A Novel Layered Aluminium Phosphate [$Co(en)_3Al_3P_4O_{16}\cdot 3H_2O$] Assembled about a Chiral Metal Complex

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The synthesis and structure of a novel layered aluminium phosphate formed about a chiral metal complex is reported.

The use of structure-directing organic molecules is a well-known strategy for synthesising materials such as zeolites and microporous aluminium phosphates.[1] Although the pores formed must be large enough to accommodate the organic molecule, it is not certain what other features the organic molecule should have to produce a particular structure-directing effect. We have recently become interested in the possibility of using metal complexes as structure-directing species for the formation of porous solids, since metal complexes could have a number of unique structure-directing features. We report here the synthesis and characterisation by X-ray crystallography of a novel layered aluminium phosphate, formed about a cobalt(III) trisethylenediamine [$Co(en)_3{}^{3+}$] complex, in which the chirality of the complex has been imprinted onto the aluminium phosphate layers. The interactions occurring between the cobalt complex and the aluminium phosphate layers suggest that the structure-directing effects of the cobalt complex may result from hydrogen bonding interactions.

In metal complexes, the ligands are organised about the metal ion in a particular spatial configuration. This provides metal complexes with several unique features. They can adopt conformations that are difficult to obtain with organic molecules, and their rigidity and flexibility are also different. In addition, the wide range of oxidation states that metal ions can achieve give complexes properties not found in organic molecules. If any of these features are important in influencing the structure-directing properties of a molecular species then microporous solids formed from metal complexes could have unusual structural architectures.

If metal complexes are to be used as templates in the synthesis of microporous zeolites and aluminium phosphates then these complexes must be stable under the reaction conditions. This excludes the use of a wide variety of metal complexes where the ligand can exchange readily. If ligand exchange does occur then insoluble metal silicates and phosphates will form under normal reaction conditions.

A number of metal complexes containing macrocyclic ligands are stable to ligand exchange. Balkus *et al.* used this property to assemble zeolites with the faujasite structure about metal complexes.[2] However, not all possible sites in the structure were occupied by the metal complex. Some metal complexes, where the metal is in a specific oxidation state, are inert and ligand exchange will be inhibited. Cobalt in the +3 oxidation state is a well-known example, and Co^{III} complexes could be useful as structure-directing species in a zeolite or $AlPO_4$ synthesis.

The layered aluminium phosphate reported here was synthesised hydrothermally at 150 °C over 1–2 days, using an aqueous mixture of $Co(en)_3{}^{3+}$ as the hydroxide, aluminium oxyhydroxide (pseudoboehmite, 0.5 g) and 85% phosphoric acid (1.9 g). The aqueous $Co(en)_3{}^{3+}$ hydroxide was isolated by filtering off the silver salts formed by the reaction of $Co(en)_3Cl_3$ (1.5 g) with Ag_2O (2 g) in water (12 ml) at 90 °C for 15 min.

The major synthetic product formed was orange needles, characterised by single crystal X-ray crystallography.† Small amounts of berlinite and bright blue concretions were also produced during the reaction. The latter component was identified by X-ray powder diffraction as being isomorphic to nickel hydrogen phosphate hydrate.[3] It is therefore probably cobalt phosphate, formed by decomposition of the metal complex. Heating of the orange crystals at 400 °C for 2 h to remove the ethylenediamine produced a deep blue compound. Although visual examination showed that the crystal morphology was retained, X-ray powder diffraction spectroscopy indicated that the compound was amorphous.

Several different layered aluminium phosphates have been characterised by single crystal X-ray diffraction.[4–7] The layers all have an identical composition ($Al_3P_4O_{16}{}^{3-}$), but a wide range of diverse structural topologies. Each aluminium is tetrahedrally coordinated by four oxygens which are bonded to phosphorous. The phosphorous is also coordinated to four other oxygens in a tetrahedral configuration, but only three of the oxygens are bonded to an aluminium. The fourth oxygen has no other bonding and is formally P=O. The most notable differences between the various layered structures occur in the network of rings formed by the aluminium and phosphorous oxygen tetrahedra. Reported structures to date include mixtures of four- and six-,[4] four- and eight-,[5] four- and twelve-,[6] and solely eight-membered rings.[7]

The structure reported here consists of three distinct four-membered rings and six distinct six-membered rings [Fig. 1(*a*)] formed into a unique macroanionic sheet, intercalated with a layer containing $Co(en)_3{}^{3+}$ cations and water molecules. The four-membered rings have a particularly unusual configuration. They form a tricyclic structural motif which is similar to a [3.3.3]propellane [Fig. 1(*b*)]. This motif is chiral as it has a distinct twist in one direction. Each of the chiral forms of this motif is repeated along one direction in the aluminium phosphate layers. Between these motifs are two similar asymmetric six-membered rings below which sits the $Co(en)_3{}^{3+}$ complex in the interlayer space [Fig. 1(*c*)]. The layer below the interlayer space is related to that above by a twofold screw axis. Thus above and below the $Co(en)_3{}^{3+}$ complex are the same two six-membered rings facing in opposite directions. The $Co(en)_3{}^{3+}$ complex therefore sits inside a chiral pocket. This chiral pocket may simply have formed as a distortion of the lattice to accommodate the chiral complex. This, however, appears unlikely as the propellane motifs have to remain chiral because of steric factors even in the absence of the complex. Also, none of the other types of layer topologies reported to date, all of which have been synthesised using non-chiral templates, show similar chiral pockets. We think that the layer topology of the AlPO reported here will only form in the presence of a chiral template.

Overall, the crystal structure of this layered aluminium phosphate is not chiral since there are equal numbers of chiral pockets of opposite handedness, containing the other enantiomer of the complex. Although most of the zeolites and microporous $AlPO_4$ contain asymmetric units, none of these except zeolite-β have chiral pockets and none to date have been synthesised in a pure chiral form. Zeolite-β is a highly intergrown hybrid of two distinct structures, the so-called polymorphs A and B. The A polymorph is chiral,[8,9] and can exist in either a left-hand or right-hand form. Davis and Lobo[10] suggest that enantiomerically enriched zeolites and microporous solids may only be synthesised with a chiral template. They base this conclusion, in part, on the preparation of a zeolite-β phase which had some enantiomeric selectivity as a catalysis.[11] They therefore assumed that the zeolite-β phase was enriched in one of the enantiomeric forms of the A polymorph.

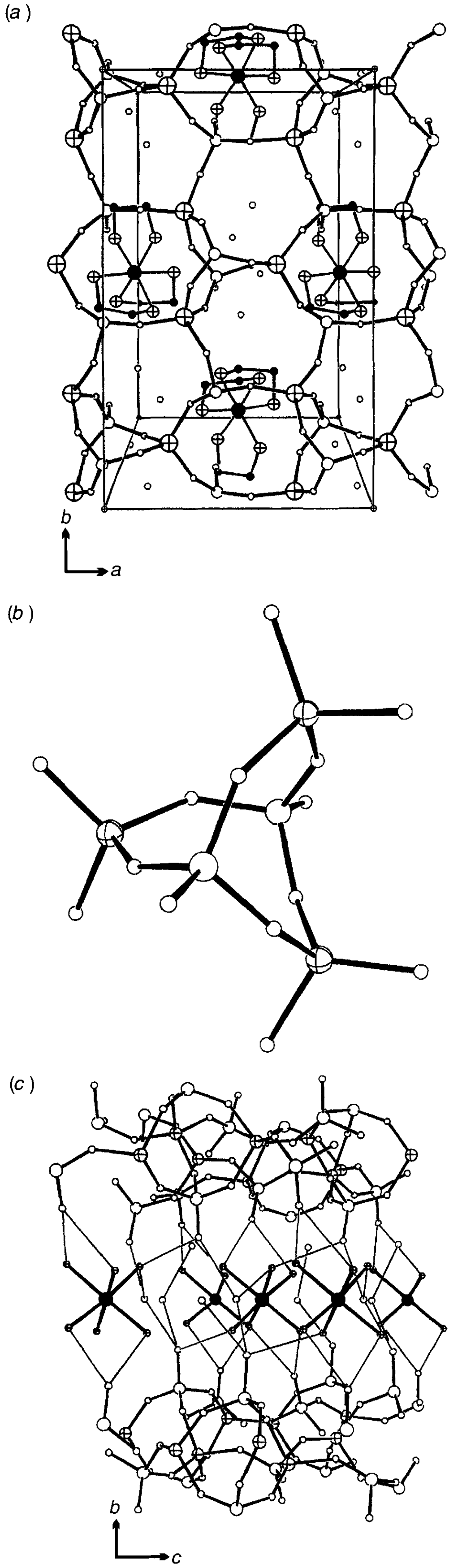

Fig. 1 Structure of the layered $AlPO_4$ (⊕ Al, ⊕ N, ● Co, ● C, ○ P, ○ O). (*a*) View normal to the plane of the layer; (*b*) propellane motif; (*c*) a view edge-on to the plane of the layer (thin lines indicate the hydrogen bonding network).

The structure reported here also provides evidence that chiral molecules can induce chiral features in a lattice, and that suitable chiral templates could form chiral zeolites and aluminium phosphates.

There is extensive hydrogen bonding between the amine groups of the cobalt complex, the interlayer water and the adjacent P=O groups [Fig. 1(*c*)]. Typical (N)–H···O=(P) distances are 1.85–2.02 Å. The hydrogen bonding appears to be the dominant interaction binding the layers together. Minimization of the electrostatic energy through hydrogen bonding interactions is probably important in determining the layer topology. Thus there is probably a direct relationship between the arrangement of the hydrogen bonding groups on the metal complex and the layer topology. It has recently been found[12] that the formation of mesoporous materials by assembly in acid media about surfactant-based structures is similarly mediated by hydrogen bonding from halides to protonated silanols. The results obtained here suggest that in the layered aluminium phosphates, the growth of the layers may primarily be determined by hydrogen bonding interactions between groups on the template and the oxygens of the phosphates.

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† *Crystal data* for $Co(en)_3Al_3P_4O_{16}\cdot 3H_2O$: orthorhombic, $Pna2_1$, a = 8.521(5), b = 13.775(5), c = 21.594(8) Å, Z = 4, ρ = 1.98 g cm^{-3}. Number of reflections collected were 1989, at 130 K, on a Nicolet P4 diffractometer using Mo-Kα radiation (λ = 0.71073, graphite monochromator). Structure was solved by a direct method (SHELXS-86) using empirical-absorption corrected data, and anisotropic temperature factors for the Co, P and Al atoms. The hydrogen atoms in calculated positions were kept in 'riding' mode with two common isotropic temperature factors. The structure was refined to a conventional R of 0.062. 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.

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