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New organically templated gallium oxalate-phosphate structures based on $Ga_4(PO_4)_4(C_2O_4)$ building unit

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Abstract

Five organic–inorganic hybrid gallium oxalate-phosphates, $[Ga_2(PO_4)_2(H_2O)(C_2O_4)_{0.5}](C_3N_2H_{12})_{0.5}(H_2O)$ (**1**), $[Ga_2(PO_4)_2(C_2O_4)_{0.5}]$ $(C_2N_2H_{10})_{0.5}(H_2O)$ (**2**), $[Ga_2(PO_4)_2(C_2O_4)_{0.5}](C_3N_2H_{12})_{0.5}$ (**3**), $[Ga_2(PO_4)_2(H_2PO_4)_{0.5}(C_2O_4)_{0.5}](C_4N_3H_{16})_{0.5}$ $(H_2O)_{1.5}$ (**4**) and $[Ga_{2.5}(PO_4)_{2.5}$ $(H_2O)_{1.5}(C_2O_4)_{0.5}](C_4N_3H_{15})_{0.5}$ (**5**), have been synthesized by using 1,3-diaminopropane, ethylenediamine and diethylene triamine as structure-directing agents under hydrothermal condition. The structures of **1**–**5** are based on $Ga_4(PO_4)_4(C_2O_4)$ building unit made up from $Ga_2O_8(C_2O_4)$ oxalate-bridging dimer and alternating PO_4 and GaO_4 tetrahedral units. Compound 1 is layered structure where the building units link together in the same orientation. Corner sharing of these similar layers result in three-dimensional (3-D) structure **2**. However, in compound **3**, the building units arrange in a wave-like way to generate two types of eight member ring (8MR) channels. Both **4** and **5** contain the layers where the building units have an opposite orientation. Those layers are linked by H_2PO_4 group and $Ga(PO_4)(H_2O)_3$ cluster, respectively, to form 3-D frameworks with 12MR large pore channels. Compounds **2**–**5** exhibit intersecting 3-D channels where the protoned amines are located.
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Keywords: Gallium oxalate-phosphates; Open framework; Hydrothermal reaction; Crystal structure; Building unit

1. Introduction

Open-framework inorganic materials are always the subject of numerous studies owing to their diverse applications in catalysis, adsorption and separation process. The initial work in this field produced aluminosilicate zeolites and aluminophosphate molecular sieves with channels and cages of various dimensionalities and sizes [1,2]. In the mid-1980s, research was extended to gallophosphates in order to discover new open-framework structures [3]. Gallium system is particularly intriguing for its tendency to exhibit various coordination configurations, including GaO_4 tetrahedra, GaO_5 trigonal bipyramids and GaO_6 octahedra. These fundamental building units can combine with phosphate tetrahedra and result in a vast number of second building units (SBUs), such as single four-ring (4R) [4], double four-ring (D4R) [5], double six-

ring (D6R) [6], single six-ring (6R) [7], $[M_3P_3]$ hexamer [8,9], and $[M_2P_2]$ tetramer [10], which are thought to be the keys to achieve novel framework topology. Incorporating oxalate anions into the gallophosphate frameworks expands the structural complexity and properties through their coordinating propensities and geometries. However, very few gallium oxalate-phosphates have been reported to date [11–17]. The incorporation of oxalate takes place in two different ways. First, the oxalate anion acts as a monobidentate ligand to each of the GaO_6 octahedron with two terminal C–O groups pendant inside the channels [11,12,17]. In the most examples, the oxalate anions play the role as bis-bidentate ligands bridging between two gallium centers [12–17].

In this paper, we report the organically templated synthesis, crystal structures and thermal behaviors of five organic–inorganic hybrid gallium oxalate-phosphates, $[Ga_2(PO_4)_2(H_2O)(C_2O_4)_{0.5}](C_3N_2H_{12})_{0.5}(H_2O)$ (**1**), $[Ga_2(PO_4)_2(C_2O_4)_{0.5}](C_2N_2H_{10})_{0.5}$ (H_2O) (**2**), $[Ga_2(PO_4)_2(C_2O_4)_{0.5}](C_3N_2H_{12})_{0.5}$ (**3**), $[Ga_2(PO_4)_2(H_2PO_4)_{0.5}(C_2O_4)_{0.5}]$

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$(C_4N_3H_{16})_{0.5}(H_2O)_{1.5}$ (**4**) and $[Ga_{2.5}(PO_4)_{2.5}(H_2O)_{1.5}$ $(C_2O_4)_{0.5}](C_4N_3H_{15})_{0.5}$ (**5**). A similar building unit Ga_4 $(PO_4)_4(C_2O_4)$ was found in all five structures.

2. Experimental section

2.1. Synthesis

All reagents were of analytical grade and were used without further purification. Compounds **1**–**5** were synthesized under hydrothermal conditions with various organic amines as structure directing agents. In a typical procedure for **1**, 0.210 g Ga_2O_3, 0.147 g H_3PO_4 (85%), 0.497 g $H_2C_2O_4 \cdot 2H_2O$ and 10.0 ml distilled water were mixed with stirring. Then 0.304 g 1,3-diaminopropane (1,3-DAP) was added until the pH of the mixture was 2.53. After the mixture was stirred at room temperature for 4 h, the resulting gel composed of Ga_2O_3: 1.14 H_3PO_4: 4.93 $H_2C_2O_4$: 496 H_2O: 3.66 1,3-DAP (in molar ratio) was heated at 160 °C for 48 h in a teflon-coated stainless-steel autoclave under autogenous pressure. Transparent columnar crystals were obtained in approximately 89.4% yield (calculated based on H_3PO_4). The X-ray powder diffraction reveals that the product 1 is pure-phase material. The pattern of the powder sample is consistent with simulated single-crystal pattern, which has relative higher intensity (Fig. 1). In the syntheses of compounds **2** and **3**, diethylene amine (en) and 1,3-DAP were employed as templates with initial gel of Ga_2O_3: 3.50 H_3PO_4: 5.57 $H_2C_2O_4$: 338 H_2O: 2.06 en and Ga_2O_3: 3.30 H_3PO_4: 5.53 $H_2C_2O_4$: 332 H_2O: 2.00 1,3-DAP, respectively. The obtained gels were heated in the autoclaves at 160 °C for 64 and 24 h, respectively. Most of products **2** were single crystals with size and shape similar to product 1. Some impurity was found from X-ray powder diffraction. Layer-like single crystals of compound **3** mixed with impurity phase were obtained. The impurity was identified to be alpha-$GaPO_4$ crystals [18] by single-crystal X-ray diffraction. In the preparation for compound **4**, diethylene triamine (DETA) were employed as a template with initial gel of Ga_2O_3: 3.50 H_3PO_4: 1.45

$H_2C_2O_4$: 334 H_2O: 2.05 DETA, heated at 140 °C for 72 h. Compound **5** was obtained as a minor phase mixed with product **4**.

2.2. Characterization

Elemental analyses were carried out on an Elementar Vario EL III microanalyzer. Thermogravimetric analyses (TGAs) were performed on a METTLER TOLEPO TGA/ SDTA851 analyzer in air atmosphere with a heating rate of 5 °C/min, from 25 to 900 °C.

2.3. Single-crystal X-ray diffraction data collection, structure solution and refinement

Suitable single crystals with varied dimensions of compounds **1**–**5** were selected for indexing and intensity data were collected at room temperature. Single-crystal structure determination by X-ray diffraction was performed on a Bruker Smart APEX area diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. A hemisphere of intensity data was collected at room temperature with a scan width of 0.60° in ω and exposure time of 20 s/frame. Empirical absorption corrections were based on SADABS program [19]. The structures were solved by direct methods and refined on F^2 using the SHELXTL-97 [20] software package. Ga and P atoms were disclosed firstly, followed by the atoms of C, N and O located on successive difference Fourier methods. Hydrogen atoms of coordinated water and HPO_4 group were directly located on final difference maps. Those of organic amines were added on asymmetric principle. Details of the final refinements are given in Table 1 and selected bond distances and angles are presented in Table 2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-294755, -294815, -294816, -294859 and -294860 (for **1**–**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk).

Compound **1** was twinned structure solved with Gemini [21]. Diprotonated 1,3-DAP cations were disordered over two sites. To normalize the internal bond distances and angles of 1,3-DAP moieties, several geometrical restrictions were used during the refinement. Most crystals of product **5** were twinned. As a consequence of the twin crystal, some reflections were from the major twin only, and some were measured from both components. The part of the minor twin in the diffraction data resulted in a little high R factor. The difference Fourier map showed many peaks of very low electronic density, which was resulted from an extensive disorder of the organic amine and water solvent molecules in the structures. Thus, the contributions from disorder guest molecules were subtracted by using
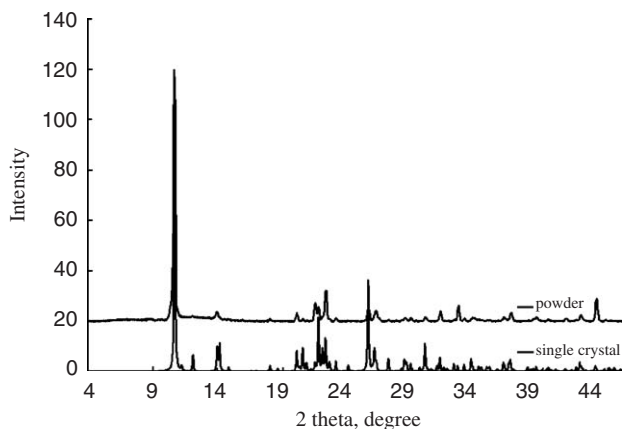

Fig. 1. X-ray powder diffraction pattern and simulated single-crystal pattern of compound **1**.

Table 1
Crystal data and structure refinement parameters for compounds **1–5**

Identification code	1	2	3	4	5
Empirical formula	$C_{2.5}H_{10}Ga_2NO_{12}P_2$	$C_2H_7Ga_2NO_{11}P_2$	$C_{2.5}H_6Ga_2NO_{10}P_2$	$C_3H_{12}Ga_2N_{1.5}O_{13.5}P_{2.5}$	$C_3H_{11.5}Ga_{2.5}N_{1.5}O_{13.5}P_{2.5}$
Formula weight	447.49	422.47	411.46	502.00	536.36
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$Pnma$ (No. 62)
a/Å	8.194(7)	7.973(2)	10.807(4)	20.131(5)	9.039(4)
b/Å	8.892(7)	8.423(2)	14.066(5)	15.670(4)	19.370(8)
c/Å	9.242(8)	8.834(2)	13.084(4)	9.097(2)	15.641(7)
α/deg	65.920(9)	116.834(2)			
β/deg	75.411(9)	100.992(3)	96.342(4)	105.988(4)	
γ/deg	78.530(10)	103.428(3)			
Volume/Å³	591.5(8)	484.2(2)	1976.6(11)	2758.6(12)	2739(2)
Z	2	2	8	8	8
ρ/g cm⁻³	2.513	2.898	2.765	2.461	2.602
μ/mm⁻¹	4.891	5.958	5.827	4.278	5.269
F(000)	440	412	1600	2024	2104
Crystal size/mm	0.10 × 0.05 × 0.04	0.15 × 0.10 × 0.04	0.10 × 0.08 × 0.08	0.10 × 0.10 × 0.05	0.10 × 0.10 × 0.08
Goodness-of-fit on F^2	1.081	1.051	1.063	0.944	1.081
Final R indices [$I > 2$ sigma(I)]^a	$R_1 = 0.0734$, $wR_2 = 0.1913$	$R_1 = 0.0307$, $wR_2 = 0.0783$	$R_1 = 0.0323$, $wR_2 = 0.0845$	$R_1 = 0.0332$, $wR_2 = 0.0767$	$R_1 = 0.0965$, $wR_2 = 0.2362$

^{a}Where $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$, $wR_2 = [\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]]^{1/2}$.

SQUEEZE subroutine of the PLATON software suite [22]. A unit cell accessible volume of about 36.3% containing 347 electrons for compound **4** was calculated, which could accommodate 0.5 protonated DETA and 1.5 water molecules in the asymmetric unit. For compound **5**, 23.7% void space containing 241 electrons was counted, which corresponded to 0.5 protonated DETA molecules in the asymmetric unit.

3. Results and discussion

3.1. Structure description

The framework of compound **1** is built up from a pseudo-rectangular shape $Ga_4(H_2O)_2(PO_4)_4(C_2O_4)$ building unit, which contains two GaO_6 octahedra, two GaO_4 tetrahedra, four PO_4 tetrahedra and one oxalate anion (Fig. 2a). The oxalate anion acts as bis-bidentate ligand to Ga(1) to form a dimer. Four gallium atoms exhibit two types of coordination. One gallium atom (Ga1) is distorted octahedrally coordinated by three phosphate oxygen atoms with the distance of Ga(1)–O(4) = 1.893(7) Å, Ga(1)–O(5) = 1.931(7) Å, Ga(1)–O(10) = 1.944(8) Å, two oxalate oxygen atoms with longer distance of Ga(1)–O(1) = 2.023(7) Å, Ga(1)–O(2) = 2.056(7) Å and one terminal oxygen atom assigned as water molecule (Ga(1)–O(3) = 1.940(7) Å). Another gallium (Ga2) is coordinated to four phosphate oxygen with typical tetrahedral Ga–O distances range from 1.816(7) to 1.848(7) Å. There are two distinct crystallographically independent phosphorus atoms P1 and P2 in nearly tetrahedral coordination with P–O distances within 1.489(8)–1.563(8) Å, among which the shortest distance of P2–O11 belong to the phosphorus–oxygen double bond. The average bond valence sums [23] calculated for Ga and P are 3.16 and 4.91, in good agreement with the usual valences (3.0 and 5.0).

The corner-sharing assembly of these $Ga_4(H_2O)_2(PO_4)_4(C_2O_4)$ building units makes up an anionic layer of formula $[Ga_2(H_2O)(PO_4)_2(C_2O_4)_{0.5}]^-$ in the (*ab*) plane (Fig. 2b). The layers are interrupted by terminal P=O groups and coordinated water molecules pointing into the interlayer space. Charge-balancing cations $[C_3N_2H_{12}]^{2+}$ and lattice water molecules occupy sites between the layers (Fig. 3a). The cohesion of the structure is mainly ensured through the hydrogen bonds between the coordinated water molecules and phosphate groups on the adjacent sheet with distance of $d_{O3\cdots O11} = 2.599(2)$ Å. Other hydrogen bond interactions occur between the terminal NH_3^+ groups of the 1,3-DAP and the oxygen atoms of the phosphate groups as well as of the lattice water molecules. Elemental analysis gives C, H, N contents of 6.57, 2.11 and 3.19% (calcd. values are C, 6.71%; H, 2.25%; N, 3.13%), which confirms the stoichiometry of 1,3-DAP.

The framework of compound **2** can be thought as arising from the similar layers in compound **1**. However, the missing of coordinated water molecules yields new

Table 2
Selected bond lengths (Å) for **1**–**5**

1		**2**		**3**		**4**		**5**	
Ga(1)–O(4)	1.893(7)	Ga(1)–O(10)	1.918(3)	Ga(1)–O(3)	1.895(3)	Ga(1)–O(3)	1.914(3)	Ga(1)–O(3)	1.908(10)
Ga(1)–O(5)#1	1.931(7)	Ga(1)–O(3)	1.924(3)	Ga(1)–O(10)	1.915(3)	Ga(1)–O(5)	1.921(3)	Ga(1)–O(7)#1	1.914(10)
Ga(1)–O(3)	1.940(7)	Ga(1)–O(4)#1	1.928(3)	Ga(1)–O(8)#1	1.935(3)	Ga(1)–O(4)	1.933(3)	Ga(1)–O(5)	1.931(10)
Ga(1)–O(10)	1.944(8)	Ga(1)–O(9)#2	1.933(3)	Ga(1)–O(4)#2	1.938(3)	Ga(1)–O(7)#1	1.936(3)	Ga(1)–O(4)	1.950(10)
Ga(1)–O(1)	2.023(7)	Ga(1)–O(1)	2.078(3)	Ga(1)–O(2)	2.045(3)	Ga(1)–O(2)	2.043(3)	Ga(1)–O(2)	2.035(11)
Ga(1)–O(2)	2.056(7)	Ga(1)–O(2)	2.089(3)	Ga(1)–O(1)	2.115(3)	Ga(1)–O(1)	2.074(3)	Ga(1)–O(1)	2.053(11)
Ga(2)–O(8)	1.816(7)	Ga(2)–O(5)#3	1.807(3)	Ga(2)–O(5)#3	1.815(3)	Ga(2)–O(10)#2	1.805(3)	Ga(2)–O(10)#2	1.790(10)
Ga(2)–O(7)	1.818(8)	Ga(2)–O(8)#4	1.830(3)	Ga(2)–O(6)	1.819(3)	Ga(2)–O(6)#3	1.807(3)	Ga(2)–O(9)	1.798(10)
Ga(2)–O(9)#2	1.820(8)	Ga(2)–O(6)	1.831(3)	Ga(2)–O(7)	1.835(3)	Ga(2)–O(8)	1.814(3)	Ga(2)–O(6)#3	1.812(10)
Ga(2)–O(6)#3	1.848(7)	Ga(2)–O(7)	1.836(3)	Ga(2)–O(9)#4	1.841(3)	Ga(2)–O(9)	1.817(3)	Ga(2)–O(8)	1.820(10)
P(1)–O(5)	1.492(7)	P(1)–O(3)	1.509(3)	P(1)–O(3)	1.513(3)	P(1)–O(7)	1.512(3)	Ga(3)–O(14)	1.855(18)
P(1)–O(4)	1.512(7)	P(1)–O(4)	1.522(3)	P(1)–O(4)	1.525(3)	P(1)–O(5)	1.514(3)	Ga(3)–O(11)	1.904(11)
P(1)–O(6)	1.551(7)	P(1)–O(5)	1.548(3)	P(1)–O(5)	1.549(3)	P(1)–O(8)	1.538(3)	Ga(3)–O(11)#4	1.904(11)
P(1)–O(7)	1.558(8)	P(1)–O(6)	1.550(3)	P(1)–O(6)	1.551(3)	P(1)–O(6)	1.540(3)	Ga(3)–O(13)#4	1.989(15)
P(2)–O(11)	1.489(8)	P(2)–O(9)	1.508(3)	P(2)–O(10)	1.490(3)	P(2)–O(4)	1.509(3)	Ga(3)–O(13)	1.989(15)
P(2)–O(10)	1.514(8)	P(2)–O(10)	1.512(3)	P(2)–O(8)	1.517(3)	P(2)–O(11)	1.510(3)	Ga(3)–O(12)	2.033(16)
P(2)–O(8)	1.555(8)	P(2)–O(8)	1.551(3)	P(2)–O(9)	1.558(3)	P(2)–O(10)	1.531(3)	P(1)–O(7)	1.516(11)
P(2)–O(9)	1.563(8)	P(2)–O(7)	1.563(3)	P(2)–O(7)	1.559(3)	P(2)–O(9)	1.532(3)	P(1)–O(5)	1.525(11)
C(1)–O(2)#4	1.235(12)	C(1)–O(1)	1.245(5)	C(1)–O(1)	1.255(4)	P(3)–O(3)#4	1.508(3)	P(1)–O(8)	1.537(10)
C(1)–O(1)	1.263(12)	C(1)–O(2)#5	1.263(5)	C(1)–C(2)	1.544(8)	P(3)–O(3)	1.508(3)	P(1)–O(6)	1.540(10)
C(1)–C(1)#4	1.572(18)	C(1)–C(1)#5	1.524(9)	C(2)–O(2)	1.249(4)	P(3)–O(12)	1.528(4)	P(2)–O(4)	1.489(11)
C(2)–N(1)	1.368(16)	C(2)–N(1)	1.455(7)	C(3)–N(1)	1.290(12)	P(3)–O(12)#4	1.528(4)	P(2)–O(11)	1.507(12)
C(2)–C(3)	1.470(19)	C(2)–C(2)#6	1.492(10)	C(3)–C(4)	1.375(12)	C(1)–O(1)	1.245(5)	P(2)–O(10)	1.562(10)
C(3)–C(3)#5	1.42(5)			C(4)–C(3)#6	1.375(12)	C(1)–O(2)#5	1.267(4)	P(2)–O(9)	1.569(11)
						C(1)–C(1)#5	1.526(8)	P(3)–O(14)	1.486(17)
								P(3)–O(3)	1.519(10)
								P(3)–O(3)#4	1.519(10)
								P(3)–O(15)	1.591(18)
								C(1)–O(1)	1.235(17)
								C(1)–O(2)#5	1.264(18)
								C(1)–C(1)#5	1.57(3)

Symmetry transformations used to generate equivalent atoms for **1**: #1 $-x+1, -y+1, -z$, #2 $-x, -y+2, -z$, #3 $-x+1, -y+2, -z$, #4 $-x, -y+1, -z$, #5 $-x+1, -y, -z+1$.

Symmetry transformations used to generate equivalent atoms for **2**: #1 $-x+1, -y, -z$, #2 $-x+2, -y+1, -z+1$, #3 $-x+1, -y+1, -z$, #4 $-x+2, -y+1, -z$, #5 $-x+1, -y+1, -z+1$, #6 $-x+2, -y+2, -z+1$.

Symmetry transformations used to generate equivalent atoms for **3**: #1 $-x+2, -y+1, -z+2$, #2 $-x+\frac{5}{2}, -y+\frac{1}{2}, -z+2$, #3 $-x+2, y, -x+\frac{5}{2}$, #4 $-x+\frac{3}{2}, -y+\frac{1}{2}, -z+2$, #5 $-x+2, y, -x+\frac{3}{2}$, #6 $-x+1, y, -z+\frac{3}{2}$.

Symmetry transformations used to generate equivalent atoms for **4**: #1 $x, -y, z+\frac{1}{2}$, #2 $-x+\frac{1}{2}, -y+\frac{1}{2}, -z$, #3 $x, -y, z-\frac{1}{2}$, #4 $-x, y, -z+\frac{1}{2}$, #5 $-x+\frac{1}{2}, -y+\frac{1}{2}, -z+1$.

Symmetry transformations used to generate equivalent atoms for **5**: #1 $x-\frac{1}{2}, y, -z+\frac{1}{2}$, #2 $-x+2, -y+1, -z$, #3 $x+\frac{1}{2}, y, -z+\frac{1}{2}$, #4 $x, -y+\frac{1}{2}, z$, #5 $-x+1, -y+1, -z$.

open-framework structure. GaO_6 octahedra are connected to the adjacent PO_4 tetrahedra by corner sharing to form a 3-D network (Fig. 3b). The structure contains intersecting 8 member ring (8MR) channels along a- and c-axis, where the protonated diethylene amine cations and lattice water are located. The framework topology of **2** is analogous to $K_2Ga_4(C_2O_4)(PO_4)_4 \cdot 2H_2O$, which was synthesized by using alkaline metal ion K^+ as a structure directing agent [14].

Crystal structure for **3** is generated by corner sharing of similar building units in compounds **1** and **2**. The connection in the (*ac*) plane results in a corrugated anionic layer (Fig. 4a), where the sequences of building units are UUDD and UDUD (UD represent up and down, respectively) along a- and c-axes, respectively. As shown in Fig. 4b, 3-D framework is formed by stacking of those wave-like layers in a parallel way along b-axis. Although this type of building units has also been found in other gallium oxalate-phosphates, such a unique arrangement is observed for the first time. There are two types of 8MR channels along [100] and [001] directions. One has the windows formed by two GaO_6, two GaO_4, three PO_4, tetrahedral, and one bridging oxalate, while the windows of the other channels are formed by two GaO_6, two GaO_4 and four PO_4 tetrahedra. Twice protonated 1,3-DAP cations are located at the intersection of two channels and interact with the framework by hydrogen bonds. No lattice water was found in compound **3**.

The occurrence of such a building unit is also observed in compound **4** and **5**. Different from structures **1**–**3**, both of them exhibit layer structures where the building units are connected to each other in an opposite orientation (Fig. 5).
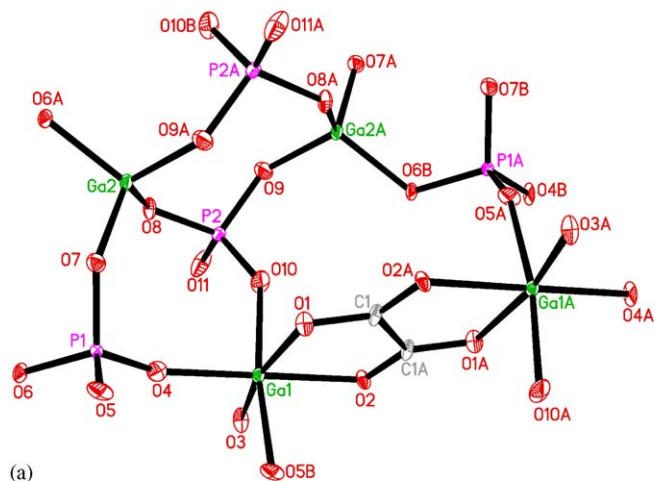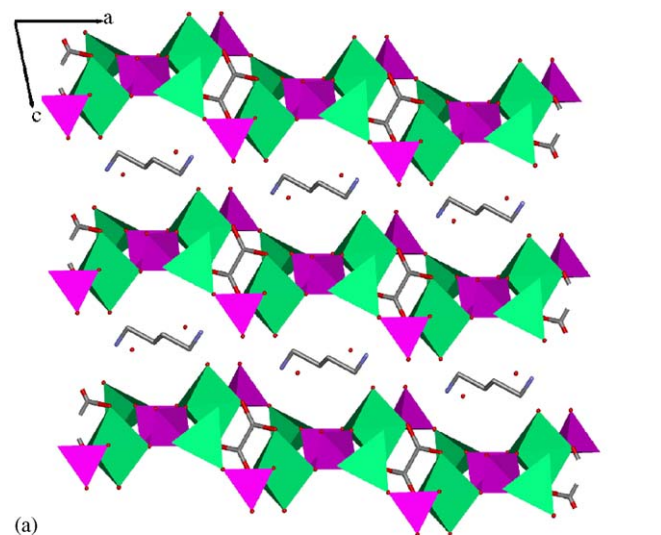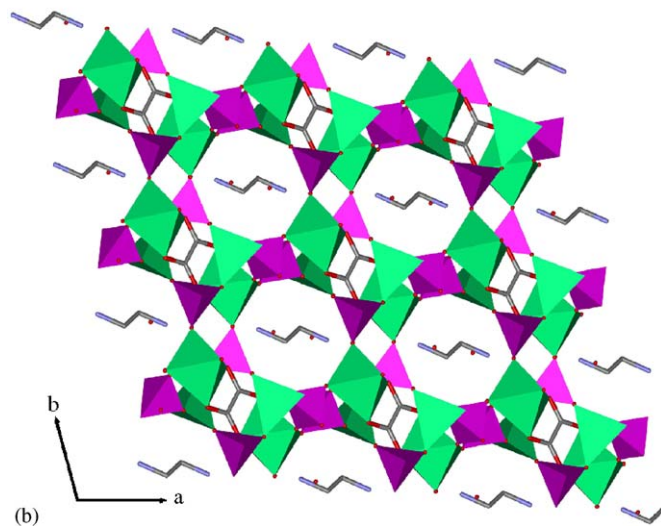
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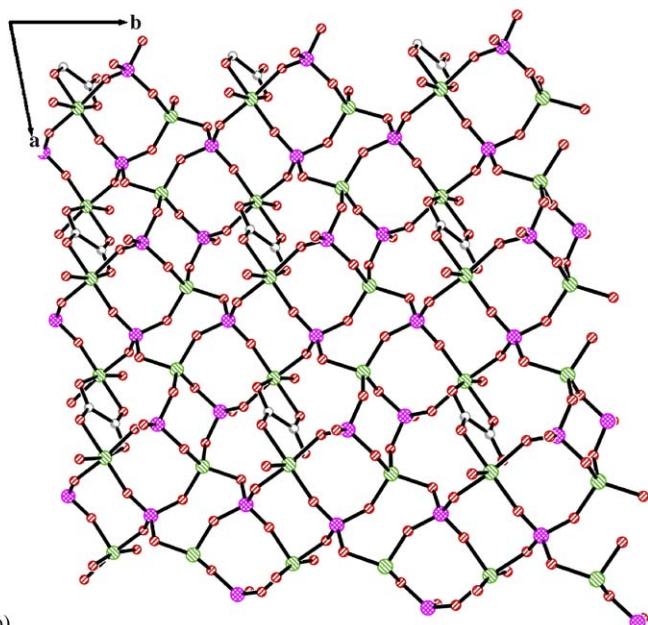
(b)

Fig. 2. (a) Details of the building unit $[Ga_4(PO_4)_4(C_2O_4)]$, showing the connections between phosphate (pink), oxalate (gray) and gallium (green) polyhedron. Thermal ellipsoids are shown at the 30% probability level. (b) One layer built up from the building units.

(a)

(b)

Fig. 3. (a) View of structure **1** along *b*-axis. (b) View of structure **2** along *c*-axis. The 2-D structure of **1** is converted into the 3-D structure of **2** by the connection of adjacent layers.

Another difference lies in the linkage between neighboring layers, which are made through additional groups called as 3-D linkers. Three kinds of 3-D linkers were observed in the previously reported gallium oxalate-phosphate compounds, including GaO_4N square pyramids [13], GaO_2X_4 ($X = OH$ or F) octahedral [16] and $MnO_2F_2(H_2O)_2$ octahedra [17]. Here compounds **4** and **5** present two novel 3-D linkers, $H_2PO_4^-$ tetrahedra and $Ga(PO_4)(H_2O)_3$ clusters respectively. In compound **4**, the phosphorous atom sits on a twofold axis, is positioned between the layers, and joins the $GaO_4(C_2O_4)$ group from adjacent layers, generating two types of alternating 8MR and 12MR channels along the [001] direction (Fig. 5a). The phosphate oxygen atom with bond valence value of 1.21 is assigned as −OH group, sticking into the 12MR apertures. When the van der Waals radius of the oxygen atoms (1.5) is taken

into account [24], the free pore diameters are 6.5×6.1 and $4.9 \times 3.4\,\text{Å}$, respectively. The 3-D linker of compound **5**, $Ga(PO_4)(H_2O)_3$ cluster, consists of corner-sharing PO_4 tetrahedron and $GaO_3(H_2O)_3$ octahedron. Structure **5** also contains adjacent and parallel 12MR and 8MR channels with the pore size of 6.5×2.1 and $4.9 \times 3.4\,\text{Å}$ (Fig. 5b). Segregation is observed in structure **4**: lattice water molecules fill in the large 12MR channels whereas amine cations reside in the 8MR channels disorderly. Considering charge balance principle, the DETA was designated as third protonated for **4** and second protonated for **5**.

3.2. TG analysis

The TGA measurements for compounds **3** and **5** were not conducted due to the impurity of the products. TG curves of compounds **1**, **2** and **4** indicated that the loss of disordered amine molecules for compound **4** occurred at a lower temperature than that for ordered ones in
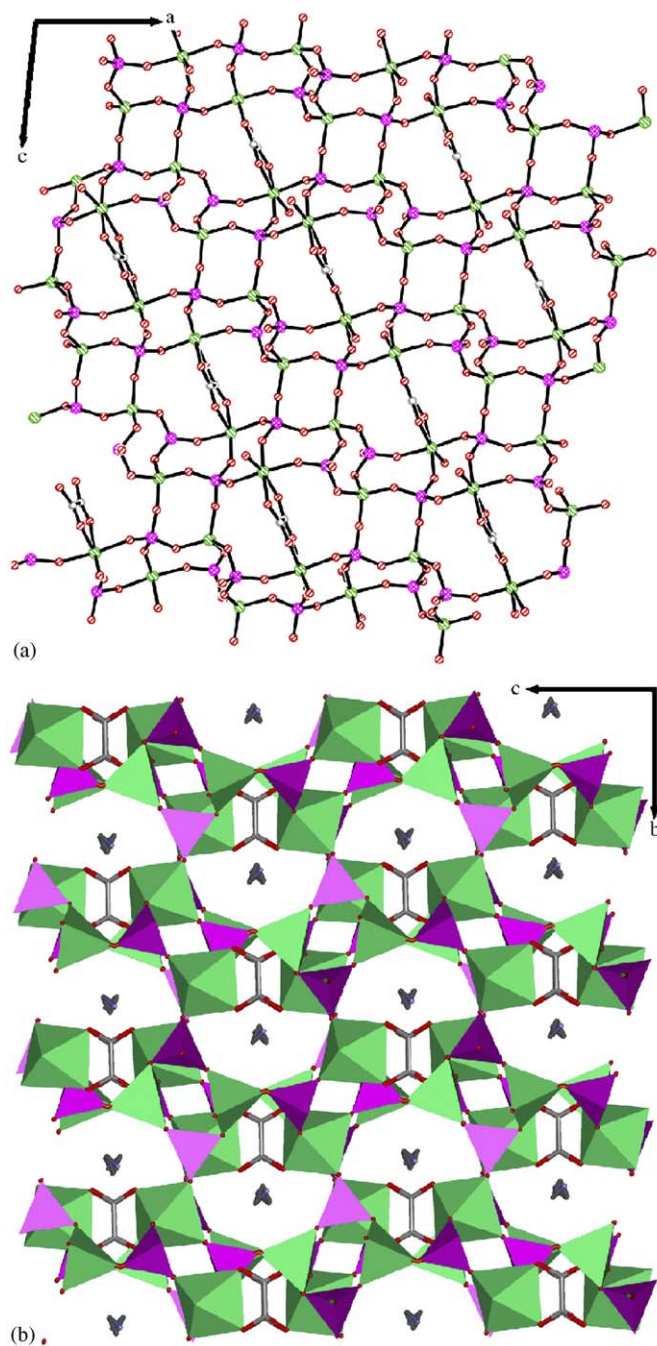
(a)

(b)

Fig. 4. (a) One layer generated by corner sharing building units in compound **3** and (b) view of structure **3**, showing 8MR channels along *a*-axis.
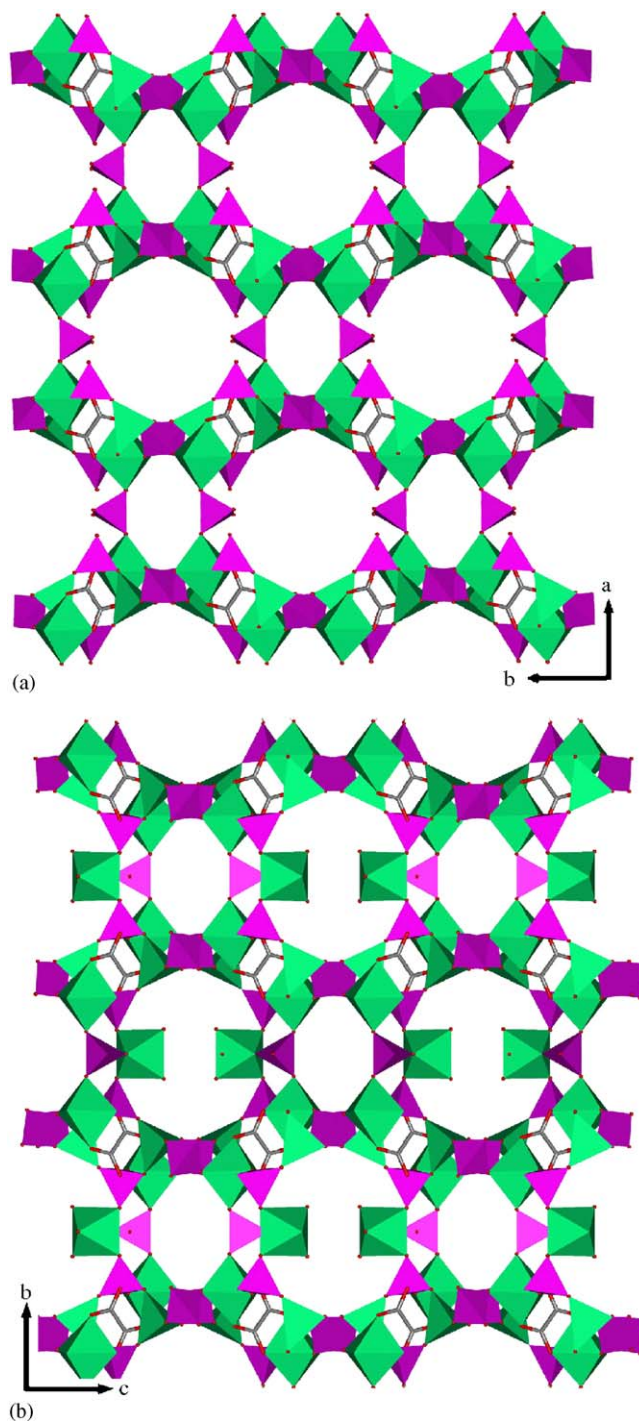

(a)

(b)

Fig. 5. View of structures **4** (a) and **5** (b), showing two types of 8MR and 12MR channel. The organic amines were omitted for clarify.

compounds **1** and **2**, which is consistent with the results based on structure refinements. The total observed weight loss, 26.5% for **1** and 21.8% for **2**, can be compared with those calculated, 26.4% from $0.5DAP + CO_2 + 2H_2O$ for compound **1** and 22.0% from $0.5en + H_2O + CO_2$ for **2**. For compound **4**, the observed weight loss is 21.2% up to 500 °C, which corresponds to the removal of lattice water and organic amines (21.5% from $0.5DETA + CO + 1.5H_2O$).

In summary, five organic–inorganic hybrid gallium oxalate-phosphates were hydrothermally synthesized by using 1,3-DAP, ethylenediamine and DETA as structure-directing agents. From the structure point of view, compound **1**–**5** share similar features. The structures of all the five materials show an arrangement of $Ga_4(PO_4)_4$ (C_2O_4) anionic building units and negative charges are balanced by the corresponding organic cations. A unique UUDD assembly of building units in compound **3** and two

novel 3-D linkers in compound **4** and **5** were observed for the first time.

Acknowledgments

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