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Comproportionation Synthesis of Bi-μ_3-oxo-capped Trimolybdenum(IV) Clusters: Structural Characterization of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$

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The reaction of $Mo_2(O_2CCH_3)_4$ with $Na_2MoO_4{\cdot}2H_2O$ (1:2 mole ratio) in acetic acid containing some acetic anhydride and a little triethylamine, followed by an aqueous workup, affords the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ cation. This has been isolated as the $CF_3SO_3^-$ salt, which has been characterized crystallographically. It is isomorphous with the tungsten analogue, crystallizing in space group $R\bar{3}c$ with $a = 11.463$ (9) Å, $c = 40.51$ (2) Å, $V = 4610$ (9) Å^3, and $Z = 6$. The cation has crystallographic 32 (D_3) symmetry but approximates closely to $\bar{6}2m$ (D_{3h}) symmetry. Important dimensions are as follows: Mo–Mo, 2.759 (1) Å; Mo–(μ_3-O), 1.994 (5) Å; Mo–O(acetate) (average), 2.082 [7] Å; Mo–O(H_2O), 2.129 (6) Å. A series of experiments were done to demonstrate that the product is obtained by a true comproportionation reaction in which molybdenum atoms from both reactants are found in the product.

Introduction

In previous publications from these laboratories we have developed the chemistry of the bicapped equilateral triangular cluster compounds of molybdenum[2-6] and tungsten.[7,8] Preparative methods previously used have generally employed one of the hexacarbonyls, $Mo(CO)_6$ or $W(CO)_6$, as the source of the metal atoms and excess of the carboxylic acid has served as the oxidizing agent. In one previous report[5] $Mo_2(O_2CCH_3)_4$ served as the source of metal with propionic acid as the oxidant, yielding $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ as the product. We have now begun to seek additional routes to the trinuclear products, and recently we have shown[9] that MoO_4^{2-} may be used as the source of metal atoms, with a reducing agent such as zinc or $W(CO)_6$ to lower the oxidation state to +4. In this paper we describe the reaction between sodium molybdate and $Mo_2(O_2CCH_3)_4$, in acetic acid, which leads to the isolated product $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$. We also present the structure of this substance thus providing for the first time the structure of a compound of molybdenum that is stoichiometrically and crystallographically the exact analogue of a bicapped tritungsten compound.[8]

Experimental Section

Preparation. A mixture of $Mo_2(O_2CCH_3)_4$ (1.00 g), $Na_2MoO_4{\cdot}2H_2O$ (1.23 g), acetic acid (70 mL), acetic anhydride (7 mL), and triethylamine (1 mL) was refluxed for 48 h under argon. The reaction mixture was cooled, diluted with 200 mL of water, and poured on a Dowex 50W-X2 cation-exchange column. The column was washed with 1 M hydrochloric acid, and the red absorbed material was eluted with 2 M trifluoromethanesulfonic acid. Good-quality crystals were obtained by slow evaporation of the eluate. Yields range from 63 to 77% (ca. 1.8 g).

Table I. Crystallographic Data and Data Collection Parameters

formula	$[Mo_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$
fw	1090.27
space group	$R\bar{3}c$
a, Å	11.463 (9)
b, Å	11.463 (9)
c, Å	40.51 (2)
α, deg	90.0
β, deg	90.0
γ, deg	120.0
V, Å^3	4610 (9)
Z	6
d_{calcd}, g/cm^3	2.356
cryst size, mm	0.3 × 0.4 × 0.2
μ(Mo Kα), cm^{-1}	14.477
data collection instrument	P$\bar{1}$ Syntex
radiation	Mo Kα
scan method	ω–2θ
data collection range	$4° \leqslant 2\theta \leqslant 50°$
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	727
no. of parameters refined	72
R[a]	0.058
R_w[b]	0.075
quality-of-fit indicator[c]	1.522
largest shift/esd, final cycle	<0.01

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$.

Studies of Stoichiometry. Several reactions were carried out under essentially the above conditions but without any attempt to isolate crystalline products. This was done to determine how much of the trinuclear product was derived from each of the reactants. In each experiment 1.0 g of $Mo_2(O_2CCH_3)_4$ was used and the quantity of $Na_2MoO_4{\cdot}2H_2O$ was such as to give the desired mole ratio. Yields were established by eluting the red trimolybdenum cation completely from the column and determining the quantity from the optical density of the eluate solution, employing the known molar extinction coefficients at several wavelengths for the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^+$ ion.

Case 1. No $Na_2MoO_4{\cdot}2H_2O$ was added. The yield of Mo_3 product was negligible.

Case 2. The $Mo_2(O_2CCH_3)_4$:$Na_2MoO_4{\cdot}2H_2O$ ratio was 1:2. The eluate would have been 3.12×10^{-3} M in the Mo_3 cation if all Mo in the reactants had been converted to this product. Concentration found: 2.83×10^{-3} M (90.7% yield).

Case 3. The molar ratio was 1:1. The observed concentration in the eluate was 1.59×10^{-3} M, compared to 3.12×10^{-3} expected for 100% conversion of all Mo to the Mo_3 cation. Unreacted $Mo_2(O_2CCH_3)_4$ recovered: 40.3% by weighing.

Reaction of $Mo_2(O_2CCH_3)_4$ with K_2CrO_4. A mixture of $Mo_2(OAc)_4$ (1.00 g), K_2CrO_4 (0.907 g), acetic acid (70 mL), and triethylamine (1 mL) was refluxed for 24 h under argon. The reaction mixture was cooled and filtered, yielding a green precipitate and a red solution. The filtrate was then diluted with 100 mL of water and poured on a Dowex 50W-X2 cation-exchange column. The column was then washed with 0.5 M hydrochloric acid, and the red band was eluted

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Table II. Positional Parameters and Their Estimated Standard Deviations for $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$

atom	*x*	*y*	*z*
Mo	0.13897 (8)	0.000	0.250
O(1)	0.000	0.000	0.2204 (2)
O(2)	0.3247 (7)	0.000	0.250
O(3)	0.1434 (5)	0.2578 (5)	0.2153 (1)
O(4)	0.2583 (5)	0.1503 (5)	0.2161 (1)
C(2)	0.3341 (9)	0.3392 (9)	0.1806 (2)
C(1)	0.2386 (8)	0.2425 (8)	0.2054 (2)
C(11)	0.333	−0.333	0.291
F	0.237 (1)	−0.4507 (8)	0.3023 (3)
S	0.333	−0.333	0.2460 (2)
O(11)	0.385 (1)	−0.1940 (8)	0.2374 (3)

with 3 M fluoboric acid. The UV–vis spectrum of the eluate was identical with that of $[Mo_3O_2(OAc)_6(H_2O)_3]^{2+}$.

Structural Characterization. A red crystal of dimensions 0.3 × 0.4 × 0.2 mm was placed in a glass capillary and mounted on a Syntex P$\bar{1}$ four-circle diffractometer. Mo Kα radiation ($\lambda = 0.710730$ Å), with a graphite-crystal monochromator in the incident beam, was used. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $15° \leq 2\theta \leq 40°$. Lorentz and polarization corrections were applied, but no absorption corrections were deemed necessary. Other parameters pertaining to the data collection and refinement procedure are summarized in Table I.

The position of the molybdenum atom was derived from the three-dimensional Patterson function. The other non-hydrogen atoms were found in a series of alternating refinements and difference maps.[10] Because of disorder in the CF_3SO_3 units, the carbon atoms were not refined anisotropically in the final cycles of refinement.

The structure factors and thermal parameters are available as supplementary material. The atomic positional parameters are listed in Table II.

Results and Discussion

Reaction Chemistry. It is well-known that trinuclear molybdenum(IV) cluster compounds having the $Mo_3O_4^{4+}$ core can be prepared by comproportionation reactions of types shown schematically as (1)[11] or (2).[12] On the other hand,

$$3Mo^{III}(aq) + 3Mo^{V}(aq) \rightarrow 2Mo_3O_4^{4+}(aq) \qquad (1)$$

$$3Mo_2^{4+}(aq) + 6MoO_4^{2-}(aq) \rightarrow 4Mo_3O_4^{4+}(aq) \qquad (2)$$

the trinuclear molybdenum(IV) cluster compounds of the bioxocapped type, i.e., based on $Mo_3O_2^{8+}$, have been obtained in nearly every case from the reaction of $Mo(CO)_6$ with a carboxylic acid,[2-6] and the $W_3O_2^{8+}$ species have been obtained similarly.[7,8] In one exceptional instance[5] $Mo_2(O_2CCH_3)_4$ was oxidized by a mixture of propionic acid and propionic anhydride to afford $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^+$. In the immediately preceding paper in this series[9] we have demonstrated the possibility of a reductive procedure, whereby the molybdate ion is reduced with zinc or $W(CO)_6$ in acetic acid to give the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^+$ ion. We now report that by use of $Mo_2(O_2CCH_3)_4$ as the starting material with lower-valent molybdenum and MoO_4^{2-} as the starting material containing high-valent molybdenum, the trinuclear bioxo-capped cation can be obtained by a comproportionation reaction.

The reaction stoichiometry is shown in eq 3, where the arrow

$$Mo_2(O_2CCH_3)_4 + 2Na_2MoO_4\cdot 2H_2O \rightarrow {}^4/_3[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+} \qquad (3)$$

implies (1) refluxing the reactants in acetic acid, (2) dilution of the cooled reaction mixture with water, (3) isolation of the red trinuclear cation on an ion-exchange column, and (4) elution of the trinuclear cation by dilute acid.

Table III. Bond Distances and Angles

Bond Distances (Å)			
Mo–Mo	2.759 (1)	C(1)–O(3)	1.255 (9)
-O(1)	1.994 (5)	-O(4)	1.262 (9)
-O(2)	2.129 (6)	-C(2)	1.493 (10)
-O(3)	2.072 (4)	C(11)-F	1.326 (7)
-O(4)	2.091 (4)	-F	1.822 (7)
		S–O(11)	1.442 (7)
Angles (deg)			
Mo′–Mo–O(1)	46.2 (1)	O(4)–Mo–O(1)	78.4 (2)
-O(3)	83.3 (1)	-O(1)′	126.1 (2)
-O(4)	81.5 (1)	-O(4)′	152.0 (3)
Mo′–O(1)–Mo	87.6 (3)	-O(1)′	73.9 (3)
O(2)–Mo–O(3)	74.9 (1)	C(2)–C(1)–O(3)	118.5 (7)
-O(4)	76.0 (1)	-O(4)	118.7 (7)
-O(1)	143.0 (2)	O(3)–C(1)–O(4)	122.7 (6)
O(3)–Mo–O(4)	88.9 (2)	S–C(11)–F	110.3 (5)
-O(4)′	83.8 (2)	F–C(11)–F′	108.6 (5)
-O(1)	78.5 (2)	C(11)–S–O(11)	104.0 (5)
-O(1)′	128.1 (2)	O(11)–S–O(11)	114.3 (4)
-O(3)′	149.7 (3)		

Since it is known that the trinuclear cation can be obtained by oxidation of a low-valent molybdenum compound, e.g., $Mo(CO)_6$ or $Mo_2(O_2CR)_4$, with a refluxing carboxylic acid or $RCO_2H/(RCO)_2O$ mixture and also that the trinuclear cation can be formed solely by the molybdenum atoms in the molybdate ion when the latter is reduced, the assertion that we have found a comproportionation reaction cannot be accepted without evidence. Such evidence has been obtained by quantitative measurements of yields. The pertinent results are as follows.

(1) When $Mo_2(O_2CCH_3)_4$ alone is refluxed with acetic acid under the same conditions as those used for the preparative reaction, only a trace of the $Mo_3O_2^{8+}$-containing cation is formed. At the reflux temperature (ca. 118 °C) of acetic acid, the rate at which acetic acid oxidizes $Mo_2(O_2CCH_3)_4$ is negligible. At the considerably higher boiling point of propanoic acid (ca. 140 °C) the required oxidation does occur, as previously reported[5] and reconfirmed by us as part of the present investigation.

(2) When a non-molybdenum-containing oxidizing agent was added to the reaction mixture, namely K_2CrO_4, substantial conversion of the $Mo_2(O_2CCH_3)_4$ to $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^+$ was observed. The green solid also isolated in this reaction was not identified positively, but it seems very likely to have been a compound containing the basic chromium acetate oxo-centered trinuclear cation $[Cr_3O(O_2CCH_3)_6]^+$.

(3) When the reactants $Mo_2(O_2CCH_3)_4$ and $Na_2MoO_4\cdot 2H_2O$ were used in the molar ratio (1:2) required by eq 3, the quantity of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^+$ formed was 91% of the possible amount based on eq 3. This demonstrates unequivocally that both of the starting materials contribute molybdenum atoms to the trinuclear product. If the molybdenum atoms in the product could come only from one or the other of the starting materials, the actual yield would be 1.8 times the theoretical yield, an obvious impossibility. The preparative reaction is thus clearly proven to be a comproportionation reaction.

(4) From the results discussed under (1) and (3), it would be expected that if one or the other reagent, $Mo_2(O_2CCH_3)_4$ or $Na_2MoO_4\cdot 2H_2O$, were present in excess, according to eq 3, this excess amount would remain unreacted. We carried out such an experiment using a 1:1 molar ratio; this means that there is a 2-fold excess of $Mo_2(O_2CCH_3)_4$. We were able to recover 81% of the expected excess.

Structural Results. We have isolated the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ion as the anhydrous salt of trifluoromethanesulfonic acid; this compound is stoichiometrically

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(10) The crystallographic programs for the structural solution and refinement from the Enraf-Nonius Structure Determination Package were used on a PDP 11/45 computer at B. A. Frenz and Associates, College Station, TX.

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Table IV. Comparison of Distances (Å) in Five $[M_3O_2(O_2CR)_6(H_2O)_3]Z$ Compounds[a]

M	R	Z	M-M	M-(μ_3-O)	M-O_2CR	M-OH_2	ref
Mo	C_2H_5	$(CF_3SO_3)_2 \cdot CF_3SO_3H \cdot 4H_2O$	2.752 [2]	1.984 [4]	2.090 [4]	2.144 [4]	5
Mo	CH_3	$Br_2 \cdot H_2O$	2.766 (2)	2.004 [6]	2.093 [3]	2.083 [10]	5
Mo	CH_3	$(CF_3SO_3)_2$	2.759 (1)	1.994 (5)	2.082 [7]	2.129 (6)	*b*
W	CH_3	$(CF_3SO_3)_2$	2.746 (1)	2.011 (5)	2.085 [7]	2.132 (6)	8
W	C_2H_5	$(BF_4)_2 \cdot 5.5H_2O$	2.745 [2]	2.000 [4]	2.090 [10]	2.090 [20]	7

[a] ( ) indicates esd of one value; [ ] indicates $\{(\Sigma\Delta_i^2)/(n(n-1))\}^{1/2}$ for several values whose unweighted arithmetic average is given. [b] This work.

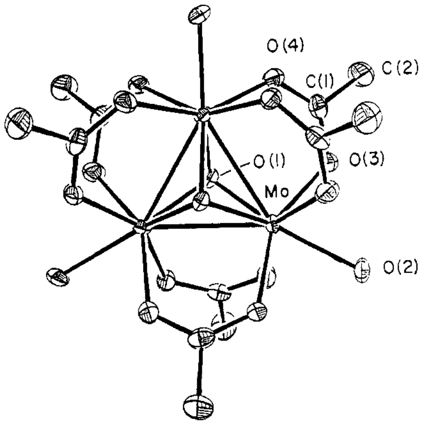

Figure 1. The $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ cation. Atoms are represented by ellipsoids of thermal vibration at the 30% probability level.

analogous to $[W_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$, which was described several years ago.[7,8] In the meantime, the trimolybdenum cation has been isolated and structurally characterized[5] in the compounds $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2 \cdot H_2O$ and $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3](CF_3SO_3)_2 \cdot CF_3SO_3H \cdot 4H_2O$, the former, of course, containing exactly the same trinuclear cation as the present compound.

Table III presents the important bond distances and angles in the present compound, which was found to be crystallographically isomorphous with its tungsten analogue. Figure 1 depicts the trinuclear cation and defines the atom-labeling scheme. Table IV compares average dimensions in this and four other similar M_3O_2 cluster species. On the whole, the five structures are very similar. There are no significant differences among the five M-(μ_3-O) distances nor among the five M-O_2CR distances. Once again, however, it is clear that in the $[Mo_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ cations the Mo-Mo bonds are characteristically *longer* than the W-W bonds. The difference for the two isomorphous compounds is 0.013 (1.4) Å, which is quite real in a statistical sense ($\Delta/\sigma \approx 10$). The average of all three Mo-Mo distances, 2.759 [4] Å, is also significantly larger than the average of the two W-W distances, 2.746 [2] Å (Δ = 0.013 (4) Å). The fact that the Mo-Mo single-bond distance is slightly longer than the W-W single-bond distance is in agreement with recent observations[13] that Mo-X single bonds (where X = Cl or PR_3) are ca. 0.02 Å (X = Cl) to 0.04 Å (X = PR_3) longer than the corresponding W-X bonds. It stands in contrast with the fact that for the much shorter triple and quadruple bonds between metal atoms the Mo to Mo bonds are ca. 0.10 Å shorter than those of their ditungsten analogues. The way in which core-core repulsions for the highly multiple bonds between two tungsten atoms give rise to the latter relationship despite the fact that for single bonds the W radius appears to be slightly the smaller has been discussed elsewhere.[14]

The variations in the M-OH_2 distances probably arise from the effects of hydrogen-bonding interactions. It is satisfying to note that for the two isomorphous compounds the Mo-OH_2 and W-OH_2 distances are not significantly different.

Finally, a few remarks are in order about the $CF_3SO_3^-$ ions in the isomorphous structures. We note first that the angle of internal rotation is again not the "ideal" value of 60°. We find an angle of 29°, which is comparable with the value of 28° found[8] in the tungsten compound, and we agree with the earlier suggestion that the demands of hydrogen bonding are responsible for this. All of the other internal angles and distances in the $CF_3SO_3^-$ ion that we have found in the molybdenum compound agree to within less than 3σ with those in the tungsten compound except for the C-S distance, for which the present value is 1.822 (7) Å compared to 1.736 (23) Å reported for the tungsten compound. Our value is in good agreement with the precise results obtained in several studies of the hydrated forms of the acid,[15-17] where five values in the range of 1.811 (4)-1.833 (4) Å have been found.

Acknowledgment. We are grateful to the U.S. National Science Foundation and the U.S.-Israel Binational Science Foundation for support.

Registry No. $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$, 76797-45-0; $Mo_2(O_2CCH_3)_4$, 14221-06-8; Na_2MoO_4, 7631-95-0.

Supplementary Material Available: A table of structure factors, tables of anisotropic thermal parameters, complete tables of bond distances and angles, and a table of rms amplitudes of vibration (12 pages). Ordering information is given on any current masthead page.

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