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The X-ray Crystal Structure of $K_2[MoO(O_2)_2(O_7C_6H_6)]\cdot\frac{1}{2}H_2O_2\cdot 3H_2O$, the First Isolated Peroxo Citrato Complex

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We have recently reported the X-ray crystal structure of $K_3[VO(O_2)_2(C_2O_4)]\cdot H_2O_2$ [1] and we now report that of $K_2[MoO(O_2)_2(O_7C_6H_6)]\cdot\frac{1}{2}H_2O_2\cdot 3H_2O$ **I**, the first peroxo citrato complex to be isolated. The complex is also of interest in view of much recent work on coordinated citrate and its involvement in the Krebs cycle [2, 3].

Yellow crystals of **I** were made by slow evaporation at 0 °C of a saturated aqueous solution of potassium molybdate with citric acid in equivalent proportions in the presence of excess hydrogen peroxide.

Crystal Data

$C_6H_{13}O_{16}K_2Mo$, monoclinic, a = 7.900(2), b = 18.772(4), c = 11.499(3) Å, β = 107.41(2)°, U = 1627.2(6) Å^3, space group $P2_1$, and Z = 4. X-ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated Cu-Kα radiation. A total of 2273 independent reflections were measured (to θ = 57°) of which 46 were judged to be 'unobserved'. Patterson and Fourier methods were used to solve the structure, and least-squares refinement has now reached R = 0.046. The program system SHELXTL was used throughout the calculations [4].

The unit cell contains two crystallographically independent complex anions, potassium cations, and hydrogen peroxide and water molecules of solvation. There are no significant differences between the two independent anions, and mean values of bond lengths are quoted. The anion, shown in the figure, has a terminal oxo atom, two bidentate peroxo groups, and a bidentate citrate ligand binding through its hydroxo atom and the central carboxylate group. It has a pentagonal bipyramidal coordination geometry with two somewhat asymmetrically bonded

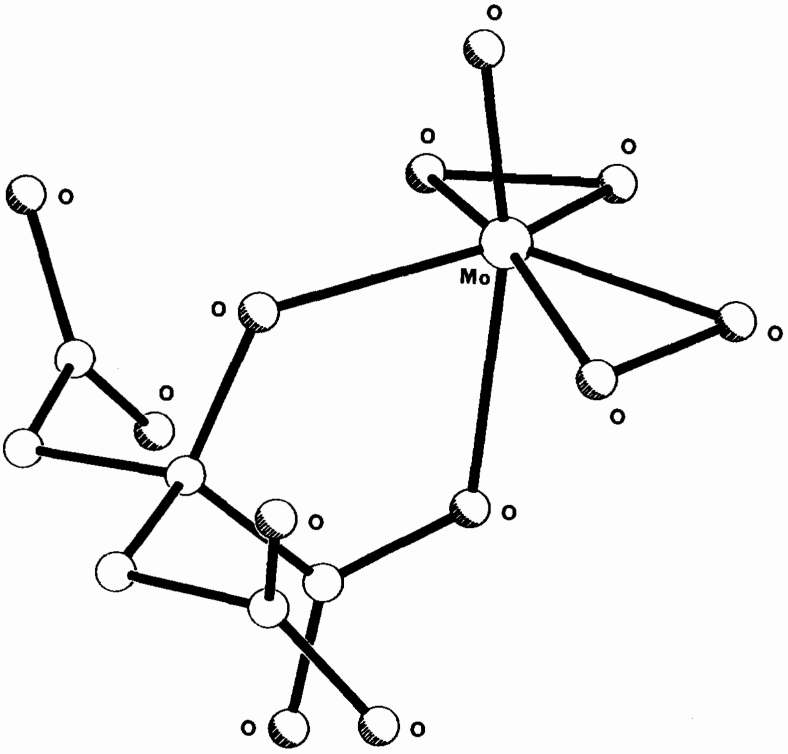

Fig. 1. Structure of the $[MoO(O_2)_2(O_7C_6H_6)]^{2-}$ anion.

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peroxo groups (mean Mo–O, 1.926(9) and 1.975(8) Å; mean O–O, 1.482(12) Å) and the deprotonated hydroxo atom from the citrate group (Mo–O, 2.011(7) Å) constituting the pentagonal equatorial plane. The axial positions are occupied by the Mo=O (1.655(8) Å) and an oxygen atom from the central deprotonated carboxylate group of the citrate (Mo–O, 2.220(8) Å).

The citrate, which normally functions as a multidentate ligand [3], is bidentate in this complex and so forms a five-membered ring with the molybdenum. This mode of coordination has been crystallographically established in only one other case [2], and in that instance the ligand was forced to adopt this mode of coordination because other sites were blocked by a tetradentate ligand. An unusual feature is the deprotonation of the coordinated hydroxo group; removal of all four ionisable protons on coordination of citrate has been observed (*e.g.* in iron(II) and iron(III) complexes) [3, 5, 6], but coordination as $C_6H_6O_7^{2-}$ with loss of only the central carboxylate and the hydroxyl protons has hitherto been proposed only in the case of *cis*-$[WOF_3(O_7C_6H_6)]^-$, on the basis of ^{19}F NMR data [7]. The deprotonation of the hydroxo group is likely to occur as a result of the formation of a strong Mo–O bond in the equational plane.

A complex network of hydrogen bonds of the type O–H···O involves the hydrogen peroxide and water molecules of solvation and some of the oxygen atoms of the complex anion.

The infrared spectrum of **I** is very complex due to the citrate modes and the extensive hydrogen bonding but, as with most peroxo complexes, the Raman spectrum of the solid is very clear. In addition to the very strong Mo=O stretch at 950 cm^{-1} the three bands associated [8] with the triangular $Mo(O_2)$ rings are clearly seen (ν(O–O) at 875 cm^{-1}, $\nu_sMo(O_2)$ at 585 and $\nu_{as}Mo(O_2)$ at 520 cm^{-1}. A band at 855 cm^{-1} is likely to be the ν(O–O) stretch [9] of the hemiperhydrate (a similar band was found at 860 cm^{-1} in *cis, trans*-$PtCl_2(OH)_2(2\text{-}NH_2Pr)_2 \cdot \frac{1}{2}H_2O_2$ [10]); its weak activity in the infrared is consistent with a skew configuration of H_2O_2. A band at 2850 cm^{-1} in the Raman may arise from ν_1, (the symmetric O–H stretch) of H_2O_2, and a broad infrared band at 2580 cm^{-1} may be due to the asymetric stretch ν_5.

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