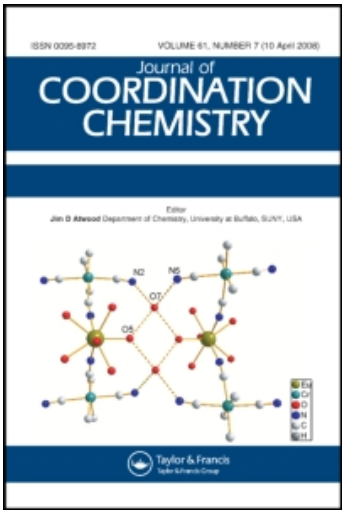

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis and crystal structure of a novel compound supported by α-Keggin units $[Cu(2,2'\text{-bipy})_2]\{W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\}\cdot 2H_2O$

Jingping Wang[a]; Yue Shen[a]; Jingyang Niu[a]
[a] School of Chemistry and Chemical Engineering, Henan University, Kaifeng, P.R. China

To cite this Article Wang, Jingping , Shen, Yue and Niu, Jingyang(2006) 'Hydrothermal synthesis and crystal structure of a novel compound supported by α-Keggin units $[Cu(2,2'\text{-bipy})_2]\{W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\}\cdot 2H_2O$', Journal of Coordination Chemistry, 59: 9, 1007 — 1014
To link to this Article: DOI: 10.1080/00958970500448283
URL: http://dx.doi.org/10.1080/00958970500448283

Journal of Coordination Chemistry
Vol. 59, No. 9, 15 June 2006, 1007–1014

Taylor & Francis
Taylor & Francis Group

Hydrothermal synthesis and crystal structure of a novel compound supported by α-Keggin units $[Cu(2,2'\text{-bipy})_2]\{AlW_{11}^{VI}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\} \cdot 2H_2O$

JINGPING WANG, YUE SHEN and JINGYANG NIU*

School of Chemistry and Chemical Engineering, Henan University, Kaifeng, 475001, P.R. China

(*Received 15 June 2005; in final form 1 August 2005*)

One of the first examples of a transition metal complex coordinated to a Keggin-type anion $[AlW_{12}O_{40}]^{5-}$: $[Cu(2,2'\text{-bipy})_2]\{AlW_{11}^{VI}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\} \cdot 2H_2O$, was prepared by the hydrothermal method. Crystal data: monoclinic, space group $P2_1/n$, $a = 18.83(3)$, $b = 20.40(4)$, $c = 21.76(4)$ Å, $\beta = 96.67(3)^\circ$, $V = 8304(2)$ Å^3, $Z = 4$, $D_c = 3.229\,Mg\,m^{-3}$, $F(000) = 7280$, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 17.402\,mm^{-1}$, $R_1 = 0.0459$, $wR_2 = 0.0902$, GOF = 1.082. The title compound is discrete, with a Keggin unit $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ linked to two transition metal coordination cations $[Cu(2,2'\text{-bipy})_2]^{2+}$ *via* two surface bridging O atoms of the Keggin unit $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$, respectively. In addition, there are discrete Cu(3) coordination cations $[Cu(2,2'\text{-bipy})_2]^{2+}$.

Keywords: Hydrothermal synthesis; Keggin structure; Crystal structure

1. Introduction

Polyoxometalates (POMs) are an important class of inorganic, anionic clusters with a diverse compositional range and significant structural versatility as well as attractive properties. They are widely used inorganic components in such diverse areas as catalysis, medicine, and materials science [1–6]. Hydrothermal methods provide a rich source of new materials both in the "traditional" inorganic framework systems and in "modern" inorganic frameworks [7, 8]. Therefore, several research efforts in polyoxometalate chemistry are focusing on the modification of polyoxoanions using various organic and/or transition metal complexes through hydrothermal synthesis [9–15]. These assemblies provide various interesting clusters [16–19]. There are relatively few reports published concerning $[AlW_{12}O_{40}]^{5-}$ [20–23] and no published report of transition metal coordination complexes supported by the Keggin unit $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$. In this article, we present the hydrothermal synthesis

*Corresponding author. Tel.: +86-378-2192443. Fax: +86-378-2853650. Email: jyniu@henu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500448283

and characterization of the Keggin heteropolymetalate compound [Cu(2,2′-bipy)$_2$]{$AlW^{VI}_{11}W^{V}O_{40}$[Cu(2,2′-bipy)$_2$]$_2$}$\cdot 2H_2O$, which is to our knowledge the first example of a transition metal complex coordinated to $[AlW^{VI}_{11}W^{V}O_{40}]^{6-}$ prepared through hydrothermal synthesis.

2. Experimental

2.1. *Materials*

All chemicals used for synthesis were reagent grade and used without further purification.

2.2. *Physical measurements and analyses*

C, H, and N elemental analyses were performed with a Perkin-Elmer 240C elemental analyzer. Thermogravimetric measurements were performed on a Exstar 6000 thermal analytical system in flowing N_2 with a heating rate of 10°C min. The IR spectra were recorded in KBr pellets with a Nicolet 170 SXFT-IR spectrometer (4000–400 cm^{-1}). The EPR spectrum was recorded with a Bruker ER-2000-DSRC10 spectrometer at the X-band at room temperature and 110 K.

2.3. *Synthesis of the title compound*

Compound **1** was prepared by the hydrothermal method from a mixture of $Cu(CH_3COO)_2\cdot 4H_2O$, $Na_2WO_4\cdot 2H_2O$, 2,2′-bipyridine, EDTA, NaOH, Al_2O_3, and H_2O in the molar ratio of 5 : 18 : 5 : 5 : 10 : 2 : 8888 heated in a Teflon-lined acid digestion bomb inside a programmable electric furnace at 180°C for three days with the starting pH = 5 adjusted by hydrochloric acid (4 M). After cooling the autoclave to room temperature for two days, black crystals were obtained. Elemental Anal. Calcd H, 1.35, C, 17.84, N, 4.16%. Found: H, 1.31, C, 17.96, N, 4.09%.

2.4. *X-ray structure determination*

A black polyhedral single crystal with dimension $0.21 \times 0.13 \times 0.12\,mm^3$ was mounted on a glass fiber for intensity data collection on a Rigaku-RAXIS-IV image plate area detector equipped with graphite monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures of the cation and anion were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL-97 program [24]. An absorption correction was performed using the SADABS program [25]. Crystal data collection parameters along with the final refinement are summarized in table 1. Selected bond lengths and bond angles are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *IR spectra*

The IR spectrum of the title compound using a KBr pellet exhibits distinctive differences in comparison with those of α-$H_5AlW_{12}O_{40}$ [20]: the vibration of the

Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_{60}H_{52}AlCu_3N_{12}O_{42}W_{12}$
Formula weight	4036.94
Temperature (K)	293(2)
Space group	$P2_1/n$
Crystal system	Monoclinic
a (nm)	1.8831(3)
b (nm)	2.0404(4)
c (nm)	2.1760(4)
β (°)	96.67(3)
Volume (nm^3)	8.304(2)
Z	4
D_c (Mgm^{-3})	3.229
μ (mm^{-1})	17.402
Reflections collected	58558
Independent reflections	14619 ($R_{int} = 0.0607$)
Parameters	1189
Goodness-of-fit on F^2	1.082
Final indices [$I > 2\sigma(I)$]	$R_1 = 0.0459$, $wR_2 = 0.0902$
R indices (all data)	$R_1 = 0.0633$, $wR_2 = 0.0958$

Table 2. Main bond lengths [nm] for the title compound.

Cu (1)–N(1)	0.198(10)	Cu(1)–N(2′)	0.199(10)
Cu(1)–N(2)	0.205(10)	Cu(1)–N(1′)	0.210(11)
Cu(1)–O(36)	0.212(8)	Cu(2)–N(3′)	0.196(10)
Cu(2)–N(4′)	0.205(12)	Cu(2)–N(3)	0.204(10)
Cu(2)–N(4)	0.198(11)	Cu(2)–O(16)	0.225(7)
Cu(3)–N(6′)	0.201(10)	Cu(3)–N(5′)	0.204(10)
Cu(3)–N(5)	0.204(10)	Cu(3)–N(6)	0.202(12)
Al(1)–O(39)	0.174(9)	Al(1)–O(38)	0.171(8)
Al(1)–O(37)	0.174(8)	Al(1)–O(40)	0.177(8)
W(1)–O(1)	0.171(8)	W(1)–O(33)	0.188(8)
W(1)–O(32)	0.189(7)	W(1)–O(14)	0.195(8)
W(1)–O(36)	0.196(7)	W(1)–O(40)	0.221(7)
W(2)–O(2)	0.171(8)	W(2)–O(30)	0.185(7)
W(2)–O(29)	0.192(8)	W(2)–O(35)	0.194(8)
W(2)–O(36)	0.198(7)	W(2)–O(40)	0.225(7)
W(3)–O(3)	0.169(8)	W(3)–O(14)	0.190(8)
W(3)–O(31)	0.191(8)	W(3)–O(35)	0.193(8)
W(3)–O(34)	0.194(7)	W(3)–O(40)	0.227(7)
W(4)–O(4)	0.171(8)	W(4)–O(25)	0.191(8)
W(4)–O(24)	0.191(7)	W(4)–O(33)	0.193(8)
W(4)–O(26)	0.195(7)	W(4)–O(39)	0.226(8)
W(5)–O(5)	0.171(8)	W(5)–O(22)	0.189(8)
W(5)–O(27)	0.189(7)	W(5)–O(23)	0.194(7)
W(5)–O(26)	0.196(8)	W(5)–O(39)	0.226(7)
W(6)–O(6)	0.172(8)	W(6)–O(26)	0.189(8)
W(6)–O(29)	0.190(8)	W(6)–O(28)	0.191(8)
W(6)–O(27)	0.197(7)	W(6)–O(39)	0.226(7)

W=O_d bonds are red shifted from 972 to 952 cm^{-1}; the W–O_b bond vibrations are red shifted from 899 to 879 cm^{-1}; and the W–O_c bond vibrations are blue shifted from 795 to 799 cm^{-1} and red shifted from 774 to 761 cm^{-1}, respectively. The results show that the solid state structure of the polyoxoanion is distorted as a result of coordination of two $[Cu(2,2'\text{-bipy})_2]^{2+}$ cations; the complex contains a third unit of

Table 3. Selected bond angles (°).

N(1)–Cu(1)–N(2′)	175.2(4)	N(1)–Cu(1)–N(2)	97.6(4)
N(2′)–Cu(1)–N(2)	80.8(4)	N(1)–Cu(1)–N(1′)	80.1(5)
N(2′)–Cu(1)–N(1′)	96.0(5)	N(2)–Cu(1)–N(1′)	109.1(4)
N(1)–Cu(1)–O(36)	87.9(4)	N(2′)–Cu(1)–O(36)	96.1(4)
N(2)–Cu(1)–O(36)	141.4(4)	N(1′)–Cu(1)–O(36)	109.5(4)
N(3′)–Cu(2)–N(4)	176.8(4)	N(3′)–Cu(2)–N(3)	81.0(4)
N(4)–Cu(2)–N(4′)	82.0(5)	N(3)–Cu(2)–N(4′)	129.8(4)
N(4)–Cu(2)–N(3)	100.5(5)	N(3′)–Cu(2)–N(4′)	99.3(5)
N(3′)–Cu(2)–O(16)	89.7(4)	N(4)–Cu(2)–O(16)	87.1(4)
N(4′)–Cu(2)–O(16)	108.8(4)	N(3)–Cu(2)–O(16)	121.4(4)
N(6′)–Cu(3)–N(6)	81.4(5)	N(6′)–Cu(3)–N(5)	110.0(4)
N(6)–Cu(3)–N(5)	144.4(5)	N(6′)–Cu(3)–N(5′)	142.2(4)
N(6)–Cu(3)–N(5′)	109.8(5)	N(5)–Cu(3)–N(5′)	82.3(4)
O(39)–Al(1)–O(37)	109.9(4)	O(39)–Al(1)–O(38)	109.4(4)
O(39)–Al(1)–O(40)	107.6(4)	O(38)–Al(1)–O(37)	109.8(4)
O(37)–Al(1)–O(40)	109.8(4)	O(38)–Al(1)–O(40)	110.4(4)

$[Cu(2,2'\text{-bipy})_2]^{2+}$ as the counter cation. Bands at 1651, 1633, 1403 cm^{-1} are assigned to characteristic vibrational modes of 2,2′-bipyridine, in which features at 1635 and 1448 are attributed to stretch vibrations of C=N bonds.

3.2. *Thermal analysis*

The TG curves of compound **2** exhibited two distinct steps. The first step, below 434°C, corresponds to the loss of lattice water and one 2,2′-bipy molecule (an exothermal peak observed at 411.5°C in the DTA curve). The second step in the range of 434 ~ 597°C corresponds to the concomitant release of five 2,2′-bipy ligands and the destruction of the skeletal framework of the polyoxoanion (two exothermal peaks observed at 466.8 and 559.6°C in DTA curve). The whole weight loss (24.35%) is in good agreement with the calculated value (24.11%).

3.3. *Electron paramagnetic resonance spectra*

The EPR spectra of the title compound at room temperature exhibit an intense signal centered at $g = 2.17$ value and a smaller one at $g = 4.49$. The intensity of the second signal progressively decreases upon cooling and almost disappears at 110 K. This can be explained by assuming the existence of a moderately strong zero-field splitting (ZFS) within the quartet state. At room temperature, two anisotropic signals within the $s = 1/2$ state and $s = 3/2$ quartet state appear, one near to the g_e value ($g = 2.25$) and other one about half-field ($g = 4.40$) [26, 27]. When the temperature is lowered to about 110 K, only the isotropic signal corresponding to the allowed transition within the $s = 1/2$ ground state remains in the spectrum. That may result from the magnetic interaction between the two closest copper(II) centers. The distance of the intramolecular Cu(3)–Cu(1) is 5.370 Å, and the shortest intermolecular Cu(3)–Cu(2) is 4.726 Å.

3.4. *Structure description*

The title compound consists of a $\{AlW_{11}^{VI}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\}^{2-}$ ion (figure 1) and a discrete $[Cu(2,2'\text{-bipy})_2]^{2+}$ cation. It is unusual that a Keggin unit $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ is

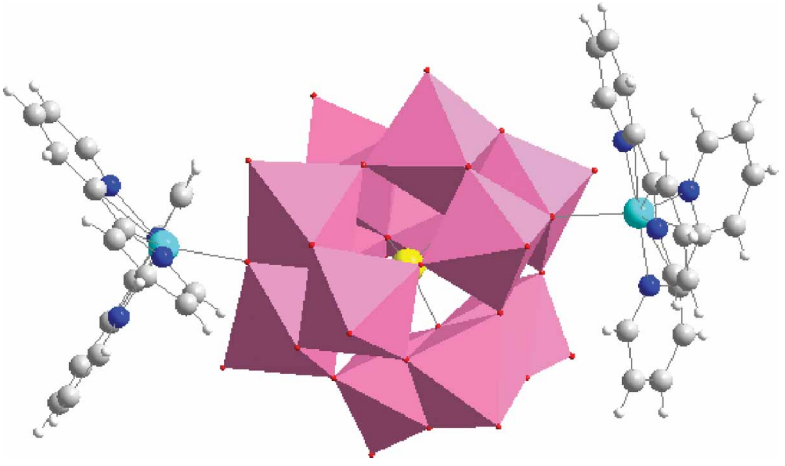

Figure 1. A polyhedral representation of the structure of $\{AlW_{11}^{VI}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\}^{2-}$ (Tungsten, cyan polyhedra; aluminium, green polyhedra; copper, purple spheres; oxygen, red spheres; nitrogen bluespheres; carbon, darkish spheres).

coordinated to two $[Cu(2,2'\text{-bipy})_2]^{2+}$ cations *via* two surface bridging O atoms [O(16) and O(36)] of the Keggin unit [28–31]. In contrast to the first reported α-Keggin heterpoloyanion coordinated to a transition metal complex [32], there are some different features: first, there is one reduced W^{V} atom in the Keggin-type heteropolyanion $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$; second, the Keggin unit and the two coordination cations $[Cu(2,2'\text{-bipy})_2]^{2+}$ are bridged *via* two surface bridging O atoms of $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ rather than terminal oxygen atoms; third, $[Cu(2,2'\text{-bipy})_2]^{2+}$ coordinated to $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ forms a five-coordinated trigonal bipyramidal moiety; last, there is a discrete square planar $[Cu(2,2'\text{-bipy})_2]^{2+}$ unit.

As expected, the $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ unit contains one AlO_4 tetrahedra and twelve WO_6 octahedra present in the four W_3O_{13} groups, in which the central Al atom is tetrahedrally coordinated by four oxygen (O_a) atoms and bridges with all 12 W atoms. Al–O bond lengths vary in the range of 1.713(8) ~ 1.769(8) Å with mean bond distance 1.740 Å, in good agreement with the literature [23]. The W–O distances vary widely, between 1.692(8) ~ 2.278(7) Å. Within the heteropolyanion, the oxygen atoms can be divided into four groups: O_t (the terminal oxygen atoms connecting only one W atom), O_b (atoms located in the share 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. Relevant W–O bonds can be classified into three categories: (1) W–O_t, 1.692(8) ~ 1.720(8) Å with mean bond distance 1.710 Å; (2) W–$O_{b,c}$, 1.850(7) ~ 1.981(7) Å with mean bond distance 1.921 Å; (3) W–O_a, 2.207(7) ~ 2.278(7) Å with mean bond distance 2.253 Å. Clearly, the W–O bond distances lengthen with increasing coordination number of the oxygen atom. In these W–O bonds, W–O(16) and W–O(36) bond distances are 1.954(8), 1.978(8) and 1.961(7), 1.981(7) Å with average distance 1.969 Å, which is longer than those of the other W–$O_{b,c}$ distances. This is attributed to the strong covalent interaction between $[Cu(2,2'\text{-bipy})_2]^{2+}$ and $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$.

Furthermore, the most interesting aspect of the title compound is that there are two kinds of Cu coordination cations (figure 2). Cu(1) and Cu(2) cations coordinated by

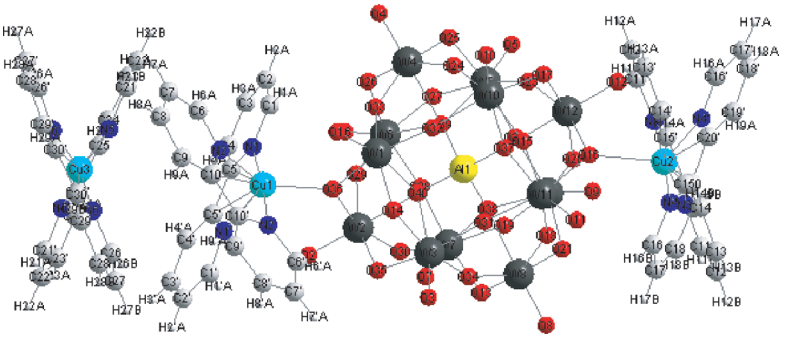

Figure 2. Structure of $[Cu(2,2'\text{-bipy})_2]\{AlW_{11}^{VI}W^{V}O_{40}[Cu(2,2'\text{-bipy})_2]_2\} \cdot 2H_2O$ (all crystal water atoms are omitted).

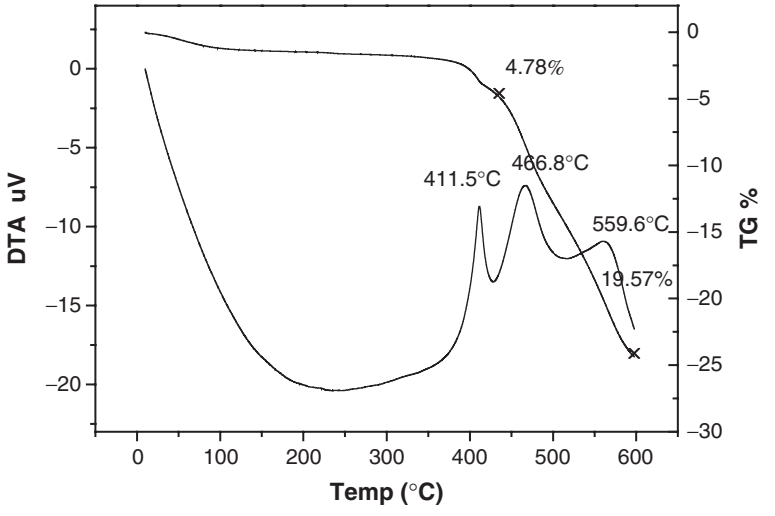

Figure 3. The TG and DTA of the title compound.

the four nitrogens of two 2,2′-bipy and one bridging O atom of the Keggin unit form two distorted trigonal bipyramid moieties, different from the typical five-coordinated copper cation [33]. Cu–N bond lengths vary in the range of 1.958(10) ~ 2.097(11) Å. N(1)–Cu(1)–N(2′) and N(3′)–Cu(2)–N(4) bond angles are 175.2(4) and 176.8(4)°, respectively. Cu–O bond lengths are 2.116(8) and 2.254(7) Å, which are much shorter than 2.421(16) Å in $[Cu(DMF)_3(H_2O)]_2[\alpha\text{-}SiW_{12}O_{40}] \cdot 3H_2O$ [32]. The reason may be that $[Cu(2,2'\text{-bipy})_2]^{2+}$ cations are linked with the Keggin unit $[AlW_{11}^{VI}W^{V}O_{40}]^{6-}$ *via* two surface bridging O atoms. In contrast, Cu(3), in the counter cation is four-coordinate with a distorted planar-square geometry, featuring Cu–N bond distances of 2.010(10) ~ 2.041(10) Å and N–Cu(3)–N bond angles ranging from 81.4(5) to 144.4(5)°. Furthermore, the dihedral angles between the ideal 2,2′-bipyridine planes in Cu(1), Cu(2) and Cu(3) are 75.9, 51.9 and 46.7°, respectively.

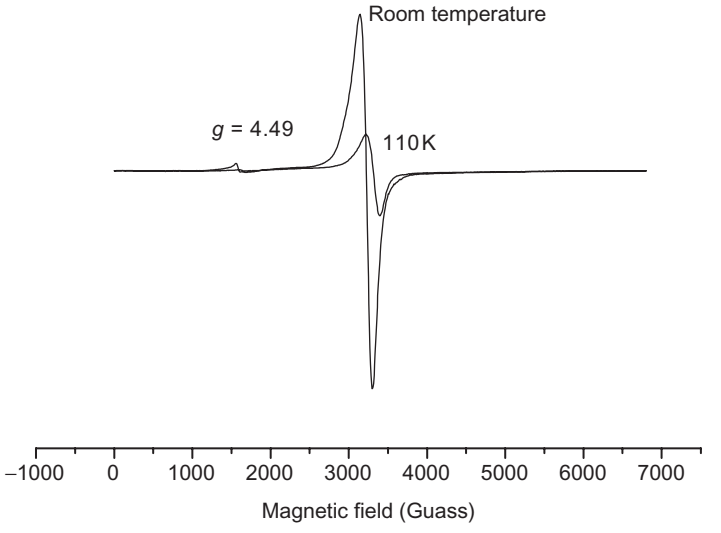

Figure 4. Room temperature (300 K) ESR spectrum of the title compound using $\nu = 9.7763$ GHZ, $g = 4.49$, $g_\xi = 2.17$, and low temperature (110 K) using $\nu = 9.4851$ GHZ, $g_\xi = 2.05$.

Supplementary material

Crystallographic data for structural analysis reported in this article have been deposited with the Cambridge Crystallographic Data Center with the deposition numbers CCDC Number 262046 for the title compound. 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; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to Special Research Fund for the Doctoral Program of Higher Education, Henan Innovation Project for University Prominent Research Talents, the Foundation of Educational Department of Henan Province and Natural Science Foundation of Henan Province.

References

[1] M.T. Pope, T. Yamase (Eds). *Polyoxometalate Chemistry for Nanocomposite Design*, Kluwer, Dordrecht (2002).
[2] A.M. Khenkin, L.J. Shimon, R. Neumann. *Inorg. Chem.*, **42**, 3331 (2003).
[3] K.F. Aguey-Zinsou, P.V. Bernhardt, U. Kappler, A.G. Mcewan. *J. Am. Chem. Soc.*, **125**, 530 (2003).
[4] D.A. Judd, J.H. Nettles, N. Nevins, J.P. Snyder, D.C. Liotta, J. Tang, J. Ermdieff, R.F. Schinazi, C.L. Hill. *J. Am. Chem. Soc.*, **123**, 886 (2001).
[5] H.D. Zeng, G.R. Newkome, C.L. Hill. *Angew. Chem.*, **112**, 1842 (2002).
[6] M. Nyman, F. Bonhomme, T.M. Alam, M.A. Rodriguez, B.R. Cherry, J.L. Krumhansl, T.M. Nenoff, A.M. Sattler. *Science*, **9**, 297 (2002).
[7] A.K. Cheetham, G. Férey, T. Loiseau. *Angew. Chem. Int. Ed.*, **38**, 3268 (1999).
[8] Z.A.D. Lethbridge, M.J. Smith, S.K. Tiwary, A. Harrison, P. Lightfoot. *Inorg. Chem.*, **43**, 11 (2004).
[9] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **38**, 2638 (1999).

[10] J.Q. Xu, R.Z. Wang, G.Y. Yang. *Chem. Commun.*, 153 (2000).
[11] Y. Xu, J.Q. Xu, K.L. Zhang, Y. Zhang, X.Z. You. *Chem. Commun.*, 153 (2000).
[12] R.G. Finke, M.W. Droege. *J. Am. Chem. Soc.*, **106**, 7274 (1984).
[13] M. Pohl, Y. Lin, T.J. R. Weakly, K. Nomiya, M. Kaneko, H. Werner, R. Finke. *Inorg. Chem.*, **34**, 767 (1995).
[14] W.S. You, E.B. Wang, Y. Xu, Y.G. Li, L. Xu, C.W. Hu. *Inorg. Chem.*, **40**, 5468 (2001).
[15] G.Y. Luan, Y.G. Li, S.T. Wang, E.B. Wang, Z.B. Han, C.W. Hu, N.H. Hu, H.Q. Jia. *Dalton Trans.*, 233 (2003).
[16] J.Y. Niu, Z.L. Wang, J.P. Wang. *Inorg. Chem. Commun.*, **6**, 1272 (2003).
[17] C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu. *J. Chem. Soc. Chem. Commun.*, 1416 (2002).
[18] A. Tripathi, T. Hughbanks, A. Clearfield. *J. Am. Chem. Soc.*, **125**, 10582 (2003).
[19] D. Hagrman, J. Zubieta. *J. Chem. Soc. Chem. Commun.*, 2005 (1998).
[20] I.A. Weinstock, J.J. Cowan, E.M.G. Barbuzzi, H.D. Zeng, C.L. Hill. *J. Am. Chem. Soc.*, **121**, 4608 (1999).
[21] M.A. Fedotov, L.P. Kazanshkii. *Izv Akad Nauk SSSR Ser Khim.*, 2000 (1988).
[22] X. López, J.M. Maestre, C. Bo, J.M. Poblet. *J. Am. Chem. Soc.*, **123**, 9571 (2001).
[23] J.M. Maestre, X. López, C. Bo, J.M. Poblet, N. Casax-Pastor. *J. Am. Chem. Soc.*, **123**, 9571 (2001).
[24] G.M. Sheldrick. *SHELXL 97*, *Program for the Refinement of Crystal Structure*, University of Göttingen, Göttingen, Germany (1997).
[25] G.M. Sheldrick. *SADABS*, University of Göttingen, Göttingen, Germany (1996).
[26] L. Banic, A. Bencini, C. Benelli, D. Gattesichi. *Inorg. Chem.*, **20**, 1399 (1981).
[27] E. Colacio, M. Dominguez-Vera, A. Escuer, R. Kivekäs, A. Romerosa. *Inorg. Chem.*, **33**, 3914 (1994).
[28] G.Y. Luan, Y.G. Li, S.T. Wang, E.B. Wang, Z.B. Han, C.W. Hu, N.H. Hu, H.Q. Jia. *Dalton Trans.*, 233 (2003).
[29] J.Y. Niu, Z.L. Wang, J.P. Wang. *Inorganic Chemistry Communications*, **6**, 1272 (2003).
[30] M. Yuan, Y.G. Li, E.B. Wang, C.G. Tian, L. Wang, C.W. Hu. *Inorg. Chem.*, **42**, 3670 (2003).
[31] Y. Lu, Y. Xu, E.B. Wang, J. Lü, C.W. Hu, L. Xu. *Crystal Growth & Design*, **5**, 257 (2005).
[32] Y. Xu, J.Q. Xu, K.L. Zhang, Y. Zhang, X.Z. You. *Chem. Comm.*, 153 (2000).
[33] J.Y. Niu, Y. Shen, J.P. Wang. *J. Molec. Struct.*, **733**, 19 (2005).