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The preparation and dynamic behaviour of platinum(IV) derivatives of macrocyclic thioethers *

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Abstract

The complexes *fac*-[$PtMe_3L$]Cl (**1**: L = 1,4,7-trithiacyclononane; **2**: L = 1,4,7,10-tetrathiacyclododecane; or **3**: L = 10-oxa-1,4,7-trithiacyclododecane) have been prepared by reaction of L with [{$PtClMe_3$}$_4$] in $CDCl_3$. Variable temperature ^1H and $^{13}C\{^1H\}$ NMR studies have shown that the complex **2** undergoes a novel ligand commutation involving exchange between metal-coordinated and uncoordinated sulphur atoms of the macrocycle. In contrast, **1** and **3** exhibit temperature-invariant NMR spectra.

Introduction

The coordination chemistry of macrocyclic thioethers has received considerable attention recently. Complexes of such ligands have been shown to possess unusual electronic [1,2], electrochemical [3] and spectroscopic [4,5] properties, and have found important applications as biological model compounds [6,7] and as solvent extraction agents [8,9]. Macrocyclic sulphur ligands can also stabilise transition metals in unusual oxidation states [10], and the chemistry of their complexes can be markedly influenced by ligand conformation [11].

A number of the complexes of macrocyclic thioethers reported to date have been shown to possess structures in which not all the sulphur atoms available were utilised for metal coordination [10,12–14]. Species of this type are potentially

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* Dedicated to Prof. Colin Eaborn on the occasion of his 65th birthday.

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fluxional via exchange of sulphur atoms between coordinated and uncoordinated environments; however, to our knowledge, dynamic behaviour of this type has not fully been characterized. In order to assess the viability of this type of fluxional process, we have investigated the reactions of 1,4,7-trithiacyclononane, 1,4,7,10-tetrathiacyclododecane and 10-oxa-1,4,7-trithiacyclododecane with $[\{PtClMe_3\}_4]$, since trimethylplatinum(IV) halide derivatives of chalcogen ligands have already been shown to exhibit a wide range of fluxional processes [15]. We now wish to report the products of these reactions, and the results of variable temperature NMR studies performed upon them. A preliminary report on this work, including the crystal structure of **1**, has recently been published [16].

Experimental

Trimethylplatinum(IV) chloride [17] and 10-oxa-1,4,7-trithiacyclododecane [18] were prepared by established routes. The ligands 1,4,7-trithiacyclononane and 1,4,7,10-tetrathiacyclododecane (Aldrich Chemical Co.) were used without further purification.

Hydrogen-1, $^{13}C\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM250 FT spectrometer operating at 250.13, 62.90 and 53.53 MHz, respectively. The preparations of complexes **1**–**3** were monitored by ^1H NMR spectroscopy using a Hitachi/Perkin–Elmer R600 60 MHz FT spectrometer. Hydrogen-1 and ^{13}C chemical shifts are quoted relative to $SiMe_4$ as internal standard, whilst ^{195}Pt chemical shifts are quoted relative to $\Xi(^{195}Pt)$ 21.414 MHz. A standard variable temperature unit was used to control the probe temperature in the variable temperature experiments; temperatures were measured immediately before and after recording the spectra, and are considered accurate to ± 1 °C.

Bandshape analyses were performed using modified versions of the program DNMR of Kleier and Binsch [19,20].

Elemental analyses were performed by Butterworth Laboratories Ltd., London.

Synthesis of complexes

Complexes **1**–**3** were prepared by similar methods, complex **1** being isolated as a dihydrate. The preparation of **2** is given as a typical example.

Trimethylplatinum(IV) chloride (0.100 g, 0.36 mmol relative to the monomeric $PtClMe_3$ unit) and 1,4,7,10-tetrathiacyclododecane (0.131 g, 0.54 mmol) were stirred

Table 1

Synthetic and microanalytical data for complexes **1**–**3**

Complex	Yield (%) [a]	Melting point (°C) [b]	Analysis (Found (calcd.)(%))	
			C	H
1 [c]	75.8	260–270 dec.	22.1 (22.0)	5.0 (5.1)
2	74.7	230–240 dec.	25.6 (25.6)	5.1 (4.9)
3	24.6	164–168 dec.	26.5 (26.4)	5.3 (5.0)

[a] Relative to $[\{PtClMe_3\}_4]$. [b] Uncorrected. [c] Analytical data are quoted for the dihydrate, $\mathbf{1}\cdot 2H_2O$.

in $CDCl_3$ (20 cm^3) until no further change was observed in the ^1H NMR spectrum of the reaction mixture (ca. 24 h). After removal of solvent at reduced pressure, the remaining white solid was washed with hexane and diethyl ether, and recrystallised from dichloromethane/light petroleum (b.p. 40–60 °C) to yield colourless crystals of *fac*-$[\mathrm{PtMe_3}\{\overline{\mathrm{S(CH_2CH_2S)_3CH_2CH_2}}\}]\mathrm{Cl}$ (**2**) (Yield 0.140 g, 74.7%).

Yields, melting points and micro-analytical data are summarised in Table 1

Results and discussion

Complexes **1**–**3** were obtained in good yield by reaction of $[\{\mathrm{PtClMe_3}\}_4]$ with the appropriate macrocycle in $CDCl_3$ at room temperature, and were isolated as colourless, crystalline, air-stable solids, complex **1** being isolated as a dihydrate. The molecular structure [16] of **1** · $2H_2O$ is shown in Fig. 1, and selected bond lengths and angles are given in Table 2. The structure reveals an essentially octahedral geometry around platinum featuring *fac*-endodentate coordination of the macrocycle. The water molecules are loosely hydrogen-bonded to the chloride counterion. Comparison of the structures of the free [21] and complexed ligand show that the bond lengths and angles within the ligand do not vary significantly on coordination. However, there is a significant reduction in the S–S nonbonded distances (from 3.451 to 3.334 Å) and the S–C–C′–S′ torsional angles (from −58 to −51.5°, average). These variations have been observed previously in complexes of 1,4,7-trithiacyclononane [22,23], and have been attributed to the increased metal-sulphur orbital overlap that pertains as a result of such distortions [22]. The platinum-sulphur bond lengths average 2.407 Å and are markedly shorter than those observed in other trimethylplatinum(IV) complexes of acyclic thioethers [24,25]. Previous studies [26,27] have shown that 1,4,7-trithiacyclononane is much more strongly coordinating than simple acyclic thioethers; for example, the cation $[\mathrm{Fe(1,4,7\text{-}trithiacyclononane)_2}]^+$ contains low-spin iron(II) [26]. The short Pt^{IV}–S bonds in **1** · $2H_2O$ are a further consequence of the strongly coordinating nature of this ligand.

Hydrogen-1 and $^{13}C\{^1H\}$ NMR parameters for complexes **1**–**3** are given in Tables 3 and 4, respectively. These data confirm that **2** and **3** also feature *fac*-endodentate coordination of the macrocycle (Fig. 2), but in which respectively one sulphur atom in **2** or the oxygen atom in **3** is uncoordinated. Thus the ^1H NMR spectrum of **1** at 20 °C shows a single platinum-methyl resonance at δ 0.92 ppm. (^2J(Pt–H) 67.5 Hz), whilst the spectra of **2** and **3** at −30 °C exhibit two platinum-methyl resonances (intensity ratio 2/1) derived from methyl groups *trans* to S^1 and S^2, respectively (Fig. 2). The values of ^2J(Pt–H) in the range 66.0–67.5 Hz, are typical for platinum-methyl groups *trans* to thioether ligands and are similar to those observed in other cationic complexes of tridentate thioethers [28]. The methylene protons of **1** gave rise to an AA′BB′ multiplet, whilst more complex multiplets were observed for the methylene protons of **2** and **3**.

The $^{13}C\{^1H\}$ NMR spectra of **1**–**3** are also consistent with the proposed structures. In particular, **2** and **3** gave rise to two platinum-methyl resonances (with ^{195}Pt satellites, although the satellites for the platinum-methyl *trans* to S^2 in **3** were not resolved). The values of ^1J(Pt–C) in the range 590.0–629.3 Hz, are typical for platinum-methyl groups *trans* to coordinated thioether ligands [25,29]. The methylene carbons of **2** and **3** gave rise to four resonances, derived from the carbons labelled A, B, C and D in Fig. 2, with the resonance due to the carbons adjacent to

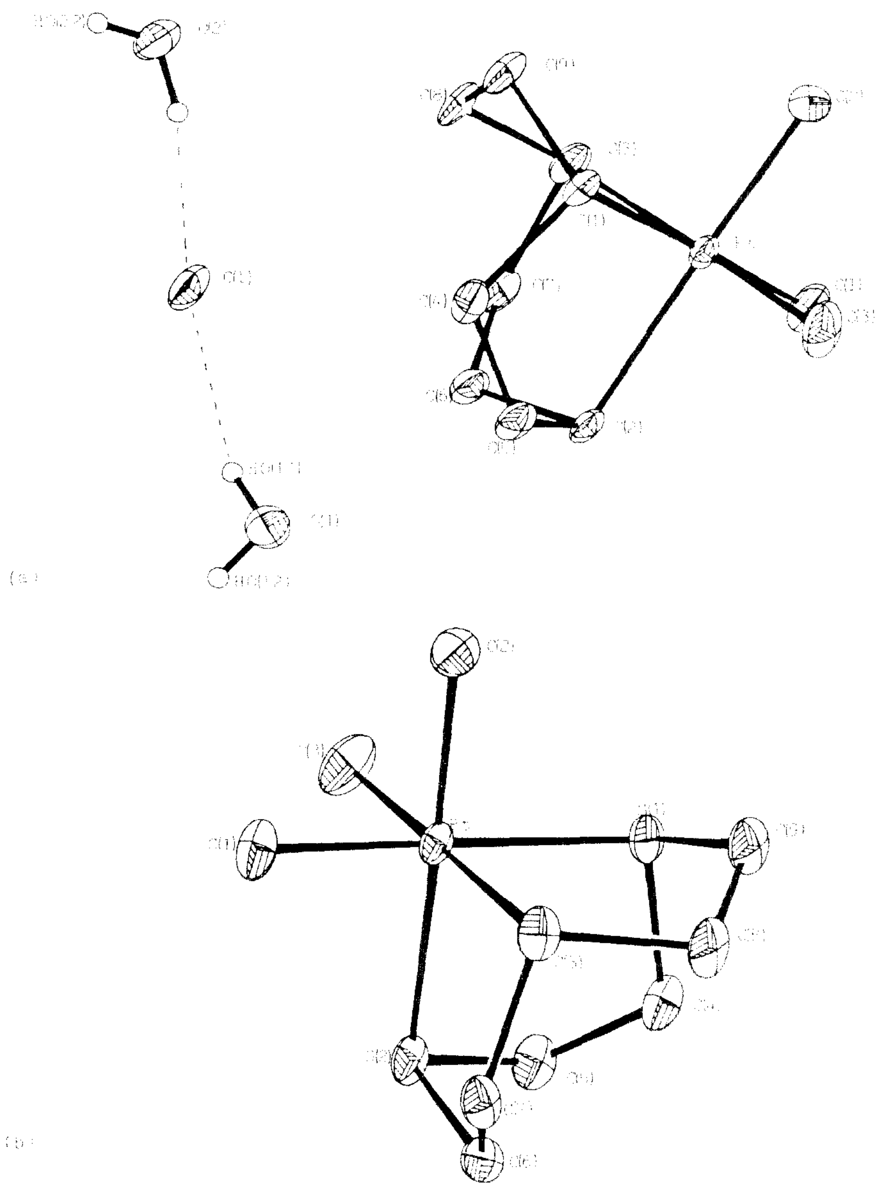

Fig. 1. The structure of $[PtMe_3(1,4,7\text{-trithiacyclonane})]Cl \cdot 2H_2O$ showing the atomic numbering scheme: (a) the complete structure; (b) an alternative view of the cation.

oxygen in **3** showing a marked upfield shift relative to the other methylene carbon signals. No clear trends are apparent in the $^{13}C\{^1H\}$ chemical shifts of either the platinum-methyl resonances or the ligand resonances in these complexes, although the platinum-methyl resonance of **1** shows a marked upfield shift in relation to similar resonances for **2** and **3**.

Table 2

Selected bond lengths (Å) and angles (deg) for the complex *fac*-[$PtMe_3$(1,4,7-trithiacyclononane)]Cl·$2H_2O$ [a]

(i) Bond lengths			
S(1)–Pt	2.411(3)	S(2)–Pt	2.405(3)
S(3)–Pt	2.405(3)	C(1)–Pt	2.073(7)
C(2)–Pt	2.087(7)	C(3)–Pt	2.075(7)
C(4)–S(1)	1.834(7)	C(9)–S(1)	1.818(7)
C(5)–S(2)	1.824(7)	C(6)–S(2)	1.827(7)
C(7)–S(3)	1.833(7)	C(8)–S(3)	1.830(7)
C(5)–C(4)	1.517(9)	C(7)–C(6)	1.510(9)
C(9)–C(8)	1.522(9)	HO(11)–O(1)	1.018(87)
HO(12)–O(1)	0.825(73)	HO(21)–O(2)	0.900(72)
HO(22)–O(2)	0.721(85)		
(ii) Bond angles			
S(2)–Pt–S(1)	87.8(1)	S(3)–Pt–S(1)	87.7(1)
S(3)–Pt–S(2)	88.4(1)	C(1)–Pt–S(1)	179.6(1)
C(1)–Pt–S(2)	91.9(3)	C(1)–Pt–S(3)	91.9(3)
C(2)–Pt–S(1)	93.2(3)	C(2)–Pt—S(2)	178.9(2)
C(2)–Pt–S(3)	92.0(3)	C(2)–Pt–C(1)	87.0(3)
C(3)–Pt–S(1)	92.7(3)	C(3)–Pt–S(2)	92.1(3)
C(3)–Pt–S(3)	179.3(2)	C(3)–Pt–C(1)	87.6(4)
C(3)–Pt–C(2)	87.4(4)	C(4)–S(1)–Pt	103.3(3)
C(9)–S(1)–Pt	99.7(3)	C(9)–S(1)–C(4)	101.9(4)
C(5)–S(2)–Pt	100.8(3)	C(6)–S(2)–Pt	103.3(3)
C(6)–S(2)–C(5)	101.6(3)	C(7)–S(3)–Pt	100.2(3)
C(8)–S(3)–Pt	103.8(3)	C(8)–S(3)–C(7)	102.5(4)
C(5)–C(4)–S(1)	113.0(4)	C(4)–C(5)–S(2)	114.4(4)
C(7)–C(6)–S(2)	114.8(4)	C(6)–C(7)–S(3)	115.4(4)
C(9)–C(8)–S(3)	112.5(5)	C(8)–C(9)–S(1)	114.9(4)
HO(12)–O(1)–HO(11)	93.1(62)	HO(22)–O(2)–HO(21)	124.3(81)

[a] Figures in parentheses are the estimated standard deviations of the least significant figures.

Platinum-195 NMR spectra have also been recorded for complexes **1**–**3** (Table 4), and in each case the spectrum consists simply of a singlet. However, the resonance observed for **1** shows a marked upfield shift relative to those observed for **2** and **3**, implying considerably stronger metal-sulphur bonding in **1** relative to **2** and **3** [30].

Table 3

Hydrogen-1 NMR parameters for the complexes **1**–**3** in $CDCl_3$

Complex	Temperature (°C)	Chemical shift δ (ppm) [a]		
		Pt–*Me* (*trans*-S^1)	Pt–*Me* (*trans*-S^2)	Methylene protons
1	20	0.92 (67.5) [b]	–	3.04–4.08 [c]
2	–30	0.86 (66.5)	1.53 (66.2)	2.78–4.55 [d]
3	–30	0.95 (67.2)	1.28 (67.5)	2.94–4.04 [d]

[a] Figures in parentheses are values of ^2J(Pt–H) in Hz. [b] Only one platinum-methyl environment for this complex. [c] AA′BB′ multiplet. [d] Complex.

Table 4

^{13}C-{^{1}H} and ^{195}Pt NMR parameters for the complexes **1–3**

Complex	Temperature (°C)	^{13}C {^{1}H} chemical shift δ (ppm) [a]			δ(^{195}Pt) (ppm)
		Pt–*Me* (*trans*-S^1)	Pt–*Me* (*trans*-S^2)	Methylene backbone carbons [b]	
1	20	−2.43 (596.6) [c]		36.03 (4.8)	730.7
2	−30	3.90 (627.3)	4.10 [d]	30.76 (D), 35.86 (12.9,C), 38.44 (B) [d], 39.46 (A) [d]	1087.8
3	−30	3.34 (629.3)	−0.53 (590.0)	33.07 (11.2,C), 34.58 (B) [d], 36.00 (A) [d], 64.27 (D)	1019.7

[a] Figures in parentheses are values of ^nJ(Pt–C) in Hz, where $n = 1$ for platinum-methyl signals, or $n = 2$ for methylene signals. [b] Assignments are based on the labelling scheme presented in Fig. 2. [c] Only one platinum-methyl environment for this complex. [d] Platinum-195 satellites not observed for this signal.

Variable temperature NMR studies

As noted above, metal complexes of macrocyclic thioethers which contain both coordinated and uncoordinated sulphur atoms offer the possibility of fluxional rearrangements involving the exchange of these coordinated and uncoordinated sulphur atoms. Accordingly, variable temperature ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded for **2** to ascertain whether this type of fluxionality indeed took place. Considering firstly the ^{1}H NMR spectra, at −30 °C the spectrum was consistent with the structure proposed in Fig. 2, featuring two platinum-methyl resonances and a complex multiplet for the methylene protons. On warming, broadening and coalescence in both regions of the spectra occurred, until at 60 °C a single platinum-methyl resonance was observed at δ 1.12 ppm (^2J(Pt–H) 66.9 Hz) together with an AA′BB′ multiplet for the methylene protons. Similar changes were observed in the ^{13}C{^{1}H} NMR spectra, so that at 60 °C a single platinum-methyl resonance was observed at δ 3.90 ppm (^1J(Pt–C) 619.2 Hz), along with a single methylene resonance at δ 35.83 ppm (^{195}Pt satellites were not resolved). The presence of a sharp singlet in both the ^{1}H and ^{13}C{^{1}H} NMR spectra, due to the presence of a small quantity of free ligand, throughout the temperature range over which spectra were recorded, confirmed the intramolecularity of the fluxionality.

These observations may be fully rationalised by the onset of a fluxionality of the type shown in Fig. 3, whereby the sulphur environments are exchanged by a ligand pivot mechanism involving a correlated series of 1,4-metallotropic shifts. Ligand pivot fluxionalities have been identified previously for bimetallic complexes of the type [(PtXMe$_3$)$_2$L] (X = Cl, Br or I), where L = 1,3,5-trithiane [31], 1,3,5,7-tetra-

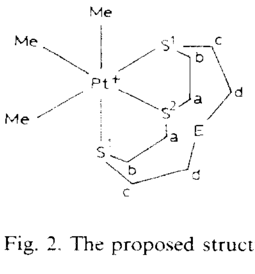

Fig. 2. The proposed structures of **2** (E = S) and **3** (E = O).

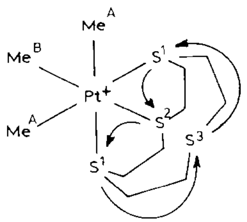

Fig. 3. The proposed mechanism of the ligand pivot fluxionality observed for **2**.

thiacane [32] or tris(methylthio)methane [33]. These fluxionalities have been shown to proceed via either 1,3- or 1,5-metal commutations, the latter mechanism applying for the complexes of tetrathiacane. Other metallotropic shifts of metal moieties in open-chain sulphur ligand complexes have involved 1,2- or 1,3-metal shifts [15]. This example thus represents the first observation of a 1,4-metallotropic shift in a transition metal complex of a sulphur ligand, and is also the first fully characterized example of a ligand pivot function in a macrocyclic thioether complex, but see ref. 14b.

Rate constants for the ligand pivot process were obtained from computer simulation of the platinum-methyl region of the variable temperature ^{1}H NMR spectra, the total spin problem being a combination of the sub-spin problems: $A \rightleftharpoons B$ (66.3%) and $AX \rightleftharpoons BX$ (33.7%). The later sub-spin set generates the ^{195}Pt satellites. Figure 4 compared the experimental and computer-synthesised spectra in this region between $-30\,°$C and $60\,°$C. The rate constants so obtained were used to calculate Arrhenius and Eyring activation parameters for the fluxionality: $E_a = 71.32 \pm 0.63$ kJ mol^{-1}, $\log_{10}A$ 15.34 ± 0.11, $\Delta H^{\ddagger}$ 68.91 ± 0.65 kJ mol^{-1}, $\Delta S^{\ddagger}$ 40.7 ± 2.2 J K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$ 56.79 ± 0.02 kJ mol^{-1} (at 298 K).

The free energy of activation $\Delta G^{\ddagger}_{298}$ for the rearrangement of **2** is the lowest observed to date for a ligand pivot fluxionality of this type; some comparative data are given in Table 5. The trends observed in the activation energies of these fluxionalities have previously been related to the degree of conformational flexibility of the coordinated ligand [15]. For example, the greater flexibility of the complexed tetrathiacane ring, relative to the complexed trithiane ring, is thought to reduce the availability of the uncoordinated sulphur atoms for involvement in the ligand pivot fluxionality, resulting in an increased activation barrier. On the basis of this argument, the low activation barrier obtained for this fluxionality in **2** suggests a relatively inflexible ligand conformation in this complex, with the uncoordinated sulphur atom favourably positioned for participation in the fluxionality.

Table 5

$\Delta G^{\ddagger}_{298}$ data for ligand pivoting in some platinum(IV) methyl complexes

Complex	$\Delta G^{\ddagger}_{298}$ (kJ mol^{-1})	Reference
2	56.79	This work
$[(PtClMe_3)_2(\overline{SCH_2SCH_2SCH_2})]$	58.79	31
$[(PtClMe_3)_2(\overline{SCH_2SCH_2SCH_2SCH_2})]$	65.82	32
$[(PtClMe_3)_2\{MeSCH(SMe)SMe\}]$	71.65	33
$[PtClMe_3\{(MeS)_2CHCH(SMe)_2\}]$	98.01	34

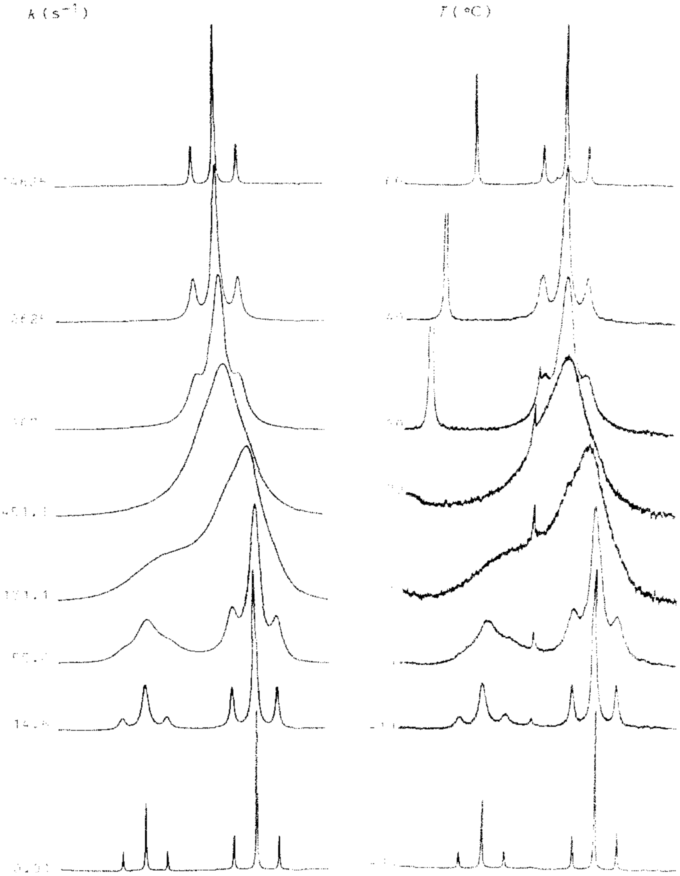

Fig. 4. Computer-simulated and experimental variable-temperature ^{1}H NMR spectra (platinum-methyl region) for **2** between −30 and +60 °C. The additional peak in the experimental spectra is due to H_2O. The static parameters (−30° C) used in the calculation off the rate constants for ligand pivoting were: ν_A 215.3 Hz, $^2J(Pt{-}H_A)$ 66.5 Hz, $\rho_A = 0.67$; ν_E 380.6 Hz, $^2J(Pt{-}H_B)$ 66.2 Hz, $\rho_B = 0.33$; T_2 0.20 s^{-1}; A represents the Pt–CH_3 protons *trans* to S^1 (Fig. 2), and B represents those *trans* to S^2.

In contrast to the results obtained for **2**, complexes **1** and **3** exhibit temperature invariant NMR spectra in the temperature range −90 °C to +60 °C. Thus, the presence of an uncoordinated sulphur atom in a complex of this type appears to be essential for low energy 1,4-metallotropic rearrangements to take place.

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References

1 E.J. Hintsa, J.R. Hartman and S.R. Cooper, J. Am. Chem. Soc., 105 (1983) 3738.
2 J.R. Hartman, E.J. Hintsa and S.R. Cooper, J. Chem. Soc., Chem. Commun., (1984) 386.

3 E.R. Dockal, T.E. Jones, W.F. Sokol, R.J. Engerer, D.B. Rorabacher and L.A. Ochrymowycz, J. Am. Chem. Soc., 98 (1976) 4322.
4 T.E. Jones, D.B. Rorabacher and L.A. Ochrymowycz, J. Am. Chem. Soc., 97 (1975) 7485.
5 N.S. Ferris, W.H. Woodruff, D.B. Rorabacher, T.E. Jones and L.A. Ochrymowycz, J. Am. Chem. Soc., 100 (1978) 5939.
6 D.F. Fenton in A.G. Sykes (Ed.), Advances in Inorganic and Bioinorganic Mechanisms, Academic Press, London, 1983, p. 187.
7 E.I. Solomon in T.G. Spiro (Ed.), Copper Proteins, Metal Ions in Biology, Wiley, New York, 1981, Vol. 3, p. 41.
8 D. Sevdić and H. Meider, J. Inorg. Nucl. Chem., 43 (1981) 153, and ref. therein.
9 K. Saito, Y. Masuda and E. Sekido, Anal. Chim. Acta, 151 (1983) 447.
10 A.J. Blake, R.O. Gould, A.J. Holder, T.I. Hyde, A.J. Lavery, M.O. Odulate and M. Schröder, J. Chem. Soc., Chem. Commun., (1987) 118.
11 T. Yoshida, T. Ueda, T. Adachi, K. Yamamoto and T. Higuchi, J. Chem. Soc., Chem. Commun., (1985) 1137.
12 M.N. Bell, A.J. Blake, M. Schröder and T.A. Stephenson, J. Chem. Soc., Chem. Commun., (1986) 471.
13 J.R. Hartman and S.R. Cooper, J. Am. Chem. Soc., 108 (1986) 1202.
14 (a) D.P. Riley and J.D. Oliver, Inorg. Chem., 22 (1983) 3361; (b) D. Parker, J.-M. Lehn and J. Rimmer, J. Chem. Soc. Dalton Trans., (1985) 1517.
15 E.W. Abel, S.K. Bhargava and K.G. Orrell, Prog. Inorg. Chem., 32 (1984) 1.
16 E.W. Abel, P.D. Beer, I. Moss, K.G. Orrell, V. Šik, P.A. Bates and M.B. Hursthouse, J. Chem. Soc., Chem. Commun., (1987) 978.
17 D.H. Goldsworthy, Ph.D. Thesis, University of Exeter, 1980.
18 J.S. Bradshaw, J.Y. Hui, B.L. Haymore and R.M. Izatt, J. Heterocyclic Chem., 10 (1973) 1.
19 D.A. Kleier and G. Binsch, J. Magn. Reson., 3 (1970) 146.
20 D.A. Kleier and G. Binsch, DNMR3 program 165, Quantum Chemistry Program Exchange, Indiana University, 1970.
21 R.S. Glass, G.S. Wilson and W.N. Setzer, J. Am. Chem. Soc., 102 (1980) 5068.
22 M.T. Ashby and D. Lichtenberger, Inorg. Chem., 24 (1985) 636.
23 W.N. Setzer, C.A. Ogle, G.S. Wilson and R.S. Glass, Inorg. Chem., 22 (1983) 266.
24 E.W. Abel, N.A. Cooley, K. Kite, K.G. Orrell, V. Šik, M.B. Hursthouse and H.M. Dawes, Polyhedron, 6 (1987) 1261.
25 E.W. Abel, I. Moss, K.G. Orrell, V. Šik, D. Stephenson, P.A. Bates and M.B. Hursthouse, J. Chem. Soc., Dalton Trans., in the press.
26 K. Wieghardt, H.J. Küppers and J. Weiss, Inorg. Chem., 24 (1985) 3067.
27 H.J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wieghardt, B. Nuber and J. Weiss, Inorg. Chem., 25 (1986) 2400.
28 E.W. Abel, K. Kite and P.S. Perkins, Polyhedron, 5 (1986) 1459.
29 E.W. Abel, K.G. Orrell and A.W.G. Platt, J. Chem. Soc., Dalton Trans., (1983) 2345.
30 P.L. Goggin, R.J. Goodfellow, S.R. Haddock, B.F. Taylor and I.R.H. Marshall, J. Chem. Soc., Dalton Trans., (1976) 459.
31 E.W. Abel, M. Booth, G.D. King, K.G. Orrell, G.M. Pring and V. Šik, J. Chem. Soc., Dalton Trans., (1981) 1846.
32 E.W. Abel, G.D. King, K.G. Orrell, V. Šik, T.S. Cameron and K. Jochem, J. Chem. Soc., Dalton Trans., (1984) 2047.
33 E.W. Abel, T.E. MacKenzie, K.G. Orrell and V. Šik, J. Chem. Soc., Dalton Trans., (1986) 2173.
34 E.W. Abel, T.P.J. Coston, K.G. Orrell and V. Šik, unpublished observations.