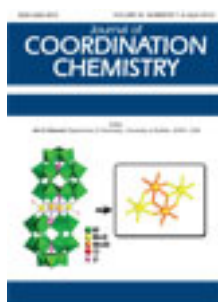


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:45

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gcoo20>

Extended structure constructed from sandwich-type tungstoantimonites fused together by water substitution on the sandwiching metal centers

Zhi-Shu Wang^a, Zhi-Ming Zhang^a, Yang-Guang Li^a, Xin-Bao Han^a, Hui Duan^a & En-Bo Wang^a

^a Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Ren Min Street No. 5268, Changchun, Jilin 130024, P.R. China

Published online: 30 Mar 2012.

To cite this article: Zhi-Shu Wang, Zhi-Ming Zhang, Yang-Guang Li, Xin-Bao Han, Hui Duan & En-Bo Wang (2012) Extended structure constructed from sandwich-type tungstoantimonites fused together by water substitution on the sandwiching metal centers, Journal of Coordination Chemistry, 65:8, 1443-1450, DOI: [10.1080/00958972.2012.674114](https://doi.org/10.1080/00958972.2012.674114)

To link to this article: <http://dx.doi.org/10.1080/00958972.2012.674114>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Extended structure constructed from sandwich-type tungstoantimonites fused together by water substitution on the sandwiching metal centers

ZHI-SHU WANG, ZHI-MING ZHANG*, YANG-GUANG LI,
XIN-BAO HAN, HUI DUAN and EN-BO WANG*

Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Ren Min Street No. 5268, Changchun, Jilin 130024, P.R. China

(Received 6 January 2012; in final form 28 February 2012)

A polyoxotungstate, $\{\text{Na}_6(\text{H}_2\text{O})_{16}\}[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{SbW}_9\text{O}_{33}\}_2] \cdot 13\text{H}_2\text{O}$ (**1**), has been synthesized and characterized by elemental analysis, IR, and single-crystal X-ray diffraction analysis. Compound **1** exhibits a 1-D chain-like structure composed of the sandwich-type tungstoantimonites fused together by water substitution on the sandwiching metal centers, rarely observed in POM chemistry. Electrocatalytic studies show that **1** has electrocatalytic activity for the reduction of nitrite.

Keywords: Polyoxotungstate; Tungstoantimonite; Extended structure; Sandwich

1. Introduction

Continual interest in the synthesis of transition metal (TM)-substituted polyoxometalates (POMs) stems from their tunable magnetic, catalytic, and optical properties as well as their applications in biochemistry and as functional materials [1–3]. Use of various lacunary POMs as inorganic multidentate O-donors to react with TM cations is an efficient way to obtain new polynuclear aggregates [4]. Within the class of TM-substituted POMs, a subfamily is sandwich-type POMs, which use different TM species and TM clusters [5–8]. POMs with controllable shape and size, high-negative charges, and oxo-enriched surfaces (such as Keggin-, Anderson-, and Lindquist-type anions) have been widely used as building blocks to construct extended framework materials. As charge density on the surface oxygen atoms of POMs increases, affinity for the polyoxoanions to coordinate to TM complexes should appear. During preparation, two strategies have been exploited to increase the surface charge density and activate the surface oxygen atoms of polyoxoanions: (1) reduce the metal centers from the highest oxidation state to a lower one, for example, from $\text{W}(\text{Mo})^{\text{VI}}$ to $\text{W}(\text{Mo})^{\text{V}}$, by introducing strong reducing reagents or (2) replace high-valence metal centers with lower-valence

*Corresponding authors. Email: zhangzm178@nenu.edu.cn; wangeb889@nenu.edu.cn

ones, for instance, from $W(Mo)^{VI}$ to V^{IV} or TM^{2+} [9]. However, the highly reduced polyoxoanions are usually unstable and oxidize in ambient conditions. For high negative charge POMs, sandwich-type heteropolytungstates are ideal candidates as they are stable and easily obtained starting materials [10–12]. Extended structure materials based on sandwich-type polyoxoanions bridged by metal-cations or the metal-organic groups have been reported. However, sandwich-type polyoxoanions fused together by water substitution on the sandwiching metal centers are rarely observed in POM chemistry [13]. In this article, a sandwich-type polyoxoanion-based 1-D chain-like structure, $\{Na_6(H_2O)_{16}\}[\{Mn_3(H_2O)_6 W(OH)_2\}\{SbW_9O_{33}\}_2] \cdot 13H_2O$ (**1**), was obtained by the elimination of two water molecules on the outer Mn centers of the sandwich-type $[\{Mn_3(H_2O)_6 W(OH)_2\}\{B-\alpha-SbW_9O_{33}\}_2]^{6-}$ and concomitant formation of Mn–O–W bonds with two adjacent POMs. The 1-D chains were further connected by $\{Na_6(H_2O)_{16}\}$ clusters into a 2-D framework.

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without purification. Elemental analyses were obtained on a PLASMA – SPEC (I) ICP atomic emission spectrometer. Infrared (IR) spectra were obtained on an Alpha Centaur FTIR spectrometer from 400 to 4000 cm^{-1} with KBr pellets. UV-Vis absorption spectra were obtained using a 752 PC UV-Vis spectrophotometer.

2.2. Synthesis of **1**

$MnCl_2 \cdot 4H_2O$ (0.20 g, 1.01 mmol), Sb_2O_3 (0.06 g, 0.21 mmol), and $Na_2WO_4 \cdot 2H_2O$ (1.32 g, 4.0 mmol) were dissolved in 20 mL of 0.5 mol L^{-1} sodium acetate buffer (pH 5.5). The mixture was heated at 85°C for 2 h with constant stirring. After cooling to room temperature, the mixture was filtered and the filtrate was left to evaporate at room temperature. Yellow crystalline products were isolated after 1 week (yield 42% based on Sb). Anal. Found (%): Na, 2.35; Mn, 3.01; Sb, 4.40; W, 61.4; Calcd (%): Na, 2.40; Mn, 2.86; Sb, 4.23; W, 61.6. IR (KBr pellet): ν_{max} (cm^{-1}): 3423 (m), 1624 (s), 947 (s), 834 (s), 770 (m), 665 (w), and 457 (w).

2.3. X-ray crystallography

Single-crystal X-ray data for **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 kW sealed tube X-ray source (Mo-K α radiation, $\lambda = 0.71073\text{ \AA}$) operating at 50 kV and 200 mA. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using *SHELXL-97* [14]. During the refinement of **1**, all hydrogen atoms on water and protonation were directly included in the molecular formula. The polyoxoanion contains site-occupancy disorder on the Mn(2)/W(10) center with occupancy ratios of 50% for Mn and 50% for W, respectively. The command “isor” was used to restrain non-H atoms with ADP and

NPD problems, which leads to a relative high restraint value (156). During the refinement, the command “omit-3 50” is used to omit the weak reflection above 50°. The highest residual peak, $4.058 \text{ e}\text{\AA}^{-3}$, is close to W(7) (0.958 \AA) and no element is suitable for this residual peak. Twenty-four lattice water molecules were found from the Fourier maps; however, there are still an accessible solvent voids ($631.5 \text{ e}\text{\AA}^{-3}$) in the crystal structure, indicating that some more water molecules should exist. PLATON analysis indicates that there were another five water molecules in the void of the structure (the SQUEEZE result is appended to the cif file). The crystal data and structure refinements of **1** are summarized in table 1, CSD reference number: 423126 for **1**.

2.4. General electrochemical materials and methods

Thrice-distilled water was used throughout the experiments. A pH 5.0, 0.2 mol L^{-1} $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer for **1** was used during the experiments. Solutions were deaerated by pure argon bubbling prior to the experiments. A CHI 660 electrochemical workstation connected to a Pentium-IV personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was glassy carbon (GC), the reference electrode was Ag/AgCl electrode, and platinum wire was used as a counter electrode. All potentials are reported *versus* the Ag/AgCl. A pHS-25B type pH meter was used for pH measurement. All the experiments were carried out at room temperature ($20\text{--}25^\circ\text{C}$).

3. Results and discussions

3.1. Synthesis and structure description

Conventional aqueous method has proved to be a powerful synthetic technique in making TM-substituted polyoxotungstates. Thousands of TM-substituted

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

Empirical formula	$\text{H}_{72}\text{Mn}_3\text{Na}_6\text{O}_{103}\text{Sb}_2\text{W}_{19}$
Formula weight	5759.99
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (\AA , $^\circ$)	
<i>a</i>	13.331(3)
<i>b</i>	14.159(3)
<i>c</i>	15.914(3)
α	104.90(3)
β	101.89(3)
γ	104.99(3)
Volume (\AA^3), <i>Z</i>	2682.0(9), 1
Calculated density (g cm^{-3})	3.566
<i>F</i> (000)	2545
Data/restraints/parameters	9374/156/560
Goodness-of-fit on F^2	1.019
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0774$, ^a $wR_2 = 0.2158$ ^b

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

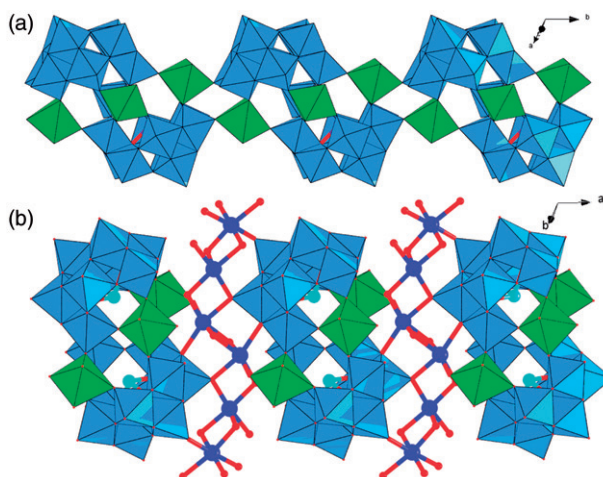


Figure 1. The 1-D chains in **1** along different directions.

polyoxotungstates have been synthesized by the use of lacunary POMs as precursors. In this article, **1** was synthesized by the simple one pot reaction with the raw materials Sb_2O_3 , Na_2WO_4 , and Mn^{2+} under conventional aqueous method; **1** exhibits a 1-D chain-like structure based on sandwich-type polyoxoanion $[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}_2]^{6-}$. Also, we have attempted to replace the Mn^{2+} with various TM cations in this reaction system. However, no similar structures were obtained. In previous work, two new Hervé-sandwich tungstoantimonates were obtained from SbCl_3 , Na_2WO_4 , and TM ions (Co^{2+} , Mn^{2+}) with the assistance of organic ligands [8c]. The reactivity of $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ toward TM has been explored under various conditions. A 1-D chain-like structure based on sandwich polyoxoanions, which are fused together by water substitution on the sandwiching metal centers, has been obtained by reaction of $[\alpha\text{-SbW}_9\text{O}_{33}]^{9-}$ with Fe^{3+} ions [13a]. However, no other similar structures were obtained by introducing other TM cations in this reaction system.

Single-crystal X-ray diffraction analysis reveals that **1** is composed of a sandwich-type polyoxoanion $[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}_2]^{6-}$, six Na^+ , and lattice water. Polyoxoanion **1** exhibits a 1-D chain-like structure with sandwich-type polyoxoanion $[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}_2]^{6-}$ (figure 1). In $[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}_2]^{6-}$, two trivalent $\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}$ units are connected by three $\{\text{MnO}_6\}$ octahedra and one $\{\text{WO}_6\}$ octahedron (each of the two opposite sites (W_{10}) is occupied by a W ion and a Mn ion with the site occupancy factor of 50%) (figure 2a). As shown in figure 1(a), the chain results from the elimination of two water molecules on the outer Mn centers of a $[\{\text{Mn}_3(\text{H}_2\text{O})_6\text{W}(\text{OH})_2\}\{\text{B-}\alpha\text{-SbW}_9\text{O}_{33}\}_2]^{6-}$ anion with the formation of Mn–O–W bonds with two adjacent POMs (figure 2). In addition, the sandwich polyoxoanions are connected by $\{\text{Na}_6(\text{H}_2\text{O})_{16}\}$ clusters into a 1-D chain-like structure. Two 1-D chains cross-link resulting in a 2-D extended layer-like structure (figure 3). Alternatively, it could be regarded that 1-D chains in the solid-state 2-D extended framework are connected by $\{\text{Na}_6(\text{H}_2\text{O})_{16}\}$ clusters into a 2-D framework structure (figure 3). In $\{\text{Na}_6(\text{H}_2\text{O})_{16}\}$, six Na^+ ions are connected by water molecules to constitute a line-like structure (figure S1). Na(1) and Na(2) are six

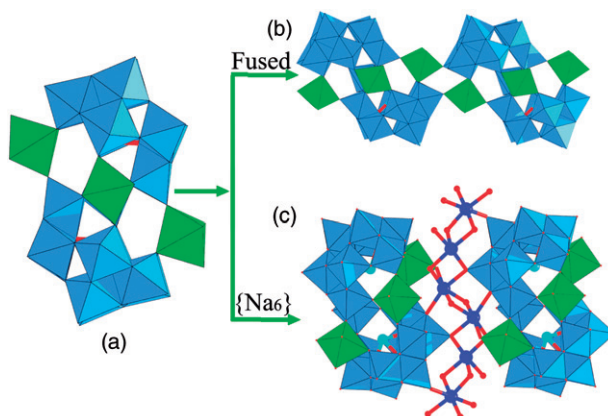


Figure 2. (a) Polyhedral representation of the sandwich-type polyoxoanion in **1**; (b), (c) polyhedral representation of the linking modes in the 1-D chains in **1**.

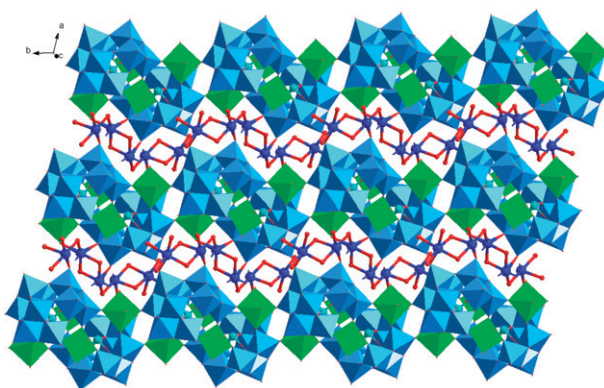


Figure 3. Mixed polyhedral and ball-and-stick representation of the 2-D framework of **1**.

coordinate and Na(3) is five coordinate. The Na–O distances are 2.33(3)–2.55(3) Å; bond lengths and angles of the tungsten-oxo framework in **1** are not unusual. Oxidation states of W, Sb, and Mn are determined on the basis of the crystal color, bond lengths and angles, charge balance consideration, and bond valence sum calculations [15], indicating that the W, Sb, and Mn sites possess +6, +3, and +2 oxidation states, respectively. Selected bond lengths and bond valence sum calculations are listed in table S1. Bond valence sum calculations also reveal that water is coordinated with Mn (Mn(1)–O(1) 2.29(3) Å; Mn(1)–O(11) 2.21(3) Å).

3.2. Aqueous solution stability and electrochemistry

The aqueous solution stabilities of **1** have been investigated by cyclic voltammetric (CV) and UV-Vis spectra (figure S2). Compound **1** was dissolved in pH 5.0 buffer solution at

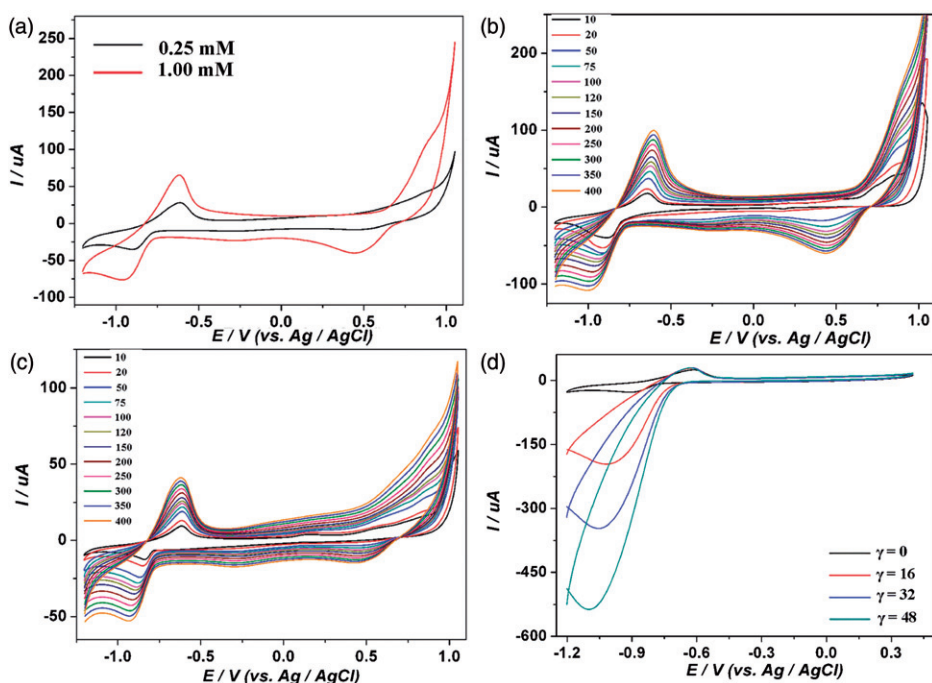


Figure 4. (a) Cyclic voltammograms of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ and $1 \times 10^{-3} \text{ mol L}^{-1}$ **1** in pH 5.0, 0.2 mol L^{-1} $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer solution at 150 mV s^{-1} ; (b) cyclic voltammograms of $1 \times 10^{-3} \text{ mol L}^{-1}$ **1** in the pH 5.0 buffer solution at different scan rates from 10 to 400 mV s^{-1} ; (c) cyclic voltammograms of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ **1** in the pH 5.0 buffer at scan rates from 10 to 400 mV s^{-1} ; (d) electrocatalysis of the reduction of NO_2^- in the presence of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ **1** at the scan rate of 150 mV s^{-1} . The working electrode was GC; the reference electrode was Ag/AgCl.

room temperature. The CV behavior of the solution was detected per 6 h for six times. These solutions show no change in voltammetric characteristics. UV-Vis spectra of the above solutions were checked simultaneously and no changes were observed during 24 h. These characterizations confirm that polyoxoanion **1** is stable in the pH 5.0 buffer solution. The CV behavior of 1 mmol L^{-1} **1** in a pH 5.0, 0.2 mol L^{-1} $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer solution exhibits two pairs of redox peaks in the potential range -1.2 V and $+1.0 \text{ V}$ with $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2 = 0.665 \text{ V}$ and -0.772 V (figure 4). The first redox peaks ($E_{1/2} = 0.665 \text{ V}$) are attributed to redox of the manganese centers in the polyoxoanion framework, which is nearly coincident with the response of free Mn^{2+} (figure S3), similar to other Mn-containing polyoxotungstates [16]. The redox process in the negative domain with $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2 = -0.772 \text{ V}$ corresponds to redox of the tungsten-oxo framework [17]. Controlled potential electrolysis confirmed that this couple corresponded to a four-electron transfer. The cyclic voltammograms of **1** at different scan rates show that the peak currents are proportional to the scan rate, indicating that the redox process on the GC electrode is surface-controlled when the scan rate does not exceed a rate of 75 mV s^{-1} . Above 100 mV s^{-1} , the peak currents were proportional to the square root of the scan rate, suggesting that the redox process is diffusion-controlled [18]. The electrochemical properties of $2.5 \times 10^{-4} \text{ mol L}^{-1}$ **1** in pH 5.0, 0.2 mol L^{-1} $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ buffer solution exhibit two redox couples in

the potential range -1.2 V and $+1.0\text{ V}$ (figure 4a and c). Many POM materials and some coordination polymers exhibit electrocatalytic activity toward the reduction of nitrite. In this article, the electrocatalytic activity of **1** toward the reduction of nitrite was detected [18b, 19]. On addition of small amounts of nitrite to the pH 5.0 buffer solution with $2.5 \times 10^{-4}\text{ mol L}^{-1}$ **1**, the reduction peak current of W centers increased while the corresponding oxidation peak current decreased, suggesting nitrite was reduced by the reduced polyoxoanion species (figure 4d) [19]. They were run at the same scan rate as a function of the excess parameter $\gamma = C_{\text{NO}_2^-}/C_{\text{POM}}$. The catalytic efficiencies CAT (defined as $\text{CAT} = 100 \times [I_{(\text{POM}+\text{NO}_2^-)}^{\text{d}} - I_{(\text{POM})}^{\text{d}}]/I_{(\text{POM})}^{\text{d}}$, where $I_{(\text{POM}+\text{NO}_2^-)}^{\text{d}}$ represents the reduction peak current observed for the polyoxoanion in the presence of nitrite and $I_{(\text{POM})}^{\text{d}}$ is the corresponding reduction peak current for POM alone) varies from 550 to 1673% when c increases from $\gamma = 16$ to $\gamma = 48$.

4. Conclusions

A sandwich-type tungstoantimonate-based 1-D chain-like structure was obtained by the one-pot reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, Sb_2O_3 , and $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$. Compound **1** exhibits a 1-D chain-like structure obtained by water substitution on the sandwiching metal centers. The 1-D chains were connected by $\{\text{Na}_6\}$ clusters into a 2-D framework structure. Electrocatalytic studies indicate that **1** displays electrocatalytic activity toward the reduction of nitrite.

Supplementary material

UV-Vis and IR spectra and additional figures, X-ray crystallographic information file (CIF) are available for **1**.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 21101022) and the Fundamental Research Funds for the Central Universities (10QNJJ009/09SSXT120).

References

- [1] (a) A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane. *Chem. Rev.*, **110**, 6009 (2010); (b) A. Dolbecq, F. Sécheresse. *Chem. Commun.*, 3477 (2006); (c) A. Proust, R. Thouvenot, P. Guozerhg. *Chem. Commun.*, 1837 (2008).
- [2] (a) D.L. Long, R. Tsunashima, L. Cronin. *Angew. Chem. Int. Ed.*, **49**, 1736 (2010); (b) J.M.C. Juan, E. Coronado. *Coord. Chem. Rev.*, **193**, 361 (1999); (c) B.S. Bassil, U. Kortz. *Dalton Trans.*, **40**, 9649 (2011).

- [3] (a) A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998); (b) Y. Kikukawa, S. Yamaguchi, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi, N. Mizuno. *J. Am. Chem. Soc.*, **130**, 5472 (2008).
- [4] (a) X.K. Fang, P. Kögerler, Y. Furukawa, M. Speldrich, M. Luban. *Angew. Chem. Int. Ed.*, **50**, 5212 (2011); (b) Z.M. Zhang, S. Yao, Y.G. Li, Y.H. Wang, Y.F. Qi, E.B. Wang. *Chem. Commun.*, 1650 (2008); (c) Z.M. Zhang, Y.F. Qi, C. Qin, Y.G. Li, E.B. Wang, X.L. Wang, Z.M. Su, L. Xu. *Inorg. Chem.*, **46**, 8162 (2007); (d) Z.M. Zhang, Y.G. Li, S. Yao, E.B. Wang. *Dalton Trans.*, **40**, 6475 (2011); (e) Z.M. Zhang, S. Yao, Y.F. Qi, Y.G. Li, Y.H. Wang, E.B. Wang. *Dalton Trans.*, 3051 (2008).
- [5] (a) C. Pichon, A. Dolbecq, P. Mialane, J. Marrot, E. Rivière, M. Goral, M. Zynek, T. McCormac, S.A. Borshch, E. Zueva, F. Sécheresse. *Chem. Eur. J.*, **14**, 3189 (2008); (b) T.M. Anderson, W.A. Neiwert, K.I. Hardcastle, C.L. Hill. *Inorg. Chem.*, **43**, 7353 (2004); (c) B. Botar, P. Kolgerler, C.L. Hill. *Inorg. Chem.*, **46**, 5398 (2007).
- [6] (a) L. Bi, U. Kortz, S. Nellutla, A.C. Stowe, J. van Tol, N.S. Dalal, B. Keita, L. Nadjo. *Inorg. Chem.*, **44**, 896 (2005); (b) B. Liu, L.L. Li, Y.P. Zhang, Y. Ma, H.M. Hu, G.L. Xue. *Inorg. Chem.*, **50**, 9172 (2011); (c) L.X. Shi, X.W. Zhang, C.D. Wu. *Dalton Trans.*, **40**, 779 (2011); (d) I. Loose, E. Droste, M. Bölsing, H. Pohlmann, M.H. Dickman, C. Rosu, M.T. Pope, B. Krebs. *Inorg. Chem.*, **38**, 2688 (1999).
- [7] (a) P.T. Witte, S.R. Chowdhury, J.E. ten Elshof, D. Sloboda-Rozner, R. Neumann, P.L. Alsters. *Chem. Commun.*, 1206 (2005); (b) J.D. Compain, P. Mialane, A. Dolbecq, I.M. Mbomekallé, J. Marrot, F. Sécheresse, E. Rivière, G. Rogez, W. Wernsdorfer. *Angew. Chem. Int. Ed.*, **48**, 3077 (2009).
- [8] (a) M. Ibrahim, Y. Lan, B.S. Bassil, Y. Xiang, A. Suchopar, A.K. Powell, U. Kortz. *Angew. Chem. Int. Ed.*, **50**, 4708 (2011); (b) J.P. Wang, P.T. Ma, J. Li, H.Y. Niu, J.Y. Niu. *Chem. Asian J.*, **3**, 822 (2008); (c) B. Chen, W. Chen, W. Liu, Y. Li, X. Wang, E. Wang. *J. Coord. Chem.*, **64**, 71 (2010).
- [9] (a) L.S. Felices, P. Vitoria, J.M. Gutiérrez-Zorrilla, L. Lezama, S. Reinoso. *Inorg. Chem.*, **45**, 7748 (2006); (b) P. Gouzerh, R. Villanneau, R. Delmont, A. Proust. *Chem. Eur. J.*, **6**, 1184 (2000).
- [10] (a) S.G. Mitchell, C. Streb, H.N. Miras, T. Boyd, D.L. Long, L. Cronin. *Nat. Chem.*, **2**, 308 (2010); (b) C. Ritchie, E.M. Burkholder, D.L. Long, D. Adam, P. Kögerler, L. Cronin. *Chem. Commun.*, 468 (2007).
- [11] (a) Z.M. Zhang, J. Liu, E.B. Wang, C. Qin, Y.G. Li, Y.F. Qi, X.L. Wang. *Dalton Trans.*, 463 (2008); (b) S.T. Zheng, D.Q. Yuan, J. Zhang, G.Y. Yang. *Inorg. Chem.*, **46**, 4569 (2007).
- [12] (a) Z.M. Zhang, Y.G. Li, Y.H. Wang, Y.F. Qi, E.B. Wang. *Inorg. Chem.*, **47**, 7615 (2008); (b) S. Yao, Z.M. Zhang, Y.G. Li, Y. Lu, E.B. Wang, Z.M. Su. *Cryst. Growth Des.*, **10**, 135 (2010); (c) Z.M. Zhang, S. Yao, Y.G. Li, Q. Shi, E.B. Wang. *J. Coord. Chem.*, **62**, 3259 (2009); (d) Z.M. Zhang, S. Yao, E.B. Wang, C. Qin, Y.F. Qi, Y.G. Li, R. Clérac. *J. Solid State Chem.*, **181**, 715 (2008).
- [13] (a) A. Dolbecq, J. Compain, P. Mialane, J. Marrot, E. Rivière, F. Sécheresse. *Inorg. Chem.*, **47**, 3371 (2008); (b) U. Kortz, S. Nellutla, A.C. Stowe, N.S. Dalal, J. Tol, B.S. Bassil. *Inorg. Chem.*, **43**, 144 (2004); (c) Z.M. Zhang, S. Yao, E.B. Wang, Q. Shi, H. Zhang. *J. Cluster Sci.*, **19**, 521 (2008); (d) B.W. Chen, W.L. Chen, Y.G. Li, E.B. Wang. *J. Cluster Sci.*, **22**, 73 (2011).
- [14] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).
- [15] The valence sum calculations are performed on a program of bond valence calculator, version 2.00 February 1993, written by C. Hormillosa with assistance from S. Healy, distributed by I.D. Brown.
- [16] (a) L. Ruhlmann, L. Nadjo, J. Canny, R. Contant, R. Thouvenot. *Eur. J. Inorg. Chem.*, 975 (2002); (b) B. Keita, P. Mialane, F. Sécheresse, P.D. Oliveira, L. Nadjo. *Electrochem. Commun.*, **9**, 164 (2007).
- [17] (a) L.-H. Bi, B. Li, Y.-Y. Bo, L.-X. Wu. *Inorg. Chim. Acta*, **362**, 1600 (2009); (b) J. Jing, B.P. Burton-Pye, L.C. Francesconi, M.R. Antonio. *Inorg. Chem.*, **47**, 6889 (2008).
- [18] (a) S.G. Mitchell, H.N. Miras, D. Long, L. Cronin. *Inorg. Chim. Acta*, **363**, 4240 (2010); (b) H. Lin, H. Hu, X. Wang, B. Mu, J. Li. *J. Coord. Chem.*, **63**, 1295 (2010).
- [19] B. Keita, I.M. Mbomekalle, L. Nadjo. *Electrochem. Commun.*, **5**, 830 (2003).