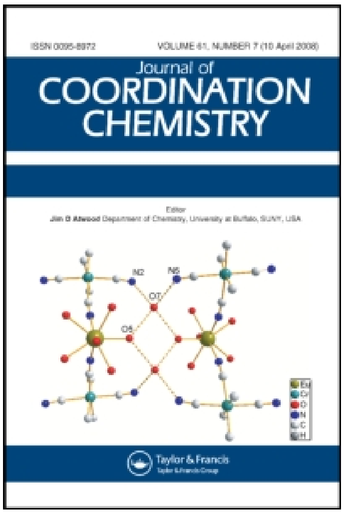

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Li, Ming-Xue , Guo, Gui-Ling and Niu, Jing-Yang(2008) 'A new organic-inorganic hybrid material constructed from Keggin polyanion and transition metal complexes: $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW^VW^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$', Journal of Coordination Chemistry, 61: 18, 2896 — 2904, First published on: 22 September 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970801986791

URL: http://dx.doi.org/10.1080/00958970801986791

Journal of Coordination Chemistry
Vol. 61, No. 18, 20 September 2008, 2896–2904

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(*Received 11 September 2007; in final form 3 December 2007*)

A new organic-inorganic hybrid compound constructed from Keggin-type polyanion clusters and transition metal complexes, $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW^VW^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$ (1), has been hydrothermally prepared and characterized by elemental analysis, IR, UV–Vis, TG-DTA and single crystal X-ray diffraction. Compound **1** crystallized in the monoclinic system, space group $C2/c$, $a = 46.995(15)$, $b = 14.487(5)$, $c = 26.205(9)$Å, $\beta = 90.000(0)^\circ$, $V = 17841(10)$Å^3, $Z = 4$. Compound **1** contains a $[SiW^VW^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]^{3-}$ polyoxoanion in which $[Co(2,2'\text{-bipy})_2(H_2O)]^{2+}$ is covalently bonded to the α-Keggin-type heteropolyanion $[SiW^VW^{VI}{}_{11}O_{40}]^{5-}$ via a terminal oxygen.

Keywords: Polyoxometalates; Hydrothermal synthesis; Dodecatungstosilicate; Keggin-type

1. Introduction

The rational design and synthesis of organic-inorganic materials has been attracting particular interest owing to their intriguing structural diversity and potential applications in the fields of catalysis, medicine and materials science [1–3]. One of the recent important advances in the design of new organic-inorganic hybrid materials is the decoration of polyoxoanions with various organic and/or transition metal complex moieties [4–6]. Owing to the remarkable features of transition metal oxide surfaces [7] and the diversities in geometric topology and oxidation state of polyoxometalate clusters [1–3, 8], it is attractive to exploit chemically robust polyoxometalate clusters as building blocks to prepare polyoxometalate-based hybrid compounds. Hydrothermal crystallization, in the presence of organic templating species, is a versatile technique for synthesis of these hybrid materials [9–10]. A large number of such materials constructed from polyoxometalate clusters and transition metal complexes have been

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970801986791

hydrothermally synthesized and characterized. Typical examples include $[\{M(phen)_2\}_2(Mo_8O_{26})]$ (M=Ni or Co) [5], $[\{Ni(H_2O)_2(4,4'\text{-bpy})_2\}_2Mo_8O_{26}]$ [11], $[\{Cu_3(4,7\text{-phen})_3\}_2Mo_{14}O_{45}]$ [12], $[\{Cu(enMe)_2\}_7\{V_{16}O_{38}(H_2O)\}_2] \cdot 4H_2O$ (enMe = 1,2-diaminopropane) [13], $[Ni(phen)_2V_4O_{11}]$ [14] and $Ni(en)_3\{V^{IV}{}_{11}V^{V}{}_5O_{38}Cl[Ni(en)_2]_3\} \cdot 8.5H_2O$ [15]. However, the hydrothermal synthesis of tungsten oxide based organic-inorganic hybrid materials remains largely unexplored, except for a few Keggin [16–17] and Dawson species [18–19]. As an expansion of organic-inorganic hybrid materials, we attempted to explore the assembly of tungstate silicates with transition metals and organodiamines under hydrothermal condition. Herein we report the hydrothermal synthesis and structural characterization of α-Keggin dodecatungstosilicate anion supported cobalt-bipyridyl complex, $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW^{V}W^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$, **1**.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased from commercial sources and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. Inductively coupled plasma (ICP) analysis was performed on a Jarrel-Ash J-A1100 spectrometer. IR spectra were recorded on a Nicolet 170FT-IR spectrometer using KBr pellets in the range 4000–400 cm^{-1}. The UV–Vis spectra were obtained on a U-4100 spectrophotometer in the range 190–850 nm. TG-DTA curves were obtained with an EXSTAR 6000 instrument under air with a heating rate of 10°C min.

2.2. *Synthesis of $[Co(2,2'\text{-bipy})_3]_{1.5}[SiW^{V}W^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)] \cdot 0.5H_2O$ (1)*

A mixture of $Na_2WO_4 \cdot 2H_2O$ (2.0 mmol, 0.66 g), $NaSiO_3 \cdot 9H_2O$ (1.5 mmol, 0.42 g), $NaCH_3COO \cdot 3H_2O$ (1.0 mmol, 0.13 g), $CoCl_2 \cdot 6H_2O$ (0.8 mmol, 0.19 g), $H_2C_2O_4 \cdot 2H_2O$ (1.5 mmol, 0.19 g), 2,2′-bipyridine (0.4 mmol, 0.06 g) and H_2O (888.9 mmol, 16 ml) was stirred for 3 h in air. Then the pH was adjusted to 4.20 by hydrochloric acid (6 mol L^{-1}) and the mixture was transferred to a 30 mL Teflon-lined autoclave and kept at 165°C for 5 days. After slow cooling to room temperature, dark red block crystals of **1** were filtered off, washed with distilled water, and dried at ambient temperature. Anal. Calcd for 1: Co, 3.62; Si, 0.69; W, 54.03; C, 19.19; H, 1.35; N, 4.47(%). Found: Co, 3.79; Si, 0.92; W, 53.76; C, 19.12; H, 1.23; N, 4.61(%).

2.3. *X-ray crystallography*

The structure of **1** was determined by single crystal X-ray diffraction. A dark red single crystal of **1** with approximate dimensions $0.12 \times 0.10 \times 0.09$ mm^3 was mounted on a glass fiber. 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 $2.07 < \theta < 25.00°$. A total of 44108(15630 unique, $R_{\text{int}} = 0.1701$) reflections were measured ($-55 \leq h \leq 55$,

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

Formula	$C_{65}H_{55}Co_{2.5}N_{13}O_{41.5}SiW_{12}$
Formula weight	4063.82
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C*2/*c*
Unit cell dimensions (Å, °)	
a	46.995(15)
b	14.487(5)
c	26.205(9)
β	90.000(0).
Volume (Å^3), Z	17841(10), 4
D_{Calcd}(Mg m^{-3})	3.024
Absorption coefficient (mm^{-1})	15.960
F(000)	14684
Crystal size (mm^3)	$0.12 \times 0.10 \times 0.09$
θ range for data collection (°)	2.07 to 25.00
Limiting indices	$-55 \le h \le 55$, $-9 \le k \le 17$, $-31 \le l \le 31$
Reflections collected	44108
Independent reflections	15630 ($R_{\mathrm{int}} = 0.1701$)
Completeness to $\theta = 25.00°$ (%)	99.5
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15630/198/1218
Goodness-of-fit on F^2	0.970
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0660$, $\omega R_2 = 0.1519$
Largest diffraction peak and hole (e Å^{-3})	3.081 and –3.882

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

$-9 \le k \le 17$, $-31 \le l \le 31$). The structures were 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. Full crystallographic information is provided in the Supporting Information in CIF format. All calculations were performed using SHELXTL-97 [20]. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

3. Result and discussion

3.1. *Synthesis*

Hydrothermal synthesis is an effective strategy in the preparation of new organic-inorganic hybrid solid materials [21–22]. Under hydrothermal conditions, factors such as the type of initial reactants, temperature, pH values, reactant stoichiometry and reaction time can influence crystal growth and composition of products. In our synthesis, $H_2C_2O_4 \cdot 2H_2O$ was used as a reducing agent and to maintain the pH of the reaction mixture; the pH was found to be critical for crystallization of products. After parallel experiments, it was found that dark red crystals of **1** could only be obtained in the pH range 4.0–4.5, and no crystalline product could be obtained beyond this pH range.

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

Co(1)–N(2′)	2.096(18)	Co(1)–N(1′)	2.111(17)
Co(1)–N(2)	2.112(19)	Co(1)–O(1W)	2.118(14)
Co(1)–N(1)	2.119(19)	Co(1)–O(5)	2.126(12)
Co(2)–N(3′)	2.103(17)	Co(2)–N(4)	2.107(15)
Co(2)–N(5′)	2.141(15)	Co(2)–N(5)	2.148(16)
Co(2)–N(3)	2.147(16)	Co(2)–N(4′)	2.147(16)
Co(3)–N(6)#1	2.104(16)	Co(3)–N(6)	2.104(16)
Co(3)–N(7′)	2.159(15)	Co(3)–N(7′)#1	2.159(15)
Co(3)–N(7)#1	2.169(18)	Co(3)–N(7)	2.169(18)
Si(1)–O(40)	1.554(12)	Si(1)–O(37)	1.567(12)
Si(1)–O(38)	1.606(14)	Si(1)–O(39)	1.634(12)
W(1)–O(1)	1.710(11)	W(1)–O(31)	1.912(13)
W(1)–O(34)	1.917(10)	W(1)–O(33)	1.939(11)
W(1)–O(32)	1.941(11)	W(1)–O(37)	2.381(11)
W(2)–O(2)	1.728(12)	W(2)–O(26)	1.912(12)
W(2)–O(13)	1.915(11)	W(2)–O(27)	1.943(11)
W(2)–O(33)	1.948(11)	W(2)–O(37)	2.370(12)
W(3)–O(3)	1.693(12)	W(3)–O(32)	1.922(11)
W(3)–O(28)	1.928(11)	W(3)–O(27)	1.929(11)
W(3)–O(17)	1.958(12)	W(3)–O(37)	2.378(11)
W(4)–O(4)	1.737(14)	W(4)–O(16)	1.896(12)
W(4)–O(18)	1.913(12)	W(4)–O(13)	1.938(11)
W(4)–O(22)	1.940(12)	W(4)–O(38)	2.381(12)
W(5)–O(5)	1.724(11)	W(5)–O(20)	1.893(11)
W(5)–O(14)	1.894(13)	W(5)–O(36)	1.910(13)
W(5)-O(18)	1.939(12)	W(5)–O(38)	2.321(11)
W(6)–O(6)	1.760(12)	W(6)–O(17)	1.886(12)
W(6)–O(15)	1.912(13)	W(6)–O(22)	1.952(11)
W(6)–O(20)	1.989(11)	W(6)–O(38)	2.340(12)
W(7)–O(7)	1.694(13)	W(7)–O(28)	1.905(11)
W(7)–O(15)	1.922(12)	W(7)–O(35)	1.947(13)
W(7)–O(30)	1.952(11)	W(7)–O(39)	2.315(11)
W(8)–O(8)	1.702(13)	W(8)–O(24)	1.900(12)
W(8)–O(30)	1.925(12)	W(8)–O(21)	1.927(12)
W(8)–O(14)	1.947(13)	W(8)–O(39)	2.361(11)
W(9)–O(9)	1.734(12)	W(9)–O(34)	1.907(10)
W(9)–O(35)	1.917(11)	W(9)–O(29)	1.928(12)
W(9)–O(21)	1.943(11)	W(9)–O(39)	2.367(11)
W(10)–O(10)	1.702(11)	W(10)–O(26)	1.902(11)
W(10)–O(19)	1.914(11)	W(10)–O(25)	1.924(12)
W(10)–O(16)	1.925(12)	W(10)–O(40)	2.374(10)
W(11)–O(11)	1.703(13)	W(11)–O(31)	1.902(13)
W(11)–O(29)	1.910(12)	W(11)–O(19)	1.913(11)
W(11)–O(23)	1.919(12)	W(11)–O(40)	2.401(10)
W(12)–O(12)	1.690(12)	W(12)–O(36)	1.896(13)
W(12)–O(24)	1.928(12)	W(12)–O(25)	1.936(12)
W(12)–O(23)	1.950(12)	W(12)–O(40)	2.346(10)
O(38)–Si(1)–O(39)	108.4(7)	O(40)–Si(1)–O(37)	110.4(7)
N(4)–Co(2)–N(5′)	169.5(6)	N(3′)–Co(2)–N(3)	76.2(7)
N(7′)–Co(3)–N(7)	76.5(6)	N(7′)–Co(3)–N(7′)#1	174.6(8)

Symmetry transformations used to generate equivalent atoms. #1: $-x+1$, y, $-z+1/2$.

3.2. *Crystal structure of 1*

Single-crystal X-ray diffraction reveals that the asymmetric unit of **1** consists of a $[SiW^{V}W^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]^{3-}$ polyoxoanion, 1.5 isolated $[Co(2,2'\text{-bipy})_2]^{2+}$ cations and 0.5 lattice water molecules (figure 1). The polyoxoanion $[SiW^{V}W^{VI}{}_{11}O_{40}Co(2,2'\text{-bipy})_2(H_2O)]^{3-}$ is composed of a reduced heteropolyanion

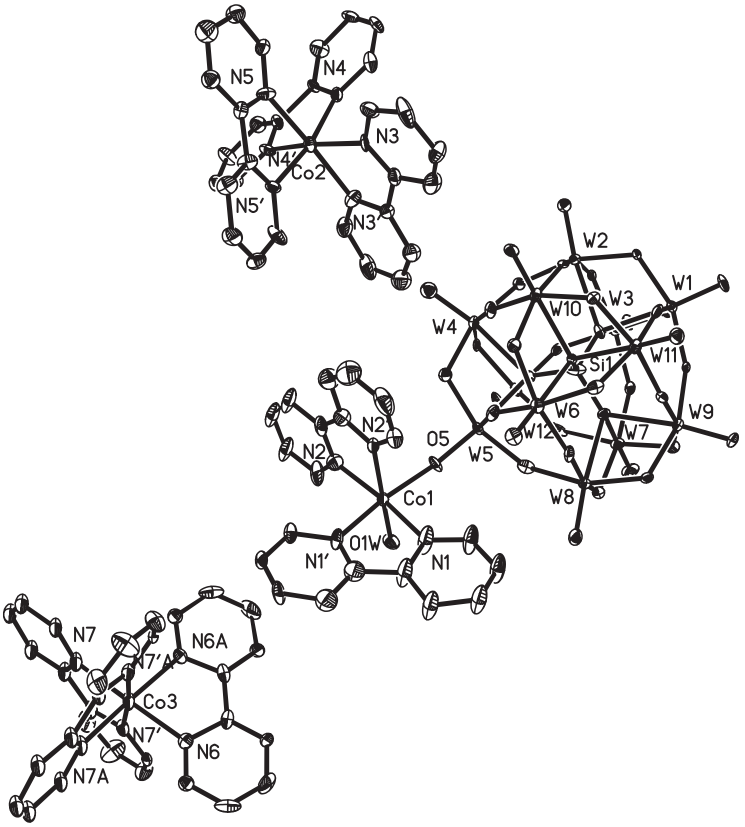

Figure 1. ORTEP view of the molecular structure of **1** with atom labeling (30% probability displacement ellipsoids). All the H atoms and lattice water molecules are omitted for clarity. Symmetry code: $-x+1$, y, $-z+1/2$.

and a covalently linked cobalt(II) complex fragment $[Co(2,2'\text{-bipy})_2(H_2O)]^{2+}$ (figure 2). The heteropolyanion $[SiW^{V}W^{VI}{}_{11}O_{40}]^{5-}$ exhibits the well-known α-Keggin-type structure, which consists of a central SiO_4 tetrahedron surrounded by twelve WO_6 octahedra. The twelve WO_6 octahedra are arranged in four W_3O_{13} groups, each of which is composed of three WO_6 octahedra in edge-sharing mode. These four W_3O_{13} groups are linked to each other by sharing corners and linked to the central SiO_4 tetrahedron. In the heteropolyanion, the oxygen atoms can be divided into five different coordination environments: Ot (terminal oxygen atoms), Ot’ (terminal oxygen atoms linked to Co), Ob (oxygen atoms located in the shared corners between two W_3O_{13} units), Oc (oxygen atoms connecting edge-sharing WO_6 octahedra in the W_3O_{13} unit) and Oa (oxygen atoms connecting the Si and W atoms). Relevant W–O bonds can be classified into four categories: W–Ot 1.690(12)–1.760(11), W–Ot′ 1.724(11), W–Ob,c 1.886(12)–1.989(11), and W–Oa 2.315(11)–2.401(10)Å. The Si–O bond lengths fall in the range 1.554(12)–1.634(12) Å, and the O–Si–O bond angles are within the 108.4(7)–110.4(7)° range. These bond lengths and bond angles are in agreement with those found in the literature [23].

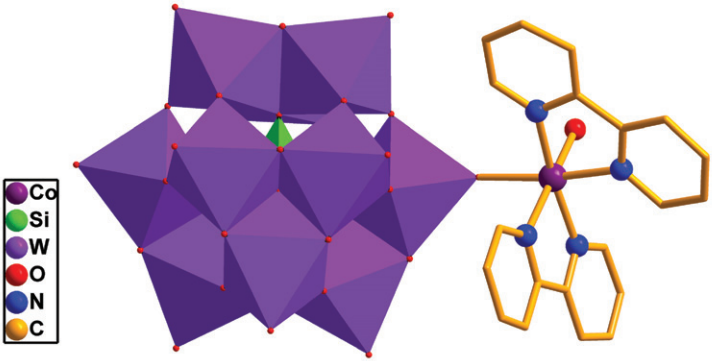

Figure 2. Polyhedral and ball-stick representation of the polyoxoanion $[SiW^{V}W^{VI}{}_{11}O_{40}Co(2,2'\text{-}bipy)_2(H_2O)]^{3-}$ in compound **1**.

The assignment of oxidation states for the W atoms in **1** has been confirmed by valence sum calculation [24] which gives values of 5.64–6.10 for W(1)–W(12), respectively (Table S1).The average value for the calculated oxidation state of W is 5.88 (the expected average value for $W^{VI}{}_{11}W^{V}$ 5.91), indicating that there is one reduced W^{5+} center with one electron delocalized within the whole $[SiW^{V}W^{VI}{}_{11}O_{40}]^{5-}$ cluster. The calculated result is consistent with the formula of **1**.

The prominent feature in the structure of 1 is that each $[SiW^{V}W^{VI}{}_{11}O_{40}]^{5-}$ cluster is linked to a $[Co(2,2'\text{-}bipy)_2(H_2O)]^{2+}$ fragment through one terminal oxygen atom of $W(5)O_6$ octahedron (Co1–O5 = 2.126(12) Å) to form a supporting complex cluster. In comparison with the Co–O distance in $[Co(en)_2]_2\{[Co(en)_2][HMo^{VI}{}_4Mo^{V}V^{IV}{}_8O_{40}(PO_4)]\}\cdot 5H_2O$ [25], the Co–O distance in **1** is much shorter, indicating that the $[Co(2,2'\text{-}bipy)_2(H_2O)]^{2+}$ is more strongly bonded to the polyoxoanions. Co1 is six-coordinate in a distorted octahedral coordination geometry, which is completed by four nitrogens from two 2,2′-bipy ligands with Co1–N distances of 2.096(18)–2.119(19) Å and N–Co1–N bond angles of 77.4(7)–171.9(7)°, one terminal oxygen atom (O5) from the Keggin-type polyoxoanions, and one water with Co1–O1W distance of 2.118(14) Å. The structure of **1** is isomorphous with $[Ni(2,2'\text{-}bipy)_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-}bipy)_2\text{-}(H_2O)]\cdot 0.5H_2O$ [6] and $[Co(2,2'\text{-}bipy)_3]_{1.5}\{[Co(2,2'\text{-}bipy)_2(H_2O)][HCoW_{12}O_{40}]\}.0.5H_2O$ [26]. The linkage between the heterometal complexes and the Keggin polyanions in **1** is similar to that in $[Ni(bipy)_3]_{1.5}[\{Ni(bipy)_2(H_2O)\}H_3W_{12}O_{40}]\cdot 0.5H_2O$ [27],$[Cu(en)_2(H_2O)]_2[\{Cu(en)_2\}H_2W_{12}O_{40}]\cdot 10H_2O$ [28], $[Cu(en)_2(H_2O)]_2[\{Cu(en)_2\}HPW_{12}O_{40}]\cdot 2H_2O$ [29] and the two reported isomorphous compounds [6, 26], but different from that in $[Zn(2,2'\text{-}bipy)_3]_2[ZnW_{12}O_{40}Zn(2,2'\text{-}bipy)_2]\cdot H_2O$ [30]. In the structure of the latter compound, the Keggin unit $[ZnW_{12}O_{40}]^{6-}$ is covalently linked to a transition metal complex through a terminal oxygen atom and a bridging atom.

Each Co in the discrete cations exhibits distorted octahedral geometry, defined by six nitrogen atoms from three 2,2′-bipy ligands with Co(2)–N and Co(3)–N distances in the range of 2.103(17)–2.148(16) Å (av. 2.132 Å) and 2.104(16)–2.169(18) Å (av. 2.144 Å), respectively. While the N–Co(2)–N and N–Co(3)–N angles are in the range of 76.2(7)–169.5(6)° and 76.5(6)–174.6(8)°, respectively.

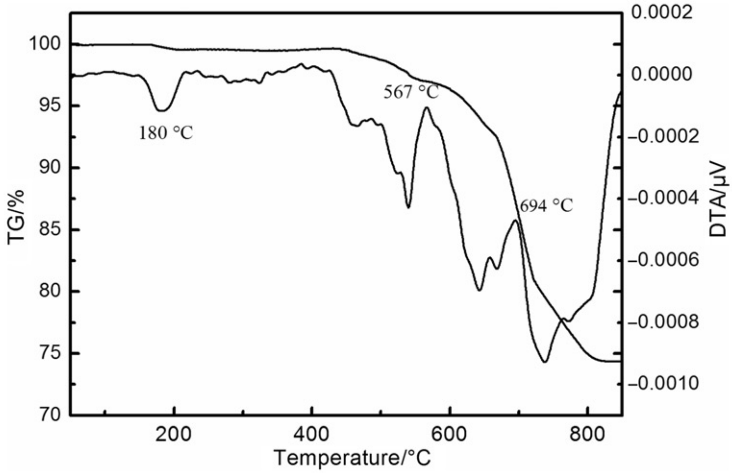

Figure 3. The TG-DTA curve of compound **1**.

3.3. *IR and UV–Vis spectra*

The IR spectrum, (fig. S1) of **1** exhibits four characteristic vibration peaks resulting from the Keggin-type heteropolyanion, namely, ν_{as} (Si–Oa), ν_{as} (W–Ob), ν_{as} (W–Oc) and ν_{as} (W = Ot), at 906; 894; 767 and 951cm^{-1}, respectively. Comparing the IR spectrum of **1** with that of α-$H_4SiW_{12}O_{40} \cdot nH_2O$ [31], the vibrational band of the Si–Oa, W=Ot and W–Oc bonds are red-shifted from 928, 981 and 785 cm^{-1} to 906, 951 and 767 cm^{-1}, respectively. The W–Ob vibration is blue-shifted from 880 to 894 cm^{-1}. These results indicate that the heteropolyanions in compound **1** still maintain basic Keggin structure but are distorted due to coordination, in agreement with the single-crystal X-ray diffraction analysis. The bands in the 1574–1104 cm^{-1} region are ascribed to characteristic vibrations of 2,2′-bipy groups. Absorptions at 1175 and 1104 cm^{-1} can be regarded as the ring stretch of 2,2′-bipy [32]; 1597 cm^{-1} can be assigned to lattice water.

The UV–Vis spectrum (fig. S2) of **1** in distilled water shows absorption bands at 192 and 255 nm (characteristic of Keggin anion), assigned to the charge-transition absorption of Ot → W and Ob,c → W [33], respectively.

3.4. *TG-DTA analysis*

As shown in figure 3, the TG curve of **1** exhibits two steps of weight loss. The first weight loss is 0.45% at 50–210°C, corresponding to release of coordinated and lattice water molecules (Calc 0.66%). There is an endothermal peak at 180°C in the corresponding DTA curve from release of water. The second weight loss of 25.20% in the temperature range 272–850°C is attributed to decomposition of 2,2′-bipy ligands (Calc 24.98%). In the second step, the DTA curve reveals two exothermal peaks at 567 and 694°C which correspond to the combustion of the 2,2′-bipy ligands and decomposition of the polyoxoanion framework, respectively. The whole weight loss (25.65%) is in agreement with the calculated value (25.64%).

4. Conclusion

Success in preparing compound **1** demonstrates that the combination of hydrothermal synthesis and incorporation of appropriate templates provides a method for isolation of hybrids containing covalently bonded transition metal complexes and polyoxotungstate clusters. The success opens up an interesting area of research in which versatile organic-inorganic hybrid compounds based on polyoxotungstate could be isolated by introducing various transition metal complex moieties and optimizing the reaction conditions. Further investigations of this work are underway.

Supplementary materials

Crystallographic data for the structural analysis reported in this paper has been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC number 659924. 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).

Acknowledgements

This work was supported by the Nature Science Foundation of China, the Program for New Century Excellent Talent in University of Hennan Province, the Foundation of Educational Department of Henan Province, and the Natural Science Foundation of Henan Province.

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