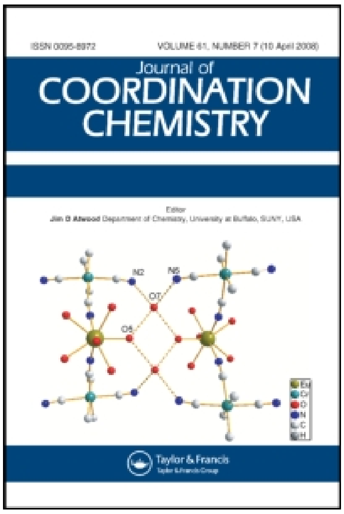

Journal of Coordination Chemistry

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

Synthesis and crystal structure of a 1D chain polyoxometalate-based complex $\{[Cu^{I}(en)_2(H_2O)]_2\{GeW_{12}O_{40}[Cu^{II}(en)_2]\}\cdot 2.5H_2O\}$*_n*

Jingping Wang[a]; Yuquan Feng[a]; Pengtao Ma[a]; Jingyang Niu[a]
[a] School of Chemistry and Chemical Engineering, Institute of Molecular and Crystal Engineering, Henan University, Kaifeng, P.R. China

To cite this Article Wang, Jingping , Feng, Yuquan , Ma, Pengtao and Niu, Jingyang(2009) 'Synthesis and crystal structure of a 1D chain polyoxometalate-based complex $\{[Cu^{I}(en)_2(H_2O)]_2\{GeW_{12}O_{40}[Cu^{II}(en)_2]\}\cdot 2.5H_2O\}$*_n*', Journal of Coordination Chemistry, 62: 12, 1895 — 1901

To link to this Article: DOI: 10.1080/00958970902721568

URL: http://dx.doi.org/10.1080/00958970902721568

Journal of Coordination Chemistry
Vol. 62, No. 12, 20 June 2009, 1895–1901

Synthesis and crystal structure of a 1D chain polyoxometalate-based complex $\{[Cu^{I}(en)_2(H_2O)]_2\{GeW_{12}O_{40}[Cu^{II}(en)_2]\}\cdot 2.5H_2O\}_n$

JINGPING WANG, YUQUAN FENG, PENGTAO MA
and JINGYANG NIU*

School of Chemistry and Chemical Engineering, Institute of Molecular and Crystal Engineering, Henan University, Kaifeng, 475004, P.R. China

(*Received 30 July 2008; in final form 16 September 2008*)

A 1-D infinite chain organic–inorganic hybrid compound, $[Cu^{I}(en)_2(H_2O)]_2\{GeW_{12}O_{40}[Cu^{II}(en)_2]\}\cdot 2.5H_2O$, was synthesized hydrothermally and characterized by IR, UV spectroscopy, TG analyses, and single-crystal X-ray diffraction. Structural analysis indicates that neighboring $[GeW_{12}O_{40}]^{4-}$ polyanions are interconnected by $[Cu(3)(en)_2]^{2+}$ subunits via W–O_t–Cu(3) bridges, generating a 1D infinite chain structure. Furthermore, the compound shows photoluminescence in the solid state at room temperature.

Keywords: Polyoxometalates; Hydrothermal synthesis; Crystal structure; Fluorescence

1. Introduction

Polyoxometalates are versatile inorganic building blocks for designing and synthesizing molecule-based materials [1–5]. Most polyoxometalates have discrete structures of definite sizes and shapes belonging to well-known structural types, such as Lindquist, Keggin, Wells-Dawson, Strandberg or Anderson [6]. Linking these discrete entities to build solid-state materials is of interest not only from a structural point of view, but also because they have potential applications in catalysis, medicine, electrical conductivity, and material science [7, 8]. A large number of inorganic–organic polyoxometalates containing infinitely extended chains constructed by Keggin-type polyanions and metal-organic cations have been reported [2, 5, 9–18]. Some examples are $[\{Ba(DMSO)_5(H_2O)\}_2(SiMo_{12}O_{40})\}$ [2], $[\{Ba(DMSO)_3(H_2O)_3\}\{Ba(DMSO)_5(H_2O)(GeMo_{12}O_{40})\}]$ [2], $[\{Ca(DMF)_5\}_2SiMo_{12}O_{40}]$ [13], $[La(DMSO)_6(H_2O)\}_2(PMo_{12}O_{40})\cdot H_2O]_n$ [16], $[\{Pr(DMSO)_6(H_2O)\}_2(PMo_{12}O_{40})\cdot CH_3CN]_n$ [17], $[\{Gd(NMP)_6\}(PMo_{12}O_{40})]_n$ [18], $[Co(dpa)_2(OH_2)_2]_2[Hdpa][PCoW_{11}O_{39}]$ [10(a)], $[Ni(DETA)_2]_3[SiNiW_{11}O_{39}]\cdot 2.5H_2O$ [10(b)], and $[H_2en]_2[Ba_{0.15}(H_2O)_2(Hen_2)]H_{1.7}[SiNaW_{11}O_{39}]\cdot 2H_2O$ [10b]. As continuation of our work [2, 10(b), 13, 16–18], in this article we report the hydrothermal synthesis and characterization of an extended 1D chain

---

*Corresponding author. Email: jyniu@henu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970902721568

$\{[Cu^I(en)_2(H_2O)]_2\{GeW_{12}O_{40}[Cu^{II}(en)_2]\}\cdot 2.5H_2O\}_n$ (**1**) built up from saturated Keggin polyanions and copper complexes.

2. Experimental

2.1. *Materials and physical measurements*

$H_4GeW_{12}O_{40}\cdot nH_2O$ was prepared by the literature method [19] and confirmed by IR spectroscopy. Other reagents were obtained from commercial sources and used without purification. C, H, and N elemental analyses were performed on a Perkin–Elmer 240C elemental analyzer. IR spectrum was recorded on a Nicolet 170 FT-IR spectrometer using KBr pellets from 4000–400 cm^{-1}. UV spectra were obtained on a U-4100 spectrometer (distilled water as solvent) from 400–190 nm. Emission/excitation spectrum was recorded on an F-7000 fluorescence spectrophotometer. TG analysis was performed on a Perkin–Elmer 7 thermal analysis instrument in flowing N_2 with a heating rate of 10°C min^{-1} from 25 to 800°C.

2.2. *Preparation of 1*

A mixture of $H_4GeW_{12}O_{40}\cdot nH_2O$ (0.50 g), $CuCl_2\cdot 2H_2O$ (0.35 g), en (0.5 mL), and water (15 mL) was stirred for half an hour in air, then the pH of the mixture was carefully adjusted to 8.27 with 4 M NaOH, and it was transferred to a Teflon-lined stainless steel autoclave (30 mL) and kept at 160°C for 10 days. After the mixture slowly cooled to room temperature, black block crystals were filtered off, washed with distilled water, and air-dried to give a yield of *ca* 57% based on $H_4GeW_{12}O_{40}\cdot nH_2O$. Anal. Calcd for **1**: C, 4.06; H, 1.62; N, 4.73%. Found: C, 4.09; H, 1.58; N, 4.71%.

2.3. *X-ray crystallography of 1*

Intensity data were collected on a Bruker APEX-II CCD area detector with Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using SHELXTL-97 software [20, 21]. All non-hydrogen atoms were refined anisotropically. Organic hydrogens were generated geometrically. A summary of crystal data and structure refinement 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. *Crystal structure of 1*

The structure of **1** consists of a 1D infinite chain built from alternating $[GeW_{12}O_{40}]^{4-}$ and $[Cu(en)_2]^{2+}$ units, two crystallographically independent $[Cu(en)_2(H_2O)]^+$ cations and 2.5 free H_2O molecules (as shown in figure 1).

Table 1. Crystallographic data structure refinement for **1**.

Empirical formula	$C_{12}H_{58}Cu_3GeN_{12}O_{44.5}W_{12}$
Molecular weight	3551.96
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	21.3268(10)
b	12.4534(5)
c	44.441(2)
β	93.4920(10)
V (Å^3)	11781.2(9)
Z	8
d_{Calcd} (g cm^{-1})	3.958
Absorption coefficient (mm^{-1})	24.985
T (K)	296(2)
Wavelength (Å)	0.71073
$R[I>2\sigma(I)]$[a]	0.0455
R_w (all data)[b]	0.0998

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

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu1–N1	2.017(18)	W4–O38	2.281(11)
Cu1–N2	1.975(17)	W5–O5	1.688(12)
Cu1–N3	2.027(16)	W5–O38	2.301(11)
Cu1–N4	2.007(15)	W6–O6	1.678(13)
Cu1–O1W	2.405(14)	W6–O38	2.309(11)
Cu2–N5	2.039(19)	W7–O7	1.698(11)
Cu2–N6	2.03(2)	W7–O39	2.29(1)
Cu2–N7	2.030(17)	W8–O8	1.702(12)
Cu2–N8	2.033(17)	W8–O39	2.261(10)
Cu2–O2W	2.39(2)	W9–O9	1.715(12)
Cu3–N9	2.00(2)	W9–O39	2.326(10)
Cu3–N10	2.084(16)	W10–O10	1.655(13)
Cu3–N11	1.970(17)	W10–O40	2.265(11)
Cu3–N12	2.052(19)	W11–O11	1.704(12)
W1–O1	1.694(13)	W11–O40	2.298(11)
W1–O37	2.308(10)	W12–O12	1.687(12)
W2–O2	1.701(12)	W12–O40	2.268(11)
W2–O37	2.276(10)	Ge1–O38	1.716(11)
W3–O3	1.687(11)	Ge1–O37	1.719(10)
W3–O37	2.313(10)	Ge1–O39	1.734(10)
N2–Cu1–N4	178.2(7)	Ge1–O40	1.745(11)
N2–Cu1–N1	86.4(7)	N11–Cu3–N9	179.0(9)
N2–Cu1–O1W	88.8(6)	N11–Cu3–N12	84.9(8)
N4–Cu1–O1W	92.9(6)	O38–Ge1–O37	108.6(5)
N7–Cu2–N8	84.0(7)	O38–Ge1–O39	109.0(5)
N6–Cu2–N8	177.8(9)	O37–Ge1–O39	111.0(5)
N6–Cu2–O2W	88.1(9)	O38–Ge1–O40	108.6(5)
N7–Cu2–O2W	101.3(9)	O37–Ge1–O40	109.2(5)
W4–O4	1.712(12)	O39–Ge1–O40	110.4(5)

There are two copper coordination environments in **1**. In the $[Cu(3)(en)_2]^{2+}$ units, the coordination number of $Cu^{2+}(3)$ is six, coordinated by four nitrogens from two en ligands with Cu–N distance of 1.970(17)–2.084(16) Å and N–Cu–N angles of 84.9(8)–179.0(9)°, and two oxygens from $[GeW_{12}O_{40}]^{4-}$ to finish its distorted

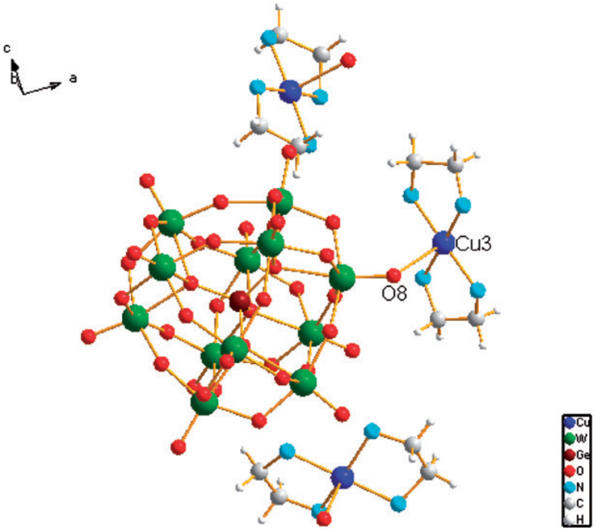

Figure 1. Molecular structure of **1**. All water molecules are omitted for clarity.

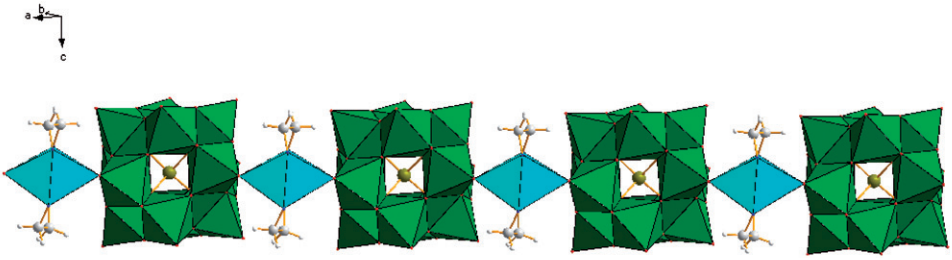

Figure 2. View of the 1-D chain in **1**. Independent $[Cu(en)_2(H_2O)]^+$ cations and all isolated water molecules are omitted for clarity. Color code: WO_6, green; CuN_4O_2, blue.

octahedral coordination environment. In two independent $[Cu(en)_2(H_2O)]^+$ cations, each Cu^+ is a distorted pyramidal geometry coordinated by four nitrogens from two en ligands and one oxygen from water. In addition, structure analysis indicates that $Cu^{2+}(3)$ connects with two terminal oxygens of $[GeW_{12}O_{40}]^{4-}$ through W(8)–O(8)–Cu(3)–O(5)–W(5) bridges (with Cu(3)–O_5/Cu(3)–O_8 distance of 2.507(13) Å/2.562(11) Å and O_5–Cu–O_8 angles of 163.8(1)°). A 1D infinite chain inorganic–organic hybrid material is formed (as shown in figure 2). Figure 3 shows the crystal packing of **1** along the *b*-axis.

The polyanion in **1** retains the well-known Keggin structure with T_d point symmetry. The central Ge, in the form of GeO_4 tetrahedron, resides in the polyanion of **1**. The Ge–O distances [1.716(11)−1.745(11) Å] and O–Ge–O angles [108.6(5)−110.0 (5)°] are consistent with the results of a previous paper [22]. The W–O_t, W–$O_{b(c)}$ and W–O_a distances vary from 1.655(13)−1.715(12) Å, 1.866(11)−1.969(12) Å and 2.261(10)−2.326(10) Å [22]. These results indicate that the GeO_4 tetrahedron and WO_6 octahedra are distorted.

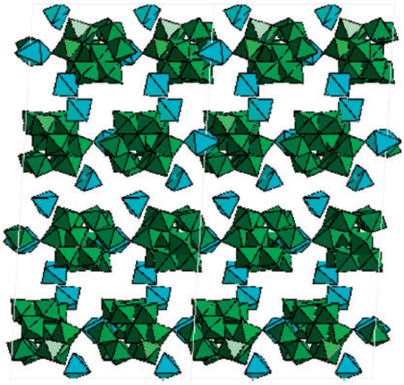

Figure 3. The crystal packing of **1** along the *b*-axis.

Bond valence sum (BVS) calculations [23] suggest that all W sites are +6 and Cu(3) sites are +2 oxidation state ($BVS_{Cu(3)} = 1.62$), while Cu(1) ($BVS_{Cu(1)} = 1.39$) and Cu(2) ($BVS_{Cu(2)} = 1.31$) sites are in the +1 oxidation state. Since the starting reagent is copper(II), some copper in **1** are +1, under hydrothermal conditions, en serves not only as a ligand but also as a reducing agent for copper(II).

3.2. *IR and UV spectra*

In the IR spectrum of **1**, there are four characteristic asymmetric vibrations resulting from polyanions with the Keggin structure, namely, $\nu_{as}(W–O_t)$, $\nu_{as}(W–O_b)$, $\nu_{as}(W–O_c)$, and $\nu_{as}(Ge–O_a)$, at 948, 869, 774, and 812 cm^{-1}, respectively. Comparing the IR spectrum of the title compound with that of $H_4GeW_{12}O_{40}$, the $W–O_t$ stretch shifted from 980 to 948 cm^{-1}; the $Ge–O_a$, $W–O_b$, and $W–O_c$ vibrations shifted from 818 to 812 cm^{-1}, 883 to 869 cm^{-1} and 760 to 774 cm^{-1} [22], indicating that $[GeW_{12}O_{40}]^{4-}$ is affected by the surrounding metal cations. This is in agreement with the result of the single-crystal X-ray diffraction analysis. In addition, vibrations at 3309, 2891, and 1627 cm^{-1} are, respectively, assigned to $\nu_{as}(N–H)$, $\nu_{as}(C–H)$ and $\delta(N–H)$ of en. In contrast to free en, the $\nu(C–N)$ has a red shift from 1000 to 1400 cm^{-1}, demonstrating coordination of en to Cu. The peak at 3450 cm^{-1} is assigned to water.

The UV absorption spectra of **1** exhibit an obvious weak peak at 258 nm, assigned to $O_{b,c} \rightarrow W$ charge transfer (Supplementary material). This peak is characteristic of the Keggin polyanion [24].

3.3. *Fluorescent property*

The emission spectrum of **1** in solid state at room temperature (Supplementary material) exhibits a broad emission band with maximum intensity at 416 nm upon excitation at about 350 nm, which may be ascribed to MLCT of $[Cu(3)(en)_2]^{2+}$ [25].

3.4. *Thermal properties*

The TG curve of **1** showed two weight loss stages (Supplementary material), giving a total loss of 12.36% in the range of 25–800°C. The first step weight loss of 2.23% at 25–124°C corresponds to release of all water molecules (Calcd 2.27%). The second step weight loss of 10.13% at 270–526°C came from loss of all en molecules (Calcd 10.16%).

Supplementary material

Crystallographic data for the structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC No. 696623. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was financially supported by the Natural Science Foundation of China, Program for New Century Excellent Talents in University of Henan Province, the Foundation of Education Department of Henan Province, and the Natural Science Foundation of Henan Province.

References

[1] (a) M.I. Khan, E. Yohannes, D. Powell. *Chem. Commun.*, 23 (1999); (b) M.I. Khan. *J. Solid State Chem.*, **152**, 105 (2000); (c) J.H. Son, H. Choi, Y.U. Kwon. *J. Am. Chem. Soc.*, **122**, 7432 (2000).

[2] J.Y. Niu, Q. Wu, J.P. Wang. *J. Chem. Soc., Dalton Trans.*, **12**, 2512 (2002).

[3] M. Sadakane, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed.*, **39**, 2914 (2000).

[4] M.P. Shores, L.G. Beauvais, J.R. Long. *Inorg. Chem.*, **38**, 1648 (1999).

[5] M.P. Shores, L.G. Beauvais, J.R. Long. *J. Am. Chem. Soc.*, **12**, 775 (1999).

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

[7] A. Dolbecq, P. Mialane, L. Lisnard, J. Marrot, F. Sécheresse. *Chem. Eur. J.*, **9**, 2914 (2003).

[8] D.E. Katsoulis. *Chem. Rev.*, **98**, 359 (1998).

[9] H.T. Evans, T.J.R. Weakley, G.B. Jameson. *J. Chem. Soc., Dalton Trans.*, 2573 (1996).

[10] (a) B. Yan, X. Xu, N.K. Bu, L.S. Goh, G.D. Chia. *J. Chem. Soc., Dalton Trans.*, 2009 (2001); (b) J.-Y. Niu, Z.-L. Wang, J.-P. Wang. *J. Solid State Chem.*, **177**, 3411 (2004).

[11] M. Sadakane, M.H. Dickman, M.T. Pope. *Angew. Chem. Int. Ed. Engl.*, **39**, 2914 (2000).

[12] J.P. Wang, J.W. Zhao, J.Y. Niu, D.J. Guo, D.B. Dang. *Sci. China (Ser. B)*, **33**, 397 (2003) (in Chinese).

[13] J.P. Wang, Q. Wu, J.Y. Niu. *Sci. China (Ser. B)*, **32**, 210 (2002) (in Chinese).

[14] D. Mialane, L. Lisnard, A. Mallard, J. Marrot, E. Antic-Fidancev, P. Aschehoug, D. Vivien, F. Sécheresse. *Inorg. Chem.*, **42**, 2102 (2003).

[15] C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu. *Chem. Commun.*, 1416 (2002).

[16] J.-P. Wang, M.-L. Wei, J.-Y. Niu. *Acta Chim. Sin.*, **8**, 1276 (2003).

[17] J.-Y. Niu, M.-L. Wei, J.-P. Wang. *J. Mol. Struct.*, **689**, 147 (2004).

[18] J.-Y. Niu, M.-L. Wei, J.-P. Wang, D.B. Dang. *J. Mol. Struct.*, **655**, 171 (2003).

[19] C. Rocchiccioli-Deltcheer, M. Fournier, R. Franck, R. Thouvenot. *Inorg. Chem.*, **22**, 207 (1983).

[20] G.M. Sheldrick. *SHELXL 97*, *Program for Crystal Structure Refinement*, University of Göttingen, Germany (1997).

[21] G.M. Sheldrick. SHELXL 97, *Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).

[22] R. Thouvenot. *Spectrosc. Lett.*, **12**, 127 (1979).
[23] I.D. Brown, D. Altermatt. *Acta Crystallogr.*, **B41**, 244 (1985).
[24] E.B. Wang, G.P. Wang, R.D. Huang. *Sci. Bull.*, **37**, 1195 (1992) (in Chinese).
[25] (a) A. Sanz-Medel, C.R. Femandez, A. Garcia. *J. Analyst*, **112**, 493 (1987); (b) K. Nakamoto, N. Ohkahu. *Inorg. Chem.*, **10**, 198 (1971); (c) K. Sugiyama, D. Yoshimura. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, **286**, 239 (1996).