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Two Multi-Copper-Containing Heteropolyoxotungstates Constructed from the Lacunary Keggin Polyoxoanion and the High-Nuclear Spin Cluster

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Two novel high-nuclear copper-substituted polyoxometalates, $Na_{16}[Cu_{14}(OH)_4(H_2O)_{16}(SiW_8O_{31})_4]\cdot 20.5H_2O$ (**1**) and $K_{10}Na_{14}[Cu_{10}(H_2O)_2(N_3)_4(GeW_9O_{34})_2(GeW_8O_{31})_2]\cdot 30H_2O$ (**2**), containing 14 Cu^{2+} ions and 10 Cu^{2+} ions, respectively, have been obtained in aqueous solution and characterized by IR, UV, TG, element analysis, electrochemistry, and single-crystal X-ray analyses. The polyoxoanion framework of **1** is composed of four [β-SiW_8O_{31}] units connected by 14 Cu^{2+} ions to constitute a tetrameric compound. In **2**, two [β-GeW_8O_{31}] anions and two [B-α-GeW_9O_{34}] anions are connected together by a $[Cu_{10}(N_3)_4O_{32}(H_2O)_2]$ $\{Cu_{10}(N_3)_4\}$ cluster to construct a novel tetrameric compound. The results of the electrocatalytic experiments reveal that the reduced species of **1** and **2** have electrocatalytic activities for nitrate reduction.

Introduction

The significant interest in high-nuclear spin clusters is not only due to their intrinsic structural characteristics but also due to their possible applications in nanomagenets, catalysis, and optical behavior.[1] Most of the work on high-nuclear spin clusters employed the polydentate organic ligands to stabilize or bridge the metal ions.[2] For example, the polydentate carboxylate is utilized to synthesize manganese oxide clusters ranging from Mn_4 to Mn_{84}, and cyanide is employed to connect metal cations to build single molecular magnets.[3] Polyoxometalates (POMs) are known as a unique class of metal-oxide clusters with impressive complexity and potential applications in catalysis, biology, magnetism, nonlinear optics, electrochemistry, and medicine.[4] Lacunary POMs possess similar capabilities, with polydentate organic ligands to coordinate with transition-metal or rare-earth-metal ions, leading to compounds with diverse nuclearities and structural features combined with interesting catalytic, electrochemical, and magnetic properties.[5,6] In the past decades, the trivacant polyoxotungstates, obtained by removing three edge-sharing or corner-sharing WO_6 octahedra from the saturated Keggin or Dawson structure, have been proven to be versatile POM

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ligands used to construct multinuclear magnetic clusters.[7] Commonly, those compounds constructed by such lacunary POM fragments have classic sandwich-type structures, and the number of the transition-metal centers among the reported examples are usually less than five. Therefore, the synthesis of high-nuclear metal clusters based on POM ligands is still a great challenge.[8]

Recently, much attention has been paid to the hexavacant species $[H_2P_2W_{12}O_{48}]^{12-}$ and the related cyclic $[H_7P_8W_{48}O_{184}]^{33-}$ tetramer, which can act as ligands for significantly larger paramagnetic clusters.[6b,6d] In 2005, Gouzerh and co-workers reported multi-iron-containing polyoxoanions based on $[H_2P_2W_{12}O_{48}]^{12-}$ units,[8e,8d] and Kortz et al. reported Cu_{20} cluster-containing anions based on the cyclic $[H_7P_8W_{48}O_{184}]^{33-}$ tetramer.[8b,8f] In the reported examples, the lacunary polyoxoanions all hold the larger coordination pocket that could provide necessary donors for the larger paramagnetic clusters and make them discrete and stabilized. Accordingly, the highly lacunary polyoxoanions might be the best candidates for the incorporation of paramagnetic centers to obtain compounds with a larger number of interacting magnetic cations. Among the various lacunary POMs, divacant polyoxoanion $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ is chosen herein because it isomerizes and decomposes easily in aqueous solution,[9] which can result in unprecedented compounds. At a certain pH value, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ could decompose in aqueous solution to form tetravacant fragments ($[\gamma\text{-}SiW_8O_{31}]$ or $[\beta\text{-}SiW_8O_{31}]$), which could embed a larger number of metal cations, such as, Co_6, Co_7, Co_{15}, and Cu_9-containing polyoxoanions, all of which exhibit interesting electrochemical and magnetic properties.[10,8c] Recently, another divacant polyoxoanion $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$ was reported in the literature.[11] Its structure and the synthetic procedure are essentially analogous to those of $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ and might possess similar reactivity with silicon analogue $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ when reacted with transition-metal cations or other electrophiles. In addition, the azido ligand can bind transition-metal cations embedded in a POM diamagnetic core, which can be regarded as an efficient way to generate interactions between metal centers.[8c,8f]

With these facts mentioned above in mind, we have focused on reactions between transition-metal ions and divacant polyoxoanions $[\gamma\text{-}XW_{10}O_{36}]^{8-}$ (X = silicon and germanium) with the expectation of getting paramagnetic metal clusters stabilized by a tetravacant Keggin anion. Here, we report the synthesis, characterization, and crystal structures of Cu_{14}− containing and the $Cu_{10}(N_3)_4$-containing POMs $Na_{16}[Cu_{14}(OH)_4(H_2O)_{16}(SiW_8O_{31})_4]\cdot 20.5H_2O$ (**1**) and $K_{10}Na_{14}[Cu_{10}(H_2O)_2(N_3)_4(GeW_9O_{34})_2(GeW_8O_{31})_2]\cdot 30H_2O$ (**2**).

Experimental Section

Materials and Methods. All of the chemicals were commercially purchased and used without further purification. $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ and $K_8[\gamma\text{-}GeW_{10}O_{36}]\cdot 6H_2O$ were synthesized according to the literature[9,11] and characterized using an IR spectrum. Elemental analyses (hydrogen and nitrogen) were performed on a PerkinElmer 2400 CHN elemental analyzer; silicon, germanium, tungsten, copper, sodium, and potassium were analyzed on a PLASMA-SPEC(I) ICP atomic emission spectrometer. IR spectra were recorded in the range 400−4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using KBr pellets.

Synthesis of 1. D-Proline (0.05 g, 0.434 mmol) and $CuCl_2\cdot 2H_2O$ (0.34 g, 1.99 mmol) were dissolved in distilled water (30 mL). The pH value of the mixture was carefully adjusted with a dilute NaOH solution (1M) to 5.30 and then stirred for 10 h. Then, 30 mL $K_8[\gamma\text{-}SiW_{10}O_{36}]\cdot 12H_2O$ (0.50 g, 0.167 mmol) solution was added dropwise with vigorous stirring, and the resulting solution was boiling for 2 h. The filtrate was kept at room temperature with slow evaporation for 2 weeks, resulting in the blue crystals of **1** (yield 21% based on silicon). Anal. Found: H, 0.68; Na, 3.81; Cu, 9.12; Si, 1.12; W, 59.2; Calcd: H, 0.78; Na, 3.69; Cu, 8.93; Si, 1.13; W, 59.0. IR (KBr pellet): ν_{max}/cm^{-1} 948 (m) and 892 (s), 740 (s), 546(w), and 498 (w).

Synthesis of 2. In a typical synthesis procedure for **2**, $K_8[\gamma\text{-}GeW_{10}O_{36}]\cdot 6H_2O$ (1.0 g, 0.35 mmol) was dissolved in 60 mL distilled water with stirring. Then, a solution of $CuCl_2\cdot 2H_2O$ (0.25 g, 1.46 mmol) in distilled water (30 mL) was added. Next, 0.12 g NaN_3 (1.84 mmol) was added, and the resulting solution was stirred for half an hour at room temperature and then filtered. The filtrate was kept at room temperature with slow evaporation for 1 week, resulting in the green crystals (Yield 32% based on germanium). Anal. Found: K, 3.06; Na, 3.21; N, 1.38; H, 0.65; Cu, 6.23; Ge, 3.06; W, 59.7; Calcd: K, 3.65; Na, 3.0; N, 1.57; H, 0.60; Cu, 5.93;

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

	1	2
empirical formula	$H_{77}Cu_{14}Na_{16}O_{164.5}Si_4W_{32}$	$H_{64}Cu_{10}Ge_4K_{10}N_{12}Na_{14}O_{162}W_{34}$
fw	9962.58	10714.15
T (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	$C2/m$	$P\bar{1}$
a (Å)	27.629(6)	12.309(3)
b (Å)	22.898(5)	17.979(4)
c (Å)	16.095(3)	21.586(4)
α (deg)	90	103.05(3)
β (deg)	113.65(3)	100.04(3)
γ (deg)	90	108.04(3)
V (Å^3)	9327(3)	4268.2(15)
Z	2	1
D_{calcd} (g cm^{-3})	3.547	4.168
μ (mm^{-1})	21.362	25.102
F000	8798	4722
Data/restraints/params	8327/93/607	14 041/381/1120
GOF on F^2	1.023	1.027
R1[a] [$I > 2\sigma(I)$]	0.0584	0.0758
wR2[b]	0.1227	0.1753

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]^{1/2}$.

Ge, 2.71; W, 58.3. IR (KBr pellet): ν_{max}/cm^{-1} 2081 (s) and 1293 (w), 940 (m), 884 (s), 773 (s), 708 (s), 515 (w), 491 (w), and 457 (w).

X-ray Crystallography. The measurements for **1** and **2** were performed on a Rigaku R-AXIS RAPID IP diffractometer. In all of the cases, the data were collected at 293 K, and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) was used. Numerical absorption corrections were applied for **1** and **2**. The structures were solved by the direct method and refined by the full-matrix least-squares on F^2 using the *SHELXL-97* software.[12] All of the hydrogen atoms for water molecules and protonation were not located but were included in the structure factor calculations. All of the structures possess apparent disorders in the range of counterions and lattice water molecules, preventing a more-precise structural analysis. However, none of these deficiencies affects the structural details and reliability of the polyoxoanion structures. Their occupancies were determined by fixing the atomic displacement parameter factors (0.08) at the beginning, and then occupancy numbers were fixed to refine their atomic displacement parameter factors. Atoms with occupancies lower than 0.1 in **1** and 0.25 in **2** were ignored. In **1**, only partial Na^+ ions can be accurately assigned from the residual electron peaks, whereas the rest were directly included in the molecular formula based on the elemental analyses. The crystal data and structure refinements of **1** and **2** are summarized in Table 1. CSD reference numbers: 417921 for **1**, 417922 for **2**.

Gel Filtration Chromatography. A gel filtration chromatography analysis carried out in the same experimental conditions as previously reported[10a] reveals that **1** and **2** eluted faster than $[P_2W_{15}Mo_2VO_{62}]^{8-}$ (ionic mass = 4055). This indicates that the molecular masses of **1** and **2** (ionic masses: 9225 for **1** and 9462 for **2**) are quite different from that of $[P_2W_{15}Mo_2VO_{62}]^{8-}$ and rules out the possibility of **1** and **2** breaking down into two dimers, four monomers. and mixtures of the two. If **1** and **2** were indeed the dimers in the solution, they have ionic masses of 4612 and 4731 g/mol, respectively, close to that of $[P_2W_{15}Mo_2VO_{62}]^{8-}$, which would elute closer together. If polyoxoanions **1** and **2** fall apart, resulting in monomers, they have the ionic masses of 2306 and 2365, respectively, and therefore would elute later.

Electrochemistry. General Electrochemical Methods and Materials. Thrice-distilled water was used throughout the experiments. The solution with pH 5 was a 0.4 M $CH_3COONa+CH_3COOH$ buffer solution. Solutions were deaerated by pure-argon bubbling prior to the experiments, and the electrochemical cell was kept under an argon atmosphere throughout the experiment.

Electrochemical Experiment. A CHI 660 electrochemical workstation connected to a Pentium-IV personal computer was used to control the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was a glassy carbon; the reference electrode was the Ag/AgCl electrode, and platinum wire was used as a counter electrode. All of the potentials were measured and reported versus the Ag/AgCl electrode. The various media of **1** and **2** were 4×10^{-4} M solutions. A pHS-25B-type pH meter was used for pH measurement. All of the experiments were conducted at room temperature (25−30 °C).

Results and Discussion

Crystal Structure of 1. 1 crystallizes in monoclinic space group $C2/m$. Its structure consists of two $[\{Cu_7(OH)_2(H_2O)_7\}(\gamma\text{-}SiW_8O_{31})_2]$ subunits (Figure 1). In each subunit, two $[\beta\text{-}SiW_8O_{31}]$ units, which were observed very recently in the cobalt and copper-substituted POMs, accommodate seven Cu^{2+} ions, to constitute a hepta-copper-substituted dimeric structure (part c of Figure S3, in the Supporting Information). Interestingly, in this dimeric structure, two equivalent $[\beta\text{-}SiW_8O_{31}]$ moieties coordinate to the central seven Cu^{2+} ions to form the dimeric structure in different ways. One of them provides 10 oxygen donor atoms that are capable of coordinating with six Cu^{2+} ions, to constitute the first six-copper-substituted Keggin polyoxoanion (part b of Figure S3, in the Supporting Information). Meanwhile, the other one provides eight oxygen donor atoms to coordinate with four Cu^{2+} ions to constitute a tetra-copper-substituted Keggin polyoxoanion $[\{Cu_2O_6\}(\gamma\text{-}Cu_2SiW_8O_{36})]$. Without regard to Cu(1) and Cu(5) in $[\{Cu_2O_6\}(\gamma\text{-}Cu_2SiW_8O_{36})]$, the remaining $[\gamma\text{-}Cu_2SiW_8O_{36}]$ unit possesses the parent $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ structure, which has been only observed in the trimeric anion $[\{SiW_8O_{31}Cu_3(OH)(H_2O)_2(N_3)\}_3(N_3)]^{19-}$ (**3**),[8c] but two terminal oxygen atoms (O(37) and O(37A)) in **1** associated to the $\{Cu_2O_6\}$ unit are replaced by an end-to-end azido ligand in **3**. Also, the tetra-copper-substituted polyoxoanion is supported by an additional Cu^{2+} ion in the Cu(6) site. The seven Cu^{2+} ions in the central metal set could be separated into two parts, a $[Cu_6O_{18}(OH)_2(H_2O)_5]$ (Cu_6) cluster and an isolated Cu^{2+}. Also, the six Cu^{2+} ions in the Cu_6 cluster can be further divided into two groups according to the positions where they are located. The first one group is composed of the Cu(3), Cu(3A), and Cu(5) ions, which are octahedrally coordinated, and the three CuO_6 octahedra are edge-sharing, to constitute a triplet. The remaining three Cu^{2+} ions lie in the same line, to constitute the second group. The two groups are connected together by two μ_3-oxo atoms, to construct the novel Cu_6 cluster (part a of Figure 3). As we know, two Cu_6-containing polyoxoanions $[(CuCl)_6(AsW_9O_{33})_2]^{12-}$ (**4**) and $[Cu_6(enMe)_2(B\text{-}a\text{-}SiW_9O_{34})_2]\}$ (**5**) have been reported in

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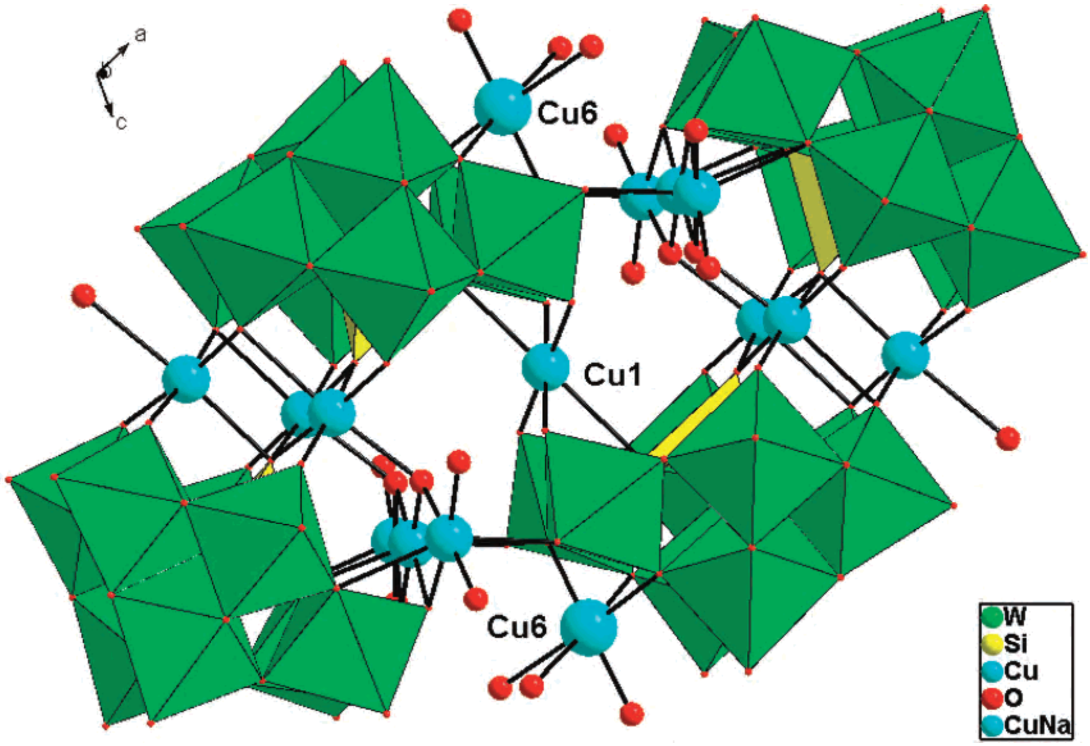

Figure 1. Combined polyhedral/ball-and-stick representation of polyanion **1**. The color codes are following: WO_6 octahedra, green; central SiO_4 tetrahedra, purple; copper atoms, blue spheres; oxygen, red spheres.

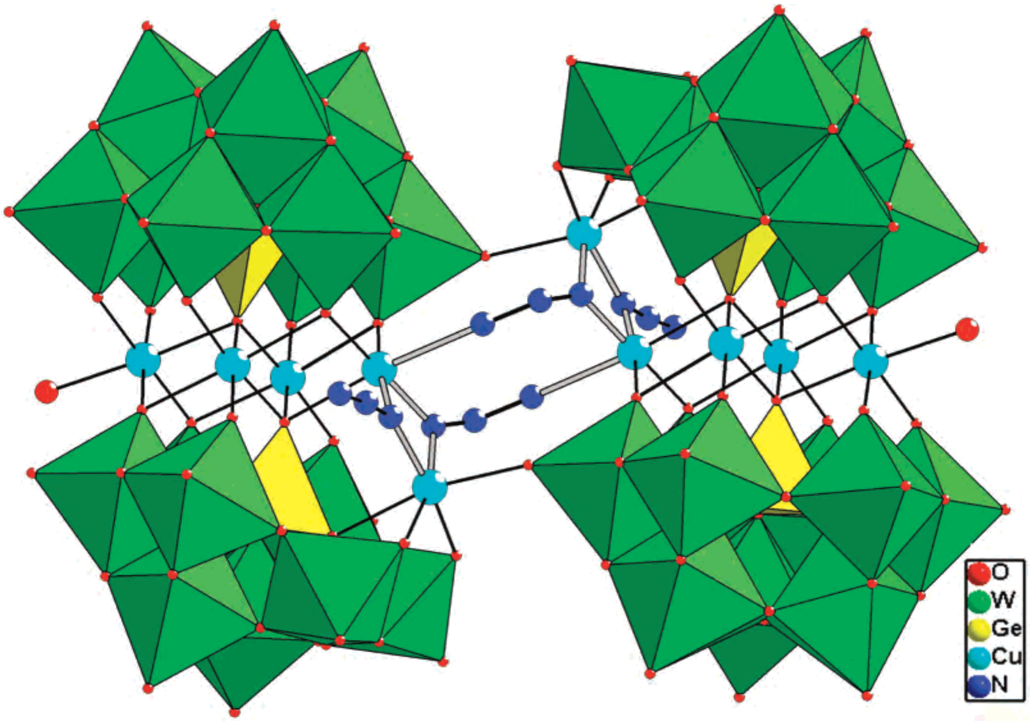

Figure 2. Combined polyhedral/ball-and-stick representation of polyanion **2**. WO_6 octahedra, green; central SiO_4, yellow; Cu atoms, blue spheres; O, red spheres.

the literature up to now,[8g,8h] but the Cu_6 clusters in these two compounds are remarkably different from that in **1**. In **4**, the Cu_6 core is a hexagonal structure made of six edge-sharing CuO_4Cl square pyramids, and in **5**, the Cu_6 core exhibits a belt-like structure with an edge-sharing combination of CuO_6 octahedra, CuO_5, and CuO_3N_2 square pyramids, and this is an inorganic−organic hybrid cluster. Very recently, two Ni_6-containing isolated polyoxoanions $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(enMe)_3(B\text{-}a\text{-}SiW_9O_{34})]$ and $[Ni_6(\mu_3\text{-}OH)_3(H_2O)_4(enMe)_3(CH_3COO)(B\text{-}a\text{-}PW_9O_{34})]$ have been reported.[8i] Although the Ni_6 cores in these two polyoxoanions are structurally similar to that of Cu_6 cluster in **1**, there are also

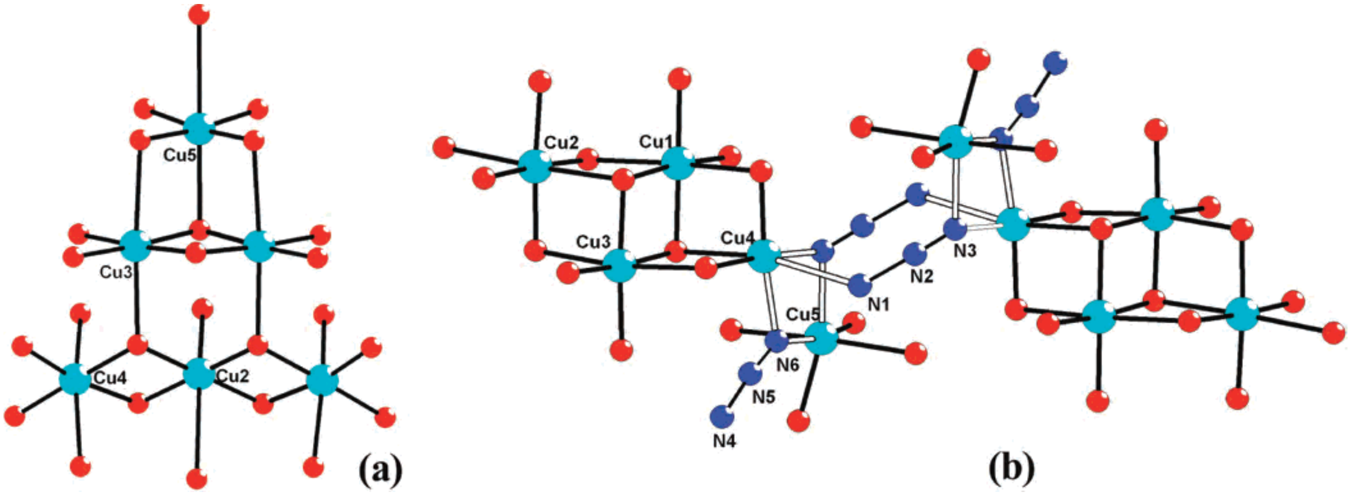

Figure 3. (a) Ball and stick representation of the $[Cu_6O_{18}(OH)_2(H_2O)_5]$ cluster in compound **1**. (b) Ball and stick representation of the central $[Cu_{10}(N_3)_4O_{32}(H_2O)_2]$ cluster in **2**.

remarkable differences between **1** and the two compounds: (1) in **1**, the Cu_6 core is an inorganic cluster, whereas the Ni_6 cores in the polyoxoanions are inorganic−organic hybrid clusters, (2) the Ni_6 cores in these two compounds are connected by only one lacunary Keggin fragment and these two compounds consist solely of Keggin polyoxotungstate monomers, whereas in **1**, the Cu_6 cluster is sandwiched by two $[SiW_8O_{31}]$ Keggin fragments, and **1** is a tetramer composed of four $[SiW_8O_{31}]$ units. Up to now, only a few complexes based on $[SiW_8O_{31}]$ have been documented, such as 9-copper-substituted trimeric polyoxoanion $[\{SiW_8O_{31}Cu_3(OH)(H_2O)_2(N_3)\}_3(N_3)]^{19-}$,[8c] and Co_9-cluster-containing trimeric polyoxoanion $[Co_6(H_2O)_{30}\{Co_9Cl_2(OH)_3(H_2O)_9(\beta\text{-}SiW_8O_{31})_3\}]^{5-}$,[10b] whereas **1** represents the first example of a 14-copper-containing tetrameric polyoxoanion based on four $[\beta\text{-}SiW_8O_{31}]$ units.

Crystal Structure of 2. **2** is made of two $[\beta\text{-}GeW_8O_{31}]$ anions, two $[B\text{-}\alpha\text{-}GeW_9O_{34}]$ anions, and a $\{Cu_{10}(N_3)_4\}$cluster (Figure 2). These could be divided into two equivalent dimeric fragments. Each dimeric fragment consists of two different lacunary polyoxoanions. One is the $[\beta\text{-}GeW_8O_{31}]$ unit, structurally similar to the first reported $[B\text{-}\beta\text{-}GeW_8O_{31}]^{10-}$ in the compound $[Cu_5(2,2'\text{-bpy})_5\text{-}(H_2O)][GeW_8O_{31}]$, which is obtained by the self-assembly of Na_2WO_4 and GeO_2 under the hydrothermal conditions.[13] However, the $[\beta\text{-}GeW_8O_{31}]$ in **2** was synthesized by routine synthetic reactions by the decomposition of $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$ in aqueous solution. The $[\beta\text{-}GeW_8O_{31}]$ anion combines with four Cu^{2+} ions to constitute the first example of the tetra-metal-substituted γ-type saturated Keggin polyoxoanion $[\gamma\text{-}GeW_8Cu_4O_{37}(N_3)_3]$. It is noteworthy that the Cu(4) center is coordinated by three oxygen atoms and three nitrogen atoms from three N_3^- ligands, leading to an axially distorted octahedral environment ($d_{Cu(4)-O(34)} = 1.91(2)$, $d_{Cu(4)-O(23)} = 1.950(16)$, $d_{Cu(4)-O(56)} = 2.486(0)$, $d_{Cu(4)-N(6)} = 1.95(3)$, $d_{Cu-N(3)} = 1.90(2)$, and $d_{Cu-N(1)} = 2.794(81)$ Å). Furthermore, Cu(5) ion is coordinated by four oxygen atoms and bridged by two end-on azido groups with Cu−N−Cu bridging angles θ equal to 96.9(10) and 95.8(10)°, to constitute the saturated γ-Keggin structure polyoxoanion (part b of Figure S4, in the Supporting Information). The polyoxoanion $[\gamma\text{-}GeW_8Cu_4O_{37}(N_3)_3]$ combines with an additional Cu^{2+} ion, to constitute the 5-copper-substituted unit. The other one is the $[B\text{-}\alpha\text{-}GeW_9O_{34}]$ Keggin unit, which is often observed in other sandwich-type POMs. The two different Keggin units are held together by a $Cu_5(N_3)_2$ cluster, to get an asymmetric dimeric structure (part c of Figure S4, in the Supporting Information). In the $Cu_5(N_3)_2$ cluster, the arrangement of the five Cu^{2+} centers is never reported in the POM chemistry. Four Cu^{2+} ions lie in the same plane, to form a centrosymmetric regular rhombuslike cluster, which has been observed in the Weakley-type sandwich structure. The tetra-copper plane and an additional Cu^{2+} ion are linked together by two end-on azido ligands, to constitute the central $Cu_5(N_3)_2$ cluster. Interestingly, the two $Cu_5(N_3)_2$ in **2** are linked together by two $\mu_{1,1,3}$-N_3 ligands with weak Cu−N bonds ($d_{Cu-N} = 2.794(81)$ Å) to construct a $\{Cu_{10}(N_3)_4\}$ cluster (part b of Figure 3). The topology of the $\{Cu_4(N_3)_4\}$ core found in the $Cu_{10}(N_3)_4$ cluster can be compared to that found in the tetranuclear complex $[(\gamma\text{-}SiW_{10}O_{36})_2Cu_4(\mu\text{-}1,1,1\text{-}N3)_2(\mu\text{-}1,1\text{-}N_3)_2]^{12-}$ (**6**) reported by Mialane et al. in 2006.[6g] In **2**, the four Cu^{2+} ions in the Cu_4 cluster are connected by two μ-1,1,3-azido ligands and two μ-1,1- azido ligands, and in **6**, the four Cu^{2+} ions are linked together by two μ-1,1,1-azido ligands and two μ-1,1- azido ligands. Furthermore, the average Cu(4)−N−Cu(5) angle is larger in **2** ($\theta_{avg} = 96.36°$) than that in **6** ($\theta_{avg} = 94.55°$). Additionally, the two asymmetric sandwich fragments are connected via two equivalent Cu−O−W′ bonds with $d_{Cu-O} = 2.321(65)$ and $d_{W-O} = 1.728(45)$ Å (besides the two weak Cu−N bonds), leading to tetrameric polyoxoanion **2**.

It is interesting to compare the structures of **2** and two co-substituted dimers $[\{Co_3(B\text{-}\alpha\text{-}SiW_9O_{33}(OH))(B\text{-}\alpha\text{-}SiW_8O_{29}(OH)_2)\}_2]^{22-}$ and $[\{(B\text{-}\beta\text{-}SiW_9O_{33}(OH))(\beta\text{-}SiW_8O_{29}(OH)_2)Co_3(H_2O)\}_2Co(H_2O)_2]^{20-}$.[10a,10c] The two cobalt-containing

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(13) Wang, C. M.; Zheng, S. T.; Yang, G. Y. *Inorg. Chem.* **2007**, *46*, 616.

polyoxoanions are composed of two equivalent tri-cobalt-substituted asymmetrical sandwich units $[Co_3(B\text{-}\alpha\text{-}SiW_9O_{33}(OH))(B\text{-}\alpha\text{-}SiW_8O_{29}(OH)_2)]^{11-}$, which has been observed for the first time by Kortz et al. The asymmetrical sandwich unit in the half unit of the two compounds is composed of a $[B\text{-}\beta\text{-}SiW_9O_{33}(OH)]$ unit and a $[B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2]$ fragment linked by a nearly equilateral triangular $\{Co_3\}$ cluster. For the former, the two $[B\text{-}\beta\text{-}SiW_9O_{33}(OH)]$ and $[B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2]$ groups are held by two Co−O−W bonds, which are arranged almost orthogonally to each other. For the latter, the two groups are connected through a $\{CoO_4(H_2O)_2\}$ group. But, in each subunit of **2**, a pentanuclear $Cu_5(N_3)_2$ cluster is encapsulated between a $[\beta\text{-}GeW_8O_{31}]$ moiety and a $[B\text{-}\alpha\text{-}GeW_9O_{34}]$ fragment, and connection between the two subunits occurs through the two equivalent Cu−O−W′ bonds with $d_{Cu-O} = 2.321(65)$ and $d_{W-O} = 1.728(45)$ Å and two weak Cu−N bonds. Accordingly, the subunits ($[B\text{-}\beta\text{-}SiW_9O_{33}(OH)]$ and $[B\text{-}\beta\text{-}SiW_8O_{29}(OH)_2]$) and the combination fashion in the two co-substituted compounds are different from those of **2**.

The bond lengths and angles of the tungsten-oxo framework in the two compounds are not unusual. The Cu^{2+} ions in the two compounds are coordinated in a strongly distorted octahedral fashion and exhibit Jahn−Teller distortion with axial elongation (the selected bond lengths and angles of Cu^{2+} in **1** and **2** are list in Table 1). The Cu(6) site in **1** is disordered, that is, the Na^+ and Cu^{2+} units share the site in-part, each with 50% occupancy. The oxidation states of tungsten and copper sites are determined on the basis of the crystal color, bond lengths and angles, charge balance consideration, and bond valence sum calculations,[14] indicating that the tungsten and copper sites possess +6 and +2 oxidation states, respectively. Bond valence sum calculations[14] also reveal that bridging oxygen atoms that link adjacent copper ions are monoprotonated, and the terminal oxygen atoms associated with the copper ions are diprotonated.

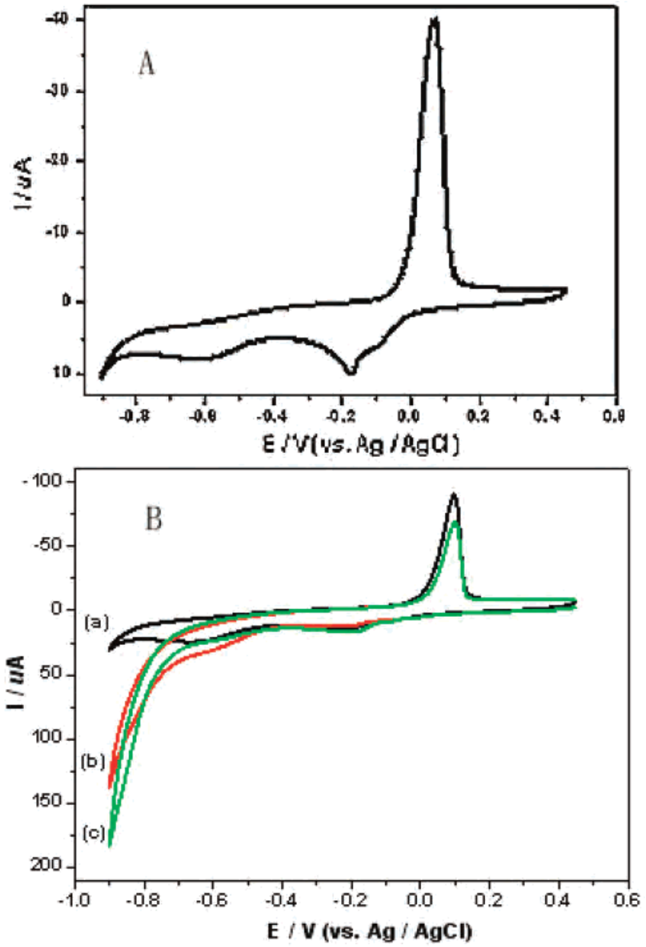

Figure 4. (A) Cyclic voltammograms of 4×10^{-4} M **1** in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution at a scan rate of 20 mV s^{-1}; (B) Electrocatalysis of the reduction of NO_3^- in the presence of 4×10^{-4} M **1** in a pH 5 medium (0.4 M $CH_3COONa+CH_3COOH$), at a scan rate of 100 mV s^{-1}, containing NO_3^- concentrations of 0.0 (a), 2.0 (b), and 3.0 (c) mM. The working electrode was glassy carbon; the reference electrode was Ag/AgCl.

Electrochemistry. Part A of Figure 4 shows the typical cyclic voltammetric behavior of **1** in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution at a scan rate of 20 mV s^{-1}. It can be clearly seen that in the potential range of +0.4 to −1.0 V, three reduction peaks appear, and the mean peak potentials are −0.114, −0.173, and −0.603 V (vs the Ag/AgCl electrode), respectively. The last redox process corresponds to the redox of the W^{VI} atoms in the polyoxoanion framework, and the domain where the wave was located was also observed in the other tungsten-containing POMs.[15,5a,10] The first two reduction waves and their oxidation counterpart, a single oxidation process located at +0.066 V, are attributed to the redox processes of the Cu^{2+} centers. The two reduction waves located at −0.114 and −0.173 V feature the two-step reduction of Cu^{2+} to Cu^0 through Cu^{1+}.[7a,16] Moreover, polyoxoanion **1** is stable in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution. When the solution was stored at room temperature and the cyclic voltammetric behavior of **1** was detected every 24 h, and detected five times totally, the same solution could be kept without any changes in the voltammetric characteristics (Figure S5, in the Supporting Information). The UV−vis spectrum of the same solution could give a complementary proof of this suggested stability (Figure S7).

The electrochemical properties of **2** are also detected in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution at the scan rate of 20 mV s^{-1} (part A of Figure 5). There are four reduction peaks that appear in the potential range of 0.4 to −1.0 V, with peak potentials located respectively at −0.119, −0.190, −0.636, and −0.795 V versus the Ag/AgCl electrode. The reduction peaks located at −0.119 and −0.190 and their oxidation counterpart located at +0.052 V correspond to the redox processes of the Cu^{2+} centers, similar

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(14) The valence sum calculations are performed on a program of a bond valence calculator, ver. 2.00 February, 1993, written by C. Hormillosa with assistance from S. Healy, distributed by I. D. Brown.

(15) (a) Bassil, B. S.; Kortz, U.; Tigan, A. S.; Clemente-Juan, J. M.; Keita, B.; Oliveira, P.; Nadjo, L. *Inorg. Chem.* **2005**, *44*, 9360. (b) Mbomekalle, I. M.; Keita, B.; Nierlich, M.; Kortz, U.; Berthet, P.; Nadjo, L. *Inorg. Chem.* **2003**, *42*, 5143.

(16) Keita, B.; Mbomekalle, I. M.; Nadjo, L. *Electrochem. Commun.* **2003**, *5*, 830.

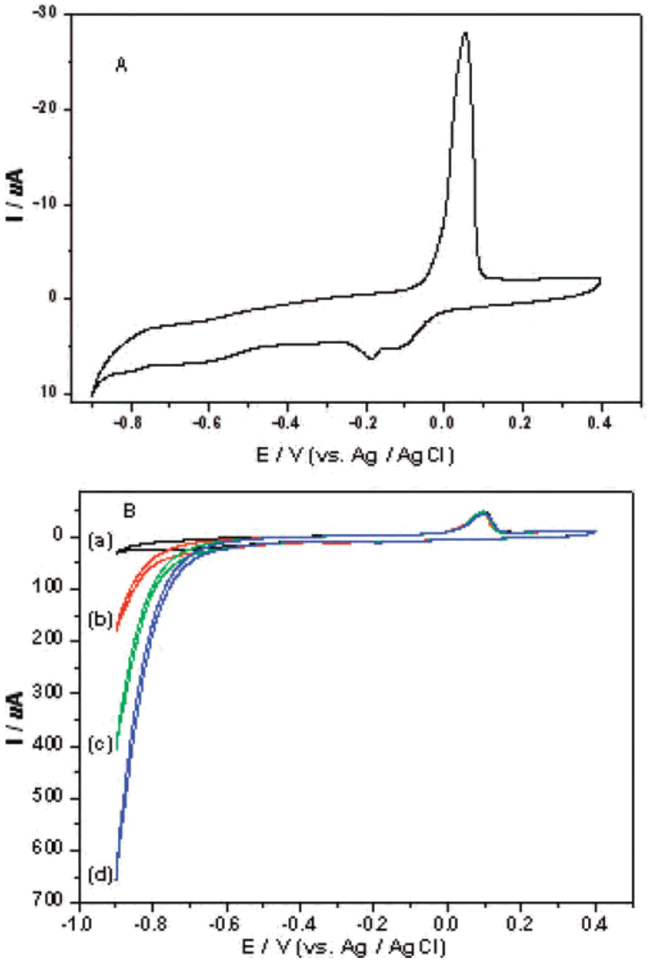

Figure 5. (A) Cyclic voltammograms of 4 × 10^{-4} M **2** in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution at a scan rate of 20 mV s^{-1}; (B) Electrocatalysis of the reduction of NO_3^- in the presence of 4 × 10^{-4} M **2** in a pH 5 medium (0.4 M $CH_3COONa+CH_3COOH$), at a scan rate was 100 mV s^{-1}, containing NO_3^- concentrations of 0.0 (a), 2.0 (b), 3.0 (c), and 4.0 (d) mM. The working electrode was glassy carbon; the reference electrode was Ag/AgCl.

to that of **1**. The last two peaks ($E_{pc} = -0.636$ and -0.795 V) are chemically reversible and are assigned to the processes of W^{VI} in the polyoxoanion framework of **2**.[15,5a,10] The stability of **2** is also studied. In the pH 5 (0.4 M CH_3-$COONa+CH_3COOH$) buffer solution, cyclic voltammetric behavior of **2** was detected every 24 h and detected five times, and the UV−vis spectra were detected every 6 h, and detected six times. These curves were virtually unchanged with time (Figures S6 and S8, in the Supporting Information), indicating that **2** is stable in the pH 5 (0.4 M CH_3-$COONa+CH_3COOH$) buffer solution.

Electrocatalysis of NO_3^- Reduction. The electrocatalytic reduction of nitrate for **1** was studied in the pH 5 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution. Polyoxoanion **1** displays electrocatalytic activity toward the reduction of nitrate. Upon the addition of modest amounts of nitrate, the reduction peak currents at the potential domain of the tungsten wave increase dramatically (part B of Figure 4). In the explored potential domain, no reduction of nitrate could be obtained on the GC electrode in the absence of POMs.[7a,17] The results indicate that the reduced species of **1** has electrocatalytic activity for nitrate reduction.

The electrocatalytic reduction of nitrate was also detected for **2** under conditions similar to that of **1** (part B of Figure 5). The results indicate that the two reduced species have electrocatalytic activity for nitrate reduction. It was also noted that the second reduced species showed better electrocatalytic activity, that is, the catalytic activity is enhanced when the extent of the polyoxoanion reduction is increased.

FTIR spectroscopy. The IR spectrum of **1** shows a broad band at 3402 cm^{-1} and strong peak at 1620 cm^{-1} attributed to the lattice and coordinated water molecules. The features at 948(m), 892 (s), 740 (s), 546(w), and 498 (w) can be attributed to ν(W−Od) ν(W−Oa), ν(W−Ob), and ν(W−Oc) in the polyoxoanion framework (Figure S9, in the Supporting Information).[4a] The IR spectrum of **2** also exhibits the characteristic bands of water molecules at ca. 3428 and 1620 cm^{-1}. The absorption band at 2081 cm^{-1} assigned to the asymmetric stretching vibration of the azido ligands (υ_{as}). The symmetric stretching vibration of the azido ligands is also observed (υ_s) at 1293 cm^{-1}.[8c,8f] The other peaks located at 940 (m), 884 (s), 773 (s), 708 (s), 515 (w), 491 (w), and 457 (w) can be attributed to the vibration of W−O in the polyoxoanion of **2** (Figure S10, in the Supporting Information).

TG Analyses. To examine the thermal stability of **1** and **2**, thermal gravimetric (TG) analyses were carried out for **1** and **2**. A TG curve of **1** (Figure S11, in the Supporting Information) shows two continuous weight loss steps from 33∼360 °C, attributed to the loss of all of the lattice and coordinated water molecules in **1**. The total weight loss is about 8.21%, a little higher than the calculated value of 6.96%. The reason could be that the solvent accessible voids of about 200 Å^3 (as determined by *PLATON* program) exist in the unit cell of **1**, which could accommodate several disordered water molecules in the formula unit, and also, there could be some solvent water molecules existing in the sample after dryness at room temperature.

The TG curve of **2** shows a weight loss of 5.28% in the range of 38∼265 °C (Calcd 5.38%), which corresponds to the loss of all non-coordinated and coordinated water molecules (Figure S12, in the Supporting Information). Another weight loss of 1.42% appears in the temperature range of 400∼495 °C, attributed to the decomposition and loss of N_3^- ligands and in agreement with the calculated value of 1.57%.

Conclusions

In conclusion, two novel high-nuclear copper-substituted tetrameric POMs have been synthesized by the reaction of Cu^{2+} ions with divacant polyoxoanions $[\gamma\text{-}XW_{10}O_{36}]^{8-}$ (X = Si and Ge). The two compounds both contain a large

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(17) Keita, B.; Abdeljalil, E.; Nadjo, L.; Contant, R.; Belghiche, R. *Electrochem. Commun.* **2001**, *3*, 56.

number of paramagnetic 3d transition-metal centers and tetravacant anions. The successful synthesis of both compounds not only provides novel examples of high-nuclear paramagnetic cluster-containing POMs but also can prove that the $[\gamma\text{-GeW}_{10}\text{O}_{36}]^{8-}$ anion might possess similar reactivity with silicon analogue $[\gamma\text{-SiW}_{10}\text{O}_{36}]^{8-}$ when reacted with transition-metal cations and could undergo an isomerization course or decompose in aqueous solution. Future research will focus on the study of the reaction between divacant polyoxoanions $[\gamma\text{-XW}_{10}\text{O}_{36}]^{8-}$ and other transition-metal or rare-earth-metal ions, in an effort to synthesize novel compounds with diverse nuclearities and structural features combined with interesting electrochemical and magnetic properties.

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Supporting Information Available: X-ray crystallographic files in CIF format, TG curves, the IR spectrum, and the additional figures for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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