Inorganic Chemistry

Article

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Synthesis and Structural Characterization of an Unprecedented Nonmetal Cation Polyborate Salt Containing Two Different “Isolated” Polyborate Anions: $[H_2en]_2[B_4O_5(OH)_4][B_7O_9(OH)_5]\cdot 3H_2O$ (en = $H_2NCH_2CH_2NH_2$)

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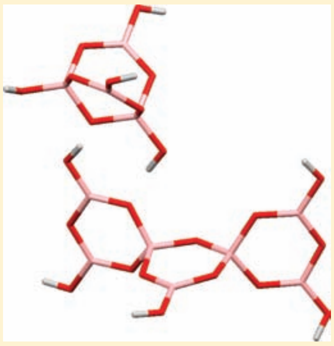
Supporting Information

ABSTRACT: The nonmetal cation polyborate salt of stoichiometry $[H_2en]_2[B_{11}O_{18}(OH)]\cdot 7H_2O$ is obtained from the reaction of 1,2-diaminoethane and boric acid (1:5 ratio) in H_2O/MeOH. An X-ray crystallographic study of the product reveals that the polyborate moiety is composed of two isolated hydrated polyborate anions: $[B_4O_5(OH)_4]^{2-}$ and $[B_7O_9(OH)_5]^{2-}$. The structure is templated by the cations with the anions forming a supramolecular H-bonded network, augmented by additional H-bonds involving the waters of crystallization and the cations.



INTRODUCTION

Most borate containing minerals (and many synthetic borate salts) contain metal cations.[1−3] The nonmetal cation (NMC) $[NH_4]^+$ has been found associated with minerals,[4,5] and in synthetic polyborate salts.[6,7] Synthetic NMC salts containing hydrated polyborate anions are enjoying a recent resurgence in interest because of their diverse intrinsic structural properties[8] and their potential applications in nonlinear optics.[7,9,10] Polyborate anions are classified as “isolated” or “condensed”, with condensed polyborates possessing infinite structural lattices arising (at least theoretically) through elimination of water from integral “isolated” polyborate moieties.[1,8] The isolated polyborate anions which have been structurally characterized to date as their NMC salts are limited in our knowledge to the following:[4,11−17] $[B_3O_3(OH)_4]^-$, $[B_4O_5(OH)_4]^-$, $[B_5O_6(OH)_4]^-$, $[B_7O_9(OH)_5]^{2-}$ (2 isomers), $[B_8O_{10}(OH)_6]^{2-}$, $[B_9O_{12}(OH)_6]^{3-}$, $[B_{14}O_{20}(OH)_6]^{4-}$, and $[B_{15}O_{20}(OH)_8]^{3-}$. Additionally, isolated polyborate anions have been found partnered with metal cations[18] and cationic metal−ligand complexes.[19−22] We have been investigating the structural properties of NMC templated polyborate salts and their thermal properties, and have recently reported a number of salts containing isolated $[B_5O_6(OH)_4]^-$ anions.[23−25] This study focuses on the nonmetal dication derived from 1,2-diaminoethane (en) which results in the formation of a NMC polyborate salt with unprecedented structural features.

RESULTS AND DISCUSSION

The reaction of 1,2-diaminoethane (en) with boric acid in aqueous solution, afforded an air stable colorless crystalline solid as a NMC templated polyborate of stoichiometry, $[H_2en]_2[B_{11}O_{18}(OH)]\cdot 7H_2O$ (**1**). A crystallographic study revealed that the polyborate did not contain an undecaborate anion but rather was composed of two previously observed isolated species: $[B_4O_5(OH)_4]^{2-}$ and $[B_7O_9(OH)_5]^{2-}$. A number of NMC pentaborate salts have previously been isolated with interstitial moieties[23,26−28] such as py, 4Me-py, H_2O, and $B(OH)_3$, but two isolated polyborate anions within one structure is unprecedented and represents a new structural motif in polyborate chemistry.

Compound **1** is an ionic compound with 2 independent $[H_2en]^{2+}$ cations partnered with $[B_4O_5(OH)_4]^{2-}$ and $[B_7O_9(OH)_5]^{2-}$ anions and 3 H_2O molecules (2 are disordered over 2 sites). An ORTEP diagram showing the ions/H_2O present in **1** is shown in Figure 1.

The isolated $[B_4O_5(OH)_4]^{2-}$ and $[B_7O_9(OH)_5]^{2-}$ anions in **1** are previously known, and bond lengths (Table 1) and bond angles (Table 2) are in accord with published data.[6,12,14,15,29] The $[B_4O_5(OH)_4]^{2-}$ anion is well-known, and is seen partnered with $2Na^+$ in borax,[30] but is less commonly partnered with NMCs.[6,12,29] Structures containing isolated heptaborate anions

Received: October 4, 2011
Published: November 3, 2011

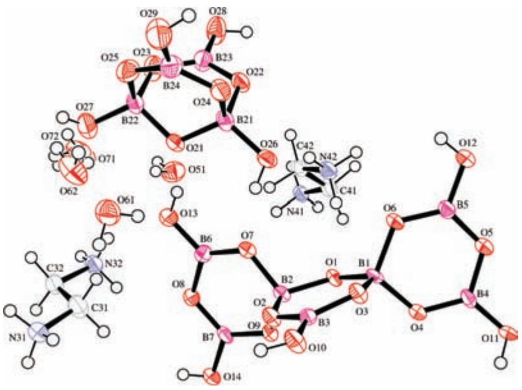


Figure 1. ORTEP drawing of **1** showing numbering scheme.

Table 1. B–O Bond Lengths (Å) for the $[B_7O_9(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ Anions Found in 1

		(i) $[B_7O_9(OH)_5]^{2-}$			
B1–O1	1.441(7)	B1–O6	1.484(6)	B1–O3	1.487(7)
B1–O4	1.487(7)	B2–O1	1.447(7)	B2–O7	1.478(7)
B2–O2	1.481(7)	B2–O9	1.488(7)	B3–O2	1.346(7)
B3–O3	1.370(7)	B3–O10	1.385(8)	B4–O4	1.354(7)
B4–O11	1.359(7)	B4–O5	1.393(7)	B5–O6	1.351(7)
B5–O12	1.372(7)	B5–O5	1.378(7)	B6–O7	1.346(7)
B6–O13	1.354(7)	B6–O8	1.405(7)	B7–O9	1.337(7)
B7–O8	1.365(7)	B7–O14	1.396(7)		
		(ii) $[B_4O_5(OH)_4]^{2-}$			
B21–O21	1.446(7)	B21–O26	1.449(7)	B21–O24	1.488(8)
B21–O22	1.517(7)	B22–O27	1.433(7)	B22–O21	1.456(8)
B22–O25	1.479(8)	B22–O23	1.498(8)	B23–O23	1.349(8)
B23–O22	1.369(8)	B23–O28	1.379(8)	B24–O24	1.358(8)
B24–O29	1.366(8)	B24–O25	1.396(8)		

are very rare and are limited to $[H_3N(CH_2)_xNH_3]$-$[B_7O_9(OH)_5)]\cdot yH_2O$ ($x = 4$, $y = 2$ and $x = 7$, $y = 1$)[14,15] and $Rb_2[B_7O_9(OH)_5)]$.[18] Two isomers of the $[B_7O_9(OH)_5)]^{2-}$ anions have been previously observed,[14,15] and this is a second example of the isomer which contains three boroxine rings linked through 2 spiro 4-coordinate B(1-) centers.

All 12 N bound H-atoms on the two $[H_2en]^{2+}$ cations are involved in H-bonds (simple or birfurcated) to borate or water acceptor sites. The unique O acceptor site (O1) of the $[B_7O_9(OH)_5]^{2-}$ anion, α to both 4-coordinate B centers, receives H-bonds from 2 cations. The 5 H-bond donor sites of the $[B_7O_9(OH)_5]^{2-}$ anion are involved with H-bonds to 2 heptaborate (O11 to O4′, O14 to O3′), 2 tetraborate (O10 to O22, O13 to O21) and 1 water acceptor site (O12 to O51). The 4 H-bond donor sites of the $[B_4O_5(OH)_4]^{2-}$ anion are linked with 2 heptaborate (O26 to O7, O28 to O2) and 2 water (O27 to O61, O29 to O61) acceptor sites. Details are given in Table 3. As has been observed in structural pentaborate chemistry,[13,16,23–25] the $R_2^2(8)$ H-bond motif (Etter)[31] links heptaborates at acceptor sites α to the spiro 4-coordinate B centers. This motif also links O21, the unique α-center between the 2 4-coordinate B atoms of the tetraborate anion, to the heptaborate anion via O13 to O21 and O26 to O7 interactions.

The anion, cations, and waters of crystallization of **1** are linked through a complex series of H-bond interactions, with the anion network templated by the cations. Figure 2 shows a view of the plane of the borate/water lattice with the cations omitted for clarity.

Table 2. B–O–B and O–B–O Internuclear Angles (deg) for the $[B_7O_9(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ Anions Found in 1

	(i) $[B_7O_9(OH)_5]^{2-}$		
O1–B1–O3	113.9(4)	O6–B1–O3	107.3(4)
O1–B1–O4	109.8(5)	O6–B1–O4	110.2(4)
O1–B1–O6	109.8(4)	O3–B1–O4	105.7(4)
O1–B2–O7	110.7(4)	O1–B2–O2	112.0(4)
O7–B2–O2	107.6(4)	O1–B2–O9	109.6(4)
O7–B2–O9	110.3(4)	O2–B2–O9	106.5(4)
O2–B3–O3	122.6(5)	O2–B3–O10	120.0(5)
O3–B3–O10	117.4(5)	O4–B4–O11	123.4(5)
O4–B4–O5	121.1(5)	O11–B4–O5	115.5(5)
O6–B5–O12	121.7(5)	O6–B5–O5	122.9(5)
O12–B5–O5	115.4(5)	O7–B6–O1	124.5(5)
O7–B6–O8	119.9(5)	O13–B6–O8	115.6(5)
O9–B7–O8	124.4(5)	O9–B7–O14	118.2(5)
O8–B7–O14	117.3(5)	B1–O1–B2	126.0(4)
B3–O2–B2	123.5(4);	B3–O3–B1	120.7(4)
B4–O4–B1	123.9(4)	B5–O5–B4	118.3(4)
B5–O6–B1	123.0(4)	B6–O7–B2	123.5(4)
B7–O8–B6	118.1(4)	B7–O9–B2	119.3(4)
	(ii) $[B_4O_5(OH)_4]^{2-}$		
O21–B21–O26	113.5(5)	O21–B21–O22	109.6(5)
O26–B21–O24	109.6(5)	O21–B21–O22	108.8(5)
O26–B21–O22	107.1(5)	O24–B21–O22	108.1(5)
O27–B22–O21	111.7(5)	O27–B22–O25	110.7(5)
O21–B22–O25	108.7(5)	O27–B22–O23	109.4(5)
O21–B22–O23	108.6(5)	O25–B22–O23	107.7(5)
O23–B23–O22	123.1(5)	O23–B23–O28	117.4(6)
O22–B23–O28	119.4(5)	O24–B24–O29	124.2(6)
O24–B24–O25	121.3(6)	O29–B24–O25	114.5(6)
B21–O21–B22	112.2(4)	B23–O22–B21	118.6(4)
B23–O23–B22	118.9(5)	B24–O24–B21	118.6(5)
B24–O25–B22	120.4(5)		

Table 3. H-Bond Interactions Arising from Polyborate Anions in 1[a]

$[B_7O_9(OH)_5]^{2-}$:	O10H10···O22, 1.87, 2.696(5), 169.3
	O11H11···O4′, 1.93, 2.772(5), 175.4
	O12H12···O51, 1.81, 2.593(5), 154.2
	O13H13···O21, 1.77, 2.575(5), 161.0
	O14H14···O3′, 2.06, 2.880(5), 163.8
$[B_4O_5(OH)_4]^{2-}$:	O26H26···O7, 1.95, 2.755(5), 160.9
	O27H27···O61, 2.23, 2.827(6), 128.2
	O28H28···O2, 1.88, 2.717(6), 175.2
	O29H29···O61, 2.35, 2.851(8), 118.7

[a] H–O distances set at 0.84 Å. Data arranged: interaction, distance (H···O) Å, distance (D···A) Å, angle DHA (deg).

The heptaborate ribbons within the planes are composed of C(8) chains. Similar C(8) chains are common in NMC pentaborate chemistry where the chain acceptor sites can be β or γ to the 4 coordinate center.[16,25] The acceptor O atoms of C(8) chains observed in **1** are adjacent to a 4 coordinate B center, but γ to the 4 coordinate center involved in the chain. The plane shown in Figure 2 is linked to neighboring planes via further borate/H_2O H-bond interactions, forming a three-dimensional (3-D) network.

IR and NMR data (^1H, ^{13}C) for **1** are consistent with the formulation. The 3 peaks which arise in the ^{11}B spectrum of **1** may be attributed to $B(OH)_3/[B(OH)_4]^-$ (18.3 ppm), $[B_3O_3(OH)_4]^-$ (12.8 ppm), and the 4-coordinate B center in

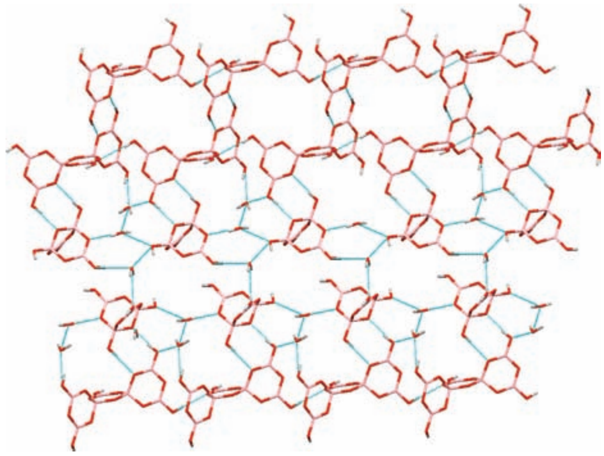


Figure 2. A "plane" of heptaborate, tetraborate, and water molecules and their "in plane" H-bond interactions. The plane is composed of 4 ribbons of polyborate anions (top and bottom ribbons are repeating but slightly displaced). $R_2^2(8)$ interactions are shown between heptaborate anions in the top ribbon to the adjacent ribbon below it. $R_2^2(8)$ interactions are shown between heptaborate and tetraborate anions in the bottom ribbon to the adjacent ribbon above it.

$[B_5O_6(OH)_4]^-$ (1.0 ppm). These species arise as the integrities of the anions in **1** are lost upon dissolution in aqueous solution as aqueous borate equilibria, appropriate to the B:base ratio, are established.[32]

Thermal studies (TGA/DSC) on compound **1** reveal that it is decomposed in air at 1000 °C to B_2O_3 (calc. residue, 56.7%, observed 56.1%) via a 2 stage process involving dehydration (<250 °C, expected weight loss 20.1%, found 19.9%) followed by oxidation of organic cation. Similar behavior has been observed in other NMC polyborate salts.[11,13−16,18−21,24,25]

The observation that two isolated polyborate moieties can coexist within one solid-state structure is of significance, and is an important new development in NMC polyborate chemistry. Thus, this possibility needs consideration for salts formulated on the basis of analytical composition without confirmation by X-ray diffraction (XRD) studies, and may be a plausible explanation for salts which have been isolated[23,33,34] with unusual or unexpected stoichiometries.

EXPERIMENTAL SECTION

Materials and Analysis. The 1,2-diaminoethane and $B(OH)_3$ chemicals were obtained commercially and used as supplied. NMR spectra were obtained on a Bruker Avance-500 spectrometer using XWIN-NMR 3.5. ^{11}B, ^{13}C, and ^1H NMR spectra were obtained at 500 MHz (^1H), 160 MHz (^{11}B), 125 MHz (^{13}C), with samples dissolved in D_2O. Fourier transform Infrared spectra (FTIR) were obtained as KBr pellets on a Perkin-Elmer 100 FTIR spectrometer over 450−4000 cm^{-1}. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) analysis were performed between 10 and 800 °C (in air) on an SDT Q600 V4.1 Build 59 instrument using Al_2O_3 crucibles, with a ramp temperature rate of 10 °C min^{-1}. CHN analysis was carried out at OEA laboratories Ltd. in Callington, Cornwall.

Synthesis of $[H_2en]_2[B_4O_5(OH)_4][B_7O_9(OH)_5]\cdot 3H_2O$ (1). 1,2-Diaminoethane (1.20 g, 20 mmol) in MeOH (100 cm^3) was added to $B(OH)_3$ (6.18 g, 100 mmol) in H_2O (100 cm^3). The $B(OH)_3$ dissolved and the solution was left to crystallize for 48 h at room temperature. The colorless crystals (0.40 g, 6%) which formed over this period were filtered and dried overnight at 110 °C. Recrystallization gave 0.22 g of colorless crystals suitable for XRD studies, $[H_2en]_2[B_4O_5(OH)_4][B_7O_9(OH)_5]\cdot 3H_2O$ (**1**). Spectroscopic analysis of the crude and recrystallized samples were identical. M.p > 300 °C, NMR: $\delta\,^1H$ (500 MHz)/ppm: 4.7, 2.9; $\delta\,^{13}C$ (125 MHz)/ppm 38.97; $\delta\,^{11}B$(160 MHz)/ppm: 1.0, 12.8, 18.3. IR/cm^{-1}: 3058, 1386, 1241, 1238, 1052, 1008, 927, 907, 838, 810, 673; Elemental analysis: Calcd for $C_4H_{35}B_{11}N_4O_{26}$: C, 7.1; H, 5.2; N, 8.31%; found: C, 7.3; H, 5.2; N, 8.3%.

Crystallographic Data for 1. A suitable crystal was selected and data were collected on a Bruker Nonius Kappa CCD area detector at the window of a Bruker Nonius FR591 rotating anode. $\lambda = Mo_{K\alpha} = 0.710\,73$ Å) driven by Collect[35] and DENZO[36,37] software at 120 K. The structure was determined and refined using SHELXS-97[38] Data: $C_4H_{35}B_{11}N_4O_{26}$, $M = 674.27$, triclinic, space group $P\bar{1}$, $a = 8.3270(7)$ Å, $\alpha = 80.415(5)°$, $b = 8.6970(9)$ Å, $\beta = 84.057(5)°$, $c = 19.164(2)$ Å, $\gamma = 86.438(6)°$, $V = 1359.7(2)$ Å^3, $Z = 2$, 16004 reflections measured, 4734 independent [$R_{int} = 0.0669$], Final R indices [$F^2 > 2\sigma(F^2)$], $R1 = 0.0896$, $wR2 = 0.1736$, R indices (all data), $R1 = 0.1334$, $wR2 = 0.1976$.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 846296 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or by application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44(0)-1223-336033 or email deposit@ccdc.cam.ac.uk).

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ACKNOWLEDGMENTS

We thank the NCS (EPSRC) University of Southampton for support.

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