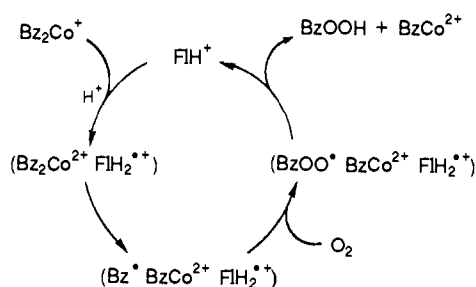


Scheme III



the latter of which may be further oxidized by the oxidant to give benzaldehyde as the final oxygenated product (Table IV). In the absence of dioxygen, the benzyl radical may react with $[\text{PhCH}_2\text{Co}(\text{bpy})_2]^{2+}$ in the cage to yield the coupling product, $\text{PhC}_2\text{H}_2\text{Ph}$ (Table III). In the case of *cis*- $[\text{R}_2\text{Co}(\text{bpy})_2]^+$ ($\text{R} = \text{Et}, \text{Me}$) as well, the cleavage of the Co-R bond upon the one-electron oxidation may occur in a stepwise manner as shown in Scheme II. However, rates of the reactions of much more reactive radicals R^* (Et^* or Me^*) with $[\text{RCo}(\text{bpy})_2]^{2+}$ as compared to benzyl radicals may be so fast that R^* radicals cannot be trapped by dioxygen and that only the net coupling of the alkyl ligands of $[\text{R}_2\text{Co}(\text{bpy})_2]^{2+}$ can occur to yield the coupling products $\text{R}-\text{R}$ exclusively. Such higher reactivities of ethyl and methyl radicals as compared to benzyl radical are known in the reactions with various thiols.⁴⁶

On the basis of the above discussion, the catalytic cycle for the coenzyme-catalyzed oxygenation of the benzyl ligand of *cis*-

$[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$ (Bz_2Co^+) in the case of FIH^+ may be shown in Scheme III. At first, an acid-catalyzed electron transfer from Bz_2Co^+ to FIH^+ occurs to give $(\text{Bz}_2\text{Co}^{2+} \text{FIH}_2^{**+})$. One cobalt-benzyl bond in $\text{Bz}_2\text{Co}^{2+}$ may be readily cleaved to give benzyl radical (Bz^*), followed by the facile trap by dioxygen to produce benzylperoxy radical (BzOO^*), which then gives benzyl hydroperoxide (BzOOH) by the abstraction of hydrogen atom from FIH_2^{**+} , accompanied by regeneration of FIH^+ . The benzyl hydroperoxide may decompose to give the final product, benzaldehyde.³¹ Essentially the same reaction scheme may be applied for the case of LH^+ . In the case of APH^+ , however, the initial electron transfer from Bz_2Co^+ to APH^+ produces APH^* instead of APH_2^{**+} as indicated by the dependence of $\log k_{\text{obs}}$ on $[\text{HClO}_4]$ (Figure 5).

Comparison of Schemes I and III reveals the origin of the difference in the oxygenation and oxidative coupling processes, that is, the much lower reactivity of benzyl radicals as compared to methyl or ethyl radicals in the coupling reactions, resulting in the trapping of benzyl radical by dioxygen to lead to the oxygenated product, benzyl hydroperoxide. As such, *cis*- $[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]^+$ is the least reactive in the one-electron oxidation in the absence of dioxygen because of the slow coupling process in Scheme II (Figure 9), but it becomes the most reactive in the coenzyme-catalyzed reaction in the presence of dioxygen in Scheme III because of the facile trapping of benzyl radical by dioxygen (Figure 8).

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Registry No. *cis*- $[(\text{PhCH}_2)_2\text{Co}(\text{bpy})_2]\text{ClO}_4$, 104013-22-1; *cis*- $[\text{Et}_2\text{Co}(\text{bpy})_2]\text{ClO}_4$, 91731-09-8; *cis*- $[\text{Me}_2\text{Co}(\text{bpy})_2]\text{ClO}_4$, 91731-08-7; HClO_4 , 7601-90-3; riboflavin-2',3',4',5'-tetraacetate, 752-13-6; riboflavin, 83-88-5; lumazine, 487-21-8; aminopterin, 54-62-6.

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New Niobium Complexes with Alkynes. 2. Tetranuclear Compounds with Nb-Nb Bonds, an Unprecedented Type of Tetracarbon Ligand, and Oxygen in a Rectangular Environment

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Abstract: Three compounds containing the tetranuclear anion $[\text{Nb}_4\text{OCl}_8\{(\text{PhC})_4\}_2]^{2-}$ have been prepared by (1) reduction of $\text{NbCl}_4(\text{THF})_2$ with Mg in the presence of PhCCPh , (2) by reduction of $\text{NbCl}_3(\text{PhCCPh})(\text{THF})_2$ with Na/Hg, and (3) by reduction of $\text{NbCl}_3(\text{PhCCPh})(\text{THF})_2$ with Na/Hg in the presence of PEt_3 . The anion consists of a planar, rectangular Nb_4 group ($\text{Nb}-\text{Nb} = 2.605$ (3) and 3.340 (3) Å) with an oxygen atom at the center (mean $\text{Nb}-\text{O} = 2.118$ (1) Å). The long $\text{Nb}\cdots\text{Nb}$ edges are doubly bridged by Cl atoms, and there is one terminal Cl atom on each Nb atom. A C-shaped $\text{PhC}-\text{C}(\text{Ph})\text{C}(\text{Ph})-\text{CPh}$ chain clasps each short $\text{Nb}-\text{Nb}$ edge at the middle and lies in a plane perpendicular to the Nb_4O plane. This C_4 chain and its mode of bonding to the pair of metal atoms has all C-C distances essentially equal at ca. 1.458 (9) Å. The four $\text{Nb}-\text{C}$ distances to terminal C atoms have an average value of 2.133 (16) Å, and the four $\text{Nb}-\text{C}$ distances to inner C atoms have an average value of 2.361 (5) Å. Crystallographic data for the three compounds are as follows: (1) $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]_2[\text{Nb}_4\text{OCl}_8\{(\text{PhC})_4\}_2] \cdot 6\text{THF}$, space group $P\bar{1}$, $a = 15.200$ (3) Å, $b = 15.515$ (4) Å, $c = 16.306$ (3) Å, $\alpha = 98.93$ (2)°, $\beta = 106.90$ (2)°, $\gamma = 102.97$ (2)°, $V = 3484$ (3) Å³, $Z = 1$; (2) $\text{Na}_2[\text{Nb}_4\text{OCl}_8\{(\text{PhC})_4\}_2] \cdot (\text{THF})_6(\text{C}_6\text{H}_6)_2$, space group $P\bar{1}$, $a = 11.802$ (3) Å, $b = 17.311$ (2) Å, $c = 22.966$ (4) Å, $\alpha = 98.91$ (1)°, $\beta = 91.61$ (1)°, $\gamma = 103.55$ (1)°, $V = 4496$ (3) Å³, $Z = 2$; (3) $(\text{HPEt}_3)_2[\text{Nb}_4\text{OCl}_8\{(\text{PhC})_4\}_2] \cdot 2\text{C}_6\text{H}_6$, space group $P\bar{1}$, $a = 12.831$ (1) Å, $b = 13.194$ (1) Å, $c = 14.219$ (1) Å, $\alpha = 68.040$ (8)°, $\beta = 66.616$ (7)°, $\gamma = 66.704$ (7)°, $V = 1961.0$ (4) Å³, $Z = 1$.

There have been previous reports of the formation of alkyne complexes of niobium and tantalum.¹⁻³ Most of these compounds

have discrete RCCR groups strongly bound to the metal atom, with $\text{M}-\text{C}$ distances in the range 2.03-2.07 Å, and it has been

proposed^{2,3} that the formation of these linkages corresponds to an increase of two units in the oxidation number of the metal atom, in a manner formally similar to the formation of $M=O$ or $M=NR$ bonds. Several examples of bridging alkynes are also known.^{2,3}

In the course of attempting to extend this type of chemistry, we have come upon some new niobium compounds that contain a tetranuclear anion, $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$. Within this anion there are two structural features that are unprecedented, so far as we know: (1) an oxygen atom that is rectangularly surrounded by four metal atoms and (2) planar, C-shaped $(PhC)_4$ units that lie perpendicular to the $M-M$ units with all carbon atoms bonded symmetrically to both metal atoms. The related questions of how to formulate the bonding of the $(PhC)_4$ units to the metal atoms and how best to assign formal oxidation states and Nb-Nb bond orders are not easy to answer unequivocally, but will be discussed.

Experimental Section

All manipulations were carried out under an atmosphere of argon. Standard Schlenk and vacuum line techniques were used. Solvents tetrahydrofuran (THF), benzene, and hexane were well dried and degassed before use in the usual way, as mentioned in the preceding paper.² Magnesium turnings were purchased from Fisher Scientific Co. Diphenylacetylene (PhCCPh) and triethylphosphine (PEt_3) were from Strem Chemical, Inc. $NbCl_5(THF)_2$ was prepared by the literature method.⁴ Preparations of sodium amalgam (1 mmol/mL) and $NbCl_3(PhCCPh)(THF)_2$ were also mentioned in the preceding paper. IR spectra were recorded on an IBM Instruments IR/44 Fourier transform spectrometer.

Preparation of $[Mg_2Cl_2(THF)_6]_2[Nb_4OCl_8\{(PhC)_4\}_2] \cdot 6THF$ (1). $NbCl_5(THF)_2$ (1.52 g, 4 mmol), Mg turnings (100 mg, 4.1 mmol), and PhCCPh (0.72 g, 4.0 mmol) were stirred overnight in THF (30 mL). Yellow $NbCl_5(THF)_2$ and Mg turnings gradually dissolved to form a dark purplish brown solution, which was then transferred to a long Schlenk tube and layered first with 10 mL of THF and then 30 mL of hexane. Brown platelike crystals started growing in a few days, but interdiffusion of the solvents and crystallization took about 1.5 months to complete. After about 3 weeks of standing, crystals were shaken off the tube walls and isolated by filtration through a fritted funnel. Longer standing caused the crystals to be contaminated by a black oily substance, which began to form on the walls in about 3 weeks. Yield: 0.7–0.9 g (ca. 30%).

IR (Nujol, NaCl plates): 1491 (w), 1450 (s), 1347 (w), 1270 (w), 1253 (w), 1074 (m), 1026 (s), 917 (m), 872 (s), 785 (w), 775 (m), 751 (w), 693 (s), 625 (s).

Some dark purple-red, block-shaped crystals (ca. 0.3 g) were also obtained by addition of 50 mL of hexane to the filtrate and several days of standing. The characterization of these crystals is in progress.

Preparation of $Na_2[Nb_4OCl_8\{(PhC)_4\}_2](THF)_6(C_6H_6)_2$ (2). $NbCl_3(PhCCPh)(THF)_2$ (0.52 g, 1 mmol) and sodium amalgam (1 mL, 1 mmol) were vigorously stirred in 20 mL of a solvent mixture (THF/ C_6H_6 , 1:1) for 24 h. The color of the solution changed rapidly from red to purplish brown. The solution was then filtered through a 4–5.5- μ m fritted funnel into a long Schlenk tube. Hexane (25 mL) was added and the solution was kept at room temperature for 1–2 weeks. After small brown, platelike crystals had developed on the walls, the tube was placed in a refrigerator at $-10^\circ C$ for about 2 weeks. During this period crystals grew to several millimeters in size and were then separated by decantation or filtration. Yield: ca. 0.10 g, 20%.

IR (Nujol, NaCl plates): 1489 (w), 1451 (s), 1180 (w), 1075 (m), 1046 (m), 1029 (m), 1014 (w), 966 (w), 914 (m), 893 (w), 853 (w), 845 (w), 785 (w), 777 (s), 694 (s), 635 (s), 611 (w).

We also tried to layer the filtrate first with THF and then with hexane and then allow the solvents to diffuse for several months. This led to a product that contained $[Nb_2\{(PhC)_4\}Cl_3(THF)_4]^+$ instead of Na^+ . A complete description of this compound will be published elsewhere.

Preparation of $(HPEt_3)_2[Nb_4OCl_8\{(PhC)_4\}_2] \cdot 2C_6H_6$ (3). $NbCl_3(PhCCPh)(THF)_2$ (0.52 g, 1 mmol), sodium amalgam (1 mL, 1 mmol), and PEt_3 (0.3 mL, 2 mmol) were stirred in 20 mL of a solvent mixture (THF/benzene, 1:1) for 24 h. The red color of the solution changed rapidly to dark brown along with the formation of a small quantity of a brown-black precipitate. The solution was filtered through a 4–5.5- μ m

Table I. Crystallographic Data

	1	2	3
formula	$Nb_2Cl_{14}Mg_4O_{19} \cdot C_{128}H_{184}$	$Nb_2Cl_8Na_2O_7 \cdot C_{92}H_{100}$	$Nb_4Cl_8P_2OC_{80} \cdot H_{84}$
formula wt	2992.10	2019.05	1778.76
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	15.200 (3)	11.802 (3)	12.831 (1)
b, Å	15.515 (4)	17.311 (2)	13.194 (1)
c, Å	16.306 (3)	22.966 (4)	14.219 (1)
α , deg	98.93 (2)	98.91 (1)	68.040 (8)
β , deg	106.90 (2)	91.61 (1)	66.616 (7)
γ , deg	102.97 (2)	103.55 (1)	66.704 (7)
V , Å ³	3484 (3)	4496 (3)	1961.0 (4)
Z	1	2	1
d_{calc} , g/cm ³	1.426	1.491	1.506
cryst size, mm	$0.4 \times 0.25 \times 0.2$	$0.50 \times 0.45 \times 0.08$	$0.53 \times 0.35 \times 0.20$
$\mu(Mo K\alpha)$, cm ⁻¹	6.534	7.754	9.024
data collection instrument	CAD-4	CAD-4	P3 equivalent
radiation (monochromated in incident beam)	Mo K α ($\lambda = 0.71073$ Å)	Mo K α ($\lambda = 0.71073$ Å)	Mo K α ($\lambda = 0.71073$ Å)
orientation	25, 30–32	25, 30–36	25, 32–36
reflections, no., range (2 θ , deg)			
temp, °C	-80	-80	20
scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
data col range (2 θ , deg)	4–46	4–46	4–46
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	9660, 7011	12457, 8494	5348, 4410
no. of parameters refined	703	1018	430
trans factors, max, min	0.9991, 0.7535	0.9984, 0.8661	0.9995, 0.9657
R^a	0.057	0.036	0.029
R_w^b	0.076	0.052	0.040
quality-of-fit indicator ^c	2.085	1.52	0.935
largest shift/esd, final cycle	0.30	0.51	0.22
largest peak, e/Å ³	1.285	0.739	0.565

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

fritted funnel into a long Schlenk tube and layered first with 5 mL of THF and then with 20 mL of hexane. After about a month of solvent interdiffusion, dark brown, well-formed rhombohedral crystals were produced and isolated by filtration. Yield: 0.2 g, 49%.

IR (Nujol, NaCl plates): 1488 (w), 1451 (s), 1263 (w), 1182 (w), 1102 (w), 1075 (m), 1043 (w), 1030 (m), 1014 (w), 965 (w), 913 (m), 893 (w), 863 (w), 843 (w), 785 (w), 776 (s), 749 (w), 695 (s), 635 (s).

We tried to relayer the filtrate with hexane in an attempt to increase the yield, but only amorphous precipitate was observed.

X-ray Crystallography. All of the crystals were air-sensitive and were examined and handled under a layer of well-degassed mineral oil on a small dish in a fritted funnel flushed constantly with a stream of argon. Crystals for data collection on a P3-equivalent diffractometer were attached with Apiezon grease under argon to cone-shaped ends of thin-walled capillaries, which were drawn to this shape on a flame and then sealed by flame. Routine procedures followed to determine the unit cell parameters and to collect intensity data were those standard in this laboratory.² The essentials are summarized in Table I. Corrections for the Lorentz factor, polarization, and absorption were applied.

$[Mg_2Cl_2(THF)_6]_2[Nb_4OCl_8\{(PhC)_4\}_2] \cdot 6THF$ (1). The coordinates of the Nb atoms and the surrounding Cl ligands were obtained from direct methods (SHELXS-86) in the acentric space group $P\bar{1}$ and then reassigned to the centric space group $P\bar{1}$. A combination of difference Fourier syntheses and least-squares refinements revealed the remaining non-hydrogen atoms. Two crystallographically independent THF molecules were found disordered around inversion centers, (0.5, 0.5, 0) and (0, 0.5, 0.5), respectively, in such a way that two atoms of each five-membered ring (C(61) and C(61)', C(65) and C(65)') were crystallographically equivalent and the remaining three atoms (O(10), C(62), and C(63), O(11), C(64), and C(66)) were located on two sets of positions related by the corresponding inversion center. It was not possible to identify

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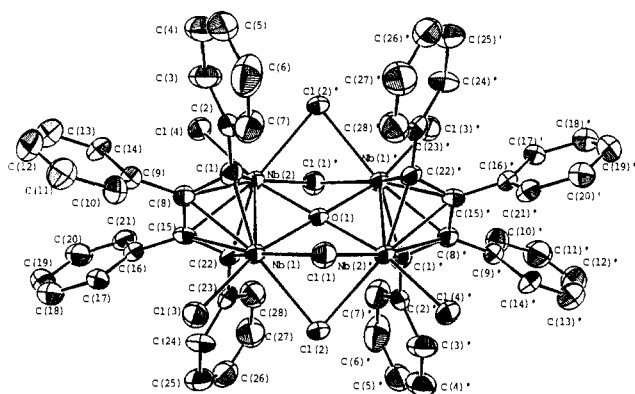


Figure 1. $[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]^{2-}$ ion as found in 1.

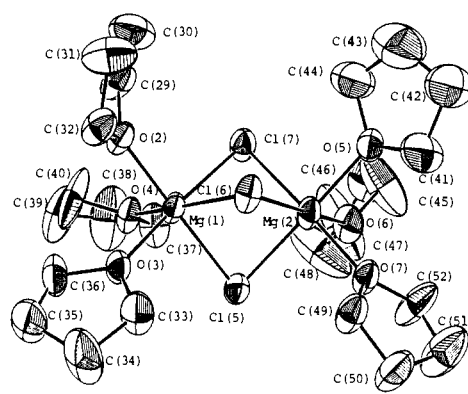


Figure 2. $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]^+$ ion as found in 1.

oxygen atoms of the THF solvent molecules. Before the final refinement, the atom having the lowest thermal parameter among the ring atoms, after they were all refined as carbon atoms, was designated as the oxygen atom. Except for these interstitial THF molecules, all other non-hydrogen atoms were refined anisotropically in the final refinement. The final difference Fourier map lacked any significant features. Among the remaining weak peaks, the highest six were around the Nb atoms.

$\text{Na}_2[\text{Nb}_4\text{OCl}_8(\text{PhC})_4] \cdot (\text{THF})_6(\text{C}_6\text{H}_6)_2$ (**2**). The approximate coordinates of the four crystallographically independent Nb atoms were obtained from a three-dimensional Patterson map. Subsequent least-squares refinements and difference Fourier syntheses located the rest of the non-hydrogen atoms. After these non-hydrogen atoms had been refined anisotropically to a convergence factor of 0.040, a difference Fourier map indicated the positions for all the phenyl hydrogen atoms and several hydrogen atoms of the THF ligand molecules and benzene solvent molecules. These phenyl hydrogen atoms were assigned thermal parameters that were 30% higher than the isotropic equivalent thermal parameters of the corresponding bonded carbon atoms and were included in the calculation of the structural factors in the final refinement. Hydrogen atoms on the THF molecules and the benzene molecules were omitted.

$(\text{HPEt}_3)_2[\text{Nb}_4\text{OCl}_8(\text{PhC})_4] \cdot 2\text{C}_6\text{H}_6$ (**3**). The positions of the two crystallographically independent Nb atoms were derived from a three-dimensional Patterson map, assuming that the space group was centric $P\bar{1}$. Alternate difference Fourier syntheses and least-squares refinements located all the remaining non-hydrogen atoms. After these atoms were refined anisotropically to a convergence factor of 0.042, a difference Fourier map revealed all the hydrogen atoms except three methylene hydrogen atoms of the phosphonium ion. The positions of these three hydrogen atoms were calculated, assuming the distances between the hydrogen atoms and the tetrahedrally hybridized methylene carbon atoms were 0.95 Å. The thermal parameters of the hydrogen atoms were set to values 30% higher than the isotropic equivalent thermal parameters of their bonded atoms, respectively. During the final refinement these hydrogen atoms, though not refined, were included in the calculation of the structural factors.

Results

Although the preparations of the three compounds differ in detail, they are essentially similar. In each case a niobium(IV) compound, $\text{NbCl}_4(\text{THF})_2$, or a niobium(V) compound, $\text{NbCl}_3(\text{PhCCPh})(\text{THF})_2$, is reduced in the presence of PhCCPh. In two cases, 1 mol of PhCCPh per mol of Nb is inherently present as part of the starting niobium compound, while in the other case it is introduced as such. In each case there is a different cation in the product, but the origin of the cation may be traced to one of the reactants.

With magnesium as the reducing agent, the product contains the $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]^+$ ion. This unusual cation was also formed in a previous reaction² where magnesium served as the reducing agent. In the preparation of **2**, where Na/Hg was used as the reducing agent, the cations in the product are Na^+ ions coordinated partly by Cl atoms and partly by THF molecules. In **3**, where PEt_3 was added to the reaction mixture (in hope that a product in which it is a ligand might be obtained), the cation present is HPEt_3^+ .

The dimerization of the PhCCPh molecules to form the PhCC(Ph)C(Ph)CPh chains occurs by a mechanism that is not known. However, dimerization,⁵ linear trimerization,⁶ and linear

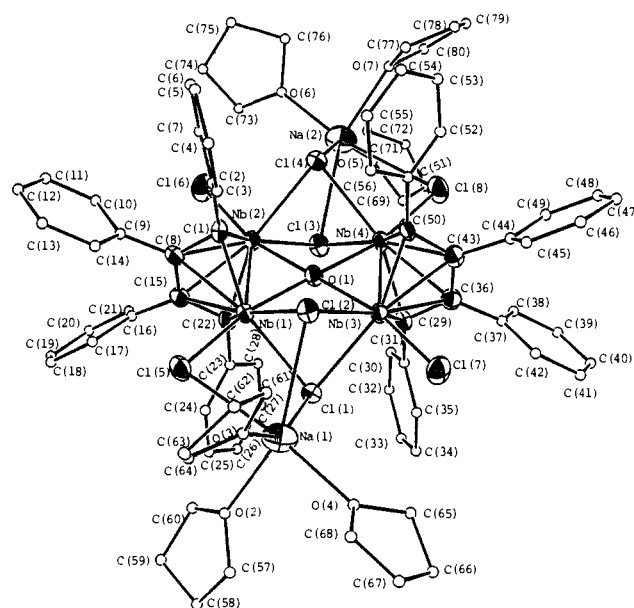


Figure 3. Asymmetric unit (excluding the benzene molecules) of **2**. The coordination of the Na^+ ions by Cl atoms of the anion and by THF molecules is shown.

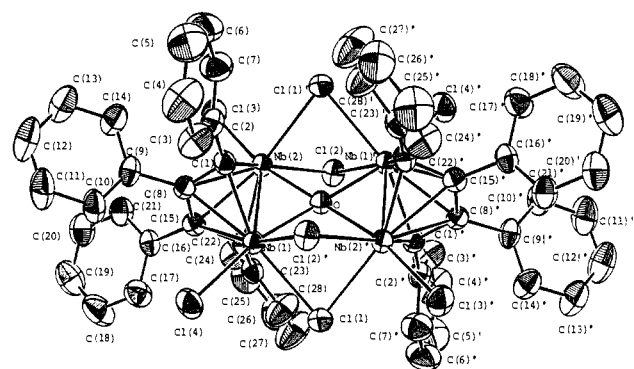


Figure 4. $[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]^{2-}$ ion as it occurs in 3.

polymerization⁷ of alkynes by transition metals (including those of group V) are already known to occur. The incorporation of oxygen atoms into compounds of the "oxophilic" early transition metals is also frequently observed though the source of the oxygen is rarely determined. Atmospheric O_2 and adventitious moisture

(5) See, for example: Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

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Table II. Selected Bond Distances (Å) and Angles (Deg) for $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]_2[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2 \cdot 6\text{THF}^a$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Nb(1)	Nb(2)	2.6082 (7)	Nb(2)	Cl(4)	2.428 (2)	Mg(1)	Cl(5)	2.491 (3)
Nb(1)	O(1)	2.1160 (6)	Nb(2)	C(1)	2.154 (7)	Mg(1)	Cl(6)	2.527 (3)
Nb(1)	Cl(1)	2.592 (2)	Nb(2)	C(8)	2.368 (7)	Mg(1)	Cl(7)	2.533 (3)
Nb(1)	Cl(2)	2.607 (2)	Nb(2)	C(15)	2.364 (6)	Mg(1)	O(2)	2.068 (5)
Nb(1)	Cl(3)	2.420 (2)	Nb(2)	C(22)	2.109 (5)	Mg(1)	O(3)	2.064 (6)
Nb(1)	C(1)	2.124 (6)	C(1)	C(2)	1.468 (9)	Mg(1)	O(4)	2.090 (6)
Nb(1)	C(8)	2.358 (7)	C(1)	C(8)	1.458 (10)	Mg(2)	Cl(5)	2.496 (3)
Nb(1)	C(15)	2.358 (8)	C(8)	C(9)	1.502 (11)	Mg(2)	Cl(6)	2.479 (3)
Nb(1)	C(22)	2.143 (7)	C(8)	C(15)	1.464 (10)	Mg(2)	Cl(7)	2.490 (3)
Nb(2)	O(1)	2.1193 (7)	C(15)	C(16)	1.516 (10)	Mg(2)	O(5)	2.104 (6)
Nb(2)	Cl(1)'	2.607 (2)	C(15)	C(22)	1.448 (11)	Mg(2)	O(6)	2.091 (5)
Nb(2)	Cl(2)'	2.598 (2)	C(22)	C(23)	1.483 (9)	Mg(2)	O(7)	2.070 (6)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
O(1)	Nb(1)	Cl(1)	79.72 (4)	C(15)	Nb(1)	C(22)	37.2 (3)	C(8)	Nb(2)	C(22)	70.1 (2)
O(1)	Nb(1)	Cl(2)	75.75 (4)	O(1)	Nb(2)	Cl(1)'	79.31 (5)	C(15)	Nb(2)	C(22)	37.2 (3)
O(1)	Nb(1)	Cl(3)	165.46 (6)	O(1)	Nb(2)	Cl(2)'	75.88 (4)	Nb(1)	O(1)	Nb(2)	76.03 (2)
O(1)	Nb(1)	C(1)	82.2 (2)	O(1)	Nb(2)	Cl(4)	165.97 (5)	Nb(1)	Cl(1)	Nb(2)	79.87 (6)
O(1)	Nb(1)	C(8)	105.9 (2)	O(1)	Nb(2)	C(1)	81.4 (2)	Nb(1)	Cl(2)	Nb(2)	79.74 (5)
O(1)	Nb(1)	C(15)	105.8 (2)	O(1)	Nb(2)	C(8)	105.4 (2)	Nb(1)	C(1)	Nb(2)	75.1 (2)
O(1)	Nb(1)	C(22)	81.6 (2)	O(1)	Nb(2)	C(15)	105.5 (2)	Nb(1)	C(1)	C(2)	145.9 (5)
Cl(1)	Nb(1)	Cl(2)	74.05 (6)	O(1)	Nb(2)	C(22)	82.3 (2)	Nb(2)	C(1)	C(2)	131.0 (4)
Cl(1)	Nb(1)	Cl(3)	90.16 (6)	Cl(1)'	Nb(2)	Cl(2)'	73.94 (6)	C(2)	C(1)	C(8)	121.6 (7)
Cl(1)	Nb(1)	C(1)	95.4 (2)	Cl(1)'	Nb(2)	Cl(4)	89.32 (7)	Nb(1)	C(8)	Nb(2)	67.0 (2)
Cl(1)	Nb(1)	C(8)	127.6 (2)	Cl(1)'	Nb(2)	C(1)	156.7 (2)	Nb(1)	C(8)	C(9)	144.8 (5)
Cl(1)	Nb(1)	C(15)	163.4 (2)	Cl(1)'	Nb(2)	C(8)	164.1 (2)	Nb(2)	C(8)	C(9)	147.5 (4)
Cl(1)	Nb(1)	C(22)	157.6 (2)	Cl(1)'	Nb(2)	C(15)	128.2 (2)	C(1)	C(8)	C(9)	117.7 (6)
Cl(2)	Nb(1)	Cl(3)	91.52 (6)	Cl(1)'	Nb(2)	C(22)	95.9 (2)	C(1)	C(8)	C(15)	125.1 (7)
Cl(2)	Nb(1)	C(1)	156.9 (2)	Cl(2)'	Nb(2)	Cl(4)	93.19 (6)	C(9)	C(8)	C(15)	117.2 (6)
Cl(2)	Nb(1)	C(8)	158.4 (2)	Cl(2)'	Nb(2)	C(1)	88.8 (2)	Nb(1)	C(15)	Nb(2)	67.0 (2)
Cl(2)	Nb(1)	C(15)	122.3 (2)	Cl(2)'	Nb(2)	C(8)	121.9 (2)	Nb(1)	C(15)	C(16)	147.6 (4)
Cl(2)	Nb(1)	C(22)	89.5 (2)	Cl(2)'	Nb(2)	C(15)	157.9 (2)	Nb(2)	C(15)	C(16)	144.8 (5)
Cl(3)	Nb(1)	C(1)	109.3 (2)	Cl(2)'	Nb(2)	C(22)	157.2 (2)	C(8)	C(15)	C(16)	116.3 (7)
Cl(3)	Nb(1)	C(8)	88.6 (2)	Cl(4)	Nb(2)	C(1)	107.5 (2)	C(8)	C(15)	C(22)	124.7 (7)
Cl(3)	Nb(1)	C(15)	86.8 (2)	Cl(4)	Nb(2)	C(8)	87.8 (2)	C(16)	C(15)	C(22)	119.0 (6)
Cl(3)	Nb(1)	C(22)	105.7 (2)	Cl(4)	Nb(2)	C(15)	87.9 (2)	Nb(1)	C(22)	Nb(2)	75.7 (2)
C(1)	Nb(1)	C(8)	37.5 (3)	Cl(4)	Nb(2)	C(22)	107.3 (2)	Nb(1)	C(22)	C(23)	131.4 (4)
C(1)	Nb(1)	C(15)	70.4 (3)	C(1)	Nb(2)	C(8)	37.2 (3)	Nb(2)	C(22)	C(23)	143.9 (5)
C(1)	Nb(1)	C(22)	94.2 (2)	C(1)	Nb(2)	C(15)	69.8 (3)	C(15)	C(22)	C(23)	122.3 (6)
C(8)	Nb(1)	C(15)	36.2 (2)	C(1)	Nb(2)	C(22)	94.3 (2)				
C(8)	Nb(1)	C(22)	69.7 (3)	C(8)	Nb(2)	C(15)	36.0 (2)				

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

are commonly recognized as possible sources, but solvents such as THF must also be considered.⁸ In the present work, THF is perhaps the most likely source, although we have no evidence, one way or the other.

We turn now to a presentation of the structural results. Atoms are numbered as indicated in Figures 1–4. The principal bond distances and bond angles for each compound are listed in Tables II–IV. We shall first describe the structure of the tetranuclear anion that occurs in all three compounds and then mention additional features, such as the structures of the accompanying cations that are peculiar to individual compounds.

Structure of the $[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2^{2-}$ Ion. Since the anion is essentially the same in all three compounds, we can discuss all three independent examples of this anion together. We first emphasize the high symmetry of the ion, with its central plane defined by the Nb_4OCl_4 set of atoms, by presenting a view along a line nearly coinciding with one of the three twofold axes that intersect at the position of the oxygen atom. The view is from slightly above this line so as to reveal, at least partially, all the atoms except for the five outer ones in each phenyl group. This is shown in Figure 5, which was drawn by using the data for 2, but essentially indistinguishable pictures are obtained for 1 and 3.

The ideal symmetry of the anion is D_{2h} , and in each compound the deviations from this are at the level of the esds. If this ideal symmetry is assumed, there are only ten different bond distances in the portion of the anion shown in Figure 5. In Table V, we list the mean value for each of these types in each structure as

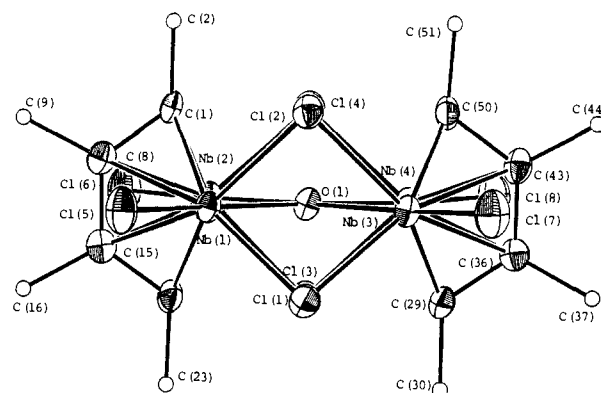


Figure 5. View of the central portion of the $[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2^{2-}$ ion drawn with the coordinates for 2.

well as the grand average for each distance averaged over all three structures. For example, in each structure we average over four equivalent Nb–O distances (though in the two centrosymmetric cases, 1 and 3, there are only two independent ones) and in the grand average we include all 12. In effect, crystallographically equivalent distances are nevertheless employed separately in computing the grand average and the mean deviation therefrom.

Particular Features of Each Structure. In 1 the cation is the binuclear $[\text{Mg}_2\text{Cl}_3(\text{THF})_6]^+$ ion, shown in Figure 2. This lies on a general position, but the inner structure, $\text{O}_3\text{MgCl}_3\text{MgO}_3$, has symmetry approximating closely to D_{3h} . Its structure is essentially the same as that previously reported² and requires no further discussion.

(8) Cotton, F. A.; Poli, R. *Polyhedron* 1987, 6, 2181.

Table III. Selected Bond Distances (Å) and Angles (Deg) for $\text{Na}_2[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2 \cdot (\text{THF})_6(\text{C}_6\text{H}_6)_2^a$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Nb(1)	Nb(2)	2.6018 (5)	Nb(3)	O(1)	2.115 (3)	C(1)	C(2)	1.470 (7)
Nb(1)	Cl(1)	2.625 (1)	Nb(3)	Cl(7)	2.400 (1)	C(1)	C(8)	1.473 (7)
Nb(1)	Cl(2)	2.618 (1)	Nb(3)	C(29)	2.157 (5)	C(8)	C(9)	1.497 (8)
Nb(1)	O(1)	2.116 (3)	Nb(3)	C(36)	2.350 (5)	C(8)	C(15)	1.457 (7)
Nb(1)	Cl(5)	2.426 (1)	Nb(3)	C(43)	2.363 (5)	C(15)	C(16)	1.499 (7)
Nb(1)	C(1)	2.111 (5)	Nb(3)	C(50)	2.130 (4)	C(15)	C(22)	1.450 (8)
Nb(1)	C(8)	2.359 (5)	Nb(4)	Cl(3)	2.623 (1)	C(22)	C(23)	1.480 (7)
Nb(1)	C(15)	2.362 (5)	Nb(4)	Cl(4)	2.624 (1)	C(29)	C(30)	1.475 (7)
Nb(1)	C(22)	2.149 (5)	Nb(4)	O(1)	2.122 (3)	C(29)	C(36)	1.459 (7)
Nb(2)	Cl(3)	2.615 (1)	Nb(4)	Cl(8)	2.423 (1)	C(36)	C(37)	1.507 (8)
Nb(2)	Cl(4)	2.634 (1)	Nb(4)	C(29)	2.103 (5)	C(36)	C(43)	1.466 (7)
Nb(2)	O(1)	2.115 (3)	Nb(4)	C(36)	2.349 (5)	C(43)	C(44)	1.497 (7)
Nb(2)	Cl(6)	2.404 (1)	Nb(4)	C(43)	2.368 (5)	C(43)	C(50)	1.460 (8)
Nb(2)	C(1)	2.159 (5)	Nb(4)	C(50)	2.158 (5)	C(50)	C(51)	1.468 (7)
Nb(2)	C(8)	2.361 (5)	Cl(1)	Na(1)	2.800 (3)	Na(1)	O(2)	2.348 (5)
Nb(2)	C(15)	2.358 (5)	Cl(2)	Na(1)	3.068 (2)	Na(1)	O(3)	2.286 (5)
Nb(2)	C(22)	2.122 (5)	Cl(3)	Na(2)	2.898 (2)	Na(1)	O(4)	2.376 (6)
Nb(3)	Nb(4)	2.6013 (5)	Cl(4)	Na(2)	2.852 (3)	Na(2)	O(5)	2.307 (5)
Nb(3)	Cl(1)	2.646 (1)	Cl(5)	Na(1)	3.065 (3)	Na(2)	O(6)	2.362 (5)
Nb(3)	Cl(2)	2.611 (1)	Cl(8)	Na(2)	3.127 (3)	Na(2)	O(7)	2.342 (5)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Nb(1)	Cl(2)	73.45 (4)	C(8)	Nb(2)	C(22)	70.1 (2)	C(29)	Nb(4)	C(50)	95.2 (2)
Cl(1)	Nb(1)	O(1)	77.23 (9)	C(15)	Nb(2)	C(22)	37.3 (2)	C(36)	Nb(4)	C(43)	36.2 (2)
Cl(1)	Nb(1)	Cl(5)	91.81 (4)	Cl(1)	Nb(3)	Cl(2)	73.24 (4)	C(36)	Nb(4)	C(50)	70.0 (2)
Cl(1)	Nb(1)	C(1)	158.1 (1)	Cl(1)	Nb(3)	O(1)	76.77 (8)	C(43)	Nb(4)	C(50)	37.3 (2)
Cl(1)	Nb(1)	C(8)	158.2 (1)	Cl(1)	Nb(3)	Cl(7)	91.73 (4)	Nb(1)	Cl(1)	Nb(3)	78.56 (3)
Cl(1)	Nb(1)	C(15)	122.2 (1)	Cl(1)	Nb(3)	C(29)	89.0 (1)	Nb(1)	Cl(2)	Nb(3)	79.32 (4)
Cl(1)	Nb(1)	C(22)	89.7 (1)	Cl(1)	Nb(3)	C(36)	121.6 (1)	Nb(2)	Cl(3)	Nb(4)	79.33 (4)
Cl(2)	Nb(1)	O(1)	79.65 (9)	Cl(1)	Nb(3)	C(43)	157.9 (1)	Nb(2)	Cl(4)	Nb(4)	78.99 (3)
Cl(2)	Nb(1)	Cl(5)	86.88 (4)	Cl(1)	Nb(3)	C(50)	158.5 (1)	Nb(1)	O(1)	Nb(2)	75.9 (1)
Cl(2)	Nb(1)	C(1)	95.5 (1)	Cl(2)	Nb(3)	O(1)	79.84 (9)	Nb(1)	O(1)	Nb(3)	104.1 (1)
Cl(2)	Nb(1)	C(8)	128.3 (1)	Cl(2)	Nb(3)	Cl(7)	87.63 (5)	Nb(1)	O(1)	Nb(4)	179.1 (2)
Cl(2)	Nb(1)	C(15)	164.0 (1)	Cl(2)	Nb(3)	C(29)	156.3 (1)	Nb(2)	O(1)	Nb(3)	179.7 (2)
Cl(2)	Nb(1)	C(22)	157.2 (2)	Cl(2)	Nb(3)	C(36)	164.8 (1)	Nb(2)	O(1)	Nb(4)	104.2 (1)
O(1)	Nb(1)	Cl(5)	164.57 (9)	Cl(2)	Nb(3)	C(43)	128.8 (1)	Nb(3)	O(1)	Nb(4)	75.7 (1)
O(1)	Nb(1)	C(1)	82.3 (2)	Cl(2)	Nb(3)	C(50)	96.7 (1)	Nb(1)	C(1)	Nb(2)	75.1 (2)
O(1)	Nb(1)	C(8)	105.8 (1)	O(1)	Nb(3)	Cl(7)	164.96 (9)	Nb(1)	C(1)	C(2)	141.8 (3)
O(1)	Nb(1)	C(15)	105.7 (1)	O(1)	Nb(3)	C(29)	80.9 (2)	Nb(2)	C(1)	C(2)	135.5 (3)
O(1)	Nb(1)	C(22)	81.8 (2)	O(1)	Nb(3)	C(36)	105.7 (1)	C(2)	C(1)	C(8)	121.9 (5)
Cl(5)	Nb(1)	C(1)	106.6 (1)	O(1)	Nb(3)	C(43)	106.2 (1)	Nb(1)	C(8)	Nb(2)	66.9 (2)
Cl(5)	Nb(1)	C(8)	88.4 (1)	O(1)	Nb(3)	C(50)	82.8 (2)	Nb(1)	C(8)	C(9)	146.3 (3)
Cl(5)	Nb(1)	C(15)	89.3 (1)	Cl(7)	Nb(3)	C(29)	108.9 (1)	Nb(2)	C(8)	C(9)	145.5 (3)
Cl(5)	Nb(1)	C(22)	109.4 (1)	Cl(7)	Nb(3)	C(36)	88.6 (1)	C(1)	C(8)	C(9)	116.2 (4)
C(1)	Nb(1)	C(8)	38.0 (2)	Cl(7)	Nb(3)	C(43)	88.1 (1)	C(1)	C(8)	C(15)	125.0 (5)
C(1)	Nb(1)	C(15)	70.8 (2)	Cl(7)	Nb(3)	C(50)	107.1 (1)	C(9)	C(8)	C(15)	118.8 (5)
C(1)	Nb(1)	C(22)	94.9 (2)	C(29)	Nb(3)	C(36)	37.5 (2)	Nb(1)	C(15)	Nb(2)	66.9 (1)
C(8)	Nb(1)	C(15)	36.0 (2)	C(29)	Nb(3)	C(43)	70.2 (2)	Nb(1)	C(15)	C(16)	146.8 (3)
C(8)	Nb(1)	C(22)	69.7 (2)	C(29)	Nb(3)	C(50)	94.5 (2)	Nb(2)	C(15)	C(16)	145.3 (3)
C(15)	Nb(1)	C(22)	37.1 (2)	C(36)	Nb(3)	C(43)	36.3 (2)	C(8)	C(15)	C(16)	117.7 (5)
Cl(3)	Nb(2)	Cl(4)	73.17 (4)	C(36)	Nb(3)	C(50)	70.4 (2)	C(8)	C(15)	C(22)	125.3 (5)
Cl(3)	Nb(2)	O(1)	80.26 (9)	C(43)	Nb(3)	C(50)	37.5 (2)	C(16)	C(15)	C(22)	117.0 (4)
Cl(3)	Nb(2)	Cl(6)	88.25 (5)	Cl(3)	Nb(4)	Cl(4)	73.21 (4)	Nb(1)	C(22)	Nb(2)	75.1 (2)
Cl(3)	Nb(2)	C(1)	157.6 (1)	Cl(3)	Nb(4)	O(1)	79.95 (9)	Nb(1)	C(22)	C(23)	128.7 (3)
Cl(3)	Nb(2)	C(8)	163.1 (1)	Cl(3)	Nb(4)	Cl(8)	88.38 (4)	Nb(2)	C(22)	C(23)	146.1 (4)
Cl(3)	Nb(2)	C(15)	127.5 (1)	Cl(3)	Nb(4)	C(29)	95.3 (1)	C(15)	C(22)	C(23)	123.6 (4)
Cl(3)	Nb(2)	C(22)	95.6 (1)	Cl(3)	Nb(4)	C(36)	127.9 (1)	Nb(3)	C(29)	Nb(4)	75.3 (2)
Cl(4)	Nb(2)	O(1)	76.28 (8)	Cl(3)	Nb(4)	Cl(43)	163.8 (1)	Nb(3)	C(29)	C(30)	134.0 (3)
Cl(4)	Nb(2)	Cl(6)	90.25 (4)	Cl(3)	Nb(4)	C(50)	157.6 (1)	Nb(4)	C(29)	C(30)	142.2 (3)
Cl(4)	Nb(2)	C(1)	90.3 (1)	Cl(4)	Nb(4)	O(1)	76.38 (9)	C(30)	C(29)	C(36)	123.1 (5)
Cl(4)	Nb(2)	C(8)	123.4 (1)	Cl(4)	Nb(4)	Cl(8)	91.50 (5)	Nb(3)	C(36)	Nb(4)	67.2 (2)
Cl(4)	Nb(2)	C(15)	159.3 (1)	Cl(4)	Nb(4)	C(29)	156.9 (1)	Nb(3)	C(36)	C(37)	145.3 (3)
Cl(4)	Nb(2)	C(22)	157.3 (1)	Cl(4)	Nb(4)	C(36)	158.9 (1)	Nb(4)	C(36)	C(37)	146.2 (3)
O(1)	Nb(2)	Cl(6)	164.31 (9)	Cl(4)	Nb(4)	C(43)	122.7 (1)	C(29)	C(36)	C(37)	116.3 (4)
O(1)	Nb(2)	C(1)	81.2 (2)	Cl(4)	Nb(4)	C(50)	89.7 (1)	C(29)	C(36)	C(43)	125.8 (5)
O(1)	Nb(2)	C(8)	105.8 (1)	O(1)	Nb(4)	Cl(8)	165.13 (9)	C(37)	C(36)	C(43)	117.9 (4)
O(1)	Nb(2)	C(15)	105.8 (1)	O(1)	Nb(4)	C(29)	82.0 (2)	Nb(3)	C(43)	Nb(4)	66.7 (1)
O(1)	Nb(2)	C(22)	82.4 (2)	O(1)	Nb(4)	C(36)	105.5 (1)	Nb(3)	C(43)	C(44)	144.5 (3)
Cl(6)	Nb(2)	C(1)	107.2 (1)	O(1)	Nb(4)	C(43)	105.8 (1)	Nb(4)	C(43)	C(44)	148.2 (3)
Cl(6)	Nb(2)	C(8)	88.2 (1)	O(1)	Nb(4)	C(50)	82.0 (2)	C(36)	C(43)	C(44)	117.3 (5)
Cl(6)	Nb(2)	C(15)	89.6 (1)	Cl(8)	Nb(4)	C(29)	108.4 (1)	C(36)	C(43)	C(50)	124.5 (5)
Cl(6)	Nb(2)	C(22)	109.5 (1)	Cl(8)	Nb(4)	C(36)	89.0 (1)	C(44)	C(43)	C(50)	118.1 (4)
C(1)	Nb(2)	C(8)	37.7 (2)	Cl(8)	Nb(4)	C(43)	87.9 (1)	Nb(3)	C(50)	Nb(4)	74.7 (2)
C(1)	Nb(2)	C(15)	70.1 (2)	Cl(8)	Nb(4)	C(50)	106.9 (1)	Nb(3)	C(50)	C(51)	146.0 (4)
C(1)	Nb(2)	C(22)	94.4 (2)	C(29)	Nb(4)	C(36)	37.8 (2)	Nb(4)	C(50)	C(51)	127.6 (3)
C(8)	Nb(2)	C(15)	36.0 (2)	C(29)	Nb(4)	C(43)	71.0 (2)	C(43)	C(50)	C(51)	125.3 (4)

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

Table IV. Important Bond Distances (Å) and Angles (Deg) for $(\text{HPEt}_3)_2[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2 \cdot 2\text{C}_6\text{H}_6^a$

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
Nb(1)	Nb(2)	2.6066 (5)	Nb(1)	C(22)	2.126 (3)	Nb(2)	C(22)	2.139 (4)
Nb(1)	Cl(1)	2.6226 (11)	Nb(2)	Cl(1)'	2.6064 (8)	C(1)	C(2)	1.485 (4)
Nb(1)	Cl(2)'	2.6255 (9)	Nb(2)	Cl(2)	2.6149 (8)	C(1)	C(8)	1.448 (4)
Nb(1)	Cl(4)	2.4266 (10)	Nb(2)	Cl(3)	2.4325 (13)	C(8)	C(9)	1.510 (4)
Nb(1)	O	2.1010 (3)	Nb(2)	O	2.1391 (4)	C(8)	C(15)	1.476 (4)
Nb(1)	C(1)	2.154 (4)	Nb(2)	C(1)	2.108 (3)	C(15)	C(16)	1.498 (4)
Nb(1)	C(8)	2.354 (4)	Nb(2)	C(8)	2.359 (3)	C(15)	C(22)	1.448 (5)
Nb(1)	C(15)	2.372 (4)	Nb(2)	C(15)	2.366 (3)	C(22)	C(23)	1.487 (4)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Cl(1)	Nb(1)	Cl(2)'	73.76 (3)	Cl(1)'	Nb(2)	Cl(3)	89.80 (4)	Nb(1)	O	Nb(2)	75.86 (1)
Cl(1)	Nb(1)	Cl(4)	88.16 (4)	Cl(1)'	Nb(2)	O	78.97 (3)	Nb(1)	C(1)	Nb(2)	75.4 (1)
Cl(1)	Nb(1)	O	79.25 (2)	Cl(1)'	Nb(2)	C(1)	94.29 (8)	Nb(1)	C(1)	C(2)	136.0 (3)
Cl(1)	Nb(1)	C(1)	158.05 (8)	Cl(1)'	Nb(2)	C(8)	127.07 (7)	Nb(2)	C(1)	C(2)	140.2 (3)
Cl(1)	Nb(1)	C(8)	162.71 (7)	Cl(1)'	Nb(2)	C(15)	163.38 (7)	C(2)	C(1)	C(8)	122.5 (3)
Cl(1)	Nb(1)	C(15)	126.57 (8)	Cl(1)'	Nb(2)	C(22)	156.9 (1)	Nb(1)	C(8)	Nb(2)	67.16 (8)
Cl(1)	Nb(1)	C(22)	94.9 (1)	Cl(2)	Nb(2)	Cl(3)	92.83 (3)	Nb(1)	C(8)	C(9)	145.6 (3)
Cl(2)'	Nb(1)	Cl(4)	89.95 (3)	Cl(2)	Nb(2)	O	76.48 (3)	Nb(2)	C(8)	C(9)	146.4 (3)
Cl(2)'	Nb(1)	O	76.85 (2)	Cl(2)	Nb(2)	C(1)	157.3 (1)	C(1)	C(8)	C(9)	117.6 (3)
Cl(2)'	Nb(1)	C(1)	90.99 (9)	Cl(2)	Nb(2)	C(8)	158.72 (8)	C(1)	C(8)	C(15)	125.4 (3)
Cl(2)'	Nb(1)	C(8)	123.21 (7)	Cl(2)	Nb(2)	C(15)	122.34 (7)	C(9)	C(8)	C(15)	117.0 (2)
Cl(2)'	Nb(1)	C(15)	159.62 (8)	Cl(2)	Nb(2)	C(22)	89.68 (8)	Nb(1)	C(15)	Nb(2)	66.76 (8)
Cl(2)'	Nb(1)	C(22)	157.86 (8)	Cl(3)	Nb(2)	O	166.18 (2)	Nb(1)	C(15)	C(16)	144.5 (3)
Cl(4)	Nb(1)	O	163.81 (4)	Cl(3)	Nb(2)	C(1)	106.9 (1)	Nb(2)	C(15)	C(16)	148.3 (3)
Cl(4)	Nb(1)	C(1)	107.92 (8)	Cl(3)	Nb(2)	C(8)	88.2 (1)	C(8)	C(15)	C(16)	116.8 (3)
Cl(4)	Nb(1)	C(8)	88.57 (9)	Cl(3)	Nb(2)	C(15)	87.9 (1)	C(8)	C(15)	C(22)	124.0 (3)
Cl(4)	Nb(1)	C(15)	89.41 (9)	Cl(3)	Nb(2)	C(22)	107.8 (1)	C(16)	C(15)	C(22)	119.2 (3)
Cl(4)	Nb(1)	C(22)	109.02 (9)	O	Nb(2)	C(1)	82.2 (1)	Nb(1)	C(22)	Nb(2)	75.34 (9)
O	Nb(1)	C(1)	81.99 (7)	O	Nb(2)	C(8)	105.0 (1)	Nb(1)	C(22)	C(23)	144.3 (4)
O	Nb(1)	C(8)	106.43 (8)	O	Nb(2)	C(15)	105.2 (1)	Nb(2)	C(22)	C(23)	128.4 (3)
O	Nb(1)	C(15)	106.24 (8)	O	Nb(2)	C(22)	81.2 (1)	C(15)	C(22)	C(23)	125.2 (3)
O	Nb(1)	C(22)	82.41 (8)	Nb(1)	Cl(1)	Nb(2)'	79.52 (3)				
Cl(1)'	Nb(2)	Cl(2)	74.20 (2)	Nb(1)	Cl(2)'	Nb(2)'	79.32 (2)				

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

Table V. Average Bond Lengths (Å) in the $[\text{Nb}_4\text{OCl}_8(\text{PhC})_4]_2^{2-}$ Ions in Compounds **1**, **2**, and **3**^a

bond type	av bond length			grand average
	1	2	3	
C–C, outer	1.453 [5]	1.461 [6]	1.448 [0]	1.458 [7]
C–C, inner	1.464 (10)	1.462 [5]	1.476 (4)	1.467 [6]
C(Ph) to C(term)	1.476 [8]	1.473 [4]	1.486 [1]	1.478 [7]
C(Ph) to C(inner)	1.509 [7]	1.500 [4]	1.504 [6]	1.504 [6]
Nb to C(term)	2.133 [16]	2.136 [20]	2.132 [15]	2.133 [16]
Nb to C(inner)	2.362 [4]	2.359 [5]	2.363 [6]	2.361 [5]
Nb–Nb (short)	2.6082 [7]	2.6015 [3]	2.6066 (5)	2.6054 [26]
Nb–O	2.1177 [17]	2.117 [3]	2.120 [19]	2.118 [1]
Nb–Cl(term)	2.424 [4]	2.413 [11]	2.430 [3]	2.422 [8]
Nb–Cl(bridge)	2.601 [6]	2.625 [8]	2.617 [7]	2.614 [7]

^a Parentheses denote esd of an individual value; square brackets denote mean deviation from the unweighted arithmetic mean; each is given for the last significant figure.

In **2** the sodium ions lie close to the long edges of the tetranuclear anion and are coordinated by the two bridging chlorine atoms and one terminal chlorine atom, which lie at three mutually cis vertices of a very distorted octahedron about each Na^+ ion. These Cl–Na–Cl angles range from 64.4 to 76.3° with a mean value of 70.2°. The Na–Cl distances range from 2.80 to 3.13 Å, with a mean value of 2.97 Å. The octahedra are completed by three THF molecules arranged with O–Na–O angles from 90.3 to 99.6° (mean = 93.5°) and Na–O distances from 2.29 to 2.38 Å (mean = 2.34 Å). For complete results on the coordination of the sodium ions, the supplementary material should be consulted. Despite the direct attachment of the Na^+ ions to the anion in a manner that tends to lower its symmetry from D_{2h} to C_{2h} , the anion in **2** is essentially identical with those in **1** and **3**, as the data in Table V show.

The HPEt_3^+ ions in **3** have a normal appearance with P–C distances of 1.81, 1.74, and 1.78 Å, each with an esd of ca. 0.02 Å.

Discussion

The Central Oxygen Atom. The central oxygen atom in this anion has an environment that is without precedent, so far as we know. It is surrounded by only four metal atoms which are coplanar and form a rectangle. The only other case we know of in which an oxygen atom has four coplanar metal atoms as neighbors also involves niobium, namely, NbO . However, in this case the arrangement is rigorously square. The Nb–O distances, 2.11 Å in NbO and 2.12 Å in our anion, are the same, however, within the experimental uncertainties.

The Ph_4C_4 Groups. We have been unable to discover any prior example of this sort of moiety related in this way to a pair of metal atoms. It should be emphasized that all C–C distances involving backbone carbon atoms, namely, the C(Ph)–C as well as the backbone C–C distances, are in the range, 1.45–1.52 Å, indicative of single bonds between sp^2 -hybridized carbon atoms. If the Ph_4C_4 skeleton is first assembled with such a set of seven C–C σ bonds, then each terminal carbon atom still has one in-plane sp^2 electron and each of the four backbone atoms has a π electron. In order not to increase the C–C bond order, we must assume that all of these six electrons are diverted into Nb–C bonding orbitals.

Electronic Structure of the Anion. Given the unprecedented nature of the Nb_2C_4 components of the structure, the problem of formulating the electronic structure of the tetranuclear anion is a difficult one. The unusual geometry about the central oxygen atom also introduces a problem. The following description of the bonding is not proposed dogmatically, and may eventually require revision, but it does not seem to have any glaring inadequacies.

The tetranuclear anion consists of two halves, each containing a direct Nb–Nb bond and united by four shared Cl atoms and a shared oxygen atom. Whether these halves or closely related derivatives are actually capable of independent existence is not known, although we are at present attempting to find out. For the purpose of discussing the bonding, we can certainly discuss only one of these halves, which we shall regard as a dinuclear species having approximately the design of a face-sharing biotetrahedron. On that basis, the six terminal ligands are all chlorine atoms and the bridging ligands are one oxygen atom and the two

halves of the PhC-C(Ph)-C(Ph)-CPh group. We can write this as $[\text{Cl}_3\text{Nb}(\mu\text{-O})(\mu\text{-C}_4\text{Ph}_4)\text{NbCl}_3]^{4-}$, and we then focus on the question of how to distribute electrons in the $[\text{Nb}_2(\text{C}_4\text{Ph}_4)]^{4+}$ unit.

We propose treating the C_4Ph_4 ligand as though it acquires two electrons from the metal atoms and thus becomes a coupled pair of four-electron donors, formally analogous to two Cl^- ions. We thus regard the $[\text{Cl}_3\text{Nb}(\mu\text{-O})(\text{C}_4\text{Ph}_4)\text{NbCl}_3]^{4-}$ ion as formally analogous to a $[\text{Cl}_3\text{Nb}(\mu\text{-O})(\mu\text{-Cl})_2\text{NbCl}_3]^{4-}$ ion. We then have the niobium atoms in oxidation state III, and these two d^2 metal ions can form a Nb=Nb double bond. The existence of such a bond is consistent with the Nb-Nb distance of 2.61 Å. In the $\text{Cl}_2(\text{Me}_2\text{S})\text{Nb}(\mu\text{-SMe}_2)(\mu\text{-Cl})_2\text{NbCl}_2(\text{SMe}_2)$ molecules, where the bridging groups are larger, the Nb-Nb distance is 2.68 Å.⁹

When seen in this simplistic way, the structure and bonding in the $[\text{Nb}_4\text{OCl}_8\{\text{PhC}\}_2]^{2-}$ ion become qualitatively under-

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standable, but it must, of course, still be recognized that the very existence of this species with its two remarkable (and apparently unprecedented) structural features is something that was not (and probably could not have been) predicted.

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Supplementary Material Available: Tables of atomic positional parameters and equivalent isotropic displacement parameters for 1-3, tables of anisotropic displacement parameters, complete tables of bond distances and angles for non-hydrogen atoms, tables of positional and isotropic thermal parameters of hydrogen atoms and the corresponding bond distances and angles, stereoviews of the unit cell contents, and a figure showing disorder modes of the THF solvent molecules (51 pages); tables of observed and calculated structure factors (102 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Biological Activity of *cis*-Diammineplatinum(II) Complexes of the DNA Intercalators 9-Aminoacridine and Chloroquine

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Abstract: The anticancer drug *cis*-diamminedichloroplatinum(II) reacts with the DNA intercalators 9-aminoacridine (9-AA) and chloroquine (CQ) to form the novel complexes *cis*-[Pt(NH₃)₂(N9-9-AA)Cl](NO₃) (1), *cis*-[Pt(NH₃)₂(N9-9-AA)₂](NO₃)₂ (2), and *cis*-[Pt(NH₃)₂(N1-HCQ)Cl](NO₃)₂ (3). Interestingly, platinum coordinates to the deprotonated exocyclic amino group of 9-aminoacridine in 1 and 2, with the proton being transferred to the endocyclic nitrogen atom N10, as revealed by X-ray crystal structure determinations. As a consequence, the acridine rings are asymmetrically positioned with respect to the platinum coordination plane, resulting in short (2.390 Å in 1·MeOH and 2.458 Å in 2·MeOH) nonbonded contacts between platinum and one of the acridine ring protons (H1). NMR spectroscopic studies demonstrated the persistence of this structure in DMF solutions of the complexes, the short Pt-H1 distances resulting in paramagnetic deshielding of the H1 protons by approximately 3.32 (1) and 2.25 (2) ppm. The Pt-H1 interactions are not agostic, however, since no reduction in the magnitude of ¹J_{C1-H1} coupling is observed. In contrast to 9-aminoacridine, chloroquine preferentially coordinates to platinum via the less hindered endocyclic N1 ring nitrogen atom. Since both diastereoisomers of 3 are observed by ¹H NMR spectroscopy, rotation about the Pt-N1 bond is slow on the NMR time scale. Complexes of the general formula *cis*-[Pt(NH₃)₂(INT)Cl]⁺⁺, where INT is a DNA intercalator such as 9-AA or CQ, have the potential to bind both covalently and intercalatively to DNA and, consequently, are potential antitumor agents. Complexes 1 and 3 were determined to be extremely toxic in animal screens, however, precluding their use as drugs.

cis-Diamminedichloroplatinum(II), *cis*-DDP, and other platinum antitumor drugs coordinate bifunctionally to DNA, inhibiting replication and transcription.¹ Biological activity in these complexes usually requires two leaving groups coordinated to platinum in *cis* positions.² Anticancer activity has also been observed in complexes of general formula *cis*-[Pt(NH₃)₂(L)Cl]⁺, where L is an N-bound pyridine, purine, pyrimidine, or piperidine ligand.³ This unanticipated discovery raised the possibility that the aromatic ligand L might intercalate between DNA base pairs adjacent to the site of platinum coordination, forming a pseudobifunctional

adduct capable of inhibiting replication.⁴ Such simultaneous intercalation and covalent coordination to DNA has been demonstrated in other classes of DNA-binding drugs such as psoralens⁵ and is also a preferred mode of binding in covalent complexes formed on DNA by *cis*-DDP and ethidium bromide.⁶

The possibility that aromatic ligands might bind intercalatively upon coordination of *cis*-[Pt(NH₃)₂(L)Cl]⁺ to DNA led us to investigate the chemistry and biological activity of analogous compounds in which L is an established intercalator. The in-

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