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Short communication

Two Keggin compounds constructed from tri —/tetra-nuclear Cu clusters linked mono copper(II)-substituted phosphomolybdates

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ABSTRACT

Two new compounds based on mono copper(II)-substituted phosphomolybdate, $[Cu_4(tea)_6(H_4PMo_{11}CuO_{39})(PMo_{12}O_{40})]_2 \cdot 33H_2O$ (**1**) and $[Cu_3(tea)_6(H_2O)_2(H_2PMo_{11}CuO_{39})_2]_2 \cdot 30H_2O$ (**2**) (tea = 2-[1,2,4]triazol-4-yl-ethylamine), have been synthesized under hydrothermal conditions. Compound **1** owns tetra-nuclear clusters $[Cu_4(tea)_6]$, linking a pair mono copper(II)-substituted and saturated Keggin anions to form a 2D structure. Compound **2** contains tri-nuclear clusters $[Cu_3(tea)_6]$, fusing four mono copper(II)-substituted anions to construct a discrete four-membered cycle structure.

At present, polyoxometalates (POMs) have attracted extensive interest because of diversity of their structures and extensive applications in catalysis [1], medicine [2], magnetism [3], materials science [4] and other fields [5]. A booming branch of POMs rests on using transition metal-organic subunits to modify POM anions under hydrothermal conditions. However, almost all these anions are saturated ones, such as saturated Keggin-type anions $[PW_{12}O_{40}]^{3-}$ and $[PMo_{12}O_{40}]^{3-}$ [6]. Thus, it becomes a new tend to form lacunary POMs and use metal organic part to substitute one or more inorganic oxide clusters, aiming to lead a new variety of mono- or multi-substituted POM-based structures. In these series, the introduction of metal organic part into lacunary POM frameworks not only can keep thermochemical and redox metal stability, but also conduce to keep the anion integrity in solution. Namely, the formations of mono- or multi-substituted POMs can construct transition metal-organic subunits modified structures with ease compared with lacunary POMs. Recently, some research groups have reported a series of metal substitute POM-based compounds modified by metal-organic subunits, usually based on mono- and tri-substituted anions [7]. For example, in 2008, Yang et al. have obtained a series of unprecedented tri-substituted Keggin anion $\{Ni_6PW_9\}$ under hydrothermal conditions, enriching POM types [8]. In 2005, Wang and co-workers have synthesized a mono-copper substituted anion based compound $[H_2bpy][Cu(4.4'\text{-bpy})]_2[HPCuMo_{11}O_{39}]$, modified by $\{Cu(4.4'\text{-bpy})\}$ subunits [9]. In this compound, the substituted copper atom links adjacent anion through Cu-*O*-Mo bond. In 2011, our group has reported a mono-substituted $\{PW_{11}CuO_{39}\}$-based compound, also using substituted copper atoms to connect adjacent anions through Cu-*O*-W bond [10]. Fortunately, in this work, we obtained another new compound, $[Cu_4(tea)_6(H_4PMo_{11}CuO_{39})(PMo_{12}O_{40})]_2 \cdot 33H_2O$ (**1**), containing both mono copper(II)-substituted and saturated Keggin anions. In these reported mono-substituted POM based compounds and **1**, almost all the substituted metal atoms connect adjacent anions through sharing terminal O atoms, but not directly link organic molecules. However, in this work, we also obtained a mono-substituted phosphomolybdate, $[Cu_3(tea)_6(H_2O)_2(H_2PMo_{11}CuO_{39})_2]_2 \cdot 30H_2O$ (**2**), in which the substituted copper(II) ion links organic ligand through Cu-N bond directly. This linking mode of mono-substituted POMs is really scarce. (See Table 1.)

Up to now, using multi-nuclear metal clusters to modify POMs [11], especially substituted POMs, is rarely observed. The selection of proper organic ligands is essential to construct multi-nuclear clusters. In this work, we choose pendant ligand 2- [1,2,4]triazol-4-yl-ethylamine (tea) as organic moiety, which owns advantages to induce multi-nuclear clusters: (i) its two apical N donors in [1,2,4]triazol group are successive, which can aggregate metal ions with ease; (ii) its ethylamine group can increase steric hindrance, assisting [1,2,4]triazol group to fuse metal ions. Fortunately, a tetra-nuclear Cu^{I} cluster and another tri-nuclear Cu^{II} cluster are actually formed by using tea ligand in this work, confirming that the selection of pendant tea ligand is rational for formation of multi-nuclear clusters.

Herein, by tuning pH, we report two new mono-substituted Keggin-based compounds $[Cu_4(tea)_6(H_4PMo_{11}CuO_{39})(PMo_{12}O_{40})]_2 \cdot 33H_2O$ (**1**) and $[Cu_3(tea)_6(H_2O)_2(H_2PMo_{11}CuO_{39})_2]_2 \cdot 30H_2O$ (**2**) (tea = 2-[1,2,4]triazol-4-yl-ethylamine). The title compounds were prepared from a mixture of $CuCl_2 \cdot 2H_2O$, $H_3PMo_{12}O_{40}$, tea and H_2O at 160 °C for 3 days, by adjusting different pH (initial pH = 3.6 for **1** and 2.5 for **2**) [12]. Single crystal X-ray diffraction analysis [13] shows that

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Table 1
Crystal data and structure refinements for compounds **1** and **2**.

	1	2
formula	$C_{48}H_{182}Cu_{10}Mo_{46}N_{48}O_{191}P_4$	$C_{48}H_{180}Cu_{10}Mo_{44}N_{48}O_{190}P_4$
Fw	9660	9451
crystal system	Monoclinic	Orthorhombic
space group	*P2₁*	*Pbca*
a (Å)	13.0097(5)	22.826(5)
b (Å)	32.8720(13)	23.852(5)
c (Å)	14.1502(6)	39.099(5)
β (°)	116.4670	90.000
V (Å^3)	5417.2(4)	21,287(7)
Z	1	4
D_c (g·cm^{-3})	2.939	2.777
μ (mm^{-1})	3.677	3.612
F(000)	4542	16,840
R_1^a [$I > 2\sigma(I)$]	0.0432	0.0650
wR_2^b (all data)	0.0972	0.1401
GOF on F^2	1.019	0.970

$^aR_1 = \sum\|F_o|-|F_c\|/\sum|F_o|$. $^b wR_2 = \{\sum[w(F_o^2 – F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

compound **1** crystallizes in a *P2₁* space group, consisting of four Cu^I ions, one mono-substituted $[PMo_{11}CuO_{39}]^{5-}$ (abbreviated to $PMo_{11}Cu$), one $[PMo_{12}O_{40}]^{3-}$ (abbreviated to PMo_{12}), six tea ligands and one crystal water molecules (Fig. S1). Both mono-substituted and saturated Keggin anions coexist in compound **1**. The $\{PMo_{11}Cu\}$ is a mono copper(II)-substituted Keggin anion, with one $\{MoO_6\}$ oxide in a classical α-Keggin type anion PMo_{12} substituted by one $\{CuO_6\}$ unit. The substituted Cu5 ion is six-coordinated by six O atoms (O55, O59, O41, O56, O65 and O29). The valence sum calculations [14] show that all Mo atoms are in +VI oxidation state. The Cu5 atom in $PMo_{11}Cu$ is in +II oxidation state, while the other copper atoms are in +I oxidation state. In order to balance charge, four protons have been added and **1** is formulated as $[Cu_4(tea)_6(H_4PMo_{11}CuO_{39})(PMo_{12}O_{40})]_2 \cdot 33H_2O$.

Except Cu5, the rest copper atoms (Cu1, Cu2, Cu3 and Cu4) are all four-coordinated in triangular pyramidal coordination geometry. Both Cu1 and Cu2 are coordinated by three N donors (N2, N5 and N9 for Cu1; N1, N14 and N17 for Cu2) from three tea ligands and one O atom (O32 for Cu1; O30 for Cu2) from a saturated PMo_{12} anion. The Cu3 and Cu4 are coordinated by three N donors (N13, N18 and N21 for Cu3; N10, N16 and N22 for Cu4) from three tea ligands, one O atom (O69 for Cu3; O79 for Cu4) from one mono-substituted $PMo_{11}Cu$ anion. The Cu-N distances are in the range of 1.956(10)-2.043(11) Å, while the Cu-O distances range from 1.926(8) to 2.544(8) Å. The *O*-Cu-O angles are in the range of 76.1(3)-169.5 (3)°, while the *O*-Cu-N angles are from 85.0(4) to 105.9(4)° (Table S1). These bond lengths and angles of Cu^I are all within the normal range [15].

In compound **1**, there are two interesting building blocks: (i) POM anionic dimmer (Fig. 1a); (ii) tetra-nuclear copper cationic cluster (Fig. 1b). In the anionic dimmer, the mono copper(II)-substituted $PMo_{11}Cu$ anion links a saturated PMo_{12} anion through Cu5-O29-Mo4 bond. In the tetra-nuclear cluster, four Cu ions (Cu1, Cu2, Cu3 and Cu4) are fused by six tea molecules by offering all the twelve apical N donors, with ethylamine groups surrounding it. In these two building blocks, the mono copper(II)-substituted anion offers O69 to link Cu3 atom of the tetra-nulcear cluster, while the saturated anion provides O32 to connect Cu1 atom of another cluster. Thus, a wave-like 1D chain is constructed with anionic dimmers and tetra-nuclear clusters arranging alternately (Fig. 2). Adjacent parallel chains connect each other through Cu2-O30 and Cu4-O79 to build a 2D network (Fig. 3). However, if those long Cu-O bonds are not considered, compound **1** is an isolated structure rather than a 2D layered structure.

Single crystal X-ray diffraction analysis [13] shows that compound **2** crystallizes in a *Pbca* space group, consisting of six copper ions, four $PMo_{11}Cu$, twelve tea ligands, four coordinated and thirty crystal water molecules (Fig. S2). In compound **2**, the $PMo_{11}Cu$ is also a mono copper(II)-substituted Keggin anion, but with one $\{MoO_6\}$ oxide in PMo_{12} substituted by one $\{CuO_5N\}$ unit. The substituted Cu ions (Cu4 and Cu5 in different anions) are six-coordinated by five O atoms from the anion and one N atom from a tea ligand (Fig. 4a). The valence sum calculations [13] show that all Mo atoms are +VI oxidation state and all the Cu atoms are in +II oxidation state [12]. In order to balance charge, eight protons have been added and **2** is formulated as $[Cu_3(tea)_6(H_2O)_2(H_2PMo_{11}CuO_{39})_2]_2 \cdot 30H_2O$.

Except substituted Cu4 and Cu5, there still exist three copper atoms (Cu1, Cu2 and Cu3), which are six-coordinated in octahedral coordination geometry. Both Cu1 and Cu3 are coordinated by three N donors (N13, N18 and N21 for Cu1; N1, N9 and N17 for Cu3) from three tea ligands, two O atoms (O38 and O67 for Cu1; O10 and O70 for Cu3) from two anions and one O1W molecule. The Cu2 is coordinated by three N donors (N2, N5 and N14) from three tea, one O70 from one anion and two water molecules (O1W and O2W). The Cu-N distance are in the range of 1.964(11)-2.199(10) Å, while the Cu-O distances range from 1.931(9) to 2.404(8) Å. The *O*-Cu-O angles are in the range of 74.8(3)-177.1(3)°, while the *O*-Cu-N angles are from 82.2(4)° to 173.2(4)° (Table S1). These bond lengths and angle of Cu^{II} are all within the normal range [16].

Different from other mono-substituted Keggin anions and compound **1**, the mono copper(II)-substituted anion in **2** links organic ligands directly through Cu-N bonds (Cu4-N22 and Cu5-N10) (Fig. 4a). This character becomes the structural feature of **2**. Furthermore, compound **2** owns a tri-nuclear Cu^{II} clusters, with three Cu^{II} ions (Cu1, Cu2 and Cu3) fused by six tea molecules (Fig. 4b). One O1W water molecule rests on the center of this tri-nuclear cluster, further stabilizing this subunit. In this tri-nuclear cluster, five tea ligans all donate two N donors to fuse two Cu^{II} ions, while the left one tea only offers one N atom to link one Cu2 ion to satisfy octahedral coordination mode of Cu2. In this cluster, the N22 and N10 donors in two tea ligands connect two mono copper(II)-substituted anions through Cu4-N22 and Cu5-N10 bonds respectively (Fig. S2). Namely, two mono-substituted anions are linked by a tri-nuclear Cu^{II} cluster to form an anionic dimmer.

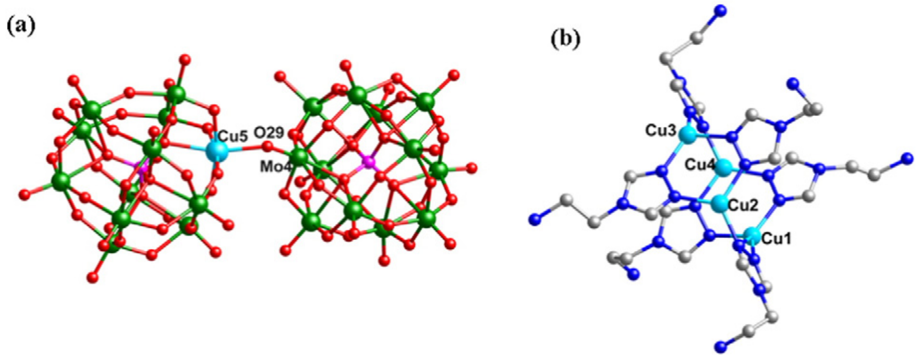

Fig. 1. (a) The POM anionic dimmer in compound **1**; (b) The tetra-nuclear Cu^I cluster.