Hydro(solvo)thermal synthesis and structure of a three-dimensional zinc fluorophosphate: $Zn_2(4,4'\text{-bipy})(PO_3F)_2$

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A new three-dimensional zinc fluorophosphate is prepared by using hydro(solvo)thermal conditions with ZnO, $(HF)_x$·py H_3PO_4 and 4,4′-bipyridyl; the single-crystal structure is determined.

Meso- and micro-porous materials are of great industrial and academic interest due to their catalytic, adsorbent, and ion-exchange properties.[1–3] A three-dimensional open framework, with uniform pores, channels and active catalytic sites, facilitates and enhances these properties. One class of these open-framework materials are transition-metal phosphates.[3–5] Various examples with metals such as V,[6] Fe,[7] Co,[8] and Mo,[3] have recently been synthesised and characterised. In contrast to the closed-shell aluminosilicates, these new materials are potential candidates for atom abstraction and redox catalysis. Many of these metal phosphates were synthesised under hydro(solvo)thermal conditions with organic templating agents.

Recently, $(HF)_x$·py [pyridinium poly(hydrogen fluoride), 70% HF by mass] has been utilised to synthesise a variety of new mixed-metal materials.[9–11] The fluoride ion not only acts as a mineralizer, but also participates in the formation and structure of the final compound. Ferey[12] used fluoride in the synthesis of new fluorinated gallophosphates, and determined that temperature, pressure, time, pH, concentration of reactants, and the nature of the template all influence the existence and nature of the microporous phases. It is our aim to synthesise new microporous fluorinated phosphate materials, and in doing so synthesise open-framework compounds with fluoride channels. Here we report the hydro(solvo)thermal synthesis and crystal structure of a new zinc fluorophosphate.

Open-framework zinc phosphates have been prepared previously by mixing $Zn(NO_3)_2$, H_3PO_4 and alkaline base, which is then heated for several days at 70 °C. Using this method, analogues of sodalite, $Na_6(H_2O)_8(ZnPO_4)_6$ and zeolite Li–A(BW), $Li_4Zn_4P_4O_{16}\cdot 4H_2O$ have been synthesized.[5] Within the metal–PO_3F^{2-} system compounds with Ni,[13] Sn,[14] Co,[15] Cu[16] and Zn,[17] have been reported. $Ni(H_2O)_6(NH_4)_2(PO_3F)_2$[13] and $SnPO_3F$[14] are molecular solids with isolated anions and cations, whereas $ZnPO_3F\cdot 2.5\ H_2O$[17] contains both tetrahedrally and octahedrally coordinated Zn^{2+}, with the tetrahedral Zn^{2+} coordinated to two oxygens and the fluorophosphate.

$Zn_2(4,4'\text{-bipy})(PO_3F)_2$ was synthesised by heating ZnO, $(HF)_x$·py, 85% H_3PO_4 and 4,4′-bipy in a 23 ml Teflon lined Parr autoclave at 180 °C.‡ It crystallises as clear colourless faceted crystals in 9% yield. The single-crystal X-ray structure determination indicates that it is a three-dimensional structure containing layers of zinc fluorophosphate moieties connected by 4,4′-bipy ligands (Fig. 1). Each zinc is tetrahedrally coordinated, bonded to three oxygens [Zn–O (av.) 1.927(3) Å] and one nitrogen [Zn–N 2.020(3) Å]. Each oxygen on the zinc is linked to a phosphorus, whereas the 4,4′-bipy ligands bridge the Zn^{2+} cations in adjacent layers [$Zn^{2+}\cdots Zn^{2+}$ 11.100(1) Å]. The 4,4′-bipy ligand is not planar, rather the rings are twisted at an angle of 15.3(3)°. The fluorophosphate group, PO_3F^{2-}, contains tetrahedrally coordinated P^{5+}. Each phosphorus is linked to three oxygens [P–O(av.) 1.501(2) Å], that bridge to the Zn^{2+}, and a terminal fluoride [P–F(av.) 1.568(2) Å]. In terms of connectivity, the compound can be formulated as $PO_{3/2}F_{1/1}^{+}$ cations linked to $Zn(4,4'\text{-bipy})_{1/2}O_{3/2}^{-}$ anions. Similarly to $CoPO_3F\cdot 3H_2O$[15] and $CuPO_3F\cdot 2H_2O$[16] the fluorophosphate groups in $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ bridge the metal exclusively through oxygen, whereas the fluorine atom is always monodentate. The bond distances and angles in PO_3F^{2-} in the reported structure are in excellent agreement with those previously reported. An interesting feature of $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ is the fluoride channel (Fig. 2). The size of this channel is a direct consequence of the Zn–(4,4′-bipy)–Zn linkage. The effect of the 4,4′-bipy ligand is twofold. First, it completes the Zn^{2+} tetrahedra by inhibiting coordination to F^-, and second it increases the distance between the Zn^{2+} and produces the observed channel. Experiments are currently in progress to

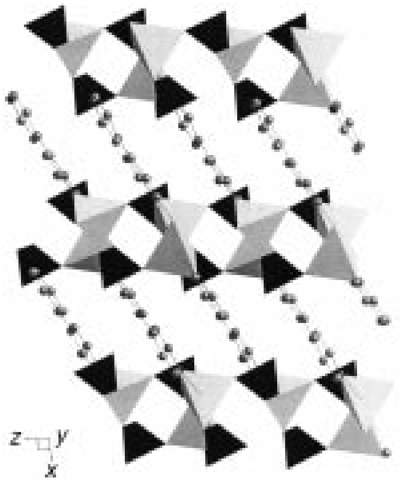

Fig. 1 View of the single-crystal structure of $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ along the crystallographic 010 direction

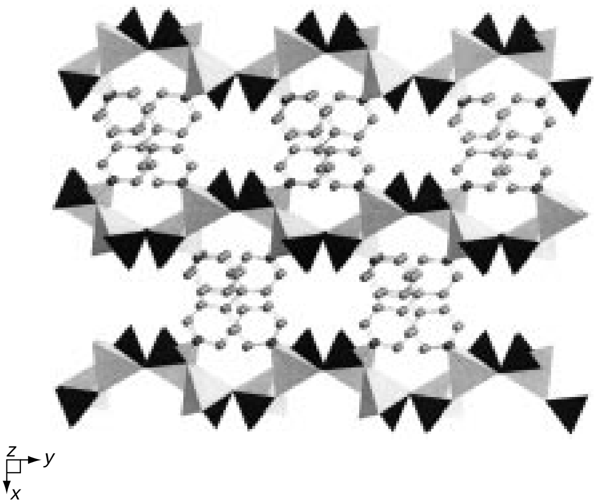

Fig. 2 View of the single-crystal structure of $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ along the crystallograpic 001 direction

increase this channel by using 1,4-bis(4-pyridyl)benzene and 1,4-bis(4-pyridylethenyl)benzene[18] as bridging ligands.

Footnotes

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‡ *Synthesis*: $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ was synthesised by adding 0.048 g ZnO, 0.51 g $(HF)_x\cdot py$, 0.40 g 85% H_3PO_4 and 0.5 g 4,4′-bipy to a 23 ml Teflon lined Parr autoclave. The autoclave was sealed and heated under static conditions for 12 h at 180 °C. To facilitate crystal growth, the reaction was cooled to room temp. over 2 h (starting Zn : $(HF)_x\cdot py : H_3PO_4$: 4,4′-bipy ratio 1 : 3.16 : 6.67 : 5.33). The product was filtered and thoroughly washed with acetone to remove recrystallised 4,4′-bipy. $Zn_2(4,4'\text{-bipy})(PO_3F)_2$ was recovered as clear colourless faceted crystals in 9% yield (0.025 g) based on ZnO. Elemental analysis, using the combustion method gave satisfactory C,H, and N values. The IR spectrum revealed P–F bands centred at 833 and 726 cm^{-1} consistent with known phases.[16]

§ *Crystal data*: monoclinic, space group $P2_1/c$, $a = 17.996(9)$, $b = 9.813(2)$, $c = 8.229(4)$ Å, $\beta = 99.727(2)°$, $U = 1432.3(3)$ Å^3, $Z = 4$, $D_c = 2.24$ g cm^{-3}, $\mu = 37.1$ cm^{-1}, crystal size *ca*. 0.40 × 0.21 × 0.19 mm, 15 188 total (2969 independent) reflections, $R = 0.031$ and $R_w = 0.030$ for 2112 reflections with $I > 5\sigma(I)$, max., min. peak in final Fourier difference map 0.54 and −0.68 e Å^{-3} respectively. Data were collected on an image-plate Enraf-Nonius DIP 2000 diffractometer using graphite-monochromated Mo-Kα radiation at 150 K; 90 frames at a step of 2° yielded 15 188 reflections, $\theta_{max} = 26°$. Corrections were made for Lorentz and polarisation effects.[19] The structure was solved by direct methods using SIR92[20] and refined using full-matrix least squares. Hydrogen atoms were fixed in geometrically idealised positions and allowed to ride on their attached carbon atoms with isotropic thermal parameters according to the atom to which they were connected (these were not refined). No correction was made for absorption. A Chebyshev weighting scheme[22] was applied in the refinement of the structure, the data corrected for the effects of anomalous dispersion and isotropic extinction (*via* an overall extinction parameter)[22] in the final stages of refinement. All crystallographic calculations were performed using the Oxford CRYSTALS system[23] running on a Silicon Graphics Indigo R4000 computer.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/418.

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