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Notes

Syntheses, Structures, and Properties of New Aluminum(III)−Molybdenum(IV) Heterometallic Clusters $M_2Al_2[Mo_3O_4(O_2CR)_8]_2 \cdot nRCO_2H$ (M = Na, K; R = Me, Et; *n* = 0, 1)

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Introduction

Of the known kinds of triangular metal−metal-bonded cluster compounds,[1−3] the incomplete cubane-type $[M_3O_4L_9]$ (M_3 = Mo_3,[4,5] Mo_2W,[6] W_3[7]) is one of the most commonly encountered. Their syntheses, structures, spectroscopy, dynamics, electrochemistry, and electronic structures have been subjects of numerous reports.[4−9] Such species contain a basic incomplete cuboidal $[M_3O_4]^{4+}$ unit which is surrounded by terminal L ligands (L = O, H_2O, $C_2O_4^{2-}$, NCS^-, edta, mida, F^-, [9]aneN_3) to complete the octahedral coordination of each metal atom (without counting M−M bonds). An alkylidyne-capped derivative with terminal pivalato ligands was also reported, which was trapped by three chromium(III) ions to form the hexanuclear cluster $W_3(CCH_2CMe_3)O_3Cr_3(O_2CCMe_3)_{12}$.[10]

Table 1. Crystallographic Data for $Na_2Al_2[Mo_3O_4(O_2CEt)_8]_2$ (**1**) and $Na_2Al_2[Mo_3O_4(O_2CCH_3)_8]_2 \cdot CH_3CO_2H$ (**2**)

empirical formula	$Al_2Mo_6O_{40}C_{48}H_{80}Na_2$	$Al_2Mo_6O_{42}C_{34}H_{51}Na_2$
fw	1972.73	1807.34
space group (No. 2)	$P\bar{1}$	$P\bar{1}$
a, Å	13.008(8)	11.528(8)
b, Å	13.896(10)	13.713(11)
c, Å	12.133(15)	11.246(9)
α, deg	109.46(9)	104.20(8)
β, deg	117.01(6)	110.86(6)
γ, deg	90.21(7)	70.10(8)
V, Å^3	1810.7	1546
Z	1	1
D_{calcd}, g cm^{-3}	1.81	1.94
T, °C	25	25
λ, Å	0.710 69	0.710 69
μ, cm^{-1}	11.1	12.9
$R(F_o)^a$	0.053	0.053
$R_w(F_o)^b$	0.064	0.062

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$.

Herein we wish to report the syntheses, structures, and properties of the three new aluminum(III)−molybdenum(IV) heterooctametallic clusters $M_2Al_2[Mo_3O_4(O_2CR)_8]_2 \cdot nRCO_2H$ (M = Na, R = Et, *n* = 0 (**1**); M = Na, R = Me, *n* = 1 (**2**); M = K, R = Et (**3**)), which possess the two incomplete cubane-type cluster units $[Mo_3O_4(O_2CR)_8]^{4-}$ bridged with two Al(III) ions. In contrast to the derivatives bridged by Cr(III) (M = Mo (**4**), W (**5**)), V(III) (M = Mo (**6**), W (**7**)), Fe(III) (M = Mo (**8**), W (**9**)) and Mo(III) (M_3 = MoW_2 (**10**), W_3 (**11**)) reported previously,[11−13] the present clusters are diamagnetic and soluble (M = K (**3**)). This work may be of additional interest in that Al-containing oxides and carboxylates have been known to have many uses in catalytic, ceramic, paper, textile, and pharmaceutical industries.[14]

Experimental Section

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

Syntheses. $Na_2Al_2[Mo_3O_4(O_2CEt)_8]_2$ (1). A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.96 g, 4.0 mmol), $Mo(CO)_6$ (0.53 g, 2.0 mmol), $AlCl_3$ (0.27 g, 2.0 mmol), and propionic anhydride (40 mL) was heated at 120 °C for 2 days. After the mixture was cooled to room temperature, well-formed black crystals of **1** (1.21 g, 61%) were isolated. IR (cm^{-1}): 811 (s), 791 (vs), 762 (s) [$\nu(Mo_3O_4)$].

$Na_2Al_2[Mo_3O_4(O_2CMe)_8]_2 \cdot MeCO_2H$ (2). $Na_2MoO_4 \cdot 2H_2O$ (0.96 g, 4.0 mmol) was refluxed in acetic anhydride (30 mL) for 3 h. To the solution obtained were added $Mo(CO)_6$ (0.53 g, 2.0 mmol), $AlCl_3$ (0.27 g, 2.0 mmol), and CH_3CO_2Na (0.1 g), and the resulting mixture was heated at 120 °C for 3 days. After the mixture was cooled to room temperature, well-formed black crystals of cluster **1** (0.31 g, 17%) were isolated.

$K_2Al_2[Mo_3O_4(O_2CEt)_8]_2 \cdot nEtCO_2H$ (3). Cluster **3** was prepared similarly to **1** using K_2MoO_4 with about 10% yield. IR (cm^{-1}): 810 (s), 791 (vs), 765 (s) [$\nu(Mo_3O_4)$]..

X-ray Crystallography. The crystallographic data for **1** and **2** are summarized in Table 1. The structures were solved by direct methods using MULTAN11/82 and refined by full-matrix least-squares proce-

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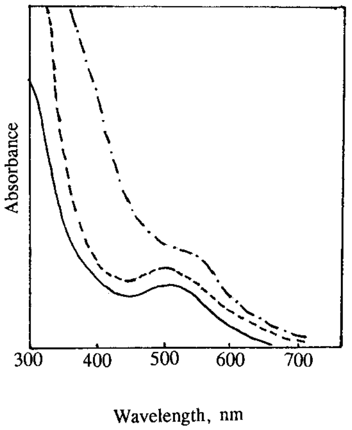

Figure 1. UV−vis spectra of **1** in HCl (2 M) (—) and DMF (—•—) solutions. The spectrum in HCl solution is very similar to that of the $[Mo_3O_4]^{4+}$ ion (- - -).

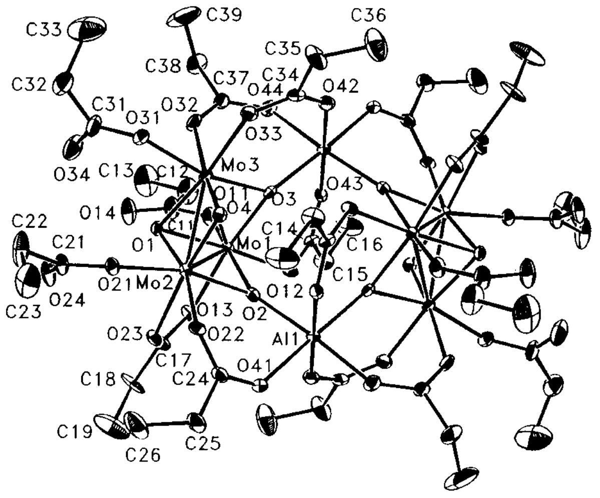

Figure 2. ORTEP drawing of the cluster dianion of **1** with 50% probability thermal ellipsoids.

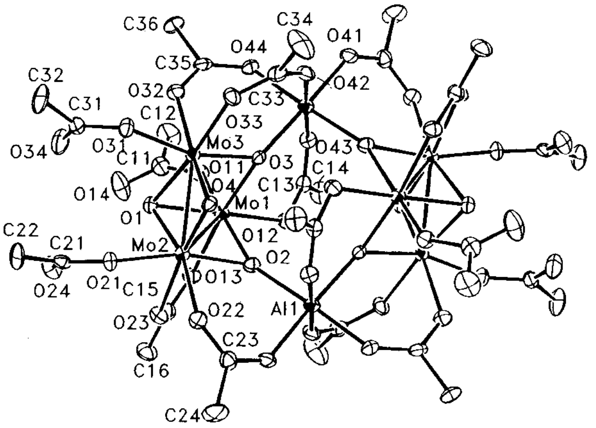

Figure 3. ORTEP drawing of the cluster dianion of **2** with 50% probability thermal ellipsoids.

dures with all non-hydrogen atoms anisotropic except those of **2**, for which a molecule of acetic acid was refined isotropically. The refinement of the acetic acid molecule of **2** based on a multiplicity of 1.0 would lead to the high-temperature factors (B_{eq} is about 25) of the oxygen atoms. On the basis of a refinement of the occupancy, a multiplicity of 0.5 was used and gave reasonable temperature factors. The highest peak in the final difference Fourier map for **2** was located around the disordered acetic acid molecule. All calculations were performed on a VAX-786 computer using the SDP program package with scattering factors taken from the *International Tables*.

Physical Methods. UV−vis spectra and IR spectra were obtained on Schimadzu UV-3000 and Digilab FTS-40 spectrophotometers.

Table 2. Positional and Thermal Parameters with Esd's for **1**

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Mo1	0.95308(8)	0.35993(7)	0.28378(8)	2.32(2)
Mo2	1.12277(8)	0.27993(7)	0.39556(8)	2.37(2)
Mo3	0.93340(8)	0.24274(7)	0.39558(9)	2.55(2)
Al1	1.2195(3)	0.5515(2)	0.5601(3)	2.63(8)
O1	0.9648(6)	0.2091(5)	0.2390(6)	3.1(2)
O2	1.1130(5)	0.4264(5)	0.4280(6)	2.4(2)
O3	0.8978(5)	0.3814(5)	0.4112(6)	2.1(2)
O4	1.0913(6)	0.2811(5)	0.5341(6)	2.6(2)
O11	0.7936(6)	0.3181(6)	0.1199(7)	3.5(2)
O12	0.9169(6)	0.5065(5)	0.2816(6)	2.7(2)
O13	1.0194(6)	0.3531(6)	0.1504(6)	3.2(2)
O14	0.7706(8)	0.1653(7)	−0.0349(8)	6.2(3)
O21	1.1707(6)	0.1399(5)	0.3620(6)	3.4(2)
O22	1.3045(5)	0.3286(5)	0.5262(6)	2.8(2)
O23	1.1753(6)	0.2894(5)	0.2563(6)	3.1(2)
O24	1.1008(7)	0.0450(6)	0.1490(7)	4.4(2)
O31	0.9231(6)	0.0934(5)	0.3741(7)	3.8(2)
O32	0.7518(6)	0.1926(6)	0.2662(7)	3.9(2)
O33	0.8937(6)	0.2607(5)	0.5512(6)	3.5(2)
O34	0.866(1)	−0.0114(7)	0.1653(9)	7.5(4)
O41	1.3423(6)	0.4910(5)	0.5450(6)	3.1(2)
O42	0.8072(6)	0.4002(5)	0.5769(6)	3.1(2)
O43	0.7579(6)	0.5020(5)	0.3061(6)	2.8(2)
O44	0.6660(6)	0.3299(6)	0.3082(7)	3.5(2)
C11	0.737(1)	0.2443(9)	0.004(1)	3.7(3)
C12	0.619(1)	0.270(1)	−0.080(1)	6.0(5)
C13	0.549(1)	0.189(1)	−0.216(2)	7.7(6)
C14	0.8173(9)	0.5269(8)	0.2596(9)	2.6(3)
C15	0.7661(9)	0.5827(8)	0.163(1)	3.5(3)
C16	0.648(1)	0.607(1)	0.142(1)	6.7(4)
C17	1.1131(9)	0.3178(9)	0.164(1)	3.7(3)
C18	1.142(1)	0.305(1)	0.052(1)	5.7(4)
C19	1.264(1)	0.288(2)	0.090(1)	9.6(6)
C21	1.154(1)	0.0546(9)	0.263(1)	4.2(3)
C22	1.204(1)	0.9687(9)	0.307(1)	6.0(4)
C23	1.329(1)	0.003(1)	0.420(2)	9.1(7)
C24	1.3740(9)	0.4062(8)	0.5492(9)	3.0(3)
C25	1.4991(9)	0.3965(9)	0.588(1)	4.9(4)
C26	1.507(1)	0.296(2)	0.494(2)	10.4(7)
C31	0.889(1)	0.0019(9)	0.277(1)	4.4(4)
C32	0.879(1)	−0.0895(9)	0.315(1)	6.3(5)
C33	0.774(2)	−0.099(1)	0.325(2)	12.8(6)
C34	0.8549(9)	0.3284(8)	0.6104(9)	3.2(3)
C35	0.867(1)	0.322(1)	0.737(1)	7.3(4)
C36	0.847(2)	0.404(1)	0.827(1)	8.6(6)
C37	0.6632(9)	0.2338(8)	0.247(1)	3.5(3)
C38	0.541(1)	0.168(1)	0.145(2)	7.2(6)
C39	0.515(2)	0.086(2)	0.178(3)	14.95(5)
Na1	0.8995(4)	0.0648(3)	0.0426(4)	4.0(1)

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

Results and Discussion

Redox reactions of $M^0(CO)_6$ and $M^{VI}O_4^{2-}$ (M = Mo, W) in refluxing carboxylic anhydride are an effective route to trinuclear dioxo-capped carboxylate clusters of molybdenum(IV) and tungsten(IV).[15−19] This reaction system was recently successfully extended to the preparation of the Mo(IV) [or W(IV)]−Cr(III) [or V(III)] mixed-metal clusters **4**−**7** using $Cr(CO)_6$ or $NaVO_3$ in place of $M(CO)_6$ or Na_2MO_4 in heating (120 °C) instead of refluxing propionic anhydride.[11,12] The formation

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(18) $Na[MoW_2O_2(O_2CMe)_9]\cdot 2H_2O$ prepared by the reaction of $Na_2WO_4\cdot 2H_2O$ and $Mo(CO)_6$ in refluxing acetic anhydride has been confirmed by a UV−vis spectrum similar to that of $[MoW_2O_2(O_2CMe)_6(H_2O)_3]^{2+}$ [20] and an X-Ray structure determination, details of which will be published elsewhere.

Table 3. Positional and Thermal Parameters with Esd's for **2**

atom	*x*	*y*	*z*	B_{eq}, Å^2
Mo1	0.29035(7)	0.13605(6)	0.44619(8)	2.00(2)
Mo2	0.38015(7)	0.27205(6)	0.61310(8)	2.00(2)
Mo3	0.42051(7)	0.22866(6)	0.39773(8)	2.00(2)
Al1	0.4783(3)	−0.0354(2)	0.2520(3)	2.22(6)
O1	0.2484(5)	0.2893(4)	0.4403(6)	2.3(1)
O2	0.4082(5)	0.1231(5)	0.6203(6)	2.2(1)
O3	0.4350(5)	0.0796(4)	0.3765(5)	1.9(1)
O4	0.5335(5)	0.2434(4)	0.5688(5)	2.1(1)
O11	0.1480(5)	0.1272(5)	0.2771(6)	2.6(2)
O12	0.2856(5)	−0.0189(4)	0.4276(6)	2.5(2)
O13	0.1394(5)	0.1797(5)	0.5301(6)	2.7(2)
O14	−0.0133(7)	0.2758(6)	0.2620(9)	5.4(3)
O21	0.3451(5)	0.4295(4)	0.6467(6)	2.4(2)
O22	0.4824(6)	0.2896(5)	0.8122(6)	2.7(2)
O23	0.2218(5)	0.2965(5)	0.6847(6)	2.8(2)
O24	0.1344(6)	0.5044(5)	0.5761(7)	3.4(2)
O31	0.4091(6)	0.3703(5)	0.3662(6)	2.8(2)
O32	0.3213(6)	0.2158(5)	0.1997(6)	2.9(2)
O33	0.5937(5)	0.1781(5)	0.3453(6)	2.9(2)
O34	0.2030(6)	0.4659(5)	0.3139(7)	4.5(2)
O41	0.4865(6)	0.1458(5)	0.8765(6)	2.9(2)
O42	0.6200(5)	0.0069(5)	0.2622(6)	2.7(2)
O43	0.3398(5)	−0.0823(5)	0.2468(6)	2.4(2)
O44	0.3663(6)	0.0447(5)	0.1205(6)	2.9(2)
C11	0.0377(9)	0.1861(8)	0.220(1)	3.3(3)
C12	−0.033(1)	0.133(1)	0.095(1)	5.0(4)
C13	0.2794(8)	−0.0782(7)	0.3221(9)	2.3(2)
C14	0.1921(8)	−0.1497(7)	0.284(1)	3.4(3)
C15	0.1349(9)	0.2481(7)	0.6258(9)	2.8(2)
C16	0.0192(9)	0.2760(9)	0.673(1)	3.8(3)
C21	0.2458(8)	0.5101(8)	0.6173(8)	2.5(2)
C22	0.276(1)	0.6130(7)	0.641(1)	3.6(3)
C23	0.4954(9)	0.2376(8)	0.898(1)	3.0(3)
C24	0.520(1)	0.2918(9)	1.035(1)	5.2(4)
C31	0.3166(9)	0.4557(7)	0.3338(9)	3.0(2)
C32	0.365(1)	0.5409(7)	0.321(1)	4.4(3)
C33	0.6580(9)	0.0883(8)	0.3045(9)	3.2(2)
C34	0.7972(9)	0.077(1)	0.312(1)	5.9(4)
C35	0.3123(8)	0.1390(8)	0.1090(8)	2.7(2)
C36	0.227(1)	0.1674(9)	−0.0242(9)	3.8(3)
Na1	0.0555(3)	0.4189(3)	0.3653(4)	3.2(1)
O51	−0.036(2)	0.454(2)	0.106(2)	9.6(7)[a]
O52	−0.155(2)	0.529(2)	−0.031(3)	11.2(8)[a]
C51	−0.144(2)	0.478(2)	0.049(2)	4.5(5)[a]
C52	−0.238(2)	0.460(2)	0.073(2)	4.5(5)[a]

[a] Atoms were refined isotropically.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

1		**2**	
Mo1−Mo2	2.500(1)	Mo1−Mo2	2.507(1)
Mo1−Mo3	2.518(1)	Mo1−Mo3	2.526(1)
Mo2−Mo3	2.515(2)	Mo2−Mo3	2.519(1)
Mo1−O1	2.007(7)	Mo1−O1	2.001(6)
Mo1−O2	1.961(7)	Mo1−O2	1.956(7)
Mo1−O3	1.924(7)	Mo1−O3	1.936(7)
Mo1−O11	2.018(8)	Mo1−O11	2.031(7)
Mo1−O12	2.098(7)	Mo1−O12	2.101(6)
Mo1−O13	2.130(8)	Mo1−O13	2.112(7)
Mo2−O1	1.999(8)	Mo2−O1	2.004(7)
Mo2−O2	1.957(8)	Mo2−O2	1.974(6)
Mo2−O4	1.897(8)	Mo2−O4	1.894(7)
Mo2−O21	2.013(8)	Mo2−O21	2.020(6)
Mo2−O22	2.105(8)	Mo2−O22	2.124(8)
Mo2−O23	2.130(8)	Mo2−O23	2.142(6)
Mo3−O1	2.027(8)	Mo3−O1	2.053(6)
Mo3−O3	1.951(7)	Mo3−O3	1.954(6)
Mo3−O4	1.894(7)	Mo3−O4	1.909(7)
Mo3−O31	1.999(8)	Mo3−O31	2.012(6)
Mo3−O32	2.103(8)	Mo3−O32	2.105(7)
Mo3−O33	2.113(8)	Mo3−O33	2.124(6)
Al1−O2	1.902(8)	Al1−O2	1.912(8)
Al1−O3	1.896(8)	Al1−O3	1.891(7)
Al1−O41	1.861(9)	Al1−O41	1.863(7)
Al1−O42	1.885(8)	Al1−O42	1.870(7)
Al1−O43	1.909(8)	Al1−O43	1.892(7)
Al1−O44	1.885(9)	Al1−O44	1.880(7)
O1−Na1	2.321(9)	O1−Na1	2.351(7)
O14−Na1	2.26(2)	O14−Na1	2.26(1)
O24−Na1	2.40(2)	O24−Na1	2.377(9)
O24−Na1	2.31(2)	O24−Na1	2.336(9)
O34−Na1	2.27(1)	O34−Na1	2.296(9)
O1−Mo1−O2	101.3(3)	O1−Mo1−O2	101.8(3)
O1−Mo1−O3	100.9(3)	O1−Mo1−O3	101.4(3)
O2−Mo1−O3	90.8(3)	O2−Mo1−O3	90.6(3)
O1−Mo2−O2	101.8(3)	O1−Mo2−O2	101.1(3)
O1−Mo2−O4	99.0(3)	O1−Mo2−O4	100.2(3)
O2−Mo2−O4	93.4(4)	O2−Mo2−O4	92.7(3)
O1−Mo3−O3	99.3(3)	O1−Mo3−O3	99.0(2)
O1−Mo3−O4	98.1(3)	O1−Mo3−O4	98.0(3)
O3−Mo3−O4	98.6(3)	O3−Mo3−O4	98.9(3)
O2−Al1−O3	94.2(3)	O2−Al1−O3	92.7(3)
O2−Al1−O41	89.4(4)	O2−Al1−O41	89.9(3)
O2−Al1−O42	88.8(4)	O2−Al1−O42	87.9(3)
O2−Al1−O43	89.1(3)	O2−Al1−O43	89.7(4)
O2−Al1−O44	175.9(4)	O2−Al1−O44	177.1(3)
O3−Al1−O41	175.8(4)	O3−Al1−O41	177.2(3)
O3−Al1−O42	91.2(3)	O3−Al1−O42	90.0(4)
O3−Al1−O43	88.8(3)	O3−Al1−O43	90.3(3)
O3−Al1−O44	89.8(4)	O3−Al1−O44	89.9(4)
O41−Al1−O42	91.1(4)	O41−Al1−O42	91.2(3)
O41−Al1−O42	89.1(4)	O41−Al1−O43	88.7(3)
O41−Al1−O44	86.6(4)	O41−Al1−O44	87.4(3)
O42−Al1−O43	177.8(4)	O42−Al1−O43	177.5(4)
O42−Al1−O44	92.2(5)	O42−Al1−O44	93.1(3)
O43−Al1−O44	90.0(4)	O43−Al1−O44	89.3(3)

of these species may be understood on the grounds that reduction of Na_2MO_4 or oxidation of $M(CO)_6$ produced the incomplete cuboidal units $[M_3O_4(O_2CEt)_8]^{4-}$ which were trapped by Cr^{3+} (or V^{3+}) and Na^+ ions in the reaction to form the insoluble chain products. These reported synthetic methods are, however, limited and are not adaptable to the preparation of, for example, the present Al(III)-bridged clusters. We thus consider using the redox reaction of Na_2MoO_4 and $Mo(CO)_6$ to produce $[Mo_3O_4(O_2CEt)_8]^{4-}$ ions which are expected to be trapped by Al^{3+} and Na^+ ions in the reaction to yield Al(III)-bridged derivatives. As might be expected, reaction of Na_2MoO_4, $Mo(CO)_6$, and $AlCl_3$ has produced the desired Al(III)-bridged cluster **1** as well-formed black crystals in excellent yield. The acetate **2** is prepared similarly using acetic anhydride but in low yield due to the simultaneous formation of a considerable amount of the insoluble dioxo-capped cluster $Na[Mo_3O_2(O_2CMe)_9]$.[15] The potassium salt **3**, which has been confirmed by the IR spectrum identical to that of **1**, can also be prepared similarly to **1** using K_2MoO_4. However, the considerable solubility in the reaction solution as will be described leads to a low yield.

The structures of the cluster dianions, $Al_2[Mo_3O_4(O_2CR)_8]_2^{2-}$ (R = Et (**1**), Me (**2**)) are shown in Figures 2 and 3, respectively. Atomic coordinates and selected bond lengths and angles for **1** and **2** are listed in Tables 2−4. Table 5 summarizes some important mean bond lengths of **1, 2, 4−11**, and related complexes for a structural comparison. As expected, the structures are identical to those of **4−7** reported.[11,12] The Al−

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Table 5. Comparison of Mean Bond Lengths (Å) in Clusters **1, 2**, **4−11**, and Related Complexes

complex	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
$Na_2Al_2[Mo_3O_4(O_2CCH_3)_8]_2$ (**1**)	2.518(1)	1.908(7)	1.957(7)	2.022(7)	2.023(7)	2.121(7)	1.901(8)	1.877(8)	this work
$Na_2Al_2[Mo_3O_4(O_2CC_2H_5)_8]_2$ (**2**)	2.511(2)	1.895(8)	1.948(8)	2.010(8)	2.011(8)	2.113(8)	1.896(8)	1.885(8)	this work
$Na_2Cr_2[Mo_3O_4(O_2CC_2H_5)_8]_2$ (**4**)	2.5198(9)	1.907(4)	1.952(5)	2.010(4)	2.026(4)	2.114(5)	1.947(4)	1.973(5)	11,12
$Na_2Cr_2[W_3O_4(O_2CC_2H_5)_8]_2$ (**5**)	2.5313(9)	1.927(9)	1.972(8)	2.012(9)	2.059(9)	2.110(9)	1.929(8)	1.986(9)	11,12
$Na_2V_2[Mo_3O_4(O_2CC_2H_5)_8]_2$ (**6**)	2.519(1)	1.905(6)	1.953(6)	2.005(6)	2.026(7)	2.119(8)	1.985(6)	1.989(8)	11,12
$Na_2V_2[W_3O_4(O_2CC_2H_5)_8]_2$ (**7**)	2.5328(6)	1.926(6)	1.974(6)	2.013(6)	2.057(6)	2.107(7)	1.962(6)	2.012(6)	11,12
$Na_2Fe_2[Mo_3O_4(O_2CC_2H_5)_8]_2$ (**8**)	2.517(1)	1.915(7)	1.957(7)	2.010(8)	2.027(7)	2.121(8)	1.992(8)	1.993(8)	13
$Na_2Fe_2[W_3O_4(O_2CC_2H_5)_8]_2$ (**9**)	2.535(1)	1.92(1)	1.98(2)	2.02(2)	2.04(2)	2.11(2)	1.98(2)	2.02(2)	13
$Na_2Mo_2[M_3O_4(O_2CC_2H_5)_8]_2$ (**10**)	2.520(1)	1.909(9)	1.959(9)	2.011(9)	2.034(9)	2.104(9)	2.028(6)	2.079(9)	13
$Na_2Mo_2[W_3O_4(O_2CC_2H_5)_8]_2$ (**11**)	2.530(2)	1.90(2)	1.97(2)	1.99(2)	2.06(2)	2.10(3)	2.03(2)	2.10(2)	13
$[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$	2.493(3)	1.915(7)			2.020(3)				5f
$[Mo_2WO_4(NCS)_9]^{4-}$	2.521(5)	1.891(15)			2.021(14)				6a
$[W_3O_4(NCS)_9]^{4-}$	2.534	1.911			2.039				7a
$[Al(ox)_3]^{3-}$							1.911(4)		21
$[Cr_3O(O_2CEt)_6F_3]^{2-}$							1.909(4)	1.974(3)	22
$[V_3O(O_2CMe)_8(THF)_3]$							1.910(6)	2.00(2)	23
$[Fe_3O(O_2CCMe_3)_6(MeOH)_3]^{+}$							1.905(5)	2.02(2)	24

[a] Bridging M atom. [a] Bridging M and M′ atoms. [c] Terminal $C_2H_5CO_2$. [d] Capping O atoms. [e] Bridging $C_2H_5CO_2$.

O_{ca} (O_2CEt) bond lengths in **1** and **2**, which are close to those in $[Al(ox)_3]^{3-}$,[21] are nearly equal to the Al−O_b* (O2 or O3) bonds, similar to the situations in **6−8** but unlike those in **4** and **5**, where the Cr−O_b* bonds are significantly shorter than the Cr−O_{ca} bonds. This may be assignable to different degrees of the M′−O_b* d−p π bonds.

The acetate **2** contains an acetic acid molecule that is weakly bound to Na^+ (Na−O = 2.83 Å). The remaining Na−O bonds [average 2.32(1) Å] are similar to those in **1** and **4−11** [average 2.31(1) Å].

Clusters **1−3** are all air stable, like **4** and **5** but in contrast to **6−11**, which are stable in air for only about 1 month. These species have different degrees of solubility or stability in acid solution. Clusters **1−3** dissolve in HCl (2 M) to produce red solutions. Interestingly, as shown in Figure **1**, the UV−vis spectrum is identical to that of red $[Mo_3O_4]^{4+}$ aqua ion reported previously,[5,6] suggesting occurrence of cleavage of the Al−O bonds and formation of isolated $[Mo_3O_4]^{4+}$ units. A similar situation applies for **6** and **8** although the peak at $\lambda_{max} = 510$ nm for **8** is not obvious, presumably caused by the effect of Fe^{3+} ions. In contrast, **4** only slowly dissolves upon heating in HCl solution and **5** is not soluble, displaying considerably higher stability in acid solution. This may be attributed to the stronger Cr−O bonding enhanced by the crystal field stabilization energy.

In contrast to the sodium salts (**1, 2, 4−9**), which are all insoluble in water and common organic solvents such as THF, DMF, or EtOH at room temperature, as expected for rather strong Na−O bonds of considerable covalence (ca. 2.31 Å vs 2.42 Å for a Na−O bond) in the infinite-chain structure, the potassium salt **3** can be easily dissolved in these solvents because of the weaker K−O ionic bonds. Nevertheless, **1−9** can all be slowly dissolved upon heating (>80 °C) in DMF, giving brown solutions, unlike the situations in acid solution as described above. These indicate that the dissolution results from cleavage of the Na(K)−O bonds only. The UV−vis spectrum of **1** in DMF solution given in Figure 1, similar to that of **3**, shows a peak at $\lambda_{max} = 560$ nm (sh) which differs clearly from that of **1** in HCl solution perhaps because of the retention of the Al−O bonds and solvent effects. Such a peak is not observed in the spectra of the V, Cr, and Fe complexes.

Cyclic voltammetry measurements of **1**−3 in DMF solution with 0.1 M Bu_4NBF_4 as supporting electrolyte show no evident redox signal in the range −1.5 to +1.5 V vs SCE, indicating the high resistance toward oxidation and reduction. This is unlike the situation in acid solution of the $[Mo_3O_4]^{4+}$ ion, where the three-electron redox process readily occurs.[8]

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Supporting Information Available: Listings of detailed crystallographic data, complete bond lengths and angles, and thermal parameters for **1** and **2** (9 pages). Ordering information is given on any current masthead page.

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