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# Weak Carbon–Hydrogen–Nitrogen Interactions Affect the Heterocyclic Ligand Bonding Modes in Barium Complexes Containing $\eta^2$-Tetrazolato and $\eta^2$-Pentazolato Ligands

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Received December 27, 2004

Treatment of Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with 2 equiv of dimethylaminotetrazole or diisopropylaminotetrazole and 1 equiv of 18-crown-6 afforded Ba[CN$_4$(NMe$_2$)]$_2$(18-crown-6) (87%) and Ba[CN$_4$(NiPr$_2$)]$_2$-(18-crown-6) (79%) as colorless crystalline solids. Ba[CN$_4$(NMe$_2$)]$_2$-(18-crown-6) contains two 1,2-$\eta^2$-tetrazolato ligands and one $\eta^6$-18-crown-6 ligand. The molecular structure of Ba[CN$_4$(NiPr$_2$)]$_2$(18-crown-6) is similar to that of Ba[CN$_4$(NMe$_2$)]$_2$(18-crown-6), except that the tetrazolato ligands exhibit the isomeric 2,3-$\eta^2$-coordination mode and the tetrazolato ligand CN$_4$ cores are bent significantly toward the 18-crown-6 ligands. Molecular orbital calculations were carried out on the model complexes Ba(azolate)$_2$(18-crown-6) (azolate = 1,2-$\eta^2$-CHN$_4$, 2,3-$\eta^2$-CHN$_4$, and $\eta^2$-N$_5$) and demonstrate that the ligand coordination modes are influenced by intramolecular interactions between filled nitrogen orbitals on the azolato ligands and empty C–H $\sigma^*$ orbitals on the 18-crown-6 ligands.

The quest to prepare isolable metal complexes containing the pentazolato (N$_5$$^-$) ligand has received considerable attention in the past several years. Theoretical studies have demonstrated the high stability of N$_5$$^-$ and have predicted that it can coordinate to different metals with $\eta^2$- and $\eta^5$-coordination modes.[1,2] The N$_5$$^-$ ion has been detected in the gas phase as an electron-induced decomposition product of aryl pentazoles.[3] In addition, the synthesis of pentazolic acid, HN$_5$, has been claimed through ceric ammonium nitrate oxidation of an aryl pentazole.[4] Despite these advances, the isolation of a stable complex containing an N$_5$$^-$ ligand

remains to be demonstrated and certainly represents a formidable synthetic challenge. As an extension of our work on pyrazolato complexes,[5] we have been exploring metal complexes containing 1,2,4-triazolato and tetrazolato ligands.[6] Our idea is that the coordination chemistry of these nitrogen-rich heterocyclic ligands should be similar to that of the N$_5$$^-$ ligand and that our efforts should identify concepts, metals, and ligands that will help to stabilize the N$_5$$^-$ ligand.
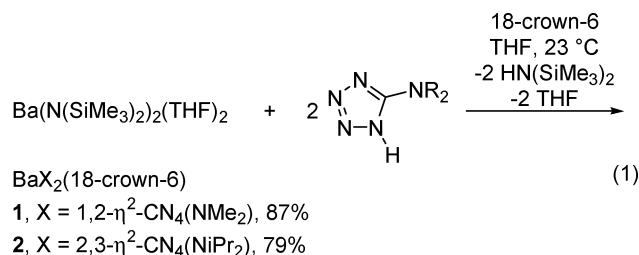
Herein, we describe the synthesis, structure, and molecular orbital calculations of barium complexes of the formula Ba-(azolate)$_2$(18-crown-6). With dimethylaminotetrazolate [CN$_4$-(NMe$_2$)], a complex containing 1,2-$\eta^2$-CN$_4$(NMe$_2$) ligands is obtained, whereas diisopropylaminotetrazolate [CN$_4$-(NiPr$_2$)] affords a complex with 2,3-$\eta^2$-CN$_4$(NiPr$_2$) ligands. Molecular orbital calculations demonstrate that these differing coordination modes can be attributed to weak C–H···N interactions between the tetrazolato and 18-crown-6 ligands. Ba(N$_5$)$_2$(18-crown-6) has been examined by molecular orbital calculations and exhibits a structure that is similar to that of the 2,3-$\eta^2$-tetrazolato complex. This work demonstrates the similarity between tetrazolato and pentazolato ligands and defines orbital interactions between C–H bonds and heteroatoms that can influence and stabilize coordination modes of ligands.

Treatment of Ba[N(SiMe$_3$)$_2$]$_2$(THF)$_2$[7] with 2 equiv of CN$_4$-(NMe$_2$)H or CN$_4$(NiPr$_2$)H and 1 equiv of 18-crown-6 afforded Ba[CN$_4$(NMe$_2$)]$_2$(18-crown-6) (**1**; 87%) and Ba-[CN$_4$(NiPr$_2$)]$_2$(18-crown-6) (**2**; 79%) as colorless crystalline solids (eq 1).

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(1) Recent leading references: (a) Carlqvist, P.; Ostmark, H.; Brinck, T. *J. Org. Chem.* **2004**, *69*, 3222. (b) Fau, S.; Wilson, K. J.; Bartlett, R. J. *J. Phys. Chem. A* **2002**, *106*, 4639.

(2) For example, see: (a) Burke, L. A.; Butler, R. N.; Stephens, J. C. *J. Chem. Soc., Perkin Trans.* **2001**, 1679. (b) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem.–Eur. J.* **2001**, *7*, 4155. (c) Zhao, J. F.; Li, N.; Li, Q. S. *Theor. Chem. Acc.* **2003**, *110*, 10.

(3) (a) Vij, A.; Pavlovich, J. G.; Wilson, W. W.; Christe, K. O. *Angew. Chem., Int. Ed.* **2002**, *41*, 3051. (b) Ostmark, H.; Wallin, S.; Brinck, T.; Carlqvist, P.; Claridge, R.; Hedlund, E.; Yudina, L. *Chem. Phys. Lett.* **2003**, *379*, 539.

(4) (a) Butler, R. N.; Stephens, J. C.; Burke, L. A. *Chem. Commun.* **2003**, 1016. (b) See also: Schroer, T.; Haiges, R.; Schneider, S.; Christe, K. O. *Chem. Commun.* **2005**, 1607.

(5) For leading references, see: (a) Sirimanne, C. T.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **2003**, *125*, 11152. (b) Gust, K. R.; Knox, J. E.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1591. (c) Perera, J. R.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1999**, *121*, 4536. (d) Pfeiffer, D.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2517. (e) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1998**, *37*, 3892. (f) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387.

(6) (a) Yélamos, C.; Gust, K. R.; Baboul, A. G.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Inorg. Chem.* **2001**, *40*, 6451. (b) Zheng, W.; Heeg, M. J.; Winter, C. H. *Angew. Chem., Int. Ed.* **2003**, *42*, 2761.

(7) Vaartstra, B. A.; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1991**, *30*, 121.

$$Ba(N(SiMe_3)_2)_2(THF)_2 \;+\; 2 \quad \underset{\substack{N-N\\H}}{\overset{\substack{N=N}}{\diagdown}}NR_2 \quad \xrightarrow[\substack{-2\,HN(SiMe_3)_2\\-2\,THF}]{\substack{18\text{-crown-}6\\THF,\,23\,°C}}$$

BaX$_2$(18-crown-6)　　　　　　　　　　　(1)

**1**, X = 1,2-$\eta^2$-CN$_4$(NMe$_2$), 87%

**2**, X = 2,3-$\eta^2$-CN$_4$(NiPr$_2$), 79%

The structures of **1** and **2** were assigned on the basis of the spectral and analytical data and also by X-ray crystallographic structure determinations.[8] ORTEP views of **1** and **2** are shown in Figure 1, along with selected bond lengths. Complex **1** contains two 1,2-$\eta^2$-tetrazolato ligands and one $\eta^6$-18-crown-6 ligand. The Ba−N bond lengths are 2.771(1) and 2.849(1) Å, which are different within the experimental uncertainty. The Ba−O bond distances are between 2.790 and 2.842 Å. The BaN$_2$/N$_2$N interplanar angles are 7.0(1)°, whereas the tetrazolato ligand CN$_4$ cores form angles of 6.4(1)° with the BaO$_6$ best plane. The molecular structure of **2** is similar to that of **1**, except that the tetrazolato ligands exhibit the isomeric 2,3-$\eta^2$-coordination mode and the CN$_4$ cores are bent significantly toward the 18-crown-6 ligands. The 2,3-$\eta^2$-tetrazolato ligands in **2** probably result from steric repulsion associated with the diisopropylamino groups. The Ba−N bond lengths are 2.869(8) and 2.885(8) Å, whereas the Ba−O bond distances range between 2.772(2) and 2.821(2) Å. The BaN$_2$/N$_2$N interplanar angles are 32.2(7) and 33.6(7)°, whereas the tetrazolato ligand CN$_4$ cores form angles of 26.9(1)° with the BaO$_6$ best plane.

To understand the bonding modes of the tetrazolato ligands, molecular orbital calculations were performed on the model complexes Ba(azolate)$_2$(18-crown-6) (**3**, azolate = 1,2-$\eta^2$-CHN$_4$; **4**, azolate = 2,3-$\eta^2$-CHN$_4$; **5**, azolate = $\eta^2$-N$_5$) using the Gaussian-03 programs.[9] The B3LYP hybrid density functional[10] was used along with the 6-311G(d,p) basis set[11] on all atoms except barium, where the MWB46 pseudo potential was used.[12] Optimization of **3** afforded asymmetric Ba−N distances of 2.782 and 2.878 Å, with BaN$_2$/N$_2$N interplanar angles of 1.7°. Similar optimization afforded Ba−N distances of 2.831 and 2.833 Å and BaN$_2$/N$_2$N interplanar angles of 18.4° for **4** and Ba−N distances of 2.864 and 2.867 Å and BaN$_2$/N$_2$N interplanar angles of 28.9° for **5**. Model **4** was 0.8 kcal/mol more stable than **3**. All three complexes possess intramolecular interactions between the azolate ligand N atoms and the 18-crown-6 C−H bonds. For natural bond order (NBO) analyses,[13] the complexes were divided into four fragments: the barium ion,
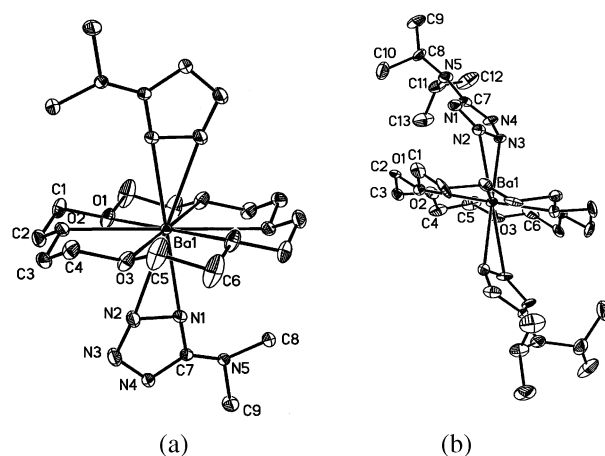


**Figure 1.** Selected bond lengths (Å) and angles (deg) for (a) **1**: Ba−N(1) 2.771(1), Ba−N(2) 2.849(1), Ba−O(1) 2.790(1), Ba−O(2) 2.842(1), Ba−O(3) 2.784(1); (b) **2**: Ba−N(2) 2.869(8), Ba−N(3) 2.885(8), Ba−O(1) 2.772(7), Ba−O(2) 2.821(2), Ba−O(3) 2.869(8).

the 18-crown-6 ligand, and the two azolato ligands. Stabilization was then calculated between the orbitals localized on the four fragments. Selected interactions are shown in Figure 2.[8] Complex **3** has a stabilization of 1.33 kcal/mol, which arises mostly from interactions of the 2- and 3-N atom lone pairs and $\pi$ orbitals mixing with the equatorial and axial C−H $\sigma^*$ orbital (Figure 2a). The asymmetric Ba−N distances arise from overlap of the 2-N atoms with an adjacent C−H bond. The majority of the 1.33 kcal/mol stabilization in **4** comes from occupied N atom p-type orbitals and lone pairs interacting with the C−H $\sigma^*$ orbitals on the crown ether (Figure 2b,c). The tetrazolato ligands bend toward the 18-crown-6 ligands to facilitate these interactions. The stabilization of **5**, 2.26 kcal/mol, is larger than that of **4**, as a result of the interaction of the N−N $\pi$ orbitals with the C−H $\sigma^*$ orbitals (Figure 2d). A further estimate of the strength of the intramolecular interactions was obtained by constraining the azolato ligands in **4** and **5** to a vertical $\eta^2$ orientation to minimize their interactions with the crown ether. This led to energy increases of 3.6 and 3.5 kcal/mol, respectively.

The crystal structures of **1** and **2** were reexamined to identify short C−H···N contacts. Complex **1** possesses many short C−H···N contacts in the range of 2.442−2.889 Å. In particular, N(2) has a short intramolecular contact to C(3)−H, which appears to be the origin of the longer Ba−N bond length to N(2). In **2**, N(1) and N(4) have numerous intramolecular and intermolecular C−H···N interactions that range between 2.422 and 2.862 Å. The sum of the van der Waals radii for N and H is about 2.7−3.0 Å,[14] which supports weak, attractive C−H···N interactions in **1** and **2**.

Herein, we have demonstrated that the coordination modes of the azolato ligands in **1−5** are determined by C−H···N interactions with the 18-crown-6 ligands, and we have used molecular orbital calculations to understand the orbital interactions and energies. The calculations can only address the intramolecular contacts, but the structures of **1** and **2**

(8) Synthetic procedures, analytical and spectroscopic data for **1** and **2**, and details of the calculations for **3**−**5** are contained in the Supporting Information.

(9) Frisch, M. J. *Gaussian 03*, revision A.1; Gaussian Inc.: Pittsburgh, PA, 2003.

(10) (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. D. *Phys. Rev. B* **1988**, *37*, 785.

(11) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(12) Kaupp, M.; Schleyer, P. V.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1991**, *94*, 1360.

(13) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(14) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Allinger, N. L.; Hirsch, J. A.; Miller, M. A.; Tyminski, I. J.; Van-Catledge, F. A. *J. Am. Chem. Soc.* **1968**, *90*, 1199.
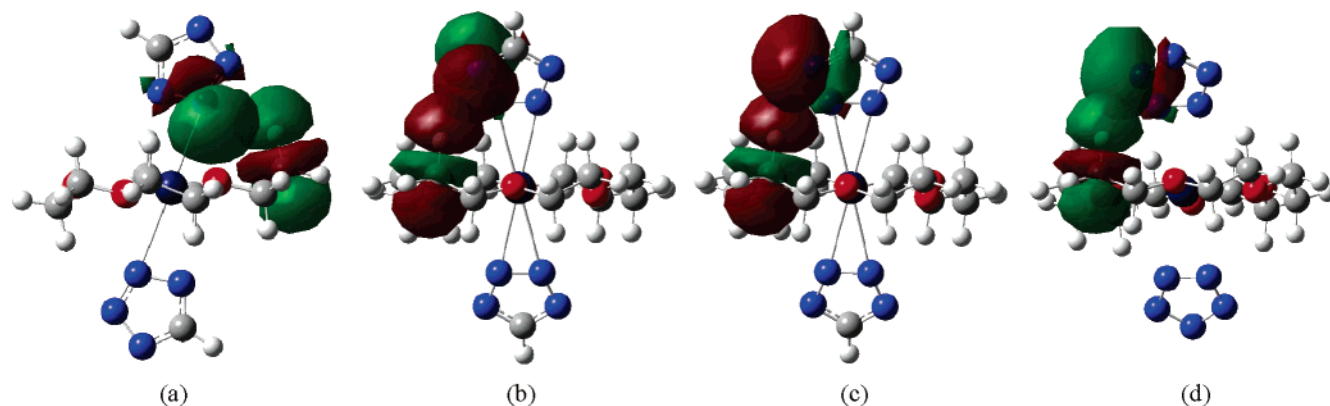
**Figure 2.** Selected orbital interactions from NBO analyses for (a) **3**, (b and c) **4**, and (c) **5**.

demonstrate that there are also intermolecular C−H···N close contacts in the solid state. The results provide insight into the weak interactions that are collectively described as crystal packing forces.[15] The C−H···N interactions provide additional thermodynamic stabilization, which should assist with efforts to isolate complexes containing $N_5^-$ ligands. For comparison, the calculated structures of $MN_5$ (M = Li, Na, K, Rb) are predicted to have all six atoms lying in the same plane and $\eta^2$ coordination of the $N_5^-$ ligand.[2c] Thus, in the absence of other ligands, the lowest energy bonding mode appears to be one where the metal ion lies in the plane of the heterocyclic core. Short C−H···E (E = N, O) interactions (also described as hydrogen bonding) are well-known in organic molecules and affect structures in many systems.[16] The effects of C−H···E interactions on metal complexes are much less documented. Intramolecular C−H···O interactions were proposed between the nitrato and 18-crown-6 ligands in $Hg(NO_3)_2$(18-crown-6) to account for the observed nitrato ligand bonding distortions.[17] The results of the present study imply that structural distortions in many reported metal complexes may originate from weak interactions between ligand heteroatoms and adjacent C−H bonds. For example, the acetylide ligands in $M(CCR)_2$(18-crown-6) (M = Ca, Sr, Ba) are bent significantly toward the 18-crown-6 ligands.[18] The bending may be due to attractive C−H···$C_\pi$ interactions between the acetylide $\pi$ system and adjacent 18-crown-6 carbon−hydrogen bonds, although other explanations are possible. Delineation of C−H···E interactions, as described herein, allows a deeper understanding of ligand coordination chemistry and the forces that lead to observed structures.

**Supporting Information Available:** Synthetic procedures and analytical and spectroscopic data for **1** and **2** and details of the molecular orbital calculations for **3**−**5**. X-ray crystallographic files for **1** and **2**, in CIF format, are also available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) For an overview, see: Martin, A.; Orpen, A. G. *J. Am. Chem. Soc.* **1996**, *118*, 1464.
(16) Selected recent examples: (a) Quinn, J. R.; Zimmerman, S. C. *Org. Lett.* **2004**, *6*, 1649. (b) Cappelli, A.; Giorgi, G.; Anzini, M.; Vomero, S.; Ristori, S.; Rossi, C.; Donati, A. *Chem.−Eur. J.* **2004**, *10*, 3177. (c) Freisinger, E.; Rother, I. B.; Luth, M. S.; Lippert, B. *Proc. Natl. Acad. Sci. U. S. A.* **2003**, *100*, 3748.
(17) Calleja, M.; Steed, J. W. *J. Chem. Crystallogr.* **2003**, *33*, 609.
(18) Green, D. C.; Englich, U.; Ruhlandt-Senge, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 354.