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# Protolytic Cleavage of Hg−C Bonds Induced by 1-Methyl-1,3-dihydro-2*H*-benzimidazole-2-selone: Synthesis and Structural Characterization of Mercury Complexes

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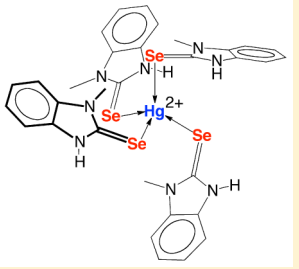
Supporting Information

**ABSTRACT:** Multinuclear ($^{1}$H, $^{77}$Se, and $^{199}$Hg) NMR spectroscopy demonstrates that 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone, H(sebenzim$^{Me}$), a structural analogue of the selenoamino acid, selenoneine, binds rapidly and reversibly to the mercury centers of $HgX_2$ (X = Cl, Br, I), while X-ray diffraction studies provide evidence for the existence of adducts of composition $[H(sebenzim^{Me})]_xHgX_2$ (X = Cl, $x$ = 2, 3, 4; X = I, $x$ = 2) in the solid state. H(sebenzim$^{Me}$) also reacts with methylmercury halides, but the reaction is accompanied by elimination of methane resulting from protolytic cleavage of the Hg−C bond, an observation that is of relevance to the report that selenoneine demethylates CysHgMe, thereby providing a mechanism for mercury detoxification. Interestingly, the structures of $[H(sebenzim^{Me})]_xHgX_2$ exhibit a variety of different hydrogen bonding patterns resulting from the ability of the N−H groups to form hydrogen bonds with chlorine, iodine, and selenium.



## INTRODUCTION

The toxicological properties of mercury[1] have been attributed to both its thiophilicity[1−4] and its selenophilicity.[4−6] With respect to the latter, selenium is an important component of antioxidants,[7,8] and the interaction between Hg(II) and selenium compounds may reduce the bioavailability of selenium *via* the formation of insoluble mercury selenide species.[4,5,8] Furthermore, mercury may bind to the active sites of selenoenzymes and thereby inhibit their functions.[4,6] For example, selenium is a component of a variety of enzymes that incorporate the amino acids selenocysteine and selenomethionine (Figure 1), as illustrated by glutathione peroxidases, thioredoxin reductases, glycine reductases, formate dehydrogenases, and selenoprotein P.[4,5,7,10] Other examples of selenium-containing biomolecules include the amino acid derivatives selenoneine[11,12] and Se-methylselenoneine[12,13] (Figure 1), of which the latter was identified in human urine and blood.

It has recently been shown that selenoamino acids (namely L-selenocysteine, L-selenoglutathione, D,L-selenopenicillamine, and L-selenomethionine) complex readily to methylmercury species[14] and that cleavage of the Hg−C bond may be achieved under physiologically relevant conditions to yield mercury selenide *via* $(MeHg)_2Se$.[15] Insoluble mercury selenide particles have also been observed in the brains of humans exposed to methylmercury species, and these particles are considered to be much less toxic than mobile, soluble methylmercury species such as CysHgMe.[16] This observation provides evidence of the neuroprotective effects of selenium with respect to the prevention of mercury-induced damage to the central nervous system. Additionally, recent *in vitro* studies have shown that selenoneine may assist cells in removal of CysHgMe.[11e] However, the interactions between mercury and selenium in biological systems are complex, and animal studies have produced contradictory results. For example, it has been observed that co-administration of diphenyl diselenide compounds with methylmercury chloride partially ameliorated methylmercury-induced oxidative damage to proteins in the livers and brains of intoxicated mice;[17] on the other hand, rats simultaneously dosed with methylmercury chloride and

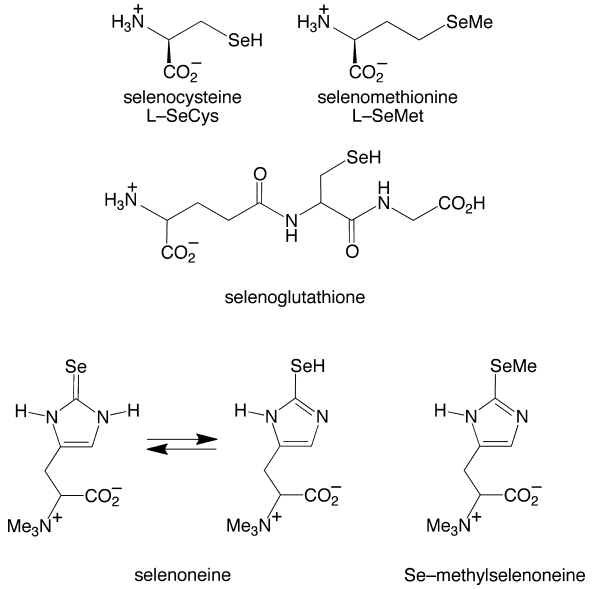



**Figure 1.** Selenium-containing derivatives of amino acids.

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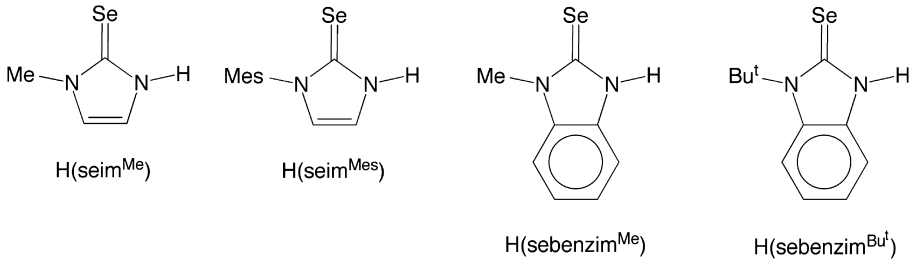


**Figure 2.** Structurally characterized imidazole-2-selones.

diphenyl diselenide were shown to suffer more severe neurological symptoms, such as motor deficits and weight loss, than rats dosed with methylmercury chloride alone.[18]

A detailed understanding of the impact of mercury on the biochemical roles of selenium would, therefore, benefit considerably from the development of the chemistry of mercury in a coordination environment that features selenium. Therefore, we describe here the reactivity of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone (Figure 2), H(sebenzim$^{Me}$),[19] a structural analogue of selenoneine, towards mercury, including the protolytic cleavage of mercury−methyl bonds.

## RESULTS AND DISCUSSION

1-R-imidazole-2-thiones, H(mim$^{R}$),[20−22] of which the methyl derivative is the well-known antithyroid drug, methimazole (tapazole),[23,24] are a widely studied class of molecules that can bind to a variety of metals,[25−27] including mercury.[27] However, in contrast to the numerous studies pertaining to 1-R-imidazole-2-thiones, there are few corresponding investigations of 1-R-imidazole-2-selones, H(seim$^{R}$).[28−32] For example, only H(seim$^{Me}$)[28,29] and H(seim$^{Mes}$),[29] and the benzannulated derivatives, H(sebenzim$^{Me}$)[30,31a] and H(sebenzim$^{Bu^t}$),[31a] have been synthesized and structurally characterized (Figure 2). Moreover, there are very few examples of structurally characterized metal complexes that feature 1-R-imidazole-2-selone ligands.[31a,33−35] It is, therefore, appropriate to develop the chemistry of this class of ligands with respect to mercury. In this regard, we recently reported an improved synthesis of H(sebenzim$^{Me}$),[31a] which has thereby allowed us to investigate the ability of this compound both to coordinate to mercury centers and to cleave mercury−carbon bonds.

**Interaction of H(sebenzim$^{Me}$) with $HgCl_2$, $HgBr_2$, and $HgI_2$.** Evidence for the ability of the imidazole-2-selone, H(sebenzim$^{Me}$), to coordinate to the mercury centers of $HgX_2$ (X = Cl, Br, I) in solution (Scheme 1) is provided by a combination of $^1$H, $^{77}$Se{$^1$H}, and $^{199}$Hg{$^1$H} NMR spectroscopies. For example, the $^{199}$Hg (Table 1) chemical shift changes progressively upon addition of H(sebenzim$^{Me}$) to a solution of $HgCl_2$ in DMSO-$d_6$. Correspondingly, the $^{77}$Se (Table 1) and $^1$H (Table 2 and Figure 3) chemical shifts associated with H(sebenzim$^{Me}$) also progressively shift upon addition to $HgCl_2$. In addition to providing evidence for coordination of H(sebenzim$^{Me}$) to mercury, the observation of a single resonance in both the $^{77}$Se{$^1$H} and $^{199}$Hg{$^1$H} NMR spectra for each concentration ratio, and also a single set of resonances in the $^1$H NMR spectra, indicates that the coordination is reversible and that the process is facile on the NMR time scale at room temperature. Furthermore, low temperature (−40 °C) spectra in DMF-$d_7$ likewise show single resonances, thereby

**Scheme 1**

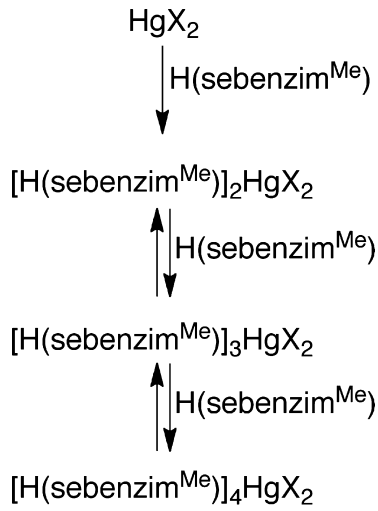


**Table 1. $^{199}$Hg and $^{77}$Se Chemical Shift Values for $HgCl_2$/H(sebenzim$^{Me}$) in DMSO-$d_6$**

| [H(sebenzim$^{Me}$)]/[$HgCl_2$] | $^{199}$Hg $\delta$ (ppm) | $^{77}$Se $\delta$ (ppm) |
|---|---|---|
| 0 | −1450 | N/A |
| 1 | −1201 | 12 |
| 2 | −1061 | 15 |
| 3 | −1013 | 33 |
| 4 | −1010 | 43 |
| ∞[a] | N/A | 83 |

[a]Value for H(sebenzim$^{Me}$).

**Table 2. $^1$H (N-$CH_3$) NMR Chemical Shift Values for $HgX_2$/H(sebenzim$^{Me}$) in DMSO-$d_6$**

| | $^1$H $\delta$ (ppm) | | |
|---|---|---|---|
| [H(sebenzim$^{Me}$)]/[$HgX_2$] | $HgCl_2$ | $HgBr_2$ | $HgI_2$ |
| 1 | 3.96 | 3.96 | 3.96 |
| 2 | 3.87 | 3.89 | 3.90 |
| 3 | 3.83 | 3.85 | 3.86 |
| 4 | 3.81 | 3.82 | 3.83 |
| 5 | 3.79 | 3.81 | 3.81 |
| 6 | 3.78 | 3.79 | 3.80 |
| 7 | 3.78 | 3.79 | 3.79 |
| 8 | 3.77 | 3.78 | 3.79 |
| 9 | 3.77 | 3.78 | 3.78 |
| 10 | 3.76 | 3.77 | 3.78 |
| 11 | 3.76 | 3.77 | 3.77 |
| ∞[a] | 3.75 | 3.75 | 3.75 |

[a]Value for H(sebenzim$^{Me}$).


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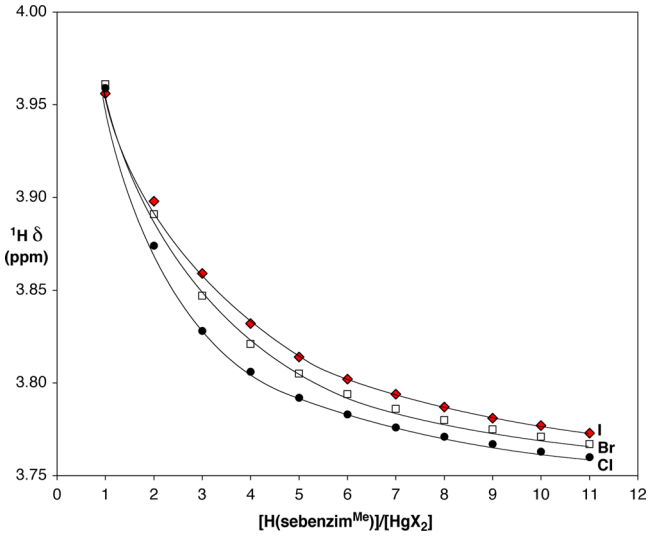


**Figure 3.** Variation of $^1$H NMR chemical shift of the methyl group of H(sebenzim$^{Me}$) in the presence of $HgX_2$ as a function of the molar ratio. Data plotted are to three significant figures.

demonstrating that the exchange is still rapid at this temperature (data not shown).

Although the fluxionality prevents identification of the precise solution composition (Scheme 1), the tetrakis, tris, and bis complexes, $[H(sebenzim^{Me})]_4HgCl_2$, $[H(sebenzim^{Me})]_3HgCl_2$, and $[H(sebenzim^{Me})]_2HgCl_2$,[31a] may be obtained by crystallization from a solution that contains the respective number of equivalents of H(sebenzim$^{Me}$).

The molecular structures of $[H(sebenzim^{Me})]_3HgCl_2$ and $[H(sebenzim^{Me})]_4HgCl_2$ have been determined by X-ray diffraction, as illustrated in Figures 4 and 5, respectively. Of these, the latter compound is particularly important because there are no structurally characterized mononuclear mercury compounds with four dative L-type[36] selenium donors currently listed in the Cambridge Structural Database

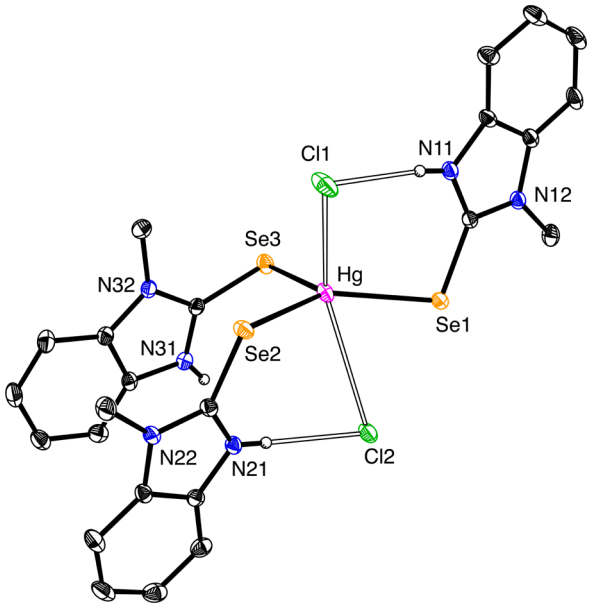


**Figure 4.** Molecular structure of $[H(sebenzim^{Me})]_3HgCl_2$, which is more appropriately represented as the ion pair, $\{[H(sebenzim^{Me})]_3HgCl\}[Cl]$.

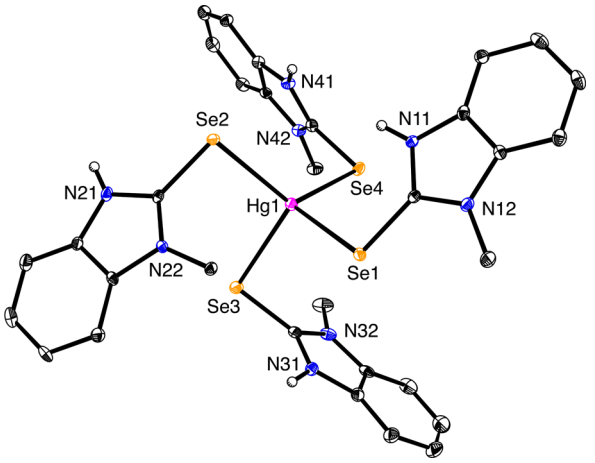


**Figure 5.** Molecular structure of the cation $\{[H(sebenzim^{Me})]_4Hg\}^{2+}$ of $\{[H(sebenzim^{Me})]_4Hg\}[Cl]_2$ (only one of the independent molecules is shown).

(CSD).[37,38] Furthermore, efforts to synthesize a tetrakis selone complex of mercury (other than for unsubstituted selenourea) have been reported to be unsuccessful.[35i,39] For example, treatment of $HgCl_2$ with 4 equiv of *N,N*-dimethylselenourea (DmSeU) was reported to yield only the bis complex, $(DmSeU)_2HgCl_2$.[35i]

In addition to $[H(sebenzim^{Me})]_4HgCl_2$ being of significance because its existence demonstrates that a mercury center can accommodate four selenium L-type donor ligands, the tris complex, $[H(sebenzim^{Me})]_3HgCl_2$, is of interest because structurally characterized mercury compounds with three L-type selenium donors are also uncommon. Thus, compounds with a $HgSe_3$ motif are typically polynuclear selenide or selenolate derivatives; there are, nevertheless a few structurally characterized mononuclear compounds that contain mercury coordinated to three dative L-type selenium ligands, of which $[(MeImSe)_3HgCl]Cl$,[35h] $\{[N(CH_2CH_2SePh)_3Hg(\kappa^2\text{-}NO_3)\}(NO_3)$,[40] and $\{[CpFe(CO)_2P(OPr^i)_2Se]_3Hg\}(ClO_4)_2$[41,42] are illustrative.

Comparison of the molecular structures of $[H(sebenzim^{Me})]_3HgCl_2$ (Figure 4) and $[H(sebenzim^{Me})]_4HgCl_2$ (Figure 5) with that of $[H(sebenzim^{Me})]_2HgCl_2$[31a] reveals interesting structural variations as a function of composition, as summarized in Figure 6. First, there is a progressive increase in the Hg−Cl distances in the sequence $[H(sebenzim^{Me})]_2HgCl_2$ < $[H(sebenzim^{Me})]_3HgCl_2$ < $[H(sebenzim^{Me})]_4HgCl_2$, as summarized in Table 3. Thus, whereas the two Hg−Cl bond lengths in the bis complex $[H(sebenzim^{Me})]_2HgCl_2$ [2.4942(7) and 2.5727(8) Å] are comparable to the mean value of 2.43 Å for structurally characterized four-coordinate mercury compounds listed in the CSD,[43] the shortest Hg···Cl distance in the tetrakis complex, $[H(sebenzim^{Me})]_4HgCl_2$, is 3.913 Å, such that the compound may be better represented as $\{[H(sebenzim^{Me})]_4Hg\}[Cl]_2$. The Hg−Cl distances in the tris complex, $[H(sebenzim^{Me})]_3HgCl_2$, are intermediate between those of $[H(sebenzim^{Me})]_2HgCl_2$ and $[H(sebenzim^{Me})]_4HgCl_2$, with values of 2.7506(10) and 3.2397(9) Å. While the latter value is sufficiently large that it cannot be considered to correspond to a Hg−Cl covalent bond, the shorter distance of 2.7506(10) Å is only 0.32 Å longer than the CSD average (*vide supra*) and may therefore be viewed as corresponding to a weak covalent interaction, such that the compound can be formulated as $\{[H(sebenzim^{Me})]_3HgCl\}[Cl]$. In accord with


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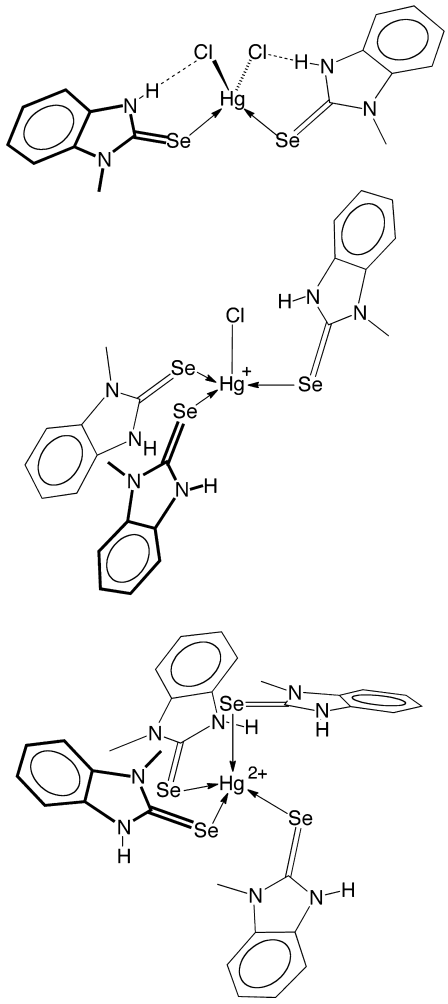

**Figure 6.** Comparison of the mercury coordination environments of $[H(sebenzim^{Me})]_2HgCl_2$ (top), $[H(sebenzim^{Me})]_3HgCl_2$ (center), and $[H(sebenzim^{Me})]_2HgCl_2$ (bottom).

the long Hg−Cl bond distance, the coordination geometry of $\{[H(sebenzim^{Me})]_3HgCl\}^+$ deviates significantly from tetrahedral. Thus, the four-coordinate $\tau_4$ index (Table 4)[44] of $\{[H(sebenzim^{Me})]_3HgCl\}^+$ (0.78) is close to that for an idealized trigonal monopyramid (0.85) in which chlorine occupies an axial position;[44] in the extreme that the axial chlorine is considered to serve the role of a counterion, the mercury would be described as approximately trigonal planar.

By comparison to the large variation in Hg−Cl interactions within $[H(sebenzim^{Me})]_xHgCl_2$, the average Hg−Se bond lengths exhibit little variation, increasing only slightly as a function of $x$, i.e., bis (2.591 Å) < tris (2.611 Å) < tetrakis (2.671 Å). These Hg−Se bond lengths are comparable to the mean value of 2.643 Å for compounds listed in the CSD,[37] but are longer than those in compounds such as $Hg(SePh)_2$ [2.480 Å][45] and $[Tm^{Bu^t}]HgSePh$ [2.524 Å],[46] which feature normal covalent bonds. The Hg−Se bond lengths in $[H(sebenzim^{Me})]_xHgCl_2$ are, nevertheless, comparable to the values in $[Tse^{Mes}]HgI$ [2.674 Å][47] and $(Pr^iImSe)_2HgCl_2$ [2.584 Å],[35i] which feature Hg←Se dative covalent bonds.[36] The latter type of interaction is recognized to be highly flexible,[48] as indicated by the fact that the Hg−Se bonds within $[Hg_2(SePh_2)_4][ClO_4]_2$ range from 2.65 to 2.92 Å.[49] As such, the variation in Hg−Se bond length within the series of $[H(sebenzim^{Me})]_xHgCl_2$ complexes may be rationalized by the dative nature of the interactions.

A common feature of all $[H(sebenzim^{Me})]_xHgCl_2$ structures is that each chloride, regardless of whether it is attached covalently to the mercury center, participates in hydrogen bonding interactions with the imidazole N−H moieties. There is, nevertheless, an interesting difference with respect to the nature of the hydrogen bonding interactions. Specifically, each chlorine that is covalently bound to mercury participates in an intramolecular N−H···Cl interaction,[50−52] whereas each outer-sphere chloride anion participates in a N−H···Cl···H−N interaction[53] that serves to link together two $H(sebenzim^{Me})$ moieties, as summarized in Figure 7.

Thus, whereas $[H(sebenzim^{Me})]_2HgCl_2$ exhibits only intramolecular N−H···Cl interactions and is a discrete mononuclear species,[31a,54] $[H(sebenzim^{Me})]_3HgCl_2$ and $[H(sebenzim^{Me})]_4HgCl_2$ also exhibit intermolecular N−H···Cl interactions. Specifically, $[H(sebenzim^{Me})]_3HgCl_2$ exhibits an intramolecular N−H···Cl interaction and intermolecular N−H···Cl···H−N interactions that bridge two molecules, thereby creating a dimeric structure (Figure 8), while $[H(sebenzim^{Me})]_4HgCl_2$ exhibits an intramolecular N−H···Cl···H−N interaction and intermolecular N−H···Cl···H−N interactions that result in a

**Table 4. Four-Coordinate $\tau_4$ Indices for $\{[H(sebenzim^{Me})]_xHg\}$ Derivatives**

| compound | $\tau_4$ |
|---|---|
| $[H(sebenzim^{Me})]_2HgCl_2$[a] | 0.94 |
| $[H(sebenzim^{Me})]_3HgCl_2$ | 0.78 |
| $[H(sebenzim^{Me})]_4HgCl_2$ | 0.88 |
| $[H(sebenzim^{Me})]_2HgI_2$ (monoclinic) | 0.88 |
| $[H(sebenzim^{Me})]_2HgI_2$ (orthorhombic) | 0.94 |
| $[H(sebenzim^{Me})_2]_2Hg$ | 0.88 |

[a]Data taken from ref 31a.

**Table 3. Selected Bond Length Data for $\{[H(sebenzim^{Me})]_xHg\}$ Compounds**

| | $d$ (Å) | |
|---|---|---|
| compound | Hg−X | Hg−Se |
| $[H(sebenzim^{Me})]_2HgCl_2$ | 2.4942(7), 2.5727(8) | 2.5732(5), 2.6090(5) |
| $[H(sebenzim^{Me})]_3HgCl_2$ | 2.7506(10), 3.2397(9) | 2.5690(4), 2.5864(4), 2.6730(4) |
| $[H(sebenzim^{Me})]_4HgCl_2$[a] | – | 2.6203(6), 2.6327(6), 2.7025(6), 27284(7), 2.6260(6), 2.6365(6), 2.6959(6), 2.7267(7) |
| $[H(sebenzim^{Me})]_2HgI_2$ (monoclinic) | 2.7280(3), 2.7463(4) | 2.6850(4), 2.6980(4) |
| $[H(sebenzim^{Me})]_2HgI_2$ (orthorhombic) | 2.7791(7), 2.8041(7) | 2.6149(10), 2.6396(10) |
| $[H(sebenzim^{Me})_2HgI$ | 2.7497(4) | 2.5466(6), 2.5748(6), 3.0904(6), 3.3215(6) |
| $[H(sebenzim^{Me})_2]_2Hg$ | – | 2.6230(12), 2.6230(12), 2.6320(12), 2.6367(13) |

[a]Values for two crystallographically independent molecules.



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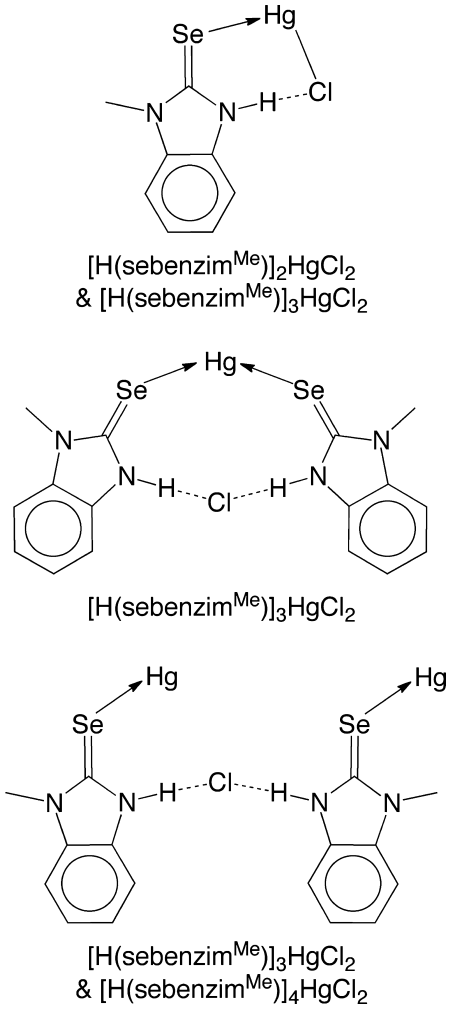


**Figure 7.** Intramolecular (top and middle) versus intermolecular (bottom) N−H···Cl hydrogen bonding interactions in $[H(sebenzim^{Me})]_xHgCl_2$ complexes.

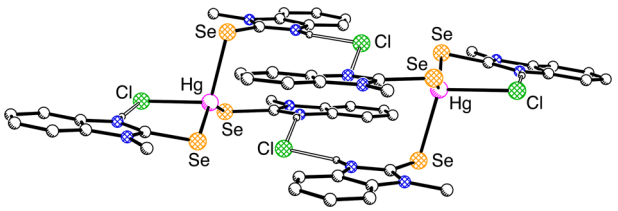


**Figure 8.** Intermolecular H−N···Cl···H−N hydrogen bonding serves to link together two $\{[H(sebenzim^{Me})]_3HgCl\}^+$ moieties.

polymeric array (Figure 9). The various hydrogen bonding N···Cl distances in $[H(sebenzim^{Me})]_xHgCl_2$ are in the range 3.031(7)−3.227(2) Å and are comparable to the values for other compounds with N−H···Cl interactions listed in the CSD [$d_{av}$(N···Cl) = 3.181 Å].[37] Furthermore, the N−H···Cl···H−N interactions that link together pairs of molecules are characterized by N···Cl···N angles in the range 100.1−119.7°, which are comparable to the average value of 99.9° for compounds listed in the CSD that feature N−H···Cl···H−N interactions wherein the chloride ion is not covalently bonded to any other atoms.[37]

The various hydrogen bonding networks in $[H(sebenzim^{Me})]_xHgCl_2$ may be described by the graph set notations[55] that are summarized in Table 5. For example, the

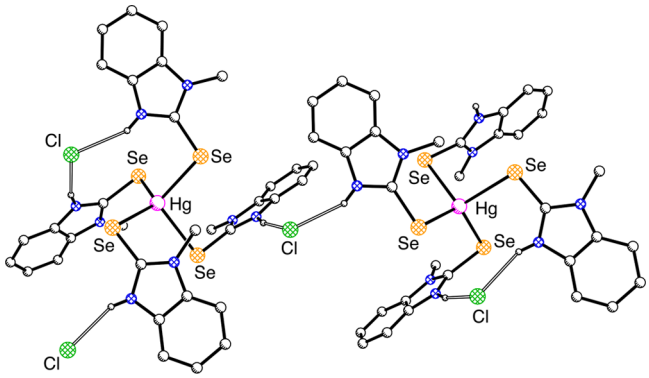


**Figure 9.** Intermolecular H−N···Cl···H−N hydrogen bonding creates a chain of $\{[H(sebenzim^{Me})]_4Hg\}[Cl]\}^+$ moieties, bridged by $Cl^-$ ions.

hydrogen-bonded dimer of $[H(sebenzim^{Me})]_3HgCl_2$ forms a 20-membered ring that is described by the unitary graph set DDS(6) and the binary graph set $R_4^2(20)$.

Coordination of $H(sebenzim^{Me})$ to $HgCl_2$ is accompanied by only relatively small increases in the lengths of the C−Se bonds. Thus, the C−Se bond lengths of $[H(sebenzim^{Me})]_2HgCl_2$ [1.862(3) and 1.864(3) Å],[31a] $[H(sebenzim^{Me})]_3HgCl_2$ [1.868(3), 1.859(3), and 1.857(3) Å], and $[H(sebenzim^{Me})]_4HgCl_2$ [1.854(12), 1.896(11), 1.851(9), 1.851(9), 1.857(11), 1.854(11), 1.869(9), and 1.856(9) Å] are only slightly longer than that of free $H(sebenzim^{Me})$ [1.838(2) Å].[31a] Despite these minor metrical changes, however, it is interesting to note that both the $^{13}C$ (see Experimental Section and ref 31a) and $^{77}Se$ NMR (Table 1) chemical shifts of the [CSe] moiety are sensitive towards the changes induced by coordination to mercury. Similar spectroscopic trends have been observed in related systems,[35i] and also for thione counterparts.[56]

NMR spectroscopic studies also demonstrate that $H(sebenzim^{Me})$ binds reversibly to $HgBr_2$ and $HgI_2$ in DMSO-$d_6$, and that the processes are facile on the NMR time scale, as indicated by the observation of single sets $^1H$ NMR chemical shifts for the $H(sebenzim^{Me})$ signals (Table 2 and Figure 3). Interestingly, the $^{77}Se$ NMR chemical shift of the $H(sebenzim^{Me})$ moiety is more sensitive towards coordination of $HgCl_2$ than to coordination of either $HgBr_2$ or $HgI_2$. For example, the $^{77}Se$ NMR chemical shifts of 2:1 mixtures of $H(sebenzim^{Me})$ and $HgX_2$ move upfield from the value of pure $H(sebenzim^{Me})$ by values of 68 ppm (X = Cl), 54 ppm (X = Br), and 35 ppm (X = I). Despite the reversibility of coordination of $H(sebenzim^{Me})$, the bis complex, $[H(sebenzim^{Me})]_2HgI_2$, may, nevertheless, be isolated from reactions performed in either acetonitrile or benzene.

Interestingly, the crystals of $[H(sebenzim^{Me})]_2HgI_2$ obtained from the two different reaction solvents are not isomorphous, and the molecules adopt different geometries, as illustrated in Figures 10 and 11. Specifically, the $H(sebenzim^{Me})$ ligands are oriented in different directions relative to both each other and the iodide ligands. Accompanying these variations in conformation are differences in the mercury coordination environments. For example, whereas the orthorhombic form of $[H(sebenzim^{Me})]_2HgI_2$ obtained from acetonitrile (Figure 10), with a $\tau_4$ index of 0.94, is close to tetrahedral ($\tau_4$ = 1.00), monoclinic $[H(sebenzim^{Me})]_2HgI_2$ obtained from benzene (Figure 11), with a $\tau_4$ index of 0.88, is distorted towards trigonal monopyramidal ($\tau_4$ = 0.85). In addition to these


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Table 5. Hydrogen Bonding Networks for $[H(sebenzim^{Me})]_xHgCl_2$ and $[H(sebenzim^{Me})]_2HgI_2$ Derivatives

| | unitary network | binary network |
|---|---|---|
| $[H(sebenzim^{Me})]_2HgCl_2$ | S(6)S(6) | – |
| $[H(sebenzim^{Me})]_3HgCl_2$ | DDS(6) | $R_4^2(20)$ |
| $[H(sebenzim^{Me})]_4HgCl_2$ | DDDDDDDD | $D_2^1(3)R_2^1(10)D_2^1(3)R_2^1(10)D_2^2(11)D_2^2(11)D_2^2(11)D_2^2(11)D_2^2(11)D_2^2(11)D_2^2(11)D_2^2(11)$ |
| $[H(sebenzim^{Me})]_2HgI_2$ (monoclinic) | $R_2^2(8)R_2^2(8)$ | C(12)C(12)$C_4^4(24)$ |
| $[H(sebenzim^{Me})]_2HgI_2$ (orthorhombic) | S(6)C(6) | – |

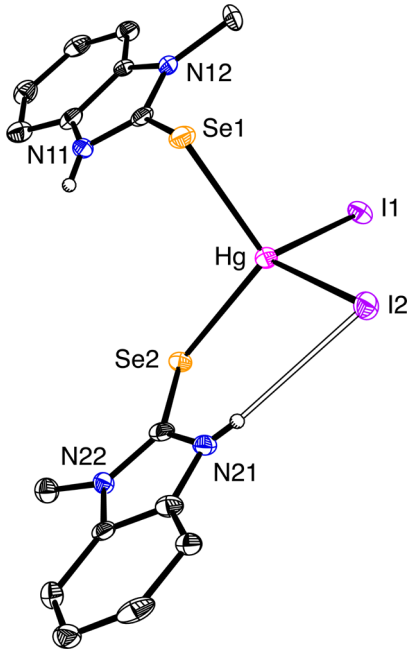


**Figure 10.** Molecular structure of orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ obtained from acetonitrile solution.

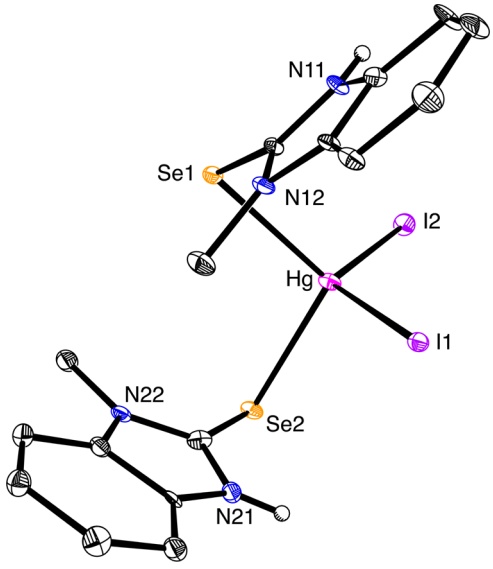


**Figure 11.** Molecular structure of monoclinic $[H(sebenzim^{Me})]_2HgI_2$ obtained from benzene solution.

angular variations, there are small differences in Hg–Se and Hg–I bond lengths. Thus, while the average Hg–I bond length of orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ (2.792 Å) is longer than that of the monoclinic version (2.737 Å), the average Hg–Se bond length of orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ (2.627 Å) is shorter than that of the monoclinic version (2.692 Å). Similarly to $HgCl_2$, coordination of $H(sebenzim^{Me})$ to $HgI_2$ is accompanied by only small increases in the lengths of the C–Se bonds. Thus, the C–Se bond lengths in $[H(sebenzim^{Me})]_2HgI_2$ [1.852(9) and 1.858(9) Å for the orthorhombic form and 1.871(3) and 1.863(3) Å for the monoclinic form] are comparable to those observed in $[H(sebenzim^{Me})]_xHgCl_2$, which range from 1.851(9) to 1.896(11) Å.

The most striking differences in the structures of orthorhombic and monoclinic $[H(sebenzim^{Me})]_2HgI_2$ do not, however, pertain to the mercury coordination environment. Rather, the differences are associated with the distinct hydrogen bonding motifs (Figures 12 and 13). Furthermore, these hydrogen bonding patterns are also different from that of the chloride counterpart, $[H(sebenzim^{Me})]_2HgCl_2$ (*vide supra*), as illustrated in Figure 14.

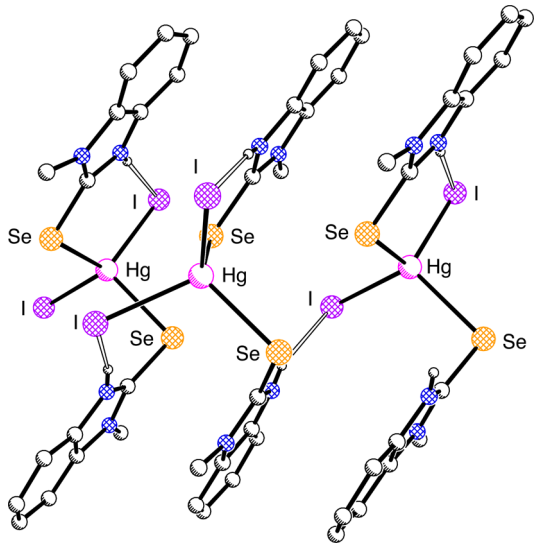


**Figure 12.** Hydrogen bonding network for orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ obtained from acetonitrile solution, illustrating intramolecular and intermolecular N–H···I interactions.

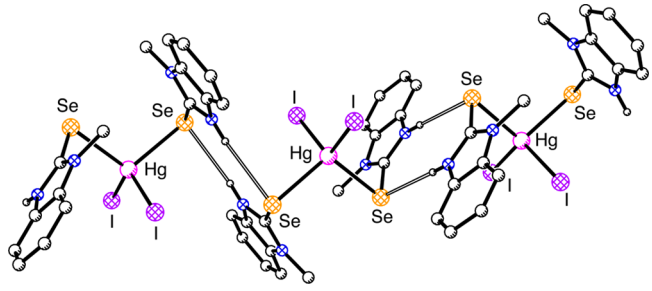


**Figure 13.** Hydrogen bonding network for monoclinic $[H(sebenzim^{Me})]_2HgI_2$ obtained from benzene solution, illustrating "head-to-head" N–H···Se interactions.



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*J. Am. Chem. Soc.* 2015, 137, 4503–4516

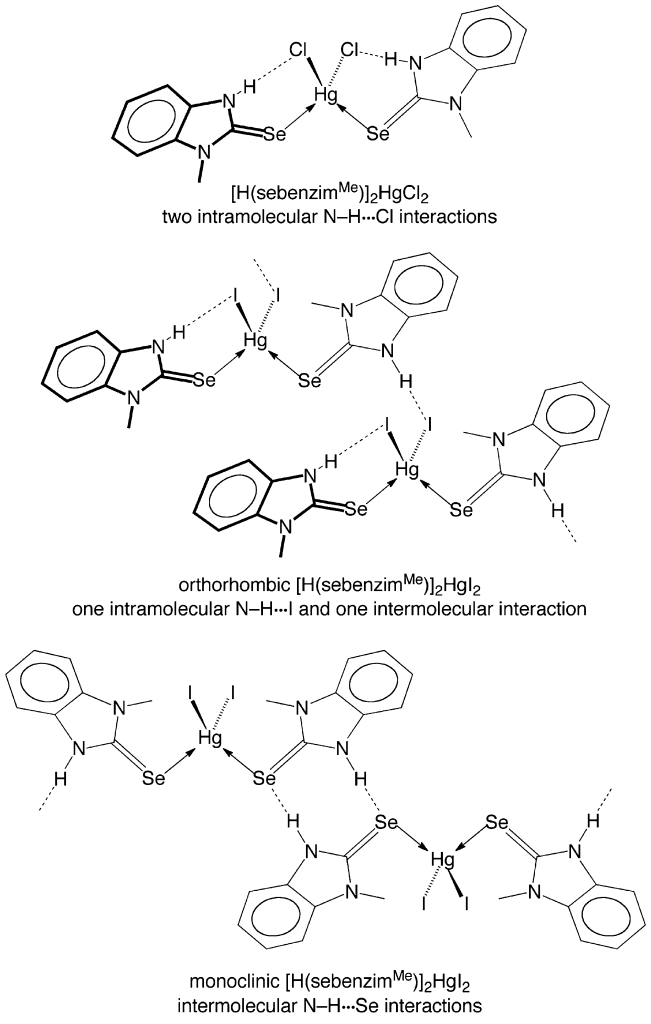


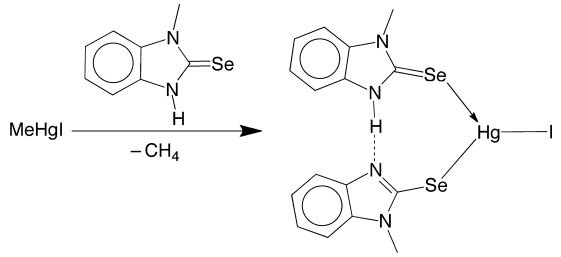

**Figure 14.** Comparison of hydrogen bonding interactions in $[H(sebenzim^{Me})]_2HgCl_2$ and $[H(sebenzim^{Me})]_2HgI_2$.

For example, whereas $[H(sebenzim^{Me})]_2HgCl_2$ is observed to have two intramolecular N−H···Cl interactions, the orthorhombic form of $[H(sebenzim^{Me})]_2HgI_2$ possesses one intramolecular and one intermolecular N−H···I interaction,[57] thereby creating a hydrogen-bonded helical chain of $[H(sebenzim^{Me})]_2HgI_2$ molecules (Figure 12).[58] In contrast to $[H(sebenzim^{Me})]_2HgCl_2$ and orthorhombic $[H(sebenzim^{Me})]_2HgI_2$, however, the monoclinic form of $[H(sebenzim^{Me})]_2HgI_2$ possesses *no* intramolecular or intermolecular N−H···I interactions. Rather, the N−H groups of the $H(sebenzim^{Me})$ ligands participate in pairs of centrosymmetric intermolecular N−H···Se interactions that link adjacent molecules together in a manner similar to that observed for certain $H(seim^R)$ derivatives in the absence of metal coordination (Figure 13).[29,59] Interestingly, $H(sebenzim^{Me})$ itself does not adopt this "head-to-head" motif, but rather adopts a polymeric "head-to-tail" structure.[31a] As such, coordination of the selenium to a metal promotes centrosymmetric N−H···Se interactions in this system, with there being no comparable structures currently listed in the CSD. The existence of this motif is undoubtedly a consequence of the fact that iodide is, by comparison to chloride, a poor hydrogen bond acceptor,[60a] such that N−H···Se interactions may compete with N−H···I interactions.

As would be expected, the hydrogen bonding N···I interactions in orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ [3.486(7) and 3.589(7) Å] are substantially longer than the analogous N···Cl interactions in $[H(sebenzim^{Me})]_2HgCl_2$. Thus, while the mean N···Cl distance in $[H(sebenzim^{Me})]_2HgCl_2$ is 3.182 Å, the mean N···I distance in orthorhombic $[H(sebenzim^{Me})]_2HgI_2$ is 3.541 Å. For reference, the mean N···Cl distance for compounds listed in the CSD with N−H···Cl interactions involving a terminal metal chloride is 3.332 Å,[52] while the analogous N···I distance is 3.707 Å.[60]

**Interaction of 2-Seleno-1-methylbenzimidazole with Methylmercury Halides.** In view of the fact that the protolytic cleavage of the Hg−C bond is a critical step in detoxification of organomercurials,[27h,i,61,62] and recognizing that $H(sebenzim^{Me})$ is an analogue of selenoneine, we have also investigated the reactivity of $H(sebenzim^{Me})$ towards methylmercury halides. Significantly, we have observed that $H(sebenzim^{Me})$ not only coordinates to the mercury center, as observed for $HgX_2$, but it is also capable of cleaving the Hg−C bonds of MeHgX. For example, $H(sebenzim^{Me})$ reacts with MeHgI at 100 °C to liberate $CH_4$ (as observed by $^1H$ NMR spectroscopy) and afford $[H(sebenzim^{Me})_2]HgI$ (Scheme 2). The importance of this observation is underscored

**Scheme 2**




by the fact that selenoneine, of which $H(sebenzim^{Me})$ is a structural analogue, has recently been shown to achieve demethylation of CysHgMe.[11e]

The molecular structure of $[H(sebenzim^{Me})_2]HgI$ has been determined by X-ray diffraction, as illustrated in Figure 15,

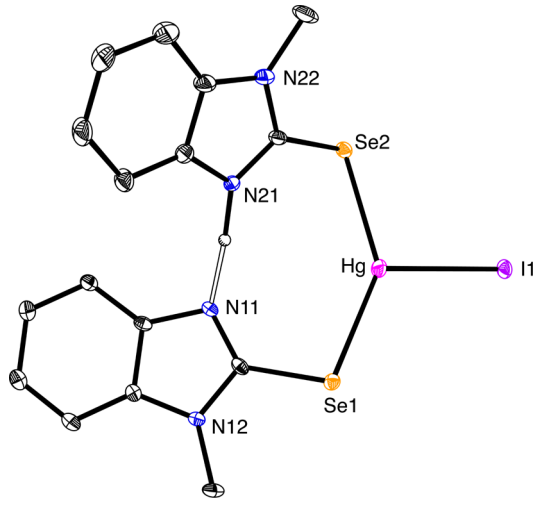



**Figure 15.** Molecular structure of the monomeric unit, $[H(sebenzim^{Me})_2]HgI$.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which demonstrates that it features mercury in an approximately trigonal planar environment, with a pyramidality ($P$) value[63] of only 0.2°. The bond angles at mercury, however, deviate from 120° [Se−Hg−Se = 140.91(2)°; Se−Hg−I = 114.87(2)° and 104.02(2)°], such that the geometry is distorted towards T-shaped, which is not uncommon for mercury.[64]

The most interesting feature of [H(sebenzim$^{Me}$)$_2$]HgI, however, pertains to the fact that the H(sebenzim$^{Me}$) and (sebenzim$^{Me}$) moieties are linked by N−H···N hydrogen bonding interactions, with a N···N distance of 2.720(6) Å.[65,66] As such, the combined fragment, [H(sebenzim$^{Me}$)$_2$], may be viewed as an LX-type ligand.[36] In this regard, the two Hg−Se bond lengths present in [H(sebenzim$^{Me}$)$_2$]HgI [2.5466(6) and 2.5748(6) Å] are very similar.

While the primary coordination environment about mercury is trigonal planar, it is evident that there are additional intermolecular Hg···Se interactions [3.0904(6) and 3.3215(6) Å] that are substantially longer than those within

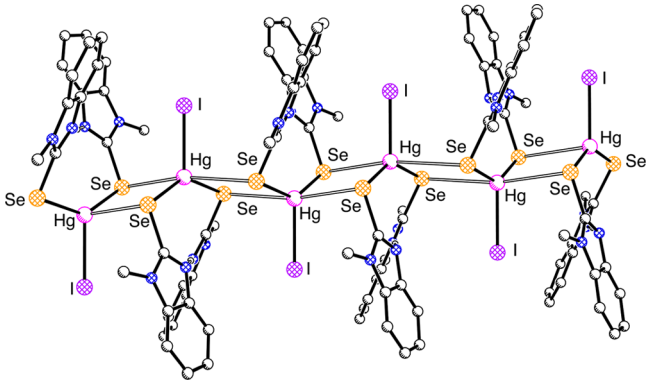



**Figure 16.** Extended structure of {[H(sebenzim$^{Me}$)$_2$]HgI}$_x$.

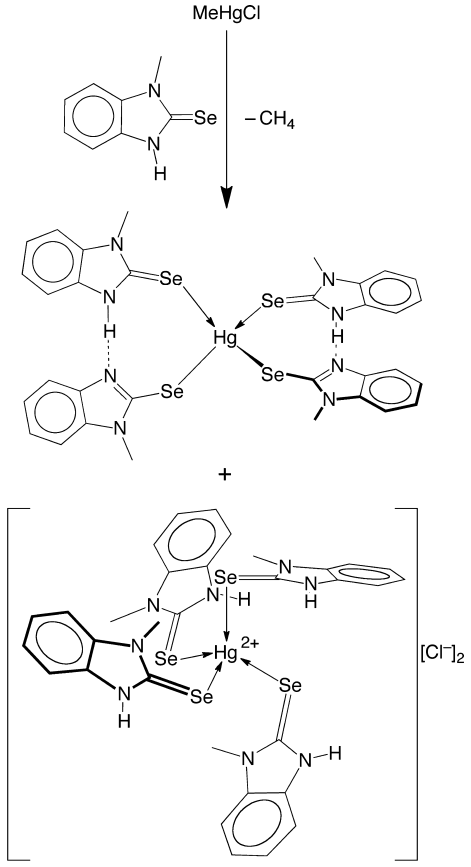
[H(sebenzim$^{Me}$)$_2$]HgI [2.5466(6) and 2.5748(6) Å], and which serve to link together adjacent molecules, as illustrated in Figure 16. In this regard, the extended coordination geometry of mercury may be viewed as five-coordinate and, with a $\tau_5$ index[67] of 0.51, is intermediate between the idealized values for square pyramidal ($\tau_5$ = 0) and trigonal bipyramidal ($\tau_5$ = 1) geometries.

In view of the kinetic stability of two-coordinate RHgX complexes towards protolytic cleavage,[68] it is likely that the mechanism for formation of [H(sebenzim$^{Me}$)$_2$]HgI involves the initial formation of an adduct, [H(sebenzim$^{Me}$)]$_x$Hg(Me)I, which undergoes either intramolecular protolytic cleavage of the Hg−Me bond, or cleavage in an intermolecular manner to afford a mercury−selenoimidazolyl species.

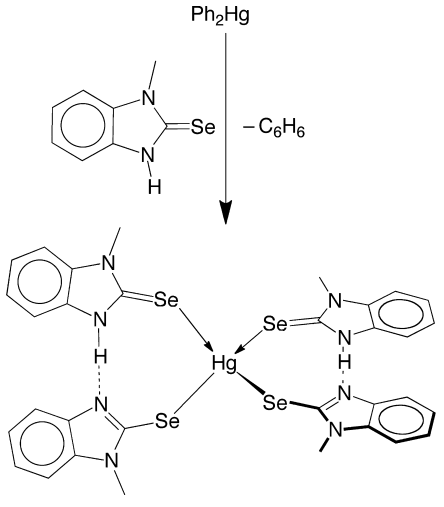
H(sebenzim$^{Me}$) is not only capable of cleaving the Hg−C bond of MeHgI, but also cleaves the Hg−C bond of MeHgCl, although the reaction follows a different course than that of MeHgI. Specifically, reaction of MeHgCl with H(sebenzim$^{Me}$) at 100 °C results in evolution of methane, as observed by $^1$H NMR spectroscopy, and the formation of a mixture of [H(sebenzim$^{Me}$)]$_4$HgCl$_2$ (*vide supra*) and [H(sebenzim$^{Me}$)$_2$]$_2$Hg (Scheme 3). The latter compound can also be obtained *via* the cleavage of the Hg−Ph bonds of Ph$_2$Hg with H(sebenzim$^{Me}$), as illustrated in Scheme 4.

The formation of [H(sebenzim$^{Me}$)]$_4$HgCl$_2$ and [H(sebenzim$^{Me}$)$_2$]$_2$Hg upon treatment of MeHgCl with H(sebenzim$^{Me}$) is indicative of a ligand redistribution process.

**Scheme 3. Protolytic Cleavage of MeHgCl by H(sebenzim$^{Me}$)**




**Scheme 4. Protolytic Cleavage of Ph$_2$Hg by H(sebenzim$^{Me}$)**




For example, one possibility is that incipient {[H(sebenzim$^{Me}$)$_2$]HgCl}, the counterpart of the above iodide derivative, could redistribute to give [H(sebenzim$^{Me}$)$_2$]$_2$Hg and HgCl$_2$, of which the latter would be trapped by H(sebenzim$^{Me}$) to afford [H(sebenzim$^{Me}$)]$_4$HgCl$_2$.[69,70]

The molecular structure of [H(sebenzim$^{Me}$)$_2$]$_2$Hg has been determined by X-ray diffraction (Figure 17), which demonstrates that pairs of H(sebenzim$^{Me}$) and (sebenzim$^{Me}$) ligands are linked together *via* hydrogen bonding interactions to produce the combined LX-type ligand,[71] [H(sebenzim$^{Me}$)$_2$], in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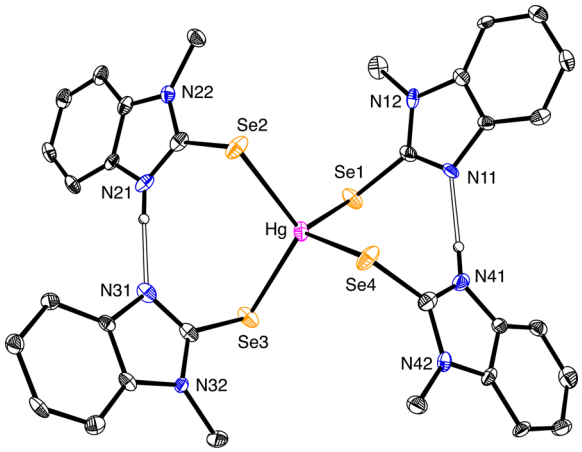


**Figure 17.** Molecular structure of $[H(sebenzim^{Me})_2]_2Hg$.

a manner akin to that observed for $[H(sebenzim^{Me})_2]HgI$. However, while the N···N distances within $[H(sebenzim^{Me})_2]_2Hg$ [2.724(14) and 2.732(14) Å] are comparable to that observed for $[H(sebenzim^{Me})_2]HgI$ [2.720(6) Å], the angles between the $H(sebenzim^{Me})$ and $(sebenzim^{Me})$ planes (76.6° and 76.5°) are distinctly larger than that in $[H(sebenzim^{Me})_2]HgI$ (47.3°). Thus, it is evident that the hydrogen-bonded $[H(sebenzim^{Me})_2]$ ligand is quite flexible with respect to the twist angles of the benzimidazole ring systems. The coordination geometry about mercury in $[H(sebenzim^{Me})_2]_2Hg$ is distorted tetrahedral ($\tau_4$ = 0.88), with Hg–Se bond lengths in a narrow range of 2.6228(12)–2.6367(13) Å.

## CONCLUSIONS

In summary, 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone, $H(sebenzim^{Me})$, is a structural analogue of selenoneine and coordinates reversibly to the metal centers of $HgX_2$ (X = Cl, Br, I). Furthermore, $H(sebenzim^{Me})$ is also capable of cleaving the Hg–C bond of methylmercury halides, thereby mimicking the role of selenoneine in demethylating CysHgMe. X-ray diffraction studies demonstrate that while two equivalents of $H(sebenzim^{Me})$ simply coordinate to mercury centers of $HgX_2$ (X = Cl, I), the third and fourth equivalents result in displacement of the chloride ligands. Thus, $[H(sebenzim^{Me})]_3HgCl_2$ and $[H(sebenzim^{Me})]_4HgCl_2$ are better represented as ion pairs, namely $\{[H(sebenzim^{Me})]_3HgCl\}[Cl]$ and $\{[H(sebenzim^{Me})]_4Hg\}[Cl]_2$, of which the latter is the first example of a structurally characterized tetrahedral mercury compound that features four L-type selenium donors. A common feature of all $[H(sebenzim^{Me})]_xHgCl_2$ structures is that each chloride, regardless of whether it is attached covalently to the mercury center or serves as a counterion, participates in hydrogen bonding interactions with the imidazole N–H moieties. The nature of the network, however, depends critically on the number of $H(sebenzim^{Me})$ donors. For example, whereas $[H(sebenzim^{Me})]_2HgCl_2$ exhibits only intramolecular N–H···Cl interactions and is a discrete mononuclear species, $[H(sebenzim^{Me})]_3HgCl_2$ exhibits an intramolecular N–H···Cl interaction and intermolecular N–H···Cl···H–N interactions that bridge two molecules, resulting in a dimeric structure, while $[H(sebenzim^{Me})]_4HgCl_2$ exhibits an intramolecular N–H···Cl···H–N interaction and intermolecular N–H···Cl···H–N interactions that result in a polymeric array. This investigation demonstrates that not only is $H(sebenzim^{Me})$ a good ligand for mercury, capable of displacing halide ligands, but is also capable of protolytically cleaving mercury–carbon bonds, a result that is of relevance to the role of selenium compounds in the detoxification of mercury compounds.

## EXPERIMENTAL SECTION

**General Considerations.** NMR spectra were measured on a Bruker Avance 500 DMX spectrometer. $^1H$ NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta$ = 0) and were referenced internally with respect to the protio solvent impurity ($\delta$ 7.16 for $C_6D_5H$ and 2.50 for DMSO-$d_5$).[72] $^{13}C$ NMR spectra are reported in ppm relative to $SiMe_4$ ($\delta$ = 0) and were referenced internally with respect to the solvent ($\delta$ 128.06 for $C_6D_6$ and 39.52 for DMSO-$d_6$).[72] $^{77}Se$ NMR spectra are reported in ppm relative to neat $Me_2Se$ ($\delta$ = 0) and were referenced using a solution of $Ph_2Se_2$ in $C_6D_6$ ($\delta$ = 460) as an external standard.[73] $^{199}Hg$ NMR spectra are reported in ppm relative to neat $Me_2Hg$ ($\delta$ = 0) and were referenced using a 1.0 M solution of $HgI_2$ in DMSO-$d_6$ ($\delta$ = −3106) as an external standard.[74] Coupling constants are given in hertz. IR spectra were recorded as KBr pellets on a Nicolet iS10 FT-IR spectrometer (ThermoScientific), and the data are reported in reciprocal centimeters. 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone was obtained by a literature method,[31a] and all other chemicals were purchased from Sigma-Aldrich.

***CAUTION!*** *All mercury compounds are toxic, and appropriate safety precautions must be taken in handling these compounds.*

**X-ray Structure Determinations.** Single-crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer, and crystal data, data collection, and refinement parameters are summarized in Table 6. 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 2013/4).[75]

**Synthesis of $[H(sebenzim^{Me})]_2HgI_2$.** A suspension of $H(sebenzim^{Me})$ (46 mg, 0.22 mmol) and $HgI_2$ (50 mg, 0.11 mmol) in $C_6D_6$ (2 mL) in an NMR tube equipped with a J. Young valve was heated overnight at 100 °C. Over this period, yellow, X-ray-quality crystals of $[H(sebenzim^{Me})]_2HgI_2$ (54 mg, 56% yield) were deposited and isolated by decanting the solution. Crystals of $[H(sebenzim^{Me})]_2HgI_2$ were also obtained from an acetonitrile solution. Anal. Calcd for $C_{16}H_{16}I_2HgN_4Se_2$: C, 21.9; H, 1.8; N, 6.4. Found: C, 22.0; H, 1.6; N, 6.4. $^1H$ NMR (DMSO-$d_6$): $\delta$ 3.90 [s, 6H of $CH_3$], 7.42 [m, 4H of $C_6H_4$], 7.51 [m, 2H of $C_6H_4$], 7.71 [m, 2H of $C_6H_4$], not observed [NH]. $^{13}C\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 33.3 [$CH_3$], 111.8 [CH of $C_6H_4$], 112.1 [CH of $C_6H_4$], 124.4 [CH of $C_6H_4$], 125.0 [CH of $C_6H_4$], 131.8 [C of $C_6H_4$], 133.6 [C of $C_6H_4$], 152.7 [CSe]. $^{77}Se\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 48 ppm. $^{199}Hg\{^1H\}$ NMR (DMSO-$d_6$): not observed. IR data (KBr pellet, $cm^{-1}$): 3172 (m), 3114 (m), 3056 (m), 2986 (w), 2929 (w), 1619 (w), 1498 (m), 1486 (m), 1447 (vs), 1391 (w), 1364 (w), 1346 (s), 1333 (m), 1246 (w), 1226 (w), 1159 (w), 1132 (m), 1091 (m), 1008 (w), 902 (vw), 804 (w), 748 (vs), 727 (w), 664 (w).

**Synthesis of $[H(sebenzim^{Me})]_3HgCl_2$.** A solution of $HgCl_2$ (17 mg, 0.06 mmol) in $CH_3CN$ (1 mL) was added to a solution of $H(sebenzim^{Me})$ (40 mg, 0.19 mmol) in $CHCl_3$ (2 mL). The pale yellow solution was allowed to stand at room temperature for 4 days at room temperature, over which period colorless crystals were deposited as the solution evaporated. X-ray-quality crystals of $[H(sebenzim^{Me})]_3HgCl_2\cdot(CH_3CN)$ were isolated by decanting the mother liquor and dried *in vacuo* (39 mg, 66% yield). Anal. Calcd for $C_{26}H_{27}Cl_2HgN_7Se_3$: C, 33.0; H, 2.9; N, 10.4. Found: C, 33.6; H, 2.3; N, 9.9. $^1H$ NMR (DMSO-$d_6$): $\delta$ 3.83 [s, 9H of $CH_3$], 7.35 [m, 6H of $C_6H_4$], 7.40 [m, 3H of $C_6H_4$], 7.62 [m, 3H of $C_6H_4$], 13.93 [br, N-H]. $^{13}C\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 32.7 [$CH_3$], 111.3 [CH of $C_6H_4$], 111.4 [CH of $C_6H_4$], 123.9 [CH of $C_6H_4$], 124.5 [CH of $C_6H_4$], 131.6 [C of $C_6H_4$], 133.4 [C of $C_6H_4$], 154.6 [CSe]. $^{77}Se\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ 35 ppm. $^{199}Hg\{^1H\}$ NMR (DMSO-$d_6$): $\delta$ −1020 ppm. IR data (KBr pellet, $cm^{-1}$): 3448 (w), 3032 (m), 2969 (m), 2918 (m), 2850 (m), 2804 (m), 2740 (m), 2693 (m), 2588 (w), 2514 (w), 1618 (w), 1502


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J. Am. Chem. Soc. 2015, 137, 4503–4516

**Table 6. Crystal, Intensity Collection, and Refinement Data**

| | $[H(sebenzim^{Me})]_3HgCl_2\cdot(MeCN)$ | $[H(sebenzim^{Me})]_4HgCl_2$ | $[H(sebenzim^{Me})]_2HgI_2$ | $[H(sebenzim^{Me})]_2HgI_2$ | $[H(sebenzim^{Me})_2]HgI\cdot0.5(benzene)$ | $[H(sebenzim^{Me})_2]_2Hg$ |
|---|---|---|---|---|---|---|
| lattice | triclinic | monoclinic | orthorhombic | monoclinic | triclinic | triclinic |
| formula | $C_{26}H_{27}Cl_2HgN_7Se_3$ | $C_{32}H_{32}Cl_2HgN_8Se_4$ | $C_{16}H_{16}HgI_2N_4Se_2$ | $C_{16}H_{16}HgI_2N_4Se_2$ | $C_{19}H_{18}HgIN_4Se_2$ | $C_{32}H_{30}HgN_8Se_4$ |
| formula weight | 945.91 | 1115.98 | 876.64 | 876.64 | 787.79 | 1043.07 |
| space group | $P\bar{1}$ | $P2_1$ | $Pbcn$ | $P2_1/c$ | $P\bar{1}$ | $P\bar{1}$ |
| $a$/Å | 10.1199(8) | 12.8918(14) | 16.884(2) | 14.0994(17) | 8.0273(8) | 8.7906(7) |
| $b$/Å | 11.9549(10) | 14.5673(15) | 8.4266(11) | 15.2939(19) | 11.7704(12) | 13.0704(10) |
| $c$/Å | 14.3848(12) | 19.000(2) | 30.211(4) | 10.1211(12) | 11.7946(12) | 15.0622(12) |
| $\alpha$/° | 74.8680(10) | 90 | 90 | 90 | 88.8410(10) | 104.4970(10) |
| $\beta$/° | 86.9400(10) | 94.939(2) | 90 | 92.800(2) | 88.2190(10) | 98.2150(10) |
| $\gamma$/° | 66.2060(10) | 90 | 90 | 90 | 73.2710(10) | 90.0560(10) |
| $V$/Å$^3$ | 1534.5(2) | 3554.9(7) | 4298.3(10) | 2179.9(5) | 1066.65(19) | 1657.1(2) |
| $Z$ | 2 | 4 | 8 | 4 | 2 | 2 |
| temperature/K | 150(2) | 150(2) | 130(2) | 130(2) | 130(2) | 150(2) |
| radiation ($\lambda$)/Å | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| $\rho$(calcd)/g cm$^{-3}$ | 2.047 | 2.085 | 2.709 | 2.671 | 2.453 | 2.090 |
| $\mu$(Mo K$\alpha$)/mm$^{-1}$ | 8.777 | 8.612 | 13.429 | 13.240 | 12.086 | 9.074 |
| $\theta_{max}$/deg | 30.721 | 30.612 | 30.034 | 30.569 | 30.034 | 31.492 |
| no. of data collected | 25209 | 42569 | 128567 | 68656 | 30304 | 28237 |
| no. of data | 9472 | 21344 | 6281 | 6679 | 6221 | 10891 |
| no. of parameters | 365 | 888 | 235 | 235 | 251 | 418 |
| $R_1$ [$I > 2\sigma I$)] | 0.0301 | 0.0409 | 0.0502 | 0.0218 | 0.0323 | 0.0810 |
| $wR_2$ [$I > 2\sigma I$] | 0.0561 | 0.0617 | 0.1081 | 0.0516 | 0.0853 | 0.1831 |
| $R_1$ [all data] | 0.0474 | 0.0684 | 0.0904 | 0.0251 | 0.0378 | 0.1123 |
| $wR_2$ [all data] | 0.0608 | 0.0688 | 0.1216 | 0.0525 | 0.0878 | 0.1869 |
| $R_{int}$ [all data] | 0.0345 | 0.0411 | 0.1616 | 0.0447 | 0.0464 | 0.1061 |
| GOF | 0.979 | 1.011 | 0.988 | 1.093 | 1.054 | 1.848 |



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J. Am. Chem. Soc. 2015, 137, 4503−4516

(s), 1449 (vs), 1399 (m), 1360 (m), 1348 (s), 1334 (s), 1258 (m), 1242 (m), 1154 (w), 1132 (w), 1096 (s), 1008 (w), 805 (w), 740 (vs).

**Synthesis of [H(sebenzim$^{Me}$)]$_4$HgCl$_2$.** A suspension of H(sebenzim$^{Me}$) (85 mg, 0.40 mmol) and $HgCl_2$ (27 mg, 0.10 mmol) in $CD_3CN$ (2 mL) in an NMR tube equipped with a J. Young valve was heated overnight at 100 °C. Over this period, pale yellow, X-ray-quality crystals of [H(sebenzim$^{Me}$)]$_4$HgCl$_2$ (94 mg, 84% yield) were deposited and isolated by decanting the solution. Anal. Calcd for $C_{32}H_{32}Cl_2HgN_8Se_4$: C, 34.4; H, 2.9; N, 10.0. Found: C, 34.7; H, 2.6; N, 10.0. $^1$H NMR (DMSO-$d_6$): $\delta$ 3.80 [s, 12H of C$\underline{H}_3$], 7.33 [m, 12H of C$_6\underline{H}_4$], 7.56 [m, 4H of C$_6$H$_4$], 13.72 [br, N-$\underline{H}$]. $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 32.5 [$\underline{C}H_3$], 111.0 [CH of $\underline{C}_6H_4$], 111.1 [CH of $\underline{C}_6H_4$], 123.6 [CH of $\underline{C}_6H_4$], 124.2 [CH of $\underline{C}_6H_4$], 131.7 [ring junction C of $\underline{C}_6H_4$], 133.5 [ring junction C of $\underline{C}_6H_4$], 156.6 [$\underline{C}$Se]. $^{77}$Se{$^1$H} NMR (DMSO-$d_6$): $\delta$ 44 ppm. $^{199}$Hg{$^1$H} NMR (DMSO-$d_6$): $\delta$ −1012 ppm. IR data (KBR pellet, cm$^{-1}$): 3424 (w), 3032 (m), 2971 (m), 2919 (m), 2849 (m), 2727 (w), 2668 (w), 1618 (w), 1498 (m), 1447 (vs), 1390 (w), 1346 (s), 1333 (m), 1247 (w), 1156 (w), 1134 (w), 1097 (m), 1009 (w), 901 (vw), 804 (w), 756 (m), 747 (s).

**Synthesis of [H(sebenzim$^{Me}$)$_2$]$_2$Hg.** A suspension of H(sebenzim$^{Me}$) (40 mg, 0.19 mmol) and $Ph_2Hg$ (17 mg, 0.05 mmol) in $CD_3CN$ (0.7 mL) in an NMR tube equipped with a J. Young valve was heated overnight at 100 °C. Over this period, very pale yellow, X-ray-quality crystals of [H(sebenzim$^{Me}$)$_2$]$_2$Hg (32 mg, 65% yield) were deposited and isolated by decanting the solution. Anal. Calcd for $C_{32}H_{30}HgN_8Se_4$: C, 36.9; H, 2.9; N, 10.7. Found: C, 36.3; H, 2.9; N, 10.4. $^1$H NMR (DMSO-$d_6$): $\delta$ 3.72 [s, 12H of C$\underline{H}_3$], 7.17 [m, 8H of C$_6\underline{H}_4$], 7.31 [m, 4H of C$_6\underline{H}_4$], 7.40 [m, 4H of C$_6\underline{H}_4$], not observed [N$\underline{H}$]. $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 32.0 [$\underline{C}H_3$], 109.7 [CH of $\underline{C}_6H_4$], 113.4 [CH of $\underline{C}_6H_4$], 121.9 [CH of $\underline{C}_6H_4$], 122.2 [CH of $\underline{C}_6H_4$], 136.4 [C of $\underline{C}_6H_4$], 156.0 [$\underline{C}$Se]. $^{77}$Se{$^1$H} NMR (DMSO-$d_6$): $\delta$ 74 ppm. $^{199}$Hg{$^1$H} NMR (DMSO-$d_6$): not observed. IR data (KBr pellet, cm$^{-1}$): 3450 (vw), 3054 (w), 2932 (w), 2461 (w), 1904 (w), 1619 (w), 1514 (m), 1466 (vs), 1432 (vs), 1392 (s), 1359 (s), 1332 (vs), 1277 (vs), 1236 (m), 1150 (w), 1113 (w), 1086 (s), 1007 (m), 912 (w), 838 (vw), 806 (w), 736 (vs), 728 (vs), 662 (vw).

**Reactivity of H(sebenzim$^{Me}$) towards MeHgI: Formation of [H(sebenzim$^{Me}$)$_2$]HgI.** A suspension of H(sebenzim$^{Me}$) (64 mg, 0.30 mmol) and MeHgI (52 mg, 0.15 mmol) in $C_6D_6$ (2 mL) in an NMR tube equipped with a J. Young valve was heated overnight at 100 °C. Over this period, pale yellow, X-ray-quality crystals of [H(sebenzim$^{Me}$)$_2$]HgI·0.5(benzene) (67 mg, 56% yield) were deposited and isolated by decanting the solution. Anal. Calcd for $C_{19}H_{18}HgIN_4Se_2$: C, 29.0; H, 2.3; N, 7.1. Found: C, 29.1; H, 2.4; N, 7.1. $^1$H NMR (DMSO-$d_6$): $\delta$ 3.75 [s, 6H of C$\underline{H}_3$], 7.21 [m, 4H of C$_6\underline{H}_4$], 7.41 [m, 2H of C$_6\underline{H}_4$], 7.45 [m, 2H of C$_6\underline{H}_4$], not observed [N$\underline{H}$]. $^{13}$C{$^1$H} NMR (DMSO-$d_6$): $\delta$ 32.7 [$\underline{C}H_3$], 110.6 [CH of $\underline{C}_6H_4$], 113.8 [CH of $\underline{C}_6H_4$], 122.9 [CH of $\underline{C}_6H_4$], 123.2 [CH of $\underline{C}_6H_4$], 134.6 [C of $\underline{C}_6H_4$], 136.6 [C of $\underline{C}_6H_4$], 151.2 [$\underline{C}$Se, $J_{Se-C}$ = 180]. $^{77}$Se{$^1$H} NMR (DMSO-$d_6$): $\delta$ 48 ppm. $^{199}$Hg{$^1$H} NMR (DMSO-$d_6$): not observed. IR data (KBr pellet, cm$^{-1}$): 3453 (vw), 3053 (w), 2932 (w), 2387 (w), 1901 (w), 1872 (w), 1863 (w), 1610 (w), 1523 (w), 1466 (vs), 1432 (vs), 1395 (s), 1336 (vs), 1277 (vs), 1236 (m), 1156 (w), 1112 (w), 1087 (s), 1007 (m), 910 (w), 846 (vw), 807 (w), 743 (vs), 736 (vs), 661 (vw).

**Reactivity of H(sebenzim$^{Me}$) towards MeHgCl: Formation of [H(sebenzim$^{Me}$)$_2$]$_2$Hg and [H(sebenzim$^{Me}$)]$_4$HgCl$_2$.** A suspension of H(sebenzim$^{Me}$) (85 mg, 0.40 mmol) and MeHgCl (25 mg, 0.10 mmol) in $CD_3CN$ (2 mL) in an NMR tube equipped with a J. Young valve was heated overnight at 100 °C. Over this period, colorless plates of [H(sebenzim$^{Me}$)$_2$]$_2$Hg and large, yellow blocks of [H(sebenzim$^{Me}$)]$_4$HgCl$_2$ were deposited and were isolated by decanting the solution. The crystals were separated manually under a microscope for purposes of performing X-ray diffraction experiments.

**$^1$H NMR Spectroscopic Study of the Titration of HgX$_2$ (X = Cl, Br, I) with H(sebenzim$^{Me}$).** A solution of $HgX_2$ (X = Cl, Br, I; 0.05 mmol) in DMSO-$d_6$ (0.6 mL) was treated with aliquots (40 $\mu$L) of a solution of H(sebenzim$^{Me}$) (126.7 mg, 0.6 mmol) in DMSO-$d_6$ (0.48 mL) and monitored by $^1$H NMR spectroscopy. The data obtained are presented in Table 2.

**$^{77}$Se{$^1$H} and $^{199}$Hg{$^1$H} NMR Spectroscopic Study of the Titration of HgCl$_2$ with H(sebenzim$^{Me}$).** A solution of $HgCl_2$ (17.0 mg, 0.063 mmol) in DMSO-$d_6$ (0.6 mL) was treated with four aliquots of H(sebenzim$^{Me}$) (13.2 mg, 0.063 mmol) and monitored by $^{77}$Se{$^1$H} and $^{199}$Hg{$^1$H} NMR spectroscopy. The results of this titration are presented in Table 1.

**$^{77}$Se{$^1$H} NMR Spectroscopic Study of HgX$_2$ (X = Cl, Br, I) with H(sebenzim$^{Me}$).** A solution of $HgX_2$ (X = Cl, Br, I) in DMSO-$d_6$ (0.05 mmol in 0.6 mL) was treated with 200 $\mu$L of a solution of H(sebenzim$^{Me}$) in DMSO-$d_6$ (0.5 mmol in 1.00 mL) and was monitored by $^{77}$Se{$^1$H} NMR spectroscopy.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Crystallographic data for all structurally characterized compounds (CIF). This material is available free of charge *via* the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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