

# Synthesis of Low-Dimensional Aluminophosphates from Higher Dimensional Precursors: Conversion of $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>]·xH<sub>2</sub>O to the Chain Compound $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·xH<sub>2</sub>O

J. D. Jasper and A. P. Wilkinson

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

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The chain compound  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·xH<sub>2</sub>O (en = 1,2-diaminoethane) was prepared by two routes: treatment of the layered material  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>]·xH<sub>2</sub>O with an aqueous sodium phosphate solution at 130 °C, and direct hydrothermal synthesis from an aluminophosphate gel. The structure of the chain compound was determined by single-crystal X-ray diffraction. The chains consist of AlO<sub>4</sub> tetrahedra linked together by doubly bridging PO<sub>4</sub> groups so that the material only has rings containing four T atoms. The chelate complexes lie between the chains and are hydrogen bonded to them. The two enantiomers of the complex are substitutionally disordered in the chain compound, but not in the layered starting material. This difference is discussed in the light of the hydrogen-bonding interactions between the chelate complexes and the AlPO chains, and the space-filling requirements of the complex.  $M_r = 564.16$ ; tetragonal,  $I42d$ ,  $a = 22.6009(7)$  Å,  $c = 8.5673(4)$  Å,  $Z = 8$ ;  $\rho_{\text{calcd}} = 1.676$  g cm<sup>-3</sup>; Mo K $\alpha$ ;  $R_F = 0.056$ .

## Introduction

Low-dimensional (0-, 1-, and 2D) aluminophosphates (AlPOs) are of interest because of their possible role in the formation of three-dimensional AlPO frameworks. Recently the syntheses and structures of several cluster-<sup>1,2</sup> and chain-containing<sup>3–8</sup> materials have been described, and Oliver et al. have discovered the solid-state transformation of the chain aluminophosphate [Al<sub>3</sub>P<sub>5</sub>O<sub>20</sub>H]<sup>5-</sup>·5[C<sub>5</sub>H<sub>9</sub>NH<sub>3</sub><sup>+</sup>] (UT-2) to a layered material, [Al<sub>2</sub>P<sub>3</sub>O<sub>12</sub>H]<sup>2-</sup>·[C<sub>5</sub>H<sub>9</sub>NH<sub>3</sub><sup>+</sup>] (UT-3).<sup>7</sup> Typically, chain structures are hydrothermally prepared from simple starting materials in predominantly nonaqueous media, although the use of aqueous media by Wang et al.<sup>4</sup> produced a product very similar to that reported by Gao and co-workers.<sup>5</sup> In the present work, we report the use of a new procedure for the synthesis of low-dimensional aluminophosphates.

We have recently reported the preparation of several aluminophosphate and gallophosphate materials using

Co(III) N-donor chelate complexes as templates.<sup>9–14</sup> Many of these materials are sheet structures with layer charge densities (4–5 e<sup>-</sup>/100 Å<sup>2</sup>) intermediate between those found for clay minerals<sup>15</sup> (1–2.7 e<sup>-</sup>/100 Å<sup>2</sup> for smectites and ~4.4 e<sup>-</sup>/100 Å<sup>2</sup> for mica) and the  $\alpha$ -zirconium phosphate family of materials<sup>16</sup> (~8.3 e<sup>-</sup>/100 Å<sup>2</sup>). Our attempts at ion exchange using the host  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>]·xH<sub>2</sub>O<sup>9,17</sup> in phosphate-containing media led to a new material,  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·xH<sub>2</sub>O (en = 1,2-diaminoethane).

## Experimental Section

**Syntheses.** Small single crystals of the new aluminophosphate were initially prepared by the treatment of unground  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>]·xH<sub>2</sub>O crystals (obtained by a procedure similar to that of Gray et al.<sup>13</sup>) with a phosphate-containing solution at 130 °C for 24 h in a Teflon-lined Parr acid digestion vessel. The phosphate solution was made by titrating a mixture of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> in distilled water (~5 g of

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**Table 1. Summary of Crystal Data and Structure Refinement**

formula/formula weight <sup>a</sup>	C <sub>6</sub> H <sub>36</sub> AlCoN <sub>6</sub> O <sub>14</sub> P <sub>2</sub> /564.16
diffractometer	SMART 1k
no. of frames/frame width	1321, 0.3°
exposure time	40 s
sample to detector distance	4.9 cm
detector 2θ	28°
wavelength/temperature	0.71073 Å/293(2) K
crystal system/space group	tetragonal/ <i>I</i> 42 <i>d</i>
unit cell dimensions	<i>a</i> = 22.6009(7) Å, <i>c</i> = 8.5673(4) Å
volume, <i>Z</i>	4376.2(3) Å <sup>3</sup> , 8
density (calcd)	1.676 g cm <sup>-3</sup>
absorption coefficient	1.045 mm <sup>-1</sup>
<i>F</i> (000)	2272
crystal size	0.05 × 0.05 × 0.3 mm <sup>3</sup>
θ range for data collection	1.80–28.28°
limiting indices	–25 ≤ <i>h</i> ≤ 30, –29 ≤ <i>k</i> ≤ 29, –11 ≤ <i>l</i> ≤ 8
reflections collected	13640
independent reflections	2662 [ <i>R</i> (int) = 0.0697] <sup>b</sup>
absorption correction	SADABS
refinement method	full-matrix least-squares on <i>F</i> <sup>2</sup>
data/restraints/parameters	2662/16/129
goodness-of-fit on <i>F</i> <sup>2</sup>	1.100
final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )] <sup>c</sup>	<i>R</i> <sub>1</sub> = 0.0561, <i>wR</i> <sub>2</sub> = 0.1324
<i>R</i> indices (all data) <sup>c</sup>	<i>R</i> <sub>1</sub> = 0.0850, <i>wR</i> <sub>2</sub> = 0.1520
absolute structure parameter	0.04(4)
largest diff. peak and hole	0.632 and –0.448 e/Å <sup>3</sup>

<sup>a</sup> Includes hydrogen that was not located crystallographically.

<sup>b</sup> *R*(int) = Σ(|*F*<sub>o</sub><sup>2</sup> – *F*<sub>m</sub><sup>2</sup>) / Σ*F*<sub>o</sub><sup>2</sup>; *m*, mean. <sup>c</sup> *R*<sub>F</sub> = Σ||*F*<sub>o</sub> – |*F*<sub>c</sub>|| / Σ|*F*<sub>o</sub>|. *R*<sub>F<sup>2</sup></sub> = {Σ[*w*(*F*<sub>o</sub><sup>2</sup> – *F*<sub>c</sub><sup>2</sup>)<sup>2</sup>] / Σ[*w*(*F*<sub>o</sub><sup>2</sup>)<sup>2</sup>]}<sup>1/2</sup>.

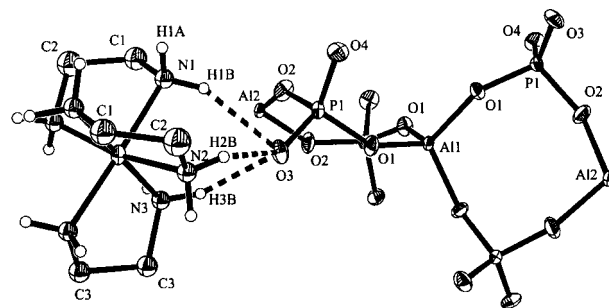
**Table 2. Atomic Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Displacement Parameter (Å<sup>2</sup> × 10<sup>3</sup>) for Λ,Δ-Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·*x*H<sub>2</sub>O**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>(eq)</sub> <sup>a</sup>
Co1 <sup>b</sup>	9794(1)	2500	1250	22(1)
N1 <sup>b</sup>	9184(3)	3108(3)	1694(8)	29(2)
N2 <sup>b</sup>	9710(3)	2232(3)	3425(5)	29(2)
N3 <sup>b</sup>	10410(2)	3069(3)	809(8)	28(2)
C1 <sup>b</sup>	9184(5)	3530(4)	361(10)	44(2)
C2 <sup>b</sup>	9259(5)	1774(5)	3645(13)	53(2)
C3 <sup>b</sup>	10974(4)	2721(5)	1918(13)	36(2)
Co2 <sup>c</sup>	9794(1)	2500	1250	22(1)
N4 <sup>c</sup>	10456(4)	2597(7)	2745(13)	25(3)
N5 <sup>c</sup>	9826(6)	3366(2)	1009(17)	26(4)
N6 <sup>c</sup>	9236(5)	2551(7)	2995(12)	25(4)
C4 <sup>c</sup>	11038(9)	2700(13)	1956(26)	36(2)
C5 <sup>c</sup>	9346(10)	3533(10)	–113(27)	44(2)
C6 <sup>c</sup>	9190(13)	1954(7)	3720(28)	53(2)
P1	9550(1)	4095(1)	5009(2)	20(1)
Al1	10000	5000	7500	16(1)
Al2	10000	5000	2500	19(1)
O1	9913(2)	4375(2)	6355(4)	29(1)
O2	9567(2)	4529(2)	3608(5)	36(1)
O3	9839(2)	3516(2)	4569(5)	37(1)
O4	8905(2)	4042(2)	5468(5)	34(1)
O5 <sup>d</sup>	8451(4)	2932(3)	5142(11)	115(3)
O6 <sup>d</sup>	7976(6)	2500	1250	189(9)
O7 <sup>d</sup>	10670(2)	3248(2)	7069(5)	43(1)
O8 <sup>d</sup>	11568(4)	2500	6250	107(4)

<sup>a</sup> *U*<sub>(eq)</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor. <sup>b</sup> These atoms have an occupancy of 70%. <sup>c</sup> These atoms have an occupancy of 30%. <sup>d</sup> Water oxygens.

each solid in 50 mL of H<sub>2</sub>O) with 1 M NaOH until the pH became 10. The product from this synthesis is hereinafter referred to as sample A. A further batch of material was prepared as a powder (sample B) by heating finely ground Λ,Δ-Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>]·*x*H<sub>2</sub>O in the phosphate buffer solution at 130 °C for 26 h.

Subsequently, an impure sample of Λ,Δ-Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·*x*H<sub>2</sub>O containing larger single crystals (sample C) was prepared from a gel with composition 1.00 Al<sub>2</sub>O<sub>3</sub>:0.33 Λ,Δ-Co(en)<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub>:

**Figure 1.** The major hydrogen-bonding interaction between the NH groups on the metal complex and the aluminophosphate chains in Λ,Δ-Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·*x*H<sub>2</sub>O.

0.17 TMAOH:14.84 H<sub>2</sub>O. Vista Catapal B (pseudoboehmite: 74.63% Al<sub>2</sub>O<sub>3</sub>) (2.25 g) was mixed with the required distilled water. After 3 h of stirring, TMAOH (tetramethylammonium hydroxide, 25% aqueous solution) was added dropwise over 15 min. After a further hour of stirring, the required amount of Λ,Δ-Co(en)<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>3</sub> was added. The gel was transferred into a Teflon-lined Parr acid digestion vessel after 4 h of additional stirring and then heated at 130 °C for ~90 h. The product was air-dried and examined by powder X-ray diffraction and optical microscopy.

**Powder X-ray Diffraction.** Powder X-ray diffraction data were collected with a Scintag X1 instrument using Cu Kα radiation and a Peltier cooled solid-state detector.

**Elemental Analysis.** The cobalt, sodium, aluminum, and phosphorus contents of sample B were obtained by ICP-AE using a Perkin-Elmer Optima 3000.

**Single-Crystal X-ray Diffraction Data Collection and Analysis.** Initially, the structure of a small crystal obtained from sample A was determined. However, the following description applies to a larger isostructural crystal that was obtained from sample C. Diffraction data were collected for a 0.05 × 0.05 × 0.3 mm<sup>3</sup> orange rod. The data were reduced using SAINT,<sup>18</sup> an absorption correction was applied using SADABS, and the final data processing was performed using XPREP.<sup>19</sup> The structure was solved in space group *I*42*d* and refined using components of the SHELXTL PC package.<sup>20</sup> A satisfactory model could not be found in the alternative space group *I*4<sub>1</sub>*md*. Examination of difference Fourier maps during the model development and refinement indicated that the Co(en)<sub>3</sub><sup>3+</sup> cation was substitutionally disordered. A two-component disorder model was constructed using difference Fourier methods and geometrical considerations. Soft constraints were applied to the Co–N, C–N, and C–C distances, and the thermal parameters of carbon atoms that were within 0.6 Å of each other in the disorder model were constrained to be the same. Hydrogen atoms were placed on the carbon and nitrogen atoms using geometrical considerations, and their positions and temperature factors were refined using a riding model. Anisotropic temperature factors were refined for the cobalt, aluminum, phosphorus, and oxygen atoms. A summary of the crystallographic details is given in Table 1, selected distances and angles are given in Table 2, and the naming scheme is illustrated in Figure 1.

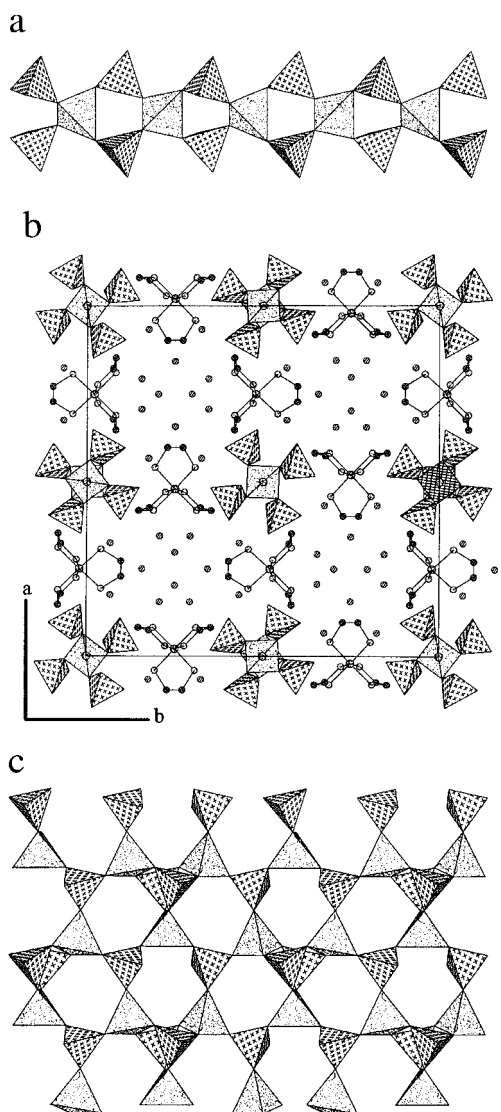
## Results

The powder X-ray diffraction data indicated that sample A contained two crystalline phases: unreacted starting material and small crystals of a new compound identified as Λ,Δ-Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>]·*x*H<sub>2</sub>O (*x* ~ 6) by single-crystal diffraction. The use of a more finely powdered

(18) *SAINT software reference manual*; Siemens Analytical X-ray Systems: Madison, WI, 1996.

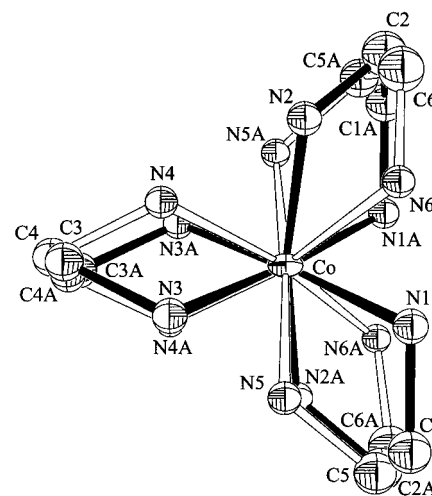
(19) *SMART software reference manual*; Siemens Analytical X-ray Systems: Madison, WI, 1996.

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**Figure 2.** (a) The chain connectivity and (b) the chain packing found in  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O. The aluminophosphate layer connectivity in  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>] $\cdot$ xH<sub>2</sub>O is shown in panel c for comparison with the chain connectivity. Only the major component in the disorder model for  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O is displayed in panel b. In all of the panels the AlO<sub>4</sub> tetrahedra are filled with random dots and the PO<sub>4</sub> tetrahedra are filled with crosses. The isolated small circles in panel b are the oxygen atoms associated with water in the structure.

batch of  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>] $\cdot$ xH<sub>2</sub>O as a starting material led to the synthesis of material (sample B) that contained  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O as the only crystalline phase. The synthesis of sample C was undertaken in an effort to obtain larger crystals of the new compound. Optical examination of this sample indicated that it contained small orange needles along with some deep blue prisms of an unidentified material. The structural details reported in this paper come from an examination of a needle obtained from sample C. The elemental analysis of sample B demonstrated that the bulk powder contained an amorphous impurity in addition to the crystalline chain compound. Typical analysis: Obsd: Co, 9.0%; Al, 14.0%; P, 23.0%; Na, 9%. Calcd for  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ 6H<sub>2</sub>O: Co, 10.5%; Al, 4.8%; P, 11%.



**Figure 3.** The relative positions of the two components in the metal complex disorder model for  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O. The major component in the disorder model is drawn with solid bonds.

## Discussion

The presence of an aluminum-containing amorphous impurity in sample B is not surprising, as the starting layered material contained considerably more aluminum per cobalt complex than the crystalline chain containing product. Treatment of the layered starting material with a solution containing Co(en)<sub>3</sub><sup>3+</sup> in addition to phosphate may have led to a cleaner product.

$\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O contains unprotonated [AlP<sub>2</sub>O<sub>8</sub><sup>3-</sup>]<sub>n</sub> chains (see Figure 2a) identical to those found in [NH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>3</sub>]<sup>2+</sup>[NH<sub>4</sub>]<sup>+</sup>[AlP<sub>2</sub>O<sub>8</sub>]<sup>3-</sup><sup>5</sup> and closely related to those in Et<sub>3</sub>NH<sup>+</sup>[H<sub>2</sub>AlP<sub>2</sub>O<sub>8</sub>]<sup>-</sup>.<sup>3</sup> The packing of the chains in the solid is illustrated in Figure 2b. The previously prepared 0D AlPOs [Al(PO<sub>4</sub>)<sub>4</sub>]<sup>9-</sup><sup>1</sup> and [Al<sub>2</sub>(HPO<sub>4</sub>)<sub>6</sub>]<sup>6-</sup><sup>2</sup> can be thought of as fragments of this chain type.

In contrast to the layered AlPOs that we have previously prepared in the presence of racemic mixtures of chelate complexes, the Co(en)<sub>3</sub><sup>3+</sup> is disordered such that both enantiomers of the complex are present at each cation site in the material (~0.70:0.30 mix of enantiomers). The two enantiomeric components in our disorder model are approximately related to one another by reflection through a plane including the cobalt and lying parallel to the triangular face defined by the three nitrogen atoms on the top or bottom of the complex (see Figure 3). However, the two enantiomers are slightly rotated with respect to each other; the plane defined by N1, N2, and N3 (disordered component 1) is at an angle of ~6° to the plane defined by N4, N5, and N6 (disordered component 2).

In the layered AlPO systems containing metal complexes that we have studied,<sup>9-13</sup> there are usually hydrogen bonds between several different framework oxygens and the NH groups on the complex, and the complexes are quite tightly packed in the interlayer space. This combination of interactions leads to the specific incorporation of one enantiomer at a given site in the structure. In  $\Lambda, \Delta$ -Co(en)<sub>3</sub>[AlP<sub>2</sub>O<sub>8</sub>] $\cdot$ xH<sub>2</sub>O there are also several hydrogen bonds between NH groups on the complexes and framework oxygens (see Table 4), but they are not sufficiently specific to drive the incorporation of one enantiomer at a given site. The primary

**Table 3. Selected Bond Lengths [Å] for  $\Lambda, \Delta\text{-Co(en)}_3[\text{AlP}_2\text{O}_8] \cdot x\text{H}_2\text{O}$** 

2 × Co1–N3	1.954(4)	2 × Co2–N6	1.959(5)
2 × Co1–N2	1.969(4)	2 × Co2–N5	1.968(5)
2 × Co1–N1	1.983(4)	2 × Co2–N4	1.981(5)
N1–C1	1.487(8)	N4–C4	1.498(10)
N2–C2	1.465(8)	N5–C5	1.498(10)
N3–C3	1.500(9)	N6–C6	1.488(10)
2 × C1–C2	1.471(9)	2 × C6–C5	1.495(10)
C3–C3	1.518(9)	C4–C4	1.510(10)
P1–O3	1.509(4)	4 × Al1–O1	1.732(3)
P1–O4	1.514(4)	4 × Al2–O2	1.730(4)
P1–O1	1.550(4)	P1–O2	1.552(4)

**Table 4. NH Hydrogen–Oxygen Short Contacts [Å] for  $\Lambda, \Delta\text{-Co(en)}_3[\text{AlP}_2\text{O}_8] \cdot x\text{H}_2\text{O}$** 

O3–H1B(N1)	2.186(8)	O7–H4B(N4)	2.181(13)
O3–H2B(N2)	2.298(8)	O3–H5A(N5)	2.263(15)
O3–H3B(N3)	2.021(8)	O3–H6A(N6)	2.051(16)
O4–H3A(N3)	2.162(7)	O4–H5B(N5)	2.215(14)
2 × O6–H1A(N1)	2.212(13)	O5–H6A(N6)	2.422(12)
O7–H2A(N2)	2.131(7)	O5–H6B(N6)	2.418(13)
O7–H4B(N4)	2.181(13)	2 × O6–H6B(N6)	2.400(18)

hydrogen-bonding interaction between the AlPO and the complex involves framework oxygen O3, lying on the pseudo-threefold axis of the complex, and the three hydrogens H1B (H4A), H2B (H5A), and H3B (H6A) (atom labels in parentheses refer to the second component in the disorder model). Clearly, hydrogen bonding of this type cannot distinguish between enantiomers of the complex. The only other AlPO metal–complex hydrogen-bonding interaction involves O4 and H3A (H5B). Inspection of the distances in Table 4 suggests that the strength of this interaction is likely to be similar for both enantiomers of the metal complex. In addition to the inability of the hydrogen bonding to differentiate between enantiomers, the two components in the disorder model occupy approximately the same location in space (see Figure 3), minimizing the preference for any particular enantiomer at a given site due to packing forces.

There are several water sites located in the space between the chains and the metal complexes. Only O7, which is involved in the strongest hydrogen-bonding interactions between the NH groups on the complexes and water (see Table 4), is well ordered.

The phosphate buffer treatment of  $\Lambda, \Delta\text{-Co(en)}_3\text{-}[\text{Al}_3\text{P}_4\text{O}_{16}] \cdot x\text{H}_2\text{O}$  to produce  $\Lambda, \Delta\text{-Co(en)}_3[\text{AlP}_2\text{O}_8] \cdot x\text{H}_2\text{O}$  is in some ways similar to the excision processes that have been employed to prepare soluble clusters from solids containing linked clusters.<sup>21</sup> Many reactions of this type fit into a formalism termed dimensional reduction<sup>22</sup> which was developed to describe the relationships between solids that can be derived from a parent structure by breaking bonds in the parent and inserting additional structure-terminating anions. However, our  $[\text{AlP}_2\text{O}_8^{3-}]_n$  chain structure is not a fragment of the  $[\text{Al}_3\text{P}_4\text{O}_{16}^{3-}]_n$  sheet structure found in the starting material (see Figure 1c), and consequently, the relationship between our product and our starting material does not fit into the dimensional reduction formalism. In our approach, the  $\Lambda, \Delta\text{-Co(en)}_3[\text{Al}_3\text{P}_4\text{O}_{16}] \cdot x\text{H}_2\text{O}$  acts as a convenient starting material for the production of the product rather than as a structural parent. It seems likely that under the synthesis conditions employed the layer is broken into small fragments that then condense to give the chain compound.

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