Synthesis and Structural Characterization of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca(THF)}_2$: Ca•••H–B interactions in a Sulfur-Rich Coordination Environment‡

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‡ Dedicated to the memory of Roberto Sánchez-Delgado, a wonderful man and an inspirational colleague.

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Abstract. The bis(mercaptoimidazolyl)hydroborato calcium compound, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca(THF)}_2$, may be obtained by the reaction of $\text{Ca(BH}_4\text{)}_2\cdot2(\text{THF})$ with 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione. X-ray diffraction demonstrates that the $[\text{Bm}^{\text{MeBenz}}]$ ligands coordinate in a $k^3–S_2H$ manner such that the calcium is eight-coordinate with a dodecahedral geometry that features two Ca•••H–B interactions.

Keywords: Calcium; bis(mercaptoimidazolyl)hydroborato; borohydride; 8-coordinate; X-ray structure.

Introduction

$\text{Bis(mercaptoimidazolyl)hydroborato}$ ligands, $[\text{Bm}^R]$ [1], provide $[S_2]$ [2] donor arrays that have found much use [3-15] as counterparts to the well-known $\text{tris(mercaptoimidazolyl)hydroborato}$ class of ligands, $[\text{Tm}^R]$ (Fig. 1) [16-19]. An important aspect of this class of ligands is that the steric and electronic properties may be significantly modified by incorporation of a diverse array of $R$ substituents (e.g. $R = \text{Me, Et, Bu',}$ 1-Ad, Bz, Cy, Ph, $p$-Tol, $o$-Tol, $p$-C$_6$H$_4$Pr$_i$, 2,6-C$_6$H$_4$Me$_2$, 2,6-C$_6$H$_4$Pr$_2$, Mes and 2-biphenyl) on the nitrogen of the imidazolyl ring [20] and by benzannulation [21,22]. Despite the fact that $[\text{Bm}^R]$ and $[\text{Tm}^R]$ ligands have been widely employed, however, the majority of investigations pertain to the chemistry of the transition metals and post-transition metals, i.e. Groups 4 – 15, while that of the alkaline earth metals has received very little attention [23]. Therefore, we report here the synthesis and structural characterization of a $\text{bis(mercaptoimidazolyl)hydroborato}$ calcium complex.

Results and discussion

Access to metal complexes containing $[\text{Bm}^R]$ and $[\text{Tm}^R]$ ligands is generally provided $via$ metathesis reactions with alkali metal derivatives, $[\text{Bm}^R]\text{M}$ and $[\text{Tm}^R]\text{M}$ ($\text{M} = \text{Li, Na, K}$), which are obtained by the reactions of MBH$_4$ with the respective 2-mercaptopimidazole compound [16-18]. We have now demonstrated that the calcium complex, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca(THF)}_2$, may be obtained directly by the reaction of $\text{Ca(BH}_4\text{)}_2\cdot2(\text{THF})$...
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[24] with 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione (Scheme 1). The molecular structure of [Bm\text{MeBenz}]_2Ca(THF)_2 has been determined by X-ray diffraction (Fig. 2 and Table 1), and is of interest for several reasons.

Firstly, there are no examples of structurally characterized [Bm\text{R}]M (M = Be, Mg, Ca, Sr, Ba) derivatives listed in the Cambridge Structural Database (CSD) [25]. Secondly, the coordination of the [Bm\text{MeBenz}] ligand to calcium is of note because the related compound, [TM\text{Me}]_2[Ca(OH)_2], is composed of discrete [TM\text{Me}]^+ anions, such that there is no interaction between calcium and the [TM\text{Me}] moiety [23]. The fact that the calcium atom of [TM\text{Me}]_2[Ca(OH)_2] coordinates preferentially to the oxygen atoms of water molecules rather than the sulfur atoms of [TM\text{Me}] is, nevertheless, in accord with the general observation that alkaline earth metal compounds which feature M–S bonds are much less common than those with M–O bonds [26, 27]. For example, there are only 31 compounds with Ca–S bonds listed in the CSD, whereas there are almost 2000 compounds with Ca–O interactions [25]. Furthermore, there are only eight compounds in the CSD that have a sulfur-rich \([S_4X_n]\) coordination environment [28,29].

The Ca–S bond lengths within [Bm\text{MeBenz}]_2Ca(THF)_2 [2.8467(15) Å – 2.8907(16) Å] compare favorably with the average value for compounds with Ca–S bonds that are listed in the CSD [2.946 Å]. For example, N,N-di-n-hexyldithiocarbamate [29a] and diphenyldithiophosphinate [28a], which are related bidentate \([S_2]\) donors with an LX Covalent Bond Classification [30], coordinate to calcium with Ca–S bond lengths in the range 2.84 – 3.04 Å. Interestingly, the Ca–S bond lengths for [Bm\text{MeBenz}]_2Ca(THF)_2 are not substantially longer than the values for calcium thiolate compounds [2.776 Å – 2.851 Å] [31] in which the thiolate ligands serve as \(X\) donors. As such, it indicates that [Bm\text{MeBenz}] is an effective ligand for calcium. The THF ligands also coordinate to calcium with Ca–O bond lengths [2.413(3) Å and 2.442(3) Å] that are comparable to the average value for Ca–THF compounds listed in the CSD [2.387 Å].

In addition to coordination by four sulfur donors and two THF ligands, the environment of calcium in [Bm\text{MeBenz}]_2Ca(THF)_2 is supplemented by two secondary Ca•••H–B interactions with Ca•••H distances of 2.45(4) Å and 2.51(4) Å, values that are comparable to the CSD average of 2.46 Å [25,32,33,34]. Each [Bm\text{MeBenz}] ligand thus possesses a \(\chi^3-S_2H\) coordination mode and thereby formally serves as an \(L_2X\) donor. As such, the eight-membered ring of each \([\text{Bm}\text{MeBenz}]_2\) moiety adopts a “boat-like” configuration, which is required to allow the B–H bond to be in proximity of the metal center [35].

Density functional theory (B3LYP) geometry optimization calculations reproduce well the overall structure of [Bm\text{MeBenz}]_2Ca(THF)_2 (Fig. 3), including the presence of Ca•••H interactions with distances of 2.469 Å and 2.471 Å [36,37]. It is also

Table 1. Selected bond lengths (Å) and angles (˚)

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca–O(1)</td>
<td>2.413(3)</td>
</tr>
<tr>
<td>Ca–O(2)</td>
<td>2.442(3)</td>
</tr>
<tr>
<td>Ca–S(1)</td>
<td>2.8467(15)</td>
</tr>
<tr>
<td>Ca–S(2)</td>
<td>2.8817(15)</td>
</tr>
<tr>
<td>Ca–S(3)</td>
<td>2.8852(16)</td>
</tr>
<tr>
<td>Ca–S(4)</td>
<td>2.8907(16)</td>
</tr>
<tr>
<td>S(1)–Ca–S(4)</td>
<td>163.32(5)</td>
</tr>
<tr>
<td>S(2)–Ca–S(3)</td>
<td>134.76(5)</td>
</tr>
<tr>
<td>H(1a)•••Ca•••H(2a)</td>
<td>64.3(13)</td>
</tr>
<tr>
<td>O(1)–Ca–O(2)</td>
<td>75.65(11)</td>
</tr>
</tbody>
</table>
worth noting that the experimental Ca•••H distances observed for [BmMeBenz]_2Ca(THF)_2 [2.45(4) Å and 2.51(4) Å] are shorter than the values that have been reported for related bis(pyrarzolyl)hydroborate compounds, namely [Bp]_2Ca(THF)_2 [2.77(2) Å and 3.01(3) Å] and [BpPr]_2Ca(THF)_2 [2.95(2) Å], which have been characterized as representing strong interactions on the basis that the distances are shorter than the sum of the van der Waals radii \cite{38,39}. Furthermore, the bis(imidazolin-2-ylidene-1-yl)hydroborate compound, [H_B(ImBu)_{2}]_2Ca(THF), also possesses Ca•••H interactions [2.83 Å and 2.97 Å] which have been described as structurally significant \cite{40}.

In view of the presence of the Ca•••H–B interactions, the calcium center of [BmMeBenz]_2Ca(THF)_2 is eight-coordinate. Examination of calcium compounds listed in the CSD indicates that calcium exhibits a variety of coordination numbers, of which six-coordinate (33.5 %) and eight-coordinate (22.7 %) are the most common (Table 2) \cite{41}. Eight-coordinate molecules are typically described in terms of one of two idealized structures, namely the \(D_{2h}\) dodecahedron and the square antiprism \cite{42}. Of these, [BmMeBenz]_2Ca(THF)_2 is best represented as possessing an idealized dodecahedral geometry (Fig. 4). A dodecahedral geometry may be identified by two mutually perpendicular trapezoids and, in this regard, the angle of 89.3˚ between the planes comprising S(2)–S(3)–O(1)–O(2) and S(1)–S(4)–H(1a)–H(2a) for [BmMeBenz]_2Ca(THF)_2 is much closer to that required for the dodecahedron (90.0˚) rather than that for the square antiprism (77.4˚) \cite{42d}. Additional support for the assignment of a dodecahedral geometry for [BmMeBenz]_2Ca(THF)_2 is provided by the value of 0.94 for the eight-coordinate geometry index parameter, \(\tau_8\) \cite{43}. Specifically, an ideal dodecahedral geometry is characterized by a \(\tau_8\) value of 1.0, whereas an ideal square antiprism is characterized by a \(\tau_8\) value of 0.0.

The dodecahedral geometry may also be described in terms of two interpenetrating tetrahedra, one of which is elongated (the A sites), and one of which is flattened (the B sites) \cite{42b,c}. In terms of this latter description, the squashed tetrahedron is occupied by the [\(S_4\)] array provided by the sulfur donors, while the elongated tetrahedron is occupied by the [\(O_2H_2\)] array provided by the THF and H–B moieties (Fig. 4). Although not common, calcium compounds that exhibit dodecahedral coordination environments are preceded \cite{44,45}. However, there are few examples of eight-coordinate calcium compounds that have a sulfur-rich coordination environment. For example, there are only four eight-coordinate compounds with an [\(S_4X_4\)] motif listed in the CSD and none of these have a dodecahedral geometry \cite{29}.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Coordination number & % \\
\hline
1 & 0.00 \\
2 & 0.26 \\
3 & 1.22 \\
4 & 5.97 \\
5 & 8.73 \\
6 & 33.50 \\
7 & 15.60 \\
8 & 22.72 \\
9 & 5.20 \\
10 & 2.18 \\
11 & 1.48 \\
12 & 2.44 \\
>12 & 0.70 \\
\hline
\end{tabular}
\caption{Distribution of calcium coordination numbers for compounds listed in the CSD.}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{DFT (B3LYP) geometry optimized structure of [BmMeBenz]_2Ca(THF)_2 (hydrogen atoms on carbon omitted for clarity).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{The dodecahedral core of [BmMeBenz]_2Ca(THF)_2. The sulfur atoms (yellow) occupy the B sites of the flattened tetrahedron, while the oxygen (red) and hydrogen (grey) atoms occupy the A sites of the elongated tetrahedron. The elongated and flattened distortions of the tetrahedra are relative to the \(C_2\) axis, which is vertical.}
\end{figure}
Summary

In summary, the first structurally characterized bis(mercaptomidazolyl)hydroborato calcium compound, [BmMeBenz\textsubscript{2}]\textsubscript{2}Ca(THF)\textsubscript{2}, has been obtained by the reaction of Ca(BH\textsubscript{4})\textsubscript{2}•2(THF) with 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione. Calcium compounds with a sulfur-rich coordination environment are not common and [BmMeBenz\textsubscript{2}]\textsubscript{2}Ca(THF)\textsubscript{2} provides an example in which the calcium also participates in two Ca•••H–B interactions, such that the calcium is eight-coordinate with a dodecahedral geometry.

Experimental section

General Considerations

All manipulations were performed using a combination of glovebox, high vacuum, and Schlenk techniques under either a nitrogen or argon atmosphere [46]. Solvents were purified and degassed using standard procedures. NMR spectra were measured on Bruker 300 DRX and Bruker 400 Cyber-enabled Avance III spectrometers. \textsuperscript{1}H NMR spectra are reported in ppm relative to SiMe\textsubscript{4} (δ = 0) and were referenced internally with respect to the proto solvent impurity (δ = 7.16 for C\textsubscript{6}D\textsubscript{5}H) [47]. \textsuperscript{13}C NMR spectra are reported in ppm relative to SiMe\textsubscript{4} (δ = 0) and were referenced internally with respect to the solvent (δ = 128.06 for C\textsubscript{6}D\textsubscript{6}) [47]. Infrared spectra were recorded on a Perkin Elmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode, and are reported in reciprocal centimeters (cm\textsuperscript{-1}). Ca(BH\textsubscript{4})\textsubscript{2}•2(THF) and 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione were obtained commercially (Aldrich) and used as received.

X-ray Structure Determination

X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, collection and refinement parameters are summarized in Table 3, and are deposited in the Cambridge Crystallographic Data Centre (CCDC #1511150). The structures were solved by using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F\textsuperscript{2} with SHELXTL (Version 2014/7) [48].

Computational Details

Calculations were carried out using DFT as implemented in the Jaguar 8.9 (release 15) [49] suite of ab initio quantum chemistry programs. Geometry optimizations were performed with the B3LYP density functional [50] using the 6-31G** (H, B, C, N, S) basis set and the LACVP (Ca) basis set [51].

Synthesis of [BmMeBenz\textsubscript{2}]\textsubscript{2}Ca(THF)\textsubscript{2}

A mixture of 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione (105 mg, 0.64 mmol) and Ca(BH\textsubscript{4})\textsubscript{2}•2(THF) (34 mg, 0.16 mmol) in a glass pressure vessel was treated with THF (ca. 4 mL) via vapor transfer from LiAlH\textsubscript{4}. The mixture was heated at 120°C for 1 day, resulting in the formation of a white precipitate. The mixture was filtered to afford [BmMeBenz\textsubscript{2}]\textsubscript{2}Ca(THF)\textsubscript{2} as a white solid which was dried in vacuo (65 mg, 47%). Anal. calc. C, 55.7%; H, 5.6%; N, 13.0%. Found: C, 55.5%; H 5.6%; N, 12.8%. Crystals of [BmMeBenz\textsubscript{2}]\textsubscript{2}Ca(THF)\textsubscript{2} suitable for X-ray diffraction were obtained from THF. \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{5}): 1.36 [m, 4H, H(2), H(3), H(5), H(6)], 6.48 [d, \textsuperscript{3}J\textsubscript{HH} = 7 Hz, 4H, H(10)\textsubscript{H}]. 4.47 [s, 4H, H(10)\textsubscript{H}], 6.87 [m, 8H, H(10)\textsubscript{H}], 5.71 [d, \textsuperscript{3}J\textsubscript{HH} = 7 Hz, 4H, H(10)\textsubscript{H}], 4.87 [s, 4H, H(10)\textsubscript{H}].
[References]


2. For \([O_2] \) and \([S_2] \) analogues, see:
   (b) Landry, V. K.; Parkin, G. Polyhedron 2007, 26, 4751-4757.

   (b) Hill, A. F.; Smith, M. K. Organometallics 2007, 26, 3900-3903.


   (b) Yurkerwich, K.; Coleman, F.; Parkin, G. Dalton Trans. 2010, 39, 6939-6942.


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(c) Vahrenkamp, H. Dalton Trans. 2007, 4751-4759.

20. See, for example:


(c) Purdy, A. P.; George, C. F. Main Group Chem. 1996, 1, 229-240.

(b) Levason, W.; Pugh, D.; Purkis, J. M.; Reid, G. Dalton Trans. 2016, 45, 7900-7911.


43. \( \tau_i = (\theta - 77.4)/12.6 \), where \( \theta \) is the dihedral angle between the two trapezoidal planes. See reference 29b.

44. (a) Geplhart, R. T., III; Williams, N. J.; Reibenspies, J. H.; Sousa, A. S. De; Hancock, R. D. *Inorg. Chem.* **2008**, *47*, 10342-10348.


(e) Huang, B.; Pei, Y. M.; Wang, L. *Acta Crystallogr.* **2008**, *E64*, m1621.


45. For calcium compounds that exhibit square antiprismatic coordination geometries, see reference 29d and:


(b) Burger, B.J.; Bercaw, J. E. in *Experimental Organometallic Chemistry*; Wayda, A. L.; Daresbury, M. Y., Eds.; American Chemical Society: Washington, DC, 1987; Chapter 4, pp 79-98.


(b) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112-122.


