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Article

A New Supramolecular Assembly Based on Triple-Dawson-Type Polyoxometalate and 3d-4f Heterometallic Cluster

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The introduction of hexavacant Dawson-type precursor $K_{12}[H_2P_2W_{12}O_{48}]\cdot 24H_2O$ into a HOAc/NaOAc (OAc^-=acetate) buffer system containing $(NH_4)_2[Ce^{IV}(NO_3)_6]$ and $Mn^{II}(OAc)_2\cdot 4H_2O$ led to the isolation of a new compound, $Na_{20}[Ce^{IV}{}_3Mn^{IV}{}_2O_6(OAc)_6(H_2O)_9]_2[Mn^{III}{}_2P_2W_{16}O_{60}]_3\cdot 21H_2O$ (**1**). Compound **1** contains unusual triple-Dawson-type polyoxoanions $[Mn^{III}{}_2P_2W_{16}O_{60}]_3{}^{24-}$ and bipyramid-like 3d−4f heterometallic clusters $[Ce^{IV}{}_3Mn^{IV}{}_2O_6(OAc)_6(H_2O)_9]^{2+}$, which are arranged in a 3-D supramolecular assembly with 1-D channels. The Na^+ cations and solvent water molecules reside in the channels. Crystal data for **1** are as follows: hexagonal, *P*6$_3$/*mcm* (No. 193), a=24.959(4) Å, c=26.923(5) Å, γ=120°, V=14525(4) Å^3, and Z=2. The electrochemical and electrocatalytic properties of compound **1** have been investigated.

Introduction

Polyoxometalates (POMs), as a unique class of metal−oxo clusters, have recently attracted extensive interest in the areas of inorganic chemistry, coordination chemistry, and materials science due to not only their unmatched structural types and attractive properties such as a controllable shape, size, high-negative charge, and nucleophilic oxygen-enriched surface but also various potential applications in catalysis, medicine, biology, and functional material science.[1,2] In the field of POM chemistry, the exploration of new POM species possessing novel structures and properties is a permanent aim that researchers have been pursuing all along. However, the rational design and synthesis of such compounds remains a realistic and great challenge. Recently, an effective strategy was developed to synthesize new POM species, that is, the use of lacunary polyoxoanions as inorganic multidentate building blocks to "capture" transition metal or rare earth metal ions, leading to novel compounds with diverse nuclearities and structural features as well as interesting properties.[3−12] In this aspect, highly lacunary POMs might be the best candidates to

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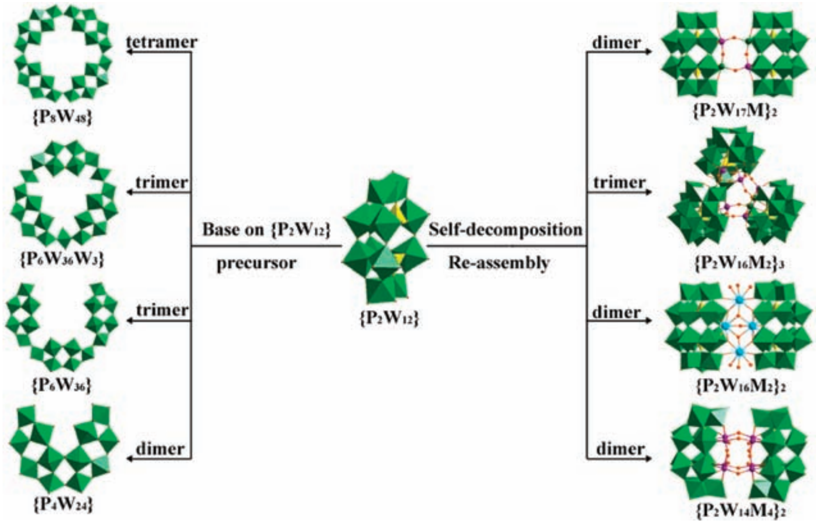
Scheme 1. Schematic View of the Giant Inorganic Aggregates Assembled from Hexa-Vacant Dawson-Type $\{P_2W_{12}\}$ Precursors



incorporate more metal centers into fascinating high-nuclear or giant inorganic aggregates. A typical precursor is the hexa-vacant derivative of the Dawson-type polyoxoanion $[P_2W_{12}O_{48}]^{14-}$ (abbreviated $\{P_2W_{12}\}$, as shown in Scheme S1, Supporting Information).[7] As reported in previous literature, $\{P_2W_{12}\}$ can be assembled into at least four types of aggregate with considerable sizes, involving the crown-type $\{P_8W_{48}\}$ tetramer and $\{P_6W_{39}\}$ trimer as well as the semi-opened $\{P_6W_{36}\}$ trimer and $\{P_4W_{24}\}$ dimer. All of these assemblies exhibit strong reactivity on their inner surfaces with various electrophilic metal ions and thus provide effective "reactors" for the assembly of huge clusters (see Scheme 1, left).[8−11] So far, a series of excellent species based on the above polymers has been reported.[8−11] It is noteworthy that the structural integrity of $\{P_2W_{12}\}$ is maintained in these compounds. On the other hand, the $\{P_2W_{12}\}$ precursor is actually metastable in solution and can transform into several other intermediate vacant Dawson-type building blocks that can be used to construct unexpected large oligomers or aggregates (see Scheme 1, right).[12] Thus, utilizing the metastable $\{P_2W_{12}\}$ precursor should provide a promising route to the design and synthesis of new POM species and enrichment of the POM family.

Following this strategy, another key factor should also be mentioned, that is, the choice of various "linkers" such as the transition metal ions, lanthanide ions, and organic or metal−organic units that can effectively connect the $\{P_2W_{12}\}$-based precursors together. In this work, we deliberately selected the $\{Ce^{IV}/Mn^{II}/OAc^-\}$ (OAc^- = acetate) mixed aqueous solution system as the starting materials instead of various simple metal salts. In such an acidic medium, various mixed valent ions such as Ce^{IV}, Ce^{III}, Mn^{IV}, Mn^{III}, and Mn^{II} ions can coexist due to the redox reaction between Ce^{IV} and Mn^{II} ions. Further, a series of building blocks such as $\{CeMn_2\}$, $\{Ce_3Mn_2\}$, $\{CeMn_6\}$, and $\{CeMn_8\}$[13] can be formed. Thus, this reaction system can provide abundant linking fragments to react with lacunary POMs. Recently, two attractive POM compounds combined with the building blocks derived from the above $\{Ce^{IV}/Mn^{II}/HOAc\}$ system have been reported by Kögerler and Fang.[14]

On the basis of the aforementioned considerations, we attempted to introduce the $\{P_2W_{12}\}$ precursor into the $\{Ce^{IV}/Mn^{II}/OAc^-\}$ mixed system in order to explore a new route to preparing novel POM compounds with unexpected structural models and interesting properties. Herein, we report a new compound, $Na_{20}[Ce_3Mn_2O_6(OAc)_6(H_2O)_9]_2[Mn_2P_2W_{16}O_{60}]_3\cdot21H_2O$ (**1**). Compound **1** contains an unusual triple-Dawson-type polyoxoanion $[Mn^{III}{}_2P_2W_{16}O_{60}]_3{}^{24-}$, representing a new structural topology in the POM chemistry. Furthermore, these polyoxoanions and the bipyramid-like 3d−4f heterometallic clusters $[Ce^{IV}{}_3Mn^{IV}{}_2O_6(OAc)_6(H_2O)_9]^{2+}$ are well-arranged into a 3-D supramolecular assembly with 1-D channels.

Experimental Section

Materials and Methods. All chemicals were commercially purchased and used without further purification. $K_{12}[H_2P_2W_{12}O_{48}]\cdot24H_2O$ was synthesized according to the literature[7] and characterized through its IR spectrum. Elemental analyses (C) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; P, W, Mn, Ce, and Na were analyzed on a PLASMA-SPEC (I) ICP atomic emission spectrometer. IR spectra were recorded in the range of 400−4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. Thermal gravimetric (TG) analyses were performed on a Perkin−Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. UV−vis absorption spectra were obtained using a 752 PC UV−vis spectrophotometer. The electrochemical measurement was

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carried out on a CHI 660 electrochemical workstation. All measurements were performed at room temperature.

Synthesis of Compound 1. An orange solution of $(NH_4)_2[Ce(NO_3)_6]$ (6.78 g, 12.4 mmol) in 9 mL of $H_2O/HOAc$ (v/v = 7/2) was slowly added to a colorless solution of $Mn(OAc)_2 \cdot 4H_2O$ (2.02 g, 8.2 mmol) in 5 mL of $H_2O/HOAc$ (v/v = 4/1), and the mixture was stirred for 30 min at room temperature. Then, 20 mL of HOAc/NaOAc buffer (0.4 M, pH = 4.2) containing freshly prepared $K_{12}[H_2P_2W_{12}O_{48}] \cdot 24H_2O$ (1.5 g, 0.38 mmol) was added dropwise to the above solution. The resulting dark brown solution (pH = 4.0) was stirred at room temperature for 24 h and filtered. The filtrate was sealed with parafilm containing tiny pores to facilitate slow evaporation at room temperature. Brown hexagonal-prism crystals of **1** were isolated after one month (yield: 0.523 g, 36% based on W). Anal. calcd for $C_{24}H_{54}O_{255}P_6W_{48}Ce_6Mn_{10}Na_{20}$, **1**: C, 1.89; P, 1.22; W, 57.74; Ce, 5.50; Mn, 3.59; Na, 3.01%. Found: C, 1.79; P, 1.31; W, 57.89; Ce, 5.34; Mn, 3.44; Na, 2.87%. IR (KBr disk, cm^{-1}): 3421 (br), 1615 (s), 1476 (m), 1427 (m), 1379 (w), 1348 (w), 1305 (w), 1202 (m), 1120 (m), 955 (s), 862 (s), 777 (s), 718 (s), 615 (s), 487 (m). TG analysis indicates that there are about 39 water molecules in compound **1**.

X-Ray Crystallography. The crystallographic data were collected at 150 K on a Rigaku R-axis Rapid IP diffractometer using graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) and IP techniques. A multiscan absorption correction was applied. The crystal data of **1** were solved by direct methods and refined by a full-matrix least-squares method on F^2 using the *SHELXL-97* crystallographic software package.[15] Anisotropic thermal parameters were used to refine all of the non-H atoms on the polyoxoanion and the 3d−4f cationic cluster. All of the sodium cations and solvent water molecules exhibit unusual thermal parameters (Ueq) with the anisotropic refinement; thus, they were only isotropically refined. The polyoxoanion contains an obvious site-occupancy disorder on the Mn_1/W_5 center with occupancy ratios of 50% for Mn and 50% for W (see Figure S1, Supporting Information). It is also noteworthy that the whole cationic cluster $[Ce_3Mn_2O_6(OAc)_6(H_2O)_9]^{2+}$ exhibits a 2-fold disorder in two positions (see Figure S2, Supporting Information), and the H atoms on acetate ligands cannot be added in the calculated positions. Thus, the H atoms on C atoms and water molecules were directly included in the final molecular formula. Further details of crystal data and structure refinement for **1** are summarized in Table 1. Selected bond lengths of **1** are given in Table 2. The CCDC reference number is 709596.

Electrochemistry. General Electrochemical Methods and Materials. Thrice-distilled water was used throughout the experiments. A 0.4 M NaOAc and HOAc buffer solution with a pH of 4.0 was used as the medium. The solution was deaerated by pure-argon bubbling prior to the experiment, and the electrochemical cell was kept under an argon atmosphere throughout the experiment.

Electrochemical Experiment. A CHI 660 electrochemical workstation connected to a Pentium-IV personal computer was used to control the electrochemical measurements and for data collection. A conventional three-electrode system was used (working electrode, glassy carbon; reference electrode, Ag/AgCl; counter electrode, platinum wire). All of the potentials were measured and reported versus the Ag/AgCl electrode. The medium of **1** was a 4×10^{-4} M solution. A pHS-25B-type pH meter was used for pH measurement. All experiments were performed at room temperature (25−30 °C).

Results and Discussion

Table 1. Crystal Data and Structural Refinements of Compound **1**

empirical formula	$C_{24}H_{54}Ce_6Mn_{10}Na_{20}O_{255}P_6W_{48}$
M	15283.21
λ/Å	0.71073
T/K	150(2)
cryst dimensions/mm	0.28 × 0.23 × 0.20
cryst syst	hexagonal
space group	$P6_3/mcm$
a/Å	24.959(4)
c/Å	26.923(5)
α/deg	90
β/deg	90
γ/deg	120
V/Å^3	14525(4)
Z	2
D_{calcd}/Mg m^{-3}	3.495
μ/mm^{-1}	20.420
F(000)	13396
θ range/deg	3.03−27.48
reflns collected/unique	107511/5899
R_{int}	0.1399
data/restraints/param	5899/54/359
R_1 ($I > 2\sigma(I)$)[a]	0.0557
ωR_2 (all data)[b]	0.0910
GOF on F^2	1.047
$\Delta\rho_{max, min}$/e Å^{-3}	2.758, −2.292

[a] $R_1 = \|F_o| - |F_c\|/|F_o|$. [b] $wR_2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

Synthesis. The reactions between lacunary polyoxoanions and various linkers such as transition metal ions, lanthanide ions, and metal−organic units have exhibited a versatile chemistry in assembling novel POM-based aggregates. In this subfield, multivacant Dawson-type polyoxoanions are excellent candidates since they contain more vacant sites that could "capture" more transition metal ions and connect them together into huge clusters. Furthermore, the metastable polyoxoanions are ideal precursors because such POMs are easy to isomerize or partly decompose in the solution and form a series of intermediate species, which are useful for the isolation of new POM-based aggregates. During our preparation of novel POM clusters with lacunary polyoxoanions, the $\{P_2W_{12}\}$ species was extensively used due to its high-vacant structural feature and its meta-stability in aqueous solution.[10a,10b,12a] Compound **1** was synthesized with such a lacunary species by carefully controlling the reaction conditions. During the assembly, the extra $\{WO_6\}$ fragments in each $\{P_2W_{16}Mn_2\}$ unit might derive from the decomposition of the $\{P_2W_{12}\}$ precursor.[8,10] As a result, the active $\{WO_6\}$ fragments could compete or connect with the Mn^{III} ions on the vacant sites of the POMs and form the {W−O−Mn} linkers, leading to the formation of large or extended Mn-substituted polyoxoanions.[9c,16] It is supposed that the pH value, reaction time, ionic concentration, and crystallization speed might play important roles for the preparation of compound **1** in this reaction system. First, the pH value should be carefully controlled since most polyoxotungstates are pH-sensitive species. In our experiment, compound **1** was isolated from the pH = 4.0 acetate buffer solution. Outside of these pH

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Table 2. Selected Bond Lengths (Å) of M−O (M = W, Mn, Ce) in **1**[a]

Polyoxoanion			
W1−O5	1.684(16)	W2−O15	1.713(11)
W1−O4A	1.832(10)	W2−O16	1.888(11)
W1−O4	1.832(10)	W2−O17A	1.896(11)
W1−O17	1.977(11)	W2−O18	1.913(11)
W1−O17A	1.977(11)	W2−O20	1.917(7)
W1−O10	2.367(14)	W2−O10	2.403(10)
W3−O14	1.710(10)	W4−O11	1.691(11)
W3−O6	1.857(11)	W4−O9	1.867(10)
W3−O8	1.900(3)	W4−O7	1.897(2)
W3−O19	1.915(7)	W4−O6	1.935(10)
W3−O18	1.923(10)	W4−O16	1.946(10)
W3−O12	2.319(9)	W4−O13	2.337(11)
W5/Mn1−O1	1.817(3)	W5/Mn1−O9	1.979(10)
W5/Mn1−O3	1.836(4)	W5/Mn1−O4	2.007(9)
W5/Mn1−O2	1.905(4)	W5/Mn1−O13	2.350(11)
3d-4f Heterometallic Cluster			
Ce1−O24	2.258(8)	Ce1−O22	2.39(3)
Ce1−O25	2.27(3)	Ce1−O28	2.55(2)
Ce1−O26B	2.28(2)	Ce1−O29	2.57(2)
Ce1−O25B	2.31(2)	Ce1−O27	2.59(3)
Ce1−O26	2.35(2)		
Mn2−O25	1.82(2)	Mn3−O26	1.84(2)
Mn2−O25B	1.82(2)	Mn3−O26B	1.84(2)
Mn2−O25C	1.82(2)	Mn3−O26C	1.84(2)
Mn2−O21	1.90(2)	Mn3−O23	1.93(3)
Mn2−O21B	1.90(2)	Mn3−O23B	1.93(3)
Mn2−O21C	1.90(2)	Mn3−O23C	1.93(3)

[a] Symmetry transformations used to generate equivalent atoms. A: y, x, z. B: $-y+1, x-y+1, z$. C: $-x+y, -x+1, z$.

conditions, compound **1** cannot be obtained. It is worth mentioning that a large amount of acetic acid was introduced into the reaction system in order to control a proper pH value and to induce the partial decomposition of $\{P_2W_{12}\}$ in such an acidic media. This method has been proved by several research groups as a useful way to isolate new POM-based high-nuclear clusters.[16] Second, a series of parallel synthetic experiments shows that a longer reaction time is necessary for the structural transformation of $\{P_2W_{12}\}$ to $\{P_2W_{16}\}$ via a process of decomposition and reconstruction. Third, the transition metal and lanthanide ions (2:3 in mole ratio) were used in excess in the reaction system; otherwise, only discrete Dawson-type $[P_2W_{18}O_{62}]^{6-}$ polyanions can be isolated. It is presumed that the excessive Mn^{III} ions might ensure the effective competition between Mn^{III} and $\{WO_6\}$ fragments on the vacant sites of the $\{P_2W_{12}\}$ units. Finally, the filtrate must be kept to a very slow evaporation, and the crystals of **1** were generally isolated after one month. Too-quick crystallization will lead to a large amount of a light-yellow byproduct of $[P_2W_{18}O_{62}]^{6-}$ and dramatically decrease the yield of compound **1**.

Structure Description. Single-crystal X-ray diffraction analysis shows that compound **1** crystallizes in the hexagonal space group *P*6$_3$/*mcm*. The basic structural unit of **1** contains one triple-Dawson-type polyoxoanion $[Mn_2P_2W_{16}O_{60}]_3^{24-}$, two cationic clusters $[Ce_3Mn_2O_6(OAc)_6(H_2O)_9]^{2+}$, 20 sodium cations, and 21 lattice water molecules. The polyoxoanion of **1** can be described as a cyclic trimer of di-Mn-substituted Dawson-type polyoxoanions (see Figure 1), representing a new triple-Dawson-type structure in POM chemistry.[17] As shown in Figure 1a, the polyoxoanion of **1** contains three $[Mn_2P_2W_{16}O_{60}]^{8-}$ subunits, and each of them possesses an unusual divacant $[P_2W_{16}O_{59}]^{12-}$ fragment (abbreviated as $\{P_2W_{16}\}$). This divacant species can be formed via the removal of two adjacent $\{WO_6\}$ octahedra from the "belt" region of its parent Dawson-type structure $\{P_2W_{18}\}$ (see Scheme S2, Supporting Information). To our knowledge, such a lacunary polyoxoanion fragment has rarely been observed in POM chemistry.[12b] Furthermore, two Mn^{III} ions reside in the two vacant sites of $\{P_2W_{16}\}$ moieties, and both exhibit the six-coordination geometry with six O atoms derived from the polyoxoanions. It is noteworthy that each Mn^{III} is connected with one W center derived from the adjacent $\{P_2W_{16}Mn_2\}$ subunit via the terminal oxygen ligand, forming the {Mn−O−W} bridges. As a result, three $\{P_2W_{16}Mn_2\}$ building blocks are fused together by six {Mn−O−W} bridges into the triple-Dawson-type polyoxoanion of **1** (see Figures 1b and 2). Furthermore, the oxidation states of W5 and Mn1 on the polyoxoanion cannot be directly determined by the bond-valence sum (BVS) calculations because the two metal centers possess site-occupancy disorder in the same position. Thus, the Mn^{III} center is confirmed by the redox titration and magnetism measurements (see Supporting Information).

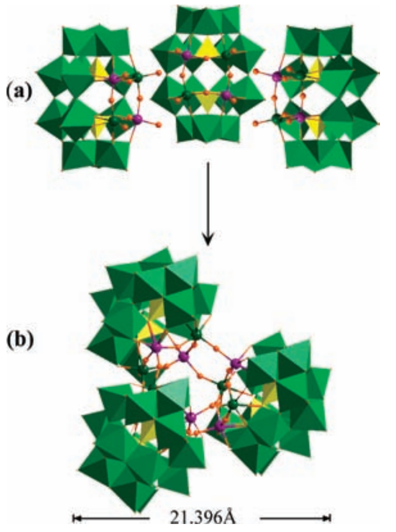

Figure 1. Polyhedral and ball-and-stick representation of (a) the basic building blocks and (b) their connection modes in the polyoxoanion of **1**. Color codes: W (green), Mn^{III} (violet), P (yellow), and O (orange).

The cationic unit $[Ce_3Mn_2O_6(OAc)_6(H_2O)_9]^{2+}$ in **1** is a 3d−4f heterometallic cluster, in which three Ce centers are sandwiched by two Mn centers, forming a pentanuclear bipyramid-like structure (see Figure 3). All of the Ce centers exhibit a nine-coordination environment with two O atoms derived from the acetate ligands, four μ_3-O bridges, and three coordinated water molecules. The bond lengths of Ce−O are in the range of 2.258(8)~2.59(3) Å. Two Mn centers possess the octahedral coordination geometry with three μ_3-O bridges and three O atoms derived from the acetate ligands. The bond lengths of Mn−O are in the range of 1.82(2)~1.93(3) Å (see Table 2).

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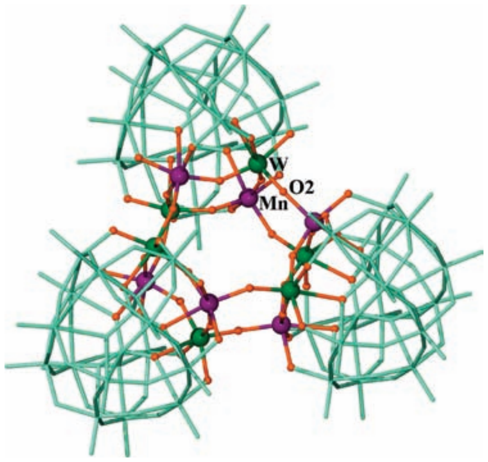

Figure 2. Ball-and-stick representation of the $\{W_6Mn_6\}$ hexagonal ring core in **1**. The inorganic POM fragments $\{P_2W_{14}\}$ are shown in the stick mode for clarity. Color codes: W (green), Mn^{III} (violet), P (yellow), and O (orange).

BVS calculations confirm that all Ce and Mn centers on the cationic clusters possess the +4 oxidation state.[18] Furthermore, their oxidation states are also determined by redox titration and the magnetism measurement. A similar neutral cluster containing the $\{Ce^{IV}{}_3Mn^{IV}{}_2\}$ core has recently been reported by Christou and co-workers.[13] In our case, partial coordination sites of three Ce^{IV} centers are occupied by nine coordinated water molecules, and thus the whole clusters acts as countercations in compound **1**.

In the packing arrangement, each triple-Dawson polyoxoanion is surrounded by six neighboring heterometallic clusters, while each heterometallic cluster is surrounded by three polyoxoanions (see Figure 4). On the basis of this arrangement, the polyoxoanions and the heterometallic clusters of **1** are well-arranged into a 2-D supramolecular assembly on the *a*+*b* plane similar to the Kagomé-type topology. Furthermore, there are two kinds of such supramolecular assemblies in **1** according to the different orientations of triple-Dawson polyoxoanions in the layer (see Figure 4a and b). These two kinds of layers are stacked together in an ABAB... mode along the *c* axis (see Figure 4c) and are notably well-overlapped so that two types of pillars coexist in **1** along the *c* axis (see Figure 4c). Pillar I is composed of the triple-Dawson-type polyoxoanions, which are arranged in a staggered fashion along the *c* axis, while pillar II consists of the heterometallic clusters stowed along the *c* axis. Hence, compound **1** possesses two sorts of potential 1-D channels. One is located in the central part of the triple-Dawson-type polyoxoanions viewed along the *c* axis with an accessible dimension of ca. 7.23 × 5.66 Å. The other exists between pillar I and pillar II, and its accessible dimension is ca. 20.76 × 20.76 Å. All of these channels are filled with sodium countercations and solvent water molecules. On the basis of the above structural feature, compound **1** can also be viewed as a new type of ionic crystal,[19] which is constructed by the cationic $\{Ce^{IV}{}_3Mn^{IV}{}_2\}$ units and the large triple-Dawson-type polyoxoanion building blocks.

Electrochemical Analyses and Electrocatalytic Activities. The aqueous solution stability of polyoxoanion **1** has been carefully investigated. Polyoxoanion **1** was dissolved in a pH = 4.0 (0.4 M NaOAc + HOAc) buffer solution and kept at room temperature. The cyclic voltammetric behavior of this solution was measured five times at 24 h intervals. After 5 days of checking, this solution was stored, and no voltammetric characteristics were changed (Figure S3, Supporting Information). Further, the UV−vis spectra of the above solution were also checked simultaneously, and no changes were observed during the five days (see Figure S4, Supporting Information). These characterizations indicate that polyoxoanion **1** is structurally stable in aqueous solution.

The electrochemical properties of **1** were investigated in the pH = 4.0 acetate buffer solution at a scan rate of 150 mV s^{-1}. As shown in Figure 5a, the cyclic voltammograms (CV) of **1** exhibit five pairs of redox peaks in the potential range of +1.15 to −1.1 V, and the mean peak potentials, $E_{1/2} = (E_{pa} + E_{pc})/2$, are +0.819, +0.368, −0.503, −0.669, and −0.847 V (vs Ag/AgCl), respectively. The first oxidation peak I (+0.926 V) and its reduction counterpart I′ (+0.712 V) are attributed to the redox process of the Mn centers.[20] The second oxidation peak II (+0.496 V) and its reduction counterpart II′ (+0.240 V) are attributed to the redox process of Ce^{IV}/Ce^{III}.[21] The third, fourth, and fifth oxidation peaks III, IV, and V (−0.504, −0.676, and −0.898 V, respectively) and their reduction counterparts III′, IV′, and V′ (−0.502, −0.662, and −0.796 V) are all ascribed to the redox process of W^{VI} centers, which are similar to those of the reported polyoxotungstates.[22]

The determination and elimination of nitrite ions in environmental and food samples has been paid considerable attention in recent years due to their distinct toxicity and suspected carcinogenicity.[23] Generally, it is difficult to directly electroreduce the nitrite ions to their corresponding reduced form with the bare electrode because this process requires high overpotential at most of the bare electrode surfaces. However, the introduction of various catalysts into the bare electrodes could speed up the electroreduction process and lower the

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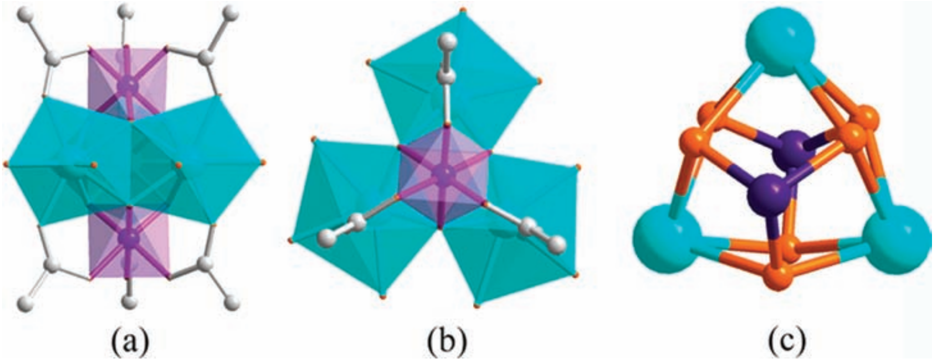

Figure 3. Polyhedral and ball-and-stick representation of the 3d−4f heterometallic cationic cluster $[Ce^{IV}_3Mn^{IV}_2O_6(CH_3COO)_6(H_2O)_9]^{2+}$ along the *b* axis (a) and along the *c* axis (b). (c) Trigonal-bipyramidal topology of the $[Ce^{IV}_3Mn^{IV}_2O_6]^{8+}$ core in **1**. Color codes: Ce (turquoise), Mn^{IV} (purple), O (orange), and C (gray-25%).

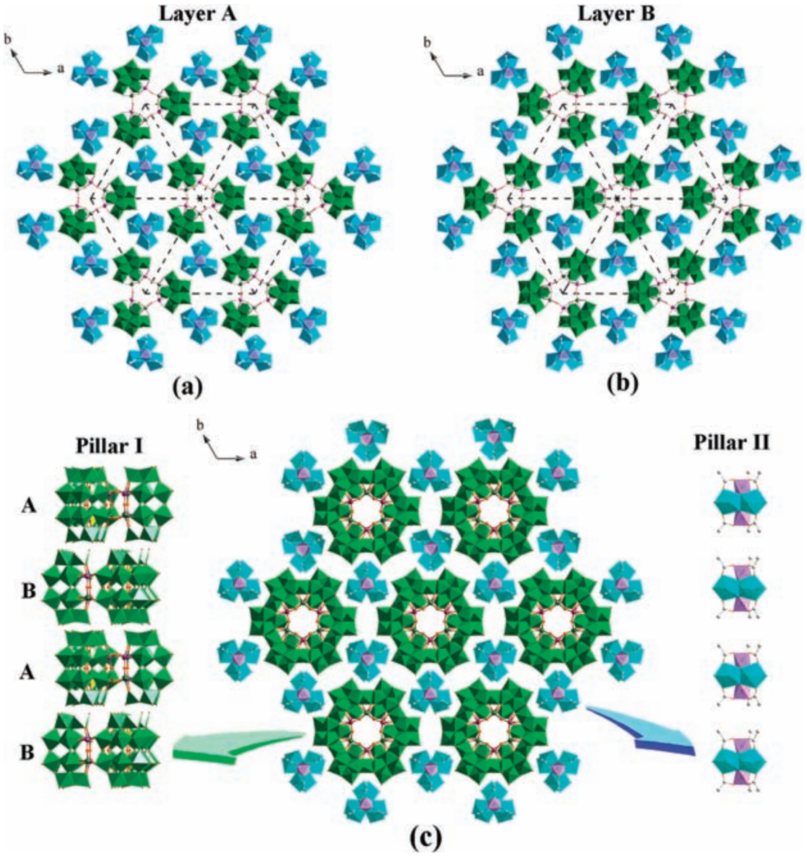

Figure 4. (a) Layer A, one 2-D supramolecular assembly of compound **1** based on POMs and cationic clusters. (b) Layer B, the other 2-D supramolecular assembly of compound **1**. (c) The packing arrangement of compound **1** viewed along the *c* axis. In this packing, pillar I contains the polyoxoanions arranged in the ABAB... mode; pillar II consists of the 3d−4f heterometallic clusters. The Na^+ cations and solvent water molecules are omitted for clarity. Color codes: W (green), Mn^{III} (violet), Mn^{IV} (purple), Ce (turquoise), P (yellow), O (orange), and C (gray).

overpotential. In this aspect, POMs are one kind of suitable catalyst candidate, because POMs are capable of delivering electrons to other species, serving as powerful electron reservoirs for multielectron reductions.[24] In this subfield, the exploration of new POM catalysts modified on the electrode is a continual research topic.

On the basis of the aforementioned background, the electrocatalytic reduction of nitrite for **1** was also studied in the same buffer solution as those employed in the CV studies. The results demonstrate that compound **1** displays moderately good electrocatalytic activity to reduce nitrite (Figure 5b). On the addition of modest amounts of nitrite, the reduction peak currents of W increased, while the corresponding oxidation peak currents dramatically decreased, suggesting that nitrite was reduced by the

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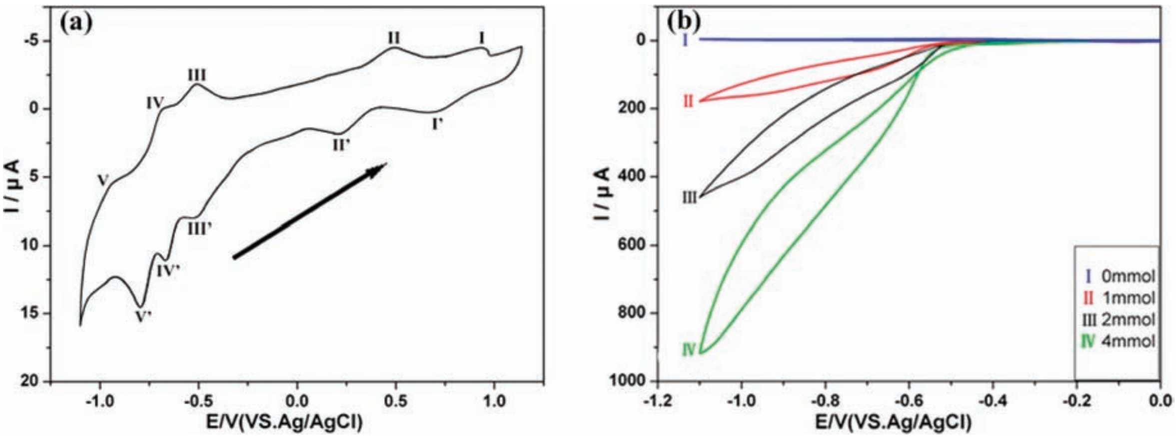

Figure 5. (a) Cyclic voltammograms of 4×10^{-4} M **1** in the pH = 4.0 (0.4 M $CH_3COONa + CH_3COOH$) buffer solution at a scan rate of 150 mV s^{-1}. (b) Electrocatalysis of the reduction of NO_2^- in the presence of 4×10^{-4} M **1** at a scan rate of 150 mV s^{-1}. The concentrations of NO_2^- are (I) 0.0, (II) 1.0, (III) 2.0, and (IV) 4.0 mM. The working electrode was glassy carbon, and the reference electrode was Ag/AgCl.

reduced POM species.[25] Notably, the second reduced species of **1** exhibits better electrocatalytic activity; that is, the catalytic activity is enhanced with the increasing extent of POM reduction. In comparison, no reduction of nitrite took place on the GC electrode in the absence of compound **1**.

FT-IR and UV−Vis Spectroscopy. The IR spectrum of **1** (Figure S5, Supporting Information) shows a broad band at 3421 cm^{-1} and a strong peak at 1615 cm^{-1} attributed to the lattice and coordinated water molecules. The bands at 1476, 1427, and 1348 are assigned to OAc$^-$ organic ligands. The absence of strong peaks around 1720 cm^{-1} indicates that all carboxylic groups are deprotonated.[26a] The value of $\Delta\nu$ (1476 − 1427 = 49 cm^{-1}) for **1** shows that the carboxylate groups coordinate to the metal atoms in bidentate fashions,[26b] which are consistent with the results of the X-ray analysis. The characteristic peak at 1202 cm^{-1} corresponds to $\nu(P-O_a)$ vibrations. The features at 955, 862, 777, and 718 cm^{-1} are attributed to $\nu(W{=}O_d)$, $\nu(W-O_b)$, and $\nu(W-O_c)$ in the polyoxoanions, respectively.[1a]

The UV−vis spectrum of compound **1** was recorded in a 0.4 M NaOAc and HOAc buffer solution at pH = 4.0 (see Figure S4, Supporting Information) and displays two absorbance bands (232 and 271 nm) in the UV region, which are attributed to the O→W ligand-to-metal charge transfer bands.[1a] Further, the band at 499 nm in the visible region might originate from the d−d electron transition of Mn^{III} ions.[26]

TG Analysis. In order to estimate the lattice−water content and the thermal stability of compound **1**, TG analysis was carried out from 25 to 800 °C. In the TG curve of compound **1** (Figure S6, Supporting Information), there are two obvious weight loss steps. The first weight loss of 2.49% in the temperature range of 50−285 °C corresponds to the release of all lattice and coordinated water molecules, which is in accordance with the calculated value of 2.47% (~39H_2O). The second weight loss of 2.33% in the temperature range of 285−510 °C is attributed to the loss of all OAc$^-$ organic ligands. The value is close to the calculated value of 2.32%. The last small weight loss after 510 °C is ascribed to the release of partial P_2O_5 derived from the combination of P and O atoms in the polyoxoanions (calcd 0.25%).

Conclusions

In conclusion, a new compound, based on cyclic triple-Dawson-type polyoxoanions $[Mn^{III}_2P_2W_{16}O_{60}]_3^{24-}$ and bipyramid-like 3d−4f heterometallic clusters $[Ce^{IV}_3Mn^{IV}_2O_6(OAc)_6(H_2O)_9]^{2+}$, has been synthesized, exhibiting a 3-D supramolecular assembly with 1-D channels. During the preparation, the introduction of hexa-vacant Dawson-type polyoxoanion $\{P_2W_{12}\}$ into the $\{Ce^{IV}/Mn^{II}/OAc^-\}$ system led to the isolation of such a new kind of POM species. Compound **1** displays moderately good electrocatalytic activity to reduce nitrite. The preparation of compound **1** may indicate new perspectives for the construction of novel POMs by carefully selecting appropriate lacunary polyoxoanions and heterometal ion sources. More research work will focus on the reaction between various lacunary POMs and the $\{Ce^{IV}/Mn^{II}/OAc^-\}$ system in order to isolate new POM species with interesting properties and functionalities.

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Supporting Information Available: X-ray crystallographic files in CIF format, the TG curve, the UV spectra, the IR spectra, and the additional figures for compound **1**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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