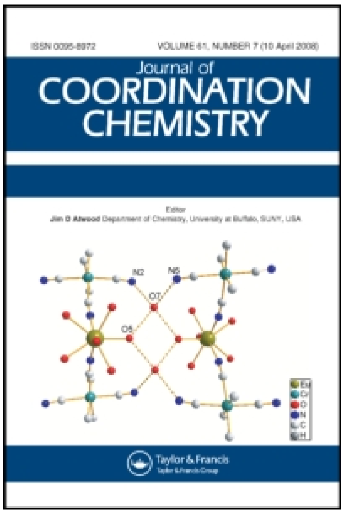

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A one-dimensional assembly of a Keggin tungstogermanate and sodium-pyridine-2-carboxylic acid: $NaH_3(C_6H_5N_2)_4[GeW_{12}O_{40}] \cdot 7H_2O$

Wen Yang[a]; Ying Liu[a]; Ganglin Xue[a]; Huaiming Hu[a]; Feng Fu[b]; Jiwu Wang[b]
[a] Department of Chemistry, Northwest University, Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Xian, China [b] Shaanxi Key Laboratory of Chemical Reaction Engineering, Yanan University, Shaanxi, China

To cite this Article Yang, Wen , Liu, Ying , Xue, Ganglin , Hu, Huaiming , Fu, Feng and Wang, Jiwu(2008) 'A one-dimensional assembly of a Keggin tungstogermanate and sodium-pyridine-2-carboxylic acid: $NaH_3(C_6H_5N_2)_4[GeW_{12}O_{40}] \cdot 7H_2O$', Journal of Coordination Chemistry, 61: 15, 2499 — 2505
To link to this Article: DOI: 10.1080/00958970801947470
URL: http://dx.doi.org/10.1080/00958970801947470

Journal of Coordination Chemistry
Vol. 61, No. 15, 10 August 2008, 2499–2505

Taylor & Francis
Taylor & Francis Group

A one-dimensional assembly of a Keggin tungstogermanate and sodium-pyridine-2-carboxylic acid: $NaH_3(C_6H_5N_2)_4[GeW_{12}O_{40}]\cdot 7H_2O$

WEN YANG†, YING LIU†, GANGLIN XUE*†, HUAIMING HU†,
FENG FU‡ and JIWU WANG‡

†Department of Chemistry, Northwest University, Shaanxi Key Laboratory of
Physico-Inorganic Chemistry, Xian, 710069, China
‡Shaanxi Key Laboratory of Chemical Reaction Engineering, Yanan University,
Yanan, Shaanxi, 716000, China

(*Received 26 September 2007; in final form 18 October 2007*)

A hybrid inorganic-organic assembly, $NaH_3(C_6H_5NO_2)_4[GeW_{12}O_{40}]\cdot 7H2O$ (**1**), has been synthesized and characterized by IR, UV, ^{1}H NMR and single crystal X-ray diffraction. Crystal data: orthorhombic, $P2_12_12_1$, $a = 12.819(2)$ Å, $b = 19.326(3)$ Å, $c = 24.164(4)$ Å, $V = 5986.4(18)$ Å^3, $Z = 4$, $R_1 = 0.0541$ ($I > 2\sigma$). The structure of **1** is based on a 1D zigzag infinite chain assembled by alternating $[GeW_{12}O_{40}]^{4-}$ and sodium-pyridine-2-carboxylic complex $[Na(C_6H_5NO_2)3(H_2O)_2]^+$ via W–O$_d$–Na–O$_d$–W.

Keywords: Polyoxometalates; Sodium-organic complexes; Pyridine-2-carboxylic; Structure

1. Introduction

Extended inorganic or hybrid inorganic-organic compounds have attracted interest for combining different characteristics of the components to get unusual structures, properties or applications [1]. Using transition metal complex subunits as bridges, 1D (one-dimension), 2D (two-dimension) and 3D (three-dimension) structures can be obtained, such as 1D chains $(NH4)[Cu(en)_2][Na(en)Cu(en)_2(H_2O)(Mo7O_{24)}]\cdot 4H_2O$ (en = ethylenediamine) [2], $Cu^I(2,2'\text{-bipy})(4,4'\text{-bipy})_{0.5}]_2[Cu^I(2,2'\text{-bipy})(4,4'\text{-Hbipy})]$, $[Cu^I(4,4'\text{-bipy})]_2[P_2W_{18}O_{62}]\cdot 3H_2O$, $[Cu^I(4,4\text{-bipy})]_3[PMo_{12}O_{40}]\cdot en\cdot 3H2O$ (2,2′-bipy = 2,2′-bipyridine, 4,4′-bipy = 4,4′-bipyridine) [3], $[\{Cu(2,2'\text{-bpy})\}_6(Mo_6O_{22})][GeMo_{12}O_{40}]\cdot H_2O$ [4], and one-dimensional zigzag chains built of $[\alpha\text{-}GeW_{11}O_{39}]^{8-}$ anions connected by Nd^{3+}/Sm^{3+} cations $[(CH_3)_4N]_2H_{1.50}[Nd_{1.50}(GeW_{11}O_{39})(H_2O)_6]\cdot 3H_2O$ and $[(CH_3)_4N]_2H_{2.25}[Sm_{1.25}(GeW_{11}O_{39})(H_2O)_4]\cdot 3.75H_2O$ [5], 2D layers $(NH_4)_3(4,4'\text{-H2bipy})[Cu^I(4,4'\text{-bipy})]_7[P_2W_{18}O_{62}]_2\cdot 10H_2O$ [6], and $\{[Cu(4\text{-phpyr})_4]_2(Mo_8O_{26})\cdot 4\text{-phpyr}\}$ [7], 3D supramolecular networks $(C_6H_5NO_2)_2Na_2[(C_6H_5NO_2)_2NaCrMo_6H_6O_{24}]$ [8], and copper phosphate $[Cu^I(2,2'\text{-bipy})$

---

*Corresponding author. Email: xglin707@163.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801947470

$(4,4'\text{-bipy})_{0.5}]_2[\mathrm{Cu^I}(4,4'\text{-bipy})]_2[\mathrm{PW_{12}O_{40}}]\cdot 0.25\mathrm{H_2O}$ [3]. The complex $(\mathrm{bbi})_{1.5}$ $[\mathrm{Cu(bbi)}]_{4.5}[\mathrm{PW_{12}O_{40}}]_{1.5}$ contains two sorts of polyoxometalates (POMs) chains, the poly-chain of $[\mathrm{Cu(bbi)}]_{4.5}[\mathrm{PW_{12}O_{40}}]$ and the single-chain of $(\mathrm{bbi})[\mathrm{PW_{12}O_{40}}]_{0.5}$ [9].

In comparison to the large number of polyoxoanion-based solid materials structurally modified by transition or lanthanide metals [10], alkali metal linkers have received less attention in self-assembly of POMs. Sodium coordination complexes are important choices in designing POM-based supramolecular compounds [11] because sodium ion and its compounds have applications in bioinorganic chemistry, various electronic, magnetic, and photosensitive materials [12].

Here we report a one-dimensional zigzag hybrid inorganic-organic compound, $\mathrm{NaH_3(C_6H_5NO_2)_4[GeW_{12}O_{40}]\cdot 7H_2O}$ (**1**), assembled by alternating $[\mathrm{GeW_{12}O_{40}}]^{4-}$ and $[\mathrm{Na(C_6H_5NO_2)_3(H_2O)_2}]^{+}$ via alternating Na-μ-Ot-W interactions.

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased commercially and used without further purification. The precursor $\alpha\text{-}\mathrm{Na_4GeW_{12}O_{34}}\cdot 14\mathrm{H_2O}$ was prepared as previously reported [13] and characterized by IR spectra. Elemental analyses (C, H, N) were determined by a PE 240Q elemental analyzer; IR spectra (4000–400 $\mathrm{cm^{-1}}$) were recorded in transmission through KBr pellets with a EQUINOX55 spectrometer. UV–Vis spectra were recorded with a Shimadzu UV2550 UV–Vis spectrophotometer. ^{1}H NMR spectra were obtained on an INOVA-400 NMR spectrometer with $\mathrm{D_2O}$ as solvent and $\mathrm{Me_4Si}$ as an internal standard.

2.2. *Synthesis of $\mathrm{NaH_3(C_6H_5NO_2)_4[GeW_{12}O_{40}]\cdot 7H_2O}$ (1)*

A 1.00 g (0.34 mmol) sample of $\alpha\text{-}\mathrm{Na_4GeW_{12}O_{34}}\cdot 14\mathrm{H_2O}$ and 0.18 g (1.02 mmol) pyridine-2-carboxylic acid were dissolved in 20 mL of water at 80°C. The pH of the solution was adjusted to 3.0 by 1M HCl and a solution of 2 mL 1 M NaCl was added, and the mixture was kept at 80°C for 1.5 h. The solution was cooled to room temperature and filtered. The colorless filtrate was kept at room temperature for several months to form 0.40 g of colorless crystals in about 66.7% yield (based on W). Anal Calcd (%) for $\mathrm{C_{24}H_{37}GeN_4NaO_{55}W_{12}}$: H, 1.04; C, 8.09; N, 1.57; Na, 0.64; Ge, 2.04; W, 61.92. Found: H, 1.06; C, 8.12; N, 1.53; Na, 0.67; Ge, 2.08; W, 61.87. IR (KBr pellets, major absorbances, $\mathrm{cm^{-1}}$): 1739 (s), 1617 (s), 1310 (m), 968 (vs), 885 (vs), 830 (s), 779 (vs), 669 (s). ^{1}H NMR (400 MHz, TMS): δ ppm 8.22 (m, $J = 0.8$ Hz, H), 8.96 (m, $J = 0.8$ Hz, H), 9.06 (m, $J = 0.8$ Hz, H), 9.27 (t, $J = 0.8$ Hz, H).

2.3. *X-ray crystallography*

A colorless single crystal of **1** with dimensions $0.20 \times 0.15 \times 0.10\ \mathrm{mm^3}$ was fixed to the end of a glass capillary which was put on a BRUKER SMART APEX II CCD diffractometer equipped with graphite monochromatic radiation used for

Table 1. Crystal data and structure refinement for $NaH_3(C_6H_5NO_2)_4[GeW_{12}O_{40}] \cdot 7H_2O$ (**1**).

Empirical formula	$C_{24}H_{37}GeN_4NaO_{55}W_{12}$
Formula weight	3563.25
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	12.819(2)
b (Å)	19.326(3)
c (Å)	24.164(4)
V (Å^3)	5986.4(18)
Z	4
D_{calc} (g cm^{-3})	3.953
Crystal size (mm^3)	$0.20 \times 0.15 \times 0.10$
θ range for data collection (°)	1.69–25.10
Index ranges	$-13 \le h \le 14$ $-22 \le k \le 23$ $-16 \le l \le 28$
Reflections collected	25765
Reflections unique	10057 [R(int) = 0.0801]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10057/0/424
Goodness-of-fit on F^2	0.948
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0541$, $wR_2 = 0.1299$
R indices (all data)	$R_1 = 0.0628$, $wR_2 = 0.1380$
Extinction coefficient	0.000104(12)
Largest diff. peak and hole (e·Å^{-3})	2.593 and −2.318

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

data collection. Data were collected at 293(2) K using Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range $1.69 < \theta < 25.10$. A total of 10057 (10057 unique, $R_{int} = 0.0801$) reflections were measured ($-13 \le h \le 14$, $-22 \le k \le 23$, $-16 \le l \le 28$). The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2. Heavy atoms (W, Ge, Na) were refined with anisotropic displacement parameters. Light atoms (O, N, C) were refined isotropically. The positions of the hydrogen atoms attached to carbon were fixed at their ideal positions, and those attached to oxygen were not located. A summary of the crystallographic data and structural determination for **1** is provided in table 1. Selected bond lengths and angles of **1** are listed in table 2.

3. Results and discussion

3.1. *Structure description*

Single crystal X-ray diffraction analysis showed that the asymmetric unit contains a α-Keggin anion $[GeW_{12}O_{40}]^{4-}$, a $[Na(C_6H_5NO_2)_3(H_2O)_2]^+$ cation, one pyridine-2-carboxylic acid and five lattice water molecules (figure 1). The classical α-Keggin-type heteropolyoxoanion $[GeW_{12}O_{40}]^{4-}$ retains the parent structure in which the central GeO_4 tetrahedron is surrounded by 12 $\{WO_6\}$ octahedra; 12 $\{WO_6\}$ octahedra are grouped into four tri-metal $\{W_3O_{13}\}$ species in edge-sharing mode, each of which is made up of three $\{WO_6\}$ octahedra in edge-sharing mode. The four tri-metallic

Table 2. Selected bond lengths (Å) and angles (°).

Ge1–O4	1.682(15)	Ge1–O1–W11	121.5(8)
Ge1–O3	1.719(13)	Ge1–O2–W6	122.9(8)
Ge1–O1	1.726(18)	Ge1–O2–W10	121.4(8)
Ge1–O2	1.750(16)	Ge1–O2–W5	121.9(8)
O29–Na1	2.52(2)	Ge1–O3–W4	123.0(7)
O39–Na1^{i}	2.44(2)	Ge1–O3–W7	122.7(7)
O42–Na1	2.83(3)	Ge1–O3–W8	122.3(7)
O43–Na1	2.43(2)	Ge1–O4–W1	124.0(8)
O44–C7	1.30(3)	Ge1–O4–W9	123.5(8)
O45–C19	1.24(3)	Ge1–O4–W12	122.8(8)
O45–Na1	2.82(3)	W10–O39–Na1^{i}	139.5(11)
O49–Na1	2.50(4)	O50–Na1–O39^{ii}	94.1(10)
O50–Na1	2.35(3)	O43–Na1–O39^{ii}	80.2(8)
Na1–O39^{ii}	2.44(2)	O39^{ii}–Na1–O49	91.8(9)
O4–Ge1–O3	109.7(7)	O50–Na1–O29	91.7(9)
O4–Ge1–O1	108.9(8)	O43–Na1–O29	85.3(8)
O3–Ge1–O1	108.5(7)	O39^{ii}–Na1–O45	72.2(8)
O4–Ge1–O2	110.6(7)	O49–Na1–O45	148.8(10)
O3–Ge1–O2	109.4(7)	29–Na1–O45	73.0(7)
Ge1–O1–W2	123.6(10)	50–Na1–O42	119.4(11)
Ge1–O1–W3	122.7(9)	43–Na1–O42	72.4(8)
O1–Ge1–O2	109.8(8)	O39^{ii}–Na1–O42	133.9(9)

Symmetry transformations used to generate equivalent atoms: (i) $0.5-x$, $2-y$, $-0.5+z$; (ii) $0.5-x$, $2-y$, $0.5+z$.

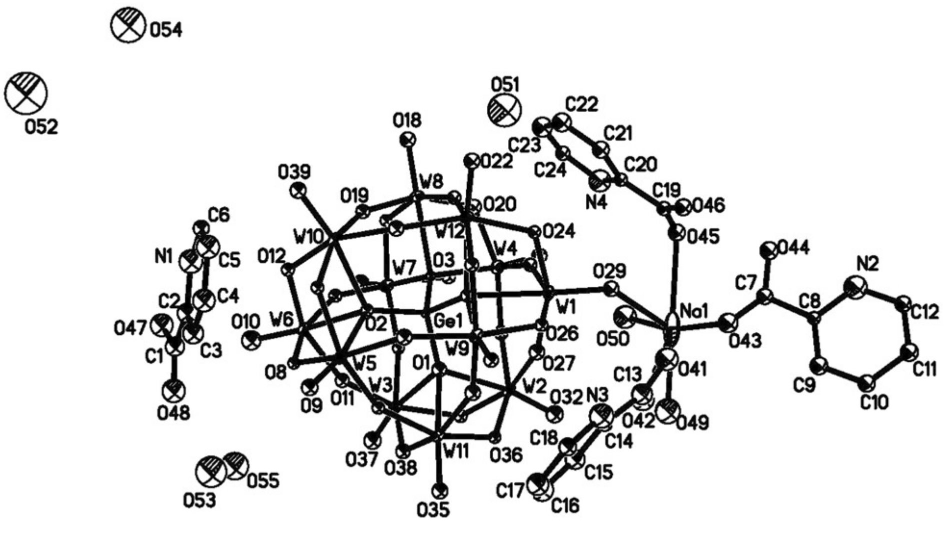

Figure 1. ORTEP drawing of the asymmetric unit in **1** with displacement ellipsoids shown at 30% probability level.

W_3O_{13} groups were linked by sharing corners and linked to the central GeO_4 tetrahedron. W–O bands can be divided into three categories: W–O_d 1.669(17)–1.707(17) Å, W–O_b 1.872(19)–1.966(18) Å, and W–O_c 2.256(17)–2.297(19) Å. The O–W–O angle is between 71.2(8)–170.9(9)°. Ge–O distances and O–Ge–O angles range from 1.698(19) to 1.753(17) Å and 109.0(9) to 110.7(10)°, respectively, showing that GeO_4 has a slight aberrance as the anion is influenced by Na^+ coordination.

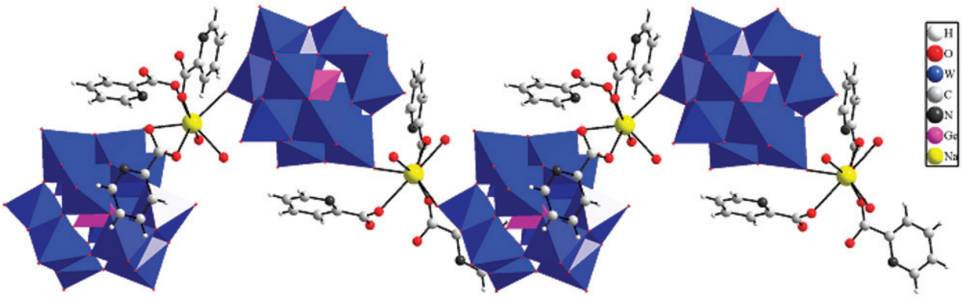

Figure 2. Polyhedral/ball-stick representation of the 1D zigzag chains in **1**.

The W(1)–O(29) and W(10)–O(39) distances which connect neighboring $[Na(C_6H_5NO_2)_3(H_2O)_2]^+$ units are 1.725(2) and 1.714(2) Å, respectively, longer than the average $W{=}O_d$ distance (1.69 Å). In $[Na(C_6H_5NO_2)_3(H_2O)_2]^+$, each Na^+ is seven-coordinate by three oxygen atoms from pyridine carboxylate molecules (O42, O43 and O45), two from adjacent POMS anions (O29 and O39) and two from water (O49 and O50), respectively, resulting in a mono-capped-triangle prism configuration. Na–O (O42, O43 and O45) average bond length is 2.69 Å, Na–O (O29 and O39) average bond length is 2.49 Å, and Na–O (O49 and O50) average bond length is 2.39 Å, meaning that the interactions between Na^+ and all coordinated oxygen atoms are very strong.

The interesting structural feature of **1** is that fused $[Na(C_6H_5NO_2)_3(H_2O)_2]^+$ fragments through the terminal oxygen of α-$[GeW_{12}O_{40}]^{4-}$ form a one-dimensional chain (figure 2). The O29–Na1–O39 bond angle 141.2 (13)° leads to formation of a hackle chain, which are further in close contact forming a three-dimensional supramolecular framework via extensive hydrogen bonding interactions among polyoxoanions, coordinated pyridine-2-carboxylic acid ligands, free pyridine-2-carboxylic acid and coordinated water molecules. Typical hydrogen bonds are as follows: $O55 \cdots O48 = 3.031$ Å, $O9 \cdots O55 = 2.870$ Å, $O29 \cdots O46 = 2.992$ Å, $O41 \cdots O43 = 2.687$ Å and $O46 \cdots O44 = 2.629$ Å.

3.2. *^{1}H NMR spectra*

^{1}H NMR spectra show clearly resolved signals which can be unambiguously assigned. The integration matches well with the pyridine-2-carboxylic acid molecule (see figure 3 and table 3). Comparing with ^{1}H NMR spectra of free pyridine-2-carboxylic acid, all protons in **1** exhibit higher chemical shifts and coupling owing to the coordination of pyridine-2-carboxylic acid molecules to Na^+ and the coexistence of coordinated and free pyridine-2-carboxylic acid molecules in the solution.

3.3. *IR and UV*

Two regions in the IR spectra of **1** are useful for identification. The 1620–1200 cm^{-1} region has characteristic vibrations of pyridine-2-carboxylic acid groups and in 1100–600 cm^{-1} there are four characteristic asymmetric vibrations from $[GeW_{12}O_{40}]^{4-}$, 968(vs) cm^{-1} for ν_{as} (W=Od), 885(vs) cm^{-1} for ν_{as} (W–Ob), 779(vs) and 669(s) cm^{-1} for ν_{as} ($W{-}O_c$), and 830(s) cm^{-1} for ν_{as} ($Ge{-}O_a$). Thus the POM anions

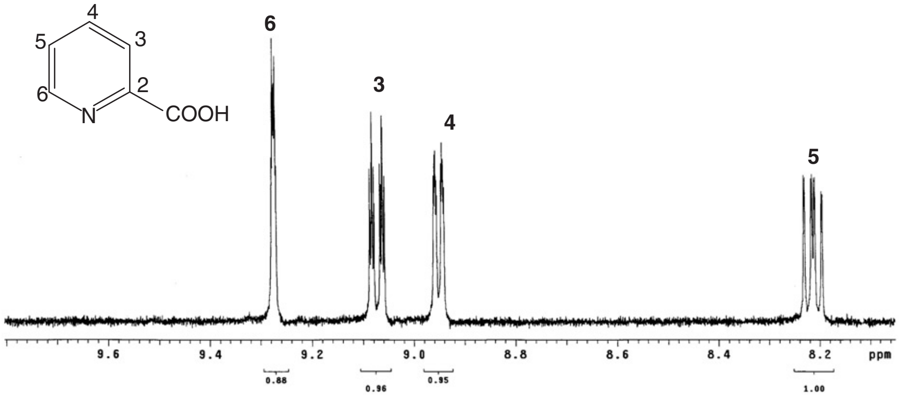

Figure 3. ^{1}H NMR spectra of **1**.

Table 3. ^{1}H NMR chemical shifts (ppm) of **1** and pyridine-2-carboxylate.

	3-H	4-H	5-H	6-H	–COOH
Pyridine-2-carboxylate	8.35	8.14	7.86	9.01	11.00
Compound **1**	9.06	8.96	8.22	9.27	

maintain a basic Keggin structure. Comparison to IR spectra of α-$Na_4GeW_{12}O_{40} \cdot 14H_2O$ shows ν_{as} ($W{=}O_d$) shifts to lower frequency by 12 cm^{-1}, due to the interaction between polyanions and $[Na(C_6H_5NO_2)_3(H_2O)_2]^+$. These results are consistent with the structural analysis.

There are two intense absorption bands in the UV spectra of the title complexes. One is at 199.7 nm, attributed to $O_d \rightarrow W$ charge transfer; another is at 262.5 nm, characteristic for a heteropolytungstate with the Keggin structure, attributed to $O_b/O_c \rightarrow W$ charge transfer.

4. Conclusion

A compound based on saturated polyoxoanion cluster and sodium coordination polymer was isolated and unequivocally characterized. The synthesis of **1** shows the utility of Keggin tungstogermanate clusters and sodium-organic complexes as precursors for self-assembly of extended supramolecular frameworks. Given the variations in the polyoxometalate clusters and alkali–metal coordination complex linkers, the scope for the further synthesis of hybrid materials based on POM and alkali–metal complex is significant.

Acknowledgements

This research was supported by the Natural Science Foundation of Shaanxi Province (2006B21) and the Education Commission of Shaanxi Province (07JK404).

References

[1] M.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer-Verlag, New York (1983); M.T. Pope, A. Müller. *Angew. Chem. Int. Ed. Engl.*, **30**, 34 (1991); M.T. Pope, A. Müller (Eds.). *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer, Dordrecht (1994); C.L. Hill (guest editor), *Chem. Rev.*, **98**, 1 (1998).

[2] Z.G. Han, H.Y. Ma, J. Peng, Y.H. Chen, E.B. Wang, N.H. Hu. *Inorg. Chem. Commun.*, **7**, 182 (2004).

[3] H. Jin, X.L. Wang, Y.F. Qi, E.B. Wang. *Inorg. Chim. Acta*, **360**, 3347 (2007).

[4] J.P. Wang, X.D. Du, J.Y. Niu. *J. Solid State Chem.*, **179**, 3260 (2006).

[5] J.P. Wang, X.Y. Duan, X.D. Du, J.Y. Niu. *Cryst. Growth Des.*, **6**, 2267 (2006).

[6] H. Jin, Y.F. Qi, D.R. Xiao, X.L. Wang, S. Chang, E.B. Wang. *J. Mol. Struct.*, **837**, 23 (2007).

[7] H. Liu, L. Xua, G.G. Gao, F.Y. Li, Y.Y. Yang, Z.K. Li, Y. Sun. *J. Solid State Chem.*, **180**, 1664 (2007).

[8] H.Y. An, D.R. Xiao, E.B. Wang, C.Y. Sun, Y.G. Li, L. Xu. *J. Mol. Struct.*, **751**, 184 (2005).

[9] B.X. Dong, J. Peng, P.P. Zhang, A.X. Tian, J. Chen, B. Xue. *Inorg. Chem. Commun.*, **10**, 839 (2007).

[10] S.T. Zheng, D.Q. Yuan, J. Zhang, G.Y. Yang. *Inorg. Chem.*, **46**, 4569 (2007); L. Lisnard, A. Dolbecq, P. Mialane, J. Marrot, E. Codjovib, F. Sécheresse. *Dalton Trans.*, 3913 (2005); H. Jin, Y.F. Qi, E.B. Wang, Y.G. Li, X.L. Wang, C. Qin, S. Chang. *Cryst. Growth Des.*, **6**, 2693 (2006); M. Yuan, Y.G. Li, E.B. Wang, C.G. Tian, L. Wang, C.W. Hu, N.H. Hu, H.G. Jia. *Inorg. Chem.*, **42**, 3670 (2003); Y. Ducommun, L. Helm, G. Laurenczy, A.E. Merbach. *Inorg. Chim. Acta*, **158**, 3 (1989); M.G.B. Drew, G.W.A. Fowles, R.W. Matthews, R.A. Walton. *J. Am. Chem. Soc.*, **91**, 7769 (1969).

[11] X.L. Wang, Y.Q. Guo, Y.G. Li, E.B. Wang, C.W. Hu, N.H. Hu. *Inorg. Chem.*, **42**, 4135 (2003).

[12] C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang. *J. Am. Chem. Soc.*, **124**, 3836 (2002); R.C. Howell, F.G. Perez, S. Jain, W.D. Horrocks, A.L. Rheingold, L.C. Francesconi. *Angew. Chem. Int. Ed.*, **40**, 4031 (2001); V. Shivaiah, P.V.N. Reddy, L. Cronin, S.K. Das. *Dalton Trans.*, 3781 (2002); M. Sadakane, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed.*, **39**, 2914 (2000); K.C. Kim, M.T. Pope. *J. Am. Chem. Soc.*, **121**, 8512 (1999); A. Müller, S.Q.N. Shah, H. Bögge, M. Schmidtmann. *Nature*, **397**, 48 (1999); D. Drewes, E.M. Limanski, B. Krebs. *Dalton Trans.*, 2087 (2004).

[13] C.R. Deltcheff, M. Fournier, R. Franck, R. Thouvenot. *Inorg. Chem.*, **22**, 207 (1983).