The Synthesis and Structure of a Chiral Layered Aluminophosphate containing the Template $Co(tn)_3^{3+}$

David A. Bruce,[a] Angus P. Wilkinson,*[a] Mark G. White[b] and J. Aaron Bertrand[a]

[a] *School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA*
[b] *School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0100, USA*

A chiral layered aluminophosphate $Co(tn)_3 \cdot Al_3P_4O_{16} \cdot 2H_2O$ containing only one enantiomer of the metal complex is synthesized using racemic $Co(tn)_3Cl_3$ as the templating agent and its structure determined using single-crystal X-ray diffraction.

The rational design and synthesis of crystalline microporous materials is still in its infancy despite the vast amount of work that has been carried out on the preparation of new materials. In the search for new frameworks, many different types of templates or structure directing agents have been tried in the synthesis of zeolites, aluminophosphates (AlPOs) and their relatives. Hydrated alkali/alkaline earth metal cations, organoamines or ammonium ions are typically used,[1–4] however, little attention has been paid to the possibility of using transition metal coordination complexes in this role.[5–7] Metal complexes can be made with a wide variety of shapes, charges, hydrogen bonding sites and, perhaps most importantly, with chirality. We are currently systematically investigating the use of chiral coordination complexes as templates for the synthesis of chiral inorganic solids.

There is considerable interest in the synthesis of chiral microporous materials for use as stationary phases in separations or as enantioselective heterogeneous catalysts. However, the introduction of chirality into a porous framework structure using traditional template molecules, such as chiral amines and ammonium ions, has proved to be particularly difficult. Zeolite β is the only example of any success in this area[8,9] The recent independent reports of syntheses for a layered aluminophosphate, DL-$Co(en)_3 \cdot Al_3P_4O_{16} \cdot nH_2O$, by Morgan *et al.*[10] and Bruce *et al.*[11] suggest that it should be possible to synthesize chiral aluminophosphates using chiral metal complexes as templates. The DL-$Co(en)_3^{3+}$ templated material contains a racemic mix of chiral AlPO layers and metal complexes. In this paper, we report the synthesis and crystal structure of a new chiral layered aluminophosphate named GTex-2, $Co(tn)_3 \cdot Al_3P_4O_{16} \cdot 2H_2O$ (tn = 1,3 diaminopropane). This material is only the second well characterized example of an aluminophosphate synthesized using a transition metal complex as a template.

Samples of GTex-2 were synthesized in Teflon/PFA digestion vessels from a gel with molar composition 1.0 Al_2O_3 : 1.0 P_2O_5 : 45 H_2O : 1 NMe_4OH : 0.25 $Co(tn)_3^{3+}$. The gel was prepared by slurrying pseudoboehmite (81.32% Al_2O_3, Catapal-B, Vista Chemical) in half of the required water and then adding orthophosphoric acid (61.56% P_2O_5, 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 h. The NMe_4OH (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 ageing continued for a further 2 h. This gel was transferred into autoclaves to a fill fraction of 80% and heated to 100–110 °C without stirring. The autoclaves were quenched after 96 h and their contents slurried in distilled water. The slurry was then centrifuged and the supernatant liquid decanted. This procedure was repeated 3–4 times until the supernatant liquid had a pH of *ca.* ~ 7. The product was dried in air at 105 °C for 24 h. A 74% yield based on cobalt was obtained.

The structure of a single crystal selected from the product was determined using X-ray diffraction techniques.[†] A powder X-ray diffraction pattern was calculated from the single crystal structure using the BIOSYM characterize software[12] and compared to the experimentally determined X-ray powder diffraction pattern.[‡] There was good agreement between the observed and calculated powder patterns indicating that the as synthesized sample was essentially pure GTex-2. Product purity was confirmed by elemental analysis.[§]

GTex-2 [$Co(tn)_3 \cdot Al_3P_4O_{16} \cdot 2H_2O$] consists of $Al_3P_4O_{16}^{3-}$ macroanionic sheets stacked in an AAAA fashion along the crystallographic *c* axis with the metal complexes acting as pillars between the layers (see Fig. 1). The layers are made up of alternating PO_4 and AlO_4 tetrahedra connected to produce a structure with four four-membered rings for every eight-membered ring (see Fig. 2). This layer connectivity is one of three previously reported $Al_3P_4O_{16}^{3-}$ layer types[11] and has been observed in aluminophosphates synthesized using either (*i*) propylamine, (*ii*) ethylenediamine/ethylene glycol, or (*iii*) 1,5-diaminopentane as templates.[13–15] Each of the PO_4 groups in the structure has three bridging and one terminal oxygen with average bond lengths of 1.530 and 1.486 Å, respectively. The latter bond length suggests that the terminal PO unit is best regarded as a phosphoryl group. The average Al–O bond length of 1.722 Å is typical of that found in AlPOs. The anisotropic temperature factors and bond lengths indicate the presence of some disorder in the ligands around the metal complex.

Remarkably, each single crystal of our material contains only one enantiomer of the metal complex template even though a racemic mix was used in the synthesis. The crystallization of racemic mixes to give a conglomerate (a mixture of crystals each containing a single enantiomer) is well known[16] and generally understood, however, it is not clear to us why GTex-2

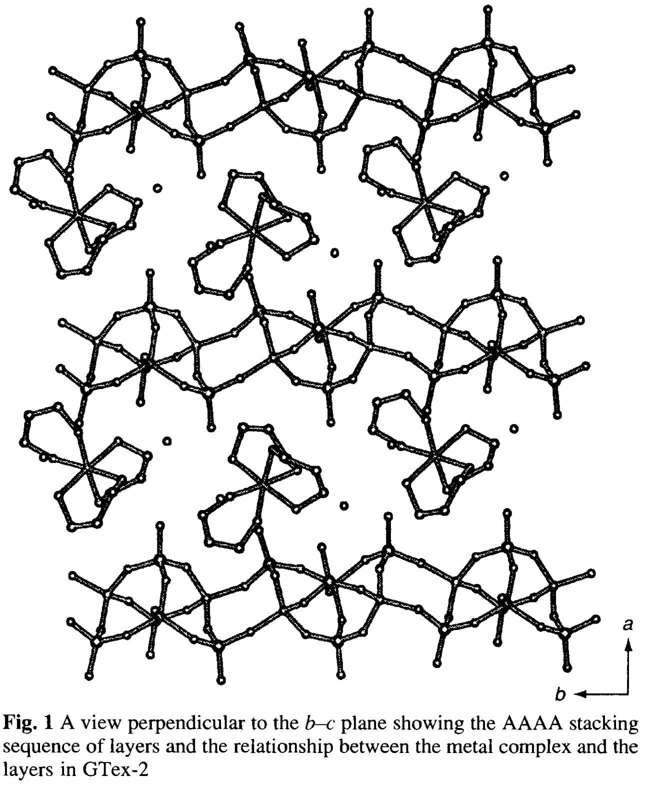

Fig. 1 A view perpendicular to the *b–c* plane showing the AAAA stacking sequence of layers and the relationship between the metal complex and the layers in GTex-2

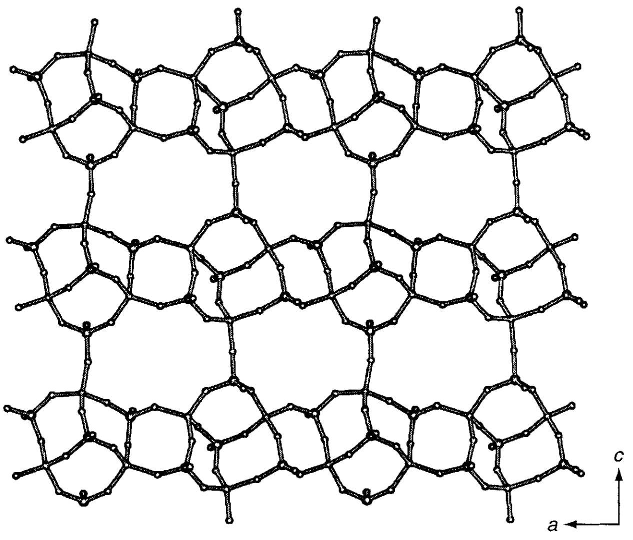

Fig. 2 A plan view of an $Al_3P_4O_{16}^{3-}$ layer in GTex-2

crystallizes in this fashion. The metal complexes are not in close proximity to each other, suggesting that they do not interact with one another directly, but they are hydrogen bonded to the aluminophosphate sheets. The AlPO layers do not have an intrinsically chiral connectivity, but their shape is modified by the presence of the metal complexes. It seems possible that an AlPO sheet mediated interaction between the complexes is responsible for the inclusion of only one enantiomer in any particular crystal.

The synthesis of chiral aluminophosphates using transition metal complexes as templates is almost unexplored and offers the possibility of preparing materials that are useful for chiral separations and catalysis. We are currently investigating the use of our aluminophosphate materials as both oxidation catalysts and stationary phases in the chromatographic separation of pharmaceuticals.

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Footnotes

† A representative crystal of GTex-2 that was of acceptable quality under stereoscopic and polarizing microscopes was selected for X-ray diffraction analysis. *Crystal data* for $Co(tn)_3 \cdot Al_3P_4O_{16} \cdot 2H_2O$; monoclinic, space group $P2_1$, $a = 8.862(4)$, $b = 14.706(3)$, $c = 11.402(5)$ Å, $\beta = 108.87(4)°$; $V = 1406.10$ Å^3; $Z = 2$, $M = 778.17$, λ(Mo-Kα) $= 0.711$ Å, $T = 296$ K, $D_c = 1.838$ g cm^3, $D_m = 1.858$ g cm^3 (measured by the flotation method using chloromethane and tetrabromoethane solvents). Data collection was performed on a Syntex $P2_1$ four-circle diffractometer using ω scans with a width of 1°, a scan rate of between 3.91 and 29.3° min^{-1} and a 2θ range of 4.3–60.0°. The unit-cell constants were determined from fifteen centred reflections within the 2θ range 10.9–22.6°. A total of 4257 reflections were collected, of which 4257 were unique and 3016 had $I > 2.5\sigma(I)$. The structure was solved using direct methods (SHELXS86) and difference Fourier syntheses. All of the hydrogen positions were located from difference Fourier maps, Full-matrix least-squares structure refinement was carried out using the NRCVAX package of programs. Anisotropic temperature factors were used for all non-hydrogen atoms. The final residuals were $R = 0.054$ and $R_w = 0.060$, respectively. The final difference Fourier map had a minimum and maximum of -0.70 and 0.72 e Å^{-3}, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Powder X-ray diffraction patterns were obtained using a Philips PW 1800 X-ray diffractometer, equipped with variable divergence slits and a graphite-monochromated Cu-Kα ($\lambda = 1.5418$ Å) radiation source.

§ Satisfactory elemental analyses were obtained.

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