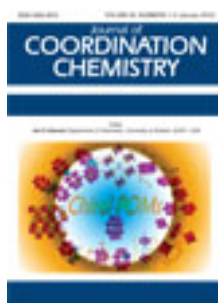


This article was downloaded by: [Renmin University of China]

On: 13 October 2013, At: 10:33

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>

A 3-D supramolecular compound based on Keggin-type polyoxometalates and potassium-sulfanilamide

Jiang Wu^a, Chunxiao Wang^a, Kai Yu^a, Zhanhua Su^a, Yang Yu^a, Yanglei Xu^a & Baibin Zhou^a

^a Key Laboratory of Design and Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province, Harbin Normal University, Harbin 150080, P. R. China

Published online: 06 Dec 2011.

To cite this article: Jiang Wu, Chunxiao Wang, Kai Yu, Zhanhua Su, Yang Yu, Yanglei Xu & Baibin Zhou (2012) A 3-D supramolecular compound based on Keggin-type polyoxometalates and potassium-sulfanilamide, *Journal of Coordination Chemistry*, 65:1, 69-77, DOI:

[10.1080/00958972.2011.640935](http://dx.doi.org/10.1080/00958972.2011.640935)

To link to this article: <http://dx.doi.org/10.1080/00958972.2011.640935>

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>

A 3-D supramolecular compound based on Keggin-type polyoxometalates and potassium-sulfanilamide

JIANG WU, CHUNXIAO WANG*, KAI YU, ZHANHUA SU, YANG YU,
YANGLEI XU and BAIBIN ZHOU*

Key Laboratory of Design and Synthesis of Functional Materials and Green Catalysis,
Colleges of Heilongjiang Province, Harbin Normal University, Harbin 150080, P. R. China

(Received 26 September 2011; in final form 4 November 2011)

A Keggin-type polyoxometalate and potassium-sulfanilamide complex, $[\{K(C_6H_{10}N_2O_2S)_2(H_2O)\}_2(SiW_{12}O_{40})_2] \cdot 2H_3O^+ \cdot 10H_2O$ (**1**), has been synthesized and characterized by elemental analyses, IR, TG, and single-crystal X-ray diffraction. Compound **1** exhibits infinite 1-D dimer chains which are constructed from Keggin units $[\alpha-SiW_{12}O_{40}]^{4-}$ bridged by potassium-sulfanilamide fragments. These 1-D chains are linked *via* π - π interactions between benzene rings of the sulfanilamides to form 2-D layers, which are further packed into 3-D supramolecular assemblies through hydrogen bonds. The electrochemical and electrocatalytic behaviors of **1** have been studied in detail.

Keywords: Keggin-type polyoxometalates; Potassium-sulfanilamide complex; Electrochemical

1. Introduction

Polyoxometalates (POMs) have attracted interest due to fascinating nano-sized structural features and potential applications in catalysis, medical agents, fluorescence, electronic, and magnetic materials [1–8]. The ligand is grafted into the framework of POM to build high-dimensional organic-inorganic hybrids materials *via* coordinate covalent bonds and weaker intermolecular forces (hydrogen bond, π - π stacking, and van der Waals forces) [9–16]. The complexes composed of weaker intermolecular forces are called supramolecular compounds. In the construction of supramolecular materials, one important strategy is the extension of low-dimensional building blocks to high-dimensional networks through weak intermolecular interactions. Among a wide variety of POMs, Keggin-type heteropolyanions have rapidly developed due to its stability and large number of oxygens as smart potential sites [17–25]. Keggin-based supramolecular architecture is promising in biology and materials science [26–31]. Extensive efforts have focused on the design and assembly of such supramolecular architectures. A few high-dimensional supramolecular assemblies have been synthesized. However, there are

*Corresponding authors. Email: wangchunxiao842@yahoo.com.cn; zhou_bai_bin@163.com

no prior reports on hybrid materials containing both Keggin-type POMs and sulfanilamide.

The selection of proper organic ligands and metals is a strategy to construct POM-based organic–inorganic hybrid compounds. Sulfonamides are widely used antibacterial agents for their low cost, low toxicity, and excellent activity against bacterial diseases [32]. Furthermore, sulfonamides containing one sulfamoyl and one amino group can be hydrogen-bonding acceptors and donors and monodentate or multidentate ligands to coordinate to various metals to give inorganic–organic hybrid materials [32–34]. Potassium, with high biological activity, is the primary cation in the cell sap, which can adjust the penetrating press of the cells and the acid–base balance of body fluids. Moreover, potassium can combine with the POMs and organic ligands containing oxygen or nitrogen to form multidimensional structures [35–39].

Based on the aforementioned considerations, herein we report a synthetic route to a supramolecular compound, $[\{K(C_6H_9N_2O_2S)_2(H_2O)\}_2(SiW_{12}O_{40})_2] \cdot 2H_3O^+ \cdot 10H_2O$ (**1**), using the α -Keggin-type polyoxoanion as inorganic building blocks. The electrochemical and electrocatalytic behaviors of **1** were also investigated.

2. Experimental

2.1. Materials and general procedures

All chemicals were obtained from commercial sources and used without purification. $K_4[\alpha-SiW_{12}O_{40}] \cdot 17H_2O$ was prepared according to the literature method [40] and verified by the IR spectrum. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. K, Si, and W analyses were performed on a PLASMA-SPEC (I) inductively coupled plasma atomic emission spectrometer. IR spectra were obtained on an Alpha Centaur Fourier transform IR (FT-IR) spectrometer with KBr pellets from 400 to 4000 cm^{-1} . The thermogravimetric analyses (TGA) were carried out in N_2 on a Perkin-Elmer DTA 1700 differential thermal analyzer with a rate of 10 $^{\circ}C\ min^{-1}$. Electrochemical measurements were performed with a CHI660 electrochemical workstation. A conventional three-electrode system was used. The working electrode was a glassy carbon electrode. Platinum gauze was used as a counter electrode and Ag/AgCl was used as reference electrode.

2.2. Synthesis of **1**

Compound **1** was prepared by routine synthetic reactions in aqueous solution: $K_4[\alpha-SiW_{12}O_{40}] \cdot 17H_2O$ (1.353 g, 0.5 mmol) was dissolved in 40 mL of water. $NH_2C_6H_4SO_2NH_2$ (1.033 g, 0.6 mmol) dissolved in 5 mL of 2 $mol\ L^{-1}$ HCl was dropped into the solution and the pH of the solution was 2.3. The mixture was heated at 80 $^{\circ}C$ for 3 h with stirring, cooled to room temperature, and filtered. The colorless crystal was obtained a few days later. The yield was 63% (based on W). Elemental Anal. Calcd (%): Si, 0.83; W, 65.17; K, 1.15; C, 4.25; H, 0.97; N, 1.65. Found (%): Si, 0.85; W, 65.20; K, 1.16; C, 4.22; H, 0.92; N, 1.61.

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

Compound	1
Chemical formula	C ₂₄ H ₆₆ O ₁₀₂ K ₂ N ₈ S ₄ Si ₂ W ₂₄
Formula weight	6773.67
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions (Å, °)	
<i>a</i>	13.952(3)
<i>b</i>	14.145(3)
<i>c</i>	15.738(3)
α	87.5440(10)
β	85.015(2)
γ	60.45
Volume (Å ³), <i>Z</i>	2691.7(10), 1
Calculated density (Mg m ⁻³)	4.179
Absorption coefficient (mm ⁻¹)	25.821
<i>F</i> (000)	2988.0
crystal size (mm ³)	0.46 × 0.42 × 0.40
θ range for data collection (°)	2.60–28.08
Reflections collected	15,667
Independent reflection	13,114 [<i>R</i> (int) = 0.0635]
Data/restraints/parameters	13,114/32/753
Goodness-of-fit on <i>F</i> ²	0.989
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> ₁ = 0.0487, <i>wR</i> ₂ = 0.0997
<i>R</i> indices (all data) ^b	<i>R</i> ₁ = 0.0886, <i>wR</i> ₂ = 0.1091

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

2.3. X-ray crystallography

Single-crystal X-ray data of **1** were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by full-matrix least-squares on *F*² using the SHELXTL-97 package [41, 42]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon and nitrogen were included at calculated positions and refined with a riding model. The crystal data and refinement parameters of **1** are summarized in table 1. Selected bond lengths and angles are listed in table S1.

3. Results and discussion

3.1. Structure description

Single-crystal X-ray analysis reveals that **1** is composed of [α -SiW₁₂O₄₀]⁴⁻ clusters, [(C₆H₉N₂O₂S)₂(H₂O)K]³⁺ units, and water. The [α -SiW₁₂O₄₀]⁴⁻ cluster is the well-known Keggin structure, which is based on a central {SiO₄} tetrahedron surrounded by twelve {WO₆} octahedra. The twelve {WO₆} octahedra may be subdivided into four {W₃O₁₃} groups, each composed of three edge-sharing {WO₆} octahedra. The four W₃O₁₃ groups are linked by sharing corners and linked to the {SiO₄} tetrahedron by the μ_4 -O atoms. The W–O bond lengths can be divided into three types: W–O_t

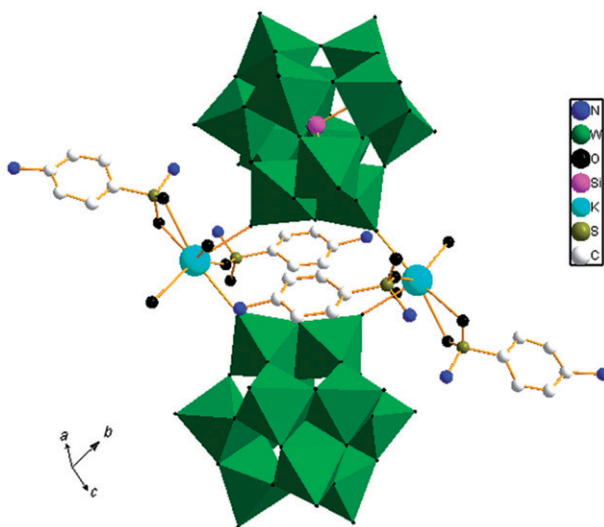


Figure 1. Polyhedral and ball-stick representation of the molecular structure unit of **1**; all hydrogen atoms and isolated water molecules are omitted for clarity.

(terminal): 1.655(14)–1.757(14) Å, W–O_{b/c} (bridge): 1.859(15)–1.984(16) Å, W–O_a (central): 2.332(14)–2.448(16) Å. The Si–O bond lengths in the {SiO₄} tetrahedron range from 1.596(15) to 1.630(16) Å; the W–O–W bond angles vary from 89.0° to 152.5°.

There is one crystallization-independent potassium ion in **1**. K(1) is seven-coordinate by two terminal oxygen atoms from two polyoxoanions (average K(1)–O 2.738(6) Å), one bridged oxygen from another polyoxoanion (K(1)–O(38)# 3.231(16) Å), one oxygen from one sulfanilamide (K(1)–O(43) 2.78(2) Å), two oxygen atoms from another sulfanilamide (average K(1)–O 2.987(10) Å), and one water molecule (K(1)–O₄₅ 2.87(2) Å) (figure S1). There are two crystallographically independent sulfanilamides adopting two different coordination modes. One is monodentate to K(1) by one oxygen of sulfamoyl. The other is bidentate coordinating to K(1) by two oxygen atoms of sulfamoyl. In this way, two sulfanilamide molecules and one potassium form a potassium–sulfanilamide complex [(C₆H₉N₂O₂S)₂(H₂O)K]³⁺.

Two [α-SiW₁₂O₄₀]⁴⁻ join to two [(C₆H₉N₂O₂S)₂(H₂O)K]³⁺ complexes by four terminal oxygen atoms of {WO₆} octahedra to form a dimer (figure 1). Each dimer connects to two neighboring ones *via* interaction between four μ-O of {WO₆} octahedra and four K⁺ ions of [(C₆H₉N₂O₂S)₂(H₂O)K]³⁺, leading to an infinite dimer chain (figure 2). These 1-D chains are linked *via* π–π interactions between benzene rings of the sulfanilamide groups to form 2-D layers (figure 3), which are further packed into 3-D supramolecular assemblies through hydrogen bonds among ligand water, lattice water, and nitrogen atoms on the sulfanilamide (figures 4, S2 and S3). In the crystal structure, the average distance between two benzene planes with π–π interactions is about 3.9477 Å. Typical hydrogen bonds between them are as follows: N1⋯O2W 2.896 Å, O2W⋯O15 2.880 Å, O2W⋯O19 2.965 Å. It is believed that the extensive hydrogen bonding (table S2) interactions and π–π interactions of **1** play an important role in stabilizing the 3-D supramolecular framework. Bond valence sum (BVS) calculations

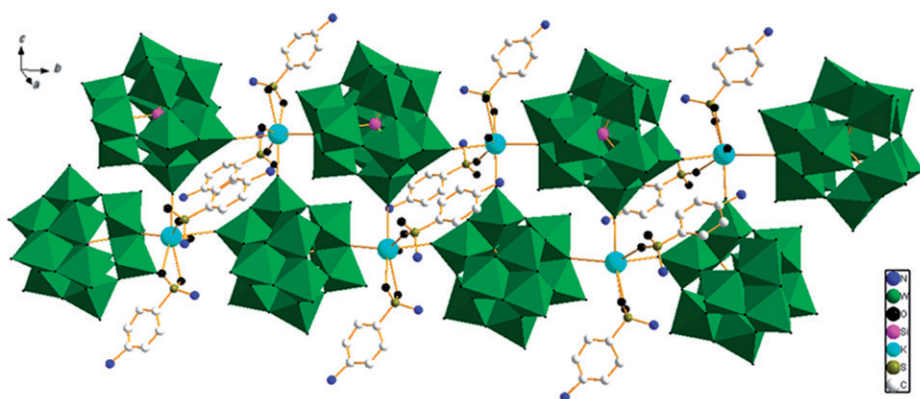


Figure 2. Polyhedral and ball-stick representation of the 1-D chain in **1**.

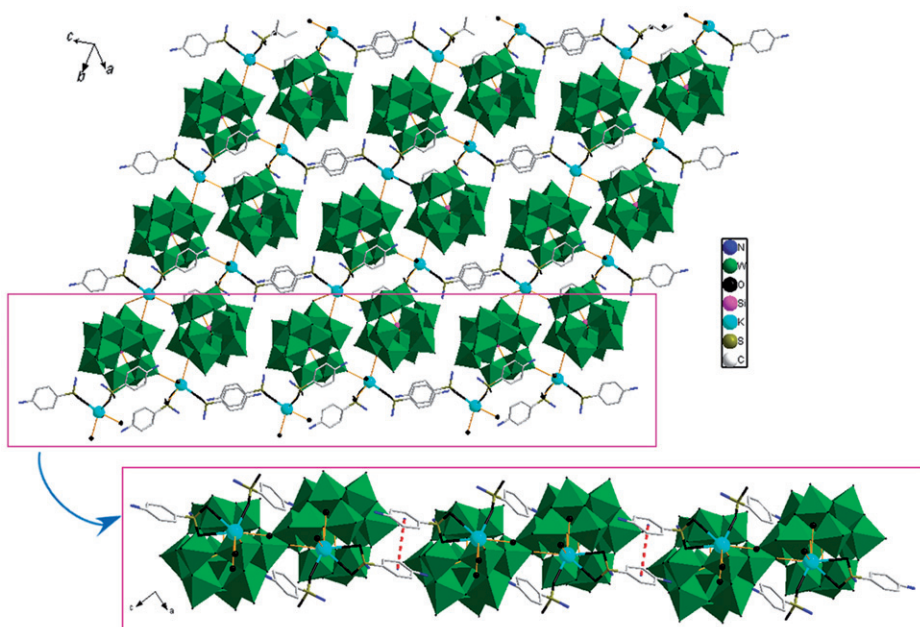


Figure 3. View of the 2-D supramolecular layer *via* π - π interactions of **1**.

[43] confirm that all W and K centers are in the oxidation states of +IV and +I, respectively.

3.2. IR spectrum

In the IR spectrum of **1** (figure S4), characteristic peaks at 792, 884, and 978 cm^{-1} are ascribed to $\nu(\text{W}-\text{Oc}-\text{W})$, $\nu(\text{W}-\text{Ob}-\text{W})$, and $\nu(\text{W}-\text{Ot})$, respectively. The peaks at 924 and

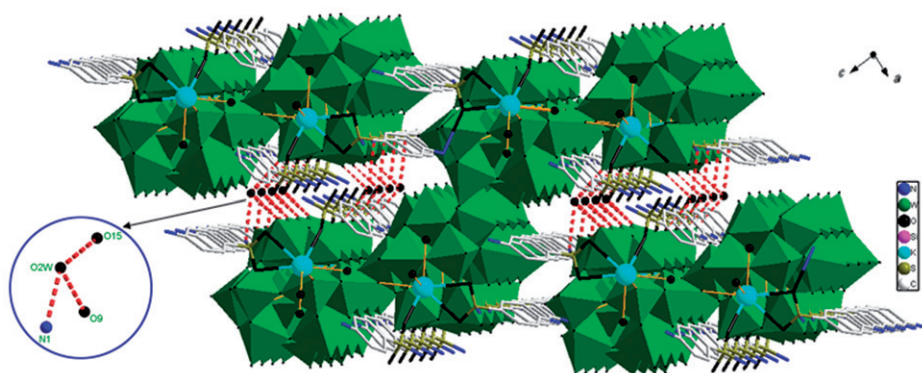


Figure 4. View of the 3-D packing of **1** along the crystallographic *b*-axis.

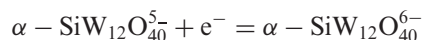
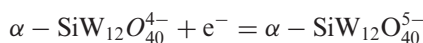
1016 cm^{-1} are attributed to $\nu(\text{Si-Oa})$. These results indicate that the polyanions in **1** still maintain the basic Keggin structure, only slightly distorted [44]. This may be due to the interaction between $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and K complexes. Peaks at 3331, 3238, and 3146 cm^{-1} can be regarded as vibrations of $\nu(\text{N-H})$, while 1306 and 1162 cm^{-1} to $\nu(\text{O=S=O})$, 1624, 1548, and 1496 cm^{-1} to $\nu(\text{C=C})$. The peak at 2590 cm^{-1} is the characteristic absorption of NH_3^+ . IR spectra are in agreement with the results of single-crystal X-ray diffraction analysis.

3.3. TG analysis

The TG curve shows a two-step weight loss (figure S5). The first weight loss of 3.74% from 309°C to 365°C corresponds to the release of all lattice and coordinated water (calculated value of 3.72%, $\sim 14 \text{ H}_2\text{O}$). The second weight loss of 10.18% from 412°C to 641°C is attributed to the loss of all sulfanilamides. The value is close to the calculated value of 10.21% (~ 4 sulfanilamide). The result of the TG analysis basically agrees with that of the structure determination.

3.4. Voltammetric behavior of **1**

The cyclic voltammogram of $10^{-3} \text{ mol L}^{-1}$ of **1** at pH 5.0 ($\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$) buffer solution at 50 mV s^{-1} shows four reversible redox peaks I-I', II-II', III-III', and IV-IV' with half-wave potentials $E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$ at 0.4805 (I-I'), -0.1821 (II-II'), -0.4275 (III-III') and -0.6264 (IV-IV') V, respectively (figure 5). Redox peaks II-II' and III-III' correspond to two consecutive one-electron processes, while I-I' and IV-IV' correspond to two, two-electron processes. Therefore, the peaks can be described by the following equations [45, 46]:



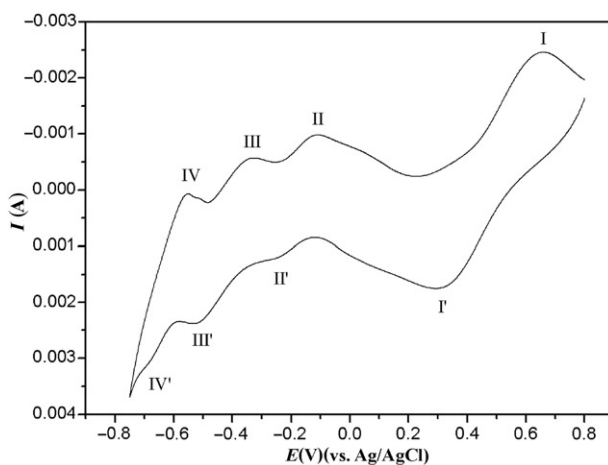


Figure 5. The cyclic voltammograms of $10^{-3} \text{ mol L}^{-1}$ of **1** at pH 5.0 ($\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$) buffer solution with a scan rate of 50 mV s^{-1} .

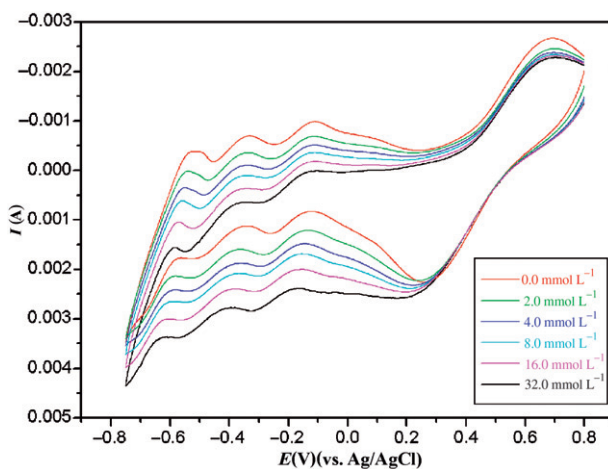
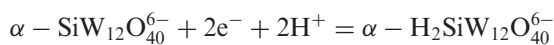
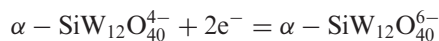


Figure 6. Electrochemical reduction of H_2O_2 in the presence of $10^{-3} \text{ mol L}^{-1}$ of **1** in a pH 5.0 medium ($\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$) at a scan rate of 50 mV s^{-1} . The concentrations of H_2O_2 are 0.0, 2.0, 4.0, 8.0, 16.0, and 32.0 mmol L^{-1} .



The peak potentials change gradually with scan rate from 50 to 260 mV s^{-1} : the cathodic peak potentials shift to the negative direction and the corresponding anodic peak potentials shift to the positive direction, increasing peak-to-peak separations; the average peak potentials do not change (figure S6a). The peak currents are proportional to scan rates (figure S6b), suggesting that the redox process of **1** is surface-controlled [47].

3.5. Electrocatalytic property of **1**

The electrocatalytic property of **1** (figure 6) indicates that **1** has good electrocatalytic activity toward the reduction of hydrogen peroxide. With the addition of H₂O₂, all reduction peak currents increased while the corresponding oxidation peak currents dramatically decreased, suggesting that the reduction of H₂O₂ is mediated by the reduced species of Keggin-ions in **1**.

4. Conclusions

A supramolecular compound based on Keggin-type POM and potassium-sulfanilamide complex has been synthesized, providing a novel example of the utility of Keggin tungstosilicate clusters as precursors for self-assembly of extended supramolecular frameworks. Furthermore, **1** exhibits electrocatalytic activity toward the reduction of hydrogen peroxide. It is promising to use as a kind of new-style electrochemical sensor.

Supplementary material

CCDC 811837 contains the supplementary crystallographic data for this article. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Email: deposit@ccdc.com.ac.uk).

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grants 20671026 and 20971032), the Study Technological Innovation Project Special Foundation of Harbin (2009RFXXG202), and Technological Innovation Team Building Program of College of Heilongjiang Province (2009td04) and Innovation Team Research Program of Harbin Normal University (KJTD200902).

References

- [1] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).
- [2] D.L. Long, R. Tsunashima, L. Cronin. *Angew. Chem. Int. Ed.*, **49**, 1736 (2010).
- [3] D.L. Long, H. Abbas, P. Kögerler, L. Cronin. *Angew. Chem. Int. Ed.*, **44**, 3415 (2005).
- [4] X.H. Wang, J.F. Liu, J.X. Li, Y. Yang, J.T. Liu, B. Li, M.T. Pope. *J. Inorg. Biochem.*, **94**, 279 (2003).
- [5] A. Forment-Aliaga, E. Coronado, M. Feliz, A. Gaita-Arino, R. Llusar, F.M. Romero. *Inorg. Chem.*, **42**, 8091 (2003).
- [6] Q.H. Zhang, C.J. Cao, T. Xu, M. Sun, J.Z. Zhang, Y. Wang, H.L. Wan. *Chem. Commun.*, 2376 (2009).
- [7] S. Pathan, A. Patel. *J. Coord. Chem.*, **63**, 4041 (2010).
- [8] G. Liu, T.B. Liu. *J. Am. Chem. Soc.*, **127**, 6942 (2005).
- [9] Y. Ishii, Y. Takenaka, K. Konishi. *Angew. Chem. Int. Ed.*, **43**, 2702 (2004).

- [10] J.R. Galán-Mascarós, C. Giménez-Saiz, S. Triki, C.J. Gómez-García, E. Coronado, L. Ouahab. *Angew. Chem. Int. Ed. Engl.*, **34**, 1460 (1995).
- [11] E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, S. Triki. *J. Am. Chem. Soc.*, **120**, 4671 (1998).
- [12] A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse. *Chem. Eur. J.*, **9**, 2914 (2003).
- [13] J.Y. Niu, M.L. Wei, J.P. Wang, D.B. Dang. *Eur. J. Inorg. Chem.*, 160 (2004).
- [14] S. Reinoso, P. Vitoria, L.S. Felices, L. Lezama, J.M. Gutiérrez-Zorrilla. *Inorg. Chem.*, **45**, 108 (2006).
- [15] J. Chen, J.Q. Sha, J. Peng, Z.Y. Shi, A.X. Tian, P.P. Zhang. *J. Mol. Struct.*, **917**, 10 (2009).
- [16] A. Dolbecq, E. Dumas, C.R. Mayer, P. Mialane. *Chem. Rev.*, **110**, 6009 (2010).
- [17] H.J. Pang, C.J. Zhang, Y.G. Chen, D.M. Shi. *J. Coord. Chem.*, **63**, 418 (2010).
- [18] W.L. Liu, H.Q. Tan, W.L. Chen, Y.G. Li, E.B. Wang. *J. Coord. Chem.*, **63**, 1833 (2010).
- [19] L.C.W. Baker, D.C. Glick. *Chem. Rev.*, **98**, 3 (1998).
- [20] P. Gouzerh, A. Proust. *Chem. Rev.*, **98**, 77 (1998).
- [21] I. Bar-Nahum, R. Neumann. *Chem. Commun.*, 2690 (2003).
- [22] D. Hagrman, P.J. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 3165 (1999).
- [23] X.Y. Wu, X.F. Kuang, Z.G. Zhao, S.C. Chen, Y.M. Xie, R.M. Yu, C.Z. Lu. *Inorg. Chim. Acta*, **363**, 1236 (2010).
- [24] H.Y. An, E.B. Wang, D.R. Xiao, Y.G. Li, Z.M. Su, L. Xu. *Angew. Chem. Int. Ed.*, **45**, 904 (2006).
- [25] G.G. Gao, L. Xu, W.J. Wang, X.S. Qu, H. Liu, Y.Y. Yang. *Inorg. Chem.*, **47**, 2325 (2008).
- [26] E. Burkholder, V. Golub, C.J. O'Connor, J. Zubieta. *Inorg. Chem.*, **42**, 6729 (2003).
- [27] C. Lei, J.G. Mao, Y.Q. Sun, J.L. Song. *Inorg. Chem.*, **43**, 1964 (2004).
- [28] B.Z. Lin, Y.M. Chen, P.D. Liu. *J. Chem. Soc., Dalton Trans.*, 2474 (2003).
- [29] M.T. Pope, A. Müller. *Angew. Chem. Int. Ed. Engl.*, **30**, 34 (1991).
- [30] E. Coronado, C.J. Gómez-García. *Chem. Rev.*, **98**, 273 (1998).
- [31] F. Yao, F.X. Meng, Y.G. Chen, C.J. Zhang. *J. Coord. Chem.*, **63**, 196 (2010).
- [32] P.A. Ajibade, G.A. Kolawole, P. O'Brien, M. Helliwell, J. Raftery. *Inorg. Chim. Acta*, **359**, 3111 (2006).
- [33] C.J. Brown, D.S. Cook, L. Sengier. *Acta Crystallogr., Sect. C*, **41**, 718 (1985).
- [34] L. Menabue, M. Saladini. *J. Inorg. Biochem.*, **49**, 201 (1993).
- [35] S. Chang, C. Qin, E.B. Wang, Y.G. Li, X.L. Wang. *Inorg. Chem. Commun.*, **9**, 727 (2006).
- [36] D.H. Li, S.X. Liu, C.Y. Sun, L.H. Xie, E.B. Wang, N.H. Hu, H.Q. Jia. *Inorg. Chem. Commun.*, **8**, 433 (2005).
- [37] E. Coronado, C. Giménez-Saiz, C.J. Gómez-García, S.C. Capelli. *Angew. Chem. Int. Ed.*, **43**, 3022 (2004).
- [38] Q.Z. Zhang, C.Z. Lu, W.B. Yang, C.D. Wu, Y.Q. Yu, Y. Yan, J.H. Liu, H. He. *J. Cluster Sci.*, **14**, 381 (2003).
- [39] J. Liu, Y.G. Li, E.B. Wang, D.G. Xiao, L.L. Fan, Z.M. Zhang, Y. Wang. *J. Mol. Struct.*, **837**, 237 (2007).
- [40] P.M. Smith, The crystal structures of potassium 12-tungstosilicate, and bis(ethylenediamine)ruthenium bis(pentaamine mu-oxoruthenium) (VI) chloride. PhD thesis, Georgetown University (1971); P.M. Smith. *Diss. Abs.* **B32**, 5136 (1972).
- [41] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany (1997).
- [42] G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany (1997).
- [43] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B*, **41**, 244 (1985).
- [44] M. Filowitz, R.K.C. Ho, W.G. Klempner, W. Shun. *Inorg. Chem.*, **18**, 93 (1970).
- [45] M. Sadakane, E. Steckhan. *Chem. Rev.*, **98**, 219 (1998).
- [46] H. Jin, C. Qin, Y.G. Li, E.B. Wang. *Inorg. Chem. Commun.*, **9**, 482 (2006).
- [47] Z.G. Han, Y.L. Zhao, P. Jun, Y.H. Feng, J.N. Yin, Q. Liu. *Electroanalysis*, **17**, 1097 (2002).