

Synthesis and Structural Characterization of Novel Thulium(III) Cyclic Organohydroborate Complex with a Weak Agostic Interaction (THF)₃Tm{(μ-H)₂(BC₈H₁₄)₃}

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Abundant studies on transition metal organohydroborate complexes have been reported.¹ However, lanthanide metal organohydroborate derivatives have received less attention.² We have been involved in the chemistry of the cyclic organohydroborate anions, and their transition metal derivatives. Recently, a series of group 4 metallocene organohydroborate complexes were synthesized.^{3,4} The M-H-B (M: transition metal) three center two electron bond is present in the organohydroborate metal complexes in which B-H or M-H bond may serve as the electron pair donor to an unsaturated metal center or a trivalent boron to form the hydrogen-bridged bond.⁵ In an effort to extend lanthanide organohydroborate chemistry, the complexes have been investigated.

Here we describe the detail of the synthesis and crystal structure of a novel thulium cyclic organohydroborate complex, (THF)₃Tm{(μ-H)₂BC₈H₁₄}₃, which was prepared in the reaction of TmCl₃ with K[H₂BC₈H₁₄]. This thulium complex has electron deficient, three center two electron bonds Tm-H-B. An interesting feature in the molecular structure of the complex is the existence of an agostic interaction between Tm(III) and the α-C-H bond of the cyclic organohydroborate H₂BC₈H₁₄ group.^{6,7}

Experimental Section

General Procedures. All operations were carried out on a standard high vacuum line or in a drybox under a nitrogen atmosphere. Diethyl ether, THF, hexane, and toluene were dried over sodium-benzophenone, distilled, and stored in a sealed flask. TmCl₃ and (μ-H)₂(BC₈H₁₄)₂ (9-borabicyclo[3,3,1]nonane, 9-BBN dimer) were purchased from Aldrich and used as received. Potassium hydride (35% dispersion in mineral oil) was purchased from Aldrich and was washed with hexane prior to use. K[H₂BC₈H₁₄] was prepared by literature procedure.⁸ NMR spectra were recorded on a Bruker AM-250 NMR spectrometer. Infrared spectra were recorded on a Mattson Polaris Fourier Transform Spectrometer with 2 cm⁻¹ resolution.

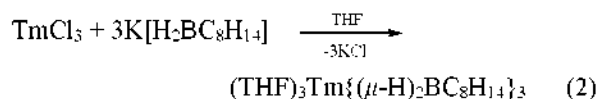
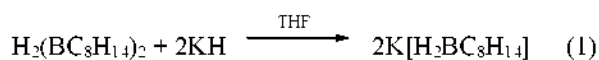
X-ray Structural Determination. Single crystal X-ray diffraction data were collected on an Enraf-Nonius Kappa CCD diffraction system, which employs graphite monochromated Mo Kα radiation (λ = 0.71073 Å). A single crystal of (THF)₃Tm{(μ-H)₂(BC₈H₁₄)₃} was mounted on the tip of a glass fiber coated with Fomblin oil (Aldrich). Unit cell parameters were

obtained by indexing the peaks in the first 10 frames and refined employing the whole data set. Data integration was carried out for Lorentz and polarization effects using the Denzo-SMN package (Nonius BV, 1999).⁹ The absorption corrections were applied using the SORTAV program¹⁰ provided by MaXus software.¹¹ The structure was solved by direct methods and refined using SHELXL-97 (difference electron density calculations and full matrix least-squares refinements) structure solution package.¹²

Preparation of (THF)₃Tm{(μ-H)₂BC₈H₁₄}₃. In the drybox 275.3 mg (1.0 mmol) of TmCl₃ and 480.3 mg (3.0 mmol) of K[H₂BC₈H₁₄] were put into a flask. After degassing, 30 mL of THF was transferred into the flask at -78 °C. The solution was warmed to room temperature and stirred for 24 hours. During this process the solution turned cloudy due to the formation of KCl which was removed by filtration. Volatile components were removed by means of dynamic high vacuum leaving a white solid. The solid was redissolved in ether and the solution was filtered to remove impurities. A white solid (THF)₃Tm{(μ-H)₂BC₈H₁₄}₃ was obtained in 65% yield upon removal of the solvent under vacuum. Crystal, suitable for X-ray diffraction, was obtained by crystallization from toluene. IR (KBr) 2922(s), 2856(s), 1702(m), 1660(m), 1446(m), 1012(m), 670(m) cm⁻¹.

Results and Discussion

The cyclic organohydroborate thulium complex (THF)₃Tm{(μ-H)₂BC₈H₁₄}₃ was obtained in the reaction of a 1:3 molar ratio of TmCl₃ with K[H₂BC₈H₁₄] at room temperature in THF (eq 1 & 2). The complex is stable in THF and toluene solution. The solid is stable under a nitrogen atmosphere at room temperature for several days while decomposition occurs when it is exposed to air.



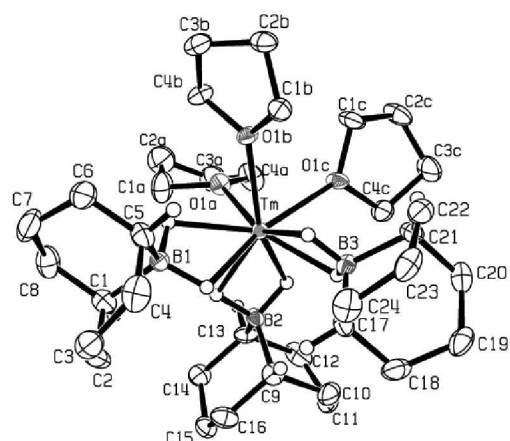


Figure 1. Molecular structure of $(\text{THF})_3\text{Tm}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{14}\}_3$ with 50% probability thermal ellipsoids. Bridging Tm-H-B and $\alpha\text{-C-H}$ hydrogens are drawn with arbitrary thermal ellipsoids. All other hydrogen atoms are omitted for clarity.

Table 1. Crystallographic Data for $(\text{THF})_3\text{Tm}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{14}\}_3$

empirical formula	$\text{C}_{36}\text{H}_{42}\text{B}_3\text{O}_3\text{Tm}$
fw	754.3
space group	$P2_1c$
a, Å	19.874(2)
b, Å	11.1305(10)
c, Å	18.4418(10)
β , deg	112.358(4)
V, Å ³	3772.8(5)
Z	4
ρ (calcd), g/cm ³	1.328
T, °C	-123
λ , Å	Mo K α (0.71073)
θ range (deg)	2.04 - 27.49
<i>hkl</i> ranges	-25 25, -14 14, -23 23
Reflections collected	77920
Independent reflections	8660
μ , mm ⁻¹	2.383
GOF	1.077
R_1 [$I > 2\sigma(I)$] ^a	0.027
wR_2 (all data) ^b	0.052

$${}^a R_1 = \sum |F_o| - F_c| / \sum |F_o|, {}^b wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)\}^{1/2}.$$

The molecular structure of the thulium complex was determined from a single crystal X-ray diffraction analysis. Crystallographic data and the selected bond distances and bond angles are provided in Table 1 and 2, respectively. The molecular structure is depicted in Figure 1. The coordination geometry about Tm(III) center can be described as a distorted octahedron formed by three cyclic organohydroborate ligands, $(\mu\text{-H})_2\text{-BC}_3\text{H}_{14}$ (9-BBN), *cis* to each other and three THF ligands. Each 9-BBN ligand is attached to Tm(III) through two Tm-H-B bridges which are three center two electron bonds. The average Tm-O, Tm-H (bridge hydrogen), and Tm-B distances are 2.3697, 2.14, and 2.681 Å, respectively. The B1-Tm-B3 angle, 99.90(9)°, is considerably distorted from the regular *cis*-octa-

Table 2. Selected bond distances (Å) and angles (°) for $(\text{THF})_3\text{Tm}\{(\mu\text{-H})_2\text{BC}_3\text{H}_{14}\}_3$

<i>bond distances</i>	
Tm-O1a	2.3889(17)
Tm-O1b	2.3627(16)
Tm-O1c	2.3574(16)
Tm-B1	2.690(3)
Tm-B2	2.639(3)
Tm-B3	2.715(3)
Tm-H1a	2.19(3)
Tm-H1b	2.161(19)
Tm-H2c	2.09(2)
Tm-H2d	2.172(19)
Tm-H3c	2.09(2)
Tm-H3d	2.14(2)
Tm-H9	3.20(2)
Tm-H13	4.20(2)
Tm-H1	3.86(2)
Tm-H5	3.64(2)
Tm-H17	3.77(2)
Tm-H21	3.88(3)
<i>bond angles</i>	
O1a-Tm-O1b	81.76(6)
O1a-Tm-O1c	76.82(6)
O1b-Tm-O1c	78.42(6)
O1a-Tm-B1	100.81(8)
O1b-Tm-B1	85.27(8)
O1c-Tm-B1	163.68(8)
O1a-Tm-B2	82.74(8)
O1b-Tm-B2	164.20(8)
O1c-Tm-B2	101.04(8)
O1a-Tm-B3	158.12(7)
O1b-Tm-B3	93.01(8)
O1c-Tm-B3	81.32(8)
B2-Tm-B1	94.59(9)
B2-Tm-B3	102.55(9)
B1-Tm-B3	99.90(9)
B1-C1-H1	108.0(14)
B1-C5-H5	111.8(16)
B2-C9-H9	112.7(14)
B2-C13-H13	113.5(13)
B3-C17-H17	113.1(14)
B3-C21-H21	114.3(14)
Tm-B1-C1	131.97(19)
Tm-B1-C5	121.25(18)
Tm-B2-C9	106.86(17)
Tm-B2-C13	145.7(2)
Tm-B3-C17	124.99(12)
Tm-B3-C21	127.85(19)

hedral angle of 90°. The steric repulsion of the two $(\mu\text{-H})_2\text{BC}_3\text{H}_{14}$ units forces the THF ligands toward each other and then the *cis*-THF angle, O1a-Tm-O1c, measures 76.82(6)°. These distances and angles fall within the ranges previously observed for other systems with bidentate Ln-H-B bridges (Ln: lanthanide metal).⁶

The bridge hydrogens of Tm-H-B were located and the position and isotropic thermal parameters were refined. The average Tm-H distance is 2.14 Å. This distance is consistent with other systems with Ln-H-B bridges (Ln: lanthanide metal).^{2,6} The paramagnetism of the Tm(III) in the complex prevented the acquisition of NMR spectra.^{2,13} The bands assigned to the bridge hydrogen Tm-H-B stretches around 1702 cm⁻¹ in IR spectrum

were observed.

The hydrogen atoms bonded to the bridgehead α -carbon atoms (C1, C5, C9, C13, C17, and C21) were refined isotropically to investigate the agostic interaction with Tm. The $(\mu\text{-H})_2\text{BC}_8\text{H}_{14}$ moieties involving B1 and B3 coordinate symmetrically to Tm. This symmetric coordination constrains the angles. Tm-B1-C1 ($131.97(19)^\circ$), Tm-B1-C5 ($121.25(18)^\circ$), Tm-B3-C17 ($124.99(12)^\circ$), and Tm-B3-C21 ($127.85(19)^\circ$), to be similar. The distances of Tm to α -hydrogens, H1 and H5 bonded to B1 and H17 and H21 bonded to B3 are 3.86, 3.64, 3.77, and 3.88 Å, respectively. However, these distances are beyond consideration for an agostic bond.¹⁴ On the other hand, the $(\mu\text{-H})_2\text{BC}_8\text{H}_{14}$ moiety involving B2 coordinates asymmetrically to Tm. The distance of Tm to α -hydrogen H9 of 3.20(2) Å is 1 Å shorter than the distance of Tm to the other α -hydrogen H13 of 4.20(2) Å. Additionally, the Tm-B2-C9 angle of $106.86(17)^\circ$ is much smaller than the corresponding Tm-B2-C13 angle of $145.7(2)^\circ$ and the O1b-Tm-B2 angle, $164.20(8)^\circ$, is considerably distorted from the regular *trans*-octahedral angle of 180° . Such distortion results from an agostic interaction between the Tm atom and the C9-H9 bond. Of the Tm-B distances, 2.690(3), 2.639(3), and 2.717(3) Å, the shortest distance is believed to be a consequence of the agostic interaction between Tm and the C(9)-H(9) bond that draws B2 closer to Tm. However, it is reasonable to consider that this is a weak agostic interaction based on the distance of Tm to α -hydrogen H9 which is not as short as that observed for other systems with the agostic interaction between the lanthanide metal and α -hydrogen.^{6,15}

Supplementary Material. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Center (CCDC No. 742704). Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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