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Novel Copper-Complex-Substituted Tungstogermanates

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Two copper-complex-substituted tungstogermanates $[Cu_5(2,2'\text{-bpy})_6(H_2O)][GeW_8O_{31}]\cdot 9H_2O$, **1**, and $\{[Cu_5(2,2'\text{-bpy})_5(H_2O)][GeW_9O_{34}]\}_2\cdot 7H_2O$, **2** (2,2′-bpy = 2,2′-bipyridyl), have been hydrothermally synthesized and structurally characterized. X-ray structural analyses show that **1** is a rare tetralacunary Keggin anion of $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ substituted by copper complexes, while dimer **2** consists of two trilacunary $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ Keggin units bridged by copper complexes. Magnetic measurement for **2** shows the presence of antiferromagnetic interactions within the dinuclear Cu^{2+} cations.

Polyoxometalates (POMs) are a unique class of metal−oxygen clusters with diverse structures and properties, applications of which include catalysis, magnetism, and medicine.[1] The current interest of the POM chemistry focuses on exploiting novel species with unexpected structures and properties. So far, the combination between transition metal complexes (TMCs) and POMs is very successful in modifying the POM structures, resulting in a large number of novel hybrids including TMCs-supported POMs[2] and extended POMs bridged by TMCs.[3] In contrast, transition-metal-substituted polyoxometalates (TMSPs) incorporating TMCs remains largely unexplored. To date, most of reported TMSPs were obtained by the reactions of lacunary POM precursors and TM ions,[4] such as $[(SiW_9O_{34})(SiW_9O_{33}(OH))(Cu(OH))_6Cu]^{11-}$,[4j] $[Cu_4K_2(H_2O)_8(\alpha\text{-}AsW_9O_{33})_2]^{8-}$,[4k] and $[Cu_{20}Cl(OH)_{24}(H_2O)_{12}(P_8W_{48}O_{184})]^{25-}$.[4m] Thus, incorporation of TMCs into TMSPs is a great challenge and chance because organic ligands may influence the coordination environments or linkage modes of substituted TMs, resulting in novel TMSPs with attractive properties.[5] The aim of our work is to assemble such TMSPs directed by TMCs under hydrothermal conditions. By this means, we successfully prepared several novel TMSPs based on arsenic−vanadium polyoxoanions incorporating zinc and cadmium complexes.[6] As a part of continuing work, we reported here two novel polyoxotungsates incorporating copper complexes: $[Cu_5(2,2'\text{-bpy})_6(H_2O)][GeW_8O_{31}]\cdot 9H_2O$, **1**, and $\{[Cu_5(2,2'\text{-bpy})_5(H_2O)][GeW_9O_{34}]\}_2\cdot 7H_2O$, **2**. Compound **1** is the first copper-complex-substituted POM based on tetralacunary Keggin anion $[GeW_8O_{31}]^{10-}$, and **2** exhibits a rare dimeric tungstogermanate constructed from trilacunary Keggin anion $[GeW_9O_{34}]^{10-}$ and a Cu complex.

The hydrothermal reaction[7] of Na_2WO_4, GeO_2, $CuCl_2$, and 2,2′-bpy at pH 9 at 160 °C for 3 days produced green crystals of **1**, while the reaction with mixed ligands of 2,2′-bpy and 4,4′-bpy formed **2**.[8] Notably, the pH is very important for the formation of **1** and **2** because basic conditions favor the

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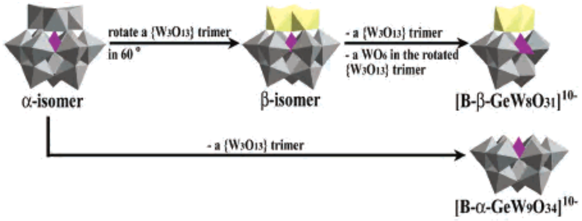
Scheme 1. Structural Relation of Lacunary Species and the Saturated Keggin Anion[a]



[a] Color code: purple, GeO_4; gray, WO_6; yellow, WO_6 in the rotated $\{W_3O_{13}\}$ trimer in the β-Keggin anion.

solution of GeO_2 and the formation of vacant species. In our cases, for a pH value of <9 or >11, no **1** and **2** were obtained (an unknown green powder was obtained). Additionally, 4,4′-bpy is crucial for making **2**.

Single-crystal X-ray diffraction analyses[9] show that the two lacunary anions, $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ in **1** and $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ in **2**, are derived from α-Keggin $[GeW_{12}O_{40}]^{4-}$. The α-Keggin isomer with T_d symmetry can bring out the β-isomer through rotating a $\{W_3O_{13}\}$ trimer 60° (Scheme 1). The $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ fragment in **1** is derived from saturated β-Keggin isomer through the removal of a $\{W_3O_{13}\}$ trimer and a adjacent WO_6 in the rotated $\{W_3O_{13}\}$ trimer. The tetralacunary species, $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$, is new blood for the POM family. The $[\beta\text{-}SiW_8O_{31}]^{10-}$ fragment was first made by Kortz et al. in a cobalt-substituted tungstosilicate in 2005.[10] Subsequently, the $[\gamma\text{-}SiW_8O_{31}]^{10-}$ fragment is observed in a Cu-azino POM.[11] So far, the tetralacunary tungstosilicates reported originate with the transformation of the lacunary $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ precursor. In addition, the $[\beta\text{-}PW_8O_{31}]^{9-}$ anion was also made recently.[12] The trilacunary $[GeW_9O_{34}]^{10-}$ anion in **2** is common and is derived from a saturated α-Keggin isomer by removal of a $\{W_3O_{13}\}$ trimer (Scheme 1). Compared with the saturated $[GeW_{12}O_{40}]^{4-}$, both tetralacunary $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ in **1** and trilacunary $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ in **2** provide an extra seven terminal O atoms, resulting in similar environments for substituted Cu complexes.

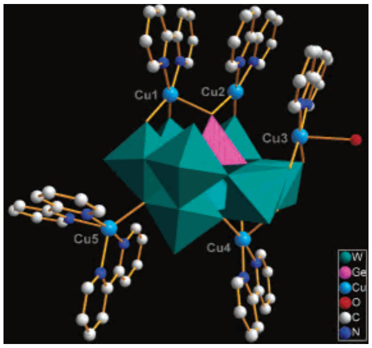


Figure 1. Molecular structure of **1**. Lattice water molecules are omitted for clarity. Color code: pink, GeO_4; green, WO_6.

Compound **1** is an isolated structure containing the tetralacunary $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion and copper complexes. The $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion acts as a multidentate ligand to link to Cu ions (Figure 1). In the $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion, the tetrahedral Ge center is defined by two μ_4-O atoms from two intact $\{W_3O_{13}\}$ trimers, a μ_3-O atom from two edge-sharing WO_6 octahedra (the remainder after removal of a WO_6 from the rotated $\{W_3O_{13}\}$ trimer of β-isomer), and an O atom bonded to Cu1/Cu2 atoms, respectively (Ge−O = 1.733(6)−1.761(6) Å). The W−O bond lengths in the WO_6 octahedra range from 1.708(6) to 2.386(5) Å. The lacunary sites of $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion are partially occupied by three [Cu(2,2′-bpy)] complexes to form a Cu-substituted POM: the Cu1 atom located in the $\{CuO_3N_2\}$ square pyramid corner-shares with two WO_6 octahedra and a GeO_4 group (Cu−O = 1.935(7)−2.265(6) Å, Cu−N = 1.994(8)−2.018(8) Å); the Cu2 atom located in the $\{CuO_2N_2\}$ planar square corner-shares with two groups of WO_6 and GeO_4 (Cu−O = 1.885(6)−1.925(7) Å, Cu−N = 2.008(9)−2.021(10) Å); and the Cu3 atom located in the $\{CuO_3N_2\}$ square pyramid bonds to a water molecule and two terminal O atoms of two remaining WO_6 octahedra in the incomplete $\{W_3O_{13}\}$ trimer (Cu−O = 1.923(7)−2.542(5) Å, Cu−N = 1.978(9)−1.985(9) Å). Each of the Cu1, Cu2, and Cu3 atoms bears a 2,2′-bpy ligand with distances of aryl planes of ∼3.5 Å. The Cu1 and Cu2 atoms are linked by an O bridge with a Cu1···Cu2 distance of 3.18 Å, while the Cu2···Cu3 distance is 4.2 Å. The Cu4 atom caps the $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion through three bridging O atoms (Figure 1, Cu−O = 1.97(6)−2.261(6) Å), while the Cu5 atom only bonds to a bridging O atom of the $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ anion (Cu−O = 2.002(6) Å). The Cu4 and Cu5 atoms located in the $\{CuO_3N_2\}$ and $\{CuON_4\}$ square pyramid link one and two 2,2′-bpy ligands, forming supporting groups of [Cu(2,2′-bpy)] and $[Cu(2,2'\text{-}bpy)_2]$, respectively (Cu−N = 1.966(7)−2.110(8) Å).

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(7) Preparation of $[Cu_5(2,2'\text{-}bpy)_6(H_2O)][GeW_8O_{31}]\cdot 9H_2O$ (**1**). A mixture of $Na_2WO_4\cdot 2H_2O$ (0.2 g, 0.6 mmol), GeO_2 (0.026 g, 0.15 mmol), $CuCl_2\cdot 2H_2O$ (0.026 g, 0.15 mmol), 2,2′-bpy (0.024 g, 0.15 mmol), and 5 mL of distilled water with a starting pH of 9.5 adjusted with 1 mol L^{-1} NaOH was sealed in a 23 mL Teflon-lined autoclave and heated for 72 h at 160 °C. After the mixture was slowly cooled to room temperature, blue green crystals of **1** were separated in a 30% yield (based on W). Anal. Calcd (Found) for **1**: C, 20.74 (20.70); H, 1.97 (1.95); N, 4.84 (4.80) %. IR (cm^{-1}) for **1**: 3440(s), 1640(m), 1495(w), 1474(w), 1450(w), 935 (m), 847(m), 730(m), 670(m), 537(m).

(8) Preparation of $\{[Cu_5(2,2'\text{-}bpy)_5(H_2O)][GeW_9O_{34}]\}_2\cdot 7H_2O$ (**2**). A mixture of $Na_2WO_4\cdot 2H_2O$ (0.2 g,0.6 mmol), GeO_2 (0.026 g, 0.15 mmol), $CuCl_2\cdot 2H_2O$ (0.026 g, 0.15 mmol), 2,2′-bpy (0.02 g, 0.13 mmol), 4,4′-bpy (0.01 g, 0.064 mmol), and 5 mL of distilled water with a starting pH of 9.5 adjusted with 1 mol L^{-1} NaOH was sealed in a 23 mL Teflon-lined autoclave and heated for 72 h at 170 °C. After the mixture was slowly cooled to room temperature, green crystals of **2** were separated in a 38% yield (based on W). Anal. Calcd (Found) for **2**: C, 17.40 (17.36); H, 1.43 (1.41); N, 4.06 (4.03) %. IR (cm^{-1}) for **2**: 3473(s), 3414(s), 1617(m), 1496(w), 1372(w), 1447(w), 1020(m), 950 (m), 810(m), 770(m), 733(m), 669(m), 629(m), 476(m).

(9) Crystal data for **1**: $C_{60}H_{68}Cu_5GeN_{12}O_{41}W_8$, $M_r = 3474.35$ g mol^{-1}, monoclinic, $P2_1/c$, $a = 19.541(3)$ Å, $b = 22.600(4)$ Å, $c = 18.760(3)$ Å, $\beta = 91.981(2)°$, $V = 8280(2)$ Å^3, $Z = 4$, $T = 293$ K, $D_c = 2.787$ g cm^{-3}, $\mu = 12.772$ mm^{-1}, R1 = 0.0382, wR2 = 0.0907, GOF = 1.056, CCDC-619149. Crystal data for **2**: $C_{100}H_{98}Cu_{10}Ge_2N_{20}O_{77}W_{18}$, $M_r = 6901.86$ g mol^{-1}, monoclinic, $C2/c$, $a = 41.336(2)$ Å, $b = 18.4930$ (7) Å, $c = 20.0884(10)$ Å, $\beta = 107.931$ (2)°, $V = 14610.3$ (12) Å^3, $Z = 4$, $T = 293$ K, $D_c = 3.138$ g cm^{-3}, $\mu = 16.029$ mm^{-1}, R1 = 0.0374, wR2 = 0.0763, GOF = 1.171, CCDC-619150.

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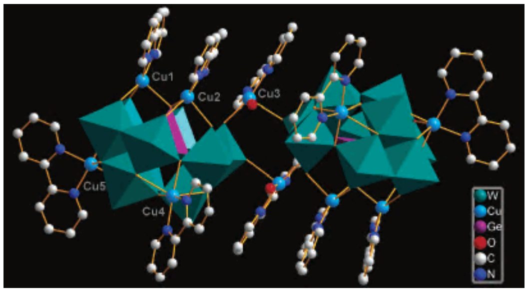

Figure 2. Molecular structure of **2**. Lattice water molecules were omitted for clarity. Color code: pink, GeO_4; green, WO_6. Ge−O = 1.721(6)−1.776(6) Å, W−O = 1.710 (6)−2.254(6) Å.

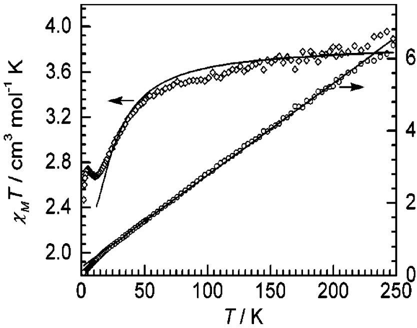

Figure 3. Temperature dependence of the reciprocal magnetic susceptibility χ_M^{-1} and the product $\chi_M T$ for compound **2**.

The centrosymmetric dimer **2** consists of trilacunary [B-α-GeW_9O_{34}]$^{10-}$ anions and [Cu(2,2′-bpy)] complexes (Figure 2). In **2**, the linkages of Cu complexes and the [B-β-GeW_9O_{34}]$^{10-}$ anion at the lacunary sites shows a subtle difference from that of **1**: (1) the Cu1- and Cu2-containing {CuO_3N_2} square pyramids corner-share with two WO_6 octahedra and a GeO_4 tetrahedron, and (2) the Cu3 as bridging atoms are bound to a water molecule and two terminal O atoms of two WO_6 groups from adjacent [B-α-GeW_9O_{34}]$^{10-}$ anions, thus forming a dimeric cluster (Cu−O = 1.903(6)−2.299(7) Å, Cu−N = 1.933(6)−2.019(8) Å). Each Cu atom bears a 2,2′-bpy ligand with distances of aryl planes of ∼3.5 Å (Cu1···Cu2 = 3.27 Å, Cu2···Cu3 = 5.75 Å). While [Cu_4-(2,2′-bpy)] and [Cu_5(2,2′-bpy)] complexes acting as capping units bond to [B-α-GeW_9O_{34}]$^{10-}$ anions by four and three μ_3-O atoms, respectively (Cu−O = 1.973(6)−2.463(6) Å, Cu−N = 1.955(9)−2.003(9) Å).

On the basis of valence sum ($\sum_s$) calculations,[13] the oxidation states of all W and Cu atoms in **1** and **2** are +6 and +2 (for W $\sum_s$ = 6.09−6.21, mean 6.15 in **1** and 5.98−6.22, mean 6.12 in **2**; for Cu $\sum_s$ = 1.69−1.89, mean 1.79 in **1** and 1.79−1.95, mean 1.86 in **2**), respectively.

The magnetic susceptibilities of **2** measured at a field of 10 kOe and in the temperature range of 2−250 K are shown in Figure 3 as the χ_M^{-1} and $\chi_M T$ versus T plots. When the sample is cooled, the $\chi_M T$ value decreases continuously to a minimum of 2.67 cm^3 mol^{-1} K at 11 K, suggesting a dominant antiferromagnetic exchange interaction. Below 11 K, a small maximum is observed at about 5.5 K, followed by a sharp drop to 2.47 cm^3 mol^{-1} K at 2 K. A Curie−Weiss fit to the data between 30 and 250 K yields a Curie constant C of 3.93 cm^3 K mol^{-1}, which is close to the theoretical value for 10 isolated Cu^{2+} ions per molecule with g = 2.05. The Weiss constant is −8.98 K.

As illustrated in the structural description, the centrosymmetrized compound **2** contains two μ_3-bridged Cu^{2+} dinuclear units (Cu1···Cu2), two chelating WO_6-group-bridged Cu^{2+} dinuclear units (Cu4···Cu5), and one nonchelating WO_6-group-bridged Cu^{2+} dinuclear unit (Cu3···Cu3A). Since the Cu1···Cu2 distance (3.27 Å) is much smaller than the other two (5.13 and 6.38 Å), the magnetic interactions between the latter can be ignored, and the experimental data approximately follow the relation

$$\chi_M T = 2[2N\beta^2 g^2/k]/(3 + \exp(-J/kT)) + 6(N\beta^2 g^2/4k)$$

which is the sum of the Bleaney−Bowers equation derived from the isotropic Hamiltonian $H = -JS_1S_2$ for two binuclear Cu^{2+} entities and the Curie law for six monomer Cu^{2+} complexes. The best-fit parameters obtained between 30 and 250 K are $J = -34.2$ cm^{-1}, $g = 2.03$, and $R = 7.9 \times 10^{-4}$ (R is the agreement factor defined as $\sum_i[(\chi_M T)\text{obsd(i)} - (\chi_M T)\text{calcd(i)}]^2/\sum_i[(\chi_M T)\text{obsd(i)}]^2$). The $\chi_M T$ value of 2.47 cm^3 mol^{-1} K at 2 K is close to that calculated for six noninteracting Cu^{2+} ions, suggesting that two pairs of Cu^{2+} centers are strongly antiferromagnetically coupled to the $S = 0$ state at low temperature, while the remaining six are largely uncorrelated. This observation is consistent with the above simplification. The magnetization versus applied field curve at 2 K approach to saturation at 70 kOe, reaching 5.97 $N\beta$ per molecule, close to the value anticipated for six independent $S = 1/2$ spin with $g = 2$. This is also in agreement with the presence of six noninteracting Cu^{2+} ions and two dinuclear Cu^{2+} moieties with significant antiferromagnetic interactions.

In summary, two Cu-substituted tungstogermanates have been made through the use of TMCs under hydrothermal conditions. Especially, the tetralacunary [B-β-GeW_8O_{31}]$^{10-}$ anion is first of its kind isolated. Notably, the TMCs can stabilize the lacunary POM species formed in situ. By further changes of the TMCs, novel TMSPs may be obtained under rational conditions.

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Supporting Information Available: Crystallographic data for **1** and **2** in CIF format and figures showing the IR spectra and the TG curves of **1** and **2** and the isothermal magnetization of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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