Synthesis, Mechanism of Formation and Characterization of a New Class of Octanuclear Mixed-metal Clusters $Na_2M'_2[M_3O_4(O_2CEt)_8]_2$ (M' = Cr or V; M = Mo or W)†

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The reaction of $Na[M_3O_2(O_2CEt)_9]$ with $Cr(CO)_6$ or $M(CO)_6$ and $CrCl_3{\cdot}6H_2O$ in propionic anhydride solution at 120 °C has resulted in the formation of the insoluble octametallic clusters $Na_2Cr_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo **1** or W **2**). The skeletal conversion of $[M_3O_2(O_2CEt)_9]^-$ into $[M_3O_4(O_2CEt)_8]^{4-}$ and the mode of formation of compounds **1** and **2** from the latter species and Cr^{3+} and Na^+ ions has been established. The vanadium analogues (M = Mo **3** or W **4**) have been synthesized by the reactions of $M(CO)_6$(M = Mo or W) with $NaVO_3{\cdot}2H_2O$ under similar reaction conditions. Clusters **1**–**4** have been characterized by X-ray crystallography, IR spectra and magnetic susceptibility measurements.

Triangular trinuclear species based on $[M_3O_2]^{n+}$ ($n = 8$, $M_3 =$ Mo_3,[1,2] Mo_2W, MoW_2[3] or W_3[2,4]; $n = 7$, $M_3 = Nb_3$[5]) and $[M_3O_4]^{4+}$ ($M_3 = Mo_3$,[6–8] Mo_2W[9] or W_3[10]) cores have been extensively researched over the past two decades. It has been well established that two $[M_3S_4]^{4+}$ units can be connected by one or two metal atoms to form the sandwich cubane-type $[M_3S_4M'S_4M_3]$ (M = Mo, M' = Mo,[11] Hg[12] or Sn[13]) or double cubane-type $[M_3S_4MM'S_4M_3]$ (M = Mo, M' = Co,[12] Cu[14] or Pd;[15] M = W, M' = Ni;[16] M = Fe,[17] M' = Mo or W) clusters. The clusters $Na_2[CrM_3O_4(O_2CEt)_8]_2$ (M = Mo or W)[18] provided the first example where the two $[M_3O_4]^{4+}$ units are bridged by two chromium(III) ions to form the circular $[M_3O_4CrCrO_4M_3]^{14+}$ cores. The work reported here has been aimed at finding other ways to prepare such octametallic species and investigating the mechanism of their formation.

For a long time the $[M_3O_2]^{8+}$-type clusters have been believed to be chemically very stable. However, the latest research has shown that the $[M_3O_2]^{8+}$-type clusters exhibit remarkable catalytic activity in the oxidation of styrene under mild conditions.[19] This, together with the irreversible reduction of such species (see below), indicates that they may be considerably reactive under reducing conditions. Herein we report the reaction between the bioxo-capped trinuclear cluster $Na[M_3O_2(O_2CEt)_9]$ with $M(CO)_6$ (M = Cr, Mo or W) and $CrCl_3{\cdot}6H_2O$ in propionic anhydride solution resulting in $Na_2Cr_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo **1** or M = W **2**). These reactions reveal the first reported skeletal conversion of the $[M_3O_2]^{8+}$ core in $[M_3O_2(O_2CEt)_9]^-$ into a $[M_3O_4]^{4+}$ core in the $[M_3O_4(O_2CEt)_8]^{4-}$ unit together with the formation of the octametallic dianion $Cr_2[M_3O_4(O_2CEt)_8]_2{}^{2-}$ from two Cr^{III} ions and two $[M_3O_4(O_2CEt)_8]^{4-}$ units. We also present the two new vanadium analogues $Na_2V_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo **3** or W **4**) synthesized by a somewhat different method and provide a detailed structural comparison of clusters **1**–**4** and the related $[M_3O_4]^{4+}$ and $[M_3O]^{7+}$ trinuclear species reported previously.

These octametallic species can also be regarded as new dichromium(III) or divanadium(III) compounds with hexadentate, trinuclear bridging ligands, which are of current interest in the area of magnetic and electronic interaction of Cr^{III} or V^{III} ions.[20]

Results and Discussion

Syntheses.—The Cr_2Mo_6 cluster can be prepared by the following three different synthetic methods shown in equations (1)–(3) by heating the reactants in propionic anhydride at 120 °C.

$$2\,Na[Mo_3O_2(O_2CEt)_9] + 2\,Cr(CO)_6 \longrightarrow Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2 \quad (1)$$

$$2\,Na[Mo_3O_2(O_2CEt)_9] + Mo(CO)_6 + 2\,CrCl_3 \longrightarrow Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2 \quad (2)$$

$$6\,Na_2MoO_4 + 2\,Cr(CO)_6 \longrightarrow Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2 \quad (3)$$

In reactions (1) and (2) the red propionic anhydride solution of the $Na[Mo_3O_2(O_2CEt)_9]$ can be obtained from the reaction of $Mo(CO)_6$ with Na_2MoO_4 in refluxing propionic anhydride solution. After pouring into diethyl ether, a copious precipitate was obtained, a mixture of a red solid and a small amount of $EtCO_2Na$. The red solid is characterized as $Na[Mo_3O_2(O_2CEt)_9]$ based on the observations that an aqueous solution of the red solid has a similar UV/VIS spectrum (Fig. 1) to that of the $[Mo_3O_2]^{8+}$ species reported previously[1c,3a] and that a similar reaction of Na_2MoO_4 with $W(CO)_6$ in refluxing acetic anhydride has been reported to produce $Na[Mo_3O_2(O_2CMe)_9]$ by Cotton and co-workers.[1a]

Based on reactions (1) and (2), the mechanism of formation of the octametallic dianion $Cr_2[Mo_3O_4(O_2CEt)_8]_2{}^{2-}$ shown in equations (4) (M = Cr or Mo) and (5) can be deduced.

$$[Mo_3O_2(O_2CEt)_9]^- + M(CO)_6 \longrightarrow [Mo_3O_4(O_2CEt)_8]^{4-} + M^{III} \quad (4)$$

$$2[Mo_3O_4(O_2CEt)_8]^{4-} + 2Cr^{III} \longrightarrow Cr_2[Mo_3O_4(O_2CEt)_8]_2{}^{2-} \quad (5)$$

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† *Supplementary data avilable:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.27 \times 10^{-24}\ J\ T^{-1}$.

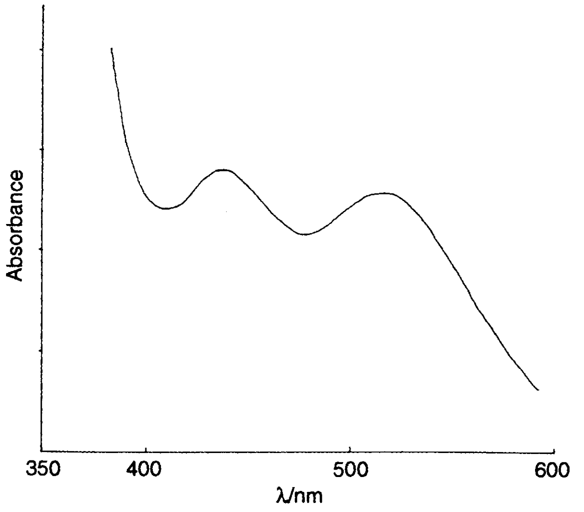

Fig. 1 Electronic absorption spectrum of an aqueous solution of the red solid of $Na[Mo_3O_2(O_2CEt)_9]$. The absorption intensity of the curve is not representative of its relative absorption coefficient since the concentration of the solution used in obtaining the spectrum was not determined. The spectrum is identical to that of $[Mo_3O_2(O_2CMe)_6(H_2O)_3]Br_2{\cdot}H_2O$ reported previously[1c]

Equation (4) shows the first reported example of the conversion of the trigonal bipyramidal $[Mo_3O_2]^{8+}$ cluster into the incomplete cuboidal cluster $[Mo_3O_4]^{4+}$. This conclusion is supported by the fact that the mixture remains unchanged for three days or more if $Mo(CO)_6$ is absent in reaction (2). To summarise, black crystals of **1** are formed from the reaction of $Mo(CO)_6$, $CrCl_3{\cdot}6H_2O$ and the red propionic anhydride solution of $Na_2[Mo_3O_2(O_2CEt)_9]$; however, the $[Mo_3O_4(O_2CEt)_8]^{4-}$ species is not obtained from the reaction of Na_2MoO_4 with $Mo(CO)_6$ in refluxing propionic anhydride solution, as, if formed, it would be trapped by the Cr^{3+} and Na^+ ions present in the reaction mixture to form the insoluble compound **1**. This has been confirmed by column chromatography of the red solid, using a Sp-Sephadex C-15 cation exchange column (0.1 mol dm^{-3} HBr as eluent) as only one red band of $[Mo_3O_2(O_2CEt)_6(H_2O)_3]^{2+}$,[1c] a hydrolysed form of $[Mo_3O_2(O_2CEt)_9]^-$,[1a] was eluted. The change in configuration shown in reaction (4) indicates that the $[Mo_3O_2]^{8+}$ skeleton can be decomposed by reduction although it is highly resistant to oxidation.[2b] This has also been suggested by electrochemical studies on $[Mo_3O_2(O_2CMe)_6(H_2O)_3]Br_2$.[1c] Unlike the $[Mo_3O_4]^{4+}$ species,[9] this cluster is irreversibly reduced as shown in Fig. 2, indicating that the $[Mo_3O_2]^{8+}$ core may have decomposed after undergoing a two-electron reduction process. A detailed decomposition mechanism is not clear at present, but the most probable pathway is the removal of two capping oxygen atoms by CO groups in $M(CO)_6$ (M = Cr or Mo) to form the reduced intermediate $[Mo_3(O_2CEt)_9]^-$ accompanied by the evolution of CO_2 and oxidation of M^0 to M^{III}. The intermediate is then oxidized to yield the more stable $[Mo_3O_4(O_2CEt)_8]^{4-}$ species because of the quasi-aromaticity in the Mo_3O_3 ring[21] and the stronger Mo–Mo bonds than those in the $[Mo_3O_2]^{8+}$ species.[1,2,6]

Reaction (5) shows the formation of the dianion $Cr_2[Mo_3O_4(O_2CEt)_8]_2{}^{2-}$ from two Cr^{III} ions and the two Mo_3 units, which can be easily understood by regarding the anion as a dichromium(III) compound with two hexadentate $[Mo_3O_4(O_2CEt)_8]^{4-}$ bridging ligands. This has been confirmed by reaction (2), in which it is assumed that the Mo_3 units resulting from the reaction of $[Mo_3O_2(O_2CEt)_9]^-$ with $Mo(CO)_6$ may be trapped by Cr^{III} ions added to the reaction solution to form the octametallic anion. The Mo_8 species has not been obtained from this experiment, indicating that the Mo^{III} ions are unstable in the propionic anhydride solution. Further evidence has been obtained using $Fe(CO)_5$, the oxidation of which gives stable Fe^{III} ions, instead of $Mo(CO)_6$ in reaction (2). As expected, the Cr–Fe mixed-metal cluster $Na_2CrFe[Mo_3O_4(O_2CEt)_8]_2$ **5** is formed.

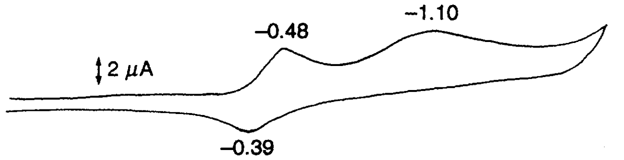

Fig. 2 Cyclic voltammogram for the reduction of $[Mo_3O_2(O_2CMe)_6(H_2O)_3]^{2+}$. Potentials in V *vs.* SCE

The above mechanism can be used to explain reaction (3). First, Na_2MoO_4 is reduced by $Cr(CO)_6$ to form $[Mo_3O_2(O_2CEt)_9]^-$, which is then converted into $[Mo_3O_4(O_2CEt)_8]^{4-}$ by $Cr(CO)_6$. This species is then trapped by the Cr^{III} ions to result in the octametallic dianion. In fact, only a red solution of the Mo_3O_2 species is obtained with only minor amounts of the black precipitate of the octametallic species if the reaction is carried out under refluxing conditions in air owing to the oxidation of most of the $Cr(CO)_6$ by O_2 to Cr^{III} ions. It should be noted that the cluster **1** can also be prepared under refluxing conditions in an N_2 atmosphere but the yield is still significantly lower than those of the methods shown in equations (1)–(3). This suggests that the presence of a controlled amount of dioxygen in the reactions improves the yield of **1** although it is not necessary for its formation.

The octametallic dianions are balanced by the Na^+ ions in the reaction mixture to form the insoluble final product $Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2$ **1** which is isolated from solution. Compound **1** is stable in air and insoluble in organic solvents, water, and acids and bases.

The Cr_2W_6 analogue $Na_2Cr_2[W_3O_4(O_2CEt)_8]_2$ **2** has been prepared similarly from Na_2WO_4 and $W(CO)_6$, indicating a similar mode of formation. However, the reaction of Na_2WO_4 with $W(CO)_6$ in refluxing carboxylic anhydride solution resulted in a blue solution rather than the yellow one expected or the W_3O_2 species.[4a,22] However, the blue solution turns yellow upon standing in air for two days owing to the formation of the bioxo-capped species $Na[W_3O_2(O_2CEt)_9]$, and this can be used to prepare **2**. This has been confirmed by column chromatography of the yellow solution using a Sp-Sephadex cation-exchange column (1 mol dm^{-3} HCl as eluent) which gives only one yellow band of $[W_3O_2(O_2CEt)_6(H_2O)_3]^{2+}$ characterized by X-ray crystallography* and a UV/VIS spectrum which is essentially indentical to that of the W_3O_2 species reported previously.[3a]

It is interesting that the vanadium analogues $Na_2V_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo or W) can be synthesized by a somewhat different method (see Experimental section). This shows that the $[M_3O_4]^{4+}$ (M = Mo or W) species can also be formed from the oxidation of $M(CO)_6$ in propionic anhydride solution by the reduction of V^{5+} to V^{3+}. It should be noted that the addition of NaCl to the reaction mixture increases the yield remarkably. The NaCl may provide sufficient Na^+ ions for the formation of the final octametallic clusters thus compensating for the Na^+ ions lost in precipitation upon refluxing.

The insoluble black crystalline products of **1**–**4** were often accompanied by minor amounts of a soluble green solid, which can easily be washed off with water. The green solid was not positively identified, but seems very likely to contain com-

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* Yellow crystals of $[W_3O_2(O_2CEt)_6(H_2O)_3][ZnCl_4]{\cdot}2H_2O$ were obtained from the evaporation of the eluent to which $ZnCl_2$ had been added and crystallized in the monoclinic system (space group *Cm*) with $a = 10.267(4)$, $b = 15.773(9)$, $c = 10.878(4)$ Å, $\beta = 96.00(3)°$, $U = 1750.2$ Å^3, $Z = 2$, $R = 0.030$ and $R' = 0.039$.

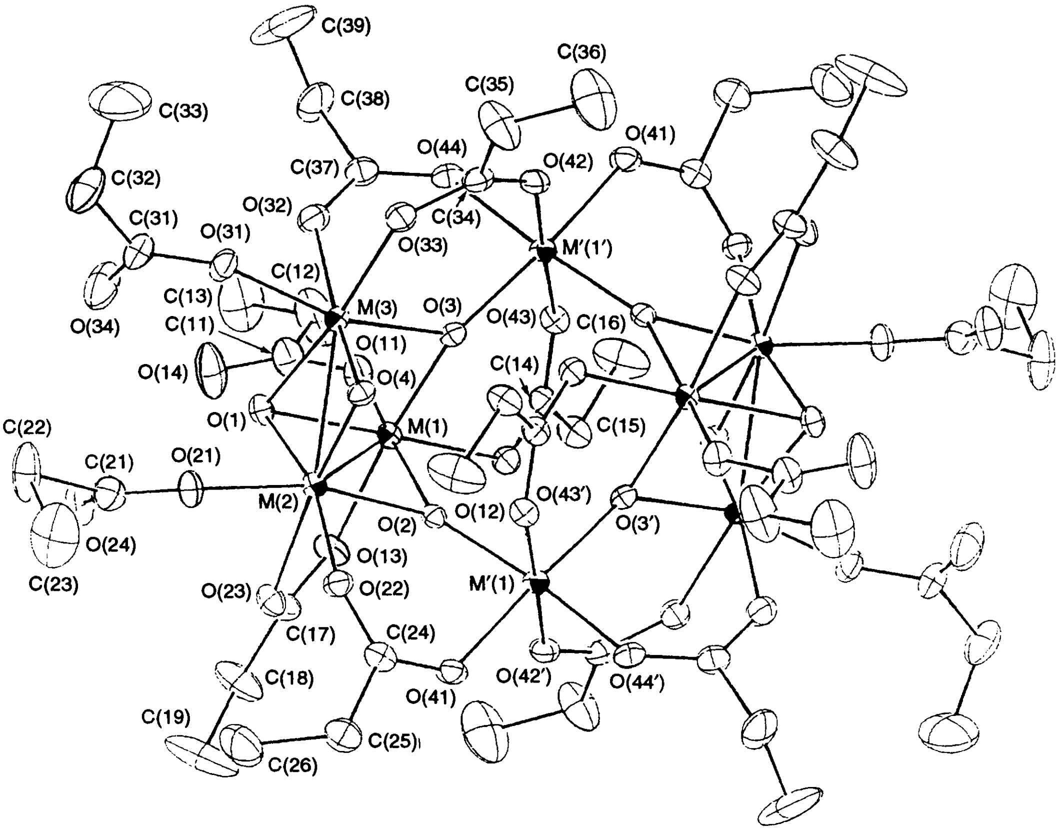

Fig. 3 Structure of the dianion $M'_2[M_3O_4(O_2CEt)_8]_2^{2-}$ (M′ = Cr, M = Mo **1** or W **2**; M′ = V, M = Mo **3** or W **4**)

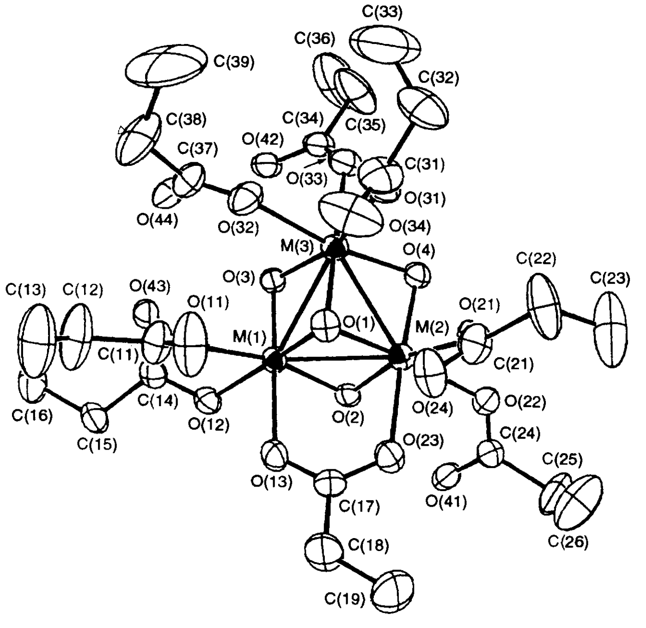

Fig. 4 Structure of the $[M_3O_4(O_2CEt)_8]^{4-}$ (M = Mo or W) units

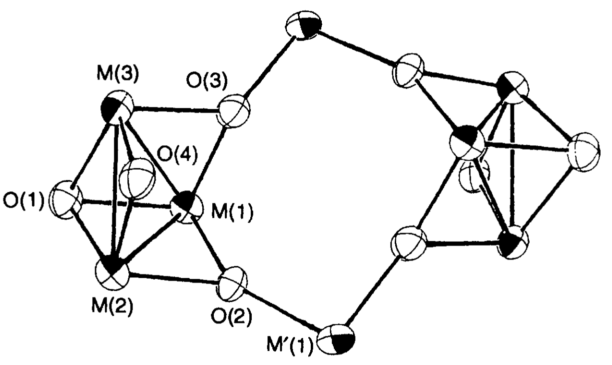

Fig. 5 Structure of the skeleton $[M_3O_4M'M'O_4M_3]^{14+}$ (M′ = Cr or V, M = Mo or W)

pounds comprising the basic oxo-centred trinuclear cations $[M_3O(O_2CEt)_6]^+$ (M = V or Cr).[23]

Crystal Structures.—The isostructural clusters **1**–**4** are each composed of two sodium ions and a centrosymetric cluster dianion, $M'_2[M_3O_4(O_2CEt)_8]_2^{2-}$ (M′ = V or Cr; M = Mo or W). The structure of the anion is shown in Fig. 3, together with the atom numbering scheme. The atomic coordinates, and the selected bond lengths and angles in clusters **1**–**4** are listed in Tables 1–5. The structure can be helpful to understand the mechanism of the formation of the octametallic dianion proposed above if it is viewed as a dinuclear species. As shown in Fig. 3, the two M′ ions are at the centre of the O_6 octahedron formed by the eight propionate oxygen atoms and the four μ-O* atoms (*i.e.* the μ-O atoms bonded to the M′ atoms) from the two M_3 units $[M_3O_4(O_2CEt)_8]^{4-}$, shown in Fig. 4, and are thus bridged by the two M_3 units to form the stable octametallic anion. Consequently, the M_3 unit, as it is an appropriate hexadentate bridging ligand, is not stable in this reaction. Alternatively, the structure can be considered to comprise two M_3 units linked by the two M′ ions to form the circular structure of the octanuclear anion. In Fig. 5 the sixteen $EtCO_2^-$ groups in the anion are omitted to give an $[M_3O_4M'M'O_4M_3]^{14+}$ skeleton. This core is formally similar to the double-cubane $[M_3S_4M'M'S_4M_3]$ species reported previously[12,14–17] although the linkage of $[M_3X_4]^{4+}$ in these two cases is different. In the former, the two M′ metal ions are each bonded to the two

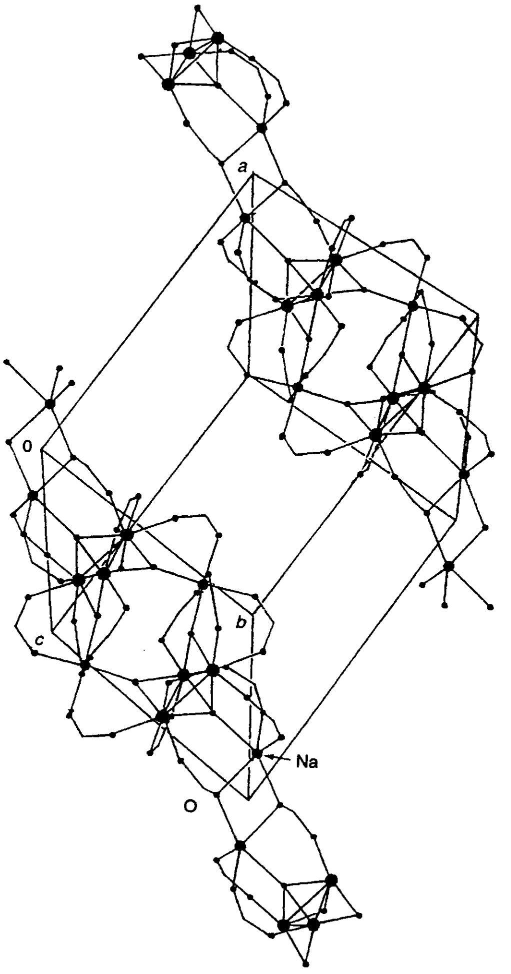

Fig. 6 Chain structure of clusters **1**–**4** with the Et groups omitted for clarity

μ-O* atoms from the two M_3 units, respectively, to constitute an approximately planar $M'_2M_2O^*_4$ eight-membered ring with deviations ranging from 0.095(1) to 0.521(7) Å [av. 0.306(7) Å]. In the other near-planar $M_2M'O^*$ units [the sum of the angles around O(2) and O(3) are 358.7(4) and 346.9(4)° respectively] similar to the CrW_2O units in $W_3(OCH_2CMe_3)O_3Cr_3(O_2CCMe_3)_{12}$,[24] the M′–M distances fall in the range 3.567–3.800 Å confirming the absence of M′–M bonds. A comparison of the average bond lengths in clusters **1**–**4** with those in the related $[M_3O_4]^{4+}$ (M = Mo or W) and $[M'_3O]^{7+}$ (M′ = Cr or V) trinuclear species is listed in Table 6. From the detailed comparison of the bond lengths given in Tables 5 and 6 the following conclusions may be drawn.

(*i*) The M–M bond lengths in the M_3 unit are very similar to those in the discrete $[M_3O_4]^{4+}$ clusters reported previously, indicating that the oxidation state of the M metal atoms is +4. Thus, by deduction, the M′ ions have a charge of +3. This is also consistent with the magnetic moments per M′ ion in **1**, **2** and **4** (3.69 in **1** and **2**, 2.48 μ_B in **4**).

(*ii*) The M–μ-O* bond lengths in **1**–**4** are *ca.* 0.05 Å longer than those of M–μ-O in these clusters and in the $[M_3O_4]^{4+}$ clusters reported previously, indicating that the three-centre d–p π bonds in the M_2O^* units are noticeably weakened as a result of the O* atoms bonding to the M′ metal ions.[21] The M′–μ-O* bond lengths in the $M'M_2O^*$ units are significantly longer than those in the $[M'_3O]^{7+}$ trinuclear complexes, indicative of much weaker d–p π bonds in the former.[23d]

(*iii*) The Cr–O* and V–O* bond lengths in the molybdenum clusters (**1** and **3**) are both found to be *ca.* 0.02 Å longer than those in the tungsten clusters (**2** and **4**). In this respect, we suppose that there are weak d–p π bonds in the $M'M_2O^*$ units. In view of the difference in electronegativity between Mo and W (Mo^{4+} 2.10, W^{4+} 1.87[25]), there will be less electron density in the M′–O* bonds in the molybdenum clusters than in the tungsten clusters, which explains the longer bond lengths in the former.

(*iv*) The Cr–O bond lengths in **1** and **2** lie in the narrow ranges 1.935(4)–1.980(5) Å and 1.916(8)–1.997(9) Å respectively, showing little Jahn-Teller distortion, which is consistent with the d^3 electronic configuration of the Cr^{III} ion. However, the V–O distances in **3** and **4** also lie within a narrow range [1.964(6)–2.006(6) Å in **3** and 1.947(6)–2.023(6) Å in **4**], although V^{III} ions (d^2) would be expected to show a greater range of values.

(*v*) The average bond lengths in clusters **1**–**4** increase in the following order: Mo–Mo < W–W, Cr–O < V–O and M–μ-O < M–μ-O* < $M–O_t$ < $M–O_{cp}$ < $M–O_{ba}$, M′–μ-O* < $M'–O_{ba}$.

The infinite chain structure of clusters **1**–**4** is shown in Fig. 6, where each Na^+ ion is co-ordinated to five oxygen atoms in an unusual distorted trigonal bipyramidal arrangement. Three of the oxygen atoms are from terminal propionato groups, one from a capping oxygen atom from one cluster anion and one is from a terminal propionato group from another adjacent cluster anion. Thus the cluster anions are connected by Na^+ ions giving an infinite chain structure with the Na_2O_2 four-membered ring lying at the crystallographic centre of symmetry (0,0,0), as shown in Fig. 6. The unexpectedly short average Na–O distance of *ca.* 2.31(1) Å in clusters **1**–**4** indicates some degree of covalent bonding, which is responsible for their being insoluble. In view of the infinite chain structure, short Na–O distances and the insolubility we believe that **1**–**4** are best regarded as new types of polymetallic cluster materials rather than simple discrete ionic complexes.

Magnetic Properties.—The magnetic moments of the metal(III) ions (3.69 μ_B in **1** and **2**, 2.48 μ_B in **4**) are slightly less than the spin-only values (Cr^{III}, d^3, 3.87 μ_B; V^{III}, d^2, 2.83 μ_B), suggesting antiferromagnetic spin-exchange coupling of the two metal(III) ions in the clusters. It is interesting that the magnetic moment (5.36 μ_B) of the metal(III) ion (*i.e.* $\frac{1}{2}Cr^{III} + \frac{1}{2}Fe^{III}$) in cluster **5** is found to be greater than that expected for a magnetically isolated metal(III) ion ($\frac{1}{2}d^3 + \frac{1}{2}d^5$, 5.00 μ_B), indicating that the spin-exchange coupling of the Cr^{III} and Fe^{III} ions may be unusually ferromagnetic.

Infrared Spectra.—The bands at 700, 740 and 780 cm^{-1} in the IR spectrum of $[W_3O_4F_9]^{5-}$ have previously been assigned[10c] to the stretching vibrations of the bridging oxygen atoms (O_b). The IR spectra of **1**–**5** show three bands in the range 700–810 cm^{-1} for **1** (812, 799 and 769 cm^{-1}) and **3** (811, 787 and 769 cm^{-1}) and four for **2** (813, 805, 766 and 743 cm^{-1}), **4** (812, 789, 761 and 743 cm^{-1}) and **5** (812, 794, 762 and 754 cm^{-1}) and these can be assigned to $\nu(M–O_b)$ vibrations in the $[M_3O_4]^{4+}$ core. The bands at 640 cm^{-1} (**1** and **2**) and 651 cm^{-1} (**5**) in the spectra of the chromium clusters are not observed in those of the vanadium clusters **3** and **4** and can therefore be assigned to $\nu(Cr–O_b)$. The similar absorption band at 662 cm^{-1} in the cation $[Cr_3O(O_2CMe)_6(H_2O)_3]^+$ has been unequivocally assigned to ν(Cr–μ-O).[23e]

Experimental

All reagents were analytical grade without further purification before use. All manipulations were carried out in air.

Syntheses.—$Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2$ **1**. *Method* A. A mixture of $Na_2MoO_4\cdot2H_2O$ (1.5 g, 6.2 mmol) and $Mo(CO)_6$ (0.81 g, 3.1 mmol) and propionic anhydride (40 cm^3) was refluxed in air for 10 h during which time dried air was bubbled through the mixture to produce a red solution of $Na[Mo_3$-

Table 1 Positional parameters for $Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2$ **1**

Atom	*x*	*y*	*z*
Mo(1)	0.952 86(4)	0.357 30(4)	0.281 77(4)
Mo(2)	1.126 01(4)	0.280 28(4)	0.395 41(4)
Mo(3)	0.934 81(4)	0.239 55(4)	0.392 00(4)
Cr(1)	1.222 51(7)	0.555 57(7)	0.565 06(8)
O(1)	0.965 6(3)	0.206 7(3)	0.236 3(3)
O(2)	1.113 9(3)	0.425 9(3)	0.426 1(3)
O(3)	0.898 2(3)	0.377 3(3)	0.408 1(3)
O(4)	1.096 0(3)	0.281 5(3)	0.532 9(3)
O(11)	0.792 3(4)	0.315 5(3)	0.118 4(4)
O(12)	0.916 0(3)	0.503 6(3)	0.282 4(3)
O(13)	1.019 1(4)	0.352 9(3)	0.153 3(3)
O(14)	0.766 2(5)	0.162 4(4)	−0.036 1(5)
O(21)	1.177 1(4)	0.142 7(3)	0.364 0(4)
O(22)	1.309 2(3)	0.332 1(3)	0.530 1(4)
O(23)	1.178 0(4)	0.292 0(3)	0.258 9(4)
O(24)	1.103 5(4)	0.048 0(4)	0.148 3(4)
O(31)	0.923 9(4)	0.089 8(3)	0.368 1(4)
O(32)	0.749 8(4)	0.187 3(3)	0.257 9(4)
O(33)	0.894 8(4)	0.255 1(3)	0.544 0(4)
O(34)	0.865 7(6)	−0.015 4(4)	0.158 4(5)
O(41)	1.354 9(3)	0.495 2(3)	0.550 8(4)
O(42)	0.805 0(3)	0.392 6(3)	0.574 5(4)
O(43)	0.751 2(3)	0.500 8(3)	0.298 7(3)
O(44)	0.657 1(4)	0.319 5(3)	0.297 4(4)
C(11)	0.734 2(6)	0.240 9(6)	0.002 1(6)
C(12)	0.616 9(8)	0.264 8(8)	−0.084 3(9)
C(13)	0.550(1)	0.190(1)	−0.222(1)
C(14)	0.814 7(5)	0.525 6(5)	0.256 7(5)
C(15)	0.769 6(6)	0.583 6(5)	0.166 8(6)
C(16)	0.650 3(7)	0.612 4(8)	0.144 6(9)
C(17)	1.113 0(5)	0.319 4(5)	0.165 3(5)
C(18)	1.145 9(7)	0.309 2(8)	0.060 1(7)
C(19)	1.270 7(8)	0.297(1)	0.098 3(9)
C(21)	1.156 2(6)	0.058 0(5)	0.263 9(6)
C(22)	1.203 7(9)	0.969 1(6)	0.306 6(8)
C(23)	1.330(1)	0.000 0(9)	0.415(1)
C(24)	1.379 2(5)	0.407 9(5)	0.552 9(5)
C(25)	1.505 3(6)	0.393 7(6)	0.584 4(9)
C(26)	1.504 7(8)	0.291 0(9)	0.489(1)
C(31)	0.887 9(7)	−0.001 4(5)	0.269 6(7)
C(32)	0.880 2(9)	−0.090 0(6)	0.311 7(8)
C(33)	0.783(1)	−0.089(1)	0.342(1)
C(34)	0.856 4(5)	0.322 5(5)	0.607 4(5)
C(35)	0.872 4(8)	0.312 6(7)	0.731 9(7)
C(36)	0.856(1)	0.399 8(9)	0.824 8(8)
C(37)	0.658 9(6)	0.226 0(5)	0.239 6(6)
C(38)	0.540 9(7)	0.154 7(7)	0.137(1)
C(39)	0.514(1)	0.082(1)	0.190(2)
Na(1)	0.898 9(2)	0.062 5(2)	0.041 9(2)

Table 2 Positional parameters for $Na_2Cr_2[W_3O_4(O_2CEt)_8]_2$ **2**

Atom	*x*	*y*	*z*
W(1)	0.952 43(4)	0.356 03(3)	0.280 81(4)
W(2)	1.126 77(4)	0.280 07(3)	0.395 39(4)
W(3)	0.933 80(4)	0.239 30(3)	0.392 22(4)
Cr(1)	1.222 7(2)	0.555 2(1)	0.565 0(2)
O(1)	0.965 6(7)	0.202 9(5)	0.233 3(7)
O(2)	1.115 7(6)	0.426 3(5)	0.426 9(6)
O(3)	0.897 6(6)	0.378 6(5)	0.409 8(6)
O(4)	1.095 9(6)	0.281 0(5)	0.534 6(7)
O(11)	0.791 7(7)	0.312 7(6)	0.116 9(7)
O(12)	0.916 0(6)	0.502 4(5)	0.279 6(7)
O(13)	1.019 5(7)	0.350 1(6)	0.150 3(7)
O(14)	0.764 4(9)	0.159 1(7)	−0.037(1)
O(21)	1.176 5(7)	0.142 3(6)	0.363 1(7)
O(22)	1.309 4(6)	0.331 6(6)	0.528 5(7)
O(23)	1.178 7(7)	0.291 4(6)	0.259 1(7)
O(24)	1.105 7(8)	0.048 0(7)	0.149 3(8)
O(31)	0.923 0(7)	0.089 3(6)	0.368 0(7)
O(32)	0.750 2(7)	0.186 8(6)	0.260 2(9)
O(33)	0.892 6(7)	0.255 1(6)	0.541 6(7)
O(34)	0.865(1)	−0.016 7(8)	0.161(1)
O(41)	1.356 2(6)	0.495 0(6)	0.552 2(7)
O(42)	0.802 9(7)	0.392 0(6)	0.574 5(7)
O(43)	0.751 6(6)	0.500 8(6)	0.298 6(7)
O(44)	0.655 3(7)	0.317 7(6)	0.296 3(8)
C(11)	0.730(1)	0.237(1)	−0.000(1)
C(12)	0.616(1)	0.265(2)	−0.084(2)
C(13)	0.549(2)	0.191(2)	−0.220(2)
C(14)	0.814 3(9)	0.525 1(8)	0.256(1)
C(15)	0.769(1)	0.583 8(9)	0.166(1)
C(16)	0.650(1)	0.611(1)	0.141(1)
C(17)	1.110(1)	0.316(1)	0.162(1)
C(18)	1.143(1)	0.306(1)	0.056(1)
C(19)	1.272(2)	0.294(2)	0.095(2)
C(21)	1.157(1)	0.059(1)	0.266(1)
C(22)	1.206(2)	0.970(1)	0.308(2)
C(23)	1.328(2)	−0.002(2)	0.415(2)
C(24)	1.383(1)	0.408 6(9)	0.554(1)
C(25)	1.508(1)	0.395(1)	0.587(2)
C(26)	1.507(1)	0.290(2)	0.493(2)
C(31)	0.890(1)	−0.002 3(9)	0.273(1)
C(32)	0.876(2)	−0.091(1)	0.313(1)
C(33)	0.776(2)	−0.094(2)	0.333(2)
C(34)	0.855(1)	0.321 9(9)	0.603(1)
C(35)	0.868(1)	0.313(1)	0.731(1)
C(36)	0.855(2)	0.400(1)	0.823(2)
C(37)	0.658(1)	0.224(1)	0.239(1)
C(38)	0.537(1)	0.152(1)	0.134(2)
C(39)	0.506(2)	0.082(2)	0.184(3)
Na(1)	0.898 2(5)	0.061 2(4)	0.042 8(5)

$O_2(O_2CEt)_9]$. To this solution was added $Cr(CO)_6$ (0.7 g, 3.2 mmol) and the mixture placed in a flask with a very narrow neck and then heated at 120 °C for 3 d. The red solution turned black green and well-formed black crystals of **1** (0.93 g, 39%) were isolated from the solution.

Method B. To the above red solution of $Na[Mo_3O_2(O_2CEt)_9]$ were added $Mo(CO)_6$ (0.85 g. 3.3 mmol) and $CrCl_3{\cdot}6H_2O$ (0.8 g, 3.0 mmol) and the reaction carried out as for method A, resulting in black crystals of **1** (1.12 g, 46.8%).

Method C.[18] A mixture of $Cr(CO)_6$ (0.7 g, 3.2 mmol), $Na_2MoO_4{\cdot}2H_2O$ (1.5 g, 6.2 mmol) and propionic anhydride (40 cm^3) was added to a 100 cm^3 closed flask with a fine-needle syringe and was heated at 120 °C for 3 d. After being cooled to room temperature well-formed black crystals of **1** were isolated from the solution (0.6 g, 29%). $\tilde{\nu}_{max}/cm^{-1}$ 812vs [$\nu(Mo–O_b)$], 799vs, 769s, 640s [$\nu(Cr–O_b)$]. λ_{max}/nm (powder) 430, 580.

$Na_2Cr_2[W_3O_4(O_2CEt)_8]_2$ **2**. Cluster **2** was synthesized similarly using $W(CO)_6$ (2.14 g, 6.1 mmol) and $Na_2WO_4{\cdot}2H_2O$ (1.02 g, 3.1 mmol). The yields for methods A, B and C were 39, 40 and 42%, respectively. $\tilde{\nu}_{max}/cm^{-1}$ 813vs [$\nu(W–O_b)$], 805vs, 766s, 743s, 640s [$\nu(Cr–O_b)$]. λ_{max}/nm (powder) 436, 504, 600.

$Na_2V_2[Mo_3O_4(O_2CEt)_8]_2$ **3**. A mixture of $NaVO_3{\cdot}2H_2O$ (1.0 g, 6.3 mmol) and propionic anhydride (40 cm^3) was refluxed for 1 h in air. After being cooled the dark green solution obtained was filtered and the filtrate treated with $Mo(CO)_6$ (1.5 g, 5.7 mmol) and NaCl (0.3 g), and the reaction carried out as for compounds **1** and **2**. After gradual cooling to room temperature the crystalline precipitate obtained was washed with diethyl ether and then with water to remove NaCl and soluble green V_3O species to produce well-formed black crystals of **3** (0.4 g, 21%). $\tilde{\nu}_{max}/cm^{-1}$ 811s, 787vs, 769s [$\nu(Mo–O_b)$].

$Na_2V_2[W_3O_4(O_2CEt)_8]_2$ **4**. The black crystals of the vanadium–tungsten complex **4** were prepared similarly using $W(CO)_6$ (2.0 g, 5.7 mmol) yielding 0.5 g, 21% of product. $\tilde{\nu}_{max}/cm^{-1}$ 812s, 789vs, 761s, 743s [$\nu(Mo–O_b)$].

Table 3 Positional parameters for $Na_2V_2[Mo_3O_4(O_2CEt)_8]_2$ **3**

Atom	*x*	*y*	*z*
Mo(1)	0.952 90(7)	0.354 90(6)	0.280 28(6)
Mo(2)	1.125 66(7)	0.279 03(5)	0.392 86(6)
Mo(3)	0.935 95(7)	0.238 79(6)	0.392 16(7)
V(1)	1.223 3(1)	0.555 9(1)	0.563 0(1)
O(1)	0.965 8(5)	0.204 8(4)	0.235 7(5)
O(2)	1.112 9(5)	0.423 3(4)	0.422 4(5)
O(3)	0.898 1(5)	0.375 6(4)	0.407 9(5)
O(4)	1.095 9(5)	0.281 4(4)	0.530 9(5)
O(11)	0.793 8(5)	0.312 1(5)	0.119 0(5)
O(12)	0.918 1(5)	0.500 5(4)	0.279 6(5)
O(13)	1.019 4(5)	0.348 8(5)	0.150 2(5)
O(14)	0.764 6(7)	0.160 3(6)	−0.034 4(7)
O(15)	1.175 9(6)	0.141 8(4)	0.361 0(5)
O(22)	1.309 1(5)	0.331 5(4)	0.526 2(5)
O(23)	1.177 3(5)	0.289 9(5)	0.256 7(5)
O(24)	1.103 7(7)	0.047 4(5)	0.147 3(6)
O(31)	0.927 3(6)	0.090 4(5)	0.369 3(6)
O(32)	0.750 4(5)	0.185 5(5)	0.260 3(6)
O(33)	0.896 9(5)	0.253 8(5)	0.544 2(5)
O(34)	0.868(1)	−0.014 1(6)	0.162 1(7)
O(41)	1.356 5(5)	0.493 7(4)	0.551 5(6)
O(42)	0.809 1(5)	0.389 3(4)	0.574 9(5)
O(43)	0.755 9(5)	0.498 7(4)	0.299 5(5)
O(44)	0.657 7(6)	0.315 6(5)	0.298 0(7)
C(11)	0.734 0(8)	0.238 9(8)	0.004 9(9)
C(12)	0.616(1)	0.258(1)	−0.082(1)
C(13)	0.546(2)	0.185(2)	−0.218(2)
C(14)	0.819 2(7)	0.525 3(6)	0.258 8(7)
C(15)	0.772 0(9)	0.583 8(7)	0.169 0(9)
C(16)	0.654(1)	0.612(1)	0.149(1)
C(17)	1.112 1(9)	0.316 4(8)	0.164 5(8)
C(18)	1.147(1)	0.307(1)	0.058 7(9)
C(19)	1.269(1)	0.296(2)	0.096(1)
C(21)	1.156 6(9)	0.058 3(7)	0.263 4(9)
C(22)	1.203(1)	0.971 6(8)	0.303(1)
C(23)	1.328(2)	0.003(1)	0.415(2)
C(24)	1.379 7(8)	0.406 6(7)	0.551 5(8)
C(25)	1.504 9(9)	0.394 9(9)	0.585(1)
C(26)	1.506(1)	0.287(1)	0.494(2)
C(31)	0.892(1)	−0.001 1(8)	0.273(1)
C(32)	0.883(1)	−0.087 9(8)	0.315(1)
C(33)	0.786(2)	−0.088(2)	0.344(2)
C(34)	0.859 9(9)	0.319 8(7)	0.607 3(8)
C(35)	0.871(1)	0.307(1)	0.729(1)
C(36)	0.858(2)	0.397(1)	0.823(1)
C(37)	0.659 6(9)	0.224 8(8)	0.242(1)
C(38)	0.541(1)	0.150(1)	0.141(2)
C(39)	0.516(2)	0.084(2)	0.197(2)
Na(1)	0.898 9(4)	0.061 0(3)	0.042 5(3)

Table 4 Positional parameters for $Na_2V_2[W_3O_4(O_2CEt)_8]_2$

Atom	*x*	*y*	*z*
W(1)	0.952 37(2)	0.354 19(2)	0.279 28(2)
W(2)	1.127 04(2)	0.279 62(2)	0.392 66(2)
W(3)	0.935 46(2)	0.237 95(2)	0.391 24(3)
V(1)	1.222 4(1)	0.556 59(9)	0.563 8(1)
O(1)	0.966 2(4)	0.202 2(4)	0.232 4(4)
O(2)	1.114 5(4)	0.425 8(4)	0.423 5(4)
O(3)	0.899 8(4)	0.376 8(3)	0.409 8(4)
O(4)	1.097 4(4)	0.279 9(4)	0.531 5(4)
O(11)	0.791 6(5)	0.310 4(4)	0.117 8(5)
O(12)	0.917 0(4)	0.498 5(4)	0.276 4(4)
O(13)	1.018 9(5)	0.348 4(4)	0.151 3(4)
O(14)	0.761 2(7)	0.156 6(6)	−0.034 8(7)
O(21)	1.178 3(5)	0.142 3(4)	0.360 5(5)
O(22)	1.308 7(4)	0.331 5(4)	0.524 6(5)
O(23)	1.178 3(4)	0.290 7(4)	0.256 1(5)
O(24)	1.105 5(5)	0.048 5(5)	0.147 2(5)
O(31)	0.925 5(5)	0.088 6(4)	0.367 2(5)
O(32)	0.751 5(5)	0.184 5(4)	0.260 7(6)
O(33)	0.896 9(5)	0.253 3(4)	0.542 7(5)
O(34)	0.868 5(8)	−0.018 3(6)	0.161 5(6)
O(41)	1.356 6(4)	0.495 2(4)	0.551 9(5)
O(42)	0.807 6(4)	0.386 9(4)	0.575 1(4)
O(43)	0.754 4(4)	0.500 0(4)	0.298 5(4)
O(44)	0.657 1(4)	0.314 4(4)	0.297 78(5)
C(11)	0.730 6(7)	0.236 1(7)	0.003 3(8)
C(12)	0.613(1)	0.260(1)	−0.079(1)
C(13)	0.547(2)	0.189(2)	−0.218(2)
C(14)	0.817 0(6)	0.524 4(6)	0.256 7(6)
C(15)	0.772 7(8)	0.585 4(6)	0.170 1(7)
C(16)	0.655 2(9)	0.613 6(9)	0.148(1)
C(17)	1.112 4(7)	0.316 2(7)	0.162 7(7)
C(18)	1.144 7(8)	0.306(1)	0.058 3(8)
C(19)	1.271(1)	0.292(2)	0.095(1)
C(21)	1.159 4(7)	0.059 2(6)	0.264 5(8)
C(22)	1.204(1)	0.968 8(8)	0.301(1)
C(23)	1.329(1)	0.002(1)	0.417(2)
C(24)	1.380 2(7)	0.407 9(7)	0.551 0(7)
C(25)	1.506 2(8)	0.394 4(8)	0.589(1)
C(26)	1.510(1)	0.292(1)	0.498(2)
C(31)	0.892 7(9)	−0.002 0(7)	0.273 3(9)
C(32)	0.881(1)	−0.090 0(7)	0.313(1)
C(33)	0.788(1)	−0.083(1)	0.353(1)
C(34)	0.858 9(7)	0.317 4(6)	0.605 8(7)
C(35)	0.873(1)	0.306 9(8)	0.729 4(9)
C(36)	0.862(1)	0.399(1)	0.826(1)
C(37)	0.658 3(7)	0.222 4(7)	0.240 9(8)
C(38)	0.543 9(9)	0.148(1)	0.141(1)
C(39)	0.511(2)	0.084(2)	0.196(3)
Na(1)	0.897 9(3)	0.059 7(3)	0.043 8(3)

$Na_2CrFe[Mo_3O_4(O_2CEt)_8]_2$ **5**. Cluster **5** was prepared similarly using $Fe(CO)_5$ (0.35 cm^3, 2.55 mmol) instead of $Mo(CO)_6$ in method B. A black solid of **5** (1.37 g, 57.8%) was obtained (Found: C, 27.8; H, 3.85; Cr, 2.70; Fe, 2.80; Mo, 27.1; Na, 2.15. $C_{48}H_{80}CrFeMo_6O_{40}$ requires C, 28.45; H, 3.85; Cr, 2.55; Fe, 2.75; Mo, 28.40; Na, 2.25%). $\tilde{v}_{max}/cm^{-1}$ 812, 794, 762, 754 [$v(Mo\text{–}O_b)$], 651 [$v(Cr\text{–}O_b)$].

Crystal Structure Determination.—The X-ray structure analyses of clusters **1** and **2** have been reported previously.[18] The structure determinations of **3** and **4** were performed similarly. Details of the crystal data, data collection and refinement are summarized in Table 7.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Physical Methods.—The magnetic susceptibilities of clusters **1**, **2**, **4** and **5** were measured at room temperature on a Gouy–Faraday magnetic balance constructed in this department. The cyclic voltammogram of $[Mo_3O_2(O_2CMe)_6(H_2O)_3]Br_2$ was recorded *vs*. the standard calomel electrode (SCE) using a platinum electrode (scan rate 0.15 mV s^{-1}) on a LZ3-204 recorder with a CV-IB potentiostat in *N,N'*-dimethylformamide solution (1.5 mmol dm^{-3}) containing 0.1 mol dm^{-3} NBu_4Cl_4. The UV/VIS solution absorption spectra of the red solid of $Na[Mo_3O_2(O_2CEt)_9]$ in H_2O and diffuse reflectance spectra of clusters **1** and **2** (as powders) (Fig. 7) were recorded on a Shimadzu UV-3000 spectrometer at room temperature and IR spectra of clusters **1**–**4** on a Digilab FTS-40 spectrometer.

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Table 5 Selected bond lengths (Å) and angles (°) for the compounds $Na_2M'_2[M_3O_4(O_2CEt)_8]_2$ **1** (M = Mo, M′ = Cr), **2** (M = W, M′ = Cr), **3** (M = Mo, M′ = V) and **4** (M = W, M′ = V)

1		**2**		**3**		**4**	
Mo(1)–Mo(2)	2.5103(8)	W(1)–W(2)	2.5177(8)	Mo(1)–Mo(2)	2.508(1)	W(1)–W(2)	2.5165(5)
Mo(1)–Mo(3)	2.5289(9)	W(1)–W(3)	2.5361(8)	Mo(1)–Mo(3)	2.533(1)	W(1)–W(3)	2.5428(6)
Mo(2)–Mo(3)	2.5203(9)	W(2)–W(3)	2.5402(9)	Mo(2)–Mo(3)	2.517(1)	W(2)–W(3)	2.5391(6)
Mo(1)–O(1)	2.019(4)	W(1)–O(1)	2.056(8)	Mo(1)–O(1)	2.020(7)	W(1)–O(1)	2.048(6)
Mo(1)–O(2)	1.956(4)	W(1)–O(2)	1.982(8)	Mo(1)–O(2)	1.953(6)	W(1)–O(2)	1.978(5)
Mo(1)–O(3)	1.934(4)	W(1)–O(3)	1.958(8)	Mo(1)–O(3)	1.943(6)	W(1)–O(3)	1.962(6)
Mo(1)–O(11)	2.009(4)	W(1)–O(11)	2.011(9)	Mo(1)–O(11)	1.997(6)	W(1)–O(11)	2.010(6)
Mo(1)–O(12)	2.103(4)	W(1)–O(12)	2.113(8)	Mo(1)–O(12)	2.106(6)	W(1)–O(12)	2.094(6)
Mo(1)–O(13)	2.109(5)	W(1)–O(13)	2.132(9)	Mo(1)–O(13)	2.127(8)	W(1)–O(13)	2.107(7)
Mo(2)–O(1)	2.015(4)	W(2)–O(1)	2.039(8)	Mo(2)–O(1)	2.013(6)	W(2)–O(1)	2.040(6)
Mo(2)–O(2)	1.963(5)	W(2)–O(2)	1.972(8)	Mo(2)–O(2)	1.959(6)	W(2)–O(2)	1.982(5)
Mo(2)–O(4)	1.901(4)	W(2)–O(4)	1.928(9)	Mo(2)–O(4)	1.906(6)	W(2)–O(4)	1.926(6)
Mo(2)–O(21)	2.013(4)	W(2)–O(21)	2.010(8)	Mo(2)–O(15)	2.014(6)	W(2)–O(15)	2.018(6)
Mo(2)–O(22)	2.106(5)	W(2)–O(22)	2.096(9)	Mo(2)–O(22)	2.117(8)	W(2)–O(22)	2.093(6)
Mo(2)–O(23)	2.132(5)	W(2)–O(23)	2.125(9)	Mo(2)–O(23)	2.115(7)	W(2)–O(23)	2.131(7)
Mo(3)–O(1)	2.044(4)	W(3)–O(1)	2.082(9)	Mo(3)–O(1)	2.045(6)	W(3)–O(1)	2.083(6)
Mo(3)–O(3)	1.954(4)	W(3)–O(3)	1.975(7)	Mo(3)–O(3)	1.956(6)	W(3)–O(3)	1.973(5)
Mo(3)–O(4)	1.913(4)	W(3)–O(4)	1.925(8)	Mo(3)–O(4)	1.905(7)	W(3)–O(4)	1.926(6)
Mo(3)–O(31)	2.007(4)	W(3)–O(31)	2.015(9)	Mo(3)–O(31)	2.003(7)	W(3)–O(31)	2.012(6)
Mo(3)–O(32)	2.123(5)	W(3)–O(32)	2.105(9)	Mo(3)–O(32)	2.136(7)	W(3)–O(32)	2.114(6)
Mo(3)–O(33)	2.111(5)	W(3)–O(33)	2.086(9)	Mo(3)–O(33)	2.110(7)	W(3)–O(33)	2.100(6)
Cr(1)–O(2)	1.959(4)	Cr(1)–O(2)	1.943(8)	V(1)–O(2)	2.006(6)	V(1)–O(2)	1.976(6)
Cr(1)–O(3)	1.935(4)	Cr(1)–O(3)	1.916(8)	V(1)–O(3)	1.964(6)	V(1)–O(3)	1.947(6)
Cr(1)–O(41)	1.976(5)	Cr(1)–O(41)	1.980(8)	V(1)–O(41)	1.989(7)	V(1)–O(41)	1.995(6)
Cr(1)–O(42)	1.969(5)	Cr(1)–O(42)	1.986(9)	V(1)–O(42)	1.971(7)	V(1)–O(42′)	2.018(6)
Cr(1)–O(43)	1.980(5)	Cr(1)–O(43)	1.981(9)	V(1)–O(43)	1.998(7)	V(1)–O(43′)	2.023(6)
Cr(1)–O(44)	1.968(5)	Cr(1)–O(44)	1.997(9)	V(1)–O(44)	1.999(8)	V(1)–O(44′)	2.011(6)
O(1)–Na(1)	2.314(5)	O(1)–Na(1)	2.267(9)	O(1)–Na(1)	2.312(7)	O(1)–Na(1)	2.267(7)
O(14)–Na(1)	2.291(7)	O(14)–Na(1)	2.29(1)	O(14)–Na(1)	2.291(9)	O(14)–Na(1)	2.31(1)
O(24)–Na(1)	2.402(6)	O(24)–Na(1)	2.43(1)	O(24)–Na(1)	2.408(9)	O(24)–Na(1)	2.428(8)
O(24′)–Na(1)	2.319(5)	O(24′)–Na(1)	2.32(1)	O(24′)–Na(1)	2.308(9)	O(24′)–Na(1)	2.317(7)
O(34)–Na(1)	2.247(8)	O(34)–Na(1)	2.27(1)	O(34)–Na(1)	2.24(1)	O(34)–Na(1)	2.25(1)
Mo(2)–Mo(1)–Mo(3)	60.02(2)	W(2)–W(1)–W(3)	60.35(2)	Mo(2)–Mo(1)–Mo(3)	59.88(3)	W(2)–W(1)–W(3)	60.24(1)
Mo(1)–Mo(2)–Mo(3)	60.35(2)	W(1)–W(2)–W(3)	60.19(3)	Mo(1)–Mo(2)–Mo(3)	60.55(3)	W(1)–W(2)–W(3)	60.40(1)
Mo(3)–Mo(3)–Mo(2)	59.63(2)	W(1)–W(3)–W(2)	59.46(3)	Mo(1)–Mo(3)–Mo(2)	59.57(3)	W(1)–W(3)–W(2)	59.37(1)
O(1)–Mo(1)–O(2)	101.6(2)	O(1)–W(1)–O(2)	101.8(3)	O(1)–Mo(1)–O(2)	101.5(3)	O(1)–W(1)–O(2)	102.2(2)
O(1)–Mo(1)–O(3)	101.0(2)	O(1)–W(1)–O(3)	102.1(3)	O(1)–Mo(1)–O(3)	100.9(3)	O(1)–W(1)–O(3)	101.9(2)
O(2)–Mo(1)–O(3)	90.7(2)	O(2)–W(1)–O(3)	90.3(3)	O(2)–Mo(1)–O(3)	90.7(3)	O(2)–W(1)–O(3)	89.6(2)
O(1)–Mo(2)–O(2)	101.4(2)	O(1)–W(2)–O(2)	102.7(3)	O(1)–Mo(2)–O(2)	101.5(3)	O(1)–W(2)–O(2)	102.4(2)
O(1)–Mo(2)–O(4)	99.8(2)	O(1)–W(2)–O(4)	100.0(3)	O(1)–Mo(2)–O(4)	99.8(3)	O(1)–W(2)–O(4)	100.0(2)
O(2)–Mo(2)–O(4)	93.5(2)	O(2)–W(2)–O(4)	93.8(3)	O(2)–Mo(2)–O(4)	93.3(3)	O(2)–W(2)–O(4)	94.1(2)
O(1)–Mo(3)–O(3)	99.4(2)	O(1)–W(3)–O(3)	100.6(3)	O(1)–Mo(3)–O(3)	99.6(2)	O(1)–W(3)–O(3)	100.4(2)
O(1)–Mo(3)–O(4)	98.4(2)	O(1)–W(3)–O(4)	98.6(3)	O(1)–Mo(3)–O(4)	98.7(3)	O(1)–W(3)–O(4)	98.6(2)
O(3)–Mo(3)–O(4)	98.0(2)	O(3)–W(3)–O(4)	98.0(3)	O(3)–Mo(3)–O(4)	98.1(3)	O(3)–W(3)–O(4)	97.7(2)
O(2)–Cr(1)–O(3′)	95.4(2)	O(2)–Cr(1)–O(3′)	95.6(3)	O(2)–V(1)–O(3′)	95.8(3)	O(2)–V(1)–O(3′)	95.7(2)
Mo(1)–O(1)–Mo(2)	77.0(1)	W(1)–O(1)–W(2)	75.9(3)	Mo(1)–O(1)–Mo(2)	76.9(3)	W(1)–O(1)–W(2)	76.0(2)
Mo(1)–O(1)–Mo(3)	77.0(1)	W(1)–O(1)–W(3)	75.7(3)	Mo(1)–O(1)–Mo(3)	77.1(2)	W(1)–O(1)–W(3)	76.0(2)
Mo(2)–O(1)–Mo(3)	76.8(1)	W(2)–O(1)–W(3)	76.1(3)	Mo(2)–O(1)–Mo(3)	76.6(3)	W(2)–O(1)–W(3)	76.0(2)
Mo(1)–O(2)–Mo(2)	79.7(2)	W(1)–O(2)–W(2)	79.1(3)	Mo(1)–O(2)–Mo(2)	79.8(2)	W(1)–O(2)–W(2)	78.9(2)
Mo(1)–O(2)–Cr(1)	147.5(2)	W(1)–O(2)–Cr(1)	147.4(4)	Mo(1)–O(2)–V(1)	147.3(3)	W(1)–O(2)–V(1)	147.9(4)
Mo(2)–O(2)–Cr(1)	132.0(2)	W(2)–O(2)–Cr(1)	132.5(4)	Mo(2)–O(2)–V(1)	132.1(3)	W(2)–O(2)–V(1)	132.1(3)
Mo(1)–O(3)–Mo(3)	81.1(2)	W(1)–O(3)–W(3)	80.4(3)	Mo(1)–O(3)–Mo(3)	81.0(2)	W(1)–O(3)–W(3)	80.5(3)
Mo(1)–O(3)–Cr(1)	134.4(2)	W(1)–O(3)–Cr(1)	134.3(4)	Mo(1)–O(3)–V(1)	134.5(3)	W(1)–O(3)–V(1′)	133.8(3)
Mo(3)–O(3)–Cr(1)	133.2(2)	W(3)–O(3)–Cr(1)	133.3(4)	Mo(3)–O(3)–V(1)	133.6(3)	W(3)–O(3)–V(1′)	133.0(3)
Mo(2)–O(4)–Mo(3)	82.7(2)	W(2)–O(4)–W(3)	82.5(3)	Mo(2)–O(4)–Mo(3)	82.6(2)	W(2)–O(4)–W(3)	82.5(2)

Table 6 Comparison of mean bond lengths in **1**–**4** and related M_3O_4 and M_3O compounds

Compound	M–M	M–μ-O[a]	M–μ-O*,[b]	M–O_t[c]	M–O_{cp}[d]	M–O_{ba}[e]	M′–μ-O*	M′–O_{ba}
$Na_2Cr_2[Mo_3O_4(O_2CEt)_8]_2$ **1**	2.5198(9)	1.907(4)	1.952(5)	2.010(4)	2.026(4)	2.114(5)	1.947(4)	1.973(5)
$Na_2Cr_2[W_3O_4(O_2CEt)_8]_2$ **2**	2.5313(9)	1.927(9)	1.972(8)	2.012(9)	2.059(9)	2.110(9)	1.929(8)	1.986(9)
$Na_2V_2[Mo_3O_4(O_2CEt)_8]_2$ **3**	2.519(1)	1.905(6)	1.953(6)	2.005(6)	2.026(7)	2.119(8)	1.985(6)	1.989(8)
$Na_2V_2[W_3O_4(O_2CEt)_8]_2$ **4**	2.5328(6)	1.926(6)	1.974(6)	2.013(6)	2.057(6)	2.107(7)	1.962(6)	2.012(6)
$[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$[f]	2.493(3)	1.915(7)			2.020(3)			
$[W_3O_4(NCS)_9]^{4-}$[g]	2.534	1.911			2.039			
$[Cr_3O(O_2CEt)_6F_3]^{2-}$[h]							1.909(4)	1.974(4)
$[V_3O(O_2CMe)_8(thf)_3]^{-}$[i]							1.910(6)	2.00(2)

[a] Bridging M atoms. [b] Bridging M and M′ atoms. [c] Terminal $EtCO_2$. [d] Capping O atoms. [e] Bridging $EtCO_2$. [f] Ref. 6(*a*). [g] Ref. 10(*a*). [h] Ref. 23(*a*). [i] Ref. 23(*c*). thf = Tetrahydrofuran.

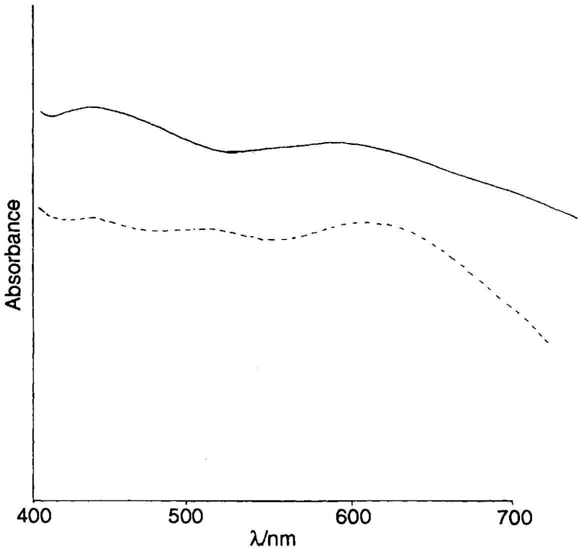

Fig. 7 Diffuse reflectance spectra of $Na_2Cr_2[M_3O_4(O_2CEt)_8]_2$ [M = Mo (——) **1** or W **2** (- - - -)]

Table 7 Crystallographic data[a] for $Na_2V_2[M_3O_4(O_2CEt)_8]_2$ (M = Mo **3** or W **4**)

Chemical formula	**3**	**4**
Crystal size/mm	0.2 × 0.1 × 0.4	0.3 × 0.3 × 0.2
M	202.65	2548.11
a/Å	12.977(7)	12.973(4)
b/Å	14.070(6)	14.063(3)
c/Å	12.338(8)	12.396(5)
α/°	109.81(4)	109.92(2)
β/°	117.20(4)	117.33(2)
γ/°	90.51(5)	90.53(2)
U/Å^3	1848.8	1851.3
F(000)	1008	1200
D_c/Mg m^{-3}	1.81	2.29
μ/cm^{-1}	12.9	98.2
Scan width	1.418 + 0.35 tan θ	1.313 + 0.35 tan θ
Absorption correction	Lorentz polarization	Lorentz polarization, line decay (0.943–1.027), empirical absorption (0.84–1.00)
Maximum and minimum transmission values	0.757–1.158	0.832–1.141
Reflections with $I \geqslant 3\sigma(I)$	3742	5499
hkl range	0 to −15, −16 to −16, −14 to −12	0 to −15, −16 to −16, −14 to −13
R[b]	0.048	0.030
R'[c]	0.054	0.036
No. of parameters	442	442
S	1.06	0.93
$(\Delta/\sigma)_{max}$	0.06	0.01
$(\Delta/\rho)_{max}$	0.53	0.97

[a] Details in common: triclinic; space group $P\bar{1}$, $Z = 1$, Mo-Kα radiation (λ = 0.710 69 Å), T = 298 K, Rigaku AFC5R diffractometer, ω–2θ collection method, absorption correction using DIFABS[26] program, 6848 unique reflections, 2θ range 3–50°. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. $w = 1/[\sigma(F_o)^2 + (0.020F_o)^2 + 1.00]$.

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