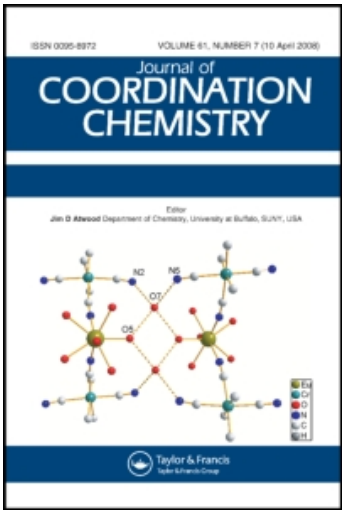

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Hydrothermal synthesis and structure characterization of a new organic-inorganic composite $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$

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HYDROTHERMAL SYNTHESIS AND STRUCTURE CHARACTERIZATION OF A NEW ORGANIC–INORGANIC COMPOSITE $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40}) \cdot 6H_2O$

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A new organic–inorganic composite $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40}) \cdot 6H_2O$ has been prepared by hydrothermal reaction and characterized by elemental analysis, IR and UV spectra, thermal analysis and single-crystal X-ray structural analysis. It belongs to the monoclinic system, space group $P2_1/c$, with $a = 18.637(4)$, $b = 14.003(3)$, $c = 26.470(5)$ Å, $\beta = 104.78(3)^\circ$, $V = 6680(2)$ Å^3, $Z = 4$. Structural analysis indicates that the title complex consists of a Keggin anion $[ZnW_{12}O_{40}]^{6-}$, 4,4′-bipyridine and water of crystallization, constructing a supramolecular system through hydrogen bonding interactions. Thermal analysis shows that the heteropolyanion $[ZnW_{12}O_{40}]^{6-}$ starts to decompose at 587.0°C.

Keywords: Polyoxometalates; Hydrothermal synthesis; Crystal structure; Zinc

INTRODUCTION

Since one of the earliest polyoxometalates of ammonium phosphomolybdate $[NH_4]_3[PMo_{12}O_{40}] \cdot xH_2O$ was synthesized by Berzelius [1] and its tungsten analogue of the Keggin compound $[H_3PW_{12}O_{40}] \cdot 5H_2O$ [2] was determined by Keggin through X-ray diffraction, the Keggin compounds continue to have an important place at the forefront of polyoxometalates because of their robust structure, remarkable electron donor–acceptor attributes, unusual magnetic properties, and potential for use in new medicines and materials [3–7]. Thus, the Keggin polyoxometalates have been widely used as building blocks in the design and synthesis of novel compounds, coupling magnetic and conducting properties with organic electric donors as ET or TTF [8–10]. Among known previously reported compounds, most heteroatoms, however, are main group elements (P, Si) [8,11] or a few transition metals (V, Co) [12,13]. Moreover, most of them are prepared by conventional aqueous solution syntheses. According to the literature, Keggin compounds containing the central $\{ZnO_4\}$ group have not yet been

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structurally characterized, except for $[Zn(2,2'\text{-bipy})_3]_2[ZnW_{12}O_{40}Zn(2,2'\text{-bipy})_2]\cdot H_2O$ [14]. Herein we report the hydrothermal synthesis and characterization of a new organic–inorganic composite $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$.

EXPERIMENTAL

Materials and Physical Measurements

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H and N elemental analyses were performed on a Perkin-Elmer 240 C elemental analyzer. An infrared spectrum was recorded as KBr pellets on a Nicolet170 SXFT-IR spectrometer in the range 400–4000 cm^{-1}. A UV spectrum was obtained on a Shimzu UV-250 spectrometer in the range 190–350 nm. Thermal analysis was performed on a Perkin-Elmer7 thermal analyzer in flowing nitrogen gas at a heating rate of $10^{\circ}C\,min^{-1}$.

Synthesis of $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$

A mixture of $Na_2WO_4\cdot 2H_2O$, $ZnCl_2$, $Zn(Ac)_2\cdot 2H_2O$, 4,4′-bipyridine and H_2O in the molar ratio 1:0.1:0.1:0.2:260 was placed in a 23-ml Teflon-lined acid digestion bomb inside a programmable electric furnace at 160°C for 96 h. After cooling to room temperature for 48 h, colorless crystals were obtained and filtered, separated mechanically and dried in air, resulting in a 60% yield based on W. Anal. Calcd. for $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$(%): C, 13.15; H, 1.37; N, 3.07. Found: C, 12.88; H, 1.21; N, 2.95.

X-ray Crystallography of the Title Compound

A colorless crystal of $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$ with dimensions $0.26\times 0.13\times 0.12$ mm was studied on a Rigaku RAXIS-IV image plate area detector using graphite-monochromated Mo Kα diffraction ($\lambda = 0.71073$ Å) at 293(2) K. The data collection was in the range $3.78\le 2\theta\le 52.00$ with $-22\le h\le 22$, $-16\le k\le 17$, $-32\le l\le 32$ and was refined by full-matrix least-squares techniques based on F^2 using SHELXTL-97 [15]. A total of 36 345 reflections were collected. The refinement converged at $R_1 = 0.0651$ for 12 713 observed reflections with $I\ge 2\sigma(I)$, $wR_2 = 0.0606$, $w = 1/\sigma^2(F_0^2)$. The structure was solved by direct methods. Nonhydrogen atoms were refined anisotropically. Hydrogen atoms were added according to the theoretical models. The maximum and minimum peaks on the final difference Fourier map correspond to 2.248 and -1.958 e $Å^{-3}$, respectively. Crystal parameters and other experimental details of the data collection are summarized in Table I. Relevant bond lengths and angles are provided in Table II.

Crystallographic data for the structural analysis of the title compound have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 220129. 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 or http://www.ccdc.cam.ac.uk).

TABLE I Crystal data and structure refinement parameters of the title compound

Empirical formula	$C_{40}H_{50}N_8O_{46}W_{12}Zn$
Formula weight	3650.45
Crystal system	Monoclinic
Space group	$P2_1/c$
T (K)	293(2)
λ (Å)	0.71073
a (Å)	18.637(4)
b (Å)	14.003(3)
c (Å)	26.470(5)
β (°)	104.78(3)
V (Å^3), Z	6680(2), 4
ρ (g cm^{-3})	3.630
μ (mm^{-1})	21.032
F(000)	6528
Total reflections	36 345
Independent reflections	12 713 [$R_{(int)} = 0.1355$]
Final R indices [$I > 2\sigma(I)$],	$R_1 = 0.0651$, $wR_2 = 0.0606$
R indices (all data)	$R_1 = 0.1755$, $wR_2 = 0.0730$

$w = 1/\sigma^2(F_o^2)$.

TABLE II Selected bond distances (Å) and bond angles (°) of the title compound

W(1)–O(1)	1.767(16)	W(1)–O(38)	2.150(15)
W(2)–O(2)	1.694(16)	W(2)–O(37)	2.135(15)
W(3)–O(3)	1.753(17)	W(3)–O(37)	2.189(15)
W(4)–O(4)	1.744(12)	W(4)–O(40)	2.155(13)
W(5)–O(5)	1.726(14)	W(5)–O(39)	2.193(13)
W(6)–O(6)	1.732(15)	W(6)–O(38)	2.174(13)
W(7)–O(7)	1.672(14)	W(7)–O(40)	2.135(15)
W(8)–O(8)	1.714(16)	W(8)–O(39)	2.140(16)
W(9)–O(9)	1.745(13)	W(9)–O(40)	2.134(15)
W(10)–O(10)	1.703(13)	W(10)–O(38)	2.159(12)
W(11)–O(11)	1.753(13)	W(11)–O(37)	2.152(12)
W(12)–O(12)	1.704(14)	W(12)–O(39)	2.193(13)
Zn(1)–O(39)	1.870(16)	Zn(1)–O(37)	1.900(13)
Zn(1)–O(38)	1.899(15)	Zn(1)–O(40)	1.940(12)
N(1′)–C(1′)	1.35(3)	N(1′)–C(5′)	1.32(3)
N(1)–C(1)	1.34(3)	N(1)–C(5)	1.39(3)
N(2)–C(6)	1.32(3)	N(2)–C(10)	1.34(3)
N(2′)–C(6′)	1.35(3)	N(2′)–C(10′)	1.35(3)
N(3′)–C(11′)	1.29(3)	N(3′)–C(15′)	1.30(3)
N(3)–C(11)	1.27(3)	N(3)–C(15)	1.31(3)
N(4′)–C(16′)	1.30(3)	N(4′)–C(20′)	1.33(3)
N(4)–C(20)	1.29(2)	N(4)–C(16)	1.37(2)
O(1)–W(1)–O(38)	165.4(6)	O(34)–W(1)–O(38)	71.0(6)
O(39)–Zn(1)–O(37)	108.7(7)	O(39)–Zn(1)–O(38)	109.9(6)
O(37)–Zn(1)–O(38)	110.8(6)	O(39)–Zn(1)–O(40)	109.4(6)
O(37)–Zn(1)–O(40)	108.9(6)	O(38)–Zn(1)–O(40)	109.1(6)

RESULTS AND DISCUSSION

Synthesis

From hydrothermal synthesis, compared to conventional aqueous solution syntheses, a number of novel complexes can be obtained with unusual structural features and good stability in air. Thus, hydrothermal syntheses have been widely combined with

the structure-directing properties of organic components to synthesize stable and novel organic–inorganic composites. However, the hydrothermal process is complex, affected by factors such as acidity of the starting reaction, structure-directing properties and the nature of the reaction materials. During the course of our investigation, we found that at the same molar ratio, good quality single crystals can only be obtained at pH 3–4; otherwise, only solid powders are obtained. We also discovered that after 2,2′-bipyridine substitutes for 4,4′-bipyridine, the final products will be red–violet crystals with a Keggin anion $[ZnW_{12}O_{40}]^{6-}$ supported the zinc-pyridine complex $[Zn(2,2'\text{-bipy})_3]_2[ZnW_{12}O_{40}Zn(2,2'\text{-bipy})_2]\cdot H_2O$ [14].

Structure Description

As shown in Fig. 1, the title compound is composed of one Keggin anion $[ZnW_{12}O_{40}]^{6-}$, four 4,4′-bipyridine molecules and six waters of crystallization. Like other Keggin anions [3], the $[ZnW_{12}O_{40}]^{6-}$ anion consists of a ZnO_4 tetrahedron surrounded by 12 WO_6 octahedra, present in four W_3O_{13} groups. According to the coordination environment of the oxygen in the Keggin anion, the oxygen atoms can be divided into four groups, O_t (the terminal oxygen atoms connecting to 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 (oxygen atoms connecting to the Zn and W atoms). The W–O_t, W–$O_{b,c}$ and W–O_a distances are 1.672(14)–1.767(16), 1.815(15)–2.035(14) and 2.134(15)–2.193(13) Å with average lengths 1.726, 1.913 and 2.159 Å, respectively. The angles in W are 71.0(6)–169.6(6)°. For the ZnO_4 tetrahedron, the Zn–O distances are in the range 1.870(16)–1.940(12) Å corresponding to an average value of 1.902 Å, while O–Zn–O angles range from 108.7(7)° to 110.8(6)° (average 109.47°). Compared with $[Zn(2,2'\text{-bipy})_3]_2[ZnW_{12}O_{40}Zn(2,2'\text{-bipy})_2]\cdot H_2O$ [14] (see Table III), the W–O_t, W–$O_{b,c}$ and W–O_a distance ranges become narrow. In particular, the average W–$O_{b,c}$ and W–O_a lengths are shortened significantly. All WO_6 octahedra and ZnO_4 tetrahedra in the Keggin anion are more regular than those reported in the literature [14] due to the

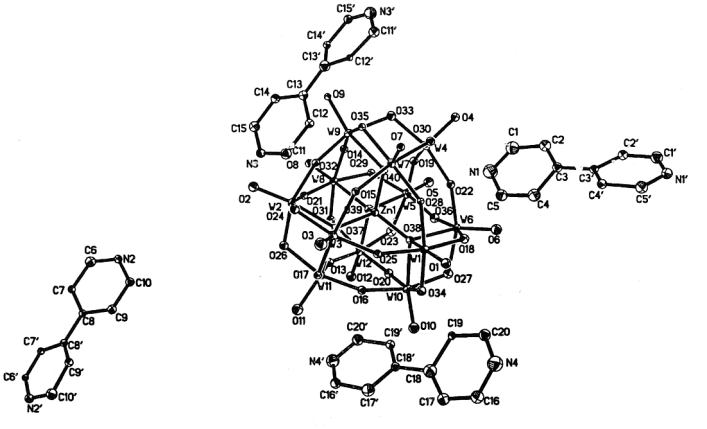

FIGURE 1 Molecular structure of $(4,4'\text{-}H_2bipy)_2(4,4'\text{-}Hbipy)_2(ZnW_{12}O_{40})\cdot 6H_2O$ with the partial labeling scheme. Water molecules and hydrogen atoms are omitted for clarity.

TABLE III Comparison of bond lengths (Å) in two compounds

Compound	$W{=}O_t$	$W{-}O_{b,c}$	$W{-}O_a$	$Zn{-}O$
$[ZnW_{12}O_{40}]^{6-}$	1.672–1.767	1.815–2.035	2.134–2.193	1.870–1.940
$[ZnW_{12}O_{40}Zn(2,2'\text{-bipy})_2]^{4-}$	1.63–1.81	1.720–2.150	1.984–2.260	1.823–1.935

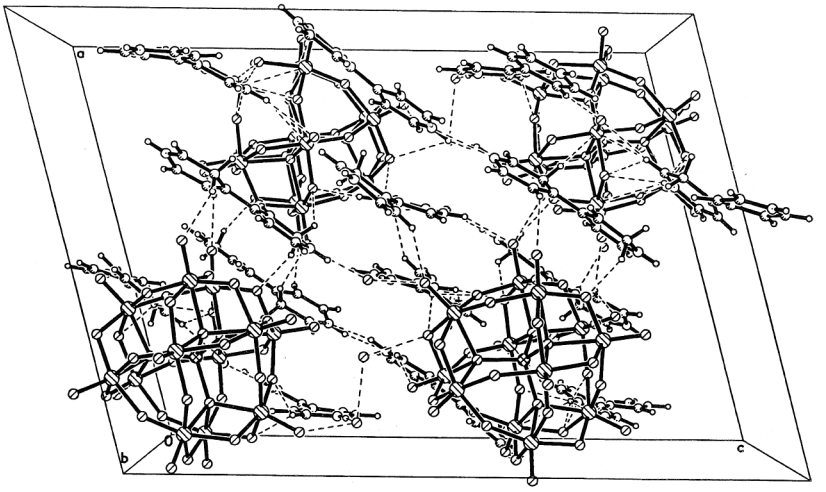

FIGURE 2 Packing diagram of the title complex along the *b*-axis.

weaker influence of 4,4′-bipyridine. It is worth mentioning that the nitrogen atoms of 4,4′-bipyridine form hydrogen bonds with bridging oxygens of $[ZnW_{12}O_{40}]^{6-}$ with N–H···O distances 2.771–2.986 Å. The nitrogen atoms also form hydrogen bonds with the water of crystallization with N–H···O distances 2.644–2.911 Å. Furthermore, the Keggin anion $[ZnW_{12}O_{40}]^{6-}$, 4,4′-bipyridine and water of crystallization construct a supramolecular complex through such hydrogen bonding as shown in Fig. 2.

IR and UV Spectra

The IR spectrum of the title compound exhibits four prominent bands at 934, 878, 746 and 451 cm^{-1} attributed to $\nu_{as}(W{=}O_t)$, $\nu_{as}(W{-}O_b)$, $\nu_{as}(W{-}O_c)$ and $\nu_{as}(Zn{-}O)$, respectively. The intense bands at 1635, 1489, 1410 and 1242 cm^{-1} are assigned to the characteristic 4,4′-bipyridine groups. In comparison with the tetrabutylammonium salts of $[N(C_4H_9)_4]H_2[ZnW_{12}O_{40}]$ [16], the $\nu(W{=}O_t)$ and $\nu(W{-}O_c)$ have a slight red shift, while the $\nu(W{-}O_b)$ and $\nu(Zn{-}O)$ have an evident blue shift, attributed to the hydrogen bonding interactions between the Keggin anion $[ZnW_{12}O_{40}]^{6-}$ and the 4,4′-bipyridine molecules. The title compound in aqueous solution exhibits two intense asymmetric absorption peaks at 195 and 240 nm (characteristic of the Keggin anion) in the UV region corresponding to charge transfer absorption of $O_t \rightarrow W$ and $O_{b,c} \rightarrow W$, respectively.

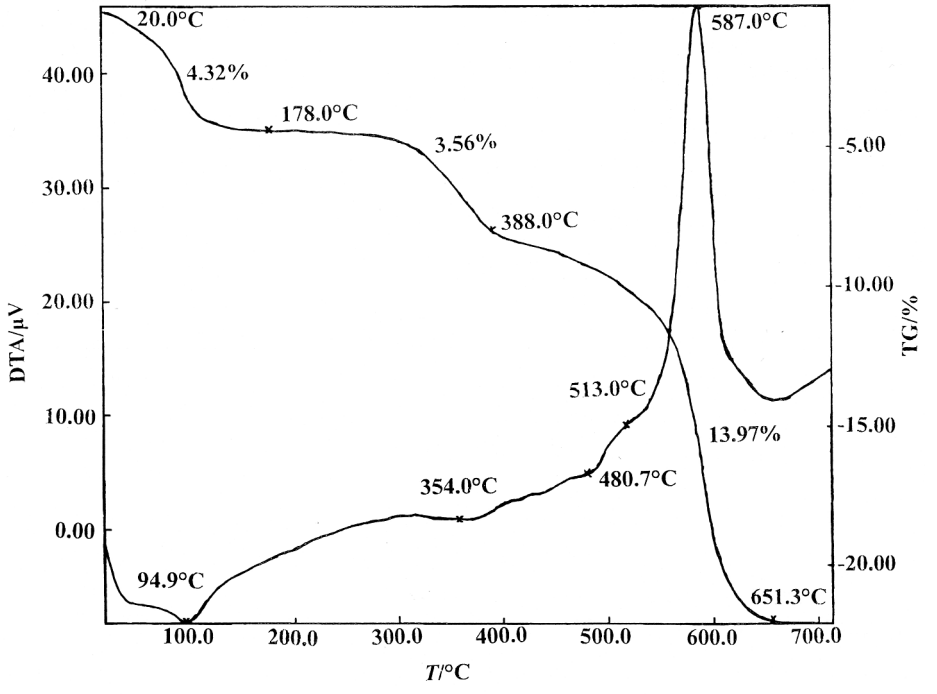

FIGURE 3 TG-DTA curve of the title compound.

Thermal Properties

The thermal decomposition profile (Fig. 3) of the title compound gives a total weight loss of 21.85% in the range of 20.0–700°C in agreement with the calculated weight loss of 21.55%, which can be divided into two stages. In the first stage, the weight loss of 4.32% in the temperature range 20.0–178.0°C is due to the loss of 6.0 waters of crystallization and 0.3 4,4′-bipyridine. In the second stage, the weight loss 17.53% in the range 178.0–700°C is assigned to the decomposition of the remaining 3.7 4,4′-bipyridines and three structural waters, corresponding to an endoenergic peak at 354.0°C and 480.7°C in the DTA curve. In addition, there is also combustion of the organic ligands giving a small exothermal peak at 513.0°C in the DTA curve. Another strong exothermal peak at 587.0°C in the DTA curve is attributed to the decomposition of the Keggin anion $[ZnW_{12}O_{40}]^6$.

Acknowledgments

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