A Novel Keggin Tungstocobaltate Framework Supported by Copperbipyridyl Complexes: $[Cu(I)(2,2'\text{-bipy})_2]\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\} \cdot 4H_2O$

Jingquan Sha[a], Li Xin[a], Baibin Zhou[b], Decheng Yu[a], Youle Qu[a,c], Shuxian Li[a],
and Fenghua Liu[a]

[a] The Provincial Key Laboratory of Biomaterials and Biological Medicine Formulation, School of Pharmacy, Jiamusi University, Jiamusi, 154007, P. R. China
[b] Department of Chemistry, Harbin Normal University, Harbin, 150025, P. R. China
[c] Zhejiang Ocean University, ZhouShan, 316004, P. R. China

Reprint requests to Dr. Jingquan Sha. E-mail: shajq2002@126.com

Z. Naturforsch. **2010**, *65b*, 1445 – 1450; received June 20, 2010

A new organic-inorganic hybrid compound based on Keggin tungstocobaltate units supported by copper complexes, $[Cu(I)(2,2'\text{-bipy})_2]\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\} \cdot 4H_2O$ (bipy = bipyridine), has been synthesized under hydrothermal conditions and characterized by elemental, IR, TG, and XPS analyses and X-ray single-crystal structure determination. The crystal structure is built up from bi-supported Keggin tungstocobaltate polyoxoanions $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}^-$, $[Cu(I)(2,2'\text{-bipy})_2]^+$ cations and water molecules. The title compound possesses a 1D tangled helical structure composed of $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}^-$ polyoxoanions *via* $\pi \cdots \pi$ interactions along the *c* axis. The electrochemical behavior of the title compound was studied.

Key words: Polyoxometalates, Tungstocobaltate, Copper Coordination Group, Electrochemistry

Introduction

Polyoxometalates (POMs), a well-known class of metal-oxygen clusters with an unmatched structural variety associated with a multitude of properties, have been attracting extensive interest in solid-state materials chemistry [1 – 16]. The decoration of POMs with transition metal complex moieties and/or various organic groups provides a powerful method for structural modification and for the synthesis of novel organic-inorganic hybrid materials that combine the features and properties of both subunits. So recently, much work has been carried out on the synthesis of novel organic-inorganic hybrids based on POMs. Due to Keggin POMs' unique structure and properties, a large number of systems covalently modified by transition metal complexes could also be presented. However, in the vast amount of reported work so far, few examples have involved transition metals as heteroatoms [17 – 20]. So the synthesis of hybrids based on Keggin POMs with transition metals as heteroatoms is a significant and formidable challenge.

Currently, hydrothermal techniques have proved to be invaluable for the synthesis of almost all kinds of important materials, in particular materials based on POMs with transition metals as heteroatoms. We have been focusing on the modification of POMs by metal-organic coordination polymers recently, and have empirically synthesized a dozen of TM cation-modified POMs [21 – 25]. During this study, our group reported six compounds based on Keggin POMs with transition metals as heteroatoms [26, 27], which suggested that surface activation could be achieved by replacing the metal centers with high oxidation state by those in a low oxidation state, *i. e.* Si/P→Co/Zn/Cu. As a part of our recent research work on the multi-grafting modification of POMs, we attempted to explore solid materials based on POMs with transition metals as heteroatoms.

On the basis of the above considerations, and to enrich the modifying chemistry of Keggin POMs, we synthesized a new organic-inorganic hybrid based on Keggin POMs with cobalt as heteroatom, $[Cu(I)(2,2'\text{-bipy})_2]\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}$, in which a Keggin tungstocobaltate polyanion is supported by two $[Cu(II)(2,2'\text{-bipy})_2]^{2+}$ coordination complexes. The electrochemical behavior of the title compound is presented.

0932–0776 / 10 / 1200–1445 \$ 06.00

Results and Discussion

Crystal structure of the title compound

The title compound (Fig. 1) consists of one $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}$ polyoxoanion, one $[Cu(I)(2,2'\text{-bipy})_2]$ coordination cation and four water molecules. Similar to other Keggin polyoxoanions, the parent $[HCoW_{12}O_{40}]^{5-}$ anion includes a CoO_4 tetrahedron surrounded by 12 WO_6 octahedra which are grouped into four $\{W_3O_{13}\}$ triads in edge-sharing mode. As usual, oxygen atoms in the polyoxoanion are divided into four groups according to the different coordination environments: O_t (terminal oxygen atoms connecting to one W atom), O_b (oxygen atoms located in shared corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge-sharing WO_6 octahedra in the W_3O_{13} unit) and O_a (oxygen atoms connecting the center Co and W atoms of a W_3O_{13} unit). The Co–O distances are in the range of 1.677(10) – 1.700(10) Å with an average bond length of 1.688(10) Å, while the O–Co–O angles vary from 109.0(5) to 110.5(5)° which are consistent with those reported in the literature [28]. Relevant W–O bonds can be classified into three groups, W–O_t bonds, W–$O_{b/c}$ bonds and W–O_a bonds, and fall in the ranges of 1.662(13) – 1.727(11), 1.879(10) – 1.991(9) and 2.285(10) – 2.357(10) Å, respectively. Comparing the W–O bonds with those of the potassium salt $K_5[HCoW_{12}O_{40}]$ [29], the W–O_t and W–$O_{b/c}$ lengths of the title compound show a certain decrease, and the mean W–O_a distances obviously an increase. Using an empirical formula of bond valence sum calculation (BVS) [3], $S = \exp[\sum -(R-R_o)/B]$ (S = bond valence, R = bond length; R_o and B are empirically determined element-specific parameters [30]), the +2 oxidation state of the cobalt atoms and the +6 oxidation state of the W atoms are deduced, while Cu(1) are in the +1 oxidation state, and Cu(2) and Cu(3) are in the +2 oxidation state, which confirms the molecular formula of the title compound. Combining the results of elemental analysis, bond valence sum calculations, coordination geometries and charge balance, the title compound is formulated as $[Cu(I)(2,2'\text{-bipy})_2]$ $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O40]\}$.

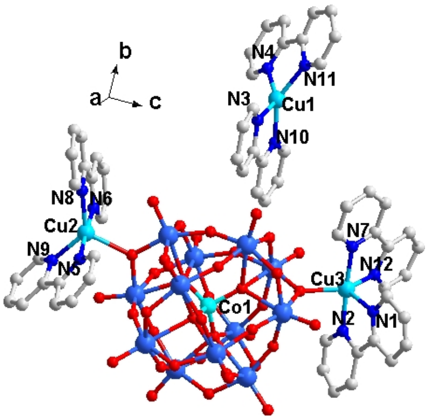

Fig. 1. Fundamental building block of the title compound. Only parts of atoms are labeled, and water molecules and all hydrogen atoms are omitted for clarity.

Note that the tungstocobaltate polyoxoanion acts as a bidentate ligand covalently bonded to two $[Cu(bipy)_2]^{2+}$ coordination subunits through bridging oxygen atoms with Cu–O distances of 2.088(11) Å. In the grafted $[Cu(bipy)_2]^{2+}$coordination unit, the Cu(2) and Cu(3) atoms are coordinated by four N atoms of two bipy ligands and one bridging oxygen atom of the Keggin anion, forming a tetragonal pyramid with Cu–N distances in the range 1.953(15) – 2.035(14) Å.

Previous investigations have shown that electron-withdrawing substituents or heteroatoms lead to a strong $\pi \cdots \pi$ interaction of arenes [31]. Aromatic nitrogen heterocycles as, *e. g.*, pyridine and bipyridines are known as electron-poor ring systems as a result of the electron-withdrawing nitrogen atoms. Nitrogen heterocycles should in principle be well suited for $\pi \cdots \pi$ interactions because of their low π-electron density, so there should be extensive $\pi \cdots \pi$ interactions in the title compound. As shown in Fig. 2, the $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}$ subunits are linked together *via* $\pi \cdots \pi$ interactions (C43···C51 =

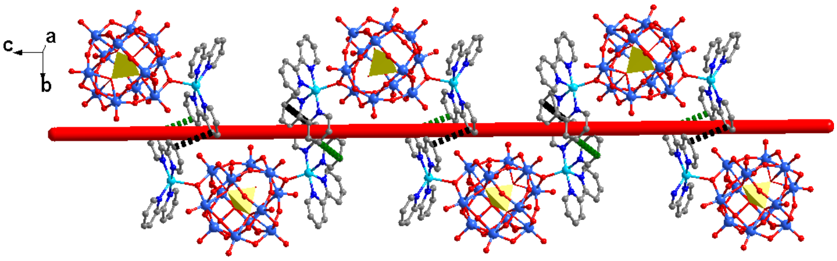

Fig. 2. Detail of the tangled helical chain structure of the title compound (all H atoms and isolated cations $[Cu(bipy)_2]^{2+}$ are omitted).

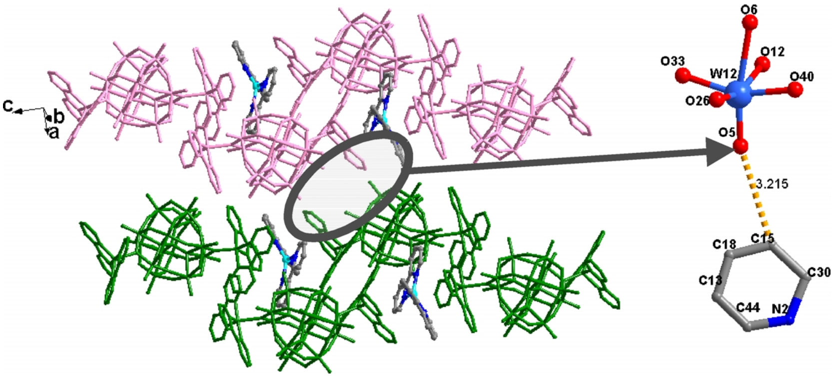

Fig. 3. Layer of the title compound formed *via* secondary interactions.

3.3619; C19$\cdots$C34 = 3.3871 Å) to from a tangled helical chain along the *c* axis.

In the solid-state structure of the title compound, additional interactions play a role to stabilize the whole structure. As shown in Fig. 3, neighboring helical chains are extended to layers *via* interactions like O5$\cdots$C15 = 3.215 Å. Furthermore, the isolated $[\mathrm{Cu(bipy)_2}]^+$ cations and water molecules fix the layers together to form a 3D supramolecular structure *via* secondary interactions.

IR spectrum, TG analysis and XPS

As shown in Fig. 4, the IR spectrum of the title compound exhibits the characteristic bands of a Keggin $[\mathrm{HCoW_{12}O_{40}}]^{5-}$ structure at 960, 889, 779, and 458 cm^{-1} attributed to ν(W-O$_t$), ν(W-O$_b$), ν(W-O$_c$), and δ(Co-O), respectively. The bands in the range 1600 – 1380 cm^{-1} are attributed to the stretching vibrations of C=N and C–N bonds. In order to characterize the compound more extensively in terms of thermal stability, its thermal behavior was studied by TG-DSC. The TG curve of the title compound is shown in Fig. 5. It exhibits three continuous weight loss stages in the range of 3 – 800 °C, corresponding to the release of water and coordinated bipy molecules, which are followed by one weak exothermic peak at 400 °C and one

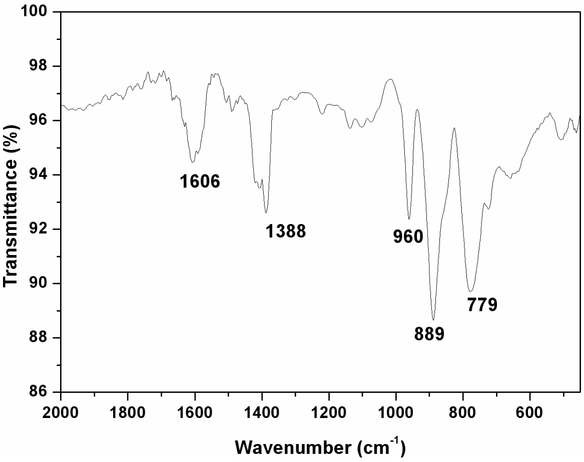

Fig. 4. IR spectrum of the title compound.

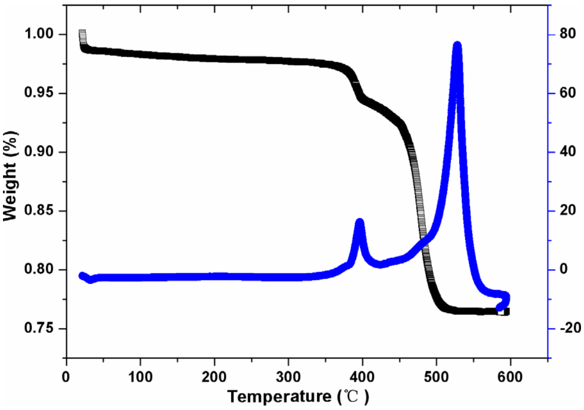

Fig. 5. TG-DSC curve of the title compound.

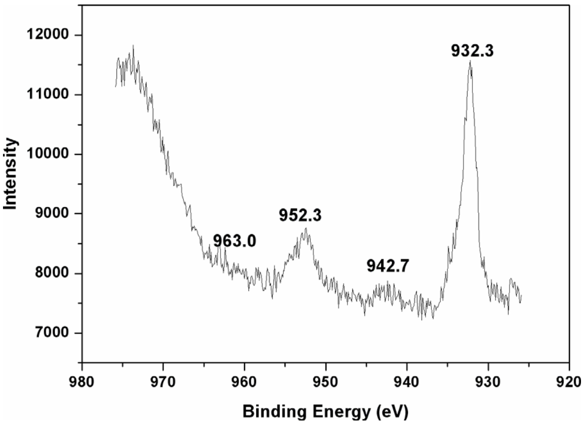

Fig. 6. XPS of Cu ions of the title compound.

strong exothermic peak at 530 °C in the DSC curve. The whole weight loss (24.5 %) is in good agreement with the calculated value (24.6 %). In order to confirm the oxidation state of the Cu atoms, XPS measurements were carried out (Fig. 6) The XPS spectrum exhibits two peaks at 932.25 and 952.34 eV, attributed to $Cu^{+}{}_{2p3/2}$ and $Cu^{+}{}_{2p5/2}$ [32], and peaks at 942.69 and 962.98 eV indicating the prescence of Cu(II) ion, which is consistent with the coordination geometries of the Cu ions and the charge balance of the compound.

Cyclic voltammetry

To study the redox properties of the title compound, we used it as a modifier to fabricate a chemically modified carbon paste electrode (**1**-*CPE*) using its insolubility in water and most organic solvents. The cyclic voltammetry (CV) of **1**-*CPE* was measured in the potential range from +1200 to −1200 mV in aqueous H_2SO_4 solution at different scan rates, as shown in Fig. 7. In the potential range, five quasi-reversible redox peaks appear, and the mean peak potentials $E_{1/2} = (Epc + Epa)/2$ are –513, –747, –1079, 182, and +856 mV, respectively. The redox peaks I-I′, II-II′ and III-III′ can be ascribed to three consecutive redox process of the tungsten atoms, and the redox peak IV-IV′ to the one-electron redox process of Co^{3+}/Co^{2+}, while the redox peak V-V′ is due to the one-electron redox process of Cu^{2+}/Cu^{+} . With the scan rate varying from 50 to 200 mV s^{-1} all peak potentials change gradually: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials to the positive direction. The peak-to-peak separation between the corresponding cathodic and anodic peaks increases with increasing scan rate, but the mean peak potentials do not change on the whole.

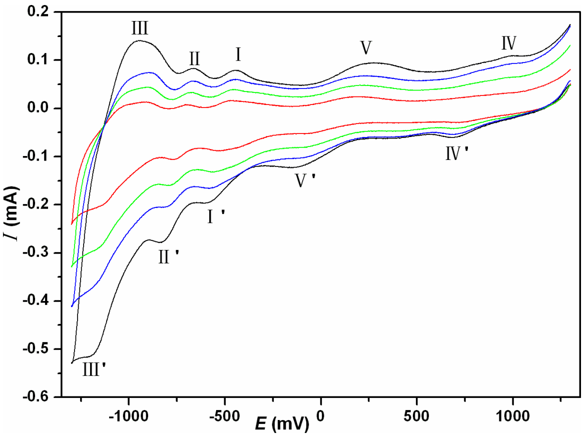

Fig. 7. The cyclic voltammograms for **1**-CPE in aqueous H_2SO_4 solution at different scan rates (from inner to outer: 50, 100, 150, 200 mV s^{-1}).

Conclusions

In summary, a new compound based on a saturated Keggin tungstocobaltate has been synthesized and characterized by routine methods. The title compound possesses a 1D tangled helical structure constructed by $\{[Cu(II)(2,2'\text{-bipy})_2]_2[HCoW_{12}O_{40}]\}^{-}$ polyoxoanions aligned *via* $\pi\cdots\pi$ interactions along the *c* axis. Although a vast amount of Keggin POMs covalently modified by transition metal complexes have been reported in recent years, few of their heteroatoms are transition metals so far. So the title compound is a good example of targeted syntheses of organic-inorganic hybrids based on POMs with transition metals as heteroatoms by the hydrothermal technique. The successful isolation of the novel compound shows perspective of extending the POM family through a reasonable choice of the POM clusters and selecting suitable second metals and organic ligands.

Experimental Section

General procedures

All reagents were purchased and used without further purification. $K_5[HCoW_{12}O_{40}]\cdot 16H_2O$ was synthesized according to the literature [29] and identified by its IR spectrum. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Cu was determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellets in the 400 – 4000 cm^{-1} region. The TG-DSC analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. XPS analyses were performed on a VG Escalab MkII spectrometer with a non-monochromatized MgK_{α} (1253.6 eV) X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at r. t. Platinum gauze was used as a counter electrode and an Ag/AgCl electrode as a reference. Chemically bulk-modified carbon paste electrodes were used as working electrodes.

Preparation of $[Cu(I)(2,2'\text{-bipy})_2]$ $\{[Cu(II)(2,2'\text{-bipy})_2]_2$-$[HCoW_{12}O_{40}]\}$

The title compound was prepared by the hydrothermal method from a mixture of $K_5[HCoW_{12}O_{40}]\cdot 16H_2O$ (0.10 mmol), $Cu(NO_3)\cdot 6H_2O$ (0.20 mmol) 2,2′-bipy

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

Empirical formula	$C_{60}H_{57}CoCu_3N_{12}O_{44}W_{12}$
M_r	4105.93
Crystal color, habit	black, block
Crystal size, mm^3	0.16 × 0.18 × 0.25
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	18.8756(11)
b, Å	20.4471(12)
c, Å	21.7845(13)
β, deg	96.8100(10)
V, Å^3	8348.4(9)
Z	4
D_{calcd}, g cm^{-3}	3.26
μ(MoK_α), cm^{-1}	25.4
F(000), e	5102
θ range data collection, deg	1.37 – 28.32
hkl range	±25, −25/+26, −29/+16
Completeness to θ = 28.32°, %	93.8
Refl. measd / unique / R_{int}	50866 / 19515 / 0.064
$R1^a$ / $wR2^b$ [$I \geq 2\,\sigma\,(I)$]	0.0543 / 0.1303
$R1^a$ / $wR2^b$ (all data)	0.1090 / 0.1544
GoF^c (F^2)	0.998
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	2.07 / −3.7

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0)+2F_c^2)/3$ and A and B are constants adjusted by the program; [c] GoF = $S = [\Sigma w(F_o^2 - F_c^2)^2/(n_{\text{obs}} - n_{\text{param}})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

(0.20 mmol), NH_4VO_3 (0.20 mmol), triethylamine (0.20 mmol), and H_2O (0.40 mol). The resulting suspension was stirred for 1 h, its pH being adjusted to 4.6 with 1 mol L^{-1} NaOH, then sealed in an 18 mL Telfon-lined reactor with 65 % filling, and heated at 170 °C for 6 d. After slow cooling to r. t. over a period of 16 h, black block-shaped crystals were filtered, washed with water, and dried at r. t. Yield: 0.065 g (*ca.* 24 % based on Cu). – Elemental analysis $C_{60}H_{57}CoCu_3N_{12}O_{44}W_{12}$ (4105.9): calcd. C 17.54, H 1.38, N 4.09, Cu 4.67; found C 17.58, H 1.42, N 4.11, Cu 4.68.

*Preparation of **1**-CPE*

100 mg graphite powder and *ca.* 20 mg of the sample were mixed and ground together by agate mortar and pestle to achieve an even, dry mixture. To the mixture 0.2 mL Nujol was added and the paste stirred with a glass rod. Then the homogenized mixture was used to pack 3 mm inner diameter glass tubes, and the surface was wiped with weighing paper. Electrical contact was established with a copper rod through the back of the electrode.

X-Ray crystallography

Crystal data for the title compound were collected on a Rigaku R-axis Rapid IP diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293 K. The structure was solved by Direct Methods and refined by full-matrix least squares on F^2 using the SHELX crystallographic software package [33]. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms at carbon atoms were calculated in idealized positions. The crystal data and parameters pertinent to data collection and structure refinement are summarized in Table 1.

CCDC 714329 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

This work was financially supported by the National Natural Science Foundation (Grant Nos. 20901031 and 20971032), the Natural Science Foundation (No. B200916) and the Education Ministry Key Teachers Foundation (1155G53) of Heilongjiang Province, and the Talent Training Fund of Jiamusi University (No. RC2009-034).

[1] E. Coronado, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, S. Triki, *J. Am. Chem. Soc.* **1998**, *120*, 4671.

[2] K. C. Kin, M. T. Pope, *J. Am. Chem. Soc.* **1999**, *121*, 8512.

[3] M. Sadakane, M. H. Dickman, M. T. Pope, *Angew. Chem.* **2000**, *112*, 3036; *Angew. Chem. Int. Ed.* **2000**, *39*, 2914.

[4] N. Honma, K. Kusaka, T. Ozeki, *Chem. Commun.* **2000**, 2896.

[5] J. Lü, E. H. Shen, M. Yuan, Y. G. Li, E. B. Wang, C. W. Hu, L. Xu, J. Peng, *Inorg. Chem.* **2003**, *42*, 6956.

[6] S. L. Zheng, J. H. Yang, X. L. Yu, X. M. Chen, W. T. Wong, *Inorg. Chem.* **2004**, *43*, 830.

[7] X. K. Fang, T. M. Anderson, C. L. Hill, *Angew. Chem.* **2005**, *117*, 3606; *Angew. Chem. Int. Ed.* **2005**, *44*, 3540.

[8] Q. Li, Y. G. Wei, J. Hao, Y. L. Zhu, L. S. Wang, *J. Am. Chem. Soc.* **2007**, *129*, 5810.

[9] C. Boglio, K. Micoine, E. Derat, R. Thouvenot, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, *J. Am. Chem. Soc.* **2008**, *130*, 4553.

[10] G. G. Gao, F. Y. Li, L. Xu, X. Z. Liu, Y. Y. Yang, *J. Am. Chem. Soc.* **2008**, *130*, 10838.

[11] H. Y. An, E. B. Wang, D. R. Xiao, Y. G. Li, Z. M. Su, L. Xu, *Angew. Chem.* **2006**, *118*, 37; *Angew. Chem. Int. Ed.* **2006**, *45*, 904.

[12] Z. M. Zhang, Y. G. Li, S. Yao, E. B. Wang, Y. H. Wang,

R. Clérac, *Angew. Chem.* **2009**, *121*, 1; *Angew. Chem. Int. Ed.* **2009**, *121*, 1609.

[13] J. Zhang, Y. F. Song, L. Cronin, T. B. Liu, *J. Am. Chem. Soc.* **2008**, *130*, 14408.

[14] S. T. Zheng, J. Zhang, G. Y. Yang, *Angew. Chem.* **2008**, *120*, 3973; *Angew. Chem. Int. Ed.* **2008**, *47*, 3909.

[15] C. D. Zhang, S. X. Liu, C. Y. Sun, F. J. Ma, Z. M. Su, *Crystal Growth & Design*, **2009**, *9*, 3655.

[16] C. Y. Sun, S. X. Liu, D. D. Liang, K. Z. Shao, Y. H. Ren, Z. M. Su, *J. Am. Chem. Soc.* **2009**, *131*, 1883.

[17] J. Y. Niu, Z. L. Wang, J. P. Wang, *Inorg. Chem. Commun.* **2003**, *6*, 1272.

[18] R. N. Devi, E. Burkholder, J. Zubieta, *Inorg. Chim. Acta* **2003**, *348*, 150.

[19] J. Y. Niu, Z. L. Wang, J. P. Wang, *Polyhedron* **2004**, *23*, 773.

[20] J. P. Wang, P. T. Ma, J. Y. Niu, *Inorg. Chem. Commun.* **2006**, *9*, 1049.

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

[22] J. Q. Sha, J. Peng, Y. Q. Lan, Z. M. Su, H. J. Pang, A. X. Tian, P. P. Zhang, M. Zhu, *Inorg. Chem.* **2008**, *47*, 5145.

[23] J. Q. Sha, J. Peng, A. X. Tian, H. S. Liu, J. Chen, P. P. Zhang, Z. M. Su, *Crystal Growth & Design* **2007**, *7*, 2535.

[24] J. Q. Sha, C. Wang, J. Peng, J. Chen, A. X. Tian, P. P. Zhang, *Inorg. Chem. Commun.* **2007**, *10*, 1321.

[25] J. Q. Sha, J. Peng, H. S. Liu, J. Chen, B. X. Dong, A. X. Tian, Z. M. Su, *Eur. J. Inorg. Chem.* **2007**, 1268.

[26] J. Q. Sha, J. Peng, J. Chen, A. X. Tian, P. P. Zhang, *Solid-State Sci.* **2007**, *9*, 1012.

[27] J. Q. Sha, J. Peng, S. J. Zhou, M. Zhu, L. Han, D. Chen, *J. Clust. Sci.* **2008**, *19*, 499.

[28] N. C. Pastor, P. Gomez-Romero, G. B. Jameson, L. C. W. Baker, *J. Am. Chem. Soc.* **1991**, *113*, 5658.

[29] L. C. W. Baker, T. P. McCutcheon, *J. Am. Chem. Soc.* **1956**, *78*, 4503.

[30] I. D. Brown, D. Altermatt, *Acta Crystallogr.* **1985**, *B41*, 244.

[31] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885.

[32] Y. H. Feng, Z. G. Han, J. Peng, X. R. Hao, *J. Mol. Struct.* **2005**, *734*, 171.

[33] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *ibid.* **2008**, *A64*, 112.