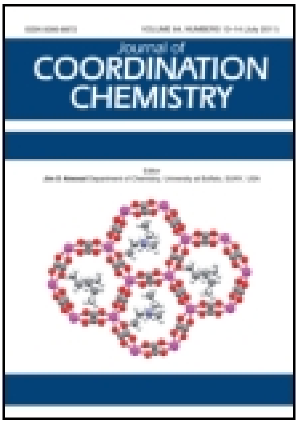
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:28
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

A 3-D inorganic-organic hybrid based on saturated Wells-Dawson polyoxoanion and K^+, linked by an Ag-Ag bond

Yanglei Xu [a], Baibin Zhou [a], Zhanhua Su [a], Kai Yu [a] & Jiang Wu [a]
[a] Key Laboratory of Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province, Harbin Normal University, Harbin 150080, P.R. China

Published online: 04 Nov 2011.

To cite this article: Yanglei Xu, Baibin Zhou, Zhanhua Su, Kai Yu & Jiang Wu (2011) A 3-D inorganic-organic hybrid based on saturated Wells-Dawson polyoxoanion and K^+, linked by an Ag-Ag bond, Journal of Coordination Chemistry, 64:21, 3670-3678, DOI: 10.1080/00958972.2011.629657

To link to this article: http://dx.doi.org/10.1080/00958972.2011.629657

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 &

Journal of Coordination Chemistry
Vol. 64, No. 21, 10 November 2011, 3670–3678

Taylor & Francis
Taylor & Francis Group

A 3-D inorganic–organic hybrid based on saturated Wells–Dawson polyoxoanion and K^+, linked by an Ag–Ag bond

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

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

(*Received 12 August 2011; in final form 14 September 2011*)

A 3-D complex $K_2[Ag_2(biim)_2]_2P_2W_{18}O_{62}$ (biim = biimidazole) (**1**) has been hydrothermally synthesized and characterized by IR, thermogravimetric, and single-crystal X-ray diffraction. Single-crystal X-ray structural analysis reveals that **1** exhibits a 1-D wavelike chain constructed from μ_3-bridging oxygen atoms of $[P_2W_{18}O_{62}]^{6-}$ and $[Ag_2(biim)_2]^{2+}$. The K^+ link to six oxygen atoms of three P_2W_{18} clusters and 12 equatorial terminal oxygen atoms of P_2W_{18} clusters link to six K^+, resulting in a 3-D framework with a relatively short Ag–Ag bond [2.836 Å]. The electrochemical behavior of **1** modified carbon paste electrode (**1**-CPE) has been studied. The results indicate that **1**-CPE has remarkable stability.

Keywords: Hydrothermal synthesis; Ag–Ag bond; Wells–Dawson polyoxometalates; 3-D

1. Introduction

Polyoxometalate (POM)-based hybrids have emerged as a major research area for rational design of new materials due to their intriguing topological structures as well as their extensive theoretical and practical applications in molecular absorption, catalysis, electron-conductance, optical, and magnetic materials [1–12]. Recently, attention has been devoted to frameworks based on POM building blocks and transition metal complexes (TMCs) [13–17]. One promising approach for the design and construction of POM hybrid materials is to build connections between the surface oxygen atoms of POMs and organic ligands or metal coordination compounds; POMs, organic ligands, and transition-metal ions all play important roles in self-assembly processes.

Compared with other classical POMs, such as Anderson- and Keggin-type anions, multidimensional structures based on Wells–Dawson anions are much less common, due to its larger size and high charge [18–25]. Exploration of feasible routes to extended frameworks based on saturated Wells–Dawson POM and transition-metal complex is appealing and challenging.

---

*Corresponding author. Email: zhou_bai_bin@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2011 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.629657

Attention has focused on the Ag complex to extend structural multiplicity and versatility. Few examples based on the Dawson-POM-Ag system have been reported because that free Ag ions are transformed to black Ag_2O or Ag with ease, increasing the synthetic difficulties [26–30]. Two Ag ions form Ag dimers, providing an opportunity to extend the structure. Few POM-based Ag dimers have been reported to date [31]. Hence, Ag ions may be a candidate to modify Wells–Dawson POMs. Composite materials constructed from Wells–Dawson POMs with 3-D network have been rarely reported. It has never been reported that 12 equatorial oxygen atoms of Wells–Dawson POMs connect with $6\,K^+$ forming a 2-D layer. Because of their various structure motifs and numerous surface oxygen atoms, constructing high-connected and high-dimensional TMCs modified Wells–Dawson POMs is still challenging.

Based on previous work, we have investigated the hydrothermal reaction of silver, potassium, biim, and Wells–Dawson POM to synthesize the highly connected new organic–inorganic hybrid compounds [32, 33]. Fortunately, we obtained a new compound $K_2[Ag_2(biim)_2]_2P_2W_{18}O_{62}$ (**1**), which represents the highest coordination number of Wells–Dawson POMs.

2. Experimental

2.1. *Materials and general procedures*

All chemicals were obtained from commercial sources and used without purification. a-$K_6P_2W_{18}O_{62} \cdot 15H_2O$ was prepared according to the literature method and verified by IR spectrum [34]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. K, P, W, and Ag analyses were performed on a PLASMA-SPEC (I) inductively coupled plasma atomic emission spectrometer. IR spectra were obtained on an Alpha Centaurt Fourier transform IR (FT-IR) spectrometer with KBr pellets from 400 to $4000\,cm^{-1}$. Thermogravimetric (TG) analyses (TG) 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 carbon paste electrode (CPE), a platinum wire as the counter electrode, and Ag/AgCl ($3\,mol\,L^{-1}$ KCl) electrode was used as a reference electrode.

2.2. *Synthesis $K_2[Ag_2(biim)_2]_2P_2W_{18}O_{62}$ (1)*

A mixture of a-$K_6P_2W_{18}O_{62} \cdot 15H_2O$ (0.1 mmol, 490 mg), biim (0.8 mmol, 106 mg), $AgNO_3$ (0.8 mmol, 136 mg), NH_4VO_3 (0.1 mmol, 12 mg), and triethylamine (0.1 mmol) was dissolved in 10 mL of distilled water at room temperature. The resulting suspension was stirred for 30 min and pH was adjusted to 2.3 with $2\,mol\,L^{-1}$ HNO_3, then sealed in an 18 mL Telfon-lined reactor and heated at 165°C for 6 days. The autoclave was cooled to room temperature. Yellow block crystals were filtered, washed with water, and dried at room temperature (Yield 60%, based on W). Anal. Calcd for $C_{12}H_8Ag_2KN_8O_{31}PW_9$ (2700.63) (%): C 5.35, Ag 8.02, K 1.43, N 4.17, O 20.68, P 1.16, W 61.46. Elemental analysis: found (%): C 5.35, Ag 8.01, K 1.44, N 4.16, P 1.15, W 61.45.

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

Empirical formula	$Ag_4K_2P_2W_{18}O_{62}C_{24}N_4H_{16}$
Formula weight	2700.63
Temperature (K)	273(2)
Crystal system	Orthorhombic
Space group	*Cmcm*
Unit cell dimensions (Å, °)	
a	21.5464(14)
b	11.8932(8)
c	32.143(2)
α	90.00
β	90.00
γ	90.00
Volume (Å^3), Z	8236.8(9), 8
Absorption coefficient (mm^{-1})	22.870
$F(000)$	9424.0
θ range for data collection (°)	2.33–28.24
Reflections collected	28,798/5318
Collected/unique	[R(int) = 0.0671]
Goodness-of-fit on F^2	1.069
$R_1[I > 2\sigma(I)]$[a]	$R_1 = 0.0346$
wR_2 (all data)[b]	0.0846

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[b] $wR = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$.

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-Kα 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. 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 in "Supplementary material."

2.4. *Preparation of 1 modified CPE (1-CPE)*

1-CPE was prepared as follows: graphite powder (0.3 g) and **1** (0.03 g) were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then nujol (0.2 mL) was added with stirring. The resulting paste was packed into a glass tube (3 mm diameter) and a copper rod was inserted through one end of the tube to make electrical contact, the other end was polished on a sheet of weighing paper.

3. Results and discussion

3.1. *Crystal structure of $K_2[Ag_2(biim)_2]_2P_2W_{18}O_{62}$ (1)*

Single-crystal X-ray diffraction analysis reveals that **1** consists of one $[P_2W_{18}O_{62}]^{6-}$ (simplified as P_2W_{18}) polyanion, two $[Ag_2(biim)_2]^{2+}$, and two K^+ in the asymmetric

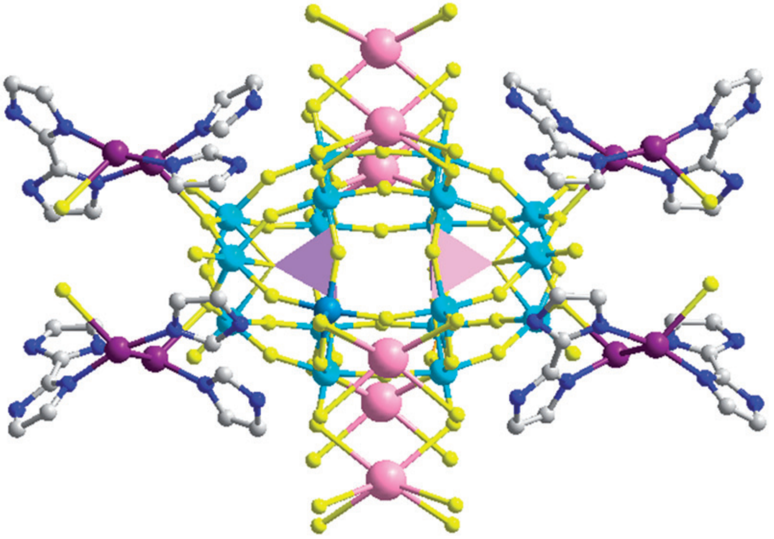


Figure 1. Combined polyhedral and ball-stick representation of the structural unit of **1**.

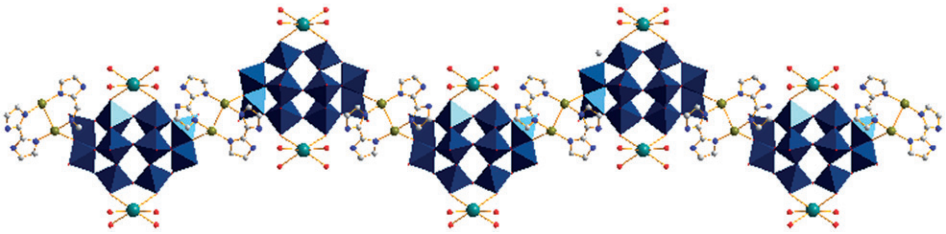


Figure 2. View of the 1-D chain of **1** constructed by POMs and $[Ag_2(biim)_2]^{2+}$.

unit (figure 1). The classical Wells–Dawson polyoxoanion, which is made up of two $[a\text{-}PW_9O_{31}]^{3-}$ units linked through corner-sharing with elimination of six oxygen atoms, contains only two structurally distinct types of tungstens (six polar and 12 equatorial) and has point group symmetry D_{3h}. Bond valence sum calculations indicate that all tungstens are in the +VI oxidation state. All W centers exhibit a $\{WO_6\}$ octahedral environment and W–O distances are 1.687(7)–1.714(7) Å for terminal oxygen atoms, 1.898(7)–1.924(7) Å for μ_2-bridging oxygen atoms and 2.379(6)–2.408(8) Å for μ_3-bridging oxygen atoms, in the normal ranges [35, 36].

Each P_2W_{18} polyanion is an inorganic ligand coordinating to four $[Ag_2(biim)_2]^{2+}$ coordination polymers along the *a*-axis to form a novel 1-D wavy chain (figure 2) and generate big vacancies. The "wave" may be due to bigger steric hindrance and polycyclic aromatic bridging of biim favoring high connectivity of the POMs. A strong metal–metal bond exists between two Ag centers. Ag_2^{2+} dimers are linked, alternately, by biim forming a $[Ag_2(biim)_2]^{2+}$ cationic chain; biim are quadridentate ligands bridging Ag (figure S1). In the dimers, Ag–Ag distance is 2.8358 Å, shorter than the sum

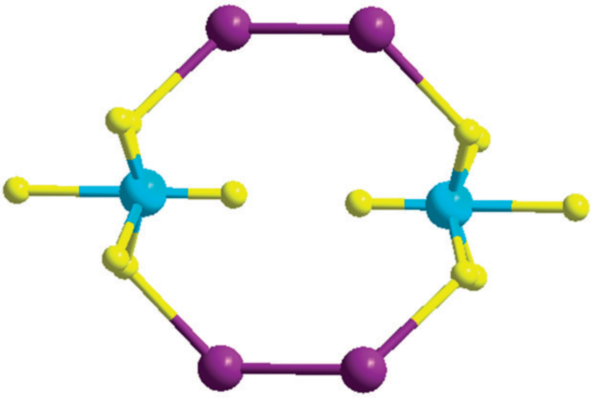


Figure 3. The ball and stick model of a 10-membered ring with four Ag(I) ions, two W(VI) ions, and four oxygen atoms.

of the van der Waals radii of two Ag atoms (3.44 Å), thus an Ag_2^{2+} dimer is formed by these significant Ag(I)–Ag(I) interactions [37, 38]. The complex forms a 10-membered ring with four Ag(I) ions [Ag(1)], two W(VI) [W(2)] ions, and four O(II) [O(3)] ions of POM (figure 3). In the P_2W_{18}/Ag chain, POMs are intercalated by double Ag–Ag bridges and silvers are linked into a –O–Ag–Ag–O– chain *via* Ag–O and Ag–Ag bonds. There are two crystallographically identical silvers, Ag(1) is four-coordinate with two nitrogen atoms [N(1) and N(4)] of two biim molecules and two oxygen atoms [O(3)] of one P_2W_{18} cluster. The bond lengths and angles around Ag are 2.109–2.125 Å for Ag–N and 84.2–92.6° for N–Ag–Ag [39, 40], deviating from the standard lengths (1.85 Å) and ideal angles (90°), due to the existence of Ag(I)–Ag(I) interactions.

In **1**, the 2-D POMs-K layers are fused by $[Ag_2(biim)_2]^{2+}$ dimers along the *a*-axis to form a 3-D framework (figure S2). There is a crystallographically unique potassium (+I), consistent with valence sum calculations and coordination environments. The K^+ are hexadentate covalently linking to six oxygen atoms of three P_2W_{18} clusters, and 12 equatorial terminal oxygen atoms of P_2W_{18} clusters link to six K^+, which result in a 2-D layer (figure 4). The K–O bond lengths are 3.423(11) (K1–O19), 2.866(7) (K1–O18), 2.877(8) (K1–O20), and the angles are 62.2(2) (O(18)–K(1)–O(9)), 71.4(2) (O(18)–K(1)–O(20)), 71.33(19) (O(9)–K(1)–O(20)), respectively. Thus, the 2-D sheets are linked by P_2W_{18} clusters to achieve a 3-D structure (figure 5).

3.2. *IR spectrum*

In the IR spectrum of **1**, four characteristic peaks of POMs 1078 cm^{-1} ascribed to ν(P–Oa), 949 cm^{-1} ascribed to ν(W–Ot), 898 cm^{-11} ascribed to ν(W–Ob–W) and 787 cm^{-1} ascribed to ν(W–Oc–W) [41, 42] show that the title polyoxoanion still retains Dawson-type structure. Characteristic bands at 1420–1620 cm^{-1} can be regarded as features of biim (figure S3).

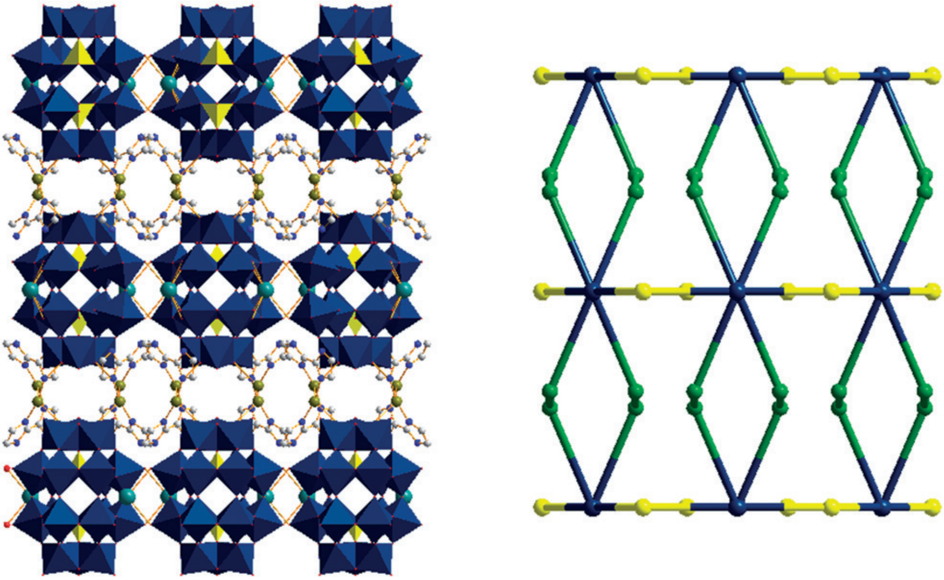


Figure 4. Left: polyhedral and ball-stick representation of the 2-D supramolecular layer in **1**. Right: diagram of 2-D structure (blue: P_2W_{18}, green: Ag, yellow: K).

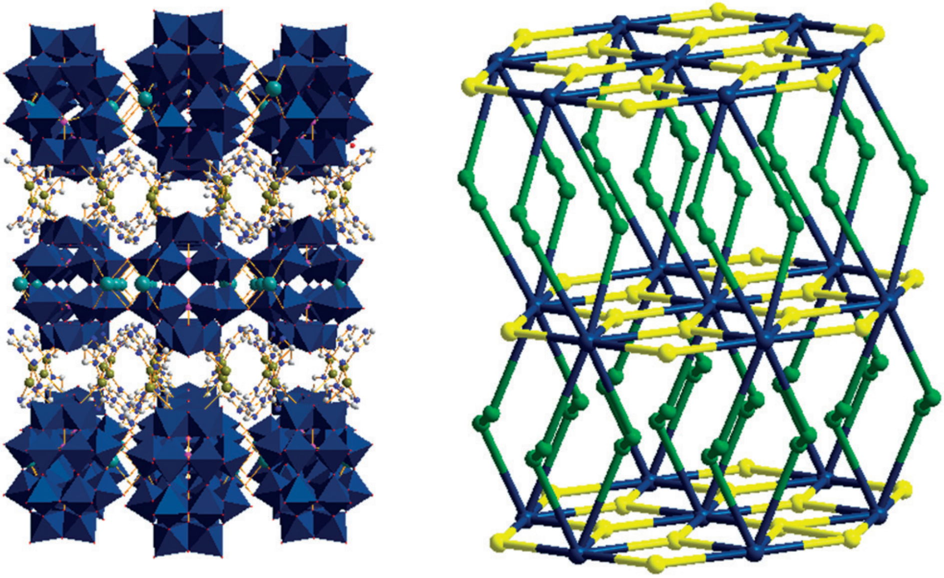


Figure 5. Left: the 3-D framework containing $[Ag_2(biim)_2]^{2+}$ chains and K^+ modifying Wells–Dawson POMs. Right: the diagram of **1** (blue: P_2W_{18}, green: Ag, yellow: K).

3.3. *TG analysis*

The thermal stabilities of **1** were investigated under N_2 from 0°C to 800°C and TG curves are provided in figure S4; **1** shows a one-step weight loss of 13.33% from 280°C

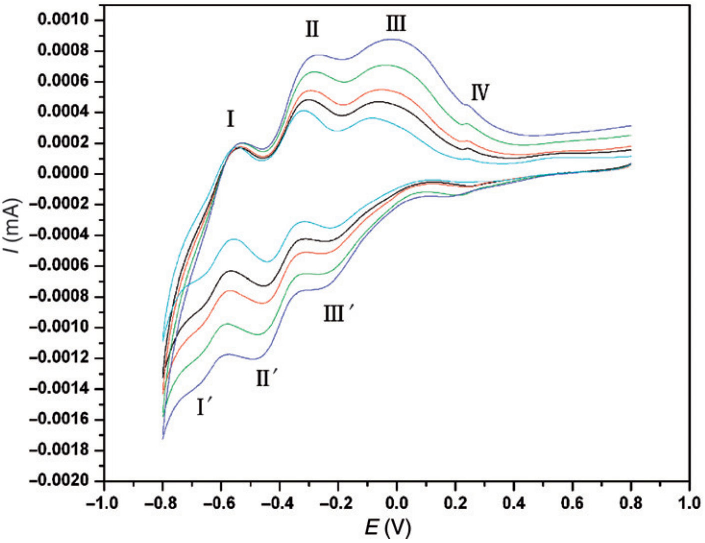


Figure 6. The CVs of **1**-CPE in 1 mol L^{-1} H_2SO_4 at different scan rates (from inner to outer: 20, 60, 100, 140, and 180 mV s^{-1}).

to 800°C ascribed to decomposition of biim, in accord with the calculated value of 13.3%.

3.4. *Voltammetric behavior of 1-CPE*

Electrochemical studies of **1**-CPE were carried out in 1 mol L^{-1} H_2SO_4 at different scan rates. Figure 6 shows the cyclic voltammograms (CVs) of **1**-CPE from −1.0 to 1.0. The fourth irreversible anodic peak corresponds to redox processes of Ag(I) [43]. Three reversible redox waves are obtained with half-wave potentials ($E_{1/2}$) of −183 (III–III′), −404(II–II′), and −613(I–I′)mV (20 mV s^{-1}), where $E_{1/2} = (E_{pc} + E_{pa})/2$; E_{pc} and E_{pa} are the cathodic and anodic peak potentials, respectively. The redox peaks, I–I′, II–II′, and III–III′ correspond to three consecutive two-electron processes of W centers [44]. When the scan rates were varied from 20 to 180 mV s^{-1} for **1**-CPE, the peak potentials change gradually; anodic peak potentials to positive direction and cathodic peak potentials toward the negative direction with increasing scan rates.

4. Conclusion

We have synthesized a complicated 3-D structure based on the saturated Wells–Dawson POM and silver units under hydrothermal conditions. In **1**, the complex forms a 10-membered ring with four Ag(I) ions, two W(VI) ions, and four oxygen atoms of POM. Neighboring anions are further linked by $[Ag_2(biim)_2]^{2+}$ in an unprecedented anionic chain. The synthesis of **1** provides a model for construction of POM-based composite materials.

Supplementary material

CCDC 814569 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 (E-mail: deposit@ccdc.com.ac.uk).

Acknowledgments

This work is supported by the National Natural Science Foundation of China (grant nos 20671026, 20971032), the Study Technological Innovation Project Special Foundation of Harbin (grant no. 2009RFXG202), The Technological innovation team building program of college of Heilongjiang Province (2009td04), and Innovation Team Research Program of Harbin Normal University (KJTD200902).

References

[1] D. Hagrman, C. Zubieta, D.J. Rose, J. Zubieta, R.C. Haushalter. *Angew. Chem., Int. Ed. Engl.*, **36**, 873 (1997).

[2] Y. Xu, J.Q. Xu, K.L. Zhang, Y. Zhang, X.Z. You. *Chem. Commun.*, **2**, 153 (2000).

[3] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer, Berlin (1983).

[4] H.T. Evans Jr. *J. Am. Chem. Soc.*, **70**, 1291 (1948).

[5] C.L. Hill. *Chem. Rev.*, **98**, 1 (1998).

[6] K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi, N. Mizuno. *Angew. Chem. Int. Ed.*, **47**, 2407 (2008).

[7] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).

[8] V. Artero, A. Proust, P. Herson, F. Villain, C. Moulin, P. Gouzerh. *J. Am. Chem. Soc.*, **12**, 11156 (2003).

[9] D.L. Long, H. Abbas, P. Kogerler, L. Cronin. *Angew. Chem. Int. Ed.*, **44**, 3415 (2005).

[10] B.B. Xu, Z.H. Peng, Y.G. Wei, D.R. Powel. *Chem. Commun.*, 2562 (2003).

[11] A. Proust, R. Thouvenot, P. Gouzerh. *Chem. Commun.*, 1837 (2008).

[12] W.L. Liu, H.Q. Tan, W.L. Chen, Y.G. Li, E.B. Wang. *J. Coord. Chem.*, **63**, 1833 (2010).

[13] H.Y. An, E.B. Wang, D.R. Xiao, Y.G. Li, Z.M. Su, L. Xu. *Angew. Chem. Int. Ed.*, **45**, 904 (2006).

[14] H.Y. An, Y.G. Li, E.B. Wang, D.R. Xiao, C.Y. Sun, L. Xu. *Inorg. Chem.*, **44**, 6062 (2005).

[15] K. Yu, B.B. Zhou, Z.H. Su, Y. Yu. *Inorg. Chem. Commun.*, **13**, 1263 (2010).

[16] Y. Chen, B.B. Zhou, J.X. Zhao, Y.G. Li, Z.H. Su, Z.F. Zhao. *Inorg. Chim. Acta*, **363**, 3897 (2010).

[17] Z.F. Zhao, B.B. Zhou, Z.H. Su. *J. Coord. Chem.*, **63**, 776 (2010).

[18] X.L. Wang, Y.G. Li, Y. Lu, H. Fu, Z.M. Su, E.B. Wang. *Cryst. Growth Des.*, **10**, 4227 (2010).

[19] H.X. Yang, S.P. Guo, J. Tao, J.X. Lin, R. Cao. *Cryst. Growth Des.*, **9**, 4735 (2009).

[20] B.Z. Lin, L.W. He, B.H. Xu, X.L. Li, Z. Li, P.D. Liu. *Cryst. Growth Des.*, **9**, 273 (2009).

[21] H.X. Yang, J.X. Lin, J.T. Chen, X.D. Zhu, S.Y. Gao, R. Cao. *Cryst. Growth Des.*, **8**, 2623 (2008).

[22] X.Y. Zhao, D.D. Liang, S.X. Liu, C.Y. Sun, R.G. Cao, C.Y. Gao, Y.H. Ren, Z.M. Su. *Inorg. Chem.*, **47**, 7133 (2008).

[23] R. Belghiche, O. Bechiri, M. Abbessi, S. Golhen, Y.L. Gal, L. Ouahab. *Inorg. Chem.*, **48**, 6026 (2009).

[24] H.Y. An, T.Q. Xu, X. Liu, C.Y. Jia. *J. Coord. Chem.*, **63**, 3028 (2010).

[25] Q. Wu, X. Fu, J.W. Zhao, S.Z. Li, J.P. Wang, J.Y. Niu. *J. Coord. Chem.*, **63**, 1844 (2010).

[26] C. Streb, C. Ritchie, D.L. Long, P. Kogerler, L. Cronin. *Angew. Chem. Int. Ed.*, **46**, 7579 (2007).

[27] Q.G. Zhai, X.Y. Wu, S.M. Chen, Z.G. Zhao, C.Z. Lu. *Inorg. Chem.*, **46**, 5046 (2007).

[28] J.Q. Sha, J. Peng, H.S. Liu, J. Chen, A.X. Tian, P.P. Zhang. *Inorg. Chem.*, **46**, 11183 (2007).

[29] X.F. Kuang, X.Y. Wu, J. Zhang, C.Z. Lu. *Chem. Commun.*, **47**, 4150 (2011).

[30] P.P. Zhang, J. Peng, H.J. Pang, J.Q. Sha, M. Zhu, D.D. Wang, M.G. Liu. *Cryst. Growth Des.*, **11**, 2736 (2011).

[31] C.J. Zhang, H.J. Pang, M.X. Hu, J. Li, Y.G. Chen. *J. Solid State Chem.*, **182**, 1772 (2009).

[32] K. Yu, B.B. Zhou, Y. Yu, Z.H. Su, G.Y. Yang. *Inorg. Chem.*, **50**, 1862 (2011).

[33] H.J. Jin, B.B. Zhou, Y. Yu, Z.F. Zhao, Z.H. Su. *CrystEngComm.*, **13**, 585 (2011).

[34] R. Contant. *Inorganic Syntheses*, Vol. 27, p. 105, Wiley & Sons, New York (1990).
[35] Y. Lu, Y. Xu, Y.G. Li, E.B. Wang, X.X. Xu, Y. Ma. *Inorg. Chem.*, **45**, 2055 (2006).
[36] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B*, **41**, 244 (1985).
[37] F. Hintermaier, S. Mihan, M. Gerdan, V. Schunemann, A. Trautwein, W. Beck. *Chem. Beu.*, **129**, 571 (1996).
[38] H.J. Pang, C.J. Zhang, J. Peng, Y.H. Wang, J.Q. Sha, A.X. Tian, P.P. Zhang, Y. Chen, M. Zhu, Z.M. Su. *Eur. J. Inorg. Chem.*, 5175 (2009).
[39] J.Q. Sha, J. Peng, Y.Q. Lan, Z.M. Su, H.J. Pang, A.X. Tian, P.P. Zhang, M. Zhu. *Inorg. Chem.*, **47**, 5145 (2008).
[40] H.J. Pang, J. Peng, J.Q. Sha, A.X. Tian, P.P. Zhang, Y. Chen, M. Zhu. *J. Mol. Struct.*, **921**, 289 (2009).
[41] H.X. Yang, S.Y. Gao, J.L.B. Xu, J.X. Lin, R. Cao. *Inorg. Chem.*, **49**, 736 (2010).
[42] J.Q. Sha, J. Peng, Y.G. Li, P.P. Zhang, H.J. Pang. *Inorg. Chem. Commun.*, **11**, 907 (2008).
[43] S. Berchmans, R.G. Nirmal, G. Prabaharan, S. Madhu, V. Yegnaraman. *J. Colloid Interface Sci.*, **303**, 604 (2006).
[44] M. Sadakane, E. Streckhan. *Chem. Rev.*, **98**, 219 (1998).