The Dipotassium Salt of the 6,6′-*commo*-Bis(tridecahydro-*nido*-6-cadmadecaborate) Dianion: A New Type of Metal-Centered *commo*-Bis(metallaborane)

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Introduction

Although the metallaboranes are a fairly well explored class of substances, the number of metallaboranes in which two borane cages are bridged by one metal atom is quite limited.[1] Known examples include $[Et_3NH][Cu(1\text{-}B_{10}H_9N_2)_2]$,[2a] derivatives of the decaborate dianion, $M(B_{12}H_{12})_2{}^{n-}$ ($n = 2$, M = Zn,[2b−d,h] Cd,[2d,e] Hg,[2d,f] Ni,[2g,h] Pd,[2h] Pt,[2h] Co;[2h] $n = 1$, M = Au[2i]), $[(B_{10}H_{12})Au(B_{10}H_{13})]^{2-}$,[2i] $M(THF)_2(B_6H_9)_2$ (M = Mg, Zn), $Cd(B_6H_9)_2$,[2j] $Cl_2Pt(B_6H_{10})_2$,[2k] $Be(B_5H_{10})_2$,[2l] and $Be(B_3H_8)_2$.[2m] Recently, through our photochemical investigations of cluster compounds, we became interested in metallaboranes in which two borane cages are bonded to one group 12 metal. Here we report the synthesis and solid state structure of $[K(18\text{-crown-}6)^+]_2[Cd(B_9H_{13})_2]$, a compound with a new type of metal-centered *commo*-bis(metallaborane) structure.

Experimental Section

Physical Measurements. All NMR spectra were recorded on samples dissolved in CD_3CN in 5 mm (o.d.) tubes. The boron (^{11}B) NMR spectra were recorded on a Bruker DPX-300 NMR spectrometer operating at 96.3 MHz. Spectra were referenced to BBr_3 at +40.0 ppm (relative to $BF_3{\cdot}Et_2O$ $\delta = 0.0$ ppm, with positive chemical shifts indicating downfield resonances) and recorded in both the ^1H-coupled and -decoupled modes. Typical ^{11}B NMR acquisition parameters employed were a relaxation delay of 0.1 ms and a 90° pulse of 10 μs. The 2D $^{11}B-^{11}B\{^1H\}$ COSY NMR spectrum, both the absolute-value and pure-phase versions, was obtained on the Bruker DPX-300 NMR spectrometer. A 90° pulse width of 10 μs was used. A previously described absolute-value-mode COSY pulse sequence[3] was used to generate the t_1, t_2 data matrix (relaxation delay $-(\pi/2)-t_1-(\pi/2)-t_2$) in which t_1 was incremented by the inverse of the sweep width in the F_1 dimension and t_2 was the usual acquisition time in a 1D experiment. The t_1, t_2 matrix was collected as 1024 × 256 data points. Data processing involved the application of a dc offset and first-point correction, shifted sine bell apodization, zero filling, Fourier transformation, and a magnitude calculation to give the 512 × 512 2D $^{11}B-^{11}B$ COSY NMR spectrum.[4] Proton (^1H) NMR spectra were recorded on the Bruker DPX-300 spectrometer operating at 300.15 MHz with chemical shifts referenced to an internal standard of tetramethylsilane at $\delta = 0.0$ ppm.

Materials. The starting cluster compound, $K_2[B_9H_{13}]$, was prepared according to the procedures previously described.[5] Tetrahydrofuran (Fisher) and diethyl ether were ACS reagent grade and were distilled under a dry nitrogen atmosphere from calcium hydride. Decaborane(14), received from Callery Chemical Co., was sublimed in vacuo at 60 °C prior to use. The cadmium chloride was dried with thionyl chloride before use. All other commercially available chemicals were used as received.

[K(18-crown-6)]$_2$[Cd(B$_9$H$_{13}$)$_2$]. In an inert atmosphere, a slurry of 226 mg (1.23 mmol) of $CdCl_2$ in 15 mL of THF was added to a solution of 466 mg (2.47 mmol) of $K_2[B_9H_{13}]$ in 15 mL of THF at −78 °C. After 16 h of warming and stirring at room temperature, a gray precipitate was filtered off. After the addition of 660 mg (2.50 mmol) of 18-crown-6, 40 mL of diethyl ether was added. The precipitate was filtered off, washed twice with THF/diethyl ether (1/1), and dried in vacuo. The product was obtained as a white powder in 38% yield (0.44 g, 0.47 mmol). ^{11}B-NMR (96.3 MHz; CD_3CN; δ, ppm): 4.6 (d, $^1J_{BH} = 135$ Hz, 2B, B8,10), −9.5 (d, $^1J_{BH} = 140$ Hz, 2B, B1,3), −11.4 (d, $^1J_{BH} = 120$ Hz, 1B, B9), −30.4 (d, $^1J_{BH} = 118$ Hz, 1B, B2), −35.6 (t, $^1J_{BH} = 100$ Hz, 2B, B5,7), −50.6 (d, $^1J_{BH} = 145$ Hz, 1B, B4).

X-ray Crystallography of [K(18-crown-6)$^+$]$_2$[1^{2-}]. A 0.33 × 0.33 × 0.20 mm^3 crystal of $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]$ was grown by condensing diethyl ether onto a THF solution of the compound. All measurements were made on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å).[6] The data collection covered a quadrant of reciprocal space by a combination of five sets of exposures with each exposure covering 0.3° in ω.[6a] Data were collected at $T = 150(1)$ K and $2.74° \leq 2\theta \leq 56.60°$. From these exposures, 23 505 reflections were read, from which 7573 unique and 6747 observed $[I > 2\sigma(I)]$ were ultimately used in the solution.[6b] The solution was accomplished by using direct methods (SHELXS86) with the refinement on $F_o{}^2$ (SHELXL93).[6c] An empirical absorption correction was applied (SADABS), and the non-hydrogen atoms were located by application of direct methods to generate a trial structure.[6d] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms at the boron cage were found by difference maps and were refined with free coordinates and displacement parameters. The final cycle of a full-matrix least-squares refinement for 618 parameters converged with $R1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.0337$ for $[I > 2\sigma(I)]$ and $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2} = 0.0668$ for all data. The crystallographic data, selected bond lengths, and selected bond angles for $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]$ are given in Tables 1−3, respectively. All atom coordinates [with U(eq)], anisotropic thermal parameters, bond distances and angles involving both non-hydrogen and hydrogen atoms, intermolecular distances, and packing diagrams for $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]$ are available as Supporting Information.

Results and Discussion

The metathesis reaction of $K_2[B_9H_{13}]^5$ and $CdCl_2$ in a 2:1 ratio in THF produces $[Cd(B_9H_{13})_2]^{2-}$, $\mathbf{1}^{2-}$, in moderate yield.

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Table 1. Crystallographic Data for [K(18-crown-6)$^+$]$_2$[**1**$^{2-}$]

empirical formula	$C_{24}H_{74}B_{18}CdK_2O_{12}$
formula weight	940.01
crystal system	orthorhombic
space group	$Pca2_1$
temperature	150 K
cell dimensions	
a	15.2570(0) Å
b	4.9067(1) Å
c	21.4155(3) Å
V	4870.56(8) Å^3
Z	4 molecules
λ(Mo Kα) (Å)	0.710 73 Å
diffractometer	Siemens SMART CCD diffractometer
ρ_{calcd}	1.282 g/cm^3
wR2 (for all data)	0.0668
R1 [(I>2σ(I)]	0.0337
total number of reflections	23 505
number of reflections with $I > 2\sigma(I)$	6747
number of variables	618
$2\theta_{max}$	56.60°
maximum shift/error in final cycle	0.00

Table 2. Selected Intramolecular Bond Distances for [K(18-crown-6)$^+$]$_2$[**1**$^{2-}$][a]

Cd(1)−B(2)	2.272(4)	B(2)−B(7)	1.868(5)
Cd(1)−B(7)	2.591(4)	B(2)−B(5)	1.863(5)
Cd(1)−B(5)	2.609(4)	B(12)−B(15)	1.885(5)
Cd(1)−B(12)	2.302(4)	B(12)−B(17)	1.865(5)
Cd(1)−B(17)	2.545(4)	B(5)−B(10)	1.973(6)
Cd(1)−B(15)	2.577(4)	B(7)−B(8)	1.954(6)
B(1)−B(2)	1.760(5)	B(2)−B(3)	1.757(5)
B(1)−B(5)	1.758(5)	B(1)−B(10)	1.727(6)
B(3)−B(7)	1.747(5)	B(3)−B(8)	1.735(6)
B(10)−H10B)	1.33(5)	B(18)−H(18B)	1.24(5)
B(9)−H(10B)	1.18(6)	B(19)−H(18B)	1.26(5)
B(8)−H(8B)	1.35(5)	B(19)−H(20B)	1.30(4)
B(9)−H(8B)	1.26(5)	B(20)−H(20B)	1.35(4)
K(1)−H(2)	2.53(3)	K(2)−H(14)	2.74(4)
K(1)−H(1)	2.95(4)	K(2)−H(20)	3.06(4)
K(2A)−H(9)	3.18(4)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 3. Selected Intramolecular Bond Angles for K(18-crown-6)$^+$]$_2$[**1**$^{2-}$][a]

B(7)−Cd(1)−B(2)	44.59(12)	B(17)−Cd(1)−B(12)	44.91(13)
B(7)−Cd(1)−B(5)	73.59(12)	B(17)−Cd(1)−B(15)	75.48(12)
B(2)−Cd(1)−B(5)	44.20(12)	B(12)−Cd(1)−B(15)	45.02(13)
B(7)−Cd(1)−B(17)	136.69(13)	B(2)−Cd(1)−B(17)	116.52(13)
B(7)−Cd(1)−B(12)	128.17(12)	B(2)−Cd(1)−B(12)	151.60(13)
B(7)−Cd(1)−B15)	134.59(13)	B(2)−Cd(1)−B(15)	163.34(12)
B(5)−Cd(1)−B(17)	123.29(13)	B(5)−Cd(1)−B(15)	120.12(12)
B(5)−Cd(1)−B(12)	158.09(12)	B(5)−B(2)−B(7)	113.2(3)
		B(15)−B(12)−B(17)	113.4(2)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

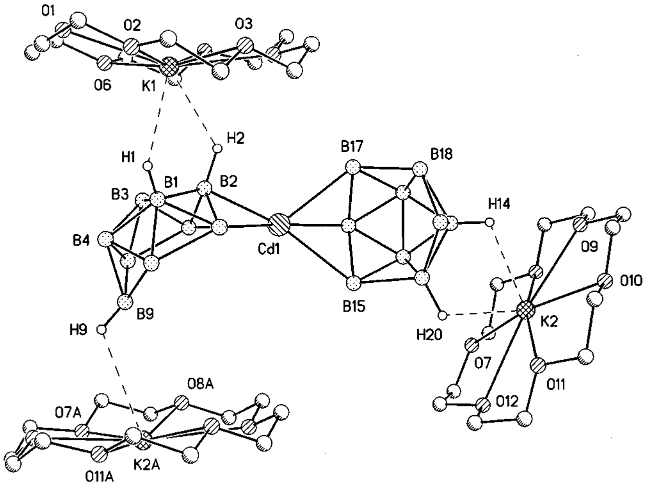

Figure 1. Plot showing the orientations and interactions between the cadmaborate cage and the [K(18-crown-6)$^+$] ions in [K(18-crown-6)$^+$]$_2$-[Cd(B_9H_{13})$_2$]$^{2-}$. (Hydrogen atoms, except those having interactions with the K$^+$ ions, have been omitted for clarity.)

The [Cd(B_9H_{13})$_2$]$^{2-}$ dianion, **1**$^{2-}$, was found to be the main cluster product (∼80−90%) in THF solution as observed in the ^{11}B-NMR spectrum of the reaction mixture. Identified side products were BH_4^- (δ(^{11}B): −47.0, q, $^1J_{BH}$ = 83 Hz)[7a] and $B_9H_{14}^-$ (δ(^{11}B): −7.2, d; −20.0, d; −22.9, d).[7b] After filtration and addition of 2 equiv of 18-crown-6, the dipotassium salt [K(18-crown-6)$^+$]$_2$[Cd(B_9H_{13})$_2$]$^{2-}$ was precipitated by the addition of diethyl ether.

Crystals of [K(18-crown-6)$^+$]$_2$[**1**$^{2-}$] were obtained by condensing diethyl ether onto a THF solution of [K(18-crown-6)$^+$]$_2$-[**1**$^{2-}$] at room temperature. The solid state structure of the compound, which has been determined by X-ray crystallography, displays a layered arrangement of the ions in the crystal packing. The unit cell contains dianionic *commo*-cluster molecules **1**$^{2-}$ and potassium cations which are complexed by 18-crown-6 units in a 1:2 ratio. The ions are not completely separated, and each dianion **1**$^{2-}$ is surrounded by three [K(18-crown-6)$^+$] ions with K−H distances between 2.53(3) and 3.18(4) Å. A plot of the [Cd(B_9H_{13})$_2$]$^{2-}$, **1**$^{2-}$, dianion showing the orientations and interactions of the cadmaborane cage and the [K(18-crown-6)$^+$] ions is given in Figure 1. Thus, the coordination number of the metallaborane dianion is 3 [K(18-crown-6)$^+$] and, since there are two types of inequivalent potassium units (one type with a coordination number of 1 and the other type with a coordination number of 2), the formal (average) coordination number of the [K(18-crown-6)$^+$] units is 1.5 in order to maintain electrical neutrality in the compound. Since the ionic radii[8a] of potassium (1.38 Å) and barium (1.35 Å) are almost identical, the interactions between K$^+$ and several of the hydrogens of **1**$^{2-}$ [H(1), H(2), H(14), H(20), and H(9)] can be compared with those of the known structures of Ba(BH_4)$_2$ compounds.[8b] In the solvates of Ba(BH_4)$_2$, the barium-bonded BH_4^- groups show Ba−H distances between 2.66(4) and 2.98(5) Å , which are approximately equivalent to those observed for [K(18-crown-6)$^+$]$_2$[**1**$^{2-}$]. It is not clear whether these shortened interactions are due to electrostatic interactions between the cadmaborane dianionic cage and the potassium ions or due to geometric packing forces. It is interesting that, even in crystals formed in a THF/Et_2O solution, the potassium cations are weakly coordinated, in addition to the 18-crown-6 system, by the cadmaborane dianions **1**$^{2-}$ rather than by ether molecules.

The molecular structure of the cadmaborane dianion **1**$^{2-}$, shown in Figure 2, is that of two *nido*-6-cadmadecaborane clusters conjoined at the common cadmium atom. Both of the $B_9H_{13}Cd^-$ subclusters are essentially identical. The best planes through the Cd(1)−B(2)−B(4)−B(9) atoms (mean deviation of 0.4 pm) and the Cd(1)−B(12)−B(14)−B(19) atoms (mean deviation of 0.5 pm) form a dihedral angle of 88.6°. The symmetry of the 19-vertex cluster dianion is thus close to C_2 point symmetry. The cadmium center displays one shorter and two longer bonds with each of the B_9H_{13} dianion cage units [average Cd(1)−B(2,12) = 2.287 Å and Cd(1)−B(5,7,15,17)

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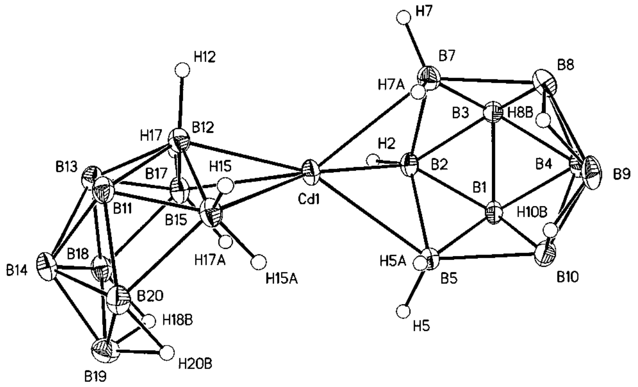

Figure 2. Molecular structure of $[Cd(B_9H_{13})_2]^{2-}$, $\mathbf{1}^{2-}$, with atomic numbering (ORTEP). (Thermal ellipsoids represent 30% probability; hydrogen atoms which are either not attached to boron atoms connected to cadmium or bridging have been omitted for clarity.)

= 2.581 Å]. This asymmetry is unusual for *nido*-6-metalladecaboranes, for which the three metal to boron distances are typically very similar. The cadmium distances to the B(2) and B(12) atoms are distinctly shorter than the Cd−B bond lengths in the known $[(OEt_2)_2Cd(B_{10}H_{12})]_2$, **2**.[9] In this decaborate derivative, **2**, the Cd−B bond distances range from 2.37(3) to 2.74(4) Å. Interestingly, the cadmium-bonded boron atoms B(5)/B(7) and B(15)/B(17) in $\mathbf{1}^{2-}$, which lie in the six-membered open faces of the 6-cadmadecaborane subunits, bind two *exo*-hydrogen atoms with B−H distances between 1.09(4) and 1.22(4) Å, typical of most $B-H_{exo}$ atom distances. The observed BH_2 units in $\mathbf{1}^{2-}$ are unusual for *nido*-6-metalladecaboranes in that these compounds typically bind to only one *exo*-hydrogen atom and one metal−boron bridging hydrogen atom rather than to two *exo*-hydrogen atoms as observed in $\mathbf{1}^{2-}$. As expected for an analogue of decaborane(14), the boron−boron bonds B(5)−B(10) and B(7)−B(8) as well as B(15)−B(20) and B(17)−B(18) in $\mathbf{1}^{2-}$ are fairly long, with an average bond distance of 1.95 Å. In addition, the B(4)−B(9) and B(14)−B(19) bonds, with an average of 1.71 Å, are shortened and the B(9)−B(8)/B(9)−B(10) and B(19)−B(18)/B(19)−B(20) bonds are bridged by hydrogen atoms in $\mathbf{1}^{2-}$, as similarly found in the parent decaborane(14) cluster.[10]

The $^{11}B\{^1H\}$-NMR spectrum of a CD_3CN solution of $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]$, shown in Figure 3, displays six signals in a ratio of 2:2:1:1:2:1. This pattern suggests that, in solution, the cadmaborane cluster can achieve a time-averaged C_{2h} symmetry structure with a mirror plane through the B(9), B(4), B(2), Cd, B(12), B(14), and B(19) atoms and with a 2-fold rotation axis through the cadmium center, perpendicular to the mirror plane. The ^{11}B-NMR resonances of $\mathbf{1}^{2-}$ have been unambiguously assigned on the basis of a 2D $^{11}B-^{11}B\{^1H\}$ COSY NMR experiment and the intensities and multiplicities of the signals in the ^{11}B NMR spectra. As expected, no cross peaks were observed between the boron atoms B(9)−B(8) and B(9)−B(10), which are bridged by hydrogen atoms, and between the boron atoms B(5)−B(10) and B(7)−B(8), which are connected by long B−B bonds.[11] The cadmium-bonded boron atoms show ^{11}B resonances at δ −30.4 [B(2)] and −35.6 [B(5),B(7)], and the resonance of B(5)/B(7) appears as a triplet in the proton-coupled ^{11}B-NMR spectrum, which is consistent with the solid state structure.

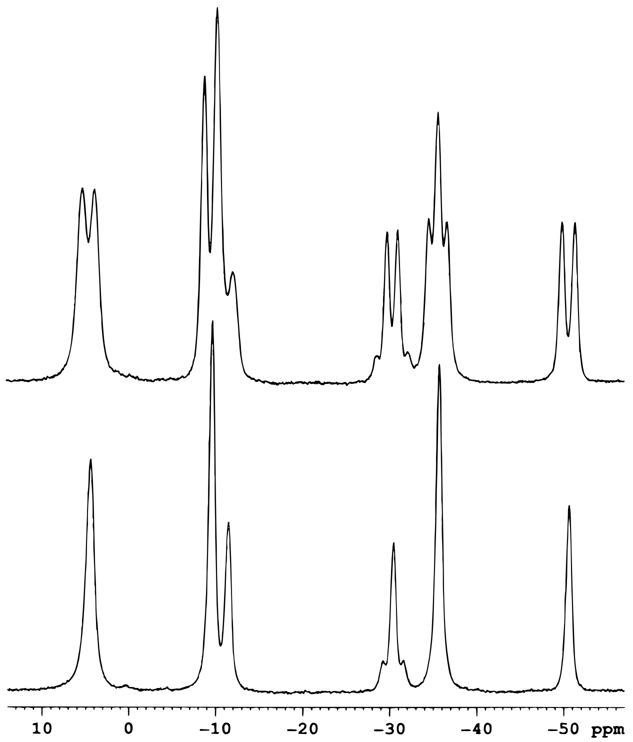

Figure 3. Room-temperature ^1H-coupled (above) and ^1H-decoupled (below) ^{11}B-NMR spectra of $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]$ in CD_3CN at 96.3 MHz.

In the two known structures of zincaboranes ($[Ph_3PMe]_2[Zn(B_{10}H_{12})_2]$[2b] and $[(MeZn)_2B_3H_7]_2$[12a]) and the only structurally characterized cadmaborane ($[(OEt_2)_2Cd(B_{10}H_{12})]_2$, **2**[9]), the group 12 metals or metal fragments formally replace bridging hydrogen atoms, while the cadmium atom of $\mathbf{1}^{2-}$ seems to be directly involved in the cluster framework. With Cd(II) formally contributing no electrons to the valence electron count, each $B_9H_{13}Cd^-$ unit thus constitutes a *nido*-cadmadecaborate with 24 valence electrons.[12b]

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Supporting Information Available: Packing diagrams and tables listing all atomic coordinates, anisotropic thermal parameters, bond distances and angles (involving both non-hydrogen and hydrogen atoms), and intermolecular distances for $[K(18\text{-crown-}6)^+]_2[\mathbf{1}^{2-}]^{2-}$ (14 pages). Ordering information is given on any current masthead page.

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