An EDTA Complex Containing Two Triangular Trimolybdenum Clusters with Mo–Mo Single Bonds

Avi Bino,[1a] F. Albert Cotton,*[1a] and Zvi Dori[1b,c]

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received November 9, 1978*

Abstract: From a solution of molybdenum(IV) in aqueous acetate buffer to which Na_2H_2EDTA is added, red crystals are obtained upon slow evaporation. This product has the composition $Na_4[Mo_6O_8(EDTA)_3]\cdot 14H_2O$. The crystals belong to the space group $P2_1/c$ with unit cell dimensions $a = 18.157$ (6) Å, $b = 16.903$ (5) Å, $c = 19.101$ (4) Å, $\beta = 91.38$ (2)°, $V = 5861$ (3) Å^3; the cell contains four formula units. The structure has been solved and refined and found to be built of anions consisting of two equivalent trinuclear units connected by EDTA groups. Each trinuclear unit consists of an equilateral triangle of Mo atoms (mean Mo–Mo = 2.51 ± 0.01 Å) capped by one triply bridging oxygen atom (mean Mo–O = 2.04 ± 0.02 Å) and three oxygen atoms that bridge pairs of molybdenum atoms (mean Mo–O = 1.93 ± 0.01 Å). Each Mo atom is then coordinated by two carboxyl oxygen atoms and a nitrogen atom from one end of an $EDTA^{4-}$ ion; each end of each $EDTA^{4-}$ ion is attached to a different Mo_3 cluster, so that two such clusters are connected by three EDTA units to form a prolate spheroid. The $Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3O_6N_3$ groups have the same geometric structure that has recently been found for the $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion.

Introduction

We have recently shown that there is an extensive chemistry of molybdenum and tungsten in the oxidation state IV involving discrete trinuclear clusters in which there are metal–metal single bonds.[2-4] A point of particular interest is the recent isolation[2] of a discrete species of the type shown in Figure 1, in which the γ positions are occupied by oxygen atoms of oxalato groups and the δ positions by water molecules. This cation, $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$, constitutes the first example of the occurrence of such a structure in discrete form, although it was previously known in several extended arrays, of which the compound $Zn_2Mo_3O_8$ provides the earliest example.[5]

Species of this kind are of interest in connection with metal atom cluster chemistry since they contain equilateral triangular clusters in which there are M–M single bonds when the metal atoms are in oxidation state IV, with interesting possibilities for variations in the electron count without loss of M–M bonding,[6] as recently exemplified by the $[Mo_3OCl_3(O_2CCH_3)_3(H_2O)_3]^{2-}$ ion.[7] They are also of interest with respect to the nature of the Mo^{IV} species that can occur in aqueous solution. There is evidence[8] that, in noncomplexing media, Mo^{IV} occurs as a dinuclear species with a total charge of +4, but the isolation of such a species in a crystalline compound has not yet been reported.

Since there are several examples of the $EDTA^{4-}$ ligand, or one of its partially protonated forms, cradling a bridged dinuclear moiety,[9] we decided to see what could be isolated from an appropriately buffered aqueous Mo^{IV} solution, prepared according to Ardon and Pernick,[8a] by adding the H_2EDTA^{2-} ion. Well-formed red crystals were obtained and their structure was determined by X-ray crystallography. This investigation is fully described in this report.

Experimental Section

Preparation of $Na_4[Mo_6O_3(EDTA)_3]\cdot 14H_2O$. A solution of Mo(IV) (150 mL, 0.01 M), prepared by the method of Ardon and Pernick,[8a] was adsorbed on a Dowex 50W × 2 cation exchange column. The red cation was then eluted with an acetate buffer solution [acetic acid (1 M), sodium acetate (1 M)]. Disodium dihydrogen ethylenediaminetetraacetate dihydrate (1 g) was added to the eluent (5 mL). The solution was stirred, filtered, and placed in a KOH desiccator. After a few days, red crystals were obtained from the red-brown solution.

X-ray Crystallography. A crystal of dimensions 0.4 × 0.2 × 0.2 mm was attached to the end of a glass fiber and mounted on a Syntex $P\bar{1}$ four-circle diffractometer. Mo Kα ($\lambda = 0.710\,730$ Å) radiation, with a graphite crystal monochromator in the incident beam, was used. Rotation photographs and ω scans of several strong reflections indicated that the crystal was of satisfactory quality. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1/c$. The unit cell dimensions were obtained by a least-squares fit of 15 strong reflections in the range $25° < 2\theta < 45°$ giving $a = 18.157$ (6) Å, $b = 16.903$ (5) Å, $c = 19.101$ (4) Å, $\beta = 91.38$ (2)°, and $V = 5861$ (3) Å^3. With these dimensions and $Z = 4$ (for the formula $Mo_6Na_4O_{46}N_6C_{30}H_{64}$, mol wt 1912) the density is calculated to be 2.17 g cm^{-3}. The density determined by flotation in a mixture of bromoform and carbon tetrachloride was 2.17 ± 0.05 g cm^{-3}. Data were measured by θ–2θ scans. A total of 7723 reflections in the range $0° < 2\theta < 45°$ were collected of which 5643 had $I > 3\sigma(I)$. General procedures for data collection have been reported elsewhere.[10] The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 13.8 cm^{-1}. No absorption correction was applied.

The heavy-atom positions were obtained by direct methods using the MULTAN program. The structure was refined[11] in space group $P2_1/c$ to convergence using anisotropic thermal parameters for Mo atoms and isotropic thermal parameters for all the nonhydrogen atoms.

The discrepancy indices used were

$$R_1 = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|}$$

$$R_2 = \frac{[\Sigma w(|F_o| - |F_c|)^2]^{1/2}}{\Sigma w|F_o|^2}$$

The final values of these indices are $R_1 = 0.087$, $R_2 = 0.133$ with an error in an observation of unit weight equal to 2.92. The final difference map showed no peaks of structural significance. A list of the observed and calculated structure factors is available as supplementary material.

Results

The positional and thermal parameters of all atoms are listed in Table I. Table II lists the interatomic distances and angles. The atomic numbering scheme used in these tables is defined in Figures 2–5, which also show the structure in detail.

The asymmetric unit contains an entire $[Mo_3O_4(EDTA)_3Mo_3O_4]^{4-}$ ion; hence, there is no crystallographic symmetry imposed on this ion. In a chemical sense, however, it possesses considerable internal symmetry. The two Mo_3O_4 units are equivalent, the three $EDTA^{4-}$ units are equivalent, and the two $-CH_2N(CH_2CO_2)_2$ halves of each $EDTA^{4-}$ moiety are equivalent. Moreover, each Mo_3O_4 unit has, effectively, C_{3v} symmetry.

In $P2_1/c$ there are fourfold general positions. Na(3), Na(4),

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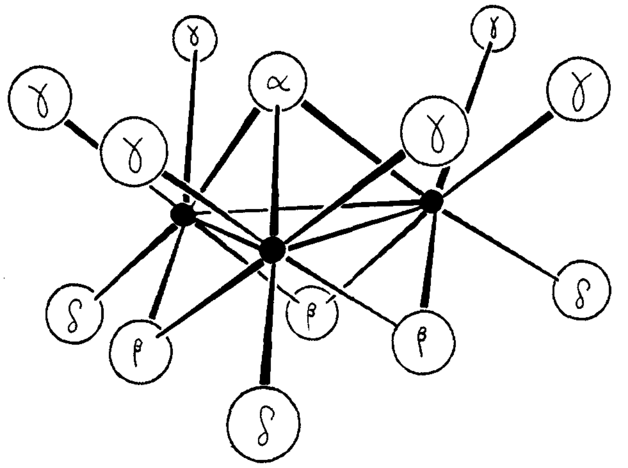

Figure 1. A general representation of the $M_3O_4X_9$ unit, where M = Mo or W, and the X's may be oxygen atoms or a variety of other suitable ligands such as Cl^-, N, etc. The four types of site are distinguished α, β, γ, and δ of which there are one, three, six, and three, respectively.

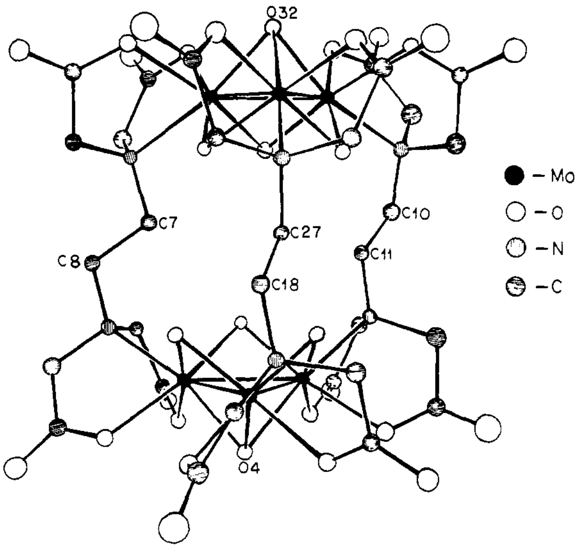

Figure 2. The entire $[(Mo_3O_4)_2(EDTA)_3]^{4-}$ ion. Sufficient atom numbers are given to clarify the positions of the subunits, shown in detail in Figures 3–5, in the complete structure. The atoms have been made arbitrarily small for the sake of clarity.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

atom	*X*	*Y*	*Z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo(1)	0.247 35 (8)	0.708 65 (9)	0.494 98 (8)	1.76 (6)	1.13 (6)	1.48 (6)	−0.11 (5)	−0.00 (5)	0.01 (5)
Mo(2)	0.178 23 (8)	0.701 34 (9)	0.606 30 (8)	1.53 (6)	1.42 (6)	1.69 (6)	−0.13 (5)	−0.05 (5)	0.19 (5)
Mo(3)	0.317 01 (8)	0.704 18 (9)	0.609 06 (8)	1.39 (6)	1.44 (6)	1.66 (6)	−0.15 (5)	−0.09 (5)	0.19 (5)
Mo(4)	0.240 02 (9)	1.068 57 (9)	0.473 73 (8)	2.61 (7)	1.24 (6)	1.89 (6)	0.02 (6)	0.04 (6)	0.10 (5)
Mo(5)	0.312 67 (9)	1.064 29 (9)	0.586 66 (8)	1.90 (7)	1.52 (6)	1.91 (6)	−0.27 (5)	0.15 (6)	−0.17 (6)
Mo(6)	0.173 61 (9)	1.062 21 (9)	0.586 49 (8)	2.17 (7)	1.30 (6)	2.08 (6)	0.22 (6)	0.07 (6)	−0.19 (5)
Na(1)	0.5000 (0)	0.5000 (0)	0.5000 (0)	6.1 (3)					
Na(2)	0.0000 (0)	0.5000 (0)	0.5000 (0)	18.0 (12)					
Na(3)	0.3742 (8)	0.4139 (8)	0.4000 (8)	8.7 (3)					
Na(4)	0.8382 (8)	0.7372 (9)	0.2858 (7)	8.7 (3)					
Na(5)	0.8685 (11)	0.6351 (11)	0.4570 (11)	13.5 (6)					
O(1)	0.1672 (6)	0.7720 (6)	0.5280 (6)	1.4 (2)					
O(2)	0.3230 (6)	0.7756 (7)	0.5312 (6)	2.0 (2)					
O(3)	0.2464 (6)	0.7689 (7)	0.6585 (6)	1.8 (2)					
O(4)	0.2478 (6)	0.6198 (7)	0.5682 (6)	2.0 (2)					
O(5)	0.4033 (7)	0.6377 (7)	0.5688 (6)	2.4 (2)					
O(6)	0.3420 (7)	0.6332 (7)	0.6939 (7)	2.6 (2)					
O(7)	0.3228 (7)	0.6495 (8)	0.4330 (7)	2.8 (3)					
O(8)	0.1733 (7)	0.6474 (7)	0.4305 (6)	2.6 (2)					
O(9)	0.0918 (8)	0.6603 (9)	0.3424 (8)	4.2 (3)					
O(10)	0.1565 (7)	0.6297 (7)	0.6903 (6)	2.3 (2)					
O(11)	0.0918 (7)	0.6319 (7)	0.5615 (6)	2.2 (2)					
O(12)	−0.0190 (7)	0.6379 (8)	0.5111 (7)	3.1 (3)					
O(13)	0.1646 (7)	1.1379 (8)	0.4156 (7)	3.0 (3)					
O(14)	0.3874 (10)	0.6583 (11)	0.3386 (10)	6.2 (4)					
O(15)	0.4339 (10)	0.5896 (10)	0.7629 (9)	5.5 (4)					
O(16)	0.5180 (8)	0.6380 (8)	0.5300 (7)	3.4 (3)					
O(17)	0.0649 (9)	0.5785 (9)	0.7515 (8)	4.5 (3)					
O(18)	0.6447 (13)	0.5107 (14)	0.4922 (12)	9.3 (6)					
O(19)	0.4627 (10)	0.5238 (11)	0.3829 (10)	6.3 (4)					
O(20)	0.9423 (12)	0.7255 (13)	0.3635 (12)	8.4 (6)					
O(21)	0.0415 (12)	0.5102 (14)	0.3885 (12)	8.8 (6)					
O(22)	0.3260 (16)	0.3028 (16)	0.4447 (15)	11.2 (8)					
O(23)	0.7608 (16)	0.6949 (17)	0.3848 (15)	11.6 (8)					
O(24)	0.1692 (14)	0.3030 (15)	0.4443 (14)	10.3 (7)					
O(25)	0.1664 (14)	0.4818 (14)	0.4914 (13)	9.9 (7)					
O(26)	0.5841 (23)	0.7088 (24)	0.4114 (23)	18.8 (14)					
O(27)	0.3156 (6)	1.1367 (7)	0.4171 (6)	2.0 (2)					
O(28)	0.3191 (6)	0.9996 (7)	0.5056 (6)	1.9 (2)					
O(29)	0.3339 (7)	1.1262 (8)	0.6801 (7)	3.0 (3)					
O(30)	0.4067 (7)	1.1254 (8)	0.5595 (7)	3.1 (3)					
O(31)	0.2434 (6)	0.9959 (6)	0.6331 (6)	1.5 (2)					
O(32)	0.2417 (7)	1.1504 (7)	0.5511 (6)	2.2 (2)					
O(33)	0.1575 (7)	1.1222 (7)	0.6822 (6)	2.4 (2)					
O(34)	0.1195 (8)	1.1050 (8)	0.7909 (7)	3.5 (3)					
O(35)	0.0768 (7)	1.1235 (7)	0.5607 (7)	2.8 (3)					
O(36)	0.1635 (6)	1.0001 (7)	0.5033 (6)	2.2 (2)					
O(37)	0.3956 (9)	1.1355 (9)	0.3339 (8)	4.6 (3)					
O(38)	0.1180 (8)	1.1673 (9)	0.3116 (8)	3.9 (3)					
O(39)	0.7298 (16)	0.7510 (18)	0.2224 (15)	12.5 (9)					
O(40)	0.5784 (17)	0.6024 (16)	0.3055 (16)	12.1 (9)					

atom	*X*	*Y*	*Z*	*B*(1,1)
O(41)	0.7108 (18)	0.5280 (19)	0.3551 (17)	13.8 (10)
O(42)	0.2551 (17)	0.4825 (19)	0.3668 (16)	13.8 (10)
O(43)	−0.0441 (9)	1.1249 (9)	0.5698 (9)	4.8 (4)
O(44)	0.8773 (19)	0.5640 (20)	0.3556 (18)	14.0 (10)
O(45)	0.3823 (9)	0.3813 (9)	0.2860 (9)	4.7 (4)
O(46)	0.5276 (9)	1.1219 (9)	0.0548 (9)	4.9 (4)
N(1)	0.4250 (8)	0.7629 (8)	0.6506 (7)	1.7 (3)
N(2)	0.2426 (8)	0.7860 (8)	0.3995 (7)	1.9 (3)
N(3)	0.0688 (8)	0.7573 (8)	0.6438 (7)	2.0 (3)
N(4)	0.2443 (8)	1.0086 (9)	0.3673 (8)	2.3 (3)
N(5)	0.3987 (8)	0.9879 (8)	0.6370 (7)	1.8 (3)
N(6)	0.0904 (8)	0.9833 (8)	0.6368 (7)	1.8 (3)
C(1)	0.1472 (10)	0.6839 (11)	0.3783 (10)	2.2 (4)
C(2)	0.1732 (10)	0.7658 (11)	0.3618 (10)	2.7 (4)
C(3)	0.0307 (10)	0.6684 (11)	0.5487 (9)	2.1 (3)
C(4)	0.1254 (10)	1.0834 (11)	0.7304 (10)	2.4 (4)
C(5)	0.0430 (11)	0.7037 (12)	0.7008 (10)	2.8 (4)
C(6)	0.0905 (10)	0.6324 (11)	0.7145 (10)	2.5 (4)
C(7)	0.1060 (10)	0.8981 (10)	0.6189 (10)	2.1 (4)
C(8)	0.0677 (10)	0.8416 (11)	0.6677 (9)	2.0 (3)
C(9)	0.0197 (10)	0.7479 (10)	0.5803 (9)	2.0 (3)
C(10)	0.2208 (11)	0.9237 (11)	0.3591 (10)	2.7 (4)
C(11)	0.2482 (10)	0.8698 (10)	0.4206 (9)	2.1 (3)
C(12)	0.3108 (12)	0.7655 (12)	0.3549 (11)	3.4 (4)
C(13)	0.3422 (11)	0.6806 (11)	0.3765 (10)	2.7 (4)
C(14)	0.4064 (11)	0.6397 (12)	0.7228 (10)	2.9 (4)
C(15)	0.4498 (10)	0.7130 (10)	0.7118 (9)	2.0 (3)
C(16)	0.4666 (10)	0.6718 (10)	0.5615 (9)	2.1 (4)
C(17)	0.4749 (11)	0.7532 (11)	0.5901 (10)	2.6 (4)
C(18)	0.4241 (10)	0.8474 (11)	0.6717 (9)	2.1 (3)
C(19)	0.0998 (10)	0.9976 (11)	0.7131 (9)	2.2 (4)
C(20)	0.0163 (11)	1.0069 (12)	0.6084 (10)	3.1 (4)
C(21)	0.3434 (10)	1.1033 (10)	0.3674 (10)	2.2 (4)
C(22)	0.3205 (12)	1.0179 (13)	0.3485 (11)	3.5 (4)
C(23)	0.1973 (13)	1.0582 (13)	0.3170 (12)	4.0 (5)
C(24)	0.1586 (11)	1.1236 (11)	0.3505 (10)	2.5 (4)
C(25)	0.3695 (10)	1.0900 (10)	0.7266 (9)	2.0 (3)
C(26)	0.3976 (10)	1.0067 (10)	0.7126 (9)	2.0 (3)
C(27)	0.3823 (9)	0.9021 (9)	0.6230 (9)	1.4 (3)
C(28)	0.4670 (10)	1.0911 (11)	0.5698 (10)	2.5 (4)
C(29)	0.4734 (10)	1.0119 (11)	0.6075 (10)	2.4 (4)
C(30)	0.0168 (10)	1.0907 (11)	0.5781 (10)	2.4 (4)

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table II. Bond Distances and Bond Angles for $Na_4[Mo_6O_8(EDTA)_3]\cdot 14H_2O$

Bond Distances

atoms	distance, Å	atoms	distance, Å	atoms	distance, Å
Mo(1)-Mo(2)	2.498 (1)				
Mo(3)	2.494 (1)	Mo(2)-Mo(3)	2.520 (1)		
O(1)	1.925 (6)	O(1)	1.922 (6)	Mo(3)-O(2)	1.920 (7)
O(2)	1.897 (7)	O(3)	1.943 (7)	O(3)	1.947 (7)
O(4)	2.052 (7)	O(4)	2.018 (7)	O(4)	2.043 (7)
O(7)	2.087 (8)	O(10)	2.056 (7)	O(5)	2.090 (7)
O(8)	2.078 (7)	O(11)	2.124 (7)	O(6)	2.059 (8)
N(2)	2.244 (8)	N(3)	2.329 (9)	N(1)	2.319 (9)
Mo(4)-Mo(5)	2.502 (1)				
Mo(6)	2.496 (1)	Mo(5)-Mo(6)	2.525 (1)		
O(13)	2.099 (8)	O(28)	1.901 (7)	Mo(6)-O(31)	1.897 (6)
O(27)	2.110 (7)	O(29)	2.097 (8)	O(32)	2.061 (7)
O(28)	1.937 (7)	O(30)	2.072 (8)	O(33)	2.117 (7)
O(32)	2.025 (7)	O(31)	1.938 (6)	O(35)	2.089 (8)
O(36)	1.905 (7)	O(32)	2.050 (7)	O(36)	1.911 (7)
N(4)	2.274 (9)	N(5)	2.227 (9)	N(6)	2.248 (9)
EDTA 1		EDTA 2		EDTA 3	
O(7)-C(13)	1.26 (1)	O(10)-C(6)	1.30 (1)	O(5)-C(16)	1.30 (1)
C(13)-O(14)	1.17 (1)	C(6)-O(17)	1.25 (1)	C(16)-O(16)	1.26 (1)
C(13)-C(12)	1.59 (2)	C(6)-C(5)	1.50 (2)	C(16)-C(17)	1.49 (1)
C(12)-N(2)	1.56 (1)	C(5)-N(3)	1.50 (1)	C(17)-N(1)	1.49 (1)
N(2)-C(2)	1.48 (1)	N(3)-C(9)	1.50 (1)	N(1)-C(15)	1.50 (1)
C(2)-C(1)	1.50 (1)	C(9)-C(3)	1.49 (1)	C(15)-C(14)	1.49 (1)
C(1)-O(8)	1.25 (1)	C(3)-O(11)	1.29 (1)	C(14)-O(6)	1.29 (1)
C(1)-O(9)	1.27 (1)	C(3)-O(12)	1.25 (1)	C(14)-O(15)	1.24 (1)
N(2)-C(11)	1.48 (1)	N(3)-C(8)	1.50 (1)	N(1)-C(18)	1.48 (1)
C(11)-C(10)	1.56 (1)	C(8)-C(7)	1.52 (1)	C(18)-C(27)	1.50 (1)
C(10)-N(4)	1.50 (1)	C(7)-N(6)	1.51 (1)	C(27)-N(5)	1.50 (1)
N(4)-C(22)	1.45 (1)	N(6)-C(19)	1.48 (1)	N(5)-C(26)	1.48 (1)
C(22)-C(21)	1.54 (2)	C(19)-C(4)	1.56 (1)	C(26)-C(25)	1.52 (1)
C(21)-O(27)	1.22 (1)	C(4)-O(33)	1.28 (1)	C(25)-O(29)	1.25 (1)
C(21)-O(37)	1.28 (1)	C(4)-O(34)	1.22 (1)	C(25)-O(45)	1.25 (1)
N(4)-C(23)	1.52 (2)	N(6)-C(20)	1.49 (1)	N(5)-C(29)	1.53 (1)
C(23)-C(24)	1.46 (2)	C(20)-C(30)	1.53 (2)	C(29)-C(28)	1.52 (1)
C(24)-O(13)	1.27 (1)	C(30)-O(35)	1.27 (1)	C(28)-O(30)	1.25 (1)
C(24)-O(38)	1.27 (1)	C(30)-O(43)	1.25 (1)	C(28)-O(46)	1.26 (1)

Bond Angles

atoms	angle, deg	atoms	angle, deg
Mo(2)-Mo(1)-Mo(3)	60.62 (3)	Mo(1)-Mo(2)-Mo(3)	59.62 (3)
O(1)-Mo(1)-O(2)	95.4 (3)	O(1)-Mo(2)-O(3)	95.0 (3)
O(4)	100.1 (3)	O(4)	101.4 (3)
O(7)	164.5 (3)	O(10)	162.9 (3)
O(8)	89.3 (3)	O(11)	88.1 (3)
N(2)	85.8 (3)	N(3)	85.0 (3)
O(2)-Mo(1)-O(4)	101.3 (3)	O(3)-Mo(2)-O(4)	100.9 (3)
O(7)	90.8 (3)	O(10)	94.4 (3)
O(8)	165.0 (3)	O(11)	171.0 (3)
N(2)	87.9 (3)	N(3)	98.1 (3)
O(4)-Mo(1)-O(7)	92.5 (3)	O(4)-Mo(2)-O(10)	90.7 (3)
O(8)	91.8 (3)	O(11)	86.6 (3)
N(2)	168.4 (3)	N(3)	159.2 (3)
O(7)-Mo(1)-O(8)	81.3 (3)	O(10)-Mo(2)-O(11)	80.5 (3)
N(2)	80.3 (3)	N(3)	79.5 (3)
O(8)-Mo(1)-N(2)	78.3 (3)	O(11)-Mo(2)-N(3)	73.8 (3)
Mo(1)-Mo(3)-Mo(2)	59.76 (3)		
O(2)-Mo(3)-O(3)	94.2 (3)		
O(4)	100.8 (3)		
O(5)	89.8 (3)		
O(6)	163.9 (3)		
N(1)	86.2 (3)		
O(3)-Mo(3)-O(4)	99.9 (3)		
O(5)	171.4 (3)		
O(6)	94.6 (3)		
N(1)	98.9 (3)		
O(4)-Mo(3)-O(5)	86.8 (3)		
O(6)	90.9 (3)		
N(1)	159.4 (3)		
O(5)-Mo(3)-O(6)	79.8 (3)		
N(1)	73.8 (3)		
O(6)-Mo(3)-N(1)	79.1 (3)		

Table II (*Continued*)

Bond Angles			
atoms	angle, deg	atoms	angle, deg
Mo(5)-Mo(4)-Mo(6)	60.69 (4)	Mo(4)-Mo(5)-Mo(6)	59.53 (4)
O(13)-Mo(4)-O(27)	81.2 (3)	O(28)-Mo(5)-O(29)	165.1 (3)
O(28)	166.3 (3)	O(30)	90.9 (3)
O(32)	90.1 (3)	O(31)	94.8 (3)
O(36)	91.4 (3)	O(32)	100.9 (3)
N(4)	79.2 (3)	N(5)	87.8 (3)
O(27)-Mo(4)-O(28)	90.2 (3)	O(29)-Mo(5)-O(30)	80.2 (3)
O(32)	90.2 (3)	O(31)	90.9 (3)
O(36)	166.4 (3)	O(32)	91.6 (3)
N(4)	75.4 (3)	N(5)	79.0 (3)
O(28)-Mo(4)-O(32)	100.6 (3)	O(30)-Mo(5)-O(31)	163.6 (3)
O(36)	94.7 (3)	O(32)	94.5 (3)
N(4)	88.4 (3)	N(5)	79.8 (3)
O(32)-Mo(4)-O(36)	101.4 (3)	O(31)-Mo(5)-O(32)	99.5 (3)
N(4)	163.1 (3)	N(5)	85.0 (3)
O(36)-Mo(4)-N(4)	92.0 (3)	O(32)-Mo(5)-N(5)	169.7 (3)
Mo(4)-Mo(6)-Mo(5)	59.78 (4)		
O(31)-Mo(6)-O(32)	100.5 (3)		
O(33)	89.0 (3)		
O(35)	162.2 (3)		
O(36)	96.6 (3)		
N(6)	84.1 (3)		
O(32)-Mo(6)-O(33)	91.9 (3)		
O(35)	94.1 (3)		
O(36)	99.9 (3)		
N(6)	169.7 (3)		
O(33)-Mo(6)-O(35)	80.4 (3)		
O(36)	165.7 (3)		
N(6)	78.9 (3)		
O(35)-Mo(6)-O(36)	90.7 (3)		
N(6)	79.9 (3)		
O(36)-Mo(6)-N(6)	88.7 (3)		
Mo(1)-O(1)-Mo(2)	81.0 (2)	Mo(4)-O(28)-Mo(5)	81.4 (3)
Mo(1)-O(2)-Mo(3)	81.6 (3)	Mo(4)-O(36)-Mo(6)	81.7 (3)
Mo(2)-O(3)-Mo(3)	80.8 (3)	Mo(5)-O(31)-Mo(6)	82.3 (2)
Mo(1)-O(4)-Mo(2)	75.7 (2)	Mo(4)-O(32)-Mo(5)	75.8 (2)
Mo(1)-O(4)-Mo(3)	75.1 (2)	Mo(4)-O(32)-Mo(6)	75.3 (2)
Mo(2)-O(4)-Mo(3)	76.7 (2)	Mo(5)-O(32)-Mo(6)	75.8 (2)
EDTA 1			
Mo(1)-O(7)-C(13)	119.1 (8)	C(11)-C(10)-N(4)	113.1 (9)
O(7)-C(13)-O(14)	128 (1)	Mo(4)-N(4)-C(10)	120.2 (9)
C(12)	120 (1)	-C(22)	103.1 (9)
O(14)-C(13)-C(12)	112 (1)	-C(23)	106.7 (9)
C(13)-C(12)-N(2)	110.0 (9)	C(10)-N(4)-C(22)	110.4 (9)
Mo(1)-N(2)-C(12)	107.4 (7)	C(23)	107.8 (9)
-C(2)	106.1 (7)	C(22)-N(4)-C(23)	108.0 (9)
-C(11)	109.6 (7)	N(4)-C(22)-C(21)	107 (1)
C(2)-N(2)-C(11)	114.1 (8)	C(22)-C(21)-O(27)	120 (1)
-C(12)	111.3 (9)	C(22)-C(21)-O(37)	119 (1)
C(11)-N(2)-C(12)	108.1 (8)	O(27)-C(21)-O(37)	121 (1)
N(2)-C(2)-C(1)	112.3 (9)	Mo(4)-O(27)-C(21)	115.6 (7)
C(2)-C(1)-O(8)	120 (1)	N(4)-C(23)-C(24)	114 (1)
-O(9)	115 (1)	C(23)-C(24)-O(13)	123 (1)
O(8)-C(1)-O(9)	124 (1)	O(38)	117 (1)
Mo(1)-O(8)-C(1)	116.8 (7)	O(13)-C(24)-O(38)	120 (1)
N(2)-C(11)-C(10)	109.6 (9)	Mo(4)-O(13)-C(24)	116.8 (7)
EDTA 2			
Mo(2)-O(10)-C(6)	117.0 (7)	C(8)-C(7)-N(6)	111.7 (9)
O(10)-C(6)-O(17)	122 (1)	Mo(6)-N(6)-C(7)	109.7 (8)
C(5)	120 (1)	C(19)	105.1 (8)
O(17)-C(6)-C(5)	118 (1)	C(20)	107.2 (8)
C(6)-C(5)-N(3)	116 (1)	C(7)-N(6)-C(19)	111.2 (8)
Mo(2)-N(3)-C(5)	105.2 (7)	C(20)	110.3 (8)
C(8)	119.9 (7)	C(19)-N(6)-C(20)	113.2 (8)
C(9)	101.7 (7)	N(6)-C(20)-C(30)	111.8 (9)
C(5)-N(3)-C(8)	110.3 (8)	C(20)-C(30)-O(35)	121 (1)
C(9)	109.6 (8)	O(43)	117 (1)
C(8)-N(3)-C(9)	109.6 (8)	O(35)-C(30)-O(43)	122 (1)
N(3)-C(9)-C(3)	110.0 (9)	Mo(6)-O(35)-C(30)	116.3 (7)
C(9)-C(3)-O(11)	118.6 (9)	N(6)-C(19)-C(4)	112.8 (9)
-O(12)	120 (1)	C(19)-C(4)-O(33)	118 (1)

Table II (*Continued*)

atoms	angle, deg	atoms	angle, deg
O(11)-C(3)-O(12)	121 (1)	O(34)	117 (1)
Mo(2)-O(11)-C(3)	115.9 (6)	O(33)-C(4)-O(34)	125 (1)
N(3)-C(8)-C(7)	113.8 (9)	Mo(6)-O(33)-C(4)	116.8 (7)
		EDTA 3	
Mo(3)-O(5)-C(16)	118.3 (7)	C(18)-C(27)-N(5)	112.8 (8)
O(5)-C(16)-O(16)	121 (1)	Mo(5)-N(5)-C(26)	105.7 (7)
-C(17)	117 (1)	C(27)	110.4 (7)
O(16)-C(16)-C(17)	122 (1)	C(29)	107.8 (7)
C(16)-C(17)-N(1)	109.2 (9)	C(26)-N(5)-C(27)	111.9 (8)
Mo(3)-N(1)-C(15)	105.2 (7)	C(29)	109.5 (8)
C(17)	102.3 (7)	C(27)-N(5)-C(29)	111.3 (8)
C(18)	119.4 (7)	N(5)-C(26)-C(25)	112.5 (9)
C(15)-N(1)-C(17)	111.3 (8)	C(26)-C(25)-O(29)	120 (1)
C(18)	109.5 (8)	O(45)	118 (1)
C(17)-N(1)-C(18)	109.0 (8)	O(29)-C(25)-O(45)	123 (1)
N(1)-C(15)-C(14)	115.3 (9)	Mo(5)-O(29)-C(25)	116.3 (7)
C(15)-C(14)-O(6)	119 (1)	N(5)-C(29)-C(28)	110.3 (9)
O(15)	117 (1)	C(29)-C(28)-O(30)	123 (1)
O(6)-C(14)-O(15)	124 (1)	O(46)	114 (1)
Mo(3)-O(6)-C(14)	118.0 (7)	O(30)-C(28)-O(46)	123 (1)
N(1)-C(18)-C(27)	115.5 (9)	Mo(5)-O(30)-C(28)	117.0 (7)

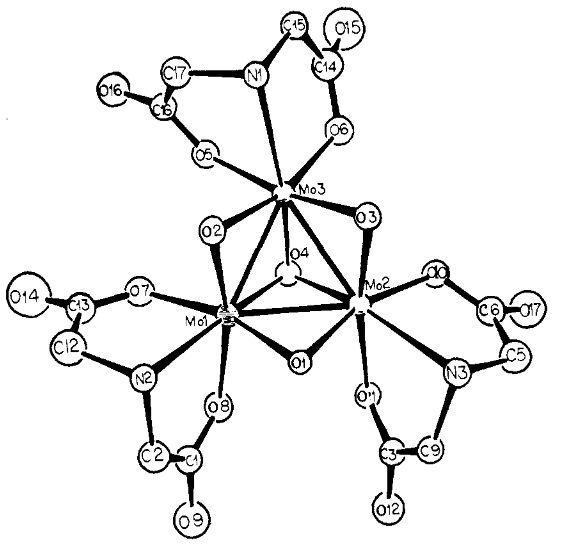

Figure 3. A detailed representation of the $Mo_3O_4[(O_2CCH_2)_2N-]_3$ portion of the structure containing Mo(1), Mo(2), and Mo(3).

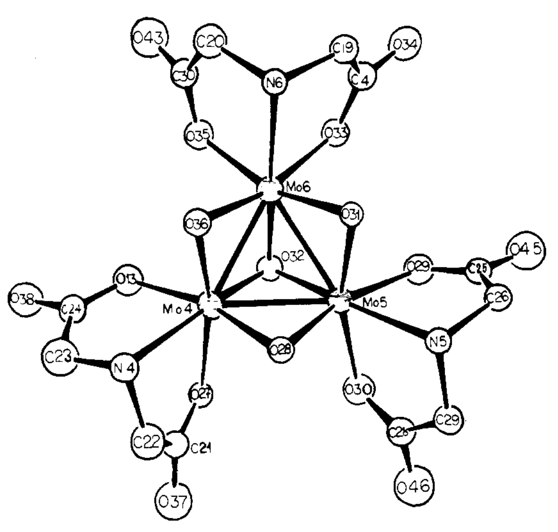

Figure 4. A detailed representation of the $Mo_3O_4[(O_2CCH_2)_2N-]_3$ portion of the structure containing Mo(4), Mo(5), and Mo(6).

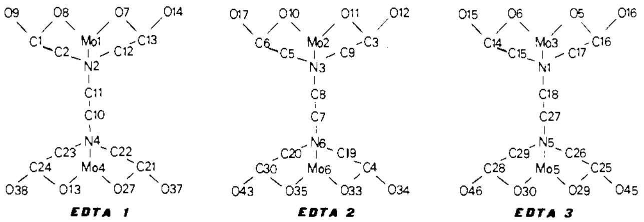

Figure 5. Sketches of the three Mo(EDTA)Mo chains showing how the atoms are numbered.

and Na(5) occupy general positions and thus account for 12 sodium atoms in the cell. Na(1) and Na(2) give half-occupancy of special positions and thus represent only four sodium atoms. In this way the required four sodium atoms per molecule are accounted for.

Discussion

Once again, the aqueous solution of Mo^{IV} prepared according to Ardon and Pernick affords a crystalline solid containing trinuclear rather than binuclear units. The Mo_3O_4 portions of the EDTA complex we have obtained are not significantly different from those previously found[2] in the $[Mo_3O_4(C_2O_4)_3(H_2O)_3]^{2-}$ ion. In the present case the γ positions of the Mo_3O_{13} unit (Figure 1) are occupied by carboxylate oxygen atoms while the δ positions are occupied by nitrogen atoms.

The isolation of a compound containing these trinuclear units, rather than dinuclear ones, is very interesting when viewed in the context of previous work on EDTA complexes of molybdenum in various oxidation states from III to VI, inclusive. The EDTA complexes of Mo^{VI}, Mo^{VI} and Mo^{V}, Mo^{V}, having the formulas $[(MoO_3)_2EDTA]^{4-}$ and $[Mo_2O_4EDTA]^{2-}$, respectively, have rather straightforward chemical and structural properties.[9,12] It is also well-known that Mo^{III}, Mo^{III} species can be prepared either by electrolytic reduction[13] or zinc amalgam reduction[14] of the Mo^{V}, Mo^{V} complex, and the structure of one of these, in which an $Mo(\mu\text{-}OH)_2Mo$ unit is cupped in an $EDTA^{4-}$ unit and also bridged by a bidentate acetate ion to form the $[Mo_2(OH)_2(O_2CCH_3)EDTA]^{-}$ ion, has been reported.[15]

Attempts to oxidize this Mo^{III}, Mo^{III} unit have been described. By using potassium azide, only half the molybdenum atoms can be oxidized to give a Mo^{III}, Mo^{IV} species that has a tetranuclear structure consisting of two $Mo_2(\mu\text{-}O)(\mu\text{-}OH)$EDTA units linked by bridging oxide ions.[16] It also appears that dinuclear Mo^{IV}, Mo^{IV} compounds can be obtained but there is no proof of structure yet available for these.[17]

The trinuclear species[2,7] we have been isolating from the Ardon and Pernick solution, including the EDTA compound reported here, do not seem related to the bi- or tetranuclear species that have been found or postulated by Sykes and his co-workers. Clearly, the solution chemistry of Mo^{IV} still holds challenges for research.

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Supplementary Material Available: A list of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Photoinduced Fragmentation of $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$

Ronald A. Epstein, Thomas R. Gaffney, Gregory L. Geoffroy,*
Wayne L. Gladfelter, and Richard S. Henderson

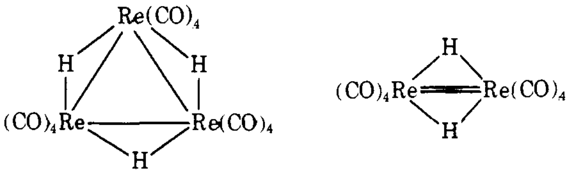
Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received December 26, 1978*

Abstract: Ultraviolet irradiation of $H_3Re_3(CO)_{12}$ in degassed solution leads to quantitative formation of $H_2Re_2(CO)_8$. Quantum yields measured at 313 and 366 nm are of the order of 0.1. Photolysis in the presence of CO also gives fragmentation and formation of $HRe(CO)_5$ and $H_2Re_2(CO)_8$, but the latter thermally reacts with CO to form $HRe(CO)_5$ and $Re_2(CO)_{10}$. The quantum yield of disappearance of $H_3Re_3(CO)_{12}$ in the presence of CO is 0.02. Photolysis of the analogous $H_3Mn_3(CO)_{12}$ cluster produces $HMn(CO)_5$, $Mn_2(CO)_{10}$, and an unidentified brown precipitate. Experiments directed toward elucidating the mechanism of these photoreactions are discussed.

The photochemistry of metal carbonyl complexes has been extensively investigated both for its mechanistic and synthetic value.[1,2] The majority of studies have focused on monomeric and dimeric complexes but relatively few reports describing the photochemistry of metal carbonyl clusters have appeared.[3-19] As with dimeric metal carbonyls, the dominant reaction mode of trimeric clusters appears to be metal–metal bond cleavage and subsequent fragmentation. $Ru_3(CO)_{12}$, for example, has been shown to yield monomeric $Ru(CO)_4L$ and $Ru(CO)_3L_2$ compounds upon photolysis in the presence of the appropriate donor ligand L,[3-6] and several $Os(CO)_3L_2$ complexes have been prepared via photolysis of $Os_3(CO)_{12}$.[7-9] Irradiation of the $RCCo_3(CO)_9$ (R = H, CH_3) clusters under an H_2 atmosphere has likewise been shown to give fragmentation and subsequent formation of $Co_4(CO)_{12}$ and CH_4 (R = H), C_2H_4, and C_2H_6 (R = CH_3).[10]

In all the cluster photoreactions reported to date, smooth conversion to tractable products occurs only in the presence of suitable substrates such as CO, H_2, and PR_3, which can capture the photoproduced intermediates.[20] In contrast, we find that photolysis of the trimeric cluster $H_3Re_3(CO)_{12}$[21,22] gives quantitative conversion to $H_2Re_2(CO)_8$,[23] eq 1, even in degassed solutions in the absence of substrate.[24] The smooth trimer to dimer conversion observed for $H_3Re_3(CO)_{12}$ suggested that this system was well suited for detailed mechanistic studies, and we describe the results of those experiments herein. The analogous $H_3Mn_3(CO)_{12}$[25,26] cluster also undergoes ready photofragmentation in degassed solution, but in this case a mixture of $HMn(CO)_5$, $Mn_2(CO)_{10}$, and an unidentified brown solid is formed.

$$2H_3Re_3(CO)_{12} \xrightarrow{h\nu} 3H_2Re_2(CO)_8 \qquad (1)$$



Experimental Section

$H_3Re_3(CO)_{12}$,[21] $H_2Re_2(CO)_8$,[23] and $H_3Mn_3(CO)_{12}$[25] were synthesized by published procedures. $H_3Re_3(CO)_{12}$ was recrystallized from hexane and $H_2Re_2(CO)_8$ from hexane/CH_2Cl_2 at −20 °C.

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