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Syntheses and Solid State Structures of Tris(pyrazolyl)methane Complexes of Sodium, Potassium, Calcium, and Strontium: Comparison of Structures with Analogous Complexes of Lead(II)

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The reaction of NaI with 2 equiv of $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ (pz = pyrazolyl ring) leads to the formation of $\{[HC(pz)_3]_2Na\}(I)$ (**1**) and $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I)$ (**2**), respectively. Both compounds have trigonally distorted octahedral arrangements about the sodium. A similar reaction of KPF_6 with $HC(3,5\text{-}Me_2pz)_3$ results in the formation of $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$ (**3**), a complex also shown crystallographically to have a trigonally distorted octahedral arrangement about the potassium, which is an unusually low coordination number for this large metal ion. The complex $\{[HC(pz)_3]_2Sr\}(BF_4)_2$ (**4**) forms in the reaction of $Sr(acac)_2$ (acac = acetylacetonate) with $HBF_4\cdot Et_2O$ followed by 2 equiv of $HC(pz)_3$. The structure is highly distorted, showing κ^3 bonding of both tris(pyrazolyl)methane ligands and, in addition, interactions with the metal from three fluorine atoms from the BF_4^- counterions. The symmetrical structure of **1** and the nine-coordinate structure of **4** are both very different from the distorted, six-coordinate structure $\{[HC(pz)_3]_2Pb\}(BF_4)_2$, indicating that for this compound the lone pair on lead(II) is influencing the structure. The reaction of $M(acac)_2$ (M = Sr, Ca) with $H\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ followed by 2 equiv of $HC(pz)_3$ produces $\{[HC(pz)_3]_2(Hacac)Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**5**) (when the reaction is done in CH_2Cl_2), $\{[HC(pz)_3]_2(Me_2CO)_2Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**6**) (when the reaction is done in acetone), and $\{[HC(pz)_3]_2(Hacac)Ca\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**7**), respectively. The structures of all three complexes show a distorted eight-coordinate arrangement of the ligands about the metal. Crystal data: **1** is orthorhombic, *Pnma*, $a = 16.931(1)$, $b = 22.368(3)$, $c = 7.937(2)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, Z = 4; **2** is trigonal, $R\bar{3}$, $a = 10.7483(8)$, $b = 10.7483(8)$, $c = 35.395(4)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120°$, Z = 3; **3** is monoclinic, $P2_1/c$, $a = 9.144(4)$, $b = 13.377(6)$, $c = 15.988(7)$ Å, $\alpha = 90$, $\beta = 92.291(10)$, $\gamma = 90°$, Z = 2; **4** is hexagonal, $P6_5$, $a = 9.42530(10)$, $b = 9.42530(10)$, $c = 55.3713(5)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120°$, Z = 6; **5** is monoclinic, *P2/n*, $a = 14.1601(3)$, $b = 13.1756(3)$, $c = 27.1826(6)$ Å, $\alpha = 90$, $\beta = 90.1744(7)$, $\gamma = 90°$, Z = 2; **6** is monoclinic, *P2/n*, $a = 14.2709(7)$, $b = 13.2646(7)$, $c = 27.4189(13)$ Å, $\alpha = 90$, $\beta = 90.3850(10)$, $\gamma = 90°$, Z = 2; **7** is monoclinic, *P2/n*, $a = 14.2388(2)$, $b = 13.1919(2)$, $c = 26.7879(3)$ Å, $\alpha = 90$, $\beta = 90.0650(8)$, $\gamma = 90°$, Z = 2.

Introduction

We have recently prepared compounds of lead(II) and cadmium(II) using tris(pyrazolyl)borate and tris(pyrazolyl)methane ligands (Chart 1).[1] The steric and electronic properties of these ligand systems can be varied systematically by changing the substituents at the 3 and/or the 5 positions on the pyrazolyl rings. Using these ligand systems, we wanted to determine the structural influence of the lone pair on lead(II) when compared to similar complexes with cadmium(II), which has no lone pair. Our studies showed the impact of the lone pair is not consistent. The complexes $[HB(3,5\text{-}Me_2pz)_3]_2Pb$[2] and $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$[3] (pz

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[1] Reger, D. L. *Comments Inorg. Chem.* **1999**, *21*, 1.

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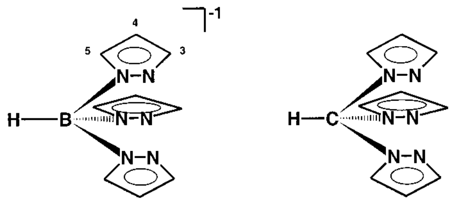
Chart 1



Tris(1-pyrazolyl)borate Tris(1-pyrazolyl)methane

= pyrazolyl ring) have octahedral structures and are isostructural to $[HB(3,5\text{-}Me_2pz)_3]_2Cd$ and $\{[HC(3,5\text{-}Me_2pz)_3]_2Cd\}(BF_4)_2$,[4] which is a surprising result given that lead(II) has the two additional valence electrons. In the two lead structures, the lone pair is clearly stereochemically inactive. In contrast, $[HB(pz)_3]_2Pb$[2] and $\{[HC(pz)_3]_2Pb\}(BF_4)_2$[3] have similar but highly distorted six-coordinate structures. In both structures, there is a gap where the lone pair of electrons is thought to be located, and there is also a pattern of long Pb−N bond distances adjacent to the proposed site of the lone pair and short distances opposite this site, the two main characteristics of lead(II) structures that contain a stereochemically active lone pair.[1,5] As expected, the cadmium(II) analogue, $[HB(pz)_3]_2Cd$, has a normal octahedral geometry about the metal.[6]

Analogous to our structural comparisons of Group 12 and 14 tris(pyrazolyl)borate and tris(pyrazolyl)methane complexes, Hanusa carried out a comparative study with Group 2 and 14 metallocene structures and found that the structures of a large number of complexes are similar. He has argued[7] that “the confinement of the metal valence electrons of the divalent Group 14 metals to non-directional orbitals of high *s*-character” limits their influence on the structures of metallocene complexes. These results encouraged us to prepare the pseudometallocene $\{[\text{tris(pyrazolyl)methane}]_2M\}^{n+}$ complexes of Group 1 and 2 metal ions that have similar ionic radii to Pb^{2+} (1.19 Å): Na^+ (1.02 Å), K^+ (1.38 Å), Ca^{2+} (1.00 Å), and Sr^{2+} (1.18 Å).[8] A number of papers on the chemistry of the analogous $[\text{tris(pyrazolyl)borate}]_2M$ complexes of Group 2 have been reported,[9] but until the recent report of $\{[HB(pz)_3]_2Na\}^-$, no tris(pyrazolyl)borate complexes of this formula had been reported for any metal in the +1 oxidation state.[10] We have shown previously that complexes of the formula $\{[\text{tris(pyrazolyl)methane}]_2M\}^+$ can be prepared for M = Ag^+,[11] Tl^+,[12] and Li^+,[13] making tris(pyrazolyl)methane ligands the logical choice for the new study. Reported here are the syntheses and solid-state structures of a series of tris(pyrazolyl)methane complexes of Na^+, K^+, Ca^{2+}, and Sr^{2+}. In addition to our interest in comparing structures to analogous lead(II) complexes, we desired to explore the types of complexes that could be prepared from metals in these two Groups with tris(pyrazolyl)methane ligands.

Experimental Section

All operations were carried out under a nitrogen atmosphere using either standard Schlenk techniques or a Vacuum Atmospheres HE−493 drybox. All solvents were dried, degassed, and distilled prior to use. ^1H NMR chemical shifts are reported in ppm versus TMS. $HC(pz)_3$, $HC(3,5\text{-}Me_2pz)_3$,[14] and $Na\{[3,5\text{-}(CF_3)_2C_6H_3]_4B\}$[15] were prepared according to our recently reported procedures. $[H(Et_2O)_2]\{[3,5\text{-}(CF_3)_2C_6H_3]_4B\}$ was prepared by previously reported methods.[16] Sodium iodide, potassium hexafluorophosphate, strontium(acetylacetonate), calcium(acetylacetonate)·hydrate, and tetrafluoroboric acid were purchased from Aldrich Chemical Co. and used as received, with the exception of the calcium(acetylacetonate)·hydrate, for which the water was removed via benzene azeotrope prior to use. Elemental analyses were performed by National Chemical Consulting, Inc. and Robertson Microlit Laboratories, Inc.

$\{[HC(pz)_3]_2Na\}(I)$ (1). A THF (10 mL) solution of NaI (0.20 g, 1.33 mmol) was treated dropwise by cannula transfer with a THF (10 mL) solution of $HC(pz)_3$ (0.57 g, 2.67 mmol). A white solid precipitated immediately from the reaction mixture. The reaction mixture was allowed to stir for several hours before cannula filtration. The remaining white solid was dried under vacuum (0.46 g, 60%); mp, 224−232 °C. Crystals suitable for an X-ray crystallographic study were grown by layering a saturated acetone solution with hexanes and allowing the two layers to slowly combine. ^1H NMR (acetone-d_6): δ 8.94 (2, s, $HC(pz)_3$), 7.95, 7.62 (6, 6; d, d; J_{HH} = 2.5 Hz, 1.5 Hz; 3,5-H pz), 6.40 (6, dd, J_{HH} = 2.4 Hz, 2.0 Hz; 4-H pz). Anal. Calcd for $C_{20}H_{20}N_{12}NaI$: C, 41.54; H, 3.48. Found C, 41.40; H, 3.24.

$\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I)$ (2). This compound was prepared (0.62 g, 83%) as described above for **1** using NaI (0.15 g, 1.00 mmol) and $HC(3,5\text{-}Me_2pz)_3$ (0.60 g, 2.01 mmol); dec, 325 °C. Crystals suitable for X-ray analysis were grown by layering a saturated CH_2Cl_2 solution with benzene and allowing the two layers to slowly combine. ^1H NMR (CD_2Cl_2): δ 7.90 (2, s, $HC(Me_2pz)_3$), 5.95 (6, s, 4-H), 1.90, 1.57 (18, 18; s, s; 3,5-Me_2). Anal. Calcd for $C_{32}H_{44}N_{12}NaI$: C, 51.48; H, 5.90. Found C, 51.01; H, 5.93.

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{[HC(3,5-Me$_2$pz)$_3$]$_2$K}(PF$_6$) (3): KPF$_6$ (0.12 g, 0.65 mmol) was suspended in THF (10 mL). This mixture was treated with a THF (20 mL) solution of HC(3,5-Me$_2$pz)$_3$ (0.40 g, 1.34 mmol). Upon addition of the ligand, the solution became homogeneous. The reaction mixture was allowed to stir overnight, during which time a white solid precipitated. The reaction mixture was filtered, and the white solid was dried under vacuum (0.19 g**,** 37%); dec, 265 °C. Crystals suitable for X-ray structural analysis were grown by slow diffusion of hexanes into a saturated acetone solution. ^{1}H NMR (acetone-d_6): δ 8.22 (2, s, *H*C(Me$_2$pz)$_3$), 5.93 (6, s, 4-*H*), 2.11, 2.04 (18, 18; s, s; 3,5-Me$_2$). Anal. Calcd for $C_{32}H_{44}N_{12}KPF_6$: C, 49.22; H, 5.67. Found C, 48.86; H, 5.88.

{[HC(pz)$_3$]$_2$Sr}(BF$_4$)$_2$ (4): Sr(acac)$_2$ (0.29 g, 1.0 mmol) was suspended in THF (10 mL). This mixture was treated with 85% HBF$_4$•Et$_2$O (0.31 mL, 2.0 mmol) and allowed to stir for 30 min. The addition of a THF (10 mL) solution of HC(pz)$_3$ (0.48 g, 2.0 mmol) by cannula transfer resulted in the precipitation of a white solid. The reaction mixture was allowed to stir several hours before cannula filtration. The white solid was washed with hexanes (3 × 10 mL) and dried under vacuum (0.41 g, 78%), mp, 219−223 °C. Crystals suitable for X-ray structural analysis were grown by slow diffusion of hexanes into a saturated acetone solution. ^{1}H NMR (acetone-d_6): δ 8.83 (2, s, *H*C(pz)$_3$), 7.93, 7.65 (6, 6; d, d; J_{HH} = 2.5 Hz, 1.5 Hz; 3,5-*H* pz), 6.41 (6, dd, J_{HH} = 1.7 Hz, 0.8 Hz; 4-*H* pz). Anal. Calcd for $C_{20}H_{20}N_{12}SrB_2F_8$: C, 34.83; H, 2.92. Found C, 34.37; H, 3.16.

{[HC(pz)$_3$]$_2$(CH$_3$COCH$_2$COCH$_3$)Sr}{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}$_2$ (5): Sr(acac)$_2$ (0.14 g, 0.49 mmol) was suspended in THF (10 mL). This mixture was treated with a THF solution (10 mL) of [H(Et$_2$O)$_2$]{[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B} (1.01 g, 0.99 mmol), and allowed to stir for 30 min, followed by the addition of a THF solution (10 mL) of HC(pz)$_3$ (0.21 g, 0.98 mmol). The homogeneous mixture was allowed to stir for 48 h before removing the solvent under vacuum. The pale yellow solid was washed with hexanes (3 × 10 mL) and collected after drying (0.93 g, 82%); mp, 154−158 °C. Crystals suitable for X-ray structural analysis were grown by slow diffusion of hexanes into a saturated CH$_2$Cl$_2$ solution. ^{1}H NMR (acetone-d_6): 8.9 (2, s, *H*C(pz)$_3$), 7.9, 7.7 (6, 6; d, d; J_{HH} = 2.4 Hz, 1.4 Hz; 3,5-*H* pz), 7.8 (8, s, *o-H* (B[C$_6$H$_3$]$_4$)$_2$), 7.7 (4, s, *p-H* (B[C$_6$H$_3$]$_4$)$_2$), 6.4 (6, dd, J_{HH} = 1.8, 1.8; 4-*H* pz), 5.6, 3.7, 2.0 (1, 1, 6; s, s, s; C*H*$_3$COC*H*$_2$COC*H*$_3$). Anal. Calcd for $C_{89}H_{52}N_{12}F_{48}B_2O_2Sr$: C, 45.63; H, 2.24. Found C, 45.91; H, 2.35.

{[HC(pz)$_3$]$_2$(Me$_2$CO)$_2$Sr}{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}$_2$ (6): Sr(acac)$_2$ (0.11 g, 0.38 mmol) was suspended in acetone (10 mL). This mixture was treated with an acetone solution (10 mL) of [H(Et$_2$O)$_2$]{[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B} (0.77 g, 0.76 mmol), and allowed to stir for 30 min, followed by the addition of an acetone solution (10 mL) of HC(pz)$_3$ (0.16 g, 0.75 mmol). The homogeneous mixture was allowed to stir overnight before removing the solvent under vacuum to yield a yellow oil. Toluene (10 mL) was added to the oil, allowed to stir for ca 15 min, and then removed under vacuum, leaving a pale yellow solid that was dried under vacuum (0.66 g, 74%); 148−151 °C. Crystals suitable for X-ray structural analysis were grown by slow diffusion of hexanes into a saturated acetone solution. ^{1}H NMR (CD$_2$Cl$_2$): 8.3 (2, s, *H*C(pz)$_3$), 7.9, 7.4 (6, 6; d, d; J_{HH} = 2.4 Hz, 1.6 Hz; 3,5-*H* pz), 7.7 (8, s, *o-H* (B[C$_6$H$_3$]$_4$)$_2$), 7.6 (4, s, *p-H* (B[C$_6$H$_3$]$_4$)$_2$), 6.4 (6, dd, J_{HH} = 1.8, 1.8; 4-*H* pz), 2.1 (6, s, C*H*$_3$-COC*H*$_3$). ES MS: *m*/*z* Calcd for {Sr[HC(3,5-Me$_2$pz)$_3$]$_2$}(B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$)$^+$: 1379.1682. Found: 1379.1653.

{[HC(pz)$_3$]$_2$(CH$_3$COCH$_2$COCH$_3$)Ca}(B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$)$_2$ (7). This compound was prepared (0.84 g, 88%) as described above for **5** using Ca(acac)$_2$ (0.10 g, 0.42 mmol), [H(Et$_2$O)$_2$]{[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$B} (0.85 g, 0.84 mmol), and HC(pz)$_3$ (0.18 g, 0.84 mmol); mp, 173−177 °C. Crystals suitable for X-ray structural analysis were grown by slow diffusion of hexanes into a saturated CH$_2$Cl$_2$ solution. ^{1}H NMR (acetone-d_6): 8.8 (2, s, *H*C(pz)$_3$), 7.9, 7.6 (6, 6; d, d; J_{HH} = 2 Hz, 2 Hz; 3,5-*H* pz), 7.8 (8, s, *o-H* (B[C$_6$H$_3$]$_4$)$_2$), 7.7 (4, s, *p-H* (B[C$_6$H$_3$]$_4$)$_2$), 6.4 (6, dd, J_{HH} = 1.8, 1.8; 4-*H* pz), 5.6, 3.8, 2.9 (1, 1, 6; s, s, s; C*H*$_3$COC*H*$_2$COC*H*$_3$). Anal. Calcd for $C_{89}H_{52}N_{12}F_{48}B_2O_2Ca$: C, 46.56; H, 2.28. Found C, 46.95; H, 2.36.

Crystallographic Structural Determination. Crystal, data collection, and refinement parameters are given in Table 1. Suitable crystals for data collection were selected and mounted with epoxy on the tip of a fine glass fiber. Data for **1** were collected using a Siemens P4 diffractometer. Data for **2**, **3**, and **6** were collected on a Bruker SMART APEX CCD-based diffractometer system, and data for **4**, **5**, and **7** on a Siemens P4 diffractometer equipped with a SMART/CCD detector.

The systematic absences of **1** are consistent with the orthorhombic space group options *Pnma* and *Pna2*$_1$. *E*-statistics suggested the centrosymmetric options for **1**, which yielded chemically reasonable and computationally stable results of refinement. Compound **2**, [(HC(Me$_2$pz)$_3$)$_2$Na]I•2C$_6$H$_6$, crystallizes in the trigonal (rhombohedral) crystal system. Systematic absences in the reflection data ruled out a c-glide operation, leaving the space groups *R*3, *R*-3, *R*3*m* and *R*-3*m*. The presence of an inversion center and the lack of mirror symmetry eventually confirmed the centrosymmetric option *R*-3. For **3**, systematic absences in the data were consistent with the monoclinic space group *P*2$_1$/*c*. The systematic absences of **4** are consistent with the reported space group. No evidence of symmetry higher than monoclinic was observed in the diffraction data of the isomorphous structures **5** and **7**. The systematic absences are consistent with the space groups *P*2*/*n and *Pn*. *E*-statistics suggested the centrosymmetric option, which yielded chemically reasonable and computationally stable results of refinement. The structures were solved using direct methods, completed by subsequent difference Fourier synthesis, and refined by full-matrix least-squares procedures. The cation of **1** lies on a crystallographic inversion center and cocrystallized with one molecule of acetone, which lies on a mirror plane. The strontium atom of **4** is involved in a strong η^1 interaction (2.450(4) Å) with one BF$_4$ anion and a weak η^2 interaction (2.662(3), 2.795(4) Å) with the other BF$_4$ anion. The absolute structure of **4** could not be reliably determined. The cations of **5** and **7** lie on two-fold rotational axes. All attempts to sufficiently model the positional disorder of the acetylacetone groups failed, which gives rise to the large thermal parameters associated with these atoms. For **5**, these atoms (O1, C31, C32, and C33) were refined isotropically. In both cases, several CF$_3$ groups of the BAr$_f$ counterion are positionally disordered and modeled as such. For **5**, the minor components of the modeled CF$_3$ groups were refined isotropically. For {[HC(pz)$_3$]$_2$(Me$_2$CO)$_2$Sr}{B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$}$_2$ (**6**), the systematic absences in the reflection data were consistent with the space groups groups *P*2*/*n or *Pn*. Therefore, *P*2*/n* was chosen, eventually solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2, using SHELXTL software package. Three of the −CF$_3$ groups of the anion were rotationally disordered over two positions. All non-hydrogen atoms, with the exception of those stated above, were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.03 or 5.10) program library (G. Sheldrick, Siemens XRD, Madison, WI).

Table 1. Crystallographic Data for $\{[HC(pz)_3]_2Na\}(I)\cdot CH_3COCH_3$ (**1**), $\{[HC(3,5Me_2pz)_3]_2Na\}(I)\cdot 2C_6H_6$ (**2**), $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$ (**3**), $\{[HC(pz)_3]_2Sr\}(BF_4)_2$ (**4**), $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**5**), $\{[HC(pz)_3]_2(Me_2CO)_2Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**6**), and $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Ca\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**7**)

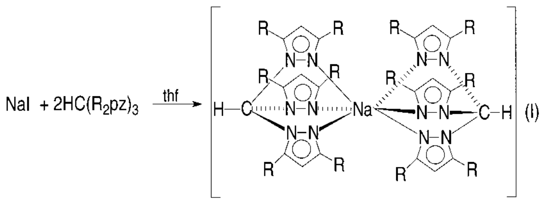
	1	**2**	**3**	**4**
empirical formula	$C_{23}H_{26}N_{12}NaIO$	$C_{44}H_{56}N_{12}NaI$	$C_{32}H_{44}N_{12}KPF_6$	$C_{20}H_{20}N_{12}SrB_2F_8$
fw, g mol^{-1}	636.45	902.90	780.86	689.72
temp, K	253(2)	293(2)	293(2)	223(2)
cryst syst	orthorhombic	trigonal	monoclinic	hexagonal
space group	*Pnma*	$R\bar{3}$	$P2_1/c$	$P6_5$
a, Å	16.931(1)	10.7483(8)	9.144(4)	9.42530(10)
b, Å	22.368(3)	10.7483(8)	13.377(6)	9.42530(10)
c, Å	7.937(2)	35.395(4)	15.988(7)	55.3713(5)
α, deg	90	90	90	90
β, deg	90	90	92.291(10)	90
γ, deg	90	120	90	120
vol, $Å^3$	3005.9(7)	3541.2(5)	1954.2(14)	4259.96(7)
Z	4	3	2	6
density, Mg/m^3 (calcd)	1.406	1.270	1.327	1.613
abs coeff, mm^{-1}	1.117	0.730	0.246	1.986
F(000)	1280	1404	816	2064
cryst size, mm^3	0.40 × 0.20 × 0.10	0.46 × 0.40 × 0.22	0.12 × 0.08 × 0.03	0.40 × 0.30 × 0.20
final *R* indices[a] $[I > 2\sigma(I)]$	R1 = 0.0357 wR2 = 0.0747	R1 = 0.0259 wR2 = 0.0683	R1 = 0.0497 wR2 = 0.1043	R1 = 0.0505 wR2 = 0.1163

	5	**6**	**7**
empirical formula	$C_{89}H_{52}N_{12}SrB_2F_{48}O_2$	$C_{90}H_{56}N_{12}SrB_2F_{48}O_2$	$C_{89}H_{52}N_{12}CaB_2F_{48}O_2$
fw, g mol^{-1}	2342.67	2358.71	2295.13
temp, K	173(2)	293(2)	203(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*P*2/*n*	*P*2/*n*	*P*2/*n*
a, Å	14.1601(3)	14.2709(7)	14.2388(2)
b, Å	13.1756(3)	13.2646(7)	13.1919(2)
c, Å	27.1826(6)	27.4189(13)	26.7879(3)
α, deg	90	90	90
β, deg	90.1744(7)	90.3850(10)	90.0650(8)
γ, deg	90	90	90
vol, $Å^3$	5071.38(19)	2190.2(4)	5031.75(16)
Z	2	2	2
density, Mg/m^3 (calcd)	1.534	1.509	1.515
abs coeff, mm^{-1}	0.672	0.657	0.204
F(000)	2332	2352	2296
cryst size, mm^3	0.35 × 0.20 x 0.010	0.44 × 0.24 × 0.18	0.35 × 0.30 × 0.30
final *R* indices[a] $[I > 2\sigma(I)]$	R1 = 0.0912 wR2 = 0.2427	R1 = 0.0762 WR2 = 0.2159	R1 = 0.0660 wR2 = 0.1992

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

Results and Discussion

Syntheses of Complexes. The reaction of NaI with 2 equiv of $HC(pz)_3$ or $HC(3,5\text{-}Me_2pz)_3$ (pz = pyrazolyl ring) in THF leads to the formation of $\{[HC(pz)_3]_2Na\}(I)$ (**1**) and $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I)$ (**2**), respectively.

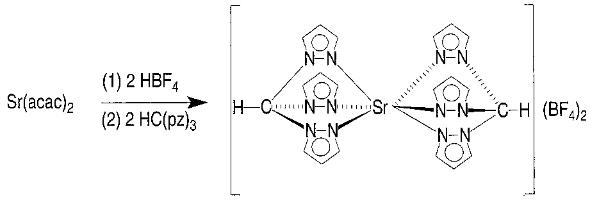


R=H, **1**
R=CH_3, **2**

These complexes are insoluble in THF and precipitate from the reaction. Complex **1** is soluble in acetone, and complex **2** is soluble in methylene chloride. Both of these complexes are air stable.

The reaction of KPF_6 with $HC(3,5\text{-}Me_2pz)_3$ in THF results in the precipitation of $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$ (**3**). The complex is air stable; however, we found that in solutions of acetone and other basic solvents, the ligand is displaced by the solvent. The analogous potassium complex with the unsubstituted $HC(pz)_3$ ligand was not obtained in similar reactions.

The complex $\{[HC(pz)_3]_2Sr\}(BF_4)_2$ (**4**) is prepared by protonation of a THF suspension of $Sr(acac)_2$ (acac = acetylacetonate) with $HBF_4\cdot Et_2O$, a reaction that forms Hacac and generates a soluble Sr^{2+} ion that reacts with added $HC(pz)_3$ to precipitate **4** in high yield. This method of preparing reactive metal ions in solution was developed earlier by us for the analogous cadmium and lead chemistry.[3]



4

Complex **4** is air and moisture sensitive. A similar reaction using the $HC(3,5\text{-}Me_2pz)_3$ ligand did not yield the analogous product, but resulted in the formation of an oil that could not be characterized.

In attempts to prepare a compound of $\{[HC(pz)_3]_2Sr\}^{2+}$ in which the cation does not interact with the counterion (vide infra), we chose to use the noncoordinating $\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}^-$ (BAr_f) anion. Reaction of $Sr(acac)_2$ with $H\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ followed by 2 equiv of $HC(pz)_3$ in THF produced $\{[HC(pz)_3]_2(Hacac)Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**5**), the Hacac adduct of the desired product, $\{[HC(pz)_3]_2Sr\}\text{-}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$. This complex is much more soluble than **4** due to the presence of the (BAr_f) counterion and is soluble in most organic solvents. After removing the THF from the reaction mixture, the product is initially an oil which solidifies after prolonged drying under vacuum. This complex is extremely air and moisture sensitive.

$$M(acac)_2 \xrightarrow[(2)\ 2\ HC(pz)_3]{(1)\ 2\ H[B(3,5\text{-}(CF_3)_2C_6H_3)_4]} [M(HC(pz)_3)_2(Hacac)]\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2 + Hacac$$
$$M = Sr,\ Ca\ (\mathbf{5},\ \mathbf{7})$$

Carrying out this same reaction in acetone yields $\{[HC(pz)_3]_2\text{-}(Me_2CO)_2Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**6**). This complex initially forms as an oil, but washing the oil in a small amount of toluene leads to the formation of a pale yellow solid once the toluene is removed under vacuum. The resulting solid is air and moisture sensitive. An analogous reaction of $Ca(acac)_2$ with $H\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$ followed by 2 equiv of $HC(pz)_3$ in THF yielded $\{[HC(pz)_3]_2(Hacac)Ca\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**7**). This complex is extremely air and moisture sensitive and is soluble in most organic solvents. As with complex **5**, the product forms initially as an oil and then solidifies after extended drying under vacuum. Similar results were obtained when the reactions to form **5** and **7** were carried out in CH_2Cl_2.

We have made several additional attempts to synthesize a six-coordinate tris(pyarazolyl)methane SrN_6 complex, and in each case, strontium has shown its preference for higher coordination. One particularly promising attempt that proved unsuccessful was an exchange reaction of SrI_2 and $\{[HC(pz)_3]_2Pb\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ in CH_2Cl_2 in which starting material was recovered. A similar reaction in acetone yields **6**. These reactions again show the desire of strontium to be at least eight coordinate.

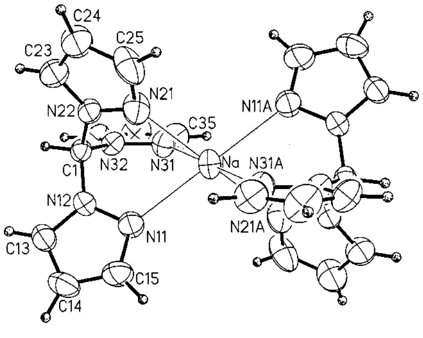


Figure 1. ORTEP diagram of the cation in $\{[HC(pz)_3]_2Na\}(I)$, **1**, at 30% probability.

Table 2. Selected Bond Distances and Angles for $\{[HC(pz)_3]_2Na\}(I)\cdot CH_3COCH_3$ (**1**)

Bond Distances (Å)	
Na−N(11)	2.501(5)
Na−N(21)	2.433(5)
Na−N(31)	2.401(4)
C(1)−N(12)	1.453(6)
C(1)−N(22)	1.439(6)
C(1)−N(32)	1.431(6)
Bond Angles (deg)	
N(11)−Na−N(21)	74.7(2)
N(11)−Na−N(31)	76.1(2)
N(21)−Na−N(31)	77.6(2)
N(11)−Na−N(21A)	105.3(2)
N(11)−Na−N(31A)	103.9(2)
N(21)−Na−N(31A)	102.4(2)
N(12)−C(1)−N(22)	110.9(4)
N(12)−C(1)−N(32)	112.5(4)
N(22)−C(1)−N(32)	113.1(4)

Solid State Structures. $\{[HC(pz)_3]_2Na\}(I)\cdot CH_3COCH_3$. Figure 1 shows the ORTEP diagram of the cation in $\{[HC(pz)_3]_2Na\}(I)$ (**1**), and selected bond distances and angles are shown in Table 2. The overall structure about the sodium is trigonally distorted octahedral. The average Na−N bond distance in **1** is 2.445 Å, with a range of values from 2.401(4) to 2.501(5) Å. The intraligand bond angles are restricted by the chelate rings of the ligand to an average of 76.1°. The interligand bond angles are all similar and average 103.9°. One molecule of the crystallization solvent is present in the unit cell.

The bond distances and angles in **1** are similar to that of the anion $\{[HB(pz)_3]_2Na\}^-$, reported by Reglinski et al., despite the difference in overall charge. In $\{[HB(pz)_3]_2Na\}^-$, the Na−N bond distances range from 2.431(8) to 2.553(8) Å, just slightly longer than the 2.401(4) to 2.501(5) Å range for **1**. The intraligand bond angles are restricted to an average of 77.7°, 1.6° larger than those in **1**.[10]

The structure of **1** shows the sodium to have a highly symmetric pseudo-octahedral arrangement of the nitrogen donor atoms similar to that of $[HB(pz)_3]_2Cd$,[6] as might be expected since the metals differ in ionic radii by only 0.07 Å. These two structures are very different from the highly distorted structures of $[HB(pz)_3]_2Pb$[2] and $\{[HC(pz)_3]_2Pb\}\text{-}(BF_4)_2$.[3]

$\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I)\cdot 2C_6H_6$. Figure 2 shows an ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}\text{-}(I)\cdot 2C_6H_6$ (**2**), and selected bond distances and angles are shown in Table 3. Similar to the structure of **1**, the sodium is six coordinate with a highly symmetric pseudo-octahedral arrangement of the nitrogen donor atoms. The crystal is in the highly symmetrical space group $R\bar{3}$ with Na−N bond distances of 2.4867(12) Å. The intraligand bond angles are restricted by the chelate rings to 77.16(4)°. The structure shows two molecules of the crystallization solvent present per cation.

The structure of **2** is nearly identical to that of $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, which crystallized in the $R\bar{3}c$ space group.[3] The lone pair in $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ is stereochemically inactive. One notable feature of these structures is the nonbonding distances between adjacent interligand 3-methyl groups, which at 3.93 Å in $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$ and 3.99 Å in **2** are nearly the sum of the van der Waals radii of two methyl groups (4.0 Å).

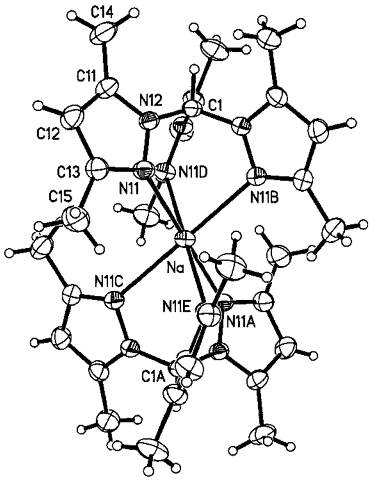


Figure 2. ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I)$, **2**, at 30% probability.

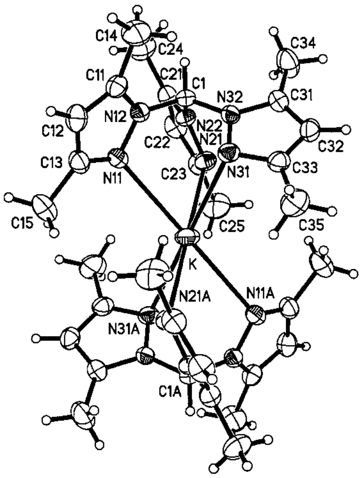


Figure 3. ORTEP diagram of the cation in $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$, **3**, at 30% probability.

Table 3. Selected Bond Distances and Angles for $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(I){\cdot}C_6H_6$ (**2**)

Bond Distances (Å)	
Na−N(11)	2.4867(12)
C(1)−N(12)	1.4417(13)
Bond Angles (deg)	
N(11)−Na−N(11B)	77.16(4)
N(11)−Na−N(11C)	102.84(4)
N(12)−C(1)−N(12D)	112.30(8)

In a different project, we found that the reaction of $HC(3,5\text{-}Me_2pz)_3$ and $NaBH_4$ in either a 1/1 or 2/1 ratio yielded $\{[HC(3,5\text{-}Me_2pz)_3]_2Na\}(BH_4)$.[17] The BH_4^- group is simply the counterion and does not interact with the sodium. The solid state structure of the cation in this complex is nearly identical to that of **2**. The average Na−N bond distance is 2.45 Å (differing by only 0.03 Å), and the intraligand bond angles average 74.8°, just 2.4° smaller than those in **2**.

$\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$. Figure 3 shows an ORTEP diagram of the cation $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$ (**3**), and selected bond distances and angles are shown in Table 4. The potassium is in a six-coordinated environment, and the overall structure is that of a trigonally distorted octahedron with the potassium sitting on a center of inversion. The average K−N bond distance is 2.82 Å, and the intraligand bond angles average 69.4°.

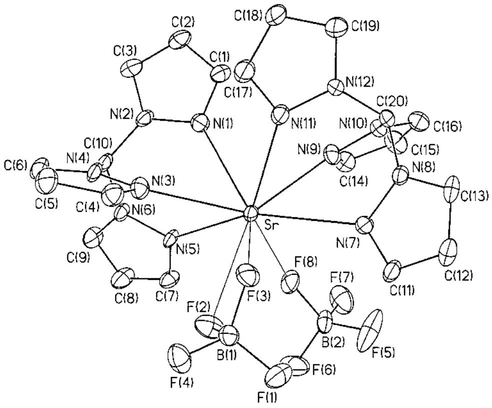


Figure 4. ORTEP diagram of $\{[HC(pz)_3]_2Sr\}(BF_4)_2$, **4**, at 30% probability.

Table 4. Selected Bond Distances and Angles for $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$ (**3**)

Bond Distances (Å)	
K−N(11)	2.800(3)
K−N(21)	2.829(3)
K−N(31)	2.834(3)
C(1)−N(12)	1.440(4)
C(1)−N(22)	1.445(4)
C(1)−N(32)	1.445(4)
Bond Angles (deg)	
N(11)−K−N(21)	68.11(9)
N(11)−K−N(31)	67.75(9)
N(21)−K−N(31)	72.40(9)
N(11)−K−N(21A)	111.89(9)
N(11)−K−N(31A)	111.25(9)
N(21)−K−N(31A)	107.60(9)
N(12)−C(1)−N(22)	111.5(3)
N(12)−C(1)−N(32)	111.7(3)
N(22)−C(1)−N(32)	110.2(3)

The structure of **3** is quite unique given the fact that K has been shown to have a preference for higher coordination. There are only a few other examples of six-coordinate KN_6 complexes.[18−20] In addition, no analogous poly(pyrazolyl)borate complexes of potassium have been prepared.

$\{[HC(pz)_3]_2Sr\}(BF_4)_2$. Figure 4 shows the ORTEP diagram of the cation in $\{[HC(pz)_3]_2Sr\}(BF_4)_2$ (**4**), and selected bond distances and angles are shown in Table 5. The structure is distorted with a highly asymmetric arrangement of the nitrogen donor atoms; the interligand N−Sr−N bond angles range from 72.6(2) to 154.99(14)°. This distortion is caused by bonding interactions with the metal from three of the fluorine atoms of the $[BF_4]^-$ counterions. The shortest Sr−F distance is 2.450(4) Å, and the longest distance is 2.795(4) Å.

The SrN_6 part of the structure in **4** is similar to that of the cation in the PbN_6 part of the structures of the analogous lead(II) complexes, $\{[HC(pz)_3]_2Pb\}(BF_4)_2$ and $\{[HC(pz)_3]_2Pb\}(B[3,5\text{-}(CF_3)_2C_6H_3]_4)_2$, both of which have a highly distorted arrangement of the nitrogen donor atoms around lead.[3,15] A major difference in the structures is that the lead(II) is six-coordinate in both cases, with no interaction from the $[BF_4]^-$ counterions in $\{[HC(pz)_3]_2Pb\}(BF_4)_2$. The shortest Pb···F distance is 3.6 Å, which is well out of bonding distance. Presumably, the lone pair on lead(II) is responsible for these

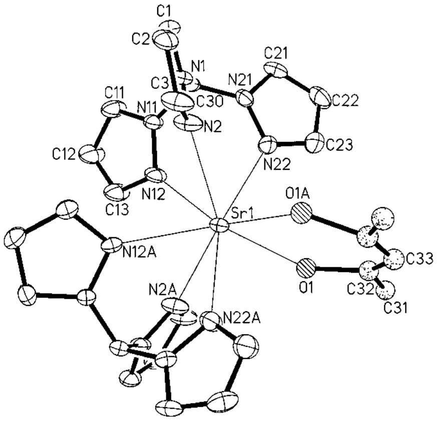


Figure 5. ORTEP diagram of the cation in $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$, **5**, at 30% probability.

Table 5. Selected Bond Distances and Angles for $\{[HC(pz)_3]_2Sr\}(BF_4)_2$ (**4**)

Bond Distances (Å)	
Sr−N(1)	2.762(5)
Sr−N(3)	2.748(5)
Sr−N(5)	2.685(4)
Sr−N(7)	2.782(4)
Sr−N(9)	2.709(5)
Sr−N(11)	2.678(4)
Sr−F(2)	2.795(4)
Sr−F(3)	2.662(3)
Sr−F(8)	2.450(4)
Bond Angles (deg)	
N(1)−Sr−N(3)	67.0(2)
N(1)−Sr−N(5)	65.38(14)
N(3)−Sr−N(5)	69.11(13)
N(7)−Sr−N(9)	65.41(14)
N(7)−Sr−N(11)	68.32(14)
N(9)−Sr−N(11)	69.27(14)
N(1)−Sr−N(7)	130.71(13)
N(1)−Sr−N(9)	73.5(2)
N(1)−Sr−N(11)	72.6(2)
N(3)−Sr−N(7)	131.96(14)
N(3)−Sr−N(9)	136.1(2)
N(3)−Sr−N(11)	81.16(14)
N(5)−Sr−N(7)	154.99(14)
N(5)−Sr−N(9)	110.78(14)
N(5)−Sr−N(11)	135.26(14)
N(2)−C(10)−N(4)	112.1(4)
N(2)−C(10)−N(6)	111.0(5)
N(4)−C(10)−N(6)	112.2(5)
F(2)−Sr−F(3)	47.98(10)
F(2)−Sr−F(8)	70.30(14)
F(3)−Sr−F(8)	102.41(14)

differences in structure between the lead and strontium complexes.

$\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$ (5). Figure 5 shows an ORTEP diagram of the cation $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$ (**5**), and selected bond distances and angles are shown in Table 6. The overall structure shows a distorted eight-coordinate arrangement of the ligands about the metal. The average Sr−N bond distance is 2.68 Å, and the Sr−O bond distance is 2.563(11) Å. The interligand N−Sr−N bond angles range from 74.7(3) to 157.1(2)°.

The fact that strontium shows a preference for higher coordination numbers is not surprising, given that most of the reported complexes show strontium in either an eight- or nine-coordinate environment. For example, $[Sr(tpy)_3]I_2$[21] shows strontium in a nine-coordinate environment, and $[Sr(bpy)_3I_2]$[22] shows strontium in an eight-coordinate environment similar to that observed in **5**. In both cases, the average Sr−N distances are similar to those observed in **5** (2.72 Å for $[Sr(tpy)_3]I_2$ and 2.73 Å for $[Sr(bpy)_3I_2]$). There is only one reported example of a six-coordinate SrN_6 complex, $[HB(3,5\text{-}Me_2pz)_3]_2Sr$, which was reported by Sohrin.[23] The overall structure is a trigonally distorted octahedron, similar to $\{[HC(3,5\text{-}Me_2pz)_3]_2Pb\}(BF_4)_2$, and the average Sr−N bond distance is 2.59 Å, just slightly shorter than that observed in **5**.

Table 6. Selected Bond Distances and Angles for $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$ (**5**)

Bond Distances (Å)	
Sr−N(2)	2.677(6)
Sr−N(12)	2.702(5)
Sr−N(22)	2.672(6)
Sr−O(1)	2.563(11)
C(30)−N(1)	1.448(8)
C(30)−N(11)	1.460(8)
C(30)−N(21)	1.446(8)
Bond Angles (deg)	
N(2)−Sr−N(12)	69.89(18)
N(2)−Sr−N(22)	68.44(18)
N(12)−Sr−N(22)	66.89(17)
N(2)−Sr−N(2A)	138.4(3)
N(12)−Sr−N(12A)	74.7(3)
N(22)−Sr−N(22A)	157.1(2)
N(11)−C(30)−N(1)	111.1(5)
N(11)−C(30)−N(21)	112.0(5)
N(1)−C(30)−N(21)	111.7(5)
N(2)−Sr−O(1)	136.5(3)
N(12)−Sr−O(1)	118.0(3)
N(22)−Sr−O(1)	76.1(3)
N(2A)−Sr−O(1)	81.6(3)
N(12A)−Sr−O(1)	145.6(3)
N(22A)−Sr−O(1)	85.3(3)
O(1)−Sr−O(1A)	70.9(5)
C(32)−C(33)−C(32A)	123(5)

$\{[HC(pz)_3]_2(Me_2CO)_2Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$. Figure 6 shows an ORTEP diagram of the cation in $\{[HC(pz)_3]_2(Me_2CO)_2Sr\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$ (**6**), and selected bond distances and angles are given in Table 7. The structure of **6** is very similar to that of **5** in that the strontium is eight coordinate, with the highly distorted $Sr{-}N_6$ core and the two additional oxygen atoms. The average Sr−N bond distance is the same in both complexes at 2.68 Å, and the Sr−O distance is nearly identical in each case.

$\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Ca\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$. Figure 7 shows an ORTEP diagram of the cation in $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Ca\}\{B[3,5-(CF_3)_2C_6H_3]_4\}_2$ (**7**), and selected bond distances and angles are shown in

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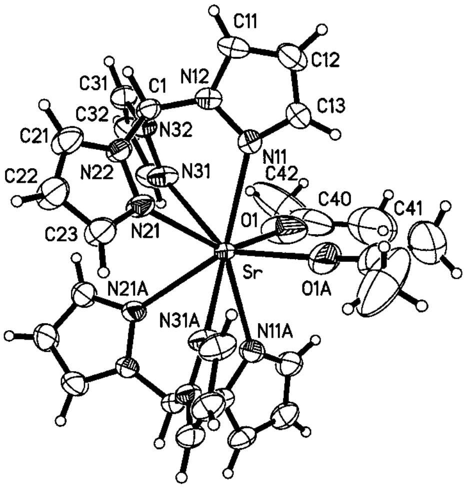

Figure 6. ORTEP diagram of the cation in $\{[HC(pz)_3]_2(Me_2CO)Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$, **6**, at 30% probability.

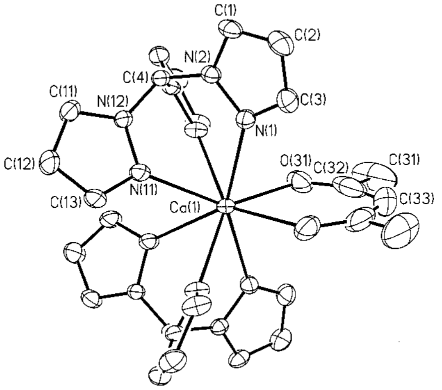

Figure 7. ORTEP diagram of the cation in $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Ca\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$, **7**, at 30% probability.

Table 7. Selected Bond Distances and Angles for $\{[HC(pz)_3]_2(Me_2CO)_2Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**6**)

Bond Distances (Å)	
Sr−N(11)	2.690(5)
Sr−N(21)	2.674(5)
Sr−N(31)	2.674(5)
Sr−O(1)	2.575(8)
C(1)−N(12)	1.443(8)
C(1)−N(22)	1.441(7)
C(1)−N(32)	1.442(7)
Bond Angles (deg)	
N(11)−Sr−N(21)	67.56(17)
N(11)−Sr−N(31)	68.61(17)
N(21)−Sr−N(31)	68.55(16)
N(11)−Sr−N(11A)	153.3(2)
N(21)−Sr−N(21A)	77.5(3)
N(31)−Sr−N(31A)	136.0(3)
N(12)−C(1)−N(22)	112.3(5)
N(12)−C(1)−N(32)	112.1(5)
N(22)−C(1)−N(32)	112.5(5)
N(11)−Sr−O(1)	85.9(2)
N(21)−Sr−O(1)	142.8(2)
N(31)−Sr−O(1)	77.8(3)
N(11A)−Sr−O(1)	74.3(2)
N(21A)−Sr−O(1)	110.9(3)
N(31A)−Sr−O(1)	139.8(2)
O(1)−Sr−O(1A)	84.7(6)

Table 8. Similar to **5**, the overall structure shows a distorted arrangement of the tris(pyrazolyl)methane ligands with coordination of Hacac. The average Ca−N bond distance is 2.56 Å, and the Ca−O bond distance 2.435(3) Å. The interligand N−Ca−N bond angles reflect the distortion and range from 72.78(15) to 155.31(13)°.

Table 8. Selected Bond Distances and Angles for $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Ca\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$ (**7**)

Bond Distances (Å)	
Ca−N(1)	2.580(3)
Ca−N(11)	2.583(3)
Ca−N(21)	2.515(3)
Ca−O(31)	2.435(3)
C(4)−N(2)	1.446(4)
C(4)−N(12)	1.454(4)
C(4)−N(22)	1.462(4)
Bond Angles (deg)	
N(1)−Ca−(N11)	68.44(9)
N(1)−Ca−N(21)	71.45(9)
N(11)−Ca−N(21)	74.46(10)
N(1)−Ca−N(1A)	155.31(13)
N(11)−Ca−N(11A)	72.78(15)
N(21)−Ca−N(21A)	145.26(14)
N(12)−C(4)−N(22)	111.8(3)
N(2)−C(4)−N(12)	112.0(3)
N(2)−C(4)−N(22)	111.9(2)
N(1)−Ca−O(31)	85.13(11)
N(11)−Ca−O(31)	146.10(11)
N(21)−Ca−O(31)	77.28(12)
N(1A)−Ca−O(31)	74.74(10)
N(11A)−Ca−O(31)	118.75(13)
N(21A)−Ca−O(31)	134.94(12)
O(31)−Ca−O(31A)	71.0(2)
C(32)−C(33)−C(32A)	118.1(9)

Similar to strontium, calcium prefers having a larger coordination sphere, as in $[Ca(tpy)_3]I_2$.[21] There are more examples of six-coordinate CaN_6 complexes (presumably because of its smaller size), including the tris(pyrazolyl)borate analogues $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ and $[HB(pz)_3]_2Ca$.[23,24] The overall structure in both of these complexes is that of a trigonally distorted octahedron. The Ca−N bond distances in $[HB(3,5\text{-}Me_2pz)_3]_2Ca$ and $[HB(pz)_3]_2Ca$ are just slightly shorter, at 2.45(2) and 2.44 Å, than those observed in **7** (2.56 Å).

Conclusions

A series of complexes of the type $\{[\text{tris(pyrazolyl)methane}]_2M\}^{n+}$ have been prepared for Na^+, K^+, Ca^{2+}, and Sr^{2+}, showing that the neutral, relatively soft tris(pyrazolyl)methane ligands will form complexes with these large, hard metals. Only for sodium were we able to make a matched pair of complexes with both the $HC(pz)_3$ and $HC(3,5\text{-}Me_2pz)_3$ ligands. The structure of $\{[HC(pz)_3]_2Na\}(I)$ shows a highly symmetrical arrangement of nitrogen donor atoms around the metal, which is very different from the distorted structure of $\{[HC(pz)_3]_2Pb\}(BF_4)_2$.[3] This result lends support to the fact that in the case of the lead(II) compound, the lone pair is significantly influencing the solid-state structure. This conclusion is supported by the structure of $\{[HC(pz)_3]_2Sr\}(BF_4)_2$. Although the $\{[HC(pz)_3]_2M\}^{2+}$ part of the structures for both $M = Pb^{2+}$ and Sr^{2+} are distorted from an octahedral arrangement and nearly identical, in the $M = Sr^{2+}$ structure three fluorine atoms from the BF_4^- counterions

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(24) Sohrin, Y.; Kokusen, H.; Kihara, S.; Matsui, M.; Kushi, Y.; Shiro, M. *J. Am. Chem. Soc.* **1993**, *115*, 4128.

interact with the metal. This type of bonding interaction is not observed for M = Pb^{2+}, again showing that the lone pair is influencing structure.

In the case of Sr^{2+} and Ca^{2+}, the expected preference for higher coordination numbers strongly influenced the chemistry of these metals. All attempts to prepare complexes of the formula $\{[\text{tris(pyrazolyl)methane}]_2M\}(X)_2$, in which the monoanionic X^- counterion was not coordinated to the metal, were unsuccessful. Products, such as $\{[HC(pz)_3]_2(CH_3COCH_2COCH_3)Sr\}\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}_2$, could only be isolated if an additional ligand, even the weakly coordinating Hacac or BF_4^- group, was present. Given these results, it is surprising that we were able to prepare a simple six-coordinate complex, $\{[HC(3,5\text{-}Me_2pz)_3]_2K\}(PF_6)$, of the large metal ion potassium.

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Supporting Information Available: Seven X-ray crystallographic files in CIF format, for compounds **1**−**7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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