Dodecahydroxy-*closo*-dodecaborate(2−)

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Abstract: The cesium salt of the icosahedral borane anion dodecahydroxy-*closo*-dodecaborate(2−), Cs_2[*closo*-$B_{12}(OH)_{12}$], Cs_2**1**, was prepared by heating cesium dodecahydro-*closo*-dodecaborate(2−), Cs_2[*closo*-$B_{12}H_{12}$], Cs_2**2**, with 30% hydrogen peroxide. The other alkali metal salts A_2**1** (A = Li, Na, K, Rb) precipitated upon addition of ACl to warm aqueous solutions of Cs_2**1**. The ammonium salt, $[NH_4]_2$**1**, and the (μ-nitrido)bis(triphenylphosphonium) salt, $[PPN]_2$**1**, were obtained similarly. The $[H_3O]_2$**1** salt precipitated upon acidification of aqueous solutions of Cs_2**1** with hydrochloric acid. The solubility of these salts in water was determined by measuring the boron content of saturated aqueous solutions of A_2**1** (A = Li, Na, K, Rb, Cs), $[H_3O]_2$**1**, and $[NH_4]_2$**1** using ICP-AES. Although these salts are derived from a dianion with twelve pendant hydroxyl groups, the alkali metal salts surprisingly displayed low water solubilities. Water solubility decreases with a decrease in the radius of A^+, except for the lithium salt, which is slightly more soluble than the potassium salt. The $[H_3O]_2$**1** and the $[NH_4]_2$**1** salts provide rare examples of water-insoluble hydronium and ammonium salts. The low water solubility of the A_2**1** salts is attributed to the dianion's pendant hydroxyl groups, which appear to function as cross-linking ligands. Four alkali metal salts, A_2**1** (A = Na, K, Rb, Cs), were characterized in the solid state by single-crystal X-ray crystallography. These data revealed intricate networks in which several anions are complexed through their hydroxyl groups to each alkali metal cation. In addition, the anions are engaged in hydrogen bonding with each other and, if present, with water of hydration. This cross-linking results in the precipitation of aggregated salts. Cation coordination numbers decrease with cation radius. Thus, cesium and rubidium are ten-coordinate, whereas potassium is seven-coordinate and sodium is six-coordinate. The geometry of anion $\mathbf{1}^{2-}$ is independent of cation identity; the B−B and B−O bond lengths of the various A_2**1** salts (A = Na, K, Rb, Cs) are identical.

The remarkable chemical, physical, and stereochemical properties of the *closo* polyhedral borane dianions and carboranes have drawn attention to these species as precursors of a new and rapidly expanding field of chemistry enriched with novel applications. Interest in these cage species is derived, in part, from the use of their polyhedral structures as molecular scaffolds stabilized by extensive electron delocalization. The essentially spherical structures of the icosahedral borane cluster modules may be used to orient exopolyhedral organic or inorganic substituents located on the cluster surface singly, in groups, or by total substitution of all available B−H and C−H vertices. The prototypical example of the latter type is provided by the perhalogenated [*closo*-$B_{12}X_{12}]^{2-}$ anions (X = Cl, Br, I).[1] Similar structures with hydrophobic substituents are represented by [*closo*-$B_{12}(CH_3)_{12}]^{2-}$,[2] {[*closo*-$B_{12}(CH_3)_{12}]^{\cdot}\}^{-}$,[3] [*closo*-$CB_{11}(CH_3)_{12}]^{-}$,[4] [*closo*-$CB_{11}(CH_3)_{12}]^{\cdot}$,[5] and *closo*-1,12-$(CH)_2B_{10}(CH_3)_{12}$.[6] Recently, we communicated the hydrophilically substituted family of icosahedral (car)borane clusters [*closo*-$(CH)_nB_{12-n}(OH)_{12-n}]^{n-2}$, ($n$ = 0−2),[7] and here we report the syntheses, structures, and solubility properties of simple alkali metal salts of [*closo*-$B_{12}(OH)_{12}]^{2-}$, A_2**1** (A = Li, Na, K, Rb, Cs), as well as $[H_3O]_2$**1**, $[NH_4]_2$**1**, and $[PPN]_2$**1**. The stepwise and easily controlled acid-catalyzed hydroxylation of [*closo*-$B_{12}H_{12}]^{2-}$, $\mathbf{2}^{2-}$, to produce mono- through tetrahydroxy derivatives has been described elsewhere.[8]

Persubstituted borane clusters of all types have potential applications as hydrophobic space-filling pharmacophores,[9] weakly coordinating anions,[10] components of radioimaging[11] or drug delivery systems, and as targets for boron neutron capture therapy.[12] The potential utility of the $\mathbf{1}^{2-}$ anion derives from its reactive pseudospherical surface to which 12 independent chains may be simultaneously attached, providing a route to a wide array of derivatives.

Experimental Section

Caution! On the scale and under the conditions described here no explosions have occurred during the synthesis of Cs_2[*closo*-$B_{12}(OH)_{12}$]. *Nevertheless, this does not preclude such an event when dealing with polyhedral boranes and hydrogen peroxide. Departure from the*

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[1] (a) Knoth, W. H.; Miller, H. C.; Sauer, J. C.; Balthis, J. H.; Chia, Y. T.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 159. (b) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; M. Dekker: New York, 1968; pp 104−168.

[2] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1999**, *121*, 5601.

[3] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Chem. Commun.* **1999**, 2039.

[4] King, B. T.; Janousek, Z.; Grüner, B.; Trammell, M.; Noll, B. C.; Michl, J. *J. Am. Chem. Soc.* **1996**, *118*, 3313.

[5] King, B. T.; Noll, B. C.; McKinley, A. J.; Michl, J. *J. Am. Chem. Soc*. **1996**, *118*, 10902.

[6] Jiang, W.; Knobler, C. B.; Mortimer, M. D.; Hawthorne, M. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1332.

[7] Peymann, T.; Herzog, A.; Knobler, C. B.; Hawthorne, M. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1062.

[8] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **2000**, *39*, 1163.

[9] Friedmann, S. H.; DeCamp, D. L.; Sijbesma, R. P.; Srdanov, G.; Wudl, F.; Kenyon, G. L. *J. Am. Chem. Soc.* **1993**, *115*, 6506.

[10] Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 133.

[11] Hawthorne, M. F.; Maderna, A. *Chem. Rev.* **2000**, *100*, 1165.

[12] Soloway, A. H.; Tjarks, W.; Barnum, B. A.; Rong, F. G.; Barth, R. F.; Codogni, I. M.; Wilson, J. G. *Chem. Rev.* **1998**, *98*, 2389.

10.1021/ja0014887 CCC: $20.00

published procedures is not recommended, and extreme precautions should always be taken to ensure the identity and purity of all reagents and the use of adequate shielding to contain possible explosions.

General Procedures. $Cs_2[closo\text{-}B_{12}H_{12}]$[13,14] and $Cs_2[closo\text{-}B_{12}H_{11}CO_2H]$[15] were obtained as gifts from DuPont. The ^{11}B NMR spectra were obtained with a Bruker AM-500 spectrometer at 160 MHz and were externally referenced to $BF_3{\cdot}Et_2O$; peaks upfield of the reference are designated as negative. Electrospray ionization mass spectra (ESI-MS) were recorded by injecting an aqueous sample solution into an ionspray source with the mass spectrometer operating in the negative-ion mode. Boron analyses were performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at the INEEL (Idaho National Engineering and Environmental Labortaory, Idaho Falls, ID).

The yields reported below were calculated, presuming anhydrous salts. The precise degree of hydration for the alkali metal salts could be expected to be highly variable and sensitive to the conditions of isolation or recrystallization. Since the primary concern was the structural determination of a series of salts, no attempt was made to determine the degree of hydration of the bulk isolated materials, and the crystal structures may not reflect the composition of the isolated salts.

$Cs_2[closo\text{-}B_{12}(OH)_{12}]$, $Cs_2$1, from $Cs_2[closo\text{-}B_{12}H_{12}]$. A suspension of $Cs_2[closo\text{-}B_{12}H_{12}]$ (1.00 g, 2.50 mmol) in 40 mL of 30% hydrogen peroxide was heated at the reflux temperature for 3 days. The resulting solution was cooled overnight in a refrigerator to precipitate crude Cs_2**1**, which was recrystallized from water. The product was collected by filtration and dried to yield pure Cs_2**1** (0.97 g, 65%) as a white powder. ^{11}B NMR (H_2O): $\delta = -17.1$ ppm (s); IR (KBr): 3370 (s, v br), 1190 (s), 1127 (s), 714 (m) cm^{-1}; ESI-MS: *m/z*: 335.1 $[H\mathbf{1}]^-$.

$Cs_2[closo\text{-}B_{12}(OH)_{12}]$, $Cs_2$1, from $Cs_2[closo\text{-}B_{12}H_{11}CO_2H]$. A suspension of $Cs_2[closo\text{-}B_{12}H_{11}CO_2H]{\cdot}H_2O$ (1.07 g, 2.27 mmol) in 40 mL of 30% hydrogen peroxide was heated at the reflux temperature for 3 days. The resulting solution was cooled overnight in a refrigerator to precipitate crude Cs_2**1**, which was recrystallized from water. The product was collected by filtration and dried to yield pure Cs_2**1** (0.94 g, 70%) as a white powder. ^{11}B NMR (H_2O): $\delta = -17.1$ ppm (s); ESI-MS: *m/z*: 335.1 $[H\mathbf{1}]^-$.

$[H_3O]_2[closo\text{-}B_{12}(OH)_{12}]$, $[H_3O]_2$1. An aqueous solution of Cs_2**1** (200 mg, 0.33 mmol) was acidified with 37.5% hydrochloric acid. A colorless precipitate formed immediately and was then collected by filtration and washed with water to yield 80 mg (0.22 mmol, 64%) of $[H_3O]_2$**1**.

$Li_2[closo\text{-}B_{12}(OH)_{12}]$, $Li_2$1. Lithium chloride (142 mg, 3.34 mmol) was added to an aqueous solution of Cs_2**1** (200 mg, 0.33 mmol). A colorless precipitate formed immediately and was then collected by filtration and washed with water to yield 99 mg (0.28 mmol, 85%) of Li_2**1**.

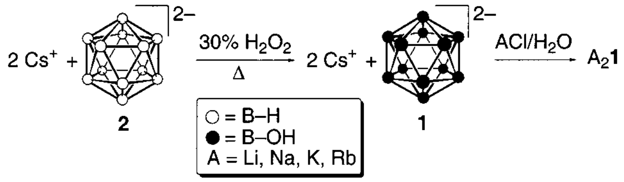
$Na_2[closo\text{-}B_{12}(OH)_{12}]$, $Na_2$1. Sodium chloride (195 mg, 3.34 mmol) was added to an aqueous solution of Cs_2**1** (200 mg, 0.33 mmol). A colorless precipitate formed immediately and was then collected by filtration and washed with water to yield 100 mg (0.26 mmol, 79%) of Na_2**1**.

$K_2[closo\text{-}B_{12}(OH)_{12}]$, $K_2$1. Potassium chloride (249 mg, 3.34 mmol) was added to an aqueous solution of Cs_2**1** (200 mg, 0.33 mmol). A colorless precipitate formed immediately and was then collected by filtration and washed with water to yield 110 mg (0.27 mmol, 81%) of K_2**1**.

$Rb_2[closo\text{-}B_{12}(OH)_{12}]$, $Rb_2$1. Rubidium chloride (404 mg, 3.34 mmol) was added to an aqueous solution of Cs_2**1** (200 mg, 0.33 mmol). The solution was refrigerated overnight at 4 °C, and the precipitated solid was collected by filtration and recrystallized from water to yield 100 mg (0.20 mmol, 60%) of Rb_2**1**.

$[PPN]_2[closo\text{-}B_{12}(OH)_{12}]$, $[PPN]_2$1. A solution of Cs_2**1** (400 mg, 0.66 mmol) in 20 mL of hot water was added to a solution of (μ-nitrido)-bis(triphenylphosphonium) chloride (766 mg, 1.33 mmol) in 20 mL of boiling water. After standing overnight at room temperature, the solid was collected by filtration and recrystallized from water. The product was dissolved in acetone and filtered. The filtrate was evaporated and dried to yield 580 mg (0.41 mmol, 63%) of $[PPN]_2$**1**.

Scheme 1



$[NH_4]_2[closo\text{-}B_{12}(OH)_{12}]$, $[NH_4]_2$1. Ammonium chloride (177 mg, 3.34 mmol) was added to an aqueous solution of Cs_2**1** (200 mg, 0.33 mmol). A colorless precipitate formed immediately and was then collected by filtration and washed with water to yield 120 mg (0.32 mmol, 97%) of $[NH_4]_2$**1**.

Determination of Aqueous Solubility. A small amount (about 20 mg) of A_2**1** (A = Li, Na, K, Rb, Cs), $[H_3O]_2$**1**, or $[NH_4]_2$**1** was suspended in water and placed in a bath sonicator for 1 h. The suspension was kept at 25 °C for 24 h and then filtered through a 0.2 μm syringe filter. The filtrate was analyzed by ICP-AES for both its boron and alkali metal content.

Results

The $[closo\text{-}B_{12}(OH)_{12}]^{2-}$ dianion ($\mathbf{1}^{2-}$) was obtained in good yield as its cesium salt simply by heating Cs_2**2** in excess 30% hydrogen peroxide at the reflux temperature (Scheme 1). The progress of the reaction could be monitored by ^{11}B NMR, with completion indicated by the collapse of the relatively complex spectra due to partially substituted species to a clean singlet at −17.1 ppm, indicative of the icosahedral symmetry of the product. Exhaustive substitution of the ion was further confirmed with IR spectroscopy (by the absence of any B−H absorption near 2500 cm^{-1}), ESI-MS ($m/z = 335.1$ for $[H\mathbf{1}]^-$), and X-ray crystallography (vide infra). Attempts to obtain informative ^1H NMR spectra for the hydroxyl groups of $\mathbf{1}^{2-}$ were unsuccessful at room temperature due to rapid proton exchange. An increase in intensity and occasional broadening of the residual water peak from the solvent were observed for hydrated salts. However, even when the spectrum was obtained under anhydrous conditions (as in the examination of $[Bu_4N]_2$**1** in dry distilled CD_3CN), the only signals detected were those for the cation, indicating that intramolecular proton exchange was sufficiently fast to render the hydroxyl hydrogen atoms unobservable.

The same product $\mathbf{1}^{2-}$ was also obtained from the reaction of the monocarboxylato derivative[15] $[closo\text{-}B_{12}H_{11}CO_2H]^{2-}$ and hydrogen peroxide. During the course of this reaction the carboxyl group was replaced by a hydroxyl group, presumably through loss of CO_2 from an intermediate peroxo acid, $[closo\text{-}B_{12}H_{11-n}(OH)_nCO_3H]^{2-}$ ($n = 0-11$), accompanied by the formation of a B−OH vertex (eq 1−4).

$$B_{12}H_{11-n}(OH)_n(CO_2H) \rightleftharpoons B_{12}H_{11-n}(OH)_n(CO)^- + OH^- \quad (1)$$

$$OH^- + H_2O_2 \rightleftharpoons H_2O + OOH^- \quad (2)$$

$$B_{12}H_{11-n}(OH)_n(CO)^- + OOH^- \rightleftharpoons B_{12}H_{11-n}(OH)_n(CO_3H)^{2-} \quad (3)$$

$$B_{12}H_{11-n}(OH)_n(CO_3H)^{2-} \rightarrow B_{12}H_{11-n}(OH)_{n+1}{}^{2-} + CO_2 \quad (4)$$

Other monosubstituted derivatives such as $[closo\text{-}B_{12}H_{11}C_6H_5]^{2-}$[16]

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[13] Pitochelli, A. R.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 3228.

[14] Miller, H. C.; Miller, N. E.; Muetterties, E. L. *Inorg. Chem.* **1964**, *3*, 1456.

[15] Knoth, W. H.; Sauer, J. C.; Balthis, J. H.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 4842.

[16] Peymann, T.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1998**, *37*, 1544.

Table 1. Water Solubility of Salts of $\mathbf{1}^{2-}$ at 25 °C

cation	μg B/ml	μg $\mathbf{1}^{2-}$/ml	[$\mathbf{1}^{2-}$], M
Li^+	390	1000	3.0×10^{-3}
Na^+	92	240	7.2×10^{-4}
K^+	360	930	2.8×10^{-3}
Rb^+	690	1800	5.4×10^{-3}
Cs^+	1000	2600	7.8×10^{-3}
NH_4^+	110	280	8.4×10^{-4}
H_3O^+	24	62	1.9×10^{-4}

Table 2. Crystallographic Data for the Alkali Metal Salts $A_2\mathbf{1}$

	$Na_2\mathbf{1}\cdot 4H_2O$	$K_2\mathbf{1}$	$Rb_2\mathbf{1}\cdot 2H_2O$	$Cs_2\mathbf{1}\cdot 2H_2O$
formula	$H_{20}B_{12}Na_2O_{16}$	$H_{12}B_{12}K_2O_{12}$	$H_{16}B_{12}O_{14}Rb_2$	$H_{16}B_{12}Cs_2O_{14}$
fw	451.86	412.02	540.79	635.66
crystal system	triclinic	monoclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$P2_1/a$
a (Å)	8.55(1)	7.168(6)	13.398(8)	13.135(9)
b (Å)	8.66(1)	10.240(9)	9.186(5)	7.342(6)
c (Å)	12.16(2)	8.969(8)	13.333(8)	8.304(6)
α (deg)	69.55(2)			
β (deg)	80.13(2)	93.69(2)	106.42(1)	97.39(2)
γ (deg)	75.67(2)			
V (Å^3)	815	657	1574	794
Z	2	2	4	4
d (g cm^{-3})	1.84	2.08	2.28	2.66
μ (cm^{-1})	2.1	7.8	63	364
R^a	0.071	0.030	0.034	0.045
$R_w{}^b$	0.172	0.057	0.093	0.124

[a] $R = \Sigma||F_o| - |F_c||/|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|^2)]^{1/2}$.

and [*closo*-$B_{12}H_{11}I]^{2-}$ [1] were degraded to boric acid when heated with 30% hydrogen peroxide at the reflux temperature.

The $Cs_2\mathbf{1}$ salt was purified by recrystallization from water. Upon addition of the alkali metal chlorides ACl (A = Li, Na, K, Rb) to warm aqueous solutions of $Cs_2\mathbf{1}$, the respective salts, $A_2\mathbf{1}$, precipitated in high yields. The hydronium and ammonium salts were precipitated by the addition of hydrochloric acid and ammonium chloride, respectively. The low water solubility of all these $\mathbf{1}^{2-}$ salts was surprising, since few alkali metal, hydronium, or ammonium salts are sparingly soluble in water. On the contrary, one would have expected the alkali metal salts of a dianion with 12 pendant hydroxyl groups to be very water soluble. In general, the larger the alkali metal cation, A^+, the lower the water solubility of a given salt.[17] The opposite phenomenon was observed for the $A_2\mathbf{1}$ salts, as their water solubility decreased with the radius of A^+ (Table 1). Thus, the cesium salt was the most water soluble, and the sodium salt was the least water soluble of the group 1 salts of $\mathbf{1}^{2-}$. Only the solubility of the lithium salt deviated markedly from this trend; it was more soluble than either the sodium or the potassium salt. The water solubility of the ammonium salt lay between that of the sodium and the potassium salts, and the hydronium ion salt was the least soluble of all $\mathbf{1}^{2-}$ salts investigated having inorganic cations. Salts of anion $\mathbf{1}^{2-}$ with organic cations, such as tetramethylammonium or methyltriphenylphosphonium, could not be obtained through metathesis because the cesium salt is less water soluble than the respective organic cation salt. Nevertheless, the $[PPN]_2\mathbf{1}$ salt, which is soluble in polar organic solvents such as acetone, acetonitrile, or DMSO, precipitated upon addition of [PPN]Cl to aqueous solutions of $Cs_2\mathbf{1}$. The tetrabutylammonium salt of **1**, which may be obtained through ion exchange, was also soluble in polar organic solvents.

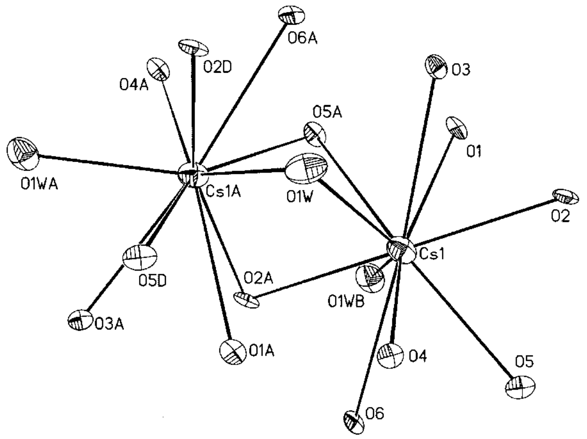

Figure 1. Coordination environment of the ten-coordinate cesium cation in $Cs_2\mathbf{1}$; thermal ellipsoids at 50% probability.

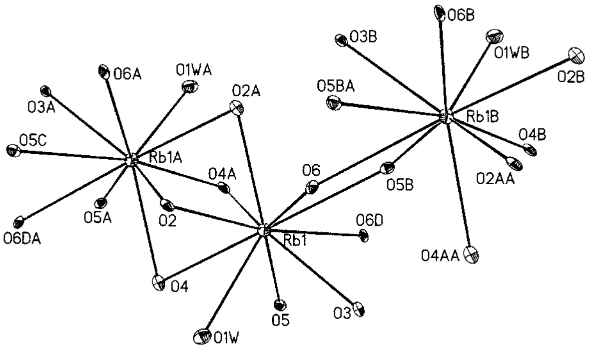

Figure 2. Coordination environment of the ten-coordinate rubidium cation in $Rb_2\mathbf{1}$; thermal ellipsoids at 50% probability.

Crystallography. Table 2 summarizes the crystallographic data pertaining to the salts, $A_2\mathbf{1}$. The $Cs_2\mathbf{1}$ salt crystallized from water as a dihydrate in the monoclinic space group $P2_1/a$. The centrosymmetric anion's B−O bond lengths range from 1.433(8) to 1.459(8) Å and the B−B distances range from 1.78(1) to 1.81(1) Å. Ten oxygen atoms surround the cesium cation (Figure 1), two from water and eight from the hydroxyl groups, with the Cs−O distances in the range of 3.067(4)−3.523(4) Å. Two of the oxygen atoms from the anion [O(2), O(5)] and one oxygen atom from water bridge two cesium cations. Three other oxygen atoms [O(2A), O(5A), O(1W)] related by an inversion center form bridges to another cesium cation; thus, all cesium cations are linked in a polymeric structure via oxygen atoms. All of the other hydroxyl groups of anion $\mathbf{1}^{2-}$ complex to only one cesium center. The Cs−Cs separation of 3.9685(9) Å, which is about twice the ionic radius (1.95 Å) of a ten-coordinate cesium ion, is unusually short.[17] The O−Cs−O angles traverse the broad range of 46.1(1)−173.8(1)°. All hydroxyl hydrogen atoms are hydrogen-bonded to other hydroxyl or water oxygen atoms with OH- -O distances spanning a range of 1.87−2.19 Å.

The $Rb_2\mathbf{1}$ salt crystallized from water as a dihydrate in the monoclinic space group $C2/c$. The anion lies on a two-fold axis. The bond lengths of the rubidium salt [B−O = 1.435(4)−1.452(4) Å; B−B = 1.776(4)−1.806(4) Å] are identical to those observed in the cesium salt. Ten oxygen atoms, one from water and nine from the hydroxyl ligands of the polyhedral borate cage, surround the rubidium cation (Figure 2). The Rb−O distances range from 2.894(2) to 3.285(2) Å. Four of the oxygen atoms [O(2), O(4), O(5), O(6)] of anion $\mathbf{1}^{2-}$ bridge two rubidium cations. Four other oxygen atoms [O(2A), O(4A), O(5A), O(6A)] are symmetry-related by a two-fold axis and form bridges to a second rubidium cation; thus, all rubidium ions are linked in a polymeric structure via oxygen atoms. The Rb−O distance of the atom O(3), which is complexed to only one rubidium cation, is the shortest [2.894(2) Å]. The atom O(1) is

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(17) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1999.

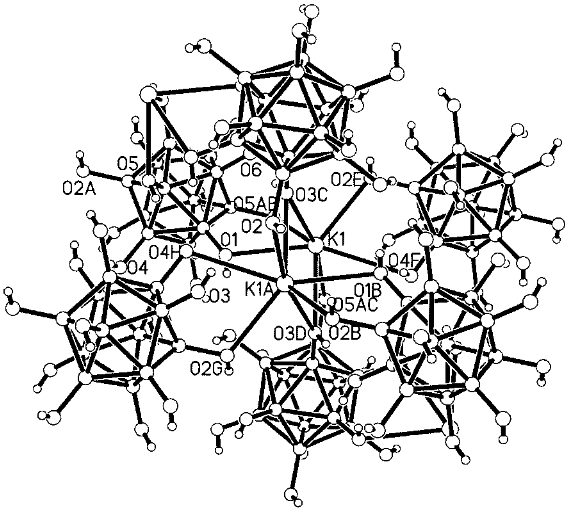

Figure 3. Crystal packing of $\mathrm{K_2}\mathbf{1}$.

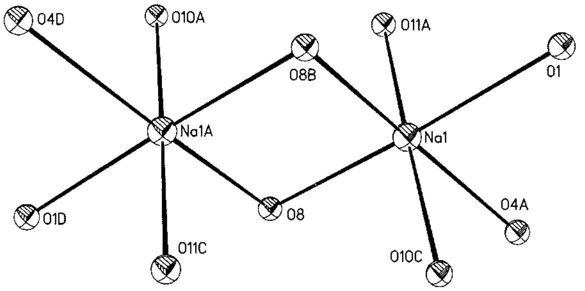

Figure 4. Coordination environment of the six-coordinate sodium cation in $\mathrm{Na_2}\mathbf{1}$; thermal ellipsoids at 50% probability.

associated with the only hydroxyl group not complexed to a rubidium cation. The unusually short Rb−Rb distance of 3.627(1) Å is about twice the ionic radius (1.80 Å) of a ten-coordinate rubidium cation.[17] The O−Rb−O angles lie in the range of 50.3(1)−171.6(1)°. The hydrogen atoms in the crystal form hydrogen bonds with OH- -O distances from 1.79 to 2.30 Å.

Unlike the salts of its other congeners, the $\mathrm{K_2}\mathbf{1}$ salt crystallized from water without incorporating solvent in the monoclinic space group $P2_1/n$. The centrosymmetric anion's geometry [B−O = 1.429(3)−1.453(3) Å; B−B = 1.775(3)−1.802(4) Å] is identical to that observed in the rubidium and cesium salts. The potassium cation in $\mathrm{K_2}\mathbf{1}$ has a lower coordination number than either the rubidium or cesium cations; seven oxygen atoms of the polyhedral borate ligand surround it (Figure 3). The K−O distances range from 2.666(2) to 3.056(3) Å. Two symmetry-related oxygen atoms [O(3C), O(3D)] of anion $\mathbf{1}^{2-}$ bridge two potassium cations; thus, all potassium cations are linked in a polymeric structure via oxygen atoms. The atom O(6) belongs to the only hydroxyl group not complexed to a potassium cation. The shortest K−K distance is 3.543(3) Å, which is noticeably more than twice the ionic radius (1.65 Å) of an eight-coordinate potassium cation.[17] The O−K−O angles are in the range of 67.47(5)−167.45(5)°. The hydrogen bond lengths (OH- -O) cover the range of 2.01−2.24 Å.

The $\mathrm{Na_2}\mathbf{1}$ salt crystallizes from water as a tetrahydrate in the triclinic space group $P\bar{1}$. The geometry of the rotationally disordered anion $\mathbf{1}^{2-}$ [B−O = 1.439(8)−1.468(8) Å; B−B = 1.775(9)−1.815(1) Å] is identical to the structures of the other alkali salts. The six-coordinate sodium cation (Figure 4) is surrounded octahedrally by oxygen atoms of the polyhedral borate ligand. The Na−O distances range from 2.357(5) to 2.460(5) Å. Two symmetry-related oxygen atoms [O(8A), O(8B)] of anion $\mathbf{1}^{2-}$ bridge two sodium cations. The Na−Na distances of 3.233(3) Å and 3.256(3) Å are distinctly more than twice the ionic radius (1.16 Å) of a six-coordinate sodium.[17] The O−Na−O angles vary from 39.2(7) to 179.4(2)° and the hydrogen bond distances (OH- -O) are on the order of 1.65−2.39 Å.

Water Solubilities. All group 1 salts of the perhydroxylated anion $\mathbf{1}^{2-}$ display low water solubility, which decreases with the cation radius. The only exception is the lithium salt; its solubility lies between that of the potassium and the rubidium salts. To our knowledge, species $\mathbf{1}^{2-}$ is the only anion known to date that forms water-insoluble salts with each alkali metal cation. Apparently, the hydration enthalpy of the ions is insufficient to compensate for the high lattice energy of the densely packed salts (exemplified in Figure 3 for the potassium salt). As the crystal structures reveal, all salts displayed an intricate polymeric network of hydrogen bonding and cation-bridging hydroxyl ligands. The smaller cations may provide a better fit for the coordinating anion and thus have a higher lattice energy. The lithium salt does not follow the general solubility trend of the alkali metal salts, because this cation has the highest hydration energy of all alkali metal cations,[17] which partially compensates for the loss of lattice energy upon solvation.

Conclusions

The perhydroxylated species dodecahydroxy-*closo*-dodecaborate(2−), $\mathbf{1}^{2-}$, may be obtained via the reaction of hydrogen peroxide with dodecahydro-*closo*-dodecaborate(2−), $\mathbf{2}^{2-}$, or the [*closo*-$\mathrm{B_{12}H_{11}CO_2H}$]$^{2-}$ ion. Potentially, the $\mathbf{1}^{2-}$ anion is a versatile synthon as its 12 hydroxyl functions should allow substitution chemistry to proceed on the spherical surface of the icosahedral borane cage. The versatility of the B−OH vertices as nucleophiles has already been demonstrated in the reactions of the lower hydroxylated derivatives [*closo*-$\mathrm{B_{12}H_{12-\mathit{n}}(OH)_\mathit{n}}$]$^{2-}$ (n = 1−3) with electrophiles.[8,18] Furthermore, the anion $\mathbf{1}^{2-}$ provides the only series of alkali metal salts known to date that exhibits low water solubility. The solid-state structures reveal that this property is due to the cross-linking achieved by the complexation of the hydroxyl ligands to the cation in addition to the hydrogen-bonding network of the anions. The higher solubility of the lithium salt deviates from the general trend that is observed for the other $\mathrm{A_2}\mathbf{1}$ salts. This anomalous behavior of the smallest cation is explained by its much higher hydration enthalpy. The compounds $\mathrm{[H_3O]_2}\mathbf{1}$ and $\mathrm{[NH_4]_2}\mathbf{1}$ are rare examples of water-insoluble hydronium and ammonium ion salts of an inorganic anion. Their insolubilities must result from extensive hydrogen bonding of their cations with the B−OH vertices leading to aggregation.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for the salts $\mathrm{Na_2}\mathbf{1}$, $\mathrm{K_2}\mathbf{1}$, $\mathrm{Rb_2}\mathbf{1}$, and $\mathrm{Cs_2}\mathbf{1}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Peymann, T.; Lork, E.; Gabel, D. *Inorg. Chem.* **1996**, *35*, 1355.