bond distance is 2.369 (3) Å. There are no short intermolecular contacts between the molecules in the unit cell.

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Supplementary Material Available: Tables of bond distances and angles, anisotropic thermal parameters, and calculated hydrogen atom positions (11 pages); a table of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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Poly(pyrazolyl)borate Complexes of Terbium, Samarium, and Erbium. X-ray Crystal Structure of $\{[\eta^3\text{-HB(pz)}_3]_2\text{Sm}(\mu\text{-O}_2\text{CPh})\}_2$ (pz = Pyrazolyl Ring)

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The reaction of MCl_3 (M = Tb, Sm, Er) with 3 equiv of $\text{K[H}_2\text{B(pz)}_2]$ yields $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{M}$. These complexes have properties similar to those of the yttrium analogue, which has been shown to have a trigonal-prismatic structure possessing weak agostic B–H···Y three-center interactions. The reaction of the metal halides with 2 equiv of $\text{K[HB(pz)}_3]$ yields $[\text{HB(pz)}_3]_2\text{MCl}$, shown to be monomeric in solution for M = Sm. A similar reaction, which in addition contains 1 equiv of $\text{Na(O}_2\text{CCH}_3)$, yields $\{[\text{HB(pz)}_3]_2\text{M(O}_2\text{CCH}_3)\}_2$. NMR spectra for all three types of these paramagnetic complexes are resolved for M = Sm and are temperature dependent, showing these molecules are fluxional in solution. The complex $\{[\text{HB(pz)}_3]_2\text{Sm(O}_2\text{CPh)}\}_2$ was also prepared and the solid-state structure determined by X-ray diffraction: monoclinic, space group $P2_1/c$, a = 13.264 (3) Å, b = 35.821 (8) Å, c = 15.544 (4) Å, β = 115.06 (2)°, V = 6690 Å^3, and Z = 4. The structure is an acetate-bridged dimer in which the geometry about the samarium atoms fails to fit any regular polyhedron. Molecular weight studies show that this complex and $\{[\text{HB(pz)}_3]_2\text{Sm(O}_2\text{CCH}_3)\}_2$ are dimers in benzene solution.

Introduction

We have recently been developing the chemistry of the early-transition metals using poly(pyrazolyl)borate ligands. With tantalum and zirconium, a variety of stable complexes containing one tris(pyrazolyl)borate ligand, such as $[\text{RB(pz)}_3]\text{TaMe}_3\text{Cl}$ (R = H, pz; pz = pyrazolyl ring),[1a] $[\text{HB(3,5-Me}_2\text{pz)}_3]\text{TaMe}_3\text{Cl}$,[1a] $[\text{RB(pz)}_3]\text{ZrCl}_3$ (R = *n*-Bu, *i*-Pr),[1b] $[\text{HB(3,5-Me}_2\text{pz)}_3]\text{Zr(O-}t\text{-Bu)}_n\text{R}_{3-n}$ (n = 1, 2; R = Cl, Me, CH_2Ph, C≡CMe),[1c] and $[\text{HB(pz)}_3]\text{CpZrCl}_2$,[1d] have been prepared. It was not possible, however, to prepare complexes containing two tris(pyrazolyl)borate ligands on tantalum or zirconium. Using the larger metals yttrium and lanthanum, we have reported the following series of complexes containing two tris(pyrazolyl)borate ligands: $[\text{HB(pz)}_3]_2\text{YCl(H}_2\text{O)}$, $[\text{HB(pz)}_3]_2\text{LaCl(H}_2\text{O)}$,[2a] $[\text{HB(pz)}_3]_2\text{YCl}$, $[\text{HB(pz)}_3]_2\text{YCl}$ (HPz), $\{[\text{HB(pz)}_3]_2\text{Y}(\mu\text{-O}_2\text{CCH}_3)\}_n$, and $\{[\text{HB(pz)}_3]\text{Y}(\mu\text{-O}_2\text{CCH}_3)_2\}_2$.[2b] $[\text{HB(pz)}_3]_2\text{YCl(H}_2\text{O)}$[2a] and $[\text{HB(pz)}_3]_2\text{YCl(Hpz)}$[2b] have been structurally characterized by X-ray crystallography and shown to have distorted-square-antiprismatic geometry. $\{[\text{HB(pz)}_3]\text{Y}(\mu\text{-O}_2\text{CCH}_3)_2\}_2$ was also structurally characterized in the solid state and is an unusual example of seven-coordinate yttrium.[2b] We have also described the synthesis and characterization of $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{Y}$,[3] a molecule that possesses three, three-center, bridging B–H···Y interactions. In the solid state, the six nitrogen donor atoms form a trigonal prism in which each rectangular face is capped by a B–H···Y agostic bond.

In addition to our work, Takats has reported the synthesis of $[\eta^3\text{-HB(pz)}_3]_2[\eta^2\text{-HB(pz)}_3]\text{M}$ complexes (M = Y, La, Ce, Pr, Sm, Gd, Er, Yb).[4a] The ytterbium derivative was characterized as eight-coordinate as indicated by the above formula in solution[4b] and in the solid state.[4c] The solid-state structure was described as a bicapped trigonal prism. The synthesis of $[\text{HB(pz)}_3]_2\text{ErCl(THF)}$ was also briefly mentioned, but no experimental details were given.[4a] Takats has also recently published the synthesis of $[\text{HB(pz)}_3]_2\text{M}$($\beta$-diketonate) (M = Yb, Lu; β-diketonate = 2,2,6,6-tetramethyl-3,5-heptanedionate (dpm), 3-(trifluoroacetyl)-*d*-camphorate).[5] The Yb–heptanedione complex was characterized by X-ray crystallography and shown to have a square-antiprismatic solid-state geometry. The synthesis of $[\text{HB(pz)}_3]_2\text{M(acac)}$ complexes (M = Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Yb, Lu; acac = acetylacetonate) has been reported by Jones and co-workers.[6] X-ray crystallographic analysis determined that the cerium complex possesses a bicapped-trigonal-prismatic geometry, while that of the ytterbium complex is derived from a square antiprism. With the exception of the $[\eta^3\text{-HB(pz)}_3]_2[\eta^2\text{-HB(pz)}_3]\text{M}$ complexes, all of these tris(pyrazolyl)borate complexes in both reports undergo dynamic rearrangements in solution.

We report here the synthesis of complexes of the type $[\text{H}(\mu\text{-H})\text{B(pz)}_2]_3\text{M}$, $[\text{HB(pz)}_3]_2\text{MCl}$, and $\{[\text{HB(pz)}_3]_2\text{M(O}_2\text{CCH}_3)\}_2$ for the lanthanide metals samarium, terbium, and erbium. The synthesis and solid-state structure of $\{[\text{HB(pz)}_3]_2\text{Sm}(\mu\text{-O}_2\text{CPh})\}_2$ is also reported.

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. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. The ^{1}H, ^{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 resonances are singlets with chemical shifts reported vs TMS by using the solvents CD_2Cl_2 and CDCl_3 as internal standards (CD_2Cl_2 resonance at 53.85 ppm; CDCl_3 resonance at 77.00 ppm). Boron-11 chemical shifts are reported in ppm vs $\text{BF}_3\cdot\text{OEt}_2$. 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 and then sealed in screw-capped 5-mm NMR tubes. Activation parameters were calculated at the coalescence temperature.[7]

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UV–visible spectra were obtained in CH_2Cl_2 by using a Cary 210 spectrometer. Accurate mass spectra were run as solids on a VG 70SQ spectrometer; low-resolution spectra were run 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. $K[HB(pz)_3]$ and $K[H_2B(pz)_2]$ were prepared by the published methods.[8] Anhydrous $TbCl_3$, $SmCl_3$, and $ErCl_3$ were purchased from Cerac/Pure Division and were used without further purification. Molecular weights were determined by freezing-point-depression measurements in an apparatus similar in basic design to that developed by Schriver.[9] The cell contains a Fenwal GB41P2 10K thermister, balanced against a Leeds & Northrup bridge circuit. A working calibration curve of ΔT verses molality was obtained by using known concentrations of doubly sublimed ferrocene. Data acquisition and processing were automated by interfacing the apparatus to a WYSE 286 computer. Typically, the mass of a sample was determined on a benchtop analytical balance and the sample then quickly transported into the drybox. The solute and the solvent were then introduced to the cryoscopy cell under the nitrogen atmosphere. Concentrations varied from approximately 5 to 30 g of solute/kg solvent.

Tris[dihydrobis(1-pyrazolyl)borato]terbium(III), $[H(\mu\text{-}H)B(pz)_2]_3Tb$ (1a). $TbCl_3$ (0.50 g, 1.9 mmol) and $K[H_2B(pz)_2]$ (1.05 g, 5.6 mmol) were placed in a 100-mL round-bottomed flask. THF (70 mL) was added by syringe. The suspension was heated to reflux for 3 h, centrifuged, and filtered, and the solvent was evaporated under vacuum. The filtrate residue was extracted with toluene (40 mL) and filtered. Addition of hexane (30 mL) and cooling (ca. 0 °C) resulted in colorless crystals (0.28 g, 0.47 mmol, 25%). IR (Nujol mull, cm^{-1}): 2455, 2440 (BH). UV–vis (λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)): 349 (1.2), 351 (1.1), 355 (1.0), 363 (0.94), 366 (0.80), 371 (0.75), 482 (0.37). The mass spectrum shows the highest cluster for $M^+ - H$ at *m/e* 599. Anal. Calcd for $C_{18}H_{24}N_{12}B_3Tb$: C, 36.04; H, 4.04. Found: C, 35.75; H, 4.09.

Bis[hydrotris(1-pyrazolyl)borato]chloroterbium(III), $[HB(pz)_3]_2TbCl$ (2a). $TbCl_3$ (0.50 g, 1.9 mmol) and $K[HB(pz)_3]$ (0.95 g, 3.8 mmol) were placed in a 100-mL round-bottomed flask. THF (50 mL) was added by syringe. The suspension was stirred at room temperature for 12 h, centrifuged, and filtered, and the solvent was evaporated under vacuum. The filtrate residue was extracted with benzene (40 mL), centrifuged, and filtered. The benzene was evaporated under vacuum to yield a white solid (0.72 g, 1.16 mmol, 62%). IR (Nujol mull, cm^{-1}): 2456 (BH). The accurate mass spectrum shows clusters for M^+ and $M^+ - Cl$. $C_{18}H_{20}N_{12}{}^{11}B_2{}^{35}ClTb$, $C_{18}H_{20}N_{12}{}^{11}B_2Tb$: calcd *m/e* 620.1062, 585.1373; found *m/e* 620.1037, 585.1397.

Bis[hydrotris(1-pyrazolyl)borato]chloro(pyrazole)terbium(III), $[HB(pz)_3]_2TbCl(Hpz)$. $TbCl_3$ (0.50 g, 1.9 mmol), $K[HB(pz)_3]$ (0.95 g, 3.8 mmol), and Hpz (0.13 g, 1.9 mmol) were placed in a 100-mL round-bottomed flask. THF (50 mL) was added by syringe. The suspension was stirred at room temperature for 6 h, centrifuged, and filtered, and the solvent was evaporated under vacuum. The filtrate residue was extracted with benzene (60 mL) and filtered. The benzene was evaporated under vacuum to yield a white solid (0.36 g, 0.52 mmol, 28%). IR (Nujol mull, cm^{-1}): 3180 (NH); 2468 (BH). The mass spectrum shows $M^+ - HCl$ and $M^+ - HBpz$ clusters at *m/e* 651 and 619. Anal. Calcd for $C_{21}H_{23}N_{14}B_2ClTb$: C, 36.69; H, 3.38. Found: C, 36.46; H, 3.58.

(Acetato)bis[hydrotris(1-pyrazolyl)borato]terbium(III), $[HB(pz)_3]_2Tb(O_2CCH_3)$ (3a). $TbCl_3$ (0.30 g, 1.1 mmol), $K[HB(pz)_3]$ (0.57 g, 2.3 mmol), and $Na(O_2CCH_3)$ (0.09 g, 1.1 mmol) were placed in a 100-mL round-bottomed flask. THF (30 mL) was added by syringe. The suspension was stirred at room temperature for 8 h, and the solvent was evaporated under vacuum. Benzene (40 mL) was added by syringe, and the suspension was stirred at room temperature for 1 h and centrifuged. Filtration and evaporation of the benzene under vacuum yielded a white solid (0.68 g, 1.1 mmol, 94%). IR (Nujol mull, cm^{-1}): 2450 (BH). The accurate mass spectrum shows a cluster for M^+. $C_{20}H_{23}N_{12}O_2{}^{11}B_2Tb$: calcd *m/e* 644.1507; found *m/e* 644.1503.

Tris[dihydrobis(1-pyrazolyl)borato]samarium(III), $[H(\mu\text{-}H)B(pz)_2]_3Sm$ (1b). This complex was prepared in 23% yield as outlined above for **1a**. ^1H NMR ($CDCl_3$): δ 10.68, 6.82, 6.53 (s, s, s; pz), 4.05 (broad BH_2). ^{13}C NMR (CD_2Cl_2): ambient temperature, δ 143.42, 135.13 (3-C, 5-C (pz)), 105.08 (4-C (pz)); −84 °C, 145.25, 137.15, 137.00 (3-C, 5-C (pz)), 107.77, 107.62 (4-C (pz)). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −16.04. IR (Nujol mull, cm^{-1}): 2455, 2440 (BH). UV–vis (λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)): 346 (7.1), 362 (4.9), 379 (5.8), 405 (10.0), 480 (3.8). The accurate mass spectrum shows $M^+ - H$ and $M^+ - BH_4$ clusters. $C_{18}H_{23}N_{12}{}^{11}B_3{}^{152}Sm$, $C_{18}H_{20}N_{12}{}^{11}B_2{}^{154}Sm$: calcd *m/e* 592.1642, 580.1342; found *m/e* 592.1664, 580.1311.

Table I. Crystallographic Data for the Structural Analysis of $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ (**4**)

formula: $(C_{25}H_{25}B_2N_{12}O_2Sm)_2$	fw = 1244.60
a = 13.264 (3) Å	space group: $P2_1/c$
b = 35.821 (8) Å	T = ambient
c = 15.544 (4) Å	λ = 0.71073 Å
α = 90°	ρ_{calc} = 1.385 g cm^{-3}
β = 115.06 (2)°	μ = 18 cm^{-1}
γ = 90°	transm coeff = 1.174–0.793
V = 6690 Å^3	R_F = 0.079
Z = 4	R_{wF} = 0.078

Bis[hydrotris(1-pyrazolyl)borato]chlorosamarium(III), $[HB(pz)_3]_2SmCl$ (2b). This complex was prepared in 44% yield as outlined above for **2a**. ^1H NMR ($CDCl_3$): δ 8.61, 5.92, 4.47 (6, 6, 6; s, s, s; pz). ^{13}C NMR ($CDCl_3$): δ 141.40, 135.80 (3-C, 5-C (pz)), 103.55 (4-C (pz)). ^{11}B NMR ($CDCl_3$): δ 2.65 (d, J_{BH} = 102 Hz, line narrowed). IR (Nujol mull, cm^{-1}): 2480 (BH). UV-vis (λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)): 345 (7.0), 362 (4.8), 377 (3.7), 404 (9.8), 478 (2.1). The accurate mass spectrum shows $M^+ - H$ and $M^+ - Cl$ clusters. $C_{18}H_{19}N_{12}{}^{11}B_2{}^{35}Cl{}^{152}Sm$, $C_{18}H_{20}N_{12}{}^{11}B_2{}^{152}Sm$: calcd *m/e* 612.0925, 578.1314; found *m/e* 612.0936, 578.1317.

(Acetato)bis[hydrotris(1-pyrazolyl)borato]samarium(III), $[HB(pz)_3]_2Sm(O_2CCH_3)$ (3b). This complex was prepared in 93% yield as outlined above for **3a**. ^1H NMR ($CDCl_3$): δ 8.31, 5.86 (s, s; two of the pz resonances, the third was not observed), 5.15 (broad CH_3). ^{13}C NMR (CD_2Cl_2): δ 141.12, 135.83 (3-C, 5-C (pz)), 103.75 (4-C (pz)). ^{11}B NMR ($CDCl_3$): δ 1.23 (d, J_{BH} = 68 Hz, line narrowed). IR (Nujol mull, cm^{-1}): 2455 (BH), 1560 (CO_2). The accurate mass spectrum shows clusters for $M^+ - H$ and $M^+ - O_2CCH_3$. $C_{20}H_{22}N_{12}O_2{}^{10}B{}^{11}B{}^{152}Sm$, $C_{18}H_{20}N_{12}{}^{10}B{}^{11}B{}^{152}Sm$: calcd *m/e* 635.1409, 577.1354; found *m/e* 635.1438, 577.1365. Anal. Calcd for $C_{20}H_{23}N_{12}O_2B_2Sm$: C, 37.80; H, 3.65. Found: C, 37.56; H, 3.58.

Bis{(μ-benzoato)bis[hydrotris(1-pyrazolyl)borato]samarium(III)}, $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ (4). This complex was prepared in 82% yield as outlined above for **3a**, substituting $Na(O_2CPh)$ for $Na(O_2CCH_3)$. ^1H NMR ($CDCl_3$): δ 8.57, 4.48 (broad, two of the pz resonances, the third was not observed), 5.89 (broad, C_6H_5). IR (benzene, cm^{-1}): 2457 (BH), 1520 (CO_2). The mass spectrum shows clusters for M^+, $M^+ - pz$, and $M^+ - O_2C(C_6H_5)$ at *m/e* 698, 632, and 578. Anal. Calcd for $C_{25}H_{25}N_{12}O_2B_2Sm$: C, 43.26; H, 3.92. Found: C, 43.02; H, 3.62.

Tris[dihydrobis(1-pyrazolyl)borato]erbium(III), $[H(\mu\text{-}H)B(pz)_2]_3Er$ (1c). This complex was prepared in 38% yield as outlined above for **1a**. IR (Nujol mull, cm^{-1}): 2455, 2440 (BH). UV–vis (λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)): 381 (22.8), 489 (5.7), 525 (13.1), 654 (5.1). Anal. Calcd for $C_{18}H_{24}N_{12}B_3Er$: C, 35.54; H, 3.99. Found: C, 35.49; H, 3.82.

Bis[hydrotris(1-pyrazolyl)borato]chloroerbium(III), $[HB(pz)_3]_2ErCl$ (2c). This complex was prepared in 48% yield as outlined above for **2a**. IR (Nujol mull, cm^{-1}: 2455 (BH). UV–vis (λ_{max}, nm (ϵ_{max}, $M^{-1}\,cm^{-1}$)): 381 (13.3), 489 (6.2), 525 (7.6), 654 (4.6). The accurate mass spectrum shows $M^+ - H$ and $M^+ - Cl$ clusters. $C_{18}H_{19}N_{12}{}^{10}B{}^{11}B{}^{35}Cl{}^{166}Er$, $C_{18}H_{20}N_{12}{}^{10}B{}^{11}B{}^{166}Er$: calcd *m/e* 625.1070, 591.1459; found *m/e* 625.1073, 591.1465.

(Acetato)bis[hydrotris(1-pyrazolyl)borato]erbium(III), $[HB(pz)_3]_2Er(O_2CCH_3)$ (3c). This complex was prepared in 40% yield as outlined above for **3a**. IR (Nujol mull, cm^{-1}): 2455 (BH), 1575 (CO_2). The accurate mass spectrum shows clusters for $M^+ - H$ and $M^+ - O_2CCH_3$. $C_{20}H_{22}N_{12}O_2{}^{10}B{}^{11}B{}^{166}Er$, $C_{18}H_{20}N_{12}{}^{10}B{}^{11}B{}^{166}Er$: calcd *m/e* 649.1514, 591.1459; found *m/e* 649.1520, 591.1444.

Crystallographic Analysis of $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ (4). A transparent prismatic crystal of **4** 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 analysis are listed in Table I. The length of one of the unit cell dimensions, b = 35.821 Å, has forced us to use a small crystal and a relatively narrow scan range to avoid reflection overlap. This may have introduced some systematic errors due to which anisotropic refinement of the light atoms resulted in nonpositive definite tensors for a few atoms. We have therefore refined the structure by using a model in which thermal motion of the light atoms was isotropic. The aromatic rings were refined as rigid bodies. Our satisfaction with the structure stems from our primary interest being the degree of oligomerization of the molecule and the geometry about the samarium atoms. The structure was solved by the heavy-atom method and refined by using SHELX 76.[10] Hydrogen atoms were placed in calculated positions and not

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Table II. Fractional Atomic Coordinates with Esd's in Parentheses and Isotropic Temperature Factors[a]

	x/a	*y/b*	*z/c*	*B*, Å^2		*x/a*	*y/b*	*z/c*	*B*, Å^2
Sm(1)	0.4328 (1)	0.1271 (0)	0.2098 (1)	3.20	C(54)	0.4996 (16)	0.1585 (4)	0.5248 (14)	7.51
Sm(2)	0.0436 (1)	0.1608 (0)	−0.0892 (1)	3.72	C(55)	0.5297 (16)	0.1201 (4)	0.5371 (14)	5.38
O(1)	0.2628 (14)	0.1471 (4)	0.2019 (11)	3.92	N(51)	0.5077 (16)	0.1050 (4)	0.4464 (14)	3.81
O(2)	0.1080 (14)	0.1571 (5)	0.0757 (12)	4.42	N(52)	0.4640 (16)	0.1339 (4)	0.3782 (14)	4.34
C(131)	0.1616 (21)	0.1477 (7)	0.1614 (17)	3.40	C(63)	0.2601 (12)	0.0449 (5)	0.2117 (9)	4.65
C(133)	−0.0234 (15)	0.1378 (5)	0.1651 (10)	5.57	C(64)	0.2521 (12)	0.0182 (5)	0.2759 (9)	5.95
C(134)	−0.0847 (15)	0.1274 (5)	0.2154 (10)	6.72	C(65)	0.3452 (12)	0.0229 (5)	0.3647 (9)	5.74
C(135)	−0.0299 (15)	0.1174 (5)	0.3109 (10)	7.94	N(61)	0.4108 (12)	0.0526 (5)	0.3554 (9)	4.43
C(136)	0.0861 (15)	0.1177 (5)	0.3561 (10)	7.36	N(62)	0.3582 (12)	0.0662 (5)	0.2609 (9)	4.02
C(137)	0.1474 (15)	0.1280 (5)	0.3058 (10)	6.20	B(2)	0.5219 (23)	0.0670 (8)	0.4281 (21)	3.38
C(132)	0.0926 (15)	0.1381 (5)	0.2104 (10)	3.81	C(73)	0.0126 (13)	0.0760 (6)	0.0183 (12)	5.72
O(3)	0.3128 (14)	0.0990 (5)	0.0709 (12)	4.20	C(74)	−0.0620 (13)	0.0459 (6)	0.0065 (12)	8.59
O(4)	0.1803 (14)	0.1136 (5)	−0.0626 (12)	4.81	C(75)	−0.1595 (13)	0.0523 (6)	−0.0782 (12)	7.97
C(141)	0.2453 (21)	0.0905 (7)	−0.0095 (18)	3.96	N(71)	−0.1453 (13)	0.0864 (6)	−0.1186 (12)	6.65
C(143)	0.1537 (15)	0.0424 (6)	−0.1325 (13)	7.94	N(72)	−0.0390 (13)	0.1010 (6)	−0.0590 (12)	5.91
C(144)	0.1486 (15)	0.0059 (6)	−0.1652 (13)	12.04	C(83)	−0.2108 (16)	0.2027 (4)	−0.1202 (13)	6.32
C(145)	0.2302 (15)	−0.0199 (6)	−0.1122 (13)	8.45	C(84)	−0.3273 (16)	0.1975 (4)	−0.1722 (13)	6.62
C(146)	0.3168 (15)	−0.0091 (6)	−0.0265 (13)	8.88	C(85)	−0.3454 (16)	0.1608 (4)	−0.2102 (13)	6.79
C(147)	0.3219 (15)	0.0274 (6)	0.0062 (13)	5.83	N(81)	−0.2401 (16)	0.1433 (4)	−0.1818 (13)	6.14
C(142)	0.2403 (15)	0.0532 (6)	−0.0468 (13)	4.00	N(82)	−0.1569 (16)	0.1692 (4)	−0.1262 (13)	4.82
C(13)	0.3289 (12)	0.2170 (5)	0.1286 (13)	5.39	C(93)	−0.0128 (13)	0.1206 (5)	−0.3106 (13)	4.98
C(14)	0.3593 (12)	0.2508 (5)	0.0981 (13)	6.81	C(94)	−0.1006 (13)	0.1031 (5)	−0.3884 (13)	6.92
C(15)	0.4676 (12)	0.2461 (5)	0.1023 (13)	7.30	C(95)	−0.1885 (13)	0.0959 (5)	−0.3615 (13)	8.50
N(11)	0.5041 (12)	0.2094 (5)	0.1354 (13)	4.85	N(91)	−0.1551 (13)	0.1088 (5)	−0.2670 (13)	5.97
N(12)	0.4184 (12)	0.1914 (5)	0.1516 (13)	4.45	N(92)	−0.0465 (13)	0.1241 (5)	−0.2355 (13)	4.90
C(23)	0.5306 (16)	0.1008 (4)	0.0355 (14)	6.85	B(3)	−0.2186 (32)	0.1072 (10)	−0.2029 (25)	5.93
C(24)	0.5941 (16)	0.1148 (4)	−0.0115 (14)	6.21	C(103)	−0.1501 (14)	0.1985 (4)	−0.3213 (13)	5.66
C(25)	0.6335 (16)	0.1508 (4)	0.0256 (14)	6.22	C(104)	−0.1780 (14)	0.2329 (4)	−0.3713 (13)	6.12
N(21)	0.5944 (16)	0.1591 (4)	0.0955 (14)	4.87	C(105)	−0.0945 (14)	0.2593 (4)	−0.3194 (13)	5.97
N(22)	0.5308 (16)	0.1282 (4)	0.1016 (14)	4.43	N(101)	−0.0150 (14)	0.2412 (4)	−0.2374 (13)	5.11
C(33)	0.6935 (16)	0.1582 (5)	0.3959 (11)	5.72	N(102)	−0.0494 (14)	0.2036 (4)	−0.2386 (13)	5.18
C(34)	0.7892 (16)	0.1797 (5)	0.4102 (11)	6.76	C(113)	0.0532 (16)	0.2391 (5)	0.0570 (11)	6.00
C(35)	0.7734 (16)	0.1955 (5)	0.3216 (11)	6.38	C(114)	0.0668 (16)	0.2785 (5)	0.0622 (11)	5.40
N(31)	0.6678 (16)	0.1838 (5)	0.2525 (11)	4.90	C(115)	0.0829 (16)	0.2903 (5)	−0.0183 (11)	5.84
N(32)	0.6184 (16)	0.1608 (5)	0.2984 (11)	5.21	N(111)	0.0793 (16)	0.2582 (5)	−0.0732 (11)	5.43
B(1)	0.6115 (26)	0.1921 (9)	0.1527 (21)	4.18	N(112)	0.0609 (16)	0.2266 (5)	−0.0267 (11)	4.82
C(43)	0.6807 (15)	0.0729 (5)	0.2785 (11)	5.31	C(123)	0.2977 (16)	0.1803 (4)	−0.1097 (14)	6.58
C(44)	0.7537 (15)	0.0506 (5)	0.3551 (11)	6.74	C(124)	0.3508 (16)	0.2089 (4)	−0.1386 (14)	7.41
C(45)	0.7045 (15)	0.0457 (5)	0.4196 (11)	5.10	C(125)	0.2805 (16)	0.2407 (4)	−0.1634 (14)	6.76
N(41)	0.6010 (15)	0.0648 (5)	0.3828 (11)	3.81	N(121)	0.1840 (16)	0.2319 (4)	−0.1498 (14)	5.57
N(42)	0.5864 (15)	0.0817 (5)	0.2955 (11)	4.18	N(122)	0.1946 (16)	0.1945 (4)	−0.1166 (14)	4.86
C(53)	0.4589 (16)	0.1670 (4)	0.4266 (14)	6.70	B(4)	0.0895 (27)	0.2575 (10)	−0.1637 (23)	4.88

[a] For samarium atoms, which were refined anisotropically, *B* values are given as $B_{eq} = {}^8/_3\pi^2\sum_i\sum_j u_{ij}a^*_i a^*_j \mathbf{a}_i\mathbf{a}_j$.

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 **4**.

Results and Discussion

Poly(pyrazolyl)borate complexes of terbium(III), samarium(III), and erbium(III) are prepared by stoichiometric combination of the appropriate metal trichloride and ligand salts (eq 1–3). The

$$MCl_3 + 3K[H_2B(pz)_2] \rightarrow \underset{\textbf{1}}{[H(\mu\text{-}H)B(pz)_2]_3M} + 3KCl \quad (1)$$

$$MCl_3 + 2K[HB(pz)_3] \rightarrow \underset{\textbf{2}}{[HB(pz)_3]_2MCl} + 2KCl \quad (2)$$

$$2MCl_3 + 4K[HB(pz)_3] + 2Na(O_2CCH_3) \rightarrow \underset{\textbf{3}}{\{[HB(pz)_3]_2M(O_2CCH_3)\}_2} + 4KCl + 2NaCl \quad (3)$$

M = Tb (**a**), Sm (**b**), Er (**c**)

new complexes, **1–3**, are freely soluble in THF, halocarbons, and aromatic hydrocarbons. They are somewhat stable in air, but complex **3** decomposes slowly and complex **2** decomposes rapidly in solution. A major decomposition product of **2** is $[HB(pz)_3]_2MCl(Hpz)$. This was verified by the direct preparation of this terbium complex by a reaction similar to that shown in eq 2 with the addition of 1 equiv of Hpz. The preparation and solid-state structure of the yttrium analogue has been reported earlier.[2b]

The UV–visible absorption spectra of complexes **1** and **2** have been studied. The spectra for the complexes of each metal are superimposable, and the spectra are not significantly different from those observed for other Tb^{3+}, Sm^{3+}, or Er^{3+} complexes.[11] The 4f orbitals of the lanthanide elements are effectively shielded from ligand effects by the filled 5s and 5p orbitals. As a result, f–f transitions do not vary appreciably from complex to complex even with substantial changes in the type of ligand.[12]

Due to the paramagnetism of these complexes, meaningful NMR spectra could only be obtained for the samarium complexes. The samarium complex $[H(\mu\text{-}H)B(pz)_2]_3Sm$ (**1b**) displays the same variable-temperature ^{13}C NMR behavior as previously reported for the yttrium complex.[3] At ambient temperature, three resonances are observed for the pyrazolyl ring carbon atoms, implying that all six rings of the three bis(pyrazolyl)borate ligands are equivalent. Lowering the temperature causes the resonances at δ 135.13 and 105.08 to broaden until at −66 °C both begin to split into two resonances. The resonance initially at δ 145.25 does not show any line broadening even at −84 °C. At this temperature the resonances at δ 135.13 and 105.08 are resolved into two equally intense resonances centered at δ 137.08 and 107.70 with separations of 11.2 and 11.4 Hz, respectively. The barrier to equilibrium as calculated from the resonance at δ 135.13 at the coalescence temperature of −47 °C is 11.7 kcal/mol. This energy barrier is essentially equal to the barrier of 11.4 kcal/mol determined for $[H(\mu\text{-}H)B(pz)_2]_3Y$.[3] Given this similarity in the NMR spectra of **1b** and the nearly superimposable IR spectra for all three type **1** complexes with that of $[H(\mu\text{-}H)B(pz)_2]_3Y$,

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(12) Cotton, F. A.; Wilkinson, G. Advanced Inorganic Chemistry, 5th ed.; John Wiley and Sons: New York, 1988; Chapter 20.

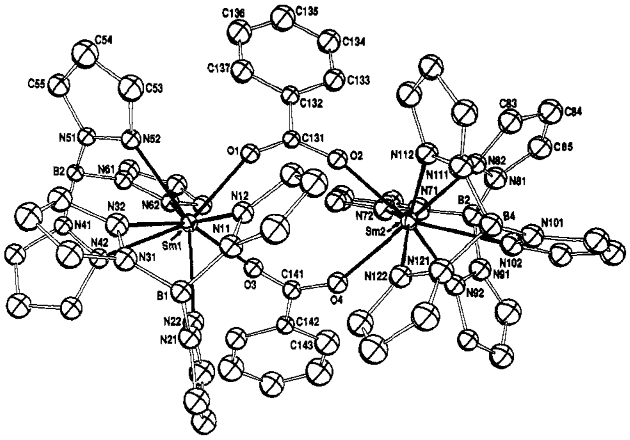

Figure 1. Numbered ORTEP drawing of $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ (**4**). Numbers for carbon atoms in many rings have been omitted for clarity. The numbering schemes for these rings are sequential as shown in the labeled rings.

it is reasonable to assume that these molecules all have the same trigonal-prismatic structure that includes the weak agostic B–H···M three-center interactions.

The samarium chloride complex **2b** shows complex temperature-dependent NMR spectra similar to that of $[HB(pz)_3]_2YCl$[2b]. Repeated attempts to obtain crystallographic quality crystals of any of these complexes have proven unsuccessful. Solution molecular weight studies (1,2-dibromoethane) with $[HB(pz)_3]_2SmCl$ show that it is a monomer. This is an interesting contrast to $[(C_5Me_5)_2YCl]_2$,[13] which is an unsymmetrical monochloride-bridged dimer. This difference in structure is most reasonably ascribed to the larger size[14] of $HB(pz)_3$ (cone angle of 184°) compared to C_5Me_5 (cone angle of 142°).

The acetate complex of samarium, **3b**, also displays complex temperature-dependent NMR spectra analogous to those of its yttrium analogue.[2b] Crystals of these complexes did not prove suitable for a solid-state structure. For this reason the phenylacetate analogue, $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ (**4**), has been prepared and characterized in the solid state by X-ray crystallography. Freezing-point-depression measurements in benzene show that $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ and $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CMe)\}_2$ are dimeric in solution.

Molecular Structure of $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$. An ORTEP drawing of **4** is shown in Figure 1; selected bond lengths and angles are shown in Table III. The molecule is a dimer with the metals bridged by the acetate ligands. The samarium atoms, separated by 5.42 Å, are eight-coordinate. Analysis of the geometry about samarium by interactive computer graphics indicates that none of the regular shapes such as a square antiprism, bicapped trigonal prism, or dodecahedron satisfactorily describe the geometry about either samarium atom. The closest analogue to the structure of **4** is $[(\eta^5\text{-}C_5H_5)_2Yb(O_2CC_6F_5)]_2$ (**5**), a molecule that is also dimeric.[15] In both structures, the bridging carboxylate ligands are not symmetrical. Thus, the Sm–O–C angles in **4** within each bridging ligand differ by 13 and 19°. Another similarity is that the tris(pyrazolyl)borate ligands on each side of the dimer are staggered (taking the boron atom as the center of the ligand), similar to the cyclopentadienyl rings in **5**.

Table III. Selected Bond Distances (Å) and Bond Angles (deg) for $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$ with Estimated Standard Deviations in Parentheses

	Bond Distances		
Sm(1)–O(1)	2.32 (1)	Sm(2)–O(2)	2.34 (2)
Sm(1)–O(3)	2.30 (2)	Sm(2)–O(4)	2.38 (2)
Sm(1)–N(12)	2.45 (2)	Sm(2)–N(72)	2.54 (2)
Sm(1)–N(22)	2.52 (2)	Sm(2)–N(82)	2.49 (1)
Sm(1)–N(32)	2.56 (2)	Sm(2)–N(92)	2.45 (2)
Sm(1)–N(42)	2.50 (2)	Sm(2)–N(102)	2.62 (2)
Sm(1)–N(52)	2.48 (2)	Sm(2)–N(112)	2.52 (2)
Sm(1)–N(62)	2.65 (2)	Sm(2)–N(122)	2.52 (1)
	Bond Angles		
O(1)–Sm(1)–O(3)	79.3 (5)	O(2)–Sm(2)–N(92)	142.6 (5)
O(1)–Sm(1)–N(12)	76.6 (5)	O(2)–Sm(2)–N(102)	145.4 (4)
O(1)–Sm(1)–N(22)	136.3 (5)	O(2)–Sm(2)–N(112)	72.5 (4)
O(1)–Sm(1)–N(32)	125.1 (5)	O(2)–Sm(2)–N(122)	105.3 (4)
O(1)–Sm(1)–N(42)	141.5 (5)	O(4)–Sm(2)–N(72)	74.1 (5)
O(1)–Sm(1)–N(52)	75.5 (5)	O(4)–Sm(2)–N(82)	141.8 (4)
O(1)–Sm(1)–N(62)	78.0 (4)	O(4)–Sm(2)–N(92)	79.5 (4)
O(3)–Sm(1)–N(12)	98.6 (4)	O(4)–Sm(2)–N(102)	127.4 (4)
O(3)–Sm(1)–N(22)	74.2 (4)	O(4)–Sm(2)–N(112)	131.1 (4)
O(3)–Sm(1)–N(32)	146.8 (4)	O(4)–Sm(2)–N(122)	76.6 (4)
O(3)–Sm(1)–N(42)	107.4 (4)	N(72)–Sm(2)–N(82)	69.0 (4)
O(3)–Sm(1)–N(52)	140.5 (5)	N(72)–Sm(2)–N(92)	68.9 (4)
O(3)–Sm(1)–N(62)	74.0 (4)	N(72)–Sm(2)–N(102)	125.5 (4)
N(12)–Sm(1)–N(22)	73.8 (4)	N(72)–Sm(2)–N(112)	133.9 (4)
N(12)–Sm(1)–N(32)	70.3 (4)	N(72)–Sm(2)–N(122)	150.5 (4)
N(12)–Sm(1)–N(42)	136.5 (4)	N(82)–Sm(2)–N(92)	78.3 (5)
N(12)–Sm(1)–N(52)	104.4 (4)	N(82)–Sm(2)–N(102)	70.6 (4)
N(12)–Sm(1)–N(62)	154.5 (3)	N(82)–Sm(2)–N(112)	83.7 (5)
N(22)–Sm(1)–N(32)	72.6 (4)	N(82)–Sm(2)–N(122)	138.5 (5)
N(22)–Sm(1)–N(42)	80.3 (4)	N(92)–Sm(2)–N(102)	68.3 (4)
N(22)–Sm(1)–N(52)	142.9 (5)	N(92)–Sm(2)–N(112)	141.8 (4)
N(22)–Sm(1)–N(62)	125.1 (4)	N(92)–Sm(2)–N(122)	102.1 (4)
N(32)–Sm(1)–N(42)	68.9 (5)	N(102)–Sm(2)–N(112)	74.1 (4)
N(32)–Sm(1)–N(52)	72.1 (5)	N(102)–Sm(2)–N(122)	71.3 (4)
N(32)–Sm(1)–N(62)	128.5 (4)	N(112)–Sm(2)–N(122)	70.7 (5)
N(42)–Sm(1)–N(52)	76.6 (5)	Sm(1)–O(1)–C(131)	150 (1)
N(42)–Sm(1)–N(62)	68.2 (4)	Sm(2)–O(2)–C(131)	163 (2)
N(52)–Sm(1)–N(62)	71.4 (4)	O(1)–C(131)–O(2)	124 (2)
O(2)–Sm(2)–O(4)	82.6 (5)	Sm(1)–O(3)–C(141)	168 (2)
O(2)–Sm(2)–N(72)	74.6 (5)	Sm(2)–O(4)–C(141)	149 (2)
O(2)–Sm(2)–N(82)	96.8 (4)	O(3)–C(141)–O(4)	121 (2)

Conclusion

A series of stable complexes with poly(pyrazolyl)borate ligands coordinated to the metals yttrium,[2,3] samarium, terbium, and erbium have been prepared and characterized: $[H(\mu\text{-}H)B(pz)_2]_3M$, $[HB(pz)_3]_2MCl$, $[HB(pz)_3]_2MCl(Hpz)$ (M = Y, Tb only), $\{[HB(pz)_3]_2M(\mu\text{-}O_2CCH_3)\}_2$ and $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$. For the $[H(\mu\text{-}H)B(pz)_2]_3M$ complexes, the M = Y complex has been characterized crystallographically[3] and shown to have a trigonal-prismatic coordination of the nitrogen donor atoms with each rectangular face capped by an agostic B–H···Y interaction. The $[HB(pz)_3]_2MCl$ complexes have not been characterized crystallographically, but have been shown to be monomers in solution. $[HB(pz)_3]YCl(Hpz)$ has been characterized in the solid state and shown to have distorted-square-antiprismatic geometry.[2b] Finally, $\{[HB(pz)_3]_2M(\mu\text{-}O_2CCH_3)\}_2$ complexes have been shown to be dimeric in solution and are presumed to be structurally similar to $\{[HB(pz)_3]_2Sm(\mu\text{-}O_2CPh)\}_2$, shown to have an acetate-bridged dimeric structure in the solid state and to also be dimeric in solution.

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Supplementary Material Available: Table SI, listing crystallographic data, and Tables SII–SV, listing complete bond distances, bond angles, thermal parameters, and positional parameters of H atoms (12 pages); tables of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

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