metal-organic papers

A new hybrid Keggin-type molybdophosphate: (H$_2$phen)[Cu(phen)$_2$][PMo$_{12}$O$_{40}$]

Ming-Xue Li, Li Yu, Dong-Qin Bi and Jing-Ping Wang*

Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng, Henan 475001, People's Republic of China

Correspondence e-mail: jpwang@henu.edu.cn

An organic–inorganic hybrid compound constructed from a Keggin-type molybdophosphate polyoxoanion, a Cu^I coordination cation and a protonated 1,10-phenanthroline subunit, namely 1,10-phenanthrolinium bis(1,10-phenanthroline)-copper(I) dodecamolybdophosphate, (C$_{12}$H$_{10}$N$_2$)-[Cu(C$_{12}$H$_8$N$_2$)$_2$][PMo$_{12}$O$_{40}$] or (H$_2$phen)[Cu(phen)$_2$]-[PMo$_{12}$O$_{40}$], has been prepared under hydrothermal conditions and structurally characterized by single-crystal X-ray diffraction. The polyoxoanion is constructed from a central PO$_4$ tetrahedron which shares its O atoms with four {Mo$_3$O$_{16}$} trinuclear groups, each of which is made up of three edge-sharing {MoO$_6$} octahedra. In the [Cu(phen)$_2$]$^+$ counter-cation, the Cu atom is coordinated by four N atoms from two 1,10-phenanthroline ligands.

Comment

Polyoxometallates have attracted attention in recent years, not only because of their remarkable structural diversity but also for their potential applications in catalysis and nanotechnology, as magnetic and photochemical materials (Pope, 1983; Misono, 1987; Ouahab, 1997; Pope & Müller, 1991). The preparation of new polyoxometallate structures is still very elusive. In this paper, we present the hydrothermal synthesis and crystal structure of an organic–inorganic hybrid compound, (H$_2$phen)[Cu(phen)$_2$][PMo$_{12}$O$_{40}$], (I).

(I)
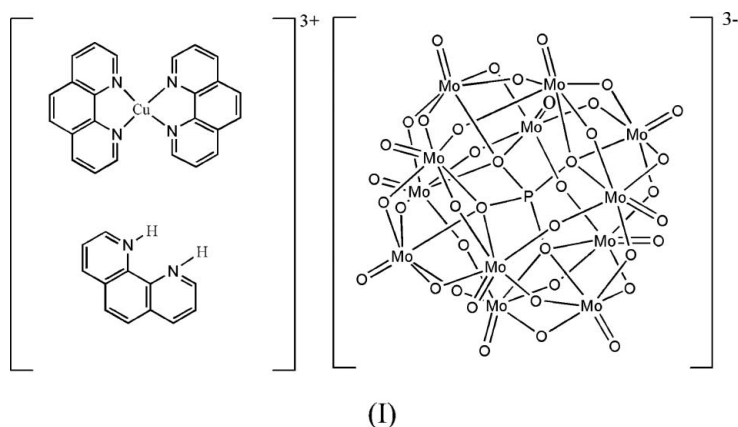
The asymmetric unit of (I) consists of a classic Keggin-type polyoxoanion [PMo$_{12}$O$_{40}$]$^{3-}$ combined with one [Cu(phen)$_2$]$^+$ and one (H$_2$phen)$^{2+}$ counter-cations. In the well known Keggin (1934) structure, there are 12 {MoO$_6$} octahedra and one PO$_4$ tetrahedron. The 12 {MoO$_6$} octahedra can be categorized into four {Mo$_3$O$_{16}$} trinuclear groups, each of which is made of three edge-sharing {MoO$_6$} octahedra, and are joined to each other by sharing corners. The PO$_4$ tetrahedron is

located in the centre of the polyoxoanion by sharing its O atoms with the four {Mo$_3$O$_{16}$} groups. Within the MoO$_6$ octahedra, the mean values of the Mo—O$_a$, Mo—O$_{b,c}$ and Mo—O$_t$ bond distances are 2.435, 1.917 and 1.674 Å, respectively (O$_a$ belong to the central PO$_4$ tetrahedron, O$_b$ are bridging between corner-sharing MoO$_6$ octahedra, O$_c$ are bridging between edge-sharing MoO$_6$ octahedra and O$_t$ are terminal). In the PO$_4$ tetrahedron, P—O bond lengths are in the range 1.531 (3)–1.536 (3) Å (average 1.534 Å), and the O—P—O angles range from 109.02 (16) to 109.88 (15)°. These data reveal that the polyoxoanion is slightly distorted. The average Mo—O$_a$, Mo—O$_{b,c}$, Mo—O$_t$ and P—O bond lengths of the title compound are correspondingly 0.007, 0.009, 0.008 and 0.005 Å longer than the previously reported values in α-H$_3$PMo$_{12}$O$_{40}$·6DMA·CH$_3$CN·0.5H$_2$O (Williamson *et al.*, 1987). The differences are very small and indicate that the different coordination environments of the polyoxoanion have very weak effects on its structure.

As shown in Fig. 1, there are two discrete counter-cations in (I). Within the [Cu(phen)$_2$]$^+$ cation, the Cu ion is coordinated by four N atoms from two 1,10-phen ligands, to give a distorted tetrahedral geometry. Although the starting reagent is a copper(II) salt, the oxidation state of the Cu atom is assigned as +1 in the title compound, since organonitrogen species generally act not only as ligands but also as reducing agents under hydrothermal conditions (Liu *et al.*, 2006), and similar trends have been observed in other compounds (Hagrman *et al.*, 1997, 1998; Wu *et al.*, 2002; Finn & Zubieta, 2001). At the same time, this result is also supported by the coordination environments, valence sum calculations (1.43 for Cu; Brese & O'Keeffe, 1991) and charge neutrality. Bond-valence sum calculations (Brown & Altermatt, 1985) for atoms N5 and N6 indicate that they are protonated, which is in good agreement with the electric charge. The polyoxoanion and the two discrete counter-cations are held together by electrostatic forces.

Experimental

A mixture of H$_3$PMo$_{12}$O$_{40}$·15H$_2$O (0.18 g), Na$_2$MoO$_4$·2H$_2$O (0.25 g), Vc (C$_8$H$_8$O$_6$; 0.02 g), Cu(CH$_3$COO)$_2$·H$_2$O (0.08 g), 1,10-phen (0.03 g) and H$_2$O (12 ml) was adjusted to pH 0.45 with HCl (6 *M*). After stirring for 4 h, the mixture was sealed in a 30 ml Teflon-lined autoclave and heated at 453 K for 4 d. The mixture was then slowly cooled to room temperature and dark-blue block crystals of (I) were obtained. In the IR (KBr pellet) spectrum, vibration modes for ν(P—O$_a$), ν(Mo—O$_t$), ν(Mo—O$_b$) and ν(Mo—O$_c$) are observed at 1055, 955, 876 and 794 cm^{-1}, respectively. The characteristic absorption bands of the organonitrogen ligands occur at 1587, 1521, 1429 and 1342 cm^{-1}.

Crystal data

(C$_{12}$H$_{10}$N$_2$)[Cu(C$_{12}$H$_8$N$_2$)$_2$]-[PMo$_{12}$O$_{40}$]	$Z = 4$
$M_r = 2428.42$	$D_x = 2.831$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 12.2382$ (15) Å	$\mu = 3.05$ mm^{-1}
$b = 21.031$ (3) Å	$T = 293$ (2) K
$c = 22.140$ (3) Å	Block, blue
$V = 5698.4$ (12) Å^3	$0.26 \times 0.18 \times 0.17$ mm

Data collection

Rigaku R-AXIS RAPID image plate diffractometer	29691 measured reflections
ω scans	10001 independent reflections
Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)	9169 reflections with $I > 2\sigma(I)$
$T_{min} = 0.504$, $T_{max} = 0.625$	$R_{int} = 0.034$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.016P)^2 + 0.1397P]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.047$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.04$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
10001 reflections	$\Delta\rho_{min} = -0.45$ e Å^{-3}
865 parameters	Absolute structure: Flack (1983), with 4446 Friedel pairs
H-atom parameters constrained	Flack parameter: −0.043 (16)

Table 1
Selected geometric parameters (Å, °).

|			
Cu—N3	1.963 (3)	Mo6—O34	1.873 (3)
Cu—N1	1.968 (4)	Mo6—O32	1.952 (3)
Cu—N2	2.014 (4)	Mo6—O29	1.959 (3)
Cu—N4	2.024 (4)	Mo6—O39	2.471 (3)
P—O38	1.531 (3)	Mo7—O7	1.664 (3)
P—O40	1.533 (3)	Mo7—O14	1.887 (3)
P—O39	1.534 (3)	Mo7—O36	1.907 (3)
P—O37	1.536 (3)	Mo7—O13	1.930 (3)
Mo1—O1	1.667 (3)	Mo7—O31	1.940 (3)
Mo1—O17	1.898 (3)	Mo7—O38	2.429 (3)
Mo1—O25	1.906 (3)	Mo8—O8	1.675 (3)
Mo1—O21	1.939 (3)	Mo8—O30	1.897 (3)
Mo1—O15	1.952 (3)	Mo8—O23	1.918 (3)
Mo1—O37	2.454 (3)	Mo8—O36	1.926 (3)
Mo2—O2	1.674 (3)	Mo8—O34	1.935 (3)
Mo2—O26	1.851 (3)	Mo8—O38	2.445 (3)
Mo2—O15	1.889 (3)	Mo9—O9	1.671 (3)
Mo2—O35	1.949 (3)	Mo9—O31	1.891 (3)
Mo2—O28	1.978 (3)	Mo9—O35	1.895 (3)
Mo2—O37	2.419 (3)	Mo9—O30	1.935 (3)
Mo3—O3	1.665 (3)	Mo9—O22	1.941 (3)
Mo3—O28	1.859 (3)	Mo9—O38	2.430 (2)
Mo3—O13	1.901 (3)	Mo10—O10	1.687 (3)
Mo3—O25	1.935 (3)	Mo10—O29	1.854 (3)
Mo3—O24	1.990 (3)	Mo10—O16	1.907 (3)
Mo3—O37	2.454 (3)	Mo10—O23	1.921 (3)
Mo4—O4	1.670 (3)	Mo10—O19	1.959 (3)
Mo4—O20	1.868 (3)	Mo10—O40	2.423 (3)
Mo4—O32	1.894 (3)	Mo11—O11	1.674 (3)
Mo4—O33	1.940 (3)	Mo11—O19	1.871 (3)
Mo4—O17	1.955 (3)	Mo11—O22	1.902 (3)
Mo4—O39	2.424 (3)	Mo11—O18	1.943 (3)
Mo5—O5	1.685 (3)	Mo11—O26	1.965 (3)
Mo5—O24	1.847 (3)	Mo11—O40	2.428 (3)
Mo5—O33	1.895 (3)	Mo12—O12	1.675 (3)
Mo5—O14	1.918 (3)	Mo12—O18	1.876 (3)
Mo5—O27	1.980 (3)	Mo12—O21	1.888 (3)
Mo5—O39	2.397 (3)	Mo12—O20	1.942 (3)
Mo6—O6	1.679 (3)	Mo12—O16	1.972 (3)
Mo6—O27	1.873 (3)	Mo12—O40	2.450 (3)
N3—Cu—N1	170.30 (15)	O38—P—O40	109.53 (15)
N3—Cu—N2	101.36 (15)	O38—P—O39	109.23 (15)
N1—Cu—N2	83.13 (15)	O40—P—O39	109.64 (15)
N3—Cu—N4	83.90 (14)	O38—P—O37	109.88 (15)
N1—Cu—N4	99.08 (15)	O40—P—O37	109.02 (16)
N2—Cu—N4	135.06 (14)	O39—P—O37	109.53 (15)

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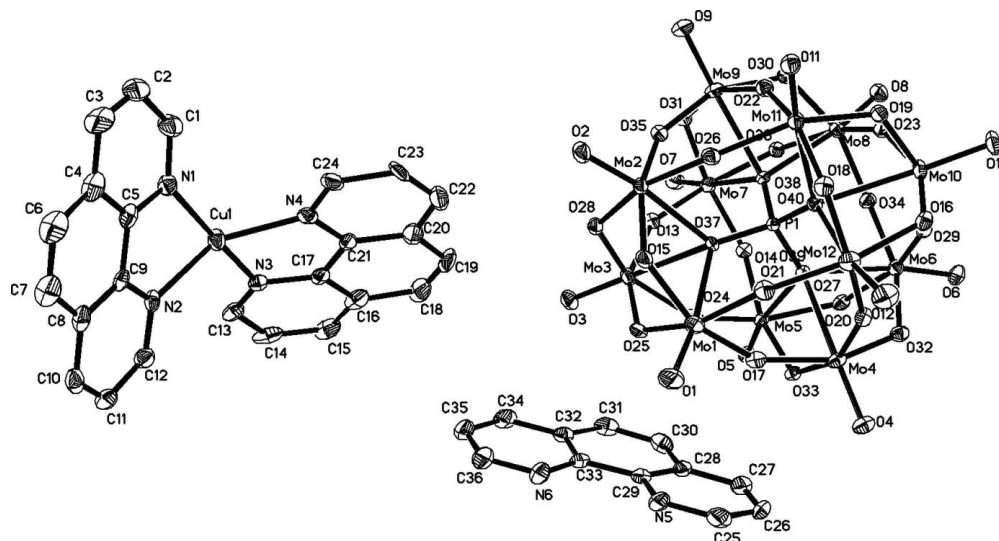
Figure 1
The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity.

H atoms bonded to C atoms were included in the refinement in calculated positions based on the riding-model approximation [C—H = 0.93 Å and $U_{iso}(H) = 1.2 U_{eq}(C)$]. N-bound H atoms were not located.

Data collection: *R-AXIS* (Molecular Structure Corporation, 1992); cell refinement: *R-AXIS*; data reduction: *R-AXIS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *TEXSAN* (Molecular Structure Corporation, 1999); software used to prepare material for publication: *TEXSAN*.

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