A new route for the synthesis of open-framework metal phosphates using organophosphates

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Use of tributylphosphate, an organophosphate, as the phosphorus source in place of phosphoric acid, has enabled the synthesis of several new open-framework zinc(II) and cobalt(II) phosphates, under solvothermal conditions.

Amongst the many inorganic open-framework structures known to-date, the metal phosphates constitute a large family.1,2 The synthesis of these compounds is generally carried out under hydrothermal conditions by taking a metal salt and phosphoric acid in the presence of an organic amine, which may act as a template or structure-directing agent. Other strategies include the use of amine phosphates.3 We have examined whether the use of an organic phosphorus source in place of H3PO4 would provide a new way to synthesize these fascinating compounds. This is of interest because the formation of open-framework structures is kinetically controlled and can be highly sensitive to the reaction conditions. In addition, the use of an organic source of phosphorus enables one to employ non-aqueous media for the synthesis. We have carried out several reactions of metal phosphates possessing different architectures. In this communication we report this new route for the synthesis of open-framework phosphates.

In a typical synthesis, zinc(II) chloride was dissolved in a butan-2-ol–water mixture. Tributylphosphate was added to the solution followed by an organic amine under constant stirring. The homogenized gel was sealed in a Parr autoclave and heated at 180 °C for 60 h. With different amines (N-(2-aminomethyl)-1,3-propanediamine in I, 4-(aminomethyl)piperidine in II and piperazine in III) the reactions yielded three-dimensional phosphates of the following compositions: [C5N3H18]–, [C4N2H12][Zn2(PO4)(H2PO4)2] I, [C5N2H10][Zn6(PO4)4]·5H2O II and [C5N2H12][Zn5(PO4)4](H2PO4)2] III. While I and II, which possess channels are new, III has been reported in the literature.

The structure of I is based on a three-dimensional network involving ZnO4 tetrahedra, PO4 and HPO4 tetrahedra with all the zinc atoms being linked to P atoms via oxygen. There are no Zn–O–Zn linkages present in the structure, hence no three-ring features are observed. The structure of I is built up of a stack of parallel layers linked by the corner-shared (CS) 4-ring chains embedded in the interlayer space (Fig. 1a). The layers in turn are made up of zigzag ladders consisting of 8-ring apertures as shown in Fig. 1b. The oxygens of the phosphate of the CS chains link on either side to the zinc tetrahedra of the layers. Such linkages between layers and CS chains result in 16-ring apertures along the c-axis, into which the terminal hydroxy groups project.

The framework of II is built up from layers and 4-ring ladders. The layers are made up of three types of chains (A, B and C) as can be visualized in Fig. 1c. The phosphate tetrahedra on the chains of type A and B add on to another set of ZnO4 tetrahedra to form the ‘tubule’ like feature, whereas the phosphate tetrahedra common to these chains and the oxygens of the newly added ZnO4 tetrahedra connect to the oxygens of the 4-ring ladder to form the three-dimensional architecture with 12- and 6-ring channels along the a-axis (Fig. 1d). The protonated amine molecule (4-(aminomethyl)piperidine decomposes to give 1,4-diaminobutane) sits in the cavities and interacts with the framework via hydrogen bonding.

For the synthesis of cobalt(II) phosphates, a known amount of CoCl2·6H2O was dissolved in butan-2-ol and tributyl phosphate added to the solution under stirring. The amine (piperazine in IV, V and diethylenetriamine in VI) was added after a few minutes and the mixture stirred until it became homogeneous. The gels were sealed in Parr autoclaves at 180 °C for 60 h.

Fig. 1 (a) Polychedral view of I, showing the 16-membered channels along the a-axis. Also marked are the CS chain and the layer forming the 16-ring channels and the pendant hydroxy groups protruding into the cavity. (b) A section of I showing the zigzag layer containing 8-ring apertures. (c) A section of II showing the layer formed of chains A, B and C. Also shown by dotted lines is the ZnO4 tetrahedron connecting to the oxygen atoms of the phosphate groups of chains (type A and B) to form the tubule. (d) Ball and stick view of 6- and 12-ring cavities of II along the a-axis.
of 3- and 4-membered rings formed by vertex linkage between

dows (Fig. 2a). Framework IV has a layered architecture. Although these cobalt phosphate are

closed by the linkage of

chains containing 4-rings running perpendicular to each other

and has a three-dimensional structure built up of infinite CS

frames with

respectively.

Such clusters are linked via six PO4 tetrahedra to other clusters
to form the structure. The clusters are arranged in such a manner that each cluster is displaced by half the length of the c-axis from its neighbour, forming a honeycomb layer. The next layer of clusters is identical to the first but is displaced along the a-axis by half the unit cell so that the honeycomb channels are
capped. This type of three-dimensional AB type stacking results in the formation of 8-membered channels at an angle to the c-axis (Fig. 2c).

The various structures obtained by using tributylphosphate as the phosphorylating agent confirm that we have found a new route for the formation of open-framework phosphates. The use of the phosphate ester enables us to carry out the reactions under non-aqueous conditions and to isolate new framework structures. It may be noted that pure open-framework Co(II) phosphates have been considered difficult to prepare. The use of the phosphate ester influences the release of phosphate ions in the solution, thereby affecting the course of the reaction and the products formed. The method can be readily extended to phosphonates, carboxylates and other systems.

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Notes and references


7 Single crystal X-ray data was collected using a Siemens SMART-CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (Mo-Kα radiation, λ = 0.71073 Å) operating at 45 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1521 frames with ω scans (width 0.30° and exposure time of 10–20 s per frame). The structure was solved by direct methods using SHELX-97 and difference Fourier syntheses. Full matrix least-squares refinement against [F2] was carried out using the SHELXTL-PLUS package of programs. Unit cell parameters: for I, space group P1 (no. 2), a = 8.4408(15), b = 9.2630(16), c = 13.8427(20), α = 81.119(15), β = 83.643(12), γ = 72.647(11)°, R = 0.037. For II, space group P21/c (no. 14), a = 5.1601(6), b = 25.0748(31), c = 14.9868(19) Å, β = 92.610(2), R = 0.046. For IV, space group P21c (no. 15), a = 13.4441(49), b = 12.8745(41), c = 8.2234(23) Å, β = 94.6402(22)°, R = 0.047. For VI, space group P1 (no. 2), a = 5.1534(7), b = 7.0578(13), c = 10.8329(14) Å, α = 96.381(2), β = 89.058(2), γ = 81.674(2), R = 0.054. For VII, space group R3 (no. 148), a = 13.4892(18), b = 13.4892(18), c = 14.9839(30) Å, γ = 120°, R = 0.066.

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See http://www.rsc.org/suppdata/cc/b1/b107898b for crystallographic data in CIF or other electronic format.

Fig. 2 (a) Structure of IV showing clover-shaped 16-ring channels. Also seen are the pipperazinium molecules in the 4-ring windows. (b) Structure of V showing a single layer. Note the presence of two types of chains D and E and the infinite Co-O-Co chains. (d) Structure of VI showing the 8-membered channels at an angle to the c-axis formed by the linkage of CoO3 clusters.