

Synthesis, Crystal Structure and Properties of the Penta-copper(II)-substituted Sandwich-type Tungstoantimonite $[\text{Cu}_5\text{Na}(\text{H}_2\text{O})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]^{7-}$ ^①

LI Jie^a MA Peng-Tao^{b②}^a (Basic Experiment Teaching Center, Henan University, Kaifeng 475004, China)^b (College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China)

ABSTRACT An organic-inorganic hybrid copper-substituted $[\text{Cu}(\text{EnMe})_2]_{1.5}\{[\text{Cu}(\text{EnMe})_2]_2\text{-}[\text{Cu}_5\text{Na}(\text{OH})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]\cdot 5.5\text{H}_2\text{O}$ (**I**, EnMe = 1,2-diaminopropane) has been hydrothermally synthesized and structurally characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Crystal data for **I**: $\text{C}_{21}\text{H}_{75}\text{Cu}_{8.50}\text{N}_{14}\text{NaO}_{75.50}\text{Sb}_2\text{W}_{18}$, $M_r = 5847.83$, triclinic, space group $P\bar{1}$, $a = 13.029(3)$, $b = 14.613(3)$, $c = 16.887(4)$ Å, $\alpha = 72.875(3)$, $\beta = 73.893(3)$, $\gamma = 74.761(3)^\circ$, $V = 2894.0(10)$ Å³, $Z = 1$, $S = 1.028$, $R = 0.0548$ and $wR = 0.1339$. Polyanion **I** consists of two $\alpha\text{-SbW}_9\text{O}_{33}$ units joined by a cyclic $\{\text{Cu}_5\text{Na}\}$ cluster. The $\{\text{Cu}_5\text{Na}\}$ cluster is stabilized by the inorganic O-donor ligand from both $\{\alpha\text{-SbW}_9\text{O}_{33}\}$ and H_2O ligand, in which the two disordered Cu/Na ions pairwise part the four copper ions to form a centrosymmetric quadrangle. In the cluster, two of the copper ions have no terminal water molecules, resulting in a tetragon configuration, while other four have terminal water molecules, leading to the square-pyramidal coordination geometry.

Keywords: tungstoantimonite, hydrothermal, crystal structure

1 INTRODUCTION

Polyoxometalates (POMs) are a unique class of metal oxygen clusters, which exhibit a fascinating variety of structures and properties including catalysis, materials science and medicine^[1-2]. These properties can be tuned thanks to the high versatility of these polyanionic structures, and the design and synthesis of new 3d transition-metal-substituted polyoxotungstates (TMSPs) remain actively explored. New POM systems are still mainly issued from the reaction of Keggin or Dawson Wells lacunary-POMs, which act as polydentate inorganic ligands toward 3d transition metal ions. The lacunary-POMs derivatives can be easily prepared in one- or two-step processes in high yields, which provide us

abundant initial materials to search and exploit the majority of aforementioned sandwich-type (TMSPs)^[3-8].

The class of Cu-containing, sandwich-type POMs is well-known, and to date numerous complexes have been reported. Most of these polyanions are dimeric and contain three or four Cu centers, e.g., $[\text{Cu}_4\text{K}_2(\text{H}_2\text{O})_8(\alpha\text{-AsW}_9\text{O}_{33})_2]^{8-}$ ^[4], $[\text{M}_4(\text{H}_2\text{O})_2\text{-}(\text{GeW}_9\text{O}_{34})_2]^{12-}$ (M = Mn, Cu, Zn, Cd)^[9], $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}_3(\text{Im})_2(\text{H}_2\text{O})\}(\text{XW}_9\text{O}_{33})_2]^{9-}$ (X = Bi or Sb)^[10] and $[\text{Cu}^{\text{II}}_4(\text{H}_2\text{O})_2(\text{B-}\alpha\text{-PW}_9\text{O}_{34})_2]^{10-}$ ^[11]. In 2008, we reported on the synthesis and magnetic properties of the tetra-copper(II) substituted tungstoantimony(III) $[\text{Na}_2\text{Cu}_4\text{Cl}(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2]^{9-}$ ^[12].

It has been proved that hydrothermal technique is a useful method in making inorganic-organic hybrid

Received 21 February 2013; accepted 16 May 2013 (CCDC 905342)

① This work was supported by the foundation of education department of Henan Province (12A150004)

② Corresponding author. Tel: 0378-3886876, E-mail: mpt@henu.edu.cn

materials in POM field. Recently, a hybrid organic-inorganic penta-Cu sandwiched polyoxotungstate (POTs), **I**, has been successfully made.

2 EXPERIMENTAL

2.1 Materials and methods

The raw material of $(\text{NH}_4)_{18}[\text{NaSb}_9\text{W}_{21}\text{O}_{86}] \cdot 24\text{H}_2\text{O}$ was prepared according to the literature^[13] and identified by IR spectrum. Elemental analyses (C, H, and N) were performed on a PerkinElmer 240C elemental analyzer. IR spectrum was recorded from a sample powder pelletized with KBr on a Bruker VERTEX 70 spectrometer over a range of 4000–400 cm^{-1} . The UV spectrum was recorded with a U-4100 spectrometer (H_2O as solvent) from 400 to 190 nm.

2.2 Synthesis of compound **I**

A mixture of $(\text{NH}_4)_{18}[\text{NaSb}_9\text{W}_{21}\text{O}_{86}] \cdot 24\text{H}_2\text{O}$ (0.70 g, 0.1 mmol), $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (0.42 g, 2.5 mmol), enMe (0.05 mL) and H_2O (15 mL) was adjusted to around pH 5.8 with 2 mol/L K_2CO_3 solution, then transferred and sealed in a 25 mL Teflon-lined stainless-steel container. The container was heated to 130 °C and held at this temperature for 6 day, then

cooled to room temperature at a rate of 5 °C/h. The dark-green block crystals of **I** were collected. C, H and N elemental analysis: calcd. (%) for $\text{C}_{21}\text{H}_{75}\text{Cu}_{8.50}\text{N}_{14}\text{NaO}_{75.50}\text{Sb}_2\text{W}_{18}$: C, 4.31; H, 1.29; N, 3.35. Found (%): C, 4.28; H, 1.35; N, 3.23.

2.3 X-ray structure determination

Intensity data were collected on a Bruker APEX-II diffractometer at 296 K using a graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods with SHELXS-97 program^[14]. Refinements were done by full-matrix least-squares on F^2 with SHELXL-97^[15]. All non-hydrogen atoms were refined anisotropically. Crystal data for **I**: crystal sizes 0.24mm × 0.16mm × 0.11mm, $F(000) = 2595$, $T = 296(2) \text{ K}$, $1.87 < \theta < 25.00^\circ$, measured reflections: 14316, independent reflections: 10056 with $R_{\text{int}} = 0.0379$, the final $R = 0.0548$, $wR = 0.1339$ ($w = 1/[\sigma^2(F_o^2) + (0.0728P)^2 + 86.4703P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 6847 observed reflections ($I > 2\sigma(I)$), $S = 1.028$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\rho)_{\text{max}} = 4.779$ and $(\Delta\rho)_{\text{min}} = -3.119 \text{ e/\AA}^3$. The selected bond lengths and bond angles are given in Table 1.

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) for **I**

Bond	Dist.	Bond	Dist.
W–O _i	1.698(17)–1.742(15)	Cu(1)–O	1.943(15)–2.023(14)
W–O _{b/c}	1.830(15)–1.991(14)	Cu(2)–O	1.973(18)–2.262(29)
W–O _a	2.265(13)–2.333(14)	Cu(3)–O	2.019(15)–2.087(15)
Sb–O	1.972(14)–2.002(13)	Cu–N	1.953(36)–2.064(19)
Angle	(°)	Angle	(°)
O–W(1)–O	72.5(5)–168.4(7)	O–Sb–O	91.0(5)–92.1(6)
O–W(2)–O	73.1(5)–168.0(6)	O–Cu(1)–O	83.8(6)–175.4(6)
O–W(3)–O	73.4(5)–170.6(7)	O–Cu(2)–O	83.5(6)–160.1(6)
O–W(4)–O	72.7(5)–166.6(6)	O–Cu(3)–O	79.7(6)–149.4(7)
O–W(5)–O	73.7(5)–167.9(6)	N–Cu(4)–N	84.8(8)–176.7(9)
O–W(6)–O	73.6(5)–170.1(6)	N–Cu(5)–N	77.3(12)–171.4(13)
O–W(7)–O	73.7(5)–171.4(6)	N–Cu(4)–O(3W)	86.5(8)–91.9(9)
O–W(8)–O	73.0(6)–171.2(7)	N–Cu(5)–O(4W)	90.9(12)–96.8(9)
O–W(9)–O	72.5(5)–166.8(6)		

3 RESULTS AND DISCUSSION

3.1 Crystal structure of the complex

Single-crystal X-ray structural analysis indicates

that the structural unit of **I** contains one di-supporting polyoxoanion fragment $\{[\text{Cu}(\text{EnMe})_2]_2\text{-}[\text{Cu}_5\text{Na}(\text{H}_2\text{O})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]\}^{3-}$, one point five discrete $[\text{Cu}(\text{EnMe})_2]^{2+}$ cations, and five point five

lattice water molecules (Fig. 1). Notice that the most striking structural feature of the polyoxoanion $\{[\text{Cu}(\text{EnMe})_2][\text{Cu}_5\text{Na}(\text{H}_2\text{O})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]\}^{3-}$ in **I** is that a sandwich-type moiety $[\text{Cu}_5\text{Na}(\text{H}_2\text{O})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]^{7-}$ is decorated by two $[\text{Cu}(\text{EnMe})_2]^{2+}$ complex cations. The sandwich-type polyoxoanion consists of two $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ moieties linked by a $\{\text{Cu}_5\text{Na}\}$ cluster. In the skeleton of sandwich-type

polyoxoanion, each $\{\text{SbW}_9\text{O}_{33}\}^{9-}$ unit provides six oxygen donors that are capable of coordinating to the central $\{\text{Cu}_5\text{Na}\}$ cluster, six Cu or Cu/Na ions lie in the center belt between two $\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}^{9-}$ anions, forming a centrosymmetric six-membered ring with an interior angle sum of 720° as a plane hexagon.

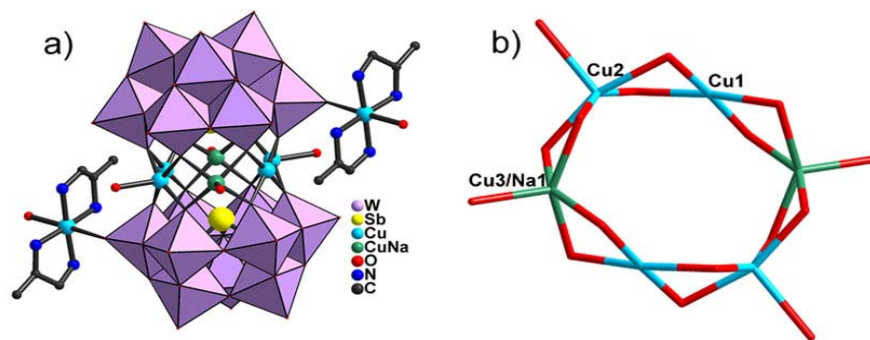


Fig. 1. a) Polyhedral/ball-and-stick representation of the molecular structural unit of **I**; b) Wire-and-stick representation of the $[\text{Cu}_5\text{Na}]$ arrangement. The isolated water molecules and H atoms attached to EnMe ligands are omitted for clarity

A novel hexacopper-substituted sandwiched POM $\{[\text{Cu}(\text{EnMe})]_3[\text{Cu}(\text{H}_2\text{O})]_3(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2\}^{6-}$ [16] recently reported by Yao S. *et al.* is similar to species **I**, and the difference lies in the coordination atoms and modes of the copper ions in the centre belt between two $\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}^{9-}$ anions. The copper ions are coordinated by oxygen and nitrogen atoms in the former, but only coordinated by oxygen atoms in **I**. In the hexagonal $\{\text{Cu}_6\}$ cluster-containing tungstoantimonite $\{[\text{Cu}(\text{EnMe})]_3[\text{Cu}(\text{H}_2\text{O})]_3(\text{B-}\alpha\text{-SbW}_9\text{O}_{33})_2\}^{6-}$, three of the Cu atoms are all coordinated by four oxygen atoms from two $\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}^{9-}$ units and a terminal water ligand, resulting in a square-pyramidal coordination, whereas another three Cu ions all exhibit trigonal bipyramidal coordination, completed by three O atoms coming from two trivalent $\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}^{9-}$ groups and two N atoms of an enMe molecule. In the $\{\text{Cu}_5\text{Na}\}$ cluster of **I**, the Cu ions can be divided into two groups according to their different coordination modes. The first group includes the Cu(2) and Cu(3)/Na(1) ions, which are all coordinated by four oxygen atoms (the average Cu–O distance is 2.024

Å) belonging to two $\{\text{SbW}_9\text{O}_{33}\}^{9-}$ ligands and an exterior H_2O molecule (the average Cu–O(H_2O) distance of 2.155 Å) in a square pyramidal geometry (Fig. 1b) [17]. The other group is composed of the two Cu(1) ions, which are both in the tetra-coordinated environment, completed by four O atoms from two trivalent $\{\text{SbW}_9\text{O}_{33}\}^{9-}$ ligands. Additionally, there are two hexa-coordinated Cu(4) ions which graft on the belt of the sandwich-type polyoxoanion. The hexa-coordinated environments are completed by four N atoms from two EnMe molecules, and two O atoms deriving from the sandwich-type polyoxoanion and a H_2O molecule, respectively. It is a pity that the hexa-coordinated Cu ions are non-coordinated with the adjacent dimeric polyoxoanions. However, the polyoxoanions in **I** are packed together through an AAAA mode to form a layer-like structure along the *c*-axis (Fig. 2).

The bond valence sum (BVS) calculations [18] indicate that the Sb site is in the +3 oxidation state, Cu site in the +2 oxidation state, and all W sites in the +6 oxidation state.

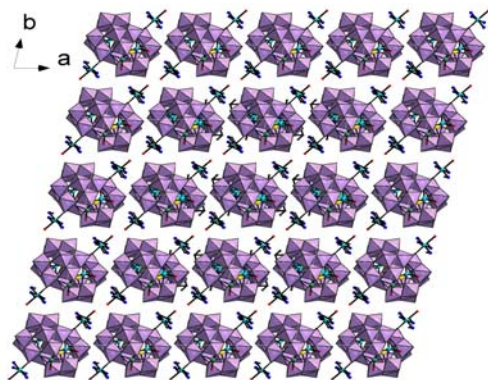


Fig. 2. Packing diagram of polyoxoanions viewed down the *c*-axis. The isolated water molecules and copper complexes are omitted

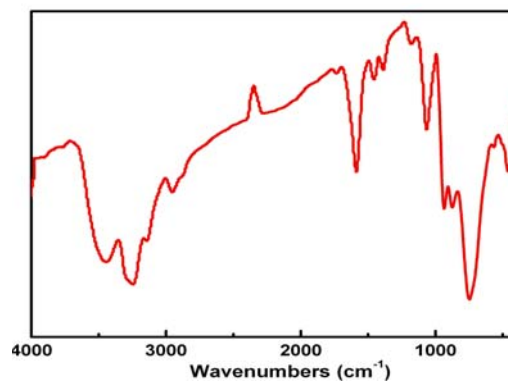


Fig. 3. IR spectrum of I

In addition, supramolecular interactions are present in the title compound regarding of hydrogen-bonding interactions between nitrogen atoms of organoamine ligands and surface oxygen atoms of polyoxoanions. Specifically, N atoms from organoamine ligands act as the proton donors, O atoms from the surface oxygen of sandwiched $[\text{Cu}_5\text{Na}(\text{H}_2\text{O})_4(\alpha\text{-SbW}_9\text{O}_{33})_2]^{7-}$ units serve as the proton acceptors, and then donors and acceptors are hydrogen-bonded

together, generating the infinite three-dimensional supramolecular framework. Within the matrix, abundant intra- and intermolecular N–H···O hydrogen bonds exist between organoamines and the surface oxygen atoms of polyoxoanions with the N···O distances in the range of 3.03–3.40 Å (Table 2). Moreover, the formation of these supramolecular interactions may be favorable for the chemical stability of the title compound.

Table 2. Hydrogen Bond Lengths (Å) and Bond Angles (°)

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
N(1)–H(1C)···O(8) ^a	0.86	2.39	3.13(2)	144.7
N(1)–H(1C)···O(31) ^a	0.86	2.47	3.14(2)	134.8
N(2)–H(2B)···O(14)	0.86	2.43	3.13(3)	139.1
N(2)–H(2B)···O(3) ^b	0.86	2.62	3.10(2)	116.9
N(3)–H(3D)···O(11) ^b	0.86	2.49	3.05(3)	122.6
N(3)–H(3D)···O(14) ^b	0.86	2.55	3.40(3)	167.2
N(4)–H(4C)···O(8) ^a	0.86	2.47	3.20(3)	143.5
N(4)–H(4C)···O(5) ^a	0.86	2.50	3.24(3)	143.7
N(5)–H(5B)···O(25) ^c	0.86	2.49	3.11(3)	130.1
N(6)–H(6D)···O(6) ^d	0.86	2.46	3.03(3)	124.9
N(7)–H(7C)···O(6) ^e	0.86	2.60	3.03(3)	111.7
N(8)–H(8B)···O(22) ^c	0.86	2.29	3.03(4)	144.0

Symmetry codes: (a) $x-1, y, z$; (b) $-x, -y+1, -z+1$; (c) $x+1, y-1, z$; (d) $x, y-1, z$; (e) $-x+1, -y+1, -z$

3.2 IR spectra

IR spectrum of **I** (Fig. 3) shows characteristic vibration patterns resulting from the sandwiched tungstoantimony framework in the range of 1000–600 cm^{-1} . Four characteristic bands are attributed to the stretching vibration of $\nu(\text{W}-\text{O}_i)$, $\nu(\text{W}-\text{O}_b)$, $\nu(\text{W}-\text{O}_c)$, and $\nu(\text{Sb}-\text{O})$, appearing at 937, 886, 750 and 697 cm^{-1} correspondingly. The $\nu(\text{N}-\text{H})$ stre-

tching band is observed at about 3243 cm^{-1} , and the $\nu(\text{C}-\text{N})$ at 1383 cm^{-1} . The characteristic peaks centered at 1581 and 1457 cm^{-1} are attributed to the bending vibration of $\nu(\text{N}-\text{H})$ and $\nu(\text{C}-\text{H})$, respectively. The appearance of these characteristic signals confirms the presence of enMe ligands in **I**, in good agreement with the single-crystal structural analysis results. In addition, the occurrence of the vibration

bands at 3453 cm^{-1} assigned to the stretching vibration $\nu(\text{O-H})$ of water molecules suggests the presence of lattice water molecules in **I**.

3.3 UV spectra

The UV spectra of the title compound **I** in aqueous solution reveal two un conspicuous bands for the ligand to metal charge transfer. More intense

bands corresponding to the $p_\pi(\text{O}_d) \rightarrow d_{\pi^*}(\text{W})$ transitions^[19] appeared at 193.2 nm for **I**. The shoulder band around 237.8 nm is assigned to a $p_\pi(\text{O}_{b,c}) \rightarrow d_{\pi^*}(\text{W})$ charge transfer transition in the tricentric bonds of POMs, which is consistent with the literature values^[3] (193.6 and 250.7 nm).

REFERENCES

- (1) Pope, M. T. *Heteropoly and Isopoly Oxometalates*. Springer-Verlag, New York **1983**.
- (2) Pope, M. T.; Muller, A. Polyoxometalate chemistry: an old field with new dimensions in several disciplines. *Angew. Chem., Int. Ed.* **1991**, 30, 34–48.
- (3) Rusu, R.; Barra, A. L.; David, L.; Rusu, C.; Cozar, O.; Marcu, G. Spectroscopic and electron paramagnetic resonance behavior of trinuclear metallic clusters encapsulated in $[\text{M}^{n+}_3(\text{H}_2\text{O})_x(\text{BiW}_9\text{O}_{33})_2]^{(18-3n)-}$ heteropolyanion ($\text{M}^{n+} = (\text{VO})^{\text{II}}$, $x = 0$ and $\text{M}^{n+} = \text{Cr}^{\text{III}}$, Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} , Cu^{II} , $x = 3$). *J. Chem. Soc., Dalton Trans.* **2001**, 2879–2887.
- (4) Kortz, U.; Nellutla, S.; Stowe, A. C.; Dalal, N. S.; van Tol, J.; Bassil, B. S. Structure and magnetism of the tetra-copper(II)-substituted heteropolyanion $[\text{Cu}_4\text{K}_2(\text{H}_2\text{O})_8(\alpha\text{-AsW}_9\text{O}_{33})_2]^{8-}$. *Inorg. Chem.* **2004**, 43, 144–154.
- (5) Ritorto, M. D.; Anderson, T. M.; Neiwert, W. A.; Hill, C. L. Decomposition of a-type sandwiches. Synthesis and characterization of new polyoxometalates incorporating multiple d-electron-centered units. *Inorg. Chem.* **2004**, 43, 44–49.
- (6) Zhao, J. W.; Wang, C. M.; Zhang, J. Combination of lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions: IX. a series of novel polyoxotungstates sandwiched by octa-copper clusters. *Chem. Eur. J.* **2008**, 14, 9223–9239.
- (7) Bi, L. H.; Kortz, U. Synthesis and structure of the pentacopper(II) substituted tungstosilicate $[\text{Cu}_5(\text{OH})_4(\text{H}_2\text{O})_2(\text{A-}\alpha\text{-SiW}_9\text{O}_{33})_2]^{10-}$. *Inorg. Chem.* **2004**, 43, 7961–7962.
- (8) Zhao, J. W.; Zhang, J.; Zheng, S. T.; Yang, G. Y. Combination between lacunary polyoxometalates and high-nuclear transition metal clusters under hydrothermal conditions: first (3,6)-connected framework constructed from sandwich-type polyoxometalate building blocks containing a novel $\{\text{Cu}_8\}$ cluster. *Chem. Commun.* **2008**, 570–572.
- (9) Kortz, U.; Nellutla, S.; Stowe, A. C.; Dalal, N. S.; Rauwald, U.; Danquah, W.; Ravot, D. Sandwich-type germanotungstates: structure and magnetic properties of the dimeric polyoxoanions $[\text{M}_4(\text{H}_2\text{O})_2(\text{GeW}_9\text{O}_{34})_2]^{12-}$ ($\text{M} = \text{Mn}^{2+}$, Cu^{2+} , Zn^{2+} , Cd^{2+}). *Inorg. Chem.* **2004**, 43, 2308–2317.
- (10) Liu, H.; Qin, C.; Wei, Y. G.; Xu, L.; Gao, G. G.; Li, F. Y.; Qu, X. S. Copper-complex-linked polytungsto-bismuthate (-antimonite) chain containing sandwich Cu(II) ions partially modified with imidazole ligand. *Inorg. Chem.* **2008**, 47, 4166–4172.
- (11) Li, B.; Zhao, J. W.; Zheng, S. T.; Yang, G. Y. Combination chemistry of hexa-copper-substituted polyoxometalates driven by the CuII -polyhedra distortion: from tetramer 1D chain to 3D framework. *Inorg. Chem.* **2008**, 47, 8294–8303.
- (12) Wang, J. P.; Ma, P. T.; Li, J.; Niu, H. Y.; Niu, J. Y. Self-assembly of $[\text{B-SbW}_9\text{O}_{33}]^{9-}$ subunit with transition metal ions (Mn^{2+} , Cu^{2+} , Co^{2+}) in aqueous solution: syntheses, structures and magnetic properties of sandwich type polyoxometalates with subvalent Sb^{III} heteroatom. *Chem. Asian J.* **2008**, 3, 822–833.
- (13) Hervéa, G.; Téazéa, A.; Liu, J.; Pope, M. T. Ammonium sodium hencosatungstonona-antimonate(III), $(\text{NH}_4)_{18}[\text{NaSb}_9\text{W}_{21}\text{O}_{86}] \cdot 24\text{H}_2\text{O}$. *Inorg. Synth.* **1990**, 27, 120.
- (14) Sheldrick, G. M. *SHELXS-97. Program for Solution of Crystal Structures*. University of Gottingen, Germany **1997**.
- (15) Sheldrick, G. M. *SHELXL-97. Program for Crystal Structure Refinement*. University of Gottingen, Germany **1997**.
- (16) Yao, S.; Zhang, Z. M.; Li, Y. G.; Wang, E. B. A $\{\text{Cu}_6\}$ -containing inorganic-metal-organic sandwich-type tungstoantimonite and its 3D supramolecular framework. *Inorg. Chem. Commun.* **2009**, 12, 937–940.
- (17) Addison, A. W.; Rao, T. N.; Reedjik, J.; Van Rijn, J.; Verschoor, C. G. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua [1,7-bis(N-methylbenzimidazol-2-yl)-2,6-dithioheptane] copper(II) perchlorate. *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
- (18) 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.
- (19) Yamase, T. Photo- and electrochromism of polyoxometalates and related materials. *Chem. Re.* **1998**, 98, 307–325.