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# Metal Alkoxides—Models for Metal Oxides. 1. Preparations and Structures of Hexadecaalkoxytetratungsten Compounds, $W_4(OR)_{16}$, Where R = Me and Et, and Octaoxotetraisopropoxytetrapyridinotetramolybdenum, $Mo_4(O)_4(\mu\text{-}O)_2(\mu_3\text{-}O)_2(O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(py)_4$

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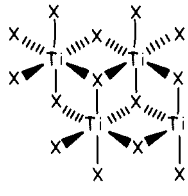
**Abstract:** In hydrocarbon solvents, $W_2(NMe_2)_6$ ($M\equiv M$) and each of the alcohols, MeOH and EtOH, react to give tetranuclear compounds, $W_4(OR)_{16}$ (R = Me and Et), by alcoholysis and oxidation of tungsten, 3+ to 4+. These new compounds have been characterized by a variety of physicochemical techniques including, for the ethoxide, a single-crystal X-ray diffraction study. By the formation of alkoxy bridges, each tungsten atom attains an octahedral coordination. The $M_4O_{16}$ skeleton is akin to those found in the anion $W_4O_{16}^{8-}$ and the neutral alkoxide $[Ti(OEt)_4]_4$, but the eight electrons associated with the four W(4+) $d^2$ atoms lead to cluster-$W_4$ bonding as evidenced by a comparison of M–M distances. From the reaction between $Mo_2(O\text{-}i\text{-}Pr)_6$ ($M\equiv M$) and molecular oxygen in pyridine, a minor product, formed in ca. 15% yield based on Mo, is shown to be $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ by a complete X-ray diffraction study. The central $Mo_4O_8O'_4N_4$ moiety is closely related to those mentioned above. The average oxidation state of molybdenum is +5, and the four electrons available for M–M bonding form two localized M–M single bonds. These new findings are compared with those of McCarley and co-workers, who found that certain mixed-metal oxides of molybdenum contain repeating $Mo_4O_{16}$ units which are structurally related to those reported here, having either 8 or 10 cluster-$M_4$ bonding electrons. These observations lead us to propose that (1) metal alkoxides provide hydrocarbon-soluble models for metal oxides and (2) there should be a large class of structurally related $M_4X_aY_bZ_c$ cluster compounds ($a + b + c = 16$) in which the metal atoms achieve an octahedral environment and, by appropriate variations of ligands and metals, have 0 through 12 electrons for M–M bonding. Crystal data for $W_4(OEt)_{16}$ are as follows: $a = 12.129$ (6) Å, $b = 10.985$ (6) Å, $c = 9.692$ (5) Å, $\alpha = 93.28$ (3)°, $\beta = 108.64$ (2)°, and $\gamma = 105.71$ (2)°, with $Z = 1$ in the space group $P\bar{1}$. Crystal data for $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4\cdot 2py$ are as follows: $a = 11.562$ (2) Å, $b = 13.915$ (3) Å, $c = 17.095$ (4) Å, $\beta = 117.75$ (1)°, with $Z = 2$ in the space group $P2_1/c$.

In 1958, Bradley[1] proposed a structural theory for metal alkoxides based on the desire of metal atoms to achieve their preferred coordination environments by the minimum degree of oligomerization. The structure of $[Ti(OEt)_4]_4$ reported by Ibers[2] in 1963 is of historic significance since it provided the first structural investigation of Bradley's proposal: each titanium atom achieves an octahedral environment, through the agency of four doubly bridging and two triply bridging alkoxy groups, as is shown in I.



1, X = OEt

We now show that this same type of structure is adopted by the compounds $W_4(OR)_{16}$, where R = Me and Et, and $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$. The only major difference between the structures arises from the number of electrons available for metal–metal bonding. A preliminary report of some of this work has appeared.[3]

## Results and Discussion

**Preparations.** $\mathbf{W_4(OR)_{16}}$. Hydrocarbon solutions of $W_2(NMe_2)_6$ ($M\equiv M$)[4] and each of the alcohols, MeOH and EtOH, react at room temperature to give dark solutions from which the tetranuclear compounds, $W_4(OR)_{16}$, are obtained by crystallization. Formation of the new compounds appears to be stoichiometric, based on eq 1.

$$2W_2(NMe_2)_6 + 16ROH \rightarrow W_4(OR)_{16} + 12HNMe_2 + 2H_2 \tag{1}$$

This contrasts with analogous reactions involving $t$-BuOH and $i$-PrOH which give $W_2(O\text{-}t\text{-}Bu)_6$[5] and $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$,[6] respectively. However, the oxidation of tungsten 3+ to 4+, in the reactions involving MeOH and EtOH, is not altogether surprising. It is quite possible, but has not been established, that $W_4(\mu\text{-}H)_2(OR)_{14}$ compounds, analogous to the isopropoxide, are intermediate in the formation of the $W_4(OR)_{16}$ compounds.

$\mathbf{Mo_4O_8(O\text{-}\mathit{i}\text{-}Pr)_4(py)_4}$. During the course of studies of reactions between $Mo_2(OR)_6$ ($M\equiv M$) compounds and molecular oxygen,[7] we discovered that, when R = $i$-Pr and the solvent was pyridine, a minor product, $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$, crystallized out of solution. This compound is formed in ca. 15% yield based on Mo: the major product is $MoO_2(O\text{-}i\text{-}Pr)_2(py)_2$ along with acetone and $i$-PrOH which arise from $i$-PrO radicals liberated during the course of the reaction. The details of these products are not pertinent to this work and will be described in detail elsewhere.[7]

**Physicochemical Properties.** The compounds $W_4(OR)_{16}$ are dark, almost black, shiny crystalline solids. They are appreciably soluble in hydrocarbon solvents and give green (R = Me) or brown (R = Et) solutions. Cryoscopic molecular weight determinations in benzene indicated that they were tetranuclear in solution. They are diamagnetic and the $^1H$ NMR spectrum of the methoxide showed eight singlets of equal intensity. This remarkable observation is consistent with the maintenance of the centrosymmetric

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[1] Bradley, D. C. *Nature (London)* **1958**, *182*, 1211.

[2] Ibers, J. A. *Nature (London)* **1963**, *197*, 686.

[3] Chisholm, M. H.; Huffman, J. C.; Leonelli, J. *J. Chem. Soc., Chem. Commun.* **1981**, 270.

[4] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4477.

[5] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

[6] Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D. *J. Am. Chem. Soc.* **1979**, *101*, 2504; **1981**, *103*, 779.

[7] Chisholm, M. H.; Huffman, J. C.; Folting, K.; Kirkpatrick, C. C.; Ratermann, A. L. *J. Am. Chem. Soc.* **1981**, *103*, 1305 and results to be published.

0002-7863/81/1503-6093$01.25/0

Table I. Fractional Coordinates for the $W_4(OEt)_{16}$ Molecule

| atom | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| W(1) | 726.9 (4) | 4463.0 (4) | 1030.5 (5) | 9 |
| W(2) | 1735.2 (4) | 6923.3 (4) | 1039 (1) | 10 |
| O(3) | 1043 (7) | 5343 (8) | −818 (9) | 9 |
| C(4) | 1356 (11) | 4888 (12) | −2029 (12) | 14 |
| C(5) | 2634 (12) | 4798 (12) | −1578 (14) | 16 |
| O(6) | 1443 (8) | 5965 (8) | 2680 (9) | 12 |
| C(7) | 1589 (11) | 6257 (13) | 4206 (13) | 16 |
| C(8) | 2913 (11) | 6495 (14) | 5162 (15) | 21 |
| O(9) | −71 (7) | 2800 (8) | −514 (9) | 10 |
| C(10) | 299 (11) | 1647 (11) | −601 (13) | 14 |
| C(11) | 399 (13) | 1341 (13) | −2065 (16) | 22 |
| O(12) | 2195 (8) | 4003 (8) | 1289 (9) | 15 |
| C(13) | 3201 (11) | 4131 (12) | 2624 (14) | 16 |
| C(14) | 4014 (14) | 3425 (14) | 2266 (17) | 28 |
| O(15) | 463 (8) | 3562 (8) | 2668 (9) | 14 |
| C(16) | 527 (11) | 2313 (11) | 2873 (13) | 12 |
| C(17) | 684 (15) | 2143 (14) | 4457 (16) | 27 |
| O(18) | 2354 (8) | 8335 (8) | 2692 (9) | 13 |
| C(19) | 2812 (13) | 9654 (12) | 2664 (15) | 20 |
| C(20) | 3263 (17) | 10341 (14) | 4244 (19) | 33 |
| O(21) | 3309 (7) | 6736 (8) | 1425 (9) | 13 |
| C(22) | 4450 (12) | 7709 (12) | 2027 (15) | 18 |
| C(23) | 5475 (12) | 7170 (14) | 2113 (19) | 28 |
| O(24) | 2076 (8) | 8136 (8) | −257 (9) | 14 |
| C(25) | 2521 (13) | 8106 (13) | −1423 (15) | 20 |
| C(26) | 3125 (15) | 9466 (14) | −1596 (18) | 28 |

[a] (1) Fractional coordinates are $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogen atoms. $B_{iso}$ values are $\times 10$. (2) Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.*, 1959, *12*, 609.

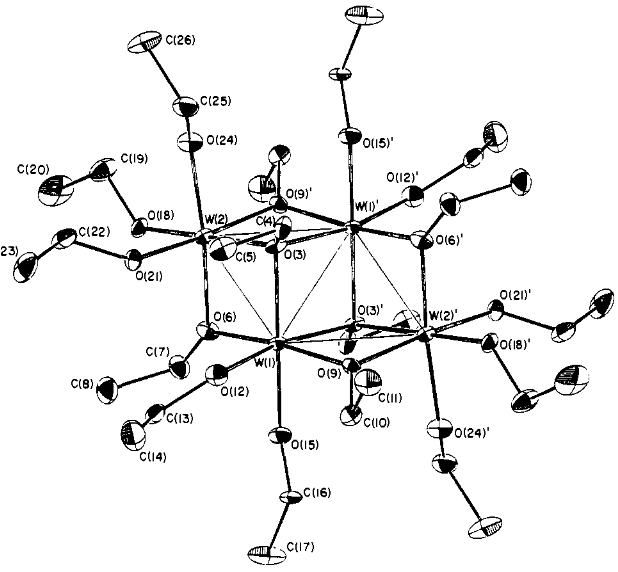

Figure 1. An ORTEP view of the centrosymmetric $W_4(OEt)_{16}$ molecule giving the atom-numbering scheme used in the tables. Atoms are represented by ellipsoids, drawn to include 50% probability of thermal displacement.

Table II. Anisotropic Thermal Parameters for the $W_4(OEt)_{16}$ Molecule[a]

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| W(1) | 13.8 (3) | 8.8 (3) | 12.9 (3) | 4.9 (2) | 5.9 (2) | 4.2 (2) |
| W(2) | 14.2 (3) | 8.9 (3) | 14.5 (3) | 2.9 (2) | 6.2 (2) | 2.7 (2) |
| O(3) | 17 (4) | 12 (4) | 11 (4) | 5 (3) | 13 (3) | 4 (3) |
| C(4) | 15 (6) | 22 (6) | 12 (5) | −1 (5) | 8 (5) | −0 (5) |
| C(5) | 28 (7) | 22 (6) | 21 (6) | 10 (5) | 19 (5) | 2 (5) |
| O(6) | 21 (4) | 21 (5) | 11 (4) | 10 (4) | 9 (4) | 4 (3) |
| C(7) | 18 (6) | 27 (7) | 15 (6) | 6 (5) | 5 (5) | 2 (5) |
| C(8) | 16 (6) | 35 (8) | 25 (7) | 3 (6) | 7 (5) | 6 (6) |
| O(9) | 11 (4) | 16 (4) | 13 (4) | 8 (3) | 5 (3) | 5 (3) |
| C(10) | 20 (6) | 13 (6) | 20 (6) | 7 (5) | 9 (5) | 1 (5) |
| C(11) | 28 (7) | 21 (7) | 38 (8) | 17 (6) | 9 (6) | 2 (6) |
| O(12) | 19 (5) | 19 (5) | 21 (5) | 9 (4) | 8 (4) | 4 (4) |
| C(13) | 19 (6) | 16 (6) | 21 (6) | −0 (5) | 8 (5) | 4 (5) |
| C(14) | 28 (8) | 28 (8) | 39 (9) | 10 (6) | −0 (7) | −1 (7) |
| O(15) | 21 (5) | 15 (4) | 22 (5) | 10 (4) | 10 (4) | 9 (4) |
| C(16) | 20 (6) | 14 (6) | 17 (6) | 8 (5) | 9 (5) | 10 (5) |
| C(17) | 63 (11) | 28 (8) | 26 (7) | 24 (7) | 23 (7) | 15 (6) |
| O(18) | 14 (4) | 8 (4) | 21 (4) | 1 (3) | 3 (4) | 0 (3) |
| C(19) | 37 (8) | 16 (6) | 23 (7) | 2 (6) | 15 (6) | 0 (5) |
| C(20) | 62 (11) | 14 (7) | 47 (10) | 11 (7) | 17 (9) | −3 (7) |
| O(21) | 7 (4) | 22 (5) | 23 (5) | 4 (3) | 7 (3) | 7 (4) |
| C(22) | 22 (6) | 16 (6) | 34 (7) | 6 (5) | 15 (6) | 10 (5) |
| C(23) | 15 (7) | 28 (8) | 63 (11) | 5 (6) | 16 (7) | 11 (7) |
| O(24) | 24 (5) | 19 (4) | 18 (4) | 12 (4) | 15 (4) | 5 (4) |
| C(25) | 30 (7) | 19 (6) | 25 (7) | 10 (6) | 6 (6) | 8 (5) |
| C(26) | 46 (9) | 21 (7) | 49 (10) | 8 (7) | 26 (8) | 18 (7) |

[a] All $U$'s are $\times 10^3$. The form of the anisotropic thermal parameter is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + hka^*b^*U_{12} + \ldots)]$.

Table III. Bond Distances (Å) for the $W_4(OEt)_{16}$ Molecule

| A | B | dist | A | B | dist |
|---|---|---|---|---|---|
| W(1) | W(1)' | 2.763 (1) | O(3) | C(4) | 1.446 (13) |
| W(1) | W(2) | 2.646 (2) | O(6) | C(7) | 1.439 (14) |
| W(1) | W(2)' | 2.936 (2) | O(9) | C(10) | 1.459 (13) |
| W(1) | O(3)' | 2.160 (8) | O(12) | C(13) | 1.435 (15) |
| W(1) | O(3) | 2.174 (8) | O(15) | C(16) | 1.417 (13) |
| W(1) | O(6) | 2.016 (8) | O(18) | C(19) | 1.409 (15) |
| W(1) | O(9) | 2.079 (8) | O(21) | C(22) | 1.417 (15) |
| W(1) | O(12) | 1.925 (8) | O(24) | C(25) | 1.401 (16) |
| W(1) | O(15) | 1.984 (8) | C(4) | C(5) | 1.502 (17) |
| W(2) | O(3) | 2.202 (8) | C(7) | C(8) | 1.516 (17) |
| W(2) | O(6) | 2.028 (8) | C(10) | C(11) | 1.490 (18) |
| W(2) | O(9)' | 2.030 (8) | C(13) | C(14) | 1.516 (19) |
| W(2) | O(18) | 1.962 (8) | C(16) | C(17) | 1.514 (17) |
| W(2) | O(21) | 1.895 (8) | C(19) | C(20) | 1.525 (20) |
| W(2) | O(24) | 1.936 (8) | C(22) | C(23) | 1.497 (18) |
|  |  |  | C(25) | C(26) | 1.521 (19) |

structure found in the solid state. Evidently, $W_4(OMe)_{16}$ is rigid on the NMR time scale, which contrasts with the fluxional $W_4(\mu\text{-}H)_2(O\text{-}i\text{-}Pr)_{14}$ molecule and the dissociation of $[Ti(OEt)_4]_4$ in solution.[8] The $^1H$ NMR spectrum of the ethoxide was complex, showing many overlapping methylene and methyl resonances. The compounds are not sublimable: in vacuo, when heated, small quantities of the monomeric $W(OR)_6$ compounds sublime, and, in the mass spectrometer, the ions of highest mass corresponded to $W(OR)_5^+$. The electronic absorption spectra revealed several bands in the UV–visible–near-IR, some of which must arise from electronic transitions involving the $W_4$–cluster molecule orbitals. Infrared data, NMR data, and $\lambda_{max}$ values (UV–visible) are recorded in the Experimental Section.

$Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ is a red crystalline solid which is insoluble in hydrocarbon solvents, pyridine, and methylene chloride. Elemental analyses and infrared data are given in the Experimental Section.

All three compounds are hydrolyzed when exposed to the atmosphere.

**Solid-State Structures. $W_4(OEt)_{16}$.** Fractional coordinates and isotropic thermal parameters are given in Table I, and anisotropic thermal parameters are given in Table II. Bond distances and bond angles are given in Tables III and IV, respectively. An ORTEP view of the molecule, giving the atom numbering scheme used in the tables, is shown in Figure 1.

In the space group $P\bar{1}$, one centrosymmetric molecule occupies the unit cell. There are two crystallographically and chemically different tungsten atoms: W(1) and W(2) have respectively two and three terminal OEt ligands. The eight crystallographically independent ethoxy ligands can be broken down into three groups: terminal (5), doubly bridging (2), and triply bridging (1). Each tungsten atom attains a distorted octahedral environment, and

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(8) Bradley, D. C.; Mehrotra, R. C.; Gaur, P. D. "Metal Alkoxides"; Academic Press: London, New York, San Francisco.

Table IV. Bond Angles (Deg) for the $W_4(OEt)_{16}$ Molecule

| A | B | C | angle |
|---|---|---|---|
| W(1)′ | W(1) | W(2) | 65.7 (0) |
| W(1)′ | W(1) | W(2)′ | 55.2 (0) |
| W(1)′ | W(1) | O(3) | 50.2 (2) |
| W(1)′ | W(1) | O(3)′ | 50.6 (2) |
| W(1)′ | W(1) | O(6) | 97.5 (2) |
| W(1)′ | W(1) | O(9) | 85.9 (2) |
| W(1)′ | W(1) | O(12) | 136.2 (3) |
| W(1)′ | W(1) | O(15) | 132.1 (2) |
| W(2) | W(1) | W(2)′ | 120.9 (0) |
| W(2) | W(1) | O(3)′ | 94.3 (2) |
| W(2) | W(1) | O(3) | 53.3 (2) |
| W(2)′ | W(1) | O(3)′ | 48.3 (2) |
| W(2)′ | W(1) | O(3) | 86.3 (2) |
| W(2) | W(1) | O(6) | 49.3 (2) |
| W(2)′ | W(1) | O(6) | 135.3 (2) |
| W(2) | W(1) | O(9) | 136.7 (2) |
| W(2)′ | W(1) | O(9) | 43.7 (2) |
| W(2) | W(1) | O(12) | 95.2 (3) |
| W(2)′ | W(1) | O(12) | 126.7 (3) |
| W(2) | W(1) | O(15) | 129.8 (3) |
| W(2)′ | W(1) | O(15) | 93.1 (3) |
| O(3)′ | W(1) | O(3) | 100.8 (3) |
| O(3) | W(1) | O(6) | 102.6 (3) |
| O(3)′ | W(1) | O(6) | 87.1 (3) |
| O(3) | W(1) | O(9) | 83.5 (3) |
| O(3)′ | W(1) | O(9) | 91.4 (3) |
| O(3)′ | W(1) | O(12) | 170.3 (3) |
| O(3) | W(1) | O(12) | 86.5 (3) |
| O(3) | W(1) | O(15) | 176.2 (3) |
| O(3)′ | W(1) | O(15) | 81.6 (3) |
| O(6) | W(1) | O(9) | 174.0 (3) |
| O(6) | W(1) | O(12) | 97.7 (3) |
| O(6) | W(1) | O(15) | 80.4 (3) |
| O(9) | W(1) | O(12) | 83.0 (3) |
| O(9) | W(1) | O(15) | 93.6 (3) |
| O(12) | W(1) | O(15) | 90.9 (3) |
| W(1) | W(2) | W(1)′ | 59.1 (0) |
| W(1)′ | W(2) | O(3) | 47.1 (2) |
| W(1) | W(2) | O(3) | 52.3 (2) |
| W(1)′ | W(2) | O(6) | 92.1 (2) |
| W(1) | W(2) | O(6) | 49.0 (2) |
| W(1) | W(2) | O(9)′ | 90.1 (2) |
| W(1)′ | W(2) | O(9)′ | 45.1 (2) |
| W(1)′ | W(2) | O(18) | 132.9 (2) |
| W(1) | W(2) | O(18) | 127.8 (2) |
| W(1) | W(2) | O(21) | 92.8 (3) |
| W(1)′ | W(2) | O(21) | 134.9 (3) |
| W(1) | W(2) | O(24) | 142.0 (3) |
| W(1)′ | W(2) | O(24) | 93.9 (3) |
| O(3) | W(2) | O(6) | 101.3 (3) |
| O(3) | W(2) | O(9)′ | 91.5 (3) |
| O(3) | W(2) | O(18) | 179.8 (3) |
| O(3) | W(2) | O(21) | 88.0 (3) |
| O(3) | W(2) | O(24) | 89.8 (3) |
| O(6) | W(2) | O(9)′ | 90.7 (3) |
| O(6) | W(2) | O(18) | 78.9 (3) |
| O(6) | W(2) | O(21) | 93.4 (3) |
| O(6) | W(2) | O(24) | 168.7 (3) |
| O(9)′ | W(2) | O(18) | 88.5 (3) |
| O(9)′ | W(2) | O(21) | 175.9 (3) |
| O(9)′ | W(2) | O(24) | 86.8 (3) |
| O(18) | W(2) | O(21) | 92.0 (4) |
| O(18) | W(2) | O(24) | 90.0 (4) |
| O(21) | W(2) | O(24) | 89.1 (4) |
| W(1)′ | O(3) | W(1) | 79.2 (3) |
| W(1)′ | O(3) | W(2) | 84.6 (3) |
| W(1) | O(3) | W(2) | 74.4 (2) |
| W(1) | O(3) | C(4) | 131.7 (7) |
| W(1)′ | O(3) | C(4) | 124.4 (7) |
| W(2) | O(3) | C(4) | 140.6 (7) |
| W(1) | O(6) | W(2) | 81.7 (3) |
| W(1) | O(6) | C(7) | 140.0 (8) |
| W(2) | O(6) | C(7) | 138.1 (8) |
| W(1) | O(9) | W(2)′ | 91.2 (3) |
| W(1) | O(9) | C(10) | 130.4 (7) |
| W(2)′ | O(9) | C(10) | 132.3 (7) |
| W(1) | O(12) | C(13) | 128.6 (7) |
| W(1) | O(15) | C(16) | 126.4 (7) |
| W(2) | O(18) | C(19) | 127.5 (8) |
| W(2) | O(21) | C(22) | 127.3 (8) |
| W(2) | O(24) | C(25) | 133.2 (8) |
| O(3) | C(4) | C(5) | 113.9 (9) |
| O(6) | C(7) | C(8) | 109.7 (10) |
| O(9) | C(10) | C(11) | 111.1 (10) |
| O(12) | C(13) | C(14) | 107.4 (10) |
| O(15) | C(16) | C(17) | 109.7 (10) |
| O(18) | C(19) | C(20) | 107.2 (11) |
| O(21) | C(22) | C(23) | 110.6 (11) |
| O(24) | C(25) | C(26) | 109.6 (11) |

the crystallographic inversion center requires that the four tungsten atoms lie in a plane.

**$Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4\cdot 2py$.** Fractional coordinates and isotropic thermal parameters are given in Table V and anisotropic thermal parameters are given in Table VI. Bond distances and bond angles are given in Tables VII and VIII, respectively. An ORTEP view of the molecule is shown in Figure 2.

The $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ molecule also possesses a center of inversion, and the molecule can be related to $W_4(OEt)_{16}$ in the following way. Molybdenum is substituted for tungsten and a pair of terminal OR groups are replaced by terminal oxo and pyridine ligands: $[W(OR)_2]_4$ is transformed to $[MoO(py)]_4$. A pair of symmetrically related bridging alkoxides in $W_4(OEt)_{16}$ are replaced by bridging oxo groups ($\mu_2$-O), and finally, the triply bridging OR ligands are replaced by triply bridging oxo groups ($\mu_3$-O).

**Comparison of Structures.** It is pertinent to discuss the interatomic parameters of these two new molecules together and, furthermore, to contrast these with other known compounds which adopt $M_4$-edge-shared octahedra of this type.[9] Particularly

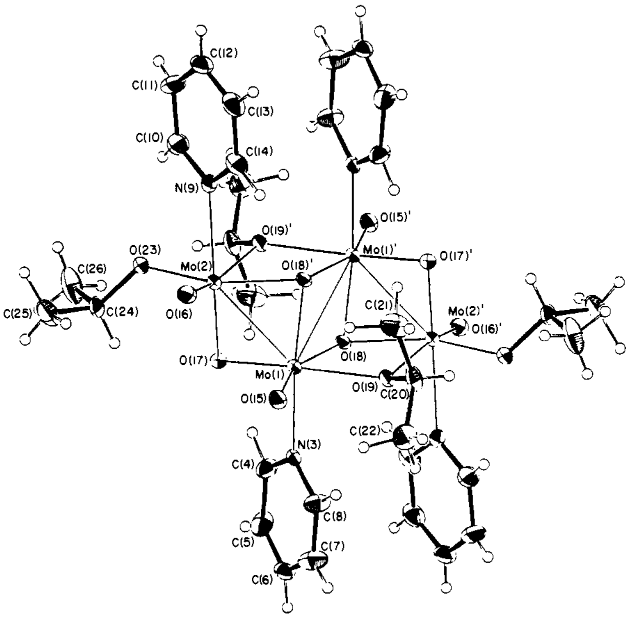

Figure 2. An ORTEP view of the $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ molecule giving the atom-numbering scheme used in the tables. Atoms are represented by ellipsoids, drawn to include 50% probability of thermal displacement. Hydrogen atoms are represented by spheres of arbitrary size.

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(9) The same structural unit is seen in $M^1Nb_4X_{11}$ compounds where $M^1$ = Cs or Rb and X = Cl or Br, but a comparison is not justified here because the very different bridging properties of the halides compared to oxo and alkoxy ligands: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, London, Sydney, Toronto, 1972; p 943 and references therein.

(10) Skarstad, P. M.; Geller, S. *Mater. Res. Bull.* **1975**, *10*, 791.

Table V. Fractional Coordinates and Isotropic Thermal Parameters for the $Mo_2O_8(O\text{-}i\text{-}Pr)_4(py)_4$ Molecule[a]

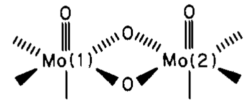
| atom | $x$ | $y$ | $z$ | $B_{iso}$, Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 16.9 (3) | 447.5 (2) | 9137.4 (2) | 10 |
| Mo(2) | 1943.8 (3) | 1210.2 (2) | 10517.3 (2) | 11 |
| N(3) | 57 (3) | −514 (2) | 8107 (2) | 12 |
| C(4) | 1024 (4) | −1133 (3) | 8290 (3) | 19 |
| C(5) | 1118 (4) | −1665 (3) | 7643 (3) | 25 |
| C(6) | 204 (4) | −1554 (3) | 6775 (3) | 20 |
| C(7) | −803 (5) | −926 (4) | 6587 (3) | 27 |
| C(8) | −844 (4) | −421 (3) | 7263 (3) | 21 |
| N(9) | 2212 (3) | 1970 (2) | 11765 (2) | 14 |
| C(10) | 3270 (4) | 1869 (4) | 12536 (3) | 23 |
| C(11) | 3448 (5) | 2362 (4) | 13281 (3) | 29 |
| C(12) | 2493 (5) | 2996 (4) | 13228 (3) | 28 |
| C(13) | 1416 (5) | 3113 (3) | 12440 (3) | 24 |
| C(14) | 1290 (4) | 2589 (3) | 11713 (3) | 21 |
| O(15) | −413 (3) | 1356 (2) | 8406 (2) | 15 |
| O(16) | 1761 (3) | 2326 (2) | 10074 (2) | 16 |
| O(17) | 1905 (2) | 330 (2) | 9627 (2) | 13 |
| O(18) | −68 (2) | −908 (2) | 9752 (2) | 11 |
| O(19) | −1973 (2) | 59 (2) | 8664 (2) | 12 |
| C(20) | 6942 (4) | 725 (3) | 8297 (3) | 19 |
| C(21) | −2830 (5) | 1591 (4) | 8881 (5) | 28 |
| C(22) | −3415 (5) | 1003 (4) | 7364 (3) | 25 |
| O(23) | 3837 (2) | 1094 (2) | 11153 (2) | 15 |
| C(24) | 4716 (4) | 890 (3) | 10805 (3) | 21 |
| C(25) | 5192 (5) | 1830 (5) | 10608 (3) | 30 |
| C(26) | 5836 (5) | 299 (4) | 11449 (5) | 35 |
| N(27) | 8031 (7) | 202 (6) | 4257 (4) | 74 |
| C(28) | 8569 (10) | 966 (5) | 4845 (5) | 65 |
| C(29) | 7943 (14) | 1291 (6) | 5261 (6) | 84 |
| C(30) | 6787 (12) | 832 (9) | 5145 (5) | 83 |
| C(31) | 6289 (7) | 90 (10) | 4625 (5) | 93 |
| C(32) | 6953 (7) | −297 (7) | 4156 (5) | 70 |
| H(1) | 162 (4) | −116 (3) | 891 (3) | 10 (8) |
| H(2) | 175 (5) | −206 (3) | 782 (3) | 28 (11) |
| H(3) | 15 (4) | −194 (3) | 634 (3) | 16 (9) |
| H(4) | −138 (5) | −85 (3) | 608 (3) | 26 (11) |
| H(5) | 851 (4) | 998 (3) | 717 (3) | 15 (9) |
| H(6) | 378 (4) | 153 (3) | 1254 (2) | 5 (8) |
| H(7) | 401 (4) | 226 (3) | 1373 (3) | 21 (11) |
| H(8) | 257 (4) | 326 (3) | 1365 (3) | 12 (9) |
| H(9) | 76 (4) | 353 (3) | 1239 (3) | 13 (9) |
| H(10) | 46 (5) | 272 (4) | 1110 (3) | 36 (11) |
| H(11) | −365 (4) | 41 (3) | 829 (3) | 19 (10) |
| H(12) | −203 (5) | 199 (4) | 893 (3) | 31 (11) |
| H(13) | −349 (5) | 205 (4) | 860 (3) | 35 (12) |
| H(14) | 745 (6) | 147 (4) | 950 (4) | 49 (15) |
| H(15) | −275 (6) | 137 (4) | 728 (4) | 42 (13) |
| H(16) | −352 (4) | 48 (3) | 703 (3) | 20 (10) |
| H(17) | −411 (5) | 141 (3) | 711 (3) | 25 (11) |
| H(18) | 431 (4) | 52 (3) | 1031 (3) | 23 (10) |
| H(19) | 579 (4) | 216 (3) | 1121 (3) | 24 (10) |
| H(20) | 565 (6) | 166 (4) | 1037 (4) | 47 (15) |
| H(21) | 448 (6) | 218 (4) | 1025 (4) | 46 (14) |
| H(22) | 556 (6) | −31 (4) | 1153 (4) | 47 (15) |
| H(23) | 647 (6) | 24 (4) | 1125 (4) | 44 (13) |
| H(24) | 624 (4) | 57 (3) | 1200 (3) | 10 (9) |

[a] (1) Fractional coordinates are $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogen atoms. $B_{iso}$ values are $\times 10$. (2) Isotropic values for those atoms refined anisotropically are calculated by using the formula given by: Hamilton, W. C. *Acta Crystallogr.* 1959, *12*, 609.

relevant for comparisons are the structures of $[Ti(OEt)_4]_4$,[2] the high temperature form of silver tungstate, $Ag_8W_4O_{16}$, which contains tetratungstate anions, $[W_4O_{16}]^{8-}$, and the ternary molybdenum oxide, $Ba_{1.13}Mo_8O_{16}$, recently prepared and structurally characterized by McCarley and his co-workers.[11] In the latter, there are infinite chains of metal clusters involving $Mo_4O_{16}$ units with the connectivity relation $Mo_4O_2O_{8/2}O_{6/3}$: the metal atoms are coplanar, being at the vertices of two triangles sharing a common edge, just as is found in the discrete coordination compounds to be considered. There are several points of interest within this grouping of compounds which include (1) the influence of $d^n$ configuration of the metal atoms and resulting metal–metal interactions and (2) the influences of the various types of oxygen donor ligands.

**Metal–Metal Distances and $d^n$ Configuration.** In the $M_4$-fused octahedra, the $t_{2g}$ atomic orbitals of the metal atoms are not involved in forming metal–ligand $\sigma$ bonds: they are, however, available for metal–metal bonding. The planar $M_4$ unit, resulting from the two triangles sharing a common edge, can be described by three distances. In Table IX, a comparison of these distances with changing $d^n$ configuration is shown. The M–M distances in $[Ti(OEt)_4]_4$ and $[W_4O_{16}]^{8-}$ are very similar and provide a basis upon which to examine the influence of introducing $t_{2g}$ electrons.

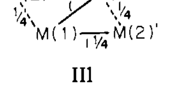
In $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$, the average oxidation for molybdenum is +5, and the four molybdenum atoms yield a total of four electrons for metal–metal bonding. These are evidently used to form two localized metal–metal single bonds between M(1) and M(2) and M(1)′ and M(2)′. It is not obvious that this should always be the case for an $M_4$-fused octahedra of the general type under consideration, but in the case of $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$, it is readily seen why this should be the case. If we consider just half the molecule, we note that the terminal oxo ligands are syn to each other as shown in II.



II

If we define the oxo–molybdenum axis as the $z$ axis, then the $d_{xz}$ and $d_{yz}$ molybdenum atomic orbitals will be used to form $\pi$ bonds to oxygen (O p-to-Mo d). The relatively short M–O (oxo) distances, 1.68 and 1.70 Å, clearly show this type of $\pi$ bonding is important.[12] Thus, the remaining $t_{2g}$ orbitals, which are not used in metal–ligand $\pi$ bonding, are the two $d_{xy}$ orbitals (one on each molybdenum) which have the appropriate symmetry to form a metal-to-metal $\sigma$ bond, $d^1$–$d^1$. One could conclude that the symmetry of the molecule and the presence of the terminal oxo groups determine that the $M_4$ unit has two localized Mo–Mo bonds, and this is certainly consistent with the observed Mo–Mo distances (Table IX).

In $W_4(OEt)_{16}$, there are four tungsten $d^2$ ions contributing a total of eight electrons for M–M bonding, and evidently, these go into cluster-type molecular orbitals, since all three M–M distances decrease from their values in $Ag_8W_4O_{16}$. The shortest distance, M(2)–M(1)′ = 2.65 Å, may be compared with the W–W double bond distances, 2.48 Å (average), found in $W_2Cl_4(OR)_4(HOR)_2$ compounds,[13] where R = Me and Et, and the M–M single bond distances, 2.73 Å (averaged), found in compounds of formula $M_2Cl_4(OR)_6$, where M = Mo[14] and W.[13] All of the latter dinuclear compounds have edge-shared octahedral structures with alkoxy bridges. Since a nonbonding distance between metal atoms bridged by alkoxy groups is typically 3.3 Å,[15] even the longest distance within the triangulo group of tungsten atoms, 2.94 Å, suggests some metal–metal bonding. A simple molecular orbital picture in these $(t_{2g}{}^n)_4$ clusters is not obvious, since there must be extensive $\sigma$, $\pi$, and $\delta$ mixing between the triangles of metal atoms. Based on bond distance considerations alone, one could reasonably partition four electron pair bonds (eight electrons) in the manner shown in III.



III

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[11] McCarley, R. E.; Luly, M. H.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* **1981**, *No. 155*, 41.

[12] For typical Mo–O distances, see: Haymore, B. L.; Nugent, W. A. *Coord. Chem. Rev.* **1980**, *31*, 123.

[13] Cotton, F. A., personal communication.

[14] Chisholm, M. H.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1981**, *20*, 871.

[15] See discussion in ref 14.

Table VI. Anisotropic Thermal Parameters for the $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_2$ Molecule ($U_{ij}$ form)[a]

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Mo(1) | 13.1 (2) | 15.9 (2) | 11.3 (2) | −0.9 (1) | 7.2 (1) | 0.1 (1) |
| Mo(2) | 13.1 (2) | 16.2 (2) | 13.0 (2) | −1.9 (1) | 7.7 (1) | −1.6 (1) |
| N(3) | 14 (2) | 20 (2) | 15 (2) | −2 (1) | 9 (1) | 1 (1) |
| C(4) | 24 (2) | 24 (2) | 23 (2) | −2 (2) | 9 (2) | −8 (2) |
| C(5) | 25 (2) | 27 (2) | 43 (3) | −3 (2) | 17 (2) | −17 (2) |
| C(6) | 39 (3) | 22 (2) | 26 (2) | −13 (2) | 24 (2) | −10 (2) |
| C(7) | 50 (3) | 30 (3) | 19 (2) | −1 (2) | 14 (2) | −0 (2) |
| C(8) | 30 (2) | 28 (2) | 18 (2) | 8 (2) | 8 (2) | −0 (2) |
| N(9) | 17 (2) | 17 (2) | 19 (2) | −4 (1) | 10 (1) | −4 (1) |
| C(10) | 23 (2) | 37 (3) | 28 (2) | 1 (2) | 14 (2) | −6 (2) |
| C(11) | 27 (3) | 62 (4) | 17 (2) | −4 (2) | 6 (2) | −11 (2) |
| C(12) | 48 (3) | 38 (3) | 33 (3) | −21 (2) | 30 (2) | −19 (2) |
| C(13) | 35 (3) | 26 (2) | 42 (3) | −1 (2) | 28 (2) | −7 (2) |
| C(14) | 30 (2) | 26 (2) | 31 (2) | 3 (2) | 20 (2) | 1 (2) |
| O(15) | 21 (1) | 20 (1) | 20 (1) | −2 (1) | 12 (1) | 1 (1) |
| O(16) | 24 (1) | 21 (2) | 19 (1) | −3 (1) | 12 (1) | −2 (1) |
| O(17) | 16 (1) | 22 (1) | 13 (1) | −3 (1) | 7 (1) | −3 (1) |
| O(18) | 17 (1) | 15 (1) | 12 (1) | −2 (1) | 9 (1) | 0 (1) |
| O(19) | 14 (1) | 19 (1) | 16 (1) | 1 (1) | 9 (1) | 2 (1) |
| C(20) | 15 (2) | 28 (2) | 30 (2) | 4 (2) | 12 (2) | 9 (2) |
| C(21) | 38 (3) | 40 (3) | 32 (3) | 17 (2) | 18 (2) | 4 (2) |
| C(22) | 28 (2) | 35 (3) | 29 (3) | 6 (2) | 9 (2) | 8 (2) |
| O(23) | 15 (1) | 26 (2) | 17 (1) | −2 (1) | 9 (1) | −3 (1) |
| C(24) | 16 (2) | 38 (3) | 33 (3) | −8 (2) | 17 (2) | −14 (2) |
| C(25) | 22 (2) | 67 (4) | 28 (3) | 6 (2) | 14 (2) | 16 (3) |
| C(26) | 31 (3) | 39 (3) | 75 (4) | 6 (2) | 36 (3) | 9 (3) |
| N(27) | 100 (5) | 125 (6) | 66 (4) | 8 (5) | 46 (4) | 18 (4) |
| C(28) | 151 (8) | 50 (4) | 66 (5) | −1 (5) | 67 (5) | 1 (4) |
| C(29) | 216 (13) | 51 (5) | 89 (6) | 53 (6) | 101 (8) | 35 (4) |
| C(30) | 129 (8) | 151 (10) | 42 (4) | 100 (8) | 44 (5) | 41 (5) |
| C(31) | 36 (4) | 261 (13) | 45 (5) | 14 (6) | 9 (3) | 11 (7) |
| C(32) | 45 (4) | 160 (9) | 42 (4) | −19 (5) | 4 (3) | −9 (5) |

[a] All $U$'s are $\times 10^3$. The form of the anisotropic thermal parameter is $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + hka^*b^*U_{12} + \ldots)]$.

Table VII. Bond Distances (Å) for the $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ Molecule

| A | B | dist | A | B | dist |
|---|---|---|---|---|---|
| Mo(1) | Mo(2) | 2.600 (1) | N(9) | C(14) | 1.341 (5) |
| Mo(1) | Mo(1)′ | 3.218 (1) | N(27) | C(28) | 1.394 (10) |
| Mo(1) | Mo(2)′ | 3.472 (1) | N(27) | C(32) | 1.366 (10) |
| Mo(1) | O(15) | 1.682 (3) | C(4) | C(5) | 1.378 (6) |
| Mo(1) | O(17) | 1.947 (3) | C(5) | C(6) | 1.372 (7) |
| Mo(1) | O(18)′ | 1.978 (2) | C(6) | C(7) | 1.368 (7) |
| Mo(1) | O(18) | 2.183 (3) | C(7) | C(8) | 1.372 (6) |
| Mo(1) | O(19) | 2.122 (2) | C(10) | C(11) | 1.375 (6) |
| Mo(1) | N(3) | 2.229 (3) | C(11) | C(12) | 1.383 (7) |
| Mo(2) | O(16) | 1.697 (3) | C(12) | C(13) | 1.352 (7) |
| Mo(2) | O(17) | 1.937 (3) | C(13) | C(14) | 1.389 (6) |
| Mo(2) | O(18)′ | 2.040 (3) | C(20) | C(21) | 1.506 (7) |
| Mo(2) | O(19)′ | 2.245 (3) | C(20) | C(22) | 1.501 (6) |
| Mo(2) | O(23) | 1.945 (3) | C(24) | C(25) | 1.516 (7) |
| Mo(2) | N(9) | 2.269 (3) | C(24) | C(26) | 1.495 (7) |
| O(19) | C(20) | 1.447 (5) | C(28) | C(29) | 1.309 (12) |
| O(23) | C(24) | 1.426 (5) | C(29) | C(30) | 1.408 (15) |
| N(3) | C(4) | 1.329 (5) | C(30) | C(31) | 1.309 (15) |
| N(3) | C(8) | 1.336 (5) | C(31) | C(32) | 1.447 (12) |
| N(9) | C(10) | 1.324 (5) | | | |

The McCarley structures, which have 8 and 10 electrons for $M_4$–cluster bonding show shorter M–M distances than those found in $W_4(OEt)_{16}$. In part, this may be attributable to the differences between oxo and alkoxy bridging groups. However, in going from 8 to 10 electrons, the M(1)–M(2) distances decrease quite singularly.

**Oxygen-to-Metal Distances.** The centrosymmetric $M_4O_{16}$ units have five terminal M–O, four doubly bridging M–$\mu_2$-O, and three triply bridging M–$\mu_3$-O unique distances. Structures which do not have a center of symmetry have twice the number of each type. Certain interesting points can be noted from a comparison of these M–O distances within the group of compounds under consideration. See Table X.

(1) The terminal M–O distances follow the order $Ba_{1.13}Mo_8O_{16}$ > RO–M in both $W_4(OEt)_{16}$ and $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ > $Ag_8W_4O_{16}$ > O≡Mo in $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$. This trend is readily understood in terms of the relative degrees of oxygen-to-metal π bonding in the series. This places the terminal RO ligands somewhere between the infinite chain oxygen donor ligands found in the ternary molybdenum oxide and the terminal oxo ligands found in $Ag_8W_4O_{16}$—which approximate to $[W_4O_{16}]^{8-}$, though each is coordinated to an $Ag^+$ countercation.

(2) M–$\mu_2$-O and M–$\mu_3$-O distances are slightly shorter than analogous M–$\mu_2$-O and M–$\mu_3$-OR distances. This general observation may, however, be masked by other factors. For example, the M–$\mu_3$-O distances in $Ag_8W_4O_{16}$ and $W_4(OEt)_{16}$ are comparable but longer than those found in McCarley's compounds. These deviations from the general rule $d_{M\text{-}\mu\text{-}OR} > d_{M\text{-}\mu\text{-}O}$, may be accounted for by considerations of trans influences[16] operating within the octahedral units. The triply bridging oxo groups in $Ag_8W_4O_{16}$ are trans to terminal W–O bonds which are short (1.79 Å average) because of multiple-bond character. An examination of the three Mo–$\mu_3$-O distances in $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ is particularly informative since the bonds are trans to three different ligands, namely, oxo, isopropoxy, and pyridine, which have different trans influences. A similar large asymmetry occurs in the M–$\mu_2$-O distances in $Ag_8W_4O_{16}$ and $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ and may be traced to the different trans influences of terminal oxo and bridging oxo ligands.

## Concluding Remarks

(1) Aside from reporting the syntheses and structures of two new interesting compounds, a structural analogy is demonstrated between alkoxide and oxide structures of molybdenum and tungsten. (2) The present work suggests that a large class of structurally related compounds of formula $M_4X_{16}$ or, in general, $M_4X_aY_bZ_c$ where $a + b + c = 16$, having 0–12 cluster electrons, should be accessible. [Twelve electrons achieves the half-filled $(Mt_{2g})_4$ molecular orbital framework for the cluster]. (3) In view of the remarkable catalytic reactivity of molybdenum and tungsten

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(16) Appleton, T. G.; Clark, H. C.; Manzer, L. M. *Coord. Chem. Rev.* **1973**, *10*, 335.

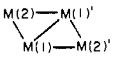
Table VIII. Bond Angles (Deg) for the $Mo_4(O)_8(O\text{-}i\text{-}Pr)_4(py)_2$ Molecule

| A | B | C | angle | A | B | C | angle |
|---|---|---|---|---|---|---|---|
| Mo(2) | Mo(1) | O(15) | 101.5 (1) | O(19)' | Mo(2) | N(9) | 79.9 (1) |
| Mo(2) | Mo(1) | O(17) | 47.8 (1) | O(23) | Mo(2) | N(9) | 83.6 (1) |
| Mo(2) | Mo(1) | O(18)' | 50.7 (1) | Mo(1) | O(17) | Mo(2) | 84.1 (1) |
| Mo(2) | Mo(1) | O(19) | 140.2 (1) | Mo(1) | O(18) | Mo(1)' | 101.2 (1) |
| Mo(2) | Mo(1) | N(3) | 129.6 (1) | Mo(1)' | O(18) | Mo(2)' | 80.6 (1) |
| O(15) | Mo(1) | O(17) | 105.5 (1) | Mo(2) | O(18) | Mo(1) | 110.6 (1) |
| O(15) | Mo(1) | O(18) | 160.5 (1) | Mo(1) | O(19) | Mo(2)' | 105.3 (1) |
| O(15) | Mo(1) | O(18)' | 109.7 (1) | Mo(1) | O(19) | C(20) | 124.7 (2) |
| O(15) | Mo(1) | O(19) | 90.8 (1) | Mo(2)' | O(19) | C(20) | 122.1 (2) |
| O(15) | Mo(1) | N(3) | 88.4 (1) | Mo(2) | O(23) | C(24) | 128.2 (2) |
| O(17) | Mo(1) | O(18) | 90.8 (1) | Mo(1) | N(3) | C(4) | 121.9 (3) |
| O(17) | Mo(1) | O(18)' | 95.0 (1) | Mo(1) | N(3) | C(8) | 120.2 (3) |
| O(17) | Mo(1) | O(19) | 160.4 (1) | C(4) | N(3) | C(8) | 117.7 (4) |
| O(17) | Mo(1) | N(3) | 81.8 (1) | Mo(2) | N(9) | C(10) | 123.1 (3) |
| O(18)' | Mo(1) | O(18) | 78.8 (1) | Mo(2) | N(9) | C(14) | 118.8 (3) |
| O(18) | Mo(1) | O(19) | 71.3 (1) | C(10) | N(9) | C(14) | 118.1 (4) |
| O(18)' | Mo(1) | N(3) | 161.8 (1) | C(28) | N(27) | C(32) | 123.6 (7) |
| O(18)' | Mo(1) | O(19) | 89.5 (1) | N(3) | C(4) | C(5) | 122.1 (4) |
| O(19) | Mo(1) | N(3) | 87.9 (1) | C(4) | C(5) | C(6) | 119.9 (4) |
| Mo(1) | Mo(2) | O(16) | 95.3 (1) | C(5) | C(6) | C(7) | 117.9 (4) |
| Mo(1) | Mo(2) | O(17) | 48.1 (1) | C(6) | C(7) | C(8) | 119.3 (4) |
| Mo(1) | Mo(2) | O(18)' | 48.6 (1) | N(3) | C(8) | C(7) | 123.0 (4) |
| Mo(1) | Mo(2) | O(19)' | 90.1 (1) | N(9) | C(10) | C(11) | 122.8 (4) |
| Mo(1) | Mo(2) | O(23) | 137.7 (1) | C(10) | C(11) | C(12) | 119.1 (4) |
| Mo(1) | Mo(2) | N(9) | 136.7 (1) | C(11) | C(12) | C(13) | 118.6 (4) |
| O(16) | Mo(2) | O(17) | 106.0 (1) | C(12) | C(13) | C(14) | 119.5 (4) |
| O(16) | Mo(2) | O(18)' | 100.9 (1) | N(9) | C(14) | C(13) | 122.0 (4) |
| O(16) | Mo(2) | O(19)' | 164.0 (1) | O(19) | C(20) | C(21) | 112.1 (4) |
| O(16) | Mo(2) | O(23) | 101.5 (1) | O(19) | C(20) | C(22) | 112.2 (4) |
| O(16) | Mo(2) | N(9) | 85.8 (1) | C(21) | C(20) | C(22) | 112.0 (4) |
| O(17) | Mo(2) | O(18)' | 93.4 (1) | O(23) | C(24) | C(25) | 108.8 (4) |
| O(17) | Mo(2) | O(19)' | 88.9 (1) | O(23) | C(24) | C(26) | 110.1 (4) |
| O(17) | Mo(2) | O(23) | 89.7 (1) | C(25) | C(24) | C(26) | 111.0 (4) |
| O(17) | Mo(2) | N(9) | 167.4 (1) | N(27) | C(28) | C(29) | 118.8 (9) |
| O(18)' | Mo(2) | O(19)' | 71.6 (1) | C(28) | C(29) | C(30) | 119.7 (9) |
| O(18)' | Mo(2) | O(23) | 155.5 (1) | C(29) | C(30) | C(31) | 122.8 (8) |
| O(18)' | Mo(2) | N(9) | 88.5 (1) | C(30) | C(31) | C(32) | 119.4 (9) |
| O(19)' | Mo(2) | Mo(1) | 90.1 (1) | N(27) | C(32) | C(31) | 115.4 (9) |
| O(19)' | Mo(2) | O(23) | 84.3 (1) | | | | |

Table IX. M-M Distances (Å) Found in Compounds Which Are Structurally Related to $W_4(OEt)_{16}$[a]

| compd | M(2)-M(1)' | M(1)-M(2) | M(1)-M(1)' | no. of $M_4$ cluster electrons | ref |
|---|---|---|---|---|---|
| $[Ti(OEt)_4]_4$ | 3.34 | 3.50 | 3.42 | 0 | *b* |
| $Ag_8W_4O_{16}$ | 3.32 | 3.23 | 3.49 | 0 | *c* |
| $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ | 3.47 | 2.60 | 3.22 | 4 | *d* |
| $W_4(OEt)_{16}$ | 2.65 | 2.94 | 2.76 | 8 | *d* |
| $Ba_{1.13}Mo_8O_{16}$ | 2.54 | 2.84 | 2.56 | 8 | *e* |
| $Ba_{1.13}Mo_8O_{16}$ | 2.61 | 2.57 | 2.58 | 10 | *e* |

[a] Distances are quoted to ±0.01 Å; the labeling scheme for M(1), M(2), and M(1)' is shown below and is such that M(1) and M(2) has respectively two and three terminal groups. [b] Ibers, J. A. *Nature (London)* 1963, *197*, 686. [c] Skarstad, P. M.; Geller, S. *Mater. Res. Bull.* 1975, *10*, 791. [d] This work. [e] McCarley, R. E.; Luly, M. H.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* 1981.



oxides, we are particularly interested in examining the reactivity of alkoxides of molybdenum and tungsten toward organic substrates. If these metal alkoxides can be viewed as oxide centers wrapped by hydrocarbons, can they model as hydrocarbon-soluble metal oxide catalysts? These considerations form the stimulus for our continuing work in this area.

## Experimental Section

General procedures and the preparation of $W_2(NMe_2)_6$[4] and $Mo_2(O\text{-}i\text{-}Pr)_6$[17] have been described.

**Prepartion of $W_4(OEt)_{16}$.** $W_2(NMe_2)_6$ (1.5 g, 2.37 mmol) was dissolved in hexane (20 mL) and ethanol (20 mL) was added: the color turned from pale yellow to dark brown. The solution was stirred for 6 h. The solvent was stripped, and the brown solids were dissolved in hexane (10 mL). The solution was cooled slowly to −15 °C, and after 24 h, brown crystals, $W_4(OEt)_{16}$ (700 mg, 40% yield based on W), were collected by filtration and dried in vacuo. IR data (Nujol mull) in the range 1400–200 cm$^{-1}$: 1370 (s sh), 1340 (m sh), 1253 (m sh), 1140 (m), 1095 (s sh), 1058 (s (br)), 1030 (s (br)), 905 (s sh), 890 (s), 870 (w), 792 (m), 715 (m sh), 578 (w (br)), 555 (w).

The $^1H$ NMR spectrum recorded in toluene-$d_8$, at +16 °C, and at 220 MHz was exceedingly complex, showing several overlapping methylene proton resonances centered at $\delta \sim 4.6$ and overlapping methyl resonances at $\delta \sim 1.4$ ($\delta$ in parts per million relative to $Me_4Si$).

The color arises from a tailing of strong absorption in the UV into the visible region of the electronic spectrum. Only one well-defined absorption was observed in the visible, centered at $\nu$ 13 790 cm$^{-1}$ with $\epsilon \sim 950$.

The mass spectrum showed $W(OEt)_5^+$ as the ion of highest *m/e* value, followed by many other mononuclear ions, including $W(OEt)_4^+$, $WO(OEt)_3^+$, $WO(OEt)_2(OH)^+$, $WO(OEt)(OH)_2^+$, and $WO(OH)_3^+$.

**Preparation of $W_4(OMe)_{16}$.** $W_2(NMe_2)_6$ (500 mg, 0.79 mmol) was dissolved in hexane (10 mL), and methanol (15 mL) was added. The color turned from pale yellow to emerald green. The solution was stirred

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(17) Chisholm, M. H.; Cotton, F. A.; Murillo, C. A.; Reichert, W. W. *Inorg. Chem.* **1977**, *16*, 1801.

Table X. Comparison of Metal-to-Oxygen Bond Distances (Å) in Compounds Which Are Structurally Related to $W_4(OEt)_{16}$[a]

| compd | M–O Terminal | M–$\mu_2$-O | M–$\mu_3$-O | ref |
|---|---|---|---|---|
| $W_4(OEt)_{16}$ | 1.96 | 2.03 | 2.17 | *b* |
| | 1.90 | 2.02 | 2.16 | |
| | 1.94 | 2.08 | 2.20 | |
| | 1.93 | 2.03 | | |
| | 1.98 | | | |
| $Ag_8W_4O_{16}$ | 1.80 | 1.86 | 2.11 | *c* |
| | 1.73 | 2.20 | 2.15 | |
| | 1.77 | 1.87 | 2.22 | |
| | 1.79 | 2.14 | | |
| | 1.83 | | | |
| $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$ | 1.68 (=O) | 1.95 (–O–) | 1.98 | *b* |
| | 1.70 (=O) | 1.94 (–O–) | 2.18 | |
| | 1.94 (OR) | 2.12 (OR) | 2.04 | |
| | | 2.24 (OR) | | |
| 10-electron $Mo_4$ cluster in $Ba_{1.13}Mo_8O_{16}$ | 2.10, 2.08 | 2.05, 2.01 | 2.06, 2.10 | *d* |
| | 2.21, 2.09 | 2.06, 2.05 | 2.03, 2.07 | |
| | 2.06, 1.99 | 1.93, 1.92 | 2.03, 2.09 | |
| | 2.11, 2.14 | 2.08, 1.95 | | |
| | 2.03, 2.06 | | | |
| 8-electron $Mo_4$ cluster in $Ba_{1.13}Mo_8O_{16}$ | 1.94, 1.85 | 1.94, 1.91 | 2.05, 2.12 | *d* |
| | 2.06, 2.10 | 2.00, 1.99 | 1.99, 2.12 | |
| | 2.10, 2.12 | 2.10, 2.00 | 1.99, 2.08 | |
| | 2.09, 2.00 | 2.10, 2.04 | | |
| | 2.11, 2.14 | | | |

[a] Distances quoted to ±0.01 Å. [b] This work. [c] Skarstad, P. M.; Geller, S. *Mater. Res. Bull.* 1975, *10*, 791. [d] McCarley, R. E.; Luly, M. H.; Ryan, T. R.; Torardi, C. C. *ACS Symp. Ser.* 1981, *No. xxx*, xxx.

for 3 h at room temperature, and then the volume of solution was reduced by vacuum distillation to ca. 15 mL. The solution was cooled slowly to –15 °C. After 24 h, dark green crystals, $W_4(OMe)_{16}$, were collected by filtration and dried in vacuo.

IR data in the range 1400–200 $cm^{-1}$ (Nujol mull) showed bands at 1372 (s sh), 1263 (m sh), 1159 (s sh), 1065 (s (br)), 1030 (s (br)), 900 (m (br)), 790 (m sh), 715 (w sh), 530 (m), 490 (s sh), and 395 (m sh).

The $^1H$ NMR spectra obtained in toluene-$d_8$ at 220 MHz were essentially invarient in the temperature range +60 to –60 °C and consisted of eight lines of equal intensity. At +16 °C, $\delta$ values are 4.50, 4.25, 4.14, 4.10, 3.89, 3.85, 3.70, and 3.62 ($\delta$ in parts per million relative to $Me_4Si$).

The color was due to intense absorption in the UV region of electronic spectrum which tails into the visible region with shoulders at 23 200 and 19 340 $cm^{-1}$ and one well-resolved absorption band at 13 300 $cm^{-1}$ with $\epsilon \sim 780$.

Elemental analyses, obtained from Canadian Microanalytical Services Ltd., repeatedly gave low observed carbon content. E.g., Anal. Calcd for $W_4(OMe)_{16}$: C, 15.59; H, 3.89. Found: C, 14.51; H, 3.71. We believe this probably reflects inadequate analytical procedures, rather than our inability to prepare bulk quantities of the compounds in analytically pure states.

Cryoscopic molecular weight determinations carried out in benzene gave $M_r$ = 1280 ± 80 (methoxide) and $M_r$ = 1486 ± 80 (ethoxide), which compared favorably with the expected molecular weights, assuming the tetrameric species is present in solution: $M_r$ = 1231 (methoxide) and $M_r$ = 1454 (ethoxide).

**Preparation of $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$.** $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.16 g, 0.29 mmol) was dissolved in pyridine (20 mL) in a 50-mL round-bottomed flask under a nitrogen atmosphere. The solution was frozen at –198 °C (liquid $N_2$) and the solution degassed by thawing in vacuo. Molecular oxygen was added by use of a calibrated vacuum manifold, and the solution was allowed to stand at room temperature under 1 atm of $O_2$ for 12 h. During this time, the solution changed from green to yellow and a small quantity of a red crystalline solid formed. The red solid (ca. 30 mg), $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4$, was collected by filtration and dried in vacuo. Anal. Calcd for $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4 \cdot 2py$: C, 41.26; H, 4.78; N, 6.87. Found: C, 41.17; H, 4.83; N, 6.71. The infrared spectrum obtained between CsI plates by using a Nujol mull showed the following peaks in the range 1700–200 $cm^{-1}$: 320 (m), 340 (w), 394 (w), 418 (w), 431 (m), 469 (s), 501 (w), 566 (m), 597 (s), 634 (m), 653 (s), 682 (s), 722 (s), 750 (s), 810 (m), 830 (m), 914 (s), 949 (vs), 968 (s), 1011 (m), 1021 (w), 1039 (m), 1065 (m), 1115 (vs), 1154 (m), 1212 (s), 1312 (m), 1572 (m), 1601 (s) $cm^{-1}$.

$Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4 \cdot 2py$ is insoluble in pyridine, hydrocarbon solvents, and dichloromethane.

**Structural Determinations.** The diffractometer, low-temperature equipment, and general procedures, as well as mathematical treatment of the data and refinement procedures, have been described in detail previously.[18]

**$W_4(OEt)_{16}$.** The crystal used for identification and data collection was a small fragment, approximately 0.12 × 0.12 × 0.12 mm, cleaved from a large crystal. The cell dimensions obtained at –164 °C from 35 reflections, using Mo K$\alpha$ ($\lambda$ 0.71069 Å), were $a$ = 12.129 (6) Å, $b$ = 10.985 (6) Å, $c$ = 9.692 (4) Å, $\alpha$ = 93.28 (3)°, $\beta$ = 108.64 (2)°, $\gamma$ = 105.71 (2)°, $Z$ = 1, $d_{calcd}$ = 2.079 g $cm^{-3}$, and space group $P\bar{1}$.

A total number of 5884 reflections were collected by using standard moving-crystal moving-detector techniques[18] with the following values: scan speed = 3 deg $min^{-1}$, scan width = 2.0 + dispersion, single background time at extremes of scan = 4 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $6° < 2\theta < 55°$. Of the 5884 reflections, 5365 were unique and 4052 reflections had $F > 3\sigma(F)$.

The structure was solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares by using the 4052 reflections having $F > 3\sigma(F)$. All nonhydrogen atoms were refined anisotropically. Almost all the hydrogen atoms were located in a difference map. The hydrogen atoms were included in fixed idealized positions. The final residuals[18] were $R(F)$ = 0.051 and $R_w(F)$ = 0.048. The goodness of fit for the last cycle was 1.141 and the maximum $\Delta/\sigma$ was 0.01. A final difference Fourier synthesis was featureless, with the largest peak being 0.75 e/Å$^3$.

No improvement in the refinement was obtained when the data were corrected for absorption ($\mu$ = 101.3 $cm^{-1}$, maximum and minimum transmission coefficients, 0.319 and 0.422, respectively). Because of the uncertainties in the crystal dimension, the uncorrected data were used in the final refinement.

**$Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4 \cdot 2py$.** A red crystal of dimensions 0.21 × 0.28 × 0.32 mm was used. The cell dimensions obtained from 42 reflections by using Mo K$\alpha$ ($\lambda$ 0.71069 Å) at –163 °C were $a$ = 11.562 (2) Å, $b$ = 13.915 (3) Å, $c$ = 17.095 (4) Å, $\beta$ = 117.75 (1)°, $Z$ = 2, $d_{calcd}$ = 1.674 g $cm^{-3}$, and space group $P2_1/c$. A total number of 5529 reflections were collected by using standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0 $min^{-1}$, scan width = 2.0 + dispersion, single background time at extremes of scan = 3 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. Of the 5529 reflections, 4312 were unique and 3752 had $F > 2.33\sigma(F)$. No absorption correction was performed ($\mu$ = 10.4 $cm^{-1}$).

The structure was solved by a combination of direct methods and Fourier techniques and refined by full-matrix least squares by using the 3752 reflections having $F > 2.33\sigma(F)$. The crystal was found to have pyridine-solvent molecules: 2 pyridines of solvent per $Mo_4$ cluster. Although the thermal parameters of the solvent molecule were large, there was no indication of disorder. All nonsolvent hydrogen atoms were located and refined isotropically; all nonhydrogen atoms were refined anisotropically. The final residuals were $R(F)$ = 0.032 and $R_w(F)$ = 0.037. The goodness of fit for the last cycle was 1.020 and the maximum $\Delta/\sigma$ for the last cycle was 0.05. A final difference Fourier synthesis was essentially featureless, with the largest peak being 0.54 e/Å$^3$.

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**Supplementary Material Available:** Observed and calculated structure factor tables for $W_4(OEt)_{16}$ and $Mo_4O_8(O\text{-}i\text{-}Pr)_4(py)_4 \cdot 2py$ (61 pages). Ordering information is given on any current masthead page.

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(18) Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* **1980**, *19*, 2755.