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Synthesis and Characterization of Indium(III) Complexes Containing Two Different Chelate Ligands of the Type [Hydrotris(3,5-dimethylpyrazolyl)borate]In[ligand]X

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The reaction of a variety of anionic, chelating ligands with $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ or $[HB(3,5\text{-}Me_2pz)_3]$-$InCl_2{\cdot}H(3,5\text{-}Me_2pz)$ leads to the formation of a series of mixed-ligand, six-coordinate indium complexes. Four complexes have been prepared with a second poly(pyrazolyl)borate ligand, $[HB(3,5\text{-}Me_2pz)_3]In[ligand]X$, where ligand = $[H_2B(pz)_2]^-$, $[H_2B(3,5\text{-}Me_2pz)_2]^-$, $[HB(pz)_3]^-$, or $[B(pz)_4]^-$. The observation of a methyl resonance shifted to high field in all of these complexes is shown by the solid-state structure of six-coordinate $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ to arise from the fact that one of the 3-position methyl groups of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is located between the aromatic rings of the $[H_2B(pz)_2]^-$ ligand. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ with other types of uninegative, bidentate ligands leads to the formation of $[HB(3,5\text{-}Me_2pz)_3]In[S_2CN(C_2H_5)_2]Cl$, $[HB(3,5\text{-}Me_2pz)_3]In(O_2CCH_3)Cl$, $[HB(3,5\text{-}Me_2pz)_3]In[((H_3C)_3CC(O))_2CH]Cl$, and $[HB(3,5\text{-}Me_2pz)_3]In$-$[((CF_3)C(O))_2CH]Cl$. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ with the dianionic ligand $[S_2C_2(CN)_2]^{2-}$ leads to the formation of $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]{\cdot}THF$, characterized as six-coordinate by X-ray crystallography. The reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}H(3,5\text{-}Me_2pz)$ and $[3,5\text{-}Bu^tC_6H_2O_2]^{2-}$ yields $[HB(3,5\text{-}Me_2pz)_3]In[3,5\text{-}Bu^t{}_2C_6H_2O_2]{\cdot}H(3,5\text{-}Me_2pz)$. Crystal data: $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$, monoclinic, $P2_1/n$, $a = 12.366(3)$ Å, $b = 15.098(2)$ Å, $c = 14.762(3)$ Å, $\beta = 96.47(2)°$, $V = 2738.5(10)$ Å^3, $Z = 4$, $T = 297$ K, $R(F) = 3.41\%$; $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]{\cdot}THF$, triclinic, $P\bar{1}$, $a = 10.050(4)$ Å, $b = 13.178(8)$ Å, $c = 15.882(8)$ Å, $\alpha = 70.34(1)°$, $\beta = 75.21(1)°$, $\gamma = 76.40(1)°$, $V = 1889(2)$ Å^3, $Z = 2$, $T = 242$ K, $R(F) = 4.10\%$.

Introduction

We have recently prepared a variety of complexes of gallium(III) and indium(III) containing one or two poly(pyrazolyl)borate ligands.[1] Our initial efforts involved the $[H_2B(pz)_2]^-$ (pz = pyrazolyl ring) ligand,[1a–c] but more recently we have prepared a variety of complexes using the potentially tridentate ligands $[HB(pz)_3]^-$, $[HB(3,5\text{-}Me_2pz)_3]^-$, and $[B(pz)_4]^-$.[1d,e] The results of these studies show that gallium(III) and indium(III) prefer to be either four- or six-coordinate. For example, $[HB(3,5\text{-}Me_2pz)_3]Ga(CH_3)_2$ is four-coordinate[1d] and $[B(pz)_4]_2InCH_3$ is six-coordinate.[1e] In both complexes, one of the potentially tridentate poly(pyrazolyl)borate ligands is coordinated in only a bidentate fashion.

As part of that work, it was noted that six-coordinate derivatives in the $[HB(3,5\text{-}Me_2pz)_3]In$ system were particularly stable. We decided to attempt to use this system to prepare a series of complexes that would contain two different chelate ligands. At the time we initiated these studies, there were no reports of well-characterized mixed-ligand [poly(pyrazolyl)borate]M(chelate ligand) complexes of the post transition metals. A few transition metal complexes of this type have been prepared.[2a,b] Reported here are the syntheses and characterizations of a series of mixed-ligand complexes of the general formula $[HB(3,5\text{-}Me_2pz)_3]In$-(ligand)X. The complexes $[HB(3,5\text{-}Me_2pz)_3In[H_2B(pz)_2]Cl$ and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]{\cdot}THF$ have been characterized crystallographically.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by standard Schlenk techniques or in a Vacuum Atmospheres HE-49 drybox. All solvents were dried, degassed, and distilled prior to use. The ^1H and ^{13}C solution NMR spectra were recorded on a Bruker AM300 or AM500 spectrometer using a 5-mm broadband probe. Proton chemical shifts are reported in ppm vs Me_4Si. Mass spectra were run on a Finnigan 4521 GC-mass spectrometer or a VG 70SQ spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. $K[H_2B(pz)_2]$,[3a] $K[HB(pz)_3]$,[3a] $K[B(pz)_4]$,[3a] $K[H_2B(3,5\text{-}Me_2pz)_2]$,[3c] $K[HB(3,5\text{-}Me_2pz)_3]$,[3b] $Na[(F_3CC(O))_2CH]$,[4] and $Na[((CH_3)_3CC(O))_2CH]$[4] were prepared according to published methods. In this paper, pz* is used as the symbol for $3,5\text{-}Me_2pz$. $Tl[S_2CN(C_2H_5)_2]$ was prepared from $Na[S_2CN(C_2H_5)_2]$ by a method analogous to that reported for $Tl[HB(3\text{-}Bu^tpz)_3]$.[3d] $Na_2[S_2C_2(CN)_2]$ was a gift from Professor Alan Davison of the Massachusetts Institute of Technology. $Na[S_2CN(C_2H_5)_2]{\cdot}3H_2O$ was purchased from Aldrich Chemical Co. $Na(O_2CCH_3)$ was purchased from Fisher. $InCl_3$ was purchased from Cerac and Strem. These reagents were used as received. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ and $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}Hpz^*$ were prepared as reported previously.[1e] Elemental analyses were

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performed by Robertson Laboratory, Inc. Melting points were measured under vacuum or through differential scanning calorimetry (DSC) when noted.

[Dihydrobis(1-pyrazolyl)borato][hydrotris(3,5-dimethylpyrazolyl)borato]chloroindium(III) $\{[H_2B(pz)_2][HB(3,5\text{-}Me_2pz)_3]InCl\}$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ (0.55 g, 1.1 mmol) and $K[H_2B(pz)_2]$ (0.21 g, 1.1 mmol) were placed into a round-bottomed flask. THF (25 mL) was added via syringe and the solution sirred for 4 h. The THF was removed under vacuum and the resulting white solid extracted with benzene (25 mL). The solution was filtered and the solvent removed to yield a white solid (0.28 g, 0.47 mmol, 43%), mp 206–208 °C. ^{1}H NMR ($CDCl_3$): δ 7.69, 7.21 (2, 2; d, d; *J* = 2.1 Hz, 1.9 Hz; 3,5-H pz); 6.15 (2; t; *J* = 2.2 Hz; 4-H pz); 5.86, 5.47 (2, 1; s, s; 4-H pz*); 2.44, 2.41, 2.33, 0.15 (6, 6, 3, 3; all s; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 151.5, 150.4, 145.5, 144.6 (2, 1, 2, 1; 3,5-C pz*); 139.6, 137.8 (3,5-C pz); 107.2, 106.5 (2, 1; 4-C pz*); 105.3 (4-C pz); 14.7, 13.3, 13.1, 8.6 (2, 2, 1, 1; 3,5-Me pz*). Mass spectrum: *m/z* 593 ($M^+ - H$), 558 ($M^+ - HCl$). Accurate mass spectrum (*m/z*) for $M^+ - H$: calcd for $C_{21}H_{29}N_{10}B_2ClIn$, 593.1490; found, 593.1500.

[Dihydrobis(3,5-dimethyl-1-pyrazolyl)borato][hydrotris(3,5-dimethylpyrazolyl)borato]chloroindium(III) $\{[H_2B(3,5\text{-}Me_2pz)_2][HB(3,5\text{-}Me_2pz)_3]InCl\}$. This compound was prepared in a method analogous to the bis(pyrazolyl)borato complex above in 61% yield, mp 234 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 5.76, 5.66, 5.57 (2, 2, 1; all s; 4-H pz*); 2.42, 2.38, 2.34, 1.23, 0.55 (6, 9, 6, 6, 3; all s; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 151.2, 151.1, 149.4, 146.0, 145.9, 144.9 (2, 2, 1, 2, 2, 1; 3,5-C pz*); 107.0, 106.6 (4, 1; 4-C pz*); 14.7, 13.6, 13.3, 13.2, 11.7, 9.3 (2, 2, 1, 2, 2, 1; 3,5-Me pz*). Mass spectrum: *m/z* 649 ($M^+ - H$); 614 ($M^+ - HCl$). Anal. Calcd for $C_{25}H_{38}N_{10}B_2ClIn$: C, 46.15; H, 5.90; N, 21.53. Found: C, 46.07; H, 5.86; N, 21.28.

[Hydrotris(1-pyrazolyl)borato][hydrotris(3,5-dimethylpyrazolyl)borato]chloroindium(III) $\{[HB(pz)_3][HB(3,5\text{-}Me_2pz)_3]InCl\}$. This compound was prepared in a method analogous to the bis(pyrazolyl)borato complex above in 84% yield, mp 298–301 °C. ^{1}H NMR ($CDCl_3$): δ 8.02, 7.90 (1, 1; d, d; *J* = 2.2 Hz, 2.2 Hz; 3,5-H noncoordinated pz); 7.39, 7.29 (2, 2; s, s; *J* = 2.3 Hz, 2.0 Hz; 3,5-H coordinated pz); 6.36 (1; t; *J* = 2.0 Hz; 4-H noncoordinated pz); 6.14 (2; t; *J* = 2.2 Hz; 4-H coordinated pz); 5.88, 5.52 (2, 1; s, s; 4-H pz*); 2.43, 2.42, 2.34, 0.38 (6, 6, 3, 3; all s; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 151.6, 150.9, 146.0, 144.8 (2, 1, 2, 1; 3,5-C pz*); 142.9, 140.0, 139.0, 136.8 (1, 2, 1, 2; 3,5-C pz); 107.3, 106.7 (2, 1; 4-C pz*); 105.5, 105.1 (2, 1; 4-C pz); 14.7, 13.3, 13.1, 9.3 (2, 2, 1, 1; 3,5-Me pz*). Mass spectrum: *m/z* 659 ($M^+ - H$), 625 ($M^+ - Cl$). Accurate mass spectrum (*m/z*) for $M^+ - H$: calcd for $C_{24}H_{31}N_{12}B_2ClIn$, 659.1708; found, 659.1713.

[Hydrotris(3,5-dimethylpyrazolyl)borato][tetrakis(1-pyrazolyl)borato]chloroindium(III) $\{[B(pz)_4][HB(3,5\text{-}Me_2pz)_3]InCl\}$. This compound was prepared in a method analogous to the bis(pyrazolyl)borato complex above in 59% yield, mp 212–215 °C. ^{1}H NMR ($CDCl_3$): δ 7.78, 7.74, 6.97, 6.63 (all 1; all br; 3,5-H noncoordinated pz); 7.48, 7.26 (2, 2; br, br; 3,5-H coordinated pz); 6.32 (2; br; 4-H coordinated pz); 6.22, 6.12 (1, 1; br, br; 4-H noncoordinated pz); 5.85, 5.56 (2, 1; s, s; 4-H pz*); 2.39, 2.36, 2.30, 0.68 (6, 6, 3, 3; all s; 3,5-Me pz*). Mass spectrum: *m/z* 725 ($M^+ - H$), 691 ($M^+ - Cl$). Accurate mass spectrum (*m/z*) for $M^+ - Cl$: calcd for $C_{27}H_{37}N_{14}B_2In$, 691.2316; found, 691.2318.

[Diethyldithiocarbamato][hydrotris(3,5-dimethyl-1-pyrazolyl)borato]chloroindium(III) $\{[S_2CN(C_2H_5)_2][HB(3,5\text{-}Me_2pz)_3]InCl\}$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}Hpz^*$ (0.35 g, 0.61 mmol) and $Tl[S_2CN(C_2H_5)_2]$ (0.22 g, 0.61 mmol) were placed into a flask along with 35 mL of THF. The mixture was stirred for 4 h. The solvent was removed under vacuum and the product extracted with benzene (30 mL). This solution was filtered and the solvent removed under vacuum to leave a yellow solid (0.27 g, 0.45 mmol, 75%), dec 287–295 °C. ^{1}H NMR ($CDCl_3$): δ 5.76, 5.75 (2, 1; s, s; 4-H pz*); 3.86 (4; m; *J* = 7.1 Hz; CH_2); 2.67, 2.47, 2.35, 2.32 (3, 6, 6, 3; s, s, s, s; 3,5-Me pz*); 1.35 (6; t; *J* = 7.1 Hz; CH_2CH_3). ^{13}C NMR ($CDCl_3$): 201.5 (S_2CN); 150.8, 150.2, 145.2, 144.6 (2, 1, 2, 1; 3,5-C pz*); 107.0, 106.8 (1, 2; 4-C pz*); 51.8 (CH_2); 13.9, 13.2, 13.1, 12.5 (2, 1, 2, 1; 3,5-Me pz*); 12.5 (CH_2CH_3). Mass spectrum: *m/z* 594 ($M^+ - H$), 560 ($M^+ - Cl$), 447 ($M^+ - S_2CN(C_2H_5)_2$). Accurate mass spectrum (*m/z*) for $M^+ - H$: calcd for $C_{20}H_{31}N_7BClInS_2$, 594.0903; found, 594.0898.

(Acetato)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]chloroindium(III) $\{[O_2CCH_3][HB(3,5\text{-}Me_2pz)_3]InCl\}$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ (0.34 g, 0.62 mmol) and $Na[O_2CCH_3]$ (0.05 g, 0.6 mmol) were charged into a flask with 35 mL of THF. The mixture was stirred for 4 h. The solvent was removed under vacuum and the product extracted with benzene (30 mL). This solution was filtered and the solvent removed under vacuum to leave a yellow solid (0.21 g, 0.42 mmol, 68%), dec 247–251 °C. ^{1}H NMR ($CDCl_3$, ambient temperature): δ 5.77 (3; s; 4-H pz*); 2.34, 2.30 (9, 9; s, s; 3,5-Me pz*); 1.94 (3; br; O_2CCH_3). ^{1}H NMR ($CDCl_3$, –45 °C): δ 5.85, 5.73 (2, 1; s, s; 4-H pz*); 4.6 (1; br; BH); 2.46, 2.36, 2.33, 2.21; (6, 6, 3, 3; all s; 3,5-Me pz*); 1.90 (3; s; O_2CCH_3). ^{13}C NMR ($CDCl_3$): δ 152.0 (O_2CCH_3); 151.0, 145.9 (3,5-C pz*); 106.9 (4-C pz*); 13.3, 13.1 (3,5-Me pz*); 13.2 (O_2CH_3). Mass spectrum: *m/z* 505 ($M^+ - H$), 471 ($M^+ - Cl$), 447 ($M^+ - O_2CCH_3$). Accurate mass spectrum (*m/z*) for $M^+ - H$: calcd for $C_{17}H_{24}N_6BClInO_2$, 505.0781; found, 505.0786.

(Hexafluoroacetylacetonato)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]chloroindium(III) $\{[(F_3CC(O))_2CH][HB(3,5\text{-}Me_2pz)_3]InCl\}$. This compound was prepared in a method analogous to the acetate complex above in 91% yield, sublimation point (753 Torr) 154 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 6.44 (1; s; CH acac); 5.85, 5.77 (2, 1; s, s; 4-H pz*); 2.43, 2.38, 2.33, 1.91 (6, 6, 3, 3; all s; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 181.3 (q; J_{CF} = 36 Hz; CO); 151.9, 150.7, 146.4; 146.0 (3,5-C pz*); 117.6 (q; J_{CF} = 285 Hz; CF_3); 107.2, 107.1 (4-C pz*); 92.6 (CH acac); 13.2, 13.1, 13.0, 12.5 (3,5-Me pz*). Mass spectrum: *m/z* 653 ($M^+ - H$), 635 ($M^+ - F$), 619 ($M^+ - Cl$). The accurate mass spectrum (*m/z*) for $M^+ - H$: calcd for $C_{20}H_{22}N_6BClF_6InO_2$, 653.0529; found, 653.0513.

(Dipivaloylmethanido)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]chloroindium(III) $\{[((CH_3)_3CC(O))_2CH][HB(3,5\text{-}Me_2pz)_3]InCl\}$. This compound was prepared in a method analogous to the acetate complex above in 95% yield, mp 244–247 °C. ^{1}H NMR ($CDCl_3$): δ 5.98 (1; s; CH acac); 5.79, 5.72 (2, 1; s, s; 4-H pz*); 2.53, 2.36, 2.33, 1.94 (6, 6, 3, 3; all s; 3,5-Me pz*); 1.19 (18; s; Bu^t). ^{13}C NMR ($CDCl_3$): δ 204.1 (CO); 151.4, 150.7, 145.5, 145.2 (3,5-C pz*); 106.7, 106.5 (4-C pz*); 92.6 (CH acac); 42.3 ($C(CH_3)_3$ acac); 28.8 ($C(CH_3)_3$ acac); 14.2, 13.2, 13.1, 12.5 (3,5-Me pz*). Mass spectrum: *m/z* 630 (M^+), 595 ($M^+ - Cl$). Anal. Calcd for $C_{26}H_{41}N_6BClInO_2$: C, 49.50; H, 6.56; N, 13.32. Found: C, 49.22; H, 6.51; N, 12.89. Accurate mass spectrum (*m/z*) for M^+: calcd for $C_{26}H_{41}N_6BClInO_2$, 630.2111; found, 630.2099.

[Hydrotris(3,5-dimethyl-1-pyrazolyl)borato](malenonitriledithiolato)(tetrahydrofuran)indium(III) $\{[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In{\cdot}THF\}$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}THF$ (0.27 g, 0.50 mmol) and $Na_2[S_2C_2(CN)_2]$ (0.10 g, 0.50 mmol) were placed into a flask with 35 mL of THF. The resulting yellow solution was heated at reflux overnight. The solvent was removed under vacuum and the product extracted with benzene (25 mL). The solution was filtered and the filtrate concentrated until yellow crystals formed (0.17 g, 0.26 mmol, 52%). Mp 165 °C (DSC). ^{1}H NMR ($CDCl_3$): δ 5.81 (3; s; 4-H pz*); 3.66, 1.85 (4, 4; m, m; THF); 2.37, 2.30 (9, 9; s, br; 3,5-Me pz*). ^{13}C NMR ($CDCl_3$): δ 151.4, 145.9 (3,5-C pz*); 121.4 (CN); 119.5 (C=C); 107.3 (4-C pz*); 68.7, 25.9 (THF); 14.2, 13.2 (3,5-Me pz*). Mass spectrum: *m/z* 552 ($M^+ - THF$), 412 ($M^+ - THF$, MNT). IR spectrum (cm^{-1}, Nujol): 2553 (BH); 2200 (CN); 1152 (CS). Accurate mass spectrum (*m/z*) for $M^+ - THF$: calcd for $C_{23}H_{30}N_8BInS_2$, 552.0541; found, 552.0548.

(3,5-Di-*tert*-butylcatecholato)[hydrotris(3,5-dimethyl-1-pyrazolyl)borato]indium(III) $\{[HB(3,5\text{-}Me_2pz)_3][3,5\text{-}Bu^t_2C_6H_2O_2]In{\cdot}H(3,5\text{-}Me_2pz)$. $[HB(3,5\text{-}Me_2pz)_3]InCl_2{\cdot}H(3,5\text{-}Me_2pz)$ (0.27 g, 0.52 mmol) was placed into a flask along with THF (30 mL) and the solution cooled to –78 °C. A THF solution of $Li_2[3,5\text{-}Bu^t_2C_6H_2O_2]$ (0.12 g, 0.52 mmol, prepared by the addition of 2 equiv. of butyllithium to a THF solution, cooled to –78 °C, of $3,5\text{-}Bu^t_2C_6H_2(OH)_2$) was added cold via cannula. The resulting yellow solution was allowed to warm to room temperature (1 h) and stirred an additional 3 h. The solvent was removed under vacuum, and the product was extracted with benzene (25 mL). The solution was filtered and the benzene removed under vacuum to leave a light green solid (0.30 g, 0.41 mmol, 79%), mp 193–195 °C. ^{1}H NMR ($CDCl_3$): δ 10.4 (1; br, *H*pz*); 6.88, 6.56 (1, 1; d, d; *J* = 2.4 Hz; 2,4-H catechol); 5.71 (3; br; 4-H pz*); 5.67 (1; s; 4-H Hpz*); 2.36, 2.00 (9, 9; br, br; 3,5-Me pz*); 2.34, 1.15 (3, 3; s, s; 3,5-Me Hpz*); 1.46, 1.28 (9, 9; s, s; 3,5-Bu^t). Mass spectrum: *m/z* 632 ($M^+ - Hpz^*$), 617 ($M^+ - Hpz^*, CH_3$). The accurate mass spectrum (*m/z*) for $M^+ - Hpz^*$: calcd for $C_{29}H_{42}N_6BInO_2$, 632.2501; found, 632.2502.

Crystallographic Analyses. Crystal, data collection, and refinement parameters for the two structures are collected in Table 1. Colorless crystals, grown from toluene/hexane for $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$, and yellow crystals, grown from benzene for $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]{\cdot}THF$, were mounted on glass fibers with epoxy cement. The unit cell parameters were obtained from the least-squares fit of 25 reflections ($20° \le 2\theta \le 25°$). Three standard reflections monitored every 197 reflections showed insignificant variations. Empirical corrections for absorptions were applied (216 ψ-scan reflections, pseudoellipsoid model). The indium atoms were located by direct methods. All hydrogen atoms were included as idealized isotropic contributions (d(CH) = 0.960 Å, U

Table 1. Crystallographic Data for the Structural Analyses

	$[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$	$[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$
formula	$C_{21}H_{30}B_2ClInN_{10}$	$C_{35}H_{42}BInN_8OS_2$
fw	594.4	780.5
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a, Å	12.366(3)	10.050(4)
b, Å	15.098(2)	13.178(8)
c, Å	14.762(3)	15.882(8)
α, deg		70.34(1)
β, deg	96.47(2)	75.21(1)
γ, deg		76.40(1)
V, Å^3	2738.5(10)	1889(2)
Z	4	2
T, K	297	242
λ, Å	0.710 73	0.710 73
ρ_{calc}, g/cm^3	1.442	1.372
abs coef, mm^{-1}	0.990	0.775
R_F, %	3.41	4.10
R_{wF}, %	4.72	5.07

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

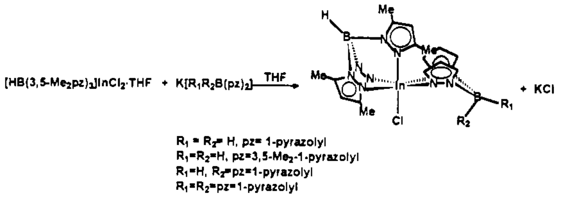
	x	y	z	U(eq)[a]
In	1723(1)	2284(1)	4443.6(1)	31(1)
Cl	1726(1)	2968.3(7)	2955.1(7)	59(1)
N(1)	1870(2)	3579(2)	5181(2)	42(1)
N(2)	1087(2)	3777(2)	5751(2)	35(1)
N(3)	1588(2)	1765(2)	5911(2)	33(1)
N(4)	960(2)	2256(2)	6444(2)	32(1)
N(5)	–95(2)	2437(2)	4436(2)	37(1)
N(6)	–479(2)	2753(2)	5215(2)	33(1)
N(7)	1579(2)	890(2)	3978(2)	36(1)
N(8)	2408(2)	426(2)	3677(2)	40(1)
N(9)	3505(2)	2020(2)	4743(2)	40(1)
N(10)	4014(2)	1345(2)	4348(2)	40(1)
B(1)	304(3)	3055(2)	6045(2)	34(1)
B(2)	3492(3)	872(3)	3469(3)	49(1)
C(1)	3326(4)	4384(3)	4476(3)	70(2)
C(2)	2416(3)	4338(2)	5065(3)	45(1)
C(3)	1991(3)	5006(2)	5554(3)	46(1)
C(4)	1149(3)	4643(2)	5969(2)	39(1)
C(5)	389(4)	5097(2)	6539(3)	56(1)
C(6)	2698(3)	380(3)	6086(3)	52(1)
C(7)	1976(3)	1074(2)	6416(2)	38(1)
C(8)	1603(3)	1122(3)	7274(2)	44(1)
C(9)	956(3)	1859(2)	7264(2)	37(1)
C(10)	295(3)	2202(3)	7980(3)	58(1)
C(11)	–889(4)	1896(4)	2907(3)	69(2)
C(12)	–970(3)	2233(2)	3853(2)	45(1)
C(13)	–1906(3)	2410(3)	4254(3)	48(1)
C(14)	–1571(3)	2737(2)	5112(2)	38(1)
C(15)	–2247(3)	3037(3)	5836(3)	55(1)
C(16)	792(3)	304(2)	4094(3)	45(1)
C(17)	1104(3)	–534(3)	3869(3)	57(1)
C(18)	2131(3)	–431(3)	3611(3)	54(1)
C(19)	4163(3)	2278(3)	5481(3)	54(1)
C(20)	5103(3)	1786(3)	5558(3)	66(2)
C(21)	4983(3)	1211(3)	4845(3)	54(1)

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

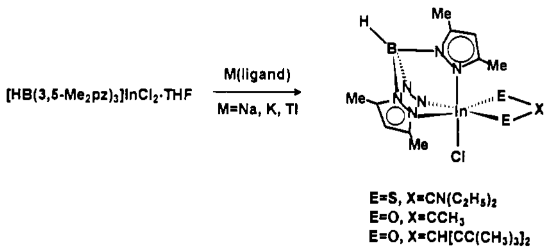
= 1.2U of attached atom). All non-hydrogen atoms were refined with anisotropic thermal parameters. All computer programs and the sources of the scattering factors are contained in the SHELXTL-PLUS program library (4.2) (G. Sheldrick, Siemens Corp., Madison, WI). Tables 2 and 3 contain the atomic coordinates and isotropic thermal parameters for $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$.

Results

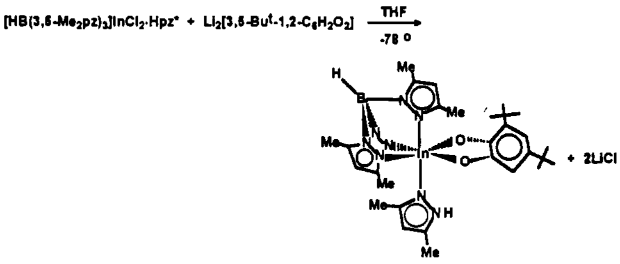
Synthesis of Complexes. Four $[HB(3,5\text{-}Me_2pz)_3]In$[poly(pyrazolyl)borato]Cl compounds were prepared in THF at room temperature by the reaction of the THF adduct of $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ with 1 equiv. of the respective poly(pyrazolyl)borate ligand salts (eq 1). Four complexes containing other types of uninegative, bidentate ligands were prepared in THF in a similar manner using the appropriate ligand salts (eq 2). Compounds of the dianionic ligands 3,5-di-*tert*-butylcatecholate and maleonitriledithiolate were also prepared in THF but at conditions other than ambient temperature. The complex $[HB(3,5\text{-}Me_2pz)_3]In[3,5\text{-}Bu^t{}_2C_6H_2O_2]\cdot H(3,5\text{-}Me_2pz)$ was prepared by adding the dilithium salt of the ligand to the dimethylpyrazolyl adduct of $[HB(3,5\text{-}Me_2pz)_3]InCl_2$ at –78 °C and slowly warming the solution to room temperature (eq 3). The complex $[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In\cdot THF$ was prepared by heating a THF solution of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ and $Na_2[S_2C_2(CN)_2]$ at reflux (eq 4). These compounds are all soluble in aromatic hydrocarbon and halocarbon solvents. Only the ketonate compounds are soluble in hydrocarbon solvents. All of the compounds with monoanionic chelate ligands are stable in both the solid and solution phases. The 3,5-di-*tert*-butylcatecholate and maleonitriledithiolate compounds decompose slowly in air in the solid phase and quickly in solution.



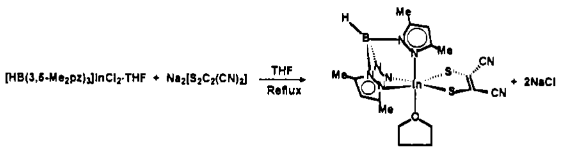
(1)



(2)



(3)



(4)

Solid-State Structures. The structures of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$ have been determined crystallographically.

$[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$. Figure 1 shows an ORTEP drawing of the compound, and Table 4 shows selected bond distances and angles. The complex is six-coordinate, and the geometry about the indium atom is a distorted octahedron. The four In–N bond lengths *cis* to the chloride ligand range from 2.216(3) to 2.260(3) Å (average 2.236 Å). The two distances from the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are 0.024 Å longer (average 2.248 Å) than those from the $[H_2B(pz)_2]^-$ ligand (average 2.224

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$

	x	*y*	*z*	*U*(eq)[a]
In	6065(1)	4525(1)	2467(1)	34(1)
S(1)	7029(1)	4991(1)	3579(1)	51(1)
S(2)	6230(1)	6442(1)	1466(1)	51(1)
O	3792(3)	4940(2)	3216(2)	48(1)
N(1)	6248(3)	2005(3)	2914(2)	35(1)
N(2)	5890(4)	2804(3)	3350(2)	38(1)
N(3)	7855(3)	2819(3)	1472(2)	40(1)
N(4)	7980(4)	3680(3)	1722(3)	43(2)
N(5)	5285(3)	3106(3)	1498(2)	35(1)
N(6)	4974(3)	4150(3)	1564(2)	36(1)
N(7)	8341(5)	7216(4)	3781(3)	70(2)
N(8)	7537(6)	8842(4)	1364(4)	81(3)
C(1)	6693(6)	−20(4)	3292(4)	65(2)
C(2)	6322(4)	1015(3)	3543(3)	42(2)
C(3)	6009(5)	1172(4)	4388(3)	47(2)
C(4)	5748(4)	2292(3)	4246(3)	40(2)
C(5)	5373(6)	2891(4)	4946(3)	57(2)
C(6)	9233(6)	1615(5)	519(4)	75(3)
C(7)	9045(5)	2522(4)	918(3)	49(2)
C(8)	9950(5)	3211(4)	820(3)	59(2)
C(9)	9271(5)	3907(4)	1392(3)	51(2)
C(10)	9799(5)	4775(5)	1500(4)	74(3)
C(11)	4489(5)	1942(4)	829(3)	54(2)
C(12)	4436(4)	2984(4)	1016(3)	41(2)
C(13)	3571(4)	3969(4)	758(3)	43(2)
C(14)	3930(4)	4669(3)	1109(3)	37(2)
C(15)	3284(4)	5832(4)	1032(3)	48(2)
C(16)	7880(5)	6834(4)	3404(3)	49(2)
C(17)	7276(4)	6319(3)	2959(3)	41(2)
C(18)	6972(4)	6888(3)	2126(3)	42(2)
C(19)	7279(5)	7981(4)	1710(3)	54(2)
C(20)	2698(5)	4283(4)	3473(4)	58(2)
C(21)	1421(6)	4967(6)	3770(6)	95(4)
C(22)	1821(6)	5784(6)	4026(5)	85(3)
C(23)	3270(6)	5901(5)	3519(4)	69(3)
B	6528(5)	2296(4)	1873(3)	36(2)
C(31)	−30(10)	1718(7)	3394(7)	116(5)
C(32)	1272(10)	1641(8)	2962(6)	121(5)
C(33)	2299(8)	1576(7)	3392(6)	107(4)
C(34)	2053(8)	1551(6)	4231(6)	87(4)
C(35)	776(11)	1654(12)	4657(7)	199(10)
C(36)	−268(9)	1732(12)	4240(9)	205(11)
C(41)	1226(11)	8944(8)	1789(11)	134(7)
C(42)	2450(13)	9145(8)	1178(8)	135(7)
C(43)	3566(9)	9172(7)	1466(8)	107(5)
C(44)	3505(9)	9019(6)	2336(8)	108(5)
C(45)	2296(13)	8852(7)	2948(7)	128(6)
C(46)	1148(10)	8797(8)	2673(9)	128(6)

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

Å). For comparison, the compound $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot NCCH_3$ has In–N bond lengths that average 2.250 Å,[5] similar to the $[HB(3,5\text{-}Me_2pz)_3]^-$ distances in $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]_2Cl$, and the complex $[H_2B(pz)_2]_3In$ has In–N distances averaging 2.241 Å. The In–Cl distance of 2.428(1) Å is similar to those in $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot NCCH_3$ of 2.428(2) and 2.429(2) Å. The In–N bond *trans* to the chloride ligand is 0.07 Å longer than the longest of the other four. This result is surprising given the low *trans* influence of a chloride ligand. Interestingly, in the similar six-coordinate structures of $[B(pz)_4]_2MCH_3$ (M = Ga, In) the M–N distance *trans* to the strong *trans* influence methyl ligand is the shortest in both complexes.[1d,e] There are no apparent packing forces in the lattices of these compounds to explain the differences. The results seem backward in both cases.

The intraligand N–In–N angles in the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand range from 81.5(1) to 86.5(1)°, with an average of 83.4°, while the intraligand angle in the $[H_2B(pz)_2]^-$ ligand is 86.3(1)°.

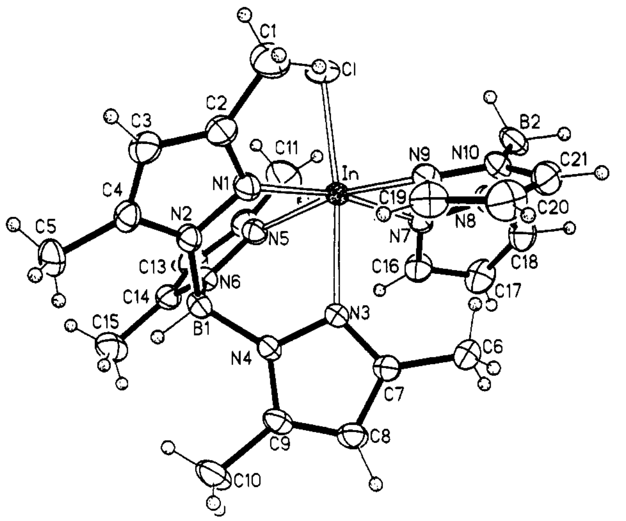


Figure 1. ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$.

There are two types of interligand N–In–N angles. The first arise from nitrogen atoms in the square plane *cis* to the chloride ligand with angles averaging 92.4° (*cis*) and 168.5° (*trans*). The second interligand angles are those involving the nitrogen atom *trans* to the chloride ligand with N–In–N angles of 85.9(1) and 87.6(1)°. The N–In–Cl angles from the $[H_2B(pz)_2]^-$ ligand average 98.2° and from the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand average 93.2° (*cis*) and 173.2(1)° (*trans*).

The six-member InN_4B ring is in the normal boat conformation with the boron atom "up" on the same side of the octahedron as the chloride ligand. This orientation of the bidentate ligand pushes its coordinated pyrazolyl rings "down" away from the chloride ligand. This arrangement causes the methyl group at C(6) of the tridentate ligand to be oriented between the pyrazolyl rings of the bidentate ligand. As discussed below, this position causes unusual chemical shifts in the NMR spectra for this methyl group.

$[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$. Figure 2 shows an ORTEP drawing of the compound, and Table 4 shows selected bond distances and angles. The compound is again six-coordinate, with the geometry around the indium a distorted octahedron. The In–N bond distances range from 2.244(5) to 2.251(3) Å (average 2.248 Å). The In–S average distance of 2.511 Å is shorter than those observed in $[HB(3,5\text{-}Me_2pz)_3]In[S_4]\cdot H(3,5\text{-}Me_2pz)$ (average 2.554 Å),[6] $[NEt_4]_2\{[S_2C_2(CN)_2]_2InCl\}$ (average 2.537 Å),[7a] and $[NEt_4]_3\{[S_2C_2(CN)_2]_3In\}$ (average 2.604 Å).[7b] The C(17)–C(18) bond distance of 1.355(6) Å is essentially the same as the two other indium maleonitriledithiolate complexes, $[NEt_4]_3\{[S_2C_2(CN)_2]_3In\}$ (average 1.36 Å) and $[NEt_4]_2\{[S_2C_2(CN)_2]_2InCl\}$ (average 1.38 Å). The average S–C distance of 1.737 Å is slightly longer than the average of 1.72 Å in the two previously mentioned structures. The average C–CN distance of 1.438 Å is in good agreement with the values of 1.42 and 1.44 Å observed in the other two structures. The S–In–S angle of 86.8(1)° is larger than those in $[NEt_4]_3\{[S_2C_2(CN)_2]_3In\}$ (average 81.5°) and in $[NEt_4]_2\{[S_2C_2(CN)_2]_2InCl\}$ (average 84.7°).[7] The N–In–N angles range from 82.4(1) to 85.0(1)° with an average of 83.7°. The N–In–S angles average 98.1° (cis) and 173.4° (trans). The N(4)–In–O angle of 161.5(2)° is somewhat distorted when compared to the N(3)–In–Cl angle of 173.2(1)° in the previous structure.

Proton and Carbon-13 NMR. In contrast to the vast majority of poly(pyrazolyl)borate complexes of the post-transition metals, ^1H NMR spectra indicate the $[HB(3,5\text{-}Me_2pz)_3]In(poly(pyrazolyl)borato)Cl$ complexes are not fluxional on the NMR

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Table 4. Selected Bond Distances and Bond Angles for $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_3]Cl$ and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$

(a) Bond Distances (Å)

$[HB(3,5\text{-}Me_2pz)_3]\text{-}In[H_2B(pz)_2]Cl$		$[HB(3,5\text{-}Me_2pz)_3]\text{-}In[S_2C_2(CN)_2]\cdot THF$	
In–N(1)	2.236(3)	In–N(2)	2.251(3)
In–N(3)	2.327(3)	In–N(4)	2.250(4)
In–N(5)	2.260(3)	In–N(6)	2.244(5)
In–N(7)	2.216(3)	In–S(1)	2.513(2)
In–N(9)	2.233(3)	In–S(2)	2.509(2)
In–Cl	2.428(1)	In–O	2.323(3)
N(1)–N(2)	1.384(4)	N(1)–N(2)	1.379(6)
N(3)–N(4)	1.382(4)	N(3)–N(4)	1.362(6)
N(5)–N(6)	1.378(4)	N(5)–N(6)	1.372(5)
N(7)–N(8)	1.357(4)	S(1)–C(17)	1.737(4)
N(9)–N(10)	1.363(4)	S(2)–C(18)	1.737(6)
N(2)–B(1)	1.553(5)	N(1)–B	1.531(6)
N(4)–B(1)	1.534(4)	N(3)–B	1.538(6)
N(6)–B(1)	1.543(4)	N(5)–B	1.543(6)
N(8)–B(2)	1.561(5)	C(17)–C(18)	1.355(6)
N(10)–B(2)	1.556(5)	C(16)–C(17)	1.438(9)
		C(18)–C(19)	1.439(7)

(b) Bond Angles (deg)

$[HB(3,5\text{-}Me_2pz)_3]\text{-}In[H_2B(pz)_2]Cl$		$[HB(3,5\text{-}Me_2pz)_3]\text{-}In[S_2C_2(CN)_2]\cdot THF$	
N(1)–In–N(3)	81.5(1)	N(2)–In–N(4)	82.4(1)
N(1)–In–N(5)	86.5(1)	N(2)–In–N(6)	85.0(1)
N(3)–In–N(5)	82.2(1)	N(4)–In–N(6)	83.6(1)
N(7)–In–N(9)	86.3(1)	S(1)–In–S(2)	86.8(1)
N(1)–In–N(7)	169.0(1)	S(2)–In–N(2)	179.0(1)
N(1)–In–N(9)	92.0(1)	S(1)–In–N(2)	94.2(1)
N(3)–In–N(7)	87.6(1)	S(2)–In–N(4)	97.7(1)
N(3)–In–N(9)	85.9(1)	S(1)–In–N(4)	102.4(1)
N(5)–In–N(7)	92.9(1)	S(2)–In–N(6)	94.0(1)
N(5)–In–N(9)	168.0(1)	S(1)–In–N(6)	173.8(1)
Cl–In–N(1)	93.4(1)	O–In–N(2)	84.4(1)
Cl–In–N(3)	173.2(1)	O–In–N(4)	161.5(2)
Cl–In–N(5)	93.1(1)	O–In–N(6)	82.3(1)
Cl–In–N(7)	97.6(1)	O–In–S(2)	95.2(1)
Cl–In–N(9)	98.8(1)	O–In–S(1)	91.4(1)
In–N(1)–N(2)	117.4(2)	In–N(2)–N(1)	116.7(2)
In–N(3)–N(4)	117.0(2)	In–N(4)–N(3)	118.4(3)
In–N(5)–N(6)	117.9(2)	In–N(6)–N(5)	117.1(3)
In–N(7)–N(8)	123.7(2)	In–S(2)–C(18)	99.6(1)
In–N(9)–N(10)	122.8(2)	In–S(1)–C(17)	99.4(2)
N(1)–N(2)–B(1)	121.3(2)	N(2)–N(1)–B	121.4(3)
N(3)–N(4)–B(1)	120.6(2)	N(4)–N(3)–B	119.6(3)
N(5)–N(6)–B(1)	121.4(3)	N(6)–N(5)–B	121.0(4)
N(7)–N(8)–B(2)	122.7(3)	S(2)–C(18)–C(17)	127.0(4)
N(9)–N(10)–B(2)	122.2(3)	S(1)–C(17)–C(18)	127.2(5)
		S(2)–C(18)–C(19)	113.9(4)
		S(1)–C(17)–C(16)	114.0(3)
		C(17)–C(18)–C(19)	119.1(5)
		C(16)–C(17)–C(18)	118.8(4)

time scale.[8] The resonances for each type of hydrogen atom in the pyrazolyl rings of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are in a 2/1 ratio (Figure 3 shows the spectrum of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$). For the second poly(pyrazolyl)borate ligand, the two pyrazolyl rings coordinated to the metal are equivalent and every additional ring is nonequivalent. Thus, the $[H_2B(pz)_2]^-$ ligand has only one set of pyrazolyl resonances (Figure 3), the $[HB(pz)_3]^-$ ligand has two types in a 2/1 ratio, and the $[B(pz)_4]^-$ ligand has three types in a 2/1/1 ratio. An interesting and important observation in the proton and carbon spectra of these complexes is the observation of a resonance for a 3-position methyl group on the unique pyrazolyl ring of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand that is significantly shifted to high field. This resonance is shifted 1.7 to 2.2 ppm in the proton spectra (Figure 3) and 4 to 5 ppm in the carbon spectra when compared to the methyl resonances in the other (3,5-Me_2pz) rings.

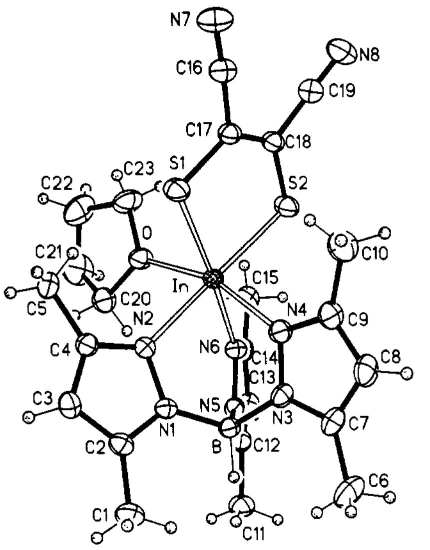

Figure 2. ORTEP drawing of $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$.

In a similar manner, the two $[HB(3,5\text{-}Me_2pz)_3]In$(acetylacetonato)Cl complexes and the diethyldithiocarbamato compound show no dynamic behavior in the NMR spectra. They show the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand resonances in a 2/1 ratio. However, the highly shielded 3-methyl resonance noted in all of the compounds with bidentate poly(pyrazolyl)borate ligands is not observed in these complexes. The complex $[HB(3,5\text{-}Me_2pz)_3]In(O_2CCH_3)Cl$ is fluxional at ambient temperature, but its ^1H NMR spectrum shows the 2/1 pattern of the pyrazolyl rings at –45 °C.

Discussion

Six-coordinate, mixed-ligand complexes of the type $[HB(3,5\text{-}Me_2pz)_3]In[\text{ligand}]X$ can be readily prepared with a variety of chelate ligands. Only a few poly(pyrazolyl)borate complexes containing a second polydentate ligand have been reported. As part of the study with the lanthanides and yttrium,[9] Takats has reported the synthesis of $[HB(pz)_3]_2M(\beta\text{-diketonate})$ (M = Yb, Lu; β-diketonate = 2,2,6,6-tetramethyl-3,5-heptadionate (dpm); 3-(trifluoroacetyl)-*d*-camphorate).[10] The synthesis of $[HB(pz)_3]_2M(acac)$ complexes (M = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Yb, Lu; acac = acetylacetonate) has also been reported by Jones and co-workers.[11] With d-block transition metals, Trofimenko and co-workers prepared a series of first-row transition metal complexes of the general formula $[HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_3]ML$, where L was a uninegative polydentate ligand. The solid-state structures were determined for M = Ni, L = $[HB(pz)_3]^-$ and $[HB(3,5\text{-}Me_2pz)_3]^-$, and M = Co, L = $[HB(3\text{-}Phpz)_3]^-$, $[H_2B(3\text{-}Phpz)_2]^-$, and $[Ph_2B(pz)_2]^-$.[2a,b] In this work, they emphasized the importance of using the moderately bulky $[HB(3\text{-}Pr^i\text{-}4\text{-}Brpz)_3]^-$ ligand to prevent the formation of L_2M complexes. This ligand also avoids the problem of the very bulky $[HB(3\text{-}Bu^tpz)_3]^-$ ligand in that $[HB(3\text{-}Bu^tpz)_3]MX$ complexes are not reactive toward other chelate ligands. Molybdenum complexes containing sulfur donor, chelate ligands,[2c-e] and a copper complex[2f] have also been reported. We have recently reported the syntheses of mixed-ligand poly(pyrazolyl)borate complexes of cadmium.[12]

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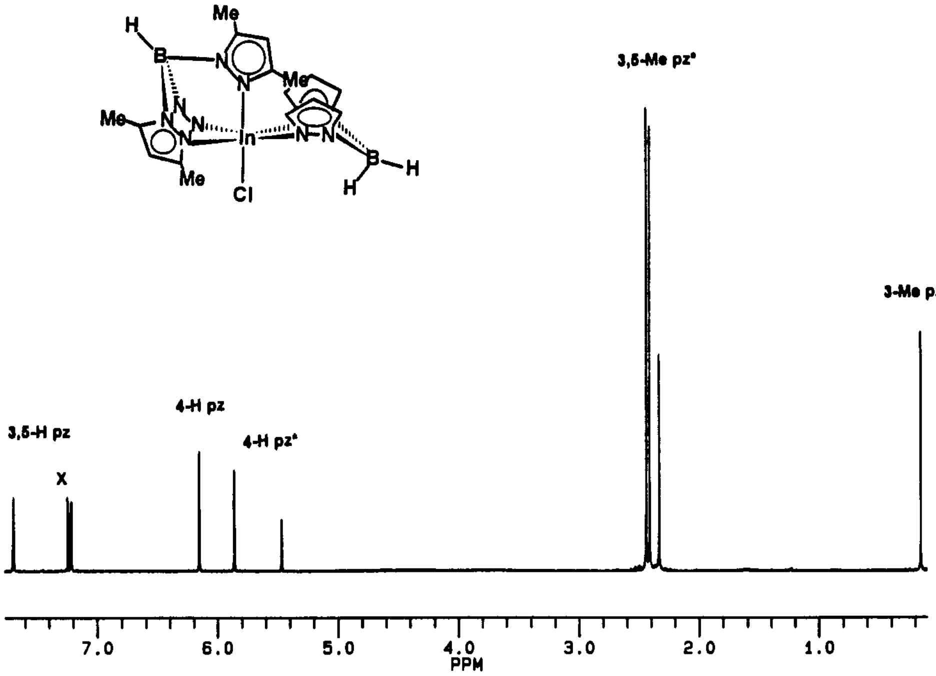

Figure 3. ^{1}H NMR spectrum of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ in $CDCl_3$. The resonance marked × is the solvent, and the resonance at δ 0.15 is the unusually shielded 3-position methyl resonance on the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand.

The complexes $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]_2Cl$ and $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$ are the first mixed-ligand, pyrazolylborate complexes to be structurally characterized for the post-transition metals. In agreement with the results quoted above for transition metal complexes, an important reason for the success of the syntheses of these novel complexes can be attributed to the fact that attempts to prepare neutral compounds of indium(III) with more than one $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand have not been successful. Reaction of $[HB(3,5\text{-}Me_2pz)_3]InCl_2\cdot THF$ with $K[HB(3,5\text{-}Me_2pz)_3]$ or $Tl[HB(3,5\text{-}Me_2pz)_3]$ leads only to the formation to the pyrazolyl adduct of the starting material. Similar results are encountered when starting from $InCl_3$ or any $RInCl_2$ compound. In contrast, we have prepared a variety of six-coordinate $[poly(pyrazolyl)borate]_2MX$ (M = Ga, In) complexes with the $[HB(pz)_3]^-$ and $[B(pz)_4]^-$ ligands.

The reasons for the failure to prepare $[HB(3,5\text{-}Me_2pz)_3]_2InX$ complexes, complexes that would also be expected to be six-coordinate, must involve a steric problem created by the 3,5-dimethylpyrazolyl rings. Formation of the $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(3,5\text{-}Me_2pz)_2]Cl$ complex demonstrates steric compatibility of two *coordinated* (3,5-Me_2pz) rings within the $[HB(3,5\text{-}Me_2pz)_3]InCl$ core. Formation of the complex $[HB(3,5\text{-}Me_2pz)_3]In[HB(pz)_3]Cl$ demonstrates compatibility of one $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand and one unsubstituted hydrotris(pyrazolyl)borate ligand. Thus, the steric problem must arise from the (3,5-Me_2pz) ring of the bidentate $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand that would be noncoordinated in a six-coordinate structure.

The structure of $[HB(3,5\text{-}Me_2pz)_3]In[H_2B(pz)_2]Cl$ can be used to explain the abnormal shielding seen in the proton and carbon NMR spectra in six-coordinate, octahedral, poly(pyrazolyl)borate complexes with one tridentate and one bidentate pyrazolylborate ligand. One 3-position methyl group of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is located between the aromatic rings of the bidentate ligand. The aromatic ring currents of the two pyrazolyl rings of the bidentate ligand cause the resonances to be shielded when compared to similar groups in a normal environment. This shielding effect for a 3-position hydrogen atom has been noted previously in the ^{1}H NMR spectra of complexes such as $[B(pz)_4]_2InCl$ and $[B(pz)_4]_2GaCH_3$.[1d,e] The effect with these complexes is not as dramatic because a hydrogen atom in this environment does not extend as far toward the aromatic rings of the bidentate ligand. We believe observation of these unusually shielded resonances can be used to assign six-coordinate structures to complexes containing two poly(pyrazolyl)borate ligands.

Both complexes of the dianionic ligands, $[HB(3,5\text{-}Me_2pz)_3]In[S_2C_2(CN)_2]\cdot THF$ and $[HB(3,5\text{-}Me_2pz)_3]In[3,5\text{-}Bu^t{}_2C_6H_2O_2]\cdot H(3,5\text{-}Me_2pz)$, retain the Lewis base adduct of their starting material to remain six-coordinate. This result follows a trend that we have observed previously in the chemistry of gallium and indium using poly(pyrazolyl)borate ligands. These compounds strongly prefer either four-coordination or six-coordination.[1d,e] Even those complexes containing more nitrogen donor atoms in the poly(pyrazolyl)borate ligands than needed to reach these coordination numbers follow the trend.

It is possible to assign different oxidation states to the metal in complexes of the catecholate and maleonitriledithiolate ligands because different forms of these ligands can be written that vary the charges between −2 and 0. Structural studies on maleonitriledithiolate complexes have correlated intraligand bond distances with the charge of the ligand.[13] The C(17)–C(18), average S–C, and C–CN bond distances are essentially the same as in two other indium maleonitriledithiolate complexes where the ligand clearly has a −2 charge, leading us to conclude that in $[HB(3,5\text{-}Me_2pz)_3][S_2C_2(CN)_2]In\cdot THF$ the maleonitriledithiolate ligand is also in the dinegative state and the metal is in the +3 oxidation state.

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Supplementary Material Available: Tables of complete data collection information, bond distances and angles, anisotropic thermal parameters, and positional parameters of H atoms (14 pages). Ordering information is given on any current masthead page.

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