Synthesis and X-Ray Structural Characterization of $[Mo_2O(S_2CNEt_2)_6]BF_4$, a μ-Oxo-bridged Mixed Oxidation State Complex of Molybdenum

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Summary The reaction of $[MoO(S_2CNEt_2)_3]BF_4$ and PPh_3 in methanol under anaerobic conditions results in the formation of $[Mo_2O(S_2CNEt_2)_6]BF_4$, an *X*-ray crystal structure of which shows a new type of μ-oxo-bridging between two molybdenum atoms each having a formal oxidation state of 4·5.

FOR the molybdenum centres in the enzymes nitrate reductase and sulphite and xanthine oxidase, current evidence suggests a sulphur environment about high oxidation state molybdenum, the presence of at least one oxo-ligand, and a mechanism of action involving oxygen atom transfer between molybdenum and substrate.[1] Two molybdenum atoms are believed to be present and e.s.r. studies of the enzymes in the presence of substrate implicate Mo^{V}. It has been suggested from redox experiments that these molybdenum atoms need not be far apart provided some mixed oxidation state binuclear complex (either V–IV or V–VI) is present.[2,3] Here we describe the first example of a mixed oxidation state μ-oxo-bridged binuclear molybdenum complex in which the other ligands are all sulphur donors. A detailed crystallographic and e.s.r. study of a μ-oxo-bridged $Mo^{IV,V}$ binuclear complex containing terminal oxo-ligands has recently been published.[4]

The reaction of $[MoO(S_2CNEt_2)_3]BF_4$ and PPh_3 in methanol under anaerobic conditions results in the formation of green-black dichroic crystals of $[Mo_2O(S_2CNEt_2)_6]BF_4$. The compound, which is air-stable in the solid state but rapidly oxidised in solution, is formulated on the basis of elemental analysis and conductance studies (in methanol, $\Lambda_0 = 80\,\Omega^{-1}\,cm^2\,mol^{-1}$, typical of 1 : 1 electrolytes). The i.r. spectrum shows the presence of bands due to bidentate $S_2CNEt_2^-$ ligands [ν(CN), 1510 cm^{-1}] and to BF_4^- (1100 cm^{-1}), and a weak band tentatively assigned to the μ-oxo-ligand (655 cm^{-1}). No bands due to terminal oxo-ligands are present. The near i.r. spectrum (in $CDCl_3$) exhibits bands at 890 (200) and 1310 (1080) nm (molar absorptivities in parentheses), the latter being tentatively assigned as an intervalence transfer band, consistent with the mixed oxidation state formulation. The electronic spectrum (in methanol) is characterised by intense absorptions at 677 (2440), 497 (19,200), 440 (14,400), and 410 (13,400) nm. Magnetic properties (μ = 2·17 B.M.) are consistent with the presence of one unpaired electron *per* molecule. The equal Mo–O bond distances and equivalent environments about the molybdenum atoms (see below) indicate that the electron is likely to be delocalised and this aspect is being further studied. Suitable crystals for an X-ray study were obtained by slow evaporation of methanolic solutions of the compound.

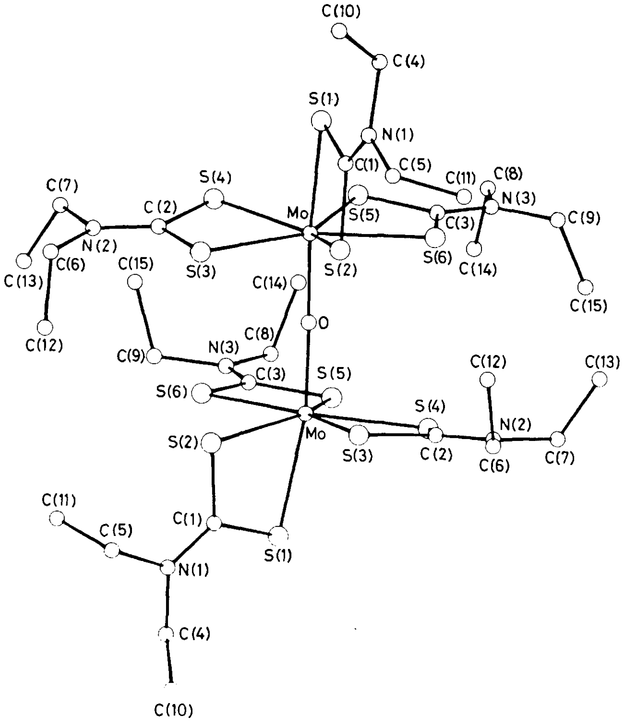

FIGURE. Structure of the cation $[Mo_2O\{S_2CNEt_2\}_6]^+$ showing the atom labelling scheme. Relevant bond lengths and angles are: Mo–O, 1·849(2); Mo–S(1), 2·526(3); Mo–S(2), 2·485(4); Mo–S(3), 2·503(3); Mo–S(4), 2·496(3); Mo–S(5), 2·519(4); Mo–S(6), 2·521(3); <S–C>, 1·722 ± 0·018 (± indicates maximum deviation from mean); <C–N> (S_2C–N bond), 1·318 ± 0·004; <N–C> (N-alkyl-C bond), 1·483 ± 0·008; <C–C>, 1·53 ± 0·02 Å; Mo–O–Mo, 175·7(6); O–Mo–S(1), 167·9(2); O–Mo–S(2), 97·6(2); O–Mo–S(3), 88·6(2); O–Mo–S(4), 96·0(1); O–Mo–S(5), 93·5(3); O–Mo–S(6), 88·5(1); S(1)–Mo–S(2), 70·51(8); S(2)–Mo–S(3), 75·4(1); S(3)–Mo–S(4), 68·7(1); S(4)–Mo–S(5), 73·51(9); S(5)–Mo–S(6), 68·08(8); S(1)–Mo–S(3), 90·31(9); S(1)–Mo–S(5), 94·72(9); S(1)–Mo–S(6), 86·34(9).

Crystal data: $C_{30}H_{60}BF_4Mo_2N_6OS_{12}$, monoclinic, space group $C2/c$, a = 13·24(1), b = 30·86(4), c = 12·42(1) Å, β = 97·89(4)°, U = 5027 Å^3, Z = 4. Data were collected on a Philips PW1100/20 diffractometer using graphite monochromated Mo-K_α radiation. The structure solution was based on 3132 reflections with $I_{obs} > 2{\cdot}0\,\sigma(I_{obs})$. The molybdenum and sulphur atom positions were determined using the MULTAN series of direct methods programs and all other non-hydrogen atoms were located in subsequent difference Fourier maps. The current value for R is 0·051.†

The structure of the cation (Figure), comprising two seven-co-ordinate $Mo(S_2CNEt_2)_3$ units bridged by an almost linear (175·7°) μ-oxo-ligand and related by a C_2 axis, is the first example of μ-oxo-bridging between molybdenum–sulphur moieties in the absence of terminal oxo- or sulphido-ligation.[5] The oxygen occupies an axial position in the pentagonal bipyramidal co-ordination geometry found around both molybdenum atoms. The Mo-O bond lengths are 1·849 Å. The Mo–S bond *trans*- to the oxo-ligand is shorter (2·528 Å) than that found in $[MoO(S_2CNEt_2)_3]^+$ (2·630 Å),[6] indicating a significant reduction in the *trans*-effect of the oxo-ligand when complexed in the bridging mode. The donor sulphur atoms in the two pentagonal planes of the dimer are in approximately 'eclipsed' positions.

While mixed valence compounds are now recognised for many elements, there are few for molybdenum and these are confined to oxyanion-type complexes.[4,7] The title complex is a class III mixed valence compound, since the two molybdenum sites are not crystallographically distinguishable. A more detailed study of the electronic spectrum is in progress along with e.s.r. and electrochemical measurements.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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