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Niobium Compounds

σ-Organoniobium Compounds with $[NbR_4]^-$ and NbR_4 Stoichiometries**

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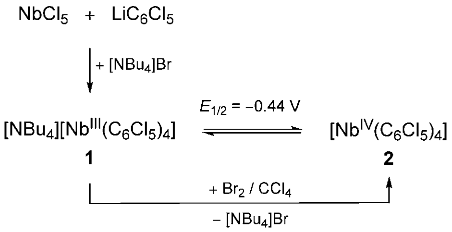
Dedicated to Prof. Dr. S. Alvarez on the occasion of his 60th birthday

Despite the well-developed organometallic chemistry of Nb,[1] homoleptic σ-organoniobium compounds remain particularly scarce and confined to extreme oxidation states. On the one hand, neutral high-valent (presumably square-pyramidal) $[Nb^{V}Me_5]$ is unstable,[2] while the more-saturated trigonal-prismatic species $[Nb^{V}Me_6]^-$ is stable enough to allow its structural characterization.[3] Little is known about the even more saturated species $[Nb^{V}Me_7]^{2-}$, which appears to have been detected only in solution.[2b] On the other hand, low-valent compounds $[Nb^{I}(CNXy)_7]^+$ (Xy = 2,6-dimethylphenyl),[4] $[Nb^{-I}(L)_6]^-$ (octahedral; L = CO,[5] CNXy[4]), and $[Nb^{-III}(CO)_5]^{3-}$ are also known,[6] all of them containing typically π-acceptor ligands and complying with the effective atomic number (18 electron) rule. Herein we report on what we believe are the first homoleptic σ-organoderivatives of Nb in intermediate oxidation states III and IV. Their properties are compared with those predicted for the homologous hydrides $[Nb^{III}H_4]^-$ and $Nb^{IV}H_4$.[7]

The low-temperature arylation of $NbCl_5$ with LiC_6Cl_5 takes place under reduction of the metal center. As a result, the homoleptic organoniobium(III) compound $[NBu_4][Nb^{III}(C_6Cl_5)_4]$ (**1**) is obtained as an air-sensitive violet solid in moderate yield (Scheme 1). This reaction is quite remarkable, since early attempts to obtain homoleptic aryl derivatives of Nb had failed—the reaction of $NbCl_5$ with $Li(2\text{-}MeC_6H_4)$ in Et_2O gave 2,2′-dimethylbiphenyl as the only identifiable product.[8] Although the reaction product of NbX_5 with LiPh was initially formulated as $Li_4[NbPh_6]$,[9] it was later found to be a heteroleptic compound containing η^2-coordinated benzyne ligands.[10] In fact, no homoleptic aryl derivative of Nb in any oxidation state has been isolated so far.



Scheme 1. Succinct synthetic procedures to obtain compounds **1** and **2** with indication of their electrochemical relationship ($E_{1/2}$ potential given vs. SCE).

The cyclic voltammogram (CV) of a CH_2Cl_2 solution of **1** between −1.6 and +1.6 V shows a quasi-reversible process occurring at $E_{1/2} = -0.44$ V (vs. SCE) with $\Delta E = 95$ mV and $i_{pa}/i_{pc} = 1.06$. In view of the moderate potential at which the electron-exchange process takes place, we treated **1** with Br_2, aiming to prepare and identify the oxidized species. As a result, the neutral organoniobium(IV) compound $[Nb^{IV}(C_6Cl_5)_4]$ (**2**) was obtained in good yield (Scheme 1). Since the CV of **2** is similar to that of **1**, it follows that both compounds are electrochemically related by the referred electron-exchange process. Oxidation of the metal center is evidenced by an increase in the X-sensitive vibration frequency in the IR spectra, which goes from 824 cm^{-1} in **1** to 842 cm^{-1} in **2**.[11] The potential of this Nb^{IV}/Nb^{III} semisystem is much lower than that observed for the corresponding V^{IV}/V^{III} one ($E_{1/2} = +0.84$ V vs. SCE).[12] This large difference ($\Delta E = 1.2$ V!) evidences a general trend within the Group 5 triad: intermediate oxidation states are relatively less stable for the heavier elements Nb (4d) and Ta (5d) than for the lighter 3d element V. No further features were observed in the CV of the $[Nb^{IV}(C_6Cl_5)_4]/[Nb^{III}(C_6Cl_5)_4]^-$ semisystem under the referred experimental conditions. Tetraaryl derivatives $[NbR'_4]$ (R′ = $2\text{-}MeC_6H_4$, $2,5\text{-}Me_2C_6H_3$) had been assumed to form by reaction of $NbCl_4$ and LiR′ or R′MgBr, but were neither isolated nor identified.[8]

The molecular structures of species $[Nb^{III}(C_6Cl_5)_4]^-$ (Figure 1) and $[Nb^{IV}(C_6Cl_5)_4]$ (Figure 2) were determined by X-ray diffraction methods on single crystals of **1** and $\mathbf{2}\cdot 2\,C_6H_{14}$, respectively.[13] In both cases, the Nb centers are located in slightly elongated tetrahedral (*T*-4) environments defined by

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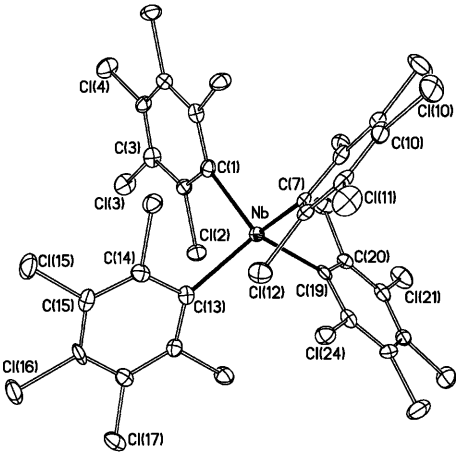

Figure 1. Thermal ellipsoid diagram (50% probability) of the $[Nb^{III}(C_6Cl_5)_4]^-$ anion in **1**. Secondary *ortho*-Cl···Nb interactions with average Nb···Cl = 304.2(1) pm are not drawn for clarity. Selected bond length [pm] and angles [°] with estimated standard deviations: average Nb–C 222.8(4); C(1)-Nb-C(7) 111.45(14), C(1)-Nb-C(13) 98.89(13), C(1)-Nb-C(19) 117.63(14), C(7)-Nb-C(13) 116.03(13), C(7)-Nb-C(19) 101.66(12), C(13)-Nb-C(19) 111.98(13).

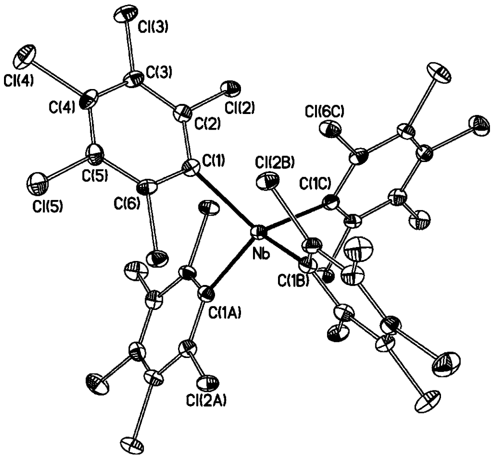

Figure 2. Thermal ellipsoid diagram (50% probability) of the neutral species $[Nb^{IV}(C_6Cl_5)_4]$ in $\mathbf{2}\cdot 2\,C_6H_{14}$. Secondary *ortho*-Cl···Nb interactions with Nb···Cl = 299.8(1) pm are not drawn for clarity (cf. Figure 3). Selected bond length [pm] and angles [°] with estimated standard deviations: Nb–C(1) 218.2(3); C(1)-Nb-C(1A) 115.70(8), C(1)-Nb-C(1B) 97.62(15), C(1)-Nb-C(1C) 115.70(8), C(1A)-Nb-C(1B) 115.70(8), C(1A)-Nb-C(1C) 97.62(15), C(1B)-Nb-C(1C) 115.70(8).

the C-donor atoms of the C_6Cl_5 groups according to the values of continuous shape measure (CShM) obtained for that geometry: $S(T\text{-}4) = 0.73$ for **1** and 1.07 for **2**.[14,15] A slightly shorter Nb–C distance was observed in **2** (218.2(3) pm) than in **1** (222.8(4) pm average), according to the different oxidation state of the metal center. Additional secondary bonding interactions were established between Nb and one of the *ortho*-Cl atoms of every C_6Cl_5 group.[16] Each interacting Cl atom caps one of the faces of the inner NbC_4 tetrahedron. This capping does not introduce any significant distortion in the NbC_4 central core geometry, thereby building a second $NbCl_4$ coordination sphere with complementary *T*-4 geometry (Figure 3). The associated Nb···Cl distances (ca. 300 pm) are much longer than those found in standard Nb–Cl covalent bonds (239 pm average)[17] and denote just a loose interaction.[18] The resulting global structure can be described as triakis tetrahedral (*TT*-8) with the following CShM values: $S(TT\text{-}8) = 1.54$ for **1** and 1.38 for **2**.[15,19] The whole $[Nb^{IV}(C_6Cl_5)_4]$ molecule has exact (crystallographically imposed) S_4 symmetry. Essentially the same symmetry was also found in the $[Nb^{III}(C_6Cl_5)_4]^-$ unit. It is interesting to note that the symmetry of the NbC_4 core in compounds **1** and **2** is similar to that theoretically predicted for the binary hydrides $[Nb^{III}H_4]^-$ and $Nb^{IV}H_4$.[7]

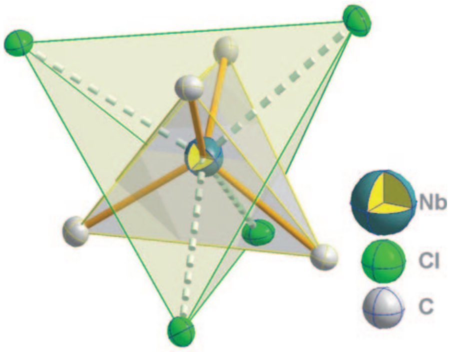

Figure 3. Local coordination environment of the Nb^{IV} center in $\mathbf{2}\cdot 2\,C_6H_{14}$ (thermal ellipsoid diagram with 50% probability) with indication of the inner NbC_4 and outer $NbCl_4$ tetrahedra. Secondary *ortho*-Cl···Nb interactions are indicated with broken lines.

In this type of compound, the interplay between structural and magnetic properties is of fundamental importance.[20] Thus, the spin states of compounds **1** and **2** were determined by isothermal magnetization measurements, $M(\mu_0 H)$, at low temperature. The dependence of the value of $M/\mu_B N_A$ (where M is the molar magnetization) on the reduced magnetic field $\mu_B H/k_B T$ at 1.8 K (Figure 4) can be described in each case by a Brillouin function with $S = 1$ and $g = 1.78(5)$ for compound **1** and $S = 1/2$ and $g = 1.94(3)$ for compound **2**. The thermal dependence of the magnetic susceptibility $\chi(T)$ was also measured for **1** and **2** in the range 1.8–273 K. The observed evolutions (Figure S1 in the Supporting Information) follow

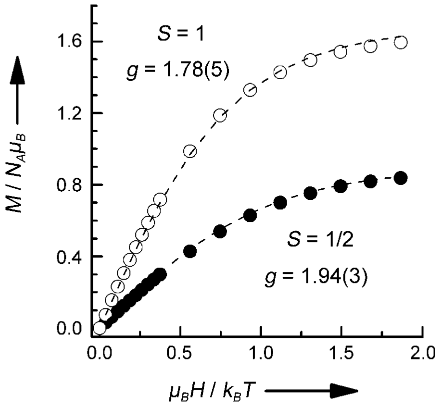

Figure 4. Dependence of $M/\mu_B N_A$ on $\mu_B H/k_B T$ for compounds **1** (○) and **2** (●) measured at 1.8 K. The dashed lines correspond to the Brillouin functions best matching the experimental data in each case. Data obtained at 5 and 78 K (not shown for clarity) overlap with those given here.

the Curie law with the following effective magnetic moments: $\mu_{\mathrm{eff}} = 2.51(5)\,\mu_B$ for compound **1** and $\mu_{\mathrm{eff}} = 1.68(5)\,\mu_B$ for compound **2**. These values nicely approach those expected for spin-only paramagnetic systems with triplet ($\mu_{\mathrm{eff}} \approx 2.83\,\mu_B$) and doublet ($\mu_{\mathrm{eff}} \approx 1.73\,\mu_B$) spin states, respectively. In view of the current results, we conclude that the secondary *ortho*-Cl···Nb bonding interactions cannot involve donation of two electrons per Cl atom because in that case, the compound would be diamagnetic (18 electrons) as in the dodecahedral pseudohalide complex $K_5[Nb^{III}(CN)_8]$.[21] Furthermore, we suggest that the singlet-spin state used for hypoelectronic $[Nb^{III}H_4]^-$ (d^2) in the calculations[7a] is a nonrealistic approach.

Compound **1** was found to be EPR-silent under our available experimental conditions.[22] Frozen solutions of compound **2** gave, in turn, a well-resolved EPR spectrum (Figure 5). This markedly anisotropic spectrum can be described by an axial spin-Hamiltonian including a hyperfine coupling contribution with the ^{93}Nb nucleus ($I = 9/2$, 100 % natural abundance). By using this approach with values of $g_{\parallel} = 1.883(2)$, $g_{\perp} = 1.969(2)$, $A_{\parallel} = 598$ MHz, and $A_{\perp} = 258(5)$ MHz, excellent agreement was obtained between calculated and experimental spectra (Figure S3 in the Supporting Information). The spectroscopically obtained value of $\langle g \rangle = 1.940(2)$ for compound **2** perfectly matches that derived from bulk magnetization measurements (Figure 4). The solid-state spectra of polycrystalline samples of **2** (Figure S2 in the Supporting Information) are also satisfactorily reproduced with the same set of parameters by applying a suitable line width in the calculation (Figures S4 and S5 in the Supporting Information). This coincidence suggests very similar (if not identical) electronic and structural environments for the Nb^{IV} center in **2** both in solution and in the solid state. An elongated *T*-4 structure was also assigned to the matrix-confined deuteride $Nb^{IV}D_4$ on the basis of its EPR spectroscopic properties.[23] Since $g_{\parallel} < g_{\perp} < g_e$ ($g_e = 2.0023$ for the free electron), it can be concluded that the ground state of compound **2** in an S_4 environment is ^{2}B, that is, the Nb^{IV} center has a $(d_{xy})^1$ electron configuration.[24] In that case, the principal values of the hyperfine coupling tensor $A_{\parallel}$ and $A_{\perp}$ are related to the principal *g* values as given in Equation (1),[12] where $P = g_e \mu_B g_N \mu_N \langle r^{-3} \rangle$.

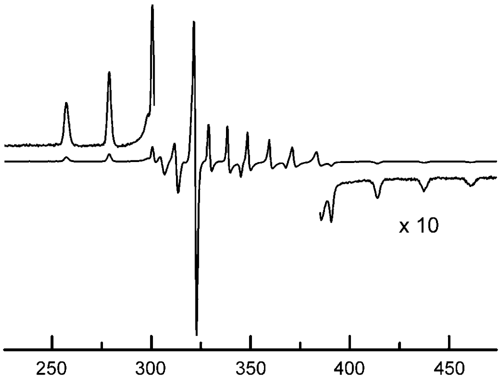

Figure 5. X-band EPR spectrum of **2** measured at 77.4 K on a chilled CH_2Cl_2/CH_2ClCH_2Cl (1:1) solution. EPR spectra of polycrystalline samples are given in Figure S2 in the Supporting Information.

$$
\begin{aligned}
A_{\parallel} &= -P\left\{\kappa + (g_e - g_{\parallel}) + \frac{3}{7}(g_e - g_{\perp}) + \frac{4}{7}\right\} \\
A_{\perp} &= -P\left\{\kappa + \frac{11}{14}(g_e - g_{\perp}) - \frac{2}{7}\right\}
\end{aligned}
\qquad (1)
$$

The κ parameter is related to the spin density in the metal nucleus, χ, through the expression: $\chi = -(2/3)\kappa \langle r^{-3} \rangle$. By introducing the experimental values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$, and $A_{\perp}$ in Equation (1), we obtain that $|P| = 352(10)$ MHz and $\kappa = 0.99(4)$; consequently, $\langle r^{-3} \rangle = 2.69(8)$ a.u. and $|\chi| = 1.8(1)$ a.u. Moreover, since the free Nb^{IV} ion has been assigned a value of $P_0 = 576$ MHz,[25] it follows that in compound **2**, $P/P_0 = 0.61$. Since a similar reduction (0.63) was observed in the V^{IV} homologous compound,[12] it follows that the outer $NbCl_4$ shell in **2** does not significantly affect the radial distribution of the unpaired-electron ground-state function. By applying the same formalism to the matrix-confined species $Nb^{IV}D_4$,[23] however, a significantly higher reduction is obtained, $P/P_0 = 0.45$, which points to more covalent metal–ligand bond character in that case. According to the structural and magnetic properties of compounds **1** and **2**, the secondary *ortho*-Cl···Nb interactions defining the outer $NbCl_4$ shell exert a shielding effect on the NbC_4 core without significantly altering its geometry or electronic state.

In summary, σ-organoderivatives with unprecedented $[Nb^{III}R_4]^-$ and $Nb^{IV}R_4$ stoichiometries were isolated and characterized. The Nb centers within the $[Nb(C_6Cl_5)_4]^{q-}$ units ($q = 0, 1$) are in S_4 sites formed by an inner NbC_4 and an outer $NbCl_4$ coordination spheres (Figure 3) with a global triakis tetrahedral structure. The geometry of the NbC_4 core is in keeping with that theoretically predicted for the homologous hydrides $[Nb^{III}H_4]^-$ and $Nb^{IV}H_4$.[7] This parallelism underlines the formal relationship between the singly charged hydride and σ-organyl ligands, regardless of the obvious difference in size. The synthesis of compounds **1** and **2** fills a gap in the exclusive family of homoleptic σ-organoniobium compounds.

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[22] From the analysis of the isothermal magnetization results (Figure 4) as well as from the linear dependence of $1/\chi(T)$ over the whole temperature range (Figure S1a), an upper limit for the zero-field splitting of approximately 50 GHz can be obtained for the non-Kramers system **1**. Following this estimate, EPR spectra would be expected to be observable as in the V^{III} case (see Ref. [12]), at least in Q band. Our failure to observe any EPR spectrum for **1** would thus not be related to the energy of the transitions involved, but rather to experimental broadening of the signals, possibly arising from manifold distribution of paramagnetic centers in the bulk sample.

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