

Unusual Structure and Novel Fluxional Rearrangements in the s-Trithian Complex $[(\text{Me}_3\text{PtCl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$; X-Ray Crystal Structure Determination

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Summary The tetrameric chlorotrimethylplatinum $[(\text{Me}_3\text{PtCl})_4]$ reacts with s-trithian to form the dinuclear complex $[(\text{Me}_3\text{PtCl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$, the crystal structure of which reveals that the 6-membered cyclic ligand is in the boat conformation rather than the more usual chair conformation; on warming a solution of the complex, the dinuclear platinum moiety commutes between pairs of sulphur atoms in an intramolecular manner, which necessitates a change in ring conformation.

We have recently reported the fluxional nature of several complexes of linear bidentate organosulphur ligands with trimethylplatinum halides.¹ These have been demonstrated to undergo a remarkable range of fluxions observable on the n.m.r. time scale, notably ring reversal, pyramidal ligand atom inversion, ligand atom commutations, and platinum-methyl scrambling.

The observation² that the individual methyl signals in the trithian complex $[\text{W}(\text{CO})_5(\text{MeCHS})_3]$ coalesce at raised temperature may be due to the metal atom undergoing 1,3-jumps from sulphur to sulphur in the ligand. We are

carrying out a detailed investigation of such metal-sulphur ligand shifts and report herein the structure of a new type of complex and its novel fluxionality.

s-Trithian undergoes reaction with the tetrameric $[(\text{Me}_3\text{PtCl})_4]$ to yield the dinuclear complex $[(\text{Me}_3\text{PtCl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$. *Crystal data:* $\text{C}_9\text{H}_{24}\text{Cl}_2\text{Pt}_2\text{S}_3$; M 689.57 monoclinic, space group $P2_1/c$; $Z = 4$; $a = 9.872(1)$, $b = 14.289(2)$, $c = 12.951(2)$ Å, $\beta = 106.83(1)^\circ$; $U = 1748.63$ Å³; $F(000) = 1264$ e; $\mu = 62.06$ cm⁻¹; $\lambda = 0.70926$ Å (Mo- K_α); $D_c = 2.628$ g cm⁻³.

The cell parameters were refined from the circle angles of 12 reflections in the range $\theta = 14$ – 16° , on a CAD-4 four-circle diffractometer. 2093 independent reflections were measured, of which 1557 had $I > 3\sigma(I)$. The data were reduced following the usual procedure.³ The structure was solved in a straightforward way using the Sheldrick X-ray system,⁴ and refined by full-matrix least-squares, with the temperature factors anisotropic for the Pt, Cl, and S atoms, and isotropic for the carbons. Hydrogen atoms were not located. The refinement converged at $R = 0.047$ with a weighting scheme $w = [\sigma^2 | F_0 | = 0.0453(F_0)^2]^{-1}$ where σ

is the individual reflection e.s.d. derived from the counting statistics. Scattering factors were taken from ref. 5, and were corrected for the anomalous dispersion effect. A view of the molecule is shown in Figure 1.†

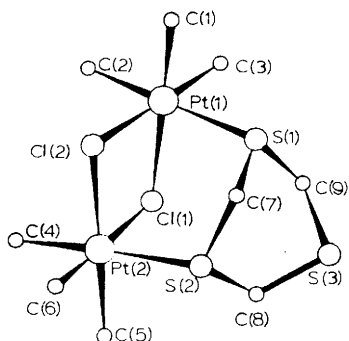


FIGURE 1. View of the complex $[(\text{Me}_3\text{PtCl})_2(\text{SCH}_2\text{SCH}_2\text{SCH}_2)]$.

The molecule contains two platinum atoms both of which have an approximate octahedral co-ordination sphere. These platinum atoms are bridged by two chlorine atoms with a $\text{Pt} \cdots \text{Pt}$ contact distance of 3.621(1) and $\text{Pt}-\text{Cl}-\text{Pt}$ angles of 92.5(2) and 93.3(2)°; thus⁶ there is clearly no $\text{Pt}-\text{Pt}$ bond.

The two platinum atoms are also bridged by the S_3C_3 ring, with $\text{Pt}(1)-\text{S}(1)$ and $\text{Pt}(2)-\text{S}(2)$ distances of 2.458(5) and 2.473(6) Å; the $\text{S}(1) \cdots \text{S}(2)$ contact distance is 3.11(1) which is considerably shorter than the $\text{Pt} \cdots \text{Pt}$ contact. The $\text{S}(1) \cdots \text{S}(3)$ and $\text{S}(2) \cdots \text{S}(3)$ distances are both 3.04(1) and the $\text{S}(1)-\text{C}(7)-\text{S}(2)$ angle is 119(1)° while the other two $\text{S}-\text{C}-\text{S}$ angles are both 113°. Thus the S_3C_3 ring is distorted by the stretching of the $\text{S}(1) \cdots \text{S}(2)$ distance to span the two platinum atoms. The ring itself has the unusual distorted boat conformation (Figure 1).

Below -30 °C the ^1H n.m.r. solution spectrum of the complex corresponds exactly to that expected for the 'static' structure (Figure 1), *i.e.* three signals (δ 1.635, 1.092, and 0.831) for the different $\text{Pt}-\text{Me}$ environments and two AB

quartet patterns (intensity ratio 2:1) centred at δ 4.459 and 4.892 respectively due to the two types of methylene groups. All the above protons show coupling to one or two ^{195}Pt nuclei. Between -30 and 30 °C the two lowest-frequency signals due to the $\text{Pt}-\text{Me}$ *trans* to the bridging Cl atoms coalesce to a single line (δ 0.959 at 30 °C), and in the methylene region the two AB quartets coalesce to a single AB quartet. The changes in both the $\text{Pt}-\text{Me}$ and methylene regions correspond to an intramolecular series of 1,3-shifts. This involves the dinuclear metallic moiety in commuting between pairs of sulphur atoms (Figure 2).

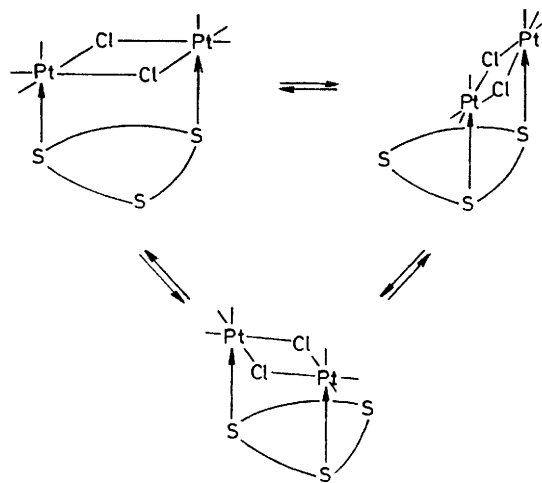


FIGURE 2. Commutation of the dinuclear $(\text{Me}_3\text{PtCl})_2$ moiety over the *s*-trithian ring.

It is notable, however, that in order to account for the above intramolecular 1,3 shifts, a change in ring conformation from boat to chair is almost certainly involved. In all these changes the retention of $^{195}\text{Pt}-\text{S}-\text{C}-^1\text{H}$ spin-spin coupling in the n.m.r. spectra emphasises the truly intramolecular non-dissociative nature of these motions.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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