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# Synthesis, structure and characterization of two new open-framework gallium phosphite-oxalates of varying dimensionality

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ABSTRACT

Using N, N-dimethyl-piperazine as structure directing agent, two new gallium phosphite-oxalates $[Ga_2(HPO_3)_2(H_2PO_3)_2(C_2O_4)](C_6N_2H_{16})$ (**I**) and $[Ga_2(HPO_3)_2(H_2PO_3)(C_2O_4)](C_6N_2H_{16})_{0.5}$ (**II**) have been synthesized under solvothermal and hydrothermal conditions, respectively and further characterized by powder X-ray diffraction, IR spectroscopy, TGA, ICP-AES and elemental analyses. Single crystal X-ray diffraction reveals that the striking feature of **I** and **II** is that they possess the same second building unit (SBU) $Ga_2P_2$ constructed from two $GaO_6$ octahedra and two $[HPO_3^{2-}]$ pseudo-pyramids sharing oxygen atoms. However, due to the different connecting fashions of SBUs, $[C_2O_4^{2-}]$ groups and $[H_2PO_3^{-}]$ pseudo-pyramids, the final frameworks of them are distinctly different. Compound **I** shows 2D layered structures with 8-membered ring (8-MR) windows in the *ab* plane while compound **II** presents a 3D open-framework with 8-MR channels along the *b* axis.



## 1. Introduction

Open-framework materials have been the subject of intense research owing to their diverse structural chemistry and potential applications as ion-exchangers, catalysts and adsorbents [1]. Of the various inorganic open-framework materials discovered in last few years, the metal phosphates with a rich structural and compositional diversity occupy a prime position, which include one-dimensional chains or ladders, two dimensional layers, and three-dimensional structures [2–4]. The introduction of rigid organic linkers, such as oxalate, as part of the inorganic framework has opened up tremendous possibilities for research in this area giving rise to new inorganic–organic hybrid compounds. In recent years, inorganic–organic hybrid compounds containing both oxalate and phosphate units have also been prepared. A number of metal phosphate-oxalates of Al, Fe, In, Ga and Mn have been reported and displayed attractive structures [5–10]. For example, NTHU-6, an unprecedented hybrid yellow phosphor, contains hexameric octahedral $Ga_6(OH)_4O_{26}$ clusters [7].

More recently, the pseudo-pyramidal phosphite $[HPO_3^{2-}]$ group has been investigated as a possible replacement for the traditional phosphate tetrahedron with great success [11–14]. Compared with phosphate $[PO_4^{3-}]$ group, the pyramidal phosphite group $[HPO_3^{2-}]$ only links three adjacent cations via P–O–M ($M$=metal) bonds, which might be expected to lead to a new class of compounds with interesting architectures. In 2005, Natarajan reported an iron phosphite-oxalate possessing infinite Fe–O–Fe chains and introduced oxalate group in metal phosphite [15]. However, compared with widely researched phosphate-oxalate hybrid networks, the exploratory research on phosphate-oxalate frameworks has only just begun [16,17]. Similar to other known hybrid structures, the phosphate-oxalate structures appear to show wide compositional and structural diversity because of the different connecting fashion of oxalate units, $MO_x$ polyhedra and $[HPO_3^{2-}]$ groups. For example, NTHU-7 contains inorganic–organic hybrid nanotubule, which is constructed from four strips of $[Ga_2(HPO_3)_2]$ 4-ring (4R) ribbons connecting through four oxalate groups to form a 16-ring (16R) aperture window at the tubule opening [18].

The rational design and synthesis of open-framework compounds are far from reality due to the interplay of many factors such as oxidation states and coordination preferences of the metal ions, stereochemistry of the ligand, solvent effects, the nature of the counter ion, etc. [19]. The earlier literature studies on metal phosphates/phosphites indicated that solvent may play an important role in the formation of open-frameworks [20]. Moreover, in our previously studies on metal phosphites, several compounds [21,22] exhibiting different structures are also synthesized with the same template under different solvent conditions. Therefore, with an aim towards searching for novel organically templated

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metal phosphites, we conducted our study on the synthesis with respect to gallium phosphite–oxalates under different solvent systems. Finally, using N, N-dimethyl-piperazine as structure directing agent, two novel open-framework gallium phosphite-oxalate compounds $[Ga_2(HPO_3)_2(H_2PO_3)_2(C_2O_4)](C_6N_2H_{16})$ (**I**) and $[Ga_2(HPO_3)_2(H_2PO_3)(C_2O_4)](C_6N_2H_{16})_{0.5}$ (**II**) are obtained by adjusting the variety of the solvents. Compound **I** is solvothermally synthesized from a mixed water–ethanol solvent system while compound **II** is hydrothermally synthesized from a single solvent system of water. It is noted that the same SBU occurs in both compounds. However, due to the different connecting fashions of SBUs, $[C_2O_4^{2-}]$ groups and $[H_2PO_3^-]$ pseudo-pyramids, the final frameworks of **I** and **II** are obviously different. Compound **I** shows 2D layered framework with 8-MR windows in the *ab* plane while compound **II** possesses 3D open-framework structure. Herein we describe the synthesis, crystal structure and characterization of **I** and **II**, along with the influence of solvents on the formation of compounds.

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. The elemental analysis was conducted on a Perkin Elmer 2400 elemental analyzer. Inductively coupled plasma-atomic emission spectroscope (ICP-AES) analysis was performed on a Perkin Elmer Optima 3300DV ICP instrument. Powder X-ray diffraction (XRD) data were obtained using SHIMADAZU XRD-6000 diffractometer with Cu-*K*α radiation ($\lambda=1.5418$ Å), with the step size and the count time of 0.02° and 4 s, respectively. FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer between 400 and 4000 $cm^{-1}$ using the KBr pellet method. Thermogravimetric analysis (TGA) was conducted on a SHIMADAZU DTG 60 thermogravimetric analyzer with a heating rate of 10 °C $min^{-1}$ from room temperature to 800 °C in air.

### 2.2. Synthesis

Both compounds **I** and **II** were prepared from a starting mixture containing gallium oxide ($Ga_2O_3$), phosphorous acid ($H_3PO_3$), oxalic acid ($H_2C_2O_4$) and N, N-dimethyl-piperazine. The difference is that compound **I** was starting with ethanol and distilled water as solvent while compound **II** was prepared with distilled water only. For compound **I**, the molar ratio of the initial mixture was $Ga_2O_3$: $H_3PO_3$: N, N-dimethyl-piperazine: $H_2C_2O_4$: $H_2O$: ethanol=1: 18.5: 5.4: 24.9: 624: 193. For compound **II**, the molar ratio of initial mixture was $Ga_2O_3$: $H_3PO_3$: N, N-dimethyl-piperazine: $H_2C_2O_4$: $H_2O$=1: 9.3: 1.4: 6.2: 521. After all the components were added, the mixture was finally further stirred for 50 min at room temperature and heated at 130 °C for 5 days in a 23 ml Teflon-lined stainless steel autoclave (filled up to 27% volume capacity), then slowly cooling down to the ambient temperature. The colorless crystalline product was collected by filtration, washed with distilled water, and then dried at room temperature. The yield of product was 65% (for **I**) and 59% (for **II**) in weight based on gallium.

### 2.3. Crystal structure determination

Suitable single-crystal with dimensions $0.20\times0.17\times0.15$ $mm^3$ of compound **I** and $0.22\times0.18\times0.15$ $mm^3$ of compound **II** were selected for single crystal XRD analysis, respectively. The intensity data were collected on a Rigaku RAXIS-RAPID IP diffractometer for **I** and a Siemens Smart CCD diffractometer for **II** using graphite-monochromatic Mo-*K*α radiation ($\lambda=0.71073$ Å) in the ω scanning mode at room temperature. No significant decay was observed during the data collection. Data processing was accomplished with the RAPID AUTO processing program for **I** and the SAINT processing program for **II**. The structure was solved by direct method with the SHELXTL 97 software package [23,24]. The gallium and phosphorus atoms were first located, and then the carbon, nitrogen and oxygen atoms were found in the difference Fourier map. The hydrogen atoms of the P–H groups and organic molecules were initially located from difference Fourier maps. All non-hydrogen atoms were refined anisotropically. The crystallographic data of **I** and **II** are given in Table 1. Selected bond lengths and angles are listed in Tables S1 and S2. CCDC-940752 and CCDC-940753 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internet) +44 1223/336 033; E-mail: deposit@ccdc.cam.ac.uk].

**Table 1**
Crystal data and structure refinement for compound **I** and **II**.

| | | |
|---|---|---|
| Empirical formula | $C_8H_{22}Ga_2N_2O_{16}P_4$ | $C_5H_{11}Ga_2NO_{13}P_3$ |
| Formula weight | 665.60 | 525.50 |
| Temperature (K) | 273(2) | 296(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/c$ | $C_2/c$ |
| *a* (Å) | 10.183(3) | 23.4617(17) |
| *b* (Å) | 12.525(4) | 8.1170(6) |
| *c* (Å) | 16.295(5) | 16.8976(12) |
| *β* (°) | 98.218(4) | 112.8730(10) |
| *V* (Å$^3$) | 2056.9(10) | 2964.9(4) |
| *Z* | 4 | 8 |
| Calculated density (mg/m$^3$) | 2.149 | 2.354 |
| Absorption coefficient | 3.015 | 4.030 |
| *F*(000) | 1336 | 2072 |
| Theta range for data collection (deg) | 2.02–26.06 | 1.88–26.12 |
| Limiting indices | $-11<=h<=12$, $-14<=k<=15$, $-20<=l<=19$ | $-28<=h<=28$, $-9<=k<=10$, $-14<=l<=20$ |
| Reflections collected/unique | 10938/4047 [*R*(int)=0.0256] | 7913/2943 [*R*(int)=0.0170] |
| Goodness-of-fit on $F^2$ | 1.052 | 1.070 |
| Final *R* indices [$I>2$sigma(I)] | *R*1=0.0330, *wR*2=0.0819 | *R*1=0.0208, *wR*2=0.0513 |
| *R* indices (all data) | *R*1=0.0424, *wR*2=0.0879 | *R*1=0.0231, *wR*2=0.0522 |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.939 and −0.383 | 1.060 and −0.434 |