Inorg. Chem. **1988**, *27*, 2347–2352

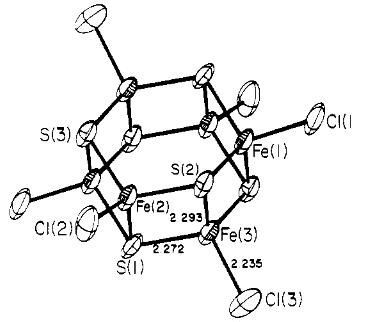

Figure 7. Structure of $[Fe_6S_6Cl_6]^{3-}$ as its PPN^+ salt, showing 50% probability ellipsoids, the atom-labeling scheme, and selected mean bond distances (Å).

identification and characterized the compound as $(PPN)_3[Fe_6S_6Cl_6]$ by X-ray crystallography. The structure of the anion, which has imposed centrosymmetry and takes the form of a slightly distorted hexagonal prism, is shown in Figure 7. Metric data[33] are in reasonable conformance with corresponding dimensions found in the Et_4N^+ salt;[8b] mean Fe–Fe and Fe–S distances are 2.791 and 2.279 Å, respectively. In a parallel experiment, reaction 8 afforded a 46% yield of $[Fe_4S_4Cl_4]^{2-}$ as its Me_4N^+ salt, thus confirming its formation in a reaction system containing sulfur and chloride. In reactions 7 and 8 cations were chosen to trap clusters as sparingly soluble salts in acetone. In each reaction, complete or nearly complete removal of phosphine from the starting cluster as Et_3PS was demonstrated by ^{31}P NMR. Of the iron content of the initial cluster in reaction 7, 85% is accounted for in identified products; at least part of the remainder occurs in an insoluble black material not further examined.

In a final experiment, reaction 12 (Figure 6), $Fe_6S_6(PEt_3)_4Cl_2$ in acetonitrile was reacted with 6 equiv each of sulfur and *p*-toluenethiolate in order to learn if a cluster with only thiolate terminal ligands could be prepared. Instead, $(Me_4N)_2[Fe_4S_4(S\text{-}p\text{-tol})_4]$ was isolated in small yield (17%). The outcome of this reaction is somewhat similar to that of reaction 13, wherein the initially formed prismane thiolate cluster $[Fe_6S_6(SR)_6]^{3-}$ rapidly transforms in a nonredox process to $[Fe_4S_4(SR)_4]^{2-}$,[8b,10] which is also accessible in high yield by the oft-utilized ligand substitution reaction 14.[23] In the present reaction, sulfur presumably acts as an oxidant, leading to formation of the stable cubane cluster. Reaction of $Fe_6S_6(PEt_3)_4Cl_2$ and thiolate affords the new clusters $Fe_6S_6(PEt_3)_4(SR)_2$,[21] which will be reported subsequently.

Summary. This research has resulted in the synthesis of a new group of iron–sulfur clusters of general formulation $Fe_6S_6(PR_3)_4X_2$ (X = halide), which contain the previously unknown basketlike core $[Fe_6S_6]^{2+}$. Full structural details of a representative cluster are provided. Current evidence suggests that, at least over short times, isoelectronic prismane and basket cores are stable and do not interconvert spontaneously. Triethylphosphine may be efficiently removed from the clusters with sulfur. Reaction products have either the prismane or cubane structures. This observation suggests that the basket configuration may be dependent on the presence of phosphine ligands and, therewith, distorted-trigonal-pyramidal coordination units and relatively short Fe–Fe separations. These clusters feature open core faces in the form of chairlike Fe_3S_3 rings, which may not be configured ideally for capping by metals. The metal-binding propensities of $Fe_6S_6(PR_3)_4X_2$ clusters in the presence and absence of sulfur or other reagents introduced to remove phosphine ligands are under examination.

Acknowledgment. This research was supported by NIH Grant GM 28856. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR02247.

Supplementary Material Available: Tables of atom positional and thermal parameters, bond distances and angles, and calculated hydrogen atom positions for $Fe(PEt_3)_2Br_2$, $Fe_6S_6(PEt_3)_4Cl_2$, and $(PPN)_3[Fe_6S_6Cl_6]$ and a stereoview of $Fe_6S_6(P\text{-}n\text{-}Bu_3)_4Cl_2$ (24 pages); tables of calculated and observed structure factors (74 pages). Ordering information is given on any current masthead page.

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Further Studies of Bi-Oxo-Capped Triniobium Cluster Complexes

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Received December 14, 1987

Synthetic and structural studies that substantially extend our knowledge of $Nb_3(\mu_3\text{-}O)_2$ complexes are reported. Treatment of $Nb_2Cl_6(THT)_3$ (THT = tetrahydrothiophene) with oxygen-free H_2SO_4 in H_2O/THF or an acetic acid/acetic anhydride mixture, followed by suitable workup procedures, allows the isolation of compounds containing the $[Nb_3(\mu_3\text{-}O)_2(SO_4)_6(H_2O)_3]^{5-}$ and $[Nb_3(\mu_3\text{-}O)_2(O_2CCH_3)_6(THF)_3]^+$ ions. The former was obtained as the compound $(NH_4)_3(H_3O)_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot nH_2O$ (**1**), which forms blocky monoclinic crystals, and as a related compound of uncertain cation content, which forms acicular hexagonal crystals. The structure of the latter was solved and refined (space group $P6_3/m$) to the point of showing clearly the complex trinuclear anion but with an intractably disordered array of cations. The monoclinic form was fully characterized by X-ray crystallography: $P2_1/m$ with a = 9.651 (3) Å, b = 9.866 (3) Å, c = 16.141 (5) Å, β = 94.07 (3)°, V = 1533 (2) Å^3, and Z = 2. The mean Nb–Nb distance is 2.870 [6] Å, and the mean Nb–(μ_3-O) distance is 2.030 [2] Å. The acetate was isolated as orthorhombic crystals (*Pnma*) of $[Nb_3O_2(O_2CCH_3)_6(C_4H_8O)_3][NbOCl_4(C_4H_8O)]$ (**2**), with unit cell dimensions a = 14.425 (5) Å, b = 16.662 (4) Å, c = 19.423 (8) Å, V = 4668 (5) Å^3, and Z = 4. The mean Nb–Nb and Nb–(μ_3-O) distances are 2.831 [3] and 2.019 [3] Å, respectively. The $[NbOCl_4(C_4H_8O)]^-$ ion has Nb=O = 1.682 (9) Å, Nb—O_{THF} = 2.384 (11) Å, and a mean Nb—Cl distance of 2.385 [2] Å. A byproduct in the preparation of **2** is $Nb_2Cl_2(OEt)(O_2CMe)_5$ (**3**), which has a novel structure in which two $(\eta^2\text{-}CH_3CO_2)_2Nb$ groups are joined by $\mu\text{-}OC_2H_5$, two μ-Cl atoms, and $\mu_2\text{-}\eta^2\text{-}CH_3CO_2$. The Nb–Nb distance, 2.789 (1) Å, is consistent with the presence of a single bond. Crystal data for **3**: space group $P2_1/n$, a = 10.057 (1) Å, b = 14.912 (3) Å, c = 13.880 (2) Å, β = 103.67 (1)°, V = 2022 (1) Å^3, Z = 4.

Introduction

Since the discovery(1) and the subsequent elucidation and development of the chemistry(2) of the trimeric bicapped M_3X_{17} clusters of molybdenum and tungsten, of the formula $[M_3X_2(O_2CR)_6L_3]^{n+}$, the existence of such clusters appeared to be limited to these group 6 metals. While trinuclear hexacarboxylates of many other transition elements are known, they are oxo centered with a planar M_3O group(3) and have no M–M bonding. It was discovered(4) in 1980 that a novel niobium sulfate compound, first

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(1) Bino, A.; Cotton, F. A.; Dori, Z.; Koch, S.; Küppers, H.; Millar, M.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3245.

(2) Cotton, F. A. *Polyhedron* **1986**, *5*, 3.

(3) (a) Mehrotra, R. C.; Bohra, R. *Metal Carboxylates*; Academic: New York, 1983. (b) Yuansheng, Jiang; Aoqing, Tang; Hoffman, R.; Jinling, Huang; Jiaxi, Lu. *Organometallics* **1985**, *4*, 27.

(4) Bino, A. *J. Am. Chem. Soc.* **1980**, *102*, 7990.

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Table I. Crystal Data[a]

	$(NH_4)_3(H_3O)_2$-$[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 3H_2O$ (**1a**)		$[Nb_3O_2(O_2CCH_3)_6(C_4H_8O)_3]$-$[NbOCl_4(C_4H_8O)]$ (**2**)	$Nb_2Cl_2(OC_2H_5)$-$(O_2CCH_3)_5$ (**3**)
formula	$Nb_3S_6O_{34}N_3H_{30}$		$Nb_4Cl_4O_{19}C_{28}H_{50}$	$Nb_2Cl_2O_{11}C_{12}H_{20}$
fw	1087.34		1204.14	597.00
space group	$P2_1/m$	$P6_3/m$	$Pnma$	$P2_1/n$
syst absences	$0k0,\ k \neq 2n$		$0kl,\ k + l \neq 2n$ $hk0,\ h \neq 2n$	$0k0,\ k \neq 2n$ $h0l,\ h + l \neq 2n$
a, Å	9.651 (3)	13.870	14.425 (5)	10.027 (1)
b, Å	9.866 (3)	13.870	16.662 (4)	14.912 (3)
c, Å	16.141 (5)	9.886	19.423 (8)	13.880 (2)
α, deg	90.0	90.0	90.0	90.0
β, deg	94.07 (3)	90.0	90.0	103.67 (1)
γ, deg	90.0	120.0	90.0	90.0
V, Å^3	1533 (2)	1647	4668 (5)	2022 (1)
Z	2	2	4	4
d_{calcd}, g/cm^3	2.355		1.713	1.960
cryst size, mm	0.3 × 0.2 × 0.1		0.35 × 0.2 × 0.05	0.3 × 0.3 × 0.05
μ(Mo Kα), cm^{-1}	15.701		12.097	14.002
data collection instrument	Syntex P3		CAD-4	Syntex P3
radiation (monochromated in incident beam)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)		Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)	Mo Kα ($\lambda_{\bar{\alpha}}$ = 0.71073 Å)
orientation reflcns: no.; range (2θ), deg	25; $17.9 < 2\theta < 28.4$		25; $18.5 < 2\theta < 29.9$	25; $17.3 < 2\theta < 29.8$
temp, °C	22		22	22
scan method	ω–2θ		ω–2θ	ω–2θ
data collcn range (2θ), deg	4–50		4–50	4–50
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2491, 2329		2948, 2178	2372, 1659
no. of params refined	220		224	244
trans factors: max, min				1.0, 0.887
R^b	0.052		0.048	0.047
$R_w{}^c$	0.079		0.061	0.059
quality-of-fit indicator[d]	1.847		1.566	1.170
largest shift/esd, final cycle	0.07		0.05	0.03
largest peak, e/Å^3	0.843		0.767	0.742

[a] The values given in the second column are unit cell parameters for the hexagonal form of the sulfate, **1b**. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

prepared[5] in 1912 by electrochemical reduction of a Nb_2O_5–H_2SO_4 solution and subsequently studied by several groups,[6] was in fact a bi-oxo-capped cluster, structurally similar to the Mo and W compounds. This gave the first indication that group 5 metals may also form the M_3X_{17} carboxyl complexes. Shortly thereafter, niobium pivalate and benzoate[7] species of this kind were prepared by reaction of $Nb_2Cl_6L_3$ with the corresponding sodium salts. However, this synthetic approach was limited since with tetramethylammonium acetate only metathesis took place and a dimeric Nb(3+)[8] complex was obtained. What seems to be a general preparative route has been found in the course of study of the systems involving low-valent Nb, usually in the oxidation state 3+, and oxo acids. The sensitivity of the former to protic media is universal, and it is a common practice to study the chemistry of the lower valent group 5 elements in inert solvents. It was observed, however, that under controlled conditions tractable products can be formed in media like alcohol or in the presence of traces of water, as exemplified by $Nb_2Cl_5(OR)(ROH)_4$[9] and $[Ta_2Cl_4(OH)(SMe_2)(dmpe)_2]Cl$.[10] We now report that the exclusion of oxygen from H_2SO_4 and acetic acid in their reaction with $Nb_2Cl_6(THT)_3$ allows the efficient preparation of the bis-oxo-capped M_3X_{17} clusters as the major products in such systems. Some of the results presented here have been published in a preliminary form.[11]

Experimental Section

All manipulations were performed under an atmosphere of argon. $Nb_2Cl_6(THT)_3$ was prepared by the literature method.[12]

$(NH_4)_3(H_3O)_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot nH_2O$ (1). A 10-mL portion of 40–70% H_2SO_4 was deoxygenated by bubbling N_2 for about 1 h, cooled on an ice bath, and added to a suspension of $Nb_2Cl_6(THT)_3$ (0.5 g, 0.80 mmol) in 25 mL of THF. After the reaction mixture turned dark green, THF was removed under vacuum. This unidentified green product was transformed into the red-brown trimeric sulfate upon standing for 1–2 weeks at 25 °C or upon being heated at 80 °C overnight. The addition of 10 mL of 1 M $(NH_4)_2SO_4$ precipitated a red-brown microcrystalline solid, which was filtered off, washed with EtOH, and dried. Yield: 0.35 g, 64%.

A convenient method of isolating the product in crystalline form involved addition of 1–2 g of $(NH_4)_2SO_4$ to the green solution and heating for 10–12 h. As the resulting brown solution cooled to room temperature, blocklike crystals, **1a**, having an apparently hexagonal cross section, but a monoclinic cell, were produced.

Slow diffusion of ammonium sulfate from aqueous solution into the red-brown sulfuric acid solution through a frit afforded thin needles with a hexagonal unit cell.

$[Nb_3O_2(O_2CCH_3)_6(THF)_3][NbOCl_4(THF)]$ (2). $Nb_2Cl_6(THT)_3$ (0.5 g, 0.80 mmol) was treated with a deoxygenated 1:1 mixture of acetic acid and acetic anhydride. Dissolution of the solid was accompanied by a color change from purple to dark red. Stirring was maintained for 12 h. After filtration the solvent was removed under vacuum. A 10-mL portion of THF was added to the solid residue, giving a red-brown solution and some orange precipitate. After the mixture had been allowed to stand for several days, the precipitate disappeared and red-brown crystals deposited in the flask. They were isolated by filtration, washed with hexane, and dried under vacuum. Yield: 0.25 g, 52%. UV–visible and NMR data are given under Results.

$Nb_2Cl_2(OC_2H_5)(O_2CCH_3)_5$ (3). This complex was a second product obtained in the above preparation. Upon storage of the THF solution from which the trimer was crystallizing for about 1–2 weeks, its color became yellow-brown. After isolation of **2**, the filtrate was layered with hexane. Upon slow interdiffusion of the solvents, yellow plates of **3** (50–100 mg, 10–20% yield) admixed with a small amount of red-brown crystals of the trimer were obtained.

X-ray Crystallography

Crystallographic procedures have been described elsewhere.[12] The intensity data were corrected for Lorentz and polarization effects. Azimuthal scans were done in all three cases, but only for **3** did the intensity of reflections vary to an extent justifying correction for absorption.

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(5) Ott, F. *Electrochem. Z.* **1912**, *18*, 349.
(6) See references in: Bino, A. *Inorg. Chem.* **1982**, *21*, 1917.
(7) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 3527.
(8) Cotton, F. A.; Diebold, M. P.; Matusz, M.; Roth, W. J. *Inorg. Chim. Acta* **1986**, *112*, 147.
(9) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3323.
(10) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1983**, *22*, 868.
(11) Cotton, F. A.; Diebold, M. P.; Llusar, R.; Roth, W. J. *J. Chem. Soc., Chem. Commun.* **1986**, 1276.
(12) Cotton, F. A.; Duraj, S. A.; Falvello, L. R.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 4389 and references therein.

Pertinent crystallographic and procedural details are summarized in Table I.

The positions of metal atoms were derived from a Patterson map for **1** and **2** and by direct methods (MULTAN 84) for **3**. All non-hydrogen atoms were subsequently located by an alternating series of difference Fourier syntheses and least-squares refinements. The following are additional comments pertaining to the individual structure determinations.

1. For both monoclinic (**1a**) and hexagonal (**1b**) forms no problems were encountered in locating and refining the trinuclear anion, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$. However, some water molecules and possibly NH_4^+ were badly disordered, which in the case of **1b** prevented satisfactory completion of the structural analysis. While the difference Fourier map contained a number of peaks that could be assigned to water oxygen atoms, they did not behave well upon refinement. The R and R_w residuals obtained with 10 atoms (one-third of the trimer and one N atom in the asymmetric unit) refined anisotropically were equal 0.079 and 0.132, respectively.

An acceptable, partly disordered model was developed for the monoclinic crystal. Among the four oxygen atom positions with overall occupancy of 2.5, O(43) and O(44) were considered nondisordered. The following occupancies were assigned to the other two positions: 0.5 for O(41) and O(41A), 0.333 for O(42), and 0.167 for O(42A). There was also the problem of distinguishing between N and O atoms because crystallography alone does not provide an adequate basis for that. The atoms considered to be nitrogen were less than 3 Å away from four to six terminal sulfate oxygen atoms, apparently due to hydrogen-bonding interactions via four tetrahedrally distributed H atoms. On the other hand, the oxygen atoms of free water molecules were close to no more than one sulfate oxygen atom.

2. There was no distinct disorder of the THF rings although they showed somewhat higher values of displacement parameters for some carbon atoms. Their anisotropic refinement was accordingly not attempted.

3. There was initially some uncertainty as to the real nature of the bridging ethoxide group. However, the possibility of this being in fact an acetate group was discounted, because the C–O bond length was too long and the residual electron density map revealed no additional atoms, except hydrogen, in the region.

Results

Syntheses and Properties of the Complexes. Solid $Nb_2Cl_6(THT)_3$ reacts very slowly with H_2SO_4 in a purely aqueous solution. The addition of a solvent that dissolves this apparently hydrophobic starting material, viz., THF, promotes a rapid reaction producing a green compound. The latter can be transformed to a red-brown substance, which was identified on the basis of its visible spectrum as containing the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ ion. The identity of the green compound is unknown, but it is probably the same material that Golibersuch and Young[13] described in their paper on the electrochemical generation of the sulfato cluster. They found that upon reduction of the red-brown trimeric complex, for which they correctly determined the average oxidation state of Nb to be $3^{2}/_{3}+$, even though they did not find the right formula, a green compound supposedly of Nb($3^{1}/_{3}+$) was obtained. In our case the red-brown compound is obtained through an oxidation process starting from Nb^{3+}, and therefore the green species is observed first, as an intermediate. Taking into account the stability of the M_3O_2 moieties, one is tempted to propose that both complexes have the same geometry with the green one having one more electron, thus being a d^5 cluster. However, we were unable to isolate it in a solid form, suitable for X-ray study. Remembering the problems with correct identification of the red-brown species, we stress that this is merely a tentative proposal for which only crystallographic analysis could provide unequivocal verification. The previous authors did report obtaining crystals from the green solution, but we suspect that these may have been the Nb($3^{2}/_{3}+$) complex since, as mentioned above, the latter forms spontaneously from its precursor. They described these crystals as dichroic with red side faces and green cross section, an appearance quite similar to that observed by us for the red-brown compound.

The sulfato cluster anion was crystallized with the ammonium cation, and like the previous authors,[13] we also obtained two forms of crystals, monoclinic and hexagonal. In both cases the presence of the trimeric hexasulfate has been demonstrated unequivocally.

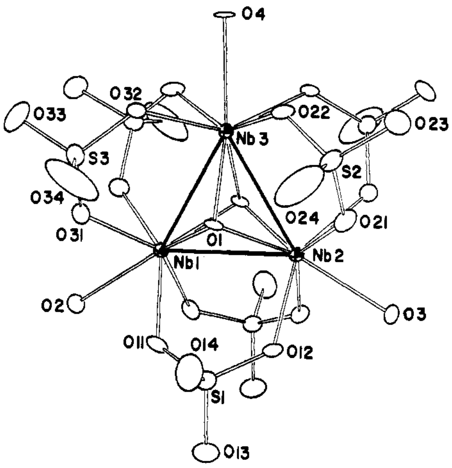

Figure 1. ORTEP drawing of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ anion in **1a**. The ellipsoids are drawn at the 30% probability level. The triangular array of the metal atoms lies on a crystallographic mirror plane.

For the monoclinic form three NH_4^+ cations per trimer have been assigned, which is consistent with the ratio of components (NH_4:SO_4:Nb) determined by Golibersuch and Young. The remaining two positive charges are provided by protons that appear to be randomly distributed among five water molecules. Consequently, the composition of compound **1a** is expressed by the formula $(NH_4)_3(H_3O)_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot3H_2O$. Some O–O distances among the free water molecules in the lattice are short enough for hydrogen bonding, and perhaps $H_5O_2^+$ ion(s) is present. The disorder of atoms in the hexagonal crystals was so severe as to prevent accurate determination of the unit cell contents beyond the sulfato cluster anion itself.

When a 1:1 mixture of acetic acid/acetic anhydride is reacted with $Nb_2Cl_6(THT)_3$, an acetate analogue of the sulfato complex is obtained. A Nb(V) species, $NbCl_4OL^-$ is also produced in this process. THF turned out to be an excellent medium for crystallization since it substitutes into the coordination sphere and the product is deposited in crystalline form. In previous syntheses of $[Nb_3O_2(O_2CR)_6(THF)_3]^+$ complexes, where R = $C(CH_3)_3$ and C_6H_5, salts of the carboxylic acids were used as reactants. This approach did not work for the acetate; it led only to substitution, giving an unoxidized Nb(III) dimer, $[Nb_2Cl_2(THT)(O_2CCH_3)_5]^-$. This difference in reactivity can be attributed to the higher stability of the acetate residue in comparison to the other two with respect to the abstraction of oxygen.

The nature of the second product, $Nb_2Cl_2(OEt)(O_2CMe)_5$, indicates that it was produced parallel to the trimer, rather than being derived from it. The source of the ethoxide ligand cannot be precisely stated, but several scenarios involving fragmentation of the anhydride or the acid can be envisioned. The presence of this Nb(4+) species, as well as the $NbOCl_4L^-$ ion, shows that in the reacting system concurrent processes take place. The latter anion was also found as counterion in the crystals of the benzoate trimer.

Molecular Structures. The atomic positional parameters for **1a**, **2**, and **3** are presented in Tables II–IV, respectively. Important interatomic dimensions are given in Tables V–VII, respectively. Full listings of bond distances and bond angles are included in the supplementary material.

$[Nb_3O_2(X_2)_6L_3]^{n\pm}$. Crystal structure determination of three new compounds containing these ions have been carried out. Drawings of the sulfate and acetate derivatives in **1a** and **2** are shown in Figures 1 and 2, respectively. Although the third structure could not be completed (vide infra), it gave a reasonably accurate model for the hexasulfate.

There are now five crystallographically characterized compounds containing the bi-oxo-capped Nb_3X_{17} molecules. All of them have virtual D_{3h} symmetry. The selected interatomic distances were averaged accordingly, and the values are compiled in Table VIII. The equivalent Nb–O distances fall within narrow ranges, independent of the residual group in the ligand. There

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(13) Golibersuch, E. W.; Young, R. C. *J. Am. Chem. Soc.* **1949**, *71*, 2402.

Table II. Positional and Isotropic Equivalent Displacement Parameters for $(NH_4)_3(H_3O)_2[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 3H_2O$ (**1a**)[a]

atom	x	y	z	B, Å^2
Nb(1)	-0.07795 (9)	0.250	-0.34335 (6)	1.49 (2)
Nb(2)	-0.08080 (9)	0.250	-0.16496 (6)	1.40 (2)
Nb(3)	0.17763 (9)	0.250	-0.24210 (5)	1.32 (2)
S(1)	-0.2914 (2)	0.4694 (2)	-0.2641 (1)	1.84 (3)
S(2)	0.1567 (2)	0.4626 (2)	-0.0846 (1)	2.28 (4)
S(3)	0.1627 (2)	0.4607 (2)	-0.4014 (1)	2.22 (4)
O(1)	0.0051 (4)	0.3690 (6)	-0.2501 (3)	1.53 (9)
O(2)	-0.1992 (8)	0.250	-0.4973 (5)	2.4 (2)
O(3)	-0.2022 (8)	0.250	-0.0505 (5)	2.1 (2)
O(4)	0.4134 (6)	0.250	-0.2289 (5)	1.6 (1)
O(11)	-0.2427 (5)	0.3930 (6)	-0.3361 (3)	2.5 (1)
O(12)	-0.2455 (5)	0.3930 (6)	-0.1870 (3)	2.3 (1)
O(13)	-0.4404 (6)	0.4739 (7)	-0.2732 (4)	3.2 (1)
O(14)	-0.2355 (8)	0.6040 (7)	-0.2613 (4)	4.1 (2)
O(21)	0.0231 (5)	0.3901 (7)	-0.0822 (3)	2.9 (1)
O(22)	0.2401 (5)	0.3930 (6)	-0.1475 (3)	1.8 (1)
O(23)	0.2300 (6)	0.452 (1)	-0.0044 (4)	6.4 (2)
O(24)	0.1328 (8)	0.6011 (8)	-0.1079 (6)	7.3 (2)
O(31)	0.0273 (6)	0.3892 (7)	-0.4173 (3)	2.8 (1)
O(32)	0.2416 (5)	0.3945 (6)	-0.3305 (3)	2.5 (1)
O(33)	0.2378 (7)	0.447 (1)	-0.4738 (4)	6.2 (2)
O(34)	0.1389 (9)	0.6007 (8)	-0.3801 (6)	7.9 (2)
N(1)	0.123 (1)	0.250	0.4020 (7)	3.9 (3)
N(2)	0.125 (1)	0.250	0.1105 (8)	5.5 (4)
N(3)	0.752 (2)	0.250	0.2396 (9)	10.4 (7)
O(41)	0.521 (2)	0.374 (2)	0.940 (1)	8.0 (5)*
O(41A)	0.523 (2)	0.455 (2)	0.916 (1)	7.0 (5)*
O(42)	0.501 (3)	0.250	0.565 (2)	8.9 (6)*
O(42A)	0.518 (5)	0.376 (6)	0.535 (3)	6 (1)*
O(43)	0.490 (3)	0.250	0.371 (2)	15.7 (9)*
O(44)	0.471 (3)	0.250	0.170 (2)	14.4 (8)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

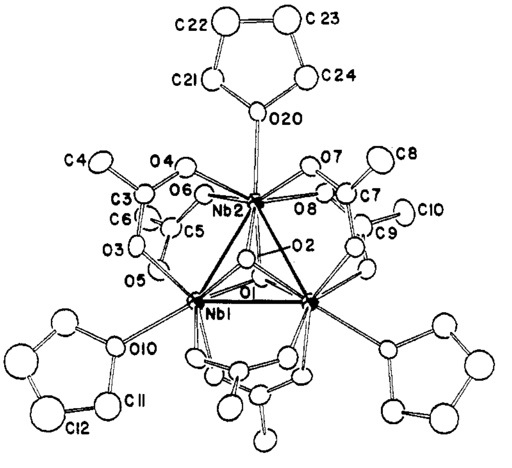

Figure 2. ORTEP drawing of the $[Nb_3O_2(O_2CCH_3)_6(THF)_3]^+$ ion in **2**. The ellipsoids enclose 30% of electron density. A crystallographic mirror plane passing through Nb(1) and μ_3-O atoms, which is perpendicular to the Nb_3 unit, relates halves of the molecule.

is a gradual increase in the M–O bond lengths, by about 0.1 Å, when going from the capping to bridging to terminal ligand. The Nb–Nb distances are somewhat longer for the sulfate than for the carboxylates. This can be attributed to the smaller bite of the latter. On the other hand, the M–M separation in the niobium acetate is considerably shorter than that in the isoelectronic, d^4, molybdenum hexaacetate and only slightly longer than that in the molybdenum d^5 homologue.[14] Both of the Mo clusters contain μ_3-alkyl ligand(s), and it is evident that electronic factors associated with ligands also affect the M–M bonding.

Table III. Positional and Isotropic Displacement Parameters for $[Nb_3O_2(O_2CCH_3)_6(THF)_3][NbOCl_4(THF)]$ (**2**)[a]

atom	x	y	z	B, Å^2
Nb(1)	0.11480 (9)	0.250	0.33496 (6)	2.73 (2)
Nb(2)	0.11150 (6)	0.16483 (4)	0.20905 (4)	2.69 (1)
Nb(3)	0.0969 (1)	0.250	-0.16445 (7)	4.02 (3)
Cl(1)	0.1214 (2)	0.3506 (2)	-0.2499 (2)	6.05 (7)
Cl(2)	0.1151 (3)	0.3504 (2)	-0.0780 (2)	7.74 (9)
O(1)	0.0300 (6)	0.250	0.2521 (4)	3.1 (2)
O(2)	0.1942 (6)	0.250	0.250	2.7 (2)
O(3)	0.2136 (5)	0.1570 (3)	0.3608 (3)	3.5 (1)
O(4)	0.2127 (5)	0.0926 (3)	0.2620 (3)	3.5 (1)
O(5)	0.0165 (5)	0.1585 (3)	0.3647 (3)	3.6 (1)
O(6)	0.0150 (4)	0.0918 (3)	0.2659 (3)	3.4 (1)
O(7)	0.2076 (5)	0.1832 (3)	0.1259 (3)	3.4 (1)
O(8)	0.0129 (5)	0.1836 (3)	0.1274 (3)	3.5 (1)
O(10)	0.1185 (8)	0.250	0.4508 (4)	4.4 (2)
O(20)	0.1088 (5)	0.0476 (3)	0.1519 (3)	3.9 (1)
O(30)	-0.0196 (8)	0.250	-0.1680 (7)	6.4 (3)
O(31)	0.2621 (9)	0.250	-0.1612 (8)	7.8 (4)
C(3)	0.2461 (7)	0.1044 (5)	0.3203 (5)	3.2 (2)
C(4)	0.3254 (7)	0.0530 (6)	0.3443 (5)	4.3 (2)
C(5)	-0.0142 (6)	0.1034 (5)	0.3264 (5)	3.2 (2)
C(6)	-0.0929 (7)	0.0524 (6)	0.3522 (5)	5.0 (3)
C(7)	0.238 (1)	0.250	0.1039 (7)	3.2 (3)
C(8)	0.312 (1)	0.250	0.0494 (8)	5.1 (4)
C(9)	-0.0154 (9)	0.250	0.1060 (7)	3.6 (3)
C(10)	-0.090 (1)	0.250	0.0496 (7)	4.6 (4)
C(11)	0.1160 (9)	0.1795 (7)	0.4945 (6)	5.7 (3)*
C(12)	0.157 (1)	0.2065 (9)	0.5620 (8)	9.5 (4)*
C(21)	0.1034 (7)	-0.0324 (6)	0.1828 (5)	4.0 (2)*
C(22)	0.1542 (9)	-0.0837 (8)	0.1318 (6)	6.2 (3)*
C(23)	0.1419 (8)	-0.0419 (7)	0.0632 (7)	6.3 (3)*
C(24)	0.1002 (7)	0.0381 (6)	0.0769 (5)	4.4 (2)*
C(31)	0.322 (1)	0.178 (1)	-0.1705 (9)	11.2 (5)*
C(32)	0.415 (1)	0.213 (1)	-0.145 (1)	14.1 (7)*

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table IV. Positional and Isotropic Equivalent Displacement Parameters for $Nb_2Cl_2(OC_2H_5)(O_2CCH_3)_5$ (**3**)[a]

atom	x	y	z	B, Å^2
Nb(1)	0.1662 (1)	0.28896 (9)	0.08037 (7)	2.44 (2)
Nb(2)	0.0180 (1)	0.28988 (9)	0.22675 (7)	2.36 (2)
Cl(1)	0.2452 (3)	0.2120 (2)	0.2459 (2)	2.98 (6)
Cl(2)	-0.0195 (3)	0.4019 (2)	0.0859 (2)	3.38 (7)
O(1)	0.0026 (7)	0.2172 (6)	0.0997 (5)	2.5 (2)
O(3)	0.2788 (8)	0.3888 (6)	0.1709 (6)	3.0 (2)
O(4)	0.1579 (8)	0.3910 (6)	0.2856 (6)	3.1 (2)
O(11)	0.2115 (8)	0.1561 (6)	0.0300 (6)	3.0 (2)
O(12)	0.3739 (8)	0.2524 (6)	0.0752 (6)	3.4 (2)
O(13)	0.2094 (8)	0.3868 (6)	-0.0233 (6)	3.4 (2)
O(14)	0.0610 (8)	0.2841 (7)	-0.0756 (6)	3.5 (2)
O(21)	-0.0280 (8)	0.1581 (6)	0.2822 (6)	3.3 (2)
O(22)	0.0679 (8)	0.2596 (6)	0.3849 (6)	3.3 (2)
O(23)	-0.1044 (8)	0.3884 (6)	0.2815 (6)	3.2 (2)
O(24)	-0.2049 (8)	0.2815 (7)	0.1851 (6)	3.5 (2)
C(1)	-0.119 (1)	0.1845 (9)	0.0230 (9)	3.4 (3)
C(2)	-0.170 (1)	0.100 (1)	0.057 (1)	4.2 (3)
C(3)	0.257 (1)	0.4186 (8)	0.251 (1)	3.0 (3)
C(4)	0.355 (1)	0.487 (1)	0.311 (1)	4.2 (3)
C(11)	0.338 (1)	0.1728 (9)	0.0466 (8)	3.1 (3)
C(12)	0.440 (1)	0.105 (1)	0.034 (1)	4.2 (3)
C(13)	0.126 (1)	0.351 (1)	-0.0951 (9)	3.4 (3)
C(14)	0.104 (2)	0.387 (1)	-0.2004 (9)	4.4 (4)
C(21)	0.027 (1)	0.180 (1)	0.3713 (9)	3.5 (3)
C(22)	0.049 (2)	0.112 (1)	0.453 (1)	4.8 (4)
C(23)	-0.214 (1)	0.352 (1)	0.238 (1)	3.7 (3)
C(24)	-0.355 (1)	0.385 (1)	0.247 (1)	4.4 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Other Molecules. In addition to the cluster ions, two more niobium-containing complexes have been characterized crystal-

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[14] Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1981**, *103*, 243.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ Ion[a]

Nb(1)–Nb(2)	2.882 (1)	Nb(2)–O(3)	2.257 (5)
Nb(1)–Nb(3)	2.861 (1)	Nb(2)–O(12)	2.136 (4)
Nb(2)–Nb(3)	2.866 (1)	Nb(2)–O(21)	2.125 (4)
Nb(1)–O(1)	2.028 (4)	Nb(3)–O(1)	2.034 (4)
Nb(1)–O(2)	2.245 (6)	Nb(3)–O(4)	2.270 (5)
Nb(1)–O(11)	2.134 (4)	Nb(3)–O(22)	2.135 (4)
Nb(1)–O(31)	2.124 (4)	Nb(3)–O(32)	2.140 (4)
Nb(2)–O(1)	2.029 (4)		

Nb(2)–Nb(1)–Nb(3)	59.87 (2)	O(3)–Nb(2)–O(12)	73.3 (2)
Nb(1)–Nb(2)–Nb(3)	59.71 (2)	O(3)–Nb(2)–O(21)	74.6 (2)
Nb(1)–Nb(3)–Nb(2)	60.42 (2)	O(12)–Nb(2)–O(12)	82.6 (2)
O(1)–Nb(1)–O(1)	70.8 (2)	O(12)–Nb(2)–O(21)	89.3 (2)
O(1)–Nb(1)–O(2)	144.6 (1)	O(12)–Nb(2)–O(21)	147.9 (2)
O(1)–Nb(1)–O(11)	80.4 (2)	O(21)–Nb(2)–O(21)	81.2 (3)
O(1)–Nb(1)–O(11)	126.8 (2)	O(1)–Nb(3)–O(1)	70.5 (2)
O(1)–Nb(1)–O(31)	82.1 (2)	O(1)–Nb(3)–O(4)	144.7 (1)
O(1)–Nb(1)–O(31)	127.7 (2)	O(1)–Nb(3)–O(22)	81.5 (1)
O(2)–Nb(1)–O(11)	72.9 (2)	O(1)–Nb(3)–O(22)	128.0 (2)
O(2)–Nb(1)–O(31)	74.9 (2)	O(1)–Nb(3)–O(32)	81.2 (2)
O(11)–Nb(1)–O(11)	82.7 (3)	O(1)–Nb(3)–O(32)	128.0 (2)
O(11)–Nb(1)–O(31)	89.5 (2)	O(4)–Nb(3)–O(22)	72.7 (1)
O(11)–Nb(1)–O(31)	147.7 (2)	O(4)–Nb(3)–O(32)	74.2 (1)
O(31)–Nb(1)–O(31)	80.6 (3)	O(22)–Nb(3)–O(22)	82.8 (2)
O(1)–Nb(2)–O(1)	70.7 (2)	O(22)–Nb(9)–O(32)	87.5 (2)
O(1)–Nb(2)–O(3)	144.6 (1)	O(22)–Nb(3)–O(32)	146.9 (1)
O(1)–Nb(2)–O(12)	80.8 (2)	O(32)–Nb(3)–O(32)	83.6 (3)
O(1)–Nb(2)–O(12)	127.2 (2)	Nb(1)–O(1)–Nb(2)	90.5 (2)
O(1)–Nb(2)–O(21)	81.5 (2)	Nb(1)–O(1)–Nb(3)	89.5 (2)
O(1)–Nb(2)–O(21)	127.3 (2)	Nb(2)–O(1)–Nb(3)	89.7 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VI. Important Bond Distances (Å) and Bond Angles (deg) for $[Nb_3O_2(O_2CCH_3)_6(THF)_3][NbOCl_4(THF)]$ (**2**)[a]

Nb(1)–Nb(2)	2.828 (1)	Nb(2)–O(4)	2.153 (5)
Nb(2)–Nb(2)	2.838 (1)	Nb(2)–O(6)	2.154 (5)
Nb(1)–O(1)	2.022 (7)	Nb(2)–O(7)	2.150 (5)
Nb(1)–O(2)	2.008 (4)	Nb(2)–O(8)	2.153 (5)
Nb(1)–O(3)	2.164 (5)	Nb(2)–O(20)	2.247 (5)
Nb(1)–O(5)	2.161 (5)	Nb(3)–Cl(1)	2.386 (2)
Nb(1)–O(10)	2.251 (7)	Nb(3)–Cl(2)	2.384 (3)
Nb(2)–O(1)	2.024 (5)	Nb(3)–O(30)	1.682 (9)
Nb(2)–O(2)	2.018 (4)	Nb(3)–O(31)	2.384 (11)

Nb(2)–Nb(1)–Nb(2)	60.24 (3)	O(2)–Nb(2)–O(20)	144.8 (2)
Nb(1)–Nb(2)–Nb(2)	59.88 (2)	O(4)–Nb(2)–O(6)	83.0 (2)
O(1)–Nb(1)–O(2)	72.0 (3)	O(4)–Nb(2)–O(7)	90.1 (2)
O(1)–Nb(1)–O(3)	125.7 (2)	O(4)–Nb(2)–O(8)	151.8 (2)
O(1)–Nb(1)–O(5)	79.4 (2)	O(4)–Nb(2)–O(20)	76.3 (2)
O(1)–Nb(1)–O(10)	144.1 (3)	O(6)–Nb(2)–O(7)	151.9 (2)
O(2)–Nb(1)–O(3)	79.4 (2)	O(6)–Nb(2)–O(8)	91.9 (2)
O(2)–Nb(1)–O(5)	126.4 (2)	O(6)–Nb(2)–O(20)	75.6 (2)
O(2)–Nb(1)–O(10)	143.9 (3)	O(7)–Nb(2)–O(8)	81.5 (2)
O(3)–Nb(1)–O(3)	91.4 (3)	O(7)–Nb(2)–O(20)	76.4 (2)
O(3)–Nb(1)–O(5)	82.2 (2)	O(8)–Nb(2)–O(20)	75.6 (2)
O(3)–Nb(1)–O(5)	151.1 (2)	Nb(1)–O(1)–Nb(2)	88.7 (3)
O(3)–Nb(1)–O(10)	75.7 (2)	Nb(2)–O(1)–Nb(2)	89.1 (3)
O(5)–Nb(1)–O(5)	89.8 (3)	Nb(1)–O(2)–Nb(2)	89.3 (2)
O(5)–Nb(1)–O(10)	75.4 (2)	Nb(2)–O(2)–Nb(2)	89.4 (2)
O(1)–Nb(2)–O(2)	71.8 (3)	Cl(1)–Nb(3)–Cl(1)	89.3 (1)
O(1)–Nb(2)–O(4)	126.1 (3)	Cl(1)–Nb(3)–Cl(2)	88.89 (9)
O(1)–Nb(2)–O(6)	79.0 (2)	Cl(1)–Nb(3)–Cl(2)	165.1 (1)
O(1)–Nb(2)–O(7)	125.8 (2)	Cl(1)–Nb(3)–O(30)	96.9 (3)
O(1)–Nb(2)–O(8)	79.5 (3)	Cl(1)–Nb(3)–O(31)	82.5 (2)
O(1)–Nb(2)–O(20)	143.5 (2)	Cl(2)–Nb(3)–Cl(2)	89.1 (1)
O(2)–Nb(2)–O(4)	78.7 (2)	Cl(2)–Nb(3)–O(30)	98.0 (3)
O(2)–Nb(2)–O(6)	125.3 (2)	Cl(2)–Nb(3)–O(31)	82.6 (2)
O(2)–Nb(2)–O(7)	79.3 (2)	O(30)–Nb(3)–O(31)	179.2 (5)
O(2)–Nb(2)–O(8)	125.4 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Important Bond Distances (Å) and Bond Angles (deg) for $Nb_2Cl_2(OC_2H_5)(O_2CCH_3)_5$ (**3**)[a]

Nb(1)–Nb(2)	2.789 (1)	Nb(2)–Cl(1)	2.521 (3)
Nb(1)–Cl(1)	2.523 (3)	Nb(2)–Cl(2)	2.531 (3)
Nb(1)–Cl(2)	2.529 (3)	Nb(2)–O(1)	2.045 (8)
Nb(1)–O(1)	2.033 (7)	Nb(2)–O(4)	2.093 (8)
Nb(1)–O(3)	2.099 (8)	Nb(2)–O(21)	2.199 (9)
Nb(1)–O(11)	2.185 (8)	Nb(2)–O(22)	2.180 (9)
Nb(1)–O(12)	2.177 (8)	Nb(2)–O(23)	2.166 (8)
Nb(1)–O(13)	2.164 (8)	Nb(2)–O(24)	2.182 (8)
Nb(1)–O(14)	2.174 (8)		

Cl(1)–Nb(1)–Cl(2)	110.6 (1)	Cl(1)–Nb(2)–O(4)	77.4 (2)
Cl(1)–Nb(1)–O(1)	74.4 (2)	Cl(1)–Nb(2)–O(21)	79.2 (2)
Cl(1)–Nb(1)–O(3)	76.6 (2)	Cl(1)–Nb(2)–O(22)	79.1 (2)
Cl(1)–Nb(1)–O(11)	80.5 (2)	Cl(1)–Nb(2)–O(23)	148.4 (2)
Cl(1)–Nb(1)–O(12)	79.5 (3)	Cl(1)–Nb(2)–O(24)	148.3 (3)
Cl(1)–Nb(1)–O(13)	147.4 (3)	Cl(2)–Nb(2)–O(1)	73.5 (3)
Cl(1)–Nb(1)–O(14)	150.0 (3)	Cl(2)–Nb(2)–O(4)	77.8 (2)
Cl(2)–Nb(1)–O(1)	73.8 (3)	Cl(2)–Nb(2)–O(21)	148.7 (2)
Cl(2)–Nb(1)–O(3)	78.9 (2)	Cl(2)–Nb(2)–O(22)	150.6 (3)
Cl(2)–Nb(1)–O(11)	145.6 (2)	Cl(2)–Nb(2)–O(23)	80.2 (2)
Cl(2)–Nb(1)–O(12)	152.8 (3)	Cl(2)–Nb(2)–O(24)	82.9 (3)
Cl(2)–Nb(1)–O(13)	80.6 (2)	O(1)–Nb(2)–O(4)	128.7 (3)
Cl(2)–Nb(1)–O(14)	82.1 (3)	O(1)–Nb(2)–O(21)	81.3 (3)
O(1)–Nb(1)–O(3)	129.3 (3)	O(1)–Nb(2)–O(22)	135.3 (4)
O(1)–Nb(1)–O(11)	78.5 (3)	O(1)–Nb(2)–O(23)	136.8 (3)
O(1)–Nb(1)–O(12)	133.2 (4)	O(1)–Nb(2)–O(24)	83.0 (3)
O(1)–Nb(1)–O(13)	137.6 (3)	O(4)–Nb(2)–O(21)	133.2 (3)
O(1)–Nb(1)–O(14)	84.0 (3)	O(4)–Nb(2)–O(22)	77.5 (3)
O(3)–Nb(1)–O(11)	135.3 (3)	O(4)–Nb(2)–O(23)	76.1 (3)
O(3)–Nb(1)–O(12)	79.1 (3)	O(4)–Nb(2)–O(24)	134.3 (4)
O(3)–Nb(1)–O(13)	75.8 (3)	O(21)–Nb(2)–O(22)	58.7 (3)
O(3)–Nb(1)–O(14)	133.3 (4)	O(21)–Nb(2)–O(23)	107.4 (3)
O(11)–Nb(1)–O(12)	59.2 (3)	O(21)–Nb(2)–O(24)	75.7 (3)
O(11)–Nb(1)–O(13)	108.0 (3)	O(22)–Nb(2)–O(23)	78.6 (3)
O(11)–Nb(1)–O(14)	74.9 (3)	O(22)–Nb(2)–O(24)	103.4 (3)
O(12)–Nb(1)–O(13)	78.6 (3)	O(23)–Nb(2)–O(24)	59.9 (3)
O(12)–Nb(1)–O(14)	101.8 (3)	Nb(1)–Cl(1)–Nb(2)	67.15 (8)
O(13)–Nb(1)–O(14)	59.2 (3)	Nb(1)–Cl(2)–Nb(2)	66.90 (8)
Cl(1)–Nb(2)–Cl(2)	110.6 (1)	Nb(1)–O(1)–Nb(2)	86.3 (3)
Cl(1)–Nb(2)–O(1)	74.3 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

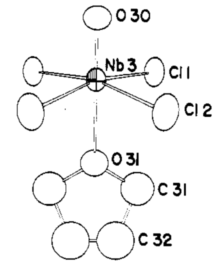

Figure 3. ORTEP drawings of the $[NbOCl_4(THF)]^-$ anion in **2** drawn at 40% probability level. A crystallographic mirror plane passes through the Nb and O atoms and is perpendicular to the plane of the drawing.

lographically. They are $[NbOCl_4(THF)]^-$, serving as the counterion in **2**, and $Nb_2Cl_2(OEt)(O_2CMe)_5$. The former, shown in Figure 3, resides on a crystallographic mirror plane, and its dimensions match closely those reported earlier.[15]

As can be seen in Figure 4, the molecule of **3** is composed of two distorted square antiprisms fused along the bases. The Nb–Nb distance is indicative of the presence of a single M–M bond, as found previously in different types of binuclear complexes of niobium(IV).[16]

Spectra and Electronic Configuration. The visible spectrum of the sulfato cluster[17] contains two bands at 510 and 710 nm, with approximate relative intensities 3:1. For the acetate we observed only one resolved but broad peak at 505 nm, with a

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(15) Aspinall, H. C.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1782.

(16) (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3319. (b) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 3592.

(17) Goroshchenko, Y. G.; Andreeva, M. I. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1966**, *11*, 1197.

Table VIII. Selected Average Interatomic Dimensions in the Bi-Oxo-Capped Triangular Clusters of Nb[a,b]

			bond dist, Å			
trinuclear ion	counterion	site symm	Nb–Nb	Nb–O_{cap}	Nb–O_x	Nb–O_l
$[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$	K^+ $H_5O_2^+$	C_1	2.885 [5]	2.051 [7]	2.134 [4]	2.240 [11]
	NH_4^+ H_3O^+	$m_{\parallel}$	2.870 [6]	2.030 [2]	2.132 [3]	2.257 [7]
	NH_4^+ H_3O^+	$\bar{6}$	2.864 (3)	2.03 (1)	2.12 (2)	2.27 (2)
$[Nb_3O_2(O_2CBu^t)_6(THF)_3]^+$	BPh_4^-	C_1	2.842 [3]	2.036 [6]	2.150 [4]	2.253 [10]
$[Nb_3O_2(O_2CCH_3)_6(THF)_3]^+$	$[NbOCl_4(THF)]^-$	$m_{\perp}$	2.831 [3]	2.019 [3]	2.156 [3]	2.248 [2]

[a] O_{cap} denotes the capping oxygen atoms; O_x and O_l are atoms from the bridging and equatorial ligands, respectively; $m_{\parallel}$ and $m_{\perp}$ refer to crystallographic mirror planes that are parallel and perpendicular, respectively, to the triangle of Nb atoms. [b] Numbers in brackets are variances, obtained from the expression $[(\sum\Delta_i/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmetic mean and *n* is the total number of values averaged.

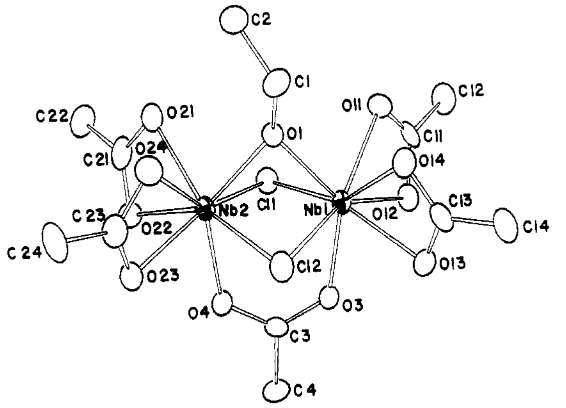

Figure 4. ORTEP drawing of the $Nb_2Cl_2(OEt)(O_2CMe)_5$ (**3**) molecule with ellipsoids enclosing 30% of electron density.

shoulder in the range 640–700 nm. The benzoate[7] had a spectrum similar to that of the sulfate with peak maxima at 520 and 727 nm. These features appear to be characteristic for all complexes within this class.

The electronic configuration of the Nb_3X_{17} clusters constitutes an intriguing issue. Since they are derived from a $Nb_3O_2^{7+}$ unit, there are four d electrons available for metal–metal bonding. If the results of MO calculations for analogous Mo systems[3b,18] were extended to the Nb complexes, either an a^2e^2 ground state with two unpaired electrons or an e^4 configuration would be obtained. As the computed energy difference between the a and e levels is small, the actual order of the orbitals is uncertain. Magnetic susceptibility measurements for the sulfate[19] gave $\mu = 1.4\ \mu_B$, which is intermediate between these two possibilities. While the pivalate showed bulk diamagnetism, a slightly paramagnetic value was obtained after appropriate corrections were applied. The ^1H NMR spectrum of the latter did not exhibit any broadening or unusual shifts that could indicate the presence of unpaired electrons, but the protons are far away from the metal centers.

The proton NMR spectrum of the niobium acetate **2** in $CDCl_3$ shows a methyl group signal at 3.28 ppm. For comparison, the diamagnetic molybdenum[20] analogue (d^6) and $Nb_2Cl_2(THT)(O_2CMe)_5$[8] give bridging acetate signals at 2.28 and 2.15 ppm, respectively. On the other hand, paramagnetic trinuclear molybdenum acetates[21] with electronic configurations d^5 (one unpaired electron) and d^4 (probably singlet–triplet mixture) exhibit large shifts with δ around 15 ppm. These data may indicate paramagnetism for the Nb acetate but only of a small magnitude. The electronic configuration accounting for this would presumably involve an e^4 ground state, but with some population of the excited a level. The separation between e and a, while comparable to kT, must be large enough to produce only a very weak overall magnetic moment. These conclusions were confirmed by MAS ^{13}C solid-state NMR spectroscopy.[22] The spectra showed a gradual decrease of paramagnetism with temperature until the sample became diamagnetic around 100 K. The solution spectrum also showed two pairs of THF signals at 1.84, 1.90, 3.89, and 3.98 ppm. The first and third resonances are probably due to free residual solvent together with the ligand in $[NbOCl_4(THF)]^-$. The second pair arises from the equatorial ligands in the trimer, and its downfield shift is associated with the weak paramagnetism. The presence of two separate signals for the THF molecules is indicative of slow exchange in solution.

Discussion

Our knowledge of the chemistry and structures of bi-oxo-capped triniobium cluster compounds is now considerably greater than it was a few years ago when the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ ion was the only such species known. Moreover, this unique species was then obtainable in only one way, and that was by a procedure giving little promise of extension to species with ligands other than sulfate. By employing the $Nb_2Cl_6(Me_2S)_3$ and $Nb_2Cl_6(THT)_3$ complexes as convenient starting materials, we have now shown that the $Nb_3(\mu_3\text{-}O)_2$ cluster complexes constitute a general class in which a variety of bridging ligands, SO_4^{2-}, $MeCO_2^-$, and other RCO_2^- ions, can be incorporated.

Table VIII summarizes the principal dimensions of the species that have been characterized by X-ray crystallography. As noted, they are all dimensionally similar. It is surprising that they consistently exist in a state with only four Nb–Nb bonding electrons, rather than the six that would allow a full set of bonds to be formed. The presence of six electrons would correspond to an oxidation state of 3+ per Nb atom, which does not seem unreasonable.

Preliminary attempts to prepare tantalum analogues of these triniobium species have been unsuccessful and unencouraging. However, some further efforts will be made. It is also likely that an HPO_4^{2-} analogue of the sulfato complex might be obtainable.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. **1a**, 114635-50-6; **2**, 114635-52-8; **3**, 114635-53-9; $Nb_2Cl_6(THT)$, 38531-73-6; Nb, 7440-03-1.

Supplementary Material Available: For the crystal structures of **1a**, **2**, and **3**, full listings of bond distances, bond angles, and anisotropic displacement parameters (10 pages); tables of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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