(1)°, which is in the range 125–160° generally observed for the M–O–X angle of coordinating tetrahedral XO_4^{n-} anions.[25]

Tridentate coordination of the ClO_4 group in nickel and cobalt perchlorates appears to be a direct consequence of the tendency of the metal atoms to retain a regular octahedral environment. Although examples of tridentate tetrahedral anions are frequently found, this type of coordination is the first to be structurally documented for the perchlorate anion.

The foregoing results are entirely consistent with infrared, Raman, and visible spectral data and magnetic measurements for $Co(ClO_4)_2$ and $Ni(ClO_4)_2$, which indicate a highly symmetrical structure and probable tridentate perchlorate.[16]

Acknowledgments. We gratefully acknowledge the help of the staff of the Laboratoire de l'Accélérateur Linéaire at Orsay, who operated the storage ring DCI. D.J.J. thanks the Royal Society of Great Britain and the French CNRS for the award of a European Exchange Fellowship. We thank Professor B. J. Hathaway (University College, Cork, Ireland) for his interest and useful comments about this work.

Registry No. $Co(ClO_4)_2$, 13455-31-7; $Ni(ClO_4)_2$, 13637-71-3.

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Contribution from the Department of Chemistry
and Molecular Structure Center,
Indiana University, Bloomington, Indiana 47405

Reactions of Metal–Metal Multiple Bonds. 14. Synthesis and Characterization of *triangulo*-W_3 and -Mo_2W Oxo-Capped Alkoxide Clusters. Comproportionation of M–M Triple Bonds ($\sigma^2\pi^4$) and d^0 Metal–Oxo Groups: $M{\equiv}M + M{\equiv}O \rightarrow M_3(\mu_3\text{-}O)$

Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman,
and Edward M. Kober

Received May 9, 1984

The early transition elements niobium, molybdenum, and tungsten have recently been found to exhibit an extensive trinuclear chemistry with a variety of ligands.[1,2] Even the Mo(IV) aquo ions has been shown by a variety of spectroscopic techniques to contain the trinuclear unit $Mo_3O_4^{4+}$.[3-5] These complexes have *triangulo*-M_3 units capped by either one or two μ_3-X groups (X may be O, S, CR, etc.). The metal atoms are coordinated to six or seven ligand atoms, and the M_3 units have four to eight cluster electrons. Our interest in these compounds was heightened by the discovery of the simple comproportionation reaction shown in eq 1.[6,7] This provided a high-yield synthesis of a new subset of triangulo cluster compounds.

$$(RO)_3M{\equiv}Mo(OR)_3 + (RO)_4MoO \rightarrow Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu\text{-}OR)_3(OR)_6 \quad (1)$$

$$R = i\text{-Pr and } CH_2\text{-}t\text{-Bu}$$

Reaction 1 has a parallel with the syntheses of dinuclear and trinuclear complexes employing metal–alkylidyne or –alkylidene fragments.[8] Reaction 1 also has a parallel with the reactions of alkynes with $Mo_2(OR)_6$ compounds, which give $Mo_2(\mu\text{-}C_2R_2)$ compounds containing the pseudotetrahedral M_2C_2 core.[9] One might well wonder whether or not one could extend comproportionation μ_3-X of type 1 to include other metal atoms and other ligands; e.g. can one replace Mo by W, O by S, NR and OR by SR, etc. We describe here our initial findings, which were prompted by these considerations.

Results and Discussion

Synthesis. $W_3O(O\text{-}i\text{-}Pr)_{10}$. Since $W_2(O\text{-}i\text{-}Pr)_6$ is not isolable in an unligated form,[10] the crystalline compound $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$[11] was used along with $WO(O\text{-}i\text{-}Pr)_4$[12] for the comproportionation reaction. Mixing the two compounds in hexane followed by heating gave a royal blue solution from which dark blue crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ were obtained.

$Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. The addition of $WO(O\text{-}i\text{-}Pr)_4$ to a hexane solution of $Mo_2(O\text{-}i\text{-}Pr)_6$ followed by heating results in an orange to green color change, and by crystallization the mixed-metal triangulo compound $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ can be isolated as green crystals.

$MoW_2O(O\text{-}i\text{-}Pr)_{10}$. In an attempt to prepare the related MoW_2-containing compound, $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were allowed to react in hexane. An immediate reaction occurred as evidenced by a color change to green. However, the reaction was more complicated than had been hoped. Attempts to crystallize the trinuclear compound failed. First fine white needles of the relatively insoluble compound $WO(O\text{-}i\text{-}Pr)_4$ were obtained. Then, from crystallization of the filtrate, blue-green crystals were obtained. The ^1H NMR spectrum of the latter indicated the presence of $W_3O(O\text{-}i\text{-}Pr)_{10}$ and other species, possibly the desired $MoW_2O(O\text{-}i\text{-}Pr)_{10}$.

Our interpretation of this is that the oxo-group-transfer reaction in eq 2 is favored and the further reaction of $WO(O\text{-}i\text{-}Pr)_4$ with $W_2(O\text{-}i\text{-}Pr)_6$ and $MoW(O\text{-}i\text{-}Pr)_6$ yields $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, respectively.

$$MoO(O\text{-}i\text{-}Pr)_4 + W_2(O\text{-}i\text{-}Pr)_6 \rightarrow MoW(O\text{-}i\text{-}Pr)_6 + WO(O\text{-}i\text{-}Pr)_4 \quad (2)$$

This suggestion finds support in the observations of Hoskins,[13] who found that, while the homonuclear *tert*-butoxides failed to react ($M_2(O\text{-}t\text{-}Bu)_6 + (t\text{-}BuO)_4MO$, M = Mo and W), the addition of $(t\text{-}BuO)_4MoO$ to $W_2(O\text{-}t\text{-}Bu)_6$ in hydrocarbon solvents yielded an immediate color change from yellow-orange to green but with time the yellow-orange color returned and by crystallization only a mixture of homonuclear, Mo_2 and W_2, and heteronuclear MoW hexa-*tert*-butoxides were obtained. The formation of $MoW(O\text{-}t\text{-}Bu)_6$ in this reaction can reliably be established by NMR spectroscopy and by mass spectrometry, but it cannot be separated from the Mo_2- or W_2-containing compounds by crystallization. Thus we believe that in the present instance $MoO(O\text{-}i\text{-}Pr)_4$ and $W_2(O\text{-}i\text{-}Pr)_6$ react to give $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ but that this is unstable with respect to dissociation to $MoW(O\text{-}i\text{-}Pr)_6$ and $WO(O\text{-}i\text{-}Pr)_4$. The latter then react to give $W_3O(O\text{-}i\text{-}Pr)_{10}$, $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$, and $Mo_2(O\text{-}i\text{-}Pr)_6$.

Attempted Preparations of $MM'_2(O\text{-}i\text{-}Pr)_{11}$ Compounds Where M = Nb, Ta and M′ = Mo, W. Since it is possible for RO ligands to cap the triangle of metal atoms once, why not twice? In attempts to prepare compounds of formula $MM'_2(\mu_3\text{-}O\text{-}i\text{-}Pr)_2(\mu\text{-}O\text{-}i\text{-}Pr)_3(O\text{-}i\text{-}Pr)_6$, hydrocarbon solutions of $M(O\text{-}i\text{-}Pr)_5$ (1 equiv), where M = Nb and Ta, and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were mixed and heated. No evidence for a com-

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for the $W_3O(O\text{-}i\text{-}Pr)_{10}$ Molecule

atom	10^4x	10^4y	10^4z	B_{iso}, Å^2	atom	10^4x	10^4y	10^4z	B_{iso}, Å^2
W(1)	2300.3 (3)	6929.0 (3)	6229 (1)	13	W(1)''	7205.8 (3)	6931.7 (3)	504 (1)	13
W(2)	3646.5 (3)	7749.1 (3)	6593 (1)	14	W(2)''	8130.7 (3)	8172.4 (3)	1706 (1)	10
W(3)	2789.1 (3)	8261.5 (3)	6602 (1)	13	W(3)''	8389.6 (3)	7146.9 (3)	1674 (1)	10
O(4)	2918 (5)	7686 (5)	7927 (8)	12	O(4)''	7586 (5)	7287 (5)	2545 (9)	15
O(5)	2911 (5)	7618 (5)	4895 (8)	14	O(5)''	8252 (5)	7549 (5)	9945 (8)	15
O(6)	3895 (5)	8775 (5)	6750 (9)	20	O(6)''	9034 (5)	8202 (5)	2514 (9)	14
O(7)	3095 (5)	6663 (5)	6102 (10)	18	O(7)''	7141 (5)	7844 (5)	688 (9)	17
O(8)	1747 (4)	7491 (5)	6270 (9)	16	O(8)''	7597 (5)	6231 (4)	569 (9)	14
O(9)	2634 (5)	8775 (5)	5312 (9)	18	O(9)''	9138 (5)	7019 (5)	838 (9)	19
O(10)	1725 (5)	6229 (5)	4616 (10)	21	O(10)''	6865 (5)	6633 (5)	−1413 (10)	20
O(11)	4332 (5)	7849 (5)	5313 (10)	22	O(11)''	8626 (5)	8983 (5)	844 (9)	17
O(12)	4260 (5)	7824 (5)	8085 (10)	18	O(12)''	8064 (5)	8715 (5)	3309 (9)	16
O(13)	2727 (6)	8851 (5)	8114 (9)	23	O(13)''	8508 (5)	6776 (5)	3204 (9)	16
O(14)	1805 (5)	6324 (5)	7413 (10)	24	O(14)''	6281 (5)	6352 (6)	983 (10)	27
C(15)	2910 (9)	7579 (8)	3443 (16)	26	O(15)''	8562 (8)	7635 (7)	−1295 (13)	13
C(16)	2184 (9)	7410 (9)	2775 (16)	29	C(16)''	8186 (8)	7894 (7)	−2179 (13)	23
C(17)	3514 (9)	8289 (10)	3201 (17)	33	C(17)''	9387 (8)	8135 (10)	−977 (18)	35
C(18)	4555 (8)	9442 (9)	6688 (21)	38	C(18)''	9700 (7)	8711 (7)	3368 (15)	16
C(19)	4337 (11)	9979 (10)	6387 (26)	57	C(19)''	9785 (8)	8438 (8)	4580 (15)	22
C(20)	5051 (11)	9662 (11)	7951 (20)	46	C(20)''	10328 (8)	8865 (9)	2532 (17)	28
C(21)	3156 (8)	6050 (7)	5570 (18)	26	C(21)''	6617 (8)	8067 (9)	379 (16)	26
C(22)	3247 (11)	6033 (10)	4114 (18)	41	C(22)''	6820 (10)	8431 (9)	−849 (17)	31
C(23)	3773 (9)	6057 (8)	6430 (21)	37	C(23)''	6623 (9)	8591 (8)	1585 (17)	27
C(24)	1040 (7)	7429 (8)	6170 (16)	22	C(24)''	7490 (9)	5533 (8)	7 (18)	29
C(25)	702 (9)	7176 (10)	4720 (17)	32	C(25)''	7841 (10)	5592 (9)	8713 (16)	33
C(26)	608 (9)	6938 (10)	7062 (17)	32	C(26)''	6710 (9)	4994 (9)	−177 (21)	41
C(27)	2577 (10)	9414 (10)	5487 (17)	35	C(27)''	9665 (7)	6890 (8)	1422 (14)	16
C(28)	1900 (11)	9327 (10)	5925 (18)	36	C(28)''	9362 (10)	6115 (9)	1469 (18)	34
C(29)	2634 (13)	9617 (12)	4075 (20)	49	C(29)''	10310 (8)	7126 (11)	672 (19)	40
C(30)	1048 (8)	5578 (8)	4468 (15)	23	C(30)''	6173 (9)	6120 (10)	−2088 (17)	36
C(31)	739 (10)	5389 (10)	3001 (19)	45	C(31)''	6287 (10)	5790 (12)	6565 (19)	48
C(32)	1164 (9)	4988 (8)	4888 (20)	33	C(32)''	5732 (12)	6483 (14)	7647 (26)	71
C(33)	4999 (11)	7883 (16)	5379 (22)	66	C(33)''	8732 (8)	9688 (7)	1172 (15)	18
C(34)	5527 (14)	8323 (29)	6169 (29)	149	C(34)''	9357 (9)	10117 (8)	2298 (15)	26
C(35)	5213 (16)	7967 (27)	3928 (28)	132	C(35)''	8878 (10)	9992 (9)	−96 (17)	32
C(36)	4217 (8)	7824 (10)	9458 (17)	31	C(36)''	8015 (8)	8570 (7)	4620 (14)	17
C(37)	4482 (10)	7328 (13)	9880 (21)	50	C(37)''	7233 (8)	8262 (9)	4910 (15)	26
C(38)	4649 (11)	8580 (12)	10306 (20)	49	C(38)''	8519 (8)	9231 (7)	5606 (14)	19
C(39)	2807 (10)	8894 (9)	9515 (17)	32	C(39)''	8083 (8)	6572 (8)	4240 (15)	24
C(40)	3142 (13)	9681 (10)	10205 (22)	55	C(40)''	8575 (10)	6626 (9)	5437 (16)	30
C(41)	2085 (11)	8460 (12)	9895 (20)	51	C(41)''	7487 (9)	5787 (9)	3722 (17)	35
C(42)	1915 (8)	6382 (8)	8835 (15)	23	C(42)''	5947 (11)	6376 (12)	2161 (22)	73
C(43)	1183 (9)	5965 (10)	9282 (17)	33	C(43)''	5286 (22)	6361 (27)	1774 (50)	171
C(44)	2405 (11)	6072 (12)	9145 (20)	46	C(44)''	5772 (23)	5773 (32)	2666 (42)	207

proportionation reaction was found by NMR spectroscopy.

Attempted Preparations of $M_2W(NPh)(O\text{-}i\text{-}Pr)_{10}$ Where M = Mo, W. Since RN ligands are isoelectronic with oxo groups and are known to be capable of bridging three metal atoms,[14] $W(NPh)(O\text{-}i\text{-}Pr)_4$ and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ were mixed in hydrocarbon solvents. No reaction was observed in either case.

Solid-State and Molecular Structures. $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. Crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ were found to be isomorphous with $Mo_3O(O\text{-}i\text{-}Pr)_{10}$, which was previously examined. The mixed-metal complex is undoubtedly disordered with respect to the disposition of molybdenum and tungsten atoms and consequently was not studied in detail. In the space group $P\bar{1}$, there are two independent $W_3O(O\text{-}i\text{-}Pr)_{10}$ molecules in the unit cell, differing only slightly with respect to the conformations of the isopropyl groups. Atomic positional parameters are given in Table I. An ORTEP view of the central $M_3O(O)_{10}$ skeleton is shown in Figure 1. The atom number system employed is the same as that used previously for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ molecule, where the two independent molecules were related by primed and unprimed numbers.

A comparison of the pertinent bond distances and bond angles for the two pairs of independent molecules for M = Mo and W is given in tables in the supplementary material. The trinuclear molybdenum and tungsten compounds are shown to be remarkably similar in many structural aspects. The W–W bond distances appear to be slightly longer than the Mo–Mo distances, though this is not really statistically significant (2.540 (6) vs. 2.534 (5) Å, respectively). This is to be contrasted to the situation found for the triangulo cluster ions $M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3^{2+}$.[15] There, the W–W bond distances were observed to be significantly shorter than the Mo–Mo distances (2.746 (2) vs. 2.759 (4) Å,

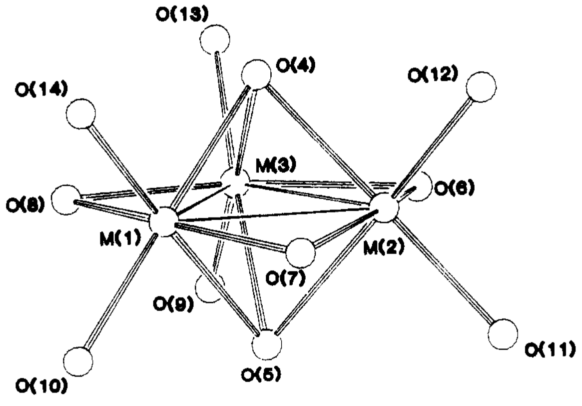

Figure 1. The central M_3O_{11} skeleton of the $W_3O(O\text{-}i\text{-}Pr)_{10}$ molecule showing the numbering scheme for the metal and oxygen atoms. This is the same numbering scheme used previously for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ molecule. O(4) is the capping oxo group.

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Table II. Electrochemical Data[a]

M_3O(O-*i*-Pr)$_{10}$	$E_{1/2}$(red), V	$E_{1/2}$, mV	E_p(ox), V
Mo_3	−1.46	110	0.48
Mo_2W	−1.57	175	0.20
W_3	−2.16	140	0.09

[a] THF solution, 0.01 M $AgNO_3(CH_3CN)$/Ag reference electrode. See Experimental Section.

respectively). It can also be seen that, for the present complexes, the W–ligand distances are consistently slightly longer than the Mo–ligand distances by 0.01–0.02 Å, though this is at the limit of statistical creditability. For the $M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3{}^{2+}$ species, no such consistent differences in M–ligand bond lengths were found.[15]

The results for metal–metal bond distances are in sharp contrast to those found for complexes containing triple or quadruple metal–metal bonds.[16] There the W–W distance is typically ca. 0.10 Å longer than the Mo–Mo distance. This has been attributed to extensive core–core repulsion interactions between the two tungsten atoms, which are separated by only ca. 2.1 Å. For the trianguio clusters, the data suggest that the W–W core–core repulsions might still be noticeable at 2.54 Å (the present species), but not at 2.75 Å (the $M_3(\mu_3\text{-}O)_2(O_2CR)_6(H_2O)_3{}^{2+}$ species).[15] More extensive comparisons are obviously needed to establish these trends, and detailed calculations will probably be necessary to determine the relative importance of core–core repulsions, orbital overlaps, and steric interactions.

Electrochemical and UV–Visible Characterizations. Previously, the electrochemical and spectroscopic properties of Mo_3O(O-*i*-Pr)$_{10}$ have been correlated with electronic structure predicted by Fenske–Hall molecular orbital calculations.[17] The latter predicted the HOMO to be of e symmetry being primarily M–M σ bonding in nature, and the LUMO was also of e symmetry but having a mixture of M–M π-bonding and metal–ligand π-antibonding character. The HOMO–LUMO gap was calculated to be rather small, ca. 1.5 eV.

A comparison of the electrochemical data is given in Table II. All three complexes exhibited a quasi-reversible reduction couple at large negative potentails. Even with internal resistance compensation, the $\Delta E_{1/2}$ ($=E_{p,a} - E_{p,c}$) value (110–175 mV) was much greater than that expected for a reversible charge-transfer process (60 mV). Approximately equimolar concentrations of ferrocene were added to each sample, and the reversible behavior of its oxidation couple under the experimental conditions implies that the present couples are inherently irreversible. Since the anodic and cathodic current peak heights are quite similar and the electrochemically generated Mo_3O(O-*i*-Pr)$_{10}{}^-$ species is stable for hours, the presumed origin of the irreversibility is slow charge-transfer kinetics.

Each complex also exhibits an irreversible oxidation wave at low positive potentials. No corresponding back-wave was observed even at scan rates of 1 V/s. Two or more product waves at negative potentails were observed to grow in upon cycling through the oxidative wave. The oxidized trimers are thereby implied to rapidly decompose, but the exact nature of these rearranged products has not been ascertained. The Mo_3 complex also exhibits a second reduction wave at ca. −2.4 V, which appears to be irreversible. No such corresponding wave was observed for the other two complexes.

The data for the three complexes show rather interesting trends. In a comparison of the Mo_3 and W_3 complexes, it is seen that both the oxidation and reduction processes occur at significantly more negative potentials for the W_3 complex. This is consistent with the generally observed phenomenon that, for medium to high oxidation states, third-row transition metals are easier to oxidize the harder to reduce than their second-row analogues. This then confirms that both the HOMO and LUMO are predominantly metal centered.

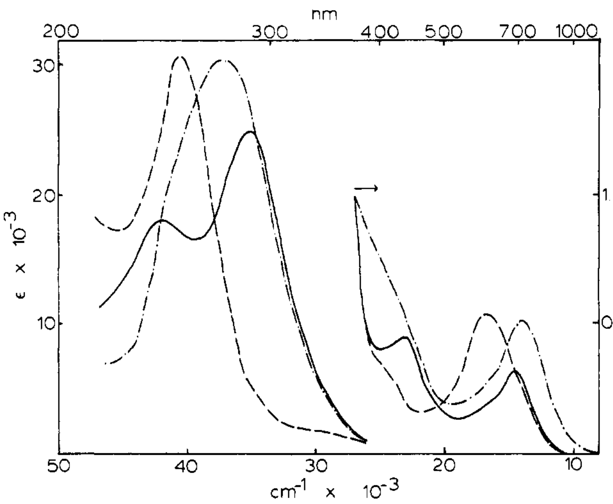

Figure 2. Comparison of the electronic absorption spectra, recorded in hexane, for the oxo-capped triangulo metal isopropoxides (—) Mo_3O(O-*i*-Pr)$_{10}$, (- - -) W_3O(O-*i*-Pr)$_{10}$, and (-··-) Mo_2WO(O-*i*-Pr)$_{10}$.

Table III. UV-Visible Absorption Spectra (Hexane Solution)

M_3O(O-*i*-Pr)$_{10}$	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
Mo_3	690 (330), 430 (560), 287 (25 000), 240 (18 000)
Mo_2W	718 (515), 420 sh (650), 270 (30 000)
W_3	600 (565), 420 sh (260), 350 sh (1600), 248 (30 000)

The couples for the Mo_2W species occur at intermediate potentials, though not at values that would be predicted on pure statistical grounds. The reduction couple occurs at only a slightly more negative value than that for the Mo_3 complex. The implication is that the reduction is more heavily centered on the Mo centers than on W. The value for the Mo_2W oxidative couple is observed to be much closer to that for W_3 than for Mo_3, which implies that the oxidation process is predominantly W centered. This behavior is consistent with the general behaviorial differences between Mo and W noted above. Presumably, the Mo–W bonds are polarized in the fashion $Mo^{\delta-}$–$W^{\delta+}$, though we cannot quantitatively demonstrate this.

A comparison of the UV–visible absorption spectra is given in Figure 2, and data are given in Table III. Qualitatively, the spectra are quite similar, consisting of two or more weak bands in the visible region and one or more very intense transitions in the UV region. The weak bands in the visible region were previously assigned for Mo_3O(O-*i*-Pr)$_{10}$ as arising from transitions between metal-centered orbitals,[17] with the lowest energy band corresponding to the allowed HOMO → LUMO transition. The low intensity of these bands results from the predominant d-orbital character of these orbitals. That the lowest energy transition for the W_3 complex occurs at higher energy and has greater intensity than for the analogous Mo_3 complex suggests greater metal–metal overlap and possibly stronger bonding interactions in the W_3 complex, which would not be unexpected.

The assignment of the intense, high-energy absorption bands is more speculative. It was previously suggested that these could be either M–M $\sigma \rightarrow \sigma^*$ transitions or alkoxide oxygen lone pair to metal charge-transfer transitions. The comparison of the Mo_3 and W_3 complexes shows a shift of these transitions to higher energy by 0.7 eV, with the Mo_2W complex exhibiting a transition at intermediate energy. Since the W_3 complex is found to be 0.7 V harder to reduce electrochemically than the Mo_3 complex, this is exactly the type of behavior expected for an O → M LMCT transition. This assignment therefore appears most likely. This places the alkoxide oxygen lone pairs approximately 2 eV lower in energy than the metal-centered HOMO, which is in good agreement with the MO calculations.[17]

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Concluding Remarks

Comproportionation reactions analogous to those previously employed for the synthesis of $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ have allowed the successful syntheses of tritungsten and tungsten–dimolybdenum oxo-capped alkoxide clusters. The new compounds are structurally and spectroscopically similar to the Mo_3-containing compounds. A number of factors may limit an extension of this approach to trinuclear cluster syntheses, two of which are seen in this work. (1) Oxo atom transfer reactions may be thermodynamically favored, and the oxo-capped trinuclear cluster may be merely an intermediate en route to products of oxo group transfer. This in some ways parallels reactions between alkynes and $(RO)_3W{\equiv}(OR)_3$ compounds, which may lead to $W_2(\mu\text{-}C_2R_2)$-containing compounds[18] or metathesis products $(RO)_3W{\equiv}CR'$.[19] (2) For either electronic or steric reasons a comproportionation may not occur. This is seen here in the failure of niobium and tantalum pentaisopropoxides to react with the $M_2(OR)_6$ compounds. However, a more obvious extension of the comproportionation reaction would involve $ReO(OR)_4$ compounds to give 7-electron clusters, analogous to the $Mo_3O(OR)_{10}^-$ anion, which may be prepared electrochemically. Also of interest to us is the substitution of S for O and SR for OR. These considerations form the basis for continuing studies in our laboratories.

Experimental Section

General Procedures and Instrumentation. Standard experimental techniques for the preparation and manipulation of air- and moisture-sensitive materials were employed. The compounds $Mo_2(O\text{-}i\text{-}Pr)_6$[20] and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$[21] were prepared by literature procedures.

Electronic absorption spectra were obtained with a Hitachi 330 recording spectrophotometer. Samples were run vs. a solvent blank in matched 1-cm or 1-mm quartz cells. The cyclic voltammograms were obtained with a PAR 173 potentiostat, a PAR 175 programmer, and a Houston 2000 XY recorder. A single-compartment cell was used with a platinum-bead or -gauze working electrode, a platinum-wire auxiliary electrode, and a 0.01 M $AgNO_3(CH_3CN)/Ag$ wire pseudo reference electrode. A 0.2 M solution of tetra-*n*-butylammonium hexafluorophosphate (TBAH) was employed as a supporting electrolyte. Scan rates were 200 mV/s. Internal resistance (IR) compensation was employed. Equimolar amounts of ferrocene were added as an internal calibrant ($E_{1/2} = +0.08$ V). The peak splitting for this couple with IR compensation was consistent with a reversible couple (60–65 mV).

Preparations. The preparations of $MO(O\text{-}i\text{-}Pr)_4$ compunds, where M = Mo[7] and W,[12] have been reported previously, but the present procedure provides the simplest and quickest syntheses.

$WO(O\text{-}i\text{-}Pr)_4$. $LiO\text{-}i\text{-}Pr$ (1.6 g, 24 mmol) was added to a solution of $WOCl_4$ (2.0 g, 5.8 mmol) in ether (40 mL) at 0 °C, with stirring. The color of the solution lightened immediately from red-orange to pale yellow and gradually became white with a copious white precipitate. The solution was stirred overnight (10 h) at room temperature. The solvent was then removed in vacuo, and from the resulting solid $WO(O\text{-}i\text{-}Pr)_4$ (2.5 g, 95% yield) was isolated by sublimation at 70 °C, 10^{-4} torr.

$MoO(O\text{-}i\text{-}Pr)_4$. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (1.0 g, 4 mmol) was suspended in hexane (10 mL). Isopropyl alcohol (1.2 mL, 16 mmol) and Et_3N (2.2 mL, 16 mmol) were mixed with hexane (10 mL), and this solution was added dropwise to the suspension of $MoOCl_4$ in hexane. The solution became yellow with a copious white precipitate, though some darker materials stuck to the side of the flask. The solution was stirred overnight (10 h) and then filtered. The solids were washed with hexane, and the filtrate was collected and concentrated in vacuo to give a yellow oil, which was distilled (55 °C, 10^{-4} torr, yielding $MoO(O\text{-}i\text{-}Pr)_4$ (0.4 g, 30% yield based on Mo).

$W_3O(O\text{-}i\text{-}Pr)_{10}$. $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (0.43 g) and $WO(O\text{-}i\text{-}Pr)_4$ (0.23 g) were combined and dissolved in hexane (10 mL). The solution was refluxed for 2 h. The color changed from a dull green to an intense royal blue. The solvent was removed in vacuo, and the solids were dissolved in CH_2Cl_2 and recrystallized. Dark blue crystals of $W_3O(O\text{-}i\text{-}Pr)_{10}$ (0.50 g, 76% yield) were obtained. Anal. Calcd for $W_3O(O\text{-}i\text{-}Pr)_{10}$: C, 31.11; H, 6.09; N, 0.00. Found: C, 31.03; H, 6.20; N, <0.03. ^1H NMR data (CD_2Cl_2, 16 °C, 220 MHz): $\delta(OCH) = 5.57$ (3 H), 5.12 (3 H), 4.55 (3 H), 3.98 (1 H) septets; $\delta(OCHMe_2) = 1.59$ (18 H), 1.32 (18 H), 1.09 (6 H), 1.01 (18 H), doublets, $J_{HH} = 7$ Hz.

Table IV. Crystal Data Summary

empirical formula	$W_3O_{11}C_{30}H_{70}$
color of cryst	black
cryst dimens, mm	0.08 × 0.07 × 0.04 mm
space group	$P\bar{1}$
cell dimens	
temp, °C	−160
a, Å	21.303 (5)
b, Å	21.809 (6)
c, Å	10.265 (2)
α, deg	98.74 (1)
β, deg	92.93 (1)
γ, deg	117.93 (1)
Z (molecules/cell)	4
volume, $Å^3$	4123.87
calcd density, g/cm^3	1.866
wavelength, Å	0.710 69
mol wt	1158.43
linear abs coeff, cm^{-1}	85.749
detector to sample dist, cm	22.5
sample to source dist, cm	23.5
av ω-scan width at half-height, deg	0.25
scan speed, deg/min	4.0
scan width (+ dispersion), deg	2.0
individual bkgd, s	6
aperture size, mm	3.0 × 4.0
2θ range, deg	6–45
total no. of reflcns collected	10 986
no. of unique intensities	10 810
no. of $F > 2.33\ \sigma(F)$	9566
$R(F)$	0.0467
$R_W(F)$	0.0487
goodness of fit for the last cycle	1.404
max Δ/σ for last cycle	0.05

$Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. $WO(O\text{-}i\text{-}Pr)_4$ (0.29 g) and $Mo_2(O\text{-}i\text{-}Pr)_6$ (0.42 g) were combined and dissolved in hexane (10 mL). The solution was refluxed for 2 h, during which time the color changed from yellow to a deep forest green. The solvent was removed in vacuo, and the solids were recrystallized from CH_2Cl_2, yielding dark green crystals of $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$ (0.55 g, 77% yield). Anal. Calcd for $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$: C, 36.67; H, 7.18; N, 0.00. Found: C, 36.66; H, 7.08; N, <0.03.

In benzene-d_6 as solvent at 21 °C, the ^1H NMR spectrum was consistent with a nonfluxional molecule having a mirror plane of symmetry. This generates seven types of O-*i*-Pr ligands in the integral ratio 1:1:1:1:2:2:2; four of the O-*i*-Pr ligands are contained in the molecular plane of symmetry, six are not. We anticipate seven methyne resonances and observe $\delta(OCH) = 5.79$ (1 H), 5.04 (2 H), 5.44 (2 H), 5.28 (1 H), 4.74 (2 H), 4.71 (1 H), and 4.08 (1 H), (septets, $J_{HH} = 7$ Hz). Ten methyl resonances of equal intensity are expected since the six O-*i*-Pr ligands not contained in the mirror plane of the molecule (2:2:2) contain diastereotopic methyl groups: $\delta(OCHMe_2) = 1.68$, 1.64, 1.63, 1.62, 1.56, 1.53, 1.24 (overlapping pair), 1.18, and 1.13 (doublets, $J_{HH} = 7$ Hz).

Attempted Preparation of $MoW_2O(O\text{-}i\text{-}Pr)_{10}$. $MoO(O\text{-}i\text{-}Pr)_4$ (0.10 g) and $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (0.25 g) were mixed and dissolved in hexane (10 mL). The solution was warmed to reflux for 2 h, during which time the solution became dark green. When the solvent was removed in vacuo, fine white needles crystallized from the solution. These were identified as $WO(O\text{-}i\text{-}Pr)_4$. The filtrate was dried in vacuo, yielding a dark green solid. The ^1H NMR spectrum in benzene-d_6 showed many overlapping septets and doublets, too many for a $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ compound. Careful recrystallization of the dark green solids from CH_2Cl_2 solutions yielded a small quantity of dark blue crystals, which were collected by filtration and identified by ^1H NMR spectroscopy as mostly $W_3O(O\text{-}i\text{-}Pr)_{10}$, but probably, contaminated by $MoW_2O(O\text{-}i\text{-}Pr)_{10}$ and other products.

Attempted Comproportionation Reactions Involving $W(NPh)(O\text{-}i\text{-}Pr)_4$. $W(NPh)(O\text{-}i\text{-}Pr)_4$ was prepared in a manner analogous to that described by Schrock and co-workers[22] for the synthesis of $W(NPh)(O\text{-}t\text{-}Bu)_4$. Stoichiometric amounts of the reagents $W(NPh)(O\text{-}i\text{-}Pr)_4$ and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (ca. 200–300 mg) were combined and dissolved in hexane. The solution was stirred for 3 days and/or heated

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to reflux for periods as long as 2 days. No apparent reaction occurred, and this was confirmed by ^1H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Attempted Comproportionation Reactions Involving $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $Wo(O\text{-}i\text{-}Pr)_2(HNMe_2)_2$. Stoichiometric amounts of the reagents $M(O\text{-}i\text{-}Pr)_5$ (M = Nb, Ta) and $Mo_2(O\text{-}i\text{-}Pr)_6$ or $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$ (ca. 200–300 mg) were dissolved together in 10–20 mL of hexane. The solutions were allowed to stir at room temperature for as long as 4 days or heated at reflux for as long as 2 days. No apparent reaction occurred, and this was confirmed by ^1H NMR spectroscopy of the solids obtained from stripping the solution to dryness.

Crystallographic Studies. General operating procedures and listings of programs have been given previously.[7] Crystal data are summarized in Table IV.

$W_3O(O\text{-}i\text{-}Pr)_{10}$ and $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$. Preliminary examination of the samples indicated that they were isomorphous with $Mo_3O(O\text{-}i\text{-}Pr)_{10}$. The mixed-metal complex is undoubtedly disordered with respect to the location of the metal atoms, and so no data were taken other than for the cell parameters (−159 °C): $a = 21.324$ (13) Å, $b = 21.874$ (14) Å, $c = 10.235$ (5) Å = 98.79 (3)°, $\beta = 92.77$ (3)°, $\gamma = 117.85$ (2)°.

Data were collected in the usual manner for the $W_3O(O\text{-}i\text{-}Pr)_{10}$ sample, and the starting coordinates for the $Mo_3O(O\text{-}i\text{-}Pr)_{10}$ sample were used. Because of the number of atoms involved in the refinement, no attempt was made to include hydrogen contributions.

A final difference Fourier synthesis was featureless, with several peaks of 0.9–1.3 e Å^{-3} located in the vicinity of the six tungsten atoms. Scans indicated no absorption correction was necessary.

Acknowledgment. We thank the Office of Naval Research and the Wrubel Computing Center for support.

Registry No. $W_3O(O\text{-}i\text{-}Pr)_{10}$, 92562-31-7; $Mo_2WO(O\text{-}i\text{-}Pr)_{10}$, 92562-32-8; $MoW_2O(O\text{-}i\text{-}Pr)_{10}$, 93862-15-8; $W_2(O\text{-}i\text{-}Pr)_6(HNMe_2)_2$, 84028-40-0; $WO(O\text{-}i\text{-}Pr)_4$, 93862-16-9; $Mo_2(O\text{-}i\text{-}Pr)_6$, 62521-20-4; $MoO(O\text{-}i\text{-}Pr)_4$, 79210-24-5; $W(NPh)(O\text{-}i\text{-}Pr)_4$, 93842-63-8; $Nb(O\text{-}i\text{-}Pr)_5$, 18368-80-4; $Ta(O\text{-}i\text{-}Pr)_5$, 16761-83-4; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Listings of a comparison of bond distances and bond angles for the $M_3O(O\text{-}i\text{-}Pr)_{10}$ molecules (M = Mo and W) and anisotropic thermal parameters, complete listings of bond distances and angles, figures showing the atom number scheme, and a table of observed and calculated structure amplitudes for $W_3O(O\text{-}i\text{-}Pr)_{10}$ (83 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Structural Studies,
Research Laboratory for Inorganic Chemistry,
Hungarian Academy of Sciences, Budapest H-1431, Hungary,
and Department of Chemistry and Institute of Materials Science,
University of Connecticut, Storrs, Connecticut 06268

Molecular Structure of Monomeric Cobalt Dibromide with Some Information on the Structure of the Dimer from Electron Diffraction

Magdolna Hargittai,*[1a] Olga V. Dorofeeva,[2]
and János Tremmel[1b]

Received June 6, 1984

As part of our research on the molecular structure of transition-metal dihalides, an electron diffraction investigation of vapor-phase cobalt dibromide has been carried out. Several first-row transition-metal dichlorides ($MnCl_2$,[3] $FeCl_2$,[4] $CoCl_2$[5]) and dibromides ($MnBr_2$,[6] $FeBr_2$,[4] $NiBr_2$[7]) have already been investigated in our Budapest laboratory. In addition to the determination of the geometrical parameters and mean vibrational amplitudes of the monomers, their bending vibrational frequencies have also been estimated. The presence of a small amount of dimeric species has also been detected in the manganese dibromide and iron dibromide experiments, and a limited amount of structural information has been gained on these species as well.

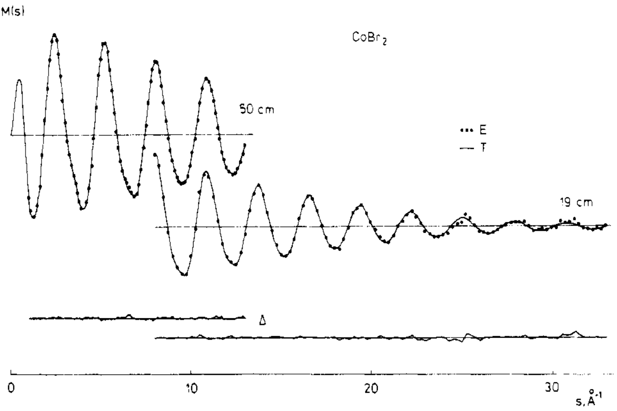

Figure 1. Experimental (E) and theoretical (T) molecular intensities, the latter for a model of 94% monomer and 6% dimer.

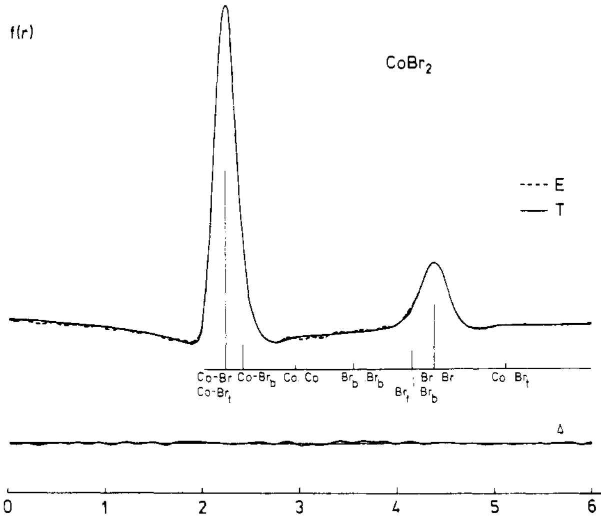

Figure 2. Radial distribution curves, corresponding to the molecular intensities of Figure 1.

Experimental Section

The sample of cobalt dibromide was a commercial product (Ventron 23149). Due to the low volatility of cobalt dibromide, relatively high-temperature conditions had to be used in the electron-scattering experiment. The composition of the vapors of transition-metal halides may be complicated, especially at high temperatures. Therefore, the combined electron diffraction/quadrupole mass spectrometric technique developed in our laboratory[8] was utilized. The choice of the nozzle material is also of importance as indeed some metals used for the nozzle showed reactions with the sample in the preliminary experiments. Finally, a molybdenum nozzle was used. The recorded mass spectra showed no indication of any reaction products in the experiments with this nozzle. However, the presence of a small amount, about 5%, of dimeric species was indicated at the electron diffraction experimental conditions.

The necessary vapor pressure for the electron diffraction experiment could be reached at a nozzle temperature of 635 °C. The so-called radiation nozzle[3] was used. All other experimental conditions, the data processing, and the source of the scattering functions were the same as in the other studies in this series.[3–7]

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(1) (a) Visiting scientist at University of Connecticut (1983/1985), on leave from the Hungarian Academy of Sciences. (b) Hungarian Academy of Sciences.

(2) Visiting scientist at the Hungarian Academy of Sciences, Fall 1982, on leave from the Institute of High Temperatures, Soviet Academy of Sciences, Moscow, U.S.S.R.

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0020-1669/85/1324-0245$01.50/0