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Bis(mercaptoimidazolyl)(pyrazolyl)hydroborato Complexes of Zinc, Cadmium, and Cobalt: Structural Evidence for the Enhanced Tendency of Zinc in Biological Systems to Adopt Tetrahedral M[S$_4$] Coordination

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The bis(2-mercapto-1-methylimidazolyl)(pyrazolyl)hydroborato derivatives $[\mathrm{pzBm^{Me}}]_2\mathrm{Zn}$, $[\mathrm{pzBm^{Me}}]_2\mathrm{Co}$, and $[\mathrm{pzBm^{Me}}]_2\mathrm{Cd}$ have been isolated and structurally characterized by X-ray diffraction. Despite their common $[\mathrm{pzBm^{Me}}]_2\mathrm{M}$ composition, each of these complexes adopts a different structure. Thus, (i) the zinc complex exhibits a tetrahedral Zn[S$_4$] structure in which only the sulfur donors coordinate to zinc, (ii) the cobalt complex exhibits a trigonal-bipyramidal Co[S$_3$NH] structure in which one of the pyrazolyl groups and one of the B−H groups coordinate to cobalt, and (iii) the cadmium complex exhibits a six-coordinate Cd[S$_4$H$_2$] structure in which both B−H groups interact with the cadmium center. These comparisons emphasize that zinc has a greater preference for tetrahedral M[S$_4$] coordination than does either cobalt or cadmium, an observation that is in accord with the prevalent role of zinc in the structural sites of enzymes.

Introduction

We have recently reported the use of bis(mercaptoimidazolyl)(pyrazolyl)hydroborato ligands to provide [SSN] coordination environments that are suitable for modeling aspects of the bioinorganic chemistry of zinc enzymes.[1] Since metal ion substitution of enzyme active sites is a commonly employed technique of providing both structural and mechanistic information,[2−4] it is important to ascertain how biologically relevant ligand complements influence the coordination geometries of different metals. In this paper, we report the syntheses and structures of bis(mercaptoimidazolyl)(pyrazolyl)hydroborato derivatives of zinc, cadmium, and cobalt.

Results and Discussion

We have recently reported the use of the hybrid bis(2-mercapto-1-methylimidazolyl)(pyrazolyl)hydroborato ligand to prepare the 1:1 zinc complexes $[\mathrm{pzBm^{Me}}]\mathrm{ZnMe}$[5] and $[\mathrm{pzBm^{Me}}]\mathrm{ZnI}$.[1a,6] Treatment of these complexes with a variety of reagents (e.g., alcohols and alkoxides) promotes ligand redistribution and the formation of the "sandwich" complex $[\mathrm{pzBm^{Me}}]_2\mathrm{Zn}$. The latter complex may also be obtained directly from the reaction of $[\mathrm{pzBm^{Me}}]\mathrm{Li}$[1a] with $\mathrm{Me_2Zn}$ using methanol as a solvent (Scheme 1).

The molecular structure of $[\mathrm{pzBm^{Me}}]_2\mathrm{Zn}$ has been determined by X-ray diffraction (Figure 1). Interestingly, rather than adopting an octahedral structure similar to that of the tris(pyrazolyl)hydroborato complex $[\mathrm{Tp^{Me_2}}]_2\mathrm{Zn}$,[7,8] the pyrazolyl groups in $[\mathrm{pzBm^{Me}}]_2\mathrm{Zn}$ do not coordinate to zinc, such that the structure is based on a tetrahedron. The Zn[S$_4$] coordination motif is similar to that of the related complex which is devoid of the additional pyrazolyl group, namely $[\mathrm{Bm^{Me}}]_2\mathrm{Zn}$.[5] The coordination motif also resembles the structural sites in a variety of zinc enzymes, such as liver alcohol dehydrogenase.[9] The Zn[S$_4$] coordination in $[\mathrm{pzBm^{Me}}]_2\mathrm{Zn}$ is also of interest because it clearly demonstrates the preference for sulfur coordination over nitrogen coordination, an observation that is in accord with the

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(6) Bis- and tris(pyrazolyl)hydroborato ligands are represented by the abbreviations $[\mathrm{Bp^{RR'}}]$ and $[\mathrm{Tp^{RR'}}]$, with the 3- and 5-alkyl substituents listed respectively as superscripts. A substituent (X) on boron other than hydrogen is listed as a prefix, i.e., $[\mathrm{XBp^{RR'}}]$ or $[\mathrm{XTp^{RR'}}]$. By analogy, we use the abbreviations $[\mathrm{Bm^{R}}]$ and $[\mathrm{Tm^{R}}]$ to represent the bis(2-mercapto-1-alkylimidazolyl)borate and tris(2-mercapto-1-alkylimidazolyl)borate ligands, respectively.

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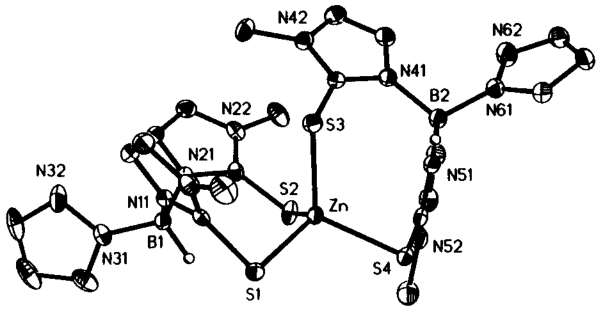
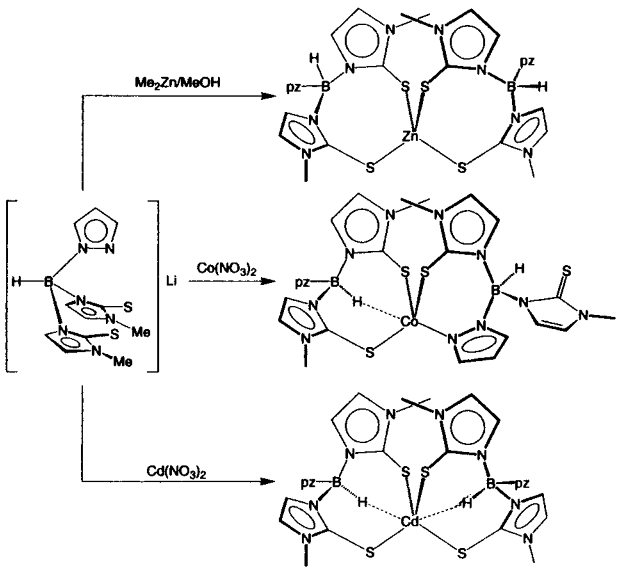


Figure 1. Molecular structure of [pzBm^{Me}]$_2$Zn. Selected bond lengths (Å) and angles (deg): Zn−S(1) 2.3392(8), Zn−S(2) 2.3389(8), Zn−S(3) 2.3432(7), Zn−S(4) 2.3404(7); S(1)−Zn−S(2) 116.43(3), S(1)−Zn−S(3) 101.37(3), S(1)−Zn−S(4) 109.90(3), S(2)−Zn−S(3) 113.40(3), S(2)−Zn−S(4) 100.96(3), S(3)−Zn−S(4) 115.39(3).

Scheme 1



prevalence of tetrahedral Zn[S$_4$] coordination in zinc enzymes.[9] Although the pyrazolyl group of [pzBm^{Me}] does not coordinate to zinc in [pzBm^{Me}]$_2$Zn, it should be noted that the pyrazolyl donor does bind in the aforementioned heteroleptic complexes of the type [pzBm^{Me}]ZnX (X = CH$_3$, I).[1a,5]

The cobalt analogue, [pzBm^{Me}]$_2$Co, has been prepared from the reaction of [pzBm^{Me}]Li with Co(NO$_3$)$_2$·6H$_2$O. Interestingly, the structure of [pzBm^{Me}]$_2$Co (Figure 2) is very different from that of the zinc counterpart; thus, rather than both [pzBm^{Me}] ligands coordinating by two sulfur donors, only one of the [pzBm^{Me}] ligands in [pzBm^{Me}]$_2$Co coordinates by both sulfur donors, while the other coordinates by one nitrogen and one sulfur donor. A further distinction is that the [pzBm^{Me}] ligand which coordinates via the two sulfur donors also participates in a 3-center-2-electron M···H−B interaction. The latter interaction is made possible by the [pzBm^{Me}] ligand adopting a configuration which results in a "boat-like" eight-membered ring, as opposed to the "chair-like" rings that are present in [pzBm^{Me}]$_2$Zn. The Co···H distance in [pzBm^{Me}]$_2$Co is 1.98(5) Å, a value which is comparable to that in the bis(pyrazolyl)hydroborato complex, [Bp^{But,Pri}]$_2$Co (1.95 Å).[10] The coordination geometry in [pzBm^{Me}]$_2$Co is, therefore, best described as trigonal bipyramidal, with the sulfur donors occupying the three equatorial sites and the nitrogen and hydrogen atoms occupying the two axial positions. It is also worth noting that the structure of [pzBm^{Me}]$_2$Co is very different from that of the phenyl-bis[(methylthio)methyl](pyrazolyl)borate derivative, [PhB(CH$_2$SMe)$_2$(pz)]$_2$Co, which has been proposed by Riordan to have an octahedral structure with coordination of all nitrogen and sulfur donors.[11]

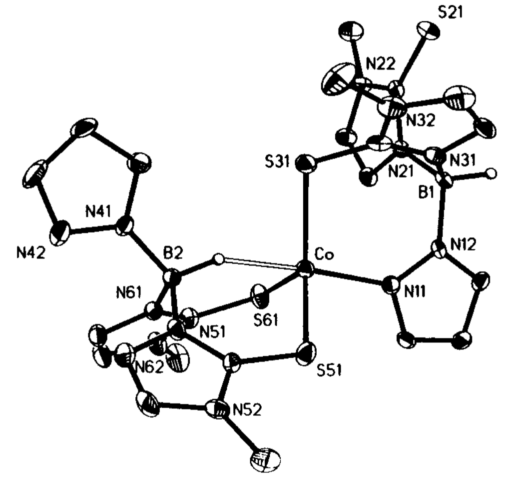


Figure 2. Molecular structure of [pzBm^{Me}]$_2$Co. Selected bond lengths (Å) and angles (deg): Co−N(11) 2.051(6), Co−S(31) 2.320(5), Co−S(51) 2.312(4), Co−S(61) 2.303(4), Co−H(2) 1.98(5); N(11)−Co−S(31) 105.2(2), N(11)−Co−S(51) 94.9(2), N(11)−Co−S(61) 94.4(2), S(31)−Co−S(51) 122.7(1), S(31)−Co−S(61) 119.9(2), S(51)−Co−S(61) 111.0(1).

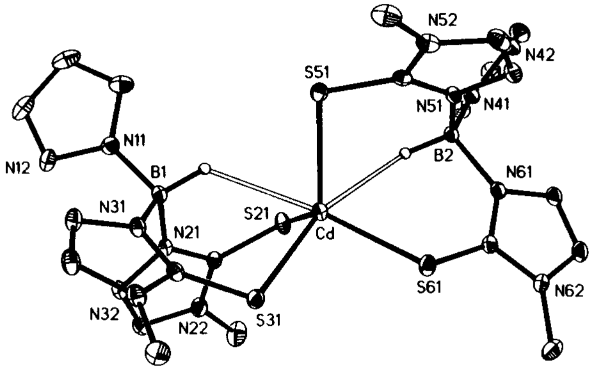


Figure 3. Molecular structure of [pzBm^{Me}]$_2$Cd. Selected bond lengths (Å) and angles (deg): Cd−S(21) 2.5259(7), Cd−S(31) 2.5660(7), Cd−S(51) 2.5365(7), Cd−S(61) 2.5723(7), Cd−H(1) 2.58(2), Cd−H(2) 2.55(2); S(21)−Cd−S(31) 105.79(2), S(21)−Cd−S(51) 112.11(2), S(21)−Cd−S(61) 123.72(2), S(31)−Cd−S(51) 118.74(2), S(31)−Cd−S(61) 86.75(2), S(51)−Cd−S(61) 108.07(2).

The cadmium derivative [pzBm^{Me}]$_2$Cd (Scheme 1) belongs to yet a different structural type of [pzBm^{Me}]$_2$M derivatives. Thus, while the structure of [pzBm^{Me}]$_2$Cd (Figure 3) is similar to that of the zinc complex (Figure 1) in that each [pzBm^{Me}] ligand coordinates through the two sulfur donors, the two structures are not superimposable. For example, a simple indication of the difference in structures is provided by examining the deviation of the S−M−S bond angles from the tetrahedral value (Table 1). Thus, the S−Zn−S bond angles in [pzBm^{Me}]$_2$Zn (100−116°) are close to the tetrahedral value, whereas the corresponding S−Cd−S bond angles in [pzBm^{Me}]$_2$Cd (87−124°) deviate considerably from the tetrahedral value. This distortion from tetrahedral geometry is accompanied by the cadmium participating in a secondary interaction with both

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Table 1. Range of S−M−S(N) Bond Angles (deg) for $[pzBm^{Me}]_2M$

$[pzBm^{Me}]_2Zn$	100−116	range = 16
$[pzBm^{Me}]_2Cd$	87−124	range = 37
$[pzBm^{Me}]_2Co$	95−123	range = 28

B−H moieties [d(Cd···H) = 2.55(2) and 2.58(2) Å]; in comparison, the corresponding values for $[pzBm^{Me}]_2Zn$ are considerably longer (3.31 and 3.34 Å). As with the cobalt derivative, the Cd···H interactions require the $[pzBm^{Me}]$ ligand to adopt a configuration which results in "boat-like" eight-membered rings.

The fact that the zinc complex $[pzBm^{Me}]_2Zn$ exhibits a structure different from those of the cobalt and cadmium complexes is of relevance to the use of these metals as spectroscopic probes for studying zinc enzymes.[2,3] For example, cobalt is frequently substituted for zinc in zinc enzymes because it has distinct electronic spectroscopic properties and also has a pronounced tendency to form tetrahedral complexes. However, even though cobalt shows a strong preference for tetrahedral coordination,[12] comparison of the structures of $[pzBm^{Me}]_2Zn$ and $[pzBm^{Me}]_2Co$ indicates that the preference for tetrahedral $M[S_4]$ coordination is actually greater for zinc. Likewise, although cadmium-substituted enzymes are studied, due to the NMR spectroscopic properties of ^{111}Cd and ^{113}Cd,[13,14] it must be recognized that the coordination geometries of the Cd active site may not be similar to those of the native zinc enzymes,[1a] thereby contributing to the dramatic differences in activity of the substituted enzymes.

Experimental Section

Table 2. Crystal, Intensity Collection, and Refinement Data

	$[pzBm^{Me}]_2Zn$	$[pzBm^{Me}]_2Cd$	$[pzBm^{Me}]_2Co$
lattice	orthorhombic	triclinic	monoclinic
formula	$C_{22}H_{28}B_2N_{12}S_4Zn$	$C_{22}H_{28}B_2N_{12}S_4Cd$	$C_{22}H_{28}B_2N_{12}S_4Co$
formula weight	675.79	722.82	669.35
space group	*Pbcn* (No. 60)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (Å)	26.702(1)	10.2206(5)	8.85(2)
b (Å)	13.0013(6)	12.2152(6)	14.75(4)
c (Å)	17.5785(9)	13.9540(7)	23.53(6)
α (deg)	90	78.083(1)	90
β (deg)	90	72.557(1)	91.64(4)
γ (deg)	90	69.113(1)	90
V (Å^3)	6102.5(5)	1543.1(1)	3071(12)
Z	8	2	4
temp (K)	293	223	233
radiation (λ, Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.471	1.556	1.448
μ (Mo Kα, mm^{-1})	1.115	1.014	0.867
θ max (deg)	28.3	28.3	28.6
no. of data	6908	6861	6357
no. of parameters	379	383	383
R1^a	0.0406	0.0307	0.0731
wR2^a	0.0963	0.0660	0.1157
GOF	1.028	1.013	1.011

[a] $R1 = [\Sigma||F_o| - |F_c||]/[\Sigma|F_o|]$ and $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/[\Sigma[w(F_o^2)^2]]^{1/2}$.

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, and Schlenk techniques.[15] Solvents were purified and degassed by standard procedures. NMR spectra were recorded on Bruker Avance 300wb DRX, Bruker Avance 400 DRX, and Bruker Avance 500 DMX spectrometers. ^1H and ^{13}C chemical shifts are reported in parts per million relative to $SiMe_4$ (δ = 0) and were referenced internally with respect to the protio solvent impurity and the ^{13}C resonances, respectively. All coupling constants are reported in Hz. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1430 or 1600 spectrophotometer and are reported in cm^{-1}. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 CHN Elemental Analyzer. Mass spectra were obtained on a Micromass Quadrupole-Time-of-Flight mass spectrometer using an electrospray ion source. $[pzBm^{Me}]Li$[1a] was obtained as previously reported.

Synthesis of $[pzBm^{Me}]_2Zn$. $[pzBm^{Me}]Li$ (390 mg, 1.3 mmol) was added to a mixture of $ZnMe_2$ (0.5 mL, 2 M in toluene) in methanol (3 mL). The mixture was stirred at room temperature for 4 h, during which a white precipitate was deposited. The volatile components were removed in vacuo, and the product was washed with toluene (16 mL), followed by extraction into chloroform (40 mL). After filtration, the solvent was removed in vacuo, giving $[pzBm^{Me}]_2Zn$ as a white powder (342 mg, 78% based on $[pzBm^{Me}]Li$). Single crystals suitable for X-ray diffraction were obtained by slow crystallization from chloroform at room temperature. *m/z*: 675 (M + 1)$^+$. IR data (KBr disk, cm^{-1}): 2513 (w) [ν(B−H)]. ^1H NMR ($CDCl_3$): δ 3.52 [s, $2(SC_3N_2H_2C\underline{H}_3)$], 6.26 [t, J_{H-H} = 2, $C_3N_2\underline{H}_3$ (1H)], 6.72 [d, J_{H-H} = 2, $2(SC_3N_2\underline{H}_2CH_3)$ (2H)], 6.88 [br, $2(SC_3N_2\underline{H}_2CH_3)$ (2H)], 7.25 [br, $C_3N_2\underline{H}_3$ (1H)], 7.96 [d, J_{H-H} = 2, $C_3N_2\underline{H}_3$ (1H)], 4.85 [br, $B\underline{H}$]. ^{13}C NMR ($CDCl_3$): δ 34.8 [q, $^1J_{C-H}$ = 141, $2(SC_3N_2H_2\underline{C}H_3)$], 118.9 [d, $^1J_{C-H}$ = 194, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)], 123.3 [d, $^1J_{C-H}$ = 195, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)], 156.5 [s, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)], 105.3 [d, $^1J_{C-H}$ = 179, $\underline{C}_3N_2H_3$ (1C)], 138.9 [d, $^1J_{C-H}$ = 202, $\underline{C}_3N_2H_3$ (1C)], 141.6 [d, $^1J_{C-H}$ = 185, $\underline{C}_3N_2H_3$ (1C)].

Synthesis of $[pzBm^{Me}]_2Cd$. A mixture of $[pzBm^{Me}]Li$ (500 mg, 1.6 mmol) and $Cd(NO_3)_2 \cdot 4H_2O$ (247 mg, 0.8 mmol) in MeOH (10 mL) was stirred for 4 h. The mixture was filtered, giving crude $[pzBm^{Me}]_2Cd$ as a white solid. The latter material was extracted into MeOH (ca. 40 mL), giving a colorless solution, which was concentrated to ca. 10 mL. The solution was allowed to stand at room temperature, depositing $[pzBm^{Me}]_2Cd$ as a white precipitate (415 mg, 72%) over a period of 2 h. Single crystals suitable for X-ray diffraction were obtained by slow crystallization from methanol at room temperature. Anal. Calcd for $[pzBm^{Me}]_2Cd$: C, 36.6; H, 3.9; N, 23.3. Found: C, 35.5; H, 3.5; N, 23.7. ^1H NMR (CD_3OD): δ 3.61 [s, $2(SC_3N_2H_2C\underline{H}_3)$], 4.90 [br, $B\underline{H}$], 6.35 [t, $J_{H-H} \approx 2$, $C_3N_2\underline{H}_3$ (1H)], 6.78 [br, $2(SC_3N_2\underline{H}_2CH_3)$ (2H)], 7.08 [d, $J_{H-H} \approx 2$, $2(SC_3N_2\underline{H}_2CH_3)$ (2H)], 7.70 [d, $J_{H-H} \approx 2$, $C_3N_2\underline{H}_3$ (1H)], 7.82 [d, $J_{H-H} \approx 2$, $C_3N_2\underline{H}_3$ (1H)]. ^{13}C NMR (CD_3OD): δ 35.2 [q, $J_{C-H} \approx 141$, $2(SC_3N_2H_2\underline{C}H_3)$], 106.6 [d, $J_{C-H} \approx 174$, $\underline{C}_3N_2H_3$ (1C)], 123.9 [d, $J_{C-H} \approx 194$, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)], 122.0 [d, $J_{C-H} \approx 197$, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)], 143.5 [d, $J_{C-H} \approx 186$, $\underline{C}_3N_2H_3$ (1C)], 139.5 [d, $J_{C-H} \approx 166.4$, $\underline{C}_3N_2H_3$ (1C)], 156.1 [s, $2(S\underline{C}_3N_2H_2CH_3)$ (2C)].

Synthesis of $[pzBm^{Me}]_2Co$. $Co(NO_3)_2 \cdot 6H_2O$ (55 mg, 0.19 mmol) was added to a solution of $[pzBm^{Me}]Li$ (175 mg, 0.56 mmol) in $CHCl_3$ (10 mL), giving a green solution. The mixture was stirred at room temperature for 2 h, during which a white precipitate was deposited. The mixture was filtered, and the volatile components were removed

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in vacuo. The product was washed with pentane (3 mL), giving [pzBm^{Me}]$_2$Co as an emerald green powder (108 mg, 86%). Crystals suitable for X-ray diffraction were obtained from CHCl$_3$/toluene. Anal. Calcd for [pzBm^{Me}]$_2$Co·C$_7$H$_8$: C, 45.7; H, 4.8; N, 22.1. Found: C, 46.4; H, 4.1; N, 22.6. IR data (KBr disk, cm^{-1}): 2429 (m) [ν(B−H)]. ^{1}H NMR (CDCl$_3$): δ 21.7, 16.1, 6.8, 3.7, 1.6 (assignments not given due to the paramagnetic nature of the sample). UV−vis in CHCl$_3$ (λ/nm and ϵ/M^{-1} cm^{-1}): 368 (8300), 511 (2440).

X-ray Structure Determinations. X-ray diffraction data for [pzBm^{Me}]$_2$M (M = Zn, Cd, Co) were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector and crystal data; data collection and refinement parameters are summarized in Table 2. The structures were solved using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (version 5.03).[16] Hydrogen atoms on carbon were included in calculated positions.

Conclusions

In summary, the structural characterization of [pzBm^{Me}]$_2$Zn, [pzBm^{Me}]$_2$Co, and [pzBm^{Me}]$_2$Cd provides an instructive comparison which indicates that zinc(II) shows a greater preference for tetrahedral M[S$_4$] coordination than does either cobalt(II) or cadmium(II). Thus, while the zinc complex exhibits a tetrahedral Zn[S$_4$] structure, the cobalt counterpart has a trigonal-bipyramidal structure of the type Co[S$_3$NH], and the cadmium derivative has a six-coordinate structure of the type Cd[S$_4$H$_2$]. In the latter example, the M···H−B interactions are made possible by the [pzBm^{Me}] ligand adopting a boatlike configuration. The greater tetrahedral M[S$_4$] coordination preference for zinc is in accord with the observation that zinc is found extensively as a tetrahedral template in molding the structures of many enzymes.

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Supporting Information Available: Crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Sheldrick, G. M. *SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*; University of Göttingen: Göttingen, Germany, 1981.