

## Isolation of Intermediates in the Acid Hydrolysis of $[\text{Pt}(\text{PPh}_3)_2(\text{O}_2)]$ ; the X-Ray Structure of $[\text{Pt}_2(\text{O}_2)(\text{OH})(\text{PPh}_3)_4][\text{ClO}_4] \cdot 2\text{C}_6\text{H}_6$

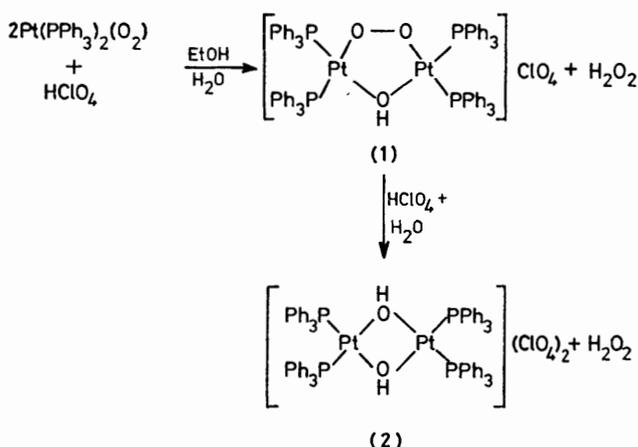
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**Summary** The hydrolysis of  $[\text{Pt}(\text{PPh}_3)_2(\text{O}_2)]$  with non-co-ordinating acids leads to the formation of  $[\text{Pt}_2(\text{O}_2)(\text{OH})(\text{PPh}_3)_4][\text{X}]$  (**1**) ( $\text{X} = \text{ClO}_4, \text{PF}_6, \text{BF}_4, \text{NO}_3$ ), and then  $[\text{Pt}_2(\text{OH})_2(\text{PPh}_3)_4][\text{X}]_2$  (**2**), with a stepwise loss of  $\text{H}_2\text{O}_2$ ; the structure of (**1**) has been confirmed by an X-ray analysis.

THE reactions of molecular oxygen, when bound to a transition metal atom, are of interest because of their relevance, as models, to the reversible oxygenation of haemoproteins and related systems.<sup>1</sup> There have been reports of the acid catalysed hydrolysis of metal complexes containing a peroxy bridge or dioxygen ligand, producing  $\text{H}_2\text{O}_2$ ,<sup>2</sup> but none of these studies describes the isolation or characterization of the intermediates involved in the reactions. We report a novel binuclear platinum intermediate, containing both bridging peroxy- and hydroxo-groups.



The addition of ethanolic HX ( $\text{X} = \text{ClO}_4, \text{BF}_4, \text{PF}_6, \text{NO}_3$ ) to a dichloromethane solution of  $[\text{Pt}(\text{O}_2)(\text{PPh}_3)_2]$  in 1:2 molar ratio leads to a colour change from orange to yellow. Yellow crystals of  $[\text{Pt}_2(\text{O}_2)(\text{OH})(\text{PPh}_3)_4][\text{X}]$  (**1**) may be deposited by the addition of diethyl ether, and recrystallized from dichloromethane-benzene. The i.r. spectrum exhibits a strong band at  $3560 \text{ cm}^{-1}$  assigned to the bridging hydroxo-group. Conductometric measurements establish that all the complexes are 1:1 electrolytes.

Further treatment of (**1**) with aqueous HX yields the known<sup>3</sup> dihydroxo-bridged complex  $[\text{Pt}_2(\text{OH})_2(\text{PPh}_3)_4][\text{X}]_2$  (**2**). Both reaction steps are accompanied by the production of  $\text{H}_2\text{O}_2$ , which has been confirmed by iodometric titration.

In order to establish the nature of the bridging groups in (**1**) a single-crystal X-ray analysis of the perchlorate derivative has been undertaken.

**Crystal data:**  $[\text{C}_{72}\text{H}_{60}\text{O}_3\text{P}_4\text{Pt}_2][\text{ClO}_4] \cdot 2\text{C}_6\text{H}_6$ ,  $M = 1743.94$ , triclinic,  $a = 14.884(3)$ ,  $b = 15.281(3)$ ,  $c = 16.744(4) \text{ \AA}$ ,  $\alpha = 90.06(2)$ ,  $\beta = 108.65(2)$ ,  $\gamma = 93.11(2)^\circ$ ,  $U = 3602.3 \text{ \AA}^3$ ,  $D_c = 1.61 \text{ g cm}^{-3}$ ,  $Z = 2$ ,  $\mu(\text{Mo-K}\alpha) = 40.64 \text{ cm}^{-1}$ , space group  $P\bar{1}$ . 10 806 intensities were recorded on a Nonius CAD4 four-circle diffractometer using zirconium-filtered Mo-K $\alpha$  radiation. A numerical absorption correction was applied, and the 5359 unique observed intensities [ $I > 2.5\sigma(I)$ ] were used in the structure solution. The two unique Pt atoms were located by multisolution  $\Sigma_2$  sign expansion, and all the non-hydrogen atoms from subsequent Fourier difference syntheses. The phenyl groups, including H atoms, were refined as rigid groups with idealised geometry

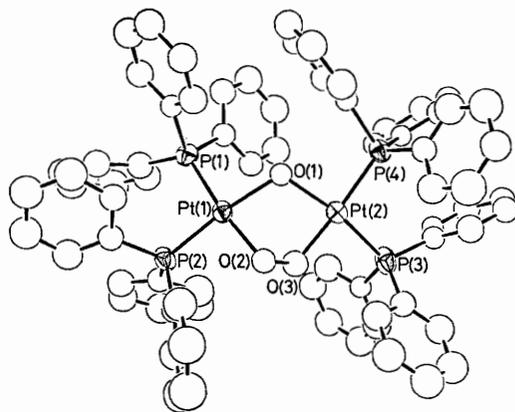


FIGURE. The molecular structure of  $[\text{Pt}_2(\text{O}_2)(\text{OH})(\text{PPh}_3)_4]^+$ . Some bond parameters are: Pt(1)-O(1), 2.077(16); Pt(1)-O(2), 1.990(21); Pt(2)-O(1), 2.096(17); Pt(2)-O(3), 2.012(19); O(2)-O(3), 1.547(21); Pt(1)-P(1), 2.245(9); Pt(1)-P(2), 2.208(7); Pt(2)-P(3), 2.274(8); Pt(2)-P(4), 2.258(7) Å;  $\angle \text{O}(1)\text{-Pt}(1)\text{-O}(2)$ , 81.0(7);  $\angle \text{O}(1)\text{-Pt}(2)\text{-O}(3)$ , 85.8(7);  $\angle \text{Pt}(1)\text{-O}(1)\text{-Pt}(2)$ , 112.7(8);  $\angle \text{Pt}(1)\text{-O}(2)\text{-O}(3)$ , 101.5(13);  $\angle \text{Pt}(2)\text{-O}(3)\text{-O}(2)$ , 104.0(12);  $\angle \text{Pt}(1)\text{-P}(1)\text{-P}(2)$ , 96.8(3);  $\angle \text{P}(3)\text{-Pt}(2)\text{-P}(4)$ , 100.0(3)°.

(C-C 1.395, C-H 1.08 Å;  $\angle \text{C-C-C}$  120, C-C-H 120°). The perchlorate oxygens were disordered, and a rigid model consisting of two interlocking tetrahedra, having occupancies of 0.64 and 0.36, with Cl-O and O...O distances fixed at 1.42 and 2.32 Å, respectively, was used in refinement. Two benzene solvent molecules were also located; one was refined as a regular hexagon, and the other, which was disordered, was fixed as two interlocking hexagons with a combined site occupancy of unity. The structure was

refined by a blocked sparse-matrix least-squares technique (with Pt, P, Cl anisotropic, C, O isotropic and H common isotropic temperature factors) to a converged  $R$  of 0.086, and a corresponding  $R_w$  [ $=\sum w^{\frac{1}{2}}\Delta/\sum w^{\frac{1}{2}}|F_o|$ ] = 0.088.†

The molecular geometry of the cation is shown in the Figure, which includes some important bond lengths and angles. Both Pt atoms exhibit planar co-ordination geometry, while the Pt...Pt distance of 3.475 Å is non-bonding. The Pt(1)–O(2)–O(3)–Pt(2) torsion angle is 79.0°, and the O(2)–O(3) distance is indicative of the presence of a peroxo-group, being in agreement with the range of values (1.45–1.53 Å) found in a number of peroxo-bridged complexes.<sup>3</sup> The bridging hydroxo-group completes the puckered  $\text{Pt}(\text{O}_2)\text{PtO}$  five-membered ring.

This structure appears to be the first crystallographic evidence for a peroxo-hydroxo-dibridged binuclear metal complex. Bridged, binuclear platinum species, with donor sulphur or halogen atoms, are known,<sup>4</sup> but bridging oxygen-containing ligands are more common for the first row transition elements, notably cobalt.<sup>5</sup>

The Pt(1)–O(2) and Pt(2)–O(3) distances are in good agreement with the Pt–O(peroxo) bond lengths of 2.006(7) Å, and 2.00 Å in  $[(\text{Ph}_3\text{P})_2\text{PtO}_2]\cdot 2\text{CHCl}_3$ <sup>6</sup> and  $[(\text{Ph}_3\text{P})_2\text{Pt}(\text{O}_2)\text{-OCMe}_2]$ ,<sup>7</sup> respectively. The Pt–O(hydroxo) bond lengths are ca. 0.01 Å longer, and similar to the value of 2.01 Å for the Pt–O(C) bond in the ketonic complex.<sup>7</sup>

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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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