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Lead(II) Complexes Containing Two Different Polydentate Ligands. Crystal and Molecular Structure of $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$ (pz = Pyrazolyl Ring), a Cationic−Anionic, Double-Coordination Complex

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The reaction in water of $PbCl_2$ with equimolar amounts of both $Na\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}$ and $K[HB(pz)_3]$ (pz = pyrazolyl ring) yields $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[HB(pz)_3]$. A similar reaction with $SnCl_2$ in CH_2Cl_2 yields $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Sn[HB(pz)_3]$. The reaction of $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$ and $[H_2B(pz)_2]_2Pb$ yields $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[H_2B(pz)_2]$. The ^{207}Pb NMR resonances for the mixed-ligand lead complexes are located fairly close to the average of the two respective symmetrical $(ligand)_2Pb$ complexes. $\{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_2\}NO_3$ is isolated from the reaction of $Pb(NO_3)_2$, $P(O)(3,5\text{-}Me_2pz)_3$, and $K[HB(3,5\text{-}Me_2pz)_3]$. In a similar reaction mixture, containing small amounts of HCl, $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$ forms, as characterized by X-ray crystallography. The structure contains a six-coordinate lead(II) cation in a capped octahedral geometry, with the lone pair on the lead atom in the capping position of the face formed by the three $3,5\text{-}Me_2pzH$ ligands and a chloride anion hydrogen bonded to the N−H groups of these $3,5\text{-}Me_2pzH$ ligands. The reaction of 1 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ and $Pb(NO_3)_2$ leads to the formation of $[HB(3,5\text{-}Me_2pz)_3]Pb(\eta^1\text{-}NO_3)$, characterized in the solid state by X-ray crystallography. The $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is tridentate and the nitrate ligand monodentate, leading to a structure best described as pseudo trigonal bipyramidal with the oxygen atom in an axial site and the stereoactive lone pair in an equatorial site. The reaction of $[HB(3,5\text{-}Me_2pz)_3]Pb(\eta^1\text{-}NO_3)$ and $[H_2B(pz)_2]^-$ yields $[HB(3,5\text{-}Me_2pz)_3]Pb[H_2B(pz)_2]$, assigned as a five coordinate complex from ^{207}Pb NMR. Crystal data: $[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)$, monoclinic, $P2_1/c$, $a = 14.218(3)$ Å, $b = 7.842(2)$ Å, $c = 18.319(6)$ Å, $\beta = 94.36(2)°$, $V = 2037$ Å^3, $Z = 4$, $R = 4.7\%$; $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$, trigonal, $P31c$, $a = 11.069(2)$ Å, $c = 17.319(3)$ Å, $V = 1838$ Å^3, $Z = 2$, $R = 2.51\%$.

Introduction

We recently reported the preparation and characterization of poly(pyrazolyl)borate complexes of lead(II).[1] Three of the complexes, $[B(pz)_4]_2Pb$, $[HB(pz)_3]_2Pb$, and $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ (pz = pyrazolyl ring), have been characterized in the solid state by X-ray crystallography. The structures of these complexes, each containing potentially tridentate ligands, are different. $[B(pz)_4]_2Pb$ has a pseudo trigonal bipyramidal geometry, with each ligand having bidentate coordination and spanning an axial and equatorial site. The lead lone pair presumably occupies the remaining equatorial vertex. In $[HB(pz)_3]_2Pb$, both ligands are tridentate, forming a six-coordinate, monomeric structure. The geometry about the lead atom is best described as a capped octahedron with the lone pair on the metal located in the capping position. $[HB(3,5\text{-}Me_2pz)_3]_2Pb$ is also six-coordinate, but the geometry about the lead atom is a trigonally distorted octahedron. The lead atom sits on a center of inversion, and the planes formed by the three nitrogen donor atoms of each ligand are parallel. The lone pair on lead is clearly stereochemically inactive. This complex represents the first example of a six-coordinate, main-group molecular compound in which the lone pair is stereochemically inactive.

In order to synthesize additional examples of lead(II) complexes with umbrella-type, potentially tridentate ligands, it was decided to attempt to prepare complexes that contain one poly(pyrazolyl)borate ligand and a second, different umbrella-type ligand. The ligands chosen were the Kläui ligand,[2] $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}^-$, and the neutral ligand $P(O)(3,5\text{-}Me_2pz)_3$.[3] The complex $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$ has been reported previously. Its solid state structure has been determined and shown to be six-coordinate with a sterically active lone pair,[4] similar to the structure of $[HB(pz)_3]_2Pb$. Mixed-ligand complexes of these ligands have not been reported for any metals. In fact, only a few mixed-ligand complexes containing poly(pyrazolyl)borate ligands have been reported.[5−7]

Reported here are the preparations of $[HB(pz)_3]M\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}$ (M = Pb, Sn) and $[H_2B(pz)_2]Pb\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}$. Attempts to prepare mixed-ligand complexes with the $P(O)(3,5\text{-}Me_2pz)_3$ ligand have led to the

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preparation of two complexes in which this ligand has decomposed by cleavage of the P—N bonds. The decomposition product isolated in the presence of HCl is $\mathrm{[HB(3,5-Me_2pz)_3]Pb(3,5-Me_2pzH)_3Cl}$. This unusual compound has been characterized by X-ray crystallography and can be described as a double-coordination compound of the lead(II) cation and the chloride anion. The complexes $\mathrm{[HB(3,5-Me_2pz)_3]Pb[H_2B(pz)_2]}$ and $\mathrm{[HB(3,5-Me_2pz)_3]Pb(\eta^1-NO_3)}$ have also been prepared, and the latter has 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-493 drybox. All solvents were dried, degassed, and distilled prior to use. The ^{1}H NMR spectra were recorded at ambient temperature on either a Bruker AM-300 spectrometer or a Bruker AM-500 spectrometer using a 5-mm broad-band probe. Abbreviations used in the assignment of ^{1}H NMR resonances are pz = pyrazolyl ring and Me$_2$pz = 3,5-dimethylpyrazolyl ring. The ^{207}Pb NMR spectra were recorded on a Bruker AM-500 spectrometer using a 5-mm broad-band probe. The ^{207}Pb NMR spectra were recorded at −49 °C using a 90° pulse width in a 1000 ppm window. Lead chemical shifts are reported (ppm) downfield from tetramethyllead using $\mathrm{PbPh_4}$ ($\delta_{\mathrm{Pb}} = -178.0$ ppm; saturated in $\mathrm{CDCl_3}$) as an external standard. Mass spectra were run on a VG 70SQ mass spectrometer. Clusters assigned to specific ions in the mass spectra show appropriate isotopic patterns as calculated for the atoms present. $\mathrm{K[H_2B(pz)_2]}$,[8] $\mathrm{K[HB(pz)_3]}$,[8] $\mathrm{K[HB(3,5-Me_2pz)_3]}$,[9] $\mathrm{Na\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$,[10] $\mathrm{P(O)(3,5-Me_2pz)_3}$,[3] $\mathrm{[H_2B(pz)_2]_2Pb}$,[1] and $\mathrm{\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb}$[4] were prepared according to the published methods. $\mathrm{PbCl_2}$, $\mathrm{Pb(NO_3)_2}$, and $\mathrm{SnCl_2}$ were purchased from Aldrich Chemical Co. and used as received. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

[Cyclopentadienyltris(diethyl phosphito-*P*)cobaltato-*O,O′,O″*][hydrotris(1-pyrazolyl)borato]lead(II), $\mathbf{[HB(pz)_3]Pb\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$. $\mathrm{PbCl_2}$ (0.20 g, 0.72 mmol), $\mathrm{Na\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$ (0.40 g, 0.72 mmol), and $\mathrm{K[HB(pz)_3]}$ (0.18 g, 0.71 mmol) were combined in a flask. Water (20 mL) was added, and the mixture was stirred overnight. The resultant solid was isolated by filtration and dissolved in benzene (10 mL), and the mixture was filtered. Evaporation of benzene under vacuum yielded a yellow solid (0.54 g, 0.57 mmol, 79%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 7.70, 7.64 (d, b; 3, 3; J = 2.0 Hz; 3,5-*H* in pz); 6.17 (t, 3, J = 2.0 Hz, 4-*H* in pz); 5.09 (s, 5, $\mathrm{C_5}H_5$); 4.06 (m, 12, $\mathrm{POC}H_2\mathrm{CH_3}$); 1.27 (t, 18, J = 7.1 Hz, $\mathrm{POCH_2C}H_3$). ^{207}Pb NMR ($\mathrm{CDCl_3}$, −49 °C), δ: −1163 ($w_{1/2}$ = 109 Hz). Anal. Calcd for $\mathrm{C_{26}H_{45}BCoN_6O_9P_3Pb}$: C, 32.68; H, 4.75. Found: C, 33.11; H, 4.62.

[Cyclopentadienyltris(diethyl phosphito-*P*)cobaltato-*O,O′,O″*]-[dihydrobis(1-pyrazolyl)borato]lead(II), $\mathbf{[H_2B(pz)_2]Pb\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$. $\mathrm{\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb}$ (0.64 g, 0.50 mmol) and $\mathrm{[H_2B(pz)_2]_2Pb}$ (0.25 g, 0.50 mmol) were combined in a flask. Toluene (30 mL) was added, and the mixture was heated at reflux overnight. The solvent was removed under vacuum, the residue was extracted with benzene (20 mL), and the extract was filtered. Evaporation of the benzene under vacuum yielded a yellow solid (0.37 g, 0.42 mmol, 42%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 7.55, 7.53 (d, d; 2, 2; J = 1.4, 1.7 Hz; 3,5-*H* in pz); 6.09 (t, 2, J = 1.7 Hz, 4-*H* in pz); 5.06 (s, 5, $\mathrm{C_5}H_5$); 4.02 (m, 12, $\mathrm{POC}H_2\mathrm{CH_3}$); 1.23 (t, 18, J = 7.1 Hz, $\mathrm{POCH_2C}H_3$). ^{207}Pb NMR ($\mathrm{CDCl_3}$, −49 °C), δ: −1049 ($w_{1/2}$ = 170 Hz). The mass spectrum shows clusters at *m/z* 889 ($\mathrm{M^+}$) and 743 ($\mathrm{M^+ - H_2B(pz)_2}$). The high-resolution mass spectrum shows $\mathrm{M^+ - H}$, *m/e* calcd for $\mathrm{C_{23}H_{42}BCoN_4O_9P_3{}^{206}Pb}$ 887.1334, found 887.1306.

[Cyclopentadienyltris(diethyl phosphito-*P*)cobaltato-*O,O′,O″*][hydrotris(1-pyrazolyl)borato]tin(II), $\mathbf{[HB(pz)_3]Sn\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$. $\mathrm{SnCl_2}$ (0.15 g, 0.79 mmol), $\mathrm{Na\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}}$ (0.44 g, 0.79 mmol), and $\mathrm{K[HB(pz)_3]}$ (0.20 g, 0.79 mmol) were combined in a flask. $\mathrm{CH_2Cl_2}$ (20 mL) was added, and the mixture was stirred overnight. The yellow solution was filtered, and the solvent was removed under vacuum to yield a yellow oil (0.60 g, 0.69 mmol, 87%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 7.54, 7.49 (b, b; 3, 3; 3,5-*H* in pz); 6.13 (t, 3, J = 2.0 Hz, 4-*H* in pz); 5.05 (s, 5, $\mathrm{C_5}H_5$); 4.02 (m, 12, $\mathrm{POC}H_2\mathrm{CH_3}$); 1.21 (t, 18, J = 7.1 Hz, $\mathrm{POCH_2C}H_3$). The mass spectrum shows clusters at *m/z* 868 ($\mathrm{M^+}$) and 655 ($\mathrm{M^+ - HB(pz)_3}$). The high-resolution mass spectrum shows $\mathrm{M^+}$, *m/e* calcd for $\mathrm{C_{26}H_{45}BCoN_6O_9P_3{}^{116}Sn}$ 864.0903, found 864.0928.

Bis(3,5-dimethylpyrazole)[hydrotris(3,5-dimethylpyrazolyl)borato]lead(II) Nitrate, $\mathbf{\{[HB(3,5-Me_2pz)_3]Pb(3,5-Me_2pzH)_2\}NO_3}$. $\mathrm{Pb(NO_3)_2}$ (0.36 g, 1.1 mmol) and $\mathrm{P(O)(3,5-Me_2pz)_3}$ (0.36 g, 1.1 mmol) were combined in a flask. Acetonitrile (20 mL) was added, and the mixture was heated at reflux for 2 h. An acetonitrile solution (20 mL) of $\mathrm{K[HB(3,5-Me_2pz)_3]}$ (0.36 g, 1.1 mmol) was added, and the mixture was stirred overnight. The solvent was removed under vacuum. The residue was extracted with $\mathrm{CH_2Cl_2}$ (40 mL) and the extract filtered. The solution was placed in a −20 °C freezer for several days, yielding light blue crystals (0.54 g, 0.71 mmol, 65%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 5.82 (s, 3, 4-*H* in $\mathrm{HB(Me_2pz)_3}$); 5.74 (s, 2, 4-*H* in $\mathrm{Me_2pzH}$); 2.37, 2.09 (s, s; 9, 9; 3,5-$(\mathrm{C}H_3)_2$ in $\mathrm{HB(Me_2pz)_3}$); 1.93 (s, 12, 3,5-$(\mathrm{C}H_3)_2$ in $\mathrm{Me_2pzH}$). ^{207}Pb NMR ($\mathrm{CDCl_3}$, −49 °C), δ: −639 ($w_{1/2}$ = 1100 Hz). Anal. Calcd for $\mathrm{C_{25}H_{38}BN_{11}O_3Pb}$: C, 39.58; H, 5.05; N, 20.31. Found: C, 39.38; H, 5.17; N, 20.51. A similar reaction with $\mathrm{P(O)(3,5-Me_2pz)_3}$ contaminated with a small amount of HCl yielded $\mathrm{[HB(3,5-Me_2pz)_3]Pb(3,5-Me_2pzH)_3Cl}$ in low yield. ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 5.83 (s, 3, 4-*H* in $\mathrm{HB(Me_2pz)_3}$); 5.79 (s, 3, 4-*H* in $\mathrm{Me_2pzH}$); 2.36, 2.31 (s, s; 9, 9; 3,5-$(\mathrm{C}H_3)_2$ in $\mathrm{HB(Me_2pz)_3}$); 2.17, 2.16 (s, s; 9, 9; 3,5-$(\mathrm{C}H_3)_2$ in $\mathrm{Me_2pzH}$). The resonance for the NH hydrogen atoms is not observed in this ambient temperature spectrum but is observed as a broad resonance at 12.6 ppm in the spectrum recorded at −50 °C.

[Hydrotris(3,5-dimethylpyrazolyl)borato]lead(II) Nitrate, $\mathbf{[HB(3,5-Me_2pz)_3]Pb(NO_3)}$. THF (20 mL) was added to a mixture of $\mathrm{Pb(NO_3)_2}$ (0.34 g, 1.0 mmol) and $\mathrm{K[HB(3,5-Me_2pz)_3]}$ (0.34 g, 1.0 mmol), and the mixture was stirred overnight. The solvent was removed under vacuum, the residue extracted with $\mathrm{CH_2Cl_2}$ (20 mL), and the extract filtered. Evaporation of the solvent under vacuum yielded a white solid (0.45 g, 0.79 mmol, 79%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 5.87 (3, s, 4-H in $\mathrm{Me_2pz}$); 2.38, 2.36 (9, 9; s, s; 3,5-$\mathrm{(CH_3)_2}$ in $\mathrm{Me_2pz}$). Anal. Calcd for $\mathrm{C_{15}H_{22}BN_7O_3Pb}$: C, 31.81; H, 3.92; N, 17.31. Found: C, 31.85; H, 3.81; N, 17.30.

[Dihydrobis(1-pyrazolyl)borato][hydrotris(3,5-dimethylpyrazolyl)borato]lead(II), $\mathbf{[HB(3,5-Me_2pz)_3]Pb[H_2B(pz)_2]}$. $\mathrm{CH_2Cl_2}$ (20 mL) was added to a mixture of $\mathrm{[HB(3,5-Me_2pz)_3]Pb(NO_3)}$ (0.20 g, 0.35 mmol) and $\mathrm{K[H_2B(pz)_2]}$ (0.070 g, 0.38 mmol), and the mixture was stirred overnight. The solution was filtered, and the solvent was removed under vacuum to yield a white solid (0.18 g, 0.28 mmol, 80%). ^{1}H NMR ($\mathrm{CDCl_3}$), δ: 7.59, 7.12 (2, 2; d, d; J = 2.0, 1.6 Hz; 3, 5-H in pz); 6.09 (2, t, J_{HH} = 2.2 Hz, 4-H in pz); 5.78 (3, s, 4-H in $\mathrm{Me_2pz}$); 2.40, 1.79 (9, 9; s, s; 3,5-$\mathrm{(CH_3)_2}$ in $\mathrm{Me_2pz}$). ^{207}Pb NMR ($\mathrm{CDCl_3}$, −49 °C), δ: −727 ($w_{1/2}$ = 150 Hz). Anal. Calcd for $\mathrm{C_{21}H_{30}B_2N_{10}Pb}$: C, 38.72; H, 4.64; N, 21.50. Found: C, 38.91; H, 4.46; N, 21.67.

X-ray Crystal Structure Determinations for $\mathbf{[HB(3,5-Me_2pz)_3]Pb(NO_3)}$ and $\mathbf{[HB(3,5-Me_2pz)_3]Pb(3,5-Me_2pzH)_3Cl}$. A colorless crystal of $\mathrm{[HB(3,5-Me_2pz)_3]Pb(NO_3)}$, grown from acetone/hexane, was mounted in a thin-walled capillary tube on a CAD-4 diffractometer. The unit cell was determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. Data were collected in the $\omega/2\theta$ scan mode with an 0.8° + (0.35 tan θ)° scan range. The structure was solved by the

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Table 1. Crystallographic Data for the Structural Analyses of $[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)$ and $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$

	$[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)$	$[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$
formula	$C_{15}H_{22}BN_7O_3Pb$	$C_{30}H_{45}BClN_{12}Pb$
fw	566.39	828.2
crystal system	monoclinic	trigonal
space group	$P2_1/n$	$P31c$
a, Å	14.218(3)	11.069(2)
b, Å	7.842(2)	
c, Å	18.319(6)	17.319(3)
β, deg	94.36(2)	
V, Å^3	2037(4)	1837.7(9)
Z	4	2
ϱ(calc), g cm^{-3}	1.85	1.497
μ(Mo Kα), mm^{-1}	8.37	4.701
T, K	293	235
R^a	0.047	0.0264
$R_w{}^b$	0.086	0.0282

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

Table 2. Atomic Coordinates and Equivalent Isotropic Temperature Factors for $[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)$

atom	x	y	z	B,[a] Å^2
Pb	0.00558(6)	0.1093(1)	0.13660(5)	2.77(2)
O1	−0.140(1)	−0.050(2)	0.0758(9)	5.6(5)
O2	−0.103(2)	0.086(3)	−0.019(1)	8.1(6)
O3	−0.177(2)	−0.144(3)	−0.032(1)	12.4(8)
N	−0.140(1)	−0.039(3)	0.008(1)	5.0(6)
N11	−0.086(1)	0.163(2)	0.297(1)	2.8(4)
N12	−0.105(1)	0.185(2)	0.222(1)	3.0(4)
N21	0.003(1)	−0.115(2)	0.288(1)	2.9(4)
N22	0.005(1)	−0.130(2)	0.2128(9)	2.6(4)
N31	0.092(1)	0.165(2)	0.313(1)	2.8(4)
N32	0.114(1)	0.195(2)	0.2424(9)	2.7(4)
C13	−0.182(2)	0.279(3)	0.215(1)	3.5(6)
C14	−0.214(2)	0.317(4)	0.284(2)	5.2(7)
C15	−0.155(1)	0.243(3)	0.334(1)	3.3(5)
C16	−0.223(2)	0.339(5)	0.141(2)	8(1)
C17	−0.154(2)	0.245(3)	0.413(1)	4.1(6)
C23	0.007(2)	−0.298(3)	0.200(1)	3.6(6)
C24	0.007(2)	−0.386(3)	0.262(1)	4.4(6)
C25	0.006(1)	−0.271(3)	0.318(1)	3.1(5)
C26	0.012(2)	−0.379(4)	0.123(2)	7.7(9)
C27	0.011(2)	−0.304(4)	0.398(2)	6.9(8)
C33	0.191(1)	0.286(3)	0.248(1)	2.8(5)
C34	0.221(2)	0.312(3)	0.320(1)	4.0(6)
C35	0.157(2)	0.235(3)	0.361(1)	4.6(7)
C36	0.238(2)	0.340(4)	0.181(2)	5.7(7)
C37	0.157(2)	0.220(4)	0.442(1)	5.8(8)
B	0.001(2)	0.064(3)	0.325(2)	3.4(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$

atom	x	y	z	U_{eq},[a] Å^2
Pb	0.6667	0.3333	0.5000	0.02945(8)
Cl	0.6667	0.3333	0.7072(2)	0.037(1)
N1	0.5425(5)	0.1540(4)	0.4018(2)	0.034(2)
N2	0.5591(4)	0.1857(4)	0.3239(2)	0.031(2)
N3	0.7533(6)	0.1421(5)	0.5483(3)	0.049(3)
N4	0.7518(6)	0.1302(6)	0.6267(3)	0.045(2)
C1	0.4751(6)	0.0709(6)	0.2828(3)	0.037(2)
C2	0.4017(6)	−0.0371(5)	0.3344(3)	0.042(2)
C3	0.4471(6)	0.0195(5)	0.4078(3)	0.039(2)
C4	0.4678(8)	0.0684(7)	0.1967(3)	0.052(3)
C5	0.4026(7)	−0.0520(7)	0.4849(3)	0.054(3)
C6	0.7775(7)	0.0429(6)	0.5230(4)	0.048(3)
C7	0.7926(7)	−0.0301(6)	0.5849(4)	0.050(3)
C8	0.7747(6)	0.0282(6)	0.6507(3)	0.045(3)
C9	0.7873(9)	0.0255(9)	0.4378(4)	0.071(4)
C10	0.7776(10)	−0.0004(10)	0.7347(4)	0.073(4)
B	0.6667	0.3333	0.2965(10)	0.034(4)

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

heavy-atom method and refined by using MolEN.[11] All hydrogen atoms were included in structure factor calculation and not refined. Full-matrix least-squares refinements were carried out for reflections with $I > 3\sigma(I)$ where $\sigma(I)$ was derived from counting statistics. Absorption corrections were made by the method of Walker and Stuart.[12] Atomic parameters are shown in Table 2.

A colorless crystal of $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$, grown from slow evaporation of a CH_2Cl_2 solution, was mounted on a fine glass fiber with epoxy cement. Preliminary photographic characterization showed that the crystal possessed trigonal Laue symmetry and systematic absences indicated space groups $P31c$ and $P\bar{3}1/c$. On the basis of E statistics, the former space group was chosen and supported by the subsequent structure solution and refinement. Crystal data, data collection, and refinement parameters are collected in Table 1. Three standard reflections monitored every 197 reflections showed insignificant variations. Semiempirical corrections for absorptions were applied. The structure was solved by direct methods and completed by difference Fourier synthesis. All non-hydrogen atoms were refined with anisotropic thermal parameters. H(4N), the hydrogen atoms bonded to the Cl anion, and H(0B), on the boron atom, were located on difference maps and refined; all other hydrogen atoms were treated as idealized, updated isotropic contributions (d(CH) = 0.960 Å, U = 1.2U of attached atom). 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). Atomic coordinates and isotropic thermal parameters are shown in Table 3.

Results and Discussion

The reaction in water of $PbCl_2$ with equimolar amounts of both $Na\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}$ and $K[HB(pz)_3]$ yields the desired mixed-ligand complex in good yield. The analogous tin(II) complex, $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Sn[HB(pz)_3]$, is prepared in a similar reaction of $SnCl_2$ in CH_2Cl_2 (eq 1).

$$MCl_2 + K[HB(pz)_3] + Na\{CpCo[P(O)(OCH_2CH_3)_2]_3\} \longrightarrow [HB(pz)_3]M\{CpCo[P(O)(OCH_2CH_3)_2]_3\} \quad (1)$$

$$M = Sn, Pb$$

A mixed-ligand complex of the dihydrobis(pyrazolyl)borate ligand is prepared by the exchange reaction of $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$ and $[H_2B(pz)_2]_2Pb$ (eq 2).

$$[H_2B(pz)_2]_2Pb + \{CpCo[P(O)(OCH_2CH_3)_2]\}_2Pb \xrightarrow[\text{reflux}]{\text{toluene}} 2[H_2B(pz)_2]Pb\{CpCo[P(O)(OCH_2CH_3)_2]_3\} \quad (2)$$

These complexes are soluble in aromatic and halocarbon solvents. Efforts to obtain single crystals have been unsuccessful and generally lead to the slow precipitation of the [poly(pyrazolyl)borate]$_2$M complex. Attempts to dissolve the new complexes in hydrocarbon solvents lead to the extraction of the extremely soluble complex $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2M$, leaving behind the respective [poly(pyrazolyl)borate]$_2$M complex.

Table 4 shows the ^{207}Pb chemical shifts for these complexes, along with the values for three poly(pyrazolyl)borate complexes reported earlier[1] and $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$. $\{(C_5H_5)$-

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(11) *MolEN: An Interactive Structure Solution Procedure*; Enraf-Nonius: Delft, The Netherlands, 1990.

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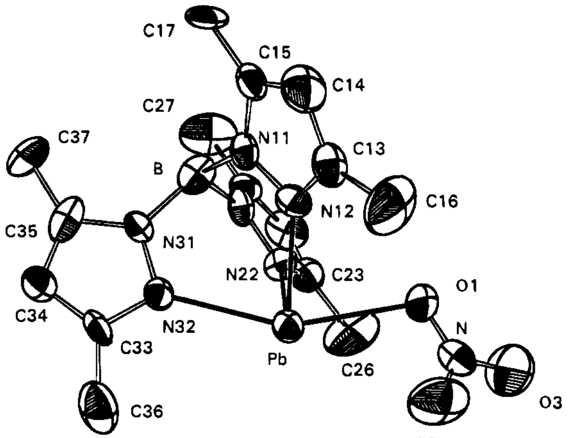

Figure 1. Molecular structure of [HB(3,5-$Me_2pz)_3$]Pb(NO_3) drawn with 50% probability ellipsoids.

Table 4. ^{207}Pb NMR Data Recorded in $CDCl_3$

compound	chem shift, ppm	$w_{1/2}$, Hz
$[H_2B(pz)_2]_2Pb$	−139	150
$[B(pz)_4]_2Pb$	−534	200
$[HB(pz)_3]_2Pb$	−895	600
$[HB(3,5\text{-}Me_2pz)_3]_2Pb$	−1481	300
$[HB(3,5\text{-}Me_2pz)_3]Pb[H_2B(pz)_2]$	−727	150
$\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$	−2034	320
$\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[H_2B(pz)_2]$	−1094	170
$\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[HB(pz)_3]$	−1613	110
$\{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_2\}(NO_3)$	−639	1100

$Co[P(O)(OC_2H_5)_2]_3\}_2Pb$, a six-coordinate complex with an O_6 donor set and a stereochemically active lone pair,[4] has the most shielded resonance. Both of the mixed-ligand complexes, $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[HB(pz)_3]$ (−1613 ppm) and $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}Pb[H_2B(pz)_2]$ (−1094 ppm), resonate fairly close (given the large chemical shift range of ^{207}Pb) to the average (−1464 and −1086 ppm) of the resonances for $\{(C_5H_5)Co[P(O)(OC_2H_5)_2]_3\}_2Pb$ and the respective [poly(pyrazolyl)borate]$_2$Pb complex.

It has not proven possible to prepare the mixed-ligand cation $\{[HB(3,5\text{-}Me_2pz)_3]PbP(O)(3,5\text{-}Me_2pz)_3\}^+$. The product that is isolated from the reaction of $Pb(NO_3)_2$, $P(O)(3,5\text{-}Me_2pz)_3$, and $K[HB(3,5\text{-}Me_2pz)_3]$ is $\{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_2\}NO_3$. This complex is insoluble in benzene and thus is likely to be ionic. The ^{207}Pb NMR shift for this complex is close to that of $[HB(3,5\text{-}Me_2pz)_3]Pb[H_2B(pz)_2]$ (vide infra), indicating a five-coordinate, N_5 environment about the lead, with the nitrate anion acting simply as the counterion. The reaction conditions used here are similar to those used in the successful preparation of $[P(O)(3,5\text{-}Me_2pz)_3]Mo(CO)_3$.[3] The reasons for ligand decomposition in the lead chemistry are not clear.

Attempts to grow crystals of $\{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_2\}NO_3$ lead to the isolation of $[HB(3,5\text{-}Me_2pz)_3]Pb(\eta^1\text{-}NO_3)$. This compound is best prepared from the direct reaction of 1 equiv of $[HB(3,5\text{-}Me_2pz)_3]^-$ and $Pb(NO_3)_2$. Its structure has been determined crystallographically. Figure 1 shows an ORTEP drawing of the molecule, and selected bond angles and distances are shown in Table 5. The $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand is tridentate and the nitrate ligand monodentate, leading to a structure best described as pseudo trigonal bipyramidal with N32 and O1 in the axial sites and N12, N22, and the stereoactive lone pair in the equatorial sites. The coordination geometry about the lead is very similar to that of $[B(pz)_4]_2Pb$.[1] The average Pb—N bond distances of 2.44 Å in $[HB(3,5\text{-}Me_2pz)_3]PbNO_3$ and 2.46 Å in $[B(pz)_4]_2Pb$ are essentially the same.

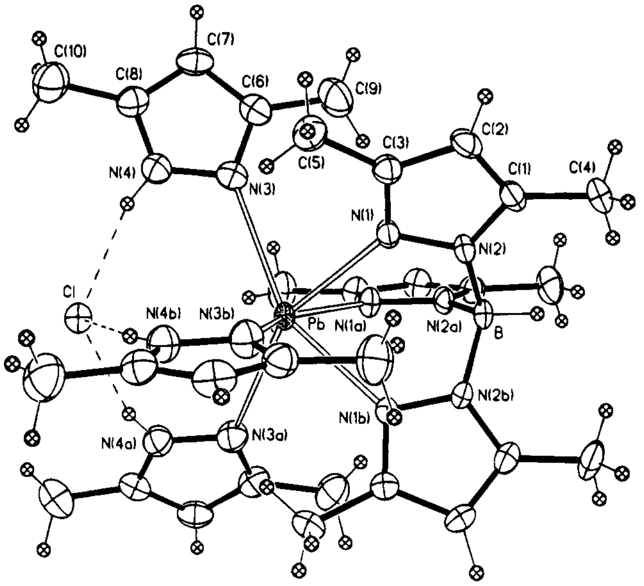

Figure 2. Molecular structure of $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$ drawn with 35% probability ellipsoids. Hydrogen bonds to Cl are shown with dashed lines.

Table 5. Selected Bonding Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)$

	Distances		
Pb−O1	2.60(2)	N11−N12	1.38(2)
Pb−N12	2.38(2)	N11−C15	1.40(3)
Pb−N22	2.34(2)	N12−C13	1.32(3)
Pb−N32	2.48(2)	C13−C14	1.40(3)
O1−N	1.24(3)	N11−B	1.52(3)
O2−N	1.23(3)	N21−B	1.56(3)
O3−N	1.19(3)	N31−B	1.55(4)
	Angles		
O1−Pb−N12	81.8(6)	O1−N−O2	119(3)
O1−Pb−N22	80.3(7)	O1−N−O3	122(3)
O1−Pb−N32	153.6(6)	O2−N−O3	119(3)
N12−Pb−N22	77.0(6)	N11−B−N21	110(2)
N12−Pb−N32	79.6(6)	N11−B−N31	111(2)
N22−Pb−N32	77.3(6)	N21−B−N31	111(2)

Table 6. Selected Bonding and Nonbonding Distances (Å) and Bond Angles (deg) for $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$

	Distances		
Pb−N1	2.448(4)	Pb···B	3.524
Pb−N3	2.851(4)	Pb···Cl	3.588
B−N2	1.538(7)	Cl−H(4N)	2.25(10)
N4−H(4N)	0.94(11)	N4···Cl	3.163
B−H(0B)	1.10(17)		
	Angles		
N1−Pb−N3	82.1(3)	N4−H(4N)−Cl	163.4(59)
N1−Pb−N1A	76.8(1)	N3−N4−H(4N)	119.9(59)
N3−Pb−N3A	111.8(3)	N1−N2−B	120.3(6)
Pb−N1−N2	121.5(3)	N2−B−H(0B)	107.9(6)
Pb−N3−N4	111.8(3)		

In a reaction of $Pb(NO_3)_2$, $P(O)(3,5\text{-}Me_2pz)_3$, and $K[HB(3,5\text{-}Me_2pz)_3]$ in which the $P(O)(3,5\text{-}Me_2pz)_3$ ligand is contaminated with HCl, the product isolated is $[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl$. The ^{1}H NMR spectrum of this complex shows the normal resonances for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand and three 3,5-Me_2pz groups and a broad resonance for the three NH hydrogen atoms at 12.6 ppm (observed at −50 °C). The structure of this complex has been definitively characterized by X-ray crystallography.

Figure 2 shows an ORTEP drawing of the compound, and the selected bond angles and distances are shown in Table 6. The lead atom is six-coordinate. The complex has crystallographically imposed 3-fold symmetry, with the rotation axis containing the chloride, lead, and boron. The $\mathrm{[HB(3,5\text{-}Me_2pz)_3]^-}$ ligand is tridentate, with intraligand N—Pb—N bond angles of 76.8(1)°. These angles are very similar to those observed in $\mathrm{[HB(3,5\text{-}Me_2pz)_3]_2Pb}$ (73.5(4)°).[1] The N—Pb—N bond angles formed by the 3,5-$\mathrm{Me_2pzH}$ ligands are large at 111.8(3)°. The Pb—N bond distances for the $\mathrm{[HB(3,5\text{-}Me_2pz)_3]^-}$ ligand are short, at 2.448(4) Å, and the Pb—N bond distances of the pyrazole ligands are long, at 2.851(4) Å. While shorter bond lengths with the anionic $\mathrm{[HB(3,5\text{-}Me_2pz)_3]^-}$ ligand would be expected on the basis of simple electrostatic considerations, the difference of over 0.40 Å is very large. For comparison, the average Y—N bond distance to the poly(pyrazolyl)borate ligands in $\mathrm{[HB(pz)_3]_2Y(pzH)Cl}$ is 2.489 Å and that to the pzH ligand is 2.613 Å, only 0.12 Å longer.[13] For $\mathrm{[HB(3,5\text{-}Me_2pz)_3]InS_4(3,5\text{-}Me_2pzH)}$, the difference is 0.06 Å (the average In—N bond distance to the $\mathrm{[HB(3,5\text{-}Me_2pz)_3]^-}$ ligand is 2.280 Å and the In—N bond distance to the 3,5-$\mathrm{Me_2pzH}$ ligand is 2.342(2) Å).[14]

These bond angles and distances about the lead atom indicate that the lone pair on the lead(II) center is stereochemically *active* and is located on the 3-fold axis pointed toward the chloride ion. The geometry about the lead is best described as a capped octahedron, with the lone pair in the capping position. It is well-known that bonds adjacent to a lone pair are long and bond angles, of course, larger.[15,16] The geometry about the lead atom is similar to that observed in the structure of $\mathrm{[HB(pz)_3]_2Pb}$, a compound with a clearly active lone pair.[1] In this compound, the average interligand bond angles (those not restrained by the chelate rings) of the face capped by the lone pair average to 134°, compared to 78° for the other face. Also, the Pb—N bond distances are much longer (average 2.73 versus 2.49 Å) adjacent to the lone pair and are similar to those observed in the structure of $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl}$.

This structure is the third we have determined in which lead(II) is bonded to six nitrogen donor atoms located in pyrazolyl rings. These compounds afford an opportunity to address the issue of whether the stereoactivity of the lone pair dramatically influences the size of the metal. From a series of structures of lead(II) coordinated to polydentate ligands, Hancock[17] has argued that the change from an inactive to an active lone pair is "accompanied by a shortening of the Pb—N bond lengths by approximately 0.3 Å". As pointed out previously, the average bond distance in $\mathrm{[HB(pz)_3]_2Pb}$ (2.61 Å), a compound with an active lone pair, is the same as that in $\mathrm{[HB(3,5\text{-}Me_2pz)_3]_2Pb}$ (2.610(5) Å), a compound with an inactive lone pair. The average Pb—N distance in the structure of $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl}$ is 2.65 Å, just slightly longer than those of the other two structures. Thus, in these three structures there is no indication of the stereoactivity of the lone pair influencing average Pb—N bond distances. We note that, in any discussion of bond lengths, the coordination number of the metal must be considered as well as the bonding characteristics of the donor atoms. In the four-coordinate structures of $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3)}$ and $\mathrm{[B(pz)_4]_2Pb}$, the average Pb—N bond distances are considerably shorter, at 2.44 and 2.46 Å, respectively. An additional example of a six-coordinate lead(II)—poly(pyrazolyl)borate complex with an inactive lone pair is needed to clarify this issue further.

In the structure of $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl}$, the chloride is hydrogen-bonded to the three NH groups of the 3,5-$\mathrm{Me_2pzH}$ ligands. The N···Cl distance is 3.163 Å, a distance considerably less than the sum of the N and Cl van der Walls radii (3.30 Å). Parkin and co-workers[18] recently published the preparation and structure of a compound, $\mathrm{\{[\eta^3\text{-}HB(3\text{-}Bu^tpzH)_3]Cl\}[AlCl_4]}$, that contains a chloride hydrogen-bonded in a very similar way to that observed here. They describe this hydrogen-bonding interaction as an unusual example of an anionic coordination complex.[19] $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(3,5\text{-}Me_2pzH)_3Cl}$ can be described as a "double-coordination compound", with a lead(II) cation coordinated to lone pairs on six nitrogen donor atoms and a chloride anion coordinated to three NH ligands.

The reaction of $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(\eta^1\text{-}NO_3)}$ and $\mathrm{[H_2B(pz)_2]^-}$ yields the mixed ligand complex $\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb[H_2B(pz)_2]}$:

$$\mathrm{[HB(3,5\text{-}Me_2pz)_3]Pb(NO_3) + K[H_2B(pz)_2] \longrightarrow [HB(3,5\text{-}Me_2pz)_3]Pb[H_2B(pz)_2] + KNO_3} \qquad (3)$$

The $^{207}\mathrm{Pb}$ NMR shift for this complex is between the ranges observed for four- and six-coordinate poly(pyrazolyl)borate complexes, indicating a five-coordinate arrangement.

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Supplementary Material Available: Tables of complete data collection information, bond distances, bond angles, anisotropic thermal parameters, and positional parameters of H atoms (12 pages). Ordering information is given on any current masthead page.

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