the W-O bond lengths are shorter by ~0.1 Å and the W-O-W bond angles are larger by ~5° than the corresponding values for the methoxy oxygen atom. Also, the W-W bond lengths of 2.514 Å opposite the bridging oxygen atoms are larger by ~0.02 Å than those in the present case. These differences indicate that the methoxy oxygen atom is bound to the metal triangle by weaker bonds than the oxo anion.

The tetrahedral $[ZnCl_4]^{2-}$ ion found in this structure has normal geometry with a mean Zn-Cl bond length of 2.259 (8) Å.

The packing forces in the unit cell between the ions and the water molecules are mainly hydrogen bonds of two types: OW-H- - -OW and OW-H- - -Cl. Bonds of the first type exist among the water molecules of hydration and also between these and the molecules of the metal cluster cation. The range of bond lengths is 2.60-2.90 Å. Bonds of the second type are formed between all four chlorine atoms of the $ZnCl_4^{2-}$ ions and some of the water molecules of hydration, the range of bonds being 3.15-3.35 Å.

Acknowledgment. We thank the National Science Foundation (U.S.) for support of this work.

Supplementary Material Available: Tables containing additional bond lengths, bond angles, and anisotropic thermal displacement parameters for **1** and **2** and a stereoview of the unit cell of **2** (9 pages); tables of observed and calculated structure factors (53 pages). Ordering information is given on any current masthead page.

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Further Studies of Low-Valent Alkoxide Complexes of Niobium. Synthesis and Structure of Dimeric Niobium(IV) Nonamethoxide

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The synthesis and properties of the niobium(IV) nonamethoxide anion, $Nb_2(OMe)_9^-$, are described. This anion is most easily prepared by reaction of $Nb_2Cl_4(OMe)_4(HOMe)_2$ (made in situ from either $NbCl_5$ or $NbCl_4(THF)_2$) with an excess of methoxide in methanol. This anion is stable only in solutions containing an excess of MeO^-; in neat methanol and in the solid state decomposition occurs to give a red compound tentatively identified as $[Nb(OMe)_4]_n$. Three salts of $Nb_2(OMe)_9^-$ were characterized by X-ray crystallography: $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), $[Mg(MeOH)_6][Nb_2(OMe)_9]I{\cdot}2CH_3OH$ (**1b**), and $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**). Crystallographic data: compound **1a**, space group *C*2 with a = 16.235 (4) Å, b = 14.453 (4) Å, c = 10.209 (3) Å, β = 94.02 (2)°, V = 2389 (1) Å^3, and Z = 2; compound **1b**, space group *Cmcm* with a = 12.397 (1) Å, b = 13.068 (6) Å, c = 24.347 (3) Å, V = 3944 (3) Å^3, and Z = 4; compound **1c**, space group *C*2/*c* with a = 17.510 (4) Å, b = 14.126 (4) Å, c = 13.932 (3) Å, β = 108.75 (2)°, V = 3263 (5) Å^3, and Z = 4. In each case the solvated cation shows disorder about a virtual 3-fold axis and an extensive network of hydrogen bonding is present. The Nb-Nb distance, 2.64 Å, is unusually short; the reason for this is discussed.

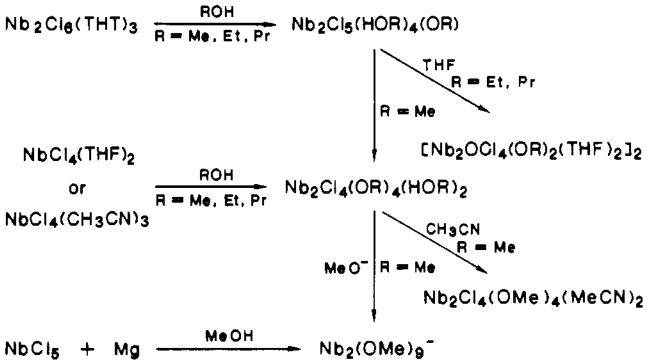
Introduction

Known complexes of niobium containing alcohol or alkoxide ligands have to date been mainly limited to those in which the metal atom is in the +5 oxidation state.[1] We have recently reported the synthesis and characterization of a number of Nb(III) and Nb(IV) alkoxide complexes, including $Nb_2Cl_5(OR)(HOR)_4$ (R = Me, Et, ^{i}Pr),[2] $[Nb_2OCl_4(OR)_2(THF)_2]_2$ (R = Et, ^{i}Pr),[2] $Nb_2Cl_4(OMe)_4(MeCN)_2$,[3] and $Nb_2Cl_4(OR)_4(HOR)_2$ (R = Me, Et, ^{i}Pr)[3] (see Scheme I). These products were obtained by using alcohols as the reactants. The reaction of $Nb_2Cl_4(OMe)_4(HOMe)_2$ with excess methoxide resulted in complete substitution of all ligating chlorides, producing an intense blue homoleptic Nb(IV) methoxide anion of the formula $Nb_2(OMe)_9^-$. We now wish to report the synthesis and properties of this compound as well as the crystal structures of this anion with a number of different counterions.

Experimental Section

All manipulations were carried out under an atmosphere of argon using standard vacuum line techniques. $NbCl_5$ was purchased from Johnson-Matthey, and $NbCl_4(THF)_2$ was prepared according to the literature method.[4] Solvents were distilled under nitrogen from appropriate drying agents prior to use. UV-visible spectra were recorded on a Cary 17d spectrometer.

Scheme I



Preparation of $Nb_2(OMe)_9^-$. (A) From $NbCl_5$. Magnesium turnings (0.88 g) and $NbCl_5$ (1.45 g, 5.36 mmol) were placed in a 100-mL round-bottomed flask and cooled with a dry-ice/acetone bath. Methanol (30 mL) was added with stirring over a period of 1 min. After 5 min the cold bath was removed and the flask allowed to warm to room temperature while the contents were rapidly stirred. Within 1 h the solution changed color to red-purple, followed by red-brown, green, and finally blue-purple. The initial red/purple complex has been identified by UV-vis spectroscopy as $Nb_2Cl_4(OMe)_4(HOMe)_2$.[2b] Should the reaction at any time become too vigorous, the solution may be cooled to −78 °C and then allowed to warm back up. After 1 h the solution was filtered from a white solid and the remaining Mg turnings. The filtrate was then placed at −20 °C overnight and, the following day, filtered from the clear crystals that had formed. When this reaction mixture was carefully layered with diethyl ether, large crystals of $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), contaminated with a white crystalline material, were

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(2) (a) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 3509. (b) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 3319.

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0020-1669/88/1327-3596$01.50/0

Table I. Crystal Data for $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), $Mg(MeOH)_6[Nb_2(OMe)_9]I\cdot nMeOH$ (**1b**), and $[Na(MeOH)_6][Nb_2(OMe)_9]$ **1c**)

formula	$Nb_2Cl_3Mg_2O_{21}C_{21}H_{75}$	$INb_2MgO_{15}C_{15}H_{51}\cdot 2CH_3OH$	$Nb_2NaO_{15}C_{15}H_{51}$
fw	1003.78	872.68	680.37
space group	*C*2	*Cmcm*	*C*2/*c*
systematic absences	$hkl\ h + k \neq 2n + 1$	$hkl,\ h + k \neq 2n$ $h0l,\ l \neq 2n$	$hkl,\ h + k \neq 2n$ $h0l,\ l \neq 2n$
a, Å	16.235 (4)	12.397 (1)	17.510 (4)
b, Å	14.453 (4)	13.068 (6)	14.126 (4)
c, Å	10.209 (3)	24.347 (3)	13.932 (3)
α, deg	90.0	90.0	90.0
β, deg	94.02 (2)	90.0	108.75 (2)
γ, deg	90.0	90.0	90.0
V, Å^3	2389 (1)	3944 (3)	3263 (5)
Z	2	4	4
d_{calc}, g/cm^3	1.396	1.469	1.385
cryst size, mm	0.3 × 0.4 × 0.5	0.55 × 0.15 × 0.15	0.2 × 0.2 × 0.4
μ(Mo Kα), cm^{-1}	7.130	13.980	7.349
data collecn instrument	Syntex P3 upgrade	CAD-4	Rigaku AFC5
radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)	Mo Kα (λ_α = 0.71073 Å)
orientation rflns: no.; range (2θ), deg	23; 18.0–30.0	25; 20.2–32.4	
temp, °C	22	22	22
scan method	ω–2θ	ω–2θ	ω–2θ
data collecn range, 2θ, deg	4–45	4–45	4–45
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1705, 1590	1863, 1389	2144, 1264
no. of params refined	216	122	180
R^a	0.037	0.045	0.061
$R_w{}^b$	0.050	0.057	0.087
quality-of-fit indicator^c	1.240	1.655	1.735
largest shift/esd, final cycle	0.25	0.20	0.02
largest peak, e/Å^3	0.45	1.124^d	0.612

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$. [d] Located around the I atoms.

obtained. Attempts to isolate **1a** in pure form were thwarted by the similarity in solubility properties of **1a** and the white crystals and by the general instability of **1a** (vide infra). Alternatively, after it was cooled overnight and filtered from the clear crystals, the solution was added to a solution of 2.4 g of NH_4I in 8 mL of methanol and the mixture allowed to stand undisturbed at room temperature. After 24 h (longer times resulted in contamination by colorless crystals) blue-purple crystals were collected on a filter stick, washed with 2 × 5 mL of cold methanol followed by 2 × 5 mL of diethyl ether, and dried under a stream of argon; yield 0.64 g (30%) of pure $[Mg(MeOH)_6][Nb_2(OMe)_9]I\cdot 2CH_3OH$ (**1b**).

(B) From $NbCl_4(THF)_2$. $NbCl_4(THF)_2$ (0.76 g, 2.0 mmol) was dissolved in 25 mL of methanol. Stirring for 6 h led to a total conversion of the starting material to $Nb_2Cl_4(OMe)_4(HOMe)_2$. A methanol solution of sodium methoxide, prepared by the reaction of 0.28 g of Na with 25 mL of methanol, was added with stirring to the purple solution of $Nb_2Cl_4(OMe)_4(HOMe)_2$. The solution immediately became blue. Solvent was removed in vacuo, the blue solid redissolved in 4 mL of methanol, and the solution filtered and placed at −20 °C. Within hours blue crystals had formed. These crystals were collected on a filter stick and washed with 3 mL of cold (−78 °C) methanol followed by 2 × 5 mL of diethyl ether; yield 0.11 g (16%) of pure $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**).

X-ray Analysis. Single-crystal X-ray analyses have been carried out following procedures routine to this laboratory, fully described elsewhere.[5,6] Relevant data pertaining to the structure determinations are summarized in Table I. Lorentz and polarization corrections were applied to all intensity data. For **1a** empirical absorption corrections based on azimuthal (ψ) scans of several reflections with Eulerian angle χ near 90° were applied to the data. For **1b** absorption corrections based on the method of Stuart and Walker[7] were applied.

In each case the niobium atom position was derived from a three-dimensional Patterson map. All non-hydrogen atoms were then located through a series of least-squares refinements and difference Fourier syntheses. Anisotropic displacement parameters were assigned to all nondisordered atoms, and the structures were refined to convergence by full-matrix least-squares techniques. Hydrogen atoms could not be located in the final difference maps and were omitted from the models refined.

Compound **1a** was solved in the noncentrosymmetric space group *C*2 with the *y* coordinate of the niobium atom fixed at zero. Attempts to refine this structure in either space group *Cm* or *C*2/*m* led to unreasonably high displacement parameters, a much poorer fit of the data, and in the case of *Cm*, disorder of the methoxide ligands. The $Nb_2(OMe)_9^-$ unit was located on a crystallographic 2-fold axis that passed perpendicular to the Nb–Nb vector and incorporated one of the bridging methoxide ligands. Chloride anions were also present in the crystals, one on a general position and the other on a 2-fold axis. The cation, $Mg(MeOH)_6^{2+}$, was located on a general position. The oxygen atoms of the alcohol molecules were disordered over two positions while the remaining non-hydrogen atoms displayed no disorder. A more complete description of this disorder will be reserved for the discussion. For all 12 oxygen atoms a common isotropic displacement parameter was assigned and the occupancy factors for the two positions were refined. The major orientation was found to have an occupancy of 0.67, while that of the minor was 0.33. With these occupancy factors fixed, the isotropic displacement parameters of the disordered atoms were allowed to vary freely and the structure was refined to convergence.

The systematic absences for **1b** indicated three possible space groups: *Cmcm* (No. 63), *Cmc*2$_1$ (No. 36), and *C*2*cm* (No. 40). The solution obtained for the centrosymmetric space group *Cmcm* showed all molecules in the lattice to be located on special crystallographic positions: $Nb_2(OMe)_9^-$ on *m*2*m*, $Mg(MeOH)_6^{2+}$ on 2/*m*, and $I\cdot nCH_3OH^-$ on *m*2*m*. The diniobium anion was very well defined. The coordination sphere of the magnesium complex was disordered in the same manner as in **1a**. In this case the disorder was crystallographically imposed and both orientations of the oxygen atoms were equally occupied. Refinement of the iodine atom presented problems since considerable residual electron density remained when the anion was placed on the *m*2*m* position with site occupancy equal to 0.25. Several possibilities were explored, and the adopted model involved a major I atom position with occupancy 0.217 slightly off the *m*2*m* symmetry element (by ca. 0.2 Å) and a second minor I atom position ca. 2.5 Å from the *m*2*m* element with an occupancy of 0.033. The first one is within hydrogen-bonding contact (3.2–3.6 Å) to two interstitial MeOH molecules. There is also room for one MeOH molecule hydrogen bonded to the I$^-$ with minor occupancy (I···HOMe located around the *m*2*m* position). The electron density associated with this MeOH molecule is so small (less than 0.05 occupancy for O and C) that it could not be distinguished from among the residual peaks in the difference Fourier map. This model gives a frac-

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(6) Calculations were made on the VAX-11/780 computer at the Department of Chemistry, Texas A&M University, College Station, TX, and on the Micro VAX computer at the Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX. VAX-SDP software was used.

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Table II. Positional and Isotropic-Equivalent Displacement Parameters for $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	occ[b]
Nb	0.07209 (3)	0.000	0.06805 (5)	1.830 (9)	0.5
O(1)	0.0916 (3)	−0.0541 (4)	0.2440 (5)	3.1 (1)	1.0
O(2)	0.1334 (3)	0.1129 (4)	0.1234 (5)	3.0 (1)	1.0
O(3)	0.1735 (3)	−0.0568 (4)	0.0095 (5)	2.9 (1)	1.0
O(4)	0.000	−0.1094 (5)	0.000	2.4 (1)	0.5
O(5)	0.0393 (3)	0.0551 (4)	−0.1158 (5)	2.4 (1)	1.0
C(1)	0.0380 (6)	−0.1071 (9)	0.3217 (9)	5.2 (2)	1.0
C(2)	0.1127 (7)	0.2072 (7)	0.112 (1)	5.5 (3)	1.0
C(3)	0.1902 (6)	−0.1028 (9)	−0.1108 (9)	5.7 (2)	1.0
C(4)	0.000	−0.1207 (8)	0.000	4.9 (3)	0.5
C(5)	0.0748 (6)	0.1055 (7)	−0.2188 (9)	4.9 (2)	1.0
Mg(1)	0.3320 (1)	0.0014 (3)	0.3268 (2)	2.23 (4)	1.0
*O(11)	0.2814 (5)	−0.1065 (6)	0.2082 (7)	2.7 (1)	0.67
*O(12)	0.2953 (5)	0.0872 (5)	0.1667 (7)	2.4 (1)	0.67
*O(13)	0.2146 (4)	0.0210 (5)	0.3892 (7)	2.6 (1)	0.67
*O(14)	0.3778 (5)	0.1131 (6)	0.4346 (8)	3.0 (1)	0.67
*O(15)	0.3629 (5)	−0.0876 (5)	0.4780 (7)	2.8 (1)	0.67
*O(16)	0.4482 (5)	−0.0165 (5)	0.2564 (7)	3.2 (1)	0.67
*O(11)′	0.249 (1)	−0.107 (1)	0.307 (2)	4.4 (4)	0.33
*O(12)′	0.309 (1)	0.025 (1)	0.135 (2)	3.7 (4)	0.33
*O(13)′	0.228 (1)	0.078 (1)	0.358 (2)	4.2 (4)	0.33
*O(14)′	0.411 (1)	0.112 (2)	0.356 (2)	5.0 (4)	0.33
*O(15)′	0.348 (1)	−0.024 (1)	0.532 (2)	4.5 (4)	0.33
*O(16)′	0.434 (1)	−0.081 (2)	0.305 (2)	5.1 (5)	0.33
C(11)	0.2608 (7)	−0.1992 (6)	0.252 (1)	5.7 (3)	1.0
C(12)	0.3355 (7)	0.0985 (9)	0.0466 (9)	5.5 (2)	1.0
C(13)	0.1846 (7)	0.0967 (8)	0.463 (1)	6.5 (2)	1.0
C(14)	0.3882 (8)	0.2049 (7)	0.394 (1)	5.5 (3)	1.0
C(15)	0.3183 (6)	−0.1056 (9)	0.5928 (9)	5.6 (2)	1.0
C(16)	0.4749 (7)	−0.0914 (8)	0.180 (1)	6.1 (2)	1.0
Cl(1)	0.500	−0.2293 (2)	0.500	4.66 (8)	0.5
Cl(2)	0.5880 (2)	0.1179 (2)	0.2731 (2)	4.65 (5)	1.0

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^{4/3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$. [b] Occupancy.

tional content of more than 1.9 molecules of the solvent, MeOH, per formula unit, and for practical purposes this was assumed to be equal to 2 exactly. As both iodine atom positions were about 3.8 Å from the carbon atoms in the bridging methoxide ligands, this particular packing in the crystal lattice appears to be affected by the attraction between CH_3 groups and I. Refinement in the two noncentrosymmetric space groups was attempted, but it did not alleviate the disorder problems; thus, the initial *Cmcm* symmetry was retained.

For compound **1c** systematic absences indicated either space group *C*2/*c* or *Cc*. Development of the structure was initiated in space group *C*2/*c*, and the correctness of this choice was subsequently confirmed by successful refinement. In this space group the $Nb_2(OMe)_9^-$ anion had crystallographic 2-fold symmetry. As in **1a** and **1b**, the oxygen atoms in the octahedral cation were disordered over two positions and in this case the major and minor occupancies were 0.73 and 0.27. Systematically higher values of calculated versus measured structure factors for the most intense low-angle reflections suggested possible complications arising from secondary extinction. An extinction parameter, which was included in the final stages of refinement, significantly reduced the residual electron density without significantly altering the positional or displacement parameters of the atoms.

Positional and isotropic-equivalent displacement parameters for **1a**–**c** are given in Tables II–IV, respectively. Tables of observed and calculated structure factors and anisotropic displacement parameters and complete listings of bond angles and distances are available as supplementary material.

Table III. Positional and Isotropic-Equivalent Displacement Parameters for $[Mg(MeOH)_6][Nb_2(OMe)_9]I{\cdot}2CH_3OH$ (**1b**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	occ[b]
Nb	0.000	−0.00835 (4)	−0.19596 (2)	2.62 (1)	0.5
O(1)	0.000	−0.1309 (4)	−0.250	3.3 (1)	0.25
O(2)	−0.1119 (4)	0.0535 (3)	−0.250	3.27 (9)	0.5
O(3)	−0.1149 (3)	−0.0701 (3)	−0.1502 (1)	3.63 (7)	1.0
O(4)	0.000	0.1163 (3)	−0.1504 (2)	3.8 (1)	0.5
C(1)	0.000	−0.2420 (8)	−0.250	5.1 (3)	0.25
C(2)	−0.2111 (7)	0.1093 (7)	−0.250	5.5 (2)	0.5
C(3)	−0.2101 (5)	−0.1234 (5)	−0.1642 (2)	6.0 (1)	1.0
C(4)	0.000	0.2228 (6)	−0.1656 (3)	5.1 (2)	0.5
Mg	0.000	0.000	0.000	3.43 (6)	0.25
O(5)	−0.0827 (6)	0.0977 (6)	−0.0518 (3)	4.8 (2)	0.5
O(6)	−0.0532 (6)	−0.1187 (5)	−0.0496 (2)	4.7 (2)	0.5
O(7)	−0.1336 (6)	0.0152 (6)	−0.0517 (3)	4.5 (2)	0.5
C(5)	−0.2004 (6)	0.1100 (7)	−0.0524 (3)	8.5 (2)	1.0
C(6)	0.000	−0.2232 (7)	−0.0524 (4)	8.2 (3)	0.5
I(1)	0.000	0.46996 (8)	−0.2430 (1)	7.56 (3)	0.217
I(2)	0.000	0.523 (1)	−0.162 (1)	13.3 (6)	0.033
*O(8)	0.042 (2)	0.551 (1)	−0.1204 (8)	16.6 (7)	0.434
*C(8)	0.000	0.485 (2)	−0.079 (1)	15.4 (7)	0.434

[a] See footnote *a* in Table II. [b] Occupancy.

Table IV. Positional and Isotropic-Equivalent Displacement Parameters for $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**)[a]

atom	*x*	*y*	*z*	*B*, Å^2	occ[b]
Nb	0.05266 (4)	0.25238 (9)	0.19963 (6)	2.52 (2)	1.0
O(1)	0.000	0.3652 (7)	0.250	3.1 (2)	0.5
O(2)	0.0617 (4)	0.1961 (6)	0.3398 (5)	3.3 (2)	1.0
O(3)	0.1599 (4)	0.3121 (6)	0.2505 (5)	3.7 (2)	1.0
O(4)	0.0301 (4)	0.3087 (6)	0.0644 (5)	4.0 (2)	1.0
O(5)	0.0972 (4)	0.1396 (5)	0.1596 (6)	3.8 (2)	1.0
C(1)	0.000	0.463 (1)	0.250 (1)	6.8 (6)	0.5
C(2)	0.1176 (8)	0.140 (1)	0.420 (1)	7.3 (4)	1.0
C(3)	0.2020 (9)	0.354 (1)	0.344 (1)	6.9 (4)	1.0
C(4)	−0.0416 (9)	0.353 (1)	−0.001 (1)	7.2 (4)	1.0
C(5)	0.082 (1)	0.039 (1)	0.170 (1)	8.6 (4)	1.0
Na	0.250	0.250	0.000	3.7 (1)	0.5
*O(1a)	0.2303 (7)	0.3714 (8)	0.1090 (9)	4.9 (3)	0.73
*O(2a)	0.3921 (6)	0.2659 (8)	0.0615 (8)	5.1 (3)	0.73
*O(3a)	0.2469 (7)	0.1462 (9)	0.1345 (8)	5.8 (3)	0.73
*O(4a)	0.339 (1)	0.119 (2)	−0.011 (2)	3.2 (6)	0.27
*O(5a)	0.281 (2)	0.244 (2)	0.180 (2)	4.6 (8)	0.27
*O(6a)	0.365 (2)	0.351 (2)	0.019 (2)	3.8 (7)	0.27
C(1a)	0.191 (1)	0.454 (1)	0.063 (1)	7.0 (5)	1.0
C(2a)	0.431 (1)	0.434 (1)	0.104 (1)	8.0 (5)	1.0
C(3a)	0.3087 (9)	0.154 (1)	0.231 (1)	8.0 (5)	1.0

[a] See footnote *a* in Table II. [b] Occupancy.

Results and Discussion

Synthesis. The reaction of $NbCl_4{\cdot}3CH_3CN$ with 4.5 equiv of KOMe in a solvent mixture of methanol and acetonitrile was reported several years ago.[8] The blue product obtained was identified as $K[Nb_2(OMe)_9]$, on the basis of the Nb content. Our experience with this system was somewhat different. While we would occasionally observe a blue intermediate, we found it to be extremely unstable and in all cases the reaction terminated with the formation of a red solution. The red oil that was isolated from these solutions was tentatively identified as $[Nb(OMe)_4]_n$, which was made previously and characterized by EPR spectroscopy.[9] Our assignment is based on an absorption maximum at 383 nm, which is close to that reported for $[Nb(OEt)_4]_n$ (380 nm), also a red oil.[10] We subsequently found that stable solutions of $Nb_2(OMe)_9^-$ were formed in methanol when a large excess of MeO^- was present.

Two methods of synthesizing $Nb_2(OMe)_9^-$ were developed. The first involved the reaction of sodium methoxide with $Nb_2Cl_4(OMe)_4(HOMe)_2$, formed in situ by reacting $NbCl_4(THF)_2$ with neat methanol. Crystals of $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**) could be isolated by cooling this solution to −20 °C, but in rather low yields. An alternative route involved the low-temperature reduction of $NbCl_5$ in methanol with a large excess of magnesium. The reaction was quite vigorous and, as evidenced by numerous color changes, proceeded through a number of intermediates, including $Nb_2Cl_4(OMe)_4(HOMe)_2$. The final result was the formation of a dark blue solution of $Nb_2(OMe)_9^-$. This solution, when layered with diethyl ether, yielded crystals of $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**), contaminated with a large number of clear crystals. Alternatively, addition of ammonium

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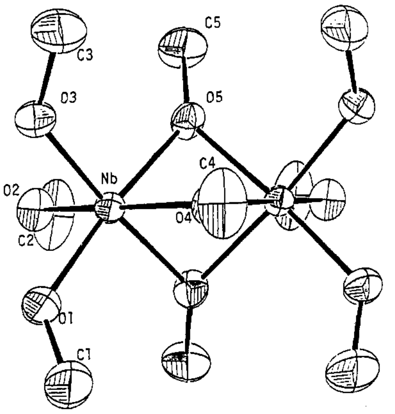

Figure 1. ORTEP view of the diniobium anion in $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**). A crystallographic 2-fold axis relates the halves of the molecule.

Table V. Average Bond Distances and Angles in the $Nb_2(OMe)_9^-$ Anion[a]

param	av[b]	range
Nb–Nb, Å	2.640 [6]	2.632–2.652
$Nb–O_b$, Å	2.069 [2]	2.019–2.076
$Nb–O_t$, Å	1.966 [5]	1.943–1.980
$O_b–C_b$, Å	1.44 [1]	1.38–1.46
$O_t–C_t$, Å	1.43 [1]	1.40–1.46
$Nb–O_b–Nb$, deg	79.3 [1]	78.7–80.0
$Nb–O_b–C_b$, deg	140.3 [1]	139.6–140.6
$Nb–O_t–C_t$, deg	131.4 [2]	130.7–132.1

[a] Averaged over the three crystal structures. [b] Values in brackets represent the variance, defined as $[\sum \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmatic mean and *n* is the number of values averaged.

iodide to the postreaction mixture gave a relatively high yield of pure $[Mg(MeOH)_6][Nb_2(OMe)_9]I \cdot 2CH_3OH$ (**1b**). In all cases the crystalline product was indefinitely stable in the mother liquor. However, redissolution of the isolated solids in neat methanol or in any other solvent, or storage under an inert atmosphere, led to the formation of a red material. Decomposition of the solid could be accelerated by grinding. Because of this instability, characterization of $Nb_2(OMe)_9^-$ was limited to solution UV–vis spectroscopy and X-ray crystal structure analysis.

Crystallographic Structures. Crystallographic analysis of three salts of $Nb_2(OMe)_9^-$ has been carried out. The anion is shown in Figure 1. It is a confacial bioctahedron and, as is usually the case for such homoleptic species, has virtual D_{3h} symmetry. The dimensions of the anion do not vary significantly from structure to structure, and averaged values for important bond distances and angles are summarized in Table V. Two structural features of this complex are quite peculiar. First, the single Nb–Nb bond arising from a d^1–d^1 configuration is unusually short. Typical single Nb–Nb bond lengths lie around 2.8 Å[11] while the value observed here, viz. 2.64 Å, falls in the range between double[12] and triple[13] M–M bonds (M = Nb, Ta). This is clearly associated with a short Nb–(μ-O) distance. We will discuss this matter in a separate section because of its relevance to the geometry and M–M bonding in M_2X_9 complexes in general.

The dimensions and bonding within the terminal Nb–OMe moieties constitute the second peculiar feature. In the several Nb-alkoxy complexes[2,3,14] that have been characterized structurally, the $Nb–O_t$ distances have been short (ca. 1.8 Å) and the $Nb–O_t–C_t$ angles quite open (ca. 150–180°). π donation from oxygen atoms to the metal center (leading to Nb–O bond orders greater than 1) has generally been considered responsible for this. In the present case the $Nb–O_t$ distances are much longer (ca. 1.9 Å) and the $Nb–O_t–C_t$ angles are around 130°, indicating less, or even negligible, π donation to the metal atom. We believe that these unexpected structural parameters may be attributed to hydrogen bonding of the terminal alkoxide ligands to the methanol molecules that solvate the cations (Mg^{2+} or Na^+). This hydrogen bonding is present in all three crystal structures and extensively links the contents of the crystal lattice. In **1b** and **1c** all six methanol ligands in each $M(MeOH)_6^{n+}$ cation are hydrogen-bonded to $Nb_2(OMe)_9^-$ anions, three each to two different $Nb_2(OMe)_9^-$ groups, forming infinite chains of $([M(MeOH)_6][Nb_2(OMe)_9])_n^{x+}$. An example of this is shown in Figure 2 for **1c**. In **1a**, three of the methanol ligands on each $Mg(MeOH)_6^{2+}$ cation are hydrogen-bonded to one $Nb_2(OMe)_9^-$ anion while the other three form hydrogen bonds to chlorine atoms present in the lattice. Each chlorine atom is hydrogen-bonded to two methanol molecules. We could not locate any hydrogen atoms in the crystal structures, which is not uncommon.[15] However, the O···O distances and the bond angles about the oxygen

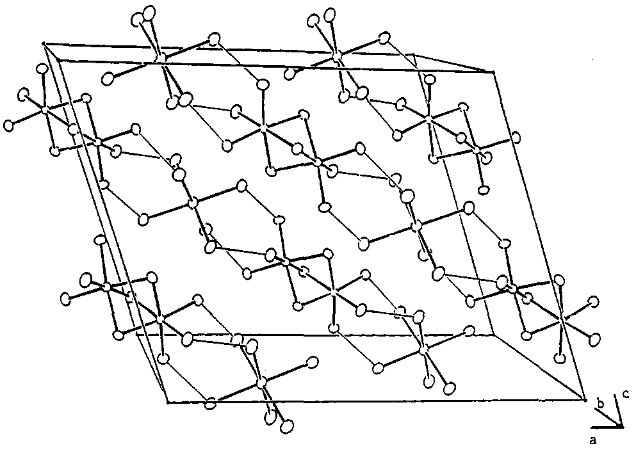

Figure 2. Unit cell packing diagram for $[Na(MeOH)_6][Nb_2(OMe)_9]$ (**1c**) detailing the formation of infinite chains. Carbon atoms have been omitted for clarity, and only the major position for the oxygen atoms in the disordered methanol ligands is shown. Light lines indicate O···O hydrogen bonds.

Table VI. Summary of Hydrogen Bond Angles and Distances in **1a–c**[a,b]

param	value[c]	range
$O_{Nb} \cdots O_M$, Å	2.72 [2]	2.62–2.82
$Cl \cdots O_M$,[d] Å	3.02 [1]	2.98–3.07
$Nb–O_{Nb} \cdots O_M$, deg	115.4 [8]	109.4–119.8
$Nb–O_{Nb}–C_{Nb}$, deg	131.5 [2]	130.6–132.0
$C_{Nb}–O_{Nb} \cdots O_M$, deg	108.7 [8]	103.8–114.0
$M–O_M \cdots O_{Nb}$, deg	114.7 [6]	109.3–118.3
$M–O_M–C_M$, deg	124.5 [13]	117.3–132.8
$C_M–O_M \cdots O_{Nb}$, deg	109.4 [5]	106.5–113.6
$Cl \cdots O_M–M$,[d] deg	94 [1]	91.3–97.4
$Cl \cdots O_M–C_M$,[d] deg	108 [2]	105.6–112.9

[a] O_{Nb} and C_{Nb} refer to atoms in the methoxide ligands bound terminally to niobium atoms. O_M and C_M refer to atoms in the alcohol ligands bound to the cation (Mg^{2+} or Na^+). [b] In all cases a disorder in O_M positions existed. Values for all disorder positions are included. [c] Values in brackets represent the variance, defined as $[\sum \Delta_i^2/n(n-1)]^{1/2}$, where Δ_i is the deviation of the *i*th value from the arithmatic mean and *n* is the number of values averaged. [d] Present only in compound **1a**.

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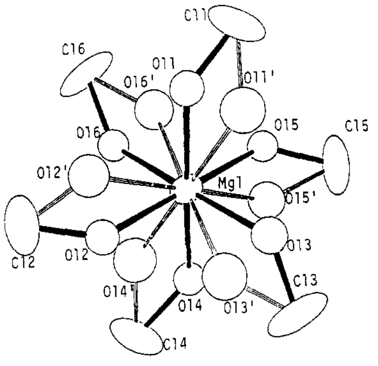

Figure 3. ORTEP view of the disordered $[Mg(MeOH)_6]^{2+}$ cation in $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]Cl_3$ (**1a**). Solid lines connect the atoms involved in the major (67%) disorder position while open lines connect the atoms involved in the minor (33%) disorder position.

atoms involved (detailed in Table VI) provide satisfactory evidence for the existence of this hydrogen bonding.

In all three cases studied crystallographically the counterions were solvated by six methanol molecules. In each case a disorder existed in the oxygen atom locations, such that two $M(MeOH)_6^{n+}$ positions were related by a 60° rotation of the oxygen atoms only about a virtual 3-fold axis of the pseudooctahedron. Although the carbon atom positions for the two orientations of the MO_6 unit were nearly identical, they did not exactly overlap. Thus, while no residual electron density peaks were located near the carbon atoms, these atoms did display high anisotropy of displacement parameters, consistent with a disorder over two or more slightly different positions. An example of this disorder is shown in Figure 3. Since the locations of the carbon atoms were nearly the same in each orientation, the overall steric requirements were essentially identical for the two positions. For **1a** and **1c** major and minor positions existed while for **1b** the two positions were equally occupied and related by crystallographic symmetry elements. It is noteworthy that hydrogen bonding persists despite this disorder, and each disorder position has a different hydrogen-bonding network associated with it. This is shown in Figure 4 for **1a**.

Finally, we note that the persistence of hydrogen bond formation in the solid state involving the terminal alkoxide ligands raises the possibility that in solution $Nb_2(OMe)_9^-$ may exist in equilibrium with a number of partially protonated species of formula $Nb_2(MeOH)_x(OMe)_{9-x}{}^{x-1}$. While we have no direct experimental evidence as to which of these species are present in solution, we believe that only those species for which x is small, if not zero, are stable. We base this on our observation that $[Nb(OMe)_4]_n$ forms spontaneously in solutions that do not contain high concentrations of MeO^-, that is, solutions where protonated metal species would be more likely.

M–M Bonding vs Geometry of Confacial Bioctahedra. In general the formation of a M–M bond causes contraction of a confacial bioctahedron along the M–M axis, while the absence of bonding allows repulsive interactions to cause elongation of the dimer.[16] In most known cases, the $M-X_b-M$ angle, which is 70.53° in an ideal bioctahedron, can provide an unequivocal criterion for establishing which situation prevails in a particular instance.

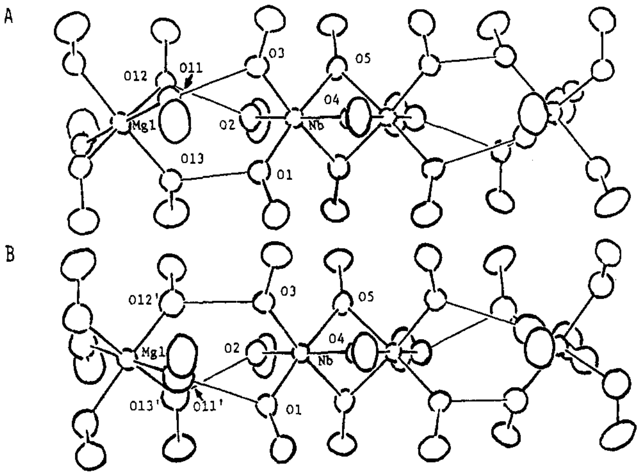

Figure 4. Hydrogen-bonding network for the $[Mg(MeOH)_6]_2[Nb_2(OMe)_9]^{3+}$ units in **1a**, showing the (A) major and (B) minor positions for the oxygen atoms in the disordered $[Mg(MeOH)_6]^{2+}$ cation. Light lines indicate O···O hydrogen bonds.

The Nb–Nb distance in $Nb_2(OMe)_9^-$ is by far the shortest for a single bond of this metal, and in fact it approaches the region of the shortest known Nb–Nb bonds of any order. On the other hand, the Nb–O–Nb angle of 79.3 [2]° in itself implies elongation of the complex as if the central atoms were repelling one another. However, this apparent inconsistency can be readily explained: in spite of contraction along the Nb–Nb axis the $Nb-O_b-Nb$ angle must remain greater than the "ideal" value because of the short fixed $Nb-O_b$ distance. What we observe here is apparently the closest approach of two Nb(+4) centers possible since such interaction appears to be the only hindrance to further contraction. An alternative, namely, that the closer approach of Nb atoms is prevented by repulsion among O atoms, is less probable since the O···O contacts are shortest between the bridging atoms (ca. 2.75 Å) while the O_t-O_b pairs are over 2.8 Å away.

Thus, the $Nb_2(OMe)_9^-$ ion provides an example of the unconventional situation in which there is an elongated (M–X–M angle greater than ideal) confacial-bioctahedral dimer with a strong M–M interaction. In the opposite unconventional case we would have a contracted dimer (M–X–M less than 70.53°) with M–M repulsion. This could happen with large bridging ligands: with a fixed M–X distance the outward movement of the central atoms would be prevented by repulsion or direct contact of the bridging atoms. Thus, the "conventional" criterion of Cotton and Ucko[16a] is applicable only in those cases where the ligands are of medium size but fails in the extreme cases of very small or very large ligands.

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Supplementary Material Available: For the crystal structures of **1a–c**, complete listings of bond distances and angles and tables of anisotropic displacement parameters (10 pages); for all three structures, tables of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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