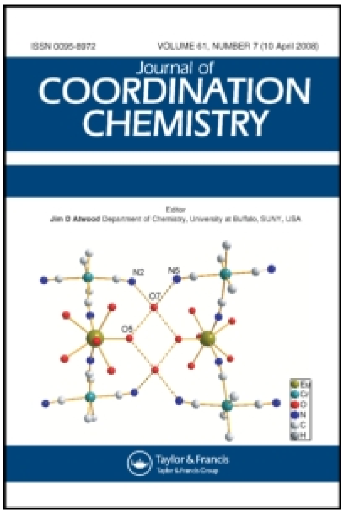

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Two α-metatungstate compounds containing supramolecular helical chains

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$[Co(bipy)_3]_3[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2] \cdot H_2O$ (**1**) and $[H_2bipy]_{0.5}[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}] \cdot H_2O$ (**2**) (bipy = 2,2′-pyridine) have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, elemental analyses, IR spectra, and TG analyses. In **1**, there exist supramolecular left/right-helical chains constructed by $[Co1(bipy)_3]^{2+}$ and these chains perpendicularly interact with a series of parallel POM double-chains composed of $[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2]^{6-}$ anions and $[Co2(bipy)_3]^{2+}$ cations forming a 3-D supramolecular network. In **2**, there also exist supramolecular left-/right-helical chains constructed by $[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}]^-$ fragments. Furthermore, these left-/right-helical chains are linked together *via* H-bonds forming interesting enantiomorphous chiral layers. Electrochemical properties of these compounds have been studied.

Keywords: Supramolecular; Polyoxometalates; Helical chain; Electrochemistry

1. Introduction

Supramolecular compounds formed through weak intermolecular forces (hydrogen bond, π–π stacking, and van der Waals forces) display diverse topologies and potential applications in catalysis, magnetism, and host-guest chemistry [1–4]. Polyoxometalates (POMs), anionic early transition metal-oxide clusters featuring special topological structures and versatile applications, have been viewed as ideal inorganic building blocks [5–15]. Supramolecular compounds based on POMs have attracted attention due to their attractive structural features and potential applications [16–18].

Helices, ubiquitous in nature and the foundation of the genetic code, have attracted increased attention in coordination chemistry and materials chemistry because of their importance in biological systems, optical devices, and asymmetric catalysis [19–24]. However, few POM-based supramolecular compounds containing helical structures have been reported [25], especially for α-metatungstate supramolecular compounds with helical structures. Compared with other classical Keggin POMs [26–28],

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α-metatungstate has higher charge density on the cluster surface because its central tetrahedral environment contains two protons rather than a heteroelement. This makes α-metatungstate a good choice to achieve the desired supramolecular structure.

As part of our longstanding efforts in the syntheses of α-metatungstate compounds [29–31], we isolated two supramolecular compounds, $[Co(bipy)_3]_3[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2] \cdot H_2O$ (**1**) and $[H_2bipy]_{0.5}[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}] \cdot H_2O$ (**2**), which possess helical structures.

2. Experimental

2.1. *Materials and general procedures*

All reagents were commercially available and used without purification. $(NH_4)_6[H_2W_{12}O_{40}] \cdot 3H_2O$ was synthesized according to the literature [32] and characterized by IR and UV-Vis spectroscopy, and TG analysis. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer and (Co, Cu, and W) were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra as KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 4000–400 cm^{-1}. TG analyses were recorded with a Netzsch STA 449C microanalyzer in an atmosphere of nitrogen at a heating rate of 10°C min^{-1}. Cyclic voltammograms (CV) were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as a counter electrode, and Ag/AgCl electrode as the reference. Chemically bulk-modified carbon paste electrode (CPE) was used as a working electrode.

2.2. *Synthesis of $[Co(bipy)_3]_3[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2] \cdot H_2O$ (1)*

A mixture of $(NH_4)_6[H_2W_{12}O_{40}] \cdot 3H_2O$ (300 mg, 0.1 mmol), $Co(CH_3COO)_2 \cdot 2H_2O$ (747 g, 0.3 mmol), bipy (60 mg, 0.3 mmol) in a molar ratio of 1 : 3 : 3 and 2 mL methanol was stirred for 30 min. The pH was then adjusted to 1.7 with 1 M oxalic acid, and the mixture was transferred to an 18 mL Teflon-lined reactor and kept under autogenous pressure at 160°C for 5 days. After the reactor was slowly cooled to room temperature at 10°C/h, brown block crystals of **1** were obtained. The crystals were picked out, washed with distilled water, and dried at room temperature (31% yield based on W). Anal. Found (%): C, 19.24; H, 1.39; N, 4.41; O, 16.59; Co, 3.54; W, 54.81. Calcd (%) for $C_{130}H_{110}Co_5N_{26}O_{83}W_{24}$ (8071.20): C, 19.36; H, 1.30; N, 4.52; O, 16.47; Co, 3.65; W, 54.71. IR (KBr): $\nu = 3431$(vs), 1605(m), 1438(m), 1316(m), 1242(w), 1161(w), 952(s), 878(s), 775(s), 675(w), 411(m).

2.3. *Synthesis of $[H_2bipy]_{0.5}[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}] \cdot H_2O$ (2)*

Compound **2** was prepared with the identical method to **1**, with $CuCl_2 \cdot 2H_2O$ (513 mg, 0.3 mmol) instead of $Co(CH_3COO)_2 \cdot 2H_2O$. The blue crystals were picked out, washed with distilled water, and dried at room temperature (40% yield based on W). Anal. Found (%): H, 1.12; C, 14.55; N, 3.49; O, 17.67; Cu, 3.58; W, 59.61. Calcd (%) for $C_{45}H_{38}Cu_2N_9O_{41}W_{12}$ (3694.03): H, 1.04; C, 14.63; N, 3.41; O, 17.76; Cu, 3.44; W, 59.72.

IR (KBr): $\upsilon = 3438$(vs), 1635(m), 1605(m), 1445(m), 1316(w), 1249(w), 1167(w), 946(s), 885(s), 761(s), 596(w), 418(m).

2.4. *Preparation of 1- and 2-CPEs*

The **1**-CPE was fabricated as follows: 48 mg of graphite powder and 8 mg of **1** were mixed and ground together by agate mortar and pestle to achieve a uniform mixture, and then 0.6 mL of nujol was added with stirring. The mixture was packed into a glass tube with a 1.2 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a copper rod through the back of the electrode. In a similar manner, **2**-CPE electrode was made with **2**.

2.5. *X-ray crystallography*

X-ray diffraction data were collected on a SMART CCD diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) at room temperature. The data collection, data reduction, and all absorption corrections were performed by using SMART, SAINT, and SADABS, respectively. The structure was solved by Direct Methods and refined by full-matrix least-squares on F^2 with the SHELXL-97 program package [33, 34]. The non-hydrogen atoms were located with difference Fourier syntheses. The organic hydrogens were generated geometrically; the hydrogens of POM moieties are similar to a reported compound [35]. The hydrogens for the waters were not located because there are too many heavy atoms in POM anions to find hydrogens in difference Fourier maps. The possible directions of hydrogens for water based on observed hydrogen bonds are shown in figure S1. The crystal data and structure refinements of **1** and **2** are summarized in table 1.

3. Results and discussion

The α-metatungstate $[H_2W_{12}O_{40}]^{6-}$ (W_{12}) is made up of 12 WO_6 octahedra arranged in four edge-shared $\{W_3O_{13}\}$ triplets, as usually observed in Keggin-type anions [35–37]. However, its central heteroatom in tetrahedral environment is replaced by two protons. Bond valence sum calculations [38] show all tungsten atoms are in +VI oxidation state, and all cobalt and copper atoms are +II. Since **1** and **2** were isolated from acidic aqueous solution, one proton was, respectively, attached to POMs to compensate for charge balance, similar to the case of $[Ag(CH_3CN)_4]\{[Ag(CH_3CN)_2]_4[H_3W_{12}O_{40}]\}$ [37]. Compounds **1** and **2** are formulated as follows:

- $[Co(bipy)_3]_3[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2] \cdot H_2O$ (**1**) and
- $[H_2bipy]_{0.5}[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}] \cdot H_2O$ (**2**).

3.1. *Crystal structure of 1*

Compound **1** consists of $[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2]^{6-}$, discrete $[Co(bipy)_3]^{2+}$ cations and lattice waters (figure 1). The W_{12} anion in **1** is decorated by a single terminal $\{Co(bipy)_2(H_2O)\}^{2+}$, in which the Co3 is six coordinate, defined by four nitrogens from

Table 1. Crystallographic data and processing paramters for **1** and **2**.

	1	**2**
Empirical formula	$C_{130}H_{110}Co_5N_{26}O_{83}W_{24}$	$C_{45}H_{38}Cu_2N_9O_{41}W_{12}$
Formula weight	8071.20	3694.03
Crystal system	Monoclinic	Monoclinic
Space group	*c2c*	*P 2(1)/n*
Unit cell dimensions (Å, °)		
a	46.640(2)	13.679(2)
b	14.302(1)	24.461(3)
c	26.098(1)	21.914(3)
β	90.235(1)	102.306(2)
Volume ($Å^3$), *Z*	17,408(7), 4	7164(3), 4
Calculated density (mg m^{-3})	3.077	3.424
Absorption coefficient (mm^{-1})	16.342	19.855
T (K)	293(2)	293(2)
F(000)	14,564	6576
θ range for data collection (°)	1.49–25.75	1.74–25.17
Reflections collected	47,148	36,755
Independent reflection	16,673 [*R*(int) = 0.0673]	12,873 [*R*(int) = 0.1100]
Data/restraints/parameters	16,673/162/1209	12,872/171/962
Goodness-of-fit on F^2	1.040	1.006
Final *R* indices [$I > 2\sigma(I)$]	$R_1^a = 0.0467$; w$R_2^b = 0.0772$	$R_1^a = 0.0552$; w$R_2^b = 0.0881$

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

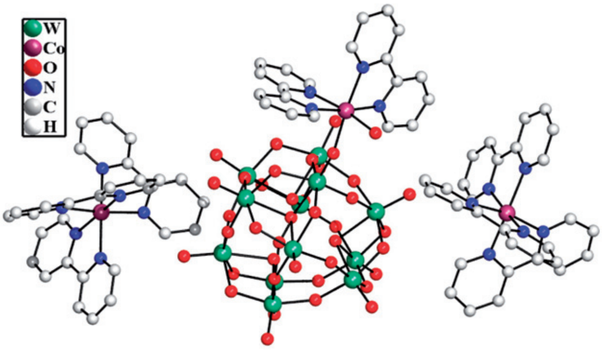

Figure 1. Combined ball/stick representation of the fundamental unit in **1**.

two bipy molecules (Co3–N = 2.085(12), 2.086(12), 2.104(11), and 2.111(12) Å), one terminal oxygen from W_{12} anion (Co3–O = 2.072(10) Å), and one H_2O (Co3–O = 2.072(8) Å). Two other cobalt ions (Co1 and Co2) are six coordinate, defined by six nitrogens from three bipy. The Co–N bond distances are between 2.099(10) and 2.135(11) Å, and the N–Co–N bond angles are between 75.4(5) and 172.0(5)°.

An interesting structural feature is the supramolecular left-/right-helical chains along the crystallographic 2_1 screw axis in the *b* direction with a pitch of 14.302 Å, constructed by $[Co1(bipy)_3]^{2+}$ cations through van der Waals forces (figure 2, left). Additionally, the $[\{Co(bipy)_2(H_2O)\}_2\{H_3W_{12}O_{40}\}_2]^{6-}$ anions are connected by $[Co2(bipy)_3]^{2+}$ cations giving a 1-D POM double-chain *via* C–H···O H-bonds between carbons of bipy and terminal/bridged oxygens of W_{12} anion, with the shortest C–H···O distance of 2.411 Å.

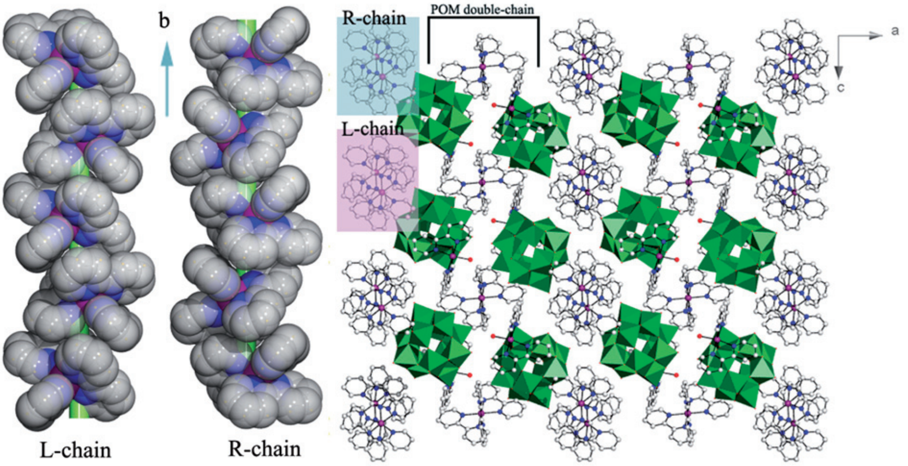

Figure 2. Space-filling representation of the left-handed (L) and right-handed (R) supramolecular helical chains in **1** (left); view of the 3-D structure in **1** (right).

A series of parallel POM double-chains perpendicularly interact with the left/right 1-D helical chains through $C_{bipy}–H\cdots O_{POM}$ H-bonds to form a 3-D supramolecular network (figure 2, right). Lattice waters also participate in extensive H-bonds and stabilize the 3-D structure further.

3.2. *Crystal structure of 2*

Compound **2** consists of $[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}]^-$ anions, protonated bipy ($[H_2bipy]^{2+}$), and lattice water (figure 3). There are two crystallographically independent Cu's with the same coordination environment. Each Cu (Cu1 or Cu2) is coordinated by four nitrogens from two bipy and an oxygen from W_{12} cluster. The Cu–N distances are in the range 1.938(1)–2.081(16) Å with N–Cu–N angles of 79.7(7)–178.9(7)° and Cu–O lengths in the range 2.045(11)–2.120(11) Å. Each W_{12} cluster is modified by two $\{Cu(bipy)_2\}^{2+}$ subunits forming $[\{Cu(bipy)_2\}_2\{H_3W_{12}O_{40}\}]^-$ fragments. These fragments are connected forming supramolecular left-/right-helical chains through $C–H\cdots O$ H-bonds with the shortest $C–H\cdots O$ distance of 2.388 Å along the crystallographic 2_1 screw axis in the b direction with a pitch of 24.461 Å (figure 4). The most attractive structural feature of **2** is the chiral layer structure. As shown in figure 5, the neighboring left-helical chains are linked *via* $C–H\cdots O$ H-bonds forming a L-chiral layer; neighboring right-helical chains are linked forming a R-chiral layer. Adjacent L- and R-chiral layers are connected alternately by the $C–H\cdots O$ H-bonds between oxygens of W_{12} clusters and hydrogens of bipy ($C–H\cdots O$ interatomic distances between 2.407 and 2.915 Å) to generate a racemic 3-D supramolecular structure. Protonated bipy and lattice water also participate in extensive H-bonds stabilizing the 3-D structure further. Only a limited number of POM-based compounds have chiral structures and most are obtained from chiral species (chiral organic linkers, chiral metal complexes or chiral POMs) as structure directing agents [39–45]. So, **2** represents a new POM-based compound with chiral layers constructed by use of achiral ligands.

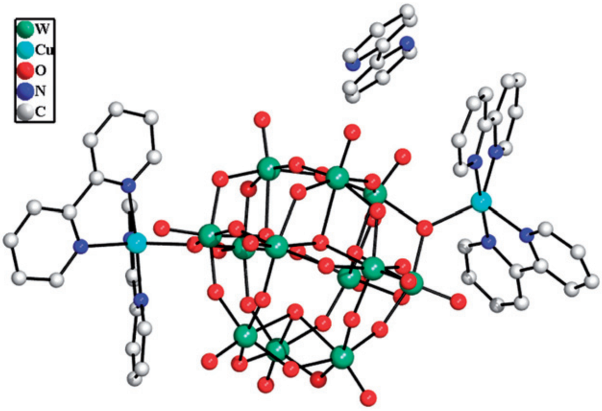

Figure 3. Combined ball/stick representation of the fundamental unit in **2**.

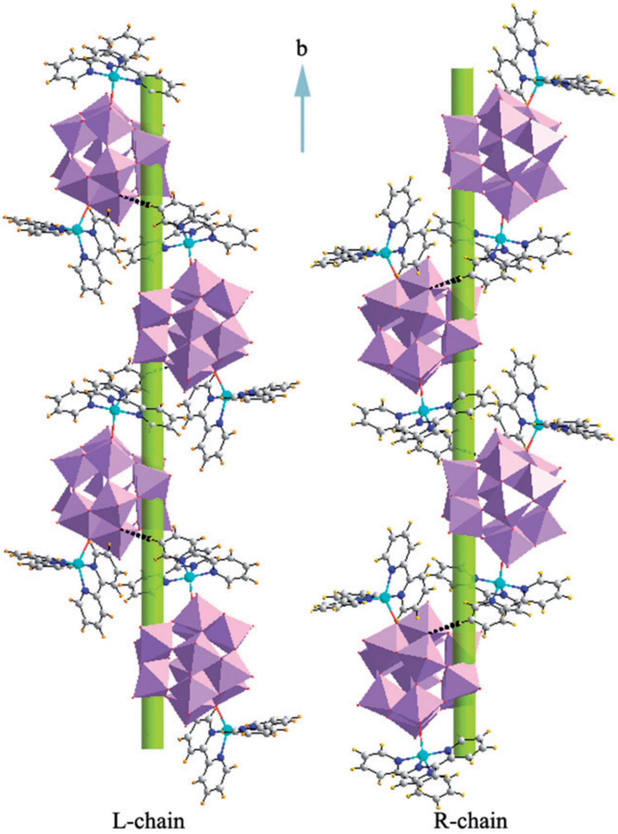

Figure 4. Combined ball/stick/polyhedron representation of the left-handed (L) and right-handed (R) supramolecular helical chains in **2**.

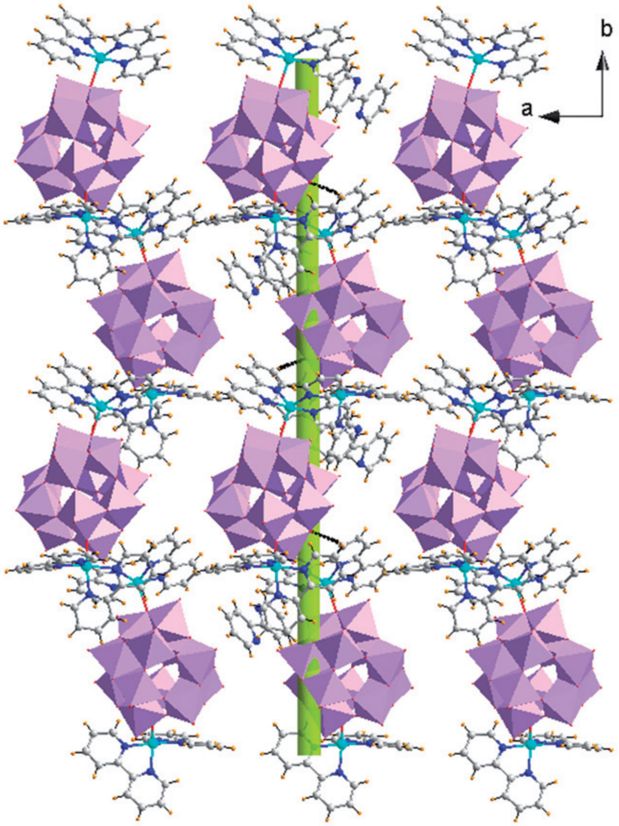

Figure 5. View of the L-chiral layer in **2**.

3.3. *XRPD patterns*

The XRPD patterns for **1** and **2** (figure S2) of both simulated and experimental patterns match well, indicating that **1** and **2** have high phase purities, which ensure the precision of other investigations.

3.4. *Thermal analysis*

The TG experiments were performed under N_2 with a heating rate of $10\,^{\circ}\mathrm{C\,min^{-1}}$ from 40 to 600°C, shown in figure S3. In the TG curve of **1**, weight loss of 27.9% (Calcd 25.8%) in the range 40–600°C corresponds to the loss of bipy. The TG curve of **2** shows two distinct weight loss steps: the first weight below 400°C corresponds to the loss of discrete H_2bipy and water. The second weight is ascribed to loss of coordinated bipy, 19.4% (Calcd 19.6%) in the range 400–600°C.

3.5. *Cyclic voltammetry*

To compare the electrochemical behavior between **1** and **2**, the POM-modified CPEs (**1-** and **2**-CPE) were studied under identical conditions: in 1 M H_2SO_4 solution at scan

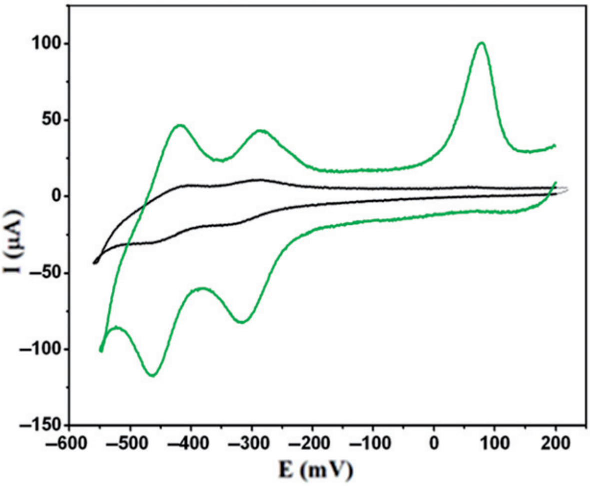

Figure 6. Comparative cyclic voltammograms of (a) **1**-CPE (black) and (b) **2**-CPE (green) in 1 M H_2SO_4. Note: Scan rate: 60 mV s^{-1}.

rate of 60 mV s^{-1} in the potential range from +200 to –600 mV. For **1**–CPE, as shown in figure 6a, there exist two reversible redox peaks I–I′ and II–II′ with the half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at −306 and −432 mV, respectively. The I–I′ and II–II′ redox waves correspond to two 2-electron reductions of W^{VI} deduced from the electrochemical behaviors of the parent compound $(NH_4)_6[H_2W_{12}O_{40}] \cdot 3H_2O$ [46, 47]. For **2**-CPE, as shown in figure 6b, there exist two reversible redox peaks with the half-wave potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ at −299 (II–II′) and −440 mV (III–III′), and one irreversible anodic wave at +79 mV (I). The II–II′ and III–III′ redox waves correspond to two 2-electron reductions of W^{VI} [43, 44] and irreversible anodic wave (I) should be assigned to the oxidation of Cu(II) [48, 49]. The values of $E_{1/2}$ in **2**-CPE are −299 and −440 mV, respectively, close to those of **1**-CPE (−306 and –432 mV). The small difference in $E_{1/2}$ of **1** and **2** suggests W_{12} cluster is the active center for electrochemical redox activity in CPE, while the corresponding complex fragments have only a slight influence on electrochemical behavior of **1**- or **2**-CPE.

3.6. *Electrocatalytic activity*

POMs have been exploited extensively in electrocatalytic reductions. For example, Keita *et al.* [50] and Toth and Anson [51] reported that Keggin POMs can be used as electrocatalysts for reduction of nitrite and hydrogen peroxide. Compounds **1** and **2** were employed to fabricate POM nanoparticle-modified electrodes to electrocatalyze reduction of nitrite.

The reduction of nitrite to ammonia involves a six-electron-eight-proton change. Owing to high overpotential required at most electrode surfaces for direct electroreduction of nitrite ion, no obvious response is observed for nitrite at bare CPE in the range from +200 to −600 mV. Figure 7a and 7b shows the CV of **1**- and **2**-CPE under scan rate 120 mV s^{-1} in an acid solution containing nitrite, indicating

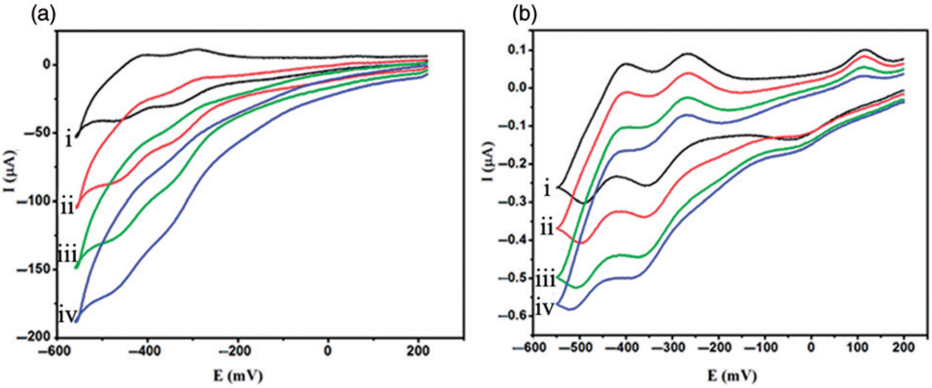

Figure 7. Cyclic voltammograms of **1**-CPE (a) and **2**-CPE (b) in 1 M H_2SO_4 containing 0 (i), 4 (ii), 8 (iii), 12 (iv) mM $NaNO_2^-$. Note: Scan rate: 120 mV s^{-1}.

that **1-** and **2**-CPE have good electrocatalytic activity for reduction of nitrite. With the addition of nitrite, the two reduction peak currents increase while the corresponding oxidation peak currents decrease, suggesting that the reduction of nitrite involves two- and four-electron-reduced species.

4. Conclusions

We have synthesized two new α-metatungstate compounds. The structural analyzes of these compounds reveal that we have incorporated nanosized α-metatungstate cluster into a helical structure through H-bonds. Compounds **1** and **2** are employed to fabricate the POM nanoparticle modified electrodes to electrocatalyze the reduction of nitrite. The results indicate that **1-** and **2**-CPE have good electrocatalytic activities toward reduction of nitrite.

Supplementary materials

The crystal structure data have been deposited in the Cambridge Crystallographic Data Center with CCDC nos. 726045 for **1** and 726046 for **2**. Supplementary data associated with this article: structural figures, X-ray diffraction patterns, TG curves for **1** and **2** and crystallographic information files (CIFs).

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