# The Preparation and Dynamic Behaviour of Platinum(IV) Derivatives of Macrocyclic Sulphides; The X-Ray Crystal Structure of *fac*-[PtMe$_3\overline{\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{SCH}_2\text{C}}\text{H}_2$]Cl·2H$_2$O

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The complexes *fac*-[PtMe$_3$L]Cl, where L = 1,4,7-trithiacyclononane (**1**), 1,4,7,10-tetrathiacyclododecane (**2**), and 10-oxa-2,4,7-trithiacyclododecane (**3**), have been prepared, and the *X*-ray crystal structure of (**1**), isolated as a dihydrate, has been obtained; variable-temperature $^1$H and $^{13}$C-{$^1$H} n.m.r. studies of (**2**) have revealed a novel ligand commutation involving exchange between metal-co-ordinated and unco-ordinated sulphur atoms of the macrocycle.

The co-ordination chemistry of macrocyclic sulphides has received considerable attention recently. Complexes of such ligands possess unusual electronic,[1] electrochemical,[2] and spectroscopic[3] properties, as well as a rich solution chemistry;[4] and they have found important applications as biological model compounds.[5] A number of complexes of such ligands have been characterised[4,6] in which not all sulphur atoms available were used for metal co-ordination. Species of this type are potentially fluxional *via* exchange of sulphur atoms between co-ordinated and unco-ordinated environments;

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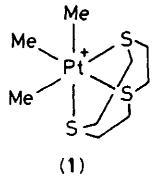
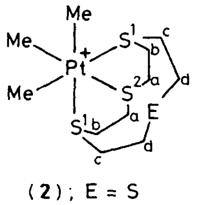
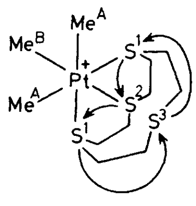


(1)



(2); E = S
(3); E = O



**Scheme 1**

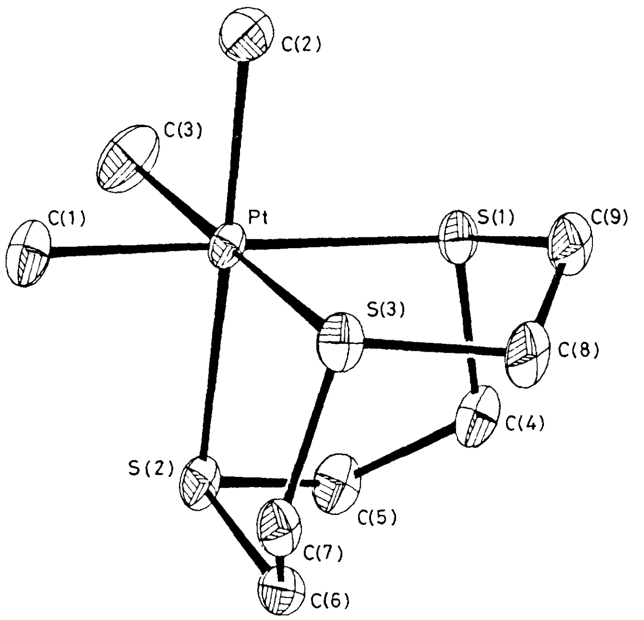


**Figure 1.** Crystal structure of the cation of (**1**), showing the atomic numbering scheme. Selected bond distances (Å) and angles (degrees) around platinum: Pt–S(1) 2.411, Pt–S(2) 2.405(3), Pt–S(3) 2.405(3), Pt–C(1) 2.073(7), Pt–C(2) 2.087(7), Pt–C(3) 2.075(7); S(2)–Pt–S(1) 87.8(1), S(3)–Pt–S(2) 88.4(1), S(3)–Pt–S(1) 87.7(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(1)–Pt–C(2) 87.0 (3), C(1)–Pt–C(3) 87.6(4). The water molecules were loosely hydrogen-bonded to the chloride counterion at a distance of 2.293 Å (average).

however, dynamic behaviour of this type has not been reported to date. 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 remarkable range of fluxional characteristics.[7] We report herein the products of these reactions, and the results of variable-temperature n.m.r. studies conducted upon them.

Reaction of $[PtClMe_3]_4$ with an excess of the appropriate macrocycle in $CDCl_3$ (24 h, room temperature), followed by removal of solvent and recrystallisation from dichloromethane–hexane, gave colourless crystals of (**1**)—(**3**) in good yield (50—70%),‡ complex (1) being isolated as a dihydrate.

The *X*-ray crystal structure§ of (**1**) (Figure 1) confirms the ionic nature of the product, with the sulphide ligand co-ordinated in a *fac*-endodentate fashion to platinum. The Pt–S bond lengths (averaging 2.407 Å) are the shortest reported to date for a trimethylplatinum(IV) derivative of a sulphide,[8] a reflection of the previously noted strongly co-ordinating nature of 1,4,7-trithiacyclononane.[9] The $^1H$ and $^{13}C$-{$^1H$} n.m.r. spectra¶ of (**2**) and (**3**) show that these complexes adopt similar structures in which, however, either one of the sulphur atoms in the tetrathiacyclododecane or the oxygen atom in the oxatrithiacyclododecane is unco-ordinated. In particular, the values of $^3J$(Pt–H) and $^2J$(Pt–C) for the platinum methyl resonances are typical for such groups when *trans* to a sulphide ligand.[10] These represent the first examples of $Pt^{IV}$ complexes of macrocyclic sulphides, although co-ordination of such ligands to Pt(II) has recently been described.[11]

The $^1H$ n.m.r. spectrum¶ of (**2**) at 243 K exhibits two platinum methyl resonances (intensity 2:1), assigned to methyl groups *trans* to $S^1$ and $S^2$ respectively, and a complex methylene signal. On warming, broadening and coalescence occurs in both regions until at 333 K a single platinum methyl signal [δ 1.12, $^3J$(Pt–H) 66.9 Hz] is observed, and the methylene resonance simplifies to an AA′BB′ multiplet.

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‡ Satisfactory n.m.r. [$^1H$, $^{13}C$-{$^1H$}, and $^{195}Pt$] and microanalytical data were obtained for all complexes.

§ *Crystal data:* $C_9H_{21}ClPtS_3 \cdot 2H_2O$, $M = 492.02$, triclinic, space group $P\bar{1}$ (No. 2), $a = 8.425(2)$, $b = 13.962(2)$, $c = 7.845(2)$ Å, $\alpha = 81.47(2)$, $\beta = 115.56(2)$, $\gamma = 101.64(1)°$; $U = 813.4(3)$ Å$^3$, $D_c = 1.357$ g cm$^{-3}$, $Z = 2$, $F(000) = 476$, $\lambda = 0.71069$ Å, $\mu$(Mo-$K_\alpha$) = 92.4 cm$^{-1}$. Crystal dimensions 0.38 × 0.18 × 0.10 mm. The structure was solved by the heavy-atom technique and refined by full-matrix least-squares, using absorption corrected data [CAD4 diffractometer, Mo-$K_\alpha$ radiation, graphite monochromator, $3 \leqslant 2\theta < 50°$, $h(-10 \rightarrow 10)$, $k\ (-16 \rightarrow 16)$, $l\ (0 \rightarrow 9)$, 3084 reflections, 2517 independent, $I \geqslant 3\sigma(I)$]. All non-hydrogen atoms were refined anisotropically. Methyl hydrogen atoms were placed in calculated positions (C–H = 0.96 Å, $U$ = 0.10 Å), while the remaining hydrogen atoms, including those of the solvated water molecules, were allowed unrestricted isotropic refinement. A total of 218 parameters were refined, and the final residuals $R$ and $R_w$ were 0.020 and 0.021 respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ *Selected n.m.r. data* [$CDCl_3$ solution, 250 MHz, δ relative to $Me_4Si$]: (**1**) $^1H$: 0.92 [9H, Pt$CH_3$, $^3J$(Pt–H) 67.5 Hz], 3.04—4.08 [AA′BB′ m, 12 H, –S$CH_2CH_2$S–] $^{13}C$-{$^1H$}: −2.43 [Pt$CH_3$, $^2J$(Pt–C) 596.6 Hz], 36.03 [–S$CH_2CH_2$S–, $^3J$(Pt–C) 4.8 Hz]. (**2**) $^1H$: 0.86 [6H, Pt$CH_3$ *trans* $S^1$, $^3J$(Pt–H) 66.5 Hz], 1.53 [3H, Pt$CH_3$ *trans* $S^2$, $^3J$(Pt–H) 66.2 Hz], 2.73—4.55 [m, 16H, –S$CH_2CH_2$S–] $^{13}C$-{$^1H$}: 3.90 [Pt$CH_3$ *trans* $S^1$, $^2J$(Pt–C) 627.3 Hz], 4.10 [Pt$CH_3$ *trans* $S^2$], 30.76 [$CH_2$, (d)], 35.86 [$CH_2$, (c), $^3J$(Pt–C) 12.9 Hz], 38.44 [$CH_2$, (b)], 39.46 [$CH_2$, (a)]. (**3**) $^1H$: 0.95 [6H, Pt$CH_3$ *trans* $S^1$, $^3J$(Pt–H) 67.2 Hz], 1.28 [3H, Pt$CH_3$ *trans* $S^2$, $^3J$(Pt–H) 67.5 Hz], 2.94—4.04 [m, 16H, –S$CH_2CH_2$S–] $^{13}C$-{$^1H$}: −0.53 [Pt$CH_3$ *trans* $S^2$, $^2J$(Pt–C) 590.0 Hz], 3.34 [Pt$CH_3$ *trans* $S^1$, $^2J$(Pt–C) 629.3 Hz], 33.07 [$CH_2$, (c), $^3J$(Pt–C) 11.2 Hz], 34.58 [$CH_2$, (b)], 36.00 [$CH_2$, (a)], 64.27 [$CH_2$, (d)]. Spectra were recorded at either 293 K [(**1**)] or 243 K [(**2**) and (**3**)].

Similar changes are seen in the $^{13}C-\{^1H\}$ n.m.r. spectra; the four methylene carbon resonances coalesce to give a *single* methylene carbon signal [δ 35.83] at 333 K, and the two platinum methyl resonances seen at 243 K coalesce to give a single resonance at 333 K [δ 3.90, $^2J$(Pt–C) 619.2 Hz]. These spectral changes are fully consistent with the onset of an intramolecular ligand rotation fluxion proceeding *via* a series of correlated 1,4-metallotropic shifts (Scheme 1). Rate constants for this fluxion were obtained by computer simulation of the platinum-methyl region of variable-temperature $^1H$ n.m.r. spectra in the temperature range 243—333 K, and $\Delta G^‡$ (298.15 K) for the fluxion was found to be 56.79 ± 0.02 kJ $mol^{-1}$. In contrast, the n.m.r. spectra of (**1**) and (**3**) were found to be invariant over the same temperature range, indicating that the presence of at least one unco-ordinated sulphur atom is necessary for the onset of this particular movement.

Ligand pivot fluxions of cyclic chalcogen ligands have been reported and well characterised previously,[7] but all have occurred *via* either 1,3- or 1,5-metal commutations; 1,4-metallotropic shifts are also unknown to date for complexes of acyclic chalcogen ligands. The value of $\Delta G^‡$ (298.15 K) obtained for the ligand rotation in (**2**) is the lowest so far observed for any such ligand pivot fluxion, and suggests a restricted degree of conformational flexibility in the co-ordinated macrocycle[7] which geometrically favours the fluxion. Although this example represents the first report of a ligand fluxion involving exchange of co-ordinated and unco-ordinated sulphur atoms in a complex of a macrocyclic sulphide, the relatively low activation barrier determined suggests that dynamic behaviour of this type may be more widespread.

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