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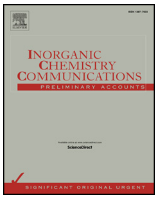

Short communication

Extended structure constructed from $\{Co_7\}$ cluster-containing sandwich-type polyoxometalate

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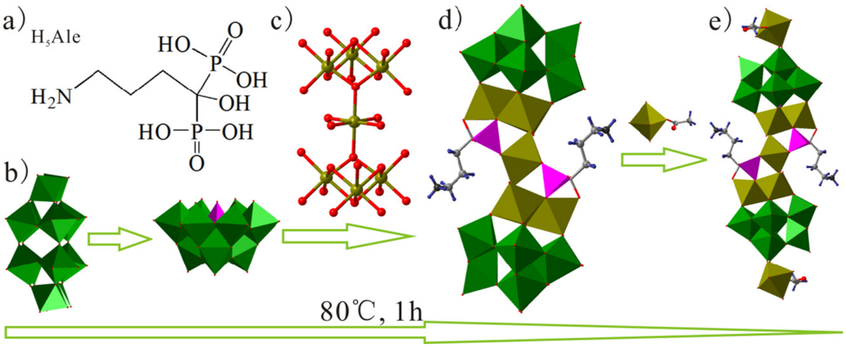
GRAPHICAL ABSTRACT

A new 2D layer-like network composed of Co_7 cluster-containing sandwich-type polyoxometalate was obtained via the transformation of hexavacant polyoxoanion to trivacant polyoxoanion.



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ABSTRACT

We report a new 2D layer-like network composed of Co_7 cluster-containing sandwich-type polyoxometalate, $Li_{10}Na_2[Co(H_2O)_3(CH_3COO)]_2\{[Co_7(H_2O)_4(OH)_2(Ale)_2][PW_9O_{34}]_2\}\cdot 20H_2O$ (**1**) {H_5Ale = Alendronic acid}, which was synthesized by the conventional aqueous solution method. Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the monoclinic $P_{2(1)/n}$ space group with unit cell a = 12.5391 (1) Å, b = 25.2531 (2) Å, c = 22.0462 (2) Å, β = 97.728(1)°, Z = 2, V = 6917.55 (10) $Å^3$. This compound was further characterized by powder X-ray diffraction (PXRD), IR spectra and thermogravimetric (TG) analyses to confirm its structure and composition. As a result, polyoxoanion in **1** consists of two $\{A\text{-}PW_9O_{34}\}^{9-}$ units, which are fused together by a $\{Co_7(H_2O)_4(OH)_2(Ale)_2\}$ {$\mathbf{Co_7}$} cluster into a sandwich-type structure. In the {$\mathbf{Co_7}$} cluster, all the Co^{2+} ions are connected together by two Ale ligands and two OH groups into the hepta-nuclear cobalt cluster {$\mathbf{Co_7}$}. Further, the sandwich-type polyoxoanions are connected together by two $\{CH_3CO_2Co(H_2O)_3\}$ units, resulting in the first 2D layer-like structure consisting of Co_7-containing sandwich polyoxoanion. Electrochemical and electro-catalytic studies reveal that **1** exhibits good electrocatalytic activity toward the reduction of H_2O_2 in neutral aqueous solution.

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Design and synthesis of new polyoxometalates (POMs) have attracted much attention as their versatile architectures and potential applications in many fields, such as catalysis, magnetism, and medicine [1–7]. POMs can also act as the support to incorporate addenda metal centers and non-metal heteroatoms to functionalize these inorganic clusters [8–11]. In this filed, lacunary polyoxotungstates represent an important subclass of the POMs for incorporating addenda functional groups as the wide existence of W-based vacant POMs. Up to date, monovacant $\{XW_{11}O_{39}\}$ (X = P, Si and Ge) and $\{P_2W_{17}O_{61}\}$, divacant $\{XW_{10}O_{39}\}$ (X = Si and Ge), trivacant $\{XW_9O_{34}\}$ (X = P, Si and Ge), $\{P_2W_{15}O_{56}\}$ and hexavacant $\{P_2W_{12}O_{48}\}$ (P_2W_{12}) polyoxotungstates have been synthesized [12–16] and widely used in constructing transition-metal-substituted POMs [17–27]. In recent years, a series of new POM clusters, such as $[Co_9(H_2O)_6(OH)_3(HPO_4)_2(PW_9O_{34})_3]^{16-}$ [21], $[Co_4(H_2O)_2(B\text{-}\alpha\text{-}PW_9O_{34})_2]^{10-}$ [22], $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ [23,24], $\{[Mn_2^{IV}Mn_6^{III}Mn_4^{II}(\mu_3\text{-}O)_6(\mu\text{-}OH)_4(H_2O)_2(CO_3)_6][B\text{-}\beta\text{-}SiW_6O_{26}]_2\}$ [25], $[Ni_7\text{-}(OH)_4(H_2O)(CO_3)_2(HCO_3)(A\text{-}\alpha\text{-}SiW_9O_{34})(\beta\text{-}SiW_{10}O_{37})]^{10-}$, $[\{Ni_6(H_2O)_4(\mu_2\text{-}H_2O)_4(\mu_3\text{-}OH)_2\}(x\text{-}SiW_9O_{34})_2]^{10-}$ [26], $\{[Cu(en)_2]_{1.5}[Cu(en)(2,20\text{-}bipy)(H_2O)_n]Ce[(\alpha\text{-}PW_{11}O_{39})_2]\}_6$ [27], $[\{Co_4(OH)_3(PO_4)\}_4(XW_9O_{34})_4]^{n-}$ (X = Si, Ge, P and As) [1,10], $[\{(B\text{-}\alpha\text{-}PW_9O_{34})Co_3(OH)(O_3PC(O(C_3H_6NH_3)PO_3)\}_2Co]^{14-}$, $[\{(B\text{-}PW_9O_{34})Ni_3(OH)(H_2O)_2(O_3PC(O)(C_3H_6NH_3)PO_3)\}_2Ni]^{14-}$ and $[\{(B\text{-}\alpha\text{-}PW_9O_{34})Ni_3(OH)(H_2O)_2(HAle)\}_2Ni]$ [28–30], were designed and synthesized. In these compounds, several cobalt, nickel and manganese clusters were stabilized by lacunary POMs to construct active photocatalysts for water splitting [10, 31–34]. Also, the Co_7, Fe_9, and Mn_6 clusters are isolated by the lacunary POM units to form transition-metal clusters with single molecule magnet behaviour. So, it is still a charming and promising field to introduce transition-metal centers into lacunary POM units to form various clusters with different structures and compositions, so as to construct multiple functional properties.

In this field, hexavacant P_2W_{12} with high-vacant sites have been regarded as an efficient building units for trapping high-nuclear transition-metal clusters [16,35]. Up to date, Cu_{20}, Fe_{27}, Fe_{16}, Nb_6, Nb_{24} and Mn_7 clusters were all synthesized and exhibited interesting functionalities [36–41]. In this field, we have focused on functionalization of the hexavacant P_2W_{12} unit with different metal centers for a long time, and a series of P_2W_{12}-based POMs, such as Ni_6, Co_6, Mn_2, Gd/Mn-containing crown-type clusters were obtained [42–44]. In the synthesis of these compounds, it could be found that the hexavacant P_2W_{12} is a metastable unit in the aqueous solution, and could transfer into trivacant POMs under the hydrothermal conditions [45], and the conversion

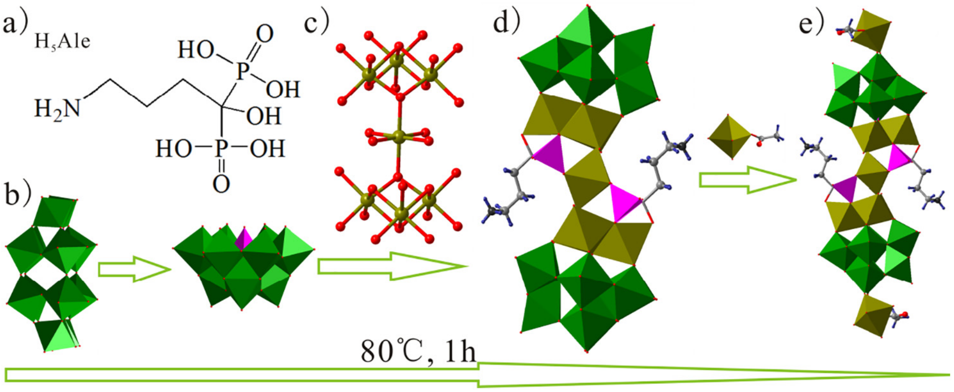

Fig. 1. Structure of (a) H_5Ale ligand, (b) hexavacant POM $[P_2W_{12}O_{48}]$, (c) $\{Co_7\}$ cluster, (d) sandwich polyoxoanion in **1**, (e) sandwich polyoxoanion decorated by two $\{Co(H_2O)_3(CH_3COO)\}$ units. Color codes: W, green octahedron; Co, brown; P, purple; C, gray; H, dark blue; N, black; O, red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

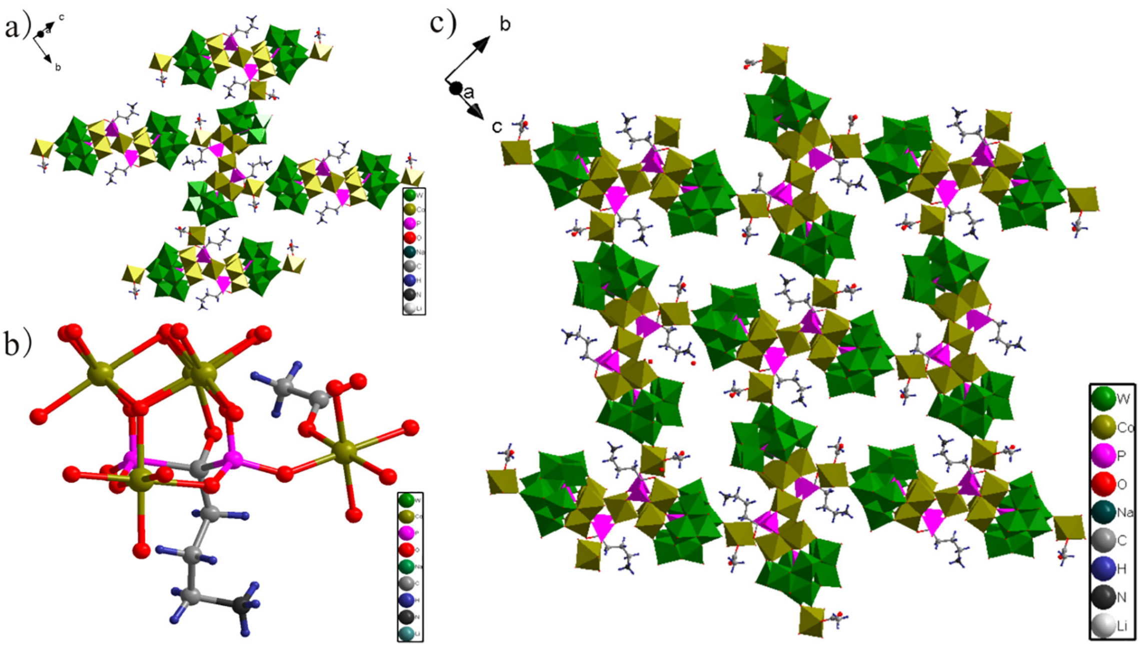

Fig. 2. (a) Linking modes between the sandwich polyoxoanions and the linking units $\{Co(H_2O)_3(CH_3COO)\}$; (b) coordination modes of Ale ligands and the central $\{Co_7\}$ cluster; (c) 2D spatial configuration of **1**.