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Hydrothermal assembly and structural characterisation of one- and two-dimensional organic/inorganic hybrid materials constructed from diphosphopentamolybdate(VI) clusters and $\{Cu(en)\}^{2+}$ complex groups

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Three novel low-dimensional organic/inorganic hybrid materials, assembled hydrothermally, are constructed from diphosphopentamolybdate(VI) clusters linked through $\{Cu(en)\}^{2+}$ groups; the initial Mo/Cu and Mo/en ratios and the use of F^- ions control the connectivity between the phosphomolybdate clusters and $\{Cu(en)\}^{2+}$ groups, and hence the dimensionality of the solid architectures.

Self-assembly of inorganic molecular precursors in a quest for supramolecular chemistry is one of the highly recognised areas of chemical research. The significant contemporary interest in the transition polyoxometalate–phosphorus based solid materials[1–5] reflects their diverse applications in the areas such as catalysis, sorption and molecular electronics.[6–9] These solids are noted not only for their rich chemical reactivity and structural complexity, but for their unique capability of allowing a variety of chemical reactions to take place in the intracrystalline region. It is evident that chemically robust clusters of polyoxometalates can be assembled through charge compensating cations forming extended structures, though the mechanism by which the assembly is organised remains elusive. A popular strategy in the realisation of materials engineering involves combined applications of hydrothermal synthesis method and structure-directing templates. The feasibility of this strategy can be demonstrated by the advancement in porous materials[10] and the development of low-dimensional and microporous transition metal phosphates.[2–5]

The chemistry of polyoxomolybdate–phosphorus has been extensively studied due to their inherent potential for the development of supramolecular chemistry.[11] The recent success in the hydrothermal assembly of low-dimensional and microporous heteropolymolybdate-based hybrid materials using transition metal coordination complexes suggests a novel approach towards rational synthesis of metal oxide/organic solids.[12] As a continuation of our effort in the hydrothermal assembly of polyoxomolybdate(VI)-based solid materials,[13] we seek to explore the assembly of phosphomolybdates in the presence of Cu^{2+} and en under the influence of a F^- switch. Here, we report the hydrothermal synthesis and structural characterisation of three novel one- and two-dimensional hybrid solids, $[H_2en]_2[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]\cdot 4H_2O$ **1**, $[H_2en][\{Cu(en)_2\}Mo_5P_2O_{22}(OH_2)]\cdot 2H_2O$ **2** and $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]\cdot 3H_2O$ **3**.

Solids **1-3** were synthesised from the hydrothermal reactions of $MoO_3\cdot H_2O$, H_3PO_4, $CuSO_4\cdot 5H_2O$, en, H_2O with and without the use of F^- ions at 160 °C for 72 h.† The concentration of F^- ions in the initial mixtures was found to be critical for the synthesis of **1**. Solid **2** was obtained from similar reaction mixtures to **1** in the absence of F^- ions. Solid **3** was obtained from reaction mixtures containing much higher Cu^{2+} and en concentrations in comparison to those of **1** and **2**. *In situ* PXRD studies‡ showed that the crystal structures of solids **1-3** remained intact until *ca.* 400 °C. The synthesis of the three solids is sensitive to the specific reaction conditions such as the Mo/Cu and Mo/en ratios, suggesting a kinetically controlled crystallisation mechanism.

The structure of $[H_2en]_2[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]\cdot 4H_2O$ **1**§ is constructed from linking of the $[Mo_5P_2O_{23}]^{6-}$ clusters and $\{Cu(en)(OH_2)O_2\}^{2+}$ square pyramids into spiral-shaped chains of $[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]^{4-}$ as shown in Fig. 1. The geometry of the $[Mo_5P_2O_{23}]^{6-}$ cluster[11] can be described as a ring of five distorted MoO_6 octahedra with two PO_4 tetrahedra capped on each side. Two adjacent $[Mo_5P_2O_{23}]^{6-}$ clusters are connected through a $\{Cu(en)(OH_2)\}^{2+}$ unit *via* corner-sharing interactions of the type PO–Cu with Cu–O 1.949(5), 2.014(5) Å. The copper site is defined by two nitrogen donors from an en molecule, two *cis*-oxo groups from two adjacent $[Mo_5P_2O_{23}]^{6-}$ clusters and one oxygen donor from a H_2O molecule. The axial Cu–O bond [Cu-OH_2 2.432(7) Å] is considerably longer than the equatorial Cu–O bonds [Cu–O 1.949(5), 2.014(5) Å] owning to Jahn–Teller distortion. The $[\{Cu(en)(OH_2)\}Mo_5P_2O_{23}]^{4-}$ chains align in parallel and are packed such that each chain is circumscribed by two groups of four alike chains, which are related by a *pseudo* 4-fold axis, giving rise to an elongated cylindrical unit. As a result, pseudo-one-dimensional channels are formed that are filled with the charge-compensating Hen_2^{2+} cations.

Modifying the reaction mixture of **1** by reducing the F^- ion content leads to the co-crystallisation of solids **1** and **2**. Monophasic crystals of **2** are produced by removing F^- ions from the reaction mixtures. Examination of the structure of $[H_2en][\{Cu(en)_2\}Mo_5P_2O_{22}(OH_2)]\cdot 2H_2O$ **2**§ reveals that it consists of the $[Mo_5P_2O_{22}(OH_2)]^{4-}$ clusters[11] linked through the $\{Cu(en)_2O_2\}^{2+}$ octahedra into a virtual one-dimensional chain of $[\{Cu(en)_2\}Mo_5P_2O_{22}(OH_2)]^{2-}$ as shown in Fig. 2. Each $[Mo_5P_2O_{22}(OH_2)]^{4-}$ cluster is connected to two $\{Cu(en)_2O_2\}^{2+}$ octahedra through the two terminal oxo groups of a common MoO_6 octahedron forming weak interactions of the type Cu–OMo with Cu–O 2.490(6), 2.503(6) Å. The two axial Cu–O bonds of the $\{Cu(en)_2O_2\}^{2+}$ octahedron are, as expected, elongated. The adjacent chains of $[\{Cu(en)_2\}Mo_5P_2O_{22}(OH_2)]^{2-}$ are in close contact forming pseudo-two-dimensional layers through weak interactions of the type P···O 3.325(6) Å as shown in Fig. 2. The striking differences between the structures of **1** and **2** lie in (i) the number of en molecules

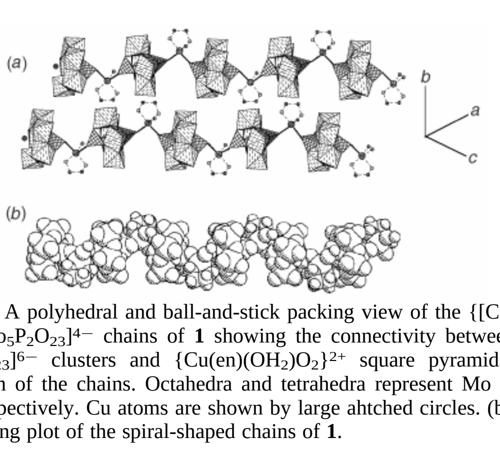

Fig. 1 (a) A polyhedral and ball-and-stick packing view of the $\{[Cu(en)(OH_2)\}Mo_5P_2O_{23}]^{4-}$ chains of **1** showing the connectivity between the $[Mo_5P_2O_{23}]^{6-}$ clusters and $\{Cu(en)(OH_2)O_2\}^{2+}$ square pyramids and orientation of the chains. Octahedra and tetrahedra represent Mo and P atoms respectively. Cu atoms are shown by large ahtched circles. (b) The space-filling plot of the spiral-shaped chains of **1**.

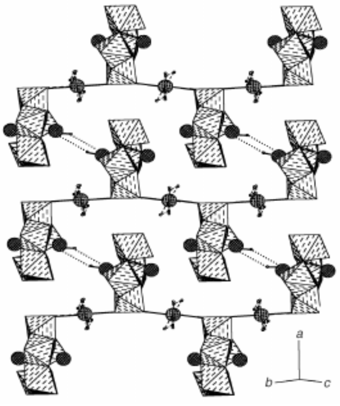

Fig. 2 A polyhedral and ball-and-stick representation of **2** showing (i) the connectivity between the $[Mo_5P_2O_{22}(OH_2)]^{4-}$ clusters and $\{Cu(en)_2O_2\}^{2+}$ octahedra; (ii) the packing and orientation of the $[\{Cu(en)_2\}Mo_5P_2O_{22}(OH_2)]^{2-}$ chains and the pseudo-layers formed as a result of interchain interactions. Octahedra represent Mo atoms. P and Cu atoms are shown by large heavy-crossed and heavy-shaded circles.

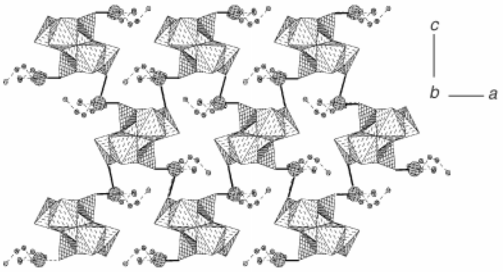

Fig. 3 A polyhedral and ball-and-stick representation of the $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]$ layer of **3** showing the connectivity between the $[Mo_5P_2O_{23}]^{6-}$ clusters and $\{Cu(en)(Hen)O_2\}^{3+}$ square pyramids and the 12-membered rings. Octahedral and tetrahedra represent Mo and P atoms respectively. Cu atoms are shown by large dotted circles.

participated in forming $\{Cu(en)\}^{2+}$ building blocks and (ii) the connectivity between $[Mo_5P_2O_{23}]^{6-}$ clusters and $\{Cu(en)\}^{2+}$ groups, namely, PO–Cu in **1** and MoO–Cu in **2**. The packing of chains gives rise to an elongated cylindrical unit in **1** and pseudo-layers in **2**. We believe that the strong coordination effect of F^- ions plays a role in controlling the reaction between Cu^{2+} center and the N donors of en molecules, and between Cu^{2+} center and the O donors of $[Mo_5P_2O_{23}]^{6-}$ clusters or H_2O molecules.

The solid architectures of **1** and **2** provide examples of different ways of connecting $[Mo_5P_2O_{23}]^{6-}$ clusters and $\{Cu(en)\}^{2+}$ groups. It suggests that further condensation of $[Mo_5P_2O_{23}]^{6-}$ clusters into higher dimensional solids through the linkage of $\{Cu(en)\}^{2-}$ groups could be feasible. Reducing the initial Mo/Cu and Mo/en ratios results in the successful crystallisation of solid **3**. The structure of $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]\cdot 3H_2O$ **3**§ is constructed from $[Mo_5P_2O_{23}]^{6-}$ clusters[11] linked through $\{Cu(en)(Hen)\}^{3+}$ groups into two-dimensional layers of $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]$ as shown in Fig. 3. Each $[Mo_5P_2O_{23}]^{6-}$ cluster is bonded to four $\{Cu(en)(Hen)\}^{3+}$ groups through two PO_4 tetrahedra and two MoO_6 octahedra forming two pairs of covalent interactions of the types Cu–OP and Cu–OMo with Cu–O 1.952(2), 2.557(2) Å respectively. The Cu^{2+} center of $\{Cu(en)(Hen)O_2\}^{3+}$ square pyramid receives contributions from three nitrogen donors belonging to one and half en molecules, one oxygen donor from a PO_4 unit and one oxygen donor from a MoO_6 unit with Cu–N 1.991(3), 2.011(3), 2.020(3) Å and Cu–O 1.952(2), 2.557(2) Å. This results in the 12-membered rings $(Mo_4P_4Cu_4)$ of the $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]$ layers of **3**. Adjacent $[\{Cu(en)(Hen)\}_2Mo_5P_2O_{23}]$ layers are separated by H_2O molecules with small interlamellar separation owing to the presence of extensive network of H-bonds. The coexistence of Cu–OP and Cu–OMo linkages plays a critical role in constructing the layer structure of **3** which contrast strikingly to the Cu–OP and Cu–OMo linkages in building up the chain structures of **1** and **2** respectively.

The successful isolation of solids **1**–**3** provides novel examples of assembling phosphomolybdate clusters through the templating effects of $\{Cu(en)\}^{2+}$ groups for design of composite oxide materials. It demonstrates that the use of hydrothermal techniques is essential for the realisation of materials design. The dimensionality of solid architectures is, to certain degree, tailorable while the key leading to the success lies on the kinetic aspect of assembly process. While the mineralising mechanism of F^- ions remains debatable, its critical role in constructing solid architectures is manifest. The present study reveals the rich hydrothermal chemistry of the phosphomolybdate–Cu–en system and the structural versatility evolving from altering reaction kinetics. This highlights the feasibility of engineering metal–organoamine–phosphomolybdate solids with potentially interesting and useful properties.

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Notes and references

† *Synthesis*: hydrothermal reactions were performed in PTFE-lined stainless steel autoclave reactors (22 mL). Mole ratios of $MoO_3\cdot H_2O$, H_3PO_4 (85 mass%), $CuSO_4\cdot 5H_2O$, en, H_2O, F^- are 3 : 4 : : 2.3 : 500 : 13.3 for **1**, 4.3 : 6.4 : 1 : 3.4 : 1730 : 0 for **2** and 1 : 2.3 : 1.8 : 3.8 : 460 : 0 for **3**.

‡ *Powder XRD data*: *in situ* PXRD patterns were collected on a Siemens D5005 diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å). Heating was conducted in the temperature range RT–1000 °C under vacuum.

§ *Crystal data*: $C_6H_{38}N_6CuMo_5P_2O_{28}$ **1**: M_w = 1247.60, monoclinic, space group *Cc*. a = 14.821(3), b = 14.419(3), c = 16.132(5) Å, β = 109.087(5)°, V = 3258.0(14) Å^3, Z = 4, D_c = 2.544 g cm^{-3}, μ = 2.716 mm^{-1}, T = 296 K. R_1 = 0.0267 for 3222 reflections. $C_6H_{32}N_6CuMo_5P_2O_{25}$ **2**: M_w = 1193.56, triclinic, space group $P\bar{1}$. a = 10.6813(14), b = 11.176(2), c = 12.852(2) Å, α = 75.568(13), β = 89.297(6), γ = 86.545(8) °, V = 1483.1(4) Å^3, Z = 2, D_c = 2.673 g cm^{-3}, μ = 2.969 mm^{-1}, T = 296 K. R_1 = 0.0496 for 5138 reflections. $C_4H_{20}N_4CuMo_{2.5}PO_{13}$ **3**: M_w = 666.60, orthorhombic, space group *Ibca*. a = 11.478(4), b = 39.171(8), c = 15.226(6) Å, V = 6845(4) Å^3, Z = 16, D_c = 2.587 g cm^{-3}, μ = 3.190 mm^{-1}, T = 296 K. R_1 = 0.0246 for 3006 reflections. The structures were solved by direct methods and refined using full-matrix least squares on F^2 using SHELXTL. The H_2O molecules of **2** and the C and N atoms of the en molecules of **2** and **3** are disordered. CCDC 182/1089. See http://www.rsc.org/suppdata/cc/1998/2733/ for crystallographic files in .cif format.

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