

A new type of layered aluminium phosphate $[\text{NH}_4]_3[\text{Co}(\text{NH}_3)_6]_3[\text{Al}_2(\text{PO}_4)_4]_2$ assembled about a cobalt(III) hexammine complex

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The formation of a novel layered aluminium phosphate containing a new type of layer stoichiometry is reported; the reaction is carried out under basic conditions using cobalt hexammine as a template.

There have been a number of reports on the synthesis of microporous solids where metal complexes have been used as templating agents. Balkus *et al.*¹ synthesized a zeolite with the faujasite structure using metal phthalocyanine complexes as templating agents. Balkus and Shepelev² have used a bis(cyclopentadienyl)cobalt(III) complex to form a nonasil molecular sieve and more recently Freyhardt *et al.*³ formed a novel large-pore high silica zeolite using bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide. In order for a metal complex to be useful as a templating agent the metal complex must be stable under the reaction conditions. Cobalt(III) complexes are inert to substitution and remain stable at relatively high temperatures. We recently used this property to form a unique layered aluminium phosphate⁴ about the chiral metal complex cobalt tris(ethylenediamine), $[\text{Co}(\text{en})_3]^{3+}$. This was the first reported example where a metal complex was used as a template to form a layered structure. Bruce *et al.* have found that the cobalt tris(propylenediamine) complex⁵ and the cobalt bis(diethylenetriamine) complex⁶ can also act as a template to form a chiral layered material. We found that if either isomers of $[\text{Co}(\text{en})_3]^{3+}$ was resolved and used as the template in the hydrothermal reaction then no crystalline material was formed. This suggests that there is no lattice compatible with the resolved complex, and that both isomers are required to obtain a stable structure.

The metal complex $[\text{Co}(\text{en})_3]^{3+}$ is reasonably stable under the hydrothermal conditions used in these types of preparations. The cobalt hexammine complex, $[\text{Co}(\text{NH}_3)_6]^{3+}$, is not as stable and undergoes decomposition in boiling water with the loss of ammonium ion. The complex is, however, stable in concentrated ammonium ion solutions at temperatures up to 150 °C.

The reaction of aluminium oxyhydroxide, (0.5 g), $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (1 g) and 85% phosphoric acid (1.9 g) in concentrated ammonium hydroxide (10 ml) at 150 °C for 12 h resulted in the formation of long orange needles, up to 1 cm in length, large purple plates and a minor amount of unidentified small blue plates. The purple plates were identified by powder XRD as NH_4CoPO_4 .⁷ Since the colour of the orange needles suggested that the complex had acted as a template for formation of the structure and not undergone decomposition, this material was further characterised by single-crystal X-ray crystallography.†

The orange needles have a layered structure with the metal complex positioned between the layers. Water and ammonium ions fill the voids between the layer and the metal complex [Fig. 1(a)]. The composition of the layers is, however, different to those layered aluminium phosphates that have been reported to date, which have either the compositions $\text{Al}_3(\text{PO}_4)_4^{3-}$ (refs. 4–6, 8–11) or $\text{Al}_2(\text{PO}_4)_3^{3-}$ (ref. 12) and a range of unique layer topologies. The composition of this new layered phase is $\text{Al}_2(\text{PO}_4)_4^{6-}$. In most of the layered aluminium phosphates, the aluminium is tetrahedrally bonded through an oxygen to four phosphorus atoms. The structure described by Chippindale *et al.*¹² is unusual as it contains both tetrahedrally and trigonal-

bipyramidal aluminium. In the $[\text{Al}_3(\text{PO}_4)_4^{3-}]_n$ ^{4–6,8–11} layered material the phosphorus is bonded through three oxygens to aluminium giving one non-coordinated P–O bond. In the $[\text{Al}_2(\text{PO}_4)_3^{3-}]_n$ ¹² layers there are two types of phosphorus. One type is bonded to four oxygens of which three are bonded to aluminium, the other is bonded to four oxygens but only two of these are bonded to aluminium.

For the structure reported here, $[\text{Al}_2(\text{PO}_4)_4^{6-}]_n$, there are two unique phosphorus atoms with each bonded to four oxygens. Only two of these oxygens are bonded to aluminium, the other two are nominally P=O double bonds. The solvent system of concentrated ammonium hydroxide used for forming the $\text{Al}_2(\text{PO}_4)_4^{6-}$ lattice is highly basic favouring P=O double bond formation. The $\text{Al}_2(\text{PO}_4)_4^{6-}$ lattice is the most basic type of the layered aluminium phosphates reported to date. There are three types of rings in the structure: two small four-membered rings and a large 20-membered ring [Fig. 1(b)]. The metal complexes reside within the larger ring. The density of the material is similar to that of the other layered aluminium phosphates.

There is an extensive hydrogen-bonding network involving the non-coordinated phosphoryl oxygens, the coordinated amines, the ammonium ions and the water molecules [O(phosphate)⋯N 2.71–2.96 Å], [O(4A)⋯O(water) 2.66 Å]. Six of the eight phosphoryl oxygens bind to more than one hydrogen. One

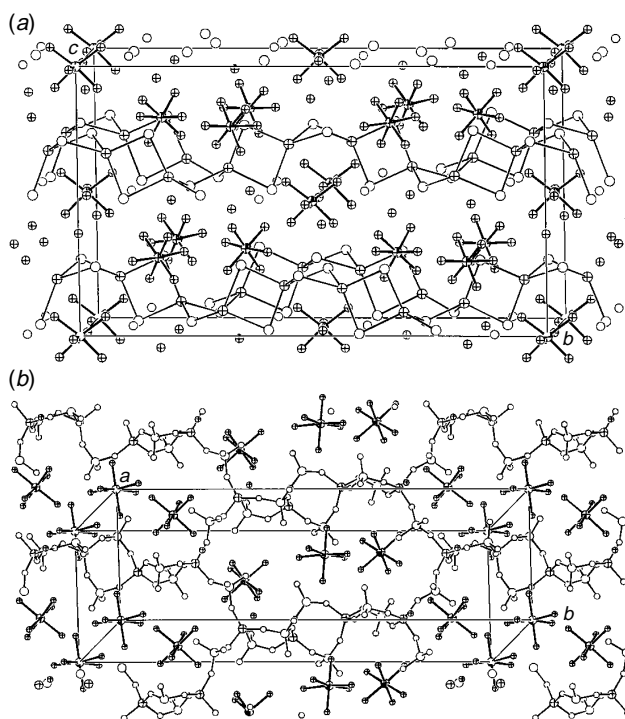


Fig. 1 Views of structure: (⊕) N, (⊕) Al, (○) P, (◊) H₂O, (⊕) Co. (a) View edge on to the $\text{Al}_2(\text{PO}_4)_4^{6-}$ layers; PO_4 and AlO_4 tetrahedron are shown linked as single atoms and hydrogens have been excluded. (b) View normal to the plane of just one layer at $z \approx 0.25$.

of the metal complexes is partially disordered and is bound weakly to one of the phosphoryl oxygens and the water molecule.

The layered phase $[\text{NH}_4]_3[\text{Co}(\text{NH}_3)_6]_3[\text{Al}_2(\text{PO}_4)_4]_2$ represents a new lattice type and layer topology. It is likely that a hydrothermal synthesis under similar basic conditions in the presence of suitable templates could yield other $\text{Al}_2(\text{PO}_4)_4^{6-}$ phases having different layer topologies.

Footnote

† *Crystal data* for $[\text{NH}_4]_3[\text{Co}(\text{NH}_3)_6]_3[\text{Al}_2(\text{PO}_4)_4]_2 \cdot 2\text{H}_2\text{O}$: orthorhombic, *Aba2*, $a = 9.502(2)$, $b = 29.699(6)$, $c = 17.210(3)$ Å, $Z = 4$, $D_c = 1.97$ g cm⁻³. 3845 reflections collected at 130(2) K on a Nicolet P4 diffractometer using Mo-K α radiation ($\lambda = 0.71073$ Å, graphite monochromator). The structure was solved by a direct method (SHELXS-90¹³) using empirical absorption-corrected data, and anisotropic temperature factors for the Co, P and Al atoms. During refinement a minor twinned component was detected; the twinned proportion parameter refined to 0.89(4).¹⁴ Located ammine hydrogen atoms were refined¹⁴ with isotropic temperature factors 1.2 times their parent nitrogen. The structure was refined on F_0^2 (358 parameters, 3324 independent reflections) to a conventional R of 0.047 [$F_0 > 4\sigma(F_0)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/300.

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