

Copper-Complex-Linked Polytungsto-Bismuthate (-Antimonite) Chain Containing Sandwich Cu(II) Ions Partially Modified with Imidazole Ligand

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Two sandwich-type complexes $\text{Na}_{9n}(\text{Cu}(\text{im})_4(\text{H}_2\text{O})_2)_{1.5n}(\text{Cu}(\text{im})_4(\text{H}_2\text{O}))_n [\{\text{Cu}(\text{im})_4\}\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})\}(\text{XW}_9\text{O}_{33})_2]_{2n} \cdot (x\text{H}_2\text{O})_n$ (im = imidazole, X = Bi (**1**), Sb (**2**), $x = 42.5$ (**1**), 40 (**2**)) have been synthesized and structurally characterized. Basic frameworks of **1** and **2** are built from sandwich-type $[\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})\}(\text{XW}_9\text{O}_{33})_2]^{9-}$ (X = Bi or Sb) anions and $[\text{Cu}(\text{im})_4]^{2+}$ cations. The Cu^{2+} and Na^+ ions in the central belt are coordinated by α - $[\text{XW}_9\text{O}_{33}]^{9-}$ units, im, and water molecules to form $\{\text{CuO}_4(\text{im})\}$, $\{\text{CuO}_4(\text{H}_2\text{O})\}$, and $\{\text{NaO}_4(\text{H}_2\text{O})_2\}$ groups in which Cu^{2+} ions are partially modified with im ligands. These groups connect alternately forming a six-membered ring including six α - $[\text{XW}_9\text{O}_{33}]^{9-}$ units. Neighboring anions are further linked by $[\text{Cu}(\text{im})_4]^{2+}$ cations to display an unprecedented anionic chain, which is first observed in sandwich-type tungsto-bismuthate (-antimonite) system. Two kinds of isolated copper complexes and sodium ions are located as counterions, which cause three-dimensional packings of **1** and **2** to present interesting cage structures. The magnetic properties for **1** and **2** both indicate dominant antiferromagnetic interactions among trinuclear Cu(II) clusters.

Introduction

Polyoxometalates (POMs) are a unique class of metal-oxide clusters with an enormous structural diversity and a variety of applications.^{1,2} Parallel to the rapid progress of POMs, particular attention has been devoted to families of transition metal-substituted POMs because of their highly tunable nature, coupled with their fascinating properties which lead to potential applications in catalysis,³ magnetism,^{4,5} and medicine.⁶ Among them, the sandwich-type species based on trivacant Keggin moieties probably represent the largest subfamily, in which the trilacunary Keggin

polyanions define the largest possible planar minisurface. Since the first sandwich-type polyoxoanion $[\text{Co}_4(\text{H}_2\text{O})_2(\text{B}-\alpha\text{-PW}_9\text{O}_{34})]^{10-}$ was discovered by Weakley et al. in 1973,⁷ many sandwich-type species have been reported including Weakley-, Hervé-, Krebs-, and Knoth-type sandwich structures. However, the known characterized structures of the sandwich-type POMs are mostly focused on trivacant tung-

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stophosphate, -silicate, and -arsenate fragments. Up to now, little research has been done on analogs containing subvalent main group atom Bi(III) or Sb(III) as heteroatom.^{8–10} In contrast to the tetrahedrally coordinated heteroatoms P(V) and As(V) of the same main group, Bi(III) or Sb(III) would give new structural information because of the stereochemical effect of the lone pair electrons located on top of the trigonal pyramid.

Moreover, in comparison to the extensive work on the modification of polyoxoanionic structures via attachment of organic groups to the surface of polyoxoanions,^{11,12} considerably less research has been conducted by using organic ligands to substitute coordinated water molecules attached to the magnetic transition metal clusters of sandwich-type heteropolyanions.^{13,14} Such modification may be an effective route to tune magnetic properties for obtaining valuable magnetic materials. Under suitable reaction conditions, some nonaqueous ligands, such as organic amine, can substitute water molecule ligands on the POM-based sandwich-type magnetic clusters, resulting in a significant change of magnetic property.¹⁵ However, this task becomes difficult in aqueous medium because of the presence of a coordinate competition between water and nonaqueous ligands. Though more sandwich-type complexes of POM are expected to arise, the development of new nonaqueous-ligand-modified magnetic POM clusters with unusual structures still remains a challenge.

Considering the above mentioned, we devoted ourselves to synthesize new types of nonaqueous-ligand modified sand-

wich-type POMs based on lacunary tungstobismuthate or tungstoantimonate anions combined with transition-metal complex moieties. In our synthetic strategy, imidazole, a readily available ligand, seized our attention because (i) compared with water ligand, it has been proved to have stronger coordination ability relative to metal ions, consequently offering the possibility of substituting coordinated water molecules so as to influence the magnetic property of the copper center; (ii) its relatively small volume may help to reduce the steric hindrance when attacking transition metal cations embedded in two polyanion cores, hence, leading themselves to coordinate with metal atoms. Fortunately, we have isolated two imidazole modified sandwich-type tungstobismuthate and tungstoantimonate by conventional methods, expressed as $\text{Na}_{9n}(\text{Cu}(\text{im})_4(\text{H}_2\text{O})_2)_{1.5n}(\text{Cu}(\text{im})_4(\text{H}_2\text{O}))_n$ [$\{\text{Cu}(\text{im})_4\}\{\text{Na}(\text{H}_2\text{O})_2\}_3\{\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})\}\{\text{XW}_9\text{O}_{33}\}_2$] $_{2n} \cdot (x-\text{H}_2\text{O})_n$ (im = imidazole, X = Bi (**1**), Sb (**2**), $x = 42.5$ (**1**), 40 (**2**)). Herein, we report on the syntheses, crystal structures, and magnetic properties of the two polyoxometalate-based complexes. The replacement of water molecule with an imidazole ligand could influence the magnetic property of the copper cluster; this should be of interest in molecular magnetism.

Experimental Section

Materials and Instrumentation. All reagents were purchased and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Bi, Sb, W, Cu, and Na were determined by a Leeman inductively coupled plasma (ICP) spectrometer. The infrared spectrum was recorded with an Alpha Centaur FT/IR spectrometer with a KBr pellet in the 4000–400 cm^{-1} region. Electronic spectra were performed in pH 7.11 (0.025 M $\text{NaH}_2\text{PO}_4 + \text{NaH}_2\text{PO}_4$) buffer solutions within a range of 190–1000 nm using an ATI Uncial-UV–vis Vision Software V3.20. A Perkin–Elmer TGA7 thermogravimetric analyzer was used to obtain TGA curves under N_2 with a temperature increasing rate of 5 $^\circ\text{C min}^{-1}$ in the range 25–800 $^\circ\text{C}$. Variable-temperature magnetic susceptibilities were performed with a Quantum Design MPMS XL-5 SQUID system.

Synthesis of 1. $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.241 g, 0.5 mmol) dissolved in 1 mL of 6 mol/L HCl was added to a solution of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (3.300 g, 10.0 mmol) in 40 mL of deionized water, and the mixture was heated to 80 $^\circ\text{C}$ for about 15 min. Then, a solution of $\text{Cu}(\text{Ac})_2 \cdot \text{H}_2\text{O}$ (0.303 g, 1.5 mmol) dissolved in 3 mL of 0.7 mol/L NaOH solution and solid imidazole (0.074 g, 1.1 mmol) were added to the clear solution successively, and the pH value was adjusted to 7.16 at 60 $^\circ\text{C}$ by addition of 1 mol/L HCl. The mixture was kept at 80 $^\circ\text{C}$ for about 2 h and then cooled to room temperature and filtered. Slow evaporation at room temperature resulted in gray-blue crystals (0.676 g, yield 35.9% based on Cu) of **1** after 10 days. Anal. Calcd for $\text{C}_{66}\text{H}_{209}\text{Bi}_4\text{Cu}_{10.5}\text{N}_{44}\text{O}_{192.5}\text{W}_{36}\text{Na}_{15}$: Cu, 4.99; Bi, 6.48; W, 51.14; Na, 2.71%; C, 6.11; N, 4.76; H, 1.53%. Found: Cu, 5.07; Bi, 6.35; W, 50.27; Na 2.62; C, 6.02; N, 4.68; H, 1.60%. IR (KBr disk): 3414 (s), 3137 (w), 2925 (w), 2854 (w), 2364 (s), 1630 (s), 1539 (w), 1494 (w), 1456 (w), 1327 (m), 1256 (m), 1171 (m), 1069 (s), 934 (s), 870 (s), 740 (s), 509 (w), 438 (m) cm^{-1} .

Synthesis of 2. Compound **2** was synthesized by the similar procedure with **1** except that the $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was replaced by SbCl_3 (0.114 g, 0.5 mmol), and the pH value was adjusted to 7.50 at 60 $^\circ\text{C}$. Purple-blue crystals of **2** (0.625 g, yield 33.7%) formed after 23 days. Anal. Calcd for $\text{C}_{66}\text{H}_{204}\text{Sb}_4\text{Cu}_{10.5}\text{N}_{44}\text{O}_{190}\text{W}_{36}\text{Na}_{15}$:

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Table 1. Crystal Data and Structure Refinement for **1** and **2**^a

compound	1	2
empirical formula	C ₆₆ H ₂₀₉ Bi ₄ Cu _{10.5} N ₄₄ ‒Na ₁₅ O _{192.5} W ₃₆	C ₆₆ H ₂₀₈ Sb ₄ Cu _{10.5} N ₄₄ ‒Na ₁₅ O ₁₉₂ W ₃₆
fw	13165.79	12771.91
<i>T</i> [K]	293(2)	190(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> [Å]	23.076(5)	22.909(6)
<i>b</i> [Å]	24.945(5)	24.833(6)
<i>c</i> [Å]	28.420(6)	28.216(7)
α [°]	70.02(3)	69.956(3)
β [°]	74.65(3)	73.716(3)
γ [°]	80.01(3)	79.628(3)
<i>V</i> [Å ³]	14764(5)	14412(6)
<i>Z</i>	1	1
ρ_{calcd} [mg m ⁻³]	2.934	2.924
μ [mm ⁻¹]	17.189 mm ⁻¹	15.544 mm ⁻¹
<i>F</i> (000)	11595	11331
crystal size [mm ³]	0.24 × 0.12 × 0.10	0.22 × 0.16 × 0.12
θ range [°]	3.01–27.47	1.58–25.00
limiting indices reflections	–29 ≤ <i>h</i> ≤ 29 –29 ≤ <i>k</i> ≤ 32 –36 ≤ <i>l</i> ≤ 36	–24 ≤ <i>h</i> ≤ 27 –29 ≤ <i>k</i> ≤ 24 –33 ≤ <i>l</i> ≤ 33
collected/unique	100115/67557 [<i>R</i> (int) = 0.0709]	72761/49982 [<i>R</i> (int) = 0.0773]
completeness to θ [%]	98.9	98.4
refinement method	full-matrix-block least-squares on <i>F</i> ²	full-matrix-block least-squares on <i>F</i> ²
data /restraints/parameters	67557/0/3058	49982/12/2573
goodness-of-fit on <i>F</i> ²	1.027	0.994
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0665 <i>wR</i> ₂ = 0.1405	<i>R</i> ₁ = 0.0687 <i>wR</i> ₂ = 0.1547
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1207 <i>wR</i> ₂ = 0.1650	<i>R</i> ₁ = 0.1467 <i>wR</i> ₂ = 0.1917
largest diff peak/hole [e Å ⁻³]	2.377/–2.611	4.397/–7.307

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. $wR = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$.

Cu, 5.13; Sb, 3.91; W, 52.33; Na, 2.62; C, 6.10; N, 4.15; H, 1.50%. Found: Cu, 5.22; Sb, 3.81; W, 51.82; Na, 2.70; C, 6.21; N, 4.83; H, 1.61%. IR (KBr disk): 3426 (s), 3130 (w), 2945 (w), 2852 (w), 2363 (w), 1647 (s), 1585 (m), 1537 (m), 1503 (w), 1426 (m), 1325 (m), 1256 (m), 1181 (s), 1068 (s), 932 (s), 870 (s), 704 (s), 517 (w), 434 (m) cm⁻¹. IR spectra of **1** and **2** were shown in Supporting Information, Figure S1.

X-ray Crystallography. Crystal data of **1** and **2** were collected on a Bruker SMART CCD APEX(II) diffractometer with a graphite-monochromated Mo K α ($\lambda = 0.71073$ Å) at 293 K. Selected data collection parameters and other crystallographic results are summarized in Table 1. All data were corrected for Lorentz polarization and absorption effects.¹⁶ The program package SHELX-97 (SHELX-TL)¹⁷ was used for structure solution and least-squares refinement on *F*². H atoms (N–H and C–H) were placed at calculated positions and were allowed to ride on the carrier-C/N atoms with *U*_{iso} = 1.2*U*_{eq}. The O atoms from water molecules are located from difference Fourier maps, but the H atoms from water molecules could not be located from difference Fourier maps and thus were not included in the final cycle of refinement. In **1**, N3, N5, C4, C8, C20, C36, C44, C65, C66, and parts of the water oxygen atoms were refined isotropically. All the imidazole molecules in **2** were refined as an idealized planar ring. CCDC–269138 **1**, CCDC–647038 **2** contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Syntheses. **1** and **2** were synthesized by treating a suspension of Na₂WO₄·2H₂O, Bi(NO₃)₃·5H₂O (or SbCl₃), Cu(Ac)₂·H₂O, and N-donor ligand imidazole at 80 °C. The successful syntheses indicate that the {Cu(im)₄} fragment is an effective linker in these reaction system. Both the molar ratio of Na₂WO₄·2H₂O to Bi(NO₃)₃·5H₂O (or SbCl₃) and the pH value are the key factors for synthesizing these two complexes. Only the molar ratio of 20:1 for Na₂WO₄·2H₂O to Bi(NO₃)₃·5H₂O (or SbCl₃) can successfully obtain complexes **1** and **2**. The pH value should be strictly controlled at 7.16 and 7.50 for **1** and **2**, respectively.

Structures. The trivacant α -B-[XW₉O₃₃]⁹⁻ unit in the two compounds derives from the parent α -Keggin structure by taking off three edge-sharing WO₆ octahedra (one edge-sharing W₃O₁₃ triad), whose structural feature is shown in the Supporting Information, Figure S2. The presence of a lone electron pair prevents the formation of the closed Keggin unit. Each α -B-[XW₉O₃₃]⁹⁻ unit provides six oxygen donor atoms coming from six W atoms to coordinate with the central metal cluster. The center heteroatom Bi(III) or Sb(III) is surrounded pyramidally by three oxygen atoms, and the lone pair orbital electrons are located on the top of the pyramid.

The structure of **1** consists of three main parts: anionic chain [(Cu(im)₄)(Na(H₂O)₂)₃(Cu₃(im)₂(H₂O))(BiW₉O₃₃)₂]_{2n} (**a**), isolated cations [Cu(im)₄(H₂O)₂]²⁺ (**b**), and [Cu(im)₄-

(16) SAINTE, Version 6.02; Bruker AXS: Madison, WI, 1999.

(17) SHELXTL, Version 5.1; Bruker AXS: Madison, WI, 1998.

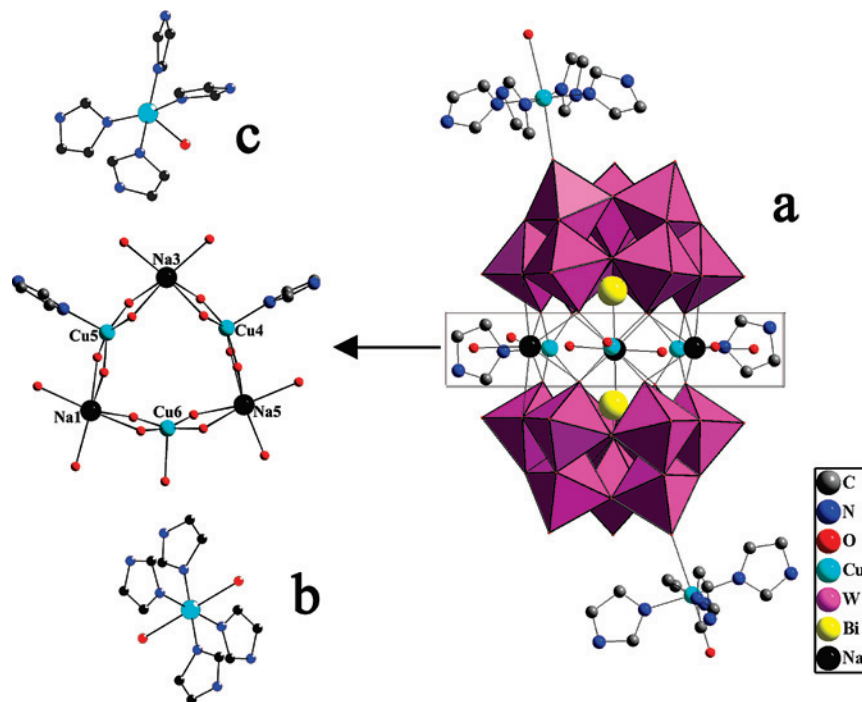


Figure 1. View of the chain motif and isolated copper complex cations located in **1**. All the H atoms, isolated water molecules, and free sodium ions are omitted.

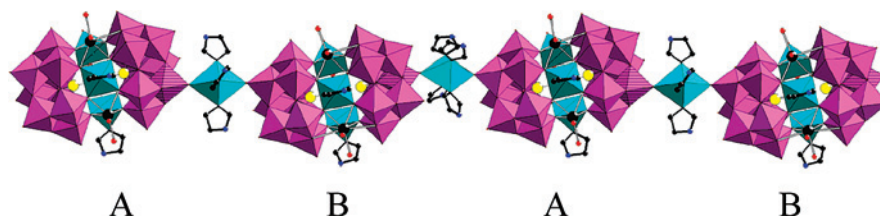


Figure 2. Chain-like structure for **1**. All the H atoms, free sodium ions, isolated water molecules, and copper complexes are omitted.

(H₂O)]²⁺ (**c**, Figure 1). As shown in Figure 1, the chain-like motif **a** is constructed by sandwich-type $\{[\text{Na}(\text{H}_2\text{O})_2]_3\{[\text{Cu}_3(\text{im})_2(\text{H}_2\text{O})](\text{BiW}_9\text{O}_{33})_2\}^9\}$ (abbr. $\{\text{Bi}_2\text{W}_{18}\text{Cu}_3\text{Na}_3\}$) anions and $[\text{Cu}(\text{im})_4]^{2+}$ cations. The novel polyanion $\{\text{Bi}_2\text{W}_{18}\text{Cu}_3\text{Na}_3\}$ consists of two trivacant $[\text{BiW}_9\text{O}_{33}]^{9-}$ moieties linked through crystallographically independent three Cu^{2+} and three Na^+ ions. For the Cu4 and Cu5 ions in the central belt, each copper ion in a square-pyramidal geometry is coordinated by four terminal oxygen atoms from four WO_6 groups of two different $[\text{BiW}_9\text{O}_{33}]^{9-}$ units with Cu–O bond lengths of 1.926(14)–2.022(15) Å and a nitrogen atom from the imidazole molecule with Cu–N bond lengths of 2.143(18)–2.160(2) Å. While for Cu6, the apical position of its square-pyramidal coordination sphere is occupied by a terminal water molecule rather than the im group. This result indicates that the coordinating water molecules can only be partially substituted by im ligands, though the im was excessively added in the reaction system. In addition to the three Cu(II) ions, polyanion **1** also incorporates three Na^+ ions within the central belt (Figure 1 left). Each sodium ion is coordinated by four oxygen atoms from two $[\text{BiW}_9\text{O}_{33}]^{9-}$ units and two terminal water molecules to furnish a $\{\text{NaO}_6\}$ octahedral geometry. Three such Na^+ ions together with three Cu^{2+} ions alternately lie in the center belt between two $[\text{BiW}_9\text{O}_{33}]^{9-}$ anions forming a six-membered ring with an interior angle sum of

720° as a plane hexagon, suggesting that the six atoms lie in the same plane. The related sandwich-type complexes with transition-metal ions in the central belt and the vacancies between them occupied by alkali metal ions have been observed in previous literature,^{13a,c,14a,18} of which two cases with the trinuclear copper moiety are worthy to be mentioned here. One is the isolated tricopper-substituted species $[\text{Cu}_3\text{Na}_3(\text{H}_2\text{O})_9(\alpha\text{-AsW}_9\text{O}_{33})_2]^{9-}$ reported by Kortz et al., in which the cyclic arrangement is formed by three equivalent Cu^{2+} ions and three Na^+ ions.^{18c} The other is the dimeric sandwich-type polyanion $[\text{Cu}_3\text{K}_3(\text{H}_2\text{O})_4(\alpha\text{-AsW}_9\text{O}_{33})_2]^{9-}$ reported by Hervé et al., which however incorporates three inequivalent copper and three inequivalent potassium ions in the central belt.^{18a} Interestingly, these sandwich-type polyanions are not discrete as is their usual fashion but are alternately linked by $[\text{Cu}(\text{im})_4]^{2+}$ cations into an anionic chain running along the $[1\ 0\ -1]$ direction, in which the linking Cu(II) ions display a $[\text{CuN}_4\text{O}_2]$ octahedral geometry as shown in Figure 2. The Cu–O distances are in the range 2.404(14)–2.593(15) Å, and the Cu–N distances are from 1.970(2) Å to 2.030(3) Å, indicating a distorted octahedron (Jahn–Teller effect).

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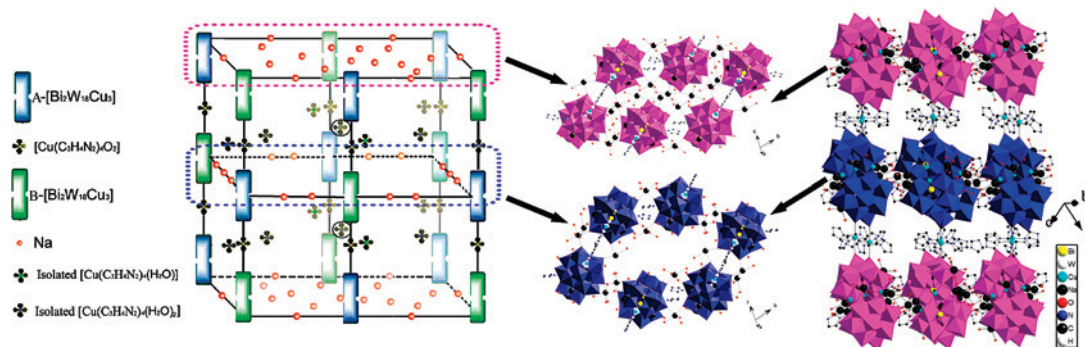


Figure 3. Schematic and perspective views of the three-dimensional framework of **1**. All the H atoms and isolated copper complex cations are omitted. The color code is the same as in Figure 1.

Further investigation reveals that the two bridging oxygen atoms of each $[\text{CuN}_4\text{O}_2]$ group do not come from the same position of the two adjacent $[\text{BiW}_9\text{O}_{33}]^{9-}$ units but change positions with each other (Figure 2), that is to say, the $\{\text{Bi}_2\text{W}_{18}\text{Cu}_3\text{Na}_3\}$ units in the same chain are arranged in an ABAB sequence. Besides the polymeric chains, there are also two kinds of discrete copper complex fragments in the crystal, namely $[\text{Cu}(\text{im})_4(\text{H}_2\text{O})_2]^{2+}$ (**b**) and $[\text{Cu}(\text{im})_4(\text{H}_2\text{O})]^{2+}$ (**c**). The former is composed of an octahedral Cu atom defined by four imidazole ligands and two water molecules (the average Cu–O and Cu–N distances are 2.627 Å and 1.988 Å) while the latter is composed of a square pyramidal Cu(II) ion ligated by four imidazole ligands and a water molecule (the average Cu–O and Cu–N distances are 2.360 Å and 1.980 Å). Hence, compound **1** includes five kinds of copper ions with different coordination environments, which to our knowledge is quite rare either in polyoxometalate chemistry or in coordination polymer chemistry. The striking structural feature of **1** is the presence of cage structures arising from the involvement of the sodium counteractions. As shown in Figure 3, adjacent chains are linked by sodium ions into a three-dimensional network along the $[1\ 0\ 1]$ direction. A more careful examination reveals that the 3D framework exhibits two types of layers which are labeled by 1 and 1', respectively. The common feature of both layers is that adjacent six $\{\text{Bi}_2\text{W}_{18}\text{Cu}_3\text{Na}_3\}$ units belonging to the different chains are connected by sodium ions in the bc plane into a closed six-unit circle. Nevertheless, the difference between them consists in that the six-unit circles in layer 1 are entirely filled with sodium clusters while in layer 1' the six-unit circles form a cavity. This unique filling fashion results in the formation of the unprecedented 18-unit cages among every three layers, 1, 1', and 1, with **c** fragments scattered in the periphery. The approximate dimensions of the enclosure are $6.6 \times 10.9 \times 34.8 \text{ \AA}^3$. Each cage encapsulates free water molecules and isolated **b** fragments and is associated with neighboring cages (Figure 3). The formation of the particular cage structure is undoubtedly attributed to the strong involvement of the sodium counteractions. The profound influences of counteractions on the ultimate structures have also been observed in other remarkable POM complexes.¹⁹

The anionic chain of **2** is very similar to that of **1** except for Sb(III) as the heteroatom. However, because of the smaller atomic radius for Sb(III), **2** still represents some

different structural features. First, the arrangement of WO_6 triads in $[\text{SbW}_9\text{O}_{33}]^{9-}$ anion is more compact. This can be reflected in the averaged Sb–O (1.955 Å) and $\text{W}\cdots\text{W}$ (3.468 Å) distances that are a little shorter than those in the $[\text{BiW}_9\text{O}_{33}]^{9-}$ unit (Bi–O 2.114 Å; $\text{W}\cdots\text{W}$ 3.586 Å). Second, affected by the compactness of anionic structure, the averaged Cu– O_t (O_t , terminal O atom) distance (1.968 Å) is evidently shorter than that of **1** (1.984 Å), suggesting that the Cu^{2+} ions are entrapped more tightly between two $[\text{SbW}_9\text{O}_{33}]^{9-}$ units. This result is also reflected by the Cu–N(im), and Cu– O_w (O_w , water O atom) distances (2.178 Å, and 2.40 Å) that are a little longer than those of **1** (2.152 Å, and 2.28 Å). Third, considering the charge balance for **2**, it should be that fifteen sodium ions are located in the asymmetry unit during the structure determination. Unfortunately, only thirteen sodium ions can be resolved in the structural refinement, which leads to an uncertainty of the packing style containing all the involved sodium ions. However, an examination of the determined sodium ions reveals that they are also located surrounding the polyoxoanions, which still helps to form the 18-unit cages similar to those of **1** (Figure 4). Interestingly, along with the compactness of the poly-anions, the distances between the neighboring chains decrease. This can be inferred from the Sb \cdots Sb distances (13.421 Å and 13.005 Å) between two nearest Sb atoms belonging to adjacent chains that are shorter than those of **1** (Bi \cdots Bi, 13.440 Å and 13.912 Å). As a result, the approximate cage dimensions also decrease to $6.2 \times 10.3 \times 32.5 \text{ \AA}^3$ as compared to **1**. Therefore, compounds **1** and **2** not only present interesting cage-like structures based on nonaqueous-ligand modified sandwich-type heteropolyanions but also show us an effective way to control the cage dimensions by adopting different heteroatoms as the polyanionic center.

Electronic Spectroscopy. Figure 5 shows the UV–vis electronic spectra of **1** and **2**. The plot contains two characteristic bands for the ligand to metal charge transfer in the polyanions. The more intense bands corresponding to

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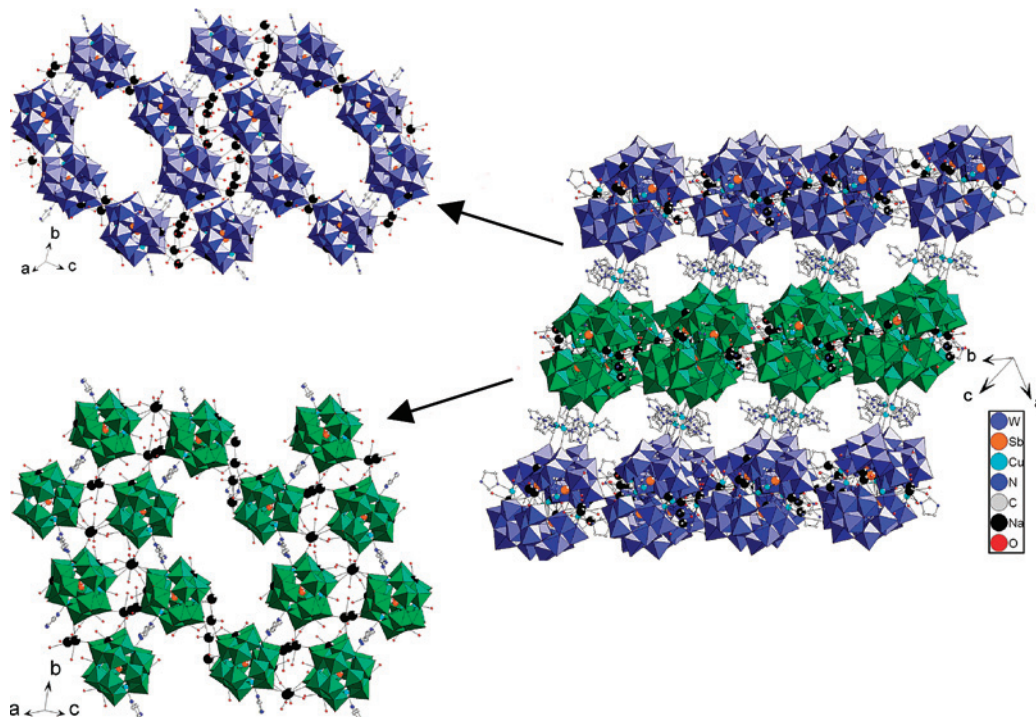


Figure 4. View of three-dimensional network of **2**. All the H atoms, isolated water molecules, and copper complexes cations are omitted. The color code is the same as in Figure 1.

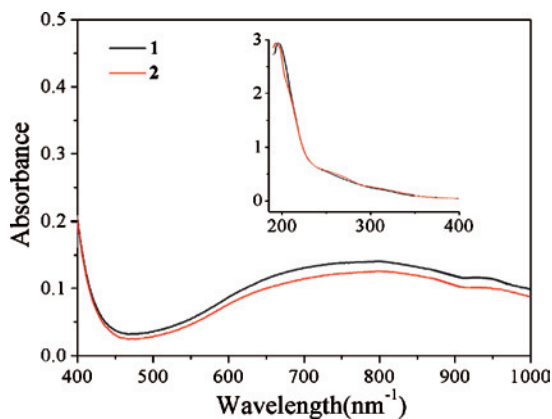


Figure 5. UV-vis spectra of **1** and **2** in pH 7.11 (0.025 M NaHPO₄ + NaH₂PO₄) buffer solutions within the range of 190–1000 nm.

the $p_{\pi}(O_d) \rightarrow d_{\pi^*}(W)$ transitions²⁰ appeared at 195.4 and 194.3 nm for **1** and **2**, respectively. The shoulder band around 250.0 nm is assigned to a $p_{\pi}(O_{b,c}) \rightarrow d_{\pi^*}(W)$ charge transfer transition in the tricentric bonds of POMs, which is consistent with the literature values (193.6 and 250.7 nm).²¹ The visible region of the electronic spectra of both **1** and **2** show the broad $B_{1g}(d_{x^2-y^2}) \rightarrow E_g(d_{xz,yz})$ transition at 799.0 nm, while the shoulders at 965.3 nm (**1**) and 966.7 nm (**2**) correspond to the $B_{1g}(d_{x^2-y^2}) \rightarrow B_{2g}(d_{xy})$ transition, which is also in agreement with the literature (965.7 nm).²²

Magnetic Properties. The plots of $\chi_m T$ versus T and χ_m^{-1} versus T of compounds **1** and **2** measured from 2 to 300 K in an applied magnetic field of 10 kOe are shown in Figure

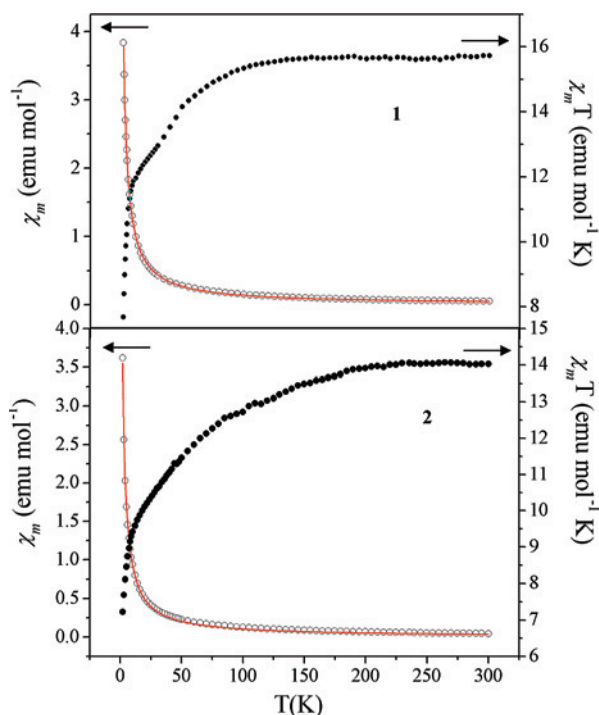


Figure 6. Plots of $\chi_m T$ versus T and χ_m^{-1} versus T from 2 to 300 K for **1** and **2** at $H = 10$ kOe.

6. The $\chi_m T$ value of **1** at room temperature is 15.74 emu K mol⁻¹ ($\mu_{\text{eff}} = 11.23 \mu_B$), substantially lower than the expected value ($\mu_{\text{eff}} = 21.98 \mu_B$) for 21 uncoupled Cu^{II} ions ($S = 1/2$, $g = 2.00$). On cooling, the $\chi_m T$ value decreases continuously to a minimum of 7.69 emu K mol⁻¹ at 2 K, suggesting a dominant antiferromagnetic exchange interaction.

As mentioned in the structural description, compound **1** contains the trinuclear Cu(II) cluster located between two

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[BiW₉O₃₃]⁹⁻ units with smaller Cu···Cu distances in the range 4.957–5.136 Å. By contrast, the other copper complexes are at a much longer distance away from the neighboring Cu(II) centers, of which the magnetic interactions can be ignored. The experimental data can approximately be fitted to a modified Heisenberg spin Hamiltonian ($S_1 = S_2 = S_3 = 1/2$) spin-coupled model assuming $H = -J [S_1S_2 + S_2S_3 + S_3S_1]$ following the equation

$$\chi_m = (Ng^2\beta^2/4kT)[(1 + 5x^{3/2})/(1 + x^{3/2})] + C/(T - \theta) \quad (1)$$

where

$$x = \exp(J/kT)$$

Here N is the Avogadro number, g the Landé g factor, β the electronic Bohr magneton, k the Boltzmann constant, and T the temperature in Kelvin. C and θ are the Curie and Weiss modifiable constants, respectively.

The best fit gives a magnetic coupling constant $J = -31.84 \text{ cm}^{-1}$ assuming $g = 2.00$, $C = 13.27 \text{ emu mol}^{-1}$, and $\theta = -1.70 \text{ K}$, with the agreement factor R {defined as $\sum_i [(\chi_m T)_{\text{obs}}(i) - (\chi_m T)_{\text{calc}}(i)]^2 / \sum_i [(\chi_m T)_{\text{obs}}(i)]^2$ } being 4.2×10^{-4} . The negative J and θ values suggests the occurrence of an antiferromagnetic Cu(II)···Cu(II) interaction in the trinuclear Cu(II) cluster of **1**, which is also in agreement with the literature result.²³ In addition, the $\chi_m T$ value of $7.69 \text{ emu K mol}^{-1}$ at 2 K is smaller than calculated for nine noninteracting Cu²⁺ ions, suggesting that the antiferromagnetic interaction among them cannot be neglected at low temperature.

As for **2**, a similar magnetic property is observed. The $\chi_m T$ value at 300 K is $14.04 \text{ emu K mol}^{-1}$ ($\mu_{\text{eff}} = 10.63 \mu_B$), which is also lower than the expected value ($\mu_{\text{eff}} = 21.98 \mu_B$) for 21 uncoupled Cu^{II} ions ($S = 1/2$, $g = 2.00$). On cooling, the $\chi_m T$ value decreases continuously to a minimum of $7.20 \text{ emu K mol}^{-1}$ at 2 K . The experimental data for **2** can also be fitted by eq 1. The best fit gives a magnetic coupling constant $J = -38.45 \text{ cm}^{-1}$ assuming $g = 2.00$, $C = 15.27 \text{ emu mol}^{-1}$, and $\theta = -1.73 \text{ K}$, with agreement factor R being 5.0×10^{-4} . Thus, the occurrence of an antiferromagnetic Cu(II)···Cu(II) interaction in trinuclear Cu(II) cluster was also confirmed. Notably, the more negative J and θ value indicate that the antiferromagnetic interaction is a little stronger than that of **1**, in agreement with sandwich Cu(II) ions of **2** embedded into the diamagnetic anions more

tightly with smaller Cu···Cu distance in the range 4.884 to 5.090 Å.

The magnetic results of the trinuclear Cu(II) cluster in **1** and **2** are similar to that of a trinuclear Cu(II) cluster reported by Kortz and co-workers, in which the weak antiferromagnetic interaction occurred between Cu(II)–Cu(II) in Na₉[Cu₃Na₃(H₂O)₉(α -AsW₉O₃₃)₂].^{18c} Because of the introduction of the imidazole ligand, however, the antiferromagnetic interaction in **1** and **2** are stronger than that reported by Kortz and co-workers. In addition, the bond angle between the neighboring magnetic metals could clearly affect the magnetic interaction in view of the dependence of the magnetic interaction on the orbital overlap. In the case of the Cu–O–Cu linkage, the angle of Cu–O–Cu directly affects their magnetic interaction. The angle at close to a right angle or smaller than a right angle could facilitate the ferromagnetic exchange interaction, and the angle over 100° often caused the antiferromagnetic exchange interaction.^{1d}

Conclusion

In this work, we represent two inorganic–organic hybrids based on sandwich-type tungsto-bismuthate (-antimonite) anions and copper(II) complex moieties. Their novel chain-like structures are built from the alternating links of sandwich-type polyoxoanions containing partially substituted imidazole groups and copper complex segments. They represent the first 1D examples in a sandwich-type tungsto-bismuthate (-antimonite) system. The results of a magnetic investigation for **1** and **2** suggest the existence of dominant antiferromagnetic coupling in trinuclear Cu(II) clusters. By the rational choice of reaction conditions, nonaqueous-ligand modified sandwich-type heteropolyanions can be successfully prepared, which affords a promising route for the development of polyoxometalate-based solid materials.

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Supporting Information Available: X-ray crystallographic files of compounds **1** and **2** in CIF format, IR spectra, the structural of the trivalent α -B-[XW₉O₃₃]⁹⁻ unit, selected bond lengths (Å) and angles (°) for complexes **1** and **2**(PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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