Syntheses and Cadmium-113 NMR Studies of Five-Coordinate Complexes with CdN_5, CdN_3O_2, and CdN_3S_2 Central Cores. Solid State Structures of $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ and $[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$ (pz = Pyrazolyl)

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The reaction of $CdCl_2$ with equimolar amounts of $K[HB(3,5\text{-}Me_2pz)_3]$ (pz = pyrazolyl) and $K[H_2B(3,5\text{-}Me_2pz)_2]$ or $K[HB(3\text{-}Phpz)_3]$ and either $K[H_2B(pz)_2]$ or $K[H_2B(3,5\text{-}Me_2pz)_2]$ yields, respectively, the five-coordinate complexes $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**1**), $[HB(3\text{-}Phpz)_3]Cd[H_2B(pz)_2]$ (**2**), and $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**3**). The structure of **3** has been characterized in the solid state by X-ray crystallography. The complex has a square pyramidal arrangement of the nitrogen donor atoms about cadmium. Solution state ^1H NMR studies indicate that this geometry is retained in solution. Complexes **1**−**3** show solution ^{113}Cd NMR resonances in the range δ 193.6−224.3 ppm (vs $Cd(ClO_4)_2$). The complexes containing the $[HB(3\text{-}Phpz)_3]^-$ ligand have the more shielded resonances. This range overlaps the region observed for poly(pyrazolyl)borate complexes with CdN_6 inner cores (δ 94.0−221.1 ppm). Six complexes with a CdN_3O_2 inner core of the formula $[HB(3\text{-}Phpz)_3]Cd[(RCO)_2CH]$ (R = Bu^t, Ph, CF_3), $[HB(3\text{-}Bu^tpz)_3]Cd[(Bu^tCO)_2CH]$, $[B(3\text{-}Pr^ipz)_4]Cd[(Bu^tCO)_2CH]$, and $[HB(3\text{-}Bu^tpz)_3]Cd(CH_3CO_2)$ have been prepared by the reaction of $CdCl_2$ or $Cd(NO_3)_2$ and the appropriate ligand salts. These complexes show solution ^{113}Cd NMR resonances in the range δ 141.8−179.8 ppm, with the $[(Bu^tCO)_2CH]^-$ ligand complexes the most deshielded and $[HB(3\text{-}Phpz)_3]Cd[(CF_3CO)_2CH]$ the most shielded. Two complexes with N_3S_2 inner cores, $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ (**10**) and $[HB(3\text{-}Phpz)_3]Cd[Et_2NCS_2]$ (**11**), have been prepared. The structure of **10** has been determined by X-ray crystallography. The donor atoms are arranged about cadmium in an irregular five-coordinate geometry. Complex **10** shows a solution ^{113}Cd signal at δ 265.7 and **11** at 237.5 ppm. Crystal data: $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$, triclinic, $P\bar{1}$, $a = 11.713(3)$ Å $b = 12.785(3)$ Å, $c = 12.922(4)$ Å, $\alpha = 102.57(3)°$, $\beta = 104.53(3)°$, $\gamma = 91.83(4)°$, $V = 1821(9)$ Å^3, $Z = 2$, $T = 298$ K, $R(F) = 3.74\%$; $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$, monoclinic, $P2_1/c$, $a = 16.707(7)$ Å, $b = 8.197(5)$ Å, $c = 20.280(11)$ Å, $\beta = 111.06(4)°$, $V = 2584(5)$ Å^3, $Z = 4$, $T = 296$ K, $R(F) = 3.70\%$.

Introduction

We are interested in the preparation of cadmium coordination complexes in which the coordination sphere about the metal can be carefully controlled by choice of ligand. An important driving force for the development of this chemistry is the fact that cadmium has two important isotopes that are NMR active with spins = $^1/_2$. A number of research groups have been using ^{113}Cd NMR as a "spin spy" in the study of zinc-containing proteins.[1] The strategy here is to replace the zinc, a metal with few good spectroscopic handles, with cadmium and use NMR to explore structure/shielding relationships and how such relationships may be useful in uncovering structure and function correlations. We are interested in the preparation of monomeric complexes in which the primary donor atom set can be controlled in a systematic manner to aid in the interpretation of both the solution and solid state ^{113}Cd NMR data[2] on samples of biological interest.

We have previously reported the syntheses of a series of complexes containing the poly(pyrazolyl)borate family of ligands with CdN_6 and CdN_4 central cores, and one compound, $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$, with a CdN_5 central core.[3] The poly(pyrazolyl)borate ligands are ideally suited for the preparation of monomeric complexes in which the coordination sphere about a metal can be carefully controlled.[4] For the syntheses of mixed-ligand complexes using these ligands, Trofimenko has recently emphasized the importance of using ligands substituted with the moderately bulky groups to prevent the formation of

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L_2M complexes.[5] We have found that the $[HB(3,5\text{-}Me_2pz)_3]^-$ and $[HB(3\text{-}Phpz)_3]^-$ ligands are just bulky enough to allow the syntheses of mixed-ligand complexes of cadmium.[3a,6] The $[HB(3\text{-}Bu^tpz)_3]^-$ ligand (and its 5-Me substituted analog) has been shown previously to be useful in the syntheses of these types of complexes of cadmium.[2c,7] Reported here are the syntheses, characterizations, and solution state ^{113}Cd NMR chemical shifts of complexes containing one of these tridentate ligands and a monoanionic, bidentate ligand to prepare complexes that contain CdN_5, CdN_3O_2, and CdN_3S_2 central cores. Two of these complexes, $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ and $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ have been characterized in the solid state by X-ray crystallography.

Experimental Section

General Procedure. The ^1H NMR spectra were recorded on a Bruker AM300, AM400, or AM500 spectrometer using a 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 resonances, pz = pyrazolyl, Me_2pz = 3,5-dimethylpyrazolyl, Phpz = 3-phenylpyrazolyl, Bu^tpz = 3-*tert*-butylpyrazolyl and Pr^ipz = 3-isopropylpyrazolyl. Mass spectral data were recorded 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. Anhydrous $CdCl_2$, dipivaloylmethane (dpmH), dibenzoylmethane, (phacacH), and hexafluoroacetylacetone (hfacacH) were purchased from Aldrich Chemicals. $K[HB(3\text{-}Phpz)_3]$,[8] $K[B(3\text{-}Pr^i pz)_4]$,[9] $K[H_2B(pz)_2]$,[4b] $K[HB(3,5\text{-}Me_2pz)_3]$,[4c] $K[H_2B(3,5\text{-}Me_2pz)_2]$,[4c] and $Tl[HB(3\text{-}Bu^tpz)_3]$[8] were prepared according to published methods. $Na[(Bu^tCO)_2CH]$ and $Na[(CF_3CO)_2CH]$ were prepared by the published procedure.[10]

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

[Hydrotris(3,5-dimethyl-1-pyrazolyl)borato][dihydrobis(3,5-dimethyl-1-pyrazolyl)borato]cadmium(II), $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (1). $CdCl_2$ (0.18 g, 1.0 mmol), $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.24 g, 1.0 mmol), and $K[HB(3,5\text{-}Me_2pz)_3]$ (0.34 g, 1.0 mmol) were placed into a round bottom Schlenk flask. THF (40 mL) was added via syringe. The mixture was allowed to stir at room temperature overnight. THF was removed under vacuum. The product was then extracted with benzene and filtered. The benzene was removed to give a white solid (0.30 g) which contained less than 5% of each homoleptic complex, $[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$ and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$. ^1H NMR ($CDCl_3$), δ: 5.75, 5.67, 5.65 (s, s, s; 1, 2, 2; 4-H (Me_2pz)); 2.44, 2.35, 2.67, 1.97, 1.82, 1.77 (all s; 3, 6, 6, 3, 6, 6; CH_3 (Me_2pz)). Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{25}H_{37}N_{10}{}^{11}B_2{}^{114}Cd$, 613.2422; found, 613.2427.

[Hydrotris(3-phenyl-1-pyrazolyl)borato][dihydrobis(1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Phpz)_3]Cd[H_2B(pz)_2]$ (2). $CdCl_2$ (0.18 g, 1.0 mmol), $K[H_2B(pz)_2]$ (0.18 g, 1.0 mmol), and $K[HB(3\text{-}Phpz)_3]$ (0.48 g, 1.0 mmol) were placed into a round bottom Schlenk flask. THF (40 mL) was added via syringe. The mixture was allowed to stir at room temperature overnight. THF was removed under vacuum. The product was then extracted with toluene and filtered. The toluene was removed to give a white solid (0.85 g) which contained 5% of $[HB(3\text{-}Phpz)_3]_2Cd$ as indicated by ^1H NMR. ^1H NMR ($CDCl_3$), δ: 7.85 (3; d; $J = 2$ Hz; 5-H (Phpz)); 7.33, 7.30 (2, 2; d, d; $J = 2$ Hz; $J= 2$ Hz; 3,5-H (pz)); 6.95; (15, m; C_6H_5); 6.45 (3; $J = 2$ Hz; 4-H (Phpz)); 5.49 (2; t; $J = 2$ Hz; 4-H (pz)). Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{33}H_{30}N_{10}{}^{11}B_2{}^{114}Cd$, 702.1875; found, 702.1877.

[Dihydrobis(3,5-dimethyl-1-pyrazolyl)borato][hydrotris(3-phenyl-1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (3). $CdCl_2$ (0.18 g, 1.0 mmol), $K[H_2B(3,5\text{-}Me_2pz)_2]$ (0.24 g, 1.0 mmol), and $K[HB(3\text{-}Phpz)_3]$ (0.48 g, 1.0 mmol) were placed into a round bottom Schlenk flask. THF (40 mL) was added via syringe. The mixture was allowed to stir at room temperature overnight. THF was removed under vacuum. The product was then extracted with toluene and filtered. The toluene was removed to give a white solid (0.40 g, 53% yield); mp = 182−183 °C. ^1H NMR ($CDCl_3$), δ: 7.85 (3; d; $J = 1.8$ Hz; 5-H (Phpz)); 7.51, 7.18 (6, 9; br, br; C_6H_5) 6.47 (3; d; $J = 1.8$ Hz; 4-H (Phpz)); 5.01 (2; s; 4-H (Me_2pz)) 2.21, 1.02 (6, 6; s, s; CH_3 (Me_2pz)). ^1H NMR (CD_2Cl_2, −51 °C), δ: 7.86, 7.83 (1, 2; s, s; 5-H (Phpz)); 7.60−6.65 (15; complex series of resonances; C_6H_5); 6.52, 6.42 (1, 2; s, s; 4-H (Phpz)); 4.94 (2; s; 4-H (Me_2pz)); 2.18, 0.95 (6, 6; s, s; CH_3 (Me_2pz)). Mass spectrum (*m/z*): 756 (M^+). Anal. Calcd for $C_{37}H_{38}N_{10}B_2Cd$: C, 58.70; H, 5.03; N, 18.50. Found: C, 58.78; H, 4.93; N, 18.27.

[Dipivaloylmethanido][hydrotris(3-phenyl-1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$ (4). $Cd(NO_3)_2$ (0.24 g, 1.0 mmol), $K[HB(3\text{-}Phpz)_3]$ (0.48 g, 1.0 mmol), and Na(dpm) (0.23 g, 1.0 mmol) were all dissolved in THF (40 mL) in a round bottom Schlenk flask. The mixture was allowed to stir at room temperature overnight. The volatiles were removed in vacuo. The product was extracted with toluene and then filtered. The toluene was removed to give 0.42 g of a white solid which contained less than 5% of $[HB(3\text{-}Phpz)_3]_2Cd$. ^1H NMR ($CDCl_3$), δ: 7.79 (3; d; $J = 2.2$ Hz; 5-H (pz)); 7.61, 7.27 (6, 9; d of d, m; C_6H_5(pz)); 6.45 (3; d; $J = 2.3$ Hz; 4-H (pz)); 5.32 (1; s; CH (dpm)) 0.63 (18; s; Bu^t). Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{38}H_{41}N_6O_2{}^{11}B^{114}Cd$, 738.2418; found, 738.2427.

[Dibenzoylmethanido][hydrotris(3-phenyl-1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Phpz)_3]Cd[(PhCO)_2CH]$ (5). $CdCl_2$ (0.18 g, 1.0 mmol), phacacH, (0.25 g, 1.0 mmol), and $K[HB(3\text{-}Phpz)_3]$ (0.48 g, 1.0 mmol) were placed into a round bottom Schlenk flask. THF (40 mL) was added via syringe. Triethylamine (0.5 mL) was slowly added to the mixture. The mixture was allowed to stir at room temperature overnight. The volatiles were removed in vacuo. The product was then extracted with toluene and filtered. The toluene was removed to give a pale yellow solid (0.35 g) which was contaminated with less than 5% of $[HB(3\text{-}Phpz)_3]_2Cd$. ^1H NMR ($CDCl_3$), δ: 7.99 (4; d; $J = 7.2$ Hz; C_6H_5 (phacac)); 7.82 (3; d; $J = 2.2$ Hz; 5-H (pz)); 7.68 (6; d; C_6H_5 (Phpz)); 7.50−7.30 (6; m; C_6H_5 (phacac)) 7.18−7.07 (9; m; C_6H_5 (Phpz)); 6.87 (1; s; *CH* (phacac)); 6.46 (3; d; $J = 2.2$ Hz; 4-H (Phpz)). Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{42}H_{33}N_6O_2{}^{11}B^{114}Cd$, 778.1792; found, 778.1805.

[Hexafluoroacetylacetonato][hydrotris(3-phenyl-1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Phpz)_3]Cd[(CF_3CO)_2CH]$ (6). This compound was prepared on a 1.0 mmol scale in the same manner as prescribed for **4** (0.34 g). The product was isolated with less than 5% of $[HB(3\text{-}Phpz)_3]_2Cd$ as indicated by ^1H NMR. ^1H NMR ($CDCl_3$), δ: 7.82 (3; d; $J = 2.2$ Hz; 5-H (Phpz)); 7.54−7.52 (15; m; C_6H_5); 6.44 (3; d; $J = 2.3$; 4-H (Phpz)); 5.53 (1; s; CH (hfacac)). Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{32}H_{23}F_6N_6O_2{}^{11}B^{114}Cd$, 762.0913; found, 762.0899.

[Dipivaloylmethanido][hydrotris(3-*tert*-butyl-1-pyrazolyl)borato]cadmium(II), $[HB(3\text{-}Bu^tpz)_3]Cd[(Bu^tCO)_2CH]$ (7). $CdCl_2$ (0.18 g, 1.0 mmol), Na(dpm) (0.23 g, 1.0 mmol), and $Tl[HB(3\text{-}Bu^tpz)_3]$ (0.59 g, 1.0 mmol) were all dissolved in THF (40 mL) in a round bottom Schlenk flask. The mixture was allowed to stir at room temperature overnight. The volatiles were removed in vacuo. The product was extracted with toluene and then filtered. The toluene was removed to give a white solid in 48% yield. ^1H NMR ($CDCl_3$), δ: 7.49 (3; d; $J = 1.9$ Hz, 5-H (pz)); 6.03 (3; d; $J = 2.0$ Hz, 4-H (pz)); 5.67 (1; s; CH

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Table 1. Crystallographic Data for $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**3**) and $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ (**10**)

	3	**10**
formula	$C_{37}H_{38}B_2CdN_{10}$	$C_{20}H_{32}BCdN_7S_2$
fw	756.8	557.9
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	11.713(3)	16.707(7)
b (Å)	12.785(3)	8.197(5)
c (Å)	12.922(4)	20.280(11)
α (deg)	102.57(3)	
β (deg)	104.53(3)	111.06(4)
γ (deg)	91.83(4)	
V (Å^3)	1821(9)	2584(5)
Z	2	4
T (K)	298	296
λ (Å)	0.710 73	0.710 73
ϱ_{calcd} (g/cm^3)	1.380	1.434
R(F)^a (%)	3.74	3.70
$R_w(F)^a$ (%)	4.81	4.80

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

(dpm)); 1.3–1.1 (45; m; Bu^t). Accurate mass spectrum (*m/z*) for M$^+$: calcd for $C_{32}H_{53}N_6O_2{}^{11}B^{114}Cd$, 678.3357; found, 678.3365.

[Dibenzoylmethanido][tetrakis(3-isopropyl-1-pyrazolyl)borato]cadmium(II), [B(3-Pr^{i}pz)$_4$]Cd[(Bu^{t}CO)$_2$CH] (8). This compound was prepared on a 1.0 mmol scale in the same manner as prescribed for **4**. As indicated by ^{1}H NMR, the product was isolated with less than 5% of $[HB(3\text{-}Pr^ipz)_3]_2Cd$. ^{1}H NMR (CDCl$_3$), *δ*: 7.50 (4; s; 5-H (Pr^{i}pz)); 6.05 (4; s; 4-H (Pr^{i}pz)); 5.72 (1; s; CH (dpm)); 3.24 (4; m; CH (Pr^i-pz)); 1.18–1.03 (42; m; Bu^t; Pr^i). Accurate mass spectrum (*m/z*) for M$^+$: calcd for $C_{39}H_{34}N_{14}O_2{}^{11}B_2{}^{114}Cd$, 834.2311; found, 834.2302.

[Acetato][hydrotris(3-*tert*-butyl-1-pyrazolyl)borato]cadmium(II), [HB(3-Bu^{t}pz)$_3$]Cd[CH$_3$CO$_2$] (9). $Cd[CH_3CO_2]_2{\cdot}2H_2O$ (0.27 g, 1.0 mmol) and $Tl[HB(3\text{-}Bu^tpz)_3]$ (0.59 g, 1.0 mmol) were charged into a round bottom Schlenk flask. CH_2Cl_2 (25 mL) was added via syringe. The mixture was allowed to stir at room temperature for 4 h. The solvent was then evaporated at reduced pressure. After extracting with benzene, the mixture was filtered. This solid was recrystallized in toluene at −20° (0.20 g, 0.36 mmol, 36%); dec pt 175–178 °C. ^{1}H NMR (CDCl$_3$), *δ*: 7.54, 6.04 (3, 3; d, d; *J* = 2.1 Hz; 4,5-H(pz)); 2.18 (3; s; CH$_3$CO$_2$); 1.33 (27; s; Bu^{t}pz). Accurate mass spectrum (*m/z*) for M$^+$: calcd for $C_{23}H_{37}N_6O_2{}^{11}B^{114}Cd$, 554.2105; found, 554.2098. Anal. Calcd for $C_{23}H_{37}N_6O_2BCd$: C, 49.96; H, 6.76; N, 15.20. Found: C, 49.48; H, 6.56; N, 15.03.

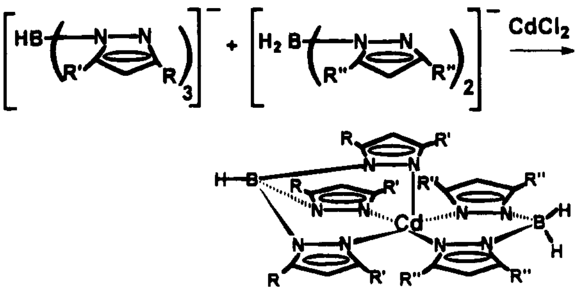
[Diethyldithiocarbamato][hydrotris(3,5-dimethyl-1-pyrazolyl)borato] cadmium(II), [HB(3,5-Me$_2$pz)$_3$]Cd[Et$_2$NCS$_2$] (10). CdCl$_2$ (0.20 g, 1.1 mmol), $K[HB(3,5\text{-}Me_2pz)_3]$ (0.37 g, 1.1 mmol), and $Na[S_2CNEt_2]{\cdot}3H_2O$ (0.25 g, 1.1 mmol) were charged into a flask along with 25 mL of THF. The yellow solution was stirred overnight. The THF was removed under vacuum and the product extracted with benzene (25 mL). The solution was filtered and the benzene removed under vacuum to leave a yellow solid (0.57 g, 1.0 mmol, 94%); dec pt = 245–253 °C. ^{1}H NMR (CDCl$_3$), *δ*: 5.71 (3; s; 4-H (Me$_2$pz)); 3.95 (4; q; *J* = 7.1 Hz; CH$_2$); 2.35, 2.33 (9, 9; s, s; CH$_3$ (Me$_2$pz)); 1.35 (6; t; *J* = 7.1 Hz; CH$_2$C*H*$_3$). ^{13}C NMR (CDCl$_3$), *δ*: 200.9 (S$_2$*C*N); 149.7, 145.2 (3,5-C (Me$_2$pz)); 105.5 (4-C(Me$_2$pz)); 51.5 (CH$_2$); 14.0, 13.3 (CH$_3$ (Me$_2$pz)); 12.6 (CH$_2$*C*H$_3$). Mass spectrum (*m/z*): 559 (M$^+$); 462 (M$^+$ − Me$_2$pz). Anal. Calcd for $C_{20}H_{32}N_7BCdS_2$: C, 43.06; H, 5.79; N, 17.58. Found: C, 43.16; H, 5.71; N, 17.37. Cryoscopic molecular weight (benzene),[2b] calcd formula weight 558 (observed molality, observed molecular weight): 0.0310, 536; 0.0316, 527.

[Diethyldithiocarbamato][hydrotris(3-phenyl-1-pyrazolyl)borato]cadmium(II), [HB(3-Phpz)$_3$]Cd[Et$_2$NCS$_2$] (11). This compound was prepared on a 1.0 mmol scale in the same manner as compound **10** (0.45 g). Impurities of $\{[Et_2NCS_2]_2Cd\}_2$ (10%) were detected by ^{1}H NMR and could not be removed. ^{1}H NMR (CDCl$_3$), *δ*: 7.77 (3; m; 5-H (Phpz)); 7.37–7.26 (15; m; C$_6$H$_5$); 6.41(3; d; *J* = 1.2; 4-H (Phpz)); 3.56 (4; q; *J* = 7.15 Hz; C*H*$_2$CH$_3$); 1.06 (6; t; *J* = 7.06; CH$_2$C*H*$_3$). Accurate mass spectrum (*m/z*) for M$^+$: calcd for $C_{32}H_{32}N_7S_2{}^{11}B^{114}Cd$ 703.1287; found, 703.1277.

Structural Determinations for 3 and 10. Crystallographic data are collected in Table 1. Both samples were mounted on glass fibers and photographically characterized. **3** was found to possess no symmetry higher than triclinic; the centrosymmetric space group $P\bar{1}$ was assumed initially and later verified by the results of refinement. **10** revealed 2/*m* Laue symmetry; the space group was uniquely defined by systematic absences in the reflection data. No corrections for absorption were required for either crystal (for both the value of the maximum/minimum transmission ratio was less than 1.1). Both structures were solved by heavy-atom methods. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized contributions. All computations used the SHELXTL software libraries (G. Sheldrick, version 4.2, Siemens XRD, Madison, WI).

Results and Discussion

Syntheses of Complexes. The reaction of either of the tridentate ligands $[HB(3,5\text{-}Me_2pz)_3]^-$ and $[HB(3\text{-}Phpz)_3]^-$, either of the bidentate ligands $[H_2B(pz)_2]^-$ and $[H_2B(3,5\text{-}Me_2pz)_2]^-$, and CdCl$_2$, all in equimolar amounts, yields the respective five-coordinate complex containing a CdN$_5$ central core (eq 1). The preparation of $[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$ was reported earlier.[3] In these reactions, some of the homoleptic complexes, [poly(pyrazolyl)borate]$_2$Cd, are also formed. It did not prove possible to separate a small amount of $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ from **1**, and $[HB(3\text{-}Phpz)_3]_2Cd$ from **2**, but complex **3** is readily isolated in pure crystalline form.

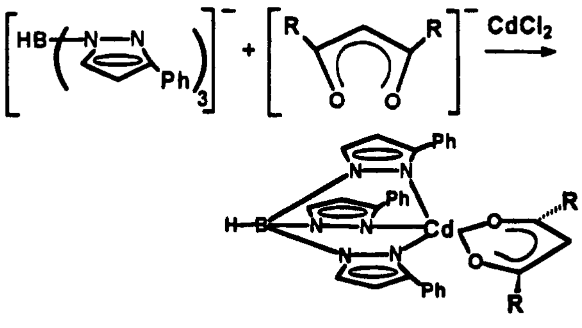


(1)

R = R' = R'' = Me, *1*
R = Ph, R' = R'' = H, *2*
R = Ph, R' = H, R'' = Me, *3*

The coordination geometry for complexes **1** and **3** can be assigned from solution state ^{1}H NMR data. At ambient temperature for **1** and at −51 °C for **3**, each type of hydrogen atom in the hydrotris(pyrazolyl)borate ligand appears in a 2:1 integrated ratio. Each type of hydrogen atom in the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand is equivalent. Two limiting geometries are reasonable for these complexes. As pictured in eq 1, in a square-based pyramidal arrangement (the structure observed in the solid state for **3**, vide infra), a 2:1 ratio is expected for the hydrotris(pyrazolyl)borate ligand because two rings are in the basal plane and the third in an axial position. The pyrazolyl rings of the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand are equivalent in this geometry. In a trigonal bipyramidal geometry, the hydrotris(pyrazolyl)borate ligand would occupy two equatorial and one axial site and the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand would occupy an axial and equatorial site. In this arrangement, a 2:1 ratio of the pyrazolyl ring resonances is predicted for the hydrotris(pyrazolyl)borate ligand, as observed, but a 1:1 ratio of the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand is predicted for this geometry. The observation of equivalent rings in ^{1}H NMR spectra for this ligand indicates the square-based pyramidal geometry observed in the solid state for **3** is retained in solution. Complex **2** is likely to have a similar geometry, but is fluxional, even at low temperatures. We have observed previously that substitution of the pyrazolyl rings substantially increases the barriers to dynamic rearrangement processes.[11]

The reaction of $[HB(3\text{-}Phpz)_3]^-$, either of the two Na salts of the diketonate ligands $[(RCO)_2CH]^-$ (R = Bu^t, CF_3) and $CdCl_2$ in equimolar amounts yields the respective five-coordinate complex containing a CdN_3O_2 core (eq 2). In situ deprotonation of $(PhCO)_2CH_2$, using triethylamine, and the use of $Cd(NO_3)_2$ as the cadmium starting material were required for the preparation of $[HB(3\text{-}Phpz)_3]Cd[(PhCO)_2CH]$ (**5**). Along with the desired CdN_3O_2 complexes, a small amount of an impurity of $[HB(3\text{-}Phpz)_3]_2Cd$ forms in these reactions. This impurity could not be removed because all efforts, to date, to crystallize these complexes lead to the precipitation of $[HB(3\text{-}Phpz)_3]_2Cd$.



(2)

R = Bu^t, 4
R = CF$_3$, 6

The solution phase structures of **4**, **5**, and **6** cannot be assigned by ^1H NMR spectroscopy. At ambient temperature, these complexes show single resonances in ^1H NMR spectra for each type of hydrogen atom in the $[HB(3\text{-}Phpz)_3]^-$ and diketonate ligands. Even at low temperatures, no line broadening was observed.

Two additional complexes of the $[(Bu^tCO)_2CH]^-$ ligand with this central core were prepared by reaction of $Tl[HB(3\text{-}Bu^tpz)_3]$ or $K[B(3\text{-}Pr^ipz)_4]$, $Na[(Bu^tCO)_2CH]$, and $CdCl_2$ (eqs 3 and 4).

$$[HB(3\text{-}Bu^tpz)_3]^- + [(Bu^tCO)_2CH]^- \xrightarrow{CdCl_2} [HB(3\text{-}Bu^tpz)_3]Cd[(Bu^tCO)_2CH] \quad (3)$$

7

$$[B(3\text{-}Pr^ipz)_4]^- + [(Bu^tCO)_2CH]^- \xrightarrow{CdCl_2} [B(3\text{-}Pr^ipz)_4]Cd[(Bu^tCO)_2CH] \quad (4)$$

8

As with the other CdN_3O_2 complexes, the solution room and low temperature ^1H NMR spectra show single resonances for each type of hydrogen atom in the $[HB(3\text{-}Bu^tpz)_3]^-$ or $[B(3\text{-}Pr^ipz)_4]^-$ and $[(Bu^tCO)_2CH]^-$ ligands.

One additional complex with a CdN_3O_2 central core, $[HB(3\text{-}Bu^tpz)_3]Cd(CH_3CO_2)$ (**9**) was also prepared by reaction of $Cd(CH_3CO_2)_2$ and equal amounts of $Tl[HB(3\text{-}Bu^tpz)_3]$ (eq 5).

$$Tl[HB(3\text{-}Bu^tpz)_3] + Cd(CH_3CO_2)_2 \rightarrow [HB(3\text{-}Bu^tpz)_3]Cd[CH_3CO_2] + Tl(CH_3CO_2) \quad (5)$$

9

The structure of this complex cannot be deduced by NMR, but it is very likely to be similar to the structure of $[HB(3\text{-}Bu^t\text{-}5\text{-}Mepz)_3]Cd(NO_3)$, previously reported in the solid state.[7]

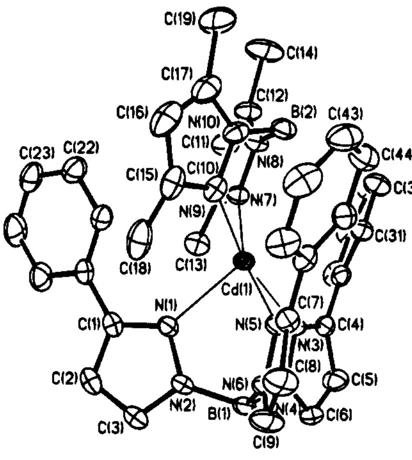
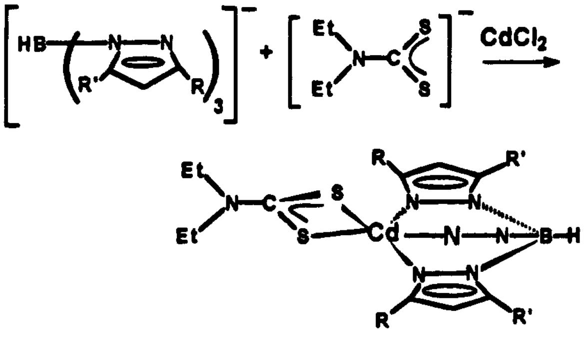


Figure 1. ORTEP diagram of $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**3**).

Complexes with a N_3S_2 inner core were prepared by the reaction of either $[HB(3,5\text{-}Me_2pz)_3]^-$ or $[HB(3\text{-}Phpz)_3]^-$, $[Et_2NCS_2]^-$, and $CdCl_2$ (eq 6). Complex **10** was purified by extractions followed by recrystallization techniques, while **11** retains small amounts of $\{[Et_2NCS_2]_2Cd\}_2$. Molecular weight studies show that **10** is monomeric in benzene solution. As observed with **4**-**6**, at ambient and low temperatures, these complexes show single resonances in ^1H NMR spectra for each type of hydrogen atom in the poly(pyrazolyl)borate and $[Et_2NCS_2]^-$ ligands.



(6)

R = R' = Me, 10
R = Ph, R' = H, 11

Solid State Structures. Figure 1 shows an ORTEP diagram of $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ and Table 4 shows selected bond distances and angles. The cadmium is five-coordinate with a surprisingly regular square pyramidal arrangement of the CdN_5 core. The donor nitrogen atoms of the bidentate $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand and N(3) and N(5) of the tridentate ligand make up the square plane. Deviations from the square plane are regular; N(3) and N(9) are displaced 0.015 Å toward the cadmium atom and N(5) and N(7) away by the same amount. The cadmium atom sits 0.30 Å above the plane. The N−Cd−N angles of adjacent donor atoms in the plane range from 81.7(1) to 97.0°. The largest deviation from the regular geometry is caused by the chelate ring of the tridentate ligand restraining the axial intraligand angles to an average of 85.8° and increasing the axial interligand angles to an average of 108.5°.

The Cd−N distances for the $[HB(3\text{-}Phpz)_3]^-$ ligand are fairly similar and average 2.34 Å, shorter than the average 2.39 Å distance observed in two six-coordinate complexes of this ligand, $[HB(3\text{-}Phpz)_3]_2Cd$ and $[HB(3\text{-}Phpz)_3]Cd[B(pz)_4]$.[6] The Cd−N distance in the bidentate ligand average 2.25 Å, shorter than observed for the tridentate ligand. We have previously noted in the mixed-ligand structure of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ that the bidentate ligand had the shorter M−N bond

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

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$

	x	*y*	*z*	*U*(eq)[a]
Cd(1)	2414.7(2)	1907.4(2)	2603.5(2)	39.9(1)
B(1)	4460(4)	360(4)	2083(4)	49(2)
B(2)	177(5)	3226(4)	2291(4)	58(2)
N(l)	4114(3)	1552(3)	3812(3)	46(1)
N(2)	4805(3)	889(3)	3307(3)	48(1)
N(3)	2231(3)	70(3)	1854(3)	44(1)
N(4)	3271(3)	−334(3)	1739(3)	47(1)
N(5)	3565(3)	1911(3)	1325(3)	45(1)
N(6)	4423(3)	1210(3)	1412(3)	51(1)
N(7)	919(3)	1920(3)	3414(3)	44(1)
N(8)	74(3)	2592(3)	3151(3)	50(1)
N(9)	2366(3)	3693(3)	2844(3)	50(1)
N(10)	1269(3)	4060(3)	2757(3)	54(1)
C(1)	4663(3)	1838(3)	4889(3)	50(2)
C(2)	5725(4)	1361(4)	5074(4)	67(2)
C(3)	5774(4)	773(4)	4069(4)	64(2)
C(4)	1426(3)	−753(3)	1608(3)	47(2)
C(5)	1940(4)	−1706(4)	1333(5)	72(2)
C(6)	3091(4)	−1398(3)	1417(4)	61(2)
C(7)	3890(3)	5609(3)	793(3)	49(2)
C(8)	4955(4)	2362(5)	561(4)	75(2)
C(9)	5248(4)	1482(5)	948(4)	76(2)
C(10)	644(4)	1456(3)	4154(3)	48(2)
C(11)	−387(4)	1826(4)	4367(4)	68(2)
C(12)	−721(4)	2535(4)	3733(4)	63(2)
C(13)	1403(4)	674(4)	4620(4)	65(2)
C(14)	−1791(5)	3153(6)	3619(6)	110(4)
C(15)	3161(5)	4546(4)	3230(4)	67(2)
C(16)	2566(7)	5459(4)	3399(5)	90(3)
C(17)	1394(6)	5129(4)	3107(4)	78(3)
C(18)	4448(5)	4407(5)	3423(4)	89(3)
C(19)	368(7)	5772(5)	3141(7)	128(4)
C(21)	3310(3)	3205(2)	5416(2)	60(2)
C(22)	2822	3796	6214	73(2)
C(23)	3170	3675	7292	81(2)
C24	4008	2962	7573	96(3)
C(25)	4497	2372	6776	78(2)
C(26)	4148	2493	5697	50(2)
C(31)	−419(3)	154(2)	1231(3)	60(2)
C(32)	−1593	244	1269	88(3)
C(33)	−2137	−454	1732	108(3)
C(34)	−1507	−1242	2157	97(3)
C(35)	−333	−1332	2119	75(2)
C(36)	211	+634	1657	51(2)
C(41)	3741(2)	4459(2)	536(3)	70(2)
C(42)	3070	5278	231	87(3)
C(43)	1837	5114	−91	83(3)
C(44)	1274	4130	−107	73(2)
C(45)	1944	3310	197	56(2)
C(46)	3178	3475	519	51(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

distances.[12] The average Cd−N bond distance of the bidentate dihydrobis(pyrazolyl)borate ligand in four-coordinate $[H_2B(pz)_2]_2Cd$ is 2.21 Å.[3b]

An interesting structural feature of **3** is the orientation of the 3-position methyl groups on the $[H_2B(3,5\text{-}Me_2pz)_2]^-$ ligand. They are each oriented over a phenyl group of the $[HB(3\text{-}Phpz)_3]^-$ ligand. Interaction of the hydrogen atoms of these methyl groups with the aromatic ring currents of the phenyl groups is evident in the ^1H NMR spectrum of **3** where these resonances are more shielded by ca 1 ppm than is normally observed.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$

	x	*y*	*z*	*U*(eq)[a]
Cd(1)	7333.0(2)	795.8(3)	1728.6(1)	34.1(1)
S(1)	5779(1)	1934(2)	1649(1)	45(1)
S(2)	7168(1)	629(2)	2924(1)	49(1)
B(1)	8490(3)	470(5)	732(2)	35(2)
N(1)	7025(2)	−574(4)	683(2)	39(1)
N(2)	7634(2)	−475(4)	377(2)	37(1)
N(3)	8689(2)	−406(4)	1987(2)	37(1)
N(4)	9013(2)	−325(4)	1452(2)	39(1)
N(5)	7924(2)	2785(4)	1290(2)	37(1)
N(6)	8319(2)	2304(4)	831(2)	36(1)
N(7)	5669(2)	1734(4)	2926(2)	37(1)
C(1)	6390(3)	−1525(5)	269(2)	43(1)
C(2)	6587(3)	−2033(6)	−310(2)	49(2)
C(3)	7373(3)	−1368(5)	−225(2)	43(2)
C(4)	5628(3)	−1921(7)	454(3)	62(2)
C(5)	7886(3)	−1529(8)	−693(3)	67(2)
C(6)	9267(3)	−1220(5)	2527(2)	46(2)
C(7)	9958(3)	−1679(6)	2339(3)	55(2)
C(8)	9787(3)	−1120(5)	1668(3)	46(2)
C(9)	9139(3)	−1508(8)	3205(3)	71(2)
C(10)	10302(3)	−1311(8)	1200(3)	77(3)
C(11)	7934(3)	4426(5)	1304(3)	44(2)
C(12)	8313(3)	5015(6)	849(3)	55(2)
C(13)	8549(3)	3668(6)	557(2)	46(2)
C(14)	7565(4)	5322(7)	1770(3)	72(3)
C(15)	8963(3)	3602(7)	15(3)	66(2)
C(16)	5950(3)	1228(6)	3673(2)	48(2)
C(17)	6403(3)	2573(8)	4172(3)	74(2)
C(18)	4808(3)	2526(5)	2637(2)	43(2)
C(19)	4083(3)	1315(6)	2392(3)	63(2)
C(20)	6147(2)	1480(5)	2536(2)	34(1)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Bond Parameters for $[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$ (**3**) and $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ (**10**)

	3	**10**
(a) Bond Distances (A)		
Cd(1)−N(1)	2.327(3)	2.288(4)
Cd(1)−N(3)	2.319(3)	2.351(4)
Cd(1)−N(5)	2.381(4)	2.249(4)
Cd(1)−N(7)	2.254(4)	
Cd(1)−N(9)	2.241(3)	
Cd(1)−S(1)		2.708(2)
Cd(1)−S(2)		2.540(2)
N(1)···N(3)	3.115(5)	3.074(5)
N(3)···N(5)	3.075(5)	3.029(5)
N(1)···N(5)	3.253(5)	3.166(5)
N(7)···N(9)	3.108(5)	
(b) Bond Angles (deg)		
N(1)−Cd(1)−N(3)	84.2(1)	83.0(1)
N(1)−Cd(1)−N(5)	87.4(1)	88.5(1)
N(1)−Cd(1)−N(7)	108.0(1)	
N(1)−Cd(1)−N(9)	108.9(1)	
N(3)−Cd(1)−N(5)	81.7(1)	82.4(1)
N(3)−Cd(1)−N(7)	97.0(1)	
N(3)−Cd(1)−N(9)	164.1(1)	
N(5)−Cd(1)−N(7)	164.3(1)	
N(5)−Cd(1)−N(9)	89.8(1)	
N(7)−Cd(1)−N(9)	87.5(1)	
N(1)−Cd(1)−S(1)		102.9(1)
N(1)−Cd(1)−S(2)		142.4(1)
N(3)−Cd(1)−S(1)		169.8(1)
N(3)−Cd(1)−S(2)		101.0(1)
N(5)−Cd(1)−S(1)		105.9(1)
N(5)−Cd(1)−S(2)		129.1 (1)
S(1)−Cd(1)−S(2)		69.2(1)

Figure 2 shows an ORTEP diagram of $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ and Table 4 shows selected bond distances and angles. The cadmium is five-coordinate with an irregular arrangement of the CdN_3S_2 core. The dithiocarbamate ligand is anisobidentate having one long (2.708(2) Å) and one short

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(12) Reger, D. L.; Mason, S. S.; Reger, L. B.; Rheingold, A. L.; Ostrander, R. L. *Inorg. Chem.* **1994**, *33*, 1811.

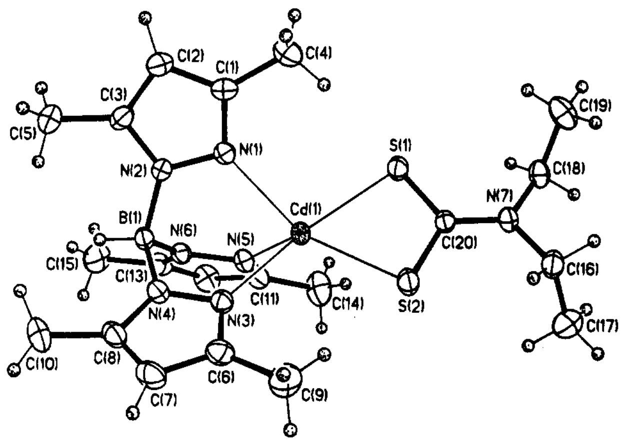

Figure 2. ORTEP diagram of $[HB(3,5\text{-}Me_2pz)_3]Cd[Et_2NCS_2]$ (**10**).

Table 5. 113-Cd Chemical Shifts versus $Cd(ClO_4)_2$

core	compound	^{113}Cd shift
N_4	$[H_2B(pz)_2]_2Cd$	298.7
	$[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$	303.3
N_5	$[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(pz)_2]$	225.1
	$[HB(3\text{-}Phpz)_3]Cd[H_2B(pz)_2]$	205.7
	$[HB(3,5\text{-}Me_2pz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$	224.3
	$[HB(3\text{-}Phpz)_3]Cd[H_2B(3,5\text{-}Me_2pz)_2]$	193.6
N_6	$[HB(pz)_3]_2Cd$	198.3
	$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	201.9
	$[HB(3\text{-}Phpz)_3]_2Cd$	94.0
	$[B(pz)_4]_2Cd$	221.1
	$[B(3\text{-}Mepz)_4]_2Cd$	202.5
N_3O_2	$[HB(3\text{-}Phpz)_3]Cd[(Bu^tCO)_2CH]$	172.4
	$[B(3\text{-}Pr^ipz)_4]Cd[(Bu^tCO)_2CH]$	168.1
	$[HB(3\text{-}Phpz)_3]Cd[(CF_3CO)_2CH]$	141.8
	$[HB(3\text{-}Phpz)_3]Cd[(PhCO)_2CH]$	155.2
	$[HB(3\text{-}Bu^tpz)_3]Cd[(Bu^tCO)_2CH]$	179.8
	$[HB(3\text{-}Bu^tpz)_3]Cd[CH_3CO_2]$	148.1
N_3S_2	$[HB(3,5\text{-}Me_2pz)_3]Cd[S_2CNEt_2]$	265.7
	$[HB(3\text{-}Phpz)_3]Cd[S_2CNEt_2]$	237.5

(2.540(2) Å) Cd−S bond distance, a structural feature noted previously in five-coordinate $[dithiocarbamate]_2CdPR_3$ structures.[13] The three Cd−N bond distances are more regular, varying only by 0.10 Å. The average Cd−N distance is 2.30 Å, shorter than observed for the tridentate $[HB(3\text{-}Phpz)_3]^-$ ligand in five-coordinate **3** of 2.34 Å and the 2.348(5) Å distance found for six-coordinate $[HB(3,5\text{-}Me_2pz)_3]_2Cd$.[3a]

The arrangement of the donor atoms could be viewed as a distorted trigonal bipyramid with S(1) and N(3) in the axial sites. The S(1)−Cd−N(3) angle is 169.8(1)° and these two donor atoms make the longer bond distances to the cadmium. The S−Cd−S angle is restricted to 68.9° by the chelate ring. The geometry in the equatorial plane is distorted by a N(1)−Cd−N(5) angle restrained to 88.5(1)° by the chelate ring and the 142.4(1)° S(2)−Cd−N(1) angle.

^{113}Cd NMR Studies. Solution state ^{113}Cd NMR spectra of the complexes reported here have been recorded and the results are presented in Table 5. Also presented in Table 5 are the chemical shifts of representative examples of other poly(pyrazolyl)borate complexes of cadmium we have reported elsewhere.[3a,6]

The chemical shifts of the complexes with CdN_5 central cores average 212 ppm and have a 31.5 ppm range. The complexes containing the $[HB(3\text{-}Phpz)_3]^-$ ligand have the more shielded chemical shifts. This ligand causes a substantial shift (ca. 50 ppm/ligand) in the shielding direction for complexes with a central N_6 core when compared to the other poly(pyrazolyl)borate ligands used in these studies, an effect that will be discussed in a separate publication.[6] However, the main rational for the increased shielding is the longer Cd−N bond distances found in $[HB(3\text{-}Phpz)_3]_2Cd$ when compared to other poly(pyrazolyl)borate ligand complexes with N_6 central cores. The shielding effect of the $[HB(3\text{-}Phpz)_3]^-$ ligand is not as great for these N_5 complexes or the other five-coordinate complexes reported here.

There is substantial overlap of the chemical shift range of the N_5 and N_6 complexes. We are studying these complexes by solid state ^{113}Cd NMR in order to determine the shifts of the individual tensors and anticipate more definitive structure/shielding correlations from these experiments. The chemical shift range for the complexes with CdN_4 cores is distinct from the CdN_5 core complexes.

The ^{113}Cd chemical shift for compounds with CdN_3O_2 cores are substantially shielded from the other five-coordinate complexes. It is well-known that ligands that bond to cadmium through oxygen cause increased shielding.[14] Given that the $[HB(3\text{-}Phpz)_3]^-$ ligand is a constant in three of the complexes, the effect of varying the diketonate ligand can be noted. As the alkyl substituent changes from an electron-donating Bu^t group to an electron-withdrawing CF_3 group, the resonances become increasingly shielded. The electron-withdrawing group will make the oxygen donor atom harder (more ionic), causing the observed shielding. A similar trend has been reported previously for a series of substituted $[Cd(1,10\text{-}phenanthroline)_3]^{3+}$ complexes.[15]

It is interesting to note that the information in Table 5 relating to compounds with CdN_3O_2 cores has been used by D. J. Darensbourg and co-workers to definitively assign the solution state coordination environment.[16] They have used ^{113}Cd NMR chemical shifts to show that propylene oxide and cyclohexene oxide adducts of $[HB(3\text{-}Phpz)_3]Cd(CH_3CO_2)$ dissociate the epoxide ligand in CH_2Cl_2 solution, as indicated by a chemical shift of 156 ppm, a shift clearly in the range of compounds with CdN_3O_2 cores reported here.

The two complexes with CdN_3S_2 central cores have chemical shifts just slightly deshielded from the range of the CdN_5 core complexes. As observed in other cases, the $[HB(3\text{-}Phpz)_3]^-$ ligand complex is more shielded. Given that previous studies have shown that "ligands which bind via sulfur produce very large deshielding",[14] a greater difference in the range of the two classes of complexes was anticipated. For comparison, the chemical shift of a series of $[Cd(SR)_2(N\text{-}donor)_2]$ complexes with CdN_2S_2 central cores are 448−474 ppm[17] compared to values of 298.7 ppm for $[H_2B(pz)_2]_2Cd$ and 303.3 ppm for $[H_2B(3,5\text{-}Me_2pz)_2]_2Cd$, complexes containing a CdN_4 central core.[3a]

Conclusion

The new complexes reported here strengthen our contention that poly(pyrazolyl)borate complexes of cadmium are ideally suited for the systematic investigation of correlations between ^{113}Cd chemical shifts and carefully controlled changes in the cadmium coordination environment. All complexes are monomeric, and by varying the substituents on the poly(pyrazolyl)borate ligands complexes with desired central core environments can be prepared and studied by crystallographic means and

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solution and solid ^{113}Cd NMR. In order for ^{113}Cd NMR spectroscopy to be useful in the delineation of the structure and function in a biological system, systems are needed that allow the study of the effects of subtle changes in the ligand of a given metal complex. This goal can be very difficult to reach with inorganic systems because changes in the ligands frequently cause the new compounds to have different bond distances and angles and possibly a completely different structure. The main exceptions to this situation are the porphyrins.[18] Here changes can be made to an axial ligand, leaving neither the angle with respect to the plane of the porphyrin nor the bond distances altered. However, the basic molecular fragment of the porphyrin remains essentially the same and may not be relevant to the biological system of interest. Using the poly(pyrazolyl)borate and related ligands, one portion of a complex can be readily changed and the new compounds do not greatly change their properties. This system provides a means to facilitate an understanding of the consequences that structural changes have on a particular property, in this case a chemical shift or element of a shielding tensor. We are attempting to prepare new complexes using the poly(pyrazolyl)borate ligands that will represent additional classes of donor atoms bonded to cadmium.

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Supporting Information Available: Complete crystallographic information, bond lengths, bond angles, and anisotropic thermal parameters, and H-atom coordinates for complexes **3** and **10** (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of this journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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