ChemComm
www.rsc.org/chemcomm

$NH_4[BPO_4F]$: A novel open-framework ammonium fluorinated borophosphate with a zeolite-like structure related to gismondine topology

Man-Rong Li, Wei Liu, Ming-Hui Ge, Hao-Hong Chen, Xin-Xin Yang and Jing-Tai Zhao*
State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai 200050, China. E-mail: jtzhao@mail.sic.ac.cn; Fax: 0086-021-52413122; Tel: 0086-021-52412073

Received (in Cambridge, UK) 26th February 2004, Accepted 8th April 2004
First published as an Advance Article on the web 29th April 2004

The title compound, synthesized in a water-free flux under mild conditions (513 K in autoclaves), exhibits a zeolite-like and chiral open-framework related to gismondine (GIS).

Borophosphates with open-framework structures analogous to the zeolites are of great interest because of their potential use as catalysts, ion-exchangers, molecuar sieves, *etc*. For example, BPO_4 itself is a good catalyst (100% conversion) for the decomposition of CCl_2F_2 (Freon 12) which is a known killer of the ozone layer.[1–3] BPO_4 is, therefore, a very promising catalyst for fluorine-containing compounds because of its durability towards fluorine due to its nonmetallic character.[4] Thus, considerable efforts have been made towards the design and synthesis of open-framework borophosphates[5–12] but only a few such structures have been found to date.[13–14] Substitution of some oxygen atoms with fluorine led to the first fluoro-boro-phosphate $(C_2H_{10}N_2)[BPO_4F_2]$, a compound with infinite chains of $[BPO_4F_2]$ separated by the protonated organic templates.[15] Along this line of research, here we report the synthesis and structure of a fluoroborophosphate with a zeolite-like open-framework structure, $NH_4[BPO_4F]$.†

The new compound was synthesized under mild conditions in a water-free flux of H_3BO_3 and $NH_4H_2PO_4$, both with low melting points of 185 and 180 °C, respectively. The reaction made of H_3BO_3, $NH_4H_2PO_4$ and NaF in a molar ratio of 3 : 3 : 2 was heated in a Teflon-lined stainless steel autoclave at 513 K. The product was washed with hot deionized water, and colorless truncated-cubelike crystals of NH_4BPO_4F were recovered as the only solid phase (yield of 77% based on F).

The crystal structure of the new compound was determined by single-crystal X-ray diffraction.‡ It reveals a new type of three-dimensional open framework. BO_3F and PO_4 tetrahedra share corners and form helical ribbons of ${}^1_\infty\{[BPO_4F]^{1-}\}$ along the 2_1 screw axes of the $P2_13$ cubic space group (Fig. 1). To our knowledge, this is the first borophosphate with such tetrahedral helical chains. The chains share common vertexes with neighboring chains and form an open-framework structure with four- and eight-membered channels along the cubic axes (Fig. 2). The latter form a three-dimensional system throughout the structure. The size of the larger channels is 4.8 × 5.5 Å measured by the O···O and F···F distances across the channel.

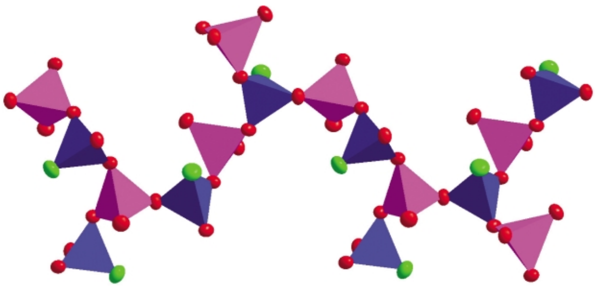

Fig. 1 Open-branched helical chain in $NH_4[BPO_4F]$, (BO_3F tetrahedra, blue; PO_4 tetrahedra, purple; F atoms, green spheres; O atoms, red spheres).

DOI: 10.1039/b402966f

The fluorine in the BO_3F tetrahedra is terminal while the three oxygen atoms are shared with neighboring PO_4 tetrahedra. The phosphate groups have one terminal oxygen atom (O2 with d_{P-O} = 1.482 Å). The average P–O, B–O, and B–F distances, 1.526, 1.460, and 1.387 Å, respectively, are consistent with values observed before. The bond valence sums (BVS) calculated for B and P, 3.17 and 4.95, respectively, are very close to their chemical valence and confirm the reliability of the determined structure.[16,17]

The ammonium cations occupy the eight-membered channels and participate in weak hydrogen bonding with the framework N–H···O hydrogen bonds with distances of 3.054–3.196 Å.[18]

The non-coplanar sequence of up (U) and down (D) linkages in the four-membered rings of two BO_3F and two PO_4 tetrahedra (Fig. 2) leads to double crankshaft (cc) chains around the eight-membered rings (Fig. 3a).[19] The coplanar linkages of the four-membered rings and adjacent parts of the eight-membered rings result in chains of bifurcated square (bs). The condensed connection of these chains gives a framework related to the topology of the known zeolite gismondine (GIS) with $I4_1/\mathrm{amd}$ symmetry (Fig. 3b).[10–16] The framework of the latter is based on a 4.8^2 net that has small cages, channels, and windows. It is extremely flexible for changes of both framework and non-framework atoms. Thus, several minerals of different compositions crystallize in various space groups such as $I112/b$, $Fddd$, $P2_1/c$, $P2_12_12_1$, $Pnma$, $I2$, $I\bar{4}$, $Pmn2_1$, and $P2_1/a$, but all have the same gismondine topology.[20] Most of them contain small cages with water molecules strongly bonded to exchangeable cations and framework oxygens. Due to

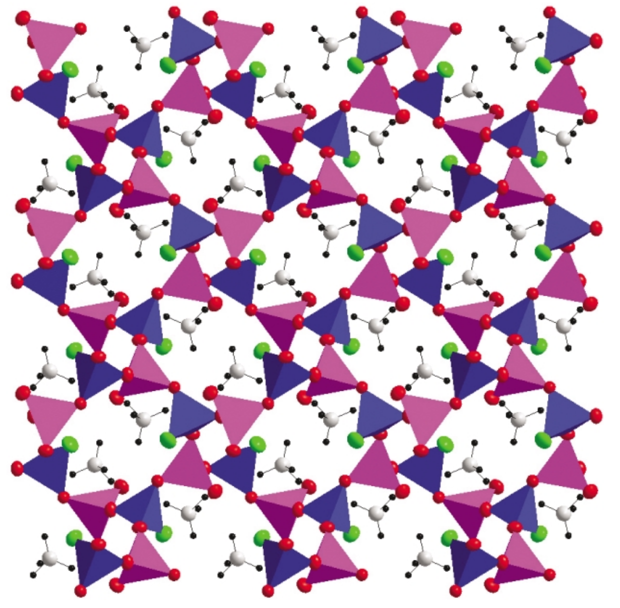

Fig. 2 Polyhedral view of the $NH_4[BPO_4F]$ structure in [100] direction, showing the three-dimensional framework with eight-membered ring channels occupied by ammonium cations (BO_3F tetrahedra, blue; PO_4 tetrahedra, purple; F atoms, green; O atoms, red; H atoms, dark; N atoms, light gray).

the presence of terminal fluorine and oxygen atoms in $NH_4[BPO_4F]$ the chains run parallel without connection leading to channels along three cubic axes instead of only one along the 4_1-axis of gismondine. This makes the structure of the title compound much more open than that of GIS.

This work was supported by the Fund for Distinguished Young Scholars and Key Project from the NNSF of China and State "863" project. The authors would like to thank Dr Yingjie Zhu and Mr Xianluo Hu for TG analysis, and Ms Linhong Weng and Zhenxia Chen for the help in X-ray single crystal data. The authors are grateful to Professor S.C. Sevov (University of Notre Dame) for very helpful suggestions on many aspects.

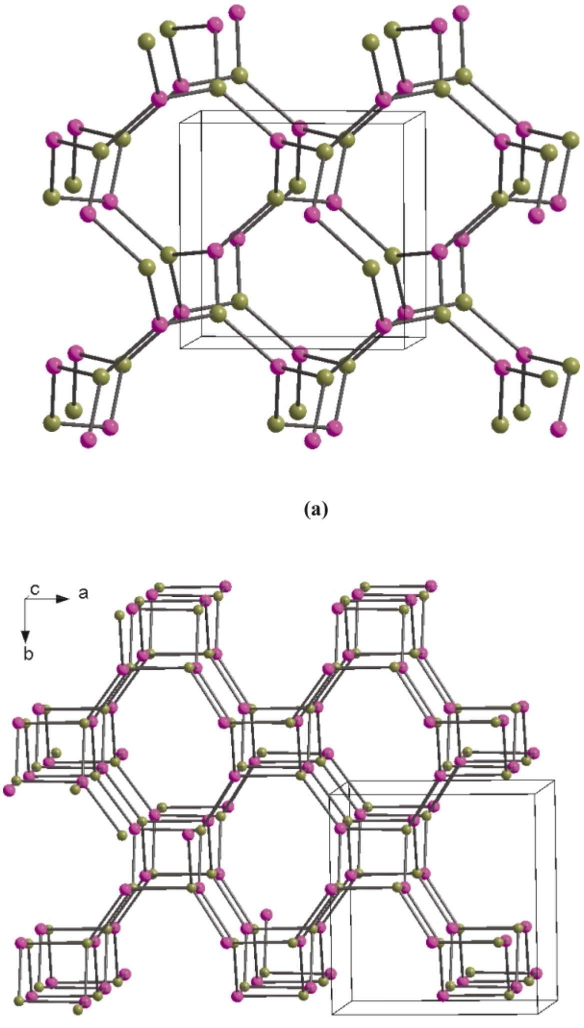

Fig. 3 Topological structure of NH_4BPO_4F represented by connections of coordination tetrahedra (PO_4, purple spheres; BO_3F, dark green spheres) (a) and GIS ($Ca_4(Al_8Si_8O_{32})(H_2O)_{16}$) ($AlO_4$, dark green spheres; SiO_4, purple spheres) (b) with $I4_1/amd$ symmetry.

Notes and references

† Selected data for $NH_4[BPO_4F]$: IR: ν_3(N–H) (3313 cm^{-1}), ν_1(N–H) (3081 cm^{-1}), $2\nu_4$(N–H) (2858 cm^{-1}), ν_4(N–H) (1430 cm^{-1}), $\nu_s(BO_3F)$ (1627 cm^{-1}, 1473 cm^{-1}), $\nu_{as}(BO_3F)$ (964 cm^{-1}), $\nu_s(PO_4)$ (1195 cm^{-1}, 1056 cm^{-1}), $\nu_{as}(PO_4)$ (995 cm^{-1}). TG-DSC study was carried out on a STA-409PC/4/H LUXX equipment up to 1273 K (heating rate 10 K min^{-1}, air atmosphere, corundum crucible). The compound is stable in air up to 669 K and then has a one-step weight loss of 27.65% from 669 K to 727 K, corresponding to the releasing of NH_3 and HF (calculated 25.94%). X-ray powder diffraction investigation of the final product indicates the presence of BPO_4.

‡ Crystal data: $NH_4[BPO_4F]$: $M = 142.818$, cubic space group $P2_13$, $a = 7.5913(9)$ Å, $V = 437.47(9)$ Å^3, $Z = 2$, $D = 2.168$ Mg m^{-3}, crystal dimension (mm): 0.02×0.02×0.02; $\mu = 10.45$ cm^{-1}, $F(000) = 288$, $T = 293(2)$ K; diffraction data collected on a Nonius Kappa CCD with graphite monochromatized MoKa radiation ($\lambda = 0.71073$ Å), $3.80° < \theta < 26.99°$, 330 unique reflections ($R_{int} = 0.0598$) and 25 parameters were used for the full-matrix, least-squares refinement of F^2 using the program package SHELXL-97/2,[21] $R1 = 0.0343$ [$I > 2\sigma(I)$], R1 = 0.0539 (all data); $wR2 = 0.0644$ [$I > 2\sigma(I)$], $wR2 = 0.0659$ (all data). CCDC 232990. See http://www.rsc.org/suppdata/cc/b4/b402966f/ for crystallographic data in .cif or other electronic format.

1 G. E. R. Schulze and F. A. Hummel, *Z. Physik Chem.*, 1934, **B24**, 215.
2 S. Sao, M. Hasegawa, T. Sodesawa and F. Nozake, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 516.
3 K. Ahmed and C. Geisert, *J. Vac. Sci. Technol. A*, 1992, **10(2)**, 313.
4 S. Imamura, K. Imakubo, S. Furuyoshi and H. Jindai, *Ind. Eng. Chem. Res.*, 1991, **30**, 2355.
5 R. P. Bontchev and S. C. Sevov, *Inorg. Chem.*, 1996, **35**, 6910.
6 S. C. Sevov, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 3641.
7 R. Kniep, H. Engelhard and C. Hauf, *Chem. Mater.*, 1998, **10**, 2930.
8 R. P. Bontchev, J. Do and A. J. Jacobson, *Angew. Chem. Int. Ed.*, 1999, **38**, 1937.
9 R. Kniep, G. Schäfer, H. Engelhardt and I. Boy, *Angew. Chem. Int. Ed.*, 1999, **38**, 3641.
10 R. P. Bontchev, J. Do and A. J. Jacobson, *Inorg. Chem.*, 2000, **39**, 4179.
11 J. Do and A. J. Jacobson, *Chem. Mater.*, 2001, **13**, 2436.
12 G.-Y. Yang and S. C. Sevov, *Inorg. Chem.*, 2001, **40**, 2214.
13 I. Boy, F. Stowasser, G. Schäfer and R. Kniep, *Chem. Eur. J.*, 2001, **7**, 834.
14 G. Schäfer, H. Borrmann and R. Kniep, *Micropor. Mesopor. Mater.*, 2002, **41**, 161.
15 Y.-X. Huang, G. Schäfer, H. Borrmann, J.-T. Zhao and R. Kniep, *Z. Anorg. Allg. Chem*, 2003, **629**, 3.
16 I. D. Brown and D. Altermatt, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1985, **B41**, 244.
17 N. E. Brese and M. O'Keeffe, *Acta Crystallogr. Sect. B: Struct. Sci.*, 1991, **B47**, 192.
18 T. Steiner, *Angew. Chem. Int. Ed.*, 2002, **41**, 48.
19 J. V. Smith, *Am. Mineral.*, 1978, **63**, 960.
20 Ch. Baerlocher, Ch. W. M. Meier and D. H. Olson, *Atlas of zeolite framework types*, Amsterdam; New York: Elsevier, 2001.
21 G. M. Sheldrick, *SHELXS-97/2, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97/2, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.