

Short communication

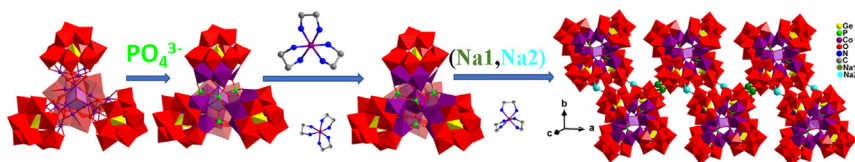
## A new inorganic-organic hybrid transition-metal-substituted polyoxometalate

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## GRAPHIC ABSTRACT



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## ABSTRACT

A new inorganic-organic hybrid transition-metal-substituted polyoxometalate  $H_{27}Na_2[Co(en)_3]_2\{[Co_4(OH)_3(PO_4)]_4(GeW_9O_{34})_4\}Cl \cdot 57H_2O$  (**1**, en = ethylenediamine) was obtained under hydrothermal conditions and characterized by single-crystal X-ray diffraction, IR spectroscopy, thermogravimetric analysis, elemental analysis, diffuse-reflectance spectroscopy and powder X-ray diffraction, respectively. Single-crystal structure analysis proved that polyanion  $[\{Co_4(OH)_3(PO_4)\}_4(GeW_9O_{34})_4]^{32-}$  (**1a**) and complex cation  $[Co(en)_3]^{2+}$  (**1b**) exist in compound **1** simultaneously, exhibiting a 1D-chain built by **1a** cluster units and  $Na^+$  cations. The cyclic voltammetry (CV) shows reversible multielectron waves from the redox of  $W^{VI}$  in **1**.

It is well-known that transition-metal-substituted polyoxometalates (TMSPs) are of great interest in the last decades owing to their controlled structures. The physical and chemical properties of different structures are applicable to diverse areas, such as magnetism, optics, catalysis, sensor, luminescence and materials science [1–3].

TMSPs with different nuclearities have been explored energetically, high-nuclearity TMSPs are usually made by bridge O/OH to assemble into cluster [4–8], meanwhile the cluster skeleton becomes unstable because of the growing degree of polymerization. So in order to make and stabilize high-nuclearity TMSPs, small inorganic ligands ( $C_2O_4^{2-}$ ,  $CO_3^{2-}$ ,  $PO_4^{3-}$ ) [9–11] or organic ligands (en, piperazine, 1,2-diaminopropane) [12–14] have been widely employed.

As an inorganic ligand,  $PO_4^{3-}$ , with abundant coordination sites, small spatial steric resistance and abundant raw materials, it has been widely used in making high-nuclearity clusters. The first  $PO_4^{3-}$  ligand used in tetrameric comprising 3d metal-containing Keggin

tungstophosphates is  $\{[Fe_{1.5}^{II}Fe_{1.5}^{III}(OH)_{12}(PO_4)_4](B-\alpha-PW_9O_{34})_4\}$  in 2007 [15]. The first Co-containing similar structure with single molecule magnet behavior  $[\{Co_4(OH)_3PO_4\}_4(PW_9O_{34})_4]^{28-}$  was made in 2011 [16]. After that,  $[\{Co_4(OH)_3PO_4\}_4(XW_9O_{34})_4]^{n-}$  ( $X = P, Ge, Si, As$ ) was produced in 2014 [17]. The above mentioned TMSPs all have a same feature, a cubane unit  $\{M_4O_4\}$  ( $M = Co, Mn, Ni$ ) locate the core of high-nuclearity TMSPs. Up to date, besides the usual cubane unit, there are some distorted cubane units such as quasi-cubane  $\{Mn_3^{III}Mn^{IV}O_3\}$  [18], double-quasi-cubane  $\{Co_7O_6\}$  [19], face-sharing-double-cubane  $\{Mn_4^{III}Mn_2^{IV}O_6\}$  [20] and so on.

Our group has made great progress in TMSPs under hydrothermal conditions [1,13–15,20]. As our continued work, herein a new inorganic-organic hybrid TMSP,  $H_{27}Na_2[Co(en)_3]_2\{[Co_4(OH)_3(PO_4)]_4(GeW_9O_{34})_4\}Cl \cdot 57H_2O$  (**1**) has been made. Compared to other similar TMSPs, it has three traits: (1) By means of hydrothermal technique, organic amines are introduced; (2) Inorganic ligand  $PO_4^{3-}$  and organic

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ligand en exist in **1** simultaneously; (3) There are two kinds of O–Na–O linkages to connect polyoxoanion form a 1-D chain.

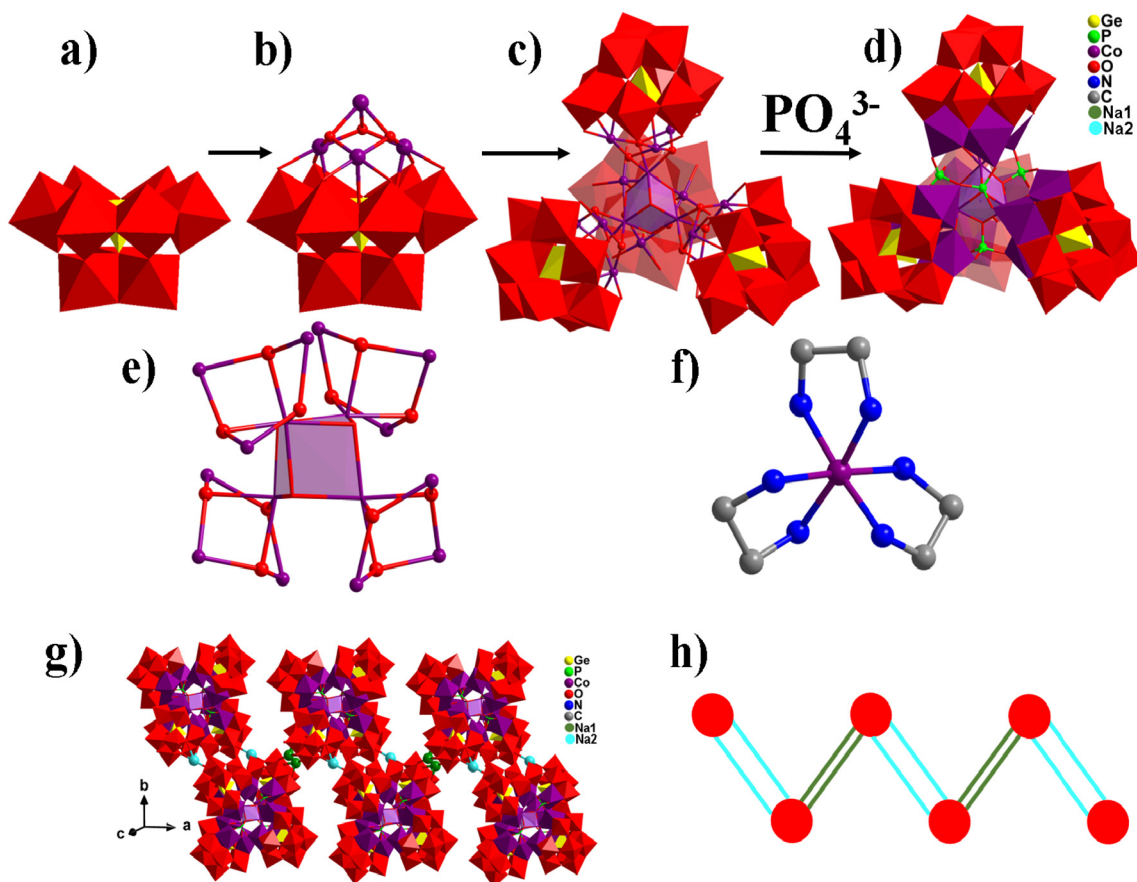
Compound **1** was hydrothermally synthesized by the reaction of  $\text{Na}_{10}[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}] \cdot 18\text{H}_2\text{O}$  (0.600 g, 0.21 mmol),  $\text{Co}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (0.365 g, 2 mmol),  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  (0.380 g, 1 mmol) in a 25 mL Teflon-lined autoclave with 8 mL distilled water. Adding 0.05 mL en to the stirring mixture, pH get to 9 with 4 M HCl. The stirring continued for 30 min at room temperature, then the resulting mixture was sealed and heated at 140 °C. After 3 days, cooled to room temperature, purple strip crystals were obtained by filtration. Then washed with distilled water and air-dried. Yield: 47% based on  $\text{Na}_{10}[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}] \cdot 18\text{H}_2\text{O}$ . Elemental analysis calcd (wt%) for **1**: C 1.17, H 1.65, N 1.37; Found: C 1.09, H 1.69, N 1.31. The phase purity of the products of **1** were proved by the powder X-ray diffraction. The experimental pattern is in good agreement with the simulated patterns from single crystal X-ray diffraction (Fig. S1).

Single-crystal X-ray diffraction reveals that **1** crystallizes in the monoclinic space group  $P2_1/c$  [21]. In the structure, the polyoxoanion  $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)\}_4(\text{GeW}_9\text{O}_{34})_4]^{32-}$  (**1a**) contains 4  $[\text{GeW}_9\text{O}_{34}]^{10-}$  fragments, 1  $\{\text{Co}_{16}(\text{OH})_{12}\}$  cluster, 4  $\text{PO}_4^{3-}$  groups, 2  $[\text{Co}(\text{en})_3]^{2+}$  complex cations, 2  $\text{Na}^+$ , 1  $\text{Cl}^-$ , 27 protons and 57 lattice water molecules (Fig. S2). The formation of the polyoxoanion **1a** (Fig. 1d) can be understood as follows: (1) Firstly, 4  $\text{Co}^{2+}$  ions connect each other by 3  $\mu_3\text{-OH}$  groups to form a  $\text{Co}_4(\text{OH})_3$  cluster and then capped on the trilacunar precursor  $[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]^{10-}$  (Fig. 1a) to form the  $\text{Co}_4$ -substituted cluster  $[\{\text{Co}_4(\text{OH})_3(\text{GeW}_9\text{O}_{34})\}]^{5-}$  (Fig. 1b). (2) Secondly, four same  $[\{\text{Co}_4(\text{OH})_3(\text{GeW}_9\text{O}_{34})\}]^{5-}$  clusters are linked by 4  $\mu_4\text{-O}$  atoms to produce the cluster  $[\{\text{Co}_4(\text{OH})_3(\mu_4\text{-O})\}_4(\text{GeW}_9\text{O}_{34})_4]^{28-}$

(Fig. 1c). Notice that the precursor  $[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]^{10-}$  keep the same conformation in the whole process of reaction. At last, four  $\text{PO}_4^{3-}$  ligands shared  $\mu_4\text{-O}$  groups to further stabilize the cluster skeleton of **1a** (Fig. 1d), of which the distorted cubane  $\{\text{Co}_4\text{O}_4\}$  in the centre of  $\{\text{Co}_{16}(\text{OH})_{12}\text{O}_4\}$  unit (Fig. 1e) consist of 4  $\mu_4\text{-O}$  atoms and 4  $\text{Co}^{2+}$  ions, each  $[\{\text{Co}_4(\text{OH})_3(\text{GeW}_9\text{O}_{34})\}]^{5-}$  cluster provide a  $\text{Co}^{2+}$  ion. As one of type of counter cations, the complex  $[\text{Co}(\text{en})_3]^{2+}$  (**1b**, Fig. 1f) contains three chelated en ligands and one  $\text{Co}^{2+}$  cation. In the asymmetric unit, two  $[\text{Co}(\text{en})_3]^{2+}$  cations distribute on the both sides of the polyoxoanion **1a** (Fig. S2). Interestingly, polyoxoanion **1a** are linked by two  $\text{Na}1^+$  and two  $\text{Na}2^+$  cations in two different directions to form a zigzag 1-D chain (Fig. 1g), and its simplified representation is shown in Fig. 1h.

The oxidation states of all cobalt ions are +2 that have been proved by BVS (bond valence sum calculations) (Table S1). There are three crystallographically independent cobalt ions with hexa-coordination modes in the asymmetric unit of **1**: (1) the  $\text{Co}^{2+}$  ions occupied the vacancy sites of precursor  $[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]^{10-}$  coordinate to 3 O atoms of trilacunar precursor, a  $\mu_4\text{-O}$  (shared with  $\text{PO}_4$  ligand), 2  $\mu_3\text{-OH}$  groups; (2) the  $\text{Co}^{2+}$  ions of  $\{\text{Co}_4\text{O}_4\}$  cubane unit are coordinated by 3  $\mu_3\text{-OH}$  groups and 3  $\mu_4\text{-O}$  (shared with  $\text{PO}_4^{3-}$  ligands); (3) the  $\text{Co}^{2+}$  ions of  $[\text{Co}(\text{en})_3]^{2+}$  complexes are completely different from fore-mentioned, coordinate to 6 N atoms of 3 en ligands.

In the structure of **1**, the Co–O–Co angles of cluster  $\{\text{Co}_{16}(\text{OH})_{12}\}$  are in the range of  $91.4(7)^\circ$ – $133.3(9)^\circ$ , which matches the range of the Co–O–Co angles of  $92.2(5)^\circ$ – $131.2(10)^\circ$  in the reported  $\text{Co}_{16}$ -cluster-substituted POM  $[\{\text{Co}_4(\text{OH})_3(\text{PO}_4)\}_4(\text{PW}_9\text{O}_{34})_4]^{28-}$  [16]. According to the structure and connection motif of magnetic centers in **1**, possibly



**Fig. 1.** (a–c) View of  $[\text{A-}\alpha\text{-GeW}_9\text{O}_{34}]^{10-}$ ,  $[\{\text{Co}_4(\text{OH})_3(\text{GeW}_9\text{O}_{34})\}]^{5-}$ , and  $[\{\text{Co}_4(\text{OH})_3(\mu_4\text{-O})\}_4(\text{GeW}_9\text{O}_{34})_4]^{28-}$ , respectively. (d) View of **1a**. (e, f) View of  $\{\text{Co}_{16}(\text{OH})_{12}\}$  unit and  $[\text{Co}(\text{en})_3]^{2+}$  cation. (g) View of the 1-D chain. Color codes:  $\text{GeO}_4$  yellow;  $\text{WO}_6$  red;  $\text{CoO}_6$  purple;  $\text{Co}_4\text{O}_4$  light purple. (h) Simplified representation of 1-D zigzag chain. **1a**, red; O–Na1–O bond, dark green; O–Na2–O bond, light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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