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The unique dual role of zinc atoms in a mixed zinc–vanadium phosphate [Zn(phen)Zn(VO)$(PO_4)_2$]

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The unique dual role of zinc atoms in a novel layered mixed zinc–vanadium phosphate has been shown by X-ray crystallography to consist of Zn/V/P/O inorganic anionic layers with cationic complex fragments in pairs attached perpendicularly to the layers.

Open-framework microporous materials have been of interest because of their traditional use in catalysis, separation, and ion-exchange and their potential applications as hybrid composite materials in nonlinear optical and sensing applications.[1] Since the first discovery of open aluminophosphates in 1982,[2] the elements constructing open-framework materials have been extended to most of the transition metals and main group. A challenge for synthetic work in open-framework metal phosphates is to synthesise mixed-metal phosphates, which can lead to interesting physical and chemical properties.[3]

Recently, an important advance in metal phosphate chemistry has been the study of the solid state co-ordination chemistry of vanadium phosphates, which are characterised by the organic components ligated to the second metal atoms or vanadium atoms.[4] While structural modification through incorporation of different organic ligands has been realised, the influence of second metal atoms on the framework has not been explored for this family of materials. The second metal atoms in those complexes reported only include cobalt, nickel and copper which play a single role, that is, linking or decorating the subunits of oxovanadium phosphate in the form of ML (M = Co, Ni or Cu, L = nitrogen-containing ligand). As a sequel to our study of the solid state co-ordination complexes of vanadium oxides[5] we present here a novel solid state co-ordination complex of mixed zinc–vanadium phosphate, namely, [Zn(phen)Zn(VO)$(PO_4)_2$] (**1**) (phen = 1,10-phenanthroline), in which the zinc atoms play an unprecedented dual role in the solid state: decorating the inorganic framework in the form of $[Zn(phen)]^{2+}$ and constituting an inorganic layered framework in the form of ZnO_4 tetrahedra together with PO_4 and VO_5 polyhedra.

A mixture of V_2O_5 (0.09 g), $Zn(OAc)_2{\cdot}2H_2O$ (0.22 g), phen (0.18 g), H_3PO_4 (0.20 g, 85%) and H_2O (10 mL) in the molar ratio of 1 : 2 : 2 : 3.5 : 1100 was stirred in air for 20 min and transferred into a Teflon-lined stainless steel reactor and heated at 160 °C for 108 h. Green crystals of **1** were recovered in 65% yield based on zinc after filtration, washing and drying in air. The initial pH was 2.4 and the final pH had increased to 3.8. The elemental analysis and IR spectra † in combination with X-ray single-crystal analysis ‡ confirmed the formula of **1**. The TGA showed that **1** has high thermal stability in air (350 °C) and the phen groups are combusted from the crystals in the range 360–620 °C with weight losses of 30.9% (calculated value of 31.7%).

There are two crystallographically distinct zinc sites and two phosphorus sites, as shown in Fig. 1. Zn(1) is located at a square-pyramidal centre, being co-ordinated by two nitrogen atoms from a phen ligand and three oxygen atoms connected to three phosphate groups. Zn(2) adopts a tetrahedral geometry formed by four oxygen atoms connected to four phosphate groups. The V(1) site features a square pyramid, being co-ordinated by one terminal apical oxygen atom (V=O 1.591(5) Å) and four bridging oxygen atoms connected to three phosphate groups. Bond valence sum and empirical formula calculations confirmed that the vanadium site is tetravalent.[6] Owing to the existence of the equilibrium $VO_2^+ + 2H^+ + e \rightleftharpoons VO^{2+} + H_2O$ ($E^o(VO_2^+/VO^{2+}) = 1.0$ V) in acidic conditions, the $E(VO_2^+/VO^{2+})$ becomes larger with a decrease in pH which makes the reduction of the VO_2^+ species easier. It has also been shown that the *N*-containing species can reduce vanadium(V) to vanadium(IV) under hydrothermal conditions[7] and thus the reductive species in this work possibly results in part from phen molecules in the reaction system. Therefore, the formation of vanadium(IV) can be attributed to the low initial pH and the existence of phen molecules. The $P(1)O_4$ and $P(2)O_4$ groups show different co-ordination modes, although both are five-connected to zinc and vanadium atoms *via* oxygen atoms. There are two μ_3- and two μ-oxygen atoms in the $P(1)O_4$ group but one μ_3- and three μ-oxygen atoms in the $P(2)O_4$ moiety.

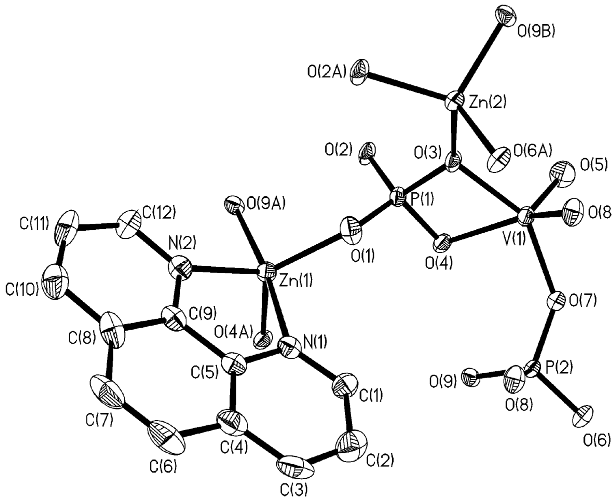

Fig. 1 View of the co-ordination environments of zinc, vanadium and phosphorus, showing the atom-labelling scheme and 50% thermal ellipsoids. Selected bond lengths (Å): av. Zn(1)–O 2.035, av. Zn(2)–O 1.958(4), V(1)–O_t 1.591(5), av. V(1)–$O_{phosphate}$ 1.991(4), av. P(1)–O 1.545(4), av. P(2)–O 1.552(4).

The structure of **1** consists of anionic mixed zinc–vanadium phosphate layers in pairs attached by cationic $[Zn(phen)]^{2+}$ complex fragments, which project perpendicularly above and below the interlayer region, as shown in Fig. 2. The anionic mixed zinc–vanadium phosphate layer with the formula $[Zn(VO)(PO_4)_2]^{2-}$ comprises double-chains interconnected by sharing the O(9) atom and its equivalents. Each double-chain consists of two single chains which are interconnected by sharing the O(3), O(8) atoms and their equivalents. The single chain is constructed by the edge-sharing or corner-sharing

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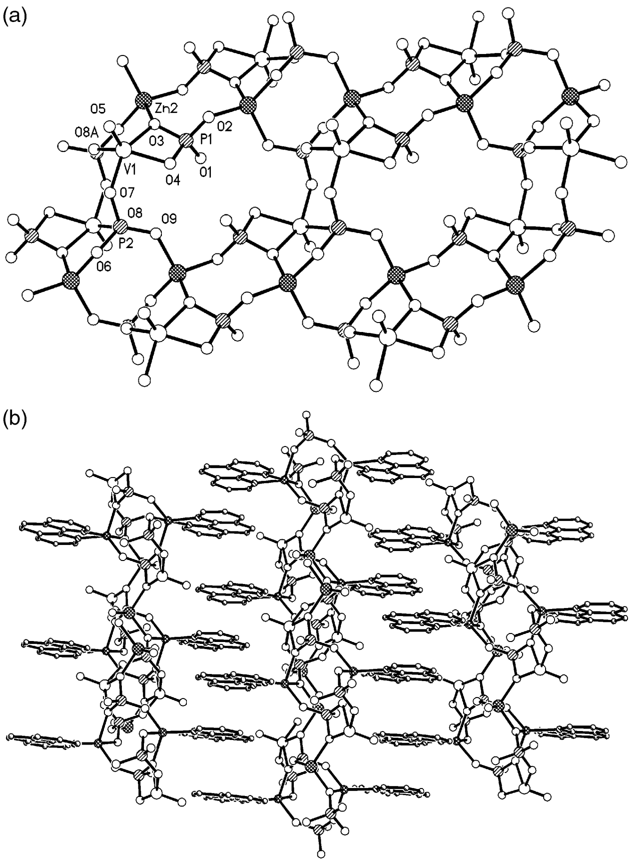

Fig. 2 Perspective views of the anionic $[Zn(VO)(PO_4)_2]^{2-}$ mixed-metal phosphate layer along the *c*-axis (a) and the intercalation of the layers into a three-dimensional supramolecular array *via* the zipper-like action of the lateral aromatic groups (b).

connections of polyhedra in the sequence ZnO_4, PO_4, VO_5 and PO_4. One consequence of the connectivity results in 3-, 4- and 8-membered rings. A pair of $[Zn(phen)]^{2+}$ complex cations are attached to one 8-membered ring *via* O(1), O(4), O(9) and their equivalents, projecting below and above the mixed-metal phosphate layer, as shown in Fig. 2b. The attachment of the complex cations evolves one 8-membered ring into four 3-membered rings and one 4-membered ring. Alternatively, the structure of **1** may be viewed as $[Zn(phen)(VO)(PO_4)_2]$ double-chains linked by $Zn(2)O_4$ tetrahedra through sharing oxygen atoms with PO_4, VO_5 and ZnN_2O_3 polyhedra to give a layered framework. Frameworks containing the zincate anion, highly charged $ZnO_4{}^{6-}$, are relatively uncommon and the presence of a high charge on the phosphorus and vanadium sites in **1** may help the charge compensation.[8]

A unique feature of **1** is that the zinc atoms in the form of ZnO_4, together with PO_4 and VO_5 polyhedra constitute a layered inorganic framework, as well as in the form of $[Zn(phen)]^{2+}$ decorate the inorganic framework. Such a dual role of zinc atoms has not been found in the known solid state co-ordination complexes of vanadium phosphates.[4] The structural variation is apparent in the incorporation of different second metal atoms which can lead to co-ordination preferences necessitating structural reorganisation of composite materials. Despite containing the same ligand, the structure of **1** is quite different from chain-like $[Cu(phen)(VO_2)PO_4]$[4b] because the Zn(II) atoms tend to four-, five- or/and six-co-ordination but the Cu(II) atoms tend towards "4 + 1" co-ordination owing to a strong Jahn–Teller effect. Another remarkable feature of **1** is that it includes seven crystallographically different rings, namely, $\{Zn(1)Zn(2)P(1)O_3\}$, $\{Zn(2)VP(2)O_3\}$, $\{Zn(1)VP(2)O_3\}$, $\{Zn(1)_2P(1)_2O_4\}$, $\{V_2P(1)_2O_4\}$, $\{Zn(2)_2P(2)_2O_4\}$ and $\{Zn(2)_2P(1)_2O_4\}$. As we know, the $\{Zn_2PO_3\}$ 3-membered rings are novel[9] and the $\{ZnVPO_3\}$ 3-membered rings have not been reported previously. Finally, it should be noted that the interlayer phen groups are intercalated with an interplanar separation of *ca.* 3.3 Å, indicating that there are very strong π–π stacking interactions involved.[5] Therefore, the two-dimensional layers of **1** are further extended into a three-dimensional supramolecular array *via* the zipper-like intercalation[10] of the lateral aromatic groups, as illustrated in Fig. 2(b).

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Notes and references

† Anal: Calc. for **1** $C_{12}H_8N_2O_9P_2VZn_2$: C, 25.38; H, 1.42; N, 4.93. Found: C, 25.17; H, 1.29; N, 4.86%. IR (KBr, cm^{-1}): 3418s, 3061w, 1620m, 1581m, 1425s, 1305w, 1081s, 1003s, 946s, 848s, 722s, 649w, 503m.

‡ Crystal data for **1**: triclinic, space group $P\bar{1}$ (no. 2), $C_{12}H_8N_2O_9P_2VZn_2$, $Mr = 567.82$, $a = 8.015(4)$, $b = 9.160(7)$, $c = 11.942(9)$ Å, $\alpha = 81.20(1)$, $\beta = 71.09(1)$, $\gamma = 74.88(1)°$, $V = 798.5(9)$ Å^3, $\mu = 3.811$ cm^{-1}, $Z = 2$, $D_c = 2.362$ g cm^{-3}. Data collection $2 \le \theta \le 26°$ for **1** were performed at 293 K on a Siemens R3m diffractometer (Mo-Kα, $\lambda = 0.71073$ Å). The structures were solved with direct methods (SHELXS-97)[11] and refined with full-matrix least-squares (SHELXL-97),[12] giving a final R_1 value of 0.0488 for 254 parameters and 2320 unique reflections with $I \ge 2\sigma(I)$ and wR_2 of 0.1264 for all 3131 reflections. CCDC reference number 163144. See http://www.rsc.org/suppdata/dt/b1/b103875n/ for crystallographic data in CIF or other electronic format.

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