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Homoleptic Group 12 Metal Bis(mercaptoimidazolyl)borate Complexes $M(Bm^R)_2$ (M = Zn, Cd, Hg)

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The sodium salt of the bis(2-mercapto-1-methylimidazolyl)borate anion $[Bm^{Me}]^-$ and those of the new bis(2-mercapto-1-alkylimidazolyl)borates $[Bm^R]^-$ (R = Bz, Bu^t, *p*-Tol) have been readily obtained from $NaBH_4$ and the appropriate 2-mercapto-1-alkylimidazoles. To contrast the binding preferences of the group 12 metals in a sulfur-rich environment, the four complete series of homoleptic complexes $M[Bm^R]_2$ (M = Zn, Cd, Hg), including the first bis(mercaptoimidazolyl)borate derivatives of cadmium and mercury, have been prepared. X-ray diffraction studies of $Cd[Bm^{Me}]_2$ and $M[Bm^{tBu}]_2$ (M = Zn, Cd, Hg) show the presence of distorted tetrahedral $[MS_4]$ central cores supplemented by two weak vicinal M···H–B bonds, interactions which appear to be a common feature in the coordination chemistry of Bm^R ligands. In the case of zinc, it has been found that only in the presence of bulky ligands, as in $Zn[Bm^{tBu}]_2$, may an unexpected expansion in the coordination number from four to six be induced. This observation suggests the viability of octahedral intermediates in the processes whereby certain zinc enzymes transfer or exchange metal ions.

Introduction

The coordination chemistry of the tris(mercaptoimidazolyl)borate ligand system (Figure 1)[1] is expanding at an accelerated pace, and recent advances include the preparation of mononuclear zinc hydroxide[2] and cadmium thiolate[3] complexes and the structural characterization of the first complete series of group 12 metal derivatives $[Tm^R]MBr$ (M = Zn, Cd, Hg; R = Me, Bu^t).[4,5] In contrast, applications of the related bis(mercaptoimidazolyl)borates (Figure 1)[6] have been more sporadic. In this regard, whereas Parkin has prepared a number of zinc complexes using the lithium or thallium reagents $M[Bm^R]$ (M = Li, Tl; R = Me, Mes),[7] Santos and co-workers have obtained several Bm^R derivatives of rhenium, technetium, and uranium.[8,9] Our entry into this arena was marked by the synthesis of paramagnetic $Ni[Bm^R]_2$ species as model compounds for the nickel center in the

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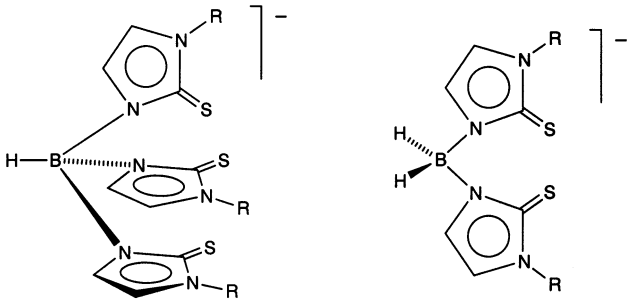


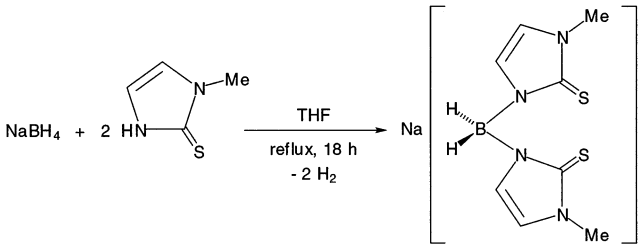
Figure 1. Tris(mercaptoimidazolyl)borate (Tm^R) and bis(mercaptoimidazolyl)borate (Bm^R) ligand systems.

active site of NiFe hydrogenases.[10] Interestingly, these complexes exhibit distorted octahedral geometries with unprecedented $[NiS_4H_2]$ cores due to the presence of two fairly strong Ni···H−B interactions. Interested in ascertaining whether such 3-center−2-electron bonds are a standard feature in Bm^R chemistry, and prompted by the fact that poly(mercaptoimidazolyl)borates are becoming increasingly attractive ligands in bioinorganic chemistry,[11] we set out to prepare new homoleptic Bm^R complexes of the group 12 metals. Such an endeavor will allow their coordination preferences in a sulfur-rich environment to be directly compared and may also provide insight into the subtle structural factors that govern the processes whereby certain cysteine-rich metalloproteins (e.g., zinc metallothioneins)[12] undergo conformational changes[13] or exchange metal ions with their heavier group congeners.[14] We describe in this paper the preparation of three new bis(mercaptoimidazolyl)borate ligands and the synthesis and structures of several homoleptic complexes of zinc, cadmium, and mercury.

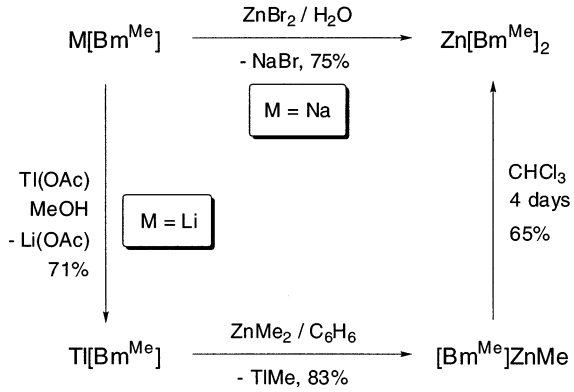
Results and Discussion

The sodium salt of the bis(2-mercapto-1-methylimidazolyl)borate anion $[Bm^{Me}]^-$ was readily prepared from $NaBH_4$ and 2 molar equiv of 2-mercapto-1-methylimidazole (methimazole) in refluxing tetrahydrofuran (THF), as illustrated in Scheme 1.[15] After partial evaporation of the solvent and addition of pentane, the desired product was isolated in spectroscopically pure form (i.e., by ^{1}H NMR

Scheme 1



Scheme 2



spectroscopy) in almost quantitative yield (ca. 95%). In a similar fashion, the new bulkier bis(mercaptoimidazolyl)borate derivatives $Na[Bm^R]$ (R = Bz, Bu^t, *p*-Tol) were also obtained in 70−90% yield starting from the appropriate 2-mercapto-1-alkylimidazoles. Although repeated attempts to obtain satisfactory elemental analyses (CHN) for these compounds have not been successful, they are all sufficiently pure for further reactions (see later discussion). The yields in which the $Na[Bm^R]$ compounds reported here are isolated compare favorably with those reported for the lithium derivatives $Li[Bm^R]$ (R = Me, 54%; R = Mes, 70%).[7] Perhaps more importantly, a potential advantage of the $Na[Bm^R]$ salts over the latter is the ease with which the sodium halide byproducts can be separated from metathetical reactions involving metal halides. $Na[Bm^R]$ (R = Me, Bz, Bu^t, *p*-Tol) species are all white, thermally robust, air-stable solids, only sparingly soluble in toluene but more so in THF, acetonitrile, dimethyl sulfoxide (DMSO), and methanol. In addition, the *p*-tolyl-substituted derivative is soluble in dichloromethane, $Na[Bm^R]$ (R = Bz, Bu^t) species are soluble in chloroform, and the methyl- and *tert*-butyl-substituted species are soluble (and stable!) in water. All four $Na[Bm^R]$ compounds are spectroscopically similar to the lithium species $Li[Bm^R]$,[7] featuring also two peaks between 6.7 and 7.2 ppm for the imidazolyl hydrogens in their ^{1}H NMR spectra and usually two distinctive bands of medium intensity in the 2300−2400 cm^{-1} range (ν_{B-H}) in their solid-state IR spectra.

The bis(mercaptoimidazolyl)borate complex $Zn[Bm^{Me}]_2$ was easily obtained by mixing aqueous solutions of zinc(II) bromide and $Na[Bm^{Me}]$ (1:2 ratio) and isolated in pure form

(9) Some complexes containing alkylbis(mercaptoimidazolyl)borate ligands $[H(R)B(mim^{Me})_2]^-$ have also been recently synthesized. See ref 8b and the following: Garcia, R.; Paulo, A.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **2001**, *632*, 41−48.

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(15) The use of higher boiling point solvents (e.g., toluene) invariably resulted in the formation of a mixture of $Na[Bm^{Me}]$ and $Na[Tm^{Me}]$, even if shorter reactions times are used.

as a white solid in 75% yield. This represents a tangible improvement over the reported three-step synthesis of $Zn[Bm^{Me}]_2$ (Scheme 2)[7] which was, prior to our work, the only known homoleptic bis(mercaptoimidazolyl)borate complex of the group 12 metals. As an extension of our more general method, all the $M[Bm^R]_2$ complexes (M = Zn, Cd, Hg; R = Me, Bz, Bu^t, *p*-Tol) were similarly prepared by combining aqueous or methanolic solutions of the metal dihalides MX_2 (X = Cl, Br, or I) with 2 equiv of the appropriate $Na[Bm^R]$ reagents (eq 1) and isolated in yields ranging from 35% to 80%. Most significantly, the four

$$MX_2 + Na[Bm^R] \xrightarrow[\substack{M = Zn, Cd, Hg \\ X = Cl, Br, I \\ R = Me, Bz, Bu^t, p\text{-Tol} \\ - NaX}]{H_2O \text{ or } MeOH} M[Bm^R]_2 \qquad (1)$$

$M[Bm^R]_2$ triads represent the first complete series of bis(mercaptoimidazolyl)borate complexes to be isolated for any group in the periodic table and include also the first such derivatives for both cadmium and mercury.

All 12 $M[Bm^R]_2$ complexes are white, air-stable, diamagnetic solids, insoluble in water and only marginally soluble in methanol. However, they tend to be moderately soluble in THF and halogenated hydrocarbons and more soluble in acetone, acetonitrile, and DMSO.[16] Unlike the zinc and cadmium complexes, the mercury compounds are moderately light-sensitive so their syntheses were performed in the dark by using glassware wrapped in aluminum foil. They were all characterized by elemental analyses (CHN) and IR and multinuclear NMR spectroscopies. For example, ^{1}H NMR data for all the complexes are qualitatively very similar to those of the corresponding free ligands, with only modest downfield chemical shifts (0.1−0.5 ppm) observed for the imidazolyl hydrogens in every case. Likewise, downfield shifts of up to 6.8 ppm for the imidazolyl carbons in their ^{13}C NMR spectra were measured upon complexation to the metals. However, upfield chemical shifts of between 3.8 and 10.4 ppm were found for the thione carbons, a phenomenon also verified for the tris(mercaptoimidazolyl)borate derivatives $[Tm^{tBu}]MBr$ (M = Zn, Cd, Hg)[5] and various other group 12 metal thione complexes.[17]

The molecular structure of $Cd[Bm^{Me}]_2$ and those of the three *tert*-butyl derivatives $M[Bm^{tBu}]_2$ (M = Zn, Cd, Hg) have been determined by single-crystal X-ray diffraction (Figures 2−5). The four isostructural complexes (also isomorphous for M = Zn, Hg) present in the solid state distorted tetrahedral geometries in which a central $[MS_4]$ core is supplemented by two adjacent M···H−B interactions of varying strength (see description later). Unlike the structure

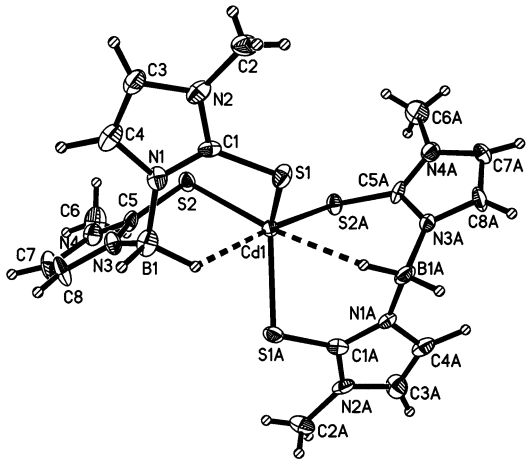

Figure 2. Molecular structure of $Cd[Bm^{Me}]_2$. Selected bond lengths (Å) and angles (deg): Cd1−S1 2.5089(13), Cd1−S2 2.5716(11), Cd1−H 2.582, S1−C1 1.735(4), S2−C5 1.708(5); S1−Cd−S1A 114.55(6), S1−Cd1−S2A 104.31(4), S1−Cd1−S2 119.21(4), S2−Cd1−S2A 94.34(5).

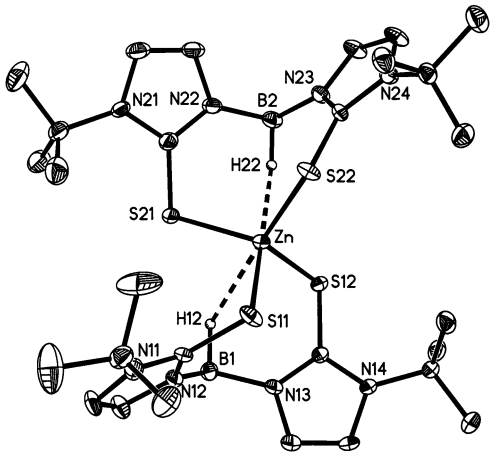

Figure 3. Molecular structure of $Zn[Bm^{tBu}]_2$. Selected bond lengths (Å) and angles (deg): Zn−S(11) 2.389(3), Zn−S(12) 2.350(2), Zn−S(21) 2.333(2), Zn−S(22) 2.372(2), Zn···H(12) 2.81(7), Zn···H(22) 2.47(7), Zn···B(1) 3.445(10), Zn···B(2) 3.230(11), S(11)−C(11) 1.737(8), S(12)−C(18) 1.738(8), S(21)−C(21) 1.735(8), S(22)−C(28) 1.715(7); S(21)−Zn−S(12) 114.61(9), S(21)−Zn−S(22) 115.82(9), S(12)−Zn−S(22) 116.83(9), S(21)−Zn−S(11) 109.77(9), S(12)−Zn−S(11) 105.70(9), S(22)−Zn−S(11) 90.52(8), S(21)−Zn−H(22) 71.0(17), S(12)−Zn−H(22) 78.6(18), S(22)−Zn−H(22) 84.2(18), S(11)−Zn−H(22) 174.4(18), S(21)−Zn−H(12) 66.4(15), S(12)−Zn−H(12) 64.1(15), S(22)−Zn−H(12) 175.6(15), S(11)−Zn−H(12) 85.1(15), H(22)−Zn−H(12) 100(2).

of the closely related nickel compound $Ni[Bm^{Me}]_2$,[10] whose geometry is better regarded as distorted octahedral (S−Ni−S trans ≈ 173°), the S−M−S bond angles in $Cd[Bm^{Me}]_2$ and $M[Bm^{tBu}]_2$ (M = Zn, Cd, Hg) span the approximate range 85−124° and imply an overall geometry much closer to tetrahedral. The aforementioned 3-center−2-electron M···H−B bonds,[18] akin to the better-known "agostic" M···H−C interactions found in metal alkyl complexes,[19] are precedented in bis(pyrazolyl)borate ($Bp^{RR'}$) chemistry.[20] However,

(16) An interesting exception to these solubility trends is provided by the $M[Bm^{p\text{-}Tol}]_2$ (M = Zn, Cd) compounds which, unlike their mercury counterpart, are soluble in benzene.

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(18) For an enlightening introduction to the coordination chemistry of B−H and other X−H bonds (X = N, P, S) see: Kubas, G. J. *Metal Dihydrogen and σ-Bond Complexes*; Kluwer Academic/Plenum Publishers: New York, 2001; Chapter 13, pp 417−439.

(19) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124.

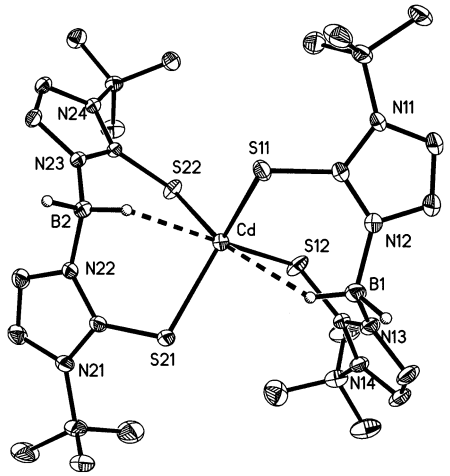

Figure 4. Molecular structure of Cd[Bm^{tBu}]$_2$. Selected bond lengths (Å) and angles (deg): Cd−S(11) 2.5407(9), Cd−S(12) 2.5646(9), Cd−S(21) 2.5356(8), Cd−S(22) 2.5954(8), Cd···H(1) 2.73(3), Cd···H(4) 2.49(3), S(11)−C(11) 1.732(3), S(12)−C(18) 1.718(3), S(21)−C(21) 1.719(3), S(22)−C(28) 1.716(3); S(11)−Cd−S(12) 111.87(3), S(11)−Cd−S(22) 114.13(3), S(12)−Cd−S(22) 85.12(3), S(21)−Cd−S(11) 116.44(3), S(21)−Cd−S(22) 114.30(3), S(21)−Cd−S(12) 110.83(3), H(4)−Cd−S(21) 72.2(7), H(4)−Cd−S(11) 76.3(7), H(4)−Cd−S(12) 167.0(7), H(4)−Cd−S(22) 82.2(7), S(21)−Cd−H(1) 78.9(6), S(11)−Cd−H(1) 67.1(6), S(12)−Cd−H(1) 77.7(6), S(22)−Cd−H(1) 161.4(7), H(4)−Cd−H(1) 115.2(9).

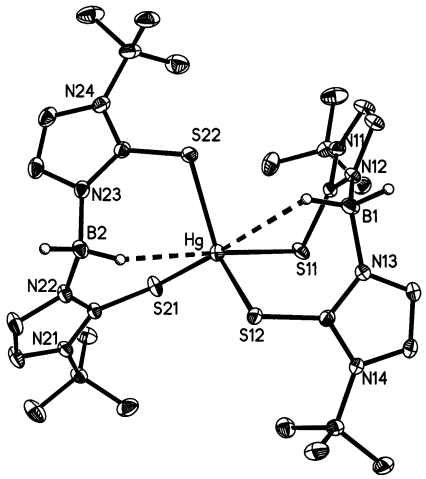

Figure 5. Molecular structure of Hg[Bm^{tBu}]$_2$. Selected bond lengths (Å) and angles (deg): Hg−S(11) 2.5919(8), Hg−S(12) 2.5557(7), Hg−S(21) 2.5526(7), Hg−S(22) 2.5374(7), Hg···H(1) 3.09(3), Hg···H(4) 2.62(3), S(11)−C(11) 1.735(3), S(12)−C(18) 1.736(3), S(21)−C(21) 1.723(3), S(22)−C(28) 1.730(3); S(22)−Hg−S(21) 112.23(3), S(22)−Hg−S(12) 110.50(2), S(21)−Hg−S(12) 123.89(3), S(22)−Hg−S(11) 112.94(3), S(21)−Hg−S(11) 94.77(2), S(12)−Hg−S(11) 100.40(3), S(22)−Hg−H(4) 70.4(6), S(21)−Hg−H(4) 79.0(6), S(12)−Hg−H(4) 82.8(6), S(11)−Hg−H(4) 173.8(6), S(22)−Hg−H(1) 66.3(5), S(21)−Hg−H(1) 174.2(5), S(12)−Hg−H(1) 61.1(5), S(11)−Hg−H(1) 81.0(5), H(4)−Hg−H(1) 105.2(8).

such a bonding motif appears to be *prevalent* in the coordination chemistry of Bm^R ligands (Table 1).[21]

For comparison purposes, included in Table 1 is the zinc complex Zn[Bm^{Me}]$_2$ already mentioned, which has a structure devoid of any significant Zn···H−B interactions, has a more limited range of S−Zn−S bond angles (ca. 101−116°), and can therefore be described as only slightly distorted tetrahedral. The observation that the presence of *tert*-butyl substituents in the 3-position of the imidazolyl rings in Zn[Bm^{tBu}]$_2$ results in a measurable change in geometry relative to Zn[Bm^{Me}]$_2$ highlights the impact that remote bulky substituents may have on the metal's immediate coordination sphere and geometry.

Table 1. M···H−B Interactions in Bm^R Complexes

complex	d(M···H)/Å	d(M···B)/Å	reference
{Li[Bm^{Mes}]}$_2$	1.86, 2.34	2.80, 3.09	7
[Bm^{Me}]Tc(CO)$_3$	1.65	2.83	8a
Ni[Bm^{Me}]$_2$	1.86	2.86	10
[Bm^{Me}]ZnI	2.06	2.94	7
[Bm^{Me}]ZnMe	1.77	2.88	7
[Bm^{Mes}]Zn(NO$_3$)	1.93	2.82	7
Zn[Bm^{Me}]$_2$	3.51	3.78	7
Zn[Bm^{tBu}]$_2$	2.47, 2.81	3.23, 3.45	this work
Cd[Bm^{Me}]$_2$	2.58	3.36	this work
Cd[Bm^{tBu}]$_2$	2.49, 2.73	3.22, 3.39	this work
Hg[Bm^{tBu}]$_2$	2.62, 3.09	3.36, 3.59	this work
{Tl[Bm^{Me}]}$_x$	2.69	3.50	7

The Zn−S bond lengths in Zn[Bm^{tBu}]$_2$ (average = 2.361 Å) are only marginally longer than those in Zn[Bm^{Me}]$_2$ (average = 2.337 Å)[7] or other Bm^R derivatives of zinc, including [Bm^{Mes}]Zn(NO$_3$) and [Bm^{Me}]ZnI (averages = 2.268 and 2.290 Å, respectively).[7] However, they are within the values found in a variety of zinc tris(mercaptoimidazolyl)-borate complexes, typically in the narrow range 2.32−2.37 Å.[22] Moreover, the Zn···H bond distances in Zn[Bm^{tBu}]$_2$ (2.47 and 2.81 Å) are clearly longer than the corresponding values observed in [Bm^{Me}]ZnX (1.77 and 2.06 Å for X = Me and I, respectively), an indication of the relative weakness of the two Zn···H−B interactions. Nevertheless, both values are smaller than either the sum of van der Waals radii of Zn and H (ca. 3.25 Å)[23] or the Zn···H separation in Zn[Bm^{Me}]$_2$ (3.51 Å).[7] The careful evaluation of M···H (or M···B) distances and S−M−S bond angles (or the deviation from ideal tetrahedral values thereof) may be the simplest way of assessing the strength of M···H−B interactions in these types of complexes. As exemplified for zinc bis(mercaptoimidazolyl)borate complexes, for which the largest number of [Bm^R]$^-$ derivatives have been structurally characterized (see Table 1), Zn···H−B interactions may be classified as strong if d(Zn···H) ≤ 2.00 Å, weak if 2.00 < d(Zn···H) < 3.25 Å, or negligible/nonexistent if d(Zn···H) ≥ 3.25 Å. The value 2.00 Å was chosen as the upper limit for "strong" Zn···H−B interactions since the Zn···H distances for such fragments

(20) See for example: Belderraín, T. R.; Paneque, M.; Carmona, E.; Gutiérrez-Puebla, E.; Monge, M. A.; Ruiz-Valero, C. *Inorg. Chem.* **2002**, *41*, 425−428 and references therein.

(21) Analogous M···H−B contacts are also present in some Tm^R complexes[21a−d] and in the related bis(mercaptoimidazolyl)(pyrazolyl)-borate complexes M[pzBm^{Me}]$_2$ (M = Co, Cd).[21e] See: (a) Santini, C.; Gioia Lobbia, G.; Pettinari, C.; Spagna, R.; Pellei, M.; Vallorani, F. *Inorg. Chim. Acta* **1999**, *285*, 81−88. (b) Gioia Lobbia, G.; Pettinari, C.; Santini, C.; Somers, N.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2001**, *319*, 15−22. (c) Bridgewater, B. M.; Parkin, G. *Inorg. Chem. Commun.* **2000**, *3*, 534−536. (d) Kimblin, C.; Churchill, D. G.; Bridgewater, B. M.; Girard, J. N.; Quarless, D. A.; Parkin, G. *Polyhedron* **2001**, *20*, 1891−1896. (e) Kimblin, C.; Bridgewater, B. M.; Churchill, D. G.; Hascall, T.; Parkin. G. *Inorg. Chem.* **2000**, *39*, 4240−4243.

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(23) Calculated from the van der Waals radii of H (1.20 Å) and Zn (2.05 Å), with the latter value estimated by adding 0.80 Å to its metallic radius. See: Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 256, 260, and 263.

in the Cambridge Structural Database are in the range 1.73−1.98 Å.[24]

With regards to the cadmium compounds, the Cd−S bond lengths in $Cd[Bm^R]_2$ (averages = 2.541 and 2.559 Å for R = Me and Bu^t, respectively) are within the 2.48−2.60 Å range observed for the corresponding values in $[Tm^R]CdX$ complexes.[25] The Cd···H bond distances in these compounds (2.58 Å for R = Me, 2.49 and 2.73 Å for R = Bu^t) are comparable to those in $M[pzBm^{Me}]_2$ (2.55 and 2.58 Å)[21e] but significantly longer than those in the only other two compounds with such interactions that appear in the Cambridge Structural Database,[24] namely $[Tp^{Me_2}]Cd(BH_4)$ (1.973 and 2.126 Å)[26] and the anionic cadmaborane $[Cd(B_9H_{13})_2]_2^-$ (2.213−2.314 Å).[27] Similarly, the average Hg−S bond distance in $Hg[Bm^{tBu}]_2$ (2.560 Å) is comparable to the corresponding values in the only two known $[Tm^R]HgBr$ complexes (averages: 2.579 and 2.573 Å for R = Me and Bu^t, respectively).[4,5] However, the strength of the Hg···H contacts in $Hg[Bm^{tBu}]_2$ (2.62 and 3.09 Å) is even harder to quantify: there are no complexes with Hg···H−B interactions in the Cambridge Structural Database.[24] Nevertheless, we note that the M···H distances in all these cadmium and mercury complexes are still within the sum of van der Waals radii of the pertinent atoms (ca. 3.41 and 3.44 Å for Cd···H and Hg···H, respectively).

Conclusions

In summary, the convenient preparation of $Na[Bm^{Me}]$ and three new bulkier $[Bm^R]^-$ ligands (R = Bz, Bu^t, *p*-Tol) expands considerably the range of bis(mercaptoimidazolyl)-borate ligands available. While this ligand system has been used in recent years to model the active sites in certain metalloenzymes (e.g., hydrogenases, alcohol dehydrogenases), it is also bound to become increasingly attractive in the study of sulfur-rich proteins such as metallothioneins and rubredoxins. We have prepared the first four complete series of homoleptic complexes $M[Bm^R]_2$ for any given group in the periodic table, including the first bis(mercaptoimidazolyl)borate complexes of both cadmium and mercury. $Cd[Bm^{Me}]_2$ and $M[Bm^{tBu}]_2$ (M = Zn, Cd, Hg) display in the solid state distorted tetrahedral structures with two ancillary M···H−B interactions, a bonding feature that appears to be widespread in Bm^R chemistry. Furthermore, we are currently extending our work to other metals and have recently verified that such interactions are also present in related transition metal derivatives $M[Bm^R]_2$ (M = Mn, Fe, Co).[28] The observation that bulky ligands (e.g., $[Bm^{tBu}]^-$) are capable of inducing zinc to expand its coordination number from four to six (i.e., $[ZnS_4]$ to $[ZnS_4H_2]$) is particularly significant in the context of the processes whereby octahedral species could mediate the transfer and exchange of metal ions in a variety of zinc-containing biomolecules.

Experimental Section

General Considerations. All reactions were performed in the air except for the syntheses of the $Na[Bm^R]$ compounds, which were carried out under argon using a combination of high-vacuum and Schlenk techniques.[29] Solvents were purified and degassed by standard procedures, and all commercially available reagents, including methimazole (Acros), were used as received. The 2-mercapto-1-alkylimidazoles $Hmim^R$ (R = Bz, Bu^t, *p*-Tol) were prepared by the acid-catalyzed cyclization of aminoacetaldehyde diethyl acetal $[H_2NCH_2CH(OEt)_2]$ and the appropriate alkylisothiocyanates (RNCS) following literature procedures.[30] ^{1}H and ^{13}C NMR spectra were obtained on General Electric QE 300 or Varian Gemini (300 MHz) FT spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$ (δ = 0 ppm) and were referenced internally with respect to the solvent resonances (^{1}H: δ 2.49 for d_5-DMSO, 7.24 for C*H*Cl$_3$. ^{13}C: δ 39.5 for DMSO, 77.0 for *C*DCl$_3$); coupling constants are given in hertz. IR spectra were recorded as KBr pellets on Bio-Rad 175C FT or Thermo Mattson Satellite 3000 FT-IR spectrophotometers and are reported in wavenumbers (cm^{-1}); relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak, sh = shoulder). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

Synthesis of Na[Bm^{Me}]. A stirred suspension of $NaBH_4$ (0.500 g, 13.217 mmol) and 2-mercapto-1-methylimidazole (3.018 g, 26.434 mmol) in THF (40 mL) was refluxed for 18 h under an atmosphere of argon. The resulting slightly cloudy solution was allowed to cool to room temperature and filtered, and the clear filtrate was concentrated under reduced pressure to ca. 5 mL, leading to the formation of a white precipitate. After addition of pentane (40 mL), the product was isolated by filtration, washed with pentane (2 × 30 mL), and dried in vacuo for 5 h (3.350 g, 97%). Mp = 220 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.33 (s, 6 H, C*H*$_3$), 6.71 (d, $^3J_{H-H}$ = 1.8, 2 H, imidazole *H*), 6.97 (d, $^3J_{H-H}$ = 1.8, 2 H, imidazole *H*), H_2B not located; ^{13}C δ 33.7 (q, $^1J_{C-H}$ = 139, 2 C, CH_3), 115.3 (d, $^1J_{C-H}$ = 190, 2 C, imidazole *C*), 123.7 (d, $^1J_{C-H}$ = 190, 2 C, imidazole *C*), 163.3 (s, 2 C, *C*=S). IR data: 3118 (m), 3081 (w), 2939 (w), 2456 (m), 2415 (w), 2358 (w), 2282 (w), 2239 (w), 1656 (w), 1618 (w), 1560 (m), 1455 (s), 1417 (m), 1378 (s), 1319 (w), 1299 (w), 1198 (s), 1165 (w), 1123 (s), 1084 (w), 1040 (w), 968 (w), 886 (w), 870 (w), 759 (w), 733 (s), 697 (w), 682 (w), 649 (w), 621 (w), 521 (w), 503 (w), 452 (w).

Synthesis of Zn[Bm^{Me}]$_2$. A stirred solution of $ZnBr_2$ (0.086 g, 0.381 mmol) in H_2O (15 mL) was treated with a solution of $Na[Bm^{Me}]$ (0.200 g, 0.763 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min, and the product was isolated by filtration and dried in vacuo for 18 h (0.156 g, 75%). Mp = 306 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.30 (s, 12 H, C*H*$_3$), 7.17 (s, 4 H, imidazole *H*), 7.21 (s, 4 H, imidazole *H*), H_2B not located; ^{13}C δ 34.5 (q, $^1J_{C-H}$ = 141, 4 C, *C*H$_3$), 120.3 (d, $^1J_{C-H}$ = 193, 4 C,

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imidazole *C*), 124.1 (d, $^1J_{C-H}$ = 201, 4 C, imidazole *C*), 152.8 (s, 4 C, *C*═S). IR data: 3147 (m), 3120 (m), 3083 (w), 2946 (w), 2493 (w), 2395 (m), 2291 (w), 1556 (m), 1459 (s), 1412 (m), 1379 (s), 1327 (w), 1302 (w), 1188 (s), 1171 (s), 1129 (s), 1086 (w), 1042 (w), 699 (w), 687 (w), 648 (w), 601 (w), 508 (w), 451 (w). Anal. Calcd for $C_{16}H_{24}B_2N_8S_4Zn$: C, 35.4; H, 4.5; N, 20.6. Found: C, 35.5; H, 4.2; N, 20.5%.

Synthesis of Cd[Bm^{Me}]$_2$. A stirred solution of $CdCl_2$ (0.105 g, 0.572 mmol) in H_2O (15 mL) was treated with a solution of Na[Bm^{Me}] (0.300 g, 1.144 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min, and the product was isolated by filtration and dried in vacuo for 18 h (0.245 g, 72%). Mp = 273 °C. NMR data (in d_6-DMSO): ^{1}H δ 3.49 (s, 12 H, C*H*$_3$), 6.98 (s, 4 H, imidazole *H*), 7.19 (s, 4 H, imidazole *H*), *H*$_2$B not located; ^{13}C δ 34.6 (q, $^1J_{C-H}$ = 141, 4 C, C*H*$_3$), 120.2 (d, $^1J_{C-H}$ = 197, 4 C, imidazole *C*), 123.3 (d, $^1J_{C-H}$ = 195, 4 C, imidazole *C*), 154.1 (s, 4 C, *C*═S). IR data: 3160 (w), 3123 (w), 2946 (w), 2407 (m), 2355 (w), 1558 (m), 1458 (s), 1416 (m), 1381 (vs), 1325 (w), 1301 (w), 1193 (s), 1166 (m), 1120 (s), 1087 (w), 1039 (w), 1014 (w), 875 (w), 730 (s), 696 (w), 680 (w), 645 (w), 516 (w), 501 (w), 454 (w), 419 (w). Anal. Calcd for $C_{16}H_{24}B_2CdN_8S_4$: C, 32.5; H, 4.1; N, 19.0. Found: C, 32.6; H, 4.3; N, 18.8%.

Synthesis of Hg[Bm^{Me}]$_2$. In the absence of light, a stirred solution of HgI_2 (0.173 g, 0.381 mmol) in methanol (10 mL) was treated with a solution of Na[Bm^{Me}] (0.200 g, 0.763 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 10 min, and the product was isolated by filtration and dried in vacuo for 4 h (0.195 g, 75%). Mp = 150 °C. NMR data (in d_6-DMSO): ^{1}H δ 3.34 (s, 12 H, C*H*$_3$), 7.16 (s, 4 H, imidazole *H*), 7.18 (s, 4 H, imidazole *H*), *H*$_2$B not located; ^{13}C δ 34.7 (q, $^1J_{C-H}$ = 141, 4 C, *C*H$_3$), 120.4 (d, $^1J_{C-H}$ = 197, 4 C, imidazole *C*), 124.3 (d, $^1J_{C-H}$ = 195, 4 C, imidazole *C*), 152.9 (s, 4 C, *C*═S). IR data: 3152 (w), 3150 (w), 3123 (w), 3115 (w), 3082 (w), 2945 (w), 2500 (m), 2402 (m), 2360 (m), 2287 (w), 1551 (s), 1457 (s), 1411 (m), 1375 (s), 1326 (m), 1297 (m), 1187 (vs), 1170 (vs), 1123 (vs), 1087 (w), 1041 (w), 1014 (w), 763 (w), 751 (m), 723 (vs), 718 (vs), 648 (w), 600 (w), 505 (m), 451 (m). Anal. Calcd for $C_{16}H_{24}B_2HgN_8S_4$: C, 28.3; H, 3.6; N, 16.5. Found: C, 28.1; H, 3.7; N, 16.2%.

Synthesis of Na[Bm^{Bz}]. A stirred suspension of $NaBH_4$ (0.099 g, 2.628 mmol) and 2-mercapto-1-benzylimidazole (1.000 g, 5.256 mmol) in THF (30 mL) was refluxed for 18 h under an atmosphere of argon. The resulting slightly cloudy solution was allowed to cool to room temperature and filtered, and the clear filtrate was concentrated under reduced pressure to ca. 5 mL, leading to the formation of a white sticky solid. After trituration with pentane (50 mL) for 2 h, the product was isolated by filtration, washed with pentane (2 × 30 mL), and dried in vacuo for 2 h (0.746 g, 69%). NMR data (in d_6-DMSO): ^{1}H δ 5.15 (s, 4 H, C*H*$_2$C$_6$H$_5$), 6.84 (d, $^3J_{H-H}$ = 1.8, 2 H, imidazole *H*), 7.02 (d, $^3J_{H-H}$ = 1.8, 2 H, imidazole *H*), 7.20−7.35 (m, 10 H, CH$_2$C$_6$*H*$_5$), *H*$_2$B not located; ^{13}C δ 48.7 (t, $^1J_{C-H}$ = 141, 2 C, *C*H$_2$C$_6$H$_5$), 116.1 (d, $^1J_{C-H}$ = 195, 2 C, imidazole *C*), 117.8 (d, $^1J_{C-H}$ = 196, 2 C, imidazole *C*), 127.2 (d, $^1J_{C-H}$ = 161, 2 C, C_p in Bz), 127.6 (d, $^1J_{C-H}$ = 159, 4 C, C_o or C_m in Bz), 128.3 (d, $^1J_{C-H}$ = 160, 4 C, C_o or C_m in Bz), 137.5 (s, 2 C, C_{ipso} in Bz), 161.3 (s, 2 C, *C*═S). IR data: 3130 (m), 3015 (m), 2921 (m), 2818 (m), 2724 (m), 2360 (m), 2339 (m), 1945 (w), 1602 (w), 1573 (vs), 1542 (w), 1495 (s), 1444 (s), 1273 (m), 1208 (m), 1033 (w), 922 (w), 770 (m), 716 (s), 679 (m), 574 (m), 524 (s), 459 (m).

Synthesis of Zn[Bm^{Bz}]$_2$. A stirred solution of $ZnBr_2$ (0.054 g, 0.241 mmol) in H_2O (15 mL) was treated with a solution of Na[Bm^{Bz}] (0.200 g, 0.483 mmol) in a mixture of water (8 mL) and methanol (3 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min, and the product was isolated by filtration and dried in vacuo for 2 h (0.130 g, 63%). Mp = 230 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.47 (br s, 4 H, *H*$_2$B), 5.00 (s, 8 H, C*H*$_2$C$_6$H$_5$), 7.20 (s, 4 H, imidazole *H*), 7.22 (s, 4 H, imidazole *H*), 7.27 (m, 20 H, CH$_2$C$_6$*H*$_5$); ^{13}C δ 51.2 (t, $^1J_{C-H}$ = 140, 4 C, *C*H$_2$), 117.8 (d, $^1J_{C-H}$ = 194, 4 C, imidazole *C*), 124.6 (d, $^1J_{C-H}$ = 195, 4 C, imidazole *C*), 127.9 (d, $^1J_{C-H}$ = 161, 4 C, C_p in Bz), 128.2 (d, $^1J_{C-H}$ = 159, 8 C, C_o or C_m in Bz), 128.6 (d, $^1J_{C-H}$ = 161, 8 C, C_o or C_m in Bz), 136.0 (s, 4 C, C_{ipso} in Bz), 155.4 (s, 4 C, *C*═S). IR data: 3156 (w), 3127 (w), 3062 (w), 3030 (w), 2932 (w), 2483 (m), 2399 (m), 2632 (m), 1558 (w), 1497 (w), 1453 (s), 1429 (m), 1399 (vs), 1356 (m), 1340 (w), 1288 (w), 1216 (m), 1171 (w), 1150 (vs), 1122 (s), 1080 (w), 1060 (w), 1029 (w), 782 (w), 718 (vs), 695 (w), 580 (w), 505 (w), 419 (w). Anal. Calcd for $C_{40}H_{40}B_2N_8S_4Zn$: C, 56.7; H, 4.8; N, 13.2. Found: C, 56.4; H, 4.5; N, 13.2%.

Synthesis of Cd[Bm^{Bz}]$_2$. A stirred solution of $CdCl_2$ (0.044 g, 0.241 mmol) in H_2O (10 mL) was treated with a solution of Na[Bm^{Bz}] (0.200 g, 0.483 mmol) in a mixture of water (10 mL) and methanol (4 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min and the product was isolated by filtration and dried in vacuo for 8 h (0.131 g, 61%). Mp = 96 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.60 (br s, 4 H, *H*$_2$B), 5.22 (s, 8 H, C*H*$_2$C$_6$H$_5$), 7.03 (s, 4 H, imidazole *H*), 7.20−7.35 (m, 24 H, imidazole *H* + CH$_2$C$_6$*H*$_5$); ^{13}C δ 50.0 (t, $^1J_{C-H}$ = 141, 4 C, *C*H$_2$), 119.2 (d, $^1J_{C-H}$ = 197, 4 C, imidazole *C*), 123.9 (d, $^1J_{C-H}$ = 195, 4 C, imidazole *C*), 127.4 (d, $^1J_{C-H}$ = 158, 4 C, C_p in Bz), 127.5 (d, $^1J_{C-H}$ = 158, 8 C, C_o or C_m in Bz), 128.4 (d, $^1J_{C-H}$ = 161, 8 C, C_o or C_m in Bz), 136.5 (s, 4 C, C_{ipso} in Bz), 154.7 (s, 4 C, *C*═S). IR data: 3160 (w), 3130 (w), 3083 (w), 3062 (w), 3031 (w), 2929 (w), 2403 (m), 2362 (m), 1559 (m), 1496 (m), 1450 (s), 1427 (m), 1401 (vs), 1358 (w), 1338 (m), 1262 (w), 1220 (m), 1174 (m), 1149 (s), 1114 (s), 1079 (w), 1059 (w), 1029 (w), 960 (w), 875 (w), 806 (w), 779 (w), 722 (vs), 682 (w), 574 (w), 516 (w), 504 (w). Anal. Calcd for $C_{40}H_{40}B_2CdN_8S_4$: C, 53.7; H, 4.5; N, 12.5. Found: C, 52.9; H, 4.4; N, 12.2%.

Synthesis of Hg[Bm^{Bz}]$_2$. In the absence of light, a stirred solution of Na[Bm^{Bz}] (0.150 g, 0.362 mmol) in methanol (8 mL) was treated with a solution of HgI_2 (0.049 g, 0.181 mmol) in the same solvent (5 mL), resulting in the formation of a white precipitate. The suspension was stirred for 10 min, and the product was isolated by filtration and dried in vacuo for 2 h (0.060 g, 36%). Mp = 169 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.60 (br s, 4 H, *H*$_2$B), 5.08 (s, 8 H, C*H*$_2$C$_6$H$_5$), 7.20−7.32 (m, 28 H, imidazole *H* + CH$_2$C$_6$*H*$_5$); ^{13}C δ 50.1 (t, $^1J_{C-H}$ = 142, 4 C, *C*H$_2$), 119.5 (d, $^1J_{C-H}$ = 197, 4 C, imidazole *C*), 124.7 (d, $^1J_{C-H}$ = 196, 4 C, imidazole *C*), 127.4 (d, $^1J_{C-H}$ = 160, 4 C, C_p in Bz), 127.5 (d, $^1J_{C-H}$ = 160, 8 C, C_o or C_m in Bz), 128.4 (d, $^1J_{C-H}$ = 160, 8 C, C_o or C_m in Bz), 136.4 (s, 4 C, C_{ipso} in Bz), 153.6 (s, 4 C, *C*═S). IR data: 3156 (w), 3126 (w), 3062 (w), 3028 (w), 2938 (w), 2486 (m), 2395 (m), 2360 (m), 2343 (m), 1558 (m), 1496 (w), 1451 (m), 1426 (m), 1395 (s), 1352 (m), 1337 (w), 1285 (w), 1214 (m), 1170 (m), 1147 (s), 1116 (s), 1080 (w), 1063 (w), 1029 (w), 922 (w), 780 (w), 715 (vs), 696 (w), 579 (w), 503 (w), 459 (w). Anal. Calcd for $C_{40}H_{40}B_2HgN_8S_4$: C, 48.9; H, 4.1; N, 11.4. Found: C, 48.3; H, 4.0; N, 11.2%.

Synthesis of Na[Bm^{tBu}]. A stirred suspension of $NaBH_4$ (0.360 g, 9.516 mmol) and 2-mercapto-1-*tert*-butylimidazole (2.978 g, 19.059 mmol) in THF (40 mL) was refluxed for 22 h under an atmosphere of argon. The resulting slightly cloudy solution was allowed to cool to room temperature and filtered, and the clear filtrate was concentrated under reduced pressure to ca. 5 mL, leading

to the formation of a white sticky solid. After trituration with pentane (50 mL) for 3 h, the product was isolated by filtration, washed with pentane (2 × 30 mL), and dried in vacuo for 2 h (2.670 g, 81%). Mp = 260 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 1.68 [s, 36 H, C(C*H*$_3$)$_3$], 6.74 (d, $^3J_{H-H}$ = 1.7, 2 H, imidazole *H*), 6.96 (d, $^3J_{H-H}$ = 1.7, 2 H, imidazole *H*), H_2B not located; ^{13}C δ 28.5 [q, $^1J_{C-H}$ = 127, 6 C, C(*C*H$_3$)$_3$], 57.9 [s, 2 C, *C*(CH$_3$)$_3$], 114.7 (d, $^1J_{C-H}$ = 193, 2 C, imidazole *C*), 120.9 (d, $^1J_{C-H}$ = 193, 2 C, imidazole *C*), 158.2 (s, 2 C, *C*═S). IR data: 3186 (w), 3155 (w), 3141 (w), 3126 (w), 3090 (w), 2977 (s), 2925 (w), 2887 (w), 2397 (m), 2350 (m), 2230 (w), 1577 (w), 1568 (w), 1483 (w), 1411 (s), 1397 (m), 1358 (vs), 1315 (w), 1283 (m), 1257 (m), 1228 (m), 1201 (s), 1165 (s), 1118 (s), 1056 (w), 1026 (w), 970 (w), 927 (w), 914 (w), 884 (w), 819 (w), 803 (w), 744 (m), 704 (s), 682 (s), 593 (w), 588 (w), 550 (w), 527 (w), 488 (w), 482 (w).

Synthesis of Zn[Bm^{tBu}]$_2$. A stirred solution of $ZnCl_2$ (0.050 g, 0.367 mmol) in methanol (15 mL) was treated with a solution of Na[Bm^{tBu}] (0.254 g, 0.733 mmol) in water (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 20 min, and the product was isolated by filtration and dried in vacuo for 1 h (0.160 g, 67%). Mp = 290 °C (dec). NMR data (in $CDCl_3$): ^{1}H δ 1.67 [s, 36 H, C(C*H*$_3$)$_3$], 3.56 (br s, 4 H, H_2B), 6.73 (d, $^3J_{H-H}$ = 1.2, 4 H, imidazole *H*), 6.83 (d, $^3J_{H-H}$ = 1.2, 4 H, imidazole *H*); ^{13}C δ 29.0 [q, $^1J_{C-H}$ = 127, 12 C, C(*C*H$_3$)$_3$], 58.5 [s, 4 C, *C*(CH$_3$)$_3$], 115.3 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 122.9 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 154.5 (s, 4 C, *C*═S). IR data: 3182 (w), 3152 (w), 2977 (s), 2929 (m), 2450 (m), 2403 (m), 2360 (m), 1560 (m), 1482 (m), 1430 (s), 1399 (m), 1365 (vs), 1301 (w), 1260 (m), 1200 (s), 1171 (s), 1154 (s), 1123 (s), 1059 (w), 819 (w), 731 (m), 709 (s), 688 (s), 545 (w), 479 (w). Anal. Calcd for $C_{28}H_{48}B_2N_8S_4Zn$: C, 47.2; H, 6.8; N, 15.7. Found: C, 47.0; H, 7.0; N, 15.5%.

Synthesis of Cd[Bm^{tBu}]$_2$. A stirred solution of $CdCl_2$ (0.066 g, 0.360 mmol) in water (15 mL) was treated with a solution of Na[Bm^{tBu}] (0.250 g, 0.722 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 30 min, and the product was isolated by filtration and dried in vacuo for 90 min (0.216 g, 79%). Mp = 280 °C (dec). NMR data (in $CDCl_3$): ^{1}H δ 1.69 [s, 36 H, C(C*H*$_3$)$_3$], 3.64 (br s, 4 H, H_2B), 6.69 (d, $^3J_{H-H}$ = 2.1, 4 H, imidazole *H*), 6.83 (d, $^3J_{H-H}$ = 2.1, 4 H, imidazole *H*), H_2B not located; ^{13}C δ 28.9 [q, $^1J_{C-H}$ = 127, 12 C, C(*C*H$_3$)$_3$], 58.5 [s, 4 C, *C*(CH$_3$)$_3$], 115.3 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 122.4 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 155.2 (s, 4 C, *C*═S). IR data: 3182 (w), 3144 (w), 2976 (m), 2927 (w), 2887 (w), 2394 (m), 2362 (w), 1561 (w), 1482 (w), 1426 (m), 1416 (m), 1397 (w), 1364 (vs), 1298 (w), 1258 (w), 1229 (w), 1199 (s), 1169 (s), 1153 (s), 1120 (s), 1057 (w), 1027 (w), 979 (w), 928 (w), 876 (w), 821 (w), 727 (w), 709 (m), 686 (s), 626 (w), 586 (w), 544 (w), 481 (w). Anal. Calcd for $C_{28}H_{48}B_2CdN_8S_4$: C, 44.3; H, 6.4; N, 14.8. Found: C, 44.0; H, 6.5; N, 14.5%.

Synthesis of Hg[Bm^{tBu}]$_2$. In the absence of light, a stirred solution of HgI_2 (0.164 g, 0.361 mmol) in water (15 mL) was treated with a solution of Na[Bm^{tBu}] (0.250 g, 0.722 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 20 min, and the product was isolated by filtration and dried in vacuo for 90 min (0.189 g, 62%). Mp = 200 °C (dec). NMR data (in $CDCl_3$): ^{1}H δ 1.66 [s, 36 H, C(C*H*$_3$)$_3$], 6.72 (d, $^3J_{H-H}$ = 2.1, 4 H, imidazole *H*), 6.83 (d, $^3J_{H-H}$ = 2.1, 4 H, imidazole *H*), H_2B not located; ^{13}C δ 29.0 [q, $^1J_{C-H}$ = 127, 12 C, C(*C*H$_3$)$_3$], 58.6 [s, 4 C, *C*(CH$_3$)$_3$], 115.5 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 122.9 (d, $^1J_{C-H}$ = 193, 4 C, imidazole *C*), 154.4 (s, 4 C, *C*═S). IR data: 3181 (w), 3153 (w), 3143 (w), 2979 (m), 2925 (w), 2442 (w), 2396 (m), 2360 (w), 2291 (w), 2269 (w), 2233(w), 1560 (w), 1481 (w), 1426 (m), 1416 (m), 1398 (w), 1360 (vs), 1299 (w), 1259 (m), 1229 (w), 1199 (s), 1169 (s), 1154 (s), 1122 (s), 1058 (w), 1028 (w), 982 (w), 929 (w), 879 (w), 821 (w), 744 (w), 732 (m), 709 (s), 689 (m), 624 (w), 588 (w), 544 (w), 480 (w). Anal. Calcd for $C_{28}H_{48}B_2HgN_8S_4$: C, 39.7; H, 5.7; N, 13.2. Found: C, 39.7; H, 5.6; N, 13.2%.

Synthesis of Na[Bm$^{p\text{-Tol}}$]. A stirred suspension of $NaBH_4$ (0.099 g, 2.617 mmol) and 2-mercapto-1-*p*-tolylimidazole (0.960 g, 5.046 mmol) in tetrahydrofuran (30 mL) was refluxed for 20 h under an atmosphere of argon. The resulting slightly cloudy solution was allowed to cool to room temperature and filtered, and the clear filtrate was concentrated under reduced pressure to ca. 10 mL, leading to the formation of a white sticky solid. After trituration with pentane (4 × 40 mL) for 2 h, the product was isolated by filtration, washed with pentane (2 × 30 mL), and dried in vacuo for 3 h (0.968 g, 93%). Mp = 205 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 2.32 (s, 6 H, C*H*$_3$), 3.39 (br s, 2 H, H_2B), 6.90 (d, $^3J_{H-H}$ = 2.3, 2 H, imidazole *H*), 7.18 (d, $^3J_{H-H}$ = 2.3, 2 H, imidazole *H*), 7.21 (d, $^3J_{H-H}$ = 8.6, 4 H, H_o or H_m in *p*-Tol), 7.48 (d, $^3J_{H-H}$ = 8.6, 4 H, H_o or H_m in *p*-Tol); ^{13}C δ 20.5 (q, $^1J_{C-H}$ = 126, 2 C, C_6H_4*C*H$_3$), 115.5 (d, $^1J_{C-H}$ = 195, 2 C, imidazole *C*), 125.2 (d, $^1J_{C-H}$ = 200, 2 C, imidazole *C*), 125.5 (d, $^1J_{C-H}$ = 152, 4 C, C_o or C_m in *p*-Tol), 128.5 (d, $^1J_{C-H}$ = 158, 4 C, C_o or C_m in *p*-Tol), 135.6 (s, 2 C, C_p in *p*-Tol), 137.2 (s, 2 C, C_{ipso} in *p*-Tol), 163.9 (s, 2 C, *C*═S). IR data: 3135 (w), 3036 (w), 2921 (w), 2856 (w), 2732 (w), 2612 (w), 2446 (sh), 2360 (m), 2274 (sh), 2129 (w), 2090 (w), 1902 (w), 1872 (w), 1641 (m), 1615 (m), 1589 (m), 1517 (s), 1422 (s), 1363 (s), 1311 (m), 1264 (m), 1191 (m), 1157 (m), 1119 (m), 1101 (m), 1020 (m), 956 (m), 909 (m), 819 (vs), 733 (s), 712 (s), 682 (s), 605 (m), 571 (s), 506 (w), 476 (w).

Synthesis of Zn[Bm$^{p\text{-Tol}}$]$_2$. A stirred solution of $ZnCl_2$ (0.037 g, 0.271 mmol) in water (10 mL) was treated with a solution of Na[Bm$^{p\text{-Tol}}$] (0.225 g, 0.543 mmol) in aqueous methanol (50% v/v, 20 mL), resulting in the formation of a white precipitate. The suspension was stirred for 20 min, and the product was isolated by filtration and dried in vacuo for 2.5 h (0.134 g, 58%). Mp = 140 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 2.33 (s, 12 H, C*H*$_3$), 3.52 (br s, 4 H, H_2B), 7.0−7.5 (m, 24 H, imidazole *H* and *p*-Tol *H*); ^{13}C δ 20.6 (q, $^1J_{C-H}$ = 127, 4 C, C_6H_4*C*H$_3$), 120.9 (d, $^1J_{C-H}$ = 205, 4 C, imidazole *C*), 125.2 (d, $^1J_{C-H}$ = 199, 4 C, imidazole *C*), 126.1 (d, $^1J_{C-H}$ = 163, 8 C, C_o or C_m in *p*-Tol), 129.3 (d, $^1J_{C-H}$ = 160, 8 C, C_o or C_m in *p*-Tol), 135.1 (s, 4 C, C_p in *p*-Tol), 137.8 (s, 4 C, C_{ipso} in *p*-Tol), 153.6 (s, 4 C, *C*═S). IR data: 3160 (w), 3135 (w), 3041 (w), 2921 (w), 2861 (w), 2411 (m), 2360 (m), 2279 (w), 1899 (w), 1586 (w), 1559 (m), 1517 (vs), 1435 (s), 1367 (vs), 1311 (m), 1273 (m), 1183 (s), 1161 (vs), 1127 (s), 1110 (m), 1041 (w), 1020 (m), 956 (m), 879 (w), 819 (vs), 733 (m), 710 (s), 688 (s), 641 (w), 598 (m), 564 (s), 504 (m), 418 (m). Anal. Calcd for $C_{40}H_{40}B_2N_8S_4Zn$: C, 56.7; H, 4.8; N, 13.2. Found: C, 56.7; H, 4.6; N, 13.2%.

Synthesis of Cd[Bm$^{p\text{-Tol}}$]$_2$. A stirred solution of $CdCl_2$ (0.052 g, 0.284 mmol) in water (15 mL) was treated with a solution of Na[Bm$^{p\text{-Tol}}$] (0.235 g, 0.567 mmol) in methanol (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min, and the product was isolated by filtration and dried in vacuo for 3 h (0.173 g, 68%). Mp = 148 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 2.34 (s, 12 H, C*H*$_3$), 3.59 (br s, 4 H, H_2B), 7.1−7.5 (m, 24 H, imidazole *H* and *p*-Tol *H*); ^{13}C δ 20.6 (q, $^1J_{C-H}$ = 127, 4 C, C_6H_4*C*H$_3$), 120.7 (d, $^1J_{C-H}$ = 199, 4 C, imidazole *C*), 124.5 (d, $^1J_{C-H}$ = 197, 4 C, imidazole *C*), 126.1 (d, $^1J_{C-H}$ = 163, 8 C, C_o or C_m in *p*-Tol), 129.3 (d, $^1J_{C-H}$ = 161, 8 C, C_o or C_m in *p*-Tol), 135.2 (s, 4 C, C_p in *p*-Tol), 138.0 (s, 4 C, C_{ipso} in *p*-Tol), 154.9 (s, 4 C, *C*═S). IR data: 3165 (w), 3135 (w), 3036 (w), 2921

Table 2. Crystallographic Data for $Cd[Bm^{Me}]_2$ and $M[Bm^tBu]_2$ (M = Zn, Cd, Hg)

	$C_{16}H_{24}B_2CdN_8S_4 \cdot Me_2SO$	$C_{28}H_{48}B_2N_8S_4Zn$	$C_{28}H_{48}B_2CdN_8S_4$	$C_{28}H_{48}B_2HgN_8S_4$
fw	668.82	711.97	759.00	847.19
cryst syst	tetragonal	triclinic	monoclinic	triclinic
cryst size, mm^3	0.45 × 0.35 × 0.30	0.30 × 0.18 × 0.05	0.36 × 0.24 × 0.24	0.48 × 0.36 × 0.24
space group	$P4_32_12$ (No. 96)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
T, K	150(1)	243(2)	243(2)	243(2)
a, Å	10.503(2)	10.031(4)	10.5846(6)	10.0007(10)
b, Å	10.503(2)	10.484(4)	36.021(2)	10.6538(11)
c, Å	26.038(5)	18.559(7)	10.3516(6)	18.9510(18)
α, deg	90	83.741(7)	90	81.699(2)
β, deg	90	78.966(7)	110.799(1)	76.592(2)
γ, deg	90	71.408(9)	90	71.855(2)
V, $Å^3$	2872.6(8)	1813.4(12)	3689.5(4)	1860.7(3)
Z	4	2	4	2
D_c, g cm^{-3}	1.546	1.304	1.366	1.512
μ (Mo Kα), cm^{-1}	11.52	9.39	8.49	43.91
θ_{max}, deg	29.7	25.51	28.31	28.18
no. data	4246	6721	8481	7919
no. params	165	405	405	405
R1/wR2 [$I > 2\sigma(I)$][a]	0.0397/0.0421[b]	0.0988/0.2419	0.0405/0.1022	0.0233/0.0572
R1/wR2 (all data)[a]	0.0479/0.0428[b]	0.1695/0.2843	0.0638/0.1086	0.0280/0.0585

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)_2]/\sum[w(F_o^2)_2]\}^{1/2}$. [b] $[I > 3\sigma(I)]$.

(w), 2856 (w), 2407 (s), 2279 (w), 1898 (w), 1516 (vs), 1426 (s), 1365 (vs), 1311 (m), 1271 (m), 1182 (s), 1157 (vs), 1021 (m), 957 (m), 875 (w), 818 (s), 731 (m), 709 (s), 684 (s), 599 (m), 562 (s), 502 (w), 468 (w). Anal. Calcd for $C_{40}H_{40}B_2CdN_8S_4$: C, 53.7; H, 4.5; N, 12.5. Found: C, 53.2; H, 4.2; N, 12.4%.

Synthesis of $Hg[Bm^{p\text{-}Tol}]_2$. A stirred solution of $HgCl_2$ (0.058 g, 0.214 mmol) in methanol (10 mL) was treated with a solution of $Na[Bm^{p\text{-}Tol}]$ (0.177 g, 0.427 mmol) in the same solvent (15 mL), resulting in the formation of a white precipitate. The suspension was stirred for 15 min, and the product was isolated by filtration and dried in vacuo for 2 h (0.112 g, 53%). Mp = 132 °C (dec). NMR data (in d_6-DMSO): ^1H δ 2.33 (s, 12 H, CH_3), 3.68 (br s, 4 H, H_2B), 7.10 (d, $^3J_{H-H} = 8.1$, 8 H, H_o or H_m in *p*-Tol), 7.20 (d, $^3J_{H-H} = 8.1$, 8 H, H_o or H_m in *p*-Tol), 7.34 (s, 4 H, imidazole *H*), 7.44 (s, 4 H, imidazole *H*); C δ 20.6 (q, $^1J_{C-H} = 127$, 4 C, $C_6H_4CH_3$), 120.9 (d, $^1J_{C-H} = 199$, 4 C, imidazole *C*), 125.3 (d, $^1J_{C-H} = 201$, 4 C, imidazole *C*), 126.1 (d, $^1J_{C-H} = 164$, 8 C, C_o or C_m in *p*-Tol), 129.2 (d, $^1J_{C-H} = 160$, 8 C, C_o or C_m in *p*-Tol), 135.1 (s, 4 C, C_p in *p*-Tol), 137.9 (s, 4 C, C_{ipso} in *p*-Tol), 153.8 (s, 4 C, C═S). IR data: 3164 (w), 3132 (w), 3039 (w), 2922 (w), 2862 (w), 2435 (m), 2399 (m), 2251 (w), 1904 (w), 1586 (w), 1550 (w), 1518 (s), 1429 (s), 1365 (vs), 1312 (w), 1272 (m), 1184 (s), 1155 (vs), 1123 (s), 1107 (s), 1019 (m), 954 (m), 878 (w), 817 (vs), 733 (m), 709 (s), 681 (m), 636 (w), 600 (m), 560 (s), 499 (w), 467 (w). Anal. Calcd for $C_{40}H_{40}B_2HgN_8S_4$: C, 48.9; H, 4.1; N, 11.4. Found: C, 48.1; H, 4.0; N, 11.0%.

X-ray Structure Determinations. A summary of crystal data collection and refinement parameters for $Cd[Bm^{Me}]_2$ and $M[Bm^tBu]_2$ (M = Zn, Cd, Hg) is given in Table 2. A crystal of the dimethyl sulfoxide solvate $Cd[Bm^{Me}]_2 \cdot Me_2SO$ suitable for data collection was selected and mounted with epoxy glue on the tip of a thin glass fiber. All measurements were made at 150 K on a Rigaku AFC8 diffractometer equipped with a Mercury CCD area detector. The lattice solvent (DMSO) molecule in $Cd[Bm^{Me}]_2 \cdot Me_2SO$ is disordered around the 2-fold axis with the oxygen atom located on the axis and the sulfur atom disordered over two sites. An absorption correction was applied, and the data were corrected for Lorentz and polarization effects. The structure was solved using direct methods, expanded with Fourier techniques, and refined by full-matrix least-squares procedures on F. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.[31]

Crystals of $M[Bm^tBu]_2$ (M = Zn, Cd, Hg) suitable for data collection were selected and mounted with epoxy glue on the tip of thin glass fibers. Data sets for $M[Bm^tBu]_2$ (M = Zn, Cd, Hg) were collected at 243 K on a Bruker P4 diffractometer equipped with a SMART CCD detector. Absorption corrections were applied using SADABS. 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 6.10).[32] Hydrogen atoms were included in calculated positions, except for hydrogen atoms on boron, which were located and refined isotropically.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of $Cd[Bm^{Me}]_2$ and $M[Bm^tBu]_2$ (M = Zn, Cd, Hg). This material is available free of charge via the Internet at http://pubs.acs.org.

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