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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding,
Texas A&M University, College Station, Texas 77843

New Niobium Complexes with Alkynes. 4. A Compound Containing both an Oxo-Centered Tetrameric Anion and a Related Dinuclear Cation

F. Albert Cotton* and Maoyu Shang

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A compound with the formula $[Nb_2(\mu\text{-}Ph_4C_4)(\mu\text{-}Cl)Cl_2(THF)_4]_2[Nb_4(\mu\text{-}Ph_4C_4)_2(\mu_4\text{-}O)(\mu\text{-}Cl)_4Cl_4]\cdot 3C_6H_6\cdot 4THF$ has been prepared and characterized. Crystal data are as follows: space group, $P2_1/c$; $a = 23.162$ (5) Å, $b = 15.235$ (4) Å, $c = 26.274$ (5) Å, $\beta = 111.91$ (2)°, $V = 8602$ (4) Å^3, and $Z = 2$. The tetranuclear anion is the same one previously described in other compounds with simpler cations. The cations in this case can be regarded as modified halves of the anion. They contain the same type of μ-PhCC(Ph)C(Ph)CPh ligand and have internal dimensions similar to those of each half of the anion. Given the structural relationship of the cation and anion, several hypotheses concerning their chemical relationship are considered.

Introduction

We have recently reported reactions of niobium(V) chloride with reducing agents in the presence of diphenylacetylene.[1-3] Some of these lead to the formation of an unprecedented tetranuclear anion containing the PhCC(Ph)C(Ph)CPh unit.[2] We addressed the question of the bonding in this anion by treating it as two halves, joined by sharing four bridging chlorine atoms and an oxygen atom (Figure 1). The bonding across the μ-Cl and μ_4-O bridges was considered to be relatively loose as compared to strong Nb-Nb multiple bonding and extensive multicenter bonding of the metal atoms to the unique C-shaped Ph_4C_4 units that form bridges between them.[4]

The clear implication of such a description is that the sturdy dinuclear unit making up each half of the tetranuclear anion ought to be capable of existence on its own, provided additional ligands, capable of supplanting the bridging ligands, are present. Concepts of this kind are often possible in structural chemistry, but despite their reasonableness and plausibility, they remain impossible to realize in the laboratory. In this paper, we report the preparation and characterization of a compound that contains both the full tetranuclear anion and, as the counterions, a pair of dinuclear cations that correspond closely to the halves of the anion.

Experimental Section

Synthetic work was carried out in 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 stored over molecular sieves and freshly distilled over Na-K-benzophenone before use. Sodium amalgam, prepared by dissolving 0.46 g of sodium in 20 mL of mercury, was assumed to have a concentration of 1 mmol of Na/mL, and handled by a syringe. $NbCl_3(PhCCPh)(THF)_2$ was prepared by using $NbCl_4(THF)_2$, sodium amalgam, and diphenylacetylene (PhCCPh) in THF, as mentioned in a previous paper.[1] IR spectra were recorded on a Perkin-Elmer 783 infrared spectrophotometer.

Preparation. $NbCl_3(PhCCPh)(THF)_2$ (0.52 g, 1 mmol) and sodium amalgam (1 mL, 1 mmol) were stirred vigorously in 15 mL of a solvent mixture (THF/C_6H_6, 1:2) for 24 h. The red color of the solution changed rapidly to purplish brown along with the formation of a small quantity of brown precipitate. The solution was filtered through a 4.5-5.5-μm fritted funnel into a Schlenk tube, layered with 5 mL of THF and then 25 mL of hexane, and then kept undisturbed at room temperature for about 3 months. Brown platelike crystals (several millimeters long) were shaken off the tube walls and washed free of accompanying brown powder by stirring up the powder precipitate and decanting the solvent. A 15-mL portion of hexane was added and the procedure repeated. When the crystals, which are air-sensitive, were crushed to fine powder, the color changed from brown to purple. Yield: 0.15 g, ca. 30%.

IR (Nujol mull, mineral oil, KBr plates, cm^{-1}): 1591 (m), 1445 (s), 1070 (m), 1025 (m), 1003 (m), 970 (w), 961 (w), 912 (m), 888 (w), 842 (s), 770 (s), 693 (s), 628 (s), 552 (m).

X-ray Crystallography. The crystals were handled under a layer of well-degassed mineral oil in an atmosphere of argon. They were attached inside thin-walled capillaries by Apiezon T grease and the capillaries sealed by flame.

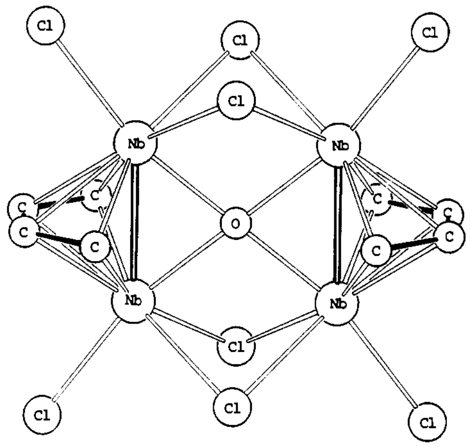

Figure 1. Two dinuclear units joined to form a tetranuclear anion by sharing four bridging chlorine atoms and an oxygen atom. Phenyl groups are omitted for clarity.

Table I. Crystal Data for $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]_2[Nb_4OCl_8\{(PhC)_4\}_2]\cdot 3C_6H_6\cdot 4THF$

compound	$[Nb_2Cl_3\{(PhC)_4\}(THF)_4]_2[Nb_4OCl_8\text{-}\{(PhC)_4\}_2]\cdot 3C_6H_6\cdot 4THF$
formula	$Nb_8Cl_{14}O_{13}C_{178}H_{194}$
fw	3781.11
space group	$P2_1/c$
a, Å	23.162 (5)
b, Å	15.235 (4)
c, Å	26.274 (5)
α, deg	90.0
β, deg	111.91 (2)
γ, deg	90.0
V, Å^3	8602 (4)
Z	2
d_{calc}, g/cm^3	1.460
μ(Mo Kα), cm^{-1}	7.660
radiation (monochromated in incident beam)	Mo Kα ($\lambda_\alpha = 0.71073$ Å)
temp, °C	20
trans factors: max; min	1.0000; 0.8719
R^a	0.065
$R_w{}^b$	0.090

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

Standard crystallographic procedures were followed.[5] Lorentz and polarization corrections and empirical absorption corrections based upon azimuthal scans were applied. An average loss of intensity of 2.7% was observed for the three standard reflections during the data collection, and an appropriate anisotropic decay correction was applied.

Direct methods (SHELXS-86) revealed the positions for all the four crystallographically independent Nb atoms and their surrounding Cl

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(1) Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 508.
(2) Cotton, F. A.; Shang, M. *J. Am. Chem. Soc.* **1990**, *112*, 1584.
(3) Cotton, F. A.; Shang, M. *Inorg. Chem.*, preceding paper in this issue.
(4) Cotton, F. A.; Feng, X. *Inorg. Chem.*, submitted for publication.

(5) (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 II. Positional and Equivalent Isotropic Displacement Parameters for $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]_2[Nb_4OCl_8\{(PhC)_4\}_2]\cdot3C_6H_6\cdot4THF$

atom	x	y	z	B,[a] Å^2	atom	x	y	z	B,[a] Å^2
Nb(1)	0.16621 (5)	0.08808 (8)	0.06182 (5)	3.49 (3)	Nb(4)	0.49167 (5)	0.56732 (8)	0.42749 (4)	3.54 (3)
Nb(2)	0.25564 (5)	0.08181 (8)	0.16308 (4)	3.51 (3)	Cl(4)	0.4868 (2)	0.5918 (2)	0.5981 (1)	4.55 (9)
Cl(1)	0.2787 (1)	0.0779 (2)	0.0785 (1)	4.53 (9)	Cl(5)	0.3881 (4)	0.4573 (2)	0.5240 (1)	4.47 (9)
Cl(2)	0.0548 (1)	0.1016 (3)	0.0203 (1)	4.9 (1)	Cl(6)	0.3490 (2)	0.6858 (2)	0.5013 (1)	5.0 (1)
Cl(3)	0.2644 (2)	0.0871 (3)	0.2574 (1)	5.6 (1)	Cl(7)	0.5004 (2)	0.6187 (3)	0.3428 (1)	5.4 (1)
C(1)	0.1965 (6)	0.1899 (8)	0.1202 (5)	3.9 (3)	O(5)	0.500	0.500	0.500	3.6 (2)
C(2)	0.2031 (6)	0.2880 (9)	0.1249 (7)	5.4 (3)	C(45)	0.4986 (5)	0.6779 (8)	0.4799 (4)	3.4 (2)
C(3)	0.1901 (9)	0.336 (1)	0.0786 (7)	8.0 (3)	C(46)	0.5498 (6)	0.7357 (9)	0.5051 (5)	4.9 (3)
C(4)	0.202 (1)	0.430 (1)	0.0847 (9)	10.1 (3)	C(47)	0.5633 (8)	0.755 (1)	0.5577 (9)	8.7 (3)
C(5)	0.223 (1)	0.467 (1)	0.137 (1)	9.8 (3)	C(48)	0.610 (2)	0.809 (2)	0.589 (1)	18.9 (3)
C(6)	0.2349 (9)	0.418 (1)	0.1831 (9)	8.1 (3)	C(49)	0.644 (1)	0.840 (1)	0.5674 (9)	13.0 (3)
C(7)	0.2250 (8)	0.326 (1)	0.1795 (7)	6.9 (3)	C(50)	0.6400 (7)	0.828 (1)	0.510 (1)	10.4 (3)
C(8)	0.1547 (6)	0.1398 (9)	0.1399 (5)	3.9 (3)	C(51)	0.5878 (6)	0.766 (1)	0.4779 (7)	6.2 (3)
C(9)	0.1119 (6)	0.1928 (9)	0.1614 (6)	4.6 (3)	C(52)	0.4460 (5)	0.7012 (7)	0.4336 (5)	3.5 (2)
C(10)	0.0680 (6)	0.246 (1)	0.1236 (7)	5.8 (3)	C(53)	0.4398 (6)	0.7980 (9)	0.4179 (6)	4.6 (3)
C(11)	0.0257 (9)	0.295 (1)	0.1389 (8)	8.5 (3)	C(54)	0.4283 (7)	0.8563 (9)	0.4545 (6)	5.7 (3)
C(12)	0.031 (1)	0.287 (1)	0.195 (1)	9.4 (3)	C(55)	0.4297 (8)	0.948 (1)	0.4434 (7)	7.0 (3)
C(13)	0.0783 (8)	0.234 (1)	0.2340 (8)	7.9 (3)	C(56)	0.4419 (9)	0.980 (1)	0.3995 (9)	8.5 (3)
C(14)	0.1202 (8)	0.185 (1)	0.2175 (7)	6.9 (3)	C(57)	0.4564 (9)	0.920 (1)	0.3651 (8)	8.2 (3)
C(15)	0.1512 (5)	0.0435 (8)	0.1414 (5)	3.6 (3)	C(58)	0.4544 (7)	0.826 (1)	0.3733 (6)	6.4 (3)
C(16)	0.1082 (6)	0.0024 (9)	0.1663 (5)	4.2 (3)	C(59)	0.3965 (5)	0.6424 (8)	0.4000 (5)	3.7 (2)
C(17)	0.0440 (6)	0.019 (1)	0.1413 (5)	4.9 (3)	C(60)	0.3440 (5)	0.6789 (8)	0.3502 (5)	3.6 (2)
C(18)	0.0064 (7)	−0.027 (1)	0.1635 (7)	7.3 (3)	C(61)	0.3370 (6)	0.6492 (9)	0.2978 (5)	4.9 (3)
C(19)	0.0302 (9)	−0.082 (1)	0.2090 (7)	8.6 (3)	C(62)	0.2868 (7)	0.677 (1)	0.2523 (6)	6.3 (3)
C(20)	0.0956 (8)	−0.095 (1)	0.2336 (7)	7.6 (3)	C(63)	0.2444 (7)	0.741 (1)	0.2581 (6)	5.9 (3)
C(21)	0.1340 (7)	−0.0522 (9)	0.2115 (5)	5.0 (3)	C(64)	0.2532 (7)	0.772 (1)	0.3087 (7)	6.4 (3)
C(22)	0.1887 (6)	−0.0131 (6)	0.1220 (5)	3.8 (3)	C(65)	0.3049 (6)	0.741 (1)	0.3577 (6)	5.7 (3)
C(23)	0.1794 (7)	−0.1096 (9)	0.1118 (5)	4.5 (3)	C(66)	0.3964 (6)	0.5488 (8)	0.4099 (5)	4.0 (3)
C(24)	0.1205 (9)	−0.154 (1)	0.1002 (8)	7.9 (3)	C(67)	0.3423 (6)	0.4894 (9)	0.3805 (5)	4.5 (3)
C(25)	0.119 (1)	−0.248 (1)	0.0877 (9)	11.8 (3)	C(68)	0.3496 (7)	0.411 (1)	0.3543 (7)	7.3 (3)
C(26)	0.167 (1)	−0.295 (2)	0.0867 (9)	11.6 (3)	C(69)	0.2981 (8)	0.356 (1)	0.3277 (7)	8.2 (3)
C(27)	0.223 (1)	−0.249 (1)	0.0974 (7)	9.0 (3)	C(70)	0.2395 (9)	0.378 (1)	0.3244 (7)	7.6 (3)
C(28)	0.2312 (8)	−0.155 (1)	0.1099 (6)	6.6 (3)	C(71)	0.2288 (7)	0.458 (1)	0.3494 (6)	7.7 (3)
O(1)	0.1669 (4)	0.1661 (6)	−0.0133 (4)	5.6 (2)	C(72)	0.2805 (6)	0.511 (1)	0.3775 (6)	6.0 (3)
C(29)	0.2221 (8)	0.204 (1)	−0.0220 (8)	8.8 (3)	C(73)	0.781 (1)	0.019 (2)	0.624 (1)	12.3 (5)*
C(30)	0.189 (1)	0.267 (2)	−0.0715 (9)	11.3 (3)	C(74)	0.835 (1)	−0.007 (2)	0.636 (1)	13.7 (5)*
C(31)	0.127 (1)	0.241 (2)	−0.098 (1)	13.4 (3)	C(75)	0.868 (1)	0.031 (2)	0.612 (1)	15.3 (5)*
C(32)	0.113 (1)	0.180 (2)	−0.0609 (8)	16.7 (3)	C(76)	0.847 (1)	0.083 (2)	0.564 (1)	13.6 (5)*
O(2)	0.1592 (4)	−0.0167 (6)	−0.0044 (4)	4.8 (2)	C(77)	0.782 (1)	0.113 (2)	0.545 (1)	13.0 (5)*
C(33)	0.2082 (7)	−0.051 (1)	−0.0223 (7)	7.6 (3)	C(78)	0.752 (1)	0.073 (2)	0.581 (1)	13.6 (5)*
C(34)	0.175 (1)	−0.118 (1)	−0.0651 (9)	10.5 (3)	O(6)	0.618 (2)	0.078 (2)	0.416 (1)	14.2 (5)*
C(35)	0.1206 (9)	−0.147 (1)	−0.0537 (9)	9.7 (3)	C(79)	0.585 (2)	0.155 (3)	0.381 (2)	10.1 (5)*
C(36)	0.1015 (7)	−0.068 (1)	−0.0275 (7)	7.0 (3)	C(80)	0.586 (3)	0.142 (4)	0.335 (2)	14.5 (6)*
O(3)	0.3424 (4)	0.1672 (7)	0.1914 (4)	5.9 (2)	C(81)	0.603 (2)	0.066 (3)	0.322 (2)	9.0 (5)*
C(37)	0.3583 (7)	0.236 (1)	0.1587 (7)	7.1 (3)	C(82)	0.628 (2)	0.016 (3)	0.384 (2)	12.8 (6)*
C(38)	0.402 (1)	0.296 (1)	0.204 (1)	11.6 (3)	O(7)	0.967 (1)	0.149 (2)	0.304 (2)	17.2 (5)*
C(39)	0.423 (1)	0.246 (2)	0.255 (1)	13.2 (4)	C(83)	0.921 (2)	0.160 (2)	0.248 (1)	15.7 (6)*
C(40)	0.3921 (8)	0.162 (2)	0.2465 (7)	10.2 (3)	C(84)	0.892 (2)	0.071 (3)	0.236 (1)	19.7 (6)*
O(4)	0.3338 (4)	−0.0155 (6)	0.1897 (3)	4.4 (2)	C(85)	0.881 (2)	0.057 (2)	0.288 (2)	12.8 (6)*
C(41)	0.3831 (6)	−0.030 (1)	0.1667 (6)	6.1 (3)	C(86)	0.942 (2)	0.081 (3)	0.329 (1)	21.6 (6)*
C(42)	0.4261 (8)	−0.095 (1)	0.2058 (8)	8.1 (3)	C(87)	−0.022 (4)	0.040 (4)	0.449 (1)	20.7 (6)*
C(43)	0.3822 (8)	−0.156 (1)	0.2235 (7)	7.5 (3)	C(88)	0.024 (3)	0.081 (2)	0.493 (3)	10.7 (6)*
C(44)	0.3355 (7)	−0.085 (1)	0.2295 (6)	6.0 (3)	C(89)	0.045 (3)	0.042 (4)	0.545 (2)	21.0 (6)*
Nb(3)	0.43091 (5)	0.59621 (8)	0.49193 (4)	3.43 (3)					

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

atoms. Subsequent least-squares refinements and difference Fourier syntheses located gradually the rest of the non-hydrogen atoms. It was not possible to distinguish oxygen atoms from carbon atoms in the interstitial THF molecules. After all the THF ring atoms were refined as carbon atoms, the atom that had the lowest displacement parameter in each ring was designated and refined as an oxygen atom in the final cycles of least-squares refinement. The highest peak (1.044 e/Å^3) in a final difference Fourier map was 0.719 Å from a solvent carbon atom (C(80)). This may be the result of large thermal motion or slight disorder of the solvent molecule. Table I lists the crystallographic data and the information pertaining the structure determination. Table II gives the positional and displacement parameters of the non-hydrogen atoms.

Results and Discussion

The crystal is made up of $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$ anions, each residing on a crystallographic inversion center, and $[Nb_2Cl_3(PhC)_4(THF)_4]^+$ cations, each residing on a general position in the unit cell. In addition there are molecules if benzene and THF

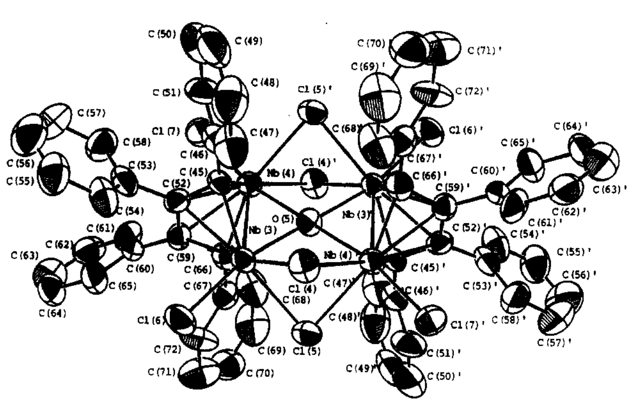


Figure 2. The cluster anion $[Nb_4OCl_8\{(PhC)_4\}_2]^{2-}$. The thermal ellipsoids enclose 50% of electron density.

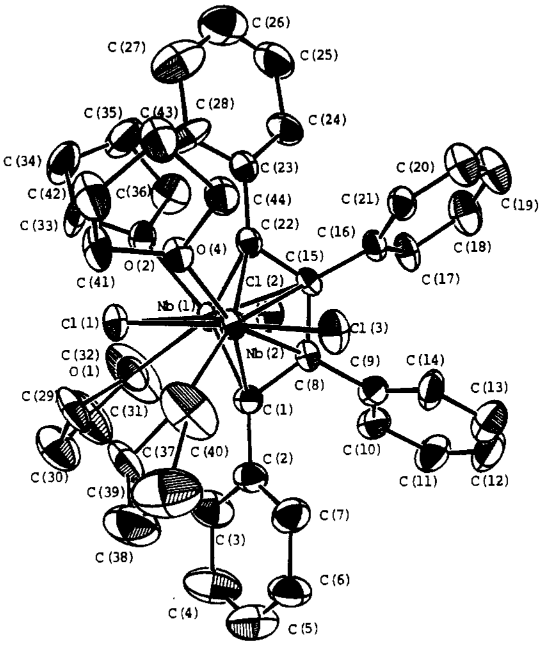


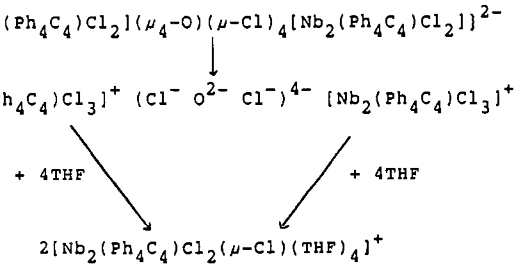
Figure 3. The cluster cation $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]^+$. Atoms are represented by their displacement ellipsoids at the 30% probability level.

Table III. Important Bond Distances (Å) for $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]_2[Nb_4OCl_8\{(PhC)_4\}_2]\cdot 3C_6H_6\cdot 4THF$[a]

Nb(1)–Nb(2)	2.6954 (13)	Nb(3)–Nb(4)	2.611 (2)
Nb(1)–Cl(1)	2.481 (3)	Nb(3)–Cl(4)	2.601 (3)
Nb(1)–Cl(2)	2.406 (3)	Nb(3)–Cl(5)	2.606 (4)
Nb(1)–Cl(1)	2.108 (13)	Nb(3)–Cl(6)	2.423 (4)
Nb(1)–C(8)	2.304 (14)	Nb(3)–O(5)	2.122 (1)
Nb(1)–C(15)	2.346 (14)	Nb(3)–C(45)	2.115 (13)
Nb(1)–C(22)	2.129 (12)	Nb(3)–C(52)	2.330 (13)
Nb(1)–O(1)	2.309 (10)	Nb(3)–C(59)	2.351 (12)
Nb(1)–O(2)	2.321 (9)	Nb(3)–C(66)	2.125 (12)
Nb(2)–Cl(1)	2.473 (4)	Nb(4)–Cl(4)′	2.614 (4)
Nb(2)–Cl(3)	2.412 (4)	Nb(4)–Cl(5)′	2.620 (3)
Nb(2)–C(1)	2.169 (12)	Nb(4)–Cl(7)	2.436 (4)
Nb(2)–C(8)	2.358 (13)	Nb(4)–O(5)	2.108 (1)
Nb(2)–C(15)	2.344 (12)	Nb(4)–C(45)	2.144 (12)
Nb(2)–C(22)	2.100 (12)	Nb(4)–C(52)	2.332 (12)
Nb(2)–O(3)	2.273 (9)	Nb(4)–C(59)	2.346 (12)
Nb(2)–O(4)	2.240 (8)	Nb(4)–C(66)	2.098 (13)
C(1)–C(2)	1.50 (2)	C(45)–C(46)	1.43 (2)
C(1)–C(8)	1.47 (2)	C(45)–C(52)	1.409 (14)
C(8)–C(9)	1.54 (2)	C(52)–C(53)	1.52 (2)
C(8)–C(15)	1.47 (2)	C(52)–C(59)	1.464 (15)
C(15)–C(16)	1.52 (2)	C(59)–C(60)	1.520 (14)
C(15)–C(22)	1.44 (2)	C(59)–C(66)	1.45 (2)
C(22)–C(23)	1.50 (2)	C(66)–C(67)	1.50 (2)

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

Scheme I



occupying interstitial positions. The anion and the cation are depicted in Figures 2 and 3, respectively; Table III lists the principal bond distances and Table IV the principal angles.

The oxo-centered tetranuclear anion is, within experimental error, identical with the ones already found[2] in other compounds accompanied by different cations. The cation, shown in Figure 3, has a structure that incorporates the main features of half of the anion, although there is one quantitative difference. The Nb–Nb distance is somewhat longer than that in the anion, namely 2.695 (1) Å versus 2.611 (2) Å, but this can very naturally be attributed to the replacement of a bridging oxygen atom by a larger bridging chlorine atom.

Table IV. Important Bond Angles (deg) for $[Nb_2Cl_3\{(PhC)_4\}(THF)_4]_2[Nb_4OCl_8\{(PhC)_4\}_2]\cdot 3C_6H_6\cdot 4THF$[a]

Cl(1)–Nb(1)–Cl(2)	164.4 (1)	Cl(4)–Nb(3)–Cl(6)	90.0 (1)
Cl(1)–Nb(1)–C(1)	82.8 (4)	Cl(4)–Nb(3)–O(5)	79.64 (9)
Cl(1)–Nb(1)–C(8)	109.1 (3)	Cl(4)–Nb(3)–C(45)	94.3 (3)
Cl(1)–Nb(1)–C(15)	108.7 (3)	Cl(4)–Nb(3)–C(52)	125.9 (3)
Cl(1)–Nb(1)–C(22)	82.8 (4)	Cl(4)–Nb(3)–C(59)	162.1 (3)
Cl(1)–Nb(1)–O(1)	80.9 (3)	Cl(4)–Nb(3)–C(66)	157.9 (3)
Cl(1)–Nb(1)–O(2)	82.2 (2)	Cl(5)–Nb(3)–Cl(6)	91.0 (1)
Cl(2)–Nb(1)–C(1)	106.0 (4)	Cl(5)–Nb(3)–O(5)	76.72 (8)
Cl(2)–Nb(1)–C(8)	85.1 (3)	Cl(5)–Nb(3)–C(45)	156.7 (3)
Cl(2)–Nb(1)–C(15)	86.5 (3)	Cl(5)–Nb(3)–C(52)	159.8 (3)
Cl(2)–Nb(1)–C(22)	108.8 (4)	Cl(5)–Nb(3)–C(59)	123.4 (3)
Cl(2)–Nb(1)–O(1)	85.2 (3)	Cl(5)–Nb(3)–C(66)	90.4 (4)
Cl(2)–Nb(1)–O(2)	87.4 (2)	Cl(6)–Nb(3)–O(5)	165.7 (1)
C(1)–Nb(1)–O(1)	97.8 (4)	Cl(6)–Nb(3)–C(45)	109.6 (3)
C(1)–Nb(1)–O(2)	164.2 (5)	Cl(6)–Nb(3)–C(52)	89.7 (3)
C(8)–Nb(1)–O(1)	128.6 (4)	Cl(6)–Nb(3)–C(59)	87.6 (3)
C(8)–Nb(1)–O(2)	154.6 (4)	Cl(6)–Nb(3)–C(66)	106.4 (4)
C(15)–Nb(1)–O(1)	164.1 (4)	O(5)–Nb(3)–C(45)	81.3 (3)
C(15)–Nb(1)–O(2)	118.5 (4)	O(5)–Nb(3)–C(52)	104.3 (3)
C(22)–Nb(1)–O(1)	158.4 (5)	O(5)–Nb(3)–C(59)	105.3 (3)
C(22)–Nb(1)–O(2)	89.3 (4)	O(5)–Nb(3)–C(66)	81.4 (3)
O(1)–Nb(1)–O(2)	74.6 (3)	Cl(4)′–Nb(4)–Cl(5)′	73.9 (1)
Cl(1)–Nb(2)–Cl(3)	164.0 (1)	Cl(4)′–Nb(4)–Cl(7)	88.5 (1)
Cl(1)–Nb(2)–C(1)	81.8 (4)	Cl(4)′–Nb(4)–O(5)	79.58 (9)
Cl(1)–Nb(2)–C(8)	107.6 (3)	Cl(4)′–Nb(4)–C(45)	156.7 (3)
Cl(1)–Nb(2)–C(15)	109.0 (3)	Cl(4)′–Nb(4)–C(52)	164.7 (3)
Cl(1)–Nb(2)–C(22)	83.6 (4)	Cl(4)′–Nb(4)–C(59)	128.4 (3)
Cl(1)–Nb(2)–O(3)	81.4 (3)	Cl(4)′–Nb(4)–C(66)	96.0 (4)
Cl(1)–Nb(2)–O(4)	81.0 (3)	Cl(5)′–Nb(4)–Cl(7)	93.1 (1)
Cl(3)–Nb(2)–C(1)	107.6 (4)	Cl(5)′–Nb(4)–O(5)	76.62 (9)
Cl(3)–Nb(2)–C(8)	87.0 (3)	Cl(5)′–Nb(4)–C(45)	89.4 (3)
Cl(3)–Nb(2)–C(15)	86.6 (3)	Cl(5)′–Nb(4)–C(52)	121.3 (3)
Cl(3)–Nb(2)–C(22)	108.3 (4)	Cl(5)′–Nb(4)–C(59)	157.8 (3)
Cl(3)–Nb(2)–O(3)	85.2 (3)	Cl(5)′–Nb(4)–C(66)	158.0 (4)
Cl(3)–Nb(2)–O(4)	87.4 (3)	Cl(7)–Nb(4)–O(5)	166.0 (1)
C(1)–Nb(2)–O(3)	92.7 (4)	Cl(7)–Nb(4)–C(45)	108.8 (4)
C(1)–Nb(2)–O(4)	160.8 (5)	Cl(7)–Nb(4)–C(52)	88.7 (4)
C(8)–Nb(2)–O(3)	122.7 (4)	Cl(7)–Nb(4)–C(59)	87.2 (3)
C(8)–Nb(2)–O(4)	159.6 (4)	Cl(7)–Nb(4)–C(66)	106.3 (4)
C(15)–Nb(2)–O(3)	158.1 (4)	O(5)–Nb(4)–C(45)	80.9 (3)
C(15)–Nb(2)–O(4)	123.5 (4)	O(5)–Nb(4)–C(52)	104.7 (3)
C(22)–Nb(2)–O(3)	163.0 (5)	O(5)–Nb(4)–C(59)	105.9 (3)
C(22)–Nb(2)–O(4)	93.5 (4)	O(5)–Nb(4)–C(66)	82.4 (4)
O(3)–Nb(2)–O(4)	76.3 (3)	Nb(3)–Cl(4)–Nb(4)′	79.3 (1)
Nb(1)–Cl(1)–Nb(2)	65.9 (1)	Nb(3)–Cl(5)–Nb(4)′	79.1 (1)
Nb(1)–C(1)–Nb(2)	78.1 (4)	Nb(3)–O(5)–Nb(4)	76.25 (5)
Nb(1)–C(1)–C(2)	142 (1)	Nb(3)–C(45)–Nb(4)	75.6 (4)
Nb(2)–C(1)–C(2)	133.4 (8)	Nb(3)–C(45)–C(46)	146 (1)
C(2)–C(1)–C(8)	123 (1)	Nb(4)–C(45)–C(46)	129 (1)
Nb(1)–C(8)–Nb(2)	70.6 (4)	C(46)–C(45)–C(52)	123 (1)
Nb(1)–C(8)–C(9)	144.2 (8)	Nb(3)–C(52)–Nb(4)	68.1 (3)
Nb(2)–C(8)–C(9)	144.4 (8)	Nb(3)–C(52)–C(53)	145 (1)
C(1)–C(8)–C(9)	117 (1)	Nb(4)–C(52)–C(53)	146 (1)
C(1)–C(8)–C(15)	125 (1)	C(45)–C(52)–C(53)	116.2 (9)
C(9)–C(8)–C(15)	118 (1)	C(45)–C(52)–C(59)	127 (1)
Nb(1)–C(15)–Nb(2)	70.2 (4)	C(53)–C(52)–C(59)	117.2 (9)
Nb(1)–C(15)–C(16)	147.6 (7)	Nb(3)–C(59)–Nb(4)	67.6 (3)
Nb(2)–C(15)–C(16)	141.6 (8)	Nb(3)–C(59)–C(60)	148 (1)
C(8)–C(15)–C(16)	118 (1)	Nb(4)–C(59)–C(60)	143 (1)
C(8)–C(15)–C(22)	123 (1)	C(52)–C(59)–C(60)	119 (1)
C(16)–C(15)–C(22)	119 (1)	C(52)–C(59)–C(66)	123.1 (9)
Nb(1)–C(22)–Nb(2)	79.2 (5)	C(60)–C(59)–C(66)	117.4 (9)
Nb(1)–C(22)–C(23)	126.8 (8)	Nb(3)–C(66)–Nb(4)	76.4 (4)
Nb(2)–C(22)–C(23)	142.9 (9)	Nb(3)–C(66)–C(67)	131 (1)
C(15)–C(22)–C(23)	126 (1)	Nb(4)–C(66)–C(67)	143 (1)
Cl(4)–Nb(3)–Cl(5)	74.3 (1)	C(59)–C(66)–C(67)	124 (1)

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

The bridging, C-shaped $(CPh)_4$ unit is essentially identical in both anion and cation, as are the positions of the two terminal chlorine atoms. In the cation the chlorine atoms that occur as bridges between the halves of the anion are replaced by THF molecules.

Structural Relationship of Cation to Anion. From a formal point of view there is a very simple and direct relationship between the structure and bonding in the cations and the same features of the anion in this compound. This is shown schematically in Scheme I. To go from the tetranuclear anion to a pair of the dinuclear cations requires (1) extrusion of the bridging oxide ion and two of the bridging chloride ions, (2) movement of one chloride ion into a bridging position between two of the strongly bonded niobium atoms, and (3) entry of four THF molecules into each dinuclear fragment.

Concluding Remarks. The isolation of a compound containing the $[Nb_2Cl_3(CPh)_4(THF)_4]^+$ ion fulfills an earlier suggestion[2,4] that half of the oxo-centered anion, with appropriate adjustments, should be a stable entity. The fact that this cation has actually been obtained in combination with the anion leads an esthetic touch to the structure that is as welcome as it was unanticipated.

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Supplementary Material Available: Tables of detailed crystal data, general displacement parameters, and complete bond distances and angles (12 pages); a table of observed and calculated structure factors (33 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Synthetic Chemistry,
Faculty of Engineering, The University of Tokyo, Hongo, Tokyo 113, Japan

Highly Active Antitumor Platinum(II) Complexes of Amino Sugars

Taro Tsubomura,*[†] Masumi Ogawa, Shigenobu Yano,*[‡] Kimiko Kobayashi,[§] Tosio Sakurai,[§]
and Sadao Yoshikawa[∥]

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The syntheses, structures, spectroscopic properties, and antitumor activities of a series of platinum(II) diamino sugar complexes, $[PtCl_2(\text{diamino sugar})]$, have been studied. The molecular structure of one of these is described. Crystal data for $[PtCl_2(\text{Me-ManNN})]\cdot H_2O$ (Me-ManNN = methyl 2,3-diamino-2,3-dideoxy-α-D-mannopyranoside) are as follows: $C_7H_{18}N_2O_5Cl_2Pt$; fw = 476.2 monoclinic, $P2_1$, $a = 10.048$ (2) Å, $b = 8.725$ (2) Å, $c = 7.584$ (2) Å, $\beta = 90.67$ (2)°, $V = 664.8$ (3) Å^3, $D_c = 2.39$ g cm^{-3}, $D_o = 2.37$ g cm^{-3}, $Z = 2$, and $\mu = 110.8$ cm^{-1} (Mo Kα). Antitumor activity was investigated against S180 and L1210 tumors. In the S180 study, the life span of mice treated with $[PtCl_2(\text{GlcNN})]\cdot H_2O$ (GlcNN = 2,3-diamino-2,3-dideoxy-D-glucose) increased, and the T/C value was up to 410%. Other compounds also showed high activities (T/C = 200–380%) against S180. The correlation between the chelate conformation of diamino sugar ligands and the antitumor activity is discussed.

Since the antitumor activity of cisplatin, *cis*-$[PtCl_2(NH_3)_2]$, was discovered by Rosenberg et al.,[1] many platinum-group metal complexes have been prepared, and their activities were examined.[2-4] Besides platinum complexes, ruthenium, rhodium, palladium, and other metal complexes such as *cis*-$[Ru^{II}Cl_2(dmso)_4]$, $[Ru^{III}(NH_3)_5(H_2O)]^{3+}$, $[Rh^I(pyR)(cod)]^+$, and $[Ti(Cp)_2Cl_2]$, where pyR = *N*-(3-pyridinylmethylene)alkylamine, cod = 1,5-cyclooctadiene, and Cp = cyclopentadienyl, were found to show antitumor activity.[2,3] Among these metal complexes, platinum(II) complexes have been most extensively studied in both preparation and clinical test. Chargeless platinum(II) complexes of the *cis*-$[PtX_2L_2]$ type generally show antitumor activity, where X_2 represents anionic monodentate or bidentate "leaving group" ligands and L_2 represents monodentate or bidentate neutral ligands. Cisplatin is effective against the tumors of bladder, testicle, ovary, etc., but it has high toxicity including nephrotoxicity, nausea, and ototoxicity.[2] In particular, kidney toxicity is the most serious problem.[5] To attain lowered toxocity and enhanced solubility, much work has been devoted to the preparation of new platinum complexes having various anionic "leaving group" ligands instead of chloride ions. These complexes include "second-generation drugs", for example, *cis*-(cyclobutanedicarboxylato)diammineplatinum(II), and (malonato)(1,2-diaminocyclohexane)platinum(II), but in almost all complexes, ammonia or simple alkylamines, which are toxic themselves, have been used as the neutral ligands.[2,3,6]

Many anticancer reagents having sugar residues such as bleomycine, adriamycin, and many antibiotics are now widely used clinically. The former two form metal complexes containing a sugar residue and have peculiar physiological activity.[7] It is therefore very interesting to examine the activity of platinum complexes having sugar residues in vivo.

As a significant part of our program to clarify the nature of sugar-transition-metal interactions,[8] we have synthesized and fully characterized several cisplatin-type complexes of diamino sugars. These platinum diamino sugar complexes show high antitumor activity against sarcoma S180. In this paper, the syntheses, structures, physical properties, and antitumor screening data of a series of platinum diamino sugar complexes are described in detail.

[†] Present address: Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino, Tokyo 180, Japan.

[‡] Present address: Department of Chemistry, Faculty of Science, Nara Women's University, Nara 630, Japan.

[§] Present address: The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351, Japan.

[∥] Present address: Applied Chemistry, Faculty of Science and Technology, Keio University, Kouhoku, Yokohama 223, Japan.

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