# Crystal and Molecular Structure of $Mo_6O_{10}(OPr^i)_{12}$: a Serpentine Chain of Molybdenum Atoms and Observation of Semibridging Alkoxy-ligands

Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman, and Charles C. Kirkpatrick
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405 U.S.A.

$Mo_6O_{10}(OPr^i)_{12}$, an intermediate in the reaction between $Mo_2(OPr^i)_6$ and molecular oxygen which yields $[MoO_2(OPr^i)_2]_n$, has been structurally characterized and found to contain a serpentine chain of molybdenum atoms connected by bridging oxo- and alkoxy-ligands; there is also a pair of alkoxy-ligands which are semibridging.

The addition of molecular oxygen to hexane solutions of $Mo_2(OBu^t)_6$ give rise to cleavage of the $Mo{\equiv}Mo$ bond as shown in equation (1).[1] No intermediates have been detected.

$$Mo_2(OBu^t)_6 + 2O_2 \rightarrow 2MoO_2(OBu^t)_2 + 2Bu^tO\cdot \qquad (1)$$
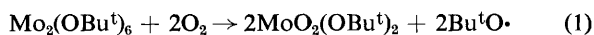
The related reaction involving $Mo_2(OPr^i)_6$ and O_2 differs in at least two respects: (i) intermediates can be detected and isolated and (ii) the final product, $MoO_2(OPr^i)_2$, is not monomeric in non-co-ordinating solvents or in the solid state, although addition of bpy (2,2′-bipyridyl) allows the isolation

of the mononuclear compound $MoO_2(OPr^i)_2(bpy)$.† An intermediate in the formation of $[MoO_2(OPr^i)_2]_n$ is $Mo_6O_{10}(OPr^i)_{12}$ which is readily isolated from the reaction between $Mo_2(OPr^i)_6$ and O_2 because it is virtually insoluble in hexane and only sparingly soluble in toluene. $[MoO_2(OPr^i)_2]_n$, which is more soluble in toluene, may be obtained either by the further

---

† Satisfactory analytical data have been obtained for the new compounds reported. All reactions were carried out using dry solvents and dry molecular oxygen.
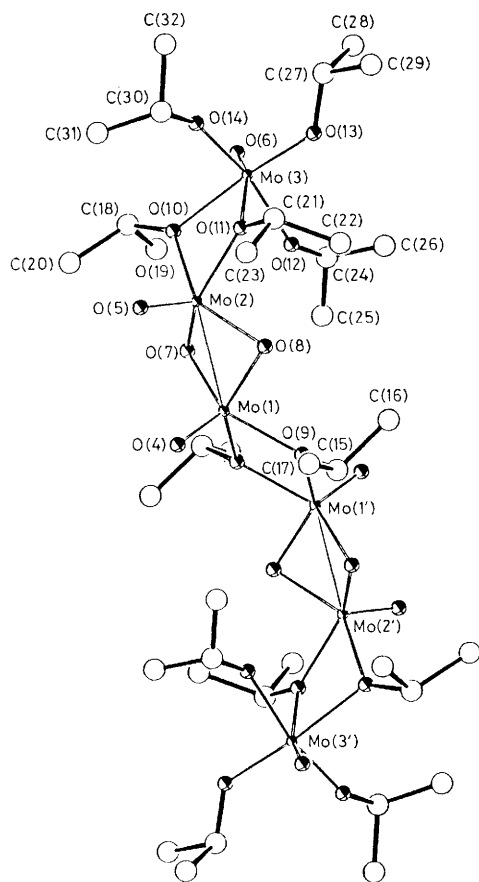
Figure 1. View of the $Mo_6O_{10}(OPr^i)_{12}$ molecule giving the atom numbering scheme. Some pertinent bond distances (Å), not quoted in the text, are for terminal oxo-molybdenum groups: Mo(1)–O(4) = 1.673(2), Mo(2)–O(5) = 1.671(2), Mo(3)–O(6) = 1.691(2); for bridging oxo-groups: Mo(1)–O(7) = 1.921(2), Mo(1)–O(8) = 1.926(2), Mo(2)–O(7) = 1.939(2), Mo(2)–O(8) = 1.939(2); for bridging alkoxy-groups: Mo(1)–O(9) = 2.058(2), Mo(1)–O(9') = 2.072(2), Mo(2)–O(10) = 2.057(2), Mo(2)–O(11) = 2.044(2), Mo(3)–O(10) = 2.128(2), Mo(3)–O(11) = 2.197(2).

reaction of $Mo_6O_{10}(OPr^i)_{12}$ with O_2 or by the addition of Pr^iOH (an excess) to $MoO_2(OBu^t)_2$.

The solid state structure of $Mo_6O_{10}(OPr^i)_{12}$ revealed a serpentine chain of six molybdenum atoms connected by bridging oxo- and alkoxy-ligands.‡ A view of the molecule giving the atom numbering scheme is shown in Figure 1 which clearly reveals the S-shaped curve of the molecule. The molecule has a rigorous centre of inversion and, to within 0.01 Å, the six molybdenum atoms lie in a plane. The Mo(1')–Mo(1)–Mo(2) and Mo(1)–Mo(2)–Mo(3) angles are 146.5(1) and 134.3(1)°, respectively. There are several other interesting structural features. The terminal molybdenum

atoms, Mo(3) and Mo(3'), are rich in alkoxy-ligands while, conversely, the internal molybdenum atoms are rich in oxo-ligands. If, per metal–ligand bond, oxidation numbers are assigned as -2 for terminal oxo, -1 for bridging oxo and terminal OR, and $-\frac{1}{2}$ for bridging OR, then Mo(3) and Mo(3') are $+6$, and Mo(1), Mo(1'), Mo(2), and Mo(2') are $+5$. Four electrons are available for metal–metal bonding and these are used to form two localized M–M single bonds as is shown by the distances Mo(1)–Mo(2) = Mo(1')–Mo(2') = 2.585(1), Mo(1)–Mo(1') = 3.353(1), and Mo(2)–Mo(3) = Mo(2')–Mo(3') = 3.285(1) Å. The geometry about the Mo^{6+} ions is approximately octahedral while that about the Mo^{5+} ions corresponds closely to a square-based pyramid. One structural feature, which has not previously been seen for metal alkoxides,[2] is the presence of semibridging alkoxy-ligands. A pair of symmetry-related alkoxy-ligands attached to each of the terminal Mo^{6+} ions are situated above/beneath the basal MoO_4 planes of the neighbouring Mo^{5+} ions such that Mo(2)–O(12) = Mo(2')–O(12') = 2.88(1) Å. The Mo(3)–O(12) distance, 1.919(2) Å, is significantly longer than either Mo(3)–O(14) = 1.865(2) Å or Mo(3)–O(13) = 1.866(2) Å. Furthermore, the angles Mo(3)–O(12)–C(24) = 127.5(1), Mo(2)–O(12)–C(24) = 137.3(1), and Mo(2)–O(12)–Mo(3) = 83.9(1)° support the view that O(12) is effectively sp^2-hybridized.

The term 'semibridging' is now commonly used in metal carbonyl chemistry[3] where semibridging carbonyls may result from either electronic[4,5] or steric[6] factors. Aside from the obvious difference that CO is a π-acceptor ligand and RO is a π-donor, the ligands share a number of common features including their abilities to act as bridging ligands (μ_2 and μ_3) and to support fluxional processes in solution whereby bridging and terminal groups are rapidly exchanged. Though it is possible to envisage that the semi-bridging OR groups in $Mo_6O_{10}(OPr^i)_{12}$ result from steric factors, we feel it is more likely that the origin is electronic in nature and that the Mo^{5+} ions can readily and willingly increase their co-ordination number from five to six. Consistent with this view is the observation that addition of pyridine (py) to $Mo_6O_{10}(OPr^i)_{12}$ breaks up the Mo_6 unit according to equation (2). The structure of $Mo_4O_8(OPr^i)_4(py)_4$ has been shown[7] to contain six-co-ordinate Mo^{5+} ions.

$$Mo_6O_{10}(OPr^i)_{12} + 6py \rightarrow 2MoO(OPr^i)_4(py) + Mo_4O_8(OPr^i)_4(py)_4 \quad (2)$$
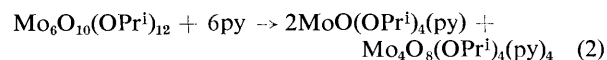
The ^1H n.m.r. spectrum of $Mo_6O_{10}(OPr^i)_{12}$ in $C_6D_5CD_3$ at $+75$ °C, 220 MHz, shows only one type of OPr^i group, consistent with rapid OPr^i group exchange.

References

1 M. H. Chisholm, K. Folting, J. C. Huffman, C. C. Kirkpatrick, and A. L. Ratermann, *J. Am. Chem. Soc.*, 1981, **103**, 1305.

2 D. C. Bradley, P. D. Gaur, and R. C. Mehrotra, 'Metal Alkoxides,' Academic Press, London, New York, San Francisco, 1978.

3 R. Colton and M. J. McCormick, *Coord. Chem. Rev.*, 1980, **31**, 1.

4 F. A. Cotton, B. A. Frenz, and L. Kruczynski, *J. Am. Chem. Soc.*, 1973, **95**, 951.

5 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, 1974, **96**, 1233.

6 W. I. Bailey, Jr., M. H. Chisholm, F. A. Cotton, and L. A. Rankel, *J. Am. Chem. Soc.*, 1978, **100**, 5764.

7 M. H. Chisholm, K. Folting, J. C. Huffman, C. C. Kirkpatrick, and J. Leonelli, *J. Am. Chem. Soc.*, 1981, **103**, 6093.