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Two New Borates Containing the First Examples of Large Isolated Polyborate Anions: Chain $[B_7O_9(OH)_5]^{2-}$ and Ring $[B_{14}O_{20}(OH)_6]^{4-}$

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Two novel hydrated borates were synthesized under mild solvothermal conditions. One is hydrated rubidium borate, $Rb_2B_7O_9(OH)_5$, which contains the first example of the isolated chain heptaborate anion, $[B_7O_9(OH)_5]^{2-}$. The other is hydrated diethylenetriamine borate, $[(C_4H_{15}N_3)]_2[B_{14}O_{20}(OH)_6]$, which contains the first example of the largest isolated ring tetradecaborate anion, $[B_{14}O_{20}(OH)_6]^{4-}$.

Borate compounds have considerable mineralogical and industrial importance.[1,2] They exist as polyborate anions composed of BO_3 planar triangle (Δ) and BO_4 tetrahedron (T) groups. These BO_3 and BO_4 groups may combine via common oxygen atoms to form isolated rings and cages or polymerize into infinite chains, sheets, and networks. Many examples of isolated polyborate anions containing one to six borons exist in mineral and synthetic borates, such as metaborates $[B(OH)_4]^-$, diborates $[B_2O(OH)_6]^{2-}$, triborates $[B_3O_3(OH)_4]^-$, tetraborates $[B_4O_5(OH)_4]^{2-}$, pentaborates $[B_5O_6(OH)_4]^-$, and hexaborates $[B_6O_7(OH)_6]^{2-}$.[1,3] However, isolated boron oxoanions having more than 6 borons are rare, and no previous examples have 7 or 14 borons.[1] Schubert et al. reported two nonaborates, $[C(NH_2)_3]_3[B_9O_{12}(OH)_6]$ and $[C_3H_5N_2]_3[B_9O_{12}(OH)_6]$, which contain the first examples of the isolated nonaborate anion, $[B_9O_{12}(OH)_6]^{3-}$.[4] It was reported that the mineral ammonioborate contains an unusual example of a large isolated anion, $[B_{15}O_{20}(OH)_8]^{3-}$,[5] but it has not be prepared in a laboratory to date. This Communication describes the synthesis and crystal structures of two new borates, hydrated rubidium borate $Rb_2B_7O_9(OH)_5$ (**I**), containing the first example of the isolated chain heptaborate anion of $[B_7O_9(OH)_5]^{2-}$, and hydrated diethylenetriamine borate of $[(C_4H_{15}N_3)]_2[B_{14}O_{20}(OH)_6]$ (**II**), containing the first example of the large isolated ring tetradecaborate anion of $[B_{14}O_{20}(OH)_6]^{4-}$.

Heptaborate **I** was synthesized by the reaction of H_3BO_3 with Rb_2CO_3 with a B/Cs molar ratio of 3 under mild solvothermal conditions:[6]

$$7H_3BO_3 + Rb_2CO_3 \xrightarrow{170\ °C} Rb_2B_7O_9(OH)_5\ (\mathbf{I}) + 8H_2O + CO_2\uparrow \quad (1)$$

Tetradecaborate **II** can be prepared by the reaction of H_3BO_3 with $C_4H_{13}N_3$ (diethylenetriamine) under mild solvothermal conditions:[7]

$$14H_3BO_3 + 2C_4H_{13}N_3 \xrightarrow{170\ °C} [(C_4H_{15}N_3)]_2[B_{14}O_{20}(OH)_6]\ (\mathbf{II}) + 16H_2O \quad (2)$$

The main absorption bands of Fourier transform infrared spectra are assigned:[8] in **I**, 3441 and 3385 cm^{-1} (OH), 1430 and 922 cm^{-1} (BO_3), and 1109 and 810 cm^{-1} (BO_4); in **II**, 3401 cm^{-1} (OH, NH_2), 1627 cm^{-1} (NH_2), 1384 and 945 cm^{-1} (BO_3), and 1062 and 818 cm^{-1} (BO_4).

The solid-state ^{11}B MAS NMR spectral data with chemical shifts (recorded on a Bruker Avance-300 spectrometer with

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(6) All reagents used in the synthesis were analytical grade. A mixture of 0.462 g of Rb_2CO_3, 0.748 g of H_3BO_3, 5.0 mL of $C_4H_{13}N_3$, 3.0 mL of pyridine (C_5H_5N), and 1.0 mL of H_2O was sealed in a Teflon-lined stainless steel autoclave, heated at 170 °C for 7 days, and then cooled to room temperature. The resulting colorless transparent crystals **I** were recovered by filtration, washed by cold deionized water, and dried in a vacuum dryer to a constant mass at room temperature (48.6% yield based on H_3BO_3).
(7) A mixture of 4.43 g of H_3BO_3, 2.0 mL of $C_4H_{13}N_3$, 2.0 mL of tetraethylenepentamine ($C_8H_{23}N_5$), 5.0 mL of pyridine, and 0.1 mL of H_2O was sealed in a Teflon-lined stainless steel autoclave, heated at 170 °C for 7 days, and then cooled to room temperature. The resulting solid powders were collected and washed thoroughly with absolute alcohol. The mixture of 0.94 g of obtained solid powders, 1.02 g of H_3BO_3, 5.0 mL of pyridine, and 0.1 mL of H_2O was sealed in a Teflon-lined stainless steel autoclave again, heated at 150 °C for 7 days, and then cooled to room temperature. The resulting colorless transparent crystals **II** were recovered by filtration, washed by absolute alcohol, and dried in a vacuum dryer to a constant mass at room temperature (31.4% yield based on $C_4H_{13}N_3$). Anal. Calcd: C, 12.25%; H, 4.59%; N, 10.72%. Found: C, 12.22%; H, 4.54%; N, 10.44%.
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10.1021/ic051580+ CCC: $33.50

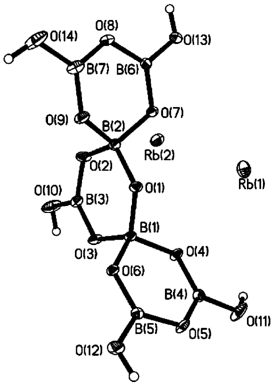

Figure 1. Structure of **I**, drawn at the 50% probability level.

a spinning speed of 10 kHz and $NaBH_4$ as the internal standard): 51.4, 75.8, 84.1, and 93.0 ppm for **I** and 56.4, 72.8, 83.0, and 90.0 ppm for **II**. These observations are consistent with the fact that each of the two borates has four kinds of different coordinated environments of boron atoms.

The simultaneous thermogravimetric analysis−differential thermal analysis (TGA−DTA) curves of **I** (carried out under a N_2 atmosphere) indicate that there is a weight loss of 9.58% between 200 and 750 °C, which corresponds to the loss of five hydroxyl groups (calcd 9.46%). In the DTA curve, the endothermic peaks at 296.2 and 689.9 °C are related to the dehydration and melting of the solid phase. The simultaneous TGA−DTA curves of **II** (carried out under an air atmosphere) show that it has a weight loss of 37.83% between 150 and 950 °C, which corresponds to the loss of six hydroxyl groups and the organics, and can be compared with the calculated value of 37.82%. This explanation is conformed by the DTA curve. The endothermic peak appearing at 303.8 °C is related to the dehydration of the hydroxyl groups, and the exothermic peak appearing at 401.2 °C is due to the oxygenolysis of organics.

Single-crystal X-ray structures of **I** and **II** are shown in Figures 1 and 2.[9] The crystal structure of **I** incorporates isolated $[B_7O_9(OH)_5]^{2-}$ polyborate anions and two rubidium ions (Figure 1). The new $[B_7O_9(OH)_5]^{2-}$ heptaborate anion consists of three six-membered rings in which five trigonal $BO_2(OH)$ [B3, B4, B5, B6, and B7] units and two tetrahedral BO_4 [B1 and B2] units are linked by common oxygen atoms. The three six-membered rings are linked through their vertexes [B1 and B2] to form chain heptaborate anion $[B_7O_9(OH)_5]^{2-}$. In the triangular borons, the B−O bonds vary from 1.333 to 1.395 Å and the mean B−O distance is 1.362 Å. In the tetrahedral borons, the B−O bonds vary from 1.420 to 1.500 Å and the mean B−O distance is 1.476 Å. The $[B_7O_9(OH)_5]^{2-}$ groups are also connected to one another through O−H···O hydrogen bonds, forming a three-dimensional framework with channels along the *a* and *b* axes, in which the Rb^+ cations are located. There are eight and nine oxygen atoms around the rubidium ions (Figure 3). Rb1 is close to two oxygen atoms [O12A and O13A] from $BO_2(OH)$ and six oxygen atoms [O1, O1A, O4, O6A, O7, and O9A] from the B−O−B bridge. Rb2 is close to four oxygen atoms [O11A, O12A, O14A, and O14B] from $BO_2(OH)$ and five oxygen atoms [O2, O5A, O6B, O7, and O8A] from the B−O−B bridge. Obviously, O7 and O12A are the two bridging oxygen atoms between Rb1 and Rb2.

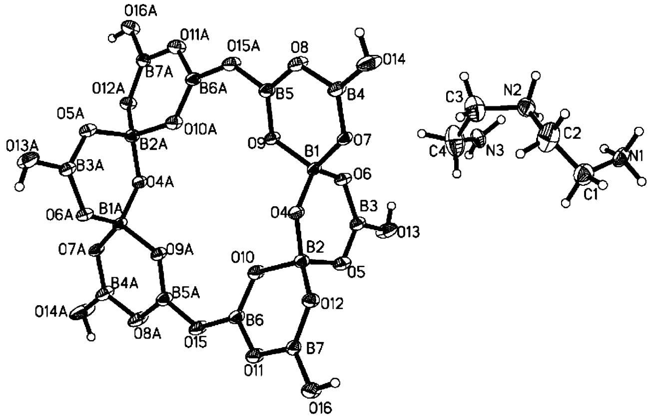

Figure 2. Asymmetric unit structure of **II**, drawn at the 50% probability level.

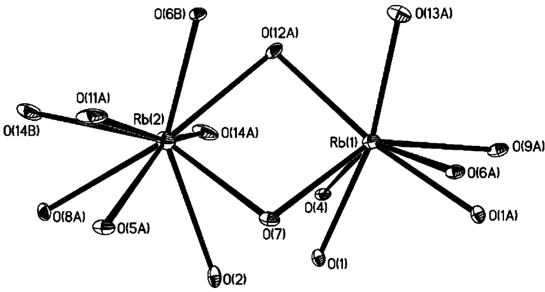

Figure 3. Coordination environments of Rb atoms in **I**.

The crystal structure of **II** consists of a large isolated $[B_{14}O_{20}(OH)_6]^{4-}$ polyborate anion and $[C_4N_3H_{15}]^{2+}$ cations (Figure 2). The $[B_{14}O_{20}(OH)_6]^{4-}$ group, a large 16-membered ring consisting of eight boron atoms and eight oxygen atoms with internal dimensions of 7.424 × 5.685 Å could be considered as two $[B_7O_{10}(OH)_3]$ clusters linked by two common oxygen atoms [O15 and O15A]. Each of the $[B_7O_{10}(OH)_3]$ clusters consists of the three six-membered rings in which two trigonal BO_3 [B5 and B6] units, three trigonal $BO_2(OH)$ [B3, B4, and B7] units, and two tetrahedral BO_4 [B1 and B2] units are linked by vertical oxygen atoms. In the triangular borons, the B−O bonds vary from 1.323 to 1.390 Å and the mean B−O distance is 1.356 Å. In the tetrahedral borons, the B−O bonds vary from 1.431 to 1.499 Å and the mean B−O distance is 1.466 Å. The $[B_{14}O_{20}(OH)_6]^{4-}$ groups are held together through a O−H···O hydrogen-bond system, forming a three-dimensional structure with the larger channels along the *b* axis, between which

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(9) All data for the crystals were collected on a Bruker Smart-1000 CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Crystal data (298 K) for **I** (CSD No. 415591): $H_5B_7Rb_2O_{14}$, $M_r = 475.65$, monoclinic, $P2_1/n$, $a = 8.047(3)$ Å, $b = 11.785(3)$ Å, $c = 13.952(4)$ Å, $\beta = 102.974(4)°$, $V = 1289.4(6)$ Å^3, $Z = 4$, GOF on $F^2 = 1.006$, final R indices [$I > 2\sigma(I)$], R1 = 0.0350, wR2 = 0.0778. Crystal data (298 K) for **II** (CCDC No. 277579): $C_8H_{36}B_{14}N_6O_{26}$, $M_r = 783.77$, monoclinic, $P2_1/n$, $a = 9.435(6)$ Å, $b = 8.752(6)$ Å, $c = 19.599(12)$ Å, $\beta = 92.263(11)°$, $V = 1617.1(18)$ Å^3, $Z = 2$, GOF on $F^2 = 1.045$, final R indices [$I > 2\sigma(I)$], R1 = 0.0604, wR2 = 0.1301.

the $[C_4N_3H_{15}]^{2+}$ cations are intercalated and interact with the $[B_{14}O_{20}(OH)_6]^{4-}$ anions by the N$-$H$\cdots$O hydrogen bonds.

The structures of $[B_{14}O_{20}(OH)_6]^{4-}$ and $[B_7O_9(OH)_5]^{2-}$ have certain similarities, as shown in Figures 1 and 2. The $[B_{14}O_{20}(OH)_6]^{4-}$ anion could be regarded as being composed of two $[B_7O_9(OH)_5]^{2-}$ units through the dehydration of four hydroxyl groups ($-$O13H and $-$O11H). According to the classification of polyborate anions proposed by Heller[10] and Christ and Clark,[11] the shorthand notation for $[B_7O_9(OH)_5]^{2-}$ is 7:5Δ+2T, isolated, and that for $[B_{14}O_{20}(OH)_6]^{4-}$ is 14: 10Δ+4T, isolated. Two new groups are isolated forms because all of the terminal hydroxyls prevent them from spreading further connections.[12] To our knowledge, $[B_{14}O_{20}(OH)_6]^{4-}$ is the largest isolated ring polyborate anion synthesized in a laboratory. Although a few even larger polyborate anions, such as $[B_{20}O_{33}(OH)_4]^{10-}$,[13] $[UO_2\{B_{16}O_{24}(OH)_8\}]^{6-}$,[14] and $[Mn_4(C_2O_4)(V_{10}B_{28}O_{74}H_8)]^{10-}$,[15] were discovered previously, none of them are isolated boron oxoanions.

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Supporting Information Available: Crystallographic files in CIF format and views of the packing structures for compounds **I** and **II**. This material is available free of charge via the Internet at http://pubs.acs.org.

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