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Synthesis and Synchrotron Microcrystal Structure of an Aluminophosphate with Chiral Layers Containing Λ Tris(ethylenediamine)cobalt(III)

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A chiral aluminophosphate, $d\text{-Co(en)}_3\cdot\text{Al}_3\text{P}_4\text{O}_{16}\cdot3\text{H}_2\text{O}$, has been synthesized using optically pure $d\text{-Co(en)}_3{}^{3+}$ as a templating agent (en = 1,2-diaminoethane). The structure of the material has been determined from a small single crystal using synchrotron radiation and imaging plate detection. The aluminophosphate contains chiral macroanionic sheets similar to those previously reported in *trans*-$\text{Co(dien)}_2\cdot\text{Al}_3\text{P}_4\text{O}_{16}\cdot x\text{H}_2\text{O}$ (dien = diethylenetriamine). $\text{Co(C}_2\text{N}_2\text{H}_8)_3\cdot\text{Al}_3\text{P}_4\text{O}_{16}\cdot3\text{H}_2\text{O}$, $M_r = 754.1$, orthorhombic, $C222_1$, $a = 8.502(6)$ Å, $b = 14.620(6)$ Å, $c = 20.890(11)$ Å, $V = 2597(3)$ Å^3, $Z = 4$, $\rho_{\text{calc}} = 1.929$ g cm^{-3}, $\rho_{\text{obs}} = 1.95$ g cm^{-3}, $\lambda = 1.2007(5)$ Å, $\mu = 9.389$ mm^{-1}, $F(000) = 1526$, $T = 293$ K, $R_F = 0.084$ for 872 reflections $I > 2\sigma(I)$.

Introduction

There is much current interest in the development of technology suitable for the enantioselective synthesis or separation of chiral intermediates for the pharmaceutical industry. In principle, the shape-selective properties of zeolitic materials, which have made them spectacularly useful in the preparation of commodity chemicals, should be extendible to enantioselective catalysis and separations. While chiral zeolitic frameworks can be readily generated by modeling techniques, the synthesis of such a material in an optically pure form has proved elusive. Many inorganic compounds, including microporous materials, crystallize as chiral solids. For example, the naturally occurring zeolite Goosecreekite[1] and a recently reported compound, $\text{NaZnPO}_4\cdot\text{H}_2\text{O}$,[2] both have chiral open frameworks. However, controlling the chirality of the material, so that predominantly one enantiomer of the framework crystallizes, is a significant challenge. The most thoroughly studied example of a chiral zeolitic material is probably polymorph A of zeolite β.[3,4] However, attempts to prepare a sample containing a significant amount of the chiral polymorph in optically enriched form have met with very limited success.[5]

Recently, there has been considerable interest in the use of coordination complexes and organometallic species as templates or structure-directing agents in the synthesis of zeolitic materials. Notably, the use of decamethylcobaltacenium led to the preparation of the first 14-ring-containing zeolite[6] (UTD-1), and the synthesis of *trans*-$\text{Co(dien)}_2\cdot\text{Al}_3\text{P}_4\text{O}_{16}\cdot x\text{H}_2\text{O}$[7] (GTex3) containing chiral aluminophosphate macroanions has been reported. We are currently exploring the use of chiral transition-metal complexes as templates for the synthesis of chiral alumino and gallophosphates.[7−9] This paper reports the preparation and characterization of $d\text{-Co(en)}_3\cdot\text{Al}_3\text{P}_4\text{O}_{16}\cdot3\text{H}_2\text{O}$ using optically pure $d\text{-Co(en)}_3{}^{3+}$ as a template cation.

The structural characterization of zeolites and related materials is often a significant problem. In many cases, it is difficult to obtain single crystals that are suitable for study by X-ray diffraction techniques. Consequently, considerable effort has been expended on the development of methods that can be used along with powder diffraction data to provide a reliable structural picture for zeolitic materials.[10] In parallel with this work, the development of synchrotron radiation sources and new X-ray detector technology has reduced the size of single crystal that can be used for structure determination.

The difficulty of collecting useful single-crystal X-ray diffraction data on a sample is a function not only of a crystal's size. It also depends upon the wavelength of the radiation used and the composition of the sample. The scattering power of a crystal, S, provides a more meaningful comparison between different samples ($S = [F_{000}/V_u]^2 V_c\lambda^3$, where V_u is the unit cell volume, and V_c

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(1) Rouse, R. C.; Peacor, D. R. *Am. Miner.* **1986**, *71*, 1494−1501.

(2) Harrison, W. T. A.; Gier, T. E.; Stucky, G. D.; Broach, R. W.; Bedard, R. A. *Chem. Mater.* **1996**, *8*, 145−151.

(3) Newsam, J. M.; Treacy, M. M. J.; Koetsier, W. T.; de Gruyter, C. B. *Proc. R. Soc. London A* **1988**, *420*, 375−405.

(4) Higgins, J. B.; LaPierre, R. B.; Schlenker, J. L.; Rohrman, A. C.; Wood, J. D.; Kerr, G. T.; Rohrbaugh, W. J. *Zeolites* **1988**, *8*, 446−452.

(5) Davis, M. E.; Lobo, R. F. *Chem. Mater.* **1992**, *4*, 756−768.

(6) Freyhardt, C. C.; Tsapatsis, M.; Lobo, R. F.; Balkus, K. J.; Davis, M. E. *Nature* **1996**, *381*, 295−298.

(7) Bruce, D. A.; Wilkinson, A. P.; White, M. G.; Bertrand, J. A. *J. Solid State Chem.* **1996**, *125*, 228−233.

(8) Bruce, D. A.; Wilkinson, A. P.; White, M. G.; Bertrand, J. A. *J. Chem. Soc., Chem. Commun.* **1995**, 2059−2060.

(9) Wilkinson, A. P.; Gray, M. J.; Stalder, S. M. *Mater. Res. Soc. Symp. Proc.* **1996**, *431*, 21−26

(10) McCusker, L. B. *Acta Crystallogr., Sect. A* **1991**, *47*, 297−313.

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is the crystal volume).[11] For diffractometers with rotating anode X-ray sources and point detectors, $S \sim 10^{17}$ ($\sim 50 \times 50 \times 50$ μm SiO_2 crystal with 1 Å radiation)[12] is near the lower limit of what is currently achievable. The very high brightness of synchrotrons, when compared to conventional X-ray sources, allows considerably smaller crystals to be studied. At second-generation synchrotron sources, microcrystals with values of S between $\sim 1 \times 10^{15}$ and $\sim 1 \times 10^{17}$ have typically been used in structural studies.[13-20] Some samples with smaller scattering powers have also been studied; see, for example, Hamada et al.[21] Very recently, Neder et al.[22] have used a 10 μm X-ray beam at the third-generation European Synchrotron Radiation Facility (ESRF) to collect data on a 0.4 μm^3 Kaolinite crystal ($S \sim 8 \times 10^{10}$).[23] The efficient collection of diffraction data on very small crystals requires the use of a position-sensitive detector: imaging plates and CCDs are now used in this role as they offer significant advantages over photographic film. As we were unable to obtain crystals of d-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ (en = 1,2-diaminoethane) of sufficient size and quality for use with our laboratory X-ray equipment, we made use of synchrotron radiation and imaging plate detection to obtain a data set suitable for structure solution.

Experimental Section

Sample Preparation. A range of synthetic conditions was explored in an attempt to prepare crystals that were large enough for diffraction studies. We report the conditions that led to the growth of the crystals used in the diffraction study along with a preparation for a pure powder sample.

Small single crystals of d-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$, for study by X-ray diffraction, were synthesized from a gel with the following composition: 1.00 Al_2O_3:1.33 P_2O_5:46.79 H_2O:1.27 TMAOH: 0.125 d-$[Co(en)_3]$ I_3. 5.40 g of Vista Catapal B (pseudoboehmite: 81.32% Al_2O_3) was mixed with 10.24 g of distilled water in a 100 mL beaker. Phosphoric acid (61.56% P_2O_5, 85% solution, Fisher) was added dropwise (over ~1.6 h), followed by the addition of the TMAOH (tetramethylammonium hydroxide, 25% aqueous solution, Aldrich) and the remaining distilled water (over ~3.7 h). During the addition of the reagents the mixture was stirred continuously. Crystals of d-$[Co(en)_3]I_3$, prepared using the method of Angelici[24] (estimated optical purity ~100%, assuming $[\alpha]_d = 89°$), were ground and added to the slurry, and the stirring was continued for an additional 4.2 h. The resulting orange gel was transferred to three 23 mL Teflon-lined Parr acid digestion vessels and placed in an oven at 130 °C. One bomb was removed after 48 h; the two remaining bombs were removed after 72 h. The contents of each vessel were slurried in distilled water, and several grams of small orange crystals were separated from the pale orange powdered product by successive resuspensions and decantations. The material was recovered by filtration and washed with distilled water until the filtrate was clear and then air-dried. The crystals recovered from the bombs heated for 72 h are subsequently referred to as sample A.

Some white material was separated from sample A by flotation in a mixture of 5 mL each of carbon tetrachloride and 1,1,2,2-tetrabromoethane. The white impurities sank to the bottom of the flask, and the orange crystals (mixed with a few white flecks) floated near the surface. Any visible white particles were removed from the orange crystals, which were then washed with ether, air-dried, and ground prior to the TGA. The density of the orange crystals was determined by the flotation method using a mixture of carbon tetrachloride and 1,1,2,2-tetrabromoethane. TGA data were recorded using a Perkin-Elmer 7 Series instrument under flowing argon between room temperature and 900 °C using a ramp rate of 10 °C/min. A powder diffraction pattern of the product was measured using a Scintag X1 diffractometer.

A pure bulk polycrystalline sample (sample B) of d-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ was prepared from a gel with the composition 1.00 Al_2O_3:1.35P_2O_5:120.04 H_2O:2.00 TMAOH:0.664 $[d$-$Co(en)_3]$-I_3. Vista Catapal B (pseudoboehmite: 72.1% Al_2O_3) was mixed with half of the required distilled water. After 15 min of stirring , phosphoric acid (86.1% solution, Baker) was added dropwise to the slurry. The mixture was then stirred for a further 2.75 h. TMAOH (25% aqueous solution, Aldrich) was combined with the remaining water and added dropwise to the solution. Ground $[d$-$Co(en)_3]I_3$ was then added in small portions over a 30 min period. The mixture was stirred for a further 1 h and allowed to stand for 2 h. The gel was transferred to Parr acid digestion bombs and heated at 130 °C for 24 h. After removal from the oven, the contents of the bombs were filtered, washed with distilled water, and air-dried. An elemental analysis of the bulk product was performed using a Perkin-Elmer Optima 3000 ICP AE spectrometer. A powder diffraction pattern of the product was recorded using a Scintag X1 diffractometer.

Structure Analysis. Several small crystals from sample A were examined by X-ray diffraction techniques at Beam Line X7B, NSLS, Brookhaven National Laboratories, using Fuji imaging plates and a BAS 2000 scanner. This beam line is equipped with a double-crystal Si(111) monochromator and a Rh-coated focusing mirror. The mirror provides a high-energy cutoff that effectively eliminates $\lambda/3$ contamination of the X-ray beam for the wavelength used in the microcrystal experiment. The X-ray wavelength was determined to be 1.2007(5) Å using a powder diffraction pattern from a NIST lanthanum hexaboride (LaB_6) standard. A 0.5 mm pinhole collimator was used for the data collection. The data for structure determination were collected using an orange rodlike microcrystal (approximately $0.02 \times 0.02 \times 0.08$ mm) mounted on a tapered glass fiber. A series of diffraction patterns were recorded by rotating an unoriented crystal in the X-ray beam. The center of the imaging plate was at $2\theta = 25°$, and an 8° segment of ϕ was recorded on each plate. Images were recorded over the range $\phi = -5$ to 179° during an initial series of scans. A second, overlapping series of scans was performed using the same method, but with ϕ ranging from -1 to 175°. An exposure time of 100 s/° was employed for all of the scans.

Indexing was performed using the program DENZO.[25] Problems were encountered with overloaded intensities due to the limited dynamic range of the BAS 2000 scanner: the overloads were rejected from the data set. Indexed data from two series of scans were then merged in space group $P1$ using SCALEPACK.[25] A total of 1950 reflections was collected

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[11] Coppens, P. *Synchrotron Radiation Crystallography*; Academic Press: San Diego, 1992.

[12] Finger, L. W. *IUCr XVII Congress and General Assembly Abstracts*; 1996; abstract C-531.

[13] Cheetham, G. M. T.; Harding, M. M.; Haggit, J. L.; Mingos, M. P.; Powell, H. R. *J. Chem. Soc., Chem. Commun.* **1993**, 1000−1001.

[14] Andrews, S. J.; Papiz, M. Z.; McMeeking, R.; Blake, A. J.; Lowe, B. M.; Franklin, K. R.; Helliwell, J. R.; Harding, M. M. *Acta Crystallogr., Sect. B* **1988**, *44*, 73−77.

[15] Harding, M. M.; Kariuki, B. M. *Acta Crystallogr., Sect. C* **1994**, *50*, 852−854.

[16] Rizkallah, P. J.; Harding, M. M.; Lindley, P. F.; Aigner, A.; Bauer, A. *Acta Crystallogr., Sect. B* **1990**, *46*, 262−266.

[17] King, H. E.; Mundi, L. A.; Strohmaier, K. G.; Haushalter, R. C. *J. Solid State Chem.* **1991**, *92*, 1−7.

[18] Ko, Y.; Tan, K.; Parise, J. B.; Darovsky, A. *Chem. Mater.* **1996**, *8*, 493−496.

[19] Tan, K.; Ko, Y.; Parise, J. B.; Darovsky, A. *Chem. Mater.* **1996**, *8*, 448−453.

[20] Tan, K.; Darovsky, A.; Parise, J. B. *J. Am. Chem. Soc.* **1995**, *117*, 7039−7040.

[21] Hamada, E.; Ishizawa, N.; Marumo, F.; Oshumi, K.; Shimizugawa, Y.; Reizen, K.; Matsunami, T. *Acta Crystallogr., Sect. B* **1996**, *52*, 266−269.

[22] Engstrom, P.; Fiedler, S.; Riekel, C. *Rev. Sci. Instrum.* **1995**, *66*, 1348−1350.

[23] Neder, R. B.; Burghammer, M.; Grasl, T.; Schulz, H. *IUCr XVII Congress and General Assembly Abstracts*; 1996; abstract C-23.

[24] Angelici, R. J. *Synthesis and Technique in Inorganic Chemistry*; Saunders: Philadelphia, 1969; pp 66−74.

[25] Otwinowski, Z. *Data Collection and Processing, Proceedings of the CCP4 study weekend*; Daresbury Laboratory: Warrington, 1993; pp 56−62.

Table 1. Crystal Data and Details of the Structure Refinement for *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O

empirical formula	$C_6H_{30}Al_3CoN_6O_{19}P_4$
formula weight	754.106[b]
temp	293(2) K
wavelength	1.2007(5) Å
crystal system	orthorhombic
space group	$C222_1$
unit cell dimensions[a]	$a = 8.502(6)$ Å $b = 14.620(6)$ Å $c = 20.890(11)$ Å
volume	2597(3) Å^3
Z	4
density (calcd)	1.929 g/cm^3[b]
density (measd)	1.950 g/cm^3
absorption coefficient	9.389 mm^{-1}
absorption correction	none
$F(000)$	1526[b]
crystal size, mm	0.02 × 0.02 × 0.08
S[c]	1.9×10^{16}
θ range for data collection	3.30 to 39.59°
index ranges	$-6 \le h \le 8, -12 \le k \le 14, -11 \le l \le 20$
reflections collected	1950
independent reflections	1287 [R(int) = 0.0662]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	1287/1/79
goodness-of-fit on F^2	1.053
final R indices [872 reflns $I > 2\sigma(I)$]	$R_F = 0.0840$, $R_{wF^2} = 0.2093$
R indices (all data)	$R_F = 0.1176$, $R_{wF^2} = 0.2534$
absolute structure parameter	0.08(3)
largest diff peak and hole	1.208 and −0.981 e Å^{-3}

[a] A unit cell was determined separately for each recorded image. The cell constants are mean values and the esds come from an analysis of the determination's repeatability. [b] Values include water hydrogen atoms that were not located in the refinement. [c] Scattering power. $R_F = \sum||F_o| - |F_c||/\sum|F_o|$, $R_{wF^2} = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2] - s_oF_o^2)^2]\}^{1/2}\}^{1/2}$.

(excluding overloads), of which 1287 were independent. Friedel pairs were not merged.

The structure was initially solved in space group $P2_1$ using SHELXS-86.[26] Model development and full-matrix least-squares refinement was subsequently performed using SHELXL-93.[27] During the refinement process, inspection of the structure showed that it was best described in the orthorhombic space group $C222_1$. The coordinates and Miller indices were transformed accordingly, taking care not to invert the sense of the axis system, and the refinement continued in this space group. The anomalous scattering coefficients for use in the refinement were calculated using the program FPRIME.[28] All the hydrogen positions on the metal complex were determined geometrically. Isotropic temperature factors were used for all of the atoms as only a small number of independent reflections with $I > 2\sigma(I)$ were available. The final residuals for reflections with $I > 2\sigma(I)$ were $R_F = 0.084$ and $R_{wF^2} = 0.209$; for all of the data $R_F = 0.118$ and $R_{wF^2} = 0.253$. The Flack absolute structure parameter[29] refined to 0.08(3), indicating that the correct absolute structure had been chosen, and inspection of the structure showed that the crystal contained *d*-[Co(en)$_3$]$^{3+}$. Details of the crystal structure refinement are summarized in Table 1, the atomic coordinates are given in Table 2, some selected interatomic distances are shown in Table 3, and hydrogen−oxygen short contacts are listed in Table 4.

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

	x	y	z	U_{iso}
Co(1)	0	−1488(3)	2500	25(1)
P(1)	−3472(5)	−22(3)	919(2)	34(1)
P(2)	−3415(5)	−3354(3)	−149(2)	37(1)
Al(1)	−4875(6)	−1403(4)	−41(3)	32(1)
Al(2)	−628(8)	0	0	33(2)
O(1)	−1797(11)	−153(8)	650(5)	27(3)
O(2)	−1828(13)	−3509(8)	168(5)	39(3)
O(3)	−3439(14)	−133(9)	1625(6)	45(3)
O(4)	−4541(12)	−725(9)	623(6)	38(3)
O(5)	−4009(15)	−2444(10)	90(7)	56(4)
O(6)	−3359(15)	−3413(9)	−858(6)	54(4)
O(7)	−4035(14)	921(9)	719(6)	47(4)
O(8)	−4500(14)	−4056(9)	140(6)	55(4)
N(1)	2308(16)	−1506(10)	2524(8)	42(4)
N(2)	−40(23)	−505(12)	3129(8)	60(5)
N(3)	162(20)	−2403(11)	3170(8)	52(5)
C(1)	1756(23)	−2470(15)	3404(10)	55(6)
C(2)	2840(24)	−2329(15)	2851(10)	52(6)
C(3)	−446(34)	367(22)	2811(9)	114(11)
O(9)[a]	−5000	813(15)	2500	74(6)
O(10)[a]	−1120(24)	−2172(14)	−1357(10)	108(7)

[a] Oxygens of water molecules in the interlayer space.

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

Co(1)−N(3) × 2	1.94(2)	Al(1)−O(5)	1.71(2)
Co(1)−N(2) × 2	1.95(2)	Al(1)−O(2)	1.69(1)
Co(1)−N(1) × 2	1.96(1)	Al(1)−O(4)	1.73(1)
P(1)−O(3)	1.48(1)	Al(1)−O(7)	1.74(1)
P(1)−O(4)	1.50(1)	Al(2)−O(1) × 2	1.70(1)
P(1)−O(7)	1.52(1)	Al(2)−O(8) × 2	1.71(1)
P(1)−O(1)	1.54(1)	N(1)−C(2)	1.46(2)
P(2)−O(6)	1.49(1)	N(2)−C(3)	1.48(3)
P(2)−O(8)	1.51(1)	N(3)−C(1)	1.44(3)
P(2)−O(5)	1.51(1)	C(1)−C(2)	1.49(3)
P(2)−O(2)	1.52(1)	C(3)−C(3)	1.50(2)

Table 4. Short Contacts (<2.80 Å) between Hydrogen and Oxygen for *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O

short contacts	distance/Å	atoms bonded to oxygen	atoms bonded to hydrogen
O(1)−H2B	2.326	P(1), Al(2)	N(2)
O(2)−H1C	2.669	P(2), Al(1)	C(1)
O(3)−H1B	1.970	P(1)	N(1)
O(3)−H2B	2.206	P(1)	N(2)
O(6)−H1A	2.792	P(2)	N(1)
O(6)−H2A	2.167	P(2)	N(2)
O(6)−H3A	1.934	P(2)	N(3)
O(9)[a]−H3B	2.109	water	N(3)
O(9)[a]−H3B	2.111	water	N(3)
O(10)[a]−H1A	2.712	water	N(1)
O(10)[a]−H2C	2.456	water	C(2)
O(10)[a]−H2D	2.682	water	C(2)
O(10)[a]−H3C	2.470	water	C(3)

[a] Oxygens of water molecules in the interlayer space.

Results and Discussion

The crude product from the hydrothermal synthesis of the single crystals (sample A) included a large amount of aluminophosphate that did not contain any metal complex, as the synthesis gel composition that was used in this preparation of *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O was optimized for crystal size rather than product purity. However, the measured density and the low-temperature weight loss for the recovered orange crystals are all consistent with the formula Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O determined from the X-ray single-crystal structure ($\rho_{obs} = 1.95$ g cm^{-3}, $\rho_{calc} = 1.929$ g cm^{-3}; observed weight loss below 275 °C ~8.5%, expected for the loss of 3H$_2$O per formula unit ~7%). Additionally, the measured powder X-ray diffraction pattern, obtained using a sample that had been purified only by suspension in water and removal of the liquid containing the small particle size material, was in agreement with that calculated from

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(26) Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Göttingen: Germany, 1986.

(27) Sheldrick, G. M. *Program for Crystal Structure Determination*; University of Göttingen: Germany, 1993

(28) Cromer, D. T. *J. Appl. Crystallogr.* **1983**, *16*, 437.

(29) Bernardinelli, G.; Flack, H. D. *Acta Crystallogr., Sect. A* **1985**, *41*, 500−511.

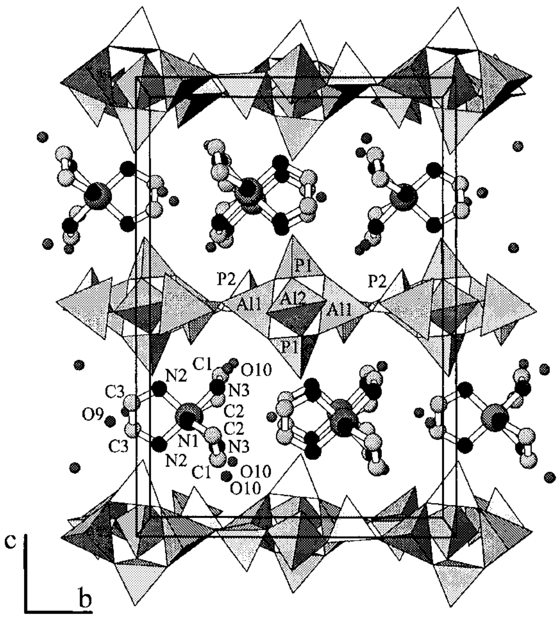

Figure 1. Perspective view along the *a*-axis of *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O showing the packing of the metal complexes between the AlPO layers and the interlayer water sites. The unit cell is outlined.

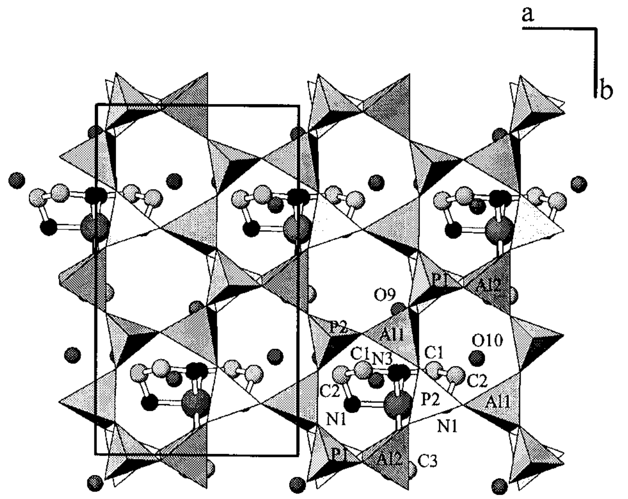

Figure 2. View along the crystallographic *c*-axis showing the layer structure in *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O and the relationship of the metal complexes to the layers. The unit cell is outlined.

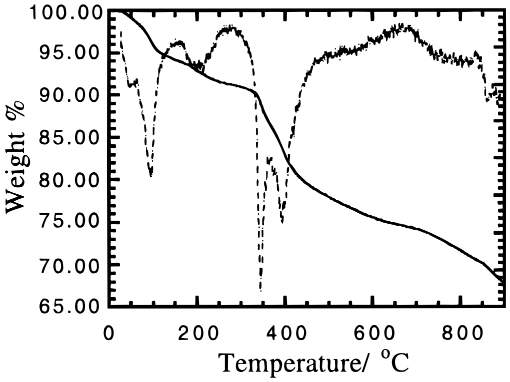

Figure 3. Thermogravimetric analysis curve for a sample of *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O heated under flowing dry argon at 10 °C/min along with the smoothed first derivative of the weight loss curve.

the single-crystal structure after taking into account preferred orientation. Simulations suggested that the majority of the sample was preferentially oriented with the crystallographic *c*-axis perpendicular to the X-ray sample holder surface; the aluminophosphate layers in *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O lie in the *a*−*b* plane. The bulk polycrystalline sample of *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O (sample B) appeared to be pure by visual inspection using a microscope. The elemental analysis indicated 8.5% Co, 16.4% P, and 10.9% Al (calculated composition 7.81% Co, 16.43% P, and 10.73% Al assuming *d*-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O). The powder diffraction pattern of this material was in good agreement with that calculated from the structure determined using single crystals from sample A.

d-Co(en)$_3$·Al$_3$P$_4$O$_{16}$·3H$_2$O consists of chiral Al$_3$P$_4$O$_{16}^{3-}$ macroanionic sheets stacked in an ABAB... fashion with the metal complexes sandwiched between the layers (see Figures 1 and 2 for the packing and layer structures). In the as-prepared sample, there is also water in the interlayer space. The TGA (Figure 3) indicates that this water is largely lost in two distinct stages as the material is heated: there is a low-temperature weight loss (<150 °C) of ~5.5% and a further weight loss of ~3% between 150 and 275 °C. In light of the TGA data, it is interesting to note that the water is split between two crystallographically distinct sites in the interlamellar region with multiplicities in the ratio 2:1. The high-multiplicity water oxygen, O(10), is not close to any hydrogen sites on the metal complex, but one of the hydrogen atoms on this water molecule is probably close to O(6) in the framework. However, the low-multiplicity water oxygen, O(9), is within hydrogen-bonding distance of two protons on N(3), and both the hydrogens of this water molecule are probably close to framework oxygen O(3) (see Table 4 for oxygen−hydrogen short contacts, and Figure 4 for the labeling scheme and hydrogen-bonding interactions). The metal complexes interact with the AlPO layers both electrostatically and by way of hydrogen bonds between the terminal P−O groups in the layer and N−H groups on the complexes (see Table 4). This later interaction is relatively strong as the terminal oxygens are considerably underbonded by the phosphorus (P−O bond valence ~1.4[30]). The metal complex appears to be well ordered in the interlayer space of the material, with the exception of the C(3)−C(3) bridge in one of the ethylenediamine ligands. The refinement strongly suggested the presence of static disorder for these carbons, probably as a consequence of the presence of two different conformations for this ethylenediamine in the crystal. A restraint was used on the C(3)−C(3) distance in the final refinement: as in its absence, this distance was unreasonably short.

The occurrence of materials containing Al$_3$P$_4$O$_{16}^{3-}$ macroanionic layers is quite common. Five different layer structures with this formulation have been reported to date,[7,31] and, in principle, there exists an infinite number of layer structures with this composition. Of the five reported structures, one of them is chiral. This chirality arises because of the relative orientations of the different terminal P−O groups in the layer. While layered AlPOs have been prepared in the presence of both metal complexes and organoamine templates, so far only chiral metal complexes have led

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(30) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244−247.

(31) Williams, I. D.; Gao, Q.; Chen, J.; Ngai, L.-Y.; Lin, Z.; Xu, R. *J. Chem. Soc., Chem. Commun.* **1996**, 1781−1782.

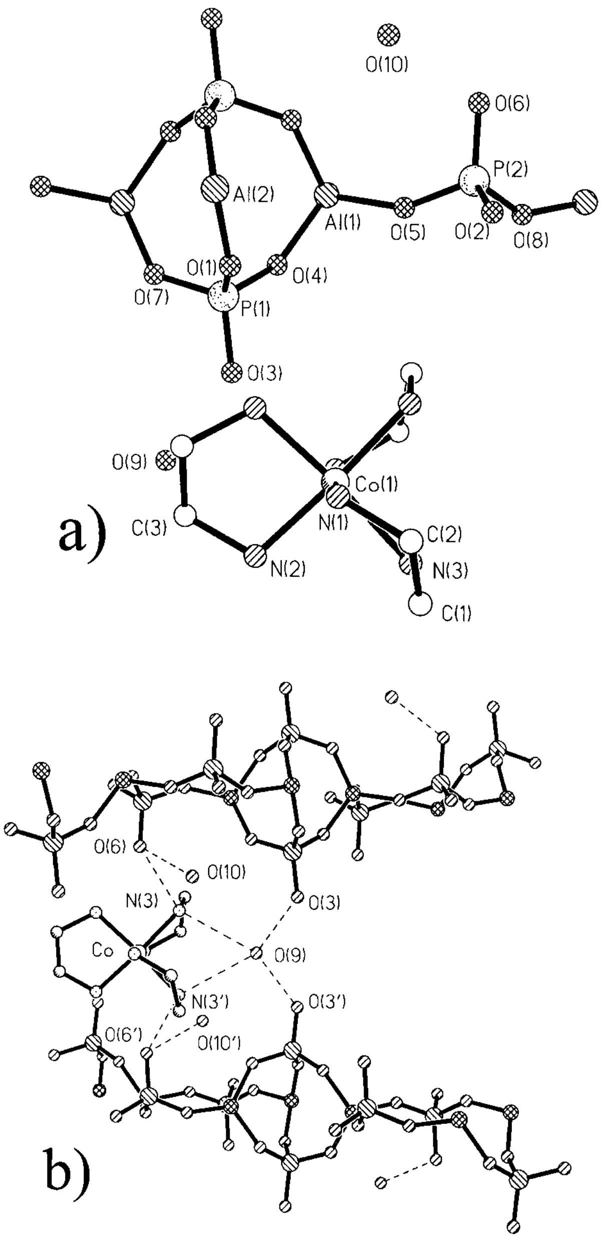

Figure 4. (a) Naming scheme and (b) hydrogen-bonding interactions involving interlamellar water for *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$.

to materials containing chiral AlPO layers. In *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$, there is only one enantiomer of the chiral AlPO macroanion in any one crystal of the material. The AlPO sheets observed in this material are different from the achiral layers found in the previously reported compound *d,l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot xH_2O$.[32,33] However, they are essentially identical with those found in *trans*-$Co(dien)_2 \cdot Al_3P_4O_{16} \cdot xH_2O$,[7] a material that also contains only one enantiomer of the chiral macroanions in any one crystal. The later compound almost certainly cannot be prepared in optically pure form; the template cation can be resolved, but it rapidly racemizes under AlPO synthesis conditions.[34] The racemization of $Co(en)_3^{3+}$ under typical AlPO synthesis conditions is considerably slower than that of *trans*-$Co(dien)_2^{3+}$, enabling, in principle, the synthesis of bulk AlPO samples that contain only one enantiomer of the metal complex.

The absolute structure determination reported in this paper demonstrates that the crystal examined contained only *d*-$Co(en)_3^{3+}$; the same enantiomer that was originally added to the synthesis gel. However, as the powder diffraction patterns of materials related as enantiomers are identical, additional evidence is required to demonstrate that the bulk sample of orange crystals contained predominantly *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ and not a significant fraction of *l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$. As optical rotation and circular dichroism experiments on powdered solids are difficult to perform and quantitatively interpret, we have chosen to rely on indirect evidence. If racemization of the $Co(en)_3^{3+}$ occurred under our synthesis conditions, the gel would contain a mixture of *d*- and *l*-$Co(en)_3^{3+}$. However, the deliberate use of racemic $Co(en)_3^{3+}$ in synthesis gels similar to the one that was used in the present study leads to the achiral material *d,l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot xH_2O$[32] rather than a mixture of *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ and *l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$. Additionally, the use of low optical purity *d*-$Co(en)_3^{3+}$ leads to a mixture of *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ and *d,l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot xH_2O$; *d,l*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot xH_2O$ is readily distinguished from *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ by powder diffraction as the latter has a smaller interlayer spacing than the former. As part of our work on the use of *d*-$Co(en)_3^{3+}$ as a template for GaPO synthesis,[35] we have examined the residual metal complex remaining in the supernatant liquid above hydrothermally synthesized GaPOs using circular dichroism spectroscopy. The presence of phosphate in the solutions containing the metal complex complicates these measurements as it is known to significantly modify the CD spectrum of $Co(en)_3^{3+}$ by coordination to the cation.[36,37] After taking into account the influence of the phosphate ions, we concluded that under synthesis conditions similar to those used for the *d*-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot 3H_2O$ in this study, $Co(en)_3^{3+}$ does not racemize significantly. However, a small amount of template decomposition and racemization is, probably, unavoidable.

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(32) Bruce, D. A. *Synthesis and Characterization of Heterogeneous Metal Oxide Catalysts on Amorphous and Molecular Sieve Supports*; Ph.D. Thesis, Georgia Institute of Technology: 1994.

(33) Morgan, K.; Gainsford, G.; Milestone, N. *J. Chem. Soc., Chem. Commun.* **1995**, 425−426.

(34) Searle, G. H.; Keene, F. R. *Inorg. Chem.* **1972**, *11*, 1006−1011.

(35) Stalder, S. M.; Wilkinson, A. P., manuscript in preparation.

(36) Smith, H. L.; Douglas, B. E. *J. Am. Chem. Soc.* **1964**, *86*, 3885−3887.

(37) Sarneski, J. E.; Urbach, F. L. *J. Am. Chem. Soc.* **1971**, *93*, 884−888.