

A novel open-framework aluminophosphate $[AlP_2O_6(OH)_2][H_3O]$ containing propeller-like chiral motifs

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A new open-framework aluminophosphate containing propeller-like chiral motifs has been synthesized solvothermally using 2-aminopyridine as the structure-directing agent and its structure is determined by single-crystal X-ray diffraction.

During recent decades, a large number of microporous aluminophosphates have been synthesized which exhibit various novel framework topologies, as well as analogous structures with known zeolites.^{1–3} However, the preparation of chiral open-framework aluminophosphates, of potentially important application in asymmetric synthesis and separation, has been less successful. The introduction of chirality into the open-framework using traditional template molecules, such as chiral organic amines, is found to be particularly difficult. However, recently the employment of chiral metal complexes as template agents has promoted the formation of a few layered compounds with chirality or chiral motifs in their porous sheets, such as GeTex1,⁴ GeTex2,⁵ GeTex3⁶ and d-Co(en)₃·Al₃P₄O₁₆·3H₂O.⁷ To our knowledge, there are no three-dimension (3D) open-framework aluminophosphates with chirality or chiral structural subunits. Here, we report a novel 3D open-framework aluminophosphate (denoted AIPO-CJ4) synthesized using 2-aminopyridine as a structure-directing agent. It consists of propeller-like chiral motifs with both Δ and Λ configurations.

Large single crystals of AIPO-CJ4 were prepared in a gel system with molar composition 1.0 Al(OPr)₃: 2.4 H₃PO₄: 2.0 2-aminopyridine: 20 2-BuOH. Typically, 1.0 g of finely ground aluminium triisopropoxide was first dispersed into 9 mL butan-2-ol solvent with stirring, followed by addition of 0.9 g of 2-aminopyridine. Phosphoric acid (85 wt%, 0.8 mL) was finally added dropwise to the above reaction mixture with stirring. A sticky gel was formed, and was transferred into a Teflon-lined stainless autoclave and heated at 180 °C for 8 days under autogeneous pressure. The product was filtered off and washed thoroughly with deionized water and dried at 70 °C. X-Ray powder diffraction patterns were recorded on a Siemens D5005 X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The experimental powder X-ray diffraction (XRD) pattern of AIPO-CJ4 accords with the simulated pattern derived from structural data (Fig. 1), establishing the as-synthesized product as a single phase.

Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300 DV ICP instrument gives Al and P contents in the product as 11.7 and 25.3%, respectively. This is in agreement with calculated values of 11.3% and 26.1% based on the formula of $[AlP_2O_6(OH)_2][H_3O]$ revealed by single-crystal structure analysis. Single crystal structure analysis, as well as elemental analysis, shows that no 2-aminopyridine is involved in the product. However, 2-aminopyridine is found to be necessary for the formation of AIPO-CJ4. If other organic amines such as 2-methylpyridine are used instead to 2-aminopyridine in the reaction mixture, only the dense phase berlinite is obtained. This demonstrates that the organic additive plays an important structure-directing role as in case of VPI-5.⁸

A single crystal of AIPO-CJ4 with dimensions of $0.08 \times 0.06 \times 0.04 \text{ mm}$ was glued to a fine glass fiber and mounted on a

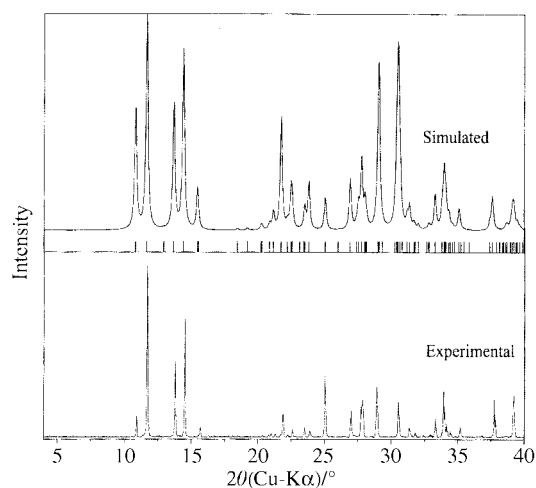


Fig. 1 Experimental and simulated powder X-ray diffraction patterns of AIPO-CJ4.

three-circle fixed Siemens diffractometer fitted with a Bruker SMART CCD detector.

Structure analysis† indicates that AIPO-CJ4 crystallizes in the $P1$ space group. The structure of AIPO-CJ4 is constructed by alternation of AlO₆ octahedra and PO₃(OH) tetrahedra via vertex oxygen atoms. To our knowledge, this is the first open-framework AIPO, in which the primary Al building unit is solely made up of AlO₆ octahedra with all six oxygen vertices being shared by adjacent P atoms. Also, it is the first 3D aluminophosphate with an Al:P ratio of 1:2, distinct from previous AlP₂O₈³⁻ aluminophosphates with 1D chain^{9,10} and 2D layer structures.^{11–13}

Interestingly, the structure of AIPO-CJ4 features chiral propeller-like motifs as found for Co(en)₃³⁺, as can be seen in Fig. 2. This chiral motif is formed by Al(2)-centered octahedra with three cyclic four-membered rings. The O–Al–O bond

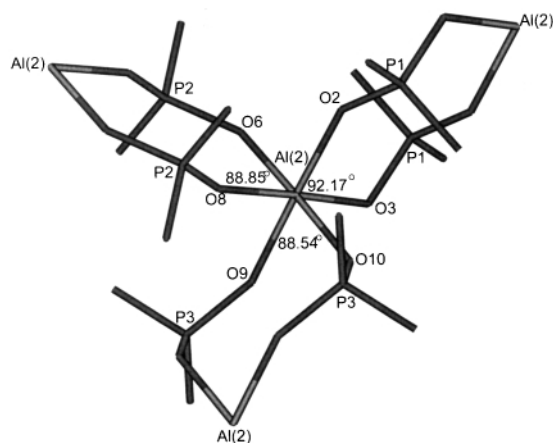


Fig. 2 A propeller-like chiral motif formed by three cyclic four-membered rings.

angles for the three blades of the propeller are 88.85, 88.54 and 92.17°. These chiral motifs are connected with each other to form a puckered 2D layer parallel to the *ab* plane, which contains double crown-like 12-membered rings as shown in Fig. 3. Each 12-membered ring is surrounded by six chiral motifs with three of Δ - and three of Λ -configuration. The 2D layers are connected *via* Al(1) atoms lying at inversion centers to form the 3D open-framework of AlPO-CJ4 (Fig. 4), with interconnecting 8-MR channels along the [100], [010] and [001] directions.

The protonated water molecules, which balance the negative charge of the framework, are trapped in the channels, and interact with the terminal oxygens attached to P atoms through

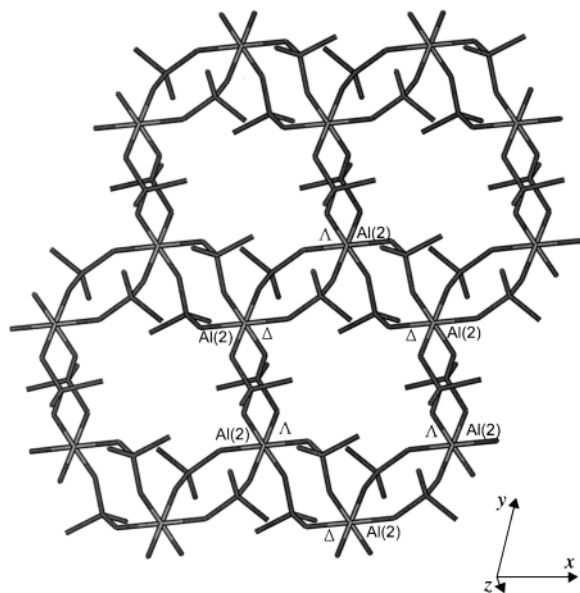


Fig. 3 2D layer formed by connecting the chiral motifs; Δ and Λ indicate the absolute configurations of the motifs.

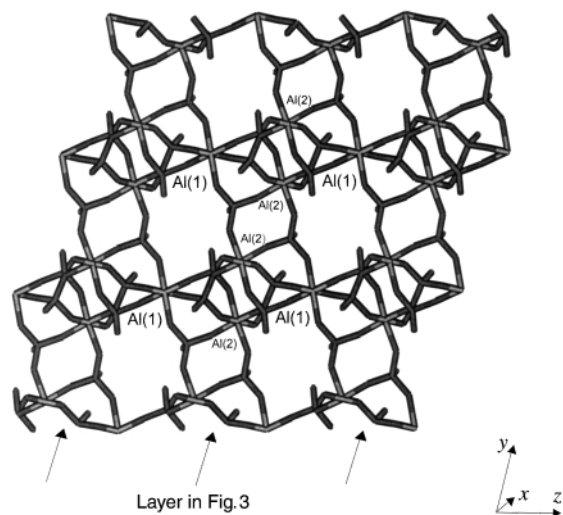


Fig. 4 3D open-framework forming by connecting the 2D layers *via* Al(1) atoms, viewed along the [100] direction. Water molecules in the channel are not shown.

H-bonds with $O_W \cdots O_{\text{terminal}}$ distances in the range 2.853–3.086 Å. Energy calculations employing Cerius² using the Burchart 1.01-Dreiding 2.21 force field^{14,15} gives the H-bonding interaction energy between the framework and occluded water molecules as $-10.0 \text{ kcal mol}^{-1}$ per unit cell. It is believed that the water molecules play an important role in the stabilization of the open-framework of AlPO-CJ4. By contrast, the structure-directing agent 2-aminopyridine is too large to be accommodated in the 8-MR channel of AlPO-CJ4 and may be the reason why 2-aminopyridine is not involved in the structure.

In summary, a novel 3D aluminophosphate compound consisting of chiral motifs was synthesized from a solvothermal system using 2-aminopyridine as a structure-directing agent. Propeller-like chiral motifs are connected to each other and form a 2D layer and further construct a 3D open-framework *via* Al(1) atoms. The discovery of such chiral structural motifs will open up the possibility for the rational design of chiral microporous materials.

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Notes and references

† Crystal data for $[\text{AlP}_2\text{O}_6(\text{OH})_2][\text{H}_3\text{O}]$: $M = 237.96$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.1177(2)$, $b = 8.6729(2)$, $c = 9.2200(3)$ Å, $\alpha = 65.108(2)$, $\beta = 70.521(1)$, $\gamma = 68.504(2)^\circ$, $U = 469.4(2)$ Å³, $T = 293(2)$ K, $Z = 3$, $\mu(\text{Mo-K}\alpha) = 0.859 \text{ mm}^{-1}$, $D_c = 2.525 \text{ g cm}^{-3}$, 1114 reflections measured, 1107 observed ($R_{\text{int}} = 0.0115$) which were used in all calculations. The final $wR(F^2_{\text{all data}})$ was 0.1098 and $R(F_{\text{all data}})$ was 0.0445. The structure was solved by direct methods using SHELXL 97.

CCDC 182/1697. See <http://www.rsc.org/suppdata/cc/b0/b004200p/> for crystallographic files in .cif format.

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