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# Coordination polymer $\{[Cu(im)_2]_3K[\beta\text{-}Mo_8O_{26}]\}_n$

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The new 1-D coordination polymer $\{[Cu(im)_2]_3K[\beta\text{-}Mo_8O_{26}]\}_n$ with modified $[Mo_8O_{26}]^{4-}$ polyanions is hydrothermally prepared and characterised by single-crystal crystallography.

Polyoxometalates are of interest because of their possible applications in catalysis, separation, medicine and materials science.[1–4] A synthetic approach to them and the concerning process have been described as self-assembly.[5–8] Organic molecules or coordination complexes may function in new materials as (1) charge-compensating units; (2) covalently bound subunits of a metal oxide framework and (3) inorganic bridges linking polyanion clusters into infinite extended networks.[7–12] Of polyoxometalates, the octamolybdate family with a variety of structural isomers including α, β, γ, η, ε, and $[\delta\text{-}Mo_8O_{26}]^{4-}$ is of special interest. Based on such isomers and organic molecules or metal complex moieties, many new organic-inorganic hybrid solids have been constructed such as the γ-form in $[Me_3N(CH_2)_6NMe_3]_2[\gamma\text{-}Mo_8O_{26}]$ and the β-form in $[NH_4]_2\{Gd[DMF]_7\}[\beta\text{-}Mo_8O_{26}]$ and $[NH_4]_2\{La[DMF]_7\}[\beta\text{-}Mo_8O_{26}]$ *etc*.[13–20] We describe here the synthesis and structural characterization of compound $\{[Cu(im)_2]_3K[\beta\text{-}Mo_8O_{26}]\}$ **1**, exhibiting 1-D polymeric structure with naked $[\beta\text{-}Mo_8O_{26}]^{4-}$ and highly modified $[\beta\text{-}Mo_8O_{26}]^{4-}$ units.

Although compounds from $[Mo_8O_{26}]^{4-}$ clusters and other constituents are numerous, the molecular modification of their surfaces with metal complexes to such an extent has never been attained. Compound **1**[†] confirms the possibility of using their surfaces and may give insight into the current use of polyoxometalates for environmentally benign catalysis and advanced materials.[21,22]

The single-crystal X-ray diffraction analysis[‡] reveals that compound **1** displays a novel 1-D polymeric structure composed of imidazole molecules, potassium ions, cuprous ions and $[Mo_8O_{26}]^{4-}$ polyanions. As shown in Figures 1 and 2, the $[Mo_8O_{26}]^{4-}$ polyanion contains eight edge-sharing $[MoO_6]$ octahedra, exhibiting the characteristic β-octamolybdate arrangement, a classical isomer of octamolybdate clusters, in which two centro-symmetrical cyclic $[Mo_4O_{13}]$ units are cross-bridged with oxygen atoms. All the molybdenum sites exhibit an octahedral coordination

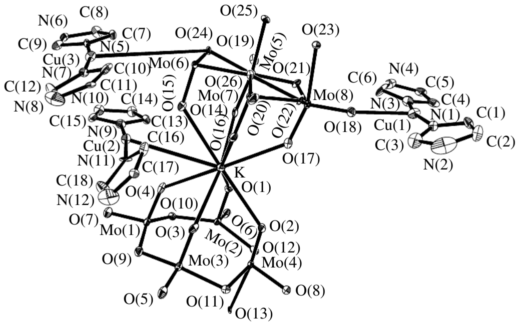

**Figure 1** Crystallographically independent unit of compound **1**. For selected bond lengths and angles see Online Supplementary Materials.

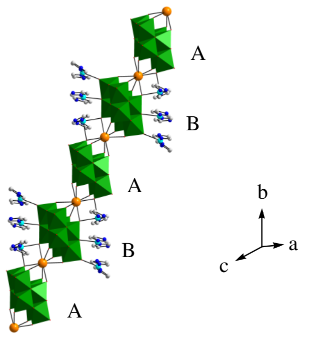

**Figure 2** Polyhedral representation of compound **1**.

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[†] Compound **1** was synthesised by a hydrothermal method with a mixture of $CuCl\cdot 2H_2O$ (1.10 g), $MoO_3$ (3.52 g), imidazole ($C_3H_4N_2$, 0.40 g), KOH (0.70 g) and distilled water (20 ml) in a 30 cm$^3$ Teflon-lined reactor. The solution was sealed and heated to 150 °C for 80 h under autogenus pressure. The obtained brown crystals were isolated from the slurry of the products and washed with distilled water (yield 25% based on imidazole). The XPS spectra show the chemical shifts 932.0 eV for Cu$^{I}$ ($2p_{3/2}$) and 232.9 for Mo$^{VI}$ ($3d_{5/2}$). The EPR measurement exhibits no signal. FTIR spectra (KBr pellets, $\nu$/cm$^{-1}$): 3237.27 (m), 3134.66 (m), 2957.54 (w), 1619.59 (m), 1540.16 (m), 1503.52 (m), 1430.05 (m), 1325.46 (m), 1261.18 (m), 1183.20 (w), 1136.96 (w), 1098.80 (s), 943.03 (vs), 910.22 (vs), 834.25 (vs), 708.74 (vs), 651.55 (vs), 571.55 (m), 553.57 (m), 517.32 (m), 476.01 (m). Bands at 500–960 cm$^{-1}$ belong to the Mo=O and Mo–O–Mo vibrations, and in the ranges 1100–1650 and 2900–3500 cm$^{-1}$ are ascribed to the organic ligands. Found (%): C, 11.90; H, 1.44; N, 9.29; Cu, 46.30; Mo, 42.34; K, 2.14. Calc. for $KMo_8O_{26}Cu_3C_{18}H_{24}N_{12}$ (%): C, 11.86; H, 1.31; N, 9.22; Cu, 46.34; Mo, 42.13; K, 2.15.

[‡] *Crystal data for* **1**: $KMo_8O_{26}Cu_3C_{18}H_{24}N_{12}$, $F_w$ = 1821.73, triclinic, space group $P\bar{1}$, $a$ = 12.614(3), $b$ = 13.824(3) and $c$ = 13.983(3) Å, $\alpha$ = = 89.79(3)°, $\beta$ = 79.34(3), $\gamma$ = 63.57(3)°, $V$ = 2137.0(7) Å$^3$, $Z$ = 2, $d_{calc}$ = = 2.831 g cm$^{-3}$, $\mu$ = 3.921, $F$(000) = 1732, crystal size of 0.15×0.20×0.23 mm. Data collection were performed with MoK$\alpha$ radiation ($\lambda$ = 0.71073 Å) on a Bruker Smart 1000 diffractometer equipped with a CCD camera. The $\omega$–$\varphi$ scan technique was used. In the $\theta$ range of 1.49 to 25.02°, a total of 13172 (7499 unique, $R_{int}$ = 0.0458) reflections were measured. The structure was solved by the direct methods with full-matrix least-squares technique (SHELXL-97). All of non-hydrogen atoms were refined anisotropically giving the final $R_1$ = 0.0599, $wR_2$ = 0.1623.

CCDC 676338 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2008.

geometry. The oxygen atoms in the $[Mo_8O_{26}]^{4-}$ units can be divided into four groups, *i.e.*, the 7×2 terminal atoms, 3×2 $\mu_2$-O atoms, 2×2 $\mu_3$-O atoms and 2×1 $\mu_5$-O atoms. The Mo–O bond distances fall into four groups in the ranges of 1.686(8)–1.716(8), 1.713(8)–2.263(7), 1.942(7)–2.337(7), 2.310(7)–2.476(7) Å, and the mean values are 1.700, 1.918, 2.098 and 2.320 Å for naked $[Mo_8O_{26}]^{4-}$ unit. For the $[Cu(im)]_2^+$ complex cation surrounded $[Mo_8O_{26}]^{4-}$ unit, it is similar. The four groups of Mo–O distances are 1.686(8)–1.716(8), 1.760(8)–1.932(8), 1.918(7)–2.315 and 2.143(8)–2.458(8) Å, the mean values are 1.696, 1.943, 2.095 and 2.313 Å, respectively. All of the $MoO_6$ octahedra are severely distorted with strong interactions between the polyanions and the $[Cu(im)_2]^+$ complex cations. The bond valence calculation gives the values of molybdenum centres to be 6.05, 6.05, 6.05 and 6.04 for Mo(1), Mo(2), Mo(3) and Mo(4) and 6.05, 6.02, 6.05 and 6.04 for Mo(5), Mo(6), Mo(7) and Mo(8), respectively, all close to +6, showing that they are all at +6 oxidation states. No signal by EPR measurement and the XPS spectra are in agreement with this.

The $\mu_8$-$K^+$ ions locate at two opposite sites of the polyanion $[Mo_8O_{26}]^{4-}$. The related K–O bond distances are from 2.713 to 2.866 Å. In addition to the two end-potassium ions, one-$[Mo_8O_{26}]^{4-}$ unit links six $[Cu(im)_2]^+$ complex cations with six oxygen atoms, of which four are monodentate-bridged, the other two exhibit $\mu_2$-connecting mode. Thus, in a chain between two neighbour $[Mo_8O_{26}]^{4-}$ units there are one $\mu_2$-$[Cu(im)_2]^+$ cation and one $K^+$ ion. The $\mu_2$-$[Cu(im)_2]^+$ complex cations seat alternately at the two sides of a chain. Therefore, any chain contains two different states of $[Mo_8O_{26}]^{4-}$ units, as shown in Figure 2, of which one is naked, and another is surrounded by six $[Cu(im)_2]^+$ complex cations. Note that the electronegative and electropositive alternations may indicate significantly a unique chemistry of the polyoxometalates.

Figure 3 shows the packing of the compound along the *a* axis.

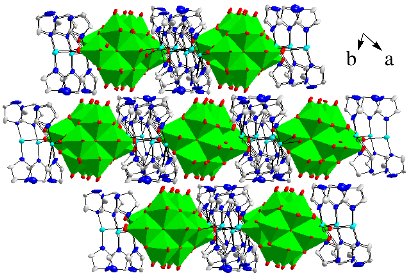

**Figure 3** Packing of compound **1**.

*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2008.05.007.

## References

1 M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer–Verlag, New York, 1983.
2 A. K. Cheetham, *Science*, 1994, **264**, 794.
3 P. Gouzerh and A. Proust, *Chem. Rev.*, 1998, **98**, 77.
4 A. Muller, F. Peters, M. T. Pope and D. Gatteschi, *Chem. Rev.*, 1998, **98**, 239.
5 D. Allis, R. Rarig, E. Burkholder and J. Zubieta, *J. Mol. Struct.*, 2004, **688**, 11.
6 D. Hagrman, P. Hagrman and J. Zubieta, *Inorg. Chim. Acta*, 2000, **212**, 300.
7 J. Greedan and J. Zubieta, *Inorg. Chem.*, 2002, **41**, 2124.
8 C. H. Springsteen, L. L. Johnston and R. L. LaDuca, *Solid State Sci.*, 2007, **9**, 804.
9 W. Yang, C. Lu and H. Zhuang, *J. Chem. Soc., Dalton Trans.*, 2002, 2879.
10 P. Hagrman, D. Hagrman and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2638.
11 A. F. Masters, S. F. Ghellu, R. T. Brownlee, M. Oconnor and A. G. Wedd, *Inorg. Chem.*, 1980, **19**, 3866.
12 M. T. Pope, *Prog. Inorg. Chem.*, 1991, **30**, 181.
13 X. Cui, K. Lu., Y. Fan., J. Xua, L. Ye, Y. Sun, Y. Lia, H. Yua and Z. Yi., *J. Mol. Struct.*, 2005, **743**, 151.
14 C. Wu, C. Lu, X. Lin, H. Zhuang and J. Huang, *Inorg. Chem. Commun.*, 2002, **5**, 664.
15 A. Kitamura, T. Ozeki and A. Yagasaki, *Inorg. Chem.*, 1997, **36**, 4275.
16 M. T. Pope and A. Muller, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 34.
17 M. L. Niven, J. J. Cruywagen and J. B. B. Heyns, *J. Chem. Soc., Dalton Trans.*, 1991, 2007.
18 R. Xi, B. Wang, K. Isobe, T. Nishioka, K. Toriumi and Y. Ozawa, *Inorg. Chem.*, 1994, **33**, 833.
19 R. S. Rarig, Jr. and J. Zubieta, *Polyhedron*, 2003, **22**,177.
20 R. S. Rarig and J. Zubieta, *Inorg. Chim. Acta*, 2001, **312**, 188.
21 M. Guo and H. Li, *Green Chem.*, 2007, **9**, 421.
22 M. Chisholm, *Chem. Rev.*, 2005, **105**, 2949.
23 N. E. Brese and M. O'Keeffe, *Acta Crystallogr.*, 1991, **B47**, 192.

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