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Graghical Abstract

Heterometallic 3d-4f Cluster-Containing Polyoxotungstate Obtained by Partial Disassembly of Preformed Large Clusters

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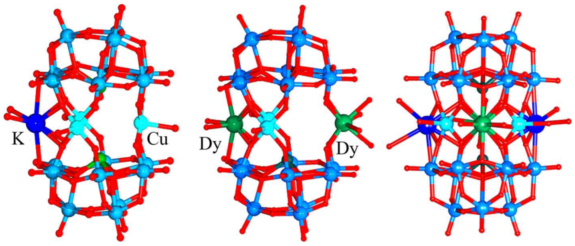

A new heterometallic 3d-4f tungstoantimonite, $KNa_5\{K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2\}\cdot 17H_2O$ (**1**) was designed and synthesized by decomposition of preformed large cluster, which further combines with two K^+ cations resulting in a ring-like 3d-4f-4p cluster $\{K_2Dy_2Cu_2(H_2O)_8\}$-containing polyoxotungstate.

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A new heterometallic 3d-4f cluster-containing polyoxotungstate $KNa_5\{K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2\}\bullet 17H_2O$ (**1**) was designed and synthesized by reaction of the preformed large cluster $[N(CH_3)_4]_{10}Na_{12}[Na_2Sb_8W_{36}O_{132}(H_2O)_4]\bullet 26H_2O$ ($\{Sb_8W_{36}\}$), transition-metal (TM) and Ln^{3+} cations. Compound **1** is the first 3d-4f heterometallic cluster-containing sandwich-type tungstoantimonite obtained by partial decomposition of preformed large cluster. Further, the sandwich-type polyoxoanion combines with two additional 4p cations resulting in a ring-like 3d-4f-4p cluster $\{K_2Dy_2Cu_2(H_2O)_8\}$-containing polyoxotungstate. The sandwich polyoxoanion $\{K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2\}$ was structural similar to the well-known anion $\{K_3Cu_3(H_2O)_{10}(SbW_9O_{33})_2\}$, inwhich one alkali metal cation and one TM cation were both replaced by the rare earth metal cations. Furthermore, the 3d-4f-4p cluster-containing polyoxoanions were bridged by the K^+ ion located at their central metal belt into a one-dimensional (1D) wavelike chain. Electrochemical study revealed that compound **1** exhibited electrocatalytic activity for reduction of the NO^{2-} and O_2, and a direct 4-electronns electrochemical reduction process of O_2 was achieved in **1**-containing aqueous solution.

Introduction

The design and synthesis of the nanoscale polynuclear metal aggregates is currently a major focus of research in the area of nanosized materials.[1,2] Polyoxometalates (POMs), as a typical class of metal–oxo clusters with unmatched structural versatility combined with applications in diverse areas, such as catalysis, magnetism and electrochemistry, have attracted much attention in the past decades.[3,4] A powerful strategy to form nanoscale POM clusters is the synthetic combination of various lacunary POMs with TM cations or Ln cations. In the past decades, the TM- or Ln-substituted POMs were usually observed by reactions of the preformed lacunary POMs with the metal linkers.[5-8] Also, the simple "one-pot" method was confirmed as an efficient synthetic approach for construction of the polynuclear metal aggregates.[9] However, the reverse of these methods, i.e., self-assembly of polynuclear metal aggregates by controlled decomposition of preformed large cluster and metal linkers was rarely explored up to now.[10]

In the field of the polynuclear aggregates, a recent aspect has focused on the construction of 3d-4f heterometallic clusters encapsulated by lacunary diamagnetic POM shells.[11-14] Until now, several strategies for the synthesis of the 3d-4f heterometallic cluster-containing POMs were explored, and a certain amount of examples were reported. However, as there is unavoidable reaction competition among the highly negative polyoxoanions, strongly oxyphilic Ln cations and relatively less active TM cations, much fewer 3d-4f heterometallic cluster-containing examples were explored compared to the 3d TM-substituted POMs. Also, it is difficult in the exploration of preformed heterometallic clusters, which could co-exist with the lacunary POMs. Typical 3d-4f heterometallic cluster-containing examples are as follows: the Ce^{IV}-Mn^{IV} clusters-containing high-nuclearity aggregate were obtained by reaction of the preformed heterometallic cluster with the lacunary Wells–Dawson POMs,[11a,11b] the $[Cu_3Ln]$ cubane was inserted in monolacunary Keggin fragments,[11c] two sandwich-type polyoxoanions containing $[\{Ce(H_2O)_2\}_2Mn_2]$ and $\{Ce^{IV}Cu_3O_{18}\}$ clusters were synthesized by replacement of TM centers with the Ln cations in the Weakley-type polyoxoanions.[12a] A three Ce^{III}-Fe^{III} bridges-containing trimeric POM aggregate and a $\{(VO_2)_2Dy(H_2O)_4\}$ cluster-containing sandwich polyoxoanion were synthesized by a one pot synthetic procedure.[13a,12b] And also, lanthanide-containing sandwich-type polyoxoanion linked by the 3d centers *via* terminal oxygen atoms resulting in the heterometals-containing POMs have also been observed.[14b]Up to date, the exploration of new synthetic method of heterometallic 3d–4f cluster-containing POMs still represents an important field of POM chemistry. In this paper, a heterometallic 3d-4f POM was firstly synthesized by decomposition of the preformed large cluster $\{Sb_8W_{36}\}$. The anion $\{K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2\}^{6-}$ in **1** was considered being obtained by replacing both the alkali metal and TM cations from the well-known anion $\{K_3Cu_3(H_2O)_{10}(SbW_9O_{33})_2\}$ by the rare earth cations. Electrochemical study revealed that the title compound exhibits electrocatalytic activity for the reduction of NO_2^- and O_2.

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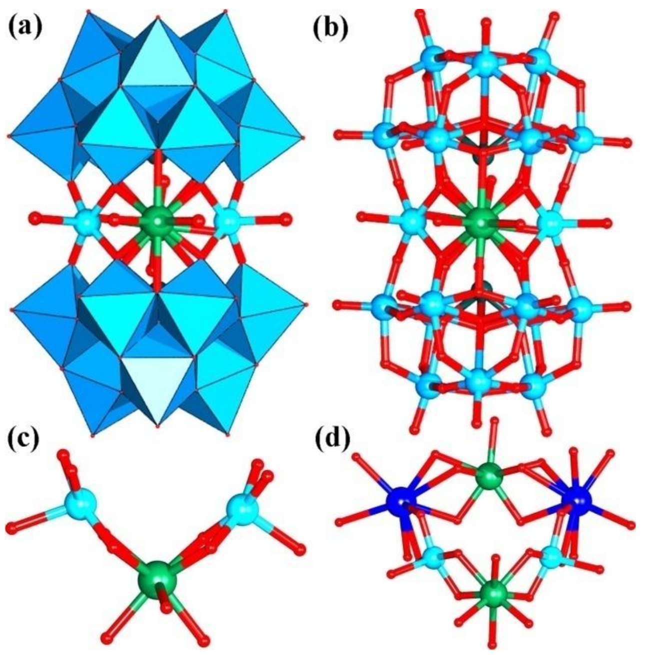

Fig. 1. (a) Polyhedral and ball-and-stick representation of polyoxoanion **1**; (b) ball-and-stick representation of polyoxoanion **1**; (c) ball-and-stick representation of {$DyCu_2$} cluster in **1**; (d) ball-and-stick representation of the ring-like 3d-4f-4p cluster {$K_2Dy_2Cu_2(H_2O)_8$} in **1**. Color codes: W azure, Dy green, Cu arctic, K blue.

Results and Discussion

Synthesis and structure. In the past decades, reaction of various lacunary POMs with TM cations or Ln cations has been proved to be a powerful strategy to form nanoscale POM clusters, as the coordination pocket of lacunary POMs with strong reactivity on their lacunary sites. The nanoscale POM clusters were confirmed to decompose into small fragments, which allowed more complicated metastable phases to exist in this system. Recent studies showed that it was a feasible method for the synthesis of high-nuclear POM clusters.[10] Additionally, previous studies showed that the presence of adapted exogenous organic ligands was a key condition for the synthesis of the 3d-4f heterometallic POMs to avoid the reaction competition among the highly negative polyoxoanions, Ln cations and TM cations, although they did not appear in the final product. In this field, Niu and Zhao et al. have isolated a series of 3d-4f heterometal-containing POMs stabilized by both the POMs and adapted exogenous organic ligands.[15] In this paper, a new heterometallic cluster-containing polyoxotungstate, $KNa_5\{K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2\}\bullet 17H_2O$ (**1**) was synthesized by reaction of the preformed large cluster {Sb_8W_{36}}, TM and Ln cations with the assistance of the proline ligands. During the experiments, other Ln cations, such as Gd^{3+}, Ho^{3+}, and Nd^{3+} were also introduced into such a reaction system. However, the corresponding compounds were not obtained except for compound **1**. And, in the absence of the proline ligand, a sandwich anion containing three $[Cu(H_2O)]^{2+}$ groups, $Na_2K_7\{K_3Cu_3(H_2O)_3(SbW_9O_{33})_2\}\bullet 17H_2O$ (**2**) was obtained with the {Sb_8W_{36}} as the start material. This sandwich-type polyoxoanion $\{Cu_3(H_2O)_3(SbW_9O_{33})_2\}^{12-}$in **2** has been reported by Kortz et al with the K^+ or Na^+ as the counter cations,[6b] and it is structural similar to the title polyoxoanion{$K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2$}. The anion {$K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2$} could be viewed as replacing one alkali metal cation and one TM cation in **2**, resulting in the 3d-4f-4p cluster-containing polyoxoanion. In the synthesis, the title compound was isolated with the assistance of L-proline or D-proline molecules. However, it is difficult to introduce the chiral functions into the clusters.

Single-crystal X-ray diffraction analyses confirm that compound **1** is a 3d-4f heterometallic {$DyCu_2$}-cluster-containing sandwich-type polyoxoanion (Fig. 1 and Fig. S1). In the sandwich structure, the [SbW_9O_{33}] unit possesses of a trivacant B-*α*-Keggin structural feature, resulting from removal of three [WO_6] octahedra from the saturated *α*-Keggin polyoxoanion. In **1**, two [SbW_9O_{33}] units were connected by a heterometallic {$DyCu_2$} cluster and a Dy^{3+} ion into a sandwich-type polyoxoanion. Additionally, the sandwich anion capture other two K^+ ions between the {$DyCu_2$} cluster and Dy^{3+} ion, forming a ring-like 3d-4f-4p cluster {$K_2Dy_2Cu_2(H_2O)_8$}. In the central 3d-4f-4p cluster, one of the Dy^{3+} ions was connected with two Cu^{2+} ions via four oxo-atoms, resulting in the heterometallic {$DyCu_2$} cluster (Fig. 1c). Further, each Cu^{2+} in this heterometallic cluster was connected with one K^+ via two oxygen atoms, and the two K^+ ions were connected with another Dy^{3+} ion via six oxygen atoms, resulting a hexa-nuclear 3d-4f-4p cluster {$K_2Dy_2Cu_2$} (Fig. 1d). In the {$K_2Dy_2Cu_2$} cluster, both of the Cu^{2+} ions exhibit the square pyramid coordination environment completed by four oxygen atoms from two trivacant [SbW_9O_{33}] units and a water molecule, and the Dy^{3+} and K^+ ions are in the 8 and 9 coordinated environments, respectively. The Cu–O distances fall into the range of 1.92(2)–2.22(2) Å, and the Dy–O and K–O distances are in the range of 2.27(2)–2.578(19) Å and 2.592(19)–3.26(2) Å, respectively. As shown in Fig. 2, the anion was structurally similar to the Cu3-containing polyoxoanion $\{K_3Cu_3(H_2O)_3(SbW_9O_{33})_2\}^{9-}$ in **2**. The anion {$K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2$} was obtained by replacing one alkali metal cation and one TM cation in $\{K_3Cu_3(H_2O)_3(SbW_9O_{33})_2\}^{9-}$. The K9 cation in **2** was replaced by the Dy1 ion in **1**, and the K-O bond lengths in **2** is in the range of 2.70(4)—2.812(15) Å, which is much longer than that of the Dy-O distance (in the range of 2.27(2)–2.578(19) Å) in **1**. So, the Dy^{3+} (Dy1) in the sandwich structure sunks into the anion, the K^+ cation bulges out of the sandwich structure. Similarly, the Cu1 site in **2** was replaced by the Dy2 cation in **1**, and the Cu1 (Cu-O bond lengths: 1.927(13)—2.31(3) Å) ion was arrange in a plane with the four linking oxygen atoms, and Dy2 cation (Dy-O bond lengths: 2.304(18)—2.527(18) Å) obviously bulges out of the plane. This arrangement of the central cations brings the two [SbW_9O_{33}] subunits parallel to each other with a similar distance. So, the replacement of both alkali metal and TM cations by the Ln cations in the POM system was firstly achieved, which will suggest a new strategy for constructing the 3d-4f heterometallic cluster-containing POMs.

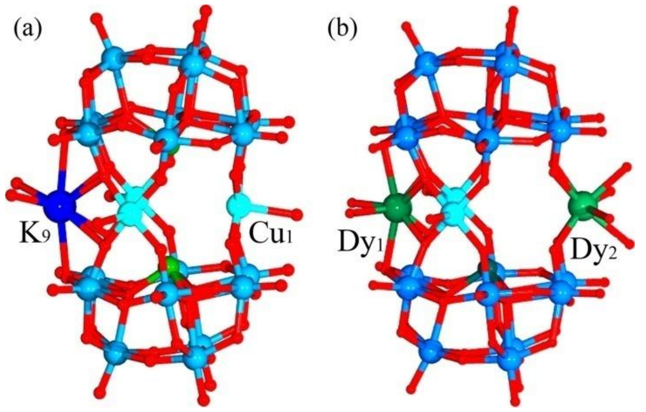

Fig. 2. Ball-and-stick representation of polyoxoanions (a) **2** and (b) **1**.

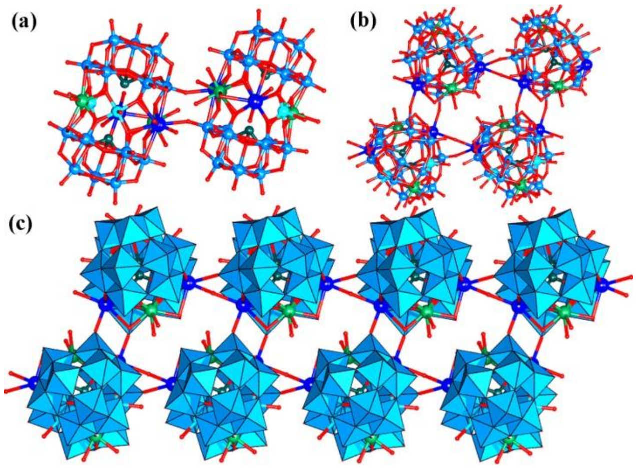

Fig. 3.(a),(b) The linking modes of K^+ linkers in the 1D chain; (c) the 1D chain structure in **1**.

Further, the 3d-4f-4p cluster-containing sandwich-type polyoxoanions were connected into a 1D chain-like structure by the K^+ ions located in the central metal belt (Fig. 3). In the packing arrangement, the 1D chains were connected by additional K^+ and Na^+ ions into a 3D structure, where all the planes of these anions are parallel with each other (Fig. S2-S4). Solvent water molecules resided in the interspaces between the sandwich-type polyoxoanions, or coordinated with alkali-metal cations or H-bonded to the surface oxygen atoms of the POMs.

Electrochemical and electrocatalytic properties. The cyclic voltammetric (CV) behavior of **1** in a pH = 4.0 0.4 M $CH_3COONa+CH_3COOH$ buffer solution exhibits five reduction peaks in the potential range -0.6 V – +0.6 V and the mean peak potentials are +0.135V, +0.032V, -0.303 V, -0.367 V and -0.500 V (vs. NHE), respectively (Fig. 4a). The three reduction peaks located at -0.303 V, -0.367 V and -0.500 V are ascribed to the reduction process of W centers in polyoxoanion **1**. The first two reduction peaks located at +0.135V and +0.032V, and the oxidation counterpart with the characteristic shape usually encountered for the oxidation of adsorbed species were attributed to the redox processes of the cooper centers in the polyoxoanion framework. The two reduction waves feature the two-step reduction of Cu^{2+} to Cu^0 through Cu^+.[16]

As well known, the TM-substituted POMs were widely studied for the electrocatalytic reduction reaction. Firstly, the NO_2^- was selected as the candidate to illustrate the electrocatalytic properties of the 3d-4f cluster-containingpolyoxoanion. On additionof a certain amount of nitrite to the pH = 4.0 0.4 M $CH_3COONa+CH_3COOH$ buffer solution containing 2×10^{-4} M anion **1**, induced a cathodic current increase after the first reduction peak of the tungsten, while the corresponding oxidation peak current decreased. These results suggested that nitrite was reduced by the reduced polyoxoanion species (Fig. 4b).

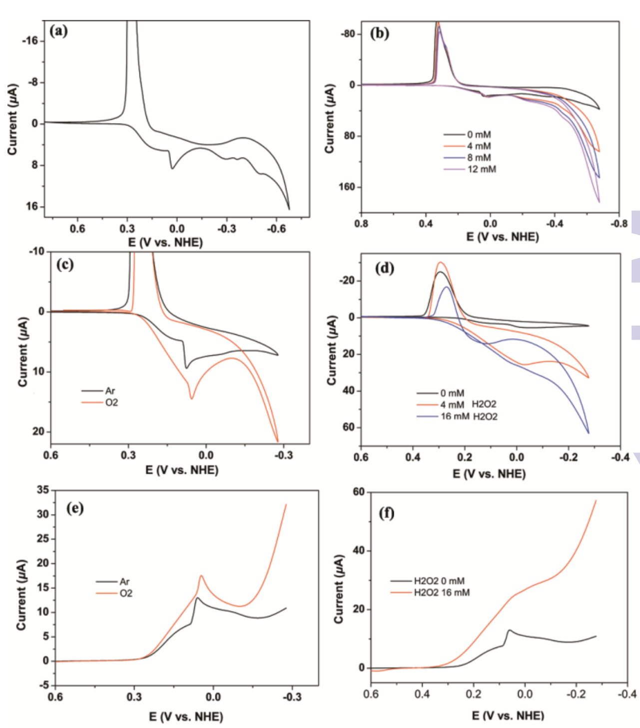

Fig. 4.(a) CV of 2×10^{-4} M**1** in the pH = 4 (0.4 M $CH_3COONa+CH_3COOH$) buffer solution at the scan rate of 5 mV s^{-1}; (b) electrocatalytic reduction of NO_2^- in the presence of 2×10^{-4} M **1** at the scan rate of 50 mV s^{-1}; (c) electrocatalytic reduction of O_2 in the presence of 2×10^{-4} M **1** at the scan rate of 10 mV s^{-1};(d) electrocatalytic reduction of H_2O_2 in the presence of 2×10^{-4} M **1** at the scan rate of 20 mV s^{-1}; (e) square wavevoltammetry (SWV) of aqueous solutions containing 2×10^{-4} M **1** bubbled by the Ar and O_2, respectively; (f) square wavevoltammetry (SWV) of aqueous solutions containing 2×10^{-4} M **1** and H_2O_2.

Oxygen is the most abundant element in the earth crust. The oxygen reduction reaction is not only an important reaction in biological system, but also for energy transformation, such as in the fuel cells. So, the development of the oxygen reduction catalysts has attracted wide attention in the past decades. And, it has attracted more and more attention of the chemists to preliminary explore the earth-abundant POM-based catalysts for the oxygen reduction reaction.[16,17] Here, compound **1** was used as electrocatalyst for the O_2 reduction reaction. As shown in Fig. 4c, when the aqueous solution was bubbled by the O_2 for 10 min, a much more striking increase of the cathodic current was detected at about -0.12V than that observed in the aqueous solution bubbled by the Ar. Also, it has a more than tripled current compared with that obtained in the Ar-saturated aqueous solution. This result suggested that an O_2 reduction process happened on the surface of the electrode. As well known, electrochemical O_2 reduction at fuel cell electrodes are complex processes. In the aqueous solutions, two pathways were usually observed for theoxygen reduction: a direct 4-electronns reduction pathway from O_2 to H_2O, and the 2-electron reduction pathway from O_2 to H_2O_2. In order to confirm the reduction process, H_2O_2 was added into to the solution in the presence of 2×10^{-4} M polyoxoanion **1**. It could find that the O_2 reduction and the H_2O_2 reduction happened in a same range of the potential, which suggested that the O_2 reduction pathway should be a direct 4-electronns reduction pathway from O_2 to H_2O.[16]

Experimental

Synthesis.

Synthesis of **1**. Dy_2O_3 (0.50 g, 1340 μmol) was added into 7.5 mL of distilled water. Then 2.5 mL of concentrated nitric acid was added. The mixture was boiling for 1 h resulting in solution A. {Sb_8W_{36}} (0.30 g, 26.5 μmol) was added into 10 mL of distilled water, which was stirred for 5 min. Then, 0.1 g $CuCl_2$•$2H_2O$, 1.0 mL aq A and 1.0 mL 2 M K_2CO_3 aqueous solution were added in the reaction system one by one. Then, the mixture was stirred or anther 10 min resulting solution B. {Sb_8W_{36}} (0.45 g, 39.75 μmol) was added into 15 mL of distilled water, which was stirred for 5 min. Then, 0.15 g $CuCl_2$•$2H_2O$, 1.5 mL aq A and 2.4 ml 2 M K_2CO_3 aqueous solution were added in the reaction system one by one. Then, the mixture was stirred for another 10 min resulting solution C. The solution B was slowly added into the solution C. The resulting mixture was further stirred for 10 min. Then, 50 mL distilled water and 0.15 g L or D-alanine were added into the mixture, which was further stirred for 5 hours at 40 ºC. Afterwards, the solution was cooled down to ambient temperature and filtered. After three weeks, green block crystals suitable for X-ray diffraction were obtained (Yields: 21 % based on W). Anal. Found (%): Dy, 5.43; K, 1.96; Cu, 2.09; Na, 2.12, Sb, 4.38; W, 57.26; Calcd: Dy, 5.66; K, 2.04; Cu, 2.21; Na, 2.00, Sb, 4.24; W, 57.61.

Conclusions

In conclusion, a new heterometallic 3d-4f polyoxotungstate was synthesized by reaction of the preformed large cluster {Sb_8W_{36}} and the mixture of 3d/4f cations, which represents the first 3d-4f heterometallic cluster-containing sandwich-type tungstoantimonite obtained by decomposition of preformed large cluster. The sandwich-type polyoxoanion combines with additional two 4p cations resulting in a ring-like 3d-4f-4p cluster {$K_2Dy_2Cu_2(H_2O)_8$}-containing polyoxotungstate. The sandwich polyoxoanion {$K_2Dy_2Cu_2(H_2O)_8(SbW_9O_{33})_2$} could also consider being obtained by both replacing the alkali metal cation and TM cation with the rare earth metal cations in the anion {$K_3Cu_3(H_2O)_{10}(SbW_9O_{33})_2$}$^{9-}$. Electrochemical study and UV-vis spectra revealed that compound **1** could be structurally stable in the pH = 4.0 buffer solution, and exhibited electrocatalytic cativity for reduction of the NO_2^-, and a direct 4-electronns electrochemical O_2 reduction process was achieved in **1**-containing aqueous solution. This study suggested a new method for constructing the 3d-4f-cluster-containing POMs, and the further study will focus on the synthesis of other heterometallic 3d-4f cluster-containing POMs by using the preformed large clusters.

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