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Crystal structure of a three-dimensional supramolecular architecture with copper molybdenum phosphate and piperazines

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A new copper molybdenum phosphate with a three-dimensional supramolecular framework has been prepared by hydrothermal synthesis and characterised by single crystal X-ray analysis.

Molybdenum phosphate is of interest in terms of catalysis, sorption, and electrical conductivity.[1,2] A new efficient method for the preparation of molybdenum phosphate is to introduce an organic component into an inorganic material.[3] Self-assembly of metal atoms and an organic amine or organophosphonate with $\{Mo_6P_4\}$ clusters resulted in remarkable diverse structures from 1D[4–11] or 2D[12,13] to 3D[14–16] frameworks. By this method, we have successfully synthesised the molybdenum phosphates $[Co(en)_3][C_4H_{12}N_2]_{0.5}[(Mo_5O_{15})(HOPO_3)_2]\cdot 3H_2O$ and $(C_4N_2H_{10})_5[Co_3Mo_{12}O_{18}(HOPO_3)_6(PO_4)_2(OH)_{12}(H_2O)_4]\cdot 9H_2O$.[17]

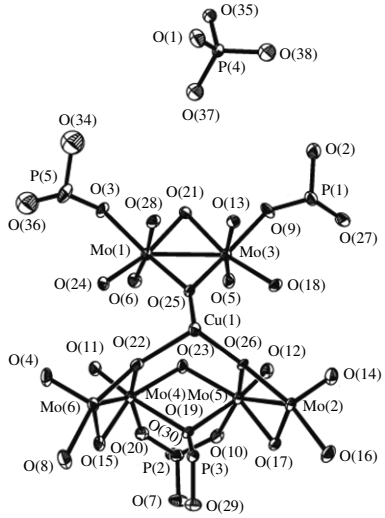

Figure 1 Asymmetry structures of the $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ cluster and the HPO_4^{2-} anion, showing the coordination environments and the atom-labeling scheme (30% probability displacement ellipsoids, H atoms have been omitted for clarity).

Copper atoms have not been incorporated into sandwich $M\{Mo_6P_4\}_2$ (M = Na, Fe, Co, Ti, Cr, Zn or Mn) clusters.[4–19] Here, we report a copper molybdenum phosphate, $(C_4N_2H_{12})_6[CuMo_{12}O_{24}(OH)_6(HPO_4)_6(PO_4)_2](HPO_4)\cdot 5H_2O$ **1**,[†] which possesses a three-dimensional framework by hydrogen bonding interactions among $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ clusters, protonated piperazine cations and lattice water molecules.

The simulation of single-crystal X-ray diffraction data corresponds to the experimental X-ray powder diffraction data (Figure S1[‡]). The IR spectrum of **1** exhibits an absorption band at 949 cm^{-1}, which is characteristic of ν(Mo=O), and bands at 735 and 1024 cm^{-1}, which are attributed to ν(Mo–O–Mo) and ν(P–O), respectively. A series of bands at 1454–1317 cm^{-1} are assigned to C–C and C–N stretching vibrations of protonated piperazine cations. A strong band at 3435 cm^{-1} was attributed to ν(O–H), and it indicates hydrogen bonding interactions in **1** (Figure S2[‡]).

Single crystal X-ray structural analysis[§] of **1** revealed the formula $(C_4N_2H_{12})_6[CuMo_{12}O_{24}(OH)_6(HPO_4)_6(PO_4)_2](HPO_4)\cdot 5H_2O$. The structure of **1** consists of $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ clusters, HPO_4^{2-} anions, protonated piperazine cations and lattice water molecules. The coordination environments and the atom-labeling scheme for the asymmetry structure of the $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ cluster is shown in Figure 1. The six Mo atoms in the $[Mo_6P_4O_{25}(OH)_6]^{6-}$ cluster, lying nearly in a plane and connected by 12 bridging O atoms, form a six-membered ring. Among the four PO_4 groups in this cluster, three HPO_4 tetrahedra lie on the periphery of the ring and the last one occupies the central position. All of the four PO_4 groups are on the same side of the plane defined by the six Mo atoms. Six Mo atoms are coordinated to oxygen atoms with Mo–O distances of 1.665(7)–2.300(7) Å and O–Mo–O band angles of 72.3(3)–171.3(3)°. There exist three short Mo–Mo contacts in the range 2.5746(12)–2.5958(12) Å. Four P atoms have P–O bond lengths in the range 1.467(10)–1.560(8) Å and O–P–O band angles in the range 105.6(5)–112.3(7)°.

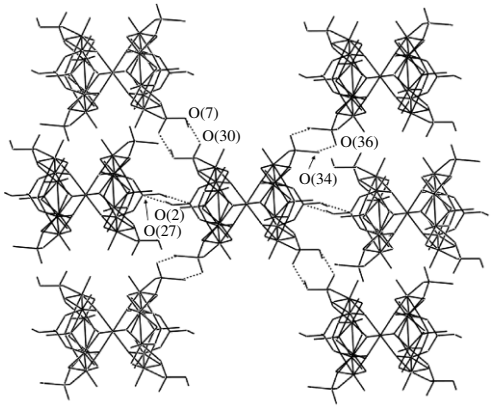

Figure 2 Connection of the $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ cluster with six adjacent clusters by 12 P–O···O strong hydrogen bonding interactions.

The dissociative HPO_4^{2-} anions in **1** are disordered. As far as we know, there are rare reports on reduced molybdenum phosphate with extra phosphonate groups. In $[Et_4N]_6[Na_{14}Mo_{24}P_{17}O_{97}(OH)_{31}]\cdot\chi H_2O$, the extra H_3PO_4 group as a unique centre is hydrogen bonded to the other phosphates.[21] In $Na_{15}Mn_{10}[(HPO_4)(PO_4)_3Mo_6O_{12}(OH)_3]_4(PO_4)\cdot 48H_2O$, the extra PO_4 group, lying on a $\bar{4}$ axis, besides the four phosphate groups, constitutes the P_4Mo_6 anion and thus plays a key role as a structure-directing agent.[16] While in **1**, the dissociative HPO_4^{2-} anions connect with a protonated piperazine cation by three hydrogen bonding interactions [N(2)–H(2D)···O(38) ($-x+1/2$, $-y+1/2$, $-z+1$), 2.75(2) Å; N(2)–H(2D)···O(35) ($x+1/2$, $-y+1/2$, $z-1/2$), 2.635(17) and N(5)–H(5D)···O(37), 2.518(18) Å].

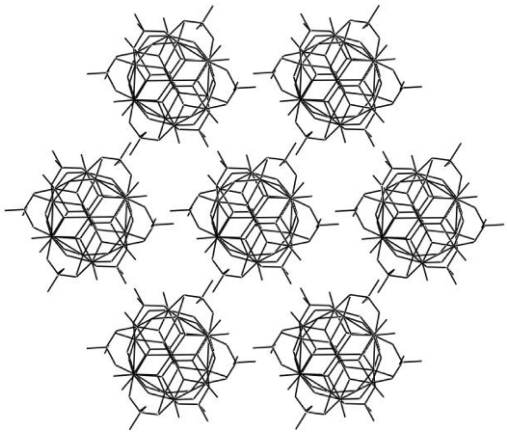

Figure 3 Crystal packing diagram of **1** viewed perpendicular to the [1 0 –1] plane showing delimits channels of the three-dimensional supramolecular architecture (HPO_4^{2-} anions, protonated piperazine cations and lattice water molecules are omitted for clarity).

[†] Compound **1** was obtained from a mixture of Mo, $Cu(OAc)_2\cdot H_2O$, H_3PO_4, $C_4N_2H_{10}$ and H_2O with a molar ratio of 1:2:30:22:500. It was heated in a Teflon-lined stainless steel autoclave at 140 °C for 96 h. After the autoclave was cooled down to room temperature for 12 h, the black block crystals were obtained. The crystals were washed with distilled water, filtered off and dried at room temperature (~70% yield based on Mo). Found (%): C, 8.83; H, 5.87; N, 5.26. Calc. for $C_{24}H_{95}N_{12}O_{71}P_{10}Cu$ (%): C, 9.10; H, 6.00; N, 5.31.

[‡] *Supplementary materials available:* Comparison of simulated and experimental powder diffraction patterns for 1 (Figure S1) and IR spectrum of 1 (Figure S2). This material is available free of charge *via* http://www.turpion.org/suppl/mc/2109/suppl2109.pdf

[§] The X-ray data were collected on a Rigaku RAXIS-RAPID diffractometer at 293 K. The structures were solved by a direct method and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. All of the crystallographic calculations were performed with the SHELXL-97 program.[20]

Crystal data for **1**: $C_{24}H_{95}CuMo_{12}N_{12}O_{71}P_9$, $M_r = 3181.53$, crystal size 0.2×0.19×0.06 mm, monoclinic, space group C_2/c, $a = 26.354(2)$, $b = 20.0290(19)$ and $c = 16.3822(17)$ Å, $\beta = 105.311(6)°$, $V = 8340.4(13)$ Å^3, $Z = 4$, $d_{calc} = 2.520$ g cm^{-3}, $2\theta_{max} = 54.84°$, MoKα ($\lambda = 0.71073$ Å), $\mu = 2.289$ mm^{-1}, $\omega/2\theta$ scans, $T = 293$ K, 8937 independent reflections, 6012 observed reflections [$I > 2.0\sigma(I)$], $R_{int} = 0.0629$, 598 refined parameters, $R_1 = 0.0696$, $R_w = 0.1006$, $\Delta\rho_{max} = 2.437$ eÅ^{-3}, $\Delta\rho_{min} = -3.195$ eÅ^{-3}.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 250412. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

In the structure of **1**, each $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ cluster connects six adjacent clusters through twelve P–O···O strong hydrogen bonding interactions [O(2)–H(2)···O(27) (*–x*, *–y*, *–z* + 1), 2.506(11) Å; O(7)–H(7)···O(30) (*–x* + 1, *–y*, *–z* + 1), 2.544(10) Å and O(34)–H(34)···O(36) (*–x* + 1/2, *–y* + 1/2, *–z* + 2), 2.690(18) Å] (Figure 2). The resulting three-dimensional supramolecular architecture delimits channels perpendicular to the [1 0 –1] plane (Figure 3). A noteworthy structural feature of **1** is that the supramolecular architecture is formed through strong hydrogen bonds among the adjacent $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ clusters. While in other three molybdenum phosphates[14,16,17] constructed from $M\{Mo_6P_4\}$ clusters, the clusters are connected through transition metal cations in the mononuclear or dimer form by covalent bonds. The structure of **1** is also stabilised by multipoint hydrogen bonding interactions among $Cu[Mo_6P_4O_{25}(OH)_6]_2^{10-}$ clusters, protonated piperazine cations and lattice water molecules.

In summary, a copper molybdenum phosphate has been synthesised under hydrothermal conditions. The result shows that the introduction of organic components into molybdenum phosphate is an interesting exploration for novel supramolecular architectures.

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References

1 R. C. Haushalter and L. A. Mundi, *Chem. Mater.*, 1992, **4**, 31.
2 P. J. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2638.
3 M. Lowe, J. Lockhart, G. Forsyth, W. Chegg and K. Fraser, *J. Chem. Soc., Dalton Trans*., 1995, 145.
4 R. C. Haushalter and F. W. Lai, *Inorg. Chem*., 1989, **28**, 2904.
5 G. Cao, R. C. Haushalter and K. G. Strohmaier, *Inorg. Chem*., 1993, **32**, 127.
6 P. Lightfoot and D. Masson, *Mater. Res. Bull*., 1995, **30**, 1005.
7 P. Lightfoot and D. Masson, *Acta Crystallogr*., 1996, **C52**, 1077.
8 Y. S. Zhou, L. J. Zhang, X. Z. You and S. Natarajan, *Int. J. Inorg. Mater*., 2001, **3**, 373.
9 Y. S. Zhou, L. J. Zhang, X. Z. You and S. Natarajan, *Inorg. Chem. Commun*., 2001, **4**, 699.
10 Y. S. Zhou, L. J. Zhang, H. K. Fun, J. L. Zuo, I. Abdul Razak, S. Chantrapromma and X. Z. You, *New J. Chem*., 2001, **25**, 1342.
11 M. Yuan, E. Wang, Y. Lu, Y. Li, C. Hu, N. Hu and H. Jia, *Inorg. Chem. Commun*., 2002, **5**, 505.
12 L. A. Mundi and R. C. Haushalter, *Inorg. Chem*., 1992, **31**, 3050.
13 M. Yuan, E. Wang, Y. Lu, Y. Li, C. Hu, N. Hu and H. Jia, *J. Solid State Chem*., 2003, **170**, 192.
14 L. A. Mundi and R. C. Haushalter, *Inorg. Chem*., 1993, **32**, 1579.
15 A. Leclaire, C. Biot, H. Rebbah, M. M. Borel and B. Raveau, *J. Mater. Chem*., 1998, **8**, 439.
16 C. D. Peloux, P. Mialane, A. Dolbecq, J. Marrot, E. Riviere and F. Secheresse, *J. Mater. Chem*., 2001, **11**, 3392.
17 X. He, P. Zhang, T. Y. Song, Z. C. Mu, J. H. Yu, Y. Wang and J. N. Xu, *Polyhedron*, 2004, **23**, 2153.
18 L. Xu, Y. Sun, E. Wang, M. Li, C. Hu and R. Huang, *J. Chem. Crystallogr*., 2000, **30**, 721.
19 L. Xu, Y. Sun, E. Wang, E. Shen, Z. Liu, C. Hu, Y. Xing, Y. Lin and H. Jia, *J. Mol. Struct*., 2000, **519**, 55.
20 G. M. Sheldrick, *SHELXL-97: A Program for Crystal Structure Determination*, University of Göttingen, Germany, 1997.
21 R. C. Haushalter and F. W. Lai, *Angew. Chem., Int. Ed. Engl*., 1989, **28**, 743.

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