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Insensitivity of the Nb−Nb Distance in a Paddle-Wheel Compound to Bond Multiplicity and Axial Ligation

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Introduction

Three-center chelating ligands (allylic type) which possess two donor atoms, a three-atom bite, one negative charge, and four π-electrons have played a visible role in the development of the chemistry of M−M multiple bond.[1] By using a very large number of substituents, a variety of combinations of donor atoms, and by incorporating the chelating frame into diversified molecular architectures, an entire class of compounds has been discovered. These compounds display a very characteristic geometry where the M−M vector is the *trait-d'union* of two dimetalla-bicyclo-pentene planar units orthogonal to each other. The appealing name of paddle-wheel or lantern-type systems has been forged for these species.

The intermetallic distances in these dinuclear compounds vary within a considerably wide range: from the so-called supershort[1,2] up to nonbonding distances.[3] Our contribution to the chemistry of these derivatives of first-row early metals was to produce evidence that ligand geometry optimization is a factor capable of determining the extent of M−M separation.[4,5] In other words, very short M−M contacts might be nothing more than ligand artifacts since the M−M interaction does not provide the expected stabilization energy and attraction force that is the distinctive characteristic of any chemical bond. The well-established paradoxical weakness of the Cr−Cr supershort quadruple bonds is a direct consequence of this unusual behavior.[4−6]

The ligation of additional molecules or anions on the intermetallic axis is another feature of paddle-wheel compounds which well reiterates the uniqueness of the M−M interaction between first row metals. The ability of axially ligated groups to stretch the M−M distances by up to 0.42 Å was observed in a consistent series of compounds.[1,7] This curious behavior was elegantly rationalized by suggesting that axial ligation may destructively impoverish the electron density of the M−M multiple bond with consequent decrease of bond order and elongation of the M−M distance.[1]

Paddle-wheel compounds of second and third row metals provide a substantially different scenario. The large amount of work produced by Chisholm[8,9] and Cotton[1] in the chemistry of Mo and W clearly indicates that the M−M interaction in these species is in fact rather substantial and satisfies the basic requisites of the definition of a chemical bond. Thus, it is reasonable to expect that axial ligation may be disfavored with these metals and, when occurring, should substantially affect the M−M bond multiplicity and distance.

In this paper we describe the preparation and characterization of a diamagnetic $[(\text{7-azaindolyl})\text{Nb}]_2$ compound which offers the ground for an interesting comparison with the two axially ligated dimeric $[(\text{7-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\text{Li(THF)}_3]\}_2$**10** and polymeric $([(\text{7-azaindolyl})_2\text{Nb}]_2\{(\mu\text{-Cl})[\mu\text{-Li(THF)}_2]\}_2)_n$**11** compounds.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenck techniques. $\text{Nb}_2\text{Cl}_5\text{Li(TMEDA)}_3$ was prepared as reported.[12] 7-Azaindole was purchased from Aldrich and used without further purification. Solvents were anhydrified and purified by using a solvent purification system (Anhydrous Engineering). Infrared spectra were recorded on a Mattson 9000 FTIR instrument from Nujol mulls prepared in a drybox. Samples for magnetic susceptibility measurements were prepared inside a drybox and sealed into calibrated tubes and measured with a Guy balance. Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

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

formula	$C_{36}H_{36}N_8Nb_2O_2$
fw	798.55
space group	triclinic, $P\bar{1}$
a (Å)	9.079(3)
b (Å)	9.551(3)
c (Å)	10.571(4)
α (deg)	83.476(6)
β (deg)	89.613(6)
γ (deg)	69.641(5)
V (Å^3)	853.3(5)
Z	1
λ (Kα Å)	0.71073
T (K)	203.2
ρ_{obsd} (g cm^{-3})	1.554
μ (cm^{-1})	0.717
R, wR^2, GoF	0.0679, 0.1447, 1.005

[a] $R = \sum|F_0| - |F_c|/\sum|F_0|$. $wR^2 = [(\sum(|F_0| - |F_c|)^2/\sum wF_0{}^2)]^{1/2}$.

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

bond distances (Å)	angles (deg)
Nb−Nb(a) = 2.2628(14)	Nb(a)−Nb−O(1) = 168.2(2)
Nb···O(1) = 3.808(13)	N(2)−Nb−N(3) = 93.40(19)
Nb−N(2) = 2.195(5)	N(2)−Nb−N(1a) = 175.8(2)
Nb(a)−N(1) = 2.273(5)	N(2)−Nb−N(4a) = 95.42(19)
Nb−N(3) = 2.240(5)	N(3)−Nb−N(1a) = 84.26(18)
Nb(a)−N(4) = 2.198(5)	N(1)−C(5)−N(2) = 123.3(5)

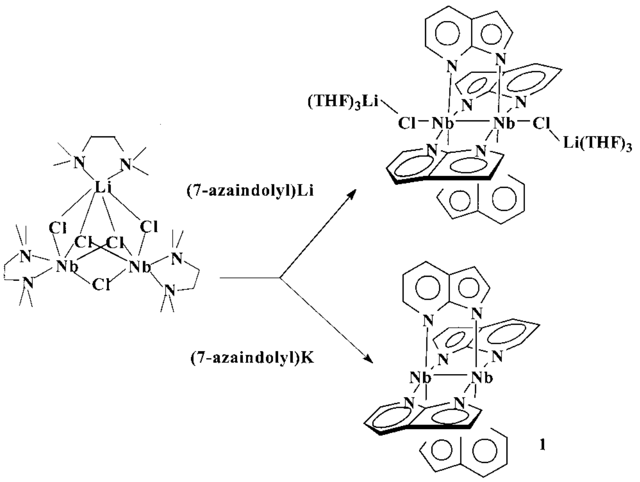
Preparation of (7-azaindolyl)$_4$Nb$_2$·2THF (1). A solution of 7-azaindole (1.3 g, 11.1 mmol) in THF (70 mL) was treated with KH (0.44 g, 11.1 mmol). After the initial vigorous gas evolution ceased, the mixture was stirred for an additional 30 min at room temperature. Solid $Nb_2Cl_5Li(TMEDA)_3$ (2.0 g, 2.8 mmol) was added and the mixture was stirred for 2 h. The resulting suspension was centrifuged and the solid was discarded. The remaining solution was allowed to stand overnight at room temperature upon which red crystals of **1** separated (1.0 g, 1.2 mmol, 43%). Anal. Calcd (found) for $C_{36}H_{36}N_8Nb_2O_2$: C, 54.15(53.95); H, 4.54(4.43), N 14.03(13.95). IR (Nujol mull, cm^{-1}) ν: 1590(s), 1554(br), 1417(m), 1405(m), 1332(s), 1278(s), 1257(s), 1141(s), 1112(br), 935(m), 910(w), 798(m), 784(m), 763(m), 727(br). ^{1}H NMR (d^6-acetone, 500 MHz, 23 °C) δ: 8.25 (d, CH, 1H), 8.02 (d, CH, 1H), 7.45 (dd, CH, 1H), 7.08 (d, CH, 1H), 6.46 (d, CH, 1H), 3.67 (m, THF, 4H), 1.89 (m, THF, 4H).

DFT Calculations. The DFT calculations on the model compound (7-azaindolyl)$_4$Nb$_2$·2THF were performed using the local spin density approach (LSDA/VWN). The basis functions were those of the double numeric basis set (DN) as provided by the SPARTAN-4 program. No model idealization or geometry optimization was performed. All the calculations were performed by using a cluster of computers available at the Department of Chemistry of the University of Ottawa.

X-ray Crystallography. Structural Determination of 1. A suitable crystal was selected, mounted on thin glass fibers using viscous 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.[13]

Despite one angle of the primitive cell being close, but not statistically equal, to 90°, no symmetry higher than triclinic was evident from the diffraction data. Solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results of refinement. The structure was solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. One 7-azaindole ligand was found end-for-end disordered with an 80/20 site occupancy distribution. Because of the proximity of the disordered, coincident atomic positions, only carbon atom C(10) could be refined in its two disordered positions. A molecule of cocrystallized THF was located in the asymmetric unit. 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 SHEXTL 5.10 program library (Sheldrick, G. M., Bruker AXS: Madison, WI, 1997).

Scheme 1



Results and Discussion

The reaction of $Nb_2Cl_5Li(TMEDA)_3$ with 4 equiv of 7-azaindolyl potassium salt afforded the novel (7-azaindolyl)$_4$Nb$_2$·2THF (**1**) which was isolated as red-orange *diamagnetic* crystals in 43% yield. Conversely, identical reaction carried out with the corresponding lithium salt afforded the blue *paramagnetic* [(7-azaindolyl)$_2$Nb]$_2${(μ-Cl)[Li(THF)$_3$]}$_2$·2THF whose characterization and VT magnetic behavior was previously reported (Scheme 1).[10] Relevant to the present discussion is also the blue-green polymeric ([(7-azaindolyl)$_2$Nb]$_2${(μ-Cl)[μ-Li(THF)$_2$]}$_2$)$_n$ compound which was obtained via reduction and ligand replacement of NbCl$_3$(DME) in a one-pot synthesis and which is also diamagnetic.[11]

The crystal structure of **1** does not display any particular feature. The characteristic paddle-wheel geometry (Figure 1) is defined by four ligands organized in the usual manner around the Nb−Nb vector. Two molecules of THF are present in the lattice with the oxygen atoms oriented toward the Nb atoms and not far from the intermetallic vector [Nb(a)−Nb−O(1) = 168.2(2)°]. However, despite the favorable orientation, there is no significant bonding contact since the Nb−O distance [Nb−O = 3.808(13) Å] is clearly outside the bonding range. The only structural feature of interest is the M−M distance [Nb−Nb(a) = 2.263(1) Å] which is surprisingly close to those observed in the paramagnetic and diamagnetic LiCl adducts [2.268(1) and 2.278(2) Å, respectively].[10,11]

The difference of magnetic behavior in the three compounds is particularly striking. In the two LiCl adducts, the degree of solvation of the alkali cation is the only factor which apparently determines the linear polymeric versus dimeric structure. Furthermore, this relatively insignificant difference is also the factor which determines the magnetic behavior. On the other hand, the diamagnetism of the polymeric compound, which incidentally has a Nb−Nb distance slightly *longer* than in the dimeric complex, was established only on the basis of the sharpness of the NMR lines of an acetone solution spectrum.[11] In addition, the paramagnetic dinuclear LiCl adduct, which displays rather broad NMR lines in THF solution, also gives a well-solved spectrum in acetone solution where, however, the complex changed its color to dark orange-brown. Thus, a LiCl dissociation process is likely to be at the basis of the alleged

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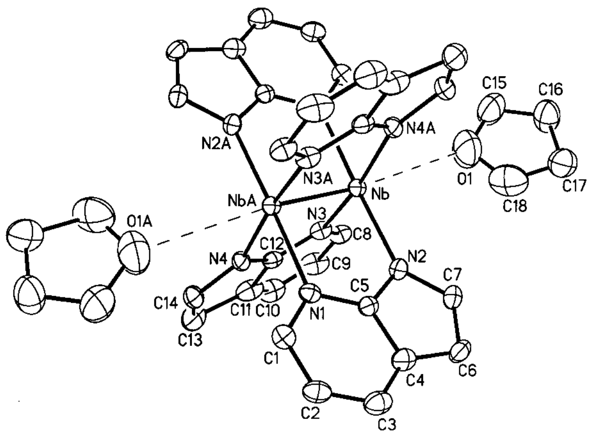
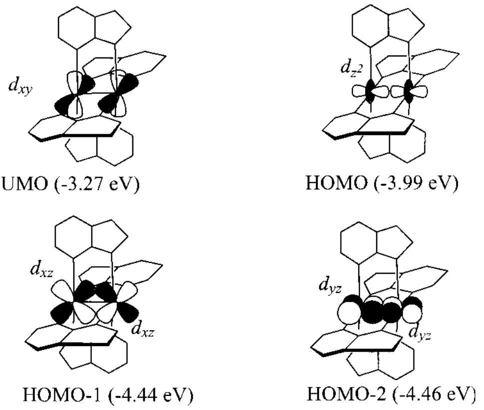


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

diamagnetism of the polymeric LiCl adduct. Conversely, complex **1** is diamagnetic in both solid state and solution. It also possesses a distinctively different color from the two LiCl adducts (red rather than blue) and, surprisingly, *does not coordinate* THF which notoriously is a Lewis base stronger than LiCl. Thus questions arise about the nature of the Nb−Nb interaction and about how axial ligation may affect these multiple bonds. The fact that the compounds with LiCl on the axis display completely different colors and magnetic behavior clearly indicates that the axial ligation has substantially modified the electronic configuration of the metal centers. Conversely, the fact that the Nb−Nb distance remains basically unchanged suggests that the axial ligation does not affect the Nb−Nb bond multiplicity.

In an attempt to solve this dichotomy, we have carried out density functional calculations on the atomic coordinates of **1** as provided by the X-ray crystal structure. Given the diamagnetism, calculations were carried out for the singlet state. The three occupied frontier orbitals are Nb−Nb centered with a metal atom contribution of predominantly *d*-orbital character (Chart 1). The HOMO−LUMO gap (0.72 eV) is sufficient to account for the observed diamagnetism in solution. Four frontier orbitals are all Nb−Nb centered. The LUMO (−3.27 eV) is a Nb−Nb δ-bond arising from the in-phase combination of the two d_{xy} atomic orbitals. The HOMO has the typical shape of a Nb−Nb σ-bond and is generated by the overlap of the $d_{z}2$ atomic orbitals. The next two occupied molecular orbital (HOMO-1 at −4.44 eV and HOMO-2 at −4.46 eV) are nearly degenerate Nb−Nb π-orbitals and are respectively formed by the overlap of the d_{xz} and d_{yz} atomic orbitals. The overall calculated Mulliken Nb−Nb *formal* bond order is 2.99. Thus the calculation clearly indicates the existence of a Nb−Nb triple bond. In addition, a geometry optimization calculation using a force field without electrostatic interactions increased the Nb−Nb distance to 2.7 Å. This is in nice agreement with the structure of the Cr derivative of the same ligand system and where the Cr−Cr interaction is likely to be very weak.[3a] Therefore, the fact that the Nb−Nb distance of **1** is considerably shorter indicates that the Nb−Nb interaction is substantial and sufficient to enforce a distortion from the normal geometry as required by the 7-azaindolyl ligand. We have recently described the results of the DFT calculation carried out on the dinuclear LiCl adduct.[10] The distribution and shape of the frontier orbitals in that case appears to be very similar to that calculated for **1**. However, the presence of the Nb−Cl−Li interactions introduces in the energy level distribution of **1** two nearly degenerate MOs which are mainly Nb−Cl−Li centered and which respectively become the HOMO and LUMO. The HOMO has a minor contribution of Nb−Nb σ-bond, thus indicating that the introduction of a weak Nb−Cl bonding interaction is done at the expenses of the Nb−Nb σ-bond. The small HOMO−LUMO gap (0.19 eV) is the cause for the paramagnetism, whereas the annihilation of the Nb−Nb σ-bond is responsible for the lower bond order (2.17) that was calculated.

Chart 1



In conclusion, there is not much doubt that complex **1** contains a Nb−Nb triple bond. The axial ligation of LiCl is obtained at the expenses of one of the Nb−Nb bonds and nicely accounts for the paramagnetism. However, the substantial decrease of Nb−Nb bond multiplicity (from triple to double) resulting from the axial coordination, surprisingly, does not correspond to any significant variation of intermetallic distance. While this is in agreement with the existence of fairly strong Nb−Nb interaction, it, on the other hand, reiterates that the relationship between multiplicity and distances of M−M bonds is not straightforward.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic thermal parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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