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Notes

Solid State Structure of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$: Comparison of the Bonding of Tris(pyrazolyl)methane and Tris(pyrazolyl)borate Ligands

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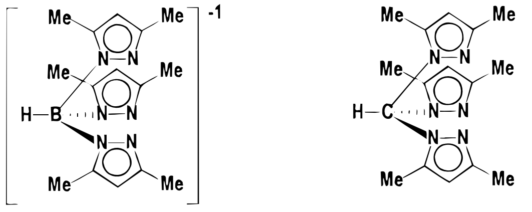
Introduction

We[1] and others[2] have developed the chemistry of cadmium(II) using poly(pyrazolyl)borate ligands (Chart 1). Our main interest is the syntheses of monomeric cadmium(II) compounds in which the coordination sphere about the cadmium atom can be carefully controlled in order to use these complexes to model the active sites in zinc metalloproteins. Cadmium has two important isotopes that are NMR active with spins = $^1/_2$, and thus NMR can be used to explore the active site of proteins in which cadmium has replaced zinc, a metal with few good spectroscopic handles.[3]

More recently, we have prepared analogous complexes using tris(pyrazolyl)methane ligands (Chart 1).[4] Complexes of the general formula $\{[\text{tris(pyrazolyl)methane}]_2Cd\}^{2+}$ are isoelectronic to $[\text{tris(pyrazolyl)borate}]_2Cd$ complexes, but because the tris(pyrazolyl)methane ligands are neutral compared to the monoanionic tris(pyrazolyl)borate ligands, the complexes have a 2+ charge. We are interested in using solid state structures and ^{113}Cd NMR chemical shifts to compare the bonding properties of these two ligand types in isoelectronic complexes.

Chart 1



Tris(3,5-dimethylpyrazolyl)borate

Tris(3,5-dimethylpyrazolyl)methane

In addition to the syntheses of these homoleptic, six-coordinate complexes, we also reported the preparation of isoelectronic, mixed-ligand complexes such as $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}(BF_4)$.[4] At that time it did not prove possible to grow single crystals of these complexes for X-ray studies, but recently we have grown suitable crystals of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$. Reported here is the solid state structure of this complex that allows a direct comparison of the two ligand types in the same complex. We compare this structure to the previously reported structures of $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$[4] and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$[1a] and contrast these three structures to the structures of the analogous lead(II) complexes $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$,[5] $[HB(3,5\text{-}Me_2pz)_3]_2Pb$,[6] and $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Pb\}^{+}$.[5]

Experimental Section

All operations were carried out under a nitrogen atmosphere either using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. $Cd(acac)_2$ was purchased from Strem Chemicals and used as received. Tetrafluoroboric acid diethyl ether complex (85%) was purchased from Aldrich and used as received. $Na\{B[C_6H_3(CF_3)_2]_4\}$,[7] $HC(3,5\text{-}Me_2pz)_3$,[8] and $[HB(3,5\text{-}Me_2pz)_3]_2Cd$[1a] were prepared according to literature procedures. ^{113}Cd NMR chemical shifts are reported in parts per million versus external 0.1 M $Cd(ClO_4)_2$. Elemental analyses were performed by National Chemical Consulting, Inc.

WARNING: *Cadmium(II) compounds are extremely toxic and care should be used when handling them. The* $Li(CF_3)_2C_6H_3$ *generated in situ in the preparation of* $Na\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ *is potentially explosive.*[9] *Its preparation should be carried out behind explosion shields, and it should be handled as dilute solutions on as small a scale as possible.*

$[Cd(thf)_3]\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$. $Cd(acac)_2$ (0.25 g; 0.80 mmol), suspended in thf (10 mL), was treated with 85% HBF_4Et_2O (0.25 mL, 1.6 mmol). This mixture was stirred for 3 h before being filtered, and the remaining solid was washed with hexanes (5 mL). A CH_2Cl_2 (25 mL) solution of $Na\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ (1.43 g; 1.6 mmol) was added to the white solid. This mixture was stirred overnight before being filtered. The solvent was evaporated and the resulting pale yellow solid

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10.1021/ic981453w CCC: $18.00

Table 1. Crystallographic Data for {[HC(3,5-$Me_2pz)_3$]-[HB(3,5-$Me_2pz)_3$]Cd}{B[3,5-$(CF_3)_2C_6H_3]_4$}

formula	$C_{63}H_{56}B_2CdF_{24}N_{12}$
fw	1571
space group	$P\bar{1}$
a, Å	10.311(6)
b, Å	19.045(5)
c, Å	19.611(6)
α, deg	108.50(2)
β, deg	96.53(5)
γ, deg	103.23(4)
V, Å^3	3482(3)
Z	2
cryst color, habit	colorless block
D(calc), g cm^{-3}	1.499
μ(Mo Kα), cm^{-1}	4.26
temp, K	244(2)
radiation	Mo Kα (*λ* = 0.710 73 Å)
$R(F)^a$, $R(wF^2)^a$	6.01, 12.73

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

dried overnight under vacuum (1.43 g; 87%); mp = 117−118 °C. ^{1}H NMR (acetone-d_6): *δ* 7.78 (br; 16; 2,6-*H* in $C_6H_3(CF_3)_2$); 7.68 (br; 8; 4-*H* in $C_6H_3(CF_3)_2$); 3.63 (m; 12; CH_2O); 1.79 (m; 12; CH_2CH_2O). Anal. Calcd for $C_{76}H_{48}B_2CdF_{48}O_3$: C, 44.42; H, 2.35. Found: C, 44.61; H, 2.40.

{[HC(3,5-$Me_2pz)_3]_2$Cd}{B[$C_6H_3(CF_3)_2]_4$}$_2$. A CH_2Cl_2 solution (10 mL) of HC(3,5-$Me_2pz)_3$ (0.48 g; 1.6 mmol) was added to a CH_2Cl_2 solution (15 mL) of [Cd(thf)$_3$]{B[$C_6H_3(CF_3)_2]_4$}$_2$ (1.65 g; 0.80 mmol). A white solid began to precipitate after several minutes of stirring. The reaction mixture was stirred overnight, followed by cannula filtration. The remaining white solid was washed with hexanes (2 × 5 mL) and dried under vacuum (1.22 g; 0.50 mmol; 62%); mp = 266−267 °C. ^{1}H NMR (acetone-d_6): *δ* 8.43 (s; 2; *H*C($Me_2pz)_3$); 7.79, 7.68 (s, s; 16, 8; 2*H*/6*H*, 4*H* in $C_6H_3(CF_3)_2$); 6.38 (s; 6; 4-*H* pz); 2.87, 2.00 (s, s; 18, 18; Me). ^{113}Cd NMR (CD_2Cl_2): *δ* 207. Crystals suitable for an analytical sample were prepared by layering an acetone solution with hexanes and allowing for slow diffusion of the two layers. Anal. Calcd for $C_{96}H_{68}B_2CdF_{48}N_{12}$: C, 47.34; H, 2.81. Found: C, 47.55; H, 2.88.

{[HC(3,5-$Me_2pz)_3$][HB(3,5-$Me_2pz)_3$]Cd}{B[$C_6H_3(CF_3)_2]_4$}. Equimolar amounts of {[HC(3,5-$Me_2pz)_3]_2$Cd}{B[$C_6H_3(CF_3)_2]_4$}$_2$ (1.62 g; 0.665 mmol) and Cd[HB(3,5-$Me_2pz)_3]_2$ (0.47 g; 0.66 mol) were combined and suspended in CH_2Cl_2 (50 mL). The mixture was heated at reflux for 16 h. After cooling to room temperature, the homogeneous solution was passed through a plug of Celite. The filtrate was concentrated to dryness, providing a white solid (1.87 g; 90%); mp = 243−247 °C. ^{1}H NMR ($CDCl_3$): *δ* 7.85 (s; 1; *H*C($Me_2pz)_3$); 7.68, 7.50 (s, s; 8, 4; 2*H*/6*H*, 4*H* in $C_6H_3(CF_3)_2$); 5.94, 5.73 (s, s; 3, 3; 4-*H* pz); 2.41, 1.82, 1.66 (s, s, s; 18, 9, 9; Me). ^{113}Cd NMR (CD_2Cl_2): *δ* 211. Crystals suitable for an analytical sample and the X-ray crystal structure were prepared by layering a CH_2Cl_2 solution with hexanes and allowing slow diffusion of the two layers. Anal. Calcd for $C_{63}H_{56}B_2CdF_{24}N_{12}$: C, 48.16; H, 3.59; N, 10.70. Found: C, 47.90; H, 3.40; N, 10.37.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. A suitable crystal for X-ray diffraction was selected and mounted with epoxy cement on a thin glass fiber. The unit cell parameters were obtained by the least-squares refinement of the angular settings of 24 reflections (20° ≤ 2*θ* ≤ 25°).

No evidence of symmetry higher than triclinic was observed in either the photographic or diffraction data. *E*-Statistics suggested the centrosymmetric space group option, $P\bar{1}$, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures. Semiempirical absorption corrections were applied. The fluorine atoms on one of the trifluoromethyl groups, F(13), F(14), and F(15), of the counterion were disordered equally over two positions. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were treated as idealized contributions. All software and sources of the scattering factors are contained in the SHELXTL (5.3) program library (G. Sheldrick, Siemens XRD, Madison, WI).

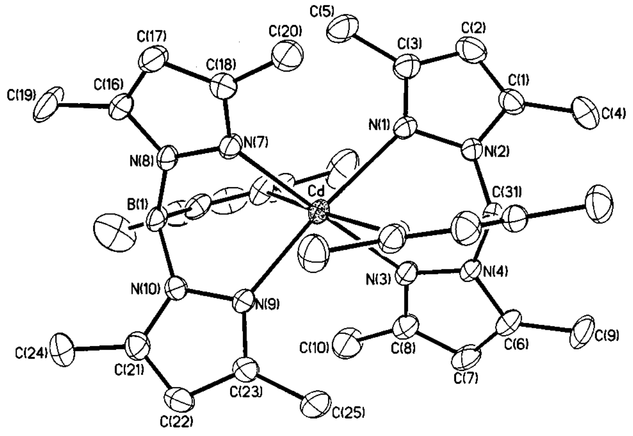
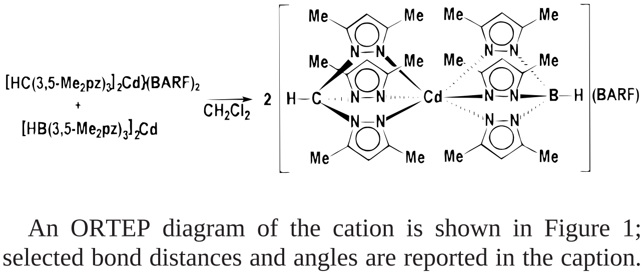


Figure 1. ORTEP diagram of {[HC(3,5-$Me_2pz)_3$][HB(3,5-$Me_2pz)_3$]-Cd}$^+$. Thermal ellipsoids are at 30% probability. Hydrogen atoms are omitted for clarity. Important distances (Å) and angles (deg): Cd−N(1) = 2.353(4), Cd−N(3) = 2.382(4), Cd−N(5) = 2.403(4), Cd−N(7) = 2.292(4), Cd−N(9) = 2.267(4), Cd−N(11) = 2.308(4), N(2)−C(31) = 1.436(5), N(4)−C(31) = 1.429(6), N(6)−C(31) = 1.443(6), N(8)−B(1) = 1.556(6), N(10)−B(1) = 1.530(6), N(12)−B(1) = 1.536(7), N(1)−Cd−N(3) = 78.4(2), N(1)−Cd−N(5) = 76.45(14), N(1)−Cd−N(7) = 100.6(2), N(1)−Cd−N(9) = 173.61(13), N(1)−Cd−N(11) = 99.0(2), N(3)−Cd−N(5) = 78.92(14), N(3)−Cd−N(7) = 179.0(2), N(3)−Cd−N(9) = 98.0(2), N(3)−Cd−N(11) = 96.5(2), N(5)−Cd−N(7) = 100.94(14), N(5)−Cd−N(9) = 97.79(14), N(5)−Cd−N(11) = 174.0(2), N(7)−Cd−N(9) = 83.1(2), N(7)−Cd−N(11) = 83.58(14), N(9)−Cd−N(11) = 86.6(2).

Results and Discussion

{[HC(3,5-$Me_2pz)_3$][HB(3,5-$Me_2pz)_3$]Cd}{B[3,5-$(CF_3)_2$-$C_6H_3]_4$} was prepared analogously to {[HC(3,5-$Me_2pz)_3$][HB-(3,5-$Me_2pz)_3$]Cd}(BF_4) reported previously.[4] Treating a thf suspension of Cd(acac)$_2$ with HBF_4Et_2O leads to [Cd_2(thf)$_5$]-($BF_4)_4$, which when treated with Na{B[3,5-$(CF_3)_2C_6H_3]_4$} yields [Cd(thf)$_3$]{B[3,5-$(CF_3)_2C_6H_3]_4$}$_2$. Reaction of this compound with 2 equiv of HC(3,5-$Me_2pz)_3$ yields {[HC(3,5-$Me_2pz)_3]_2$Cd}-{B[$C_6H_3(CF_3)_2]_4$}$_2$, which undergoes an exchange reaction with [HB(3,5-$Me_2pz)_3]_2$Cd to yield the desired complex (BARF = {B[3,5-$(CF_3)_2C_6H_3]_4$}$^+$).



An ORTEP diagram of the cation is shown in Figure 1; selected bond distances and angles are reported in the caption. The cadmium is bonded to the six nitrogen donor atoms in a trigonally distorted octahedral arrangement. The two ligands can be distinguished by the smaller covalent radius of carbon versus boron.[10] The C(methyne)−N bond lengths are 0.1 Å shorter than the B−N bond lengths (Table 2). The three Cd−N bond distances from [HB(3,5-$Me_2pz)_3$]$^-$ are shorter than those from HC(3,5-$Me_2pz)_3$, with the average distances being 2.29 versus 2.38 Å.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ (**A**), $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ (**B**), and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$ (**C**)

	A	**B**[a]	**C**
Distances			
Cd−N(methane)		2.38	2.321(10)
Cd−N(borate)	2.348(5)	2.29	
C(methyne)−N		1.44	1.439(7)
B−N	1.533(6)	1.54	
Angles			
N−Cd−N(methane intraligand)		80	80.0(4)
N−Cd−N(borate intraligand)	82.7(7)	84	
N−Cd−N(*trans*-interligand)	180.0(1)	173	180.0(1)
N−Cd−N(*cis*-interligand)	97.3(1)	99	100.0(4)
N−C(methyne)−N		112	109.6(4)
N−B−N	110.6(4)	110	

[a] Average values.

Table 2 compares the structural parameters of this complex with those for $[HB(3,5\text{-}Me_2pz)_3]_2Cd$[1a] and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}^{2+}$.[4] The Cd−N distances are essentially identical in the two homoleptic structures. From these two structures of homoleptic complexes the bonding of the two ligand types to cadmium(II) seems similar. The structure of the mixed-ligand complex indicates that the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand coordinates more strongly to cadmium(II), demonstrating that a true comparison of the two ligands must be made *in the same complex*. Interestingly, the *average* Cd−N distance of 2.33 Å in $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ is very similar to those in the homoleptic structures. This similarity in average Cd−N bond distances was predicted previously because the ^{113}Cd NMR chemical shift values for these three compounds are nearly identical.[4] All other parameters in the structures are also very similar.

The structures of the three analogous complexes of lead(II) have been reported. The complexes $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}^{2+}$ [5] and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$[6] are isostructural to their cadmium analogues, a surprising result given that lead(II) has two additional valence electrons. As with the cadmium complexes, the Pb−N distances in these two structures are very similar. The structure of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Pb\}^+$ [5] is very different from these two structures and the structure of $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}^+$ reported here. The lead(II) ion is five coordinate bonded to a tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand and a bidentate $HC(3,5\text{-}Me_2pz)_3$ ligand. The three Pb−N bonding distances from the tridentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are short (average 2.43 Å), while both Pb−N bonding distances from $HC(3,5\text{-}Me_2pz)_3$ are much longer (2.745(7) and 2.827(7) Å). As observed to a lesser degree in the mixed-ligand cadmium(II) structure, in this lead(II) structure the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand coordinates much more strongly than the $HC(3,5\text{-}Me_2pz)_3$ ligand. Enemark[11] has also commented in comparing the chemistry of molybdenum complexes of the $HC(3,5\text{-}Me_2pz)_3$ ligand with similar complexes of tris(pyrazolyl)borate ligands that the $HC(3,5\text{-}Me_2pz)_3$ ligand is “much more labile.”

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Supporting Information Available: An X-ray crystallographic file in CIF format for complex $\{[HC(3,5\text{-}Me_2pz)_3][HB(3,5\text{-}Me_2pz)_3]Cd\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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