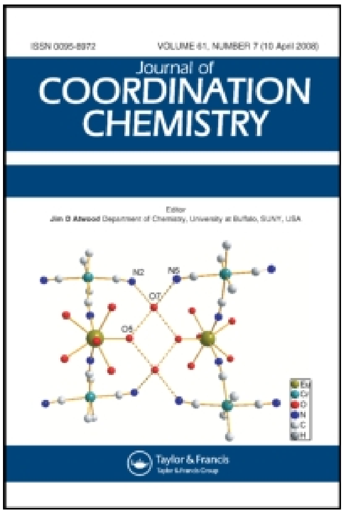

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Synthesis, crystal structure, and electrochemistry of a polymeric ladder-like compound based on and [Cu(OOCCH$_2$NH$_2$)$_2$]$_{2<i>n</i>}$

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Synthesis, crystal structure, and electrochemistry of a polymeric ladder-like compound based on $[H_2W_{12}O_{42}]_n^{10n-}$ and $[Cu(OOCCH_2NH_2)_2]_{2n}$

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An inorganic–organic hybrid compound, consisting of $[H_2W_{12}O_{42}]_n^{10n-}$ polyanions and glycine decorated $Cu(OOCCH_2NH_2)_{2n}$ units, was synthesized. X-ray single-crystal diffraction was carried out, giving a defined chemical structure of $Na_8(NH_4)_2[\{Cu(OOCCH_2NH_2)_2\}_2(H_2W_{12}O_{42})] \cdot 21H_2O$. Structure analysis indicates that $[H_2W_{12}O_{42}]^{10-}$ clusters were connected by $Cu(OOCCH_2NH_2)_2$ components on both sides through Cu–O bonds, forming a polymeric ladder-like structure in the crystal. The hybrid compound was further characterized by infrared (IR) spectrum, elemental analysis, and thermogravimetric analysis (TGA). The electrochemical behavior was investigated in pH 4.8 buffer.

Keywords: Paradodecatungstate-B; Copper; Glycine; Ladder-like structure

1. Introduction

Polyoxometalates (POMs) represent prominent polyanion clusters due to their potential applications in catalysis, magnetism, electrochemistry, and optical materials [1]. Although various POMs have been synthesized, most are crystallized in discrete clusters [2]. Current study of POMs chemistry focuses on decorating additional organic and/or inorganic components on polyoxometalates to construct diverse topological supramolecular architectures. One branch of this field involving transition metals, especially copper ions, plays important roles in the construction of various topologic structures [3]. Copper ions exhibit three, four, five, and six coordination, modifying the geometric and packing of POMs, and incorporating functionalities into the structures, such as redox and magnetic properties [4, 5]. Use of different organic ligands with various functions enriches the derivatives of POMs; among all organic ligands, amine, and pyridine derivatives are the most frequently employed ligands [6]. In contrast with other ligands, amino acids are rarely introduced into extended POMs, even the simplest one, glycine [7].

Considering the activity of the terminal oxygens paradodecatungstate-B anion, $[H_2W_{12}O_{42}]^{10-}$, is a useful building block to construct extended POMs.

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Several transition and lanthanide cations have been applied as effective bridges to link discrete paradodecatungstate-B anions to form 1-, 2-, and 3-D compounds [8]. While most of these extended POMs are connected by inorganic ions, inorganic–organic complexes as bridges of hybrid compounds are quite rare [9]. Therefore, we tried to introduce both copper and organic components into POMs to obtain hybrid extended POMs. In the present article, we describe the synthesis, crystal structure, and electrochemical behavior of a polymeric ladder-like compound, $Na_8(NH_4)_2[\{Cu(OOCCH_2NH_2)_2\}_2(H_2W_{12}O_{42})]\cdot 21H_2O$ (**1**), based on $[H_2W_{12}O_{42}]^{10-}$ and glycine decorated $[Cu(OOCCH_2NH_2)_2]$ units.

2. Experimental

2.1. *Materials and measurements*

Doubly-distilled water was used throughout the experiments. All reagents were commercially available and used without purification.

Elemental analysis (Na, Cu, and W) was performed on a PLASMA-SPEC (I) inductively coupled plasma (ICP) spectrometer. IR spectrum was carried out on a Bruker Vertex 80V FT-IR spectrometer equipped with a DTGS detector (32 scans) with a resolution of $4\,cm^{-1}$ in KBr pellets. Thermogravimetric (TG) analysis was performed on a Perkin-Elmer TGA-7 instrument in flowing air with a heating rate of $10^{\circ}C\,min^{-1}$. All electrochemical experiments were recorded on a CHI 660C 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 an Ag/AgCl electrode as the reference. The GCE was polished with 1.0, 0.3, and 0.05 µm α-Al_2O_3 powders successively and sonicated in water for *ca* 15 min after each polishing step. Finally, the electrode was washed with acetone and dried with a nitrogen stream immediately before use.

2.2. *Synthesis*

$Cu(NO_3)_2\cdot 6H_2O$ (0.9 g, 3 mmol) and glycine (0.5 g, 6 mmol) were dissolved in H_2O (30 mL). The mixture was stirred for 10 min and then $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$ (3.6 g, 1 mmol), which was synthesized according to the method given in [10], was added. The solution was heated to 50°C and kept at this temperature for 30 min and then NH_4Cl (0.1 g, 2 mmol) was added. The resulting solution was cooled to room temperature and blue block crystals were obtained 1 week later. Elemental analysis Calcd for **1** (%): C, 2.38; H, 2.05; N, 2.09; Na, 4.57; Cu, 3.16; W, 54.77. Found (%): C, 2.35; H, 2.01; N, 2.12; Na, 4.72; Cu, 3.05; W, 55.62.

2.3. *Crystallographic data collection and refinement*

Single crystal data of **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Empirical absorption corrections based on equivalent reflections were applied. The structure was

Table 1. Crystal data and structure refinements for **1**.

Compound	$Na_8(NH_4)_2[\{Cu(OOCCH_2NH_2)_2\}_2(H_2W_{12}O_{42})]\cdot 21H_2O$
Formula weight	3901.88
Temperature (K)	293(2)
λ (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12067(3)
b	12.136(5)
c	12.235(4)
α	76.130(14)
β	87.940(11)
γ	88.290(15)
Volume (Å^3)	1738.0(10)
Z	1
D_{Calcd} (g cm^{-3})	3.728
Absorption coefficient (mm^{-1})	20.544
R_{int}	0.0308
$F(000)$	1760
Goodness-of-fit on F^2	1.069
R [$I > 2\sigma(I)$]	0.0362
R_w [$I > 2\sigma(I)$]	0.0900
R (all data)	0.0427
R_w (all data)	0.0929

$R = ||F_o| - |F_c||/|F_o|$. $R_w = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2}$.

solved by direct methods and refined by full-matrix least-squares fitting on F^2 using SHELXTL-97. No hydrogens associated with water were located from the difference Fourier map. Positions of the hydrogen atoms attached to the carbon atom were geometrically placed. A summary of the crystallographic data and structural refinement for **1** is listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single crystal X-ray diffraction indicates that **1** crystallizes in the triclinic system, $P\bar{1}$ space group. The asymmetric unit consists of half of a paradodecatungstate-B, one $[Cu(OOCCH_2NH_2)_2]$ fragment, four sodium ions, one ammonium ion, and some lattice water molecules. Except for lattice water molecules, all the other atoms were refined anisotropically.

The paradodecatungstate-B cluster in **1** is composed of four corner-sharing $\{W_3O_{13}\}$ units with two protons. Based on different coordination environments, the oxygens can be divided into three groups: tungsten-terminal oxygens with W–O bond lengths from 1.608(6) to 1.789(6) Å; tungsten-bibridged oxygens with distances between tungsten and oxygen atoms of 1.730(6) and 2.122(6) Å; and tungsten-tribridged oxygens with W–O bond lengths in the range of 1.779(6)–2.304(6) Å. All the W–O distances and W–O–W angles are in the normal range [8]. In **1**, each $[H_2W_{12}O_{42}]^{10-}$ coordinates with four $[Cu(OOCCH_2NH_2)_2]$ fragments *via* four terminal oxygens, as shown in figure 1. In the

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu(1)–O(2)	2.564(12)	Cu(1)–O(12)#1	2.704(13)	Cu(1)–O(23)	1.862(7)
Cu(1)–O(24)	1.899(7)	Cu(1)–N(1)	1.952(9)	Cu(1)–N(2)	1.878(9)

O(2)–Cu(1)–O(12)#1	168.70(38)	O(23)–Cu(1)–O(2)	84.37(30)
O(24)–Cu(1)–O(2)	82.27(31)	N(1)–Cu(1)–O(2)	103.02(34)
N(2)–Cu(1)–O(2)	88.61(33)	O(23)–Cu(1)–O(12)#1	106.05(34)
O(24)–Cu(1)–O(12)#1	92.56(33)	N(1)–Cu(1)–O(12)#1	83.04(33)
N(2)–Cu(1)–O(12)#1	80.73(30)	O(24)–Cu(1)–O(23)	93.43(32)
N(1)–Cu(1)–O(23)	82.53(32)	N(2)–Cu(1)–O(23)	172.33(32)
N(1)–Cu(1)–O(24)	172.93(35)	N(2)–Cu(1)–O(24)	82.55(35)
N(2)–Cu(1)–N(1)	102.11(37)		

Symmetry code: #1; $2-x$, $2-y$, $-z$.

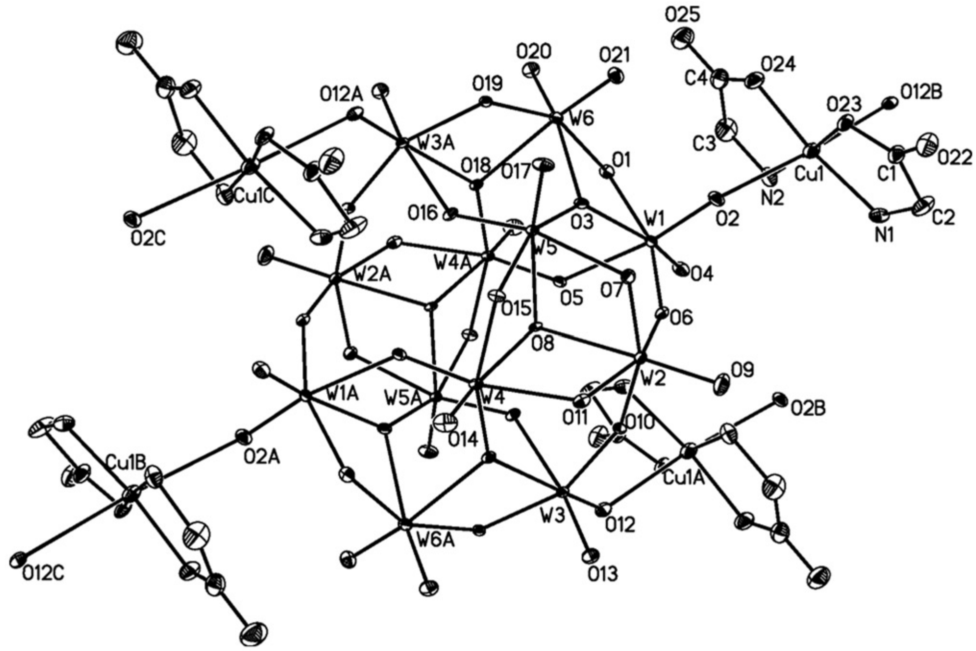

Figure 1. Fragment of **1** with the atomic labeling scheme (thermal ellipsoids shown at 30% probability).

structure, each copper is six-coordinate by two oxygens from two $[H_2W_{12}O_{42}]^{10-}$ clusters, and two oxygens and two nitrogens from two glycines. The copper of **1** exhibits a 4 + 2 coordination with marked axial distances (2.564(12) and 2.704(13) Å) from coordination of the terminal oxygens of paradodecatungstate-B. These distances are obviously longer than the equatorial ones (1.862(7)–1.952(9) Å, with a mean value of 1.898 Å) from coordination of glycine. All the distances for the $\{CuO_4N_2\}$ group are similar with those of Cu-containing POMs and glycine-coordinated compounds [7]. Based on Na–O bond lengths, the water molecules coordinated with sodium can be divided into strong sodium-coordinated water (Na–O bond lengths are shorter than 2.3 Å) and weak sodium-coordinated water (Na–O bond lengths are longer than 2.3 Å).

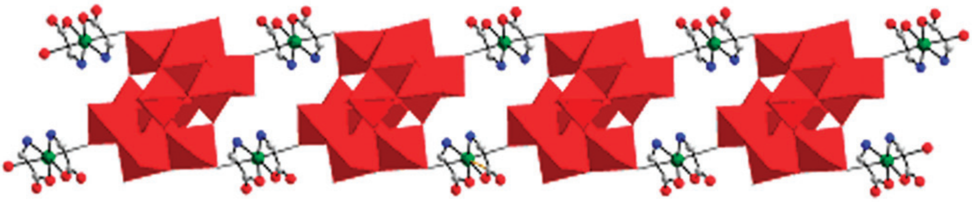

Figure 2. Polyhedral and ball-and-stick representation of 1-D structure of **1** based on Cu ions and paradodecatungstate-B clusters.

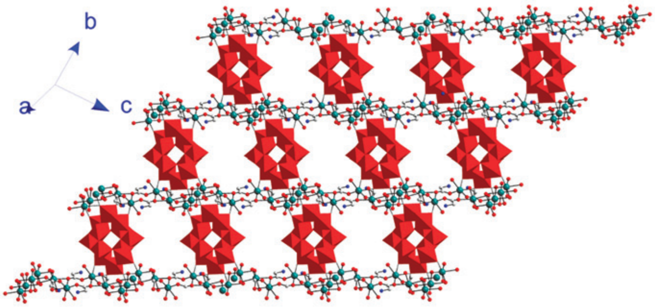

Figure 3. Polyhedral and ball-and-stick representation of 2-D structure of **1** based on Na ions and paradodecatungstate-B clusters.

Bond valence sum calculation reveals that all tungstens are +6, copper is +2, and oxygens of the polyanion are −2 except the tribridged O8 with an oxidation value of −1.49, may be protonated.

As shown in the top of figure 2, two weak Cu–O bonds link neighboring paradodecatungstate-B clusters and $[Cu(OOCCH_2NH_2)_2]$ fragments, leading to a ladder-like polymeric chain along *a*. The average Cu–Cu distance between neighboring chains is 6.898(12) Å, with no obvious Cu–Cu interaction in **1**. The differences between the present and reported 1-D compound, $Na_8[Cu(H_2O)_2(H_2W_{12}O_{42})] \cdot 30H_2O$ [11], are as follows. In our previous compound, every paradodecatungstate-B unit is tetradentate coordinating with two Cu ions. In addition, the Cu exhibits a typical chelated structure with terminal oxygens of paradodecatungstate-B at Cu–O distances of 1.919(6) and 2.516(8) Å, respectively. However, in **1**, the paradodecatungstate-B units connect with $[Cu(OOCCH_2NH_2)_2]$ fragments through two weak Cu–O bonds making it possible that two $[Cu(OOCCH_2NH_2)_2]$ fragments to exist between the paradodecatungstate-B units. As a consequence, the hybrid structure exhibits a ladder-like chain and each ladder packs in a parallel orientation along the *a*-axis. The side rails of the ladder-like structure are provided by $[Cu(OOCCH_2NH_2)_2]$ units and rungs by paradodecatungstate-B clusters. The nearest Cu–Cu distances are 12.07(18) Å for the rail direction and 6.90(10) Å for the rung direction, providing the inter-rung distance and width of the ladder.

If only the Na ions are considered as connecting metals, a 2-D network can be found in **1**, as shown in figure 3. The copper ions link the paradodecatungstate-B clusters of two adjacent layers *via* O2 and O12 atoms, forming a 3-D topology. The ammonium

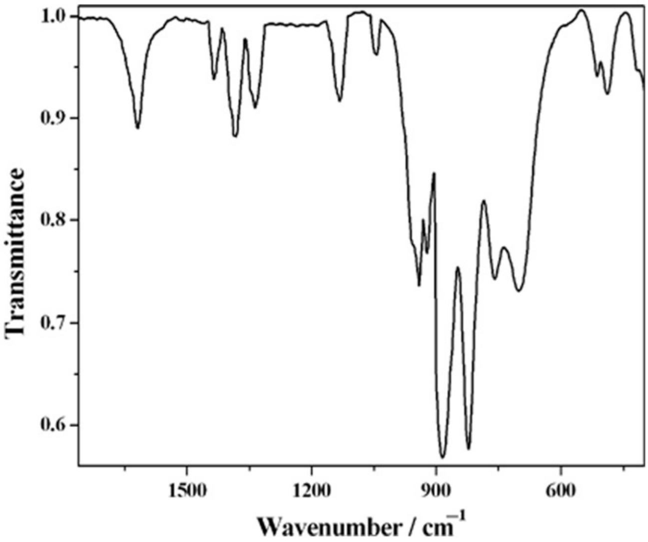

Figure 4. IR spectrum of **1** in KBr pellet.

ions are located in the crystal structure, balancing the negative charges and stabilizing the backbone of **1**.

3.2. *IR and TG*

IR spectrum of **1** in the low wavenumber region shows characteristic vibrations of paradodecatungstate-B clusters (figure 4). Bands at 941 and 922 cm^{-1} can be assigned to terminal W–O vibrations, in which the band splitting should be derived from the different coordination environments, coordinated and non-coordinated with Cu. The bridging W–O–W vibration in $[H_2W_{12}O_{42}]^{10-}$ separates into bands of 883 and 823 cm^{-1} due to the lower symmetry of the anions. A peak at 1600 cm^{-1} is attributed to combination vibrations of amine and carbonyl. The absorption at 1132 cm^{-1}, attributed to C–N vibration, confirms the presence of glycine [12].

The TG curve of **1** (Supplementary material) exhibits a total weight loss of 16.4%, slightly larger than the calculated value of 15.2% from crystal structure data. The excess weight is perhaps derived from the dried sample's physical surface absorption of moisture in the air. Two plateaus in the weight loss curve appear in the temperature range 40–500°C. The first loss of 5.9% before 236°C corresponds to removal of absorbed and crystallized water, slightly larger than the expected value (Calcd 5.4%). The second mass loss of 10.5% between 236 and 492°C arises from strong sodium-coordinated water and decomposition of organic ligands (Calcd 9.8%).

3.3. *Electrochemistry*

The electrochemical study of **1** was carried out in 0.5 M of NaAc+HAc buffer solution (pH 4.8). The stability was assessed by monitoring the cyclic voltammetric behavior for every 24 h, for three times and is stable under the experimental conditions.

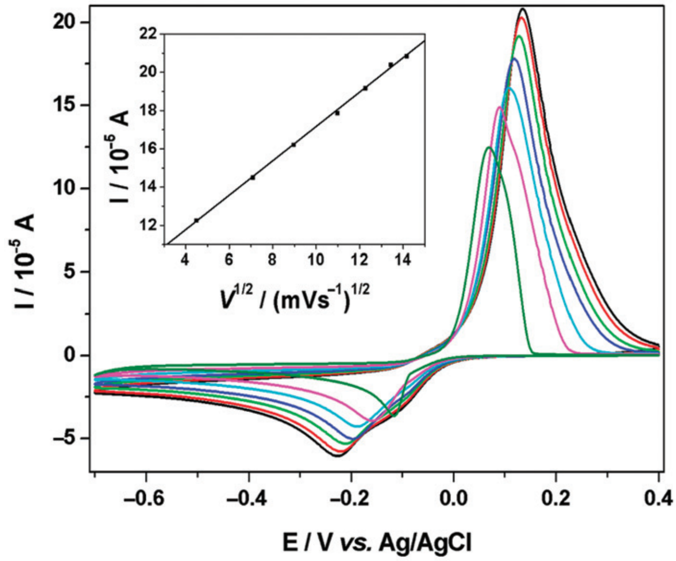

Figure 5. Cyclic voltammograms of 5×10^{-4} M **1** at scan rates of 20, 50, 80, 120, 150, 180, and 200 mV s^{-1} (from inner to outer) in 0.5 M NaAc+HAc of buffer solution (pH 4.8). The inset is the dependence of anodic peak current with the square root of the scan rates.

Figure S1 shows the typical cyclic voltammetric behavior of **1** at a scan rate of 100 mV s^{-1}. Unfortunately, we could not distinguish the oxidation wave of W due to the little current intensity [13]. In the potential range of −0.7 to +0.4 V, only a strong single oxidation process can be distinguished at +0.101 V, attributed to the redox of Cu. Two reduction peaks at −0.089 and −0.179 V feature the two-step reduction of Cu^{II} to Cu^0 through Cu^I [14]. The peak potential difference of the two reduction processes is 0.090 V, indicating the presence of ligands [15].

The cyclic voltammograms of **1** at different scan rates under the same pH were investigated and the results are shown in figure 5. By taking the oxidation peak currents of Cu centers in the compound, the peak currents are linearly proportional to the square root of the scan rate when the scan rates change from 20 to 200 mV s^{-1}, as shown in the inset of figure 5, indicating that the redox process is diffusion-controlled [16]. Oxidation waves move to the positive direction while the reduction peaks move negative with increase of scan rates, indicating that the redox process is quasi-reversible.

4. Conclusion

We report a polymeric inorganic–organic hybrid compound with $Cu(OOCCH_2NH_2)_2$-supported paradodecatungstate-B clusters, where $[Cu(OOCCH_2NH_2)_2]_2$ units are sides and paradodecatungstate-B clusters are rungs, forming a ladder-like chain along *a*. IR and TG results support the analysis of the crystal structure of the compound. The electrochemistry of **1** reveals the redox properties. Further research on the inorganic–organic hybrid and extended compounds based on the different POMs is currently underway.

Supplementary material

CCDC No. 690109 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email for inquiry: fileserv@ccdc.cam.ac.uk

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