

Hydrothermal synthesis and structure of a three-dimensional open-framework cobalt molybdenum(vi) phosphate containing ethylenediammonium ions: $(C_2H_9N_2)_6[Co_3Mo_4P_4O_{28}]$

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The first microporous cobalt molybdenum(vi) phosphate, crystallised under hydrothermal conditions, is constructed from unique $CoMo_2P$ tetrahedral units connected by CoO_4 tetrahedra and by sharing corners; the framework contains interlocking cavity units and unusual 7-ring intersecting channels that are filled with charge-compensating ethylenediammonium ions.

While the synthesis and characterisation of three-dimensional framework aluminosilicate zeolites¹ and aluminophosphate materials² has been an actively pursued area of materials chemistry, only in recent years have other open-framework inorganic materials started to emerge. The driving force behind the effort is to engineer open-framework materials with desired chemical and catalytic reactivities. One of the strategies adopted is to incorporate d-block elements into these materials as stoichiometric framework constituents through the combined effects of hydrothermal synthesis and amine templates. Practicing this strategy results in the successful synthesis of open-framework reduced molybdenum phosphates,³ mixed valent molybdenotungsten phosphates,⁴ vanadium phosphates,⁵ cobalt phosphates,⁶ vanadium oxides,⁷ non-oxide solids⁸ and a number of layered molybdenum(vi) solids.⁹ However, three-dimensional open-framework molybdenum(vi) solids remain largely unexplored except for a hexagonal molybdenum trioxide phase.¹⁰

In the course of our investigation on the synthesis of molybdenum(vi) polyoxoanion based solid materials, we have hydrothermally synthesised a series of novel one- and two-dimensional organically templated solids.¹¹ Extending this idea, we explored the incorporation of 'heteroatoms' as tetrahedral tethers and applied the 'magic' F^- mineraliser¹² to assemble molybdenum(vi) polyoxoanions forming three-dimensional open frameworks. Here, we report the synthesis and structural characterisation of the first open-framework cobalt molybdenum phosphate with entrenched charge-compensating ethylenediammonium ions, $(C_2H_9N_2)_6[Co_3Mo_4P_4O_{28}]$ **1**.

Compound **1** was prepared from the hydrothermal reaction of $CoCl_2 \cdot 6H_2O$, $MoO_3 \cdot H_2O$, H_3PO_4 (85 mass%), NaF, ethylenediamine and H_2O in a mole ratio of 1 : 2.2 : 3.3 : 3.1 : 1.2 : 407. Ethylenediamine was introduced at the last stage into the clear solution of $CoCl_2 \cdot 6H_2O$, $MoO_3 \cdot H_2O$, H_3PO_4 , NaF and H_2O resulting in a pinkish slurry. Crystallisation was carried out in a sealed Teflon-lined stainless-steel autoclave reactor at 160 °C and autogenous pressure for 3 days. The presence of NaF was found to be critical for the successful synthesis of **1**. The use of $Co(NO_3)_2 \cdot 6H_2O$ instead of $CoCl_2 \cdot 6H_2O$ resulted in the crystallisation of the same product **1**. The chemical analysis in combination with the single crystal X-ray structure determination[‡] and thermogravimetric analysis confirmed the chemical formula of $C_3H_{13.5}N_3Co_{0.75}MoPO_7$ and the absence of F^- ions from the crystal structure of **1**. Simultaneous TG/DT analysis and *in-situ* powder XRD studies[§] indicated that ethylenediamine can be removed at 360 °C and the structure of **1** remained intact until *ca.* 700 °C. By replacing the heteroatom Co^{2+} with Al^{3+} and Zn^{2+} , a few new organic/MoPO hybrid phases

crystallised as identified by both the single and powder X-ray diffraction methods. One of the organic/MoPO hybrid phases, $(C_2N_2H_{10})_2[Mo_5P_2O_{22}] \cdot H_2O$, crystallised in monoclinic symmetry.[¶]

As shown in Fig. 1, the three-dimensional framework of **1** is constructed from the unique $CoMo_2P$ pseudo-tetrahedral building units (Fig. 1 inset) which consist of crystallographically independent one MoO_6 octahedron, one PO_4 tetrahedron and a half CoO_6 octahedron. The $CoMo_2P$ units are linked into a covalently bonded three-dimensional framework through (i) direct and (ii) indirect connection modes as shown in Fig. 2(a). The direct connection mode refers to the connection between two adjacent $CoMo_2P$ units by corner-sharing Mo and Co atoms. The indirect connection mode refers to the connection of four 4₁-screw-axis-related $CoMo_2P$ units, each linking to a common CoO_4 tetrahedron *via* a corner-shared oxygen atom from PO_4 of the respective $CoMo_2P$ unit. This gives rise to two cavity units, A and B, of **1** as shown in Fig. 2(b). The cavity A is circumscribed by four MoO_6 , four CoO_6 , four PO_4 and two CoO_4 units and contains four identical 3- and 7-ring windows. In the cavity B, five MoO_6 , five PO_4 , two CoO_6 and two CoO_4 units are linked up *via* corner-shared oxygen atoms forming one 8-ring window, three distinct 3-ring windows and three 7-ring windows of two distinct types (I: $Mo_2Co_3P_2$ and II: $Mo_3Co_2P_2$). The cavities A and B are interlocked by a single 7-ring window encircled by one CoO_4 , two PO_4 , two MoO_6 and two CoO_6 units (highlighted). The three-dimensional framework of **1** can also

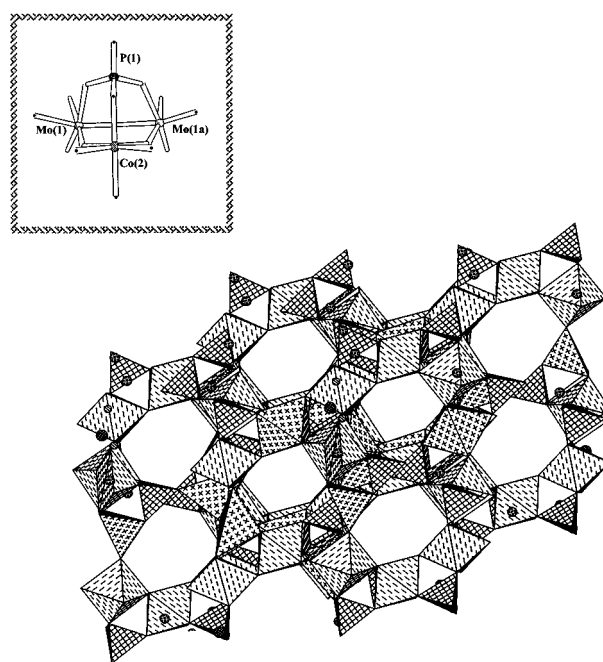


Fig. 1 A polyhedral view of $(C_2H_9N_2)_6[Co_3Mo_4P_4O_{28}]$ **1** showing the intersecting 7-ring channels. Inset shows the $CoMo_2P$ tetrahedral unit.

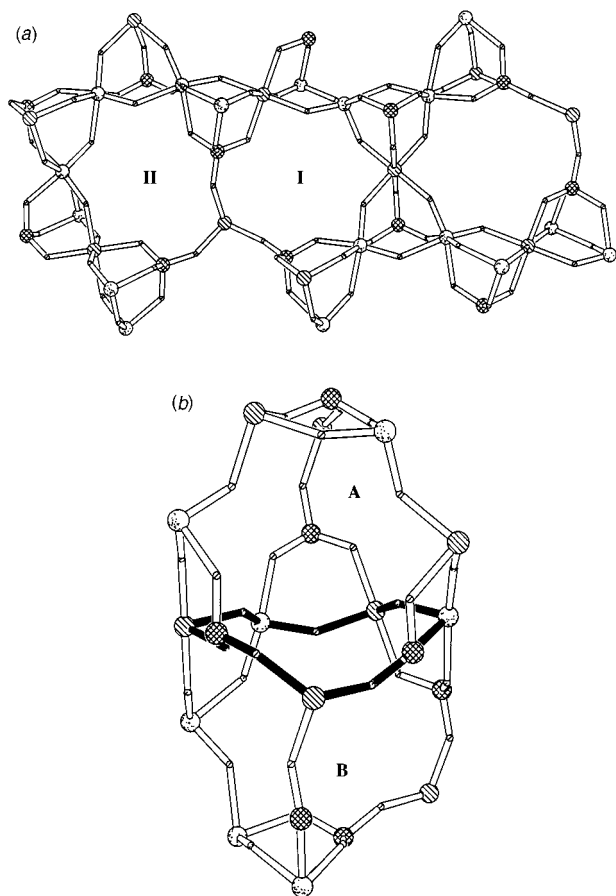


Fig. 2 (a) A general view of $(\text{C}_2\text{H}_5\text{N}_2)_6[\text{Co}_3\text{Mo}_4\text{P}_4\text{O}_{28}]$ **1** showing the two types of connection modes of the CoMo_2P units and two types of 7-ring windows. (b) A view of interlocked cavities **A** and **B** by a single 7-ring window (with highlighted bonds) showing the 3-, 7- and 8-ring windows. The atoms shown are: dotted circles for Mo, cross-hatched circles for P, shaded circles for Co and small circles for O.

be envisioned as being built up in space group $I4_1/a$ from the aforementioned interlocking cavity units [**A** + **B**] by sharing the CoMo_2P units. Two types of intersecting 7-ring channels are formed in the so-packed cobalt molybdenum phosphate framework as shown in Fig. 1 and 2(a).

The 7-ring channels of **I** are filled with partially protonated ethylenediamine molecules. The ethylenediammonium ions interact with the framework through contacts between the N atoms of the ethylenediammonium ions and the O atoms of the framework with $\text{N}(\text{H})\cdots\text{O}$ 2.82–2.94 Å. One of the two nitrogen atoms of the ethylenediammonium ion is found to be involved in the $\text{N}(\text{H})\cdots\text{O}$ interactions, supporting the assignment of partial protonation of ethylenediamine molecules. However, uncertainty is encountered in locating H atoms attached to the N atoms due to the severe disordering of the ethylenediammonium ions in the crystal packing of **1**.

The asymmetric unit of **1** consists of one MoO_6 octahedron, one PO_4 tetrahedron, a half CoO_6 octahedron, a quarter CoO_4 tetrahedron, and one and a half ethylenediammonium ions. The coordination geometry of the three framework atoms, Mo, P and Co, is exclusively defined by unsymmetrically corner-shared oxo groups. The geometric parameters of the cobalt molybdenum phosphate framework which are reasonably well determined (data:parameters ratio *ca.* 10:1) show that the Mo–O contacts are in the range 1.767(3)–2.198(3) Å, the P–O contacts in the range 1.517(4)–1.556(3) Å, the Co(1)–O contact 1.928(4) Å (tetrahedral Co, T_{Co}) and the Co(2)–O contacts in the range 2.066(3)–2.102(3) Å (octahedral Co, O_{Co}). The P–O and Co–O (at both T_{Co} and O_{Co} sites) contacts are within the expected range.^{6a,13} The molybdenum site exhibits short-to-medium

bond length pattern regardless of the absence of terminal oxo groups which is not uncommon to molybdenum(vi) oxides containing unsymmetrical bridging oxo groups.¹⁴ This may also be attributed to the existence of moderate hydrogen bonds involving some of the O atoms of the MoO_6 units.

The cobalt molybdenum phosphate **1** reported here represents the first successful synthesis and characterisation of covalently bonded three-dimensional open-framework structure in the metal molybdenum(vi) phosphate compositional domain. The enhanced solvating effect of water and mineralising effect of F^- under the hydrothermal autogenous conditions evidently provide the environment required for the assembly of an open-framework from molecular precursors. It opens up the possibility of applying this method for assembling other three-dimensional metal molybdenum phosphates with potentially interesting or useful properties.

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Notes and References

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‡ *Crystal data* for $(\text{C}_2\text{H}_5\text{N}_2)_6[\text{Co}_3\text{Mo}_4\text{P}_4\text{O}_{28}]$ **1**: $\text{C}_3\text{H}_{13.5}\text{N}_3\text{Co}_{0.75}\text{MoPO}_7$, $M_w = 374.78$, tetragonal, space group $I4_1/a$, $a = 17.163(2)$, $c = 10.764(2)$ Å, $V = 3170.7(9)$ Å³, $Z = 16$, $D_c = 3.140$ g cm⁻³, $\mu = 3.40$ mm⁻¹, $T = 296$ K, dark blue prism, crystal size *ca.* 0.15 × 0.10 × 0.08 mm, and max., min. peak on final Fourier difference map 0.647, -0.994 e Å⁻³ respectively. Intensity data were collected by $\theta/2\theta$ scans on a Siemens P4 X-ray diffractometer with graphite-monochromated Mo-K α radiation. Empirical absorption corrections were made from ψ -scan data using an applied program at the data reduction stage along with the correction of Lorentz and polarization factors. The structure was solved by direct methods and refined using full-matrix least squares on F^2 using the SHELXTL-PLUS package. The final refinement was based on 1384 reflections with $I > 2.0\sigma(I)$ for 135 parameters and converged to $R_1/wR_2 = 0.0303/0.0742$ ($R_1/wR_2 = 0.0388/0.0896$ for all data). CCDC 182/933.

§ *Powder XRD data*: *in situ* XRD patterns were collected on a Siemens D5005 diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.5406$ Å). Heating was conducted in the temperature range room temp.–1000 °C under vacuum.

¶ *Crystal data* for the monoclinic $(\text{C}_2\text{N}_2\text{H}_{10})_2[\text{Mo}_5\text{P}_2\text{O}_{22}]\cdot\text{H}_2\text{O}$ phase: $M_w = 1035.9$, space group $C2/c$ with unit cell dimensions $a = 17.642(4)$, $b = 10.039(2)$, $c = 13.777(3)$ Å, $\beta = 96.92(3)^\circ$, $V = 2422.4(8)$ Å³.

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