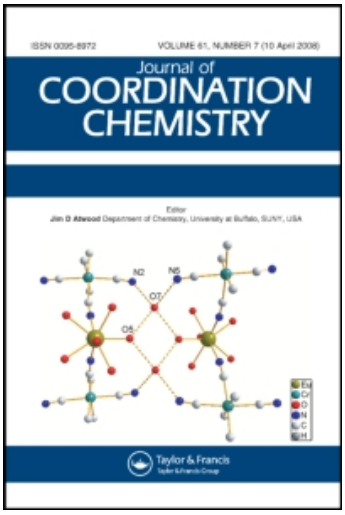

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CLUSTER CONVERSION OF $[MoW_2O_2(O_2CEt)_9]^-$ TO $[MoW_2O_4(O_2\ CEt)_8]^{4-}$ BY CHROMIUM HEXACARBONYL CRYSTAL STRUCTURES OF $Na[MoW_2O_2(O_2CMe)_9] \cdot H_2O$, $[MoW_2O_2(O_2CEt)_6(H_2O)_3]ZnCl_4 \cdot 2H_2O$, AND $Na_2Cr_2[MoW_2O_4(O_2CEt)_8]_2$

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Reactions of $Mo(CO)_6$ with $Na_2WO_4 \cdot 2H_2O$ in refluxing carboxylic anhydride produce the triangular bioxo-capped mixed-metal carboxylate clusters $Na[MoW_2O_2(O_2CR)_9]$ (R = Me, **1**; Et, **2**), the propionate being hydrolyzed in 2M HCl containing $ZnCl_2$ to form $[MoW_2O_2(O_2CEt)_6(H_2O)_3]ZnCl_4 \cdot 2H_2O$ (**3**). Cluster **2** is converted to the incomplete cuboidal tetraanion $[MoW_2O_4(O_2CEt)_8]^{4-}$ upon reacting with $Cr(CO)_6$ in propionic anhydride at 120°, the latter species being trapped by Cr^{3+} and Na^+ ions in the reaction mixture to afford the octanuclear heterometallic chain-like cluster $Na_2Cr_2[MoW_2O_4(O_2CEt)_8]_2$ (**4**). Clusters **1**, **3** and **4** have been characterized by X-ray crystallography with the following crystal data, for **1**: monoclinic, space group $P2_1/c$, $a = 16.666(8)$, $b = 11.096(3)$, $c = 16.541(7)$ Å, $\beta = 94.60(4)°$, $V = 3048.9$ Å^3, $Z = 4$, R, $Rw = 0.070$, 0.079; for **3**, monoclinic, space group Cm, $a = 10.259(3)$, $b = 15.756(3)$, $c = 10.870(3)$ Å, $\beta = 96.18(3)°$, $V = 1746.8$ Å^3, $Z = 2$, R, $Rw = 0.028$, 0.034; for **4**, triclinic, space group $P\text{-}1$, $a = 13.013(5)$, $b = 14.005(4)$, $c = 12.357(4)$ Å, $\alpha = 109.71(2)$, $\beta = 117.77(3)$, $\gamma = 90.41(3)°$, $V = 1838.9$ Å^3, $Z = 1$, R, $Rw = 0.037$, 0.042.

Keywords: chromium; molybdenum; tungsten; carboxylate; clusters; crystal structure

INTRODUCTION

Two principal types of triangular metal-metal bonded clusters of molybdenum and tungsten, namely those with bioxo-caps $[M_3O_2(\mu\text{-}O_2CR)_6]^{2+}$ and incomplete cubane-like $[M_3O_4]^{4+}$(M = Mo, W) cores have been extensively researched over the past two decades.[1] Both types are very stable in aqueous solution or solid solid but have

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different redox properties. The former is highly resistant to oxidation; for example, with R = Ph, they can be fully nitrated in phenyl groups in a mixture of concentrated H_2SO_4 and HNO_3 without observable decomposition.[1,2] Those of the latter type are stable toward reduction.[3] However, we recently found that the former clusters have irreversible redox properties,[4] which, together with their remarkable catalytic activity in the oxidation of styrene under mild conditions,[5] aroused our interest in investigating their reactivity under reducing conditions. As might be expected, this kind of cluster is reduction-active and the results of the investigation are presented in this paper.

EXPERIMENTAL SECTION

All reagents were analytical grade and used without further purification. All manipulations were carried out in air.

Synthesis of $Na[MoW_2O_2(O_2CCH_3)_9]\cdot H_2O$ (1)

A mixture of $Na_2WO_4\cdot 2H_2O$ (1.98 g, 6 mmol), $Mo(CO)_6$ (0.79 g, 3 mmol) and acetic anhydride ($60cm^3$) was refluxed in air for ten hours. After being cooled to room temperature, the resulting solution was poured into ether ($200cm^3$) to produce an orange solid which, together with the orange precipitate (1.6 g) isolated from the reaction solution, gave a total of 2.8 g of **1** (89%). Orange-red crystals of **1** were obtained by slow evaporation of a solution in MeOH/EtOH (1:1) Anal. calcd. for $MoW_2O_{21}C_{18}H_{29}Na$: Mo, 8.99; C, 20.22; H, 2.71: Found: Mo, 8.18; C, 20.13; H, 2.22%.

Synthesis of $Na[MoW_2O_2(O_2CEt)_9]$ (2) and $[MoW_2O_2(O_2CEt)_6(H_2O)_3]ZnCl_4\cdot 2H_2O$ (3)

The orange-red propionic anhydride solution of **2** was prepared similarly using propionic anhydride. The solution was poured into ether (200 cm^3) to yield orange-red, solid **2** (3.3 g, *ca* 94%). It was hydrolyzed in 2M HCl containing $ZnCl_2$ (0.4 g) and the resulting solution was evaporated slowly in air to produce orange-red crystals of **3** (1.9 g, 51% based on $Mo(CO)_6$).

Synthesis of $Na_2Cr_2[MoW_2O_4(O_2CEt)_8]_2$ (4)

To the propionic anhydride solution of **2**, which was obtained from refluxing a mixture of $Na_2WO_4\cdot 2H_2O$ (1.3 g, 3.9 mmol), $Mo(CO)_6$ (0.5g, 1.9 mmol) and

propionic anhydride (50cm^3) for six hours, $Cr(CO)_6$ (0.5 g, 2.3 mmol) was added and the mixture was heated at 120°C for three days. After being cooled to room temperature, well-formed, black crystals of **4** were isolated from a resulting green-black reaction solution (0.57 g, 26% based on $Mo(CO)_6$) Anal: calcd. for $Cr_2Mo_2W_4O_{40}C_{48}H_{80}Na_2$: Cr, 4.38; Mo, 8.08; C, 24.26; H, 3.36; Na, 1.94. Found: Cr, 4.17; Mo, 7.22; C, 23.90; H, 3.47; Na, 1.83%.

X-ray Crystallography

The crystallographic data for clusters **1**, **3** and **4** are summarized in Table I. The intensity data were collected on a Rigaku AFC5R diffractometer using graphite-monochromated MoKα radiation (λ = 0.71069 Å) at 298K and $\omega/2\theta$ scan mode ($3° < 2\theta < 50°$) with scan speed 16° min^{-1}. Accurate unit cell dimensions were determined from least-squares refinement on diffractometer angles for 20 automatically centred reflections. The structures were solved by direct methods (Mo and W atoms), followed by heavy atom procedures. The Mo and W atoms of the triangular M_3 unit in the three clusters were all found to be disordered and treated as M = 0.33Mo + 0.67W to give reasonable temperature factors for the metal atoms. The structures were refined by full-matrix least-squares with some of the non-hydrogen atoms (for **1** and **3**) or all non-hydrogen atoms (for **4**) anisotropic. The weighing scheme w was $1/[\sigma(F_o)^2 + (0.020F_o)^2 + 1.000]$ with $\sigma(F_o)$ from counting statistics. All calculations were performed on a VAX 785 computer using the SDP program package with scattering factors taken from the *International Tables*.

RESULTS AND DISCUSSION

Synthesis

The trinuclear mixed-metal cluster $[MoW_2O_2(O_2CMe)_6(H_2O)_3]^{2+}$ was first prepared by Sasaki and co-workers as one of three principal products (the other two being Mo_2W and W_3 analogues) by reaction of Na_2MoO_4, Na_2WO_4 and zinc dust in refluxing acetic anhydride.[6] The improved synthetic method, namely reaction of Na_2WO_4 and $Mo(CO)_6$ in refluxing acetic anhydride was developed in this laboratory[7] and found to produce $Na[MoW_2O_2(O_2CMe)_9]$ (**1**) exclusively in excellent yield. The propionate **2** was prepared similarly using propionic anhydride but it did not precipitate from the reaction solution due to its solubility. However, it can be easily isolated by the addition of ether and has been confirmed by electronic

TABLE I Crystallographic Data for **1**, **3** and **4**

	1	*3*	*4*
formula	$MoW_2O_{21}C_{18}H_{29}Na$	$MoW_2O_{23}C_{18}H_{48}ZnCl_4$	$Cr_2Mo_2W_4O_{40}C_{48}H_{80}Na_2$
f.w.	1068.05	1231.3	2374.4
$F(000)$	2024	1176	1138
crystal size	$0.4 \times 0.1 \times 0.2$	$0.3 \times 0.2 \times 0.1$	$0.4 \times 0.3 \times 0.2$
space group	$P2_1/c$	Cm	$P\bar{1}$
a, Å	16.666(8)	10.259(3)	13.013(5)
b, Å	11.096(3)	15.756(3)	14.005(4)
c, Å	16.541(7)	10.870(3)	12.357(4)
α deg			109.71(2)
β deg	94.60(4)	96.18(3)	117.77(3)
γ deg			90.41(3)
V, Å^3	3048.9	1746.8	1838.9
Z	4	2	1
Dc, gm^{-3}	2.33	2.34	2.14
μ cm^{-1}	81.8	81.3	70.6
scan width	1.08	1.10	1.11
unique reflns	5682	1702	6790
observed reflns ($I > 3\sigma(I)$)	2651	1530	4807
refined parameters	301	215	442
R, Rw[a]	0.070, 0.079	0.028, 0.034	0.037, 0.042
GOF[b]	1.42	1.19	1.01
$(\Delta/\sigma)_{max}$	0.03	0.01	0.04
$(\Delta/\rho)_{max}$	1.42	1.34	1.07

[a] $R = \Sigma(|F_o|-|F_c|)/|F_o|$, $R_w = [w(|F_o|-|F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$ [b] $GOF = [w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$

spectrum which is essentially identical to that reported[6] as well as column chromatography techniques described below. In order to investigate whether the $[M_3O_4]^{4+}$ species was formed or not, cation exchange column chromatography of the reaction solution using Sephadex-C25 with 2M HCl as eluent was employed. As a result, only a single red-orange band of cation **3** was observed. The addition of $ZnCl_2$ to the eluate gave rise to red-orange crystals of **3** after exposure to air for several days.

To the red-orange propionic anhydride solution of **2**, $Cr(CO)_6$ was added and the resulting mixture was heated to produce black crystals of **4**, $Na_2Cr_2[MoW_2O_4(O_2CEt)_8]_2$, in moderate yield. The cuboidal unit, $[MoW_2O_4(O_2CEt)_8]^{4-}$, unambiguously results from the conversion of the cluster monoanion of **2**, $[MoW_2O_2(O_2CEt)_9]^-$, with the MoW_2 metal framework remaining intact. Such cluster conversion may be ascribable to the M_3-μ_3O antibonding character in the HOMO of **2**, which may also be responsible for the irreversible redox properties and the catalytic oxidation activity of such species. It is thereby reasonable to consider that the conversion starts with reductive cleavage of the M_3-μ_3O bond by $Cr(CO)_6$, followed by oxidation of the intermediate and the formation of the $[MoW_2O_4]^{4+}$ core. In addition to the abovementioned kinetic origin, the reaction is also thermodynamically supported,as revealed by the resulting cuboidal unit being reduction-stable and the insolubility of the octanuclear reaction product.

Structure

The structures of cluster ions of **1** and **3** are shown in Figure **1** and Figure **2**. Selected bond lengths and angles are given in Table II. Positional parameters are given in Table III and Table IV. Cluster **1** has no crystallographically imposed symmetry. It is structurally similar to the tritugsten clusters $M[W_3O_2(O_2CMe)_9]$ (M = H^8, Cs^9) previously reported although the terminal $MeCO_2$ planes have different orientations. The Na^+ ion is five-coordinate with a mean Na-O bond of 2.44(4) Å. The structure of the cation of **3**, which has C_m symmetry, is identical to that of $[Mo_3O_2CO_2CEt)_6(H_2O)_3]^{2+}$ [10] although the symmetries are different. The M-M bonds [*av.* 2.748(1) Å] in **3** are shorter than those in **1** [av. 2.774(2) Å] due to the effect of the terminal acetates in the latter species.

The structures of the cuboidal unit and cluster dianion of **4** are shown in Figure **3** and Figure **4**. Selected bond lengths and angles are listed in Table II and positional parameters in Table V. The structures are similar to those of the chromium analogues[11,12] and further discussion is not necessary. It is of interest to compare the structures shown in Figures **1** and **3** to see how the conversion of $[MoW_2O_2(O_2CEt)_9]^-$, which can be safely considered as having the same structure as that of the anion of **1**, to $[MoW_2O_4(O_2CEt)_8]^{4-}$ proceeds. It can be easily seen

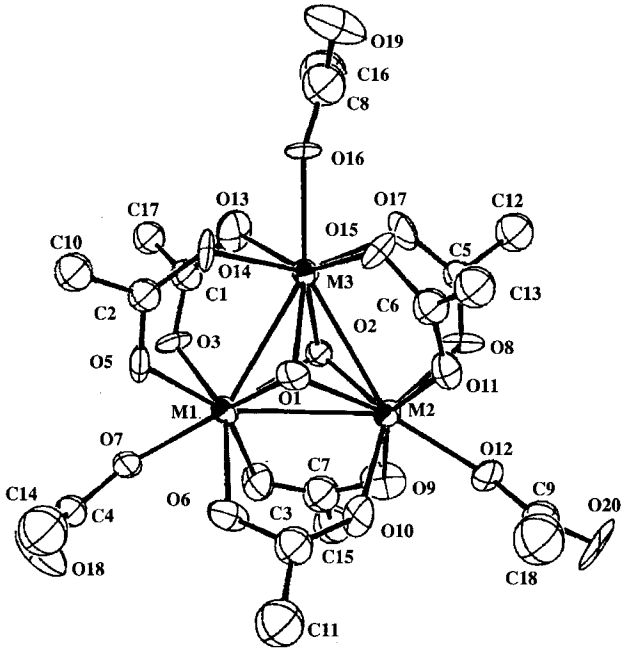

FIGURE 1 Structure of $[MoW_2O_2(O_2CCH_3)_9]^-$ with 50% probability thermal ellipsoids.

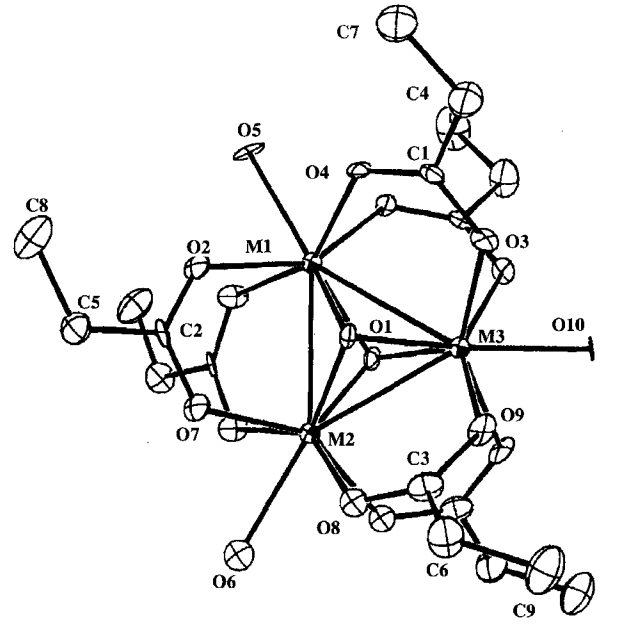

FIGURE 2 Structure of $[MoW_2O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ with 50% probability thermal ellipsoids.

that the MoW_2 metal framework, one capping oxygen atom, three terminal carboxylato groups and one carboxylato bridge in the former species are preserved in the latter. The other capping oxygen atom and two of the six bridging carboxylato groups in the former are replaced by three μ_2O atoms. The remaining four bridging carboxylato groups in the former become terminal ones, two being bound to one M atom and the remaining two to the other two M atoms, respectively.

TABLE II Selected band distances (Å) and angles (°) for clusters **1**, **3** and **4**

1		*3*		*4*	
M1-M2	2.774(2)	M1-M2	2.740(1)	M1-M2	2.5193(7)
M1-M3	2.763(2)	M1-M3	2.7619(9)	M1-M3	2.5395(7)
M2-M3	2.784(2)	M2-M3	2.743(1)	M2-M3	2.5458(7)
M1-O1	1.98(1)	M1-O1	2.014(6)	M1-Ol	2.029(7)
M1-O2	2.04(1)	M1-O2	2.125(7)	M1-O2	1.972(7)
M1-O3	2.09(1)	M1-O4	2.089(6)	M1-O3	1.957(7)
M1-O4	2.14(2)	M1-O5	2.098(9)	M1-O11	2.005(7)
M1-O5	2.12(2)	M2-O1	2.003(7)	M1-O12	2.092(7)
M1-O6	2.11(2)	M2-O6	2.18(1)	M1-O13	2.105(7)
M1-O7	2.02(1)	M2-O7	2.085(6)	M2-Ol	2.025(7)
M2-O1	2.04(2)	M2-O8	2.097(6)	M2-O2	1.984(7)
M2-O2	1.96(1)	M3-O1	2.003(6)	M2-O4	1.915(7)
M2-O8	2.09(1)	M3-O3	2.081(6)	M2-O21	2.010(8)
M2-O9	2.13(1)	M3-O9	2.116(6)	M2-O22	2.088(7)
M2-O10	2.07(2)	M3-O10	2.069(9)	M2-O23	2.128(8)
M2-O11	2.07(1)	Znl-C11	2.266(5)	M3-O1	2.062(7)
M2-O12	2.00(1)	Znl-C12	2.274(5)	M3-O3	1.972(7)
M3-O1	1.99(1)	Znl-C13	2.276(4)	M3-O4	1.920(7)
M3-O2	1.95(1)			M3-O31	2.005(7)
M3-O13	2.11(2)			M3-O32	2.116(8)
M3-O14	2.08(1)			M3-O33	2.101(8)
M3-O15	2.09(2)			Cr1-O2	1.950(7)
M3-O16	2.04(1)			Cr1-O3	1.929(7)
M3-O17	2.13(1)			Cr1-O41	1.984(7)
O7-Na1	2.36(3)			Cr1-O42	1.957(8)
O16-Na1	2.31(4)			Cr1-O43	1.981(7)
O18-Na1	2.68(3)			Cr1-O44	1.966(7)
O19-Na1	2.59(3			Ol-Nal	2.291(8)
O20-Na1	2.26(3)			O14-Na1	2.29(2)
				O24-Nal	2.41(1)
				O24'-Na1	2.327(9)
				O34-Nal	2.25(1)
M2-M1-M3	60.38(4)	M2-M1-M3	59.81(2)	M2-M1-M3	60.43(2)
M1-M2-M3	59.64(4)	M1-M2-M3	60.50(2)	M1-M2-M3	60.19(2)
M1-M3-M2	59.98(4)	M1-M3-M2	59.69(2)	M1-M3-M2	59.39(3)
O1-M1-O2	72.1(6)	O1-M1-O1'	75.2(4)	O1-M1-O2	101.9(3)
O1-M2-O2	72.7(6)	O1-M 2-O1'	75.8(4)	O1-M1-O3	101.6(3)
O1-M3-O2	74.0(7)	O1-M 3-O1'	75.8(4)	O2-1-O1'	90.0(3)
M1-O1-M2	87.4(6)	M1- O1-M 2	86.0(3)	O1-M2-O2	101.7(3)
M2-O1-M3	87.9(6)	M1-O1-M3	86.8(3)	O1-M2-O4	99.4(3)
M1-Ol-M3	88.4(6)	M2-O1-M3	86.4(2)	O2-M2-O4	93.8(3)

TABLE II *(Continued)*

1		*3*		*4*	
M1-O2-M2	87.7(6)	C11-Zn1-Cl2	117.4(2)	O1-M3-O3	99.9(3)
M1-O2-M3	87.6(6)	C11-Zn1-Cl3	108.1(2)	O1-M3-O4	97.9(3)
M2-O2-M3	90.7(7)	Cl2-Zn1-Cl3	107.5(1)	O3-M3-O4	97.5(3)
O7-Na1-O16	145(2)	Cl3-Zn1-Cl3	108.2(2)	O2-Cr1-O3	94.8(3)
O7-Na1-O18	50(2)			M1-O1-M2	76.8(2)
O7-Na1-O19	131(3)			M1-O1-M3	76.7(2)
O7- Na1-O20	121(2)			M2-O1-M3	77.0(2)
O16-Na1-O18	50(2)			M1-O2-M2	79.1(2)
O16-Na1-O19	51(3)			M1-O2-Cr1	148.1(4)
O16-Na1-O20	92(2)			M2-O2-Cr1	131.6(4)
O18-Na1-O19	178(2)			M1-O3-M3	80.5(2)
O18-Na1-O20	93(3)			M1-O3-Cr1	133.9(4)
O19-Na1-O20	85(3)			M3-O3-Cr1	132.5(3)
				M2-O4-M3	83.2(3)

TABLE III Positional and thermal parameters for $Na[MoW_2O_2(O_2CCH_3)_9] \cdot H_2O$, **1**

Atom	*x/a*	*y/b*	*z/c*	$B_{eq}(Å^2)$
MW1	0.70562(9)	0.0915(1)	0.88733(8)	1.81(3)
MW2	0.74997(9)	–0.0691(1)	1.01145(8)	1.80(3)
MW3	0.79027(9)	0.1738(1)	1.02696(8)	1.66(2)
O1	0.687(1)	0.088(2)	1.004(1)	2.2(4)
O2	0.811(1)	0.046(1)	0.9504(8)	1.8(3) *
O3	0.786(1)	0.201(1)	0.830(1)	2.6(4)
O4	0.746(1)	–0.053(2)	0.815(1)	3.0(4)
O5	0.639(1)	0.251(2)	0.903(1)	2.5(4)
O6	0.597(1)	–0.006(2)	0.886(1)	3.2(4)
O7	0.656(1)	0.122(2)	0.774(1)	2.4(4)
O8	0.869(1)	–0.089(1)	1.061(1)	2.5(4)
O9	0.787(1)	–0.178(2)	0.915(1)	3.6(4)
O10	0.633(1)	–0.128(2)	0.985(1)	2.7(4)
O11	0.720(1)	–0.046(2)	1.130(1)	2.8(4)
O12	0.752(1)	–0.238(2)	1.054(1)	2.6(4)
O13	0.855(1)	0.270(2)	0.944(1)	3.5(4)
O14	0.707(1)	0.313(2)	1.015(1)	2.5(4)
O15	0.752(1)	0.151(1)	1.143(1)	2.7(4)
O16	0.838(1)	0.314(2)	1.095(1)	2.6(4)
O17	0.902(1)	0.103(2)	1.077(1)	3.1(4)
O18	0.587(1)	0.111(3)	0.657(1)	6.2(7)
O19	0.903(2)	0.423(3)	1.186(1)	6.2(6)
O20	0.750(2)	–0.421(2)	1.102(1)	5.0(5)
O21	0.204(2)	0.452(3)	0.075(1)	8.7(9)
C1	0.841(2)	0.261(2)	0.864(2)	2.7(5) *
C2	0.651(2)	0.329(2)	0.961(1)	2.5(5) *
C3	0.582(2)	–0.092(3)	0.936(2)	3.4(6) *
C4	0.588(2)	0.137(2)	0.731(2)	2.5(5) *
C5	0.917(2)	–0.011(2)	1.082(1)	2.1(5) *
C6	0.720(2)	0.050(3)	1.168(2)	2.9(6) *

TABLE III *(Continued)*

Atom	*x/a*	*y/b*	*z /c*	$B_{eq}(Å^2)$
C7	0.783(2)	−0.143(3)	0.839(2)	3.5(6) *
C8	0.904(2)	0.360(3)	1.126(2)	4.4(7) *
C9	0.720(2)	−0.324(3)	1.092(2)	3.3(6) *
C10	0.595(2)	0.433(3)	0.961(2)	3.2(6) *
C11	0.495(2)	−0.138(3)	0.930(2)	4.9(8) *
C12	1.004(2)	−0.038(3)	1.117(2)	3.9(7) *
C13	0.682(2)	0.055(3)	1.251(2)	3.5(6) *
C14	0.506(2)	0.168(4)	0.764(2)	5.6(8) *
C15	0.827(2)	−0.221(3)	0.782(2)	4.0(7) *
C16	0.984(2)	0.356(3)	1.080(2)	5.3(8) *
C17	0.895(2)	0.332(3)	0.816(2)	2.9(5) *
C18	0.641(2)	−0.301(4)	1.134(2)	5.5(9) *
Na1	0.7479(8)	0.407(1)	0.1741(7)	4.2(3) *

Starred atoms were refined isotropically. $B_{eq} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2)\ ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE IV Positional and thermal parameters for $[MoW_2O_2(O_2CC_2H_5)_6(H_2O)_3]ZnCl_4 \cdot 2H_2O$, **3**

Atom	*x/a*	*y/b*	*z /c*	$B_{eq}(Å^2)$
MW1	1.0097(0)	0.0000(0)	1.0078(0)	0.87(1)
MW2	1.24748(7)	0.0000(0)	1.14908(7)	0.95(1)
MW3	1.23903(7)	0.0000(0)	0.89601(7)	0.99(1)
O1	1.1660(6)	0.0780(4)	1.0170(6)	1.0(1)
O2	0.9642(7)	0.0896(5)	1.1429(7)	1.5(1)
O3	1.1371(7)	0.0877(5)	0.7791(6)	1.4(1)
O4	0.9516(6)	−0.0894(4)	0.8710(6)	1.1(1)
O5	0.8042(9)	0.0000(0)	0.995(1)	2.0(2)
O6	1.360(1)	0.0000(0)	1.3310(9)	1.9(2) *
O7	1.1566(6)	0.0893(5)	1.2528(7)	1.5(1)
O8	1.3948(6)	0.0910(4)	1.1373(7)	1.5(1) *
O9	1.3896(6)	0.0913(5)	0.9321(7)	1.5(1)
O10	1.3367(9)	0.0000(0)	0.7392(8)	1.7(2)
C1	1.022(1)	0.1164(6)	0.7888(9)	1.2(2)
C2	1.0405(9)	0.1152(6)	1.2323(8)	0.9(2)
C3	1.431(1)	0.1199(7)	1.038(1)	1.8(2)
C4	0.972(1)	0.1805(8)	0.695(1)	2.5(2)
C5	0.995(1)	0.1795(7)	1.321(1)	1.9(2)
C6	1.523(1)	0.1954(8)	1.047(1)	2.5(2)
C7	0.840(1)	0.2214(9)	0.715(1)	3.5(3)
C8	0.854(1)	0.2081(8)	1.298(1)	2.8(3)
C9	1.627(1)	0.1927(7)	0.960(1)	3.0(2)
Zn1	0.1626(2)	0.5000(0)	0.5396(2)	1.78(3)
C11	0.3704(4)	0.5000(0)	0.4871(6)	3.8(1)
C12	0.1367(4)	0.5000(0)	0.7447(4)	3.3(1)
C13	0.0589(4)	0.3830(2)	0.4544(4)	4.19(8)
Ow1	0.183(1)	0.5000(0)	0.198(1)	3.8(3) *
Ow2	0.193(2)	0.0000(0)	0.527(2)	6.5(5) *

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the same form as in Table III.

TABLE V Positional and thermal parameters for $Na_2Cr_2[MoW_2O_4(O_2CC_2H_5)_8]_2$, **4**

Atom	*x*	*y*	*z*	$B_{eq}(Å^2)$
M1	0.95281(3)	0.35673(3)	0.28073(3)	2.207(9)
M2	1.12733(3)	0.28070(3)	0.39499(3)	2.202(9)
M3	0.93470(3)	0.23913(3)	0.39134(4)	2.216(9)
Cr1	1.2224(1)	0.5562(1)	0.5659(1)	3.04(4)
O1	0.9665(5)	0.2057(5)	0.2352(5)	3.4(2)
O2	1.1148(5)	0.4275(5)	0.4259(5)	3.1(1)
O3	0.8996(5)	0.3787(5)	0.4100(5)	3.1(2)
O4	1.0965(5)	0.2810(5)	0.5323(5)	3.2(2)
O11	0.7923(5)	0.3131(6)	0.1179(6)	4.1(2)
O12	0.9173(5)	0.5022(5)	0.2811(5)	3.4(2)
O13	1.0178(5)	0.3506(6)	0.1516(6)	4.1(2)
O14	0.7651(8)	0.1601(7)	−0.0362(8)	7.3(3)
O21	1.1771(6)	0.1429(5)	0.3630(6)	4.0(2)
O22	1.3085(5)	0.3334(5)	0.5296(6)	3.6(2)
O23	1.1787(6)	0.2929(6)	0.2592(6)	4.3(2)
O24	1.1042(7)	0.0479(6)	0.1479(7)	5.2(2)
O31	0.9248(6)	0.0897(5)	0.3668(6)	4.1(2)
O32	0.7504(6)	0.1873(6)	0.2582(7)	4.7(2)
O33	0.8941(6)	0.2544(5)	0.5414(6)	4.5(2)
O34	0.8661(9)	−0.0159(7)	0.1590(8)	7.9(3)
O41	1.3562(5)	0.4961(5)	0.5539(6)	3.9(2)
O42	0.8051(5)	0.3918(5)	0.5718(6)	3.9(2)
O43	0.7518(5)	0.4999(5)	0.2981(6)	3.7(2)
O44	0.6594(6)	0.3180(5)	0.2965(7)	4.2(2)
C11	0.7327(9)	0.2386(8)	0.002(1)	4.6(3)
C12	0.614(1)	0.263(1)	−0.085(1)	8.4(5)
C13	0.547(2)	0.188(2)	−0.221(2)	11.5(8)
C14	0.8156(8)	0.5251(8)	0.2562(8)	3.4(2)
C15	0.7704(8)	0.5860(9)	0.1689(9)	4.7(3)
C16	0.651(1)	0.614(1)	0.144(1)	7.9(4)
C17	1.1125(8)	0.3164(8)	0.1634(9)	4.1(3)
C18	1.1436(9)	0.309(1)	0.058(1)	6.6(4)
C19	1.271(1)	0.296(2)	0.098(1)	10.5(6)
C21	1.1564(9)	0.0577(9)	0.2631(9)	4.3(3)
C22	1.205(1)	0.970(1)	0.305(1)	7.1(4)
C23	1.332(2)	0.003(1)	0.418(2)	10.3(6)
C(24)	1.3819(8)	0.4090(8)	0.5551(9)	3.6(2)
C25	1.5063(9)	0.396(1)	0.587(1)	5.9(4)
C26	1.507(1)	0.294(1)	0.493(2)	9.3(6)
C31	0.890(1)	−0.0031(9)	0.270(1)	5.1(3)
C32	0.882(1)	−0.092(1)	0.310(1)	6.6(4)
C33	0.785(2)	−0.092(2)	0.342(2)	12.2(7)
C34	0.8552(8)	0.3207(8)	0.6038(9)	4.1(3)
C35	0.871(1)	0.311(1)	0.730(1)	6.6(3)
C36	0.853(1)	0.400(1)	0.823(1)	9.3(5)
C37	0.6576(8)	0.2253(8)	0.2381(9)	4.0(3)
C38	0.541(1)	0.151(1)	0.135(1)	6.7(4)
C39	0.507(2)	0.085(2)	0.188(2)	16.4(9)
Na1	0.8991(4)	0.0620(4)	0.0435(4)	4.9(1)

Equivalent thermal parameter are in the same form as in Table III.

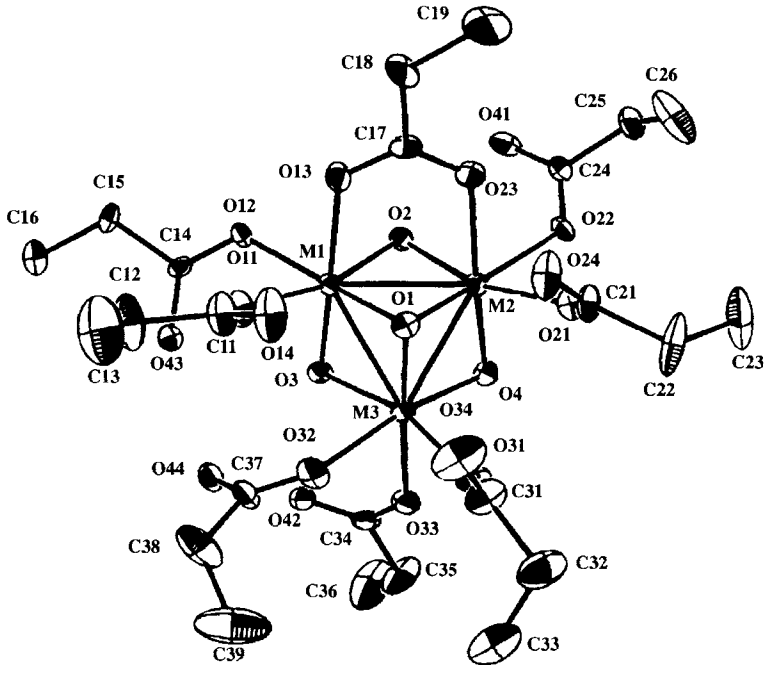

FIGURE 3 Structure of $[MoW_2O_4(O_2CC_2H_5)_8]^{4-}$ with 50% probability thermal ellipsoids.

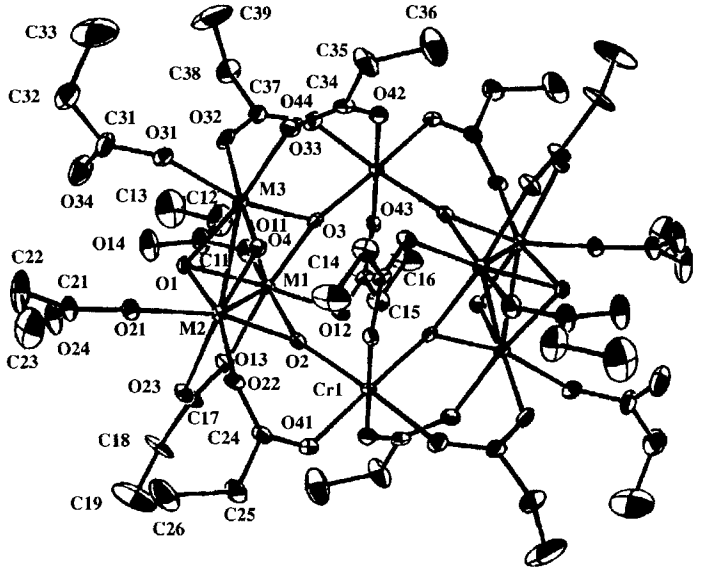

FIGURE 4 Structure of $Cr_2[MoW_2O_2(O_2CC_2H_5)_8]_2^{2-}$ with 50% probability thermal ellipsoids.

Acknowledgments

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SUPPLEMENTARY DATA

Full lists of H atom positions, bond lengths and angles, anisotropic thermal parameters and observed and calculated structure factors are available from the authors upon request.