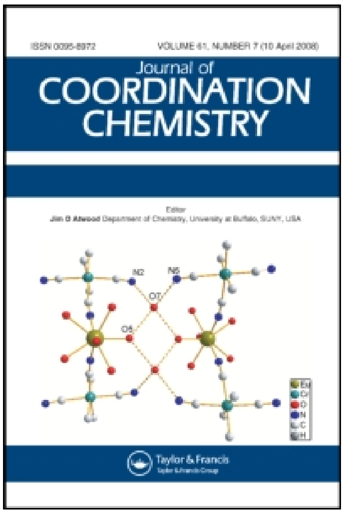

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Wang, Juan , Li, Feng-Biao , Tian, Li-Hong and Cheng, Shi-Yuan(2008) 'Synthesis, structure and electrochemical behavior of an organic-inorganic hybrid compound based on Dawson-type polyoxometalates', Journal of Coordination Chemistry, 61: 13, 2122 — 2131

To link to this Article: DOI: 10.1080/00958970801891330

URL: http://dx.doi.org/10.1080/00958970801891330

Journal of Coordination Chemistry
Vol. 61, No. 13, 10 July 2008, 2122–2131

Synthesis, structure and electrochemical behavior of an organic-inorganic hybrid compound based on Dawson-type polyoxometalates

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(*Received 20 August 2007; in final form 3 October 2007*)

An organic-inorganic hybrid compound constructed from Wells-Dawson polyanion clusters and metal-organic complex subunits, $[Cu(phen)_3][Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})] \cdot 2H_2O$ (**1**) has been prepared hydrothermally and characterized by elemental analysis, IR, UV, cyclic voltammetry (CV) and single-crystal X-ray diffraction. Crystal structural analysis indicates that two terminal oxygen atoms of the Wells-Dawson polyanion located in the "belt" site coordinate with Cu^{2+}. Three Cu ions have different coordination environments: Cu1 and Cu2 are five-coordinate, while Cu3 is six-coordinate. The bisupporting polyoxoanions $[Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]^{2-}$ are polymerized into a 1D chain by hydrogen bonding interactions, then the chains are stacked into a two-dimensional structure via offset, face-to-face, $\pi \cdots \pi$ stacking interactions. CV reveals that **1** exhibits three chemically-reversible processes.

Keywords: Crystal structure; Hydrothermal synthesis; Wells-Dawson polyoxometalate; 1,10-phenanthroline; Cyclic voltammetry

1. Introduction

Polyoxometalates (POMs) exhibit many properties [1, 2] that make them attractive for applications in catalysis for chemical transformation [3], molecular conductivity [4], magnetism [5], luminescence, photochromism and electrochromism [6], etc. The incorporation of metal-organic moieties into inorganic oxide clusters provides a powerful method for structural modification and synthesis of materials that combine the features of both substructures. Stability constants for binding of transition metal or rare-earth elements with $[P_2W_{18}O_{62}]^{6-}$ are low [7–9]. The poor complexing of $[P_2W_{18}O_{62}]^{6-}$ is attributed to the weakly basic oxygen atoms on the anion's surface in combination with the lack of suitable inner-sphere coordination sites [10]. In contrast, the monovacant, lacunary Wells-Dawson polyoxoanion $[P_2W_{17}O_{61}]^{10-}$,

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801891330

obtained by removal of one $[W(VI){=}O]^{4+}$ group from $[P_2W_{18}O_{62}]^{6-}$, is a tetradentate ligand [11–18] with four strongly basic O donor atoms directed at the vacant site left by the removal of $[WO]^{4+}$, and binds transition metals to form stable complexes [19–21]. There are a few organic-inorganic hybrid compounds based on $[X_2M_{18}O_{62}]^{6-}$ (X = P, As) and transition metal. For example, a dimeric polyoxotungstate $[Cu(2,2'\text{-bipy})_3]_4H_2[Cu(H_2O)_4(As_2W_{18}O_{62})_2]$ has two $[As_2W_{18}O_{62}]^{6-}$ blocks linked by one $[Cu(H_2O)_4]^{2+}$ fragment [22].

To the best of our knowledge, organic-inorganic hybrid compounds containing Dawson anion $[P_2M_{18}O_{62}]^{6-}$ and 1,10-phenanthroline as a ligand have not been reported except for $[Zn(phen)_2(H_2O)_2][\{Zn(phen)_2\}\{Zn(phen)_2(H_2O)\}\{P_2W_{18}O_{62}\}]\cdot 8H_2O$ and $[Cd(phen)_2(H_2O)_2][\{Cd(phen)_2\}\{Cd(phen)(H_2O)_3\}\{P_2W_{18}O_{62}\}]\cdot 4H_2O$ [23]. Herein, we report the synthesis, crystal structure, and characterization of an organic-inorganic hybrid compound $[Cu(phen)_3][Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]\cdot 2H_2O$ (phen = 1,10-phenanthroline). Furthermore, the electrochemical behavior of **1** is reported.

2. Experimental

2.1. *Materials and physical measurement*

All materials and organic solvents were of analytical grade and used without further purification. Distilled, deionized water was used throughout. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHNSO elemental analyzer. The infrared spectrum was recorded as a KBr pellet on a Nicolet 170SXFT-IR spectrometer in the 4000–400 cm^{-1} range. The electronic absorption spectra were taken on a Shimadzu UV-240 spectrophotometer. Cyclic voltammograms were obtained on a model CHI660 electrochemical analyzer (CH Instruments, Austin, TX, USA) controlled by a personal computer at room temperature. A three-electrode system was used for the measurements, with a bare GCE (3 mm diameter) or C-Ni/GCE used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. All experiments were performed at room temperature.

2.2. *Synthesis of $[Cu(phen)_3][Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]\cdot 2H_2O$ (1)*

A mixture of $Na_2WO_4\cdot 2H_2O$ (0.9857 g, 2.99 mmol), H_3PO_4 (0.3 mL, 85%), $Cu(CH_3COO)_2\cdot H_2O$ (0.0385 g, 0.19 mmol), 1,10-phen (0.0991 g, 0.50 mmol) and H_2O (15 mL) was stirred for half an hour in air and the pH of the solution was adjusted to 4.6 by addition of KOH (0.5 M) solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170°C for 4 days. After the autoclave cooled to room temperature, green block-shaped crystals were filtered off, washed with distilled water, and air-dried to give a yield of 10.7% based on W. Anal. Calcd for $C_{84}H_{60}Cu_3W_{18}N_{14}O_{64}P_2$ (%): C, 17.23; H, 1.03; N, 3.35. Found: C, 17.28; H, 1.01; N, 3.43.

2.3. *X-ray crystallography*

Single-crystal X-ray crystallographic analysis of **1** with approximate dimensions $0.14 \times 0.16 \times 0.28\,\mathrm{mm}^3$ was performed at 291(2) K on a Bruker SMART APEX CCD sealed tube diffractometer with graphite monochromated Mo-Kα (0.71073 Å) radiation. Data collection, indexing, and initial cell refinements were carried out using SMART software [24]. Frame integration and final cell refinements were carried out using SAINT software [25]. Absorption corrections for each data set were applied using SADABS [26]. Structure solution, refinement, and generation of publication materials were performed using SHELXTL-97 [27]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms except several oxygen, carbon and nitrogen atoms. Hydrogen atoms were located at their ideal positions as a riding mode. The crystallographic data and structure determination parameters for $[Cu(phen)_3][Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})] \cdot 2H_2O$ are summarized in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

Hydrothermal reactions have been utilized to synthesize many organic-inorganic hybrid materials, although syntheses and complete characterization of the polyoxometalates are not easy. The hydrothermal technique has many variables, such as the kind and stoichiometry of starting materials, temperature, pH, filling volume and reaction time, which can affect the result. Many groups used Wells-Dawson POM α-$K_6P_2W_{18}O_{62} \cdot nH_2O$ as the precursor to prepare organic-inorganic hybrid complexes. In our experiments, we used $Na_2WO_4 \cdot 2H_2O$ and H_3PO_4 as starting materials instead of α-$K_6P_2W_{18}O_{62} \cdot nH_2O$ and obtained a green product, suggesting that $Na_2WO_4 \cdot 2H_2O$ and H_3PO_4 as starting materials is also an effective strategy. The 1,10-phen molecules in the preparation of **1** act as a ligand coordinated to Cu atoms, incorporated into the metal oxide backbone as peripheral moieties.

3.2. *Crystal structure*

Single crystal X-ray diffraction analysis reveals that **1** is composed of a polyoxoanion $[Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]^{2-}$, one discrete $[Cu(phen)_3]^{2+}$ cation and two free water molecules. The polyoxoanion $[Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]^{2-}$ consists of a Dawson polyoxoanion $[P_2W_{18}O_{62}]^{6-}$, on which two $[Cu(phen)_2]^{2+}$ groups are supported (see figure 1). $[P_2W_{18}O_{62}]^{6-}$ in **1** has a normal Wells-Dawson structure built from edge- and corner-sharing octahedral encapsulating two phosphorus atoms. Oxygen atoms in $[P_2W_{18}O_{62}]^{6-}$ can be divided into four groups according to their coordination number [28]: O_t (terminal oxygen atoms connecting only one W atom), O_b (oxygen atoms located in corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge sharing WO_6 octahedra in the same W_3O_{13} unit) and O_a (oxygen atoms connecting the P heteroatom and W atoms). Relevant W–O bond distances in the anion can be classified into three groups: W–O_t 1.730(7)–1.760(7) Å,

Table 1. Crystallographic data for **1**.

Empirical formula	$C_{84}H_{6}0Cu_{3}W_{18}N_{14}O_{64}P_{2}$
Formula weight	5851.32
Temperature (K)	291(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	54.671(4)
b	13.6761(9)
c	32.037(2)
α	90
β	97.112(2)
γ	90
Volume (Å^3)	23769(3)
Z	8
Density (calculated) (g · cm^{-3})	3.270
Absorption coefficient (mm^{-1})	17.990
$F(000)$	20984
Crystal size (mm^3)	0.14 × 0.16 × 0.28
θ range for data collection (°)	1.3 to 26.0
Index ranges	$-67 \le h \le 67$; $-16 \le k \le 16$; $-39 \le l \le 39$
Reflections collected	120660
Independent reflections	23332 ($R_{\text{int}} = 0.049$)
Completeness to $\theta = 26.0°$	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	23332/0/1684
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0501$, $wR_2 = 0.1021$
R indices (all data)	$R_1 = 0.0710$, $wR_2 = 0.1076$
Largest diffraction peak and hole (e•Å^{-3})	0.83 and −0.74

$R_1 = \sum \lVert F_o \rvert - F_c \rVert / \sum |F_o|$; $wR_2 = \sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$.
$w^{-1} = [\sigma^2(F_o)^2 + (0.06P)^2 + 1.99P]$, $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths (Å) and angles (°).

Wl–01	1.740(8)	W8–O8	1.752(7)
Wl–019	1.871(7)	W8–O24	1.930(8)
Wl–021	1.877(8)	W8–O29	1.933(7)
W1–022	1.887(7)	W8–O30	1.982(6)
W1–027	2.003(7)	W8–O36	1.858(7)
Wl–055	2.368(7)	W8–O56	2.387(8)
Cul–Nl	2.125(9)	Cu2–N5	2.077(10)
Cul–N2	2.061(9)	Cu2–N6	2.156(10)
Cul–N3	2.087(10)	Cu2–N7	2.156(9)
Cul–N4	2.175(11)	Cu2–N8	2.066(9)
Cul–05	2.122(7)	Cu2–O13	2.085(7)
Cu3–N9	2.049(10)	Cu3–N10	2.236(9)
Cu3–Nll	1.942(9)	Cu3–N12	2.217(9)
Cu3–N13	1.994(10)	Cu3–N14	2.098(10)
Pl–055	1.571(7)	P2–O59	1.572(9)
Pl–056	1.509(8)	P2–O60	1.528(8)
Pl–057	1.544(8)	P2–O61	1.565(8)
Pl–058	1.523(7)	P2 –062	1.548(9)
W5–O5–Cul	28.0(4)	W13–O13–Cu2	132.9(4)
N3–Cul–N4	81.2(4)	N5–Cu2–N6	81.7(4)
Nl–Cul–05	85.2(3)	N6–Cu2–N7	104.8(4)
N2–Cul–N3	98.6(3)	O13–Cu2–N8	84.7(3)

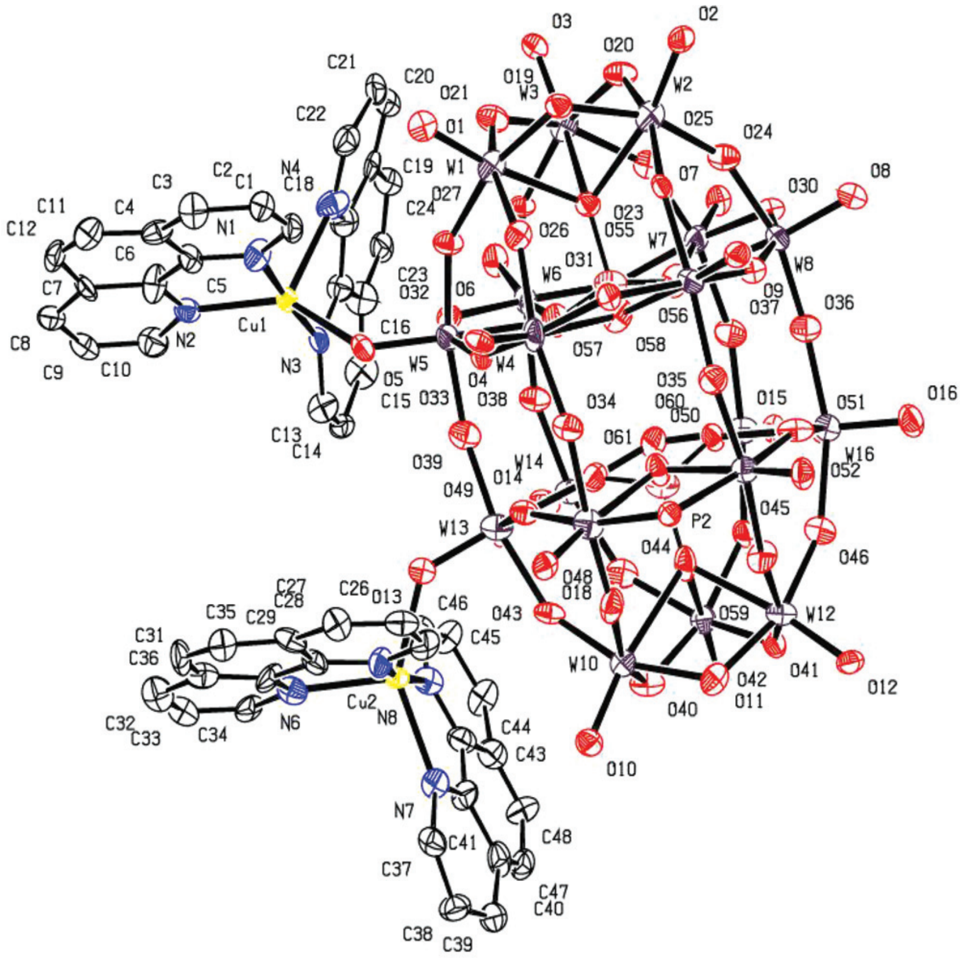

Figure 1. Structure of the polyoxoanion [Cu(phen)$_2$Cu(phen)$_2$(P2W18O62)]^2. All hydrogen atoms and water molecules are omitted for clarity.

W–O$_{b,c}$ 1.836(7)–2.42(6) Å, W–O$_a$ 2.345(7)–2.410 (9) Å. Their mean bond distances are 1.740(3) Å, 1.975(3) Å, and 2.379(2) Å, respectively; W–O–W bond angles vary from 71.5(3)–174.3(3)°. For the PO$_4$ tetrahedron, the P–O distances are 1.509(8)–1.572(9) Å with an average bond distance of 1.545(8) Å, while O–P–O angles vary from 106.2(5)–113.2(5)°. The results indicate that WO$_6$ octahedra and central PO$_4$ tetrahedra in the Dawson anion are distorted, attributed to the strong covalent interaction between [Cu(phen)$_2$]$^{2+}$ and [P$_2$W$_{18}$O$_{62}$]$^{6-}$.

In **1**, three Cu ions have different coordination environments: Cu1 and Cu2, located on the hemispheres of one [P$_2$W$_{18}$O$_{62}$]$^{6-}$ anion are five-coordinate, with four nitrogen atoms from two 1,10-phen molecules and one terminal oxygen on each Cu^{2+} with Cu1–N and Cu2–N bond distances in the range of 2.061(9)–2.175(11) and 2.066(9)–2.156(10) Å, Cu–O bond distances are 2.122(7) and 2.085(7) Å; bond angles around Cu1 and Cu2 are 83.4(3)–177.6(3)° and 78.6(4)–169.2(4)°. The dihedral angle between the two 1,10-phen molecules for [Cu1(phen)$_2$]$^{2+}$ and [Cu2(phen)$_2$]$^{2+}$

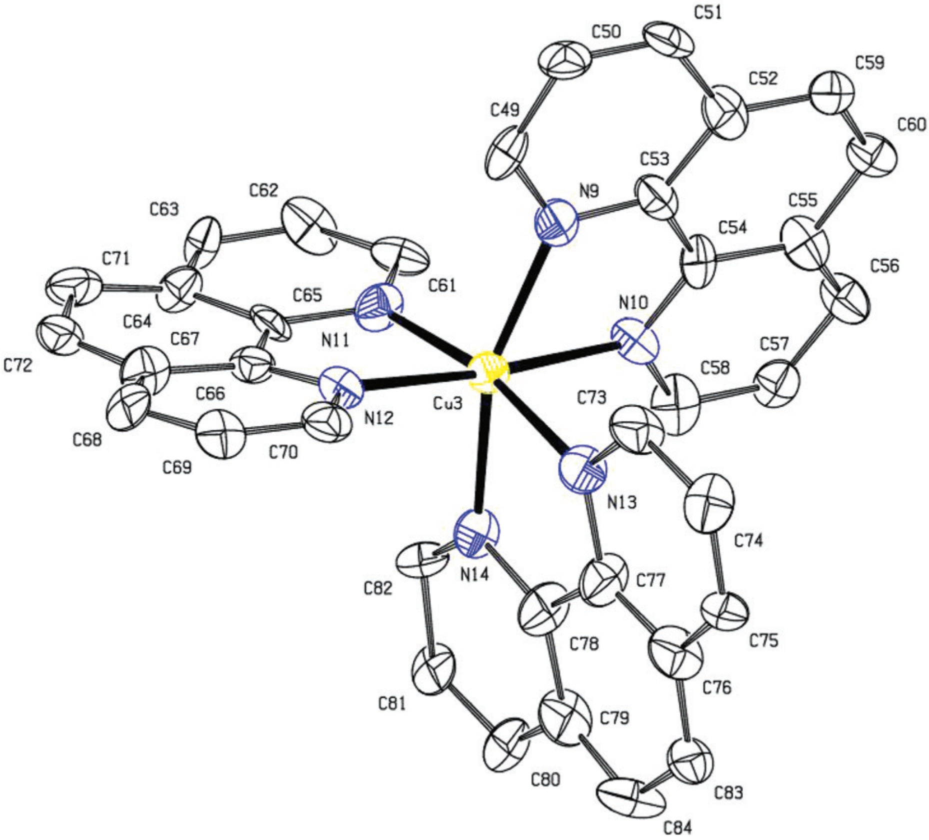

Figure 2. Coordination environment of Cu in **1**.

are 109° and 77°, respectively. The dihedral angle between two 1,10-phen molecules from different $[Cu(phen)_2]^{2+}$ grafted on the same $[P_2W_{18}O_{62}]^{6-}$ cluster, namely 1,10-phen (N1, N2) and 1,10-phen (N5, N6), is 9.9°. Cu3 is six-coordinate (see figure 2), coordinated by three 1,10-phen molecules with Cu3–N distances of 1.942(9)–2.217(9) Å and bond angles of 73.7(4)–174.9(4)°. The dihedral angles among the three 1,10-phenanthroline planes are 69.7°, 71.1°, and 81.4°.

As shown in figure 3, the bisupporting polyoxoanions, $[Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]^{2-}$, are polymerized to form a 1D chain through hydrogen bonds (O65–H65C $\cdots$ O2^{i} 2.700(18) Å, O66–H66D $\cdots$ O65 2.74(2) Å, O66–H66C $\cdots$ O12^{ii} 2.343(17) Å; symmetry codes: (i) x, $-1+y$, z and (ii) x, $1-y$, $1/2+z$, respectively. The chains are then stacked into a two-dimensional structure by offset, face-to-face, $\pi \cdots \pi$ stacking interactions (see figure 4). The shortest distance between the offset, face-to-face (interior alternate angle is 57.94°), aromatic rings of neighboring 1,10-phen's is 3.384 Å (see figure 5). Extensive $\pi \cdots \pi$ stacking and hydrogen bonding interactions increase the stability of the structure. Discrete $Cu(phen)_3^{2+}$ fill the space between two chains and balance the negative charges on the bisupporting polyoxoanion $[Cu(phen)_2Cu(phen)_2(P_2W_{18}O_{62})]^{2-}$.

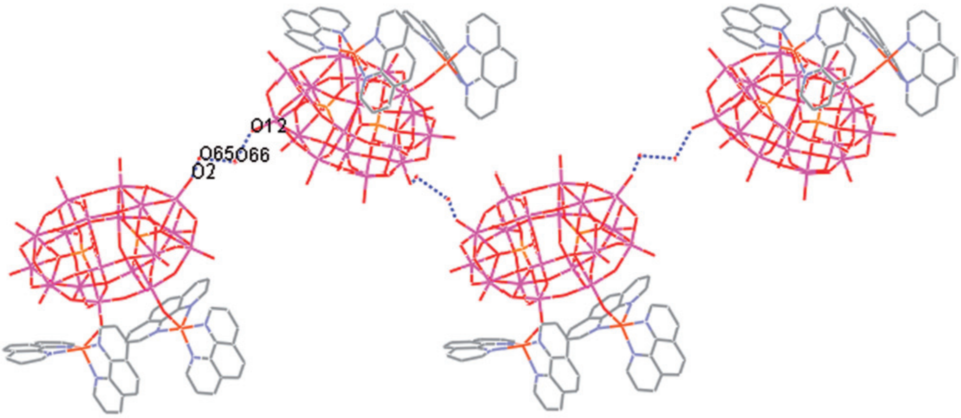

Figure 3. The 1D chain structure of **1**. All hydrogen atoms and water molecules are omitted for clarity.

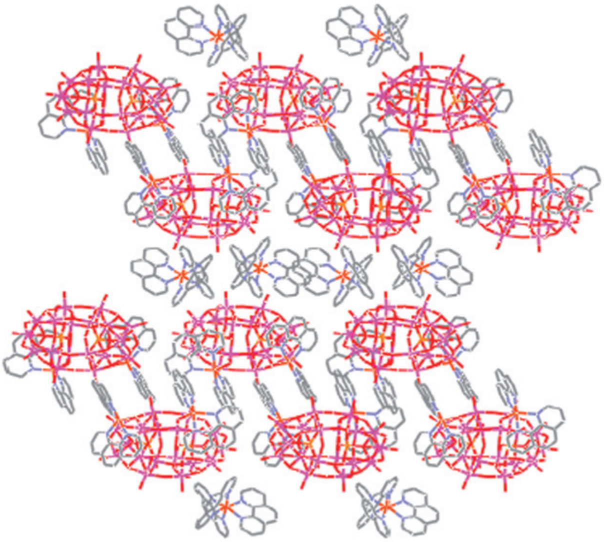

Figure 4. Molecular packing arrangement viewed down the *b* axis in **1**. All hydrogen atoms and water molecules are omitted for clarity.

3.3. *IR spectrum*

IR spectra of **1** exhibit four characteristic (W–O_d, P–O_a, W–O_b–W, W–O_c–W) asymmetric stretching vibrations for heteropolyanions with the Dawson structure at 1093, 964, 916, and 788 cm^{-1}. Comparing the IR spectra of **1** with that of α-$H_6P_2W_{18}O_{62} \cdot nH_2O$ [29], the vibrations are blue-shifted with W–O_d, P–O_a and W–O_b–W by 2 cm^{-1} and W–O_c–W by 13 cm^{-1}. These results indicate that the polyanions of **1** retain the basic Wells-Dawson structure, but are distorted due to coordination, in agreement with the results of the single crystal X-ray diffraction analysis. The compound also shows characteristic bands of 1,10-phen at 1425 and 1517 cm^{-1}. The peaks at 3438 and 1625 cm^{-1} can be assigned to O–H stretching, and the bending vibration of crystallization water molecules [30], respectively. Peaks at 2848 and 2917 cm^{-1} may be attributed to stretching of the CH_2 groups [31].

3.4. *UV spectrum*

Comparison of the u.v. spectrum of **1** with those of free α-$H_6P_2W_{18}O_{62} \cdot nH_2O$ and 1,10-phen indicates that interactions between 1,10-phen and the polyoxometalate are fairly strong. The 1,10-phen peaks at 200, 226 and 264 nm [32] and the characteristic absorption peaks of the Wells-Dawson type polyanion (210, 325 nm) [33] are absent for **1**, with a new relatively strong broad peak around 260~310 nm (figure 6),

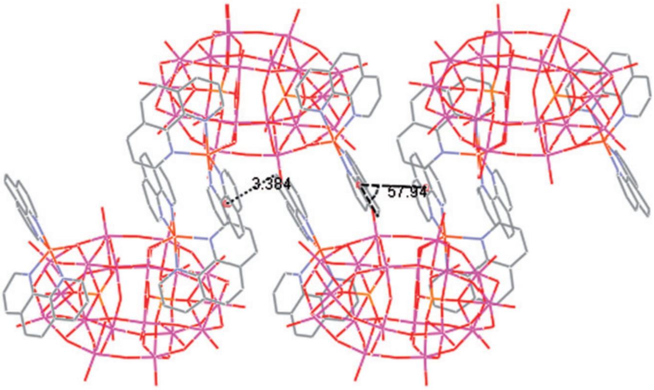

Figure 5. $\pi \cdots \pi$ stacking interactions among the molecules.

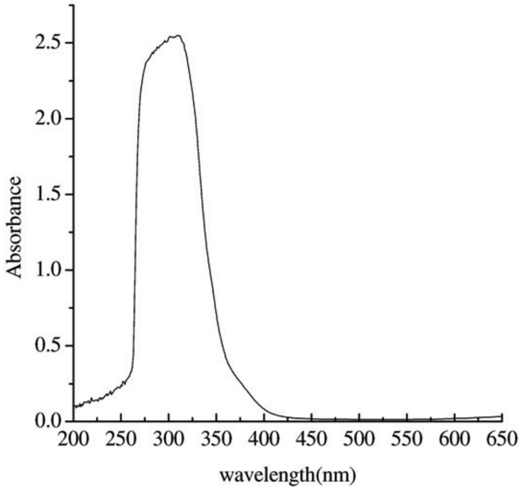

Figure 6. UV spectrum of **1** in DMF.

suggesting that a new conjugated system has been created between the organic and inorganic moieties.

3.5. *Electrochemical behavior of [$P_2W_{18}O_{62}$]$^{6-}$*

A cyclic voltammogram at a scan rate (υ) of 100 mV s^{-1} for reduction of **1** (0.5 mM) in DMF (0.1 M H_2SO_4) at a glassy carbon macrodisk electrode over the potential range 0.3 and −0.9 V exhibits three chemically reversible processes (figure 7), E_{pc} (−0.308, −0.505, −0.743), E_{pa} (−0.289, −0.483, −0.711), and $E_{1/2} = [(E_{pc} + E_{pa})/2]$ ($E_{1/2}$ = half-wave potential, E_{pc} = reduction peak potential, E_{pa} = oxidation peak potential) values of −0.299(I), −0.494(II) and −0.727 V(III). The first one-electron redox potential of $K_6P_2W_{18}O_{62}$ shows solvent effects (negative shift in DMF compared with aqueous medium) as for $K_4SiW_{12}O_{40}$ [34]; the first two one-electron waves are independent of pH [35]. Generally, cations in solution have no effect on the first two one-electron waves, thus when $[P_2W_{18}O_{62}]^{6-}$ is in solution, addition of the first two electrons is not followed by protonation, while the third and fourth reversible two-electron reductions are accompanied by protonations. In our experiment we observe three redox pairs but not four; the second one-electron wave merges with the first one-electron wave into one two-electron wave, resulting in a cyclic voltammogram of three two-electron waves [34, 36, 37]. The three reversible redox waves are summarized, as shown in equations (1)–(3).

$$[P_2W_{18}O_{62}]^{6-} + 2e^- = [P_2W_{18}O_{62}]^{8-} \tag{1}$$

$$[P_2W_{18}O_{62}]^{6-} + 2e^- + 2H = [P_2W_{18}O_{62}]^{8-} \tag{2}$$

$$[P_2W_{18}O_{62}]^{6-} + 2e^- + 2H^+ = [P_2W_{18}O_{62}]^{8-}. \tag{3}$$

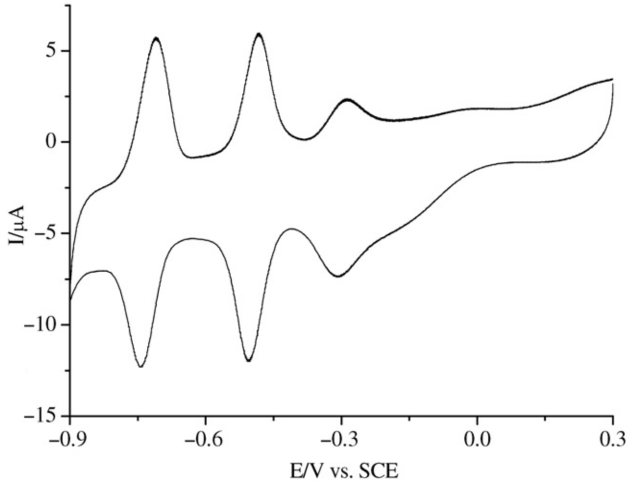

Figure 7. Cyclic voltammograms of **1** (0.5 mM) in DMF+0.1M H2SO4; scan rate: 100 mV s $^{-1}$; working electrode : glassy carbon disk.

Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. 640864. Copies of the data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

References

[1] M.T. Pope, A. Müller (Eds.). *Polyoxometalates: From Platonic Solids to Antiretroviral Activity*, Kluwer Academic Publications, Dordrecht (1994).
[2] C.L. Hill. *Chem. Rev.*, **1**, 98 (1998).
[3] O.V. Branytska, R.J. Neumann. *J. Org. Chem.*, **9510**, 68 (2003).
[4] E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. GómezGarcía, E. Martínez-Ferrero, M. Almeida, E.B. Lopes. *Adv. Mater.*, **324**, 16 (2004).
[5] E. Coronado, M. Clemente-León, J.R. Galán-Mascarós, C. Giménezsaiz, C.J. Gómez-García, E.J. Martínez-Ferrero. *J. Chem. Soc., Dalton Trans.*, **3955**, 21 (2000).
[6] T. Yamase. *Mol. Eng.*, **241**, 3 (1993).
[7] A. Saito, G.R. Choppin. *Inorg. Chem.*, **4563**, 30 (1991).
[8] V.P. Shilov, L.N. Astafurova, N.N. Krot. *Radiochemistry* (Engl. Transl.), **266**, 36 (1994).
[9] S. Lis. *Acta Phys. Pol., A.*, **275**, 90 (1996).
[10] Q.-H. Luo, R.C. Howell, M. Dankova, J. Bartis, C.W. Williams, W.D. Horrocks Jr, V.G. Young Jr, A.L. Rheingold, L.C. Francesconi, M.R. Antonio. *Inorg. Chem.*, **1894**, 40 (2001).
[11] J. Bartis, M. Dankova, J.J. Lessmann, Q.H. Luo, W. Horrocks Jr, L.C. Francesconi. *Inorg. Chem.*, **1042**, 38 (1999).
[12] J.P. Ciabrini, R. Contant. *J. Chem. Res.*, (M) **2720**, (S), 391 (1993).
[13] T.L. Jorris, M. Kozik, N. Casan-Pastor, P.J. Domaille, R.G. Finke, W.K. Miller, L.C.W. Baker. *J. Am. Chem. Soc.*, **7402**, 109 (1987).
[14] L. Qu, S. Wang, J. Peng, Y. Chen, G. Wang. *Polyhedron*, **2645**, 11 (1992).
[15] N. Haraguchi, Y. Okaue, T. Isobe, Y. Matsuda. *Inorg. Chem.*, **115**, 33 (1994).
[16] B.-B. Yan, Y. Xu, X.-H. Bu, N.K. Goh, L.S. Chia, G.D. Stucky. *J. Chem. Soc., Dalton Trans.*, **2009**, 13 (2001).
[17] B. Keita, F. Girard, L. Nadjo, R. Contant, J. Canny, M. Richet. *J. Electroanal. Chem.*, **76**, 478 (1999).
[18] R. Contant, M. Abbessi, J. Canny, A. Belhouari, B. Keita, L. Nadjo. *Inorg. Chem.*, **4961**, 36 (1997).
[19] J. Bartis, Y. Kunina, M. Blumenstein, L.C. Francesconi. *Inorg. Chem.*, **1497**, 35 (1996).
[20] J.-P. Wang, W. Wang, J.-Y. Niu. *Inorg. Chem. Commun.*, **520**, 10 (2007).
[21] Y.-H. Luo, H.-K. Lin, H. Lin. *Transition Met. Chem.*, **103**, 31 (2006).
[22] H.-K. Lin, Y.-H. Luo, H. Lin. *Transition Met. Chem.*, **690**, 31 (2006).
[23] A.-X. Tian, Z.-G. Han, J. Peng, B.-X. Dong, J.-Q. Sha, B. Li. *J. Mol. Struct.*, **117**, 832 (2007).
[24] SMART, version 5.624, Bruker AXS, Inc., Madison, WI (2002).
[25] SAINT, version 6.36 A, Bruker AXS, Inc., Madison, WI (2002).
[26] G. Sheldrick. SADABS, version 2.10, University of Göttingen, Germany (2003).
[27] G.M. Sheldrick. *SHELXTL-97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[28] J.-Y. Niu, Z.-L. Wang, J.-P. Wang. *Inorg. Chem. Commun.*, **1272**, 6 (2003).
[29] Y.-S. Zhou, J. Peng, E.-B. Wang. *Transition Met. Chem.*, **125**, 23 (1998).
[30] S. Lis. *J. Alloys Compounds.*, **88**, 300 (2000).
[31] S.-T. Zheng, J. Zhang, G.-Y. Yang. *J. Mol. Struct.*, **25**, 752 (2005).
[32] M. Hölscher, U. Englert, B. Zibrowius, W.F. Hölderich. *Angew. Chem. Int. Ed.*, **2491**, 33 (1994).
[33] V.I. Spitsyn, L.P. Kazanskii, E.A. Torchenkova. *Sov. Sci. Rev. Sect. B.*, **111**, 3 (1981).
[34] M. Sadakane, E. Steckhan. *Chem. Rev.*, **219**, 98 (1998).
[35] M.T. Pope, E. Papaconstantinou. *Inorg. Chem.*, **1147**, 6 (1967).
[36] P.D. Prenzler, C. Boskovic, A.M. Bond, A.G. Wedd. *Anal. Chem.*, **3650**, 71 (1999).
[37] A. Papadakis, A. Souliotis, E. Papaconstantinou. *J. Electroanal. Chem.*, **17**, 435 (1997).