

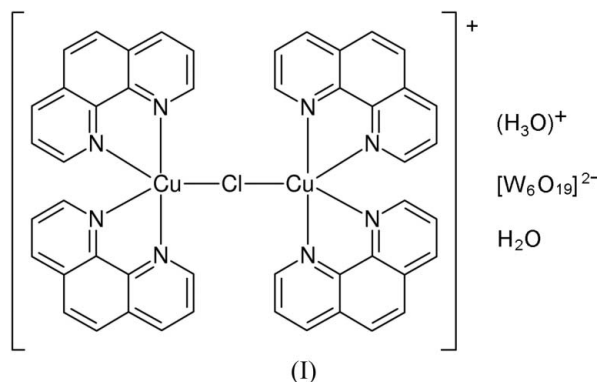
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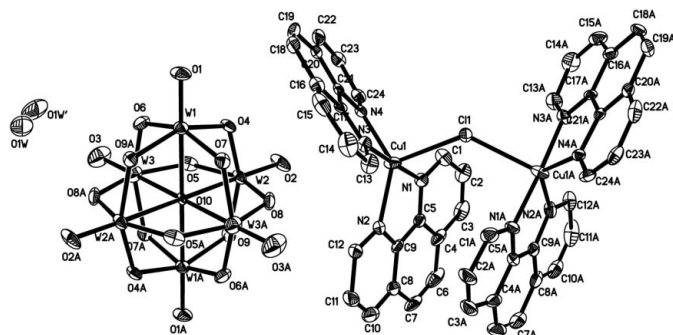
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Key indicators

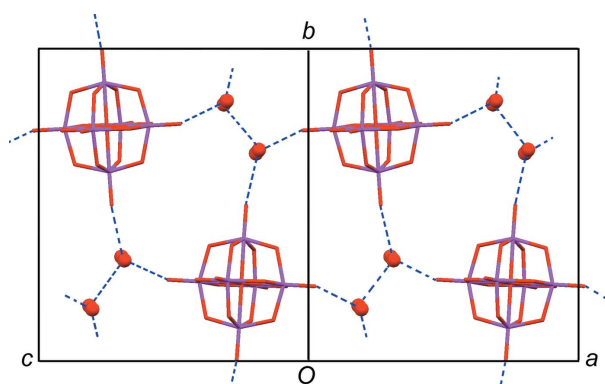
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.018$ Å
H-atom completeness 87%
Disorder in solvent or counterion
 R factor = 0.041
 wR factor = 0.123
Data-to-parameter ratio = 11.7For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hydronium μ -chloro-bis[bis(1,10-phenanthroline)copper(I)] hexatungstate monohydrateThe title compound, $(\text{H}_3\text{O})[\text{Cu}_2\text{Cl}(\text{C}_{12}\text{H}_8\text{N}_2)_4][\text{W}_6\text{O}_{19}]\cdot\text{H}_2\text{O}$, has been synthesized hydrothermally. The structure contains a dicopper(I) complex cation comprising two $[\text{Cu}(\text{phen})_2]^+$ units bridged by a chloride ion lying on a twofold rotation axis, a Lindquist isopolyanion, $[\text{W}_6\text{O}_{19}]^{2-}$, lying on a centre of inversion, one hydronium cation, and one uncoordinated water molecule per formula unit.Received 26 June 2006
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Comment

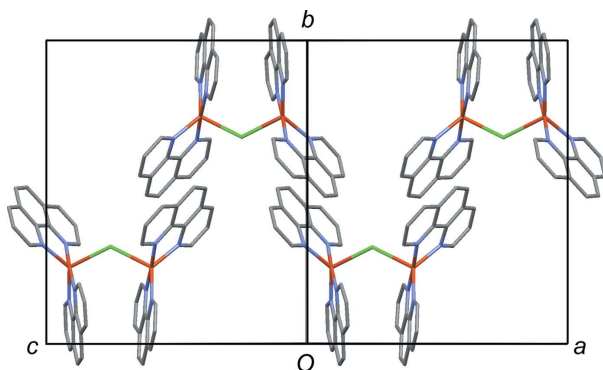
Polyoxometalates (POMs), *i.e.* early transition-metal/oxygen clusters, have attracted attention in recent years due to their fascinating properties and potential applications in materials science, medicine and catalysis (Yamase, 1998; Judd *et al.*, 2001; Hill, 2004). As well known electron acceptors (Sadakane & Steckhan, 1998), POMs have been applied in the preparation of charge-transfer salts with organic cation donors (Torres *et al.*, 2000; Liu *et al.*, 2002). Although numerous charge-transfer salts based on metal-organic complex cations and POM clusters have been described, charge-transfer hybrids based on the Lindquist polyanion $[\text{W}_6\text{O}_{19}]^{2-}$ are still scarce (Dietrich *et al.*, 1999). We report here the structure of a hydrothermally synthesized charge-transfer hybrid $[\text{Cu}_2(\text{phen})_4\text{Cl}](\text{H}_3\text{O})[\text{W}_6\text{O}_{19}]\cdot\text{H}_2\text{O}$ (phen = 1,10-phenanthroline), (I), which contains the Lindquist polyanion.The structure of (I) comprises a twofold-symmetric dicopper(I) complex cation, $[\text{Cu}_2(\text{phen})_4\text{Cl}]^+$, and a centrosymmetric Lindquist polyanion, $[\text{W}_6\text{O}_{19}]^{2-}$, with two disordered O atoms also present per formula unit (Fig. 1). In the $[\text{Cu}_2(\text{phen})_4\text{Cl}]^+$ cation, Cu1 adopts a square pyramidal coordination geometry, coordinated by two phen ligands and one bridging chloride ion (Table 1). The presence of Cu^{I} was established by X-ray photo-electron spectroscopy and is supported by bond-valence calculations (Brese & O'Keeffe, 1991). Charge balance requires the presence of one hydro-


Figure 1

The structural components of (I), showing displacement ellipsoids at the 30% probability level. H atoms have been omitted. Atoms O1W and O1W' are separate disorder components that comprise the hydronium ion and uncoordinated water molecule.

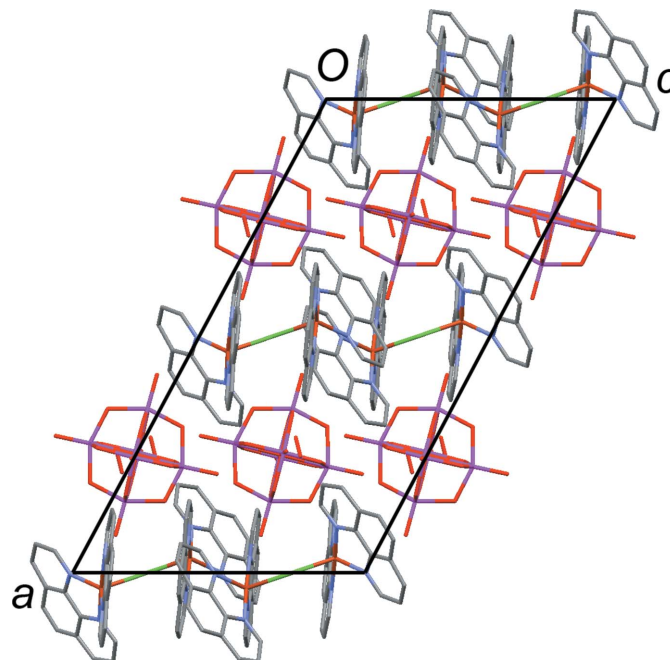

Figure 2

Projection approximately on to (100), showing one layer of $[W_6O_{19}]^{2-}$ anions linked through O1W and O1W'. The dashed lines denote hydrogen bonds. The environment of O1W and O1W' is suitable for one hydronium ion and one water molecule in any one site between the $[W_6O_{19}]^{2-}$ anions. H atoms have been omitted.


Figure 3

Projection approximately on to (100), showing one layer of $[Cu_2(phen)_4Cl]^+$ cations, forming π - π stacking interactions between the phen groups. H atoms have been omitted.

nium ion and one uncoordinated water molecule per formula unit. The environment of O1W/O1W' is suitable for such an assignment, forming a total of five $O \cdots O$ contacts suitable for $O-H \cdots O$ hydrogen bonding per pair of O1W/O1W' atoms between the $[W_6O_{19}]^{2-}$ anions (Fig. 2 and Table 2). It was not possible to locate H atoms in this vicinity.


Figure 4

Projection of (I) along b , showing the layered structure. H atoms have been omitted.

The $[W_6O_{19}]^{2-}$ polyanion comprises six edge-shared WO_6 octahedra and exhibits approximate O_h point symmetry. The O atoms can be divided into three groups: O_t (terminal oxygen, connected to one W atom), O_b (bridging oxygen, connecting edge-shared WO_6 octahedra) and O_c (the central O atom, common to all six WO_6 octahedra). The W—O bond lengths lie in the range 1.697 (10)–1.733 (8) Å (average 1.713 Å) for O_t , 1.895 (9)–1.949 (7) Å (average 1.923 Å) for O_b , and 2.322 (4)–2.331 (5) Å (average 2.326 Å) for O_c .

The $[Cu_2(phen)_4Cl]^+$ cations lie in layers in the (200) planes, forming π - π stacking interactions between the phen groups (Fig. 3). The $[W_6O_{19}]^{2-}$ anions and hydronium ions/water molecules occupy the interlamellar space (Fig. 4).

Experimental

A mixture of $CuCl_2 \cdot 2H_2O$ (1 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol), phen (1.5 mmol), $Na_2WO_4 \cdot 2H_2O$ (24 mmol) and water (60 ml) (molar ratio 1:1:1.5:24:3333) was adjusted to pH = 4.11 with aqueous HCl, and placed in an autoclave at 458 K for 4 d. After allowing the autoclave to stand at room temperature for 32 h, green block-shaped crystals were obtained. The X-ray photo-electron spectrum of (I) exhibits a signal at 932.4 eV, which is attributed to the $2p_{3/2}$ peak of Cu^I (Ghijssen *et al.*, 1988).

Crystal data

$(H_3O)[Cu_2Cl(C_{12}H_8N_2)_4] \cdot [W_6O_{19}] \cdot H_2O$
 $M_r = 2327.48$
 Monoclinic, $C2/c$
 $a = 26.135$ (2) Å
 $b = 16.2883$ (14) Å
 $c = 14.1273$ (13) Å
 $\beta = 118.138$ (1)°

$V = 5303.2$ (8) Å³
 $Z = 4$
 $D_x = 2.914$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 13.88$ mm⁻¹
 $T = 293$ (2) K
 Block, green
 $0.11 \times 0.11 \times 0.09$ mm

Data collection

Rigaku R-AXIS IV diffractometer
 φ scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.242$, $T_{\max} = 0.287$

13441 measured reflections
 4659 independent reflections
 3729 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.123$
 $S = 1.07$
 4659 reflections
 399 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 13.1567P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.69 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -3.80 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu1—N1	1.986 (7)	Cu1—N4	2.054 (7)
Cu1—N2	2.069 (8)	Cu1—Cl1	2.535 (2)
Cu1—N3	1.983 (7)		
N3—Cu1—N1	177.2 (3)	N3—Cu1—Cl1	88.9 (2)
N3—Cu1—N4	82.0 (3)	N1—Cu1—Cl1	88.3 (2)
N1—Cu1—N4	99.2 (3)	N4—Cu1—Cl1	106.0 (2)
N3—Cu1—N2	99.3 (3)	N2—Cu1—Cl1	119.8 (2)
N1—Cu1—N2	81.7 (3)	Cu1—Cl1—Cu1 ⁱ	128.24 (14)
N4—Cu1—N2	134.2 (3)		

Symmetry code: (i) $-x, y, -z + \frac{3}{2}$.

Table 2

Hydrogen-bond geometry (\AA).

$D-H\cdots A$	$D\cdots A$	$D-H\cdots A$	$D\cdots A$
O1W ⁱ ...O1 ⁱⁱ	3.00 (3)	O1W ⁱ ...O1 ⁱⁱ	2.84 (3)
O1W ⁱ ...O3	2.64 (3)	O1W ⁱ ...O3	2.72 (3)
O1W ⁱ ...O1W ⁱⁱⁱ	3.00 (8)	O1W ⁱ ...O1W ⁱⁱⁱ	3.51 (7)
O1W ⁱ ...O1W ⁱⁱⁱ	3.13 (4)		

Symmetry codes: (ii) $x, -y, z - \frac{1}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

H atoms were placed in calculated positions, with C—H = 0.93 \AA , and allowed to ride during subsequent refinement, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Atom O1W was modelled as disordered over two closely spaced sites (O1W and O1Wⁱ), with site occupancy factors 0.55 and 0.45. It was not possible to locate the H atoms in this vicinity. The highest difference peak and deepest hole lie in the vicinity of W2 and W3, respectively.

Data collection: R-AXIS (Molecular Structure Corporation, 1992); cell refinement: R-AXIS; data reduction: TEXSAN (Molecular Structure Corporation, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: TEXSAN; software used to prepare material for publication: TEXSAN.

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