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X-Ray Structure of $[Be\{B(pz)_4\}_2]$ and $[Be_3(OH)_3\{HB(pz)_3\}_3]$. Different Structures and Multiple-Point Bindings in Polypyrazolylborate Complexes

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Two novel polypyrazolylborate complexes of beryllium, $[Be\{B(pz)_4\}_2]$ (**1**) and $[Be_3(OH)_3\{HB(pz)_3\}_3]$ (**2**), have been prepared in aqueous solution, and their X-ray crystal structures have been determined. Complex **1** contains a tetrahedral Be^{2+} with each ligand having bidentate coordination. In complex **2**, each $HB(pz)_3^-$ is attached to a cyclic $[Be_3(OH)_3]^{3+}$ moiety by two Be-N coordination bonds and one OH-N hydrogen bond.

Polypyrazolylborate ligands have produced many attractive coordination compounds of not only transition metals but also main-group elements.[1] We report here the preparation and structure of beryllium complexes of tetrakis(1-pyrazolyl)borate, $[Be\{B(pz)_4\}_2]$ (**1**), and of hydrotris(1-pyrazolyl)borate, $[Be_3(OH)_3\{HB(pz)_3\}_3]$ (**2**). The central Be^{2+} of these complexes has the smallest ionic radius and has the highest charge to radius ratio among the central metal ions of the polypyrazolylborate chelates that have been prepared. Complexes **1** and **2** are the very rare example of beryllium complexes of which stable Be-N bonds are formed in aqueous solution.[2] Complex **1** is extracted into dichloromethane from aqueous solution of pH 4.5 containing 0.02 M of $BeCl_2$ and 0.044 M of $K[B(pz)_4]$.[3] When $K[HB(pz)_3]$ is used in stead of $K[B(pz)_4]$ under the same condition, **2** is the dominant extracted species of beryllium. Although both $B(pz)_4^-$ and $HB(pz)_3^-$ act as a bidentate ligand for Be^{2+}, the forth pyrazolyl ring causes formation of totally different complexes of the same metal. Such very different structures of complexes of the same metal with $B(pz)_4^-$ and $HB(pz)_3^-$ have so far been reported only for lead(II).[4] Furthermore, **2** contains a cyclic $[Be_3(OH)_3]^{3+}$ moiety, which is the dominant species of

beryllium in aqueous solution in the course of hydrolysis of Be^{2+}.[5] In complex **2**, each $HB(pz)_3^-$ is bound to the $[Be_3(OH)_3]^{3+}$ moiety by one OH-N hydrogen bond through the third pyrazolyl ring in addition to two Be-N bonds. Complex **2** is the demonstration for the first time that polypyrazolylborates can stabilize a molecule by multiple-point bindings.

Colorless crystals of **1** and **2** suitable for X-ray diffraction were afforded by recrystallization from a mixture of chloroform and hexane in a 1:2 volume ratio. In the crystal of **1**,[6] there are three crystallographically independent molecules within a unit cell. Figure 1 shows the structure of one of these molecules. The structure of the other two molecules is quite similar to Fig. 1. The complex contains the tetrahedral beryllium atom coordinated by four nitrogen atoms. Concerning the chelate ring, the average Be-N distance is 1.70 Å, N-Be-N angles is 103.2°, and "bite size" (distance between donor atoms) is 2.66 Å. The Be-N distance is shorter than that (1.73-1.77 Å) about the tetrahedral beryllium atoms in $Be(NH_2)_2$[7] or that (1.78-1.81 Å) in $\{\eta^3$-HB(3-$Bu^tpz)_3\}BeX$ (X = H, Br), where the polypyrazolylborate is tridentate.[8]

The structure of **2**[9] consists of a cyclic $[Be_3(OH)_3]^{3+}$ moiety and has C_3 symmetry as shown in Fig. 2. The cyclic structure of $[Be_3(OH)_3]^{3+}$ has been determined in $[Be_3(OH)_3(C_5H_4NCOO)_3]\cdot H_2O$ (**3**).[10] Although the dimensions of $[Be_3(OH)_3]^{3+}$ in **2** are similar to those in **3**, $[Be_3(OH)_3]^{3+}$ in **2** is more puckered than that in **3**. With respect to dimensions of the chelate ring in **2**, while the bite size (2.66 Å) is similar to that of **1**, the Be-N

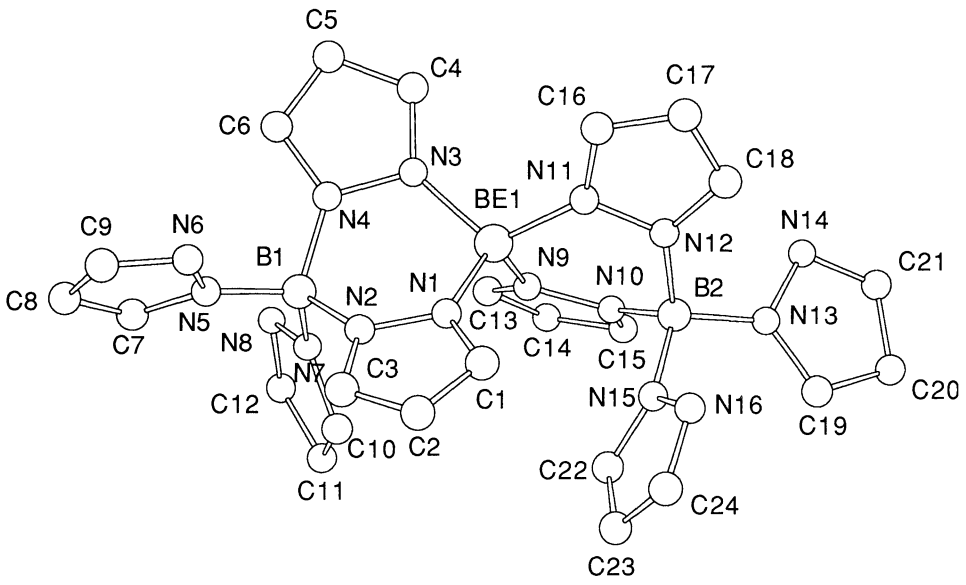

Fig. 1. Perspective drawing of $[Be\{B(pz)_4\}_2]$ (**1**). Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): N1-BE1, 1.718(7); N2-B1, 1.528(8); N3-BE1, 1.690(9); N4-B1, 1.555(7); N9-BE1, 1.709(8); N11-BE1, 1.675(7); N2-N1-BE1, 122.1(4); N1-N2-B1, 121.5(3); N2-B1-N4, 108.5(4); N2-B1-N5, 110.0(4); N2-B1-N7, 107.8(5); N5-B1-N7, 110.7(4); N1-BE1-N3, 102.8(4); N1-BE1-N9, 116.4(4); N1-BE1-N11, 111.5(5).

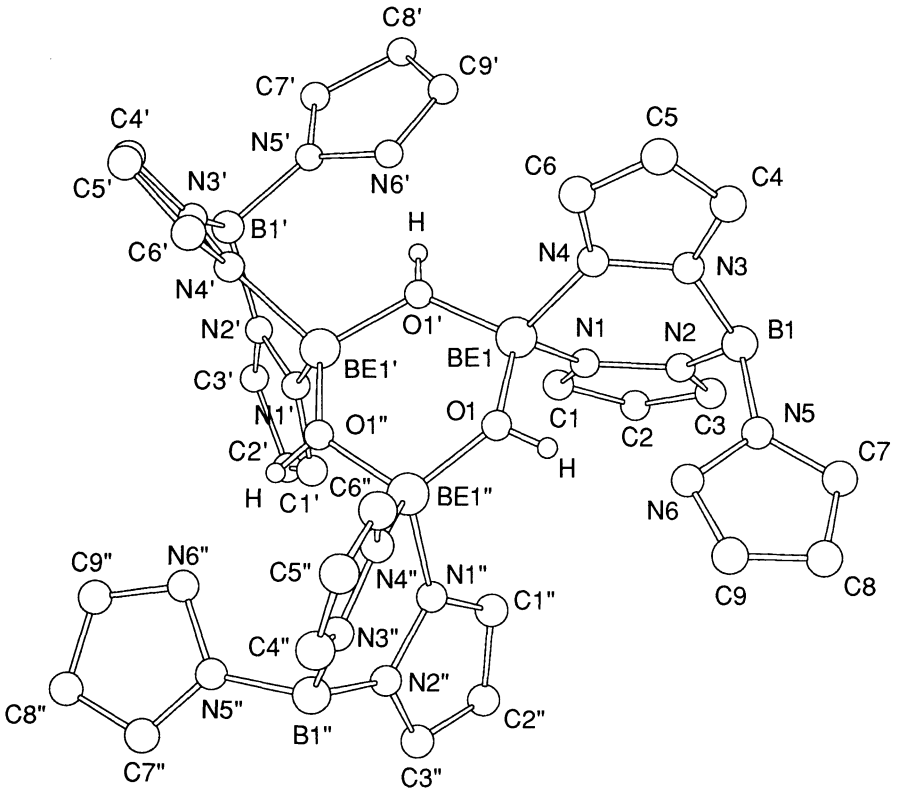

Fig. 2. Perspective drawing of $[Be_3(OH)_3\{HB(pz)_3\}_3]$ (**2**). Hydrogen atoms bonded to boron and carbon atoms are omitted for clarity. Selected distances (Å) and angles (deg): O1-BE1, 1.595(4); O1'-BE1, 1.581(4); N1-BE1, 1.742(4); N4-BE1, 1.741(4); BE1-O1-BE1", 127.0(2); N2-N1-BE1, 123.5(2); N1-N2-B1, 122.8(2); N6-N5-B1, 122.9(2); N2-B1-N3, 109.6(2); N2-B1-N5, 110.7(3); N3-B1-N5, 111.2(3); O1-BE1-O1', 108.8(2); O1-BE1-N1, 114.1(2); O1-BE1-N4, 108.0(2); N1-BE1-N4, 99.5(2).

distance (1.74 Å) is longer and the N-Be-N angle (99.5°) is smaller than those of **1**. The N5-N6 bond of noncoordinated pyrazolyl ring is almost coplanar to BE1-O1 bond (dihedral angle of N5-N6-O1-BE1 is 4.0°). The distance of O1-N6 is 2.85 Å, and angles of O1-H-N6 and N5-N6-H are 168.4° and 122.4°, respectively. IR spectrum shows a broad absorption of the hydroxide group at 3200 cm^{-1}. In ^1H NMR, the chemical shift of the hydroxide protons is 7.72 ppm. These facts show that hydrogen bondings of OH-N exist in **2**.

$B(pz)_4^-$ is a more effective ligand for Be^{2+} than $HB(pz)_3^-$, because $B(pz)_4^-$ substitutes all hydroxide ions bound to Be^{2+} but $HB(pz)_3^-$ does not under the same condition. This can not be attributed to the difference in basicity of donor atoms, since the acid dissociation constants for the mono-protonated ligands were proved to be 6.06 for $H[B(pz)_4]$ and 6.92 for $H[HB(pz)_3]$. Detailed discussion on the factors that control the structure and stability of group 2 metal complexes of polypyrazolylborates will be reported in a subsequent paper.

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6) Analytical and spectroscopic data for **1**. Anal. Found: C, 49.47; H, 4.26; N, 38.47; B, 3.85; Be, 1.57%. Calcd for $C_{24}H_{24}N_{16}B_2Be$: C, 50.82; H, 4.27; N, 39.51; B, 3.81; Be, 1.59%. ^{1}H NMR spectrum at 25 °C in $CDCl_3$: δ 6.25 (4H, t), 6.26 (4H, t), 6.62 (4H, d), 6.69 (4H, d), 7.35 (4H, d), 7.77 (4H, d). Crystal data for **1**: M = 567.19, monoclinic, space group $P2_1/c$, a = 21.813(6), b = 16.556(7), c = 26.267(5) Å, β = 112.82(1)°, V = 8743(4) Å^3, D_c = 1.293 g cm^{-3} at 23 °C; Z = 12. Least-squares refinement of 1291 variables led to R = 0.054 and R_w = 0.069 for 5417 reflections with $I > 3\sigma(I)$.

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9) Analytical and spectroscopic data for **2**. Anal. Found: C, 44.46; H, 4.78; N, 34.90; B, 4.77; Be, 3.83%. Calcd for $C_{27}H_{33}N_{18}O_3B_3Be_3$: C, 45.21; H, 4.65; N, 35.16; B, 4.52; Be, 3.77%. ^{1}H NMR spectrum at 25 °C in $CDCl_3$: δ 6.00 (3H, t), 6.21 (6H, t), 6.96 (3H, d), 7.60 (6H, d), 7.66 (6H, d), 7.68 (3H, d), 7.72 (3H, br). The peak for borate protons was not identified. Crystal data for **2**: M = 717.14, rhombohedral (hexagonal axes), space group R3(h), a = 19.037(2), c = 17.194(6) Å, V = 5397(2) Å^3, D_c = 1.324 g cm^{-3} at 23 °C; Z = 6. Least-squares refinement of 196 variables led to R = 0.045 and R_w = 0.072 for 1352 reflections with $I > 3\sigma(I)$. For **1** and **2**, intensity data were collected on a Rigaku AFC5R diffractometer.

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