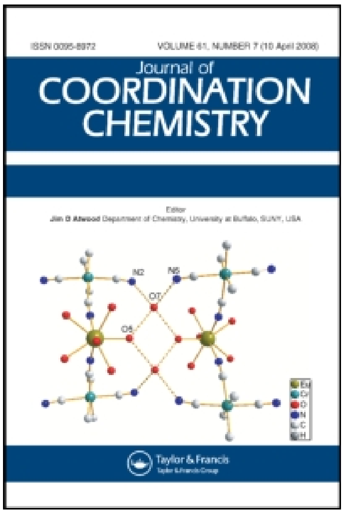

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Hydrothermal synthesis and crystal structure of a heteropolyoxotungstate formed by sandwich-type heteropolyanion $[Gd(PW_{11}O_{39})_2]^{11}$- and reduced $[Cu(en)_2]$+ cations

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Hydrothermal synthesis and crystal structure of a heteropolyoxotungstate formed by sandwich-type heteropolyanion $[Gd(PW_{11}O_{39})_2]^{11-}$ and reduced $[Cu(en)_2]^+$ cations

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A heteropolyoxotungstate, $[Cu(en)_2]_2H_8[Gd(PW_{11}O_{39})_2]\cdot(H_2en)_{0.5}\cdot 3H_2O$ (**1**), has been hydrothermally synthesized and characterized by IR, XPS, TGA and single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.651(2)$ Å^3, $b = 20.559(3)$ Å^3, $c = 21.729(3)$ Å^3, $\alpha = 71.379(2)$, $\beta = 82.829(2)$, $\gamma = 75.532(2)^\circ$, $V = 5179.5(14)$ Å^3, $Z = 2$, $R_1 = 0.0702$ and $\omega R_2 = 0.1479$. The heteropolyanion is composed of two monovacant $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ Keggin moieties linked via a Gd atom leading to a sandwich-type structure. The Gd center is in a distorted square antiprismatic coordination environment with eight oxygen atoms, four from each of the two $[\alpha\text{-}PW_{11}O_{39}]^{7-}$moieties.

Keywords: Polyoxometalates; Lanthanide; Sandwich-type; Hydrothermal synthesis

1. Introduction

Polyoxometalates (POMs) are a rich class of metal-oxygen clusters with intriguing structural diversity and unique properties that give rise to a variety of applications in fields ranging from materials science to medicine [1–4]. Attention has focused on rational syntheses and characterization of POMs with unexpected structures and properties. Incorporation of lanthanide (Ln) into POMs can be a viable route to new classes of functional materials with useful luminescent, optical and magnetic properties [5–8]. The $Ln^{III/IV}$-containing, lacunary POMs is well-known, and a number of complexes have been reported [9–18]. Within the class of lanthanopolyoxometalates (LnPOMs), complexes containing sandwich-type monolacunary POMs are an important subclass, in which two $[XM_{11}O_{39}]^{n-}$ ($X = P^V, Ge^{IV}, Si^{IV}$; $M = W, Mo$) groups sandwich a $Ln^{III/IV}$ $K_{11}H_2[Dy(SiMo_{11}O_{39})_2]\cdot 29H_2O$ [19], $K_7H_6[Nd(GeMo_{11}O_{39})_2]\cdot 27H_2O$ [20], $(NH_4)_{11}[Ln(PMo_{11}O_{39})_2]\cdot 16H_2O(Ln = Ce^{III}, Sm^{III}, Dy^{III}$ or $Lu^{III})$ [21], $K_{13}[Ce^{III}(GeW_{11}O_{39})_2]\cdot 21H_2O$ [22], $K_{12}[Ce^{IV}(SiW_{11}O_{39})_2]\cdot 28H_2O$ [23],

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$(NH_4)_2\,[N(CH_3)_4]_6Na[Ce(PW_{11}O_{39})_2]\cdot 14H_2O$ [24]. The aforementioned compounds are synthesized by traditional aqueous reactions and with alkaline or ammonium as cations, but no analogous compound containing sandwich-type heteropolyanions with a transition metal complex as countercation has been synthesized. Herein we describe the hydrothermal synthesis and crystal structure of $[Cu(en)_2]_2H_8[Gd(PW_{11}O_{39})_2]\cdot(H_2en)_{0.5}\cdot 3H_2O$, which represents the first composite containing sandwich Keggin-type polyoxotungstophosphates containing Ln prepared under hydrothermal condition, with charge balance provided by transition metal cations.

2. Experimental section

2.1. *General materials*

All reagents were purchased from commercial sources and used without further purification.

2.1.1. Synthesis of $[Cu(en)_2]_2H_8[Gd(PW_{11}O_{39})_2]\cdot(H_2en)_{0.5}\cdot 3H_2O$ (1). A mixture of Gd_2O_3 (0.02 g, 0.05 mmol), CH_3COOH (0.06 g, 1.0 mmol), $Na_2WO_4{\cdot}2H_2O$ (0.33 g, 1.0 mmol), H_3BO_3 (0.25 g, 4.0 mmol), H_3PO_4 (0.10g, 1.0 mmol), $CuCl_2{\cdot}2H_2O$ (0.10 g, 0.6 mmol), en (1.35 g, 22.4 mmol) and H_2O (16.0g, 888.9 mmol) was neutralized to pH = 4.23 with hydrochloric acid (6 mol L^{-1}). The mixture was then transferred to a 30 ml Teflon-lined autoclave inside a programmable electric furnace and reacted at 180°C for 4 days. After cooling the autoclave to room temperature over 48 h, purple block crystals of **1** were obtained, filtered off, washed with distilled water, and dried at ambient temperature (yield 60%, based on W). Elemental analysis, Calcd (%): C, 1.81; H, 0.85; N, 2.11. Found: C, 1.75; H, 0.97; N, 2.02.

2.1.2. Physical measurements. C, H and N elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. IR spectra were recorded on a Nicolet 170FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. TG curves were obtained with an EXSTAR 6000 instrument under air at a heating rate of 10°C/min. XPS analyses were performed on a AXIS ULTRA spectrometer with a Al-Kα ($h\nu = 1486.7$ eV) achromatic X-ray source.

2.1.3. *Crystal structure determination*

A purple single crystal of **1** with approximate dimensions $0.11\times 0.11\times 0.10\,mm^3$ was mounted on a glass fiber. The data were collected on a Bruker APEX-II CCD detector with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2)K in the range of $1.89 < \theta < 24.72°$. A total of 24895 (17046 unique, $R_{int} = 0.0662$) reflections were measured ($-13 \le h \le 14$, $-23 \le k \le 24$, $-25 \le l \le 24$). The structure was solved by direct methods and refined using full-matrix least-squares calculations with anistropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were performed

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

Formula	$C_9H_{51}Cu_2GdN_9O_{81}P_2W_{22}$
Formula weight	5972.55
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.651(2)
b	20.559(3)
c	21.729(3)
α	71.379(2)
β	82.829(2)
γ	75.532(2)
Volume (Å^3)	5179.5(14)
Z	2
Density (calculated) (Mg m^{-3})	3.829
Absorption coefficient (mm^{-1})	25.470
$F(000)$	5189
Crystal size (mm^3)	0.11 × 0.11 × 0.10
θ range for data collection (°)	1.89 to 24.72
Limiting indices	$-13 \le h \le 14$, $-23 \le k \le 24$, $-25 \le l \le 24$
Reflections collected	24895
Independent reflections	17046 ($R_{int} = 0.0662$)
Completeness to $\theta = 24.72°$ (%)	96.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17046/347/1183
Goodness-of-fit on F^2	0.902
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0702$, $\omega R_2 = 0.1479$
Largest diffraction peak and hole (e Å^{-3})	3.933 and –2.703

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

with SHELXTL-97 [25]. Crystallographic data are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Description of structure*

Single-crystal X-ray diffraction analysis reveals that **1** consists of one $[Gd(PW_{11}O_{39})_2]^{11-}$ heteropolyanion, two reduced cations $[Cu(en)_2]^+$, half of a diprotonated en, eight protons and three lattice water molecules. As shown in figure 1, the heteropolyanion $[Gd(PW_{11}O_{39})_2]^{11-}$ contains a Gd^{3+} cation sandwiched between two lacunary Keggin-type $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anions. The Gd^{3+} cation has a coordination number of eight and exhibits square antiprismatic geometry. The monovacant polyoxoanion $[PW_{11}O_{39}]^{7-}$ is obtained by removal of one {W = Ot} group from a saturated Keggin-type $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ anion. In the heteropolyanion $[Gd(PW_{11}O_{39})_2]^{11-}$, each monolacunary $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ is tetradentate via its four unsaturated oxygen atoms to coordinate with the Gd^{3+}. The crystal structure of **1** is similar to $[Ln(PMo_{11}O_{39})_2]^{11-}$ (Ln = Ce^{III}, Sm^{III}, Dy^{III} or Lu^{III}) reported recently by Gaunt *et al.* [21]. The sandwich-type heteropolyanion $[Ln(PW_{11}O_{39})_2]^{n-}$ was originally isolated by Peacock and Weakley [23].

Table 2. Relevant bond distances (Å) and angles (°).

Cu(1)–N(1)	1.92(3)	Cu(1)–N(3)	1.95(3)
Cu(1)–N(2)	2.04(3)	Cu(1)–N(4)	2.04(3)
Cu(2)–N(6)	1.96(3)	Cu(2)–N(6)#1	1.96(3)
Cu(2)–N(5)#1	2.09(3)	Cu(2)–N(5)	2.09(3)
Cu(3)–N(7)	2.00(2)	Cu(3)–N(7)#2	2.00(2)
Cu(3)–N(8)	2.05(3)	Cu(3)–N(8)#2	2.05(3)
P(1)–O(73)	1.50(2)	P(1)–O(72)	1.504(19)
P(2)–O(76)	1.57(2)	P(2)–O(77)	1.575(18)
Gd(1)–O(65)	2.368(19)	Gd(1)–O(68)	2.391(19)
Gd(1)–O(64)	2.39(2)	Gd(1)–O(67)	2.398(19)
Gd(1)–O(66)	2.40(2)	Gd(1)–O(70)	2.44(2)
Gd(1)–O(63)	2.45(2)	Gd(1)–O(69)	2.456(18)
W(1)–O(1)	1.66(2)	W(1)–O(63)	1.706(19)
W(1)–O(37)	1.91(2)	W(1)–O(39)	1.942(19)
W(1)–O(36)	2.09(2)	W(1)–O(71)	2.463(17)
W(2)–O(2)	1.73(2)	W(2)–O(34)	1.88(2)
W(2)–O(35)	1.882(18)	W(2)–O(32)	1.927(18)
W(2)–O(37)	1.948(19)	W(2)–O(71)	2.389(18)
W(3)–O(3)	1.75(2)	W(3)–O(23)	1.86(2)
W(3)–O(36)	1.863(18)	W(3)–O(32)	1.932(18)
W(3)–O(28)	1.965(18)	W(3)–O(71)	2.458(18)
W(4)–O(4)	1.71(2)	W(4)–O(24)	1.85(2)
W(4)–O(29)	1.883(19)	W(4)–O(35)	1.923(17)
W(4)–O(40)	2.05(2)	W(4)–O(72)	2.472(18)
W(5)–O(5)	1.66(2)	W(5)–O(40)	1.881(19)
W(5)–O(28)	1.884(18)	W(5)–O(27)	1.89(2)
W(5)–O(38)	1.952(19)	W(5)–O(72)	2.424(19)
W(6)–O(6)	1.68(2)	W(6)–O(41)	1.84(2)
W(6)–O(33)	1.907(19)	W(6)–O(29)	1.924(19)
W(6)–O(27)	1.95(2)	W(6)–O(72)	2.461(17)
W(7)–O(7)	1.73(2)	W(7)–O(26)	1.84(2)
W(7)–O(38)	1.860(19)	W(7)–O(25)	1.89(2)
W(7)–O(23)	1.961(19)	W(7)–O(73)	2.505(19)
W(8)–O(8)	1.703(18)	W(8)–O(31)	1.82(2)
W(8)–O(42)	1.908(18)	W(8)–O(33)	1.92(2)
W(8)–O(25)	1.96(2)	W(8)–O(73)	2.437(19)
W(9)–O(9)	1.62(2)	W(9)–O(64)	1.77(2)
W(9)–O(39)	1.86(2)	W(9)–O(31)	2.04(2)
W(9)–O(26)	2.07(2)	W(9)–O(73)	2.473(19)
W(10)–O(10)	1.691(18)	W(10)–O(65)	1.79(2)
W(10)–O(42)	1.885(18)	W(10)–O(30)	1.95(2)
W(10)–O(41)	2.05(2)	W(10)–O(74)	2.315(17)
W(11)–O(11)	1.726(17)	W(11)–O(66)	1.78(2)
W(11)–O(30)	1.906(19)	W(11)–O(34)	1.95(2)
W(11)–O(24)	2.08(2)	W(11)–O(74)	2.321(17)
W(12)–O(12)	1.74(2)	W(12)–O(68)	1.769(18)
W(12)–O(50)	1.907(18)	W(12)–O(43)	1.92(2)
W(12)–O(56)	2.077(18)	W(12)–O(75)	2.453(18)
W(14)–O(56)	1.815(19)	W(14)–O(61)	1.89(2)
W(20)–O(20)	1.79(2)	W(20)–O(55)	2.103(19)
O(73)–P(1)–O(74)	111.7(11)	O(75)–P(2)–O(77)	107.0(10)
O(68)–Gd(1)–O(67)	69.8(6)	O(63)–Gd(1)–O(69)	144.7(6)

Symmetry codes. #1: $-x$, $-y+2$, $-z+2$; #2: $-x$, $-y+2$, $-z+1$.

The heteropolyanion $[Gd(PW_{11}O_{39})_2]^{11-}$contains two central P atoms in the tetrahedral coordination environment of PO_4 with P–O bond lengths in the range of 1.50(2)–1.575(18) Å, and O–P–O bond angles of 107.0(10)–111.7(11)°. These data indicate that the PO_4 tetrahedra have distorted to some extent because of the replacement of $\{W=O\}^{4+}$ with Gd^{3+} cation. In the anion, every W center has a

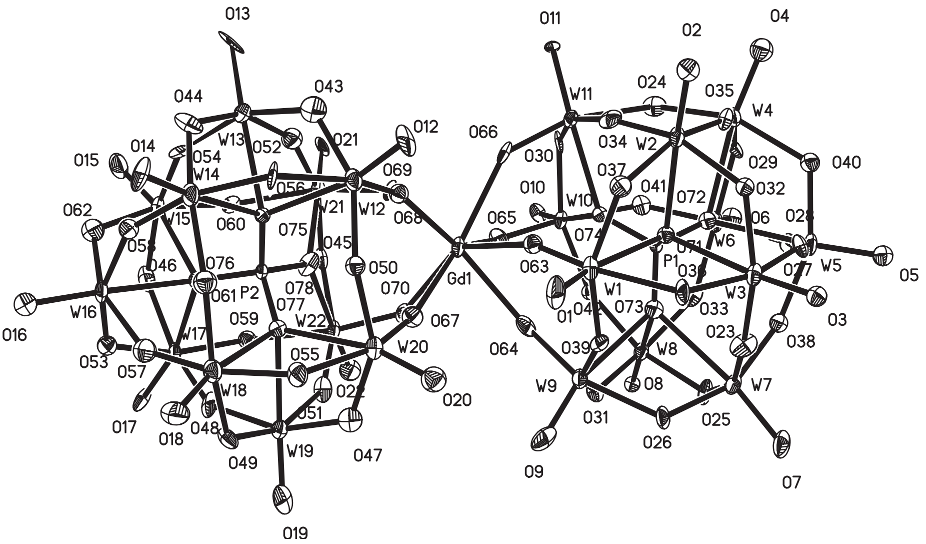

Figure 1. ORTEP view of the heteropolyanion of **1** with atom labeling, showing 30% probability displacement ellipsids.

distorted WO_6 octahedral coordination geometry, and the oxygen atom can be divided into four types according to their different coordination environments: Ot (terminal oxygen atom); Ob/c (Ob, oxygen atoms located in the shared corners between two W_3O_{13} units and Oc, oxygen atoms connecting edge-sharing WO6 octahedra in the W_3O_{13} units); Oa (oxygen atoms connecting the P and W atoms) and $O_{W(Gd)}$ (oxygen atoms connecting a W atom and a Gd atom). Thus, the W–O distances fall into four classes: W–Ot, 1.62(2)–1.79(2) Å; W–Ob/c, 1.815(19)–2.103(19) Å; W–Oa, 2.315(17)–2.505(19) Å and W–$O_{W(Gd)}$, 1.706(19)–1.79(2) Å. Two kinds of Gd–O bonds can be distinguished by their lengths for **1**. There are four "long" Gd–O bonds and four "short" ones. The "long" and "short" Gd–O bond lengths are in the ranges 2.368(19)–2.398(19) Å (av. 2.386 Å) and 2.40(2)–2.456(18) Å (av. 2.436 Å), respectively. The O–Gd–O angles are in the range of 69.8(6)–144.7(6)°. The "long" and "short" Gd–O bonds cause a distortion in the square antiprismatic geometry of GdO_8 as observed in other lanthanide complexes of lacunary polyoxometalates [19–21]. Valence sum calculations [26] confirm that in **1**, all W sites are in the +6 oxidation state and the P sites are in the +5 oxidation state. The bond valences [26] of oxygen atoms in the heteropolyanion are between 1.57 and 2.23 (average 1.91), indicating that all the oxygen atoms are unprotonated. According to the consideration of charge balance, there should be eight protons in the structural unit of **1**.

The copper in the discrete cation $[Cu(en)_2]^+$ adopts a nearly square-planar geometry, coordinated by four nitrogen donors from two en molecules with Cu-N distance of 1.92(3)–2.09(3) Å, comparable to the Cu–N distance in $[Cu^I(phen)_2]^+$ [27]. There exist strong contacts between discrete cations $[Cu(en)_2]^+$ and the $[Gd(PW_{11}O_{39})_2]^{11-}$ clusters with $Cu\cdots O$ distances of 2.644(2)–2.818(2) Å. As shown in figure 2, the $[Gd(PW_{11}O_{39})_2]^{11-}$ clusters which connect with discrete Cu1 groups are linked together by Cu2 and Cu3 fragments, alternately, through the terminal oxygen atoms to form a 1D chain, and the chains are arranged in layers parallel to the bc plane. The Cu2 and Cu3 atoms are disordered with an occupancy of 0.5. Valence sum calculations [28]

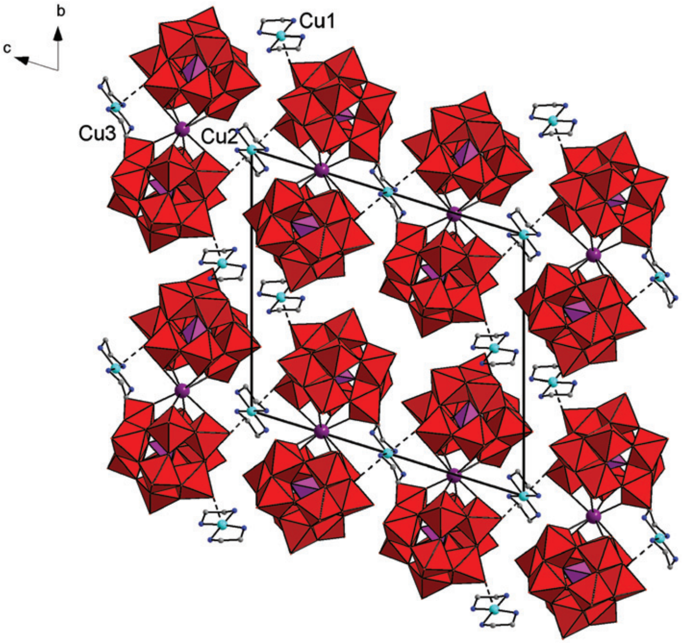

Figure 2. The packing diagram of **1** with unit cell outlines, viewed along the a-axis. Dashed lines indicate Cu…O bonds. All the water molecules and H atoms are omitted for clarity. Color code online: PO_4, purple; WO_6, red; Cu, turquiose; N, blue; C, gray.

resulted in an oxidation state in the range 1.30–1.46 (av. 1.36) for the copper centers, suggesting that all copper sites in **1** have been reduced to Cu(I). The ethylenediamine molecule in this hydrothermal reaction acts not only as ligands but also as an effective reductive agent. It is a common feature that high oxide-state metals are reduced by organic amines under hydrothermal conditions [29,30].

3.2. *IR, XPS spectra and TG analysis*

The IR spectrum of **1** exhibits bands at 1615, 1592, 1456, 1401, 1281, 1098, 1044, 948, 833, 776 and 726 cm^{-1}. There are four characteristic vibrations resulting from heteropolyanion with Keggin structure: ν_{as} (P–Oa), ν_{as} (W=Ot), ν_{as} (W–Ob) and ν_{as} (W–Oc). Comparing the IR spectrum of compound **1** with those of monovacant $[\alpha\text{-}PW_{11}O_{39}]^{7-}$ anion [1], vibration of the P–Oa bonds blue-shifted from 1085 and 1040 cm^{-1} to 1098 and 1044 cm^{-1}, respectively. The two peaks at 948 and 833 cm^{-1} should be attributed to $\nu_{as}(W=Ot)$ and ν_{as}(W–Ob), respectively. Bands at 776 and 726 cm^{-1} can be assigned to ν_{as}(W–Oc).The features at 1615, 1592, 1456, 1401 and 1281 cm^{-1} are assigned to characteristic vibrations of en.

The XPS spectra of **1** (figure 3) gives one peak at 932.7eV, ascribed to $Cu^{+}2p_{3/2}$ [31], two peaks at 35.1 and 37.2 eV, attributable to $W^{6+}4f_{5/2}$ and $W^{6+}4f_{7/2}$ [32], respectively. These results further confirm the composition of compound **1**.

The thermal analysis of **1** (figure 4) gives a loss of 5.67% in the range of 50–650°. Weight loss of 1.52% at 50–202° corresponds to the loss of water and the half free en (Calcd 1.40%). The weight loss of 4.15% at 202–650° arises to the decomposition of en ligands (Calcd 4.03%).

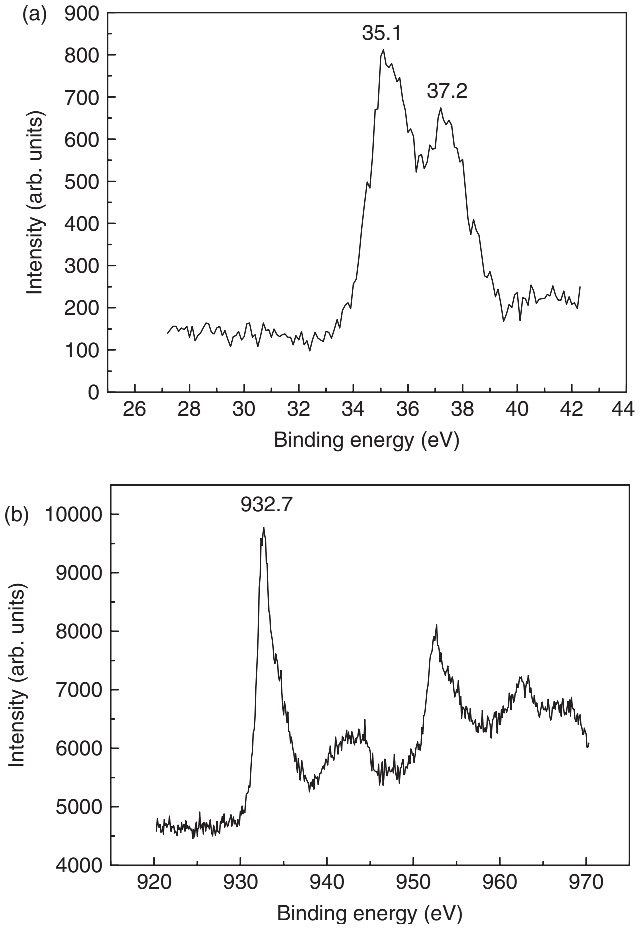

Figure 3. (a) XPS for W(VI) in **1**, (b) XPS for Cu(I) in **1**.

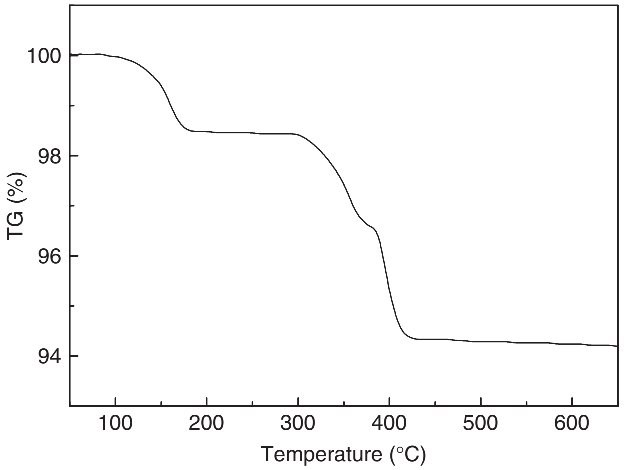

Figure 4. TG curve of **1**.

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 number 648870. 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).

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