Synthesis and Characterization of a Chiral 3D-Framework Material: *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$

S. M. Stalder and A. P. Wilkinson*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

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A chiral material, *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$ (en = 1,2-diaminoethane), with a three-dimensionally connected framework has been prepared hydrothermally, using optically pure *d*-$Co(en)_3^{3+}$ as a structure directing agent, and the structure characterized by X-ray diffraction. Aluminum-containing analogues of this material have also been synthesized. The material can be thought of as a diamondlike network, consisting of tetrahedrally coordinated gallium sites linked by doubly bridging phosphates, with the metal complex sitting in the interstices. $Co(C_2N_2H_8)_3[H_3Ga_2P_4O_{16}]$, $M_r = 761.56$, monoclinic, $I2$, $a = 9.580(2)$Å, $b = 12.6789(5)$Å, $c = 9.9631(6)$Å, $\beta = 97.85(2)°$, $Z = 2$, $\rho_{calc} = 2.109$ g cm^{-3}, $\rho_{obs} = 2.11$ g cm^{-3}, Cu Kα, $R_F = 0.032$. $Co(C_2N_2H_8)_3[H_3Ga_{1.25}Al_{0.75}P_4O_{16}]$, $M_r = 729.51$, monoclinic, $I2$, $a = 9.567(1)$Å, $b = 12.6923(5)$Å, $c = 9.9241(5)$Å, $\beta = 97.601(8)°$, $Z = 2$, $\rho_{calc} = 2.028$ g cm^{-3}, $\rho_{obs} = 2.08$ g cm^{-3}, Cu Kα, $R_F = 0.026$.

Introduction

The availability of economically viable routes to optically pure chiral organic compounds is important for the production of many pharmaceuticals. One-quarter of all drugs administered to humans are mixtures of the therapeutic agent and isomers of it, in most cases, a racemate of enantiomers.[1] The pharmacokinetics and/or pharmacodynamics of the nontherapeutic enantiomer are in some cases different from the desirable one. Consequently, there is considerable regulatory pressure to move toward formulations that contain only the therapeutically beneficial enantiomer.

In principle, chiral zeolitic materials could be of use in the preparation of optically pure chiral products and intermediates. However, an optically pure chiral zeolitic material has never been prepared. The selection of chiral templates that are capable of transferring their chirality to a growing 3D inorganic framework presents a significant challenge. We report in this paper the synthesis and characterization of a chiral 3D framework gallophosphate, *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$ (en = 1,2-diaminoethane), using an optically pure template species.

A large number of zeolitic frameworks have been prepared.[2] However, the occurrence of chiral frameworks is uncommon, and full control of framework chirality has never been achieved. A small number of chiral microporous materials have been reported. These include gooscreekite (GOO),[3] "chiral zinc phosphate" (CZP),[4] and the chiral polymorphs of both zeolite β[5−7] and the titanosilicate ETS-10.[8] However, both zeolite β and ETS-10 are usually prepared as heavily intergrown materials, and only one of the polymorphic forms present in the intergrowth is chiral. We are not aware of any attempts to control the chirality of GOO or CZP and, hence, prepare the materials in optically pure form. Davis et al. have attempted to prepare samples of zeolite β that contain predominantly one enantiomer of the chiral polymorph (polymorph A). This approach met with limited success; the synthesis apparently yielded an excess of polymorph A, although it was impossible to tell from the crystallographic data if there was any enantiomeric enrichment. Using the acid form of the material as a catalysts for the ring opening of *trans*-stilbene oxide yielded the *S*,*S* form of the diol in 5% enantiomeric excess, while a typical zeolite β sample gave none. It was therefore inferred that the zeolite itself possessed a slight enantiomeric excess of one enantiomer of the A polymorph.[9]

As the use of chiral organic templates has met with limited success, we have been examining inorganic chiral chelate complexes containing transition-metal ions that are kinetically inert to ligand substitution reactions as alternative template species. Chiral chelate complexes in racemic form have previously been used to synthesize *d*,*l*-$Co(en)_3[Al_3P_4O_{16}]\cdot xH_2O$,[10,11] *d*,*l*-$Co(en)_3[Ga_3P_4O_{16}]\cdot xH_2O$,[12] $Co(tn)_3[Al_3P_4O_{16}]\cdot xH_2O$,[13] and trans-$Co(dien)_2[Al_3P_4O_{16}]\cdot xH_2O$[14] (tn = 1,3-diaminopropane, dien = bis(2-aminoethyl)amine). Our experiments using tris(1,2-diaminoethane)cobalt(III) in optically pure

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form have led to the preparation of a layered chiral solid *d*-$Co(en)_3[Al_3P_4O_{16}]\cdot xH_2O$,[15] and a chiral 3D framework material *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$. The latter compound and our attempts to prepare aluminum-containing analogues of it are the subject of the current paper.

Experimental Section

Synthesis. We have attempted the preparation of *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$ using a number of different gallium sources. The material was first prepared using a gel made by the hydrolysis of a $GaCl_3$ solution. The thermal decomposition of $Ga(NO_3)_3$ also produced a viable precursor. However, we were unable to synthesize the material using gallium oxyhydroxide prepared by the reaction of gallium metal and water in an autoclave. Our attempts at the preparation of a pure aluminum analogue of *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$ were unsuccessful, but we were able to prepare materials containing both aluminum and gallium in the framework.

Preparation of a gallium source from $GaCl_3$: 12 g of $GaCl_3$ was dissolved in 70 mL of distilled water, and the solution cooled. Concentrated aqueous ammonia was added dropwise until the maximum amount of gelatinous material was formed. The gel was filtered and washed with distilled water. It was then oven dried (~100 °C) and ground. The solid was heated in a vacuum oven at 120 °C overnight to remove any material that was sublimable. The gallium content (as Ga_2O_3) of the product was estimated thermogravimetrically.

Preparation of a gallium source from $Ga(NO_3)_3\cdot xH_2O$: 25 g portions of the nitrate, in an evaporating basin, were decomposed using a heating mantle. The gallium oxide content of the resulting solid was then determined.

Preparation of d-$Co(en)_3[H_2PO_4]_3$: the tartrate salt of *d*-$Co(en)_3^{3+}$ was prepared according to the method of Angelici.[16] Sodium dihydrogen phosphate was added to a hot solution of the tartrate, and *d*-$Co(en)_3[H_2PO_4]_3$ was recovered after allowing the solution to cool slowly. Elemental analysis of the resulting product by ICPAE was in good agreement with that expected for the proposed formula (experimental 10.9% Co, 17.75% P; predicted 11.08% Co, 17.54% P); however, traces of sodium were detectable.

Preparation of d-$Co(en)_3[H_3Ga_2P_4O_{16}]$: A gel with composition 0.7 Ga_2O_3:1.0 P_2O_5:2.0 TMAOH:0.5 *d*-$Co(en)_3[H_2PO_4]_3$:90 H_2O was used for the synthesis (TMAOH = tetramethylammonium hydroxide). Orthophosphoric acid (85% solution) was diluted with half of the required water and then slowly added to 5 g of the powdered gallium source (a nitrate-derived source was used for the preparation of the single crystals studied by X-ray diffraction) mixed with the remaining water. The resulting gel (pH ~ 3) was stirred for ~3.5 h. The TMAOH (25% aqueous solution) was then added, to adjust the gel pH, and the stirring continued for another hour. The metal complex was added to the gel, and after 20 min of stirring the mixture was transferred to Teflon-lined acid digestion vessels. The bombs were heated at 130 °C for 4 days. A deep orange product was recovered from the bombs by filtration along with a colorless crystalline material. The orange material was separated from the colorless material by suspension of the mixture in water and decantation of the liquid; the colorless material stayed suspended longer than the orange material. The orange material was then air-dried.

d-$Co(en)_3[H_3(Ga_{2-x}Al_x)P_4O_{16}]$: Materials isostructural with the gallophosphate, containing a mixture of aluminum and gallium, were synthesized by a procedure similar to that outlined above using metal sources prepared by the thermal decomposition of mixtures of aluminum and gallium nitrates or by the hydrolysis of solutions containing both aluminum and gallium chlorides. A metal source containing a 1:1 mixture of aluminum and gallium was used for the preparation of the *d*-$Co(en)_3[H_3(Ga_{1.25}Al_{0.75})P_4O_{16}]$ crystal that was studied by X-ray diffraction.

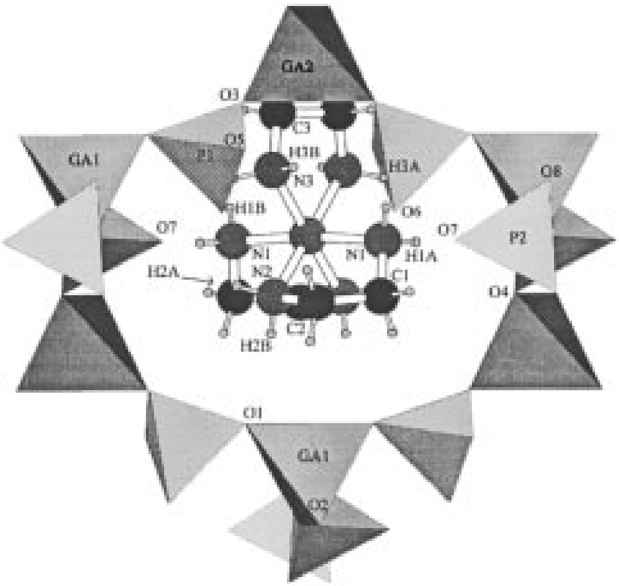

Figure 1. Naming scheme used to describe *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$. Only hydrogen atoms bound to nitrogen are labeled in this figure.

X-ray Diffraction Data Collection and Analysis. *d-$Co(en)_3[H_3Ga_2P_4O_{16}]$*: Unit-cell constants for the material were determined from 25 centered reflections in the θ range 11.5−47.6°. Data were collected using an Enraf-Nonius CAD4 diffractometer. Data reduction was performed using programs from the NRCVAX package.[17] The structure was solved using SHELXS-86,[18] developed using difference Fourier techniques and refined using SHELXL-93.[19] Anisotropic temperature factors were used for Ga, P, O, and Co; isotropic temperature factors were used for N and C due to the limited extent of the data set. Hydrogen atoms were placed on the nitrogen and carbon atoms of the metal complex using geometrical considerations and refined using a riding model. See Table 1 for a summary of the crystallographic details, Figure 1 for the naming scheme, Table 2 for refined coordinates, Table 3 for selected distances and angles, and Table 4 for a list of short hydrogen−oxygen contacts. Anisotropic temperature factors, hydrogen coordinates, a full distance and angle listing, and structure factor tables are available as Supporting Information.

d-$Co(en)_3[H_3(Ga_{1.25}Al_{0.75})P_4O_{16}]$: Unit-cell constants were determined from 25 centered reflections in the θ range 21.8−47.8°. Diffraction data were collected, and the structure was solved and refined as described in the previous paragraph. The distribution of the aluminum/gallium between the two metal sites, as well as their positions were also refined. See Table 1 for a summary of crystallographic details, Table 5 for the refined coordinates, Figure 1 for the naming scheme, and Table 3 for selected distances and angles. Anisotropic temperature factors, a full distance and angle listing, hydrogen atom coordinates, hydrogen−oxygen short contacts, and structure factor tables are available as Supporting Information.

Examination of Residual Complex in the Supernatant for Racemization. Our procedure for the preparation of *d*-$Co(en)_3[H_3Ga_2P_4O_{16}]$ does not lead to complete incorporation of the metal complex into the solid products from the hydrothermal synthesis. Some of the supernatant above the solid products was examined using polarimetric techniques so that the extent of racemization could be estimated. The analysis is complicated by the presence of phosphate in the supernatant; this ion is known to dramatically influence the CD

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Table 1. Crystal Data and Structure Refinement for *d*-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] and *d*-Co(en)$_3$[H$_3$(Ga$_{1.25}$Al$_{0.75}$)P$_4$O$_{16}$]

empirical formula	$CoN_6C_6H_{27}Ga_2P_4O_{16}$[a]	$CoN_6C_6H_{27}Ga_{1.25}Al_{0.75}P_4O_{16}$[a]
formula weight	761.56[a]	729.51[a]
temperature	ambient	ambient
wavelength	1.540 56 Å	1.540 56 Å
crystal system	monoclinic	monoclinic
space group	*I*2	*I*2
unit-cell dimensions	$a = 9.580(2)$ Å	$a = 9.5670(10)$ Å
	$b = 12.6789(5)$ Å	$b = 12.6923(5)$ Å
	$c = 9.9631(6)$ Å	$c = 9.9241(5)$ Å
	$\beta = 97.85(2)°$	$\beta = 97.601(8)°$
volume	1198.8(3) Å^3	1194.5 (2) Å^3
Z	2	2
density (calculated)	2.109 g/cm^3 [a]	2.028 g/cm^3[a]
density (measured)	2.11 g/cm^3	2.08 g/cm^3
absorption coefficient	11.304 mm^{-1}	10.721 mm^{-1}
absorption correction	semiempirical	semiempirical
F(000)	761[a]	734[a]
crystal size	0.20 × 0.25 × 0.30 mm^3	0.15 × 0.15 × 0.15 mm^3
θ range for data collection	5.68−74.48°	5.69−74.70°
index ranges	$-11 \leq h \leq 11$	$-11 \leq h \leq 11$
	$-1 \leq k \leq 15$	$-1 \leq k \leq 15$
	$-12 \leq l \leq 12$	$-12 \leq l \leq 12$
reflections collected	1636	1568
independent reflections	1407 (R(int) = 0.031[b])	1393 (R(int) = 0.020[b])
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	1407/1/130	1393/1/132
goodness-of-fit on F^2	1.056	1.071
R indexes [$I > 2\sigma(I)$][c]	$R_F = 0.0320$, $wR_F{}^2 = 0.0853$	$R_F = 0.0256$, $wR_F{}^2 = 0.0698$
R indexes (all data)[c]	$R_F = 0.0321$, $wR_F{}^2 = 0.0853$	$R_F = 0.0260$, $wR_F{}^2 = 0.0700$
absolute structure param	0.006(6)	−0.004(5)
largest difference map peak and hole	0.653 and −0.940 e$^-$/Å^3	0.660 and −0.441 e$^-$/Å^3

[a] Based on a formula including three charge balancing hydrogens that were not found crystallographically. [b] $R(\text{int}) = \sum|(I_0 - I_m)|/\sum I_0$. [c] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{F^2} = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for *d*-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$][a]

atom	*x*	*y*	*z*	$U_{(eq)}$
Ga(1)	10000(0)	−3073(1)	5000(0)	22(1)
Ga(2)	5000(0)	−344(1)	5000(0)	22(1)
P(1)	4848(1)	1289(1)	7053(0)	25(1)
P(2)	7035(1)	−2204(1)	5262(1)	29(1)
O(1)	5029(4)	1022(3)	8593(3)	31(1)
O(2)	8506(4)	−2218(4)	4775(4)	40(1)
O(3)	5740(3)	445(3)	6459(3)	30(1)
O(4)	6358(4)	−1213(4)	4543(4)	37(1)
O(5)	3363(4)	1270(4)	6398(4)	37(1)
O(6)	5503(5)	2397(3)	6895(4)	40(1)
O(7)	7123(4)	−2121(4)	6782(4)	42(1)
O(8)	6213(5)	−3184(4)	4695(5)	50(1)
Co(1)	5000(0)	−2204(1)	10000(0)	25(1)
N(1)	3626(5)	−2120(4)	8350(4)	32(1)[b]
N(2)	6200(4)	−1158(4)	9248(4)	30(1)[b]
N(3)	6046(5)	−3355(4)	9220(5)	39(1)[b]
C(1)	2730(5)	−1166(5)	8394(5)	35(1)[b]
C(2)	7589(6)	−1065(5)	10170(5)	37(1)[b]
C(3)	5272(8)	−4354(7)	9328(7)	56(2)[b]

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic temperature factors.

Table 3. Selected Bond Lengths (Å) for *d*-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] and *d*-Co(en)$_3$[H$_3$(Ga$_{1.25}$Al$_{0.75}$)P$_4$O$_{16}$]

atoms	bond lengths (Å) for d-Co(en)$_3$-[H$_3$Ga$_2$P$_4$O$_{16}$]	bond lengths (Å) for d-Co(en)$_3$-[H$_3$(Ga$_{1.25}$Al$_{0.75}$)P$_4$O$_{16}$]
2 × M(1)−O(2)	1.785(4)	1.748(3)
2 × M(1)−O(1)	1.815(4)	1.783(3)
2 × M(2)−O(4)	1.810(4)	1.798(3)
2 × M(2)−O(3)	1.826(4)	1.799(3)
P(1)−O(5)	1.482(4)	1.488(3)
P(1)−O(3)	1.538(4)	1.539(3)
P(1)−O(6)	1.555(4)	1.559(3)
P(1)−O(1)	1.558(3)	1.550(3)
P(2)−O(7)	1.509(4)	1.511(3)
P(2)−O(8)	1.536(5)	1.534(3)
P(2)−O(4)	1.545(4)	1.536(3)
P(2)−O(2)	1.552(4)	1.548(3)
2 × Co−N(1)	1.964(4)	1.968(3)
2 × Co−N(2)	1.969(4)	1.967(4)
2 × Co−N(3)	1.988(5)	1.978(3)
N(1)−C(1)	1.487(7)	1.483(5)
N(2)−C(2)	1.515(7)	1.496(5)
N(3)−C(3)	1.479(10)	1.490(7)
2 × C(1)−C(2)	1.508(7)	1.515(6)
C(3)−C(3)	1.502(14)	1.504(10)

Table 4. O···H Contacts (Å) Less Than 2.5 Å for *d*-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$]

atoms	distance (A)	atoms	distance (A)
O4−HN1A	2.410(6)	O1−HN2B	2.141(6)
O5−HN1B	1.959(6)	O7−HN3A	2.387(7)
O7−HN2A	2.109(6)	O5−HN3B	2.091(6)

spectrum of the complex,[20] as a consequence of ion pairing changing the equilibrium distribution of conformations in solution.[21,22] However, it has been reported that the effect of phosphate saturates at ~0.05M.[20] Reference solutions of the starting *d*-Co(en)$_3$[H$_2$PO$_4$]$_3$ and a sample of the supernatant were diluted using an aqueous solution of Na$_2$HPO$_4$ so that the concentration of the phosphate species in all of the samples was 0.5 M. UV−vis spectroscopy, along with a molar extinction coefficient derived from the reference solutions of *d*-Co(en)$_3$[H$_2$PO$_4$]$_3$, was used to estimate the concentration of *d*-Co(en)$_3{}^{3+}$ in the diluted supernatant. Measurements of the optical rotation (JASCO DIP-360 polarimeter) for the supernatant sample were compared with those obtained from the reference solutions of *d*-Co(en)$_3$[H$_2$PO$_4$]$_3$ so that the extent of racemization could be estimated.

TGA and DSC. A TGA experiment was performed in flowing air on a sample of *d*-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] using a Perkin-Elmer TGA 7, heating from 25 to 600 °C with a temperature ramp of 10 °C/min. A DSC experiment was also performed using a Perkin-Elmer DSC 7 over a similar temperature range.

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Table 5. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times 10^3$) for d-Co(en)$_3$[H$_3$(Ga$_{1.25}$Al$_{0.75}$)P$_4$O$_{16}$][a]

atom	x	y	z	$U_{(eq)}$	occupancy
Ga(1)	10000(0)	−3062(1)	5000(0)	22(1)	0.489(6)
Al(1)	10000(0)	−3062(1)	5000(0)	22(1)	0.511(6)
Ga(2)	5000(0)	−358(1)	5000(0)	24(1)	0.764(6)
Al(2)	5000(0)	−358(1)	5000(0)	24(1)	0.236(6)
P(1)	4814(1)	1288(1)	7047(1)	26(1)	
P(2)	7041(1)	−2215(1)	5298(1)	30(1)	
O(1)	4999(3)	1061(2)	8596(3)	32(1)	
O(2)	8523(3)	−2239(3)	4836(3)	40(1)	
O(3)	5674(3)	416(3)	6461(3)	33(1)	
O(4)	6379(3)	−1219(3)	4601(3)	37(1)	
O(5)	3316(3)	1288(3)	6409(3)	39(1)	
O(6)	5508(4)	2378(3)	6844(3)	41(1)	
O(7)	7120(3)	−2151(3)	6827(3)	42(1)	
O(8)	6223(4)	−3185(3)	4706(4)	47(1)	
Co	5000(0)	−2179(1)	10000(0)	25(1)	
N(1)	3642(4)	−2102(3)	8331(3)	33(1)[b]	
N(2)	6211(4)	−1130(3)	9264(3)	32(1)[b]	
N(3)	6057(4)	−3323(3)	9234(4)	37(1)[b]	
C(1)	2743(4)	−1154(4)	8368(4)	37(1)[b]	
C(2)	7577(5)	−1047(4)	10184(4)	39(1)[b]	
C(3)	5278(6)	−4331(5)	9326(5)	51(1)[b]	

[a] $U_{(eq)}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor. [b] Isotropic temperature factors.

Other Modes of Characterization. Powder diffraction patterns of the products were recorded using a Scintag X1 diffractometer equipped with a Peltier-cooled solid-state detector. Inductively coupled plasma atomic emission spectroscopy (Perkin-Elmer Optima 3000) was used to estimate the composition of the sample that the crystal of d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] was obtained from. Crystal density measurements were made using the flotation method with a mixture of carbon tetrachloride and 1,1,2,2-tetrabromoethane.

Results and Discussion

The X-ray diffraction study of the orange product from the hydrothermal gallophosphate synthesis demonstrated that the crystals examined were the chiral material d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$]. While the three hydrogens per formula unit associated with the framework were not located crystallographically, their presence as charge-balancing species is consistent with the elemental analysis (experimental 7.4% Co, 17.6% Ga, and 16.3% P; expected for the proposed formula 7.7% Co, 18.3% Ga, and 16.3% P by weight) and experimental crystal density (experimental 2.11 g/cm^3, expected for the proposed formula 2.109 g/cm^3). A comparison of the experimental powder X-ray diffraction pattern of the bulk orange product from the synthesis with that calculated from the single-crystal structure indicated that the bulk product had the same structure as the crystals. The white material produced during the hydrothermal synthesis was identified as a previously characterized gallophosphate,[23] isostructural with both leucophosphite (KFe$_2$(PO$_4$)$_2$(OH)·2H$_2$O)[24] and AlPO-15,[25] by comparison of the observed powder diffraction pattern with those in the ICDD powder diffraction file.

The synthesis of d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] employed a metal-to-phosphorus ratio (0.7:1) somewhat greater than that usually used for AlPOs and GaPOs. We did not produce any of this product in the small number of experiments that we performed with a 1:1 metal-to-phosphorus ratio. The primary role of the tetramethylammonium hydroxide in the preparation is probably pH adjustment, as none of the TMA cation is incorporated into the product. We have not investigated the use of other bases in the synthesis of d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$], but Bruce[10] has previously shown that the layered material d,l-Co(en)$_3$[Al$_3$P$_4$O$_{16}$]·xH$_2$O can be prepared using dipropylamine, tripropylamine, tetrabutylammonium hydroxide, or tetramethylammonium hydroxide as a synthesis gel additive.

d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] consists of a three-dimensional gallophosphate framework with the metal complex included within the pores of this framework (see Figures1 and 2). There are two crystallographically distinct gallium sites and two distinct phosphorus sites in the compound. Each gallium is linked to four phosphate groups (average Ga−O distance 1.809 Å) that bridge between two galliums (average bridging P−O distance 1.548 Å). The metal complex interacts with the framework electrostatically and through hydrogen bonds between the N−H groups on the metal complex and both terminal (O5 and O7) and bridging oxygens (O1 and O4) in the framework. There are short contacts (less than 2.5 Å see Table 4 and Figure 1) between all 12 N−H groups on each complex and framework oxygens. Only one of the two terminal oxygens on each of the phosphate groups is involved in hydrogen bonding with the complex. It should be noted that the terminal oxygens involved in H-bonding (O5 and O7) have short oxygen phosphorus bonds (1.48 and 1.51 Å, respectively), indicating P=O character, whereas the terminal oxygens that are not involved in hydrogen bonding (O6 and O8) have longer oxygen−phosphorus bonds (1.56 and 1.54 Å, respectively), suggesting that the charge-balancing hydrogen ions that were not located crystallographically are bound to these oxygen atoms. However, there are fewer hydrogen ions required for charge balancing than there are terminal oxygens not involved in H-bonding, so the hydrogen ions are probably disordered over the available terminal oxygens.

The thermal stability of the product was investigated using TGA and DSC. The TGA trace showed a weight loss of approximately 2% occurring at less than 200 °C, which is attributed to water loss. As no water oxygen atoms were located crystallographically, this water either is adsorbed on the surface of the material or is highly disordered and present within the pores of the compound. At about 350 °C a weight loss of ~20% is observed, indicating decomposition of the metal complex. Additionally, powder X-ray diffraction indicates that this weight loss is associated with a loss of crystallinity. The DSC showed events at temperatures similar to those seen in the TGA; heat flow events occurred at less than 200 °C and at approximately 350 °C. The events were not reversible.

Two crystals of the gallophosphate material were examined by single-crystal diffraction techniques, and their absolute structures determined. In both cases they contained d-Co(en)$_3^{3+}$. However, this does not guarantee that the bulk orange product contained only this enantiomer. The determination of optical purity for a solid such as d-Co(en)$_3$[H$_3$Ga$_2$P$_4$O$_{16}$] is not straightforward. Powder diffraction is not capable of distinguishing between enantiomers. Direct optical measurements on the powdered solid are complicated by the lack

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(25) Parise, J. B. *Acta Crystallogr. C* **1984**, *40*, 1641.

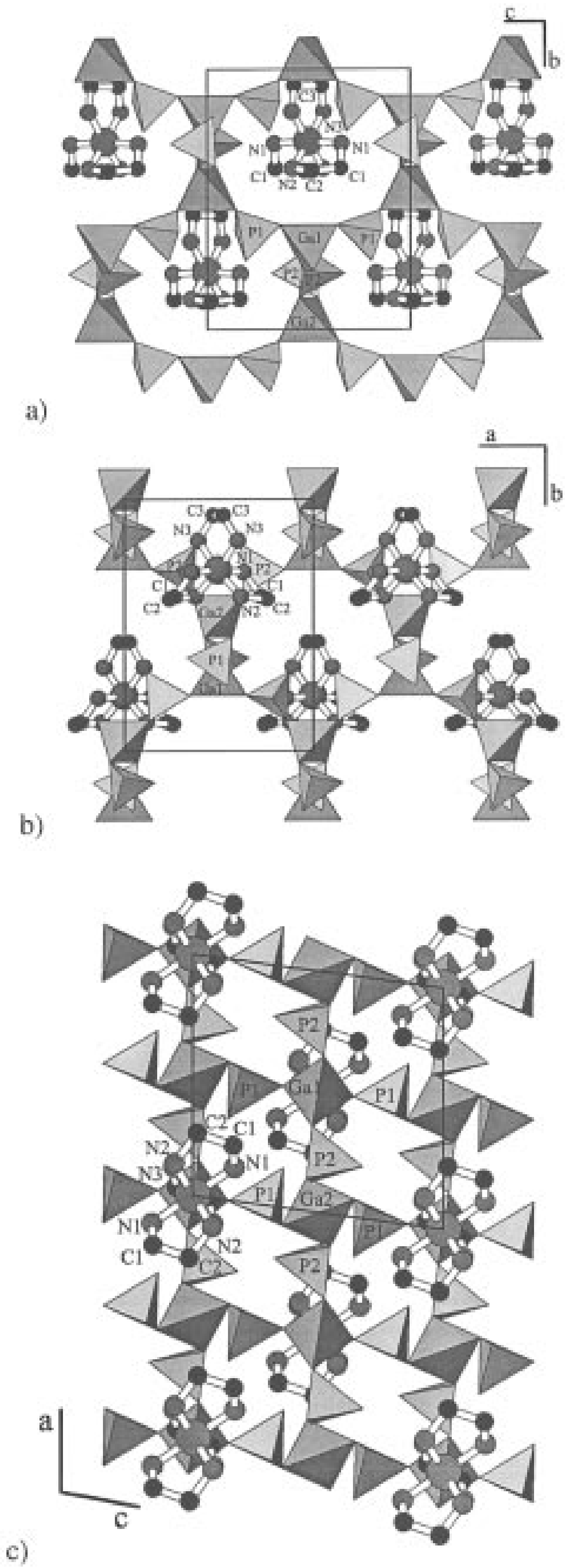

Figure 2. Views of d-Co(en)$_3$[$H_3Ga_2P_4O_{16}$] along the (a) crystallographic *a* axis, (b) crystallographic *c* axis, and (c) crystallographic *b* axis.

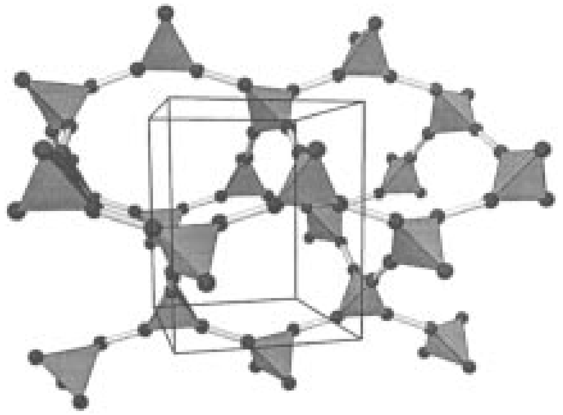

Figure 3. Framework connectivity of d-Co(en)$_3$[$H_3Ga_2P_4O_{16}$].

of reference values for the optically pure material, the optical anisotropy of the solid compound, and the possibility that a pressed transparent disk of polycrystalline material would display preferred orientation. We chose to examine the optical purity of the solid indirectly. For the product to contain a mixture of enantiomers the template species must racemize. Our examination of the supernatant liquid from the hydrothermal synthesis indicates that approximately 10% of the original d-Co(en)$_3{}^{3+}$ was converted to l-Co(en)$_3{}^{3+}$ during the gallophosphate synthesis, at 130 °C for 96 h, and subsequent handling prior to analysis.

It is interesting to examine the chirality of the structure. The presence of a single enantiomer of the metal complex in any given crystal of the material dictates that the crystal will be chiral, but it does not guarantee that the gallophosphate framework will be chiral. An examination of just the gallophosphate framework with MISSYM[17] demonstrates that there are no symmetry elements beyond those required for space group *I*2; this indicates that the complete framework is chiral in the absence of the complex. As each phosphate group in the structure acts as a bridge between only two GaO_4 units, the structure can be viewed as a fully connected network of linked GaO_4 tetrahedra. Inspection of this network (see Figure 3) indicates that the framework connectivity is the same as that of diamond, an achiral structure. An F-centered pseudocubic unit cell ($a = 14.735$ Å, $b = 12.679$ Å, $c = 12.844$ Å, $\alpha = 90°$, $\beta = 92.27°$, $\gamma = 90°$), analogous to the F-centered unit cell used to describe diamond, can be readily derived from the I-centered monoclinic unit cell. The chirality of the complete gallophosphate framework is a consequence of the phosphate groups' orientation and buckling of the connected PO_4 and GaO_4 network.

The structure of the crystal obtained from the mixed aluminum/gallium preparation is essentially the same as that of the gallophosphate. However, it is interesting to note that the Al/Ga ratio in the crystal, as determined from the diffraction data, differs considerably from that of the synthesis gel and the distribution of the aluminum over the two crystallographically inequivalent metal sites (as determined by a site occupancy refinement) is not statistical (for site M1 Ga/Al $\sim$ 1, and for site M2 Ga/Al $\sim$ 3). The inequivalence of the two tetrahedrally coordinated metal sites makes the network of linked MO_4 tetrahedra formally equivalent to cubic ZnS rather than diamond. The average M1−O and M2−O distances of 1.766 and 1.799 Å, respectively, are also consistent with their being more aluminum on site M1 than on site M2. It should be noted that the density calculated on the basis of the crystal structure is not in good agreement with the measured density of a crystal from the same batch; this may indicate some compositional variation within the batch.

The present work indicates that it is possible to prepare chiral three-dimensional frameworks using transition-metal complexes as templates. However, the nature of the chirality and the stability of the framework in the absence of the template need careful consideration. We are currently exploring other metal complex template species and framework types in an effort to prepare robust materials that are chiral by virtue of their connectivity.

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Supporting Information Available: Anisotropic temperature factors, hydrogen coordinates, and a full distance and angle listing (15 pages); structure factor tables (8 pages) are available as Supporting Information. Ordering information is given on any current masthead page.

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