4376 *Inorg. Chem.* **1994**, *33*, 4376−4383

New Mode of Ion Size Discrimination for Group 2 Metals Using Poly(pyrazolyl)borate Ligands. 2. Control of Stability and Structure of Chelate Complexes by Intra- and Interligand Contact and Shielding Effect

Yoshiki Sohrin,[*,†] Masakazu Matsui,[†] Yasuo Hata,[†] Hiroshi Hasegawa,[‡] and Hisao Kokusen[§]

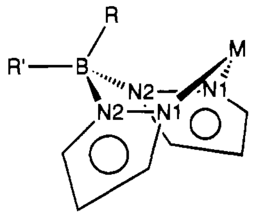
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan, Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780, Japan, and Faculty of Education, Tokyo Gakugei University, Koganei, Tokyo 184, Japan

Received May 4, 1994[®]

Selectivity of $[HB(3,5\text{-}Me_2pz)_3]^-$ (pz = 1-pyrazolyl) for group 2 metal ions has been studied by liquid−liquid extraction and compared with that of $[HB(pz)_3]^-$ and $[B(pz)_4]^-$. Although all the extracted species of Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} are distorted octahedral A_2M (A = poly(pyrazolyl)borate), the selectivity is highly dependent on the ligand. The selectivity of $[HB(pz)_3]^-$ is in the order $Mg^{2+} > Ca^{2+} > Sr^{2+}$. $[B(pz)_4]^-$ is specific to Mg^{2+} and hardly extracts the larger metal ions. $[HB(3,5\text{-}Me_2pz)_3]^-$ shows the selectivity order $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$. The steric properties responsible for the selectivity have been elucidated by X-ray diffraction, ^1H and ^{13}C NMR, and molecular mechanics calculations. The results confirm the following conclusions: (i) the selectivity is principally governed by the stability of A_2M complexes; (ii) the stability of $[B(pz)_4]_2M$ markedly decreases with the increase in ion size because of the intraligand contact between pyrazolyl rings; (iii) the 3-methyl group of $[HB(3,5\text{-}Me_2pz)_3]^-$ stabilizes the complex with a large metal ion through shielding effects and destabilizes the complex with a small metal ion through interligand contact. For the very small ion Be^{2+}, which takes tetrahedral geometry, the structures of extracted species are distinct. With $[HB(3,5\text{-}Me_2pz)_3]^-$, $[HB(3,5\text{-}Me_2pz)_3]BeOH$ is the dominant extracted species, which cyclizes to $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ in diethyl ether. In contrast, $[B(pz)_4]^-$ forms $[B(pz)_4]_2Be$, and $[HB(pz)_3]^-$ forms $[HB(pz)_3]_2Be$ and $[(HB(pz)_3)BeOH]_3$ depending on the initial concentration of Be^{2+}. Structure variation in Be^{2+} complexes also arises from the intra- and interligand contact and shielding effects.

Introduction

The coordination chemistry of poly(pyrazolyl)borate ligands is being extensively studied, and they form a variety of interesting complexes with most metals and metalloids.[1] Many unusual features of the ligands are largely derived from their unique structure. All poly(pyrazolyl)borate complexes contain the six membered ring $RR'B(\mu\text{-}pz)_2M$ structure (**1**), where R and R′ can be pz, H, alkyl, aryl, and so forth (pz = 1-pyrazolyl). The chelate ring has a boat configuration, which enables the R group to approach the metal and bond to it. Trofimenko has termed the ligands "scorpionate", since the $(\mu\text{-}pz)_2$ moiety looks like claws and the pseudoaxial R group looks like the stinger of the curving tail.[1a]



1

It is fundamentally important in poly(pyrazolyl)borate chemistry to determine how the scorpionate discriminates its prey (metal ion). However, few studies have been reported on the selectivity of the ligands for metal ions and on the stability of their complexes.[2] We have been studying the liquid−liquid extraction of group 2 metal ions with poly(pyrazolyl)borates and have found that selectivity trends are different from those for conventional chelating ligands. These selectivity trends are derived from the different mode of ion size discrimination. Conventional chelating ligands discriminate ion sizes based on the chelate ring size.[3] The chelate ring size is principally determined by the kind and number of atoms, and the order of bonds contained in the ring. For hard metal ions, such as group 2 and lanthanide, the stability constants of conventional chelating complexes decrease gradually with the increase in ion size.[4] In a previous paper,[2c] we showed that $[B(pz)_4]^-$ extracts Mg^{2+} but

---

[*] To whom correspondence should be addressed.

[†] Kyoto University.

[‡] Kochi University.

[§] Tokyo Gakugei University.

[®] Abstract published in *Advance ACS Abstracts,* August 15, 1994.

(1) (a) Trofimenko, S. *Chem. Rev.* **1993**, *93*, 943. (b) Anderson, S.; Hill, A. F.; Slawin, A. M. Z.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1993**, 266. (c) Das, A.; Maher, J. P.; McCleverty, J. A.; Navas Badiola, J. A.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1993**, 681. (d) Gulino, A.; Ciliberto, E.; Di Bella, S.; Fragalà, I. *Inorg. Chem.* **1993**, *32*, 3759. (e) Halcrow, M. A.; Chaudret, B.; Trofimenko, S. *J. Chem. Soc., Chem. Commun.* **1993**, 465. (f) Jones, W. D.; Hessell, E. T. *J. Am. Chem. Soc.* **1993**, *115*, 554. (g) Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496. (h) Kitajima, N.; Moro-oka, Y. *J. Chem. Soc., Dalton Trans.* **1993**, 2665. (i) LeCloux, D. D.; Tolman, W. B. *J. Am. Chem. Soc.* **1993**, *115*, 1153. (j) Long, G. J.; Grandjean, F.; Trofimenko, S. *Inorg. Chem.* **1993**, *32*, 1055. (k) Looney, A.; Han, R.; McNeill, K.; Parkin, G. *J. Am. Chem. Soc.* **1993**, *115*, 4690. (l) Protasiewicz, J. D.; Theopold, K. H. *J. Am. Chem. Soc.* **1993**, *115*, 5559. (m) Skagestad, V.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 5077. (n)Wlodarczyk, A.; Kurek, S. S.; Moss, M. A. J.; Tolley, M. S.; Batsanov, A. S.; Howard, J. A. K.; McCleverty, J. A. *J. Chem. Soc., Dalton Trans.* **1993**, 2027.

(2) (a) Jezorek, J. R.; McCurdy, W. H., Jr. *Inorg. Chem.* **1975**, *14*, 1939. (b) Yasuda, N.; Kokusen, H.; Sohrin, Y.; Kihara, S.; Matsui, M. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 781. (c) Sohrin, Y.; Kokusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4128.

(3) (a) Hancock, R. D.; Martell, A. E. *Chem. Rev.* **1989**, *89*, 1875. (b) Hancock, R. D. *Prog. Inorg. Chem.* **1989**, *37*, 187.

0020-1669/94/1333-4376$04.50/0

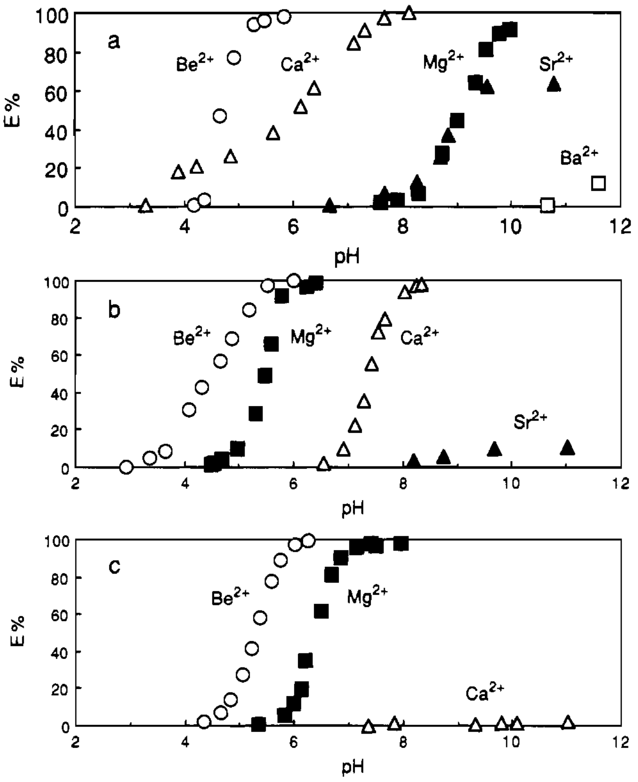


Figure 1. Effect of pH on the extraction of group 2 metal ions. Aqueous phase: 1 × 10^{-2} M KA, 1 × 10^{-2} M buffer, 1 × 10^{-4} M M^{2+} (10 mL). Organic phase: chloroform (10 mL). Key: (a) K[HB(3,5-$Me_2pz)_3$]; (b) K[HB$(pz)_3$]; (c) K[B$(pz)_4$].

hardly extracts Ca^{2+}. It was suggested on the basis of X-ray crystallography that the stability and structure of $[B(pz)_4]^-$ complexes are dominated by intraligand contact between the pyrazolyl rings. In the present work, liquid–liquid extraction data with $[HB(3,5\text{-}Me_2pz)_3]^-$, ^1H and ^{13}C NMR data of its complexes, and the X-ray crystal structures of $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**), $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**), and $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**) are presented. It should be noted that $[HB(3,5\text{-}Me_2pz)_3]^-$ is selective for Ca^{2+} over Mg^{2+} in contrast with $[HB(pz)_3]^-$ and $[B(pz)_4]^-$. The results indicate that the stability and structure of $[HB(3,5\text{-}Me_2pz)_3]^-$ complexes are dominated by interligand contact and the shielding effect of the 3-methyl group on the pyrazolyl ring. Further, the steric energy assessed by molecular mechanics calculations for the ligands and complexes of $[HB(pz)_3]^-$, $[B(pz)_4]^-$, and $[HB(3,5\text{-}Me_2pz)_3]^-$ is presented to substantiate the intra- and interligand contact. This work is the first attempt to clarify the effect of steric factors on the chemistry of poly(pyrazolyl)borates using molecular mechanics.

Experimental Section

General Procedure. $K[HB(3,5\text{-}Me_2pz)_3]$ was synthesized by the literature method.[5] All other chemicals were reagent grade, and distilled water was used throughout. Acid dissociation constants of the $H_2[HB(3,5\text{-}Me_2pz)_3]^+$ were determined by potentiometric titration. Twenty milliliters of aqueous solution containing 2 × 10^{-2} M $K[HB(3,5\text{-}Me_2pz)_3]$ was titrated with 0.1 M hydrochloric acid under a nitrogen atmosphere at 25.0 ± 0.1 °C. Metal ion and boron concentrations were determined with a Japan Jarrel Ash ICAP-500 inductively coupled argon plasma emission spectrometer. ^1H and ^{13}C NMR spectra were obtained at 25 ± 1 °C with Varian VXR 200 and JEOL JNM-GX400 FT NMR spectrometers. Chemical shifts are reported (ppm) downfield from TMS using the solvents $CDCl_3$ (δ_H = 7.25 ppm, δ_C = 77 ppm) as an internal standard.

Extraction of Group 2 Metal Ions. Five milliliters of aqueous phase containing a group 2 metal ion (1 × 10^{-6} mol) and a buffer (1 × 10^{-4} mol), which was acetic acid, 2-morpholinoethanesulfonic acid (MES), 3-morpholino-1-propanesulfonic acid (MOPS), 3-[(tris(hydroxymethyl)-methyl)amino]-1-propanesulfonic acid (TAPS), 2-(cyclohexylamino)-ethanesulfonic acid (CHES) or 3-(cyclohexylamino)propanesulfonic acid (CAPS), was taken in a 30 mL glass tube. Five milliliters of freshly prepared 2 × 10^{-2} M aqueous $K[HB(3,5\text{-}Me_2pz)_3]$ was added, and the mixture was allowed to stand for 20 min at 25 ± 1 °C. After addition of 10 mL of chloroform, both phases were shaken for 5 min at 25 ± 1 °C. The two phases were separated centrifugally, and the pH of the aqueous phase was measured. The metal concentration in the aqueous phase was determined using the ICAP-500. The concentration in the organic phase was measured after back-extraction into 1 M nitric acid.

Bis[hydrotris(3,5-dimethylpyrazolyl)borato]magnesium, $[HB(3,5\text{-}Me_2pz)_3]_2Mg$ (2). Twenty milliliters of an aqueous solution of $K[HB(3,5\text{-}Me_2pz)_3]$ (0.67 g, 2 mmol) was added to an acidic aqueous solution (50 mL) of $MgCl_2{\cdot}6H_2O$ (0.20 g, 1 mmol). Sodium hydroxide solution (0.1 M) was added with mixing, until a white precipitate no longer formed (pH 10). After 20 min, the white precipitate was filtered off and washed with distilled water and methanol. Colorless crystals for the X-ray structure were obtained by recrystallization from chloroform. The structure was identical to that reported by Han and Parkin,[6] although they prepared **2** through ligand redistribution reaction of $[HB(3,5\text{-}Me_2pz)_3]MgR$ (R = CH_3, etc) in hot benzene. Anal. Calcd for $C_{30}H_{44}N_{12}B_2Mg$: C, 58.24; H, 7.17; N, 27.17. Found: C, 58.28; H, 7.24; N, 27.35. ^1H NMR ($CDCl_3$, δ): 1.38 (18; s; 3-Me); 2.41 (18; s; 5-Me); 5.56 (6; s; 4-H (pz)). ^{13}C NMR ($CDCl_3$, δ): 11.8, 12.8 (3-Me, 5-Me); 104.5 (4-C (pz)); 143.1, 149.2 (3-C, 5-C (pz)).

Bis[hydrotris(3,5-dimethylpyrazolyl)borato]calcium, $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (3). Twenty milliliters of an aqueous solution of $K[HB(3,5\text{-}Me_2pz)_3]$ (0.67 g, 2 mmol) was added to an acidic aqueous solution (50 mL) of $CaCl_2{\cdot}2H_2O$ (0.15 g, 1 mmol). Sodium hydroxide solution (0.1 M) was added with mixing, until a white precipitate no longer formed (pH 8.6). After 20 min, the white precipitate was filtered off and washed with distilled water and methanol. Colorless crystals for the X-ray structure were obtained by recrystallization from benzene at 40 °C. Anal. Calcd for $C_{30}H_{44}N_{12}B_2Ca$: C, 56.79; H, 6.99; N, 26.49. Found: C, 56.80; H, 6.97; N, 26.31. ^1H NMR ($CDCl_3$, δ): 1.83 (18; s; 3-Me); 2.41 (18; s; 5-Me); 5.63 (6; s; 4-H (pz)). ^{13}C NMR ($CDCl_3$, δ): 12.8, 13.2 (3-Me, 5-Me); 104.2 (4-C (pz)); 144.7, 148.6 (3-C, 5-C (pz)).

Bis[hydrotris(3,5-dimethylpyrazolyl)borato]strontium, $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (4). Twenty milliliters of an aqueous solution of $K[HB(3,5\text{-}Me_2pz)_3]$ (0.67 g, 2 mmol) was added to an acidic aqueous solution (50 mL) of $SrCl_2{\cdot}6H_2O$ (0.27 g, 1 mmol). Sodium hydroxide solution (0.1 M) was added with mixing, until a white precipitate no longer formed (pH 11). After 20 min, the white precipitate was filtered off and washed with distilled water and methanol. Anal. Calcd for $C_{30}H_{44}N_{12}B_2Sr$: C, 52.83; H, 6.50; N, 24.65. Found: C, 51.63; H, 6.39; N, 24.24. ^1H NMR ($CDCl_3$, δ): 1.97 (18; s; 3-Me); 2.39 (18; s; 5-Me); 5.66 (6; s; 4-H (pz)). ^{13}C NMR ($CDCl_3$, δ): 13.0, 13.2 (3-Me, 5-Me); 104.3 (4-C (pz)); 145.1, 147.9 (3-C, 5-C (pz)). Colorless crystals for the X-ray structure were obtained by recrystallization from benzene.

[Hydrotris(3,5-dimethylpyrazolyl)borato]hydroxyberyllium, $[HB(3,5\text{-}Me_2pz)_3]BeOH$ (5). Twenty milliliters of an aqueous solution of $K[HB(3,5\text{-}Me_2pz)_3]$ (0.67 g, 2 mmol) was added to a 0.24 M hydrochloric acid solution (50 mL) of Be (9.0 mg, 1 mmol). Sodium hydroxide solution (0.1 M) was added with mixing, until a white precipitate no longer formed (pH 6.2). After 20 min, the white precipitate was filtered off and washed with distilled water and methanol. ^1H NMR ($CDCl_3$, δ): 2.30 (9; s; 3-Me); 2.40 (9; s; 5-Me); 5.64 (3; s; 4-H (pz)).

Tris[hydrotris(3,5-dimethylpyrazolyl)borato]cyclotris((μ-hydroxy)-beryllium), $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (6). Compound **5** was dissolved

---

(4) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980. (b) Huheey, J. E.; Keiter, E. A.; Keiter R. L. *Inorganic Chemistry*, 4th ed.; Harper Collins College Publishers: New York, 1983.

(5) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288.

(6) Han, R.; Parkin, G. *J. Organomet. Chem.* **1990**, *393*, C43.

Table 1. Crystallographic Data for $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**), $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**), and $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**)

	3	**4**	**6**
formula	$C_{30}H_{44}N_{12}B_2Ca$	$C_{42}H_{56}N_{12}B_2Sr$	$C_{45}H_{69}N_{18}O_3B_3Be_3$
fw	634.46	838.22	969.63
cryst syst	trigonal	monoclinic	trigonal
space group	$R\bar{3}$ (No. 148)	*C*2/*m* (No. 12)	$R\bar{3}$ (No. 148)
a, Å	11.046(2)	24.955(3)	21.826(5)
b, Å		10.476(3)	
c, Å	24.964(3)	8.591(3)	19.636(4)
α, deg			
β, deg		90.66(2)	
γ, deg			
V, Å^3	2638.1(3)	2246.0(9)	8100(1)
Z	3	2	6
cryst size, mm	0.20 × 0.20 × 0.40	0.15 × 0.15 × 0.38	0.40 × 0.20 × 0.40
D_{calc}, g cm^{-3}	1.198	1.239	1.192
μ(Cu Kα), cm^{-1}	18.42	19.96	6.15
2*θ* range, deg	5−140	5−120	3−120
no. of reflcns collcd	1218	1672	2757
no. of indep reflcns	1105	1630	2575
no. of indep reflcns obsd	959	1321	1919
R, R_w	0.044, 0.068	0.046, 0.057	0.046, 0.067
goodness of fit	1.84	1.33	1.75

in diethyl ether and placed at room temperature, giving a colorless crystal of **6**. Anal. Calcd for $C_{45}H_{69}N_{18}O_3B_3Be_3$: C, 55.74; H, 7.17; N, 26.00. Found: C, 56.18; H, 7.52; N, 25.84. ^{1}H NMR ($CDCl_3$, δ): 1.36, 1.95 (9, 18; s, s, 3-Me), 2.24, 2.50 (18, 9; s, s, 5-Me), 5.54, 5.59 (3, 6; s, s; 4-H (pz)), 9.30 (3; s; OH).

X-ray Crystal Structure Determination. Crystallographic data are summarized in Table 1. Colorless crystals of **3** and **6** were each mounted on fine glass fibers with epoxy cement. A Crystal of **4** was sealed in a glass capillary with a drop of recrystallization solvent. The lattice parameters and intensity data were measured on a Rigaku AFC7R four-circle diffractometer with Ni-filtered Cu Kα radiation (λ = 1.541 78 Å) at 20 ± 1 °C. The $\omega-2\theta$ scan technique to a maximum 2θ value of 120 or 140° was used. An empirical absorption correction using the program DIFABS[7] was applied to the data sets. The data were corrected for Lorentz and polarization effects, and a correction for secondary extinction was applied. Structures were solved by direct methods[8] and expanded using Fourier techniques.[9] The non-hydrogen atoms were refined anisotropically. Methyl hydrogens were fixed at the positions generated by calculation, and the positions of the remaining hydrogens were refined. All calculations were performed using the TeXsan crystallographic software package developed by the Molecular Structure Corp.

Figures 2−4 show ORTEP drawings of **3**, **4**, and **6**, respectively. Tables 2−4 contain selected bond distances and bond angles for **3**, **4** and **6**, respectively. Mean dimensions of chelate rings for the group 2 metal complexes are summarized in Table 5; the labeling of atoms is given in structure **1**.

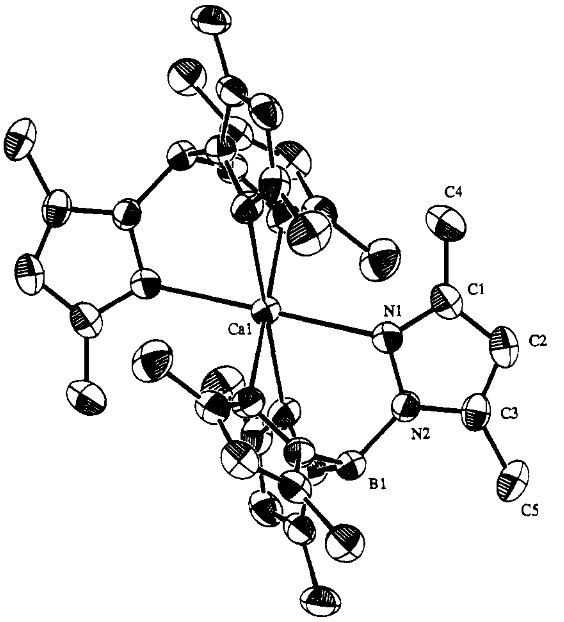


Figure 2. ORTEP view of $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**) (50% probability). Hydrogen atoms are omitted for clarity.

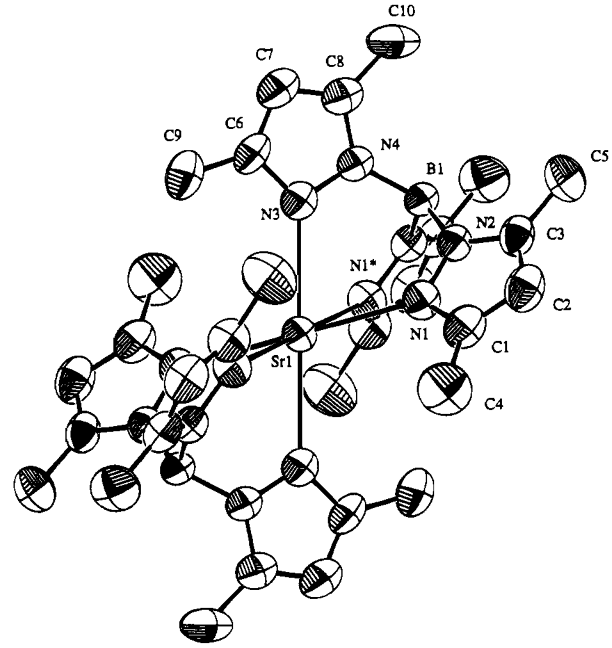


Figure 3. ORTEP view of $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**) (50% probability). Hydrogen atoms are omitted for clarity.

Molecular Mechanics Calculations. These were carried out using a CAChe system (version 3.0, CAChe Scientific) on a Macintosh Quadra 800. The program was based on Allinger's MM2 force field[10] and computed the net force acting on a molecule as the sum of energy terms of bond stretch, bond angle, dihedral angle, improper torsion, van der Waals, electrostatics, and hydrogen bond. The augmented force field parameters by CAChe were used without modification. Charges of −1 and +2 were assigned to boron and group 2 metal atoms, respectively. Octahedral geometry was adopted for the metal atoms. M−N bonds were described as coordinate bonds. In this condition, pyrazole rings were treated as aromatic.

Global energy minimum conformation of free poly(pyrazolyl)borates was searched by changing three dihedral angles of N−N−B−H or N−N−B−N. The conformation for tripodal coordination was modeled in such a way that the ligand was of C_3 symmetry. The bite sizes (distance between donor atoms) were adjusted to a given value, and the three dihedral angles of N−N−B−H or N−N−B−N were adjusted to 180°. These bite sizes and dihedral angles were locked while the rest of the geometry was optimized. (The locking assigns a large force

---

(7) Walker, N; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(8) (a) Sheldrick, G. M. In *Crystallographic Computing*, Sheldrick, G. M., Kruger C., Goddard, R., Eds.; Oxford University Press: Oxford, England, 1985; Vol. 3, pp 175−189. (b) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389.

(9) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nijmegen: The Netherlands, 1992.

(10) (a) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127. (b) Burkert, U.; Allinger, N. L. *Molecular Mechanics*; the American Chemical Society: Washington, DC; 1982.

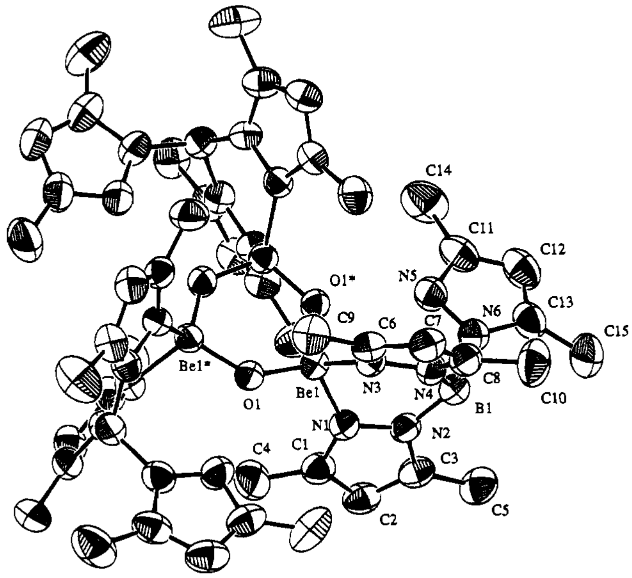


Figure 4. ORTEP view of $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**) (50% probability). Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**)

	Bond Distances		
Ca1–N1	2.454(2)	N1–N2	1.378(2)
N1–C1	1.333(3)	N2–C3	1.349(3)
N2–B1	1.545(2)	C1–C2	1.396(3)
C1–C4	1.494(3)	C2–C3	1.368(3)
C3–C5	1.496(3)		
	Bond Angles		
N1–Ca1–N1a	79.98(6)	N1–Ca1–N1b	180.00
N1a–Ca1–N1b	100.02(6)	Ca–N1–N2	116.0(1)
Ca1–N1–C1	134.4(1)	N2–N1–C1	106.2(2)
N1–N2–C3	109.9(2)	N1–N2–B1	121.7(2)
C3–N2–B1	128.4(2)	N1–C1–C2	110.0(2)
N1–C1–C4	121.0(2)	C2–C1–C4	129.0(2)
C1–C2–C3	106.1(2)	N2–C3–C2	107.8(2)
N2–C3–C5	123.0(2)	C2–C3–C5	129.2(2)
N2–B1–N2a	110.7(1)		

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**)

	Bond Distances		
Sr1–N1	2.600(3)	Sr1–N3	2.593(5)
N1–N2	1.381(4)	N2–B1	1.550(5)
N3–N4	1.379(6)	N4–B1	1.542(9)
	Bond Angles		
N1–Sr1–N1a	72.7(1)	N1–Sr1–N1b	180.00
N1a–Sr1–N1b	107.3(1)	N1–Sr1–N3	75.3(1)
N1b–Sr1–N3	104.7(1)	N3–Sr1–N3c	180.00
Sr1–N1–N2	121.6(2)	N1–N2–B1	121.4(4)
Sr1–N3–N4	121.2(4)	N3–N4–B1	122.3(5)
N2–B1–N2a	110.9(5)	N2–B1–N4	111.6(3)

constant and sets the geometry to be a given value.) Then, the locking was removed, and the energy for the strained conformation was calculated.

X-ray structure was used as an initial conformation for calculation of the complex. The $[B(pz)_4]_2Ca$ model was deduced from the structure of $[HB(pz)_3]_2Ca$ (**9**), and $[HB(pz)_3]_2Sr$ and $[B(pz)_4]_2Sr$ were modeled on the basis of **4**. Optimization of the geometry was carried out with locking of the six M–N–C–C dihedral angles. This locking was necessary to maintain local C_3 symmetry of the complexes while the optimization. However, the presence and absence of the locking had only a minor effect on the steric energy of the optimized geometry.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**)

	Bond Distances		
O1–Be1	1.564(4)	O1a–Be1	1.595(4)
N1–N2	1.376(3)	N1–Be1	1.759(4)
N2–B1	1.546(4)	N3–N4	1.378(3)
N3–Be1	1.764(4)	N4–B1	1.554(4)
N5–N6	1.364(3)	N6–B1	1.544(4)
	Bond Angles		
Be1–O1–Be1b	131.0(2)	N2–N1–Be1	119.7(2)
N1–N2–B1	124.9(2)	N4–N3–Be1	120.1(2)
N3–N4–B1	124.8(2)	N5–N6–B1	120.2(2)
N2–B1–N4	110.1(2)	N2–B1–N6	111.0(2)
N4–B1–N6	111.9(2)	O1–Be1–O1a	109.0(2)
O1–Be1–N1	114.0(2)	O1–Be1–N3	114.3(2)
O1a–Be1–N1	110.5(2)	O1a–Be1–N3	110.0(2)
N1–Be1–N3	98.7(2)		

Results

Acid Dissociation Constants of the Protonated Poly(pyrazolyl)borates. The poly(pyrazolyl)borates are polyacidic bases. The acid dissociation constants are defined as

$$K_{a1} = [H^+][A^-]/[HA] \qquad (1)$$

$$K_{a2} = [H^+][HA]/[H_2A^+] \qquad (2)$$

where brackets represent the molar concentration in aqueous solution and A^- stands for a poly(pyrazolyl)borate anion. For $[HB(3,5\text{-}Me_2pz)_3]^-$, pK_{a1} and pK_{a2} were found to be 10.12 ± 0.05 and 5.58 ± 0.10, respectively. These values are higher than those of $[HB(pz)_3]^-$ ($pK_{a1} = 6.92 \pm 0.04$; $pK_{a2} = 3.64 \pm 0.10$) and $[B(pz)_4]^-$ ($pK_{a1} = 6.06 \pm 0.05$; $pK_{a2} = 3.04 \pm 0.10$). $[HB(3,5\text{-}Me_2pz)_3]^-$ rather quickly hydrolyzed into 3,5-dimethylpyrazole and boric acid in aqueous solution around neutral pH; the ligand in 10^{-3} M D_2O solution was completely decomposed within 2 h. The pK_{a2} of $[HB(3,5\text{-}Me_2pz)_3]^-$ is somewhat uncertain because of this decomposition.

Extraction of Group 2 Metal Ions. Figure 1 shows the relationship between extracted percentage of a metal ion (*E* %) and pH of the aqueous phase. The data for $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ systems are taken from the previous paper.[2c] In these systems, the aqueous phase was shaken with chloroform immediately after preparation. In the $[HB(3,5\text{-}Me_2pz)_3]^-$ system, however, the *E* % scattered when the same procedure was followed, but allowing the aqueous phase to stand for 20 min before shaking gave reproducible results. Excessively prolonged shaking time decreased the *E* %. In the absence of buffer, the *E* % of Ca^{2+} was enhanced between pH 4 and pH 7. Be^{2+} and Ca^{2+} were quantitatively extracted into the organic phase. Maximum *E* % was 91% for Mg^{2+} and 64% for Sr^{2+}. An appreciable percentage of Ba^{2+} was extracted from alkaline solution.

Syntheses of Complexes. Complexes with two $[HB(3,5\text{-}Me_2pz)_3]^-$ ligands coordinated to Mg^{2+}, Ca^{2+}, and Sr^{2+} were produced according to the following equation:

$$M^2 + 2H[HB(3,5\text{-}Me_2pz)_3] \rightleftharpoons [HB(3,5\text{-}Me_2pz)_3]_2M + 2H^+ \qquad (3)$$

Although these complexes were obtained as precipitates and dissolved into chloroform, dichloromethane, and benzene, the solubility was lower than that of $[HB(pz)_3]_2M$.

The precipitated species of Be^{2+} with $[HB(3,5\text{-}Me_2pz)_3]^-$ was $[HB(3,5\text{-}Me_2pz)_3]BeOH$ (**5**), even if a sufficient quantity of the ligand was present to form $[HB(3,5\text{-}Me_2pz)_3]_2Be$. When **5** was

Table 5. Mean Dimensions (Å or deg) of Chelate Rings in $[HB(3,5\text{-}Me_2pz)_3]_2Mg$ (**2**), $[HB(pz)_3]_2Mg$ (**7**), $[B(pz)_4]_2Mg$ (**8**), $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**), $[HB(pz)_3]_2Ca$ (**9**), $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**), $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**), $[(HB(pz)_3)BeOH]_3$ (**10**), and $[B(pz)_4]_2Be$ (**11**)

	2	**7**[a]	**8**[a]	**3**	**9**[a]	**4**	**6**	**10**[a]	**11**[a]
M—N1	2.18(1)	2.19(3)	2.16(3)	2.45(1)	2.44(2)	2.60(1)	1.76(1)	1.74(1)	1.70(2)
N1—N2	1.37(1)	1.36(1)	1.37(1)	1.38(1)	1.36(1)	1.38(1)	1.38(1)	1.36(1)	1.37(1)
N2—B	1.54(1)	1.54(1)	1.55(1)	1.55(1)	1.54(1)	1.55(1)	1.56(1)	1.54(1)	1.54(1)
N1···N1	2.98(2)	2.94(4)	2.91(1)	3.15(1)	3.11(6)	3.14(4)	2.67(1)	2.66(1)	2.67(1)
M···B	3.20(1)	3.24(1)	3.24(1)	3.44(1)	3.46(1)	3.66(1)	3.16(1)	3.17(1)	3.08(2)
N1—M—N1	86.0(0.5)	84.7(2.0)	84.7(1.1)	80.0(0.1)	79.2(2.1)	74.4(1.2)	98.7(0.2)	99.5(0.2)	103.2(0.6)
M—N1—N2	116.7(0.4)	118.2(0.7)	119.5(1.4)	116.0(0.1)	118.2(0.6)	121.5(0.2)	119.9(0.2)	122.8(0.7)	121.6(0.8)
N1—N2—B	120.3(0.6)	120.7(0.6)	119.5(2.1)	121.7(0.2)	122.8(0.4)	121.7(0.4)	124.9(0.1)	123.7(0.9)	121.7(0.8)
N2—B—N2	109.6(0.6)	108.9(1.2)	108.7(1.3)	110.7(0.1)	110.3(0.5)	111.4(0.3)	110.0(0.2)	109.6(0.2)	108.4(0.5)

[a] Data taken from ref 2c.

recrystallized from diethyl ether and chloroform, it formed $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**). The latter complex dissolved in solvents more sparingly than the former complex.

All five complexes were stable in air.

Structure of $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (3). Figure 2 shows an ORTEP drawing of **3**; Table 2 shows selected bond distances and angles. The molecule has C_3 symmetry. The calcium atom sits on a center of inversion. Both ligands are tridentate, and the geometry about the calcium atom is a trigonally distorted octahedron. The mean dimensions of the chelate rings of **3** are nearly equal to those of $[HB(pz)_3]_2Ca$ (**9**)[2c] (Table 5).

Structure of $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (4). The crystals contained two molecules of benzene for each molecule of **4**. Figure 3 shows an ORTEP drawing of **4**; Table 3 shows selected bond distances and angles. The molecule has C_{2h} symmetry. Both ligands are tridentate, forming a six-coordinated, monomeric structure. The trigonal distortion of **4** is more enhanced than the distortion of **2** and **3**. The N—Sr—N angles in the chelate ring (74.4(1.2)°) are smaller than the N—Ca—N angles of **3** (Table 5). Of the coordination polyhedra examined, the mean interligand N—N distance is 7%, 19%, and 32% longer than the mean intraligand N—N distance (bite size) for **2**, **3** and **4**, respectively.

Structure of $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (6). Complex **6** lies on a 3-fold axis in the crystal. Figure 4 shows an ORTEP drawing of **6**; Table 4 shows selected bond distances and angles. The structure of **6** consists of a cyclic $[BeOH]_3{}^{3+}$ moiety and is analogous to $[(HB(pz)_3)BeOH]_3$ (**10**).[2c,11] The $[HB(3,5\text{-}Me_2pz)_3]^-$ in **6** is bidentate, and the geometry about the beryllium atom is a distorted tetrahedron. The Be—N distance (1.76(1) Å) is longer and the N—Be—N angle (98.7(0.2)°) is smaller than those of $[B(pz)_4]_2Be$ (**11**, Table 5).[2c,11] Similarly to **10**, there is an OH—N hydrogen bonding between the bridged hydroxide and noncoordinated pyrazolyl ring. The N5—N6 bond of the noncoordinated pyrazolyl ring is almost coplanar to the Be1—O1a bond (dihedral angle of N6—N5—O1a—Be1 is 3.5°). The distance O1a—N5 is 2.71 Å, and angles O1a—H—N5 and N6—N5—H are 171.9 and 122.1°, respectively. In ^1H NMR, the resonance of the hydroxide proton appears at 9.30 ppm.

Molecular Mechanics Calculations. The global minimum in steric energy of free ligand ($U_{A^-,min}$) was 8.4 kcal/mol for $[HB(pz)_3]^-$, 9.6 kcal/mol for $[B(pz)_4]^-$, and −4.1 kcal/mol for $[HB(3,5\text{-}Me_2pz)_3]^-$. The global minimum configuration of $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ is shown in Figure 5. The configuration of $[B(pz)_4]^-$ is similar to the X-ray structure of the ligand in the crystals of sodium and potassium salts.[12] Two pyrazolyl groups form a shallow V-wing. The third ring is oriented so as to bisect the wing. The fourth ring is nearly perpendicular to the third ring. The global minimum configuration of $[HB(pz)_3]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$ is like a propeller. The energy barrier to rotation of pyrazolyl rings around the N—B bond was much lower for $[HB(pz)_3]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$ than that for $[B(pz)_4]^-$.

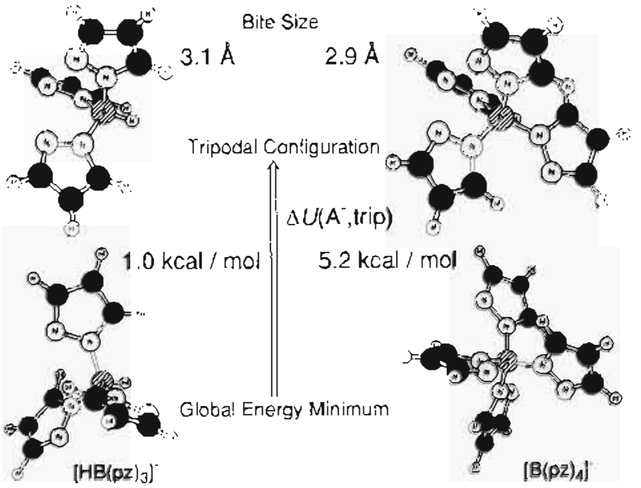


Figure 5. Minimum energy and tripodal configuration of $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ generated by molecular mechanics.

When the ligand molecule takes a conformation suitable for tripodal coordination, the steric energy increases (Figure 5). The increase is expressed as

$$\Delta U(A^-,trip) = U_{A^-,trip} - U_{A^-,min} \tag{4}$$

where $U_{A^-,trip}$ means the steric energy for tripodal conformation. The dependency of $\Delta U(A^-,trip)$ on bite size is shown in Figure 6.

The change in steric energy on A_2M complex formation ($\Delta U(A_2M)$) was assessed on the basis of

$$M^{2+} + 2A^- \rightleftharpoons A_2M \tag{5}$$

$$\Delta U(A_2M) = U_{A_2M} - U_{M^{2+}} - 2U_{A^-,min} \tag{6}$$

where U_{A_2M} and $U_{M^{2+}}$ are steric energies of the complex and metal ion, respectively. We assumed $U_{M^{2+}}$ to be zero for simplicity. U_{A_2M} was obtained by optimizing the X-ray structure in the force field. Differences in dimensions between the optimized and X-ray structures were less than 4% with a few exceptions. $\Delta U(A_2M)$ values are listed in Table 6.

Discussion

Extraction of Group 2 Metal Ions. The extraction of Mg^{2+} and Ca^{2+} with $[HB(pz)_3]^-$ and Mg^{2+} with $[B(pz)_4]^-$ can be

---

(11) Sohrin, Y.; Kokusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *Chem. Lett.* **1992**, 1461.

(12) Lopez, C.; Claramunt, R. M.; Sanz, D.; Foces, C. F.; Cano, F. H.; Faure, R.; Cayon, E.; Elguero, J. *Inorg. Chim. Acta* **1990**, *176*, 195.

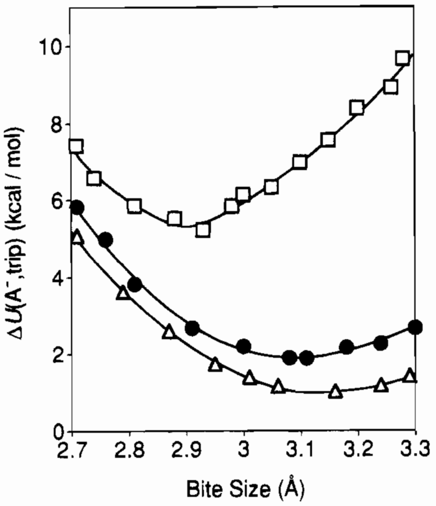


Figure 6. Change in steric energy of free ligands taking from the minimum energy configuration into the tripodal configuration (ΔU(A$^-$,trip)), as a function of the bite size. Key: (△) [HB(pz)$_3$]$^-$; (□), [B(pz)$_4$]$^-$; (●) [HB(3,5-Me$_2$pz)$_3$]$^-$.

analyzed as an equilibrium, and the extracted species were proved to be A$_2$M.[2c] The extraction with [HB(3,5-Me$_2$pz)$_3$]$^-$ cannot be treated as equilibrium, since the complex formation was slow and the ligand rather quickly decomposed. However, the extracted species of Mg^{2+}, Ca^{2+}, and Sr^{2+} with [HB(3,5-Me$_2$pz)$_3$]$^-$ are also A$_2$M and are formed according to eq 3. The extracted species of these systems are identical with the complexes synthesized for X-ray crystallography. NMR data show that the solution structures of these complexes are octahedral similarly to that observed in the crystals. All of the [HB(pz)$_3$]$^-$, [B(pz)$_4$]$^-$, and [HB(3,5-Me$_2$pz)$_3$]$^-$ anions act as a tripodal ligand and form six-membered BN$_4$M rings. Thus, it is astonishing that the selectivity of the three ligands is very different. [HB(pz)$_3$]$^-$ extracts Mg^{2+} and Ca^{2+} quantitatively and Sr^{2+} slightly. The extraction behavior resembles that of conventional chelating ligands.[13] [B(pz)$_4$]$^-$ extracts Mg^{2+} quantitatively but hardly extracts Ca^{2+}. [HB(3,5-Me$_2$pz)$_3$]$^-$ is selective for Ca^{2+} over Mg^{2+} and has improved extractability for Sr^{2+} and Ba^{2+}. We have not succeeded in determining the stability constants of the complexes owing to the ligand decomposition. Nevertheless, there is no doubt that the stability of the complexes is principally responsible for the selectivity. Judging from the pK_a values, the basicity of donor atoms of [HB(3,5-Me$_2$pz)$_3$]$^-$ is higher than that of [HB(pz)$_3$]$^-$ and [B(pz)$_4$]$^-$ because of the inductive effect of the methyl groups. The high basicity of donor atoms should stabilize the N—M bond. It is usual, however, that the increase in stability of complexes caused by electrolytic factor does not enhance extractability since the effect of increased stability is canceled by the increase in pK_a.[13] Therefore, the unique selectivity pattern of poly(pyrazolyl)borates must originate from a unique stability pattern controlled by steric factors.

Intraligand Contacts. Dimensions of the BN$_4$M chelate ring depend on the metal ion size (Table 5). The M—N1 distance is nearly equal to the sum of Shannon's ionic radii: 1.73 Å for Be—N, 2.18 Å for Mg—N, 2.46 Å for Ca—N, and 2.64 for Sr—N.[14] The bite size (N1⋯N1) widens when the ligand coordinates to a large metal ion. Widening of the bite size is realized by increasing the N1—N2—B and N2—B—N2 angles, which results in opening of the tripod of the coordinated pyrazolyl groups. When [B(pz)$_4$]$^-$ coordinates to Ca^{2+}, opening the tripod should cause severe steric contact between the coordinated and noncoordinated pyrazolyl rings.[2c]

This intraligand contact is clearly demonstrated in Figure 6. Figure 6 shows the increase in steric energy of the free ligand when it is taken from the lowest steric energy state into a conformation suitable for tripodal coordination (ΔU(A$^-$,trip)). For [HB(pz)$_3$]$^-$, ΔU(A$^-$,trip) is low and has a minimum at a bite size of around 3.1 Å . The ΔU(A$^-$,trip) of [B(pz)$_4$]$^-$ is substantially higher because of steric crowding about the boron atom. The minimum is 5.2 kcal/mol at a bite size of 2.9 Å. The steric energy sharply increases with the increase in bite size, making the complex formation more disadvantageous. In accordance with X-ray crystallography, while the bite size of [HB(pz)$_3$]$_2$Ca (**9**) is 3.11 Å,[2c] the average bite sizes of tridentate [B(pz)$_4$]$^-$ in previously reported complexes are smaller than 3.0 Å[15] with the only exception being [B(pz)$_4$]$_2$Cd.[16]

ΔU(A$^-$,trip) also increases for all ligands, when the bite size is reduced. This increase is derived chiefly from van der Waals repulsion between the coordinating pyrazolyl rings. The repulsion is relieved to a considerable extent when a chelate ring is formed. Hence, the increase in ΔU(A$^-$,trip) may not be so serious for complex formation with a small bite size. Actually, the bite size of [HB(3-Bu^{t}pz)$_3$]BeX (X = Br, H), which have been prepared by Han and Parkin, is as small as 2.73—2.79 Å.[17]

Table 6 summarizes the increase in steric energy accompanying A$_2$M complex formation (ΔU(A$_2$M); eqs 5 and 6). Because $U_{\mathrm{M}^{2+}}$ is assumed to be zero for all metals, comparison of the absolute values of ΔU(A$_2$M) is not meaningful. We noted the difference between ΔU([B(pz)$_4$]$_2$M) and ΔU([HB(pz)$_3$]$_2$M) for a given metal:

$$\Delta(\Delta U)_4 = \Delta U([\mathrm{B(pz)_4}]_2\mathrm{M}) - \Delta U([\mathrm{HB(pz)_3}]_2\mathrm{M}) \quad (7)$$

The term $U_{\mathrm{M}^{2+}}$ is canceled in $\Delta(\Delta U)_4$, so that it can be compared between metals. $\Delta(\Delta U)_4$ of Ca^{2+} and Sr^{2+} is 10—12 kcal/mol, more than twice that for Mg^{2+}. The results indicate severe intraligand contact between coordinated and noncoordinated pyrazolyl rings. In the above calculation, solvation is neglected and electron distribution in molecules is simplified. Nevertheless, it is very probable that the above steric energy change dominates the stability in the real systems.

Interligand Contact and Shielding Effect. Figure 6 shows that the energetics of [HB(3,5-Me$_2$pz)$_3$]$^-$ parallel that of [HB(pz)$_3$]$^-$ when the free ligand takes the tripodal conformation. The differences in stability of [HB(3,5-Me$_2$pz)$_3$]$^-$ and [HB(pz)$_3$]$^-$ complexes arise from steric factors related to ligand—solvent and/or ligand—ligand interactions. The methyl groups on a 3-position of the pyrazolyl rings, which are arrayed around the equator of metal in [HB(3,5-Me$_2$pz)$_3$]$_2$M (Figures 2 and 3), play an important role in such steric factors.

Figure 7 shows space-filling models of the X-ray structures of A$_2$M complexes. The models are viewed from the same direction. It is apparent that the metal atoms of [HB(3,5-Me$_2$pz)$_3$]$_2$M are shielded by the 3-methyl groups whereas those of [HB(pz)$_3$]$_2$M are exposed. While the poly(pyrazolyl)borate

---

(13) (a) Starý, J. *The Solvent Extraction of Metal Chelates*; Pergamon Press: Oxford, England, 1964. (b) Sekine, T.; Hasegawa, Y. *Solvent Extraction Chemistry*; Marcel Dekker: New York, 1977.

(14) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751. The radius of the nitrogen atom is taken as 1.32 Å of four-coordinate N^{3-}.

(15) (a) Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Inorg. Chem.* **1975**, *14*, 3046. (b) De Gil, E. R.; Rivera, A. V.; Noguera, H. *Acta Crystallogr., Sect. B* **1977**, *33*, 2653. (c) Cocivera, M.; Desmond, T. J.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J. *Organometallics* **1982**, *1*, 1125. (d) Cocivera, M.; Ferguson, G.; Kaitner, B.; Lalor, F. J.; O'Sullivan, D. J.; Parvez, M.; Ruhl, B. *Organometallics* **1982**, *1*, 1132.

(16) Reger, D. L.; Mason, S. S.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1993**, *32*, 5216.

(17) Han, R.; Parkin, G. *Inorg. Chem.* **1992**, *31*, 983.

Table 6. Steric Energy Change (kcal/mol) for Complex Formation

	$\Delta U([HB(pz)_3]_2M)$	$\Delta U([B(pz)_4]_2M)$	$\Delta(\Delta U)_4$	$\Delta U([HB(3,5\text{-}Me_2p)_3]_2M)$	$\Delta(\Delta U)_{Me}$
Mg^{2+}	−25.2	−20.5	4.7	−23.2	2.0
Ca^{2+}	−4.8	5.5	10.3	−5.2	−0.4
Sr^{2+}	6.1	17.7	11.6	5.9	−0.2

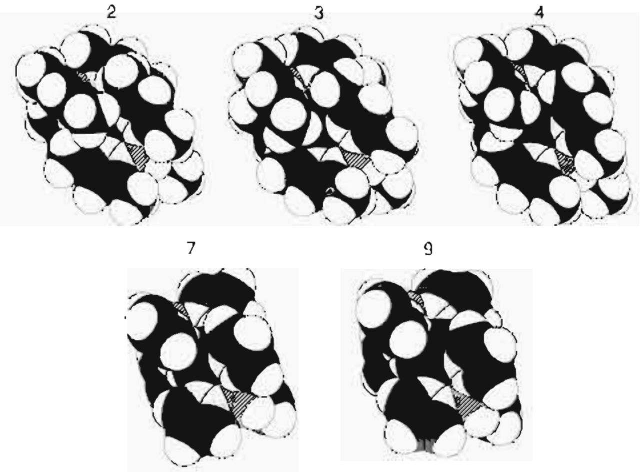


Figure 7. Space-filling views of $[HB(3,5\text{-}Me_2pz)_3]_2Mg$ (**2**), $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**), $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**), $[HB(pz)_3]_2Mg$ (**7**), and $[HB(pz)_3]_2Ca$ (**9**). The central metals are shown by black balls.

ligands widen the bite size on coordination to a large metal ion, there is a limitation in the widening. In fact, the bite size of $[HB(3,5\text{-}Me_2pz)_3]_2Sr$ (**4**) is the same as that of $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ (**3**, Table 5). The limitation enhances the trigonal distortion. If $[HB(pz)_3]_2Sr$ was formed in aqueous solution, it would not be stable. This is because the trigonal distortion makes the metal atom subject to attack by water molecules. For $[HB(3,5\text{-}Me_2pz)_3]_2M$, the array of 3-methyl groups prevents water molecules from approaching the metal atom. This is the shielding effect of 3-methyl groups, which stabilizes $[HB(3,5\text{-}Me_2pz)_3]_2M$ complexes of large metal ions.

The interligand distance between 3-methyl carbons (Me–Me) decreases as the metal ion size decreases. The mean interligand Me–Me distance is 3.99(18) Å for **4**, 3.93(1) Å for **3**, and 3.73(4) Å for $[HB(3,5\text{-}Me_2pz)_3]_2Mg$ (**2**). The Me–Me distance of **2** is considerably short taking into account the van der Waals radius of the methyl group (2.0 Å).[18] The interligand contact between 3-methyl groups can occur and hinder complex formation. The steric energy change for $[HB(3,5\text{-}Me_2pz)_3]_2M$ is listed in Table 6. $\Delta(\Delta U)_{Me}$ is defined as

$$\Delta(\Delta U)_{Me} = \Delta U([HB(3,5\text{-}Me_2pz)_3]_2M) - \Delta U([HB(pz)_3]_2M) \quad (8)$$

The values of $\Delta(\Delta U)_{Me}$ are nearly zero for Ca^{2+} and Sr^{2+}. The results indicate that introduction of 3-methyl groups does not increase the steric energy of Ca^{2+} and Sr^{2+} complexes. The shielding effect, of course, is not evaluated in this calculation. On the other hand, the presence of 3-methyl groups increases $\Delta(\Delta U)_{Me}$ of Mg^{2+} by 2.0 kcal/mol. It should be noted that $\Delta U([HB(3,5\text{-}Me_2pz)_3]_2M)$ is assessed for the minimum energy structure of $[HB(3,5\text{-}Me_2pz)_3]_2M$. Rotation of 3-methyl groups can bring about more steric hindrance. The effect of the rotation on steric energy was investigated while the rest of the geometries were maintained. The rotation increased the steric energy of **2** maximally by 3.4 kcal/mol, whereas the increase was as low as 1.3–1.7 kcal/mol for **3** and **4**. Thus, the interligand contact is unfavorable for the formation of **2**.

Although the above discussion is on thermodynamics, kinetics also may affect the selectivity of $[HB(3,5\text{-}Me_2pz)_3]^-$. The time required for Mg^{2+} tended to be longer than for Ca^{2+} before E % reached a constant value. The interligand contact of methyl groups probably hinders the formation of the bis(ligand) complex of a small ion not only thermodynamically but also kinetically.

Structure of Be^{2+} Complexes. In Figure 1, the pH range in which Be^{2+} is extracted is similar among $[HB(pz)_3]^-$, $[B(pz)_4]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$. It has been found, however, that the composition and structure of Be^{2+} complexes depend on the ligand.

The extracted species of 10^{-4} M Be^{2+} with $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ are considered to be A_2Be.[2c] $[B(pz)_4]_2Be$ (**11**) was crystallized and its X-ray structure was determined. When the concentration of Be^{2+} was 10^{-2} M, $[HB(pz)_3]^-$ formed not $[HB(pz)_3]_2Be$ but $[(HB(pz)_3)BeOH]_3$ (**10**). The cyclic $[BeOH]_3^{3+}$ is the dominant species of beryllium in aqueous solution in the course of hydrolysis of 10^{-2} M Be^{2+}.[19] The small size of Be^{2+} favors tetrahedral coordination. Poly(pyrazolyl)borates reduce the bite size needed to coordinate to Be^{2+}. $[B(pz)_4]^-$ is suitable for bidentate coordination in a compact arrangement because of steric crowding around the boron atom. For $[HB(pz)_3]^-$, bidentate conformation with a small bite size is unfavorable, since intraligand contact between the coordinating pyrazolyl rings increases the steric energy. As a result, $[HB(pz)_3]^-$ is a somewhat weaker ligand for Be^{2+} than hydroxide ion and forms $[HB(pz)_3]_2Be$ and **10** according to the dominant species of beryllium in aqueous solution.

The species extracted with $[HB(3,5\text{-}Me_2pz)_3]^-$ is not an A_2Be type, whereas we lack evidence on equilibrium. When $[HB(3,5\text{-}Me_2pz)_3]^-$ bidentately coordinates to Be^{2+} and forms an analogous complex to **11**, one of the interligand Me–Me distance decreases to 2.7–3.3 Å. The interligand contact cannot be avoided in tetrahedral coordination because of the V-shaped conformation of coordinating pyrazolyl rings. It is favorable for $[HB(3,5\text{-}Me_2pz)_3]^-$ that the ligand acts in a tridentate fashion and forms $[HB(3,5\text{-}Me_2pz)_3]BeOH$ (**5**) to avoid the interligand contact. **5** was synthesized in 10^{-2} M Be^{2+} aqueous solution and characterized by ^1H NMR. The structure of **5** should resemble that of $[HB(3\text{-}Bu^tpz)_3]BeX$ (X = Br, H).[17] Although recrystallization of **5** was tried from chloroform and diethyl ether, **5** always gave the crystal of $[(HB(3,5\text{-}Me_2pz)_3)BeOH]_3$ (**6**). The result is attributable to the much lower solubility of **6**.

It has been reported that the comparable ligands, namely $[HB(pz)_3]^-$, $[B(pz)_4]^-$, and $[HB(3,5\text{-}Me_2pz)_3]^-$, form different structures of complexes for a large metal ion, such as Pb^{2+} and Sn^{2+}.[20] This work demonstrates for the first time that these three ligands also produce totally different complexes for a small metal ion.

Conclusion

Stability of poly(pyrazolyl)borates complexes with group 2 metals is controlled by the steric effects of the substituents.

---

(18) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(19) (a) Kakihana, H.; Sillén, L. G. *Acta Chem. Scand.* **1956**, *10*, 985. (b) Ishiguro, S.; Maeda, M.; Ono, S.; Kakihana, H. *Denki Kagaku* **1978**, *46*, 553. (c) Brown, P. L.; Ellis, J.; Sylva, R. N. *J. Chem. Soc., Dalton Trans.* **1983**, 2001. (d) Faure, R.; Bertin, F.; Loiseleur, H.; Thomas-David, G. *Acta Crystallogr., Sect. B* **1974**, *30*, 462.

Because $[HB(pz)_3]^-$ has no specific steric effect on formation of the octahedral A_2M complex, its stability decreases in the order $Mg^{2+} > Ca^{2+} > Sr^{2+}$ which is the usual pattern for chelating ligands. The stability for $[B(pz)_4]^-$ remarkably drops between Mg^{2+} and Ca^{2+}. The complex formation with a large metal ion is prohibited by the intraligand contact due to steric crowding around the boron atom. For $[HB(3,5\text{-}Me_2pz)_3]^-$, methyl groups on the 3-position of the pyrazolyl ring hinder A_2M complex formation for small metal ions through interligand contact, while they stabilize the complex of large metal ions through the shielding effect. As a result, the order of stability is $Ca^{2+} > Mg^{2+} > Sr^{2+} > Ba^{2+}$. These steric factors make $[B(pz)_4]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$ unique ligands in selectivity for the metal ions. It has also been proved that these steric factors produce distinct compositions and structures for Be^{2+} complexes.

We believe that the intra- and interligand contact and shielding effects are essential in the chemistry of poly(pyrazolyl)borates. The intra- and interligand contacts can affect the electronic structure of the central metal and cause spin crossover[1d] and a stereochemically inactive lone pair.[20c] Bulky substituents on the 3-position favor the formation of AMX type complexes because of the interligand contact and shielding effect,[1a] where X can be various ligands and the reactivity of the metal ion is strangely modified by the steric hindrance.[1f,l,m] Moreover, the shielding effect stabilizes unusual heteroleptic complexes, such as O_2[1h] and CO_3[1g,k] complexes. The fine-tuning of the steric factors of poly(pyrazolyl)borate will further extend the frontier of its coordination chemistry.

Acknowledgment. This research was supported by Grants-in-Aid (Nos. 03453042, 05854071) from the Ministry of Education, Science, and Culture, Japan. We are particularly grateful to Professor D. L. Reger, University of South Carolina, for helpful discussions.

Supplementary Material Available: Text detailing the structure solution and tables of crystallographic details, positional and thermal parameters, temperature factors, bond distances, and bond angles for **3**, **4**, and **6** (31 pages). Ordering information is given on any current masthead page.

---

(20) (a) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Carrano, C. J. *J. Organomet. Chem.* **1988**, *341*, C27. (b) Reger, D. L.; Knox, S. J.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 1754. (c) Reger, D. L.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 579.