Structural Comparison of Oxobis(benzene-1,2-dithiolato)molybdenum-(V) and -(IV) Complexes

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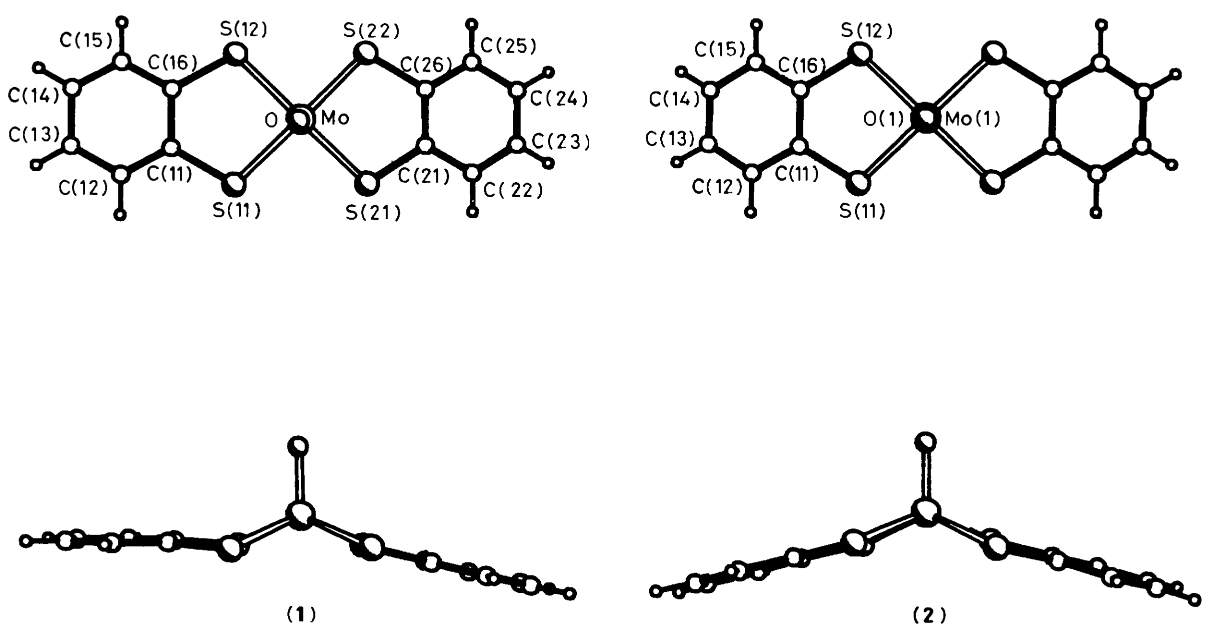
The $[MoO(bdt)_2]^-/[MoO(bdt)_2]^{2-}$ (H_2bdt = benzene-1,2-dithiol) redox couple, in dimethylformamide solution, is a fully reversible process at $E_{\frac{1}{2}} = -350$ mV *vs.* standard calomel electrode and each of these anions has been characterised by *X*-ray crystallography; the metal–ligand bond lengths of the former are slightly shorter than those of the latter, Mo^V–O = 1.668(3) Å, Mo^{IV}–O = 1.699(6) Å, mean Mo^V–S = 2.377(1) Å, Mo^{IV}–S = 2.388(2) Å.

Molybdenum K-edge e.x.a.f.s. studies, accomplished for the reduced forms of several of the oxomolybdoenzymes, have indicated that this metal has a co-ordination environment consisting of a single terminal oxygen (Mo–O *ca.* 1.68 Å) and approximately three sulphur atoms (Mo–S *ca.* 2.38 Å).[1] These forms of the enzymes are generally accepted as involving Mo^{IV}. E.s.r. signals of the corresponding Mo^V centres have been detected during enzyme catalysis and are consistent with a co-ordination environment very similar to that proposed for the Mo^{IV} centres.[2] Partial characterisation of the molybdenum cofactor of these enzymes has led to the suggestion that two of the sulphur atoms detected in the molybdenum K-edge e.x.a.f.s. studies belong to a 1,2-dithiolene group which is part of the C-6 substituent of a reduced pterin.[3] Metal complexes of such ligands (metal dithiolenes[4]) have not been identified in any other biological system but, in view of the reversible electron-transfer properties of these complexes,[4] the presence of such a group at the active site of these oxido-reductase enzymes could aid the redox changes associated with their catalytic activity.

We have investigated the chemistry of oxomolybdenum dithiolene complexes as potential models for the spectroscopic



(1) (2)

Figure 1. Comparison of the structures of the anions of $[PPh_4][MoO(bdt)_2]$ (**1**) and $[NEt_4]_2[MoO(bdt)_2]$ (**2**) (anion I).

properties and chemical reactivity of the catalytic site of the oxomolybdoenzymes. Herein, we report the syntheses and structures of the benzene-1,2-dithiolato (bdt) complexes $[MoO(bdt)_2]^-$ and $[MoO(bdt)_2]^{2-}$. These are the first oxobis-(dithiolene)metallate complexes to be characterised by *X*-ray crystallography and these data provide the first structural comparison between members of an $Mo^VOS_4/Mo^{IV}OS_4$ redox couple.

$[PPh_4][MoO(bdt)_2]$ (**1**) was prepared by the reaction[5] of $[PPh_4][MoO(SPh)_4]$[6] with H_2bdt (1:2) in CH_2Cl_2. $[MoO(bdt)_2]^{2-}$ was prepared by the reaction[7] of $K_4[MoO_2(CN)_4]\cdot 6H_2O$[8] with H_2bdt (1:2) in H_2O–EtOH (1:1) and isolated as $[NEt_4]_2[MoO(bdt)_2]$ (**2**) by addition of $[NEt_4]Br$ to this solution. Crystals of (**1**) and (**2**) proved to be suitable for investigation by *X*-ray crystallography.† The anions of (**1**) are identical but (**2**) contains two independent anions, each with crystallographic C_2 symmetry. The structures of the anions of (**1**) and (**2**) (anion I) are illustrated in Figure 1 and selected dimensions are compared in Table 1. $[MoO(bdt)_2]^-$ and $[MoO(bdt)_2]^{2-}$ have virtually identical structures; both anions possess approximately square pyramidal geometry (C_{2v} symmetry) with the oxygen atom at the apex and the molybdenum atom raised slightly above the basal (S_4) plane. The dimensions of the two anions are very similar and these values and the nature of the co-ordination geometry closely resemble those of $Mo^VO(thiolate)_4$ complexes.[5,6,9] Also, both the Mo–O and Mo–S distances closely correspond to the values obtained[1] from molybdenum K-edge e.x.a.f.s. studies of the reduced forms of the oxomolybdoenzymes.

Table 1. Comparison of selected dimensions[a] (Å, degrees) for the anions of $[PPh_4][MoO(bdt)_2]$ (**1**) and $[NEt_4]_2[MoO(bdt)_2]$ (**2**) (anion I).[b]

	(1)	(2)
Mo–O	1.668(3)	1.699(6)
Mean Mo–S	2.377(1)	2.388(2)
Mean S–C	1.763(4)	1.767(6)
Diplacement of Mo from S_4 plane	0.736(1)	0.745(2)
Ligand bite	3.192(2)	3.168(2)
Mean O–Mo–S	108.1(1)	108.2(1)
Mean S–Mo–$S_{intraligand}$	84.4(1)	83.1(1)
Mean S–Mo–$S_{interligand}$	84.6(1)	85.8(1)
S–Mo–$S_{interligand}$	143.9(1)	143.7(1)

[a] E.s.d.s. given in parentheses represent the precision of individual values rather than their concordance. [b] Dimensions of anion II are not significantly different from those of anion I.

Addition of one electron to $[MoO(bdt)_2]^-$ results in a slight increase in all of the metal–ligand bond lengths, the change being greater for Mo–O than Mo–S, whilst the dimensions of the bdt ligands are not changed to any significant extent. These results, when taken together with the electronic structure of Mo^VOL_4 centres[10] and the diamagnetic nature of $[MoO(bdt)_2]^{2-}$, are consistent with the electron being added to an orbital of a_1 symmetry based on the molybdenum $4d_{x^2-y^2}$ orbital which is essentially metal–ligand non-bonding. The increase in the length of the Mo–O bond upon reduction of $[MoO(bdt)_2]^-$ presumably arises from a reduction in the $O(2p\pi) \rightarrow Mo(4d\pi)$ donation and the implied reduction in bond strength is also reflected in the decrease in the i.r. stretching frequency of ν(Mo–O) from 944 cm^{-1} in (**1**) to 905 cm^{-1} in (**2**).

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† *Crystal data:* (**1**), $C_{36}H_{28}MoOPS_4$, monoclinic, space group *Cc*, $Z = 4$, $a = 12.7543(5)$, $b = 15.6222(7)$, $c = 16.5149(6)$ Å, $\beta = 93.136(4)°$, $U = 3285.7$ Å^3, $D_c = 1.479$ g cm^{-3}, $F(000) = 1492$, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu(Mo\text{-}K_\alpha) = 0.71$ mm^{-1}. (**2**), $C_{28}H_{48}MoN_2OS_4$, monoclinic, space group $P2/n$, $Z = 4$, $a = 18.522(1)$, $b = 9.2341(6)$, $c = 18.986(1)$ Å, $\beta = 93.379(6)°$, $U = 3241.6$ Å^3, $D_c = 1.388$, $F(000) = 1376$, Mo-K_α radiation, $\lambda = 0.71073$ Å, $\mu(Mo\text{-}K_\alpha) = 0.66$ mm^{-1}. The structures were solved by normal heavy-atom methods and refined by weighted least-squares [$w^{-1} = \sigma^2(F) + gF^2$; (**1**) $g = 0.00017$, (**2**) $g = 0.0006$]; anisotropic thermal parmeters were used for all non-hydrogen atoms. Hydrogen atoms were included with all C–H = 0.96 Å; aromatic hydrogens were placed on the external bisectors of ring angles and aliphatic hydrogens included with H–C–H = 109.5°. The refinement for (**1**) [(**2**)] converged with $R = 0.0337$ [0.0595] and $R_w = 0.0345$ [0.0758] for 5414 [4098] unique reflections with $F_0 > 4\sigma(F_0)$. 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, 1986.

The electrochemical behaviour of (**1**) and (**2**) in dimethylformamide solution has been investigated by cyclic voltammetry. The $[MoO(bdt)_2]^-/[MoO(bdt)_2]^{2-}$ couple is observed as a fully reversible process ($i_{pa}/i_{pc} = 1.0 \pm 0.05$; $\Delta E_p = 60$ mV independent of scan rate) at $E_{\frac{1}{2}} = -350$ mV *vs.* standard calomel electrode. These anions can be interconverted chemically by oxidation of $[MoO(bdt)_2]^{2-}$ with I_2 and by reduction of $[MoO(bdt)_2]^-$ with zinc amalgam.

The very small differences in the geometry about molybdenum in $[MoO(bdt)_2]^-$ as compared with $[MoO(bdt)_2]^{2-}$ suggest that the Mo^V centres of the oxomolybdoenzymes, observed by e.s.r. spectroscopy,[2] and the corresponding Mo^{IV} centres, observed by molybdenum K-edge e.x.a.f.s.,[1] may be more structurally similar than assumed hitherto.

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