metal-organic papers

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Key indicators

Single-crystal X-ray study T = 293 K Mean σ (C–C) = 0.007 Å H-atom completeness 93% R factor = 0.026 wR factor = 0.047 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.

A new hybrid Keggin-type molybdophosphate: (H₂phen)[Cu(phen)₂][PMo₁₂O₄₀]

An organic-inorganic hybrid compound constructed from a Keggin-type molybdophosphate polyoxoanion, a Cu¹ coordination cation and a protonated 1,10-phenanthroline subunit, 1,10-phenanthrolinium bis(1,10-phenanthroline)namely copper(I) dodecamolybdophosphate, $(C_{12}H_{10}N_2)$ - $[Cu(C_{12}H_8N_2)_2][PMo_{12}O_{40}]$ (H₂phen)[Cu(phen)₂]or [PMo₁₂O₄₀], 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 $\{MO_3O_{16}\}$ trinuclear groups, each of which is made up of three edgesharing $\{MoO_6\}$ octahedra. In the $[Cu(phen)_2]^+$ countercation, 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, (H₂phen)[Cu(phen)₂][PMo₁₂O₄₀], (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 $(H_2phen)^{2+}$ counter-cations. In the well known Keggin (1934) structure, there are 12 {MoO₆} octahedra and one PO₄ tetrahedron. The 12 {MoO₆} octahedra can be categorized into four {Mo₃O₁₆} trinuclear groups, each of which is made of three edge-sharing {MoO₆} octahedra, and are joined to each other by sharing corners. The PO₄ tetrahedron is

© 2006 International Union of Crystallography All rights reserved Received 30 July 2006 Accepted 8 September 2006 located in the centre of the polyoxoanion by sharing its O atoms with the four $\{MO_3O_{16}\}$ 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 PO₄ tetrahedron, O_b are bridging between corner-sharing MoO₆ octahedra, O_c are bridging between edge-sharing MoO₆ 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 -H₃PMo₁₂O₄₀·6DMA·CH₃CN·0.5H₂O (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. Bondvalence 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 H₃PMo₁₂O₄₀·15H₂O (0.18 g), Na₂MoO₄·2H₂O (0.25 g), Vc ($C_8H_8O_6$; 0.02 g), Cu(CH₃COO)₂·H₂O (0.08 g), 1,10-phen (0.03 g) and H₂O (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 v(P- O_a , $\nu(Mo-O_t)$, $\nu(Mo-O_b)$ and $\nu(Mo-O_c)$ are observed at 1055, 955, 876 and 794 $\rm cm^{-1}$, respectively. The characteristic absorption bands of the organonitrogen ligands occur at 1587, 1521, 1429 and 1342 cm^{-1} .

Crystal data

$(C_{12}H_{10}N_2)[Cu(C_{12}H_8N_2)_2]$ -	Z = 4
[PMo ₁₂ O ₄₀]	$D_x = 2.831 \text{ Mg m}^{-3}$
$M_r = 2428.42$	Mo $K\alpha$ radiation
Orthorhombic, $P2_12_12_1$	$\mu = 3.05 \text{ mm}^{-1}$
a = 12.2382 (15) Å	T = 293 (2) K
b = 21.031 (3) Å	Block, blue
c = 22.140 (3) Å	$0.26 \times 0.18 \times 0.17 \text{ mm}$
$V = 5698.4 (12) \text{ Å}^3$	

Data collection

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Rigaku R-AXIS RAPID image
  plate diffractometer
(i) scans
Absorption correction: empirical
  (using intensity measurements)
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(ABSCOR: Higashi, 1995) $T_{\min} = 0.504, \ T_{\max} = 0.625$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.026$ $wR(F^2) = 0.047$ S = 1.0410001 reflections 865 parameters H-atom parameters constrained 29691 measured reflections 10001 independent reflections 9169 reflections with $I > 2\sigma(I)$ $R_{\rm int}=0.034$ $\theta_{\rm max} = 25.0^{\circ}$

 $w = 1/[\sigma^2(F_0^2) + (0.016P)^2]$ + 0.1397P] where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\rm max} = 0.003$ _3 $\Delta \rho_{\rm max} = 0.43 \ {\rm e} \ {\rm \AA}$ $\Delta \rho_{\rm min} = -0.45 \text{ e } \text{\AA}^{-3}$ Absolute structure: Flack (1983). with 4446 Friedel pairs Flack parameter: -0.043 (16)

Table 1 Selected geometric parameters (Å, °).

$\begin{array}{cccccccccccccccccccccccccccccccccccc$				
$\begin{array}{c} \mathrm{Cu-N1} & 1.968 \ (4) & \mathrm{Mo6}-032 & 1.952 \ (3) \\ \mathrm{Cu-N2} & 2.014 \ (4) & \mathrm{Mo6}-029 & 1.959 \ (3) \\ \mathrm{Cu-N4} & 2.024 \ (4) & \mathrm{Mo6}-039 & 2.471 \ (3) \\ \mathrm{P}-038 & 1.531 \ (3) & \mathrm{Mo7}-07 & 1.664 \ (3) \\ \mathrm{P}-040 & 1.533 \ (3) & \mathrm{Mo7}-014 & 1.887 \ (3) \\ \mathrm{P}-039 & 1.534 \ (3) & \mathrm{Mo7}-036 & 1.907 \ (3) \\ \mathrm{P}-037 & 1.536 \ (3) & \mathrm{Mo7}-031 & 1.940 \ (3) \\ \mathrm{Mo1}-011 & 1.667 \ (3) & \mathrm{Mo7}-031 & 1.940 \ (3) \\ \mathrm{Mo1}-021 & 1.939 \ (3) & \mathrm{Mo8}-038 & 1.675 \ (3) \\ \mathrm{Mo1}-021 & 1.939 \ (3) & \mathrm{Mo8}-030 & 1.897 \ (3) \\ \mathrm{Mo1}-037 & 2.454 \ (3) & \mathrm{Mo8}-036 & 1.926 \ (3) \\ \mathrm{Mo2}-026 & 1.851 \ (3) & \mathrm{Mo8}-034 & 1.935 \ (3) \\ \mathrm{Mo2}-026 & 1.851 \ (3) & \mathrm{Mo8}-038 & 2.445 \ (3) \\ \mathrm{Mo2}-026 & 1.851 \ (3) & \mathrm{Mo8}-038 & 2.445 \ (3) \\ \mathrm{Mo2}-028 & 1.978 \ (3) & \mathrm{Mo9}-031 & 1.891 \ (3) \\ \mathrm{Mo3}-03 & 1.665 \ (3) & \mathrm{Mo9}-031 & 1.891 \ (3) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo9}-038 & 2.4430 \ (2) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo9}-038 & 2.4430 \ (2) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo9}-038 & 2.4430 \ (2) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo9}-038 & 2.4430 \ (2) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo1}-010 & 1.687 \ (3) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo1}-029 & 1.884 \ (3) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo1}-029 & 1.884 \ (3) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo1}-029 & 1.884 \ (3) \\ \mathrm{Mo3}-028 & 1.889 \ (3) & \mathrm{Mo1}-010 & 1.687 \ (3) \\ \mathrm{Mo3}-037 & 2.454 \ (3) & \mathrm{Mo1}-010 & 1.687 \ (3) \\ \mathrm{Mo4}-04 & 1.670 \ (3) & \mathrm{Mo1}-011 & 1.674 \ (3) \\ \mathrm{Mo4}-033 & 1.940 \ (3) & \mathrm{Mo1}-018 & 1.943 \ (3) \\ \mathrm{Mo4}-033 & 1.940 \ (3) & \mathrm{Mo1}-018 & 1.943 \ (3) \\ \mathrm{Mo4}-033 & 1.940 \ (3) & \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-05 & 1.685 \ (3) & \mathrm{Mo1}-021 & 1.675 \ (3) \\ \mathrm{Mo5}-014 & 1.918 \ (3) & \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-033 & 1.895 \ (3) & \mathrm{Mo1}-021 & 1.675 \ (3) \\ \mathrm{Mo5}-033 & 1.895 \ (3) & \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-033 & 1.895 \ (3) & \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-040 & -2428 \ (3) \ \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-07 & 1.980 \ (3) & \mathrm{Mo1}-018 & 1.9438 \ (3) \\ \mathrm{Mo5}-07 & 1.980 \ (3) & \mathrm{Mo1}-021 & 1.675 \ (3)$	Cu-N3	1.963 (3)	Mo6-O34	1.873 (3)
$\begin{array}{c} \mathrm{Cu}-\mathrm{N2} & 2.014 \ (4) & \mathrm{Mo6}-\mathrm{O29} & 1.959 \ (3) \\ \mathrm{Cu}-\mathrm{N4} & 2.024 \ (4) & \mathrm{Mo6}-\mathrm{O39} & 2.471 \ (3) \\ \mathrm{P}-\mathrm{O38} & 1.531 \ (3) & \mathrm{Mo7}-\mathrm{O7} & 1.664 \ (3) \\ \mathrm{P}-\mathrm{O40} & 1.533 \ (3) & \mathrm{Mo7}-\mathrm{O14} & 1.887 \ (3) \\ \mathrm{P}-\mathrm{O39} & 1.534 \ (3) & \mathrm{Mo7}-\mathrm{O36} & 1.907 \ (3) \\ \mathrm{P}-\mathrm{O37} & 1.536 \ (3) & \mathrm{Mo7}-\mathrm{O31} & 1.930 \ (3) \\ \mathrm{Mo1}-\mathrm{O1} & 1.667 \ (3) & \mathrm{Mo7}-\mathrm{O31} & 1.940 \ (3) \\ \mathrm{Mo1}-\mathrm{O12} & 1.996 \ (3) & \mathrm{Mo8}-\mathrm{O8} & 1.675 \ (3) \\ \mathrm{Mo1}-\mathrm{O21} & 1.939 \ (3) & \mathrm{Mo8}-\mathrm{O30} & 1.897 \ (3) \\ \mathrm{Mo1}-\mathrm{O15} & 1.952 \ (3) & \mathrm{Mo8}-\mathrm{O30} & 1.897 \ (3) \\ \mathrm{Mo2}-\mathrm{O22} & 1.674 \ (3) & \mathrm{Mo8}-\mathrm{O34} & 1.925 \ (3) \\ \mathrm{Mo2}-\mathrm{O22} & 1.674 \ (3) & \mathrm{Mo8}-\mathrm{O34} & 1.925 \ (3) \\ \mathrm{Mo2}-\mathrm{O22} & 1.674 \ (3) & \mathrm{Mo8}-\mathrm{O34} & 1.935 \ (3) \\ \mathrm{Mo2}-\mathrm{O25} & 1.949 \ (3) & \mathrm{Mo9}-\mathrm{O31} & 1.891 \ (3) \\ \mathrm{Mo2}-\mathrm{O25} & 1.949 \ (3) & \mathrm{Mo9}-\mathrm{O31} & 1.891 \ (3) \\ \mathrm{Mo2}-\mathrm{O25} & 1.949 \ (3) & \mathrm{Mo9}-\mathrm{O31} & 1.891 \ (3) \\ \mathrm{Mo2}-\mathrm{O35} & 1.949 \ (3) & \mathrm{Mo9}-\mathrm{O30} & 1.935 \ (3) \\ \mathrm{Mo3}-\mathrm{O3} & 1.665 \ (3) & \mathrm{Mo9}-\mathrm{O38} & 2.430 \ (2) \\ \mathrm{Mo3}-\mathrm{O13} & 1.691 \ (3) & \mathrm{Mo10}-\mathrm{O10} & 1.687 \ (3) \\ \mathrm{Mo3}-\mathrm{O25} & 1.935 \ (3) & \mathrm{Mo10}-\mathrm{O29} & 1.854 \ (3) \\ \mathrm{Mo3}-\mathrm{O26} & 1.851 \ (3) & \mathrm{Mo10}-\mathrm{O10} & 1.687 \ (3) \\ \mathrm{Mo3}-\mathrm{O37} & 2.445 \ (3) & \mathrm{Mo10}-\mathrm{O10} & 1.687 \ (3) \\ \mathrm{Mo3}-\mathrm{O37} & 2.445 \ (3) & \mathrm{Mo10}-\mathrm{O10} & 1.687 \ (3) \\ \mathrm{Mo3}-\mathrm{O27} & 1.990 \ (3) & \mathrm{Mo10}-\mathrm{O16} & 1.907 \ (3) \\ \mathrm{Mo4}-\mathrm{O20} & 1.868 \ (3) & \mathrm{Mo1}-\mathrm{O11} & 1.674 \ (3) \\ \mathrm{Mo4}-\mathrm{O33} & 1.940 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo4}-\mathrm{O33} & 1.940 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo4}-\mathrm{O39} & 2.424 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo5}-\mathrm{O5} & 1.685 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo5}-\mathrm{O5} & 1.685 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo5}-\mathrm{O5} & 1.685 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo5}-\mathrm{O5} & 1.685 \ (3) & \mathrm{Mo1}-\mathrm{O18} & 1.943 \ (3) \\ \mathrm{Mo5}-\mathrm{O21} & 1.988 \ (3) \\ \mathrm{Mo5}-\mathrm{O21}$	Cu-N1	1.968 (4)	Mo6-O32	1.952 (3)
Cu - N4 2.024 (4) Mo6-O39 2.471 (3) P - O38 1.531 (3) Mo7-O7 1.664 (3) P - O39 1.534 (3) Mo7-O14 1.887 (3) Mo1-O1 1.667 (3) Mo7-O36 1.907 (3) Mo1-O1 1.667 (3) Mo7-O38 2.429 (3) Mo1-O17 1.898 (3) Mo7-O38 2.429 (3) Mo1-O25 1.906 (3) Mo8-O30 1.897 (3) Mo1-O15 1.952 (3) Mo8-O34 1.935 (3) Mo1-O37 2.454 (3) Mo8-O34 1.935 (3) Mo2-O26 1.851 (3) Mo8-O38 2.445 (3) Mo2-O15 1.889 (3) Mo9-O31 1.891 (3) Mo2-O28 1.978 (3) Mo9-O31 1.891 (3) Mo2-O28 1.978 (3) Mo9-O31 1.891 (3) Mo3-O28 1.859 (3) Mo9-O31 1.891 (3) Mo3-O28 1.859 (3) Mo9-O31 1.991 (3) Mo3-O28 1.859 (3) Mo9-O31 1.991 (3) Mo3-O29 1.984 (3) Mo10-	Cu-N2	2.014 (4)	Mo6-O29	1.959 (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-O31 1.940 (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-O30 1.897 (3) Mo1-O21 1.939 (3) Mo8-O30 1.897 (3) Mo1-O37 2.454 (3) Mo8-O34 1.935 (3) Mo2-O20 1.674 (3) Mo8-O38 2.445 (3) Mo2-O35 1.949 (3) Mo9-O31 1.891 (3) Mo2-O35 1.949 (3) Mo9-O31 1.891 (3) Mo2-O37 2.419 (3) Mo9-O32 1.941 (3) Mo3-O28 1.859 (3) Mo9-O38 2.430 (2) Mo3-O28 1.859 (3) Mo9-O38 2.430 (2) Mo3-O25 1.935 (3) Mo10-O10 1.687 (3) Mo3-O24 1.990 (3) Mo10-O10 <td>Cu-N4</td> <td>2.024 (4)</td> <td>Mo6-O39</td> <td>2.471 (3)</td>	Cu-N4	2.024 (4)	Mo6-O39	2.471 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P-O38	1.531 (3)	Mo7-O7	1.664 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P-O40	1.533 (3)	Mo7-O14	1.887 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P-O39	1.534 (3)	Mo7-O36	1.907 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	P-O37	1.536 (3)	Mo7-O13	1.930 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo1-O1	1.667 (3)	Mo7-O31	1.940 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo1-O17	1.898 (3)	Mo7-O38	2.429 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo1-O25	1.906 (3)	Mo8-O8	1.675 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo1 - O21	1.939 (3)	Mo8-O30	1.897 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_{01} - 015$	1 952 (3)	Mo8-023	1 918 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo1-O37	2.454(3)	Mo8-O36	1.926 (3)
No2O261851 (3)No8O382.445 (3)Mo2-O261.851 (3)Mo8-O382.445 (3)Mo2-O351.949 (3)Mo9-O91.671 (3)Mo2-O351.949 (3)Mo9-O311.891 (3)Mo2-O372.419 (3)Mo9-O351.895 (3)Mo3-O31.665 (3)Mo9-O321.941 (3)Mo3-O281.859 (3)Mo9-O382.430 (2)Mo3-O281.859 (3)Mo10-O101.687 (3)Mo3-O251.935 (3)Mo10-O101.687 (3)Mo3-O241.990 (3)Mo10-O161.907 (3)Mo3-O372.454 (3)Mo10-O191.929 (3)Mo4-O41.670 (3)Mo10-O191.929 (3)Mo4-O41.670 (3)Mo11-O111.674 (3)Mo4-O321.894 (3)Mo11-O191.871 (3)Mo4-O331.940 (3)Mo11-O191.871 (3)Mo4-O392.424 (3)Mo11-O261.965 (3)Mo5-O51.685 (3)Mo11-O261.965 (3)Mo5-O51.685 (3)Mo12-O121.675 (3)Mo5-O241.847 (3)Mo12-O121.876 (3)Mo5-O271.980 (3)Mo12-O161.972 (3)Mo5-O271.980 (3)Mo12-O161.972 (3)Mo5-O271.873 (3)Mo12-O161.972 (3)Mo5-O271.873 (3)Mo12-O161.972 (3)Mo5-O271.873 (3)Mo12-O161.972 (3)Mo5-O282.977 (3)Mo12-O161.972 (3)Mo5-O292.937 (3)Mo12-O161.972 (3) <td< td=""><td>$Mo^2 = O^2$</td><td>1.674(3)</td><td>Mo8-034</td><td>1.935 (3)</td></td<>	$Mo^2 = O^2$	1.674(3)	Mo8-034	1.935 (3)
No2OLS1.05OLS1.161No2O151.889(3)Mo9O91.671Mo2O251.949(3)Mo9O91.671Mo2O251.949(3)Mo9Mo9O311.891Mo2O281.978(3)Mo9Mo9O351.895Mo3O272.419(3)Mo9O221.941(3)Mo3O281.859(3)Mo9O221.941(3)Mo3O281.859(3)Mo10O101.687(3)Mo3O251.935(3)Mo10O101.687(3)Mo3O251.935(3)Mo10O191.997(3)Mo4O41.670(3)Mo10O191.997(3)Mo4O41.670(3)Mo10O191.997(3)Mo4O41.670(3)Mo10O191.997(3)Mo4O321.894(3)Mo11O111.674(3)Mo4O331.940(3)Mo11 <o19< td="">1.871(3)Mo4O331.940(3)Mo11<o12< td="">1.902(3)Mo5O51.685(3)Mo11<o26< td="">1.965(3)Mo5O241.847(3)Mo11<o12< td="">1.675(3)Mo5O331.895(3)Mo12<o12< td="">1.675(3)Mo5O331.895(3)Mo1</o12<></o12<></o26<></o12<></o19<>	$M_{02} = 0.26$	1.671(3)	Mo8-038	2445(3)
M02-013 100 (3) M09-031 1.81 (3) M02-028 1.978 (3) M09-031 1.81 (3) M02-037 2.419 (3) M09-030 1.935 (3) M03-03 1.665 (3) M09-030 1.935 (3) M03-028 1.859 (3) M09-030 1.935 (3) M03-028 1.859 (3) M09-038 2.430 (2) M03-013 1.901 (3) M010-010 1.687 (3) M03-024 1.990 (3) M010-029 1.854 (3) M03-024 1.990 (3) M010-016 1.907 (3) M04-020 1.868 (3) M010-019 1.957 (3) M04-032 1.894 (3) M011-011 1.674 (3) M04-033 1.940 (3) M011-019 1.871 (3) M04-033 1.940 (3) M011-018 1.943 (3) M05-05 1.685 (3) M011-022 1.902 (3) M04-039 2.424 (3) M011-018 1.943 (3) M05-024 1.847 (3) M011-040 2.428 (3) M05-024 1.847 (3) M012-012 1.675 (3) M05-033 1.895 (3) M012-0	$M_{02} = 020$ $M_{02} = 015$	1.001(0) 1.889(3)	$M_{0}^{0} = O_{0}^{0}$	1.671(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo2 035	1.009(3)	Mo9_031	1.071(3) 1.801(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo2 028	1.979(3) 1 078(3)	Mo9_035	1.091(3) 1.805(3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_{02} = 0.23$ $M_{02} = 0.27$	2,410 (3)	Mo0_020	1.095(3) 1.025(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_{02} = 037$	2.419(3)	Mo9-030	1.935(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_{03} = 0.000$	1.003(3) 1.850(2)	Mo9-022	1.941(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$M_{-2} = 0.12$	1.039 (3)	Mo9-038	2.430 (2)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M03-015	1.901(3)	Mo10-010 M-10-020	1.087(3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M03-025	1.955 (5)	Mo10-029	1.834 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M03-024	1.990(3)	Mo10-016	1.907 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	M03-03/	2.454 (3)	M010-023	1.921 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	M04-04	1.6/0 (3)	M010-019	1.959 (3)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo4-O20	1.868 (3)	Mo10-040	2.423 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo4-032	1.894 (3)	Mol1-Oll	1.674 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo4-O33	1.940 (3)	Mo11-019	1.8/1 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo4-O17	1.955 (3)	Mo11-O22	1.902 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo4-O39	2.424 (3)	Mo11-O18	1.943 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O5	1.685 (3)	Mo11-O26	1.965 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O24	1.847 (3)	Mo11-O40	2.428 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O33	1.895 (3)	Mo12-O12	1.675 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O14	1.918 (3)	Mo12-O18	1.876 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O27	1.980 (3)	Mo12-O21	1.888 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo5-O39	2.397 (3)	Mo12-O20	1.942 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo6-O6	1.679 (3)	Mo12-O16	1.972 (3)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Mo6-O27	1.873 (3)	Mo12-O40	2.450 (3)
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)	N3-Cu-N1	170.30 (15)	O38-P-O40	109.53 (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)	N3-Cu-N2	101.36 (15)	O38-P-O39	109.23 (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)	N1-Cu-N2	83.13 (15)	O40-P-O39	109.64 (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)	N3-Cu-N4	83.90 (14)	O38-P-O37	109.88 (15)
N2-Cu-N4 135.06 (14) $O39-P-O37$ 109.53 (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)



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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