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Elucidation of Tetraboric Acid with a New Borate Fundamental Building Block in a Chiral Uranyl Fluoroborate

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Supporting Information

ABSTRACT: A new neutral borate species, $H_2B_4O_7$ (also known as tetraboric acid), with a one-dimensional chain structure, is found in the interlayer spacing in $Rb_2[(UO_2)_2B_8O_{12}F_6]\cdot H_2B_4O_7$ (**RbUBOF-2**) derived from boric acid flux reaction of uranyl(VI) nitrate with $RbBF_4$. This new form of tetraboric acid possesses a novel borate fundamental building block with the symbol $4\Delta{:}\langle 3\Delta\rangle\Delta$.

The term "boric acid" generally refers to orthoboric acid with the chemical formula H_3BO_3. The naturally occurring form of orthoboric acid, namely, mineral sassolite, is known to crystallize in space group $P\bar{1}$ and adopts a two-dimensional sheet structure formed by H_3BO_3 molecules connected via hydrogen bonds.[1] A modified polytype of orthoboric acid that crystallizes in space group $P3_2$ with the actual chemical formula $H_6B_2O_6$ has also been reported.[2] However, several other ternary compounds containing H, B, and O were also added to the category of boric acids, which are mostly represented by metaboric acid HBO_2. Three different types of metaboric acid have been discovered that crystallize in space groups of *Pbnm* (α phase), $P2_1/c$ (β), and $P\bar{4}3n$ (γ), respectively.[3] All of these compounds only contain B^{III} centers. In addition, several ternary compounds containing B^{II} centers were isolated and structurally determined.[4,5] One of these, with a chemical moiety of $B_2(OH)_4$, is named as diboric acid. The crystal structure of diboric acid contains molecules of $B_2(OH)_4$ hydrogen-bonded to two-dimensional sheets similar to H_3BO_3.[5]

The melting point of orthoboric acid was determined to be 170.6 °C.[6] Thermogravimetric data suggest that orthoboric acid transforms to metaboric acid when the dehydration temperature is below 150 °C.[6] When the temperature is above 150 °C, metaboric acid further loses water and boron oxide (B_2O_3) is gradually formed.[6] Alvarez-Valdes et al. studied the thermal decomposition mechanism of orthoboric acid using different ambient conditions and heating sources.[7] On the basis of the thermogravimetric data, they proposed that a new species, namely, tetraboric acid or pyroboric acid with the chemical formula of $H_2B_4O_7$, forms between 160 and 210 °C in moist air. Furthermore, the absorption bands at 3400, 1715, and 1620 cm^{-1} in the IR spectrum of $H_2B_4O_7$ are not observed for H_3BO_3 and HBO_2. Nevertheless, no structural information is reported for $H_2B_4O_7$, which cannot exclude the possibility that "$H_2B_4O_7$" being observed is actually an intermediate state involving both HBO_2 and B_2O_3. In addition, the molecular structure proposed for $H_2B_4O_7$ is questionable with 2-fold coordination for B^{III} centers.[8,9]

We have recently explored the syntheses, structures, spectroscopy, and stability of actinide borates from thorium to plutonium with the aim of uncovering the solubility-limiting phases of actinides in some repositories such as the Waste Isolation Pilot Plant.[10,11] During the course of synthesizing new actinide fluoroborates,[10] in order to improve the physicochemical properties of actinide borates,[11] an isolated tetraboric acid unit is observed for the first time in the crystal structure of $Rb_2[(UO_2)_2B_8O_{12}F_6]\cdot H_2B_4O_7$ (**RbUBOF-2**), which also represents a new type of borate fundamental building block (FBB). **RbUBOF-2** was obtained in the boric acid flux reaction of uranyl(VI) nitrate with $RbBF_4$.[12] It should be noted that **RbUBOF-2** was not isolated in reactions starting with RbF, where $Rb[(UO_2)B_5O_8(OH)F]$ (**RbUBOF-1**) was present as the sole product.[10] It is possible that the fluoroborate anions are primarily formed via partial hydrolysis of the BF_4^- anion in **RbUBOF-2**, while in **RbUBOF-1**, only fluorination of borates affords the fluoroborate anions.

RbUBOF-2 crystallizes in the chiral space group *P*1, as shown by single-crystal X-ray diffraction studies.[13] In our previous report, we demonstrated that partial F substitution for O in BO_4 tetrahedra reduces the symmetry of the basic building block; therefore, a noncentrosymmetric structure could yield a larger nonlinear-optical response based on polarization of the B−F bond. $Tl[(UO_2)B_5O_8(OH)F]$ (**TlUBOF-1**), which crystallizes in *P*1, is a good example.[10] The crystal structure of **RbUBOF-2** is based on two-dimensional sheets containing uranyl cations, BO_3 triangles, and BO_3F tetrahedra (Figure 1a). Within the sheet, as observed in typical uranyl(VI) borate compounds,[11] uranyl cations form UO_8 hexagonal bipyramids.

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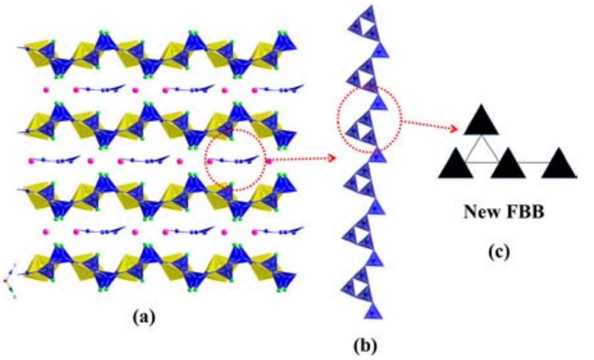

Figure 1. Views of the crystal structure of **RbUBOF-2** in *bc* plane (a), a one-dimensional tetraboric acid unit (b), and a representation of the new borate FBB found in the new tetraboric acid (c). UO_8 polyhedra are shown in yellow, borates in blue, F atoms in green, and Rb atoms in purple.

There are nine neighboring borate/fluoroborate units in the first coordination sphere of the uranyl cations. Among these, six are BO_3F tetrahedra, while three are BO_3 triangles. This type of actinide borate sheet topology (G type) was previously observed in the structure of $Ag[(UO_2)B_5O_8(OH)_2]$,[11d] as well as $K[(UO_2)B_5O_8(OH)F]$ (**KUBOF-1**).[10] There are no extra BO_3 triangles extending perpendicular to the sheets. Therefore, the structural hierarchy can be described as 1L−0−0−0, according to our symbolic representation summarized for actinide borate compounds.[11d]

As is observed in several actinide fluoroborate compounds, the B−F bonds are only present at four-coordinated B atoms to form BO_3F tetrahedra. F-substituted BO_3 triangles have not been observed to date. The B−F bond distances range from 1.39(1) to 1.44(1) Å with an average of 1.41(1) Å, which is significantly shorter than the average B−O bond distance of 1.46(1) Å in BO_3F tetrahedra.[10] Along with the crystallographic thermal parameter information, this observation serves as two of the most important data points to assign F atoms in the crystal structure because isoelectronic F^- and O^{2-} are otherwise difficult to distinguish by X-rays. Moreover, the presence of F in **RbUBOF-2** is supported by the scanning electron microscopy energy-dispersive spectrometry (SEM-EDS) measurements (see the Supporting Information).

The most important structural features of **RbUBOF-2** are the moieties observed in the interlayer space. There are two types of units in the interlayer space (Figure 1b). One is the Rb^+ cation, which compensates for the negative charge provided by the uranyl(VI) fluoroborate sheet. The other one is an unbound neutral borate unit with a one-dimensional chain structure consisting of four crystallographically independent B atoms (Figure 1b). All of these B atoms are determined to have the BO_3 triangle geometry, and the one-dimensional borate chain can be described as BO six-membered rings connected through additional BO_3 triangles via O-atom corner sharing. According to the symbolic representation of borate FBBs summarized initially by Burns et al.[14] followed by Yuan and Xue,[15] the borate chain structure can be represented by the symbol $4\Delta{:}\langle 3\Delta\rangle\Delta$ (Figure 1c), which has not been reported in any other borate materials. Bond-valence-sum calculations on all seven unique O atoms in the borate chains demonstrate that two of these O atoms are protonated (O22 and O23). As a result, the chemical formula of this borate chain is $H_2B_4O_7$; thus, it can be referred to as tetraboric or pyroboric acid. This is the first time that such a species has been found in a crystal structure. Also, what we observed further indicates the incorrectness of the previously proposed molecular structure of tetraboric acid.[8]

In addition to the Rb compound, the boric acid flux reactions of uranyl(VI) nitrate with ABF_4 (A = Na, Ag, and Cs) yielded three new members of the uranyl(VI) fluoroborate family with the formula $A[(UO_2)B_5O_8(OH)F]$ (called **NaUBOF-2**, **AgUBOF-1**, and **CsUBOF-1**, respectively; Supporting Information), which are isotypic with the previously reported **KUBOF-1**.[10] All of these compounds contain two-dimensional layer structures with G-type sheet topology and a structural hierarchy of 1L−1−1−0.[11d]

To compare our observation of tetraboric acid with that proposed by Alvarez-Valdes et al. from thermogravimetric data of boric acid,[7] we have measured the IR spectra of the four new uranyl(VI) fluoroborates from single crystals. The spectra are shown in Figure 2. **RbUBOF-2** produces two broad absorption features in the IR spectrum at 3100 and 3580 cm^{-1}, respectively, which could both be assigned to the stretching mode of OH^- groups. Note that the 3100 cm^{-1} feature is not observed in **NaUBOF-2**, **AgUBOF-1**, and **CsUBOF-1**. It should be mentioned that the OH^- moiety in **RbUBOF-2** is only within the tetraboric acid unit, whereas **NaUBOF-2**, **AgUBOF-1**, and **CsUBOF-1** contain only one unique hydroxyl group associated with one BO_3 triangle within the uranyl(VI) fluoroborate sheet and they solely contain the OH^- stretching mode at 3580 cm^{-1} in the IR spectra. It is worth mentioning that the OH^- stretch in solids of orthoboric acid, orthorhombic metaboric acid, and monoclinic metaboric acid are at 3200, 3280, and 3070 cm^{-1}, respectively.[16,17]

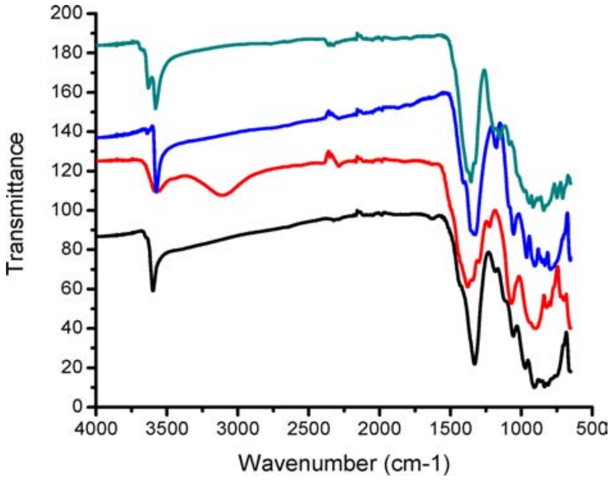

Figure 2. IR spectra of **NaUBOF-2** (black), **RbUBOF-2** (red), **AgUBOF-1** (blue), and **CsUBOF-1** (green) obtained from single crystals.

The density functional theory vibrational calculations on the isolated repeating unit of the $H_2B_4O_7$ moiety observed in the structure of **RbUBOF-2** yields calculated symmetric and asymmetric OH^- stretches of 3898 and 3879 cm^{-1}, respectively (Supporting Information). Further calculations based on the optimized structure can lower these values to 3619 cm^{-1}, which is still significantly larger than the experimental values. This difference is also observed for orthoboric acid in the solid state (OH^- stretch at 3200 cm^{-1}) containing hydrogen bonding and a gas phase (OH^- stretch at 3705 cm^{-1}) in which hydrogen bonding is excluded.[18] Therefore, it is also conceivable that the intercalation of tetraboric acid into the interlayer space of the uranyl(VI) fluoroborate structure can significantly shift the absorption feature of the hydroxyl group because both hydroxyl groups are involved in hydrogen bonding with F atoms on the adjacent BO_3F tetrahedra. The corresponding O−F distances range from 2.99(1) to 3.20(1) Å.

Notably, the feature at 3100 cm^{-1} is also absent in the spectrum reported by Alvarez-Valdes et al., where they observe a OH^- stretch mode at 3400 cm^{-1} assigned to $H_2B_4O_7$.[7] This may originate from the different strengths of the hydrogen bonds present in **RbUBOF-2** and $H_2B_4O_7$ prepared by thermolysis of boric acid. However, our efforts to repeat the synthesis of $H_2B_4O_7$ under the same conditions fail to reproduce the 3400 cm^{-1} feature in the IR spectrum, which casts doubt on the conclusion by Alvarez-Valdes et al.

In conclusion, the first crystallographically characterized tetraboric acid species has been observed in the structure of the new chiral uranyl(VI) fluoroborate compound **RbUBOF-2**, which also provides a new type of borate FBB. Until now, there is no solid evidence for the existence of the previously proposed structure of tetraboric acid, which contains two-coordinated B centers.[8] Because evidence for the two coordinated B atoms is still not substantiated,[9] the structure of tetraboric acid present in **RbUBOF-2** is far more reliable. Considering thermal decomposition of boric acid, which has a zero-dimensional molecular structure, to the final product B_2O_3, which contains a three-dimensional framework structure, the one-dimensional chain structure of $H_2B_4O_7$ is still possible as the intermediate phase during thermal decomposition of boric acid.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files for **NaUBOF-2**, **RbUBOF-2**, **AgUBOF-1**, and **CsUBOF-1**, synthetic details for **NaUBOF-2**, **AgUBOF-1**, and **CsUBOF-1**, UV−vis−near-IR spectra, fluorescence spectra, powder X-ray diffraction pattern, and SEM-EDS results of all four phases. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(12) Synthetic details: $UO_2(NO_3)_2 \cdot 6H_2O$ (0.2 g, 0.398 mmol), boric acid (0.194 g, 3.18 mmol), and $RbBF_4$ (0.274 g, 1.59 mmol) were loaded into a 23 mL autoclave with 50 μL of deionized water in a Rb:U:B molar ratio of 4:1:8. The autoclave was sealed and heated in a box furnace for 5 days at 220 °C. The autoclave was then cooled to ambient temperature at a rate of 5 °C/h. The product was washed with boiling water to remove excess boric acid and rinsed with ethanol. Yellow-green crystals in the form of tablets formed in the products, along with an abundance of yellow amorphous materials.

(13) Crystallographic data for $K[(NpO_2)B_{10}O_{14}(OH)_4]$ (**1**): yellow-green tablet crystals, 0.077 × 0.075 × 0.007 mm, triclinic, $P1$, $Z = 1$, $a = 6.448(4)$ Å, $b = 10.392(6)$ Å, $c = 10.397(6)$ Å, $\alpha = 107.456(5)°$, $\beta = 107.898(6)°$, $\gamma = 107.865(6)°$, $V = 568.0(5)$ $Å^3$ [$T = 100(2)$ K], $\mu = 186.49$ cm^{-1}, R1 = 0.0282, wR2 = 0.0641. *SAINT* software was used for data integration including Lorentz and polarization corrections. Semiempirical absorption corrections were applied using the program *SCALE* (*SADABS*).[19] The structures were solved using the *SHELX* program suite.[20]

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