

Two layered gallophosphates assembled about the chiral metal complexes: $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$

Yu Wang, Jihong Yu,* Yu Du, and Ruren Xu¹

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Jiefang Road 119, Changchun 130023, People's Republic of China

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Abstract

Two new layered gallophosphates $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ (**1**) and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (**2**) have been hydrothermally synthesized using the racemic mixture of chiral metal complex $\text{Co}(\text{en})_3\text{Cl}_3$ and $\text{Co}(\text{dien})_2\text{Cl}_3$ as the structure-directing agent, respectively. Their structures are determined by single-crystal X-ray diffraction analysis and further characterized by X-ray powder diffraction, ICP, elemental, and TG analyses. The structures of **1** and **2** consist of vertex-linking GaO_4 and $\text{PO}_3(=\text{O})$ tetrahedral units forming macroanionic $[\text{Ga}_3\text{P}_4\text{O}_{16}]^{3-}$ sheets with a 4.6-net. The 4.6-net is characteristic of chiral [3.3.3] propellane-like structural motifs. The sheets of **1** stack in an *ABAB* sequence, with a pair of enantiomers of chiral $\text{Co}(\text{en})_3^{3+}$ cations residing in the interlayer region. The sheets of **2** array in a helical fashion with an *ABCDEF* stacking sequence, with only one enantiomer of chiral $\text{Co}(\text{dien})_2^{3+}$ cations residing in the interlayer region. Structural elucidation of **1** and **2** reveals that there exist stereo-specific correspondence between the metal complex template and the structure of the inorganic host. Crystal data: **1**, $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$, orthorhombic, *Pnna* (No. 52), $a = 8.6618(2) \text{ \AA}$, $b = 21.6071(5) \text{ \AA}$, $c = 13.7426(4) \text{ \AA}$, $Z = 4$, $R_1 = 0.0337$ ($I > 2\sigma(I)$), $wR_2 = 0.0985$ (all data); **2**, $\text{Co}(\text{dien})_2 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$, hexagonal, *P6₅22* (No. 179), $a = 8.5152(7) \text{ \AA}$, $b = 8.5152(7) \text{ \AA}$, $c = 63.278(8) \text{ \AA}$, $R_1 = 0.1183$ ($I > 2\sigma(I)$), $wR_2 = 0.2864$ (all data) and $Z = 6$.

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1. Introduction

The synthesis of chiral open-framework materials is of considerable interest because of their potential application in enantio-selective catalysis and separations [1–6]. A small number of enantiomeric mixtures of chiral open-framework metal phosphates have been known using achiral structure-directing agents, such as $[\text{Na}_{12}(\text{H}_2\text{O})_{12}]$ ($\text{Zn}_{12}\text{P}_{12}\text{O}_{48}$) [7], $[\text{NH}_3(\text{CH}_2)_2\text{NH}_2(\text{CH}_2)_2\text{NH}_3]$ [$(\text{ZnPO}_4)(\text{HPO}_4)$] [8], $[\text{CN}_3\text{H}_6][\text{Sn}_4\text{P}_3\text{O}_{12}]$ [9], $[(\text{CH}_3)_2\text{NH}_2]\text{K}_4[\text{V}_{10}\text{O}_{10}(\text{H}_2\text{O})_2(\text{OH})_4(\text{PO}_4)_7] \cdot 4\text{H}_2\text{O}$ [10], and UCSB-7 [11].

Recently, the use of chiral metal complex template has greatly facilitated the formation of chiral open-framework metal phosphates. Employing an optically pure or a racemic mix of chiral metal complex as the structure-direction agent, a number of metal phosphates have been prepared including aluminophosphates [12–15], boron phosphate $[\text{Co}(\text{en})_3][\text{B}_2\text{P}_3\text{O}_{11}(\text{OH})_2]$ [16], gallium phosphates [*d*- $\text{Co}(\text{en})_3][\text{H}_3\text{Ga}_2\text{P}_4\text{O}_{16}]$ [17] and $[\text{Co}(\text{en})_3][\text{Ga}_3(\text{H}_2\text{PO}_4)_6(\text{HPO}_4)_3]$, [18] and zincophosphates $[\text{Co}^{\text{II}}(\text{en})_3]_2[\text{Zn}_6\text{P}_8\text{O}_{32}\text{H}_8]$, [19] $[\text{Co}^{\text{III}}(\text{en})_3][\text{Zn}_8\text{P}_6\text{O}_{24}\text{Cl}] \cdot 2\text{H}_2\text{O}$, [19] $[\text{H}_3\text{O}] \cdot [\text{Co}^{\text{II}}(\text{dien})_2][\text{Zn}_2(\text{HPO}_4)]$ [20] and $\text{Co}^{\text{II}}(\text{en})_3[\text{Zn}_4(\text{H}_2\text{PO}_4)_3(\text{HPO}_4)_2(\text{PO}_4)] \cdot 2\text{H}_2\text{O}$ [21]. We find that the rigid octahedrally coordinated chiral metal amine complexes can imprint their chiral characters into the inorganic host through H-bonding, thus revealing the chirality transference and molecular recognition between the host framework and the guest chiral templating agent [21].

*Corresponding author. Fax: +86-431-5671974.

E-mail addresses: jihong@mail.jlu.edu.cn (J. Yu), rrxu@mail.jlu.edu.cn (R. Xu).

¹Also for correspondence.

In this work we report two new layered gallophosphates $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ (**1**) and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (**2**) by using the racemic mixture of chiral metal complexes $\text{Co}(\text{en})_3\text{Cl}_3$ and $\text{Co}(\text{dien})_2\text{Cl}_3$ as the structure–direction agent, respectively. Both **1** and **2** consist of a 4.6-net sheet. However, their sheet stacking sequences are different. Even though **1** and **2** have an analogous structure to layered aluminophosphates $\text{Co}(\text{en})_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (Gtex-1) [12] and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (Gtex-3) [14], respectively, they exhibit new types of layered structures in gallium phosphates [22–24]. Structural elucidation of **1** and **2** reveals a good stereo-specific correspondence between the metal complex template and the structure of the inorganic host.

2. Experimental section

Compound **1** was prepared by a hydrothermal reaction of a mixture of $\text{GaO}(\text{OH})$, H_3PO_4 , $\text{Co}(\text{en})_3\text{Cl}_3$, TMAOH and H_2O in a molar ratio of 1.0:2.3:0.4:1.68:150. Typically, $\text{GaO}(\text{OH})$ (0.3 g, 70%) was first dissolved in H_2O (8 mL), and then H_3PO_4 (85 wt%, 0.46 mL) was added with stirring followed by addition of $\text{Co}(\text{en})_3\text{Cl}_3$ (0.47 g). Finally, TMAOH (2.5 mL, 10%) was added to the above reaction mixture. The resulting gel with a pH value 4.5 was stirred for one hour until it was homogeneous, and was then sealed in a Teflon-lined stainless-steel autoclave and heated at 110°C for 6 days under static condition. The product containing orange plate-like single crystals was separated by sonication and further washed by distilled water and then air-dried. The X-ray diffraction pattern of the product was in good agreement with that generated from single-crystal structural data, confirming the phase purity of the as-synthesized product.

Compound **2** was prepared by a hydrothermal reaction of a mixture of $\text{GaO}(\text{OH})$, H_3PO_4 , $\text{Co}(\text{dien})_2\text{Cl}_3$, TMAOH and H_2O in a molar ratio of 1.0:1.5:0.34:2.24:226. Typically, $\text{GaO}(\text{OH})$ (0.25 g, 70%) was first dissolved in H_2O (10 mL), and then H_3PO_4 (85 wt%, 0.25 mL) was added with stirring followed by addition of $\text{Co}(\text{dien})_2\text{Cl}_3$ (0.31 g). Finally, TMAOH (5 mL, 10%) was added to the above reaction mixture. The resulting gel with a pH value of 7 was stirred for 1 h until it was homogeneous, and was then sealed in a Teflon-lined stainless-steel autoclave and heated at 80°C for 6 days under static condition. The product containing orange plate-like single crystals was separated by sonication and further washed by distilled water and then air-dried. The X-ray diffraction pattern of the product was in good agreement with that generated from single-crystal structural data.

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) analyses were performed on a Perkin-Elmer Optima 3300DV spectrometer. The determined data of **1** (Ga: 24.01 wt%, P: 14.26 wt%, Co: 6.82 wt%) and **2** (Ga: 23.31 wt%, P: 13.46 wt%, Co: 6.42 wt%) were in agreement with those calculated values of **1** (Ga: 22.78 wt%, P: 13.50 wt%, Co: 6.42 wt%) and **2** (Ga: 23.02 wt%, P: 13.65 wt%, Co: 6.50 wt%), respectively. The elemental analyses were conducted on a Perkin-Elmer 2400 elemental analyzer. The determined data of **1** (C: 8.08 wt%, H: 3.15 wt%, N: 9.45 wt%) and **2** (C: 9.98 wt%, H: 3.35 wt%, N: 9.45 wt%) were in agreement with those calculated values of **1** (C: 7.85 wt%, H: 3.70 wt%, N: 9.15 wt%) and **2** (C: 10.57 wt%, H: 3.52 wt%, N: 9.25 wt%), respectively.

A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 10°C/min. A weight loss in a total of 20% (calcd 21.5%) for **1** and 27.52% for **2** (calcd 28.62%) occurring at 200–660°C was observed, respectively, which was attributed to the dehydration of the product and the decomposition of the metal complex.

Suitable single crystals with dimensions of $0.3 \times 0.06 \times 0.04 \text{ mm}^3$ for **1** and $0.3 \times 0.3 \times 0.04 \text{ mm}^3$ for **2** were selected for single-crystal X-ray diffraction analysis, respectively. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing were accomplished with the SAINT processing program [25]. The structures of compounds **1** and **2** (one selected crystal) were solved in the space group *Pnna* and *P6₅22*, respectively, by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97 [26]. The Flack parameter for compound **2** was 0.1326. Specific rotation measurement of compound **2** dissolved in the HNO_3 solution shows that the as-made compound **2** was racemic, suggesting the bulk product was a 50:50 mixture of enantiomeric crystals crystallized in the *P6₁22* and *P6₅22* space groups. All Ga, Co, P, and O atoms were easily located. H atoms attached to the metal complex cations were placed geometrically and refined using a riding model. H atoms in the water molecules were not added. All non-hydrogen atoms were refined anisotropically. Experimental details for the structure determination were presented in Table 1. The selected bond distances and angles for compounds **1** and **2** are presented in Tables 2 and 3, respectively.

3. Result and discussion

The structure of compound **1**, $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$, consists of macroanionic $[\text{Ga}_3\text{P}_4\text{O}_{16}]^{3-}$ sheets. Charge neutrality of the framework is achieved by the complex $\text{Co}(\text{en})_3^{3+}$ cations residing in the interlayer

Table 1
Crystal data and structure refinement for **1** and **2**

Identification code	1	2
Empirical formula	C ₃ H ₁₇ Co _{0.50} Ga _{1.50} N ₃ O _{10.50} P ₂	C ₄ H ₁₆ Co _{0.50} Ga _{1.50} N ₃ O _{9.50} P ₂
Formula weight	459.18	454.18
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Hexagonal
Space group	<i>Pnna</i>	<i>P6₃22</i>
Unit cell dimensions	$a = 8.6618(2) \text{ \AA}; \alpha = 90^\circ$ $b = 21.6071(5) \text{ \AA}; \beta = 90^\circ$ $c = 13.7426(4) \text{ \AA}; \gamma = 90^\circ$	$A = 8.5152(7) \text{ \AA}; \alpha = 90^\circ$ $b = 8.5152(7) \text{ \AA}; \beta = 90^\circ$ $C = 63.278(8) \text{ \AA}; \gamma = 120^\circ$
Volume	2572.02(11) Å ³	3973.5(7) Å ³
Z, Calculated density	8, 2.372 Mg/m ³	12, 2.278 Mg/m ³
Absorption coefficient	4.096 mm ⁻¹	3.971 mm ⁻¹
<i>F</i> (000)	1840	2724
Crystal size	0.3 × 0.06 × 0.04 mm ³	0.3 × 0.3 × 0.04 mm ³
θ range for data collection	1.88–23.24°	1.93–23.64°
Limiting indices	$-9 \leq h \leq 9$, $-22 \leq k \leq 23$, $-13 \leq l \leq 15$	$-9 \leq h \leq 9$ $-9 \leq k \leq 9$ $-70 \leq l \leq 47$
Reflections collected/unique	11415/1846 [<i>R</i> (int) = 0.0553]	18844/1985 [<i>R</i> (int) = 0.1434]
Completeness to $\theta = 23.24^\circ$	99.9%	99.3%
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1846/0/187	1985/78/187
Goodness-of-fit on <i>F</i> ²	1.052	1.351
Final <i>R</i> indices [<i>I</i> > $\sigma(I)$]	<i>R</i> ₁ = 0.0337, <i>wR</i> ₂ = 0.0950	<i>R</i> ₁ = 0.1183, <i>wR</i> ₂ = 0.2852
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0433, <i>wR</i> ₂ = 0.0985	<i>R</i> ₁ = 0.1207, <i>wR</i> ₂ = 0.2864
Largest diff. peak and hole	1.075 and -0.772 e Å ⁻³	1.387 and -1.937 e Å ⁻³

Table 2
Selected bond lengths (Å) and angles (°) for compound **1**

Ga(1)–O(1)	1.822(4)	Ga(1)–O(1)#2	1.822(4)
Ga(1)–O(2)#2	1.840(4)	Ga(1)–O(2)	1.840(4)
Ga(2)–O(6)	1.804(4)	Ga(2)–O(7)	1.813(4)
Ga(2)–O(4)	1.825(4)	Ga(2)–O(5)	1.827(4)
P(1)–O(3)	1.496(4)	P(1)–O(2)	1.537(4)
P(1)–O(4)	1.543(4)	P(1)–O(5)#2	1.543(4)
P(2)–O(8)	1.486(4)	P(2)–O(6)#3	1.538(4)
P(2)–O(7)	1.543(5)	P(2)–O(1)#4	1.545(4)
O(1)–Ga(1)–O(1)#2	116.4(3)	O(1)–Ga(1)–O(2)#2	109.26(19)
O(1)#2–Ga(1)–O(2)#2	105.03(18)	O(1)–Ga(1)–O(2)	105.03(18)
O(1)#2–Ga(1)–O(2)	109.26(18)	O(2)#2–Ga(1)–O(2)	112.0(2)
O(6)–Ga(2)–O(7)	111.9(2)	O(6)–Ga(2)–O(4)	110.11(18)
O(7)–Ga(2)–O(4)	108.67(19)	O(6)–Ga(2)–O(5)	107.14(18)
O(7)–Ga(2)–O(5)	107.2(2)	O(4)–Ga(2)–O(5)	111.78(19)
O(3)–P(1)–O(2)	110.0(2)	O(3)–P(1)–O(4)	111.2(3)
O(2)–P(1)–O(4)	109.5(2)	O(3)–P(1)–O(5)#2	109.5(2)
O(2)–P(1)–O(5)#2	109.0(2)	O(4)–P(1)–O(5)#2	107.4(2)
O(8)–P(2)–O(6)#3	113.8(2)	O(8)–P(2)–O(7)	110.4(3)
O(6)#3–P(2)–O(7)	107.1(2)	O(8)–P(2)–O(1)#4	112.5(2)
O(6)#3–P(2)–O(1)#4	105.3(2)	O(7)–P(2)–O(1)#4	107.4(2)
P(2)#3–O(1)–Ga(1)	127.4(3)	P(1)–O(2)–Ga(1)	135.7(3)
P(1)–O(4)–Ga(2)	132.7(3)	P(1)#2–O(5)–Ga(2)	137.7(3)
P(2)#4–O(6)–Ga(2)	137.7(3)	P(2)–O(7)–Ga(2)	133.3(3)
H-bonding			
<i>D</i> – <i>H</i> ⋯ <i>A</i>	<i>d</i> (<i>D</i> ⋯ <i>A</i>)		<(DHA)
N(1)–H(1B)⋯O(8)#6	2.791(6)		161.5
N(2)–H(2A)⋯O(3)#5	2.926(6)		167.3
N(2)–H(2B)⋯O(3W)#7	2.961(7)		154.8

Symmetry transformations used to generate equivalent atoms: #1 – $x + 3/2, -y + 2, z$ #2 $x, -y + 3/2, -z + 1/2$ #3 $x + 1/2, y, -z + 1$
#4 $x - 1/2, -y + 3/2, z + 1/2$ #5 $x + 1/2, -y + 3/2, z - 1/2$ #6 $x - 1/2, y, -z + 1$ #7 – $x + 1/2, -y + 1, z$.

Table 3
Selected bond lengths (Å) and angles (°) for compound **2**

Ga(1)–O(7)#2	1.811(18)	Ga(1)–O(7)#3	1.811(18)
Ga(1)–O(1)#4	1.830(15)	Ga(1)–O(1)	1.830(15)
Ga(2)–O(8)#5	1.783(15)	Ga(2)–O(5)	1.806(17)
Ga(2)–O(3)	1.812(16)	Ga(2)–O(2)	1.830(16)
P(1)–O(4)	1.495(16)	P(1)–O(1)	1.535(16)
P(1)–O(2)#4	1.546(17)	P(1)–O(3)	1.552(17)
P(2)–O(6)	1.475(17)	P(2)–O(8)	1.530(17)
P(2)–O(5)	1.575(17)	P(2)–O(7)	1.605(19)
O(2)–P(1)#4	1.546(17)	O(7)–Ga(1)#6	1.811(18)
O(8)–Ga(2)#7	1.783(15)	O(7)#2–Ga(1)–O(1)#4	110.1(7)
O(7)#2–Ga(1)–O(7)#3	113.9(12)	O(7)#3–Ga(1)–O(1)#4	106.7(8)
O(7)#2–Ga(1)–O(1)	106.7(8)	O(7)#3–Ga(1)–O(1)	110.1(7)
O(1)#4–Ga(1)–O(1)	109.4(10)	O(8)#5–Ga(2)–O(5)	114.4(7)
O(8)#5–Ga(2)–O(3)	110.9(7)	O(5)–Ga(2)–O(3)	105.8(7)
O(8)#5–Ga(2)–O(2)	105.7(7)	O(5)–Ga(2)–O(2)	111.8(7)
O(3)–Ga(2)–O(2)	108.1(7)	O(4)–P(1)–O(1)	111.3(9)
O(4)–P(1)–O(2)#4	110.4(9)	O(1)–P(1)–O(2)#4	107.2(9)
O(4)–P(1)–O(3)	111.8(10)	O(1)–P(1)–O(3)	109.9(9)
O(2)#4–P(1)–O(3)	106.1(9)	O(6)–P(2)–O(8)	113.1(10)
O(6)–P(2)–O(5)	113.9(11)	O(8)–P(2)–O(5)	103.9(9)
O(6)–P(2)–O(7)	118.1(11)	O(8)–P(2)–O(7)	105.0(10)
O(5)–P(2)–O(7)	101.3(9)	P(1)–O(1)–Ga(1)	130.5(10)
P(1)#4–O(2)–Ga(2)	132.9(10)	P(1)–O(3)–Ga(2)	129.8(10)
P(2)–O(5)–Ga(2)	127.9(10)	P(2)–O(7)–Ga(1)#6	131.5(11)
P(2)–O(8)–Ga(2)#7	140.5(9)		
H-bond			
$D-H\cdots A$	$d(D\cdots A)$		<(DHA)
N(1)–H(1C) \cdots O(6)#5	2.79(3)		161.3
N(1)–H(1D) \cdots O(2W)#8	2.98(3)		151.6
N(2)–H(2C) \cdots O(6)#5	3.02(3)		136.6

Symmetry transformations used to generate equivalent atoms: #1 $-y + 1, -x + 1, -z + 1/6$ #2 $x + 1, y, z$ #3 $x - y + 1, -y, -z$ #4 $x - y, -y, -z$ #5 $x - y + 1, 1y + 1, -z$ #6 $x - 1, y, z$ #7 $x - y, -y + 1, -z$.

region. Single-crystal X-ray diffraction analysis indicates it crystallizes in the orthorhombic space group $Pnma$ (No. 52) with $a = 8.6618(2)$ Å, $b = 21.6071(5)$ Å, $c = 13.7426(4)$ Å, and $Z = 4$. The asymmetric unit, as seen in Fig. 1a, contains two crystallographically distinct Ga atoms and two P atoms. The Ga atoms are tetrahedrally coordinated by oxygen atoms, sharing four vertex oxygen atoms with adjacent P atoms. Ga(2) is located at a general position, while Ga(1) at a special position with C_2 symmetry. The Ga–O distances are in the range of 1.804(4)–1.840(4) Å. The O–Ga–O angles are in the range of 105.03(18)–116.4(3)°. The P atoms are tetrahedrally coordinated by oxygen atoms, sharing three oxygen atoms with adjacent Ga atoms, with one oxygen atom being terminal. The P–O_{bridging} distances are in the range of 1.537(4)–1.545(4) Å, and the shorter P=O distances in the range of 1.486(4)–1.496(4) Å. There are one crystallographically distinct Co atom and one crystallographically water molecule O(3W) lying at special position on the two-fold axis.

The structure of **1** is built from strictly alternating GaO_4 and $PO_3(=O)$ tetrahedral units that are linked through their vertexes, giving rise to the two-dimen-

sional layered structure with a 4.6-net. As shown in Fig. 2, the 4.6-net sheet has been found in layered aluminophosphates Gtex-1 [12] and Gtex-3, [14] but has not yet been found in gallophosphates. The sheet contains a series of [3.3.3] propellane-like chiral structural motifs, which is composed of three four-membered rings twisted in one direction. Since the sheet structure is center symmetric, a pair of enantiomers of such chiral motif exists in the structure.

Fig. 3 shows the packing of the inorganic sheets along the [100] direction with an $ABAB$ stacking sequence. A pair of enantiomers of chiral $Co(en)_3^{3+}$ cation resides in the interlayer regions. There are hydrogen-bonding interactions between the amino groups of the complex cations and the lattice oxygen atoms, with the N \cdots O distances in the range of 2.791(6)–2.9619(7) Å. We cannot locate the H atoms in the water molecules but they take part in H-bond network with the O(3W) \cdots O(8) separation of 2.666 Å measured by Cerius² software package [27].

The structure of compound **2**, $Co(dien)_2 \cdot Ga_3P_4O_{16} \cdot 3H_2O$, consists of macroanionic $[Ga_3P_4O_{16}]^{3-}$ sheets intercalating with complex $trans-Co(dien)_2^{3+}$ cations.

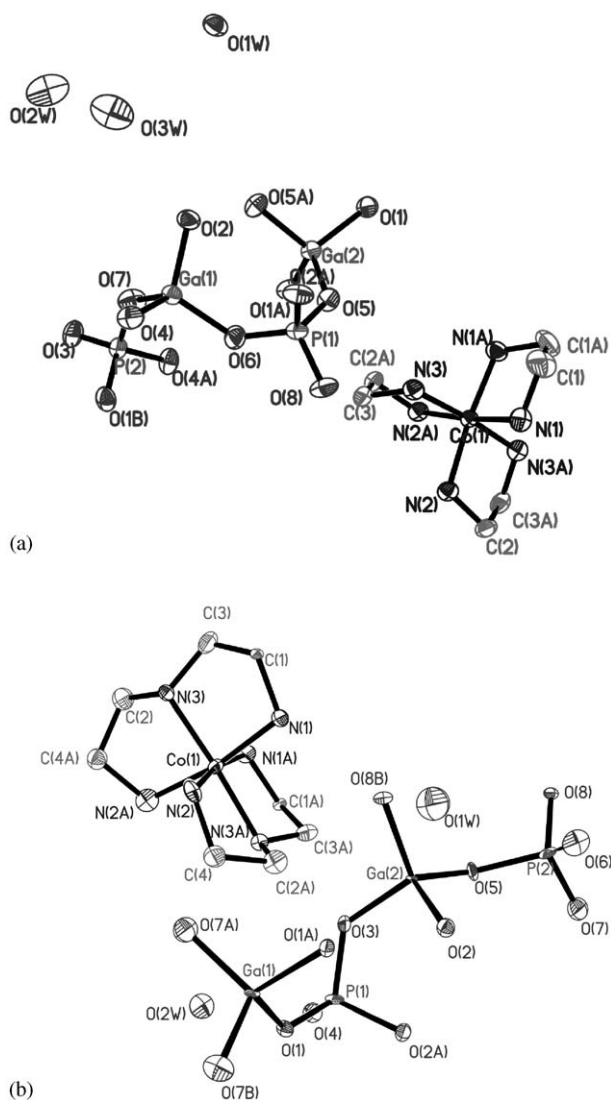


Fig. 1. Thermal ellipsoid plot (50%) showing the atomic labeling scheme of: compound **1** (a) and compound **2** (b).

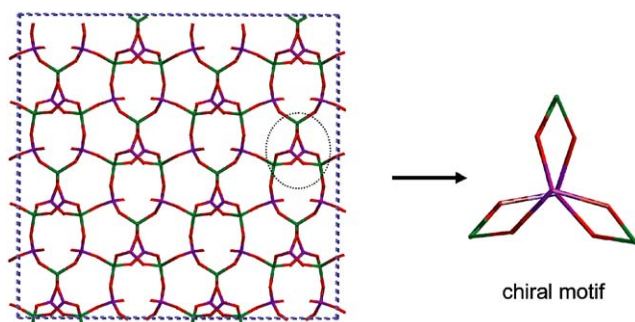


Fig. 2. The 4.6-net sheet structure of **1** parallel to the (010) plane, characteristic of [3.3.3] propellane-like chiral structural motifs.

Single-crystal X-ray diffraction analysis for one selected crystal in the batch of product **2** indicates it crystallizes in the hexagonal space group $P6_522$ with $a = 8.5152(7) \text{ \AA}$, $b = 8.5152(7) \text{ \AA}$, $c = 63.278(8) \text{ \AA}$, and

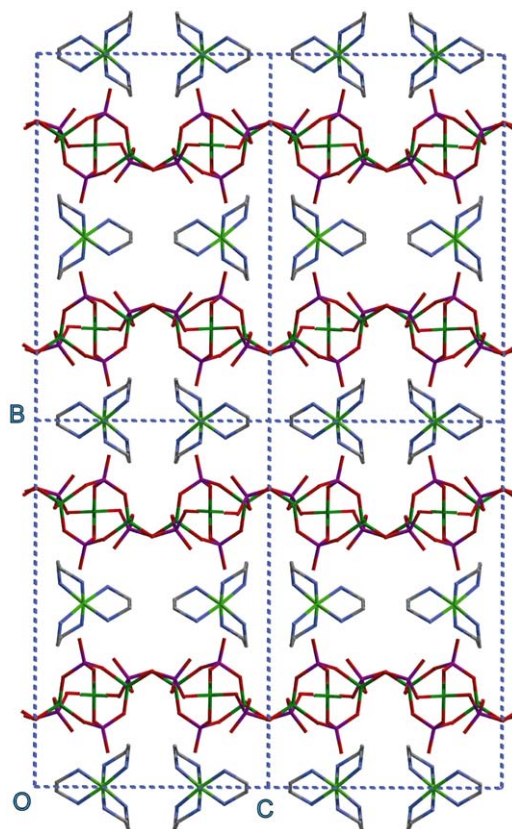


Fig. 3. Packing of the gallophosphate sheets in **1** in an ABAB stacking sequence along [100] direction, with Co(en)₃³⁺ cations in the interlayer region.

$Z = 6$. The asymmetric unit, as seen in Fig. 1b, contains two crystallographically distinct Ga atoms and two P atoms. Ga(1) is located at a general position, while Ga(2) at a special position with C_2 symmetry. The Ga–O distances are in the range of 1.806(17)–1.830(16) Å. The O–Ga–O angles are in the range of 105.8(7)–115.4(7)°. The P atoms are tetrahedrally coordinated by oxygen atoms, sharing three oxygen atoms with adjacent Ga atoms, with one oxygen atom being terminal. The P–O_{bridging} distances are in the range of 1.530(17)–1.605(19) Å, and the shorter P=O distances in the range of 1.475(17)–1.495(16) Å. There are one crystallographically distinct Co atom and one crystallographically distinct water O(2W) molecule lying at special position on the two-fold axis. As with **1**, **2** consists of macroanionic [Ga₃P₄O₁₆]^{3−} sheets with a 4.6-net. In contrast to **1**, the individual sheet of **2** is chiral, which contains only one enantiomer of [3.3.3] propellane-like chiral structural motifs. Interestingly, the sheets of **2** array in a helical fashion with an ABCDEF stacking sequence along the [010] direction as shown in Fig. 4. Only one enantiomer of chiral complex Co(dien)₂³⁺ cations resides in the interlayer region. There are extensive hydrogen-bonding interactions between the

amino groups of the complex cations and the lattice oxygen atoms, with the N...O distances in the range of 2.79(5)–3.02 Å. The water molecules also take part in H-bond network with the O(2W)...O(3) separation of 2.681 Å measured by Cerius² software package [27].

The structures of **1** and **2** both contain a 4.6-net sheet that is characteristic of [3.3.3] propellane-like chiral structural motifs. In **1**, a pair of enantiomers of chiral structural motif is induced by a pair of enantiomers of chiral complex $\text{Co}(\text{en})_3^{3+}$ cation. It is noted that both the chiral complex cations and the inorganic structural motifs have the C_2 symmetry. In **2**, an enantiomer of chiral complex $\text{Co}(\text{dien})_2^{3+}$ cation induces an enantiomer of chiral inorganic structural motif. Both the chiral complex cations and the inorganic structural motifs have the C_2 symmetry. The structures of **1** and **2** show a good stereo-specific correspondence between the metal complex template and the structure of the inorganic structural motifs, as seen in Fig. 5. This further demonstrates that the chiral metal complex template can impose their symmetry and configuration information into the inorganic host through chiral transference and molecular recognition effect.

4. Conclusions

Using the racemic mixture of chiral metal complex cations $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{dien})_2^{3+}$ as the structure-directing agent, respectively, two new types of layered gallophosphates $\text{Co}(\text{en})_3 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ (**1**) and *trans*- $\text{Co}(\text{dien})_2 \cdot \text{Ga}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (**2**) have been hydrothermally

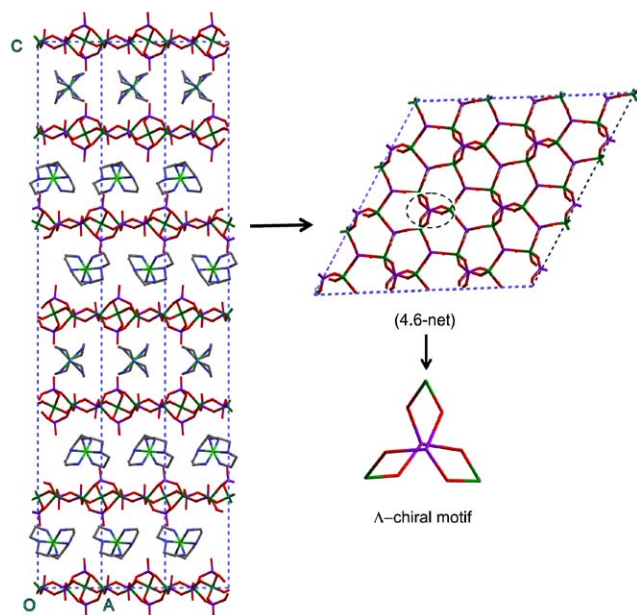


Fig. 4. Packing of the gallophosphate sheets in **2** in an *ABCDEF* stacking sequence along [010] direction, with *trans*- $\text{Co}(\text{dien})_3^{3+}$ cations in the interlayer region.

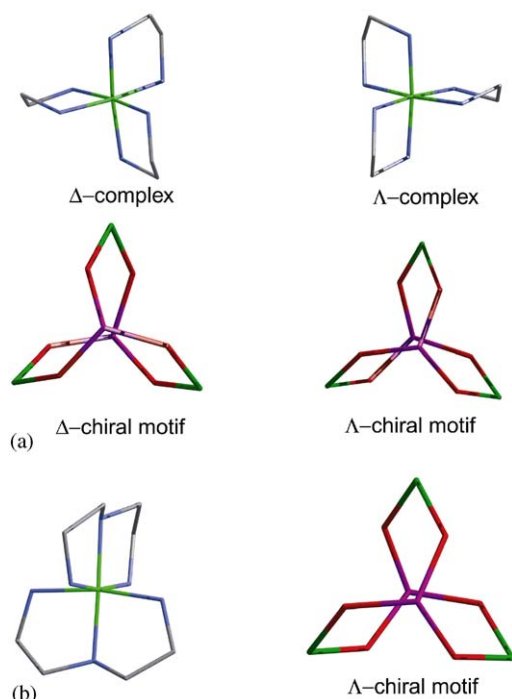


Fig. 5. The stereo-specific correspondence between the metal complex templates and the structure of the inorganic structural motifs in **1** and **2**.

prepared. The structures of **1** and **2** both consist of the 4.6-net sheets that are characteristic of [3.3.3] propellane-like chiral structural motifs. In **1**, the gallophosphate layers are assembled about a pair of enantiomers of chiral complex $\text{Co}(\text{en})_3^{3+}$ cations. As a consequence, a pair of enantiomers of chiral inorganic structural motifs exists. In **2**, the gallophosphate layers are assembled about one enantiomer of chiral complex $\text{Co}(\text{dien})_2^{3+}$ cation. As a consequence, only one enantiomer of chiral inorganic structural motif exists. Moreover, the point symmetry of the inorganic structural motifs conforms with that of the cobalt complex cations, revealing the chiral transference and molecular recognition effect between the host inorganic framework and the guest chiral templating agent.

Acknowledgments

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