

# New Tetrameric Alkylmetal Boryloxides $[(\mu^3\text{-R}_2\text{BO})\text{MR}']_4$ of Zinc and Cadmium with Heterocubane Structure

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The treatment of diethylzinc with  $(9\text{-BBN})_2\text{O}$  afforded a tetrameric species  $[(\mu^3\text{-9-BBN-9-O})\text{ZnEt}]_4$  (**1**) in high yield due to the selective cleavage of metal–carbon bond whereas  $\text{Bu}_2\text{Zn}$  was found to be inert toward  $(9\text{-BBN})_2\text{O}$ . The reaction of dimethylcadmium with  $(9\text{-BBN})_2\text{O}$  resulted in the formation of the analogue  $[(\mu^3\text{-9-BBN-9-O})\text{CdMe}]_4$  (**2**). Reactions of tetraethyldiboroxane  $\text{Et}_4\text{B}_2\text{O}$  with  $\text{Et}_2\text{Zn}$ ,  $\text{Bu}_2\text{Zn}$  and  $\text{Me}_2\text{Cd}$  were also investigated showing its different behavior in each case. The structures of **1** and **2** were determined by X-ray diffraction, and they are the first for group 12 metal boryloxides with a cubane-like  $\text{M}_4\text{O}_4$  core. The boron–oxygen interaction affecting deformation of the central core is discussed based on X-ray as well as multinuclear NMR spectroscopy data.

## Introduction

The chemistry of metal diorganoboryloxides  $[\text{M}(\text{OBR}_2)_n]_m$  was not extensively studied up to now. This is quite surprising since the expected weaker  $\pi$ -donor properties of the oxygen atom in the quasi-alkoxide  $\text{R}_2\text{BO}$  ligand versus typical alkoxide ligands might be especially interesting from the structural point of view. Different bonding properties and the presence of the coordinatively unsaturated boron atom may also be responsible for potential reactivity of these compounds. So far only several reports covering this area have been published, and they concern mainly the synthesis and structure of main group metal boryloxides, e.g.,  $[\text{9-BBN-9-OLi}]_m$ ,<sup>1</sup>  $[\text{Mes}_2\text{BOLi}(\text{THF})]_2$ ,<sup>2</sup>  $[(\text{Me}_3\text{-Si})_2\text{CH})_2\text{BOLi}]_2$ ,<sup>3</sup>  $[\text{9-BBN-9-ONa}(\text{THF})]_4$ ,<sup>4</sup> and  $[(\mu\text{-R}_2\text{BO})\text{-AlX}_2]_2$ , where  $\text{R} = \text{Et}$ ,  $\text{R}_2 = \text{cyclooctane-1,5-diyl}$ , and  $\text{X} = \text{Cl}$  or  $\text{Br}$ .<sup>5</sup> Some other examples are also known for silicon, tin, and mercury,<sup>6</sup> but they have not been characterized by X-ray diffraction, or cannot be considered as simple metal or organometal boryloxides.<sup>7</sup> In principle, the chemistry of transition metal diorganoboryloxides is not recognized as only two structures of the homoleptic species  $[\text{Fe}(\text{OBMes}_2)_2]_2$  and  $[\text{Mn}(\text{OBTrip}_2)_2]_2$  were reported.<sup>8</sup>

The interest in our laboratory has focused on synthesis and structural characterization of alkylmetal boryloxides. Recently, several group 13 alkylmetal boryloxides of the formula  $[(\mu\text{-9-BBN-9-O})\text{MR}_2]_2$  ( $\text{M} = \text{Al}$ ,  $\text{Ga}$ ,  $\text{In}$ ) have been synthesized and

characterized by our group.<sup>9</sup> In this paper we describe the preparation and structure of related group 12 alkylmetal diorganoboryloxides of the formula  $[(\mu\text{-R}_2\text{BO})\text{MR}']_4$ , where  $\text{R} = \text{Et}$ ,  $\text{R}_2 = 9\text{-BBN}$ ,  $\text{M} = \text{Zn}$  or  $\text{Cd}$ , and  $\text{R}' = \text{Me}$  or  $\text{Et}$ .

## Experimental Section

**General Comments.**  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{11}\text{B}$ , and  $^{113}\text{Cd}$  NMR spectra were recorded at room temperature on a Varian Unity Plus 200 spectrometer using benzene- $d_6$  as the solvent; chemical shifts are given relative to  $\text{C}_6\text{D}_5\text{H}$  ( $\delta = 7.17$  ppm),  $\text{Et}_2\text{O}\cdot\text{BF}_3$ , and  $\text{Me}_2\text{Cd}$ , respectively.  $^{17}\text{O}$  NMR spectra were recorded on a Varian Unity Plus 500 using  $\text{CD}_3\text{NO}_2$  as an external standard ( $\delta = 590$  ppm). Multinuclear NMR ( $^{11}\text{B}$ ,  $^{17}\text{O}$ ,  $^{113}\text{Cd}$ ) data are collected in Table 1. Molecular weight determinations were performed cryoscopically in benzene. Diethylzinc (Aldrich) was used as received. Boron-containing reagents 9-(OH)-9-BBN,<sup>10</sup>  $\text{Et}_2\text{-BOH}$ ,<sup>11</sup>  $(9\text{-BBN})_2\text{O}$ ,<sup>12</sup>  $\text{Et}_4\text{B}_2\text{O}$ ,<sup>13</sup> dimethylcadmium,<sup>14</sup> and bis(*tert*-butyl)-zinc<sup>15</sup> have been prepared according to the literature descriptions. Solvents were dried with sodium- or potassium-benzophenone ketyl, distilled, and stored under argon. All reactions were carried out under argon atmosphere using the standard Schlenk techniques.

**Preparation of  $[(\mu^3\text{-9-BBN-9-O})\text{ZnEt}]_4$  (**1**) and  $[(\mu^3\text{-9-BBN-9-O})\text{-CdMe}]_4$  (**2**).** A stirred solution of  $(9\text{-BBN})_2\text{O}$  (2.92 g, 11.3 mmol) in toluene (25 mL) was treated with  $\text{Et}_2\text{Zn}$  (1.36 g, 11.1 mmol) in toluene (5 mL) at room temperature. Precipitation of a colorless crystalline solid was observed immediately. The suspension was warmed to dissolve a precipitate (ca. 90 °C). Slow cooling afforded well-formed colorless crystals of **1** (1.96 g, yield 76%), mp 206–210 °C dec. Anal. Calcd for  $\text{C}_{10}\text{H}_{19}\text{BOZn}$ : C, 51.89; H, 8.27. Found: C, 50.39; H, 8.14.  $^1\text{H}$  NMR:  $\delta$  1.97, 1.47, 1.29, 1.16 (9-BBN), 0.67 (q, 2H,  $\text{ZnCH}_2$ ) ppm.  $^{11}\text{B}$  NMR:  $\delta$  62.6 ppm.

The compound  $[(\mu^3\text{-9-BBN-9-O})\text{CdMe}]_4$  (**2**) was prepared similarly starting from  $(9\text{-BBN})_2\text{O}$  (1.69 g, 6.6 mmol) and  $\text{Me}_2\text{Cd}$  (1.32 g, 9.3 mmol), in toluene (15 mL). However, precipitation of the product was observed only after 30 min while the mixture was kept at room temperature. The yield of **2** was 1.24 g (72%), mp 230–235 °C dec. Anal. Calcd for  $\text{C}_9\text{H}_{17}\text{BCdO}$ : C, 40.88; H, 6.48. Found: C, 39.03; H,

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**Table 1.**  $^{11}\text{B}$ ,  $^{17}\text{O}$  and  $^{113}\text{Cd}$  NMR Chemical Shifts,  $\delta$ [Ppm], for 1-4.

	$\text{Et}_4\text{B}_2\text{O}$	$(9\text{-BBN})_2\text{O}$	1	2	3	4
$^{11}\text{B}$	52.8	58.0	62.6	60.7	60.2	58.4
$^{17}\text{O}$	223 <sup>a</sup>	207 <sup>a</sup>			135.9	154.5
$^{113}\text{Cd}$				-323		-327

<sup>a</sup> Reference 21.

6.17.  $^1\text{H}$  NMR:  $\delta$  1.91, 1.41, 1.22 (14H, 9-BBN), 0.16 (s, 3H, CdMe),  $^2J(^{111,113}\text{Cd}-^1\text{H}) = 86.9$  Hz ppm.  $^{11}\text{B}$  NMR:  $\delta$  60.7 ppm.  $^{113}\text{Cd}$  NMR:  $\delta$  -323 ppm.

**Preparation of  $[(\mu^3\text{-Et}_2\text{BO})\text{ZnEt}]_4$  (3).**  $\text{Et}_4\text{B}_2\text{O}$  (1.23 g, 8.0 mmol) was added dropwise to the stirred solution of  $\text{Et}_2\text{Zn}$  (1.01 g, 8.2 mmol) in toluene (5 mL) at 0 °C. The solution was stirred for 30 min at ambient temperature, and then volatiles were removed under reduced pressure. The product **3** was obtained as a white waxy solid in 1.41 g yield (98%).  $^1\text{H}$  NMR (200 MHz):  $\delta$  1.34 (t, 3H,  $\text{ZnCH}_2\text{CH}_3$ ), 1.03 (m, 10H,  $\text{BEt}_2$ ), 0.52 (q, 2H,  $\text{ZnCH}_2$ ) ppm.  $^{13}\text{C}$  NMR (50.24 MHz):  $\delta$  17.33 ( $\text{BCH}_2$ ), 12.40 ( $\text{ZnCH}_2\text{CH}_3$ ), 9.02 ( $\text{BCH}_2\text{CH}_3$ ), 2.91 ( $\text{ZnCH}_2$ ) ppm.  $^{11}\text{B}$  NMR:  $\delta$  60.2 ppm.  $^{17}\text{O}$  NMR:  $\delta$  135.9 ppm.

**Preparation of  $[(\mu^3\text{-Et}_2\text{BO})\text{CdMe}]_4$  (4).**  $\text{Et}_2\text{BOH}$  (0.84 g, 9.8 mmol) was added dropwise to the stirred solution of  $\text{Me}_2\text{Cd}$  (1.77 g, 12.5 mmol) in toluene (10 mL) at -20 °C. Methane evolution was observed during the addition. The solution was allowed to warm to room temperature and was stirred for a further 30 min to complete the reaction. Then volatiles were removed under reduced pressure. The product **4** was obtained as a colorless oil in 2.05 g yield (98%).  $^1\text{H}$  NMR (200 MHz):  $\delta$  1.07-0.91 (m, 10H,  $\text{BEt}_2$ ), -0.01 (s, 3H, CdMe),  $^2J(^{111,113}\text{Cd}-^1\text{H}) = 87.4$  Hz ppm.  $^{13}\text{C}$  NMR (50.28 MHz):  $\delta$  17.66 ( $\text{BCH}_2$ ), 9.08 ( $\text{BCH}_2\text{CH}_3$ ), -10.64 ( $\text{CdCH}_3$ ),  $^1J(^{111}\text{Cd}-^{13}\text{C}) = 1037.9$  Hz,  $^1J(^{113}\text{Cd}-^{13}\text{C}) = 1085.6$  Hz ppm.  $^{11}\text{B}$  NMR:  $\delta$  58.4 ppm.  $^{17}\text{O}$  NMR:  $\delta$  154.5 ppm.  $^{113}\text{Cd}$  NMR:  $\delta$  -327 ppm.

**Crystal structure determination of 1 and 2.** Single crystals of **1** and **2**, suitable for X-ray diffraction studies, were placed in a thin-walled capillary tube (Lindemann glass 0.5 mm) in an inert atmosphere. The tube was plugged with grease, then flame-sealed, and mounted on a goniometer head of a four-circle P3 (Siemens AG) diffractometer. The crystal class and the orientation matrix were obtained from the least-squares refinement of 30 reflections using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The intensities were corrected for Lorentz and polarization factors. An analytical absorption correction (Gaussian integration)<sup>16</sup> was applied on the basis of the crystal shape.

The structures were solved by direct methods using the SHELXS-86 program,<sup>17</sup> which revealed the positions of the metal (Zn or Cd), oxygen, boron, and several carbon atoms. Full-matrix least-squares refinement method against  $F^2$  values was carried out by using the SHELXL-97 program.<sup>18</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined with fixed geometry, riding on their carrier atoms, with a fixed isotropic displacement parameter. Difference Fourier maps, calculated during refinement, indicated disorder of two 9-BBN groups in structure **2**. Final results were obtained with a restraint model in which atoms of these groups were disordered over two sets of positions rotated around the B-O bond, with adjusted occupancy factors (the final SOF values were equal to 0.52(2) (residue 3) and 0.67(2) (residue 4) for major conformers). In the case of **1** all 9-BBN groups showed large thermal parameters and significant electron density features close to the carbon atoms, which implied some kind of disorder, but no satisfactory multisite model was derived. Owing to partial overlapping of the atoms of the disordered groups, geometrical restraints were introduced. Chemically equivalent B-C and C-C distances were assumed to be equal for two disordered 9-BBN groups in **2** and for all groups in **1**. The selected crystallographic data and the parameters of data collection

**Table 2.** Crystal Data and Structure Refinement for 1 and 2

	1	2
formula	$\text{C}_{10}\text{H}_{19}\text{BOZn}$	$\text{C}_9\text{H}_{17}\text{BOCd}$
formula weight	231.43	264.44
crystal system	monoclinic	triclinic
space group	$P2_1/c$	P1
<i>a</i> , Å	20.197(3)	10.5614(19)
<i>b</i> , Å	11.1513(19)	10.5994(18)
<i>c</i> , Å	20.479(3)	20.248(3)
$\alpha$ , deg	90.00	96.483(13)
$\beta$ , deg	95.045(13)	96.481(14)
$\gamma$ , deg	90.00	98.362(14)
<i>V</i> , Å <sup>3</sup>	4594.5(13)	2208.9(6)
<i>Z</i>	16	8
<i>F</i> (000)	1952	1056
<i>d</i> (calcd), g cm <sup>-3</sup>	1.338	1.590
temperature, K		293(2)
$\lambda$ , Å		0.71073
$\mu$ , mm <sup>-1</sup>	2.099	1.932
crystal size, mm	0.48 × 0.24 × 0.20	0.15 × 0.14 × 0.11
$\theta$ range, deg	2.00 to 25.00	2.04 to 25.07
index ranges	0 ≤ <i>h</i> ≤ 24 0 ≤ <i>k</i> ≤ 13 -24 ≤ <i>l</i> ≤ 24	0 ≤ <i>h</i> ≤ 12 -12 ≤ <i>k</i> ≤ 12 -24 ≤ <i>l</i> ≤ 23
no. of reflections collected	8324	7157
no. of independent reflections	8079 [ <i>R</i> (int) = 0.0286]	6739 [ <i>R</i> (int) = 0.0167]
no. of reflections obsd. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	4464	4685
no. of data/restraints /parameters	8079/ 104/472	6739/288/586
goodness-of-fit on $F^2$ <sup>a</sup>	1.014	1.154
<i>R</i> indices [ $F_o > 4\sigma(F_o)$ ] <sup>b</sup>	<i>R</i> 1 = 0.0739 <i>wR</i> 2 = 0.1888	<i>R</i> 1 = 0.0551 <i>wR</i> 2 = 0.1087
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1355 <i>wR</i> 2 = 0.2212	<i>R</i> 1 = 0.0869 <i>wR</i> 2 = 0.1213
largest diffraction peak and hole, e Å <sup>-3</sup>	0.795 and -0.522	0.508 and -0.460
weighting scheme <sup>c</sup>	0.1255, 0.0000	0.0443, 3.8326

<sup>a</sup> GOF =  $[\sum w(F_o^2 - F_c^2)^2 / (n - p)]^{1/2}$  (where *n* is the number of reflections and *p* is the number of refined parameters). <sup>b</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$ . <sup>c</sup>  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = (F_o^2 + 2F_c^2) / 3$ .

and refinement procedures are presented in Table 2. Selected bond distances and angles are given in Table 3.

## Results and Discussion

**Synthesis.** The reaction of diethylzinc with  $(9\text{-BBN})_2\text{O}$  proceeds smoothly at ambient temperature. The product  $[(\mu\text{-}9\text{-BBN-}9\text{-O})\text{ZnEt}]_4$  (**1**) was isolated from the toluene solution as a colorless crystalline material, whereas the formation of 9-Et-9-BBN was confirmed by the  $^{11}\text{B}$  NMR analysis of the reaction mixture. Thus, the selective cleavage of one zinc-carbon bond as well as one boron-oxygen bond was observed. This suggests a mechanism involving the initial formation of the  $(9\text{-BBN})_2\text{O} \cdot \text{ZnEt}_2$  complex, subsequent ethyl group transfer from zinc to boron, and stabilization of a monomeric species,  $(9\text{-BBN-}9\text{-O})\text{ZnEt}$ , through auto-association as shown in Scheme 1. The reaction of  $(9\text{-BBN})_2\text{O}$  with  $\text{Bu}'_2\text{Zn}$  does not proceed, which lends support to the above mechanism. The steric hindrance of *tert*-butyl groups apparently prevents the formation of the  $(9\text{-BBN})_2\text{O} \cdot \text{ZnBu}'_2$  complex.<sup>19</sup> We have also investigated the reaction of  $(9\text{-BBN})_2\text{O}$  with  $\text{Me}_2\text{Cd}$ . The crystalline compound  $[(\mu^3\text{-}9\text{-BBN-}9\text{-O})\text{CdMe}]_4$  was obtained in good yield. The formation of the byproduct 9-Me-9-BBN was established from the  $^{11}\text{B}$  NMR spectrum of the reaction mixture. Clearly, the mechanism of the reaction remains the same. However, the

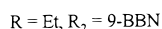
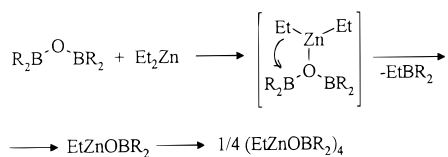
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(19) However, the compound  $[(\mu\text{-}9\text{-BBN-}9\text{-O})\text{ZnBu}'_4]$  was obtained when  $\text{Bu}'_2\text{Zn}$  was treated with 9-(OH)-9-BBN, but the structure could not be refined due to crystal decay.

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for **1** (Columns 1–4) and **2** (Columns 5–8)

Zn(1)–O(2)	2.094(5)	O(2)–Zn(1)–O(3)	83.7(2)	Cd(1)–O(3)	2.311(5)	O(3)–Cd(1)–O(2)	79.6(2)
Zn(1)–O(3)	2.097(5)	O(2)–Zn(1)–O(4)	85.1(2)	Cd(1)–O(2)	2.318(5)	O(3)–Cd(1)–O(1)	80.0(2)
Zn(1)–O(4)	2.143(5)	O(3)–Zn(1)–O(4)	82.1(2)	Cd(1)–O(1)	2.322(5)	O(2)–Cd(1)–O(1)	79.2(2)
Zn(2)–O(3)	2.082(5)	O(3)–Zn(2)–O(4)	83.6(2)	Cd(2)–O(2)	2.301(5)	O(2)–Cd(2)–O(4)	80.4(2)
Zn(2)–O(4)	2.096(5)	O(3)–Zn(2)–O(1)	85.0(2)	Cd(2)–O(4)	2.302(5)	O(2)–Cd(2)–O(1)	79.6(2)
Zn(2)–O(1)	2.136(5)	O(4)–Zn(2)–O(1)	82.0(2)	Cd(2)–O(1)	2.318(5)	O(4)–Cd(2)–O(1)	79.8(2)
Zn(3)–O(4)	2.091(5)	O(1)–Zn(3)–O(2)	81.9(2)	Cd(3)–O(3)	2.285(5)	O(3)–Cd(3)–O(4)	81.9(2)
Zn(3)–O(1)	2.110(5)	O(4)–Zn(3)–O(1)	82.7(2)	Cd(3)–O(4)	2.309(5)	O(3)–Cd(3)–O(2)	80.3(2)
Zn(3)–O(2)	2.126(5)	O(4)–Zn(3)–O(2)	85.6(2)	Cd(3)–O(2)	2.309(5)	O(4)–Cd(3)–O(2)	80.1(2)
Zn(4)–O(1)	2.075(5)	O(1)–Zn(4)–O(2)	83.0(2)	Cd(4)–O(4)	2.294(5)	O(4)–Cd(4)–O(3)	81.9(2)
Zn(4)–O(2)	2.114(5)	O(1)–Zn(4)–O(3)	84.8(2)	Cd(4)–O(3)	2.300(5)	O(4)–Cd(4)–O(1)	80.0(2)
Zn(4)–O(3)	2.149(5)	O(2)–Zn(4)–O(3)	82.0(2)	Cd(4)–O(1)	2.312(5)	O(3)–Cd(4)–O(1)	80.5(2)
Zn(1)–C(18)	1.94(1)	Zn(3)–O(1)–Zn(2)	96.6(2)	Cd(1)–C(18)	2.125(9)	Cd(4)–O(1)–Cd(2)	99.0(2)
Zn(2)–C(28)	1.95(1)	Zn(4)–O(1)–Zn(3)	98.2(2)	Cd(2)–C(28)	2.119(8)	Cd(4)–O(1)–Cd(1)	98.7(2)
Zn(3)–C(38)	1.95(1)	Zn(4)–O(1)–Zn(2)	94.5(2)	Cd(3)–C(38)	2.09(1)	Cd(2)–O(1)–Cd(1)	99.4(2)
Zn(4)–C(48)	1.93(1)	Zn(1)–O(2)–Zn(4)	97.5(2)	Cd(4)–C(48)	2.12(1)	Cd(2)–O(2)–Cd(3)	99.1(2)
O(1)–B(1)	1.36(1)	Zn(1)–O(2)–Zn(3)	93.9(2)	O(1)–B(1)	1.35(1)	Cd(2)–O(2)–Cd(1)	100.1(2)
O(2)–B(2)	1.35(1)	Zn(4)–O(2)–Zn(3)	96.5(2)	O(2)–B(2)	1.37(1)	Cd(3)–O(2)–Cd(1)	98.9(2)
O(3)–B(3)	1.40(1)	Zn(1)–O(3)–Zn(4)	96.4(2)	O(3)–B(3)	1.341(9)	Cd(3)–O(3)–Cd(4)	97.4(2)
O(4)–B(4)	1.37(1)	Zn(2)–O(3)–Zn(1)	97.9(2)	O(4)–B(4)	1.350(9)	Cd(3)–O(3)–Cd(1)	99.8(2)
		Zn(2)–O(3)–Zn(4)	93.9(2)			Cd(4)–O(3)–Cd(1)	99.3(2)
		Zn(3)–O(4)–Zn(2)	98.4(2)			Cd(4)–O(4)–Cd(2)	100.0(2)
		Zn(3)–O(4)–Zn(1)	93.5(2)			Cd(4)–O(4)–Cd(3)	96.9(2)
		Zn(2)–O(4)–Zn(1)	96.0(2)			Cd(2)–O(4)–Cd(3)	99.0(2)

**Scheme 1**

reaction is considerably slower in the case of dimethylcadmium. Presumably, this is due to the weaker Lewis acid properties of dimethylcadmium with respect to diethylzinc, which results in a weaker donor–acceptor interaction of the former with the oxygen atom of (9-BBN)<sub>2</sub>O.

In addition we have investigated reactions of tetraethylboroxane (Et<sub>4</sub>B<sub>2</sub>O) with zinc and cadmium alkyls. The compound [(Et<sub>2</sub>BO)ZnEt]<sub>4</sub> (**3**) was obtained from the reaction of Et<sub>4</sub>B<sub>2</sub>O with Et<sub>2</sub>Zn as a waxy white solid very soluble in hydrocarbons. The formation of the tetrameric associates of **3** was proved cryoscopically. No reaction was observed with Bu<sub>2</sub>Zn. Both results indicate that Et<sub>4</sub>B<sub>2</sub>O behaves similarly to (9-BBN)<sub>2</sub>O when treated with zinc alkyls; i.e., no substituent influence on the reactivity of the B–O–B linkage was found. When **3** was heated with Et<sub>4</sub>B<sub>2</sub>O in toluene at 100 °C, the reactants remained almost unchanged, and only traces of Et<sub>3</sub>B were detected in the reaction mixture. A difference in reactivity of the examined diboroxanes appeared when dimethylcadmium was used. Et<sub>4</sub>B<sub>2</sub>O does not cleave Me<sub>2</sub>Cd at ambient temperature. The heating of the reaction mixture at 70 °C to accelerate the desired reaction failed. The analysis of the mixture revealed the presence of triethylborane (Et<sub>3</sub>B) and triethylboroxin ((EtBO)<sub>3</sub>) as well as unchanged substrates. Tetraalkyldiboroxanes possessing open-chain alkyl rests readily undergo dismutation, e.g., in the presence of diborane (six) catalysts (R<sub>2</sub>BH)<sub>2</sub>,<sup>20</sup> or when heated with B<sub>2</sub>O<sub>3</sub> or even powdered glass.<sup>21</sup> The catalytic effect of Me<sub>2</sub>Cd is not clear enough. Presumably, dismutation is induced by free radicals which are generated

owing to the decomposition of dimethylcadmium during heating. The instability of Me<sub>2</sub>Cd at elevated temperature<sup>22</sup> lends support to this suggestion. The synthesis of [(μ<sup>3</sup>-Et<sub>2</sub>BO)CdMe]<sub>4</sub> (**4**) was accomplished using diethylborinic acid (Et<sub>2</sub>BOH). The reaction is rapid so that the methane evolution is complete at ambient temperature. It is also selective, and neither cleavage of the second cadmium–carbon bond nor boron alkylation is observed. Compound **4** is an oily, colorless liquid, highly soluble in hydrocarbons.

The difference in reactivity of Et<sub>4</sub>B<sub>2</sub>O and (9-BBN)<sub>2</sub>O revealed in reaction with dimethylcadmium can be explained in terms of different acid–base properties of the examined diboroxanes. (9-BBN)<sub>2</sub>O should be the stronger acid and/or base as this facilitates the formation of the four-center transition state and its conversion to the products. This is apparently due to the weaker π-bonding in (9-BBN)<sub>2</sub>O with respect to Et<sub>4</sub>B<sub>2</sub>O. Generally, diboroxanes are known as weaker bases with respect to ethers, which is due to pp(π) interaction, reducing charge density on the oxygen atom. This is well reflected by <sup>17</sup>O NMR chemical shifts showing strong deshielding of diboroxane oxygen versus ether oxygen.<sup>21</sup> The better shielding of the oxygen in (9-BBN)<sub>2</sub>O relative to Et<sub>4</sub>B<sub>2</sub>O (<sup>17</sup>O NMR: δ 207 and 223 ppm, respectively) suggests that the former is a stronger base. The stronger acidity of the boron in (9-BBN)<sub>2</sub>O with respect to Et<sub>4</sub>B<sub>2</sub>O arising from the ring strain is also reflected by its distinct deshielding (<sup>11</sup>B NMR: δ 58 and 52.8 ppm, respectively).

**Crystal Structures of 1 and 2.** The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are collected in Table 3. The general folding of the molecule is very similar for both compounds although they crystallize in different space groups, **1** in monoclinic *P*2<sub>1</sub>/*c* and **2** in triclinic *P*1̄. The main structural feature of **1** and **2** is the distorted M<sub>4</sub>O<sub>4</sub> heterocubane central core which can be well compared in a topological way with structural fragments observed in NaCl-like metal oxides ZnO (high-pressure form)<sup>23</sup> and CdO (monteponite).<sup>24</sup> Metal atoms possess highly distorted tetrahedral coordination and lie at the corners of a tetrahedron. The atom arrangement in **1** is very close to the structures observed for related tetrameric alkylzinc

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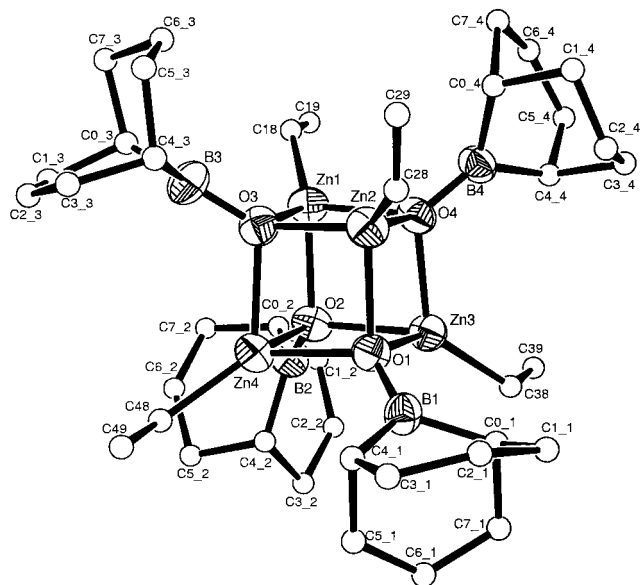
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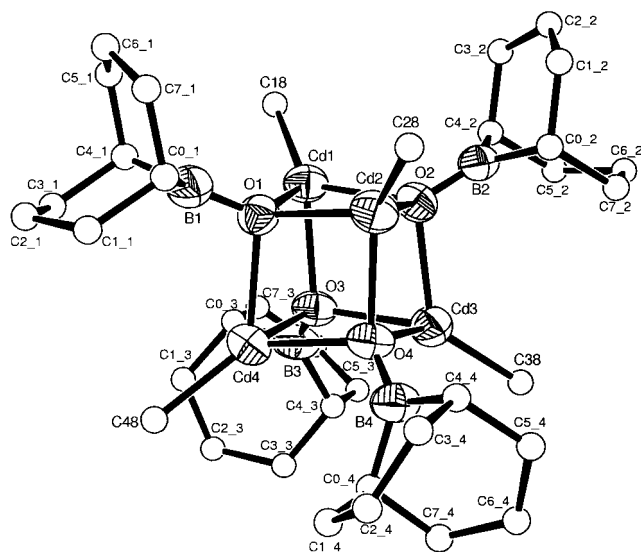
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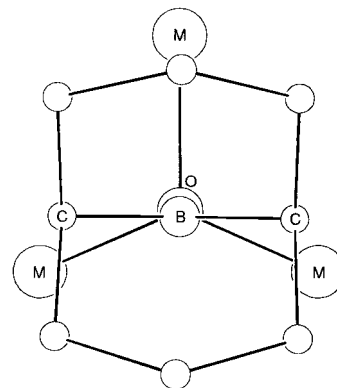


**Figure 1.** Ortep<sup>30</sup> plot of the molecular structure of **1**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms are shown only as balls, and hydrogen atoms are omitted for clarity.



**Figure 2.** Ortep<sup>30</sup> plot of the molecular structure of **2**. Thermal ellipsoids are drawn at the 50% probability level. Carbon atoms are shown only as balls, and hydrogen atoms are omitted for clarity.

alkoxides, e.g., [MeZnOMe]<sub>4</sub>,<sup>25</sup> [MeZnOBu]<sub>4</sub>,<sup>26</sup> and [Me<sub>3</sub>-SiCH<sub>2</sub>Zn(O-*i*-Ad)]<sub>4</sub>.<sup>27</sup> The entire molecule shows *S*<sub>4</sub> quasi-symmetry with a symmetry axis passing through the centers of two parallel cube faces, Zn(1)–O(2)–Zn(3)–O(4) and Zn(2)–O(3)–Zn(4)–O(1). The distortion of the Zn<sub>4</sub>O<sub>4</sub> heterocubane (the average Zn–O–Zn and O–Zn–O angles are 94° and 87°, respectively) can be described in terms of outward movements of zinc atoms along the *S*<sub>4</sub> axis. Nevertheless, the mentioned valence angles reveal that the atomic orbitals of zinc used in forming bonds to oxygen have mostly p character. The distortion leads to butterfly-like cube faces with two different sets of



**Figure 3.** Preferred orientation of the 9-BBN ligand toward the central M<sub>4</sub>O<sub>4</sub> core.

torsion angles Zn–O–O–Zn (four angles from 5.6(3)° to 6.2(3)° and two larger angles equal to 13.7(3)° and 13.8(3)°). The Zn···Zn distances range from 3.084(1) to 3.165(1) Å, with an average value of 3.137 Å, and are considerably greater than observed for methylzinc methoxide (3.086 Å) and zinc oxide (high-pressure form) (3.026 Å). The Zn–O distances varying from 2.075(5) to 2.149(5) Å (mean value 2.109 Å) are comparable with the distance of 2.140 Å observed in zinc oxide (high-pressure form). The three such bonds to each zinc atom show tendency for one to fall at the lower end of this range, one at the upper end, and one in the middle. The Zn–C distances are equal within experimental error and have a mean of 1.94 Å.

The central core of **2** corresponds well to the previously reported structure of [C<sub>6</sub>F<sub>5</sub>Cd(OH)]<sub>4</sub>,<sup>28</sup> but the entire molecule displays only approximate *C*<sub>2</sub> point group symmetry. The distortion of Cd<sub>4</sub>O<sub>4</sub> heterocubane can be characterized as outward movements of cadmium atoms along the cube space diagonals with torsion angles Cd–O–O–Cd varying from 10.7(2)° to 13.9(2)°. The average Cd···Cd contact of 3.507(1) Å is also greater than observed in CdO (monteponite) (3.320 Å). The Cd–O distances range from 2.285(5) to 2.322(5) Å (mean value 2.307 Å) and are only slightly shorter than for CdO (2.347 Å). The Cd–C distances may be regarded as the same with a mean of 2.11 Å, and they are typical.

The B–O bond distances in **1** range from 1.35(1) to 1.40(1) Å and in **2** from 1.341(9) to 1.37(1) Å. The mean B–O bond distances are equal within the experimental error to 1.37 Å for **1** and 1.35 Å for **2**. It is difficult to draw any conclusions from the small difference in the averaged values. However, the shortening of B–O bonds in **2** could be expected as this is consistent with the lower acidity of cadmium. The stronger ionic character of the Cd–O bond versus the Zn–O bond should lead to the stronger  $\pi$ -bonding between boron and oxygen. The notable shortening of the B–O distance of 1.31 Å observed in analogous tetrameric sodium compound [9-BBN-9-ONa(THF)]<sub>4</sub><sup>4</sup> lends support to this conclusion. Similarly, the stronger B–O bonds in **2** could also be reflected by the <sup>11</sup>B NMR chemical shifts of **1** and **2** as the boron atom in **2** is more shielded than that in **1**. Unfortunately, the actual difference in chemical shifts is only 1.9 ppm and cannot be meaningfully interpreted given the variety of factors that can affect chemical shifts. However, it should here be noted that the analogous trend was also found for related group 13 alkylmetal boryloxides.<sup>9</sup> Similarly, the very short B–O distance in [9-BBN-9-ONa(THF)]<sub>4</sub> corresponds to the strong shielding of the boron atom (<sup>11</sup>B NMR:  $\delta$  48 ppm). Borabicyclo[3.3.1]non-9-yl ligand orientation toward a central core is not random, and as shown in Figure 3 it has an affinity

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to put the  $C_2BO$  mean plane almost perpendicular with one of the BOM planes, which in the case of **1** comprises the longest Zn–O bond in a row. The preferred conformation is also revealed for disordered ligands in **2**.

As mentioned before, the  $pp(\pi)$  interaction results in a strong deshielding of the oxygen atom of the diboroxane. In **3** and **4** the oxygen is much more shielded due to its coordination number increasing from 2 to 4. On the other hand, the boron atom in compounds **1–4** is deshielded by 3–7 ppm in relation to the parent diboroxanes (Table 1). This could be expected as both lone pairs of oxygen donate to the metal atoms of the  $M_4O_4$  core. The structures **2** and **4** were also confirmed by  $^{113}Cd$  NMR spectroscopy. The spectra exhibit only one signal, and the  $^{113}Cd$  NMR chemical shifts as well as  $^2J(^{111,113}Cd-^1H)$  and  $^1J(^{113}Cd-^{13}C)$  coupling constant values point to the tetrahedral environment of the cadmium atom.<sup>29</sup>

In conclusion, it is well-known that most alkylzinc and alkylcadmium alkoxides have tetrameric structure, and our result demonstrates that there is no significant difference between quasi-alkoxide ligand  $R_2BO$  and typical alkoxide ligands. The

assumption that the  $pp(\pi)$  interaction between boron and oxygen may reduce  $\pi$ -donor properties of the latter, and as a result may decrease the tendency for auto-association, was not confirmed. However, the apparent influence of the boron atoms on the  $Zn_4O_4$  core in **1** should be noted. This influence, which could be described in terms of the  $p-\sigma$  interaction (hyperconjugation) between boron and oxygen, leads to the significant variation of Zn–O bond distances. It is expressed much more weakly for the cadmium analogue **2**, where it is presumably due to more ionic bonding within the  $Cd_4O_4$  core when compared to the  $Zn_4O_4$  core in **1**. However, the specific conformation of 9-BBN moieties toward the core in **2** is retained.

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**Supporting Information Available:** Listings of crystal and refinement data, atomic coordinates, bond distances and angles, anisotropic displacement parameters for all non-hydrogen atoms, and hydrogen atom coordinates with isotropic displacement parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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