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New Niobium Complexes with Alkynes. 6. Two Compounds Containing Nb_2[PhCC(Ph)C(Ph)CPh] Units Joined in Unorthodox Ways[†]

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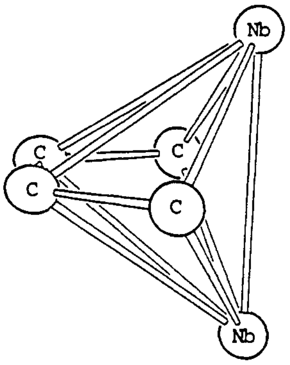
Two new compounds are described that contain the recently discovered Nb_2[PhCC(Ph)C(Ph)CPh] moiety. In each of these the manner in which two of these are joined to form a tetranuclear species is unsymmetrical and thus unorthodox in comparison to the very symmetrical linking across one μ_4-O and four μ_2-Cl bridges previously observed. Compound 1, $[Nb_4O_2Cl_4\{(PhC)_4\}_2(THF)_4]\cdot 2THF$, contains centrosymmetric tetranuclear molecules in which the equivalent halves, $Nb_2\{(PhC)_4\}Cl_2(THF)_2O$, are joined solely by having the μ-O atom of each half form a strong donor bond to one of the Nb atoms of the other half. This compound crystallizes in space group $P2_1/c$ with $Z = 2$ and has been refined to $R = 0.049$ and $R_w = 0.066$. The unit cell dimensions are $a = 13.409$ (2) Å, $b = 27.421$ (5) Å, $c = 10.805$ (3) Å, and $\beta = 106.76$ (2)°. Compound 2, $[Mg_2Cl_3(THF)_6][Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]\cdot THF$, crystallizes in space group $P\bar{1}$ with $Z = 2$ and no rigorous molecular symmetry. The unit cell dimensions are $a = 12.614$ (2) Å, $b = 16.706$ (3) Å, $c = 27.153$ (5) Å, $\alpha = 107.45$ (1)°, $\beta = 99.11$ (1)°, and $\gamma = 90.61$ (2)°. The two $Nb_2(PhC)_4$ moieties are arranged to form a rectangle with a μ_4-O atom at the center and two μ-Cl atoms bridging one long edge, essentially as in the previously described symmetrical $[Nb_4O\{(PhC)_4\}_2Cl_8]^{2-}$ anions. The other long edge is spanned by an oxygen atom and has an $Mg(THF)_3$ unit attached to this oxygen atom and to one terminal pair of the neighboring Cl atoms, to give a distorted octahedron about Mg.

Introduction

We have recently reported a variety of reactions of lower valent niobium with tolan (PhC≡CPh). In some cases[1] the tolan molecule remained discrete but served as a ligand to one or two niobium atoms. However, the strength of these interactions caused appreciable changes in the shape and dimensions of the tolan molecule. In another investigation[2] it was found that the tolan molecules were dimerized to cyclic ligands (which may somewhat loosely be called tetraphenylcyclobutadiene) and each of these cyclic ligands became strongly and symmetrically bound to one niobium atom. Yet a third type of reaction led to the formation of PhCC(Ph)C(Ph)CPh chains that are bent into a planar C shape and attached symmetrically and perpendicularly across an Nb–Nb unit, as shown schematically in I. The local symmetry of this moiety is C_{2v}. In the first compounds containing I that we isolated,[3] two such units were joined by four bridging chlorine atoms and a quadruply bridging, planar oxygen atom to form the anion $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$. It was implicit in our description of the electronic structure of this anion that the essential and characteristic features were those within each half, while the linking of the halves was relatively loose and subject to modification—or even, mutatis mutandis, to abolition. In confirmation of this view, we isolated and characterized a compound[4] that contained in cationic form the dinuclear moiety $[Nb_2\{(PhC)_4\}Cl_3(THF)_4]^+$ in association with the tetranuclear anion.



I

In keeping with the view that the essential unit, in which the unique character and stability of the tetranuclear anion are to be found, is the $Nb_2\{(PhC)_4\}L_n$ moiety, one might also propose that compounds might be found in which these units would be associated in ways other than the highly symmetrical one originally seen in the $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anion. In this paper we report exactly such results, namely, two compounds in which there are two of the dinuclear moieties linked in ways different from and less symmetrical than that previously described.

Experimental Section

All synthetic work was carried out under an atmosphere of argon by using standard Schlenk and vacuum-line techniques or in a nitrogen-filled drybox. Solvents tetrahydrofuran (THF), benzene, and hexane were dried over molecular sieves for at least 4 weeks and deoxygenated by refluxing over Na–K–benzophenone ketyl for at least 8 h and distilling before use. Magnesium turnings were purchased from Fisher Scientific Co. Diphenylacetylene (PhCCPh) and dimethylphenylphosphine were from Strem Chemical, Inc. $NbCl_4(THF)_2$ was prepared according to the literature method.[5] Preparations of sodium amalgam (1 mmol/mL) and $NbCl_3(PhCCPh)(THF)_2$ were mentioned in a preceding paper.[1] IR spectra were recorded on a Perkin-Elmer 783 infrared spectrophotometer.

Preparation of $[Nb_4O_2Cl_4\{(PhC)_4\}_2(THF)_4]\cdot 2THF$ (1). $NbCl_3(PhCCPh)(THF)_2$ (0.52 g, 1 mmol), sodium amalgam (1 mL, 1 mmol), and PMe_2Ph (0.3 mL, 2.1 mmol) were stirred in 20 mL

[†] This paper is dedicated to Professor F. G. A. Stone on the occasion of his 65th birthday.

(1) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990,** *29,* 508.
(2) Cotton, F. A.; Shang, M. *Inorg. Chem.,* in press.
(3) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1990,** *112,* 1584.
(4) Cotton, F. A.; Shang, M. *Inorg. Chem.,* in press.
(5) Manzer, L. E. *Inorg. Chem.* **1977,** *16,* 525.

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Table I. Crystallographic Data for Compounds 1 and 2

	1	2
formula	$Nb_4Cl_4O_8C_{80}H_{88}$	$Nb_4Cl_{10}Mg_3O_{12}C_{96}H_{120}$
fw	1691.02	2265.11
space group	$P2_1/c$	$P\bar{1}$
syst absences	$h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$	none
a, Å	13.409 (2)	12.614 (2)
b, Å	27.421 (5)	16.706 (3)
c, Å	10.805 (3)	27.153 (5)
α, deg	90.0	107.45 (1)
β, deg	106.76 (2)	99.11 (1)
γ, deg	90.0	90.61 (2)
V, Å^3	3804 (3)	5380 (3)
Z	2	2
d_{calcd}, g/cm^3	1.476	1.398
cryst size, mm	0.30 × 0.20 × 0.20	0.45 × 0.23 × 0.15
μ(Mo Kα), cm^{-1}	7.551	7.164
data collcn instrument	Rigaku AFC5R	CAD4
radiation (monochromated in incident beam)	Mo Kα ($\lambda\alpha$ = 0.71073 Å)	
orientation rflns: no.; range (2θ), deg	25; 32–39	25; 16.5–35.0
temp, °C	20	−80
scan method	ω	ω
data collcn range, 2θ, deg	4–50	4–36
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6733, 4188	14873, 9445
no. of params refined	408	1094
transmissn factors: max, min	1.000, 0.9499	0.9985, 0.9172
R^a	0.049	0.068
$R_w{}^b$	0.066	0.097
quality-of-fit indicator^c	1.44	1.317
largest shift/esd, final cycle	0.26	0.21
largest peak e/Å^3	0.691	0.848

[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 $= [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{params})]^{1/2}$.

Table II. Positional and Equivalent Isotropic Displacement Parameters for $[Nb_4O_2Cl_4\{(PhC)_4\}_2(THF)_4]\bullet 2THF^a$

atom	x	y	z	B, Å^2
Nb(1)	0.34134 (5)	0.06618 (2)	0.06115 (5)	3.10 (1)
Nb(2)	0.42555 (5)	0.03361 (2)	−0.11143 (5)	3.08 (1)
Cl(1)	0.2044 (1)	0.11944 (7)	0.0915 (2)	4.57 (4)
Cl(2)	0.4255 (2)	0.03924 (8)	−0.3354 (2)	5.54 (5)
O(1)	0.4618 (3)	0.0183 (2)	0.0836 (4)	3.6 (1)
C(1)	0.2719 (5)	0.0223 (2)	−0.1048 (6)	3.4 (1)
C(2)	0.1938 (6)	−0.0180 (2)	−0.1314 (6)	4.0 (2)
C(3)	0.2244 (7)	−0.0646 (3)	−0.1563 (8)	5.5 (2)
C(4)	0.1527 (8)	−0.1039 (3)	−0.1696 (9)	7.3 (3)
C(5)	0.0542 (7)	−0.0962 (4)	−0.1575 (9)	7.1 (3)
C(6)	0.0247 (7)	−0.0500 (3)	−0.1324 (8)	6.0 (2)
C(7)	0.0926 (5)	−0.0110 (3)	−0.1194 (7)	4.8 (2)
C(8)	0.2542 (5)	0.0695 (2)	−0.1669 (6)	3.3 (1)
C(9)	0.1532 (5)	0.0776 (2)	−0.2730 (6)	3.7 (2)
C(10)	0.0753 (6)	0.1073 (3)	−0.2526 (7)	5.2 (2)
C(11)	−0.0174 (7)	0.1124 (4)	−0.3533 (9)	6.7 (2)
C(12)	−0.0305 (8)	0.0912 (4)	−0.4698 (8)	6.8 (3)
C(13)	0.0475 (9)	0.0610 (4)	−0.4880 (9)	8.0 (3)
C(14)	0.1389 (7)	0.0547 (4)	−0.3896 (8)	6.4 (2)
C(15)	0.3285 (5)	0.1084 (2)	−0.1371 (6)	3.4 (1)
C(16)	0.3005 (5)	0.1556 (3)	−0.2123 (6)	3.8 (2)
C(17)	0.2603 (8)	0.1941 (3)	−0.1629 (8)	6.5 (2)
C(18)	0.2411 (8)	0.2383 (3)	−0.2276 (9)	7.1 (3)
C(19)	0.2603 (7)	0.2436 (3)	−0.3433 (9)	6.8 (2)
C(20)	0.2992 (9)	0.2054 (4)	−0.394 (1)	10.5 (3)
C(21)	0.3210 (8)	0.1612 (3)	−0.3275 (9)	8.8 (2)
C(22)	0.4285 (5)	0.1067 (2)	−0.0411 (6)	3.2 (1)
C(23)	0.5039 (6)	0.1471 (3)	−0.0188 (8)	5.0 (2)
C(24)	0.5745 (7)	0.1503 (4)	−0.093 (1)	9.4 (3)
C(25)	0.6470 (8)	0.1896 (4)	−0.064 (2)	14.5 (5)
C(26)	0.647 (1)	0.2253 (4)	0.018 (2)	12.7 (5)
C(27)	0.574 (1)	0.2229 (4)	0.089 (1)	12.2 (4)
C(28)	0.4956 (9)	0.1847 (3)	0.0654 (9)	8.1 (3)
O(2)	0.2917 (4)	0.0141 (2)	0.1985 (4)	4.4 (1)
C(29)	0.2757 (7)	0.0257 (3)	0.3221 (7)	6.3 (2)
C(30)	0.2220 (8)	−0.0201 (4)	0.3561 (9)	8.4 (3)
C(31)	0.250 (1)	−0.0602 (4)	0.276 (1)	13.1 (3)
C(32)	0.2910 (7)	−0.0388 (3)	0.1819 (8)	6.2 (2)
O(3)	0.4386 (4)	0.0977 (2)	0.2601 (4)	4.7 (1)
C(33)	0.5503 (7)	0.0921 (4)	0.304 (1)	7.0 (3)
C(34)	0.5908 (8)	0.1335 (4)	0.3985 (9)	8.4 (3)
C(35)	0.5023 (8)	0.1477 (5)	0.444 (1)	10.3 (3)
C(36)	0.4061 (8)	0.1334 (4)	0.3472 (9)	7.6 (3)
O(4)	0.134 (1)	0.7796 (8)	0.190 (2)	26.6 (7)*
C(37)	0.058 (2)	0.8003 (9)	0.072 (2)	19.6 (8)*
C(38)	0.009 (3)	0.757 (1)	0.008 (3)	32 (1)*
C(39)	0.014 (2)	0.724 (1)	0.105 (2)	25 (1)*
C(40)	0.133 (2)	0.723 (1)	0.132 (2)	24 (1)*

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

of a solvent mixture (THF/benzene, 1:1) for about 24 h. The red solution changed rapidly to dark brown with the formation of a small quantity of brown-black precipitate during the reaction. After the solution was filtered into a Schlenk tube, it was layered first with 5 mL of THF and then with 25 mL of hexane. Brown-black long parallelepiped-shaped crystals started growing in 1 week, and then the tube was moved into a refrigerator at −10 °C for 2 weeks. Crystals were isolated by either filtration or decantation; yield ca. 0.15 g, 35%. IR (Nujol mull, KBr plates): 1665 (w), 1655 (w), 1594 (m), 1571 (w), 1559 (w), 1543 (w), 1535 (w), 1450 (s), 1345 (w), 1296 (w), 1245 (m), 1197 (w), 1136 (m), 1102 (w), 1071 (m), 1016 (s), 889 (m), 835 (s), 755 (m), 693 (s), 540 (w), 445 (m) cm^{-1}.

Preparation of $[Mg_2Cl_3(THF)_6][Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]\cdot THF$ (2). $NbCl_4(THF)_2$ (1.52 g, 4 mmol), Mg turnings (0.15 g, 6.2 mmol), and PhCCPh (1.5 g, 8.4 mmol) were stirred in 60 mL of THF for 18 h. Mg and yellow $NbCl_4(THF)_2$ gradually dissolved, and a dark brown solution resulted, which was then filtered into a Schlenk tube and layered with 30 mL of hexane. After 2 weeks of standing a large quantity of greenish brown crystals grew on the walls of the tube along with much oily black deposit. They were removed by filtration, and the crystals were confirmed later by X-ray crystallography to be $[Mg_2Cl_3(THF)_6]_2[Nb_4OCl_8\{(PhC)_4\}_2]\cdot 6THF$, reported previously.[3] The filtrate was relayered in a Schlenk tube with 40 mL of hexane. After another 2 weeks of standing, irregular brown crystals appeared on the walls of the hexane layer, which were isolated by decantation and confirmed to be the title compound by X-ray crystallography; yield 0.3–0.4 g, ca. 15%.

X-ray Crystallography. These air-sensitive crystals were examined and handled under a layer of sodium-treated mineral oil on a small dish in a fritted funnel flushed constantly with a stream of argon. Crystals for data collection on a Rigaku AFC5R diffractometer were attached with Apiezon grease under argon to cone-shaped ends of thin-walled capillaries and sealed by flame. Routine procedures that have already been fully reported elsewhere[6] were used to determine the unit cell parameters and to collect data. Corrections for Lorentz factor, polarization, and absorption were applied. A correction for crystal decay (12.3%) was also applied to the data of 1.

$[Nb_4O_2Cl_4\{(PhC)_4\}_2(THF)_4]\cdot 2THF$ (1). The interpretation of a supersharp Patterson map (SHELXS-86) gave the positions for most of the non-hydrogen atoms. The coordinates of the remaining non-hydrogen atoms were found by combination of difference Fourier syntheses and least-squares refinements. Before the final refinement, the atom that had the lowest thermal parameter of the ring atoms in the interstitial THF molecule, after they were refined as carbon atoms, was designated as the oxygen atom. A final difference Fourier map showed the positions for

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(6) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

Table III. Positional and Equivalent Isotropic Displacement Parameters for $[Mg_2Cl_3(THF)_6][Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]\cdot THF$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
Nb(1)	0.69351 (7)	0.29367 (6)	0.22472 (3)	2.28 (2)	C(54)	0.283 (2)	0.461 (1)	0.0861 (6)	10.0 (7)
Nb(2)	0.52381 (7)	0.28776 (5)	0.26923 (3)	2.07 (2)	C(55)	0.275 (3)	0.532 (2)	0.1236 (7)	22 (1)
Nb(3)	0.51400 (7)	0.48995 (6)	0.29781 (3)	2.39 (2)	C(56)	0.351 (2)	0.559 (1)	0.1700 (7)	16 (1)
Nb(4)	0.67764 (8)	0.50325 (6)	0.25113 (3)	2.79 (3)	Mg(1)	0.3271 (3)	0.4345 (2)	0.3455 (1)	3.09 (9)
O(1)	0.6030 (5)	0.3928 (4)	0.2592 (2)	2.3 (2)	O(3)	0.3552 (7)	0.3783 (6)	0.4043 (3)	5.0 (3)
O(2)	0.4454 (5)	0.3848 (4)	0.3046 (2)	2.7 (2)	O(4)	0.2121 (6)	0.3459 (5)	0.2985 (3)	4.2 (2)
Cl(1)	0.8233 (2)	0.2091 (2)	0.1787 (1)	4.35 (9)	O(5)	0.2013 (6)	0.4995 (5)	0.3808 (3)	4.1 (2)
Cl(2)	0.6932 (2)	0.3881 (2)	0.16359 (9)	2.90 (6)	C(57)	0.460 (1)	0.343 (1)	0.4155 (6)	6.9 (6)
Cl(3)	0.8406 (2)	0.4147 (2)	0.2721 (1)	3.57 (7)	C(58)	0.464 (1)	0.337 (1)	0.4684 (6)	8.0 (6)
Cl(4)	0.4039 (2)	0.1895 (2)	0.2864 (1)	3.82 (8)	C(59)	0.350 (1)	0.344 (1)	0.4808 (5)	6.8 (5)
Cl(5)	0.3144 (2)	0.5249 (2)	0.2858 (1)	3.41 (7)	C(60)	0.295 (1)	0.394 (1)	0.4487 (6)	7.3 (6)
Cl(6)	0.4734 (2)	0.5443 (2)	0.3932 (1)	4.04 (8)	C(61)	0.188 (1)	0.3324 (8)	0.2424 (5)	5.0 (4)
Cl(7)	0.7904 (3)	0.6001 (2)	0.2287 (1)	5.9 (1)	C(62)	0.120 (1)	0.248 (1)	0.2217 (8)	8.0 (6)
C(1)	0.6854 (7)	0.2610 (7)	0.2941 (4)	2.8 (3)	C(63)	0.074 (1)	0.237 (1)	0.2663 (7)	7.7 (6)
C(2)	0.6528 (8)	0.1804 (6)	0.2548 (4)	2.6 (3)	C(64)	0.150 (1)	0.285 (1)	0.3155 (7)	6.5 (5)
C(3)	0.5832 (8)	0.1683 (6)	0.2061 (4)	2.6 (3)	C(65)	0.221 (1)	0.578 (1)	0.4228 (7)	7.0 (5)
C(4)	0.5349 (7)	0.2365 (6)	0.1892 (4)	2.5 (3)	C(66)	0.162 (3)	0.632 (2)	0.399 (1)	15 (2)
C(5)	0.6706 (9)	0.5485 (6)	0.3328 (4)	3.1 (3)	C(67)	0.083 (2)	0.589 (2)	0.355 (1)	12 (1)
C(6)	0.625 (1)	0.6174 (7)	0.3163 (4)	4.3 (3)	C(68)	0.094 (1)	0.501 (1)	0.3507 (6)	5.9 (5)
C(7)	0.549 (1)	0.6069 (7)	0.2668 (5)	4.3 (4)	Mg(2)	0.1146 (3)	0.7278 (2)	0.0113 (1)	3.3 (1)
C(8)	0.5167 (9)	0.5278 (6)	0.2284 (4)	3.1 (3)	Mg(3)	0.0107 (5)	0.7757 (3)	0.1125 (2)	5.6 (1)
C(9)	0.7512 (8)	0.2654 (7)	0.3462 (4)	3.3 (3)	Cl(8)	0.0346 (3)	0.6348 (2)	0.0548 (1)	4.61 (9)
C(10)	0.8611 (9)	0.2873 (8)	0.3562 (4)	4.1 (3)	Cl(9)	−0.0449 (4)	0.8097 (3)	0.0302 (2)	7.4 (1)
C(11)	0.923 (1)	0.287 (1)	0.4025 (5)	5.6 (4)	Cl(10)	0.1963 (4)	0.8083 (4)	0.1026 (2)	10.2 (2)
C(12)	0.876 (1)	0.265 (1)	0.4408 (5)	6.6 (5)	O(6)	0.1744 (6)	0.8196 (4)	−0.0172 (3)	3.8 (2)
C(13)	0.763 (1)	0.245 (1)	0.4314 (6)	8.1 (7)	O(7)	0.2499 (9)	0.6621 (8)	0.0042 (6)	11.0 (6)
C(14)	0.702 (1)	0.245 (1)	0.3840 (5)	5.9 (5)	O(8)	0.0498 (9)	0.6563 (7)	−0.0612 (3)	7.9 (3)
C(15)	0.6979 (9)	0.1025 (7)	0.2670 (5)	3.8 (3)	O(9)	0.008 (2)	0.9051 (8)	0.1602 (5)	14.1 (7)
C(16)	0.634 (1)	0.054 (1)	0.285 (1)	10.1 (9)	O(10)	0.051 (1)	0.7461 (8)	0.1810 (3)	9.5 (4)
C(17)	0.677 (1)	−0.018 (1)	0.296 (1)	10.8 (9)	O(11)	−0.150 (1)	0.7500 (8)	0.1172 (6)	10.4 (6)
C(18)	0.780 (2)	−0.039 (1)	0.2884 (8)	8.8 (7)	C(69)	0.104 (1)	0.8775 (9)	−0.0402 (6)	6.9 (5)
C(19)	0.842 (2)	0.016 (1)	0.2743 (9)	10.9 (9)	C(70)	0.160 (2)	0.964 (1)	−0.0182 (9)	10.1 (7)
C(20)	0.802 (1)	0.087 (1)	0.2637 (7)	8.2 (6)	C(71)	0.268 (2)	0.953 (1)	0.011 (1)	10.4 (8)
C(21)	0.5597 (9)	0.0803 (7)	0.1701 (4)	3.3 (3)	C(72)	0.284 (1)	0.8575 (9)	0.0002 (7)	6.4 (5)
C(22)	0.469 (1)	0.0344 (8)	0.1722 (6)	6.5 (5)	C(73)	0.328 (2)	0.664 (1)	0.0585 (7)	4.0 (5)*
C(23)	0.443 (1)	−0.0490 (9)	0.1387 (6)	6.6 (5)	C(74)	0.412 (2)	0.601 (1)	0.0401 (9)	4.2 (5)*
C(24)	0.510 (1)	−0.0848 (8)	0.1043 (5)	5.6 (4)	C(75)	0.407 (2)	0.589 (2)	−0.0154 (9)	11.0 (9)
C(25)	0.600 (1)	−0.038 (1)	0.1009 (6)	7.1 (5)	C(76)	0.333 (1)	0.650 (1)	−0.0249 (7)	7.0 (5)
C(26)	0.626 (1)	0.0458 (9)	0.1346 (5)	5.9 (4)	C(77)	0.050 (1)	0.6701 (9)	−0.1106 (5)	7.0 (5)
C(27)	0.4626 (8)	0.2178 (6)	0.1386 (4)	2.7 (3)	C(78)	0.003 (1)	0.5881 (8)	−0.1519 (5)	5.3 (4)
C(28)	0.503 (1)	0.2105 (8)	0.0927 (4)	4.3 (3)	C(79)	0.056 (2)	0.521 (1)	−0.1260 (7)	3.4 (4)*
C(29)	0.431 (1)	0.1862 (9)	0.0427 (5)	5.8 (4)	C(80)	0.048 (1)	0.556 (1)	−0.0677 (6)	2.1 (3)*
C(30)	0.320 (1)	0.1734 (8)	0.0410 (5)	4.4 (3)	C(81)	0.126 (4)	0.946 (2)	0.1963 (9)	24 (2)
C(31)	0.281 (1)	0.1835 (8)	0.0865 (5)	4.5 (4)	C(82)	0.139 (3)	1.017 (1)	0.175 (1)	15 (1)
C(32)	0.3503 (9)	0.2042 (8)	0.1353 (5)	4.2 (3)	C(83)	0.030 (2)	1.024 (1)	0.142 (1)	11.5 (9)
C(33)	0.7451 (8)	0.5544 (8)	0.3806 (4)	3.7 (3)	C(84)	−0.055 (3)	0.966 (1)	0.138 (1)	14 (1)
C(34)	0.7396 (9)	0.4871 (9)	0.4013 (4)	4.3 (3)	C(85)	−0.023 (2)	0.765 (1)	0.2238 (7)	12 (1)
C(35)	0.814 (1)	0.490 (1)	0.4467 (5)	6.0 (5)	C(86)	0.056 (2)	0.743 (2)	0.2669 (9)	16 (1)
C(36)	0.888 (2)	0.553 (2)	0.4706 (7)	9.7 (8)	C(87)	0.114 (2)	0.670 (2)	0.2377 (9)	15 (1)
C(37)	0.889 (2)	0.619 (2)	0.449 (1)	11.3 (9)	C(88)	0.145 (2)	0.725 (2)	0.2026 (9)	11 (1)
C(38)	0.823 (1)	0.622 (1)	0.4042 (6)	6.9 (5)	C(89)	−0.208 (2)	0.663 (1)	0.092 (1)	21 (2)
C(39)	0.651 (1)	0.7068 (7)	0.3527 (5)	6.1 (5)	C(90)	−0.324 (3)	0.640 (2)	0.093 (1)	6.8 (7)*
C(40)	0.613 (1)	0.7304 (8)	0.3991 (5)	6.5 (5)	C(91)	−0.353 (4)	0.721 (3)	0.093 (2)	9 (1)*
C(41)	0.648 (2)	0.808 (1)	0.4366 (7)	9.7 (7)	C(92)	−0.254 (2)	0.792 (2)	0.112 (1)	6.0 (6)*
C(42)	0.714 (3)	0.862 (1)	0.4226 (8)	17 (1)	C(73)′	0.209 (2)	0.565 (1)	−0.031 (1)	7.5 (8)*
C(43)	0.762 (3)	0.839 (1)	0.3764 (7)	19 (1)	C(74)′	0.312 (2)	0.522 (2)	−0.049 (1)	7.4 (8)*
C(44)	0.720 (2)	0.756 (1)	0.3376 (7)	11.7 (8)	C(79)′	−0.103 (3)	0.598 (2)	−0.139 (1)	6.4 (7)*
C(45)	0.506 (1)	0.6877 (8)	0.2593 (6)	6.6 (5)	C(80)′	−0.074 (2)	0.626 (2)	−0.0793 (9)	5.7 (6)*
C(46)	0.435 (1)	0.7297 (7)	0.2890 (5)	4.7 (4)	C(90)′	−0.295 (3)	0.723 (2)	0.119 (1)	7.9 (9)*
C(47)	0.399 (2)	0.8061 (9)	0.2793 (7)	7.4 (6)	C(91)′	−0.272 (2)	0.797 (2)	0.171 (1)	7.3 (8)*
C(48)	0.430 (2)	0.836 (1)	0.242 (1)	12 (1)	C(92)′	−0.151 (2)	0.801 (2)	0.1753 (8)	10 (1)*
C(49)	0.496 (3)	0.786 (2)	0.211 (1)	17 (1)	O(12)	0.233 (4)	0.047 (3)	0.342 (2)	10 (1)*
C(50)	0.538 (2)	0.715 (1)	0.2186 (9)	12 (1)	C(93)	0.262 (4)	0.099 (4)	0.396 (2)	11 (2)*
C(51)	0.435 (1)	0.5105 (8)	0.1802 (4)	4.2 (4)	C(94)	0.160 (5)	0.119 (4)	0.414 (2)	9 (2)*
C(52)	0.4314 (9)	0.4322 (8)	0.1433 (5)	4.3 (4)	C(95)	0.086 (4)	0.104 (4)	0.364 (2)	9 (2)*
C(53)	0.3578 (9)	0.4091 (8)	0.0968 (5)	4.6 (4)	C(96)	0.121 (4)	0.014 (3)	0.343 (2)	9 (2)*

[a] See footnote *a* of Table II.

some of the phenyl hydrogen atoms, but no effort was made to locate these hydrogen atoms.

$[Mg_2Cl_3(THF)_6][Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]\cdot THF$ (2). The four crystallographically independent Nb atoms were located also by the interpretation of a supersharp Patterson map (SHELXS-86) in the centric space group $P\bar{1}$. The structure was gradually developed by difference Fourier syntheses and least-squares refinements. After the convergence factor fell below 8%, a difference Fourier synthesis revealed that seven carbon atoms from the THF ligands in the magnesium dimer cation $[Mg_2Cl_3(THF)_6]^+$ (C(73), C(74), C(79), C(80), C(90), C(91), C(92)) were disordered over two sets of positions, each of which was then assigned a site occupancy factor of 0.5. The oxygen atom was designated in the same way for the interstitial THF molecule as

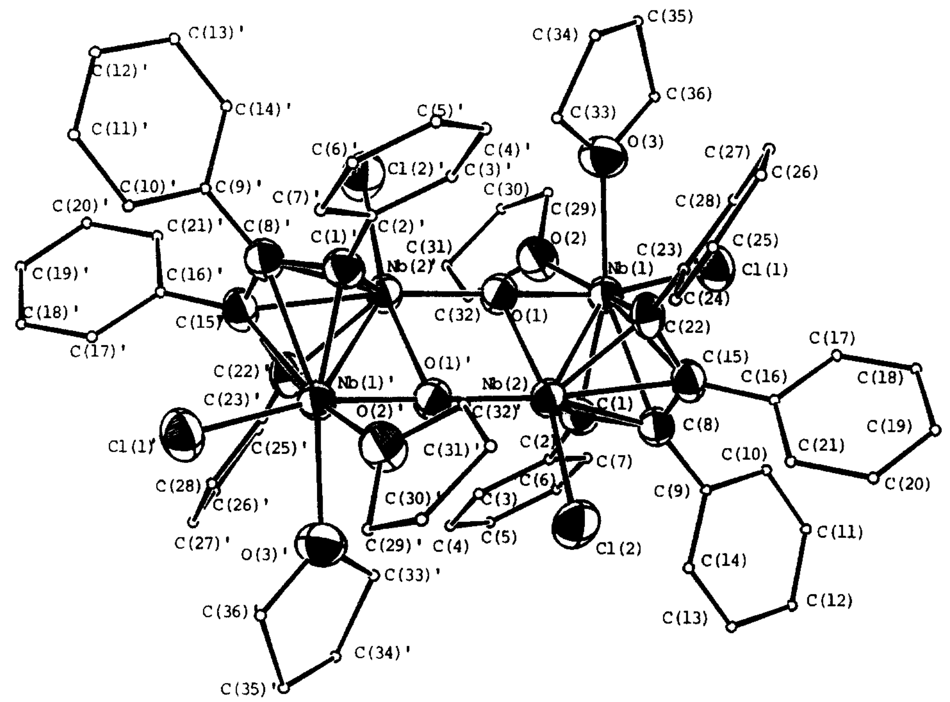

Figure 1. Neutral niobium tetramer [Nb$_4$O$_2$Cl$_4${(PhC)$_4$}$_2$(THF)$_4$] as found in compound 1.

that in 1. These disordered carbon atoms and the atoms from the interstitial THF solvent molecule were treated only isotropically in the final least-squares refinement. A few highest peaks (ca. 0.8 e/Å^3) in a final difference Fourier map were found around the interstitial THF molecule, which was indicative of a slight disorder. However, no effort was made to model the disorder.

The usual particulars pertaining to crystal parameters and the collection and refinement of data are set forth in Table I. Tables II and III list the positional and isotropic-equivalent thermal parameters for compounds 1 and 2, respectively.

Results and Discussion

In our previous paper, we reported a series of compounds that contain the rectangular tetranuclear cluster anion [[(NbCl)$_2$(μ-PhCC(Ph)C(Ph)CPh)]$_2$(μ_4-O)(μ-Cl)$_4$]$^{2-}$.[3,4] They were prepared by the stoichiometric reduction of NbCl$_4$(THF)$_2$ with Mg or of NbCl$_3$(PhCCPh)(THF)$_2$ with Na/Hg. Cations generated in situ, such as Na$^+$, [Mg$_2$Cl$_3$(THF)$_6$]$^+$, and (HPEt$_3$)$^+$, then combined with the anion in the corresponding crystal forms. Successful synthesis[4] of the structurally related Nb dimer cation [Nb$_2$Cl$_3$(PhC)$_4$(THF)$_2$]$^+$ provided clear proof that half of the above tetrameric anion, with appropriate adjustment, is a stable entity. Of course, one may expect combination of such halves to form structurally similar tetramers by an appropriate workup. The preparation of 1 is essentially the same as the preparation of (HPEt$_3$)$_2$[Nb$_4$OCl$_8${(PhC)$_4$}$_2$] except for the use of the phosphine.[3] The preparation of 2 is very similar to the preparation of [Mg$_2$Cl$_3$(THF)$_6$]$_2$[Nb$_4$OCl$_8${(PhC)$_4$}$_2$]·6THF except for the quantity of Mg reducing agent used.[3] However, the fact that these reactions gave bis(oxo)-bridged tetramers instead of compounds of [Nb$_4$OCl$_8${(PhC)$_4$}$_2$]$^{2-}$ was unexpected, even though these new products are understandable once found. The use of more reducing agent in the reaction did not lower the oxidation state of the Nb atoms at all. However, it provides more Mg^{2+} cations and facilitates the formation of products with higher Mg content. No doubt, many subtle factors play important roles in the manner of association of the dimer entities.

Structure of Compound 1. The solid is made up of neutral tetranuclear molecules together with two interstitial THF molecules per Nb$_4$ molecule. The Nb$_4$ molecule is depicted in Figure 1. It has crystallographic inversion symmetry, and primed and unprimed atoms of the same number are so related. The principal dimensions of the molecule are given in Table IV.

The halves of the molecule are in many ways very similar to the halves of the [Nb$_4$OCl$_8${(PhC)$_4$}$_2$]$^{2-}$ anion.[3,4] The short Nb–Nb distance, 2.601 (1) Å, is effectively the same as that in the anion (ca. 2.61 Å), and the entire central Nb$_2$(PhC)$_4$(μ-O) unit is essentially the same. The four carbon atoms that are bound to the metal atoms and the μ-O atom are coplanar to within 0.02 Å. These two planes are in turn within 1° of being perpendicular to the mean plane defined by the four niobium atoms and the two bridging oxygen atoms. The four niobium atoms are, of course, rigorously coplanar while the O(1) atoms lie 0.073 (4) Å above and below this plane. This is reflected in the fact that the sum of the Nb–O–Nb angles is 356.6°.

The set of four niobium atoms defines a rhombus with angles of 52.37 (2)° at Nb(1) and 127.63 (2)° at Nb(2), whereas in the [Nb$_4$OCl$_8${(PhC)$_4$}]$^{2-}$ ion the four metal atoms defined a rectangle.

Another qualitative difference between this structure and that of the rectangular anion has to do with the arrangement of nonbridging ligand atoms about the niobium atoms. The arrangement about Nb(1), of two oxygen atoms and one Cl atom instead of three chlorine atoms, is actually quite similar. The THF oxygen atoms, O(2) and O(3), lie equal distances above and below the Nb$_4$O$_2$ mean plane, and Cl(1) lies only slightly (0.13 Å) out of it. About Nb(2), however, there are only two other ligands. One is the O(1) atom that bridges the other Nb$_2$(PhC)$_4$ unit, and the other is Cl(2). The arrangement about Nb(2) can be roughly described as trigonal bipyramidal (with O(1) and Cl(2) being apical) in the same sense that the arrangement about Nb(1) can be described as octahedral. In each case the description employs the formal assignment of the center of each outer C–C bond of the C$_4$ unit to a coordination position. This formalism has been presented and discussed in previous papers in this series.[3]

Structure of Compound 2. The cation and the anion are shown in Figures 2 and 3, respectively. The

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) for $[Nb_4O_2Cl_4\{(PhC)_4\}_2(THF)_4]\cdot 2THF$[a]

Nb(1)-Nb(2)	2.6008 (9)	Nb(1)-O(3)	2.334 (4)	C(1)-C(2)	1.495 (10)
Nb(1)-Cl(1)	2.442 (2)	Nb(2)-Cl(2)	2.425 (2)	C(1)-C(8)	1.445 (9)
Nb(1)-O(1)	2.041 (4)	Nb(2)-O(1)	2.065 (4)	C(8)-C(9)	1.517 (8)
Nb(1)-C(1)	2.137 (6)	Nb(2)-O(1)′	2.034 (4)	C(8)-C(15)	1.432 (9)
Nb(1)-C(8)	2.405 (6)	Nb(2)-C(1)	2.104 (7)	C(15)-C(16)	1.515 (9)
Nb(1)-C(15)	2.397 (6)	Nb(2)-C(8)	2.410 (6)	C(15)-C(22)	1.440 (8)
Nb(1)-C(22)	2.137 (7)	Nb(2)-C(15)	2.403 (6)	C(22)-C(23)	1.472 (10)
Nb(1)-O(2)	2.292 (5)	Nb(2)-C(22)	2.140 (6)		
Cl(1)-Nb(1)-O(1)	165.7 (1)	C(22)-Nb(1)-O(2)	164.4 (2)	Nb(1)-O(1)-Nb(2)′	175.1 (3)
Cl(1)-Nb(1)-C(1)	106.7 (2)	C(22)-Nb(1)-O(3)	92.3 (2)	Nb(2)-O(1)-Nb(2)′	103.9 (2)
Cl(1)-Nb(1)-C(8)	87.3 (2)	O(2)-Nb(1)-O(3)	79.8 (2)	Nb(1)-C(1)-C(2)	133.6 (5)
Cl(1)-Nb(1)-C(15)	88.2 (2)	Cl(2)-Nb(2)-O(1)	164.5 (1)	Nb(2)-C(1)-C(2)	137.9 (5)
Cl(1)-Nb(1)-C(22)	107.7 (2)	Cl(2)-Nb(2)-O(1)′	88.8 (1)	C(2)-C(1)-C(8)	124.2 (5)
Cl(1)-Nb(1)-O(2)	85.1 (1)	Cl(2)-Nb(2)-C(1)	109.0 (2)	Nb(1)-C(8)-C(9)	147.5 (5)
Cl(1)-Nb(1)-O(3)	84.1 (1)	Cl(2)-Nb(2)-C(8)	90.0 (2)	Nb(2)-C(8)-C(9)	145.8 (5)
O(1)-Nb(1)-C(1)	82.9 (2)	Cl(2)-Nb(2)-C(15)	89.2 (2)	C(1)-C(8)-C(9)	118.3 (5)
O(1)-Nb(1)-C(8)	106.3 (2)	Cl(2)-Nb(2)-C(22)	106.8 (2)	C(1)-C(8)-C(15)	123.5 (5)
O(1)-Nb(1)-C(15)	105.5 (2)	O(1)-Nb(2)-O(1)′	76.1 (2)	C(9)-C(8)-C(15)	118.1 (5)
O(1)-Nb(1)-C(22)	82.2 (2)	O(1)-Nb(2)-C(1)	83.1 (2)	Nb(1)-C(15)-C(16)	146.6 (5)
O(1)-Nb(1)-O(2)	83.7 (2)	O(1)-Nb(2)-C(8)	105.3 (2)	Nb(2)-C(15)-C(16)	146.3 (5)
O(1)-Nb(1)-O(3)	85.2 (2)	O(1)-Nb(2)-C(15)	104.6 (2)	C(8)-C(15)-C(16)	117.8 (5)
C(1)-Nb(1)-O(2)	93.2 (2)	O(1)-Nb(2)-C(22)	81.6 (2)	C(8)-C(15)-C(22)	125.5 (6)
C(1)-Nb(1)-O(3)	166.8 (2)	O(1)′-Nb(2)-C(1)	125.8 (2)	C(16)-C(15)-C(22)	116.7 (5)
C(8)-Nb(1)-O(2)	122.8 (2)	O(1)′-Nb(2)-C(8)	159.5 (2)	Nb(1)-C(22)-C(23)	139.3 (5)
C(8)-Nb(1)-O(3)	155.0 (2)	O(1)′-Nb(2)-C(15)	165.8 (2)	Nb(2)-C(22)-C(23)	134.8 (5)
C(15)-Nb(1)-O(2)	156.9 (2)	O(1)′-Nb(2)-C(22)	131.8 (2)	C(15)-C(22)-C(23)	123.1 (6)
C(15)-Nb(1)-O(3)	121.4 (2)	Nb(1)-O(1)-Nb(2)	78.6 (1)		

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

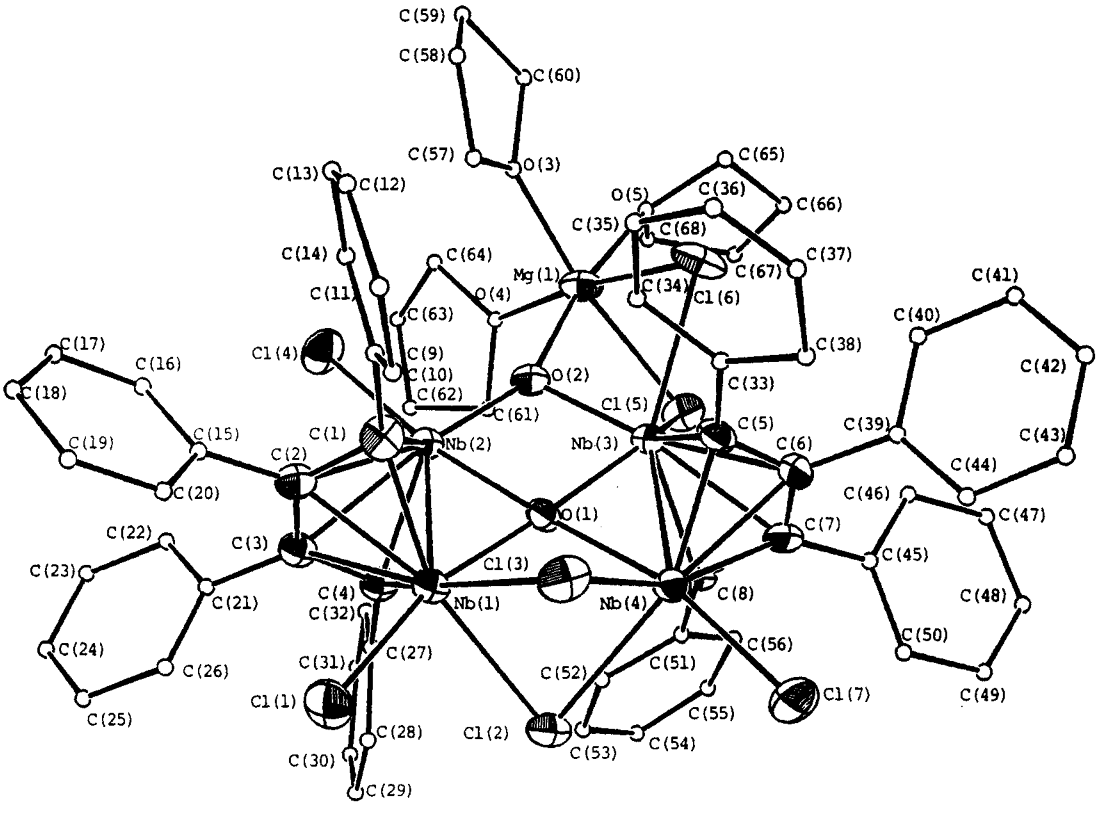

Figure 2. Cluster anion $[Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]^-$ as found in compound 2.

$[Mg_2Cl_3(THF)_6]^+$ ion has been found before in cases where magnesium metal was used as a reducing agent for a metal chloride in THF solution[1,3] or $MgCl_2(THF)_2$ was used as a source of counterion for a metal complex anion in THF solution.[7] There are also analogous vanadium species.[8] The present example shows no unusual features.

The tetraniobium anion has no overall symmetry, but nevertheless, it has a great deal of internal regularity. The principal bond distances and angles are listed in Table V.

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[7] (a) Sobota, P.; Utko, J.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1984**, 2077. (b) Sobota, P.; Pluzinski, T.; Lis, T. *Z. Anorg. Allg. Chem.* **1986**, *533*, 215.

[8] (a) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1988**, *7*, 737. (b) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1987**, *6*, 1433. (c) Cotton, F. A.; Duraj, S. A.; Manzer, L. E.; Roth, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 3850. (d) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1985**, *24*, 913. (e) Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715. (f) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[Mg_2Cl_3(THF)_6][Nb_4O_2Cl_7\{(PhC)_4\}_2\{Mg(THF)_3\}]\cdot THF^a$

Nb(1)-Nb(2)	2.634 (1)	Nb(3)-O(2)	2.020 (7)	C(1)-C(2)	1.453 (12)
Nb(1)-O(1)	2.091 (6)	Nb(3)-Cl(5)	2.583 (3)	C(1)-C(9)	1.504 (14)
Nb(1)-Cl(1)	2.425 (3)	Nb(3)-Cl(6)	2.612 (3)	C(2)-C(3)	1.424 (13)
Nb(1)-Cl(2)	2.610 (3)	Nb(3)-C(5)	2.137 (10)	C(2)-C(15)	1.53 (2)
Nb(1)-Cl(3)	2.605 (3)	Nb(3)-C(6)	2.413 (12)	C(3)-C(4)	1.456 (15)
Nb(1)-C(1)	2.128 (12)	Nb(3)-C(7)	2.410 (14)	C(3)-C(21)	1.497 (13)
Nb(1)-C(2)	2.356 (12)	Nb(3)-C(8)	2.165 (11)	C(4)-C(27)	1.467 (13)
Nb(1)-C(3)	2.378 (10)	Nb(4)-O(1)	2.148 (7)	C(5)-C(6)	1.45 (2)
Nb(1)-C(4)	2.154 (9)	Nb(4)-Cl(2)	2.608 (2)	C(5)-C(33)	1.454 (14)
Nb(2)-O(1)	2.118 (7)	Nb(4)-Cl(3)	2.634 (3)	C(6)-C(7)	1.49 (2)
Nb(2)-O(2)	1.982 (6)	Nb(4)-Cl(7)	2.414 (4)	C(6)-C(39)	1.522 (14)
Nb(2)-Cl(4)	2.414 (3)	Nb(4)-C(5)	2.133 (10)	C(7)-C(8)	1.425 (13)
Nb(2)-C(1)	2.138 (9)	Nb(4)-C(6)	2.363 (11)	C(7)-C(45)	1.52 (2)
Nb(2)-C(2)	2.421 (10)	Nb(4)-C(7)	2.377 (13)	C(8)-C(51)	1.484 (15)
Nb(2)-C(3)	2.422 (9)	Nb(4)-C(8)	2.108 (12)	Mg(1)-O(3)	2.068 (11)
Nb(2)-C(4)	2.113 (10)	O(2)-Mg(1)	2.038 (8)	Mg(1)-O(4)	2.040 (7)
Nb(3)-Nb(4)	2.628 (1)	Cl(5)-Mg(1)	2.515 (5)	Mg(1)-O(5)	2.123 (9)
Nb(3)-O(1)	2.094 (6)	Cl(6)-Mg(1)	2.489 (4)		

O(1)-Nb(1)-Cl(1)	164.2 (2)	O(2)-Nb(3)-Cl(5)	80.3 (2)	Nb(2)-O(2)-Mg(1)	151.4 (4)
O(1)-Nb(1)-Cl(2)	77.7 (2)	O(2)-Nb(3)-Cl(6)	79.0 (2)	Nb(3)-O(2)-Mg(1)	100.5 (3)
O(1)-Nb(1)-Cl(3)	77.5 (2)	O(2)-Nb(3)-C(5)	128.5 (4)	Nb(1)-Cl(2)-Nb(4)	80.50 (8)
O(1)-Nb(1)-C(1)	82.9 (3)	O(2)-Nb(3)-C(6)	162.1 (3)	Nb(1)-Cl(3)-Nb(4)	80.11 (8)
O(1)-Nb(1)-C(2)	107.1 (3)	O(2)-Nb(3)-C(7)	161.7 (3)	Nb(1)-C(1)-Nb(2)	76.3 (4)
O(1)-Nb(1)-C(3)	106.3 (3)	O(2)-Nb(3)-C(8)	129.2 (3)	Nb(1)-C(1)-C(9)	141.7 (8)
O(1)-Nb(1)—C(4)	81.1 (3)	Cl(5)-Nb(3)-Cl(6)	75.88 (9)	Nb(2)-C(1)-C(9)	134.3 (7)
Cl(1)-Nb(1)-Cl(2)	88.8 (1)	Cl(5)-Nb(3)-C(5)	141.0 (3)	C(2)-C(1)-C(9)	121 (1)
Cl(1)-Nb(1)-Cl(3)	90.90 (9)	Cl(5)-Nb(3)-C(6)	108.8 (3)	Nb(1)-C(2)-Nb(2)	66.9 (3)
Cl(1)-Nb(1)-C(1)	108.8 (3)	Cl(5)-Nb(3)-C(7)	86.5 (3)	Nb(1)-C(2)-C(15)	143.7 (8)
Cl(1)-Nb(1)-C(2)	88.4 (3)	Cl(5)-Nb(3)-C(8)	84.3 (3)	Nb(2)-C(2)-C(15)	147.9 (8)
Cl(1)-Nb(1)-C(3)	88.2 (3)	Cl(6)-Nb(3)-C(5)	84.1 (3)	C(1)-C(2)-C(3)	125 (1)
Cl(1)-Nb(1)-C(4)	108.4 (3)	Cl(6)-Nb(3)-C(6)	88.3 (3)	C(1)-C(2)-C(15)	116.8 (9)
Cl(2)-Nb(1)-Cl(3)	73.76 (9)	Cl(6)-Nb(3)-C(7)	110.1 (3)	C(3)-C(2)-C(15)	117.8 (8)
Cl(2)-Nb(1)-C(1)	158.6 (3)	Cl(6)-Nb(3)-C(8)	142.2 (3)	Nb(1)-C(3)-Nb(2)	66.6 (2)
Cl(2)-Nb(1)-C(2)	160.4 (2)	O(1)-Nb(4)-Cl(2)	76.8 (2)	Nb(1)-C(3)-C(21)	144.0 (8)
Cl(2)-Nb(1)-C(3)	125.5 (3)	O(1)-Nb(4)-Cl(3)	76.0 (2)	Nb(2)-C(3)-C(21)	148.3 (8)
Cl(2)-Nb(1)-C(4)	94.1 (3)	O(1)-Nb(4)-Cl(7)	164.6 (2)	C(2)-C(3)-C(4)	123.9 (8)
Cl(3)-Nb(1)-C(1)	93.3 (3)	O(1)-Nb(4)-C(5)	81.3 (3)	C(2)-C(3)-C(21)	118 (1)
Cl(3)-Nb(1)-C(2)	125.7 (2)	O(1)-Nb(4)-C(6)	105.5 (4)	C(4)-C(3)-C(21)	118.4 (8)
Cl(3)-Nb(1)-C(3)	160.7 (3)	O(1)-Nb(4)-C(7)	105.3 (4)	Nb(1)-C(4)-Nb(2)	76.2 (3)
Cl(3)-Nb(1)-C(4)	157.3 (3)	O(1)-Nb(4)-C(8)	82.5 (4)	Nb(1)-C(4)-C(27)	138.7 (8)
O(1)-Nb(2)-O(2)	75.8 (3)	Cl(2)-Nb(4)-Cl(3)	73.33 (8)	Nb(2)-C(4)-C(27)	137.2 (7)
O(1)-Nb(2)-Cl(4)	167.4 (2)	Cl(2)-Nb(4)-Cl(7)	90.0 (1)	C(3)-C(4)-C(27)	119.9 (8)
O(1)-Nb(2)-C(1)	82.1 (4)	Cl(2)-Nb(4)-C(5)	154.7 (3)	Nb(3)-C(5)-Nb(4)	76.0 (3)
O(1)-Nb(2)-C(2)	103.9 (3)	Cl(2)-Nb(4)-C(6)	164.8 (3)	Nb(3)-C(5)-C(33)	135.5 (9)
O(1)-Nb(2)-C(3)	103.9 (3)	Cl(2)-Nb(4)-C(7)	128.3 (3)	Nb(4)-C(5)-C(33)	134.9 (8)
O(1)-Nb(2)-C(4)	81.5 (3)	Cl(2)-Nb(4)-C(8)	96.0 (3)	C(6)-C(5)-C(33)	127.0 (9)
O(2)-Nb(2)-Cl(4)	91.9 (2)	Cl(3)-Nb(4)-Cl(7)	92.8 (1)	Nb(3)-C(6)-Nb(4)	66.8 (3)
O(2)-Nb(2)-C(1)	126.7 (3)	Cl(3)-Nb(4)-C(5)	89.1 (3)	Nb(3)-C(6)-C(39)	145 (1)
O(2)-Nb(2)-C(2)	161.2 (3)	Cl(3)-Nb(4)-C(6)	121.8 (3)	Nb(4)-C(6)-C(39)	148 (1)
O(2)-Nb(2)-C(3)	164.6 (3)	Cl(3)-Nb(4)-C(7)	158.3 (3)	C(5)-C(6)-C(7)	124.3 (9)
O(2)-Nb(2)-C(4)	129.9 (3)	Cl(3)-Nb(4)-C(8)	157.6 (3)	C(5)-C(6)-C(39)	119 (1)
Cl(4)-Nb(2)-C(1)	108.1 (3)	Cl(7)-Nb(4)-C(5)	109.4 (3)	C(7)-C(6)-C(39)	117 (1)
Cl(4)-Nb(2)-C(2)	88.6 (3)	Cl(7)-Nb(4)-C(6)	89.3 (3)	Nb(3)-C(7)-Nb(4)	66.6 (4)
Cl(4)-Nb(2)-C(3)	87.1 (3)	Cl(7)-Nb(4)-C(7)	89.1 (4)	Nb(3)-C(7)-C(45)	145 (1)
Cl(4)-Nb(2)-C(4)	104.9 (3)	Cl(7)-Nb(4)-C(8)	107.2 (3)	Nb(4)-C(7)-C(45)	149 (1)
O(1)-Nb(3)-O(2)	75.5 (3)	Nb(1)-O(1)-Nb(2)	77.5 (2)	C(6)-C(7)-C(8)	124 (1)
O(1)-Nb(3)-Cl(5)	134.9 (2)	Nb(1)-O(1)-Nb(3)	176.6 (4)	C(6)-C(7)-C(45)	115 (1)
O(1)-Nb(3)-Cl(6)	133.8 (2)	Nb(1)-O(1)-Nb(4)	105.4 (3)	C(8)-C(7)-C(45)	121 (1)
O(1)-Nb(3)-C(5)	82.5 (3)	Nb(2)-O(1)-Nb(3)	100.6 (3)	Nb(3)-C(8)-Nb(4)	75.9 (4)
O(1)-Nb(3)-C(6)	105.6 (4)	Nb(2)-O(1)-Nb(4)	177.1 (3)	Nb(3)-C(8)-C(51)	129.4 (9)
O(1)-Nb(3)-C(7)	105.9 (4)	Nb(3)-O(1)-Nb(4)	76.5 (2)	Nb(4)-C(8)-C(51)	139.3 (8)
O(1)-Nb(3)-C(8)	82.4 (3)	Nb(2)-O(2)-Nb(3)	108.1 (3)	C(7)-C(8)-C(51)	128 (1)

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

The four niobium atoms form a nearly perfect rectangle, with short edges (i.e., niobium–niobium bonds) that are 2.634 (2) and 2.629 (2) Å in length. The four Nb atoms are not precisely coplanar, but none deviates by more than 0.025 (1) Å from the best mean plane through them. In fact, the four Nb atoms together with O(1) and O(2) are practically coplanar, with none of these six atoms lying more than 0.031 (1) Å from the best mean plane. The eight carbon atoms forming the two C-shaped units and the central oxygen atoms, O(1), are also essentially coplanar, and this plane is perpendicular, to within less than 1°, to the Nb_4O_2 plane.

One long edge of the Nb_4 rectangle is symmetrically bridged by the two chlorine atoms Cl(2) and Cl(3), which lie 1.50 and 1.65 Å, respectively, on opposite sides of the central Nb_4O_2 plane. The four Nb–Cl distances in this set are essentially equal, lying in the range 2.60–2.65 Å. Similarly, the two terminal Nb–Cl distances, Nb(1)–Cl(1) and Nb(4)–Cl(7), are essentially equal at 2.42 ± 0.01 Å, and both of these terminal Cl atoms are within less than 0.05 Å of the central Nb_4O_2 plane. The Nb–O(1) distances vary somewhat, ranging from 2.09 to 2.14 Å.

It is along the Nb(2)···Nb(3) edge of the structure that there is a marked asymmetry. The magnesium ion Mg(1)

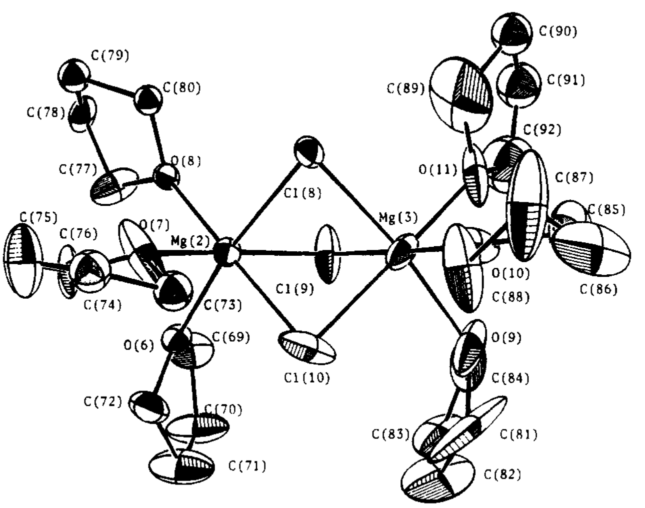

Figure 3. Magnesium dimer cation $[Mg_2Cl_3(THF)_6]^+$ as found in compound 2.

is attached to the bridging oxygen atom O(2) and also to the two chlorine atoms Cl(5) and Cl(6). These three atoms occupy a facial set of positions of an octahedron that is completed by the three THF ligands also attached to Mg(1). This unsymmetrical arrangement causes the bridging oxygen atom to form unequal bonds to the niobium atoms, with Nb(2)-O(2) = 1.971 (7) Å and Nb(3)-O(2) = 2.020 (8) Å. The two chlorine atoms Cl(5) and Cl(6) are roughly equal distances above and below the central Nb_4O_2 plane, viz., 1.53 and 1.67 Å.

Another feature of the marked asymmetry in this part of the anion is the presence of only one terminal Cl atom, Cl(4), on Nb(2), while there are two such atoms on Nb(3). This Cl(4) atom lies very close (0.14 Å) to the central Nb_4O_2 plane. Two of the THF ligands on the Mg(1) atom encroach on the regions above and below the central plane, so that it would not appear possible for Nb(2) to have had two terminal chlorine atoms without other changes having occurred.

It has previously been noted[3] that, in the symmetrical $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anion, the halves could be regarded formally as face-sharing bioctahedra, with the six eclipsed terminal positions occupied by Cl atoms and the three bridge positions by the central oxygen atom and two of the C-C bonds. In the present case, neither half of the molecule can be described in this way. In the Nb(3)-Nb(4) half, there is a distorted octahedron about one metal atom, Nb(4), but a distorted trigonal prism about the other, Nb(3). On the other side there is again one distorted octahedron, but there are only five coordination positions (in the sense we have been using this concept with regard to the $(PhC)_4$ groups) about the other, Nb(2). For what it is worth, a description of this arrangement as a trigonal bipyramid with O(1) and Cl(4) in axial positions can be given.

Concluding Remarks. The presently reported compounds emphasize further the point already evident in our previous studies. The reaction of PhCCPh with reduced solutions of niobium chloride has as its chief product the $Nb_2(PhC)_4$ unit (I), to which other ligands such as Cl, O, and THF then coordinate to fill either three or four addition positions about each Nb atom. These units, in turn, may remain as such (viz., the $[Nb_2Cl_3(PhC)_4(THF)_4]^+$ ion) or they may associate via shared ligands, either symmetrically (viz., the $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anion) or unsymmetrically, as in the two compounds described here. The details of what happens to the $Nb_2(PhC)_4$ unit seem quite varied and seem of much less importance than the formation and stability of that unit itself.

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Supplementary Material Available: Tables of anisotropic displacements and complete bond distances and angles for compounds 1 and 2 and stereoviews of unit cell contents for compound 1 (21 pages); tables of calculated and observed structure factors for compounds 1 and 2 (69 pages). Ordering information is given on any current masthead page.

Cleavage of Poly(diorganosiloxanes) by Trimethylaluminum

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The interaction of $AlMe_3$ at elevated temperatures with poly(diorganosiloxanes), $(RMeSiO)_x$ (R = Me, n-$C_{18}H_{37}$, $-CH_2CH_2CF_3$, Ph), leads to rupture of the silicon-oxygen framework and yields the dimeric aluminum siloxides $[Me_2Al(OSiMe_2R)]_2$. The molecular structure of $[Me_2Al(OSiMe_2Ph)]_2$ has been confirmed by X-ray crystallography. The compound $[Me_2Al(OSiMe_2Ph)]_2$ crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 7.970$ (3) Å, $b = 24.563$ (10) Å, $c = 13.322$ (4) Å, $\beta = 105.05$ (3)°, $Z = 4$, 2754 observed data, $R = 0.0478$, and $R_w = 0.0639$. At ambient temperatures the cyclic trisiloxane $(Me_2SiO)_3$ forms a highly fluxional 1:1 Lewis acid-base adduct with $AlMe_3$.

Introduction

It is widely known that reactions of $AlMe_3$ result in the leaching of silicon grease, primarily $(Me_2SiO)_x$, from joints and stopcocks.[1] In addition, we have observed the presence of an unidentified impurity in the reaction products, whose ^1H NMR spectrum consists of two peaks in a 3:2 ratio (δ 0.10 and 0.66, respectively).

In 1959 Jenkner reported[2] that the interaction of $(Me_2SiO)_x$ with 5% $AlEt_3$, at 175 °C, led upon hydrolysis to ethyl-substituted polysiloxanes, presumably via alkyl-

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(1) Eisch, J. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K. 1986; Vol. 1, p 668.

(2) Jenkner, H. *Z. Naturforsch.* **1959**, *146*, 133.

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