the correct positions. Inspection of Fourier maps causes us to doubt the significance of any deviation of B(1) from the midpoint between U(1) and U(2). We would expect a significantly longer U(1)–U(2) distance if B(1) were singly bridged to one and triply bridged to the other. Finally, this model would give an unprecedented coordination number of 15 hydrogen atoms to U(2). Thus, while the diffraction data are not as definite as we would like, we recognize no acceptable alternative for the assignment of hydrogen neighbors.

The poor definition of the carbon atoms we believe reflects real variability of the positions of the propyl groups in the crystal structure.

A discussion of the volatility properties of this material must involve the molecular constitution of the vapor phase, which is not yet established. The discovery of this curious unsymmetrical dimer tends to complicate, rather than simplify, this question.

Registry No. $U(BH_4)_4$, 38903-76-3; $[U(BH_4)_4{\cdot}O(n\text{-}C_3H_7)_2]_2$, 65150-34-7.

Supplementary Material Available: Data processing formulas, a table of thermal parameters, coordinates and bond distances from the unrestrained refinements, and a listing of observed structure factors (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) This work was done with support from the U.S. Energy Research and Development Administration.
(2) R. R. Rietz and N. M. Edelstein, to be submitted for publication.
(3) R. R. Rietz, A. Zalkin, D. H. Templeton, N. M. Edelstein, and L. K. Templeton, companion paper, this issue.
(4) R. R. Rietz, N. M. Edelstein, H. Ruben, D. H. Templeton, and A. Zalkin, companion paper, this issue.
(5) H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, **75**, 219 (1953).
(6) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(7) J. Waser, *Acta Crystallogr.*, **16**, 1091 (1963).
(8) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).
(9) D. T. Cromer and J. T. Waber, *Acta Crystallogr., Sect. A*, **18**, 104 (1965).
(10) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(11) E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, *Inorg. Chem.*, **11**, 3009 (1972).

Contribution from the Laboratoire de Chimie Minérale Moléculaire, Equipe de Recherche Associée au CNRS,
Parc de Valrose, 06034 Nice Cedex, France, and the Institut de Cristallographie,
Université de Lausanne, BSP, Dorigny, 1015 Lausanne, Switzerland

Structural and Stereodynamic Studies on Molecular Early Transition Metal Derivatives. 4. Synthesis, Crystal Structure, and Molecular Constitution of Solutions of Bis(alkoxo)trichloroniobium(V)–Hexamethylphosphortriamide Adducts

LILIANE HUBERT-PFALZGRAF,*[1a] ALAN A. PINKERTON,[1b] and JEAN G. RIESS[1a]

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Compounds $NbCl_3(OR)_2{\cdot}HMPA$ (R = Me, *i*-Pr; HMPA = $OP(NMe_2)_3$) were obtained by disproportionation of $[NbCl_2(OR)_3]_2$ in methylene chloride or ether in the presence of HMPA. The products are characterized by IR, NMR, and mass spectrometry. An x-ray analysis on $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}HMPA$ shows that it crystallizes in the monoclinic space group $P2_1/n$ with unit cell dimensions a = 8.570 (2) Å, b = 14.087 (3) Å, c = 19.374 (3) Å, β = 94.80 (1)°, and Z = 4. The structure refined to R = 0.068. The crystal is built up of the meridional isomer; the two alkoxo groups are cis to each other, one of them being trans to the HMPA ligand. The two Nb–O-*i*-Pr bonds have comparable lengths and their shortness (1.81 Å average) implies a considerable d_π–p_π contribution to the implicit bonding. A trans weakening was observed for the Nb–Cl bond trans to an alkoxo group. The same geometrical isomer was always found to be the predominant species in fresh solutions, while oxo species were detected in aged solutions.

Introduction

We wish to report the unexpected isolation of the dialkoxotrichloroniobium adducts $NbCl_3(OR)_2{\cdot}OP(NMe_2)_3$ (R = Me, *i*-Pr) which resulted from the reaction of trialkoxodichloroniobium $[NbCl_2(OR)_3]_2$ with hexamethylphosphortriamide (HMPA) in dichloromethane or diethyl ether. Our initial aim was in fact to prepare the niobium oxoalkoxides $NbO(OR)_3$ or their adducts through an oxygen vs. chlorine exchange reaction between $[NbCl_2(OR)_3]_2$ and an oxo-type ligand such as dimethyl sulfoxide (Me_2SO) or HMPA. This exchange reaction, which is known to occur with the niobium pentahalides[2a] and methylniobium tetrahalides,[2b] was expected to provide a second synthetic route as an alternative to the reaction of $NbOCl_3$ with the alcohol in the presence of ammonia, which failed to give us the desired niobium oxoalkoxide in the case where R = Me.

Several niobium(V) halide alkoxides have already been isolated, but there is no information available about their structure, the molecular constitution of their solutions, and their coordination properties. Adducts $NbCl_4(OR){\cdot}MeCN$[3–5] (R = Me, Et) and $NbCl_3(OMe)_2{\cdot}MeCN$[3] had been obtained when the niobium pentachloride and pentaalkoxide were mixed in the appropriate ratio in acetonitrile. Compound $NbCl_3(OEt)_2{\cdot}MeCOOEt$ was isolated by reacting MeCOCl with $[NbCl_2(OEt)_3]_2$ and further afforded $NbCl_3(OEt)_2{\cdot}py$ by addition of pyridine.[4] On the other hand, a phosphine adduct, $NbCl_3(OEt)_2{\cdot}PPh_3$, was prepared by reacting $NbCl_5{\cdot}PPh_3$ with EtOH in CCl_4.[6]

The present paper describes the reaction of $[NbCl_2(OR)_3]_2$ with HMPA, the isolation and spectral characterization of the redistribution products $NbCl_3(OR)_2{\cdot}HMPA$ (R = Me, *i*-Pr), an x-ray diffraction structure of the adduct where R = *i*-Pr, and a preliminary picture of the molecular constitution of their solutions.

Experimental Section

All handling of compounds was carried out under dry argon. HMPA (gift from Pierrefitte), Me_2SO, and solvents were purified and dried according to standard methods. Niobium pentachloride was obtained by chlorination of the metal (gift from Produits Chimiques Ugine Kuhlmann). $NbCl_2(OMe)_3$ was prepared by reaction of an excess of methanol with $NbCl_5$ in benzene and recrystallized in a mixture of methylene chloride and toluene.

The ^1H NMR spectra were measured on solutions kept in sealed tubes with a JEOL C-60 HL spectrometer equipped with a variable-temperature system. Me_4Si was used as an internal reference. The infrared spectra were recorded on Nujol mulls on a Perkin-Elmer 577 spectrometer. The conductance measurements were performed with a Taccussel CDN6 conductometer. The molecular weight data were obtained on a Knauer vapor pressure osmometer. The mass

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spectra were obtained at 70 eV on a MS-30-AEI spectrometer. The elemental analyses were performed by the Centre de Microanalyse du CNRS.

A. Preparation and Characterization of Compounds. Synthesis of $NbCl_3(OMe)_2$·HMPA. Methanol (2 mL, 49.5 mmol) is added to a suspension of niobium pentachloride (2.1 g, 7.8 mmol) in methylene chloride. After 1 h, the clear solution is evaporated to dryness. The crude product is redissolved in 10 mL of CH_2Cl_2 and 1.5 mL (8.6 mmol) of HMPA is added at room temperature. The solution is stirred for 15 min and petroleum ether is then added until the solution becomes cloudy ($\simeq$10 mL). Crystallization occurs after 2 days at −30 °C. The crystals are removed by filtration and washed with petroleum ether. A second crop of white crystals of $NbCl_3(OMe)_2$·HMPA was obtained after a week (1.18 g, 35%, mp 92 °C). They are insoluble in ether and carbon tetrachloride and soluble in dichloromethane, acetone, and acetonitrile. Anal. Calcd for $C_8H_{24}O_3N_3Cl_3NbP$: C, 21.78; H, 5.48; Cl, 24.16; N, 9.53; P, 7.03. Found: C, 21.80; H, 5.45; Cl, 23.85; N, 9.54; P, 7.19.

IR (Nujol, cm^{-1}): 1188 (m), 1172 (m), 1145 (m) (ν_{as}(C—N)); 1070 (s), 1052 (s), 1040 (s) (ν(C—O—R)); 995 (s) (ν(P=O)); 940 (sh) (ν_s(P—N)); 765 (m), 752 (m), 721 (m) (ν_{as}(P—N)); 660 (w) (N—P—N bending); 570 (s), 552 (s) (ν(Nb—OR)); 473 (P—O bending); 382 (m), 330 (m), 290 (m), 240 (m) (ν(Nb—Cl)).

Mass spectrum (70 eV, 80 °C): M − OMe (6%), M − Cl (5%), M − Cl − $NHMe_2$ (2%), M − HCl − $OP(NMe_2)_3$ (5%), $OP(NMe_2)_3^+$ (45%), $OP(NMe_2)_2^+$ (100%), $NbOH_3^+$ (10%), Nb^+ (10%).

Synthesis of $NbCl_3$(O-*i*-Pr)$_2$·HMPA. The same procedure was used, but the addition of the ligand was carried out at −30 °C. White crystals of $NbCl_3$(O-*i*-Pr)$_2$·HMPA (30%, mp 113 °C) are obtained. Anal. Calcd for $C_{12}H_{32}O_3N_3Cl_3NbP$: C, 28.99; H, 6.49; Cl, 21.44; N, 8.45; P, 6.24. Found: C, 28.96; H, 6.31; Cl, 20.48; N, 9.06; P, 7.57.

IR (Nujol, cm^{-1}): 1118 (s), 1170 (s), 1132 (s) (ν_{as}(C—N)); 1106 (s), 1080 (vs), 1070 (sh), 1010 (vs) (ν(C—OR)); 990 (s) (ν(P=O)); 937 (s) (ν_s(P—N)); 862 (s), 760 (s), 763 (s) (ν_{as}(P—N)); 659 (m) (N—P—N bending), 600 (s), 539 (m) (ν(Nb—OR)); 480 (s) (PO bending); 380 (s), 330 (m) (ν(Nb—Cl)).

Mass spectrum (70 eV, 100 °C): M − Cl (9%), P − OPr (1%), M − $O(Pr)_2$ − Cl (12%), M − $OP(NMe_2)_3$ − Cl (3%), M − $OP(NMe_2)_3$ − Cl − OPr (11%), $OP(NMe_2)_3$ (58%), $OP(NMe_2)_2^+$ (100%), NbO^+ (3%), Nb^+ (24%).

B. X-Ray Measurements. Crystals of $NbCl_3$(O-*i*-Pr)$_2$·HMPA suitable for an x-ray diffraction analysis grew in the CH_2Cl_2 reaction mixture at −30 °C.

Crystal Data. A crystal with approximate dimensions 0.25 × 0.24 × 0.16 mm was mounted in a Lindemann tube under dry argon. The unit cell was determined on the diffractometer to be monoclinic with cell dimensions a = 8.570 (2) Å, b = 14.087 (3) Å, c = 19.374 (3) Å, and β = 94.80 (1)°, containing 4 formula units. The measurement temperature is 24 ± 1 °C. The density d = 1.45 g cm^{-3} was measured by flotation in a mixture of $CFCl_2CF_2Cl$ and ether (d_{calcd} = 1.42 g cm^{-3} for Z = 4). The space group was determined to be $P2_1/n$ by systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$).

Crystallographic Procedures. The intensities of 3062 unique reflections, of which 1225 were less than the 3σ limit, were measured with a Syntex $P2_1$ automated diffractometer using Mo Kα radiation monochromatized with niobium filters and a profile interpretation technique[7] to a maximum of $(\sin \theta)/\lambda$ 0.540 Å^{-1}, operating in the scan mode θ–2θ (range 2°). No absorption correction was applied (μ = 9.3 cm^{-1}). Scattering factors for the neutral atoms and anomalous dispersion factors for Nb, Cl, O, and P atoms were taken from literature.[8] All computer programs were taken from the "X-Ray 72" program system.[9] The figure was drawn using the program ORTEP.[10]

Solution of the Structure. The position of the niobium was found from the interpretation of a three-dimensional Patterson map. Two difference Fourier syntheses were required to find unequivocally all the medium weight atoms. A cycle of full-matrix least-squares refinement followed by another difference Fourier located all the light nonhydrogen atoms. The carbon atoms of the isopropoxo groups were seen to be rather diffuse. The resulting structure was refined on the structure factors $|F|$ by block-matrix least squares. The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure factors, respectively. The weights used were $1/\sigma^2$ where the esd's (σ) of the structure factors were derived from counting statistics and the variations in the intensities of the periodically measured check reflections. The refinement converged to an $R = \sum||F_o| - |F_c||/\sum|F_o| = \sum|\Delta F|/\sum|F_o|$ of 0.068 and an $R_w = [\sum(w\Delta F)^2/\sum(wF_o)^2]^{1/2}$ of 0.071 (goodness of fit $[\sum w(\Delta F)^2/N_{ref} - N_v]^{1/2}$ of 3.53 (N_{ref} and N_v are respectively the number of reflections and the number of variables)). In the final cycles the carbon atoms were allowed to vibrate isotropically and all other atoms anisotropically. The maximal shift–error ratio was 0.7 on the final cycle. The number of observations per refined parameter was 20. A compilation of observed and calculated structure factors is available.

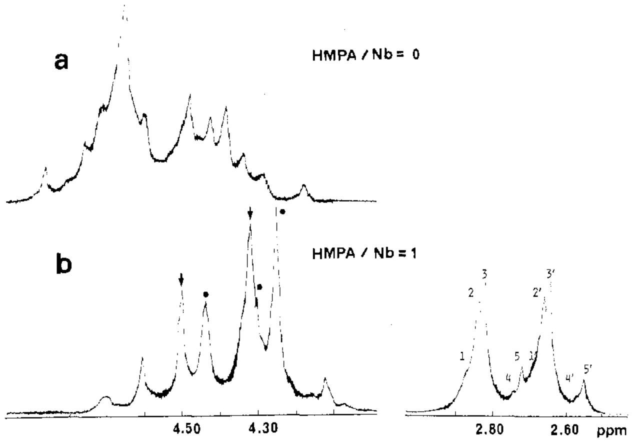


Figure 1. Proton NMR spectra measured at −35 °C (methoxo and ligand regions) on a 0.3 M solution of $[NbCl_2(OMe)_3]_2$ in CD_2Cl_2 and for various R = HMPA:Nb molar ratios. ↓ stands for $NbCl_3(OMe)_2$·HMPA resonances and ● for those of NbCl(OMe)$_4$·HMPA; doublet 5 corresponds to the free ligand.

Results and Discussion

The Reaction of $[NbCl_2(OR)_3]_2$ with HMPA. When the reaction between $[NbCl_2(OR)_3]_2$ and HMPA or Me_2SO in CD_2Cl_2 or $CDCl_3$ at −35 °C was monitored by ^1H NMR, it revealed very intricate behavior.

To start with the NMR spectrum of a recrystallized sample of $[NbCl_2(OMe)_3]_2$ (sharp melting point at 162 °C) exhibited several signals (Figure 1a), the relative areas of which depend on the solvent and concentration, which means that they belong to different molecular species. These species are in fast dynamic equilibrium among themselves on the NMR time scale, since all signals coalesce above 63 °C (in $CDCl_3$). Slow evaporation of the solutions in CD_2Cl_2 or $CDCl_3$ gives back the initial product (identical melting point and IR spectra). No change in the aspect of the spectra of these solutions was found after a month at room temperature. There was in particular no methyl ether detectable nor any ν(Nb=O) absorption in the infrared. The various species in equilibrium can be either isomers or redistribution products. It has been shown that the presence of isomers in dynamic equilibrium can be expected for this type of early transition metal derivatives.[11] On the other hand, no indications could be obtained concerning the extent of redistribution reactions on $[NbCl_2(OMe)_3]_2$ in nonpolar media.

Upon addition of 1 equiv of HMPA at −35 °C (Figure 1b), the spectrum immediately undergoes a drastic change in the methoxo region, and five doublets appear in the ligand region. The main constituents (assignments given on Figure 1b) are $NbCl_3(OMe)_2$·HMPA (40%) and NbCl(OMe)$_4$·HMPA (40%). These assignments result from independent studies of solutions of these two species (see below and ref 12). No direct evidence for the presence of $NbCl_2(OMe)_3$·HMPA could be obtained, although its presence in small amounts cannot be excluded. Since all signals coalesce both in the methoxo and in the HMPA regions (above 50 and 35 °C), this means that the redistribution of MeO vs. Cl substituents is rapid on the NMR time scale as well as the exchange between the free and the coordinated ligand.

Table I. Atomic Parameters for $NbCl_3(O\text{-}i\text{-}Pr)_2OP(NMe_2)_3$ with Standard Deviations in Parentheses[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
NB	0.5377 (1)	0.23840 (8)	0.40329 (5)	0.0750 (8)	0.0735 (8)	0.0431 (5)	0.0180 (8)	0.0112 (5)	0.0044 (7)
Cl1	0.3752 (4)	0.0998 (2)	0.4064 (2)	0.099 (3)	0.100 (3)	0.087 (2)	−0.000 (2)	0.029 (2)	0.022 (2)
Cl2	0.4166 (4)	0.2706 (2)	0.2864 (1)	0.081 (2)	0.102 (3)	0.056 (2)	0.005 (2)	0.001 (2)	0.018 (2)
Cl3	0.7147 (4)	0.3683 (2)	0.3868 (2)	0.103 (3)	0.073 (2)	0.091 (2)	0.000 (2)	0.005 (2)	−0.005 (2)
P1	0.7448 (4)	0.0764 (2)	0.3083 (1)	0.060 (2)	0.069 (2)	0.049 (2)	0.004 (2)	0.010 (2)	−0.005 (2)
O1	0.6911 (8)	0.1544 (5)	0.3550 (3)	0.070 (6)	0.071 (5)	0.050 (4)	0.012 (5)	0.009 (4)	−0.005 (4)
O2	0.388 (1)	0.3119 (6)	0.4353 (4)	0.082 (6)	0.101 (6)	0.061 (5)	0.035 (6)	0.021 (5)	0.004 (4)
O3	0.6386 (9)	0.2129 (5)	0.4872 (3)	0.101 (7)	0.088 (6)	0.041 (4)	0.022 (5)	0.004 (4)	0.004 (4)
N1	0.635 (1)	0.0523 (6)	0.2388 (4)	0.077 (8)	0.064 (7)	0.051 (6)	−0.006 (6)	0.012 (6)	−0.004 (5)
N2	0.909 (1)	0.1106 (7)	0.2847 (5)	0.070 (8)	0.084 (8)	0.106 (8)	−0.004 (7)	0.040 (7)	−0.035 (7)
N3	0.752 (1)	−0.0219 (7)	0.3511 (4)	0.12 (1)	0.069 (7)	0.054 (6)	0.020 (7)	0.011 (6)	0.005 (6)

Atom	x	y	z	U, Å^2	Atom	x	y	z	U, Å^2
C1	0.485 (2)	0.003 (1)	0.2419 (7)	0.099 (5)	C7	0.240 (2)	0.362 (1)	0.4309 (7)	0.111 (5)
C2	0.638 (2)	0.1078 (9)	0.1729 (6)	0.083 (4)	C8	0.280 (2)	0.465 (1)	0.4434 (8)	0.151 (7)
C3	0.987 (2)	0.199 (1)	0.3035 (7)	0.111 (5)	C9	0.137 (2)	0.314 (1)	0.4787 (9)	0.155 (7)
C4	1.011 (2)	0.045 (1)	0.2501 (7)	0.112 (5)	C10	0.674 (3)	0.194 (2)	0.563 (1)	0.22 (1)
C5	0.778 (2)	−0.117 (1)	0.3197 (6)	0.095 (4)	C11	0.810 (4)	0.164 (2)	0.578 (1)	0.24 (1)
C6	0.786 (2)	−0.0214 (9)	0.4293 (7)	0.100 (5)	C12	0.611 (3)	0.269 (2)	0.597 (1)	0.24 (1)

[a] The expression for the temperature factors has the form $\exp(-T)$ where $T = 8\pi^2 U(\sin^2 \theta)/\lambda^2$ for isotropic atoms and $T = 2\pi^2 \Sigma h_i h_j U_{ij} a_i^* a_j^*$ for anisotropic atoms.

When more than 1 equiv of ligand is used, some methyl ether starts to become detectable, indicating the formation of some oxoniobium species, as further evidenced by the apparition of the ν(Nb=O) absorption at 940 cm^{-1} in the IR. Simultaneously new peaks develop in the MeO region while those of the free ligand increase in the HMPA region. However, the formation of the oxoniobium compounds does not proceed through the expected exchange of chlorine vs. oxygen between the niobium chlorides alkoxides and the ligand, as no $Cl_2P(NMe_2)_3$ was detected. It is worthwhile to stress this important difference in the lability of the methoxo groups between the niobium haloalkoxides and pentaalkoxides, where no Me_2O was obtained even in the presence of a high excess of the same oxo ligands.[13]

Some differences were noted with Me_2SO as the oxo ligand. In CH_2Cl_2 and for an $R = Me_2SO{:}Nb$ molar ratio <1, scrambling reactions are also observed, but the evolution of Me_2O occurs already for smaller amounts of the oxo ligand present. On the other hand, a white precipitate was formed. Attempts to isolate the niobium species for $R = 1$ gave a product whose analysis was close to $NbCl_2(OMe)_3{\cdot}Me_2SO$. However, the low solubility of the various niobium–dimethyl sulfoxide adducts prevented further purification by crystallization.

The dialkoxotrichloro adducts $NbCl_3(OR)_2{\cdot}$HMPA could be isolated from dichloromethane or diethyl ether solutions in 30–35% yields in the case where R = Me and *i*-Pr. They were characterized by elemental analyses and IR and mass spectrometry. The infrared spectra of the solid show numerous absorptions bands. Those at 995 cm^{-1} (R = Me) and 990 cm^{-1} (R = *i*-Pr) were tentatively assigned to the ν(P=O) vibration.[14] The Nb–O(R) stretching region presents two absorptions respectively located at 570 and 552 cm^{-1} for R = Me and at 600 and 530 cm^{-1} for R = *i*-Pr.[15]

The products are relatively volatile, which allowed their mass spectra to be measured. The molecular ions were not detected and the parent peaks correspond to the loss of a chlorine atom or an alkoxo group. Furthermore the peak resulting from the loss of an alkoxo group is less abundant for R = *i*-Pr than for R = Me, while the base peak is in both cases m/e 135 ($OP(NMe_2)_2^+$). These observations are in agreement with the x-ray results which suggest that the niobium–isopropoxo bond is stronger than the niobium–methoxo bond.

In order to ascertain that the isolated solid consists of one single molecular species and to recognize which is the isomer present in the solid state, we performed an x-ray structure determination on $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}$HMPA. This crystal structure was also expected to shed some light on the p_π–d_π contribution in the niobium–alkoxo bond.

Table II. Bond Lengths (Å) and Angles (deg) for $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}$HMPA with Standard Deviations in Parentheses

	Coordination Polyhedron		
Nb–Cl1	2.401 (4)	Nb–O1	2.051 (7)
Nb–Cl2	2.452 (3)	Nb–O2	1.801 (8)
Nb–Cl3	2.415 (4)	Nb–O3	1.811 (6)
Cl1–Nb–Cl2	88.4 (1)	Cl3–Nb–O1	86.8 (2)
Cl1–Nb–Cl3	172.4 (1)	Cl3–Nb–O2	94.9 (3)
Cl1–Nb–O1	86.4 (2)	Cl3–Nb–O3	90.6 (3)
Cl1–Nb–O2	91.5 (3)	O1–Nb–O2	172.7 (3)
Cl1–Nb–O3	92.9 (3)	O1–Nb–O3	91.1 (3)
Cl2–Nb–Cl3	87.7 (1)	O2–Nb–O3	96.1 (3)
Cl2–Nb–O1	85.6 (2)	Nb–O1–P1	157.9 (5)
Cl2–Nb–O2	87.3 (2)	Nb–O2–C7	155.2 (7)
Cl2–Nb–O3	176.4 (2)	Nb–O3–C10	163 (1)
	Isopropoxo groups		
O2–C7	1.45 (2)	O3–C10	1.49 (2)
C7–C8	1.50 (2)	C10–C11	1.26 (4)
C7–C9	1.49 (2)	C10–C12	1.38 (4)
O2–C7–C8	106 (1)	O3–C10–C11	113 (2)
O2–C7–C9	107 (1)	O3–C10–C12	106 (2)
C8–C7–C9	119 (1)	C11–C10–C12	122 (2)
	HMPA Ligand		
O1–P1	1.519 (7)	N1–C2	1.50 (1)
P1–N1	1.61 (1)	N2–C3	1.45 (2)
P1–N2	1.59 (1)	N2–C4	1.47 (2)
P1–N3	1.61 (1)	N3–C5	1.50 (2)
N1–C1	1.47 (2)	N3–C6	1.52 (1)
O1–P1–N1	117.8 (5)	C1–N1–C2	110.9 (9)
O1–P1–N2	105.8 (5)	P1–N2–C3	125.9 (9)
O1–P1–N3	108.4 (4)	P1–N2–C4	120.8 (9)
N1–P1–N2	106.8 (5)	C3–N2–C4	112.5 (1.1)
N1–P1–N3	104.1 (5)	P1–N3–C5	124.2 (7)
N2–P1–N3	114.3 (5)	P1–N3–C6	120.3 (8)
P1–N1–C1	121.0 (8)	C5–N3–C6	112.7 (9)
P1–N1–C2	123.7 (8)		

Molecular Structure of $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}$HMPA. The molecular structure of $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}$HMPA is shown in Figure 2, which also defines the atom numbering scheme. The atomic positional parameters and thermal parameters are listed in Table I. The calculated bond lengths and angles are presented in Table II.

The crystal structure is built up of monomeric $NbCl_3(O\text{-}i\text{-}Pr)_2{\cdot}$HMPA molecules. The only intermolecular interactions are the van der Waals contacts. The niobium atom is at the center of a distorted coordination octahedron, consisting of

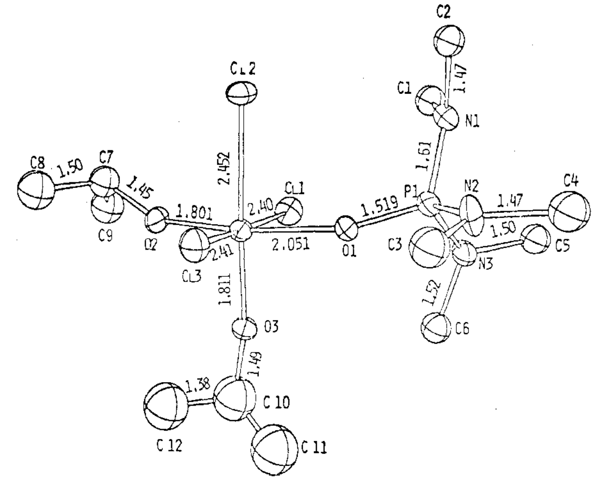


Figure 2. ORTEP view of $NbCl_3(O\text{-}i\text{-}Pr)_2\cdot HMPA$ with bond lengths (Å).

three chlorine, two alkoxo groups, and one HMPA ligand. The two isopropoxo groups are cis to each other, one of them being trans to the HMPA ligand. The coordination polyhedron is less distorted than for $NbOCl_3\cdot(HMPA)_2$[16] (Cl_1NbCl_3 angle 172.4 (1)° vs. 168.14 (8)°).

Despite the fact that the isopropoxo groups occupy nonequivalent positions, one being trans to a chlorine, the other to the HMPA ligand, no significant difference was found between the two Nb–OR distances. These lengths (1.806 (7) Å av) are comparable to those obtained on *fac*-Nb(NCS)(O-*i*-Pr)$_3$dbm[17] (dbm = dibenzoylmethane) (1.835 (5) Å average) and are significantly shorter than the sum of the covalent radii (2.07 Å). They are also shorter than those found for the terminal niobium–alkoxo bonds in $[Nb(OMe)_5]_2$ (1.899 (7) Å)[18] and $NbCl(OMe)_2(S_2CNEt_2)_2$ (1.88 (1) Å)[19] or in $NbOCl_2(OEt)\cdot bpy$ (1.87 (1) Å).[20] It is also noticeable that the Nb–O-*i*-Pr distance is only 0.12 Å longer than the niobium–oxo bond in the $NbOCl_3(HMPA)_2$ adduct. This remarkably short Nb–O-*i*-Pr distance implies a considerable d_π–p_π contribution to the niobium–isopropoxo linkage, and the large NbOC angles (159 (1)° average) are consistent with this scheme. The carbon atoms of the isopropoxo group trans to the chlorine are poorly defined and show high thermal motion.

The niobium–chlorine distances depend on the nature of the ligand in the trans position; the weakest bond is observed for the Nb–Cl bond trans to an isopropoxo group (2.452 (3) Å as compared to 2.408 (4) Å for the two other Nb–Cl bonds). All Nb–Cl distances are large with respect to the sum of their covalent radii (2.33 Å) or to the values found for the terminal Nb–Cl bond in $[NbCl_5]_2$ (2.302 (5) or 2.250 (6) Å).[21] However, a distance of 2.460 (5) Å has already been reported for the Nb–Cl bond trans to a methoxo group in $NbCl(OMe)_2(S_2CNEt_2)_2$.[19] On the other hand the Nb–Cl lengths of the chlorine trans to each other are similar to those obtained on $NbOCl_3(HMPA)_2$; in this case, however, no weakening was observed on the Nb–Cl bond trans to the Nb–O(P) linkage and therefore it seems that the trans weakening produced by the Nb–OR bond is higher than that resulting from the Nb–O(P) coordination bond. This is in agreement with the predictions of Buslaev,[22] who suggests that the trans weakening increases with the multiplicity of the trans directing bond.

Steric hindrance between the two bulky isopropoxo groups is evidenced by a close intramolecular $O_2\cdots O_3$ contact (2.68 (1) vs. 2.80 Å for the van der Waals radii) despite a rather large O_2NbO_3 angle (96.1 (3)°). On the other hand, small contacts are observed between the oxygen atoms of the phosphoryl ligand and its cis neighboring isopropoxo group ($O_1\cdots O_3$ 2.76 (1) Å). Thus it appears that cis configuration of the alkoxo groups is favored in the niobium(V) mixed alkoxides, as also illustrated in *fac*-Nb(NCS)(O-*i*-Pr)$_3$dbm[17] or $NbCl(OMe)_2(S_2CNEt_2)_2$,[19] even when steric hindrance is present and seems essentially to be attributable to electronic factors.

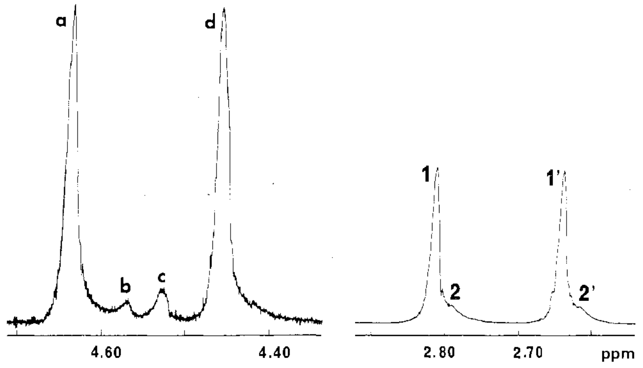
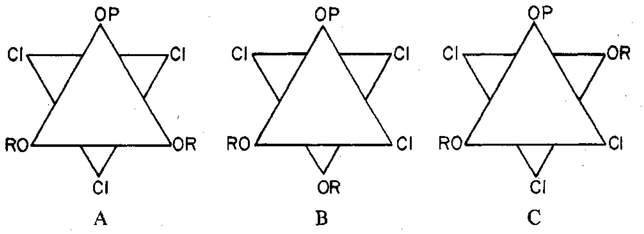


Figure 3. Proton NMR measured at 20 °C on a 0.3 M solution of $NbCl_3(OMe)_2\cdot HMPA$ in CD_2Cl_2 (intensity ratio 10:1 between the methoxo and the HMPA ligand region).

The Nb–O(P) coordination bond is strong, as shown by its short length (2.051 (7) Å), while the NbOP angle is quite large (157.9 (5)°). These data are comparable with those previously reported on $MoO_5\cdot py\cdot(HMPA)$,[23] $NbOCl_3(HMPA)_2$,[16] or $MoOCl_3(HMPA)_2$.[24] Structural x-ray data on hexamethylphosphortriamide adducts are scarce, and they are nonexistent as yet for the free ligand; however, the P–O bond length for the HMPA ligand in $NbCl_3(O\text{-}i\text{-}Pr)_2\cdot HMPA$ (1.519 (7) Å) is in agreement with the 1.51-Å bond distance predicted for the free ligand on the basis of CNDO/2 calculations.[25] On the other hand, the P–N bond length for the complexed ligand is significantly shorter (av 1.60 (1) Å) than the one predicted for the free ligand (1.69 Å) from these calculations, which would mean that the electron donation from the nitrogen to the phosphorus atom contributes to maintain the P=O bond order practically unchanged.[16] The average sum of the angles (358°) around the nitrogen atoms indicates that they have essentially planar configuration and is consistent with this back-donation scheme.

Molecular Constitution of the Solutions of $NbCl_3(OR)_2\cdot$HMPA. As illustrated in previous papers,[11] coordination compounds of the early transition metals having a single well-defined molecular structure in the solid often undergo drastic changes in nature and give complex mixtures once they are put in solution. We therefore investigated the molecular constitution of solutions of the isolated crystalline $NbCl_3(OR)_2\cdot HMPA$ adducts, of which the x-ray structures were now determined. The ^1H NMR spectra of $NbCl_3(OMe)_2\cdot HMPA$ measured at 20 °C on a 0.3 M solution in CD_2Cl_2 (Figure 3) immediately showed four signals (a, b, c, d) in the methoxo region, and two doublets ($J_{H-P} = 9.8 \pm 0.5$ Hz) for the ligand. While the relative areas of most of these signals vary when the experimental conditions are changed (nature of the solvent, concentration, addition of an excess of HMPA), resonances a and d always remain of comparable area and keep a 1:3 area ratio with respect to doublet 1. Signals a and d and doublet 1 are therefore assigned to a same molecular species. No free ligand was detected. The same general pattern is observed in acetonitrile but with only three resonances in the methoxo region, two of them being largely predominant (85% of the total peak area) and always keeping comparable area.

These observations and the fact that $NbCl_3(OMe)_2\cdot HMPA$ is monomeric (vapor pressure osmometry: found 460, calcd 440.7) and nonconducting in acetonitrile, which implies that the niobium atom is hexacoordinated, are tentatively interpreted to mean that these solutions mainly consist of mixtures of the three possible octahedral isomers A, B, and C.



facial meridional

OP = OP[NMe_2]$_3$

Resonances a and d, and doublet 1, which represent 90% of the total peak area, are assigned to the meridional isomer B in which the alkoxo groups occupy nonequivalent positions, one being trans to a chlorine atom and the other to the HMPA ligand. This isomer is also the one which is found in the solid state for $NbCl_3(O\text{-}i\text{-}Pr)_2 \cdot$HMPA. Signals b and c and doublet 2 are assigned to isomers A and C, but the NMR data do not allow one to specify which is which. Since HMPA is trans to a chlorine atom in both A and C, it is expected to have very similar chemical shifts in both isomers, which would account for the fact that it shows only one doublet, the area of which is, as expected, three times that of signals b and c taken together.

No interconversion among these three species occurs on the NMR time scale up to 70 °C. The presence of redistribution products in fresh solutions is unlikely, as the formation of $NbCl_3(OMe)_2 \cdot$HMPA from $[NbCl_2(OMe)_3]_2$ is strongly favored and as no peak corresponding to $NbCl_2(OMe)_3 \cdot$HMPA (2:1 ratio expected) was detected.

The molecular constitution of $NbCl_3(O\text{-}i\text{-}Pr)_2 \cdot$HMPA in CH_3CN or CD_2Cl_2 further supports this scheme. In a 0.3 M CH_3CN solution, isomer B ($\delta_{C\text{-}H} = 5.21$ and 5.19 ppm, $\delta_{CH_3} = 1.39$ and 1.34 ppm, $J_{C\text{-}H} = 6 \pm 0.5$ Hz, HMPA ligand $\delta = 2.75$ ppm) is favored (90%). A second species, which exhibits a sextuplet at 5.18 ppm, a doublet at 1.12 ppm, and an HMPA ligand at 2.68 ppm, was also detected.

An evolution of the $NbCl_3(OR)_2 \cdot$HMPA solutions was observed in all cases, with new signals becoming detectable after ca. 1 week at room temperature. This evolution was favored by CH_3CN or an excess of HMPA. In the methoxo region, the proportion of isomer B decreases while those of other species increase and several new peaks appear. Simultaneously, new doublets are observed in the HMPA region, and Me_2O ($\delta = 3.36$ ppm, also characterized by its IR) becomes detectable. These modifications are very complex and are presumably to be attributed to some isomerizations and to the formation of niobium–oxo species as evidenced by the apparition of ν(Nb═O) absorptions (940, 935 cm^{-1}) in the IR.

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Registry No. $NbCl_3(OMe)_2 \cdot$HMPA, 65149-39-5; $NbCl_3(O\text{-}i\text{-}Pr)_2 \cdot$HMPA, 65120-52-7; $[NbCl_2(OMe)_3]_2$, 25970-86-9; $[NbCl_2(O\text{-}i\text{-}Pr)_3]_2$, 65120-53-8.

Supplementary Material Available: A listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Equipe de Recherche Associée au CNRS. (b) Université de Lausanne.
(2) (a) D. L. Keppert, "The Early Transition Metals", Academic Press, London, 1972; D. B. Copley, F. Fairbrother, K. H. Grundy, and A. Thompson, *J. Less-Common Met.*, **6**, 407 (1964); D. Brown, J. Hill, and C. E. F. Richard, *ibid.*, **20**, 57 (1970); J. R. Dorschner, *J. Inorg. Nucl. Chem.*, **34**, 2665 (1972); (b) C. Santini-Scampucci and J. G. Riess, *J. Chem. Soc., Dalton Trans.*, 1433 (1974).
(3) M. Schönhern and L. Kolditz, *Z. Chem.*, **10**, 72 (1970).
(4) L. Kolditz and M. Schönhern, *Z. Chem.*, **9**, 349 (1965).
(5) R. Gut, H. Buser, and E. Schmid, *Helv. Chim. Acta*, **48**, 878 (1965).
(6) M. A. Glushkova, M. M. Ershova, N. A. Ovchinnikova, and Yu. A. Buslaev, *Zh. Neorg. Khim.*, **17**, 147 (1972).
(7) H. Blessing, P. Coppens, and P. Becker, *J. Appl. Crystallogr.*, **7**, 488 (1972); D. Schwarzenbach, TWOTHLEH, a SYNTEX-P2$_1$ data collection program including scan profile interpretation.
(8) D. T. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968); D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).
(9) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "X-Ray 72" system, Technical Report TR-192, Computing Science Center, University of Maryland, June 1972 (as modified by D. Schwarzenbach).
(10) C. K. Johnson, Report ORNL-3794 Oak Ridge National Laboratory, Oak Ridge, Tenn., 1971.
(11) J. G. Riess, R. Muller, and M. Postel, *Inorg. Chem.*, **13**, 1802 (1974); L. G. Hubert-Pfalzgraf, R. C. Muller, M. Postel, and J. G. Riess, *ibid.*, **15**, 40 (1976).
(12) L. G. Hubert-Pfalzgraf and J. G. Riess, to be submitted for publication.
(13) L. G. Hubert-Pfalzgraf, *Inorg. Chim. Acta*, **12**, 229 (1975); L. G. Hubert-Pfalzgraf and J. G. Riess, *Chimia*, **30**, 481 (1976).
(14) M. W. G. de Bolster and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, **90**, 477 (1971).
(15) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1951).
(16) L. G. Hubert-Pfalzgraf and A. A. Pinkerton, *Inorg. Chem.*, **16**, 1895 (1977).
(17) F. Dahan, R. Kergoat, M. C. Sénéchal-Toquer, and J. E. Guerchais, *J. Chem. Soc., Dalton Trans.*, 2202 (1976).
(18) A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, and J. G. Riess, *Inorg. Chem.*, **15**, 1196 (1976).
(19) J. W. Moncrief, D. C. Pantaleo, and N. E. Smith, *Inorg. Nucl. Chem. Lett.*, 7, 255 (1971).
(20) B. Kamenar and C. K. Prout, *J. Chem. Soc. A*, 2379 (1970).
(21) A. Zalkin and D. E. Sands, *Acta Crystallogr.*, **11**, 615 (1958).
(22) E. M. Shustorovich, M. A. Parai-Koshits, and Yu. A. Buslaev, *Coord. Chem. Rev.*, **17**, 1 (1975).
(23) J. M. Le Carpentier, R. Schlupp, and R. Weiss, *Acta Crystallogr., Sect. B*, **28**, 1278 (1972).
(24) C. D. Garner, P. Lambert, F. E. Mabbs, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1191 (1977); P. Khadadad, B. Viossat, and N. Raddi, *Acta Crystallogr., Sect. B*, **33**, 1035 (1977).
(25) R. Dorschner and G. Kaufman, *Inorg. Chim. Acta*, **15**, 71 (1975).