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# A hybrid open-framework structure: Hydrothermal synthesis and characterization of zinc (II) ethylaceto-acetate phosphate

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**ABSTRACT**

A novel inorganic-organic hybrid open- framework zinc ethylacetoacetate phosphate ($Zn_2(CH_3COCHCO_2C_2H_5)_{0.5}$ $(H_2PO_4)_3$), has been synthesized at $60^oC$ in the presence of a β-keto ester (ethylacetoacetate), under hydrothermal conditions. The compound has been characterized by powder X-ray diffraction analysis, scanning electron microscopy, energy dispersive analysis by X-ray and infrared spectroscopy and its thermal properties studied by thermogravimetric analysis under nitrogen atmosphere. The PXRD pattern indicates phase purity and a novel phase while the EDAX indicates a Zn / P ratio of 2: 3. SEM shows that the compound consists of hexagonal crystals with a particle size of 1.5μ. The infrared spectrum clearly shows the presence of the vibrational band characteristics of (-O-C-O-) group around 1626 $cm^{-1}$.

**Keywords:** Open-framework solids, hybrid materials, hydrothermal synthesis.

## INTRODUCTION

The synthesis of hybrid solids whose frameworks are built up by the connection of inorganic moieties with organic molecules having complexing functional groups such as phosphonates, carboxylates or sulfonates is currently a very important area of research [Robl, 1992; Clearfield, 1996; Yaghi, *et al.*, 1998]. The design of such hybrid solids is attractive not only because it takes advantage of the metal coordination, but also because of the flexibility of the organic linkers, which helps in the formation of inorganic sub-network with different dimensionalities [Ferey, 2001; Barthelet *et al.*, 2003; Rao *et al.*, 2004). A large variety of coordination polymers have been synthesized by classical solution chemistry [Jones, 1998]. Nevertheless, using hydrothermal techniques can considerably extend the range of structural types accessible for each metal-organic system. Because of the diminution of the water dielectric constant, interactions between organic and inorganic partners are different under hydrothermal conditions from those under mild ones [Barrer, 1982; Whittingham, 1996]. For positively charged organic molecules (protonated amine or alkylammonium cation) the condensation of the inorganic network is oriented via weak interactions between the inorganic skeleton and the organic component. This behaviour is called templating effect and gives rise to a variety of products (Jones, 1989; Davis and Lobo, 1992; Cheetham *et al.*, 1999). With negatively charged species (e.g. carboxylate, phosphonate ions) the presence of an electron pair donor (Lewis base) leads to the formation of coordination bonds. The organic component belongs to the framework and creates most of the time, neutral open networks. Thus using a β-keto ester (ethylacetoacetate), we have been able to create an extended hybrid solid**:** $[Zn_2(H_2PO_4)_3(C_6H_9O_3)_{0.5}H_2O]$, **I,** with open frameworks. In this article we report the synthesis, characterization and thermal properties of this hybrid solid.

## EXPERIMENTAL

In the sythesis of compound **I**, 0.125g of ZnO was dispersed in 2.2ml of distilled water followed by addition of 0.25ml of conc. HCl as a mineralizing agent .To this mixture, 0.16ml of $H_3PO_4$ was added under effective stirring and finally 0.58ml of ethylacetoacetate was added and the stirring continued for 10 mins. The resultant mixture of composition ZnO: $3C_6H_{10}O_3$:$2H_3PO_4$; 2HCl: $80H_2O$, with a pH=3 was sealed in a pyrex glass pressure bomb and kept at $60^oC$ for 24h. The resultant products were filtered, washed, and dried at room temperature.

## CHARACTERIZATION

**Powder x-ray diffraction analysis**: Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $Cuk_\alpha$

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radiation (λ = 1.5406Å). The step size was 0.02 and the count time was 4s.

**Thermogrametric analysis**: This was performed using Mettler-Toledo TGA analyser under flowing nitrogen from room temperature to 700$^{O}$C.

**SEM/EDAX**: The surface morphology of the as-synthesized compound and its metal-phosphorous ratio was checked using LEICA S440I Scanning Electron Microscope equipped with energy dispersive analyzer.

**Infrared spectroscopy**: The infrared spectrum was recorded within 400- 4000cm$^{-1}$ regions on a Nicolet Impact 410FTIR spectrometer using KBr pellets.

## RESULTS AND DISCUSSION

The SEM image of compound I (Fig.1) shows a uniform chunky hexagonal crystal of size 1.5µ. The PXRD pattern (Fig. 2) indicates phase purity as well as a novel open-framework phase. EDAX result (Fig.3) shows a Zn/P ratio of 2:3. Chemical analysis of the sample gave the following results: C, 7.41%, H, 2.28%. These values agree well with those calculated from the proposed formula $(C_6H_9O_3)_{.0.5}[Zn_2(H_2PO_4)_3.H_2O]$. The presence of an electron pair donor: the ethylcetoacetate dianions leads to the formation of coordination bonds. The acetoacetate dianion contributes –2 x 0.5 = 1 charge while each $H_2PO_4$ group contributes –1 giving a total of –4 charge. This –4 charge is being balanced by the presence of two zinc atoms in the framework.

The thermal analysis under flowing nitrogen gas (heating rate 10$^{O}$ per min.) between room temperature up to 700$^{O}$C (Fig. 4) shows two weight losses at 74.6$^{O}$C and 296.5$^{O}$C which correspond to the removal of ethylacetoacetate and lattice water with respective loss of 14.72 and 5.41%. These experimental values are on the whole in good agreement with the theoretical value of 13.28% for the removal of ethylacetoacetate group and 3.7% for loss of water molecule. The calcined sample was weakly diffracting indicating the collapse of the framework after the removal of these components. This analysis coupled with the chemical analyses: Zn, 26.89% (25.98%), P, 19.11% (20.65%), C, 7.41% (7.33%,), H,2.18% (2.28%), supports the proposed formula of this material as $(C_6H_9O_3)_{.0.5}[Zn_2(H_2PO_4)_3.H_2O$ .

The infrared spectrum (Fig.5) clearly shows the presence of the vibrational band characteristics of the framework -(-O-C-O-)- groups (Barthelet *et al., 2003* ) around 1626cm$^{-1}$ . The strong absorption bands at 1175 and 1088 cm$^{-1}$ are associated with the asymmetric stretching vibration of $PO_4$ groups whereas those at 962 and 730cm$^{-1}$ correspond to its bending mode ( Nakamoto, 1997; Gao *et al.*, 1996,). The bands at 541 and 504cm$^{-1}$ are associated with the vibration modes of a four-membered (tetrahedral) ring of $ZnO_4$. The band at 1664cm$^{-1}$ is associated with the stretching vibration of C=O group while the band at 1316cm$^{-1}$ is due to the symmetric stretching mode of -$CH_3$ (Vaidhyanathan *et al.*, 2003). The broad band at 3272cm$^{-1}$ is due to the presence of water molecules in the structure.

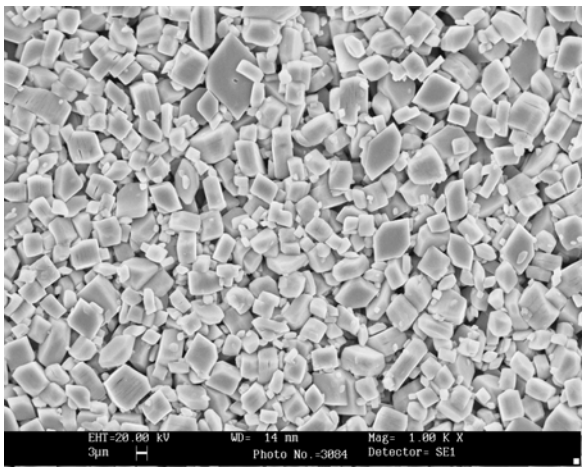


**Fig. 1. The SEM image of compound I.**

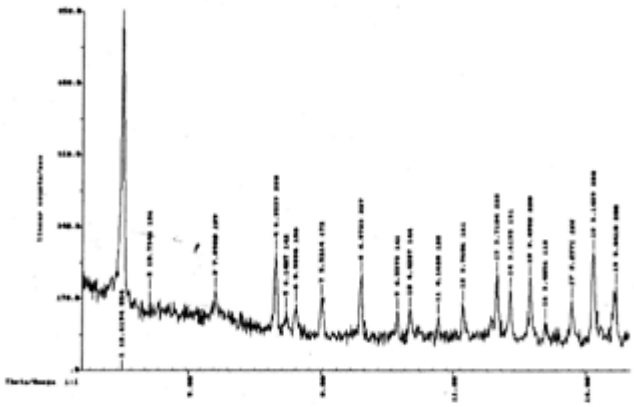

**Fig. 2. PXRD pattern of $[C_6H_9O_3]_{0.5}[Zn_2(H_2PO_4)_3].H_2O$**

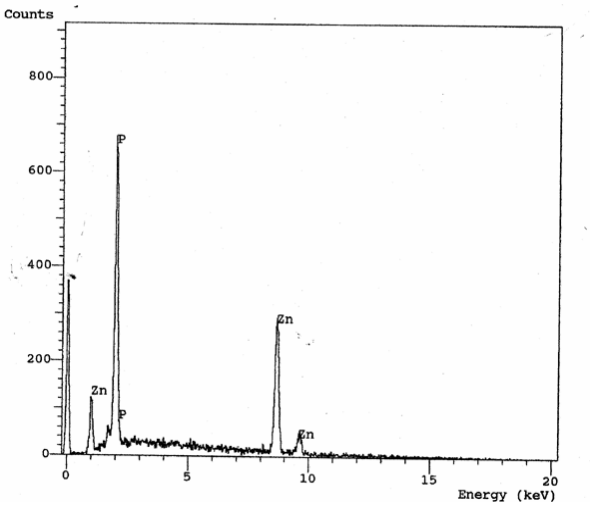


**Fig. 3. EDAX spectrum of $[C_6H_9O_3]_{0.5}[Zn_2(H_2PO_4)_3].H_2O$**

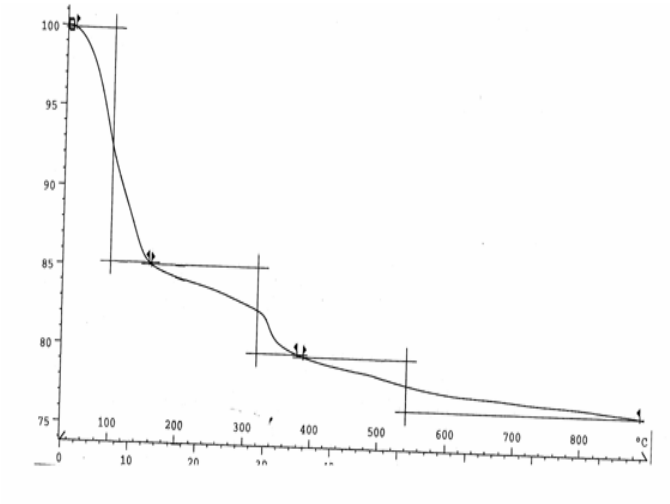

**Fig. 4. TGA curve of $[C_6H_9O_3]_{0.5}[Zn_2(H_2PO_4)_3].H_2O$**

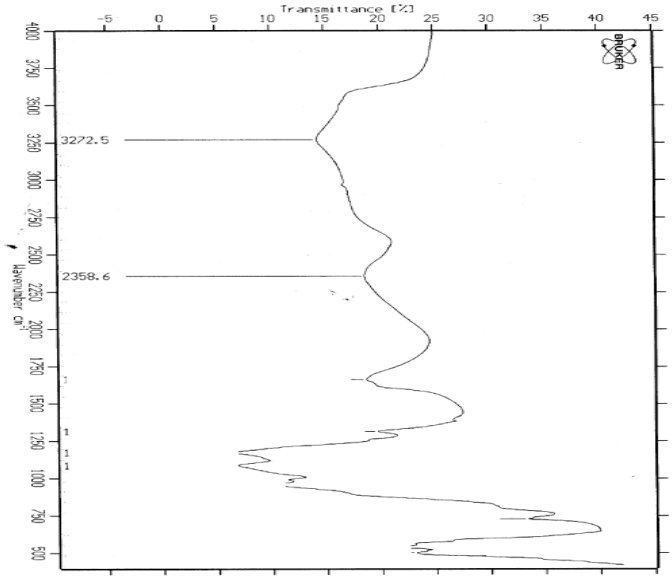


**Fig. 5: IR spectrum of $[C_6H_9O_3]_{0.5}[Zn_2(H_2PO_4)_3].H_2O$**

In conclusion, a new hybrid material in the zincophosphate-ethylacetoacetate family has been synthesized via solution-mediated mechanism under hydrothermal conditions. This is a potential material for catalysis, adsorption and ion-exchange studies. Research is underway to isolate good quality single crystals of **I** for structure determination by X-ray crystallography.

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