Oxidation Catalysts produced by Catalytic Oxidation: Preparation, Reactivity and X-Ray Crystal Structures of $[WO(O_2)_2(pyO)_2]$ and $[MoO(O_2)_2(pyO)_2]$

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The X-ray crystal structures of the pentagonal bipyramidal title complexes are reported (pyO = pyridine-*N*-oxide); these complexes were made by the oxidation by H_2O_2 of pyridine, catalysed by $[MoO_4]^{2-}$ and $[WO_4]^{2-}$, and are themselves catalysts for oxidations by H_2O_2.

Here, we report the first example of a system in which the metal-catalysed oxidation of an organic substrate gives a product that coordinates to the metal, the resulting complex itself being an oxidation catalyst. During studies on transition metal catalysed oxidations by hydrogen peroxide we attempted to prepare complexes of the type $[MO(O_2)_2(py)_2]$ and $[MO(O_2)(py)(H_2O)]$ (M = Mo, W); one such species, $[WO(O_2)_2(py)(H_2O)]$, has been reported in the patent literature.[1] Despite many attempts we have been unable to isolate such compounds, but have found that the reaction of pyridine with H_2O_2 in the presence of $[WO_4]^{2-}$ or $[MoO_4]^{2-}$ leads to rapid oxidation to the *N*-oxide. The complexes $[WO(O_2)_2(pyO)_2]$ **1** and $[MoO(O_2)_2(pyO)_2]$ **2** can be isolated from such solutions.

1 was obtained by dissolving $WO_3 \cdot H_2O$ in a 30% w/v solution of hydrogen peroxide, followed by slow addition of pyridine at 0 °C; white crystals of **1** were formed over a period of weeks. Pale yellow crystals of **2** were obtained by an analogous procedure using $MoO_3 \cdot H_2O$. Complex **2** has been previously prepared by direct reaction of $MoO_3 \cdot H_2O$, H_2O_2 and pyridine-*N*-oxide, but these workers were unable to isolate **1** in a pure form by this route.[2]

Single crystal X-ray analyses† show that **1** and **2** are not isomorphous but are structurally very similar (Fig. 1). The basic structure in both cases in pentagonal bipyramidal, the axial positions being occupied by oxo [W=O 1.712(5) Å, Mo=O 1.676(3) Å] and pyO [W–O 2.221(5) Å, Mo–O 2.245(2) Å] ligands. The two peroxo ligands (in η^2 side-bound configurations) and the other pyO ligand occupy equatorial positions within the distorted pentagonal plane. The oxygen atoms that define the equatorial plane are, in both complexes, coplanar to within 0.10 Å with the W and Mo atoms displaced by 0.29 and 0.31 Å respectively towards the oxo ligand. There is also, in both structures a small bend in the O(1′)–M–O(6) axis [165.8(3) in **1** and 164.8(1)° in **2**]. The M–O(pyO) bonds *trans* to the oxo ligands are, as expected, substantially longer than their equatorial counterparts [2.085(6) Å for W and 2.120(2) Å for Mo]. The Mo–O and W–O(peroxo) bond distances are normal. The small differences in the geometries of the complexes are caused by variations in the orientations of the C_5-N planes with respect to the coordination polyhedra, probably due to packing effects associated with the different crystal systems.

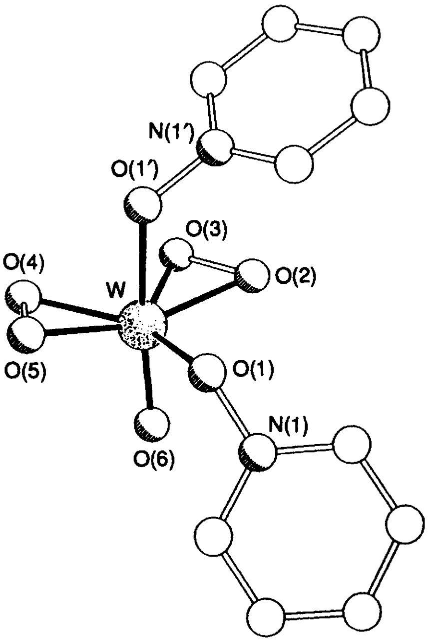

Fig. 1 The molecular structure of $[WO(O_2)_2(pyO)_2]$. Selected bond lengths (Å) and angles (°) for **1** and **2** [] respectively: M–O(1) 2.085(6), [2.120(2)]; M–O(2) 1.968(5), [1.942(3)], M–O(3) 1.926(6), [1.926(3)], M–O(4) 1.934(6) [1.913(2)], M–O(5) 1.951(5) [1.944(2)], M–O(6) 1.712(5) [1.676(3)], O(2)–O(3) 1.513(9) [1.460(3)], O(4)–O(5) 1.494(9) [1.458(4)], O(1′)–M–O(6) 165.8(3) [164.8(1)], O(1′)–M–O(1) 75.9(2) [75.3(1)], O(2)–M–O(3) 45.7(3) [44.4(1)], O(4)–M–O(5) 45.2(3) [44.4(1)].

The profiles of the Raman spectra of **1** and **2** in the solid state and aqueous solutions are very similar {*e.g.* ν(M=O) at 962 and 976 cm^{-1}; ν(O–O) at 852 and 851 cm^{-1}; $\nu_{as}[M(O_2)]$} at 598 and 616 cm^{-1} and $\nu_s[M(O_2)$ at 560 and 545 cm^{-1} for **1** and **2** respectively in solution} and are consistent with the solution Raman data for other comparable peroxo complexes.[3] This suggests that the solid state structures are retained in solution; Raman data have been used to show that pentagonal bipyramidal oxovanadium(v) diperoxo complexes retain their structures in aqueous solution.[4] Surprisingly, both **1** and **2** appear to be stable in aqueous base, as shown by their Raman spectra in a pH 10.0 (bicarbonate) buffer solution.

Further evidence for the retention of the solid state structures is provided by the ^{13}C NMR spectra of the complexes in the solid state and solution. In ^2H_2O **1** and **2** exhibit resonances at δ 141.6, 135.3, 130.0 and 141.7, 136.1, 130.1 (all δ values *vs.* $SiMe_4$) respectively. These are slightly shifted from those observed in free pyridine-*N*-oxide, which resonate at δ 141.5, 134.9 and 129.9 respectively. The ^{13}C CPMAS solid state NMR spectra show corresponding resonances at δ 142.9, 141.0 and 129.5 for **1**, while for **2** only two resonances are resolved, at δ 142.0 and 129.7, close to values observed in other pyridine-*N*-oxide complexes.[5]

Pyridine is reported to be inert to hydrogen peroxide alone,[6] which we have confirmed by ^{1}H and ^{13}C NMR studies. The catalysed oxidation of pyridine (1.43 mol dm^{-3}) with H_2O_2 (3.5 mol dm^{-3}) and $[MO_4]^{2-}$ (6.4×10^{-3} mol dm^{-3}) was followed by ^{13}C NMR. The rate of reaction was first order in both pyridine and hydrogen peroxide. The reaction was relatively fast in the presence of $[WO_4]^{2-}$ with an approximate second-order rate constant, k, of 9×10^{-6} dm^3 mol^{-1} s^{-1}. The $[MoO_4]^{2-}$ catalysed oxidation was markedly slower ($k = 3 \times 10^{-6}$ dm^3 mol^{-1} s^{-1}).

Both **1** and **2** show mild catalytic activity in the oxidations of model organic pigments by H_2O_2. The rate law for the bleaching of phenolphthalein[7] at pH 10.0 and 21.0 °C consists of a second order term for the oxidation by hydrogen peroxide alone ($k_{uncat} = 5.44 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}), and a term for the catalysed reaction which was first order in each of phenolphthalein (1×10^{-5} to 3×10^{-5} mol dm^{-3}), hydrogen peroxide (3.3×10^{-3} to 1.2×10^{-2} mol dm^{-3}) and $[MO(O_2)_2(pyO)_2]$ (1.3×10^{-5} to 8.5×10^{-5} mol dm^{-3}). The third order rate constants were 30 and 43 $dm^6 mol^{-2} s^{-1}$ for the reactions with **1** and **2** respectively.

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† *Crystal data*: **1**. $C_{10}H_{10}N_2O_7W$, $M = 454.1$, triclinic, $a = 7.127(3)$, $b = 7.422(3)$, $c = 12.893(6)$ Å, $\alpha = 76.78(3)$, $\beta = 84.86(2)$, $\gamma = 77.00(2)°$, $V = 646.3(5)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 2.33$ g cm^{-3}, μ(Mo–Kα) = 89.7 cm^{-1}, F(000) = 428. **2**. $C_{10}H_{10}MoN_2O_7$, $M = 366.1$, monoclinic, $a = 6.561(2)$, $b = 12.729(6)$, $c = 15.419(7)$ Å, $\beta = 94.36(2)°$, $V = 1284(1)$ Å^3, space group $P2_1/c$, $Z = 4$, $D_c = 1.89$ g cm^{-3}, μ(Mo–Kα) = 10.6 cm^{-1}, $F(000) = 728$. Data for both compounds were measured on a Siemens P4/PC diffractometer with Mo–Kα radiation (graphite monochromator) using ω-scans. The structures were solved by direct methods and the non-hydrogen atoms refined anisotropically to give for **1** (using absorption corrected data) $R = 0.0275$, $R_w = 0.0286$ for 2034 independent observed reflections and for **2** $R = 0.0272$, $R_w = 0.0296$ for 2002 independent observed reflections $[|F_0| > 4\sigma(|F_0|), 2\theta \leq 50°]$. Atomic coordinates, bond lenghts and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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