X-RAY STUDIES, SPECTRAL CHARACTERIZATION AND THERMAL BEHAVIOUR OF A TWO-DIMENSIONAL ZINC PHOSPHATE TEMPLATED BY TRIS (2-AMINOETHYL) AMINE [C₆H₂₁N₄][Zn₆(PO₄)₃] (HPO₄)₃]. H₂O.

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ABSTRACT

A two-dimensional (2D) layered zinc phosphate hydrate [C₆H₂₁N₄][Zn₆ (PO₄)₃](HPO₄)₃]. H₂O. I. was synthesized by reacting Zn²⁺ ions with tri-(2-aminoethyl) amine phosphate [C₆H₂₁N₄]⁺[PO₄]⁻]. H₂O. The compound was characterized by powder x-ray diffraction analysis, energy dispersive analysis by x-ray and infrared spectroscopy. The thermal behaviour of compound I was studied under flowing nitrogen and the structure determined by single crystal x-ray crystallography. Compound I crystallizes in the orthorhombic space group Pna2₁(No. 33). a = 18.785(2), b = 8.273(5), c = 18.747(2). volume = 2915(4) Å³, z = 4. The structure consists of a network of Zn₆, PO₄ and HPO₄ tetrahedra which are connected to form a layer with interlamellar region occupied by the protonated amine and water molecules.

KEYWORDS. Metal phosphates. open-framework solids. amine phosphates route. layered structure

INTRODUCTION

The synthesis and characterization of crystalline microporous materials is attractive, not only because of its fascinating structural diversity and many practical applications ranging from catalysis, separation and sensor technology to waste water treatment [Yaghi et al., 1998; Kistiakowski and Kondo, 1998; Lercher and Jencks, 2004; Logar and Kaucic, 2006], but also because they may be nanostructured with respect to pore diameters and overall size of the particles [Breck, 1974. van Grieken et al., 2000, Redig et al., 2003]. Zeolites, which are crystalline inorganic polymers based on a three-dimensional arrangement of SiO₄ and AlO₄ tetrahedra represent the well-known family of microporous materials. After the seminal work of Wilson et al., 1982 on the synthesis of aluminophosphates, whose frameworks are formed from vertex-sharing of AlO₄ and PO₄ tetrahedra, extensive investigations in the last two decades have enabled the synthesis of a variety of novel inorganic materials with open framework structures (Cheetham et al., 1999). By replacing Al³⁺ ions with Zn²⁺ ions, a large number of zinc phosphates encompass a variety of architectures have been isolated and characterized. They include zero-, one-, two- and three-dimensional network structures [Neeraj et al., 1999, 2000, Ayi et al., 2000, 2001, 2002, 2005, Harrison et al., 1992, 1997, 1998]. These materials are generally synthesized hydrothermally in the presence of organic amines as structure directing or templating agents. Neeraj et al., (1959), discovered that phosphates of organic amines are intermediates in the formation of open-framework structures. The versatility of this synthetic route to hybrid open-framework materials has been proven through facile reactions between the amine phosphates and metal ions [Neeraj et al., 2000, Rao, et al. 2000, Ayi et al., 2005]. In this paper, we report the synthesis of an organically templated layered zinc phosphate via amine phosphate route.

Experimental

A layered zinc phosphate of the formula [C₆H₁₃₃N₄][Zn₆(PO₄)₃]. H₂O was isolated via amine phosphate route. The amine phosphate tris(2-aminophosphino)amine (Trenphos) was prepared by following standard procedures of Neeraj et al. (1999) and Ayi (2007). The amine phosphate was then interacted with an aqueous solution of Zn²⁺ ions. In a typical synthesis of compound I, 0.214g Zn(CH₃COO)₂ was dispersed in 2 ml of H₂O followed by addition of 0.342g of Trenphos under effective stirring. The resulting thick gel having a pH of 5 was sealed in a steel autoclave and heated at 160 °C for 48 h. The colourless single crystals formed, were vacuum filtered, washed with distilled water and dried at 30°C.

Characterization

Powder X-ray Diffraction Analysis Powder X-ray diffraction (PXRD) data were collected using Philipsaher model XRD-3000XT. CuKα, Ni filter 40kV x 30mA

Thermogravimetric analysis (TGA)

This was carried out using a Mettler Toledo TG50 instrument under flowing nitrogen with a heating rate of 5° per minute.

Infrared Spectroscopy

The Fourier Transform Infrared (FTIR) spectrum was recorded within 400 - 4000 cm⁻¹ on IFS 66V/S beam spectrometer Measurements were carried out by diffuse reflectance method (DRIFTS).

Determination of Crystal Structure

A single crystal with dimensions 0.05 x 0.05 x 0.20mm was selected under polarizing microscope and glued to a thin glass fibre with cryoacrylate (super glue) adhesive. Single crystal structure determination by X-ray diffraction was performed on a Siemens Smart 1 CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (MoKα, radiation. λ = 0.71073Å) operating at 50kV and 40mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with 20 scans (width of 0.30° and exposure time of 20s per frame) in the 2θ range 3 to 45.5°. Pertinent experimental details for the structure determinations are presented in Table 1.

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### Table 1: Crystal data and structure refinement parameters for compound I

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**Unique data**
- 3157

**Data [1 > 2σ(1)]**
- Full-matrix least-square on F²

**Refinement method**
- R_m = 0.1251
- R_1 > 2σ(1) = 0.0669;
- wR² = 0.1518
- R (all data) = 0.1022;
- wR² = 0.1727

**Goodness of fit**
- 1.010

**No. of variable**
- 194

**Largest diff. map peak and hole eÅ⁻³**
- 1.097 and -1.372

The structure was solved by direct methods using SHELXS - 86 (Sheldrick, 1986) and difference Fourier synthesis. An empirical absorption correction based on symmetry equivalent reflections was applied using SADABS program (Sheldrick, 1994). All the hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. Full-matrix-least-squares structures refinement against F² was carried out using the SHELX TL - PLUS package of programs (Sheldrick, 1993).

**RESULTS AND DISCUSSION**

On the basis of the Weissenberg photographs, the powder pattern was indexed in the orthorhombic space group Pna2 (no. 33). The least-squares refinement was carried out over the powder X-ray data. A least-square fit of the PXRD (Cu - Kα) lines, using the hkl indices generated from single crystal X-ray data gave the following unit cell dimensions: a = 18.785(2), b = 8.2783 (7), c = 18.747(2) Å which are in good agreement with that determined using single-crystal XRD.

The TGA reveals a two-step weight loss (Fig. 1). The weight loss of 2.82% during the first step from 90°C to 180°C corresponds to the removal of the guest water molecule (Calculated: 2.62%). The weight loss of 22.78% during the second step from 180°C to 600°C is attributed to the complete removal of the amine molecules (Calculated: 21.65%). The calcined product was weakly diffracting indicating collapse of the framework.
Fig. 1: TGA Curve of compound I

The IR Spectrum of compound 1 (Fig. 2) reveals the presence of vibrational bands at 1112 – 1015 cm⁻¹ which are characteristic of the asymmetric stretching mode of the PO₄ units. The absorption at 955 cm⁻¹ is due to the symmetric vibrations of the PO₄ groups. The bands at 762 – 602 cm⁻¹ are attributed to the bending vibration of the PO₄ units [Nakamoto, 1997]. The bands due to the template cations are also observed. The asymmetric vibration of the N-H group (νₐₙ) is observed at 2919 cm⁻¹ while the symmetric stretching is observed at 2851 cm⁻¹. The in-plane vibration of the N-H group νₐₕ appears at 1635 cm⁻¹. The absorption at 3622 cm⁻¹ is due to the lattice water molecules (Craver, 1982; Sociates, 1950).

Fig. 2: Infrared Spectrum of Compound I
The atomic coordinates, selected bond lengths and bond angles for the single crystal data are presented in Tables 2 and 3, respectively. The single-crystal structure analysis revealed that compound I [(CH₂H₂N₂)_2][Zn₆(PO₄)₄(HPO₄)₂H₂O] is a 2D layered open-framework material. The fundamental building units of I (Fig. 3) include six crystallographically independent Zn atoms and six P atoms belonging to the inorganic framework, four N atoms, six C atoms and one O atom belonging to the guest molecules.

### Table 2: Atomic coordinates [x 10⁴] and equivalent isotropic displacement parameters [Å² x 10⁴] for [CH₂H₂N₂][Zn₆(PO₄)₄(HPO₄)₂H₂O].

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### Table 3: Selected bond distances and angles in [(CH₂H₂N₂)_2][Zn₆(PO₄)₄(HPO₄)₂H₂O].

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Summary Transformations used to generate equivalent atoms:
=1x-1/2,-y-1/2z #2x,y+1/2,-z #3x,y-1,z #4x+1/2,-y-1/2,z
=5x+1/2,-y+3/2,z #6x-1/2,-y+1/2,z #7x+1/2,-y+1/2,z #8x-1/2,-y-3/2,z

Fig. 3: ORTEP Plot of $[\text{C}_6\text{H}_2\text{N}_4][\text{Zn}_6(\text{P}_0\text{A})_3(\text{HP}_0\text{A})_3] \cdot \text{H}_2\text{O}$
Each Zn atom is tetrahedrally coordinated with four oxygen atoms with Zn–O bond distances in the range 1.890(2) – 2.022 (14) Å (av. Zn-O) = 1.961 Å. The O–Zn–O bond angles are in the range 97.6(6) – 127.3(7)° (av. O–Zn–O) = 109.5°. Of the six independent P atoms, P(1), P(2), P(3), and P(4) are connected to Zn atoms via four Zn-O-P linkages, while P(5) and P(6) are connected via three Zn–O–P linkages with one terminal P-O bond. The average P–O distances of 1.545, 1.540, 1.545, 1.533, 1.525 and 1.533 Å result for P(1), P(2), P(3), and P(4), P(5) and P(6) respectively (Table 3). The O-P-O bond angles are in the range 103.9(9) – 113.5(9)° (av. O–P–O) = 109.5°. The geometrical parameters observed in the present compound are in good agreement with similar open-framework zinc phosphates [Neeraj et al., 2000, Ayi et al., 2001].

The inorganic framework [Zn6(PO4)3(HPO4)] is anionic with -3 charge. The charge neutrality is achieved by the incorporation of the triply protonated amine molecule. The structure of this, consists of a network of ZnO6, PO4 and HPO4 moieties forming a layer with the interlamellar region occupied by the protonated amine and water molecules (Fig. 4).

In conclusion, by employing aminephosphosphate route, we have been able to isolate a 2D layered zinc phosphate similar to that obtained by Ayi et al. (2001) as a transformation product of a zero-dimensional monomer [CaH2·H2O] [Zn(HPO4)·(H3PO4)2]. Since compound I was obtained in high yield, we have been able to study the framework vibrations and its thermal properties in detail.

ACKNOWLEDGEMENT

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