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Three new supramolecular sandwich-type compounds constructed from $[SbW_9O_{33}]^{9-}$

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Three new tungstoantimonates, $[\{Na_2(H_2O)_4(OH)_2\}\{Na(H_2O)_4\}_2\{(Zn(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 8H_2O$ (**1**) $[\{Na_2(H_2O)_4(OH)_2\}\ \{Na(H_2O)_4\}_2\{(Ni(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 16H_2O$ (**2**) and $[\{Na_2(H_2O)_3(OH)_3\}_2\{(Mn(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 4H_3O\cdot 12H_2O$ (**3**), have been synthesized by the routine synthetic reactions in aqueous solution and structurally characterized by elemental analysis, IR, XRD, TG and single-crystal X-ray diffraction. Compounds **1** and **2** are isomorphic. The frameworks of **1–3** are constructed from two trivacant $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ linked by two $[W(H_2O)_2]^{4+}$ segments and two $[M(H_2O)_3]^{2+}$ (M = Zn, Ni, Mn) groups leading to $[M_2Sb_2W_{20}]$. The units are bonded by binuclear sodium cluster $\{Na_2(H_2O)_4(OH)_2\}$ and $\{Na(H_2O)_4\}$ linker (for **1** and **2**) or by binuclear $\{Na_2(H_2O)_3(OH)_3\}$ linker (for **3**) to form infinite 1-D chains. These chains are further packed into various interesting 3-D supramolecular frameworks via hydrogen bonding interactions. Compounds **1** and **2** are supramolecular structures with large voids. The electrochemical and electrocatalytic behaviors of **1–3** have also been investigated.

Keywords: Polyoxometalates; Sandwich-type structure; Electrochemical property

1. Introduction

Polyoxometalates (POMs) constitute a class of metal–oxygen clusters with a variety of fascinating structures and exciting properties, applications of which include catalysis, analytical chemistry, electronic devices, medicine, etc. [1–4]. Transition-metal substituted POMs (TMSPs) have attracted attention because of their highly tunable nature and excellent properties [5–7]. For TMSPs, sandwich-type POMs contain a certain number of transition-metal cations sandwiched by two lacunary fragments. The sandwich-type species based on trivacant Keggin $[XM_9O_{34or33}]^{n-}$ (X = Si, Ge, P, As, Sb, Bi, Zn, Fe) represent the largest subfamily. Weakley- [8–11], Hervé- [12–14], Krebs- [15, 16], and Knoth- [17–19] sandwich-type polyoxoanions have been obtained.

Sb^{III}-containing POMs has been known for a long time [20–22]. The lone pair of electrons on the hetero atom does not allow the closed Keggin unit to form, resulting in some unexpected structures, for example $[NaSb_9W_{21}O_{86}]^{18-}$ and $[Na_2Sb_8W_{36}O_{132}(H_2O)_4]^{22-}$ [23]. $[SbW_9O_{33}]^{9-}$ are the most studied Sb^{III}-containing POM. Sandwich-type species based

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on trivacant Keggin $[SbW_9O_{33}]^{9-}$ moieties represent the largest subfamily [24–28]. $[SbW_9O_{33}]^{9-}$, which possess two isomers B-α and B-β, contain a pyramidal heteroatom with a lone pair of electrons. Compounds of sandwich-type based on $[B\text{-}\alpha\text{-}SbW_9O_{33}]^{9-}$ which contain mono-, bi-, tri-, tetra- and hexa-supported sandwich-type polyanions have been reported [29–34]. In comparison to extensive work on sandwich-type species based on $[B\text{-}\alpha\text{-}SbW_9O_{33}]^{9-}$, considerably less research has been accomplished on Krebs-type polyoxoanions. There has been recent upsurge in interest in investigating Krebs-type polyoxoanions. The first Krebs-type sandwich structure $[(WO_2)_4(OH)_2(\beta\text{-}SbW_9O_{33})_2]^{12-}$ was discovered by Krebs *et al.* [35]. Subsequently, the authors obtained some isostructural derivatives, $[(WO_2)_2M_2(H_2O)_6(\beta\text{-}SbW_9O_{33})_2]^{(14-2n)-}$ ($M^{n+} = Fe^{3+}$, Co^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+}) [36]. Some Krebs-type tungstoantimonates have been reported, such as $[Sb_2W_{20}O_{70}(RuC_{10}H_{14})_2]^{10-}$, $[Sb_2W_{20}O_{70}(RuC_6H_6)_2]^{10-}$, $[Sb_2W_{20}Ru_2(H_2O)_2(dmso)_6O_{68}]^{4-}$, $[\{Y(H_2O)_7\}_4Sb_2W_{22}O_{76}]^{2-}$, $[\{Sn(CH_3)_2(H_2O)_2\}_3(\beta\text{-}SbW_9O_{33})_2]^{3-}$, $[Fe_4(H_2O)_{10}(\beta\text{-}SbW_9O_{33})_2]^{6-}$ and $[Fe_4(C_2O_4)_4(H_2O)_2(SbW_9O_{33})_2]^{14-}$ with $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ [37–42]. However, most are discrete structures [43]. Extended structures of Krebs-type polyoxoanions linked by bridging groups are less common. Recently, our group described a 1-D chain based on $\{M_2Bi_2W_{20}\}$ anions and Na^+ linker [44], extended structures of tungstoantimonates connected by bisodium clusters to form supramolecular sandwich-type compounds.

>Here we report three new sandwich-type tungstoantimonates, $[\{Na_2(H_2O)_4(OH)_2\}\{Na(H_2O)_4\}_2\{(Zn(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 8H_2O$ (**1**) $[\{Na_2(H_2O)_4(OH)_2\}\{Na(H_2O)_4\}_2\{(Ni(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 16H_2O$ (**2**) and $[\{Na_2(H_2O)_3(OH)_3\}_2\{(Mn(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2\}]\cdot 4H_3O\cdot 12H_2O$ (**3**). The electrochemistry of **1–3** are studied in detail.

2. Experimental

2.1. *Materials and general procedures*

All reagents were purchased and used without purification. Elemental analyzes (H) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Na, Sb, Mn, Co and W were obtained with a Leaman inductively coupled plasma spectrometer. IR spectra were recorded from 4000 to 400 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer with pressed KBr pellets. X-ray powder diffraction data were collected on a Bruker AXS D8 Advance diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å) in the 2θ range of 5°–50° with a step size of 0.02°. TG analyzes were performed on a Perkin–Elmer TGA7 instrument in flowing N_2 at a heating rate of 10 °C min^{-1}. The electrochemical measurement was carried out on a CHI 660 electrochemical workstation at room temperature (25–30 °C). The working electrode was a glassy carbon electrode. Platinum gauze was used as a counter electrode and Ag/AgCl as a reference electrode.

2.2. *Synthesis of 1*

$SbCl_3$ (0.228 g, 1.0 mmol) dissolved in 1 mL of 6 M HCl, was added to a solution of $Na_2WO_4\cdot 2H_2O$ (3.300 g, 10.0 mmol) in 40 mL of deionized water and the mixture was heated to 60 °C for 10 min. Then, a solution of $ZnSO_4\cdot 7H_2O$ (1.0 mmol) dissolved in 4 mL water was added to the clear solution. The pH of the solution was adjusted to 6.2 at room temperature by addition of 1 M HCl. The mixture was kept at 60 °C for 2 h and then cooled to room temperature and filtered. White crystals were obtained after 7 days. (Yield: 45.2% based on Zn). Anal. Calcd for $H_{60}Na_4Sb_2W_{20}Zn_2O_{98}$: H, 1.07; Zn, 2.29; Sb, 4.26; W, 64.38; Na, 1.61%. Found: H, 1.09; Zn, 2.31; Sb, 4.30; W, 64.61; Na, 1.56%.

2.3. *Synthesis of 2*

Compound **2** was synthesized by similar procedure to **1** except that $ZnSO_4{\cdot}7H_2O$ was replaced by $NiCl_2{\cdot}6H_2O$ (0.7 mmol). Green crystals were obtained after 8 days. (Yield: 47.5% based on Ni). Anal. Calcd for $H_{76}Na_4Sb_2W_{20}Ni_2O_{106}$: H, 1.32; Ni, 2.01; Sb, 7.09; W, 62.44; Na, 0.78%. Found: H, 1.33; Ni, 2.10; Sb, 6.89; W, 62.83; Na, 0.73%.

2.4. *Synthesis of 3*

Compound **3** was synthesized by similar procedure to **1** except that $ZnSO_4{\cdot}7H_2O$ was replaced by $MnCl_2{\cdot}4H_2O$ (0.7 mmol). The pH of the solution was adjusted to 6.8; yellow crystals were obtained after 8 days. (Yield: 54.2% based on Mn). Anal. Calcd (%) for $H_{58}Na_4Sb_2W_{20}Mn_2O_{104}$: H, 1.14; Mn, 1.98; Sb, 7.03; W, 61.87; Na, 0.77. Found (%): H, 1.18; Mn, 2.07; Sb, 6.78; W, 62.59; Na, 0.71.

2.5. *X-ray crystallography*

Crystal data of **1–3** were collected on a Bruker SMART CCD APEX(II) diffractometer equipped with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å) at 293 K. Data processing was accomplished with the PROCESS-AUTO program. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 crystallographic software package [45]. The final refinement includes anisotropic displacement parameters for non-hydrogen atoms.

CCDC Nos. 854790, 877834 and 877833 for **1**, **2** and **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. *Crystal structures of 1, 2 and 3*

Single-crystal X-ray diffraction analysis reveals that **1–3** are sandwich-type structures composed of two $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ units. The W–O distances can be grouped into three sets: W–O_d (terminal): 1.703(12)–1.735(11) Å for **1**, 1.701(17)–1.767(18) Å for **2**, 1.681–1.765 Å for **3**; W–$O_{b/c}$ (bridge): 1.726(11)–2.113(11) Å for **1**, 1.770(16)–2.078(16) Å for **2**, 1.79(3)–2.07(3) Å for **3**; W–O_a (central): 2.166(12)–2.357(10) Å for **1**, 2.256(15)–2.330(16) Å for **2**, 2.26(2)–2.35(3) Å for **3**. As shown in figure 1, two $[B\text{-}\beta\text{–}SbW_9O_{33}]^{9-}$ units are linked by two corner-sharing WO_6 octahedra and two octahedral $M^{n+}O_4(H_2O)_2$ ($M^{n+} = Zn^{2+}$, Mn^{2+}, Ni^{2+}) groups forming Krebs-type polyoxoanions. Each M^{n+} is six-coordinate by three

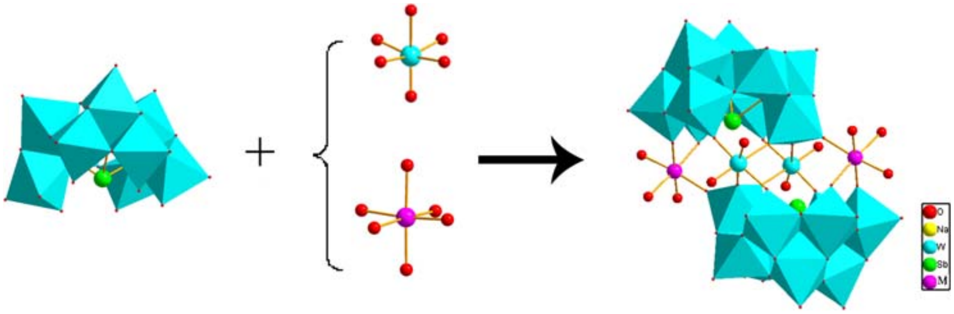

Figure 1. Polyhedral and ball-and-stick representation of the transition-metal-disubstituted polyoxoanions $[\{M(H_2O)_3\}_2\{W(OH)_2\}_2(SbW_9O_{33})_2]^{6-}$.

terminal oxygens derived from two $[B–\beta-SbW_9O_{33}]^{9-}$ units and three terminal waters. The Zn–O bond lengths vary from 2.043(11) to 2.123(13) Å, whereas angles are in the range 84.3 (5)°–177.7(6)° for **1**. Ni–O bond lengths vary from 2.011(17) to 2.068(18) Å and O–Ni–O angles are 85.5(7)°–176.9(7)° (for **2**). The Mn–O distances are 2.09(3)–2.23(4) Å and O–Mn–O angles from 80.2(12)° to 170.6(14)° (for **3**); all are in common ranges.

Compounds **1** and **2** are isomorphic with only slight differences in substituted transition metal and the number of lattice waters. As shown in figure 2(a), the terminal oxygen and the bridging oxygen of $[B-\beta–SbW_9O_{33}]^{9-}$ are connected, respectively, by $\{Na(H_2O)_4\}^+$ and $[Na_2(H_2O)_4(OH)_2]$. Compounds **1** and **2** are linked in a 1-D chain by two $[Na(H_2O)_4]^+$ groups and one $[Na_2(H_2O)_4(OH)_2]$. The 1-D sandwich-type polyoxoanions are linked into a 2-D layer by extensive hydrogen bonding interactions between H_2O and polyoxoanion

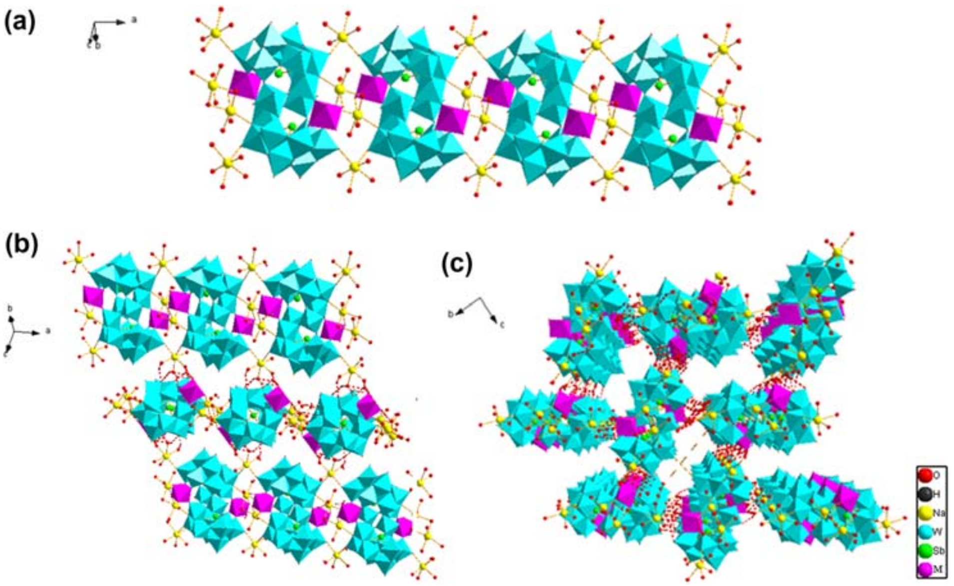

Figure 2. (a) Polyhedral and ball–stick representation of the 1-D chain in **1** and **2**. (b) Polyhedral and ball–stick representation of the 2-D layers in **1** and **2**. (c) Polyhedral and ball–stick representation of the 3-D supramolecular structures of **1** and **2**.

(figure 2(b)). The 2-D layer is further connected into a 3-D supramolecular network with large voids via Na^+ and extensive $O\cdots O_{POMs}$ hydrogen-bonding interactions (O50···O41, 3.02(2) Å; O54···O27, 3.21(3) Å; O49···O19, 3.02(3) Å) (figure 2(c)). The void dimensions are 3.4387 × 27.5222 Å. Compared to $Na_9[\{Na(H_2O)_2\}_3\{M(C_4H_6N_2)\}_3(SbW_9O_{33})_2]\cdot 28H_2O$ (M = Co(1); M = Mn(2) complexes [46]), **1** and **2** are based on two $[B\text{–}\beta\text{-}SbW_9O_{33}]^{9-}$ units which are linked by two transition metal ions and two tungstens, while sandwich-type structures in the reported compounds are based on two $[B\text{-}\alpha\text{-}SbW_9O_{33}]^{9-}$ units connected by three transition metal ions and three sodium ions. Compounds **1** and **2** exhibit a new linking mode from reported compounds, which are extended into 1-D chains via hydrogen-bonding interactions between organic groups and oxygen of POMs. However, **1** and **2** are packed into 1-D chains via Na-O-Na covalent bonds.

Polyanion **3** can be described as $[(Mn(H_2O)_3)_2(W(H_2O)_2)_2(SbW_9O_{33})_2]^{2-}$ linked by two $[Na_2(H_2O)_3(OH)_3]^-$ into a 1-D chain (figure 3(a)). In $\{Na_2(H_2O)_3(OH)_3\}$, Na (2) is five coordinate, linked by two terminal oxygens of $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ and Na (1) is six coordinate. Na (2) and Na (1) form a binuclear molecule through three OH^-. **3** is further connected into 2-D layer and 3-D supramolecular networks via Na^+ and extensive $O\cdots O_{POMs}$ hydrogen-bonding interactions (O10···O35, 2.74(4) Å; O7···O8, 2.85(5) Å; O1···O33, 2.79(6) Å) (figure 3(b) and (c)). Comparing to $[Na_6(H_2O)_{16}][\{Mn_3(H_2O)_6W(OH)_2\}\{SbW_9O_{33}\}_2]\cdot 13H_2O$ [47], in **3** two $[B\text{-}\beta\text{-}SbW_9O_{33}]^{9-}$ units are linked by two $\{MnO_6\}$ octahedra and two $\{WO_6\}$ octahedra while in reported compounds, two trivacant $[B\text{–}\beta\text{-}SbW_9O_{33}]^{9-}$ units are connected by three $\{MnO_6\}$ octahedra and one $\{WO_6\}$ octahedron. Compound **3** exhibits a new linking mode, extended into 1-D chain and 2-D layer via Mn–O–W bonds and Na–O–Na covalent bonds, respectively. However, **3** is packed into a 1-D chain and 2-D layer via Na–O–Na covalent bond and hydrogen-bonding interactions, respectively.

All hydrogen bonds are O–H···O and typical distances (O···O) are 2.705(18)–3.46(3) Å for **1**, 2.34(4)–3.26(3) Å for **2** and 2.74(4)–2.86(4) Å for **3**.

The crystallographic and structural data of **1**, **2** and **3** are summarized in table 1. Selected hydrogen-bond distances are given in tables S1–S3. Selected bond distances and angles are given in tables S4–S6 for **1–3**, respectively. Bond valence sum (BVS) calculations [48]

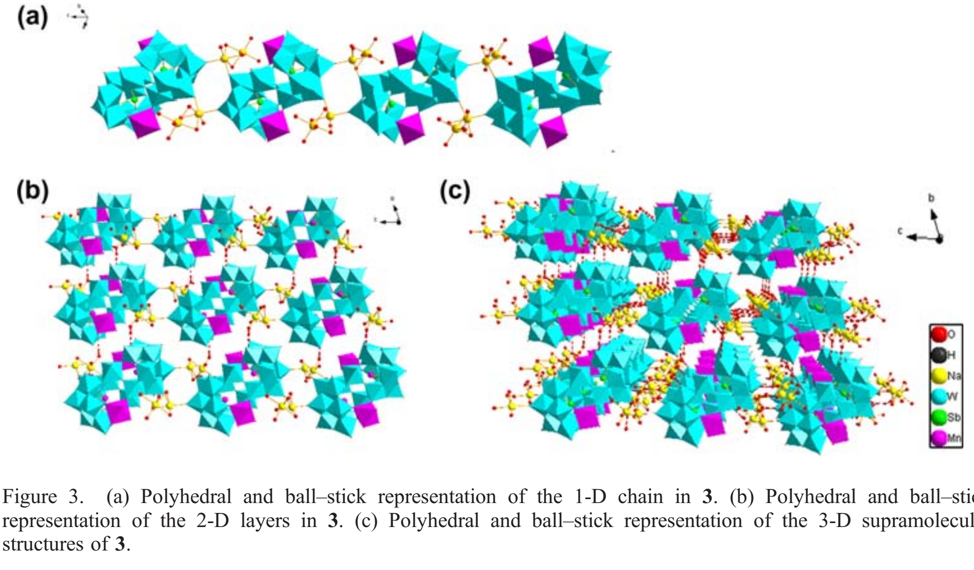

Figure 3. (a) Polyhedral and ball–stick representation of the 1-D chain in **3**. (b) Polyhedral and ball–stick representation of the 2-D layers in **3**. (c) Polyhedral and ball–stick representation of the 3-D supramolecular structures of **3**.

Table 1. Crystal data and structure refinement parameters for **1**, **2** and **3**.

Compound	**1**	**2**	**3**
Formula	$H_{60}Na_4Sb_2W_{20}Zn_2O_{98}$	$H_{76}Na_4Sb_2W_{20}Ni_2O_{106}$	$H_{58}Na_4Sb_2W_{20}Mn_2O_{104}$
Mr	5763.48	5894.21	5772.56
Crystal. size, mm^3	0.26 × 0.20 × 0.20	0.38 × 0.32 × 0.30	0.26 × 0.22 × 0.20
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	*P21/n*	*P21/n*	*P−1*
a, Å	12.8999(9)	12.916(2)	12.485(3)
b, Å	25.2473(17)	25.211(4)	13.766(3)
c, Å	16.2418(11)	16.107(3)	17.101(4)
β, deg	94.1710(10)	94.189(2)	83.031(3)
V (Å^3)	5275.7(6)	5230.8(15)	2493.3(10)
Z	2	2	1
D_{calcd}, g cm^{-3}	3.63	3.74	3.85
μ(MoK*α*), cm^{-1}	2.3	2.3	2.4
F(000), *e*	5044	5196	2526
θ range, deg/°	2.53–28.28	2.53–28.31	2.46–25.00
Reflns. collected/unique/Rint	42,202/12,980/0.0777	37,085/12,728/0.1067	15,743/8331/0.1043
Data/restraints/parameters	12,980/1038/568	12,728/1122/604	8331/1374/577
R_1/wR_2 $[I \geq 2\sigma(I)]^a$	0.0485/0.1199	0.0872/0.2306	0.0829/0.2143
$R(F)$/w$R(F^2)^a$ (all refl.)	0.0846/0.1279	0.1070/0.2466	0.1472/0.2515
GoF $(F^2)^a$	1.088	1.031	1.043
*Δρ*fin (max/min), e Å^{-3}	4.67/−4.13	6.10/−12.78	4.51/−9.25

$^aR_1 = \sum||F_0|-|F_C||/\sum|F_0|$; $wR_2 = \sum[w(F_0^2-F_C^2)^2]/\sum[w(F_0^2)^2]^{1/2}$, $w = [\sigma^2(F_0^2)+(0.484P)^2+24.2999P]^{-1}$, where $P = (\mathrm{Max}(F_0^2,0)+2F_C^2)/3$, $\mathrm{GoF} = [\sum w(F_0^2-F_C^2)^2/(n_{obs}-n_{param})]^{1/2}$.

confirm that all Sb and W centers are + 3 and + 6, respectively. The Zn, Ni, and Mn cations in **1–3** are in + 2 oxidation states. BVS calculations for O linked to Na centers present hydroxyl (0.56–0.72) and water (0.22–0.34). Four extra protons should be added to isolated waters of **3** for charge balance.

3.2. *IR spectrum and XRD*

Compounds **1**, **2** and **3** have similar IR spectra (figure S1). Peaks at 1629 and 3422 cm^{-1} are characteristic of water. Characteristic peaks for **1**, **2** and **3**, respectively (670, 700, 648 cm^{-1}), are ascribed to ν(W–O$_a$), (950, 941, 940 cm^{-1}) corresponding to ν(W=O$_d$) (873, 851, 871 cm^{-1}), associated with ν(W–O$_b$–W), and (806, 760 cm^{-1}), (804, 767 cm^{-1}) and (821, 767 cm^{-1}) attributed to ν(W–O$_c$–W) [35, 49].

The powder XRD pattern of **1**, **2** and **3** and their simulated XRD pattern are shown in figure S2. Diffraction peaks on the pattern correspond in position, confirming that the product is a pure phase. The differences in reflection intensity are probably due to preferred orientation in the powder samples.

3.3. *TG analysis*

Thermal gravimetric analysis has been performed for **1–3** between 20 and 800 °C (figure S3). The TG curve of **1** shows a weight loss of 8.82% from 48 to 546 °C (calcd 8.74%), which corresponds to removal of all lattice and coordinated water (figure S3). Compound **2** has similar weight loss steps. The weight loss of 10.87% (calcd 10.98%) from 38 to 687 °C corresponds to removal of all water. Similarly, **3** shows a weight loss of 9.05% from 31 to 679 °C corresponding with the calculated value of 9.34% (figure S3).

3.4. *Voltammetric behavior*

The cyclic voltammetric studies of **1–3** were investigated in a buffer solution (0.4 M $CH_3COONa + CH_3COOH$) at pH 4. Figure 4 shows the cyclic voltammetry of **1–3** in the potential range −1.0–1.0 V. There exist three reversible redox peaks I–I′, II–II′ and III–III′ with the half-wave potentials $E_{1/2} = (Epa + Epc)/2$ at + 0.515 V (I–I′), + 0.071 V (II–II′) and − 0.318 V (III–III′) for **1**, 0.523 V (I–I′), − 0.00625 V (II–II′) and − 0.279 V (III–III′) for **2**, + 0.552 V (I–I′), + 0.0665 V (II–II′) and − 0.324 V (III–III′) for **3** (scan rate: 60 mV s^{-1}). Redox peaks I–I′ and II–II′ correspond to two consecutive one-electron processes of W atoms, while III–III′ correspond to a two-electron process [50]. The electrochemical behaviors of **1–3** are similar except for some slight potential shift, which may relate to the effect of transitional metal [51].

3.5. *Electrocatalytic property*

The electrocatalytic properties indicate that **1–3** have good electrocatalytic activities toward the reduction of hydrogen peroxide (see figure 5). With the addition of H_2O_2, all reduction peak currents increased while the corresponding oxidation peak currents dramatically decreased, suggesting that H_2O_2 was reduced by all four reduced polyoxoanion species. It

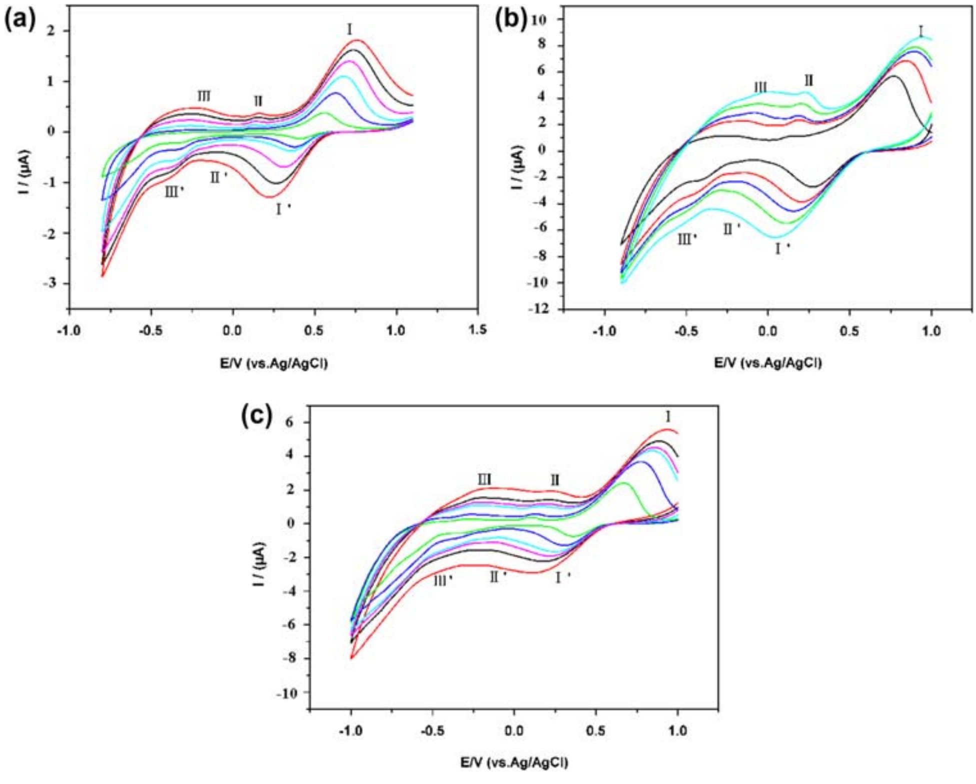

Figure 4. Cyclic voltammograms of 1.0 mM of **1–3** ((a) **1**, (b) **2**, (c) **3**) at pH 4 (0.4 M $CH_3COONa + CH_3COOH$) at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120 mV s^{-1}). The working electrode was glassy carbon and the reference electrode Ag/AgCl.

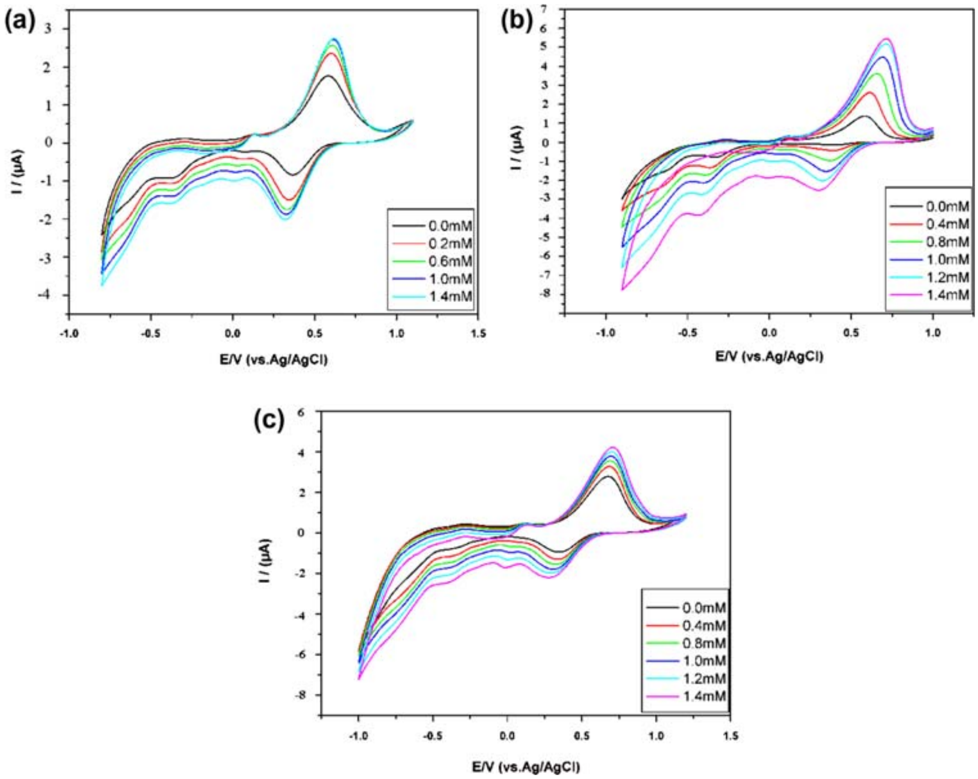

Figure 5. Electrocatalysis of the reduction of H_2O_2 of **1–3** ((a) **1**, (b) **2**, (c) **3**) in a pH 4.0 medium ($CH_3COONa + CH_3COOH$) at a scan rate of 20 mV s^{-1}. The concentration of H_2O_2 is 0.0, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 mM.

has been noted that the catalytic activities were enhanced with the increasing extent of the anion reduction.

4. Conclusions

In this paper, we report three 1-D chains based on $[M_2Sb_2W_{20}]$ which connected by binuclear $\{Na_2(H_2O)_4(OH)_2\}$ and $\{Na(H_2O)_4\}$ linker or by $\{Na_2(H_2O)_3(OH)_3\}$ linker. These chains are further packed into various interesting supramolecular frameworks via hydrogen bond interactions. Electrochemical analysis shows unique redox properties and good electrocatalytic activity to reduce H_2O_2.

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References

[1] N. Zamstein, A. Tarantul, B. Tsukerblat. *Inorg. Chem.*, **46**, 8851 (2007).
[2] J.P. Wang, P.T. Ma, J. Li, H.Y. Niu, J.Y. Niu. *Chem. Asian J.*, **3**, 822 (2008).
[3] L.H. Bi, B. Li, S. Bi, L.X. Wu. *J. Solid State Chem.*, **182**, 1401 (2009).
[4] E. Antonova, C. Näther, P. Kögerler, W. Bensch. *Dalton Trans.*, **41**, 1338 (2012).
[5] D. Volkmer, B. Bredenkötter, J. Tellenbrköer, P. Kögerler, D.G. Kurth, P. Lehmann, H. Schnablegger, D. Schwahn, B. Krebs. *J. Am. Chem. Soc.*, **124**, 10489 (2002).
[6] S.S. Mal, U. Kortz. *Angew. Chem. Int. Ed.*, **44**, 3777 (2005).
[7] S.T. Zheng, D.Q. Yuan, H.P. Jia, J. Zhang, G.Y. Yang. *Chem. Commun.*, **1858**, (2007).
[8] T.J.R. Weakley, H.T. Evans, J.S. Showell, G.F. Tourné, C.M. Tourné. *J. Chem. Soc., Chem. Commun.*, 139 (1973).
[9] T.J.R. Weakley, R.G. Finke. *Inorg. Chem.*, **29**, 1235 (1990).
[10] L.H. Bi, E.B. Wang, J. Peng, R.D. Huang, L. Xu, C.W. Hu. *Inorg. Chem.*, **39**, 671 (2000).
[11] U. Kortz, S. Isber, M.H. Dickman, D. Ravot. *Inorg. Chem.*, **39**, 2915 (2000).
[12] F. Robert, M. Leyrie, G. Herve. *Acta Crystallogr., Sect. B*, **38**, 358 (1982).
[13] M. Bösing, A. Nöh, I. Loose, B. Krebs. *J. Am. Chem. Soc.*, **120**, 7252 (1998).
[14] B. Botar, T. Yamase, E. Ishikawa. *Inorg. Chem. Commun.*, **4**, 551 (2001).
[15] E.M. Limanski, D. Drewes, E. Droste, R. Bohner, B. Krebs. *J. Mol. Struct.*, **656**, 17 (2003).
[16] D. Drewes, E.M. Limanski, M. Piepnbrink, B. Krebs. *Z. Anorg. Allg. Chem.*, **630**, 58 (2004).
[17] W.H. Knoth, P.J. Domaille, R.D. Farlee. *Organometallics*, **4**, 62 (1985).
[18] F.B. Xin, M.T. Pope. *J. Am. Chem. Soc.*, **118**, 7731 (1996).
[19] R.G. Finke, B. Rapko, T.J.R. Weakley. *Inorg. Chem.*, **28**, 1573 (1989).
[20] J. Fischer, L. Ricard, R. Weiss. *J. Am. Chem. Soc.*, **98**, 3050 (1976).
[21] E. Antonova, C. Näther, P. Kögerler, W. Bensch. *Angew. Chem. Int. Ed.*, **50**, 764 (2011).
[22] E. Antonova, C. Näther, P. Kögerler, W. Bensch. *Inorg. Chem.*, **51**, 2311 (2012).
[23] J. Fischer, L. Richard, R. Weiss. *J. Am. Chem. Soc.*, **98**, 3050 (1976).
[24] H. Liu, C. Qin, L. Xu, G.G. Gao, F.Y. Li, X.S. Qu. *Inorg. Chem.*, **47**, 4166 (2008).
[25] J.W. Zhao, C.M. Wang, J. Zhang, S.T. Zheng, G.Y. Yang. *Chem. Eur. J.*, **14**, 9223 (2008).
[26] T. McGlone, L. Vilà-Nadal, H.N. Miras, D.L. Long, J.M. Poblet, L. Cronin. *Dalton Trans.*, 11599 (2010).
[27] M. Ibrahim, S.S. Mal, B.S. Bassil, A. Banerjee, U. Kortz. *Inorg. Chem.*, **50**, 956 (2011).
[28] K.S. Boland, S.D. Conradson, A.L. Costello, A.J. Gaunt, S.A. Kozimor, I. May, D.D. Schnaars. *Dalton Trans.*, **41**, 2003 (2012).
[29] U. Kortz, N.K. Al-kassem, M.G. Savelieff, N.A. AlKadi, M. Sadakane. *Inorg. Chem.*, **40**, 4742 (2001).
[30] A.J. Gaunt, I. May, R. Copping, A.I. Bhatt, D. Collison, O.D. Fox, K.T. Holman, M.T. Pope. *Dalton Trans.*, 3009 (2003).
[31] E.M. Limanski, D. Drewes, B. Krebs. *Z. Anorg. Allg. Chem.*, **630**, 523 (2004).
[32] A. Dolbecq, J.D. Compain, P. Mialane, J. Marrot, E. Rivière, F. Sècheresse. *Inorg. Chem.*, **47**, 3371 (2008).
[33] T. Yamase, H. Ishikawa, H. Abe, K. Fukaya, H. Nojire, H. Takeuchi. *Inorg. Chem.*, **51**, 4606 (2012).
[34] Z.G. Han, Q.X. Zhang, Y.Z. Gao, J.J. Wu, X.L. Zhai. *Dalton Trans.*, 1332 (2012).
[35] M. Bösing, I. Loose, H. Pohlmann, B. Krebs. *Chem. Eur. J.*, **3**, 1232 (1997).
[36] I. Loose, E. Droste, M. Bösing, H. Pohlmann, M.H. Dickman, C. Rosu, B. Krebs. *Inorg. Chem.*, **38**, 2688 (1999).
[37] U. Kortz, M.G. Savelieff, B.S. Bassil, B. Keita, L. Nadjo. *Inorg. Chem.*, **41**, 783 (2002).
[38] F. Hussain, M. Reicke, U. Kortz. *Eur. J. Inorg. Chem.*, **2733**, (2004).
[39] L.F. Chen, K. Zhu, L.H. Bi, A. Suchopar, M. Reicke, G. Mathys, H. Jaensch, R.M. Richards. *Inorg. Chem.*, **46**, 8457 (2007).
[40] L.H. Bi, G.F. Hou, Y.Y. Bao, B. Li, L.X. Wu, Z.M. Gao, T. McCormac, S.S. Mal, U. Kortz. *Eur. J. Inorg. Chem.*, **5259**, (2009).
[41] L.H. Bi, G.A. Kadamany, E.V. Chubarova, M.H. Dickman, L.F. Chen, D.S. Gopala, R.M. Richards, B. Keita, L. Nadjo, H. Jaensch, U. Kortz. *Inorg. Chem.*, **48**, 10068 (2009).
[42] N. Anwar, T. McMormac, J.D. Compain, P. Mialane, A. Dolbecq, F. Laffir. *Electrochim. Acta*, **59**, 1 (2012).
[43] L. Lisnard, P. Mialane, A. Dolbecq, J. Marrot, J.M. Clemente-Juan, E. Coronado, B. Keita, L. Nadjo. *Sécheresse. Chem. Eur. J.*, **13**, 3525 (2007).
[44] J. Wu, C.X. Wang, Z.H. Su, K. Yu, Y.L. Xu, B.B. Zhou. *Chinese. J. Struct. Chem.*, **31**, 271 (2012).
[45] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Germany (1997).
[46] B.W. Chen, W.L. Chen, W.L. Liu, Y.G. Li, X.L. Wang, E.B. Wang. *J. Coord. Chem.*, **64**, 71 (2011).
[47] Z.S. Wang, Z.M. Zhang, Y.G. Li, X.B. Han, H. Duan, E.B. Wang. *J. Coord. Chem.*, **65**, 1443 (2012).
[48] I.D. Brown, D. Altermatt. *Acta Crystallogr. Sect. B.*, **41**, 244 (1985).
[49] B.W. Chen, W.L. Chen, Y.G. Li, E.B. Wang. *J. Clust. Sci.*, **22**, 73 (2011).
[50] A.X. Tian, J. Ying, J. Peng, J.Q. Sha, H.J. Pang, P.P. Zhang, Y. Chen, Z.M. Su. *Inorg. Chem.*, **48**, 100 (2009).
[51] K. Yu, W.L. Chen, B.B. Zhou, Y.Y. Li, Y. Yu, Z.H. Su, Y. Chen. *Cryst. Eng. Comm.*, **13**, 3417 (2011).