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An Unprecedented Polyborate Ester Anion: X-ray Diffraction Studies on $[1,8\text{-}C_{10}H_6(NMe_2)_2H][B_5O_6(OMe)_4]$

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The slow hydrolysis of $B(OMe)_3$ in a CH_2Cl_2 solution in the presence of $1,8\text{-}C_{10}H_6(NMe_2)_2$ (5:1 ratio) led to the formation of the novel isolated pentaborate ester anion $[B_5O_6(OMe)_4]^-$, which was characterized by a single-crystal X-ray diffraction study as the salt $[1,8\text{-}C_{10}H_6(NMe_2)_2H][B_5O_6(OMe)_4]$.

Polyborate systems are a class of compounds that are undergoing a rapid resurgence of academic interest because of the richness of diversity of their intrinsic structures, their potential as precursors to new porous materials, and their practical applications in fluorescence, piezoelectric, and second-harmonic-generation optical materials.[1] We have recently been exploring solid-state pentaborate chemistry and are currently investigating structure-directing effects of a variety of “non-innocent” substituted alkylammonium cations.[2] During the course of these investigations, we examined the conjugate acid of 1,8-bis(dimethylamino)naphthalene (proton sponge, PS) as a potential cation. We anticipated that under ambient conditions the pentaborate salt $[C_{10}H_6(NMe_2)_2H][B_5O_6(OH)_4]$ would be formed from controlled slow hydrolysis of the borate ester $B(OMe)_3$ in a nonaqueous solvent, CH_2Cl_2.[3] Unexpectedly, the novel tetramethoxypentaborate ester salt $[C_{10}H_6(NMe_2)_2H][B_5O_6(OMe)_4]$ (**1**) was obtained, and this Communication describes its serindipitous synthesis and subsequent characterization by a single-crystal X-ray diffraction study.

Well-characterized homoleptic methoxyborate systems have hitherto been restricted to the borate esters $B(OMe)_3$,[4a] $B_2(OMe)_4$,[5] and $B_3O_3(OMe)_3$[4b] and the anion[6] in $M[B(OMe)_4]$ ($M = Li$, K, $^1/_2Sr$). $B_2(OMe)_4$ is unique within the series because it contains a B−B bond. A less-well-characterized polyborate, $B_8O_9(OMe)_6$, has also been described;[7] it is believed to contain boroxyl (B_3O_3) rings but is unlikely to be a pure compound. To our knowledge, **1** is the first structurally characterized anionic polyborate ester. It is also the first compound containing a spirocyclic tetraalkoxypentaborate(1−) anion and as such is a rare example of a spirocyclic nonhydroxypentaborate(1−) anion; the few previously characterized examples have been hydrolytically stabilized by B−C bonds.[8]

The reaction of the proton sponge with $B(OMe)_3$ in reagent-grade CH_2Cl_2 in a 1:5 ratio gave, after 2 weeks and evaporation of ∼50% of the solvent, a purple solution and a high yield of a “wet” crystalline solid.[9] Crystals of **1** suitable for a single-crystal X-ray diffraction[10] study were obtained directly from this crude material. Elemental analysis data of the isolated solid were inconsistent with the structural

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data, and subsequent NMR analysis in saturated CD_3OD and D_2O solutions revealed that the solid was a mixture of (several) compounds.[11] Consistent with the formation of **1**, a broad peak at δ 15 ppm (three-coordinate B) was observed in the $^{11}B\{^1H\}$ NMR spectrum of a saturated CD_3OD solution of the isolated solid, and a singlet at δ 3.37 ppm (MeOB) was observed in its ^1H NMR spectrum. Attempts to recrystallize or further purify the solid in order to isolate **1** were unsuccessful.

The structure of **1** is shown in Figure 1. The unit cell comprises four repeating $[(MeO)_4B_5O_6]^-$ anions and four repeating $[C_{10}H_6(NMe_2)_2H]^+$ cations with no hydrogen-bonding interactions between the cations and anions. There is a strong unsymmetrical hydrogen-bonding intermolecular interaction within the cation. The N11···N12 distance in the cation of **1** is at 2.588(3) Å, with the N11−H11···N12 angle at 156° and N11−H11 and H11···N12 distances at 1.05(3) and 1.59(3) Å, respectively, consistent with literature data[12] on structures containing this cation. The tetramethoxypentaborate(1−) anion has the gross spirobicyclic ring structure commonly observed in $[B_5O_6(OH)_4]^-$ compounds but with methyl groups replacing H atoms. However, in contrast to $[B_5O_6(OH)_4]^-$ salts, which generally contain "isolated" pentaborate anions as hydrogen-bonded supramolecular poly(pentaborate) structures, the anions in **1** are truly isolated. Selected anion structural data for **1** are given in the caption of Figure 1.

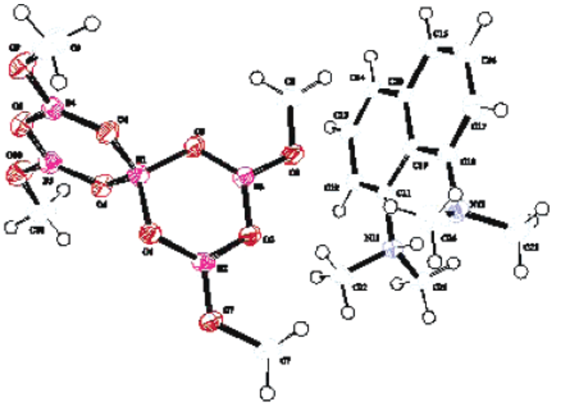

Figure 1. ORTEP drawing of **1** showing the atomic numbering scheme. Selected bond lengths (Å) and angles (deg) of the $[B_5O_6(OMe)_4]^-$ anion in **1**: B1−O4, 1.472(4); B1−O1, 1.473(4); B1−O6, 1.473(4); B1−O3, 1.483(4); B2−O1, 1.346(4); B2−O7, 1.373(3); B2−O2, 1.374(3); B3−O3, 1.335(4); B3−O8, 1.365(4); B3−O2, 1.385(3); B4−O4, 1.344(4); B4−O9, 1.361(4); B4−O5, 1.384(4); B5−O6, 1.338(4); B5−O10, 1.371(4); B5−O5, 1.379(4); O1−B1−O3, 110.7(2); O6−B1−O3, 108.5(2); O4−B1−O1, 109.4(2); O4−B1−O6, 111.1(2); O4−B1−O3, 108.0(2); O1−B1−O6, 109.2(2); O1−B2−O2, 122.8(2); O1−B2−O7, 119.3(2); O7−B2−O2, 117.9(3); O3−B3−O8, 124.3(3); O3−B3−O2, 122.1(3); O8−B3−O2, 113.6(2); O4−B4−O9, 123.0(3); O4−B4−O5, 122.2(3); O9−B4−O5, 114.7(3); O6−B5−O10, 122.7(3); O6−B5−O5, 122.7(3); O10−B5−O5, 114.5(3); B2−O1−B1, 121.5(2); B2−O2−B3, 117.8(2); B3−O3−B1, 122.3(2); B4−O4−B1, 123.1(2); B5−O5−B4, 117.7(2); B5−O6−B1, 123.0(2).

Table 1. Average B−O Distances (Å) in **1** and Related Compounds

compound	$B(sp^2){-}O^{\alpha}$	$B{-}O^{\beta}$	$B{-}O^{\gamma}$	$B(sp^3){-}O^{\alpha}$
1	1.341	1.368	1.381	1.475
$Na[B_5O_6(OH)_4]\cdot 3H_2O$[16]	1.356	1.367	1.383	1.468
$[H_2NMe_2][B_5O_6(OH)_4]$[17]	1.359	1.355	1.384	1.468
$[Rh(cod)(PPh_3)_2][B_5O_6(OH)_4]$[8a]	1.34	1.36	1.39	1.47

Average B−O bond lengths for **1** are compared with those for some related but supramolecular poly(pentaborate) systems in Table 1, where data involving the trigonal B atoms are grouped as $B{-}O^{\alpha}$, $B{-}O^{\beta}$, and $B{-}O^{\gamma}$, with O^{β} being exo to the ring and O^{α} bridging to the four-coordinate B atom. It is evident from the data presented that isolation of the pentaborate anion, albeit with methyl groups replacing H atoms, has an insignificant impact on the B−O bond lengths of the exo B−O and spirobicyclic pentaborate ring system.

It has long been believed that hydrolysis of orthoborate esters is a facile stepwise process, proceeding via four-coordinate boron intermediates.[13] In a few exceptional cases, $(RO)B(OH)_2$ derivatives have been isolated, whereas $(RO)_2B(OH)$ derivatives have yet to be reported.[13,14] In nonaqueous

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(9) To a solution of $C_{10}H_6(NMe_2)_2$ (1.15 g, 5.35 mmol) in undried reagent-grade CH_2Cl_2 (10 mL) was added $B(OMe)_3$ (3.00 mL, 26.76 mmol) via a syringe. The solution was stirred, sealed, and left at room temperature for 2 weeks. This resulted in the formation of a pale-purple solution and few colorless crystals of **1**. The flask was left open to air to facilitate slow evaporation of the solvent, and the product was obtained as a crop of "wet" colorless crystals (1.75 g, 65%). A crystal suitable for X-ray diffraction was obtained directly from this crude product. Mp: 170−173 °C.

(10) Crystal 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* (Hooft, R. *Collect: Data collection software*; Nonius BV: Delft, The Netherlands, 1998) and *DENZO* (Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, 276; *Macromolecular Crystallography*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; part A, pp 307−326) software at 120 K. The structure was determined in *SHELXS-97* (Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467−473) and refined using *SHELXL-97* (Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997). Data: $C_{18}H_{31}B_5N_2O_{10}$, $M = 489.50$, monoclinic, space group = $P2_1/c$, $a = 9.8513(5)$ Å, $b = 16.2689(6)$ Å, $c = 16.0216(8)$ Å, $\beta = 107.749(2)°$, $U = 2445.6(2)$ Å^3, $Z = 4$, μ(Mo Kα) = 0.102 mm^{-1}, 31 132 reflections measured, 5608 unique ($R_{int} = 0.1451$), which were used in all calculations. Final R1 = 0.0676, wR2 = 0.1155 [$F^2 > 2\sigma(F^2)$]; R1 = 0.1493, wR2 = 0.1404 (all data). Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 638456. Copies of the data can be obtained, free of charge, upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44(0)-1223-336033 or e-mail deposit@ccdc.cam.ac.uk).

(11) Saturated solutions of the "wet" solid in CD_3OD and D_2O were used for ^1H (500 MHz), ^{13}C (125 MHz), and ^{11}B (160 MHz) NMR spectra. ^1H NMR (CD_3OD): δ 2.78 (s, 12H, MeN, PS), 3.19 (s, 8H, MeN, PSH$^+$), 3.37 (s, 6H, MeO), 6.95 (d, 2H, Ar−CH, J = 7.6 Hz, PS), 7.26 (t, 2H, Ar−CH, J = 7.6 Hz, PS), 7.33 (d, 2H, Ar−CH, J = 7.9 Hz, PS), 7.72 (t, 1.3H, Ar−CH, J = 7.9 Hz, PSH$^+$), 8.00 (d, 1.3H, Ar−CH, J = 7.6 Hz, PSH$^+$), 8.06 (d, 1.3H, Ar−CH, J = 8.2 Hz, PSH$^+$). ^{11}B NMR (CD_3OD): δ 15.6 (96%), 18.7 (4%). ^{11}B NMR (D_2O): δ 12.9 (61%), 17.36 (39%). ^{13}C NMR (CD_3OD): δ 44.91 (MeN, PS), 46.68 (MeN, PSH$^+$), 113.90 (Ar−CH, PS), 120.37 (Ar−CH, PSH$^+$), 122.05 (Ar−CH, PS), 122.71 (Ar−CH, PSH$^+$), 122.94 (Ar−CH, PS), 126.45 (Ar−CH, PS), 128.24 (Ar−CH, PSH$^+$), 130.64 (Ar−CH, PSH$^+$), 137.09 (Ar−CH, PSH$^+$), 139.32 (Ar−C, PS), 145.59 (Ar−CH, PSH$^+$), 151.99 (Ar−C, PS). Integration of the CD_3OD ^1H NMR spectra suggests a PS/PSH$^+$ ratio of 3:2, corresponding to an overall sample composition of ~3:15:2 PS/$B(OH)_3$/**1**. Elem anal. Calcd for **1** ($C_{18}H_{31}B_5N_2O_{10}$): C, 44.2; H, 6.4; N, 5.7. Calcd for 3:15:2 PS/$B(OH)_3$/**1** ($C_{78}H_{161}B_{25}N_{10}O_{65}$): C, 36.8; H, 6.4; N, 5.5. Found: C, 33.9; H, 6.0; N, 5.5.

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solvents, limited hydrolysis of orthoborate esters leads to condensation and the formation of $B_3O_3(OR)_3$ or polyborates.[3,13] A possible mechanism of this reaction has also been proposed and the reaction's outcome attributed, in the absence of excess H_2O, to limited stability associated with B centers possessing one alkoxy substituent.[6] The isolation of **1** from our reaction mixture further supports this proposal. Dissolution of our isolated solid in D_2O (rather than CD_3OD) results in a different ^{11}B NMR spectrum. Although ^{11}B NMR spectra of aqueous polyborate systems are difficult to interpret because of the many complex equilibria present,[15] the observed spectrum is consistent with full hydrolysis of **1** to the expected hydroxyborate products $[B_3O_3(OH)_4]^-$ and $B(OH)_3$.

The existence of **1**, and related compounds with B−C bonds, clearly demonstrates that the synthesis of hybrid inorganic/organic polyborate systems is possible, and further research in this area is ongoing. The physical and chemical properties of these new materials needs further research because in time they may well rival the industrial importance and applications associated with inorganic polyborate compounds.

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Supporting Information Available: Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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