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New Bi-Oxo-Capped Triangular Trinuclear Cluster Compounds of Niobium

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Abstract: The compounds [Nb$_3$O$_2$(O$_2$CC$_6$H$_5$)$_6$(C$_4$H$_8$O)$_3$][NbOCl$_4$(C$_4$H$_8$O)] (**1**) and [Nb$_3$O$_2$(O$_2$CCMe$_3$)$_6$(C$_4$H$_8$O)$_3$][B(C$_6$H$_5$)$_4$] (**2**) have been prepared by reactions of the sodium carboxylates with Nb$_2$Cl$_6$(Me$_2$S)$_3$. Crystals of **1** were unstable (solvent loss?) and diffracted poorly. The structure was solved and refined sufficiently to define the trinuclear cation and the anion unambiguously, but not accurately. Compound **2** formed excellent crystals which allowed a complete and accurate structure determination. The trinuclear cation has no crystallographically imposed symmetry but in its essentials approximates to the D_{3h} symmetry found for M$_3$O$_2$(O$_2$CR)$_6$L$_3$ species formed by Mo and W; it is clearly closely related to the previously known [Nb$_3$O$_2$(SO$_4$)$_6$(H$_2$O)$_3$]$^{5-}$ ion. The mean values of important structural parameters are the following: Nb–Nb, 2.842 [3] Å; Nb–O(cap), 2.035 [6] Å; Nb–O(carbox), 2.150 [4] Å; Nb–O(THF), 2.25 [1] Å; and Nb–O(cap)–Nb, 88.5 [3]°. Compound **2** crystallizes in space group *Pbca* with a = 27.033 (5) Å, b = 26.251 (4) Å, c = 20.609 (3) Å, V = 14,625 (7) Å^3, and Z = 8. The ^{1}H NMR spectrum of **2** is consistent with the composition and structure established crystallographically, and together with an Evans method measurement it shows the compound to be diamagnetic in solution. The solid is also diamagnetic, but when a correction is made for the diamagnetic contributions of all the atoms, it is concluded that the cation has μ_{eff} = 1.3 μ_B. No epr signal was detected at liquid nitrogen temperature. All data are consistent with a spin triplet ground state and a Nb–Nb bond order of $^2/_3$ (i.e., ground configuration of a^{2}e^2 or e^{3}a).

In recent years the existence of molybdenum and tungsten compounds of the type [M$_3$(μ_3-O)$_2$(O$_2$CR)$_6$(H$_2$O)$_3$]$^+$ has been discovered and extensively investigated.[1-11] These species have six electrons available for M–M bonding (core electrons) and thus a set of three single M–M bonds may be expected to exist. This expectation is supported by molecular orbital calculations.[12] In all of these compounds the M–M bond length, for both the molybdenum and tungsten compounds, is ca. 2.75 Å. In addition, there are structurally homologous molybdenum compounds in which one[5,13] or both[14] capping oxygen atoms are replaced by CH$_3$C groups and the total number of core electrons is 5 or 4, giving bond orders of $^5/_6$ and $^2/_3$ and bond lengths of ca. 2.82 and 2.89 Å, respectively. The essential structure in all of these species is shown in Figure 1.

It is interesting that the discovery of these molybdenum and tungsten bicapped triangular cluster species was antedated by many years by the discovery of a similar niobium cluster compound in which the six bridging bidentate ligands are sulfate ions rather than carboxylate ions. While the preparation of the niobium cluster compounds was first reported[15] in 1912, and later studied chemically by others,[16] the correct structure became known only in 1980 through the work of A. Bino.[17] In his structural study of K$_4$(H$_5$O$_2$)[Nb$_3$O$_2$(SO$_4$)$_6$(H$_2$O)$_3$]·5H$_2$O, Bino showed conclusively that the extent of oxidation of the metal atoms is such as to leave four core electrons (giving a Nb–Nb bond order of $^2/_3$) and he found, in accord with this, a Nb–Nb distance of 2.885 (7) Å.

When we reflected upon the facts just summarized, it seemed to us that bicapped triniobium compounds (and also tritantalum compounds) other than the sulfato species just described might reasonably be expected to exist. We therefore undertook the preparation of carboxylato-bridged species, which if isolelectronic with the sulfato anion would have formulas of the type [Nb$_3$O$_2$(O$_2$CR)$_6$L$_3$]$^+$, in which L is a neutral ligand. In this paper we report that this undertaking has been successful, the species with L = C$_4$H$_8$O and R = C$_6$H$_5$ or *tert*-butyl having been obtained and characterized.

Experimental Section

All manipulations were performed under an atmosphere of argon with use of standard Schlenk techniques. Nb$_2$Cl$_6$(SMe$_2$)$_3$ was prepared according to the literature method used for preparation of the analogous complex Ta$_2$Cl$_6$(THT)$_3$.[18] Sodium benzoate and pivalate were deaerated under vacuum at 100 °C, and sodium tetraphenylborate was deaerated under vacuum at room temperature. Elemental analyses were performed by Galbraith Microanalytical Laboratories. ^{1}H spectra were obtained on a Varian XL 200 spectrometer.

[Nb$_3$(μ_3-O)$_2$(O$_2$CC$_6$H$_5$)$_6$(THF)$_3$][NbOCl$_4$(THF)]·*n* (THF) (1). Nb$_2$Cl$_6$(SMe$_2$)$_3$ (0.60 g, 1.0 mmol) was dissolved in 20 mL of a 1:1 benzene–THF mixture. The solution was filtered, and to the resulting mixture sodium benzoate was added (0.60 g, 4.0 mmol). Upon stirring, the color of the reaction mixture changed from purple to dark red within several minutes. Stirring of the mixture was continued at room temperature for 12 h. After that period, the reaction mixture was filtered into a Schlenk tube, leaving a white solid behind. This dark red solution was carefully covered with a layer of hexane and allowed to stand undisturbed. Interdiffusion of solvents was accompanied by the formation of a crystalline deposit of **1** (yield, 36%; ca. 0.3 g).

[Nb$_3$(μ_3-O)$_2$(O$_2$CC(CH$_3$)$_3$)$_6$(THF)$_3$][B(C$_6$H$_5$)$_4$] (2). A solution of Nb$_2$Cl$_6$(SMe$_2$)$_3$ (0.60 g, 1.0 mmol) in 20 mL of a 1:1 benzene–THF mixture was filtered, and sodium pivalate (0.50 g, 4.0 mmol) was added. The color of the solution changed from purple to dark red immediately. After being stirred for 12 h at room temperature, the reaction mixture was filtered to remove a white solid. Dry sodium tetraphenylborate (0.25 g, 0.73 mmol) was added to the filtrate, and the reaction mixture was again stirred for several hours. The mixture was filtered, and the filtrate was evaporated to dryness. The oily residue was dissolved in 4 mL of THF, and 1 mL of benzene and then 50 mL of hexane were carefully added on top of this solution. The flask was placed in a refrigerator, and after a period of 1–2 days, a red crystalline solid was obtained. The

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Table I. Crystallographic Data

formula	$Nb_4Cl_4O_{20}C_{62}H_{70}$ (**1**)	$Nb_3O_{17}C_{66}BH_{98}$ (**2**)
formula wt	1648.67	1453.04
space group	$P2_1/m$	$Pbca$
systematic absenses	$0k0$, $k = 2n + 1$	$0kl$, $k = 2n + 1$ $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$
a, Å	19.214 (11)	27.033 (5)
b, Å	17.812 (5)	26.251 (4)
c, Å	24.466 (9)	20.609 (3)
α, deg	90.0	90.0
β, deg	112.86 (4)	90.0
γ, deg	90.0	90.0
V, Å^3	7715 (33)	14625 (7)
Z	4	8
d_{calcd}, g/cm^3	1.419	1.320
crystal size, mm	0.1 × 0.15 × 0.2	0.2 × 0.3 × 0.3
μ, cm^{-1}	7.530	43.498
data collection instrument	CAD-4	Syntext P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ 0.71073 Å)	Cu Kα (λ 1.54184 Å)
orientation reflections, no., range (2θ)		15, $40.85 < 2\theta < 47.31$
temperature, °C		0
scan method		ω–2θ
data collect. range, 2θ, deg		$5 < 2\theta < 130$
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$		5969 5217
no. of parameters refined		653
trans. factors, max, min		99.95, 90.45
R^a		0.0518
R_w^b		0.0680
quality-of-fit indicator^c		1.359
largest shift/esd, final cycle		0.81
largest peak, e/Å^3		0.777

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

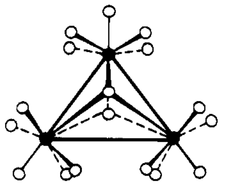

Figure 1. The general $M_3(\mu_3\text{-}X)_2Y_{15}$-type structure.

solvents were siphoned off with use of cannula, the solid was washed with fresh hexane (3 × 10 mL), and this entire purification procedure was repeated twice (yields, 35–45%; ca. 0.4 g).

Anal. Calcd for $C_{66}H_{98}BO_{17}Nb_3$: C, 54.55; H, 6.80; B, 0.74. Found: C, 54.75; H, 6.56; B, 0.71. ^{1}H NMR (THF/Me$_4$Si): δ 1.26 (s, H54), 1.71–1.88 (m, H12), 3.54–3.72 (m, H12), 6.60–7.44 (m, H20). EPR: no signal was obtained between 1000 and 5000 G.

Crystallographic quality crystals can be prepared by the procedure described above or by careful layering, with hexane, of the benzene–THF reaction mixture containing $NaB(C_6H_5)_4$. Large, dark red, acicular crystals of **2** are formed upon slow mixing of the solvents within 2–3 weeks (0.2 g, yield 20%).

X-ray Crystallographic Procedures. Structure determinations have been carried out by application of general procedures that have already been fully described elsewhere.[19]

Crystals of **1** disintegrated rapidly when removed from the mother liquor, probably by loss of solvent molecules. It was found that this problem could be alleviated by collecting data at −100 °C, but unfortuantely the crystals appeared to be of very mediocre quality. The intensity data were poor and satisfactory completion of the structure was not possible. However, we were able to identify the compound, determine its empirical formula, and define the major structural features. All atoms of interest to us were located in a three-dimensional difference Fourier map, but it is possible—even probable—that not all solvent molecules present in the lattice were detected. Least-squares refinement gave unsatisfactory residuals even when a rigid body model for the phenyl groups was introduced.

Basic information about data collection and structure refinement for **2**, as well as selected data concerning **1**, are summarized in Table I. Polarization, Lorentz, and absorption corrections were applied to the intensity data.

For **2**, the position of one niobium atom was obtained from a three-dimensional Patterson function. The remainder of the structure was developed by a series of Fourier syntheses and least-squares refinements. Two of the six *tert*-butyl groups present were disordered over two positions. Initially equal fractional occupancy of $^1/_2$ was assigned to both orientations and then by additional refinement they were adjusted to 0.6 [C(12) to C(14)], 0.4 [C(12A) to C(14A)], 0.55 [C(62) to C(64)], and 0.45 [C(62A) to C(64A)]. Full-matrix least-squares refinement was completed with the disordered methyl carbon atoms and the atoms in the anion having isotropic thermal parameters while all remaining atoms were assigned anisotropic parameters. A complete list of structure factors and a table of anisotropic thermal parameters are available as supplementary material.

Magnetic Measurements. By the Faraday method at 22 °C $\chi_g = 0.059 \times 10^{-6}$ cgsu. From which $\chi_M = -85.7$ cgsu and $\chi_M^{corr} = 730 \times 10^{-6}$ cgsu.

Results and Discussion

Of the two compounds described here only the pivalato complex, **2** could be characterized satisfactorily. The importance of **1** is associated with it being the first bi-oxo-capped niobium carboxylate to be isolated and identified. It showed the feasibility of preparation of such compounds and constituted a starting point in a search for related complexes which would be easier to work with.

Compound **1** was found to have the empirical formula $[Nb_3O_2(O_2CC_6H_5)_6(C_4H_8O)_3][NbOCl_4(C_4H_8O)]\cdot nC_4H_8O$, where n could not be determined with certainty but is probably equal to 1. There are two crystallographically independent trimers in the asymmetric unit, each one positioned on a mirror plane. For one of them the Nb_3 triangle lies in the plane while the other one has the mirror plane perpendicular to it. The trinuclear cations in **1** closely resemble the one in **2**, both qualitatively and in terms of bond lengths and angles. The anion, $[NbOCl_4(THF)]^-$, is a pseudooctahedral Nb(V) species with THF molecules trans to the oxygen atom.

Compound **2**, with the formula $[Nb_3O_2(O_2CC_4H_9)_6(C_4H_8O)_3][B(C_6H_5)_4]$, is composed of discrete trinuclear cations and tetraphenylborate anions, both located on general crystallographic positions. The final atomic positional and isotropic equivalent thermal parameters are presented in Table II. Table III and IV list important interatomic distances and angles. The remaining interatomic distances and angles are included in the supplementary

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(19) See, for example: Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

Table II. Positional and Isotropic Equivalent Thermal Parameters for **2**[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Nb(1)	0.01860 (3)	0.10786 (3)	0.23678 (4)	2.86 (2)	C(103)	0.0726 (4)	0.4137 (5)	0.4812 (6)	4.9 (3)*
Nb(2)	0.00126 (3)	0.19137 (3)	0.32093 (4)	2.90 (2)	C(14)	0.101 (1)	0.048 (1)	0.420 (1)	8.5 (8)*
Nb(3)	−0.07841 (3)	0.12651 (3)	0.28611 (4)	2.92 (2)	C(12A)	0.177 (2)	0.131 (2)	0.385 (2)	11 (1)*
O(1)	−0.0112 (2)	0.1152 (2)	0.3275 (3)	2.9 (1)	C(13A)	0.112 (1)	0.119 (1)	0.471 (1)	6.3 (7)*
O(2)	−0.0275 (2)	0.1691 (2)	0.2354 (3)	2.9 (1)	C(14A)	0.146 (1)	0.052 (1)	0.381 (2)	8.5 (9)*
O(10)	0.0833 (2)	0.0990 (2)	0.2985 (3)	3.6 (2)	C(20)	0.0689 (4)	0.2098 (4)	0.2028 (5)	3.5 (2)
O(11)	0.0694 (2)	0.1654 (3)	0.3629 (3)	3.7 (2)	C(21)	0.0981 (4)	0.2445 (4)	0.1580 (5)	4.4 (3)
O(20)	0.0642 (2)	0.1626 (2)	0.1890 (3)	3.4 (2)	C(22)	0.1036 (6)	0.2193 (5)	0.0891 (6)	7.9 (4)
O(21)	0.0509 (3)	0.2290 (3)	0.2534 (3)	3.9 (2)	C(23)	0.1495 (5)	0.2499 (7)	0.1889 (7)	9.2 (4)
O(30)	−0.0020 (3)	0.0307 (2)	0.2572 (3)	3.7 (2)	C(24)	0.0718 (7)	0.2948 (5)	0.1502 (7)	9.4 (5)
O(31)	−0.0775 (2)	0.0453 (3)	0.2969 (3)	4.0 (2)	C(30)	−0.0394 (4)	0.0169 (4)	0.2871 (5)	3.9 (2)
O(40)	−0.0221 (3)	0.0971 (2)	0.1474 (3)	3.7 (2)	C(31)	−0.0420 (4)	−0.0373 (4)	0.3176 (6)	4.8 (3)
O(41)	−0.0975 (2)	0.1101 (3)	0.1879 (3)	3.6 (2)	C(32)	−0.0337 (7)	−0.0306 (6)	0.3897 (7)	9.4 (5)
O(50)	−0.0328 (3)	0.1858 (3)	0.4143 (3)	3.8 (2)	C(33)	−0.0014 (6)	−0.0704 (5)	0.2870 (9)	9.3 (4)
O(51)	−0.0955 (2)	0.1356 (3)	0.3870 (3)	3.9 (2)	C(34)	−0.0951 (5)	−0.0602 (5)	0.3040 (8)	8.0 (4)
O(60)	−0.0545 (2)	0.2490 (3)	0.3065 (3)	3.6 (2)	C(40)	−0.0674 (4)	0.1099 (4)	0.1405 (5)	3.8 (2)
O(61)	−0.1171 (2)	0.1983 (2)	0.2796 (3)	3.7 (2)	C(41)	−0.0847 (4)	0.1308 (4)	0.0743 (5)	4.5 (3)
O(70)	0.0712 (2)	0.0609 (3)	0.1769 (3)	3.9 (2)	C(42)	−0.0574 (7)	0.1832 (5)	0.0670 (8)	10.3 (5)
O(80)	0.0271 (3)	0.2615 (3)	0.3758 (3)	4.5 (2)	C(43)	−0.0678 (6)	0.0941 (7)	0.0214 (6)	9.0 (5)
O(90)	−0.1581 (2)	0.1036 (3)	0.2905 (3)	4.0 (2)	C(44)	−0.1415 (6)	0.1380 (8)	0.0755 (8)	11.3 (6)
C(10)	0.0903 (4)	0.1238 (4)	0.3496 (5)	3.7 (2)	C(50)	−0.0677 (4)	0.1571 (4)	0.4289 (5)	3.5 (2)
C(11)	0.1260 (4)	0.1018 (4)	0.4000 (6)	4.7 (3)	C(51)	−0.0793 (4)	0.1476 (4)	0.5010 (5)	4.3 (3)
C(12)	0.1363 (9)	0.1383 (9)	0.454 (1)	6.3 (6)*	C(52)	−0.1291 (4)	0.1749 (6)	0.5150 (6)	6.5 (4)
C(13)	0.174 (1)	0.086 (1)	0.368 (1)	7.6 (7)*	C(53)	−0.0378 (5)	0.1690 (5)	0.5423 (5)	5.5 (3)
C(60)	−0.0983 (4)	0.2420 (4)	0.2872 (5)	3.1 (2)	C(54)	−0.0834 (5)	0.0885 (4)	0.5103 (6)	6.2 (3)
C(61)	−0.1304 (5)	0.2889 (4)	0.2749 (6)	5.1 (3)	C(104)	0.0504 (5)	0.4492 (5)	0.4395 (6)	5.7 (3)*
C(62)	−0.102 (1)	0.328 (1)	0.238 (1)	9.9 (8)*	C(105)	0.0799 (5)	0.4730 (5)	0.3919 (6)	5.7 (3)*
C(63)	−0.147 (1)	0.307 (1)	0.344 (1)	9.2 (8)*	C(106)	0.1317 (4)	0.4626 (4)	0.3883 (6)	4.5 (2)*
C(64)	−0.1765 (9)	0.277 (1)	0.233 (1)	8.1 (7)*	C(107)	0.2280 (4)	0.3598 (4)	0.4575 (5)	4.1 (2)*
C(62A)	0.384 (1)	0.335 (1)	0.186 (2)	7.6 (9)*	C(108)	0.2397 (5)	0.3202 (5)	0.4151 (6)	5.2 (3)*
C(63A)	0.316 (1)	0.279 (1)	0.205 (2)	8 (1)*	C(109)	0.2483 (5)	0.2708 (6)	0.4366 (7)	6.9 (3)*
C(64A)	0.368 (2)	0.297 (2)	0.299 (2)	11 (1)*	C(110)	0.2471 (5)	0.2603 (6)	0.5019 (7)	7.1 (4)*
C(71)	0.0572 (4)	0.0154 (4)	0.1384 (6)	5.1 (3)	C(111)	0.2368 (5)	0.2991 (5)	0.5472 (6)	6.2 (3)*
C(72)	0.1059 (5)	−0.0103 (5)	0.1221 (8)	8.4 (4)	C(112)	0.2282 (4)	0.3485 (5)	0.5241 (6)	4.6 (3)*
C(73)	0.1459 (5)	0.0275 (5)	0.1355 (7)	5.8 (3)	C(113)	0.2393 (4)	0.4630 (4)	0.4800 (5)	4.2 (2)*
C(74)	0.1247 (4)	0.0712 (5)	0.1699 (7)	7.2 (4)	C(114)	0.2182 (4)	0.5104 (5)	0.4868 (6)	5.0 (3)*
C(81)	0.0332 (6)	0.3160 (5)	0.3456 (7)	8.2 (4)	C(115)	0.2395 (5)	0.5478 (6)	0.5276 (7)	6.6 (3)*
C(82)	0.0874 (6)	0.3241 (5)	0.3498 (7)	7.8 (4)	C(116)	0.2840 (5)	0.5371 (5)	0.5599 (6)	5.9 (3)*
C(83)	0.1072 (6)	0.2837 (6)	0.3996 (9)	9.4 (5)	C(117)	0.3041 (5)	0.4908 (5)	0.5540 (6)	6.1 (3)*
C(84)	0.0596 (6)	0.2638 (6)	0.4296 (7)	8.7 (5)	C(118)	0.2846 (4)	0.4532 (5)	0.5136 (6)	4.9 (3)*
C(91)	−0.1970 (4)	0.1299 (5)	0.3275 (6)	5.3 (3)	C(119)	0.2380 (4)	0.4243 (4)	0.3562 (5)	4.2 (2)*
C(92)	−0.2452 (5)	0.1100 (7)	0.2990 (8)	9.7 (5)	C(120)	0.2855 (5)	0.4432 (5)	0.3463 (6)	5.3 (3)*
C(93)	−0.2329 (5)	0.0669 (7)	0.258 (1)	10.5 (5)	C(121)	0.3048 (5)	0.4437 (5)	0.2819 (6)	6.1 (3)*
C(94)	−0.1794 (4)	0.0587 (5)	0.2553 (6)	5.8 (3)	C(122)	0.2771 (5)	0.4266 (5)	0.2287 (6)	5.6 (3)*
B	0.2147 (5)	0.4181 (6)	0.4299 (7)	4.5 (3)*	C(123)	0.2315 (5)	0.4086 (5)	0.2390 (6)	5.7 (3)*
C(101)	0.1553 (4)	0.4271 (4)	0.4311 (5)	3.5 (2)*	C(124)	0.2122 (5)	0.4055 (5)	0.3024 (6)	5.6 (3)*
C(102)	0.1241 (4)	0.4034 (4)	0.4771 (5)	4.0 (2)*					

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

material. An ORTEP drawing of the cation, in which the labeling scheme is defined, is shown in Figure 2.

At the core of the trinuclear cation is a trigonal-bipyramidal $Nb_3O_2^{7+}$ unit with oxygen atoms 1.204 [1] Å above and below the equatorial Nb_3 plane. Two $(CH_3)_3CCO_2^-$ ligands bridge each edge of the triangle, and three THF molecules occupy the axial positions. The coordination sphere has virtual D_{3h} symmetry. Table V lists averaged values of important interatomic dimensions. The Nb–O bond lengths agree well with those found in the sulfato complex. The peripheral atoms do not conform rigorously to the D_{3h} symmetry. For example, the α-carbon atoms of the six pivalato ligands are located at different distances from the corresponding ONbNb′O′ planes. As is clearly evident in Figure 2, two axial THF ligands are essentially in the Nb_3 plane, while the third is roughly perpendicular to it. This apparent uniqueness of Nb(2) seems to be manifested also in a slightly elongated Nb(1)–Nb(3) bond as compared to the other two metal–metal distances. However, this effect is very small and may in fact have no real significance. The NMR spectrum indicates that in solution all three axial ligands become equivalent. Similarly the presence of only one signal for methyl protons shows the equivalency of the pivalato groups in solution.

Table III. Important Bond Distances (Å) for **2**[a]

Nb(1)–Nb(2)	2.834 (1)	Nb(1)–O(20)	2.134 (6)
Nb(3)	2.855 (1)	O(30)	2.143 (6)
O(1)	2.045 (5)	O(40)	2.163 (6)
O(2)	2.033 (5)	O(70)	2.250 (6)
O(10)	2.175 (6)		
Nb(2)–Nb(3)	2.838 (1)	Nb(2)–O(21)	2.171 (6)
O(1)	2.034 (5)	O(50)	2.138 (6)
O(2)	2.013 (5)	O(60)	2.158 (6)
O(11)	2.145 (6)	O(80)	2.271 (6)
Nb(3)–O(1)	2.029 (5)	Nb(3)–O(51)	2.144 (6)
O(2)	2.058 (5)	O(61)	2.159 (6)
O(31)	2.143 (6)	O(90)	2.238 (6)
O(41)	2.133 (6)		

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

All three bi-oxo-capped trimers of niobium, namely **1**, **2**, and the sulfato complex, have the same formal charge on the Nb_3 core, viz., 11+, and the mean oxidation state of the metal is +3 $^2/_3$. However, it is more useful to look at the electronic structure of

Table IV. Important Bond Angles (deg) for **2**[a]

Nb(2)-Nb(1)-Nb(3)	59.84 (3)	Nb(1)-Nb(2)-Nb(3)	60.44 (3)
O(1)	45.8 (2)	O(1)	46.2 (2)
O(2)	45.2 (2)	O(2)	45.8 (2)
O(10)	81.9 (2)	O(11)	81.9 (2)
O(20)	81.8 (2)	O(21)	81.8 (2)
O(30)	124.6 (2)	O(50)	124.7 (2)
O(40)	122.5 (2)	O(60)	125.0 (2)
O(70)	149.8 (2)	O(80)	151.7 (2)
Nb(3)-Nb(1)-O(1)	45.3 (2)	Nb(3)-Nb(2)-O(1)	45.6 (2)
O(2)	46.1 (2)	O(2)	46.5 (2)
O(10)	123.3 (2)	O(11)	124.2 (2)
O(20)	125.4 (2)	O(21)	125.5 (2)
O(30)	81.6 (2)	O(50)	81.9 (2)
O(40)	81.9 (2)	O(60)	81.7 (2)
O(70)	150.4 (2)	O(80)	147.8 (2)
O(1)-Nb(1)-O(2)	72.4 (2)	O(1)-Nb(2)-O(2)	73.1 (2)
O(10)	78.0 (2)	O(11)	78.6 (2)
O(20)	125.9 (2)	O(21)	126.4 (2)
O(30)	78.8 (2)	O(50)	78.5 (2)
O(40)	126.2 (2)	O(60)	125.7 (2)
O(70)	143.3 (2)	O(80)	144.6 (2)
O(2)-Nb(1)-O(10)	125.8 (2)	O(2)-Nb(2)-O(11)	126.3 (2)
O(20)	79.3 (2)	O(21)	79.1 (2)
O(30)	126.2 (2)	O(50)	127.0 (2)
O(40)	77.3 (2)	O(60)	79.3 (2)
O(70)	144.3 (2)	O(80)	142.2 (2)
O(10)-Nb(1)-O(20)	83.0 (2)	O(11)-Nb(2)-O(21)	82.7 (2)
O(30)	89.6 (2)	O(50)	89.1 (2)
O(40)	153.2 (2)	O(60)	151.5 (2)
O(70)	75.7 (2)	O(80)	78.1 (2)
O(20)-Nb(1)-O(30)	151.3 (2)	O(21)-Nb(2)-O(50)	150.9 (2)
O(40)	89.3 (2)	O(60)	91.4 (2)
O(70)	75.6 (2)	O(80)	76.1 (2)
O(30)-Nb(1)-O(40)	85.0 (2)	O(50)-Nb(2)-O(60)	82.6 (2)
O(70)	75.7 (2)	O(80)	74.9 (2)
O(40)-Nb(1)-O(70)	77.5 (2)	O(60)-Nb(2)-O(80)	73.4 (3)
Nb(1)-Nb(3)-Nb(2)	59.73 (3)	O(2)-Nb(3)-O(31)	125.8 (2)
O(1)	45.8 (2)	O(41)	77.9 (2)
O(2)	45.4 (2)	O(51)	125.2 (2)
O(31)	81.7 (2)	O(61)	79.6 (2)
O(41)	81.4 (2)	O(90)	144.1 (2)
O(51)	124.3 (2)	O(31)-Nb(3)-O(41)	84.3 (2)
O(61)	124.9 (2)	O(51)	90.7 (2)
O(90)	148.5 (2)	O(61)	151.6 (2)
Nb(2)-Nb(3)-O(1)	45.8 (2)	O(90)	74.9 (2)
O(2)	45.2 (2)	O(41)-Nb(3)-O(51)	153.0 (2)
O(31)	124.2 (2)	O(61)	90.0 (2)
O(41)	123.0 (2)	O(90)	75.6 (2)
O(51)	81.5 (2)	O(51)-Nb(3)-O(61)	81.8 (2)
O(61)	81.9 (2)	O(90)	77.4 (2)
O(90)	151.8 (2)	O(61)-Nb(3)-O(90)	76.7 (2)
O(1)-Nb(3)-O(2)	72.2 (2)	Nb(1)-O(1)-Nb(2)	88.0 (2)
O(31)	78.4 (2)	Nb(3)	88.9 (2)
O(41)	125.9 (2)	Nb(2)-O(1)-Nb(3)	88.6 (2)
O(51)	78.6 (2)	Nb(1)-O(2)-Nb(2)	88.9 (2)
O(61)	126.0 (2)	Nb(3)	88.5 (2)
O(90)	143.6 (2)	Nb(2)-O(2)-Nb(3)	88.4 (2)

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

Table V. Averaged Values of Selected Interatomic Dimensions in Niobium Trimers with a $Nb_3O_2^{7+}$ Core[a]

	trinuclear ion	
atoms, unit	$[Nb_3O_2(O_2CC_4H_9)_6(THF)_3]^+$	$[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$
Nb-Nb, Å	2.842 [3]	2.885 [5]
$Nb-O_{cap}$, Å	2.035 [6]	2.051 [7]
$Nb-O_{carbax.}$, Å	2.150 [4]	2.134 [4]
$Nb-O_{axial}$, Å	2.253 [10]	2.240 [11]
$Nb-O_{cap}-Nb$, deg	88.5 [3]	89.4 [3]

[a] 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 ith value from the arithmetic mean and n is the total number of values averaged.

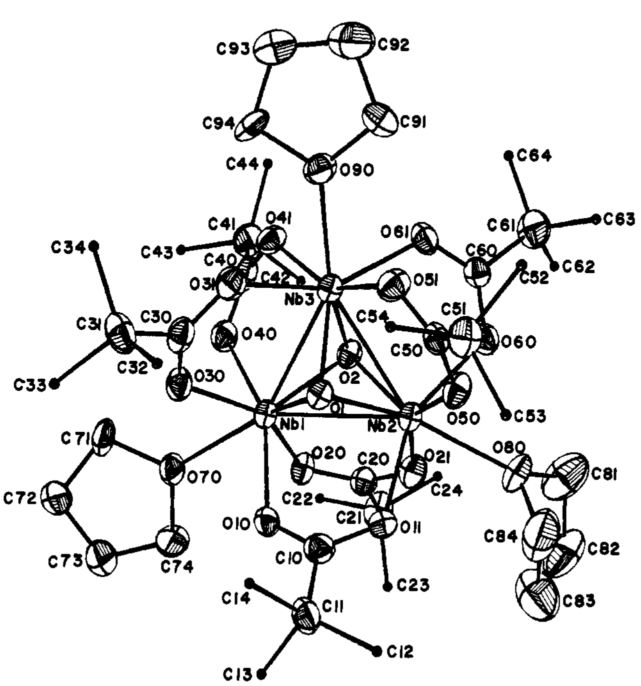

Figure 2. An ORTEP drawing of the $[Nb_3O_2(O_2CC_4H_9)_6(C_4H_8O)_3]^+$ cation, which also defines the labeling scheme. The thermal ellipsoids enclose 35% of the electron density. Methyl carbon atoms were assigned arbitrarily small thermal ellipsoids for the sake of clarity.

the Nb_3 cluster as a whole. Since a set of three neutral niobium atoms would have 15 electrons, the Nb_3^{11+} unit has four electrons available for metal–metal bond formation. The presence of four d electrons within the system should lead to the formation of bonds of order $^2/_3$ between the metal atoms.

This assignment of bond order is fully consistent with the observed Nb–Nb bond lengths, which have a mean value of 2.842 [3] Å. This may be compared with the value of 2.885 (7) Å in the sulfato-bridged case[17] where the same bond order is proposed. The somewhat smaller bite of the carboxylate ligands could account for the slightly shorter distance in the present case. Comparison can also be made with various carboxylato-bridged $Mo_3X_2^{n+}$ species, where it has been shown that the Mo–Mo bond length is a consistent function of the Mo–Mo bond order.[4,14] Thus, for systems with 6, 5, and 4 cluster electrons, the Mo–Mo bond lengths are typically 2.75, 2.82, and 2.88 Å, respectively. The Nb–Nb distance of 2.84 Å for a $^2/_3$ bond order may be shorter than those for Mo_3 species because in the latter case the formal charge on the metal atoms ($+4^2/_3$) is higher than for the Nb_3 case ($+3^2/_3$), thus leading to greater metal–metal repulsive forces.

According to MO calculations[12,20] for $Mo_3X_2^{n+}$ species, the two highest filled orbitals in a six-electron system of this kind should be an a_1' and an e' orbital and these are calculated to be very similar in energy, with the question of the ordering being "too close to call". Thus for a 4-electron system we might reasonably expect either an e'^3a_1' or an $a_1'^2e_1^2$ configuration, and thus two unpaired electrons giving rise to a spin triplet ground state.

Physical measurements are consistent with this as a first approximation, but suggest that in detail a more complicated situation may prevail. No EPR signal was observed for **2** at 77 K in the magnetic field range of 1000–5000 G with use of an X-band spectrometer, but this is not surprising for a spin-triplet ground state. Measurements of the bulk magnetic susceptibility showed that compound **2** is diamagnetic and so also did a measurement on the dissolved compound by the Evans NMR method. However, the diamagnetic susceptibility is very small and when corrected for the diamagnetism of all of its components, a magnetic moment of 1.3 μ_B is indicated. This result may be compared with the weak paramagnetism reported for the $[Nb_3O_2(SO_4)_6(H_2O)_3]^{5-}$ ion[21] and also for the 4-electron trimolybdenum species $[Mo_3(CH_3C)_2$-

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$(O_2CCH_3)_6(H_2O)_3]^{2+}$, although in the latter the NMR spectrum showed some line shape and chemical shift effects as well.[14] In the case of compound **2**, the ^{1}H NMR spectrum has a perfectly normal appearance, indicating that unpaired spin density does not reach the pivalate protons.

The mechanism and factors contributing to the formation of the trinuclear complexes of niobium are still rather obscure. Analogous Mo and W compounds form under a variety of conditions and show unusual stability. Once formed they are chemically inert, and the replacement of axial ligands or substitution reactions on phenyl groups of the RCO_2 ligands are the only chemical changes short of disintegration to monomers they are known to undergo. The niobium compounds are less stable, but nevertheless, their "self-assembly" suggests that all such systems have a special stability relative to mononuclear or binuclear species.

So far the source of capping oxygen atoms has not been identified with certainty for any bi-oxo-capped trimer. The most viable possibility is that oxygen atoms are extracted from carboxylato groups. However, since no definite evidence is available yet we cannot rule out some other sources, e.g., hydrolysis due to the presence of traces of water in solvents. On the other hand, the latter does not account for the oxidation of Nb(III) to species with $3^2/_3$ oxidate state. In general rather complex reaction paths are probably taking place in systems which produce compounds with an $M_3X_2^{n+}$ core. Unexpected formation of $NbOCl_4(THF)^-$ in the Nb-benzoate reaction is a further indication that complex chemical transformations are occurring.

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Registry No. 1, 89746-82-7; **2**, 89746-84-9; $Nb_2Cl_6(SMe_2)_3$, 61069-51-0.

Supplementary Material Available: Tables of structure factors, anisotropic thermal vibration parameters, and additional bond distances and angles (33 pages). Ordering information is given on any current masthead page.

MNDO Study of S_N2 Reactions and Related Processes[1]

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Abstract: Recent experimental and theoretical work has shown that S_N2 reactions of anions commonly take place with little or no activation in the gas phase, indicating that the barriers in solution are due primarily to desolvation of the ion. This conflicts with current theories of S_N2 reaction rates where the solvent is assumed to play a minor role. Detailed MNDO calculations for S_N2 reactions of chloride ion with alkyl chlorides, benzyl chlorides, allyl chloride, and chloroacetaldehyde, and of various anions with methyl chloride, have now suggested an explanation and have also elucidated the roles of alkyl and +E groups. The S_N2' reaction of chloride ion with allyl chloride is predicted to take place without activation, its lower rate in solution being an expected consequence of solvation. According to simple MO theory, the S_N2 and S_N2' reactions should *both* take place without activation. The S_N2 barriers are now attributed to the small size of the carbon atom which inhibits binding to five ligands.

Nucleophilic aliphatic substitution has been studied more intensively than any other organic reaction, and the results form the basis of much of the currently accepted theory concerning the mechanisms of organic reactions in solution and the effects of solvents on their rates. Some years ago, however, doubt was thrown on these conclusions by the discovery that many S_N2 reactions of anions take place with little or no activation in the gas phase.[2-4] The activation barriers in solution must therefore be attributed to the energy required to remove solvent molecules from the anion so that the alkyl derivative can approach it. Yet, as Ingold pointed out many years ago,[5] the solvent seems to have only a minor effect on reactions of this kind when they are carried out in solution. The situation was further confused by studies[6,7] of the interactions between halide ions and alkyl halides in the gas phase which seemed to suggest that the trigonal-bipyramidal species commonly regarded as the transition states (TS) in S_N2 reactions are in fact stable intermediates. These conclusions, if true, would moreover throw doubt on the entire current theory of reactions of anions in solution because *any* such reaction of an anion with a neutral molecule must involve analogous desolvation of the ion and its rate must be correspondingly reduced. *Any* reaction of an anion that takes place as rapidly in solution as its S_N2 reaction with methyl chloride should also then take place without activation in the gas phase.

Since resolution of this paradox clearly represented a very pressing problem, we decided some years ago to undertake detailed calculations for a wide range of S_N2 reactions in the hope of finding a solution. In the period since this work started, ab initio calculations[8] and detailed experimental studies[10] have in fact clarified the situation, showing that the S_N2 reaction itself is not as anomalous in this respect as Dougherty et al.[6,7] had supposed. Both theory and experiment now indicate that the reaction profile for the S_N2 reaction of chloride ion with methyl chloride has the form indicated in Figure 1a. The reactants first combine to form a charge/dipole (CD) complex (the species observed by Dougherty et al.[6,7]) which undergoes conversion to the products via the trigonal-bipyramidal TS commonly postulated. The activation energy in the gas phase under the conditions used in the ICR studies[9] is small because the energy liberated in the exothermic

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