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Isolation and Characterization of $[Zn_2(O_2CCH_3)_3][Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]\cdot 2H_2O$, an Anionic Trimolybdenum(IV) Cluster Compound Containing an Unusual Cation

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The reaction of sodium molybdate with zinc dust in refluxing acetic anhydride affords a red powder. Upon recrystallization of this powder from methanol, the red crystalline title compound is obtained. The anion in this compound is a typical bicapped $[Mo_3(\mu_3\text{-}O)_2(O_2CR)_6X_3]$ cluster species with a six-electron cluster bonding configuration, but it is novel in being the first such species to have as X groups alkoxide ions (OCH_3^-). The cation consists of two zinc(II) ions bridged by three acetate ions, and the crystal structure consists of infinite zigzag chains of alternating binuclear cations and cluster anions. The compound forms orthorhombic crystals in space group *Pnma* with cell dimensions a = 20.733 (6) Å, b = 14.042 (5) Å, c = 13.285 (5) Å, V = 3868 (4) Å^3, and Z = 4. In the cluster anion two of the OCH_3 oxygen atoms form donor bonds to zinc ions; these have longer O–Mo bonds, 2.01 (1) and 2.06 (1) Å, than the third one, 1.95 (1) Å. In a corresponding way the Mo–Mo bonds within the cluster also differ: the one between the two Mo atoms that have longer Mo–OMe bonds is shorter, 2.763 (3) Å, than the other two, 2.801 (3) and 2.817 (3) Å.

Introduction

We recently reported that trimolybdenum cluster species of the general type $[Mo_3(\mu_3\text{-}O)_2(O_2CCH_3)_6X_3]^q$ can be obtained by reducing sodium molybdate in acetic anhydride with use of either $W(CO)_6$ or zinc as the reducing agent.[2] In that study the compound ultimately characterized by crystallography was $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O$, but this was obtained only after hydrolysis of the initial product of the $W(CO)_6$ reduction, namely a red solid of composition $Na[Mo_3O_2(O_2CCH_3)_9]$, according to elemental analysis. In the case of zinc reduction the initial product was also a red precipitate that was evidently very similar to the one just mentioned but could not have been identical. We have now studied the zinc reduction process further with the goal of identifying the material formed initially, as well as those formed directly therefrom under various workup conditions. This has enabled us to isolate the first anionic cluster species of the type $[Mo_3O_2(O_2CR)_6X_3]$ in which X is an alkoxide ion, viz., methoxide. In the crystal, the cluster anions are linked by the cationic aggregates, $[Zn_2(O_2CCH_3)_3]^+$, into infinite chains.

Experimental Section

Preparation. Freshly prepared sodium molybdate dihydrate (1.0 g) and zinc dust (2.0 g) were added to 100 mL of acetic anhydride, and the mixture was held at reflux temperature for 4 h. As the mixture cooled, a red powder (product A) was precipitated. This powder was isolated by filtration, dried by pumping at room temperature, and dissolved in methanol. After about 12 h a red crystalline material (product B) had come out of solution. These crystals, which were not satisfactory for X-ray crystallography, gave analytical results corresponding approximately to the formula $Zn_2(O_2CCH_3)_3[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]\cdot 2H_2O$. Anal. Calcd for $C_{21}H_{40}O_{25}Mo_3Zn_2$: C, 22.70; H, 3.63. Found: C, 23.07; H, 3.46.

To obtain crystals of better quality, product B was dissolved in a mixture of methanol and ethanol (1:1 by volume) and the solution allowed to evaporate slowly in an open vessel.

X-ray Crystallography. All crystals examined were found to be twinned on (001). A thin red plate of approximate dimensions 0.20 × 0.20 × 0.06 mm was eventually selected and used for intensity measurements since the contributions of one component of this particular twin to the diffracted intensities appeared to be very small. The crystal was mounted on a Philips PW 1100/20 four-circle diffractometer, and accurate cell parameters were derived from 24 carefully centered reflections. Intensities were collected with graphite-monochromated Mo Kα radiation. Pertinent details of all crystallographic measurements are given in Table I. Lorentz and polarization but not absorption corrections were applied to the intensities, and these were reduced to structure factors. The systematic absences were consistent with space groups *Pnma* or *Pna*2_1. The Patterson map and the intensity distribution implied the former, and this was confirmed by the successful refinement.

Table I. Pertinent Crystallographic Data for Intensity Collection and Structure Refinement

formula	$[Mo_3O_2(CH_3COO)_6(CH_3O)_3]$-$Zn_2(CH_3COO)_3\cdot 2H_2O$
mol wt	1111.03
lattice	orthorhombic
a	20.733 (6) Å
b	14.042 (5) Å
c	13.285 (5) Å
space group	*Pnma* (No. 62)
Z	4
d(measd) in (*s*-tetrabromoethane + toluene)	1.900 g cm^{-3}
d(calcd)	1.909 g cm^{-3}
radiation	Mo Kα (graphite monochromated)
scan mode	$\omega/2\theta$
scanning range for 2θ	$5° < 2\theta < 45°$
scan speed	1.5° min^{-1}
scan width in ω	1.15°
no. of unique reflcns	2537
no. of reflcns for which $F_o > 2\sigma(F_o)$	1780
weighting scheme	$1.052/(\sigma^2(F_o) + 0.001(F_o)^2)$
no. of variables	271
$R(F)^a$	0.090
$R_w(F)^b$	0.081

^{a} $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w(F) = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = \sigma(F_o)^{-2}$.

Structure solution was carried out with use of the SHELX-77 program package. The three Mo atoms were located from the Patterson synthesis and the remaining atoms from successive Fourier difference maps. The structure was refined with use of unit weights in the initial stages and statistical weights in the final stages. After anisotropic refinement of all heavy and light atoms (R = 0.10) residual electron densities of ca. 1 e Å^{-3} were detected in the difference maps. These were ascribed to water molecules filling the vacancies in the structure in a disordered way. Eight different positions were found for these peaks. Their occupancies add up to eight water molecules per cell, as confirmed by chemical analysis and density measurement. At this stage, all possible water positions with their various fixed occupancies were refined isotropically and the remaining atoms anisotropically. The refinement converged at R = 0.090. A table of observed and calculated structure factors is available as supplementary material.

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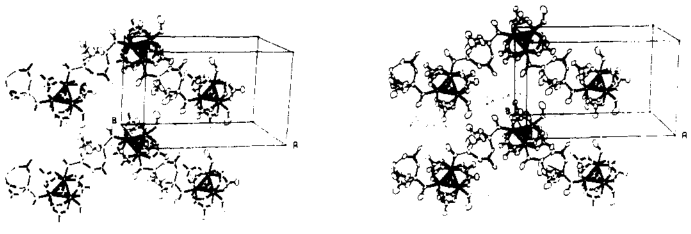

Figure 1. Stereoview of the unit cell showing how the infinite chains of alternating $[Zn_2(O_2CCH_3)_3]^+$ and $[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]^-$ are arranged.

Table II. Final Positional Parameters[a,b]

atom	*x*	*y*	*z*
Mo(1)	−729 (1)	2500 (0)	320 (2)
Mo(2)	144 (1)	2500 (0)	−1252 (2)
Mo(3)	594 (1)	2500 (0)	749 (2)
Zn(1)	−2290 (2)	2500 (0)	−423 (3)
Zn(2)	−3704 (2)	2500 (0)	−1913 (3)
O	6 (5)	3350 (8)	−73 (10)
O(11)	−1181 (5)	3553 (9)	−597 (10)
O(12)	−486 (6)	3519 (9)	−1864 (10)
C(11)	−982 (11)	3840 (14)	−1416 (15)
C(12)	−1383 (10)	4645 (16)	−1926 (16)
O(21)	900 (6)	3522 (9)	−1444 (10)
O(22)	1234 (6)	3529 (9)	164 (11)
C(21)	1262 (9)	3824 (15)	−725 (18)
C(22)	1729 (10)	4647 (15)	−1001 (18)
O(31)	288 (6)	3515 (9)	1838 (10)
O(32)	−763 (5)	3510 (9)	1481 (9)
C(31)	−282 (9)	3819 (14)	1975 (18)
C(32)	−394 (9)	4572 (16)	2791 (17)
O(41)	−2811 (7)	3635 (11)	−120 (13)
O(42)	−3672 (7)	3648 (12)	−1032 (12)
C(41)	−3340 (10)	3947 (18)	−357 (16)
C(42)	−3547 (14)	4915 (20)	67 (24)
O(51)	−2083 (8)	2500 (0)	−1837 (16)
O(52)	−2962 (9)	2500 (0)	−2805 (16)
C(51)	−2340 (13)	2500 (0)	−2666 (28)
C(52)	−1957 (15)	2500 (0)	−3609 (22)
OM(1)	−1673 (8)	2500 (0)	670 (14)
CM(1)	−1932 (22)	2500 (0)	1683 (33)
OM(2)	378 (8)	2500 (0)	−2756 (15)
CM(2)	−59 (18)	2500 (0)	−3619 (34)
OM(3)	1314 (9)	2500 (0)	1697 (14)
CM(3)	1295 (20)	2500 (0)	2911 (36)
OWA	248 (2)	250 (0)	109 (4)
OWB	252 (3)	345 (5)	116 (5)
OWC	255 (12)	250 (0)	195 (19)
OWD	280 (6)	346 (9)	171 (10)
OWE	492 (11)	250 (0)	68 (17)
OWF	402 (9)	250 (0)	88 (14)
OWG	296 (11)	250 (0)	162 (15)
OWH	354 (3)	205 (4)	112 (4)

[a] Positional parameters are $\times 10^4$ for heavy and light atoms and $\times 10^3$ for water oxygen atoms. [b] Occupancies of water molecules: OWA = 0.187; OWC = 0.0625; OWE = 0.0625; OWG = 0.0625; OWB = 0.25; OWD = 0.125; OWF = 0.0625; OWH = 0.187.

Results and Discussion

Preparative Procedure. Metallic zinc functions as a reducing agent to convert the molybdenum(VI) in sodium molybdate to molybdenum(IV) in the bicapped trimolybdenum cluster. The first red precipitate, product A, is believed to consist of a mixture of $Na[Mo_3O_2(O_2CCH_3)_9]$ and $Zn(O_2CCH_3)_2$. It has a visible spectrum essentially identical with that of $Na[Mo_3O_2(O_2CCH_3)_9]$ obtained in the $W(CO)_6$ reduction of sodium molybdate.[2] It must, of course, also contain zinc in order to account for the appearance of zinc in the title compound, product B, obtained when product A reacts with methanol. To confirm this, a mixture of $Na[Mo_3O_2(O_2CCH_3)_9]$ and $Zn(O_2CCH_3)_2$ in 1:2 molar ratio was made and found to behave exactly as does product A, affording product B upon dissolution in and reaction with methanol.

Table III. Important Bond Lengths in Å

Mo(1)–Mo(2)	2.763 (3)	C(21)–C(22)	1.55 (2)
Mo(1)–Mo(3)	2.801 (3)	O(31)–C(31)	1.27 (2)
Mo(2)–Mo(3)	2.817 (3)	O(32)–C(31)	1.27 (2)
Mo(1)–O	2.00 (1)	C(31)–C(32)	1.53 (3)
Mo(1)–O(11)	2.13 (1)	O(41)–C(41)	1.22 (2)
Mo(1)–O(32)	2.10 (1)	C(42)–C(41)	1.21 (2)
Mo(2)–O	1.99 (1)	C(41)–C(42)	1.53 (3)
Mo(2)–O(12)	2.10 (1)	O(51)–C(51)	1.22 (4)
Mo(2)–O(21)	2.14 (1)	O(52)–C(51)	1.30 (3)
Mo(3)–O	2.03 (1)	C(51)–C(52)	1.48 (4)
Mo(3)–O(22)	2.11 (1)	OM(1)–CM(1)	1.45 (4)
Mo(3)–O(31)	2.13 (1)	OM(2)–CM(2)	1.46 (4)
Mo(1)–OM(1)	2.01 (1)	OM(3)–CM(3)	1.61 (5)
Mo(2)–OM(2)	2.06 (1)	Zn(1)–O(41)	1.97 (1)
Mo(3)–OM(3)	1.95 (1)	Zn(1)–O(51)	1.93 (2)
O(11)–C(11)	1.23 (2)	Zn(1)–OM(1)	1.94 (1)
O(12)–C(11)	1.27 (2)	Zn(2)–O(42)	1.99 (1)
C(11)–C(12)	1.56 (2)	Zn(2)–O(52)	1.94 (1)
O(21)–C(21)	1.29 (2)	Zn(2)–OM(2)[a]	1.95 (1)
O(22)–C(21)	1.25 (2)		

[a] Atom generated by *n* glide and translated along −*a* and −*c*.

Table IV. Important Bond Angles in deg

Mo(2)–Mo(1)–Mo(3)	60.84 (8)	Mo(1)–Mo(3)–O(31)	81.2 (3)
Mo(2)–Mo(1)–O	46.0 (3)	Mo(1)–Mo(3)–OM(3)	151.6 (5)
Mo(2)–Mo(1)–O(11)	81.8 (3)	Mo(2)–Mo(3)–O	44.9 (3)
Mo(2)–Mo(1)–O(32)	125.3 (3)	Mo(2)–Mo(3)–O(22)	82.0 (3)
Mo(2)–Mo(1)–OM(1)	144.3 (5)	Mo(2)–Mo(3)–O(31)	122.9 (3)
Mo(3)–Mo(1)–O	46.3 (3)	Mo(2)–Mo(3)–OM(3)	149.4 (5)
Mo(3)–Mo(1)–O(11)	123.2 (3)	O–Mo(3)–O(22)	77.1 (4)
Mo(3)–Mo(1)–O(32)	83.3 (3)	O–Mo(3)–O(31)	78.0 (4)
Mo(3)–Mo(1)–OM(1)	154.8 (5)	O–Mo(3)–O′	72.2 (4)
O–Mo(1)–O(11)	76.9 (4)	O–Mo(3)–OM(3)	143.9 (3)
O–Mo(1)–O(32)	79.3 (4)	O(22)–Mo(3)–O(31)	88.8 (4)
O–Mo(1)–O′	73.1 (4)	O(22)–Mo(3)–O(22)′	86.4 (5)
O–Mo(1)–OM(1)	143.1 (3)	O(22)–Mo(3)–OM(3)	75.9 (5)
O(11)–Mo(1)–O(32)	86.4 (4)	O(31)–Mo(3)–O(31)′	84.1 (4)
O(11)–Mo(1)–O(11)′	87.8 (4)	O(31)–Mo(3)–OM(3)	77.8 (5)
O(11)–Mo(1)–OM(1)	72.8 (4)	O(11)–C(11)–O(12)	125 (1)
O(32)–Mo(1)–O(32)′	85.1 (4)	O(11)–C(11)–C(12)	116 (1)
O(32)–Mo(1)–OM(1)	78.3 (5)	O(12)–C(11)–C(12)	119 (1)
Mo(1)–Mo(2)–Mo(3)	60.24 (8)	O(21)–C(21)–O(22)	124 (1)
Mo(1)–Mo(2)–O	46.4 (3)	O(21)–C(21)–C(22)	116 (1)
Mo(1)–Mo(2)–O(12)	83.4 (3)	O(22)–C(21)–C(22)	120 (1)
Mo(1)–Mo(2)–O(21)	124.7 (3)	O(31)–C(31)–O(32)	123 (1)

It is clear, then, that the cluster anion $[Mo_3O_2(O_2CCH_3)_9]^-$ is subject to solvolysis by either water or methanol. In a previous report[2] we described reaction 1, in which hydrated

$$[Mo_3O_2(O_2CCH_3)_9]^- + 19H_2O \rightarrow [Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]\cdot 16H_2O + 2CH_3COOH + CH_3CO_2^- \quad (1)$$

$$[Mo_3O_2(O_2CCH_3)_9]^- + 2Zn(O_2CCH_3)_2 + 3CH_3OH + 2H_2O \rightarrow [Zn_2(O_2CH_3)_3][Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]\cdot 2H_2O + 3CH_3CO_2H + CH_3CO_2^- \quad (2)$$

crystals containing the neutral molecule $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]$ were obtained. In the present study we have obtained the principal product shown in eq 2. We do

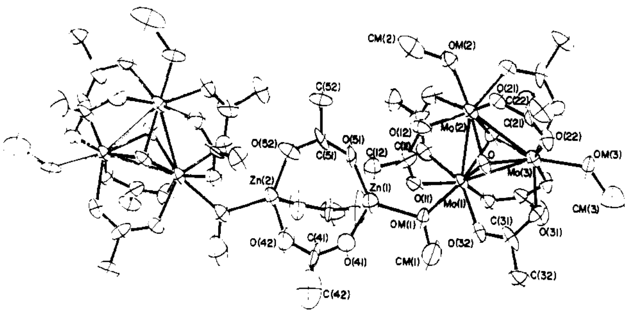

Figure 2. Computer-drawn view of the asymmetric unit showing the atomic numbering scheme. In addition, one adjacent $[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]^-$ unit is shown to give a more complete picture of the chain formation. Atoms are represented by their ellipsoids of thermal vibration at the 50% probability level.

not actually know whether the acetate groups appear in the forms shown or whether some esterification occurs to afford methyl acetate.

Structural Results. The positional and thermal parameters are presented in Tables II and IIS (Table IIS is given in the supplementary material). The structure consists of infinite zigzag chains of alternating $[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]^-$ ions and $[Zn_2(O_2CCH_3)_3]^+$ ions, arranged in space as shown in the stereo drawing presented in Figure 1. An enlarged view of a representative portion of the chain is presented in Figure 2. The numbering scheme for one asymmetric unit is defined, and the linking to an adjacent $[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]^-$ unit is shown. The linkages are all formed by Mo(1)–OM(1)–Zn(1) and Zn(2)–OM(2)–Mo(2) sets of atoms. The methoxide units OM(3)–CM(3) do not participate in any such linking.

The infinite sinuous chains extend along the *a* direction. They are translated along *c* to form layers parallel to *ac* at $y = {}^1/_4, {}^3/_4$. There is some space between the chains, which is filled by water molecules in a disordered array such that several positions are partially occupied, as detailed in Table II.

Turning now to structural details, let us dispose first of the $[Zn_2(O_2CCH_3)_3]^+$ group before giving our full attention to the trimolybdenum cluster anions. This cationic unit consists of two zinc ions bridged by three acetate groups. There is a plane of symmetry containing the zinc atoms and one acetate group. The O–Zn–O angles are all in the range 107.9–109.4°, and the zinc atoms are separated by 3.538 Å. The Zn–O(acetate) bond lengths range from 1.93 (2) to 1.99 (1) Å. The bonds from the zinc atoms to the methoxide oxygen atoms are similar in length, 1.94 (1) and 1.95 (1) Å, but their directions are far from those required to complete regular tetrahedra. In each case there is one large O(acetate)–Zn–O(methoxide) angle of 125 or 129° and two small ones of 99.5 or 102°. These distortions evidently arise from packing contacts between the $[Zn_2(O_2CCH_3)_3]^+$ cations and the cluster anions to which they are attached, as is evident in Figure 2.

The trimolybdenum cluster anion is interesting in several respects. It is the first anionic species of its type to be structurally characterized, although the existence of the $[Mo_3O_2(O_2CCH_3)_9]^-$ ion is well established chemically.[2] The anion is found in a low-symmetry environment in this compound, and the perturbations caused in the structure are significant and important. Ideally, the $[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]^-$ ion would be expected to have D_{3h} symmetry aside from deviations caused by the orientations of the methoxy and acetate methyl groups. In this crystalline compound the plane of symmetry, containing the three Mo atoms as well as both O and C atoms of all three methoxy groups, is present as a rigorous crystallographic mirror plane. The other elements of D_{3h} symmetry have been abolished by the use of lone pairs on two of the methoxy oxygen atoms to form bonds to zinc ions. The symmetry has been degraded to something approximating to C_{2v}, in which the approximate C_2 axis would coincide with the Mo(3)–OM(3) bond and bisect the Mo(1)–Mo(2) bond.

The most notable and important effects of this degradation of symmetry are to be found in the inequalities in Mo(*n*)–OM(*n*) and Mo(*n*)–Mo(*m*) bond lengths. The participation of two of the methoxy groups in bridging to the zinc ions leads, expectedly, to a lengthening of their bonds to the molybdenum atoms. Thus, we find the Mo(1)–OM(1) and Mo(2)–OM(2) bond lengths, 2.01 (1) and 2.06 (1) Å, are nearly the same and both are longer than the Mo(3)–OM(3) distance, 1.95 (1) Å, which involves the methoxy group not engaged in bridging to zinc ions. It appears that the differences in these Mo–O bond strengths induce inverse effects on the Mo–Mo bonds. The two molybdenum atoms that form the weaker Mo–OCH_3 bonds, Mo(1) and Mo(2), have the shortest metal–metal bond, 2.763 (3) Å, while the other two Mo–Mo bonds, each of which involves Mo(3) with its shorter Mo–O-CH_3 bond, are nearly equal and are much longer, viz., 2.801 (3) and 2.817 (3) Å.

This sort of inverse relationship between the equatorial Mo–O and Mo–Mo bond lengths was noted previously in the $[Mo_3O_2(O_2CCH_3)_6(H_2O)(OH)_2]$ molecule,[2] although in that case it was partially masked by a disorder which resulted in there being only one unequivocal Mo–OH position while the other two equatorial bonds were seen as a random (i.e., 1:1) mixture of Mo–OH and Mo–OH_2. From earlier work[3] it was known that Mo–OH_2 bond lengths are in the range 2.08–2.14 Å, whereas the ordered Mo–OH bond length in the above molecule was 1.979 (7) Å. The observed average of the Mo–OH and Mo–OH_2 values, 2.049 (5) Å, was thus about as expected. Corresponding with these differences in equatorial Mo–O bond lengths were Mo–Mo bond lengths 2.773 (1) Å and (twice) 2.796 (1) Å. The pattern of relationships between equatorial Mo–O bond lengths and Mo–Mo bond lengths is essentially the same in both this case and the present one, and there can now be no doubt that the inverse relationship between equatorial Mo–X bond lengths and Mo–Mo bond lengths is real. The magnitude of the difference in Mo–Mo bond lengths in the present case, ca. 0.046 Å, is large enough to be very important when attempts are made to relate Mo–Mo bond lengths to the number of metal–metal bonding electrons in the cluster. It has been previously shown[4] that a change of one electron results in an Mo–Mo bond length change of ca. 0.07 Å.

Other evidences of symmetry degradation from D_{3h} to C_{2v}, as in Mo–(μ_3-O) and Mo–O(acetate) bond lengths, and in bond angles, are absent or are at the border line of statistical significance. The Mo–(μ_3-O) distances range from 1.99 (1) to 2.03 (1) Å; the mean value, 2.01 [1] Å, is not significantly different from those previously reported[3] in related compounds.

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Registry No. $Zn_2(O_2CCH_3)_3[Mo_3O_2(O_2CCH_3)_6(OCH_3)_3]\cdot 2H_2O$, 89655-96-9; $Na[Mo_3O_2(O_2CCH_3)_9]$, 86695-77-4; Zn, 7440-66-6; sodium molybdate, 7631-95-0.

Supplementary Material Available: A table of thermal vibration parameters and a list of structure factors (12 pages). Ordering information is given on any current masthead page.

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