34 卷 8 期　　结 构 化 学（*JIEGOU HUAXUE*）　　Vol. 34, No. 8
2015. 8　　*Chinese J. Struct. Chem.*　　1247─1252

A New Organic-inorganic Hybrid Arsenatotungstate $[\{Cu(phen)(en)\}\{Cu(phen)\}\{Cu_3(phen)_3(a\text{-}AsW_9O_{33})\}](OH)\cdot 3H_2O$①

LI Jie　TIAN Shu-Fang　ZHOU Hui　MA Peng-Tao②
(*Key Laboratory of Polyoxometalate Chemistry of Henan Province,*
Institute of Molecular and Crystal Engineering, College of Chemistry
and Chemical Engineering, Henan University, Kaifeng, Henan 475004, *China*)

ABSTRACT A new organic-inorganic hybrid copper-substituted arsenatotungstate complex formulated as $[\{Cu(phen)(en)\}\{Cu(phen)\}\{Cu_3(phen)_3(a\text{-}AsW_9O_{33})\}](OH)\cdot 3H_2O$ (**1**, en = ethylenediamine, 1,10-phen = 1,10-phenanthroline) has been synthesized by controlling the reaction process and characterized by infrared (IR) spectroscopy, elemental analysis, and thermogravimetric (TG) analysis. Crystal data for **1**: $C_{62}H_{56}AsCu_5N_{12}O_{37}W_9$, $M_r = 3608.46$, monoclinic, space group $P2_1/n$, $a = 13.245(4)$, $b = 25.692(9)$, $c = 24.670(8)$ Å, $b = 99.251(6)$°, $V = 8286(5)$ Å^3, $Z = 4$, $GOOF = 1.103$, $R = 0.0560$, $wR = 0.1285$. In **1**, the vacant sites of the trivacant Keggin anion $[a\text{-}AsW_9O_{33}]^{9-}$ are occupied by three same copper coordination cations $[Cu(phen)]^{2+}$. Meanwhile, the lacunary anion $[a\text{-}AsW_9O_{33}]^{9-}$ is capped by two kinds of copper coordination cations $[Cu(phen)]^{2+}$ and $[Cu(phen)(en)]^{2+}$, resulting in an unprecedented polycation structure with C_s symmetry.

Keywords: tungstoarsenate, hydrothermal, crystal structure;
DOI: 10.14102/j.cnki.0254-5861.2011-0652

1 INTRODUCTION

Polyoxometalates (POMs) are metal oxygen cluster species that exhibit a fascinating variety of structures and properties including catalysis, medicine, and materials science[1-5]. A new area of interest is the decoration of polyoxoanions with various organic and/or transition-metal complexes (TMCs), which is also driven by the manifold applications in areas as diverse as catalysis and magnetism[6, 7]. Hitherto, the combination between TMCs and POMs is extraordinarily successful in modifying the POM structures, leading to a large number of novel hybrids including TMCs-supported POMs[8-10] and extended POMs bridged by TMCs[11-13].

The POMs supported by trivacant subunits (formulized as $[XM_9O_{34}or_{33}]^{n-}$) represent a large subfamily of transition-metal substituted polyoxometalates (TMSPs), which are often easily synthesized by the self-assembly reaction of transition-metal (TM) ions with appropriate trivacant polyoxotungstate (POW) precursors. Nevertheless, reports on incorporating TMCs into the vacant sites of $[XM_9O_{34/33}]^{n-}$ fragments are limited, and the reported were decorated by single TM-aliphatic amine complexes or TM-aromatic amine complexes[14-18]. Therefore, the construction of TMCs-incorporated POMs remains a longstanding challenge. As we know, organic ligands, as structure-stabilizing agents

---

Received 29 January 2015; accepted 29 April 2015 (**CCDC 1043034**)

① This work was supported by the Foundation of Education Department of Henan Province (14A150028)

② Corresponding author. E-mail: mpt@henu.edu.cn or structure-directing agents, influence on the coordination geometries or modes of transition-metals in the vacant sites of trivacant POTs, which further construct novel organic-inorganic hybrid TMSPs[19, 20]. Therefore, the aim of our work focuses on assembling lacunary POM fragments directed by mixed types of TMCs, which act as decorated cations coordinating to the surface oxygen atoms of POM matrixes, or function as bridges to construct multi-dimensional extended frameworks. On the basis of the above-mentioned consideration, we have recently launched the exploration on the reaction under hydrothermal conditions, which could combine the inorganic compound precursors with TM cations in the presence of two kinds of organic components (aliphatic amine and aromatic amine). Herein, we report a novel organic-inorganic hybrid polyoxotungstate, **1**, whose polycation consists of a trivacant [a-AsW_9O_{33}]$^{9-}$ moiety supported by mixed type complex cations [Cu(phen)(en)]$^{2+}$ and copper-aromatic complex cations [Cu(phen)]$^{2+}$.

2 EXPERIMENTAL

2. 1 Instruments

All chemicals and solvents were used as purchased without further purification. C, H, and N elemental analyses were performed by using a PerkinElmer 2400-II CHNS/O analyzer. The Infrared spectra (using KBr in pellets) were recorded in a Bruker VERTEX 70 IR spectrometer (4000～400 cm^{-1}). The TG analyses were measured under nitrogen atmosphere on a Mettler-Toledo TGA/SDTA851e instrument at a heating rate of 10 ℃/min from 25 to 1000 ℃.

2. 2 Extraction and isolation

A mixture of As_2O_3 (0.12 g, 0.6 mmol), $Na_2WO_4·2H_2O$ (0.66 g, 2.0 mmol), $Cu(Ac)_2·H_2O$ (0.14 g, 0.7 mmol), $CuCl_2·2H_2O$ (0.12 g, 0.7 mmol), 1,10-phen (0.06 g, 0.3 mmol) and en (0.10 mL) in 23 mL H_2O was stirred for 3 h at room temperature, and adjusted to around pH = 6.20 with 2 mol/L HCl solution. And then, the mixture was sealed into a 30 mL poly(tetrafluoroethylene)-lined stainless steel container under autogenous pressure, heated at 160 ℃ for 5 days and cooled to room temperature at a rate of 5 ℃/h. The dark-green block crystals of **1** were collected. C, H and N elemental analysis for $C_{62}H_{56}AsCu_5N_{12}O_{37}W_9$: calcd. (%): C, 20.64; H, 1.56; N, 4.66. Found (%): C, 21.15; H, 1.67; N, 4.88.

2. 3 X-ray crystallography

Crystallographic data were collected with a Bruker SMART-CCD Apex II diffractometer with graphite-monochromated Mo$K\alpha$ radiation (l = 0.71073 Å) with the following index ranges: $-12 \leqslant h \leqslant 15$, $-30 \leqslant k \leqslant 28$ and $-27 \leqslant l \leqslant 29$. The single-crystal X-ray analysis reveals that the crystal crystallizes in monoclinic space group $P2_1/n$, with a = 13.245(4), b = 25.692(9), c = 24.670(8) Å, b = 99.251(6)º, M_r = 3608.46, V = 8286(5) Å^3, Z = 4, and $F(000)$ = 6608. A total of 41872 reflections were measured by an ω scan mode at 296(2) K within $1.67 \leqslant q \leqslant 25.00°$, of which 14563 were independent with R_{int} = 0.0779 and 14563 were observed with $I > 2s(I)$. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms using SHELXTL[21]. The final R = 0.0560 and wR = 0.1285 ($w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 32.7047P]$, where $P = (F_o^2 + 2F_c^2)/3$). The maximum and minimum peaks on the final difference Fourier map are 4.938 and –2.288 e/Å^3, respectively. The selected bond lengths and bond angles are given in Table 1.

Table 1. Bond Lengths (A) and Bond Angles (°) of 1

Bond	Dist.	Bond	Dist.
W–O_t	1.681(13)～1.722(11)	As–O	1.750(10)～1.767(10)
W–$O_{b/c}$	1.718(12)～2.115(11)	Cu–O	1.871(11)～2.301(11)
W–O_a	2.304(10)～2.404(10)	Cu–N	1.956(14)～2.114(15)
Angle	(°)	Angle	(°)
O–W–O_{cis}	72.0(4)～105.1(5)	O–As–O	98.7(5)～100.4(5)
O–W–O_{trans}	155.8(5)～172.3(4)	N–Cu–N_{cis}	81.9(6)～95.8(7)
O–Cu–O_{cis}	72.3(4)～93.6(5)	N–Cu–N_{trans}	168.6(7)～169.4(7)
O–Cu–O_{trans}	128.2(4)		

3 RESULTS AND DISCUSSION

3.1 Structural description

Single-crystal X-ray diffraction reveals that **1** crystallizes in the monoclinic space group $P2_1/n$, which is composed of organic-inorganic hybrid polycation $[\{Cu(phen)(en)\}\{Cu(phen)\}\{Cu_3(phen)_3(a\text{-}AsW_9O_{33})\}]^+$, one hydroxyl ion and three dissociative water molecules. It should be noted that the most striking structural feature of the infrequent polycation$[\{Cu(phen)(en)\}\{Cu(phen)\}\{Cu_3(phen)_3(a\text{-}AsW_9O_{33})\}]^+$ is present in **1**. The polycation contains a classical trivacant Keggin moiety $[a\text{-}AsW_9O_{33}]^{9-}$, in which three $[Cu(phen)]^{2+}$ units occupy the defect sites of the polyanion fragment $[a\text{-}AsW_9O_{33}]^{9-}$; synchronously, another complex cation $[Cu(phen)]^+$ and a mixed organic amine complex $[Cu(phen)(en)]^{2+}$ were grifted on the trivacant polyanion fragment $[a\text{-}AsW_9O_{33}]^{9-}$. As seen from Fig. 1, the $[Cu(phen)]^{2+}$ fragment for Cu(1) coordinates to the lacuna position of the $[a\text{-}AsW_9O_{33}]^{9-}$ subunit through two terminal oxygen atoms and an additional m_2-O atom for Cu(1), whereas another two $[Cu(phen)]^{2+}$ fragments for Cu(2) and Cu(3) are inserted in vacant sites of the trivacant polyanion skeleton. In addition, the $[Cu(5)(phen)(en)]^{2+}$ and $[Cu(4)(phen)]^{2+}$ fragments graft on two sides of the polyanion $[a\text{-}AsW_9O_{33}]^{9-}$ subunit *via* one and four bridging oxygen atoms, respectively. As a result, such structural conformation results in the formation of an infrequent polycation structure with C_s symmetry.

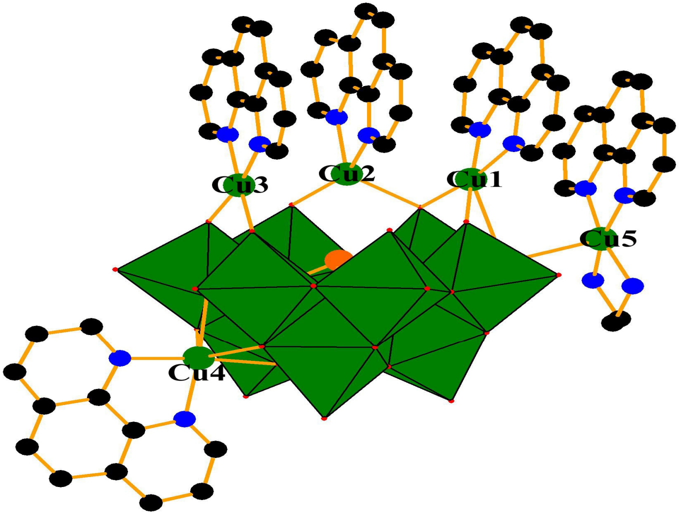

Fig. 1. Polyhedral/ball-and-stick representation of 1. The atoms with suffix A are generated by symmetry operation: $-x, -y, -z$ (Color code: WO_6 = green octahedra; Cu = green spheres; As = orange spheres; O = red spheres; C = black spheres; N = blue spheres). The hydrogen atoms and lattice water molecules are omitted for clarity

The bond valence sum (BVS) calculations[22] indicate that the As atom is in the +3 oxidation state, Cu site in the +2 oxidation state, and all W sites in the +6 oxidation state. The five Cu^{II} ions in **1** exhibit three types of coordination environments (Fig. 2): the Cu(2) and Cu(3) ions reside in a four-coordinate distorted quadrangle geometry with two nitrogen atoms from a bidentate phen ligand (Cu–N: 1.960(14)～2.112(15) Å) and two terminal W=O oxygen atoms of one $[a\text{-}AsW_9O_{33}]^{9-}$ subunit ($Cu–O_d$: 1.867(12)～2.112(12) Å); Both Cu(1) and Cu(5) atoms adopt square pyramidal configurations, which display two kinds of square pyramidal environments in **1**. The Cu(1) ion is bonded to two nitrogen atoms from a bidentate phen ligand (Cu–N: 1.987(15) and 1.991(14) Å), two terminal W=O oxygen atoms of one $[a\text{-}AsW_9O_{33}]^{9-}$ subunit ($Cu–O_d$: 1.912(12) and 1.913(11) Å) and one m_2-O atom (2.8824(117) Å); and square pyramidal geometry of the Cu(5) ion is defined by four nitrogen atoms from an aromatic amine phen (Cu–N: 2.0380(185) and 1.9651(206) Å), an aliphatic amine en (Cu–N: 1.9852(207) and 1.9946(197) Å) and one μ_2-O atom of one $[a\text{-}AsW_9O_{33}]^{9-}$ subunit (2.7261(124) Å). The rings of the above-mentioned three [Cu(phen)]$^{2+}$ fragments are nearly parallel with the dihedral angle ranges between 1.13 and 10.024°. The third type Cu(4) is a six-coordinate distorted octahedral geometry with one nitrogen atom from a bidentate phen ligand (Cu(4)–N(8): 1.984(15) Å) and one m_2-O atom from one [*a*-AsW_9O_{33}]$^{9-}$ subunit in the axial positions (Cu–m_2-O: 2.006(11) Å), and the other nitrogen atom (Cu(4)–N(7): 2.033(14) Å) and three μ_2-O atoms from the same [*a*-AsW_9O_{33}]$^{9-}$ subunit building the equatorial plane (Cu–m_2-O: 2.000(11), 2.266(12), 2.299(11) Å).

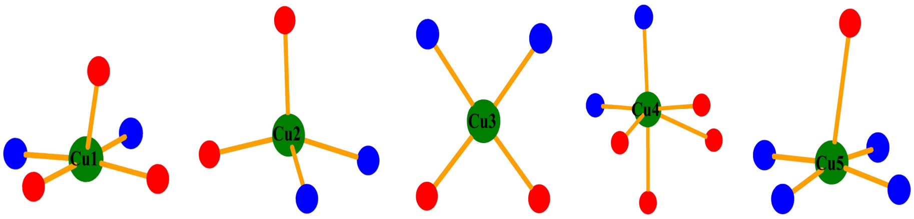

Fig. 2. Coordination environments of the Cu^{II} ions

It should be noted that every copper ion bears one phen ligand in the polycation skeleton of **1**, so stronger *p-p* interactions occur between the adjacent phen ligands (Fig. 3). In the solid-state structure of **1**, adjacent polycations are closely aligned *via* the offsetting *p-p* interactions between the neighboring *p-p* ligands on the Cu(1), Cu(2), Cu(3) and Cu(5) complex groups with the centroid separations of adjacent *p-p* ligands falling in the range of 3.498(1)～3.694(1) Å, which contributes to the stability of the crystal structure.

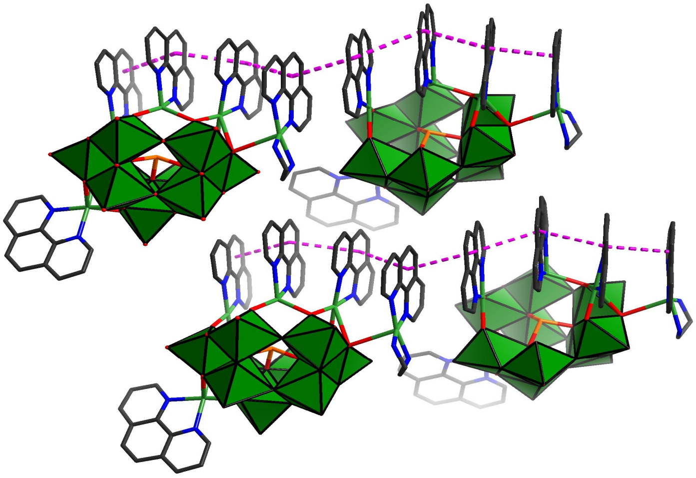

Fig. 3. *π–π* packing interactions in 1. The hydrogen atoms and lattice water molecules are omitted for clarity

3. 2 IR spectra

The IR spectrum (Fig. 4) of **1** shows characteristic vibration patterns resulting from the trivacant polyanion in the range of 1000～700 cm^{-1}. Four groups of characteristic vibration absorption bands are observed at 940, 874, 793, and 714 cm^{-1} in **1**, which are attributed to the stretching vibration of *v*(W=O_t), *v*(As−O_a), *v*(W−O_b), and *v*(W–O_c), respectively[23, 24]. The peaks centered at 3424, 3246, and 3056 cm^{-1} are assigned to the stretching vibration of *v*(O–H), *v*(N–H) and *v*(C–H); whereas the bands appearing at 1624, 1580 and 1516 cm^{-1} are attributed to the bending vibration of *d*(O–H), *d*(N–H) and *d*(C–H), respectively[24]. The characteristic vibration peak at 1425 cm^{-1} is attributed to the C–N stretching modes. Bands in the range of 1040～1624 cm^{-1} are attributed to the phen aromatic ligands. These results indicate the presence of en and phen ligands together with the lattice water molecules in **1**.

3. 3 TG analyses

The TG curve of **1** is divided into two stages with a total weight loss of 32.97% (calcd. 31.16%), as shown in Fig. 5. The first stage weight loss of 3.68% occurring from 25 to 110 ℃ can be ascribed to the removal of the surface adsorbed water and three lattice water molecules. The second weight loss of 29.29% (calcd. 29.66%) in the range of 110～890 ℃ could be attributed to the decomposition of the arsenatotungstate framework. According to the suppositional reaction $\{Cu(phen)(en)\}\{Cu(phen)\}[\{Cu(phen)\}_3(\alpha\text{-}AsW_9O_{33})](OH) \rightarrow 1/2As_2O_3\uparrow + 9WO_3 + 5CuO + 1/2H_2O\uparrow + 5phen\uparrow + en\uparrow$, the second weight loss process corresponds to the departure of one en molecule, five phen molecules and a hydroxide ion, together with the sublimation of half a As_2O_3 molecule.

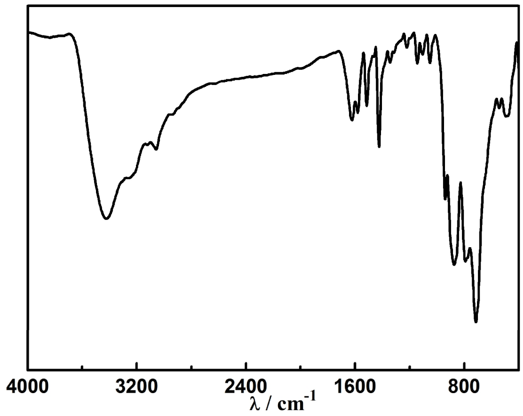

Fig. 4. IR spectrum of 1

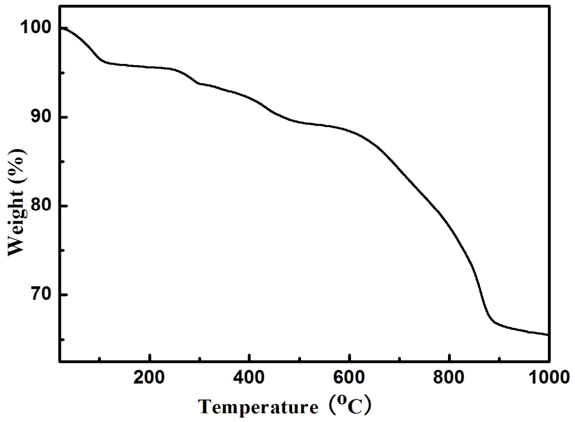

Fig. 5. TG curve of 1

REFERENCES

(1) Kozhevnikov, I. V. Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions. *Chem. Rev.* **1998**, 98, 171–198.

(2) Pope, M. T.; Müller, A. *Polyoxometalate Chemistry: from Topology via Self-assembly to Applications*; Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands **2001**, 1–424.

(3) Pope, M. T.; Müller, A. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands **1994**, 1–408.

(4) Pope, M. T.; Müller, A. Polyoxometalate chemistry: an old field with new dimensions in several disciplines. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 34–48.

(5) Pope, M. T. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag: Berlin **1983**.

(6) Hill, C. L.; Prosser-McCartha, C. M. Homogeneous catalysis by transition metal oxygen anion clusters. *Coord. Chem. Rev.* **1995**, 143, 407–455.

(7) Clemente-Juan, J. M.; Coronado, E. Magnetic clusters from polyoxometalate complexes. *Coord. Chem. Rev.* **1999**, 361, 193–195.

(8) Lisnard, L.; Dolbecq, A.; Mialane, P.; Marrot, J.; Codjovi, E.; Sécheresse, F. Molecular and multidimensional polyoxotungstates functionalized by $\{Cu(bpy)\}^{2+}$ groups. *Dalton Trans.* **2005**, 3913–3920.

(9) Zheng, S. T.; Zhang, J.; Yang, G. Y. $[\{Zn(enMe)_2\}_2(enMe)_2\{Zn_2As_8V_{12}O_{40}(H_2O)\}]\cdot 4H_2O$: a hybrid molecular material based on covalently linked inorganic Zn-As-V clusters and transition metal complexes via enMe ligands. *Eur. J. Inorg. Chem.* **2004**, 2004, 2004–2007.

(10) Xu, Y.; Xu, J. Q.; Zhang, K.; Zhang, Y.; You, X. Z. Keggin unit supported transition metal complexes: hydrothermal synthesis and characterization of $[Ni(2,2'\text{-}bipy)_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-}bipy)_2(H_2O)]\cdot 0.5H_2O$ and $[Co(1,10'\text{-}phen)_3]_{1.5}[PMo_{12}O_{40}Co(1,10'\text{-}phen)_2(H_2O)]\cdot 0.5H_2O$. *Chem. Commun.* **2000**, 153–154.

(11) Hagrman, P. J.; Hagrman, D.; Zubieta, J. Organic-inorganic hybrid materials: from “simple” coordination polymers to organodiamine-templated molybdenum oxides. *Angew. Chem., Int. Ed.* **1999**, 38, 2638–2684.

(12) Khan, M. I.; Yohannes, E.; Powell, D. Synthesis and characterization of a new mixed-metal oxide framework material composed of vanadium oxide clusters: X-ray crystal structure of $(N_2H_5)_2[Zn_3V^{IV}{}_{12}V^{V}{}_6O_{42}(SO_4)(H_2O)_{12}]\cdot 24H_2O$. *Chem. Commun.* **1999**, 23–24.

(13) Zheng, P.; Ren, Y.; Long, L.; Huang, R.; Zheng, L. pH-dependent assembly of Keggin-based supramolecular architecture. *Inorg. Chem.* **2005**, 44, 1190–1192.

(14) Zhao, J. W.; Shi, D. Y.; Chen, L. J.; Ma, P. T.; Wang, J. P.; Niu, J. Y. Two 1-D multi-nickel substituted arsenotungstate aggregates. *Cryst. Eng. Comm.* **2011**, 13, 3462−3469.

(15) Yang, L.; Ma, X.; Ma, P. T.; Hua, J. A.; Niu, J. Y. A series of arsenotungstates based on the $[HAs_2W_8O_{31}]^{7-}$ building block: syntheses by control of the reaction process. *Cryst. Growth Des.* **2013**, 13, 2982−2989.

(16) Niu, J. Y.; Ma, X.; Zhao, J. W.; Ma, P. T.; Zhang, C.; Wang, J. P. A novel organic-inorganic hybrid turbine-shaped hexa-Zn sandwiched tungstoarsenate(III). *Cryst. Eng. Comm.* **2011**, 13, 4834–4837.

(17) Zhao, J. W.; Shi, D. Y.; Chen, L. J.; Cai, X. M.; Wang, Z. Q.; Ma, P. T.; Wang, J. P.; Niu, J. Y. Two organic-inorganic hybrid 1-D and 3-D polyoxotungstates constructed from hexa-Cu^{II} substituted sandwich-type arsenotungstate units. *Cryst. Eng. Comm.* **2012**, 14, 2797−2806.

(18) Fan, L. L.; Wang, E. B.; Li, Y. G.; An, H. Y.; Xiao, D. R.; Wang, X. L. Wells-Dawson anion, a useful building block to construct one-dimensional chain as a chelate ligand coordinating with transition metal cations. *J. Mol. Struct.* **2007**, 841, 28–33.

(19) Wang, J. P.; Ma, P. T.; Li, J.; Niu, J. Y. A novel organic-inorganic hybrid based on tungstoantimonate: synthesis, crystal structure, and properties of $Na[\{Cu(2,2'\text{-}bpy)(H_2O)\}_2\{Cu(2,2'\text{-}bpy)\}_2(B\text{-}a\text{-}SbW_9O_{33})]\cdot 2H_2O$. *Chem. Lett.* **2006**, 35, 994–995.

(20) Zhao, J. W.; Jia, H. P.; Zhang, J.; Zheng, S. T.; Yang, G. Y. A combination of lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions. part II: from double cluster, dimer, and tetramer to three-dimensional frameworks. *Chem. Eur. J.* **2007**, 13, 10030–10045.

(21) Sheldrick, G. M. *SHELXTL-97, Program for X-ray Crystal Structure Solution*. University of Göttingen, Germany **1997**.

(22) Brownand, I. D.; Altermatt, D. Bond-valance parameters obtained from a systematic analysis of an inorganic crystal structure database. *Acta Cryst.* **1985**, B41, 244–247.

(23) Rocchiccioli-Deltcheff, C.; Fournier, M.; Franck, R.; Thouvenot, R. Vibrational investigations of polyoxometalates. 2. evidence for anion-anion interactions in molybdenum(VI) and tungsten(VI) compounds related to the Keggin structure. *Inorg. Chem.* **1983**, 22, 207−216.

(24) Wang, J. P.; Wang, W.; Niu, J. Y. Self-assembly of $[b\text{-}As(V)W_8O_{31}]^{9-}$ subunit in hydrothermal system with moderate acidity: synthesis, crystal structure and characterizations of dimeric arsenotungstate $H_2[\{Cu(phen)\}_8(b\text{-}AsW_8O_{31})_2]\cdot 2.5H_2O$. *Inorg. Chem. Commun.* **2007**, 10, 1054–1057