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Key indicators

Single-crystal X-ray study
 T = 283 K
 Mean $\sigma(C-C)$ = 0.017 Å
 R factor = 0.052
 wR factor = 0.127
 Data-to-parameter ratio = 11.6

For details of how these key indicators were
 automatically derived from the article, see
<http://journals.iucr.org/e>.

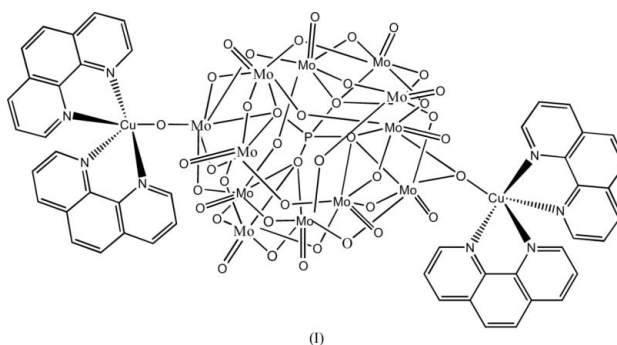
**μ -Hexatriacontaoxophosphatododecamolybdate-
 bis[bis(1,10-phenanthroline)copper(II)]**

The title compound, $[Cu_2Mo_{12}O_{40}P(C_{12}H_8N_2)_4]$, was obtained by the hydrothermal reaction of $Na_2MoO_4 \cdot 2H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, NH_4VO_3 , 1,10-phenanthroline (phen) and H_3PO_4 . The structure determination shows that two $\{Cu(phen)_2\}$ fragments are supported by the reduced α -Keggin polyoxoanion $[PMo^{VI}_{11}Mo^VO_{40}]^{4-}$ through a terminal O atom and a bridging oxygen atom from opposite sides of the Keggin structure.

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Comment

There has been considerable interest in polyoxometalates (POMs) owing to their interesting structural features and various potential applications in catalysis, sorption, electrical conductivity, magnetism and photochemistry [Pope *et al.*, 1983, Hill *et al.*, 1998]. Recently, an important advance in polyoxometalate chemistry has been the study of heteropolyoxoanions substituted by transition-metal and heteropolyoxoanion-supported inorganic or organometallic complexes since their properties can possibly be modified due to their constituents at the molecular level; examples include $[PW_{10}^{VI}W_2^VO_{40}Ni(2,2'-bipy)_2(H_2O)]^{3-}$ (Xu *et al.* 2000), $[PMo_6^{VI}Mo_2^V V_8^{IV}O_{44}\{Co(2,2'-bipy)_2(H_2O)\}_4][PMo_4^{VI}Mo_4^V V_8^{IV}O_{44}\{Co(2,2'-bipy)_2(H_2O)\}_2] \cdot 4H_2O$ (Yuan *et al.* 2003) and $\{[Ni(phen)_2(H_2O)]_2[Ni(phen)_2][V_8^{IV}Mo_6^{VI}Mo_2^VO_{40}(PO_4)]\}_n^{n+}$ (Liu *et al.* 2004). However, except for $[ZnW_{12}O_{40}Zn(2,2'-bipy)_2]^{4-}$ [(Niu *et al.* 2003), a singly supporting heteropolyoxoanion, these heteropolyoxoanions can use only terminal oxygen or bridging oxygen to form supporting structures. To our knowledge, no previous structural examples of multiply supporting heteropolyoxoanions simultaneously linked through terminal oxygen and bridging oxygen have been reported.



We report here the hydrothermal synthesis and crystal structure of a novel reduced α -Keggin unit supporting two copper-phenanthroline complexes, $\{PMo^{VI}_{11}Mo^VO_{40}[Cu(phen)_2]_2\}$, (I). In the crystal structure, two $\{Cu(phen)_2\}$ fragments are bonded to the reduced α -Keggin-type poly-

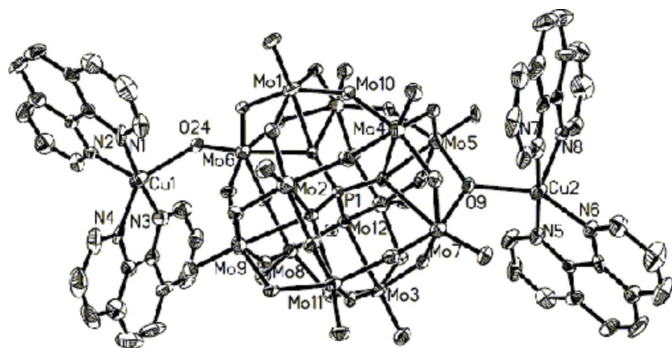


Figure 1

A view of the structure of the asymmetric unit of the title compound. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted, and only selected atoms are labeled for clarity.

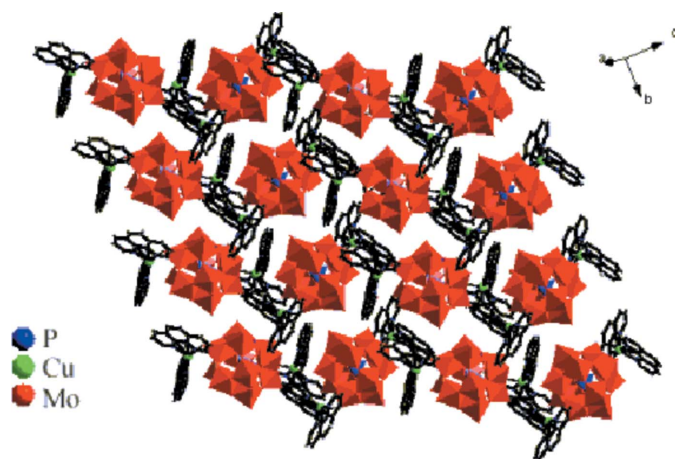


Figure 2

A view of the packing arrangement of the three-dimensional network of the title compound.

oxoanion $[\text{PMo}_{11}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]^{4-}$ via a terminal oxygen atom and a bridging oxygen atom from opposite sides of the Keggin structure; this is the first example of a doubly supporting heteropolyoxoanion. As shown in Fig. 1, there are two crystallographically independent Cu centers and one $[\text{PMo}_{11}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]^{4-}$ polyoxoanion in the asymmetric unit. As in other well known Keggin structures, the reduced heteropolyoxoanion $[\text{PMo}_{11}^{\text{VI}}\text{Mo}^{\text{V}}\text{O}_{40}]^{4-}$ is formed from twelve MoO_6 octahedra and one PO_4 tetrahedron. The P–O distances vary from 1.525 (6) to 1.530 (6) Å, while the O–P–O angles are in the range 108.5 (3) to 110.7 (3)°. The Mo–O distances can be divided into three groups: Mo–O_t (terminal) 1.652 (7)–1.694 (6) Å, Mo–O_b (bridging) 1.846 (6)–2.006 (6) Å and Mo–O_c (central) 2.399 (6)–2.445 (5) Å. The central PO_4 tetrahedron shares its O atoms with four $\{\text{Mo}_3\text{O}_{13}\}$ groups, each of which is made up of three edge-sharing $\{\text{MoO}_6\}$ octahedra. The $\{\text{Mo}_3\text{O}_{13}\}$ subunits are joined to each other in a corner-sharing mode. A valence-sum calculation (Brown & Altermatt, 1985) gives the average value of 5.92 for the oxidation state of Mo. This calculation shows that 1 out of 12 Mo atoms is in the +5 oxidation state, with one electron delocalized within the whole metal-oxide cluster.

An unusual structural feature is that the Keggin polyoxoanion supports two $\{\text{Cu}(\text{phen})_2\}^{2+}$ fragments through a terminal O atom (O24) and a bridging O atom (O9) from the opposite sides of the Keggin unit [$\text{Cu1}–\text{O24}$ 2.187 (6) Å, and $\text{Cu2}–\text{O9}$ 2.160 (6) Å]. Previously, transition metals have been linked only through terminal or surface bridging oxygen donors (Liu *et al.*, 2002; Luan *et al.*, 2003). The Cu1 and Cu2 centers each adopt a distorted trigonal-bipyramidal geometry, being coordinated by four N atoms of two phen groups [$\text{Cu}–\text{N}$ 1.952 (8)–2.178 (8) Å], and one O atom of the Keggin unit. The τ values for Cu1 and Cu2 are 0.61 and 0.47 respectively (Addison *et al.*, 1984). Furthermore, an extended three-dimensional supramolecular network in the crystal structure of the title compound is formed through $\text{O} \cdots \text{O}$ short contacts and $\pi–\pi$ interactions (Fig. 2).

Experimental

A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.178 g), $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.115 g), NH_4VO_3 (0.067 g), H_3PO_4 (0.5 ml), phen (0.135 g) and H_2O (9 ml) was stirred for 20 min in air. The mixture was then transferred to a 20 ml Teflon-lined autoclave, and kept at 433 K for 4 days. After slowly cooling to room temperature, black block crystals were isolated as a major phase (50% yield based on Mo). The crystals were manually selected for structure determination and further characterization. Analysis calculated for $\text{C}_{48}\text{H}_{32}\text{Cu}_2\text{Mo}_{12}\text{N}_8\text{O}_{40}\text{P}$: C 21.56, H 1.20, N 4.19, P 1.16, Mo 43.13, Cu 4.79%; found: C 21.60, H 1.24, N 4.15, P 1.14, Mo 43.18, Cu 4.81%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

Crystal data

$[\text{Cu}_2\text{Mo}_{12}\text{O}_{40}\text{P}(\text{C}_{12}\text{H}_8\text{N}_2)_4]$
 $M_r = 2670.15$
 Monoclinic, $P2_1/c$
 $a = 25.975$ (5) Å
 $b = 11.545$ (2) Å
 $c = 23.286$ (5) Å
 $\beta = 108.81$ (3)°
 $V = 6610$ (2) Å³
 $Z = 4$

$D_x = 2.683$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 48954 reflections
 $\theta = 3.1–25.0^\circ$
 $\mu = 2.95$ mm⁻¹
 $T = 283$ (2) K
 Block, black
 $0.22 \times 0.16 \times 0.14$ mm

Data collection

Rigaku R-Axis RAPID IP diffractometer
 ω scans
 Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
 $T_{\text{min}} = 0.573$, $T_{\text{max}} = 0.661$
 48954 measured reflections

11597 independent reflections
 7806 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.090$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -30 \rightarrow 30$
 $k = -13 \rightarrow 13$
 $l = -27 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.127$
 $S = 1.02$
 11597 reflections
 1000 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0552P)^2 + 18.0365P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.010$
 $\Delta\rho_{\text{max}} = 1.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.03$ e Å⁻³

H atoms were included in calculated positions and treated as riding atoms, with $\text{C}–\text{H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest density peak and deepest hole in the final difference map are located 1.00 and 0.64 Å, respectively, from atom Mo5.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalStructure* (Rigaku/MSC, 2002); software used to prepare material for publication: *CrystalStructure*.

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