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NMR INVESTIGATIONS OF PYRAMIDAL ATOMIC INVERSION AND OTHER INTRAMOLECULAR REARRANGEMENTS IN THE HALOGENOTRIMETHYLPLATINUM COMPLEXES OF 2,4,6-TRITHIAHEPTANE

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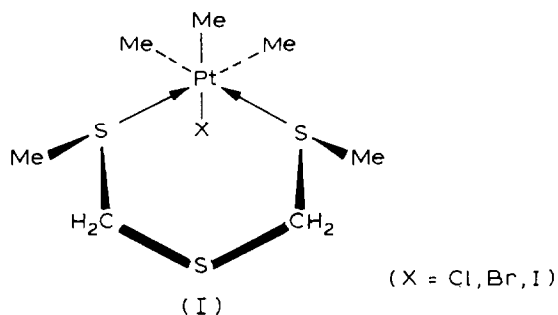
Summary

The mononuclear six-membered ring complexes $[(PtXMe_3)(MeSCH_2SCH_2SMe)]$ ($X = Cl, Br$ and I) have been synthesised and studied by dynamic NMR methods. The separate energy barriers associated with the pyramidal inversion of the sulphur atoms, platinum-methyl scrambling and chelate ligand rotation were measured by complete band-shape analyses.

Introduction

As part of an investigation of the factors which govern the energy barriers of fluxional movements in sulphur and selenium ligand coordination complexes, we have previously synthesised and studied complexes where the $(PtXMe_3)$ moiety has been chelated with the ligands $MeE(CH_2)_nEMe$ ($E = S$ or Se and $n = 2$ or 3 [1]) and $MeSZSeMe$ ($Z = (CH_2)_2$ or $o-C_6H_4$) [2]. In these mononuclear complexes the chalcogen atoms have been shown to be inverting essentially independently, and all possible invertomers were detected at low temperatures [2,3]. At temperatures above those at which chalcogen inversions were rapid, the NMR line shapes were further changed by complete platinum-methyl scrambling. Such a process was regarded as integral with an overall 180° rotation of the bidentate ligand, but the complexity of the ligand back-bone NMR spectra hampered a direct study of the ligand movements. In order to obtain more direct evidence of the ligand fluxion the complexes $[(PtXMe_3)(MeSCH_2SCH_2SMe)]$ ($X = Cl, Br$ and I) were prepared. The ligand behaved in a bidentate manner, with the central sulphur atom redundant; as illustrated in I. The uncoupled methylene groups of the ligand give uncomplicated spectra of an AB type, very suitable for DNMR studies.

These complexes were examined at low temperatures to detect the number of invertomers and to calculate accurate energy barriers for pyramidal sulphur inver-



sion. At high temperatures, when sulphur inversion was rapid, changes of NMR line shapes in the different spectral regions were used in separate studies of Pt-Me scrambling and chelate ligand rotation.

Experimental

Materials. The trimethylplatinum(IV) halides were prepared by previously reported methods [4,5]. The ligand 2,4,6-trithiaheptane was prepared by literature methods [6,7], and was a pale yellow oil (yield 49%), b.p. 104–108°C/15 mmHg (lit. b.p. 106°C/5 mmHg [8], 100–103°C/3.5 mmHg [9]). ^1H NMR δ (ppm) 2.15 (S-Me) and 3.77 (CH₂).

The platinum complexes were prepared as outlined below.

A slight excess of 2,4,6-trithiaheptane (120 mg, 0.77 mmol) was added to the tetrameric chlorotrimethylplatinum (200 mg, 0.73 mmol, based on the monomer unit PtClMe₃) in chloroform (10 cm³), and the stirred suspension was heated under reflux for 6 h. Reduction of solution volume to ca. 1 cm³ under vacuum, was followed by addition of petroleum spirit (10 cm³) (b.p. 40–60°C) to produce a white precipitate. Solvent was decanted and the product recrystallized from chloroform/petroleum spirit (50/50) at -20°C as fine white crystals of chloro(2,4,6-trithiaheptane)trimethylplatinum(IV) (253 mg, 81%). The crystals of bromo(2,4,6-trithiaheptane)trimethylplatinum(IV) (300 mg, 87%) and iodo(2,4,6-trithiaheptane)trimethylplatinum(IV) (362 mg, 96%), were obtained in similar manner from the appropriate trimethylplatinum halides (Table 1).

The compounds are air stable and soluble in most polar organic solvents. All ^1H NMR signals of the complexes were coupled with the spin active platinum-195

TABLE 1
ANALYTICAL DATA FOR THE COMPLEXES [PtXMe₃L]

Compound	M.p. (°C)	Analysis (Found(calcd.)(%))	
		C	H
[PtClMe ₃ {MeS(CH ₂ S) ₂ Me}]	174-176	19.30 (19.55)	4.41 (4.45)
[PtBrMe ₃ {MeS(CH ₂ S) ₂ Me}]	183-185	17.55 (17.72)	3.97 (4.03)
[PtI Me ₃ {MeS(CH ₂ S) ₂ Me}]	190-192	15.90 (16.12)	3.12 (3.67)

TABLE 2

 ^1H NMR DATA FOR $\{[\text{PtXMe}_3]\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}\}$ IN CD_2Cl_2 AT ROOM TEMPERATURE^a

X	-CH ₂ - region		SMe region				PtMe <i>trans</i> to S		PtMe <i>trans</i> to X		
	δ_A (ppm) ^b	δ_B (ppm)	2J (Hz) ^c	3J (Hz) ^d	3J (Hz) ^e	δ (ppm)	3J (Hz) ^f	δ (ppm)	2J (Hz) ^g	δ (ppm)	2J (Hz)
Cl	5.02,4.88	3.82,3.68	13.55	2.00	9.7	2.38	13.3	1.18	69.1	0.89	72.7
Br	5.08,4.94	3.88,3.75	13.60	2.11	10.7	2.40	13.7	1.25	69.3	1.01	71.9
I	5.12,4.98	3.98,3.84	13.55	2.18	11.9	2.45	14.4	1.32	70.1	1.15	69.6

^a Room temperature was not measured precisely. ^b Chemical shifts were measured relative to SiMe_4 . ^c $^2J(^1\text{H}-\text{C}-^1\text{H})$. ^d $^3J(^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H}_A)$. ^e $^3J(^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H}_B)$. ^f $^3J(^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H})$. ^g $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$.

isotope (33.7%). Room temperature spectra consisted of three regions, the ligand methylenes (AB quartet), the sulphur methyls (singlet) and platinum methyls (two singlets in intensity ratio 2/1). These ^1H NMR data for the three complexes are given in Table 2.

Spectra. NMR spectra were recorded using a JEOL PS/PFT-100 spectrometer operating in the Fourier-transform mode at 100 MHz for ^1H studies. A JES-VT-3 variable temperature unit was used to control the probe temperature. Temperatures were measured immediately before and after the recording of spectra, using a digital thermometer (Comark 5000) based on a precisely calibrated copper-constantan thermocouple. All temperatures quoted are considered accurate to $\leq 1^\circ\text{C}$. A mixture of CD_2Cl_2 and CS_2 was used as solvent for all complexes in the temperature range -75 to 40°C . For higher temperature studies, a mixture of $\text{C}_6\text{D}_5\text{NO}_2$ and C_6D_6 was used. Computations of NMR band-shapes were carried out according to the DNMR program developed by Kleier and Binsch [10].

Results

Low temperature studies. The coordinated sulphur atoms in these six-membered rings are centres of chirality, and thus in the absence of any internal exchange process, four diastereoisomers can exist. These are two different *meso* forms and a pair of *dl* forms (Fig. 1). Evidence for the existence of these invertomers came from the low temperature spectra of the complexes. The spectra of $[(\text{PtClMe}_3)\text{-(MeSCH}_2\text{SCH}_2\text{SMe)}]$ are typical of those for the series.

At ca. -60°C the methylene region consisted of four AB quartets (plus ^{195}Pt satellites), which can be attributed to the three spectroscopically distinct invertomers, one of which is the degenerate *dl* pair. Further evidence for four diastereoisomers came from the SMe region of the spectrum, where four signals (plus ^{195}Pt satellites) were predicted and observed for all four complexes, $[(\text{PtXMe}_3)\text{-}$

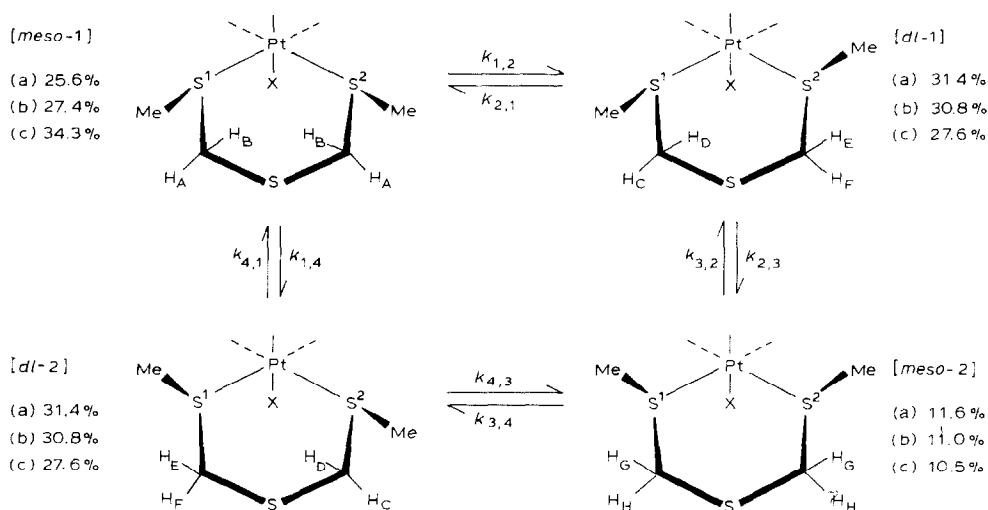


Fig. 1. Interconversion of isomers by inversion of coordinated sulphur atoms. Percentage populations refer to the complexes (a) X = Cl, (b) X = Br, and (c) X = I at ca. -65°C .

(MeSCH₂SCH₂SMe)] (X = Cl, Br and I). On warming there was coalescence of signals, until at ca. 30°C only a single averaged AB quartet (plus ¹⁹⁵Pt satellites) in the methylene region, and an averaged singlet (plus ¹⁹⁵Pt satellites) in the SMe region were observable. These particular changes of line shape are due entirely to the increasing rate of pyramidal inversion at sulphur with rise in temperature.

In the Pt–Me region of the ¹H NMR spectrum seven signals are to be expected, three for methyls *trans* to halogen and four for methyls *trans* to sulphur. In these studies only five or six signals were normally observed due to fortuitous chemical shift overlaps.

Whilst both the SMe and methylene regions could in principle be used for band shape analyses, a slight overlapping of two of the SMe signals with ¹⁹⁵Pt satellites made the accurate calculation of isomer populations difficult, and the methylene region only was used for such studies. Since the *dl* isomers are structurally and energetically identical, their populations in any complex will be the same. Moreover, it was observed in previous work on six-membered dithioether complexes [3] that the population of the *meso*-1 isomer grew with increasing size of the halogen present.

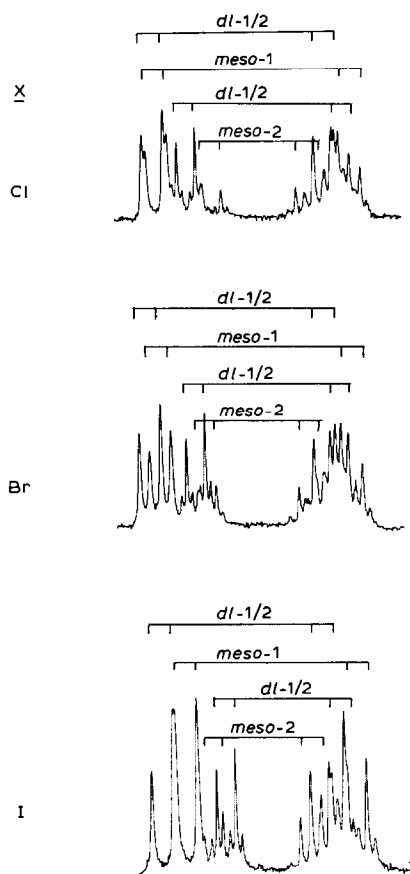


Fig. 2. ¹H methylene region spectra of [PtXMe₃(MeS(CH₂S)₂Me)] at low temperature showing the halogen dependences of individual invertomers.

TABLE 3
 STATIC PARAMETERS USED IN THE COMPUTER-SIMULATION OF THE METHYLENE SPECTRA FOR PYRAMIDAL INVERSION STUDY IN
 $[(\text{PtXMe}_3)(\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3)]^a$

X	Temperature (°C)	Isomer	ν_i (Hz) ^b	ν_j (Hz)	2J (Hz) ^c	3J (Hz) ^d	3J (Hz) ^e	$p\%$ ^f	T_2^* (s)		
Cl	-62.2	<i>meso</i> -1	501.3	370.1	14.9	2.0	8.5	25.6			
		<i>dl</i> -1/2	503.7	387.3	14.4	2.0	12.5	31.4			
		<i>meso</i> -2	480.9	376.3	12.3	6.6	8.5	31.4			
			463.6	400.5	12.8	8.0	11.0	11.6			
		Br	-61.8	<i>meso</i> -1	504.2	374.6	14.8	2.1	9.5	27.4	
				<i>dl</i> -1/2	511.2	393.1	14.5	2.2	12.7	30.8	
<i>meso</i> -2	480.2			383.1	12.6	7.3	8.7	30.8			
	472.9	404.4	12.5	8.5	13.2	11.0					
I	-76.5	<i>meso</i> -1	500.4	385.4	15.1	2.5	11.2	34.3			
		<i>dl</i> -1/2	516.6	408.5	15.2	2.6	12.5	27.6			
			473.3	397.1	12.6	7.9	8.5	27.6			
		<i>meso</i> -2	482.2	416.3	13.1	8.0	11.0	10.5			

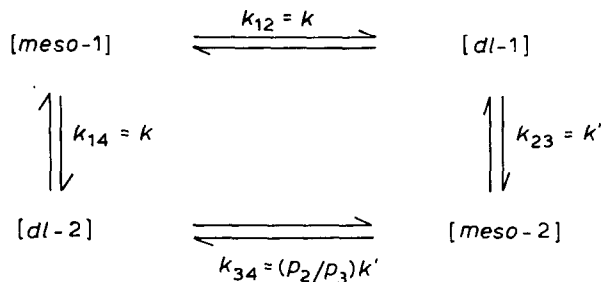
^a Solvent was $\text{CD}_2\text{Cl}_2/\text{CS}_2$ mixture. ^b Chemical shifts (ν_i and ν_j) were measured relative to SiMe_4 . ^c 2J ($^1\text{H}-\text{C}-^1\text{H}$). ^d 3J ($^1\text{H}-\text{C}-^1\text{H}$). ^e 3J ($^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H}_A$). ^f 3J ($^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H}_B$).
^f Populations of isomers (± 0.005).

With these points in mind, the assignments of the individual AB quartets were made with confidence. The spectra of the methylene regions, together with the assignments for the three different halogen complexes, are shown in Fig. 2.

It is notable that for the chloro and bromo complexes, the sequence of populations is $dl-1 = dl-2 > meso-1 > meso-2$, whereas in the iodo complex there is a change to $meso-1 > dl-1 = dl-2 > meso-2$.

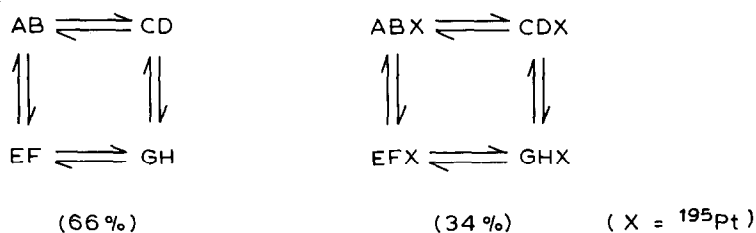
The complexes were cooled to -90°C to seek further changes in the NMR spectra resulting from the slowing down of the chair-to-chair reversal of the six-membered ring. However, no such changes were observed implying that the ring reversal process was very fast, even at low temperature, on the NMR time scale, or that one of the conformers overwhelmingly predominated in solution.

As the sample temperature was raised, pyramidal inversion became rapid, and the different environments of the methylene protons became averaged. This is illustrated in the cyclic scheme in Fig. 1, where inversion is considered to occur at each coordinated sulphur atom independently, in an uncorrelated manner. Assuming a very low possibility for synchronous double-site inversion of both sulphur atoms, then direct interconversion between *meso*-1 and *meso*-2, and between *dl*-1 and *dl*-2 was neglected ($k_{13} = k_{24} = 0$). There is no reason why the *meso*-1 \rightarrow *dl*-1 barrier should be identical to that of *dl*-1 \rightarrow *meso*-2, and the spectra were therefore simulated using different rate constants k and k' for these two steps. This is illustrated in Scheme 1 where p_2 is the population of *dl*-1 and p_3 is the population of *meso*-2.



SCHEME 1

In practice, the spectral line-shapes, on simulation, were found sensitive to both of the rate constants. The dynamic process under investigation involves interconversions between four distinct chemical configurations, each consisting of two spins which are coupled to one another. Since in 33.7% of the molecules the spins are also coupled with ^{195}Pt , the total spin problem for the methylene protons can be represented as Scheme 2, where the labelling refers to Fig. 1.



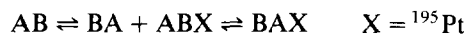
SCHEME 2

Table 3 records the static parameters from the ^1H spectra of the three complexes. The experimental and simulated variable temperature spectra for $[(\text{PtClMe}_3)-(\text{MeSCH}_2\text{SCH}_2\text{SMe})]$ are illustrated in Fig. 3, and the 'best-fit' rate constant values for k and k' are given in Table 4. The excellent agreement between line-shapes in Fig. 3 justifies the assumption of independent inversions at the two coordinated sulphur atoms.

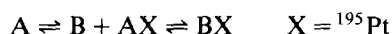
High temperature studies. On increasing the temperature of the complexes in $\text{C}_6\text{D}_5\text{NO}_2/\text{C}_6\text{D}_6$ solution above ca. 50°C further changes of line shapes took place in both the ligand methylene and platinum-methyl regions. The methylene AB quartet coalesced at ca. 110°C and was averaged to a singlet at ca. 130°C . Similarly the two PtMe signals coalesced to one. Both changes were completely reversible on lowering the temperature, and ^{195}Pt couplings to Pt-Me protons and methylene protons were retained throughout all the changes.

These observations require that the intramolecular movements bring about a complete scrambling of all three platinum methyl groups, and an effective 180° "pancake" rotation of the chelating ligand. It is likely that the two processes are part of a single overall mechanism, but as the changes are observed in quite different regions of the NMR spectra they can be separately characterized and quantified.

The spin problem of the exchanging methylene AB system coupled with ^{195}Pt can be represented as:



Since the chemical shifts of two platinum methyls are identical, and the populations of all three methyls are equal the spin problem was computed as:



with normalised weighting factors of 0.667 and 0.333 for A and B respectively.

The static parameters of the three complexes are collected in Table 5 for the ligand methylene region and in Table 6 for the platinum-methyl region. The

TABLE 4

RATE CONSTANTS USED IN THE COMPUTER-SIMULATION OF THE METHYLENE REGION OF $[(\text{PtClMe}_3)\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}]$ FOR PYRAMIDAL INVERSION STUDIES

Spectrum No. ^a	Temperature ($^\circ\text{C}$)	k (s^{-1})	k' (s^{-1})
1	-62.2	0.001	0.001
^b	-43.4	0.6	0.3
^b	-38.2	2.0	0.8
2	-31.8	4.4	1.8
3	-26.6	8.0	3.2
4	-20.7	15.4	6.2
^b	-14.4	29.0	14.5
5	-4.5	95.0	32.0
6	+3.5	170.0	70.0
7	+12.2	360.0	144.0
^b	+20.1	726.0	288.0
^b	+26.4	1200.0	480.0

^a See Fig. 3. ^b Spectra not shown in Fig. 3.

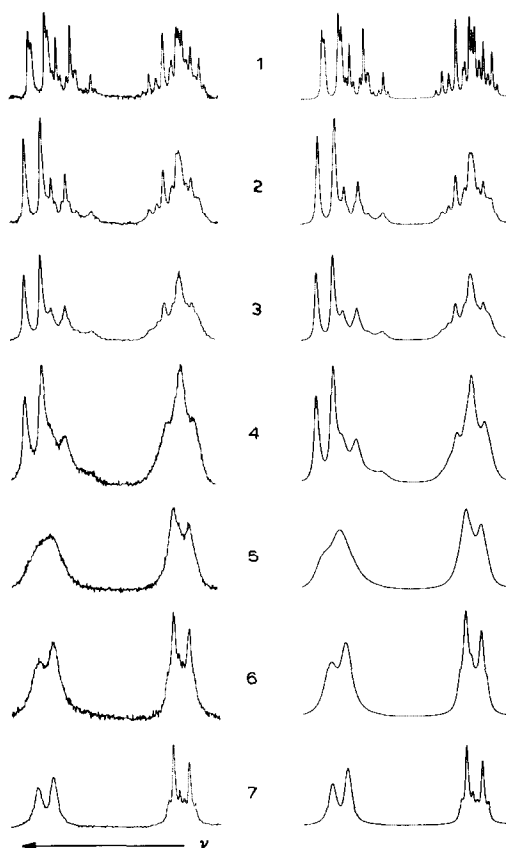


Fig. 3. Experimental and computer synthesised spectra of the methylene region of $[\text{PtClMe}_3\text{-(MeS(CH}_2\text{S)}_2\text{Me)}]$ showing the effects of sulphur inversion.

experimental and simulated variable temperature spectra for $[(\text{PtClMe}_3)\text{-(MeSCH}_2\text{SCH}_2\text{SMe)}]$ are illustrated for the ligand methylene region in Figure 4 and the platinum-methyl region in Figure 5. The rate constants (usually eight to ten, but a minimum of six) extracted from the line shape fittings of the three processes for

TABLE 5

STATIC PARAMETERS USED IN THE COMPUTER-SIMULATION OF METHYLENE REGION FOR LIGAND ROTATION STUDY IN $[\text{PtXMe}_3\{\text{CH}_3\text{S(CH}_2\text{S)}_2\text{CH}_3\}]^a$

X	Temperature (°C)	ν_A (Hz) ^b	ν_B (Hz)	2J (Hz) ^c	3J (Hz) ^d	3J (Hz) ^e	T_2^* (s)
Cl	49.5	489.2	374.3	13.7	3.5	9.9	0.40
Br	53.6	493.5	380.0	13.4	3.7	11.1	0.39
I	62.1	497.3	387.2	13.7	3.8	12.2	0.38

^a Solvent was $\text{C}_6\text{D}_5\text{NO}_2\text{-C}_6\text{D}_6$ mixture. ^b Chemical shifts (ν_i) measured relative to $\text{Me}_3\text{SiOSiMe}_3$. ^c $^2J(^1\text{H-C-}^1\text{H})$. ^d $^3J(^{195}\text{Pt-S-C-}^1\text{H}_A)$. ^e $^3J(^{195}\text{Pt-S-C-}^1\text{H}_B)$.

TABLE 6

STATIC PARAMETERS USED IN THE COMPUTER-SYNTHESIS OF PLATINUM-METHYL SPECTRA FOR METHYL SCRAMBLING STUDY IN $[\text{PtXMe}_3\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}]^a$

X	Temperature (°C)	PtMe <i>trans</i> to S			PtMe <i>trans</i> to X			T_{22}^* (s)
		ν (Hz) ^b	2J (Hz) ^c	p ^d	ν (Hz)	2J (Hz)	p	
Cl	57.4	118.0	69.3	0.667	88.8	72.5	0.333	0.337
Br	51.0	124.1	69.2	0.667	100.3	71.9	0.333	0.286
I	52.3	138.2	70.2	0.667	116.9	69.5	0.333	0.382

^a Solvent was $\text{C}_6\text{D}_5\text{NO}_2/\text{C}_6\text{D}_6$ mixture. ^b Chemical shifts (ν_i) measured relative to $\text{Me}_3\text{SiOSiMe}_3$. ^c $^2J(^{195}\text{Pt}-\text{C}-^1\text{H})$. ^d Fractional populations.

chloro, bromo and iodo complexes were used for the calculation of the barrier energies from a plot of $\ln k$ against T^{-1} and $\ln(k/T)$ against T^{-1} . Error limits quoted are based upon linear regression analyses of equally weighted graphical points.

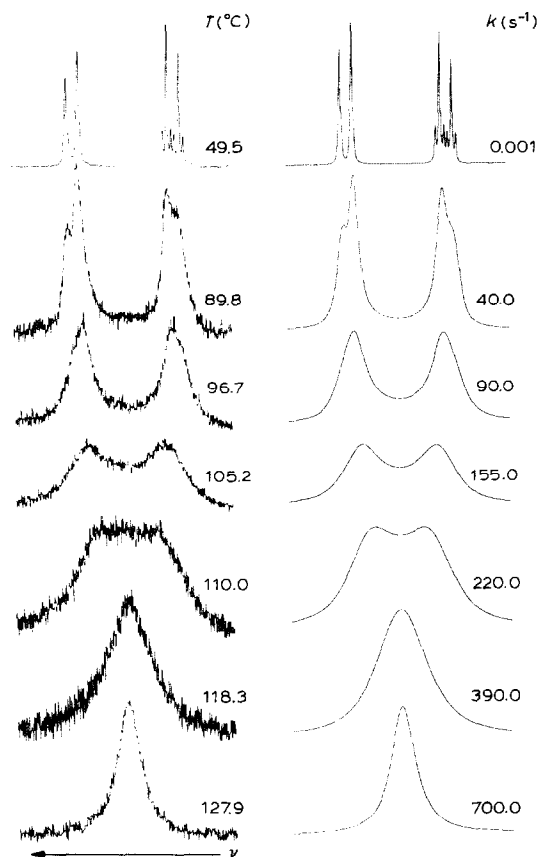


Fig. 4. Experimental and computer synthesised spectra of the methylene region of $[\text{PtClMe}_3\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$ showing the effects of ligand rotation.

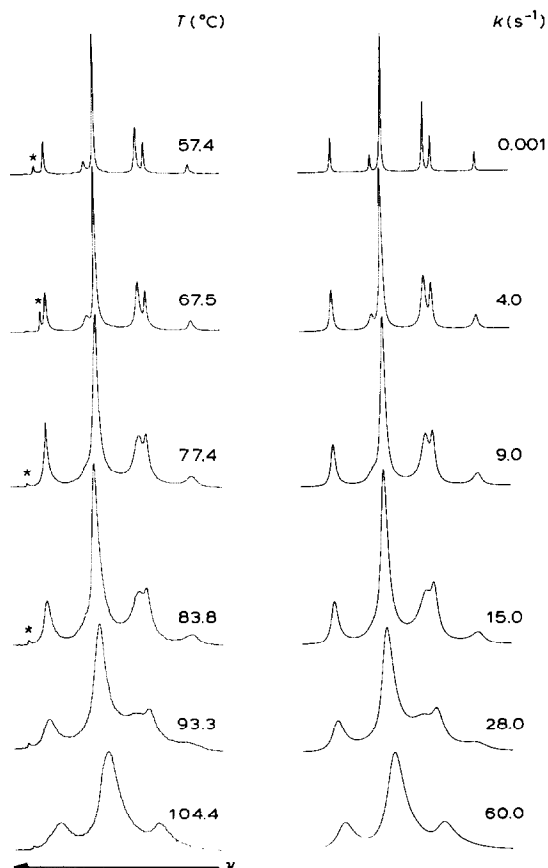


Fig. 5. Experimental and computer synthesised spectra of $[\text{PtClMe}_3\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$ showing the effects of platinum-methyl scrambling. The band marked with asterisk is due to water in the solvent.

Discussion

Pyramidal inversion. The Arrhenius and Eyring activation parameters for pyramidal inversions are presented in Table 7, and have comparable values to those observed for other platinum(IV) complexes. The inversion energies are of virtually equal magnitude to those recorded for the analogous complexes of 2,6-dithiaheptane [3], indicating that the presence of the extra redundant sulphur atom in the 2,4,6-trithiaheptane complexes has a negligible effect upon the inversions of the coordinated sulphur atoms. No appreciable difference in barrier energy was found between chloro and bromo complexes, suggesting that there is no significant *cis*-halogen influence upon inversion, as also noted for analogous compounds [2,3].

The ground state energies of the *meso*-1 and *meso*-2 isomers relative to the *dl* isomers have been calculated from the standard equation $\Delta G^\ominus = -RT \ln K^\ominus$, where K^\ominus is the ratio of the population of the appropriate *meso* isomer to *dl* isomer, and are presented in Table 8. These values along with the barrier energies (ΔG^\ddagger) reported in Table 7 enable approximate potential energy profiles for the inversions

TABLE 7

ARRHENIUS AND EYRING ACTIVATION PARAMETERS FOR PYRAMIDAL SULPHUR INVERSION IN $[(\text{PtXMe}_3)(\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3)]$

X	Interconversions	E_a (kJ mol ⁻¹)	$\log_{10} A$	ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (J K ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹) ^a
Cl	<i>meso</i> -1 → <i>dl</i> -1/2	57.91 ± 0.78	13.17 ± 0.16	55.77 ± 0.79	0.21 ± 3.07	55.71 ± 0.12
	<i>dl</i> -1/2 → <i>meso</i> -2	57.55 ± 0.84	12.71 ± 0.17	55.40 ± 0.86	-8.71 ± 3.34	58.00 ± 0.14
Br	<i>meso</i> -1 → <i>dl</i> -1/2	59.08 ± 0.62	13.27 ± 0.12	56.83 ± 0.63	1.56 ± 2.34	56.36 ± 0.06
	<i>dl</i> -1/2 → <i>meso</i> -2	60.78 ± 1.00	13.20 ± 0.19	58.53 ± 1.00	0.38 ± 3.72	58.42 ± 0.10

^a Calculated at 298.15 K.

TABLE 8

GROUND STATE ENERGIES (ΔG°) OF THE *MESO* ISOMERS (relative to *dl* isomers) OF $[\text{PtXMe}_3\{\text{MeS}(\text{CH}_2\text{S})_2\text{Me}\}]$ AT 298.15 K

X	ΔG° (kJ mol ⁻¹)	
	<i>meso</i> -1	<i>meso</i> -2
Cl	0.51	2.47
Br	0.29	2.55
I	-0.54	2.40

to be obtained, and that for $[(\text{PtClMe}_3)(\text{MeSCH}_2\text{SCH}_2\text{SMe})]$ is drawn in Fig. 6.

Other fluxional rearrangements. The barrier energies associated with ligand rotation and platinum-methyl scrambling are collected in Table 9. The values of ΔG^\ddagger are ca. 20 kJ mol⁻¹ higher than those for pyramidal atomic inversion in the same complexes, and are essentially halogen independent.

The barrier energies for the ligand rotation observation and the methyl scrambling observation are so close as to suggest that the two processes are correlated, and perhaps have the same transition state.

A number of dissociative and non-dissociative mechanisms are possible for the observed changes. Halogen dissociation would give a highly fluxional five coordinate intermediate which would allow ligand rotation and methyl scrambling. However, a halogen exchange experiment at 130°C showed no evidence of halogen dissociation, and in any case the presence of such a dissociation in the mechanism would be reflected in a halogen dependence of barrier energies. Thus a halogen dissociation in the transition state has no support. The formation of a five coordinate species is also possible by the breaking and reforming of individual Pt-S coordination bonds. Whilst this would retain the Pt-S-C-H couplings, they would be approximately halved in magnitude during such a process. Since no changes in $^3J(\text{Pt-S-C-H})$ values were observed the partial sulphur ligand dissociation appears ruled out. Similarly, the complete retention of unchanged $^2J(\text{Pt-C-H})$ rules out platinum-methyl dissociations.

Several non-dissociative mechanisms are possible to explain these experimental observations. A highly fluxional pseudo-eight-coordinate transition state allows scrambling of the platinum methyl groups, and 180° rotation of the chelating ligand [2]. Alternatively, a succession of ligand trigonal shifts (Bailar twists) or ligand rhombic shifts (Ray-Dutt twists) permit the platinum methyl exchanges and effect

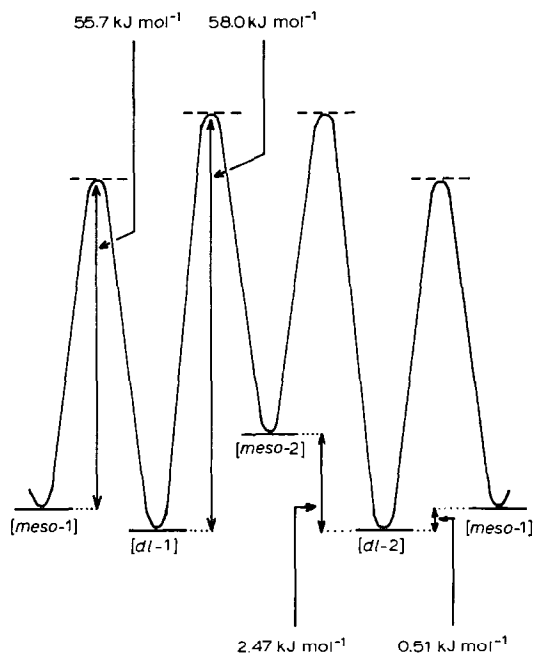


Fig. 6. Approximate energy profile for the interconversions of the invertomers of $[\text{PtClMe}_3(\text{MeS}(\text{CH}_2\text{S})_2\text{Me})]$.

ligand rotation, via pyramidal six coordinate transition configurations [11].

Whichever mechanism is operating, the high temperature spectra of these 2,4,6-trithiaheptane complexes provide the first direct evidence of an effective ligand rotation fluxion in S-chelate complexes. Such a fluxion has been postulated to be occurring in conjunction with platinum-methyl scrambling in open chain chelate complexes, e.g. $[\text{PtXMe}_3\{\text{MeE}(\text{CH}_2)_2\text{E}'\text{Me}\}]$ ($\text{E} = \text{E}' = \text{S}$ or Se , $\text{E} = \text{S}$, $\text{E} = \text{Se}$) [2]. However, it has proved impossible until now to compute its activation energy separately from that of the methyl scrambling fluxion.

TABLE 9

ARRHENIUS AND THERMODYNAMIC ACTIVATION ENERGIES FOR LIGAND ROTATION AND PLATINUM-METHYL SCRAMBLING IN $\{[\text{PtXMe}_3]\{\text{CH}_3\text{S}(\text{CH}_2\text{S})_2\text{CH}_3\}\}$

X	Process	E_a (kJ mol^{-1})	$\log_{10} A$	ΔH^\ddagger (kJ mol^{-1})	ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$)	ΔG^\ddagger (kJ mol^{-1}) ^a
Cl	Rotation	81.79 ± 1.32	13.49 ± 0.18	78.62 ± 1.31	3.10 ± 3.41	77.69 ± 0.29
	Scrambling	78.04 ± 1.11	12.58 ± 0.16	75.07 ± 1.13	-13.93 ± 3.16	79.22 ± 0.19
Br	Rotation	80.82 ± 3.42	13.27 ± 0.46	77.65 ± 3.39	-1.13 ± 8.89	77.99 ± 0.75
	Scrambling	81.38 ± 7.67	13.16 ± 1.08	78.31 ± 7.66	-2.99 ± 20.71	79.20 ± 1.49
I	Rotation	80.18 ± 4.68	13.14 ± 0.64	77.01 ± 4.64	-3.71 ± 12.18	78.12 ± 1.01
	Scrambling	82.70 ± 2.13	13.40 ± 0.31	79.68 ± 2.12	1.74 ± 5.84	79.16 ± 0.38

^a Calculated at 298.15 K.

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