Syntheses of Cationic, Six-Coordinate Cadmium(II) Complexes Containing Tris(pyrazolyl)methane Ligands. Influence of Charge on Cadmium-113 NMR Chemical Shifts

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Treating a thf (thf = tetrahydrofuran) suspension of Cd(acac)$_2$ (acac = acetylacetonate) with 2 equiv of HBF$_4$•Et$_2$O results in the immediate formation of [Cd$_2$(thf)$_5$](BF$_4$)$_4$ (**1**). Crystallization of this complex from thf/CH$_2$Cl$_2$ yields [Cd(thf)$_4$](BF$_4$)$_2$ (**2**), a complex characterized in the solid state by X-ray crystallography. Crystal data: monoclinic, $P2_1/n$, $a = 7.784(2)$ Å, $b = 10.408(2)$ Å, $c = 14.632(7)$ Å, $\beta = 94.64(3)°$, $V = 1181.5(6)$ Å^3, $Z = 2$, $R = 0.0484$. The geometry about the cadmium is octahedral with a square planar arrangement of the thf ligands and a fluorine from each (BF$_4$)$^-$ occupying the remaining two octahedral sites. Reactions of [Cd$_2$(thf)$_5$](BF$_4$)$_4$ with either HC(3,5-Me$_2$pz)$_3$ or HC(3-Phpz)$_3$ yield the dicationic, homoleptic compounds {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ (**3**) and {[HC(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$_2$ (**4**) (pz = 1-pyrazolyl). The solid state structure of **3** has been determined by X-ray crystallography. Crystal data: rhombohedral, R$\bar{3}$, $a = 12.236(8)$ Å, $c = 22.69(3)$ Å, $V = 2924(4)$ Å^3, $Z = 3$, $R = 0.0548$. The cadmium is bonded to the six nitrogen donor atoms in a trigonally distorted octahedral arrangement. Four monocationic, mixed ligand tris(pyrazolyl)methane−tris(pyrazolyl)borate complexes {[HC(3,5-Me$_2$pz)$_3$][HB(3,5-Me$_2$pz)$_3$]Cd}(BF$_4$) (**5**), {[HC(3,5-Me$_2$pz)$_3$][HB(3-Phpz)$_3$]Cd}(BF$_4$) (**6**), {[HC(3-Phpz)$_3$][HB(3,5-Me$_2$pz)$_3$]Cd}(BF$_4$) (**7**), and {[HC(3-Phpz)$_3$][HB(3-Phpz)$_3$]Cd}(BF$_4$) (**8**) are prepared by appropriate conproportionation reactions of **3** or **4** with equimolar amounts of the appropriate homoleptic neutral tris(pyrazolyl)borate complexes [HB(3,5-Me$_2$pz)$_3$]$_2$Cd or [HB(3-Phpz)$_3$]$_2$Cd. Solution ^{113}Cd NMR studies on complexes **3**−**8** demonstrate that the chemical shifts of the new cationic, tris(pyrazolyl)methane complexes are very similar to the neutral tris(pyrazolyl)borate complexes that contain similar substitution of the pyrazolyl rings.

Introduction

We have initiated an investigation into the design, synthesis, and characterization of monomeric cadmium(II) compounds in which the coordination sphere about the cadmium atom is carefully controlled to prepare model complexes for zinc metalloprotein sites.[1] The main impetus 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.[2] 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. To date, much of our effort has focused on neutral cadmium(II) coordination complexes supported by the versatile poly(pyrazolyl)borate ligands.[1] Because the local charge of a protein can alter upon change in pH, we decided to determine if the chemical shift ranges, established for our neutral cadmium(II) complexes, remain constant in similar complexes that are charged.

Attractive alternatives to the anionic poly(pyrazolyl)borate ligands are the isoelectronic neutral poly(pyrazolyl)methane analogs, ligands derived from replacing the central boron atom with a carbon atom. An early account of the syntheses of several poly(pyrazolyl)methane ligands was reported by Trofimenko.[3] Trofimenko demonstrated that as with the poly(pyrazolyl)borate analogs, these neutral ligands bind both early (Cr, Mo, W, and Mn) and late transition metals (Co, Ni, and Pd).[3] Later, Elguero et. al. developed an improved procedure for the syntheses of these ligands.[4] A number of papers using the HC(pz)$_3$ ligand with transition metals have appeared[5] as have the syntheses of the group 12 metal complexes {[HC(pz)$_3$]$_2$M}$^{+2}$ (M = Zn, Cd).[6] These group 12 complexes have limited solubility and the ligands are displaced by donor solvents, such

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as DMSO, in which they will dissolve. Very recently, an account of several molybdenum complexes prepared from the HC(3,5-Me$_2$pz)$_3$ ligand has appeared.[7]

We are studying the chemistry of HC(3,5-Me$_2$pz)$_3$[8] and the new ligands HC(3-Phpz)$_3$[9] and HC(3-Bu^{t}pz)$_3$[10] ("relatives" of the bulky second generation poly(pyrazolyl)borate ligands[11]) with a variety of the post-transition metals. Reported here is the preparation of [Cd$_2$(thf)$_5$](BF$_4$)$_4$ (thf = tetrahydrofuran), a useful starting material for the synthesis of cadmium(II) complexes in nonaqueous solution. The syntheses of the dicationic, cadmium(II) coordination complexes [L$_2$Cd]$^{2+}$ (L = HC(3,5-Me$_2$pz)$_3$ or HC(3-Phpz)$_3$) are reported as well as all four possible monocationic, mixed-ligand complexes of these two tris(pyrazolyl)methane ligands with the poly(pyrazolyl)borate analogs, [HB(3,5-Me$_2$pz)$_3$]$^-$ and [HB(3-Phpz)$_3$]$^-$. The solution ^{113}Cd NMR chemical shifts of the new complexes are also reported. In addition, the solid state structures of {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ and [Cd(thf)$_4$](BF$_4$)$_2$ have been determined.

Experimental Section

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed and distilled prior to use. ^{1}H and ^{13}C NMR chemical shifts are reported in ppm vs TMS. ^{113}Cd NMR chemical shifts are reported in ppm vs external 0.1 *M* Cd(ClO$_4$)$_2$. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. Cd(acac)$_2$ was purchased from Strem Chemicals and used as received. HC(Me$_2$pz)$_3$,[4] HC(3-Phpz)$_3$,[9] [HB(3,5-Me$_2$pz)$_3$]$_2$Cd[1a], and [HB(3-Phpz)$_3$]$_2$Cd[1f] were prepared according to literature procedures. Elemental analyses were performed by National Chemical Consulting, Inc.

Caution! Cadmium(II) compounds are extremely toxic and care should be used when handling them.

[Cd$_2$(thf)$_5$](BF$_4$)$_4$ (1). A thf (8 mL) suspension of Cd(acac)$_2$ (0.50 g; 1.6 mmol) was treated with 85% HBF$_4$·Et$_2$O (0.51 mL, 3.2 mmol). The resulting reaction mixture was stirred for 2 h, followed by cannula filtration. The remaining white solid was washed with hexanes (5 mL) and dried under vacuum (0.663 g; 0.71 mmol; 88%). ^{1}H NMR (acetone-*d*$_6$): δ 3.64 (m; 4; CH$_2$O); 1.79 (m; 4; C*H*$_2$CH$_2$O). Anal Calcd for C$_{20}$H$_{40}$B$_4$Cd$_2$F$_{16}$: C, 25.76; H, 4.32. Found: C, 25.92; H, 4.51. Crystals of [Cd(thf)$_4$](BF$_4$)$_2$ were obtained by layering a saturated CH$_2$Cl$_2$ solution of [Cd$_2$(thf)$_5$](BF$_4$)$_4$ with thf; mp = 183−187 °C. These crystals decompose in air.

{[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ (3). An acetone solution (8 mL) of HC(3,5-Me$_2$pz)$_3$ (0.42 g; 1.4 mmol) was added to an acetone solution (8 mL) of [Cd$_2$(thf)$_5$](BF$_4$)$_4$ (0.33 g; 0.35 mmol). A white solid began to precipitate after stirring for several minutes. The reaction mixture was allowed to stir overnight, followed by cannula filtration. The remaining white solid was washed with hexanes (2 × 5 mL) and dried under vacuum (0.37 g; 0.42 mmol; 65%); mp = 385−390 °C. ^{1}H NMR (acetone-*d*$_6$): δ 8.42 (s; 2; *H*C(Me$_2$pz)$_3$); 6.38 (s; 6; 4-*H* pz); 2.86, 2.00 (s, s; 18, 18; Me). ^{13}C NMR (acetone-*d*$_6$): 153.7, 144.8 (3,5-*C* pz); 108.3 (4-*C* pz); 68.9 (H*C*(Me$_2$pz)$_3$); 12.3, 11.0 (*C*H$_3$). ^{113}Cd NMR (CD$_2$Cl$_2$): δ 207. Mass spectrum (FAB): *m/z* 707 ({[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}$^{+2}$ − H$^+$); 727 ({[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(F)$^+$); 795 ({[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$^+$). Accurate FAB high resolution mass spectrum for {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$^+$ (*m/z*): calcd for C$_{32}$H$_{44}$^{11}B^{116}CdF$_4$N$_{12}$, 799.2889; found, 799.2888.

{[HC(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$_2$ (4). This complex was prepared using [Cd$_2$(thf)$_5$](BF$_4$)$_4$ (0.37 g; 0.40 mmol) and HC(3-Phpz)$_3$ (0.71 g; 1.6 mmol) as described above for **3** (0.53 g; 0.21 mmol; 56%); mp = 235−240 °C. ^{1}H NMR (CD$_2$Cl$_2$): δ 9.75 (s; 2; *H*C(3-Phpz)$_3$); 8.74 (m; 6; 5-H pz); 7.07, 6.98, 6.67 (m, m, m; 6, 12, 12; C$_6$*H*$_5$); 6.56 (m; 6; 4-H pz). ^{13}C NMR (CD$_2$Cl$_2$): δ 158.0, 136.7 (3,5-C pz); 129.9, 128.1, 127.7, 126.8 (*C*$_6$H$_5$); 107.4 (4-C pz); 77.9 (H*C*(3-Phpz)$_3$). ^{113}Cd NMR (CD$_2$Cl$_2$): δ 116. Mass spectrum (FAB): *m/z* 995 ({[HC(3-Phpz)$_3$]$_2$Cd}$^{+2}$ − H$^+$); 1015 ({[HC(3-Phpz)$_3$]$_2$Cd}(F)$^+$); 1083 ({[HC-(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$^+$). Accurate FAB high resolution mass spectrum for {[HC(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$^+$ (*m/z*): calcd for C$_{56}$H$_{44}$^{11}B^{116}CdF$_4$N$_{12}$, 1087.2853; found, 1087.2889.

{[HC(3,5-Me$_2$pz)$_3$][HB(3,5-Me$_2$pz)$_3$]Cd}(BF$_4$) (5). Equimolar amounts of {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ (0.200 g; 0.227 mmol) and Cd[HB(3,5-Me$_2$pz)$_3$]$_2$ (0.160 g; 0.226 mol) were combined and suspended in CH$_2$Cl$_2$ (50 mL). The mixture was heated at reflux for 16 h. After cooling to room temperature, the homogenous solution was passed through a plug of Celite. The filtrate was concentrated to dryness providing a white solid (0.31 g; 86%); mp = 346−348 °C. ^{1}H NMR (acetone-*d*$_6$): δ 8.34 (s; 1; *H*C(Me$_2$pz)$_3$); 6.28, 5.87 (s, s; 3, 3; 4-*H* pz); 2.82, 2.47, 1.88, 1.76 (s, s, s, s; 9, 9, 9, 9; Me). ^{13}C NMR (CD$_2$Cl$_2$): 153.5, 149.1, 146.1, 142.2 (3,5-*C* pz); 108.0, 105.4 (4-*C* pz); 68.6 (H*C*(Me$_2$pz)$_3$); 13.2, 12.6, 12.5, 11.4 (*C*H$_3$). ^{113}Cd NMR (CD$_2$Cl$_2$): δ 211. Accurate FAB high resolution mass spectrum for {[HC(3,5-Me$_2$pz)$_3$]Cd[HB(3,5-Me$_2$pz)$_3$]}$^+$ (*m/z*): calcd for C$_{31}$H$_{44}$^{11}B-^{114}CdN$_{12}$, 709.2938; found, 709.2916.

{[HC(3,5-Me$_2$pz)$_3$][HB(3-Phpz)$_3$]Cd}BF$_4$ (6). [HB(3-Phpz)$_3$]$_2$Cd (0.29 g, 0.25 mmol) and {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ (0.22 g, 0.25 mmol) were charged into a round bottom Schlenk flask in the drybox. The two solids were suspended in CH$_2$Cl$_2$ (15 mL) and were heated at reflux for 3 h. After the mixture was filtered through Celite, the CH$_2$Cl$_2$ was removed under reduced pressure. The remaining white solid was washed with toluene to remove unreacted [HB(3-Phpz)$_3$]$_2$Cd. The solid was extracted with chloroform, filtered and the solvent removed to yield a white solid (0.050 g; 12%); decomposes above 255 °C. ^{1}H NMR (CDCl$_3$): δ 8.19 (1; s; *H*C(Me$_2$pz)$_3$); 7.92 (3; d,. $J = 2.3$ Hz; 5-H 3-Phpz); 7.15 (6; d, $J = 7.2$; *o*-C$_6$H$_5$); 7.02 (3; t, $J = 7.5$ Hz; *p*-C$_6$H$_5$); 6.72 (6; t, $J = 7.6$ Hz; *m*-C$_6$H$_5$); 6.52 (6; d, $J = 2.3$ Hz; 4-H 3-Phpz); 5.53 (3; s; 4-H 3,5-Me$_2$); 2.72, 1.36 (9; 9; s; s; Me). ^{113}Cd NMR (CDCl$_3$): δ 140. Accurate FAB mass spectrum for {[HC(3,5-Me$_2$pz)$_3$]Cd[HB(3-Phpz)$_3$]}$^+$ (*m/z*): calcd for C$_{43}$H$_{44}$N$_{12}$^{11}B^{114}Cd, 853.2939; found, 853.2933.

{[HC(3-Phpz)$_3$][HB(3,5-Me$_2$pz)$_3$]Cd}BF$_4$ (7). [HB(3,5-Me$_2$pz)$_3$]$_2$Cd (0.085 g, 0.120 mmol) and {[HC(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$_2$ (0.150 g, 0.129 mmol) were charged into a round bottom Schlenk flask in the drybox. The two solids were suspended in CH$_2$Cl$_2$ (30 mL) and were allowed to react at reflux temperature for 2 days. This solution was allowed to come to room temperature, and hexanes (15 mL) were added to precipitate a white powder. This powder was collected and dried (0.11 g, 54%). ^{1}H NMR (CDCl$_3$): δ 9.48 (1; s; *H*C(3-Phpz)$_3$); 8.71 (3; d, $J = 2.7$ Hz; 5-H 3-Phpz); 7.29−6.71 (m; 15; Ph); 6.71 (3; d, $J = 2.7$ Hz; 4-H 3-Phpz); 5.33 (3; s; 4-H Me$_2$pz); 2.45, 1.17 (s, s; 9, 9; Me). ^{113}Cd NMR (CDCl$_3$): δ 168. Accurate FAB mass spectrum for {[HB(3,5-Me$_2$pz)$_3$]Cd[HC(3-Phpz)$_3$]}$^+$ (*m/z*): calcd for C$_{42}$H$_{44}$N$_{12}$^{11}B-^{114}Cd, 853.2939; found, 853.2956.

{[HC(3-Phpz)$_3$][HB(3-Phpz)$_3$]Cd}BF$_4$ (8). [HB(3-Phpz)$_3$]$_2$Cd (0.017 g, 0.017 mmol) and {[HC(3-Phpz)$_3$]$_2$Cd}(BF$_4$)$_2$ (0.019 g, 0.017 mmol) were charged into a round bottom Schlenk flask in the drybox. The two solids were suspended in CH$_2$Cl$_2$ (15 mL) and were heated at reflux overnight. The volatiles were removed under reduced pressure. The product was then washed with toluene to remove unreacted [HB(3-Phpz)$_3$]$_2$Cd. Following filtration, a white solid was dried and collected (0.015 g; 45%); mp = 172−180 °C. ^{1}H NMR (CDCl$_3$), δ: 9.60 (1; s; *H*C(Me$_2$pz)$_3$); 8.62 (3; d, $J = 2.6$ Hz; 5-H in HC(3-Phpz)$_3$); 7.89 (3; d, $J = 2.3$ Hz; 5-H in HB(3-Phpz)$_3$); 7.09−6.47 (30; m; C$_6$*H*$_5$); 6.37 (3; d, $J = 2.6$ Hz; 4-H in HC(3-Phpz)$_3$); 6.17 (3; d, $J = 2.3$ Hz; 4-H in

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Table 1. Crystallographic Data for the Structural Analyses

	2	**3**
chem formula	$C_{16}H_{32}B_2CdF_8O_4$	$C_{32}H_{44}B_2CdF_8N_{12}$
fw	574.44	882.81
cryst syst	monoclinic	rhombohedral
space group	$P2_1/n$	$R\bar{3}$
a (Å)	7.784(2)	12.236(8)
b (Å)	10.408(2)	
c (Å)	14.632(7)	22.69(3)
β (deg)	94.64(3)	
V (Å^3)	1181.5(6)	2942(4)
Z	2	3
ρ_{calcd}, (g cm^{-3})	1.615	1.495
μ(Mo Kα) (cm^{-1})	10.05	6.36
range of 2θ (deg)	4−45	4−45
temp (°C)	−35	20
no. of observns ($I > 4\sigma(I)$)	1121	761
goodness of Fit	1.03	1.601
residuals: $R(F)$;[a] $R_w(F^2)$[b]	0.0484; 0.1343	0.0548; 0.1182

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

HB(3-Phpz)$_3$). ^{113}Cd NMR ($CDCl_3$): δ 110. Accurate FAB mass spectrum for $\{[HC(3\text{-}Phpz)_3]Cd[HB(3\text{-}Phpz)_3]\}^+$ (*m/z*): calcd for $C_{55}H_{44}N_{12}{}^{11}B^{114}Cd$, 997.2939; found, 997.2983.

Crystal Structure of $[Cd(thf)_4](BF_4)_2$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$. Crystals of $[Cd(thf)_4](BF_4)_2$ were grown by dissolving $[Cd_2(thf)_5](BF_4)_4$ in CH_2Cl_2, followed by filtering this solution through Celite and layering it with thf. These crystals lose thf when dried. Crystals of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ were grown by layering a CH_2Cl_2 solution with hexanes. Suitable crystals for X-ray diffraction were selected and mounted with epoxy cement in a thin-walled glass capillary flushed with nitrogen for $[Cd(thf)_4](BF_4)_2$ and on a thin glass fiber for $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$. The unit cell parameters were obtained by the least squares refinement of the angular settings of 24 reflections ($20° \le 2\theta \le 25°$).

Systematic absences in the diffraction data for $[Cd(thf)_4](BF_4)_2$ are uniquely consistent for the space group $P2_1/n$. The unit-cell parameters, photographic data, systematic absences, and occurrences of equivalent reflections in $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ are consistent with rhombohedral space groups without c-glide absences. Chemical composition suggested the space group, $R\bar{3}$, and this solution gave chemically reasonable results during refinement.

The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Absorption corrections were not necessary.

The cadmium atom in $[Cd(thf)_4](BF_4)_2$ is located on an inversion center. Carbons C(5), C(6), C(7), and C(8) are disordered over two positions with an occupancy of 60/40. The hydrogen atoms on the disordered carbon atoms were ignored and the remaining hydrogen atoms were treated as idealized contributions.

The cadmium atom in $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ is located on a 3-fold axis and an inversion center. The boron atom and one of the fluorine atoms of the counterions are located on a three-fold axis. The N(1), C(2), C(3), C(4), and C(5) atoms of the pyrazole ring are disordered over two positions, with an occupancy of 50/50. All non-hydrogen atoms were refined with anisotropic displacement parameters.

All software and sources of the scattering factors are contained in either the SHELXTL (5.1) or the SHELXTL PLUS (4.2) program libraries (G. Sheldrick, Siemens XRD, Madison, WI). Crystallographic data are given in Table 1.

Results

Syntheses of Complexes. Treating a thf suspension of $Cd(acac)_2$ with $HBF_4\cdot Et_2O$ leads to the formation of $[Cd_2(thf)_5](BF_4)_4$, isolated as a white powder (eq 1). This empirical

$$2Cd(acac)_2 + 4HBF_4\cdot Et_2O \xrightarrow{\text{thf}} [Cd_2(thf)_5](BF_4)_4 + 4Hacac \quad (1)$$

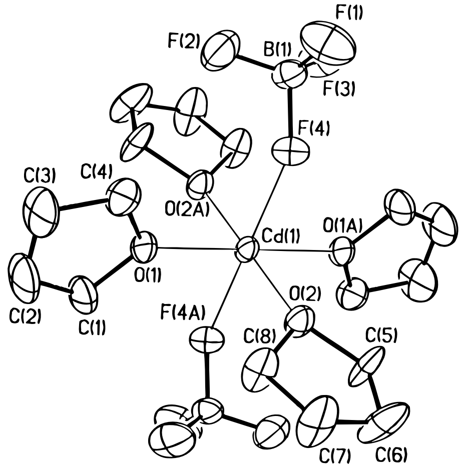


Figure 1. ORTEP diagram of $[Cd(thf)_4](BF_4)_2$.

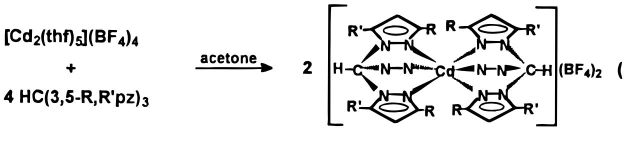
Table 2. Selected Bond Distances (Å) and Angles (deg) for $[Cd(thf)_4](BF_4)_2$

	Bond Distances		
Cd(1)−O(1)	2.263(5)	Cd(1)−F(4)	2.307(4)
Cd(1)−O(2)	2.219(4)		
	Bond Angles		
O(1)−Cd(1)−O(2)	89.8(2)	O(2)−Cd(1)−O(1A)	90.2(2)
O(1)−Cd(1)−F(4)	89.6(2)	F(4)−Cd(1)−O(1A)	90.4(2)
O(1)−Cd(1)−O(2A)	90.2(2)	F(4)−Cd(1)−O(2A)	92.7(2)
O(2)−Cd(1)−F(4)	87.3(2)		

formula was determined by elemental analysis. $[Cd_2(thf)_5](BF_4)_4$ is insoluble in thf and soluble in acetone and CH_2Cl_2.

Crystallization of $[Cd_2(thf)_5](BF_4)_4$ from CH_2Cl_2/thf leads to the formation of $[Cd(thf)_4](BF_4)_2$ (**2**), as shown by an X-ray structural analysis. Figure 1 shows an ORTEP drawing of the compound and Table 2 shows important bond angles and distances. The thf molecules coordinate to the cadmium in a square planar arrangement, with a fluorine atom from each BF_4^- ion filling the remaining two sites of an octahedron. The Cd−O bond distances average 2.24 Å, just slightly shorter than those observed in octahedral $[Cd(DMSO)_6]^{2+}$ (2.29 Å)[12] and $[Cd(H_2O)_6]^{2+}$ (2.28 Å).[13] The Cd−F distances of 2.307(4) Å are just slightly longer than the average Cd−O distance. Given that the size of oxygen and fluorine are similar,[14] this distance indicates a significant bonding interaction.

Reactions of $[Cd_2(thf)_5](BF_4)_4$ with tris(pyrazolyl)methane ligands in acetone result in the immediate precipitation of the respective dications (eq 2). A similar reaction of $HC(3,5\text{-}Me_2pz)_3$ and $Cd(NO_3)_2\cdot 4H_2O$ in thf is not successful, indicating the usefulness of the thf adduct starting material. These dications were characterized by ^{1}H, ^{13}C and ^{113}Cd NMR as well as mass spectral analyses. High resolution mass spectra were obtained for the monocationic $\{[tris(pyrazolyl)methane]_2Cd(BF_4)\}^+$ spe-



(2)

(3) R = R' = Me
(4) R = Ph, R' = H

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(12) Sandström, M. *Acta Chem. Scand. A* **1978**, *32*, 519.

(13) (a) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1964**, *17*, 1295. (b) Montgomery, H.; Lingafelter, E. C. *Acta Crystallogr.* **1966**, *20*, 728.

(14) Huheey, J. E.; Keiter, E. A.; Keiter, R. *Inorganic Chemistry, 4th ed.*; Harper Collins: New York, 1993; p 292.

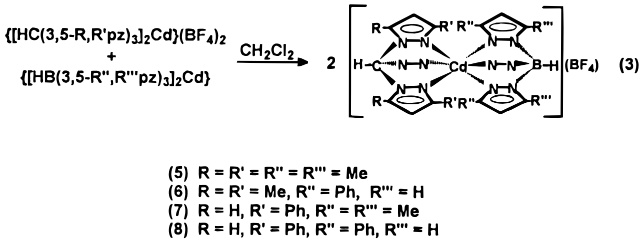
Table 3. Cadmium-113 Chemical Shifts[a]

compound	chem shift	compound	chem shift
$\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$	207	$[HB(3,5\text{-}Me_2pz)_3]_2Cd$	202
$\{[HC(3\text{-}Phpz)_3]_2Cd\}^{2+}$	116	$[HB(3\text{-}Phpz)_3]_2Cd$	94
$\{[HC(3,5\text{-}Me_2pz)_3][HB(3\text{-}Phpz)_3]Cd\}^{+}$	140	$[HB(3,5\text{-}Me_2pz)_3][HB(3\text{-}Phpz)_3]Cd$	148
$\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$	211		
$\{[HC(3\text{-}Phpz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$	168		
$\{[HC(3\text{-}Phpz)_3][HB(3\text{-}Phpz)_3]Cd\}^{+}$	110		

[a] Spectra were run at a concentration of 0.06 M at 25 °C.

cies observed in the FAB spectra of both dications. Both complexes are air stable and soluble in acetone and CH_2Cl_2. We have not been able to prepare the $\{[HC(3,5\text{-}Me_2pz)_3][HC(3\text{-}Phpz)_3]Cd\}^{2+}$ complex. Heating an equimolar mixture of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ and $\{[HC(3\text{-}Phpz)_3]_2Cd\}(BF_4)_2$ in CH_2Cl_2 leads to reisolation of these two starting materials.

Mixed monocationic tris(pyrazolyl)borate/tris(pyrazolyl)methane complexes of cadmium(II) are prepared by the conproportionation reactions of the dicationic poly(pyrazolyl)methane complexes with neutral poly(pyrazolyl)borate complexes in refluxing CH_2Cl_2 (eq 3). These complexes were characterized by ^1H, ^{13}C and ^{113}Cd NMR as well as mass spectral analyses.


(3)

Ligand Exchange Studies. As expected from the results of the exchange studies, these complexes exchange tris(pyrazolyl)methane ligands on the chemical time scale. Mixing $\{[HC(3\text{-}Phpz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$ with $HC(3,5\text{-}Me_2pz)_3$ leads to exchange of the $HC(3\text{-}Phpz)_3$ ligand and formation of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$. The NMR spectrum of a mixture of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$ and $HC(3\text{-}Phpz)_3$ shows both compounds with no exchange products observed. A mixture of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^{+}$ and $HC(3,5\text{-}Me_2pz)_3$ shows separate ^1H NMR signals for the free and coordinated $HC(3,5\text{-}Me_2pz)_3$. Also, the ^{113}Cd NMR resonance observed for this mixture is the same as for the pure complex (vide infra).

Preferential bonding of the $HC(3,5\text{-}Me_2pz)_3$ ligand is also shown with the dications. The ^1H NMR spectrum of a mixture of $HC(3\text{-}Phpz)_3$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ shows the spectra of the individual two compounds and the ^{113}Cd NMR spectrum shows the resonance for pure $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$. The same spectra are observed for a mixture of $\{[HC(3\text{-}Phpz)_3]_2Cd\}^{2+}$ and $HC(3,5\text{-}Me_2pz)_3$ showing that the $HC(3,5\text{-}Me_2pz)_3$ ligand completely displaced the $HC(3\text{-}Phpz)_3$ leading to the formation of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ and free $HC(3\text{-}Phpz)_3$. In neither of these experiments (or experiments carried out with limited amounts of $HC(3,5\text{-}Me_2pz)_3$ added to $\{[HC(3\text{-}Phpz)_3]_2Cd\}^{2+}$) was any of the mixed-ligand compound $\{[HC(3,5\text{-}Me_2pz)_3][HC(3\text{-}Phpz)_3]Cd\}^{2+}$ observed.

^{113}Cd NMR. The solution state ^{113}Cd NMR spectra for all cationic complexes were obtained and are tabulated in Table 3. Also included in the table are the chemical shifts of the analogous tris(pyrazolyl)borate complexes. The spectra of the neutral hydrotris(pyrazolyl)borate complexes were reported in $CDCl_3$, but deuterated methylene chloride was required for some of the cationic compounds to insure appreciable solubility. We have demonstrated that negligible solvent effects are observed upon switching from $CDCl_3$ to CD_2Cl_2.[15]

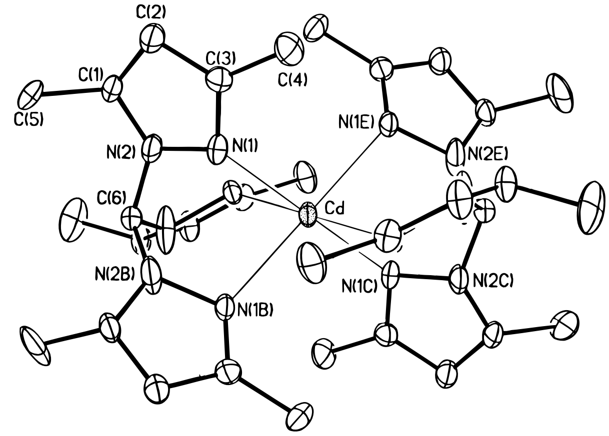


Figure 2. ORTEP diagram of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ Bond Distances in Å

	$\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$	$\{[HB(3,5\text{-}Me_2pz)_3]_2Cd\}$[a]
	Bond Distances	
Cd−N(1)	2.321(10)	2.348(5)
C(6)− or B−N(2)	1.439(7)	1.533(6)
N(1)−N(2)	1.507(11)	1.397(6)
N(2)−C(1)	1.328(8)	1.381(1)
C(2)−C(3)	1.43(2)	1.391(10)
C(3)−N(1)	1.33(2)	1.357(10)
C(1)−C(5)	1.49(2)	1.497(9)
C(3)−C(4)	1.51(2)	1.505(1)
Cd···C(6) or B	3.320	3.328
N(1)···N(1a)	2.98	3.10
	Bond Angles	
N(1)−Cd−N(1a)	80.0(4)	82.7(7)
N(1)−Cd−N(1c)	180.0(1)	180.0(1)
N(1)−Cd−N(1d)	100.0(4)	97.3(1)
Cd−N(1)−N(2)	109.0(6)	114.8(3)
C(6)− or B−N(2)−N(1)	113.7(7)	120.7(5)

[a] Assignments are based on using a numbering scheme analogous to that shown for $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ in Figure 2.

Solid State Structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$. The solid state structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$ was determined by X-ray crystallography. An ORTEP diagram of the dication is shown in Figure 2. Crystallographic data is presented in Table 1, while selected bond distances and angles are reported in Table 4, along with the comparable information for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$.[1a] In the structure of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$, the atoms in the pyrazolyl rings are disorder in a

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(15) We have previously reported the ^{113}Cd NMR chemical shift for $Cd[HB(3,5\text{-}Me_2pz)_3]_2$ in $CDCl_3$ as 201.9 ppm vs $Cd(ClO_4)_2$ (see ref 1a). In CD_2Cl_2, a signal for $Cd[HB(3,5\text{-}Me_2pz)_3]_2$ was observed at 201.5 ppm.

(16) Reger, D. L.; Huff, M. F.; Rheingold, A. L.; Haggerty, B. S. *J. Am. Chem. Soc.* **1992**, *114*, 579.

50:50 ratio over two sites. The cadmium is bonded to the six nitrogen donor atoms in a trigonally distorted octahedral arrangement. The space group is $R\bar{3}$, the same as with [HB(3,5-Me$_2$pz)$_3$]$_2$Cd. The Cd−N bond distances (2.321(10) Å) in this structure are just slightly shorter than those reported for [HB(3,5-Me$_2$pz)$_3$]$_2$Cd (2.348(5) Å).[1a] Intraligand N−Cd−N bond angles (80.0(4)°), C−N bond distances (1.439(7) Å) and N−C(6)−N angles (109.6(4)°) are also just slightly smaller than the analogous ones observed for [HB(3,5-Me$_2$pz)$_3$]$_2$Cd (82.7°; the comparable B−N distance is 1.533(6) Å and the N−B−N bond angle is 110.6(4)°).

One significant difference between the two structures is the degree of tilting the pyrazole rings make with respect to the C_3 axis formed by the metal and the two methyne carbon (or boron) atoms (a propeller-like distortion). Ideally, for maximum overlap with the lone pair on the donor nitrogen atoms the metal would lie in the plane of each pyrazole ring. Any deviation where the metal lies out of this planarity can be measured by the CdN−NC1 torsion angle, an angle that is ideally 180° in these planar rings. Tilting in the present structure is pronounced with a CdN−NC torsion angle of 141°, while in [HB(3,5-Me$_2$pz)$_3$]$_2$Cd this angle is 159°.

Discussion

The main result of these studies is the determination of the ^{113}Cd chemical shifts, shown in Table 3, of monocationic and dicationic tris(pyrazolyl)methane complexes. The substitution on the pyrazolyl rings is the same as some of our previously reported neutral tris(pyrazolyl)borate complexes.[1a,f] The charge on the complexes is varied by replacing one or two tris(pyrazolyl)borate ligands with tris(pyrazolyl)methane ligands. *Only small differences in the chemical shifts are observed with changes in the charges, for complexes that have the same substitution on the pyrazolyl rings*. These results are very surprising given the 900 ppm chemical shift range observed in ^{113}Cd NMR.[2]

The first line of Table 3 shows that the chemical shifts of [HB(3,5-Me$_2$pz)$_3$]$_2$Cd and {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}$^{2+}$ are only different by 5 ppm. The shift for the analogous monocation, {[HC(3,5-Me$_2$pz)$_3$][HB(3,5-Me$_2$pz)$_3$]Cd}$^{+}$, is also similar. The three complexes with 3-phenyl substitution on both ligands also have similar chemical shifts (the spread is a little larger at 22 ppm), but the average shift of these three complexes is 100 ppm different from the average of the three complexes with methyl substitution on the pyrazolyl rings. The average chemical shift of the complexes with one ligand having methyl substitution and the other having phenyl substitution are within 5 ppm of the average of the other two classes of complexes (one class with all methyl substitution and the second with all phenyl substitution on the pyrazolyl rings). Clearly, the ^{113}Cd chemical shifts are much more sensitive to changes in ligand substitution than to changes in the charge of the complexes. We have previously shown in a series of six-coordinate complexes of the general formula [poly(pyrazolyl)borate]$_2$Cd (poly(pyrazolyl)borate = [HB(pz)$_3$]$^-$, [HB(3,5-Me$_2$pz)$_3$]$^-$, [B(pz)$_4$]$^-$, and [HB(3-Phpz)$_3$]$^-$) that the chemical shift of the complexes are highly correlated with the measured Cd−N bond distances, with longer bonds in complexes containing the [HB(3-Phpz)$_3$]$^-$ ligand leading to shielding of the ^{113}Cd resonance.[1f]

The second important result of these studies is that the structure of {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$, taken with our previously published structure of [HB(3,5-Me$_2$pz)$_3$]$_2$Cd,[1a] allows the first direct comparison of parallel structures of complexes of analogous hydrotris(pyrazolyl)methane and hydrotris(pyrazolyl)borate ligands. As shown in Table 4, the structure of the cation in {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ closely resembles that of [HB(3,5-Me$_2$pz)$_3$]$_2$Cd. The Cd−N bond distances differ by only 0.03 Å. Thus by combining the ^{113}Cd NMR studies and the structural results, we have shown that complexes with different charges can have similar ^{113}Cd chemical shifts, if the ligand environment about the cadmium remains constant. This result is important for the use of ^{113}Cd NMR to probe structure and bonding relationships in compounds of biological interest.

Table 5. Average MN−NC Torsion Angles (deg), Average M−N Bond Distances (Å) and Average Intraligand N···N Distances (Å) of Selected Complexes

compound	av MN−NC torsion angle	M−N dist	av N···N dist	ref
{[HC(3,5-Me$_2$pz)$_3$]$_2$Tl}(PF$_6$)	123.2	2.92	3.24	8
{[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$	141.1	2.32	2.98	this work
{[HC(3,5-Me$_2$pz)$_3$]Tl}(PF$_6$)	155.5	2.67	3.03	8
[HC(3,5-Me$_2$pz)$_3$]MoI$_3$	177.3	2.20	2.92	7
[HB(3,5-Me$_2$pz)$_3$]$_2$Pb	159.4	2.61	3.18	16
[HB(3,5-Me$_2$pz)$_3$]$_2$Cd	158.6	2.35	3.10	1a
[HB(3,5-Me$_2$pz)$_3$]$_2$Zn	174.6	2.17	2.98	18
[HB(3,5-Bu$^t{}_2$pz)$_3$]Tl	132.9	2.57	3.24	17b

Although the structures of {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ and [HB(3,5-Me$_2$pz)$_3$]$_2$Cd are similar, there are two important differences. The smaller covalent radius of carbon vs boron[14] is reflected in the C(6)−N(2) bond length in {[HC(3,5-Me$_2$pz)$_3$]$_2$Cd}(BF$_4$)$_2$ being 0.09 Å shorter than the B-N bond distance in [HB(3,5-Me$_2$pz)$_3$]$_2$Cd. This shortening coupled with a 1° lower N−C(6)−N angle compared to the N−B−N angle causes the intrinsic "bite" of the HC(3,5-Me$_2$pz)$_3$ ligand to be smaller than the [HB(3,5-Me$_2$pz)$_3$]$^-$ ligand. This lowering is reflected in the shorter N···N intraligand nonbonding distance (2.98 vs 3.10 Å).

The second difference, a difference related to the first, involves tilting of the pyrazole rings along the C_3 axis with respect to the metal. We and others have previously commented on this tilting feature.[8,17] In the previous discussions by others of the tilting in poly(pyrazolyl)borate ligand complexes, the main cause of the tilting was attributed to unfavorable nonbonding interactions caused by bulky substituents, such as tert-butyl groups, on the pyrazolyl rings. Table 5 summarizes data for four structures containing the HC(3,5-Me$_2$pz)$_3$ ligand as well as three representative [HB(3,5-Me$_2$-pz)$_3$]$_2$M structures. Included are the average MN−NC torsion angles, M−N bond distances and N···N intraligand nonbonding distances for each compound. Presumably, the tilting observed with 3,5-dimethyl-substituted ligands is *not* mainly related to the relatively small methyl substituents on the pyrazolyl rings. In the two structures of this type with short M−N distances, the torsion angles are near the ideal C_{3v} value of 180°. In the four structures with M−N bond distances in the range of 2.32 to 2.67 Å, the distortions are moderate. In the structure of {[HC(3,5-Me$_2$pz)$_3$]$_2$Tl}PF$_6$, the case with very long M−N bond distances, the distortions are pronounced. The tilting is also very pronounced in the structure of [HB(3,5-Bu$^t{}_2$pz)$_3$]Tl. This distortion was attributed to the bulky substituent at the 5-position,[17b] but the large size of the metal also contributes. The importance of the size of the metal has been noted previously with complexes of the [HB(Mementhpz)$_3$]$^-$ ligand.[17c]

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(17) (a) LeCloux, D. D.; Tokar, C. J.; Osawa, M.; Houser, R. P.; Keyes, M. C.; Tolman, W. B. *Organometallics* **1994**, *13*, 2855. (b) Dowling, C. M.; Leslie, D.; Chisholm, M. H.; Parkin, G. *Main Group Chem.* **1995**, *1*, 29. (c) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.

(18) Looney, A.; Han, R.; Gorrell, I. B.; Cornebise, M.; Yoon, K.; Parkin, G.; Rheingold, A. L. *Organometallics* **1995**, *14*, 274.

In comparing {$[HC(3,5\text{-}Me_2pz)_3]_2Cd$}$(BF_4)_2$ and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$, the greater tilting is observed with the $HC(3,5\text{-}Me_2pz)_3$ ligand. This result is explained by the smaller intrinsic “bite” of the tris(pyrazolyl)methane ligands. Thus, for these ligands with relatively small substituents on the pyrazolyl rings, the tilting is caused by the size of the metal atom being large in comparison to the intrinsic “bite” of the ligand.

Four other aspects of this work are important. First, an interesting conclusion from these structural and ^{113}Cd chemical shift data is that the charge in poly(pyrazolyl)borate ligands is highly localized on the boron atom. Second, the development of this chemistry, especially the ability to prepare complexes containing both the tris(pyrazolyl)methane and tris(pyrazolyl)borate ligands indicates that the tris(pyrazolyl)methane ligands show promise in the development of new coordination chemistry of the post transition metals. Third, the new starting material $[Cd_2(thf)_5](BF_4)_4$ has been prepared and is very useful in the preparation of new cadmium(II) complexes in non-aqueous solutions. Fourth, the ligand exchange studies show that $HC(3,5\text{-}Me_2pz)_3$ preferentially bonds to cadmium(II) over $HC(3\text{-}Phpz)_3$.

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Supporting Information Available: Tables of complete data collection information, bond distances, bond angles, positional parameters, and anisotropic thermal parameters (11 pages). Ordering information is given on any current masthead page.

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