible high-temperature limit of *ca.* 423 K. For this reason the two-dimensional EXSY experiments were preferred for the kinetic analysis. Free energies of activation for the Pt-methyl scrambling fluxion are given in Table 3 alongside the sulphur inversion-energy data.

The $\Delta G^‡$ values for both dynamic processes are very similar in magnitude to those obtained for the mononuclear complexes.[1,2] In the case of sulphur inversion, the values are identical, within experimental error, to those due to the *cis*-1 isomer of the complexes $[PtXMe_3\{(MeS)_2CHCH(SMe)_2\}]$ (X = Br or I).[1] Since the values for the *trans* isomers of the above complexes are somewhat different, this suggests that the dinuclear complexes are based on a mononuclear *cis*-1 template structure in which the methine protons adopt a *cis* relationship both to each other and to the halogen of the $PtXMe_3$ moiety.

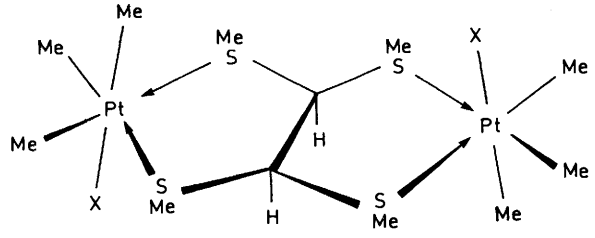
Solution Structures.—Five distinct configurational isomers of $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ can be envisaged depending on (*i*) the mutual relationship of the two methine protons, (*ii*) the mutual relationship of the two $PtXMe_3$ moieties, and (*iii*) the relationship between the methine and $PtXMe_3$ moieties. The structures based on a *trans*-$(MeS)_2CHCH(SMe)_2$ backbone, however, are unlikely as they would require the five-membered chelate rings to adopt highly strained non-planar geometries. The very close similarity in activation energies for sulphur inversion in the dinuclear complexes and the mononuclear *cis*-1 complexes suggests that the *cis*-1 mononuclear geometry forms the basis for the dinuclear complex geometry. A further argument in support of a *cis*-1 geometry comes from the observation that in the preparation of the mononuclear complexes[1] there is clearly a link between the amount of *cis*-1 complex formed and the amount of dinuclear complex formed as a by-product. With increasing halogen size, the *cis*-1 isomer was less favoured and, similarly, less dinuclear complex by-product was formed. It is therefore proposed that the dinuclear complexes arise from a second $PtXMe_3$ moiety attaching to the *cis*-1 mononuclear template.

Two possible structures, differing only in the mutual relationship of the $PtXMe_3$ moieties, need to be considered (Figure 4). It is not possible to rule unambiguously in favour of one of these structures but (**2a**) in which the methine protons adopt a *cis*-1 relationship to *both* $PtXMe_3$ moieties appears more favourable on steric grounds. Furthermore, the ^1H n.m.r. spectra of these complexes at room temperature indicate only a single type of $PtXMe_3$ environment whereas structure (**2b**) (Figure 4) contains in theory *two* different environments for this moiety.

In order to account for the n.m.r. bandshape changes accompanying sulphur inversion in these complexes it is necessary to consider the possible static invertomers of the favoured *cis*-1 isomer. There are seven n.m.r.-distinct species, three *meso* forms and four DL pairs. These are depicted in Figure 5, with only single members of the DL pairs being shown. The ^{1}H n.m.r. spectra at low temperatures consist of a single methine signal, two equal-intensity S-methyl signals, and three equal intensity Pt-methyl signals. The only structure compatible with such a set of signals is *meso*-2 (Figure 5). This structure is also greatly preferred on steric grounds on account of the *anti* relationships of all adjacent S-methyls. Pyramidal inversion of individual S atoms will convert *meso*-2 into one or more of the other invertomers but, as there is no spectral evidence for any of these being present in solution in detectable abundance, the S inversion process in essence involves exchange between *meso*-2 and its topomeric partner[11] *meso*-2′ (Figure 6). This leads to a collapse of the two S-methyl signals into one, and a similar collapse of the two equatorial Pt-methyl signals. The effect on the methine absorption is more subtle, however. When inversion is slow, two magnitudes of ^{3}J(PtH) are possible depending on whether the coupling is *via* a sulphur with its attached methyl *cis* or *trans* to halogen. In the fast-inversion limit a single averaged magnitude of coupling will be observed, which accounts for the more clearly resolved quintet structure of the methine signal at room temperature compared to 213 K.



(**2a**)

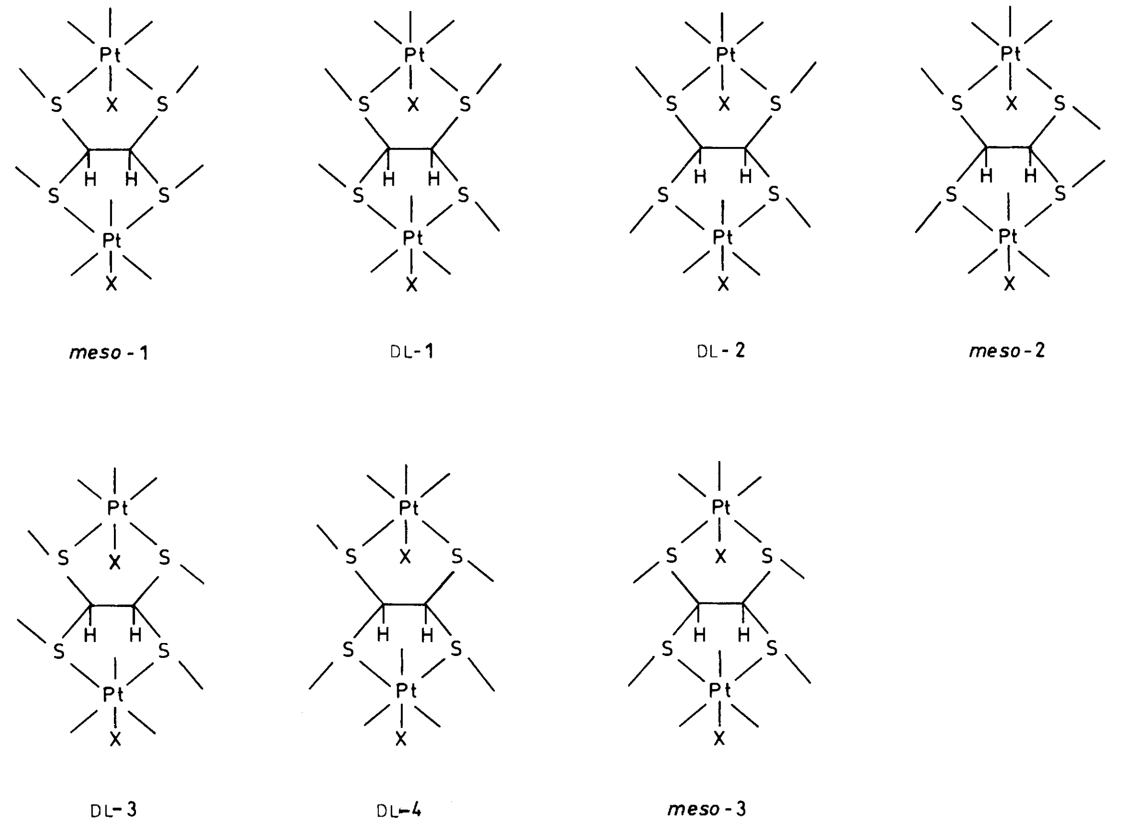


(**2b**)

Figure 4. Most likely isomeric forms of $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$

A careful analysis of the ^{1}H n.m.r. spectral features of the dinuclear complexes $[(PtXMe_3)_2\{(MeS)_2CHCH(SMe)_2\}]$ (X = Cl, Br, or I) in $CDCl_3$ solution makes it possible therefore to conclude with a high degree of certainty that the complexes exist solely as species based on the *cis*-1 mononuclear complexes, with the methine protons *cis* to each other and to the halogens of both $PtXMe_3$ moieties. At ambient temperatures, sulphur inversion occurs rapidly on the ^{1}H n.m.r. time-scale and results in exchange between a pair of topomeric *meso*-2 species in which the four S-methyls adopt a staggered relationship to each other.

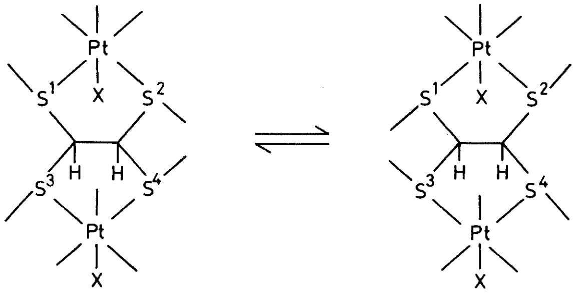
$[Me_3XPt\{(MeS)_2CHCH(SMe)_2\}PtX'Me_3]$ (X ≠ X′) *Complexes.*—Following the successful preparation of the homohalogeno complexes (X = X′ = Cl, Br, or I), attempts were made to synthesise the three mixed halogeno species, *viz.* X = Cl, X′ = Br; X = Cl, X′ = I; and X = Br, X′ = I. In all cases, however, equilibrium mixtures of the homo- and heterohalogeno complexes were obtained, according to equation (1).



meso-1 DL-1 DL-2 *meso*-2

DL-3 DL-4 *meso*-3

Figure 5. The seven n.m.r.-distinct static invertomers of the *cis*-1 isomer (**2a**) (Figure 4)



meso - 2 *meso* - 2′

Figure 6. Topomerisation of the *meso*-2 structures resulting from pyramidal inversion of the co-ordinated S atoms

$$3[PtXMe_3L] + \tfrac{3}{4}[(PtX'Me_3)_4] \longrightarrow [(PtXMe_3)_2L] + [(PtXMe_3)L(PtX'Me_3)] + [(PtX'Me_3)_2L] \quad (1)$$

Thus, in an attempt to prepare the X = Cl, X′ = I complex, the X = X′ = Cl and I complexes were also produced, and the resulting mixture could not be separated. The n.m.r. spectral differences between the homo-and hetero-halogeno species in all cases were so slight that no confident spectral analyses could be achieved.

Such mixtures of products would suggest that labile $PtXMe_3$ and $PtX'Me_3$ moieties, derived from the mononuclear complexes and the tetramers, are present in solution, with like and unlike pairs of these moieties becoming attached to ligand molecules. The established existence of fluxionality in these mononuclear complexes[1,2] and the very likely existence of Pt-methyl fluxionality in the trimethylplatinum(IV) halide tetramers[12] may facilitate the formation of these labile $PtXMe_3$ or $PtX'Me_3$ moieties and so account for the formation of equilibrium mixtures of these dinuclear complexes.

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Received 27*th April* 1989; *Paper* 9/01794A