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Synthesis and Structural Characterization of *Tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato Cadmium Halide Complexes, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ and $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$: A Rare Example of Cadmium in a Trigonal Bipyramidal Sulfur-Rich Coordination Environment

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Abstract

The *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato cadmium complexes, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ and $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$, have been synthesized *via* the reactions of $[\text{Tm}^{\text{MeBenz}}]\text{K}$ with CdCl_2 and CdI_2 , respectively. While X-ray diffraction studies demonstrate that the iodide derivative, $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$, is a monomer, the chloride derivative, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$, exists as a dimer, which is unprecedented for Group 12 $[\text{Tm}^{\text{R}}]\text{MX}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) compounds. Furthermore, the cadmium centers of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ are trigonal bipyramidal, which is an uncommon motif for cadmium complexes with a $[\text{S}_3\text{Cl}_2]$ coordination sphere.

INTRODUCTION

We have previously utilized the *tris*(mercaptoimidazolyl)hydroborato $[\text{S}_3]$ donor ligand system, $[\text{Tm}^{\text{R}}]$,^{1,2,3,4} to model aspects of metalloenzymes that feature sulfur-rich active sites. For example, the zinc compound $[\text{Tm}^{\text{Ph}}]\text{ZnOH}$ serves as a synthetic analogue for 5-aminolevulinic acid dehydratase (ALAD),^{5,6} while $[\text{Tm}^{\text{R}}]\text{ZnSPh}$ ($\text{R} = \text{Bu}^t, \text{Ph}$)⁷ and $[\text{Tm}^{\text{R}}]\text{ZnSCH}_2\text{C}(\text{O})\text{N}(\text{H})\text{Ph}$ ⁸ are synthetic analogues of the ADA DNA repair protein. However, while zinc is essential for humans, its congeners, cadmium and mercury, and related divalent metal ions such as lead, are most toxic.^{9–12} Since the toxicity of such metals is often linked to their ability to bind effectively to the cysteine thiolate groups of proteins,¹³ thereby perturbing their functions, the $[\text{Tm}^{\text{R}}]$ ligand also provides a means to investigate such interactions. For example, we have demonstrated that Pb^{2+} efficiently replaces the zinc in $\{[\text{Tm}^{\text{Ph}}]\text{Zn}(\text{NCMe})\}^+$ to give $\{[\text{Tm}^{\text{Ph}}]\text{Pb}\}^+$, and have noted that the reduced Lewis acidity of the lead center, which is associated with the stereochemically active lone pair, is an important factor that contributes towards deactivating ALAD.^{6b,14} Furthermore, we have also demonstrated that mercury binds effectively to the $[\text{Tm}^{\text{Bu}^t}]$ ligand and that such coordination promotes the protolytic cleavage of the mercury–carbon bond in $[\text{Tm}^{\text{Bu}^t}]\text{HgR}$

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compounds, thereby providing insight into the mechanism of action of organomercurial lyase (*Mer B*).^{15,16} Here we report that coordination of the *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato ligand, [Tm^{MeBenz}], to cadmium results in two very different classes of {[Tm^{MeBenz}]Cd} compounds depending upon the nature of the co-ligand attached to cadmium. Specifically, whereas the iodide derivative [Tm^{MeBenz}]CdI is a discrete monomer, the chloride derivative {[Tm^{MeBenz}]Cd(μ-Cl)}₂ is dimeric, with a trigonal bipyramidal geometry that has not been previously observed for {[Tm^R]Cd} compounds.

RESULTS AND DISCUSSION

An attractive feature of the [Tm^R] ligand system is that the steric and electronic properties may be readily modified by varying the R-substituent.^{17,18} Furthermore, we recently reported that benzannulation of this ligand system is possible and that [Tm^{RBenz}] derivatives may exhibit different types of structures to those of the non-benzannulated counterparts.¹⁹ With this perspective, we have now investigated the reactivity of the *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato complex, [Tm^{MeBenz}]K,^{19b} towards CdCl₂ and CdI₂, as illustrated in Scheme 1.

The molecular structures of the products, namely [Tm^{MeBenz}]CdI (Figure 1) and {[Tm^{MeBenz}]Cd(μ-Cl)}₂ (Figure 2), have been determined by single crystal X-ray diffraction, and while the [Tm^{MeBenz}] ligand exhibits the κ³-coordination mode that is commonly observed for [Tm^R] ligands,²⁰ a striking feature is that the iodide compound is a monomer, whereas the chloride derivative is a dimer with two μ-Cl bridges. Of note, the molecular structure of the chloroform solvate, {[Tm^{MeBenz}]Cd(μ-Cl)}₂•6(CHCl₃), has also been determined and exhibits a similar structure for both of the crystallographically independent molecules (Figure 3 and Figure 4), thereby indicating that packing effects are not responsible for the dimeric structure of the chloride derivative.

Selected bond lengths and angles for [Tm^{MeBenz}]CdI are presented in Table 1, from which it is evident that the coordination geometry of cadmium is approximately tetrahedral, possessing a four-coordinate τ₄ geometry index²¹ of 0.89 (for which an ideal tetrahedron has a value of 1.00). Furthermore, the B•••Cd–I angle is 175.23°, indicating that the iodide ligand lies close to the C₃ axis as defined by the B•••Cd vector (Table 2). In this regard, the structure of [Tm^{MeBenz}]CdI is similar to that of [Tm^{Bu^t}]CdI. For example, not only are the Cd–I bond length [2.7105(3) Å] and Cd–S bond lengths [2.5470(7) Å, 2.5506(6) Å and 2.5564(7) Å] of [Tm^{Bu^t}]CdI comparable to those of [Tm^{MeBenz}]CdI (Table 1), but so are the τ₄ and B•••Cd–I values (Table 2); the only noteworthy difference between these two compounds is that the B•••Cd–I angle for [Tm^{MeBenz}]CdI (175.23°) is larger than that for [Tm^{Bu^t}]CdI (172.36°), such that [Tm^{MeBenz}]CdI adopts a structure that is closer to C₃ symmetric.

The coordination geometry observed for cadmium in [Tm^{MeBenz}]CdI is also similar to those of all other structurally characterized zinc, cadmium and mercury halide complexes of the type [Tm^R]MX. However, while all of the [Tm^R]MX compounds have approximately tetrahedral geometries, distortions are evident from the spread of τ₄ geometry indices (0.80

to 0.98) and $B\cdots M-X$ angles ($164.70^\circ - 180.00^\circ$), as summarized in Table 1. Not surprisingly, the deviation of the τ_4 index from unity correlates with the deviation of the $B\cdots M-X$ angle from 180° , as illustrated in Figure 5. These data indicate that the distortion from tetrahedral geometry is greater for cadmium and mercury than for zinc, as has been noted for $[Tm^{Me}]MX$ derivatives.^{16b} None of these compounds, however, have $B\cdots Cd-X$ angles as small as the average values observed for the axial (124°) or equatorial (151°) $B\cdots Cd-Cl$ angles for $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$, indicating that both of the possible monomeric $[Tm^{MeBenz}]CdCl$ units within the dimer are grossly distorted from tetrahedral.

Although no other zinc, cadmium or mercury compounds have been reported to possess a dinuclear $\{[Tm^R]M(\mu-X)\}_2$ motif, this type of structure has, nevertheless, been observed for some transition metal halide complexes, namely $\{[Tm^{Me}]Mn(\mu-Cl)\}_2$, $\{[Tm^{Me}]Ni(\mu-Cl)\}_2$ and $\{[Tm^{Me}]Ni(\mu-Br)\}_2$.²² In addition to being dinuclear, another interesting feature of $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ is that the cadmium centers are five-coordinate, which is a comparatively rare coordination number for cadmium. For example, only 8.2 % of the cadmium compounds listed in the Cambridge Structural Database (CSD)²³ have a coordination number of five, with the majority being six-coordinate, as illustrated in Figure 6.

Selected bond lengths and angles for $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ are presented in Table 3 and 4, with the angles indicating that the five-coordinate cadmium center is best described as a trigonal bipyramid, in which the axial sites are occupied by chlorine and sulfur atoms. For example, the $S(1)-Cd-Cl'$ bond angle of $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ (crystal #1) is $174.53(6)^\circ$, while the τ_5 five-coordinate geometry index²⁴ is 0.73, with the latter being much closer to the value for an idealized trigonal bipyramidal (1.00) than for a square pyramidal geometry (0.00).²⁵ With respect to the observation of a trigonal bipyramidal geometry for $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$, it is pertinent to note that examination of the CSD indicates that five-coordinate cadmium compounds more typically have approximately square pyramidal geometries (Figure 7). For example, 72.6 % of such compounds have τ_5 values in the range $0 < \tau_5 < 0.5$, with an average value of 0.18, and may therefore be broadly classified as belonging to the distorted square pyramidal geometry regime.²⁶

Mononuclear cadmium compounds that feature a trigonal bipyramidal geometry with the $[S_3Cl_2]$ motif observed for $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ are most uncommon, with there being only one other such compound that features an L_2X tripodal ligand, namely the phenyltris[(*t*-butylthio)methyl]borate complex, $\{[PhTt^{Bu^t}]Cd(\mu-Cl)\}_2$, as reported by Riordan.^{27,28}

The $Cd-Cl$ bonds within $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ are asymmetric, with the average axial bond on each cadmium center [$d(Cd-Cl_{ax}) = 2.838 \text{ \AA}$] being longer than the equatorial bond [$d(Cd-Cl_{eq}) = 2.500 \text{ \AA}$].²⁹ Likewise, the average axial $Cd-S$ bond [$d(Cd-S_{ax}) = 2.666 \text{ \AA}$] is also longer than the equatorial $Cd-S$ bonds [$d(Cd-S_{eq}) = 2.556 \text{ \AA}$ and $2.575 \text{ \AA}$]. $\{[PhTt^{Bu^t}]Cd(\mu-Cl)\}_2$ exhibits a similar trend with respect to possessing longer axial bond lengths, but the magnitude of the asymmetry of the $[Cd_2Cl_2]$ core is greater for $[Tm^{MeBenz}]Cd(\mu-Cl)_2$. Specifically, whereas the difference in $Cd-Cl$ bond lengths for

$\{[\text{PhTt}^{\text{Bu}^{\dagger}}]\text{Cd}(\mu\text{-Cl})\}_2$ is 0.18 Å, the average difference for $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ is 0.34 Å.

Density functional theory calculations reproduce the trigonal bipyramidal geometry of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$, as illustrated in Figure 8. For comparison, the geometry-optimized structure of monomeric $[\text{Tm}^{\text{MeBenz}}]\text{CdCl}$ (Figure 9) exhibits a well-defined pseudotetrahedral geometry in which the chlorine is coincident with the $\text{B}\cdots\text{Cd}$ vector, *i.e.* the $\text{B}\cdots\text{Cd}\text{-Cl}$ angle is 180°. In contrast, neither of the computed $\text{B}\cdots\text{Cd}\text{-Cl}$ angles (125.9° and 148.9°) for dinuclear $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ are close to 180°, which illustrates the distortion that is introduced upon forming the dimer. Furthermore, the computed $\text{Cd}\text{-Cl}$ bond in the monomer (2.429 Å) is shorter than those in the dimer (2.589 Å and 2.734 Å). Nevertheless, the calculations indicate that formation of the dimer is enthalpically favored, with $E = -10.7$ kcal per mole of dimer.³⁰

Corresponding density functional theory calculations have also been performed on the iodide compounds, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-I})\}_2$ (Figure 10) and $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$ (Figure 11). As observed for the chloride system, the $\text{Cd}\text{-I}$ bond in the monomer (2.776 Å) is shorter than both of the $\text{Cd}\text{-I}$ bonds in the dimer (2.919 Å and 3.227 Å). However, an important difference with the chloride system is that the formation of the dimer is not strongly favored enthalpically, with $E = -0.7$ kcal per mole of dimer.³¹ As such, the calculations are in accord with the experimental observation of a dimer in the solid state for the chloride, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$, but a monomer for the iodide, $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$.

CONCLUSIONS

In summary, whereas the *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato cadmium iodide complex, $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$, exists as a monomer, the chloride derivative, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$, exists as a dimer with two $\mu\text{-Cl}$ bridges. As such, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ possesses trigonal bipyramidal cadmium in an uncommon sulfur-rich coordination environment. The dimeric structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ contrasts with all other Group 12 $[\text{Tm}^{\text{R}}]\text{MX}$ halide compounds, which have been structurally characterized as monomeric species. However, it is reasonable to expect that the motif observed for $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ could also exist for other $[\text{Tm}^{\text{R}}]\text{MX}$ complexes, and since cadmium and mercury show a greater propensity to exhibit a distortion from tetrahedral geometry than does zinc, it is probable that such complexes are more likely to be discovered for the heavier congeners.

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 (δ 7.26 for CDCl_3 and 2.50 for $\text{Me}_2\text{SO}-d_5$).³² ^{13}C NMR spectra are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the solvent (δ 77.16 for CDCl_3).³² Coupling constants are given in hertz. IR spectra were recorded in diffuse reflectance (DR) mode on a Thermo Nicolet 6700 spectrometer

(ThermoScientific) equipped with a smart collector accessory, and the data are reported in reciprocal centimeters. Samples were finely ground with KBr and a similarly prepared sample of KBr was used to obtain a background spectrum. All chemicals were purchased from Sigma-Aldrich. $[\text{Tm}^{\text{MeBenz}}]\text{K}$ was prepared by the literature method.^{19b}

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 5. 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 6.12 and Version 2013/4).³³

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.7 (release 107) suite of *ab initio* quantum chemistry programs.³⁴ Geometry optimizations were performed with the B3LYP density functional³⁵ using the 6-31G** (H, B, C, N, S, Cl) and LAV3P (Cd, I) basis sets. The energies of the optimized structures were re-evaluated by additional single point calculations on each optimized geometry using the cc-pVTZ(-f) correlation consistent triple- ζ (H, B, C, N, S, Cl) and LAV3P (Cd, I) basis sets.³⁶ Basis set superposition errors were taken into account by using the Boys-Bernardi counterpoise correction.³⁷

Synthesis of $[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})_2$

A suspension of $[\text{Tm}^{\text{MeBenz}}]\text{K}$ (11 mg, 0.020 mmol) in CDCl_3 (0.7 mL) was treated with CdCl_2 (60 mg, 0.327 mmol) in an NMR tube equipped with a J. Young valve, and the mixture was heated for 1 day at 60°C. The white suspension was filtered and the solvent was then removed *in vacuo* from the filtrate to give $[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})_2$ as a white solid (3 mg, 23% yield). Colorless crystals of composition $[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})_2$ suitable for X-ray diffraction were obtained *via* slow diffusion of hexanes into a solution in CHCl_3 , while crystals of composition $[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})_2 \cdot 6(\text{CHCl}_3)$ suitable for X-ray diffraction were obtained *via* evaporation of a solution in CHCl_3 . Anal. calcd. for $[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})_2$: C, 44.4; H, 3.4; N, 12.9. Found: C, 43.2; H, 3.3; N, 12.5. ^1H NMR (CDCl_3): δ 3.84 [s, 18H of 6NCH_3], 5.64 [br s, 2H of 2BH], 7.22 [m, 6H of $6\text{C}_6\text{H}_4$], 7.34 [m, 18H of $6\text{C}_6\text{H}_4$]. ^{13}C NMR (CDCl_3): δ 31.7 [CH_3 of NCH_3], 110.0 [CH of C_6H_4], 113.6 [CH of C_6H_4], 124.1 [CH of C_6H_4], 124.2 [CH of C_6H_4], 133.7 [C of C_6H_4], 136.1 [C of C_6H_4], 165.1 [$\text{C}=\text{S}$]. IR (DR, KBr, cm^{-1}): 3059 (w), 3033 (w), 2944 (w), 2432 (w), 2380 (w), 2256 (w), 1960 (vw), 1942 (vw), 1902 (vw), 1862 (vw), 1780 (vw), 1597 (w), 1481 (m), 1440 (s), 1402 (s), 1393 (m), 1366 (s), 1351 (s), 1330 (m), 1296 (m), 1235 (m), 1194 (m), 1155 (m), 1143 (m), 1126 (m), 1097 (m), 1012 (w), 1002 (w), 968 (w), 933 (vw), 928 (vw), 853 (w), 810 (m), 759 (m), 747 (s), 704 (vw), 671 (vw).

Synthesis of $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$

A suspension of $[\text{Tm}^{\text{MeBenz}}]\text{K}$ (80 mg, 0.148 mmol) in CHCl_3 (6 mL) was treated with CdI_2 (65 mg, 0.177 mmol) in a pressure vessel, and the mixture was heated for 6 days at 90°C.

The mixture was filtered and the precipitate was extracted with CHCl_3 (50 mL), after which hexanes (80 mL) was added to the combined filtrate and extract. The solution was then placed in a freezer overnight at -15°C , thereby depositing a precipitate. The mixture was filtered to give $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$ as an off-white solid which was dried *in vacuo* (30 mg, 27% yield). Colorless crystals of composition $[\text{Tm}^{\text{MeBenz}}]\text{CdI}\cdot 4(\text{C}_6\text{H}_6)$ suitable for X-ray diffraction were obtained *via* cooling of a hot solution in C_6H_6 . Anal. calcd. for $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$: C, 38.8; H, 2.6; N, 10.4. Found: C, 39.2; H, 3.3; N, 10.6. ^1H NMR (CDCl_3): δ 3.83 [s, 9H of 3NCH_3], 5.70 [br, 1H of BH], 7.22 [m, 3H of $3\text{C}_6\text{H}_4$], 7.34 [m, 9H of $3\text{C}_6\text{H}_4$]. ^{13}C NMR (CDCl_3): δ 31.7 [CH_3 of NCH_3], 110.0 [CH of C_6H_4], 113.6 [CH of C_6H_4], 124.0 [CH of C_6H_4], 124.1 [CH of C_6H_4], 133.7 [C of C_6H_4], 136.1 [C of C_6H_4], 165.3 [$\text{C}=\text{S}$]. IR (DR, KBr, cm^{-1}): 3061 (w), 2942 (w), 2451 (w), 2427 (w), 2251 (w), 1614 (w), 1480 (m), 1441 (s), 1401 (m), 1365 (s), 1350 (s), 1328 (w), 1295 (m), 1248 (w), 1235 (w), 1192 (w), 1157 (m), 1140 (w), 1126 (w), 1097 (w), 1013 (w), 999 (w), 970 (w), 854 (m), 810 (m), 758 (m), 745 (s).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Molecular structure of $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$.

Figure 2.
Molecular structure of $\{[Tm^{MeBenz}]Cd(\mu-Cl)\}_2$ (Crystal #1).

Figure 3.
Molecular structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ (Crystal #2, molecule #1).

Figure 4.
Molecular structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ (Crystal #2, molecule #2).

Figure 5. Correlation between the $B \cdots M-X$ angle and the τ_4 index of $[Tm^R]MX$ ($M = Zn, Cd, Hg$) compounds.

Figure 6.
Distribution of cadmium coordination numbers for compounds listed in the CSD.

Figure 7.
Distribution of τ_5 parameters for five-coordinate cadmium compounds.

Figure 8.
Geometry optimized structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$.

Figure 9.
Geometry optimized structure of $[\text{Tm}^{\text{MeBenz}}]\text{CdCl}$.

Figure 10.
Geometry optimized structure of $\{[Tm^{MeBenz}]Cd(\mu-I)\}_2$.

Figure 11.
Geometry optimized structure of $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$.

Scheme 1.

Table 1Selected bond lengths (Å) and angle (°) data for [Tm^{MeBenz}]CdI.

Cd–I	2.7094(5)	S(1)–Cd–I	117.426(18)
Cd–S(1)	2.5431(7)	S(2)–Cd–I	117.266(15)
Cd–S(1)	2.5657(7)	S(3)–Cd–I	110.518(16)
Cd–S(1)	2.5585(8)	S(1)–Cd–S(2)	102.81(2)
		S(1)–Cd–S(3)	103.620(19)
		S(2)–Cd–S(3)	103.479(18)

Table 2Structurally characterized $[\text{Tm}^{\text{R}}]\text{MX}$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) compounds and their τ_4 values.

	τ_4	$\text{B}\cdots\text{M}-\text{X}/^\circ$	Reference
$[\text{Tm}^{\text{Bu}^t}]\text{ZnF}$	0.98	180.00	2d
$[\text{Tm}^{\text{Me}}]\text{ZnCl}$	0.94	177.89	16b
$[\text{Tm}^{\text{Et}}]\text{ZnCl}$	0.91	174.13	17f
$[\text{Tm}^{\text{Bu}^t}]\text{ZnCl}$	0.94	175.53	17d
$[\text{Tm}^{\text{Mes}}]\text{ZnCl}$	0.91 0.96	172.49 178.51	17c
$[\text{Tm}^{\text{Xyl}}]\text{ZnCl}$	0.95	175.05	17g
$[\text{Tm}^{\text{Me}}]\text{ZnBr}$	0.95	180.00	16b
$[\text{Tm}^{\text{CH}_2\text{Ph}}]\text{ZnBr}$	0.95	180.00	17j
$[\text{Tm}^{\text{Bu}^t}]\text{ZnBr}$	0.93	173.71	17k
$[\text{Tm}^{\text{Me}}]\text{ZnI}$	0.92	176.29	16b
$[\text{Tm}^{\text{Bu}^t}]\text{ZnI}$	0.92	174.95	17e
$[\text{Tm}^{\text{Ad}}]\text{ZnI}$	0.93	180.00	17a
$[\text{Tm}^{\text{Mes}}]\text{ZnI}$	0.95	175.13	17c
$[\text{Tm}^{\text{Ph}}]\text{ZnI}$	0.93	175.90	17c
$[\text{Tm}^{\text{Me}}]\text{CdBr}$	0.80	164.70	16b
$[\text{Tm}^{\text{Et}}]\text{CdBr}$	0.89	175.35	17f
$[\text{Tm}^{\text{CH}_2\text{Ph}}]\text{CdBr}$	0.88	172.22	16a
$[\text{Tm}^{\text{Bu}^t}]\text{CdBr}$	0.86	170.22	16a
$[\text{Tm}^{\text{Bu}^t}]\text{CdI}$	0.85	172.36	17i
$[\text{Tm}^{\text{MeBenz}}]\text{CdI}$	0.89	175.23	this work
$[\text{Tm}^{\text{Bu}^t}]\text{HgCl}$	0.83	166.22	15c
$[\text{Tm}^{\text{Me}}]\text{HgBr}$	0.81	166.05	16b
$[\text{Tm}^{\text{Bu}^t}]\text{HgBr}$	0.85	173.54	16a
$[\text{Tm}^{\text{Bu}^t}]\text{HgI}$	0.82	170.57	15a

Table 3

Selected bond length and angle data for $\{[\text{Tm}^{\text{MeBenz}}\text{Cd}(\mu\text{-Cl})]\}_2$.

	Crystal #1	Crystal #2		Average
		Molecule #1	Molecule #2	
	Cd	Cd1	Cd2	Cd3
Cd(X)-S(X1)	2.661(2)	2.656(2)	2.673(2)	2.674(2)
Cd(X)-S(X2)	2.559(2)	2.565(2)	2.543(2)	2.555(2)
Cd(X)-S(X3)	2.593(2)	2.587(2)	2.562(2)	2.557(2)
Cd(X)-Cl(X)	2.496(2)	2.521(2)	2.491(2)	2.489(2)
Cd(X)-Cl(X')	2.886(2)	2.750(2)	2.857(2)	^a 2.860(2) ^b
				2.838

^(a) Cl(X') = Cl(3)

^(b) Cl(X') = Cl(2)

Selected bond angle data for $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$.

$$\begin{aligned} (a) \quad & \text{Cl}(X') = \text{Cl}(3) \\ (b) \quad & \text{Cl}(X') = \text{Cl}(2) \end{aligned}$$

Table 5

Crystal, intensity collection and refinement data.

	Crystal #1	Crystal #2	
	$\{[\text{Tm}^{\text{MeBenz}}]\text{CdCl}\}_2$	$\{[\text{Tm}^{\text{MeBenz}}]\text{CdCl}\}_2 \cdot 6\text{CHCl}_3$	$[\text{Tm}^{\text{MeBenz}}]\text{CdI} \cdot 4(\text{C}_6\text{H}_6)$
lattice	Triclinic	Triclinic	Triclinic
formula	$\text{C}_{48}\text{H}_{44}\text{B}_2\text{Cd}_2\text{Cl}_2\text{N}_{12}\text{S}_6$	$\text{C}_{54}\text{H}_{50}\text{B}_2\text{Cd}_2\text{Cl}_{20}\text{N}_{12}\text{S}_6$	$\text{C}_{48}\text{H}_{46}\text{BCdIN}_6\text{S}_3$
formula weight	1298.63	2014.84	1053.20
space group	$\text{P}\bar{1}$	$\text{P}\bar{1}$	$\text{P}\bar{1}$
$a/\text{\AA}$	11.242(6)	12.773(3)	12.414(3)
$b/\text{\AA}$	11.922(6)	20.555(5)	12.870(3)
$c/\text{\AA}$	12.005(6)	24.286(6)	15.611(3)
$\alpha/^\circ$	79.932(7)	104.902(4)	77.113(3)
$\beta/^\circ$	82.909(8)	94.113(4)	77.354(3)
$\gamma/^\circ$	62.842(7)	104.429(4)	78.370(3)
$V/\text{\AA}^3$	1407.8(12)	5904(3)	2341.6(8)
Z	1	3	2
temperature (K)	130(2)	130(2)	130(2)
radiation (λ , $\text{\AA}$)	0.71073	0.71073	0.71073
$\rho(\text{calcd.}) \text{ g cm}^{-3}$	1.532	1.700	1.494
$\mu(\text{Mo K}\alpha), \text{ mm}^{-1}$	1.118	1.423	1.299
θ max, deg.	25.02	26.37	30.51
no. of data collected	13521	70908	38324
no. of data	4982	24139	14251
no. of parameters	331	1315	603
$R_I [I > 2\sigma(I)]$	0.0711	0.0833	0.0317
$wR_2 [I > 2\sigma(I)]$	0.1679	0.2156	0.0722
R_I [all data]	0.1034	0.0974	0.0441
wR_2 [all data]	0.1873	0.2266	0.0795
R_{int}	0.0879	0.0395	0.0318
GOF	1.026	1.122	1.037