

A one-dimensional organic–inorganic hybrid based on the bimolecular $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$ polyoxometalate

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Abstract

A one-dimensional coordination polymer $[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\} \cdot 4.5\text{H}_2\text{O}$ (en = ethylenediamine), which represents the first example of one-dimensional organic–inorganic hybrid based on the bimolecular Keggin polyoxometalates $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$ has been hydrothermally synthesized and characterized by elemental analyses, IR, TG and single crystal X-ray diffraction. Crystal data: $\text{C}_{24}\text{H}_{85}\text{Cu}_8\text{N}_{24}\text{O}_{84.5}\text{Si}_2\text{W}_{22}$, monoclinic, $P2_1/c$, $a = 18.8126(3)$, $b = 23.0896(4)$, $c = 26.0711(4)$ Å, $\beta = 96.3790(10)^\circ$, $V = 11254.5(3)$ Å³, $T = 293(2)$ K; $Z = 4$, $\mu = 23.983$ mm⁻¹, $R_1 = 0.0628$, $wR_2 = 0.1210$ [$I > 2\sigma$], $R_1 = 0.0854$, $wR_2 = 0.1285$ (all data).

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Keywords: Polyoxometalates; One-dimensional hybrid; Bimolecular; Crystal structure

1. Introduction

The design and synthesis of organic–inorganic hybrid have attracted increasing interest in recent years owing to the possibility of combining the different characteristics of the components to get unusual structures or properties [1,2]. Polyoxometalates (POMs) are one of the most widely used inorganic components owing to their extreme variability of composition, structure, electronic properties and applications [3,4]. In this way, the design of new composite materials by incorporating POMs and transition/rare-earth metal complex moieties constitutes an emerging area of interest [5,6]. To date, several hybrid compounds based on the typical heteropolyanions [7,8] or the vanadium/molybdenum isopolyanions [9,10] have been explored. However, hybrid supramolecular arrays based on their derivatives as the inorganic component have not been extensively studied.

Herein, we report the synthesis, crystal structure and magnetic properties of the compound $[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\} \cdot 4.5\text{H}_2\text{O}$ (**1**), which is

the first one-dimensional (1D) hybrid based on the rare bimolecular Keggin POMs $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$.

2. Experimental

2.1. Synthesis of $[\text{Cu}(\text{en})_2]_2[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]_2\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\} \cdot 4.5\text{H}_2\text{O}$

All reagents were purchased commercially and used without further purification. Compound **1** was prepared from a mixture of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (0.21 g, 1.34 mmol), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (2.23 g, 6.76 mmol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.55 g, 2.28 mmol), ethylenediamine (0.1 mL, 1.5 mmol), KF (0.3 g, 5.1 mmol) and distilled water (20 mL) in the mole ratio 1.3:6.8:2.3:1.5:5.1:1100, heated in a Teflon-lined steel autoclave inside a programmable electric furnace at 130 °C for 6 days with a starting pH of 4.8, adjusted with hydrochloric acid (2 mol/L). After cooling the autoclave to room temperature for 48 h, green crystals were obtained, filtered, washed several times with distilled water and dried in air (Yield: 75%). $\text{C}_{24}\text{H}_{85}\text{Cu}_8\text{N}_{24}\text{O}_{84.5}\text{Si}_2\text{W}_{22}$ (6671.06): calcd. C 4.32, H 1.28, N 5.04; Found: C 4.50, H 1.45, N 4.60.

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2.2. General methods

The elemental analyses were conducted on a Perkin-Elmer 240C element analyzer. The infrared (IR) spectrum was obtained from a sample powder palletized with KBr on Nicolet AVATAR 360 FTIR spectrophotometer over the range 4000–400 cm^{-1} . The thermal analysis was conducted on Exstar 6000 analyzer in the nitrogen gas atmosphere with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The variable-temperature magnetic susceptibility data on polycrystalline samples of compound **1** was measured with a quantum design MPMS7 SQUID magnetometer in the temperature region of 2–300 K at the field of 0.1 T.

2.3. Structure determination

A suitable green single crystal with dimensions $0.15 \times 0.12 \times 0.11$ mm was selected and intensity data were collected with a Rigaku RAXIS-IV image plate area detector using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 293(2) K. A total of 75082 reflections were measured in the range of $1.80^{\circ} \leq \theta \leq 25.00^{\circ}$ with $-22 \leq h \leq 22$, $-24 \leq k \leq 27$, $-30 \leq l \leq 30$, 19 640 of which ($R_{\text{int}} = 0.0830$) were used in the refinement. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 package [11]. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. The maximum and minimum peaks on the final difference Fourier map are corresponding to 2.958 and $-2.866 \text{ e}\text{\AA}^{-3}$. The crystallographic data and structure determination parameters for compound **1** are summarized in Table 1. CCDC reference number: 618479.

Table 1
Crystal data and structure refinement parameters for compound **1**

Empirical formula	$\text{C}_{24}\text{H}_{85}\text{Cu}_8\text{N}_{24}\text{O}_{84.5}\text{Si}_2\text{W}_{22}$
Formula weight	6671.06
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	18.8126(3)
$b/\text{\AA}$	23.0896(4)
$c/\text{\AA}$	26.0711(4)
β/deg	96.3790(10)
$V/\text{\AA}^3$	11 254.5(3)
Z	4
$D_c/\text{mg}/\text{m}^3$	3.937
Abs coeff/ mm^{-1}	23.983
T/K	293(2)
No. of refls collected	75082
No. of independent refls	19 640
Data/restraints/params	19 640/294/ 1513
GOF on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0628$, $wR_2 = 0.1210$
R indices (all data)	$R_1 = 0.0854$, $wR_2 = 0.1285$
Largest diff peak and hole ($\text{e}\text{\AA}^{-3}$)	2.958 and -2.866

3. Results and discussion

3.1. Structure description

Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with 1 $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$ building block, 2 $[\text{Cu}(\text{en})_2]^{2+}$, 2 $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ cations and 4.5 water of hydration in the asymmetric unit (Fig. 1). The bimolecular cluster fragment $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$ can be described as the condensation product of a couple of $\{[\text{Cu}(\text{en})_2][\text{CuSiW}_{11}\text{O}_{34}]\}^{4-}$ subunits by sharing one oxygen atom bound the Cu(W) (Cu7(W9) and Cu9(W21)) atoms. Each $\{[\text{Cu}(\text{en})_2][\text{CuSiW}_{11}\text{O}_{34}]\}^{4-}$ subunit is made of a copper-mono substituted α -Keggin polyanion as the inorganic building block and the $[\text{Cu}(\text{en})_2]^{2+}$ cation as the metalorganic cation which is anchored to the POM through an apical position via a POM terminal oxygen atom. Thus, the metalorganic cation and the POM are bound by a Cu–O–W bridge (123.3° for Cu1–O5–W5 and 127.7° for Cu2–O14–W14), while the Cu1–O5, Cu2–O14, W5–O5 and W14–O14 are 2.386, 2.359, 1.722 and 1.716 Å, respectively.

In each subunit α - $[\text{SiW}_{11}\text{O}_{39}\text{Cu}]^{6-}$, the copper ion is disordered over two positions on two opposite $\{\text{W}_3\text{O}_{13}\}$ units (Cu7, Cu8 for subunit 1 and Cu9, Cu10 for subunit 2) with half occupancies. Thus, the two Keggin subunits are bound by a Cu–O–W bridge with the Cu (W)–O lengths ranging from 1.89 (2) to 2.389 (14) Å (the mean value is 2.02 Å) and Cu–O–W angle (Cu7(W9)–O–W21(Cu9)) 159.0 (10°) to form an interesting bimolecular POM $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$. The structural arrangement is similar to that in Ref. [12,13], which shows the isolated bimolecular TM-substituted Keggin POMs, however, compound **1** shows the first example of 1D chain based on the bimolecular Keggin POMs.

In comparison with the optimized polyanions $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ [12], the W–O distances become shorter (Table 2) for the bimolecular POM $[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]^{12-}$ in **1**, which displays a little distortion in the whole skeleton of the Keggin anion. In addition, there are three kinds of Cu coordination centers in compound **1** (Fig. 1): (i) Six-coordinated Cu centers (Cu(7)–Cu(10)). These Cu atoms occupy the sites for W centers of the Keggin structure and thus adopt the octahedral geometry. It should be noted that in these octahedra one Cu atom together with one W atom locate at one position with each occupancy 0.5. (ii) Five-coordinated Cu centers (Cu(1), Cu(2), Cu(5) and Cu(6)) adopting the square pyramidal geometry. Each is bonded with four nitrogen atoms from two ethylenediamine ligands and one oxygen atom with the Cu–N average distances of 2.00 Å for Cu(1) and Cu(2), 2.01 Å for Cu(5) and Cu(6). The difference is that the oxygen atoms coordinated to Cu(1) and Cu(2) come from the terminal oxygen atoms of the $[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]^{12-}$ skeleton with the Cu–O average distance of 2.373 Å, whereas the others are from the isolated water molecules with the Cu–O average distance of 2.289 Å. (iii) Four-coordinated Cu(3) and

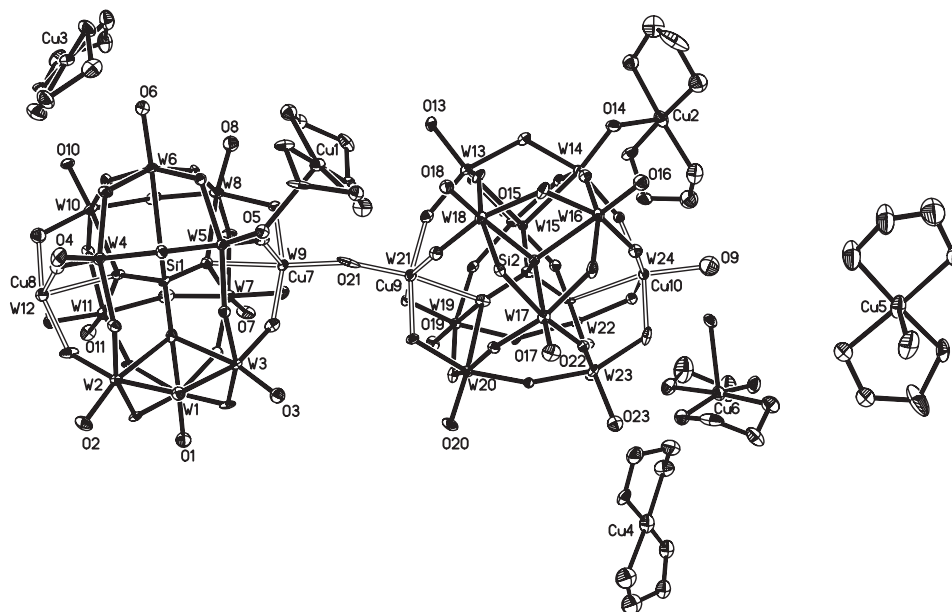


Fig. 1. Molecular structure unit of compound **1**. Water molecules and all hydrogen atoms are omitted for clarity. Displacement ellipsoids are scaled to enclose 30% probability.

Table 2

Ranges and [mean] M–O bond lengths [Å] for the $[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]^{12-}$ polyanion in compound **1** and for the optimized polyanions^a

	Compound 1 : $[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]^{12-}$		Optimized polyanions $[\text{SiW}_{12}\text{O}_{40}]^{4-}$
	Subunit 1	Subunit 2	
W–O _a	2.25–2.38 [2.33]	2.31–2.40 [2.34]	2.393
W–O _b	1.84–1.99 [1.90]	1.83–1.97 [1.90]	1.923
W–O _c	1.87–1.98 [1.93]	1.88–1.97 [1.92]	1.935
W–O _t	1.70–1.74 [1.72]	1.70–1.74 [1.72]	1.740
Si–O _a	1.61–1.64 [1.63]	1.60–1.63 [1.61]	1.650
Cu(W)–O _a	2.340, 2.389	2.336, 2.369	
Cu(W)–O _b	1.924–1.984 [1.94]	1.924–1.964 [1.95]	
Cu(W)–O _c	1.911–1.952 [1.93]	1.952–1.981 [1.97]	
Cu(W)–O _t	1.940, 2.06	1.89, 1.99	

^aO_a: oxygen atoms belonging to the central SiO₄ tetrahedron; O_b: bridging oxygen atoms between corner-sharing MO₆ octahedra; O_c: bridging oxygen atoms between edge-sharing MO₆ octahedra; O_t: terminal oxygen atoms.

Cu(4). Each is defined by four nitrogen atoms from two ethylenediamine molecules with the Cu–N average distances ranging from 1.96(2) to 2.04(3) Å and the mean value 2.01 Å.

Furthermore, the oxygen atom (O9) bound to the copper atom (Cu10) in subunit 2 of the bimolecular unit connects the opposite copper position in subunit 1 of the neighboring bimolecular unit (W12) to form an interesting metalorganic complex supported infinite chain $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}_n^{8n-}$ (Fig. 2). The subsequent formation of the Cu–O–W bridge connects the two unit which are rotated by 162.9 (12)° (Cu10–O–W12#2) with respect to each other. Although this type of TM–O–W bridge has been observed in several chainlike polymolecular Keggin POMs [14–18] with TM = Mn, Co or Cu, to our knowledge, there is only one other example of high-dimensional hybrid connected by the metalorganic cation

based on the monomolecular TM-substituted Keggin POM, unlike compound **1**, is not decorated with TM complexes.

As shown in Fig. 3, the bimolecular building block of compound **1** form chains along the *c*-axis. The isolated $[\text{Cu}(\text{en})_2]^{2+}$, $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})]^{2+}$ cations and water molecules are located between the chains. Thus, the crystal packing of the compound displays a 3D network arrangement through an extended hydrogen-bonding network (Table 3) that involves the metalorganic cation, isolated water molecules and the POMs terminal oxygen atoms.

3.2. IR spectral characterization

In the low wavenumber region ($\nu < 1000 \text{ cm}^{-1}$) of the IR spectrum, compound **1** displays the characteristic vibration patterns of Keggin-type structure [19], namely, $\nu_{\text{as}}(\text{W–O}_d)$,

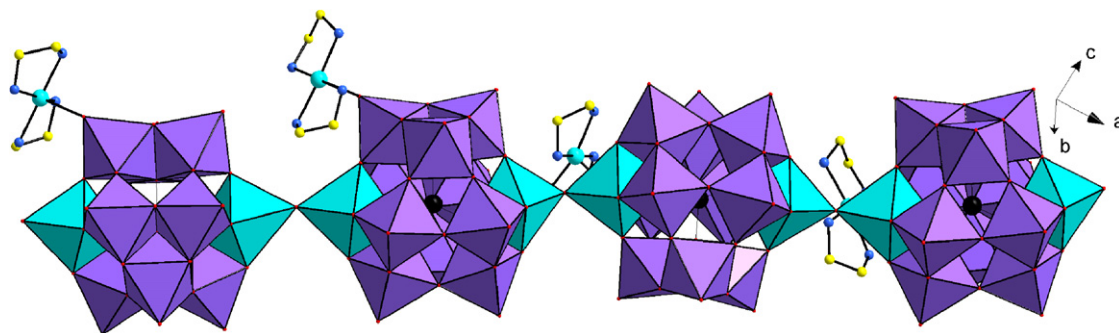


Fig. 2. Polyhedral representation of compound **1**. Key: WO_6 (purple), $\text{Cu}(\text{W})\text{O}_6$ (cyan), Cu (cyan), N (blue) and C (yellow). The isolated coordination cations and water molecules are omitted for clarity.

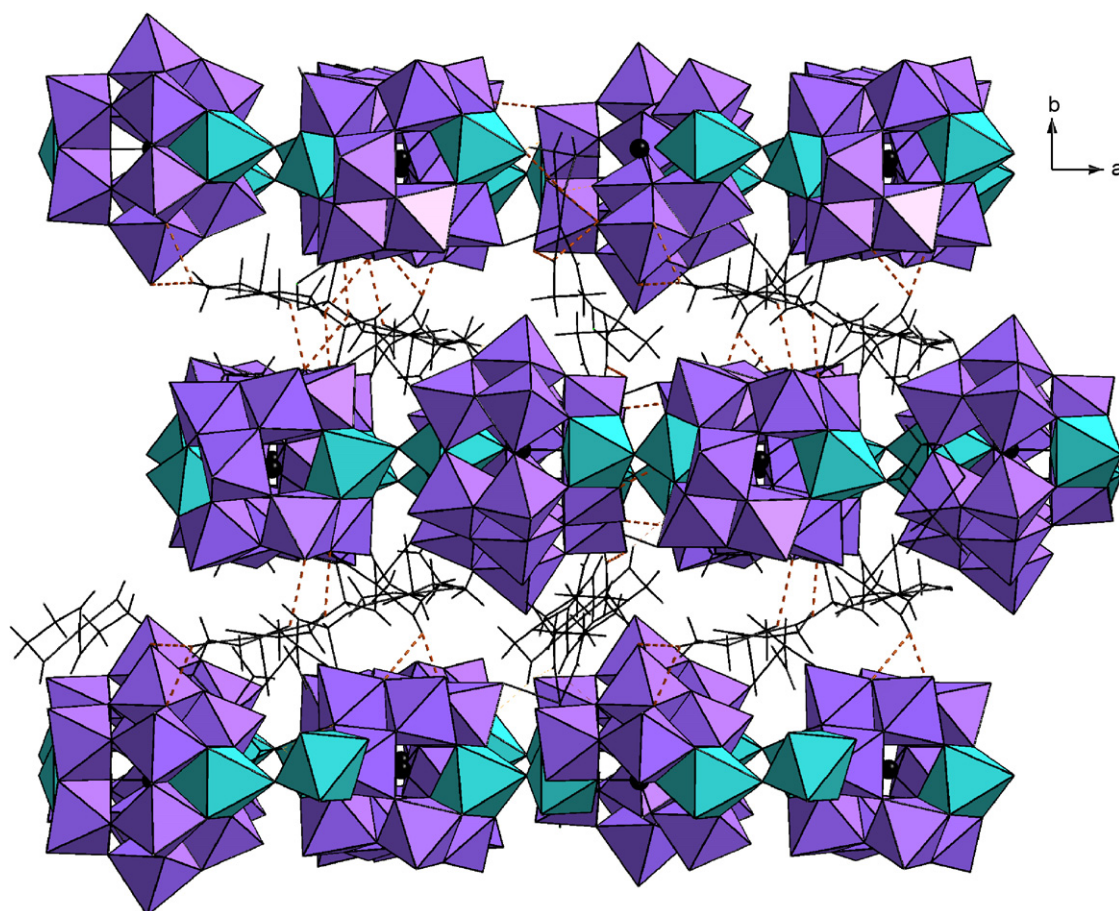


Fig. 3. Crystal packing of compound **1** viewed along the ab plane with a detailed view of the linking through the H-bonding network to give a 3D arrangement. The hydrogen bond was displayed as red dotted line.

$\nu_{\text{as}}(\text{Si}-\text{O}_a)$, $\nu_{\text{as}}(\text{W}-\text{O}_b)$ and $\nu_{\text{as}}(\text{W}-\text{O}_c)$, appearing at 946, 897, 781 and 687 cm^{-1} . On the other hand, the bands around 3455, 3306, 3249, 1584 and 1462 cm^{-1} are originated from the organic group ethylenediamine in compound **1**.

3.3. Magnetic properties

The thermal evolution of the magnetic molar susceptibility and the $\chi_{\text{M}}T$ product for compound **1** is displayed in

Fig. 4. The χ_{M} increases continuously with decreasing temperature and no maximum is observed. At high temperature ($T > 120$ K), the susceptibility data are well described by Curie–Weiss expressions, being $C_{\text{M}} = 4.81 \text{ emu K mol}^{-1}$, $\theta = -180.9$ K. The values of $\chi_{\text{M}}T$ at 300 K is 3.03 emu K mol^{-1} , which is in good agreement with the presence of eight uncoupled Cu^{II} ions (3.00 emu K mol^{-1} , considering $g = 2$). Additionally, when the system is cooled down from 300 to 2 K, the $\chi_{\text{M}}T$ product decreases reaching values close to 0.99 emu K mol^{-1} . This behavior indicates

Table 3
Hydrogen bonds for compound **1**

D–H	d(D–H)	d(H...A)	<DHA	d(D...A)	A
N1–H1C	0.860	2.612	131.03	3.243	O21
N1–H1C	0.860	2.630	144.25	3.366	O55
N2–H2C	0.860	2.228	163.64	3.063	O61
N2–H2C	0.860	2.551	128.13	3.155	O57
N3–H3C	0.860	2.261	166.03	3.102	O19
N4–H4C	0.860	2.654	136.95	3.335	O6W
N6–H6C	0.860	2.503	156.25	3.308	O31
N6–H6C	0.860	2.595	120.89	3.125	O38
N9–H9C	0.860	2.333	168.06	3.179	O7W
N10–H10C	0.860	2.659	127.91	3.259	O50
N11–H11C	0.860	2.570	112.24	3.003	O20
N15–H15C	0.860	2.337	136.13	3.016	O47
N16–H16C	0.860	2.291	176.13	3.150	O6W
N17–H17C	0.860	2.599	119.76	3.116	O10
N18–H18C	0.860	2.496	162.38	3.325	O17
N18–H18C	0.860	2.552	125.40	3.130	O68
N20–H20C	0.860	2.518	112.65	2.958	O45
N21–H21C	0.860	2.528	126.52	3.118	O22
N23–H23C	0.860	2.174	157.74	2.987	O37
N23–H23C	0.860	2.657	128.51	3.262	O46
N24–H24C	0.860	2.608	122.75	3.157	O53

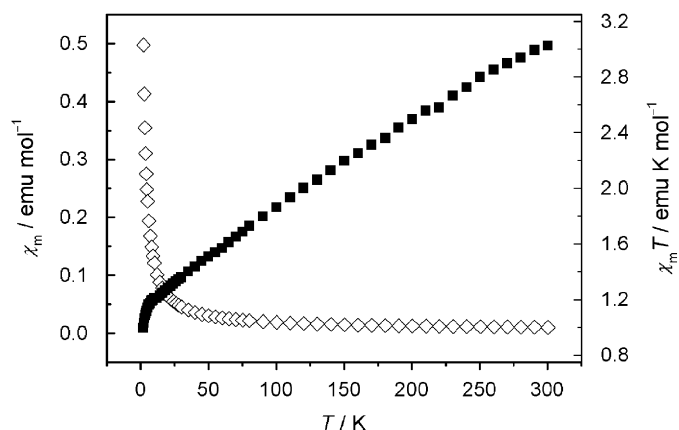


Fig. 4. Thermal evolution of the magnetic molar susceptibility and the $\chi_M T$ product for compound **1**.

the presence of relatively strong antiferromagnetic interactions between the Cu^{II} ions. The bond valence sum (BVS) [20] calculations of all the tungsten atoms except the four disordered Cu (W) position in compound **1** (6.257, 6.055, 5.971, 6.204, 6.114, 6.221, 6.087, 5.946, 6.031, 6.012, 6.133, 6.130, 6.191, 6.042, 6.019, 6.141, 6.162, 6.17, 6.033 and 5.986 for W1–W8, W10–W11, W13–W20, W22, W23, respectively) indicates these W atoms are fully oxidized. In addition, in the compound, six of the eight paramagnetic centers are completely isolated from one another. For the single-ion zero-field splitting is not paramount for Cu^{2+} (d_9) ions, thus, the observed antiferromagnetic exchange may predicated on the Cu–O–Cu dimeric linkages adjoining neighboring polyoxoanions, in the 50% case where Cu atoms occupy both of those sites. Nevertheless, due to the

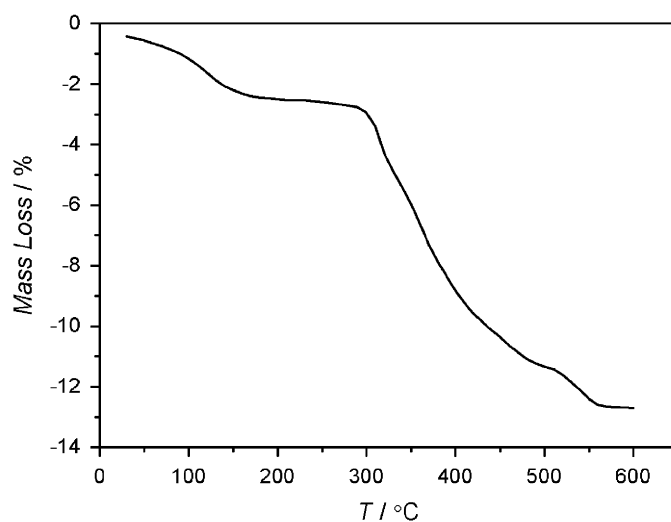


Fig. 5. The TG curve for compound **1**.

complexity of the system, it is difficult to model the magnetic property, and the deeper treatment of magnetism in such a potentially interesting system is in progress.

3.4. Thermal analysis

The TG curve of compound **1** (Fig. 5) shows two-step weight loss, giving a total loss of 12.69% (calcd. 12.74%) in the range of 30–600 °C. The first weight loss 2.46% (30–175 °C), corresponding to the release of 6.5 water and 1 ethylenediamine molecules (calcd. 2.65%). The second weight loss of 9.91% (176–600 °C) is attributed to the oxidation combustion of the other 11 ethylenediamine organic groups.

4. Conclusions

A 1D organic–inorganic hybrid based on the rare bimolecular Keggin POMs $\{[\text{Cu}(\text{en})_2]_2[\text{Cu}_2\text{Si}_2\text{W}_{22}\text{O}_{78}]\}^{8-}$ has been hydrothermally synthesized and displays a relatively strong antiferromagnetic interactions between the Cu^{II} ions according to the magnetic study, which may have much more potentially importance during the further magnetism study.

Acknowledgments

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.02.004.

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