Synthesis and Structural Characterization of 0D Vanadium Borophosphate [Co(en)$_3$]$_2$[V$_3$P$_3$BO$_{19}$][H$_2$PO$_4$]·4H$_2$O and 1D Vanadium Oxides [Co(en)$_3$][V$_3$O$_9$]·H$_2$O and [Co(dien)$_2$][V$_3$O$_9$]·H$_2$O Templated by Cobalt Complexes: Cooperative Organization of the Complexes and the Inorganic Networks

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A 0D vanadium borophosphate [Co(en)$_3$]$_2$[V$_3$P$_3$BO$_{19}$][H$_2$PO$_4$]·4H$_2$O (**1**) and two 1D vanadium oxides [Co(en)$_3$][V$_3$O$_9$]· H$_2$O (**2**) and [Co(dien)$_2$][V$_3$O$_9$]·H$_2$O (**3**) have been synthesized hydrothermally from the reaction mixture of V$_2$O$_5$– H$_3$PO$_4$–H$_3$BO$_3$–CoCl$_2$–R–H$_2$O at 110 °C (R: en or dien). The complex cations Co(en)$_3$$^{3+}$ and Co(dien)$_2$$^{3+}$ are cooperatively organized in the reaction medium to play a structure-directing role in the formation of the inorganic clusters and chains. The structures are determined by single-crystal X-ray diffraction analysis and further characterized by X-ray powder diffraction, ICP, and TG analyses. The structure of **1** contains isolated [V$_3$P$_3$BO$_{19}$]$^{5-}$ cluster anions, H$_2$PO$_4$$^-$ anions, racemic Co(en)$_3$$^{3+}$ cations, and H$_2$O molecules, which form a complex H-bond network. **2** and **3** both contain chains of corner-sharing VO$_4$ tetrahedra running along the 2$_1$ screw axis. The complex cations located in the interchain region interact with the chains through H-bonds. **2** is crystallized in an enantiomorphic space group and only one enantiomer of Co(en)$_3$$^{3+}$ is involved in the structure. Crystal data: **1**, monoclinic, *C*2/*c*, *a* = 32.8492(14) Å, *b* = 11.9601(3) Å, *c* = 22.6001(7) Å, *β* = 108.9630(8)°, *Z* = 8; **2**, orthorhombic, *P*2$_1$2$_1$2$_1$, *a* = 8.1587(16) Å, *b* = 12.675(3) Å, *c* = 18.046(4) Å, *Z* = 4; **3**, monoclinic, *P*2$_1$/*c*, *a* = 16.1663(10) Å, *b* = 8.7028(3) Å, *c* = 13.9773(5) Å, *β* = 103.1340(18)°, *Z* = 4.

Introduction

There has been much continuous interest in preparing new vanadium oxides because of their promising applications as anodes in secondary lithium batteries and electrochromic devices,[1–3] and as heterogeneous catalysts. The hydrothermal synthetic techniques in the presence of templates have led to the development of a variety of organic-based vanadium oxides[4–17] and vanadium oxides incorporating borophosphate

units[18–24] with 3D open frameworks, 2D layers, 1D chains, and 0D discrete clusters. Notable examples are chained

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$[NH_3(CH_2)_4NH_3](VO_3)_2$ with corner-sharing VO_4 tetrahedra,[6] layered $(C_6H_{14}N_2)V_6O_{14} \cdot H_2O$ composed of a unique arrangement of edge-shared VO_5 square pyramids that are corner-shared with VO_4 tetrahedra,[10] layered $(H_3N(CH_2)_3NH_3)$-$[V_4O_{10}]$ with electronic and magnetic properties,[12] layered $[N(CH_3)_4]_5V_{18}O_{46}$ with a supercell structure,[15] 3D framework vanadium borophosphate $(H_3NCH_2CH_2NH_3)_2[(VO)_5(H_2O)$-$BO_2(PO_4)_2] \cdot 1.5H_2O$,[18] cluster anions $(N_2C_6H_{14})_2[VO(PO_3$-$OH)_4(B_3O_3OH)] \cdot 4H_2O$,[19] and $(C_4H_{12}N_2)_6[(VO)_2BP_2O_{10}]_4 \cdot nH_2O$.[20] These compounds exhibit interesting structural characteristics with vanadium adopting a variety of coordination geometries in various oxidation states.

The nature of the template is one of the most important factors in determining the structures. The mechanism by which the inorganic frameworks assemble around the organic template under hydrothermal conditions is currently the subject of intense research but is not yet well-understood. We are interested in the study of the use of chiral metal complex as a template to imprint its chiral information onto the inorganic lattices and aim to explore the chiral recognition between the host and the guest and its origin. To date, several metal phosphates templated by chiral metal complexes have been reported including layered aluminophosphates,[25−29] gallium phosphates $[d$-Co(en)$_3][H_3Ga_2P_4O_{16}]$[30] and $[Co(en)_3]$-$[Ga_3(H_2PO_4)_6(HPO_4)_3]$,[31] boron phosphate $[Co(en)_3][B_2P_3O_{11}$-$(OH)_2]$,[32] and zinc phosphates $[Co(en)_3]_2[Zn_6P_8O_{32}H_8]$ and $[Co(en)_3][Zn_8P_6O_{24}Cl] \cdot 2H_2O$[33] 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)$_3$, and Ir− or Co−(1, 2-diaminocyclohexane)$_3$. More recently, using a racemix mix of chiral Co(dien)$_2$Cl$_3$ complex as the template, an interesting open-framework zinc phosphate $[Zn_2(HPO_4)_4][Co(dien)_2] \cdot H_3O$ has been prepared with multidirectional helical channels.[34] The rigid octahedrally coordinated metal amine complex is chiral, existing in both the Δ and Λ enantiomers. These structures show that the chiral template might induce an asymmetric microenvironment in the inorganic host or a chiral structure.

In an effort to further investigate the influence of the chiral metal complex on the structure of vanadium oxides, we have carried out synthesis in the system of $V_2O_5 - H_3PO_4 - H_3$-$BO_3 - CoCl_2 - R - H_2O$ (R: en and dien) and obtained a new 0D vanadium borophosphate $[Co(en)_3]_2[V_3P_3BO_{19}][H_2PO_4] \cdot 4H_2O$ (**1**) and two new 1D vanadium oxides $[Co(en)_3][V_3O_9] \cdot H_2O$ (**2**) and $[Co(dien)_2][V_3O_9] \cdot H_2O$ (**3**). Their synthesis and single-crystal structures are reported here. All of these compounds contain cobalt complexes which are cooperatively organized with the inorganic networks.

Experimental Section

Synthesis of $[Co(en)_3]_2[V_3P_3BO_{19}][H_2PO_4] \cdot 4H_2O$ (1). 1 was prepared by a hydrothermal reaction of a mixture of V_2O_5, H_3PO_4, H_3BO_3, $CoCl_2 \cdot 6H_2O$, en, and H_2O. Typically, 0.25 g of V_2O_5 and 0.68 g of H_3BO_3 were first dissolved in 10 mL of H_2O and then 0.326 g of $CoCl_2 \cdot 6H_2O$ was added followed by the addition of 0.578 mL of ethylenediamine. Finally, 0.556 mL of H_3PO_4 (85 wt %) was added dropwise with stirring. A gel was formed and stirred for 1 h until it was homogeneous, and then it was sealed in a Teflon-lined stainless steel autoclave and heated at 110 °C for 6 days under static conditions. The product containing uniform orange-yellow rod-shaped single crystals in a yield of ca. 30% was formed. The crystals were stable when kept in the mother liquid, but changed to amorphous after separation because of hydrolysis of the crystals.

Synthesis of $[Co(en)_3][V_3O_9] \cdot H_2O$ (2). A mixture of V_2O_5, H_3PO_4, H_3BO_3, $CoCl_2 \cdot 6H_2O$, en, and H_2O in the mole ratio of 1.0:2.0:2.0:1.0:4.0:404 was heated at 110 °C for 6 days. The product containing orange-yellow plate-shaped single crystals in a yield of ca. 23% was isolated by sonication and further washed by distilled water and then air-dried. The experimental X-ray diffraction pattern of the isolated product is in agreement with the simulated one generated by single-crystal structural data.

Synthesis of $[Co(dien)_2][V_3O_9] \cdot H_2O$ (3). A mixture of V_2O_5, H_3PO_4, H_3BO_3, $CoCl_2 \cdot 6H_2O$, dien, and H_2O in the mole ratio of 1.0:1.0:6.0:1.0:8.0:404 was heated at 110 °C for 6 days. The product containing orange-yellow plate-shaped single crystals in a yield of ca. 15% was separated by sonication and further washed by distilled water and then air-dried. The experimental X-ray diffraction pattern of the isolated product is in agreement with the simulated one generated by single-crystal structural data.

Characterization. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

The metal ion, boron, and phosphorus contents were measured by inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300DV spectrometer. The elemental analysis for C, H, and N was conducted on a Perkin-Elmer 2400 elemental analyzer. Analysis results for **2**: 27.1% V, 10.3% Co, 12.8% C, 4.8% H, and 14.8% N (calcd: 27.61% V, 10.65% Co, 13.01% C, 4.69% H, 15.24% N). Analysis results for **3**: 26.0% V, 10.1% Co, 16.4% C, 5.0% H, 14.1% N (calcd: 26.28% V, 10.14% Co, 16.51% C, 4.81% H, 14.50% N).

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. The weight loss of 34.53% and 36.56% occurring at 100−450 °C for **2** and **3**, respectively, was observed, which is attributed to the release of the water molecules and the decomposition of the occluded metal complexes in the product. Their structures collapse upon decomposition of the occluded complexes. The final products upon calcination above 800 °C are a mixture of V and Co oxides.

The valence state of +3 for Co in the products was confirmed by mangnetic measurement carried out on the Squids MPMS XL-5T Instrument.

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Table 1. Crystallographic Data and Refinement Details for Compounds **1**, **2**, and **3**

empirical formula	$[Co(en)_3]_2[V_3P_3B_1O_{19}][H_2PO_4]\cdot 4H_2O$	$[Co(en)_3][V_3O_9]\cdot H_2O$	$[Co(dien)_2][V_3O_9]\cdot H_2O$
formula weight	1144.07	554.08	582.13
temperature(K)	293(2)	293(2)	293(2)
wavelength(Å)	0.71073	0.71073	0.71073
crystal system,	monoclinic	monoclinic,	orthorhombic
space group	$C2/c$	$P2_12_12_1$	$P2_1/c$
unit cell dimensions (Å, deg)	$a = 32.8492(14)$	$a = 8.1587(16)$	$a = 16.1663(10)$
	$b = 11.9601(3)$	$b = 12.675(3)$	$b = 8.7028(3)$
	$c = 22.6001(7)$	$c = 18.046(4)$	$c = 13.9773(5)$
	$\beta = 108.9630(8)$		$\beta = 103.1340(18)$
volume (Å³)	8397.2(5)	1866.3(6)	1915.05(15)
Z	8	4	4
calculated density (Mg/m³)	1.810	1.97	2.019
absorption coefficient (mm⁻¹)	1.660	2.387	2.332
$F(000)$	4688	1120	1184
crystal size (mm)	$0.18 \times 0.06 \times 0.06$	$0.4 \times 0.050 \times 0.050$	$0.1 \times 0.08 \times 0.06$
θ range for data collection (deg)	1.31–27.48	1.96–27.42	1.29–27.43
limiting indices	$0 \leq h \leq 42$	$-10 \leq h \leq 10$	$-20 \leq h \leq 20$
	$0 \leq k \leq 15$	$-16 \leq k \leq 16$	$-11 \leq k \leq 11$
	$-29 \leq l \leq 27$	$-23 \leq l \leq 23$	$-18 \leq l \leq 18$
reflections collected/unique	9591/9591	4205/4205	7674/4151
R(int)	0	0	0.0629
completeness to θ (27.48°)	99.5%	98.4%	94.9%
refinement method	F^2	F^2	F^2
data/restraints /parameters	9591/0/550	4205/0/235	4151/0/256
goodness-of-fit on F^2	0.954	0.891	0.837
final R indices [$I > 2\sigma(I)$]	R1 = 0.0514	R1 = 0.0264	R1 = 0.0470,
	wR2 = 0.1429	wR2 = 0.0503	wR2 = 0.0601
R indices (all data)	R1 = 0.0937	R1 = 0.036	R1 = 0.1327
	wR2 = 0.1668	wR2 = 0.0644	wR2 = 0.0697
largest diff. peak and hole (e Å⁻³)	2.761 and −0.777	0.668 and −0.340	0.982 and −0.587

Structural Determination. Three suitable single crystals with dimensions $0.18 \times 0.06 \times 0.06$, $0.4 \times 0.05 \times 0.05$, and $0.10 \times 0.08 \times 0.06$ mm were selected for single-crystal X-ray diffraction analysis for **1**, **2**, and **3**, respectively. The intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer by oscillation scans using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Cell refinement and data reduction were accomplished with the RAPID AUTO program. The structures were solved by the direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97.[35] The V, Co, and P atoms were first located, and the B, O, N, and C atoms were then subsequently located in the difference Fourier maps. The C—H hydrogen atoms were located geometrically. The H atoms associated with the water molecules were not located. All non-hydrogen atoms were refined with anisotropically thermal parameters. Experimental details for the structure determinations are presented in Table 1. The atomic coordinates for compounds **1**, **2**, and **3** are listed in Tables 2–4, and their selected bond distances and bond angles are presented in Tables 5–7, respectively.

Result and Discussion

Synthesis of [Co(en)₃]₂[V₃P₃BO₁₉][H₂PO₄]·4H₂O (1), [Co(en)₃][V₃O₉]·H₂O (2), and [Co(dien)₂][V₃O₉]·H₂O (3). Compounds **1**, **2**, and **3** are all crystallized in the reaction mixture of V_2O_5, H_3PO_4, H_3BO_3, $CoCl_2\cdot 6H_2O$, amine, and H_2O at 110 °C. Table 8 presents the synthesis conditions and results. Compound **1** can be obtained in the reaction mixtures with molar compositions 1.0:(4–6):(4–10):1.0: (6–8):404 V_2O_5:H_3PO_4:H_3BO_3:$CoCl_2\cdot 6H_2O$:en:H_2O. The pH values of the initial reaction mixture are in the range of 5–6. When the amounts of H_3PO_4 and H_3BO_3 are reduced, compounds **2** and **3** are formed in the reaction mixtures with

pH values of 7–8 and 7–10, respectively. It is noted that **2** and **3** do not include B and P species. The above results show that even though three solids are obtained in the same system, their behaviors are different. This must be related to the pH value of the reactant media. At low pH the complexation contents of V by B and P species are sufficiently high to lead **1**. Increasing pH destroys the corresponding complexes; as a consequence, no B and P species are involved in **2** and **3**. Furthermore, it is noted that H_3PO_4 or H_3BO_3 acids are not necessary to the formation of **2** and **3** because HCl can also be used to adjust the pH value of the reactant instead of them. Thus, the addition of H_3PO_4 and H_3BO_3 plays a role in adjusting the pH value of the reaction media of **2** and **3**.

Interestingly, it is noted that $Co(en)_3^{3+}$ and $Co(dien)_2^{3+}$ complex cations are self-organized in the reaction medium and play a structure-directing role in the formation of compounds **1**, **2**, and **3**. The Co^{2+} ions in the initial reaction mixture are oxidized to Co^{3+} ions by V_2O_5. With use of a racemic mix of $Co(en)_3Cl_3$ as a template, compound **2** can be crystallized in the reaction mixture of V_2O_5, H_3PO_4, H_3BO_3, $Co(en)_3Cl_3$, and H_2O. This indicates that the cobalt and the organic amine species might be first organized to a complex and then play a structure-directing agent role in the formation of the inorganic networks. This reflects a cooperative effect between the complex and the inorganic networks.

Structures of [Co(en)₃]₂[V₃P₃BO₁₉][H₂PO₄]·4H₂O (1), [Co(en)₃][V₃O₉]·H₂O (2), and [Co(dien)₂][V₃O₉]·H₂O (3). The structure of $[Co(en)_3]_2[V_3P_3BO_{19}][H_2PO_4]\cdot 4H_2O$ (**1**) consists of isolated $[V_3P_3BO_{19}]^{5-}$ cluster anions, $H_2PO_4^-$ anions, water molecules, and $Co(en)_3^{3+}$ cations. An extended network of H-bonds among anions, cations, and water

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Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement parameters ($\text{Å}^2 \times 10^3$) for Compound **1**

atoms	x	y	z	U(eq)
V(1)	1174(1)	−891(1)	7319(1)	21(1)
V(2)	1730(1)	−1011(1)	6478(1)	20(1)
V(3)	1743(1)	1048(1)	7249(1)	20(1)
P(1)	722(1)	−1515(1)	5923(1)	18(1)
P(2)	1585(1)	1255(1)	5790(1)	21(1)
P(3)	781(1)	1547(1)	7005(1)	19(1)
P(4)	1320(1)	4345(2)	4441(1)	38(1)
B(1)	908(2)	608(5)	6050(3)	18(1)
Co(1)	1706(1)	4993(1)	1819(1)	19(1)
Co(2)	779(1)	8123(1)	3971(1)	21(1)
O(1)	1250(1)	136(3)	6569(2)	17(1)
O(2)	627(1)	−285(3)	5681(2)	20(1)
O(3)	1080(1)	1260(3)	5628(2)	22(1)
O(4)	637(1)	1375(3)	6281(2)	21(1)
O(5)	714(1)	−1558(3)	6599(2)	21(1)
O(6)	1180(5)	−1806(3)	5914(2)	21(1)
O(7)	392(1)	−2264(3)	5495(2)	24(1)
O(8)	1720(1)	8(3)	5796(2)	26(1)
O(9)	1773(1)	1781(3)	6442(2)	24(1)
O(10)	1702(1)	1895(3)	5305(2)	32(1)
O(11)	774(1)	408(3)	7317(2)	24(1)
O(12)	1245(1)	2023(3)	7216(2)	23(1)
O(13)	478(1)	2338(3)	7157(2)	28(1)
O(14)	1569(1)	−1706(3)	7126(2)	24(1)
O(15)	2074(1)	−86(3)	7040(2)	23(1)
O(16)	1609(1)	135(3)	7770(2)	24(1)
O(17)	1087(1)	−1581(3)	7868(2)	33(1)
O(18)	2050(1)	−1934(3)	6367(2)	29(1)
O(19)	2102(1)	1887(3)	7688(2)	28(1)
O(20)	917(2)	3534(6)	4141(3)	81(2)
O(21)	1729(2)	3604(5)	4591(3)	70(2)
O(22)	1324(2)	5133(4)	3936(3)	58(2)
O(23)	1268(2)	4848(4)	5012(2)	43(1)
N(1)	1312(2)	6051(4)	1250(2)	24(1)
N(2)	1199(2)	4043(4)	1663(2)	26(1)
N(3)	1615(2)	5681(4)	2552(2)	27(1)
N(4)	2049(2)	3891(4)	2419(2)	25(1)
N(5)	2201(2)	5979(4)	1903(2)	26(1)
N(6)	1850(2)	4310(4)	1124(2)	27(1)
N(7)	365(2)	8925(5)	3279(3)	42(1)
N(8)	792(2)	9505(5)	4440(3)	46(2)
N(9)	1220(2)	7429(6)	4681(3)	45(2)
N(10)	1267(2)	8595(5)	3710(3)	51(2)
N(11)	709(2)	6787(5)	3451(2)	45(1)
N(12)	321(2)	7495(6)	4238(3)	44(2)
C(1)	865(2)	5773(5)	1208(3)	29(1)
C(2)	830(2)	4528(5)	1151(3)	32(1)
C(3)	1961(2)	5319(5)	3126(3)	31(1)
C(4)	2020(2)	4070(5)	3054(3)	33(1)
C(5)	2336(2)	5904(5)	1337(3)	35(1)
C(6)	2285(2)	4700(6)	1133(3)	38(2)
C(7)	319(3)	10107(6)	3463(4)	51(2)
C(8)	382(3)	10142(6)	4135(4)	50(2)
C(9)	1654(2)	7885(7)	4712(3)	44(2)
C(10)	1657(2)	7944(6)	4052(3)	40(2)
C(11)	331(2)	6114(6)	3470(3)	33(1)
C(12)	303(2)	6260(5)	4128(3)	35(2)
O(1W)	162(2)	3043(6)	1983(4)	93(2)
O(2W)	1501(3)	862(5)	4171(3)	98(3)
O(3W)	462(2)	2811(5)	4829(3)	66(2)
O(4W)	846(2)	4426(5)	2687(3)	64(2)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Compound **2**[a]

atoms	x	y	z	U(eq)
V(1)	7193(1)	−554(1)	3602(1)	29(1)
V(2)	4486(1)	−2312(1)	3097(1)	31(1)
V(3)	3784(1)	−3001(1)	1373(1)	31(1)
Co(1)	359(1)	385(1)	1318(1)	23(1)
O(1)	7545(6)	−738(4)	4472(3)	74(2)
O(2)	8597(4)	−1165(3)	3121(2)	43(1)
O(3)	7262(5)	816(3)	3365(3)	61(1)
O(4)	5215(4)	−1045(3)	3381(3)	54(1)
O(5)	5382(4)	−3224(3)	3592(2)	46(1)
O(6)	2513(4)	−2377(3)	3247(2)	43(1)
O(7)	4951(5)	−2536(5)	2151(3)	73(2)
O(8)	2454(5)	−2109(3)	1125(2)	55(1)
O(9)	4990(5)	−3220(4)	690(3)	58(1)
N(1)	2473(5)	74(3)	1782(3)	31(1)
N(2)	−206(5)	1035(3)	2271(2)	34(1)
N(3)	1060(5)	1775(3)	962(3)	36(1)
N(4)	1146(5)	−157(3)	354(3)	35(1)
N(5)	−1875(5)	620(3)	967(3)	35(1)
N(6)	−418(5)	−1036(3)	1588(3)	32(1)
C(1)	2333(6)	224(4)	2595(3)	39(1)
C(2)	1283(6)	1187(4)	2728(3)	36(1)
C(3)	1263(7)	1723(4)	139(3)	41(1)
C(4)	2079(6)	696(5)	−30(3)	43(1)
C(5)	−2951(5)	−251(4)	1241(3)	40(1)
C(6)	−1985(6)	−1254(4)	1193(4)	44(2)
O(1W)	4629(9)	−1279(6)	−268(4)	107(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Compound **3**[a]

atoms	x	y	z	U(eq)
V(1)	2503(1)	552(1)	6638(1)	23(1)
V(2)	2133(1)	1575(1)	4334(1)	19(1)
V(3)	3372(1)	3650(1)	7775(1)	18(1)
Co(1)	0	5000	5000	14(1)
Co(2)	5000	5000	5000	14(1)
O(1)	1581(2)	1250(6)	6613(3)	56(1)
O(2)	3387(2)	4689(4)	6811(2)	33(1)
O(3)	2562(3)	−1216(4)	7054(2)	48(1)
O(4)	2342(2)	3416(4)	4468(2)	32(1)
O(5)	4258(2)	3873(4)	8608(2)	34(1)
O(6)	2485(2)	4198(4)	8284(2)	24(1)
O(7)	1102(2)	1357(4)	4144(2)	27(1)
O(8)	2673(2)	567(4)	5415(2)	30(1)
O(9)	3332(2)	1638(4)	7478(2)	26(1)
C(1)	78(4)	3183(7)	6690(4)	40(2)
C(2)	3452(3)	6614(6)	4376(4)	24(1)
C(3)	3883(3)	7411(6)	5316(4)	25(1)
C(4)	396(4)	5420(6)	3147(3)	32(2)
C(5)	−1460(4)	3079(6)	4922(4)	33(2)
C(6)	−691(4)	2078(6)	5054(4)	32(2)
C(7)	5507(3)	3206(6)	6707(3)	28(2)
C(8)	4794(3)	2253(6)	6084(4)	27(2)
N(1)	1233(3)	5354(5)	5390(3)	31(1)
N(2)	4095(3)	5806(4)	3934(3)	17(1)
N(3)	137(3)	4174(5)	3743(3)	25(1)
N(4)	4543(3)	6353(5)	5886(3)	20(1)
N(5)	4305(3)	3281(5)	5298(3)	21(1)
N(6)	49(3)	2968(5)	5608(3)	30(1)
O(1W)	1526(2)	−3376(4)	7467(2)	30(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

molecules links the structure in three dimensions. The asymmetric unit, as seen in Figure 1, contains three vanadium atoms, four phosphorus atoms, one B atom, and two Co atoms. The vanadium atoms are all coordinated by six oxygen atoms to form distorted octahedra with one short vanadyl (V=O) bond (1.591−1.621 Å). Each VO$_6$ octahedron is linked to two PO$_4$ tetrahedra, three VO$_6$ octahedra, and one BO$_4$ tetrahedron via vertex oxygen atoms. The V−O distances range between 1.763 and 2.173 Å and are typical

for structures containing six-coordinated V atoms. It is noted that O(1) is shared by three V atoms and one B atom. Bond valence calculations[36] give a bond valence sum for V(1),

(36) Brese, N. E.; O'Keefe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound **1**[a]

V(1)−O(17)	1.591(4)	V(1)−O(14)	1.788(4)
V(1)−O(16)	1.908(4)	V(1)−O(5)	1.992(4)
V(1)−O(11)	2.033(4)	V(1)−O(1)	2.173(4)
V(2)−O(18)	1.600(4)	V(2)−O(15)	1.783(4)
V(2)−O(14)	1.900(4)	V(2)−O(8)	1.958(4)
V(2)−O(6)	2.072(4)	V(2)−O(1)	2.148(3)
V(3)−O(19)	1.621(4)	V(3)−O(16)	1.763(4)
V(3)−O(15)	1.892(4)	V(3)−O(12)	1.988(4)
V(3)−O(9)	2.054(4)	V(3)−O(1)	2.133(4)
P(1)−O(7)	1.494(4)	P(1)−O(5)	1.539(4)
P(1)−O(6)	1.551(4)	P(1)−O(2)	1.565(4)
P(2)−O(10)	1.485(4)	P(2)−O(9)	1.535(4)
P(2)−O(8)	1.554(4)	P(2)−O(3)	1.579(4)
P(3)−O(13)	1.493(4)	P(3)−O(11)	1.537(4)
P(3)−O(12)	1.550(4)	P(3)−O(4)	1.563(4)
P(4)−O(22)	1.484(5)	P(4)−O(23)	1.484(5)
P(4)−O(21)	1.550(5)	P(4)−O(20)	1.605(6)
B(1)−O(1)	1.451(6)	B(1)−O(2)	1.479(7)
B(1)−O(3)	1.479(7)	B(1)−O(4)	1.485(7)
Co(1)−N(2)	1.951(5)	Co(1)−N(3)	1.958(5)
Co(1)−N(6)	1.959(5)	Co(1)−N(4)	1.961(5)
Co(1)−N(1)	1.962(4)	Co(1)−N(5)	1.967(5)
Co(2)−N(12)	1.942(6)	Co(2)−N(11)	1.954(6)
Co(2)−N(8)	1.955(6)	Co(2)−N(7)	1.959(6)
Co(2)−N(9)	1.963(6)	Co(2)−N(10)	1.965(7)
O(20)−H(20)	0.8200	O(21)−H(21)	0.8200
B(1)−O(1)−V(3)	126.2(3)	B(1)−O(1)−V(2)	124.9(3)
V(3)−O(1)−V(2)	89.32(13)	B(1)−O(1)−V(1)	126.5(3)
V(3)−O(1)−V(1)	88.89(13)	V(2)−O(1)−V(1)	89.28(13)
B(1)−O(2)−P(1)	117.7(3)	B(1)−O(3)−P(2)	116.2(3)
B(1)−O(4)−P(3)	115.9(3)	P(1)−O(5)−V(1)	123.0(2)
P(1)−O(6)−V(2)	123.0(2)	P(2)−O(8)−V(2)	122.4(2)
P(2)−O(9)−V(3)	123.8(2)	P(3)−O(11)−V(1)	124.9(2)
P(3)−O(12)−V(3)	120.6(2)	V(1)−O(14)−V(2)	110.78(19)
V(2)−O(15)−V(3)	109.84(18)	V(3)−O(16)−V(1)	110.38(19)

H-Bonds

D−H...A	d(D...A)	∠(DHA)
O(21)−H(21)...O(10)	2.624(7)	162.1
N(1)−H(1A)...O(9)#1	2.962(6)	146.9
N(1)−H(1B)...O(23)#1	2.956(7)	151.7
N(2)−H(2A)...O(14)#2	3.092(6)	134.2
N(2)−H(2B)...O(4W)	2.943(7)	157.7
N(3)−H(3A)...O(12)#1	2.998(6)	147.6
N(3)−H(3B)...O(4W)	3.037(8)	160.3
N(4)−H(4A)...O(14)#2	3.012(6)	160.0
N(4)−H(4B)...O(19)#3	3.023(6)	148.3
N(4)−H(4B)...O(15)#3	3.091(6)	136.2
N(5)−H(5A)...O(9)#1	3.048(6)	143.6
N(5)−H(5B)...O(15)#3	2.971(6)	171.3
N(6)−H(6A)...O(18)#2	2.928(6)	162.2
N(6)−H(6B)...O(23)#1	2.804(7)	170.4
N(7)−H(7A)...O(11)#1	3.011(7)	155.0
N(7)−H(7A)...O(13)#1	3.076(7)	138.3
N(7)−H(7B)...O(13)#4	3.024(7)	173.1

[a] Symmetry transformations used to generate equivalent atoms: (#1) x, $-y + 1$, $z - \frac{1}{2}$; (#2) x, $-y$, $z - \frac{1}{2}$; (#3) $-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + 1$; (#4) $-x$, $-y + 1$, $-z + 1$.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound **2**[a]

Co(1)−N(3)	1.956(4)	Co(1)−N(5)	1.959(4)
Co(1)−N(2)	1.961(4)	Co(1)−N(1)	1.964(4)
Co(1)−N(6)	1.967(4)	Co(1)−N(4)	1.978(4)
V(1)−O(1)	1.614(5)	V(1)−O(2)	1.635(4)
V(1)−O(4)	1.781(4)	V(1)−O(3)	1.784(4)
V(2)−O(5)	1.633(4)	V(2)−O(6)	1.641(3)
V(2)−O(7)	1.773(5)	V(2)−O(4)	1.783(4)
V(3)−O(9)	1.605(4)	V(3)−O(8)	1.631(4)
V(3)−O(3)#1	1.788(4)	V(3)−O(7)	1.797(5)
O(3)−V(3)#2	1.788(4)	V(1)−O(3)−V(3)#2	137.1(3)
V(1)−O(4)−V(2)	133.1(2)	V(2)−O(7)−V(3)	133.7(3)

H-Bond

D−H...A	d(D−H)	∠(DHA)
N(1)−H(1C)...O(4)#3	2.765(5)	164.0
N(1)−H(1D)...O(9)#4	2.967(5)	162.3
N(2)−H(2C)...O(3)#5	2.888(5)	170.0
N(2)−H(2D)...O(7)	2.828(5)	159.5
N(3)−H(3C)...O(6)#3	2.951(5)	129.7
N(3)−H(3D)...O(7)	3.020(5)	148.7
N(4)−H(4C)...O(8)#6	2.993(6)	156.3
N(4)−H(4D)...O(3)#6	3.120(5)	116.8
N(5)−H(5C)...O(8)#6	2.840(5)	163.0
N(5)−H(5D)...O(7)	3.011(5)	152.2
N(6)−H(6C)...O(1)#5	2.885(6)	135.6
N(6)−H(6D)...O(9)#4	2.911(5)	153.9

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x + 1$, $y + \frac{1}{2}$, $-z - \frac{1}{2}$; (#2) $-x + 1$, $y - \frac{1}{2}$, $-z - \frac{1}{2}$; (#3) $x + \frac{1}{2}$, $-y - \frac{1}{2}$, $-z$; (#4) $x + 1$, $y - 1$, z; (#5) $-x + 2$, $y - \frac{1}{2}$, $-z - \frac{1}{2}$; (#6) x, $y - 1$, z.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for Compound **3**[a]

V(1)−O(1)	1.603(4)	V(1)−O(3)	1.640(4)
V(1)−O(8)	1.791(3)	V(1)−O(9)	1.831(3)
V(2)−O(7)	1.638(3)	V(2)−O(4)	1.639(4)
V(2)−O(8)	1.793(3)	V(2)−O(6)#3	1.819(3)
V(3)−O(2)	1.628(3)	V(3)−O(5)	1.639(3)
V(3)−O(9)	1.797(3)	V(3)−O(6)	1.803(4)
Co(1)−N(6)	1.956(4)	Co(1)−N(3)	1.957(4)
Co(1)−N(1)	1.967(4)	Co(2)−N(2)	1.965(4)
Co(2)−N(4)	1.971(4)	Co(2)−N(5)	1.972(4)
V(1)−O(8)−V(2)	131.0(2)	V(3)−O(9)−V(1)	129.36(19)
V(3)−O(6)−V(2)#4	129.97(19)		

H-Bonds

D−H...A	d(D−H)	∠(DHA)
N(6)−H(6)...O(1)	2.960(6)	133.4
N(5)−H(5A)...O(2)	3.097(5)	144.5
N(5)−H(5B)...O(5)#3	3.004(5)	153.7
N(4)−H(4A)...O(2)	2.891(5)	157.8
N(4)−H(4B)...O(5)#5	2.906(6)	148.4
N(5)−H(5A)...O(4)	3.123(5)	122.8
N(3)−H(3C)...O(7)	2.891(5)	161.6
N(3)−H(3D)...O(1W)#6	2.917(5)	165.3
N(2)−H(2)...O(9)#3	3.007(5)	167.4
N(1)−H(1A)...O(1W)#7	3.042(5)	142.1
N(1)−H(1B)...O(4)	2.962(6)	165.6

[a] Symmetry transformations used to generate equivalent atoms: (#1) $-x$, $-y + 1$, $-z + 1$; (#2) $-x + 1$, $-y + 1$, $-z + 1$; (#3) x, $-y + \frac{1}{2}$, $z - \frac{1}{2}$; (#4) x, $-y + \frac{1}{2}$, $z + \frac{1}{2}$; (#5) $-x + 1$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$; (#6) $-x$, $-y$, $-z + 1$; (#7) x, $y + 1$, z.

V(2), and V(3) of 5.1, respectively, confirming that all vanadium atoms are present in the V^{5+} oxidation state.

The three phosphorus atoms in the cluster anion are each coordinated by three bridging oxygen atoms and one terminal oxygen atom. Two oxygen atoms are shared with two VO_6 octahedra and the third is shared with a BO_4 tetrahedron. The P−O distances are in the range of 1.535−1.579 Å. The remaining oxygen atom belongs to the terminal P=O group with shorter bond lengths of 1.485−1.494 Å. The boron atom is coordinated by four oxygen atoms, three of which are linked to three P atoms and one to three V atoms. The B−O distances are in the range of 1.451−1.485 Å.

The $[V_3P_3BO_{19}]^{5-}$ cluster has been found in the vanadium borophosphate $(NH_4)_5[V_3BP_3O_{19}]H_2O$.[37] Differently from this

(37) Bontchev, R. P.; Do, J.; Jacobson, A. J. *Inorg. Chem.* **2000**, *39*, 4179.

Table 8. Synthesis Conditions and Products[a]

| | | | gel composition (molar ratio) | | | | | |
| | | | CoCl$_2$·6H$_2$O(a) | en or | | | | |
run	V$_2$O$_5$	H$_3$PO$_4$	H$_3$BO$_3$	Co(en)$_3$Cl$_3$ (b)	dien*	H$_2$O	pH	product
1	1	4−6	4	1(a)	6−8(c)	404	5	**1**
2	1	4−6	8	1(a)	6−8(c)	404	6	**1**
3	1	4−6	10	1(a)	6−8(c)	404	6	**1**
4	1	1	0	1(a)	3−8(c)	404	8−9	**2**
5	1	3	0	1(a)	4−8(c)	404	7−8	**2**
6	1	0	2	1(a)	3−4(c)	404	7−8	**2**
7	1	0.5	2	1(a)	3−4(c)	404	7−8	**2**
8	1	1	4	1(a)	3−4(c)	404	7−8	**2**
9	1	3	4	1(a)	3−8(c)	404	7−8	**2**
10	1	1−2	4	0.5(b)	7−8(c)	404	8	**2**
11	1	4−5	4	0.5(b)	7−8(c)	404	8	**2**
12	1	4−5	8	0.5(b)	7−8(c)	404	8	**2**
13	1	0−2	12	0.5(b)	7−8(c)	404	10	**2**
14	1	2	2	1(a)	3−8(d)	404	7−10	**3**
15	1	0.5	6	1(a)	3−8(d)	404	7−10	**3**
16	1	1	6	1(a)	3−8(d)	404	7−10	**3**

[a] Crystallization temperature, 110 °C; crystallization time, 6 days.
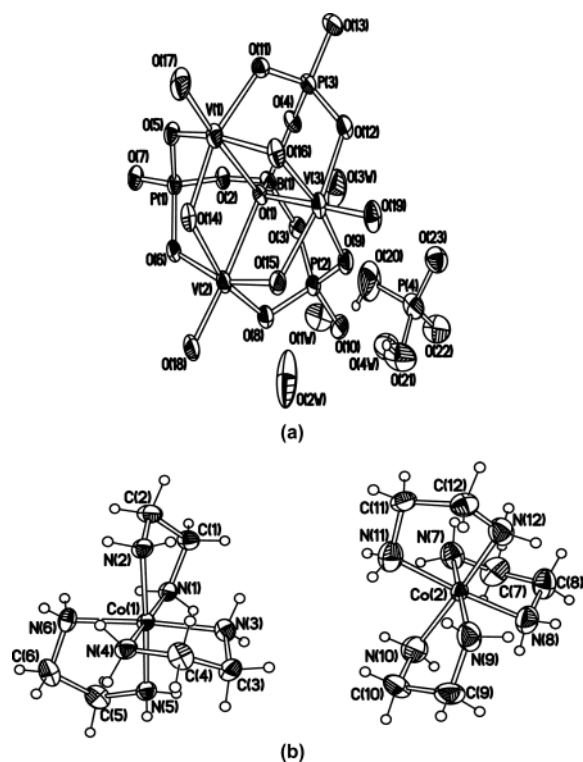
Figure 1. Thermal ellipsoid plot (50%) showing atom labeling scheme in **1**: (a) V, P, B, and O atoms and (b) Co, C, and N atoms.

Figure 2. Structure of **1** viewed along the [010] direction, showing the discrete cluster anions, H$_2$PO$_4^-$ anions, Co(en)$_3^{3+}$ cations, and H$_2$O molecules.

Figure 3. A pair of enantiomers of Co(en)$_3^{3+}$ cation and a pair of enantiomers of [V$_3$P$_3$BO$_{19}$]$^{5-}$ cluster anion in **1**.

compound, **1** contains isolated H$_2$PO$_4^-$ anions and complex cations which are self-organized around the cluster anions in the reaction system. Figure 2 shows the structure of **1** viewed along the [010] direction. It is noted that each Co-(en)$_3^{3+}$ cation is paired with a H$_2$PO$_4^-$ anion or a [V$_3$P$_3$BO$_{19}$]$^{5-}$ cluster anion. Each Co(en)$_3^{3+}$ cation and the cluster anion are chiral with a point group of $C1$. Interestingly, the chiral complex cations having the Δ configuration are associated with the chiral cluster anions with a same configuration, while the chiral complex cations having the Λ configuration are associated with the chiral cluster anions having the same configuration. As seen in Figure 3, a pair of enantiomers of
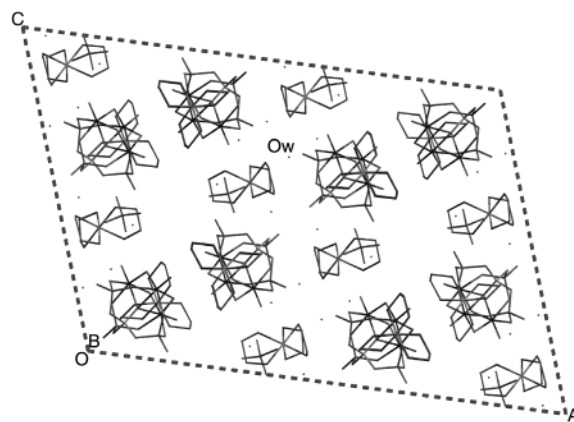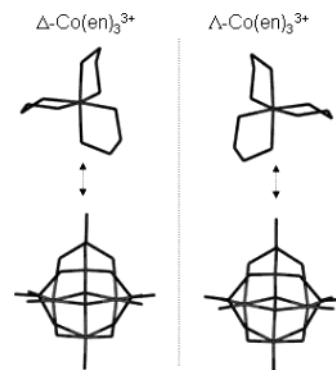
Co(en)$_3^{3+}$ is associated with a pair of enantiomers of the cluster anion.

The [V$_3$P$_3$BO$_{19}$]$^{5-}$ cluster anions, H$_2$PO$_4^-$ anions, the Co(en)$_3^{3+}$ cations, and water molecules form a complex H-bond network of N···O$_{cluster}$, N···O$_w$, N···O(H$_2$PO$_4^-$), Ow···Ow, and Ow···O(H$_2$PO$_4^-$). Table 5 summarizes the H-bonding information. Interestingly, the chiral metal complexes associated with the chiral cluster anions only form H-bonds with the chiral cluster anions having the same configuration. This reflects a chiral recognition phenomenon between the chiral metal complexes and the chiral cluster anions.

[Co(en)$_3$][V$_3$O$_9$]·H$_2$O (**2**) is crystallized in an enantiomorphic space group $P2_12_12_1$, and only one enantiomer of Co-(en)$_3^{3+}$ is involved in the structure (Figure 4). It contains chiral chains of corner-sharing VO$_4$ tetrahedra running along the 2_1 screw axis, with the Co(en)$_3^{3+}$ cations intercalated between them. It is noted that only the Δ-Co(en)$_3^{3+}$ cations are involved in the structure.

The vanadium atoms occupy three independent positions and are coordinated by four oxygen atoms in a distorted tetrahedron. Each VO$_4$ tetrahedron shares two oxygen atoms with two adjacent VO$_4$ tetrahedra with longer V−O distances of 1.773−1.797 Å. The V−O−V bond angles are in the range of 133.1−137.1°. The other two oxygen atoms are two terminal with shorter V=O distances of 1.605−1.641 Å. Bond valence calculations give a bond valence sum for V(1),
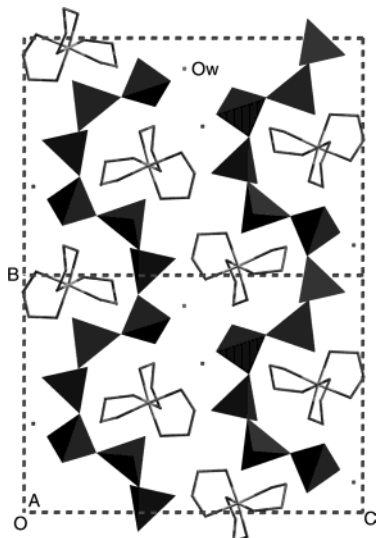
Figure 4. Structure of **2** viewed along the [100] direction. The Co(en)$_3$$^{3+}$ cations in the interchain region are exclusively with Δ configuration.

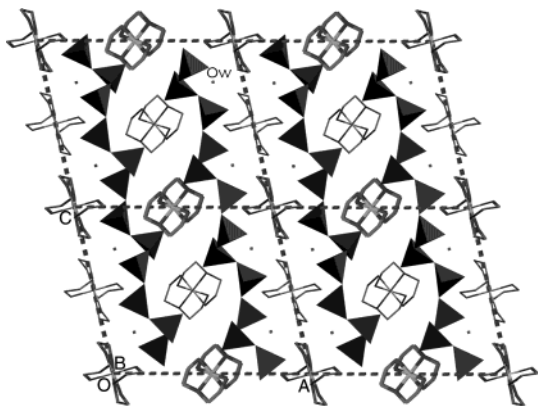**Figure 5.** Structure of **3** viewed along the [010] direction.

V(2), and V(3) of 5.3, 5.3, and 5.4, respectively, confirming that all vanadium atoms are present in the V^{5+} oxidation state.

The same chain type is also encountered for some compounds where the cations are mono- or divalent organic cations. Compound **2** is the first example with chiral chains between which only one enantiomer of the chiral Co(en)$_3$$^{3+}$ cations locates. H-bonds exist between the anionic chains and the complex cations. Each $-$NH$_2$ group of Co(en)$_3$$^{3+}$ cation, serving as a H-bond donor, forms two H-bonds to the oxygen atoms of the anionic chains. Table 6 summarizes the H-bonding information.

[Co(dien)$_2$][V$_3$O$_9$]·H$_2$O (**3**) is crystallized in the space group $P2_1/c$. It has the same type of chain structure as **2**, with the Co(dien)$_2$$^{3+}$ cations in the interchain region (Figure 5). Two crystallographically distinct Co atoms occupy an inversion center, respectively. The V$-$O$_{bridging}$ distances for tetrahedra V(1), V(2), and V(3) atoms are in the range of 1.791$-$1.831 Å, and the terminal short V=O distances are

in the range of 1.603$-$1.640 Å. The V$-$O$-$V bond angles are in the range of 129.4$-$131.0°. There exist H-bonds among the chain anions and the complex cations. Table 7 summarizes the H-bonding information.

Despite the similar chain topologies of **2** and **3**, it is noted that **2** is noncentric and **3** centric. Taking into consideration the fact that Co(en)$_3$$^{3+}$ in **2** is chiral noncentric and Co(dien)$_2$$^{3+}$ in **3** is centric, it reveals a stereospecific correspondence between the metal complex template and the structure of the inorganic host, which clearly indicates that there exists a molecular recognition between the guest and the host.

The anionic clusters in **1** and the anionic chains in **2** and **3** are all formed around the cobalt complex cations which are self-organized in the reaction medium to play to a structure-directing role in the formation of the inorganic networks. The cobalt complex-templated compounds have been found for a number of metal phosphates templated by an optically pure or a racemic mix of chiral metal complex.[25−33] Of particular interest is that the rigid chiral cobalt complex might induce its chirality to the inorganic lattice. As seen in compound **1**, a racemic mix of the chiral metal complex induces a pair of enantiomers of inorganic cluster anion, while an optically pure chiral metal complex induces a chiral inorganic lattice as seen in compound **2**. This implies a chiral recognition phenomenon between the host$-$guest.

Conclusions

Syntheses of a new vanadium borophosphate cluster [Co(en)$_3$]$_2$[V$_3$P$_3$BO$_{19}$][H$_2$PO$_4$]·4H$_2$O (**1**) and two new 1D vanadium oxide chains [Co(en)$_3$][V$_3$O$_9$]·H$_2$O (**2**) and [Co(dien)$_2$][V$_3$O$_9$]·H$_2$O (**3**) have been accomplished under hydrothermal conditions. The metal complex cations and the inorganic networks are cooperatively organized through extensive H-bonds. A pair of enantiomers of chiral Co(en)$_3$$^{3+}$ cations are involved in the structure of **1**, whereas only one enantiomer of chiral Co(en)$_3$$^{3+}$ cation is involved in the structure of **2** which enables compound **2** to be potentially used in the separation of the enantiomers of the chiral Co(en)$_3$$^{3+}$ cations. Further understanding the role of a chiral template in determining an inorganic framework structure will promote the development of chiral inorganic crystalline materials.

Supporting Information Available: Crystallographic data for compounds **1**, **2**, and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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