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# Complexes of the [K(18-Crown-6)]$^+$ Fragment with Bis(tetrazolyl)borate Ligands: Unexpected Boron−Nitrogen Bond Isomerism and Associated Enforcement of $\kappa^3$-N,N′,H-Ligand Chelation

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The syntheses and solid-state structures of $K(BH_2(RCN_4)_2)$-(18-crown-6) (R = H, Me, $NMe_2$, and $NiPr_2$) are described. Complexes where R = H and Me have B−N bonds to $N^1$ of the tetrazolyl groups and form one-dimensional polymers, whereas those with R = $NMe_2$ and $NiPr_2$ possess isomeric B−N bonds to $N^2$ of the tetrazolyl moieties and adopt chelating $\kappa^3$-N,N′,H-coordination modes to the potassium ion.

Metal tetrazolate complexes have attracted attention for application as energetic materials because of their positive heats of formation, large volumes of $N_2$ that are generated upon decomposition, and the potential for good thermal stabilities.[1,2] In principle, the tetrazolate ligand (**1**) can release 2 equiv of $N_2$ per negative charge, while tetrazolate ligands containing nitrogen-based substituents (**2**) on the core carbon atom can evolve larger amounts of $N_2$ and other gases per negative charge (Chart 1).[2] Poly(azolyl)borates based on a variety of pyrazoles and triazoles have found broad application as ligands.[3−6] However, only a few reports have described metal complexes containing the bis(5-H-tetrazolyl)-borate ligand (**3a**, R = H).[7] Isomeric **3b** remains unknown. As depicted in Chart 1, **3a** and **3b** can liberate up to 4 equiv of $N_2$ per negative charge. Hence, **3a** and **3b** represent interesting candidates for the construction of new energetic metal complexes.

The bis(5-H-tetrazolyl)borate ligand has exclusively served as a bridging ligand between metal centers[7] rather than adopting the chelating $\kappa^3$-N,N′,H-coordination mode that has been commonly observed in bis(pyrazolyl)borate ligands.[3,4] The reluctance of the bis(5-H-tetrazolyl)borate ligand to coordinate with the $\kappa^3$-N,N′,H mode was ascribed to the higher basicity of $N^4$ compared to $N^2$ (**3a**; Chart 1).[7c] Our laboratory is interested in the development of tetrazole-based metal complexes that might serve as new classes of energetic materials.[2i,8] Herein, we report the synthesis, structure, and properties of

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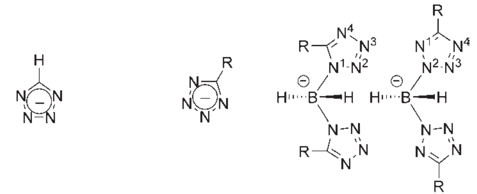
**Chart 1.** Equivalents of $N_2$ per Negative Charge for Various Nitrogen Ligands



**1**, tetrazolate
2 $N_2$/negative charge

**2**, R = nitrogen-based
>2 $N_2$/negative charge

**3a,b**, bis(tetrazolyl)borate
4 $N_2$/negative charge

the complexes $K(BH_2(RCN_4)_2)$(18-crown-6), where R = H, Me, $NMe_2$, and $NiPr_2$. Complexes with R = H and Me form ligands of the general structure **3a** and adopt bridging coordination modes, consistent with previous reports of the bis(5-H-tetrazolyl)borate ligand.[7] By contrast, complexes with R = $NMe_2$ and $NiPr_2$ form isomeric B−N bonds to $N^2$ of the tetrazolyl rings (**3b**; Chart 1). Isomeric ligands **3b** can only adopt the chelating $\kappa^3$-$N^3$,$N^{3'}$,H-coordination mode to the potassium ion because coordination of $N^1$ and $N^4$ to adjacent metal centers is blocked sterically by the carbon atom substituents.

Complexes **4**−**7** were prepared according to eq 1.[9] Solid mixtures of $KBH_4$ and two equivalents of each tetrazole were heated at 100−130 °C until gas evolution ceased, and then the resultant white solids were treated with 1 equiv of 18-crown-6 in tetrahydrofuran to afford $K(BH_2(HCN_4)_2)$(18-crown-6) (**4**, 97%), $K(BH_2(MeCN_4)_2)$(18-crown-6)•$(C_7H_8)_{0.5}$ (**5**, 64%), $K(BH_2(Me_2NCN_4)_2)$(18-crown-6) (**6**, 77%), and $K(BH_2(iPr_2NCN_4)_2)$(18-crown-6) (**7**, 80%) as colorless crystalline solids. Despite many attempts with 3:1 or 4:1 tetrazole to $KBH_4$ stoichiometry, it was not possible to prepare complexes containing tris(tetrazolyl)borate or tetrakis(tetrazolyl)borate ligands by this thermolysis route, and only **4**-**7** were isolated. This observation is similar to the findings by Janiak.[7] The structures and compositions of **4**-**7** were established by spectroscopic and analytical methods, and by X-ray crystal structure determinations. Singlets were observed in $^1H$ NMR spectra of **4**-**6** for the H, Me, and $NMe_2$ substituents of the tetrazolyl groups, and a septet and a doublet were observed for the $NiPr_2$ groups in **7**. In addition, the 18-crown-6 $^1H$ NMR resonances in **4**-**7** were observed as sharp singlets, suggesting dynamic processes in solution at room temperature that lead to exchange of the diastereotopic methylene hydrogen atoms. The $^{11}B$ NMR resonances for **4**-**7** appeared as broad singlets between −7.9 and −12.52 ppm, relative to $BF_3$•$Et_2O$ as the external standard. $^{11}B$ NMR chemical shifts of poly(pyrazolyl)borates and poly(triazolyl)borates usually appear upfield of $BF_3$•$Et_2O$ in the same region as **4**-**7**.[10] The infrared spectra of **4**-**7** exhibited absorptions attributable to boron−hydrogen stretches between 2483 and 2409 $cm^{-1}$, which are similar to values in complexes containing bis(pyrazolyl)borate ligands.[11]

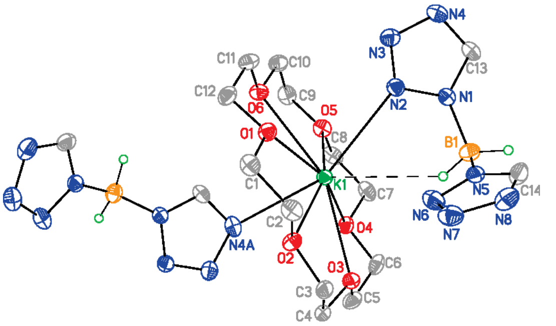
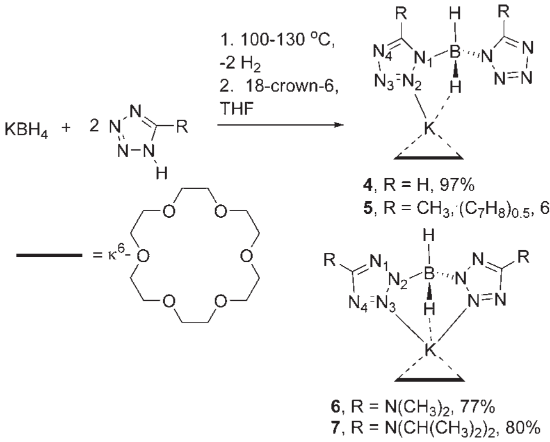


**Figure 1.** Perspective view of **4** with probability ellipsoids at the 50% level, showing a portion of the polymeric chain. Selected interatomic distances (Å) and angles (deg): K−N2 3.040(1), K−N4′ 2.928(1), K−O1 2.803(1), K−O2 2.857(1), K−O3 2.840(1), K−O4 2.909(1), K−O5 2.897(1), K−O6 2.955(1), B−N1 1.568(2), B−N5 1.568(2), K−B1 3.875(2), K−H 3.17(2); N1−B−N5 108.0(1), K−N2−N1 117.38(9), K−N2−N3 135.3(1), B−N1−N2 123.2(1), B−N5−N6 122.6(1), N2−K−N4′ 156.16(4).



(1)

Complex **4** exists as a one-dimensional polymer that forms through bridging of N2 and N4 between potassium ions (Figure 1). The K−N distances are 3.040(1) and 2.928(1) Å, respectively. The nitrogen atoms of the other tetrazolyl group are not coordinated to the potassium ion. The B−N bonds in **4** are to N1 and N5, which correspond to the $N^1$ atoms of the tetrazolyl groups (**3a**; Chart 1) and are consistent with previous structures of complexes containing this ligand.[7] One of the boron-bound hydrogen atoms is directed toward the potassium ion, with K−H and K−B distances of 3.17(2) and 3.875(2) Å, respectively. Thus, the bis(5-H-tetrazolyl)borate ligand in **4** adopts a $\kappa^2$-N2,H-coordination mode to each potassium ion and further has a $\mu_2$-N2,N4-bridging coordination mode between potassium ions. This is a new coordination mode for the bis(5-H-tetrazolyl)borate ligand.[7] The K−O bond distances range between 2.803(1) and 2.955(1) Å. The molecular structure of **5** exists as a one-dimensional polymer that is formed through K−N bonds to $N^2$ and $N^{3'}$ of the bis(methyltetrazolyl)borate ligands. Unlike **4**, both tetrazolyl rings have K−N bonds. The K−B and boron-bound K−H distances are 4.056(1) and 3.34(2) Å, respectively, which are longer than those in **4**. As in **4**, the B−N bonds in **5** are to the $N^1$ atoms of the methyltetrazolyl moieties.

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(9) Experimental procedures and spectral and analytical data are containing in the Supporting Information. ***Caution!*** *The compounds described herein have high nitrogen contents and are potentially energetic. Safety precautions such as a face shields, a leather apron and gloves, and hearing protection should be employed.*

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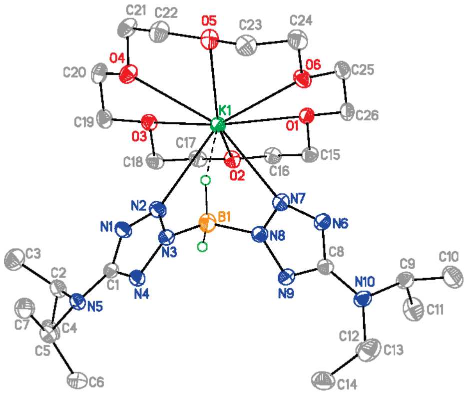

**Figure 2.** Perspective view of **7** with probability ellipsoids at the 50% level. Selected interatomic distances (Å) and angles (deg): K−N2 2.965(1), K−N7 2.990(1), K−O1 2.968(1), K−O2 2.837(1), K−O3 2.909(1), K−O4 2.893(1), K−O5 2.897(1), K−O6 2.887(1), B−N3 1.566(2), B−N8 1.569(2), K−B 3.719(2), K−H 3.08(2); N2−K−N7 71.29(4), K−N2−N3 116.85(9), K−N2−N1 135.27(9), K−N7−N8 114.92(9), K−N7−N6 134.88(9), B−N3−N2 121.7(1), B−N8−N7 122.2(1).

Complex **7** adopts a molecular structure that consists of isolated monomeric complexes, with $\kappa^3$-N2,N7,H coordination of the bis[(diisopropylamino)tetrazolyl]borate ligand to the potassium ion (Figure 2). In addition, the B−N bonds in **7** are to N3 and N8, which correspond to the N$^2$ atoms of the tetrazolyl groups (**3b**; Chart 1). By contrast, the B−N bonds in **4**, **5**, and previous structures containing the bis(5-H-tetrazolyl)borate ligand[7] are to the N$^1$ atoms of the tetrazolyl groups. The K−N distances are 2.965(1) and 2.990(1) Å. The K−B and boron-bound K−H distances are 3.719(2) and 3.08(2) Å, respectively, which are shorter than the values in **4** and **5**. The K−O distances in **7** range from 2.837(1) to 2.968(1) Å and are similar to those in **4**. Complex **6** has a monomeric structure similar to that of **7** with $\kappa^3$-N$^3$,N$^{3\prime}$,H coordination of the bis[(dimethylamino)tetrazolyl]borate ligand. The K−B and boron-bound K−H distances are 3.464(3) and 2.87(3) Å, respectively, which are the shortest among the series **4**−**7**. Like in **7**, the B−N bonds of **6** are formed to N$^2$ of each (dimethylamino)tetrazolyl group (**3b**; Chart 1).

The K−H distances and K−N$^2$−N$^1$ or K−N$^3$−N$^2$ angles increase in the order **6** [2.87(3) Å; 103.5(1) and 107.5(1)°] < **7** [3.08(2) Å; 114.92(9) and 116.85(9)°] < **4** [3.17(2) Å; 117.38(9)°] < **5** [3.34(2) Å; 124.06(6)°], whereas the B−N−N angles fall between 121.7 and 123.5°. Clearly, the K−N bonds act as the "hinge" for the B−H interaction,[3,4] which is probably facilitated by the ionic bonding between the potassium ion and the nitrogen atoms. The K−H distances in **4**−**7** are longer than those in K(BH$_4$)(18-crown-6) [avg = 2.74(8) Å],[12] but the value in **6** is similar to that in K(BH$_2$(HCN$_4$)$_2$) [2.89(3) Å].[7d]

Complexes **4**−**7** melt without decomposition within 2 °C ranges between 111 and 158 °C. Samples of **4**−**7** (~5 mg) did not explode upon being struck hard with a hammer or upon scraping across 150 grit sandpaper with a spatula. Placing ~10 mg samples of **4**−**7** into a Bunsen burner flame led to rapid burning with intense light and little smoke. Passing sparks from a Tesla coil through ~5 mg samples of **4**−**7** on an aluminum plate did not lead to explosions or burning. These experiments suggest that **4**−**7** are not primary energetic materials, although they contain considerable energy, as evidenced by rapid burning. The onset of thermal decomposition of **4**−**7** started between 210 and 220 °C, as determined by thermogravimetric analysis (TGA) under a nitrogen atmosphere between 50 and 700 °C with a heating rate of 5 °C/min. The weight loss events for **4**−**7** appear to involve 18-crown-6 evolution and bis(tetrazolyl)borate ligand decomposition, as judged by residual weights upon reaching 450 °C.

A major discovery herein is the isomeric B−N bonds that form in **6** and **7**, compared to those found in **4** and **5** and in previous reports of complexes containing bis(5-H-tetrazolyl)borate ligands.[7] The isomeric B−N bond positions in **6** and **7** probably originate from unfavorable steric interactions at the tetrazole N$^1$ atoms during hydrogen evolution and B−N bond formation, compared to the more favorable situation at N$^2$. The tetrazolyl ring carbon atom substituents in **6** and **7** sterically block coordination of the N$^1$ and N$^4$ atoms to the potassium ions, which leaves the N$^3$ positions as the only donor atoms and affords the $\kappa^3$-N$^3$,N$^{3\prime}$,H-coordination mode. As a result, the ligands in **6** and **7** are likely to coordinate to many different metal ions with the chelating $\kappa^3$-N$^3$,N$^{3\prime}$,H-coordination mode. The coordination chemistry of the new isomeric bis(tetrazolyl)borate ligands should therefore resemble that of the extensively studied bis(pyrazolyl)borate and other poly(azolyl)borate ligands. Because bis(tetrazolyl)borate and tetrazolate ligands have the same charge, use of ligands of the general formula **3a** and **3b** may lead to metal complexes that can be used to develop new classes of high-energy-density materials. In this vein, a recent theoretical study has suggested that metal salts of BH(N$_5$)$_3^-$ should be promising high-energy-density materials if a synthetic route becomes available.[13] Energetic silver and azolium salts of bis(1,2,4-triazolyl)borate and tris(1,2,4-triazolyl)borate have been reported.[14] Finally, metal complexes containing the bis(3-nitro-1,2,4-triazolyl)borate ligand have been structurally characterized.[15]

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**Supporting Information Available:** X-ray crystallographic data in CIF format, synthetic procedures, and analytical and spectroscopic data for **4**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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