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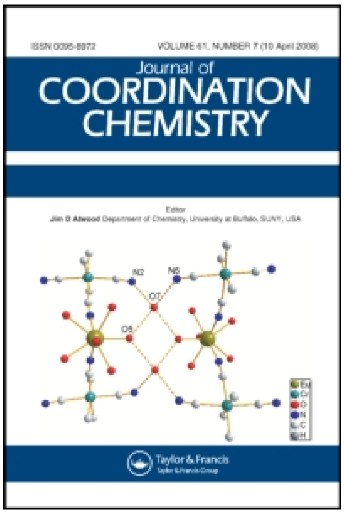

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Metal–oxo cluster-supported transition metal complexes: hydrothermal synthesis and characterization of $[\{Cu(phen)_2\}_2SiW_{12}O_{40}]$

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A new neutral α-Keggin polyoxometalate, $[\{Cu(phen)_2\}_2SiW_{12}O_{40}]$ (**1**) (phen = 1,10-phenanthroline) was hydrothermally synthesized and characterized by IR, TG and single-crystal X-ray diffraction. The compound is monoclinic, space group $P2_1/c$ with $a = 26.065(5)$, $b = 11.867(2)$, $c = 23.385(5)$ Å, $\beta = 113.78(3)°$, $V = 6619$ Å^3, $Z = 4$. X-ray analysis showed that both $[Cu(phen)_2]^{2+}$ units are supported on the α-Keggin polyoxoanion $[SiW_{12}O_{40}]^{4-}$ via the surface bridging and terminal oxygen atoms of two non-adjacent WO6 octahedra; these show unusual coordination environments. One Cu ion displays distorted trigonal bipyramidal geometry and the other square pyramidal. The unusual coexistence of complexes with different geometries is most likely caused by steric effects involving surface oxygen atoms of the heteropolytungstate and phen, which prevent the presence of a sixth coordinating atom. Weak π–π stacking interactions between phen groups give a 1D chain-like structure and hydrogen bonds are responsible for extended 2D and 3D motifs in the crystal.

Keywords: Hydrothermal synthesis; Keggin structure; Organic–inorganic hybrids; Polyoxotungstate; Copper; Crystal structure

1. Introduction

Polyoxometalates (POMs) have been known for more than 200 years, but continue to receive attention due to their intriguing structures and applications in medicine, materials science, catalysis, separation and imaging [1–3]. Decoration of polyoxoanion with various organic and transition metal complexes [4–6], which may enrich the discrete framework, leads to new and more selective applications in many fields. The mechanism of formation of decorated polyoxoanions is still poorly understood and usually described as self-assembly, and direct modification of the surface of POM clusters remains a great challenge. At the present time, there are four kinds of decorated

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POMs, capped [7], supporting [8], organic-metal compound [9] and functional organic group [10]. An important advance in POM chemistry concerns polyoxoanion-supported transition metal complexes and several hybrid compounds based on polyoxomolybdates have been reported [11]. In contrast, the number of examples incorporating polyoxotungstates is significantly lower [12] and heteropolyoxotungstate-supported inorganic-organic hybrids solids are hardly known, perhaps due to difficulties in modifying the surface of the heteropolyoxoanions. Structually characterized examples include $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$[13], $[PW_9V_3O_{40}\{Ag(2,2'\text{-bipy})\}_2\{Ag_2(2,2'\text{-bipy})_3\}_2]$ [14], $[Zn(2\text{-}2'\text{-bipy})_3]_2[ZnW_{12}O_{40}Zn(2\text{-}2'\text{-bipy})_2]\cdot H_2O$ [15], and $[Cu(en)_2(OH_2)]_2[Cu(en)_2]_{0.5}[H_2en]_{0.5}[\{[Cu(en)]_2P_2CuW_{17}O_{61}\}]\cdot 5H_2O$ [16]. Currently, we are interested in the applicability of a Keggin heteropolyanion, $[SiW_{12}O_{40}]^{4-}$, and exploiting its linking propensity with metal ions to obtain extended structures and new materials. We have succeeded in connecting this versatile building unit to $[Cu(phen)_2]^{2+}$ (phen = 1,10-phenanthroline) to form a new type of supramolecular compound $[\{Cu(phen)_2\}_2 SiW_{12}O_{40}]$ (**1**). In **1**, both $[Cu(phen)_2]^{2+}$ groups are coordinated to the α-Keggin-type polyoxoanion $[SiW_{12}O_{40}]^{4-}$ via the surface bridging and terminal oxygen atoms of two nonadjacent WO_6 octahedra. To the best of our knowledge, it has been rarely reported that α-Keggin heteropolyotungstates simultaneously support transition metal complex moieties that display different geometry geometries construction. There are two crystallographically independent copper sites with two different coordination environments in the present case, reported below.

2. Experimental

All chemicals purchased were of reagent grade as received from commercial sources and used without further purification. $H_4SiW_{12}O_{40}\cdot nH_2O$ was prepared according to a literature method [17]. Distilled water was used in the reaction. Elemental analyses (CHN) were performed on a Perkin-Elmer 2400 system. W, Cu and Si were determined by a Leaman ICP spectrometer. IR spectra (KBr pellets) were recorded in the range 400–4000 cm^{-1} on an Alpha Centauri FTIR spectrophotometer. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$.

2.1. *Synthesis*

Good quality crystals of **1** were prepared from a mixture of $CuSO_4\cdot 5H_2O$ (0.3055 g), phen (0.3740 g), $Na_3VO_4\cdot 2H_2O$ (0.5751 g), $H_4SiW_{12}O_{40}\cdot nH_2O$ (1.6138 g) and 15 cm^3 of water. The mixture was adjusted to pH 2.8 by addition aqueous 4M HCl aqueous solution and stirred for 30 mins in air. The final solution was transferred into a 25 cm^3 Teflon-lined autoclave, heated at 160°C for 5 days and cooled at $10^{\circ}C\,h^{-1}$ to room temperature. The resulting green blocky crystals were filtered off, washed with distilled water and air dried (54% yield based on W). Anal. Calcd for $C_{48}H_{32}Cu_2N_8O_{40}Si_1W_{12}$ (%): C, 15.49; H, 0.87; N, 3.01; W, 59.26; Si, 0.75; Cu, 3.42. Found: C, 15.56; H, 0.95; N, 2.97; W, 59.35; Si, 0.71; Cu, 3.36.

Table 1. Crystal data and structure refinement details for **1**.

Empirical formula	$C_{48}H_{32}N_8O_{40}SiCu_2W_{12}$
Formula weight	3722.19
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)	
a	26.065(5)
b	11.867(2)
c	23.385(5)
β	113.78(3)
Volume (Å^3)	6619(2)
Z	4
Calculated density (Mg m^{-3})	3.735
Absorption coefficient (mm^{-1})	21.506
F(000)	6624
Crystal size (mm^3)	$0.225 \times 0.130 \times 0.100$
Theta range for data collection (°)	3.03–27.48
Limiting indices	$-33 \le h \le 33$, $-15 \le k \le 15$, $-30 \le l \le 30$
Reflections collected/unique	60095/14976 [R(int) = 0.0724]
Completeness to $\theta = 27.48$	98.7%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	14976/0/1001
Goodness-of-fit on F^2	0.993
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0442$, $wR_2 = 0.1010$
R indices (all data)	$R_1 = 0.0652$, $wR_2 = 0.1100$
Extinction coefficient	0.000054(9)
Largest diff. peak and hole (e Å^{-3})	2.337 and −2.163

2.2. *X-ray crystallography*

A crystal with approximate dimensions $0.225 \times 0.130 \times 0.100\,\text{mm}^3$ was mounted on a glass fibre. X-ray diffraction data were measured on a R-axis RAPID IP diffractometer equipped with a normal focus, 18 kW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å). Data processing was accomplished with the RAXWISH processing program. An empirical absorption correction was applied. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL 97 [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located from different Fourier maps. A summary of crystal data is provided in table 1. Selected bond lengths and angles are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Synthesis*

The isolation of **1** relies on hydrothermal techniques. Hydrothermal synthesis has recently been proved as a useful technique in the preparation of a large number of organic–inorganic hybrids [19, 20]. In the hydrothermal environment, a variety of simple organic and/or inorganic template agents can be introduced [21, 22]. However, hydrothermal synthesis is still a relatively complex process. During the preparation of **1**,

Table 2. Selected bond lengths (Å) for **1**.

W(1)–O(33)	1.692(8)	W(2)–O(35)	1.699(8)
W(1)–O(27)	1.886(8)	W(2)–O(20)	1.863(8)
W(1)–O(14)	1.896(8)	W(2)–O(19)	1.877(7)
W(1)–O(1)	1.937(7)	W(2)–O(15)	1.933(7)
W(1)–O(23)	1.944(7)	W(2)–O(22)	1.959(8)
W(1)–O(29)	2.362(7)	W(2)–O(28)	2.361(7)
W(3)–O(2)	1.705(8)	W(4)–O(34)	1.680(8)
W(3)–O(24)	1.895(8)	W(4)–O(23)	1.853(8)
W(3)–O(17)	1.917(8)	W(4)–O(16)	1.900(7)
W(3)–O(1)	1.914(7)	W(4)–O(3)	1.946(8)
W(3)–O(11)	1.929(8)	W(4)–O(37)	1.960(7)
W(3)–O(29)	2.335(7)	W(4)–O(6)	2.326(7)
W(5)–O(36)	1.705(8)	W(6)–O(13)	1.730(8)
W(5)–O(16)	1.881(7)	W(6)–O(22)	1.873(8)
W(5)–O(39)	1.884(8)	W(6)–O(7)	1.887(7)
W(5)–O(27)	1.932(8)	W(6)–O(26)	1.901(7)
W(5)–O(9)	1.938(8)	W(6)–O(39)	1.948(8)
W(5)–O(30)	2.389(7)	W(6)–O(30)	2.279(7)
W(7)–O(4)	1.697(7)	W(8)–O(10)	1.688(8)
W(7)–O(21)	1.858(8)	W(8)–O(3)	1.885(7)
W(7)–O(15)	1.907(8)	W(8)–O(26)	1.905(7)
W(7)–O(25)	1.911(8)	W(8)–O(18)	1.924(7)
W(7)–O(5)	2.035(8)	W(8)–O(19)	1.934(7)
W(7)–O(28)	2.319(6)	W(8)–O(6)	2.380(8)
W(9)–O(8)	1.680(8)	W(10)–O(40)	1.665(7)
W(9)–O(11)	1.879(8)	W(10)–O(31)	1.862(8)
W(9)–O(25)	1.891(8)	W(10)–O(9)	1.897(8)
W(9)–O(31)	1.924(8)	W(10)–O(21)	1.931(8)
W(9)–O(14)	1.946(8)	W(10)–O(7)	1.939(8)
W(9)–O(29)	2.337(7)	W(10)–O(30)	2.378(7)
W(11)–O(12)	1.697(8)	W(12)–O(32)	1.690(8)
W(11)–O(38)	1.894(7)	W(12)–O(38)	1.891(7)
W(11)–O(17)	1.900(8)	W(12)–O(24)	1.900(8)
W(11)–O(18)	1.900(8)	W(12)–O(20)	1.950(8)
W(11)–O(37)	1.964(7)	W(12)–O(5)	1.970(7)
W(11)–O(6)	2.350(7)	W(12)–O(28)	2.356(7)
Si(1)–O(6)	1.608(7)	Cu(1)–N(4)	1.976(10)
Si(1)–O(29)	1.617(8)	Cu(1)–N(3)	2.000(9)
Si(1)–O(30)	1.626(8)	Cu(1)–N(5)	2.006(9)
Si(1)–O(28)	1.633(7)	Cu(1)–O(13)	2.055(8)
Cu(2)–N(6)	1.958(10)	Cu(1)–N(2)	2.199(9)
Cu(2)–N(7)	2.041(11)	Cu(2)–O(37)	2.270(7)
Cu(2)–N(8)	1.975(10)	Cu(2)–N(1)	2.155(10)

we found that final products are sensitive to the pH of the starting solution. The pH was controlled at 2.5–3.5 to obtain pure crystalline product and outside this range no crystals were obtained. Changing the amounts of other reagents, temperature (150–170°C) and reaction time (4–6 days) had little effect. In the experiment, we used $Na_3VO_4 \cdot 2H_2O$ to try to synthesise vanadium-capped Keggin derivatives, but vanadium is not incorporated in the structure.

3.2. *Structure*

Complex **1** consists of two $[Cu(phen)_2]^{2+}$ cations and one $[SiW_{12}O_{40}]^{4-}$ polyanion (figure 1a). The $[SiW_{12}O_{40}]^{4-}$ anion consists of 12 WO_6 octahedra and one

Table 3. Selected bond angles (°) for **1**.

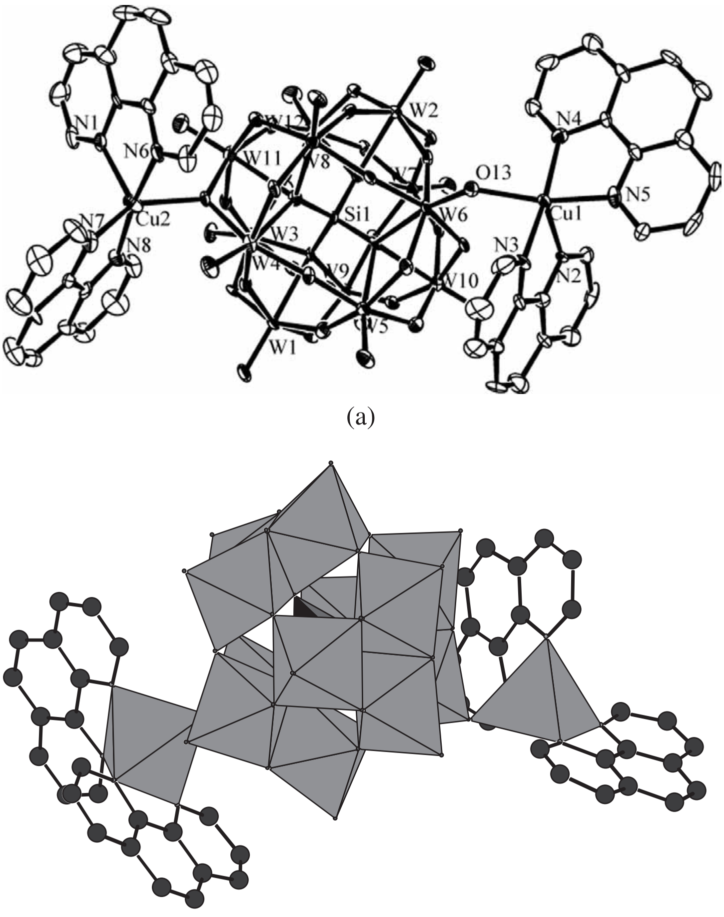
O(33)–W(1)–O(27)	102.6(4)	O(35)–W(2)–O(20)	101.5(4)
O(33)–W(1)–O(14)	99.8(4)	O(35)–W(2)–O(19)	102.7(4)
O(27)–W(1)–O(14)	92.8(3)	O(20)–W(2)–O(19)	91.4(3)
O(33)–W(1)–O(1)	99.6(4)	O(35)–W(2)–O(15)	100.7(3)
O(27)–W(1)–O(1)	157.3(3)	O(20)–W(2)–O(15)	88.1(3)
O(14)–W(1)–O(1)	87.8(3)	O(19)–W(2)–O(15)	156.1(3)
O(33)–W(1)–O(23)	102.9(4)	O(35)–W(2)–O(22)	100.5(4)
O(27)–W(1)–O(23)	84.9(3)	O(20)–W(2)–O(22)	157.9(3)
O(14)–W(1)–O(23)	157.2(3)	O(19)–W(2)–O(22)	85.7(3)
O(1)–W(1)–O(23)	85.8(3)	O(15)–W(2)–O(22)	85.9(3)
O(33)–W(1)–O(29)	170.0(4)	O(35)–W(2)–O(28)	171.5(3)
O(27)–W(1)–O(29)	85.3(3)	O(20)–W(2)–O(28)	74.1(3)
O(14)–W(1)–O(29)	73.6(3)	O(19)–W(2)–O(28)	84.8(3)
O(1)–W(1)–O(29)	73.0(3)	O(15)–W(2)–O(28)	72.1(3)
O(23)–W(1)–O(29)	83.6(3)	O(22)–W(2)–O(28)	83.8(3)
O(2)–W(3)–O(24)	102.1(4)	O(34)–W(4)–O(23)	103.1(4)
O(2)–W(3)–O(17)	102.9(3)	O(34)–W(4)–O(16)	103.4(4)
O(24)–W(3)–O(17)	85.2(3)	O(23)–W(4)–O(16)	86.7(3)
O(2)–W(3)–O(1)	99.5(4)	O(34)–W(4)–O(3)	99.7(4)
O(24)–W(3)–O(1)	158.3(3)	O(23)–W(4)–O(3)	157.2(3)
O(17)–W(3)–O(1)	90.7(3)	O(16)–W(4)–O(3)	87.1(3)
O(2)–W(3)–O(11)	97.6(4)	O(34)–W(4)–O(37)	95.4(4)
O(24)–W(3)–O(11)	88.1(3)	O(23)–W(4)–O(37)	92.0(3)
O(17)–W(3)–O(11)	159.3(3)	O(16)–W(4)–O(37)	160.9(3)
O(1)–W(3)–O(11)	88.5(3)	O(3)–W(4)–O(37)	86.8(3)
O(2)–W(3)–O(29)	168.7(3)	O(34)–W(4)–O(6)	168.3(4)
O(24)–W(3)–O(29)	84.5(3)	O(23)–W(4)–O(6)	84.4(3)
O(17)–W(3)–O(29)	86.7(3)	O(16)–W(4)–O(6)	85.8(3)
O(1)–W(3)–O(29)	74.1(3)	O(3)–W(4)–O(6)	73.2(3)
O(11)–W(3)–O(29)	73.2(3)	O(37)–W(4)–O(6)	75.2(3)
O(36)–W(5)–O(16)	103.3(4)	O(13)–W(6)–O(22)	100.2(4)
O(36)–W(5)–O(39)	100.9(4)	O(13)–W(6)–O(7)	98.5(3)
O(16)–W(5)–O(39)	92.4(3)	O(22)–W(6)–O(7)	91.2(3)
O(36)–W(5)–O(27)	102.6(4)	O(13)–W(6)–O(26)	103.1(3)
O(16)–W(5)–O(27)	84.9(3)	O(22)–W(6)–O(26)	85.4(3)
O(39)–W(5)–O(27)	156.3(3)	O(7)–W(6)–O(26)	158.3(3)
O(36)–W(5)–O(9)	99.0(4)	O(13)–W(6)–O(39)	99.2(3)
O(16)–W(5)–O(9)	157.5(3)	O(22)–W(6)–O(39)	160.4(3)
O(39)–W(5)–O(9)	86.7(3)	O(7)–W(6)–O(39)	88.4(3)
O(27)–W(5)–O(9)	86.9(3)	O(26)–W(6)–O(39)	87.8(3)
O(36)–W(5)–O(30)	170.0(3)	O(13)–W(6)–O(30)	170.4(3)
O(16)–W(5)–O(30)	85.0(3)	O(22)–W(6)–O(30)	86.8(3)
O(39)–W(5)–O(30)	72.7(3)	O(7)–W(6)–O(30)	74.6(3)
O(27)–W(5)–O(30)	83.6(3)	O(26)–W(6)–O(30)	83.8(3)
O(9)–W(5)–O(30)	73.3(3)	O(39)–W(6)–O(30)	74.2(3)
O(4)–W(7)–O(21)	103.8(4)	O(10)–W(8)–O(3)	100.9(4)
O(4)–W(7)–O(15)	98.9(4)	O(10)–W(8)–O(26)	100.8(4)
O(21)–W(7)–O(15)	93.4(3)	O(3)–W(8)–O(26)	91.2(3)
O(4)–W(7)–O(25)	101.8(4)	O(10)–W(8)–O(18)	101.4(4)
O(21)–W(7)–O(25)	87.4(3)	O(3)–W(8)–O(18)	87.7(3)
O(15)–W(7)–O(25)	158.5(3)	O(26)–W(8)–O(18)	157.6(3)
O(4)–W(7)–O(5)	96.3(4)	O(10)–W(8)–O(19)	102.2(4)
O(21)–W(7)–O(5)	159.8(3)	O(3)–W(8)–O(19)	156.8(3)
O(15)–W(7)–O(5)	85.7(3)	O(26)–W(8)–O(19)	84.3(3)
O(25)–W(7)–O(5)	86.1(3)	O(18)–W(8)–O(19)	87.9(3)
O(4)–W(7)–O(28)	166.8(3)	O(10)–W(8)–O(6)	171.9(3)
O(21)–W(7)–O(28)	87.7(3)	O(3)–W(8)–O(6)	73.0(3)
O(15)–W(7)–O(28)	73.5(3)	O(26)–W(8)–O(6)	84.9(3)
O(25)–W(7)–O(28)	85.0(3)	O(18)–W(8)–O(6)	73.4(3)
O(5)–W(7)–O(28)	72.7(3)	O(19)–W(8)–O(6)	84.0(3)

(*continued*)

Table 3. Continued.

O(8)–W(9)–O(11)	100.5(4)	O(40)–W(10)–O(31)	101.4(4)
O(8)–W(9)–O(25)	102.7(4)	O(40)–W(10)–O(9)	101.3(4)
O(11)–W(9)–O(25)	90.7(3)	O(31)–W(10)–O(9)	93.8(3)
O(8)–W(9)–O(31)	102.5(4)	O(40)–W(10)–O(21)	100.8(4)
O(11)–W(9)–O(31)	156.9(3)	O(31)–W(10)–O(21)	85.3(3)
O(25)–W(9)–O(31)	86.3(3)	O(9)–W(10)–O(21)	157.6(3)
O(8)–W(9)–O(14)	98.9(4)	O(40)–W(10)–O(7)	101.4(4)
O(11)–W(9)–O(14)	87.8(3)	O(31)–W(10)–O(7)	156.5(3)
O(25)–W(9)–O(14)	158.2(3)	O(9)–W(10)–O(7)	87.3(3)
O(31)–W(9)–O(14)	86.6(3)	O(21)–W(10)–O(7)	84.9(3)
O(8)–W(9)–O(29)	170.5(3)	O(40)–W(10)–O(30)	171.4(4)
O(11)–W(9)–O(29)	74.0(3)	O(31)–W(10)–O(30)	86.3(3)
O(25)–W(9)–O(29)	85.3(3)	O(9)–W(10)–O(30)	74.2(3)
O(31)–W(9)–O(29)	83.0(3)	O(21)–W(10)–O(30)	83.4(3)
O(14)–W(9)–O(29)	73.4(3)	O(7)–W(10)–O(30)	71.4(3)
O(12)–W(11)–O(38)	101.5(4)	O(32)–W(12)–O(38)	103.5(4)
O(12)–W(11)–O(17)	102.2(4)	O(32)–W(12)–O(24)	102.2(4)
O(38)–W(11)–O(17)	86.1(3)	O(38)–W(12)–O(24)	87.5(3)
O(12)–W(11)–O(18)	100.5(4)	O(32)–W(12)–O(20)	101.5(4)
O(38)–W(11)–O(18)	90.3(3)	O(38)–W(12)–O(20)	88.8(3)
O(17)–W(11)–O(18)	157.3(3)	O(24)–W(12)–O(20)	156.2(3)
O(12)–W(11)–O(37)	98.6(4)	O(32)–W(12)–O(5)	97.9(4)
O(38)–W(11)–O(37)	159.9(3)	O(38)–W(12)–O(5)	158.5(3)
O(17)–W(11)–O(37)	88.6(3)	O(24)–W(12)–O(5)	88.9(3)
O(18)–W(11)–O(37)	87.2(3)	O(20)–W(12)–O(5)	86.0(3)
O(12)–W(11)–O(6)	171.5(3)	O(32)–W(12)–O(28)	169.4(4)
O(38)–W(11)–O(6)	85.6(3)	O(38)–W(12)–O(28)	85.6(3)
O(17)–W(11)–O(6)	82.9(3)	O(24)–W(12)–O(28)	83.4(3)
O(18)–W(11)–O(6)	74.5(3)	O(20)–W(12)–O(28)	72.8(3)
O(37)–W(11)–O(6)	74.5(3)	O(5)–W(12)–O(28)	73.0(3)
N(6)–Cu(2)–N(8)	172.9(4)	N(4)–Cu(1)–N(3)	170.7(4)
N(6)–Cu(2)–N(7)	98.6(4)	N(4)–Cu(1)–N(5)	83.3(4)
N(8)–Cu(2)–N(7)	82.3(4)	N(3)–Cu(1)–N(5)	97.9(4)
N(6)–Cu(2)–N(1)	80.3(4)	N(4)–Cu(1)–O(13)	89.5(4)
N(8)–Cu(2)–N(1)	105.8(4)	N(3)–Cu(1)–O(13)	87.0(4)
N(7)–Cu(2)–N(1)	115.3(4)	N(5)–Cu(1)–O(13)	164.3(4)
N(6)–Cu(2)–O(37)	86.3(3)	N(4)–Cu(1)–N(2)	110.0(4)
N(8)–Cu(2)–O(37)	89.1(4)	N(3)–Cu(1)–N(2)	79.2(4)
N(7)–Cu(2)–O(37)	146.6(3)	N(5)–Cu(1)–N(2)	93.8(4)
N(1)–Cu(2)–O(37)	98.0(3)	O(13)–Cu(1)–N(2)	101.8(3)
O(6)–Si(1)–O(28)	111.4(4)	O(6)–Si(1)–O(29)	109.0(4)
O(29)–Si(1)–O(28)	108.6(4)	O(6)–Si(1)–O(30)	109.0(4)
O(30)–Si(1)–O(28)	109.3(4)	O(29)–Si(1)–O(30)	109.5(4)

SiO_4 tetrahedron. For the latter, Si–O distances vary from 1.605(8) to 1.636(8) Å with an average of 1.623 Å, 0.007 Å shorter than that of a previous report [23]. The average O–Si–O angle of 109.45° is 0.22° larger than that in $H_4SiW_{12}O_{40}$ [23]. The central SiO_4 tetrahedron shares its oxygen atoms with four $\{W_3O_{13}\}$ groups, each of which is made up of three edge-sharingWO$_6$ octahedra. W_3O_{13} subnits are joined by corner sharing. Oxygen atoms in $[SiW_{12}O_{40}]^{4-}$ can be divided into four groups according to their coordination number; O_t terminal oxygen atoms connect to one W atom, O_b atoms share corners between two W_3O_{13} units, O_c atoms connecting edge-sharing WO_6 octahedra in the same W_3O_{13} unit and O_a atoms connecting the Si and three W atoms. Relevant W–O bond distances in the anion can be classified into three groups: W–O_t 1.678–1.737 Å, mean 1.696 Å, W–$O_{b,c}$ 1.854–1.971 Å, mean 1.914 Å and W–O_a



(a)

(b)

Figure 1. (a) ORTEP drawing of $[\{Cu(phen)_2\}_2SiW_{12}O_{40}]$ depicted at the 50% probability level; only some atoms are labelled and H atoms are omitted for clarity; (b) polyhedral representation of compound **1**.

2.276–2.384 Å, mean 2.352 Å. These are 0.039, 0.021 and 0.005 Å shorter, respectively, than corresponding values in the literature [24], indicating that the polyanion maintains the basic Keggin structure, However, compared with the averages, $W(6)–O_t(13)$ (1.730 Å) and $W(4)–O_c(37)$ (1.960 Å) bonds are lengthened (table 2), this is caused by the coordination of copper to surface oxygen atoms of the polyanion.

The most unusual structural feature of **1** is that a surface bridging and a terminal oxygen atom of the polyoxoanion are coordinated to two $[Cu(phen)_2]^{2+}$ cations, respectively. To our knowledge, such an α-Keggin anion simultaneously supporting two transition metal complexes has rarely been observed. It is interesting that there are two distinct copper(II) coordination geometries in **1** as shown in figure 1(b). Cu(1) exhibits square pyramidal geometry with the square plane defined by three nitrogen atoms from two phen ligands and a terminal oxygen atom of the anion; the apical site is occupied by the remaining nitrogen atom of a phen ligand. Cu(2) exhibits distorted trigonal

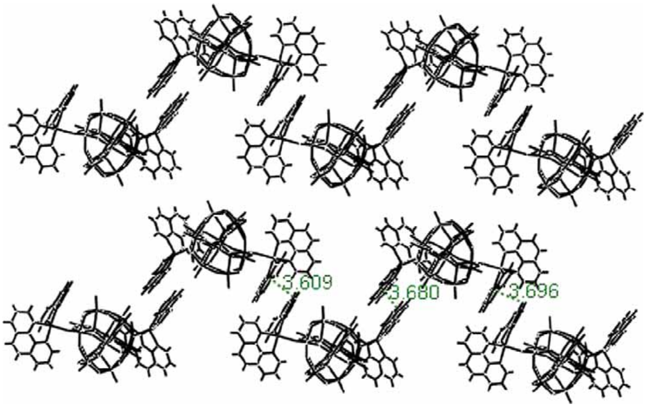


Figure 2. A view of the extended structure of $[\{Cu(phen)_2\}_2SiW_{12}O_{40}]$ showing the 1D toothed chain structure connected by π–π stacking interactions.

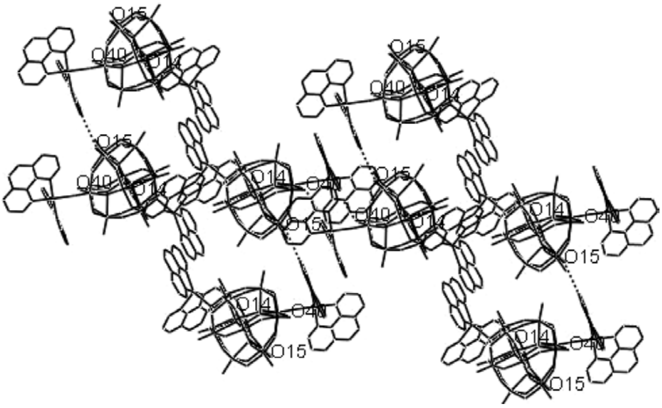


Figure 3. A view of the 2D planar structure in **1** connected through hydrogen bonding and π–π stacking interactions; all H atoms are omitted for clarity.

bipyramidal geometry, in which the equatorial plane is defined by three nitrogen atoms from two phen ligands, while axial positions are occupied by the remaining nitrogen atom and the bridging oxygen atom of the polyoxotungstate. The difference is most likely caused by steric effects induced by the surface oxygen atoms of the Keggin anion.

Molecules of **1** are joined together by π–π stacking interactions involving phen groups and extensive hydrogen bonding contacts between hydrogen atoms on the phen ligands and oxygen atoms of polyanions, with C–H$\cdots$O distances in the range 2.324–2.526 Å; the closest contact between adjacent aromatic rings is 3.609 Å. Thus the structure forms a 1D, toothed, chain-like arrangement via weak π–π stacking (figure 2). Hydrogen bonds link the chains to give an infinite 2D planar structure (figure 3) and further such interactions serve to assemble a 3D supramolecular network (figure 4). The extensive hydrogen bonding array no doubt contributes to the stability of the structure.

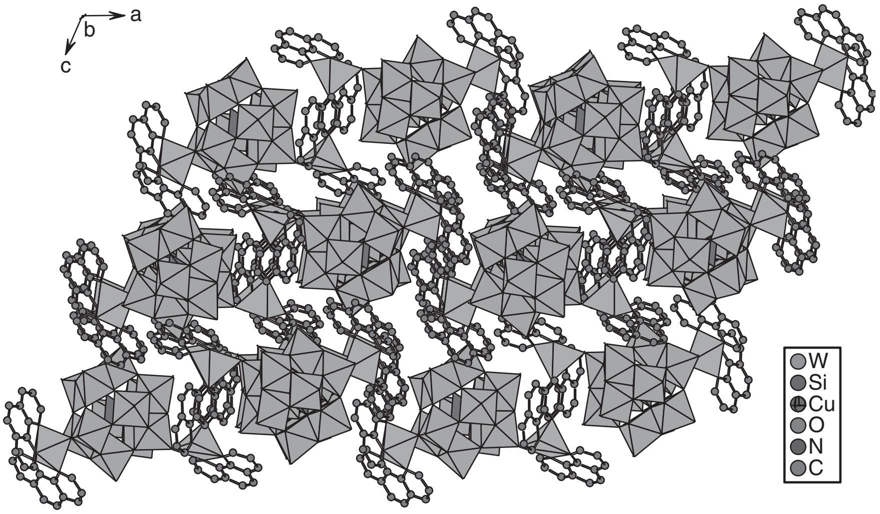


Figure 4. The packing arrangement in **1** viewed down the *b* axis; H atoms are omitted for clarity.

3.3. *Other data*

In IR, cations bands (1100–1600 cm^{-1} associated with phen) and four characteristic asymmetric vibrations of $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ [ν_{as}(Si–O$_a$), ν_{as}(W = O$_t$), ν_{as}(W–O$_b$) and ν_{as}(W–O$_c$)] are observed; the latter appear at 920, 971, 850 and 790 cm^{-1}, respectively. Comparison of the IR spectrum of **1** with that of $(\text{TBA})_4[\text{SiW}_{12}\text{O}_{40}]$ [25], shows that W–O$_c$ and W–O$_b$ bands are red-shifted. This indicates that bridge oxygen bonds are weakened due to coordination to $[\text{Cu(phen)}_2]^{2+}$ and formation of hydrogen bonds. Thermogravimetric analysis over the temperature range 440 to 645°C indicates one weight loss due to release of phen ligands (found: 20.6; Calcd 21.3%).

Supplementary material

Crystallographic data (excluding structure factors) have been deposited with Cambridge Crystallographic Data Centre as Supplementary publication CCDC 275684. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44 1223 336033; Email:deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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