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Tri- and Tetravalent and Mixed-Valence Niobium Complexes Supported by a Tripodal Tripyrrolylmethane Trianion

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The reaction of $Nb_2Cl_6(TMEDA)_2$ with the potassium salt of tripyrrolylmethane in a 1:1 ratio afforded two products which have been isolated and characterized. The first compound is the dinuclear $\{[HC(C_4H_3N)_3]Nb(THF)\}_2{\cdot}2THF$ (**1**), with two trivalent and diamagnetic metal centers bridged by two tripyrrolyl trianions. Each of the two ligands adopted a rather unusual bridging mode, with two rings each σ-bonding one of the two metal centers and the third both π-bonded to one of the two niobium atoms and σ-bonded to the other. The second product of the reaction is $\{([H(C_4H_3N)_3]_2NbK)_2\}\{Nb_4Cl_{11}[K(THF)_2]_2\}{\cdot}2THF$ (**2**), which displays some unusual features. The complex is ionic, with the cationic $\{Nb_4Cl_{11}[K(THF)_2]_2\}^{2+}$ unit containing the metal in a mixed-valence state. The two positive charges of the cationic moiety are balanced by two identical anionic $\{([HC(C_4H_3N)_3]_2NbK)_2\}^-$ units, each containing Nb in the tetravalent state. Each anion is connected to an identical one by the bridging potassium atom, thus assembling a linear and anionic polymeric array. A similar reaction carried out with the lithium salt of the tripyrrolide anion led instead to the simple monomeric and tetravalent complex $\{[HC(C_4H_3N)_3]_2Nb\}\{Li(THF)_4\}_2$ (**3**).

Introduction

Complexes containing Nb and Ta in the oxidation states +2 and +3 are both highly reactive and surprisingly rare. Besides the cyclopentadienyl derivatives, for which a rather extensive series of compounds is available,[1] only a few low-valent derivatives have been isolated and fully characterized for these metals. Low-valent non-Cp complexes of Nb and Ta remain basically limited to two recently reported amides,[2] the bulky silanolate derivatives,[3] a series of halides and related clusters,[4] one amidinate−borohydride,[5] two lantern-type compounds,[6] and one thiolate.[7] Conversely, a wealth of promising reactivity and a remarkable variety of attractive transformations, almost invariably involving molecular activation processes, has been obtained by using mainly in situ generated low-valent complexes.[8] One of the most desirable characteristics of the reactivity of low-valent Nb and Ta complexes is a unique ability to perform C−N single bond cleavage[2a,b,3,8f−h,9] and nitrogen abstraction.[10]

Metal−metal bonding is another important and recurrent feature of the chemistry of low-valent Nb and Ta.[11] Di- and trivalent Nb and Ta complexes display a variety of M−M distances, which range from very short[6] to rather long.[4] In analogy to the case of first-row transition metals, the geometry of the ligand system seems to play a critical role in determining the extent of electronic coupling, the magnetic properties and the intermetallic distance thus affecting the M−M bond multiplicity.[12]

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A possible reason for the rarity of low-valent niobium and tantalum compounds may reside in another interesting characteristic of these systems: that is, a tendency to disproportionate and/or to give substrate reduction via complex reaction pathways involving in some cases the participation of more metals. For example, the above-mentioned denitrogenation of the pyrrolide anion[10] required the occurrence of a parallel transformation involving both C−H and C−N bond activation in order to balance the number of electrons involved in the redox process.

In this paper we describe the results of the reaction of low-valent niobium salts with a novel tripodal tripyrrolyl trianion. The study was prompted by the observation of the ability of pyrrolide anions to be involved at the same time in both the reactivity and stabilization of the metal center via formation of π-bonded complexes.[10] Conversely, polypyrrole anions have recently proven to be more resistant to strongly reducing metals, to have an enhanced tendency toward π-donation,[13] and to support clusterification reactions[14] and even dinitrogen fixation/activation.[15]The particular tripodal geometry of the trianionic ligand employed for this preliminary study seemed especially promising to us for enhancing the chemical reactivity of niobium toward M−M bond formation and/or molecular activation processes via pyramidalization of the metal center. Herein we report our observations.

Experimental Section

All operations were carried out under nitrogen using standard Schlenk techniques, or in a nitrogen-filled drybox. $NbCl_3(DME)$[16] and $Nb_2Cl_6(TMEDA)_2$[4f] were prepared according to published procedures. Pyrrole-2-carboxaldeyde (Aldrich) was used as received. DME and TMEDA (Aldrich) were distilled under N_2 prior to use over $LiAlH_4$ and molten potassium, respectively. 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 the drybox and sealed into calibrated tubes. Magnetic measurements were carried out with a Gouy balance (Johnson Matthey) at room temperature. The magnetic moments were calculated by standard methods,[17] and corrections for underlying diamagnetism were applied to the data.[18] Elemental analyses were carried out with a Perkin-Elmer 2400 CHN analyzer. NMR spectra were recorded with a Bruker AMX 500 MHz spectrometer.

Preparation of $HC(C_4H_4N)_3$. A solution of pyrrole-2-carboxaldeyde (4.0 g, 42 mmol) and pyrrole (19.3 g, 0.23 mol) in $CHCl_3$ (30 mL) was allowed to stand at room temperature under nitrogen for 10 min. The solution was cooled to 0 °C, treated with a few drops of CH_3SO_3H, and allowed to rest at room temperature overnight. The solvent was removed under vacuum and the crude product purified by column chromatography by using silica gel and $CHCl_3$ as eluant, yielding analytically pure tripyrrolylmethane, $HC(C_4H_4N)_3$ (4.1 g, 18.9 mmol, 45%). IR (Nujol, KBr; cm^{-1}): ν 3448 (s), 3370 (s, br), 3127 (w), 3110 (w), 3005 (w), 3095(w), 1560 (s), 1398 (m), 1358 (s), 1311 (m), 1271 (w), 1267 (s), 1122 (m), 1091 (s), 1027 (vs), 973 (m), 887 (w), 817 (m), 777 (w), 736 (w), 765 (vs), 727 (vs). ^1H NMR ($CDCl_3$, 500 MHz, 23 °C): δ 7.91 (s, N−H pyrrole, 3H), 6.62 (d, C−H pyrrole, 3H), 6.15 (m, C−H pyrrole, 3H), 6.05 (d, C−H pyrrole, 3H), 5.45 (s, C−H methine, 1H). ^{13}C NMR ($CDCl_3$, 125.72 MHz, 23 °C): δ 249.81 (C−H methine), 171.18 (quaternary C pyrrole), 156.31 (C−H pyrrole), 144.05 (C−H pyrrole), 143.14 (C−H pyrrole). Anal. Calcd (found) for $C_{13}H_{13}N_3$: C, 73.91 (73.88); H, 6.20 (6.17); N, 19.89 (19.83). MS (EI): *m/e* 211.

Preparation of $\{[HC(C_4H_3N)_3]Nb(THF)\}_2 \cdot 2THF$ (1). A solution of tripyrrolylmethane (1.0 g, 4.5 mmol) in THF (150 mL) was stirred with KH (0.5 g, 13.5 mmol). A vigorous gas evolution was observed upon mixing, and stirring was continued at room temperature for 1 h. The addition of $NbCl_3(DME)$ (1.3 g, 4.5 mmol) to the resulting suspension resulted in a color change to dark green. After it wa stirred for 10 min, the green solution was filtered to remove a small amount of light-colored material, and the resulting solution was concentrated to small volume (10 mL) and transferred into a layering tube. Red crystals of **1** separated upon slow diffusion with ether (50 mL) at room temperature over a period of 7 days (0.8 g, 0.8 mmol, 40%). IR (Nujol mull, cm^{-1}): ν 1396 (w), 1274 (w), 1241 (w), 1209 (s), 1180 (s), 1160 (s), 1132 (s), 1101 (vs), 1052 (br), 1025 (vs), 973 (w), 960 (s), 948 (w), 892 (br), 800 (vs), 767 (s), 721 (vs), 692 (w), 676 (w). ^1H NMR (d_8-THF, 500 MHz, 23 °C): δ 6.56 (d, C−H pyrrolyl, 3H), 5.91 (m, C−H pyrrolyl, 3H), 5.73 (d, C−H pyrrolyl, 3H), 5.37 (s, methine, 1H), 3.61 (broad s, coord THF, 4H), 3.58 (broad s, free THF, 4H), 1.79 (broad s., coord THF, 4H), 1.75 (broad s, free THF, 4H). ^{13}C NMR (d_8-THF, 500 MHz, 23 °C): δ 212.81 (C−H methine), 134.17 (quaternary C pyrrolyl), 117.33 (C−H pyrrolyl), 107.80 (C−H pyrrolyl), 106.89 (C−H pyrrolyl), 68.22 (CH_2 free THF), 67.45 (CH_2 coord THF), 26.38 (CH_2 coord THF), 25.48 (CH_2 free THF). Anal. Calcd (found) for $C_{42}H_{52}N_6Nb_2O_4$: C, 56.63 (56.48); H, 5.88 (5.83); N, 9.44 (9.39).

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$C_{42}H_{52}N_6O_4Nb_2$	$C_{100}H_{152}Cl_{11}K_4N_{20}Nb_6O_6$	$C_{58}H_{84}Li_2N_6NbO_8$
M_w	890.72	2834.23	1100.10
space group	monoclinic, $P2_1/c$	monoclinic, $C2/c$	triclinic, $P\bar{1}$
a (Å)	12.688(2)	44.482(4)	10.562(2)
b (Å)	12.908(2)	12.800(1)	12.247(3)
c (Å)	12.607(2	26.560(2)	12.799(3)
α (deg)			117.166(3)
β (deg)	110.511(3)	125.204(1)	90.288(4)
γ (deg)			96.559(4)
V (Å^3)	1933.7(6)	12356(2)	1460.1(6)
Z	2	4	1
radiation (Kα)	0.710 73	0.710 73	0.710 73
T (K)	203(2)	203(2)	203(2)
D_{calcd} (g cm^{-3})	1.530	1.524	1.251
μ_{calcd} (cm^{-1})	6.44	9.76	2.62
F_{000}	920	5796	585
R1, wR2,[a] GOF	0.0609, 0.1203, 1.020	0.0873, 0.2237, 1.084	0.0709, 0.1612, 1.030

[a] $R = \sum F_o - F_c/\sum F_o$; wR2 $= [\sum(F_o - F_c)^2/\sum wF_o^2\,]^{1/2}$.

Isolation of {([HC(C_4H_3N)$_3$]$_2$NbK)$_2$}{Nb_4Cl_{11}[K(THF)$_2$]$_2$}·2THF (2). A solution of tripyrrolylmethane (1.0 g, 4.5 mmol) in THF (150 mL) was treated with KH (0.5 g, 13.5 mmol). A vigorous gas evolution was observed upon mixing. The mixture was stirred at room temperature for 1 h and treated with solid Nb_2Cl_6(TMEDA)$_2$ (1.4 g, 2.2 mmol). The resulting suspension was refluxed overnight. The mixture was cooled and filtered to eliminate a small amount of insoluble material and the resulting solution allowed to stand overnight at room temperature, upon which a crystalline solid mass separated. The solid was composed of red and orange crystals of distinct shape present as the major and minor components, respectively. The red crystals were identified as **1** by comparison of the IR and NMR spectra with those of analytically pure samples prepared as described above. The crystallographic cell parameters were also identical. The orange crystals of **2** were physically separated from **1** with the help of a stereomicroscope and characterized. Anal. Calcd (found) for $C_{100}H_{152}Cl_{11}K_4N_{20}Nb_6O_6$: C, 42.38 (42.27); H, 5.41 (5.39); N, 9.88 (9.84). $\mu_{eff} = 1.77\ \mu_B$ per formula unit.

Preparation of {[HC(C_4H_3N)$_3$]$_2$Nb}{Li(THF)$_4$}$_2$ (3). A solution of MeLi (9.7 mL, 1.39 M, 13.5 mmol) was added dropwise to a solution of tripyrrolylmethane (1.0 g, 4.5 mmol) in THF (150 mL) at 0 °C. After this mixture was stirred for 30 min, solid Nb_2Cl_6(TMEDA)$_2$ (1.4 g, 2.2 mmol) was added to the resulting solution, forming a dark purple slurry. When the mixture was refluxed overnight, the purple starting material disappeared to afford a reddish brown solution and a small amount of Nb_2Cl_5 (TMEDA)$_2$,[2a] which was identified by comparison of the IR spectrum with that of an analytically pure sample. The solution was concentrated to about 50 mL and layered with diethyl ether (30 mL). Red crystals of **3** separated upon standing a few days at room temperature (0.8 mg, 0.73 mmol, 17%). IR (Nujol mull, cm^{-1}): ν 1396 (m), 1376 (s), 1344 (w), 1290 (w), 1274 (m), 1258 (w), 1234 (m), 1207 (s), 1178 (s), 1170 (s), 1139 (vs), 1099 (s), 1037 (br), 1020 (s), 970 (s), 958 (s), 916 (w), 885 (br), 804 (s), 736 (w), 742 (m), 709 (s), 676 (s). Anal. Calcd (found) for $C_{58}H_{84}N_6O_8Li_2Nb$: C, 63.32 (62.78); H, 7.70 (7.57); N, 7.64 (7.56). $\mu_{eff} = 1.89\ \mu_B$.

Molecular Orbital Calculations. DFT-MO calculations were carried out on the geometrical parameters of **2**, as obtained from the crystal structures by using a Silicon Graphics workstation and the Spartan 4.0 software package.[19] The program's default parameters were used for the calculations. The fractional atomic coordinates of the crystal structures were converted to the corresponding Cartesian coordinates by using the XP program of the SHELXTL program library.

X-ray Crystallography. Suitable crystals were selected, mounted on thin, glass fibers using paraffin oil, and cooled to the data collection temperature. The structures were 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, except the carbon atoms in **2**, which were refined isotropically to conserve a favorable data/parameter ratio. All hydrogen atoms were treated as idealized contributions. Relevant crystal data are reported in Table 1. Selected bond distances and angles are given in Table 2.

Complex 1. Complex **1** is a symmetry-generated dimer with two niobium atoms bridged by two tripyrrolylmethane anions (Figure 1). Each niobium is also coordinated to one molecule of THF substantially deviating from the intermetallic vector (Nb−O(1) = 2.258(5) Å, Nb(a)−Nb−O(1) = 140.43(15)°). One interstitial molecule of THF completes the asymmetric unit. Each tripyrrolylmethane triyl trianion (C(4)−C(13)−C(8) = 108.3(7)°, C(12)−C(13)−C(8) = 108.6(7)°, C(4)−C(13)−C(12) = 114.6(7)°) adopts a curious bridging mode. Two of the three pyrrolyl rings are σ-bonded each to one of the two Nb atoms (N(1)−Nb(a) = 2.176(7) Å, N(2)−Nb = 2.208(7) Å), while the third is π-bonded to one of the two Nb (Nb−N(3) = 2.262(6) Å, Nb−C(9) = 2.347(7) Å, Nb−C(10) = 2.487(8) Å, Nb−C(11) = 2.498(8) Å, Nb−C(12) = 2.363(8) Å). The π-bonded pyrrolyl ring also forms a σ-bond with the second Nb atom (Nb−N(1a) = 2.176(7) Å). As a result, the coordination geometry around each Nb is rather distorted square-pyramidal with the oxygen atom and three nitrogen atoms of σ-bonded pyrrolyl rings defining the basal plane (O(1)−Nb−N(2) = 74.4(2)°, O(1)−Nb−N(1a) = 76.2(2)°, O(1)−Nb−N(3a) = 86.6(2)°, N(2)−Nb−N(3a) = 87.4(2)°, N(2)−Nb−N(1a) = 149.5(2)°, N(1a)−Nb−N(3a) = 82.6(2)°) and the centroid of the π-bonded pyrrolyl ring on the apical position. The Nb−Nb distance (Nb−Nb(a) = 2.6583(15) Å) is fairly short and falls in the range expected for M−M bonding.

Complex 2. The complex is ionic. The anionic part is composed by a linear polymer formed by discrete [HC(C_4H_3N)$_3$]$_2$Nb units bridged by a potassium atom which forms a network of π-bonds with four pyrrolyl rings from two ligands of two units (Figure 2). The asymmetric unit of the anionic polymer consists of a distorted-octahedral niobium atom (N(1)−Nb(1)−N(2) = 81.7(4)°, N(1)−Nb(1)−N(3) = 86.6(4)°, N(1)−Nb(1)−N(4) = 166.9(4)°, N(3)−Nb(1)−N(6) = 162.8(4)°, N(2)−Nb(1)−N(5) = 162.0(4)°, N(2)−Nb(1)−N(3) = 84.8(4)°) surrounded by two [HC(C_4H_3N)$_3$]$^{3-}$ ligands each adopting a regular tripodal-like geometry (C(4)−C(13)−C(8) = 109.5(11)°, C(4)−C(13)−C(12) = 110.2(11)°, C(8)−C(13)−C(12) = 111.4(11)°). The six N atoms of the σ-bonded pyrrolyl rings from the two ligands (Nb(1)−N(1) = 2.156(11) Å, Nb(1)−N(2) = 2.159(10) Å, Nb-

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[19] All the calculations were performed with the software package SPARTAN 4.0, from Wavefunction, Inc., 18401 Von Karman Ave., #370, Irvine, CA 92715, 1995.

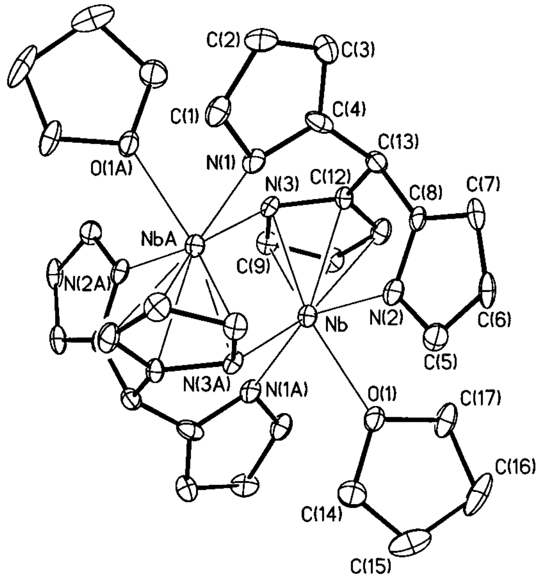


Figure 1. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1−3

	Compound **1**		
Nb−N(1a)	2.176(7)	Nb−C(10)	2.487(8)
Nb−N(2)	2.208(7)	Nb−C(11)	2.498(8)
Nb−O(1)	2.258(5)	Nb−C(12)	2.363(8)
Nb−N(3)	2.262(6)	Nb−Nb(a)	2.6583(15)
Nb−C(9)	2.347(7)	Nb−N(3a)	2.242(6)
N(1a)−Nb−N(3a)	82.6(2)	N(3a)−Nb−N(2)	87.4(2)
N(1a)−Nb−N(2)	149.5(2)	N(3a)−Nb−O(1)	86.6(2)
N(1a)−Nb−O(1)	76.2(2)	N(2)−Nb−O(1)	74.4(2)
	Compound **2**		
Nb(1)−N(1)	2.156(11)	K(1)−C(25a)	3.027(14)
Nb(1)−N(2)	2.159(10)	K(1)−C(24a)	3.150(14)
Nb(1)−N(3)	2.095(10)	Nb(2)−Nb(3)	2.506(2)
Nb(1)−N(4)	2.130(11)	Nb(2)−Cl(3)	2.524(4)
Nb(1)−N(5)	2.144(10)	Nb(2)−Cl(4)	2.474(4)
Nb(1)−N(6)	2.166(11)	Nb(2)−Cl(5)	2.507(6)
K(1)−N(1)	3.207(11)	Nb(2)−Nb(3)	2.506(2)
K(1)−C(1)	3.324(14)	Cl(1)−K(2)	3.042(6)
K(1)−C(2)	3.293(14)	Cl(1)−K(2a)	3.306(6)
K(1)−C(3)	3.141(14)	K(2)−Cl(2)	3.041(10)
K(1)−C(4)	3.096(13)	K(2)−Cl(5)	3.561(8)
K(1)−N(2)	3.099(11)		
N(1)−Nb(1)−N(2)	81.7(4)	N(2)−Nb(1)−N(6)	87.2(4)
N(1)−Nb(1)−N(3)	86.6(4)	N(3)−Nb(1)−N(4)	85.2(4)
N(1)−Nb(1)−N(4)	166.9(4)	N(5)−Nb(1)−N(6)	83.7(4)
N(1)−Nb(1)−N(5)	86.2(4)	Cl(1)−Nb(2)−Cl(3)	178.43(15)
N(1)−Nb(1)−N(6)	107.2(4)	Cl(1)−Nb(2)−Cl(4)	90.09(18)
N(2)−Nb(1)−N(3)	84.8(4)	Cl(1)−Nb(2)−Cl(5)	87.47(17)
N(2)−Nb(1)−N(4)	107.7(4)	Cl(1)−Nb(2)−Cl(3)	178.43(15)
N(2)−Nb(1)−N(5)	162.0(4)	Nb(2)−Cl(1)−K(2)	95.21(18)
	Compound **3**		
Nb−N(1)	2.123(5)	Nb−N(3)	2.135(4)
Nb−N(2)	2.144(5)	Li−O(1)	1.911(17)
N(1)−Nb−N(2)	84.1(2)	N(1)−Nb−N(1a)	180.0(3)
N(1)−Nb−N(3)	84.51(18)	N(1)−Nb−N(2a)	84.1(2)
N(2)−Nb−N(3)	83.97(18)	N(1)−Nb−N(3a)	84.51(18)

(1)−N(3) = 2.095(10) Å, Nb(1)−N(4) = 2.130(11) Å, Nb(1)−N(5) = 2.144(10) Å, Nb(1)−N(6) = 2.166(11) Å) define the coordination octahedron. Two pyrrolyl rings of one ligand are also π-bonded to one potassium atom (K(1)−N(1) = 3.207(11) Å, K(1)−C(1) = 3.324(14) Å, K(1)−C(2) = 3.293(14) Å, K(1)−C(3) = 3.141(14) Å, K(1)−C(4) = 3.096(13) Å), which in turn is π-coordinated to two other pyrrolyl rings of the next unit (K(1)−N(6a) = 3.197(11) Å, K(1)−C(25a) = 3.027(14) Å, K(1)−C(24a) = 3.150(14) Å, K(1)−C(22a) = 3.410(14) Å, K(1)−C(23a) = 3.412(15) Å, K(1)−C(16a) = 3.285(16) Å, K(1)−C(17a) = 3.244(13) Å, K(1)−N(4a) = 3.583(11) Å, K(1)−C(14a) = 3.774(16) Å, K(1)−C(15a) = 3.636(16) Å, thus assembling a polymeric polyanionic structure. The coordination environment of the alkali-metal cation is rather unique and is defined by four π-bonded pyrrolyl rings.

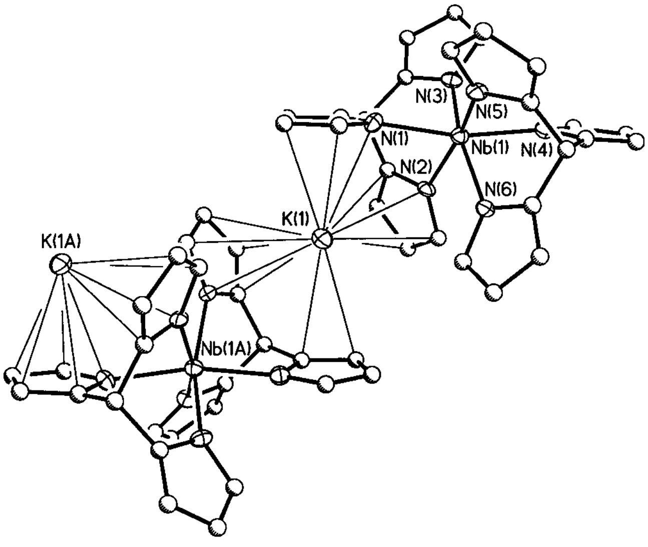


Figure 2. Partial thermal ellipsoid drawing of **2** (anionic moiety). Thermal ellipsoids are drawn at the 30% probability level.

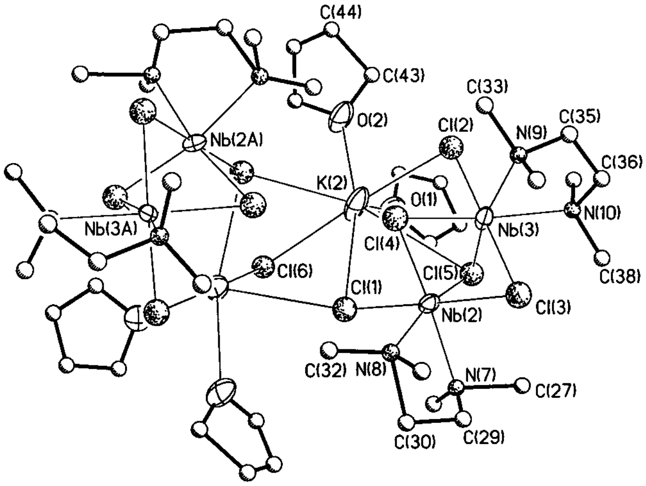


Figure 3. Partial thermal ellipsoid drawing of **2** (cationic moiety). Thermal ellipsoids are drawn at the 30% probability level.

The cationic tetramer (Figure 3) is composed of two identical $[(TMEDA)Nb]_2Cl_5$ units, similar to the recently reported mixed valence $[(TMEDA)Nb]_2Cl_5$[2a] and forming a comparable Nb−Nb distance (Nb(2)−Nb(3) = 2.506(2) Å). The two identical units are held together by a network of bridging interactions established by a formal $[(THF)K]_2Cl$ unit located between the two diniobium moieties. Each $(TMEDA)_2Nb_2Cl_5$ unit displays a face-sharing bioctahedral structure with each niobium atom in a fairly regular octahedral environment (Cl(1)−Nb(2)−Cl(3) = 178.43(15)°, N(7)−Nb(2)−Cl(4) = 166.5(10)°, N(8)−Nb(2)−Cl(5) = 167.6(8)°). The bridging between each pair of niobium atoms is realized by three chlorine atoms (Nb(2)−Cl(3) = 2.524(4) Å, Nb(2)−Cl(4) = 2.474(4) Å, Nb(2)−Cl(5) = 2.507(6) Å). The other two chlorine atoms bridge Nb to K (Nb(2)−Cl(1) = 2.498(4) Å, Cl(1)−K(2) = 3.042(6) Å). One additional chlorine atom bridges the two heptacoordinated

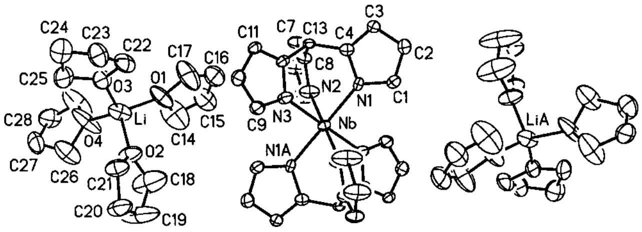


Figure 4. ORTEP drawing of **4**. Thermal ellipsoids are drawn at the 30% probability level.

potassium atoms (K(2)−Cl(6)−K(2a) = 78.1(6)°). The bridging interactions between the two potassium cations are provided by three chlorine atoms. The heptacoordination of each potassium atom is defined by two terminally bonded molecules of THF and five chlorine atoms. Each pair of anionic $[HC(C_4H_3N)_3]_2Nb$ units is counterbalanced by one tetranuclear cationic $[(TMEDA)Nb]_4(\mu\text{-}Cl)_{11}[K(THF)_2]_2$ aggregate. Two molecules of interstitial THF complete the structure.

Complex 3. The structure is composed of one octahedral $\{[HC(C_4H_3N)_3]_2Nb\}^{2-}$ dianion and two tetrahedral $[Li(THF)_4]^+$ cations (Li−O(1) = 1.911(17) Å, O(1)−Li−O(2) = 109.2(8)°) (Figure 4). The niobium atom is located in the center of a slightly distorted octahedron (N(1)−Nb−N(2) = 84.1(2)°, N(1)−Nb−N(3) = 84.51(18)°, N(2)−Nb−N(3) = 83.97(18)°, N(3)−Nb−N(3a) = 180.0(3)°) defined by the N-donor atom (Nb−N(1) = 2.123(5) Å, Nb−N(2) = 2.144(5) Å, Nb−N(3) = 2.135(4) Å) of the two tripyrrolylmethane triyl anions. The two ligands adopted a tripodal-like bonding mode with niobium (C(4)−C(13)−C(12) = 110.6(4)°, C(4)−C(13)−C(8) = 110.2(4)°, C(8)−C(13)−C(12) = 109.8(5)°). All the other bond distances and angles compare rather well with those of the polymeric anionic moiety of **2**.

Results and Discussion

The reaction of $Nb_2Cl_6(TMEDA)_2$ with 2 equiv of the tripyrrolylmethane triyl anion afforded a mixture from where two products have been isolated and characterized (Scheme 1). The first complex is the diamagnetic and dinuclear $\{[HC(C_4H_3N)_3]Nb(THF)\}_2\cdot 2THF$ (**1**). The dinuclear structure of this complex is hold together by the two $[HC(C_4H_3N)_3]^{3-}$ anions, each adopting a curious bridging mode between the two niobium atoms. Each ligand caps the dimetallic unit using two of the three pyrrolyl rings to form a σ-bond with each of the two niobium atoms, while the third ring is both π-bonded to one of the two niobium atoms and σ-bonded to the second. Complex **2** could also be more conveniently prepared under similar conditions in analytically pure form free of byproducts by using $NbCl_3(DME)$ as the starting material.

Complex **1** displays a Nb−Nb distance (2.6583(15) Å0 which suggests the existence of a possible Nb−Nb bonding interaction. The d^2 electronic configuration of the two trivalent Nb centers and the diamagnetism of the complex might indicate the presence of a *formal* Nb−Nb double bond. DFT calculations were carried out on the atomic coordinates as provided by the crystal structure. The substantial HOMO−LUMO gap (1.66 eV) nicely accounts for the observed diamagnetism (Chart 1). Both orbitals display some extent of Nb−Nb π-bond character. In the LUMO (−2.58 eV), however, the Nb−Nb bond component is rather marginal, while the major feature is the π-interaction of Nb with the pyrrolyl ligand. Conversely, the HOMO (−4.24 eV) appears to be an almost "pure" Nb−Nb π-bond arising from the overlap of the niobium d_{xz} orbitals. Another orbital which displays a rather substantial Nb−Nb π-bond character is HOMO-9 (−5.92 eV), where the π-bond is still realized by the overlap of the niobium d_{xz} orbitals but with a major participation of the p_z orbitals of the nitrogen atom of one of the σ-bonded pyrrolyl ligands attached to each niobium. The Nb−Nb σ-bonding interaction is realized via three main MO's. All three MO's rely on the overlap of the d_{z^2} orbitals. In the first (HOMO-3, −4.97 eV), the σ-bond contribution is only a minor component of the Nb−ligand interactions. The contribution of the overlap of the two d_{z^2} orbitals turns out to be the dominant feature of the second (HOMO-5, −5.32 eV). In the third (HOMO-8, −5.92 eV), the Nb−Nb σ-bond is similar in shape to HOMO-5 except that the Nb−Nb σ-interaction is realized via the overlap of hybrid combinations of d_{z^2} and d_{yz} atomic orbitals. Both HOMO-5 and HOMO-8 display a minor yet significant involvement of the ligand. Thus, the DFT calculation supports the existence of a Nb−Nb double bond. A second complex was isolated as a byproduct of the reaction mixture, but in contrast to **1**, its preparation could not be obtained through a selective synthetic procedure. Thus, its characterization remains necessarily limited. Nonetheless, the product presents some unique features. The complex is ionic with the anionic moiety formed by two identical tetravalent $[HC(C_4H_3N)_3]_2NbK$ units bridged together by potassium cations and composing an infinite *zigzag* polymeric structure. The corresponding dication is a discrete $(TMEDA)_4Nb_4Cl_{11}K_2(THF)_4$ species, *formally* arising from the aggregation of *two* identical $(TMEDA)_2Nb_2Cl_5K(THF)$ units linked together by one additional chlorine atom, and is structurally reminiscent of the divalent $(TMEDA)_2Nb_2Cl_5Li(TMEDA)$[4t] and mixed-valence $(TMEDA)_2Nb_2Cl_5$ derivative.[2a] The ligand system (11 chlorides and 4 tripyrrolide trianions) accounts for 23 negative charges, which are balanced by four potassium and six niobium atoms. A possible rationalization of the structure of **2** is to assume that each niobium atom of the anionic polymer is present in the tetravalent state. This possibility is also substantiated by the close structural similarity with complex **3** (vide infra), which doubtlessly contains tetravalent niobium. Given that the structure of **2** consists of *two* anionic moieties, the tetrametallic cation must necessarily bear a +2 charge. As a result, the cation has three of the four niobium atoms still present in the original +3 oxidation state, while the fourth is the formal divalent state. Regardless, the formation of **2** requires elimination of one electron and implies that another species must be present in the reaction mixture as a result of the reduction process.

An interesting comparison can be made between the $\{(TMEDA)_4Nb_4Cl_{11}K_2\}^{2+}$ dication and the neutral and tetranuclear $Nb_4Cl_{10}(PR_3)_8$ cluster.[4u] Despite having the niobium atoms in a slightly higher oxidation state, the dicationic cluster possesses a significantly shorter Nb−Nb distance (Nb−Nb = 2.506 Å), indicative of the presence of two Nb−Nb double bonds. In contrast, the tetranuclear $Nb_4Cl_{10}(PR_3)_8$ cluster shows long Nb−Nb distances (Nb−Nb = 2.904 and 2.934 Å), indicating the absence of a Nb−Nb bonding interaction.

Reactions carried out under identical conditions but using the trilithium salt of the tripyrrole ligand led to

Scheme 1

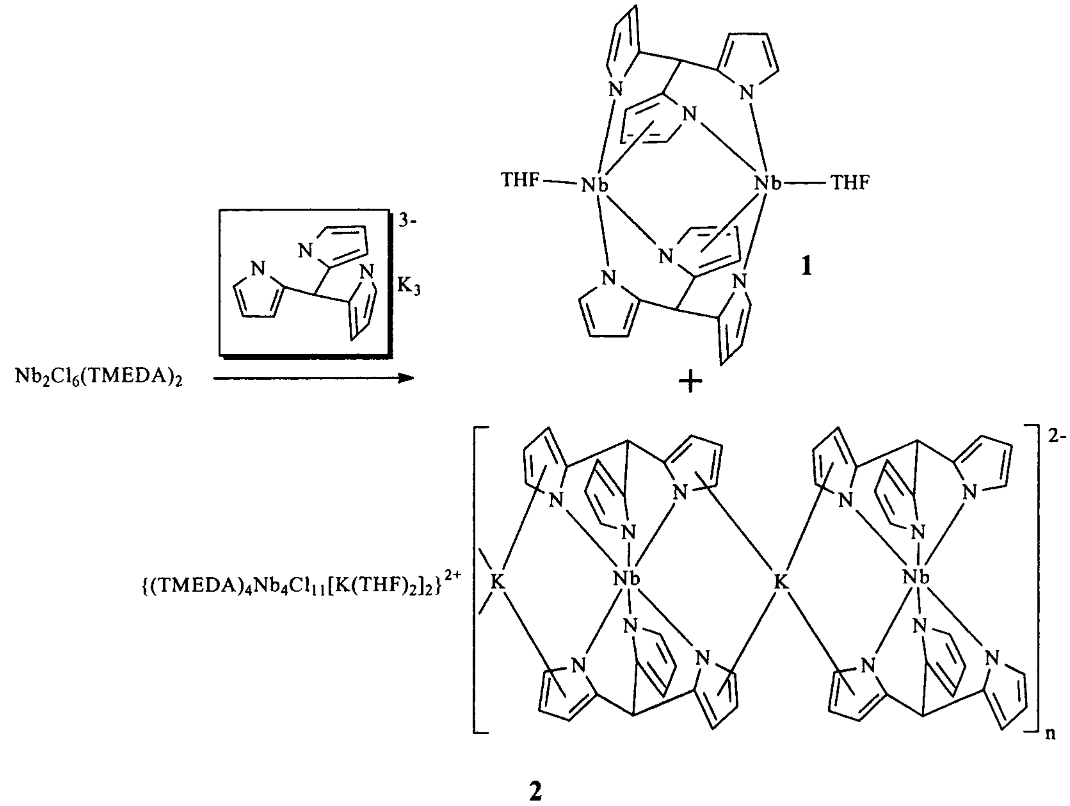
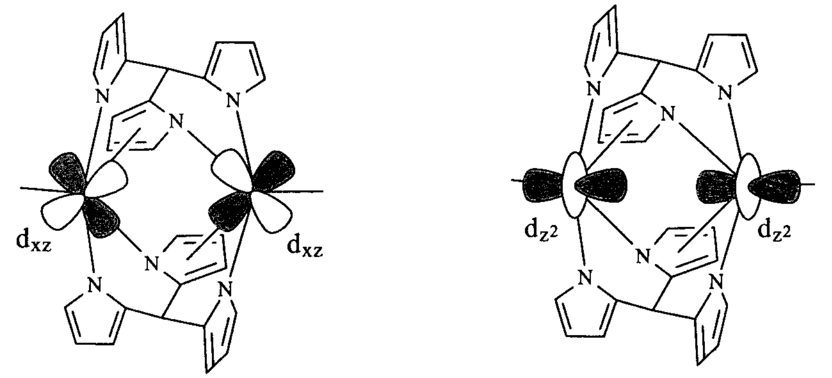
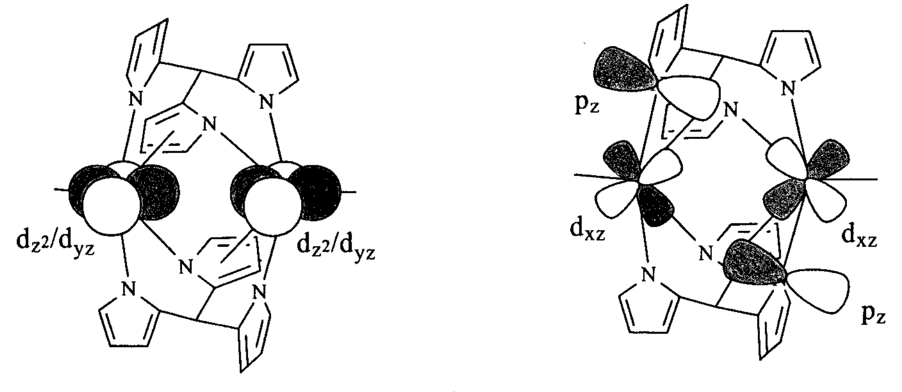


Chart 1



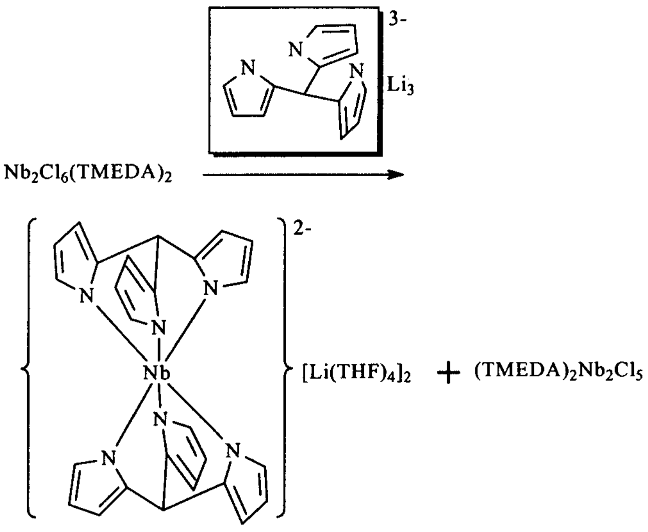
HOMO (-4.24 eV, Nb-Nb π-bond) **HOMO-5 (-5.32 eV, Nb-Nb σ-bond)**



HOMO-8 (-5.68 eV, "hybrid" σ-bond) **HOMO-9 (-5.92 eV, "hybrid" π-bond)**

a simple mononuclear tetravalent niobium complex with the metal encapsulated by two ligands and two solvated lithium cations in the lattice (Scheme 2). In this case, the oxidation of one tetravalent niobium to Nb(III) was

Scheme 2



3

accompanied by the formation of the insoluble, mixed-valence Nb(II)/Nb(III) species $Nb_2Cl_5(TMEDA)_2$,[2a] resulting from the one-electron reduction of $Nb_2Cl_6(TMEDA)_2$. Complex **3** is paramagnetic, with a magnetic moment as expected for the d^1 electronic configuration (spin-only) of a mononuclear Nb(IV) complex.

Conclusions

In this work we have examined the reaction of trivalent Nb halides with the tripodal tripyrrolyl trianion. The preeminent features of this ligand can be summarized as (1) the ability to cap a dimetallic unit with an unusual bridging mode and stabilize the trivalent state of Nb, (2) an apparent inertness to reactivity of the trivalent Nb center, and (3) the ability to support formation of Nb–Nb bonds with and without participation of ligand orbitals in the formation of the Nb–Nb MO's. The possibility of coordinating one of the three pyrrolyl rings in a π-bonding fashion is probably the key for understanding the versatility of this ligand and its ability to prevent destructive reactivity patterns such as ring opening,[2,8b–f] C–N cleavage,[2,8,9] and denitrogenation reactions.[10] The trianion also supports the regular pyramidal bonding mode. In this particular case, however, the tendency to encapsulate the metal by combining two ligands to create an octahedral pocket is accompanied by a tendency to promote complex disproportionation reactions. A crucial role in this respect is played by the nature of the ancillary ligand around the Nb starting material (TMEDA versus DME) and by the nature of the alkali-metal cation employed (K versus Li). Similar to other transformations involving low-valent niobium,[10] these reactions involve the participation of several metal centers in a complex redox pattern. Further studies to fully exploit the potential of this ligand system will be carried out by increasing the steric hindrance of the tripodal system to prevent encapsulation of the metal center.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Council of Canada (NSERC).

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for **1**–**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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