One-dimensional Chainlike Organic–Inorganic Polymer Constructed from Sandwich-type Germanotungstates Linked by $[Cu(en)_2]^{2+}$ Cations

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A novel one-dimensional chainlike organic–inorganic polymer $[Cu(en)_2]_3[Cu(en)_2(H_2O)]_2\{[Cu_4(GeW_9O_{34})_2][Cu(en)_2]\}\cdot 9.5H_2O$ (en = ethylenediamine) has been synthesized by hydrothermal reaction in good yield, and characterized by elemental analysis, IR, TG-DTA, EPR, magnetic properties, and single-crystal X-ray diffraction. The diffraction analysis reveals that the polymer represents the first high-dimensional organic–inorganic hybrid based on the sandwich-type polyoxometalates linked by transition-metal coordination cations.

Polyoxometalates (POMs) are metal–oxygen cluster species with a diverse compositional range and an enormous structural variety and the Keggin series has been the most studied,[1] therefore structural design of novel POMs and derivation of known POMs has provoked great interest for synthetic chemists.[2] Recent years, transition-metal- or rare earth metal-substituted polyoxometalates have been widely explored because of their highly tunable nature, as well as their fascinating properties resulting in potential applications in catalysis, material science, and medicine.[3,4] Within the class of transition-metal-substituted polyoxometalates, the sandwich-type compounds represents the largest subclass.[1b] And such species are of particular interest in catalysis and magnetism. For another, hybrid organic–inorganic compounds have attracted an increasing interest during the possibility of combing the different characteristics of the components to get unusual structures, properties, or applications. Numerous hybrid compounds based on the typical heteropolyanions or the vanadium/molybdenum isopolyanions have been explored,[5–7] but examples of high-dimensional POMs based on the sandwich-type polyoxometalates are rarely observed. Here, we report on the synthesis, crystal structure,[8] and properties of the compound $[Cu(en)_2]_3[Cu(en)_2(H_2O)]_2\{[Cu_4(GeW_9O_{34})_2][Cu(en)_2]\}\cdot 9.5H_2O$ (**1**), which represents the first example of the 1D chain-like organic–inorganic hybrid based on the sandwich-type polyoxometalates linked by transition-metal coordination cations.

X-ray analysis revealed that the crystal structure of **1** consists of 1 heterometallic cluster $\{[Cu_4(GeW_9O_{34})_2][Cu(en)_2]\}^{10-}$, $3[Cu(en)_2]^{2+}$, $2[Cu(en)(H_2O)]^{2+}$ coordination cations, and 9.5 hydration water (Figure 1). In the polymer, two neighboring building blocks $[Cu_4(GeW_9O_{34})_2]^{12-}$ are linked by $[Cu(en)_2]^{2+}$ coordination cations into one-dimensional zigzag-shaped chains (Figure 2).

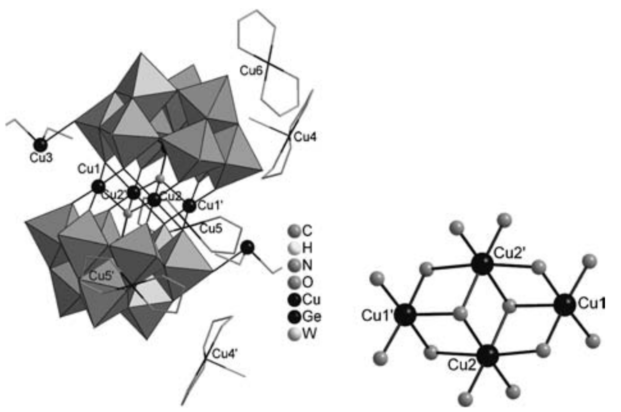

Figure 1. (left) Molecular structure of compound **1**, the H atoms and hydration water are omitted for clarity; (right) ball and stick representation of the central Cu_4O_{14} fragment in the subunit $[Cu_4(GeW_9O_{34})_2]^{12-}$. Key: WO_6 (gray), Cu (black), C and N (gray).

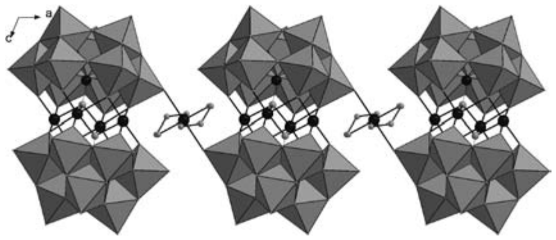

Figure 2. The 1D chain-like framework of compound **1**; Key: WO_6 (gray), Cu (black), C and N (gray). The isolated coordination cations are omitted for clarity.

The most remarkable feature of compound **1** is that in the heterometallic cluster $\{[Cu_4(GeW_9O_{34})_2][Cu(en)_2]\}^{10-}$, one coordination cation $[Cu(en)_2]^{2+}$ is supported by one $[Cu_4(GeW_9O_{34})_2]^{12-}$ which is rarely observed in the sandwich-type transition-metal-substituted polyoxoanion families. The $[Cu_4(GeW_9O_{34})_2]^{12-}$ subunit contains two lacunary $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ Keggin moieties linked via a rhomblike Cu_4O_{14} group (Figure 1) leading to a sandwich-type structure, which bears some similarity to that of the well-known Weakly-type sandwich polyanion $[M_4(H_2O)_2(XW_9O_{34})_2]^{12-/10-}$ (X = P, Si, As, and Ge).[6] The tungsten-oxo bond distances and angles within the two fragments $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ in **1** are within the usual ranges.[9] In the Cu_4O_{14} group, the Cu–O bond lengths are in the range of 1.908(11)–2.438(12) Å, and the Cu–O–Cu bond angles vary from 78.8(5) to 176.3(4)°.

There are five crystallographically unique Cu atoms in the asymmetric unit (Figure 1): (1) the square pyramidal coordination Cu(1) and octahedral coordinated Cu(2), which are coordinated by five and six oxygen atoms, respectively. Both of them are located at the sandwich site of the building block $[Cu_4(GeW_9O_{34})_2]^{12-}$. The coordination mode are similar to one of the largest transition-metal-substituted polyoxoanion $[M_4(H_2O)_2(XW_9O_{34})_2]^{12-/10-}$ (X = P, As, Si, and Ge). The only difference is that the Cu(2) is five coordinated and is not

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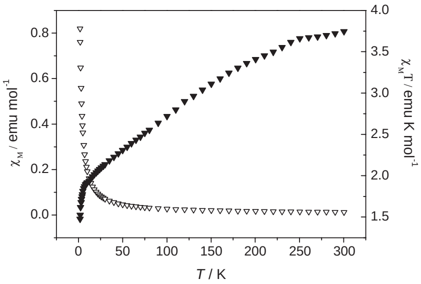

Figure 3. The thermal evolution of the magnetic molar susceptibility and the $\chi_M T$ product for compound **1**.

bound to another water oxygen partially due to the steric hindrance of the coordination cation bridge $[Cu(3)(en)_2]^{2+}$; (2) the octahedral coordinated Cu(3) which links to four nitrogen donors from two en ligands and two terminal oxygen atoms from two centrosymmetric fragments [B-α-$GeW_9O_{34}]^{10-}$ of two neighboring subunits $[Cu_4(GeW_9O_{34})_2]^{12-}$ with the Cu–N average distance of 2.025 Å and the Cu–O average distance of 2.433(8) Å; (3) the Cu(4) center is coordinated by four nitrogen atoms from two en ligands and one water oxygen with the Cu–N average distance of 2.011 Å and the Cu–O distance of 2.350(15) Å; (4) the last two are four-coordinated Cu centers (Cu(5) and Cu(6)) adopting the square-planar geometry, and both of them are defined by four nitrogen donors from two en molecules with the Cu–N average distance of 2.028 Å. The other copper centers Cu(1′), Cu(2′), Cu(4′), and Cu(5′) are centrosymmetric to Cu(1), Cu(2), Cu(4), and Cu(5), respectively.

Compound **1** was obtained by hydrothermal synthesis[10] based on the starting material of α-$K_8GeW_{11}O_{39}$. But the product is constructed of the subunit $[Cu_4(GeW_9O_{34})_2]^{12-}$, thus we may infer that the pH of the reaction system is very important to the product.

The thermal evolution of the magnetic molar susceptibility and the $\chi_M T$ product for compound **1** is displayed in Figure 3. The χ_M increases continuously with decreasing temperature and no maximum is observed. At high temperature ($T >$ 120 K), the susceptibility data are well described by Curie–Weiss expressions, being $Cm = 4.75$ emu K mol^{-1}, $\theta = -78.1$ K. The values of $\chi_M T$ at 300 K is 3.746 emu K mol^{-1}, which is in good agreement with the presence of ten uncoupled Cu^{II} ions (3.75 emu K mol^{-1}, considering $g = 2$). Additionally, when the system is cooled down from 300 to 2 K, the $\chi_M T$ product decreases reaching values close to 1.48 emu K mol^{-1}. This behavior indicates the presence of relatively strong antiferromagnetic interactions between the Cu^{II} ions.

The X-band EPR spectra of compound **1** recorded at 300 and 110 K both display one broad resonance centered at approximately 3200 G (with $g = 2.12$ and 2.13, respectively), as expected for copper(II) systems.

The TG curve of the compound **1** showed two weight loss stages, giving a total loss of 15.05% in the range of 30–900 °C, which approximately agrees with the calculated value of 15.19%. The weight loss (3.14%) of the first step (30–277 °C) corresponds to the release of the 9.5 crystal water and 2 coordination water molecules. In the corresponding DTA curve, there is a strong endothermal peak at 298 °C, resulting from the removal of coordination organic groups ethylenediamine in compound **1**. The exothermal peak observed at 795 °C in the DTA curve indicates the collapse of the polyanion framework. All the data above illustrate that compound **1** retains a comparatively good thermal stability.

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8 Crystal Data for **1**: $C_{24}H_{119}N_{24}O_{79.5}Cu_{10}Ge_2W_{18}$, triclinic, space group $P\bar{1}$, $M_r = 6106.12$, $a = 13.0014(10)$, $b = 13.8546(11)$, $c = 17.1074(14)$ Å; $\alpha = 94.6500(10)°$, $\beta = 110.1820(10)°$, $\gamma = 101.0990(10)°$, $V = 2801.6(4)$ Å^3, $T = 292(2)$ K; $Z = 1$, $\mu =$ 20.871 mm^{-1}, $R_1 = 0.0581$, $wR_2 = 0.1455$ [$I > 2\sigma(I)$]. 14319 reflections measured, 9435 independent ($R_{int} = 0.1187$). CCDC: 618905.

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10 Synthesis of **1**: The precursor α-$K_8GeW_{11}O_{39}$ was synthesized as described in reference[11] and confirmed by IR spectrum. Other reagents were purchased commercially and used without further purification. Compound **1** was prepared from a mixture of α-$K_8GeW_{11}O_{39}$, $Cu(NO_3)_2 \cdot 3H_2O$, $KF \cdot 2H_2O$, en and distilled water in the mole ratio 0.6:2:7:1.3:1100, heated in a Teflon-lined steel autoclave inside a programmable electric furnace at 160 °C, for 120 h with a starting pH of 4.9, adjusted with hydrochloric acid (2 mol/L). After cooling the autoclave to room temperature for 48 h, brown crystals were obtained, filtered, washed with distilled water and dried in air. Yield: 75%. $C_{24}H_{119}N_{24}O_{79.5}Cu_{10}Ge_2W_{18}$ (6106.12): calcd. C, 4.72; H, 1.90; N, 5.51%. Found: C, 4.38; H, 1.44; N, 4.85%. IR (KBr pellets, υ/cm^{-1}): 3446(s), 3259(s), 1590(m), 1458(w), 1399(m), 1110(w), 1048(m), 928(m), 908(w), 885(m), 833(w), 775(s), 715(s), 508(w), 454(w), 412(w).

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