2442 *Inorg. Chem.* **2001,** *40,* 2442−2445

Preparation and Characterization of a Tetranuclear and Mixed-Valence Nb(II)/Nb(III) Diamagnetic $Nb_4Cl_{12}Li_2(THF)_8$ Cluster

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Received November 14, 2000

Introduction

Extreme chemical reactivity is the primary characteristic of the few low-valent Nb and Ta compounds reported in the literature to date.[1−4] In spite of being very diversified in terms of chemical behavior, these species remain surprisingly limited due to the fact that suitable low-valent starting materials are hardly available. An effective strategy to overcome this problem consists of in situ generating highly reactive low-valent moieties thus affording the desired transformation in the presence of the target substrate.[5]

Another intriguing characteristic of low-valent Nb and Ta systems is their tendency to form M−M bonded species. For example, the di- and trivalent niobium compounds reported to date, with the only exception of the sterically demanding siloxyl derivatives[6] and pyridine[7] or chelating dimethoxyethane adducts,[8] typically display di- or polynuclear structures.[2e,3d,e,4j,9,10] The intermetallic distances vary significantly, the nature of the bridging ligands being a primary factor in determining the Nb−Nb separation.[2e,3d,4j,9q−u,10c] In sharp contrast, when the Nb−Nb distance is in the very short range, minor modifications at the periphery of the molecule are sufficient to significantly modify the magnetic behavior of these compounds while leaving the Nb−Nb distance unchanged.[9s,t,10c] Thus, in these cases, both the M−M distance and the magnetic properties do not provide a sufficiently conclusive criterion to evaluate the nature of the Nb−Nb bond.

A few years ago we described the reaction of trivalent $Nb_2Cl_6(TMEDA)_2$ with LDA (LDA = lithium diisopropyl amide) affording the divalent and dinuclear $Nb_2Cl_5Li(TMEDA)_3$.[9r] The reaction could be carried out on a very large scale and provided access to the chemistry of the divalent state and to a variety of transformations. [2e,3d,e,4j,9r−t] The utilization of alkali amides as reducing agents has a few literature precedents and was pioneered by Chisholm with the preparation of low-valent Mo and W compounds.[11] By reacting the tetravalent $NbCl_4(THF)_2$ compound with Cy_2NLi we have now obtained a mixed-valence Nb(II)/(III) tetranuclear and diamagnetic cluster.

Our observations are described herein.

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10.1021/ic001253w CCC: $20.00

Table 1. Crystal Data and Structure Analysis Results for **1**

formula	$C_{32}H_{64}Cl_{12}Li_2Nb_4O_8$	V (Å^3)	2596.6(7)
fw	1387.75	Z	2
space group	$P2(1)/n$	λ (Kα Å)	0.71073
a (Å)	12.763(2)	T (K)	193
b (Å)	10.989(2)	ρ_{calcd} (g cm^{-3})	1.775
c (Å)	18.517(3)	μ (cm^{-1})	15.20
β (deg)	91.068(3)	R1, wR2	0.0625, 0.0675

$R1 = \sum[(F_o) - (F_c)]/\sum(F_o)$. $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$.

Experimental Section

All operations were performed in an inert atmosphere using standard Schlenk techniques. $NbCl_4(THF)_2$[12] and $(Cy_2N)Li$[13] were prepared following published procedures. Infrared spectra of samples prepared in a drybox as Nujol mulls were recorded on a Mattson 9000 FTIR instrument. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes. The magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature by using standard methods[14] and applying data corrections for underlying diamagnetism.[15] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer.

Preparation of $Nb_4Cl_{12}Li_2(THF)_8$ (1). A solution of Cy_2NLi (2.0 g, 11.1 mmol) in THF (100 mL) was treated with $NbCl_4(THF)_2$ (2.1 g, 5.5 mmol). The resulting greenish slurry was stirred for 1 h, during which it turned into a reddish brown solution. The reaction mixture was stirred for another 3 h. After centrifugation, the volume of the solution was reduced to about 70 mL. Layering with diethyl ether (30 mL) and standing at room temperature for a few days afforded diamagnetic dark-red crystals of **1** (0.15 g, 0.11 mmol, 10%). Elemental anal. Calcd (found) for $C_{32}H_{64}Cl_{12}Li_2O_8Nb_4$: C 27.7 (27.19), H 4.65 (4.62). IR (Nujol, KBr plates, cm^{-1}): ν 1343 (s), 1318 (w), 1293 (m), 1247 (m), 1178 (s), 1140 (w), 1044 (s), 1025 (s), 1012 (s), 964 (w), 915 (m), 858 (m), 679 (s).

DFT Calculations. DFT calculations were carried out on the atomic coordinates as obtained from the X-ray crystal structure by using the local spin density approximation and using a double numerical basis set. The model was treated as a singlet to account for the observed diamagnetism. The convergence criterion was 10^{-6} of the root mean square of the change in the density matrix (program default).

X-ray Crystallography. Structural Determination of 1. A suitable crystal was selected, mounted on a thin, glass fiber using paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AX SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[16] Systematic absences in the diffraction data and unit-cell parameters were uniquely consistent with the reported space group. The structure was solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 5.10 program library (Sheldrick, G. M., Bruker AXS, Madison, WI, 1997).

Details on crystal data and structure refinement are given in Table 1 while relevant bond distances and angles are given in Table 2.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

bond distances (Å)		angles (deg)	
Nb(1)−Cl(6)	2.4360(18)	O(1)−Nb(1)-Cl(6)	90.96(12)
Nb(1)−Cl(1)	2.4322(19)	O(1)−Nb(1)-Cl(1)	164.52(13)
Nb(1)−Cl(2)	2.4566(18)	Cl(6)−Nb(1)-Cl(1)	93.19(6)
Nb(1)−Cl(4)	2.5416(18)	O(1)−Nb(1)-Cl(2)	84.23(13)
Nb(1)−Nb(2)	2.8615(9)	Cl(6)−Nb(1)-Cl(2)	109.76(6)
Nb(1A)-Nb(2)	2.9152(10)	Cl(1)−Nb(1)-Cl(2)	108.26(6)
Nb(2)−Nb(2A)	2.9947(12)	O(1)−Nb(1)-Cl(4)	82.32(12)
Nb(1)−Li	3.451(13)	Cl(6)−Nb(1)-Cl(4)	164.11(7)
Nb(2)−Cl(5)	2.5055(19)	Cl(1)−Nb(1)-Cl(4)	89.79(6)
Cl(3)−Li	2.317(13)	Cl(2)−Nb(1)-Cl(4)	83.98(6)
		Cl(1)−Nb(1)-Cl(3)	83.43(6)
		Cl(2)−Nb(1)-Cl(3)	162.83(6)
		Cl(4)−Nb(1)-Cl(3)	83.52(6)
		Cl(1)−Nb(1A)-Nb(1)	52.76(5)
		Nb(1)−Cl(1)-Nb(2)	72.60(5)
		Nb(1)−Cl(2)-Nb(2)	72.04(5)

Results and Discussion

The reaction of $NbCl_4(THF)_2$ with 2 equiv of Cy_2NLi in THF gave, upon mixing, a rapid color change to green followed by a slow change to dark-red. The diamagnetic tetranuclear niobium cluster $[Nb_4Cl_{12}Li_2(THF)_8]$ (**1**) was crystallized from THF/ether in a modest but significant yield (10%). The IR spectrum and combustion analysis data clearly ruled out the presence of the amide ligand while the connectivity was elucidated by an X-ray crystal structure.

The structure of **1** consists of a symmetry-generated tetramer with a planar Nb_4 core (Figure 1). The overall frame may be conveniently visualized in terms of a face-sharing dicuboidal structure where each cuboid is *sine* one metal corner. Of the four niobium atoms two are located on two opposite corners of the shared face of the dicuboid, while the other two are located each on the opposite side of the plane containing the shared face. The two sets of niobium atoms display different octahedral coordination environments. The geometry of the two metals located in the center of the molecule is defined by the oxygen atom of one coordinated THF [Nb(2)−O(2) = 2.255(4) Å], one terminal chlorine [Nb(2)−Cl(5) = 2.5055(19) Å], two μ^2-chlorine atoms [Nb(2)−Cl(1) = 2.4917(18) Å, Nb(2)−Cl(6a) = 2.4974(19) Å] located trans to each other [Cl(1)−Nb(2)−Cl(6a) = 167.50(6)°], and two μ^3-chlorine atoms [Nb(2)−Cl(2) = 2.5001(18) Å, Nb(2)−Cl(2a) = 2.4862(18) Å] occupying the remaining two cis positions [Cl(2)−Nb(2)−Cl(2a) = 106.18(5)°]. The second set of Nb atoms also carries one terminally bonded THF [Nb(1)−O(1) = 2.212(4) Å] but has two cis μ^2-chlorine atoms [Nb(1)−Cl(6) = 2.4360(18) Å, Nb(1)−Cl(1) = 2.4322(19) Å, Nb(1)−Cl(1)−Nb(2) = 72.60(5)°, Nb(1)−Cl(6)−Nb(2a) = 70.89(5)°, Cl(1)−Nb(1)−Cl(6) = 93.19(6)°] and only one μ^3-chlorine atom [Nb(1)−Cl(2) = 2.4566(18) Å]. The last two μ^2-chlorine atoms [Nb(1)−Cl(3)

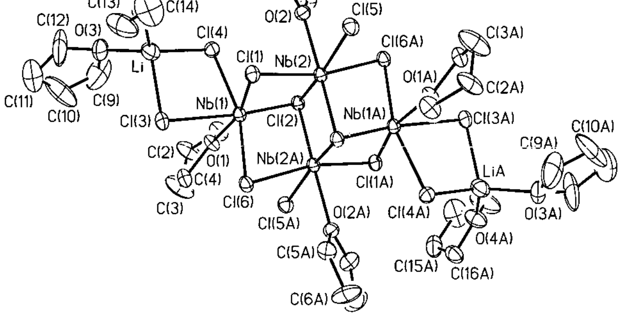

Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

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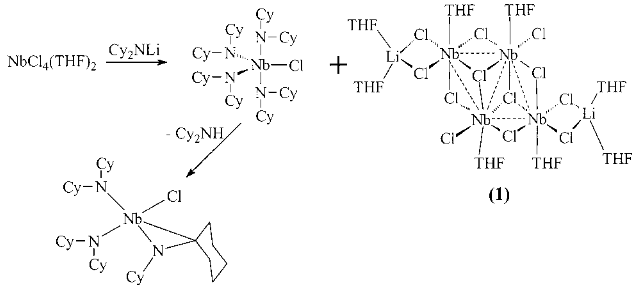
Scheme 1

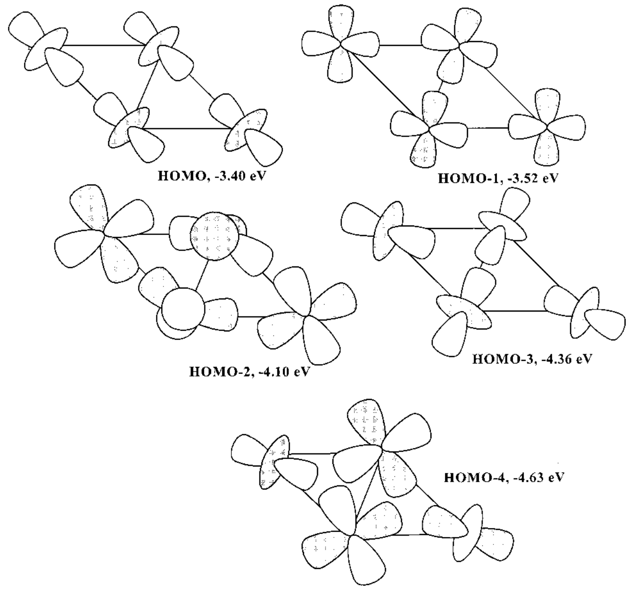


= 2.5841(18) Å, Nb(1)−Cl(4) = 2.5416(18) Å], also cis to each other [Cl(3)−Nb(1)−Cl(4) = 83.52(6)°], point toward the exterior of the cluster and bridge a tetracoordinated Li atom [Li−Cl(3) = 2.317(13) Å; Nb(1)−Cl(3)−Li = 89.3(3)°] solvated by two molecules of THF.

Complex **1** is a mixed-valent species. As previously mentioned, the utilization of anionic organic amides as reducing agents has a few precedents in the literature.[11] In this particular case, the formation of **1** is rather surprising given that the same reaction carried out in toluene with a larger amount of amide afforded the pentavalent niobaaziridine derivative $(Cy_2N)_2Nb(CyNC_6H_{10})Cl$ instead.[17] The formation of this species was accompanied by partial evolution of H_2 with no indication that other products were being formed. Conversely, the low yield of **1** suggests that another species may well be present in the reaction mixture. A reasonable explanation for the formation of **1** can perhaps be found in the analogy of the behavior of $VCl_3(THF)_3$ in its reaction with Cy_2NLi in THF. Two different trivalent compounds, the mononuclear $(Cy_2N)_2VCl(THF)$ and dinuclear $[(Cy_2N)_2V(\mu\text{-}Cl)]_2$, arising from the expected replacement of two chlorine atoms by two amides were formed.[18] However, when the reaction was carried out with a vanadium to amide stoichiometric ratio of 1:1, a disproportionation reaction took place with formation of $(Cy_2N)_2VCl_2$ and "VCl_2".[18] Thus if we assume that a similar disproportionative pathway takes place in the case of $NbCl_4(THF)_2$, a mixture of pentavalent $(Cy_2N)_4NbCl$ [eventually evolving toward the previously reported niobaaziridine derivative $(Cy_2N)_2Nb(CyNC_6H_{10})Cl$]][17] and low-valent species may be formed (Scheme 1). In agreement with this proposal, a reaction carried out in toluene with the same stoichiometric ratio initially afforded a small amount of the insoluble **1**, which was isolated by recrystallization from THF. The ^1H NMR spectrum of the residue obtained from the evaporation of the mother liquor clearly indicated the presence of the niobaaziridine derivative.

A few tetrametallic niobium clusters have been described in the literature of the higher oxidation states, and less than a handful of thiolates,[19] alkoxides,[20] and carboxylates[21] have been reported. The present mixed-valence compound is *formally* composed of two trivalent and two divalent niobium atoms and has in a phosphine derivative reported a few years ago, $(Me_3P)_6Nb_4Cl_{10}$, one of the very few related precedents.[22] Unfortunately, the magnetic properties were not reported for this particular complex and thus the presence of five Nb−Nb single bonds argued on the exclusive basis of the intermetallic distances remains putative.

Chart 1



Indeed complex **1** contains five Nb−Nb contacts ranging from 2.8615(9) to 2.995(1) Å and which might be regarded as being within the bonding range. It is interesting to compare **1** to the previously reported $[Nb_2Cl_5Li(TMEDA)_3]^{(+)}$ and also mixed-valence Nb(II/III).[3d,e] Both compounds contain octahedral Nb atoms with both bridging and terminally bonded chlorine. The cationic complex is dinuclear and contains a considerably shorter intermetallic distance [2.545(1) Å]. Thus, the nature of the Lewis base coordinated to the metal (THF versus TMEDA) and the presence of the LiCl unit retained in the structure appear to be the only factors determining both the nuclearity and the extent of intermetallic separation in these compounds. While we have no explanation for this behavior, we have here attempted to clarify the nature of the Nb−Nb interaction in complex **1.** Density functional theory (DFT) calculations were carried out on the atomic coordinates as obtained from the X-ray crystal structure. Given the diamagnetism, calculations were carried out on the singlet state. The HOMO−LUMO gap (0.68 eV) is rather small yet sufficient to account for the observed diamagnetism. The LUMO (−2.72 eV) is basically a Nb−Cl centered MO. Conversely the next five frontier orbitals are mainly Nb-centered. All these orbitals are formed by the overlap of complex hybrid combinations of several atomic orbitals of the four niobium atoms. The HOMO (−3.40 eV) shows two lobes along two parallel Nb−Nb vectors both closely reminiscent in shape of Nb−Nb σ-bonds (Chart 1). The HOMO-1 (−3.52 eV) is also generated by hybrid combinations and is very similar in shape to the HOMO. However, the two lobes are placed along the other two edges of the tetrametallic rhombus while a small lobe is present alongside the shortest diagonal. The next (HOMO-2, −4.10 eV) presents four lobes each along one edge but with a nodal plane bisecting the two Nb atoms located on the longest diagonal. HOMO-3 (−4.36 eV) is formed by the overlap of four similar hybrids each orienting one of the four lobes toward the center of the tetrametallic rhombus and featuring a large lobe delocalized in the center of the tetrametallic unit. The last

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(HOMO-4, −4.63 eV) is rather similar in shape to HOMO-2 except that the nodal plane is placed along the shortest diagonal. Another MO located lower in energy (HOMO-8, −5.91 eV) is mainly chlorine centered but displays a minor Nb−Nb σ-bond component along the shortest diagonal. All the Nb−Nb bond centered molecular orbitals can be considered in first approximation as Nb−Nb σ-bonds. The average calculated Mulliken bond order is 0.85 for the Nb−Nb bonds thus confirming the existence of five M−M single bonds.

In conclusion a tetranuclear niobium Nb(II/III) planar cluster was obtained as a result of a complex series of disproportionation reactions. The diamagnetism of this mixed-valence complex can be rationalized in terms of the presence of five Nb−Nb single bonds.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC). The authors are indebted with Prof. A. StAmant for his assistance with DFT calculations.

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001253W