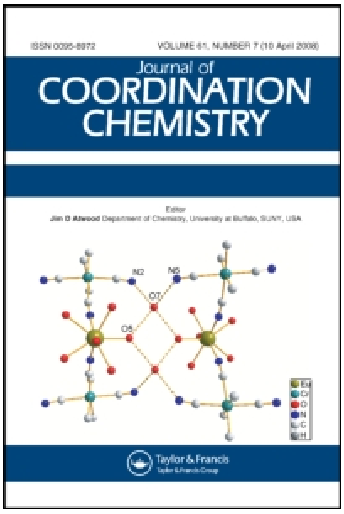
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



**Journal of Coordination Chemistry**

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

# Hydrothermal synthesis and structural characterization of two inorganic-organic composite sandwich-type tungstogermanates

Jingping Wang[a]; Jiangping Liu[a]; Jingyang Niu[a]
[a] Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, P.R. China

First published on: 10 December 2009

**To cite this Article** Wang, Jingping , Liu, Jiangping and Niu, Jingyang(2009) 'Hydrothermal synthesis and structural characterization of two inorganic-organic composite sandwich-type tungstogermanates', Journal of Coordination Chemistry, 62: 22, 3599 — 3605, First published on: 10 December 2009 (iFirst)

**To link to this Article: DOI:** 10.1080/00958970903176879

**URL:** http://dx.doi.org/10.1080/00958970903176879

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Journal of Coordination Chemistry*
Vol. 62, No. 22, 20 November 2009, 3599–3605

# Hydrothermal synthesis and structural characterization of two inorganic–organic composite sandwich-type tungstogermanates

JINGPING WANG, JIANGPING LIU and JINGYANG NIU*

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

(*Received 15 February 2009; in final form 25 May 2009*)

Two new inorganic–organic hybrid polyoxotungstates $[enH_2][C_8N_4H_{22}]_3H_2[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 6H_2O$ (**1**) and $[Co(en)_3]_2H_6[Co_4(enH)_2(GeW_9O_{34})_2] \cdot 14H_2O$ (**2**) (en = ethylenediamine) have been synthesized by hydrothermal methods and characterized by IR, TG, XRD, XPS, elemental analysis, and single-crystal X-ray analysis. The polyoxoanion frameworks of the two compounds consist of two classical tetra-Co sandwiched polyoxoanions $[Co_4(H_2O)_2(GeW_9O_{34})_2]$ in which two organic ligands substitute two water molecules. The tetra-Co clusters in **1** and **2** exhibit the familiar structural type of a $\beta$-junction at the sites of metal incorporation. Compound **1** is of interest owing to its $C_8N_4H_{20}$ ligands resulting from the reaggregation of triethylenetetramine which occurs under 160°C.

*Keywords*: Heteropolyoxotungstates; Cobalt; Sandwich-type structure; Hydrothermal synthesis

## 1. Introduction

Polyoxometalate (POM) chemistry attracts interest for their diverse properties which endows them with applications in catalysis, electrochemistry, electrochromism, and magnetism [1, 2]. Lacunary polyoxoanion precursors, as favorable multidentate ligands and allowing the inclusion of the transition metal (TM) cations, have attracted considerable attention [3–7]. Exploration of magnetic and electrochemically-active metal clusters from polyoxoanions has been a focus in transition-metal-substituted POMs (TMSPs) [8, 9]. To date, TMSPs were obtained by the reactions of lacunary POM precursors and TM ions, such as $K_4Na_4[Co_2(H_2O)_{10}Co_4(H_2O)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2] \cdot 28.5H_2O$ [5], $K_{10}Na_2[Co_4(H_2O)_2(B\text{-}\alpha GeW_9O_{34})_2] \cdot 20H_2O$ [7], $K_2Na_2Mn_2(H_2O)_{12}[Mn_2(H_2O)_{10}Mn_4(H_2O)_2(GeW_9O_{34})_2] \cdot 18H_2O$ [10], and $Na_4[Mn_4(H_2O)_{18}Mn_4(H_2O)_2(GeW_9O_{34})_2] \cdot 22H_2O$ [10]. Thus, because organic ligands may influence the coordination environments or linkage modes of substituted TMs, the direct method of assembling TMSPs with transition-metal complexes (TMCs) is

---

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

*Journal of Coordination Chemistry*
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970903176879

a challenge [11, 12]. We have attempted to search for an effective synthetic strategy, i.e., using the TMCs directly to induce the formation of TMSPs, as well as multidentate amines as structure stabilizing agents to stabilize TM oligomers, to further construct inorganic–organic composite POMs under hydrothermal conditions. In this article, we report the synthesis, structure, and characterization of two discrete compounds built from the tetra-cobalt-substituted sandwich-type $[Co_4(enH)_2(GeW_9O_{34})_2]^{10-}$ cluster.

## 2. Experimental

### 2.1. *General considerations*

All chemicals were commercially purchased and used without purification. The elemental analyses (C, H, and N) were performed using a Perkin–Elmer 2400 Series II CHNS/O elemental analyzer. Infrared spectra were obtained on a Nicolet 170SXFT-IR spectrometer with KBr pellets from 400 to 4000 $cm^{-1}$. The thermogravimetric (TG) curve was obtained with Exstar 6000 analyzer in nitrogen with a heating rate of 10°C $min^{-1}$ from room temperature to 700°C.

### 2.2. *Synthesis of 1*

$Na_2WO_4 \cdot 2H_2O$ (0.6 mmol), $GeO_2$ (0.15 mmol), and $CoCl_2 \cdot 6H_2O$ (0.15 mmol) were successively dissolved in $H_2O$ (5 mL), and triethylenetetramine (TETA) (0.05 mL) was added under stirring and the pH was adjusted to 8.91 by 4 M NaOH. The resulting mixture was stirred for 5 h, sealed in a Teflon-lined stainless steel autoclave (25 mL), kept at 160°C for 3 days and then cooled to room temperature. Purple block crystals were filtered and washed with distilled water. Yield: *ca* 23% (based on W). Anal. Calcd for $C_{30}H_{108}N_{18}O_{74}Co_4Ge_2W_{18}$ (wt%): C, 6.44; H, 1.95; N, 4.5. Found (wt%): C, 6.38; H, 2.02; N, 4.43.

### 2.3. *Synthesis of 2*

Compound **2** was isolated by the reaction of $Na_2WO_4 \cdot 2H_2O$ (0.6 mmol), $GeO_2$ (0.15 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.15 mmol), $H_2O$ (5 mL), and ethylenediamine (0.05 mL) in an analogous way to **1** at 160°C (pH = 11.04). Yield: *ca* 20% (based on W). Anal. Calcd for $C_{16}H_{100}N_{16}O_{82}Co_6Ge_2W_{18}$ (wt%): C, 3.4; H, 1.79; N, 3.98. Found (wt%): C, 3.46; H, 1.83; N, 3.95. Powder X-ray diffraction patterns of the bulk product **2** are in agreement with the calculated patterns based on single-crystal X-ray diffraction (Supplementary material).

### 2.4. *X-ray crystallography*

Purple single crystals of **1** and **2** with dimensions of $0.25 \times 0.18 \times 0.15\ mm^3$ (**1**), $0.16 \times 0.13 \times 0.11\ mm^3$ (**2**) were fixed to the end of a glass capillary. Intensity data were collected on a Bruker APEX-II CCD detector with Mo-K$\alpha$ radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares

Table 1. X-ray crystallographic data and refinements of **1** and **2**.

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{30}H_{108}N_{18}O_{74}Co_4Ge_2W_{18}$ | $C_{16}H_{100}N_{16}O_{82}Co_6Ge_2W_{18}$ |
| Formula weight | 5595.3282 | 5636.9630 |
| Crystal system | Triclinic | Monoclinic |
| Space group | *P-1* | *C2/c* |
| Unit cell dimensions (Å, °) | | |
| $a$ | 12.5837(15) | 22.569(2) |
| $b$ | 12.9233(15) | 15.5931(14) |
| $c$ | 17.441(2) | 28.746(3) |
| $\alpha$ | 74.148(2) | 90 |
| $\beta$ | 83.301(2) | 100.556(2) |
| $\gamma$ | 62.717(2) | 90 |
| Volume (Å$^3$), $Z$ | 2424.8(5), 1 | 9945.4(15), 4 |
| Calculated density (g cm$^{-3}$) | 3.822 | 3.741 |
| Absorption coefficient (mm$^{-1}$) | 22.631 | 22.395 |
| Limiting indices | $-14 \le h \le 14$; $-15 \le k \le 15$; $-20 \le l \le 13$ | $-22 \le h \le 26$; $-18 \le k \le 13$; $-34 \le l \le 34$ |
| Reflections collected | 12,537 | 25,028 |
| Independent reflections | 8466 | 8739 |
| $R_{\text{int}}$ | 0.0243 | 0.0799 |
| Refined parameters | 669 | 643 |
| Refinement method | Full-matrix least-squares on $F^2$ | Full-matrix least-squares on $F^2$ |
| $R$ | 0.0327 | 0.0508 |
| $wR$ | 0.0818 | 0.1143 |

Scheme 1. The reaction equation for the rearrangement of TETA.

on $F^2$ using the SHELXTL-97 package [13]. The organic hydrogens were generated geometrically. A summary of crystal data and structure refinement for **1** and **2** are provided in table 1.

## 3. Results and discussion

### 3.1. *Synthesis*

Compounds **1** and **2** were synthesized by the hydrothermal reaction from $Na_2WO_4 \cdot 2H_2O$, $GeO_2$, and $Co^{2+}$ in the presence of en or TETA at different pH values. The structures and procedures of the synthesis of the two compounds were essentially analogous. $[enH_2]^{2+}$ and $[C_8N_4H_{22}]^{2+}$ are countercations in **1**, but two $[Co(en)_3]^{2+}$ in **2**. In **1** $C_8N_4H_{20}$ resulted from the reaggregation of TETA which occurs under 160°C (scheme 1).

### 3.2. *Description of the crystal structures*

Single-crystal structural analyses reveal that **1** and **2** are almost isostructural but crystallize in different space group (triclinic space group *P-1* for **1** and monoclinic

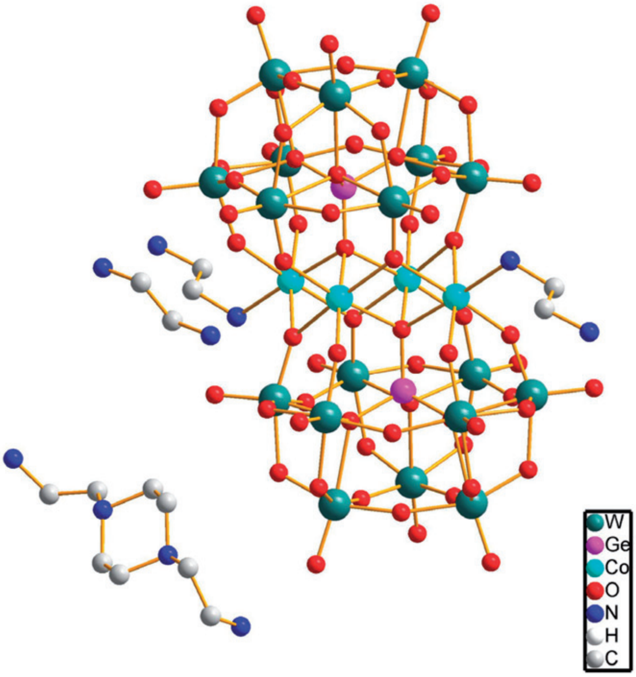


Figure 1. The ball-and-stick representation of the molecular structure of **1**. The H atoms are omitted for clarity.

space group *C2/c* for **2**). Compounds **1** and **2** contain the polyoxoanion $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$ composed of two trivacant $[B\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ subunits linked via a regular rhomblike $Co_4O_{14}N_2$ cluster leading to a sandwich-type structure where two monoprotonated ethylenediamine ligands coordinate with two Co1 ions. As shown in figure 1, the molecular structure of **1** consists of a tetra-cobalt sandwiched $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$ polyoxoanion, one diprotonated en molecule, three diprotonated $[C_8N_4H_{20}]$ molecules, two protons, and 6 lattice waters. The $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$ polyanion has the general structure of $[Co_4(H_2O)_2(GeW_9O_{34})_2]^{12-}$ but with two water molecules on the external cobalt replaced by protonated en (figure 2). The $Co_4O_{14}N_2$ cluster (Supplementary material) is defined by 14 bridging O atoms (two $\mu_4$-O from $GeO_4$ group and 12 $\mu_2$-O from 12 $WO_6$ clusters) and two nitrogens from en. Both Co1 and Co2 ions in the sandwiched core are distorted octahedrally with Co–O bond lengths in the ranges 2.074(5)–2.173(5) Å for Co1 and 1.999(6)–2.153(5) Å for Co2. Co1 is also coordinated with nitrogen with Co–N distance of 2.176(7) Å. This structural type was first reported in 1973 by Weakley *et al.* [14] for $[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$. This Keggin-based dimeric sandwich-type framework is known for most first-row TM and it is possible to substitute tetrahedral heteroelements, phosphorus(V) [15–20] by arsenic(V) [21–23], germanium(IV), and silicon(IV) [24–26]. Therefore, this structural type represents one of the largest TMSP classes. To the best of our knowledge, **1** represents the first sandwich-type germanotungstate example with chelate TETA complex cations as the charge balance cations.

Compound **2** (Supplementary material) is composed of a tetra-cobalt sandwiched polyoxoanion $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$, two $[Co(en)_3]^{2+}$ cations, six protons and

14 lattice waters. Similar to **1**, the Co1 and Co2 in the sandwich belt adopt a distorted octahedral geometry with the Co–O distances falling in the ranges 2.073(8)–2.167(8) Å for Co1 ion and 1.983(9)–2.128(8) Å for Co2 ion, and the Co1–N bond length is 2.093(10) Å. The isolated $[Co(en)_3]^{2+}$ cation is coordinated with six nitrogens from en with Co3–N distances of 1.933–1.98 Å.

In $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]^{10-}$, the heptadentate B-type trivacant Keggin cluster $[B\text{-}\alpha\text{-}XW_9O_{34}]$ can be considered as a derivative of the parent Keggin structure $[\alpha\text{-}XW_{12}O_{40}]^{4-}$ by removing three edge-sharing $WO_6$ octahedra, each providing seven oxygen donors (one from the central $XO_4$ group and one each from the six W atoms) that allows coordination to the $Co_4(enH)_2$ cluster whose four $Co^{2+}$ ions are coplanar and construct a centrosymmetric rhomblike cluster leading to the dimeric structure. In $[Co_4(enH)_2(B\text{-}\alpha\text{-}GeW_9O_{34})_2]$ there are four kinds of W–O distances: W–$O_t$, W–$O_{W2}$, W–$O_{W3Ge}$, and W–$O_{Wco}$ [27], and their bond lengths vary from 1.710(6) to 2.386(5) Å for **1** and from 1.687(10) to 2.383(8) Å for **2**. The $GeO_4$ tetrahedra in the central cavity have Ge–O distances from 1.731(4) to 1.759(5) Å for **1** and 1.728(8) to 1.753(8) Å for **2**, in good agreement with previous reports [7]. Bond valence calculations [28] for **1** and **2** confirm that the cobalts in the core of the polyoxoanion and the free Co in **2** are in the +2 oxidation state, the terminal nitrogens associated to the Co ion in the central belt of the anion are protonated and the organoamine cations are all diprotonated. Organoamine cations or cobalt–organoamine cations fill the gaps of the polyoxoanions in **1** and **2**, and hydrogen-bonding interactions exist between organoamine cations or cobalt–organoamine cations and oxygens of the polyoxoanions or lattice waters with N···O distances from 2.56 to 3.339 Å for **1** and 2.87 to 3.32 Å for **2**.

### 3.3. *IR spectra of 1 and 2*

A comparison of IR spectra of **1** and **2** is provided in "Supplementary material". In the low-wavenumber region of the IR spectra ($\nu < 1000\,cm^{-1}$), **1** displays similar patterns with **2** with four characteristic bands attributable to $\nu(W\text{–}O_t)$, $\nu(Ge\text{–}O_a)$, $\nu(W\text{–}O_b)$, and $\nu(W\text{–}O_c)$ at 935, 823, 861, and 767 $cm^{-1}$, respectively [29]. However, there are subtle differences in bands between 600 and 800 $cm^{-1}$, which distinguish the two complexes. The $\nu(W\text{–}O_c)$ stretching vibrations split into two or three bands. Stretching bands of $-OH$ and $-NH_2$ are observed at 3425–3445 $cm^{-1}$ and 3137–2846 $cm^{-1}$, respectively. Bending vibrations of $-NH_2$ and $-CH_2$ appear at 1631–1603 $cm^{-1}$ and 1455–1465 $cm^{-1}$, respectively [30].

### 3.4. *XPS spectrum of 2*

The XPS of spectrum of **2** (Supplementary material) gives one pair of peaks at 779.3 and 795.2 eV, attributable to $Co^{2+}$ $2p_{3/2}$ and $Co^{2+}$ $2p_{1/2}$, respectively [31].

### 3.5. *TG analysis of 1*

The thermal decomposition profile (Supplementary material) of **1** gives a total weight loss of 14.98% in the range of 25–700°C in agreement with the calculated weight loss of 14.89%, which can be divided into three stages. In the first step, the weight loss of

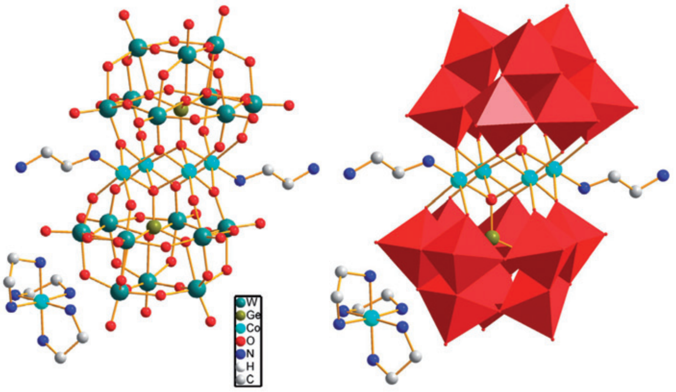


Figure 2. The ball-and-stick (left) and the polyhedral representations of the molecular structure of **2**. The H atoms are omitted for clarity.

3.66% from 25 to 300°C is due to the loss of six waters of crystallization, one structural water, and one ethylenediamine molecule. In the second stage, the weight loss of 9.95% in the range of 300–530°C is assigned to the decomposition of the remaining three $C_8N_4H_{22}$ molecules, and in the last step (530–700°C) the loss of two coordinated ethylenediamines, weight loss of 1.37%, is observed.

## 4. Conclusions

Two new heteropolyoxotungstates (**1** and **2**), synthesized hydrothermally, are comprised of two trivacant Keggin [B-$\alpha$-$GeW_9O_{34}$] fragments linked via a centro-symmetric tetrametallic unit $Co_4O_{14}N_2$ to construct a sandwich-type structure. The synthesis of two compounds using raw materials in subtle differences provides examples of paramagnetic cluster containing sandwich-type tungstogermanates. Further research will focus on the study of the reaction between raw materials and the other TM, even rare-earth metal ions, expecting to synthesize compounds with diverse nuclearities and structural features.

## Supplementary material

Supplementary data have been deposited with the Cambridge Crystallographic Centre, CCDC Nos 708525 and 708526. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44123336033; 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.T. Pope. *Heteropoly and Isopoly Oxometalates*, Springer, Berlin (1983); (b) M.T. Pope, A. Müller. *Polyoxometalates: From Platonic Solids to Anti-retroviral Activity*, Kluwer, Dordrecht, The Netherlands (1994); (c) K. Fukaya, T. Yamase. *Angew. Chem. Int. Ed.*, **42**, 654 (2003); (d) P. Mialane, A. Dolbecq, F. Sécheresse. *Chem. Commun.*, 3477 (2006).
[2] (a) C.L. Hill. *Chem. Rev.*, **98**, 1 (1998); (b) M.T. Pope, A. Müller. *Polyoxometalate Chemistry: From Topology via Self-assembly to Applications*, Kluwer, Dordrecht, The Netherlands (2001); (c) B.B. Xu, Z.H. Peng, Y.G.. Wei, D.R. Powell. *Chem. Commun.*, 2562 (2003); (d) D.L. Long, E. Burkholder, L. Cronin. *Chem. Soc. Rev.*, **36**, 105 (2007).
[3] C.L. Wang, S.X. Liu, C.Y. Sun, L.H. Xie, Y.H. Ren, D.D. Liang, H.Y. Cheng. *J. Mol. Struct.*, **841**, 88 (2007).
[4] A. Dolbecp, J.D. Compain, P. Mialane, J. Marrot, E. Rivière, F. Sécheresse. *Inorg. Chem.*, **47**, 3371 (2008).
[5] Z.M. Zhang, E.B. Wang, Y.G. Li, H.Y. An, Y.F. Qi, L. Xu. *J. Mol. Struct.*, **872**, 176 (2008).
[6] J.W. Zhao, B. Li, S.T. Zheng, G.Y. Yang. *Cryst. Growth Des.*, **7**, 2658 (2007).
[7] Z.M. Zhang, Y.F. Qi, E.B. Wang, Y.G. Li, H.Q. Tan. *Inorg. Chim. Acta*, **361**, 1797 (2008).
[8] N. Casañ-Pastor, J. Bas-Serra, E. Coronado, G. Pourroy, L.C.W. Baker. *J. Am. Chem. Soc.*, **114**, 10380 (1992).
[9] (a) C.J. Gómez-Garcia, E. Coronado, J. Borrás-Almenar. *Inorg. Chem.*, **31**, 1667 (1992); (b) H. Andres, J.M. Clemente-Juan, M. Aebersold, H.U. Güdel, E. Coronado, H. Bulttner, C. Kearly, J. Melero, R. Burriel. *J. Am. Chem. Soc.*, **121**, 10028 (1999).
[10] Z.M. Zhang, S. Yao, E.B. Wang, C. Qin, Y.F. Qi, Y.G. Li, R. Clérac. *J. Solid State Chem.*, **181**, 715 (2008).
[11] C.M. Wang, S.T. Zheng, G.Y. Yang. *Inorg. Chem.*, **46**, 616 (2007).
[12] (a) N. Belai, M.T. Pope. *Chem. Commun.*, 5760 (2005); (b) S. Reinoso, P. Vitoria, J.M. Gutierrez-Zorrilla, L. Lezama, L. San Felices, J.I. Beitia. *Inorg. Chem.*, **44**, 1190 (2005); (c) P. Mialane, A. Dolbecq, F. Sécheresse. *Chem. Commun.*, 3477 (2006).
[13] G.M. Sheldrick. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany (1997).
[14] T.J.R. Weakley, H.T. Evans Jr, J.S. Showell, G.F. Tourné, C.M. Tourné. *J. Chem. Soc., Chem. Commun.*, 139 (1973).
[15] U. Kortz, I.M. Mbomekalle, B. Keita, L. Nadjo. *Inorg. Chem.*, **41**, 6412 (2002).
[16] R.G. Finke, M. Droege, J.R. Hutchinson, O. Gansow. *J. Am. Chem. Soc.*, **103**, 1587 (1981).
[17] W.H. Knoth, P.J. Domaille, R.L. Harlow. *Inorg. Chem.*, **25**, 1577 (1986).
[18] C.J. Gómez-García, E. Coronado, P. Gómez-Romero, N. Casañ-Pastor. *Inorg. Chem.*, **32**, 3378 (1993).
[19] J.M. Clemente-Juan, E. Coronado, J.R. Galán-Mascarös, C.J. Gömez-García. *Inorg. Chem.*, **38**, 55 (1999).
[20] M.D. Ritorto, T.M. Anderson, W.A. Neiwert, C.L. Hill. *Inorg. Chem.*, **43**, 44 (2004).
[21] H.T. Evans, C.M. Tourné, G.F. Tourné, T.J.R. Weakley. *J. Chem. Soc., Dalton Trans.*, 2699 (1986).
[22] L.H. Bi, E.B. Wang, J. Peng, R.D. Huang, L. Xu, C.W. Hu. *Inorg. Chem.*, **39**, 671 (2000).
[23] L.H. Bi, R.D. Huang, J. Peng, E.B. Wang, Y.H. Wang, C.W. Hu. *J. Chem. Soc., Dalton Trans.*, 121 (2001).
[24] U. Kortz, S. Isber, M.H. Dickman, D. Ravot. *Inorg. Chem.*, **39**, 2915 (2000).
[25] E.M. Limanski, M. Piepenbrink, E. Droste, K. Burgemeister, B. Krebs. *J. Cluster Sci.*, **13**, 369 (2002).
[26] C. Rosu, D.C. Crans, T.J.R. Weakley. *Polyhedron*, **21**, 959 (2002).
[27] (a) $O_t$ is double bonded with a tungsten atom; (b) $O_{W2}$ is combined with two tungsten atoms; (c) $O_{W3Ge}$ is linked to three tungsten and one germanium atoms; (d) $O_{WCo}$ is connected with one tungsten and one or two Co atoms.
[28] I.D. Brown, D. Altermatt. *Acta Crystallogr., Sect. B*, **41**, 244 (1985).
[29] R. Thouvenot, M. Fournier, R. Franck, C. Rocchiccioli-Deltcheff. *Inorg. Chem.*, **23**, 598 (1984).
[30] G.Y. Yang, S.C. Sevov. *Inorg. Chem.*, **40**, 221 (2001).
[31] Y.B. Liu, X.B. Cui, J.Q. Xu, Y.K. Lu, J. Liu, Q.B. Zhang, T.G. Wang. *J. Mol. Struct.*, **825**, 45 (2006).