A Novel Organic–Inorganic Hybrid Based on Tungstoantimonate: Synthesis, Crystal Structure, and Properties of $Na[\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{Cu(2,2'\text{-bpy})\}_2(\textit{B}\text{-}\alpha\text{-}SbW_9O_{33})]\cdot 2H_2O$

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A novel organic–inorganic hybrid tungstoantimonate $Na[\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{Cu(2,2'\text{-bpy})\}_2(B\text{-}\alpha\text{-}SbW_9O_{33})]\cdot 2H_2O$ (2,2′-bpy = 2,2′-bipyridine) was synthesized hydrothermally and characterized by elemental analyses, IR, EPR, TG, and X-ray single-crystal diffraction, whose polyoxoanion consists of two $[Cu(2,2'\text{-bpy})]^{2+}$ and two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ complex groups grafted on a trivacant polyoxoanion $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton.

Polyoxometalates (POMs) as anionic early transition-metal oxide clusters, constitute a large family with intriguing variety of architectures, the diversity of electronic structures and topologies,[1] which endow them with fascinating properties in material science,[2] medicine,[3] catalysis,[4] etc. A new area of interest is the decoration of polyoxoanions with various organic and/or transition-metal complex moieties, which is also driven by the manifold applications in areas as diverse as catalysis and magnetism.[5] Recently, organic–inorganic hybrids based on complicated POM–organic system constitute an important subclass in the fields of materials chemistry and attract increasing attention.[6] At the same time it must be pointed out, numerous transition-metal-substituted POMs with topological beauty and the associated multitude of properties are constructed mostly from trivacant POMs building blocks.[7] To date, among the POMs supported by trivacant $[XM_9O_{34\text{or}33}]^{q-}$ subunits, the most often used are polyoxotungstates as precursors with X = Si, P, and As. However, the investigation on tungstoantimonates with $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ fragments is rather scarce, maybe because of the steric interactions between the $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ fragment and transition-metal complex moieties, which is prone to isomerize $B\text{-}\beta\text{-}[SbW_9O_{33}]^{9-}$ skeleton.[8] Moreover, the hybrids composed of tungstoantimonate fragment are still in the infancy.[9] The organic–inorganic hybrids based on trivacant tungstoantimonate $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ with transition-metal complex groups grafted on it are not found hitherto.

Herein, we report on a novel hybrid $Na[\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{Cu(2,2'\text{-bpy})\}_2(B\text{-}\alpha\text{-}SbW_9O_{33})]\cdot 2H_2O$ (**1**) (2,2′-bpy = 2,2′-bipyridine),[10] whose polyoxoanion consists of a trivacant $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ moiety supporting two $[Cu(2,2'\text{-bpy})]^{2+}$ and two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ complex cations.

The single-crystal X-ray diffraction analysis[11] of compound **1** revealed that the polyoxoanion consists of a trivacant polyoxoanion $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ fragment to which two $[Cu(2,2'\text{-bpy})]^{2+}$ and two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ groups are coordinated resulting in an unprecedented polyoxoanion structure with C_s symmetry (see Figure 1). Interestingly, the two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ units are coordinated at the lacuna of the polyoxoanion via two Cu–O(W) bonds, whereas the other two $[Cu(2,2'\text{-bpy})]^{2+}$ units are capped on the opposite positions through the four bridging oxygen atoms from the $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton. This indicates that the lacunary sites of the polyoxoanion do not allow binding of more than two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ groups, most likely owing to steric effects. Therefore, the other two $[Cu(2,2'\text{-bpy})]^{2+}$ groups attach to the two square windows of polyoxoanion between the three W_3O_{13} triads.

The most remarkable feature of **1** is that the structural conformation of trivacant polyoxoanion $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ is obviously different from $B\text{-}\beta\text{-}[SbW_9O_{33}]^{9-}$ building block fused together by three corner-shared W_3O_{13} triads, which comprises three edge-shared W_3O_{13} fragments anchoring a Sb^{III} center linked by quadruply bridging oxygen atoms. The trivacant polyoxoanion $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ fragment of **1** is isomer of $B\text{-}\beta\text{-}[SbW_9O_{33}]^{9-}$ skeleton,[8b] which is obtained and observed for the first time under hydrothermal conditions missing any POM precursor.

Another feature of the polyoxoanion of **1** is that there are two kinds of Cu coordination centers: six-coordinate Cu(1) and five-coordinate Cu(2). Every octahedrally coordinated Cu(1) center is bonded with four oxygen donors from $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ fragment and two nitrogen atoms from one 2,2′-bipyridine molecule, corresponding bond distances of Cu(1)–O and Cu(1)–N are in the range of 2.019(7)–2.411(7) and 1.970(9)–2.006(9) Å, respectively. Whereas, each of two square pyramidal coordinated Cu(2) atom is defined by one water molecules located at two positions as a result of vibrational disorder, two oxygen atoms from the vacant oxygen atoms of $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton and two nitrogen dornors from one 2,2′-bipyridine ligand. The bond lengths of Cu(2)–N are 2.013 Å, and Cu(2)–O distances range from 1.922(8) to 2.31(2) Å.

By means of the polyoxoanion $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton

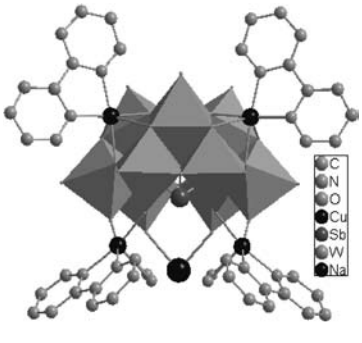

Figure 1. Polyhedral and ball-and-stick representation of polyoxoanion of **1**. The hydrogen atoms are omitted for clarity.

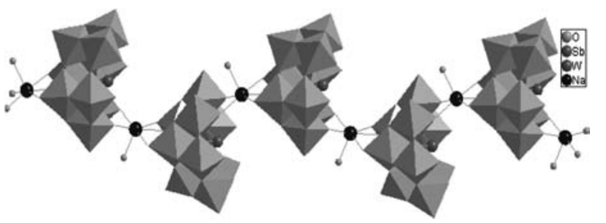

Figure 2. Polyhedral and ball-and-stick representation indicating the linkages of neighboring polyoxoanions via Na junctions in **1**. The Cu, C, N, and H atoms are omitted for clarity.

to which two $[Cu(2,2'\text{-bpy})]^{2+}$ and two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ groups grafted, the flower-shaped paramagnetic copper(II)-participating antimony-based polyoxoanion $[\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{Cu(2,2'\text{-bpy})\}_2(B\text{-}\alpha\text{-}SbW_9O_{33})]^-$ comes into being. In addition, besides two $[Cu(2,2'\text{-bpy})(H_2O)]^{2+}$ complex cations, there is a Na^+ ion incorporated into the third lacunary site of $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton via another two vacant oxygen atoms, and adjacent polyoxoanions $[\{Cu(2,2'\text{-bpy})(H_2O)\}_2\{Cu(2,2'\text{-bpy})\}_2(B\text{-}\alpha\text{-}SbW_9O_{33})]^-$ are interconnected together generating 1D infinitely chain-like construction fashion in the help of the Na^+ ion (Figure 2). The Na atom is defined by six oxygen atoms, one from disordered water molecule, two from vacant oxygen atoms of $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton and three from oxygen atoms at "cap" site of adjacent $B\text{-}\alpha\text{-}[SbW_9O_{33}]^{9-}$ skeleton, respectively.

Preliminary mangnetic studies of complex **1** in the range of 2–300 K are shown as the χ_M, $\chi_M T$, and $1/\chi_M$ versus T plots in Figure 3. The room temperature $\chi_M T$ value 1.12 emu·K·mol^{-1} is slightly smaller than the spin-only value of 1.50 emu·K·mol^{-1} for four uncoupled Cu^{II} ions ($S = 1/2$), indicative of antiferromagnetic coupling. When the temperature is decreased, $\chi_M T$ gradually increases and reaches a maximum of 1.39 emu·K·mol^{-1} at 80 K, indicating the presence of ferromagnetic coupling. Subsequently, the $\chi_M T$ value decreases rapidly and reaches the first minimum value of 0.96 emu·K·mol^{-1} at 12 K, and then increases rapidly to 0.97 emu·K·mol^{-1} at 6 K, finally decreases continuingly and reaches the last minimum value of 0.82 emu·K·mol^{-1} at 2 K. The magnetic susceptibility obeys the Curie–Weiss law in the range of 110–300 K with Curie constant $C = 3.00$ emu·K·mol^{-1} and Weiss constant $\theta = 40.5$ K, characteristic of an overall ferromagnetic interaction.

The X-band EPR spectra of **1** at 300 and 110 K give only one signal with $g = 2.147$ and $g = 2.145$, respectively, indicating the characteristic of an isolated Cu^{II} chromophore with an axial g tensor which is originated by Cu^{II}-supported POMs.[12]

TGA study shows that the complex has two step weight loss. The first weight loss 2.13% ranges from 78 to 195 °C, corresponding to the removal of four water molecules (calcd 2.20%). The second weight loss of 18.82% between 263 and 552 °C is attributed to the oxidation combustion of the four 2,2-bipyridine organic groups.

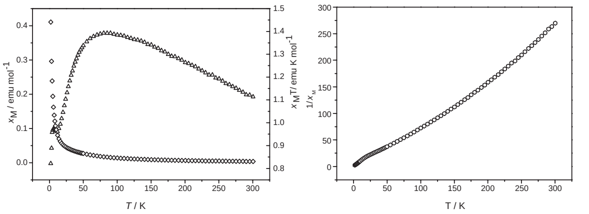

Figure 3. Plots of the temperature dependence of χ_M, $\chi_M T$, and $1/\chi_M$.

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10 Preparation of **1**: The mixture of Sb_2O_3, $Na_2WO_4\cdot 2H_2O$, $CuCl_2\cdot 2H_2O$, 2,2′-bipyridine, and H_2O in the molar ratio of 1:24:8:8:2222 was heated in a Teflon-lined bomb inside a programmable electric furnace at 180 °C for six days with starting pH = 6.94 adjusted by hydrochloric acid (1 mol/L). After cooling the autoclave to room temperature over two days, blue single crystals suitable for X-ray crystallography were obtained. The crystals were filtered off, washed with distilled water and dried in air to give **1** in 57% yield based on W. Anal. Calcd for $C_{40}H_{40}Cu_4N_8NaO_{37}SbW_9$ **1**: C, 14.65; H, 1.22; N, 3.42%. Found: C, 14.43; H, 1.20; N, 3.45%. IR (KBr pellets, ν/cm^{-1}): 1603(s), 1475(m), 1445(s), 1399(w), 942(s), 884(vs), 789(s), 730(s), 710(s), 538(w), 492(m), and 452(w).

11 Crystal data for **1**: $C_{40}H_{40}Cu_4N_8NaO_{37}SbW_9$, $M_r = 3278.27$, orthorhombic, $a = 17.174(2)$, $b = 24.572(4)$, $c = 15.267(2)$ Å, $V = 6442.3(16)$ Å^3, $T = 293(2)$ K, space group *Pnma*, $Z = 4$, $\mu = 17.801$ mm^{-1}, 36676 reflections measured, 5766 independent ($R_{int} = 0.0983$). $R_1 = 0.0401$ ($I > 2\sigma(I)$), $wR_2 = 0.1079$ (all data). CCDC: 297738.

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