The First Molecular Borophosphonate Cage: Synthesis, Spectroscopy, and Single-Crystal X-ray Structure[†]

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*Summary: The synthesis of the first molecular borophosphonate, [t-BuPO$_3$BEt]$_4$ (**1**), has been achieved from the reaction of tert-butylphosphonic acid and triethylboron in refluxing toluene/1,4-dioxane. The inorganic B$_4$O$_{12}$P$_4$ cubic framework in **1** is enveloped by butyl and ethyl groups, making the compound highly soluble in common organic solvents. The reactive B−C bonds present in the four corners of **1** might offer the possibility of the use of this compound as a starting material for building supramoleclar borophosphonate/phosphate structures.*

The synthesis of materials having specifically designed properties has been an active field of research in the last few decades.[1] In particular, the metal organophosphonates have received considerable attention because of their structural chemistry, intercalation behavior, ion-exchange properties, and catalytic applications. The early studies on phosphates and phosphonates have focused on the incorporation of transition metals (such as V, Zr, and Zn) in the frameworks.[2,3] However, the discovery of a new group of aluminophosphate molecular sieves by Wilson et al.[4] with exceptional properties has recently shifted the focus toward the synthesis of a variety of group 13 phosphates and phosphonates.[5] Most of these materials are synthesized either by hydrothermal conditions (in the presence of structure-directing organic templates) or by high-temperature solid-state synthesis routes. Almost all of these materials are insoluble in most organic solvents.

Although, Al-, Ga-, and In-containing layered phosphates have been studied in detail over the last few years, the corresponding boron-containing compounds have received little attention. It has recently been shown that the mineral luneburgite contains anions of the type O$_3$BOPO$_3$$^{6-}$ and the mineral seamanite is made up of separate BO$_4$ and PO$_4$ tetrahedra.[6] A few of the mixed-metal phosphates which contain small quantities of boron are known as good catalysts in organic transformations such as conversion of aldehydes to diolefins, dehydration of alcohols, hydration of olefins, and carbonylation of methanol.[7] Recently, several metal borophosphate materials with extended structures have been synthesized and structurally characterized.[8] However, to the best of our knowledge, in the molecular domain there are no known examples of organic-soluble borophosphates or borophosphonates.

Our recent experience in the synthesis of a multitude of group 13 framework silicates[9] prompted us to extend this approach to the isoelectronic phosphate and phosphonate chemistry. Continuing our studies,[10] in this communication we wish to report on the synthesis and X-ray crystal structure of the first soluble borophosphonate molecule. This compound, existing in the form of a three-dimensional cage, is a small molecular building unit (SBU) in the eventual formation of crystalline solid-state borophophonate materials.

[†] Dedicated to Professor Günter Schmid on the occasion of his 60th birthday.

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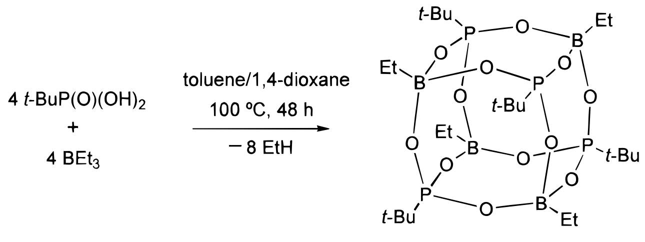
Scheme 1



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The reaction between *tert*-butylphosphonic acid and an equimolar quantity of BEt_3 in a mixture of toluene and 1,4-dioxane (4:1) at 100 °C for 48 h yields the title compound $[t\text{-}BuPO_3BEt]_4$ (**1**) in 80% yield (Scheme 1).[11] As has been recently demonstrated in the case of metallasiloxane chemistry,[9] the alkane elimination reaction between a metal alkyl and an acidic hydrogen containing compound proved to be the most facile route for synthesizing the title compound in very good yields. On the other hand, when the reaction is carried out in other solvents or at lower reaction temperatures (for example, in THF at 65 °C), substantial amounts of unreacted starting materials are left in the reaction mixture. Although this observation is in contrast to the instantaneous reaction between *tert*-butylphosphonic acid and aluminum alkyls at ambient temperature even in solvents such as *n*-hexane,[10] it is consistent with the higher reactivity of the Al—C bond compared to the B—C bond.[12]

Compound **1** has been fully characterized by means of analytical and spectroscopic techniques[13] and a single-crystal X-ray diffraction study.[14] It is of interest to note that under electron impact mass spectral conditions (70 eV), the cubic framework of **1** is intact and shows a peak due to the molecular ion (M^+) at *m/e* 704 (2%). The subsequent fragmentations are due to the loss of methyl (5%) and ethyl (100%, base peak) groups. The IR spectrum is devoid of any absorption in the region 3000−3500 cm^{-1}, indicating complete reaction of all P—OH groups with BEt_3.

The integrated ^1H NMR intensities reveal that there is only one ethyl group remaining on each boron. The methylene protons appear as a doublet of a quartet centered at δ 0.78 ppm as a result of the coupling with methyl protons and the boron nucleus (Figure 1). The protons of the *tert*-butyl group couple with phosphorus and appear as a doublet ($^3J_{PH}$ = 18.2 Hz). The ^{31}P and ^{11}B NMR spectra show a single resonance at δ 7.3 and 4.1 ppm ($\nu_{1/2}$ = 385 Hz), respectively, indicating the equivalence of all four P or B atoms in the molecule. It should be noted that the ^{31}P NMR chemical shift for the corresponding aluminophosphonate cage is downfield-shifted and occurs at δ 16.9 ppm.[10]

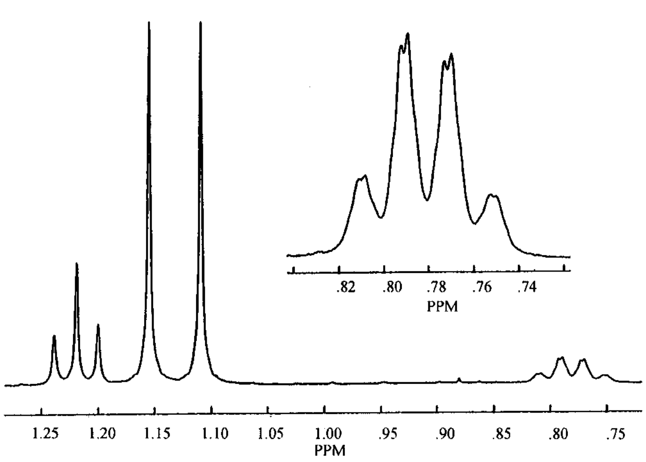

Figure 1. ^1H NMR (400 MHz, C_6D_6) spectrum of **1**.

The cubic borophosphonate **1** crystallizes in the centrosymmetric tetragonal space group $I4_1/a$ with one-fourth of the molecule in the asymmetric part of the unit cell. The final refined molecular structure is shown in Figure 2, along with selected structural parameters. In the structure of **1**, a cube-shaped polyhedron can be defined as the central core which is made up of four boron and four phosphorus atoms occupying the alternate vertices. Each of the B···P edges of the polyhedron is bridged by an oxygen atom in a μ_2 fashion, which results in the formation of six nonplanar $B_2O_4P_2$ eight-membered rings. Each of these eight-membered rings adopts a pseudo-C_4 crown conformation. While the two B and two P atoms are coplanar, the four oxygen atoms of the ring form another almost parallel plane (dihedral angle 0.7°) just above (0.30 Å) the former plane. The periphery of the central $B_4O_{12}P_4$ polyhedron is surrounded by hydrophobic *tert*-butyl and ethyl groups, explaining the high solubility of **1** in common organic solvents.

There are no formal P—O and P═O bonds in the molecule. The observed average P—O bond length (1.50 Å) is much shorter than a formal P—O bond (1.59−1.60 Å) and considerably longer than a formal P═O bond (1.45−1.46 Å).[15] Moreover, the observed values are slightly shorter than the P—O distances found in many

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[11] Synthesis of $[t\text{-}BuPO_3BEt]_4$ (**1**). To a solution of *tert*-butylphosphonic acid (138 mg, 1 mmol) in toluene (20 mL) and 1,4-dioxane (5 mL) was slowly added BEt_3 (1 mL of 1 M solution in THF, 1 mmol) via a syringe at room temperature, and the mixture was stirred for 2 h. No evolution of ethane gas was noted during this period. The reaction mixture was subsequently heated under reflux for 48 h, during which the evolution of ethane gas ceased. After the reaction mixture was cooled, the solvent was removed under reduced pressure at room temperature and the residue was redissolved in a THF (6 mL)/hexane (2 mL) mixture and cooled to −20 °C to yield 140 mg (0.2 mmol, 80%) of analytically pure **1** as a microcrystalline solid.

[12] Although B—C bonds are less reactive compared to Al—C, Ga—C, or In—C bonds, there are reports in the literature using the reactivity of triethylboron in estimating the hydration number of many inorganic salts. See: (a) Köster, R.; Fenzl, W. *Justus Liebigs Ann. Chem.* **1974**, 9. (b) *Inorganic Chemistry of the Main-group Elements*; Specialist Periodical Reports; The Chemical Society: London, 1976; Vol. 3, p 141.

[13] Characterization data for **1**: mp 311 °C. Anal. Calcd for $C_{24}H_{56}B_4O_{12}P_4$: C, 40.96; H, 8.02. Found: C, 41.5; H, 8.2. MS (EI, 70 eV): *m/e* 704 (2%, M^+), 689 (5%, $M^+ - Me$), 675 (100%, $M^+ - Et$). IR (Nujol): 1299 w, 1262 s, 1213 w, 1193 w, 1097 s, 1079 s, 1049 s, 1028 s, 1017 s, 937 s, 802 s, 723 s, 661 w, 650 w, 620 w, 538 w, 497 w cm^{-1}. ^1H NMR (C_6D_6, 400 MHz, external standard $SiMe_4$): δ 0.78 (dq, BCH_2, 8H, $^3J_{HH}$ = 7.8 Hz, $^2J_{BH}$ = 1.1 Hz), 1.13 (d, $C(CH_3)_3$, 36H, $^3J_{PH}$ = 18.2 Hz), 1.22 (t, BCH_2CH_3, 12H, $^3J_{HH}$ = 7.8 Hz). ^{11}B NMR (C_6D_6, 128 MHz, external standard $BF_3{\cdot}Et_2O$): δ 4.1 (br, $\nu_{1/2}$ = 385 Hz). ^{31}P NMR (C_6D_6, 162 MHz, external standard 85% H_3PO_4): δ 7.3 (s).

[14] Crystals of **1** suitable for X-ray diffraction studies were grown from a dilute 3:1 THF/*n*-hexane solution at −10 °C over 24 h. Crystal data: $C_{24}H_{56}B_4O_{12}P_4$, $M_r = 703.81$, tetragonal, space group $I4_1/a$, $a = b = 19.124(3)$ Å, $c = 10.290(2)$ Å, $V = 3763(1)$ Å^3, $Z = 4$, density (calcd) = 1.242 Mg/m^3, $F(000) = 1504$, $\lambda = 0.710\,73$ Å, $T = 210$ K, μ(Mo Kα) = 0.252 mm^{-1}. Intensity data were collected on a Siemens-Stoe AED2 four-circle diffractometer using a 0.7 × 0.3 × 0.3 mm crystal. The data were collected using the $\omega-2\theta$ scan mode in the range $7.0 \le 2\theta \le 45.0$, $-22 \le h \le 22$, $-22 \le k \le 22$, $-2 \le l \le 12$. Of 1513 reflections collected, 1227 were independent. The structure solution (direct methods) and refinement (by full-matrix least squares on F^2) were carried out using the SHELXTL-PLUS program. All non-hydrogens were refined anisotropically, and the hydrogen atoms were placed on calculated positions and refined isotropically. Final R1 ($I > 2\sigma(I)$) = 0.040; wR2(all data) = 0.1096. Maximum and minimum heights in final Fourier difference map were 0.302 and −0.286 e Å^{-3}.

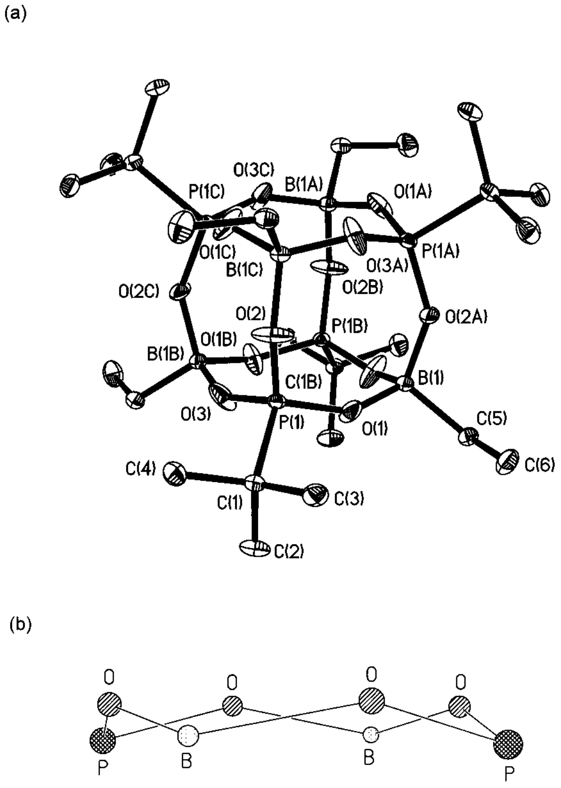

Figure 2. (a) Molecular structure of the cubic borophosphonate **1**. Selected bond lengths (Å) and bond angles (deg): P(1)–O(1) = 1.500(2), P(1)–O(2) = 1.503(2), P(1)–O(3) = 1.498(2), B(1)–O(1) = 1.472(4), B(1)–O(2A) = 1.469(4), B(1)–O(3B) = 1.469(4); P(1)–O(1)–B(1) = 148.0(2), P(1)–O(2)–B(1C) = 146.1, P(1)–O(3)–B(1B) = 149.3. (b) The shape of the $B_2O_4P_2$ face of the cube revealing the C_4-crown conformation.

phosphates and phosphonates (1.506–1.543 Å).[5] The average B–O distance in the molecule is 1.470 Å. The observed B–O distances in **1** are much longer than those found in the eight-membered-ring borosiloxane [t-$Bu_2SiO_2BPh]_2$ (average 1.35 Å)[16] and other borosiloxanes.[17] The average B–O–P angle (147.8°) is comparable to the M–O–Si angles fond in many of the cubic heterosiloxanes described in the literature. The B and P atoms adopt nearly ideal tetrahedral geometries with the average angles around them being 109.5 and 109.4°, respectively. The average length of the B···P edge of the cube is 2.85 Å. While the average length of the face diagonal in the B···B direction is 4.12 Å, the corresponding length along the P···P vector is 3.92 Å. The length of the body diagonal of the B_4P_4 cube is 4.93 Å.

In this communication we have demonstrated the use of commonly available starting materials as precursors for framework borophosphonates through a facile alkane elimination reaction. We are currently investigating the use of compound **1** as the secondary building unit (SBU) in synthesizing supramolecular borophosphate structures through cage fusion reactions utilizing the reactive B–C bonds located on the four vertices of the cube. In this direction, we also plan to develop synthetic routes to cubic borophosphonates that are fully functionalized at all the vertices of the cube (for example, P–N bonds at the phosphorus vertices). Moreover, owing to the well-known use of oligophosphate-based boron compounds in boron neutron capture therapy (BNCT),[18] it should also be possible to extend the chemistry described in this paper to develop new water-soluble borophosphonate superstructures and study their use in cancer therapy.

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Supporting Information Available: Tables giving positional and thermal parameters and estimated standard deviations for all atoms, bond distances and angles, and anisotropic thermal parameters for **1** (5 pages). Ordering information is given on any current masthead page.

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