Inorg. Chem. **1993,** *32,* 5216–5222

Syntheses, Structures, ^{113}Cd Solution NMR Chemical Shifts, and Investigations of Fluxional Processes of Bis[poly(pyrazolyl)borato]cadmium Complexes

Danial L. Reger* and Scott S. Mason

Department of Chemistry and Biochemistry, University of South Carolina,
Columbia, South Carolina 29208

Arnold L. Rheingold and Robert L. Ostrander

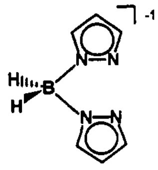
Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716

Received June 3, 1993®

The reactions of 2 equiv of $K[H_2B(pz)_2]$, $K[HB(pz)_3]$, $K[B(pz)_4]$, $K[H_2B(3,5\text{-}Me_2pz)_2]$, $K[HB(3,5\text{-}Me_2pz)_3]$, and $K[B(3\text{-}Mepz)_4]$ with $CdCl_2$ lead to the formation of the respective $[\text{poly(pyrazolyl)borato}]_2Cd$ complexes in high yields. A similar reaction with a 1/1 mixture of $K[HB(3,5\text{-}Me_2pz)_3]$ and either $K[H_2B(pz)_2]$ or $K[B(pz)_4]$ yields $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ (**7**) or $[HB(3,5\text{-}Me_2pz)_3]Cd[B(pz)_4]$ (**8**), respectively. The solid-state structures of $[B(pz)_4]_2Cd$ (**3**), $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (**5**), and $[B(3\text{-}Mepz)_4]_2Cd{\cdot}2C_7H_8$ (**6**) have been determined crystallographically. All three complexes show a distorted octahedral arrangement of the nitrogen donor atoms, with the cadmium atom located on a center of symmetry. For **5**, all Cd–N bonding distances are equal, but for **3** and **6**, three different Cd–N bond distances, with the differences being as large as 0.103 Å for **3**, are observed. The solution ^{113}Cd chemical shifts for the six-coordinate complexes range from 198.3 to 221.1 ppm, the resonance for the five-coordinate complex **7** is at 225.1 ppm, and the resonances for the four-coordinate complexes $[H_2B(pz)_2]_2Cd$ (**1**) and $[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$ (**4**) are at 298.7 and 303.3 ppm, respectively. Variable-temperature ^{1}H NMR spectra show that complexes **1**, **3**, **4**, and **6**–**8** are dynamic in solution. For **3**, **6**, and **8** all of the pyrazolyl rings of the tetrakis(pyrazolyl)borate ligands are equivalent at high temperatures with a 3/1 pattern observed at low temperatures. A mechanism that exchanges a coordinated with the noncoordinated pyrazolyl ring for the tetrakis(pyrazolyl)borate ligands is presented to explain these data. For the mixed-ligand complex **7**, at low temperatures each resonance type for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand appears as two resonances in a 2/1 ratio, resonances that coalesce at higher temperatures. The pyrazolyl ring resonances for the $[H_2B(pz)_2]^-$ ligand resonances remain equivalent at low temperatures, indicating a five-coordinate, square pyramidal arrangement of the nitrogen donor atoms. For **8**, the resonances for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand remain equivalent at low temperatures, indicating that the complex is six-coordinate. Crystal data: $[B(pz)_4]_2Cd$, monoclinic, $P2_1/c$, $a = 7.744(2)$ Å, $b = 10.029(2)$ Å, $c = 17.807(5)$ Å, $\beta = 92.80(2)^\circ$, $V = 1381.4(5)$ Å^3, $Z = 2$, $R(F) = 3.79\%$; $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, rhombohedral, $R\bar{3}$, $a = 11.003(2)$ Å, $c = 24.784(5)$ Å, $V = 2598.4(10)$ Å^3, $Z = 3$, $R(F) = 5.50\%$; $[B(3\text{-}Mepz)_4]_2Cd{\cdot}2C_7H_8$, monoclinic, $P2_1/c$, $a = 13.925(3)$ Å, $b = 12.412(2)$ Å, $c = 14.024(3)$ Å, $\beta = 92.62(2)^\circ$, $V = 2421.3(8)$ Å^3, $Z = 2$, $R(F) = 7.72\%$.

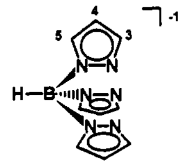
Introduction

We have undertaken an investigation into the coordination and organometallic chemistry of the post transition metals using the unique properties of the poly(pyrazolyl)borate ligand system.[1] These ligands are extremely versatile because the number of donor atoms in each ligand can be varied from 2 to 3 in going from the bidentate ligands **A** to the potentially tridentate ligands **B** and **C**. The steric requirements of the ligands can also be varied dramatically by substitution of the pyrazolyl ring at the 3-position with substituents ranging from methyl[1] to *tert*-butyl.[2] As shown in our recent studies with complexes of tin(II) and lead(II), varying the fourth boron substituent from hydrogen (**B**) to a pyrazolyl ring (**C**) can also change the coordination mode of the ligand.[3]



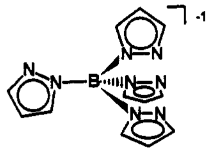
A

$[H_2B(pz)_2]^-$



B

$[HB(pz)_3]^-$



C

$[B(pz)_4]^-$

Our initial efforts were with the metals gallium(III)[4] and indium(III)[5] in group 13 and tin(II)[3a] and lead(II)[3b] in group 14 using the dihydrobis(pyrazolyl)borate ligand, **A**. These investigation clearly demonstrated that the poly(pyrazolyl)borate ligands form extremely stable, monomeric complexes with these post transition metals. For example, $[H_2B(pz)_2]In(CH_3)_2$ (pz = pyrazolyl ring) is monomeric and air stable.[5] In expanding these studies to the potentially tridentate ligands **B** and **C**, we were initially surprised to find that these ligands, particularly the ligand **C**, frequently coordinate in only a bidentate fashion, even in complexes of low coordination number. Thus, the complex $[B(pz)_4]_2Sn$[3a] is only four-coordinate in solution and the solid

---

® Abstract published in *Advance ACS Abstracts,* October 1, 1993.

(1) (a) Trofimenko, S. *Acc. Chem. Res.* **1971**, *4*, 17. (b) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170. (c) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288. (d) Shaver, A. *J. Organomet. Chem. Lib.* **1976**, *3*, 157. (e) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.

(2) (a) Trofimenko, S.; Calabrese, J. C.; Thompson, J. S. *Inorg. Chem.* **1987**, *26*, 1507. (b) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010. (c) Gorell, I. B.; Parkin, G. *Inorg. Chem.* **1990**, *29*, 2452.

(3) (a) Reger, D. L.; Knox, S. J.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *Inorg. Chem.* **1991**, *30*, 1754. (b) Reger, D. L.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 579.

(4) (a) Reger, D. L.; Knox, S. J.; Lebioda, L. *Inorg. Chem.* **1989**, *28*, 3092. (b) Reger, D. L.; Knox, S. J.; Lebioda, L. *Organometallics* **1990**, *9*, 2218.

(5) Reger, D. L.; Knox, S. J.; Rheingold, A. L.; Haggerty, B. S. *Organometallics* **1990**, *9*, 2581.

0020-1669/93/1332-5216$04.00/0

phase, and it has been shown by others that $[HB(3,5\text{-}Me_2pz)_3]_2Sn$[6] is five-coordinate in the solid state, a coordination number that it retains in the solution phase.[3a] More recently, we determined that $[B(pz)_4]_2InCH_3$ is six-coordinate, with one tridentate and one bidentate tetrakis(pyrazolyl)borate ligand.[7]

We have expanded these studies to the chemistry of cadmium(II)[8] for a number of reasons. With the group 14 metals in the +2 oxidation state, the geometry of the complexes and the overall chemistry are significantly influenced by the lone pair on the metal. In group 13, neutral complexes require three anionic ligands. Thus, the presence of the lone pair in $[B(pz)_4]_2Sn$ and the methyl ligand in $[B(pz)_4]_2InCH_3$ presumably influence the coordination behavior of the tetrakis(pyrazolyl)borate ligands. This influence is removed in the chemistry of cadmium(II). We are particularly interested in the comparison of analogous complexes of cadmium(II) and tin(II) because of the similarity in size between these two metals in the +2 oxidation state.[9] We showed previously that the size of the metal has an important influence on the coordination chemistry of the poly(pyrazolyl)borate ligands.[10]

Another important driving force for the development of this chemistry is the fact that cadmium has two important isotopes that are NMR active with spins = $^1/_2$. We have been able to show that the coordination number of the analogous tin(II) complexes can be correlated with the solution ^{119}Sn chemical shifts[10b] and expected to be able to do similar correlations using ^{113}Cd NMR. Also, a number of research groups have been using ^{113}Cd NMR as a "spin spy" in the study of zinc-containing proteins.[11] The strategy here is to replace the zinc, a metal with few good spectroscopic handles, with cadmium and use NMR to explore the properties of the proteins. We are interested in the preparation of monomeric complexes in which the donor atom set can be controlled in a systematic manner to aid in the interpretation of both solution and the solid-state NMR data on samples of biological interest.

The synthesis and characterization of a series of $[\text{poly(pyrazolyl)borato}]_2Cd$ complexes are reported here. We report the solid-state structures of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, $[B(3\text{-}Mepz)_4]_2Cd\cdot 2C_7H_8$, and $[B(pz)_4]_2Cd$. The solution ^{113}Cd NMR chemical shifts of these complexes are also reported. Many of the complexes are fluxional in solution, and the dynamic processes responsible for this behavior have been probed by variable-temperature NMR studies.

Experimental Section

General Procedure. The ^1H NMR spectra were recorded on a Bruker AM300 or AM500 spectrometer (all variable-temperature data) using a 5-mm broad-band probe. Proton chemical shifts are reported in ppm vs internal Me_4Si. ^{113}Cd NMR spectra were recorded in $CDCl_3$ on a Bruker AM500 spectrometer using a 5-mm broad-band probe, and the chemical shifts are reported in ppm vs external 0.1 M $Cd(ClO_4)_2$. In the assignment of ^1H NMR measurements, pz = pyrazolyl ring, pz* = $3,5\text{-}Me_2pz$ ring, pz** = 3-Mepz ring. Mass spectra were run on a Finnigan 4521 GC mass spectrometer or a VG 70SQ spectrometer using electron impact ionization. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present.

$K[H_2B(pz)_2]$,[1b] $K[HB(pz)_3]$,[1b] $K[B(pz)_4]$,[1b] $K[H_2B(3,5\text{-}Me_2pz)_2]$,[1c] $K[HB(3,5\text{-}Me_2pz)_3]$,[1c] and $K[B(3\text{-}Mepz)_4]$[12] were prepared according to the published methods. Anhydrous $CdCl_2$ was purchased from Aldrich Chemical Co. and used as received. Elemental analyses were performed by Robertson Laboratory, Inc., Madison, NJ.

Note! Cadmium compounds and their wastes are extremely toxic and must be handled carefully.

Bis[dihydrobis(1-pyrazolyl)borato]cadmium(II), $[H_2B(pz)_2]_2Cd$ (1). $CdCl_2$ (0.10 g, 0.54 mmol) was dissolved in H_2O (25 mL), and $K[H_2B(pz)_2]$ (0.20 g, 1.1 mmol), in THF (25 mL). The two solutions were combined, along with an additional 25 mL of H_2O, in a separatory funnel; the mixture was shaken and then extracted with CH_2Cl_2 (25 mL). The CH_2Cl_2 layer was separated from the mixture and the solvent removed to reveal a white solid (0.21 g, 0.52 mmol, 96%); dec pt 153–156 °C. ^1H NMR ($CDCl_3$) (δ): 7.70, 7.51 (4, 4; d, d; J = 2.1, 1.8 Hz; 3,5-H (pz)); 6.25 (4; t; J = 2.0 Hz; 4-H (pz)); 3.8 (4; broad; BH_2). ^{13}C NMR ($CDCl_3$) (δ): 141.2, 137.1 (3,5-C (pz)); 105.8 (4-C (pz)). Mass spectrum: m/z 405 ($M^+ - H$). Anal. Calcd for $C_{12}H_{16}N_8B_2Cd$: C, 35.43; H, 3.96. Found: C, 35.33; H, 4.05.

Bis[hydrotris(1-pyrazolyl)borato]cadmium(II), $[HB(pz)_3]_2Cd$ (2). This complex was prepared as above for **1** in 80% yield; mp 284–286 °C (lit. mp 285–286 °C[1b]). ^1H NMR ($CDCl_3$) (δ): 7.75, 7.35 (6, 6; d, d; J = 1.6, 1.4 Hz; 3,5-H (pz)); 6.15 (6; t; J = 2.0 Hz; 4-H (pz)). Mass spectrum: m/z 537 ($M^+ - H$), 471 ($M^+ - pz$). Anal. Calcd for $C_{18}H_{20}N_{12}B_2Cd$: C, 40.10; H, 3.74. Found: C, 40.25; H, 3.87.

Bis[tetrakis(1-pyrazolyl)borato]cadmium(II), $[B(pz)_4]_2Cd$ (3). This complex was prepared as above for **1** in 85% yield; mp 308–311 °C (lit. mp 328–329 °C[1b]). ^1H NMR ($CDCl_3$, ambient temperature (δ): 7.74, 7.51 (4, 4; s, s; 3,5-H (pz)); 6.27 (4; s; 4-H (pz)). ^1H NMR (CD_2Cl_2, –89 °C) (δ): 8.11, 7.96, 7.52, 7.37 (s, s, s, s; 1, 1, 3, 3; 3,5-H (pz)); 6.60, 6.18 (s, s; 1, 3; 4-H (pz)). Mass spectrum: m/z 670 (M^+), 603 ($M^+ -$ pz).

Bis[dihydrobis(3,5-dimethyl-1-pyrazolyl)borato]cadmium(II), $[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$ (4). This complex was prepared as above for **1** in 85% yield; dec pt 191–194 °C. ^1H NMR ($CDCl_3$) (δ): 5.76 (4; s; 4-H (pz*)); 3.6 (4; br; BH_2); 2.36, 2.00 (12, 12; s, s; 3,5-Me (pz*)). Mass spectrum: m/z 517 ($M^+ - H$). Anal. Calcd for $C_{20}H_{32}N_8B_2Cd$: C, 46.31; H, 6.23; N, 21.61. Found: C, 46.56; H, 6.40; N, 21.43.

Bis[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]cadmium(II), $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (5). This complex was prepared as above for **1** in 90% yield; dec pt 318–320 °C. ^1H NMR ($CDCl_3$) (δ): 5.62 (6; s; 4-H (pz*)); 2.40, 1.66 (18, 18; s, s; 3,5-Me (pz*)). ^{13}C NMR ($CDCl_3$) (δ): 149.1, 144.0 (3,5-C (pz*)); 104.6 (4-C (pz*)); 13.5, 12.6 (3,5-Me (pz*)). Mass spectrum: m/z 706 (M^+), 611 ($M^+ -$ pz*). Anal. Calcd for $C_{30}H_{44}N_{12}B_2Cd$: C, 50.93; H, 6.27; N, 23.76. Found: C, 50.71; H, 6.10; N, 23.43.

Bis[tetrakis(3-methyl-1-pyrazolyl)borato]cadmium(II), $[B(3\text{-}Mepz)_4]_2Cd$ (6). $CdCl_2$ (0.10 g, 0.54 mmol) and $K[B(3\text{-}Mepz)_4]$ (0.41 g, 1.1 mmol) were placed in a flask. THF (30 mL) was added via syringe, and the mixture was stirred 4 h. THF was removed under vacuum, the product was extracted with benzene (30 mL), and the extract was filtered. Benzene was removed under vacuum to reveal a white solid (0.37 g, 0.47 mmol, 87%); dec pt 210–215 °C. ^1H NMR ($CDCl_3$) (δ): 7.88, 7.50 (d, d; 2, 6; J = 2.2 Hz; 5-H (pz**)); 6.29, 5.90 (d, d; 2, 6; J = 2.1, 1.9 Hz; 4-H (pz**)); 2.46, 1.71 (s, s; 6, 18; 3-Me (pz**)). ^{13}C NMR ($CDCl_3$) (δ): 151.4 (3-C (coordinated pz**)); 151.3 (3-C (noncoordinated pz**)), 138.0 (5-C (noncoordinated pz**)); 136.1 (5-C (coordinated pz**)); 106.4 (4-C (noncoordinated pz**)); 105.0 (4-C (coordinated pz**)); 14.4 (3-Me (noncoordinated pz**)); 12.8 (3-Me (coordinated pz**)). Mass spectrum: m/z 782 (M^+), 701 ($M^+ -$ pz**). Anal. Calcd for $C_{32}H_{40}N_{16}B_2Cd$: C, 49.09; H, 5.16; N, 28.63. Found: C, 49.30; H, 5.22; N, 28.87.

[Dihydrobis(1-pyrazolyl)borato][hydrotris(3,5-dimethyl-1-pyrazolyl)borato]cadmium(II), $[H_2B(pz)_2]Cd[HB(3,5\text{-}Me_2pz)_3]$ (7). $CdCl_2$ (0.50 g, 2.7 mmol), $K[H_2B(pz)_2]$ (0.50 g, 2.7 mmol), and $K[HB(3,5\text{-}Me_2pz)_3]$ (0.91 g, 2.7 mmol) were placed in a flask. THF (30 mL) was added via syringe, and the mixture was stirred overnight. THF was removed under vacuum, the product was extracted with benzene (30 mL), and the extract was filtered. Benzene was removed under vacuum, leaving a white solid (0.63 g, 1.1 mmol, 42%). The ^1H NMR spectrum of this solid indicates the presence of a 5% impurity of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, which could not be removed. ^1H NMR ($CDCl_3$, ambient temperature) (δ): 7.65, 7.35 (d, d; 2, 2; J = 1.8 Hz; 3,5-H (pz)); 6.15 (t; 2; J = 2.1 Hz; 4-H (pz)); 5.71 (s; 3; 4-H (pz*)); 2.40, 1.80 (s, s; 9, 9; 3,5-Me (pz*)). ^1H NMR (CD_2Cl_2, –89 °C) (δ): 7.68, 7.37 (s, s; 2, 2; 3,5-H (pz)); 6.19 (s; 2; 4-H (pz)); 5.88, 5.73 (s, s; 1, 2; 4-H (pz*)); 4.65 (br; 1; BH (pz*)); 4.07, 3.66 (br, br; 1, 1; BH_2 (pz)); 2.37, 2.32, 1.88, 1.67 (s, s, s, s; 3, 6, 3, 6; 3,5-Me (pz*)). ^{13}C NMR ($CDCl_3$) (δ): 149.6, 145.5 (3,5-C (pz*)); 139.7, 135.5,

---

(6) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Carrano, C. J. *J. Organomet. Chem.* **1988**, *341*, C27.

(7) Reger, D. L.; Mason, S. S.; Rheingold, A. L. *Inorg. Chem.*, submitted for publication.

(8) Reger, D. L.; Mason, S. S. *Organometallics* **1993**, *12*, 2600.

(9) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

(10) (a) Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1890, 3923. (b) Reger, D. L. *Synlett* **1992**, 469.

(11) (a) Ellis, P. D. *J. Biol. Chem.* **1989**, *264*, 3108. (b) Kennedy, M. A.; Ellis, P. D. *J. Am. Chem. Soc.* **1989**, *111*, 3195. (c) Rivera, E.; Kennedy, M. A.; Ellis, P. D. *Adv. Magn. Reson.* **1989**, *13*, 257.

(12) Niedenzu, K.; Niedenzu, P. M.; Warner, K. R. *Inorg. Chem.* **1985**, *24*, 1604.

Table I. Crystallograpic Data for the Structural Analyses

	3	**5**	**6**
formula	$C_{24}H_{24}B_2N_{16}Cd$	$C_{30}H_{44}B_2N_{12}Cd$	$C_{32}H_{40}B_2N_{16}Cd{\cdot}2C_7H_8$
fw	670.6	706.8	967.1
cryst syst	monoclinic	rhombohedral	monoclinic
space group	$P2_1/c$	$R\bar{3}$	$P2_1/c$
a, Å	7.744(2)	11.003(2)	13.925(3)
b, Å	10.029(2)		12.412(2)
c, Å	17.807(5)	24.784(5)	14.024(3)
β, deg	92.80(2)		92.62(2)
V, Å^3	1381.4(5)	2598.4(10)	2421.5(9)
Z	2	3	2
T, °C	−39	25	25
λ, Å	0.710 73	0.710 73	0.710 73
ρ_{calc}, g/cm^3	1.612	1.351	1.327
abs coeff, cm^{-1}	8.39	6.70	5.01
R_F,[a] %	3.79	5.50	7.72
R_{wF},[a] %	4.08	9.09	9.29

[a] $R = \sum||F_o| - F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/[\sum w|F_o|^2]^{1/2}$.

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$

	x	*y*	*z*	*U*(eq)[a]
Cd(1)	0	0	0	31(1)
N(1)	837(7)	1876(5)	612(2)	44(2)
N(2)	437(6)	1485(5)	1148(2)	42(2)
B(1)	0	0	1343(3)	34(2)
C(1)	1114(8)	3224(7)	589(3)	49(2)
C(2)	992(8)	3690(7)	1097(3)	53(2)
C(3)	510(6)	2604(7)	1428(2)	44(2)
C(4)	1613(13)	4015(10)	66(3)	77(3)
C(5)	156(8)	2484(9)	2016(3)	56(3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

(3,5-C (pz)); 105.4 (4-C (pz*)); 105.1 (4-C (pz)); 13.4, 13.3 (3,5-Me (pz*)). Mass spectrum: *m/z* 555 (M$^+$ − H), 461 (M$^+$ − pz*).

[Hydrotris(3,5-dimethyl-1-pyrazolyl)borato][tetrakis(1-pyrazolyl)borato]cadmium(II), $[HB(3,5\text{-}Me_2pz)_3Cd[B(pz)_4]$ (8). $CdCl_2$ (0.25 g, 1.4 mmol), $K[HB(3,5\text{-}Me_2pz)_3]$ (0.46 g, 1.4 mmol), and $K[B(pz)_4]$ (0.43 g, 1.4 mmol) were placed in a flask. THF (25 mL) was added via syringe, and the mixture was stirred overnight. THF was removed under vacuum, the product was extracted with benzene (30 mL), and the extract was filtered. Benzene was removed under vacuum, leaving a white solid (0.26 g, 0.38 mmol, 28%). The ^{1}H NMR spectrum of this solid indicates the presence of a 5% impurity of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, which could not be removed. ^{1}H NMR ($CDCl_3$, ambient temperature) (δ): 8.01, 7.74, 7.62, 7.44 (br, br, br, br; 1, 1, 3, 3; 3,5-H(pz)); 6.55, 6.14 (br, br; 1, 3; 4-H(pz)); 5.69 (s; 3; 4-H (pz*)); 2.43, 1.58 (s, s; 9, 9; 3,5-Me (pz*)). ^{1}H NMR (CD_2Cl_2, −89 °C) (δ): 8.11, 7.94, 7.47, 7.35 (s, s, s, s; 1, 1, 3, 3; 3,5-H (pz)); 6.58, 6.14 (s, s; 1, 3; 4-H (pz)); 5.75 (s; 3; 4-H (pz*)); 4.70 (br; 1; BH (pz*)); 2.38, 1.52 (s, s; 9, 9; 3,5-Me (pz*)). Mass spectrum: *m/z* 688 (M$^+$), 620 (M$^+$ − Hpz), 593 (M$^+$ − pz*).

Crystallographic Analyses. Crystal, data collection, and refinement parameters for the three structures are collected in Table I. Colorless crystals, grown from methylene chloride for **3**, from chloroform for **5**, and from toluene for **6**, were mounted on glass fibers with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections (20° ≤ 2θ ≤ 25°). In **6**, two molecules of toluene were found for each full Cd complex. The C_7H_8 molecules were disordered over at least two sites which, although coplanar, differed in the orientation of the CH_3 group. Three standard reflections monitored every 197 reflections showed insignificant variations. Empirical corrections for absorptions were applied (216 ψ-scan reflections, pseudoellipsoid model). The metal atom was located from Patterson syntheses. All hydrogen atoms were included as idealized isotropic contributions (*d*(CH) = 0.960 Å, *U* = 1.2*U* of attached atom). All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors are contained in the SHELXTL-PLUS program library (4.2) (G. Sheldrick, Siemens Corp., Madison, WI). Tables II–IV contain the atomic coordinates and isotropic thermal parameters for **5**, **6**, and **3**, respectively.

Table III. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[B(3\text{-}Me_2pz)_4]_2Cd$

	x	*y*	*z*	*U*(eq)[a]
Cd	5000	5000	5000	33.50(9)
N(1)	7007(4)	5276(3)	4092(2)	42(1)
N(2)	7060(3)	6427(3)	3679(2)	29.5(8)
N(3)	6353(4)	7037(3)	5397(2)	37.1(9)
N(4)	6920(3)	7833(3)	4841(1)	27.4(7)
N(5)	3394(4)	6512(3)	4307(2)	36.3(9)
N(6)	4228(3)	7538(3)	3978(1)	27.8(7)
N(7)	6831(5)	8954(3)	2831(2)	50(1)
N(8)	6631(3)	8967(3)	3590(2)	30.1(8)
C(1)	7895(5)	4367(4)	3729(2)	44(1)
C(2)	8530(5)	4899(5)	3083(2)	46(1)
C(3)	7966(5)	6195(4)	3069(2)	38(1)
C(4)	7354(5)	7303(4)	6011(2)	43(1)
C(5)	8565(5)	8263(4)	5861(2)	45(1)
C(6)	8266(5)	8565(4)	5118(2)	38(1)
C(7)	1705(5)	6725(4)	4182(2)	41(1)
C(8)	1434(5)	7882(4)	3768(2)	47(1)
C(9)	3051(4)	8369(4)	3647(2)	39(1)
C(10)	6690(6)	10221(4)	2615(2)	56(1)
C(11)	6365(6)	11057(4)	3208(3)	51(1)
C(12)	6327(5)	10244(3)	3816(2)	44(1)
B(1)	6234(4)	7689(3)	4011(2)	26(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[B(pz)_4]_2Cd$

	x	*y*	*z*	*U*(eq)[a]
Cd	0	0	0	39.6(3)
N(1)	−1123(5)	250(6)	−1295(7)	47(3)
N(2)	−1439(5)	1275(7)	−1395(6)	41(3)
N(3)	−1277(5)	640(7)	827(6)	40(3)
N(4)	−1832(5)	1393(7)	366(6)	38(3)
N(5)	269(6)	1860(7)	−241(7)	49(3)
N(6)	−497(5)	2531(6)	−304(6)	38(3)
N(7)	−2315(5)	3808(7)	−235(7)	49(3)
N(8)	−2277(5)	2889(6)	−750(7)	43(3)
B(1)	−1501(7)	2027(8)	−528(9)	34(4)
C(1)	−1091(7)	−194(8)	−2188(9)	51(4)
C(2)	−1371(8)	618(9)	−2853(9)	54(4)
C(3)	−1569(8)	1502(10)	−2324(9)	54(4)
C(4)	−785(9)	−1319(10)	−2354(10)	72(5)
C(5)	−1764(7)	296(7)	1573(8)	46(4)
C(6)	−2640(7)	844(9)	1583(9)	56(4)
C(7)	−2650(7)	1524(9)	817(9)	54(4)
C(8)	−1370(10)	−526(11)	2240(11)	79(6)
C(9)	1052(7)	2464(8)	−42(8)	41(4)
C(10)	781(7)	3540(9)	−2(9)	50(4)
C(11)	−193(6)	3544(8)	−158(9)	49(4)
C(12)	2030(7)	1977(9)	90(11)	70(5)
C(13)	−3195(7)	4218(9)	−405(10)	60(5)
C(14)	−3744(8)	3546(10)	−1031(10)	60(4)
C(15)	−3153(7)	2708(10)	−1232(9)	51(4)
C(16)	−3464(8)	5258(10)	56(12)	87(6)
C(21)	3682(16)	1603(24)	2416(17)	81(7)
C(22)	3567	706	1823	130(15)
C(23)	4061	645	981	235(26)
C(24)	4670	1481	733	144(15)
C(25)	4785	2379	1326	74(8)
C(26)	4292	2439	2168	276(42)
C(27)	4394(63)	3355(69)	2460(56)	207(30)
C(21′)	4642(18)	1920(21)	1345(17)	103(11)
C(22′)	4995	2950	1551	93(10)
C(23′)	4676	3512	2337	136(18)
C(24′)	4003	3044	2917	93(10)
C(25′)	3650	2015	2711	101(19)
C(26′)	3970	1452	1925	109(11)
C(27′)	4180(90)	669(86)	1223(83)	198(61)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results

Syntheses of Complexes. The [poly(pyrazolyl)borato]$_2$Cd complexes **1**–**5** are readily prepared in water–THF using the

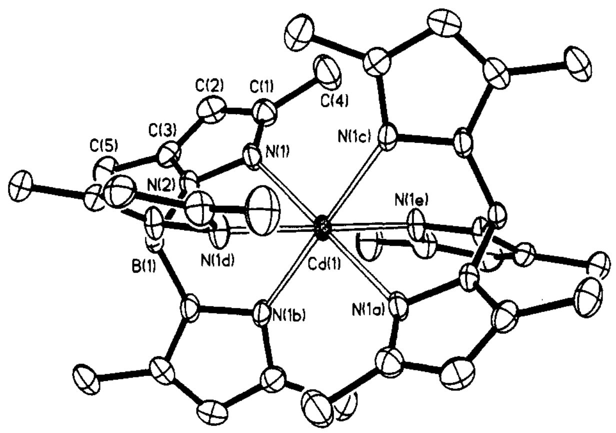


Figure 1. ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (**5**), with 35% thermal ellipsoids.

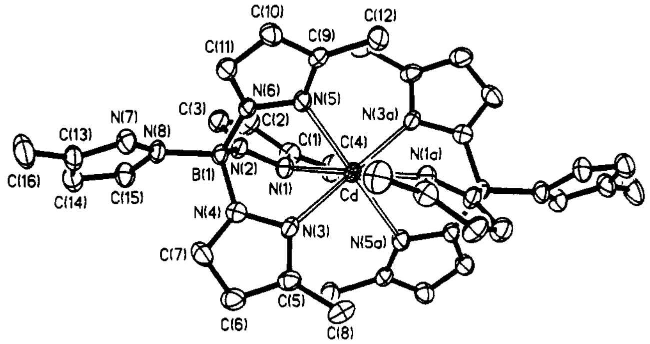


Figure 2. ORTEP drawing of $[B(3\text{-}Mepz)_4]_2Cd$ (**6**), with 35% thermal ellipsoids.

stoichiometry of eq 1 and are isolated in high yield by extraction

$$CdCl_2 + 2K[R_1R_2Bpz'_2] \longrightarrow Cd[R_1R_2Bpz'_2]_2 + 2KCl \quad (1)$$

1 $R_1 = R_2 = H$, pz' = 1-pyrazolyl
2 $R_1 = H$, R_2 = pz' = 1-pyrazolyl
3 $R_1 = R_2$ = pz' = 1-pyrazolyl
4 $R_1 = R_2 = H$, pz' = 3,5-Me_2-1-pyrazolyl
5 $R_1 = H$, R_2 = pz' = 3,5-Me_2-1-pyrazolyl
6 $R_1 = R_2$ = pz' = 3-Me-1-pyrazolyl

with CH_2Cl_2. Compounds **1**–**3** have been mentioned previously in the literature,[1b] but no NMR or structural data were reported. After submission of this paper, a preparation in water using 1/1 stoichiometry of a slightly impure sample (analytical data) of **5** was reported.[13] Although no yield of isolated product was given, our use of a mixed solvent system and the stoichiometry of eq 1 appear to be the preferred route for the preparation of **5**.

Compound **6** is prepared in THF. The mixed ligand complexes, **7** and **8**, are also prepared in THF (eq 2). In these reactions, a

$$CdCl_2 + K[HB(3,5\text{-}Me_2pz)_3] + K[R_1R_2Bpz_2] \longrightarrow [HB(3,5\text{-}Me_2pz)_3]Cd[R_1R_2Bpz_2] + 2KCl \quad (2)$$

7 $R_1 = R_2 = H$
8 $R_1 = R_2$ = pz

mixture of the [poly(pyrazolyl)borato]$_2$Cd and mixed-ligand complexes is isolated in statistical amounts in reactions run for 2 h, but in reactions run overnight, the mixed-ligand complexes are isolated, contaminated by a small amount of **5**.

Table V. Selected Bond Distances and Angles

	3	5	6
	Bond Distances (Å)		
Cd–N(1)	2.314(3)	2.348(5)	2.362(8)
Cd–N(3)	2.387(3)		2.308(8)
Cd–N(5)	2.284(3)		2.365(8)
N(1)–N(2)	1.370(4)	1.397(6)	1.352(11)
N(3)–N(4)	1.360(4)		1.357(11)
N(5)–N(6)	1.362(4)		1.353(11)
N(2)–B(1)	1.548(4)	1.533(6)	1.573(15)
N(4)–B(1)	1.553(4)		1.568(15)
N(6)–B(1)	1.559(4)		1.551(12)
N(1)··N(1b or 3)	2.981	3.103	3.033
N(1)··N(5)	3.101		3.110
N(3)··N(5)	2.977		3.076
	Bond Angles (deg)		
N(1)–Cd–N(1b or 3)	78.7(1)	82.7(1)	81.0(3)
N(1)–Cd–N(5)	84.8(1)		82.3(3)
N(3)–Cd–N(5)	79.1(1)		82.3(3)
N(1)–Cd–N(1a)	180.0(1)	180.0(1)	180.0(1)
N(3)–Cd–N(3a)	180.0(1)		180.0(1)
N(5)–Cd–N(5a)	180.0(1)		180.0(1)
N(1)–Cd–N(1c or 3a)	101.3(1)	97.3(1)	99.0(3)
N(1)–Cd–N(5a)	95.2(1)		97.7(3)
N(3)–Cd–N(5a)	100.9(1)		97.7(3)
Cd–N(1)–N(2)	121.0(2)	114.8(3)	113.8(6)
Cd–N(3)–N(4)	116.1(2)		115.6(6)
Cd–N(5)–N(6)	118.5(2)		118.7(6)
B(1)–N(2)–N(1)	117.4(3)	120.7(5)	121.3(8)
B(1)–N(4)–N(3)	122.0(3)		123.0(7)
B(1)–N(6)–N(5)	123.3(2)		117.7(7)
N(2)–B(1)–N(2a or 4)	108.1(2)	110.6(4)	110.9(8)
N(2)–B(1)–N(6)	109.6(2)		108.8(8)
N(4)–B(1)–N(6)	109.8(2)		109.6(8)

These cadmium complexes are air stable in both the solid and solution phases. They are soluble in aromatic or halocarbon solvents but only sparingly soluble in hydrocarbons.

Solid-State Structures. The structures of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (**5**), $[B(3\text{-}Mepz)_4]_2Cd\cdot 2C_7H_8$ (**6**), and $[B(pz)_4]_2Cd$ (**3**) have been determined crystallographically.

$[HB(3,5\text{-}Me_2pz)_3]_2Cd$. Figure 1 shows an ORTEP drawing of **5**, and Table V shows selected bond distances and angles. The complex is six-coordinate, and the geometry about the cadmium atom is a trigonally distorted octahedron. The cadmium atom sits on a center of inversion, and the planes formed by the three nitrogen donor atoms of each ligand are parallel. All Cd–N distances are equivalent at 2.348(5) Å. Intraligand N–Cd–N bond angles are all 82.7(1)°, and the interligand N–Cd–N bond angles are 97.3(1)° (cis) and 180(1)° (trans). Although the molecular geometry is quite symmetrical, there is an interesting canting of the pyrazolyl rings with respect to the B(1)··Cd··B(1a) axis, shown best in Figure 1 by the ring containing N(1d). This feature appears to be general for $[HB(3,5\text{-}Me_2pz)_3]_2M$ structures.[3b,14] The crystal structure of **5**, in which severe disorder problems were encountered, was just recently published.[13]

$[B(3\text{-}Mepz)_4]_2Cd\cdot 2C_7H_8$. Figure 2 shows an ORTEP drawing of **6**, and Table V shows selected bond distances and angles. As with **5**, the structure is a distorted octahedron in which the cadmium atom sits on a center of inversion. The structure is much less symmetrical, with three pairs of Cd–N distances ranging from 2.308(8) to 2.362(8) to 2.365(8) Å. The average Cd–N distance of 2.345(8) Å is the same as in complex **5**. The intraligand N–Cd–N angles are very similar, ranging from 81.0(3) to 82.3(3)°, with an average of 81.9°, similar to that observed with **5**. The interligand N–Cd–N angles are also very similar, ranging

---

[13] McWhinnie, W. R.; Monsef-Mirzai, Z.; Perry, M. C.; Shaikh, N.; Hamor, T. A. *Polyhedron* **1993**, *12*, 1193.

[14] (a) Oliver, J. D.; Mullica, D. F.; Hutchinson, B. B.; Milligan, W. O. *Inorg. Chem.* **1980**, *19*, 165. (b) Han, R.; Parkin, G. *J. Organomet. Chem.* **1990**, *393*, C43.

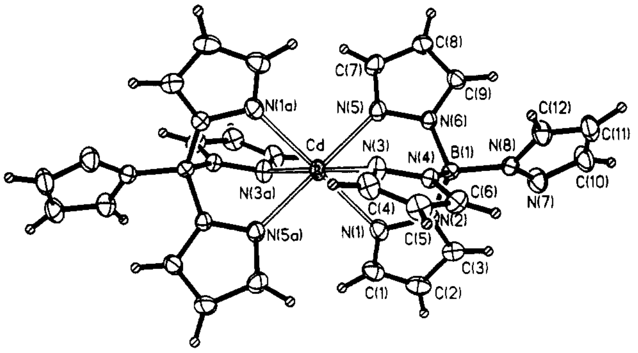


Figure 3. ORTEP drawing of $[B(pz)_4]_2Cd$ (**3**), with 35% thermal ellipsoids.

Table VI. ^{113}Cd NMR Chemical Shifts (ppm) versus 0.1 M $Cd(ClO_4)_2$

no.	compd	core	^{113}Cd soln chem shift
1	$[H_2B(pz)_2]_2Cd$	N_4	298.7
2	$[HB(pz)_3]_2Cd$	N_6	198.3
3	$[B(pz)_4]_2Cd$	N_6	221.1
4	$[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$	N_4	303.3
5	$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	N_6	201.9
6	$[B(3\text{-}Mepz)_4]_2Cd$	N_6	202.5
7	$[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$	N_5	225.1
8	$[HB(3,5\text{-}Me_2pz)_3]Cd[B(pz)_4]$	N_6	209.0

from 97.7(3) to 99.0(3)°, with an average of 98.1°, again similar to that observed with **5**.

$[B(pz)_4]_2Cd$. Figure 3 shows an ORTEP drawing of **3**, and Table V shows selected bond distances and angles. Again, the cadmium atom is located on an inversion center, but this structure is considerably less symmetrical than the structures of **5** and **6**. The three independent Cd–N bond lengths are 2.284(3), 2.314(3), and 2.387(3) Å (average = 2.328 Å). The shortest bond distance is 0.024 Å shorter than the shortest distance in **6**, and the longest is 0.022 Å longer than the longest distance in **6**. The bond angles also differ significantly, with intraligand angles ranging from 78.7(1) to 84.8(1)° (average = 80.9°) and interligand angles ranging from 95.2(1) to 101.3(1)° (average = 99.1°).

Cadmium-113 NMR. Table VI shows the ^{113}Cd chemical shifts for these compounds. The values are within the general range of chemical shifts expected for cadmium bonded to nitrogen donor atoms of 200–380 ppm versus 0.1 M $Cd(ClO_4)_2$.[15]

Trends in chemical shift versus coordination number are evident in the table. The four-coordinate complexes $[H_2B(pz)_2]_2Cd$ (**1**) and $[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$ (**4**) have chemical shifts of 298.7 and 303.3 ppm, very different from the others in the table. Complexes **3**, **5**, and **6**, shown to be six-coordinate in the solid state, and **2** which is also clearly six-coordinate, span a chemical shift range of 198.3–221.1 ppm. In this group, **3**, the complex with the greatest asymmetry in the solid state, is notably different at 221.1 ppm from the other three (average shift of 200.9 ppm). The mixed-ligand complex **8**, shown by variable-temperature NMR studies to also be six-coordinate (vide infra), has a shift of 209.0 ppm. Complex **7**, $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$, shown by variable-temperature NMR studies to be five-coordinate, has a shift of 225.1 ppm. This shift is very different from those of the four-coordinate **1** and **4** but not very different from those of the six-coordinate compounds, especially asymmetric **3**.

Variable-Temperature NMR Studies. It has been observed previously that many poly(pyrazolyl)borate complexes show dynamic behavior on the NMR time scale.[1,3] Because of the high symmetry of the octahedral complexes **2** and **5**, the rings are all equivalent and no such processes are expected or observed. In contrast, the other six complexes all have the potential to show fluxional behavior.

The $[B(3\text{-}Mepz)_4]_2Cd$ (**6**) complex shows a 3/1 ratio (three coordinated pyrazolyl rings and one free pyrazolyl ring for each ligand) of the resonances for each type of hydrogen atom at ambient temperature, as expected from the solid-state structure. At higher temperatures, each of the resonance types broadens and coalesces. The barrier is 18 kcal/mol at 94 °C, as measured on the most deshielded resonance.

In contrast to **6**, for $[B(pz)_4]_2Cd$ (**3**) all of the pyrazolyl rings are equivalent at ambient temperature. At –89 °C each type of hydrogen atom shows as two resonances in a 3/1 ratio. These resonances broaden and coalesce at higher temperatures. The barrier to the dynamic process is 9.7 kcal/mol, as measured at the coalescence temperature of –60 °C for the 4-H resonances.

The tetrahedral complex, **1**, has equivalent pyrazolyl rings, but because of the boat arrangement of the six-membered CdN_4B rings, the BH_2 hydrogen atoms are potentially nonequivalent. At ambient temperature, the resonance for these hydrogen atoms is broad due to quadrupolar coupling and relaxation effects from the boron atom, but at low temperatures the boron becomes self-decoupled from the hydrogen atoms, leading to sharper resonances.[16] At –61 °C, only a single BH_2 resonance is observed, a resonance that broadens slightly at –89 °C, the lowest temperature studied. The BH_2 region for compound **4** likewise shows a single resonance in the –62 °C spectrum.

At ambient temperature, for $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ (**7**) the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand shows equivalent pyrazolyl rings, and the two rings of the $[H_2B(pz)_2]^-$ ligand are equivalent. At –89 °C, each type of hydrogen atom of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand shows as two resonances in a 2/1 ratio. The barrier to the dynamic process is 10.0 kcal/mol, as measured at the coalescence temperature of –60 °C for the more shielded methyl resonances.

The resonances for the two rings of the $[H_2B(pz)_2]^-$ ligand remain equivalent at –89 °C, with no indication of resonance broadening, but the BH_2 hydrogen atoms appear as two resonances, separated by 209 Hz (Figure 4). These resonances coalesce at –46 °C with a measured barrier to the dynamic process of 10.4 kcal/mol.

For $[HB(3,5\text{-}Me_2pz)_3]Cd[B(pz)_4]$ (**8**), the three rings of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand show equivalent resonances at all temperatures studied (–89 to +27 °C). At low temperatures, each type of hydrogen atom in the four rings of the $[B(pz)_4]^-$ ligand appears as two resonances in a 3/1 ratio. These resonances broaden and coalesce above 0 °C. The barrier to the fluxional process is 14 kcal/mol as measured at 27 °C for the most deshielded hydrogen resonance.

Discussion

The structure of **5**, coupled with the previous structures of $[HB(3,5\text{-}Me_2pz)_3]_2M$ (M = Sn, Pb), allows a comparison of similar complexes in which one (Sn) has an active lone pair, one has an inactive lone pair (Pb), and one (Cd) has no lone pair on the central metal. The effect of the active lone pair in the tin complex, compared to **5**, is to change the coordination number from 6 to 5. The tin lone pair and the changes in geometry cause an increase in M–N bond lengths in comparison to those for the equally sized cadmium by an average of 0.112 Å. This increase in bond length is mainly due to an increase in the Sn–N bonds *cis* to the lone pair. In contrast, the structures of **5** and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ are isomorphous, with the bond lengths 0.262 Å longer in the lead complex, a distance essentially equal to the difference in size of cadmium(II) and lead(II).[9] ***The lone pair on lead does not cause significant differences in structure between the two compounds.***

---

[15] Summers, M. F. *Coord. Chem. Rev.* **1988**, *86*, 43.

[16] Harris, R. K. *Nuclear Resonance Spectroscopy*; Pitman: London, 1983; Chapter 3.

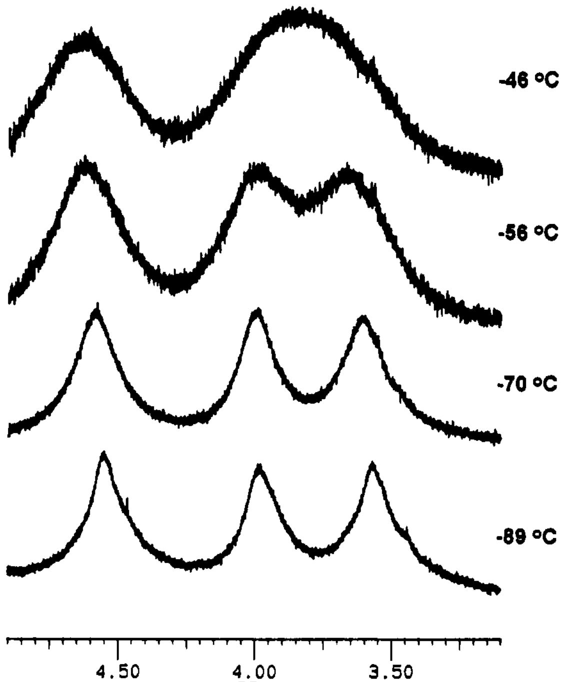
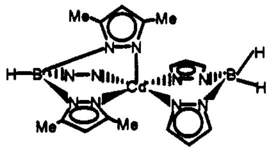


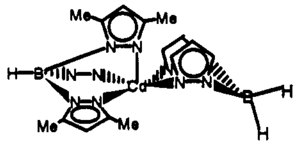
Figure 4. Variable-temperature ^{1}H NMR spectra of the BH resonances for [HB(3,5-Me$_2$pz)$_3$]Cd[H$_2$B(pz)$_2$]. The resonance on the left arises from the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand, and those on the right, from the [H$_2$B(pz)$_2$]$^-$ ligand.

There are no apparent features in the structures of **3** and **6** that account for the observed greater asymmetry in **3**. The free pyrazolyl ring in each ligand is expected to reduce the symmetry in comparison to **5**, but the ligand with the larger 3-methylpyrazolyl rings might have been expected to have the greater asymmetry. The fact that **3** shows a ^{113}Cd chemical shift that is different from the other six-coordinate complexes **2**, **5**, and **6** indicates that this asymmetry likely persists in solution. The similarity in the shifts of **3** and five-coordinate **7** also shows that solution ^{113}Cd NMR data are not sufficient, by themselves, to distinguish five- from six-coordination. The chemical shifts for **1** and **4** indicate that four-coordination versus higher coordination numbers can be assigned on the basis of solution ^{113}Cd NMR data. We are carrying out solid-state ^{113}Cd NMR studies to determine if those data are a more definitive measure of structure.

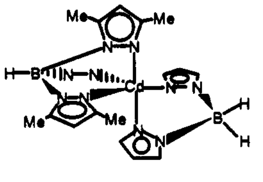
The mixed-ligand complex **7** shows two types of changes with temperature in its ^{1}H NMR spectra. The rings in the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand go to a 2/1 ratio at low temperatures, while the two rings of the [H$_2$B(pz)$_2$]$^-$ ligand remain equivalent. These data are best accounted for by square pyramidal structures, **A** and **B**, that differ only in the orientation of the boat configuration, conformations that are generally found for the six-membered CdN$_4$B ring in the [H$_2$B(pz)$_2$]$^-$ ligand. A trigonal bipyramidal structure **C** is ruled out because the rings of the [H$_2$B(pz)$_2$]$^-$ ligand would be nonequivalent. The equivalence of the these rings at low temperature also rules out a tetrahedral structure, **D**, in which one of the 3,5-Me$_2$pz rings is not coordinated to the metal. The ^{113}Cd chemical shift is 89.7 ppm different from that of four-coordinate **1** and also argues against a tetrahedral structure.



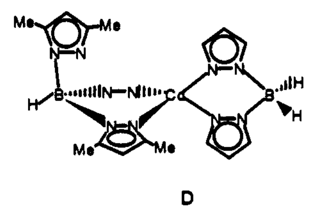
A



B



C



D

Two explanations are reasonable for the observed nonequivalence of the BH$_2$ resonances at low temperatures, resonances that coalesce with essentially the same barrier as the resonances of the rings in the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand. We previously interpreted the analogous freezing out of two BH$_2$ resonances in the variable-temperature spectra of [H$_2$B(pz)$_2$]$_2$Sn as being due to stopping the boat–boat flip of the SnN$_4$B ring,[3a] rendering the BH$_2$ hydrogen atoms nonequivalent because of their axial and equatorial orientations. A second interpretation of the data is possible based on the fact that in both of the compounds the BH$_2$ hydrogen atoms are nonequivalent *even if the boat–boat flip is fast on the NMR time scale* if the polyhedral structures of the compounds are not changing. For **7**, one of the BH$_2$ hydrogen atoms remains proximate to the unique 3,5-Me$_2$pz ring while the other is proximate to the bottom space in the square pyramid, even if the boat–boat flip equilibrates structures **A** and **B** rapidly. The nonequivalence at −89 °C of the rings in the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand demonstrates that the rearrangement of the polyhedral structure is slow on the NMR time scale at this temperature. At higher temperatures, the polyhedral structure must rearrange fast on the NMR time scale, causing equilibration of both the rings and the BH$_2$ hydrogen atoms, assuming the boat–boat flip is fast at these temperatures. The similarity of the barrier to the equilibration of the pyrazolyl rings and the BH$_2$ hydrogen atoms makes the polyhedral rearrangement process a reasonable mechanism to explain the dynamic behavior of both types of resonances.

The polyhedral rearrangement must involve the entire polyhedron. Simple rotation of the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand around the Cd···B axis, a process that would equilibrate the 3,5-Me$_2$pz rings, does not equilibrate the BH$_2$ hydrogen atoms. Examples of such a rotation have been observed with the [HB(pz)$_3$]$^-$ ligand in complexes such as [HB(pz)$_3$]ZrCl$_2$(OBu^t), but the analogous [HB(3,5-Me$_2$pz)$_3$]ZrCl$_2$(OBu^t) complex is static, presumably because the additional steric effects of the 3-methyl groups prevent such a rotation.[17]

In the tetrahedral structures of **1** and **4**, stopping the boat–boat flip is necessary to render the BH$_2$ hydrogen atoms nonequivalent. Little line broadening is observed for the single BH$_2$ resonances at low temperatures. Although these results show that the barrier for the boat–boat flip of the CdN$_4$B rings is likely to be less than ca. 8–9 kcal/mol for **1** and **4**, this barrier is not directly comparable to the situation for **7** discussed above, because the two arrangements of the ring, **A** and **B**, differ in energy, whereas in **1** and **4** they are degenerate.

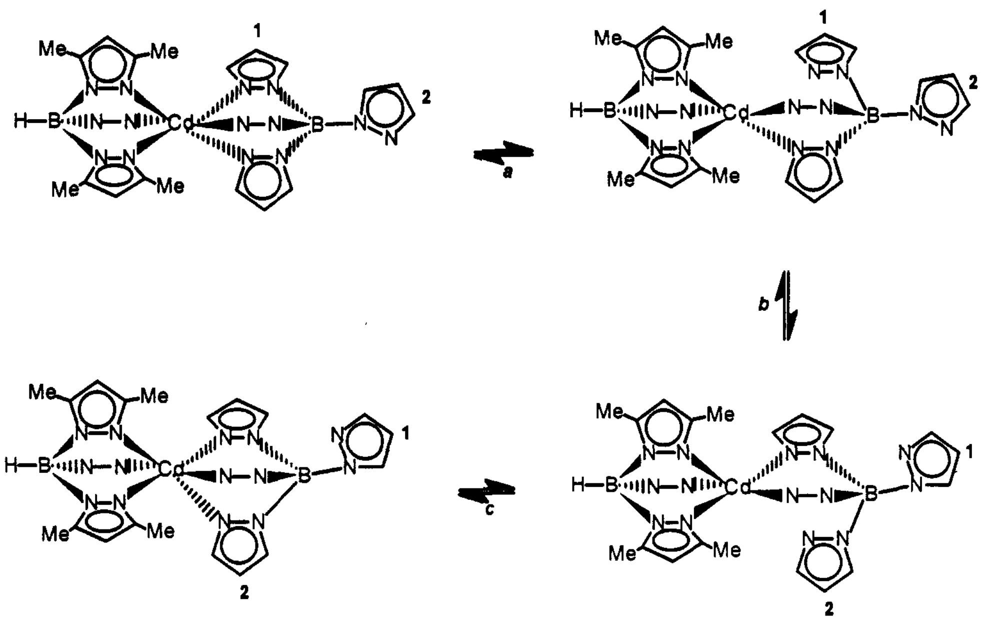
In contrast to **7**, the observation of equivalent 3,5-Me$_2$pz rings in **8** at all temperatures studied and the 3/1 pattern observed for the [B(pz)$_4$]$^-$ ligand below ambient temperatures indicate six-coordination for **8**, analogous to **2**, **3**, **5**, and **6**. If **8** were five-coordinate, analogous to **7**, it would be anticipated that the variable-temperature behaviors of the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligands would be similar for both, contrary to that observed.

In a six-coordinate structure for **3**, **6**, and **8**, equilibration of the rings of the tetrakis(pyrazolyl)borate ligand at higher temperatures occurs (as pictured for **8** in Scheme I) through rupture of the Cd–N bond for ring 1 (process a), a boat–boat flip (b), and coordination of ring 2 (c), which is now close to the cadmium atom. Given the low barrier for the boat–boat flip, the barriers (measured at different temperatures) of 9.7 kcal/mol

---

(17) Reger, D. L.; Tarquini, M. E. *Inorg. Chem.* **1983**, *22*, 1064.

Scheme I



for 3, 14 kcal/mol for 8, and 18 kcal/mol for 6 are a very rough measure of the energy needed to break the Cd–N bond.[18] The lower barrier for 3 versus 6 can be correlated with the solid-state structures, which show that one of the three Cd–N bond distances for 3 is considerably longer than those in 6.

The determination that the $[B(pz)_4]^-$ and $[B(3\text{-}Mepz)_4]^-$ ligands in 3, 6, and 8 show tridentate coordination is somewhat unexpected, given the bidentate coordination found in $[B(pz)_4]_2M$ (M = Sn, Pb) complexes. In the group 14 papers, we have argued that a driving force for bidentate coordination of the tetrakis(pyrazolyl)borate ligands is unfavorable intraligand steric interactions when the ligands are tridentate. Working with poly(pyrazolyl)borate complexes of group 2 metals, Sohrin and co-workers recently quantitated these unfavorable intraligand steric interactions by relating them to the bite size (intraligand N···N distances) of the ligand.[19] It was argued that because of these unfavorable intraligand steric interactions the tetrakis(pyrazolyl)borate ligands cannot readily accommodate intraligand N···N distances greater than 3.0 Å in *tridentate* coordination. The intraligand N···N distances for 3 range from 2.981 to 3.101 Å and for 6 range from 3.033 to 3.110 Å (they are 3.103 Å for 5). The fact that the tetrakis(pyrazolyl)borate ligands show tridentate coordination despite the relatively long N···N distances demonstrates that the *cadmium atom in these complexes clearly prefers six-coordination.*

Acknowledgment is made to the National Science Foundation (Grant CHE-9115158) and to the National Institutes of Health (Grant GM-26295) for support. The NSF (Grants CHE-8411172 and CHE-8904942) and NIH (Grant RR-02425) supplied funds to support the NMR equipment and the NIH (Grant RR-02849) supplies funds to support the mass spectrometry equipment at the University of South Carolina. We thank Dr. Paul S. Coan for valuable discussions on the interpretations of our variable-temperature NMR data.

Supplementary Material Available: Tables of complete data collection information, bond distances, bond angles, anisotropic thermal parameters, and positional parameters of H atoms (17 pages). Ordering information is given on any current masthead page.

---

(18) The strength of the C–H···Mo interaction in $[Et_2B(pz)_2]Mo(CO)_2(\eta^3\text{-allyl})$ complexes has been estimated previously from the barrier to a similar fluxional process: Cotton, F. A.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 5074.

(19) Sohrin, Y.; Koskusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4128.