Model Compounds for the Active Sites of Oxo-transfer Molybdoenzymes. Synthesis, Structural Characterization, and Electrochemical Properties of $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$

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$[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]\cdot 2H_2O$ has been prepared and its crystal structure solved, providing the first example of a co-ordinatively saturated molybdenum complex which reacts readily and reversibly with organophosphines at room temperature in water or methanol; its variable-temperature $^{13}C\{^1H\}$ NMR spectra and electrochemical properties are presented.

The well known complex $MoO_2(S_2CNEt)_2$[1] undergoes the first recognized example for a molybdenum complex of an oxo-transfer reaction with organophosphines, but it is unsuitable as a model system for oxo-type molybdoenzymes because a stable and unreactive oxo-bridged Mo^V dimer readily forms in solution.[2] More recently, Berg and Holm have synthesized a five-co-ordinated unsaturated dioxomolybdenum(VI) complex $MoO_2(LNS_2)$ [LNS_2 = 2,6-bis(2,2-diphenyl-2-mercaptoethyl)pyridine (2−)] which is quite effective in oxidizing Ph_3P, and forming a stable $MoO(LNS_2)$(dmf) (dmf = dimethylformamide) complex.[3] The phenyl rings adjacent to the ligating sulphur atoms provide steric hindrance and prevent dimerization upon reduction.

These and other complexes[4] that have been reported to act as oxo-transfer agents are similar in that they contain sulphur-donor ligands. Herein we describe a monomeric hexavalent Mo^{VI} complex derived from the sterically hindered 2,2-diphenyl-2-mercaptoacetic acid, which is anionic, slightly soluble in H_2O, and very soluble in MeOH or other polar organic solvents. Addition of a stoicheiometric amount of this ligand, prepared as described previously,[5] to a H_2O–MeOH (1:10) solution of $(NH_4)_2MoO_4$ yielded a stable yellow microcrystalline solid.

X-Ray analysis (Figure 1) shows that the Mo^{VI} complex contains discrete monomeric ions,† which are composed of two carboxylato–diphenylmethylthiolato ligands co-ordinated

† *Crystal data*: $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]\cdot 2H_2O$, M = 684.6, monoclinic, space group $P2_1/c$, a = 8.190(7), b = 14.367(3), c = 24.816(3) Å, β = 92.49(3)°, V = 2917 Å^3, Z = 4, D_c = 1.56 g cm^{-3}, λ(Mo-K_α) = 0.7093 Å, μ(Mo-K_α) = 5.67 cm^{-1}. The intensities of 5117 reflections were measured at room temperature ($0 \leqslant 2\theta \leqslant 50°$) on a CAD-4 diffractometer using monochromated Mo-K_α radiation. The structure was solved by direct methods using MULTAN-84[9] and refined with SHELX-76.[10] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms except those of one of the two water molecules were located in difference Fourier syntheses but were not refined and only used as a fixed contribution to F_c. For 4205 unique observed reflections with $I \geqslant 3\sigma(I)$, R = 0.032, R_w = 0.038 [$w = 1/\sigma^2(F) + 0.001F^2$]. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

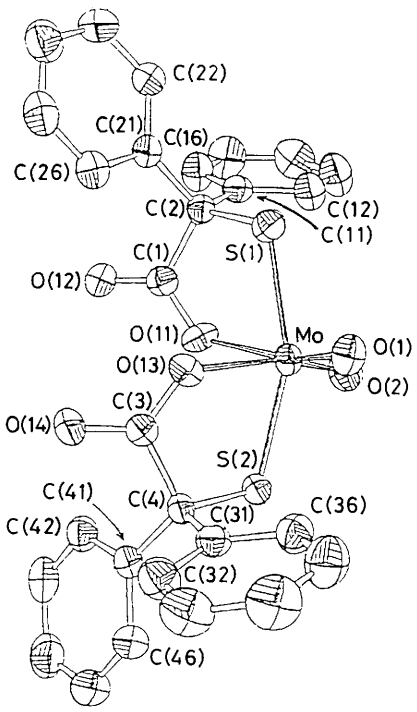

Figure 1. Perspective view of the complex anion $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$; ORTEP drawing with 50% probability ellipsoids. Selected distances (Å) and angles (°): Mo–S(1), 2.429(1); Mo–S(2), 2.415(1); Mo–O(1), 1.715(2); Mo–O(2), 1.709(2); Mo–O(11), 2.174; Mo–O(13), 2.176; S(1)–Mo–S(2), 158.7(1); S(1)–Mo–O(1), 87.9(1); S(1)–Mo–O(2), 106.9(1); S(1)–Mo–O(11), 77.0(1); S(1)–Mo–O(13), 85.6(1); O(1)–Mo–O(2), 104.4(1); O(1)–Mo–O(11), 161.9; O(1)–Mo–O(13), 91.4; O(11)–Mo–O(13), 77.6(1).

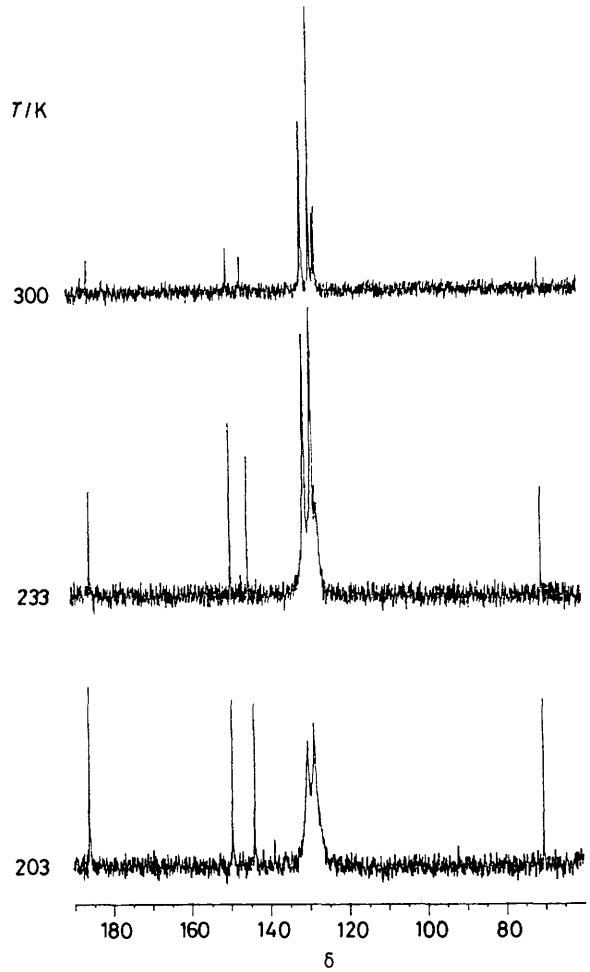

Figure 2. Variable temperature ^{13}C NMR spectra of $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ in methanol.

with a *cis*-MoO_2 core through S(1) and S(2) of the deprotonated thiolate groups and O(11) and O(13) of the adjacent carboxylate groups.

Although no symmetry is imposed on the anion, it possesses a twofold axis that bisects the O(11)–Mo–O(13) and O(1)–Mo–O(2) angles. Bond lengths and angles related by this axis are identical within experimental error. Molybdenum–oxygen (Mo=O, Mo–OCO) and molybdenum–sulphur bond distances are normal,[6] falling within the narrow range of 2.41—2.47 Å found for Mo–S in enzymatic Mo sites from EXAFS analysis.[7]

Each terminal oxo atom is sterically hindered by one phenyl ring in the direction of a potential Mo–O–Mo bond. The paramount relevance of these steric factors has been demonstrated recently by Holm.[8]

Co-ordination of the carboxylate and thiolate groups is also consistent with the large low-field shifts (~10 p.p.m.) in their ^{13}C NMR signals compared with resonances for the free ligand (Figure 2). Molecular C_2 symmetry in solution (CD_3OD) is also indicated by the number and intensity of the resonances due to the two co-ordinated ligands. The variable temperature NMR spectra (Figure 2) show clearly that the phenyl rings are fluxional on the NMR time-scale.

The cyclic voltammogram (CV) of this complex in water is unusual, and is unique in studies which included a range of solvents (dmf, MeOH, and MeCN). As shown in Figure 3, the CV using a hanging mercury drop electrode (HMDE) displays a reversible wave at −0.3 V *vs.* standard calomel electrode (SCE) as well as an irreversible cathodic wave at −0.86 V associated with an oxidation process at −0.35 V. However, at a glassy carbon electrode, the peak potentials shifted towards more negative values and the first reduction became irreversible. Controlled-potential coulometry in methanol and water at −0.57 V corresponding to the first reduction wave using a carbon electrode proceeded smoothly and consumed two faradays/mol Mo^{VI}.

The reaction with Ph_3P mentioned in the introduction[3a] also occurred. The reaction was carried out in refluxing MeOH at 50 °C with a three-fold excess of Ph_3P in the presence of air [Ph_3P (1.5 mmol); complex (0.5 mmol); MeOH (10 ml)]. As shown by using ^{31}P NMR spectroscopy, after 5 h, the three-fold excess of Ph_3P (δ 0.0 p.p.m.) had been completely oxidized to Ph_3PO (δ 38.12 p.p.m.) and to a small amount of Ph_3PS (δ 48.74 p.p.m.). After the reaction, 54% of the starting Mo^{VI} was recovered by chromatography. Since there was no appreciable reaction between Ph_3P and O_2 in the absence of the complex, equations (1) and (2) describe the catalytic cycle responsible for the oxidation of the Ph_3P in excess.

$$[MoO_2(X)_2]^{2-} + Ph_3P \rightarrow Ph_3PO + [MoO(X)_2]^{2-} \quad (1)$$

$$[MoO(X)_2]^{2-} + O_2 \rightarrow MoO_2(X)_2]^{2-} \quad (2)$$

$$X = O_2CC(S)Ph_2$$

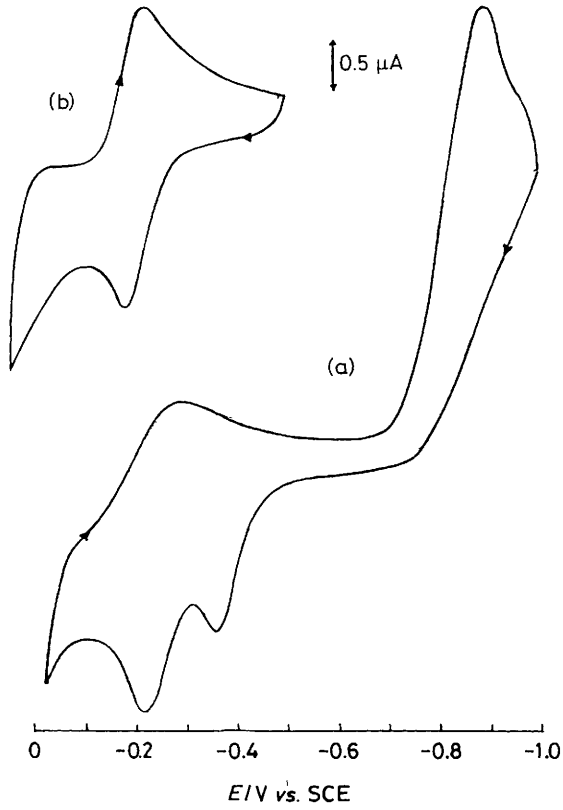

Figure 3. Cyclic voltammogram of $[NH_4]_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ (10^{-3} mol dm^{-3}) in water; pH 4.1 (0.2 mol dm^{-3} AcOH/AcONa buffer); HMDE as working electrode; scan rate: (a) 0.14; (b) 0.36 V s^{-1} (*vs.* SCE).

From all these results we consider that this co-ordinatively saturated complex behaves as would be expected for a chemical model of oxo-type molybdoenzymes.

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