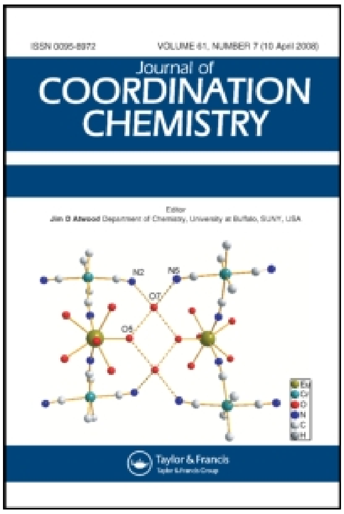

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Solvothermal synthesis, structure and properties of two new compounds based on Keggin polyoxometalates decorated by copper complexes

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Solvothermal synthesis, structure and properties of two new compounds based on Keggin polyoxometalates decorated by copper complexes

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Two new organic-inorganic hybrid compounds based on polyoxometalate building blocks, $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo_3^{V}Mo_9^{VI}O_{40}\}$ (**1**), $H[Cu(bpy)(H_2O)]\{[Cu(bpy)]_4(PO_4)_2\}\{PW_{11}CuO_{39}\} \cdot H_2O$ (**2**) (bpy = 2,2′-bipyridine), have been solvothermally synthesized and characterized by elemental analyses, IR, and TG analysis. Single crystal X-ray diffraction reveals that **1** is built from the reduced α-Keggin polyoxoanion $[PMo_3^{V}Mo_9^{VI}O_{40}]^{6-}$ bicapped by two $[Cu^{II}(bpy)]^{2+}$ through four bridging oxo groups on two opposite $[Mo_4O_4]$ faces. **1** shows mild photoluminescence in the solid state at room temperature. **2** is based on monovacant Keggin anion $\{PW_{11}CuO_{39}\}^{5-}$ linked through $Cu(bpy)^{2+}$ andPO_4^{3-}, generating a one-dimensional chain. Magnetism indicates predominantly antiferromagnetic interaction in **2**.

Keywords: Polyoxometalates; Organic–inorganic hybrid material; Solvothermal synthesis; One-dimensional chain; Magnetic property

1. Introduction

Polyoxometalates (POMs) [1], as early transition metal oxide clusters, have interest in solid state materials chemistry due to their structural and compositional diversity and potential applications in catalysis, sorption, ion exchange, optical, electro- and magnetic materials [2]. Attention has been paid toward construction of organic–inorganic materials based on POMs. Systematic structural design of composite materials possessing unique structures and potentially useful magnetic and luminescent properties remains extremely challenging. However, several successful strategies have been developed to design such materials [3]. One utilizes polyoxometalates's coordination ability to produce polyoxoanion-supported or bridged by transition metal or lanthanide cations under hydrothermal or solvothermal conditions, providing

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charge-compensation, space-filling, passivating and structure-directing roles [4]. Many examples have been explored, including discrete clusters [5], one-dimensional chains [6], two-dimensional networks [7] and three-dimensional frameworks [8].

Especially, Zubieta's and Wang's groups have reported series of such hybrid materials consisting of polyoxomolybdate and phosphomolybdate clusters attached to various transition metal complexes such as $[Ni(phen)_3][PMo_9^{VI}Mo_3^{V}O_{40}\{Ni(phen)\}_2]$ [5b], $[Cu(phen)]_2[V^{IV}V_4^{V}As_2O_{19}]\cdot 0.5H_2O$ [7a], $Na_2[\{Mn(phen)_2(H_2O)\}\{Mn(phen)_2\}_3\{MnMo_{12}O_{24}(HPO_4)_6(PO_4)(OH)_6\}]\cdot 4H_2O$ [7b], $[\{Cu_3(trz)_2\}V_4O_{12}]$ [8a] etc. We reported two compounds based on the $\{P_2Mo_5\}$ clusters linked by copper complexes, $[Cu(phen)(H_2O)]_3[(PO_4)_2Mo_5O_{15}]\cdot 5H_2O$ and $HNa[Cu(bpy)(H_2O)]_2[(PO_4)_2Mo_5O_{15}]\cdot 6H_2O$, with one-dimensional chains [6d]. Herein, we present syntheses and structures of two compounds based on polyoxometalate building blocks, $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo_3^{V}Mo_9^{VI}O_{40}\}$ (**1**) and $H[Cu(bpy)(H_2O)]\{[Cu(bpy)]_4(PO_4)_2\}\{PW_{11}CuO_{39}\}\cdot H_2O$ (**2**).

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased from commercial sources and used without further purification. Elemental analyses (C, N, and H) were performed on a Perkin-Elmer 2400 elemental analyzer and P, Cu, W and Mo were analyzed on a PLASMA-SPEC ICP atomic emission spectrometer. FT-IR spectra were recorded in the range 4000–400 cm^{-1} on an EQUINOX-55 spectrometer using KBr pellets. Thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$. XPS analysis was performed on a VG Scientific ESCALab220i-XL spectrometer with an Al Kα achromatic X-ray source. Binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. Excitation and emission spectra were obtained on a RF-5301PC spectrofluorometer equipped with a 450 W xenon lamp as the excitation source, and the measurements were performed at room temperature. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range 2–300 K at 1000 Oe. Samples for the magnetic measurements were ground into powder in order to avoid anisotropy effects.

2.2. *Synthesis*

2.2.1. Preparation of $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo_3^{V}Mo_9^{VI}]O_{40}\}$ (1). A mixture of $Na_2MoO_4\cdot 2H_2O$ (1.115 g, 4.61 mmol), $CuCl_2\cdot 2H_2O$ (0.323 g, 1.89 mmol), 2,2′-bipyridine (0.183 g, 1.17 mmol), oxalic acid ($C_2H_4O_2\cdot 2H_2O$) (0.138 g, 1.44 mmol), H_3PO_4 (85%) (0.470 g), H_2O (15 mL), and CH_3OH (15 mL) was stirred (the initial pH value was adjusted to 3–4 with 2M HCl) and then sealed in a 50 mL Teflon-lined autoclave, which was heated at 140°C for two days. After slow cooling to room temperature, black block crystals of **1** were obtained in 40% yield (based on Cu). The elemental analyses found (%): Cu, 8.56; P, 1.25; Mo, 38.02; C, 23.32; H, 2.01;

N, 5.97. Anal. Calcd: Cu, 8.43; P, 1.03; Mo, 38.20; C, 23.91; H, 1.61; N, 5.58. Selected FT-IR data (KBr, cm^{-1}): 491(m), 763(m), 945(s), 1029(m), 1057(m), 1174(m), 1311(m), 1439(m), 1597(m), 3448(w).

2.2.2. Preparation of $H[Cu(bpy)(H_2O)]\{[Cu(bpy)]_4(PO_4)_2\}\{PW_{11}CuO_{39}\} \cdot H_2O$ (2). Compound **2** was prepared by a procedure similar to that for **1**, but with $Na_2WO_4 \cdot 2H_2O$ (1.24 g, 3.76 mmol), 2,2′-bipyridine (0.233 g, 1.49 mmol) and $Cu(NO_3)_2 \cdot 6H_2O$ (0.360 g, 1.22 mmol) (the initial pH value was adjusted to 2–3 with 85% H_3PO_4). Yield: 60% (based on Cu). The elemental analyses found (%): Cu, 8.99; P, 2.87; W, 49.03; C, 14.21; H, 1.32; N, 3.03. Anal. Calcd: Cu, 9.38; P, 2.29; W, 49.73; C, 14.77; H, 1.12; N, 3.44. Selected FT-IR data (KBr, cm^{-1}): 520(m), 814(s), 882(m), 957(s), 1061(m), 1094(m), 1448(m), 1474(m), 1604(m), 3448(br).

2.3. *X-ray crystallography*

Intensity data collection was carried out with a Bruker Smart APEXII diffractometer equipped with a CCD detector using Mo K_α monochromated radiation ($\lambda = 0.71073$ Å) at room temperature. All data were corrected for absorption using SADABS [9]. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL-97 software package [10]. All non-hydrogen atoms in **1** and **2** were refined anisotropically. Positions of hydrogen atoms attached to carbon were fixed at their ideal positions, and those attached to oxygen could not be located. A summary of the crystallographic data and structure determinations for **1** and **2** is provided in table 1. Selected bond lengths and angles for **1** and **2** are listed in table 2.

Table 1. Crystal data and structure refinement of **1** and **2**.

	Compound **1**	Compound **2**
Empirical formula	$C_{60}H_{48}Cu_4Mo_{12}N_{12}O_{40}P$	$C_{50}H_{45}Cu_6N_{10}O_{49}P_3W_{11}$
Formula weight	3013.53	4066.49
Crystal size (mm^3)	0.42 × 0.38 × 0.12	0.42 × 0.36 × 0.24
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*n*
Unit cell dimension (Å, °)		
a	13.2629 (7)	15.7837 (5)
b	29.7181 (15)	24.1950 (7)
c	21.4910 (10)	21.4063 (7)
β	103.021 (2)	95.252 (2)
Volume (Å^3), *Z*	8252.8 (7), 4	8140.5 (4), 4
D_{calcd} ($g\,cm^{-3}$)	2.425	3.315
μ (mm^{-1}), *F* (000)	2.878, 5788	17.164, 7344
Reflections collected	85278	84037
Unique reflections	20286	20310
R_{int}	0.0596	0.1013
Final *R* indices	$R_1 = 0.0542$	$R_1 = 0.0569$
$[I > 2\sigma(I)]^a$	$wR_2 = 0.1089$	$wR_2 = 0.1323$
R indices	$R_1 = 0.0968$	$R_1 = 0.1164$
[all data]	$wR_2 = 0.1310$	$wR_2 = 0.1530$
Goodness-of-fit on F^2	1.033	1.032

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

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

Compound **1**			
Cu(1)–O (17)	1.999 (4)	O (37)–Mo (8)–O (22)	81.17 (17)
Cu (1)–N (2)	1.999 (5)	Mo (1)–O (18)–Mo (2)	122.72 (19)
Cu (1)–O (18)	2.372 (4)	Mo (4)–O (27)–Cu (2)	96.76 (17)
Mo (8)–O (22)	1.999 (4)	Cu (1)–O (17)–Mo (9)	106.85 (18)
Mo (1)–O (18)	1.955 (4)	Mo (9)–O (37)–Cu (1)	97.11 (17)
Cu (2)–O (32)	2.035 (4)	Mo (11)–O (32)–Mo (6)	143.9 (2)
Cu (2)–O (40)	2.366 (4)	Mo (1)–O (18)–Cu (1)	95.98 (17)
Cu (2)–N (3)	1.987 (5)	Mo (8)–O (3)–Mo (7)	88.15 (13)
Mo (11)–O (40)	1.971 (4)	P (1)–O (4)–Mo (12)	126.9 (2)
Mo (4)–O (27)	1.963 (4)	O (4)–P (1)–O (3)	109.2 (2)
Cu (3)–N (5)	2.005 (7)	O (27)–Cu (2)–O (40)	126.98 (13)
Cu (4)–N (9)	2.037 (7)	N (4)–Cu (2)–O (27)	111.85 (18)
Compound **2**$^{\text{a}}$			
Cu (1)–O (39)	1.983 (11)	W (2)–O (39)–Cu (1)	118.5 (6)
Cu (2)–O (38)	2.311 (10)	W (5)–O (9)–Cu (5)	159.0 (7)
Cu (3)–O (45)#1	1.906 (10)	Cu (1)–O (39)–Cu (3)	114.5 (5)
Cu (4)–O (43)#2	1.901 (11)	P (1)–O (1)–Cu (1)	120.4 (6)
Cu (5)–O (44)	1.985 (10)	Cu (1)–O (1)–W (1)	87.1 (4)
Cu (6)–O (19)#2	2.356 (10)	P (3)–O (44)–Cu (5)	125.5 (6)
W (5)–O (9)	1.733 (12)	Cu (5)–O (44)–Cu (4)	115.1 (5)
W (2)–O (39)	1.809 (11)	P (2)–O (40)–Cu (2)	109.5 (6)
P (2)–O (40)	1.531 (12)	P (3)–O (46)–Cu (2)#2	130.2 (7)
P (3)–O (44)	1.574 (12)	P (2)–O (43)–Cu (4)#1	128.7 (7)

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

3. Results and discussion

3.1. *Synthesis*

The isolation of **1** and **2** depended on solvothermal techniques [3–8], because differential solubilities of organic and inorganic precursors can be minimized. However, factors such as temperature, starting materials, pressure, acidity, reactant stoichiometry, and time of reaction can influence the reaction [4–8]. Parallel experiments show that starting pH and the choice of starting materials are crucial for isolation of **1** and **2**, which could only be obtained in the pH range 3–4 and 2–3, respectively. At higher pH (5–7) no crystal was formed except a mixture of powders, probably due to decomposition of the polyanion at high pH. Oxalic acid is essential for preparation of **1**, acting as a reducing agent for Mo(VI) in the reagent to Mo(V). For **2**, if $Cu(NO_3)_2 \cdot 6H_2O$ was replaced by $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$ or $CuAc_2 \cdot 2H_2O$ in identical hydrothermal reaction environments, we could not obtain **2**.

3.2. *Crystal structure*

3.2.1. $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo^{V}_3Mo^{VI}_9O_{40}\}$ (1). The structure of **1** (figure 1) consists of a bicapped bisupporting $\{[Cu^{II}(bpy)]_2PMo^{V}_3Mo^{VI}_9O_{40}\}^{2-}$ heteropolyoxoanion and two $[Cu^{I}(bpy)_2]^{+}$ countercations. The polyoxoanion $\{[Cu^{II}(bpy)]_2PMo^{V}_3Mo^{VI}_9O_{40}\}^{2-}$ is composed of a reduced bicapped Keggin $[PMo^{V}_3Mo^{VI}_9O_{40}]^{6-}$ and two $[Cu^{II}(bpy)]^{2+}$ units linking to it through bridging oxo groups. As in other well-known Keggin structures, the reduced polyoxoanion is constructed from a central

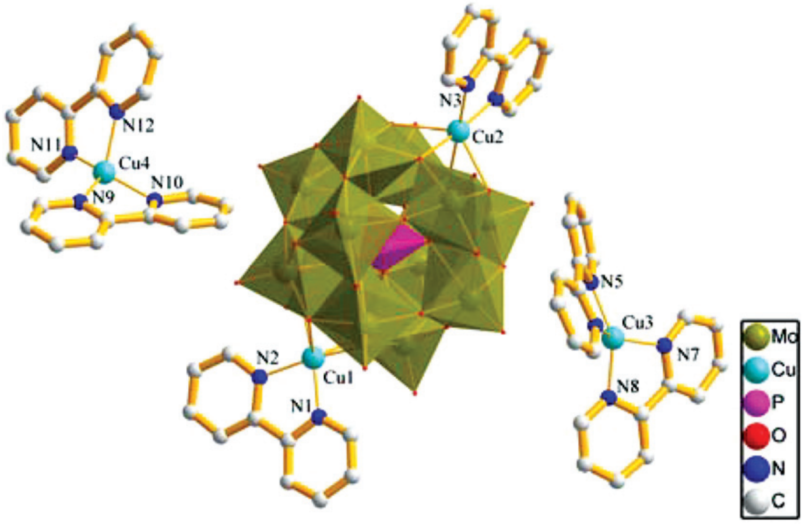

Figure 1. The molecular structure of **1** [Cu^I is Cu(3) and Cu(4) whereas Cu^{II} is Cu(1) and Cu(2)]. Octahedra, $\{MoO_6\}$; Tetrahedra, $\{PO_4\}$.

PO_4 tetrahedron which shares its oxygens with four Mo_3O_{13} groups, each of which is made up of three edge-sharing MoO_6 octahera. Valence sum calculations [11] give the average value of 5.70 for Mo atoms (the expected average value for $Mo^V_3Mo^{VI}_9$ is 5.75), showing 3 of 12 Mo atoms in +5 oxidation state with three electrons delocalized within the whole metal-oxide cluster. A typical feature of the structure is that the Keggin polyoxoanion is capped by two $[Cu^{II}(bpy)]^{2+}$ (Cu1, Cu2) through four bridging oxo groups on two opposite $\{Mo_4O_4\}$ faces, with Cu–O distance of 1.999(4)–2.372(4) Å and Cu–N distance of 1.987(5)–2.001(5), forming a $\{CuO_4N_2\}$ octahedron. However, Cu(3, 4) ions are coordinated by four nitrogen atoms from two bpy ligands [Cu–N, 1.992(7)–2.052(8)], with a distorted tetrahedral geometry $\{CuN_4\}$, as countercations in the crystal structure. The valence sum calculations indicate that Cu(1, 2) and Cu(3, 4) are +2 and +1, respectively. The Cu^I atom is commonly three- or four-coordinate, while Cu^{II} is five- or six-coordinate.

3.2.2. $H[Cu(bpy)(H_2O)]\{[Cu(bpy)]_4(PO_4)_2\}\{PW_{11}CuO_{39}\}\cdot H_2O$ (2). The basic building block of **2**, shown in figure 2, is composed of one heteropolyoxoanion $\{PW_{11}CuO_{39}\}^{5-}$, two PO_4^{3-} and five $Cu(bpy)^{2+}$ ions. The valence sum calculations confirm that all W and Cu atoms are +6 and +2. The heteropolyoxoanion $\{PW_{11}CuO_{39}\}^{5-}$ has Cu1 occupying the vacancy of a defective $\{PW_{11}O_{39}\}^{7-}$ anion and bound to the POM by five oxygen atoms (O1, O19, O33, O38, O39). As illustrated in figure 3(a), an unusual structural feature of **2** is that the monovacant Keggin anion $\{PW_{11}CuO_{39}\}^{5-}$ is linked by five $Cu(bpy)^{2+}$ and two PO_4^{3-}, generating a one-dimensional chain. The coordination environments of Cu^{2+} and PO_4^{3-} are shown in figure 3(b). One PO_4 (P2) has a non-bonded terminal (O42), two μ_2 (O41, O43) and one μ_3 (O40) oxygens. The other PO_4 (P3) tetrahedron has two μ_2 (O45, O47) and two μ_3 (O46, O44) oxygen atoms. According to their coordination-type, Cu atoms can be

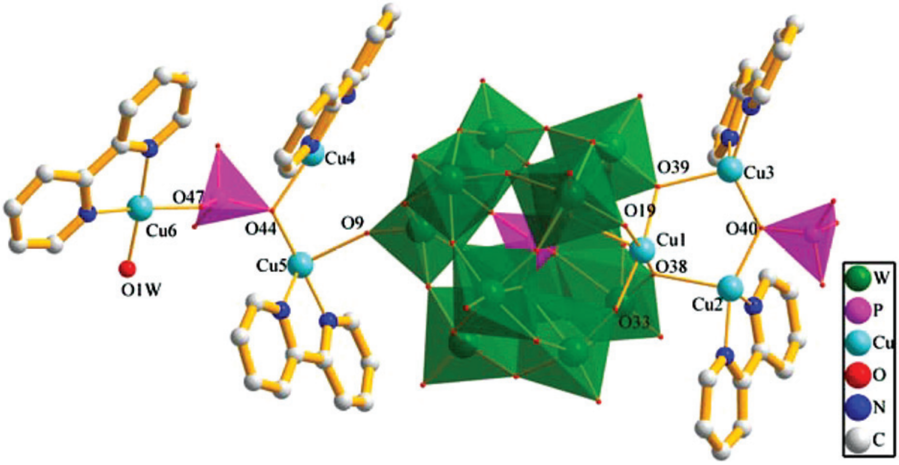

Figure 2. The basic building block of **2**. H atoms and lattice water are omitted for clarity. Octahedra, $\{WO_6\}$; Tetrahedra, $\{PO_4\}$.

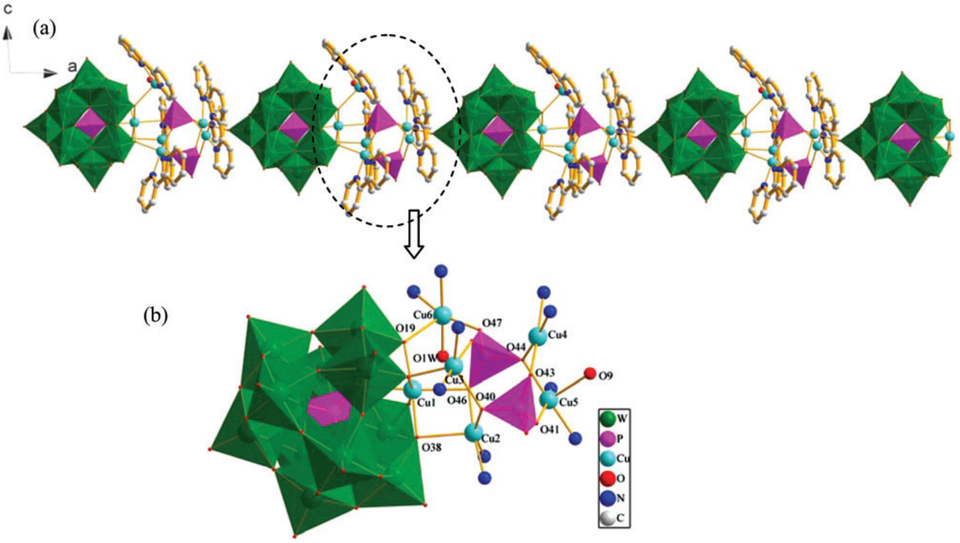

Figure 3. (a) View of the one-dimensional chain in **2**; (b) the coordination environments of Cu(II) and PO_4^{3-} in **2**. All C and H atoms are omitted for clarity.

divided into three groups: (i) Cu1 is a $\{CuO_6\}$ distorted octahedral geometry with five oxygens from $\{PW_{11}O_{39}\}^{7-}$ and one oxygen from PO_4^{3-}, with Cu–O distances of 1.938(11)–2.325(11) Å; (ii) Cu4 is four-coordinate, with two nitrogens from bpy and two oxygens from different PO_4 tetrahedra, with Cu–O distances 1.901(11)–2.018(10) Å and Cu–N distance of 1.977(14)–1.980(14); (iii) Cu (2, 3, 5, 6) are coordinated by two nitrogen atoms from bpy and three oxygen atoms, showing square-pyramidal geometry in the form of $\{CuN_2O_3\}$, with Cu–O distance of 1.902(11)–2.356(10) Å and Cu–N distance of 1.954(15)–2.034(14). Cu5 is bound to the terminal oxygen atom (O9) of the POM, resulting in the one-dimensional chain in **2**.

3.3. *Thermal analysis and IR spectra*

The thermal gravimetric analysis (TGA) of **1** shows two weight losses. The first in the temperature range 331–523°C corresponds to release of four bpy molecules, 19.5% (calcd 20.8%); the second at 542–663°C is ascribed to decomposition of the other two bpy ligands, 10.1% (calcd 10.4%), respectively. For **2**, TGA shows that chemical decomposition starts at 435°C and ends at 752°C with weight loss of 19.7%, equivalent to loss of organic ligand (calcd 19.2%) (see figure S3).

The infrared spectra of **1** and **2** (see figures S1 and S2) recorded between 4000 and 400 $\mathrm{cm^{-1}}$ exhibit two strong bands in the 750–960 $\mathrm{cm^{-1}}$ range associated with $\nu_{\mathrm{sym}}(\mathrm{M{=}O})$ and $\nu_{\mathrm{asym}}(\mathrm{M{=}O})$ and a medium to strong intensity band in the 490–520 $\mathrm{cm^{-1}}$ region attributed to $\nu(\mathrm{M–O–M})$ (M = Mo, W). A series of medium intensity bands in the 1000–1620 $\mathrm{cm^{-1}}$ range is associated with organic ligands. A broad band at 3448 $\mathrm{cm^{-1}}$ for **2** is associated with the water of crystallization.

3.4. *XPS and photoluminescence for 1*

In the XPS spectrum for **1**, figure 4(a) shows the shoulder peaks of $2p_{3/2}$ and $2p_{1/2}$ at 934.3 and 954.1 eV, respectively, suggesting the presence of $\mathrm{Cu^{I}}$. Satellite peaks at 943.2 and 962.2 eV indicate that the compound also contains $\mathrm{Cu^{II}}$ [12]. The XPS spectrum of Mo for **1** [figure 4(b)] displays four partially overlapped peaks, and curve fitting gives positions of these four peaks at 231.2 eV (a), 232.4 eV (b), 234.3 eV (c) and 235.5 eV (d), ascribed to $\mathrm{Mo^{V}}3d_{5/2}$, $\mathrm{Mo^{VI}}3d_{5/2}$, $\mathrm{Mo^{V}}3d_{3/2}$ and $\mathrm{Mo^{VI}}3d_{3/2}$, respectively [13]. These results further confirm the valence of copper and molybdenum.

The emission spectrum of **1** in the solid state at room temperature, depicted in figure 5, exhibits mild blue fluorescent emission bands at ca 390 nm upon excitation at ca 246 nm. It is assigned to ($\mathrm{Cu^{I}}$)-to-ligand charge-transfer (MLCT) band [$\mathrm{d^{10}}$-π^*], according to the literature [14]. The fluorescence indicates that **1** may be a candidate for photoluminescence materials.

3.5. *Magnetic property for (2)*

The magnetic behavior of **2** was studied between 2 and 300 K at a field of 1000 Oe; the thermal variations of $\chi_{\mathrm{M}}T$ and $1/\chi_{\mathrm{M}}$ are displayed in figure 6. The $\chi_{\mathrm{M}}T$ curve exhibits continuous decrease from 3.42 $\mathrm{cm^3\,mol^{-1}\,K}$ at 300 K to 1.04 $\mathrm{cm^3\,mol^{-1}\,K}$ at 5 K, characteristic of antiferromagnetic interactions among $\mathrm{Cu^{II}}$ ions. However, the curve increases a little below 5 K, indicating a very weak ferromagnetic interaction exists in **2** at lower temperatures. Above 20 K, the magnetic susceptibility of **2** follows the Curie-Weiss law, $\chi_{\mathrm{M}} = C/(T-\theta)$ ($C = 3.60\ \mathrm{cm^3\,K\,mol^{-1}}$, $\theta = -39.71$ K), illustrating predominantly antiferromagnetic coupling between $\mathrm{Cu^{II}}$ centers.

Since $\mathrm{W^{VI}}$ ($\mathrm{5d^0}$, S = 0) ions do not possess a magnetic moment, they do not contribute to the bulk properties; the magnetism of **2** may be attributed solely to the presence of $\mathrm{Cu^{II}}$ ions ($\mathrm{3d^9}$; $S = 1/2$) which reside on chains of the compound. According to the crystal structure of **2**, the magnetic behavior may be due to superexchange interactions between hexanuclear $\mathrm{Cu^{II}}$ clusters. Unfortunately, it is too difficult to fit the

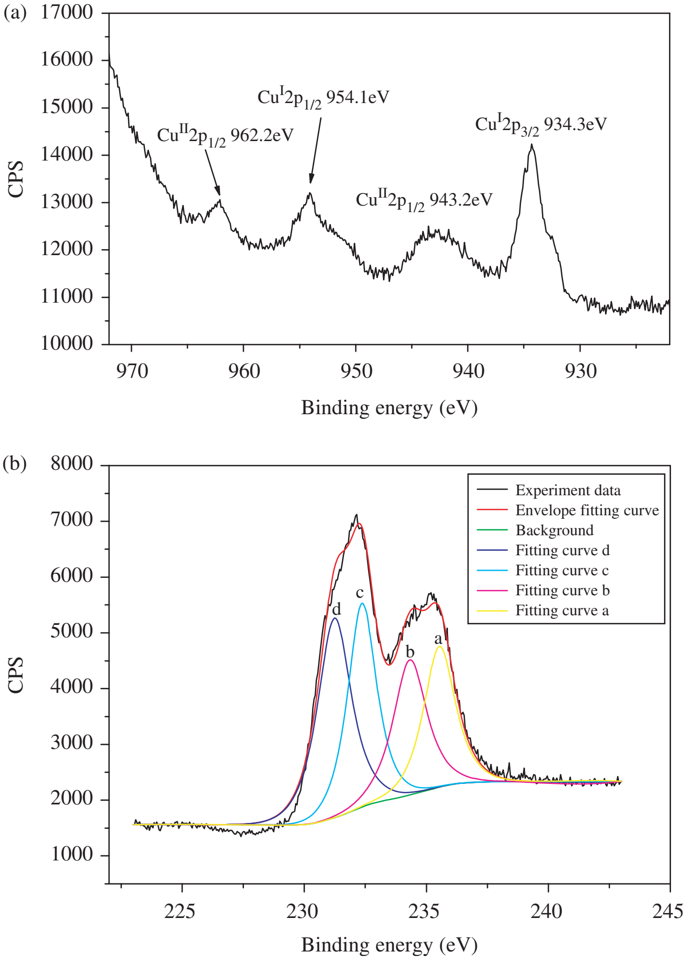

Figure 4. (a) The XPS spectrum of Cu in **1**. (b) The XPS spectrum of Mo in **1** and the fitting of it. The peak positions from curve fitting: a 231.2 eV; b 232.4 eV; c 234.3 eV; d 235.5 eV.

experimental magnetic data of the one-dimensional compound spin system using a suitable theoretical model.

4. Conclusions

We report synthesis and characterization of two new decorated polyoxometalate derivatives, $[Cu^{I}(bpy)_2]_2\{[Cu^{II}(bpy)]_2PMo_3^{V}Mo_9^{VI}O_{40}\}$ (**1**) and $H[Cu(bpy)(H_2O)]\{[Cu(bpy)]_4(PO_4)_2\}\{PW_{11}CuO_{39}\}\cdot H_2O$ (**2**). **1** shows mild photoluminescence in the solid state at room temperature and **2** has predominantly antiferromagnetic interaction between Cu^{II} centers.

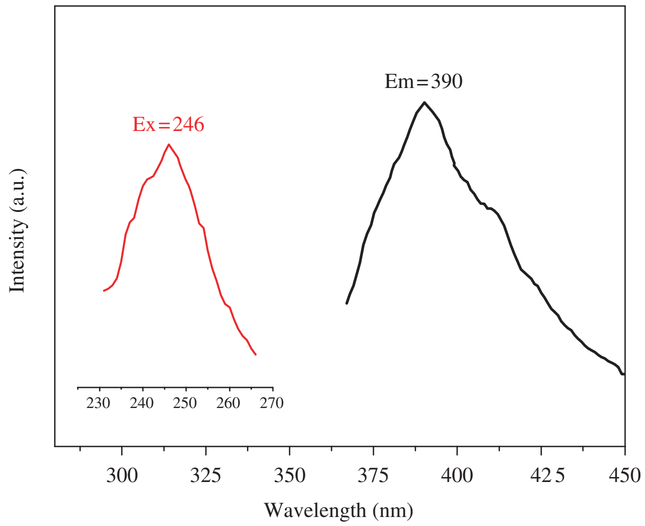

Figure 5. The excitation and emission spectra of **1** in the solid state at room temperature.

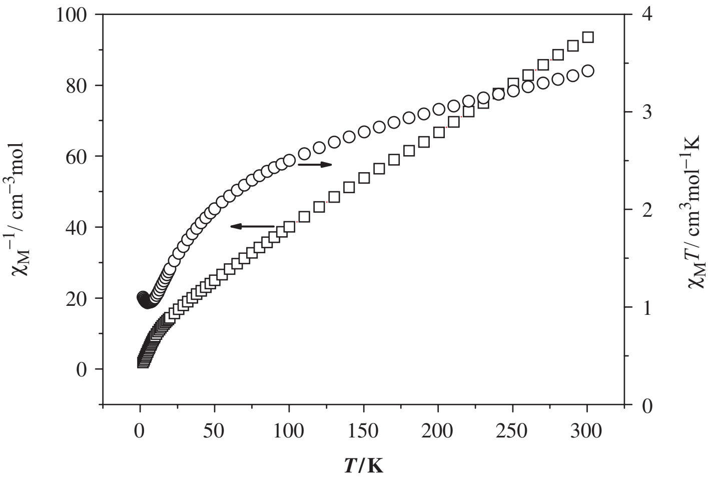

Figure 6. Temperature dependence of $1/\chi_M$ and $\chi_M T$ for **2** in an applied field of 1 kOe between 2 and 300 K.

Supplementary materials

The IR spectrum (figure S1 and figure S2) and TG curves (figure S3) of **1** and **2**, and the wide survey XPS (figure S4) for **1**, can be found in supplementary data. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre with CCDC No. 631873 for **1** and 633134 for **2**. Supplementary crystallographic data associated with this article can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif

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