A Novel Open-framework Sodium Zincophosphate with Isomorphous Cobalt(II) Substitution

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A novel anionic cobalt-substituted zincophosphate framework with a hexagonal unit cell of composition $Na_6[Co_{0.2}Zn_{0.8}PO_4]_6 \cdot 9H_2O$ is synthesised and its crystal structure determined by single crystal X-ray diffraction.

In recent years much effort has been devoted to the investigation of new open-framework compositions of oxides other than the aluminosilicate or aluminophosphate materials. In this context, zinc phosphates belong to a group of compounds that are of some potential interest, *i.e.* like silicon and aluminium, zinc and phosphorus commonly bond tetrahedrally to oxygen, and a hypothetical zincophosphate framework formula unit is electronically equivalent to the known aluminosilicate one. Harrison and coworkers[1–5] have prepared and characterised a number of new open-framework zincophosphates, some of which have structures analogous to those of zeolites, while others have no counterparts. More recently, Song *et al.*[6] synthesised a novel open-framework zinc phosphate from a non-aqueous system.

In comparison to zeolites, in which the transition metal ions are never constituents of the aluminosilicate network, various transition metal ions can be incorporated into the aluminophosphate framework. This feature offers many possibilities of designing materials possessing desirable catalytic properties. With this in mind, we explored the possibility of incorporating cobalt(II) into the open-framework zincophosphate network. This paper describes the crystal structure of a new cobalt-substituted zincophosphate phase (CoZnPO) crystallising from an Na_2O–ZnO–CoO–P_2O_5–H_2O system under ambient conditions.

The reaction gel of composition $1.75Na_2O : 0.8ZnO : 0.2CoO : 0.62P_2O_5 : 160H_2O$ (after being stirred intensively for *ca.* 30 min) was left standing overnight at room temperature and ambient pressure. Royal blue prism-shaped crystals were obtained, whose chemical analysis yielded the formula $Na_6[Co_{0.2}Zn_{0.8}PO_4]_6 \cdot 9H_2O$. Diffuse reflectance spectroscopy confirmed the tetrahedral coordination of Co^{II}. A suitable crystal was selected for a structure determination by single crystal X-ray diffraction.†

The structure's framework is built up from ZnO_4, CoO_4 and PO_4 tetrahedra, forming a three-dimensionl network in which all the vertices are shared. Chemical and crystallographic data indicate the isomorphous substitution of Co^{II} on two crystallographically distinct Zn sites. The refinement of the population parameters suggests that the isomorphous replacement of Zn by Co occurred predominantly at the Zn(1) site, although we must emphasise that this result is not very reliable because of small amount of diffraction data. The ratio of zinc/cobalt : phosphorus is unity and $(Zn_{0.8}Co_{0.2})$ and P tetrahedral units alternate throughout the structure. Neglecting the amount of incorporated Co, this mode of connectivity generates the anionic framework structure $[ZnPO_4]^-$, with charge compensation provided by the extra-framework Na^+ species. The same framework stoichiometry has been observed in a number of microporous phosphates with divalent non-transition and transition metals.[5,7,8] This zincophosphate framework is electronically equivalent to the aluminosilicate $[AlSiO_4]^-$, in contrast to some newly obtained layered zinc phosphates[3,4] where a variety of tetrahedral groups (ZnO_4, ZnO_3OH_2, PO_4, PO_3OH) form a new family of structures which are much less common in microporous aluminosilicate structures.

In the title compound the topology consists of four- and six-membered rings, building six-membered ring channels spreading in the [001] direction (Fig. 1). The channels are not of a regular diameter but consist of small cavities which are connected by the six-membered pore openings and where the Na^+ cations and water molecules are trapped. The framework-atom geometries are in accordance with the expected behaviour for these species. The tetrahedral Zn–O and P–O bond lengths are in the ranges 1.92(3)–2.01(5) and 1.45(4)–1.56(2) Å, respectively. All eight framework oxygen atoms participate in Zn(Co)–O–P linkages.

Six of the eight framework O atoms form bonds with one of the two guest Na cations. The Na(1) is bonded to four framework oxygens at expected distances [2.34(5)–2.46(5) Å]. This fact most likely suggests a tetrahedral coordination. However, it is reasonable to assume that the two accompanying

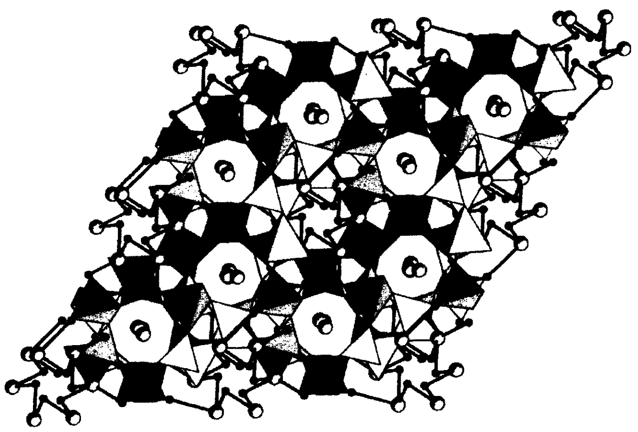

Fig. 1 The framework topology with Zn(Co) and P tetrahedra building a three-dimensional complex network and occluded Na cations (large open circles) and water molecules (small black circles)

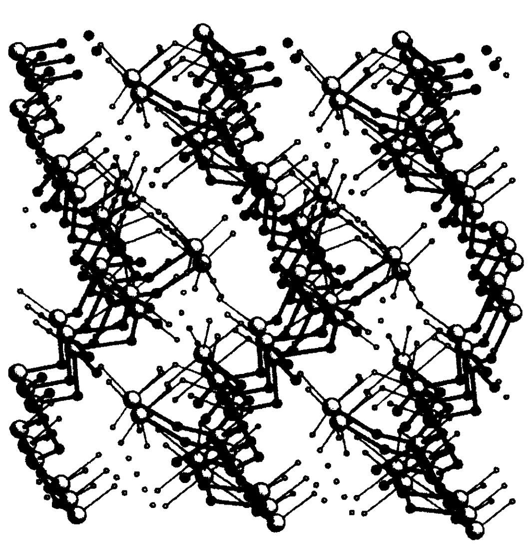

Fig. 2 Representation of the extra-framework Na cations and water oxygens forming an infinite helix located in the framework openings, projected on the *bc* plane. Bonding of the framework O atoms to the Na species is presented by thin lines. Other framework atoms are omitted for clarity.

oxygen atoms at distances of 2.75(5) and 2.57(9) Å (water oxygen) are also coordinated to some degree. Therefore, this coordination polyhedron can also be considered as distorted octahedral (such is the case in most related structures). A similar situation appears when considering the coordination of the Na(2) atom: it is surrounded by two framework oxygen atoms and three water molecules at distances from 2.00(9) to 2.41(7) Å, and one additional water molecule coordinates to it at the slightly greater distance of 2.59(9) Å.

The sodium cations and water molecules form an infinite helix, which is located in the six-ring channel running in the [001] direction (Fig. 2). The Na(2) atoms and water molecules form a chain of NaO_4 units, each of which is bonded to two framework oxygen atoms to complete the octahedral coordination of sodium. Each Na(1) octahedron is connected to the helix through one of its vertices, resulting in an additional stabilisation of the helix in the structure. All three water molecules participate in hydrogen bonding to framework oxygens. A similar helical arrangement of template molecules has been found in the aluminophosphate VPI-5 structure,[9] where a triple helix of water molecules inside the 18-ring channel has been established.

To conclude, the structure determination yielded a novel structure, which could be described as a complex zincophosphate framework with small pores and occluded H_2O molecules, together with the Na^+ cations balancing the framework charge.

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† *Crystal data* for $Na_6[Co_{0.2}Zn_{0.8}PO_4]_6 \cdot 9H_2O$, hexagonal, space group $P6_1$ (no. 169), a = 10.477(3), c = 15.049(5) Å, V = 1430.6(10) Å^3, Z = 6, D_c = 2.917 g cm^{-3}, μ(Mo-Kα) = 5.30 mm^{-1}, λ = 0.71069 Å, crystal dimensions 0.12 × 0.06 × 0.04 mm, R = 0.070, R_w = 0.061. The data were collected on an Enraf-Nonius CAD4 diffractometer at 20 °C in the range 1.00 < 2θ < 28.00 ° using an ω–2θ scan technique. A total of 10566 reflection intensities were measured, of which 527 were considered to be observed [$I \geqslant 2.5\sigma(I)$]. The complete sphere of reflection with an index range $-15 \leqslant h \leqslant 15$, $-15 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 19$ was measured, and three standard reflections were monitored every 20 000 s with an intensity change of 0.70%. No absorption correction was applied because of the small size of the crystal. The structure was elucidated by direct methods (MULTAN88)[10] followed by Fourier calculations. The refinement was straightforward for the Zn, P and O atomic sites assigned to a framework. During the course of the crystal structure analysis it also proved possible to locate most of the extra-framework atoms, suggesting chemically meaningful bond distances and the realistic corresponding thermal parameters. The Xtal 3.2 system[11] was used for all further calculations and interpretation. All calculations were done at the University Computer Centre, Ljubljana.

The lack of crystal intensity data is evident from a low reflection: parameter ratio and the relatively high final R values. The framework and non-framework atoms were refined isotropically using full-matrix least-squares methods. Occupancy factors < 1 of the two Zn sites (after some trial refinement) and the examination of the difference Fourier map with minimum height peaks located in Zn positions were in accordance with the partial replacement of Zn by an atom of lower atomic number (Co). The difference map also revealed a variety of positions that could be attributed to hydrogen atoms, which were not included in the refinement. Large temperature factors at non-framework atoms might indicate a lower symmetry of the group, but an attempt to refine the structure in a lower symmetry resulted in no significant improvement, due to the increased number of variables. The structure was refined by 527 reflections and 68 parameters.

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