Syntheses, Crystal Structures, and Properties of Novel Heterooctametallic Clusters $Na_2M'_2[M_3O_4(O_2CEt)_8]_2$ (M' = Fe, Cr, Mo; $M_3 = Mo_3, MoW_2, W_3$)

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Abstract: A mixture of Na_2MO_4, $M(CO)_6$, $FeCl_3 \cdot 6H_2O$, and $(EtCO)_2O$ was heated at 120 °C to produce the heterooctanuclear clusters $Na_2Fe_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo, **1**; W, **2**). The bioxo-capped clusters $Na[M_3O_2(O_2CEt)_9]$ ($M_3 = MoW_2, W_3$) were treated with $Fe(CO)_5$, $Cr(CO)_6$, and $Mo(CO)_6$ in $(EtCO)_2O$ at 120 °C to afford $Na_2M'_2[MoW_2O_4(O_2CEt)_8]_2$ (M' = Fe, **3**; Cr, **4**; Mo, **5**) and $Na_2Mo_2[W_3O_4(O_2CEt)_8]_2$ (**6**), respectively. The isomorphous clusters **1**, **2**, **5**, and **6** were characterized by X-ray crystallography. The structures, similar to those of the analogues $Na_2Cr_2[M_3O_4(O_2CEt)_8]$ (M = Mo, **7**; W, **8**) and $Na_2V_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo, **9**; W, **10**), consist of two incomplete cubane-type $[M_3O_4(O_2Et)_8]^{4-}$ units centrosymmetrically bridged by two M'(III) metal ions through μ-oxo and propionate groups; the resulting cluster dianions are linked by Na^+ ions into infinite chains. Clusters **1**–**10** do not dissolve in water and common organic solvents at room temperature. Unlike the chromium(III) clusters **7** and **8**, the iron(III) and vanadium(III) clusters **1** and **9** are soluble in aqueous acid solution, as a result of their decomposition into isolated $[Mo_3O_4]^{4+}$ cluster units. Temperature-dependent magnetic susceptibilities of **1**, **2**, and **7**–**10** were measured over the range 2–200 K and modeled by means of the spin-Hamiltonian $H = -2J\boldsymbol{S}_1\boldsymbol{S}_2$ to give spin exchange coupling constants J/k of −0.60, −0.72, −1.76, −1.31, −4.80, and −1.46 K, respectively. These figures show that antiferromagnetic spin exchange coupling interactions between the magnetic, bridging M'(III) ions are very weak. These species show characteristic bands in the IR spectra at 740–820 cm^{-1}, which can probably be assigned to $\tilde{\nu}(M-\mu\text{-}O)$.

Keywords
chromium · clusters · iron · molybdenum · tungsten

Introduction

Recently, we reported a novel class of the paramagnetic heterooctametallic chain clusters $Na_2M'_2[M_3O_4(O_2CR)_8]_2$,[1,2] which consist of two incomplete cubane-type cluster units $[M^{IV}_3O_4(O_2CR)_8]^{4-}$ (M = Mo, W) bridged by two M'(III) metal ions through μ-oxo and carboxylate groups. These clusters are of interest because they add to the extensive and developing chemistry of $[M_3O_4]$ (M = Mo, W) cluster units.[3–11] However, because of the lack of general and efficient synthetic methods, the species of this type thus far reported are limited to chromium(III)- and vanadium(III)-bridged clusters containing homonuclear triangular units,[1,2] and little is known about their magnetic properties and stability toward aqueous acid solution. Herein we report on a new general route to such species and crystal structures of four new members of this series—$Na_2Fe_2[Mo_3O_4(O_2CEt)_8]_2$ (**1**), $Na_2Fe_2[W_3O_4(O_2CEt)_8]_2$ (**2**), $Na_2Mo_2[MoW_2O_4(O_2CEt)_8]_2$ (**5**), and $Na_2Mo_2[W_3O_4(O_2CEt)_8]_2$ (**6**). The magnetic exchange interactions between the bridging metal(III) ions in trinuclear units and solution stabilities have also been investigated.

Results and Discussion

Synthesis: The syntheses of clusters **1**–**10** are summarized in Scheme 1. All these preparative reactions involve the redox reaction system $Na_2MO_4/M'(CO)_6/(RCO)_2O$, which was previously used in the effective synthesis of triangular bioxo-capped carboxylate clusters of molybdenum(IV) and tungsten(IV).[12–16] One such reaction (M = Mo, M' = W, R = Me) was first reported by Cotton et al. to yield a mixture of the triangular bioxo-capped acetates $Na[Mo_xW_{3-x}O_2(O_2CMe)_9]$ ($x = 1-3$).[12,13] The reverse reactions (M = W, M' = Mo, R = Me, Et) were found to result in the exclusive formation of the mixed-metal cluster species $Na[MoW_2O_2(O_2CR)_9]$ (R = Me, Et).[14–16] This reaction system was recently successfully extended to the preparation of the Mo(W)–Cr(V) mixed-metal clusters $Na_2M'_2[M_3O_4(O_2CEt)_8]_2$ (M' = Cr, M = Mo, **7**, M = W, **8**; M' = V, M = Mo, **9**, M = W, **10**) by using $Cr(CO)_6$ or $NaVO_3$ in place of $M(CO)_6$ or Na_2MO_4 in heated (120 °C)

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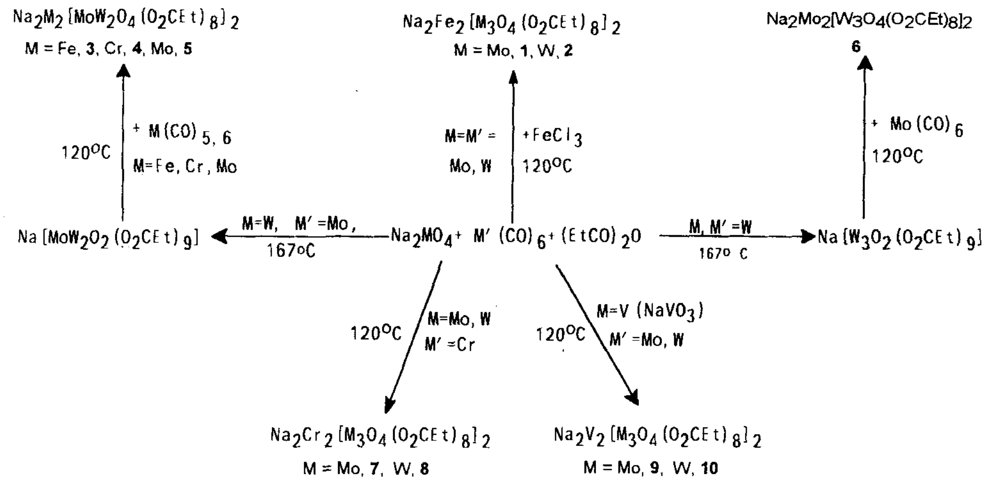

Scheme 1. Syntheses of clusters **1**–**10**

instead of refluxing $(EtCO)_2O$.[1,2] It is interesting to note that both reduction of Na_2MO_4 and oxidation of $M(CO)_6$ produced the incomplete cubane-type units $[M_3O_4(O_2CEt)_8]^{4-}$ rather than the aforementioned bioxo-capped species, which were previously considered to predominate for Mo^{IV} and W^{IV} in carboxylic anhydrides, since the former cuboidal units could be trapped by Cr^{3+} (or V^{3+}) and Na^+ ions in the reaction mixtures to give the insoluble heterooctanuclear infinite chain clusters. However, these two methods are limited and cannot be employed to prepare, for example, the present Fe^{III}-bridged derivatives effectively. We thus considered designing an alternative route based on the redox reaction of Na_2MO_4 and $M(CO)_6$ to produce the incomplete cuboidal units $[M_3O_4(O_2CEt)_8]^{4-}$ in the presence of iron(III) complexes as a source of Fe^{3+} ions. As might be expected, reaction of Na_2MO_4, $M(CO)_6$, and $FeCl_3 \cdot 6H_2O$ in heated (120 °C) propionic anhydride yielded the desired iron(III)-bridged derivatives $Na_2Fe_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo, **1**; W, **2**) in good yields. This reaction should provide a more general route to such heterooctametallic series than the above-mentioned methods, because a far wider variety of metal(III) complexes are available compared to metalates or metal carbonyls. For instance, one can prepare cluster **7** easily and in similar yields by replacing $FeCl_3 \cdot 6H_2O$ with $CrCl_3 \cdot 6H_2O$.

The syntheses of clusters **3**–**6** from the hetero- or homonuclear bioxo-capped propionates $Na[M_3O_2(O_2CEt)_9]$ ($M_3 = MoW_2$ or W_3) as starting materials are of special interest, because they confirm that the cuboidal units $[M_3O_4(O_2CEt)_8]^{4-}$ ($M_3 = MoW_2$, W_3) in **3**–**6** result from the cluster conversion of the bioxo-capped species with the metal triangle remaining intact.

It is noteworthy that, in addition to the above-mentioned Mo^{IV} clusters, this reaction system can also produce the interesting dinuclear Mo^V and trinuclear $Mo^{II,III,III}$ carboxylates, $Na_2Mo_2O_2(\mu\text{-}O_2CCF_3)_{10} \cdot 4CF_3CO_2H$ and $Na_2[Mo_3O(\mu,\eta^2\text{-}O_2CMe)_5(\mu,\eta^1\text{-}O_2CMe)(O_2CMe)_2(H_2O)]$.[17,18]

Stability: Unlike the chromium-bridged species, which are stable for at least six months (monitored by IR spectroscopy), the iron(III)-, molybdenum(III)-, and vanadium(III)-bridged clusters are only stable in air for a few days. Like clusters **7**–**10**, **1**–**6** are insoluble in water and common organic solvents at room temperature. However, clusters **1** and **9** can be dissolved in aqueous hydrochloric acid to produce red solutions. It is interesting to note that the UV/Vis spectrum of **9** (Figure 1) is similar to that of red $[Mo_3O_4]^{4+}$ aqua ions reported previously;[8a] this indicates that the V cations dissociate from the trinuclear centers with formation of isolated $[Mo_3O_4]^{4+}$ units. The peak at ca. 510 nm is flatter for **1**, presumably because of the presence of Fe^{3+} ions. These results suggest that the solubility in aqueous acid solution is a consequence of the decomposition of the octametallic clusters to give $[Mo_3O_4]^{4+}$ species. In contrast to the above-mentioned iron and vanadium clusters, the chromium cluster **7** dissolves only very slowly in hot HCl, and **8** is insoluble; these clusters thus display considerably higher stability toward aqueous acid solution. A similar trend was observed for the stability in air.

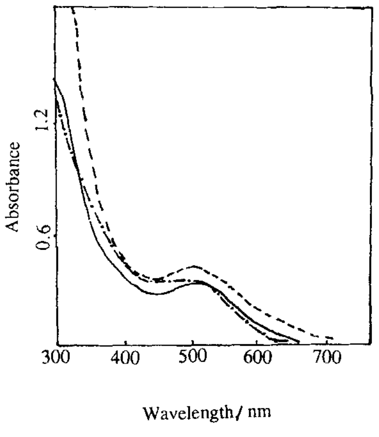

Figure 1. UV/Vis spectra of **1** (- · · · -, 0.001 M) and **9** (—, 0.001 M) in 2 M HCl (optical path = 1 cm); the latter is similar to that of $[Mo_3O_4]^{4+}$ aqua ions (- - -).

Abstract in Chinese:

混合物 Na_2MO_4, $M(CO)_6$, $FeCl_3$ $6H_2O$ 和$(EtCO)_2O$在 120°C 加热生成异八金属簇合物 $Na_2Fe_2[M_3O_4(O_2CEt)_2]_2$ (M = Mo, 1, W, 2)。 双氧帽簇合物 $Na[M_3O_2(O_2CEt)_9]$ ($M_3 = MoW_2$, W_3) 与 $Fe(CO)_5$, $Cr(CO)_6$ 和 $Mo(CO)_6$ 在 120°C 的$(EtCO)_2O$ 溶液中反应分别得到 $Na_2M'_2[MoW_2O_4(O_2CEt)_8]_2$ (M' = Fe, 3, Cr, 4, Mo, 5) 和 $Na_2Mo_2[W_3O_4(O_2CEt)_8]_2$ (6). 异质同晶簇合物 1 ， 2 ， 5 ， 6 被 X-ray 结晶学表征。其结构由两个金属 (III) 离子 (M')和由其对称桥联的两个不完全立方烷单元$[M_3O_4(O_2CEt)_8]^{4-}$组成。所形成的两价簇阴离子被 Na^+联结成无限链。簇合物 1-6 在常温下不溶于水及一般有机溶剂，类似于$Na_2Cr_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo, 7, W, 8)和 $Na_2V_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo, 9, W, 10)。簇合物 1 ， 9 溶于酸性水溶液并同时分解为分离的$[Mo_3O_4]^{4+}$单元。然而， 簇合物 7 ， 8 在酸性水溶液中具有高度的稳定性 (不溶性) 。采用自旋偶合哈密顿量 $H = -2JS_1 S_2$ 对簇合物 1 ， 2, 7-10 在 2-200K 的变温磁化率数据进行模拟得到其自旋交换偶合常数 J/k 分别为-0.60, -0.72, -1.76, -1.31, -4.80 和-1.46K ， 表明 M'(III)磁性离子间具有很弱的反铁磁自旋交换偶合作用。簇合物在 600-820cm^{-1} 区间的特征红外光谱被归属。

Presumably, this can be explained in terms of the stronger Cr–O bonds, owing to the high crystal-field activation energy of Cr^{III} ions.

Crystal Structure: The isomorphous clusters **1**, **2**, **5**, and **6** have been characterized by X-ray crystallography. The $[Mo_3O_4(O_2CEt)_8]^{4-}$ unit, the $[FeMo_3O_4]_2^{14+}$ skeleton, the $Fe_2[Mo_3O_4(O_2CEt)_8]_2^{2-}$ dianion, and the infinite chain of cluster **1** are shown in Figures 2–5, respectively. Table 1 lists the selected bond lengths and angles. A comparison of important averaged bond lengths in **1**–**10** and related clusters is given in Table 2. An unusual feature of the trinuclear unit shown in Figure 2 is the single bridging propionate ligand, which has not been found in isolated $[M_3O_4]^{4+}$-type clusters previously reported. The average bond lengths in the $[M_3O_4]^{4+}$ cores of **1**, **2**, **5**, and **6** are similar to the corresponding bond lengths in the other compounds shown in Table 2. The M–O_b^* (O2 or O3) bonds are significantly lengthened compared to the M–O_b bonds. This implies that d–p π bonds in the $Mo_2O_b^*$ arrays are considerably weakened by the bonding of O_b^* atoms to the bridging metal M′(III) ions. Unlike the formal sulfur analogues $[M'M_3S_4]_2$ of double cubane-type structure,[4] the $[FeMo_3O_4]_2^{14+}$ skeleton shown in Figure 3 possesses a centrosymmetric cyclic structure characteristic of $Fe_2Mo_2O_4$ eight-membered rings (the average deviation of ring atoms from the least-squares plane is about 0.3 Å). The four $FeMo_2O$ arrays are nearly planar (the sum of the M′-O-M angles are 346 and 359° for Fe1/Mo1/Mo3/O3 and Fe1/Mo1/Mo2/O2, respectively; Table 1), as is also observed for the CrW_2O units in $W_3(CCH_2tBu)O_3Cr_3(O_2CtBu)_{12}$.[19] This arrangement is believed to be a result of both the strong repulsion between the Mo^{IV} and Fe^{III} ions and the small radius of the oxygen atom. In fact, no $[M_3M'O_4]$ (M = Mo or W) cubane-type clusters with three or more metal–metal bonds have been prepared by far. As shown in Figure 4 and Table 1, the four $EtCO_2$ groups from each trinuclear unit complete a rather regular O_6 octahedron for the M′(III) ions with the O-M′-O angles within 5° of the expected values for an octahedron and six similar M′–O bond lengths. It is noteworthy that Fe–O_b^* and Mo–O_b^* bond lengths in **1**, **2**, **5**, and **6** are much longer than corresponding Fe–O_b and Mo–O_b ones in $[Fe_3O]^{7+}$ and $[Mo_3O_4]^{4+}$ units, respectively; this indicates that the former bonds lack significant d–p π bonding.

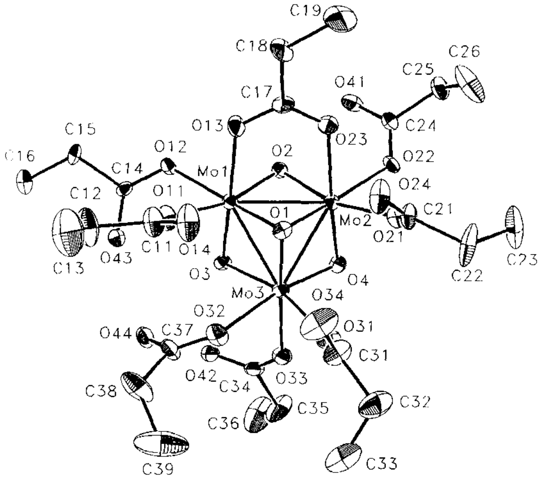

Figure 2. Structure of the triangular unit $[Mo_3O_4(O_2CEt)_8]^{4-}$ of **1**.

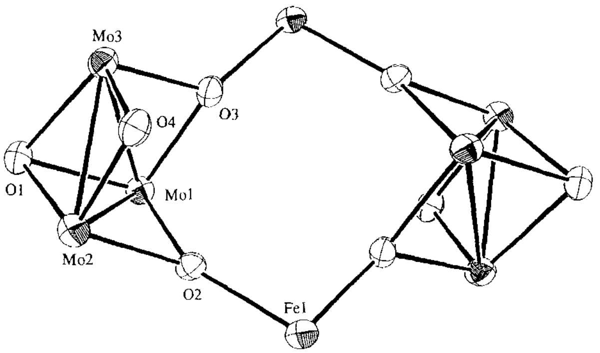

Figure 3. Structure of the $[FeMo_3O_4]_2^{14+}$ skeleton of **1**.

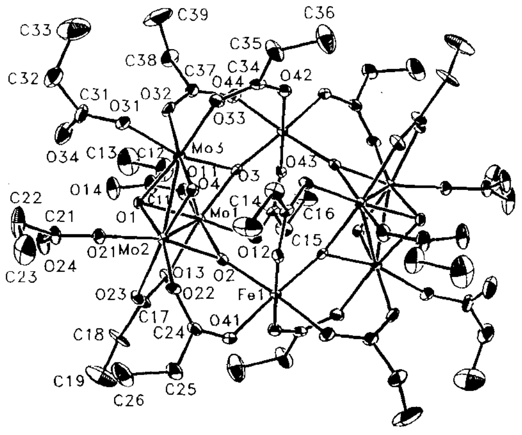

Figure 4. ORTEP drawing of the octametallic dianion $Fe_2[Mo_3O_4(O_2CEt)_8]_2^{2-}$ of **1** (thermal ellipsoids at the 50% probability level).

The octanuclear dianions shown in Figure 4 are linked by Na^+ ions into infinite chains characteristic of centrosymmetric Na_2O_2 four-membered rings (Figure 5). Each Na^+ ions is coordinated to four terminal propionate oxygen atoms and one capping oxygen atom in a distorted trigonal bipyramidal arrangement with rather short Na–O bonds (ca. 2.31 Å), compared to

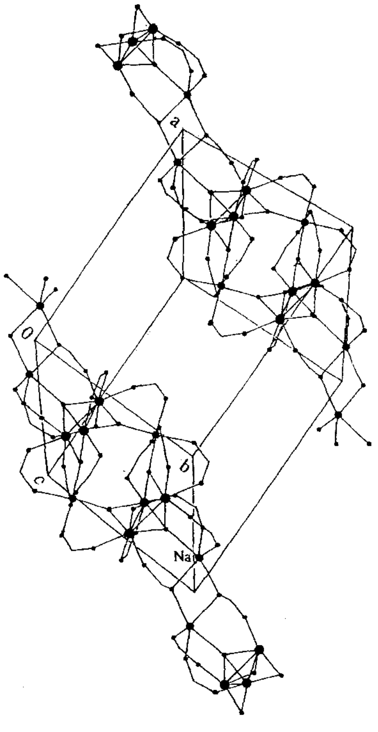

Figure 5. Perspective view of infinite chains of cluster **1** with the Et groups omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for clusters **1**, **2**, **5**, and **6**.

Cluster **1**		Cluster **2**		Cluster **5**		Cluster **6**	
Mo1–Mo2	2.506(1)	W1–W2	2.5182(9)	M1–M2	2.5045(9)	W1–W2	2.517(2)
Mo1–Mo3	2.529(1)	W1–W3	2.5442(9)	M1–M3	2.533(1)	W1–W3	2.539(1)
Mo2–Mo3	2.517(1)	W2–W3	2.542(1)	M2–M3	2.523(1)	W2–W3	2.535(2)
Mo1–O1	2.014(7)	W1–O1	2.043(9)	M1–O1	2.022(8)	W1–O1	2.03(2)
Mo1–O2	1.957(7)	W1–O2	1.96(1)	M1–O2	1.959(6)	W1–O2	1.96(2)
Mo1–O3	1.950(7)	W1–O3	1.98(1)	M1–O3	1.959(9)	W1–O3	1.96(2)
Mo1–O11	1.991(8)	W1–O11	2.01(2)	M1–O11	2.004(6)	W1–O11	1.99(2)
Mo1–O12	2.105(7)	W1–O12	2.09(2)	M1–O12	2.094(8)	W1–O12	2.09(2)
Mo1–O13	2.136(7)	W1–O13	2.11(2)	M1–O13	2.11(1)	W1–O13	2.12(2)
Mo2–O1	2.013(7)	W2–O1	2.02(2)	M2–O1	2.021(6)	W2–O1	2.04(2)
Mo2–O2	1.952(7)	W2–O2	1.980(9)	M2–O2	1.965(8)	W2–O2	1.97(1)
Mo2–O4	1.911(7)	W2–O4	1.923(9)	M2–O4	1.918(9)	W2–O4	1.91(2)
Mo2–O21	2.018(7)	W2–O21	2.02(1)	M2–O21	2.019(8)	W2–O21	2.00(2)
Mo2–O22	2.109(8)	W2–O22	2.10(2)	M2–O22	2.098(7)	W2–O22	2.05(2)
Mo2–O23	2.145(7)	W2–O23	2.15(1)	M2–O23	2.12(2)	W2–O23	2.13(2)
Mo3–O1	2.055(7)	W3–O1	2.068(9)	M3–O1	2.059(9)	W3–O1	2.10(2)
Mo3–O3	1.975(7)	W3–O3	1.99(1)	M3–O3	1.952(8)	W3–O3	2.00(2)
Mo3–O4	1.918(7)	W3–O4	1.92(2)	M3–O4	1.901(7)	W3–O4	1.89(2)
Mo3–O31	2.022(7)	W3–O31	2.04(2)	M3–O31	2.010(9)	W3–O31	1.98(2)
Mo3–O32	2.116(8)	W3–O32	2.09(1)	M3–O32	2.102(7)	W3–O32	2.11(3)
Mo3–O33	2.116(7)	W3–O33	2.10(2)	M3–O33	2.10(2)	W3–O33	2.12(2)
Fe1–O2	2.011(7)	Fe1–O2	1.994(9)	Mo1–O2	2.044(6)	Mo1–O2	2.05(1)
Fe1–O3	1.973(8)	Fe1–O3	1.96(2)	Mo1–O3	2.011(3)	Mo1–O3	2.00(2)
Fe1–O41	1.975(8)	Fe1–O41	1.99(2)	Mo1–O41	2.083(9)	Mo1–O41	2.13(2)
Fe1–O42	1.989(7)	Fe1–O42	2.02(1)	Mo1–O42	2.083(8)	Mo1–O42	2.09(2)
Fe1–O43	2.010(7)	Fe1–O43	2.02(1)	Mo1–O43	2.085(7)	Mo1–O43	2.08(2)
Fe1–O44	1.999(8)	Fe1–O44	2.03(2)	Mo1–O44	2.064(8)	Mo1–O44	2.10(2)
O1–Na1	2.310(8)	O1–Na1	2.30(1)	O1–Na1	2.277(7)	O1–Na1	2.28(2)
O14–Na1	2.25(2)	O14–Na1	2.30(2)	O14–Na1	2.27(1)	O14–Na1	2.34(2)
O24–Na1	2.40(2)	O24–Na1	2.41(2)	O24–Na1	2.41(2)	O24–Na1	2.39(3)
O24–Na1	2.305(8)	O24–Na1	2.32(1)	O24–Na1	2.31(2)	O24–Na1	2.31(2)
O34–Na1	2.23(1)	O34–Na1	2.25(2)	O34–Na1	2.24(2)	O34–Na1	2.27(3)
O2-Fe1-O3	93.8(3)	O2-Fe1-O3	94.6(4)	O2-Mo1-O3	96.8(4)	O2-Mo1-O3	96.0(7)
O2-Fe1-O3	93.8(3)	O2-Fe1-O3	94.6(4)	O2-Mo1-O3	96.8(4)	O2-Mo1-O3	96.0(7)
O2-Fe1-O41	88.3(3)	O2-Fe1-O41	88.8(4)	O2-Mo1-O41	87.5(3)	O2-Mo1-O41	86.9(6)
O2-Fe1-O42	89.0(4)	O2-Fe1-O42	89.6(5)	O2-Mo1-O42	89.6(2)	O2-Mo1-O42	90.5(6)
O2-Fe1-O43	89.3(3)	O2-Fe1-O43	91.4(4)	O2-Mo1-O43	89.6(2)	O2-Mo1-O43	88.9(7)
O2-Fe1-O44	176.4(3)	O2-Fe1-O44	175.6(4)	O2-Mo1-O44	175.9(2)	O2-Mo1-O44	176.8(7)
O3-Fe1-O41	176.5(3)	O3-Fe1-O41	175.8(5)	O3-Mo1-O41	175.0(2)	O3-Mo1-O41	175.7(6)
O3-Fe1-O42	89.1(3)	O3-Fe1-O42	88.4(4)	O3-Mo1-O42	88.3(2)	O3-Mo1-O42	90.1(7)
O3-Fe1-O43	87.9(3)	O3-Fe1-O43	88.2(5)	O3-Mo1-O43	89.6(2)	O3-Mo1-O43	88.8(7)
O3-Fe1-O44	89.7(3)	O3-Fe1-O44	89.7(4)	O3-Mo1-O44	87.3(3)	O3-Mo1-O44	87.1(7)
O41-Fe1-O42	93.7(3)	O41-Fe1-O42	94.1(4)	O41-Mo1-O42	94.3(3)	O41-Mo1-O42	93.0(7)
O41-Fe1-O43	89.4(4)	O41-Fe1-O43	89.2(4)	O41-Mo1-O43	87.9(2)	O41-Mo1-O43	88.2(7)
O41-Fe1-O44	88.2(3)	O41-Fe1-O44	87.1(5)	O41-Mo1-O44	88.3(3)	O41-Mo1-O44	90.0(7)
O42-Fe1-O43	176.4(3)	O42-Fe1-O43	176.6(4)	O42-Mo1-O43	177.6(3)	O42-Mo1-O43	178.6(7)
O42-Fe1-O44	90.7(3)	O42-Fe1-O44	89.4(4)	O42-Mo1-O44	90.6(2)	O42-Mo1-O44	88.6(8)
O43-Fe1-O44	91.2(3)	O43-Fe1-O44	90.0(4)	O43-Mo1-O44	90.4(3)	O43-Mo1-O44	92.2(7)
Mo1-O2-Mo2	79.7(3)	W1-O2-W2	79.4(3)	M1-O2-M2	79.3(2)	W1-O2-W2	79.6(6)
Mo1-O2-Fe1	147.3(4)	W1-O2-Fe1	148.0(6)	M1-O2-Mo1	147.1(4)	W1-O2-Mo1	147.1(8)
Mo2-O2-Fe1	132.1(4)	W2-O2-Fe1	131.1(5)	M2-O2-Mo1	132.3(3)	W2-O2-Mo1	132.2(8)
Mo1-O3-Mo3	80.3(4)	W1-O3-W3	79.8(4)	M1-O3-M3	80.7(4)	W1-O3-W3	80.0(6)
Mo1-O3-Fe1	134.3(2)	W1-O3-Fe1	132.7(5)	M1-O3-Mo1	133.4(5)	W1-O3-Mo1	135.2(8)
Mo3-O3-Fe1	131.9(4)	W3-O3-Fe1	132.2(5)	M3-O3-Mo1	134.1(6)	W3-O3-Mo1	132.8(9)

Table 2. A comparison of mean bond lengths (Å) in clusters **1**, **2**, **5–10**, and related compounds.

	$M-M$	$M-O_b$ [a]	$M-O_b^*$ [b]	$M-O_t$ [c]	$M-O_{cp}$ [d]	$M-O_{ba}$ [e]	$M'-O_b^*$	$M'-O_{ba}$	Ref.
$Na_2Fe_2[Mo_3O_4(O_2CEt)_8]_2$ (**1**)	2.517(1)	1.915(7)	1.957(7)	2.010(8)	2.027(7)	2.121(8)	1.992(8)	1.993(8)	this work
$Na_2Fe_2[W_3O_4(O_2CEt)_8]_2$ (**2**)	2.535(1)	1.92(1)	1.98(2)	2.02(2)	2.04(2)	2.11(2)	1.98(2)	2.02(2)	this work
$Na_2Mo_2[M_3O_4(O_2CEt)_8]_2$ (**5**)	2.520(1)	1.909(9)	1.959(9)	2.011(9)	2.034(9)	2.104(9)	2.028(6)	2.079(9)	this work
$Na_2Mo_2[W_3O_4(O_2CEt)_8]_2$ (**6**)	2.530(2)	1.90(2)	1.97(2)	1.99(2)	2.06(2)	2.10(3)	2.03(2)	2.10(2)	this work
$Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2$ (**7**)	2.5198(9)	1.907(4)	1.952(5)	2.010(4)	2.026(4)	2.114(5)	1.947(4)	1.973(5)	[1,2]
$Na_2Cr_2[W_3O_4(O_2CEt)_8]_2$ (**8**)	2.5313(9)	1.927(9)	1.972(8)	2.012(9)	2.059(9)	2.110(9)	1.929(8)	1.986(9)	[1,2]
$Na_2V_2[Mo_3O_4(O_2CEt)_8]_2$ (**9**)	2.519(1)	1.905(6)	1.953(6)	2.005(6)	2.026(7)	2.119(8)	1.985(6)	1.989(8)	[2]
$Na_2V_2[W_3O_4(O_2CEt)_8]_2$ (**10**)	2.5328(6)	1.926(6)	1.974(6)	2.013(6)	2.057(6)	2.107(7)	1.962(6)	2.012(6)	[2]
$[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$	2.493(3)	1.915(7)			2.020(3)				[7f]
$[Mo_2WO_4(NCS)_9]^{4-}$	2.521(5)	1.891(15)			2.021(14)				[8b]
$[W_3O_4(NCS)_9]^{4-}$	2.534	1.911			2.039				[9a]
$[Fe_3O(O_2CCMe_3)_6(MeOH)_3]^+$							1.905(5)	2.02(2)	[21]
$[Cr_3O(O_2CEt)_6F_3]^{2-}$							1.909(4)	1.974(3)	[22]
$[V_3O(O_2CMe)_6(THF)_3]^+$							1.910(6)	2.00(2)	[23]

[a] Bridging M atoms. [b] Bridging M and M′ atoms. [c] Terminal $EtCO_2$. [d] Capping O atoms. [e] Bridging $EtCO_2$.

usual Na–O bonds (2.42 Å). These features are believed to be responsible for the ready formation and for the insolubility of the heterooctanuclear species described.

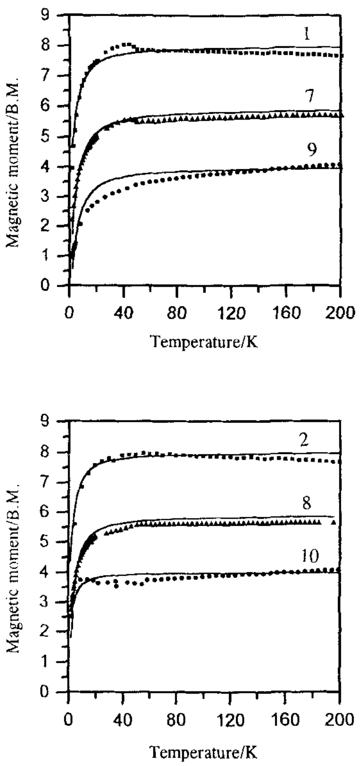

Figure 6. Plots of effective moments of **1**, **2**, and **7**–**10** versus temperature over the range 2–200 K. the solid line is a best fit of the experimental data.

Magnetic Properties: Plots of the magnetic moments of **1**, **2**, and **7**–**10** between 2 and 200 K are given in Figure 6. At 200 K the magnetic moments per M′(III) ion in **1**, **2**, and **7**–**10** are 5.71, 5.72, 4.02, 3.98, 2.87, and 2.87 μ_B, respectively, close to the spin-only values for the magnetically isolated high-spin Fe^{3+} (5.92 μ_B), Cr^{3+} (3.87 μ_B), and V^{3+} (2.83 μ_B) ions. The values for the iron and chromium clusters **1**, **2**, **7**, and **8** are almost constant over the range 200–40 K and then decrease to 2.80, 3.90 (4 K), 1.54, and 1.78 μ_B at about 2 K. The vanadium clusters **9** and **10** behave somewhat differently. For **9**, the magnetic moment sharply decreases from 2.87 μ_B at 200 K to 0.67 μ_B at 2 K. The magnetic moment of **10** varies slightly over the range 200–9 K (200 K, 2.87 μ_B; 35 K, 2.50 μ_B; 9 K, 2.64 μ_B) and then decreases to 2.18 μ_B at 4 K. The susceptibility data of these clusters have been modeled with the isotropic Heisenberg–Dirac–Van Vleck model with the spin-Hamiltonian $H = -2JS_1S_2$. A best fit of the data (g is fixed to 2.0) leads to the spin exchange coupling constants J/k of −0.60, −0.72, −1.76, −1.31, −4.80, and −1.46 K for **1**, **2**, and **7**–**10**, respectively. These figures show that the antiferromagnetic spin exchange coupling interactions between the bridging M′(III) ions are very weak, as expected for long M′(III)–M′(III) distances (ca. 5.7 Å).

Infrared Spectra: The heterooctanuclear clusters in this series display several characteristic IR absorptions in the range 700–820 cm^{-1}. For the oxofluorotungsten species $[W_3O_4F_9]^{5-}$, the IR bands at 780, 740, and 700 cm^{-1} have been previously assigned to the stretching vibrations of the $W-O_b$ bonds in the W_3O_4 core.[9b] The corresponding bands, assigned to $M-O_b$ stretching vibrations in the clusters **1**–**4** and **7**–**10**, are observed at the higher wavenumbers [811 (s), 785 (ms), and 753 (ms) cm^{-1} (**1**); 812 (s), 784 (ms), and 754 (ms) cm^{-1} (**2**); 812 (s), 783 (ms), 754 (ms) cm^{-1} (**3**), 814 (s), 805 (s), 767 (m), 747 (m) cm^{-1} (**4**); 812 (s), 799 (s), and 769 (m) cm^{-1} (**7**); 813 (s), 805 (s), 766 (m), and 743 (m) cm^{-1} (**8**); 811 (s), 787 (m), and 769 (m) cm^{-1} (**9**); 812 (s), 789 (s), 761 (m), and 743 (m) cm^{-1} (**10**)].[2] All these spectra are very similar, even though they are for different cores, namely, W_3O_4 (**6**, **8**, **10**), Mo_3O_4 (**1**, **7**, **9**), and MoW_2O_4 (**3**, **4**). This is rather surprising, since the stretching force constants in isostructural species involving Mo and W are always larger for latter than for the former. However, a similarly unexpected behavior has also been observed in the case of the triangular bioxo-capped carboxylates $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ (M = Mo, W; R = Me, Et). The band $\nu(Fe-\mu_3\text{-}O)$ for $[Fe_3O(O_2CCH_3)_6(H_2O)_3]^+$ appears at 600 cm^{-1},[20] but $\nu(Fe-O^*_b)$ for **1** and **2** are not found in this region, owing to the fact that the $Fe-O^*_b$ bonds are remarkably weak.

Experimental Procedure

All manipulations were carried in air. All reagents were A. R. grade and were used without further purification before use.

$Na_2Fe_2[Mo_3O_4(O_2CEt)_8]_2$ (1): A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.63 g, 2.60 mmol), $Mo(CO)_6$ (0.40 g, 1.50 mmol), $FeCl_3 \cdot 6H_2O$ (0.35 g, 1.30 mmol), and propionic anhydride (60 mL) was placed in a flask with a fine-needle syringe and heated at 120 °C for 3 d. After the reaction had been allowed to cool to room temperature, well-formed black crystals of cluster **1** were obtained (0.95 g, 72% based on $FeCl_3 \cdot 6H_2O$). $Fe_2Mo_6O_{40}C_{48}H_{80}Na_2$ (2030.5), calcd Fe 5.50, Na 2.26, C 28.39, H 3.97; found Fe 5.41, Na 2.03, C 28.67, H 4.11.

$Na_2Fe_2[W_3O_4(O_2CEt)_8]_2$ (2): The tungsten cluster **2** was prepared similarly to **1** by using $Na_2WO_4 \cdot 2H_2O$ (0.86 g, 2.60 mmol) and $W(CO)_6$ (0.43 g, 1.5 mmol). Yield: 21%. $Fe_2W_6O_{40}C_{48}H_{80}Na_2$ (2557.9), calcd Fe 4.37, Na 1.80, C 22.54, H 3.15; found Fe 4.33, Na 1.61, C 22.83, H 3.22.

$Na_2Fe_2[MoW_2O_4(O_2CEt)_8]_2$ (3): An orange-red solution of $Na[MoW_2O_2(O_2CEt)_9]$ in propionic anhydride (50 mL) was obtained by refluxing $Na_2WO_4 \cdot 2H_2O$ (1.3 g, 4.0 mmol), and $Mo(CO)_6$ (0.53 g, 2.0 mmol) for ten hours in air. $Fe(CO)_5$ (0.35 mL, 2.55 mmol) was added, and the mixture was heated at 90 °C for 3 d. After the reaction had been allowed to cool to room temperature, black microcrystalline **3** was isolated from the solution (0.43 g, 18% base on $Mo(CO)_6$). $Fe_2Mo_2W_4O_{40}C_{48}H_{80}Na_2$ (2382.1), calcd Fe 4.69, Mo 8.06, Na 1.93, C 24.21, H 3.39; found Fe 4.66, Mo 7.81, Na 1.69, C 24.67, H 3.45.

$Na_2Cr_2[MoW_2O_4(O_2CEt)_8]_2$ (4): This cluster was synthesized similarly to **3** by using $Cr(CO)_6$ (0.5 g, 2.3 mmol). Yield: ca. 26% (0.57 g). $Cr_2Mo_2W_4O_{40}C_{48}H_{80}Na_2$ (2374.4), calcd Cr 4.38, Mo 8.08, Na 1.94, C 24.28, H 3.40; found Cr 4.17, Mo 7.22, Na 1.83, C 23.90, H 3.47.

$Na_2Mo_2[MoW_2O_4(O_2CEt)_8]_2$ (5): This cluster was synthesized similarly to **3** using $Mo(CO)_6$ (0.53 g, 2.0 mmol). Yield: ca. 6%. $Mo_4W_4O_{40}C_{48}H_{80}Na_2$ (2462.3), calcd Mo 15.57, Na 1.87; found Mo 15.19, Na 1.87.

$Na_2Mo_2[W_3O_4(O_2CEt)_8]_2$ (6): A yellow solution of $Na[W_3O_2(O_2CEt)_9]$ in propionic anhydride (50 mL) was prepared by refluxing a mixture of $Na_2WO_4 \cdot 2H_2O$ (1.3 g, 4 mmol) and $W(CO)_6$ (0.66 g, 2.0 mmol) in propionic anhydride for 10 h in air. $Mo(CO)_6$ was added, and the mixture heated at 120 °C for 3 d. After the reaction had been allowed to cool to room temperature, black crystals of **6** precipitated from the solution in 8% yield.

X-Ray Crystallography: The crystallographic data for clusters **1**, **2**, **5**, and **6** are summarized in Table 3. The reflection intensities were collected on a Rigaku AFC5R diffractometer, by using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å) at room temperature and $\omega/2\theta$ scan mode ($3 < 2\theta < 50°$) with a scan speed of 8° min^{-1}. The structures were solved by direct methods using MULTAN 11/82 and refined by full-matrix least-squares with all non-hydrogen atoms anisotropic except for in **5**, where some of the non-hydrogen atoms were refined isotropically, owing to the low number of observable reflections. The Mo and W atoms of the trinuclear unit in **5** are disordered and treated as M = 0.33 Mo + 0.67 W, giving the reasonable temperature factors. The weighting scheme w was $1/[\sigma(F_o)^2 + (0.02\,F_o)^2 + 1.000]$. All calculations were performed on a Compaq Prolinea 4/66 with the Molen program package with scattering factors taken from the International Tables.

Table 3. Crystallographic Data for **1**, **2**, **5**, and **6**.

	1	**2**	**5**	**6**
M_r	2030.5	2557.9	2462.3	2638.1
$F(000)$	1014	1206	1174	1238
crystal size, mm	0.2 × 0.3 × 0.3	0.3 × 0.2 × 0.4	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.3
space	group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}P\bar{1}$
a, Å	12.988(6)	12.984(6)	12.805(4)	12.904(13)
b, Å	14.021(7)	14.072(7)	14.100(3)	14.144(16)
c, Å	12.378(9)	12.436(9)	12.396(3)	12.467(14)
α, °	109.79(5)	109.91(5)	109.97(2)	109.91(9)
β, °	117.50(4)	117.54(4)	117.87(2)	118.09(8)
γ, °	90.52(5)	90.50(5)	90.43(2)	90.42(1)
V, Å^3	1844.2	1856.2	1821.7	1848.3
Z	1	1	1	1
ρ_{calcd}, g cm^{-3}	1.83	2.29	2.24	2.37
μ, cm^{-1}	14.4	99.4	71.8	99.2
scan width	1.32	1.63	1.15	1.26
unique reflns	6826	6863	6169	6842
reflns $I \geq 3\sigma(I)$	3518	4586	4529	2964
no. of parameters	442	442	442	442
R [a]	0.056	0.045	0.042	0.063
wR [b]	0.062	0.052	0.053	0.069
GOF [c]	1.31	1.24	1.40	1.37
$(\Delta\sigma)_{max}$	0.04	0.05	0.05	0.03
$(\Delta\rho)_{max}$	0.85	1.80	1.78	2.14

[a] $R = \sum||F_o| - |F_c||/|F_o|$. [b] $wR = [w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. [c] GOF = $[w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-1220-45. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

Magnetic Susceptibility, UV/Vis, and IR Spectra: The temperature-dependent magnetic susceptibilities of polycrystalline samples of **1**, **2**, and **7–10** were measured on PPMS Model-6000 over the range 2–200 K. The data were corrected for diamagnetism of the samples by using Pascal's constants. UV/Vis and IR spectra were recorded on a Schimazhu UV-3000 and Digilab FTS-40 spectrophotometers with KBr pellet, respectively.

Acknowledgements: This work was supported by the grant from the National Science of Foundation of China.

Received: June 13, 1996 [F392]

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