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Coordination of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone to zinc and cadmium: Monotonic and non-monotonic bond length variations for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MCl}_2$ complexes ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$)[‡]

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Abstract

The reactions of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone, $\text{H}(\text{sebenzim}^{\text{Me}})$, towards the zinc and cadmium halides, MX_2 ($\text{M} = \text{Zn}, \text{Cd}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), afford the adducts, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MX}_2$, which have been structurally characterized by X-ray diffraction. The halide ligands of each of these complexes participate in hydrogen bonding interactions with the imidazole N–H moieties, although the nature of the interactions depends on the halide. Specifically, the chloride and bromide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$ ($\text{X} = \text{Cl}, \text{Br}$), exhibit two intramolecular N–H $\cdots$ X interactions, whereas the iodide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, exhibit only one intramolecular N–H $\cdots$ I interaction. Comparison of the M–Se and M–Cl bond lengths of the chloride series, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MCl}_2$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$), indicates that while the average M–Cl bond lengths progressively increase as the metal becomes heavier, the variation in M–Se bond length exhibits a non-monotonic trend, with the Cd–Se bond being the longest. These different trends provide an interesting subtlety concerned with use of covalent radii in predicting bond length differences. In addition to tetrahedral $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$, $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2 \cdot [\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$, which features both five-coordinate and six-coordinate centers, has also been structurally characterized. Finally, the reaction between CdI_2 and $\text{H}(\text{sebenzim}^{\text{Me}})$ at elevated temperatures affords the 1-methylbenzimidazole complex, $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{--}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$, a transformation that is associated with cleavage of the C–Se bond.

[‡]Dedicated to William D. Jones on the occasion of his 65th birthday. Happy birthday, Bill!

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APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC #1872851-1872858). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.xxxxxx>.

Graphical Abstract

The reactions of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone, H(sebenzim^{Me}), towards the zinc and cadmium halides, MX₂ (M = Zn, Cd; X = Cl, Br, I), afford the adducts, [H(sebenzim^{Me})₂MX₂]. Comparison of the M–Se and M–Cl bond lengths of the chloride series, [H(sebenzim^{Me})₂MCl₂] (M = Zn, Cd, Hg), indicates that while the average M–Cl bond lengths progressively increase as the metal becomes heavier, the variation in M–Se bond length exhibits a non-monotonic trend, with the Cd–Se bond being the longest. These different trends provide an interesting subtlety concerned with use of covalent radii in predicting bond length differences.

INTRODUCTION

1-*R*-imidazole-2-thiones, H(mim^R)^{1,2} and 1-*R*-imidazole-2-selones, H(seim^R)^{3–8} are five-membered heterocyclic nitrogen compounds that respectively feature C=S and C=Se moieties (Figure 1).⁹ Of these, the former has been investigated most extensively, in part due to the fact that the methyl derivative is the well-known antithyroid drug, methimazole (tapazole).¹⁰ By comparison, the selenium counterparts have been studied relatively little. However, they have received attention with respect to their potential for antithyroid activity,^{3,8} and the heterocyclic motif is present in the biomolecules selenoneine^{11,12} and Se-methylselenoneine.^{12,13} Furthermore, while there are numerous applications of 1-*R*-imidazole-2-thiones in coordination chemistry,^{14–18} there are very few reports of metal complexes that feature 1-*R*-imidazole-2-selone ligands.^{6,7,19,20} For example, the only structurally characterized examples listed in the Cambridge Structural Database (CSD)²¹ are gold¹⁹ and mercury⁶ complexes. Prompted by the many uses of 1-*R*-imidazole-2-thiones,^{2,14–16} it is evident that 1-*R*-imidazole-2-selone ligands offer much potential for complementing the use of other selenium ligands, such as selenolate,²² selenoether,^{23,24} pyridine selenolates²⁵ and, in particular, 1,3-dialkylimidazole-2-selones²⁶ and their saturated counterparts.²⁷ Moreover, 1-*R*-imidazole-2-selones are also of interest because they can be elaborated into bidentate and tridentate bis- and tris(selenoimidazolyl)hydroborato ligands.^{28,29,30} Here, we describe the application of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone, H(sebenzim^{Me}),³¹ towards the chemistry of zinc and cadmium, with the specific intention of providing a comparison for the aforementioned mercury system.

RESULTS AND DISCUSSION

1. Synthesis and Structural Characterization of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$

We have previously reported that $\text{H}(\text{sebenzim}^{\text{Me}})$ is an effective ligand for mercury, as illustrated by the structural characterization of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{HgCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{HgI}_2$.⁶ As an extension of this investigation, we report here that $\text{H}(\text{sebenzim}^{\text{Me}})$ likewise coordinates to zinc and cadmium. For example, treatment of ZnX_2 and CdX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) with two equivalents of $\text{H}(\text{sebenzim}^{\text{Me}})$ affords the respective adducts, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$, as illustrated in Scheme 1.¹⁶ $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$ have been structurally characterized by X-ray diffraction (Figure 2 – Figure 7), which demonstrates that the metal centers adopt slightly distorted tetrahedral geometries with τ_4 and τ_8 indices³² in the ranges of 0.93–0.95 and 0.88–0.92, respectively (Table 1).^{33,34,35}

As would be expected, coordination of $\text{H}(\text{sebenzim}^{\text{Me}})$ to the MX_2 metal centers is accompanied by a lengthening of the C–Se bond, albeit small. Specifically, the C–Se bond lengths of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MX}_2$ range from 1.855(9) to 1.867(3) Å, compared to the value of 1.838(2) Å for $\text{H}(\text{sebenzim}^{\text{Me}})$.^{6a} For reference, the C–Se single bond length in the diselenide $(\text{sebenzim}^{\text{Me}})_2$ is 1.89 Å.^{6a} As such, the singly bonded zwitterionic form C^+-Se^- (Figure 1) is an important component for the description of the bonding in both $\text{H}(\text{sebenzim}^{\text{Me}})$ and the adducts, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MX}_2$.

A common feature of the structures of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MX}_2$ is that the halide ligands participate in hydrogen bonding interactions with the imidazole N–H moieties (Table 2), although the nature of the interactions depends on the halide. Specifically, the chloride and bromide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$ ($\text{X} = \text{Cl}, \text{Br}$), exhibit two intramolecular N–H $\cdots$ X interactions,^{36,37,38,39} whereas the iodide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, exhibit only one intramolecular N–H $\cdots$ I interaction.^{40,41} A difference between $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, however, is that one of the $\text{H}(\text{sebenzim}^{\text{Me}})$ ligands of the zinc complex exhibits a hydrogen bonding interaction with MeCN,⁴² whereas that in the cadmium complex exhibits a hydrogen bonding interaction with an iodide ligand of an adjacent molecule, thereby resulting in a polymeric structure (Figure 8). Differences in hydrogen bonding interactions as a function of the halide ligand are also observed in the mercury system, for which $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{HgCl}_2$ is monomeric with two intramolecular N–H $\cdots$ Cl interactions, whereas $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{HgI}_2$ adopts two structures, of which one (obtained from acetonitrile solution) is similar to that of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, with one intramolecular and one intermolecular N–H $\cdots$ I interaction per mercury, while the other (obtained from benzene solution) exhibits no N–H $\cdots$ I interactions, but rather exhibits a polymeric structure by virtue of centrosymmetric N–H $\cdots$ Se interactions.⁶

As would be expected, the hydrogen-bonding N–H $\cdots$ X interactions increase in length as the halogen becomes heavier (Table 2). For reference, the mean N $\cdots$ X distances for compounds listed in the Cambridge Structural Database with N–H $\cdots$ X interactions involving a terminal metal halide ligand are 3.34 Å (Cl), 3.48 Å (Br) and 3.71 Å (I).

Comparison of the M–Se and M–Cl bond lengths of the chloride series (Table 1), [H(sebenzim^{Me})]₂MCl₂ (M = Zn, Cd, Hg), is particularly interesting. Specifically, while the average M–Cl bond lengths progressively increase as the metal becomes heavier, the variation in M–Se bond length exhibits a non-monotonic trend, with the Cd–Se bond being the longest, *i.e.* 2.471 Å (Zn), 2.626 Å (Cd) and 2.591 Å (Hg), as illustrated in Figure 9. A similar non-monotonic trend is also observed in the variation of M–SePh bond lengths in [Tm^{Bu^t}]₂MSePh, *i.e.* 2.394 Å (Zn),⁴³ 2.560 Å (Cd)⁴⁴ and 2.524 Å (Hg).⁴⁵ The M–Se bond lengths in [Tm^{Bu^t}]₂MSePh are, nevertheless, consistently shorter than those for [H(sebenzim^{Me})]₂MCl₂ due to the fact that the M–Se interactions in [Tm^{Bu^t}]₂MSePh are normal covalent bonds, whereas those in [H(sebenzim^{Me})]₂MCl₂ are dative covalent bonds (*i.e.* X *versus* L interactions according to the covalent bond classification),⁴⁶ in this regard, the lengths of dative covalent bonds are known to be both more variable and longer than corresponding normal covalent bonds.⁴⁷

The non-monotonic variation in M–Se bond lengths is in accord with the variation in covalent radii of these elements, *i.e.* Zn (1.22 Å) < Cd (1.44 Å) > Hg (1.32 Å),⁴⁸ an observation that is normally rationalized in terms of the lanthanide contraction and relativistic effects for mercury.^{49,50} Thus, the Hg–X bond in a mercury compound is often shorter than the Cd–X bond in the cadmium counterpart, as illustrated by the M–CH₃ bonds in M(CH₃)₂,⁴⁹ the M–Sn bonds in [MeSi{SiMe₂N(p-Tol)}₃Sn]₂M,⁵¹ and the M–M bonds in ArM–MAr.⁵² In addition to these two-coordinate compounds, the same trend is observed for the M–halogen bonds in tetrahedral [Tp^{Prⁱ2}]₂MCl,⁵³ [Tm^R]₂MBr (R = Me, Bu^t),^{54,55} and [Tse^{Mes}]₂MI.^{28a}

With this perspective, it is evident that it is the monotonic trend in the M–Cl bond lengths of [H(sebenzim^{Me})]₂MCl₂ that should be considered unusual. However, examination of the literature indicates that this trend is also preceded in certain other compounds. For example, the average Cd–X bond lengths in [CdX₄]^{2–} (X = Cl, Br, I) are shorter than the average Hg–X bond lengths in the mercury counterparts, [HgX₄]^{2–}.⁴⁵

Interestingly, other systems also behave in a similar manner to [H(sebenzim^{Me})]₂MCl₂ by exhibiting two different trends in bond lengths. In particular, the mercaptoimidazole adducts [H(mim^{Me})]₂MCl₂^{16b,f} and [H(mim^{Bu^t})]₂MBr₂^{16g} exhibit a non-monotonic variation in M–S bond length, but a monotonic variation in M–halogen bond length. Likewise, the Cd–X bond lengths in (Ph₃P)₂CdX₂ (X = Cl,⁵⁶ I⁵⁷) are shorter than the corresponding Hg–X bond lengths in (Ph₃P)₂HgX₂ (X = Cl,⁵⁸ I⁵⁹), whereas the Cd–P bonds are longer than the Hg–P bonds. Another example is provided by [Tm^{Bu^t}]₂MSePh, in which the M–S bond lengths exhibit a monotonic trend, whereas the M–Se bond lengths exhibit a non-monotonic trend.⁴⁵ The observation that [H(sebenzim^{Me})]₂MCl₂, [H(mim^{Me})]₂MCl₂, [Tm^{Bu^t}]₂MSePh and (Ph₃P)₂MX₂ each exhibit two different trends in bond length variation presents an interesting subtlety concerned with use of covalent radii in predicting bond length differences.

2. Synthesis and Structural Characterization of $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2 \cdot [\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$

In addition to $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{HgX}_2$, compounds of composition $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{HgCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{HgCl}_2$ were also reported for the mercury system.^{6b} Cadmium complexes with 3:1 and 4:1 compositions, *i.e.* $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$, have also been obtained by treatment of CdCl_2 with excess $\text{H}(\text{sebenzim}^{\text{Me}})$ as illustrated in Scheme 2; however, the two compounds have not been isolated independently but are rather components of the same crystal, *i.e.* $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2 \cdot [\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$.

The molecular structures of $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$ are respectively illustrated in Figure 10 and Figure 11, and demonstrate that the former possesses a distorted trigonal bipyramidal geometry, while the latter adopts a distorted octahedral arrangement. An illustration of the distortion of $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ is provided by the fact that the axial $\text{Cl}-\text{Cd}-\text{Cl}$ group is not orthogonal to the $[\text{CdSe}_3]$ plane, as illustrated by the observation that the $\text{Cl}21-\text{Cd}2-\text{Se}21$ and $\text{Cl}22-\text{Cd}2-\text{Se}21$ angles are 97.9° and 78.9° . Despite this distortion, however, $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ is characterized by a τ_5 five-coordinate geometry index⁶⁰ of 0.90, which is much closer to that for an idealized trigonal bipyramidal (1.00) than that for a square pyramidal geometry (0.00). This observation is of note because most five-coordinate cadmium compounds possess τ_5 values that correspond more closely to a square pyramidal rather than trigonal bipyramidal geometry.^{61,62}

With respect to six-coordinate $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$, the distortion from octahedral geometry is made evident by the fact that while the $\text{Se}-\text{Cd}-\text{Se}$ bond angles are close to 90° , the $\text{Cl}-\text{Cd}-\text{Se}$ bond angles deviate considerably, such that the $\text{Cl}-\text{Cd}-\text{Cl}$ unit is not orthogonal to the $[\text{CdSe}_4]$ plane. For example, the $\text{Cl}-\text{Cd}-\text{Se}$ bond angles range from $79.45(3)^\circ$ to $100.55(3)^\circ$.

In common with tetrahedral $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$, the chloride ligands of $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$ also participate in intramolecular hydrogen bonding interactions with the imidazole $\text{N}-\text{H}$ moieties. Metrical data for $[\text{H}(\text{sebenzim}^{\text{Me}})]_x\text{CdCl}_2$ ($x = 2, 3, 4$), which illustrate some interesting differences, are compared in Table 3. Firstly, the increase in coordination number is accompanied by a progressive increase in $\text{Cd}-\text{Se}$ bond length (2.61 Å for $x = 2$; 2.68 Å for $x = 3$; 2.80 Å for $x = 4$). A significant increase in $\text{Cd}-\text{Cl}$ bond length is also observed upon progressing from $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$ (2.44 Å) to $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ (2.68 Å), but there is little subsequent change (and, in fact, a slight decrease) upon progressing to $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$ (2.67 Å). Also of note, the increase in $\text{Cd}-\text{Cl}$ bond length between $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ (0.23 Å) is substantially larger than the increase in $\text{Cd}-\text{Se}$ bond length (0.08 Å). In contrast to these changes $\text{Cd}-\text{Cl}$ and $\text{Cd}-\text{Se}$ bond lengths, there is relatively little variation in the $\text{N}-\text{H} \cdots \text{Cl}$ hydrogen bonding interactions (Table 3).

Finally, with respect to the structures of $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$, it is interesting to point out that while the compositions of these

molecules correspond to those observed for the mercury system, *i.e.* $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{HgCl}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{HgCl}_2$, the structures are actually very different. Specifically, whereas the cadmium compounds are discrete molecular species, the mercury counterparts are ionic. Thus, with the shortest $\text{Hg}\cdots\text{Cl}$ distance in $[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{HgCl}_2$ being 3.913 Å, the compound is best represented as $\{[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{Hg}\}[\text{Cl}]_2$, with a tetrahedral coordination geometry. Likewise, with a $\text{Hg}\cdots\text{Cl}$ distance of 3.240 Å for one of the interactions,⁶³ $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{HgCl}_2$ is best formulated as $\{[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{HgCl}\}[\text{Cl}]$, with a trigonal monopyramidal geometry.

3. Synthesis and Structural Characterization of $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$

While the reaction between CdI_2 and $\text{H}(\text{sebenzim}^{\text{Me}})$ at room temperature affords the simple adduct, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, the 1-methylbenzimidazole complex, $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$, (Scheme 3) is also formed at elevated temperatures and has been structurally characterized by X-ray diffraction (Figure 12). The formation of $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$ is associated with cleavage of the C–Se bond,⁶⁴ and $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$ may also be directly obtained by the reaction of CdI_2 with an equimolar mixture of $\text{H}(\text{sebenzim}^{\text{Me}})$ and 1-methylbenzimidazole (Scheme 3).

The cadmium center in $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$ adopts a distorted tetrahedral geometry with τ_4 and τ_5 indices of 0.88 and 0.85 respectively. The Cd–Se [2.6817(9) Å] and Cd–I [2.7448(9) Å and 2.7550(7) Å] bond lengths are similar to those observed in $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, and the Cd–N bond length [2.249(4) Å] is comparable to the average Cd–N_{benzimidazole} bond length found in the CSD (2.266 Å)²¹ for cadmium complexes that also feature two iodide ligands.⁶⁵ In contrast to $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, however, the N–H moiety of the $\text{H}(\text{sebenzim}^{\text{Me}})$ ligand does not participate in a hydrogen bonding interaction with the iodide ligand, but does exhibit an interaction with a molecule of acetonitrile with a $\text{N}\cdots\text{N}$ distance of 2.953 Å, similar to that described above for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$.

CONCLUSIONS

In summary, the reactions of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-selone towards the zinc and cadmium halides, MX_2 (M = Zn, Cd; X = Cl, Br, I) afford the adducts, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MX}_2$, in which the halide ligands participate in hydrogen bonding interactions with the imidazole N–H moieties. The nature of the interactions, however, depend on the halide, such that the chloride and bromide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnX}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdX}_2$ (X = Cl, Br), exhibit two intramolecular $\text{N}\cdots\text{H}\cdots\text{X}$ interactions, whereas the iodide derivatives, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$ and $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$, exhibit only one intramolecular $\text{N}\cdots\text{H}\cdots\text{I}$ interaction.

Comparison of the M–Se and M–Cl bond lengths of the chloride series, $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{MCl}_2$ (M = Zn, Cd, Hg), indicates that while the average M–Cl bond lengths progressively increase as the metal becomes heavier, the variation in M–Se bond length exhibits a non-monotonic trend, with the Cd–Se bond being the longest. Although the latter trend is in accord with that expected by the lanthanide contraction, the observation of

two different trends in bond lengths provides an interesting subtlety concerned with use of covalent radii in predicting bond length differences. In addition to tetrahedral $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$, $[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{CdCl}_2 \cdot [\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{CdCl}_2$, which features both five-coordinate and six-coordinate coordinate centers has also been structurally characterized. Finally, the reaction between CdI_2 and $\text{H}(\text{sebenzim}^{\text{Me}})$ at elevated temperatures affords the 1-methylbenzimidazole complex, $[\text{H}(\text{sebenzim}^{\text{Me}})]\text{-}[\text{H}(\text{benzim}^{\text{Me}})]\text{CdI}_2$, a transformation that is associated with cleavage of the C–Se bond.

EXPERIMENTAL SECTION

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum and Schlenk techniques under a nitrogen or argon atmosphere.⁶⁶ Solvents were purified and degassed by standard procedures. NMR spectra were measured on Bruker Avance III 300, Bruker Avance III 400, and Bruker Avance III 500 spectrometers. ^1H NMR spectra are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.26$ for CDCl_3 , $\delta = 7.16$ for $\text{C}_6\text{D}_5\text{H}$, and $\delta = 1.94$ for CD_2HCN).⁶⁷ Coupling constants are reported in hertz. $\text{H}(\text{sebenzim}^{\text{Me}})$ was prepared by the literature procedure,^{6a} while 1-methylbenzimidazole was purchased from Alfa Aesar and all other chemicals were purchased from Sigma Aldrich and used as supplied.

X-ray Structure Determinations

X-ray diffraction data were collected on a Bruker Apex II diffractometer. The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7).⁶⁸ Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC #1872851-1872858).

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnCl}_2$

A mixture of ZnCl_2 (11 mg, 0.081 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (35 mg, 0.166 mmol) in acetonitrile (*ca.* 8 mL) was stirred for 18 hours. After this period, the white precipitate was isolated by decantation, washed with pentane (1×2 mL) and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnCl}_2$ as a white powder (31 mg, 69%). Colorless crystals suitable for X-ray diffraction were obtained *via* slow evaporation of a solution in chloroform. Anal. calcd. for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnCl}_2$: C, 34.4%; H, 2.9%; N, 10.0%. Found: C, 34.6%; H, 3.2%; N, 9.9%. ^1H NMR (CD_3CN): 3.79 [s, 6H of CH_3], 7.23–7.43 [m, 8H of C_6H_4], 11.22 [broad s, 2H of N–H].

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnBr}_2$

A mixture of ZnBr_2 (15 mg, 0.067 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (29 mg, 0.129 mmol) in acetonitrile (*ca.* 8 mL) was stirred for 18 hours. After this period, the precipitate was isolated by decantation, washed with pentane (1 × 2 mL) and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnBr}_2$ as a white powder (15 mg, 35%). Colorless crystals suitable for X-ray diffraction were obtained *via* slow evaporation of solution in acetonitrile. Anal. calcd. for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnBr}_2$: C, 29.7%; H, 2.5%; N, 8.7%. Found: C, 30.0%; H, 2.5%; N, 8.5%.

^1H NMR (CD_3CN): 3.79 [s, 6H of CH_3 , 7.25-7.44 [m, 8H of C_6H_4 , 11.25 [broad s, 2H of N-H].

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$

A mixture of ZnI_2 (16 mg, 0.05 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (21 mg, 0.10 mmol) was dissolved in acetonitrile (*ca.* 1.5 mL). The volatile components were removed *in vacuo* and the solid obtained was washed with pentane (1×2 mL) and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{ZnI}_2$ as a white powder (15 mg, 41%). Colorless crystals suitable for X-ray diffraction were obtained *via* slow evaporation of solution in acetonitrile. ^1H NMR (CD_3CN): 3.82 [s, 6H of CH_3 , 7.28-7.44 [m, 8H of C_6H_4 , 11.05 [broad s, 2H of N-H].

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$

A mixture of CdCl_2 (22 mg, 0.120 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (50 mg, 0.237 mmol) in acetonitrile (*ca.* 8 mL) was stirred for 18 hours. After this period, the precipitate was isolated by decantation, washed with pentane (1×2 mL) and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$ as a white powder (55 mg, 76%). Colorless crystals suitable for X-ray diffraction were obtained from a solution in acetonitrile. Anal. calcd for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdCl}_2$: C, 31.7%; H, 2.7%; N, 9.3%. Found: C, 31.4%; H, 2.8%; N, 9.1%. ^1H NMR (CD_3CN): 3.77 [s, 6H of CH_3 , 7.23-7.46 [m, 8H of C_6H_4 , 11.49 [broad s, 2H of N-H].

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdBr}_2$

A mixture of CdBr_2 (32 mg, 0.118 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (50 mg, 0.237 mmol) in acetonitrile (*ca.* 8 mL) and stirred for 18 hours. After this period, the precipitate was isolated by decantation, washed with pentane (1×2 mL) and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdBr}_2$ as a white powder (61 mg, 75%). Colorless crystals suitable for X-ray diffraction were obtained *via* vapor diffusion of pentane into a dichloromethane solution. Anal. calcd for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdBr}_2$: C, 27.7%; H, 2.3%; N, 8.1%. Found: C, 27.3%, H, 2.2%; N, 7.7%. ^1H NMR (CD_3CN): 3.79 [s, 6H of CH_3 , 7.31-7.46 [m, 8H of C_6H_3 , 11.79 [broad s, 2H of N-H].

Synthesis of $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$

A mixture of CdI_2 (43 mg, 0.117 mmol) and $\text{H}(\text{sebenzim}^{\text{Me}})$ (50 mg, 0.237 mmol) was stirred in acetonitrile (*ca.* 8 mL) for 18 hours resulting in a colorless solution. After this period, the solution was concentrated *in vacuo* to a small volume (*ca.* 2 mL), and diethyl ether (*ca.* 15 mL) was added resulting in the precipitation of a white solid. The solid was isolated by filtration and dried *in vacuo* to afford $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$ as a white powder (40 mg, 43%). Colorless crystals suitable for X-ray diffraction were obtained *via* slow evaporation of a dichloromethane solution. Anal. calcd. for $[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{CdI}_2$: C, 24.4%; H, 2.1%; N, 7.1%. Found: C, 23.4%; H, 2.6%; N, 6.6%. ^1H NMR (CD_3CN): 3.82 [s, 6H of CH_3 , 7.31-7.48 [m, 8H of C_6H_4 , 11.32 [broad s, 2H of N-H].

Synthesis of $[H(sebenzim^{Me})]_3CdCl_2 \cdot [H(sebenzim^{Me})]_4CdCl_2$

A mixture of $CdCl_2$ (22 mg, 0.120 mmol) and $H(sebenzim^{Me})$ (100 mg, 0.474 mmol) was dissolved in acetonitrile (*ca.* 8 mL) to form a colorless solution that was stirred for 18 hours at 100°C. Upon cooling, colorless crystals were deposited on the walls of the reaction vessel. When examined under a microscope, large colorless cubic crystals of $[H(sebenzim^{Me})]_3CdCl_2 \cdot [H(sebenzim^{Me})]_4CdCl_2$ suitable for X-ray diffraction were easily identified over the needle shaped crystals of $[H(sebenzim^{Me})]_2CdCl_2$.

Synthesis of $[H(sebenzim^{Me})]-(benzim^{Me})CdI_2$

(a) A mixture of CdI_2 (35 mg, 0.096 mmol), $H(sebenzim^{Me})$ (20 mg, 0.095 mmol), and 1-methylbenzimidazole (13 mg, 0.098 mmol) was dissolved in acetonitrile (*ca.* 8 mL) to form a colorless solution that was stirred for 18 hours at 100°C. Upon cooling, colorless crystals of $[H(sebenzim^{Me})]-(benzim^{Me})CdI_2$ suitable for X-ray diffraction were deposited on the walls of the reaction vessel (20 mg, 30%). Anal. calcd. For $[H(sebenzim^{Me})]-(benzim^{Me})CdI_2 \cdot MeCN$: C, 28.7%; H, 2.6%; N, 9.3%. Found: C, 28.6%, H, 2.7%; N, 9.0%. 1H NMR ($CDCl_3$): 3.85 [s, 3H of $H(sebenzim^{Me})CH_3$], 3.90 [s, 3H of $(benzim^{Me})CH_3$], 7.29-7.47 [m, 6H of overlapping C_6H_4], 7.57 [m, 1H of C_6H_4], 8.11 [d, 1H of C_6H_4 , $^3J_{H-H} = 8$], 8.40 [s, 1H of $(benzim^{Me})NCHN$], 11.96 [broad s, 1H of $N-H$]. (b) A solution of CdI_2 (8 mg, 0.022 mmol) and $H(sebenzim^{Me})$ (20 mg, 0.095 mmol) in CD_3CN (*ca.* 0.7 mL) in an NMR tube equipped with a J. Young valve was heated at 100°C for 3 days, resulting in the formation of a grey precipitate. The sample was examined by 1H NMR spectroscopy, thereby demonstrating the formation of $[H(sebenzim^{Me})]-(benzim^{Me})CdI_2$. In addition, colorless crystals were obtained upon cooling and identified as $[H(sebenzim^{Me})]-(benzim^{Me})CdI_2$ by X-ray diffraction.

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Figure 1.
1-R-imidazole-2-thiones and 1-R-imidazole-2-selones.

Figure 2.
Molecular structure of $[H(sebenzim^{Me})]_2ZnCl_2$ (open bonds correspond to hydrogen bonding interactions).

Figure 3.
Molecular structure of $[H(sebenzim^{Me})]_2ZnBr_2$ (open bonds correspond to hydrogen bonding interactions).

Figure 4.
Molecular structure of $[H(sebenzim^{Me})]_2ZnI_2 \cdot MeCN$ (open bond corresponds to a hydrogen bonding interaction and hydrogen bonded acetonitrile is not shown).

Figure 5.
Molecular structure of $[H(sebenzim^{Me})]_2CdCl_2$ (open bonds correspond to hydrogen bonding interactions).

Figure 6.
Molecular structure of $[H(sebenzim^{Me})]_2CdBr_2$ (open bonds correspond to hydrogen bonding interactions).

Figure 7.
Molecular structure of $[H(sebenzim^{Me})]_2CdI_2$ (open bond corresponds to a hydrogen bonding interaction).

Figure 8. Hydrogen bonding network for $[H(sebenzim^{Me})]_2CdI_2$ illustrating intramolecular and intermolecular N-H...I interactions (as illustrated by open bonds).

Figure 9. Variation in M–Cl (monotonic) and M–Se (non-monotonic) bond lengths in $[H(\text{sebenzim}^{\text{Me}})]_2MCl_2$.

Figure 10.
Molecular structure of $[H(sebenzim^{Me})]_3CdCl_2$ present in $[H(sebenzim^{Me})]_2CdCl_2 \cdot [H(sebenzim)]_4CdCl_2$ (open bonds corresponds to hydrogen bonding interactions).

Figure 11. Molecular structure of $[H(sebenzim^{Me})]_4CdCl_2$ present in $[H(sebenzim^{Me})], CdCl_2 \cdot [H(sebenzim^{Me})]_4CdCl_2$, (open bonds corresponds to hydrogen bonding interactions).

Figure 12.
Molecular structure of $[H(sebenzim^{Me})] \cdot [H(benzim^{Me})]CdI_2 \cdot MeCN$ (acetonitrile not shown).

Scheme 1.

Scheme 2.

Scheme 3.

Table 1.Metrical data for [H(sebenzim^{Me})]₂MX₂.

	$d(\text{M-Se})_{\text{av}}/\text{\AA}$	$d(\text{M-X})_{\text{av}}/\text{\AA}$	$d(\text{C-Se})_{\text{av}}/\text{\AA}$	τ_4	τ_8	Ref
[H(sebenzim ^{Me})] ₂ ZnCl ₂	2.471	2.279	1.864	0.93	0.90	<i>a</i>
[H(sebenzim ^{Me})] ₂ ZnBr ₂	2.479	2.412	1.860	0.93	0.88	<i>a</i>
[H(sebenzim ^{Me})] ₂ ZnI ₂	2.483	2.585	1.861	0.93	0.89	<i>a</i>
[H(sebenzim ^{Me})] ₂ CdCl ₂	2.630	2.470	1.862	0.94	0.93	<i>a</i>
[H(sebenzim ^{Me})] ₂ CdBr ₂	2.643	2.596	1.864	0.95	0.91	<i>a</i>
[H(sebenzim ^{Me})] ₂ CdI ₂	2.642	2.773	1.864	0.95	0.92	<i>a</i>
[H(sebenzim ^{Me})] ₂ HgCl ₂	2.591	2.534	1.863	0.94	0.92	6a
[H(sebenzim ^{Me})] ₂ HgI ₂ ^{<i>b</i>}	2.628	2.792	1.855	0.94	0.90	6b
[H(sebenzim ^{Me})] ₂ HgI ₂ ^{<i>c</i>}	2.692	2.737	1.867	0.87	0.81	6b

^(a) this work.^(b) Data for orthorhombic form of [H(sebenzim^{Me})]₂HgI₂.^(c) Data for monoclinic form of [H(sebenzim^{Me})]₂HgI₂.

Table 2.Hydrogen bonding data for [H(sebenzim^{Me})]₂MX₂.

	<i>d</i> (N•••X)/Å	Ref.
[H(sebenzim ^{Me})] ₂ ZnCl ₂	3.215, 3.135	this work
[H(sebenzim ^{Me})] ₂ ZnBr ₂	3.272, 3.344	this work
[H(sebenzim ^{Me})] ₂ ZnI ₂	3.710	this work
[H(sebenzim ^{Me})] ₂ CdCl ₂	3.153, 3.245	this work
[H(sebenzim ^{Me})] ₂ CdBr ₂	3.300, 3.386	this work
[H(sebenzim ^{Me})] ₂ CdI ₂	3.606 (intra), 3.498 (inter)	this work
[H(sebenzim ^{Me})] ₂ HgCl ₂	3.137, 3.227	6a
[H(sebenzim ^{Me})] ₂ HgI ₂ ^a	3.590 (intra), 3.489 (inter)	6b

^(a) values for orthorhombic form from acetonitrile.

Table 3.

Bond length data for $[\text{H}(\text{sebenzim}^{\text{Me}})]_x\text{MX}_2$ ($x = 2, 3, 4$).

	$[\text{H}(\text{sebenzim}^{\text{Me}})]_2\text{-CdCl}_2$	$[\text{H}(\text{sebenzim}^{\text{Me}})]_3\text{-CdCl}_2$	$[\text{H}(\text{sebenzim}^{\text{Me}})]_4\text{-CdCl}_2$
$d(\text{Cd-Se})_{\text{av}}/\text{\AA}$	2.630	2.692	2.811
$d(\text{Cd-Cl})_{\text{av}}/\text{\AA}$	2.469	2.679	2.672
$d(\text{N}\cdots\text{Cl})_{\text{av}}/\text{\AA}$	3.199	3.126	3.138