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Synthesis and Structure of the Pentacopper(II) Substituted Tungstosilicate $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$

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The dimeric, pentacopper(II) substituted tungstosilicate $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (**1**) has been synthesized in good yield using a one-pot procedure by reaction of Cu^{2+} ions with the trilacunary precursor salt $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$. The title polyanion represents the first polyoxotungstate substituted by 5 copper centers and the central copper–hydroxo–aqua fragment is completely unprecedented. In the course of the reaction, two $[A\text{-}\alpha\text{-}SiW_9O_{34}]^{10-}$ Keggin half-units have fused in an asymmetrical fashion resulting in the lacunary polyoxotungstate $[Si_2W_{18}O_{66}]^{16-}$. The vacancy in this species is stabilized by a magnetic cluster of five octahedrally coordinated Cu^{2+} ions resulting in polyanion **1** with C_{2v} symmetry.

Polyoxometalates (POMs) are metal−oxygen cluster species with a diverse compositional range and an enormous structural variety.[1−6] Although the class of POMs has been known for about 200 years, the mechanism of formation of POMs is not well understood and is commonly described as self-assembly. Therefore, systematic structural design of novel POMs and derivatization of known POMs remains a challenge for synthetic chemists.

Transitional metal substituted polyoxometalates (TMSPs) have attracted increasing attention in recent years because of their highly tunable nature, coupled with their fascinating properties resulting in potential applications in catalysis, material science, and medicine.[7−10] Within the class of TMSPs, the sandwich-type compounds represent the largest subclass.[11] To date the Weakley-, Hervé-, Krebs-, and Knoth-type sandwich polyanions can be distinguished. However, considering that formation of polyanions occurs via self-assembly, the discovery of novel TMSPs with fundamentally novel structures continues to be a focus of considerable ongoing research. These synthetic efforts are often accompanied by attempts to incorporate a large number of paramagnetic transition metal ions in lacunary polyanion fragments, in order to obtain products with interesting magnetic and/or redox properties.

The class of Cu^{2+}-containing, sandwich-type POMs is well-known, and to date numerous complexes have been reported. Most of these polyanions are dimeric and contain three or four Cu^{2+} centers, e.g., $[Cu_3(H_2O)_3(XW_9O_{33})_2]^{12-}$ ($X = As^{III}, Sb^{III}$), $[Cu_4(H_2O)_2(XW_9O_{34})_2]^{n-}$ ($X = P^V, As^V, n = 10$; $X = Si^{IV}, n = 12$).[12] Very recently, we reported on the synthesis and magnetic properties of the tetracopper(II) substituted tungstoarsenate(III) $[Cu_4K_2(H_2O)_8(\alpha\text{-}AsW_9O_{33})_2]^{8-}$.[13] Recently, Mialane et al. reported on a tetrameric Cu_{14}-containing tungstosilicate.[14] Here we report on the first pentacopper(II) substituted polyoxoanion.

Reaction of 0.076 g (0.44 mmol) of $CuCl_2 \cdot 2H_2O$ and 0.50 g (0.16 mmol) of $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$[15] in 20 mL of 0.5 M NaAc buffer (pH 4.8) at 80 °C for 1 h followed by slow evaporation at room temperature resulted in green single

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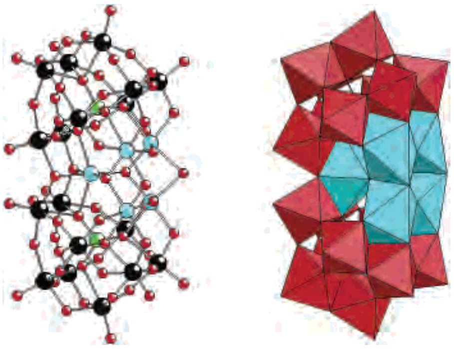

Figure 1. Ball and stick (left) and polyhedral (right) representations of **1**. The color code is as follows: copper (turquoise), tungsten (black), silicon (green), and oxygen (red).

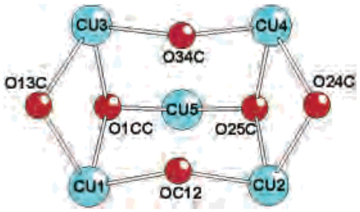

Figure 2. Ball and stick representation of the central $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ fragment of **1**.

crystals of $K_{10}[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]\cdot 18.5H_2O$ (**K-1**, 0.28 g, yield 63%) suitable for X-ray diffraction,[16] FTIR spectroscopy,[17] and elemental analysis.[18]

The dimeric title polyanion $[Cu_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ (**1**) consists of two $A\text{-}\alpha\text{-}[SiW_9O_{34}]^{10-}$ Keggin moieties which are linked via two adjacent W−O−W bonds and stabilized by a central $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ fragment leading to a structure with idealized C_{2v} symmetry (see Figure 1). Polyanion **1** is stable in a very large pH range (pH 1−7) as shown by UV−vis and IR. The tungsten−oxo fragment of **1** is best described as $[Si_2W_{18}O_{66}]^{16-}$ which represents a multilacunary precursor. Interestingly, the potassium salt of this species has been reported recently by Hervé et al.[19] Furthermore, these authors described the structure of the dicobalt derivative $[\{Co(H_2O)\}\{Co(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{11-}$. In this polyanion, the center of the lacunary site is occupied by a potassium ion, and the two inequivalent cobalt(II) ions are located in external positions of the cavity.[19] On the other hand, in **1** the vacancy of $[Si_2W_{18}O_{66}]^{16-}$ is tightly filled with the novel and cationic copper−oxo cluster $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$. Such an arrangement of oxo-bridged transition metal centers has never been observed before in polyoxoanion chemistry. Therefore, the structural details of this unprecedented $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ fragment are of interest (see Figure 2). The bond lengths and angles of the $[Si_2W_{18}O_{66}]^{16-}$ tungsten−oxo framework are not unusual. Bond valence sum (BVS) calculations indicate that all bridging oxo groups linking adjacent copper atoms are either mono- or diprotonated.[20] Specifically, oxygen atoms O1CC, OC12, O25C, and O34C are monoprotonated (OH) whereas oxygen atoms O13C and O24C are diprotonated (H_2O). As expected, the octahedral coordination spheres of all copper(II) centers are Jahn−Teller distorted. The equatorial Cu−O distances range from 1.907 to 2.084(13) Å, whereas the axial Cu−O distances are 2.280−2.387(13) Å. The unique Cu−O−Cu angles of the central $\{Cu_5(OH)_4(H_2O)_2\}^{6+}$ fragment are 83.6(5)° (O24C), 85.0(5)° (O13C), 128.4(6)° (OC12), and 129.3(7)° (O34C), respectively. The angles around O1CC and O25C range from 100.2 to 123.2(6)° and 99.5−123.1(6)°, respectively. The Cu··Cu separations in **1** are as follows: Cu1··Cu2, 3.48 Å; Cu3··Cu4, 3.49 Å; Cu1··Cu3, 3.15 Å; Cu2··Cu4, 3.11 Å; Cu1··Cu5, 3.56 Å; Cu2··Cu5, 3.54 Å; Cu3··Cu5, 3.49 Å; Cu4··Cu5, 3.52 Å.

We also tried to synthesize other first-row transition metal derivatives of **1** by using the same synthetic procedure. We have isolated the Mn-containing analogue $[Mn_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]^{10-}$ as based on IR.[21] Unfortunately, our single crystals of this compound were not of sufficient quality for X-ray diffraction. On the other hand, reaction of Ni^{2+} and Co^{2+} with $K_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$ did not result in isostructural derivatives of **1**. On the basis of single crystal X-ray diffraction we obtained the mononickel substituted $[\{Ni(H_2O)\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{13-}$ (**2**)[22] and the dicobalt substituted $[\{Co(H_2O)\}\{Co(H_2O)_4\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]^{11-}$, respectively. The structure of the former is closely related to the latter, which has already been reported by Hervé et al.[19] However, **2** contains only one nickel center in the lacunary site in addition to the potassium ion.

In summary, we have synthesized the novel pentacopper substituted polyanion **1** and the mononickel substituted derivative **2**. Polyanion **1** contains an unprecedented copper−oxo cluster, and therefore, **1** is highly interesting for magnetic, EPR, electrochemical, and electrocatalysis studies. All this work is currently in progress, and the results will be reported in due time.

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Supporting Information Available: X-ray crystallographic data for **K-1** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Crystal data for **K-1**: $Cu_5H_{45}K_{10}O_{90.5}Si_2W_{18}$, $M = 5567.6$, triclinic, space group $P\bar{1}$, $a = 13.4108(7)$ Å, $b = 15.5496(8)$ Å, $c = 24.1156(12)$ Å, $\alpha = 100.0840(10)°$, $\beta = 101.9270(10)°$, $\gamma = 103.3990(10)°$, $V = 4653.2(4)$ Å^3, $Z = 2$, $T = 173$ K, $D_{calc} = 3.823$ g·cm^{-3}, μ (Mo Kα) = 23.65 mm^{-1}, 33458 measured and 22732 unique reflections ($R_{int} = 0.033$). Final R1 = 0.069 for 19331 observations with $F_o > 4\sigma(F_o)$, R1 = 0.079 (wR2 = 0.179) for all unique data.

(17) IR for **K-1**: 1008, 945, 915, 885, 810, 768, 698, 595, 546, 524 cm^{-1}.

(18) Anal. Calcd (Found) for **K-1**: K 7.0 (7.2), Cu 5.7 (5.6), W 59.4 (59.8), Si 1.0 (1.1).

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(21) IR for $Na_{10}[Mn_5(OH)_4(H_2O)_2(A\text{-}\alpha\text{-}SiW_9O_{33})_2]$: 999, 957, 904, 815, 800, 758, 700, 538, 521 cm^{-1}.

(22) Crystal data for $Rb_3Na_{10}[\{Ni(H_2O)\}\{K(H_2O)_2\}(Si_2W_{18}O_{66})]\cdot 29H_2O$: triclinic, space group $P1$, $a = 12.8710(6)$ Å, $b = 18.6869(8)$ Å, $c = 21.0566(9)$ Å, $\alpha = 69.056(1)°$, $\beta = 87.243(1)°$, $\gamma = 81.251(1)°$, $V = 4674.8(4)$ Å^3, $Z = 2$, $T = 173$ K.