

A New Type of Divalent Niobium Compound: The First Nb–Nb Triple Bond in a Tetragonal Lantern Environment

F. Albert Cotton,*[†] John H. Matonic,[†] and Carlos A. Murillo*^{‡,§}

Laboratory for Molecular Structure and Bonding and
Department of Chemistry, Texas A&M University
College Station, Texas 77843-3255
Department of Chemistry, University of Costa Rica
Ciudad Universitaria, Costa Rica

Received April 12, 1997

Divalent compounds of the heavier group 5 elements (Nb, Ta) can be classified as three types: mononuclear, polynuclear, and organometallic.¹ There are relatively few examples of each type. Paramagnetic, octahedral MX_2L_4 species with $\text{M} = \text{Nb}$ or Ta and $\text{X} = \text{Cl}$, $\text{L} = \text{PMe}_3$ or $1/2\text{dmpe}^2$ and niobium complexes with $\text{X} = \text{OAr}$ and $\text{L} = 1/2\text{dmpe}^3$ can be prepared by reduction of higher oxidation state metal chlorides or aryloxides with Na/Hg ; KC_8 works best for the reduction of $\text{NbCl}_4(\text{THF})_2$ in pyridine to prepare *trans*- $\text{NbCl}_2(\text{py})_4$.⁴

A few anionic species of the type $[\text{M}_2\text{X}_6(\text{THT})_3]^{2-}$ or $[\text{Nb}_2\text{Cl}_5(\text{THT})(\text{py})_3]^-$ are also known.⁵ In these face-sharing bioctahedral complexes (FSBO) there are formal triple bonds between the metal atoms, but the metal–metal distances are rather long, ca. 2.6 Å. There are multiple metal–metal bonds in other FSBO species,⁵ such as $\text{W}_2\text{Cl}_9^{3-}$, but these are always rather long, and there is no M–M distance within this structural type shorter than 2.43 Å. Species of this type are interesting and important in their own right, but in their chemistry and electronic structures they have significant differences from compounds where M–M multiple bonds are supported by ligands that do not form bridges at all (as in $\text{Mo}_2\text{Cl}_8^{4-}$) or form less intrusive bridges by linking pairs of coordinated atoms through three-atom chains (as in $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$). It is the latter class with which we are here concerned.

We have been interested in the preparation of compounds with a $\sigma^2\pi^4$ triple bond between Group 5 elements which should be shorter than those found in FSBO complexes, much as we previously showed for the vanadium(II) tetraformamidinate compound.⁶ Unfortunately, we have been unable to prepare the analogous $\text{M}_2(\text{formamidinato})_4$ by reacting $\text{NbCl}_2(\text{THF})_n$ solutions and lithium formamidinate salts, as was done for the vanadium analogs. We have found that for the heavier elements a reaction resulting in cleavage of the formamidinate ligand is prevalent.⁷ In this reaction (or reactions, depending on conditions) the cleavage is typically at a C–N bond. One or both of the fragments ArN , ArNC are often incorporated into the isolated products.

[†] Texas A&M University.

[‡] University of Costa Rica.

(1) See, for example: (a) Calderazzo, F.; Pampaloni, G.; Rocchi, L.; Strähle, J.; Wurst, K. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 102. (b) Calderazzo, F.; Englert, U.; Pampaloni, G.; Rocchi, L.; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1235.

(2) Luetkens, M. L., Jr.; Elcesser, W. L.; Huffman, J. C.; Sattelberger, A. P. *Inorg. Chem.* **1984**, *23*, 1718.

(3) (a) Coffindaffer, T. W.; Steffy, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 4742. (b) Coffindaffer, T. W.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1519.

(4) Araya, M. A.; Cotton, F. A.; Matonic, J. H.; Murillo, C. A. *Inorg. Chem.* **1995**, *34*, 5424.

(5) See for example: Cotton, F. A.; Shang, M. *Inorg. Chim. Acta* **1994**, *227*, 191 and references therein.

(6) Cotton, F. A.; Daniels, L. M.; Murillo, C. A. *Inorg. Chem.* **1993**, *32*, 2881.

(7) (a) Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1997**, *36*, 896. (b) Cotton, F. A.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Bull. Soc. Chim. Fr.* **1996**, *133*, 711.

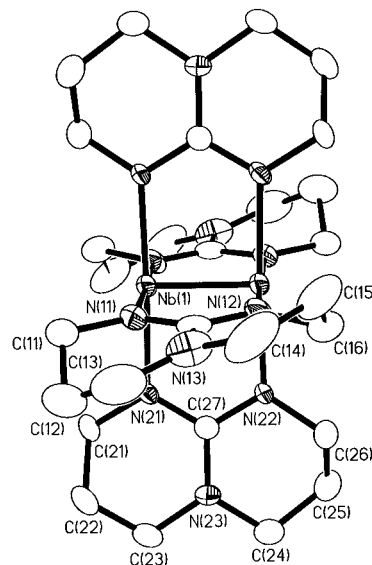
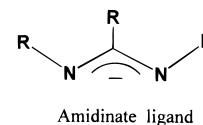
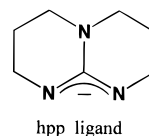


Figure 1. Thermal ellipsoid plot of **1**, atoms are drawn at the 50% probability level. Selected bond distances and angles: Nb(1)–Nb(1a)···2.2035(9) Å, Nb(1)–N(11)···2.201(4) Å, Nb(1)–N(21)···2.201(4) Å, Nb(1a)–N(12)···2.198(4) Å, N(11)–Nb(1)–N(21)···89.1(2)°, N(12a)–Nb(1)–N(11)···176.6(2)°, N(12)–C(17)–N(11)···119.0(5)°.

To avoid such cleavage, we decided to use a ligand which would be more resistant toward cleavage because of the support provided by other bonds within it. Such a ligand is the hpp anion, hpp = 1,3,4,6,7,8-hexahydropyrimido[1,2-a]pyrimidinate, which has already been shown to be effective in the stabilization of dinuclear units in complexes such as $\text{M}_2(\text{hpp})_4$, $\text{M} = \text{V}$, Cr , and Mo ⁸ and $\text{Ru}_2(\text{hpp})_4\text{Cl}_2$.⁹



We report here that a reaction of $\text{NbCl}_3(\text{DME})^{10a}$ with a mixture of Lihpp and KC_8 in THF produces green crystals of the diamagnetic complex $\text{Nb}_2(\text{hpp})_4$, **1**.^{10b} The structure¹¹ of the centrosymmetric complex is shown in Figure 1. There are four hpp ligands, each of which forms a bridge between the niobium atoms, resulting in a lantern-type complex, very similar to that found in the V, Cr, and Mo complexes. The metal–metal bond length of 2.2035(9) Å is by far the shortest known Nb–Nb distance, ca. 0.4 Å shorter than the corresponding distances found in FSBO complexes (*vide supra*). It is 0.27 Å longer than that found in the isostructural vanadium complex and is also 0.35 and 0.14 Å longer than the corresponding distances found in the quadruply bonded chromium and molybdenum analogs, respectively. Another interesting comparison is that between the congeneric pairs of compounds, V_2

(8) Cotton, F. A.; Timmons, D. J. *Polyhedron* **1997**, accepted.

(9) Bear, J. L.; Li, Y.; Han, B.; Kadish, K. M. *Inorg. Chem.* **1996**, *35*, 1395.

(10) (a) Pedersen, S. F. *Inorg. Syn.* **1992**, *29*, 119. (b) Preparation of **1**: $\text{NbCl}_3(\text{DME})$ (0.5 g, 1.7 mmol) was added to a mixture of Lihpp (0.622 g, 4.3 mmol) and KC_8 (0.27 g, 2.0 mmol) in THF (15 mL). The mixture was stirred for 3 h at room temperature and was filtered through Celite. The resulting THF solution was then layered with 20 mL of hexanes. Green crystals of **1** appeared after several days. The yield of the reaction was 0.10 g (16%) and has not yet been optimized. ¹H-NMR (ppm, C_6D_6): 3.09(t), 2.57(t), 1.53(q); elemental analysis gave satisfactory results.

(11) The compound crystallizes in space group $P1$ with the following unit cell parameters: $a = 8.437(1)$ Å, $b = 9.615(2)$ Å, $c = 10.268(1)$ Å, $\alpha = 87.26(3)^\circ$, $\beta = 70.530(5)^\circ$, $\gamma = 80.77(1)^\circ$, $V = 775.1(2)$ Å³, and $Z = 1$. Refinement converged for 1944 unique reflections and 190 parameters to give $R1 = 0.039$ and $wR2 = 0.089$ and a goodness-of-fit (Goof) = 1.081.

(hpp)₄/Nb₂(hpp)₄ and Cr₂(hpp)₄/Mo₂(hpp)₄. Within each of these pairs the increase in M–M distance is 0.28 and 0.23 Å, respectively. The reason for the somewhat greater increase for the pair from group 5 is not clear.

Another point of interest is the comparison of this structure with the one recently predicted (genuinely, before the compound was made) by density functional theory.¹² The calculated Nb–Nb distance was 2.225 Å for the closely related Nb₂(HNCHNH)₄ and the calculated Nb–N distances were 2.20 Å. The agreement with those just found (2.20 Å for Nb–Nb and 2.20 Å for Nb–N) is impressive.

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),¹³ 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 Re₂Cl₈²⁻, for comparison, the FSR is 0.87.

(12) Cotton, F. A.; Feng, X. *J. Am. Chem. Soc.* **1997**, *119*, 7514–7520.

(13) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Oxford University Press: Oxford, UK, 1993.

In conclusion, it is notable that the preparation of this compound is more than “just another M–M multiple bond”. It is the first step toward opening up what has been the most difficult and resistant area, namely the stabilization of such bonds in the earliest transition metal groups, 4 and 5. While the preparation of V≡V bonds was already accomplished several years ago, the question of whether congeneric compounds of niobium and tantalum could be obtained was far from answered, because while the heavier elements are more prone to M–M bond formation, they are much less prone to exist in very low oxidation states. We are now very optimistic that a tantalum analog to this niobium compound will be obtainable and also cautiously optimistic about the accessibility of similar compounds (with double bonds) in group 4.

Acknowledgment. We are grateful to the National Science Foundation for support of work done at Texas A&M University and the University of Costa Rica.

Supporting Information Available: Table of crystallographic data including final coordinates, bond lengths, bond angles, and anisotropic displacement parameters (7 pages). See any current masthead page for ordering and Internet access instructions.

JA9715152