## *Experimental Section*

**1:** Method A: A solution of potassium diphenylmethyldipyrrolide (1.3 g, 3.4 mmol) in THF (100 mL) was treated under $N_2$ with $[SmI_2(thf)_2]$ (1.8 g, 3.4 mmol). The color immediately changed to dark purple-brown. Stirring was continued for 12 h after which the solution was filtered to eliminate a small amount of insoluble material. The filtrate was concentrated to 50 mL and layered with toluene (50 mL). After the mixture had been left to stand at room temperature for 24 h, large, red-brown crystals of **1** (1.3 g, 0.66 mmol, 78%) were obtained. Elemental analysis (%) calcd for $Sm_4C_{92}H_{80}O_2N_{10}$: C 56.40, H 4.12, N 7.15; found: C 56.35, H 4.08, N 7.09; IR (Nujol mull): $\tilde{\nu}$ = 3048 w, 1597 w, 1491 m, 1464 s, 1417 w, 1377 s, 1261 w, 1182 w, 1147 m, 1078 w, 1043 s, 985 w, 874 w, 798 m, 785 m, 756 s, 740 s, 696 s, 658 w, 640 m cm$^{-1}$. $\mu_{eff} = 6.55\,\mu_B$ per formula unit.

Method B: A solution of **2** (0.7 g, 0.25 mmol) in THF (50 mL) under $N_2$ was treated with KH (0.050 g, 1.2 mmol). A vigorous reaction with effervescence and a color change to purple-brown was immediately observed. The solution was allowed to stir for 30 min, followed by filtration to remove a small amount of insoluble material. After the mixture had been layered with toluene and left to stand at room temperature for three days, crystals of **1** were obtained (Yield 76%).

**2:** A solution of diphenylmethyldipyrrolide (1.0 g, 3.4 mmol) in THF (100 mL) was stirred with KH (0.3 g, 6.7 mmol) for 30 min at room temperature under argon. Subsequent addition of $[SmI_2(thf)_2]$ (1.8 g, 3.4 mmol) resulted in an immediate color change to dark brown. After stirring overnight the solution was filtered to eliminate a small amount of dark insoluble material, concentrated to 50 mL, and layered with toluene (25 mL). The mixture was allowed to stand for 24 h at room temperature, which resulted in the precipitation of large, dark red crystals of **2** (1.0 g, 0.22 mmol, 53% calculated relative to Sm). Elemental analysis (%) calcd for $Sm_8N_{14}O_7C_{206.5}H_{205.5}$: C 59.07, H 4.93, N 4.67; found: C 58.88, H 4.81, N 4.59; IR (Nujol mull): $\tilde{\nu}$ = 3049 w, 1595 w, 1489 m, 1464 s, 1419 w, 1377 s, 1263 w, 1234 w, 1184 w, 1151 m, 1076 m, 1038 s, 980 w, 964 w, 926 w, 891 m, 848 m, 789 m, 748 s, 704 s, 658 w, 634 m cm$^{-1}$. $\mu_{eff} = 9.14\,\mu_B$ per formula unit.

**3:** A solution of diphenylmethyldipyrrolide (1.1 g, 3.7 mmol) in THF (100 mL) was treated with KH (0.3 g, 7.5 mmol). Stirring was continued at room temperature for 30 min until all of the KH had been consumed. Subsequent addition of $[SmCl_3(thf)_3]$ (1.7 g, 3.7 mmol) resulted in the formation of a yellow suspension which was stirred for 1 h. Potassium metal (0.15 g, 3.8 mmol) was then added to the reaction mixture together with a catalytic amount of naphthalene (0.01 g, 78 μmol). Within minutes the color began to deepen to reddish-brown. After 4 h all the potassium had been consumed. The solution was filtered to remove a small amount of insoluble material. The dark brown filtrate was concentrated to 50 mL and layered with toluene (30 mL). After the mixture had been left to stand at room temperature for two days, large, dark brown crystals of **3** were obtained (1.2 g, 0.5 mmol, 58%). Elemental analysis (%) calcd for $C_{104}H_{104}N_8O_5KClSm_4$: C 56.21, H 4.72, N 5.04; found: C 56.11, H 4.66, N 4.97; IR (Nujol mull): $\tilde{\nu}$ = 3050 w, 1597 w, 1493 m, 1464 s, 1415 w, 1377 s, 1261 m, 1236 w, 1182 w, 1151 m, 1091 m, 1078 m, 1039 s, 980 w, 924 w, 879 w, 849 m, 795 m, 760 s, 700 s, 660 m, 636 m cm$^{-1}$. $\mu_{eff} = 7.02\,\mu_B$ per tetramer.

Crystal data for **1**: $Sm_4C_{92}H_{80}O_2N_{10}$, $M_r = 1059.32$, monoclinic, $C2/m$, $a = 21.542(6)$, $b = 19.232(6)$, $c = 12.437(3)$ Å, $\beta = 116.96(3)^\circ$, $V = 4593(2)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.405$ Mg m$^{-3}$; absorption coefficient 2.567 mm$^{-1}$, $F(000) = 1900$, reflections collected 17557, independent reflections 5668, GOF = 1.007, $R = 0.0546$, $wR^2 = 0.1696$.

Crystal data for **2**: $Sm_8N_{14}O_7C_{206.5}H_{205.5}$, $M_r = 4451.95$, monoclinic, $P2(1)/c$, $a = 18.186(2)$, $b = 23.349(2)$, $c = 43.492(4)$ Å, $\beta = 90.169(2)^\circ$, $V = 18467(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.601$ Mg m$^{-3}$; absorption coefficient 2.895 mm$^{-1}$, $F(000) = 8802$, reflections collected 145877, independent reflections 44562, GOF = 1.018, $R = 0.0553$, $wR^2 = 0.1086$.

Crystal data for **3**: $C_{104}H_{104}N_8O_5KClSm_4$, $M_r = 2221.90$, triclinic, $P\bar{1}$, $a = 13.462(1)$, $b = 17.534(2)$, $c = 20.970(2)$ Å, $\alpha = 110.006(1)$, $\beta = 100.343(2)$, $\gamma = 90.421(1)^\circ$, $V = 4562.8(7)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.617$ Mg m$^{-3}$; absorption coefficient 2.670 mm$^{-1}$, $F(000) = 2216$, reflections collected 35786, independent reflections 11862, GOF = 1.047, $R = 0.0385$, $wR^2 = 0.1010$.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-117425 (**1**), CCDC-117426 (**2**), CCDC-117427 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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# A Paramagnetic Diniobium Complex with a Very Short Nb–Nb Distance: Evidence for a Pseudo Nb–Nb Triple Bond?**

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Low-valent second- and third-row transition metals typically form significant and robust M–M bonds.[1, 2] Divalent Group 5 metals provide a puzzling exception. In principle, the d$^3$ electronic configuration makes them good candidates for the formation of triple bonds. Exceedingly short V≡V triple bonds were indeed observed in a few dinuclear V$^{II}$ complexes,[3] although these bonds seem to display the same paradoxical weakness[4] that was previously observed for quadruply bonded dichromium compounds.[5] Conversely, for the heavier Nb and Ta homologues no such information is

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available, since the few known di- and polynuclear $M^{II}$ compounds are para- or diamagnetic and have long M–M distances.[6–8] An $Nb^{II}$ complex of a three-center chelating pyrimidinate ligand[9] has a characteristic paddle-wheel shape and the shortest Nb–Nb distance (2.2035(9) Å). On the basis of its diamagnetism, the existence of an "intrinsically stable" Nb≡Nb bond was proposed.[10h] In an attempt to probe the strength of the Nb–Nb interaction, we attempted the preparation of another paddle-wheel diniobium complex. However, we selected the 7-azaindolyl anion as a ligand whose bite usually accommodates long intermetallic distances.[10]

Reaction of $[Nb_2Cl_5Li(tmeda)_3]$ (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with four equivalents of 7-azaindolyllithium in THF afforded a deep blue solution, from which dark blue crystals of $[(7\text{-azaindolyl})_4Nb_2\{(\mu\text{-Cl})Li(thf)_3\}_2]\cdot 2\,THF$ (**1**) were isolated in good yield. The complex is dinuclear, and the two Nb atoms are bridged by four 7-azaindolyl anions, which together with the $Nb_2$ unit, adopt the characteristic paddle-wheel configuration (Figure 1). However, in contrast to the previously reported pyrimidinate complex,[9] **1** bears two terminally bound LiCl units on the intermetallic axis, which provide the niobium atoms with a formal pyramidal coordination geometry. The Nb–Nb distance is only 0.065 Å longer than that of the pyrimidinate complex. The long Nb–Cl distance suggests that the coordination of the axial $(thf)_3LiCl$ moiety is rather weak.

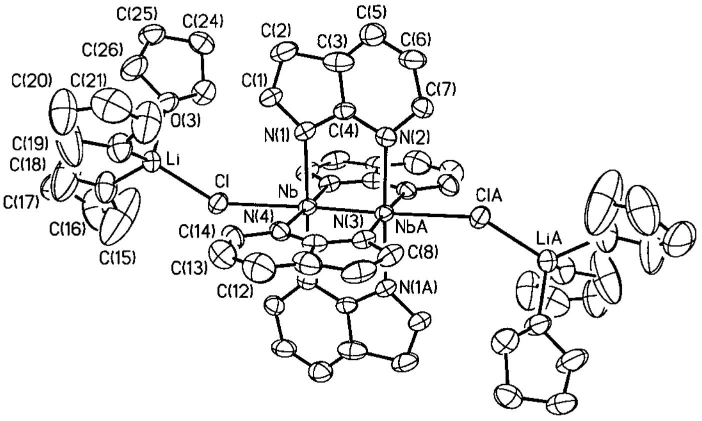

Figure 1. ORTEP drawing of **1** (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Nb–NbA 2.2683(13), Nb–Cl 2.733(2), Nb–N(1) 2.247(6), Nb–N(4) 2.266(6), Li–Cl 2.279(15); N(1)-Nb-N(4) 90.9(2), N(1)-Nb-N(3a) 88.3(2), N(1)-Nb-N(2a) 177.6(2), N(4)-Nb-N(3a) 177.4(2), N(1)-Nb-Cl 91.04(17), N(4)-Nb-Cl 88.37(18), Nb-Cl-Li 142.2(4), Nb(a)-Nb-Cl 177.56(6).

While this work was in progress, an $Nb^{II}$ complex of of the same ligand was reported.[10h] In spite of the close similarity of the $Nb_2$ cores, the two compounds display remarkable structural differences. Complex **1** is composed of discrete dimeric units, while the other is a linear polymer. On the basis of the sharpness of the NMR signals in acetone solution, it was concluded that the polymeric complex was diamagnetic, in line with the alleged existence of an "intrinsically stable" Nb–Nb triple bond.[10h] To our surprise, **1** is paramagnetic in the solid state and, to a small extent, in solution, in spite of having an Nb–Nb distance that is even slightly shorter than that of the linear polymeric complex. Measurement of the magnetic moment (SQUID magnetometer) as a function of temperature on a sample in a sealed quartz tube showed the presence of residual paramagnetism at 4.5 K ($0.6\,\mu_B\,mol^{-1}$; Figure 2). The magnetic moment increases sharply with increasing temperature, reaches a maximum of $1.8\,\mu_B$ at 200 K, and then remains roughly constant up to 300 K. This behavior is most unusual and could imply the presence of an antiferromagnetically coupled dinuclear system. However, the behavior does not conform to that expected for a $d^3-d^3$, $d^2-d^2$, or a $d^1-d^1$ antiferromagnetic system. A magnetization study at 3.0 K as a function of field strength (0–5.0 T) gave a linear response, and this suggests the absence of any ferromagnetic coupling. Even though a complete interpretation of the magnetic behavior is not possible at this stage, we can confidently conclude that **1** is paramagnetic and tends towards an $S=0$ ground state at low temperature. In THF solution, the NMR spectrum showed rather broad lines. A well-resolved spectrum was obtained only in acetone solution, in which, however, the color of the complex changed to dark orange-brown.

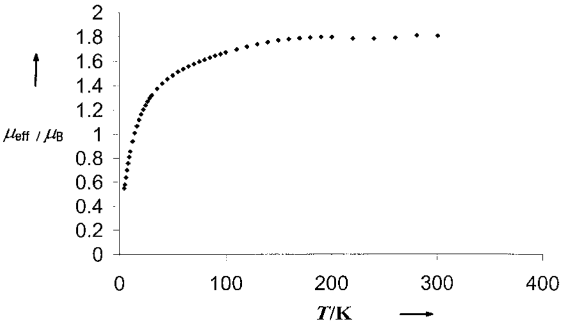

Figure 2. Magnetic moment of **1** as a function of temperature.

The paramagnetism of **1** may be inconsistent with the presence of a significant Nb≡Nb bond and is in sharp contrast to the short Nb–Nb distance. However, a geometry optimization calculation, starting with the atomic coordinates of both **1** and the pyrimidinate complex[9] and using a force field without electrostatic interactions, predicted Nb–Nb distances of 2.7 and 2.5 Å, respectively. The value calculated for the 7-azaindolyl complex is in good agreement with that observed for the "superlong" quadruple bond of the dichromium complex and other derivatives of the same ligand[10a] once the different dimensions of the metal atoms are taken into consideration. Hence the presence in both complexes of Nb–Nb distances in the range of 2.2 Å clearly indicates a substantial attractive force between the two metal centers. However, the complex nature of the paramagnetism of **1** indicates that other factors in addition to a Nb–Nb bond may contribute to the nature of the metal–metal interaction.

The density functional calculations (DFT) calculations on the singlet and triplet states yielded consistent results. The singlet state has a total energy value of which is only $1.8\,kcal\,mol^{-1}$ smaller than that of the triplet state. This small difference, together with the small HOMO–LUMO gap in the singlet state (0.19 eV), accounts for the paramagnetism in terms of a low-lying and thermally accessible triplet state. Both HOMO and LUMO are mainly lithium-centered molecular orbitals (Figure 3). The LUMO (−2.69 eV) is almost exclusively formed by an out-of-phase combination of one lithium 2s (87 %) and one chlorine $3p_z$ (10 %) atomic orbital. A similar situation was observed for the HOMO (−2.88 eV), which has large contributions from the other lithium 2s orbital (68 %) and a second chlorine $3s/3p_z$ hybrid (21 %). However, the two niobium $d_{z^2}$ atomic orbitals also participate in this orbital with an in-phase combination that provides an almost negligeable Nb–Nb σ-bond character (10 %). The next frontier orbitals HOMO − 1 (−3.04 eV) and HOMO − 2 (−3.11 eV) are nearly degenerate Nb–Nb-centered π orbitals and are respectively formed by the overlap of the $d_{xz}$ and $d_{yz}$ orbitals. The overall calculated Mulliken Nb–Nb bond order is 2.17. The fact that the HOMO and LUMO orbitals are mainly Li-centered suggests that the presence of LiCl on the intermetallic axis is responsible for the destabilization and virtual disappearance of the Nb–Nb σ bond and, ultimately, for the observed paramagnetism. The pyrimidinate complex with no LiCl on the axis is indeed diamagnetic.[9] The question arises whether the small variation in intermetallic distance between the two complexes is sufficient to cause such a remarkable difference in magnetic properties. Calculations on the same model compound of **1** but without LiCl and with Nb–Nb distances of 2.268 and 2.203 Å gave increased Nb–Nb bond orders of 2.97 and 3.02, respectively, and showed the presence of an MO with a clear Nb–Nb σ-bond character. This confirms that the presence of LiCl on the intermetallic axis is indeed the factor responsible for decreasing the formal Nb–Nb bond order and implies that the presumably weak coordination of LiCl is preferred to the formation of a presumably strong Nb–Nb σ bond. These observations remind us of the oddities and intricacies in metal–metal bonding, and on the basis of these findings, the alleged stability of Nb≡Nb bonds should perhaps be reconsidered.

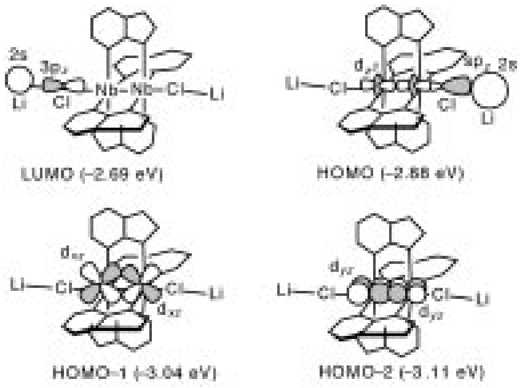

Figure 3. Molecular orbitals of **1** (DFT calculations).

## *Experimental Section*

A solution of 7-azaindole (1.3 g, 11.1 mmol) in diethyl ether (70 mL) was treated with a solution of methyllithium (8 mL, 1.4 M) at 0 °C. The mixture was stirred for 20 min. The solvent was removed in vacuo and replaced by THF (70 mL). $[Nb_2Cl_5Li(tmeda)_3]$ (2.0 g, 2.8 mmol)[7a] was added, and the mixture stirred for 12 h. After filtration and allowing the resulting solution to stand at −30 °C, blue crystals of **1** separated (1.4 g, 1.1 mmol, 39 %). Elemental analysis calcd (found) for $C_{60}H_{84}O_8N_8Nb_2Li_2Cl_2$: C 54.76 (54.33), H 6.43 (6.28), N 8.52 (8.45); IR (Nujol, NaCl) [$cm^{-1}$]: $\tilde{\nu}$ = 1591(s), 1556(s), 1417(m), 1334(s), 1199(s), 1147(s), 1113(s), 933(s), 912(s), 889(s), 798(s), 783(s), 757(s); $H^1$ NMR ([D$_8$]THF, 500 MHz, 23 °C): $\delta$ = 8.40 (brs, 1H), 7.93 (brm, 2H), 6.75 (brt, 1H), 6.11 (brs, 1H); $H^1$ NMR ([D$_6$]acetone, 500 MHz, 23 °C): $\delta$ = 8.20 (d), 7.93 (dd), 7.44 (d), 7.00 (dd), 6.45 (d).

Crystal data for **1** ($C_{60}H_{84}O_8N_8Nb_2Li_2Cl_2$): $M_r$ = 1315.95, monoclinic, space group $P2_1/n$, $a$ = 14.280(1), $b$ = 12.9435(9), $c$ = 18.307(1) Å, $\beta$ = 108.264(1)°, $V$ = 3213.4(4) Å$^3$, $Z$ = 2, $\rho_{calcd}$ = 1.360 g cm$^{-3}$, absorption coefficient 0.497 mm$^{-1}$, $F(000)$ = 1372, reflections collected 25 347, independent reflections 4187, GOF = 1.028, $R$ = 0.0572, $wR_2$ = 0.1730. The molecule was located on an inversion center. One of the two 7-azaindolyl ligands was "end-over-end" disordered. The disorder was modeled by refining the C(5) atom over the two disordered positions with a 60/40 site occupancy. The other disordered ring atoms could not be located, presumably because of close proximity to the primary contributing atom positions. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were treated as idealized contributions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-118120. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam. ac.uk).

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