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A New Decaoxidooctaborate(2−) Anion, $[B_8O_{10}(OH)_6]^{2-}$: Synthesis and Characterization of $[Co(en)_3][B_5O_6(OH)_4][B_8O_{10}(OH)_6)]\cdot 5H_2O$ (en = 1,2-Diaminoethane)

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Supporting Information

ABSTRACT: The synthesis and X-ray diffraction structure of $[Co(en)_3][B_5O_6(OH)_4][B_8O_{10}(OH)_6]\cdot 5H_2O$ (**1**) are reported. Compound **1** arises through a selective-templating process from a Dynamic Combinatorial Library of polyborate anions. Compound **1** contains two different polyborate species, with $[B_8O_{10}(OH)_6]^{2-}$ being particularly novel. It is comprised of fused tetraborate and pentaborate anions with a 4-coordinate B atom and a 3-coordinate O atom in common.

Polyborate salts are well-known for their diverse structural types[1] and for their bulk and specialized industrial applications.[2] Borate (more correctly named oxidoborate) anions may be classified as hydrated or anhydrous, with hydrated species bearing hydroxyl groups. Structurally oxidoborates present themselves as polymeric systems or discrete ("isolated") anions.[3,4] Structural motifs observed in "isolated" oxidoborate chemistry are limited to relatively few examples, e.g., $[B_3O_3(OH)_4]^-$,[5] $[B_4O_5(OH)_4]^{2-}$,[6] $[B_5O_6(OH)_4]^-$,[7] $[B_6O_7(OH)_4]^{2-}$,[8] $[B_7O_9(OH)_5]^{2-}$ (two isomers),[9,10] $[B_8O_{10}(OH)_6]^{2-}$,[11] $[B_9O_{12}(OH)_6]^{2-}$,[4,12] and $[B_{14}O_{20}(OH)_6]^{4-}$,[13] and new structural motifs are always of interest. Herein, we present the synthesis, from a Dynamic Combinatorial Library (DCL),[14] of aqueous oxidoborate anions,[15] and the structural characterization of a polyborate salt containing a novel decaoxidooctaborate(2−) dianion. This salt, $[Co(en)_3][B_5O_6(OH)_4][B_8O_{10}(OH)_6]\cdot 5H_2O$ (**1**), is of structural interest in that it contains two different isolated oxidoborate anions, with the larger of the two being previously unobserved. It also possesses several unique structural features.

Orange crystals, identified by X-ray diffraction (XRD) studies as **1**, were obtained in moderate (40%) yield from the addition of $B(OH)_3$ to a H_2O/MeOH solution of $[Co(en)_3][OH]_3$.[16] Compound **1** was characterized[16] by satisfactory elemental analysis data, spectroscopy (NMR, IR, and UV/vis), thermal measurements [thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)], and single-crystal XRD studies.[17] TGA reveals that **1** is decomposed to an orange glassy solid, with the obtained residual mass consistent with the formation of $CoB_{13}O_{21}$. The TGA trace indicates that it is a multistep process, which can be attributed to dehydration followed by oxidation. This was consistent with the DSC curve, which is consistent with previous observations on polyborate salts.[18]

An XRD study[17] of **1** revealed that it is an ionic salt of composition $[Co(en)_3][B_5O_6(OH)_4][B_8O_{10}(OH)_6].5H_2O$ comprised of discrete $[B_5O_6(OH)_4]^-$ and $[B_8O_{10}(OH)_6]^{2-}$ anions partnered with a $[Co(en)_3]^{3+}$ cation and five molecules of H_2O. Line drawings on the oxidoborate anions present in **1** are shown in Figure 1, and a "stick" diagram showing the ions/H_2O present in **1** is shown in Figure 2.

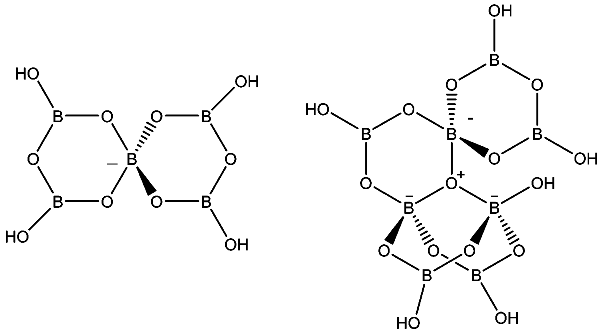

Figure 1. Schematic drawings of the pentaborate(1−) and octaborate(2−) anions observed in **1**.

The pentaborate(1−) anion is frequently observed in oxidoborate chemistry, but it has never been observed before cocrystallized with another polyborate anion. The observation of two different oxidoborates in one structure is very rare, with only one other known example, $[H_2en]_2[B_4O_5(OH)_4][B_7O_9(OH)_5]\cdot 3H_2O$, which contains both tetraborate(2−) and heptaborate(2−) anions.[19]

The octaborate anion $[B_8O_{10}(OH)_6]^{2-}$ observed in **1** is unique and possesses several interesting structural features, which are discussed in more detail below. An isomeric anion of this stoichiometry[11] has previously been observed in $[H_3N(CH_2)_7NH_3][B_8O_{10}(OH)_6]\cdot 2B(OH)_3$ (**2**). The isomeric octaborate anions in **1** and **2** may be considered to be derived from condensation reactions of different smaller oxidoborate anions. Thus, **2** may be considered to be consist with a simple condensation product of $[B_5O_6(OH)_4]^-$/$[B_3O_3(OH)_4]^-$ anions, whereas **1** may be considered as arising from condensation of

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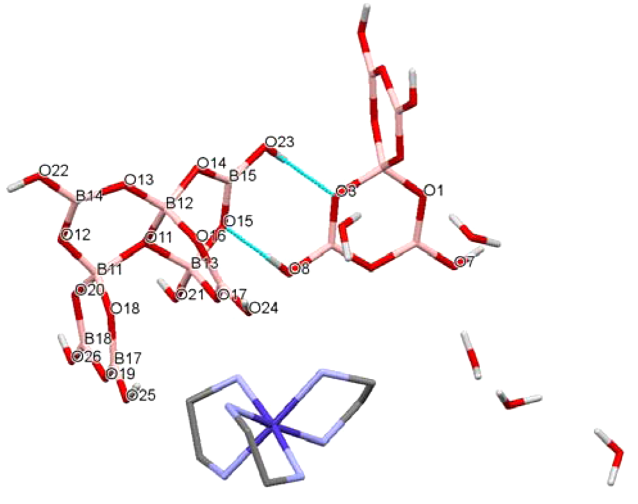

Figure 2. XRD "stick" view of ions present in **1**. The numbering scheme for atoms present in the $[B_8O_{10}(OH)_6]^{2-}$ anion is shown, together with selected other atoms. One $R_2^2(8)$ reciprocal hydrogen-bonding interaction is shown (O23H−O*3/O*8H−O15). H atoms on the cation are removed for clarity.

$[B_5O_6(OH)_4]^-$ with an unknown linear triborate, $[(HO)_2BOB(OH)_2OB(OH)_2]^-$. Alternatively, the anion in **1** can be viewed as a "fusion" of $[B_4O_5(OH)_4]^{2-}/[B_5O_6(OH)_4]^-$ anions with two O atoms and one B atom in common (Figure 3). The anion contains four boroxole (B_3O_3) rings. One O atom, with the formal positive charge (O11), is a constituent of three of the boroxole rings. O atoms with formal positive charges have been previously observed in hexaborate anions, e.g., $Mg[B_6O_7(OH)_6]\cdot 5H_2O$,[8] and heptaborate anions, e.g., $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5]\cdot H_2O$.[10]

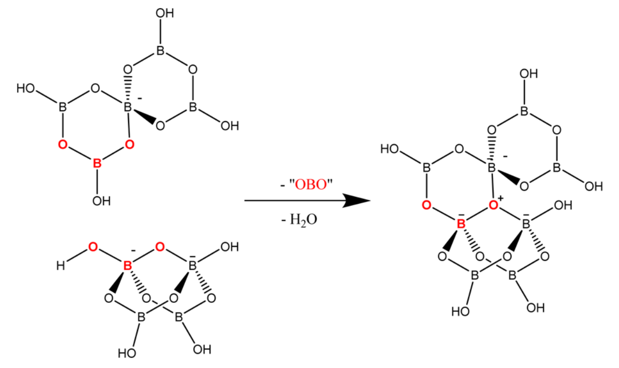

Figure 3. Decaoxidooctaborate(2−) anion structurally formally composed of fused pentaoxidotetraborate(2−) and hexaoxidopentaborate(1−) anions with two O and one B atoms in common.

Selected bond lengths and bond angles for the new decaoxidooctaborate(2−) anion (Figure 3), as found in **1**, are given in Table 1. The anion is comprised of three 4-coordinate B (sp^3) centers, five 3-coordinate B (sp^2) centers, 10 bridging O atoms, and six *exo*-OH groups. As expected, B−O bond lengths to 4-coordinate B atoms [1.423(3)−1.565(3) Å] are significantly longer than those to 3-coordinate B centers [1.344(4)−1.398(4) Å].[20] O11, with a formal positive charge, is bound to all three 4-coordinate B centers and has the three longest B−O bonds in the anion (av. 1.554 Å). Coordination about O11 is pyramidal, with a distance of 0.357 Å perpendicular to the plane containing B11, B12, and B13 and with a sum of its BOB angles of 344.54°. This deviation from planarity is greater than that previously observed in $[H_3N(CH_2)_7NH_3][B_7O_9(OH)_5]\cdot H_2O$, $[\mathit{cyclo}\text{-}C_6H_{11}NH_3]_2[B_7O_9(OH)_5]\cdot 3H_2O.B(OH)_3$, and $[\mathit{cyclo}\text{-}C_7H_{13}NH_3]_2[B_7O_9(OH)_5)]\cdot 2H_2O\cdot 2B(OH)_3$.[10] As a consequence of the pyramidal O11, the octaborate anion in **1** is chiral, but the solid-state structure is racemic because the octaborate anions are arranged as centrosymmetric (enantiomeric) pairs in the crystalline lattice. The OBO angles at 3-coordinate B centers are appropriate for sp^2 B atoms [116.6(2)−122.5(3)°], and likewise OBO angles at 4-coordinate B centers [105.34(19)−112.3(2)°] are appropriate for sp^3-hybridized B atoms.[20] The largest deviations occur for B18 and B13, respectively. BOB angles at ring O atoms (excluding O11) range from 118.6(2) to 124.1(2)°, with O15 being the highest and furthest away from 120°. Bond lengths and angles for the pentaborate(1−) anion found in **1** are available in the Supporting Information (SI), are consistent with previously reported data,[7,18,21] and are not discussed further here.

Table 1. Selected Bond Lengths (Å) and Angles (deg) Found in the Octaborate(2−) Anion in 1

B11−O11	1.554(3)	B12−O11−B11	115.79(19)
B12−O11	1.543(3)	B12−O11−B13	108.60(18)
B13−O21	1.423(3)	B11−O11−B13	120.15(19)
B13−O17	1.453(3)	B15−O14−B12	118.6(2)
B13−O15	1.475(3)		
B13−O11	1.565(3)	B18−O20	1.369(4)
B18−O26	1.344(4)	B18−O19	1.398(4)

There are many hydrogen-bonding interactions to be found in the solid-state structure of **1**. These include cation/anion, anion/anion, H_2O/anion, and H_2O/H_2O hydrogen bonds. There are 16 potential hydrogen-bond-acceptor sites on the $[B_8O_{10}(OH)_6]^{2-}$ anion, and all, with the exception of O13 and O26, are acceptors.

One motif that is commonly observed in polyborate structures has the Etter[22] description $R_2^2(8)$. There are six hydrogen-bond-donor sites in the octaborate anion in **1**, and these are all involved in $R_2^2(8)$ interactions: two link with pentaborate acceptors (O22H−O*1/O*7H−O12 and O23H−O3/O8H−O15) and four link with octaborate acceptors (O21H−O*20/O*26H−O11 and O24H−O*18/O*25H−O16). One of these interactions is shown in Figure 2.

O11, the formally 3-coordinate O atom, effectively becomes 4-coordinate in **1** because it accepts a hydrogen bond from O*26H. This interaction is approximately linear (173.2°), with $d(D\cdots A)$ and $d(H\cdots A)$ distances of 2.853(3) and 2.02 Å, respectively. The $R_2^2(8)$ interaction involving O11 is unusual in that the heavy (BO) $R_2^2(8)$ atoms are nonplanar (half-chair) with the 3-coordinate O center (O11) out of the plane by 0.98 Å. As a further consequence of these hydrogen-bonding interactions, there is a short (non-hydrogen-bond) O20⋯O*21 distance of 2.823 Å. These structural aspects have not been observed in polyborates before.

The amino groups of the coordinated 1,2-diaminoethane are also hydrogen-bond donors to the polyborate anions. Hydrogen-bonding interaction details are in the SI. It is believed that these interactions are important in the formation of this unusual templated polyborate compound.

In summary, compound **1** is a novel compound showing two different isolated polyborate anions, with the larger octaborate(2−) being previously unobserved. It is formed, as a consequence of favorable solid-state energetics, as a crystalline material from aqueous solution, where the $[Co(en)_3]^{3+}$ cation templates its formation from the DCL of the oxidoborate anions present. The cation's high charge, high steric volume, and ability to form hydrogen bonds all play important roles in this structure-directing selective reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CCDC 1034719 containing supplementary X-ray crystallographic data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org. These data can also be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge CB2 1EZ, U.K. [fax (+44) 1223-336-033 or e-mail deposit@ccdc.cam.ac.uk].

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Notes

The authors declare no competing financial interest.

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(16) $[Co(en)_3]Cl_3\cdot 2H_2O$ (1.01g, 2.66 mmol) was added to an aqueous (50 mL) suspension of excess activated Dowex 550A anion-exchange resin and stirred for 24 h. The resin was separated (solution kept) and washed with H_2O (4 × 5 mL). The aqueous solution containing $[Co(en)_3][OH]_3$ was reduced in volume to ~15 mL and MeOH (15 mL added), followed by $B(OH)_3$ (2.46 g, 39.9 mmol). The reaction mixture was gently warmed for 3 h, and then the solvent was reduced to 5 mL. The concentrated solution was left to crystallize (40 day), and **1** (0.97 g, 41%) was obtained as orange crystals, which were suitable for XRD studies. Elem. anal. Calcd for **1** ($C_6H_{44}B_{13}CoN_6O_{31}$): C, 8.0; H, 5.0; N, 9.4. Found: C, 8.2; H, 5.0; N, 9.6. ^{1}H NMR (400 MHz, D_2O): δ 2.73 (12H, m). ^{13}C NMR (101 MHz, D_2O): δ 44.55. ^{11}B NMR (128 M Hz, D_2O): δ 13.4, 16.5. IR (ν_{max}/cm^{-1}): 3461, 3265, 3149, 1611, 1394, 1324, 1170, 1059, 1033, 939, 863, 811, 779, 711. TGA: 100−180 °C loss 9.7% (10.0% calcd for five H_2O molecules of crystallization), at 800 °C residue 60.0% (59.76% calcd for $CoB_{13}O_{21}$).

(17) Crystallographic data for **1**: A suitable crystal was selected, and data were collected following a standard method[23] on a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum rotating-anode generator with HF Varimax optics (100 μm focus). T = 100(2) K; λ = 0.71075 Å. Cell determination and data collection, data reduction, cell refinement and absorption correction,[24] structure solution,[25] and refinement.[26] Data: $C_6H_{44}B_{13}CoN_6O_{31}$, M = 895.93, triclinic, space group $P\bar{1}$, a = 11.2993(8) Å, α = 88.272(4)°, b = 11.5139(8) Å, β = 76.220(4)°, c = 13.7574(10) Å, γ = 88.984(4)°, V = 1737.4(2) Å^3, Z = 2, 27217 reflections measured, 7900 independent [R_{int} = 0.0491], final R indices [$F^2 > 2\sigma(F^2)$], R1 = 0.0463, wR2 = 0.1182, R indices (all data), R1 = 0.0645, wR2 = 0.1280.

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