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Synthesis and crystal structure of a 3-D zinc phosphate, $[C_5N_2H_{14}][Zn_2(PO_3(OH))_3]$, containing (4.8) net sheets

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Abstract

A new 3-D zinc phosphate, $[C_5N_2H_{14}][Zn_2(PO_3(OH))_3]$, has been synthesised under solvothermal conditions in the presence of 1-methylpiperazine. The structure, determined by single-crystal X-ray diffraction at 293 K (RMM = 520.9, orthorhombic, space group $P2_1\,2_1\,2_1$; a = 10.0517(2) Å, b =10.4293(2) Å and c = 14.9050(5) Å; V = 1562.52 Å^3; Z = 4; $R(F)$ = 2.60%, $wR(F)$ = 2.93%), consists of vertex linked ZnO_4 and $PO_3(OH)$ tetrahedra assembled into (4.8) net sheets which in turn are linked through further $PO_3(OH)$ units to generate a 3-D framework. 1-Methylpiperazinium cations reside within the 3-D channel system, held in place by a strong network of hydrogen bonds. The (4.8) net sheets occur in a number of zeolite structures e.g. ABW and GIS and related zinc phosphate phases. ***To cite this articles: F.O.M.Gaslain, A.M.Chippindale, C.R.Chimie 8 (2005).***

Résumé

Un nouveau composé zincophosphate, $[C_5N_2H_{14}][Zn_2(PO_3(OH))_3]$, adoptant une structure tridimensionnelle, a été préparé en présence de 1-méthylpipérazine comme agent structurant et en utilisant des conditions solvothermales. L'étude cristallographique réalisée à 293 K par diffraction des rayons X d'un monocristal montre que le composé est orthorhombique, avec une maille de dimensions : a = 10.0517(2) Å, b = 10.4293(2) Å et c = 14.9050(5) Å; V = 1562.52 Å^3. Le groupe spatial est $P2_12_12_1$, avec Z = 4. La détermination de l'arrangement atomique aboutit au résultat final $R(F)$ = 2.60%, $wR(F)$ = 2.93%. La structure décrite consiste en l'assemblage par leurs coins de tétraèdres de ZnO_4 et de $PO_3(OH)$ pour former des feuillets poreux de type (4.8). Ces feuillets sont ensuite reliés ensemble par des tétraèdres de $PO_3(OH)$ pour générer une structure tridimensionnelle. Les cations 1-méthylpipérazinium résident à l'intérieur du réseau poreux tridimensionnel et sont maintenus en place grâce à un important nombre de liaisons hydrogène. Les feuillets poreux de type (4.8) se retrouvent dans un nombre important de structures zéolithiques, notamment ABW et GIS, ainsi que d'autres composés zincophosphates. ***Pour citer cet article : F.O.M.Gaslain, A.M. Chippindale, C.R. Chimie 8 (2005).***

Keywords: Zinc phosphate; Solvothermal synthesis; Open-framework structure; 1-Methylpiperazine; Crystal structure

Mots clés : Phosphate de zinc ; Synthèse solvothermale ; Structure à architecture ouverte ; 1-Méthylpipérazine ; Structure cristalline

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1. Introduction

Since the discovery of the first microporous zinc phosphates (ZnPOs) by Gier and Stucky [1] in 1991, much effort has been devoted to preparing novel structures within the zinc-phosphate system. Hydro- or solvothermal synthesis conditions are often employed using organic amines as the structure directing agents or templates and these are usually incorporated, in their protonated forms, into pores or cavities within anionic zinc-phosphate frameworks. Over 100 templated ZnPOs have now been characterised, making this the fastest growing class of open-framework phosphates, and they exhibit great structural diversity with ZnO_4 tetrahedra linked via PO_4 units to generate 0-D (monomer), 1-D (chain, ladder), 2-D (layer) and 3-D architectures. As well as direct synthesis, a number of ZnPOs of higher dimensionalities have been prepared from low dimensional phases. For example, monomer [2], chain [3] and layered [4] ZnPOs transform to 3-D structures on heating under modest conditions, especially in the presence of additional amine. These transformations have thrown some light on the assembly mechanisms of 3-D ZnPO phases as structural units present in low dimensional frameworks are retained during the condensation processes [5,6]. Interestingly, some of these reactions are reversible, with 3-D frameworks forming 1-D ladders under acidic conditions [7].

Of the many 3-D zinc phosphates reported, particularly eye catching examples include $[TH_2][Zn_3(PO_4)_2(HPO_4)]\cdot 2H_2O$ (T = 1,2-diaminocyclohexane) (ND-1) [8], containing large-pore 1-D channels bounded by 24-membered rings (24 MR) of alternating ZnO_4 and PO_4 units and $[TH_2][Zn_4(HPO_4)_2]\cdot 3H_2O$ (T = 1,6-diaminohexane), containing isolated trimers of ZnO_4 groups together with 5- and 20-MR [9]. The range of stoichiometries found in the 3-D frameworks is now quite wide with examples known having P:Zn ratios of 3:4, 4:5, 5:6, 6:7, 1:1, 5:4, 4:3, 3:2 and 2:1. Pertinent to the present work are 3-D materials with P:Zn ratio of 3:2, of which six examples containing organic amine cations have been reported to date; namely, $[TH]_2[Zn_2(HPO_4)_3$ (T = ethylamine) [10], $[TH_2][Zn_2(HPO_4)_3]\cdot xH_2O$ (x = 0, T = ethylenediamine [11], 1,2-diaminopropane [12] and piperazine [13]; x = 1, T = 1,4-diazacycloheptane (homopiperazine) [14]), and $[TH_2][Zn_2(PO_4)(H_{1.5}PO_4)_2]$ (T = piperazine [13,15]). Here we report the synthesis and characterisation of a new zinc phosphate, $[C_5N_2H_{14}][Zn_2(HPO_4)_3]$, with P:Zn ratio 3:2 and containing the cyclic amine, 1-methylpiperazine. The relationship of this structure to two 3-D ZnPOs with the same stoichiometry [12,14] is discussed.

2. Synthesis

Single crystals of the title compound, $[C_5N_2H_{14}][Zn_2(HPO_4)_3]$, were synthesised under predominantly non-aqueous solvothermal conditions. ZnO (0.36 g) was dispersed in 6.00 cm^3 of ethylene glycol by stirring. 1-Methylpiperazine (0.42 cm^3) and orthophosphoric acid (0.70 cm^3, 85 wt.%) were then added with further stirring. Finally, hydrochloric acid (0.20 cm^3) was added to form a thick gel with the overall composition ZnO: 24.32 $HO(CH_2)_2OH$: 0.86 $C_5N_2H_{12}$: 2.31 H_3PO_4(aq): 0.55 HCl(aq). The gel was sealed in a 23 cm^3 Teflon-lined stainless steel autoclave and placed in an oven at 433 K for 7 days. The solid product obtained from this synthesis consisted of a very hard dark glass-type material of unknown composition with a few large colourless blocks of the title product. The crystals could be recovered manually by adding deionised water to the glassy material. This operation trans-

Table 1
Crystallographic data for $[C_5N_2H_{14}][Zn_2(PO_3(OH))_3]$

Formula	$[C_5N_2H_{14}][Zn_2P_3O_{12}H_3]$
M_r	520.90
Crystal size (mm)	0.16 × 0.28 × 0.40
Crystal habit	Colourless plate
Crystal system	Orthorhombic, $P2_12_12_1$
a (Å)	10.0517(2)
b (Å)	10.4293(2)
c (Å)	14.9050(5)
Cell volume (Å^3)	1562.52
Z	4
Temperature (K)	293(2)
ρ_{calc} ($mg\ m^{-3}$), μ(Mo Kα) (mm^{-1})	2.214, 3.442
Radiation, wavelength (Å)	Mo Kα, 0.71073
Unique data, observed data ($I > 3\sigma(I)$)	3490, 3238
R_{int}	0.01
Residual electron density (min, max) (e Å^{-3})	–0.86, 0.70
Number of parameters refined	227
$R(F)$, $wR(F)$	0.0260, 0.0293