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The First Nitro-Substituted Heteroscorpionate Ligand

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The new dihydridobis(3-nitro-1,2,4-triazolyl)borate ligand, $[H_2B(tz^{NO2})_2]^-$, has been synthesized in dimethylacetamide solution, using 3-nitro-1,2,4-triazole and KBH_4 through careful temperature control, and characterized as its potassium salt. The zinc(II) and cadmium(II) complexes, $\{M[H_2B(tz^{NO2})_2]Cl(H_2O)_2\}$, have been prepared by metathesis of $[H_2B(tz^{NO2})_2]K$ with $ZnCl_2$ and $CdCl_2$, respectively. The complexes likely contain a metal core in which the ligand is coordinated to the metal ions in the κ^2-N,N′ or κ^4-N,N′,O,O′ fashion. A single-crystal structural characterization is reported for the potassium dihydrobis(3-nitro-1,2,4-triazolyl)borate. The potassium salt is polymeric and shows several K···N and K···O interactions.

Since the first report of Trofimenko,[1] poly(pyrazolyl)borates and related scorpionate ligands[2] have been extensively employed as anionic σ-donor ligands in a wide variety of metal complexes, and they have found wide application in coordination, organometallic, and bioinorganic chemistry.[3] Very little has been done on poly(pyrazolyl)borate systems bearing electron withdrawing substituents.[4] In 1995, Dias[5] and Venanzi[6] reported the synthesis of ligands containing highly electron withdrawing trifluoromethyl substituents, and over the past few years, Dias and others[7] reported the synthesis and/or uses of several poly(pyrazolyl)borates containing fluoroalkyl substituents. The electron withdrawing substituents in polyfluorinated ligands commonly improve the volatility, oxidation resistance, thermal stability, and solubility of metal complexes. Considering this success, we decided to investigate a new class of electron withdrawing substituted poly(azolyl)borate ligands, derived from nitro-substituted heterocyclic rings. In this Communication, we report the synthesis and characterization of an unprecedent heteroscorpionate ligand, dihydridobis(3-nitro-1,2,4-triazolyl)borate, $[H_2B(tz^{NO2})_2]^-$. To our knowledge, to date, no poly(azolyl)borates containing a $-NO_2$ function have been prepared, presumably due to difficulties in the synthesis of ligands having both a hydride and a nitro group. However, a bis(triazolyl)borate containing a $-NO_2$ substituent could be of interest due to its high coordinative flexibility from κ^2- to κ^4-N_2O_2 coordination ability.

This new ligand represents the 3-nitro-substituted analogues of one of the most widely used dihydridobis(1,2,4-triazolyl)borate[8] and dihydridobis(1,2,3-benzotriazolyl)borate ligands.[9]

The potassium salt of [dihydridobis(3-nitro-1,2,4-triazolyl)borate], **1**, has been synthesized by treating KBH_4 with 3-nitro-1,2,4-triazole in DMAC solvent.[10] Compound **1** is an air- and moisture-stable colorless solid; it is soluble in

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(10) Synthesis of $K[H_2B(tz^{NO2})_2]$, **1**, follows: KBH_4 (0.791 g, 14.7 mmol) and 3-nitro-1,2,4-triazole (5.367 g, 47.0 mmol) were mixed in *N,N*-dimethylacetammide (10 mL), and the mixture was heated slowly to 110 °C. After 2 h, the mixture was frozen at room temperature; chloroform was added to obtain a colorless precipitate, which was filtered and recrystallized from acetone/diethyl ether (1:3). Yield: 65%. Mp: 241−244 °C. ^{1}H NMR (CD_3OD, 293 K): δ 8.36 (s, 2H, 5C-*H*). ^{1}H NMR (D_2O, 293 K): δ 8.25 (s, 2H, 5C-*H*). ^{13}C NMR (CD_3OD, 293 K): 151.28 (s, 5-*C*H), 165.37 (s, 3-*C*NO$_2$). IR (Nujol, cm^{-1}): 3128w (CH); 2469m, 2440m (BH); 1670sbr, 1633sbr (C=C + C=N); 1538sbr ($\nu_{as}(NO_2)$); 1304s ($\nu_s(NO_2)$). ESIMS (CH_3OH): (−) 239 (100) $[H_2B(tz^{NO2})_2]^-$. ESIMS (CH_3OH): (+) 317 (100) $\{K_2[H_2B(tz^{NO2})_2]\}^+$, 595 (80) $\{K_3[H_2B(tz^{NO2})_2]_2\}^+$. Anal. Calcd for $C_4H_4BKN_8O_4$: C, 17.28; H, 1.45; N, 40.30. Found: C, 17.12; H, 1.47; N, 40.28.

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acetone, and in protic solvents as water, methanol, and ethanol. The reaction of **1** with KH in THF solution results in the reduction of the nitro to ammine groups and formation of an oligomer mixture of the composition $[H_2B(tz^{NH2})_2]_n$ species ($n = 2-4$) identified by mass spectrometry, in which the dimeric triazabole, $[H_2B(tz^{NH2})_2BH_2]$, is the major species.[11] From the interaction of 1 equiv of **1** with 1 equiv of zinc(II) chloride or cadmium(II) chloride, in acetone at room temperature, the complexes $\{Zn[H_2B(tz^{NO2})_2]Cl(H_2O)_2\}$, **2**, and $\{Cd[H_2B(tz^{NO2})_2]Cl(H_2O)_2\}$, **3**, have been obtained in high yield:

$$K[H_2B(tz^{NO2})_2] + MCl_2 \rightarrow M[H_2B(tz^{NO2})_2]Cl(H_2O)_2 + KCl$$

$$\mathbf{2}, M = Zn(II); \mathbf{3}, M = Cd(II)$$

The same compounds have been obtained even when an excess of ligand **1** was employed. Both the colorless compounds **2** and **3** are soluble in methanol and in water solution and air stable even as in solutions. This property offers the possibility of applications in bioinorganic study.[12]

Ligand **1** and complexes **2** and **3** have been isolated in high yield and characterized by ^1H and ^{13}C NMR and FT-IR spectroscopy, electrospray ionization mass spectroscopy (ESI-MS), and elemental analysis.

In the infrared spectrum of **1**, the B−H stretching appears at 2469 and 2440 cm^{-1}, and the asymmetric and symmetric stretching of $-NO_2$ group appears at 1538 and 1304 cm^{-1}. The asymmetric and symmetric stretchings of the $-NO_2$ group appear at 1520 and 1310 cm^{-1} in the neutral nitrotriazole. These bands are only slightly shifted upon coordination, consistent with a weak interaction in the solid state between the nitro group and the zinc or cadmium metal center. The ^{13}C chemical shifts of 5-*C*H and 3-*C*NO$_2$ carbons (in CD_3OD solution) at δ 151.28 and 165.37, respectively, are close to those of the starting triazole (δ 146.20 and 163.20 in DMSO-d_6).

Electrospray ionization mass spectroscopy was used to probe the existence of aggregates of the scorpionate ligand **1** with zinc(II) and cadmium(II) in solution. Both positive-ion and negative-ion spectra of ligand **1** and the related derivatives **2** and **3**, dissolved in methanol, were recorded at low fragmentor voltage; in these conditions the dissociation is minimal, and a high proportion of the analyte is transported to the mass spectrometer as the intact molecular species. The positive-ion spectrum of ligand **1** and compounds **2** and **3** in methanol is dominated by a fragment at m/z 317 (100%) attributable to the aggregation of two potassium ions to the ligand.

The ligand ion (m/z 239, 100%) dominates the negative-ion ESI-MS spectra of **1**−**3**. In the positive-ion spectrum of compounds **2** and **3**, some further peaks due to the aggregates of Zn(II) and Cd(II) with scorpionate ligand, chloride, and water have also been detected and identified by the characteristic isotope distribution patterns. For the cadmium derivative **3**, the ^{113}Cd NMR spectrum in water solution has been obtained and a unique absorption has been detected which falls at 46.15 ppm, in the typical region of five- or six-coordinate cadmium species.[13]

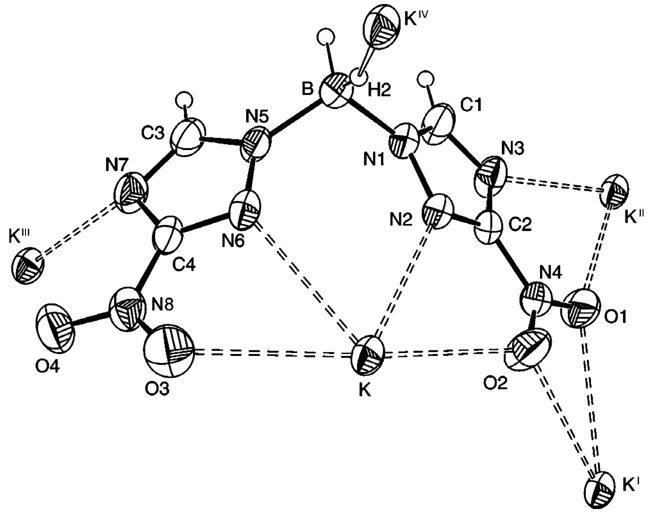

Figure 1. Structure of the anion, bonded to the potassium ions. Selected bond distances (Å) and angles (deg) for $[H_2B(tz^{NO2})_2]^-$ anion: N(4)−O(1) 1.217(3), N(4)−O(2) 1.215(3), N(8)−O(3) 1.224(3), N(8)−O(4) 1.226(3), B−N(1) 1.567(4), B−N(5) 1.559(3), N(1)−C(1) 1.330(4), N(1)−N(2) 1.357(3), N(2)−C(2) 1.319(3), C(2)−N(3) 1.325(3), C(1)−N(3) 1.331(4), C(2)−N(4) 1.449(5), N(5)−N(6) 1.356(3), N(5)−C(3) 1.339(3), C(3)−N(7) 1.325(3), C(4)−N(6) 1.313(3), C(4)−N(7) 1.339(3), C(4)−N(8) 1.445(3); N(1)−B−N(5) 109.1(5), O(1)−N(4)−O(2) 123.5(2), O(1)−N(4)−C(2) 118.3(2), O(2)−N(4)−C(2) 118.1(2), O(3)−N(8)−O(4) 124.7(2), O(3)−N(8)−C(4) 117.9(2), O(4)−N(8)−C(4) 117.4(2).

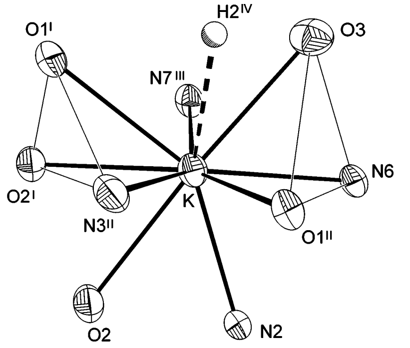

Figure 2. Potassium coordination polyhedron. Selected bond lengths (Å): K−O(2) 2.970(3), K−N(2) 2.912(2), K−N(6) 2.979(2), K−O(3) 3.162(3), K−O(1)^I 3.100(2), K−O(2)^I 3.049(3), K−O(1)^{II} 2.873(3), K−N(3)^{II} 2.882(2), K−N(7)^{III} 2.923(2), K−H(2)^{IV} 3.03(3). (Symmetry codes: I, $1 - x$, $-y$, $-z$; II, $0.5 - x$, $0.5 + y$, $-z$; III, $1 - x$, $-y$, $1 - z$, IV, $-0.5 + x$, $0.5 - y$, z.)

The crystal and molecular structure of $[H_2B(tz^{NO2})_2]K$ has been determined by X-ray analysis.[14] Figure 1 shows an ORTEP view of the anion coordinated to the potassium ions. The resulting coordination polyhedron is a rather irregular tricapped trigonal prism, distorted for the insertion of the agostic B−H···K bond (shown as dotted line but not considered in the coordination polyhedron) (Figure 2).

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(14) Crystal data for $C_4H_4N_8O_4BK$ follow: $M = 278.04$, monoclinic, space group $P2_1/a$ (No. 14), $a = 9.931(2)$ Å, $b = 10.952(3)$ Å, $c = 10.448(2)$ Å, $\beta = 106.77(2)°$, $V = 1088.0(4)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_c = 1.697$ g cm^{-3}, μ(Mo Kα) = 0.51 mm^{-1}, 2600 reflections measured, 2415 unique reflections. The final R_1 value was 0.0449 and $R_w(F^2)$ was 0.1197 for $I \geq 2\sigma I$. The corresponding values for all data are $R_1 = 0.456$ and $R_w(F^2) = 0.1197$.

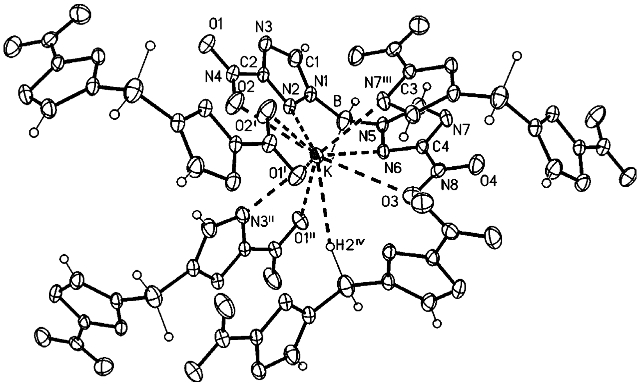

Figure 3. Network of the ligands around potassium ion.

Similar agostic interactions have been reported for related tetrazolyl derivative $[H_2B(CHN_4)_2]K$.[15] The two nitro functionalities of the ligand are coplanar to the respective triazolyl ring, while the latter is inclined 64.4(1)° with respect to the other.

Due to the sharing of the ligand between different cationic units, the whole structure is formed by the three-dimensional net-work presented in Figure 3.

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Supporting Information Available: Synthetic procedures for compounds **2** and **3** and crystallographic data in CIF format for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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