



# Synthesis and characterization of three-layered zinc phosphites containing *tert*-octylamine molecules with template and ligand roles



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## ARTICLE INFO

### Article history:

Received 27 February 2013

Received in revised form

30 April 2013

Accepted 5 May 2013

Available online 18 May 2013

### Keywords:

Zinc phosphite

Hydrothermal synthesis

Solvothermal synthesis

Ligand and template

## ABSTRACT

Three-layered zinc phosphites containing single monoamine molecules with different roles have been synthesized using hydro(solvo)thermal methods and characterized by single-crystal X-ray diffraction, thermogravimetric analysis, and infrared spectroscopy. Compound **1**,  $(C_8H_{17}NH_3)_4Zn_3(HPO_3)_5 \cdot 3H_2O$ , consists of 20-ring layer structures sandwiched by water molecules and protonated *tert*-octylamine molecules. The structure of  $Zn(C_8H_{17}NH_2)(HPO_3)$  (compound **2**) is composed of  $4.8^2$  network structures, wherein the *tert*-octylamines are coordinated to the Zn atom as pendant groups. Compound **3**,  $(C_8H_{17}NH_3)_2Zn_4(C_8H_{17}NH_2)(HPO_3)_5$ , was prepared in which the amine plays a dual role as both a ligand and a counteranion. In addition, compound **1** is the first layered metal phosphite with large 20-ring windows. This group of substances represents the first example of the preparation of compounds in which the reactivity of incorporated single amine molecules is varied by adjusting the synthesis conditions.

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## 1. Introduction

Great effort has been devoted to the synthesis of metal phosphates in the presence of organic amines because of the interesting structural features and potential applications of the resulting compounds in intercalation, catalysis, and ion exchange applications [1,2]. The amines usually play two different roles in the formation of metal phosphate structures: (1) as templates or space-filling counterions, which is the most common; and (2) as ligands that bind to the metal, as in  $[In_5F_3(PO_4)_4(H_2O)_2(en)_3]$  [3]. It is less common that amines take on both roles in one structure. Only two phosphates have been previously reported that exhibit this behavior: a zincophosphate with 1,3-diaminopropane molecules and a gallophosphate with 1,2-diaminocyclohexane molecules [4,5].

Recently, the pseudotetrahedral phosphite group  $HPO_3^{2-}$  has been employed as a replacement building unit for the tetrahedral phosphate group. The  $HPO_3^{2-}$  group gives rise to new classes of organic–inorganic hybrid compounds and crystalline materials with extra-large pores [6–15]. In addition to the synthesis of these interesting compounds, one interesting research field involves the study of the influence of amines on the inorganic composition of these materials. A variety of organic amines display versatile

structural features and play different roles in the formation of interesting structures, including roles as ligands and templates, depending on the synthesis conditions, which results in forming new materials with different chemical compositions and structural topologies.

Herein, we report the synthesis of three new layered zinc phosphites using hydro(solvo)thermal methods that contain the monoamine *tert*-octylamine (TOA), which perform different roles in each compound. This group of compounds represents the first example where a single monoamine molecule plays different roles in three zinc phosphites owing to changes in the reaction conditions. Compound (**1**),  $(C_8H_{17}NH_3)_4Zn_3(HPO_3)_5 \cdot 3H_2O$ , possesses a sheet structure with 20-membered rings sandwiched by water molecules and protonated (HTOA)<sup>+</sup> templates; compound (**2**),  $Zn(C_8H_{17}NH_2)(HPO_3)$ , has an undulated layer structure with the neutral TOA ligands coordinated to the Zn as pendent groups; and compound (**3**),  $(C_8H_{17}NH_3)_2Zn_4(C_8H_{17}NH_2)(HPO_3)_5$ , contains TOA molecules that act as both neutral ligands and protonated templates in the structure.

## 2. Experimental section

### 2.1. Synthesis and characterization

The hydro(solvo)thermal reactions were carried out in Teflon-lined stainless steel Parr acid digestion bombs at 120 °C for 3 d.

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Colorless block crystals of **1** were obtained by heating a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol),  $\text{HF}(\text{aq})$  (0.5 mmol, 48% solution),  $\text{H}_3\text{PO}_3$  (7 mmol, 8 M solution), *tert*-octylamine (12 mmol),  $\text{H}_2\text{O}$  (1 mL), and ethylene glycol (4 mL). Colorless tablet crystals of **2** were prepared by heating a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.5 mmol),  $\text{HF}(\text{aq})$  (2 mmol, 48% solution),  $\text{H}_3\text{PO}_3$  (3 mmol, 8 M solution), *tert*-octylamine (12 mmol), and  $\text{H}_2\text{O}$  (5 mL). Colorless tablet crystals of **3** were synthesized by heating a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.4 mmol),  $\text{HF}(\text{aq})$  (2 mmol, 48% solution),  $\text{H}_3\text{PO}_3$  (6 mmol, 8 M solution), *tert*-octylamine (12 mmol),  $\text{H}_2\text{O}$  (1.4 mL), and ethylene glycol (5.6 mL). The addition of ethylene glycol (1–2 mL) to the same reaction condition of **2** led the formation of the mixture of **1** and **2**. Attempts to synthesize **1** and **3** without ethylene glycol were unsuccessful.

Powder X-ray diffraction patterns of the bulk products **1**, **2**, and **3** are in good agreement with the calculated patterns based on the results of single-crystal X-ray diffraction analyses (Figs. S1–S3). Energy-dispersive X-ray fluorescence spectroscopy of several colorless crystals of **1**, **2**, and **3** confirmed the presence of Zn and P. Elemental analysis results for the bulk products are consistent with the formulas presented for the compounds. Anal. Found (calcd) for **1**: C, 33.03% (32.92%); H, 7.99% (7.86%); N, 4.89% (4.80%). Anal. Found (calcd) for **2**: C, 35.37% (35.16%); H, 7.49% (7.38%); N, 5.26% (5.13%). Anal. Found (calcd) for **3**: C, 27.62% (27.56%); H, 6.29% (6.17%); N, 4.24% (4.02%).

Thermogravimetric analysis (TGA) using a Perkin Elmer TGA7 thermal analyzer was performed on powder samples of **1**, **2**, and **3** in  $\text{O}_2$  over a temperature range of 40–900 °C at a heating rate of 10 °C  $\text{min}^{-1}$  (Figs. S4–S6). In the case of **1**, a first weight loss of 4.56% occurred in the range of 50–137 °C, which corresponds to the loss of the free water molecules (calcd. 4.63%). The X-ray powder patterns of the final decomposition products from the TG analyses showed the presence of  $\text{Zn}_2\text{P}_2\text{O}_7$  (JCPDS: 34-0623) for **1**,  $\text{Zn}_2\text{P}_2\text{O}_7$  (JCPDS: 72-1702) for **2** and for **3**, and several unidentified products. The TGA curves show a number of overlapping weight losses, indicating the complex decomposition processes. The observed overall weight loss of 51.15% for **1** (for **2**: 42.55%; for **3**: 36.29%) is different from the calculated value of 55.88% for the weight loss of 4 ( $\text{C}_8\text{H}_{17}\text{NH}_2$ ) units and 7.5  $\text{H}_2\text{O}$  molecules (for **2**: 50.60% for the loss of 1 ( $\text{C}_8\text{H}_{17}\text{NH}_2$ ) and 0.5  $\text{H}_2\text{O}$ ; for **3**: 43.11% for the loss of 3 ( $\text{C}_8\text{H}_{17}\text{NH}_2$ ) and 3.5  $\text{H}_2\text{O}$ ). The difference between the observed and calculated weight losses can be attributed to the oxidation from  $\text{P}^{\text{III}}$  to  $\text{P}^{\text{V}}$  during the decomposition process. The calculated weight gain for the oxidation from  $\text{P}^{\text{III}}$  to  $\text{P}^{\text{V}}$  is 6.86% for **1**, 5.86% for **2**, and 7.66% for **3**. Therefore, the total weight loss would be the observed weight loss plus the calculated weight gain for the oxidation from  $\text{P}^{\text{III}}$  to  $\text{P}^{\text{V}}$ : for **1**, 58.01%  $\{(51.15\%+6.86\%)\}$ ; for **2**, 48.41%  $\{(42.55\%+5.86\%)\}$ ; and for **3**, 43.95%  $\{(36.29\%+7.66\%)\}$ . These results are close to the calculated values for the total weight loss of each compound: 55.88% for **1**, 50.60% for **2**, and 43.11% for **3**. Differential scanning calorimetry (DSC) analysis was performed on powder samples of **1**, **2**, and **3** in  $\text{O}_2$  over a temperature range of 30–300 °C at a heating rate of 5 °C  $\text{min}^{-1}$ . For **1**, the endothermic peak at 118 °C can be interpreted by the loss of the lattice-water molecules. The TGA analysis shows the main weight loss of three compounds in the range of 150–300 °C. So, the DSC peaks at 244 and 269 °C for **1**; 221 °C for **2**; 271 °C for **3** can be attributed to the decomposition and loss of amine molecules. From the results of TGA and DSC thermal analysis, the total decomposition process can be written as the following equations: for **1**:  $[(\text{C}_8\text{H}_{17}\text{NH}_3)_4\text{Zn}_3(\text{HPO}_3)_5] \cdot 3\text{H}_2\text{O} + 101/2\text{O}_2 \rightarrow 3/2 \text{Zn}_2\text{P}_2\text{O}_7 + \text{P}_2\text{O}_5 + 4\text{NH}_3 + 32 \text{CO}_2 + 79/2 \text{H}_2\text{O}$ ; for **2**:  $[\text{Zn}(\text{C}_8\text{H}_{17}\text{NH}_2)(\text{HPO}_3)] + 25/2 \text{O}_2 \rightarrow 1/2 \text{Zn}_2\text{P}_2\text{O}_7 + \text{NH}_3 + 8\text{CO}_2 + 17/2 \text{H}_2\text{O}$ ; and for **3**:  $[(\text{C}_8\text{H}_{17}\text{NH}_3)_2\text{Zn}_4(\text{C}_8\text{H}_{17}\text{NH}_2)(\text{HPO}_3)_5] + 77/2 \text{O}_2 \rightarrow 2 \text{Zn}_2\text{P}_2\text{O}_7 + 1/2 \text{P}_2\text{O}_5 + 3 \text{NH}_3 + 24 \text{CO}_2 + 55/2 \text{H}_2\text{O}$ .

The infrared studies of three compounds were recorded by the KBr pellet method in the range of 400–4000  $\text{cm}^{-1}$ . The spectrum of **1** shows characteristic bands of lattice water molecules at

3550  $\text{cm}^{-1}$  ( $\nu_s$ ) and 1630  $\text{cm}^{-1}$  ( $\delta_{\text{as}}$ ), which is in agreement with the presence of water molecules in **1** as analyzed from single-crystal X-ray diffraction and thermogravimetric analysis. The other absorption bands with a few variations correspond to the organic amines, and the  $\text{HPO}_3$  moiety in their respective peaks (Fig. S7). IR (KBr):  $\nu_s(\text{N-H})=3090\text{--}3410 \text{ cm}^{-1}$ ,  $\nu(\text{C-H})=2780\text{--}2950 \text{ cm}^{-1}$ ,  $\nu_s(\text{P-H})=2360\text{--}2390 \text{ cm}^{-1}$ ,  $\nu_s(\text{N-H})=1595\text{--}1600 \text{ cm}^{-1}$ ,  $\delta_s(\text{C-H})=1470\text{--}1500 \text{ cm}^{-1}$ ,  $\delta_s(\text{C-N})=1360\text{--}1400 \text{ cm}^{-1}$ ,  $\nu_{\text{as}}(\text{P-O})=1080\text{--}1140 \text{ cm}^{-1}$ ,  $\delta_{\text{as}}(\text{P-H})=1070\text{--}1080 \text{ cm}^{-1}$ ,  $\nu_s(\text{P-O})=999\text{--}1026 \text{ cm}^{-1}$ ,  $\delta_s(\text{P-O})=579\text{--}596 \text{ cm}^{-1}$ ,  $\delta_{\text{as}}(\text{P-O})=455\text{--}517 \text{ cm}^{-1}$ .

## 2.2. Single-crystal X-ray diffraction

Colorless crystals (0.20 × 0.15 × 0.10  $\text{mm}^3$  for **1**, 0.15 × 0.15 × 0.10  $\text{mm}^3$  for **2**, and 0.20 × 0.20 × 0.15  $\text{mm}^3$  for **3**) were selected for each compound for indexing and intensity data collection on a Bruker X8 Apex2 CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected in 1271 frames with  $\omega$  scans (width: 0.30° per frame). Empirical absorption corrections based on symmetry equivalents were applied. On the basis of systematic absences and successful solution and refinement of the structures, the space groups were determined to be *P*-1 (No. 2) for **1**, *P*<sub>2</sub>/c (No. 14) for **2**, and *P*ca2<sub>1</sub> (No. 29) for **3**. The crystal structures were solved by direct methods followed by difference Fourier syntheses and refined using SHELXTL 5.1 software. The H atoms associated with the P atoms, with the N atoms in the *tert*-octylamine molecules of the three compounds except N(4) in **1**, and with the water oxygen atoms in **1** could be located in the difference maps. Atoms C(22), C(23), C(24), C(27), C(28), C(31), C(32), and N(4) in **1** and C(8) and C(15) in **3** are disordered over two sites with equal occupancy. The H atoms bonded to the C atoms in the *tert*-octylamine molecules for the three compounds were positioned geometrically and refined using a riding model with fixed isotropic thermal parameters. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters of H atoms converged at  $R_1=0.0551$ ,  $wR_2=0.1612$ , and  $S=1.05$  for **1**;  $R_1=0.0398$ ,  $wR_2=0.1028$ , and  $S=1.00$  for **2**; and  $R_1=0.0482$ ,  $wR_2=0.1123$ , and  $S=1.03$  for **3**. All the calculations were performed using the SHELXTL Version 5.1 software package. The crystal data and selected bond lengths are given in Tables 1 and 2, respectively. CCDC reference numbers 919156, 919157 and 919158.

## 3. Results and discussion

### 3.1. Description of the structures

The three title compounds are interesting examples containing single amines with different roles, as templates in **1**, as ligands in **2**, and as both templates and ligands in **3**, and were obtained by adjusting the synthesis conditions. As shown in Fig. S8, the asymmetric unit of **1** contains three distinct  $\text{ZnO}_4$  tetrahedra, five phosphate pseudotetrahedra, four protonated ( $\text{HTOA}$ )<sup>+</sup> cations, and three water molecules. The P(2) and P(5) atoms link to three Zn atoms via oxygen atoms and one hydrogen atom (P–H). All P(1), P(3), and P(4) atoms individually bridge two Zn atoms through oxygen atoms, leaving one terminal P=O group and one P–H bond. Every Zn atom is coordinated by  $\text{HPO}_3$  units through oxygen atoms to form a 4-membered ring, which is further linked through the corners to form a layered structure with 20-membered rectangular windows (Fig. 1a). The Zn–O and P–O(P=O) bond distances are in the range from 1.907(3) Å and from 1.498(3) to 1.535(3) Å, respectively. Each anionic planar sheet is interleaved by

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