

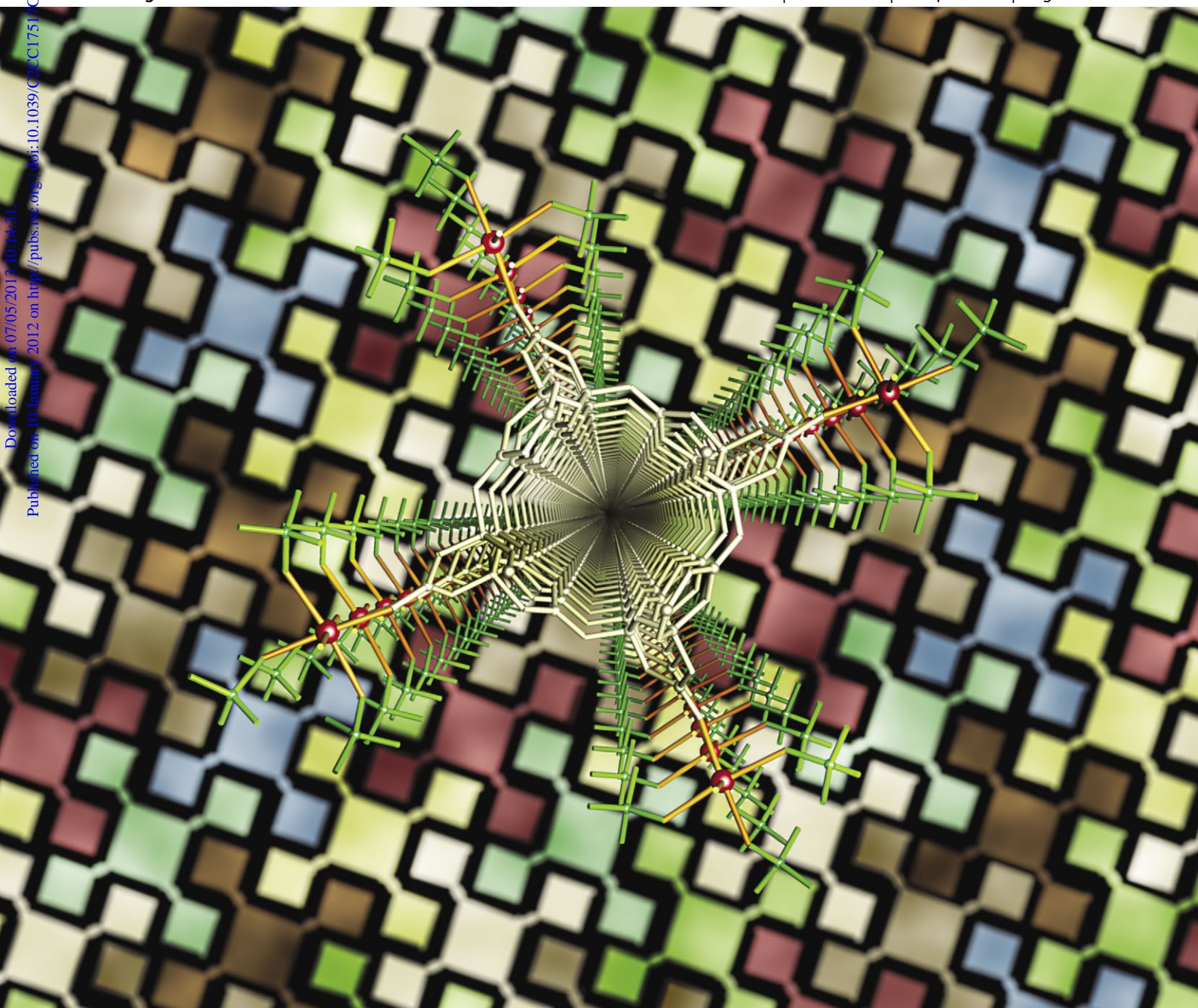
ChemComm

Chemical Communications

www.rsc.org/chemcomm

Volume 48 | Number 29 | 11 April 2012 | Pages 3465–3564

Downloaded on 07/05/2013 10:14:31.
Published on 10 January 2012 on <http://pubs.rsc.org>. DOI: 10.1039/C2CC17517G



ISSN 1359-7345

RSC Publishing

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1359-7345(2012)48:29;1-5

Cite this: *Chem. Commun.*, 2012, **48**, 3479–3481

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COMMUNICATION

Complex clover cross-sectioned nanotubes exist in the structure of the first uranium borate phosphate†

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Received 1st December 2011, Accepted 6th January 2012

DOI: 10.1039/c2cc17517g

An actinide borate phosphate was prepared *via* a high temperature solid-state reaction. This phase exhibits unprecedented complex inorganic nanotubular fragments with an external diameter of $\sim 2 \times 2$ nm. The nanotubular aggregates are based on borate tubes where the exterior of the tubes is decorated with $\text{UO}_2(\text{PO}_4)_3$ moieties to form a complex shape with a cross-section similar to the clover cross.

Nanostructured phases have been the focus of considerable interest since the discovery of carbon nanotubes.¹ Numerous different topologies with nano-scale features have been found in the past two decades: nanotubes, nanorods, nanospheres, *etc.* Nanotubes are especially interesting owing to their unique chemical and physical properties.² Most of these phases are not periodically ordered and are present in forms of fully or partially disordered arrays. Novel crystalline materials based on nanotubular fragments were observed recently in metal-organic hybrid materials and purely inorganic compounds.³ The family of inorganic phases based on nanotubular fragments is relatively small. It includes $\text{Na}_2\text{V}_3\text{O}_7$,^{3d} $\text{K}_5[(\text{UO}_2)_3(\text{SeO}_4)_5](\text{NO}_3)(\text{H}_2\text{O})_{3.5}$,^{3e} SbPS_4 ,^{3f} and $\text{Na}_2\text{EuSiSe}_4$.^{3g} In addition, two organically-templated hybrid phases were reported with the following compositions: $(\text{C}_4\text{H}_{12}\text{N})_{14}[(\text{UO}_2)_{10}(\text{SeO}_4)_{17}(\text{H}_2\text{O})]^{3h}$ and $(\text{H}_3\text{O})_2\text{K}[(\text{H}_3\text{O})@([\text{18}]\text{crown-6})][(\text{UO}_2)_3(\text{SeO}_4)_5](\text{H}_2\text{O})_4$.³ⁱ The nanotubules in the aforementioned phases possess classical tubular shapes with spherical, elliptical, or square-like cross-sections. The outer diameter of the tubes varies from 1 to 3.5 nm with internal dimensions from 0.5 to 1.5 nm. In an attempt to synthesize

crystalline phases that might exist in vitrified nuclear waste,⁴ we synthesized a complex uranium(vi) borate phosphate, $\text{Ba}_5[(\text{UO}_2)(\text{PO}_4)_3(\text{B}_5\text{O}_9)] \cdot n\text{H}_2\text{O}$ (**BaBPUI**).[‡] This compound has an unprecedented structure with nanotubular fragments. Borophosphates form a large group of inorganic phases with borate groups (triangles or tetrahedra) that are directly linked to PO_4 groups. Borate phosphates are rather rare, and contain isolated borate and phosphate groups.⁵ There are no known actinide borophosphates or borate phosphates.

Crystals of **BaBPUI** were obtained from a high-temperature solid-state reaction, and characterized by X-ray diffraction and by several spectroscopic methods. A view of the **BaBPUI** crystal structure is shown in Fig. 1a.

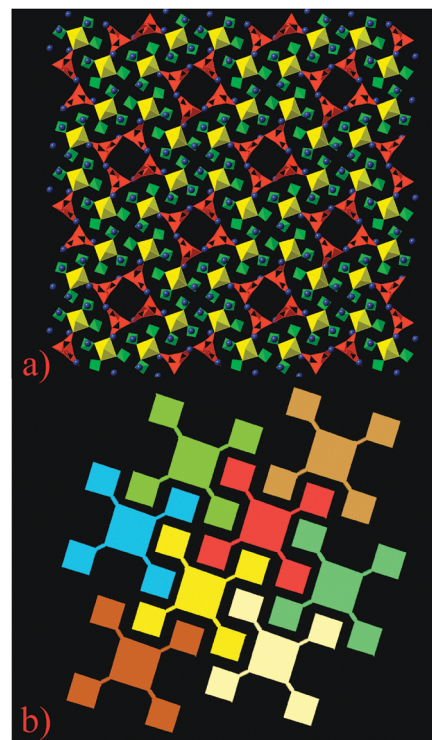


Fig. 1 View of **BaBPUI** (a) and its schematic representation (see the text for details) (b). U polyhedra are shown in yellow, phosphate tetrahedra are shown in green, borate groups in red and Ba atoms are in blue (the color scheme refers to parts (a) and (b) only). Projection on (001).

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† Electronic supplementary information (ESI) available: CIF file for $\text{Ba}_5[(\text{UO}_2)(\text{PO}_4)_3(\text{B}_5\text{O}_9)](\text{H}_2\text{O})_{0.125}$. ICSID 423800. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2cc17517g

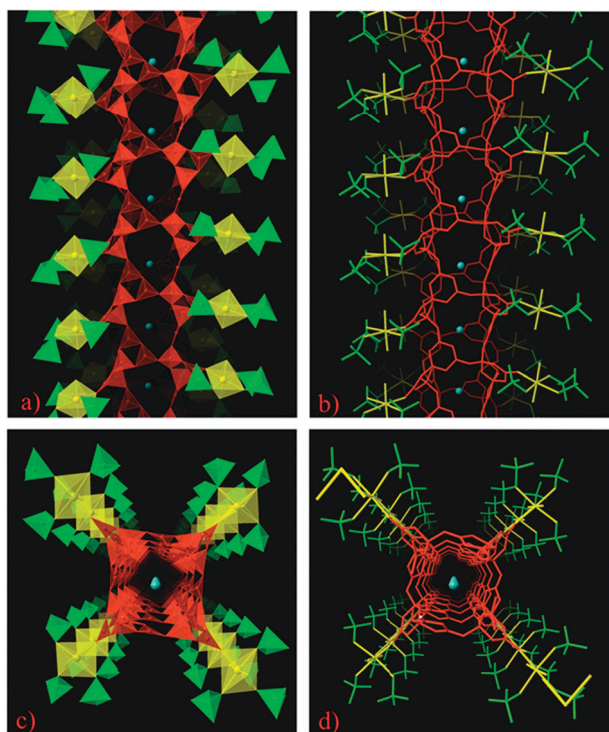


Fig. 2 The structure of nanotubes in **BaBPU1**. The polyhedral and skeletal view of side (a and b) and top projections (c and d). Colours are the same with those in Fig. 1, water molecules are light-blue.

The structure of **BaBPU1** is based on complex nanotubular fragments with the composition of $[(\text{UO}_2)(\text{PO}_4)_3(\text{B}_5\text{O}_9)]_1 \infty^-$ linked by Ba^{2+} cations into a quasi 3D structure. The nanotubes have a complex shape that can be described as having a four-leafed clover cross-section. The external dimensions of the nanotubes are $\sim 2 \times 2$ nm, with an internal size approximately $\sim 0.6 \times 0.6$ nm (measured from atom centers). Two main fragments can be separated within the structure of the nanotubes in **BaBPU1**. The first is a borate tubular porous net (shown in red in Fig. 2). The borate net is based on the pentaborate $[\text{B}_5\text{O}_{11}]$ anion, which can be viewed as a fundamental building block (FBB). The FBBs are linked *via* corner-sharing into polymeric tubules with a complex topology. The borate tubes have an external size of 1×1 nm. Water molecules occupy positions within the borate tube channels. The internal diameter is large enough to absorb water molecules directly from the air under standard conditions. The tubes are open from the sides and have nine-membered windows with an approximate size of 5×6.5 Å. The Ba^{2+} cations reside in the pores. A skeletal view demonstrates that the topology of the nanotubes body in **BaBPU1** is similar to those found in organic and metal-organic nanotubular phases with side pores.^{3a,b} Other inorganic nanotubes do not have pores on the sides. The borate nanotubular fragment in **BaBPU1** is the only known example from borate chemistry to date.

The second fragment of this complex nanotubule is the $\text{UO}_2(\text{PO}_4)_3$ cluster (UO_6 shown in yellow and PO_4 in green in Fig. 2). This fragment is quite well-known in uranyl phosphate chemistry and is based on almost linear uranyl groups corner-shared with PO_4 tetrahedra. The uranyl groups are surrounded by only phosphate tetrahedra in all known

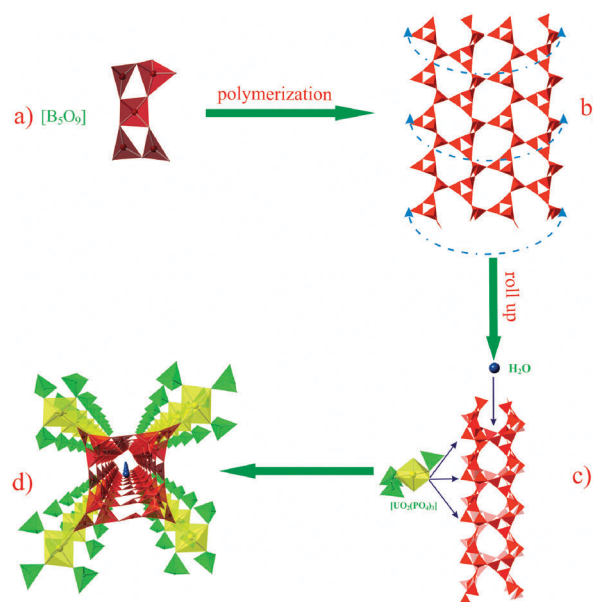


Fig. 3 A schematic representation of fragments hierarchy in **BaBPU1** nanotubes.

uranyl phosphate-based materials. However, in **BaBPU1**, the fourth PO_4 group is substituted by one BO_3 triangle from the polyborate tubules.

The $\text{U}=\text{O}$ bond distances in the uranyl groups are approximately 1.812(4) Å, whereas the equatorial bonds range from 2.159(44) Å to 2.322(4) Å. The $\text{U}-\text{O}$ bond to the coordinating oxygen atom from the BO_3 triangle has the shortest distance of 2.159(4) Å. The bonds in the PO_4 and BO_4 tetrahedra are in the ranges of 1.511(4)–1.581(4) Å and 1.414(8)–1.497(8) Å, respectively. The bonds in BO_3 triangles are shorter and occur from 1.323(8)–1.395(8) Å.

The formation of the nanotubular fragment in **BaBPU1** from simple groups to a complex aggregate is schematically shown in Fig. 3. The FBBs of polyborate nanotubes are $[\text{B}_5\text{O}_{11}]$ pentamers shown in Fig. 3a. This fragment is based on three BO_3 triangles corner-linked with two BO_4 tetrahedra, and can be described as $3\Delta 2\Box: (\Delta 2\Box) - (\Delta 2\Box)$ according to the borate classification system.⁶ Corner-sharing polymerization of such groups gives a hypothetical 2D sheet with the structure shown in Fig. 3b. The layer has nine-membered holes similar to those we observed in recently described actinide borates.⁴ The sheet topology has been known in borate chemistry for natural biringuccite and several synthetic compounds.⁷ The process of converting layers into tubes can be described as simple rolling up. A similar process was described for vanadate nanotubes and was proposed for several other inorganic nanotubular materials.^{3,8} The resulting borate nanotubes (Fig. 3d) are surrounded by $\text{UO}_2(\text{PO}_4)_3$ groups *via* their interaction with the external BO_3 triangles (Fig. 3c). Those $\text{UO}_2(\text{PO}_4)_3$ clusters facing each other (the angle between them is 180°) are shifted by $\frac{1}{2}c$ in a relation to the neighbouring groups (90°). This shift results in a stepwise shape. The resulting nanotubes have a complex shape with a cut similar to the clover (Celtic) cross.

We suggest that water molecules residing inside the tubes are absorbed from air during cooling. This is based on the

synthetic method we used (the temperature of the synthesis was 1000 °C). It is obvious that water is driven off at such high temperatures and the only way for it to enter the nanotubes is water absorption after or during the process of crystal cooling.⁹ The water molecules occupy half of their positions inside the tubes. They are strongly distorted because the internal diameter of the nanotubes is slightly larger than the size of H₂O molecules. The presence of water in molecular form was confirmed by absorptions near 1600 cm⁻¹ and 3500 cm⁻¹ in the IR spectrum.

The packing mode of these complex nanotubes in the structure of **BaBPUI** is unusual (Fig. 1a and b). Normally, nanotubular fragments are packed in crystal structures with hexagonal or tetragonal packing. Such simple packing is impossible in **BaBPUI** because of the cross-like forms of the UO₂(PO₄)₃ groups attached to the borate-based nanotubes. Generally, one can name the packing mode in **BaBPUI** as a 3D puzzle assemblage. A schematic projection of nanotubes packing is shown in Fig. 1b (borate nanotubes and UO₂(PO₄)₃ are shown in the form of large and small squares, respectively). Each UO₂(PO₄)₃ group from a single nanotube is inserted into the free space between the UO₂(PO₄)₃ groups of neighbouring nanotubes (for example yellow to red). The identical group from a third nanotube (cream colored) locks with the yellow UO₂(PO₄)₃ unit by inserting into the free space of the yellow nanotube. Simultaneously, the yellow UO₂(PO₄)₃ groups are locking the red ones by insertion into the free space of the pale greenish nanotube (Fig. 3c). All other nanotubes are locked in the same manner and form a zipper-like structure. Thus, the structure is stabilized not only by Ba²⁺ cations but also *via* coupling of the cross-shaped nanotubes. This makes the structure of **BaBPUI** unique in the class of nanotubular based compounds.

This work was supported by Deutsche Forschungsgemeinschaft within the DE 412/43-1 and the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, Heavy Elements Program, U.S. Department of Energy, under Grant DE-SC0002215.

Notes and references

† Synthesis: the crystals of Ba₅[(UO₂)(PO₄)₃(B₅O₉)](H₂O)_{0.125} were obtained from a high-temperature solid state reaction. The following compounds were used as initial components: H₃BO₃ (61.38 mg); BPO₄ (52.89 mg); UO₂(NO₃)₂·6H₂O (251.05 mg); Ba(CO₃)₂ (197.34 mg). The components were ground in an agate mortar, placed into a platinum crucible, heated to 1000 °C and then slowly (5 °C h⁻¹) cooled to the room temperature. The resulting mixture consisted of **BaBPUI** crystals (estimated yield 8–10%) and a glassy mass. Crystallographic data for Ba₅[(UO₂)(PO₄)₃(B₅O₉)](H₂O)_{0.125}: green needle, 0.28 × 0.09 × 0.08 mm, tetragonal, *M*_r = 1441.89, *P*₄₂/*n*, *Z* = 8, *a* = *b* = 24.934(4) Å, *c* = 6.7732(6) Å, *V* = 4211.0(9) Å³ (*T* = 293(2) K), *μ* = 172.05 cm⁻¹, *N*_{ref} = 55046/4643, *R*_{int} = 0.139, *R*₁ = 0.0254 for *F*_o² > 2σ(*F*_o²), *wR*₂ = 0.0437 for all data. Infrared spectra of **BaBPUI** exhibit strong absorption bands at 1320 and 1280 cm⁻¹ which can be assigned to ν_{as} of BO₄ and BO₃ groups. The ν_s of BO₄ and BO₃ groups are in the range 600–810 cm⁻¹. The vibrations of UO₂²⁺ groups are in the range from 848 to 966 cm⁻¹. The bands of PO₄ are in the range 1000–1066 cm⁻¹. The presence of water is confirmed by the bands at 1633 and 3474 cm⁻¹. The UV-vis-NIR and

fluorescence spectra of **BaBPUI** are also typical for the presence of UO₂²⁺ (see ESI†).

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