

Synthesis and Structural Characterization of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$: $\text{Ca}\cdots\text{H}-\text{B}$ 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, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$, may be obtained by the reaction of $\text{Ca}(\text{BH}_4)_2\cdot 2(\text{THF})$ with 1-methyl-1,3-dihydro-2H-benzimidazole-2-thione. X-ray diffraction demonstrates that the $[\text{Bm}^{\text{MeBenz}}]$ ligands coordinate in a κ^3-S_2H manner such that the calcium is eight-coordinate with a dodecahedral geometry that features two $\text{Ca}\cdots\text{H}-\text{B}$ interactions.

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

Resumen. El compuesto *bis*(mercaptoimidazolil) hidrobórato calcio, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$, puede obtenerse por reacción de $\text{Ca}(\text{BH}_4)_2\cdot 2(\text{THF})$ con 1-metil-1,3-dihidro-2H-bencimidazol-2-tiona. La difracción de rayos X demuestra que los ligandos de $[\text{Bm}^{\text{MeBenz}}]$ se coordinan de una manera κ^3-S_2H de tal manera que el calcio presenta una coordinación ocho con una geometría dodecaédrica que presenta dos interacciones $\text{Ca}\cdots\text{H}-\text{B}$.

Palabras clave: Calcio; borohidrato de *bis*(mercaptoimidazolil); borohidruro; octacoordinado; estructura de rayos X.

Introduction

Bis(mercaptoimidazolyl)hydroborato ligands, $[\text{Bm}^{\text{R}}]$ [1], provide $[S_2]$ [2] donor arrays that have found much use [3-15] as counterparts to the well-known *tris*(mercaptoimidazolyl)hydroborato class of ligands, $[\text{Tm}^{\text{R}}]$ (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 = Me, Et, Bu^t, 1-Ad, Bz, Cy, Ph, *p*-Tol, *o*-Tol, *p*-C₆H₄Prⁱ, 2,6-C₆H₃Me₂, 2,6-C₆H₃Prⁱ₂, Mes and 2-biphenyl) on the nitrogen of the imidazolyl ring [20] and by benzannulation [21,22]. Despite the fact that $[\text{Bm}^{\text{R}}]$ and $[\text{Tm}^{\text{R}}]$ 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 *bis*(mercaptoimidazolyl)hydroborato calcium complex.

Results and discussion

Access to metal complexes containing $[\text{Bm}^{\text{R}}]$ and $[\text{Tm}^{\text{R}}]$ ligands is generally provided *via* metathesis reactions with alkali metal derivatives, $[\text{Bm}^{\text{R}}]\text{M}$ and $[\text{Tm}^{\text{R}}]\text{M}$ (M = Li, Na, K), which are obtained by the reactions of MBH_4 with the respective 2-mercaptoimidazole compound [16-18]. We have now demonstrated that the calcium complex, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$, may be obtained directly by the reaction of $\text{Ca}(\text{BH}_4)_2\cdot 2(\text{THF})$

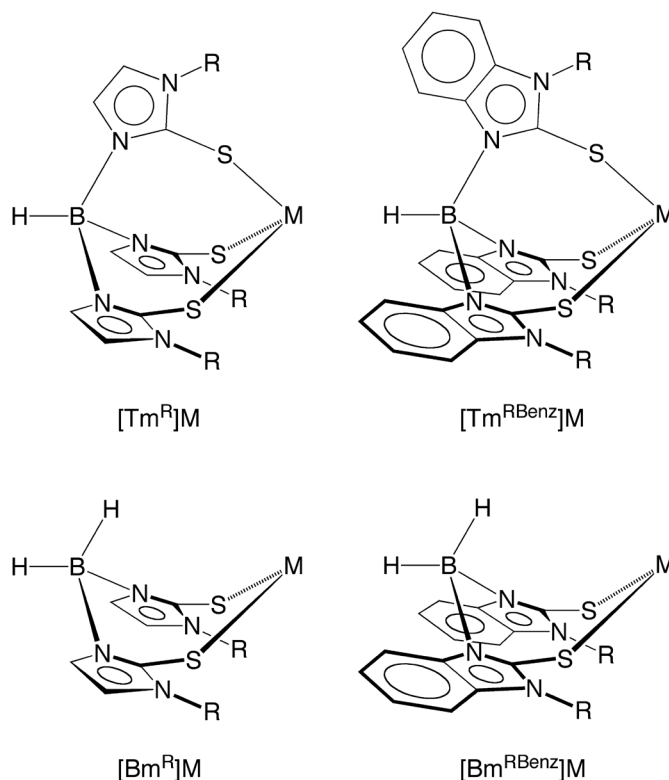
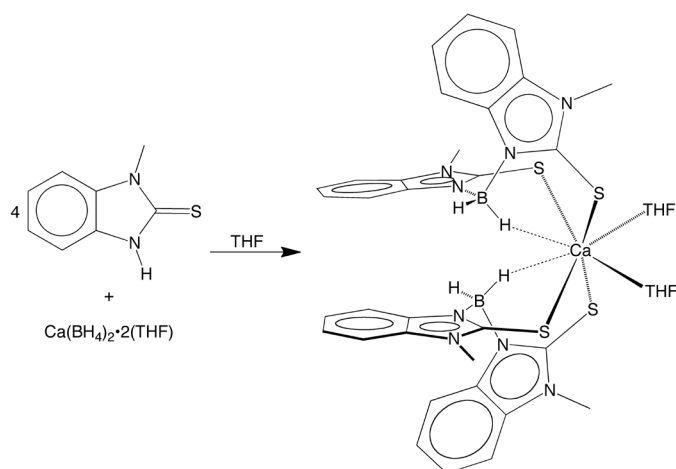


Fig. 1. Coordination of *bis* and *tris*(mercaptoimidazolyl)hydroborato ligands to metal centers.

[24] with 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-thione (Scheme 1). The molecular structure of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ 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 $[\text{Bm}^{\text{R}}]\text{M}$ ($\text{M} = \text{Be}, \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$) derivatives listed in the Cambridge Structural Database (CSD) [25]. Secondly, the coordination of the $[\text{Bm}^{\text{MeBenz}}]$ ligand to calcium is of note because the related compound, $[\text{Tm}^{\text{Me}}]_2[\text{Ca}(\text{OH}_2)_6]$, is composed of discrete $[\text{Tm}^{\text{Me}}]^-$ anions, such that there is no interaction between calcium and the $[\text{Tm}^{\text{Me}}]$ moiety [23]. The fact that the calcium atom of $[\text{Tm}^{\text{Me}}]_2[\text{Ca}(\text{OH}_2)_6]$ coordinates preferentially to the oxygen atoms of water molecules rather than the sulfur atoms of $[\text{Tm}^{\text{Me}}]$ is, nevertheless, in accord with the general observation that alkaline earth metal compounds which feature $\text{M}-\text{S}$ bonds are much less common than those with $\text{M}-\text{O}$ bonds



Scheme 1. Synthesis of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$.

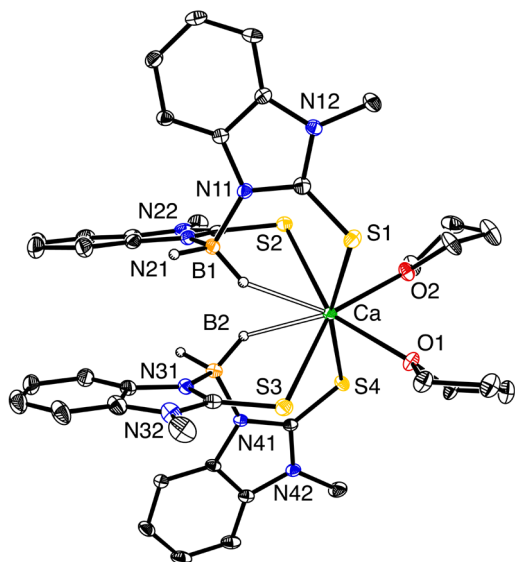


Fig. 2. Molecular structure of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$.

Table 1. Selected bond lengths (Å) and angles (°) for $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$.

Ca–O(1)	2.413(3)
Ca–O(2)	2.442(3)
Ca–S(1)	2.8467(15)
Ca–S(2)	2.8817(15)
Ca–S(3)	2.8852(16)
Ca–S(4)	2.8907(16)
Ca \cdots H(1a)	2.51(4)
Ca \cdots H(2a)	2.45(4)
S(1)–Ca–S(4)	163.32(5)
S(2)–Ca–S(3)	134.76(5)
H(1a) \cdots Ca \cdots H(2a)	64.3(13)
O(1)–Ca–O(2)	75.65(11)

[26, 27]. For example, there are only 31 compounds with $\text{Ca}-\text{S}$ bonds listed in the CSD, whereas there are almost 2000 compounds with $\text{Ca}-\text{O}$ interactions [25]. Furthermore, there are only eight compounds in the CSD that have a sulfur-rich $[\text{S}_4\text{X}_n]$ coordination environment [28,29].

The $\text{Ca}-\text{S}$ bond lengths within $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ [2.8467(15) Å – 2.8907(16) Å] compare favorably with the average value for compounds with $\text{Ca}-\text{S}$ bonds that are listed in the CSD [2.946 Å]. For example, *N,N*-di-*n*-hexyldithiocarbamate [29a] and diphenyldithiophosphate [28a], which are related bidentate $[\text{S}_2]$ donors with an LX Covalent Bond Classification [30], coordinate to calcium with $\text{Ca}-\text{S}$ bond lengths in the range 2.84 – 3.04 Å. Interestingly, the $\text{Ca}-\text{S}$ bond lengths for $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ 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 $[\text{Bm}^{\text{MeBenz}}]$ is an effective ligand for calcium. The THF ligands also coordinate to calcium with $\text{Ca}-\text{O}$ bond lengths [2.413(3) Å and 2.442(3) Å] that are comparable to the average value for $\text{Ca}-\text{THF}$ 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 $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ is supplemented by two secondary $\text{Ca}\cdots\text{H}-\text{B}$ interactions with $\text{Ca}\cdots\text{H}$ 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 $[\text{Bm}^{\text{MeBenz}}]$ ligand thus possesses a $\kappa^3-\text{S}_2\text{H}$ coordination mode and thereby formally serves as an L_2X donor. As such, the eight-membered ring of each $\{[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}\}$ moiety adopts a “boat-like” configuration, which is required to allow the $\text{B}-\text{H}$ bond to be in proximity of the metal center [35].

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

worth noting that the experimental Ca•••H distances observed for $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ [2.45(4) Å and 2.51(4) Å] are shorter than the values that have been reported for related *bis*(pyrazolyl)hydroborate compounds, namely $[\text{Bp}]_2\text{Ca}(\text{THF})_2$ [2.77(2) Å and 3.01(3) Å] and $[\text{Bp}^{\text{Pr}}]_2\text{Ca}(\text{THF})_2$ [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 [38,39]. Furthermore, the *bis*(imidazolin-2-ylidene-1-yl)hydroborate compound, $[\text{H}_2\text{B}(\text{Im}^{\text{Bu}})_2]_2\text{Ca}(\text{THF})_2$, also possesses Ca•••H interactions [2.83 Å and 2.97 Å] which have been described as structurally significant [40].

In view of the presence of the Ca•••H–B interactions, the calcium center of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ 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) [41]. Eight-coordinate molecules are typically described in terms of one of two idealized structures, namely the D_{2d} dodecahedron and the square antiprism [42]. Of these, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ 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 $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ is much closer to that required for the dodecahedron (90.0°) rather than that for the square antiprism (77.4°) [42d]. Additional support for the assignment of a dodecahedral geometry for $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ is provided by the value of 0.94 for the eight-coordinate geometry index parameter, τ_8 [43]. Specifically, an ideal dodecahedral geometry is characterized by a τ_8 value of 1.0, whereas an ideal square antiprism is characterized by a τ_8 value of 0.0.

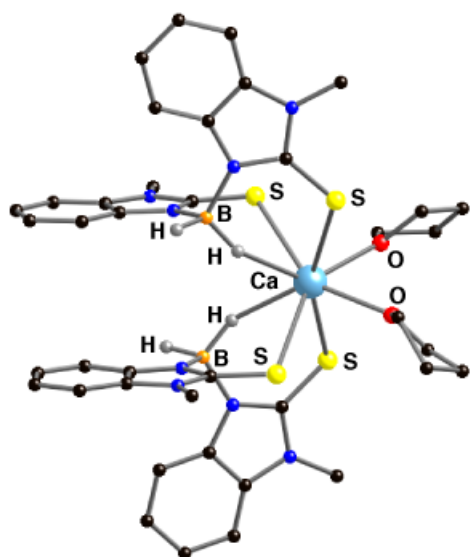


Fig. 3. DFT (B3LYP) geometry optimized structure of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ (hydrogen atoms on carbon omitted for clarity).

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) [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 [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 [29].

Table 2. Distribution of calcium coordination numbers for compounds listed in the CSD.

Coordination number	%
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

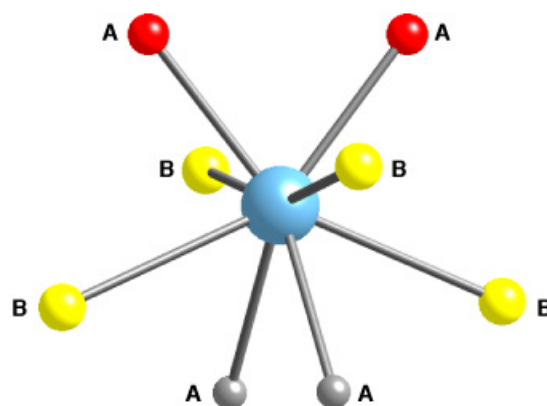


Fig. 4. The dodecahedral core of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$. The sulfur atoms (yellow) occupy the B sites of the flattened tetrahedron, while the oxygen (red) and hydrogen (grey) atoms occupy the A sites of the elongated tetrahedron. The elongated and flattened distortions of the tetrahedra are relative to the C_2 axis, which is vertical.

Summary

In summary, the first structurally characterized *bis*(mercaptoimidazolyl)hydroborato calcium compound, $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$, has been obtained by the reaction of $\text{Ca}(\text{BH}_4)_2 \cdot 2(\text{THF})$ with 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-thione. Calcium compounds with a sulfur-rich coordination environment are not common and $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ provides an example in which the calcium also participates in two $\text{Ca}\cdots\text{H}-\text{B}$ 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. ^1H NMR spectra are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the protio solvent impurity ($\delta = 7.16$ for $\text{C}_6\text{D}_5\text{H}$) [47]. ^{13}C NMR spectra are reported in ppm relative to SiMe_4 ($\delta = 0$) and were referenced internally with respect to the solvent ($\delta = 128.06$ for C_6D_6) [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^{-1}). $\text{Ca}(\text{BH}_4)_2 \cdot 2(\text{THF})$ and 1-methyl-1,3-dihydro-2*H*-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, 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^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 $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$

A mixture of 1-methyl-1,3-dihydro-2*H*-benzimidazole-2-thione (105 mg, 0.64 mmol) and $\text{Ca}(\text{BH}_4)_2 \cdot 2(\text{THF})$ (34 mg,

Table 3. Crystal, intensity collection, and refinement data.

	$[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$
lattice	Orthorhombic
formula	$\text{C}_{40}\text{H}_{48}\text{B}_2\text{CaN}_8\text{O}_2\text{S}_4$
formula weight	862.80
space group	$\text{P}2_12_12_1$
$a/\text{\AA}$	9.4345(15)
$b/\text{\AA}$	18.240(3)
$c/\text{\AA}$	24.635(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	4239.4(12)
Z	4
temperature (K)	130(2)
radiation (λ , \AA)	0.71073
ρ (calcd.) g cm^{-3}	1.352
μ (Mo $\text{K}\alpha$), mm^{-1}	0.391
θ max, deg.	30.640
no. of data collected	69816
no. of data	13037
no. of parameters	534
$R_1 [I > 2\sigma(I)]$	0.0587
$wR_2 [I > 2\sigma(I)]$	0.1080
R_1 [all data]	0.1201
wR_2 [all data]	0.1297
GOF	1.009
R_{int}	0.1486
Absolute struct param.	0.00(3)

0.16 mmol) in a glass pressure vessel was treated with THF (*ca.* 4 mL) *via* vapor transfer from LiAlH_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 $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ as a white solid which was dried *in vacuo* (65 mg, 47%). Anal. calcd. C, 55.7%; H, 5.6%; N, 13.0%. Found: C, 55.5%; H 5.6%; N, 12.8%. Crystals of $[\text{Bm}^{\text{MeBenz}}]_2\text{Ca}(\text{THF})_2$ suitable for X-ray diffraction were obtained from THF. ^1H NMR (C_6D_6): 1.36 [m, 8H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 3.03 [s, 12H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 3.79 [m, 8H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 4.47 [s, 4H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 6.48 [d, $^3J_{\text{H-H}} = 7$ Hz, 4H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 6.87 [m, 8H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 7.61 [d, $^3J_{\text{H-H}} = 7$ Hz, 4H, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$]. ^{13}C $\{^1\text{H}\}$ NMR (C_6D_6): 25.6 [s, 4C, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 30.5 [s, 4C, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$], 68.7 [s, 4C, $[\text{H}_2\text{B}\{\text{C}_4\text{H}_4\text{C}_2\text{N}_2(\text{CH}_3)\text{CS}\}_2]_2\text{Ca}(\text{C}_4\text{H}_8\text{O})_2$],

108.9 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 113.5 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 121.9 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 122.6 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 134.4 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 137.4 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂], 170.3 [s, 4C, [H₂B{C₄H₄C₂N₂(CH₃)CS}₂]₂Ca(C₄H₈O)₂]. IR (ATR, cm⁻¹): 3072 (w), 2826 (w), 2552 (w), 2213 (w), 1674 (s), 1601 (w), 1582 (w), 1497 (w), 1454 (w), 1421 (m), 1324 (m), 1288 (s), 1186 (m), 1127 (m), 1073 (w), 1027 (w), 933 (m), 807 (m), 732 (w), 702 (s), 685 (w), 666 (m).

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