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Synthesis and characterization of a new layered gallium phosphate [Co(en)₃][Ga₃(H₂PO₄)₆(HPO₄)₃] templated by cobalt complex

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Abstract

A new layered gallium phosphate [Co(en)₃][Ga₃(H₂PO₄)₆(HPO₄)₃], denoted as GaPO-CJ14, has been synthesized solvothermally by using a racemic mix of chiral metal complex Co(en)₃Cl₃ as a template. Its structure was determined by single-crystal X-ray diffraction analysis and further characterized by X-ray powder diffraction, ICP, and TG analyses. The compound crystallizes in the monoclinic space group *P*2₁/*m* (No. 11) with *a* = 9.2103(3), *b* = 22.0936(8), *c* = 9.5458(4) Å, β = 108.278(2)°, *Z* = 2, *R*₁ = 0.0497 and *wR*₂ = 0.1122 for all data. The inorganic layer is built up by alternation of Ga-centered octahedra (GaO₆) and P-centered tetrahedra (PO₃(OH), PO₂(OH)₂, PO₂(=O)(OH) and PO(=O)(OH)₂) forming a 4.12-net. The sheet structure is featured by a series of structural units composed of two centrosymmetrically related [3.3.3] propellane-like chiral motifs. The metal complex cations locate in the interlayer region and interact with the host network through H-bonds.

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Keywords: Layer; Gallium phosphate; Synthesis; Structure; Metal complex

1. Introduction

The interest in open-framework metal phosphates has been continuously growing because of their potential applications in catalysis, adsorption and separation [1,2]. So far, a large numbers of open-framework aluminophosphates [3–7], gallium phosphates [8–11], zinc phosphates [12–16], cobalt phosphates [17,18], titanium phosphates [19,20], and iron phosphates [21,22], etc. have been prepared. These materials are typically synthesized under hydrothermal or solvothermal conditions in the presence of various organic amines as a structure-directing agent.

Metal phosphates that are templated by transition-metal complexes are rare. Such compounds are known as a few aluminophosphates [23–27], gallium phosphate [*d*-Co(en)₃][H₃Ga₂P₄O₁₆] [28], boron phosphate [Co(en)₃][B₂P₃O₁₁(OH)₂] [29], and zinc phosphates [Co(en)₃]₂[Zn₆P₈O₃₂H₈] and [Co(en)₃][Zn₈P₆O₂₄Cl]·2H₂O [30] templated by an optically pure or a racemic mix of Co and Ir complexes such as Co(en)₃, Co(tn)₃,

Co(dien)₂, Ir(en)₃, Ir- or Co-(1, 2-diaminocyclohexane)₃. Interestingly, the rigid octahedrally coordinated metal amine complex has a chiral feature. It appears that the chirality of the metal complex can be imprinted into the inorganic frameworks as has been demonstrated in Morgan's [23] and our recent work [30]. This phenomenon has important implications concerning the expression of the chirality of the templating agents into the host framework.

We are interested in understanding the role of a chiral complex in determining an inorganic framework structure. In this work a racemic mix of chiral metal complex Co(en)₃Cl₃ has been used in the synthesis of a new gallium phosphate [Co(en)₃][Ga₃(H₂PO₄)₆(HPO₄)₃]. It is the second gallium phosphate templated by the metal complex. In the structure the Co(en)₃³⁺ cations locate in the interlayer region and interact with the host network through extensive H-bonds.

2. Experimental section

The title compound was prepared by a solvothermal reaction of a mixture of GaO(OH), H₃PO₄, Co(en)₃Cl₃ and 2-BuOH. Typically, 0.357 g GaO(OH) was first

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dissolved in 10 mL of 2-BuOH and then 0.684 mL of H_3PO_4 (85 wt%) was added with stirring. Finally, 0.396 g $\text{Co}(\text{en})_3\text{Cl}_3$ was added to the above reaction mixture. A gel was formed and stirred for 1 h until it was homogeneous, and then was sealed in a Teflon-lined stainless-steel autoclave and heated at 110°C for 3 d under static conditions. The orange plate-shaped single crystals in 70% yield in the product were separated by sonication and further washed by distilled water and then air-dried.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$).

Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of $10^\circ\text{C}/\text{min}$.

A suitable single crystal with dimensions $0.4 \times 0.4 \times 0.2 \text{ mm}^3$ was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were collected at temperature of $20 \pm 2^\circ\text{C}$. Intensity data of 9062 reflections in which 2734 were independent ($-9 \leq h \leq 10$, $-24 \leq k \leq 24$, $-10 \leq l \leq 7$) were collected in the ω scan mode ($R_{\text{int}} = 0.0694$). Data processing was accomplished with the SAINT processing program [31]. The structure was solved in the space group $P2_1/m$ by the direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97 [32]. No adsorption correction was applied. The heaviest atoms Ga, Co and

Table 1
Crystal data and structure refinement for GaPO-CJ14

Empirical formula	$\text{C}_6 \text{H}_{39} \text{Co}_1 \text{Ga}_3 \text{N}_6 \text{O}_{36} \text{P}_9$
Formula weight	1318.26
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system, space group	Monoclinic, $P2_1/m$
Unit-cell dimensions	$a = 9.2103(3) \text{ \AA}$, $\alpha = 90^\circ$ $b = 22.0936(8) \text{ \AA}$, $\beta = 108.278(2)^\circ$ $c = 9.5458(4) \text{ \AA}$, $\gamma = 90^\circ$
Volume	1844.46(12) \AA^3
Z, Calculated density	2, 2.374 Mg/m^3
Absorption coefficient	3.132 mm^{-1}
$F(000)$	1320
Crystal size	$0.40 \times 0.40 \times 0.20 \text{ mm}^3$
Theta range for data collection	$1.84\text{--}23.25^\circ$
Limiting indices	$-9 \leq h \leq 10$, $-24 \leq k \leq 24$, $-10 \leq l \leq 7$
Reflections collected/unique	9062/2734 [$R_{\text{int}} = 0.0694$]
Completeness to $\theta = 23.25$	100.0%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2734/0/313
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0418$, $wR_2 = 0.1091$
R indices (all data)	$R_1 = 0.0497$, $wR_2 = 0.1122$
Largest diff. peak and hole	0.729 and $-0.813 \text{ e \AA}^{-3}$

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{ \AA}^2 \times 10^3$) for GaPO-CJ14. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x	y	z	U_{eq}
Ga(1)	5000	5000	5000	12(1)
Ga(2)	4148(1)	3952(1)	667(1)	12(1)
Co(1)	2028(1)	7500	1449(1)	15(1)
P(1)	3194(2)	6016(1)	6219(2)	14(1)
P(2)	2290(2)	4118(1)	2969(2)	16(1)
P(3)	4222(2)	5435(1)	1620(2)	12(1)
P(4)	4202(2)	2500	1254(2)	13(1)
P(5)	1283(2)	4278(1)	-2157(2)	15(1)
O(1)	2998(5)	6706(2)	5858(5)	24(1)
O(2)	1538(5)	5757(2)	5763(5)	27(1)
O(3)	4061(5)	5748(2)	5251(4)	18(1)
O(4)	2955(4)	4686(2)	3782(4)	17(1)
O(5)	5298(4)	5338(2)	3184(4)	16(1)
O(6)	3215(4)	3768(2)	2194(4)	16(1)
O(7)	1962(6)	3645(2)	4059(6)	37(1)
O(8)	753(5)	4263(2)	1771(6)	39(1)
O(9)	3721(4)	4852(2)	763(4)	15(1)
O(10)	2710(5)	5767(2)	1672(4)	19(1)
O(11)	6129(4)	4064(2)	2138(4)	17(1)
O(12)	5080(5)	4106(2)	-852(4)	17(1)
O(13)	4444(5)	3063(2)	450(4)	18(1)
O(14)	5204(7)	2500	2852(7)	27(2)
O(15)	2483(7)	2500	1286(8)	33(2)
O(16)	2132(4)	3887(2)	-863(4)	18(1)
O(17)	-375(5)	4142(2)	-2810(5)	22(1)
O(18)	1975(5)	4218(2)	-3460(5)	26(1)
O(19)	1501(5)	4954(2)	-1657(5)	25(1)
C(1)	-775(12)	7500	2100(12)	45(3)
C(2)	376(13)	7500	3492(14)	81(6)
C(3)	5030(9)	7164(4)	3193(10)	58(3)
C(4)	1267(9)	7159(4)	-1558(8)	43(2)
N(1)	148(12)	7052(5)	1348(12)	26(3)
N(2)	1569(12)	7019(5)	2961(12)	22(2)
N(3)	3304(12)	6945(5)	2931(12)	22(2)
N(3')	3927(12)	7057(5)	1735(13)	25(3)
N(4)	2311(12)	6997(5)	-162(12)	23(3)
N(4')	899(14)	6944(5)	-109(13)	28(3)

P were easily located. O, C and N atoms were subsequently located in the difference Fourier maps and H atoms attached to the terminal P–O groups and to the metal complex cations were placed geometrically and refined using a riding model. It was noted that part of the C and N atoms of the $\text{Co}(\text{en})_3^{3+}$ cation were disordered. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination are presented in Table 1. The final atomic coordinates, and the selected bond distance and bond angles are presented in Tables 2 and 3, respectively.

3. Results and discussion

Large orange single crystals of GaPO-CJ14 can be crystallized from reaction gels with molar composition

Table 3
Bond lengths (Å) and bond angles (°) for GaPO-CJ14

Ga(1)–O(3)#1	1.915(4)
Ga(1)–O(3)	1.915(4)
Ga(1)–O(5)	1.984(4)
Ga(1)–O(5)#1	1.984(4)
Ga(1)–O(4)#1	2.002(4)
Ga(1)–O(4)	2.002(4)
Ga(2)–O(12)	1.934(4)
Ga(2)–O(11)	1.938(4)
Ga(2)–O(6)	1.952(4)
Ga(2)–O(16)	1.975(4)
Ga(2)–O(13)	2.001(4)
Ga(2)–O(9)	2.035(4)
P(1)–O(11)#1	1.506(4)
P(1)–O(3)	1.518(4)
P(1)–O(2)	1.558(4)
P(1)–O(1)	1.560(4)
P(2)–O(4)	1.502(4)
P(2)–O(6)	1.505(4)
P(2)–O(8)	1.549(5)
P(2)–O(7)	1.569(5)
P(3)–O(12)#3	1.509(4)
P(3)–O(9)	1.518(4)
P(3)–O(5)	1.527(4)
P(3)–O(10)	1.588(4)
P(4)–O(13)#4	1.515(4)
P(4)–O(13)	1.515(4)
P(4)–O(14)	1.515(6)
P(4)–O(15)	1.593(6)
P(5)–O(17)	1.488(4)
P(5)–O(16)	1.509(4)
P(5)–O(19)	1.561(5)
P(5)–O(18)	1.571(4)
P(1)–O(3)–Ga(1)	139.2(3)
P(2)–O(4)–Ga(1)	138.4(3)
P(3)–O(5)–Ga(1)	133.0(2)
P(2)–O(6)–Ga(2)	135.3(3)
P(3)–O(9)–Ga(2)	145.4(3)
P(1)#1–O(11)–Ga(2)	136.7(3)
P(3)#3–O(12)–Ga(2)	147.1(3)
P(4)–O(13)–Ga(2)	135.0(3)
P(5)–O(16)–Ga(2)	133.6(3)

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

1.0 GaO(OH): (6.0–12.0) H₃PO₄: 0.5 Co(en)₃Cl₃: 66 2-BuOH at 110°C. An unidentified gallium phosphatete powder phase that can be separated from GaPO-CJ14 is frequently accompanied with GaPO-CJ14. Using other solvents such as water, ethylene glycol instead of 2-butanol, GaPO-CJ14 cannot be obtained.

ICP analysis for the separated pure GaPO-CJ14 crystals gives that the contents of Ga as 15.31 wt% (calcd. 15.87 wt%), P as 20.05 wt% (calcd. 21.14 wt%), and Co as 4.23 wt% (calcd. 4.47 wt%). Elemental analysis indicates the sample contains 5.10, 2.68 and 6.11 wt% of C, H and N, respectively. These are in agreement with those calculated values of 5.47, 2.96 and

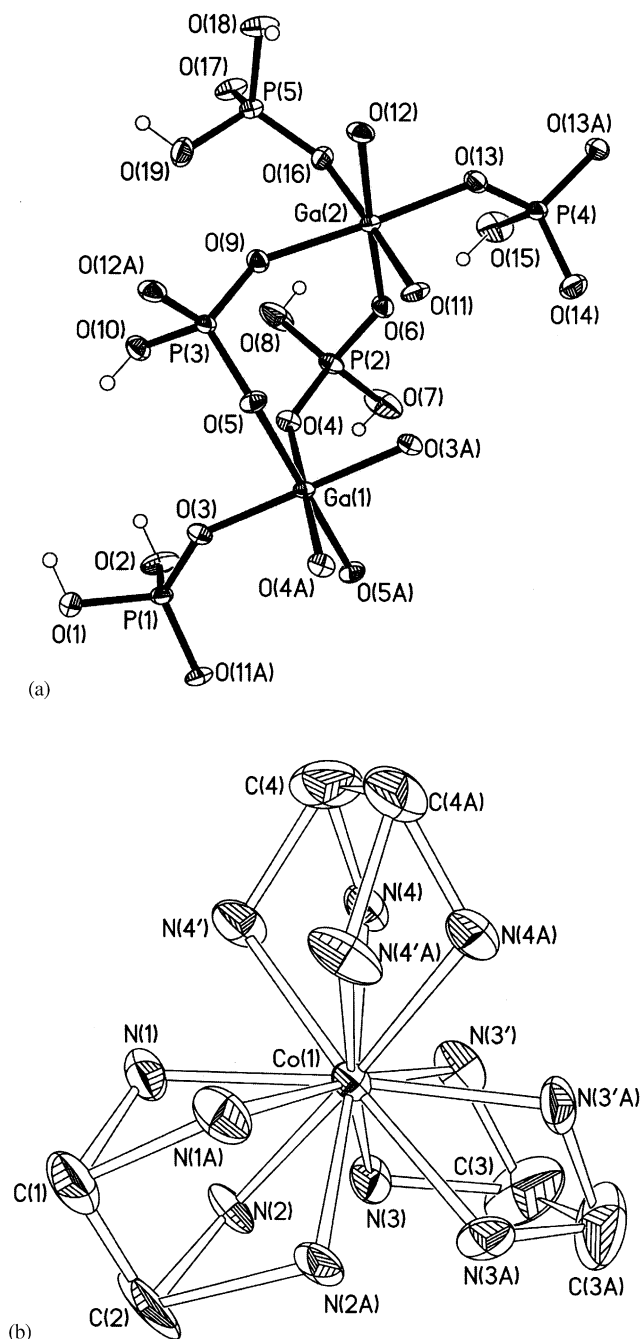


Fig. 1. Thermal ellipsoid plot (50%) showing atom labeling scheme in GaPO-CJ14: (a) the Ga, P, O and H atoms in the inorganic network; (b) the Co, N and C atoms in the complex.

6.38 wt% of C, H, and N, respectively, on the basis of the empirical formula [Co(en)₃][Ga₃(H₂PO₄)₆(HPO₄)₃] given by single-crystal structure analysis.

TGA shows a major weight loss of 12.8 wt% (calcd. 13.7 wt%) occurring at ca 320°C, which is attributed to the decomposition of the metal complexes. X-ray powder diffraction analysis indicates that the inorganic sheet structure is not stable upon decomposition of the occluded metal complex templates.

The structure of GaPO-CJ14 consists of macroanionic $[\text{Ga}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_3]^{3-}$ sheets. The charge neutrality is achieved by the $\text{Co}(\text{en})_3^{3+}$ cations located in the interlayer region. So far there are three types of 2-D layered gallium phosphates intercalated by the guest templating agents [33–35]. This compound exhibits one more new type with an interesting layered structural architecture. The asymmetric unit, as seen in Fig. 1a, contains two crystallographically distinct Ga atoms. Each Ga atom is coordinated to six oxygen atoms. Ga(1) atom lies on an inversion center, and the $\text{Ga}(1)\text{O}_6$ unit has a regular octahedral geometry with the Ga–O bond lengths in the range of 1.915–2.002(4) Å. The O–Ga–O bond angle for two oxygens at the *trans* positions is 180° . The $\text{Ga}(2)\text{O}_6$ unit is slightly distorted with the Ga–O distances in the range of 1.934–2.035(4) Å. The O–Ga–O angles for two oxygens at the *trans* positions are in the range of 176.1 – $178.2(2)^\circ$. Of the

five distinct tetrahedrally coordinated P atoms, P(4) lies on a mirror plane, while other P atoms are on a general position. P(1) and P(2) each makes two P–O–Ga links and possesses two terminal P–OH bonds. P(3) makes three P–O–Ga links and one terminal P–OH bond. P(4) makes two P–O–Ga links, one terminal P–OH bond and one terminal P=O bond (1.515(6) Å). P(5) makes only one P–O–Ga link and possesses two terminal P–OH bonds and one terminal P=O bond (1.488(4) Å). The P–O_{bridging} and P–OH bond distances are in the ranges of 1.502(4)–1.527(4) Å and 1.549(5)–1.593(6) Å, respectively. As seen in Fig. 1b, each asymmetric unit also contains one crystallographically distinct Co atom lying on a mirror plane. Since the $\text{Co}(\text{en})_3^{3+}$ cation itself has no mirror symmetry, it is either the Δ or the Λ enantiomer of a chiral identity, the $\text{Co}(\text{en})_3^{3+}$ cation in this structure has to be disordered. As a consequence, the two isomers randomly occupy the lattice positions.

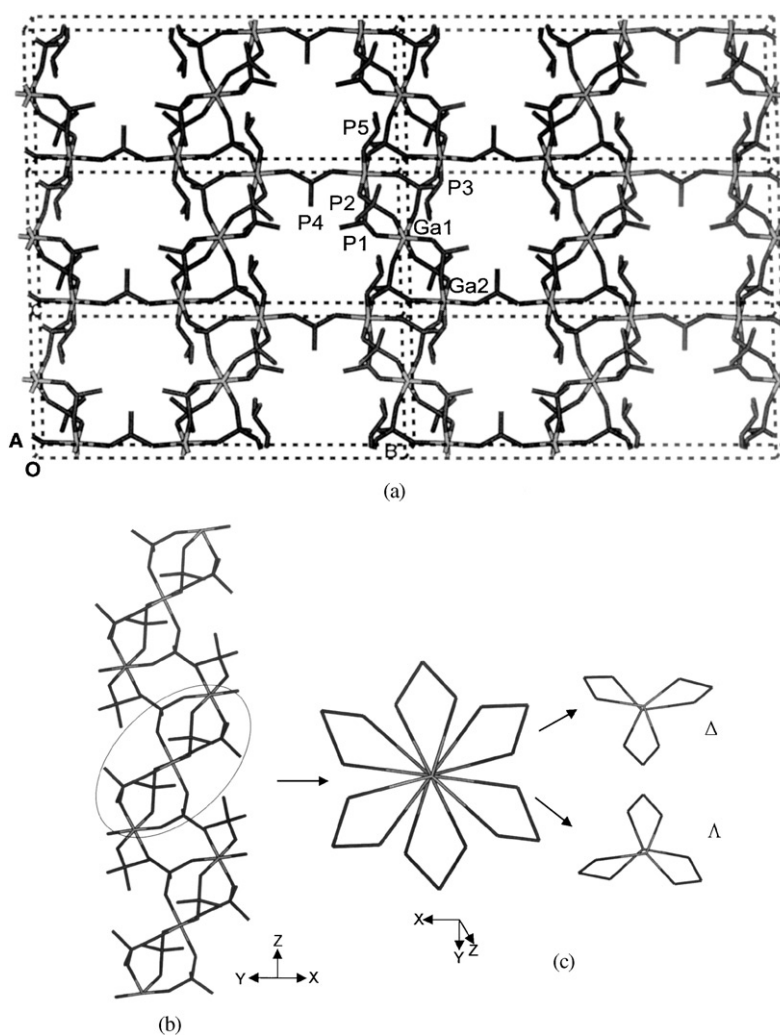


Fig. 2. (a) The 4.12-net sheet structure parallel to the *bc* plane in GaPO-CJ14; (b) a chain made up of solely four-membered rings along the *c*-axis; (c) a characteristic structural unit in GaPO-CJ14 composed of two centrosymmetrically related [3.3.3] propellane-like chiral motifs existing in Δ and Λ configurations, respectively.

The strict alternation of Ga-centered octahedra (GaO_6) and P-centered tetrahedra ($\text{PO}_3(\text{OH})$, $\text{PO}_2(\text{OH})_2$, $\text{PO}_2(=\text{O})(\text{OH})$ and $\text{PO}(=\text{O})(\text{OH})_2$) forms a 2-D sheet parallel to the bc plane containing 4- and 12-membered rings, designated a 4.12-net (Fig. 2a). The sheet structure can be viewed as a series of chains interconnected with each other via P(4) tetrahedra. Fig. 2b shows such a chain made up of solely four-membered rings along the c -axis. It is noted that the structure of the compound is characteristic of a series of structural unit composed of two centrosymmetrically related [3.3.3] propellane-like chiral motifs (Fig. 2c). Each [3.3.3] propellane-like motif composed of three four-membered rings is chiral since it has a distinct twist in one direction. Such chiral structural motif has been found in layered aluminophosphates $[\text{Co}(\text{en})_3][\text{Al}_3\text{P}_4\text{O}_{16}] \cdot 3\text{H}_2\text{O}$ [23] and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ [24], and layered zinc phosphate $[\text{Co}(\text{en})_3]_2 \cdot [\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$ [30]. Two motifs sharing a common Ga(1) atom at the inversion center are a pair of enantiomers. Insight into those structures templated by chiral metal complexes, it is found that an asymmetric microenvironment in the inorganic host can be induced by the chiral complex template.

As seen in Fig. 3, the inorganic sheets stack in an AAAA sequence along the [100] direction, with the metal complex cations residing in the interlayer region. The complex cations interact with the terminal OH groups in the inorganic network through H-bonds with the N...O separation in the range of 2.682(6)–3.058(12) Å. There are also H-bonds between the bridging oxygen atoms and the terminal OH groups inside the inorganic network with the O...O separation

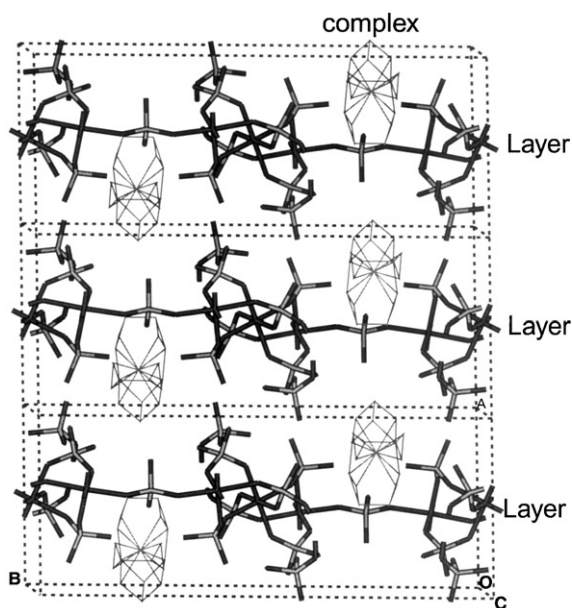


Fig. 3. Packing of the inorganic sheets in an AAAA sequence along the [100] direction.

Table 4
Hydrogen bonds for GaPO-CJ14 (Å and °)

$D\text{--}H\cdots A$	$d(D\text{--}H)$	$d(H\cdots A)$	$d(D\cdots A)$	$\angle(DHA)$
O(1)–H(1)···N(2)	0.82	1.95	2.753(11)	167.7
O(1)–H(1)···N(3)	0.82	2.26	2.943(11)	141.5
O(2)–H(2)···O(17)#5	0.82	1.87	2.693(6)	175.1
O(7)–H(7)···O(18)#6	0.82	2.13	2.682(6)	124.1
O(10)–H(10)···N(3)	0.82	2.04	2.848(12)	169.6
O(10)–H(10)···N(3')	0.82	2.41	3.058(12)	136.1
O(15)–H(15)···O(6)	0.82	2.28	2.948(5)	139.2
O(18)–H(18)···O(5)#3	0.82	1.87	2.632(6)	155.2
O(19)–H(19)···O(2)#7	0.82	2.32	3.044(6)	147.7

Symmetry transformations used to generate equivalent atoms: #3: $-x + 1, -y + 1, -z$; #5: $-x, -y + 1, -z$; #6: $x, y, z + 1$; #7: $x, y, z - 1$.

of 2.632(6)–3.044(6) Å. Table 4 summarizes the H-bond informations.

4. Conclusions

Solvothermal synthesis of a new layered gallium phosphate $[\text{Co}(\text{en})_3][\text{Ga}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_3]$ has been accomplished in a gel system using a racemic mix of a chiral metal complex as the template. The structure is characteristic of a structural unit composed of a pair of enantiomers of chiral [3.3.3] propellane-like structural motifs. The guest metal complexes located in the interlayer regions interact with the host network through H-bonds. We believe that the hydrogen bonding is responsible for the stereo-specific structural arrangement of the host network and the guest metal complexes.

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