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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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 $^2/_3$

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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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Table I. Positional Parameters and Estimated Standard Deviations for $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O^a$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Nb(1)	0.4778 (1)	0.25000 (0)	0.3062 (1)	O(33)	0.646 (1)	0.0677 (5)	0.773 (1)
Nb(2)	0.3711 (1)	0.23835 (8)	0.5252 (1)	O(34)	0.639 (1)	0.1389 (5)	0.973 (1)
Nb(3)	0.6920 (1)	0.26554 (8)	0.6264 (1)	O(41)	0.6705 (9)	0.3469 (5)	0.771 (1)
K(1)	0.4853 (4)	0.4984 (2)	0.4973 (4)	O(42)	0.407 (1)	0.3152 (5)	0.698 (1)
K(2)	0.8285 (3)	0.2488 (2)	0.1612 (3)	O(43)	0.493 (1)	0.4392 (6)	0.760 (1)
K(3)	0.5006 (4)	0.0642 (2)	0.0990 (4)	O(44)	0.584 (1)	0.3453 (5)	0.959 (1)
K(4)	0.1528 (4)	0.4174 (2)	0.5471 (4)	O(51)	0.7897 (9)	0.3463 (5)	0.544 (1)
S(1)	0.2122 (3)	0.1219 (2)	0.2356 (3)	O(52)	0.605 (1)	0.3363 (5)	0.279 (1)
S(2)	0.1698 (3)	0.3476 (2)	0.2282 (3)	O(53)	0.681 (1)	0.4563 (6)	0.393 (1)
S(3)	0.6155 (3)	0.1398 (2)	0.8195 (3)	O(54)	0.858 (1)	0.3807 (6)	0.354 (1)
S(4)	0.5399 (3)	0.3633 (2)	0.8011 (3)	O(61)	0.831 (1)	0.1917 (5)	0.577 (1)
S(5)	0.7359 (3)	0.3823 (2)	0.3927 (3)	O(62)	0.659 (1)	0.1838 (5)	0.309 (1)
S(6)	0.7910 (3)	0.1458 (2)	0.4400 (3)	O(63)	0.9158 (9)	0.1479 (5)	0.4054 (9)
O(1)	0.4919 (9)	0.3175 (4)	0.4765 (9)	O(64)	0.746 (1)	0.0713 (5)	0.456 (1)
O(2)	0.5347 (9)	0.1867 (4)	0.4956 (9)	OW(1)	0.4317 (9)	0.2459 (5)	0.0633 (9)
O(11)	0.326 (1)	0.1590 (5)	0.201 (1)	OW(2)	0.1774 (9)	0.2268 (5)	0.5741 (9)
O(12)	0.2401 (9)	0.1483 (5)	0.388 (1)	OW(3)	0.9337 (9)	0.2835 (4)	0.8119 (9)
O(13)	0.058 (1)	0.1423 (5)	0.121 (1)	OW(4)	0.387 (1)	0.4548 (6)	0.034 (1)
O(14)	0.240 (1)	0.0429 (6)	0.241 (1)	OW(5)	0.179 (1)	0.1874 (5)	0.832 (1)
O(21)	0.182 (1)	0.3008 (5)	0.360 (1)	OW(6)	1.128 (1)	0.9683 (6)	0.974 (1)
O(22)	0.277 (1)	0.3150 (5)	0.181 (1)	OW(7)	0.948 (1)	1.0699 (6)	0.864 (1)
O(23)	0.013 (1)	0.3392 (5)	0.103 (1)	OW(8)	0.989 (1)	0.5098 (7)	0.634 (1)
O(24)	0.206 (1)	0.4237 (5)	0.279 (1)	OW(9)	0.257 (2)	0.0449 (8)	0.805 (2)
O(31)	0.7188 (9)	0.1967 (5)	0.8090 (9)	OW(10)	0.118 (1)	0.3885 (8)	0.814 (2)
O(32)	0.455 (1)	0.1618 (5)	0.712 (1)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

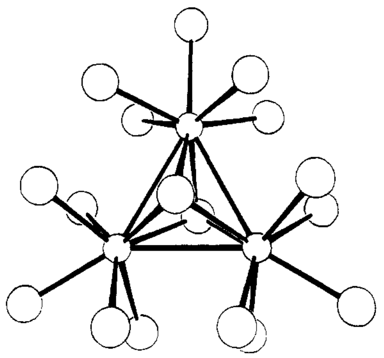

Figure 1. The M_3X_{17} structure.

type that has been found in several molybdenum and tungsten compounds.[6] Niobium forms a similar structure in Nb_3X_8 (X = Cl, Br, I), but unlike the group 6 clusters, which are discrete entities, the unit Nb_3X_{13} occurs in these compounds in a chainlike structure.[9]

The second structural type, M_3X_{17}, is shown in Figure 1. It occurs in several molybdenum and tungsten compounds, all of which have been obtained by reaction of the hexacarbonyls with carboxylic acids.[7,8]

The known tungsten compounds are all in oxidation state +4 with two capping oxygen atoms. Molybdenum forms clusters with either oxygen capping atoms or alkylidyne capping groups and oxidation states from +4 to $+4^2/_3$. Compounds of this structural type have not been found outside of group 6.

The present work was undertaken with the purpose of exploring the possibility that discrete triangular clusters may occur in species of other transition elements of the second and third row.

The X-ray crystallographic study of the first species of this type, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$, has been reported in a preliminary communication. It was found that this much-investigated niobium sulfate complex[1-5] is in fact a trinuclear, triangular cluster possessing the M_3X_{17} structural type (Figure 1) and that previously proposed structures were erroneous. We report here the full details of the structure of this cluster as it appears in the potassium salt $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$.

Experimental Section

Preparation. A red-brown solution of niobium in oxidation state +3.66 in 70% sulfuric acid was obtained by electrolytic reduction at a mercury cathode, after Golibersuch and Young.[3]

Crystals, suitable for X-ray crystallographic study, were obtained by layering a solution of 1 M K_2SO_4 on top of the reduced solution under nitrogen. Red-brown crystals were deposited after a few hours at room temperature.

X-ray Crystallography. A crystal of dimensions 0.12 × 0.1 × 0.1 mm was attached to the end of a glass fiber, coated with epoxy glue, and mounted on a Philips PW 1100 four-circle computer-controlled diffractometer. Mo Kα (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. Preliminary examination showed that the crystal belonged to the monoclinic system, space group $P2_1/m$ or $P2_1$. The unit cell dimensions, a = 9.961 (2) Å, b = 18.088 (3) Å, c = 10.036 (2) Å, β = 118.84 (2)°, and V = 1584 (2) Å^3, were obtained by a least-squares fit of 25 reflections in the range 12° < θ < 16°. With Z = 2 and a molecular weight of 1224.6, the calculated density is 2.568 g cm^{-3}.

Data were measured by using a ω–2θ motion. A total of 2829 reflections in the range 3° < 2θ < 50° were collected, 2645 of which having $I > 3[\sigma(I)]$ were used to solve and refine the structure. During data collection three intensity standards were measured after every hour. No decay was observed. The data were corrected for Lorentz and polarization effects. The linear absorption coefficient is 19.3 cm^{-1}; no absorption correction was applied.

The niobium atoms were located by using the results of MULTAN direct-method analysis,[11] and all nonhydrogen atoms were located in a series of difference Fourier maps. The structure was refined[12a] in space group $P2_1$ to convergence with use of anisotropic thermal parameters for all niobium, potassium, and sulfur atoms and isotropic parameters for all oxygen atoms. The acentric space group $P2_1$ rather than the centric $P2_1/m$ was chosen (a) because of the statistical

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(12) (a) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University of Jerusalem with use of the SHELX 1977 structure determination package. (b) The values of R_1 and R_2 for the incorrect enantiometer are 0.038 and 0.045, respectively.

indication of an acentric space group and (b) on the basis of the distribution of peaks in the Patterson function. It is confirmed by the successful refinement. The refinement of the mirror image of the original structure suggested that the original choice of enantiomorph was right.[12b] The discrepancy indices, $R_1 = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, had final values of $R_1 = 0.037$ and $R_2 = 0.044$. The final difference map showed no peaks of structural significance. A list of observed and calculated structure factors is available as supplementary material.

Results and Discussion

The atomic positional parameters are listed in Table I. Figure 2 shows a stereoview of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ unit and defines the numbering scheme, while Figure 3 gives a stereoview of the contents of the entire unit cell. Important interatomic distances and angles are listed in Table II.

With the two molecules in the cell of space group $P2_1$, there is no crystallographic symmetry imposed upon the complex. However, the ion nearly possesses D_{3h} symmetry. Each niobium atom in this structure forms nine bonds, of which two are Nb–Nb bonds and seven are Nb–O bonds in the usual arrangement found in other M_3X_{17} structures.[6–8] The mean distance of niobium atom to capping oxygen atom is 2.051 (9) Å, and the mean Nb–O(H_2O) distance is 2.240 (9) Å. The main structural difference between the niobium cluster and the group 6 M_3X_{17} clusters is the replacement of the six bridging carboxylates by six bridging sulfates. Such bridging sulfates have not been observed before in metal clusters. The bond distances and angles in the SO_4^{2-} ligands are similar to those found in bridging sulfates in dinuclear complexes,[13] and they are listed in a table included in the supplementary material.

The three edges of the Nb_3 triangle differ slightly (but significantly) from each other [2.875 (1), 2.889 (1), 2.892 (1) Å]. This distortion is probably the result of asymmetric electrostatic forces acting on the trimer as the result of the asymmetric hydrogen-bonding network and the potassium–oxygen interactions. The hydrogen-bonding network includes five lattice water molecules, three coordinated water ligands, one $H_5O_2^+$ unit, and twelve exo S=O oxygen atoms. In addition to the $H_5O_2^+$ ion there are four K^+ ions in the lattice that are surrounded by six to eight oxygen atoms from neighboring water molecules or exo S=O oxygen atoms. All the hydrogen bonds are within the normal range of 2.62 (1)–2.78 (1) Å, and the K^+–O distances are between 2.65 (1) and 3.1 (1) Å.

The O···H···O distance in the $H_5O_2^+$ unit is 2.43 (1) Å. This result is within the average range of 2.41–2.43 Å found in other compounds containing the diaquahydrogen ion.[14]

The electronic spectrum of $K_5(H_2O_5)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$ was measured on a sample ground with KBr and pressed into a pellet. This spectrum showed absorption lines at 510 and 700 nm and is identical with the spectrum of the mother liquid and the spectrum of a solution prepared by the dissolution of this salt in 60% H_2SO_4. This, together with the fact that the red-brown solid is precipitated quantitatively from the red-brown solution by the addition of K_2SO_4, strongly supports the assumption that the species present in solution is identical with the ion found in the crystal, namely, $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$. The same electronic spectrum was reported earlier by Goroshchenko and Andreeva but wrongly assigned to a postulated $Nb_6O_3(SO_4)_8$.[5]

Golibersuch and Young determined the oxidation state of the niobium atom in the red-brown complex by a permanganatometric titration and found it to be +3.7 in the mother liquid and +3.68 ± 0.02 in its alkali salts.[3] This oxidation number is confirmed by the crystallographic results

Table II. Important Bond Lengths and Bond Distances for $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot 5H_2O$

Important Bond Lengths (A)

Nb(1)-Nb(2)	2.875 (1)	Nb(2)-O(21)	2.136 (7)
-Nb(3)	2.889 (1)	-O(32)	2.150 (9)
-O(1)	2.049 (8)	-O(42)	2.115 (9)
-O(2)	2.051 (8)	-OW(2)	2.22 (1)
-O(11)	2.139 (8)	Nb(3)-O(1)	2.055 (6)
-O(22)	2.129 (8)	-O(2)	2.056 (7)
-O(52)	2.11 (1)	-O(31)	2.124 (9)
-O(62)	2.15 (1)	-O(41)	2.15 (1)
-OW(1)	2.254 (9)	-O(51)	2.13 (1)
Nb(2)-Nb(3)	2.892 (1)	-O(61)	2.15 (1)
-O(1)	2.075 (9)	-OW(3)	2.246 (6)
-O(2)	2.022 (9)	OW(6)-OW(7)	2.43 (1)
-O(12)	2.126 (8)		

Important Angles (Deg)

Nb(2)-Nb(1)-Nb(3)	60.23 (4)	O(2)-Nb(2)-O(12)	80.6 (4)
-O(1)	46.2 (2)	-O(21)	127.1 (4)
-O(2)	44.7 (2)	-O(32)	80.2 (4)
-O(11)	83.5 (2)	-O(42)	126.5 (5)
-O(22)	84.4 (2)	-OW(2)	146.9 (3)
-O(52)	128.3 (3)	O(12)-Nb(2)-O(21)	82.3 (4)
-O(62)	124.4 (3)	-O(32)	86.0 (4)
-OW(1)	150.1 (3)	-O(42)	147.6 (3)
Nb(3)-Nb(1)-O(1)	45.4 (3)	-OW(2)	75.1 (3)
-O(2)	45.4 (3)	O(21)-Nb(2)-O(32)	147.5 (4)
-O(11)	126.3 (3)	-O(42)	91.5 (4)
-O(22)	125.5 (3)	-OW(2)	71.6 (4)
-O(52)	84.5 (4)	O(32)-Nb(2)-O(42)	82.4 (4)
-O(62)	82.8 (3)	-OW(2)	76.1 (4)
-OW(1)	149.6 (3)	O(42)-Nb(2)-OW(2)	72.7 (4)
O(1)-Nb(1)-O(2)	71.5 (3)	Nb(1)-Nb(3)-Nb(2)	59.64 (4)
-O(11)	128.2 (3)	-O(1)	45.2 (2)
-O(22)	80.2 (4)	-O(2)	45.2 (3)
-O(52)	82.1 (3)	-O(31)	128.4 (3)
-O(62)	126.8 (5)	-O(41)	123.9 (3)
-OW(1)	144.9 (4)	-O(51)	82.3 (4)
O(2)-Nb(1)-O(11)	80.9 (4)	-O(61)	84.0 (4)
-O(22)	128.0 (3)	-OW(3)	149.0 (2)
-O(52)	128.2 (5)	Nb(2)-Nb(3)-O(1)	45.8 (2)
-O(62)	79.7 (4)	-O(2)	44.4 (2)
-OW(1)	143.6 (3)	-O(31)	82.0 (3)
O(11)-Nb(1)-O(22)	83.9 (4)	-O(41)	84.3 (3)
-O(52)	146.3 (4)	-O(51)	127.9 (3)
-O(62)	88.1 (4)	-O(61)	122.7 (3)
-OW(1)	73.3 (4)	-OW(3)	151.3 (2)
O(22)-Nb(1)-O(52)	88.1 (4)	O(1)-Nb(3)-O(2)	71.2 (4)
-O(62)	149.1 (4)	-O(31)	125.0 (4)
-OW(1)	74.8 (4)	-O(41)	78.7 (4)
O(52)-Nb(1)-O(62)	82.2 (4)	-O(51)	82.3 (4)
-OW(1)	72.9 (4)	-O(61)	128.4 (4)
O(62)-Nb(1)-OW(1)	74.3 (4)	-OW(3)	144.5 (3)
Nb(1)-Nb(2)-Nb(3)	60.13 (4)	O(2)-Nb(3)-O(31)	83.3 (4)
-O(1)	45.4 (2)	-O(41)	127.8 (4)
-O(2)	45.5 (3)	-O(51)	125.3 (4)
-O(12)	84.2 (2)	-O(61)	78.4 (4)
-O(21)	83.2 (2)	-OW(3)	144.2 (4)
-O(32)	125.7 (2)	O(31)-Nb(3)-O(41)	80.2 (4)
-O(42)	126.9 (2)	-O(51)	147.8 (5)
-OW(2)	149.1 (3)	-O(61)	90.4 (4)
Nb(3)-Nb(2)-O(1)	45.3 (3)	-OW(3)	74.4 (4)
-O(2)	45.3 (3)	O(41)-Nb(3)-O(51)	90.4 (3)
-O(12)	125.9 (3)	-O(61)	150.1 (5)
-O(21)	126.5 (2)	-OW(3)	76.0 (4)
-O(32)	84.5 (3)	O(51)-Nb(3)-O(61)	82.6 (3)
-O(42)	83.0 (3)	-OW(3)	73.5 (4)
-OW(2)	150.5 (3)	O(61)-Nb(3)-OW(3)	74.2 (4)
O(1)-Nb(2)-O(2)	71.5 (3)	Nb(1)-O(1)-Nb(2)	88.4 (3)
-O(12)	128.3 (4)	-Nb(3)	89.5 (3)
-O(21)	81.3 (4)	Nb(2)-O(1)-Nb(3)	88.9 (3)
-O(32)	128.7 (5)	Nb(1)-O(2)-Nb(2)	89.8 (4)
-O(42)	81.5 (3)	-Nb(3)	89.4 (3)
-OW(2)	141.5 (3)	Nb(2)-O(2)-Nb(3)	90.3 (3)

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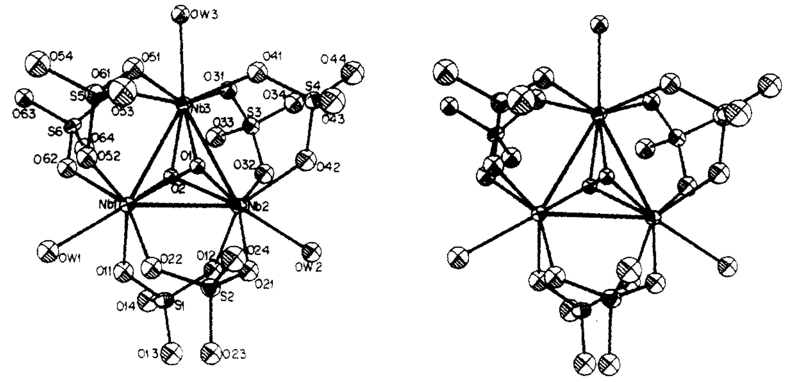

Figure 2. Stereoview of $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$.

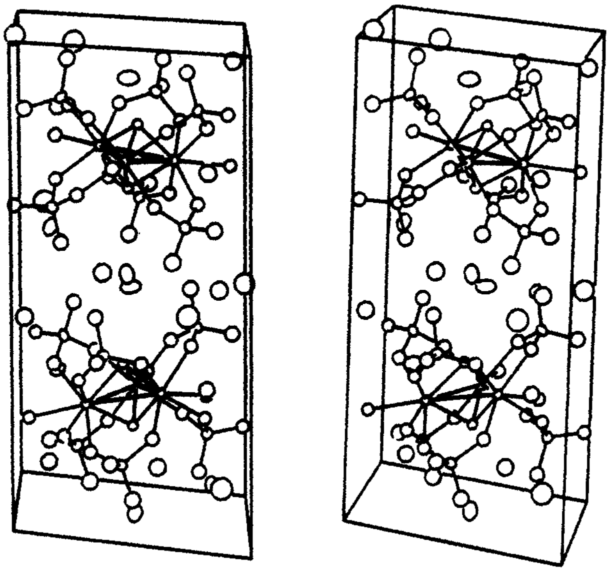

Figure 3. Stereoview of the contents of the unit cell of $K_4(H_5O_2)$-$[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot5H_2O$.

presented here; the 5− charge of the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ ion necessitates an oxidation number of $+3^2/_3$ for each Nb atom. Formally, one could assume that one of the metal atoms is in the +3 oxidation state and two are in the +4 oxidation state. However, the crystallographic data clearly suggest that the three metal atoms are equivalent, and therefore a better description would be an oxidation state of $+3^2/_3$ with four electrons available for M–M orbitals. Calculations[15] suggest that the four electrons will occupy bonding orbitals, and the resulting bond order in this complex is $^2/_3$ with an average Nb–Nb distance of 2.885 (7) Å.

Recent work on triangular molybdenum cluster of the M_3X_{17} type showed the existence of a series of three species differing in the number of d electrons in the M–M orbitals.[8] $[Mo_3O(CCH_3)(OAc)_6(H_2O)_3]^+$, $[Mo_3(CCH_3)_2(OAc)_6(H_2O)_3]^+$, and $[Mo_3(CCH_3)_2(OAc)_6(H_2O)_3]^{2+}$ contain six, five, and four electrons, respectively, in the molecular orbitals that provide the Mo–Mo bonding. When six electrons are present, the bond order is 1.0 and three sets of Mo–Mo single bonds exist. When the total number of electrons drops to 6 and then to 4, the bond orders drop to $^5/_6$ and then to $^2/_3$. As a result of the decrease in bond order the M–M distances increase from 2.753 (1) to 2.815 (7) and 2.883 (1) Å, respectively. A comparison of the four-electron Nb cluster with its four-electron molybdenum analogue $[Mo_3(CCH_3)_2(OAc)_6(H_2O)_3]^{2+}$ shows a very good agreement with the pattern described here. For the same bond order of $^2/_3$ the M–M distances are identical within the esd's, i.e., 2.885 Å. The close agreement between the M–M bond lengths of these Nb and Mo clusters is all the more striking if one considers the fact that the coordinating ligands of the Mo and the Nb atoms in the two clusters are quite different. It seems that the bond length in metal clusters of this type is determined almost exclusively by the M–M bond order.

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Registry No. $K_4(H_5O_2)[Nb_3O_2(SO_4)_6(H_2O)_3]\cdot5H_2O$, 80738-34-7.

Supplementary Material Available: Tables of thermal parameters, structure factors, and bond distances and angles in the SO_4^{2-} ligands (20 pages). Ordering information is given on any current masthead page.

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(15) Unpublished work by B. E. Bursten, A. Fang, and M. B. Hall.