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A Novel Dumbbell-like Polyoxometalate Assembled of Copper(II)-Disubstituted Monovacant Keggin Polyoxoanions with a Tetranuclear Copper Cluster

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Supporting Information

ABSTRACT: A dimeric Keggin polyoxometalate, $[Cu(bpy)(\mu_2\text{-}OH)]_4[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]_2\cdot 2CH_3CH_2OH\cdot 10H_2O$ (**1**), constructed from two dicopper(II)-substituted monovacant Keggin polyoxoanions bridged by a Cu_4 cluster, has been hydrothermally synthesized. Magnetic analysis indicates predominantly an antiferromagnetic interaction between copper(II) centers. Compound **1** also shows very high catalytic activity for the esterification of phosphoric acid with equimolar lauryl alcohol to monoalkyl phosphate ester.

Polyoxometalates (POMs), as a fascinating family of metal—oxygen clusters, have been extensively researched because of their unmatched structural versatility and potential applications in fields as diverse as catalysis, magnetism, luminescence, materials science, molecular electronics, etc.[1] The massive range of applications has led to many deliberate assembly tactics for the design and synthesis of novel POM-based hybrids by introducing transition-metal-coordinated complexes as linkers and modifiers with consideration of the structure direction or charge compensation.[2] As an advance in this field, many POM-based compounds with variable topologies and dimensionalities have been prepared hydrothermally.[3] As an important branch of POMs, Keggin-type POMs, represent an important place at the forefront of the POM field because of their unusual structural diversity and electronic versatility.[4] The system containing transition-metal cations and monovacant Keggin-type polyoxoanions has been paid more and more attention since monovacant Keggin species $[PW_{11}O_{39}]^{7-}$ was reported by Kehrmann et al. in 1892.[5] In 1995, Coronado et al. found the poly-Keggin compound based on the manganese-monosubstituted Keggin unit $\{PW_{11}MnO_{39}\}$.[6] Recently, Gutiérrez-Zorrilla et al. acquired and characterized a series of hybrids constructed from monocopper(II)-substituted Keggin polyoxoanions by means of monovacant Keggin precursors in acetic acid.[7] We can discover that the condensation of POMs is a charge-driven progress because all of these polymeric structures are based on transition-metal-substituted POM units whereby a low-valence metal substitutes a high-valence early transition metal.[8]

However, the progress of this research field is still laggardly, and the system including transition-metal cations and lacunary polyoxoanions remains mostly unexplored. To the best of our knowledge, few studies on the ditransition-metal-substituted monovacant Keggin polyoxoanions have been reported. Recently, we began the research in this filed, and fortunately we have successfully prepared a novel dumbbell-like transition-metal coordination fragment derivative of the monovacant Keggin POM $[Cu(bpy)(\mu_2\text{-}OH)]_4[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]_2\cdot 2C_2H_5OH\cdot 10H_2O$ (**1**; bpy = bipyridine) through a conventional hydrothermal method. As far as we know, compound **1** is the first dicopper(II)-substituted monovacant Keggin polyoxoanion that bridged with a Cu_4 cluster to construct a dimeric Keggin polyoxoanion. Magnetic analysis indicates predominantly an antiferromagnetic interaction between Cu^{2+} ions in **1**. More interestingly, compound **1** shows very high catalytic activity for the esterification of phosphoric acid with equimolar lauryl alcohol to monoalkyl phosphate ester.

Compound **1** crystallizes in the triclinic space group $P\bar{1}$. The fundamental building unit of **1** contains two dicopper(II)-substituted monovacant Keggin polyoxoanions $[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]^{2-}$, a Cu_4 cluster, two ethyl alcohol molecules, and 10 lattice water molecules (Figure S1 in the Supporting Information, SI). In $\{HPW_{11}Cu_2O_{39}\}$, the central phosphorus atom is surrounded by four oxygen atoms (O4, O12, O18, and O26). Average distance of the P—O bonds is in the usual region of 1.528 Å, and the O—P—O bond angle is in the range of 107.1(4)—111.5(4)°. The distances of the W—O bonds can be divided into three groups: $W-O_t$, 1.705(8)—1.748(7) Å; $W-O_b$, 1.771(8)—2.047(8) Å; $W-O_a$, 2.396(7)—2.509(7) Å, which is in the range of reported monovacant Keggin polyoxoanions.[9−11] Bond-valence-sum calculations[12] show that all of the tungsten sites exhibit a 6+ oxidation state and all of the copper ions have a 2+ oxidation state in the disubstituted $\{HPW_{11}Cu_2O_{39}\}$ units. In compound **1**, it is interesting that PW_{11} is formed from the saturated Keggin cluster PW_{12} under hydrothermal conditions[8] and two copper(II) (Cu1 and Cu2) cations chelated by the 2,2′-bpy ligands respectively physically occupy the vacant position of PW_{11} to generate an anionic $[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]^{2-}$ unit. To our knowledge, $[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]^{2-}$ in **1** is the first dicopper(II)-substituted monovacant Keggin polyoxoanion. Cu1 exhibits a

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distorted square-planar geometry defined by two oxygen atoms from one polyoxoanion [Cu−O$_b$ = 1.901(7)−1.961(4) Å] and two nitrogen atoms from one 2,2′-bpy ligand [Cu−N = 1.957(10)−2.023(9) Å], while Cu2 displays a square-pyramidal geometry in which the basic plane is the same as that of Cu1 and the axial vertex is occupied by a oxygen atom from one water molecule.

A remarkable structure feature of compound **1** is the presence of the chair form $[Cu(\mu_2\text{-}OH)]_4^{4+}$ unit comprising three four-membered Cu_2O_2 rings (Figure 1). Each copper ion is chelated by one 2,2′-bpy ligand to form $[Cu(bpy)(\mu_2\text{-}OH)]_4^{4+}$ cations. Two crystallographically independent copper(II) (Cu3 and Cu4) cations are in the cluster: both Cu3 and Cu4 display a square-pyramidal geometry, with the basic plane defined by two oxygen atoms from two hydroxyl groups and two nitrogen atoms from one 2,2′-bpy ligand, while the axial vertex of Cu3 and Cu4 are occupied by one oxygen atom from one hydroxyl group and a terminal oxygen atom from one polyoxoanion, respectively.[13] Interestingly, two dicopper(II)-substituted $[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]^{2-}$ are bridged through the chair form $[Cu(bpy)(\mu_2\text{-}OH)]_4^{4+}$ cations to give a dimeric Keggin polyoxoanion $\{[Cu(bpy)(\mu_2\text{-}OH)]_4[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]_2\}$, as shown in Figure 1. With all of the bpy ligands and two water molecules omitted, the dimer can be better appreciated as a dumbbell, as presented in Figure 2, in which the overall length is 28.43(4) Å and the stick is 12.80(3) Å; this ratio compares well with the scale of the real dumbbell. The dimers are parallelly packed and interact with each other through hydrogen bonds and π···π interactions, which leads to the formation of a 3D supramolecular architecture (Figure 3).

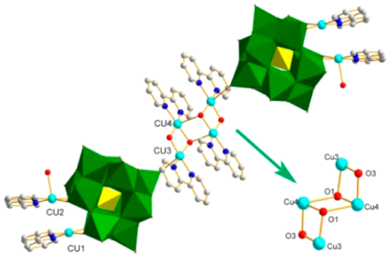

Figure 1. Dimeric $\{[Cu(bpy)(\mu_2\text{-}OH)]_4[(H_2O)(bpy)_2HPW_{11}Cu_2O_{39}]_2\}$ unit and the chair form $[Cu(\mu_2\text{-}OH)]_4^{4+}$ unit in **1**.

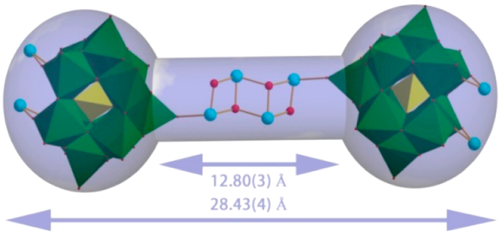

Figure 2. Dumbbell-like structure of **1**.

Powder X-ray diffraction (XRD) measurements for **1** were determined at room temperature (Figure S2 in the SI), and the diffraction peak positions of the experimental XRD patterns of **1** are in agreement with that of simulated XRD patterns, which indicate the phase purity of compound **1**.

POM-based hybrids with copper(II) ions and conjugated ligands are of interest owing to their excellent luminescence performance.[15,16] The luminescence studies of compound **1** and the 2,2′-bpy ligand are explored in the solid state at room temperature. The spectrum exhibits fluorescent emission bands at ca. 466 nm upon excitation at ca. 357 nm, which are associated with ligand-centered π*−π electronic transitions (Figure 4). The emission spectra of compound **1** red-shifted with the free 2,2′-bpy ligand display an emission at 408 nm (λ_{ex} = 337 nm), which may be assigned to the charge-transfer transitions between ligands and metal-ion centers.[14−16] Compared with the free organic ligands, the emission intensity decreases, which may be assigned to the hydrogen-bonding interactions between the guest water molecules and organic ligands.

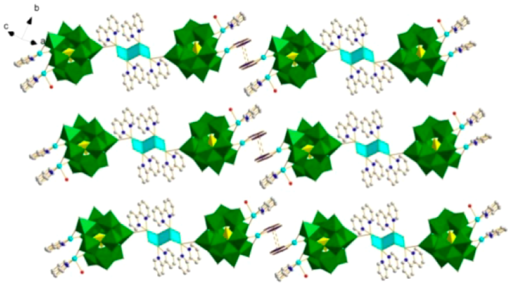

Figure 3. 3D supramolecular architecture built by the dimers. Hydrogen atoms and lattice water and ethyl alcohol molecules are omitted for clarity.

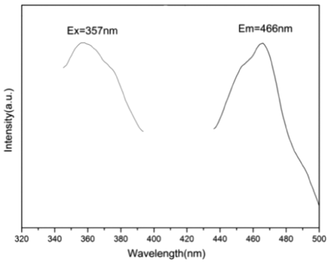

Figure 4. Excitation and emission spectra of compound **1** in the solid state at room temperature.

On the basis of the superinteraction through the tetracopper(II) nucleus in compound **1**, which may potentially possess magnetic features, the magnetic behavior of **1** has been investigated at 500 Oe in the temperature range 2−300 K (Figure 5). The value of χ_M slowly increases from 9.53 × 10^{-3} cm^3 mol^{-1} at 300 K to 3.18 × 10^{-2} cm^3 mol^{-1} at 25 K and then exponentially to the maximum of 0.32 cm^3 mol^{-1} at 2 K. The $\chi_M T$ curve displays a continuous decrease upon cooling from 2.88 cm^3 mol^{-1}K at 300 K, which is a little lower than the calculated value

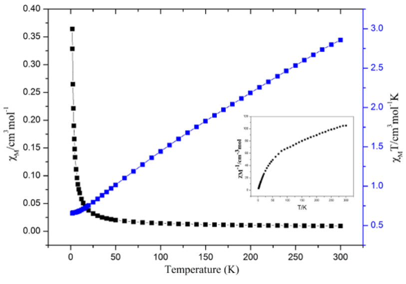

Figure 5. Temperature dependence of $\chi_M T$ (blue) and χ_M (black) (inset, χ_M^{-1}) for compound **1**.

of 2.99 cm^3 mol^{-1} K for the eight uncoupled Cu^{2+} centers (S = $^1/_2$, assuming g = 2.0), to 0.65 cm^3 mol^{-1}K at 2 K, indicating significant antiferromagnetic exchange interactions within the Cu^{2+} ions. In addition, the plot of $\chi_M{}^{-1}$ versus T in the range of 80−300 K obeys the Curie−Weiss law and give the Weiss constant θ = −262.04 K and the Curie constant C = 5.21 cm^3 mol^{-1} K. The large and negative value of θ indicates a dominant antiferromagnetic coupling interaction between the neighboring spins of Cu^{2+} centers, which are stronger than the other reported multicopper clusters.[15,16]

The thermogravimetric analysis (TGA) of **1** (Figure S4 in the SI) exhibits two steps of weight loss processes with a total loss of 19.85% (calcd 20.78%). The TGA curve for **1** shows an initial weight loss of 3.93% (calcd 4.11%) from 70 to 260 °C corresponding to the removal of water and ethyl alcohol molecules, while the weight loss at 260−720 °C, 15.92% (calcd 16.67%), is ascribed to decomposition of the 2,2′-bpy ligands.

A large number of ecofriendly POM-based solid acids and their salts have been employed as catalysts in many organic reactions, particularly in green esterification, oxidation of styrene and acetylation of phenols with acetic anhydride, and nitration of phenols.[17−19] By linking copper complexes and monovacant Keggin polyoxoanion to the novel structure, this approach will offer a way to fine-tune potential catalytic properties. Our experimental results figure that a high yield of 90.5% and selectivity of 97.8% for monododecyl phosphate were achieved with toluene as the dehydrant when the direct esterification of phosphoric acid with lauryl alcohol was carried out at 110 °C for 24 h under an optimum catalyst dosage of 0.5% (mass fraction).

In summary, we have successfully obtained a dumbbell-like dimeric Keggin polyoxoanion that contains the first dicopper(II)-substituted monovacant Keggin polyoxoanion under hydrothermal conditions, which leads to a deeper understanding of the lacunary polyoxoanions. Compound **1** demonstrates the efficiency of hydrothermal methods for the synthesis of new novel POMs and exhibits unprecedented and extended vacant molecular structures. A tetranuclear copper(II) cluster sandwiched between two monovacant phosphotungstates has thus been isolated, and a magnetic model has observed a strong antiferromagnetic interaction between copper(II) centers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, experimental section, synthetic discussion, crystal data, catalytic activity experimental details, IR, TGA, XRD, and selected bond length tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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