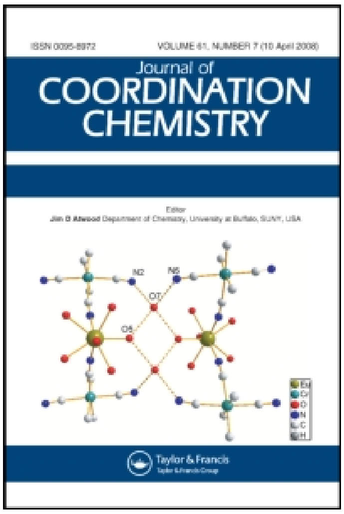

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Yong Cui[a]; Jin-Shun Huang[a]
[a] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian, P.R. China

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PREPARATION, STRUCTURE AND PROPERTIES OF THE ONE-DIMENSIONAL POLYMERIC COMPLEX $Na_2[AlW_3O_4(O_2CEt)_8]_2$

YONG CUI and JIN-SHUN HUANG*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, Fujian, 350002, P.R. China

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The heterometallic polymeric cluster $Na_2[AlW_3O_4(O_2CEt)_8]_2$ (**1**) has been prepared by reaction of $W(CO)_6$ and $NaWO_4 \cdot 2H_2O$ with $AlCl_3$ at 120°C in propionic anhydride and characterized by X-ray crystallography, with the following crystal data: triclinic, space group $P1$, $a = 12.205(5)$, $b = 13.032(4)$, $c = 13.925(3)$ Å, $\alpha = 90.21(3)°$, $\beta = 109.53(5)°$, $\gamma = 117.26(6)°$, $V = 1822.8(1)$ Å^3, $Z = 1$, $R = 0.038$ and $R_w = 0.101$. The structure consists of two triangular $[W_3O_4(O_2CEt)_8]^{4-}$ cluster unit, which act as polydenate ligands to link Al^{3+} and Na^+ ions forming a one-dimensional chain structure. IR spectra show characteristic $[W_3O_4]^{4+}$ bands at 746–815 cm^{-1}. Thermal analysis reveals that the complex is air stable up to 250°C. Cluster **1** decomposes in hot aqueous 2 M HCl solution to produce discrete $[W_3O_4]^{4+}$ units.

Keywords: Aluminum; tungsten; cluster; carboxylate; crystal structure; polymeric complex

INTRODUCTION

Heterometallic chemistry of $[M_3S_4]^{4+}$ (M = Mo, W) cuboidal cluster units has been well established in recent years especially in aspects of synthesis, structure and bonding. Up to 16 heterometals have been incorporated into the units to give mixed-metal $[M'M_3S_4]$-type clusters of single, edge-linked or corner-shared double cube structures.[1–3] All such species were prepared directly from the addiction of $[M_3S_4]^{4+}$ units to metal elements or compounds. On the other hand, no similar reaction is established for similar $[M_3O_4]^{4+}$ units to form $[M'M_3O_4]$-type clusters. However, we recently

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* Corresponding author.

obtained a series of novel mixed-metal chain clusters, formulated as $Na_2[M'M_3O_4(O_2CEt)_8]_2$ (M = Mo, W; M′ = V, Cr, Mn, Fe, Mo), with two $[M_3O_4(O_2CEt)_8]^{4-}$ units bridged by two M′(III) metal ions via oxo and carboxylate groups forming cyclic cores, from the redox reaction system of MO_4^{2} and $M(CO)_6$.[4,5] The clusters $Na_2[CrM_3O_4(O_2CEt)_8]_2$ (M = Mo, W) are the first two examples of this type of compounds.[4] These clusters are of great interest because they not only introduce a new $[M'M_3O_4]$ ring chemistry as a counterpart of the well-studied $[M'M_3S_4]$ cubane-type cluster chemistry but also add to the extensive and developing chemistry of $[M_3O_4]$ cluster units, including for example $Zn_2Mo_3O_8$,[6] $[Mo_3O_4]^{4+}$,[7] $[Mo_2WO_4]^{4+}$[8] and $[W_3O_4]^{4+}$.[9] Very recently, some main group metals have also been successfully incorporated into this family in this laboratory and the Al–Mo, Ga–W and In–W species have been reported.[10] Herein we presented a new tungsten–aluminum mixed-metal derivative $Na_2[AlW_3O_4(O_2CEt)_8]_2$, and described its synthesis, X-ray structure and properties.

EXPERIMENTAL SECTION

All starting chemical reagents were commercially available and were of reagent grade. Elemental analyses were performed by the Analytic Chemistry Group of this Institute. The proportions of W, and Al were determined by ICP-AES and by atomic absorption on a Perkin-Elmer 306 spectrophotometer. IR spectra were recorded on a Digilab FTS-40 instrument. The thermogravimetric analysis was carried out using a Perkin-Elmer D5C-4 in air.

Synthesis of $Na_2[AlW_3O_4(O_2CEt)_8]_2$ (1)

A mixture of $NaWO_4 \cdot 2H_2O$ (1.33 g, 4.0 mmol), $W(CO)_6$ (0.70 g, 2.0 mmol) $AlCl_3$ (0.27 g, 2.0 mmol) and propionic anhydride (60 cm^3) was heated at 120°C for 4 days. After cooling the mixture to room temperature, well-formed black crystals of **1** were isolated. Yield: 0.61 g, 30%. *Anal.*: Calcd. for $C_{48}H_{80}O_{40}Al_2Na_2W_6$%: C, 23.06; H, 3.23; Al, 2.16; W, 44.12. Found: C, 22.98; H, 3.19; Al, 2.06; W, 43.84. IR (cm^{-1}): 1672 s, 1626 s, 1565 s, 1469 s, 1442 s, 1381 s, 1304 s, 1236 s [ν(C=O)], 813 s, 804 ms, 768 ms, 746 ms [$\nu(W_3O_4)$], 644 m [ν(Al–O)].

X-ray Crystallography

The intensity data for **1** were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo*Kα* radiation

TABLE I Crystallographic data for $Na_2[AlW_3O_4(O_2CEt)_8]_2$

Formula	$C_{48}H_{80}O_{40}Al_2Na_2W_6$
Crystal size (mm^3)	$0.30 \times 0.30 \times 0.20$
f. w.	2500.16
Crystal system	Triclinic
Space group	$P1$
a, Å	12.205(5)
b, Å	13.032(4)
c, Å	13.925(3)
α, deg	90.21(3)
β, deg	109.53(5)
γ, deg	117.26(5)
V, $Å^3$	1822.8(10)
Z	1
D_c $g\,cm^{-3}$	2.278
$\mu(MoK\alpha)$, cm^{-1}	9.556
$F(000)$	1180
$2\theta_{max}(°)$	50
h, k, l ranges	0 to 14, −15 to 13, −16 to 15
Unique reflections	6389
Observed reflections ($I > 2\sigma(I)$)	5162
No. of parameters	442
R	0.038
R_w[a]	0.101
S	1.039
$(\Delta/\sigma)_{max}$	0.001
$(\Delta/\rho)_{max}$	1.215

[a] $R_w = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0668P)^2)]$ with $P = (F_o^2 + 2F_c^2)/3$.

($\lambda = 0.71073$ Å) at 298 K and corrected for Lorentz and polarization using empirical scan data. Accurate unit cell dimensions were determined from least-square refinement of diffractionmeter angles for 20 automatically centred reflections. The structure was solved by direct methods, followed by heavy atom procedures, and refined by full-matrix least-squares techniques on F^2 with anisotropical thermal parameters for all non-hydrogen atoms. All calculations were performed on an HP/586 computer with the SHELXTL-PC program[14] with scattering factors taken from *International Tables for Crystallography* (Vol. C). The crystallographic data are summarized in Table I.

RESULTS AND DISCUSSION

Synthesis

Redox reactions of $M^0(CO)_6$ with $M^{VI}O_4^{2-}$ ($M = Mo$, W) in refluxing carboxylic anhydride is an effective route to the well-known trinuclear bioxo-capped carboxylate clusters of molybdenum(IV) and tungsten(IV).[11] Based on this kind of reaction, several different routes to the $Na_2[M'M_3O_4(O_2CEt)_8]_2$ system, including reactions of $NaMO_4$ and $Cr(CO)_6$, $NaVO_3$ and $Mo(CO)_6$, $Na[M_3O_2(O_2CEt)_9]$ and $Cr(CO)_6$, as well as $NaMO_4$, $M(CO)_6$ and $M'Cl_3$ (M = Mo, W) in hot propionic anhydride solution, have been described in our laboratory.[4,5,10] The formation of these species may be understood on the grounds of the reduction of $NaMO_4$ or oxidation of $M(CO)_6$ to produce the triangular cluster $[M_3O_4(O_2CEt)_8]^{4-}$ anions which are trapped by M'^{3+} and Na^+ ions to form chain products, where the M'^{3+} ions come from the corresponding redox reaction or starting materials $M'Cl_3$. The last route may be more general than the other three, because a far wider variety of metal(III) complexes are easily available compared to metallates or metal carbonyls. As expected, complex **1** was obtained readily from the redox reaction self-assembly of $NaWO_4$–$W(CO)_6$–$(EtCO)_2O$ in the presence of $AlCl_3$, indicative of the generality of the preparative method. The yield of **1** (30%) is much lower than that of the Al–Mo analogue,[11a] as a consequence of the poor redox properties of tungsten. All attempts to prepare other trivalent main group metal ions such as Sb^{3+} and Bi^{3+} bridged derivatives using $SbCl_3$ or $BiCl_3$ in place of $AlCl_3$ have failed. Preparations of Sn^{2+} derivatives such as $Mg_2[SnW_3O_4(O_2CEt)_8]_2$ using $MgWO_4$ and $SnCl_2$ in place of Na_2WO_4 and $AlCl_3$, respectively, also failed.

Crystal Structure

Complex **1** comprises two sodium ions and a centrosymmetric dianion $\{[AlW_3O_4(O_2CEt)_8]_2\}^{2-}$. The structures of the $\{[AlW_3O_4(O_2CEt)_8]_2\}^{2-}$ dianion, the $[W_3O_4(O_2CEt)_8]^{4-}$ unit and the infinite chain of cluster **1** are shown in Figures 1–3, respectively. Selected bond lengths and angles are listed in Table II. Positional parameters are given in Table III. The structure has crystallographically imposed C_i symmetry and is essentially similar to that of the Al–Mo analog reported previously.[11a] Unlike the sulfur analogues $[M'M_3S_4]_2$, species of edge-shared cubane structure,[1c] the oxo-bridged cluster skeleton $[AlW_3O_4]_2^{14+}$ in the cluster dianion possesses an eight-membered ring, $Al_2W_2O_4$, where metals Mo and Al deviate ~ 1.0 and 0.4 Å from the O4 plane, respectively. The $Al_2W_2O_4$ ring contains two types of planar oxo-centered AlW_2O triangular arrays with the sum of the W–O–Al angles being 359.2° and 347.8°, respectively, reminiscent of oxo-centred $[M_3O(O_2CR)_6L_3]^{n+}$ complexes.[12] Such an arrangement is reasonable considering the strong static repulsion of W^{4+} and Al^{3+} and the small atomic volume of oxygen. An unusual feature of the trinuclear unit shown

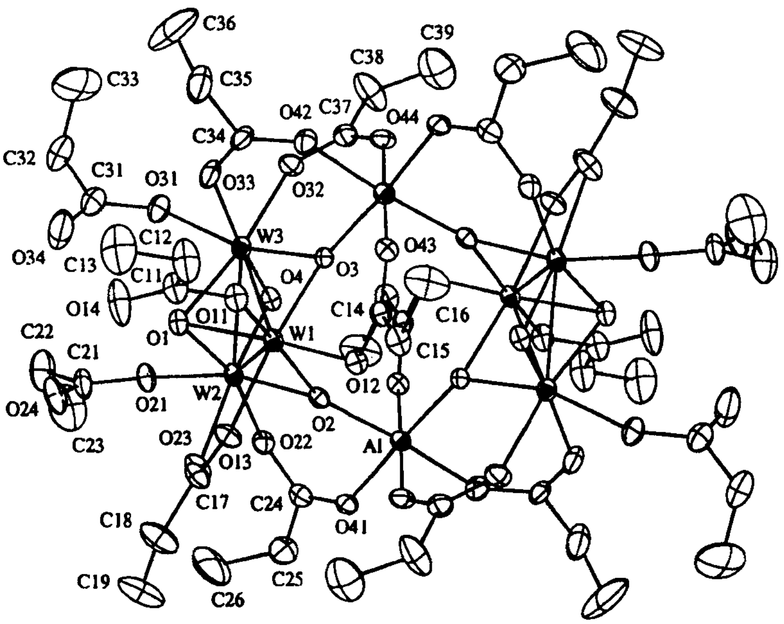

FIGURE 1 Structure of the cluster dianion $[AlW_3O_4(O_2CEt)_8]_2$ of 1 drawn with 35% thermal probability ellipsoids.

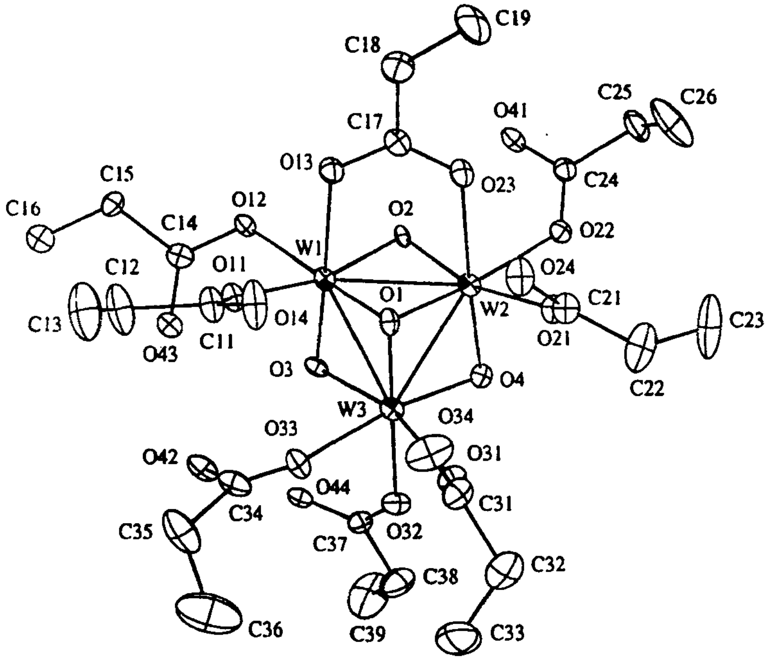

FIGURE 2 Structure of the triangular unit $[W_3O_4(O_2CEt)_8]^{4-}$ of 1.

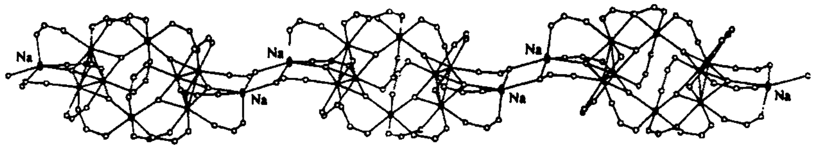

FIGURE 3 Perspective view of the one-dimensional chain structure of 1 with the Et groups omitted for clarity.

in Figure 2 is the single bridging ligand μ_2–O_2CEt, which has not been found in discrete W_3O_4 carboxylates.[9] W–W bonds are not significantly different from those in isolated W_3O_4 complexes.[9] It should be noted that the W–μ_3O bonds in AlW_2O arrays are significantly lengthened compared to the W–μ_2O bonds in $[W_3O_4]^{4+}$ units, implying that the former bonds lack significant d–p π bonding. The octahedron around Al^{3+} ions, completed by six oxygen atoms from two μ_3–O and four propionate bridges, is rather regular with six similar Al–O bonds and all O–Al–O angles within 5° of the ideal octahedral values. The Al–O bond lengths [av. 1.892(2)Å] in 1 are comparable with the Al–O bonds in $[Al(ox)_3]^{3-}$ and the Al–Mo analogue.[10,13]

Each Na^+ ion is coordinated to one capping oxygen atom and four terminal propionate oxygen atoms in a distorted trigonal bipyramid with rather short Na–O bonds [av. 2.304(11) Å], compared to the usual Na–O bonds [2.42 Å]. The octanuclear dianions $[AlW_3O_4(O_2CEt)_8]_2^{2-}$ are thus connected by Na^+ ions to constitute a chain structure characteristic of centrosymmetric Na_2O_2 four-membered rings, as shown in Figure 3. The short Na–O distances and the chain structure are believed to be responsible for the ready formation and insolubility of the compound.

Infrared Spectrum

Cluster 1 exhibits several IR strong bands in the range 1100–1700 cm^{-1} attributable to ν(C=O) of the propionate ligands. The characteristic W–O stretching vibrations in $[W_3O_4]^{4+}$ cores appear at 813, 804, 768 and 746 cm^{-1}, analogous to those of $[W_3O_4F_9]^{5-}$ and other tungsten analogues.[4,9,10] By comparison with the IR spectra of V, Cr, Fe and Ga analogues.[5,10a] the peak at 645 cm^{-1} is tentatively assigned to ν(Al–O).

Solid and Solution Stability

Product 1 is air-stable at least for a month and insoluble in water and common organic solvents such as EtOH, MeOH, EtCN, DMSO and DMF.

TABLE II Selected bond lengths (Å) and angles (°) for $Na_2[AlW_3O_4(O_2CEt)_8]_2$

W(1)-W(2)	2.511(2)	W(3)-O(3)	1.972(6)
W(1)-W(3)	2.5307(11)	W(3)-O(4)	1.940(7)
W(2)-W(3)	2.5347(10)	W(3)-O(31)	2.009(7)
W(1)-O(1)	2.048(7)	W(3)-O(32)	2.009(7)
W(1)-O(2)	1.980(7)	W(3)-O(33)	2.121(8)
W(1)-O(3)	1.965(6)	Al-O(2)	1.884(7)
W(1)-O(11)	2.009(7)	Al-O(3a)	1.863(7)
W(1)-O(12)	2.088(7)	Al-O(41)	1.881(7)
W(1)-O(13)	2.131(7)	Al-O(42a)	1.905(8)
W(2)-O(1)	2.052(7)	Al-O(43a)	1.904(7)
W(2)-O(2)	1.978(7)	Al-O(44a)	1.907(8)
W(2)-O(4)	1.913(7)	Na-O(1)	2.260(8)
W(2)-O(21)	2.016(7)	Na-O(14)	2.283(10)
W(2)-O(22)	2.093(7)	Na-O(24)	2.424(10)
W(2)-O(23)	2.140(7)	Na-O(24b)	2.309(9)
W(3)-O(1)	2.077(7)	Na-O(34)	2.248(12)
W(2)-W(1)-W(3)	60.36(3)	O(1)-W(2)-O(4)	100.5(3)
W(1)-W(2)-W(3)	60.20(3)	O(1)-W(2)-O(21)	86.7(3)
W(1)-W(3)-W(2)	59.45(4)	O(1)-W(2)-O(22)	163.9(3)
O(1)-W(1)-O(2)	102.7(3)	O(1)-W(2)-O(23)	86.3(3)
O(1)-W(1)-O(3)	102.1(3)	O(2)-W(2)-O(4)	93.8(3)
O(1)-W(1)-O(11)	87.8(3)	O(2)-W(2)-O(21)	165.0(3)
O(1)-W(1)-O(12)	165.4(3)	O(2)-W(2)-O(22)	87.2(3)
O(1)-W(1)-O(13)	83.8(3)	O(2)-W(2)-O(23)	83.9(3)
O(2)-W(1)-O(3)	90.3(3)	O(4)-W(2)-O(21)	96.1(3)
O(2)-W(1)-O(11)	165.5(3)	O(4)-W(2)-O(22)	91.5(3)
O(2)-W(1)-O(12)	88.4(3)	O(4)-W(2)-O(23)	173.2(3)
O(2)-W(1)-O(13)	86.3(3)	O(21)-W(2)-O(22)	81.3(3)
O(3)-W(1)-O(11)	97.3(3)	O(21)-W(2)-O(23)	85.0(3)
O(3)-W(1)-O(12)	87.2(3)	O(22)-W(2)-O(23)	82.0(3)
O(3)-W(1)-O(13)	173.8(3)	O(1)-W(3)-O(3)	100.8(3)
O(11)-W(1)-O(12)	79.8(3)	O(1)-W(3)-O(4)	98.7(3)
O(11)-W(1)-O(13)	85.0(3)	O(1)-W(3)-O(31)	88.9(3)
O(12)-W(1)-O(13)	87.5(3)	O(1)-W(3)-O(32)	172.4(3)
O(1)-W(2)-O(2)	102.6(3)	O(1)-W(3)-O(33)	90.0(3)
O(3)-W(3)-O(4)	98.2(3)	O(42a)-Al-O(44a)	91.1(4)
O(3)-W(3)-O(31)	163.0(3)	O(43a)-Al-O(44a)	179.2(4)
O(3)-W(3)-O(32)	85.5(3)	W(1)-O(1)-W(2)	75.6(2)
O(3)-W(3)-O(33)	84.7(3)	W(1)-O(1)-W(3)	75.7(2)
O(4)-W(3)-O(31)	94.1(3)	W(2)-O(1)-W(3)	75.7(2)
O(4)-W(3)-O(32)	84.5(3)	Al-O(2)-W(1)	147.9(4)
O(4)-W(3)-O(33)	170.1(3)	Al-O(2)-W(2)	132.4(4)
O(31)-W(3)-O(32)	84.0(3)	W(2)-O(2)-W(1)	78.8(2)
O(31)-W(3)-O(33)	81.4(3)	W(1)-O(3)-Al(a)	134.3(4)
O(32)-W(3)-O(33)	86.3(3)	W(3)-O(3)-Al(a)	133.3(4)
O(2)-Al-O(3a)	94.9(3)	W(1)-O(3)-W(3)	80.0(2)
O(2)-Al-O(41)	89.4(3)	W(2)-O(4)-W(3)	82.3(3)
O(2)-Al-O(42a)	174.8(3)	O(1)-Na-O(14)	80.7(3)
O(2)-Al-O(43a)	90.2(3)	O(1)-Na-O(24)	82.3(3)
O(2)-Al-O(44a)	89.1(3)	O(1)-Na-O(24b)	156.4(4)
O(3a)-Al-O(41)	175.6(4)	O(1)-Na-O(34)	83.0(3)
O(3a)-Al-O(42a)	90.3(3)	O(14)-Na-O(24)	147.2(4)
O(3a)-Al-O(43a)	90.0(3)	O(14)-Na-O(24b)	102.2(4)
O(3a)-Al-O(44a)	90.4(3)	O(14)-Na-O(34)	116.8(5)
O(41)-Al-O(42a)	85.4(3)	O(24)-Na-O(24b)	83.2(3)
O(41)-Al-O(43a)	89.0(3)	O(24)-Na-O(34)	88.5(5)
O(41)-Al-O(44a)	90.6(3)	O(24)-Na-O(34)	115.1(4)
O(42a)-Al-O(43a)	89.6(3)		

Symmetry codes a: $-x+1, -y, -z$; b: $-x+2, -y, -z+1$.

TABLE III Final position and equivalent thermal parameters for $Na_2[AlW_3O_4(O_2CEt)_8]_2$

Atom	x/a	y/b	z/c	U_{eq}
A1	−0.4380(3)	0.2181(3)	0.0524(2)	0.0321(7)
W1	0.71777(4)	0.04683(3)	0.14047(3)	0.03000(12)
W2	0.60467(4)	−0.124612(4)	0.21928(3)	0.03070(12)
W3	0.60626(4)	0.06635(4)	0.25811(3)	0.03265(13)
O1	0.7672(7)	0.0362(6)	0.2944(5)	0.036(2)
O2	0.5721(6)	−0.1144(6)	0.0715(5)	0.0311(15)
O3	0.5872(7)	0.1018(6)	0.1177(5)	0.0310(15)
O4	0.4644(7)	−0.0956(6)	0.2186(5)	0.034(2)
O11	0.8813(7)	0.2057(6)	0.1823(6)	0.040(2)
O12	0.1796(7)	0.0826(6)	−0.0052(5)	0.035(2)
O13	0.8502(7)	−0.0194(6)	0.1474(6)	0.041(2)
O14	1.0358(9)	0.2316(8)	0.3347(7)	0.078(3)
O21	0.6373(7)	−0.1739(6)	0.3587(5)	0.040(2)
O22	0.4732(7)	−0.3053(6)	0.1698(5)	0.037(2)
O23	0.7434(8)	−0.1770(7)	0.2089(6)	0.047(2)
O24	0.8519(8)	−0.0127(8)	0.4545(7)	0.060(2)
O31	0.6299(8)	0.0770(7)	0.4083(5)	0.047(2)
O32	0.4536(8)	0.1062(7)	0.2423(6)	0.045(2)
O33	0.7387(8)	0.2495(6)	0.3087(5)	0.047(2)
O34	0.8394(11)	0.1327(12)	0.5146(7)	0.097(4)
O41	0.4511(7)	−0.3442(6)	0.0054(5)	0.037(2)
O42	0.6964(8)	0.3342(6)	0.1718(6)	0.044(2)
O43	0.6941(7)	0.2417(6)	−0.0019(5)	0.034(2)
O44	0.4280(8)	0.1940(6)	0.1047(6)	0.039(2)
C11	0.9982(11)	0.2650(10)	0.2569(9)	0.048(3)
C12	1.0856(14)	0.3798(12)	0.2291(11)	0.079(5)
C13	1.2203(16)	0.4510(14)	0.3089(14)	0.107(7)
C14	0.7400(10)	0.1837(9)	−0.0283(8)	0.035(2)
C15	0.8328(11)	0.2327(10)	−0.0853(9)	0.046(3)
C16	0.8573(17)	0.3501(12)	−0.1112(14)	0.083(5)
C17	0.8389(12)	−0.1107(10)	0.1843(9)	0.046(3)
C18	0.9454(14)	−0.1427(13)	0.1959(14)	0.073(4)
C19	0.9108(19)	−0.2638(15)	0.2112(17)	0.105(7)
C21	0.7351(13)	−0.1576(11)	0.4423(9)	0.053(3)
C22	0.6917(15)	−0.2071(14)	0.5289(11)	0.078(5)
C23	0.5843(20)	−0.3303(17)	0.4993(16)	0.116(7)
C24	0.4466(10)	−0.3746(9)	0.0888(9)	0.041(3)
C25	0.4140(15)	−0.4974(11)	0.1017(10)	0.063(4)
C26	0.5052(21)	−0.5070(16)	0.1978(16)	0.120(8)
C31	0.7275(15)	0.1108(13)	0.5002(10)	0.059(3)
C32	0.6855(15)	0.1219(14)	0.5883(10)	0.072(4)
C33	0.6668(27)	0.2218(20)	0.5918(17)	0.139(10)
C34	0.7562(12)	0.3378(9)	0.2653(8)	0.044(3)
C35	0.8528(17)	0.4551(12)	0.3338(11)	0.083(5)
C36	0.8178(26)	0.4866(20)	0.4085(17)	0.169(12)
C37	0.3931(11)	0.1457(10)	0.1749(9)	0.042(3)
C38	0.2685(15)	0.1340(17)	0.1797(13)	0.084(5)
C39	0.1771(17)	0.1492(18)	0.0971(15)	0.105(6)
Na	0.9573(4)	0.1010(4)	0.4356(4)	0.0509(12)

Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Thermogravimetric analysis shows that the complex is stable up to 250°C in air and then starts to decompose. The decomposition comprises only one step in the temperature range 310–435°C and the remaining weight was 62.52%, according to Na_2O, Al_2O_3 and WO_3 (calc. 62.18%). The thermal data were consistent with above crystal structure data.

Unlike the molybdenum–aluminum analogue, cluster **1** cannot be dissolved in aqueous 2 M hydrochloric acid at room temperature. However, it is soluble in hot (> 50°C) aqueous 2 M HCl solution to produce a red-purple solution. The electronic spectrum gives a peak at 450 nm characteristic of $[W_3O_4(H_2O)_9]^{3+}$ aqua ions,[9,11] indicating dissociation of Al^{3+} ions from the trinuclear cores and formation of isolated $[W_3O_4]^{4+}$ units, as in the case of the molybdenum analogues.[5,10a] This suggests that the solubility in aqueous acid solution is a consequence of the decomposition of the clusters to generate $[W_3O_4]^{4+}$ species, and supports the assumption that such octanuclear dianions are formed through the combination of the triangular cluster units with the heterometals.

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Supplementary Data

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

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