



Synthesis, crystal structure, and property of one- and two-dimensional complexes based on paradodecatungstate-B cluster

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ABSTRACT

Three polyoxotungstates, $\text{Na}_8[\text{Cu}(\text{H}_2\text{O})_2(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 30\text{H}_2\text{O}$ (**1**), $\text{Na}_8[\text{Cd}(\text{H}_2\text{O})_2(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 20\text{H}_2\text{O}$ (**2**), and $\text{Na}_{7.4}[\text{Cd}_{1.3}(\text{H}_2\text{O})_2(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 24\text{H}_2\text{O}$ (**3**), were synthesized and characterized by elemental and thermogravimetric (TG) analysis, infrared spectroscopy and X-ray single-crystal analysis. Both complexes **1** and **2** exhibit one-dimensional structure with two neighboring paradodecatungstate-B clusters, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, linked by $[\text{Cu}(\text{H}_2\text{O})_2]^{2+}$ or $[\text{Cd}(\text{H}_2\text{O})_2]^{2+}$ units, while complex **3** displays a two-dimensional network structure. The electrochemical behaviors of complexes **1** and **3** were investigated in the buffer solution of pH 4.8. The results of electrocatalysis reveal that the reduced species of complexes **1** and **3** are electrocatalytically active for the reduction of nitrate. Complex **1** exhibits the electrocatalytic activity for the reduction of nitrate as well. The surface photovoltage spectroscopy (SPS) and electric field-induced SPS (EFISPS) measurements show that the surface photovoltage behavior of complex **1** is complicated while complex **3** bears the property of n-type semiconductor.

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1. Introduction

Polyoxometalates (POMs) have been one of the remarkable and rich classes of inorganic clusters, which are usually constructed by early transition metals, especially tungsten, molybdenum and vanadium [1]. In the past several years, much attention has been paid on the design and synthesis of the complexes with novel crystal structure and functional properties, while most of which exist in discrete cluster state [2]. Due to the diverse potential applications in the interdisciplinary areas, especially in functional materials, extended POMs researches become more attractive based on a fundamental interest, such as linked or cross-linked POMs [3]. Generally, there are two types of polymeric POMs, one of which is that the clusters join with each other directly without the introduction of any other metals [4]. The other is that the clusters are connected by additional metal ions, especially those transition and lanthanide metal ions [5]. Comparing with the polymeric POMs without additional binding metal ions, the POMs networks with extra binding metal ions have been developed more widely due to the convenience and facility to connect discrete clusters. Such polymeric structures are surely important because of the multiformity of structure and function for these bonded clusters. To date, various metal-supporting POMs have been synthesized and characterized, such as $(\text{NH}_4)_2[\text{Ni}_4$

$(1,2\text{-diaminopropane})_2(\text{PW}_9\text{O}_{34})_2] \cdot 9\text{H}_2\text{O}$ [6], $\text{Co}_2(4,4\text{-bipy})_6(\text{W}_6\text{O}_{19})_2$ [7], $[\text{Cu}_3(4,7\text{-phen})_3]_2\text{Mo}_{14}\text{O}_{45}$ [8], $[\text{Zn}_2(\text{terephthalate})(4,4\text{-bipy})\text{-V}_2\text{O}_6]$ [9] and $[\text{Cu}(\text{enMe})_2]_7[\text{V}_{16}\text{O}_{38}(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$ [10], which display rich and interesting structural and functional features. However, the design and synthesis of extended POMs are still a challenge and it is necessary to find an effective way by selecting an appropriate discrete cluster as basic unit for the construction of polymeric POMs. Considering coordination capability, we selected the paradodecatungstate-B cluster, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$, to be the primary building block. Several paradodecatungstate-B complexes with different counter ions have been synthesized and characterized [11–15]. This kind of anion is composed of four corner-sharing W_3O_{13} groups with two protons. Due to its stable structure and high reactive activity of the terminal oxygen atoms, paradodecatungstate-B cluster, as an ideal building block, has been also employed for the construction of extended metal bridged polyoxoanion, such as $\text{H}_2\{[\text{K}(\text{H}_2\text{O})_2]_2[\text{Ln}(\text{H}_2\text{O})_5]_2(\text{H}_2\text{M}_{12}\text{O}_{42})\}$ ($M = \text{W}, \text{Mo}$), $[(\text{Co}(\text{H}_2\text{O})_4)_2(\text{H}_2\text{W}_{12}\text{O}_{42})]_n^{6n-}$, and $[\text{Cu}(\text{en})_2]_3[\text{Cu}(\text{en})_2(\text{H}_2\text{W}_{12}\text{O}_{42})] \cdot 12\text{H}_2\text{O}$ [16–20].

To explore new structures based on paradodecatungstate-B clusters, we tried the reactions under controlled conditions and we really obtained some interesting complexes. In this paper, we described the synthesis, crystal structure, electrochemistry and photovoltage property of one copper (II) connected POM complex **1**, and two cadmium (II) connected POM complexes **2** and **3**. The frameworks of the complexes are supported by paradodecatungstate-B clusters. Because the structure of complex **2** is quite similar to the one that has been described in the literature [21],

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we mainly concentrate our description and discussion on complexes **1** and **3**.

2. Experimental

2.1. Materials and physical measurements

Doubly distilled water was used throughout the experiments. All reagents were commercially available and used without further purification. Buffer solution was prepared from 0.5 M NaAc and 0.5 M HAc. For the electrocatalysis experiments, the solutions of NaNO₃ and NaNO₂ were freshly prepared before use. All solutions were degassed with pure nitrogen gas for at least 30 min before use.

Elemental analysis (Na, Cu, Cd and W) were performed on a PLASMA-SPEC (I) inductively coupled plasma (ICP) spectrometer. FT-IR spectra were carried out on a Bruker Vertex 80V FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of 4 cm⁻¹ on KBr pellets. Thermogravimetric (TG) analyses were performed on a Perkin-Elmer TGA-7 instrument in flowing air with a heating rate of 10 °C min⁻¹. All electrochemical experiments were performed on a LK98BII electrochemical workstation at room temperature. A three-electrode electrochemical cell was used with a glassy carbon electrode (GCE) as the working electrode, a platinum wire as the counter and a Ag/AgCl electrode as the reference. The GCE was polished with 1.0, 0.3 and 0.05 μm α-Al₂O₃ powders successively, and sonicated in water for about 15 min after each polishing step. Finally, the electrode was washed with acetone and dried with a nitrogen stream immediately before use. Formal potentials (*E_f*) were estimated as average values of anodic (*E_{pa}*) and cathodic (*E_{pc}*) peak potentials, i.e., *E_f* = (*E_{pa}* + *E_{pc}*)/2. The surface photovoltage (SPV) spectroscopic instrument was home-made and composed of xenon lamp of 500 W, precision monochromators, SRS-830 Lock-in amplifier, chopper and computer.

2.2. Synthesis

2.2.1. Na₈[Cu(H₂O)₂(H₂W₁₂O₄₂)] · 30H₂O (**1**)

Na₂WO₄ · 2H₂O (3.298 g, 10 mmol) and V₂O₅ (0.182 g, 1 mmol) were dissolved in 30 mL of water, and the pH of the mixture was adjusted to 4.8 by adding dilute HCl. The solution was then heated to 80 °C and kept at this temperature for 15 min. A clear solution was obtained, and to the solution was added Cu(NO₃)₂ · 6H₂O (0.591 g, 2 mmol) subsequently. Diluted HCl was added again when turbidity occurs and the final pH was adjusted to 4.8. About 20 min later, the solution was cooled to room temperature and filtered. Slow evaporation of the filtrate generates light green block crystals. The yield was 60% (based on Cu(NO₃)₂ · 6H₂O). Anal. calc. (Found) (%) for Na₈[Cu(H₂O)₂(H₂W₁₂O₄₂)] · 30H₂O (**1**): Na 4.97 (5.09), W 59.56 (60.84), Cu 1.72 (1.78). IR (KBr pellet, cm⁻¹): 1630, 1579, 1417, 943, 875, 835, 806, 710, 501, 440.

2.2.2. Na₈[Cd(H₂O)₂(H₂W₁₂O₄₂)] · 20H₂O (**2**)

Similar procedures were taken as mentioned above by using CdCl₂ · 2.5H₂O (0.456 g, 2 mmol) instead of Cu(NO₃)₂ · 6H₂O. Colorless crystals were obtained in 2 weeks. The yield was 45% (based on CdCl₂ · 2.5H₂O). Anal. Calc. (Found) (%) for Na₈[Cd(H₂O)₂(H₂W₁₂O₄₂)] · 20H₂O (**2**): Na 5.15 (5.26), W 61.75 (63.07), Cd 3.15 (3.26). IR (KBr pellet, cm⁻¹): 1635, 1576, 1415, 935, 887, 837, 798, 702, 499, 441.

2.2.3. Na_{7.4}[Cd_{1.3}(H₂O)₂(H₂W₁₂O₄₂)] · 24H₂O (**3**)

Na₂WO₄ · 2H₂O (3.298 g, 10 mmol) and V₂O₅ (0.182 g, 1 mmol) were added to 1 M of CH₃COONa/CH₃COOH buffer solution (pH

4.8), and the mixture was heated to 80 °C and then CdCl₂ · 2.5H₂O (0.456 g, 2 mmol) was added. The mixture was stirred and heated for an hour at this temperature. During this period, the solution kept clear. After that, the solution was cooled to room temperature and filtered, the filtrate was kept in air and a colorless crystal was obtained in 2 weeks. The yield was 65% (based on CdCl₂ · 2.5H₂O). Anal. calc. (Found) (%) for Na_{7.4}[Cd_{1.3}(H₂O)₂(H₂W₁₂O₄₂)] · 24H₂O (**3**): Na 4.64 (4.80), W 60.20 (61.71), Cd 3.99 (4.10). IR (KBr pellet, cm⁻¹): 1631, 1577, 1419, 945, 906, 875, 835, 804, 708, 501, 438.

2.2.4. Crystallographic data collection and refinement

A light green block single crystal of complex **1** (0.052 × 0.056 × 0.062 mm³) was set on the end of a glass capillary, and the data were collected on a Rigaku R-Axis RAPID IP diffractometer with graphite monochromated MoKα radiation (λ = 0.71073 Å) at 293 K in the range of 3.14° < θ < 27.48°. Empirical absorption correction based on equivalent reflections was applied. A total of 31,023 (14,405 unique, *R_{int}* = 0.0610) reflections were measured (-16 ≤ *h* ≤ 16, -16 ≤ *k* ≤ 17, -26 ≤ *l* ≤ 26). A colorless block single crystal of complex **2** (0.085 × 0.096 × 0.101 mm³) was fixed to the glass capillary, the data were obtained on the same diffractometer under the same condition of complex **1** in the range of 3.03° < θ < 27.49°. Empirical absorption correction based on equivalent reflections was applied. A total of 13,593 (6235 unique, *R_{int}* = 0.0524) reflections were measured (-14 ≤ *h* ≤ 14, -15 ≤ *k* ≤ 15, -15 ≤ *l* ≤ 15). Indexing and intensity data collection for **3** (colorless block, 0.035 × 0.036 × 0.039 mm³) were also performed on the same diffractometer in the range of 3.04° < θ < 27.50° under the same condition as complex **1**. Empirical absorption correction based on equivalent reflections was applied. A total of 14,716 (6790 unique, *R_{int}* = 0.0481) reflections were measured (-14 ≤ *h* ≤ 14, -16 ≤ *k* ≤ 16, -15 ≤ *l* ≤ 16).

The three complexes were all solved by direct method and refined by full-matrix least-squares fitting on *F*² using the SHELXTL-97 software. A summary of the crystallographic data and structural refinements for complexes **1**, **2** and **3** are listed in

Table 1
Crystal data and structure refinement of complexes **1**, **2** and **3**

Complex	1	2	3
Formula weight	3704.02	3572.74	3664.73
Temperature (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	13.081(4)	11.243(5)	10.973(4)
<i>b</i> (Å)	13.160(6)	11.961(5)	12.836(6)
<i>c</i> (Å)	20.127(6)	12.034(5)	13.014(5)
α (deg)	78.294(12)	64.510(17)	65.700(17)
β (deg)	78.524(11)	71.570(15)	67.410(14)
γ (deg)	72.593(11)	74.550(19)	69.150(18)
Volume (Å ³)	3201.7(17)	1369.7(10)	1499.2(10)
<i>Z</i>	2	1	1
<i>d</i> _{calcd} (g/cm ³)	3.907	4.332	4.059
Abs. coeff. (mm ⁻¹)	21.975	25.656	23.548
<i>R</i> _{int}	0.0610	0.0525	0.0482
<i>F</i> (0 0 0)	3450	1582	1630
GOOF on <i>F</i> ²	1.067	1.045	0.963
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0429	0.0412	0.0470
<i>R</i> _w (all data) ^b	0.1160	0.0978	0.1212
(Residues) _{max} (e/Å ³)	1.890	2.102	3.693
(Residues) _{min} (e/Å ³)	-2.983	-4.493	-4.762

^a *R* = ||*F*_o - *F*_c||/||*F*_o||.

^b *R*_w = [w(*F*_o² - *F*_c²)/w(*F*_o²)]^{1/2}.

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