Synthesis and Characterization of $(R\text{-}C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$, a Layered Gallium Phosphatooxalate Containing a Chiral Amine

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The first metal phosphatooxalate containing a chiral amine, $(R\text{-}C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction and ^{31}P MAS NMR spectroscopy. It crystallizes in the monoclinic space group $P2_1$ (No. 4) with $a = 8.0248(4)$ Å, $b = 25.955(1)$ Å, $c = 9.0127(5)$ Å, $\beta = 100.151(1)°$, and $Z = 2$. The structure consists of GaO_6 octahedra and GaO_4 tetrahedra connected by coordinating $C_2O_4^{2-}$ and phosphate anions to form anionic sheets in the *ac* plane with charge-compensating diprotonated *R*-2-methylpiperazinium cations and water molecules between the layers. There is a good correlation between the NMR spectrum and the structure.

Introduction

Open-framework materials have been the subject of intense research owing to their interesting structural chemistry and potential applications as ion-exchangers, catalysts, and adsorbents.[1−3] A large number of these materials are synthesized in the presence of organic amines as structure-directing agents.[4−7] Recently, many research activities have focused on the synthesis of inorganic−organic hybrid frameworks.[8−13] Compared with inorganic ligands, the advantage of using organic multidentate ligands is the efficacy of rational design of crystalline solids through their coordinating propensities and geometries. We and others have synthesized a number of inorganic−organic hybrid frameworks, namely, phosphatooxalates of Fe,[14−16] V,[17] Al,[18] Ga,[19] and In.[20] A tin phosphonate−oxalate was also reported.[21] The gallium system appears rather interesting among these compounds. For example, the structure of $[Ga_5(OH)_2(C_{10}H_9N_2)(C_2O_4)(PO_4)_4]\cdot 2H_2O$[19] consists of GaO_4 tetrahedra and GaO_6 octahedra linked by phosphate and oxalate groups to form two-dimensional sheets between which are the GaO_4N trigonal bipyramids, generating tunnels in which the monoprotonated 4,4′-bipyridinium cations reside. ^{71}Ga MAS NMR spectroscopy confirms the presence of four-, five-, and six-coordinate Ga atoms in the structure.

Recently, we reported a one-dimensional gallophosphate, $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$, which is the first metal phosphate containing a chiral amine.[22] Several three-dimensional aluminophosphates and gallophosphates prepared by using optically pure metal complex *d*-$Co(en)_3^{3+}$ as a structure-directing agent were reported.[23,24] However, the use of chiral organic amines as structure-directing agents to prepare three-dimensional microporous materials has not been successful. In an attempt to synthesize a chiral open-framework phosphatooxalate, we have synthesized a new gallium compound, $(R\text{-}C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$ (**1**), which possesses a two-dimensional layer structure with diprotonated *R*-2-methylpiperazinium cations located between the layers. It is the first example of a phosphatooxalate containing a chiral organic amine and is also a good example that shows how ^{31}P MAS NMR spectroscopy helps determine the composition.

Experimental Section

Synthesis and Initial Characterization. In a typical hydrothermal synthesis, a mixture of $Ga(NO_3)_3\cdot 4H_2O$, *R*-2-methylpiperazine, $C_2H_2O_4\cdot 2H_2O$, H_3PO_4, and H_2O in the molar ratio of 1:5:4:5:555 was

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sealed in a Teflon lined acid digestion bomb and heated at 165 °C for 3 days followed by slow cooling at 10 °C h^{-1} to room temperature. The resulting product consists of colorless plate-shaped crystals of **1** in a 64% yield based on Ga. A suitable plate crystal was carefully selected for structure determination by single-crystal X-ray diffraction. The product is monophasic because its powder X-ray diffraction pattern can be completely indexed based on the unit cell parameters from single-crystal X-ray studies. However, the intensities of $0k0$ reflections are considerably greater than the values simulated from single-crystal data because of the preferred orientation of crystals within the powder specimen. Energy dispersive X-ray (EDX) analysis shows the presence of Ga and P. Elemental analysis confirms the stoichiometry. Anal. Found: C, 12.27; H, 3.04; N, 4.71. Calcd: C, 12.20; H, 3.07; N, 4.74. Thermogravimetric analysis was carried out using a Perkin-Elmer TGA7 thermal analyzer from room temperature to 900 ˚C under flowing air. The sample lost weight gradually in several overlapping steps. The first weight loss began at ca. 100 °C and was complete by ca. 350 °C. The observed weight loss of 3.11% is in good agreement with the value calculated for the loss of two molecules of lattice water per formula unit (calcd 3.05%). Further weight loss began at ca. 350 °C, had a maximum rate at ca. 430 °C, and was incomplete by 900 °C.

Single-Crystal X-ray Diffraction. Colorless plate crystals of **1** with the dimensions 0.68 mm × 0.12 mm × 0.02 mm was mounted on a Siemens Smart-CCD diffractometer equipped with a normal focus, 3 kW sealed-tube X-ray source. Intensity data were collected in 1271 frames with increasing ω (width of 0.30° per frame). The orientation matrix and unit cell dimensions were determined by a least-squares fit of 7375 reflections. Octants collected and $2\theta_{\max}$: $-10 \leq h \leq 10$, $-24 < k \leq 34$, $-10 \leq l \leq 11$ and 56.5°. Number of measured reflections and observed unique reflections [$I > 2\sigma(I)$]: 11003 and 5458. Empirical absorption corrections were performed by using the SADABS program for Siemens area detector ($T_{\min,\ \max}$: 0.609, 0.912).[25] On the basis of systematic absences, statistics for intensity distribution, and successful solution and refinement of the structure, the space group was determined to be $P2_1$ (No. 4). The structure was solved by direct methods. The Ga and P atoms were first located, and the C, N, and O atoms were found in difference Fourier maps. The Flack x parameter was 0.024(12), indicative of a correct absolute structure. The H atoms were not located. Ow(1) and Ow(2), which are located at sites between layers of gallium phosphatooxalate, are water oxygen atoms. The final cycles of least-squares refinement converged at R1 = 0.0348 and wR2 = 0.0976. The final difference Fourier maps were flat ($\Delta r_{\max,\ \min} = 0.81$, -0.72 e/Å^3). Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed using SHELXTL programs.[26]

Solid-State NMR Measurements. Room-temperature ^{31}P MAS NMR spectrum of **1** was acquired at a ^{31}P frequency of 161.73 MHz on a Bruker DSX-400 spectrometer equipped with a Bruker double-tuned 4 mm probe, under conditions of high-power proton decoupling. A pulse length of 12 μs and repetition time of 100 s were used. The ^{31}P chemical shifts were reported relative to 85% H_3PO_4 as an external reference. A cross-polarization (CP) pulse sequence followed by ^{1}H high-power decoupling was used to measure the ^{31}P CP MAS spectra. As shown in Figure 1, two resonances at 0.7 and −9.0 ppm with relative intensities of 1.0:2.08 are observed. Figure 2 shows the contact time dependence of a ^{31}P CP MAS spectrum.

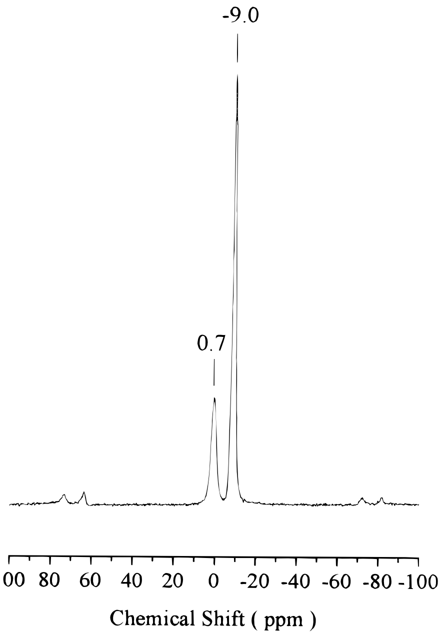

Figure 1. Proton-decoupled ^{1}P MAS NMR spectrum of **1** acquired at a spinning speed of 10 kHz.

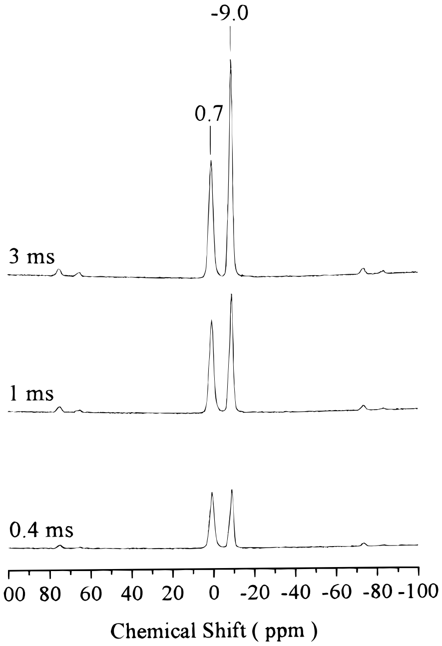

Figure 2. $^1H \rightarrow {}^{31}P$ CP/MAS NMR spectra of **1** obtained at three different contact times.

Results and Discussion

The crystallographic data are summarized in Table 1. The atomic coordinates and bond lengths are given in Tables 2 and 3, respectively. Figure 3 shows the asymmetric unit of **1**. This compound crystallizes in the enantiomorphic space group $P2_1$. The Ga atoms are six- and four-coordinated. Bond-valence calculations indicate that both Ga atoms are trivalent, O(12), O(14), O(15), O(16), O(18), O(19), O(20), and O(24) have valence sums of 1.30, 1.41, 1.23, 1.14, 1.37, 1.20, 1.10 and 1.41, respectively, and all other oxygen atoms have values close to 2.[27] The valence sums of O(12), O(14), O(18), and O(24) can be satisfied by forming hydrogen bonds with hydrogen phosphate groups and R-2-methylpiperazinium cations [O(12)···O(15) = 2.49 Å, O(12)···N(3) = 2.75 Å, O(14)···N(1) = 2.69 Å, O(14)···N(4) = 2.81 Å, O(18)···N(2) = 2.78 Å, O(18)···N(3) = 2.73 Å, O(24)···O(19) = 2.49 Å, O(24)···N(1) = 2.73 Å]. To balance charge, all other O atoms with undersaturated valence sums are hydroxo oxygens. Therefore, P(1), P(2), P(3), and P(6) form PO_4 groups, and P(4) and P(5) are H_2PO_4 groups. The presence of two types of monophosphate in the structure is confirmed by ^{31}P MAS NMR spectroscopy (vide infra).

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Table 1. Crystallographic Data for $(R\text{-}C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$

empirical formula	$C_{12}H_{36}N_4O_{30}P_6Ga_4$
fw	1181.15
space group	$P2_1$
a, Å	8.0248(4)
b, Å	25.955(1)
c, Å	9.0127(5)
β, deg	100.151(1)
vol, Å^3	1847.8(3)
Z	2
D_{calc}, g cm^{-3}	2.123
μ, mm^{-1}	3.26
temp, °C	22
λ, Å	0.710 73
R1[a]	0.0348
wR2[b]	0.0976

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(|F_o|^2 - |F_c|^2)^2]/[w(|F_o|^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 1.31P]$ and $P = [\max(F_o^2,0) + 2F_c^2]/3$.

Table 2. Atomic Coordinates and Thermal Parameters (Å^2) for $(R\text{-}C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$

atom	x	y	z	U_{eq}[a]
Ga(1)	0.00934(8)	0.28503	0.67147(7)	0.0120(2)
Ga(2)	0.50180(8)	0.39120(3)	0.81704(7)	0.0120(2)
Ga(3)	0.01355(8)	0.34913(4)	0.22190(7)	0.0134(2)
Ga(4)	0.49963(8)	0.32627(4)	0.26741(7)	0.0130(2)
P(1)	0.2164(2)	0.33268(7)	0.9804(2)	0.0115(3)
P(2)	0.2952(2)	0.34319(7)	0.5086(2)	0.0114(3)
P(3)	0.8279(2)	0.26044(8)	0.3259(2)	0.0136(4)
P(4)	0.1635(2)	0.17398(9)	0.6075(2)	0.0214(4)
P(5)	0.3536(2)	0.50208(8)	0.8880(2)	0.0203(4)
P(6)	0.6854(2)	0.41554(8)	0.1640(2)	0.0138(4)
O(1)	0.1553(5)	0.2894(2)	0.8700(4)	0.015(1)
O(2)	0.3123(6)	0.3751(2)	0.9151(5)	0.017(1)
O(3)	0.3248(5)	0.3065(2)	0.1172(4)	0.016(1)
O(4)	0.0677(5)	0.3600(2)	0.0363(4)	0.019(1)
O(5)	0.3544(6)	0.3857(2)	0.6194(5)	0.019(1)
O(6)	0.2009(5)	0.3004(2)	0.5728(5)	0.018(1)
O(7)	0.1845(6)	0.3701(2)	0.3714(5)	0.019(1)
O(8)	0.4434(5)	0.3164(2)	0.4525(4)	0.016(1)
O(9)	0.8536(6)	0.2839(2)	0.4818(5)	0.023(1)
O(10)	0.9614(6)	0.2816(2)	0.2367(5)	0.021(1)
O(11)	0.6538(5)	0.2784(2)	0.2396(5)	0.021(1)
O(12)	0.8325(6)	0.2019(2)	0.3219(5)	0.024(1)
O(13)	0.0548(6)	0.2127(2)	0.6737(5)	0.020(1)
O(14)	0.2361(7)	0.1329(4)	0.7160(3)	0.031(1)
O(15)	0.0638(8)	0.1480(3)	0.4644(6)	0.040(2)
O(16)	0.3150(8)	0.2040(3)	0.5586(8)	0.049(2)
O(17)	0.4522(6)	0.4638(2)	0.8127(5)	0.021(1)
O(18)	0.2675(7)	0.5427(2)	0.7824(6)	0.030(1)
O(19)	0.4712(8)	0.5299(2)	0.0193(5)	0.034(1)
O(20)	0.2139(8)	0.4724(3)	0.9592(8)	0.046(2)
O(21)	0.6601(5)	0.3949(2)	0.0064(4)	0.022(1)
O(22)	0.5478(6)	0.3938(2)	0.2483(5)	0.022(1)
O(23)	0.8589(6)	0.3972(2)	0.2505(5)	0.024(1)
O(24)	0.6845(6)	0.4731(2)	0.1747(6)	0.026(1)
O(25)	0.8036(5)	0.2731(2)	0.7704(5)	0.017(1)
O(26)	0.9373(5)	0.3595(2)	0.6821(5)	0.017(1)
O(27)	0.5741(6)	0.3170(2)	0.8078(5)	0.017(1)
O(28)	0.7064(6)	0.4033(2)	0.7178(5)	0.019(1)
N(1)	0.1041(9)	0.0385(3)	0.6456(8)	0.037(1)
N(2)	0.1583(8)	0.4798(3)	0.5352(7)	0.028(2)
C(1)	0.976(1)	0.4720(4)	0.5506(9)	0.030(2)
C(2)	0.181(1)	0.4963(3)	0.3802(8)	0.032(2)
C(3)	0.363(1)	0.5065(4)	0.379(1)	0.056(2)
C(4)	0.119(1)	0.0212(4)	0.4881(9)	0.035(2)
C(5)	−0.076(1)	0.0464(4)	0.660(1)	0.038(2)
N(3)	0.3978(8)	0.6385(3)	0.8523(7)	0.025(1)
N(4)	0.331(1)	0.1958(3)	0.9699(8)	0.038(2)
C(6)	0.212(1)	0.6568(3)	0.0345(9)	0.045(2)
C(7)	0.392(1)	0.6509(4)	0.0172(8)	0.035(2)
C(8)	0.578(1)	0.6323(4)	−0.174(1)	0.036(2)
C(9)	0.509(1)	0.2029(4)	−0.0519(9)	0.037(2)
C(10)	0.678(1)	0.6814(5)	−0.1328(9)	0.046(3)
C(11)	0.7928(8)	0.3629(3)	0.7169(6)	0.012(1)
C(12)	0.7163(8)	0.3122(3)	0.7680(6)	0.016(1)
Ow(1)	−0.120(1)	0.5317(6)	0.939(2)	0.149(6)
Ow(2)	0.630(1)	0.1492(4)	0.537(1)	0.085(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

A polyhedral plot of the complete crystal structure of **1** is shown in Figure 4. It consists of anionic sheets of the formula $[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]^{4-}$ with charge compensating diprotonated *R*-2-methylpiperazinium cations and water molecules between the layers. Each layer is constructed from two types of infinite chains; one is made of $Ga(1)O_6$ and $Ga(2)O_6$ octahedra, phosphate tetrahedra, and oxalate anions, while the other is made of $Ga(3)O_4$, $Ga(4)O_4$, and phosphate tetrahedra. The infinite chains, both parallel to the *a* axis, are linked via coordinating PO_4^{3-} to form a layer in the *ac* plane (Figure 5). The $H_2P(4)O_4^-$ and $H_2P(5)O_4^-$ groups are connected to $Ga(1)O_6$ and $Ga(2)O_6$ octahedra, respectively, and extend from the layer as pendant groups. Each layer encompasses a six-membered window formed by the edges of two GaO_6 octahedra, a GaO_4 tetrahedron, an oxalate anion, and two phosphate tetrahedra. Adjacent layers, which are symmetry-related by the 2_1 axis, are not aligned to form straight tunnels along the *b* axis. Oxalate anions act as bisbidentate ligands to both Ga(1) and Ga(2) to form dimers of GaO_6 octahedra; the connectivity between dimers is made via bridging $P(1)O_4^{3-}$ and $P(2)O_4^{3-}$. The coordination by the oxalate leads to a distorted octahedron for Ga(1) and Ga(2), as indicated by the wide range of Ga−O bond lengths [1.914−2.028 Å for Ga(1) and 1.923−2.037 Å for Ga(2)] and the O−Ga−O bond angle [82.21° for Ga(1) and 82.54° for Ga(2)] subtended by the oxalate group. Diprotonated 2-methylpiperazinium cations are locked in position by hydrogen bonds to phosphates, namely, $P(3)O_4^{3-}$, $P(6)O_4^{3-}$, $H_2P(4)O_4^-$, and $H_2P(5)O_4^-$, that protrude from the layers as indicated by the short N···O distances [N(1)···O(14) = 2.69 Å, N(1)···O(24) = 2.73 Å, N(2)···O(5) = 2.93 Å, N(2)···O(18) = 2.78 Å, N(3)···O(12) = 2.75 Å, N(3)···O(18) = 2.73 Å, N(4)···O(1) = 2.87 Å, N(4)···O(14) = 2.81 Å]. The 2-methylpiperazininium cations run in rows parallel to the *a* axis and alternate along *c* with rows of alternate water molecules and pendant $H_2P(4)O_4$ (or $H_2P(5)O_4$) groups. Ow(2) is more involved in hydrogen-bonding to phosphate oxygens than Ow(1), as is indicated from a comparison of Ow···O distances. This accounts for the larger thermal parameters of Ow(1).

The ^{31}P MAS NMR spectrum shows two peaks at 0.7 and −9.0 ppm with relative intensities close to 1:2. These signals correspond to the two different types of phosphate. In studies of a series of layered Ti, Zr, and Al phosphates by MAS NMR spectroscopy, Nakayama et al. reported that the isotropic ^{31}P chemical shifts of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} groups appear around −10, −20, and −30 ppm, respectively.[28] The isotropic ^{31}P chemical shifts move to high-field values with decreasing protonation. Turner et al. noted that with increasing radius of the metal ion within one group of elements the ^{31}P signal shifts downfield (BPO_4, −29.5 ppm; $AlPO_4$, −24.5 ppm; $GaPO_4$, −9.8 ppm).[29] On the basis of the previous studies, it is clearly indicated that the peak at −9 ppm is attributed to PO_4^{3-} groups

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Table 3. Selected Bond Lengths (Å) for (R-$C_5H_{14}N_2)_2[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]\cdot 2H_2O$[a]

Ga(1)−O(13)	1.912(5)	Ga(1)−O(1)	1.961(4)
Ga(1)−O(9)a	1.932(5)	Ga(1)−O(26)a	2.025(5)
Ga(1)−O(6)	1.948(4)	Ga(1)−O(25)a	2.033(4)
Ga(2)−O(17)	1.925(6)	Ga(2)−O(5)	1.962(4)
Ga(2)−O(2)	1.934(4)	Ga(2)−O(27)	2.018(5)
Ga(2)−O(21)b	1.942(4)	Ga(2)−O(28)	2.028(4)
Ga(3)−O(23)a	1.810(5)	Ga(3)−O(4)	1.822(4)
Ga(3)−O(10)a	1.812(6)	Ga(3)−O(7)	1.828(5)
Ga(4)−O(11)	1.802(5)	Ga(4)−O(8)	1.822(4)
Ga(4)−O(22)	1.810(6)	Ga(4)−O(3)	1.842(4)
P(1)−O(2)	1.521(5)	P(1)−O(3)a	1.536(4)
P(1)−O(1)	1.524(5)	P(1)−O(4)a	1.545(4)
P(2)−O(5)	1.507(5)	P(2)−O(8)	1.539(4)
P(2)−O(6)	1.515(5)	P(2)−O(7)	1.555(5)
P(3)−O(9)	1.512(5)	P(3)−O(11)	1.546(5)
P(3)−O(12)	1.521(6)	P(3)−O(10)	1.549(4)
P(4)−O(14)	1.493(6)	P(4)−O(15)	1.548(6)
P(4)−O(13)	1.520(5)	P(4)−O(16)	1.571(6)
P(5)−O(17)	1.504(5)	P(5)−O(19)b	1.555(6)
P(5)−O(18)	1.504(6)	P(5)−O(20)	1.586(6)
P(6)−O(24)	1.498(6)	P(6)−O(23)	1.546(5)
P(6)−O(21)	1.498(4)	P(6)−O(22)	1.553(4)
N(1)−C(5)	1.49(1)	N(1)−C(4)	1.51(1)
N(2)−C(2)	1.503(9)	N(2)−C(1)a	1.51(1)
C(1)−C(4)c	1.50(1)	C(2)−C(3)	1.48(1)
C(2)−C(5)d	1.56(1)	N(3)−C(8)b	1.52(1)
N(3)−C(7)b	1.529(9)	N(4)−C(9)b	1.49(1)
N(4)−C(10)e	1.53(1)	C(6)−C(7)	1.49(1)
C(7)−C(9)f	1.57(1)	C(8)−C(10)	1.52(1)
C(11)−C(12)	1.557(6)	C(11)−O(28)	1.256(8)
C(11)−O(26)	1.257(7)	C(12)−O(25)	1.230(9)
C(12)−O(27)	1.261(7)		

[a] Symmetry codes: (a) $x-1, y, z$; (b) $x, y, z+1$; (c) $-x+1, y+{}^1/_2, -z+1$; (d) $-x, y+{}^1/_2, -z+1$; (e) $-x+1, y-{}^1/_2, -z+1$; (f) $-x+1, y+{}^1/_2, -z$.

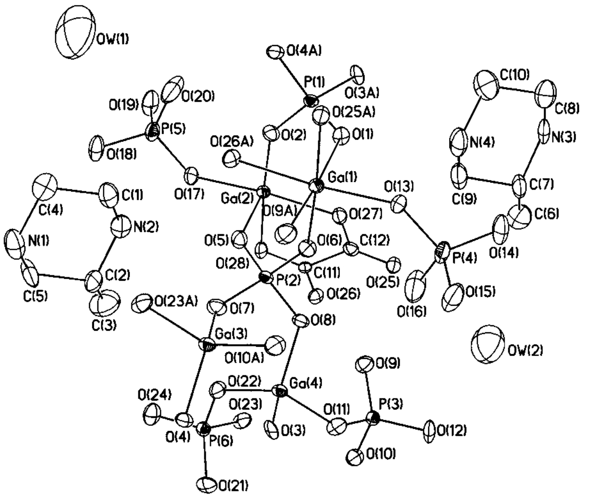

Figure 3. Fragment of the structure of **1** (50% thermal ellipsoids) showing the atom labeling scheme.

(P(1), P(2), P(3) and P(6)) and the peak at −0.7 ppm to $H_2PO_4^-$ groups (P(4) and P(5)), which is also in agreement with the relative intensities. The contact time dependence of the CP MAS spectrum is shown in Figure 2. The poor CP efficiency for the resonance at −9.0 ppm indicates that the phosphorus atom is not in proximity to the protons, consistent with the assignment of this resonance to the PO_4^{3-} group. On the other hand, an enhancement of signal intensity for the resonance at 0.7 ppm at short times is observed. This indicates that this resonance is attributed to phosphate groups associated with protons. Therefore, there is a good correlation between the NMR spectrum and the structure.

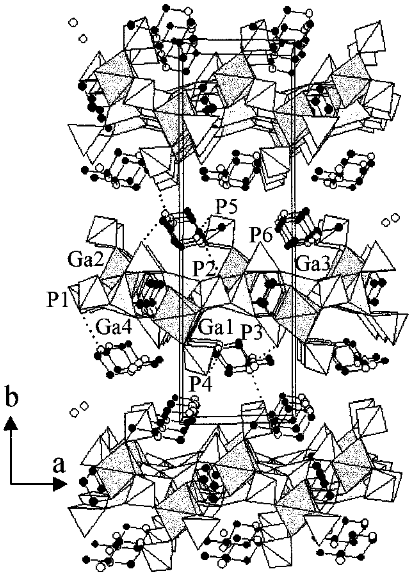

Figure 4. Polyhedral plot of the structure of **1** along the *c* axis. GaO_6 octahedra are dark-gray, GaO_4 tetrahedra are medium-gray, and PO_4 tetrahedra are without gray shading. Solid circles and stippled circles are C and N atoms of *R*-2-methylpiperazinium cations, respectively. Open circles are water oxygen atoms. The short O···N distances are shown as dotted lines.

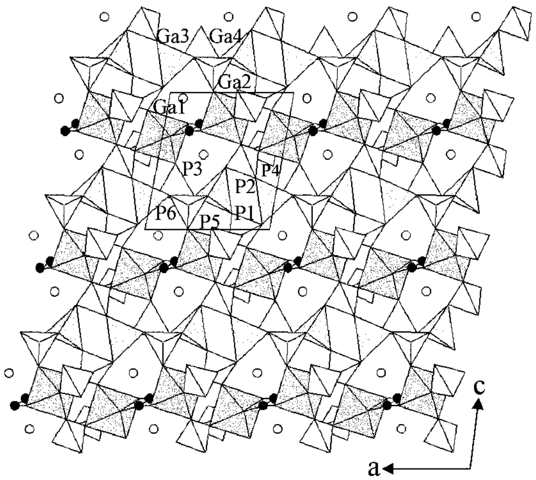

Figure 5. Section of a layer in **1** viewed along the *b* axis.

We have reported previously the gallophosphate [(1*R*,2*R*)-$C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ in an attempt to synthesize chiral microporous materials.[22] It is the first metal phosphate containing a chiral amine. It adopts a 1-D chain structure, and each chain contains a zigzag Ga−O(H)−Ga−O(H) backbone with alternating short and long Ga−O(H) bonds (1.967 and 2.007 Å). However, an alternation of the Al−O bond length (1.930, 1.946 Å) along the chain axis is also present in the analogous compound $CaMgAl(OH)(PO_4)_2(H_2O)_4$, although it crystallizes in a centrosymmetric space group.[30] Therefore, such bond alternation does not necessarily result from the presence of a chiral template, and the degree to which chirality of the organic amine is transferred to the $[Ga(OH)(HPO_4)_2]_\infty$ chain is small. It is unlikely in this case that the amine cations can be removed or ion-exchanged without collapse of the structure or loss of chirality.

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(30) Moore, P. B.; Araki, T. *Am. Mineral.* **1977**, *62*, 692.

Summary

We have extended this research to the system of gallium phosphatooxalate. The title compound is the first example in this system that contains a chiral amine. It adopts a 2-D layer structure with the chiral amine located between layers. Adjacent layers are symmetry-related by the 2_1 axis and are held together via the H-bonding of the organic amine to those phosphates that protrude from the layers. The amine cations are located at two unique sites that are surrounded by $P(3)O_4^{3-}$, $H_2P(4)O_4^{-}$, and $H_2P(5)O_4^{-}$; and $H_2P(4)O_4^{-}$, $H_2P(5)O_4^{-}$, and $P(6)O_4^{3-}$, respectively. On closer examination of the atomic coordinates, pairs of Ga and P atoms are nearly *n*-glide-related if the origin of the unit cell is displaced by (0.25, −0.338, −0.25). This implies that the chirality of the organic amine is hardly transferred to the inorganic host structure. Upon ion exchange with, for example, piperazinium cations, the structure may become centrosymmetric with an *n*-glide plane passing through each $[Ga_4(C_2O_4)(H_2PO_4)_2(PO_4)_4]_\infty$ layer. The synthesis of a chiral microporous material using chiral amine as a structure-directing agent is a significant challenge. The material will be potentially useful if the open framework does not collapse and if the chirality remains when the templates are removed or exchanged. Further work on this theme is in progress.

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Supporting Information Available: One X-ray crystallographic file in CIF format, a table of indexed powder diffraction data, observed and calculated powder patterns, and a figure showing the TGA curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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