$[(1S,2S)\text{-}H_2DACH][Ga_2(1S,2S\text{-}DACH)(HPO_4)(PO_4)_2]$: A Layered Chiral Gallophosphate Containing Chiral Ligand and Chiral Template

Chia-Her Lin and Sue-Lein Wang*,†

Department of Chemistry, National Tsing Hua University,
Hsinchu 300, Taiwan

Received November 8, 2000

Introduction

Synthesis of chiral zeolitic and microporous inorganic solids is of great interest with respect to their potential applications in enantioselective catalysis and separation.[1,2] Synthetic approaches, to date, include the encapsulation of chiral transition-metal complexes in open-framework materials and the selection of optically pure organic amines as templates.[3] Both approaches have met with limited success. The only examples in the GaPO system included the incorporation of optically pure tris(1,2-diaminoethane) cobalt(III) into the 3D chiral framework of *d*-Co(en)$_3$[$H_3Ga_2P_4O_{16}$],[4] and the use of (1*R*,2*R*)-1,2-diaminocyclohexane and (*R*)-2-methylpiperazine for preparing the chained [(1*R*,2*R*)-$C_6H_{10}(NH_3)_2$][$Ga(OH)(HPO_4)_2$]·H_2O[5] and the layered [(*R*)-$C_5H_{14}N_2$]$_2$[$Ga_4(C_2O_4)(H_2PO_4)_4$]·2H_2O,[6] respectively. In all cases the availability of optically pure reagents is practically a limitation. The search for viable routes to homochiral materials is still a great challenge for synthetic chemists.

Here we report the hydrothermal synthesis and characterization of a chiral structure, [(1*S*,2*S*)-H_2DACH][Ga_2(1*S*,2*S*-DACH)(HPO_4)(PO_4)$_2$] (**1**), which has been obtained from a mixture of achiral cis and racemic trans isomers of 1,2-diaminocyclohexane (DACH) as the structure-directing agent. The mixture of DACH isomers is inexpensively accessible and can be selectively separated via mild hydrothermal routes. Previous works[7,8] showed that the trans DACH could be included in the open framework of metal phosphates whereas the cis was entirely excluded. The trans species has two enantiomers, namely, (1*S*,2*S*)-DACH and (1*R*,2*R*)-DACH. By referring to the synthetic conditions previously used for the preparation of a racemic GaPO phase, [*trans*-H_2DACH][$Ga(OH)(HPO_4)_2$]·H_2O,[5] a less acidic and less polar solvent system was pursued for further discrimination between the *R* and *S* two enantiomers in trans DACH. This approach has led to the unique chiral structure of **1**. It is the first example where chiral amine molecules play dual roles as both metal ligands and countercations. In this paper, the synthesis, crystal structure, thermal analysis, and solid-state ^{31}P and ^{71}Ga MAS NMR data of **1** are described and discussed.

Experimental Section

Synthesis and Compositional Characterization. Chemicals of reagent grade were used as received. Compound **1** was obtained by heating a mixture of DACH (1.1 mL, 9.0 mmol), Ga_2O_3 (0.2812 g, 1.5 mmol), 3 M H_3PO_4 (2.0 mL, 6.0 mmol), Si(OEt)$_4$ (0.05 mL), EG (ethylene glycol, 8 mL), and H_2O (2 mL) at an initial pH value of ∼6.8 in a Teflon-lined digestion bomb at 150 °C under autogenous pressure for 2 days followed by a slow cooling at 6 °C h^{-1} to room temperature. The resulting product contained a major phase of colorless plate-shaped crystals of **1** plus a tiny amount of unidentified powder. The solvent EG played an important role for the crystallization of the desired product. Both the quantity and quality of the crystals of **1** would degrade drastically when an insufficient amount of EG was added to the solvent system. A suitable plate crystal was carefully selected for single-crystal structure analysis. The Ga:P ratio determined from single-crystal analysis (see below) was further confirmed by EPMA analysis. Elemental analysis was carried out to verify organic contents. Anal. Found: C, 22.19; H, 4.96; N, 8.26. Calcd: C, 22.05; H, 4.47; N, 8.57.

Single-Crystal X-ray Structure Analysis. A crystal of dimensions 0.02 × 0.10 × 0.30 mm was selected for indexing and intensity data collection at 293 K. The measurements were performed on a Siemens Smart-CCD diffractometer system equipped with a normal focus, 3 kW sealed-tube X-ray source ($\lambda = 0.71073$ Å). Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 3832 reflections. After Lorentz polarization and empirical absorption corrections, 7568 independent reflections ($\theta_{max} = 28.30°$) were obtained, and among these 5855 reflections ($I > 3\sigma(I)$) were considered observed ($R_{int} = 0.0342$). The empirical absorption correction was performed on the basis of 3311 symmetry-equivalent reflections using the SADABS program.[9] On the basis of systematic absences, statistics of intensity distribution, and later successful structure refinements, the acentric space group $P2_1$ was chosen. Direct methods were used to locate the Ga, P, and a few oxygen atoms with the remaining non-hydrogen atoms found from successive difference Fourier maps. The results of bond-length and bond-strength calculation[10] were used to identify the hydroxo oxygen atom, O(3) in hydrogen phosphate groups. The atomic coordinates of all H atoms on DACH molecules were calculated on the basis of a riding model. The hydroxo H on O(3), H(1), was located directly on a difference map. Structural parameters were refined on the basis of F^2. The final cycle of refinement, including the atomic coordinates and anisotropic thermal parameters for all non-H atoms and fixed atomic coordinate and isotropic thermal parameter for hydrogen atoms, converged at $R = 0.0477$. Corrections for secondary extinction and anomalous dispersion were applied. Neutral-atom scattering factors for all atoms were taken from the standard sources. All calculations were performed by using SHELXTL programs.[11] Crystallographic data of **1** are given in Table 1. Other details for the refinement are given in the Supporting Information.

Thermogravimetric Analysis. Thermal analyses (TGA/DTA), using a Seiko TG/DTA 300 analyzer, were performed on a powder sample (2.46 mg) under flowing N_2 with a heating rate of 10 °C min^{-1}. As indicated by the TGA/DTA curves shown in Figure 1, **1** was thermally stable up to ∼330 °C. Two stages of mass loss was observed over the ranges 350−500 °C and 950−1100 °C. The first stage should be attributed to the dehydration of HPO_4^{2-} groups and the removal of

---

[†] E-mail: slwang@mx.nthu.edu.tw. Tel: 886-35-721074. Fax: 886-35-711082.

(1) (a) Li, H.; Edaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (b) Bu, X.; Feng, P.; Stucky, G. D. *Science* **1997**, *278*, 2080. (c) Feng, P.; Bu, X.; Stucky, G. D. *Nature* **1997**, *388*, 735. (d) Gier, T. E.; Bu, X.; Wang, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1996**, *118*, 3039. (e) Davis, M. E.; Lobo, R. F. *Chem. Mater*. **1992**, *4*, 756.

(2) (a) Reineke, T. M.; Eddaoudi, M.; O'Keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed*. **1999**, *38*, 2590. (b) Thomas, J. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3588.

(3) (a) Kepert, C. J.; Prior, T. J.; Rosseinsky, M. J. *J. Am. Chem. Soc.* **2000**, *122*, 5158. (b) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (c) R. A. Sheldon, *Curr. Opin. Solid State Mater. Sci*. **1996**, *1*, 101.

(4) Stalder, S. M.; Wilkinson, A. P. *Chem. Mater*. **1997**, *9*, 2168.

(5) Lin, H. M.; Lii, K. H. *Inorg. Chem*. **1998**, *37*, 4220.

(6) Lii, K. H.; Chen, C. Y. Submitted.

(7) Yang, G. Y.; Sevov, S. C. *J. Am. Chem. Soc*. **1999**, *121*, 8389.

(8) Lin, C. H.; Wang, S. L. *Chem. Mater*., in press.

(9) Sheldrick, G. M. *SADABS*: *Siemens Area Dector Absorption Correction Software*; University of Göttingen: Göttingen, Germany, 1998.

(10) Brown, I. D.; Altermann, D. *Acta Crystallogr*. **1985**, *B41*, 244.

(11) Sheldrick, G. M. *SHELXTL-Plus NT crystallographic system*, release 5.10; Brucker Analytical X-ray Instrument Division: Madison, WI, 1998.

10.1021/ic001234m CCC: $20.00

Table 1. Crystallographic Data for **1**

formula	$C_{12}H_{31}Ga_2N_4O_{12}P_3$
fw	655.76
space group	$P2_1$
a, Å	9.780(1)
b, Å	9.104(1)
c, Å	13.924(1)
β, deg	108.02(1)
vol, Å^3	1178.9(2)
Z	2
N(reflns collected)	7568 (5855 > $3\sigma(I)$)
D_{calcd}, g cm^{-3}	1.847
μ, mm^{-1}	2.554
T, °C	22
λ, Å	0.71073
R1^a	0.0477
wR2^b	0.1392

^{a} R1 $= \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 $= [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + 0.0846P]^2 + 2.74P]$.

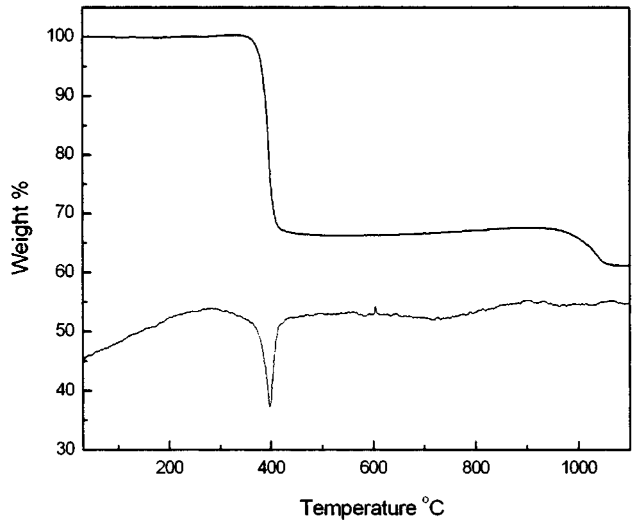

Figure 1. TGA (top) and DTA (bottom) curves of $[(1S,2S)\text{-}H_2DACH][Ga_2(1S,2S\text{-}DACH)(HPO_4)(PO_4)_2]$ (**1**).

organic contents (calcd 4.12% for $1.5H_2O$ and 34.77% for two molecules of DACH). However, the observed mass loss (33.6%) was lower than that expected (38.89%). The lower reduction in this stage was due to the retention of carbon in the solid residue (black in color). The second stage with a mass loss of 5.2% beyond 950 °C should correspond to the removal of carbon from the black solid residue. The total observed weight loss (38.8%) for the two stages compared well with that calculated on the basis of the above interpretation. The post-TGA residue was amorphous and could not be identified.

Solid-State NMR Measurements. ^{71}Ga and ^{31}P MAS NMR spectra were performed on a Bruker DSX 400 spectrometer equipped with a standard Bruker 4-mm MAS probe head at 9.4 T. Sample spinning speeds of 12 kHz for Ga and 7 kHz for P were applied. Chemical shifts were respectively reported relative to 1.0 M $Ga(NO_3)_3$ and 85% H_3PO_4 solutions as external references. The ^{31}P MAS NMR data revealed two resonance peaks located at δ −1.3 and δ −5.5 ppm with a 1:2 intensity ratio. The ^{71}Ga MAS NMR spectra showed one small resonance peak at 127 ppm and a much larger one at 4.4 ppm.

Results and Discussion

The asymmetric unit of **1**, as depicted in Figure 2, contains two Ga centers, one HPO_4 and two PO_4 tetrahedra, and one neutral and one diprotonated DACH molecules. The refinement on absolute structure (Flack parameter 0.01(2))[12] indicates that the crystal of **1** grown from achiral cis and racemic trans DACH is an *S* enantiomer. Although the thermal ellipsoids of several C atoms are large, a static disorder model for the carbon atoms could not be refined. In the structure of **1**, half of the (1*S*,2*S*)-DACH molecules are neutral and bind in a bidentate fashion to the octahedral Ga(1) center. The other half are diprotonated acting as countercations. Organic diamine usually can play three different roles in metal phosphates: (I) as space-filling counterions (i.e., unbound amine cations), as in the general cases; (II) to bind metal as a bidentate ligand (i.e., bound amine molecules), as in $[In_5F_3(PO_4)_4(H_2O)_2(en)_3]$[13] and $[In_4(4,4'\text{-bipy})_3(HPO_4)_4(H_2PO_4)_4\cdot nH_2O$;[14] and (III) partially protonated but also acting as a monodentate ligand to metal (i.e., bound amine cation), as in $[Ga_5(OH)_2(C_{10}H_9N_2)(C_2O_4)(PO_4)_4]\cdot 2H_2O$.[15] It is less common that diamine molecules play dual roles in one structure. To the best of our knowledge, the only example documented previously was the zincophosphate, $[H_2en]_2[Zn_{12}(Hen)2(OH)_2(PO_4)_{10}]$,[16] in which ethylenediamine molecules played both roles I and III. The structure of **1** sets another example where (1*S*,2*S*)-DACH molecules plays dual roles I and II.

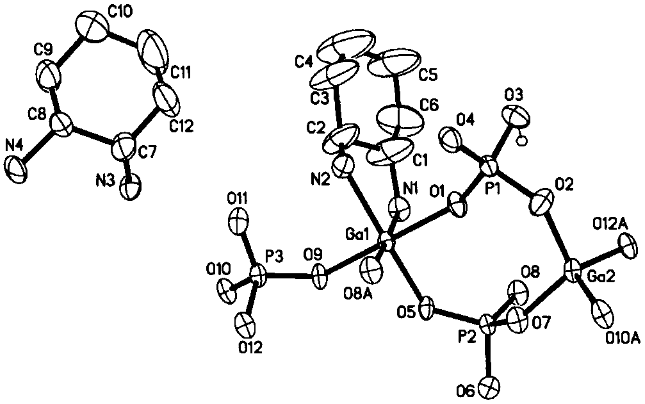

Figure 2. ORTEP drawing of the building unit in $[(1S,2S)\text{-}H_2DACH][Ga_2(1S,2S\text{-}DACH)(HPO_4)(PO_4)_2]$ (**1**). Thermal ellipsoids are given at the 50% level. Average bond distances (Å): Ga(1)−O = 1.952(5); Ga(1)−N = 2.096(7); Ga(2)−O = 1.819(6); P(1)−O = 1.535(6); P(2)−O = 1.530(6); P(3)−O = 1.534(7).

In the crystal of **1**, the Ga−O polyhedra alternate with PO_4 tetrahedra in a corner-shared manner to form $^{\infty}_{2}$[GaPO] sheets where 8-rings and 4-rings delimited by $Ga(1)O_4N_2$ octahedra, $Ga(1)O_4$ and PO_4 tetrahedra in a 1:1:2 ratio are observed (see Figure 3a). Pendent HPO_4 groups, each connecting two Ga centers (one $Ga(1)O_4N_2$ octahedron and one $Ga(2)O_4$ tetradedron), appear on both sides of the $^{\infty}_{2}$[GaPO] sheets. The arrangement results in anionic $[Ga_4(1S,2S\text{-}DACH)_2(HPO_4)_2(PO_4)_4]^{4-}$ sheets that are stacking in an AAA... sequence along the *c*-axis (Figure 3b). Between the sheets are (1*S*,2*S*)-H_2DACH cations. It is noted that the $[Ga_4(1S,2S\text{-}DACH)_2(HPO_4)_2(PO_4)_4]^{4-}$ sheet is sandwiched by (1*S*,2*S*)-H_2DACH cations with the cyclic hydrophobic rings pointing toward the interlayer region. Thus, another view of the structure can be a stacking of composite $\{[\text{cation}]^{2+}[\text{anion}]^{4-}[\text{cation}]^{2+}\}$ layers which are associated with each other solely by van der Waals forces. Strong H-bonds exist between the pendent HPO_4 groups and (1*S*,2*S*)-H_2DACH cations: (O(3)···N(4), 2.588 Å and N(4)···H(1), 1.661 Å). H-bonding interactions also likely exist

---

(12) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876.

(13) Du, H.; Chen, J.; Pang, W.; Yu, J.; Williams, I. D. *Chem. Commun.* **1997**, 781.

(14) Lii, K. H.; Huang, Y. F. *Inorg. Chem.* **1999**, *38*, 1348.

(15) Chen, C. Y.; Chu, P. P.; Lii, K. H. *Chem. Commun.* **1999**, 1473.

(16) Vaidhyanathan, R. S.; Natarajan, S.; Rao, C. N. R. *J. Mater. Chem.* **1999**, *9*, 2789.

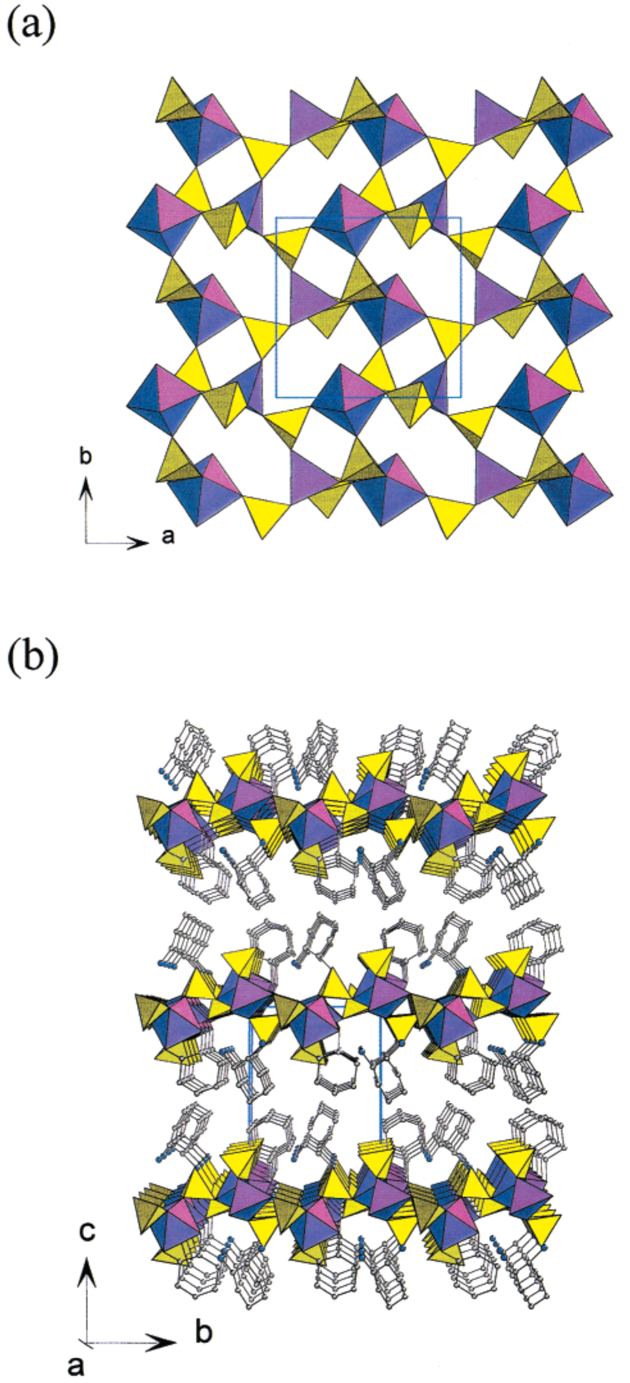

Figure 3. Polyhedral representations of **1**. (a) Section of the anionic $[Ga_4(1S,2S\text{-}DACH)_2(HPO_4)_2(PO_4)_4]^{4-}$ sheet showing two types of 4-rings and one 8-ring. (b) The neutral composite layers (in brackets) stacking along the *c*-axis direction with hydrophobic rings of the H_2-$DACH^{2+}$ cations pointing toward each other. In the plots, the darker polyhedra are GaO_4 and GaO_4N_2, the lighter HPO_4 and PO_4, open circles are C atoms and dark circles are N atoms.

between PO_4 tetrahedra and amine cations due to a short contact of 2.707 Å between N(3) and O(11).

The presence of two different Ga and P centers in **1** are confirmed by NMR data. ^{71}Ga MAS NMR spectrum (Figure 4) showed two distinct peaks: the resonance at δ 127 ppm corresponds to the 4-coordinated Ga in GaO_4, in accordance with the data in other structures;[8,15,17] the resonance at $\delta \sim 4.4$ corresponds to the 6-coordinate gallium in the GaO_4N_2 octahedron. The large upfield shift relative to that of GaO_6 should be probably due to the strong shielding by two directly bonded nitrogens.[15] In the ^{31}P MAS NMR spectrum the resonance peaks located at δ −1.3 and δ −5.5 ppm respectively correspond to the HPO_4^{2-} and PO_4^{3-} as the isotropic ^{31}P chemical shifts will move to high field with decreasing protonation.[18,19]

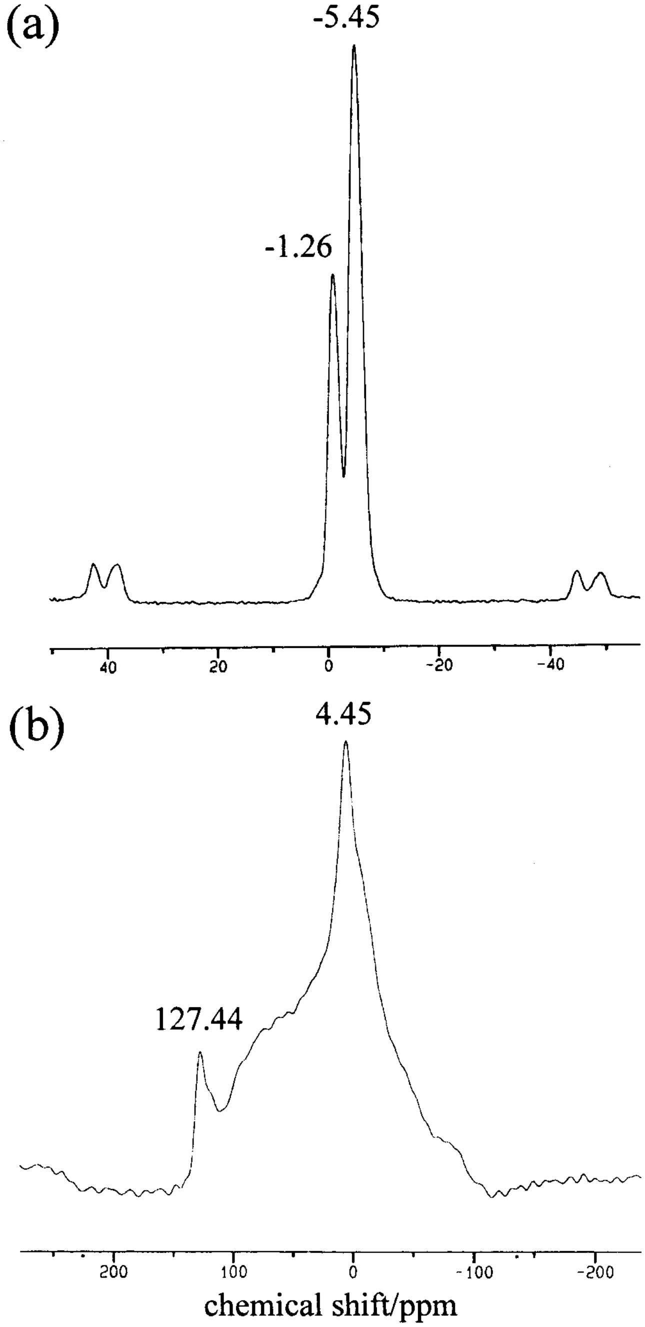

Figure 4. MAS solid-state NMR spectra of **1**: (a) ^{31}P and (b) ^{71}Ga resonance peaks.

To date, only two organically templated GaPO materials[20,21] adopt layer structures. Compound **1** adds not only one more unique layered topology without any precedent counterpart

---

[17] Lin, C. H.; Wang, S. L. Unpublished results.

[18] Nakayama, H.; Eguchi, T.; Nakamura, N.; Yamaguchi, S.; Danjyo, M.; Tsuhako, M. *J. Mater. Chem.* **1997**, *7*, 1063.

[19] Wesels, T.; McCusker, L. B.; Baerlocher, Ch.; Reinert, P.; Patarin, J. *Microporous Mesoporous Mater.* **1998**, *23*, 67.

[20] Jones, R. H.; Thomas, J. M.; Huo, Q.; Xu, R.; Hursthuose, M. H.; Chen, J. *J. Chem. Soc., Chem. Commun.* **1991**, 1520.

[21] Leech, M. A.; Cowley, A. R.; Prout, K.; Chippindale, A. M. *Chem. Mater*. **1998**, *10*, 451

among GaPO's and AlPO's but also the first layered structure with a Ga:P ratio of 2:3. The chiral nature of **1** can be the consequence of a novel templating effect due to the chirality of the trans DACH molecule. Either the *S* or the *R* enantiomer could act as the template to the layered structure.[22] By employing the same synthetic strategy we have also prepared a titanium phosphate compound in which the two trans DACH enantiomers were also isolated.[23] Progress in pursuing more chiral metal phosphate structures is currently being undertaken.

Acknowledgment. We are grateful to the National Science Council of the Republic of China for support of this work (NSC 89-2113-M-007 −079).

Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC001234M

---

(22) The [(1*R*,2*R*)-H_2DACH][Ga_2(1*R*,2*R*-DACH)(HPO_4)(PO_4)$_2$] phase also crystallized in the product. However, the crystal quality of the (1*R*,2*R*) enantiomer was rather poor based on our single-crystal structure analysis.

(23) [(1*S*,2*S*)-H_2DACH][Ti(OH)(HPO_4)$_2$]·H_2O, an orthorhombic phase with space group $Pca2_1$ and $a = 21.954(2)$ Å, $b = 8.6045(9)$ Å, $c = 7.2720(8)$ Å, $V = 1373.7(3)$ Å^3, and $Z = 4$. C. H. Lin, S. L. Wang, unpublished results.