Si–N stretching vibration and those near 1135 cm^{-1} to the N–H deformation vibration. The strong intensity of the latter bands may be the result of mixing of the Si–N stretching motion with the N–H deformation vibration as has been found in the IR spectrum of $(Me_3Si)_2NH$.[25]

The IR spectrum of $[Me(Cl)GaN(H)SiMe_3]_2$ contains six intense bands which are primarily associated with the stretching vibrations of the skeletal structure $[C(Cl)GaN(H)Si]_2$. If the skeletal structure has a symmetry of C_i, then the selection rules predict 15 IR-active vibrations of which six are principally stretching motions. For the symmetries of C_s and C_{2v}, a significantly larger number of IR-active vibrations would be expected. Thus, the IR spectrum of $[Me(Cl)GaN(H)SiMe_3]_2$ supports the presence of the trans–trans structure as the predominate isomer in the solid state. Confirmation of this structure by Raman spectroscopy was prevented by the rather substantial fluorescence which the solid dimer exhibited.

In conclusion, the IR, melting point, and crystallographic data indicate that the trans–trans isomer of $[Me(Cl)GaN(H)SiMe_3]_2$ crystallized from a methylene chloride solution of the reaction mixture. The major signals in the ^1H NMR spectrum of a benzene solution of $[Me(Cl)GaN(H)SiMe_3]_2$ are consistent with the trans–trans isomer although other isomers may be present in low concentrations. The *trans*-$[Me_2GaN(Me)Ph]_2$ has also been found to be the predominate isomer in benzene and thermodynamically more stable than the cis isomer.[17] A comparison of the major features in the IR spectra of both alkyl((trimethylsilyl)amino)gallium chlorides suggests that $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$ probably has a trans–trans structure in the solid state.

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Registry No. $[Me(Cl)GaN(H)SiMe_3]_2$, 80765-15-7; $[n\text{-}Bu(Cl)GaN(H)SiMe_3]_2$, 80765-16-8; $MeGaCl_2$, 6917-74-4; $n\text{-}BuGaCl_2$, 73873-08-2; $(Me_3Si)_2NH$, 999-97-3.

Supplementary Material Available: Tabulations of observed and calculated structure factors and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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Triangular Trinuclear Molybdenum(IV) Cluster Compounds with Two Capping Oxygen Atoms

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The preparation and structural characterization of two trinuclear molybdenum(IV) cluster compounds with capping oxygen atoms are reported. Reaction of $Mo(CO)_6$ with acetic acid under O_2 allows the isolation, after suitable workup by cation-exchange resin chromatography of **1**, $[Mo_3O_2(OAc)_6(H_2O)_3]Br_2\cdot H_2O$. This forms rhombohedral crystals in space group $R\bar{3}m$ with unit cell dimensions $a = 11.784$ (5) Å, $\alpha = 106.34$ (5)°, $V = 1386.6$ (1) Å^3, and $Z = 2$. The structure consists of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ ions having effectively D_{3h} symmetry residing on crystallographic positions of C_{3v} symmetry. The metal atoms form an equilateral triangle capped above and below by oxygen atoms. The edges of the triangle are each bridged by two acetate ions, and there is a water molecule coordinated to each metal atom with the Mo–OH_2 bond direction intersecting the center of the opposite Mo–Mo bond. The bromide ions and the additional H_2O are disordered over several positions in the rhombohedral cell. Reaction of $Mo_2(O_2CCH_3)_4$ with a mixture of propionic acid and propionic anhydride followed by cation column chromatography using CF_3SO_3H to elute gives $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3](CF_3SO_3)_2(CF_3SO_3H)(H_2O)_4$. This forms triclinic crystals in space group $P\bar{1}$ with $a = 15.760$ (5) Å, $b = 14.848$ (5) Å, $c = 13.632$ (4) Å, $\alpha = 70.4$ (2)°, $\beta = 118.5$ (2)°, $\gamma = 123.1$ (2)°, $V = 2336.6$ (1) Å^3, and $Z = 2$. The trinuclear cation resides on a general position but is very similar to the one in the acetate and has essentially D_{3h} symmetry. The important dimensions within the $[Mo_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ ions are virtually identical in the two cases, with Mo–Mo = 2.766 (2) Å in the acetate and averaging 2.752 (3) Å in the propionate. This type of trinuclear cation can be formulated electronically as having six electrons for Mo–Mo bonding and bond orders of 1. They are very similar to the analogous $[W_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ cations described earlier.

Introduction

The past five years have witnessed the discovery of a remarkable new area in the chemistry of molybdenum and tungsten.[2-14] that of compounds containing discrete triangular trinuclear clusters with the metal atoms in oxidation states of, or close to, +4. There are two, structurally different, principal types of compounds as represented by the general structures

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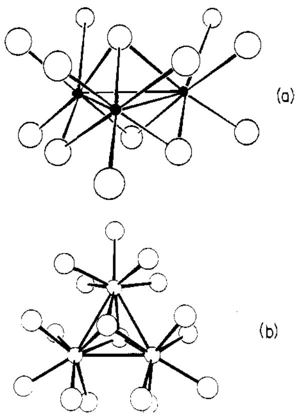

Figure 1. Two principal types of trinuclear Mo_3 and W_3 cluster structures presently known: (a) the monocapped structure, $M_3(\mu_3\text{-}X)(\mu\text{-}Y)_3Z_9$; (b) the bicapped structure, $M_3(\mu_3\text{-}X)_2Y_{12}Z_3$.

(a and b) of Figure 1. In structure a there is one capping atom (a μ_3-X atom) and three μ_2-Y atoms; we shall call this the monocapped structure. In structure b there are two capping atoms; we shall call this the bicapped structure.

Compounds crystallized from aqueous solutions of Mo^{IV} have been found to contain a structure of type a, in which both μ_3-X and μ_2-Y are oxygen atoms, and it is therefore a reasonable hypothesis that such a structure is present in solutions of the molybdenum(IV) aquo ion. There are also several tungsten compounds that have been shown to have a structure of type a.[5-8]

The type b structure, with two μ_3-O groups, has thus far been demonstrated for several tungsten compounds, all of which are obtained by reaction of $W(CO)_6$ with acetic acid, usually followed by workup employing aqueous media and cation exchange columns.[9] There are the following four compounds: $[W_3O_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$, $[W_3O_2(O_2CC_2H_5)_6(H_2O)_3](BF_4)_2 \cdot 5.5H_2O$, $[W_3O_2(O_2CCMe_3)_6(Me_3CCO_2)_2(H_2O)](Me_3CCO_2H)$, and $Cs[W_3O_2(O_2CCH_3)_6(CH_3CO_2)_3] \cdot 3H_2O$.

We have recently reported the existence of a number of molybdenum compounds of type b, including species with two CCH_3 capping groups,[10,12] species with one μ_3-O and one μ_3-CCH_3,[10,11] and a species with two μ_3-O groups,[10] viz., $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$, but no detailed report on molybdenum compounds with two μ_3-O groups has previously been published. In this paper we describe two compounds in detail, one containing the cation just mentioned and the other containing the $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ cation.

Experimental Section

Preparation of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2 \cdot H_2O$ (1). The dark brown solution obtained from the reaction of $Mo(CO)_6$ with acetic acid as described previously[10-12] was left to stand in the air for several weeks and then passed through a Dowex 50W-X2 cation-exchange column. Elution of the adsorbed material showed the presence of only two ions. The first, which was eluted with 0.1 M HBr, was shown to be the $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]^+$ ion.[10,12] The second ion, which was red, eluted with 2 M HBr. Slow evaporation of the red solution gave good quality red crystals whose elemental analysis agrees well with the assigned formula. Anal. Calcd for $C_{12}H_{28}Br_2Mo_3O_{19}$: C, 15.58; H, 3.03; Br, 17.29. Found: C, 15.62; H, 3.13; Br, 17.02. This complex can also be obtained in high yield if air is bubbled through the solution throughout the refluxing of $Mo(CO)_6$ with acetic acid. The cation column chromatography may then be carried out immediately.

Preparation of $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3](CF_3SO_3)_2 \cdot CF_3SO_3H \cdot H_2O$ (2). A mixture of $Mo_2(O_2CCH_3)_4$ (1.0 g), propionic acid (50 mL), and propionic anhydride (50 mL) was refluxed for 12 h under nitrogen. The reaction mixture was cooled, diluted with 100 mL of water, and poured through a column of Dowex 50 W-X2 cation-exchange resin. The column was washed with 1 M hydrochloric acid, and the red adsorbed material was eluted with 2 M trifluoromethylsulfonic acid. Good quality crystals were obtained by slow evaporation of the eluate under vacuum.

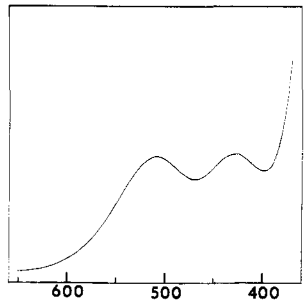

Figure 2. Electronic absorption spectrum of a ca. 10^{-3} M aqueous solution of $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2 \cdot H_2O$.

Table I. Pertinent Information about Data Collection and Structure Refinement

	1	2
space group	$R\bar{3}m$ (No. 166, rhombohedral axes)	$P\bar{1}$
a, Å	11.784 (5)	15.760 (5)
b, Å		14.848 (5)
c, Å		13.632 (4)
α, deg	106.34 (5)	70.4 (2)
β, deg		118.5 (2)
γ, deg		123.1 (2)
V, Å^3	1386.58	2336.6
molecular formula	$Mo_3C_6H_{26}O_{18}Br_2$	$Mo_3C_{15}H_{45}O_{30}F_9S_3$
formula wt	905.8	1331
Z	2	2
ρ(measd),[a] g cm^{-3}	2.18	
ρ(calcd), g cm^{-3}	2.17	1.89
radiation used for data collctn	Mo Kα (λ = 0.71069 Å)	
scanning range for 2θ, deg	$4 \leq 2\theta \leq 48$	$5 \leq 2\theta \leq 42$
stds for intens control	$[0\bar{1}1, \bar{1}01, \bar{1}10]$	$[\bar{1}22, 4\bar{3}\bar{2}, 110]$
scan mode	$\omega/2\theta$	$\omega/2\theta$
scan speed, deg/min	3	1.5
scan width, deg	1.3 (in ω)	1.2
no. of unique reflctns used in the last cycle of least squares	895	4921
no. of variables	82	471
final R(F)[b]	0.066	0.083

[a] Measured by flotation in toluene-1,1,2,2-tetrabromoethane.
[b] $R(F) = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

Electronic Absorption Spectrum. The UV–visible spectra of aqueous solutions of the two compounds are identical within experimental error. That of an approximately 10^{-3} M solution of **1** is presented in Figure 2. The two maxima are described numerically as follows: (1) λ = 509 nm, $\bar{\nu}$ = 19.6 × 10^3 cm^{-1}, ϵ 450; (2) λ = 428 nm, $\bar{\nu}$ = 23.4 × 10^3 cm^{-1}, ϵ 460.

X-ray Measurements. In each case the red crystals were unstable on the diffractometer over long periods of time in the air and it was necessary to place them in Lindemann glass capillaries. Crystals were approximately 0.2 × 0.2 × 0.3 mm in each case, and all data were collected on a Phillips PW-1100 four-circle automated diffractometer. Pertinent details are given in Table I. Unit cell dimensions were determined by centering 25 strong high-angle reflections and are given in Table I. Lorentz and polarization corrections were made; absorption corrections were omitted.

Structure of 1. The rhombohedral crystals showed no systematic absences, thus making $R\bar{3}$ and $R\bar{3}m$ the possible space groups. The statistics of the intensity distribution strongly suggested the centric group, $R\bar{3}m$. Solution of the structure was expedited by the direct methods program MULTAN (1977 version of Main, Woolfson, Lessinger, Germain, and DeClerq). All further crystallographic calculations were carried out with Sheldrick's SHELX-76 program package.

The trinuclear cation was found and refined routinely, but the four Br^- ions in the cell were found to be disordered. Two of them were assigned to a general (12-fold) position and the other two to a special (sixfold) position. With appropriate occupancy factors (i.e., $^1/_6$ and

Table II. Positional Parameters for Compound 1 (×10^4 for Nonhydrogen Atoms; ×10^3 for the Hydrogen Atoms)

	x	*y*	*z*
Mo	2943 (1)	2943 (1)	1477 (1)
O(1)	1564 (10)	1564 (10)	1564 (10)
O(2)	3358 (10)	3358 (10)	3358 (10)
OW	3579 (9)	3579 (9)	0200 (10)
OA1	4916 (6)	3372 (5)	2188 (5)
OA2	1302 (6)	2873 (6)	0124 (6)
CA1	0289 (9)	2848 (11)	0289 (9)
CA2	−0797 (11)	2823 (14)	−0797 (11)
CA3	5485 (12)	2942 (9)	2942 (9)
CA4	6903 (12)	3346 (11)	3346 (11)
Br(1)	3698 (3)	6302 (3)	0[a]
Br(2)	7849 (12)	4851 (12)	0946 (11)
O(3)	5948 (36)	4052 (36)	0[a]
H(1)	418 (10)	369 (11)	028 (11)
H(2)[b]	−170	233	−077
H(3)[b]	−078	359	−078
H(4)[b]	713	349	256
H(5)[b]	748	408	408

[a] Atoms Br(1) and O(3) are located on a twofold axis.
[b] Theoretically calculated positions; not refined.

$^1/_3$) they refined satisfactorily. However, because of correlation between temperature factors and occupancy factors, this exact 2:2 partitioning of the Br^- ions on the two sites may not be exactly correct. There appear to be hydrogen bonds from the cluster water molecules to the Br^- ions with distances of 3.250 (9) and 3.156 (9) Å.

A difference Fourier map was now calculated, and a residual peak having electron density of about 2 e/Å^3 was observed on a special (sixfold) position. This density was assigned to two disordered water molecules per unit cell. This assignment is supported by the fact that the distance between this peak and the water molecules directly coordinated to the molybdenum atoms, 2.780 (12) Å, is consistent with the existence of a hydrogen bond between them. Moreover, with the presence of two water molecules per unit cell the calculated density of 2.17 g cm^{-3} agrees well with the measured density of 2.18 g cm^{-3}. These water molecules also relate in a sterically reasonable way to the Br^- ions.

The oxygen atom of the lattice water molecules was refined only isotropically. Hydrogen atoms were also introduced at calculated positions except for those on the water molecules directly coordinated to the molybdenum atoms which were found in a difference Fourier map. The calculated hydrogen atoms were not refined. With all these atoms included the unit-weighted residual was lowered to a final value of 0.066. The observed and calculated structure factors as well as the anisotropic thermal parameters are available as supplementary material. The atomic positional parameters are presented in Table II.

Structure of 2. This structure was solved straightforwardly from a Patterson function, which yielded the positions of the molybdenum atoms, followed by an alternation of difference Fourier maps and cycles of refinement. In this way all nonhydrogen atoms were located and refined; hydrogen atoms were omitted. There was evidence for minor disorder in the CF_3SO_3 units, especially of the fluorine atoms. In the final cycles of refinement, therefore, only the sulfur atoms in these units were refined anisotropically, as were all nonhydrogen atoms in the cations. This gave a data to parameter ratio of 10.5 and the final unit-weighted *R* value was 0.083.

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

Results and Discussion

The work reported here establishes the existence and the structural parameters of trinuclear cations of the type $[Mo_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ with R = CH_3 and C_2H_5. These cluster species are of type (b) in Figure 1 and are analogous to those of tungsten previously reported.[9] The oxidation state of the molybdenum atoms is +4 which means that there are six electrons available for Mo–Mo bonding and a set of three single bonds may be assumed to exist. Before comparing these oxo-capped trimolybdenum cations with other bicapped trimolybdenum cluster species and with their tungsten analogues, we shall first examine each of the new compounds and its structure in detail.

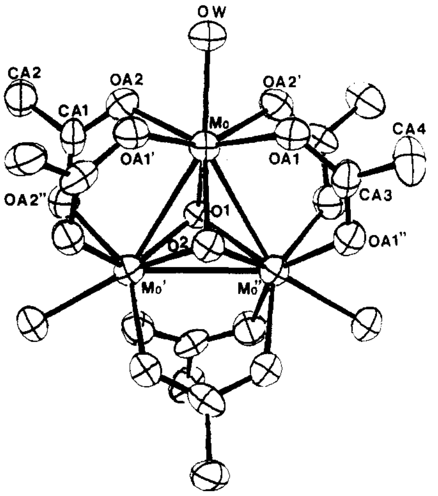

Figure 3. View of the $[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ cation in compound **1**. The thermal ellipsoids are of 50% probability.

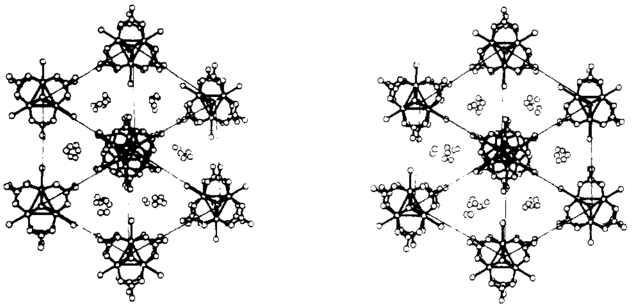

Figure 4. Packing diagram of compound **1** in the equivalent hexagonal system (viewed down the unique axis). The disordered water molecules (O(3)) were omitted for clarity.

$[Mo_3O_2(O_2CCH_3)_6(H_2O)_3]Br_2 \cdot H_2O$ (1). The disordered arrangement of the Br^- ions and the H_2O of solvation have been adequately discussed in the Experimental Section. We turn attention now to the trinuclear cation. The structure and the atom labeling scheme are shown in Figure 3. A stereoview of the packing arrangement using the equivalent hexagonal unit cell is presented in Figure 4. A list of important interatomic distances and angles is given in Table IV.

The cation has rigorous crystallographic $3m$ (C_{3v}) symmetry and approximates closely to the D_{3h} symmetry that would result if a mirror plane coinciding with the Mo_3 plane were added. Thus, the two sets of Mo–(μ_3-O) distances differ by 0.012 (12) Å, a difference that is statistically negligible by the 3σ criterion. Similarly, the two sets of nonequivalent Mo–O distances to the acetate ions differ by only 0.006 (8) Å, which, statistically speaking, means they are equal.

$[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3](CF_3SO_3)_2 \cdot CF_3SO_3H \cdot 4H_2O$ (2). This compound crystallizes in the space group $P\bar{1}$ and has the trinuclear cation on a general position, with no imposed symmetry. The cation and the atom labeling scheme are shown in Figure 5. Bond lengths for both the cation and the anions are listed in Table V, and the bond angles are given in Table VI.

As noted in the Experimental Section, the F and O atoms of the F_3CSO_3 groups, especially the former, showed evidence of disorder and/or very large amplitudes of thermal motion. As a consequence, the distances and angles in these anions cannot be accurately determined and tend to vary over wide ranges. However, the mean values[15] of C–F = 1.30 [10] Å,

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(15) We use $[x]$ to specify the estimated uncertainty of an average of n independent values, defined as $[x]^2 = (\sum \Delta_i^2)/n(n-1)$.

Table III. Positional Parameters for Compound 2 ($\times 10^4$)

atom	*x*	*y*	*z*
Mo(1)	2977 (1)	1088 (1)	2355 (1)
Mo(2)	3861 (1)	3026 (1)	3128 (1)
Mo(3)	3924 (1)	3000 (1)	1153 (1)
O(1)	4449 (7)	2365 (7)	2714 (7)
O(2)	2735 (7)	2368 (7)	1710 (7)
O(3)	3816 (8)	654 (7)	1936 (8)
O(4)	3779 (8)	682 (7)	4031 (8)
O(5)	1775 (7)	663 (7)	769 (7)
O(6)	1745 (7)	673 (7)	2867 (8)
O(7)	2164 (8)	−637 (7)	2534 (8)
O(8)	3439 (7)	4263 (7)	2186 (7)
O(9)	4202 (7)	3907 (7)	4344 (7)
O(10)	5516 (7)	4208 (7)	3468 (7)
O(11)	2441 (7)	2249 (7)	3475 (8)
O(12)	4496 (8)	2249 (7)	4658 (7)
O(13)	5520 (7)	4245 (7)	1821 (7)
O(14)	3452 (7)	4208 (7)	578 (7)
O(15)	4375 (7)	3858 (7)	−287 (7)
O(16)	2560 (7)	2217 (7)	−190 (7)
O(17)	4588 (7)	2212 (8)	956 (8)
C(1)	4410 (13)	1339 (14)	4764 (12)
C(2)	5140 (15)	969 (13)	5854 (14)
C(3)	6044 (17)	1810 (16)	6635 (16)
C(4)	1700 (12)	1296 (13)	3288 (12)
C(5)	661 (14)	818 (14)	3535 (16)
C(6)	676 (18)	1529 (19)	4111 (20)
C(7)	4441 (12)	1267 (13)	1394 (13)
C(8)	5012 (16)	767 (15)	1262 (16)
C(9)	5802 (19)	1539 (19)	670 (21)
C(10)	1767 (12)	1295 (12)	−127 (12)
C(11)	730 (12)	911 (13)	−1158 (12)
C(12)	746 (14)	1781 (14)	−2163 (15)
C(13)	3254 (10)	4557 (10)	1137 (11)
C(14)	2804 (13)	5341 (12)	554 (12)
C(15)	2461 (16)	5490 (16)	−726 (14)
C(16)	6015 (11)	4519 (10)	2810 (11)
C(17)	7218 (11)	5234 (13)	3179 (13)
C(18)	7794 (14)	5463 (16)	4431 (15)
S(1)	4005 (4)	2722 (4)	7209 (4)
S(2)	412 (4)	−2501 (4)	−4 (4)
S(3)	2089 (6)	7478 (5)	5379 (6)
O(18)	3504 (11)	3035 (11)	6041 (11)
O(19)	3855 (13)	3059 (13)	7949 (13)
O(20)	5088 (11)	2894 (11)	7533 (11)
O(21)	98 (18)	−3647 (18)	211 (18)
O(22)	780 (15)	−2061 (15)	980 (16)
O(23)	−387 (18)	−2378 (18)	−1024 (18)
O(24)	1317 (21)	6324 (21)	5408 (21)
O(25)	3262 (22)	7907 (22)	6169 (23)
O(26)	1896 (18)	7877 (17)	4215 (18)
O(27)	3636 (9)	5473 (9)	3755 (9)
O(28)	1367 (12)	4172 (12)	2495 (12)
O(29)	111 (16)	4603 (16)	6628 (17)
O(30)	344 (19)	5132 (19)	2049 (20)
C(19)	3195 (27)	1163 (26)	7302 (30)
C(20)	1637 (34)	−1916 (37)	−329 (38)
C(21)	1519 (23)	7910 (23)	5740 (24)
F(1)	2188 (14)	956 (13)	7063 (14)
F(2)	3589 (20)	849 (20)	8278 (23)
F(3)	3240 (19)	886 (19)	6572 (21)
F(4)	1392 (18)	−2291 (18)	−1212 (19)
F(5)	2337 (19)	−2193 (18)	488 (20)
F(6)	1959 (25)	−931 (27)	−479 (25)
F(7)	532 (22)	7688 (20)	5158 (21)
F(8)	2033 (16)	8472 (16)	6563 (17)
F(9)	2038 (25)	9155 (27)	5385 (27)

S–O = 1.44 [3] Å, and C–S = 1.81 [14] Å are all in agreement with the typical values[16] for these linkages.

Purely for convenience, we have written the formula of compound **2** with two $CF_3SO_3^-$ ions, one CF_3SO_3H molecule of crystallization and four H_2O of crystallization, but we have

Table IV. Bond Lengths (Å) and Angles (Deg) in Compound 1

Mo–Mo	2.766 (2)	OA2–CA1	1.256 (8)
Mo–O(1)	1.998 (8)	CA1–CA2	1.521 (17)
Mo–O(2)	2.010 (9)	CA3–CA4	1.491 (17)
Mo–OW	2.083 (10)	OW–Br(1)	3.250 (9)
Mo–OA1	2.090 (6)	OW–Br(2)	3.156 (9)
Mo–OA2	2.096 (6)	OW–O(3)	2.780 (12)
OA1–CA3	1.267 (8)		
O(1)–Mo–O(2)	74.3 (4)	O(1)–Mo–OA2	79.1 (3)
O(1)–Mo–OW	143.0 (4)	O(2)–Mo–OA2	127.2 (2)
O(2)–Mo–OW	142.7 (4)	OW–Mo–OA1	75.3 (3)
O(1)–Mo–OA1	127.4 (2)	OW–Mo–OA2	75.0 (3)
O(2)–Mo–OA1	78.2 (3)	OA1–Mo–OA2	150.2 (2)
Mo–OA1–CA3	125.5 (6)	OA2–CA1–CA2	117.8 (5)
Mo–OA2–CA1	125.3 (6)	OA1–CA3–CA4	118.2 (6)
Mo–O(1)–Mo′	87.6 (4)	Mo–O(2)–Mo′	87.0 (4)

Table V. Bond Lengths (Å) in Compound 2

Mo(1)–Mo(2)	2.755 (1)	O(17)–C(7)	1.26 (2)
Mo(1)–Mo(3)	2.748 (1)	C(1)–C(2)	1.53 (2)
Mo(1)–O(1)	1.987 (6)	C(2)–C(3)	1.49 (2)
Mo(1)–O(2)	1.97 (1)	C(4)–C(5)	1.55 (3)
Mo(1)–O(3)	2.09 (1)	C(5)–C(6)	1.50 (4)
Mo(1)–O(4)	2.082 (8)	C(7)–C(8)	1.54 (4)
Mo(1)–O(5)	2.089 (7)	C(8)–C(9)	1.51 (3)
Mo(1)–O(6)	2.08 (1)	C(10)–C(11)	1.52 (1)
Mo(1)–O(7)	2.133 (8)	C(11)–C(12)	1.54 (2)
Mo(2)–Mo(3)	2.754 (2)	C(13)–C(14)	1.49 (2)
Mo(2)–O(1)	2.00 (1)	C(14)–C(15)	1.54 (2)
Mo(2)–O(2)	1.986 (7)	C(16)–C(17)	1.49 (1)
Mo(2)–O(8)	2.10 (1)	C(17)–C(18)	1.56 (2)
Mo(2)–O(9)	2.14 (1)	S(1)–O(18)	1.44 (1)
Mo(2)–O(10)	2.118 (8)	S(1)–O(19)	1.42 (2)
Mo(2)–O(11)	2.09 (1)	S(1)–O(20)	1.43 (1)
Mo(2)–O(12)	2.084 (8)	S(2)–O(21)	1.45 (2)
Mo(3)–O(1)	1.982 (7)	S(2)–O(22)	1.41 (2)
Mo(3)–O(2)	1.98 (1)	S(2)–O(23)	1.40 (2)
Mo(3)–O(13)	2.107 (7)	S(3)–O(24)	1.46 (2)
Mo(3)–O(14)	2.08 (1)	S(3)–O(25)	1.50 (2)
Mo(3)–O(15)	2.16 (1)	S(3)–O(26)	1.44 (2)
Mo(3)–O(16)	2.067 (7)	C(19)–F(1)	1.33 (4)
Mo(3)–O(17)	2.09 (1)	C(19)–F(2)	1.22 (4)
O(3)–C(7)	1.27 (2)	C(19)–F(3)	1.24 (6)
O(4)–C(1)	1.26 (1)	C(20)–F(4)	1.30 (6)
O(5)–C(10)	1.27 (1)	C(20)–F(5)	1.28 (5)
O(6)–C(4)	1.29 (2)	C(20)–F(6)	1.24 (6)
O(8)–C(13)	1.28 (1)	C(21)–F(7)	1.26 (4)
O(10)–C(16)	1.28 (2)	C(21)–F(8)	1.28 (4)
O(11)–C(4)	1.26 (1)	C(21)–F(9)	1.56 (4)
O(12)–C(1)	1.24 (2)	S(1)–C(19)	1.93 (3)
O(13)–C(16)	1.27 (1)	S(2)–C(20)	1.84 (5)
O(14)–C(13)	1.27 (2)	S(3)–C(21)	1.65 (4)
O(16)–C(10)	1.26 (1)		

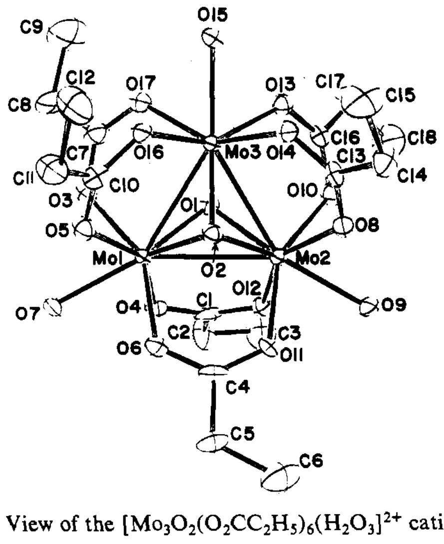

Figure 5. View of the $[Mo_3O_2(O_2CC_2H_5)_6(H_2O)_3]^{2+}$ cation in compound **2**.

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(16) "Interatomic Distances Supplement", *Spec. Publ.—Chem. Soc.* **1965**, *No. 18.*

Table VI. Bond Angles (Deg) in Compound 2

Mo(2)-Mo(1)-Mo(3)	60.05 (5)	Mo(3)-Mo(2)-O(9)	150.1 (3)	O(2)-Mo(3)-O(14)	78.2 (4)	O(16)-C(10)-C(11)	119 (1)
Mo(2)-Mo(1)-O(1)	46.5 (2)	Mo(3)-Mo(2)-O(10)	83.8 (2)	O(2)-Mo(3)-O(15)	143.2 (5)	C(10)-C(11)-C(12)	113 (2)
Mo(2)-Mo(1)-O(2)	46.1 (4)	Mo(3)-Mo(2)-O(11)	124.8 (4)	O(2)-Mo(3)-O(16)	77.8 (5)	O(8)-C(13)-O(14)	121 (1)
Mo(2)-Mo(1)-O(3)	124.5 (4)	Mo(3)-Mo(2)-O(12)	123.7 (2)	O(2)-Mo(3)-O(17)	128.3 (5)	O(8)-C(13)-C(14)	119 (1)
Mo(2)-Mo(1)-O(4)	82.5 (3)	O(1)-Mo(2)-O(2)	73.2 (4)	O(13)-Mo(3)-O(14)	85.5 (5)	O(14)-C(13)-C(14)	118 (1)
Mo(2)-Mo(1)-O(5)	123.7 (3)	O(1)-Mo(2)-O(8)	126.9 (4)	O(13)-Mo(3)-O(15)	75.9 (5)	C(13)-C(14)-C(15)	113 (1)
Mo(2)-Mo(1)-O(6)	82.5 (4)	O(1)-Mo(2)-O(9)	144.2 (5)	O(13)-Mo(3)-O(16)	151.3 (4)	O(10)-C(16)-O(13)	122 (2)
Mo(2)-Mo(1)-O(7)	150.6 (3)	O(1)-Mo(2)-O(10)	77.0 (4)	O(13)-Mo(3)-O(17)	88.4 (5)	O(10)-C(16)-C(17)	120 (1)
Mo(3)-Mo(1)-O(1)	46.1 (3)	O(1)-Mo(2)-O(11)	127.8 (5)	O(14)-Mo(3)-O(15)	74.9 (3)	O(13)-C(16)-C(17)	116 (1)
Mo(3)-Mo(1)-O(2)	46.1 (3)	O(1)-Mo(2)-O(12)	77.8 (4)	O(14)-Mo(3)-O(16)	85.5 (5)	C(16)-C(17)-C(18)	114 (1)
Mo(3)-Mo(1)-O(3)	82.0 (3)	O(2)-Mo(2)-O(8)	78.6 (5)	O(14)-Mo(3)-O(17)	148.9 (4)	O(18)-S(1)-O(19)	113 (1)
Mo(3)-Mo(1)-O(4)	123.6 (4)	O(2)-Mo(2)-O(9)	142.5 (4)	O(15)-Mo(3)-O(16)	75.4 (5)	O(18)-S(1)-O(20)	114 (1)
Mo(3)-Mo(1)-O(5)	82.8 (4)	O(2)-Mo(2)-O(10)	128.9 (4)	O(15)-Mo(3)-O(17)	74.1 (4)	O(18)-S(1)-C(19)	102 (1)
Mo(3)-Mo(1)-O(6)	125.0 (3)	O(2)-Mo(2)-O(11)	78.9 (5)	O(16)-Mo(3)-O(17)	85.3 (5)	O(19)-S(1)-O(20)	115 (1)
Mo(3)-Mo(1)-O(7)	149.3 (3)	O(2)-Mo(2)-O(12)	127.4 (5)	Mo(1)-O(1)-Mo(2)	87.4 (4)	O(19)-S(1)-C(19)	107 (1)
O(1)-Mo(1)-O(2)	73.8 (5)	O(8)-Mo(2)-O(9)	75.0 (4)	Mo(1)-O(1)-Mo(3)	87.6 (5)	O(20)-S(1)-C(19)	101 (1)
O(1)-Mo(1)-O(3)	78.0 (5)	O(8)-Mo(2)-O(10)	87.6 (5)	Mo(2)-O(1)-Mo(3)	87.5 (4)	O(21)-S(2)-O(22)	111 (1)
O(1)-Mo(1)-O(4)	77.5 (5)	O(8)-Mo(2)-O(11)	88.0 (5)	Mo(1)-O(2)-Mo(2)	88.3 (5)	O(21)-S(2)-O(23)	105 (2)
O(1)-Mo(1)-O(5)	127.6 (5)	O(8)-Mo(2)-O(12)	151.2 (4)	Mo(1)-O(2)-Mo(3)	88.1 (3)	O(21)-S(2)-C(20)	102 (2)
O(1)-Mo(1)-O(6)	127.4 (4)	O(9)-Mo(2)-O(10)	76.1 (4)	Mo(2)-O(2)-Mo(3)	87.9 (6)	O(22)-S(2)-O(23)	124 (1)
O(1)-Mo(1)-O(7)	142.7 (5)	O(9)-Mo(2)-O(11)	74.2 (5)	Mo(1)-O(3)-C(7)	125 (1)	O(22)-S(2)-C(20)	105 (2)
O(2)-Mo(1)-O(3)	126.6 (4)	O(9)-Mo(2)-O(12)	76.3 (4)	Mo(1)-O(4)-C(1)	123 (1)	O(23)-S(2)-C(20)	104 (2)
O(2)-Mo(1)-O(4)	127.4 (4)	O(10)-Mo(2)-O(11)	150.1 (4)	Mo(1)-O(5)-C(10)	124 (1)	O(24)-S(3)-O(25)	122 (2)
O(2)-Mo(1)-O(5)	77.6 (5)	O(10)-Mo(2)-O(12)	83.9 (5)	Mo(1)-O(6)-C(4)	126 (1)	O(24)-S(3)-O(26)	106 (2)
O(2)-Mo(1)-O(6)	78.9 (4)	O(11)-Mo(2)-O(12)	85.9 (5)	Mo(2)-O(8)-C(13)	126.0 (7)	O(24)-S(3)-C(21)	98 (2)
O(2)-Mo(1)-O(7)	143.4 (6)	Mo(1)-Mo(3)-Mo(2)	60.10 (5)	Mo(2)-O(10)-C(16)	124 (1)	O(25)-S(3)-O(26)	116 (2)
O(3)-Mo(1)-O(4)	87.9 (4)	Mo(1)-Mo(3)-O(1)	46.3 (4)	Mo(2)-O(11)-C(4)	125.4 (8)	O(25)-S(3)-C(21)	106 (2)
O(3)-Mo(1)-O(5)	85.3 (5)	Mo(1)-Mo(3)-O(2)	45.8 (3)	Mo(2)-O(12)-C(1)	123 (1)	O(26)-S(3)-C(21)	104 (1)
O(3)-Mo(1)-O(6)	150.9 (5)	Mo(1)-Mo(3)-O(13)	124.4 (3)	Mo(3)-O(13)-C(16)	126 (1)	S(1)-C(19)-F(1)	103 (2)
O(3)-Mo(1)-O(7)	75.1 (5)	Mo(1)-Mo(3)-O(14)	124.0 (3)	Mo(3)-O(14)-C(13)	125 (1)	S(1)-C(19)-F(2)	105 (4)
O(4)-Mo(1)-O(5)	151.5 (5)	Mo(1)-Mo(3)-O(15)	150.1 (3)	Mo(3)-O(16)-C(10)	125 (1)	S(1)-C(19)-F(3)	106 (3)
O(4)-Mo(1)-O(6)	85.0 (5)	Mo(1)-Mo(3)-O(16)	82.8 (3)	Mo(3)-O(17)-C(7)	123 (1)	F(1)-C(19)-F(2)	110 (3)
O(4)-Mo(1)-O(7)	76.2 (6)	Mo(1)-Mo(3)-O(17)	84.0 (4)	O(4)-C(1)-O(12)	125 (2)	F(1)-C(19)-F(3)	111 (5)
O(5)-Mo(1)-O(6)	87.6 (5)	Mo(2)-Mo(3)-O(1)	46.6 (2)	O(4)-C(1)-C(2)	115 (1)	F(2)-C(19)-F(3)	117 (3)
O(5)-Mo(1)-O(7)	75.3 (5)	Mo(2)-Mo(3)-O(2)	46.1 (4)	O(12)-C(1)-C(2)	119 (2)	S(2)-C(20)-F(4)	110 (5)
O(6)-Mo(1)-O(7)	75.8 (4)	Mo(2)-Mo(3)-O(13)	81.9 (2)	C(1)-C(2)-C(3)	116 (2)	S(2)-C(20)-F(5)	109 (4)
Mo(1)-Mo(2)-Mo(3)	59.85 (5)	Mo(2)-Mo(3)-O(14)	83.3 (2)	O(6)-C(4)-O(11)	122 (1)	S(2)-C(20)-F(6)	104 (3)
Mo(1)-Mo(2)-O(1)	46.1 (4)	Mo(2)-Mo(3)-O(15)	149.8 (3)	O(6)-C(4)-C(5)	116 (2)	F(4)-C(20)-F(5)	107 (3)
Mo(1)-Mo(2)-O(2)	45.7 (3)	Mo(2)-Mo(3)-O(16)	123.9 (3)	O(11)-C(4)-C(5)	120 (1)	F(4)-C(20)-F(6)	112 (5)
Mo(1)-Mo(2)-O(8)	124.2 (4)	Mo(2)-Mo(3)-O(17)	125.9 (3)	C(4)-C(5)-C(6)	114 (2)	F(5)-C(20)-F(6)	113 (6)
Mo(1)-Mo(2)-O(9)	150.1 (3)	O(1)-Mo(3)-O(2)	73.7 (5)	O(3)-C(7)-O(17)	124 (1)	S(3)-C(21)-F(7)	117 (3)
Mo(1)-Mo(2)-O(10)	123.1 (2)	O(1)-Mo(3)-O(13)	78.2 (5)	O(3)-C(7)-C(8)	115 (1)	S(3)-C(21)-F(8)	123 (3)
Mo(1)-Mo(2)-O(11)	83.2 (3)	O(1)-Mo(3)-O(14)	128.6 (3)	O(17)-C(7)-C(8)	120 (1)	S(3)-C(21)-F(9)	104 (2)
Mo(1)-Mo(2)-O(12)	82.9 (3)	O(1)-Mo(3)-O(15)	143.1 (5)	C(7)-C(8)-C(9)	113 (2)	F(7)-C(21)-F(8)	118 (2)
Mo(3)-Mo(2)-O(1)	46.0 (3)	O(1)-Mo(3)-O(16)	127.7 (5)	O(5)-C(10)-O(16)	123 (2)	F(7)-C(21)-F(9)	97 (3)
Mo(3)-Mo(2)-O(2)	46.0 (3)	O(1)-Mo(3)-O(17)	79.4 (4)	O(5)-C(10)-C(11)	116 (2)	F(8)-C(21)-F(9)	66 (3)
Mo(3)-Mo(2)-O(8)	82.4 (2)	O(2)-Mo(3)-O(13)	126.6 (4)				

Table VII. Nonbonded Contacts (Å) Shorter than 2.8 Å in Compound 2

O(7)-O(26)	2.61 (2)	O(21)-O(30) (66602)	2.55 (3)
O(7)-O(22) (65602)[a]	2.70 (2)	O(28)-O(30)	2.45 (4)
O(9)-O(18)	2.66 (2)	O(29)-O(30) (56602)	2.44 (4)
O(9)-O(27)	2.68 (2)	F(3)-F(9)	2.71 (5)
O(15)-O(19) (55401)	2.61 (2)		

[a] The reference atoms (those whose coordinates are given in Table II) are denoted as 555, translations along the axes are specified by adding or subtracting integers from the reference code. The sequence of the symmetry elements is that given in the "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1952.

no evidence that this is preferable to $(CF_3SO_3^-)_3 \cdot H_3O^+ \cdot 3H_2O$, or still other arrangements. From the structure and spectroscopic properties of the compound we know that the cation has a charge of 2+, and hence that a net charge of 2− must be accommodated over the remaining constituents of the compound. Unfortunately, the accuracy of this part of the structure is insufficient to afford an unequivocal indication of where to place the ninth hydrogen atom beyond the eight that belong to the four water molecules.

Table VII gives a list of the O···O distances below 2.80 Å, which we assume to be conclusively indicative of hydrogen bonds; there could, of course, be additional hydrogen bonds at greater O···O distances. We also mention in this table one fairly short F···F distance of 2.71 (5) Å. However, this is not less than twice the van der Waals radius of fluorine (2.70 Å) and we do not think it implies anything more than a firm non-bonded contact.

The data in Table VII provide some basis for believing that an H_3O^+ ion, containing O(30) may be present. This oxygen atom has two very close hydrogen bonds to other lattice water molecules, O(28) at 2.45 Å and O(29) at 2.44 Å, and another short one to O(21), which belongs to one of the $CF_3SO_3^-$ ions.

Table VIII. Comparison of Some Key Dimensions (Å) for Several $[M_3O_2(O_2CR)_6(H_2O)_3]Z$ Compounds[a]

M	R	Z	M-M	M-(μ_3-O)	M-O_2CR	M-OH_2	ref
Mo	CH_3	$Br_2 \cdot H_2O$	2.766 (2)	2.004 [6]	2.093 [3]	2.083 (10)	*b*
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]	*b*
W	CH_3	$(CF_3SO_3)_2$	2.746 (1)	2.011 (5)	2.085 [7]	2.132 (6)	9
W	C_2H_5	$(BF_4)_2 \cdot 5.5H_2O$	2.745 [2]	2.000 [4]	2.09 [1]	2.09 [2]	9

[a] Numbers in parentheses are esd's of individual values; numbers in brackets are defined in ref 15. [b] This work.

The other five O···O distances listed in Table VII involve water molecules belonging to the cation. Atom O(9) is H bonded to one $CF_3SO_3^-$ ion and to the remaining lattice water molecule, O(27). Atom O(15) is H bonded to a $CF_3SO_3^-$ ion, and atom O(7) is H bonded to two $CF_3SO_3^-$ oxygen atoms from different anions.

Comparison of Structures. Table VIII summarizes the principal dimensions of the trinuclear cations of the type $[M_3O_2(O_2CR)_6(H_2O)_3]^{2+}$ that have been characterized X-ray crystallographically. The variations range from minor to insignificant. There is no statistically significant variation of the M–(μ_3-O) bond lengths or the M–O_2CR bond lengths over the four structures. There are statistically significant variations in the M–OH_2 bond lengths, but the largest ones are between the pairs of compounds containing the same metal atoms; very probably, these variations are a consequence of hydrogen bonding of these water molecules to their surroundings being different from one compound to another. Finally, among the M–M distances, only the Mo–Mo distance in the bromide is significantly (in a statistical sense) different from the others, one Mo–Mo and two W–W, which do not differ significantly from one another. Even this statistically significant difference is at the very threshold of the 3σ criterion and does not appear to have any chemical significance.

This set of M–M bond lengths, 2.745–2.766 Å includes the Mo–Mo bond length, 2.753 (1) Å, in $[Mo_3O(CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4\cdot 9H_2O$, which also contains a cation in which there are M–M bonds of order 1. This suggests that the M–M distance is essentially a function of the bond order and not appreciably dependent on a change of the capping groups from O to CH_3C.

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Registry No. 1, 76811-28-4; **2**, 80754-11-6; $Mo_6(O_2CCH_3)_4$, 14221-06-8; $Mo(CO)_6$, 13939-06-5.

Supplementary Material Available: Tables of structure factors and of anisotropic thermal vibration parameters for both compounds (36 pages). Ordering information is given on any current masthead page.

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A Trinuclear Niobium Cluster with Six Bridging Sulfates and Metal to Metal Bond Order of $^2/_3$

AVI BINO

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Upon addition of K_2SO_4 to the red-brown solution produced by the electrochemical reduction of Nb(V) in 70% H_2SO_4, a red-brown, crystalline product is precipitated. X-ray crystallographic study has defined this substance as $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$. It crystallizes in the monoclinic space group $P2_1$ with the cell dimensions $a = 9.961$ (2) Å, $b = 18.088$ (3) Å, $c = 10.036$ (2) Å, $\beta = 118.84$ (2)°, $V = 1584$ (1) Å^3, and $Z = 2$. The structure was refined by full-matrtix least-squares methods to residuals of $R_1 = 0.037$ and $R_2 = 0.044$. It consists of a discrete trinuclear, triangular niobium cluster of the type M_3X_{17} that has been found in metal clusters of group 6 elements. The three niobium atoms in the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ ion are triply bridged by two μ_3-O atoms, above and below the triangle plane, and each pair of Nb atoms is bridged by two μ-SO_4^{2-} groups. The trimer possesses a near D_{3h} symmetry. The mean Nb–Nb distance is 2.885 (7) Å, and the average oxidation state of the Nb atom is $+3^2/_3$. Four electrons occupy M–M bonding orbitals, resulting in a bond order of $^2/_3$.

Introduction

It has been known for a long time that the electrochemical reduction of pentavalent niobium in sulfuric acid solutions produces a red-brown species.[1] Several attempts have been made to identify the complex responsible for this color by isolating well-defined compounds from the reduced solution.[1-5] Ott prepared a red compound to which he assigned the formula $Nb_2(SO_4)_3\cdot(NH_4)_2SO_4\cdot H_2SO_4\cdot 6H_2O$.[1] Kiehl, Fox, and Hardt reported the preparation of a red crystalline compound to which they gave the tentative formula $4K_2O\cdot N_2O_5\cdot 2NbO_2O_3\cdot 12H_2SO_4\cdot 12H_2O$.[2c] Golibersuch and Young favored a hexanuclear structure and proposed the formula $K_8Nb_6(OH)_6(SO_4)_{12}\cdot 18H_2O$ for this salt.[3] They assigned an average oxidation state of $+3^2/_3$ to the niobium atoms in the complex. Later, the hexanuclear structure was adopted by others who formulated its ammonium salt as $(NH_4)_8[Nb_6O_3(SO_4)_{12}]\cdot x H_2O$.[4,5] Krylov and Kalugina measured the magnetic susceptibility of what they believed to be $K_8[Nb_6O_3(SO_4)_{12}]\cdot 21H_2O$ and found that the molecule contains "two types of niobium atoms, two are paramagnetic with $\mu_{eff} = 1.4\ \mu_B$ per Nb atom and four are diamagnetic".[4] Goroshchenko and Andreeva formulated the complex as $Nb_6O_3(SO_4)_8\cdot 12H_2O$ and stated that all the salts containing potassium or ammonium can be regarded as double salts of this complex.[5]

In the past few years, work on molybdenum and tungsten revealed the existence of trinuclear, triangular metal clusters in oxidation states between +3 and +5 with M–M bonds of order <1.[6-8] From a structural point of view there are two different types of clusters. The first is the well-known M_3X_{13}

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