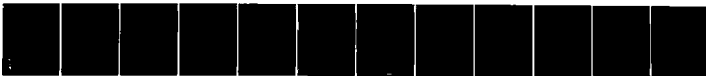


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CRYSTAL AND MOLECULAR STRUCTURE OF $\text{Mo}_6\text{S}_{10}(\text{OPr}^i)_{12}$:
A SERPENTINE CHAIN OF MOLYBDENUM ATOMS
AND OBSERVATION OF SEMIBRIDGING ALKOXY LIGANDS.

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Crystal and Molecular Structure of $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$:
 A Serpentine Chain of Molybdenum Atoms
 and Observation of Semibridging Alkoxy Ligands

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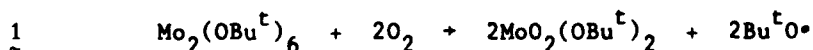
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Summary $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$, an intermediate in the reaction between $\text{Mo}_2(\text{OPr}^i)_6$ and molecular oxygen which yields $[\text{MoO}_2(\text{OPr}^i)_2]_n$, has been structurally characterized and found to contain 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 $\text{Mo}_2(\text{OBu}^t)_6$ gives rise to cleavage of the $\text{Mo}\equiv\text{Mo}$ bond as shown in equation 1 below.¹ No intermediates have been detected.



The related reaction involving $\text{Mo}_2(\text{OPr}^i)_6$ and O_2 differs in at least two respects: (i) intermediates can be detected and isolated and (ii) the final product, $\text{MoO}_2(\text{OPr}^i)_2$, is not monomeric in non-coordinating solvents or in the solid state, though addition of bpy (2,2'-bipyridyl) allows the isolation of the

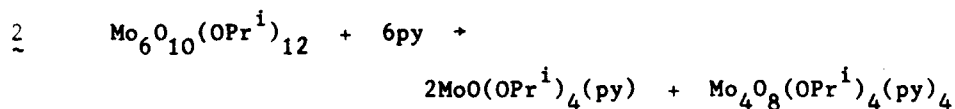
mononuclear compound $\text{MoO}_2(\text{OPr}^i)_2(\text{bpy})$.[†] An intermediate in the formation of $[\text{MoO}_2(\text{OPr}^i)_2]_n$ is $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ which is readily isolated from the reaction between $\text{Mo}_2(\text{OPr}^i)_6$ and O_2 because it is virtually insoluble in hexane and only sparingly soluble in toluene. $[\text{MoO}_2(\text{OPr}^i)_2]_n$, which is more soluble in toluene, may be obtained by either the further reaction of $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ with O_2 or by the addition of Pr^iOH (excess) to $\text{MoO}_2(\text{O}^t\text{Bu})_2$.

The solid state structure of $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ 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 and a stereoview of the molecule, which clearly reveals the S-shaped curve of the molecule, is shown in Figure 2. The molecule has a rigorous center of inversion and, to within 0.01 Å, the six molybdenum atoms lie in a plane. The $\text{Mo}(1)'\text{-Mo}(1)\text{-Mo}(2)$ and $\text{Mo}(1)\text{-Mo}(2)\text{-Mo}(3)$ angles are $146.5(1)^\circ$ and $134.3(1)^\circ$, respectively. There are several other interesting structural features. The terminal molybdenum atoms, $\text{Mo}(3)$ and $\text{Mo}(3)'$, 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 -2 for terminal oxo, -1 for bridging oxo and terminal OR and $-\frac{1}{2}$ for bridging OR, then $\text{Mo}(3)$ and $\text{Mo}(3)'$ are +6, and, $\text{Mo}(1)$, $\text{Mo}(1)'$, $\text{Mo}(2)$ and $\text{Mo}(2)'$ are +5. Four electrons are available for metal-metal bonding and these are used to form two localized M-M single bonds

as evidenced by the distances $\text{Mo}(1)\text{--}\text{Mo}(2) = \text{Mo}(1)'\text{--}\text{Mo}(2)' = 2.585(1) \text{ \AA}$, $\text{Mo}(1)\text{--}\text{Mo}(1)' = 3.353(1) \text{ \AA}$ and $\text{Mo}(2)\text{--}\text{Mo}(3) = \text{Mo}(2)'\text{--}\text{Mo}(3)' = 3.285(1) \text{ \AA}$. The geometry about the $\text{Mo}(6+)$ ions is approximately octahedral while that about the $\text{Mo}(5+)$ 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 $\text{Mo}(6+)$ ions are situated above/beneath the basal MoO_4 planes of the neighboring $\text{Mo}(5+)$ ions such that $\text{Mo}(2)\text{--}\text{O}(12) = \text{Mo}(2)'\text{--}\text{Mo}(12)' = 2.88(1) \text{ \AA}$. The $\text{Mo}(3)\text{--}\text{O}(12)$ distance, $1.919(2) \text{ \AA}$ is significantly longer than either $\text{Mo}(3)\text{--}\text{O}(14) = 1.865(2) \text{ \AA}$ or $\text{Mo}(3)\text{--}\text{O}(13) = 1.866(2) \text{ \AA}$. Furthermore, the angles $\text{Mo}(3)\text{--}\text{O}(12)\text{--}\text{C}(24) = 127.5(1)$, $\text{Mo}(2)\text{--}\text{O}(12)\text{--}\text{C}(24) = 137.3(1)$ and $\text{Mo}(2)\text{--}\text{O}(12)\text{--}\text{Mo}(3) = 83.9(1)^\circ$ support the view that $\text{O}(12)$ is effectively sp^2 hybridized.

The term semibridging is now commonly used in metal carbonyl chemistry³ where semibridging carbonyls may result from either electronic^{4,5} or steric⁶ 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 semibridging OR groups in $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ 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 coordination number from five to six. Consistent with this view is the observation that addition of pyridine (py) to $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ breaks up the Mo_6 unit according to equation 2. The structure of $\text{Mo}_4\text{O}_8(\text{OPr}^i)_4(\text{py})_4$ has been shown⁷ to contain six coordinate Mo(5+) ions.



The ^1H NMR spectrum of $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ in toluene- d_8 at $+75^\circ\text{C}$, 220 MHz, shows only one type of OPr^i group consistent with rapid OPr^i group exchange.

We thank the Office of Naval Research for support of this work. CCK is the 1980/81 Indiana University SOHIO Fellow.

†Satisfactory analytical data have been obtained for the new compounds reported. All reactions were carried out using dry solvents and dry molecular oxygen.

*Crystal data (at -162°C) for $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$: space group = $\overline{\text{P}}1$, $a = 13.082(3)$, $b = 11.478(2)$, $c = 9.760(2)$ Å, $\alpha = 106.40(1)^\circ$, $\beta = 91.85(1)^\circ$, $\gamma = 99.81(1)^\circ$, $D_c = 1.738$ g cm $^{-3}$, $Z = 1$. The structure was solved by Patterson and Fourier techniques using 4891 unique intensities collected on an automated diffractometer

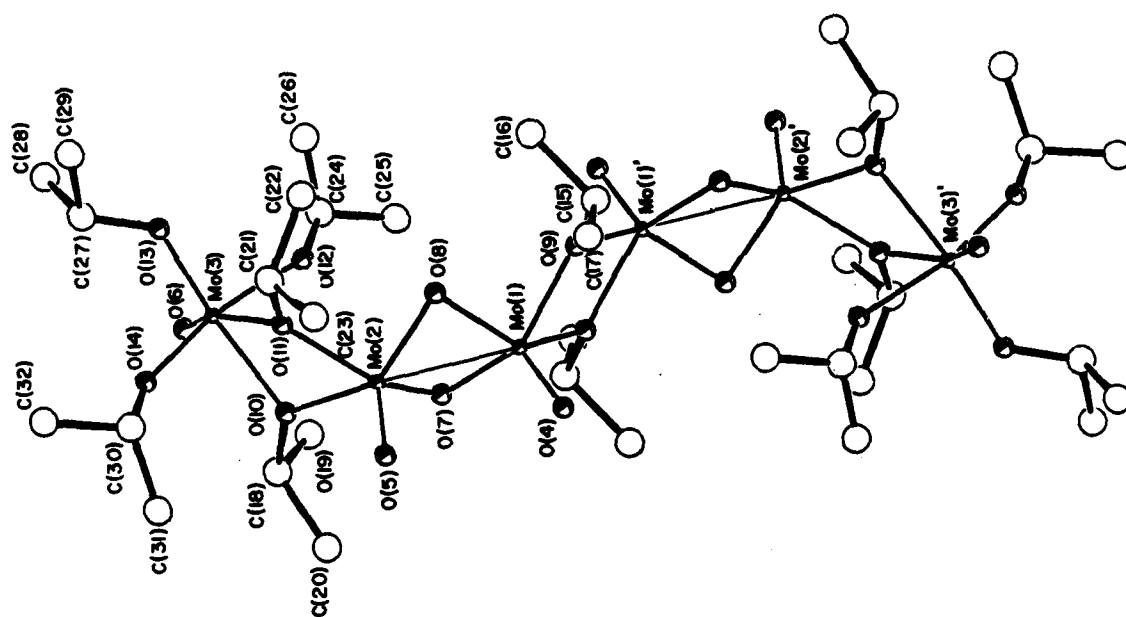
using Mo K α radiation for $5^\circ \leq 2\theta \leq 50^\circ$. All hydrogen atoms were located and refined. Final refinement utilized anisotropic thermal parameters for all nonhydrogen atoms and converged to $R(F) = 0.027$ and $R_w(F) = 0.036$. The atomic coordinates and a complete listing of bonding distances for this work are available upon request. See J. Chem. Soc. Chem. Commun. 1981, 3. Any request should be accompanied by the full literature citation for this communication.

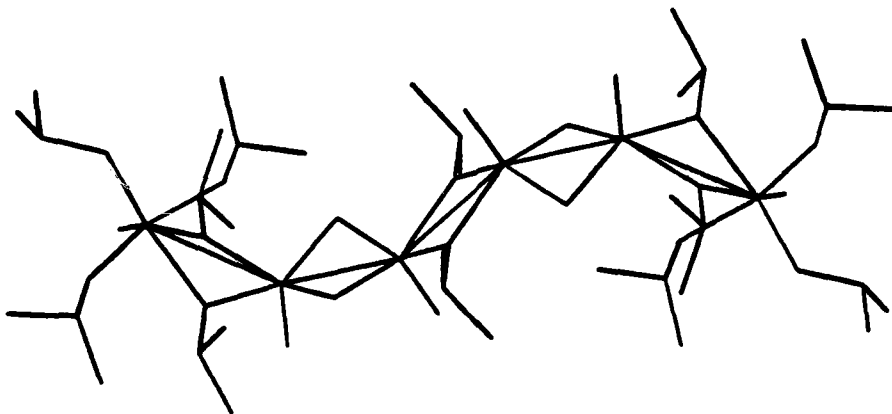
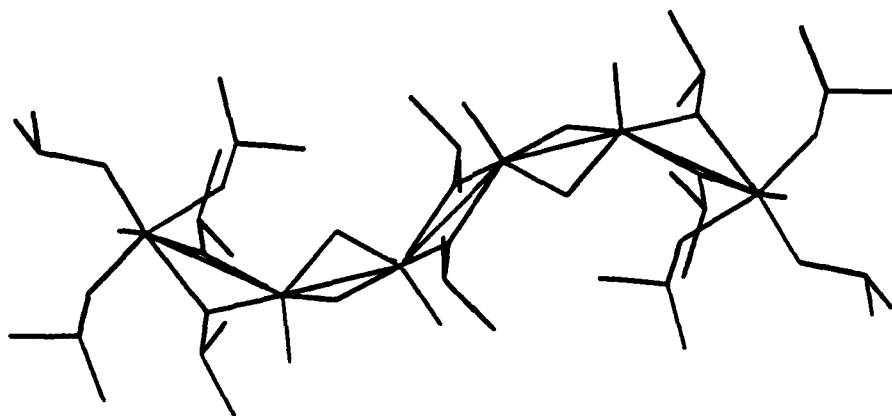
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Captions to Figures

Figure 1. View of the $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ molecule giving the atom numbering scheme. Some pertinent bond distances ($\text{\AA}$), not quoted in text, are for terminal oxo-molybdenum groups: $\text{Mo}(1)-\text{O}(4) = 1.673(2)$, $\text{Mo}(2)-\text{O}(5) = 1.671(2)$, $\text{Mo}(3)-\text{O}(6) = 1.691(2)$; for bridging oxo groups: $\text{Mo}(1)-\text{O}(7) = 1.921(2)$, $\text{Mo}(1)-\text{O}(8) = 1.926(2)$, $\text{Mo}(2)-\text{O}(7) = 1.939(2)$, $\text{Mo}(2)-\text{O}(8) = 1.939(2)$; for bridging alkoxy groups: $\text{Mo}(1)-\text{O}(9) = 2.058(2)$, $\text{Mo}(1)-\text{O}(9)' = 2.072(2)$, $\text{Mo}(2)-\text{O}(10) = 2.057(2)$, $\text{Mo}(2)-\text{O}(11) = 2.044(2)$, $\text{Mo}(3)-\text{O}(10) = 2.128(2)$, $\text{Mo}(3)-\text{O}(11) = 2.197(2)$.

Figure 2. Stereoview of $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ showing the S-curve shape of the molecule.





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Table of Bond Distances ($\text{\AA}$) for the $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ Molecule.

A	B	Distance	A	B	Distance
Mo(1)	Mo(1)'	3.353(1)	O(9)	C(15)	1.476(4)
Mo(2)	Mo(3)	3.285(1)	O(10)	C(18)	1.462(4)
Mo(1)	Mo(2)	2.585(1)	O(11)	C(21)	1.454(4)
Mo(1)	O(4)	1.673(2)	O(12)	C(24)	1.443(4)
Mo(1)	O(7)	1.921(2)	O(13)	C(27)	1.434(4)
Mo(1)	O(8)	1.926(2)	O(14)	C(30)	1.433(4)
Mo(1)	O(9)	1.058(2)	C(15)	C(16)	1.489(6)
Mo(1)	O(9)'	2.072(2)	C(15)	C(17)	1.496(6)
Mo(2)	O(5)	1.671(2)	C(18)	C(19)	1.513(5)
Mo(2)	O(7)	1.939(2)	C(18)	C(20)	1.505(5)
Mo(2)	O(8)	1.939(2)	C(21)	C(22)	1.522(5)
Mo(2)	O(10)	2.057(2)	C(21)	C(23)	1.518(5)
Mo(2)	O(11)	2.044(2)	C(24)	C(25)	1.485(6)
Mo(3)	O(6)	1.691(2)	C(24)	C(26)	1.483(7)
Mo(3)	O(10)	2.128(2)	C(27)	C(28)	1.531(7)
Mo(3)	O(11)	2.197(2)	C(27)	C(29)	1.506(7)
Mo(3)	O(12)	1.919(2)	C(30)	C(31)	1.512(6)
Mo(3)	O(13)	1.866(2)	C(30)	C(32)	1.510(6)
Mo(3)	O(14)	1.865(2)			

Table of Fractional Coordinates for the $\text{Mo}_6\text{O}_{10}(\text{OPr}^i)_{12}$ Molecule.

Atom	x	y	z
Mo(1)	1285.4(2)	104.2(3)	-124.9(3)
Mo(2)	2776.6(2)	-1044.0(3)	-1053.6(3)
Mo(3)	2878.3(2)	-3886.8(3)	-2919.9(3)
O(4)	1897(2)	1560(2)	656(3)
O(5)	3811(2)	102(2)	-527(3)
O(6)	2425(2)	-4552(2)	-4658(3)
O(7)	1723(2)	9518(2)	7983(2)
O(8)	1935(2)	-1041(2)	546(2)
O(9)	-88(2)	191(2)	-1148(2)
O(10)	3086(2)	-2044(2)	-3053(2)
O(11)	3323(2)	-2541(2)	-797(2)
O(12)	1582(2)	-3505(2)	-2230(3)
O(13)	2821(2)	-5233(2)	-2193(3)
O(14)	4301(2)	-3763(2)	-3129(3)
C(15)	-160(3)	424(4)	-2556(4)
C(16)	-13(4)	1728(5)	-2328(5)
C(17)	-1117(4)	-345(4)	-3459(5)
C(18)	3121(3)	-1741(3)	-4410(4)
C(19)	2043(3)	-2031(4)	-5174(4)
C(20)	3629(3)	9592(4)	5860(5)
C(21)	3510(3)	-2893(3)	495(4)
C(22)	2519(3)	-3539(4)	945(4)
C(23)	4065(3)	-1766(4)	1671(4)
C(24)	547(3)	-4068(4)	-2897(4)
C(25)	9870(4)	6875(5)	7355(9)
C(26)	152(5)	-5113(6)	-2327(10)
C(27)	3328(3)	-6280(4)	-2573(5)
C(28)	2669(4)	-7252(4)	-3843(5)
C(29)	3445(4)	-6718(5)	-1270(6)
C(30)	5313(3)	-3166(4)	-2432(4)
C(31)	5664(3)	-1997(4)	-2848(6)
C(32)	6040(4)	-4076(5)	-2843(6)

Note: (1) Fractional coordinates are $\times 10^4$ for nonhydrogen atoms.

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