

# The Synthesis and Characterization of an Aluminophosphate with Chiral Layers; *trans*-Co(dien)<sub>2</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 3H<sub>2</sub>O

David A. Bruce,\*<sup>1</sup> Angus P. Wilkinson,\* Mark G. White,† and J. Aaron Bertrand\*

\*School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400; and †School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

Received February 26, 1996; in revised form March 1, 1996; accepted May 31, 1996

*trans*-Co(dien)<sub>2</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 3H<sub>2</sub>O (GTex3) (dien - bis-(2-aminoethyl)amine) was prepared hydrothermally using Co(dien)<sub>2</sub>Cl<sub>3</sub> as a structure-directing agent in an aluminophosphate gel. The structure of GTex3 was determined using single-crystal X-ray diffraction. It contains chiral layers distinct from, but related to, those previously found in *d,l*-Co(en)<sub>3</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · *x*H<sub>2</sub>O. They are stacked in a helical fashion with only one enantiomer of the aluminophosphate macroanion in any one crystal. Co(C<sub>4</sub>N<sub>3</sub>H<sub>13</sub>)<sub>2</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 3H<sub>2</sub>O, *M<sub>r</sub>* = 780.1, hexagonal, *P* 6<sub>2</sub> 2 2, *a* = *b* = 8.457(3), *c* = 63.27(2) Å, *V* = 3920(2) Å<sup>3</sup>, *Z* = 6, ρ<sub>x</sub> = 1.98 gcm<sup>-3</sup>, ρ<sub>e</sub> = 1.95 gcm<sup>-3</sup>, λ(MoKα) = 0.71073 Å, μ = 10.99 cm<sup>-1</sup>, *F*(000) = 2396, *T* = 293 K, *R*<sub>1</sub> = 0.0954 for 2277 reflections *F* > 4σ(*F*). © 1996 Academic Press, Inc.

## INTRODUCTION

Chiral catalysts and sorbents play an important role in the preparation of many high-value organic compounds such as pharmaceuticals. The demand for optically pure fine chemicals is increasing rapidly, largely as a result of regulatory pressure (1). Typically, enantioselective catalytic processes are performed in homogeneous systems (2–5). However, the significant economic advantages associated with the use of heterogeneous catalysts have led to considerable interest in their development (6). Alternatives to the chiral sorbents currently employed in separations are also of great interest.

The use of chiral microporous materials is an attractive approach to both enantioselective catalytic and separations applications, as such materials may combine good shape and size selectivity with various types of catalytic activity. While it is easy to postulate chiral zeolitic frameworks, efforts to prepare them using conventional structure-directing agents, such as alkylammonium salts and alkylamines, have encountered problems (7, 8). The only chiral zeolitic material that we are aware of is a component of

zeolite β. This material crystallizes as an intergrowth of two polymorphs, only one of which is chiral (9, 10). Attempts to prepare zeolite β samples with a large excess of one enantiomer of this polymorph have met with limited success, but enantioselective catalysis has been demonstrated (7, 8).

Chiral microporous materials can, in principle, be prepared in a number of ways. Recently, there has been considerable interest in the construction of microporous solids from molecular building blocks by a self-assembly process (11). Both organic molecules (12, 13) and metal complexes (14, 15) have been used for this, and the selection of appropriate geometry building blocks could give rise to chiral structures. For many applications the greater stability of aluminosilicates and aluminophosphates (AIPOs) would be beneficial. Such materials are usually synthesized from gels in the presence of a structure-directing or template species (7, 16–18). The use of chiral amines or alkylammonium ions can in principle lead to chiral solids; however this approach has not been very successful. We are currently exploring the use of chiral metal complexes as alternative structure directing agents. Various metal complexes have been used in zeolite and AIPO syntheses (19–24), but we are not aware of any other work using chiral metal complexes as templates for chiral inorganic solids.

We have started by examining the synthesis of AIPO materials using kinetically inert cobalt (III) complexes as templates. Such species are reasonably stable under the acidic conditions typically employed in AIPO syntheses and the use of chelating ligands facilitates the introduction of chirality. This work (25) has led to the preparation and characterization of several new materials including *d,l*-Co(en)<sub>3</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · *x*H<sub>2</sub>O (GTex1) (26, 27), Co(tn)<sub>3</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 2H<sub>2</sub>O (GTex2) (28), and, the subject of this report, *trans*-Co(dien)<sub>2</sub> · Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub> · 3H<sub>2</sub>O (GTex3) [en-1,2-diaminoethane, tn- 1,3-diaminopropane, dien- bis-(2-aminoethyl)amine]. GTex2 is a chiral solid; however, it is chiral because of the presence of a single enantiomer of the complex inbetween its layers. The anionic sheets do not have an intrinsically chiral connectivity. However, GTex3

<sup>1</sup> Current address: Department of Chemical Engineering, Clemson University, Clemson, SC 29634-0909.

TABLE 1  
Crystal Data

Empirical formula	Co N <sub>6</sub> C <sub>8</sub> H <sub>32</sub> Al <sub>3</sub> P <sub>4</sub> O <sub>19</sub> <sup>a</sup>
Formula weight	780.10 <sup>a</sup>
Temperature	293 K
Wavelength	0.71073 Å (graphite monochromated MoKα)
Crystal system	Hexagonal
Space group	<i>P</i> 6 <sub>5</sub> 2 2
Unit cell dimensions	<i>a</i> = 8.457(3) Å $\alpha$ = 90° <i>b</i> = 8.457(3) Å $\beta$ = 90° <i>c</i> = 63.27(2) Å $\gamma$ = 120°
Volume	3920(2) Å <sup>3</sup>
<i>Z</i>	6
Density (calculated)	1.98 g/cm <sup>3a</sup>
Density (measured)	1.95 g/cm <sup>3</sup>
Absorption coefficient	10.99 cm <sup>-1</sup>
<i>F</i> (000)	2396 <sup>a</sup>
Crystal size	0.4 × 0.4 × 0.034 mm <sup>3</sup>
Theta range for data collection	2.78 to 30.11°.
Index ranges	0 ≤ <i>h</i> ≤ 10, 0 ≤ <i>k</i> ≤ 9, 0 ≤ <i>l</i> ≤ 89
Reflections collected	3992
Independent reflections	3844 [ <i>R</i> (int) = 0.0263]
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	3844/0/104
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.006
<i>R</i> indices [2277 reflections <i>F</i> > 4σ( <i>F</i> )]	<i>R</i> <sub>1</sub> = 0.0954, w <i>R</i> <sub>2</sub> = 0.2196 <sup>b</sup>
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.2028, w <i>R</i> <sub>2</sub> = 0.2491 <sup>b</sup>
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.118P)^2]$ $P = [2F_o^2 + \text{Max}(F_o^2, 0)]/3$
Absolute structure parameter	0.01(7)
Largest diff. peak and hole	0.803 and -0.714 e.Å <sup>-3</sup>

<sup>a</sup> Values include water hydrogen atoms that were not located in the refinement.

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$  and  $wR_2 = (\sum [w(F_o^2 - F_c^2)]^2/\sum [w(F_o^2)]^2)^{1/2}$ .

crystals contain only one enantiomer of an intrinsically chiral anion.

## EXPERIMENTAL

Samples of GTex3 were synthesized in Teflon digestion vessels from a gel with molar composition 1.0 Al<sub>2</sub>O<sub>3</sub>: 1.0 P<sub>2</sub>O<sub>5</sub>: 45 H<sub>2</sub>O: 1 TMAOH: 0.25 Co(dien)<sub>2</sub>Cl<sub>3</sub> (TMAOH-tetramethylammonium hydroxide). The Co(dien)<sub>2</sub>Cl<sub>3</sub> was prepared using an adaptation of Work's synthesis of Co(en)<sub>3</sub>Cl<sub>3</sub> (29); hydrogen peroxide rather than air was used to oxidize the cobalt. This procedure produces a mixture containing three diastereoisomers of Co(dien)<sub>2</sub><sup>3+</sup> (30–33), two of which are chiral. The aluminophosphate gel was prepared by slurrying pseudoboehmite (81.3% Al<sub>2</sub>O<sub>3</sub>, Catapal-B, Vista Chemical) in half of the required water and then adding *ortho*-phosphoric acid (61.6% P<sub>2</sub>O<sub>5</sub>, 85% sol., Fisher), that had been diluted with the remaining distilled water, while stirring vigorously. The resulting thick white gel was aged while stirring at 25°C for 2 hours. The

TMAOH (25% aq. sol., Aldrich) was then added and the mixture stirred for several minutes. The metal complex template was stirred into the gel and the aging continued for an additional 2 hours. This gel was transferred into autoclaves to a fill fraction of 80% and heated to 150°C without stirring. The autoclaves were quenched after 72 hours and their contents slurried in distilled water. The slurry was then centrifuged and the supernatant liquid decanted. This process was repeated 3–4 times until the supernatant liquid had a pH of ~7. The orange product was dried in air at 105°C for 24 hours.

The density of several representative crystals was determined by the flotation method. A crystal of GTex3 that was of acceptable quality under stereoscopic and polarizing microscopes was selected for X-ray diffraction analysis. Data collection was performed on a Syntex P2<sub>1</sub> four-circle diffractometer using omega scans with a width of 1° and a scan rate of between 3.91 and 29.3°/min. The unit cell constants were determined from fifteen centered reflections within the range 9.7–23.3° 2θ. A total of 3992 reflections were collected, of which 3844 were independent (~50% of these were Friedel equivalents) and 2277 had

TABLE 2  
Atomic Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Displacement Parameters (Å<sup>2</sup> × 10<sup>3</sup>) for *trans*-Co(dien)<sub>2</sub>·Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>·3H<sub>2</sub>O

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Co	2385(1)	7615(1)	833	14(1)
C(1)	4363(14)	11308(14)	726(1)	23(2)
C(2)	-196(14)	4333(14)	657(1)	24(2)
C(3)	3075(13)	10456(13)	545(1)	23(2)
C(4)	1585(14)	4458(15)	596(2)	29(2)
N(1)	118(10)	5276(10)	860(1)	17(1)
N(2)	2991(10)	6375(10)	607(1)	18(2)
N(3)	1521(11)	8683(11)	618(1)	19(2)
P(1)	110(3)	2674(3)	1367(1)	11(1)
P(2)	-3301(3)	5898(3)	1683(1)	12(1)
Al(1)	0	-226(4)	1667	11(1)
Al(2)	-2814(4)	2599(4)	1645(1)	13(1)
O(1)	-1864(9)	2060(9)	1435(1)	20(1)
O(2)	608(9)	1282(8)	1455(1)	17(1)
O(3)	341(9)	2825(9)	1132(1)	19(1)
O(4)	1333(9)	4536(9)	1473(1)	17(1)
O(5)	1045(10)	6801(10)	249(1)	29(2)
O(6)	-3094(9)	4421(9)	1566(1)	19(1)
O(7)	-1829(8)	7753(9)	1591(1)	17(1)
O(8)	-5133(10)	5619(9)	1608(1)	23(2)
O(9) <sup>b</sup>	6341(15)	5669(15)	503(2)	60(3)
O(10) <sup>b</sup>	-313(7)	10313(7)	833	29(2)

Note. *U*<sub>eq</sub> is defined as one third of the trace of the orthogonalized *U*<sub>ij</sub> tensor.

<sup>a</sup> All atoms other than Co, Al, and P were refined isotropically and their quoted temperature factors are *U*<sub>iso</sub>.

<sup>b</sup> Oxygens of water molecules in the interlayer space.

TABLE 3  
Selected Bond Lengths  
[Å] for *trans*-Co(dien)<sub>2</sub>·  
Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>·3H<sub>2</sub>O

2 × Co–N(1)	1.956(8)
2 × Co–N(3)	1.968(7)
2 × Co–N(2)	1.987(7)
C(1)–N(1)	1.476(12)
C(1)–C(3)	1.492(12)
C(2)–N(1)	1.463(11)
C(2)–C(4)	1.507(14)
C(3)–N(3)	1.488(12)
C(4)–N(2)	1.456(13)
P(1)–O(3)	1.500(6)
P(1)–O(2)	1.538(7)
P(1)–O(4)	1.538(7)
P(1)–O(1)	1.541(7)
P(2)–O(5)	1.481(7)
P(2)–O(8)	1.522(7)
P(2)–O(6)	1.537(7)
P(2)–O(7)	1.549(7)
Al(1)–O(7)	1.703(7)
Al(1)–O(2)	1.742(6)
Al(2)–O(1)	1.728(6)
Al(2)–O(8)	1.731(7)
Al(2)–O(4)	1.745(6)
Al(2)–O(6)	1.746(7)

$F > 4\sigma(F)$ . No absorption correction was applied. The structure was solved using direct methods (SHELXS-86) and difference Fourier syntheses. All of the hydrogen atoms were geometrically placed. Full-matrix least-squares structure refinement on  $F_o^2$  was carried out using SHELXL-93. Anisotropic temperature factors were used for Co, Al, and P. Isotropic temperature factors were used for the C, N, and O atoms as a limited amount of data was available from the weakly diffracting crystal. The hydrogen atom temperature factors were constrained to be  $1.2\times$  that of the atom they rode on. Further details of the data collection, data analysis, and relevant crystal data are summarized in Table 1. The coordinates and isotropic temperature factors resulting from the final refinement are given in Table 2, and selected bond lengths are shown in Table 3. Observed and calculated structure factors, anisotropic temperature factors, hydrogen atom coordinates and temperature factors, and a full listing of distances and angles are available as supplementary material.<sup>2</sup>

<sup>2</sup> See NAPS document no. 05325 for 17 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance \$4.00 for microfiche copy or for photocopy, \$7.75 up to 20 pages plus \$0.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of \$15. Foreign orders add \$4.50 for postage and handling, for the first 20 pages, and \$1.00 for additional 10 pages of material, \$1.50 for postage of any microfiche orders.

Analyses for carbon, nitrogen, and hydrogen were performed by Atlantic Microlab, Inc. in Norcross, Georgia. Analyses for metals were performed by Applied Technical Services, Inc. in Marietta, Georgia. The powder diffraction pattern of the product was measured using a Phillips PW 1800 X-ray diffractometer.

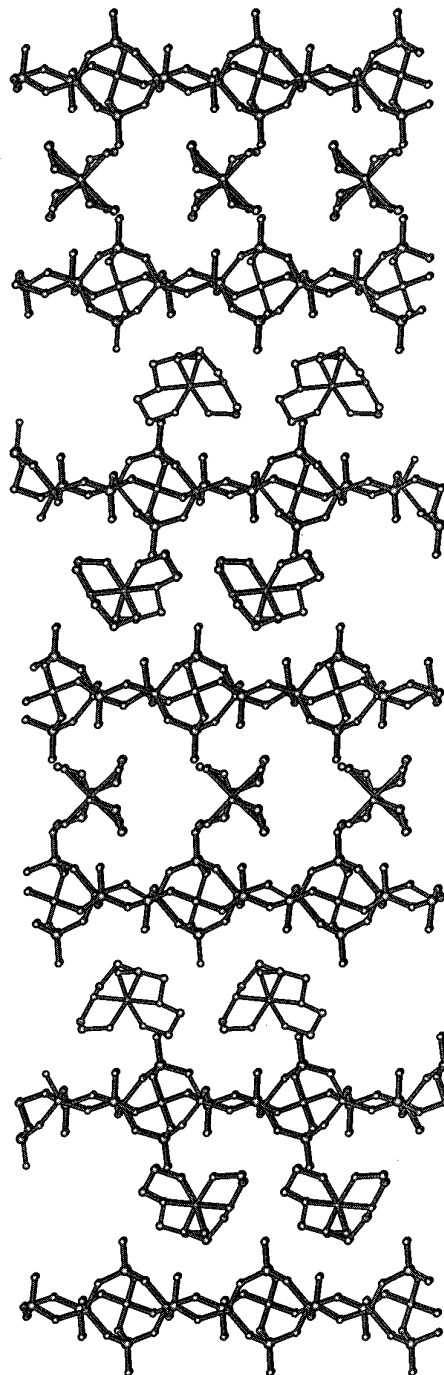
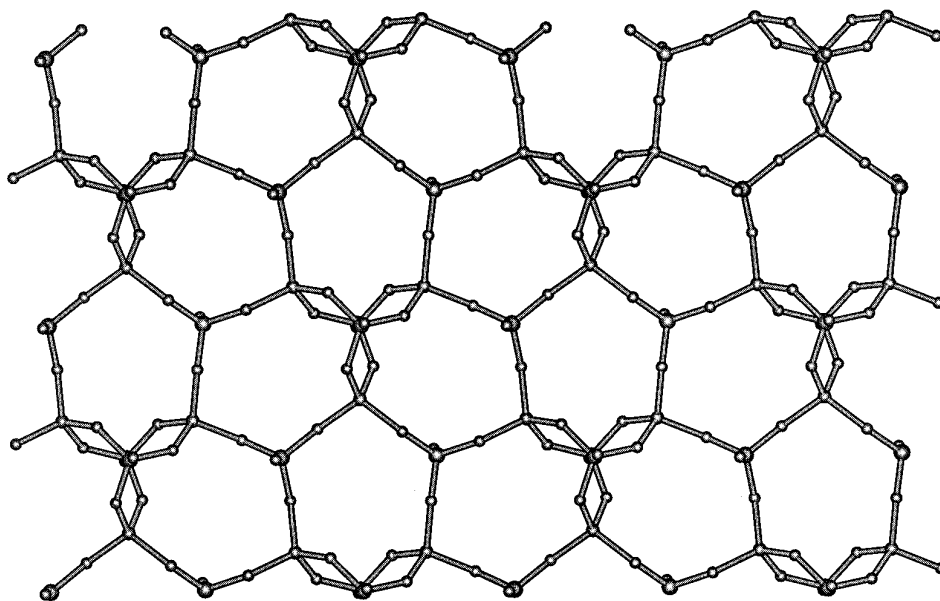
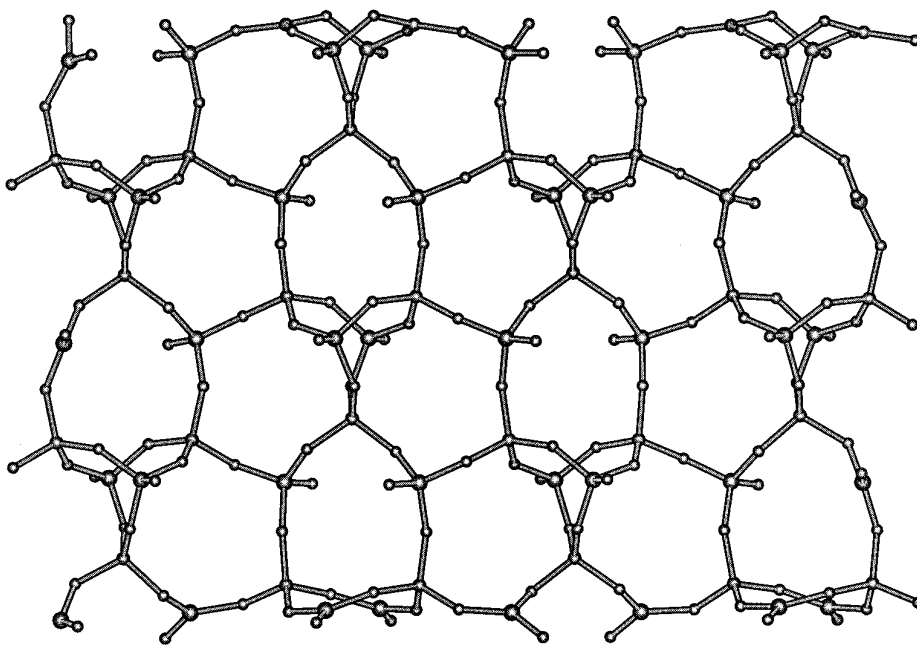


FIG. 1. A view of *trans*-Co(dien)<sub>2</sub>·Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>·3H<sub>2</sub>O down the crystallographic *b* axis showing the layer stacking sequence. Interlayer water molecules and all hydrogen positions have been omitted for clarity.



a



b

FIG. 2. Plan views of the  $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$  layers found in (a)  $\text{trans-Co}(\text{dien})_2 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$  (GTex3) and (b)  $d,l\text{-Co}(\text{en})_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$  (GTex1). The view of GTex1 is a projection onto the crystallographic  $a$ - $c$  plane. The drawing of GTex1 was produced from the refinement results of Bruce *et al.* (26) in space group  $Pnna$ ,  $a = 8.561(4)$ ,  $b = 21.323(9)$ ,  $c = 13.813(5)$  Å.

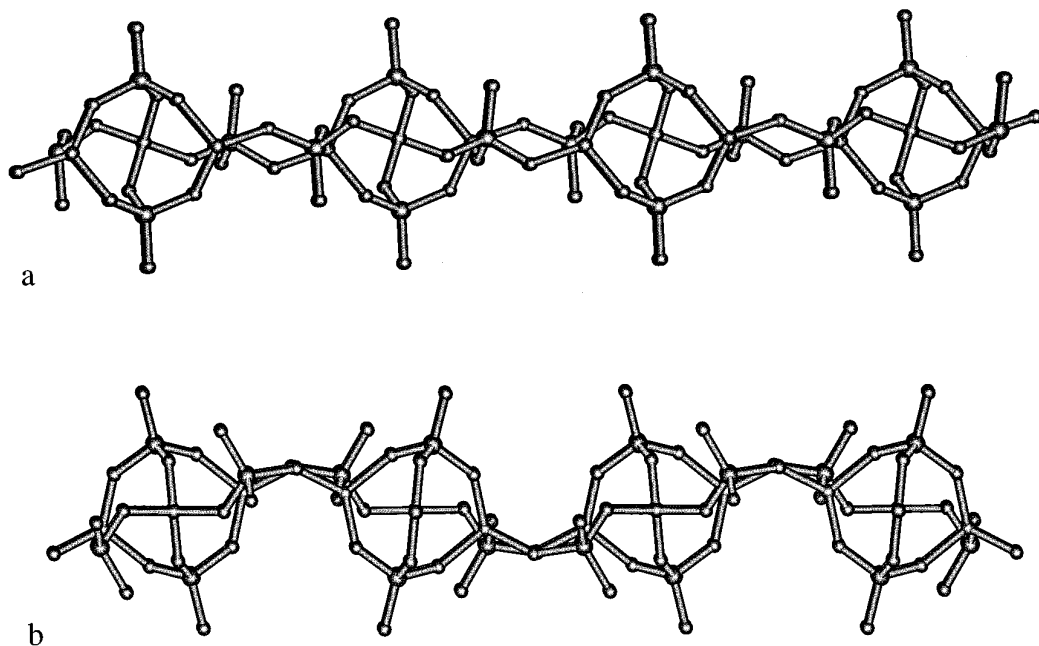


FIG. 3. Side views of the  $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$  layers found in (a)  $\text{trans-Co}(\text{dien})_2 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot 3\text{H}_2\text{O}$  (GTex3) and (b)  $d,l\text{-Co}(\text{en})_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$  (GTex1). Both drawings are projections down the crystallographic  $a$  axes of the materials. The drawing of GTex1 was produced from the refinement results of Bruce *et al.* (26) in space group  $Pnna$ ,  $a = 8.561(4)$ ,  $b = 21.323(9)$ ,  $c = 13.813(5)\text{\AA}$ .

## DISCUSSION

The crystal examined by X-ray diffraction was found to have a unique architecture consisting of chiral aluminophosphate (AIPO) layers stacked (see Fig. 1) in a helical fashion with a single enantiomer of  $\text{trans-Co}(\text{dien})_2^{3+}$  present between the layers. The elemental analysis for the bulk sample was in reasonable agreement with that expected on the basis of the crystal structure for GTex3 [observed and expected composition, 12.34 (12.61)% C, 10.75 (11.03)% N, 7.5 (7.73)% Co, 11.2 (10.62)% Al, 16.6 (16.26)% P] and the powder diffraction pattern calculated from the single-crystal structure was also in good agreement with the measured pattern after taking preferred orientation into account. These observations suggest that the other isomers of the metal complex that were present in the synthesis gel were either incorporated into solid products with crystal structures closely related to that of GTex3 (other materials with  $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$  macroanionic layers) or they remained in solution. We are currently trying to prepare pure samples of each of the  $\text{Co}(\text{dien})_2^{3+}$  diastereoisomers so that their fate during AIPO synthesis can be determined. The preparation of a chiral AIPO using the, chiral,  $u\text{-cis-Co}(\text{dien})_2^{3+}$  complex as a structure directing agent would be more interesting than material that we report here as the  $u\text{-cis}$ -diastereomer can be resolved (31–33) and it should be stable to racemization under AIPO synthesis conditions. Unfortunately, while  $\text{trans-Co}(\text{dien})_2^{3+}$  can be

resolved (31–33) it is susceptible to racemization (34) under AIPO synthesis conditions, effectively precluding the synthesis of a bulk GTex3 sample in optically pure form.

The inclusion of a single isomer of the complex into a crystal of GTex3 suggests a very high degree of specificity in the crystal growth process. This specificity combined with the chirality of the layers demonstrates that chiral metal complexes have great potential for the template synthesis of chiral inorganic solids. The layers in GTex3 consist of  $\text{PO}_4$  and  $\text{AlO}_4$  tetrahedra linked in a strictly alternating pattern. Each  $\text{PO}_4$  tetrahedron has three bridging (average bond length 1.538  $\text{\AA}$ ) and one terminal phosphoryl oxygen (average bond length 1.491  $\text{\AA}$ ) while all of the oxygens connected to Al are bridging (average bond length 1.730  $\text{\AA}$ ).  $\text{Al}_3\text{P}_4\text{O}_{16}^{3-}$  macroanions have been reported before, and even materials with the same connectivity have been observed, for example  $d,l\text{-Co}(\text{en})_3 \cdot \text{Al}_3\text{P}_4\text{O}_{16} \cdot x\text{H}_2\text{O}$  (GTex1), but the orientation of the terminal P–O bonds relative to the plane of the layer makes the structure of GTex3 unique. The layer structures of GTex1 and GTex3 are compared in Figs. 2 and 3. As far as we are aware, GTex3 is the first material to be characterized that contains a single enantiomer of a chiral sheet anion in any one crystal.

Several distinct AIPO layer structures are known (19, 26, 28, 35–38) and apparently subtle changes in the structure-directing agent can lead to different layer types. It is not clear which of the interactions between the structure-di-

recting agent and the layers are responsible for these differences. However, all of the layered AIPOs that we have prepared using metal complexes as templates display hydrogen bonds between the complex and terminal P–O groups of the layers. In GTex3, there are short contacts between the five distinct N–H hydrogens and either phosphoryl oxygens or water in the interlamella space (contacts between 1.87 and 2.47 Å). The shortest contacts involve hydrogens on two of the three crystallographically distinct ligand nitrogens and the two types of phosphoryl oxygens in the structure (both around 1.88 Å).

The development of new microporous materials suitable for use in enantioselective catalytic and separations applications could have a major impact on the production of high-value chiral products. We believe that the synthesis of GTex3 demonstrates that the use of chiral transition metal complexes as structure-directing agents offers a valuable new approach to preparing such materials.

### ACKNOWLEDGMENTS

This work was partially funded by Texaco and the Georgia Institute of Technology. Additionally, acknowledgment is made to the Donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are grateful to Dr. D. Vanderveer for assistance with the X-ray data collection.

### REFERENCES

1. S. C. Stinson, *Chem. Eng. News* (October 9th), 44 (1995).
2. W. A. Nugent, T. V. RajanBabu, and M. J. Burk, *Science* **259**, 479 (1993).
3. G. W. Parshall and W. A. Nugent, *CHEMTECH* (March), 184 (1988).
4. J. M. Brown, in "Insights into Speciality Inorganic Chemicals," (D. Thompson, Ed.), p. 123. Royal Chem. Soc., London, 1995
5. I. Ojima, "Catalytic Asymmetric Synthesis." VCH, Weinheim/New York, 1993.
6. K. T. Wan and M. E. Davis, *Nature* **370**, 449 (1994).
7. M. E. Davis and R. F. Lobo, *Chem. Mater.* **4**, 756 (1992).
8. M. E. Davis, *Acc. Chem. Res.* **26**, 111 (1993).
9. J. M. Newsam, M. M. J. Treacy, W. T. Koetsier, and C. B. de Gruyter, *Proc. R. Soc. London A* **420**, 375 (1988).
10. M. M. J. Treacy and J. M. Newsam, *Nature* **332**, 249 (1988).
11. M. D. Ward, *Nature* **374**, 764 (1995).
12. J. S. Moore, *Nature* **374**, 495 (1995).
13. D. Venkataraman, S. Lee, J. Zhang, and J. S. Moore, *Nature* **371**, 591 (1994).
14. B. F. Abrahams, B. F. Hoskins, D. M. Michail, and R. Robson, *Nature* **369**, 727 (1994).
15. G. Gardner, D. Venkataraman, J. S. Moore, and S. Lee, *Nature* **374**, 792 (1995).
16. J.-P. Gilson, in "Zeolite Microporous Solids: Synthesis, Structure, and Reactivity" (E. G. Derouane, F. Lemos, C. Naccache, and F. R. Ribeiro, Eds.), p. 19. Kluwer, Dordrecht, 1992.
17. J. L. Guth, P. Caultet, A. Seive, J. Patarin, and F. Delprato, in "Guidelines for Mastering the Properties of Molecular Sieves," (D. Barthomeuf, Ed.), p. 69. Plenum, New York, 1990.
18. B. M. Lok, T. R. Cannan, and C. A. Messina, *Zeolites* **3**, 282 (1983).
19. D. A. Bruce, J. A. Bertrand, M. L. Occelli, M. G. White, and F. Mertens, in "Catalysis of Organic Reactions" (M. G. Scaros and M. L. Prunier, Eds.), p. 545. Dekker, New York, 1995.
20. K. J. Balkus and S. Kowalak, U.S. Patent 5 167 942 (1992).
21. E. W. Valyocik, U.S. Patent 4 568 654 (1986).
22. K. J. Balkus, A. G. Gavriellov, N. Sandler, and T. Jacob, "North American Catalysis Society, Snowbird, Utah, Meeting Abstracts," T115, 1995.
23. K. J. Balkus and S. Shepelev, *Prepr. Pap. Am. Chem. Soc. Div. Petr.* **38**, 512 (1993).
24. K. J. Balkus, S. Kowalak, K.T. Ly, and D. C. Hargis, *Stud. Surf. Sci. Catal.* **69**, 93 (1991).
25. D. A. Bruce, "Synthesis and Characterization of Heterogeneous Metal Oxide Catalysts on Amorphous and Molecular Sieve Supports," Ph.D. thesis, Georgia Institute of Technology, 1994.
26. D. A. Bruce, A. P. Wilkinson, J. A. Bertrand, M. G. White, and J. C. Edwards, submitted for publication.
27. K. Morgan, G. Gainsford, and N. Milestone, *J. Chem. Soc. Chem. Commun.*, 425 (1995).
28. D. A. Bruce, A. P. Wilkinson, M. G. White, and J. A. Bertrand, *J. Chem. Soc. Chem. Commun.*, 2059 (1995).
29. J. B. Work, *Inorg. Synth.* **2**, 221 (1946).
30. F. R. Keene and G. H. Searle, *Inorg. Chem.* **13**, 2173 (1974).
31. F. R. Keene and G. H. Searle, *Inorg. Chem.* **11**, 148 (1972).
32. F. R. Keene, G. H. Searle, Y. Yoshikawa, A. Imai, and K. Yamasaki, *J. Chem. Soc. Chem. Commun.*, 784 (1970).
33. F. R. Keene, G. H. Searle, and S. F. Mason, *J. Chem. Soc. Chem. Commun.*, 893 (1970).
34. G. H. Searle and F. R. Keene, *Inorg. Chem.* **11**, 1006 (1972).
35. A. M. Chippindale, S. Natarajan, J. M. Thomas, and R. H. Jones, *J. Solid State Chem.* **111**, 18 (1994).
36. R. H. Jones, J. M. Thomas, R. Xu, Q. Huo, A. K. Cheetham, and A. V. Powell, *J. Chem. Soc. Chem. Commun.*, 1266 (1991).
37. R. H. Jones, A. M. Chippindale, S. Natarajan, and J. M. Thomas, *J. Chem. Soc. Chem. Commun.*, 565 (1994).
38. J. M. Thomas, R. H. Jones, R. Xu, J. Chen, A. M. Chippindale, S. Natarajan, and A. K. Cheetham, *J. Chem. Soc. Chem. Commun.*, 929 (1992).