

Hydrothermal synthesis and structure of a new layered zincophosphate intercalated with 3-Methylaminopropylamine cations

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Abstract: A novel layered zincophosphate (ZnPO–MPA) was prepared by hydrothermal crystallization using 3-methylaminopropylamine (MPA) as a structure-directing agent. The structure consists of macroanion $[\text{Zn}_2\text{P}_3\text{O}_8(\text{OH})_3]^{2-}$ layers which are built up of 4-membered ring channels. The channels (of about 3.7 Å diameter) arise through the connection of the neighbouring rings by two oxygen bridges. The negative charge of the layers is compensated by diprotonated MPA molecules which are stacked parallel to the ring channels. ZnPO–MPA is stable up to 300 °C. At higher temperatures MPA decomposition begins followed by a dehydration, which occurs through condensation of the framework hydroxyl groups. The activation energy of the MPA decomposition is high due to the fact that the layers and MPA cations are held together by strong hydrogen bonds.

Keywords: inorganic compounds, chemical synthesis, electron microscopy, X-ray diffraction, crystal structure.

INTRODUCTION

Open-framework metallophosphates are of great interest not only due to their structural diversity but also to their potential application in the areas of sorption, separation and catalysis. Generally, these solids are formed under hydrothermal conditions. Hydrothermal crystallization seems to be a promising route for the production of inorganic solids with extended architectures since the composition and temperature of the reaction mixture can be varied over a wide range. Also, the presence of an organic amine in the reaction mixture has a crucial structure-directing role. Usually, these species exert structural specificity enabling inorganic moieties to connect themselves in a specific manner.

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In recent years, a variety of zincophosphates with neutral frameworks or anionic chains, layers and frameworks have been reported.^{1–9} They are mainly built up of alternating Zn polyhedra (ZnO_4 , ZnO_5 , ZnO_6) and P tetrahedra [such as PO_4 , $\text{PO}_2\text{O}(\text{OH})$, $\text{PO}_2(\text{OH})_2$, *etc.*], which leads to different Zn/P ratios and to compositional diversity due to various manner in which the Zn units can be connected with the adjacent P tetrahedra *via* oxygen atoms. Interesting features of the zincophosphate chemistry are also the Zn–O–Zn chains,⁵ which additionally expand the structural complexity. Moreover, there are zincophosphates with unique structural features – *e.g.*, the two systems exhibiting gigantic pore structure: 24-membered rings and 20-membered ring channels.⁷ Finally, zeolite analogs have also been found among zincophosphates.^{10–13}

In this paper, the hydrothermal crystallization of a zincophosphate in the presence of 3-methylaminopropylamine (MPA) was investigated. Until now this organic compound has not been employed as a structure-directing agent in the synthesis of metallophosphates.

EXPERIMENTAL

Synthesis

The synthesis was carried out hydrothermally in poly tetrafluoroethylene-lined stainless-steel containers. Two reaction mixtures, A and B, were used.

Mixture A:

From a mixture of relative molar composition of $\text{Zn}(\text{ac})_2 : 5.5\text{H}_3\text{PO}_4 : 2\text{MPA} : 100\text{H}_2\text{O}$, where $\text{Zn}(\text{ac})_2$ is zinc acetate dihydrate (Aldrich) and 3-methylaminopropylamine is a 98 % solution (Fluka), a white suspension resulted. The mixture was prepared by successive additions of phosphoric acid and MPA to a vigorously stirred solution of zinc acetate in water. The initial pH was about 2.5 and it has slightly increased to 3 by the end of the reaction. Crystallization was performed at 120° and 160 °C for 2–12 days.

Mixture B:

A similarly prepared mixture with a relative molar composition of $\text{Zn}(\text{ac})_2 : 3\text{H}_3\text{PO}_4 : 2\text{MPA} : 100\text{H}_2\text{O}$ gave a thick white suspension. The initial pH was 5.5 and it had not changed by the end of the reaction. Crystallization was performed at 120° and 160 °C for 2–12 days.

The products were filtered and washed with distilled water, then ultrasonically treated in order to remove amorphous impurities, and air-dried.

Instrumentation

The crystal morphology analysis and elemental analysis (Zn and P) of the products were conducted by inductively coupled plasma emission spectroscopy. Carbon, hydrogen and nitrogen were determined using a standard C–H–N analyzer. The crystal morphology was examined using a JEOL 5800 scanning electron microscope (SEM). Fourier transformed infrared (FTIR) spectra were recorded in the 4000 to 400 cm^{-1} range on a Digilab-FTS-80 spectrophotometer, using the KBr wafer technique. Thermogravimetric analysis and differential scanning calorimetry (TGA and DSC, respectively) were performed using a SDT 2960 Simultaneous DSC–TGA instrument (TA Instruments) at a heating rate of 5 °C/min under a helium flow.

X-Ray powder diffraction patterns were obtained on a Philips PW 1710 Diffractometer using $\text{CuK}\alpha$ radiation of 0.04° 2 θ steps from 5 to 55° 2 θ with 1 s per step.

A colorless prismatic-like single crystal ($0.05 \times 0.05 \times 0.022 \text{ mm}^3$) was selected for single-crystal X-ray structural analysis. The structural parameters and details of the crystallographic data will be published elsewhere.

RESULTS AND DISCUSSION

The XRD pattern of the product obtained by crystallization of reaction mixture A at 120°C showed the crystalline phase to be the hopeite modification of zinc phosphate. It is interesting to note that it is known that hopeite is formed not only as a precursor phase during hydrothermal crystallization of an open-framework zincophosphate¹⁴ (indicating that the crystallization of this phase is kinetically favoured) but also by transformation of open-framework zincophosphates during chemical treatments,¹⁵ or even during the washing procedure.⁹

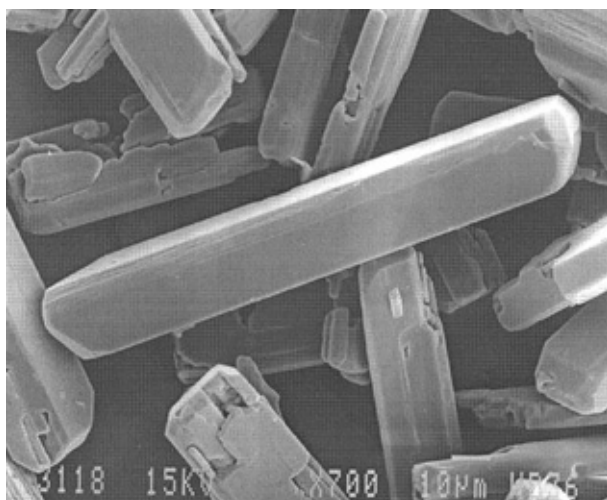


Fig. 1. A SEM photograph of ZnPO-MPA, magnification 700x.

Crystallization of mixture A at 160°C , as well as of mixture B at both employed temperatures gave only one crystalline phase (in the ensuing text it is designated as ZnPO-MPA). A SEM photo of ZnPO-MPA is given in Fig. 1 from which it can be seen that the crystals consisted of parallelepipeds with an average size of about $100 \mu\text{m}$.

The FTIR spectrum of ZnPO-MPA (Fig. 2) shows vibrational features of entrapped organic molecules: the intense bands in the range $3200\text{--}2000 \text{ cm}^{-1}$ mainly arise from amine groups. The strong band at about 1540 cm^{-1} can be assigned to NH_3^+ ions,¹⁶ indicating that the organic species is protonated and, accordingly, the zincophosphate network is anionic. There are also three strong bands at 1100 , 1065 and 1030 cm^{-1} corresponding to the asymmetric stretching vibrations of PO_2 groups. The same bands appeared in the spectrum of an aluminophosphate with a chain structure in which two oxygen atoms from the phosphorous coordination sphere were bonded to aluminium atoms, while the other two oxygens belonged to P=O bonds.¹⁷ The peaks at about 600 , 565 , 520 and 460 cm^{-1} are attributed to bending vibrations of PO_4 groups.¹⁸

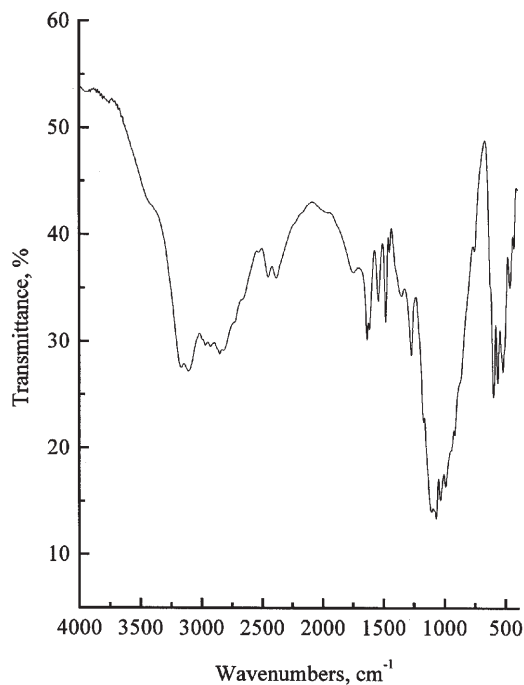


Fig. 2. The FTIR spectrum of ZnPO-MPA.

Single-crystal analysis showed that the structure of ZnPO-MPA consists of anionic sheets $[\text{Zn}_2\text{P}_3\text{O}_8(\text{OH})_3]^{2-}$ in (101) crystal planes with charge compensating

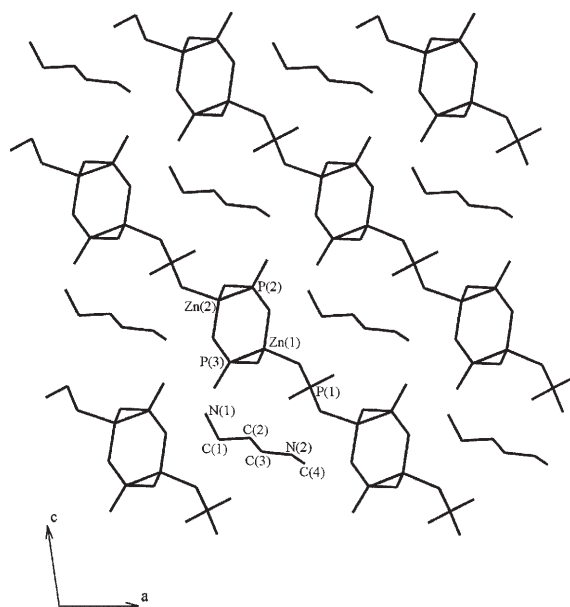


Fig. 3. A schematic representation of the ZnPO-MPA structure viewed down the *b* crystallographic axis. The hydrogen atoms are omitted for clarity.

diprotonated MPA species between the sheets. The sheets are built up of 4-membered ring channels, which extend along the *b* axis, as shown in Fig. 3. Recently, Rao and co-workers found¹⁹ that the four-membered ring is a genuine basic building unit in open-framework metallophosphates. The results presented here obviously give support to such a finding. Diprotonated MPA molecules are stacked parallel to the ring channels and in effect hold together adjacent zinc phosphate sheets by interacting with them through strong N \cdots O hydrogen bonds. Each protonated diamine forms 5 such N \cdots O short contacts, their length ranging from 2.82(1) to 3.08(1) Å.

The asymmetric unit contains two crystallographically distinct Zn atoms and three P atoms, as shown in Fig. 4. All the zinc atoms are tetrahedrally coordinated by their oxygen neighbours with Zn–O distances in the range 1.909(3)–1.965(4) Å and O–Zn–O angles in the range 99.6(2) to 121.5(2)°, which is in accordance with

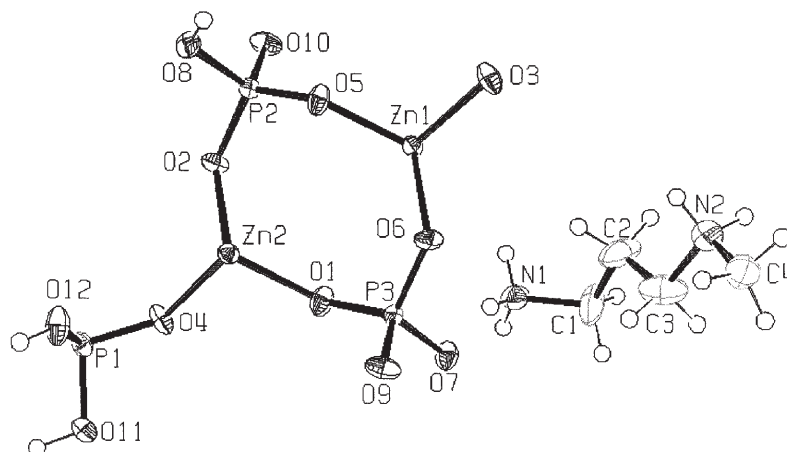


Fig. 4. Asymmetric unit of the structure of the zincophosphate ZnPO-MPA showing the atom-labelling scheme and 50% thermal ellipsoids. The open circles represent hydrogen atoms.

literature values.^{9,18} Of the three independent P atoms, P(1) forms only two P–O–Zn linkages and has two terminal P–O bonds, whereas P(2) and P(3) are connected to Zn *via* three P–O–Zn linkages, and have one terminal P–O bond each. The P–O distances are in the range 1.502(4)–1.567(4) Å and the O–P–O angles are in the range of 105.3(2)–115.6(2)°. These geometric parameters are also in good accord with those of open-framework zinc phosphates.^{9,18}

The linkage Zn(1)–O–P(3)–O–Zn(2)–O–P(2)–O gives rise to the 4-membered rings. The neighbouring rings are connected by two oxygen bridges resulting in channels of about 3.7 Å diameter (Fig. 5). The adjacent channels are linked into a layer by Zn(1)–O–P(1)–O–Zn(2) bridges.

TGA of ZnPO-MPA shows an overall weight loss of about 23 wt.% (Fig. 6), which is in agreement with the elemental analysis. It is evident that the sample was thermally stable up to 300 °C. At higher temperatures, the decomposition of organic species begins, causing also a structural change, which is evident in the XRD

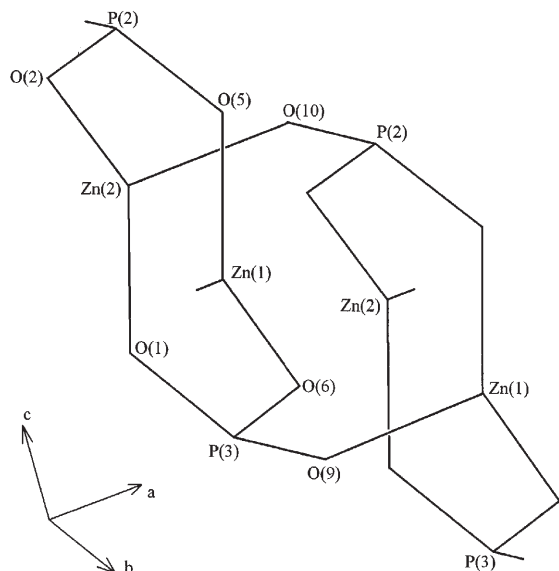


Fig. 5. The connection mode of neighbouring rings giving rise to channels within a layer.

pattern. There were two mass losses. The first mass loss took place in the 295–465 °C temperature range ($\approx 17.2\%$) and the second one in the 465–550 °C temperature range ($\approx 6\%$). According to the C–H–N analyses, the first weight loss corresponds to MPA decomposition whereas the second loss is due to a dehydration process, which occurs through the condensation of the framework hydroxyl groups.

As the DTG curve shows (Fig. 6), MPA decomposition is a three-step process. A kinetics analysis of the TG data reveals that the three-step decomposition can be

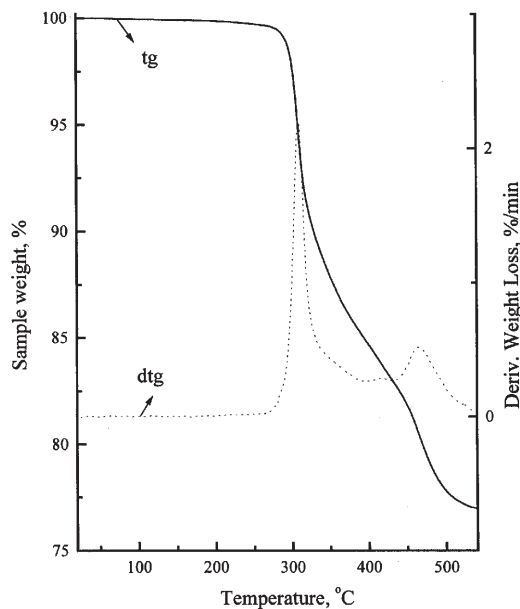


Fig. 6. The TG curve of ZnPO-MPA.

described as follows. The first step occurred in the 295–344 °C temperature range, the second one in the 345–444 °C temperature range and the third step in the 445–465 °C temperature range. If the rate expression for a non-isothermal reaction is represented as:

$$\frac{d\alpha}{dt} = Ae^{-E/RT} f(\alpha)$$

where α is the degree of conversion, then the first step can be best described using the Coats-Redfern model:²⁰

$$f(\alpha) = (1 - \alpha)^n$$

with a reaction order $n = 2$. The second step is best described by the Valensi diffusion model:²¹

$$f(\alpha) = [-\ln(1 - \alpha)]^{-1}$$

while the third step is best described by the parabolic diffusion law²¹:

$$f(\alpha) = 1/\alpha$$

The dehydration process (condensation of the framework hydroxyl groups) occurred in the 430–505 °C temperature range (Fig. 6) and is best described by the Valensi diffusion model. The activation energies (E), the frequency factors (A) and the R_f factors of the least-squares linear regression fit for the decomposition of MPA and for the dehydration are presented in Table I. The activation energy of 343 kJ/mol for the first step of the MPA decomposition is rather large, which is in agreement with the fact that the anionic layers and MPA cations are held together by strong hydrogen bonds. Regarding the A values for the three steps, it has been, somewhat speculatively, suggested^{22,23} that in solid state reactions, a high A value refers to a case where the activated complex has a greater degree of freedom than the reactants; *e.g.*, it could be an activated complex that extends itself from the reactant surface and both rotates and translates parallel to the surface. The low A value, according to this suggestion, is characteristic for processes that are mainly surface reactions. In terms of such an interpretation, the first step of the decomposition of MPA would feature a rather “free” activated complex, whereas the second and third step of the MPA decomposition, as well as the dehydration process occur as surface reactions.

TABLE I. Kinetic data for the decomposition of the MPA template and for the dehydration

Temperature range/°C	$E/\text{kJ mol}^{-1}$	A/s^{-1}	R_f
295–344	343	4.8×10^{28}	0.989
345–444	31.3	1.5×10^{-1}	0.997
445–465	28.7	4.0×10^{-2}	0.996
430–505	42.9	6.43×10^{-1}	0.995

CONCLUSION

3-Methylaminopropylamine exerts a templating role in the formation of a novel zincophosphate structure. This demonstrates again the versatility of the chemistry of zinc phosphate. The formation of 4-membered rings, which were found to act as the basic building units in open-framework phosphate-based structures, indicates that 3-methylaminopropylamine could be a suitable template not only for layer zincophosphates but also for 3-D frameworks. In this sense, further work will be directed toward the investigation of crystallization conditions for the formation of open-framework zincophosphates.

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ИЗВОД

ХИДРОТЕРМАЛНА СИНТЕЗА И СТРУКТУРА ЈЕДНОГ НОВОГ СЛОЈЕВИТОГ
ЦИНКОФОСФАТА ИНТЕРКАЛИРАНОГ СА
3-МЕТИЛАМИНОПРОПИЛАМИН-КАТЈОНОМ

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Један нови слојевити цинкофосфат (ZnPO–MPA) добијен је хидротермалном кристаллизацијом коришћењем 3-метиламинопропиламина (MPA) као агенса за усмеравање структуре. Структура се састоји од макроанјонских слојева $[Zn_2P_3O_8(OH)_3]^{2-}$ који су изграђени од канала у виду четворочланог прстена. Канали (пречника око 3,7 Å) настају повезивањем суседних прстенова преко кисеоничних мостова. Негативно наелектрисање слојева компензовано је двопротонованим MPA који су наслагани паралелно прстенастим каналима. ZnPO–MPA је стабилан до 300 °C. На вишим температурама почиње разлагање MPA које је праћено дехидратацијом, а ова се дешава путем кондензације хидроксилних група решетке. Енергија активације разлагања MPA је велика због тога што се слојеви и катјони MPA узајамно држе јаким водоничним везама.

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