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Influence of Benzannulation on Metal Coordination Geometries: Synthesis and Structural Characterization of *Tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato Cadmium Bromide, $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$

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Abstract

The *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato cadmium complex, $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$, may be synthesized *via* the reaction of $[Tm^{MeBenz}]K$ with $CdBr_2$. X-ray diffraction demonstrates that $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ exists as a dimer, which is in marked contrast to the monomeric structure of the non-benzannulated counterpart, $[Tm^{Me}]CdBr$, and thereby demonstrates that benzannulation of *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato ligands can have a distinct impact on the molecular structure of their metal complexes. In accord with this observation, density functional theory calculations indicate that the benzannulated dimers, $\{[Tm^{MeBenz}]Cd(\mu-X)\}_2$ ($X = Cl, Br, I$), are more stable with respect to dissociation than are their non-benzannulated counterparts, $\{[Tm^{Me}]Cd(\mu-X)\}_2$. Furthermore, the calculations also indicate that the stability of the dimer depends on the nature of X , such that the dimer becomes more stable in the sequence $I < Br < Cl$.

Keywords

Cadmium; *tris*(2-mercaptoimidazolyl)hydroborato; halide; benzannulation; benzannulation; trigonal-bipyramidal

INTRODUCTION

The *tris*(mercaptoimidazolyl)hydroborato class of ligands, $[Tm^R]$, as introduced by Reglinski and Spicer,^{1,2,3} has proven to be of much use in coordination chemistry by virtue of its ability to provide a well-defined $[S_3]$ donor platform, which provides a valuable

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APPENDIX A. Supplementary Data

Crystallographic data in CIF format (CCDC # 1021454). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/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.molstruct.xxxxxx>.

complement to Trofimenko's $[N_3]$ donor *tris*(pyrazolyl)hydroborato class of ligands.^{4,5,6} For example, we have used $[Tm^R]$ ligands both to (i) model aspects of metalloenzymes that feature sulfur-rich active sites and (ii) mimic the interactions of toxic metals such as mercury, cadmium and lead with cysteine thiolate groups.^{7–12} One reason for the widespread use of $[Tm^R]$ ligands is the fact that the properties of the ligand can be readily tailored by variation of the R substituents, in a manner akin to that of the *tris*(pyrazolyl)hydroborato $[N_3]$ donor ligand system.^{4,5} In this regard, while the most common variation pertains to the nature of the 1-R substituent,¹³ we recently introduced *tris*(mercaptoimidazolyl)hydroborato ligands, namely $[Tm^{MeBenz}]$ and $[Tm^{Bu^tBenz}]$, in which the imidazolyl groups are benzannulated.¹⁴ Here, we describe the impact of benzannulation in cadmium chemistry.

RESULTS AND DISCUSSION

Treatment of the *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato potassium complex, $[Tm^{MeBenz}]K$,^{14b} with $CdBr_2$ results in the formation of $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$, as illustrated in Scheme 1.

The molecular structure of $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ has been determined by single crystal X-ray diffraction (Figure 1), thereby demonstrating that the $[Tm^{MeBenz}]$ ligand exhibits κ^3 -coordination, as is most commonly observed for $[Tm^R]$ ligands.^{1–3} Most interesting, however, is the observation that the compound is dimeric, in contrast to the monomeric structure observed for the analogous non-benzannulated derivative, $[Tm^{Me}]CdBr$.¹⁵ The significance of this result is underscored by the fact that there are no structurally characterized compounds listed in the Cambridge Structural Database (CSD)¹⁶ that feature cadmium in a $[S_3Br_2]$ coordination environment. Furthermore, there are only six structurally characterized complexes listed in the CSD that feature any metal in a $[S_3Br_2]$ environment,¹⁷ while there are only nine examples of dimeric cadmium complexes that feature 5-coordinate cadmium with two $\mu-Br$ bridges.¹⁸ The direct comparison of the molecular structures of $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ and $[Tm^{Me}]CdBr$, therefore, makes it evident that benzannulation of a *tris*(2-mercaptoimidazolyl)hydroborato ligand can have a notable impact on the coordination chemistry of cadmium.

Selected bond lengths and angles for $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ are presented in Table 1, from which it is evident that the coordination geometry of cadmium is approximately trigonal bipyramidal, with a τ_5 five-coordinate geometry index¹⁹ of 0.72; this value is much closer to that for an idealized trigonal bipyramidal (1.00) than for a square pyramidal geometry (0.00). The axial sites in $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ are occupied by one bromine and one sulfur atom, while the equatorial sites are occupied by one bromine and two sulfur atoms. For example, the S(1)–Cd–Br' bond angle of $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ is close to 180° [$171.15(2)^\circ$], while the Br–Cd–Br' bond angle is close to 90° [$84.80(2)^\circ$]. The Cd–Br bonds within $\{[Tm^{MeBenz}]Cd(\mu-Br)\}_2$ are asymmetric, such that the axial bond on each cadmium center [$d(Cd-Br_{ax}) = 2.8977(6) \text{ \AA}$] is longer than the equatorial bond [$d(Cd-Br_{eq}) = 2.6336(7) \text{ \AA}$].* Correspondingly, the axial Cd–S bond length [$2.6473(9) \text{ \AA}$] is longer than

*For comparison, the average Cd–Br bond length for compounds listed in the Cambridge Structural Database is $2.662 \text{ \AA}$.

the equatorial Cd–S bonds [2.5724(8) Å and 2.5812(8) Å], albeit that this difference is less than that for the Cd–Br bond lengths.

Density functional theory (DFT) calculations performed on the molecule in the gas phase are in accord with the experimental structure and reproduce both the trigonal bipyramidal geometry of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ (Figure 2) and also the difference in axial (2.963 Å) and equatorial (2.761 Å) Cd–Br bond lengths. Furthermore, the calculations indicate that formation of the dimer is enthalpically favored over that of the monomer, $[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$ (Figure 3), by 7.2 kcal mol^{−1} (Scheme 2).[†] Monomeric $[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$ exhibits a well-defined pseudotetrahedral geometry, with a four-coordinate τ_4 geometry index of 0.86 (for which an ideal tetrahedron has a value of 1.00),²⁰ in which the bromine is coincident with the B...Cd vector, *i.e.* the B...Cd–Br angle is 179.8°. Also of note, the Cd–Br bond of $[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$ (2.605 Å) is shorter than both the axial and equatorial bonds of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ (2.761 Å and 2.963 Å).

Corresponding density functional theory calculations have also been performed on the non-benzannulated counterparts, $\{[\text{Tm}^{\text{Me}}]\text{Cd}(\mu\text{-Br})\}_2$ (Figure 4) and $[\text{Tm}^{\text{Me}}]\text{CdBr}$ (Figure 5), which exhibit similar structural differences to those of the $[\text{Tm}^{\text{MeBenz}}]$ derivatives. For example, as observed for the $[\text{Tm}^{\text{MeBenz}}]$ system, the calculated Cd–Br bond in the monomer (2.613 Å) is shorter than those in the dimer (2.750 Å and 3.006 Å). However, an important difference with the benzannulated system is that the formation of the dimer is less strongly favored enthalpically, with $E = -3.9$ kcal mol^{−1}, *i.e.* $K_{\text{dimer}}[\text{Tm}^{\text{MeBenz}}] > K_{\text{dimer}}[\text{Tm}^{\text{Me}}]$ (Scheme 2). As such, the calculations are in accord with the experimental observation (Table 2) of a dimer in the solid state for the benzannulated complex, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$, but a monomer for the non-benzannulated compound, $[\text{Tm}^{\text{Me}}]\text{CdBr}$.

It is also pertinent to compare the dimerization energies of $[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$ and $[\text{Tm}^{\text{Me}}]\text{CdBr}$ with those of the chloride and iodide counterparts (Table 3). In each case, the benzannulated derivatives show a greater tendency to form a dimeric structure. Furthermore, the tendency to form the dimeric structure increases in the sequence I < Br < Cl. The latter trend is in accord with the experimental observation that $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ and $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Cl})\}_2$ ¹² exist as dimers in the solid state, but $[\text{Tm}^{\text{MeBenz}}]\text{CdI}$ ¹² is a monomer.

The observation that the benzannulated dimers, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-X})\}_2$, are more stable with respect to dissociation than are their non-benzannulated counterparts, $\{[\text{Tm}^{\text{Me}}]\text{Cd}(\mu\text{-X})\}_2$, provides an interesting illustration of how benzannulation can modify the nature of a system. In this regard, the example complements several other reports concerned with benzannulated $[\text{Tm}^{\text{RBenz}}]$ ligands. For example, the benzannulated *tris*(mercaptoimidazoly)borohydride ligand of $\{[\text{Tm}^{\text{MeBenz}}]\text{Na}\}_2(\mu\text{-THF})_3$ coordinates in a κ^3 -manner, which is in marked contrast to the κ^2 -, κ^1 - and κ^0 -modes that have been reported for various non-benzannulated $[\text{Tm}^{\text{Me}}]\text{Na}$ derivatives.^{14a} Furthermore, whereas $[\text{Tm}^{\text{Me}}]\text{K}\cdot 4\text{H}_2\text{O}$ possesses a polymeric structure in which each $[\text{Tm}^{\text{Me}}]$ ligand bridges two

[†]This value refers to the formation of one mole of dimer.

potassium centers, benzannulated $[\text{Tm}^{\text{MeBenz}}]\text{K}(\text{OCMe}_2)_3$ exists as a discrete monomeric species in which the $[\text{Tm}^{\text{MeBenz}}]$ ligand coordinates in a novel $\kappa^4\text{-S}_3\text{H}$ manner.^{14b} Finally, whereas $[\text{Tm}^{\text{R}}]\text{Tl}$ compounds exist as dinuclear molecules in which two of the sulfur donors coordinate to different thallium centers, all three sulfur donors of the $[\text{Tm}^{\text{RBenz}}]$ ligands of both $[\text{Tm}^{\text{MeBenz}}]\text{Tl}$ and $[\text{Tm}^{\text{Bu}^{\text{t}}\text{Benz}}]\text{Tl}$ chelate to thallium.^{14b}

CONCLUSIONS

In summary, treatment of the *tris*(2-mercapto-1-methylbenzimidazolyl)hydroborato potassium complex, $[\text{Tm}^{\text{MeBenz}}]\text{K}$, with CdBr_2 , results in the formation of the bromide bridged dimer, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$, which is the first example of a 5-coordinate cadmium compound that possesses a $[\text{S}_3\text{Br}_2]$ coordination environment. In this regard, the structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ is distinct from that of the non-benzannulated counterpart, $[\text{Tm}^{\text{Me}}]\text{CdBr}$, which exists as a tetrahedral monomer, thereby demonstrating that benzannulation can have a notable impact on cadmium chemistry. Density functional theory calculations indicate that the benzannulated dimers, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-X})\}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), are more stable with respect to dissociation than are their non-benzannulated counterparts, $\{[\text{Tm}^{\text{Me}}]\text{Cd}(\mu\text{-X})\}_2$, a result that is in accord with the experimental observations. Furthermore, the calculations also indicate that the stability of the dimer depends on the nature of X , and becomes more stable in the sequence $\text{I} < \text{Br} < \text{Cl}$.

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).²¹ ^{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).²¹ 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. All chemicals were purchased from Sigma-Aldrich. $[\text{Tm}^{\text{MeBenz}}]\text{K}$ was prepared by the literature method.^{14b}

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 4. 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).²²

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 7.7 (release 107) suite of *ab initio* quantum chemistry programs.²³ Geometry optimizations were performed with the B3LYP density functional²⁴ using the 6-31G** ($\text{H}, \text{B}, \text{C}, \text{N}, \text{S}, \text{Cl}$) and LAV3P ($\text{Cd}, \text{Br}, \text{I}$) 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, Br) and LAV3P (Cd, I) basis sets.²⁵ Basis set superposition errors were taken into account by using the Boys-Bernardi counterpoise correction.²⁶

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

A suspension of $[\text{Tm}^{\text{MeBenz}}]\text{K}$ (15 mg, 0.028 mmol) in CDCl_3 (0.7 mL) was treated with CdBr_2 (23 mg, 0.084 mmol) in an NMR tube equipped with a J. Young valve, and the mixture was heated for 4 days at 100°C. The white suspension was filtered and the solvent was then removed from the filtrate *in vacuo* to give $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2 \cdot \text{CDCl}_3$ as a white solid (6 mg, 29% yield). Colorless crystals of composition $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2 \cdot \text{C}_6\text{H}_6$, suitable for X-ray diffraction, were obtained *via* cooling of a hot, saturated solution in C_6H_6 . Anal. calcd. for $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2 \cdot \text{CHCl}_3$: C, 39.1; H, 3.0; N, 11.2. Found: C, 39.9; H, 3.0; N, 11.2. ^1H NMR (CDCl_3): δ 3.84 [s, 18H of 6NCH_3], 5.65 [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], 165.2 [$\text{C}=\text{S}$]. IR (KBr pellet, cm^{-1}): 3059 (vw), 2930 (w), 2850 (vw), 1481 (m), 1459 (m), 1439 (m), 1401 (m), 1363 (s), 1349 (s), 1296 (m), 1235 (w), 1191 (w), 1155 (m), 1140 (m), 1096 (w), 1014 (w), 998 (w), 855 (w), 811 (w), 743 (m).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgment

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Highlights

- The cadmium complex, $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ has been synthesized.
- X-ray diffraction demonstrates that $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$ exists as a dimer.
- Benzannulation of $[\text{Tm}^{\text{Me}}]\text{CdX}$ stabilizes the dimeric form $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-X})\}_2$.
- The dimeric form becomes more stable in the sequence $\text{I} < \text{Br} < \text{Cl}$.

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

Figure 2.
Geometry optimized structure of $\{[\text{Tm}^{\text{MeBenz}}]\text{Cd}(\mu\text{-Br})\}_2$.

Figure 3.
Geometry optimized structure of $[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$.

Figure 4.
Geometry optimized structure of $\{[\text{Tm}^{\text{Me}}]\text{Cd}(\mu\text{-Br})\}_2$.

Figure 5.
Geometry optimized structure of $[\text{Tm}^{\text{Me}}]\text{CdBr}$.

Scheme 2.

Table 1Selected bond lengths (Å) and angles (°) for {[Tm^{MeBenz}]Cd(μ-Br)}₂.

Cd-Br	2.6336(7)	S(1)-Cd-Br	88.91(2)
Cd-Br'	2.8977(6)	S(2)-Cd-Br	125.78(2)
Cd-S(1)	2.6473(9)	S(3)-Cd-Br	128.24(2)
Cd-S(2)	2.5724(8)	S(1)-Cd-S(2)	96.97(3)
Cd-S(3)	2.5812(8)	S(1)-Cd-S(3)	98.05(3)
		S(2)-Cd-S(3)	104.29(3)
		S(1)-Cd-Br'	171.150(17)
		S(2)-Cd-Br'	81.78(2)
		S(3)-Cd-Br'	90.74(2)
		Br-Cd-Br'	84.797(16)

Table 2

Monomer *versus* dimer nature of experimentally determined structures of $\{[\text{Tm}^{\text{R}}]\text{CdX}\}_n$.

$\{[\text{Tm}^{\text{R}}]\text{CdX}\}_n$		
X	$[\text{Tm}^{\text{Me}}]$	$[\text{Tm}^{\text{MeBenz}}]$
Cl	— ^a	dimer ^c
Br	monomer ^b	dimer ^d
I	— ^a	monomer ^c

(a) data not available.

(b) reference 15.

(c) reference 12.

(d) this work.

Table 3Energetics for dimerization of $[\text{Tm}^{\text{R}}]\text{CdX}$.

Compound	$E_{\text{dimerization}}$ (kcal mol ⁻¹)
$[\text{Tm}^{\text{Me}}]\text{CdCl}$	-7.7
$[\text{Tm}^{\text{Me}}]\text{CdBr}$	-3.9
$[\text{Tm}^{\text{Me}}]\text{CdI}$	1.2
$[\text{Tm}^{\text{MeBenz}}]\text{CdCl}^a$	-10.7
$[\text{Tm}^{\text{MeBenz}}]\text{CdBr}$	-7.2
$[\text{Tm}^{\text{MeBenz}}]\text{CdI}^a$	-0.7

^(a) data taken from reference 12.

Table 4

Crystal, intensity collection and refinement data.

$\{[\text{Tm}^{\text{MeBenz}}]\text{CdBr}\}_2 \cdot \text{C}_6\text{H}_6$	
lattice	Triclinic
formula	$\text{C}_{54}\text{H}_{50}\text{B}_2\text{Br}_2\text{Cd}_2\text{N}_{12}\text{S}_6$
formula weight	1465.66
space group	$\text{P}\bar{1}$
$a/\text{\AA}$	11.226(3)
$b/\text{\AA}$	11.930(3)
$c/\text{\AA}$	12.139(3)
$\alpha/^\circ$	86.970(3)
$\beta/^\circ$	80.445(3)
$\gamma/^\circ$	63.629(3)
$V/\text{\AA}^3$	1435.9(6)
Z	1
temperature (K)	130(2)
radiation (λ , $\text{\AA}$)	0.71073
$\rho(\text{calcd.}) \text{ g cm}^{-3}$	1.695
$\mu(\text{Mo K}\alpha), \text{ mm}^{-1}$	2.399
$\theta_{\text{max}}, \text{ deg.}$	30.507
no. of data collected	49072
no. of data	8755
no. of parameters	359
$R_I [I > 2\sigma(I)]$	0.0389
$wR_2 [I > 2\sigma(I)]$	0.0790
$R_I [\text{all data}]$	0.0597
$wR_2 [\text{all data}]$	0.0841
R_{int}	0.0690
GOF	1.016