Inorg. Chem. **1998,** *37,* 363−365 **363**

Hexahydro-*closo*-hexaborate as a Ligand in Coordination Compounds: Synthesis and Crystal Structure of $(n\text{-Bu}_4\text{N})_2[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]\cdot 2\text{CH}_2\text{Cl}_2$

Tanja Schaper and Wilhelm Preetz*

Institut für Anorganische Chemie der Universität Kiel,
Olshausenstrasse 40, D-24098 Kiel, Germany

Received August 15, 1997

Introduction

Many derivatives of the smallest and moderately stable *closo*-$[\text{B}_6\text{H}_6]^{2-}$ have been synthesized; however, only a few examples are published in which the dianion or other *closo*-borates are coordinated to metal centers. Recently we described the first η^3 complexes with transition metals: $(\text{Ph}_4\text{P})[\text{Hg}(\eta^3\text{-B}_6\text{H}_6)\text{Ph}]$,[1] $[\text{M}_2(\mu\text{-bis-}\eta^3\text{-B}_6\text{H}_6)_2(\text{PPh}_3)_2]$ (M = Cu, Au).[2] While the Hg(II) cation is coordinated to only one hexaborate anion in an η^3 fashion with the short distance to the B_3 plane being 2.17 Å, in the case of Cu(I) and Au(I) the hexaborate functions as a bridging ligand, coordinated to the metal centers with two opposite B_3 facets in symmetrical η^3 fashion with the distance 1.92 and 2.10 Å, respectively.

In this paper we report the syntheses of another new type of a coordination compound, $[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]^{2-}$. By X-ray diffraction analysis, it has been confirmed that the Cd(II) cation is symmetrically coordinated with two hexaborate clusters, each η^3-bound via one B_3 facet. The new compound has been further characterized by ^{11}B NMR investigations.

Experimental Section

General Procedures. Solvents were dried and distilled by standard procedures. Unless otherwise noted, reagents were obtained from commercial suppliers and used as received. The compounds $(n\text{-Bu}_4\text{N})_2[\text{B}_6\text{H}_6]$ [3,4] and $[\text{CdCl}_2(\text{PPh}_3)_2]$ [5] were prepared according to the literature procedures. ^{11}B NMR: Bruker AM 400 (128.38 MHz) with $\text{BF}_3\cdot\text{OEt}_2$ as external standard. IR: Matson Genesis FT-IR.

$(n\text{-Bu}_4\text{N})_2[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]$ (1). A solution of $[\text{CdCl}_2(\text{PPh}_3)_2]$ (0.14 g, 0.2 mmol) in CH_2Cl_2 (10 mL) was added to a solution of $(n\text{-Bu}_4\text{N})_2[\text{B}_6\text{H}_6]$ (0.2 g, 0.4 mmol) in CH_2Cl_2 (10 mL) at 40 °C. After the mixture was stirred for 48 h, the solution was evaporated to dryness. The colorless residue was dissolved in CH_2Cl_2 (5 mL), filtered, and layered with petroleum ether. After few days $(n\text{-Bu}_4\text{N})_2[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]$ (**1**), precipitated as a colorless crystalline material, was collected, washed with diethyl ether (10 mL), and dried *in vacuo.* Yield: 0.1 g (55%). Crystals of $\mathbf{1}\cdot 2\text{CH}_2\text{Cl}_2$ suitable for X-ray diffraction analysis were grown by slow diffusion of petroleum ether into a CH_2Cl_2 solution of **1**. ^{11}B NMR (CD_2Cl_2, 128.38 MHz, 298 K): δ −16.34 (d, 12B, J_{BH} = 129 Hz). IR (KBr, cm^{-1}): 2519, 2498, 2456 (s, B−H). Raman: 2523, 2500, 2456 (m, B−H).

Table 1. Crystallographic Data for $(n\text{-Bu}_4\text{N})_2[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]\cdot 2\text{CH}_2\text{Cl}_2$

empirical formula	$\text{C}_{34}\text{H}_{88}\text{B}_{12}\text{CdCl}_4\text{N}_2$
fw	908.99
cryst syst	triclinic
space group (No.)	$P\bar{1}$ (No. 2)
a (Å)	9.80(5)
b (Å)	10.18(5)
c (Å)	14.37(2)
α (deg)	84.2(2)
β (deg)	72.4(2)
γ (deg)	72.3(4)
V (Å^3)	1302(9)
Z	1
λ (Å)	Mo Kα 0.710 69
T (°C)	−65
ρ_{calc} (g/cm^3)	1.160
μ (cm^{-1})	6.50
2θ range (deg)	4−50
index ranges	$+h, \mp k, \mp l$
no. of reflcns collcd	4933
no. of reflcns with $[I > 2\sigma(I)]$	4627 [R(int) = 0.0337]
no. of refined parameters	265
GOF on F^2	1.083
final R indices $[I > 2\sigma(I)]$[a]	R1 = 0.0456, wR2 = 0.1275
R indices (all data)[a]	R1 = 0.0519, wR2 = 0.1325
largest diff peak and hole (e$^-$/Å^3)	0.923 and −0.664

[a] $\text{R1} = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $\text{wR2} = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[wF_o^4]]^{1/2}$.

Table 2. Atomic Coodinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^3 × 10^3) for $(n\text{-Bu}_4\text{N})_2[\text{Cd}(\eta^3\text{-B}_6\text{H}_6)_2]\cdot 2\text{CH}_2\text{Cl}_2$[a] ($U_{\text{eq}}$ Defined as One-Third of the Trace of the Orthogonalized $\mathbf{U}_{ij}$ Tensor)

atom	x	y	z	U_{eq}
Cd	10000	0	0	39(1)
B(1)	8163(4)	1160(4)	1405(3)	37(1)
B(2)	8361(4)	2297(4)	362(3)	39(1)
B(3)	7297(4)	1116(4)	487(3)	37(1)
B(4)	6273(4)	1741(4)	1620(3)	42(1)
B(5)	7300(4)	2881(4)	1499(3)	38(1)
B(6)	6464(4)	2844(4)	622(3)	42(1)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 2, -y, -z$.

Crystal Structure Determination. Diffraction data were collected on an Enraf-Nonius CAD4 four-circle diffractometer with a graphite-monochromated Mo Kα radiation source (λ = 0.710 69 Å). A suitable single crystal was affixed to a glass fiber using silicone grease. Lattice parameters were obtained from least-squares analysis of 25 machine-centered reflections. The intensities recorded at 208 K were corrected for Lorentz and polarization factors.[6] Three standard reflections were measured every 200 reflections to monitor crystal deterioration and X-ray beam intensity. The structure was solved by using the direct method, program SHELXS-86[7] and optimized by full-matrix weighted least-squares refinement on F^2 (SHELXL-93).[8] The crystallographic calculation was performed using the program XANADU.[9] The positions of all non-hydrogen atoms were refined anisotropically, the hydrogen atoms of the cluster were refined isotropically, whereas the hydrogen atoms of the cations were placed on calculated positions using a "riding" model.

---

* Corresponding author. Fax: +49 (0)431 880.1520. E-mail: Preetz@talos.ac.uni-kiel.de.

(1) Schaper, T.; Preetz, W. *Z. Naturforsch.* **1997**, *52B*, 57−60.
(2) Schaper, T.; Preetz, W. *Chem. Ber.* **1997**, *130*, 405−407.
(3) Preetz, W.; Heinrich, A.; Thesing J. *Z. Naturforsch.* **1988**, *43B*, 1319−1326.
(4) Kabbani, R. M. *Polyhedron* **1996**, *15*, 1951−1955.
(5) Blackburn, J. R.; Nordberg, R.; Stevie, F.; Albridge, R. G.; Jones, M. M. *Inorg. Chem.* **1970**, *9*, 2374−2376.
(6) Enraf-Nonius. *CAD-4-PC*, Version 1.5; Enraf-Nonius: Delft, The Netherlands, 1994.
(7) Sheldrick, G. M. *SHELXS-86: Program for Crystal Structure Solution*; University of Göttingen: Germany, 1986.
(8) Sheldrick, G. M. *SHELXL-93: Program for Crystal Structure Refinement*; University of Göttingen: Germany, 1993.
(9) Roberts, P.; Sheldrick, G. M. *XANADU: Program for Crystallographic Calculations*; Cambridge University: Cambridge, U.K., 1975.

S0020-1669(97)01039-2 CCC: $15.00

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(n\text{-}Bu_4N)_2[Cd(\eta^3\text{-}B_6H_6)_2]\cdot 2CH_2Cl_2$

Distances			
Cd−B(1)	2.388(10)	B(2)−B(3)	1.780(9)
Cd−B(2)	2.404(14)	B(2)−B(5)	1.703(7)
Cd−B(3)	2.451(14)	B(2)−B(6)	1.702(11)
Cd−H(1)	2.50(6)	B(3)−H(3)	1.04(4)
Cd−H(2)	2.48(4)	B(3)−B(4)	1.701(7)
Cd−H(3)	2.36(4)	B(3)−B(6)	1.702(10)
B(1)−B(2)	1.798(7)	B(4)−H(4)	1.10(5)
B(1)−B(3)	1.783(6)	B(4)−B(5)	1.718(9)
B(1)−B(4)	1.703(11)	B(4)−B(6)	1.729(7)
B(1)−B(5)	1.697(10)	B(5)−B(6)	1.708(6)
B(1)−H(1)	1.03(6)	B(5)−H(5)	1.15(4)
B(2)−H(2)	1.17(4)	B(6)−H(6)	1.06(4)
Angles			
B(1)−Cd−B(2)	44.1(3)	B(1)−B(2)−Cd	67.5(3)
B(1)−Cd−B(3)	43.2(2)	B(3)−B(2)−Cd	69.9(4)
B(2)−Cd−B(3)	43.0(3)	B(5)−B(2)−Cd	124.9(3)
B(1)−Cd−H(1)	24.3(14)	B(6)−B(2)−Cd	128.2(4)
B(2)−Cd−H(2)	27.6(10)	H(2)−B(2)−Cd	80(2)
B(3)−Cd−H(3)	24.8(10)	B(1)−B(3)−Cd	66.5(3)
B(2)−B(1)−Cd	68.4(4)	B(2)−B(3)−Cd	67.1(4)
B(3)−B(1)−Cd	70.3(3)	B(4)−B(3)−Cd	124.7(3)
B(4)−B(1)−Cd	128.3(3)	B(6)−B(3)−Cd	125.4(4)
B(5)−B(1)−Cd	126.1(4)	H(3)−B(3)−Cd	73(2)
H(1)−B(1)−Cd	84(3)		

Crystallographic data are summarized in Table 1. Atomic coordinates and U_{eq} values for $\mathbf{1}\cdot 2CH_2Cl_2$, excluding those of cations, lattice solvents, and hydrogen atoms, are given in Table 2, whereas selected bond distances and angles are given in Table 3.

Results and Discussion

Reaction of $(n\text{-}Bu_4N)_2[B_6H_6]$ with $[CdCl_2(PPh_3)_2]$ in dichloromethane led to **1**, which was isolated as a colorless solid

$$2(n\text{-}Bu_4N)_2[B_6H_6] + [CdCl_2(PPh_3)_2] + 2\,CH_2Cl_2 \rightarrow (n\text{-}Bu_4N)_2[Cd(\eta^3\text{-}B_6H_6)_2]\cdot 2CH_2Cl_2\ (\mathbf{1}) + 2(n\text{-}Bu_4N)Cl + 2PPh_3$$

soluble in dichloromethane and acetonitrile and insoluble in water. Complex **1** is airstable up to 100 °C and decomposes at higher temperature.

By slow diffusion of petroleum ether into a solution of **1** in CH_2Cl_2, single crystals suitable for X-ray structure determinations were obtained. The cadmium complex crystallizes in space group $P\bar{1}$. The molecular structure with atom labeling is shown in Figure 1.

Crystallographic Studies. The structure consists of two $\{CdB_6H_6\}$ fragments fused about a common Cd vertex. The metal atom located on a crystallographic inversion center displays a trigonal-prismatic co-ordination geometry with the angles B2−Cd−B3 (43.0°) and B2−Cd−B3#1 (137.0°). Because of the high degree of electron delocalization over the framework, which allows one to regard the cluster, like fullerenes,[10] as a three-dimensional aromatic system,[11] **1** may be considered as a cadmium(II) sandwich complex.

The cadmium atom lies only 2.18 Å above the B_3 facet. In contrast to other synthezised η^3 complexes $[Hg(\eta^3\text{-}B_6H_6)Ph]^-$,[1] $[Cu_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)_2(PPh_3)_2]$,[2] and $[Au_2(\mu\text{-bis-}\eta^3\text{-}B_6H_6)_2(PPh_3)_2]$,[2] with all M−B distances shorter than the M−H distances and therefore no M−H−B bridge bondings, the Cd−H distances in $\mathbf{1}\cdot 2CH_2Cl_2$ of 2.36−2.50 Å are in the same range of the Cd−B bond lengths of 2.39−2.45 Å. Compounds with M−H−B bridges display substantially shorter M−H bond lengths than M−B distances, as has been pointed out for $[Cu(BH_4)(PPh_3)_2]$ with 2.02 and 2.18 Å[12] and $[Cu(B_3H_8)(PPh_3)_2]$ with 1.84 and 2.30 Å, respectively.[13] In **1** the Cd−B1 and Cd−B2 bond lengths are shorter than their corresponding Cd−H distances while Cd−B3 is longer than Cd−H3 so that in $\mathbf{1}\cdot 2CH_2Cl_2$ two additional M−H−B bridges may be discussed. The bond lengths within the boron clusters are comparable and fall in the normal range (Table 3). The influence of the metal atom on the geometry of the clusters is shown by an expansion of the metal-bonded facets, B−B distances of which are about 6% longer than those between the other neighboring boron atoms. In contrast to $[Hg(\eta^3\text{-}B_6H_6)Ph]^-$ there is no expansion of the facets opposite to the metal-bonded B_3 facets. To date, there have been no reports on coordination of cadmium with *closo*-borates but only with *nido*-borates.[14−16]

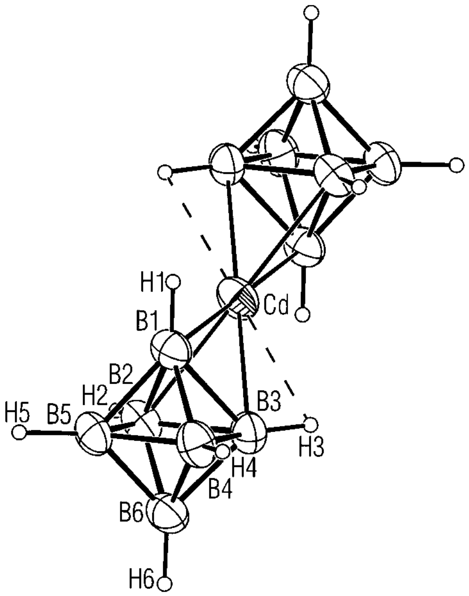

Figure 1. Molecular structure of the complex anion $[Cd(\eta^3\text{-}B_6H_6)_2]^{2-}$ in the crystal, showing the 50% probability thermal ellipsoids.

NMR Spectrum. The ^{11}B NMR spectrum exhibits only one doublet, indicating the ambient equivalence of all B nuclei. We conclude that the clusters are rotating at ambient temperature, as has been supposed for $[Hg(\eta^3\text{-}B_6H_6)Ph]^-$.[1] As a result of coordination to the metal center, a downfield shift and a concomitant decrease of the coupling constant $^1J_{BH}$ are observed: $\delta = -16.34$ [129 Hz] (**1**), compared with $\delta = -17.2$ [145 Hz] in $[B_6H_7]^-$.

IR Spectrum. Until now it has been impossible to prepare alkali salts so that the IR and Raman spectra of **1** show strong bands due to $(n\text{-}Bu_4N)^+$, such that the assignment of modes in the framework area below 1100 cm^{-1} is not possible. The BH stretching vibrations, observed for $(n\text{-}Bu_4N)_2[B_6H_6]$ at 2414 cm^{-1},[3] are split and shifted to higher energy, appearing as strong but broad IR bands for **1** at 2456, 2498, and 2519 cm^{-1}, while the protonated $[B_6H_7]^-$ anion exhibits υ(BH) in the region of 2509 and 2530 cm^{-1}.[3]

---

(10) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160−1161.
(11) King, R. B. *J. Math. Chem.* **1990**, *4*, 69−85.
(12) Lippard, S. L.; Melmed K. M. *Inorg. Chem.* **1967**, *6*, 2223−2228.
(13) Lippard, S. L.; Melmed K. M. *Inorg. Chem.* **1969**, *8*, 2755−2762.
(14) Greenwood, N. N.; Staves J. *J. Chem. Soc., Dalton Trans.* **1977**, 1786−1788.
(15) Greenwood, N. N.; McGinnety, J. A.; Owen, J. D. *J. Chem. Soc., Dalton Trans.* **1972**, 989−992.
(16) Greenwood, N. N.; Travers, N. F. *J. Chem. Soc. A* **1967**, 880−884.

Acknowledgment. This work was kindly supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: The X-ray crystallographic data of **1**·$2CH_2Cl_2$, in CIF format, is available. Ordering information is given on any current masthead page. Further details of the crystal structure investigation are also available on request from Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-406912.

IC971039G