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Inorganic Chemistry Article

Synthesis and Characterization of the First Organically Templated Metal Oxalatophosphonate: $(C_3H_{12}N_2)_{0.5}[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot 0.5H_2O$

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The first organically templated gallium oxalatophosphonate has been synthesized under hydrothermal conditions and characterized by single-crystal X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. The structure consists of GaO_6 octahedra and GaO_4 tetrahedra connected by methylphosphonate and bis-bidentate oxalate anions to form anionic sheets in the *ab* plane with the charge-compensating propylenediammonium cations and water molecules between the sheets. The methyl groups of the phosphonate ligands extend from both sides of the layers into the interlamellar region. Crystal data: monoclinic, space group $P2_1/n$ (No. 14), $a = 8.8514(4)$ Å, $b = 16.3030(7)$ Å, $c = 15.0816(7)$ Å, $\beta = 97.539(1)°$, and $Z = 4$.

Introduction

The synthesis of open-framework metal phosphates and metal phosphonates has been extensively studied, owing to potential applications in ion exchange and catalysis. This research has led to a vast number of new compounds, displaying wide structural variations.[1−4] Recently, many research activities have focused on the synthesis of organic−inorganic hybrid compounds by incorporating organic ligands in the structures of metal phosphates. As compared with inorganic phosphates, the organic molecules have larger sizes and a wide variety of means of connection. This idea is currently used by a number of groups and leads to a large number of oxalatophosphates of transition metals and main-group elements.[5] Most of these compounds are synthesized in the presence of an organic amine as the structure-directing agent. They commonly adopt 3-D framework structures, whereas only a few have 2-D layer or 1-D chain structures. However, very few reports in the literature illustrate the use of oxalate anions forming part of the structure with the phosphonate groups, although this area of metal phosphonate chemistry has been the focus of intense research for many years. We report herein an organically templated oxalatophosphonate, $(C_3H_{12}N_2)_{0.5}[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot 0.5H_2O$, with a layer structure. This compound is original in that methylphosphonate and oxalate anions, associated with a group 13 element, are incorporated into the skeleton of a layer structure templated with an amine. Two compounds were published which had the characteristics of the title compound concerning the two anions with metals, namely, the tin compounds $Sn_2(O_3PCH_3)(C_2O_4)$ and $Sn_4(O_3PCH_2CH_2CO_2)_2(C_2O_4)$.[6,7] The former has a 2D layer structure, and the latter adopts a 3D framework structure which consists of two different bifunctional linkers, phosphonopropionate and oxalate anions. However, organic templates are not included in these structures.

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Experimental Section

Synthesis and Preliminary Characterization. The hydrothermal reactions were carried out in Teflon-lined stainless steel Parr acid digestion bombs with an internal volume of 23 mL. All chemicals were purchased from Aldrich. Colorless long thin plate crystals of $(C_3H_{12}N_2)_{0.5}[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot 0.5H_2O$ (**1**) were obtained by heating a mixture of gallium nitrate hydrate (1 mmol), methylphosphonic acid (3 mmol), oxalic acid (2 mmol), 1,3-diaminopropane (2.8 mmol), sodium chloride (2 mmol), and water (10 mL) at 165 °C for 3 d and very slow cooling to 70 °C at 1 °C/h followed by fast cooling to room temperature by turning off the power of the oven. The pH after the reaction was 2.9, and the yield was 19% based on gallium. We have also carried out retrosyntheses without NaCl, with 1 and 3 mmol of NaCl, and with 2 mmol of KCl; the resulting product from the reaction with 1 mmol of NaCl contains colorless thin plate crystals of **1** in 24% yield, whereas the other products are a mixture of **1** in smaller crystal sizes and a small amount of unidentified side products. It appears that the addition of 1 or 2 mmol of NaCl helps grow larger crystals of **1** with better quality. A reaction with 2 mmol of NaF did not produce **1**, as indicated from powder X-ray diffraction. Energy-dispersive X-ray fluorescence spectroscopy of several plate crystals did not reveal any Na and confirms the presence of Ga and P. Powder X-ray data were collected on a Shimadzu XRD-6000 automated powder diffractometer with Cu Kα radiation equipped with a scintillation detector. Data were collected in the range $5° < 2\theta \leq 50°$ at a very slow scan speed of 0.1 deg/min in 2θ using the $\theta-2\theta$ mode in a flat plate geometry. The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern on the basis of the results from single-crystal X-ray diffraction (see Figure S1 in the Supporting Information). However, the intensities of the 00*l* reflections are considerably greater than the values in the simulated pattern because of the preferred orientation of the crystallites within the powder specimen. Most peaks in the diffraction pattern are broadened. The 00*l* reflections appear to have narrower profiles. The broadened reflection profiles could be due to disordering of the layers in the stacking direction in some very thin plate crystals in the sample. Elementary analysis results of the bulk product are consistent with the stoichiometry (Found: C, 12.77; H, 2.44; N, 1.72. Calcd for $C_{7.5}Ga_3H_{19}NO_{16.5}P_4$: C, 12.51; H, 2.66; N, 1.94).

The infrared spectrum was recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer using the KBr pellet method. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA7 thermal analyzer. The sample was heated from 40 to 900 °C at 5 °C min^{-1} in flowing N_2 or O_2.

Single-Crystal X-ray Diffraction. A colorless crystal of dimensions $0.21 \times 0.09 \times 0.06$ mm^3 was selected for indexing and intensity data collection on a Siemens Smart CCD diffractometer equipped with a normal-focus, 3 kW sealed tube X-ray source. Most crystals in the reaction product were twinned because of the platey morphology. A number of crystals were selected and checked for reflection profiles before a satisfactory one was obtained. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). The number of observed unique reflections ($F_o > 4\sigma(F_o)$) is 4450 ($2\theta_{max} = 56.63°$, $R_{int} = 0.035$). Empirical absorption corrections based on symmetry equivalents were performed by using the SADABS program for the Siemens area detector ($T_{min,max} = 0.735, 0.960$). On the basis of systematic absences, the statistics of intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P2_1/n$ (No. 14). The structure was solved by direct methods: The metal and P atoms were first located, and the C, N, and O atoms were found from difference Fourier maps. The propylenediammonium cation is statistically distributed over four positions. The molecule is located on sites close to an inversion center. Each atom in the molecule is disordered over two positions, so that four alternative orientations are generated by an inversion center. A lattice water oxygen atom site with 50% occupancy was also located. The H atoms were not located. The final cycles of least-squares refinement including the atomic coordinates and anisotropic thermal parameters of all atoms in the skeleton of the layer structure and isotropic thermal parameters for all atoms in the amine molecule converged at R1 = 0.0402, wR2 = 0.1041, and $S = 1.146$. $\Delta\rho_{max,min} = 0.69, -0.40$ $e\cdot Å^{-3}$. Neutral atom scattering factors were used for all the atoms. Anomalous dispersion and secondary extinction corrections were applied. All calculations were carried out with the PC version of the SHELXTL program package.[8] The crystallographic data are given in Table 1 and selected bond lengths in Table 2.

Table 1. Crystallographic Data for $(C_3H_{12}N_2)_{0.5}[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot 0.5H_2O$

empirical formula	$C_{7.5}Ga_3H_{19}NO_{16.5}P_4$
a/Å	8.8514(4)
b/Å	16.3030(7)
c/Å	15.0816(7)
β/deg	97.539(1)
V/Å^3	2157.5(3)
Z	4
fw	720.28
space group	$P2_1/n$ (No. 14)
T/°C	23
λ(Mo Kα)/Å	0.71073
D_{calcd}/g·cm^{-3}	2.217
μ(Mo Kα)/cm^{-1}	41.0
R1[a]	0.0402
wR2[b]	0.1041

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\max(F_o, 0) + 2(F_c)^2]/3$, $a = 0.0422$, and $b = 2.55$.

Table 2. Bond Lengths (Å) for $(C_3H_{12}N_2)_{0.5}[Ga_3(C_2O_4)(CH_3PO_3)_4]\cdot 0.5H_2O$

Ga(1)−O(2)	1.930(3)	Ga(1)−O(6)	1.883(3)
Ga(1)−O(7)	1.950(3)	Ga(1)−O(12)	1.948(3)
Ga(1)−O(14)	2.032(3)	Ga(1)−O(15)	2.070(3)
Ga(2)−O(1)	1.794(3)	Ga(2)−O(4)	1.821(3)
Ga(2)−O(9)	1.835(3)	Ga(2)−O(11)	1.806(3)
Ga(3)−O(3)	1.919(3)	Ga(3)−O(5)	1.904(3)
Ga(3)−O(8)	1.905(3)	Ga(3)−O(10)	1.957(3)
Ga(3)−O(13)	2.024(3)	Ga(3)−O(16)	2.042(3)
P(1)−O(1)	1.542(3)	P(1)−O(2)	1.507(3)
P(1)−O(3)	1.494(3)	P(1)−C(1)	1.794(5)
P(2)−O(4)	1.535(3)	P(2)−O(5)	1.513(3)
P(2)−O(6)	1.508(3)	P(2)−C(2)	1.782(5)
P(3)−O(7)	1.523(3)	P(3)−O(8)	1.505(3)
P(3)−O(9)	1.539(3)	P(3)−C(3)	1.782(5)
P(4)−O(10)	1.511(3)	P(4)−O(11)	1.540(3)
P(4)−O(12)	1.528(3)	P(4)−C(4)	1.780(6)
C(5)−O(13)	1.252(5)	C(5)−O(14)	1.281(5)
C(6)−O(15)	1.259(5)	C(6)−O(16)	1.254(5)

Results and Discussion

Characterization. The FTIR spectrum (Figure 1) displays bands characteristic of a H-bonded H_2O molecule [ν(O−H) ≈ 3400 cm^{-1}], an RNH_3^+ group [ν(N−H) ≈ 3100 cm^{-1}], an oxalate ligand [ν(C−O) = 1690, 1367, 1307 cm^{-1}], a CH_2 group [δ_{as}(C−H) = 1495 cm^{-1}], and a CH_3 group

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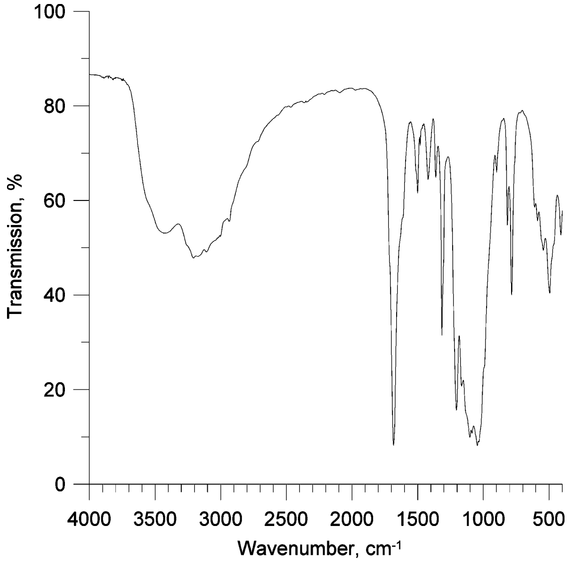

Figure 1. FTIR spectrum of **1**.

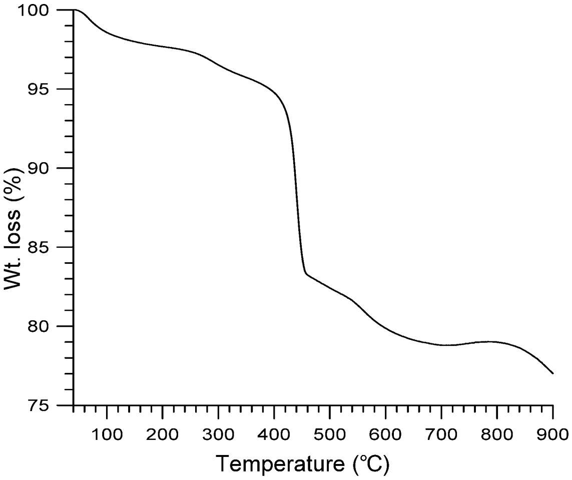

Figure 2. Thermogravimetric analysis of **1** in flowing nitrogen at 5 °C min^{-1}.

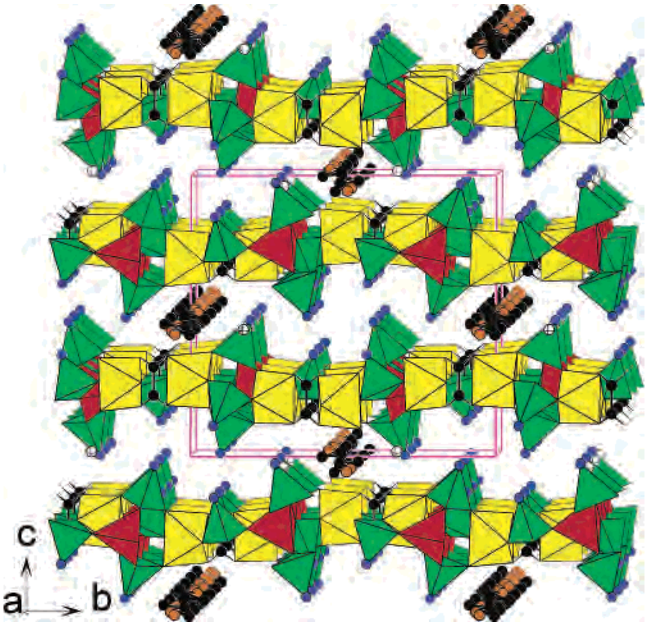

Figure 3. Structure of **1** viewed along the *a* axis. The yellow, red, and green polyhedra are GaO_6 octahedra, GaO_4 tetrahedra, and CPO_3 tetrahedra, respectively. Black circles are C atoms, orange circles are N atoms, blue circles are C atoms of CPO_3 tetrahedra, and white circles with principal ellipses are water oxygen atoms. H atoms are not shown.

[δ_s(C−H) = 1420 cm^{-1}, δ_{as}(C−H) at about 1310 cm^{-1}], thus confirming the presence of organic components and a water molecule. A group of peaks around 1100 cm^{-1} correspond to the stretching of $-PO_3$ groups.

The TGA curve shows a number of weight losses, indicating a complex process of decomposition (Figure 2). The weight loss commences at room temperature. This is due to the loss of a lattice water molecule. We can attribute this facile loss of lattice water to the low degree of hydrogen bonding holding the water in the crystal lattice. There are several overlapping weight losses between 100 and 420 °C. They can be attributed to the deprotonation and volatilization of the organic amine. The observed weight loss between 40 and 420 °C is 6.0%, which is close to that calculated for the loss of 0.5 mol of $C_3H_{10}N_2$ and 0.5 mol of H_2O (6.39%). The rapid weight loss of 10.5% between 420 and 450 °C is attributed to the loss of $1CO_{(g)}$, $1CO_{2(g)}$, and $0.5H_2O$, calculated as 11.25%. The weight loss above 450 °C can be assigned to the decomposition of methylphosphonate groups. The slight weight gain at about 750 °C is unclear to us. Another TGA experiment was performed in which the sample was heated in flowing O_2. The TGA curve is similar to that measured in N_2, but does not show any weight gain at about 750 °C. The decomposition was incomplete by 900 °C in both experiments.

The XRD patterns of a sample that has been heated at 95 and 200 °C show that the framework is maintained after loss of water of crystallization (see Figure S2 in the Supporting Information). The decomposition step between 420 and 450 °C is supported by the TGA data for $K_2[Ga_4(C_2O_4)(PO_4)_4]\cdot 2H_2O$,[9] which shows the weight loss due to the decomposition of oxalate at about 500 °C. The IR spectrum of **1** that was heated at 450 °C does not display the peaks at 1690 and 1367 cm^{-1} due to ν(C−O) of the oxalate and the sharp peak at 1495 cm^{-1} due to δ_{as}(C−H) of the CH_2 group (see Figure S3 in the Supporting Information). Therefore, the loss of the amine and oxalate above 450 °C is confirmed. The peaks due to δ_s(C−H) and δ_{as}(C−H) of the phosphonate methyl group remain in the spectrum. To identify the final decomposition products, a separate sample was heated in flowing N_2 at 900 °C for 3 h. The products contained $GaPO_4$ (JCPDS 31-546) and black glassy carbon, as indicated from powder X-ray diffraction and the color. CHN analysis of the decomposition product of a sample that had been heated in flowing N_2 at 700 °C for 1 h gave C, 4.63; H, 0.28; N, 0.24. The results indicate complete loss of the organic amine molecules and oxalate units and partial decomposition of methylphosphonate ligands.

Structure. A polyhedral plot of the complete crystal structure is shown in Figure 3. It consists of anionic sheets of the formula $[Ga_3(C_2O_4)(CH_3PO_3)_4]^-$ with charge-compensating propylenediammonium cations and water molecules between the layers. There are two sheets per unit cell

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(9) Hung, L.-C.; Kao, H.-M.; Lii, K.-H. *Chem. Mater.* **2000**, *12*, 2411.

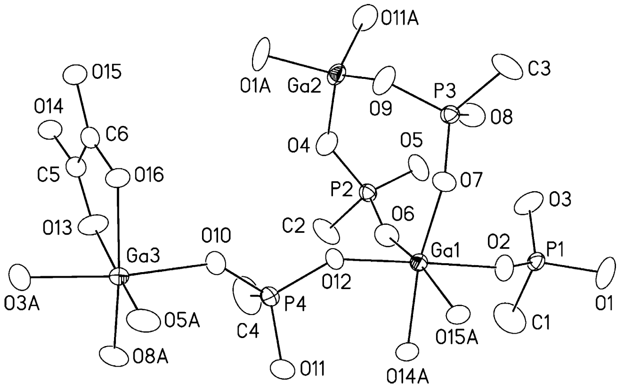

Figure 4. Coordination environments of the Ga atoms in the structure of **1** showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability. H atoms are not shown.

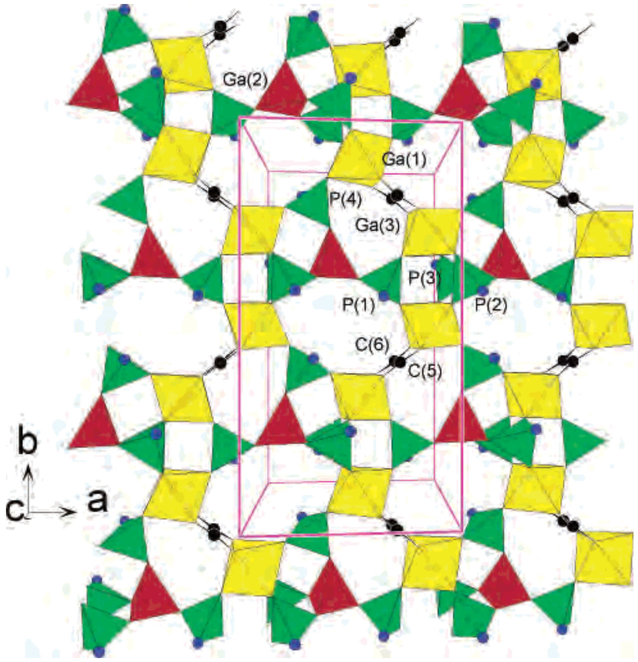

Figure 5. Section of a gallium oxalatophosphonate layer in **1** viewed along the *c* axis.

length along the *c* axis. Adjacent sheets are related by an inversion center. The asymmetric unit is constructed from the following structural elements: three Ga atoms, one oxalate, and four methylphosphonate ligands, all of which are at general positions in the unit cell (Figures 4 and 5). Both Ga(1) and Ga(3) are octahedrally coordinated by one bidentate oxalate and four methylphosphonate units. In contrast, Ga(2) is tetrahedrally coordinated by four methylphosphonate units. The Ga−O bond lengths vary from 1.883(3) to 2.070(3) Å for Ga(1), from 1.794(3) to 1.835(3) Å for Ga(2), and from 1.904(3) to 2.042(3) Å for Ga(3). The coordination by the oxalate leads to a distorted octahedron for Ga(1) and Ga(3), as indicated by the wide range of Ga−O bond lengths and the O−Ga−O bond angles [80.6° for Ga(1) and 81.2° for Ga(3)] subtended by the oxalate group. The distortion is slightly more pronounced than that in $[(R)\text{-}C_5H_{14}N_2]_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$,[10] which is a layered gallium oxalatophosphate containing both GaO_6 octahedra and GaO_4 tetrahedra. The ranges of Ga−O bond lengths in the GaO_4 tetrahedra in both structures are comparable. In the structure of **1** each oxalate unit is a bis-bidentate ligand to one Ga(1) and one Ga(3) atom. This is a common type of oxalate coordination in the structures of oxalatophosphates. The coordination environments of four distinct methylphosphonate units are chemically similar. Each methylphosphonate coordinates to one tetrahedral Ga and two octahedral Ga atoms, with the methyl group being directed toward the interlamellar region. The P−O and P−C bond lengths agree well with those found in other metal phosphonates. Four-, six-, and eight-membered rings are formed within the layer structure, with the latter consisting of three GaO_6 octahedra, one GaO_4 tetrahedron, one oxalate, and three CH_3PO_3 units. The propylenediammonium cations and lattice water molecules reside in the interlamellar region and are disordered. Each organic cation forms hydrogen-bonding interaction with a framework oxygen atom, as inferred from the short N(1A)···O(12) distance of 2.74 Å. The cation is disordered because it is not stabilized via extensive hydrogen bonds to the framework atoms. The water molecule is disordered over two positions with 50% occupancy and is also H-bonded to a framework oxygen atom (Ow(1)···O(5) = 2.83 Å).

A large number of organically templated oxalatophosphates have been reported. Most of them adopt 3-D framework structures, whereas only a few have 2-D sheet or 1-D chain structures. In most cases, the 3-D frameworks are formed of metal phosphate layers connected by bis-bidentate oxalate bridges. The oxalate units are out-of-plane with respect to the inorganic layers. In contrast, the incorporation of oxalate units within the layers (in-plane) has been observed in only three layer structures, namely, $(NH_4)_2[VO(HPO_4)]_2(C_2O_4)\cdot H_2O$,[11] $[(R)\text{-}C_5H_{14}N_2]_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$,[10] and $(H_3TREN)[M_2(HPO_4)(C_2O_4)_{2.5}]\cdot 3H_2O$ (M = Mn and Fe).[12] $Sn_2(O_3PCH_3)(C_2O_4)$ is the first example reported in the literature which uses an oxalate ligand to form part of the framework along with the phosphonate group.[6] The compound consists of infinite chains of vertex-linked SnO_4 and O_3PC units which are connected via in-plane oxalate groups, forming the 2-D corrugated layer structure. The oxalate anion is incorporated by the decomposition of the tin oxalate used in the starting material. Although *n*-butylamine was added in the starting mixture, the organic template is not included in the structure. In the course of our synthesis of metal oxalate−organophosphonates, we noted that most compounds form thin, flat, easily separated sheets, indicating that they have 2-D layer structures. Presumably, they consist of layers of metal centers linked through CPO_3 tetrahedra and oxalate units. The organic components of organophosphonate groups extend from both sides of the layers and hinder metal ligation by out-of-plane oxalate linkages. To promote the formation of 3-D covalent connectivities, organodiphosphonate ligands can be used. The organic tethers of the diphosphonate groups might project

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outward from both sides of the M/Ox/P/O sheet to produce a 3-D covalent framework. Recently, three organically templated gallium methylenediphosphonates were reported.[13] However, all three materials contain a corrugated layer motif composed of octahedral $GaO_5(OH)$ units that are linked together by the diphosphonate groups. It would be interesting to learn about the role of the diphosphonate group in the structure along with the other structural moieties, viz., oxalate anions. Further work on this theme is in progress.

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Supporting Information Available: Crystallographic data in CIF format, and X-ray powder patterns and IR spectrum (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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