Synthesis and Structure of [(1*R*,2*R*)-$C_6H_{10}(NH_3)_2$][Ga(OH)$(HPO_4)_2$]·H_2O, the First Metal Phosphate Containing a Chiral Amine

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The first metal phosphate containing a chiral amine, [(1*R*,2*R*)-$C_6H_{10}(NH_3)_2$][Ga(OH)$(HPO_4)_2$]·H_2O, has been synthesized hydrothermally and characterized by single-crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1$ with $a = 8.7202(2)$ Å, $b = 7.1276(2)$ Å, $c = 11.1411(4)$ Å, $\beta = 96.129(1)°$, and $Z = 2$. The structure consists of infinite chains of *trans*-corner-sharing $GaO_5(OH)$ octahedra with the adjacent octahedra being bridged by HPO_4 groups, which are H-bonded with amine groups of the organic cations and the lattice water. The Ga−O bond lengths along the backbone of the chain are alternately short and long. For comparison, the gallophosphate-containing racemic mix is also synthesized. [*trans*-1,2-$C_6H_{10}(NH_3)_2$][Ga(OH)$(HPO_4)_2$]·H_2O crystallizes in the centrosymmetric, orthorhombic space group *Pbcm* with $a = 8.6993(2)$ Å, $b = 21.8612(1)$ Å, $c = 7.1557(2)$ Å, $V = 1360.85(5)$ Å^3, and $Z = 4$.

Introduction

Catalytic asymmetric synthesis of enantiomerically pure compounds is of increasing importance to the fine chemical and pharmaceutical industries. A number of successful homogeneous catalysts of actual or potential industrial applications have been developed.[1] However, the number of solid catalysts that can perform enantioselective catalysis are very limited.[2] One approach to prepare solid catalysts for asymmetric synthesis is to encapsulate chiral metal complexes in open-framework materials such as zeolites.[3] Another approach is the synthesis of chiral microporous materials, which may combine good shape and size selectivity with various types of catalytic activity. The synthesis of microporous materials usually involves the use of templates or structure-directing agents added to the synthesis gels. The selection of chiral templates that are capable of transferring their chirality to a growing 3-dimensional framework presents a significant challenge. To date an optically pure chiral zeolite has never been prepared. Several chiral aluminophosphates and gallophosphates prepared by using optically pure *d*-$Co(en)_3^{3+}$ as a structure-directing agent were reported.[4] However, the use of chiral organic templates has not been successful. Here we report the synthesis and structure of [(1*R*,2*R*)-$C_6H_{10}(NH_3)_2$][Ga(OH)$(HPO_4)_2$]·H_2O (**1**), which is the first example of metal phosphate containing a chiral organic amine. For comparison, the gallophosphate-containing racemic *trans*-1,2-diaminocyclohexane, [*trans*-1,2-$C_6H_{10}(NH_3)_2$][Ga(OH)$(HPO_4)_2$]·H_2O (**2**), was also synthesized and structurally characterized.

Experimental Section

Synthesis and Initial Characterization. Hydrothermal reactions of $Ga(NO_3)_3$·$4H_2O$, H_3PO_4, (1*R*,2*R*)-(−)-1,2-diaminocyclohexane, and H_2O in the molar ratio 1:12.5:8.75:555 at 120 °C for 2 d yielded colorless plate crystals and powder. A plate crystal was used to determine its structure by single-crystal X-ray diffraction (vide infra). Energy-dispersive X-ray fluorescence confirmed the presence of Ga and P in the plate crystals. The product was a single phase of **1** as indicated by comparison of the X-ray powder pattern of the bulk product to the pattern simulated from the atomic coordinates derived from the single-crystal study. Chemical analysis confirmed the stoichiometry. Anal. Found: C, 17.60; H, 5.13; N, 6.85%. Calcd: C, 17.45; H, 5.13; N, 6.79. Colorless plate crystals of **2** were obtained by hydrothermal treatment of $Ga(NO_3)_3$·$4H_2O$ (1 mmol), H_3PO_4 (13 mmol), *trans*-1,2-diaminocyclohexane (9 mmol), and H_2O (555 mmol) under the same reaction conditions as those for **1**. The iron analogues of **1** and **2** have also been synthesized.

Single-Crystal X-ray Diffraction. Both compounds crystallized in very thin plates. Most of the crystals were unsuitable for single-crystal X-ray structure analysis as indicated from peak profile analysis. Many were selected before a satisfactory crystal was obtained. Colorless plate crystals of dimensions 0.38 × 0.06 × 0.02 mm for **1** and 0.22 × 0.09 × 0.02 mm for **2** were 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 matrixes and unit cell dimensions were determined by a least-squares fit of 2295 and 2598 reflections for **1** and **2**, respectively. Octants collected: $-8 \le h \le 11$, $-9 \le k \le 8$, $-14 \le l \le 14$ for **1** and $-5 \le h < 11$, $-28 \le k \le 27$, $-9 \le l \le 9$ for **2**. $2\theta_{max} = 56.2°$. Number of measured reflections and observed unique reflections [$I > 2\sigma(I)$]: 4090, 2118 for **1**; 7930, 1087 for **2**. Empirical absorption corrections were performed by using the SADABS program for Siemens area detector ($T_{min, max}$: 0.863, 0.919 for **1** and 0.720, 0.942 for **2**). On the basis of systematic absences, statistics of intensity distribution, and successful solution and refinement of the structures, the space groups were determined to be $P2_1$ (No. 4) and *Pbcm* (No. 57) for **1** and **2**, respectively. The structures were 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 H atoms were not located. For **1** the Flack x parameter was 0.066(39), indicative of a correct absolute structure. For **2** the C(2), C(5), and N(1) atoms were refined in a general position with a half-occupancy. The other C and N atoms sit on a mirror plane. The diastereoisomers of *trans*-1,2-diaminocyclohexane are symmetry related by a mirror plane each with an occupancy

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Table 1. Crystallographic Data for $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**1**) and $[trans\text{-}1,2\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**2**)

	1	**2**
chem formula	$C_6GaH_{21}N_2O_{10}P_2$	$C_6GaH_{21}N_2O_{10}P_2$
fw	412.91	412.91
space group	$P2_1$ (No. 4)	*Pbcm* (No. 57)
a, Å	8.7208(2)	8.6993(2)
b, Å	7.1276(2)	21.8612(1)
c, Å	11.1411(4)	7.1557(2)
β, deg	96.129(1)	
V, Å^3	688.55(5)	1360.85(5)
Z	2	4
T, °C	23	23
ρ_{calcd}, g cm^{-3}	1.992	2.015
λ, Å	0.710 73	0.710 73
μ(Mo Kα), cm^{-1}	22.8	23.1
$R1^a$	0.0514	0.0591
$wR2^b$	0.1317	0.1324

[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 $w = 1/[\sigma^2(F_o^2) + (0.0807P)^2 + 0.53P]$ for **1** and $w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 6.90P]$ for **2** with $P = (\mathrm{Max}(F_o^2) + 2F_c^2)/3$.

Table 2. Atomic Coordinates and Thermal Parameters for $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**1**) and $[trans\text{-}1,2\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**2**)

atom	*x*	*y*	*z*	$U_{eq}{}^a$ (Å^2 × 100)
		Compound **1**		
Ga	−0.0011(2)	0.1396	−0.0034(1)	1.26(2)
P(1)	−0.2824(2)	−0.1118(7)	−0.1379(1)	1.33(4)
P(2)	0.1217(2)	−0.1149(6)	−0.2112(1)	1.42(4)
O(1)	−0.2718(6)	−0.127(2)	−0.2785(4)	2.4(1)
O(2)	−0.201(1)	0.069(1)	−0.0923(7)	1.7(2)
O(3)	−0.4511(5)	−0.108(2)	−0.1209(4)	2.1(1)
O(4)	−0.202(1)	−0.283(1)	−0.0796(8)	2.1(2)
O(5)	0.112(1)	0.058(1)	−0.1351(8)	2.5(2)
O(6)	0.2823(5)	−0.118(1)	−0.2632(4)	2.0(1)
O(7)	0.113(1)	−0.289(1)	−0.1305(7)	1.9(2)
O(8)	0.0059(6)	−0.122(2)	−0.3230(4)	2.7(1)
O(9)	−0.0235(5)	0.389(1)	−0.0787(4)	1.53(9)
N(1)	0.3856(6)	−0.105(2)	0.0733(5)	1.8(1)
N(2)	0.2351(8)	−0.062(1)	0.2968(6)	2.7(2)
C(1)	0.4771(9)	−0.064(1)	0.1949(7)	1.8(2)
C(2)	0.3953(9)	−0.146(2)	0.2969(7)	2.4(3)
C(3)	0.4889(9)	−0.103(3)	0.4180(7)	2.6(2)
C(4)	0.649(1)	−0.199(2)	0.4192(8)	3.3(2)
C(5)	0.7343(8)	−0.107(3)	0.3171(7)	2.7(2)
C(6)	0.6370(9)	−0.147(1)	0.1930(8)	2.2(3)
Ow	−0.0959(9)	0.228(1)	−0.4609(6)	3.9(2)
		Compound **2**		
Ga	0	0	0	1.51(3)
P(1)	0.1525(3)	0.1061(1)	0.75	1.59(6)
P(2)	−0.2643(3)	0.0698(1)	0.75	1.44(6)
O(1)	0.1320(5)	0.0668(2)	0.9240(7)	2.3(1)
O(2)	0.3224(8)	0.1318(3)	0.75	2.3(2)
O(3)	0.0503(8)	0.1618(3)	0.75	2.7(2)
O(4)	−0.1894(5)	0.0446(2)	0.9256(7)	2.3(1)
O(5)	−0.2372(9)	0.1417(3)	0.75	3.3(2)
O(6)	−0.4346(8)	0.0607(3)	0.75	2.3(2)
O(7)	−0.0113(8)	0.0405(3)	0.25	1.9(2)
C(1)	0.644(1)	0.1518(5)	0.25	6.9(6)
C(2)^b	0.553(2)	0.1006(6)	0.296(2)	2.2(5)
C(3)	0.387(1)	0.1003(5)	0.25	3.7(3)
C(4)	0.311(1)	0.1634(5)	0.25	3.1(3)
C(5)^b	0.404(2)	0.2140(6)	0.167(3)	3.5(5)
C(6)	0.571(1)	0.2144(5)	0.25	2.8(3)
N(1)^b	0.811(1)	0.1540(5)	0.213(3)	2.4(6)
N(2)	0.623(1)	0.0390(4)	0.25	2.2(2)
Ow^c	−0.055(3)	0.259(2)	0.533(5)	2.9(4)
Ow′^{c}	−0.033(3)	0.236(2)	0.437(5)	2.9(4)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] The occupancy factor is 0.5. [c] The occupancy factor is 0.25.

factor of 0.5. The lattice water molecule is disordered over two unique sites at a general position with a quarter occupancy. The final cycles of least-squares refinement converged at $R1 = 0.0516$ for **1** and 0.0598 for **2**. The final difference Fourier maps were flat ($\Delta\rho_{max,\ min} = 0.73$, -0.68 e/Å^3 for **1** and 0.82, -0.44 e/Å^3 for **2**). Neutral-atom scattering factors for all atoms were used. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed by using SHELXTL PC programs.[5]

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.

$[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$. This compound crystallizes in the enantiomorphic space group $P2_1$. The Ga and P atoms are six- and four-coordinated, respectively. Bond-valence calculations indicated that O(1), O(3), O(6), O(8), and O(9) had valence sums of 1.10, 1.36, 1.13, 1.31, and 1.00, respectively, and all other oxygen atoms had values close to 2.[6] O(1), O(6), and O(9) are hydroxo oxygens. The valence sums of O(3) and O(8) are satisfied by forming hydrogen bonds [O(3)···O(6) = 2.67, O(3)···N(1) = 2.71 Å; O(8)···O(1) = 2.52, O(8)···Ow = 2.81 Å]. One lattice water site, labeled Ow, was located in the structural channel surrounded by chains of gallium phosphate and organic cations. The structure is shown in Figure 1. It consists of infinite chains of *trans*-corner-sharing $GaO_5(OH)$ octahedra running parallel to the *b*-axis, as shown in Figure 2. The central axis of each chain is a 2_1-screw axis. There are two octahedra per chain of unit cell length along the *b*-axis. The Ga atoms are linked together by means of single bridges of hydroxo groups to produce a zigzag Ga−O(H)−Ga−O(H)− backbone with alternating short and long Ga−O(H) bonds (1.967 and 2.007 Å). The bond angle at the shared O atom between two Ga atoms is 127.5(2)°. The hydrogen atom of the hydroxo bridge is involved in hydrogen bonding with phosphate oxygens. Adjacent octahedra within a chain are bridged by phosphate groups in the same way as those in $Na_3M(OH)(HPO_4)(PO_4)$ (M = Al, Ga),[7] $Na_4Al(PO_4)_2(OH)$,[8] and those $[M(TO_4)_2\phi]$ chains (T, 4-coordinate cation; ϕ, O, OH, F) in phosphate, sulfate, and silicate minerals.[9] An alternation of the Al−O bond length (1.930, 1.946 Å) along the chain axis is also present in the mineral overite, $CaMgAl(OH)(PO_4)_2(H_2O)_4$, although it crystallizes in a centrosymmetric space group.[10] Therefore, such bond alternation does not necessarily result from the presence of chiral template. In the case of **1** the degree to which the chirality of the template is transferred to the lattice appears small.

Each tetrahedron in **1** has a hydroxo group (O(1)H for $HP(1)O_4$ and O(6)H for $HP(2)O_4$) and a free oxygen vertex (O(3) for $HP(1)O_4$ and O(8) for $HP(2)O_4$). The gallium phosphate chains are linked to organic cations and lattice water molecules by hydrogen bonds. On the basis of the O···O distances, all oxygen atoms are involved in hydrogen bonding. The organic cation is also nested via a hydrogen-bonded network. There are two $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2]^{2+}$ cations at general positions in a unit cell, which are symmetry related by a 2_1-screw axis.

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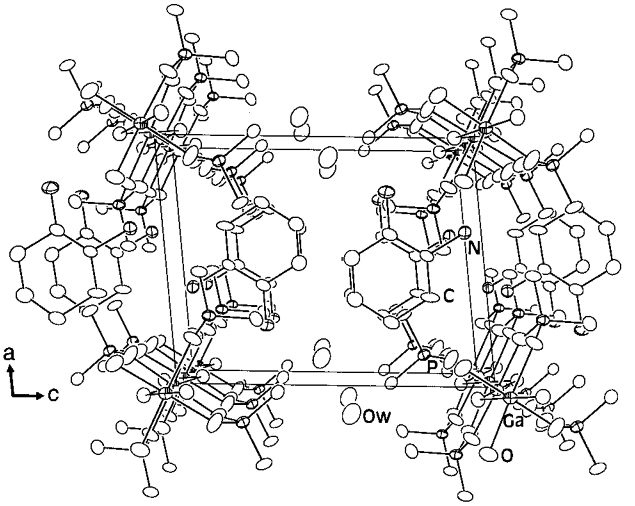

Figure 1. Structure of **1** viewed along the *b*-axis. Thermal ellipsoids are shown at 60% probability.

Table 3. Bond Lengths (Å) for $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**1**) and $[trans\text{-}1,2\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$ (**2**)

	Compound **1**		
Ga−O(2)	1.977(8)	Ga−O(4)	1.989(9)
Ga−O(5)	1.941(9)	Ga−O(7)	1.934(9)
Ga−O(9)	1.968(9)	Ga−O(9)	2.006(9)
P(1)−O(1)	1.583(5)	P(1)−O(2)	1.531(7)
P(1)−O(3)	1.503(5)	P(1)−O(4)	1.519(8)
P(2)−O(5)	1.507(9)	P(2)−O(6)	1.572(5)
P(2)−O(7)	1.537(8)	P(2)−O(8)	1.518(5)
N(1)−C(1)	1.52(1)	N(2)−C(2)	1.52(1)
C(1)−C(2)	1.52(1)	C(1)−C(6)	1.51(1)
C(2)−C(3)	1.53(1)	C(3)−C(4)	1.56(1)
C(4)−C(5)	1.57(1)	C(5)−C(6)	1.57(1)
	Compound **2**		
Ga−O(1)	1.937(5) (2×)	Ga−O(4)	1.988(5) (2×)
Ga−O(7)	1.999(3) (2×)	P(1)−O(1)	1.523(5) (2×)
P(1)−O(2)	1.582(7)	P(1)−O(3)	1.508(7)
P(2)−O(4)	1.519(5) (2×)	P(2)−O(5)	1.588(7)
P(2)−O(6)	1.495(7)	N(1)−C(1)	1.47(2)
N(2)−C(2)	1.51(1)	C(1)−C(2)	1.41(2)
C(1)−C(6)	1.51(2)	C(2)−C(3)	1.48(2)
C(3)−C(4)	1.53(1)	C(4)−C(5)	1.49(2)
C(5)−C(6)	1.57(2)		

$[trans\text{-}1,2\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$. This compound crystallizes in the centrosymmetric space group *Pbcm* with nearly twice the unit cell volume of **1**. O(2), O(5), and O(7) are hydroxo oxygens. The lattice water molecule is disordered over two unique sites with a quarter occupancy. The structure also consists of $[M(TO_4)_2\phi]$ chains which are topologically identical to those in **1**. However, each chain sits on a 2-fold screw axis with center of symmetry with equal Ga−O(7) bond length (1.999 Å) along the Ga−O(H)-Ga−O(H)− backbone. The Ga−O(7)−Ga bond angle is 127.0(3)°, which is essentially the same as that in **1**. As shown in Figure 3, the $[trans\text{-}1,2\text{-}C_6H_{10}(NH_3)_2]^{2+}$ cations are arranged in a way different from that in **1** such that there are four cations in a unit cell and the nearest neighboring cations are symmetry related by *c*-glide planes. The cation site is occupied by mirror plane-related diastereoisomers each with an occupancy factor of 50%. On the basis of the O···O and O···N distances, there is also extensive hydrogen bonding among the phosphate oxygens, amine groups of the cation, and the lattice water molecules. There is probably a direct relationship between the arrangement of the hydrogen bonding groups on the organic cations and the topology of the structure.

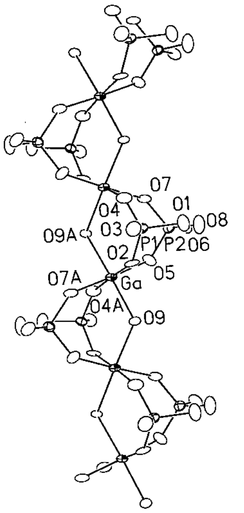

Figure 2. Section of an infinite chain in **1**, viewed in a direction perpendicular to the *b*-axis.

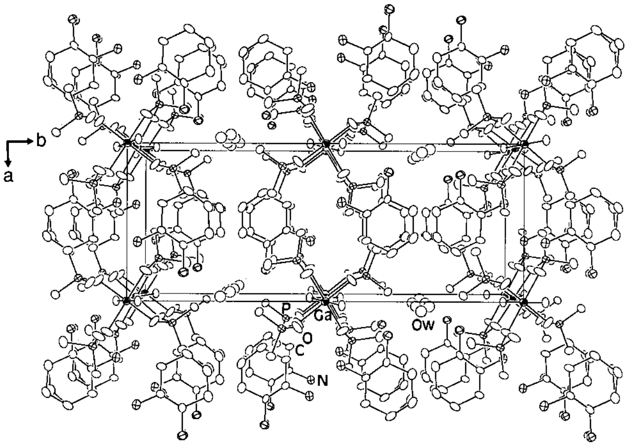

Figure 3. Structure of **2** viewed along the *c*-axis. Thermal ellipsoids are shown at 60% probability.

We have described the synthesis and structure of the first metal phosphate containing a chiral amine, $[(1R,2R)\text{-}C_6H_{10}(NH_3)_2][Ga(OH)(HPO_4)_2]\cdot H_2O$. But it adopts a one-dimensional chain structure, and it is unlikely that the amine cations can be removed without collapse of the structure. However, we believe that the use of chiral amines as structure-directing agents is a feasible route to prepare chiral open frameworks, which will be useful if the chirality remains when the templates are removed. We are continuing the exploratory synthesis of metal phosphate frameworks with chiral templating agents.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters and anisotropic thermal parameters, and bond lengths and bond angles (8 pages). Ordering information is given on any current masthead page.

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