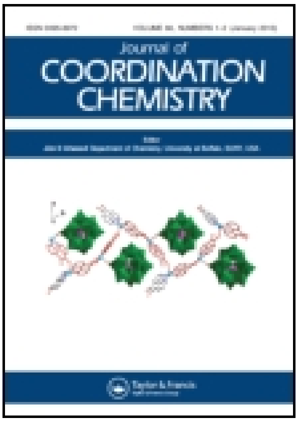
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:53
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

A new $\{P_2W_{18}\}$ polyoxometalate cluster modified with copper complex based on pz, 2,2-bipy, and in situ amino acid

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

Accepted author version posted online: 05 Mar 2013.Published online: 05 Apr 2013.

To cite this article: Yanglei Xu , Kai Yu , Baibin Zhou , Zhanhua Su & Jiang Wu (2013) A new $\{P_2W_{18}\}$ polyoxometalate cluster modified with copper complex based on pz, 2,2-bipy, and in situ amino acid, Journal of Coordination Chemistry, 66:8, 1303-1310, DOI: 10.1080/00958972.2013.781160

To link to this article: http://dx.doi.org/10.1080/00958972.2013.781160

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

Journal of Coordination Chemistry, 2013
Vol. 66, No. 8, 1303–1310, http://dx.doi.org/10.1080/00958972.2013.781160

Taylor & Francis
Taylor & Francis Group

A new $\{P_2W_{18}\}$ polyoxometalate cluster modified with copper complex based on pz, 2,2–bipy, and *in situ* amino acid

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

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

(*Received 5 October 2012; in final form 4 January 2013*)

A new organic–inorganic hybrid compound, $[\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2P_2W_{18}O_{62}]\cdot H_2O$ (bipy = bipyridine, pz = pyrazine, gly = glycine) (**1**), has been hydrothermally synthesized and characterized by elemental analysis, IR, thermal gravimetric, and single- crystal X-ray diffraction. Compound **1** is an infinite one-dimensional (1-D) chain constructed from $[P_2W_{18}O_{62}]^{6-}$ clusters and $\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2^{6+}$ linker exhibiting an alternating-type structure via equatorial terminal oxygens of the polyanion. The 1-D chains are further extended into 2-D layers and 3-D supramolecular network via weak interactions. The copper complex of **1** consists of three ligands, in which an *in situ* glycine from pyrazine precursor was observed. Additionally, the electrochemical and electrocatalytic properties of **1** have been studied.

Keywords: Hydrothermal synthesis; Wells–Dawson polyoxometalates; *In situ* ligand

1. Introduction

Polyoxometalates (POMs) are anionic metal–oxygen clusters with a variety of robust structures, properties and a multitude of potential applications [1–12]. One approach for the construction of POM hybrid materials is to build connections between the surface oxygens of POMs and organic ligands or metal coordination compounds [13–16]. Transition-metal-substituted POMs (TMCs) have received attention. In comparison with Keggin-, Anderson- and Lindquist-type POM clusters, Dawson-type hybrids are relatively few due to its larger size and high charge [17–24], but have been used in preparation of various complexes retaining its structural integrity under hydrothermal conditions. Hence, interesting research is the exploration of feasible synthetic routes to construct an extended framework based on saturated Wells-Dawson polyoxometalate and TMCs. The selection of ligand and transition metal is an important step to construct TMCs POMs. Cu(II) possesses flexible coordination number and favors N and O donors, which make Cu(II) a good candidate in constructing TMCs. However, most copper-based hybrids are mononuclear [25–28]; multinuclear TMCs for modifying POM-based inorganic–organic hybrid compounds are less common [29, 30]. Multinuclear TMC subunits in reported POM-based compounds are usually built from one type of ligand. It is relatively rare that multinuclear

---

*Corresponding author. Email: zhou_bai_bin@163.com

TMCs and mixed ligands are linkers for the construction of POM-based compounds. As an extension of our ongoing effort in the design of POM-templated multinuclear TMCs with mixed–ligands, we select two organonitrogen ligands, 2,2′–bipyridine- and pyrazine. They contain adjacent nitrogens and tend to bridge TM ions forming multinuclear coordination polymers. Moreover, they may generate ligands through dehydrogenative and hydroxylation via *in situ* ligand synthesis under hydrothermal conditions.

In situ ligand synthesis is of interest because it may produce new structures and provide evidence for organic reaction mechanisms [31, 32]. Systematic designs of coordination polymers involving *in situ* ligand syntheses are not common, compared with those with ligands maintaining integrity, especially in modified POMs. Based on the mentioned considerations and previous work [33–36], we have investigated the hydrothermal reaction of copper, pyrazine, 2,2′–bipyridine, and Wells–Dawson polyoxometalate. Here, we prepared $[\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2P_2W_{18}O_6]\cdot H_2O$, which represents the first Wells–Dawson-type chain linked by tetranuclear TMC subunits and mixed–ligands.

2. Experimental

2.1. *Materials and general procedures*

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 [37]. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. P, W, and Cu 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}. Thermal gravimetric analyses were carried out in N_2 on a Perkin–Elmer DTA 1700 differential thermal analyzer with a rate of 10 °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 was the counter electrode and Ag/AgCl (3 M KCl) electrode, was used as a reference electrode.

2.2. *Synthesis of $[\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2P_2W_{18}O_62]\cdot H_2O$*

A mixture of a-$K_6P_2W_{18}O_{62}\cdot 15H_2O$ (0.10 mM, 490 mg), $Cu(NO_3)_2$ (0.99 mM, 180 mg), pz (0.67 mM, 60 mg), and 2,2′–bipy (0.7 mM, 96 mg) was dissolved in 25 mL of distilled water at room temperature. The resulting suspension was stirred for 30 min, then sealed in an 30- mL Teflon-lined reactor and heated at 160 °C for 3 days. The autoclave was cooled to room temperature. Blue black crystals were filtered, washed with water, and dried at room temperature (Yield 60%, based on W). Anal. Calcd for $C_{52}H_{48}Cu_4N_{14}O_{67}P_2W_{18}$ (5566.28): C, 11.21; H, 0.86; N, 3.52; Cu, 4.55; P, 1.11; W, 59.45%. Elemental analysis: found: C, 11.20; H, 0.84; N, 3.55; Cu, 4.56; P, 1.12; W, 59.46%.

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 (λ = 0.71073 Å). The structure

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

Empirical formula	$C_{52}H_{48}Cu_4N_{14}O_{67}P_2W_{18}$
Formula weight	5566.28
Temperature/K	273(2)
Crystal system	Monoclinic
Space group	P n
a (Å)	13.4789(13)
b (Å)	22.551(2)
c (Å)	16.4302(16)
α (°)	90.00
β (°)	104.6120(10)
γ (°)	90.00
V (Å^3)	4832.6(8)
Z	2
μ (mm^{-1})	22.324
F (0 0 0)	4944.0
θ Range (°)	2.39–28.27
Reflections	23,934/5126
Collected/unique	[R(int) = 0.0473]
GOF on F^2	1.030
R_1 ($I > 2\sigma(I)$)[a]	R1 = 0.0525
wR_2 (all data)[b]	0.1159

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

was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 package [38, 39]. All non-hydrogen atoms were refined anisotropically. Hydrogens 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. *Crystal structure of [{Cu$_2$(2,2′–bipy)$_2$(pz)(gly)}$_2$P$_2$W$_{18}$O$_{62}$]·H$_2$O*

Single-crystal X-ray diffraction analysis shows that **1** consists of a mixed ligand cation $\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2^{6+}$, a polyoxoanion $[P_2W_{18}O_{62}]^{6-}$ (simplified as P_2W_{18}) and a lattice water. The basic building unit Wells–Dawson polyoxoanion, which is made up of two $[a\text{-}PW_9O_{31}]^{3-}$ units linked through corner-sharing with elimination of six oxygens, contains only two structurally distinct types of tungsten (6 polar and 12 equatorial) and has the point group symmetry D_{3h}. Bond valence sum calculations indicate that all tungstens are in the + VI oxidation state. All W exhibit a $\{WO_6\}$ octahedral environment and W–O distances are 1.687(16)–1.729(18) Å for terminal oxygens, 1.876(16)–1.987(16) Å for u_2-bridging oxygens and 2.329(16)–2.410(15) Å for u_3-bridging oxygens, in the normal ranges [40, 41]. $\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2^{6+}$ is coordinated by three ligands, 2,2′–bipy, pz and gly, in which the gly was formed *in situ* (figure 1), generated from a POMs-mediated reaction through simultaneous dehydrogenative coupling and hydroxylation of pyrazine (scheme 1).

In $\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2^{6+}$, there are two pairs of crystallographically identical coppers segregated to two pairs of centrosymmetric positions. All coppers are + 2 oxidation

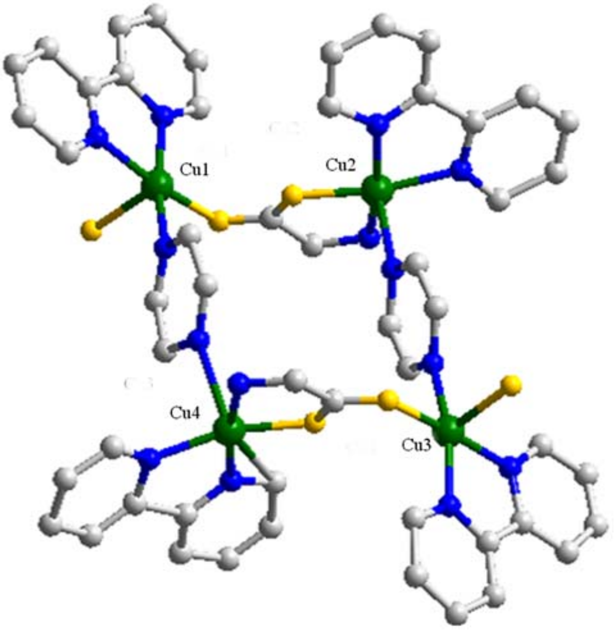
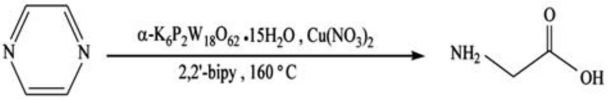


Figure 1. Combined polyhedral and ball-stick representation of the structure unit of $\{Cu_2(2,2'\text{–bipy})_2(pz)(gly)\}_2^{6+}$.



Scheme 1. *In situ* generation of glycine from pyrazine ligands.

state, consistent with valence sum calculations and coordination environments, and each is five-coordinate with square pyramid geometry; Cu1 and Cu3 are five-coordinate with two nitrogens from 2,2′–bipy, an oxygen from glycine, a nitrogen from pyrazine and a terminal oxygen located in the equatorial site of $[P_2W_{18}O_{62}]^{6-}$, while Cu2 and Cu4 are five-coordinate with two N from 2,2′–bipy, a nitrogen from pyrazine and an oxygen and nitrogen from glycine. The Cu–O distances are 1.96(2) – 1.998(14) Å and Cu–N lengths are 1.97(2) – 2.04(2) [42–44]. Glycine, which is synthesized from pyrazine, is formed at central positions linking coppers. In **1**, $\{P_2W_{18}O_{62}\}^{6-}$ polyanions are bidentate connecting two coppers [45] (see figure S1).

The four metal centers are linked by four μ-O, two μ-N and four μ_3-N bridges to form tetranuclear complexes with a quadrate hole composed of four coppers, two pyrazines, and two glycines. The pz and glycine as bridging linkers connect adjacent Cu ions to form a mixedligand $\{Cu_2(pz)(gly)\}_2$ ring.

Each Wells–Dawson cluster is connected to two adjacent copper-organic complexes to form infinite 1-D chains via two Cu–O bonds between equatorial terminal O of polyanion and copper (Cu1–O27 = 2.218(16), Cu3–O54 = 2.293(16)). The tetranuclear complexes are counter-charge ions and also link the Wells-Dawson cluster to form ABAB-type structure (figure 2). Thus, 1-D chains are linked by Cu2 and Cu4 to achieve a 2-D layer. Another

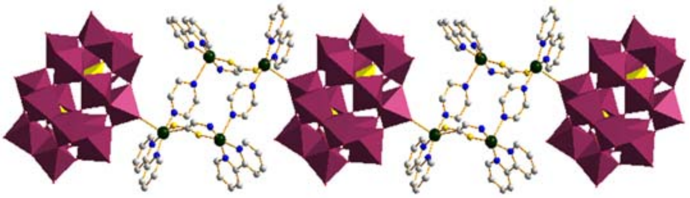


Figure 2. View of the 1D chain of **1** constructed by POMs and $\{Cu_2(2,2'–bipy)_2(pz)(gly)\}_2^{6+}$.

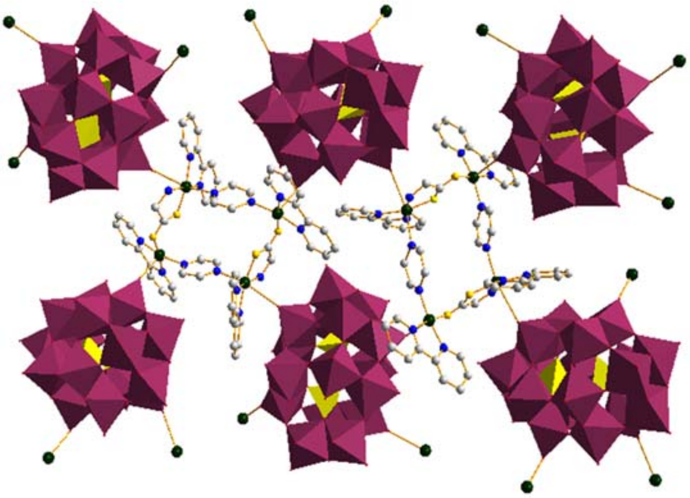


Figure 3. View of the 2D frame of **1**.

remarkable aspect of **1** is that these 2-D layers are further extended by P2W18 via connecting the O(20)/O(46) to form 3-D frames. The distances of these weak interactions are: Cu4…O41 2.854(16) Å, Cu2…O29 2.807(12) Å, O20…O46 3.032 Å (see figure 3) [46–48]. These adjacent 2-D layers and 3-D frames are further supported by supramolecular interactions (see figure S2).

3.2. *IR spectrum*

In the IR spectrum of **1**, there are four characteristic peaks of POMs, 1190 cm^{-1} ascribed to ν(P-Oa), 950 cm^{-1} ascribed to ν(W–Ot), 869 cm^{-1} ascribed to ν(W–Ob–W) and 799 cm^{-1} ascribed to ν(W–Oc–W), showing that the title polyoxoanion still retains Dawson-type structure [49]. Bands from 1459 to 1630 cm^{-1} are characteristic of pyrazine, glycine, and 2,2′–bipy (see figure S3).

3.3. *TG analysis*

Thermal gravimetric curve of **1** is shown in figure S4 with four weight loss processes. The first (0.32%) from 0 to 250 °C is attributed to loss of one lattice water (Calcd: 0.32%).

The second (2.69%) from 250 to 300 °C is in accord with the removal of two glycines (Calcd: 2.70%). The third weight loss (2.88%) from 300 to 500 °C is equivalent to the loss of the two pz (Calcd: 2.89%). The fourth (11.12%) from 500 to 800 °C is attributed to the loss of four 2,2′–bipy (Calcd: 11.22%). The final residual substance is $P_2W_{18}O_{62}$.

3.4. *Voltammetric behavior of 1-CPE*

Compound **1** is insoluble in water and most organic solvents. Thus, **1**-bulk-modified carbon paste electrode (**1**-CPE) was fabricated as the working electrode to study redox properties. The electrochemical studies of **1**-CPE were carried out in 1 M H_2SO_4 at different scan rates. Figure 4 shows the cyclic voltammogram of **1**-CPE from −0.8 to 0.6 V. The fourth oxidation peak (IV) at 210 mV (20 mV s^{-1}) is attributed to redox processes of the Cu(II). Three reversible redox waves are obtained with half-wave potentials ($E_{1/2}$) of −140(III–III′), −360(II–II′), and −600(I–I′) mV (20 mVs^{-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* [50]. When scan rates were varied from 20 to 140 mV s^{-1} for **1**-CPE, the peak potentials change gradually with the corresponding anodic peak potentials to the positive direction and the cathodic peak potentials to the negative direction. Peak-to-peak separations between the corresponding cathodic and anodic peaks increase, but the average peak potentials do not change [51, 52]. The cyclic voltammetry measurements indicate that **1** retains the redox properties of the parent polyanion.

3.5. *Electrocatalytic activity of CPE for reduction of H_2O_2*

Figure S5 shows the cyclic voltammograms of **1**-CPE in 1 M H_2SO_4 aqueous solution in the absence and presence of H_2O_2. With the addition of hydrogen peroxide, for the redox

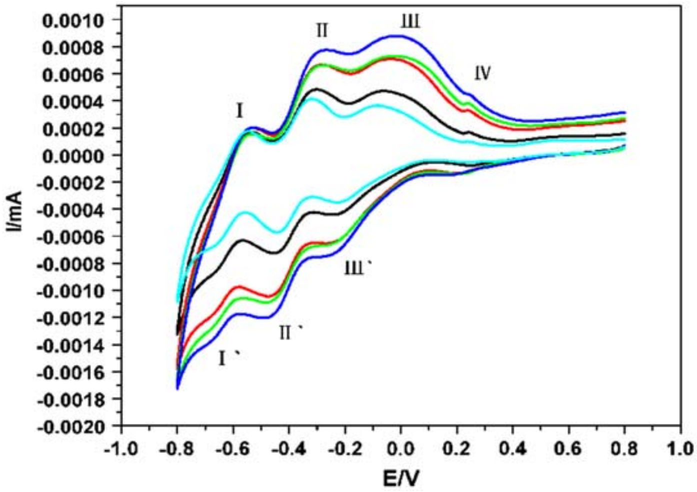


Figure 4. The cyclic voltammograms of **1**-CPE in 1 M H_2SO_4 at different scan rates (from inner to outer: 20, 50, 80, 110 and 140 mV s^{-1}).

couples at −0.52 V, cathodic peak currents increased, while the corresponding anodic peak currents decreased; the other two cathodic peak currents of **1**-CPE redox couple were almost unchanged, suggesting that H_2O_2 is mainly reduced by the six-electron-reduced species of P_2W_{18} polyanion [53–55]. **1**-CPEs exhibit electrocatalytic activity toward the reduction of H_2O_2.

4. Conclusions

We have synthesized a 1-D chain based on saturated Wells–Dawson POMs and tetranuclear copper units under hydrothermal conditions. Compound **1** represents the first Wells–Dawson-type chain linked by tetranuclear TMC subunits with mixed ligands. The copper complex consists of three ligands and has a quadrate hole with Cu, pyrazine, and glycine. Electrochemical analysis shows that **1**-CPE displays good electrocatalytic activity to reduce hydrogen peroxide. The synthesis of **1** may provide a new model for the construction of POM-based TMCs.

Supplementary material

CCDC 830810 contains the Supplementary material.doc 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.cam.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] 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] T. Howard, J. Evans. *Chem. Rev.*, **70**, 1291 (1984).
[5] K. Kamata, S. Yamaguchi, M. Kotani, K. Yamaguchi, N. Mizuno. *Angew. Chem., Int. Ed.*, **47**, 2407 (2008).
[6] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).
[7] A. Müller, S. Roy. *Coord. Chem. Rev.*, **245**, 153 (2003).
[8] T. Yamase, K. Fukaya, H. Nojiri, Y. Ohshima. *Inorg. Chem.*, **45**, 7698 (2006).
[9] V. Artero, A. Proust, P. Herson, F. Villain, C. Moulin, P. Gouzerh. *J. Am. Chem. Soc.*, **125**, 11156 (2003).
[10] D.L. Long, H. Abbas, P. Kogerler, L. Cronin. *Angew. Chem., Int. Ed.*, **44**, 3415 (2005).
[11] B.B. Xu, Z.H. Peng, Y.G. Wei, D.R. Powel. *Chem. Commun.*, 2562 (2003).
[12] A. Proust, R. Thouvenot, P. Gouzerh. *Chem. Commun.*, **44**, 1837 (2008).
[13] P.J. Hagrman, J. Zubieta. *Inorg. Chem.*, **39**, 3252 (2000).
[14] M.I. Khan, E. Yohannes, R.J. Doedens. *Angew. Chem. Int. Ed. Engl.*, **38**, 1292 (1999).
[15] H.Y. An, Y.G. Li, E.B. Wang, D.R. Xiao, C.Y. Sun, L. Xu. *Inorg. Chem.*, **44**, 6062 (2005).
[16] H.X. Yang, S.P. Guo, J. Tao, J.X. Lin, R. Cao. *Cryst. Growth Des.*, **9**, 4735 (2009).
[17] B.Z. Lin, L.W. He, B.H. Xu, X.L. Li, Z. Li, P.D. Liu. *Cryst. Growth Des.*, **9**, 273 (2009).

[18] 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).
[19] H.X. Yang, S.Y. Gao, J. Lu, B. Xu, J.X. Lin, R. Cao. *Inorg. Chem.*, **49**, 736 (2010).
[20] X.L. Wang, H.L. Hu, A.X. Tian, H.Y. Lin, J. Li. *Inorg. Chem.*, **49**, 10299 (2010).
[21] X.F. Kuang, X.Y. Wu, J. Zhang, C.Z. Lu. *Chem. Commun.*, **47**, 4150 (2011).
[22] X.L. Wang, Y.G. Li, Y. Lu, H. Fu, Z.M. Su, E.B. Wang. *Cryst. Growth Des.*, **10**, 4227 (2010).
[23] C. Liang, Y. Lu, H. Fu, W.L. Chen, E.B. Wang. *J. Coord. Chem.*, **65**, 3254 (2012).
[24] Y.L. Xu, B.B. Zhou, Z.H. Su, K. Yu, J. Wu. *J. Coord. Chem.*, **64**, 3670 (2011).
[25] H.J. Pang, J. Peng, C.J. Zhang, Y.G. Li, P.P. Zhang, H.Y. Ma, Z.M. Su. *Chem. Commun.*, **46**, 5097 (2010).
[26] H.X. Yang, T.F. Liu, M.N. Cao, H.F. Li, S.Y. Gao, R. Cao. *Chem. Commun.*, **46**, 2429 (2010).
[27] J.P. Zhang, X.M. Chen. *Chem. Commun.*, **42**, 1689 (2006).
[28] Z.M. Zhang, Y.G. Li, Y.H. Wang, Y.F. Qi, E.B. Wang. *Inorg. Chem.*, **47**, 7615 (2008).
[29] X.L. Wang, C. Qin, E.B. Wang, Z.M. Su, Y.G. Li, L. Xu. *Angew. Chem. Int. Ed.*, **45**, 7411 (2006).
[30] C.Y. Sun, S.X. Liu, D.D. Liang, K.Z. Shao, Y.H. Ren, Z.M. Su. *J. Am. Chem. Soc.*, **131**, 1883 (2009).
[31] X.L. Wang, Q. Gao, G.C. Liu, H.Y. Lin, A.X. Tian, J. Li. *Inorg. Chem. Commun.*, **14**, 745 (2011).
[32] J.X. Meng, X.L. Wang, E.B. Wang, Y.G. Li, C. Qin, X.X. Xu. *Inorg. Chim. Acta*, **361**, 2447 (2008).
[33] K. Yu, B.B. Zhou, Z.H. Su, Y. Inorg. *Chem. Commun.*, **13**, 1263 (2010).
[34] Y. Chen, B.B. Zhou, J.X. Zhao, Y.G. Li, Z.H. Su, Z.F. Zhao. *Inorg. Chim. Acta*, **363**, 3897 (2010).
[35] K. Yu, B.B. Zhou, Y. Yu, Z.H. Su, G.Y. Yang. *Inorg. Chem.*, **50**, 1862 (2011).
[36] H.J. Jin, B.B. Zhou, Y. Yu, Z.F. Zhao, Z.H. Su. *Cryst. Eng. Commun.*, **13**, 585 (2011).
[37] R.G. Finke, M.W. Droege, P.J. Domaille. *Inorg. Chem.*, **26**, 3886 (1987).
[38] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen (1997).
[39] G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen (1997).
[40] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B: Struct. Sci.*, **41**, 244 (1985).
[41] Y. Lu, Y. Xu, Y.G. Li, E.B. Wang, X.X. Xu, Y. Ma. *Inorg. Chem.*, **45**, 2055 (2006).
[42] F. Hintermaier, S. Mihan, M. Gerdan, V. Schunemann, A. Trautwein, W. Beck. *Chem. Ber.*, **129**, 571 (1996).
[43] L. Hou, W.J. Shi, Y.Y. Wang, B. Liu, W.H. Huang, Q.Z. Shi. *Cryst. Growth Des.*, **12**, 4365 (2010).
[44] S.T. Zheng, G.Y. Yang. *Dalton Trans.*, **39**, 700 (2010).
[45] S.Z. Li, P.T. Ma, J.P. Wang, Y.Y. Guo, H.Z. Niu, J.W. Zhao, J.Y. Niu. *Cryst. Eng. Commun.*, **12**, 1718 (2010).
[46] H. Fu, Y.G. Li, Y. Lu, W.L. Chen, Q. Wu, J.X. Meng, X.L. Wang, Z.M. Zhang, E.B. Wang. *Cryst. Growth Des.*, **11**, 458 (2011).
[47] H.X. Yang, X. Lin, B. Xu, Y.L.J. You, M.N. Cao, S.Y. Gao, R. Cao. *J. Mol. Struct.*, **966**, 33 (2010).
[48] X.L. Wang, Y. Lu, J.X. Meng, E.B. Wang, H. Fu. *Transition Met. Chem.*, **36**, 201 (2011).
[49] F. Yu, Y.X. Long, Y.P. Ren, X.J. Kong, L.S. Long, R.B. Huang, L.S. Zheng. *Dalton Trans.*, **39**, 7588 (2010).
[50] 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).
[51] J.Q. Sha, C. Wang, J. Peng, J. Chen, A.X. Tian, P.P. Zhang. *Inorg. Chem. Commun.*, **10**, 1132 (2007).
[52] J.Q. Sha, L.Y. Liang, Z.W. Yang, C. Wang, Y.L. Qu, Y.G. Lv. *Inorg. Chem. Commun.*, **13**, 840 (2010).
[53] A. Mahmoud, B. Keita, L. Nadjo, O. Oung, R. Contant, S. Brown, Y. DeKouchkovsky. *J. Electroanal. Chem.*, **463**, 129 (1999).
[54] B. Keita, A. Belhouari, L. Nadjo, R. Contant. *J. Electroanal. Chem.*, **381**, 243 (1995).
[55] X.D. Xi, S.J. Dong. *J. Mol. Catal. A: Chem.*, **14**, 257 (1996).