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Triply Bonded Nb_2^{4+} Tetragonal Lantern Compounds: Some Accompanied by Novel B−H···Na^+ Interactions

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Abstract: The diniobium tetragonal lantern compound $Nb_2(hpp)_4$, **1**, has been prepared in high yields by the reaction of $NbCl_3(DME)$, DME = dimethoxyethane, with a mixture of lithium naphthalenide and Li(hpp), hpp = the anion of 1,3,4,6,7,8-hexahydropyrimido[1,2-a]pyrimidine. Compound **1** interacts with two equivalents of $NaEt_3BH$ to give the bis-adduct, **1**·$2NaEt_3BH$. In a refluxing mixture of THF/toluene, **1**·$2NaEt_3BH$ loses one $NaEt_3BH$ molecule to give **1**·$NaEt_3BH$. Both adducts contain short Na to N−C−N "pseudo-allylic" interactions to the coordinated hpp ligand. Very little variation can be seen in the Nb−Nb bond distances, which are 2.2035(9), 2.2064(3), and 2.2187(7) Å for **1**, **1**·$2NaEt_3BH$ and **1**·$NaEt_3BH$, respectively. By a synthetic route similar to that used to make **1**, $Nb_2(azin)_4$·2LiCl·4THF, **2**, was prepared using the anion of 7-azaindole; the Cl^- ions are loosely coordinated to the Nb atoms. This ligand tends to give long metal−metal distances, and the Nb−Nb distance of 2.278(2) Å is 0.07 Å longer than that in **1**.

Introduction

Dinuclear metal−metal bonded compounds of the lantern type—those containing four bridging ligands in an approximately D_{4h} arrangement—have been extensively studied; they are well-known for the heavier transition elements of groups 6−11. The bond orders can range from 0.0, 0.5, or 1.0 in Pt_2^{4+}, Pt_2^{5+}, or Pt_2^{6+} units to 4 in compounds containing Mo_2^{4+} units.[1] For the first row transition elements, as well as for the early transition metals, the situation is significantly different. In the first transition series, up to 1992, this type of complex was known only for several dichromium compounds and one cobalt compound.[2] However, the preparation of the cobalt compound proved to be nongeneral and did not work for the synthesis of analogues. Since then, rational design of synthetic procedures has yielded systematic preparations of metal-to-metal bonded compounds for V,[3] Fe,[4] and Co.[5]

Our observations indicate that the choice of starting materials is often critical for the successful isolation of dinuclear species. Once formed, however, they tend to be chemically and thermally stable. Apparently, the outcome in the competition between the formation of classical coordination compounds and the formation of metal−metal bonded species is dependent on several factors, of which, the nature of the solvent, the other coordinated ligands, and the reaction pathway are critical. For example, the reaction of a THF solution of $FeCl_2$ and Li(PhNCHNPh) yields an oxidized tris-chelated species of the type $Fe(PhNCHNPh)_3$ while the corresponding triazine analogue forms a mononuclear Fe^{II} species, $Li(THF)_4[Fe(PhNNNPh)_3]$;.[6] However, when reactions are carried out with $MCl_2(formamidine)_2$ (M = Fe, Co) and LiMe, in a noncoordinating solvent, the products are exclusively dinuclear.[4,5]

For vanadium, reactions of *trans*-$VCl_2(py)_4$ and formamidinate anions gave only mononuclear complexes of the type *trans*-$V(formamidinato)_2(py)_2$.[7] Reactions of species containing triply bridged $[VCl_3V]^+$ units always failed to produce isolable materials with formamidinates. It was not until we were able to generate solutions of $VCl_2(THF)_n$ that the triply bonded tetragonal lantern species containing divanadium units were isolated.[3]

The heavier group 5 elements, Nb and Ta, present a different challenge. Divalent compounds of these elements, whether mononuclear, binuclear, cluster, or organometallic complexes, are scarce. Coordination species such as MCl_2L_4 for M = Nb and Ta, L = PMe_3[8] or $^1/_2$ dmpe[8] and $Nb(OAr)_2(dmpe)_2$[9] have been prepared by reduction of higher-valent chlorides or aryloxides with Na/Hg. Potassium graphite works best for the reduction of $NbCl_4(THF)_2$ in THF/py to prepare *trans*-$NbCl_2(py)_4$.[10] There are also triply bonded species of the face-sharing

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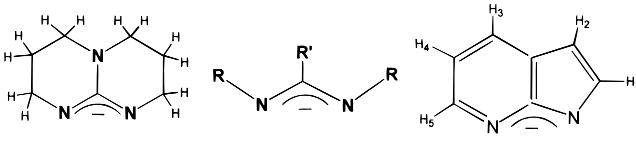
Scheme 1



hpp ligand Amidinate ligand 7-azaindolate ligand

bioctahedral type such as $[Cl_3M(\mu\text{-THT})_3MCl_3]^{2-}$ and $[Nb_2Cl_5(THT)(py)_3]^+$ that have long M−M distances[11] of ca. 2.6 Å. An amine-containing species, $Li(tmeda)_3Nb_2Cl_5$, that has a shorter Nb−Nb distance of 2.4001(5) Å is also known.[12] Moreover, none of the previously known compounds has proved to be a suitable starting material for the preparation of the desired dinuclear products.

While reacting formamidinates (Scheme 1) and compounds of the heavier group 5 elements it was, of course, necessary to reduce the higher-valent complexes. However, such procedures generally gave dinuclear complexes containing doubly bonded M_2^{6+} units which typically reacted with the formamidinate anions by an oxidative addition pathway, cleaving a C−N bond of the formamidinate anion,[13] thus preventing the formation of the target M_2(formamidinate)$_4$ complexes and giving products containing M^{III} or M^{IV} and fragments such as ArN and ArNC.

In the hope of circumventing the cleavage, a more robust ligand, namely the anion of 1,3,4,6,7,8 hexahydropyrimido[1,2-*a*]pyrimidine, hpp$^-$, (Scheme 1) was used. The ligand, hpp, like the amidine ligands also has an $(N-C-N)^-$ unit, but because of its fused ring structure is more robust. With hpp, we were able to prepare, in low yield, the first triply bonded Nb_2^{4+} compound, $Nb_2(hpp)_4$, **1**, of which a preliminary report has appeared.[14]

We now report a high yield synthesis of $Nb_2(hpp)_4$ as well as the isolation of two new crystalline forms containing one and two interstitial sodium triethylborohydride entities per dinuclear unit: **1**·$NaEt_3BH$ and **1**·$2NaEt_3BH$, respectively. In both of these compounds, there are interesting interactions between sodium ions, BEt_3H^- ions, and the nitrogen atoms of the hpp ligand which give rise to significant conformational modifications but have very little effect on the Nb−Nb distances.

Another example of a lantern Nb_2^{4+} complex, $Nb_2(azin)_4$·2LiCl·4THF, **2** (azin = the anion of 7-azaindole, see Scheme 1), which contains a ligand that typically produces relatively long metal−metal bonds is also reported. The Nb−Nb bond length of 2.278(2) Å is about 0.07 Å longer than that of $Nb_2(hpp)_4$.

Experimental Section

General Procedures. All syntheses and sample manipulation were carried out under an atmosphere of dry and deoxygenated argon with standard Schlenk and glovebox techniques. Solvents were distilled under N_2 from Na/K−benzophenone. $NbCl_3$(DME) was prepared as reported[15] and was stored at −40 °C prior to use; older samples left at room temperature were less reactive. Methyllithium (1 M solution in THF/cumene) and $NaEt_3BH$ (1 M solution in THF) were purchased from Aldrich Chemical Co. 7-Azaindole (HAzin) and 1,3,4,6,7,8-hexahydropyrimido[1,2-*a*]pyrimidine (Hhpp) were purchased from Aldrich Chemical Co. and sublimed prior to use. NMR spectra were recorded on a Varian XL-200 spectrometer. Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 16PC FT-IR spectrophotometer. UV−vis data were recorded on a Cary-17 spectrometer. Elemental analyses were performed by Canadian Microanalytical Services Ltd.; they were satisfactory.

Preparation of $Nb_2(hpp)_4$, 1. A solution of lithium naphthalenide, Li(nap), was prepared by stirring thinly crushed pieces of Li (0.025 g, 3.6 mmol) and 0.463 g (3.6 mmol) of naphthalene in THF (10 mL) for 3 h at room temperature. The solution was then cooled to −40 °C. Lihpp was prepared by dissolving Hhpp (0.97 g, 6.9 mmol) in THF (10 mL), cooling to −77 °C, and adding MeLi (6.9 mL). The deprotonation of Hhpp was essentially complete upon warming to room temperature. The THF solutions of Li(nap) and Li(hpp) were combined and cooled to −77 °C. $NbCl_3$(DME) (1.0 g, 3.6 mmol) was then added to the mixture. The solution was stirred at −77 °C for 3 h and then at 0 °C for 10 h. Green microcrystalline **1**, was then filtered, washed with cold THF (2 × 5 mL), and dried under vacuum. Yield: 0.60 g, 47%. IR (cm^{-1}): 2930 (s), 2808 (s), 1618 (m), 1512 (s), 1467 (s), 1439 (s), 1372 (s), 1315 (sh), 1302 (s), 1250 (m), 1218 (m), 1193 (s), 1134 (s), 1113 (m), 1071 (s), 1022 (m), 915 (w), 898 (w), 729 (s), 590 (w), 550 (w), 460 (w). ^1H NMR (C_6D_6, ppm): 1.90 (p), 2.90 (t), 3.71 (t). λ_{max}, (benzene, ϵ): 442 nm (995 M^{-1} cm^{-1}).

Preparation of $Nb_2(hpp)_4$·$2NaEt_3BH$. To $Nb_2(hpp)_4$ (0.100 g, 0.135 mmol) was added 7 mL of toluene. The temperature of the flask was then lowered to −77 °C, and $NaEt_3BH$ (0.27 mL) was added. The mixture was allowed to warm to room temperature. As the temperature increased, the mixture changed from a light green suspension to a dark green solution. After 1 h of stirring at room temperature, the reaction solution was carefully layered with 15 mL of hexanes. Green needle-shaped crystals of **1**·$2NaEt_3BH$ grew overnight. Yield: 0.110 g, 87%. IR (cm^{-1}): 2928 (s), 2850 (s), 1999 (sh), 1919 (s), 1613 (m), 1526 (s), 1485 (s), 1468 (s), 1440 (s), 1376 (s), 1318 (s), 1305 (s), 1282 (s), 1203 (s), 1131 (m), 1113 (m), 1058 (m), 1024 (m), 905 (w), 854 (w), 804 (w), 745 (m), 725 (m), 713 (sh), 464 (w).

Preparation of $Nb_2(hpp)_4$·$NaEt_3BH$. To $Nb_2(hpp)_4$·$2NaEt_3BH$ (0.100 g, 0.107 mmol) were added 5 mL of toluene and 2 mL of THF. The green solution was then heated to reflux for 2 h. After cooling the solution to room temperature, hexanes were then layered on to the solution. Within 1 week large green, block-shaped crystals of **1**·$NaEt_3BH$ formed. IR (cm^{-1}): 2927 (s), 2886 (s), 2845 (s), 1998 (sh), 1947 (m), 1612 (m), 1522 (s), 1497 (s), 1467 (s), 1440 (s), 1375 (s), 1317 (sh), 1303 (s), 1282 (s), 1220 (sh), 1197 (s), 1130 (s), 1113 (m), 1066 (m), 917 (w), 902 (w), 880 (w), 747 (sh), 733 (s), 592 (w), 464 (w).

Preparation of $Nb_2(azin)_4$·2LiCl·4THF. In the drybox, a solution of lithium naphthalenide was prepared by introducing thin pieces of lithium (0.025 g, 3.62 mmol) to a solution of naphthalene (0.500 g, 3.9 mmol) in THF (10 mL). To ensure complete consumption of the Li, the mixture was stirred at room temperature for 3 h. Li(azin) was prepared by dissolving 0.81 g (6.9 mmol) of 7-azaindole in THF (5 mL), followed by addition of MeLi (6.9 mL, 6.9 mmol) at low temperature (−77 °C). The deprotonation was completed by the time the reaction mixture reached room temperature. The THF was then removed under vacuum, and the Li(azin) was added to the Li(nap) solution. The mixture was cooled to −40 °C before adding 1.0 g (6.9 mmol) of $NbCl_3$(DME). This mixture was transferred to a Schlenk line and stirred at 0 °C for 12 h. A blue-green precipitate which formed was filtered and then dissolved in THF (7 mL), and this solution was layered with hexanes (15 mL). Black needle crystals of **2** formed within 2 days. Yield: 0.35 g, 20%. ^1H NMR (acetone-d_6, ppm): 1.78 (p, 4H), 3.65 (t, 4H), 6.42 (d, 1H), 7.05 (m, 1H), 7.50 (m, 1H), 7.90 (m, 1H), 8.20 (m, 1H).

X-ray Crystallography. Data collection for all crystals was carried out on a Nonius FAST area detector diffractometer with each crystal mounted on the tip of a glass fiber under a stream of nitrogen at −60 °C.[16] Cell parameters were obtained by least-squares refinement of

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Table 1. Crystal Data and Structure Refinement

	1	**1**·$NaEt_3BH$	**1**·$2NaEt_3BH$	**2**
empirical formula	$C_{28}H_{48}N_{12}Nb_2$	$C_{34}H_{48}BN_{12}NaNb_2$	$C_{40}H_{80}B_2N_{12}Na_2Nb_2$	$C_{48}H_{48}Cl_2Li_2N_8Nb_2O_2$
formula weight	738.60	844.46	982.58	1039.54
space group	$P\bar{1}$	C2/c	$P2_1/c$	$I\bar{4}$
a (Å)	8.437(1)	14.930(3)	9.228(2)	14.100(2)
b (Å)	9.615(2)	14.370(3)	10.963(2)	14.100(2)
c (Å)	10.268(1)	19.160(4)	23.401(5)	11.614(2)
α (deg)	87.26(3)	90	90	90
β (deg)	70.530(5)	98.13(3)	95.18(3)	90
γ (deg)	80.77(1)	90	90	90
V ($Å^3$)	775.1(2)	4069.4(14)	2357.7(8)	2309.1(7)
Z	1	4	2	2
d_{calc} (g/cm^{-1})	1.582	1.378	1.384	1.495
cryst size (mm)	0.15 × 0.15 × 0.10	0.4 × 0.25 × 0.25	0.35 × 0.30 × 0.30	0.20 × 0.10 × 0.10
abs coeff (mm^{-1})	0.780	0.613	0.547	0.660
data collection instrument	Nonius-Fast	Nonius-Fast	Nonius-Fast	Nonius-Fast
temp	213(2) K	213(2) K	213(2) K	213(2) K
θ range (data collection)	2.15 to 22.51	2.77 to 24.96	2.55 to 25.14	2.27 to 22.49
reflections collected	3948	11231	12648	4880
independent reflections	1944 [*R*(int) = 0.0493]	3524 [*R*(int) = 0.0516]	3982 [*R*(int) = 0.0475]	1508 [*R*(int) = 0.0591]
data/restraints/parameters	1944/0/190	3524/3/322	3978/0/383	1505/0/130
max and min transmission	0.990 and 0.650			0.998 and 0.720
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.039, wR2 = 0.089	R1 = 0.037, wR2 = 0.094	R1 = 0.036, wR2 = 0.083	R1 = 0.052, wR2 = 0.127
R indices (all data)	R1 = 0.044, wR2 = 0.093	R1 = 0.041, wR2 = 0.098	R1 = 0.042, wR2 = 0.091	R1 = 0.061, wR2 = 0.139
goodness-of-fit on F^2	1.081	1.110	1.154	1.146
largest shift/esd, final cycle	0.000	−0.139	−0.065	0.223
largest peak, final cycle	0.54(9) e/$Å^3$	1.02(9)	0.93(8)	0.59(10)

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $wR2 = [\sum w[(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o^2 \text{ or } 0) + 2(F_c^2)]/3$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **1**, **1**·$2NaEt_3BH$, and **1**·$NaEt_3BH$

	1	**1**·$2NaEt_3BH$	**1**·$NaEt_3BH$
	Bond Lengths		
Nb(1)−Nb(1a)	2.2035(9)	2.2064(6)	2.2187(7)
Nb(1)−N(11)	2.201(4)	2.215(3)	2.198(3)
Nb(1)−N(12a)	2.198(4)	2.226(3)	2.219(3)
Nb(1)−N(21)	2.201(4)	2.214(3)	2.255(3)
Nb(1)−N(22a)	2.204(4)	2.213(3)	2.261(3)
Nb(1)−Na(1)		3.4121(14)	3.420(2)
Na(1)−Nb(1a)		3.461(2)	3.467(2)
	Bond Angles		
N(12a)−Nb(1)−N(21)	88.6(2)	85.15(10)	177.88(9)
N(12a)−Nb(1)−N(11)	176.6(2)	172.33(9)	91.71(11)
N(21)−Nb(1)−N(11)	89.1(2)	87.49(10)	88.28(10)
N(12a)−Nb(1)−Nb(1a)	91.47(12)	92.45(7)	91.09(7)
N(21)−Nb(1)−Nb(1a)	91.67(11)	92.21(7)	91.03(7)
N(11)−Nb(1)−Nb(1a)	91.23(11)	89.99(7)	91.36(7)
N(12a)−Nb(1)−N(22a)	88.8(2)	87.91(10)	87.82(10)
N(21)−Nb(1)−N(22a)	176.3(2)	172.79(9)	92.08(10)
N(11)−Nb(1)−N(22a)	93.3(2)	99.37(10)	177.14(9)
Nb(1a)−Nb(1)−N(22a)	91.09(11)	172.79(9)	91.47(7)

Table 3. Selected Bond Lengths [Å] and Angles [deg] for **2**

Nb(1)−Nb(1a)	2.278(2)	Nb(1)−N(2a)	2.241(10)
Nb(1)−N(1a)	2.238(10)	Nb(1)−N(2a)	2.241(10)
Nb(1)−N(1)	2.238(10)	Nb(1)−Cl(1)	2.849(3)
N(1a)−Nb(1)−N(1)	176.0(7)	N(1a)−Nb(1)−N(2a)	91.6(5)
N(1)−Nb(1)−N(2a)	88.4(5)	N(1a)−Nb(1)−N(2a)	88.4(5)
N(1)−Nb(1)−N(2a)	91.6(5)	N(2a)−Nb(1)−N(2)#3	179.5(9)
N(1a)−Nb(1)−Nb(1a)	92.0(4)	N(1)−Nb(1)−Nb(1a)	92.0(4)
N(2a)−Nb(1)−Nb(1a)	90.3(5)	N(2a)−Nb(1)−Nb(1a)	90.3(5)
N(1a)−Nb(1)−Cl(1)	88.0(4)	N(1)−Nb(1)−Cl(1)	88.0(4)
N(2a)−Nb(1)−Cl(1)	89.7(5)	N(2a)−Nb(1)−Cl(1)	89.7(5)
Nb(1a)−Nb(1)−Cl(1)	180.0		

250 reflections ranging in 2*θ* from 15 to 41°. Laue groups and centering conditions were confirmed by axial images. Data were collected using 0.2° intervals in *ϕ* for the range 0 ≤ *ϕ* ≤ 220° and 0.2° intervals in *ω* for two different regions in the range 0 ≤ *ω* ≤ 72°; in this way, nearly a full sphere of data was collected. The highly redundant data set was corrected for Lorentz and polarization effects, and the program Sortav was used to correct for absorption in compounds **1** and **2**.[17] No absorption correction was applied to **1**·$NaEt_3BH$ or **1**·$2NaEt_3BH$.

The positions of the Nb atoms were taken from a direct-methods E-map. All other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles. The hydrogen atom bound to B(1) in the structure of **1**·$2NaEt_3BH$ was found in a difference Fourier E-map and refined isotropically. All other hydrogen atoms were included in idealized positions for the purpose of structure factor calculations.

Refinement of structure **1** and **1**·$2NaEt_3BH$ proceeded very smoothly to give *R* values of 0.039 and 0.036, respectively. For compound **1**·$NaEt_3BH$, the Et_3B group was found to be disordered on a 2-fold axis. This disorder was satisfactorily modeled by refining the disordered atoms at 0.5 occupancy. For this reason the boron hydrogen atom was not refined, although a peak with 1.02 e/$Å^3$, 1.2 Å away from B(1), was found in the difference Fourier maps. For compound **2**, several space group choices were possible; $I\bar{4}$ allowed for an alternating head-to-tail arrangement of the 7-azaindole ligand, and refinement was best for this space group. However, final refinement cycles suggested a small amount of racemic twinning in the crystal. The Flack parameter refined to a value of 0.183.[18] Final *R* values were R1 = 0.037 (on *F*) and wR2 = 0.094 (on F^2).

Crystal data are listed in Table 1. Selected bond distances and angles for **1**, **1**·$2NaEt_3BH$, and **1**·$NaEt_3BH$ are given in Table 2. Selected bond distances and angles for **2** are found in Table 3.

Results and Discussion

Synthetic Considerations. Our earlier attempts to prepare compounds with a $\sigma^2\pi^4$ triple bond between the heavier group 5 elements, analogous to V_2(formamidinato)$_4$, were stymied by a lack of divalent species which could be used as starting materials. Furthermore, reduction of higher-valent complexes in the presence of the formamidinate ligands failed to produce such complexes. A systematic study of synthetic routes that employ starting materials containing trivalent and doubly bonded Ta_2^{6+} units such as those in $Ta_2Cl_6(SMe_2)_3$, demonstrated that the Ta═Ta unit reacts with the formamidinate anions to produce

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a C−N bond cleavage. Thus only Ta complexes with one or both of the corresponding $ArN{=}CH^-$ and NAr^{2-} fragments were isolated.[13] Such cleavage was also observed in attempts to reduce $TaCl_5$ with various reducing agents, e.g., Zn, KC_8, $NaEt_3BH$, and $LiBH_4$.[19] Similarly, reduction of higher-valent Nb halide complexes failed to produce the Nb_2^{4+} species. Attempts to reduce $NbCl_4(THF)_2$ in the presence of Li(formamidinate) were also unsuccessful. The reaction of $Nb_2(\mu\text{-}SMe_2)_3Cl_6$ and Li(formamidinate) in the presence of a reducing agent such as $NaEt_3BH$, demethylates the SMe_2 unit to give a doubly bonded compound $Nb_2(\mu\text{-}SMe)_2(\mu\text{-formamidinate})_2(\eta^2\text{-formamidinate})_2$.[20] Furthermore, no isolable compounds have been recovered from reactions of *trans*-$NbCl_2(py)_4$ and formamidinate anions.

However, the reaction of $NbCl_3(DME)$ with a mixture of Lihpp and KC_8 in THF produced green crystals of the diamagnetic complex $Nb_2(hpp)_4$ in low yields (ca. 16%). We have now found that if lithium naphthalenide is used as the reducing agent, the yield of the reaction increases to ca. 47%. We believe that this difference in yields is due to the solubility properties of the diniobium compound, which is not very soluble in THF and thus precipitates. Both lithium chloride and naphthalene are sufficiently soluble in THF to be filtered. Consequently, a simple filtration produces a clean product (as observed by NMR and elemental analysis). In the reduction with KC_8, the $Nb_2(hpp)_4$ precipitated on the graphite thus making the separation more difficult.

Since $Nb_2(hpp)_4$ has a $\sigma^2\pi^4$ triple bond between the Nb atoms, we attempted a reduction using 2 equiv of $NaEt_3BH$ with the hope of obtaining the quadruply bonded species $Nb_2(hpp)_4^{2-}$. Not surprisingly, it was found that no reaction occurred at low temperatures. However, it is remarkable that the solubility properties change dramatically. While $Nb_2(hpp)_4$ is relatively insoluble in THF but soluble in toluene, a new species was formed which is soluble in THF but insoluble in toluene. A crystallographic study (vide infra) revealed that this species combines one $Nb_2(hpp)_4$ molecule and two $NaEt_3BH$ molecules in the crystal. Upon heating a suspension of this compound in a mixture of THF/toluene to reflux, a new crystalline form was obtained which contains only one $NaEt_3BH$ molecule per $Nb_2(hpp)_4$ unit. The morphologies of the crystals of **1**·$NaEt_3BH$ and **1**·$2NaEt_3BH$ are very different; crystals of only one type are present in each reaction vessel. This is also supported by the IR data discussed below.

To test the generality of the synthetic method to the production of Nb_2^{4+} species, we attempted a reaction of $NbCl_3(DME)$, Li(azin), and lithium naphthalenide and found that it yields the corresponding $Nb_2(azin)_4$ unit in the compound $Nb_2(azin)_4\cdot 2LiCl\cdot 4THF$. The isolated yield of only ca. 20%, lower than that obtained for $Nb_2(hpp)_4$, is mainly due to the higher solubility of **2** in THF. Compound **2** is diamagnetic, as determined by the sharp signals in the ^1H NMR spectrum, which are found at 6.42, 7.05, 7.50, 7.90, and 8.20 ppm for the azin ligands. Following the studies on $Mo_2(acetate)_2(azin)_2$ and Hazin done by Allaire and Beauchamp,[21] they can be assigned to the protons attached to the carbon atoms labeled in Scheme 1 as H_2, H_4, H_1, H_3, and H_5, respectively. The signals at 1.78 and 3.65 ppm correspond to the THF molecules; they integrate in accord with a 1:1 Azin:THF ratio, just as in the crystal structure.

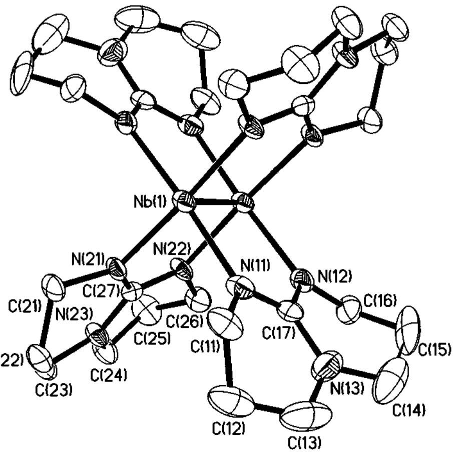

Figure 1. Thermal ellipsoid plot of **1**, atoms are shown at the 50% probability level.

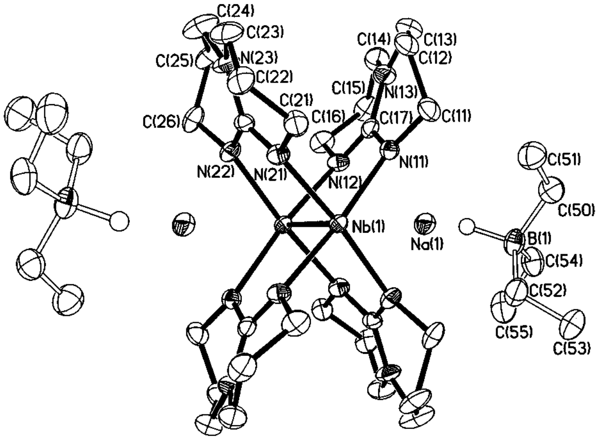

Figure 2. Thermal ellipsoid plot of **1**·$2NaEt_3BH$, atoms are shown at the 50% probability level.

Crystallographic and Spectroscopic Considerations. In all four compounds there are two niobium atoms bridged by four ligands, either hpp^- or $azin^-$. Compound **1** has one molecule per unit cell, an inversion center bisects the Nb−Nb bond as shown in Figure 1. The Nb−Nb distance of 2.2035(9) Å is considerably shorter than that found in triply bonded face-sharing bioctahedral (FSBO) species such as $[Nb_2(\mu\text{-}Cl_2)_2(\mu\text{-}THT)Cl_3py_3]^-$ or $[Nb_2Cl_2(THT)_3]^{2-}$ which have Nb−Nb distances of ca. 2.6 Å.[11] In $Li(tmeda)[(tmeda)ClNb]_2(\mu\text{-}Cl)_3$, the Nb−Nb distance is 0.2 Å longer than that of **1**.[12]

To further put the Nb−Nb triple bond distance in context, we may note that at 2.20 Å it is enormously shorter than the Nb−Nb distances in the metal itself (2.85 Å) which is one of the most refractory ones known (mp 2468 °C). Also, in terms of the *formal shortness ratio* (FSR),[1b] whereby the length of a given chemical bond is normalized to the sizes of the metal atoms themselves by using Pauling's R_1 values, we have in this case 0.820. The only class of compounds characterized by lower values are the quadruply bonded dichromium compounds (0.76−0.79) and the triple bonded divanadium compounds with FSRs of 0.79−0.81. In $Re_2Cl_8^{2-}$, for comparison, the FSR is 0.87.

Figure 2 shows the structure of **1**·$2NaEt_3BH$; an inversion center is located at the midpoint of the Nb−Nb bond. Each of the crystallographically independent sodium atoms is located near one of the lantern faces. It is bound to two "pseudo-allylic" N−C−N units of the hpp ligands at distances that vary from 2.542(3) to 2.708(3) Å and also to the hydrogen atom of the triethylborohydride anion. The presence of the sodium atoms

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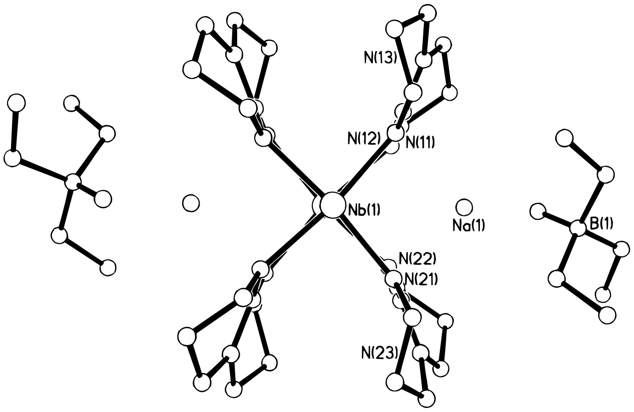

Figure 3. A drawing of **1**·$2NaEt_3BH$, showing the "puckering" in the hpp ligands.

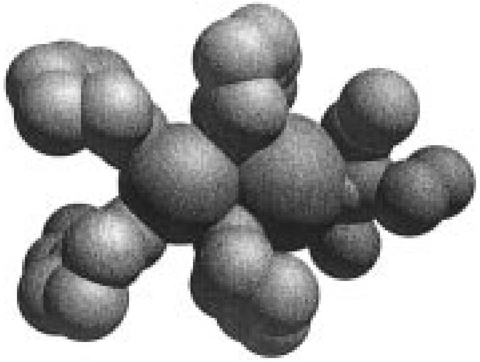

Figure 4. A space-filling drawing of **1**·$NaEt_3BH$, showing the "puckering" in two of the hpp ligands.

has important consequences for the conformation adopted by the hpp ligands as shown in Figures 3 and 4. For **1**, the angle between the planes formed by the Nb atoms and the two nitrogen atoms bound to the metal centers and that formed by the three nitrogen atoms of the ligands is less than 8°. However, those angles are 22.3(2)° and 22.8(2)° for **1**·$2NaEt_3BH$. A similar folding of the ligands is observed for **1**·$NaEt_3BH$ as shown in Figure 4. In this compound, there is a crystallographic 2-fold axis that bisects the Nb−Nb bond and includes the boron and sodium atoms. Since there is a sodium atom on only one face of the lantern, only two of the ligands are puckered, while the other two retain nearly planar configurations similar to those found in **1**. The angles between the planes formed by the atoms Nb(1), Nb(1a), N(11), N(12) and N(11), N(12), N(13) are 8.6(2)° and the corresponding angles for the ligands next to the sodium atoms are 23.9(1)°.

The type of coordination at the sodium atom of both **1**·$2NaEt_3BH$ and **1**·$NaEt_3BH$ is rather unusual. It bears some resemblence to that found in a zirconium complex containing a phorphyrinogen ligand and NaH, namely $[\{(\eta^5\text{-}\eta^1\text{-}\eta^1\text{-}\eta^1\text{-}Et_8N)Zr(CH_2CH_3)\}_2(\mu\text{-}NaH)_2$.[21] In this complex, the sodium atom is σ-bonded to some nitrogen atoms and η^3 and η^2 bonded to carbon and nitrogen atoms of the pyrrole groups at distances the vary from 2.543(3) to 3.216(3) Å. Significantly shorter distances to sodium are found in species containing $Na(cryptate)^+$ ions; the Na−O, Na−N distances are 2.27−2.38 Å.[23] Short Na to ligand distances are also found in crown ether analogues[24] or nitrogen-containing phenolates such as $[NaOC_6H_4(2\text{-}CH_2NMe_2)]_6$.[25]

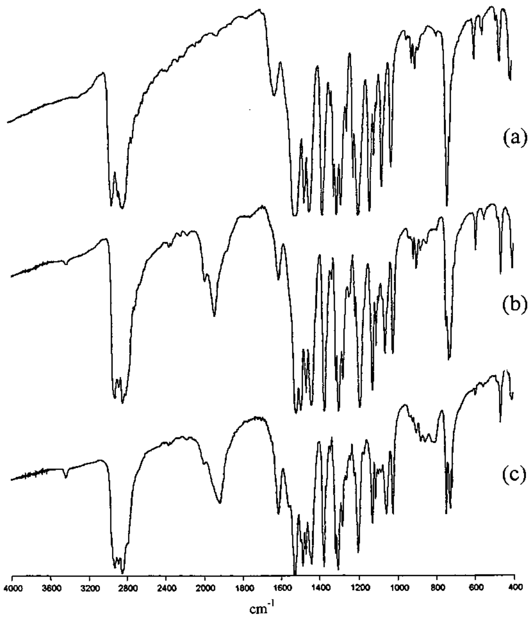

Figure 5. Infrared spectra of (a) **1**, (b) **1**·$NaEt_3BH$, and (c) **1**·$2NaEt_3BH$. See the Experimental Section for the precise wavenumbers.

It is remarkable the Nb−Nb distances of 2.2064(3) and 2.2187(7) Å for **1**·$2NaEt_3BH$ and **1**·$NaEt_3BH$ are essentially the same as that of **1**, which is 2.2035(9) Å. The Nb−N distances are also similar for all three compounds.

The crystallographic features of the Et_3BH^- anion resemble those found in a study of the structure of $(NaEt_3BH\cdot mesitylene)_4$.[26] Similarly, the infrared spectroscopic spectra, shown in Figure 5, agree with the solid state formulation. The strong bands centered at 1919 and 1948 cm^{-1} found in the spectra of **1**·$2NaEt_3BH$ and **1**·$NaEt_3BH$, respectively, correspond to B−H stretching vibrations. Those bands are known to be very sensitive to the B−H environment. For example, they are found at 1870, 1835, and 1950 cm^{-1} for $MHBEt_3$ compounds, M = Li (in KBr), Na (in cyclohexane), and K (in toluene), respectively.[27] For comparison, the ν_{BH} bands for $NaHBPr^n_3$ are at 1830 cm^{-1} in cyclohexane solution and 1975 cm^{-1} in diglyme solution; they are found at significantly higher energies for other coordinated RBH_3^- groups, e.g., 2320−2360 cm^{-1} for R = CN.[28] In coordination compounds containing bidentate BH_4^- anions, the B−H stretching vibrations can also vary; for example in $[Na(DME)][V(BH_4)_4]$ they are found at 2470, 2410, and 2090 cm^{-1}.[29] There are other small but significant differences in the IR spectra. The well-studied formamidinate ligands show bands at ca. 1588 cm^{-1} which have been assigned to ν_{CN}.[30] By analogy, the bands at 1513, 1526, and 1522 cm^{-1} for **1**, **1**·$2NaEt_3BH$, and **1**·$NaEt_3BH$, respectively, can be assigned to the corresponding C=N stretching vibrations of the hpp ligands.

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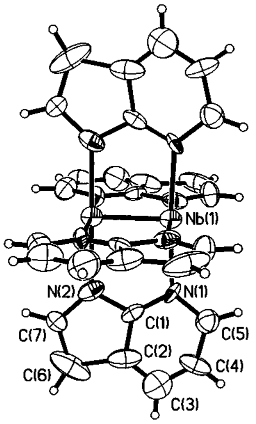

Figure 6. Thermal ellipsoid plot of the dinuclear unit in **2**.

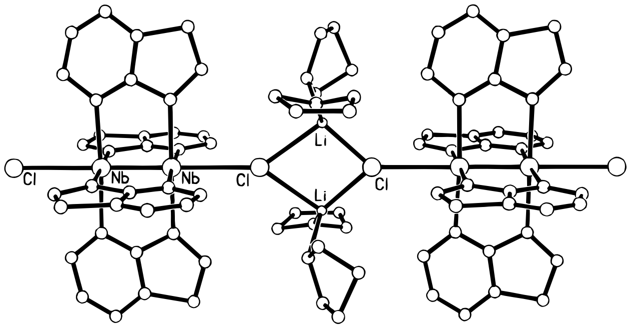

Figure 7. A drawing showing the packing along **c** in **2**.

The reaction of $NbCl_3(DME)$, Li(azin) and Li(nap) yields $Nb_2(azin)_4 \cdot 2LiCl \cdot 4THF$. The $Nb_2(azin)_4$ unit, shown in Figure 6 contains four bridging ligands, all related by a $\bar{4}$ axis located along the Nb−Nb bond. There are also two weak interactions to axially located chlorine atoms (Figure 7) which are interconnected by crystallographically disordered $Li(THF)_2$ units. The Nb−Nb distance of 2.278(2) Å is distinctly longer than the Nb−Nb distances in the hpp derivatives discussed earlier. This elongation is to be expected due to the geometrical characteristics of the azin ligand which imposes a wider bite and may be compared to the increase of 0.05 Å in going from $Mo_2(hpp)_4$ to $Mo_2(azin)_4$.[31] Also, in $Mo_2(acetate)_2(azin)_2$ the Mo−Mo distance is ca. 0.02 Å longer than that of $Mo_2(acetate)_4$. Similarly, the W−W distance in $W_2(azin)_4$ is the longest so far observed for a ligand of any type in W_2^{4+} species.[32] For $Cr_2(formamidinate)_4$, the Cr−Cr distances range from 1.8 to 1.9 Å; however, for $Cr_2(azin)_4(dmf)_2$ the Cr−Cr distance is 2.604 (2) Å.[33] In the latter, the significant elongation of the bond is due to the combined effect of the ligand bite and the effect of the axial ligation by the dmf molecules trans to the metal−metal bond. Since **2** also has weakly coordinated axial chloride ligands, it is actually surprising that the elongation of the Nb−Nb distance relative to that for $Nb_2(hpp)_4$ is only 0.08 Å.

Concluding Remarks. A systematic approach to the preparation of triply bonded diniobium compounds with the electronic configuration of the type $\sigma^2\pi^4$ have been designed. The isolation of the $Nb_2(hpp)_4$ molecule and its thermal stability, which allows the cocrystallization with the reactive $NaEt_3BH$, even after refluxing in THF, are remarkable observations. The very short Nb−Nb distances, even with ligands that tend to give long metal−metal distances, attest to the stability of the long sought Nb_2^{4+} unit. This work provides further evidence of the influence of the starting materials, solvent type, and reaction pathways in the formation of metal−metal bonds. It also shows that the Nb−Nb bonds are intrinsically stable once formed. We are currently pursuing the synthesis of the Ta analogues as well as similar compounds of the group 4 elements.

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Supporting Information Available: Tables of crystallographic data including diffractometer and refinement data, atomic coordinates, bond lengths, bond angles, and anisotropic displacement parameters (36 pages, print/PDF). An X-ray crystallographic file, in CIF format, is available through the Web only. See any current masthead page for ordering information and Web access instructions.

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