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Tris(pyrazolyl)borate Complexes of Yttrium. X-ray Crystal Structures of $[HB(pz)_3]_2YCl(Hpz)$ and $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ (pz = Pyrazolyl Ring)

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Reaction of YCl_3 with 2 equiv of $K[HB(pz)_3]$ (pz = pyrazolyl ring) in THF yields the unsolvated complex $\{[HB(pz)_3]_2YCl\}_x$ (**1**). In solution, the molecular weight is concentration dependent, showing that this complex is in a monomer–dimer equilibrium. In a similar reaction to which 1 equiv of pyrazole, Hpz, has been added, the adduct $[HB(pz)_3]_2YCl(Hpz)$ (**2**) is formed. The molecular structure of **2** has been determined by single-crystal X-ray diffraction: orthorhombic, space group *Pbca*, $a = 9.197$ (2) Å, $b = 15.560$ (3) Å, $c = 36.770$ (7) Å, $V = 5262$ Å^3, $Z = 8$. The structure is best described as a square antiprism, distorted in the direction of a bicapped trigonal prism. The two mixed tris(pyrazolyl)borate–acetate complexes $\{[HB(pz)_3]_2Y(\mu\text{-}O_2CCH_3)\}_3$ (**3**) and $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ (**4**) are prepared from the reaction of YCl_3, $K[HB(pz)_3]$, and $Na(O_2CCH_3)$ in the respective stoichiometric amounts. The trimeric formulation of **3** was determined from solution-state molecular weight studies. The solid-state structure of **4** has been determined crystallographically: monoclinic, space group $P2_1/c$, $a = 10.945$ (2) Å, $b = 7.876$ (1) Å, $c = 24.498$ (4) Å, $\beta = 98.50$ (2)°, $V = 2088$ Å^3, $Z = 4$. The structure of this centrosymmetric dimer can be described as a sandwich complex where each yttrium atom is between the parallel planes formed by the three nitrogen donor atoms of the tris(pyrazolyl)borate ligand and the square plane formed by the oxygen atoms from the bridging acetate ligands. Alternatively, the geometry about each yttrium atom can be described as a capped trigonal prism with one of the nitrogen atoms in the capping position. All four of these complexes show dynamic NMR behavior. The only mechanism for these dynamic processes that can clearly be assigned is the reversible dissociation of the pyrazole ligand in complex **2**.

Introduction

The synthesis and characterization of poly(pyrazolyl)borate complexes of the early transition metals is an area of continuing interest. Using this flexible ligand system, we have prepared new complexes and precursors to organometallic compounds analogous to those containing the ubiquitous cyclopentadienyl, Cp^-, and pentamethylcyclopentadienyl, $C_5Me_5^-$, ligands. To date, we have prepared and studied several complexes containing one tris(pyrazolyl)borate ligand: $[RB(pz)_3]TaMe_3Cl$ (R = H, pz; pz = pyrazolyl ring);[1a] $[HB(3,5\text{-}Me_2pz)_3]TaMe_3Cl$;[1a] $[RB(pz)_3]ZrCl_3$ (R = *n*-Bu, *i*-Pr);[1b] $[HB(3,5\text{-}Me_2pz)_3]Zr(O\text{-}t\text{-}Bu)_nR_{3-n}$ ($n = 1$, 2; R = Cl, Me, CH_2Ph, C≡CMe);[1c] $[HB(pz)_3]CpZrCl_2$.[1d] It was not possible, however, to prepare complexes containing two tris(pyrazolyl)borate ligands, such as $[HB(pz)_3]_2MX_n$, of tantalum or zirconium.

The tris(pyrazolyl)borate ligands are formally six-electron donors analogous to Cp^- but have large steric requirements more similar to those of $C_5Me_5^-$.[2] In order to prepare complexes containing two tris(pyrazolyl)borate ligands, we extended our study to the chemistry of yttrium. The larger ionic radius of yttrium should allow the coordination of two of these bulky ligands. Also, sterically demanding ligands have been shown to be assets in the chemistry of the prelanthanide and lanthanide elements, giving stability through steric saturation, which is difficult to achieve by electronic saturation only.[3] Of particular interest is the fact that Takats has reported the synthesis of a series of $[HB(pz)_3]_3M$ complexes (M = Y, La, Ce, Pr, Sm, Gd, Er, Yb, Lu).[4] The ytterbium complex is eight-coordinate, $[\eta^3\text{-}HB(pz)_3]_2[\eta^2\text{-}HB(pz)_3]Yb$, both in the solid state[4b] and in solution.[4c] The initial report also briefly mentioned the preparation of $[HB(pz)_3]_2ErCl(THF)$.

Two reports have recently appeared in the literature describing the synthesis and solid-state characterization of bis[hydrotris(pyrazolyl)borato]lanthanide complexes containing β-diketonate ligands. The first report by Takats describes the synthesis of $[HB(pz)_3]_2M(\beta\text{-diketonate})$ (M = Yb, Lu; β-diketonate = 2,2,6,6-tetramethyl-3,5-heptanedionate, dpm; 3-(trifluoroacetyl)-*d*-camphorate).[4d] The crystal structure of the ytterbium heptanedionate complex was determined by X-ray analysis. The complex has a square-antiprismatic coordination geometry, SAP. In the second report, Jones and co-workers discuss the preparation of acetylacetonate complexes for the entire lanthanide series, $[HB(pz)_3]_2M(acac)$ (M = La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Yb, Lu, Y; acac = acetylacetonate).[5] Two of these complexes have been structurally characterized. Interestingly, they possess different molecular geometries. The cerium complex has a bicapped-trigonal-prismatic geometry, BCTP, while that of the ytterbium complex is derived from a SAP geometry. NMR studies in both reports show the eight-coordinate complexes to be fluxional in solution, equilibrating the pyrazolyl rings of the $[HB(pz)_3]^-$ ligands.

We have recently described the synthesis and characterization of $[H(\mu\text{-}H)B(pz)_2]_3Y$ and $[H(\mu\text{-}H)B(3,5\text{-}Me_2pz)_2]_3Y$,[6a] molecules that possess three three-center, bridging B–H···Y interactions. In the solid state, the six nitrogen donor atoms form a trigonal prism with each rectangular face capped by a B–H···Y agostic bond. In solution, the molecule is distorted toward an octahedral geometry and undergoes a fluxional process that equilibrates the boron hydrogens. Our initial synthetic efforts toward bis[tris(pyrazolyl)borate] compounds resulted in the preparation of $[HB(pz)_3]_2YCl(H_2O)$ and $[HB(pz)_3]_2LaCl(H_2O)$.[6b] Both of these eight-coordinate complexes are fluxional in solution. Reported here are the syntheses and properties of anhydrous $\{[HB(pz)_3]_2YCl\}_x$, $[HB(pz)_3]_2YCl(Hpz)$, $\{HB(pz)_3]_2Y(\mu\text{-}O_2CCH_3)\}_3$, and $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$. $[HB(pz)_3]_2YCl(Hpz)$ and $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ have been structurally characterized by X-ray crystallography.

Experimental Section

General Procedure. All operations were carried out under a nitrogen atmosphere either by using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 drybox. All solvents were dried, degassed, and distilled prior to use. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ^1H, ^{11}B, and ^{13}C solution NMR spectra were recorded on a Bruker AM300 spectrometer using a 5-mm broad-band probe. An IBM NR-80 spectrometer was also used to collect ^{13}C NMR data. Proton chemical shifts are reported in ppm vs Me_4Si. All carbon

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resonances are singlets unless otherwise noted. Carbon chemical shifts are reported vs TMS with the solvents CD_2Cl_2 and $CDCl_3$ as internal standards (CD_2Cl_2 resonance at 53.85 ppm, $CDCl_3$ at 77.00 ppm). Boron-11 chemical shifts are reported in ppm vs $BF_3{\cdot}OEt_2$. Proton and ^{13}C variable-temperature NMR analyses were also performed on the Bruker AM300 NMR spectrometer at resonant frequencies of 300.13 and 75.47 MHz, respectively. The samples for variable-temperature studies were dissolved in CD_2Cl_2; then the solutions were sealed in screw-capped 5-mm NMR tubes. Activation parameters were calculated at the coalescence temperature.[7] Solution molecular weight studies were conducted in CH_2Cl_2 by the isopiestic method using a Signer apparatus.[8] Accurate mass spectra were run as solids on a VG 70SQ spectrometer; low-resolution spectra, on a Finnigan 4521 GC-mass spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Elemental analyses were performed by Robertson Laboratory, Inc. $K[HB(pz)_3]$ was prepared by the published method.[9] Anhydrous YCl_3 was purchased from Cerac/Pure Division and was used without further purification.

^{89}Y NMR Spectra. ^{89}Y NMR experiments were performed by using a Bruker AM300 spectrometer equipped with a broad-band 10-mm probe at a resonant frequency of 14.71 MHz. Pulse widths were determined on a 1.0 M sample of YCl_3 in D_2O with a 90° pulse of 31.0 μs and a 180° pulse off 62.8 μs. Chemical shifts are reported in ppm versus the same 1.0 M YCl_3 in D_2O standard. The sample concentrations ranged from 0.12 to 0.23 M in $CDCl_3$. The direct acquisition experiments utilized a 6° pulse (2.2 μs) and a relaxation delay of 0.001 s with total acquisition times of 5–7 h.

Bis[hydrotris(1-pyrazolyl)borato]chloroyttrium(III), $[HB(pz)_3]_2YCl$ (1). YCl_3 (0.20 g, 1.0 mmol) and $KHB(pz)_3$ (0.47 g, 1.9 mmol) were placed in a 50-mL round-bottomed flask, and THF (45 mL) was added by syringe. The solution was stirred at room temperature for 5 h. The precipitate was allowed to settle out before the solution was filtered, and the filtrate was reduced to dryness under vacuum. The residue was extracted with benzene (40 mL). The insoluble salts were again allowed to settle out completely before the solution was filtered. The benzene was evaporated under vacuum to yield a white solid (0.37 g, 0.67 mmol, 72%). ^1H NMR ($CDCl_3$): δ 7.66 and 7.19 (6, 6; d, d; J = 2.11, 1.80 Hz; 3-H, 5-H (pz)), 6.01 (6, t, J = 2.10 Hz, 5-H (pz)), 4.69 (broad, BH). ^{13}C NMR (ambient temperature, $CDCl_3$, 20.13 MHz): δ 140.65 and 135.23 (3-C, 5-C (pz)), 104.25 (4-C (pz)). ^{13}C NMR (−81 °C, CD_2Cl_2): δ 141.88 and 135.12 (m, s; 3-C, 5-C (pz)), 103.76 (4-C (pz)). ^{11}B NMR ($CDCl_3$): δ −3.31 (d, J_{BH} = 102 Hz, line narrowed). ^{89}Y NMR ($CDCl_3$): δ 116.0. IR (Nujol mull), cm^{-1}: 2460 (BH). The accurate mass spectrum shows $M^+ - H$ and $M^+ - Cl$ clusters. *m/e*: calcd for $C_{18}H_{19}N_{12}{}^{10}B^{11}B^{35}ClY$ and $C_{18}H_{20}N_{12}{}^{10}B^{11}BY$, 548.0825 and 514.1215; found, 548.0807 and 514.1279.

Bis[hydrotris(1-pyrazolyl)borato]chloro(pyrazole)yttrium(III), $[HB(pz)_3]_2YCl(Hpz)$ (2). YCl_3 (0.20 g, 1.0 mmol), $KHB(pz)_3$ (0.52 g, 2.1 mmol), and Hpz (0.070 g, 1.0 mmol) were combined in a 50-mL round-bottomed flask, and THF (30 mL) was added by syringe. The solution was stirred at room temperature for 4 h and filtered, and the solvent was evaporated under vacuum. The filtrate residue was extracted with benzene (50 mL). The insoluble salts were allowed to settle out completely before the solution was filtered. The benzene was evaporated under vacuum to yield a white solid (0.48 g, 0.78 mmol, 78%). Recrystallization from a CH_2Cl_2/hexane solution gave clear crystals suitable for X-ray analysis. ^1H NMR ($CDCl_3$): δ 7.64 and 7.00 (6, 6; d, d; J = 1.86, 1.75 Hz; 3-H, 5-H (pz)), 7.30 (2, s, 3-H, 5-H (Hpz)), 6.17 (1, s, 4-H (Hpz)), 5.97 (6, t, J = 2.10 Hz, 4-H (pz)), 4.70 (broad s, BH). ^{13}C NMR (ambient temperature, CD_2Cl_2): δ 142.78 and 135.59 (3-C, 5-C (pz)), 134.41 (3-C, 5-C (Hpz)), 105.95 (4-C (Hpz)), 104.37 (4-C (pz)). ^{13}C NMR (−86 °C, CD_2Cl_2): δ 142.07, 141.93, and 135.13 (3-C, 5-C (pz)), 139.21 and 128.94 (3-C, 5-C (Hpz)), 105.52 (4-C (Hpz)), 103.76 (4-C (pz)). ^{11}B NMR ($CDCl_3$): δ −3.15 (d, J_{BH} = 108 Hz, line narrowed). IR (Nujol mull), cm^{-1}: 3125 (NH), 2455 (BH). The accurate mass spectrum shows $M^+ - H_2Cl$ and $M^+ - H_2pz$ clusters. *m/e*: calcd for $C_{21}H_{22}N_{14}{}^{11}B_2Y$ and $C_{18}H_{19}N_{12}{}^{11}B_2{}^{35}ClY$, 581.1396 and 549.0789; found, 581.1369 and 549.0803.

Tris{(μ-acetato)bis[hydrotris(1-pyrazolyl)borato]yttrium(III)}, $\{[HB(pz)_3]_2Y(\mu\text{-}O_2CCH_3)\}_3$ (3). YCl_3 (0.20 g, 1.0 mmol), $KHB(pz)_3$ (0.52 g, 2.0 mmol), and NaO_2CCH_3 (0.082 g, 1.0 mmol) were placed in a 50-mL round-bottomed flask, and THF (25 mL) was added by syringe. The solution was heated at reflux for 4 h and allowed to cool, and the solvent was evaporated under vacuum. The residue was extracted with benzene (25 mL). The insoluble salts were allowed to settle out completely before the solution was filtered. The benzene was evaporated under vacuum to yield a white solid (0.39 g, 0.68 mmol, 68%). ^1H NMR ($CDCl_3$): δ 7.65 and 7.09 (6, 6; d, d; J = 2.1, 1.9 Hz; 3-H, 5-H (pz)), 6.01 (6, t, J = 2.1 Hz, 4-H (pz)), 4.7 (2, broad s, BH), 2.09 (3, s, CH_3). ^{13}C NMR ($CDCl_3$ with $Cr(acac)_3$): δ 188.49 (O_2CCH_3), 140.62 and 135.27 (3-C, 5-C (pz)), 104.29 (4-C (pz)), 24.68 (CH_3). ^{13}C NMR (−86 °C, CD_2Cl_2): δ 188.58 (O_2CCH_3), 140.31, 140.17, and 135.53 (3-C, 5-C (pz)), 104.67 (4-C (pz)), 24.39 (CH_3). ^{11}B NMR ($CDCl_3$): δ −3.13 (d, J_{BH} = 102 Hz, line narrowed). ^{89}Y NMR ($CDCl_3$): δ 117.2 (s). IR (Nujol mull), cm^{-1}: 2455 (BH), 1560 (CO_2). The low-resolution mass spectrum shows clusters for monomer(1+) − H and monomer(1+) − HO_2CCH_3 at *m/e* 573 and 515, respectively. Anal. Calcd. for $C_{20}H_{23}N_{12}B_2O_2Y$: C, 41.85; H, 4.04. Found: C, 42.07; H, 4.21.

Table I. Crystallographic Data for the Structural Analyses

compd	2	4
formula	$C_{21}H_{24}B_2ClN_{14}Y$	$(C_{13}H_{16}BN_6O_4Y)_2{\cdot}2CH_2Cl_2$
space group	*Pbca*	*P*2$_1$/*c*
a, Å	9.197 (2)	10.945 (2)
b, Å	15.560 (3)	7.876 (1)
c, Å	36.770 (7)	24.498 (4)
β, deg		98.50 (2)
V, Å^3	5262	2088
Z	8	4
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
temp	−100 °C	ambient
linear abs coeff, cm^{-1}	23.7	30.9
transmission factors: max, min, av	1.109, 0.828, 0.991	1.154, 0.667, 0.946
R_F	0.038	0.043
R_{wF}	0.042	0.041

Bis{bis(μ-acetato)[hydrotris(1-pyrazolyl)borato]yttrium(III)}, $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ (4). YCl_3 (0.31 g, 1.5 mmol), $KHB(pz)_3$, (0.39 g, 1.5 mmol), and NaO_2CCH_3 (0.28 g, 3.4 mmol) were placed in a 100-mL round-bottomed flask, and THF (60 mL) was added by syringe. The solution was heated at reflux for 4 h and allowed to cool, and the solvent was evaporated under vacuum. The residue was extracted with benzene (50 mL). The insoluble salts were allowed to settle out completely before the solution was filtered. The crude product was recrystallized from CH_2Cl_2 to yield a white solid (0.26 g, 0.31 mmol, 41%). Recrystallization from CH_2Cl_2 gave crystals suitable for X-ray analysis. ^1H NMR ($CDCl_3$): δ 7.91 and 7.65 (6, 6; d, d; J = 1.24, 1.75 Hz; 3-H, 5-H (pz)), 6.14 (6, t, J = 2.06 Hz, 4-H (pz)), 4.63 (broad s, BH), 1.93 (12, s, CH_3). ^{13}C NMR (ambient temperature, CD_2Cl_2): δ 181.54 (O_2CCH_3), 142.44 and 135.94 (3-C, 5-C (pz)), 104.33 (4-C (pz)), 24.19 (CH_3). ^{13}C NMR (−87 °C, CD_2Cl_2): δ 181.38 (O_2CCH_3); 141.50 and 135.38 (3-C, 5-C (pz)), 103.78 and 103.60 (4-C (pz)), 23.92 (m, CH_3). ^{11}B NMR ($CDCl_3$): δ −2.81. ^{89}Y NMR ($CDCl_3$): δ 69.4. IR (Nujol mull), cm^{-1}: 2465 (BH), 1600 (CO_2). The accurate mass spectrum shows the $M^+ - O_2CCH_3$ cluster. *m/e*: calcd for $C_{24}H_{29}N_{12}O_6{}^{11}B_2Y_2$, 781.0636; found, 781.0579.

Crystallographic Analysis of $[HB(pz)_3]_2YCl(Hpz)$ (2) and $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ (4). Transparent prisms of **2** and **4** were mounted in thin-walled capillaries on a CAD-4 diffractometer. The unit cells were determined and refined from 25 general reflections. Crystal data, data collection parameters, and results of the analysis are listed in Table I. The structures were solved by the heavy-atom method. The structure of **2** was refined by using SDP.[9] For **4**, the data were reduced by using SDP and refined by using SHELX 76.[10] The crystals of **4** contain one lattice molecule of methylene chloride per asymmetric unit. The relatively high temperature factors suggest some mobility of this molecule. Hydrogen atoms were placed in calculated positions and not refined. Full-matrix least-squares refinements were carried out with weights $w = (\sigma^2(F) + 0.0004F^2)^{-1}$ for reflections with $I > 3\sigma(I)$. Table II shows atomic parameters for **2**, and Table III, those for **4**. Geometry analyses were performed by using a PS 330 Evans and Sutherland interactive computer graphics system.

Results

Preparation of the new complexes is carried out by the stoi-

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Table II. Positional Parameters for $[HB(pz)_3]_2YCl(Hpz)$ with Esd's in Parentheses

atom	*X/a*	*Y/b*	*Z/c*	*B*, Å^2
Y(1)	0.13542 (6)	0.07062 (4)	0.13083 (1)	1.26
Cl(1)	0.3349 (2)	−0.0382 (1)	0.16023 (4)	1.97
N(11)	−0.2267 (5)	0.0289 (3)	0.1264 (1)	1.43
N(12)	−0.0965 (5)	0.0077 (3)	0.1103 (1)	1.60
N(21)	−0.1734 (5)	0.1649 (3)	0.1609 (1)	1.48
N(22)	−0.0446 (5)	0.1829 (3)	0.1440 (1)	1.67
N(31)	−0.1405 (6)	0.0215 (3)	0.1902 (1)	1.56
N(32)	0.0036 (6)	0.0074 (3)	0.1843 (1)	1.49
N(41)	0.1459 (6)	0.1335 (3)	0.0402 (1)	1.53
N(42)	0.0642 (5)	0.1415 (3)	0.0710 (1)	1.54
N(51)	0.2889 (5)	0.0008 (3)	0.0514 (1)	1.36
N(52)	0.2186 (6)	−0.0260 (3)	0.0822 (1)	1.80
N(61)	0.3896 (5)	0.1442 (3)	0.0701 (1)	1.57
N(62)	0.3492 (5)	0.1504 (3)	0.1059 (1)	1.55
N(71)	0.2385 (6)	0.1541 (3)	0.1868 (1)	1.69
N(72)	0.3441 (6)	0.1177 (3)	0.2066 (1)	2.51
C(13)	−0.1325 (7)	−0.0330 (4)	0.0797 (2)	2.26
C(14)	−0.2817 (7)	−0.0378 (4)	0.0754 (2)	2.15
C(15)	−0.3368 (7)	0.0011 (4)	0.1054 (2)	2.14
C(23)	−0.0343 (7)	0.2680 (4)	0.1424 (2)	2.06
C(24)	−0.1517 (7)	0.3065 (4)	0.1596 (2)	2.34
C(25)	−0.2369 (7)	0.2395 (4)	0.1704 (2)	2.12
C(33)	0.0462 (7)	−0.0450 (4)	0.2110 (2)	2.14
C(34)	−0.0685 (7)	−0.0643 (5)	0.2344 (2)	2.64
C(35)	−0.1853 (7)	−0.0214 (4)	0.2199 (2)	2.10
C(43)	−0.0647 (7)	0.1725 (4)	0.0599 (2)	2.36
C(44)	−0.0659 (6)	0.1846 (4)	0.0226 (2)	2.67
C(45)	0.0684 (7)	0.1578 (4)	0.0109 (2)	1.85
C(53)	0.2315 (7)	−0.1115 (4)	0.0825 (2)	2.05
C(54)	0.3094 (7)	−0.1409 (4)	0.0535 (2)	2.60
C(55)	0.3441 (7)	−0.0681 (5)	0.0338 (2)	2.26
C(63)	0.4477 (7)	0.2003 (4)	0.1216 (2)	1.83
C(64)	0.5514 (7)	0.2284 (4)	0.0967 (2)	2.11
C(65)	0.5092 (7)	0.1912 (4)	0.0646 (2)	1.65
C(73)	0.3856 (8)	0.1674 (5)	0.2343 (2)	2.94
C(74)	0.3034 (8)	0.2405 (5)	0.2331 (2)	2.79
C(75)	0.2129 (7)	0.2288 (4)	0.2033 (2)	2.21
B(1)	−0.2333 (8)	0.0740 (5)	0.1639 (2)	1.79
B(2)	0.3000 (8)	0.0960 (5)	0.0421 (2)	1.80

chiometric combination of YCl_3 and the appropriate ligand salts in THF (eq 1–4). Complex **3** can also be prepared by the reaction

$$\mathrm{YCl_3 + 2KHB(pz)_3 \rightarrow \underset{\mathbf{1}}{[HB(pz)_3]_2YCl} + 2KCl} \tag{1}$$

$$\mathrm{YCl_3 + 2KHB(pz)_3 + Hpz \rightarrow \underset{\mathbf{2}}{[HB(pz)_3]_2YCl(Hpz)} + 2KCl} \tag{2}$$

$$\mathrm{3YCl_3 + 6KHB(pz)_3 + 3NaO_2CCH_3 \rightarrow \underset{\mathbf{3}}{\{[HB(pz)_3]_2Y(\mu\text{-}O_2CCH_3)\}_3} + 6KCl + 3NaCl} \tag{3}$$

$$\mathrm{2YCl_3 + 2KHB(pz)_3 + 4NaO_2CCH_3 \rightarrow \underset{\mathbf{4}}{\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2} + 2KCl + 4NaCl} \tag{4}$$

of **1** with $Na(O_2CCH_3)$. Interestingly, **1** is not a THF adduct even though isolated from this solvent. The analogous $(C_5Me_5)_2YCl(THF)$ complex is isolated as an adduct.[13] However, Lewis acid–base pairs containing **1** such as the pyrazole adduct $[HB(pz)_3]_2YCl(Hpz)$ (**2**) and the previously reported water adduct $[HB(pz)_3]_2YCl(H_2O)$ can be prepared.[6b]

All of the complexes are soluble in THF, halocarbons, and aromatic hydrocarbon solvents. The acetate derivatives, **3** and **4**, are slightly soluble in saturated hydrocarbons; **1** and **2** are insoluble. The solids can be handled briefly in air, but decompose partially in ca. 6 months in an inert-atmosphere box, as indicated by the appearance of pyrazole in NMR spectra. Complex **2** is considerably more stable than the other three and is a product of the decomposition of **1**.

Table III. Positional Parameters for $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2 \cdot 2CH_2Cl_2$ with Esd's in Parentheses

atom	*x*	*y*	*z*	*B*, Å^2
Y(1)	0.16434 (7)	−0.02199 (8)	0.04913 (3)	3.16 (1)
O(11)	0.0191 (5)	0.0759 (7)	0.0987 (2)	4.2 (1)
O(12)	0.1533 (6)	−0.1188 (7)	−0.0391 (3)	4.9 (1)
O(21)	0.0654 (5)	−0.2755 (7)	0.0593 (2)	5.1 (1)
O(22)	0.0966 (7)	0.2017 (8)	−0.0050 (2)	5.9 (2)
N(11)	0.3675 (6)	−0.0961 (7)	0.1654 (3)	3.0 (1)
N(12)	0.2508 (6)	−0.1278 (7)	0.1417 (3)	3.3 (1)
N(21)	0.4102 (5)	0.1819 (7)	0.1219 (3)	3.4 (1)
N(22)	0.2990 (6)	0.2087 (6)	0.0938 (3)	3.7 (1)
N(31)	0.4729 (6)	−0.0987 (7)	0.0825 (3)	3.2 (1)
N(32)	0.3732 (6)	−0.1283 (8)	0.0418 (3)	4.0 (2)
C(11)	−0.0933 (9)	0.1133 (9)	0.0866 (5)	3.7 (2)
C(12)	−0.164 (1)	0.154 (1)	0.1307 (5)	5.4 (2)
C(13)	0.2032 (9)	−0.216 (1)	0.1799 (3)	4.6 (2)
C(14)	0.2830 (9)	−0.246 (1)	0.2254 (3)	4.0 (2)
C(15)	0.3895 (8)	−0.1630 (8)	0.2145 (4)	3.4 (2)
C(21)	−0.0426 (8)	−0.2954 (8)	0.0407 (3)	2.9 (2)
C(22)	−0.114 (1)	−0.435 (1)	0.0578 (5)	6.2 (3)
C(23)	0.2770 (9)	0.3736 (7)	0.0921 (4)	3.6 (2)
C(24)	0.3847 (8)	0.4577 (9)	0.1179 (3)	4.1 (2)
C(25)	0.4637 (9)	0.332 (1)	0.1356 (4)	4.4 (2)
C(33)	0.4162 (7)	−0.224 (1)	0.0054 (3)	3.9 (2)
C(34)	0.5372 (7)	−0.2573 (9)	0.0185 (3)	3.8 (2)
C(35)	0.5691 (7)	−0.1728 (9)	0.0664 (3)	3.7 (2)
B(1)	0.4626 (8)	0.001 (1)	0.1365 (3)	3.2 (2)
Cl(1)	0.0632 (5)	0.3858 (6)	0.2295 (3)	12.1 (1)
Cl(2)	0.2585 (9)	0.1816 (7)	0.2902 (2)	16.6 (2)
C(1)	0.182 (2)	0.240 (2)	0.2256 (6)	12.6 (4)

Isopiestic molecular weight studies were undertaken to determine if these tris(pyrazolyl)borate complexes oligomerized in solution. Experiments involving the chloride complex, **1**, indicate the presence of a monomer–dimer equilibrium in solution. In an experiment with a final concentration of **1** of 0.035 M the molecular weight was 686 whereas at a final concentration of 0.065 M the molecular weight was 917. The molecular weight of the monomer is 550. For the monoacetate complex, **3**, the molecular weight was observed to be 1700, very close to that calculated for a trimer (1722). For the bis(acetate) complex, **4**, the observed molecular weight was 750, close to that calculated for a dimer (840).

Variable-Temperature NMR Studies. In solution, all four complexes undergo dynamic rearrangements that equilibrate the pyrazolyl rings of the $[HB(pz)_3]^-$ ligands. The ambient-temperature proton and carbon NMR spectra of the complexes show only one resonance for each of the three aromatic ring hydrogen or carbon atom types.

Variable-temperature analyses of both the ^1H and ^{13}C spectra of the chloride complex, **1**, yield similar data. In each case, one of the resonances (the δ 7.19 resonance for hydrogen and δ 140.65 for carbon) assigned to either the 3- or 5-position of the pyrazolyl rings (they are not readily distinguishable) collapses, starting at ca. −20 °C to a complex set of resonances at −87 °C. The other two resonances do not noticeably change with temperature in either spectra.

For the pyrazole adduct, **2**, both the tris(pyrazolyl)borate and the pyrazole ligands show dynamic behavior in solution. The ambient-temperature proton and carbon NMR spectra show three resonances for the equivalent pyrazolyl rings of the tris(pyrazolyl)borate ligands and two resonances in a 2:1 ratio for the coordinated pyrazole. As best seen in the carbon spectra, Figure 1, two of the three resonances of the $[HB(pz)_3]^-$ ligands remain sharp even at the lowest temperature, but the resonance at δ 142.78 loses intensity and broadens until ca. −58 °C, where it begins to resolve into two resonances. At −86 °C, these two resonances are sharp and separated by 11.1 Hz. The barrier to equilibration of the two resonances as calculated at the coalescence temperature of −50 °C is 11.5 kcal/mol. For the pyrazole ligand, the more deshielded resonance (relative intensity of 2) at ambient temperature collapses into the base line and at ca. −86 °C two equally intense broad resonances are observed at δ 139.21 and 128.94.

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(13) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

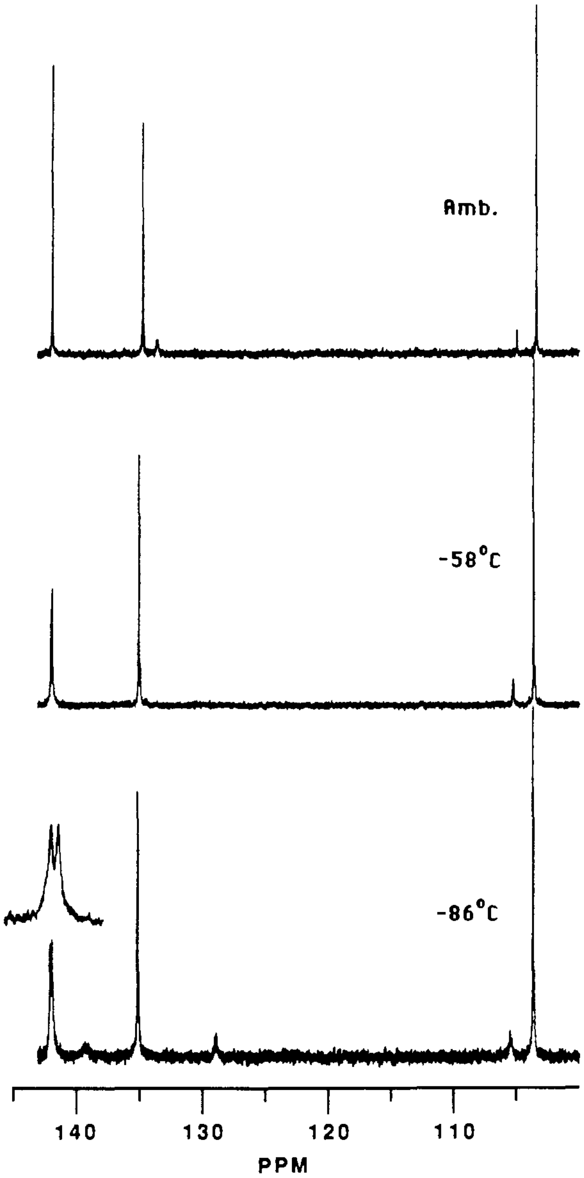

Figure 1. Variable-temperature ^{13}C NMR spectra of $[HB(pz)_3]_2YCl(Hpz)$ (**2**). Insert in the −86 °C spectrum is an expansion of the δ 142 resonance.

The barrier to equilibration of these two resonances as calculated at the coalescence temperature of −50 °C is 9.6 kcal/mol.

The ^1H NMR spectra of the monoacetate complex, **3**, do not change with temperature. In fact, the doublet, doublet, triplet pattern of the tris(pyrazolyl)borate ligands is still resolved even at −87 °C. In the carbon variable-temperature experiment, the only resonance that changes with temperature is the most deshielded pyrazolyl ring resonance. This resonance splits into two resonances at ca. −53 °C. At −86 °C these resonances are separated by 10.6 Hz.

For the bis(acetate) complex, **4**, there is no observable change in the ^1H NMR spectra between ambient temperature and −87 °C. In the ^{13}C spectra, both the δ 142.47 and 104.36 resonances of the pyrazolyl rings split into two resonances at ca. −55 °C. These resonances are separated by 4.0 and 13.3 Hz, respectively, at −87 °C. Though not observed for **3**, the methyl carbon resonance of the acetate groups of **4** also collapses into a complex resonance at low temperature.

Crystallographic Studies. Molecular Structure of $[HB(pz)_3]_2YCl(Hpz)$. The molecular structure of **2** has been determined by X-ray crystallography. Figure 2 shows an ORTEP drawing of **2**. Tables IV and V, respectively, list selected bond lengths and bonds angles for **2**. Because of the frequently cited analogy between tridentate poly(pyrazolyl)borate and cyclopentadienyl (for steric considerations the pentamethylcyclopentadienyl) ligands, it is reasonable to attempt to describe the structure of **2** as a bent sandwich complex. In accordance with this description, the nitrogen donor atoms of each $[HB(pz)_3]^-$ ligand form a plane having a dihedral angle of 134.1°, very similar to the angle of that in $(C_5Me_5)_2YCl(THF)$ at 134.6°.[13] The pyrazolyl rings of each ligand are staggered with respect to one another, with the closest interligand contact being 2.395 Å (both N(12) and N(22) from N(42)). For the pyrazolylborate nitrogens, the Y–N bond lengths range from 2.456 (5) to 2.546 (4) Å, with an average Y–N bond distance of 2.489 Å. The Y–N(71) (pyrazole) distance is longer at 2.613 (4) Å. A very interesting structural feature is that the coordinated pyrazole is nearly coplanar with the Y, Cl, and N(71) plane (dihedral angle of 2.51°) such that N(72) is only 0.040 Å above that plane, placing N(72) in close proximity to Cl. This orientation and the short N(72)–Cl interatomic distance of 2.935 Å suggest the possibility of an intramolecular hydrogen bond between the pyrazole hydrogen atom and Cl. The NH stretching frequency in the IR spectrum

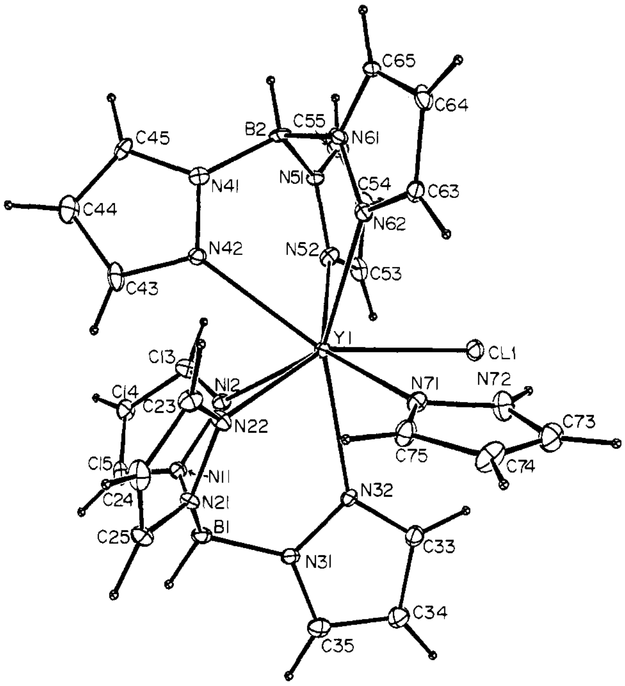

Figure 2. Numbered ORTEP drawing of $[HB(pz)_3]_2YCl(Hpz)$ (**2**).

Table IV. Bond Distances (Å) for $[HB(pz)_3]_2YCl(Hpz)$ with Esd's in Parentheses

Y(1)–Cl(1)	2.721 (2)	N(51)–N(52)	1.369 (6)
Y(1)–N(12)	2.465 (5)	N(51)–C(55)	1.351 (9)
Y(1)–N(22)	2.456 (5)	N(51)–B(2)	1.524 (9)
Y(1)–N(32)	2.511 (4)	N(52)–C(53)	1.336 (8)
Y(1)–N(42)	2.546 (4)	N(61)–N(62)	1.371 (5)
Y(1)–N(52)	2.457 (4)	N(61)–C(65)	1.336 (8)
Y(1)–N(62)	2.499 (5)	N(61)–B(2)	1.517 (9)
Y(1)–N(71)	2.613 (4)	N(62)–C(63)	1.325 (8)
N(11)–N(12)	1.376 (6)	N(71)–N(72)	1.339 (7)
N(11)–C(15)	1.345 (8)	N(71)–C(75)	1.332 (8)
N(11)–B(1)	1.548 (8)	N(72)–C(73)	1.335 (9)
N(12)–C(13)	1.333 (8)	C(13)–C(14)	1.383 (9)
N(21)–N(22)	1.367 (6)	C(14)–C(15)	1.36 (1)
N(21)–C(25)	1.346 (8)	C(23)–C(24)	1.387 (9)
N(21)–B(1)	1.522 (9)	C(24)–C(25)	1.363 (9)
N(22)–C(23)	1.329 (8)	C(33)–C(34)	1.39 (1)
N(31)–N(32)	1.361 (8)	C(34)–C(35)	1.37 (1)
N(31)–C(35)	1.345 (8)	C(43)–C(44)	1.38 (1)
N(31)–B(1)	1.527 (9)	C(44)–C(45)	1.37 (1)
N(32)–C(33)	1.335 (8)	C(53)–C(54)	1.36 (1)
N(41)–N(42)	1.365 (6)	C(54)–C(55)	1.38 (1)
N(41)–C(45)	1.346 (8)	C(63)–C(64)	1.39 (1)
N(41)–B(2)	1.534 (9)	C(64)–C(65)	1.37 (1)
N(42)–C(43)	1.343 (8)	C(73)–C(74)	1.37 (1)
		C(74)–C(75)	1.39 (1)

Table V. Bond Angles (deg) for $[HB(pz)_3]_2YCl(Hpz)$ with Esd's in Parentheses

Cl(1)-Y(1)-N(12)	117.3 (1)	Y(1)-N(12)-N(11)	121.8 (3)
Cl(1)-Y(1)-N(22)	145.0 (1)	Y(1)-N(12)-C(13)	131.4 (4)
Cl(1)-Y(1)-N(32)	76.7 (1)	N(22)-N(21)-B(1)	122.5 (5)
Cl(1)-Y(1)-N(42)	141.8 (1)	C(25)-N(21)-B(1)	128.7 (5)
Cl(1)-Y(1)-N(52)	72.4 (1)	Y(1)-N(22)-N(21)	121.9 (3)
Cl(1)-Y(1)-N(62)	85.6 (1)	Y(1)-N(22)-C(23)	130.7 (4)
Cl(1)-Y(1)-N(71)	75.6 (1)	N(32)-N(31)-B(1)	122.0 (5)
N(12)-Y(1)-N(22)	76.1 (1)	C(35)-N(31)-B(1)	127.5 (5)
N(12)-Y(1)-N(32)	70.5 (2)	Y(1)-N(32)-N(31)	122.1 (3)
N(12)-Y(1)-N(42)	71.7 (1)	Y(1)-N(32)-C(33)	132.3 (4)
N(12)-Y(1)-N(52)	78.7 (2)	N(42)-N(41)-B(2)	120.4 (5)
N(12)-Y(1)-N(62)	140.0 (1)	C(45)-N(41)-B(2)	129.2 (5)
N(12)-Y(1)-N(71)	138.8 (1)	Y(1)-N(42)-N(41)	122.4 (3)
N(22)-Y(1)-N(32)	78.4 (2)	Y(1)-N(42)-C(43)	130.2 (4)
N(22)-Y(1)-N(42)	71.9 (1)	N(52)-N(51)-B(2)	120.9 (5)
N(22)-Y(1)-N(52)	142.1 (2)	C(55)-N(51)-B(2)	129.7 (5)
N(22)-Y(1)-N(62)	104.4 (1)	Y(1)-N(52)-N(51)	124.2 (3)
N(22)-Y(1)-N(71)	74.6 (1)	Y(1)-N(52)-C(53)	129.1 (4)
N(32)-Y(1)-N(42)	136.2 (2)	N(62)-N(61)-B(2)	122.5 (5)
N(32)-Y(1)-N(52)	118.7 (2)	C(65)-N(61)-B(2)	128.0 (5)
N(32)-Y(1)-N(62)	149.5 (2)	Y(1)-N(62)-N(61)	122.0 (3)
N(32)-Y(1)-N(71)	75.7 (2)	Y(1)-N(62)-C(63)	132.0 (4)
N(42)-Y(1)-N(52)	73.6 (2)	Y(1)-N(71)-N(72)	118.8 (3)
N(42)-Y(1)-N(62)	70.8 (1)	Y(1)-N(71)-C(75)	136.8 (4)
N(42)-Y(1)-N(71)	124.0 (1)	N(11)-B(1)-N(21)	110.0 (5)
N(52)-Y(1)-N(62)	78.0 (2)	N(11)-B(1)-N(31)	107.4 (5)
N(52)-Y(1)-N(71)	139.8 (2)	N(21)-B(1)-N(31)	109.9 (5)
N(62)-Y(1)-N(71)	75.9 (1)	N(41)-B(2)-N(51)	108.5 (5)
N(12)-N(11)-B(1)	121.7 (5)	N(41)-B(2)-N(61)	110.2 (5)
C(15)-N(11)-B(1)	128.9 (5)	N(51)-B(2)-N(61)	111.4 (5)

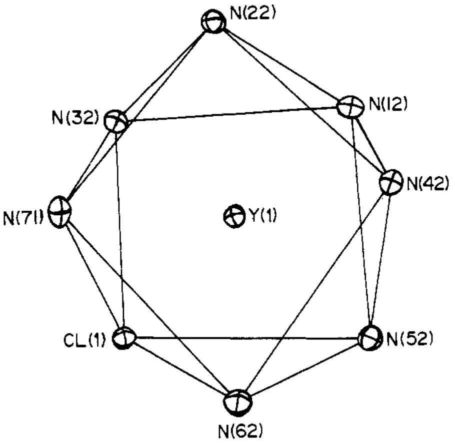

Figure 3. ORTEP drawing showing only the donor atoms in $[HB(pz)_3]_2YCl(Hpz)$. The view is perpendicular to one of the square faces of the square-antiprism coordination geometry.

occurs at 3125 cm^{-1}, in the expected region for hydrogen bonding.

Although useful conceptually, there is a problem with describing the structure of **2** as a bent sandwich complex. In Cp_2MXY complexes, the dihedral angle of the (center of Cp)-M-(center of Cp) and X-M-Y planes is found to be very close to 90°.[14] For **2**, with the boron atom taken as the center point of the poly(pyrazolyl)borate ligands, the dihedral angle of the B(1)-Y-B(2) and Cl-Y-N(71) planes is 69.2°. This is a significant distortion from the bent sandwich geometry.

Table VI. Shape Parameters[a] (deg) for **2** and Those Calculated for the Three Regular Eight-Coordinate Polyhedra

	DOD	BCTP	SAP	**2**
δ	29.5, 29.5	0, 21.8	0.0, 0.0	4.11, 17.63
	29.5, 29.5	48.2, 48.2	52.4, 52.4	54.34, 53.82
ϕ	0	14.1	24.5	16.78, 18.06

[a] For a definition of the shape parameters see ref 15a.

Table VII. Bond Distances (Å) for $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ with Esd's in Parentheses

Y(1)-O(11)	2.273 (5)	N(21)-C(25)	1.34 (2)
Y(1)-O(12)	2.279 (6)	N(21)-B(1)	1.560 (9)
Y(1)-O(21)	2.302 (5)	N(22)-C(23)	1.321 (7)
Y(1)-O(22)	2.262 (5)	N(31)-N(32)	1.385 (8)
Y(1)-N(12)	2.469 (5)	N(31)-C(35)	1.315 (8)
Y(1)-N(22)	2.488 (6)	N(31)-B(1)	1.56 (1)
Y(1)-N(32)	2.465 (6)	N(32)-C(33)	1.308 (9)
O(11)-C(11)	1.26 (1)	C(11)-C(12)	1.46 (1)
O(12)-C(11)	1.25 (1)	C(13)-C(14)	1.33 (2)
O(21)-C(21)	1.213 (9)	C(14)-C(15)	1.40 (2)
O(22)-C(21)	1.228 (8)	C(21)-C(22)	1.46 (1)
N(11)-N(12)	1.346 (7)	C(25)-C(24)	1.34 (2)
N(11)-C(15)	1.303 (9)	C(24)-C(23)	1.42 (2)
N(11)-B(1)	1.54 (2)	C(33)-C(34)	1.34 (2)
N(12)-C(13)	1.334 (9)	C(34)-C(35)	1.35 (1)
N(21)-N(22)	1.324 (7)		

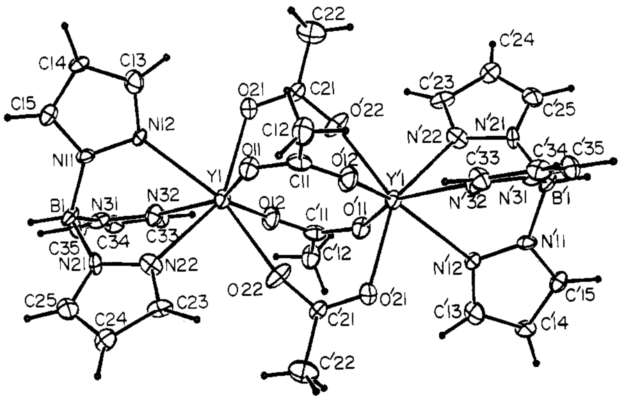

Figure 4. Numbered ORTEP drawing of $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ (**4**). The view is perpendicular to the Y-Y axis.

Examination of the structure using interactive computer graphics clearly indicates that the most reasonable geometry for describing the coordination polyhedron is a square antiprism, distorted somewhat toward a bicapped trigonal prism. Figure 3 shows a view of the donor atoms perpendicular to the square faces. The face formed by Cl, N(32), N(12), and N(52) is nearly planar (root-mean-square deviation of 0.0395 Å), with the largest deviation from the least-squares plane being 0.0415 Å for N(12). The N(71), N(22), N(42), N(62) face is less planar (root-mean-square deviation of 0.1517 Å), with the largest deviation of 0.160 Å for N(42). The dihedral angle of these planes is 5.71°. The length of the edges of the squares ranges from 2.870 Å (N(12)-N(32)) to 3.251 Å (N(32)-Cl).

Three polyhedra have been used to describe eight-coordinate molecules: the D_{2d} dodecahedron, the C_{4v} bicapped trigonal prism, and the D_{4d} square antiprism used here to describe **2**. A formal outline of shape parameters to characterize these three geometries has been depicted by Muetterties and Guggenberger,[15a] expanding on the work of Porai-Koshits and Aslanov.[15b] Shape parameters as defined in this work[15a] are given in Table VI. Although a fairly good match of the geometry of **2** with the square antiprism is observed, there is clearly a distortion in the direction of a bicapped trigonal prism.

Molecular Structure of $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$. The solid state structure of **4** has also been determined by X-ray crystallography. Figure 4 shows a numbered ORTEP diagram of **4**. Tables VII and VIII, respectively, list selected bond lengths and bond angles for **4**. The structure is a centrosymmetric dimer with all four acetate ligands bridging the yttrium atoms. The yttrium atoms are separated by 4.037 Å. Figure 5 is a view of the molecule down the yttrium-yttrium axis. As is evident in this view, the boron atoms are nearly collinear with this axis, making the yttrium-yttrium-boron angle 172.6°. The yttrium atoms are in an

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(14) Evans, W. J.; Dominguez, R.; Levan, K. R.; Doedens, R. J. *Organometallics* **1985**, *4*, 1836.

(15) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748. (b) Porai-Koshits, M. A.; Aslanov, L. A. *Zh. Strukt. Khim.* **1972**, *13*, 266.

Table VIII. Bond Angles (deg) for $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ with Esd's in Parentheses

O(11)–Y(1)–O(12)	132.6 (2)	N(22)–N(21)–B(1)	122.9 (6)
O(11)–Y(1)–O(21)	81.9 (2)	C(25)–N(21)–B(1)	128.2 (6)
O(11)–Y(1)–O(22)	81.6 (2)	N(21)–N(22)–C(23)	108.9 (6)
O(11)–Y(1)–N(12)	80.1 (2)	N(32)–N(31)–C(35)	107.0 (5)
O(11)–Y(1)–N(22)	86.2 (2)	N(32)–N(31)–B(1)	123.2 (6)
O(11)–Y(1)–N(23)	152.0 (2)	C(35)–N(31)–B(1)	129.8 (7)
O(12)–Y(1)–O(21)	81.5 (2)	N(31)–N(32)–C(33)	105.2 (5)
O(12)–Y(1)–O(22)	74.8 (2)	O(11)–C(11)–O(12)′	126.1 (7)
O(12)–Y(1)–N(12)	135.9 (2)	O(11)–C(11)–C(12)	119.1 (8)
O(12)–Y(1)–N(22)	127.3 (2)	O(12)′–C(11)–C(12)	144.8 (7)
O(12)–Y(1)–N(32)	74.8 (2)	N(12)–C(13)–C(14)	113.8 (6)
O(21)–Y(1)–O(22)	128.3 (2)	C(13)–C(14)–C(15)	102.7 (6)
O(21)–Y(1)–N(12)	74.4 (2)	N(11)–C(15)–C(14)	108.7 (6)
O(21)–Y(1)–N(22)	147.5 (2)	O(21)–C(21)–O(22)′	122.0 (7)
O(21)–Y(1)–N(23)	99.7 (2)	O(21)–C(21)–C(22)	121.8 (7)
O(22)–Y(1)–N(12)	148.1 (2)	O(22)′–C(21)–C(22)	116.1 (8)
O(22)–Y(1)–N(22)	79.1 (2)	N(21)–C(25)–C(24)	109.5 (7)
O(22)–Y(1)–N(23)	116.7 (2)	C(23)–C(24)–C(25)	104.6 (6)
N(12)–Y(1)–N(22)	73.8 (2)	N(22)–C(23)–C(24)	108.0 (7)
N(12)–Y(1)–N(32)	73.6 (2)	N(32)–C(33)–C(34)	113.0 (7)
N(22)–Y(1)–N(32)	77.6 (2)	C(33)–C(34)–C(35)	103.5 (6)
N(12)–N(11)–C(15)	111.0 (6)	N(31)–C(35)–C(34)	111.3 (7)
N(12)–N(11)–B(1)	123.6 (5)	N(11)–B(1)–N(21)	107.9 (6)
C(15)–N(11)–B(1)	125.4 (6)	N(11)–B(1)–N(31)	106.3 (6)
N(11)–N(12)–C(13)	103.8 (6)	N(21)–B(1)–N(31)	109.5 (5)
N(22)–N(21)–C(25)	109.0 (5)		

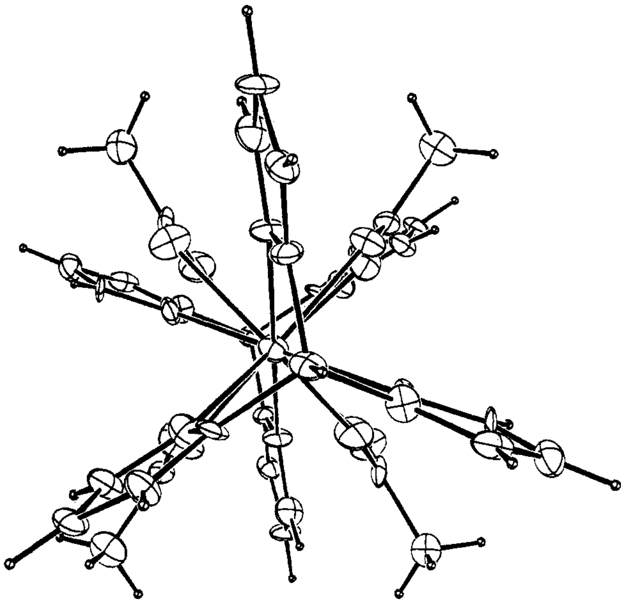

Figure 5. ORTEP drawing of $\{[HB(pz)_3]Y(\mu\text{-}O_2CCH_3)_2\}_2$ as viewed down the Y–Y axis.

unusual seven-coordinate polyhedron. Each yttrium atom is sandwiched between a square plane of oxygen atoms from the acetate ligands and a triangular plane of nitrogen atoms from a tris(pyrazolyl)borate ligand. The oxygen atoms form a nearly perfect square plane, with the largest deviation from the plane being 0.042 Å. The yttrium atom is 0.952 Å out of this plane and 1.759 Å out of the N(12), N(22), and N(32) plane. These two planes are nearly parallel, with a dihedral angle of 6.36°.

An alternative description of the geometry about yttrium suggested from the analysis by interactive computer graphics is as a monocapped trigonal prism. In this description, the four oxygen ligands make up one square face, and the other two square faces are formed with N(22) and N(32), placing N(12) in the capping position of the O(11), O(21), N(22), N(32) rectangular face. The two triangular faces (O(11), O(22), N(22) and O(12), O(21), N(32)) are at a dihedral angle of 6.6° and make nearly 90° angles with the 4-fold faces. The twist angle between the triangular faces is near zero, as expected for a trigonal prism. The largest distortion from this geometry is the relatively long distance between O(21) and N(32).

Discussion

The new $[HB(pz)_3]_2Y$ complexes **1**–**3** reported in this work add to a growing number of molecules of this general formula prepared with yttrium and the lanthanides. $[HB(pz)_3]_2YCl(Hpz)$ (**2**) is the sixth member of the series to be characterized in the solid state by X-ray crystallography. Two of these complexes, $[\eta^3\text{-}HB(pz)_3]_2[\eta^2\text{-}HB(pz)_3]Yb$ (**5**)[4b] and $[HB(pz)_3]_2Ce(acac)$ (**6**),[5] have been shown to have a bicapped-trigonal-prismatic (BCTP) geometry. Alternatively, they can also be described as having bent sandwich geometry analogous to Cp_2MX_2 complexes. In contrast to these structures, $[HB(pz)_3]_2Yb(dpm)$[4d] and $[HB(pz)_3]_2Yb(acac)$[5] have been described as having a square-antiprismatic (SAP) geometry. Although the structure of $[HB(pz)_3]_2YCl(H_2O)$ was initially described as a bent sandwich type geometry,[6b] further analysis of the structure by interactive computer graphics clearly shows that this structure can be better described as a distorted SAP. Thus, **2** is the fourth member of the series to be a distorted SAP. The factors that determine the geometry of this class of molecules are not yet clear. It is not unexpected that complex **6** has a different structure from the yttrium and ytterbium complexes because of the much larger size of cerium, but the difference in structure between **5** and the four other complexes with similarly sized metals is surprising. Complex **5** is also the only member of this class of molecules that does not show ambient-temperature fluxional behavior in solution (vide infra). Possibly, this difference can be explained by the $[\eta^2\text{-}HB(pz)_3]$ ligand being considerably more bulky than the analogous ligand(s) in the four complexes with SAP geometry.

With the exception of complex **5**, this entire class of molecules shows dynamic behavior of the tris(pyrazolyl)borate ligands in solution. In each case, all of the pyrazolyl rings of the two tris(pyrazolyl)borate ligands appear equivalent in ambient-temperature spectra. Complete detailed analyses of these fluxional processes have not yet appeared. A problem is the difficulty in obtaining limiting low-temperature spectra due to the low energy barrier of the rearrangement processes.[4d] Takats has proposed an interesting way to equilibrate the rings that involves a SAP–BCTP–SAP rearrangement.[4d] On the basis of our work with $[RB(pz)_3]Zr(OR)Cl_2$ and related complexes,[1] another reasonable dynamic process for these molecules is a trigonal-twist rotation of the poly(pyrazolyl)borate ligands about the M–B axis.

For complex **1**, at least one resonance in both the ^1H and ^{13}C NMR spectra collapses to a complex set of resonances at low temperature. Any interpretation of these data also needs to take into consideration the solution molecular weight studies that indicate a monomer–dimer equilibrium. While it has not proven possible to structurally characterize this complex in the solid state (the crystals of **1** decompose in the X-ray beam), a reasonable structure of the dimer is as an unsymmetrical, monochloride-bridged species analogous to $[(C_5Me_5)_2YCl]_2$.[16] Considering the large number of nonequivalent pyrazolyl rings that would be expected from both the monomer and an unsymmetrical structure such as this, complex static NMR spectra are expected. Mechanisms for equilibration of the rings at higher temperatures could involve both intra- and intermolecular processes that cannot be evaluated from the current data.

As outlined above, the structure of **2** in the solid state is best described as a SAP. An interesting feature is the near planarity of the Cl, Y, and coordinated pyrazole ring, with the ring rotated such that the NH hydrogen atom is pointed toward the chlorine ligand, forming an intramolecular hydrogen-bonding interaction. Hydrogen bonding is also indicated by the infrared spectrum. In the structure of $[HB(pz)_3]_2YCl(H_2O)$, intermolecular hydrogen bonding was observed.[6b]

Two dynamic processes are observed by NMR spectroscopy for **2**. The 3- and 5-positions of the coordinated pyrazole ligand are equivalent at ambient temperature. This indicates that the pyrazole is undergoing dissociation from yttrium and tautomerism of the NH proton in solution, equilibrating the 3- and 5-positions

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on the ring. The pyrazolyl rings of the tris(pyrazolyl)borate ligands also equilibrate with a slightly higher barrier. The two processes do not seem to be correlated. Thus, it is not clear whether the eight-coordinate structure observed in the solid state or a seven-coordinate species formed upon dissociation of the pyrazole is the dynamic species responsible for the equilibration of the $[HB(pz)_3]^-$ pyrazolyl rings.

The mixed acetate–tris(pyrazolyl)borate complexes of yttrium form readily. A chelating ligand such as acetate or acac[4d,5] seems to be necessary to form stable $[HB(pz)_3]_2Y$(ligand) complexes because we have been unable to prepare seven-coordinate $[HB(pz)_3]_2Y(OR)$ complexes even with bulky alkoxide ligands.[17] Molecular weight studies indicate that **3** is a trimer in solution. The closest analogue is $[Cp_2YbO_2CC_6F_5]_2$, which is a dimer in the solid state.[18] A series of similar cyclopentadienyl complexes of the lanthanides have also been shown to be dimers in solution.[19] The trimeric structure of **3** may reflect the increased steric bulk of the tris(pyrazolyl)borate ligand when compared to the cyclopentadienyl ligand.[2] Trimers are favored for complexes having excessively bulky ligands.[20]

Yttrium is stabilized in a seven-coordinate environment in complex **4**. This tetraacetate-bridged dimer does not appear to have an analogue in cyclopentadienyl chemistry of yttrium or the lanthanides. Two examples of similar complexes of early metals, $[CpV(O_2CCF_3)_2]_2$ and $[CpTi(O_2CPh)_2]_2$,[21] have been structurally characterized. Both **3** and **4** show equal-intensity resonances for two types of pyrazolyl rings in low-temperature NMR spectra. For **3**, the acetate methyl groups remain equivalent at low temperature, but for **4**, two methyl resonances are observed. It seems unlikely that limiting low-temperature spectra of these complexes are being observed in either case even at ca. −87 °C. It is difficult to formulate a static structure for either **3** or **4** in which the pyrazolyl rings form a 1/1 equivalent set unless the two $[HB(pz)_3]^-$ ligands are inequivalent but are undergoing a fluxional process to equilibrate the pz rings within each ligand. In fact, in the solid-state structure of **4** the rings form a 1/1/1 set in the centrosymmetric dimer unit. Given that these molecules could demonstrate dynamic behavior by rotation of the tris(pyrazolyl)borate ligands, by rearrangement of the coordination polyhedra, by equilibria involving breaking and re-forming of the acetate bridges or combinations thereof, speculation on the mechanism(s) of these dynamic processes seems unwarranted at this time.

Finally, the preparation of mixed poly(pyrazolyl)borate–cyclopentadienyl complexes of yttrium, like those of zirconium,[1d] have been attempted. Although spectral evidence for complexes such as $[HB(pz)_3]CpYCl$ has been obtained, definitive isolation has not proven possible, to date.[17] Poly(pyrazolyl)borate complexes of several lanthanides analogous to those reported here are also under investigation.[22]

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Supplementary Material Available: Tables of crystallographic data for structural analysis, positional parameters of H atoms, and anisotropic thermal parameters (9 pages); listings of structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Lanthanide Complexes of Potentially Heptadentate Ligands Including the Structure of [Tris(3-aza-4-methylhept-4-ene-6-on-1-yl)amine]tris(nitrato)gadolinium(III)

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Several potentially heptacoordinate N_4O_3 ligands have been prepared and characterized, as has a series of their lanthanide (Ln) complexes. The ligands are the Schiff base condensation products of tris(2-aminoethyl)amine with 3 equiv of either acetylacetone or a hydroxyacetophenone. The ligands are believed to be heptadentate in Ln complexes if the starting lanthanide salt contains a poorly coordinating anion (e.g. Cl^-) and an early (large) Ln; several Ln(L) (Ln = La, Pr; different Ls) complexes have been isolated. When the anion is NO_3^-, the resulting complexes are of the form $Ln(H_3L)(NO_3)_3$ where Ln is from across the series and the ligand is tridentate with the three O atoms coordinating Ln and a hydrogen atom bridging across each of the three N,O arms of the ligand. A Gd complex, $[N(CH_2CH_2NHC(Me)CHC(Me)O)_3]Gd(NO_3)_3$, of the latter type has been studied by single-crystal X-ray diffraction. It is nine-coordinate, and each of the bidentate nitrates is trans to a ligand O rendering the geometry pseudo-*fac*-octahedral if each nitrate is considered to occupy one coordination position. $Gd(C_{21}H_{36}N_4O_3)(NO_3)_3$ crystallizes in the monoclinic space group *Cc* with the crystal parameters $a = 16.617$ (3) Å, $b = 17.083$ (1) Å, $c = 10.901$ (1) Å, $\beta = 101.13$ (1)°, and $Z = 4$. The data were refined by using 5028 reflections with $I \geq 3\sigma(I)$ to R and R_w values of 0.022 and 0.024, respectively.

Introduction

We have been pursuing a continuing project to detail the coordination chemistry of main-group complexes that are water soluble, hydrolytically stable, and lipophilic.[1] Because of their great mobility in vivo, the compounds have presented interesting opportunities for the study of some of these metals in the etiology and diagnosis of disease.[2,3] In an effort to extend these properties

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