[Mn(TRP)] these angles do not differ as dramatically, having values of 95.15 and 96.01°, respectively, but the difference between the Mn–N bonds (0.094 Å) is greater than that in the iron complex (0.053 Å). In each complex the triangle formed from the pyrrole nitrogens [N(1)] is smaller than that from the imine nitrogen atoms [N(7)]. The sides of these triangles have lengths of 3.03 and 3.19 Å in [Mn(TRP)] and 2.81 and 3.00 Å in [Fe(TRP)].

Magnetically coupled d^5–d^9 complexes have been of considerable interest as cytochrome *c* oxidase models[8–13] because of the enzyme's anomalous magnetic properties, which could be rationalized in terms of a strong Fe–Cu coupling, $J \sim -300\ \mathrm{cm}^{-1}$. However, no proven models for such a system yet exist. Synthetic coupled d^5–d^9 complexes, of which we have made the first and the most strongly coupled,[12] have only shown coupling constants about an order of magnitude too small. On treatment with CN^- the resting oxidase exhibits a temperature-dependent magnetic moment which can be interpreted in terms of a coupled low-spin d^5–d^9 system, with $J \sim -40\ \mathrm{cm}^{-1}$.[9] A d^4 high-spin–low-spin equilibrium in a d^4–d^{10} [Fe(IV)–Cu(I)] system with the metals well separated would adequately explain the magnetic properties, and a d^4–d^{10} model is otherwise at least as plausible, based on recent work with the enzyme.[13] Such an explanation has not come readily to mind in the past in the absence of evidence for d^4 spin crossovers. With the clear observation of a spin equilibrium in d^4, both models must now seriously be considered and compared.

Acknowledgment. Support received under NSF Grant CHE77-01372 is gratefully acknowledged.

Supplementary Material Available: A listing of F_o and F_c (3 pages). Ordering information is given on any current masthead page.

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A New Aqueous Chemistry of Organometallic, Trinuclear Cluster Compounds of Molybdenum

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The reactions of $Mo(CO)_6$ and $W(CO)_6$ with acetic acid are important, interesting and, especially for $Mo(CO)_6$, complicated. We have previously reported[1,2] that for $W(CO)_6$ products can be isolated that contain either the trinuclear cluster species $[W_3(\mu_3\text{-}O)_2(OAc)_6(H_2O)_3]^{2+}$ or a substitution product thereof with H_2O replaced by, e.g., OAc^-. The reaction of $Mo(CO)_6$ yields

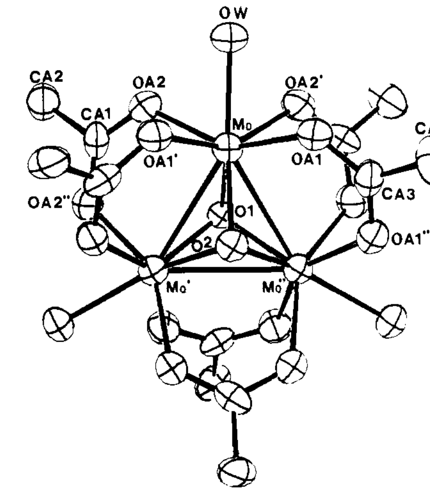

Figure 1. $[Mo_3O_2(OAc)_6(H_2O)_3]^{2+}$ ion found in compounds **1** and **2**.

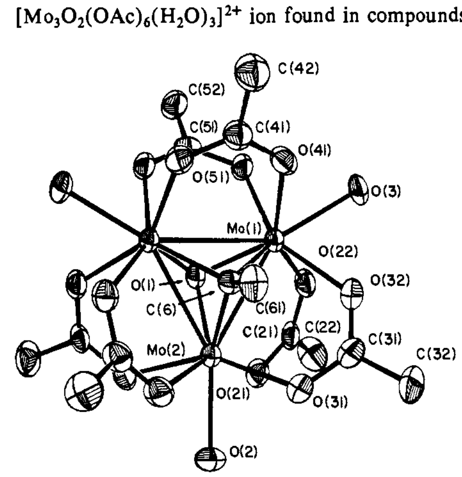

Figure 2. $[Mo_3O(CCH_3)(OAc)_6(H_2O)_3]^+$ ion found in compound **3**.

$Mo_2(OAc)_4$ (ca. 15%) and a solution from which several trinuclear products can be isolated, either directly or following reaction with an oxidizing agent. One of these was previously reported[3] and assigned the formula $[Mo_3(OEt)_2(OAc)_6(H_2O)_3](CF_3SO_3)_2$. A thorough reinvestigation of this system has led to the recognition of a remarkable class of new compounds and shows that the above formula should be revised.

We describe six representative compounds that illustrate the nature and range of the field. All are obtained from the reaction of $Mo(CO)_6$ with a refluxing mixture of AcOH and $(AcO)_2O$, followed by suitable workup,[4] and have been identified by

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(4) The ions of compounds **4** and **5** were obtained as previously described.[3] Elution of the cation-exchange column with $NaSbF_6$, CF_3SO_3H, or $CH_3C_6H_4SO_3H$ followed by slow evaporation afforded **4**, **5**, or **6**, respectively, in crystalline form. Compounds **1** and **2** are best obtained by refluxing $Mo(CO)_6$ in an $AcOH/(AcO)_2O$ mixture for 24 h with constant bubbling of air. After being cooled, the solution was filtered, diluted with water, and passed through a Dowex 50W-X2 cation-exchange column. Elution of the adsorbed red ion with 0.5 M HBr or CF_3SO_3H followed by slow evaporation led to compounds **1** and **2**. When the $M(CO)_6$ reaction is carried out in the presence of NaOAc, an orange solid was obtained upon evaporation of the mother liquor. This solid was dissolved in water and the solution treated as described above. Elution of the orange ion with 0.1 M HBF_4 followed by slow evaporation led to the isolation of compound **3**. In all cases small amounts of $Mo_2(OAc)_4$ precipitated from the reaction mixture and were separated by filtration.

(5) Satisfactory elemental analyses have been obtained for all new compounds. To illustrate how analytical data support CH_3C caps, are less compatible with CH_3CH_2O caps, and rule out CH_3O caps, we give carbon analyses (%) for **5** and **6**. The percentages found are averages of several, highly reproducible analyses. Anal. (for compound **5**) Calcd: CH_3C, 20.63; CH_3CH_2O, 19.94; CH_3O, 18.19. Found: 20.62 ± 0.06. (for compound **6**) Calcd: CH_3C, 28.46; CH_3CH_2O, 27.66; CH_3O, 26.38. Found: 28.66 ± 0.06. In the case of **1** the oxidation number of molybdenum was shown by permanganate titration, similar to that used for the tungsten compounds,[1] to be +4.0 ± 0.1.

Table I. Structural Data for $[Mo_3(\mu_3\text{-}X)(\mu_3\text{-}Y)(OAc)_6(H_2O)_3](Anion)_x \cdot yH_2O$ Compounds

compd no.	X	Y	anion	x	y	bond distances, Å[a] Mo-Mo	Mo-(μ_3-C)	Mo-(μ_3-O)	C-CH_3	electron count
1	O	O	Br^-	2	1	2.767 (2)		2.006 (9)		
2	O	O	$CF_3SO_3^-$	2	0	2.757 (1)		1.981 (9)		6
3	O	CCH_3	BF_4^-	1	9	2.753 (1)	2.054 (16)	1.982 (11)	1.514 (12)	
4	CCH_3	CCH_3	SbF_6^-	1	3	2.815 (7)	2.06 (1)		1.54 (2)	5
5	CCH_3	CCH_3	$CF_3SO_3^-$	2	0	2.883 (1)	2.075 (2)		1.491 (4)	4
6	CCH_3	CCH_3	$C_7H_7SO_3^-$	2	10	2.892 (1)	2.074 (9)		1.49 (1)	

[a] Numbers in parentheses are esd's occurring in the last significant figure. Crystallographically distinct but chemically equivalent distances have been averaged.

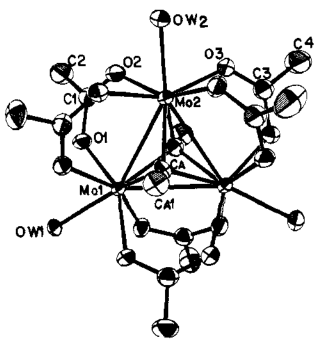

Figure 3. $[Mo_3(CCH_3)_2(OAc)_3(H_2O)_3]^{2+}$ ion found in compounds 5 and 6. Trinuclear cation in 4 is very similar.

chemical[5] and physical[6] methods including X-ray crystallographic structure determinations,[7] the principal results of which are given in Table I.

Compounds 1 and 2 are analogous to the previously described dioxotritungsten compounds;[1,2] the trinuclear cation is shown in Figure 1. Compound 2 is isomorphous with its tungsten analogue[2], and the Mo-Mo and W-W distances are very similar, 2.757 (1) and 2.747 (1) Å, respectively. They have six electrons in the Mo_3 cluster for M-M binding, giving a bond order of 1.

The remaining four compounds differ from any previously known Mo or W compounds in having μ_3-alkylidyne capping ligands and, for 4, 5, and 6, in having less than six cluster electrons and, hence, bond orders <1. Evidence for the CH_3C capping groups (rather than CH_3CH_2O or CH_3O) is as follows.

(1) Chemical analyses are consistent only with CH_3C groups and not with CH_3CH_2O or CH_3O groups.[5]

(2) The agreement of calculated (from structure) and measured densities is satisfactory only for CH_3C or CH_3O, but not CH_3CH_2O, capping groups.[6] Thus (1) and (2) together leave only CH_3C as an acceptable capping group (other than O where it occurs).

(3) In each case, 3–6, refinement of the CH_3C groups as CH_3O or CH_3CH_2O groups gives unreasonably large thermal ellipsoids for the capping atom and no refinable β-carbon atoms can be found. As shown in Figures 2 and 3 the capping carbon atoms, when refined as such, give ellipsoids comparable to those for the true oxygen atoms, whereas these atoms appear 2–3 times larger if refined as oxygen atoms. Furthermore, in most cases, packing leaves no room for β-CH_3 groups.

(4) NMR spectra are consistent with all proposed structures and formulas.[8] In 3, for example, when all carbon positions are enriched with ^{13}C, the signal for the CH_3 groups of H_3CC shows satellites due to the ^{13}C capping atoms.

Preliminary magnetic susceptibility measurements as well as NMR spectra confirm the diamagnetism of 1, 2, and 3 and the paramagnetism of 4, 5, and 6. The increasing Mo-Mo distances, from about 2.76 Å for the $6e^-$ clusters to 2.82 for the $5e^-$ cluster to 2.89 for the $4e^-$ clusters, are consistent with the decrease in Mo-Mo bond order from 1.0 to $^5/_6$ to $^2/_3$.

There have been some previous reports of μ-alkylidyne-bridged triangular metal atom clusters, viz., the $XCCo_3(CO)_9$ and $RCCo_3(\eta^5\text{-}C_5H_5)_3CO$ types,[9] some $XCRu_3H_3(CO)_9$[10a,b] and $XCOs_3H_3(CO)_3$[10c,d,e] types, the nickel[11a] and rhodium[11b] species $XCNi_3(\eta^5\text{-}C_5H_5)_3$ and $[HCRh_3(\eta^5\text{-}C_5H_5)_3(CO)_2]^+$, and a number of mixed species such as $RCMo(\eta^5\text{-}C_5H_5)Co_2(CO)_6$[11c] and $CH_3CFeCo_2(CO)_9H$.[11d] These, however, are rather different in character from the molybdenum compounds we are reporting, since they involve zero- or low-valent metal atoms, are nonionic (except on an outer carbon atom), have no simple aqueous chemistry, and show no variability in electron population.[12] Moreover, some of the new compounds contain *two* capping ethylidyne groups, and this has never been observed before. The new aqueous chemistry of 4-valent to $4^2/_3$-valent molybdenum is essentially an unprecedented area for both organometallic chemistry and metal-atom-cluster chemistry. A series of future papers will provide full reports on the compounds described here and on many others that have been discovered.

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Supplementary Material Available: Tables of crystallographic data (space groups, unit cell dimensions, etc.) and atomic positional parameters for all six compounds (9 pages). Ordering information is given on any current masthead page.

(6) Measured densities (g cm^{-3}) agree well with those calculated from crystal structure analyses. For 5 and 6 these measurements rule out CH_3CH_2O capping groups. For 5: d(obsd), 2.16 ± 0.01; d(calcd) for CH_3C, 2.16; for CH_3O, 2.18; for CH_3CH_2O, 2.23. for 6: d(obsd), 2.15 ± 0.01; d(calcd) for CH_3C, 2.16; for CH_3O, 2.18; for CH_3CH_2O, 2.24. All d(calcd) values are precise to ±0.002 g cm^{-3}.

(7) The six structures, along with a number of others, have been thoroughly refined. Details of the space groups, unit cell dimensions, and lists of atomic positional and thermal parameters are available as supplementary material.

(8) For 3, for example, the ^1H spectrum has three signals of relative intensities of 1:3:3 at 2.400, 2.195, and 2.128 ppm downfield from Me_4Si corresponding to the CH_3C and two kinds of CH_3CO_2 methyl groups. The ^{13}C spectrum has a doublet (Δ = 10 Hz) at 21.0 ppm (downfield) from Me_4Si for the O_2CCH_3 atoms, a singlet at 29.3 ppm for the CCH_3 atoms, with the relative intensities of three signals being approximately 3:3:1. There is a doublet (Δ = 51 Hz) at 182.5 ppm for the two kinds of O_2CCH_3 atoms and a singlet at 295.8 ppm for the capping ethylidyne carbon atom.

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(12) For carbonyl-type systems oxidizing agents destroy the cluster whereas in the molybdenum systems even strong reagents like permanganate remove electrons from the cluster but leave the structure, including the alkylidyne bridges, intact.