A novel extended architecture with $4^6 \cdot 6^4$ topology based on mixed-valence Wells–Dawson arsenotungstate and mixed-ligand Cu(I) units

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ABSTRACT

A novel inorganic–organic hybrid compound based on mixed-valence Wells–Dawson arsenotungstate and mixed-ligand Cu(I) units, $Cu_8^I(imi)_4(bpy)_6(H_2O)[As_2^V W_2^V W_{16}^{VI} O_{62}] \cdot 2H_2O$ (**1**) (bpy = 4,4′-bipydine; imi = imidazole), has been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy, thermal gravimetric analysis, luminescent spectrum and single crystal X-ray diffraction. Single-crystal X-ray diffraction revealed that four terminal and three bridging oxygen atoms of the Wells–Dawson cluster are coordinated to Cu(I) ions and form an unprecedented hepta-supporting polyoxometalate. The functionalized arsenotungstates are further connected by two kinds of tridentate linkers, Imi–Cu–(bpy)–Cu–(bpy)–Cu–(bpy)–Cu–Imi and Imi–Cu–(bpy)–Cu–(bpy)–Cu–H_2O, to construct a 3D framework with $4^6 \cdot 6^4$ topology. The hybrid material has an intense emission at about 397 nm.

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1. Introduction

Polyoxometalates (POMs) exhibit an enormous variety of structures, which leads to interesting and often unexpected properties in a variety of areas, including catalysis, medicine and materials science [1–4]. The inorganic–organic hybrid compounds based on POMs are becoming a new generation of solid-state materials that have promising applications in gas storage, catalysis and porous materials owing to their chemical and structural diversity [5]. Up to now, a wealth of 1-D, 2-D, and 3-D POM-based compounds constructed from the combination of POMs and transition metal complex have been reported [6]. Compared with lots of inorganic–organic hybrids based on the well-known structure types, such as Lindquist and Keggin type anions, those derived from Dawson-type anions have seldom been used as a molecular building unit in this field owing to its bigger volume in spite of their potential large number coordination O atoms (18 terminal and 36 μ_2-O atoms) making the steric orientations of the coordination sites more flexible. To date only have some examples been structurally characterized [7–22], such as, $[Cu_4^{II} Cu_2^I (PO_4)_2 (H_2O)_2 (bpy)_6](H_3O)_2 [P_2W_{18}O_{62}]$ [7], $\{[Cu^I(4,4′-bpy)]_3[Cu^{II}(en)_2]_2[As_2W_3^V W_{15}^{VI} O_{62}]\}_2$ [9], $[\{Cu(en)_2(H_2O)\}_2\{Cu(en)_2\}(P_2W_{18}O_{61})_2]^{6-}$ [10], $[\{Cu(enMe)_2(H_2O)\}\{Cu(enMe)_2\}_3 P_2W_{18}O_{62}]$ [11], $Cu_6(btp)_3((P_2W_{18}O_{62})) \cdot 3H_2O$ [13], in which most of them are 0-D and 1-D hybrids based on

phosphotungstates and transition metal complexes (TMCs). And the first 2-D example, $(NH_4)_3(4,4′-H_2bipy)[Cu(4,4′-bipy)]_7[P_2-W_{18}O_{62}]_2 \cdot 10H_2O$ [12], was reported by the Wang et al. Recently, Peng depicted the structure of the first 3-D hybrid materials based on Dawson-type POM $[Cu(4,4′-bipy)]_2[H_4P_2W_{18}O_{62}] \cdot 2H_2O$ [17]. Very recently, Peng et al. and Cao et al. synthesized and reported other four examples of the 3-D hybrid compounds [13–16]. However, only one 3-D hybrid compound based on Dawson-type arsenotungstate has been reported up to date [9]. Here we report the synthesis, structure and some characterization of a novel 3-D structure based on mixed-valence Wells–Dawson type arsenotungstate and mixed-ligand Cu(I) units, $Cu_8^I(imi)_4(bpy)_6 (H_2O)[As_2^V W_2^V W_{15}^{VI} O_{62}] \cdot 2H_2O$, which presents a five-connected $4^6 \cdot 6^4$ topology framework. To the best of our knowledge, the compound is the first example of hepta-supporting functionalized Dawson polyoxometalates.

2. Experimental

2.1. Chemicals and methods

All reagents used were of analytical grade and obtained from commercial sources without further purification. Infrared spectra of the compound was recorded on a Nicolet AVATAR 360 FTIR spectrophotometer (KBr pellets in 400–4000 cm^{-1} region). The TG measurement was performed on a model Q600SDT analyzer in

the N_2 atmosphere with a heating rate of 15 °C /min from ambient temperature to 990 °C. Luminescent spectrum was measured at room temperature on a Hitachi F4500 fluorescence spectro-photometer.

2.2. Synthesis of $Cu_8^I(imi)_4(bpy)_6(H_2O)[As_2^VW_2^VW_{16}^{VI}O_{62}] \cdot 2H_2O$

The mixture of As_2O_3 (0.025 g, 0.13 mmol), WO_3 (0.23 g, 0.99 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (0.10 g, 0.50 mmol), bpy (0.019 g, 0.12 mmol), imi (0.017 g, 0.25 mmol) and H_2O (10 mL) were stirred for 0.5 h, the solution was put into a Teflon-lined autoclave and kept under autogenous pressure at 160 °C for 4 days. After slow cooling to room temperature, orange red strip crystals were filtered and washed with distilled water (yield 25% based on Cu). Anal. Calcd: C 13.90, As 2.41, N 4.50, Cu 8.17, W 53.18 (%) for $C_{72}H_{70}N_{20}As_2Cu_8O_{65}W_{18}$. Anal. Found: C 13.95, As 2.37, N 4.61, Cu 7.99, W 53.39 (%).

2.3. X-ray crystallography

The X-ray crystallographic data of **1** was collected on a BRUKER SMART APEX II CCD diffractometer with graphite-monochroma-tized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) radiation at 296(2) K. The structure was solved by direct methods and refined on F^2 by full matrix least-squares using the SHELXTL-97 program package. All heavy atoms (W, Cu and As) and the framework oxygen atoms (except O10 and O36) of the arsenotungstate were refined anisotropically. Other atoms (C, N and the oxygen atoms of free water molecules) were refined isotropically. Hydrogen atoms of organic ligands were included at calculated positions and refined with a riding model. The crystal data and refinement parameters for **1** are listed in Table 1. Selected bond lengths and angles are listed in Table S1.

3. Results and discussion

3.1. Synthesis

The compound $Cu_8^I(imi)_4(bpy)_6(H_2O)[As_2^VW_2^VW_{16}^{VI}O_{62}] \cdot 2H_2O$ was synthesized under the hydrothermal condition by reacting the mixture of WO_3, $Cu(CH_3COO)_2 \cdot H_2O$, imi and bpy with As_2O_3 at pH value of 6.5. It is noticeable that the complicated redox reaction was taken place in the preparation of **1**, and all copper ions were reduced from +2 of the reactant to +1 of the product,

one-ninth of W atoms were reduced from +6 to +5, and the valence of arsenic was changed from +3 to +5. It is rare that the valence of three or more elements was changed in the preparation of inorganic–organic hybrid compounds based POMs. It has been reported that the valence of arsenic was oxidized from +3 to +5 in the preparation of $[Cu_4(Hen)_2As_2W_{18}O_{68}] \cdot 4 H_2en \cdot 18H_2O$ [23] by the reaction of $Na_2WO_4 \cdot 2H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ and ethylene-diamine with As_2O_3 at pH=4.0 under hydrothermal condition. In fact, the electromotive force value of AsO_4^{3-}/AsO_3^{3-} increases with pH decrease, therefore As(III) can be oxidized to As(V) easily in mildly acidic condition. And the nitrogen-containing ligand acting as reducing agents is not unusual in the preparation of other POM-based inorganic–organic hybrid materials under hydrother-mal conditions [24]. However, compared with polyoxomolybdates and polyoxovanadates, reduction of partial metal sites in hydro-thermally generated polyoxotungstates is rare [10,11,25] and it appeared that a higher pH value under acidic, hydrothermal conditions is helpful to form a mixed-valence Wells–Dawson polyoxotungstate [10].

3.2. Structure description

Single crystal X-ray diffraction analysis suggests that the molecular structure unit of **1** consists of one Wells–Dawson $[As_2^VW_2^VW_{16}^{VI}O_{62}]^{8-}$ polyoxoanion, eight Cu^I ions, four imi ligands, six bpy ligands, one crystal water molecule and two free water molecules (Fig. 1 and Fig. S1). The reduced-polyanion $[As_2W_{18}O_{62}]^{8-}$ acts as a hepta-dentate ligand which offers four terminal O atoms and three bridging O atoms to coordinate seven Cu(I) centers located in almost parallel Cu(I) complex chains surrounding the reduced-polyanion. There are two kinds of tridentate linkers bridging the neighboring Dawson polyoxotungstates, namely, Imi–Cu(3)–(bpy)–Cu(1)–(bpy)–Cu(8)–(bpy)–Cu(5)–Imi and Imi–Cu(2)–(bpy)–Cu(6)–(bpy)–Cu(7)–H_2O. The length of the linkers is proportional to the number of Cu(I) ions, and extended by bidentate linear bpy ligands and terminated by monodentate imi or water molecule. The first connects neighboring three arsenotungstates, by Cu(3), Cu(1) and Cu(5) atoms (Fig. 2a) and the second by Cu(2), Cu(6) and Cu(7) atoms (Fig. 2b) to construct a complex 3D inorganic–organic framework. A better insight into this fascinating structure can be achieved by the application of topology analysis. If the heterometallic cluster $As_2W_{18}O_{62}Cu_6$ being simplified to an entity

Table 1
Crystal data and refinement parameters for compound **1**.

Empirical formula	$C_{72}H_{70}N_{20}As_2Cu_8O_{65}W_{18}$
Formula weight	6222.94
Temperature (K)	296(2)
Crystal system	triclinic
Space group	P-1
a (Å)	15.4671(9)
b (Å)	17.5861(11)
c (Å)	23.0647(14)
α (deg.)	74.827(1)
β (deg.)	89.224(1)
γ (deg.)	81.079(1)
V (Å^3)	5979.4(6)
Z	2
D_{calcl} (g cm^{-3})	3.456
GOF on F^2	1.030
$R1$, $wR2$ [$I > 2\sigma(I)$]	$R1 = 0.0543$, $wR2 = 0.1556$
$R1$, $wR2$ (all data)	$R1 = 0.0843$, $wR2 = 0.1809$

$R1 = [\Sigma|F_o| - |F_c|]/[\Sigma|F_c|]$. $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{1/2}$.

Fig. 1. View of the coordination environment of eight Cu(I) ions around the Wells–Dawson cluster. H atoms are omitted for clarity.
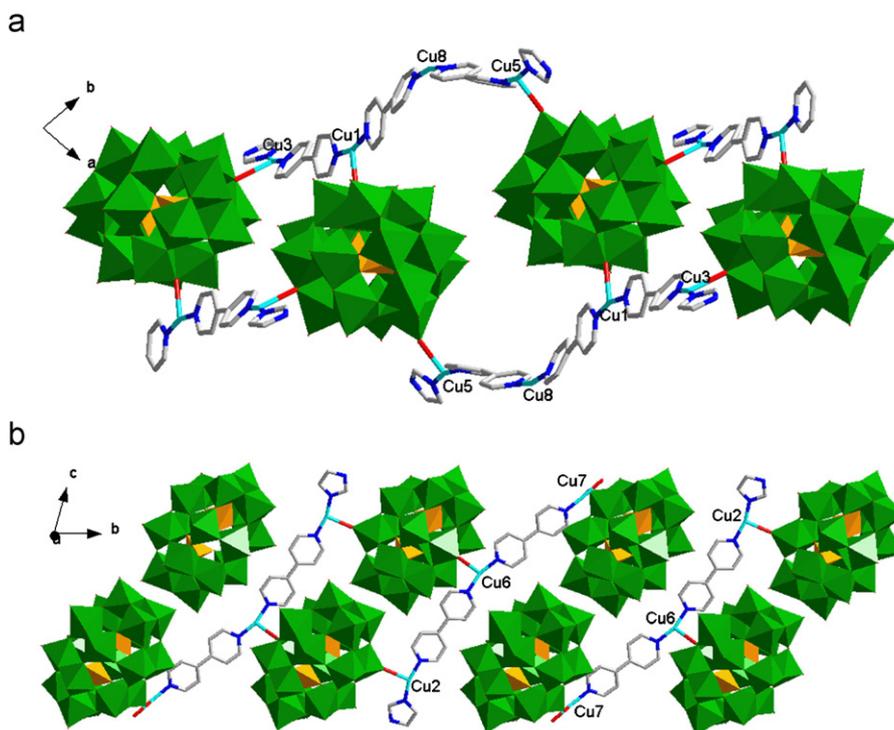
Fig. 2. The two kinds of chains connects neighboring three arsenotungstates in different directions.
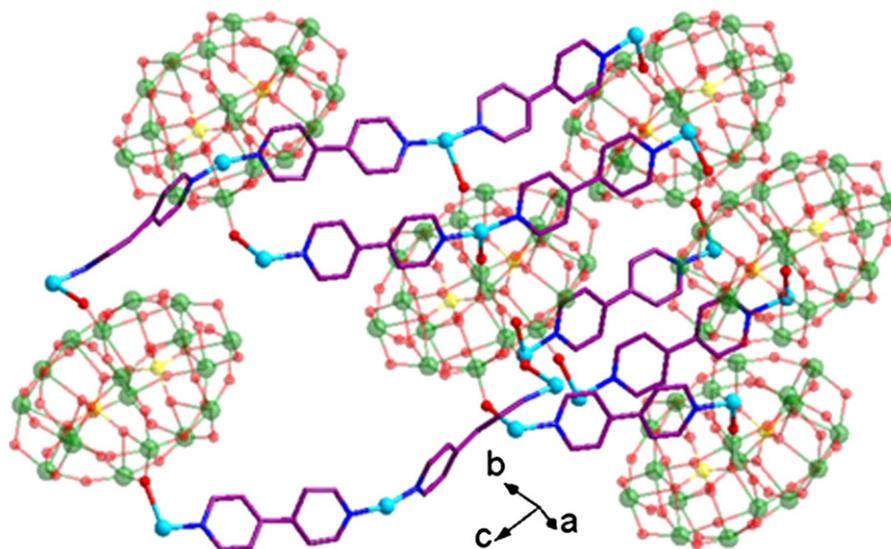
Fig. 3. View of the five-connected node of heterometallic cluster $As_2W_{18}Cu_6$, and its connectors.

and, accordingly, the bpy ligand and bpy-Cu8-bpy fragment acting as two-connected linkers, each node is connected to five equivalent nodes by eight linkers (six bpy ligands and two bpy-Cu8-bpy fragments) and three pairs are connected by double linkers (Fig. 3). Therefore, the title architecture represents a five-connected node and the overall 3D inorganic–organic network topology can be described as a boron nitride topology with the Schläfli symbol $(4^6 \cdot 6^4)$ (Fig. 4 and Fig. S2). The 5-connected net is rarely observed in coordination polymers up to now [26]. To the best of our knowledge, the boron nitride network has never been reported so far in the inorganic–organic hybrid compounds based on POMs.

The parent Wells–Dawson cluster is close to the D_{3h} symmetry which contains two [AsW$_9$O$_{31}$] moiety derived from the well-known Keggin $[AsW_{12}O_{40}]^{3-}$ anion by removing three corner-sharing WO$_6$ octahedra from three separate W$_3$O$_{13}$ triads. In compound **1**, the W–O bond distances are in the range 1.682(14)–2.375(10) Å, and the As–O distances are from 1.655(11) to 1.711(11) Å. The eight crystallogically independent Cu atoms have two different coordination numbers. Seven (Cu(1)–Cu(7)) of eight Cu atoms are three coordinated, in which Cu(1) and Cu(6) atoms are coordinated by one O atom from polyoxoanion and two N atoms from two bpy ligands, and Cu(7) coordinated by one N atom from a bpy ligand, one O$_w$ atom and one O atom from the polyanion, and the other four Cu ions coordinated by one O atom from the polyanion and two N atoms from a bpy and an imi molecule. The bond distances and angles of
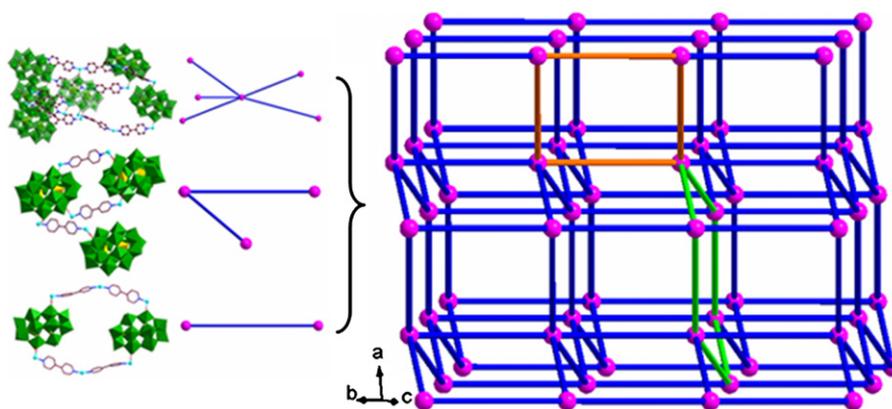
Fig. 4. Topological representation of compound **1** showing the $(4^6 \cdot 6^4)$ topology, and the shortest 4- and 6- circle loops.

the copper ions are in the range of 1.802(12)–1.975(6) Å for Cu–N, 1.982(18)–2.784(14)Å for Cu–O, 161.2(6)–174.9(5)° for N–Cu–N, 89.8(4)–103.0(7)° for N–Cu–O, respectively. The remaining Cu(8) shows a distorted linear {CuN2} coordination geometry coordinating to two N atoms from two bpy ligands (Cu–N=1.837(6)–1.890(2) Å) with the N–Cu–N angle of 163.8(9)°.

On the basis of valence sum calculations, the oxidation states of all Cu and As atoms in **1** are +1 and +5 (for Cu, $\sum S_{ij}=0.82-1.22$, mean 0.98; for As, $\sum S_{ij}=5.00-5.14$, mean 5.07). And the average value of W atoms is 6.08, which is close to those in the known mixed-valence polyoxotungstates. However, the average value of W atom in the hybrid organic–inorganic compounds based on non-reduced Dawson ions is in the range 6.18–6.40, which is much larger than 6.0 (Table S2). In addition, the values of BVS calculations cannot identify the reduced W sites, and generally the delocalization of the d electrons exists in the reduced polyoxotungstate [2].

3.3. IR spectra

IR spectrum of compound **1** exhibits four characteristic absorptions below 1000 cm^{-1} at 951, 858, 819 and 762 cm^{-1}, attributed to the characteristic absorption of $\nu(W-O_d)$, $\nu(W-O_b-W)$, $\nu(As-O_a)$ and $\nu(W-O_c-W)$, respectively. In addition, the absorptions at 1610, 1530, 1486, 1415 and 1280 cm^{-1} are assigned to characteristic vibrations of bpy and imi ligands.

3.4. Thermal analysis

The TG curve (Fig. S3) shows that the weight loss of the compound can be divided into two steps. The first weight-loss of 3.2% occurs between 35 and 310 °C, which is due to the loss of three water molecules and one molecule of bpy (cacl. 3.4%). The second weight loss is 16.7% from 310 to 840 °C, assigned to the decomposition of four imi molecules and other five bpy ligands (cacl. 16.9%). The observed total weight loss (19.9%) is in good agreement with the calculated values (20.3%).

3.5. Fluorescent property

The emission spectra of compound **1** and the starting materials, free ligand bpy, imi molecule and $K_6[As_2W_{18}O_{62}]\cdot 14H_2O$ [27] in solid state at room temperature upon excitation at 294 nm, are compared in Fig. 5. There is a weak emission at ca.364 nm for bpy ligand, and a strong broad emission at ca.398 nm for imi [28], both of them are attributed to the emissions between HOMO and LUMO energy levels of the ligand
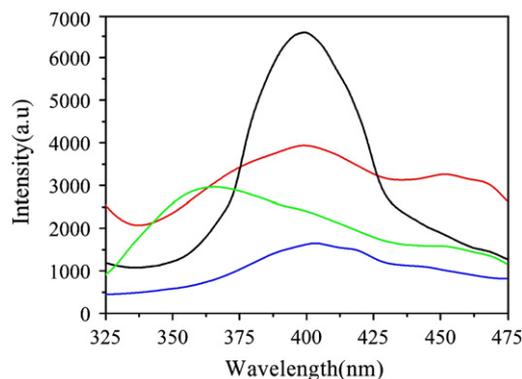
Fig. 5. The emission spectra of the compound **1** (black), bpy (green), imi (red) and $K_6[As_2W_{18}O_{62}]\cdot 14H_2O$ (blue) in the solid state at room temperature (excitation at 294 nm). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

molecules. For $K_6[As_2W_{18}O_{62}]\cdot 14H_2O$, there is a weak broad emission band at ca.402 nm assigned to O→W charge-transfer transition. Compared with the starting materials, compound **1** exhibits very intensive emission band at ca.397 nm, which is mainly due to O→W charge-transfer transition and metal-to-ligand charge transfer [29]. The title compound has an intense emission at about 397 nm and may be an excellent candidate for potential solid-state photoluminescent material.

4. Conclusions

In summary, we firstly reported a novel 3D inorganic–organic hybrid compound based on the mixed-valence Wells–Dawson arsenotungstate and mixed-ligand Cu(I) unit. The polyanion offers four terminal O atoms and three bridging O atoms to coordinate seven Cu(I) centers. The functionalized arsenotungstates are further connected by two kinds of tridentate linkers, Imi–Cu–(bpy)–Cu–(bpy)–Cu–(bpy)–Cu–Imi and Imi–Cu–(bpy)–Cu–(bpy)–Cu–H$_2$O, to construct a 3-D framework with $4^6 \cdot 6^4$ topology.

Appendix A. Supplementary Material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.07.004.

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