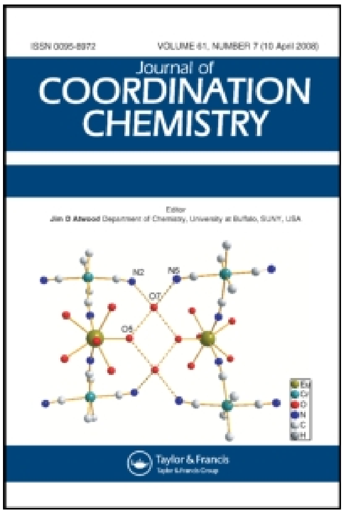

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Two new ladder-like inorganic chains constructed from Cu-containing sandwich polyoxoanions

Zhi-Ming Zhang[a]; Shuang Yao[a]; Yang-Guang Li[a]; En-Bo Wang
[a] Department of Chemistry, Northeast Normal University, Key Laboratory of Polyoxometalate Science of Ministry of Education, Changchun, PR China

To cite this Article Zhang, Zhi-Ming , Yao, Shuang , Li, Yang-Guang and Wang, En-Bo(2009) 'Two new ladder-like inorganic chains constructed from Cu-containing sandwich polyoxoanions', Journal of Coordination Chemistry, 62: 9, 1415 — 1422

To link to this Article: DOI: 10.1080/00958970802627204

URL: http://dx.doi.org/10.1080/00958970802627204

Journal of Coordination Chemistry
Vol. 62, No. 9, 10 May 2009, 1415–1422

Taylor & Francis
Taylor & Francis Group

Two new ladder-like inorganic chains constructed from Cu-containing sandwich polyoxoanions

ZHI-MING ZHANG, SHUANG YAO,
YANG-GUANG LI and EN-BO WANG*

Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, PR China

(*Received 23 June 2008; in final form 27 August 2008*)

Two heteropolyoxotungstates, $K_4Na_4[Cu_2(H_2O)_8Cu_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]14H_2O$ (**1**) and $K_8[Cu_2(H_2O)_8Cu_4(H_2O)_2(B\text{-}\alpha\text{-}SiW_9O_{34})_2]4H_2O$ (**2**), have been obtained in aqueous solution and characterized by IR, TG, elemental analysis, magnetism, and single-crystal X-ray analysis. The two compounds are one-dimensional (1-D) inorganic polymers composed of Cu-containing sandwich polyoxoanions, linked by additional Cu^{2+} ions to construct 1-D ladder-like chain structures. To the best of our knowledge, it is the first example of a 1-D ladder-like chain based on sandwich-type anions and Cu^{2+} linkers. Furthermore, the chains in **1** are further connected by K^+ into an extensive three-dimensional (3-D) framework. The magnetic studies of **1** indicate that antiferromagnetic interactions exist in the central tetra-metal set of the sandwich-type polyoxoanion.

Keywords: Heteropolyoxotungstates; Copper; Sandwich-type; Ladder-like structure

1. Introduction

Polyoxometalates (POMs), as metal oxide clusters with nanosizes and abundant topologies, attract interest in fields such as catalysis, electrochemistry, electrochromism, and magnetism [1, 2]. POMs have been used as the building blocks to construct 1-D chain, 2-D layer, and 3-D network architectures with functional properties. To date, POM building blocks still largely focus on well-known Keggin-, Wells–Dawson-, Anderson-, Silverton-, and Lindquist-type anions [3–7]. Most extended frameworks based on these polyoxoanions are achieved via bridges of secondary metal–organic complexes [8]. Very recently, bridging suitable metal oxide building blocks (such as the lacunary or transition-metal substituted polyoxoanions) by simple metal cations as the linking units to generate true metal oxide surfaces and framework materials without the incorporation of additional conventional ligands have attracted considerable attention [9]. Materials based on such POM clusters have shown 1-D chain-like structure by direct condensation to form oxo-bridged arrays of clusters or through

---

*Corresponding author. Email: wangenbo@public.cc.jl.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970802627204

lanthanide cations and transition metal cations acting as inorganic bridging ligands. Such 1-D chain-like structures consisting of sandwich-type polyoxoanions with a linker of lanthanide or transition metal cations were seldom observed [10]. Sandwich polyoxoanions, obtained by the reaction of lacunary polyoxoanions with transition metal cations, possess larger volume and more negative charge than those of commonly used POMs, allowing formation of higher coordination numbers with metal cations and should be excellent precursors for constructing extended materials [10e]. In our group, we have obtained examples such as $Na_4[Mn_4(H_2O)_{18}Mn_4(H_2O)_2(XW_9O_{34})_2]22H_2O$ ($X = $ Ge and Si) and $K_4Na_2[\{Ce(H_2O)_7\}_2Mn_4Si_2W_{18}O_{68}(H_2O)_2]21 \cdot 5H_2O$ [11]. Incorporation of the sandwich polyoxoanions into an inorganic polymer has introduced centers of magnetism and electrochemistry into the extended structure for functional materials.

In this article, we report two new inorganic polymers $K_4Na_4[Cu_2(H_2O)_8Cu_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]14H_2O$ (**1**) and $K_8[Cu_2(H_2O)_8Cu_4(H_2O)_2(B\text{-}\alpha\text{-}SiW_9O_{34})_2]4H_2O$ (**2**). Single-crystal X-ray diffraction analysis reveals that the compounds exhibit 1-D ladder-like chain structures, composed of the $[Cu_4(XW_9O_{34})_2]^{12-}$ ($X = $ Ge, Si) anions linked by Cu^{2+}.

2. Experimental

2.1. *Materials and methods*

All chemicals were commercially purchased and used without purification. $K_8[\gamma\text{-}SiW_{10}O_{36}]12H_2O$ and $K_8[\gamma\text{-}GeW_{10}O_{36}]6H_2O$ were synthesized according to literature [12] and characterized by IR spectrum. Elemental analyses (H) were performed on a Perkin–Elmer 2400 CHN elemental analyzer; Ge, Si, W, Cu, Na, and K were analyzed on a PLASMA-SPEC(I) inductively coupled plasma (ICP) atomic emission spectrometer. IR spectra were recorded from 400–4000 cm^{-1} on an Alpha Centauri Fourier transform infrared (FTIR) spectrophotometer using KBr pellets. Magnetic susceptibility measurements of **1** were performed with a Quantum Design Superconducting quantum interference device (SQUID) magnetometer (MPMS-XL). DC measurements were conducted from 2 to 300 K at 0.1 T. The measurements were performed on polycrystalline samples. A pHS-25B type pH meter was used for pH measurements.

2.2. *Synthesis of compounds*

2.2.1. Synthesis of 1. In a typical synthesis for **1**, $K_8[\gamma\text{-}GeW_{10}O_{36}]6H_2O$ (1.0 g) was dissolved in 60 mL of distilled water with stirring and 4 mL of 1 M $CuCl_2$ (4 mM) solution was added dropwise with vigorous stirring and the mixture boiled for 2.5 h. After cooling to room temperature, the solution was filtered and the filtrate was slowly evaporated at room temperature for 3 days, resulting in the blue block crystalline product (yield of 51% based on Ge). Anal. Calcd for **1** (%): K, 2.78; Na, 1.64; H, 0.89; Cu, 6.80; Ge, 2.59; W, 58.1. Found: K, 3.08; Na, 1.54; H, 1.09; Cu, 6.51; Ge, 2.89; W, 57.8. IR (KBr pellet): 945 (m), 887 (m), 773 (s), 704 (m), 492 (w), 455 (w) cm^{-1}.

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$H_{48}Cu_6Ge_2K_4Na_4O_{92}W_{18}$	$H_{28}Cu_6Si_2K_8O_{92}W_{18}$
Formula mass	5604.46	5559.74
Temperature [K]	150(2)	150(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimension (Å, °)		
a	11.669(2)	11.751(2)
b	12.408(3)	12.339(3)
c	17.076(3)	15.531(3)
α	76.40(3)	101.31(3)
β	71.59(3)	100.18(3)
γ	77.04(3)	102.30(3)
V (Å^3)	2249.8(1)	2100.6(7)
Z	1	1
D_{calcd} (g cm^{-3})	4.137	4. 395
μ (mm^{-1})	25.261	26.559
$F(000)$	2474	2450
Data/restraints/parameters	7901/36/561	4238/252/523
Goodness-of-fit on F^2	1.047	0.943
$R_1{}^{a}$ [$I > 2\sigma(I)$]	0.0419	0.0865
$wR_2{}^{b}$	0.0945	0.1864

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

2.2.2. Synthesis of 2. The preparation of **2** was similar to that of **1** except that $K_8[\gamma\text{-SiW}_{10}O_{36}]12H_2O$ was used instead of $K_8[\gamma\text{-GeW}_{10}O_{36}]6H_2O$.

2.3. *X-ray crystallography*

Single-crystal X-ray data for **1** and **2** were collected on a Rigaku R-AXIS RAPID IP diffractometer equipped with a normal focus 18 KW sealed tube X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 KV and 200 mA. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL-97 software [13]. Further details of the X-ray structural analyses are given in table 1. Details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; Email: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-419602 for **1** and CSD-419603 for **2**.

3. Results and discussion

3.1. *Synthesis*

The divacant polyoxoanion $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ decomposes easily and usually undergoes isomerization in aqueous solution. Recently, the $[\gamma\text{-GeW}_{10}O_{36}]^{8-}$ was obtained by decomposition of $[\beta\text{-GeW}_{11}O_{36}]^{8-}$. The structures and procedures of the synthesis of the two polyoxoanions ($[\gamma\text{-GeW}_{10}O_{36}]^{8-}$ and $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$) were analogous. Both react with transition metal cations giving a series of compounds with diverse nuclearities and structural features combined with interesting catalytic, electrochemical, and magnetic properties. Herein, $[\gamma\text{-}X\text{W}_{10}O_{36}]^{8-}$ ($X=\text{Ge}$, Si) reacts with Cu^{2+} ions, giving **1** and **2**. The successful synthesis of **1** confirms that $[\gamma\text{-GeW}_{10}O_{36}]^{8-}$ possesses similar reactivity with Si analogs $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ when reacted with transition-metal cations [11a].

3.2. *Structure description*

3.2.1. Structure analysis. Single-crystal X-ray diffraction analysis reveals that **1** and **2** are isostructural and crystallize in the same space group $P\bar{1}$. Therefore, we discuss only the structure of **1** here. Compound **1** exhibits a 1-D ladder-like chain built up of sandwich anions $[Cu_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ and Cu^{2+} (figure 1). In this polymeric chain, four Cu^{2+} linkers coordinate to a sandwich-type anion by four μ_2-O atoms and link two neighboring anions to constitute the 1-D ladder-like chain along the *b* axis, representing the first example of a 1-D ladder-like chain based on sandwich-type anions and Cu^{2+} linkers. The coordination geometry of the four linking Cu^{2+} ions is octahedral, completed by two oxygens coming from two neighboring sandwich-type $[Cu_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ anions and four water molecules. The bond lengths of Cu–O of the four linking Cu^{2+} ions are in the range 1.956(12)–2.616(26) Å. The sandwich-type polyoxoanion in this chain was composed of a rhomblike Cu_4O_{16} and two $[B\text{-}\alpha\text{-GeW}_9O_{34}]^{10-}$ units (figure 2). The $[B\text{-}\alpha\text{-GeW}_9O_{34}]^{10-}$ unit provides seven oxygen donor atoms (one from the central GeO_4 group and one each from the six W atoms) that are capable of coordinating to the central $\{Cu_4\}$ cluster to form the Weakley-type sandwich structure. All the W and Cu centers in the $[Cu_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ cluster exhibit octahedral coordination environments. The W–O bond lengths are in the range 1.702(9)–2.381(10) Å and the Cu–O bond lengths in the central cluster are in the range 1.926(10)–2.371(11) Å.

In the unit cell of **1**, two types of functionalized potassium cations with different coordinated environment are observed. On the *ac* plane, adjacent ladder-like chains are connected by K^{2+} which exhibit eight-coordination with six O atoms derived from two different polyoxoanions and two water molecules to form a 2-D framework (Supplemental Material). Furthermore, the 2-D layers are connected by additional potassium cations (K^{1+}) into a 3-D open framework (figure 3). K^{1+} is also eight-coordinate, however, it coordinates to six oxo atoms coming from three different

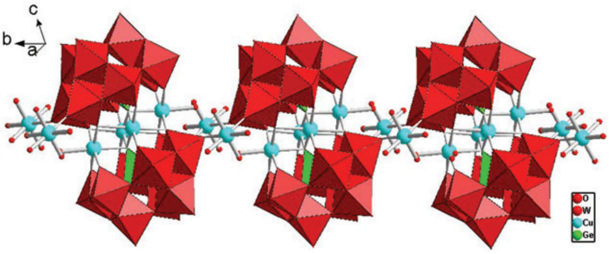

Figure 1. View of the 1-D ladder-like chain of **1**.

polyoxoanions and two waters. The bond lengths of K-O_{POM} are in the range 2.747(11) ~ 3.288(12) Å, while the distances of K-Ow from 2.710(3) ~ 2.826(11) Å. Thus, the potassium cations can be viewed as μ_2-bridges (K^{2+}) and μ_3-bridges (K^{1+}). The oxidation states of W and Cu sites are +6 and +2, respectively, based on the crystal color (blue), bond lengths and angles, charge balance considerations, and bond valence sum calculations [14].

3.3. *TG analysis*

Thermogravimetric (TG) analysis, on a Perkin–Elmer TGA7 instrument under N_2 atmosphere, of **1** (Supplemental Material) shows a weight loss of 8.33% between 40 and 350°C corresponding to loss of all lattice and coordinated water molecules, in

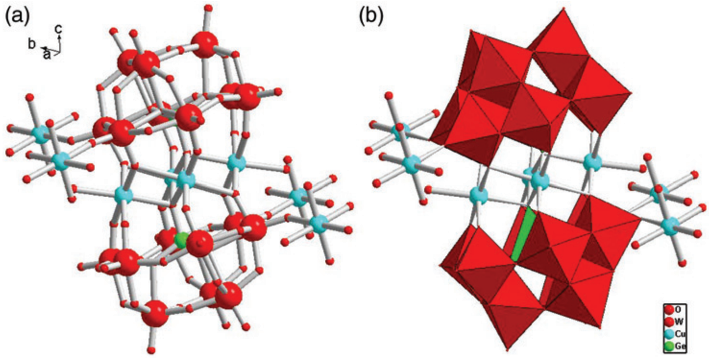

Figure 2. (a) Ball-and-stick representation of polyoxoanion **1**. (b) Polyhedral and ball-and-stick representation of polyoxoanion **1**.

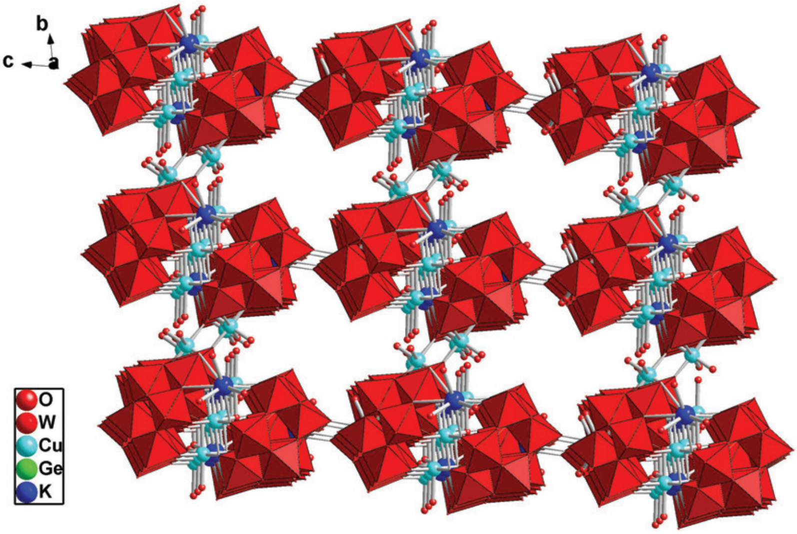

Figure 3. Polyhedral and ball-and-stick view of the 3-D open framework along the *a* axis (polyoxoanion **1**).

agreement with the calculated value of 7.71%. The TG curve of **2** shows weight loss of 5.43% in the range 30–250°C (Calcd 4.53%), attributed to loss of all noncoordinated and coordinated water molecules (Supplemental Material).

3.4. *Magnetic properties*

Magnetic susceptibility of **1** was investigated at $H = 0.1\,\mathrm{T}$ and $T = 2.0 \sim 300\,\mathrm{K}$. $\chi_M T$ is $2.47\,\mathrm{cm^3\,K\,mol^{-1}}$ at 300 K, consistent with the expected value for six uncoupled Cu^{2+} centers ($\chi_M T = 2.48\,\mathrm{cm^3\,K\,mol^{-1}}$ assuming $g = 2.1$, $S = 1/2$). Figure 4 shows the temperature dependence of χT and χ of **1** over 2.0–300 K. The $\chi_M T$ *versus* T plot slowly decreases from $2.47\,\mathrm{cm^3\,K\,mol^{-1}}$ at 300 K, to $2.06\,\mathrm{cm^3\,K\,mol^{-1}}$ at 10 K, and then increases and rapidly drops to $0.295\,\mathrm{cm^3\,K\,mol^{-1}}$ at 2 K. This behavior indicates antiferromagnetic interactions are dominant in **1**.

The χ^{-1} *versus* T plot is fitted by the Curie–Weiss law in the whole temperature range with $C = 2.49\,\mathrm{cm^3\,K\,mol^{-1}}$ and $\theta = -8.04\,\mathrm{K}$, confirming the presence of antiferromagnetic coupling between Cu^{2+} ions. Based on the connection modes of Cu(II) ions in the polyoxoanion of **1**, the susceptibility was simulated by a tetrameric Cu model with the following isotropic Heisenberg spin Hamiltonian:

$$H = -2J_1(S_1S_2 + S_2S_3 + S_3S_4 + S_4S_1) - 2J_2S_2S_4 \tag{1}$$

where S_i are the spin operators for each metal ion ($S_i = 1/2$ for $\mathrm{Cu^{II}}$ with $i = 1$–4); J_1 and J_2 are the magnetic interaction between the two central Cu(II) sites. The molar magnetic susceptibility of the $\{\mathrm{Cu_4}\}$ cluster is described as:

$$\chi_M = \frac{Ng^2\beta^2}{3kT} \times \frac{\sum_S S_T(S_T+1)(2S_T+1)e^{-E(S_T)/kT}}{\sum_S (2S_T+1)e^{-E(S_T)/kT}} \tag{2}$$

where the N, g, μ_B and k_B have their usual meanings.

The susceptibility data of **2** is simulated with the following equation (3):

$$\chi = \chi_M + 2Ng^2{\mu_B}^2 S(S+1)/3k_B T \tag{3}$$

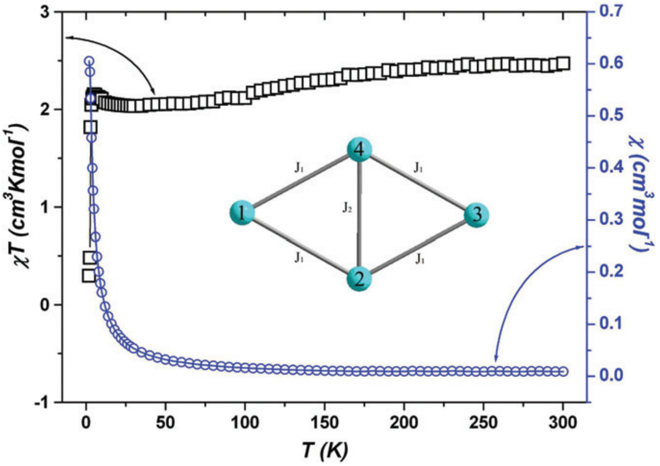

Figure 4. χT *vs.* T (black □) and χ *vs.* T (blue ○) curves of **1**.

where the first term refers to the susceptibility of the central tetrameric $\{Cu_4\}$ cluster of the sandwich-type polyoxoanion and the second one to the Curie contribution for two isolated Cu(II) metal ions ($S = 1/2$). N, g, μ_B and k_B have their usual meanings. The fit is good in the whole temperature range with the parameters: $g = 2.06$, $J_1 = -0.052$ and $J_2 = -0.19$ K. The results indicate that the paramagnetic behavior of **1** is consistent with its structure.

4. Conclusions

In summary, two heteropolyoxotungstates with 1-D ladder-like and chain-like structures have been obtained in aqueous solution. The two compounds are composed of sandwich-type anions $[Cu_4(H_2O)_2(XW_9O_{34})_2]^{12-}$ ($X = $ Ge, Si) and Cu^{2+} linkers, which represents the first example of the 1-D ladder-like chain based on sandwich-type anions and Cu^{2+}. Meanwhile, **1** is further connected by potassium cations into a 3-D open framework. The synthesis of the two compounds enriches the system of POM-based extended frameworks. The subsequent synthesis of 3-D extended materials, with the introduction of other magnetic and electrochemical active centers, could open the way to new functional materials. This research is currently going on in our group.

Supplementary materials

X-ray crystallographic files in CIF format; TG curves and the IR spectra; polyhedral and ball-and-stick representations of polyoxoanion **2**; and polyhedral and ball-and-stick view of the coordination modes of two independent potassium cations in **1** are available online.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No. 20701005); the Postdoctoral station Foundation of Ministry of Education (No. 20060200002); the Program for Changjiang Scholars and Innovative Research Team in University.

References

[1] (a) M.L. Wei, C. He, W.J. Hua, C.Y. Duan, S.H. Li, Q.J. Meng. *J. Am. Chem. Soc.*, **128**, 13318 (2006); (b) K. Uehara, H. Nakao, R. Kawamoto, S. Hikichi, N. Mizuno. *Inorg. Chem.*, **45**, 9448 (2006); (c) Y. Ishii, Y. Takenaka, K. Konishi. *Angew. Chem. Int. Ed.*, **43**, 2702 (2004); (d) J.M. Knaust, C. Inman, S.W. Keller. *Chem. Commun.*, 492 (2004); (e) R. Kawamoto, S. Uchida, N. Mizuno. *J. Am. Chem. Soc.*, **127**, 10560 (2005).

[2] (a) M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer, Berlin (1983); (b) C.L. Hill. *Chem. Rev.*, **98**, 1 (1998); (c) L.C. Baker, D.C. Glick. *Chem. Rev.*, **98**, 3 (1998); (d) A. Müller, S.Q.N. Shah, H. Bögge, M. Schmidtmann. *Nature*, **397**, 48 (1999); (e) K. Fukaya, T. Yamase. *Angew. Chem. Int. Ed.*, **42**, 654

(2003); (f) E. Coronado, G. García. *Chem. Rev.*, **98**, 273 (1998); (g) D.L. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).

[3] (a) M. Sadakane, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed.*, **39**, 2914 (2000); (b) J.M. Galan-Mascaros, C. Gimenez-Saiz, S. Triki, C.J. Gomez-Garcia, E. Coronado, L. Ouahab. *Angew. Chem. Int. Ed.*, **34**, 1460 (1995); (c) X.L. Wang, C. Qin, E.B. Wang, Z.M. Su, Y.G. Li, L. Xu. *Angew. Chem. Int. Ed.*, **45**, 1 (2006).

[4] J.Y. Niu, D.J. Guo, J.P. Wang, J.W. Zhao. *Cryst. Growth Des.*, **5**, 837 (2005).

[5] (a) V. Shivaiah, P.V. Reddy, L. Cronin, S.K. Das. *J. Chem. Soc., Dalton Trans.*, 3781 (2002); (b) H.Y. An, Y.G. Li, E.B. Wang, D.R. Xiao, C.Y. Sun, L. Xu. *Inorg. Chem.*, **17**, 6062 (2005).

[6] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang. *J. Am. Chem. Soc.*, **124**, 3836 (2002).

[7] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 3165 (1999).

[8] (a) Y. Lu, Y. Xu, E.B. Wang, J. Lu, C.W. Hu, L. Xu. *Cryst. Growth Des.*, **5**, 257 (2005); (b) C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu. *Chem. Commun.*, 1416 (2002).

[9] (a) M.I. Khan, E. Yohannes, D. Powell. *Chem. Commun.*, 23 (1999); (b) M.I. Khan, E. Yohannes, J.R. Doedens. *Angew. Chem. Int. Ed.*, **38**, 1292 (1999); (c) X.B. Cui, J.Q. Xu, H. Meng, S.T. Zheng, G.Y. Yang. *Inorg. Chem.*, **43**, 8005 (2004).

[10] (a) J.P. Wang, X.D. Du, J.Y. Niu. *Chem. Lett.*, **35**, 1408 (2006); (b) X. Zhang, Q. Chen, D.C. Duncan, C.F. Campana, C.L. Hill. *Inorg. Chem.*, **36**, 4208 (1997); (c) S.T. Zheng, D.Q. Yuan, J. Zhang, G.Y. Yang. *Inorg. Chem.*, **46**, 4569 (2007); (d) U. Kortz, S. Nellutla, A.C. Stowe, N.S. Dalal, J. Tol, B.S. Bassil. *Inorg. Chem.*, **43**, 144 (2004); (e) J.W. Zhao, H.P. Jia, J. Zhang, S.T. Zheng, G.Y. Yang. *Chem. Eur. J.*, **13**, 10030 (2007).

[11] (a) Z.M. Zhang, S. Yao, E.B. Wang. *J. Solid State Chem.*, **181**, 715 (2008); (b) W.L. Chen, Y.G. Li, Y.H. Wang, E.B. Wang. *Eur. J. Inorg. Chem.*, **15**, 2216 (2007).

[12] (a) A. Tézé, G. Hervé. *Inorg. Synth.*, **27**, 85 (1990); (b) J. Canny, A. Tézé, R. Thouvenot, G. Hervé. *Inorg. Chem.*, **25**, 2114 (1986); (c) N.H. Nsouli, B.S. Bassil, M.H. Dickman, U. Kortz, B. Keita, L. Nadjo. *Inorg. Chem.*, **45**, 3858 (2006).

[13] (a) G.M. Sheldrick. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997); (b) G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).

[14] I.D. Brown, D. Altermatt. *Acta Crystallogr.*, **B41**, 244 (1985).