

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 ions with tributylphosphate, both in alcohol and aqueous media, and obtained several open-framework cobalt, zinc and iron 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-aminoethyl)-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][Zn₃(HPO₄)₃(PO₄)₄] **I**, [C₄N₂H₁₄]₄[Zn₅(PO₄)₄]₄·5H₂O, **II** and [C₄N₂H₁₂][Zn₂(PO₄)(H₂PO₄)₂] **III**. While **I** and **II**, which possess channels are new, **III** has been reported in the literature.³

The structure of **I** is based on a three-dimensional network involving ZnO₄, 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 layer in turn is 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 diethylentriamine 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. By

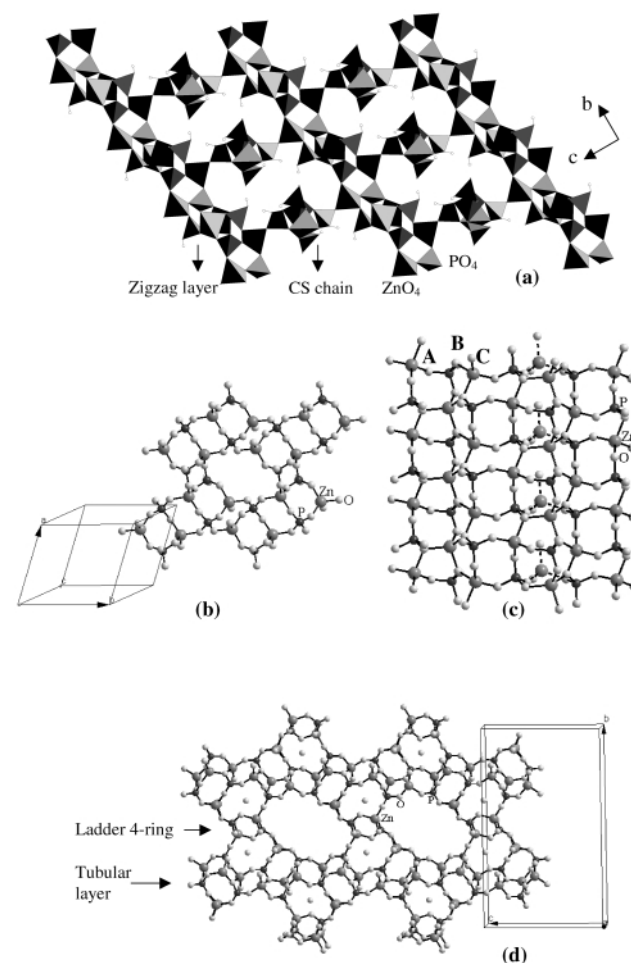


Fig. 1 (a) Polyhedral view of **I**, showing the 16-membered channels along the *a*-axis. Also marked are the CS chain and the layer forming the 16-ring channels and the pendant hydroxy groups protruding into the cavity. (b) A section of **I** showing the zigzag layer containing 8-ring apertures. (c) 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.

such reactions, we obtained three new open-framework cobalt phosphates $[C_4N_2H_{11}][Co_2(PO_4)(H_2PO_4)_2]$ **IV**, $[C_4N_2H_{12}][Co_2(PO_4)_2]$ **V** and $[C_6N_4H_{22}][Co_7(PO_4)_6]$ **VI**. Of these, **IV** and **VI** possess three-dimensional frameworks and **V** has a layered architecture. Although these cobalt phosphates are new, their zinc phosphate analogues are known in the literature.^{3–5} We have also synthesized a known mixed valence iron phosphate⁶ by this route.

Framework **IV** is isostructural with the zinc phosphate **III** and has a three-dimensional structure built up of infinite CS chains containing 4-rings running perpendicular to each other and connected at various junctions.³ Four such junctions form a 16-membered clover-shaped aperture, with the pendant hydroxyl groups from the phosphorus projecting in the cavities. The protonated piperazinium cations occupy the 4-ring windows (Fig. 2a). Framework **V** has a layered topology made up of 3- and 4-membered rings formed by vertex linkage between

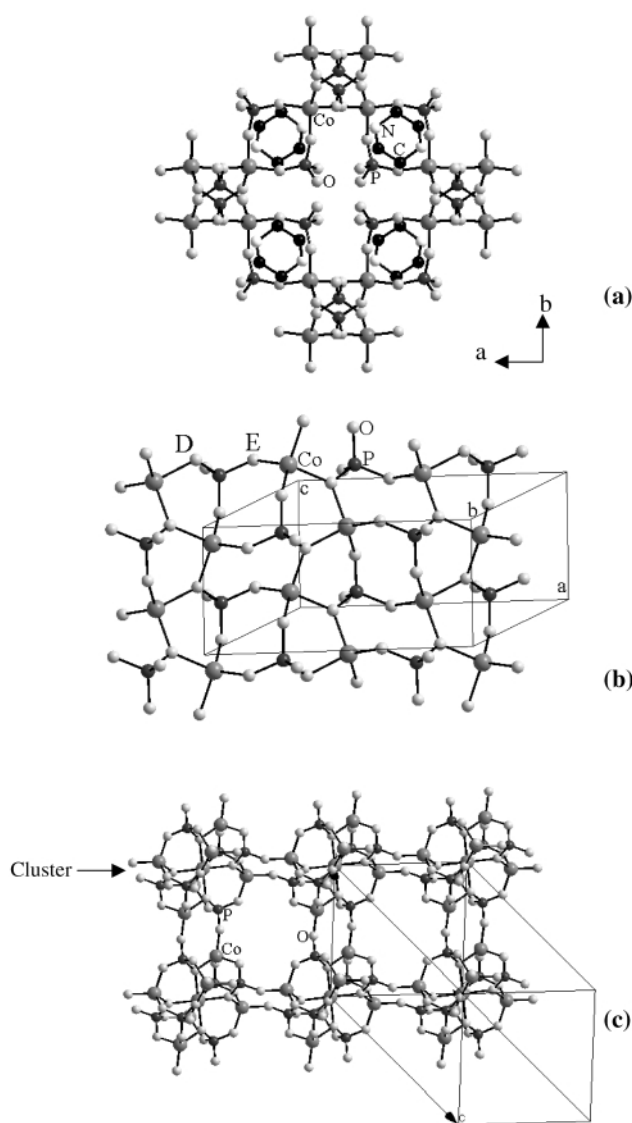


Fig. 2 (a) Structure of **IV** showing clover-shaped 16-ring channels. Also seen are the piperazinium molecules in the 4-ring windows. (b) Structure of **V** showing a single layer. Note the presence of two types of chains **D** and **E** and the infinite Co–O–Co chains. (d) Structure of **VI** showing the 8-membered channels at an angle to the *c*-axis formed by the linkage of Co_7O_6 clusters.

CoO_4 and PO_4 tetrahedral units. The anionic layer is built up of two kinds of chains, **D** and **E**, made from 3- and 4-rings (Fig. 2b). The presence of a 3-ring chain results in a step-like feature in the layer due to the strain involved in accommodating it and also gives rise to an infinite one-dimensional Co–O–Co chain.

Compound **VI** possesses a three-dimensional architecture and is made of CoO_6 , CoO_4 and PO_4 polyhedra, which connect to give rise to a Co_7O_6 cluster. The cobalt octahedron is surrounded by six cobalt tetrahedra to form the Co_7 cluster. Such clusters are linked *via* six PO_4 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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- 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-K α radiation, $\lambda = 0.71073$ Å) operating at 45 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 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 $|F_o|$ was carried out using the SHELXTL-PLUS package of programs. *Unit cell parameters*: for **I**: space group $P\bar{1}$ (no. 2), $a = 8.4408(13)$, $b = 9.2630(16)$, $c = 13.8427(20)$ Å, $\alpha = 81.119(15)$, $\beta = 83.643(12)$, $\gamma = 72.647(11)^\circ$, $R = 0.037$. For **II**: space group $P2_1/n$ (no. 14), $a = 5.1601(6)$, $b = 25.0748(31)$, $c = 14.9860(19)$ Å, $\beta = 92.610(2)^\circ$, $R = 0.046$. For **IV**: space group $C2/c$ (no. 15), $a = 13.4441(49)$, $b = 12.8745(41)$, $c = 8.2243(23)$ Å, $\beta = 94.640(22)^\circ$, $R = 0.047$. For **V**: space group $P\bar{1}$ (no. 2), $a = 5.1534(7)$, $b = 10.7578(13)$, $c = 10.8329(14)$ Å, $\alpha = 66.381(2)$, $\beta = 89.058(2)$, $\gamma = 81.674(2)^\circ$, $R = 0.054$. For **VI**: space group $R\bar{3}$ (no. 148), $a = 13.4892(18)$, $b = 13.4892(18)$, $c = 14.9839(30)$ Å, $\gamma = 120^\circ$, $R = 0.066$.

CCDC reference numbers 168260–168264 for **I**, **II**, **IV**, **V** and **VI** respectively.

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