H-Bonding Directs H₂O₂ Oxidation of Platinum(II) to a *cis*-Dihydroxo Platinum(IV) Complex

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The use of ligands with proximate hydrogen bonding substituents in the oxidation of platinum(II) dimethyl complexes with H₂O₂ leads to the exclusive formation of an unusual *cis*-dihydroxo platinum(IV) complex, which can dehydrate to form a trinuclear metalla-azacrown complex.

The selective oxidation of methane to methanol, catalysed by electrophilic late transition metals such as platinum, has attracted much interest since the first observations by Shilov and Gol'dshleger in the late 1960s.^{1,2} The mechanism of the overall reaction (Eq. 1), as proposed by Shilov,^{3,4} consists of three steps: 1) C-H activation at a Pt(II) centre generating a Pt-Me bond^{5,6} 2) oxidation of the Pt(II) centre to Pt(IV) and 3) functionalisation of the methyl group *via* reductive elimination of methanol and regeneration of the Pt(II) complex.⁴ In the original Shilov reaction, the second step was carried out by a stoichiometric Pt(IV) oxidant. Several alternative oxidants have been investigated, but so far with limited success, for example O₂,⁷ Cl₂,⁸ SO₃⁹ and H₂O₂.¹⁰ We have investigated here the reaction between H₂O₂ and dimethylplatinum(II) complexes with the aim to generate *cis*-dihydroxo platinum(IV) dimethyl complexes that can subsequently generate methanol *via* a C-O reductive elimination process (Eq. 2).

The oxidative addition reaction of H₂O₂ or related compounds of the type RXXR, where X = O, S or Se, generally results in the formation of *trans*-L₂Pt(XXR)₂ complexes.¹¹⁻¹⁷ Octahedral *trans*-dihydroxo Pt(IV) complexes are plentiful and rather unreactive due to the low spin d⁶ configuration and the weak *trans* effect of the hydroxo ligand. If the oxidative addition reaction of H₂O₂ could be directed to the more reactive *cis*-dihydroxo Pt(IV) alkyl intermediate, this would offer the possibility of tuning the Pt-C and Pt-O bond strengths by the ancillary ligand and induce a C-O reductive elimination to the desired methanol product.¹⁸ However, only in a few cases, for example in the reaction of PhOCOCOPh or PhSSPh with [(phen)PtMe₂] (phen = phenanthroline), minor amounts of the *cis* isomer have been observed alongside the major *trans* isomer.¹⁵ The first exclusive formation of a *cis*-dihydroxo Pt(IV) alkyl complex was recently reported by Vedernikov and co-workers. By using a facially coordinating tridentate ligand which forces the two hydroxo ligands *cis* to each other, they indeed observed the formation of methanol.¹⁹

We have targeted here the synthesis of *cis*-dihydroxo Pt(IV) dimethyl complexes *via* the oxidative addition reaction of H₂O₂ with platinum(II) dimethyl complexes containing ligands with H-bonding amine substituents.²⁰⁻²³ The role of these H-bonding substituents is to stabilise *cis*-dihydroxo platinum(IV) intermediates and prevent their rearrangement to *trans*-dihydroxy Pt(IV) complexes.

The addition of an excess of H₂O₂ (35 wt% aqueous solution) to the complex [(6,6'-diaminobipy)Pt(II)Me₂] **1** in acetone as the solvent at room temperature results in the immediate precipitation of a yellow product. This compound **2** is sparingly soluble in acetone but readily dissolves in a D₂O/d⁶-acetone mixture. The ¹H NMR spectrum in this solvent mixture shows two signals of equal intensity at δ = 1.68 ppm (²J_{H-Pt} = 67.5 Hz) and 0.93 ppm (²J_{H-Pt} = 65.9 Hz), which suggest two distinctly different Pt(IV)-CH₃ groups. When the yellow compound **2** is dissolved in d⁷-DMF, the ¹H and ¹³C NMR spectra show six Pt(IV)-CH₃ signals of equal intensity and a complex pattern in the aromatic region (see Figure S1). X-ray analysis of crystals, grown by cooling a saturated acetone solution, revealed that complex **2** is a trinuclear Pt(IV) complex with three linked PtMe₂(OH)(L) units joined together by N-Pt bonds to form a 12-membered metalla-azacrown complex (see Equation 3 and Figure 1).[‡] One of the NH₂ substituents on the bipyridine ligand of one PtMe₂(OH)(L) unit has been deprotonated and binds to the platinum centre of the next, and so on. The possibility of 3-fold symmetry for the trinuclear complex is broken by the chirality of the individual complexes. In the stereoisomer shown in Figure 1, for both Pt(1) and Pt(2) the ligand orientation results in *S* configuration, whilst for Pt(3) the ligands are oriented to give an *R* configuration. There does not appear to be any steric reason for this preferred arrangement. In d⁷-DMF solution, this trinuclear structure of **2** is maintained resulting in six distinct Pt-Me signals due to the lack of symmetry.

The trinuclear complex **2** is only sparingly soluble in acetone, but upon the addition of H₂O, the equilibrium due to the loss of water as shown in Eq. 3 is reversed. This results in the exclusive formation of the *cis*-dihydroxo Pt(IV) dimethyl complex *cis*-**3** (present as a mixture of enantiomers), as shown by the two distinct Pt-Me signals in the ¹H and ¹³C NMR spectra in D₂O/d⁶-acetone (see Figure S5).

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Figure 1

The equatorial hydroxo ligand at each Pt centre occupies a coordination site that places it proximal to the NH₂ substituent of the bipyridine unit bound to the same metal centre with N...O distances of 2.68(3), 2.77(2) and 2.73(2) Å for O(1)...N(13), O(2)...N(33) and O(3)...N(53) respectively. These distances suggest intramolecular O...H...N hydrogen bonding interactions,¹⁴ but the quality of the data set did not allow the exact location of the H atoms (see SI for further details). We have previously established in the solid state structure of [(6-aminobipy)PtMe₂] complex **4** (shown in Eq. 4), that the lone pair on the amino nitrogen atom is tied up in the delocalised π -system of the ligand, resulting in a planar sp² hybridized nitrogen atom.²³ The interconversion shown in Eq. 3 between complex *cis*-**3** and the trinuclear complex **2**, indicates that the NH₂ protons are weakly acidic and that the OH ligands on the platinum centre are basic. It is on the basis of these observations that we suggest the HNH...OH hydrogen bonding as shown in Eq. 3, rather than the OH...NH₂ alternative, which would result in a pyramidalisation of the amino nitrogen atom.

Although the formation of the trinuclear compound **2** via the loss of H₂O was rather unexpected, it should be mentioned that trinuclear metal complexes of this type are not without precedent. Several of these so-called metalla-azacrown compounds have been discovered during the last decade containing metals such as Ru(II),^{24, 25} Rh(III),^{24, 25} Pd(II),²⁶ Pt(II)²⁷⁻²⁹ and one example for Pt(IV)³⁰. In these trimeric complexes the ligands are in all cases nucleobases or related model compounds.

In order to gain further support for the H-bonding effect in oxidation reactions with H₂O₂ and its influence on the *cis*/*trans* ratio of the dihydroxo Pt(IV) complex, the reaction of [(6-aminobipy)PtMe₂] (**4**) with H₂O₂ in acetone solution was also investigated. This reaction results in the formation of a mixture of exactly 50 % of the *cis* dihydroxo Pt(IV) isomer *cis*-**5** (present as a mixture of enantiomers) and 50 % of the *trans* dihydroxo Pt(IV) complex *trans*-**5'** (Eq. 4). These products could not be separated but are easily identified by their characteristic ¹H and ¹³C NMR data (see Figures S6-S9).

The results presented here provide strong evidence that hydrogen-bonding can be used to generate exclusively *cis*-dihydroxo platinum(IV) complexes. In order to rule out any possible electronic or steric effects, we also investigated the reaction of H₂O₂ with the following complexes: [(4-aminobipy)PtMe₂] (**6**) [(6-methylbipy)PtMe₂] (**7**) and [(2,9-dimethylphen)PtMe₂] (**8**). In all cases, a *trans*-dihydroxo Pt(IV) dimethyl complex was the only product observed (Eq. 5-7 and Figures S10-S13). Substantial decomposition was observed in the reaction of complex **8**, probably due to the severe steric distortions of the dimethylphenanthroline coordination and the consequent instability of the complex.³¹

The ability of hydrogen bonding to direct the outcome of the oxidation reaction of Pt(II) complexes with H₂O₂ has also important mechanistic implications. The mechanism of the oxidative addition reaction of H₂O₂ and Pt(II) complexes has been the subject of some debate and two reaction pathways have been proposed: a) *via* axial electrophilic attack by the oxidant at the square planar Pt(II) complex, followed by a heterolytic cleavage of the O–O bond and subsequent attack of the hydroxide anion or b) *via* a concerted three-centered transition state and homolytic cleavage of the O–O bond to give a *cis*-dihydroxo complex as the initial kinetic product, which subsequently rapidly isomerises to the thermodynamically more stable *trans*-dihydroxo Pt(IV) complex (Scheme 1).^{12, 13, 17}

Scheme 1

In an attempt to explain the observed reaction products in the oxidative addition reactions of H₂O₂ with complexes **1** and **4**, we postulate a *cis*-concerted mechanism (pathway b). In the case of the reaction of complex **1** with H₂O₂, a *cis* concerted addition of H₂O₂ leads to only one possible intermediate, which upon oxidative addition results in a single *cis*-dihydroxo Pt(IV) complex *cis*-**3** (Eq. 8). In the case of complex **4** where only one amine substituent is present, the reaction with H₂O₂ generates initially two isomeric *cis* complexes *cis*-**5** and *cis*-**5'** (Eqs. 9a and 9b). Complex *cis*-**5'**, which is not observed, rearranges immediately to a *trans*-dihydroxo Pt(IV) complex *trans*-**5'** due to the absence of hydrogen bonding in the equatorial plane.

In conclusion, we have shown that hydrogen-bonding substituents in the proximity of a metal centre can have a dramatic effect on the outcome of a reaction. The reaction of H_2O_2 with a platinum(II) dimethyl complex containing a 6,6'-diaminobipyridine ligand results in exclusive formation of the *cis*-dihydroxo Pt(IV) dimethyl complex. Instead of methanol formation via C-O coupling and reduction of the Pt(IV) centre, deprotonation of the diamino-bipyridine ligand was observed, resulting in the formation of an unusual trinuclear Pt(IV) complex. We are continuing our investigations into the properties of these novel *cis*-dihydroxy Pt(IV) dimethyl complexes, with the aim to develop alkane oxidation catalysts using cheap and environmentally benign oxidants such as H_2O_2 .

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Notes and references

†Electronic Supplementary Information (ESI) available: This material includes synthetic procedures, analytical data, crystallographic information as well as an ORTEP diagram for **2** and NMR spectra.

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*Crystal data for **2**: $\text{C}_{36}\text{H}_{48}\text{N}_{12}\text{O}_3\text{Pt}_3 \cdot 2\text{Me}_2\text{CO}$, $M = 1398.29$, orthorhombic, *Pbca* (no. 61), $a = 8.9391(5)$, $b = 23.5173(17)$, $c = 44.243(5)$ Å, $V = 9300.9(13)$ Å³, $Z = 8$, $\rho_{\text{calcd}} = 1.997$ g cm⁻³, $\mu(\text{MoK}\alpha) = 9.059$ mm⁻¹, $T = 173$ K, yellow needles, Oxford Diffraction Xcalibur 3 diffractometer; 15245 independent measured reflections, F^2 refinement, $R_1 = 0.153$, $wR_2 = 0.289$, 11772 independent observed reflections [$|F_o| > 4\sigma(|F_o|)$], $2\theta_{\text{max}} = 64^\circ$, 588 parameters. CCDC 658926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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