

Supporting Information for:

Complexes of the [K(18-Crown-6)]⁺ Fragment with Bis(tetrazolyl)borate Ligands: Unexpected Boron-Nitrogen Bond Isomerism and Associated Enforcement of κ^3 -N,N',H-Ligand Chelation**

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Experimental Details

Complexes **4-7** are air stable and all reactions were performed under ambient conditions unless stated otherwise. A 3 wt. % solution of 1-*H*-tetrazole in acetonitrile was purchased from Aldrich Chemical Company. The acetonitrile was removed under reduced pressure, and the 1-*H*-tetrazole was used as a solid. 5-Methyl-1-*H*-tetrazole was purchased from Aldrich Chemical Company and was used without further purification. 5-Dimethylamino-1-*H*-tetrazole and 5-diisopropylamino-1-*H*-tetrazole were prepared as described in literature procedures.^{1,2} ¹H, ¹³C{¹H} and ¹¹B NMR spectra were obtained at 500, 125, and 160 MHz, respectively. Chemical shifts for ¹¹B NMR were measured in ppm using BF₃·Et₂O as the external reference. Infrared spectra were obtained using Nujol as the medium. Elemental analyses were performed by Midwest Microlab, Indianapolis, IN. Melting points were obtained on a Thermo Scientific Mel-Temp 3.0 melting point apparatus and are uncorrected. Thermogravimetric analyses were conducted on a Perkin-Elmer Pyris 1 TGA system between 50 and 700 °C for **4-7**, using nitrogen as the flow gas with a heating rate of 5 °C /min. **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. In addition, only experienced personnel should be allowed to carry out the syntheses.**

General procedure for the preparation of 4-7. A 100-mL Schlenk flask, equipped with a stir bar and reflux condenser, was charged with potassium borohydride and two equivalents of the tetrazole as a fine powder. The flask was purged with argon to avoid reaction of potassium borohydride with the moisture in ambient air. The solid mixture was then heated under stirring to 100 °C for **4** and **5**, and 130 °C for **6** and **7**, until about two equivalents of gas evolved. An equimolar quantity of 18-crown-6 was added to the crude white solid, and

tetrahydrofuran (30 mL) was then added. The resultant mixture was refluxed for 1 h and then filtered through a 2-cm pad of Celite on a coarse glass frit. The clear filtrate was concentrated to about 10 mL, and was then layered with hexane (80 mL). After slow diffusion of the two solvents, colorless crystalline solids were obtained for **4**, **6**, and **7**, and the crystals were suitable for X-ray crystallographic studies. Crystals of **5** were grown from a concentrated toluene/THF solution at -25 °C. The crystalline samples were also used for the microanalyses.

K(BH₂(HCN₄)₂)(18-crown-6) (4). Prepared from potassium borohydride (0.100 g, 1.85 mmol), 1-*H*-tetrazole (0.260 g, 3.71 mmol), and 18-crown-6 (0.490 g, 1.85 mmol) to afford **4** in 97% yield as a colorless crystalline solid. Mp: 121-123 °C; IR (Nujol, cm⁻¹): □ = 3133 (s), 2431 (s), 2422 (s), 2295 (w), 2254 (w), 1588 (w), 1351 (s), 1284 (s), 1251 (s), 1235 (s), 1185 (s), 1170 (s), 1160 (s), 1136 (s), 1107 (s), 1030 (s), 975 (m), 960 (s), 896 (m), 886 (m), 862 (m), 838 (s), 770 (w), 743 (m), 716 (s), 682 (w), 651 (m), 634 (s); ¹H NMR (D₂O, 23 °C): δ = 8.81 (s, 2H, HCN₄), 3.52 (s, 24H, OCH₂CH₂O); ¹³C{¹H} NMR (D₂O, 23 °C): δ = 148.20 (s, HCN₄), 69.86 (s, OCH₂CH₂O); ¹¹B NMR (D₂O, 23 °C): δ = -11.23 (s, br, BH₂); elemental analysis calculated for C₁₄H₂₈BKN₈O₆ (%): C 37.01, H 6.21, N 24.66; found: C 37.23, H 5.98, N 24.82.

K(BH₂(MeCN₄)₂)(18-crown-6)•(C₇H₈)_{0.5} (5). Prepared from potassium borohydride (0.100 g, 1.85 mmol), 5-methyl-1-*H*-tetrazole (0.312 g, 3.71 mmol), and 18-crown-6 (0.490 g, 1.85 mmol) to afford **5** in 64% yield as a colorless crystalline solid. Mp: 109-111 °C; IR (Nujol mull, cm⁻¹): □ = 2437 (s), 2417 (s), 2256 (w), 1602 (w), 1505 (s), 1402 (s), 1352 (s), 1286 (s), 1251 (s), 1194 (s), 1134 (s), 1105 (s), 994 (m), 961 (s), 879 (w), 866 (m), 839 (s), 746 (s), 737 (m), 726 (s), 703 (m), 624 (s); ¹H NMR (CD₃OD, 23 °C): δ = 7.21-7.08 (m, 2.5H, C₆H₅CH₃), 3.60 (s, 24H, OCH₂CH₂O), 2.55 (s, 6H, CH₃CN₄), 2.31 (s, 1.5H, C₆H₅CH₃); ¹³C{¹H} NMR (CD₃OD, 23 °C): δ = 157.13 (s, CH₃CN₄), 138.92 (s, *ipso*-C₆H₅CH₃), 129.93 (s, *o*-C₆H₅CH₃), 129.22 (s, *m*-C₆H₅CH₃), 126.30 (s, *p*-C₆H₅CH₃), 71.30 (s, OCH₂CH₂O), 21.47 (s, C₆H₅CH₃), 9.80 (s, CH₃CN₄); ¹¹B NMR (D₂O, 23 °C): δ = -12.52 (s, br, BH₂); elemental analysis calculated for C_{19.5}H₃₆BKN₈O₆ (%): C 44.32, H 6.87, N, 21.20; found: C 44.38, H 6.79, N 21.25.

K(BH₂(Me₂NCN₄)₂)(18-crown-6) (6). Prepared from potassium borohydride (0.100 g, 1.85 mmol), 5-dimethylamino-1-*H*-tetrazole (0.368 g, 3.71 mmol), and 18-crown-6 (0.490 g, 1.85 mmol) to afford **6** in 77% yield as a colorless crystalline solid. Mp: 138-140 °C; IR (Nujol mull, cm⁻¹): □ = 2457 (s), 2410 (s), 2266 (w), 1571 (s), 1503 (w), 1400 (s), 1353 (s), 1301 (m), 1286 (m), 1254 (s), 1217 (w), 1179 (m), 1143 (s), 1112 (s), 1068 (s), 1031 (m), 1021 (s), 964 (s), 884 (w), 868 (m), 839 (s), 761 (m), 740 (m), 699 (m), 675 (w), 665 (m); ¹H NMR (D₂O, 23 °C): δ = 3.51 (s, 24H, OCH₂CH₂O), 2.79 (s, 12H, (CH₃)₂NCN₄); ¹³C{¹H} NMR (D₂O, 23 °C): δ = 170.00 (s, (CH₃)₂NCN₄), 69.85 (s, OCH₂CH₂O), 39.04 (s, (CH₃)₂NCN₄); ¹¹B NMR (D₂O, 23 °C): δ = -10.24 (s, br, BH₂); elemental analysis calculated for C₁₈H₃₈BKN₁₀O₆ (%): C 40.00, H 7.09, N 25.92; found: C 40.19, H 6.94, N 26.07.

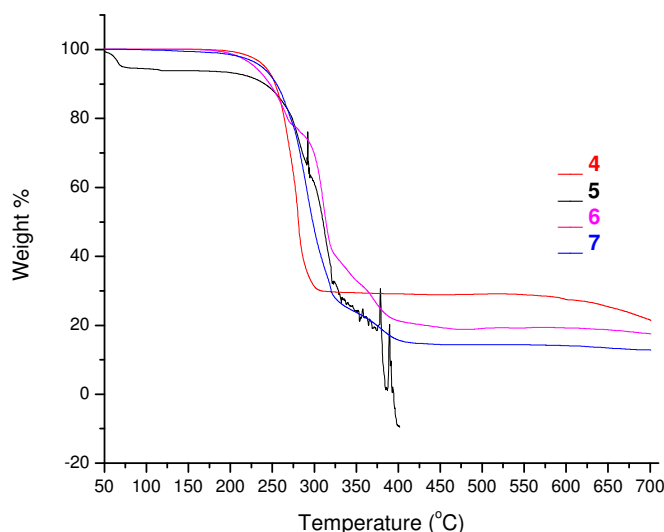
K(BH₂(iPr₂NCN₄)₂)(18-crown-6) (7). Prepared from potassium borohydride (0.100 g, 1.85

mmol), 5-diisopropylamino-1-*H*-tetrazole (0.620 g, 3.71 mmol), and 18-crown-6 (0.490 g, 1.85 mmol) to afford **7** in 80% yield as a colorless crystalline solid. Mp: 156-158 °C; IR (Nujol mull, cm^{-1}): \square = 2483 (s), 2409 (s), 2285 (w), 1563 (s), 1547 (s), 1543 (s), 1539 (s), 1505 (w), 1406 (s), 1352 (s), 1287 (s), 1253 (m), 1238 (w), 1204 (s), 1189 (m), 1176 (m), 1146 (s), 1134 (s), 1111 (s), 1032 (s), 963 (s), 889 (w), 871 (w), 861 (w), 837 (s), 758 (m), 700 (m), 679 (m); ^1H NMR (CD_2Cl_2 , 23 °C): δ = 4.04 (septet, J = 6.8 Hz, 4H, CH_3CHCH_3), 3.66 (s, 24H, $\text{OCH}_2\text{CH}_2\text{O}$), 1.26 (d, J = 6.5 Hz, 24H, CH_3CHCH_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 23°C): δ = 167.41 (s, $i\text{Pr}_2\text{NCN}_4$), 70.44 (s, $\text{OCH}_2\text{CH}_2\text{O}$), 47.20 (s, CH_3CHCH_3), 20.78 (s, CH_3CHCH_3); ^{11}B NMR (CD_2Cl_2 , 23 °C): δ = -7.87 (s, br, BH_2); elemental analysis calculated for $\text{C}_{26}\text{H}_{54}\text{BKN}_{10}\text{O}_6$ (%): C 47.85, H 8.34, N 21.46; found: C 48.17, H 8.11, N 21.04.

Reference

1. Garbrecht, W. L.; Herbst, R. M. *J. Org. Chem.* **1953**, *18*, 1003-1013.
2. Koguro, K.; Oga, T.; Mitsui, S.; Orita, R. *Synthesis* **1998**, 910-914.

Figure 1. Thermogravimetric Analysis (TGA) Curves of **4-7**.



Complex **5** possibly detonated at about 350 °C during the TGA analysis. For safety reasons, this analysis was not repeated and the data are presented herein as obtained.