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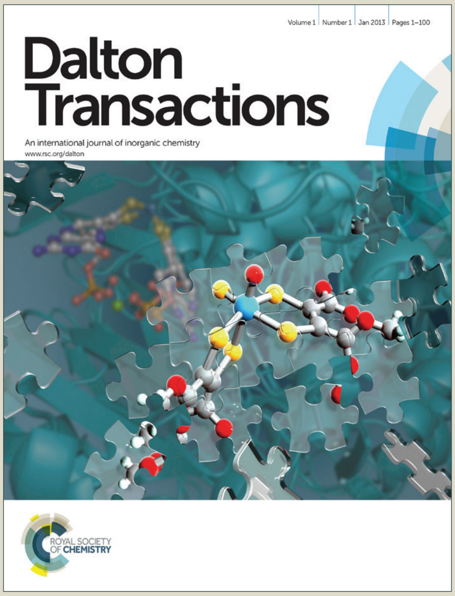

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ARTICLE TYPE

A novel poly(polyoxometalate) built by $\{Cu_9\}/\{Cu_5\}$ clusters and $\{PW_9\}/\{PW_{10}\}/\{PW_{11}\}$ lacunary fragments

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The hydrothermal reactions of $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$ with $CuCl_2\cdot 2H_2O$ in the presence of ethanediamine (en) and acetate afforded a novel poly(polyoxotungstate)s cotaining different lacunary fragments: monolacunary $\{\alpha\text{-}PW_{11}O_{39}\}$, dilacunary $\{\alpha\text{-}PW_{10}O_{37}\}$, and trilacunary $\{B\text{-}\alpha\text{-}PW_9O_{34}\}$, etc. In addition, cockhorse-like nona-copper $\{Cu_9\}$ slab is incorporated. Magnetic investigation indicates overall antiferromagnetic interactions in this compound.

Polyoxometalates (POMs) represent a class of polyanionic metal oxo clusters based on tungsten, molybdenum, vanadium, and niobium.[1] Polynuclear transition-metal (TM) clusters may possess large spin ground state and may exhibit single-molecule magnetism.[2] The synthesis of combined POMs and TM clusters is predominantly driven not only in their structural diversity but also in their rich catalytic, electrochemical and magnetic properties.[3] To date, many researchers have devoted great efforts to explore synthetic strategies for making TM substituted polyoxotungstates (TMSPs).[4] One effective approach is to encapsulate high-nuclearity TM clusters into the lacunary poly(polyoxotungstate)s (poly(POT)s), such as Fe_{27}[4a] Co_{16},[4b] Mn_{40},[4c] Nb_{16},[5] Ni_{40},[6] and Zr_{24}.[7]

Compared with the above TM-substituted POTs, the chemistry of Cu-substituted POTs has attracted considerable attention.[8] On one hand, Cu ions adopt flexible coordination geometries.[9] On the other hand, the axial distortion of the Jahn-Teller and pseudo-Jahn-Teller effect would overcome larger steric hindrance and help to stabilize the in situ formed larger aggregates.[8a] Moreover, it allows multi-dimensional organizations *via* long Cu–O/N bonds. So far, the highest number of Cu ions incorporated in the sandwiched POTs is eight.[10] The tetrameric wheel-shaped Cu_{20}-substituted poly(POT)s represent the highest number of Cu ions among Cu-substituted poly(POT)s.[11] During the last decade, we have made some progress in TM-cluster-substituted poly(POT)s by structure-directing of the lacunary sites of POTs,[12] the synergistic directing of different trilacunary fragments,[4g, 9] as well as the cooperation between the structure-directing of the lacunary sites of POTs and the directing assembly of the organic ligands.[4h] Recently, the giant cluster-based Ni_{40}-,[6] and Zr_{24}-[7]substituted poly(POT)s are reported under the guidance of these strategies. In continuation with the study of Cu-substitued poly(POT)s, we present herein an unprecedented poly(POT)s, $(H_2en)[Cu(en)_2(H_2O)]_2\{[Cu_5(en)_2(OH)_2(CH_3COO)_2(H_2O)_8][Cu_{10.75}(en)_6(OH)_4(H_2O)_5(\alpha\text{-}PW_{11}O_{39})(\alpha\text{-}PW_{10.25}O_{37})(B\text{-}\alpha\text{-}PW_9O_{34})]_2\}\cdot 18H_2O$ (**1**). The poly(POT)s not only contains three distinct types of Keggin vacant POT fragments, but also include nona-copper slab.

Dark green crystals of **1** were hydrothermally synthesized‡ and structurally characterized using single-crystal X-ray diffraction.§ The morphology and crystallinity of the sample retains since 2009, which revealing its exceptional stability in air (Fig. S1, Table S1). Its composition and purity has been demonstrated by elemental analysis, ICP, IR spectrum (Fig. S2) and powder X-ray diffraction (PXRD) (Fig. S3). The numbers of Cu and W atoms are not integer for crystallographic refinement resulted in occupancy factors of 0.75 for Cu9 and 0.25 for W31,[4a] which is confirmed by the results of chemical analysis. All hydroxyl bridges and coordination water molecules are localized by bond valence sum (BVS) calculations.[13] The detailed structure of this large molecule will be presented like peeling the onion. **1** contains a polyanion of $[Cu_{26.5}(en)_{14}(OH)_{10}(CH_3COO)_2(H_2O)_{18}P_6W_{60.5}O_{220}]^{6-}$ (**1a**), two $[Cu(en)_2(H_2O)]^{2+}$ complexes and one doubly protonated en as the countercations (Fig. S4). The polyanion (Fig. 1a) with a size of 2.1×4.1 nm can be viewed as two symmetry-related half units ligated by "S"-shaped penta-copper segment.

The half unit is a combination of $[Cu(en)_2(H_2O)]^{2+}$ decorated $\{Cu_6(en)_3(OH)_3(H_2O)_3PW_9O_{34}\}$ ($\{Cu_6PW_9\}$), $\{Cu_{2.75}(en)(OH)(H_2O)PW_{10.25}O_{37}\}$ ($\{Cu_3PW_{10}\}$) and mono-Cu substituted $\{\alpha\text{-}PW_{11}O_{39}\}$ ($\{CuPW_{11}\}$). All of three parts are associated by Cu-O=W bridges. One pertinent feature of the half unit is the coexistence of three distinct Keggin POT fragments. The structure transformation of divacant $[\gamma\text{-}SiW_{10}O_{36}]^{8-}$ to three inequivalent lacunary silicotungstates have reported by Cronin et al in aqueous solution.[14] Similar transformation of phosphotungstates is observed herein in hydrothermal condition. $\{Cu_6PW_9\}$ is a trilacunary POTs capped by a equilateral triangle $\{Cu_6(en)_3(OH)_3(H_2O)_3\}$ ($\{Cu_6\}$) core. The skeleton of $\{Cu_6\}$ is built by three truncated cubanes shared one edge with each other, and all sharing a common vertex (μ_4-O7). All of the six copper ions (Cu1-Cu6) reside in six-coordinated octahedron. Three interior octahedra (Cu2, Cu3, Cu5) are located at the trivacant sites of $B\text{-}\alpha\text{-}PW_9O_{34}{}^{9-}$. While the three exterior ones are attached to interior triad *via* three μ_3-OH bridges (Fig. S5). The $\{Cu_3PW_{10}\}$ is a dilacunary POTs capped by a $[Cu_{2.75}(en)(OH)(H_2O)]$ ($\{Cu_3\}$) core. Cu7 and Cu9 ions are located in the vacant sites of $\{\alpha\text{-}PW_{10}O_{37}\}$, while Cu8 occupies four membered ring windows between two W_2CuO_{13} units (Fig. S6). Notably, the Cu8 ion resides in a seven-coordinate monocapped trigonal prismatic

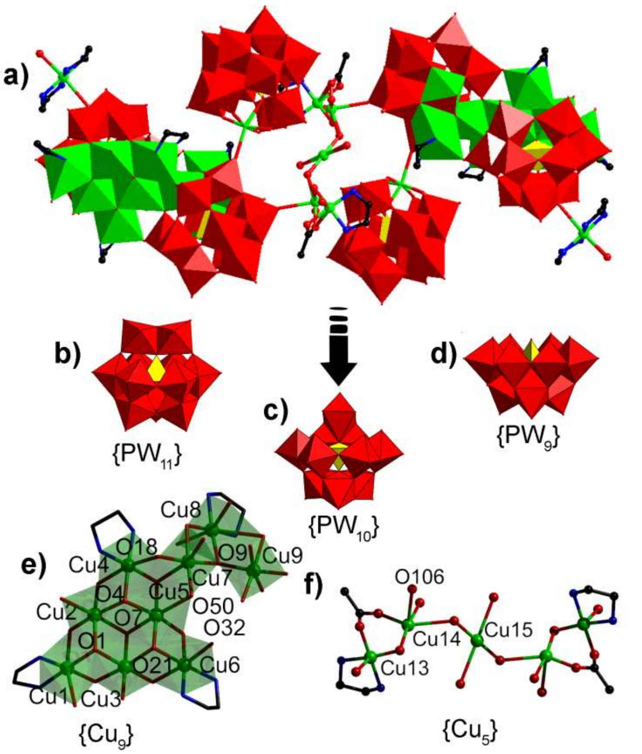

Fig. 1 (a) Structure of **1a** with idealized C_i symmetry; (b-d) Polyhedral view of three lacunary POTs: {PW_{11}}, {PW_{10}}, and {PW_9}; (e-f) Ball-stick view of the cockhorse-like nona-copper cluster and S-shaped penta-copper segment. Color code: WO_6 red, PO_4 yellow, CuO_xN_y green, Cu green, C black, N blue, O red.

geometry. The coordinate environment is completed by one μ_3-OH [Cu8-μ_3-OH: 2.030(11) Å], three μ_3-O atoms [Cu8-μ_3-O: 2.023(11)-2.967(12) Å] from {α-$PW_{10}O_{37}$} unit, a terminal oxygen atom from adjacent {B-PW_9} unit [Cu8-O_t: 2.345(12) Å], and one en molecule [Cu8-N: 1.975(14)-2.032(16) Å]. Although seven-coordinate mode of Cu atoms is common in coordination polymers,[15] it is rare in TMSPs. Though the [A-α-PW_9O_{34}]$^{9-}$ ({A-PW_9}) fragment was used as the starting material, **1a** contains mono-lacunary [α-$PW_{11}O_{39}$]$^{7-}$ ({PW_{11}}, Fig. 1b), dilacunary [α-$PW_{10}O_{37}$]$^{9-}$ ({PW_{10}}, Fig. 1c) and trilacunary [B-α-PW_9O_{34}]$^{9-}$ ({B-PW_9}, Fig. 1d). The transformations of {A-PW_9}→{PW_{11}},[16] {A-PW_9}→{PW_{10}},[17] and {A-PW_9}→{B-PW_9}[8a] have been reported, separately. However, it is firstly found that three of them are synchronously incorporated into a poly(POT). The sequence of these transformations can't precisely identify, while the rapidly inter-exchangeable, highly reactive intermediates of POMs could serve as inorganic supporting ligands to ligate TM clusters formed *in situ*.

Another remarkable feature of the half unit is the occurrence of nona-Cu slab, in which the hexa- and tri-Cu cluster capped on {PW_9} and {PW_{10}} moieties are joined together by three μ_3-O (O18, O32, O50) atoms (Fig. 1e). The typical structural types of sandwiched Cu-substituted POT dimers range from tri-,[18] tetra-,[19] penta-,[20] hexa-,[8a, 21] to octa-nuclear (Fig. S7).[9-10, 22] Till now, the largest number of metal atoms in the sandwich belts is eight. In addtion, Cu6 and Cu8 coordinate to the terminal oxygen atoms of neighboring Keggin units through two parallel Cu-O=W bridges compensating the weak axial Cu-O bonds and strengthen the stability of the slab.

As shown in Fig. 1f, the S-shaped penta-Cu segment contains three independent Cu atoms: five-coordinated Cu13, Cu14, and four-coordinate Cu15. It is noteworthy that the connectivity between Cu14 and a terminal oxygen atom [Cu14-O106: 2.566Å] of {α-$PW_{10}O_{37}$}, plays a crucial role in the construction of the poly(POT)s. In the packing arrangement in the *ab* plane, the poly(POT)s are arranged in the −AAA− fashion (Fig. S8). Projection along the *a*-axis shows channels with the porosity about 13.3% of the total unit cell volume, which is occupied by counterions and lattice water molecules. The number of lattice water molecules is confirmed by a combination of chemical analysis and thermogravimetric analysis (Fig. S9).

To study the preliminary magnetic property of the semi-conductor (band gap = 3.89 eV, Fig. S10), variable-temperature magnetic susceptibilities was measured (Fig. 2). The experimental $\chi_M T$ value of 10.43 emu·mol^{-1}·K at 300 K is in good agreement with the sum of the spin-only contribution (10.69 emu·mol^{-1}·K) for 28.5 uncoupled high-spin Cu^{2+} ions with S = 1/2 and g = 2.0 per formula unit. Upon cooling until 45 K, the $\chi_M T$ value shows a slowly decrease. Then, the $\chi_M T$ value decreases rapidly to reach the minimum of 5.86 emu·mol^{-1}·K at 2 K, where the sudden decrease might be mainly attributed to the presence of zero-field splitting and inter-cluster magnetic interactions. Such magnetic behavior suggests the overall antiferromagnetic interactions within Cu^{II} centers. The temperature dependence of the reciprocal susceptibilities ($1/\chi_M$) obeys the Curie-Weiss law above 30 K with negative Weiss constant θ = -7.93 K (Fig. S11), which confirms the presence of overall anti-ferromagnetic coupling within Cu^{II} centers. The Curie constant C = 10.68 emu·mol^{-1}·K is also reasonable for 28.5 Cu^{II} ions per formula unit.

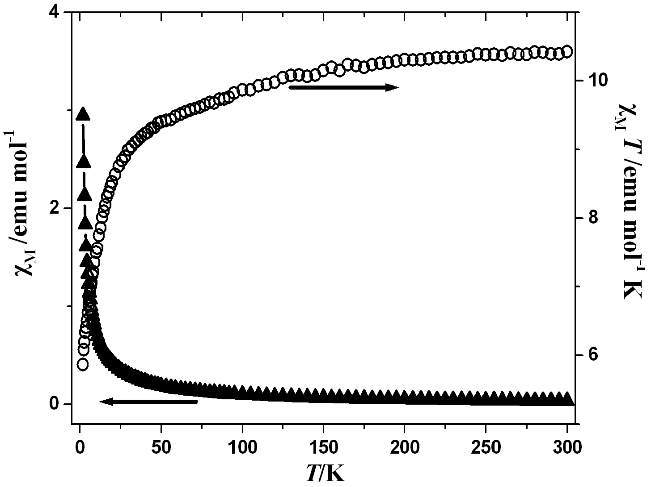

Fig. 2 Temperature dependence of χ_M (▲) and $\chi_M T$ (O) values for **1**.

In summary, the poly(POT)s contains multi-lacunary clusters, nona-Cu slab, and S-shaped penta-Cu clusters are successfully made under hydrothermal condition. The isolation of this poly(POT)s demonstrates that the combination of hydrothermal techniques and lacunary POT structure direct agents affords an effective strategy for making large Cu-substituted poly(POT)s . And such synthetic method may be extended to other similar members of TM-substituted POT family. In view of the stability and semi-conductivity as well as the bareness of the nona-Cu slab, the poly(POT)s may possess potential catalytic activity. Investigation on the catalytic behavior of a series of poly(POT)s is in progress.

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Notes and references

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† Electronic Supplementary Information (ESI) available: X-Ray structure data in CIF files for compound **1** (CCDC-807965); Materials and physical measurements; photographs of crystals; IR spectrum; TGA curve; PXRD patterns; uv-vis spectrum. See DOI: 10.1039/b000000x/

‡ Synthesis of **1**: $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}]\cdot 7H_2O$ (PW_9)[23] (0.256 g, 0.1 mmol), $CuCl_2\cdot 2\ H_2O$ (0.170 g, 1.0 mmol), en (0.05 mL, 0.75 mmol), and acetate (0.10 mL, 1.75 mmol) were successively added into distilled water (5 mL, 278 mmol). Being stirred at room temperature for 30 min (pH 3.9), the mixture was sealed in a 30 mL Teflon-lined stainless steel autoclave, heated under autogeneous pressure at 100 ºC for 5 days, and then cooled to room temperature naturally in air (pH 3.8). Green strips of crystals were collected by filtration, washed with distilled water, and dried in air. Yield: 13% (based on PW_9). To optimize the experimental parameters and improve the yield of reaction, a series of comparative experiments were carried out. When the reaction temperature raise to 120ºC, 140ºC or even higher, only amorphous powders were received. While reducing temperature to 80ºC resulted in $[\{Cu_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_3\}(B\text{-}\alpha\text{-}PW_9O_{34})]\cdot 7\ H_2O$.[10] When the dosage of acetate was set to 0.20, 0.40, 0.60, 0.8 mL, green crystals of hexa-copper sandwiched POTs were always obtained.[8a, 10] The attempts of replace en by other amines, like 1,2-diaminopropane, diethylenetriamine to make isostructures were field. It shows the synthesis of poly(POT)s should perform under harsh conditions. However, it's encouraging that the sample can be reproduced (once about 30 mg in an autoclave). Chemical analysis calcd (%) for $C_{42}H_{246}N_{38}O_{272}Cu_{28.5}P_6W_{60.5}$: C 2.69, H 1.30, N 2.84, P 0.99, Cu 9.67, W 59.41; found: C 3.01, H 1.54, N 3.14, P 1.08, Cu 9.38, W 58.87.

§ Crystal data for **1**: $C_{42}H_{246}N_{38}O_{272}Cu_{28.5}P_6W_{60.5}$, Mr = 18756.40, triclinic, space group $P\bar{1}$, a = 12.159(3), b = 22.224(4), c = 30.636(6) Å, α = 92.391(3), β = 97.373(3), γ = 95.874(3)°, V = 8154(3) Å^3, T = 293(2) K, Z = 1, ρ = 3.820 g·cm^{-3}, μ = 23.185 mm^{-1}, $F(000)$ = 8334, GOF = 1.031. A total of 52071 reflections were collected, 27447 of which were independent (R_{int} = 0.0525). $R1/wR_2$ = 0.0532/0.1302 for 1950 parameters and 21646 reflections ($I>2\sigma(I)$).

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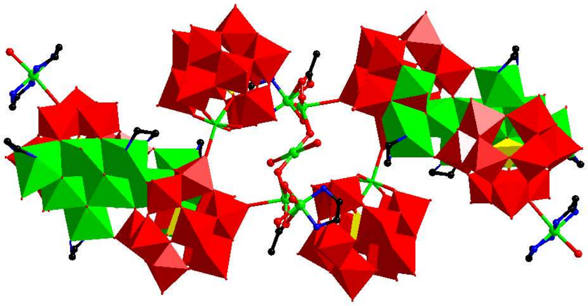

The synergistic directing effect of six multi-lacunary Keggin fragments leads to the formation of a $Cu_{28.5}$-based poly(polyoxotungstate)s (poly(POT)s), not only showing the largest Cu-substituted POTs, but also representing typical example of poly(POT)s comprising three types of Keggin vacant units. In addition, cockhorse-like $\{Cu_9\}$ cluster and S-shaped $\{Cu_5\}$ bridge are incorporated.