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Ferromagnetically Coupled Dimer of Cu^{II}-Substituted γ-Decatungstosilicate

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A novel copper-substituted polyoxoanion $[Cu_4(H_2O)_2(OH)_4Si_2W_{16}O_{58}]^{8-}$ (**1**) has been synthesized as its sodium salt, Na_8-**1**·$26H_2O$ (Na-**1**), potassium salt, K_8-**1**·$28H_2O$(K-**1**), and calcium salt, Ca_4-**1**·$48H_2O$ (Ca-**1**). Compound **1** is the first dimer of dicopper-substituted γ-decatungstosilicate fused in an unprecedented side-by-side dimerization mode with a ferromagnetic coupling property.

Since the first polyoxometalate (POM) was found by Berzelius in 1826,[1] POMs of the early transition elements have witnessed a huge development.[2] Although thousands of POMs have been described, their structures are limited to the basic frameworks such as the Keggin, Wells−Dawson, and Anderson−Evans types or their lacunary fragments, and the formation mechanisms of some new POMs are still not well understand and are commonly described as self-assembly. The rational synthesis of mixed hetero-POMs and of magnetic clusters with diverse nuclearities and geometry morphologies remains a big challenge.[3]

The lacunary heteropolyanions (LHPAs) can be seen as polydentate oxo ligands that can coordinate most transition-metal ions, resulting in an enormous variety of structures with improved magnetic, catalytic, and electrochemical properties.[1,4] The LHPAs and their active binding sites have been well investigated and reviewed.[5] Metastable lacunary POMs, such as the Keggin species $[XM_9O_{34}]^{n-}$, $[XM_{10}O_{36}]^{n-}$, or $[XM_{11}O_{39}]^{n-}$ and the Wells−Dawson species $[X_2M_{15}O_{56}]^{12-}$ or $[X_2M_{17}O_{61}]^{10-}$ (X = P, S, Si, ...; M = W, Mo, V, ...), can coordinate to transition-metal ions (Z) to reconstitute the complete (saturated) HPA or to form high-nuclearity cluster structures. Nevertheless, transition-metal-substituted LHPAs, such as $[XM_{9-x}Z_xO_{34}]^{n-}$, $[XM_{10-x}Z_xO_{36}]^{n-}$, or $[XM_{11-x}Z_xO_{39}]^{n-}$, in which the LHPA constituent atoms (M) are partly replaced by transition-metal atoms (Z) while the original lacunary skeletons are maintained, have not been observed to date.

When transition-metal atoms with low oxidation states replace the M atoms, the negative charge of the substituted LHPA cluster increases and becomes more basic and reactive than that of the unsubstituted LHPA. This property can be used to obtain extended structures and to functionalize the polyanion fragments via their active positions. Surprisingly, little research has been done in this area.

Among the hundreds of known LHPAs, the dilacunary Keggin polyoxoanion, $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ (γ-SiW_{10}), first reported by Hervé et al. in 1986,[6] has recently become a focus of research because of its structural flexibility, which has allowed the synthesis of plenty of derivatives starting from γ-SiW_{10}. In most of them, the saturated γ skeleton was kept or isomerized to the β isomer[7−10] or to sandwich-type

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species.[11a] Recently, several copper−chloro- and copper−azido-containing high-nuclearity clusters with the {SiW_8M_2} fragment have been reported by Mialane, Kortz, and co-workers:[10,11b,c] [{Co_3(B-β-SiW_9O_{33}(OH))(B-β-$SiW_8O_{29}(OH)_2$)}$_2$]$^{22-}$, [$Co_6(H_2O)_{30}${$Co_9Cl_2(OH)_3(H_2O)_9$(β-$SiW_8O_{31})_3$}]$^{5-}$, [(γ-$SiW_{10}O_{36}$)(β-SiW_8O_{30}(OH))$Co_4(OH)(H_2O)_7$]$^{10-}$, and [{(γ-SiW_8O_{31})$Cu_3(OH)(H_2O)_2$-(N_3)}$_3$(N_3)]$^{19-}$.

In these examples, the {SiW_8} fragments are coordinated to a Z_3O_{13} triad (Z = Cu, Co); therefore, they do not belong to the [$XM_{10-x}(Z)_xO_{36}$]$^{n-}$ type. The small chloro and azido ligands may have an important effect on the construction of these complexes. In fact, the controllable synthesis of the substituted LHPAs represents a remarkable challenge because the LHPA precursors generally decompose or isomerize very easily and the factors governing the final structure are not well understood. An additional interest in the chemistry of metal-substituted and vacant POMs comes from their ability to self-assemble in order to build up novel structures with high nuclearities.

In our recent research work on γ-SiW_{10}-based derivatives, we have observed that factors such as the pH, the temperature, and the presence of metal ions must be controlled in order to slow down decomposition and isomerization reactions of γ-SiW_{10}.[7d] We have used various metal ions in an acidic aqueous medium to react with the γ-SiW_{10} polyanion and found that Cu^{II} ions can stabilize the (γ-SiW_8O_{31})[≡(β-SiW_8O_{31})] fragment in γ-$SiW_8Cu_2O_{36}$ to recover the γ-SiW_{10} skeleton. Thus, by mixing γ-SiW_{10} with Cu^{2+} in a 2:5 molar ratio in an acidic 1 M NaCl (KCl or $CaCl_2$) solution (pH = 4.5) at 50 °C, we have obtained novel substituted LHPA complexes where the γ-SiW_{10} skeleton is preserved although two adjacent W^{VI} atoms are replaced by two Cu^{2+} ions, giving rise to the γ-SiW_8Cu_2 dimeric polyanion, [$Cu_4(H_2O)_2(OH)_4Si_2W_{16}O_{58}$]$^{8-}$ (**1**), isolated as the corresponding sodium, potassium, and calcium salts: Na-**1**, K-**1**, and Ca-**1** (see the Supporting Information). Electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) provides evidence for the dimeric species (Figure S3 in the Supporting Information). When an organic solvent or a bigger cation such as Rb^+ or Cs^+ was used, the reaction did not produce any expected salt.

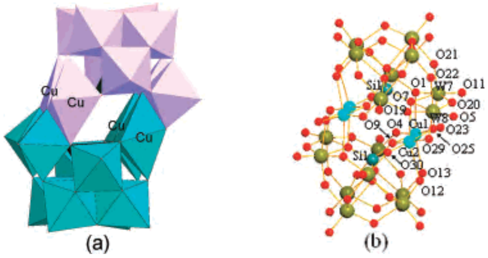
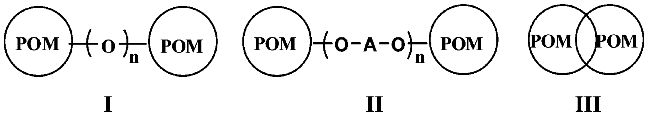


Figure 1. (a) Polyhedral representation of **1** showing the two **1a** subunits in different colors. (b) Ball-and-stick representation of **1**. Color code: Cu, blue; W, yellow-green; O, red; Si, dark blue.

Scheme 1. Different Combination Modes of POM Subunits



Single-crystal X-ray diffraction analyses[12] show that the polyanion **1** can be regarded as a dimer composed of two equivalent {$SiW_8Cu_2O_{36}$} (**1a**) subunits (Figure 1), which are fused through two edge-sharing WO_6 octahedra and two edge-sharing CuO_6 octahedra from two **1**a subunits, giving rise to an overall ideal symmetry of C_i. To the best of our knowledge, the polymerization mode of the two **1a** subunits in the polyanions **1** is original because the POM subunits are usually linked in a head-to-head mode: POM−(O)$_n$−POM (mode **I**, in Scheme 1) or POM−(O−A−O)$_n$−POM (A = addenda or heteroatom; mode **II**, in Scheme 1). In these two models, the polyanion subunits are connected by sharing O atom(s). The typical examples are the Well−Dawson structure and various sandwich structures (e.g., Weakley, Hervé, Krebs, and Knoth type). Surprisingly, in **1** the two {SiW_8Cu_2} subunits are combined by edge-sharing {WO_6} and {CuO_6} octahedra, i.e., the side-by-side mode, a way never observed in POM chemistry (mode **III** in Scheme 1).

Each **1a** subunit can be described as a fragment derived from the parent γ-SiW_{10} polyanion, where a pair of edge-sharing {WO_6} octahedra is replaced by a pair of edge-sharing distorted {CuO_6} octahedra. This dimerization can be easily explained by the fact that the potential sharing O atoms, four bridging O_b (O1, O4, O19, and O30), two O_a (O7 and O9), and four $O_{d'}$ (O1A, O7A, O25, and O29) (Ob, Oa, and Od′, initially marked by Hervé[6]) atoms in **1a**, are more basic than those in the parent γ-SiW_{10}. Therefore, they are more reactive toward protonation and coordination (or polymerization).[13] In Na-**1**, the two **1a** subunits are connected via eight shared O atoms (O1, O7, O25, O29, O1A, O7A,

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(12) Crystal data for Na-**1**: $H_{60}Na_8Cu_4Si_2W_{16}O_{90}$, M_r = 4936.3 g·mol^{-1}, monoclinic, $P2_1/n$, a = 17.965(8) Å, b = 10.722(5) Å, c = 21.757(6) Å, β = 101.943(6)°, V = 4100(3) Å^3, Z = 2, T = 193 K, D_c = 3.950 g·cm^{-3}, μ = 23.552 mm^{-1}, R1 = 0.0770, wR2 = 0.1789, CSD 418246. Crystal data for K-**1**: $H_{64}K_8Cu_4Si_2W_{16}O_{92}$, M_r = 5101.2 g·mol^{-1}, monoclinic, $P2_1/n$, a = 10.8635(12) Å, b = 19.810(2) Å, c = 18.502(2) Å, β = 90.774(2)°, V = 3981.4(7) Å^3, Z = 2, T = 193 K, D_c = 4.201 g·cm^{-3}, μ = 24.631 mm^{-1}, R1 = 0.0759, wR2 = 0.1982, CSD 418247. Crystal data for Ca-**1**: $H_{104}Ca_4Cu_4Si_2W_{16}O_{112}$, M_r = 5309.03 g·mol^{-1}, triclinic, $P\bar{1}$, a = 10.9084(8) Å, b = 13.1056(10) Å, c = 17.8439(14) Å, α = 69.628(1)°, β = 101.943(6)°, γ = 88.869(1)°, V = 2280.3(3) Å^3, Z = 1, T = 193 K, D_c = 3.790 g·cm^{-3}, μ = 21.389 mm^{-1}, R1 = 0.0675, wR2 = 0.1854, CSD 418248.

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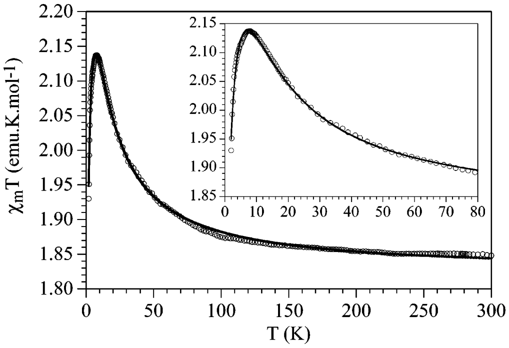

Figure 2. Temperature dependence of the $\chi_m T$ product for Na-**1**. The inset shows the low-temperature region. The solid line represents the best fit to the model (see the text).

O25A, and O29A), leading to the dimeric structure observed in **1**. The atoms Cu2, W7A, and W8A represent a triad (a group of three edge-sharing octahedra) that is connected to one central $\{SiO_4\}$ tetrahedron by the μ_4-O_a (O7) bridging O atom. Cu1, Cu2, and W7A also form a triad connected to another central $\{SiO_4\}$ tetrahedron by the μ_3-O_a (O9) bridge; the four central atoms (W7, W8, Cu1, and Cu2) are almost in the same plane (Figure 1b).

In **1a**, the CuO_6 octahedra are very elongated; the axial Cu−O bond lengths [2.600(2) and 2.41(2) Å for Cu1 and 2.461(2) and 2.470(2) Å for Cu2] are much longer than the average lengths of the equatorial Cu−O bonds (1.964 and 1.952 Å for Cu1 and Cu2, respectively). The other W(Cu)−Oa(b,c,d) bond lengths and angles are within the normal values observed in the precursor SiW_{10}.[6]

Bond-valence-sum calculations (BVSCs) indicate that the polyanion **1** has eight protons,[14] located in the two $\{Cu_2O_{10}\}$ groups. Each Cu_2O_{10} group has two hydroxo bridges: a μ_2-O13 bridge (BVSC = 1.054) connecting Cu and W centers (Cu1−O13−W5) and a μ_3-O25 (BVSC = 1.246) bridge, which is shared by three metals (Cu1, Cu2, and W7A). O23 is a terminal water ligand (BVSC = 0.477). This assignment reduces the total negative charge of **1** from −16 to −8, in agreement with the presence of eight Na atoms located by the X-ray diffraction analysis.

We suggest that the formation of **1** involves a $\gamma\text{-SiW}_{10} \rightarrow \text{B-}\beta\text{-SiW}_8 \rightarrow \gamma\text{-SiW}_8\text{Cu}_2 \rightarrow \{\gamma\text{-SiW}_8\text{Cu}_2\}_2$ process. Through our research, we have found that Cu^{2+} ions have a suitable size to enter into the vacancies and to stabilize the γ-SiW_8 fragment under the reaction conditions. Smaller counterions, higher temperatures, and longer reaction times favor further isomerizations of the POM matrix. Kortz et al. have found that Cu^{2+} stabilizes B-α-SiW_9O_{34}.[11b] In fact, we also have obtained the $[Cu_4(H_2O)_2(\text{B-}\alpha\text{-}SiW_9O_{34})_2]^{12-}$ species by prolonging the reaction time or increasing the pH value.

The magnetic susceptibility of Na-**1** measured at a field of 0.1 T in the temperature range of 2−300 K is shown in Figure 2 as the thermal variation of the product of the molar susceptibility per four Cu^{II} atoms times the temperature ($\chi_m T$). When the sample is cooled, the $\chi_m T$ product gradually increases from ca. 1.84 emu·K·mol^{-1} at 300 K and reaches a maximum of ca. 2.14 emu·K·mol^{-1} at ca. 8 K. Below 8 K, the $\chi_m T$ product decreases to a value of ca. 1.93 emu·K·mol^{-1} at 2 K. This behavior indicates the presence of ferromagnetic intradimer exchange interactions (J) with antiferromagnetic interdimer interactions (j), accounting for the decrease in the $\chi_m T$ product at low temperatures. Accordingly, we have fitted the magnetic data to a simple dimer model with an interdimer coupling using the molecular field approximation.[16] This model[17] (the Hamiltonian is written as $-JS_1S_2$) shows a very good agreement over the whole temperature range, only when a monomeric contribution is included in the fitting procedure, with the following set of parameters: $g = 2.205(1)$, $J = 13.7(2)$ cm^{-1}, $j = -0.03(1)$ cm^{-1}, and a monomeric contribution of ca. 6% (solid line in Figure 2). This monomeric contribution may be due to the presence of some vacancies in the Cu positions, leading to isolated Cu^{II} ions, and/or to the presence of some Cu^{2+} cations replacing some of the Na^+ ions, in agreement with the slight copper excess found in the elemental analysis.

The ferromagnetic intradimer and the antiferromagnetic interdimer exchange interactions can be easily explained in terms of the exchange pathways and the bond angles. Thus, the intradimer exchange implies one hydroxo bridge with a Cu1−O25−Cu2 angle of 93.6(7)°, which should give rise to a medium-strong ferromagnetic interaction,[10a,17] and an oxo bridge with a Cu1−O9−Cu2 bond angle of 99.5(8)°, which should produce a weak antiferromagnetic coupling,[18] giving an overall ferromagnetic intradimer interaction. The interdimer coupling pathway implies two long bridges, Cu−O−W−O−Cu and Cu−O−Si−O−Cu, which are expected to give rise to weak antiferromagnetic interactions.

In summary, we have synthesized a novel ferromagnetically coupled dimer of Cu^{II}-substituted γ-decatungstosilicate. The structure of this POM shows the possibility of replacing W atoms with the first-row transition-metal atoms in an already lacunary POM. It is also the first example of a dimer of classical lacunary Keggin POM combined in an unprecedented side-by-side mode. Further work will focus on the multiply substituted LHPA with interesting magnetic properties.

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Supporting Information Available: Experimental section, X-ray crystallographic files in CIF format, IR spectra, thermogravimetric analyses of Na/K/Ca-**1**, ORTEP diagram of **1**, and the ESI FT-ICR MS of Na-**1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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