originate from their small ionic radius. The ligand edtp is able apparently to fold itself almost optimally around the nickel and cobalt ions. With the larger metal ions (Fe, Mn, and Cd) six-coordinate octahedral coordination by the ligand edtp becomes too unfavorable, even when distorted, resulting in seven-coordinate "bicapped octahedral" geometries around the metal ions. The zinc compounds appear to be intermediate cases (see the coordination numbers in Table IV).

Concluding Remarks. The pyrazole derivative of ethylenediamine, edtp, appears to be a hexadentate nitrogen donor ligand toward first-row transition-metal ions. Except for the small nickel(II) ion the ligand edtp has a too restricted geometrical configuration to be able to form regular coordination octahedrons. Coordination numbers show a direct correlation with the ionic radii of the metal ions: The larger ions are seven-coordinate and the smaller ions are six-coordinate with Zn(II) in an intermediate position.

Acknowledgment. The authors are indebted to S. Gorter for the collection of the crystallographic data.

Registry No. Mn(edtp)$(ClO_4)_2$, 91670-09-6; Mn(edtp)$(BF_4)_2$, 91670-11-0; Fe(edtp)$(ClO_4)_2$, 91686-34-9; Fe(edtp)$(BF_4)_2$, 91670-12-1; Cd(edtp)$(ClO_4)_2$, 91670-14-3; Cd(edtp)$(BF_4)_2$, 91686-36-1; Zn(edtp)$(ClO_4)_2$, 91670-16-5; Zn(edtp)$(BF_4)_2$, 91670-18-7; Co(edtp)$(ClO_4)_2$, 91670-20-1; Co(edtp)$(Br_4)_2$, 91670-21-2; Ni(edtp)$(ClO_4)_2$, 91670-23-4; Ni(edtp)$(BF_4)_2$, 91670-24-5; Cu(edtp)$(ClO_4)_2$, 91670-26-7; Cu(edtp)$(BF_4)_2$, 91670-27-8.

Supplementary Material Available: Listings of bond lengths, bond angles, fractional coordinates of the hydrogen atoms, anisotropic thermal parameters of the non-hydrogen atoms, observed and calculated structure factors, and analytical data (13 pages). Ordering information is given on any current masthead page.

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Further Studies of the Phosphine Complexes of Niobium(IV) Chloride

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Three compounds of empirical formula $NbCl_4(PR_3)_2$, two of which (**1** and **2**) were previously reported and one of which (**3**) is new, have been structurally characterized. Compound **1**, $Nb_2Cl_8(PMe_3)_4$, is dinuclear, consisting of two square-antiprismatic $NbCl_6(PMe_3)_2$ units fused on a common square face formed by four Cl atoms. The molecule has crystallographic *mmm* (D_{2h}) symmetry in the cubic space group *Im*3 with $a = 16.372$ [4] Å and $Z = 6$. The Nb-Nb distance is 2.833 (1) Å and the metal to ligand distances are Nb-Cl_b = 2.541 (1) Å, Nb-Cl_t = 2.502 (1) Å, and Nb-P = 2.671 (1) Å. Compound **2**, *trans*-$NbCl_4(PEt_3)_2$, forms monoclinic crystals ($P2_1/n$) with unit cell dimensions of $a = 7.224$ (2) Å, $b = 12.131$ (4) Å, $c = 12.017$ (2) Å, $\beta = 90.74$ (2)°, and $Z = 2$. Compound **3**, *trans*-$NbCl_4(PEtPh_2)_2$, also forms monoclinic crystals ($P2_1/n$) with $a = 9.851$ (2) Å, $b = 16.010$ (3) Å, $c = 9.367$ (2) Å, $\beta = 98.67$ (1)°, and $Z = 2$. In both **2** and **3** there is crystallographic inversion symmetry imposed on the molecule, and the mean dimensions (for **2** and **3** in that order) are Nb-Cl = 2.366 [9], 2.367 [34] Å and Nb-P = 2.664 (3), 2.706 (1) Å. Observations on the colors, visible spectra, and EPR spectra of solutions of these compounds are reported and partially interpreted. Compound **1** and the previously reported $Nb_2Cl_8(PMe_2Ph)_4$ exist in concentration-dependent equilibrium with EPR-active monomers, although the exact nature of the latter is uncertain.

Introduction

Our knowledge of the fundamental chemistry of the elements niobium and tantalum still has surprising lacunae. One of these is in the area of the phosphine adducts of the tri- and tetrahalides.[1-4] The existence of the compounds has been recognized since at least 1976,[2] but information on their molecular structures, bonding, or chemical behavior is very incomplete. A program in this laboratory to explore new areas in the chemistry of these elements has brought us to the realization that we are often lacking the kind of basic information on which we wish to build. With regard to the chemistry of "simple" phosphine adducts, we decided to remedy this need ourselves. Happily, we have found that the subject is intrinsically quite interesting since the behavior of some of these compounds is not at all "simple".

In this paper we are concerned only with some bis(phosphine) adducts of niobium(IV) chloride, "$NbCl_4(PR_3)_2$". Manzer[2] reported those with PEt_3 and PMe_3 in 1977 as orange or brown solids. He also reported that "$NbCl_4(PMe_3)_2$" had a μ_{eff} value at room temperature of only 0.50 μ_B. Samuel and co-workers[3] have reported the EPR spectra of the compounds with R = butyl, isobutyl, and ethyl in both fluid and frozen solutions. They found all three compounds to have similar spectra and argued that the only reasonable interpretation of these required the assumption of trans structures with a spin Hamiltonian based on D_{4h} symmetry. While their argument was plausible, it did not seem to us to be conclusive, and moreover, we had observed puzzling color changes with other compounds of this class on going from solid to solution. Furthermore, Manzer's magnetic data for $NbCl_4(PMe_3)_2$ were not explicable by such a structure. When we found here that (a) "$NbCl_4(PMe_2Ph)_2$" is actually dinuclear[4] and that (b) $TaCl_4(PMe_2Ph)_2$ is cis,[5] it was clear that a good deal more remained to be learned about this class of compounds. This paper is the first of several in which we hope to sort out some of the basic questions in this area.

Experimental Section

All manipulations were carried out under an atmosphere of argon. Standard vacuum-line techniques were used. $NbCl_5$ and the phosphine ligands were purchased from Aldrich and Strem Chemicals, Inc.,

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(1) Luetkens, M. L.; Huffman, J. C.; Sattelberger, A. P. *J. Am. Chem. Soc.* **1983**, *105*, 4474 and references cited therein.

(2) Manzer, L. E. *Inorg. Chem.* **1977**, *16*, 525.

(3) (a) Samuel, E.; Labauze, G.; Livage, J. *Nouv. J. Chim.* **1977**, *1*, 93. (b) Labauze, G.; Samuel, E.; Livage, J. *Inorg. Chem.* **1980**, *19*, 1384.

(4) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 945.

(5) Cotton, F. A.; Roth, W. J., to be submitted for publication.

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Table I. Crystallographic Data

	$Nb_2Cl_8(PMe_3)_4$ (**1**)	$NbCl_4(PEt_3)_2$ (**2**)	$NbCl_4(PEtPh_2)_2$ (**3**)
formula	$Nb_2Cl_8P_4C_{12}H_{36}$	$NbCl_4P_2C_{12}H_{30}$	$NbCl_4P_2C_{28}H_{30}$
fw	773.76	471.04	663.22
space group	$Im3$ (No. 204)	$P2_1/n$	$P2_1/n$
systematic absences	$hkl, h + k + l \neq 2n$	$0k0, k \neq 2n; h0l, h + l \neq 2n$	$0k0, k \neq 2n; h0l, h + l \neq 2n$
a, Å	16.372 [4]	7.224 (2)	9.851 (2)
b, Å		12.131 (4)	16.010 (3)
c, Å		12.017 (2)	9.367 (2)
α, deg	90.00	90.0	90.0
β, deg		90.74 (2)	98.67 (1)
γ, deg		90.0	90.0
V, Å^3	4388 (3)	1053 (1)	1460 (2)
Z	6	2	2
d_{calcd}, g/cm^3	1.757	1.485	1.508
cryst size, mm	0.35 × 0.3 × 0.25	0.3 × 0.25 × 0.15	0.5 × 0.4 × 0.2
μ(Mo Kα), cm^{-1}	17.071	11.992	80.801 (for Cu Kα)
data collcn instrument	CAD-4	Syntex P$\bar{1}$	Syntex P$\bar{1}$
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 84 Å)
orientation reflcns no. range (2θ)	25, $18.3 \leq 2\theta \leq 31.0$	15, $17.31 \leq 2\theta \leq 31.40$	15, $40.45 \leq 2\theta \leq 79.13$
temp, °C	22	22	0
scan method	ω–2θ	ω–2θ	ω–2θ
data collcn range (2θ), deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 50$	$5 \leq 2\theta \leq 130$
no. of unique data	667	874	1887
no. of data with $F_o^2 > 3\sigma(F_o^2)$	557	702	1819
no. of params refined	57	88	220
transmittance factors: max, min			0.9986, 0.6426
R^a	0.0222	0.0465	0.035
$R_w{}^b$	0.0287	0.0625	0.056
quality-of-fit indicator^c	0.773	1.249	1.476
largest shift/esd, final cycle	0.02	0.02	0.21
largest peak, e/Å^3	0.506	0.535	0.90

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

respectively, and used as received. $NbCl_4(THF)_2$ was prepared according to the literature method.[2] All products were extremely sensitive to oxygen and/or moisture, and traces of air caused immediate formation of blue oily deposits.

Visible and EPR spectra were recorded on a Cary 17D spectrophotometer and an X-band Varian E-6S EPR spectrometer, respectively.

Preparation of $NbCl_4(PMe_3)_2$ (1). The literature method was used.[2] Crystals suitable for X-ray diffraction were formed when the reaction mixture was left undisturbed after the reactants were mixed together. DPPH was used as a *g*-value marker.

Preparation of $NbCl_4(PEt_3)_2$ (2). The literature method[2] was slightly modified. To a slurry of $NbCl_4(THF)_2$ (2.0 g, 5.3 mmol) in 10 mL of toluene was added PEt_3 (1.5 mL, 10.3 mmol). The solution turned brown, and a small amount of solid was still present. Addition of 10 mL of toluene resulted in a homogeneous solution. After filtration, the solution was reduced in volume to ca. 5 mL and stored at −5 °C. An abundant red precipitate was obtained overnight (ca. 1.0 g). The liquid was decanted, reduced in volume to ca. 3 mL, and again stored at −5 °C. The solid samples were dried under vacuum. The combined yield was 1.9 g, ca. 4 mmol, 76%. This procedure afforded crystals suitable for X-ray diffraction.

The EPR spectrum of this compound was measured and found to be essentially similar to the one already published.[3b]

Preparation of $NbCl_4(PEtPh_2)_2$ (3). The synthetic procedure employed was analogous to the one previously described[4] for preparing the $NbCl_4(PMe_2Ph)_2$ compound. Quite similar behavior of the reaction mixture, especially with respect to color changes, was observed in both cases.

$NbCl_5$ (2.0 g, 7.4 mmol) was placed in a 100-mL flask to which 40 mL of toluene, $PEtPh_2$ (3.5 mL, 16 mmol), and sodium amalgam (0.17 g, 7.4 mmol of Na in 5 mL of mercurry) were subsequently added. Vigorous stirring was applied. The initial red color changed to green and then slowly to red-brown. After 12 h of stirring, the solution was filtered and the solvent removed under vacuum. The oily residue was redissolved in benzene (20 mL). The solution was filtered into a Schlenk tube and covered with a layer of hexane. As with the PMe_2Ph adduct, the interdiffusion of solvents was accompanied by an upward migration of a green band. A large amount of the product deposited in the form of oily material, but red crystals suitable for X-ray diffraction were produced as well (ca. 0.5 g, 10% yield).

The use of $NbCl_4(THF)_2$ as a starting material for this compound was tried, but it proved inferior to the above procedure since only oils or the original THF adduct were obtained.

X-ray Crystallography. Single-crystal X-ray analyses have been carried out by application of general procedures that are fully described elsewhere.[6] The relevant data pertaining to the structure determination are summarized in Table I. All intensity data were corrected for polarization and Lorentz effects. In the case of **1** and **2** no absorption correction was made since ψ scans of selected reflections showed less than 10% variation in intensity.

$Nb_2Cl_8(PMe_3)_4$ (1). The position of the Nb atom was determined by a combination of Patterson synthesis with direct methods. The remaining atoms, including hydrogens, were located in a difference Fourier map.

$NbCl_4(PEt_3)_2$ (2). Since the β angle was very close to 90°, the possibility of an orthorhombic rather than a monoclinic cell was considered. However, the appearance of axial photographs, showing only one mirror plane, ruled out the former possibility. On the basis of the Patterson function, the metal atom was placed on a crystallographic inversion center at 0, 0, 0. The rest of the structure was developed by least-squares refinements and difference Fourier syntheses.

$NbCl_4(PEtPh_2)_2$ (3). The collection of data was carried out for a unit cell with c = 18.734 Å, which was justified by the pattern observed on the axial photograph. It showed intense spots defining horizontal lines with spacings corresponding to c equal one-half the above value, but there were a few weak spots between these layers, suggesting, perhaps, that the c-axis length be doubled. However, among the reflections that would have odd l indices in this doubled cell, only a few had intensity, I, greater than $3\sigma(I)$. Furthermore, the Patterson function was dominated by two vectors with coordinates equal to 0, 0, $^1/_2$ and $^1/_2$, $^1/_2$, $^3/_4$. In view of this, the structure was first solved for a cell with c reduced to 9.367 Å and in space group $P1$. On the basis of the Patterson map, two Nb atoms were placed

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

Table II. Positional and Isotropic Equivalent Thermal Parameters for $Nb_2Cl_8(PMe_3)_4$, $NbCl_4(PEt_3)_2$, and $NbCl_4(PEtPh_2)_2$[a]

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				a. $Nb_2Cl_8(PMe_3)_4$					
Nb	0.41349 (3)	0.000	0.000	1.308 (9)	H(1)	0.082 (2)	0.294 (2)	0.240 (2)	4.3 (9)*
Cl(1)	0.500	0.09148 (6)	0.09077 (7)	2.04 (2)	H(2)	0.321 (2)	0.370 (3)	0.185 (2)	5 (1)*
Cl(2)	0.32877 (7)	0.000	0.12719 (7)	2.28 (2)	H(3)	0.415 (2)	0.115 (2)	0.272 (2)	5.4 (9)*
P	0.32189 (7)	0.13501 (7)	0.000	2.03 (2)	H(4)	0.191 (3)	0.172 (4)	0.000	6 (2)*
C(1)	0.3326 (2)	0.2039 (2)	0.0856 (2)	3.59 (8)	H(5)	0.203 (2)	0.091 (2)	0.042 (2)	8 (1)*
C(2)	0.2124 (3)	0.1136 (3)	0.000	3.2 (1)					
				b. $NbCl_4(PEt_3)_2$					
Nb	0.000	0.000	0.000	2.92 (3)	C(2)	−0.362 (2)	−0.370 (1)	0.018 (1)	5.8 (4)
Cl(1)	0.1585 (5)	0.0030 (3)	−0.1702 (2)	5.40 (8)	C(3)	−0.048 (2)	−0.273 (1)	−0.160 (1)	4.7 (3)
Cl(2)	0.2353 (6)	−0.1141 (3)	0.0777 (3)	5.08 (8)	C(4)	0.108 (2)	−0.334 (1)	−0.098 (1)	6.7 (4)
P	−0.1812 (5)	−0.1787 (3)	−0.0702 (2)	3.14 (7)	C(5)	−0.396 (2)	−0.149 (1)	−0.155 (1)	5.0 (3)
C(1)	−0.263 (2)	−0.259 (1)	0.047 (1)	4.4 (3)	C(6)	−0.347 (2)	−0.101 (1)	−0.268 (1)	5.9 (4)
				c. $NbCl_4(PEtPh_2)_2$					
Nb	0.000	0.000	0.000	2.509 (8)	C(14)	0.2244 (5)	−0.0168 (3)	0.4289 (5)	4.8 (1)
Cl(1)	−0.16341 (9)	0.10438 (5)	−0.0627 (1)	3.57 (2)	H(2)	0.365 (4)	0.010 (2)	0.132 (4)	2.3 (7)*
Cl(2)	0.12931 (9)	0.05161 (6)	−0.1791 (1)	3.98 (2)	H(3)	0.593 (4)	0.035 (2)	0.147 (4)	4.4 (9)*
P	0.13735 (9)	0.09974 (5)	0.20611 (9)	2.74 (2)	H(4)	0.673 (4)	0.168 (2)	0.178 (5)	5 (1)*
C(1)	0.3157 (4)	0.1258 (2)	0.1923 (4)	2.94 (7)	H(5)	0.535 (4)	0.281 (2)	0.221 (4)	4.2 (9)*
C(2)	0.4048 (4)	0.0637 (2)	0.1597 (4)	3.60 (8)	H(6)	0.308 (4)	0.247 (3)	0.238 (5)	5 (1)*
C(3)	0.5408 (4)	0.0816 (3)	0.1541 (5)	4.03 (8)	H(8)	−0.013 (4)	0.193 (2)	0.388 (4)	4.4 (9)*
C(4)	0.5904 (4)	0.1616 (3)	0.1789 (4)	4.32 (9)	H(9)	−0.110 (6)	0.326 (3)	0.383 (7)	9 (2)*
C(5)	0.5026 (4)	0.2240 (2)	0.2098 (4)	4.17 (8)	H(10)	−0.113 (4)	0.407 (2)	0.199 (4)	4.4 (9)*
C(6)	0.3668 (4)	0.2066 (2)	0.2174 (4)	3.62 (8)	H(11)	−0.009 (4)	0.358 (2)	0.011 (4)	4.1 (9)*
C(7)	0.0529 (4)	0.2010 (2)	0.2061 (4)	3.10 (7)	H(12)	0.086 (4)	0.239 (2)	−0.003 (4)	3.6 (8)*
C(8)	−0.0161 (4)	0.2268 (3)	0.3158 (4)	4.05 (8)	H(13)	0.046 (4)	0.053 (2)	0.402 (4)	4.4 (9)*
C(9)	−0.0812 (5)	0.3042 (3)	0.3082 (5)	5.2 (1)	H(14)	0.183 (4)	0.108 (2)	0.458 (4)	3.8 (8)*
C(10)	−0.0758 (5)	0.3555 (3)	0.1911 (5)	4.77 (9)	H(15)	0.193 (4)	−0.058 (2)	0.366 (4)	5 (1)*
C(11)	−0.0097 (4)	0.3301 (2)	0.0819 (5)	4.34 (9)	H(16)	0.225 (4)	−0.033 (2)	0.531 (4)	4.2 (8)*
C(12)	0.0540 (4)	0.2526 (2)	0.0870 (4)	3.65 (8)	H(17)	0.311 (4)	−0.014 (2)	0.416 (4)	4.0 (9)*
C(13)	0.1426 (4)	0.0614 (2)	0.3929 (4)	3.83 (8)					

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

Table III. Selected Bond Distances (Å) and Angles (deg) in *trans*-$NbCl_4L_2$ Complexes[a]

	L = $PEtPh_2$	L = PEt_3
	A. Bond Distances	
Nb-Cl(1)	2.333 (1)	2.357 (3)
Nb-Cl(2)	2.401 (1)	2.374 (4)
Nb-P(1)	2.706 (1)	2.664 (3)
	B. Bond Angles[b]	
Cl(1)-Nb-Cl(2)	89.79 (3)	89.8 (1)
Cl(1)-Nb-P	90.51 (2)	88.8 (1)
Cl(2)-Nb-P	91.98 (3)	89.8 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] The molecule is positioned on an inversion center, making angles of the type L-Nb-L′ equal to 180.0°.

Table IV. Comparison of Important Interatomic Distances (Å) in Molecules of the Type $Nb_2Cl_8L_4$[a]

	L = PMe_3	L = PMe_2Ph[b]
	A. Bonding Contacts	
Nb-Nb′	2.833 (1)	2.838 (1)
Nb-Cl_b	2.541 (1)	2.541 [6]
Nb-Cl_t	2.502 (1)	2.484 [10]
Nb-P	2.671 (1)	2.700 [3]
	B. Short Non-Bonding Contacts	
Cl_b-Cl'_b	2.984 [12]	2.981 [8]
Cl_b-Cl_t	3.234 (1)	3.244 [7]
Cl_b-P	3.350 (1)	3.335 [16]
Cl_t-P	3.039 (1)	3.057 [7]

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Averaged values from ref 4.

Table V. Selected Bond Angles (deg) in the $Nb_2Cl_8(PMe_3)_4$ Molecule[a]

Nb′-Nb-Cl(1)	56.13 (2)	Cl(1)-Nb-Cl(2)′	142.72 (3)
Nb′-Nb-Cl(2)	123.67 (3)	Cl(1)-Nb-P	79.93 (3)
Nb′-Nb-P	124.15 (3)	Cl(1)-Nb-P′	143.19 (3)
Cl(1)-Nb-Cl(1)′	112.25 (4)	Cl(2)-Nb-Cl(2)′	112.67 (7)
Cl(1)-Nb-Cl(1)″	71.57 (6)	Cl(2)-Nb-P	71.87 (2)
Cl(1)-Nb-Cl(1)‴	72.23 (5)	P-Nb-P′	111.69 (7)
Cl(1)-Nb-Cl(2)	79.76 (3)	Nb-Cl(1)-Nb′	67.75 (4)

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

at the origin and in the center of the cell. Scale factor refinement gave relatively high values of residuals, apparently because the metal atom alone did not provide adequate phasing. Subsequent series of difference Fourier syntheses and least-squares refinements revealed the positions of the remaining non-hydrogen atoms. Two molecules of $NbCl_4(PEtPh_2)_2$ were found in the unit cell, and the arrangement of atoms was consistent with $P2_1/n$ symmetry. Refinement in that space group with the metal atom positioned on an inversion center confirmed the correctness of this assignment. All expected hydrogen atoms were located in a difference Fourier map and included in the refinement. Since the developed model refined well and the lack of disorder ruled out the possibility of a significant superlattice effect, it was concluded that for the purpose of obtaining a correct and accurate molecular structure there was no need to double the length of the *c* axis, and the few odd reflections that suggested this longer axis were disregarded.

Results and Discussion

Solid-State Structures. Positional and isotropic equivalent thermal parameters are listed in Table IIa–c. Tables III–V present important interatomic distances and angles. Tables of anisotropic thermal parameters, *B*'s, and complete listings of bond distances and angles are included in the supplementary material. ORTEP drawings of each of the three molecules are shown in Figures 1 and 2.

The chemical similarity of the two *trans*-$NbCl_4(PR_3)_2$ compounds, **2** and **3**, is matched by crystallographic similarities. Both crystallize in the space group $P2_1/n$ and have two molecules per unit cell with the metal atom located on a crystallographic inversion center. Although individual Nb–Cl_t distances (Table III) vary within each compound, the averages

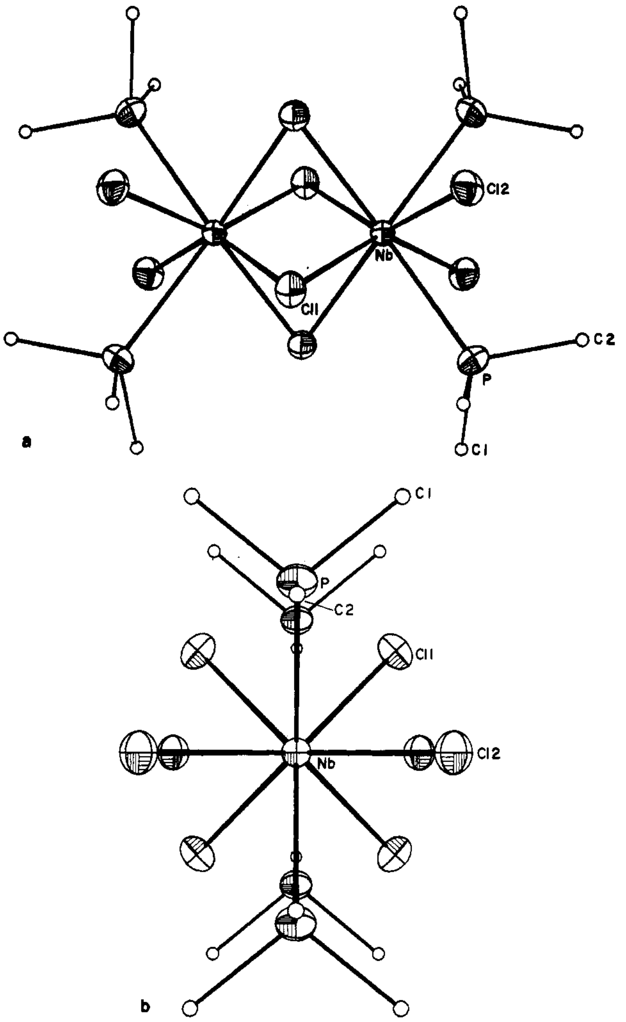

Figure 1. (a) ORTEP drawing of the $Nb_2Cl_8(PMe_3)_4$ molecule. Thermal ellipsoids enclose 50% of electron density. Methyl carbon atoms were assigned arbitrarily small thermal parameters for the sake of clarity. (b) As above. A view along the Nb–Nb axis.

are very close and equal to 2.367 [34] and 2.366 [9] Å for $PEtPh_2$ and PEt_3, respectively. All angles between nonequivalent atoms are very close to 90°, and in this sense the molecules might be described as octahedral. However, there is a substantial tetragonal distortion, with the Nb–P bonds being more than 0.3 Å longer than the Nb–Cl bonds. The Nb–P bond length has a small dependence upon the type of R groups, as will be discussed later.

The molecule of $Nb_2Cl_8(PMe_3)_4$ (**1**) has a structure analogous to that of the previously reported[4] $Nb_2Cl_8(PMe_2Ph)_4$. It consists of two square-antiprismatic $Nb(PMe_3)_2Cl_6$ units sharing a square Cl_4 face. The center of the molecule is located on a special position of *mmm* (D_{2h}) symmetry. The niobium atoms lie at the intersection of two crystallographic mirror planes, one of which incorporates the terminal chlorine atoms while the second incorporates phosphorus atoms together with one carbon and one hydrogen atom of each phosphine ligand. The bridging chlorine atoms lie in the mirror plane perpendicular to these two planes. Interatomic distances, which are compiled in Table IV, clearly show that the two compounds have practically identical bond lengths and separations between atoms. As with the complex involving PMe_2Ph, the existence of a single bond between the niobium atoms seems reasonable. The bond angles in **1**, which are also very similar to those in the PMe_2Ph analogue, are listed in Table V.

Comparison of the Nb–P distances in all four phosphine adducts shows that there is a certain pattern independent of the overall geometry of a complex. Thus, when one of the R groups is phenyl, the length of a Nb–P bond is ca. 2.700 Å. If the phosphine is entirely aliphatic, this bond is ca. 0.03 Å shorter. Since there are only two examples for each case, it is not certain whether this trend is general. If real, it may most probably be attributed to the different electron-donating abilities of the phosphines.

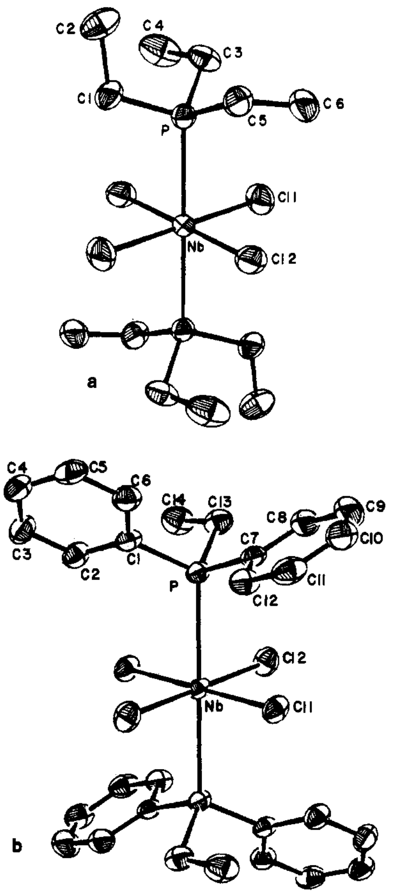

Figure 2. ORTEP drawings of the *trans*-$NbCl_4L_2$ complexes: (a) L = PEt_3; (b) L = $PEtPh_2$. Thermal ellipsoids enclose 40% of electron density. Nb atoms are located on an inversion center that relates the halves of the molecule.

Among the four phosphine adducts of $NbCl_4$ whose structures are now known, two crystallize as discrete monomeric, trans species and the other two are remarkable dimers with eight-coordinate Nb atoms connected by a single metal–metal bond. The crucial factor seems to be the bulkiness of the phosphine ligands. The phosphines that are sterically less demanding give dimeric species, whereas the bulkier ones give centrosymmetric trans complexes. Since the PEt_3 and $PEtPh_2$ ligands are too large to allow dimerization, it is doubtful that many other dimers will be found in the $NbCl_4(PR_3)_2$ series, although compounds with $PMeEt_2$, PMe_2Et, and possibly $PMePh_2$ may be possibilities. The question of whether any $NbBr_4(PR_3)_2$ compounds could form dimers is also of interest and is currently under investigation. It must also be recognized that there may be phosphines that for steric or other reasons may favor a *cis*-$NbX_4(PR_3)_2$ structure. Finally, of course, there may be structures in solution that are not the same as those found in the crystals.

$NbCl_4(PR_3)_2$ Compounds in Solution. These compounds exhibit complex and puzzling behavior in solution, an observation that has been made before by other authors.[2,3] It has been found that those solids that have red, brown, or related colors can give green solutions. This phenomenon is solvent dependent and was nicely elucidated for *trans*-$NbCl_4(i\text{-}Bu_3P)_2$.[3b] A change of color from brown to green observed upon addition of THF to a toluene solution of the *i*-Bu_3P

Table VI. Summary of the EPR Data for the $Nb_2Cl_8L_4$ Complexes in Solution[a]

T, °C	$L = PMe_3$		$L = PMe_2Ph$	
22	g_{iso}	1.83	g_{iso}	1.88
	$A_{iso}{}^{Nb}$	133 G	$A_{iso}{}^{Nb}$	143 G
−196	A^P	25 G	$g_{\parallel}$	1.97[b]
			$A_{\parallel}{}^{Nb}$	198 G[b]

[a] Because of the complexity of the EPR spectra only partial information could be obtained. [b] Values determined on the basis of the low-field part of the spectrum.

adduct was attributed to the substitution of one phosphine ligand by a THF molecule. The EPR spectrum of the toluene solution showed triplet superhyperfine structure (two phosphorus atoms coupled to Nb) while in the presence of THF these changed to doublets. We have observed that for the PEt_3 adduct also, addition of THF causes a color change from brown to green. It therefore seems that this phenomenon of phosphine substitution by THF and the accompanying change of color are common to all trans adducts.

The complexes that are dimers in the solid state also give green solutions, but apparently as a result of more complex processes. When the PMe_3 adduct (**1**) is prepared by addition of the phosphine to a slurry of $NbCl_4(THF)_2$ in CH_2Cl_2 or THF, the orange solid dimer and a green solution are obtained. The EPR spectrum of the solution at room temperature shows 10 lines characteristic of coupling to a niobium-93 nucleus ($I = {}^9/_2$, 100%). The spectrum is very similar to those previously reported for similar compounds.[3] This and other EPR data are recorded in Table VI. Although some of the lines appear doubled, this spectrum can be considered as typical for $Nb(d^1)$ systems. A spectrum of the same solution at −196 °C (where it remains green) is very complex, and only its low-field half is reasonably resolved. It shows five partially overlapping major signals (probably coupling to Nb) each with extensive fine structure, viz. five to six peaks, all about 25 G apart (typical for P coupling). These results are tentatively interpreted as indicating the presence of mononuclear Nb^{IV} adducts, e.g. $NbCl_4(PMe_3)_m$, $NbCl_4(PMe_3)_n(THF)_m$, etc.; coordination numbers higher than 6 cannot be neglected. More detailed characterization of this system is obstructed by the very low solubility of the solid product.

The previously reported dimer, $Nb_2Cl_8(PMe_2Ph)_4$, is more suitable for solution study. While it is only slightly soluble in benzene and toluene (to give slight green colorations), it dissolves readily in CH_2Cl_2 and THF. With THF a green solution is obtained initially, but over several hours the color changes to red. This color change, monitored by visible spectra, is due to the gradual disappearance of a band at 640 nm and concomitant growth of a new band at 450 nm. The low-energy band had disappeared entirely after ca. 21 h, and two isosbestic points, at 550 and 800 nm, were observed. This peculiar behavior, which is apparently associated with the coordinating ability of THF, requires further study.

In CH_2Cl_2, $Nb_2Cl_8(PMe_2Ph)_4$ gives solutions whose color is independent of time. However, it changes with concentration. It should be noted that measurements of electronic spectra were possible only down to ca. 400–500 nm as an intense band was present in that region. Concentrated solutions (ca. 8% w/v of $Nb_2Cl_8(PMe_2Ph)_4$) are brown and have no distinct features in the region 500–850 nm except for a shoulder at ca. 550 nm. Its EPR spectrum at room temperature is composed of 10 lines, unsymmetric with regard to intensity. At −196 °C there are 13 bands, apparently due to overlap of perpendicular and parallel components, but there is no resolution of the coupling to phosphorus. The separation of signals in the low-field region is ca. 200 G, which is consistent with $A_{\parallel}$ observed for monomeric $NbCl_4(phosphine)_2$ complexes. When this solution is diluted about 10-fold, it takes on a distinctly green coloration. There are two bands in the region 450–850 nm, at 705 and 575 nm. However, EPR spectra of the dilute and concentrated solutions at −196 °C are very similar, which indicates the presence of the same paramagnetic species. The above results are consistent with the occurrence of an equilibrium between monomers and dimers. The dimer is brown and the monomer green. The appearance of similar EPR signals at all concentrations would be due to the fact that the monomer is solely responsible for the EPR spectrum, with the dimer being EPR silent. The structure of the monomer is uncertain; it may be cis or trans but also seven- or eight-coordinate if there is partial decomposition. Control of decomposition is very difficult as CH_2Cl_2 is slightly oxidizing, the phosphine adducts are extremely sensitive to such agents, and a large amount of the solvent must be used to effect the color change.

In conclusion, the behavior of the dimeric $Nb_2Cl_8L_4$ complexes in solution can be explained, at least in part, by the equilibrium

$$Nb_2Cl_8L_4 \rightleftarrows 2NbCl_4L_2$$

The monomer may be involved in further reactions, thus giving a mixture of several mononuclear compounds. Further understanding of these systems will require thorough quantitative measurements for which the compounds now available are not very suitable. They are not soluble in totally inert solvents like benzene or toluene, and as mentioned, in media like CH_2Cl_2 or THF there is a possibility for additional, complicating, interactions and processes. Furthermore, one has to take into account that decomposition of the phosphine adducts yields blue products, which may contribute to the apparent green color of solutions.

Clearly, while the work reported here serves to clarify some aspects of this chemistry, especially by showing that dimers are possible and by confirming that compounds previously formulated as trans monomers on the basis of EPR spectra really are so constituted, it also demonstrates the need for a good deal more work before the full complexity of these deceptively "simple" systems is mapped out.

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Registry No. **1**, 92125-99-0; **2**, 73135-97-4; **3**, 92126-00-6; $Nb_2Cl_8(PMe_2Ph)_4$, 88801-80-3; $NbCl_5$, 10026-12-7; Nb, 7440-03-1.

Supplementary Material Available: Tables of structure factors and anisotropic thermal parameters, B's, and a full list of bond distances and angles for all three compounds (24 pages). Ordering information is given on any current masthead page.