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Tris(pyrazolyl)hydroborato Complexes of Cadmium: A Bidentate Nitrate Derivative and Its Relevance to Carbonic Anhydrase Activity

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The synthesis and structures of a series of [tris(pyrazolyl)hydroborato]cadmium complexes, $\{\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3\}$CdI, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$CdI, $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$CdCH$_3$, and $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO), are reported. The complex $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO) exhibits bidentate coordination of the nitrate ligand [2.272(6) and 2.295(7) Å], in contrast to the unidentate coordination mode that is observed in the related zinc derivative [η^3-HB(3-Bu^{t}pz)$_3\}$Zn(η^1-ONO$_2$). Cadmium-substituted carbonic anhydrase is less active than the zinc enzyme, and although many factors, such as the higher pK_a of the coordinated water, may be responsible for the lower activity, the observation of bidentate coordination in $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO) supports the notion that facile access to a unidentate bicarbonate intermediate may be an important requirement for carbonic anhydrase activity. $\{\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3\}$CdI is monoclinic, $P2_1/m$ (No. 11), with a = 9.840(2) Å, b = 16.449(9) Å, c = 10.633(2) Å, β = 103.04(2)°, V = 1677(1) Å^3, and Z = 2. $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$CdI is tetragonal, $P\bar{4}2_1m$ (No. 113), with a = b = 16.938(2) Å, c = 9.915(2) Å, V = 2845(1) Å^3, and Z = 4. $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$CdCH$_3$ is cubic, $I\bar{4}3d$ (No. 220), with a = 22.747(2) Å, V = 11770(2) Å^3, and Z = 16. $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO) is monoclinic, $P2_1/n$ (No. 14), with a = 10.690(1) Å, b = 17.233(3) Å, c = 16.272(2) Å, β = 91.70(1)°, V = 2996(1) Å^3, and Z = 4.

Introduction

We recently reported the application of sterically-demanding tris(pyrazolyl)hydroborato ligands [HB(3,5-RR′pz)$_3$]$^-$ (RR′pz = substituted pyrazole)^1 to an investigation of the chemistry of a series of monomeric alkyl, hydride, and hydroxide derivatives of zinc, such as $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ZnCH$_3$, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$ZnH, and $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH (3-Bu^{t}pz = 3-C$_3$N$_2$-Bu^{t}H$_2$; 3-Bu^t-5-Mepz = 3-Bu^t-5-MeC$_3$N$_2$H).$^{2-7}$ Our specific interest in the hydroxide derivative $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH$^{4-7}$ derives from its structural relationship to that of the active site of the enzyme carbonic anhydrase [(His)$_3$Zn(OH$_2$)]$^{2+}$ (His = histidine).^{8,9} Thus, the three nitrogen atom donors of the tris(pyrazolyl)hydroborato ligand bind to the zinc center in $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH by a manner closely analogous to those of the histidine imidazole groups in carbonic anhydrase. Further to the structural relationship, reactivity studies on $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$ZnOH have also revealed a functional equivalence to the enzyme.$^{4-7,10}$

Metal-substituted (e.g., Mn, Co, Ni, Cu, Cd, and Hg) carbonic anhydrases have also been actively investigated in order to provide information concerned with both enzyme structure and activity.$^{9,11-13}$ Such studies are in part a consequence of the lack of suitable spectroscopic probes for the diamagnetic d^{10} Zn(II) center of the native enzyme. In this regard, cadmium-substituted carbonic anhydrase has been studied by ^{113}Cd NMR spectroscopy.^{14,15} However, the activity of cadmium-substituted carbonic anhydrase is reduced substantially from that of the zinc enzyme at pH 7.^{13,16} Prompted by the reduced activity for the cadmium-substituted enzyme, we have initiated a study of [tris(pyrazolyl)-

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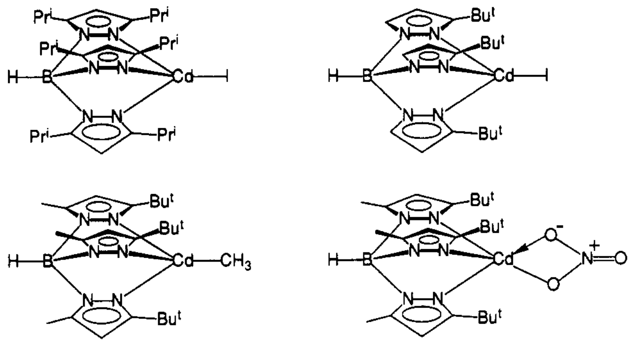

Figure 1. Structures of $\{\eta^3\text{-HB(3,5-RR'pz)}_3\}\text{CdX}$ complexes.

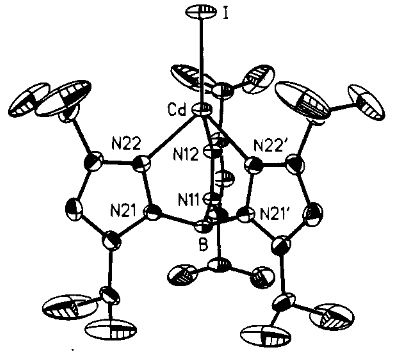

Figure 2. Molecular structure of $\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{CdI}$.

hydroborato]cadmium complexes in order to provide information that may explain the origin of the difference in activity between the zinc and cadmium enzymes. In this paper, we describe the synthesis and structures of some alkyl, halide, and nitrate derivatives of cadmium that are supported by tris(pyrazolyl)hydroborato ligation. In particular, the coordination mode of the nitrate ligand in the complex $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$ will be of central importance.

Results

[Tris(pyrazolyl)hydroborato]cadmium complexes of the type $\{\eta^3\text{-HB(3,5-RR'pz)}_3\}\text{CdX}$ [3,5-RR′pz = 3-Bu^{t}pz, 3-Bu^t-5-Mepz, 3,5-Pr$^i{}_2$pz; X = CH$_3$, I, NO$_3$], as shown in Figure 1, have been synthesized by the reaction between CdX$_2$ and either the potassium or thallium reagent $\text{M\{HB(3,5-RR'pz)}_3\}$ (M = K, Tl), as illustrated by eqs 1–4. The molecular structures of each of the derivatives $\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{CdI}$, $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{CdI}$, $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$, and $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$ have been determined by X-ray diffraction as shown in Figures 2–5. Selected bond lengths and angles are presented in Tables 1–8, with atomic coordinates in Tables 9–12.

$$\text{CdI}_2 + \text{K\{HB(3,5-Pr}^i{}_2\text{pz)}_3\} \rightarrow \{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{CdI} + \text{KI} \quad (1)$$

$$\text{CdI}_2 + \text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\} \rightarrow \{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{CdI} + \text{TlI} \quad (2)$$

$$\text{Cd(NO}_3)_2 + \text{K\{HB(3-Bu}^t\text{-5-Mepz)}_3\} \rightarrow \{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO}) + \text{KNO}_3 \quad (3)$$

$$\text{Cd(CH}_3)_2 + \text{Tl}\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\} \rightarrow \{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3 + [\text{TlCH}_3]_{\text{dec}} \quad (4)$$

Discussion

Recent attempts to synthesize the complexes $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}\text{CdX}$ (X = Cl, I) have met with only limited success due to facile contamination with the six-coordinate sandwich complex $\{\eta^3\text{-HB(3,5-Me}_2\text{pz)}_3\}_2\text{Cd}$.[17] However, by the use of more sterically-demanding tris(pyrazolyl)hydroborato ligands, we have found that cadmium complexes of the type $[\eta^3\text{-HB(3,5-RR'pz)}_3\}\text{CdX}$ may be readily synthesized by metathesis reactions (eqs 1–4). The synthesis of the alkyl derivative $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$ is based on the method that we had developed

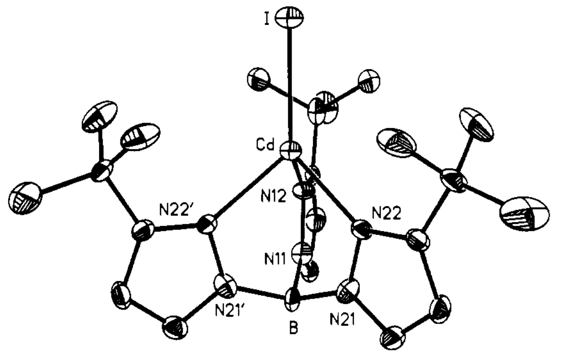

Figure 3. Molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{CdI}$.

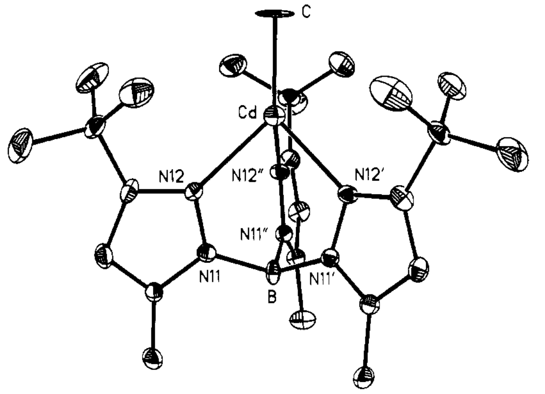

Figure 4. Molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$.

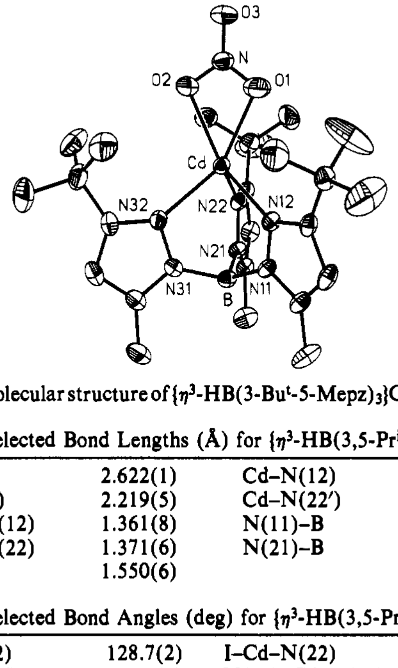

Figure 5. Molecular structure of $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$.

Table 1. Selected Bond Lengths (Å) for $\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{CdI}$

Cd–I	2.622(1)	Cd–N(12)	2.221(5)
Cd–N(22)	2.219(5)	Cd–N(22′)	2.219(5)
N(11)–N(12)	1.361(8)	N(11)–B	1.556(10)
N(21)–N(22)	1.371(6)	N(21)–B	1.550(6)
N(21′)–B	1.550(6)		

Table 2. Selected Bond Angles (deg) for $\{\eta^3\text{-HB(3,5-Pr}^i{}_2\text{pz)}_3\}\text{CdI}$

I–Cd–N(12)	128.7(2)	I–Cd–N(22)	127.7(1)
I–Cd–N(22′)	127.7(1)	N(12)–Cd–N(22)	85.8(2)
N(12)–Cd–N(22′)	85.8(2)	N(22)–Cd–N(22′)	86.3(2)
N(11)–B–N(21)	109.8(4)	N(11)–B–N(21′)	109.8(4)
N(21)–B–N(21′)	110.8(5)		

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Table 3. Selected Bond Lengths (Å) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$

Cd–I	2.673(2)	Cd–N(12)	2.232(17)
Cd–N(22)	2.255(12)	Cd–N(22′)	2.255(12)
N(11)–N(12)	1.377(26)	N(11)–B	1.520(42)
N(21)–N(22)	1.400(18)	N(21)–B	1.555(25)
B–N(21′)	1.555(25)		

Table 4. Selected Bond Angles (deg) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$

I–Cd–N(12)	124.2(4)	I–Cd–N(22)	127.4(3)
N(12)–Cd–N(22)	88.8(4)	I–Cd–N(22′)	127.4(3)
N(12)–Cd–N(22′)	88.8(4)	N(22)–Cd–N(22′)	87.8(6)
N(11)–B–N(21)	109.6(17)	N(11)–B–N(21′)	109.6(17)
N(21)–B–N(21′)	108.7(24)		

Table 5. Selected Bond Lengths (Å) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{CdCH}_3$

Cd–C	2.074(19)	Cd–N(12)	2.311(7)
N(11)–N(12)	1.364(13)	N(11)–B	1.573(11)

Table 6. Selected Bond Angles (deg) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{CdCH}_3$

C–Cd–N(12)	128.6(2)	C–Cd–N(12′)	128.6(2)
N(12)–Cd–N(12′)	85.2(4)	C–Cd–N(12″)	128.6(2)
N(12)–Cd–N(12″)	85.2(4)	N(12′)–Cd–N(12″)	85.2(4)
N(11)–B–N(11′)	109.5(9)	N(11)–B–N(11′)	109.5(9)
N(11′)–B–N(11′)	109.5(9)		

Table 7. Selected Bond Lengths (Å) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$

Cd–O(1)	2.272(6)	Cd–O(2)	2.295(7)
Cd–N(12)	2.245(3)	Cd–N(22)	2.250(4)
Cd–N(32)	2.230(4)	O(1)–N	1.145(10)
O(2)–N	1.160(7)	O(3)–N	1.207(6)
N(11)–N(12)	1.372(5)	N(11)–B	1.541(6)
N(21)–N(22)	1.363(5)	N(21)–B	1.552(6)
N(31)–N(32)	1.387(6)	N(31)–B	1.554(7)

Table 8. Selected Bond Angles (deg) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$

O(1)–Cd–O(2)	48.1(3)	O(1)–Cd–N(12)	107.0(2)
O(2)–Cd–N(12)	142.3(3)	O(1)–Cd–N(12)	113.2(2)
O(2)–Cd–N(22)	122.1(2)	N(12)–Cd–N(22)	92.2(1)
O(1)–Cd–N(32)	151.6(2)	O(2)–Cd–N(32)	106.3(2)
N(12)–Cd–N(32)	86.8(1)	N(22)–Cd–N(32)	90.4(1)
Cd–O(1)–N	102.9(5)	Cd–O(2)–N	101.1(5)
O(1)–N–O(2)	107.8(6)	O(1)–N–O(3)	125.9(5)
O(2)–N–O(3)	126.3(6)	N(11)–B–N(21)	111.7(4)
N(11)–B–N(31)	111.3(4)	N(21)–B–N(31)	110.5(4)

Table 9. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for $\{\eta^3\text{-HB}(3,5\text{-Pr}^i{}_2\text{pz})_3\}\text{CdI}$

atom	*x*	*y*	*z*	*U*[a]
Cd	9531(1)	2500	8945(1)	57(1)
I	9557(1)	2500	6484(1)	113(1)
N(11)	11008(6)	2500	11824(5)	48(2)
N(12)	11324(6)	2500	10642(5)	54(2)
N(21)	8717(4)	1724(3)	11309(4)	52(1)
N(22)	8598(4)	1577(3)	10019(4)	56(2)
C(11)	12226(8)	2500	12751(7)	58(3)
C(12)	13308(9)	2500	12126(8)	72(3)
C(13)	12716(8)	2500	10819(7)	60(3)
C(14)	12280(8)	2500	14188(7)	70(3)
C(15)	13371(9)	2500	9672(9)	74(3)
C(16)	12915(16)	3246(7)	14792(8)	205(8)
C(17)	14113(24)	3098(11)	9567(16)	529(20)
C(21)	8108(6)	1106(4)	11816(5)	65(2)
C(22)	7626(7)	573(4)	10838(6)	83(3)
C(23)	7938(6)	872(4)	9737(5)	66(2)
C(24)	8054(7)	1060(4)	13230(6)	80(3)
C(25)	7668(8)	538(4)	8393(7)	91(3)
C(26)	6742(11)	1261(11)	13481(10)	219(9)
C(27)	8546(18)	304(11)	13803(10)	350(15)
C(28)	6323(11)	665(12)	7668(10)	260(10)
C(29)	8303(14)	−233(9)	8337(11)	230(9)
B	9463(8)	2500	11946(7)	45(3)

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

Table 10. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$

atom	*x*	*y*	*z*	*U*[a]
Cd	7958(1)	2958(1)	5383(2)	45(1)
I	9043(1)	4043(1)	4749(2)	69(1)
N(11)	6753(8)	1753(8)	4490(19)	49(5)
N(12)	7267(7)	2267(7)	3871(17)	43(5)
C(11)	6334(11)	1334(11)	3495(27)	52(7)
C(12)	6616(11)	1616(11)	2262(32)	64(9)
C(13)	7151(10)	2151(10)	2517(21)	42(6)
C(14)	7623(11)	2623(11)	1510(26)	58(7)
C(15)	7415(16)	2415(16)	108(27)	96(8)
C(16)	7462(11)	3513(10)	1778(22)	74(8)
N(21)	7446(8)	1390(7)	6644(13)	50(5)
N(22)	8141(7)	1835(7)	6565(12)	44(4)
C(21)	7583(11)	726(10)	7319(18)	59(6)
C(22)	8367(11)	718(11)	7680(17)	63(7)
C(23)	8693(10)	1431(11)	7238(16)	50(6)
C(24)	9534(9)	1703(12)	7330(19)	73(7)
C(25)	9912(14)	1779(15)	5976(20)	104(10)
C(26)	9996(15)	1088(18)	8227(30)	182(16)
C(27)	9539(10)	2555(12)	7955(22)	95(9)
B	6649(15)	1649(15)	6002(38)	58(9)

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

previously for the preparation of the related magnesium and zinc derivatives $\{\eta^3\text{-HB}(3,5\text{-RR}'\text{pz})_3\}\text{MR}$ (M = Mg, Zn), namely the reaction between MR_2 and the thallium reagent $\text{Tl}\{\eta^3\text{-HB}(3,5\text{-RR}'\text{pz})_3\}$.[2,18] The thallium derivative $\text{Tl}\{\eta^3\text{-HB}(3,5\text{-RR}'\text{pz})_3\}$ is generally the reagent of choice because the deposition of Tl, due to decomposition of unstable [TlR], provides an effective driving force for the reaction.[19] More recently, using a similar procedure, Reger synthesized an extensive series of cadmium alkyl derivatives of the less sterically-demanding tris(3,5-dimethylpyrazolyl)hydroborato ligand $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}\text{CdR}$.[20]

The molecular structures of the complexes $\{\eta^3\text{-HB}(3,5\text{-Pr}^i{}_2\text{pz})_3\}\text{CdI}$, $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$, $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{CdCH}_3$, and $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$ are illustrated in Figures 2–5. Each of the complexes exhibit a similar coordination of the tris(pyrazolyl)hydroborato ligands to the cadmium center, as evidenced by the average Cd–N bond lengths and N–Cd–N bond angles: $\{\eta^3\text{-HB}(3,5\text{-Pr}^i{}_2\text{pz})_3\}\text{CdI}$ [2.22 Å, 86.0°], $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$ [2.25 Å, 88.5°], $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{CdCH}_3$ [2.31 Å, 85.2°], and $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$ [2.24 Å, 89.8°]. It is noteworthy that the Cd–N bond lengths in these complexes are shorter than those in the six-coordinate sandwich complex $\{\eta^3\text{-HB}(3,5\text{-Me}_2\text{pz})_3\}_2\text{Cd}$ [2.36(1) and 2.43(2) Å].[17,21]

The Cd-I bond lengths in $\{\eta^3\text{-HB}(3,5\text{-Pr}^i{}_2\text{pz})_3\}\text{CdI}$ and $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{pz})_3\}\text{CdI}$ are 2.622(1) and 2.673(2) Å, respectively, and are both shorter than the sum of covalent radii (2.81 Å).[22] Since these complexes represent well-defined examples of four-coordinate cadmium, these results may suggest that a more appropriate value for the covalent radius of cadmium in such complexes is *ca.* 1.32 Å [on the basis that $r_{\text{cov}}(\text{I}) = 1.33$ Å], rather than the literature value of 1.48 Å.[22] Similarly, the Cd–CH_3 bond length of 2.07(2) Å in $\{\eta^3\text{-HB}(3\text{-Bu}^t\text{-5-Mepz})_3\}\text{CdCH}_3$ is also shorter than the sum of the covalent radii (2.25 Å)[22] but is close to the value of 2.09 Å that is obtained by assuming a modified covalent radius of 1.32 Å for cadmium. Moreover, the Cd–CH_3 bond length of 2.07(2) Å is also close to the established range for other Cd–CH_3 bond lengths (2.09–2.11 Å). For reference, Cd–C bond lengths for some alkyl, aryl, and cyclopentadienyl derivatives are listed in Table 13. However, it should be noted that the thermal parameters of the carbon atom of the Cd–CH_3 group are

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(18) Han, R.; Parkin, G. *Organometallics* **1991**, *10*, 1010–1020.
(19) Gilman, H.; Jones, R. G. *J. Am. Chem. Soc.* **1946**, *68*, 517–520.
(20) Reger, D. L.; Mason, S. S. *Organometallics* **1993**, *12*, 2600–2603.

Table 11. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$

atom	*x*	*y*	*z*	*U*[a]
Cd	411(1)	411(1)	411(1)	47(1)
C	938(5)	938(5)	938(5)	105(7)
N(11)	−17(4)	−822(3)	−30(4)	35(3)
N(12)	422(5)	−600(3)	314(4)	37(3)
C(11)	−47(5)	−1412(4)	6(5)	38(4)
C(12)	394(5)	−1578(4)	383(6)	50(4)
C(13)	675(5)	−1059(5)	581(5)	48(4)
C(14)	−470(5)	−1785(5)	−311(6)	55(5)
C(15)	1187(5)	−981(6)	997(5)	51(4)
C(16)	957(8)	−681(9)	1554(6)	104(9)
C(17)	1441(8)	−1590(7)	1140(8)	101(8)
C(18)	1671(6)	−600(8)	713(7)	86(7)
B	−422(6)	−422(6)	−422(6)	36(3)

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

Table 12. Atom Coordinates ($\times 10^4$) and Temperature Factors (Å^2 $\times 10^3$) for $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$

atom	*x*	*y*	*z*	*U*[a]
Cd	2353(1)	7168(1)	7183(1)	51(1)
O(1)	271(6)	6900(5)	7125(5)	236(5)
O(2)	1233(5)	6175(4)	6576(6)	223(5)
O(3)	−718(4)	5980(3)	6570(3)	103(2)
N	220(4)	6342(3)	6742(3)	75(2)
N(11)	3772(4)	8224(2)	8349(2)	54(1)
N(12)	2768(4)	7733(2)	8404(2)	56(1)
N(21)	3908(4)	8579(2)	6827(2)	53(1)
N(22)	2851(4)	8251(2)	6494(2)	54(1)
N(31)	5128(4)	7418(2)	7404(2)	55(1)
N(32)	4351(4)	6796(2)	7209(2)	59(1)
C(11)	3957(5)	8591(3)	9072(3)	66(2)
C(12)	3068(6)	8342(3)	9589(3)	74(2)
C(13)	2327(5)	7804(3)	9166(3)	60(2)
C(14)	4963(7)	9175(4)	9232(4)	106(3)
C(15)	1247(5)	7336(3)	9472(3)	68(2)
C(16)	1097(13)	7463(8)	10361(5)	226(7)
C(17)	82(8)	7549(9)	9042(7)	222(7)
C(18)	1492(8)	6499(5)	9339(6)	142(4)
C(21)	4220(5)	9210(3)	6378(3)	61(2)
C(22)	3366(5)	9281(3)	5751(3)	71(2)
C(23)	2517(5)	8673(3)	5829(3)	60(2)
C(24)	5337(6)	9700(4)	6577(4)	92(3)
C(25)	1380(6)	8491(3)	5295(3)	82(2)
C(26)	201(6)	8541(6)	5772(5)	150(4)
C(27)	1296(9)	9052(6)	4577(5)	201(6)
C(28)	1496(7)	7689(4)	4935(4)	106(3)
C(31)	6317(5)	7186(3)	7420(3)	70(2)
C(32)	6324(5)	6410(4)	7232(3)	77(2)
C(33)	5098(5)	6176(3)	7114(3)	68(2)
C(34)	7403(5)	7707(4)	7595(5)	100(3)
C(35)	4576(7)	5383(3)	6900(4)	95(3)
C(36)	3596(7)	5137(4)	7499(4)	116(3)
C(37)	4008(8)	5398(4)	6034(4)	133(4)
C(38)	5649(8)	4794(5)	6943(7)	196(6)
B	4609(5)	8239(4)	7594(3)	57(2)

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

not particularly well-behaved, so that the derived bond length should be regarded with a degree of caution.[23]

The methyl derivative $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$ has also been studied by ^{1}H and ^{13}C NMR spectroscopy. In particular, the ^{1}H NMR signal of the Cd–CH$_3$ group is characterized by the observation of both ^{111}Cd ($^2J_{\text{Cd-H}} = 71$ Hz) and ^{113}Cd ($^2J_{\text{Cd-H}} = 74$ Hz) satellites,[24] as shown in Figure 6. The $^2J_{\text{Cd-H}}$ coupling constants for $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$ are greater than those for the two-coordinate alkyls R$_2$Cd (50-53 Hz)[25] but less than those for tetrameric alkoxides $[\text{(RO)CdCH}_3]_4$ (80–90 Hz).[26,27]

Table 13. Some Cd–C Bond Lengths

compound	*d*(Cd–C), Å	ref
$(\text{CH}_3)_2\text{Cd}$	2.112(4)[a]	*b*
$[(\text{CH}_2{=}\text{CHMe}_2\text{Si})(\text{Me}_3\text{Si})_2\text{C}]_2\text{Cd}$	2.172(3)	*c*
$[(\text{CH}_3)_2\text{Cd(1,4-dioxane)}]_n$	2.09(2)	*d*
$(\text{CH}_3)_2\text{Cd(bipy)}$	2.17(3)	*e*
	2.15(2)	
$(\text{Me}_3\text{SiCH}_2)_2\text{Cd(bipy)}$	2.19(6)	*f*
	2.09(5)	
$\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{CdCH}_3$	2.07(2)	this work
$[(\text{NC}_5\text{H}_4)\text{SiMe}_3)_2\text{C}]_2\text{Cd}$	2.27	*g*
$[2\text{-(Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{Cd}$	2.154(8)	*h*
$[2,4,6\text{-(CF}_3)_3\text{C}_6\text{H}_2]_2\text{Cd(MeCN)}$	2.184(3)	*i*
	2.181(3)	
$\text{Cp}_2\text{Cd(NC}_5\text{H}_5)_2$	2.353(5)	*j*
	2.307(5)	
$\{\text{Cp*Cd}[\mu\text{-N(SiMe}_3)_2]\}_2$	2.220(6)	*k*

[a] Raman studies in gas phase. [b] Rao, K. S.; Stoicheff, B. P.; Turner, R. *Can. J. Phys.* **1960**, *38*, 1516. [c] Ayoko, G. A.; Buttrus, N. H.; Eaborn, C.; Hitchcock, P. B.; Smith, J. D. *J. Organomet. Chem.* **1987**, *320*, 137–143. [d] Almond, M. J.; Beer, M. P.; Drew, M. G. B.; Rice, D. A. *J. Organomet. Chem.* **1991**, *421*, 129–136. [e] Almond, M. J.; Beer, M. P.; Drew, M. G. B.; Rice, D. A. *Organometallics* **1991**, *10*, 2072–2076. [f] Bushnell, G. W.; Stobart, S. R. *Can. J. Chem.* **1980**, *58*, 574–578. [g] Henderson, M. J.; Papasergio, R. I.; Raston, C. L.; White, A. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1986**, 672–674. [h] (i) Khan, O. F. Z.; Frigo, D. M.; O'Brien, P.; Howes, A.; Hursthouse, M. B. *J. Organomet. Chem.* **1987**, *334*, C27–C30. (ii) Atwood, J. L.; Berry, D. E.; Stobart, S. R.; Zaworotko, M. J. *Inorg. Chem.* **1983**, *22*, 3480–3482. [i] Brooker, S.; Bertel, N.; Stalke, D.; Noltemeyer, M.; Roesky, H. W.; Sheldrick, G. M.; Edelmann, F. T. *Organometallics* **1992**, *11*, 192–195. [j] (i) Smeets, W. J. J.; Spek, A. L.; Fischer, B.; van Mier, G. P. M.; Boersma, J. *Acta Crystallogr.* **1987**, *C43*, 893–895. (ii) Fischer, B.; van Mier, G. P. M.; Boersma, J.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *322*, C37–C40. [k] Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1991**, *10*, 3781–3785.

The coordination mode of the nitrate ligand in $\{\eta^3\text{-HB(3-Bu}^t\text{-5-Mepz)}_3\}\text{Cd}(\eta^2\text{-O}_2\text{NO})$ is of particular interest to the present study. We have recently suggested that, among other factors, the coordination mode (*i.e.* unidentate *versus* bidentate) exhibited in the bicarbonate intermediate of the carbonic anhydrase catalytic cycle may be an important factor in influencing the activity of metal-substituted enzymes.[6,7] We also proposed that the changes in coordination mode of nitrate ligands in a series of structurally related metal complexes may provide an indication of the relative preferences for unidentate *versus* bidentate bicarbonate intermediates in the catalytic cycles of metal-substituted carbonic anhydrases.[6,7] The basis of this suggestion is the observation that the variation of the coordination mode of the nitrate ligands in the complexes $\{\eta^3\text{-HB(3-Bu}^t\text{pz)}_3\}\text{M(NO}_3)$ (M = Co, Ni, Cu,

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(21) Some other Cd–N bond lengths: $(\text{1-Me-imid})_2\text{Cd(SR)}_2$ (R = 2,4,6-$\text{Pr}^i{}_3\text{C}_6\text{H}_2$), 2.28 (1) Å;[21a] $\text{C}_2\text{H}_4[\text{MeNCH}_2\text{(3,5-Me}_2\text{pz)}]_2\text{CdCl}_2$, 2.431(3) and 2.478(3) Å;[21b] $\{\eta^3\text{-O}[\text{CH}_2\text{CH}_2\text{(3,5-Me}_2\text{pz)}]_2\}\text{Cd}(\eta^2\text{-NO}_3)_2$, 2.26 Å (average);[21c] $\{\eta^3\text{-HN}[\text{CH}_2\text{CH}_2\text{(3,5-Me}_2\text{pz)}]_2\}\text{Cd}(\eta^2\text{-NO}_3)_2$, 2.31 Å (average);[21c] $\text{Cd}_2\text{(bddo)}_2\text{(NCS)}_4$, 2.32 Å (average);[21d] $[\text{Cd(1-Me-imid)}_6]^{2+}$, 2.35 Å (average).[21e] (a) Corwin, D. T., Jr.; Gruff, E. S.; Koch, S. A. *J. Chem. Soc., Chem. Commun.* **1987**, 966–967. (b) Paap, F.; Erdonmez, A.; Driessen, W. L.; Reedijk, J. *Acta Crystallogr.* **1986**, *C42*, 783–785. (c) Griffith, E. A. H.; Charles, N. G.; Lewinski, K.; Amma, E. L.; Rodesiler, P. *Inorg. Chem.* **1987**, *26*, 3983–3989. (d) Haanstra, W. G.; Driessen, W. L.; Reedijk, J.; Turpeinen, U.; Hämäläinen, R. *J. Chem. Soc., Dalton Trans.* **1989**, 2309–2314. (e) Rodesiler, P. F.; Charles, N. G.; Griffith, E. A. H.; Lewinski, K.; Amma, E. L. *Acta Crystallogr.* **1986**, *C42*, 396–399.

(22) $r_{\text{cov}}(\text{Cd}) = 1.48$ Å, $r_{\text{cov}}(\text{Zn}) = 1.31$ Å, $r_{\text{cov}}(\text{C}) = 0.77$ Å, $r_{\text{cov}}(\text{I}) = 1.33$ Å. See: Pauling, L. *The Nature of the Chemical Bond*, Cornell University Press: Ithaca, NY, 1960.

(23) The ill-behaved thermal parameter may be a consequence of (i) a poor absorption correction, (ii) cocrystallization with an unidentified isostructural impurity, or (iii) disorder of a different nature. See: (a) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455–460. (b) Parkin, G. *Chem. Rev.* **1993**, *93*, 887–911.

(24) ^{111}Cd ($I = {}^1/_2$, 12.75%, $\gamma = -5.7046 \times 10^7$ rad s^{-1} T^{-1}) and ^{113}Cd ($I = {}^1/_2$, 12.26%, $\gamma = -5.9609 \times 10^7$ rad s^{-1} T^{-1}). The ratio $^2J_{^{111}\text{Cd-H}}/^2J_{^{113}\text{Cd-H}}$ (0.96) is close to that predicted by the ratio $\gamma(^{111}\text{Cd})/\gamma(^{113}\text{Cd}) = 0.957$.

(25) Turner, C. J.; White, R. F. M. *J. Magn. Reson.* **1977**, *26*, 1–5.

(26) Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Perkin Trans. 2*, **1977**, 1187–1191.

(27) It has been suggested that changes in $J_{\text{Cd-H}}$ correlate with effective nuclear charge at cadmium. See ref 26 and: Kennedy, J. D.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1976**, 1219–1223.

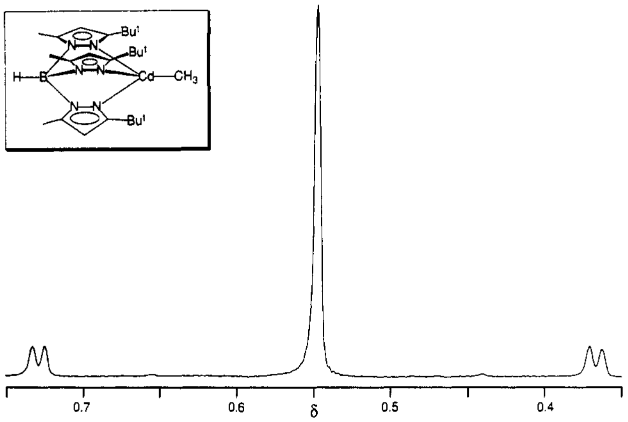

Figure 6. ^{1}H NMR signal of the Cd–CH$_3$ group in {η^3-HB(3-Bu^{t}pz)$_3$}-CdCH$_3$.

Zn) correlates with the activity of the metal-substituted carbonic anhydrases. Thus, the nitrate ligand coordination mode in {η^3-HB(3-Bu^{t}pz)$_3$}M(NO$_3$) (M = Co, Ni, Cu, Zn) varies from unidentate for Zn to symmetric bidentate for Ni and Cu, with the cobalt derivative exhibiting an asymmetric coordination mode.[28] Significantly, the activity of the metal-substituted enzymes also decreases across the series Zn > Co ≫ Ni and Cu,[11–13] a sequence that therefore correlates with the coordination mode of the nitrate ligands in the model complexes {η^3-HB(3-Bu^{t}pz)$_3$}M(NO$_3$) (M = Co, Ni, Cu, Zn).[29] Indeed, subsequent to our original report on the model complex {η^3-HB(3-Bu^{t}pz)$_3$}-Zn(η^1-ONO$_2$),[30] the X-ray structure of the nitrate derivative of human carbonic anhydrase II has shown that the nitrate ligand is coordinated to the zinc center *via* only one of its oxygen atoms.[31]

Cadmium-substituted carbonic anhydrase is less active than the zinc enzyme.[13,16] Many factors, such as the higher pK_a of the coordinated water,[13,16,32] may be responsible for the lower activity of cadmium-substituted carbonic anhydrase. Nevertheless, it was of interest to determine the coordination mode of the nitrate ligand in a related cadmium complex in order to examine the previously observed correlation between enzyme activity and the ease with a metal center may stabilize bidentate coordination.[6,7,33,34]

As illustrated in Figure 5, the cadmium derivative {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO) exhibits bidentate coordination of the nitrate ligand, with very similar Cd–O bond lengths of 2.272(6) and 2.295(7) Å.[35] The observation of an almost symmetric bidentate coordination mode in {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO) contrasts with the significantly different Zn–O interactions [1.978(3) and 2.581(3) Å] in the related zinc complex {η^3-HB(3-Bu^{t}pz)$_3$}Zn(η^1-ONO$_2$). The ability of cadmium to stabilize the bidentate coordination mode is presumably a reflection of larger size of Cd compared to its lighter congener Zn.[36,37] Thus, in line with the reduced activity of cadmium-substituted carbonic anhydrase, it is significant that the cadmium derivative {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO) also exhibits bidentate coordination of the nitrate ligand. As such, this observation thereby provides further support for the proposal that it is important to consider the nature of the bicarbonate intermediate (*i.e.* unidentate *versus* bidentate) when one evaluates the origin of the different activities of metal-substituted carbonic anhydrases. However, it is not intended to suggest that this factor alone is responsible for influencing the activity of metal-substituted carbonic anhydrases, and other factors, such as the coordination environment and the pK_a of the coordinated water, must naturally also be considered.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[38] Solvents were purified and degassed by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as KBr pellets or Nujol mulls between KBr disks on a Perkin-Elmer 1420 spectrophotometer and are reported in cm^{-1}. Mass spectra were obtained on a Nermag R10-10 mass spectrometer using chemical ionization (NH$_3$ or CH$_4$) techniques. Elemental analyses were obtained using a Perkin-Elmer 2400 CHN elemental analyzer. K{HB(3-Bu^{t}pz)$_3$},[39] Tl{η^3-HB(3-Bu^{t}pz)$_3$},[39] K{HB(3-Bu^t-5-Mepz)$_3$},[40] Tl{η^3-HB(3-Bu^t-5-Mepz)$_3$},[40] K{HB(3,5-Pr$^i_2$pz)$_3$},[41] and Cd(CH$_3$)$_2$[42] were prepared by literature methods.

Synthesis of {η^3-HB(3,5-Pr$^i_2$pz)$_3$}CdI. A solution of K{HB(3,5-Pr$^i_2$-pz)$_3$} (0.50 g, 0.99 mmol) in C$_6$H$_6$ (20 mL) was added dropwise to a suspension of CdI$_2$ (0.44 g, 1.18 mmol) in C$_6$H$_6$ (20 mL), resulting in the immediate formation of a yellow precipitate. The mixture was stirred overnight at room temperature and filtered. The filtrate was concentrated and placed at 0 °C, giving a crop of colorless crystals. The crystals of {η^3-HB(3,5-Pr$^i_2$pz)$_3$}CdI were isolated by filtration and dried *in vacuo* (0.38 g, 54%). Anal. Calcd for {η^3-HB(3,5-Pr$^i_2$pz)$_3$}CdI: C, 46.0; H, 6.6; N, 11.9. Found: C, 45.7; H, 6.1; N 11.9. ^{1}H NMR (C$_6$D$_6$): δ 1.12 [18H, d, $^3J_{H-H}$ = 7, η^3-HB{C$_3$N$_2$H(CH*Me*$_2$)$_2$}$_3$], 1.18 [18H, d, $^3J_{H-H}$ = 7, η^3-HB{C$_3$N$_2$H(CH*Me*$_2$)$_2$}$_3$], 3.45 [3H, spt, $^3J_{H-H}$ = 7, η^3-HB{C$_3$N$_2$H-(C*H*Me$_2$)$_2$}$_3$], 3.55 [3H, spt, $^3J_{H-H}$ = 7, η^3-HB{C$_3$N$_2$H(C*H*Me$_2$)$_2$}$_3$], 5.83 [3H, s, η^3-HB{C$_3$N$_2$*H*(CHMe$_2$)$_2$}$_3$]. ^{13}C NMR (C$_6$D$_6$): δ 23.5 [6C, q, $^1J_{C-H}$ = 126, η^3-HB{C$_3$N$_2$H(CH*Me*$_2$)$_2$}$_3$], 23.6 [6C, q, $^1J_{C-H}$ = 127, η^3-

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(28) For further information on nitrate coordination modes see: (a) Addison, C. C.; Logan, N.; Wallwork, S. C.; Garner, C. D. *Q. Rev., Chem. Soc.* **1971**, *25*, 289–322. (b) Kleywegt, G. J.; Wiesmeijer, W. G. R.; Van Driel, G. J.; Driessen, W. L.; Reedijk, J.; Noordik, J. H. *J. Chem. Soc., Dalton Trans.* **1985**, 2177–2184. (c) Suslick, K. S.; Watson, R. A. *Inorg. Chem.* **1991**, *30*, 912–919.

(29) Furthermore, Kitajima recently reported similar structural changes for a series of binuclear bridging carbonate complexes, [{η^3-HB(3,5-Pr$^i_2$-pz)$_3$}M]$_2$(μ-CO$_3$) (M = Fe, Co, Ni, Cu, Zn): Kitajima, N.; Hikichi, S.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1993**, *115*, 5496–5508.

(30) Han, R.; Parkin, G. *J. Am. Chem. Soc.* **1991**, *113*, 9707–9708.

(31) The Zn–O distance is 2.8 Å, indicating a relatively weak association. Moreover, the nitrate ligand does not displace the coordinated water from the zinc center. See: Mangani, S.; Håkansson, K. *Eur. J. Biochem.* **1992**, *210*, 867–871.

(32) Garmer, D. R.; Krauss, M. *J. Am. Chem. Soc.* **1992**, *114*, 6487–6493.

(33) We emphasize that it is the structural *changes* of nitrate coordination mode that provide an indication of the *changes* that may be expected for the corresponding bicarbonate complexes. Thus, this argument does not require that a nitrate coordination mode must be identical to that of the corresponding bicarbonate complex.

(34) We also note that Mn(II)-substituted carbonic anhydrase, which is less active than the zinc enzyme, has also been proposed to exhibit bidentate bicarbonate coordination. See: (a) Led, J. J.; Neesgaard, E. *Biochemistry* **1987**, *26*, 183–192. (b) Led, J. J.; Neesgaard, E.; Johansen, J. T. *FEBS Lett.* **1982**, *147*, 74–80.

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(37) An interesting example where a cadmium derivative exhibits unidentate nitrate coordination when the zinc derivative exhibits bidentate coordination is provided by the complexes Cd(OenNdienH$_4$)(η^1-NO$_3$)$_2$ and Zn(OenNdienH$_4$)(η^1-NO$_3$)(η^2-NO$_3$). However, in this case the macrocyclic OenNdienH$_4$ ligand also adopts different coordination modes. See: Adam, K. R.; Dancey, K. P.; Leong, A. J.; Lindoy, L. F.; McCool, B. J.; McPartlin, M.; Tasker, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 8471–8477.

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Table 14. Crystal and Intensity Collection Data

	L^{I}CdI^a	L^{II}CdI^a	L^{III}CdCH$_3$^{a}	L^{III}Cd(O$_2$NO)^a
formula	$C_{27}H_{46}N_6BCdI$	$C_{21}H_{34}N_6BICd$	$C_{25}H_{43}N_6BCd$	$C_{24}H_{40}N_7BO_3Cd$
fw	704.8	620.7	550.9	597.9
lattice	monoclinic	tetragonal	cubic	monoclinic
cell constants				
a, Å	9.840(2)	16.938(2)	22.747(2)	10.690(1)
b, Å	16.449(9)	16.938(2)	22.747(2)	17.233(3)
c, Å	10.633(2)	9.915(2)	22.747(2)	16.272(2)
α, deg	90.0	90.0	90.0	90.0
β, deg	103.04(2)	90.0	90.0	91.70(1)
γ, deg	90.0	90.0	90.0	90.0
V, Å^3	1677(1)	2845(1)	11 770(2)	2996(1)
Z	2	4	16	4
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
space group	$P2_1/m$ (No. 11)	$P\bar{4}2_1m$ (No. 113)	$I\bar{4}3d$ (No. 220)	$P2_1/n$ (No. 14)
ρ(calcd), g cm^{-3}	1.40	1.45	1.24	1.33
μ(Mo Kα), cm^{-1}	16.0	18.8	7.6	7.6
2θ range, deg.	3–50	3–50	3–50	3–50
no. of data [$F > 6\sigma(F)$]	2331	934	577	3583
no. of parameters	182	152	103	330
goodness of fit	1.772	1.491	1.162	1.239
R	0.0460	0.0522	0.0433	0.0395
R_w^{b}	0.0689	0.0623	0.0504	0.0525

^{a} L^{I} = {η^3-HB(3,5-Pr$^i_2$pz)$_3$}, L^{II} = {η^3-HB(3-Bu^{t}pz)$_3$}, L^{III} = {η^3-HB(3-Bu^t-5-Mepz)$_3$}. ^{b} Weighting scheme: $w = [\sigma^2(F) + gF^2]^{-1}$.

HB{C$_3$N$_2$H(CH*Me*$_2$)$_2$}$_3$], 26.7 [3C, d, $^1J_{C-H}$ = 127, η^3-HB{C$_3$N$_2$H(*C*HMe$_2$)$_2$}$_3$], 28.4 [3C, d, $^1J_{C-H}$ = 127, η^3-HB{C$_3$N$_2$H(*C*HMe$_2$)$_2$}$_3$], 98.1 [3C, d, $^1J_{C-H}$ = 172, η^3-HB{*C*$_3$N$_2$H(CHMe$_2$)$_2$}$_3$], 157.1 [3C, s, η^3-HB{*C*$_3$N$_2$H(CHMe$_2$)$_2$}$_3$], 161.0 [3C, s, η^3-HB{*C*$_3$N$_2$H(CHMe$_2$)$_2$}$_3$]. IR data: 2552 (ν_{B-H}).

Synthesis of {η^3-HB(3-Bu^{t}pz)$_3$}CdI. A suspension of Tl{η^3-HB(3-Bu^t-pz)$_3$} (1.50 g, 2.6 mmol) in THF (*ca.* 30 mL) was added to a suspension of CdI$_2$ (1.00 g, 2.7 mmol) in THF (*ca.* 20 mL). A yellow precipitate of TlI was immediately deposited. The mixture was stirred at room temperature for 30 min and filtered. The filtrate was concentrated and placed at 0 °C, giving colorless crystals of {η^3-HB(3-Bu^{t}pz)$_3$}CdI, which were isolated by filtration and dried in vacuo (1.0 g, 62%). Anal. Calcd for {η^3-HB(3-Bu^{t}pz)$_3$}CdI: C, 40.6; H, 5.5; N, 13.5. Found: C, 39.3; H, 5.1; N, 11.9 (nitrogen analysis was consistently low). IR data: 2946 (ν_{B-H}). ^{1}H NMR (C$_6$D$_6$): δ 1.44 [27H, s, {η^3-HB{C$_3$N$_2$H$_2$C(C*H*$_3$)$_3$}$_3$], 5.83 [3H, d, $^3J_{H-H}$ = 2.6, η^3-HB{C$_3$N$_2$*H*$_2$C(CH$_3$)$_3$}], 7.36 [3H, d, $^3J_{H-H}$ = 2.6, η^3-HB{C$_3$N$_2$*H*$_2$C(CH$_3$)$_3$}$_3$]. ^{13}C NMR (C$_6$D$_6$): δ 31.5 [q, $^1J_{C-H}$ = 126, η^3-HB{C$_3$N$_2$H$_2$C(*C*H$_3$)$_3$}$_3$], 32.2 [s, η^3-HB{C$_3$N$_2$H$_2$*C*(CH$_3$)$_3$}$_3$], 102.3 [d, $^1J_{C-H}$ = 176; d, $^2J_{C-H}$ = 8; η^3-HB{*C*$_3$N$_2$H$_2$C(CH$_3$)$_3$}$_3$], 132.0 [d, $^1J_{C-H}$ = 185; d, $^2J_{C-H}$ = 5; η^3-HB{*C*$_3$N$_2$H$_2$C(CH$_3$)$_3$}$_3$], 165.3 [s, η^3-HB{*C*$_3$N$_2$H$_2$C(CH$_3$)$_3$}$_3$].

Synthesis of {η^3-HB(3-Bu^t-5-Mepz)$_3$}CdCH$_3$. A solution of Cd(CH$_3$)$_2$ (excess) in toluene was added to a solution of Tl{η^3-HB(3-Bu^t-5-Mepz)$_3$} (0.50 g, 0.8 mmol) in Et$_2$O (30 mL), resulting in the formation of a black deposit. The mixture was stirred for 1 h at room temperature and filtered. The solvent was removed from the filtrate under reduced pressure and cooled to 0 °C, giving a crop of colorless crystals. The crystals of {η^3-HB(3-Bu^t-5-Mepz)$_3$}CdCH$_3$ were isolated by filtration and dried *in vacuo* (0.24 g, 55%). Anal. Calcd for {η^3-HB(3-Bu^t-5-Mepz)$_3$}CdCH$_3$: C, 54.5; H, 7.9; N, 15.3. Found: C, 53.9; H, 7.4; N, 14.6. ^{1}H NMR (C$_6$D$_6$): δ 0.56 [3H, s, Cd–C*H*$_3$, $^2J_{Cd-H}$ = 71 and 74], 1.40 [27H, s, η^3-HB{C$_3$N$_2$H(CH$_3$)C*Me*$_3$}$_3$], 2.20 [9H, s, η^3-HB{C$_3$N$_2$H(C*H*$_3$)CMe$_3$}$_3$], 5.72 [3H, s, η^3-HB{C$_3$N$_2$*H*(CH$_3$)CMe$_3$}$_3$]. ^{13}C NMR (C$_6$D$_6$): δ –6.1 [q, $^1J_{C-H}$ = 126, Cd–*C*H$_3$], 13.1 [q, $^1J_{C-H}$ = 128, η^3-HB{C$_2$N$_2$CH(*CH*$_3$)CMe$_3$}$_3$], 30.8 [q, $^1J_{C-H}$ = 127, η^3-HB{C$_2$N$_2$CH(CH$_3$)C*Me*$_3$}$_3$], 31.7 [s, η^3-HB{C$_2$N$_2$CH(CH$_3$)*C*Me$_3$}$_3$], 102.8 [d, $^1J_{C-H}$ = 172, η^3-HB{C$_2$N$_2$*C*H-(CH$_3$)CMe$_3$}$_3$], 144.1 and 162.4 [s, η^3-HB{*C*$_2$N$_2$CH(CH$_3$)CMe$_3$}$_3$]. IR data: 2565 (ν_{B-H}).

Synthesis of {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO). A fine suspension of K{HB(3-Bu^t-5-Mepz)$_3$} (0.75 g, 1.62 mmol) in THF (20 mL) was added to a solution of Cd(NO$_3$)$_2$·4(H$_2$O) (0.68 g, 2.2 mmol) in THF (10 mL). The mixture was stirred overnight at room temperature, giving a white precipitate, which was removed by filtration. The filtrate was concentrated under reduced pressure and placed at 0 °C, giving {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO) as colorless crystals. {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO) was isolated by filtration and dried *in vacuo* (0.5 g, 52%). Anal. Calcd for {η^3-HB(3-Bu^t-5-Mepz)$_3$}Cd(η^2-O$_2$NO): C, 48.2; H, 6.7; N, 16.4. Found: C, 48.2; H, 6.5; N, 15.7. ^{1}H NMR (C$_6$D$_6$): δ 1.32 [27H, s, η^3-HB{C$_3$N$_2$H(CH$_3$)C*Me*$_3$}$_3$], 2.08 [9H, s, η^3-HB{C$_3$N$_2$H(C*H*$_3$)CMe$_3$}$_3$], 5.64 [3H, s, η^3-HB{C$_3$N$_2$*H*(CH$_3$)CMe$_3$}$_3$]. ^{13}C NMR (C$_6$D$_6$): δ 13.1 [q, $^1J_{C-H}$ = 128, η^3-HB{C$_2$N$_2$CH(*C*H$_3$)CMe$_3$}$_3$], 30.3 [q, $^1J_{C-H}$ = 128, η^3-HB{C$_2$N$_2$CH(CH$_3$)C*Me*$_3$}$_3$], 31.5 [s, η^3-HB{C$_2$N$_2$CH(CH$_3$)*C*Me$_3$}$_3$], 103.5 [d, $^1J_{C-H}$ = 174, η^3-HB{C$_2$N$_2$*C*H-(CH$_3$)CMe$_3$}$_3$], 145.7 and 163.7 [s, η^3-HB{*C*$_2$N$_2$CH(CH$_3$)CMe$_3$}$_3$]. IR data: 2574 (ν_{B-H}).

X-ray Structure Determination of {η^3-HB(3,5-Pr$^i_2$pz)$_3$}CdI. Crystal data and data collection and refinement parameters for {η^3-HB(3,5-Pr$^i_2$-pz)$_3$}CdI are summarized in Table 14. A single crystal of {η^3-HB(3,5-Pr$^i_2$pz)$_3$}CdI was mounted in a glass capillary that was then placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.710 73 Å). Check relections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects (based on ψ scans). The structure was solved using direct methods and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[43] Systematic absences were consistent with the space groups $P2_1/m$ (No. 11) and $P2_1$ (No. 4), but the structure was successfully solved with the choice $P2_1/m$ (No. 11). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions (d_{C-H} = 0.96 Å; U_{iso}(H) = 1.2U_{iso}(C)). Block-diagonal least-squares refinement converged to R = 0.0460 (R_w = 0.0689). Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 9, and selected bond distances and angles are listed in Tables 1 and 2.

X-ray Structure Determination of {η^3-HB(3-Bu^{t}pz)$_3$}CdI. Crystal data and data collection and refinement parameters are summarized in Table 14, and the general procedure is as described for {η^3-HB(3,5-Pr$^i_2$pz)$_3$}-CdI. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects (based on ψ scans). Systematic absences were consistent with the space groups $P\bar{4}2_1m$ (No. 113) and $P42_12$ (No. 90), but the structure was successfully solved with the choice $P\bar{4}2_1m$ (No. 113). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions (d_{C-H} = 0.96 Å; U_{iso}(H) = 1.2 U_{iso}(C)). Block-diagonal least-squares refinement converged to R = 0.0522 (R_w = 0.0623). Inversion of configuration indicated the correct choice of enantiomorph. Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 10, and selected bond distances and angles are listed in Tables 3 and 4.

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X-ray Structure Determination of $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$CdCH$_3$. Crystal data and data collection and refinement parameters are summarized in Table 14, and the general procedure is as described for $\{\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3\}$CdI. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects (based on ψ scans). Systematic absences were consistent uniquely with the space group $I\bar{4}3d$ (No. 220). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions ($d_{\text{C-H}}$ = 0.96 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$). Block-diagonal least-squares refinement converged to $R = 0.0433$ ($R_w = 0.0504$). Inversion of configuration indicated the correct choice of enantiomorph. Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 11, and selected bond distances and angles are listed in Tables 5 and 6.

X-ray Structure Determination of $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO). Crystal data and data collection and refinement parameters are summarized in Table 14, and the general procedure is as described for $\{\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3\}$CdI. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption effects (based on ψ scans). Systematic absences were consistent uniquely with the space group $P2_1/n$ (No. 14). Most of the hydrogen atoms were located in the difference map after all the non-hydrogen atoms were located and refined anisotropically, but hydrogens on carbon were allowed to refine in calculated positions ($d_{\text{C-H}}$ = 0.96 Å; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$). Block-diagonal least-squares refinement converged to $R = 0.0395$ ($R_w = 0.0525$). Atomic coordinates and thermal parameters for non-hydrogen atoms are listed in Table 12, and selected bond distances and angles are listed in Tables 7 and 8.

Conclusion

In summary, a series of [tris(pyrazolyl)hydroborato]cadmium complexes of the type $\{\eta^3$-HB(3,5-RR′pz)$_3\}$CdX [3,5-RR′pz = 3-Bu^{t}pz, 3-Bu^t-5-Mepz, 3,5-Pr$^i{}_2$pz; X = CH$_3$, I, NO$_3$] have been synthesized by the reaction between CdX$_2$ and either the potassium or thallium reagent M{HB(3,5-RR′pz)$_3$} (M = K, Tl). The complex $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO) exhibits bidentate coordination of the nitrate ligand, in contrast to the unidentate coordination mode that is observed in the related zinc derivative $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$Zn(η^1-ONO$_2$). In view of the lower activity of cadmium-substituted carbonic anhydrase compared with the zinc enzyme, this result supports the notion that facile access to a unidentate bicarbonate intermediate may be a critical requirement for carbonic anhydrase activity.

Note Added in Proof. Since submission of this manuscript, two other papers concerned with tris(pyrazolyl)hydroborato complexes of cadmium have appeared.[44]

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Supplementary Material Available: Tables of complete crystal and intensity collection data, hydrogen atomic coordinates and temperature factors, bond distances and angles, and anisotropic displacement parameters for $\{\eta^3$-HB(3,5-Pr$^i{}_2$pz)$_3\}$CdI, $\{\eta^3$-HB(3-Bu^{t}pz)$_3\}$CdI, $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$CdCH$_3$, and $\{\eta^3$-HB(3-Bu^t-5-Mepz)$_3\}$Cd(η^2-O$_2$NO) (21 pages). Ordering information is given on any current masthead page.

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