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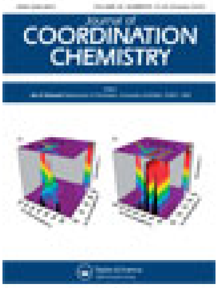

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Hydrothermal synthesis and structural characterization of two new reduced phosphomolybdates based on an organoamine template and copper ion

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Hydrothermal synthesis and structural characterization of two new reduced phosphomolybdates based on an organoamine template and copper ion

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Two new compounds, $(H_2en)_3(H_2enMe)_4(H_3O)\{Cu^I[Mo^V{}_6O_{12}(OH)_3(HPO_4)(PO_4)_3]_2\}\cdot 6H_2O$ (**1**) and $(H_2enMe)_4\{Cu^ICu^{II}[Mo^V{}_6O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\}\cdot 3H_2O$ (**2**), were hydrothermally synthesized and characterized by elemental analysis, IR, TGA, and single-crystal X-ray diffraction analysis. Crystallographic analysis reveals that **1** is constructed from cluster anions $\{Cu^I[Mo^V{}_6O_{12}(OH)_3(HPO_4)(PO_4)_3]_2\}^{15-}$, protonated organic amines, and water molecules. Each cluster is bridged through hydrogen bonds to form a 3-D supermolecular structure. For **2**, $\{Cu^I[Mo^V{}_6O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\}^{11-}$ are connected by Cu^{II} cations to form an infinite chain. The formation of **1** and **2** reveals that organoamines influence the structures of the crystals.

Keywords: Hydrothermal synthesis; Phosphomolybdates; Crystal structure; Copper ion; Organoamine-templated

1. Introduction

Phosphomolybdates attract attention for their interesting topological structures and promising applications in catalysis, photochemical activity, magnetism, and materials science [1–9]. As a branch of molybdenum phosphates, reduced phosphomolybdates have a sandwich formation which is constructed from two $[P_4Mo_6]$ units linked by a center atom; introduction of transition-metals to phosphomolybdates has become appealing to construct high-dimensional compounds. Transition metals act as counter ions and bridging ligands connecting phosphomolybdates *via* covalent bonds [10]. Transition-metal complexes can also influence the oxide microstructure [11]. A series of hybrid transition-metal molybdenum phosphates have been obtained by hydrothermal synthesis [12–21]. However, reduced phosphomolybdates including Cu^I are seldom reported [19–21]. Organoamines are structure-directing reagents which control the structure of polyoxometalates and play important roles in the reaction system; they are also organic ligands taking part in coordination and bridging inorganic fragments.

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In addition, as cations they can balance the charge of system. No mixed organic amine-templated phosphomolybdate was reported.

We report two new compounds based on organoamines and reduced copper phosphomolybdates, $(H_2en)_3(H_2enMe)_4(H_3O)\{Cu^I[Mo^V{}_6O_{12}(OH)_3(HPO_4)(PO_4)_3]_2\} \cdot 6H_2O$ (**1**) and $(H_2enMe)_4\{Cu^ICu^{II}[Mo^V{}_6O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\} \cdot 3H_2O$ (**2**) (H_2en = ethylenediamine, H_2enMe = 1,2-diaminopropane). For **1** and **2**, despite slight distinction of organoamine, the effects of organoamine template lead them to have different topological structures. Both en and enMe are found in **1**, while mixed valence Cu(I) and Cu(II) connect phosphomolybdates to form infinite chains in **2**.

2. Experimental

2.1. *Materials and equipment*

All chemicals purchased were of reagent grade and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra of **1** and **2** were recorded with a Nicolet Impact 410 FTIR spectrometer with pressed KBr pellets from 4000 to 450 cm^{-1}. TG measurement was carried out on a Diamond thermogravimetric analyzer in flowing N_2 from 40°C to 700°C with a heating rate of 10°C min^{-1}.

2.2. *Syntheses of the complexes*

2.2.1. $(H_2en)_3(H_2enMe)_4(H_3O)\{Cu^I[Mo^V{}_6O_{12}(OH)_3(HPO_4)(PO_4)_3]_2\} \cdot 6H_2O$ (1). A mixture of $Na_2MoO_4 \cdot 2H_2O$ (0.6150 g), ethylenediamine (1.0476 g), 1,2-diaminopropane (1.2656 g), copper acetate (0.4248 g), and deionized water (5 mL) was stirred for 20 min in air and 50% H_3PO_4 was added to the mixture; the final pH was 6. Then the solution was stirred for another 20 min and transferred to a 20 mL Teflon-lined autoclave and heated to 160°C for 7 days. After being cooled to room temperature, black block-like crystals were filtered, washed with deionized water, and dried in air (0.3527 g, yield 39% based on Mo). Elemental analysis: Found C 7.10%, H 3.42%, and N 6.48% (Calcd C 7.02%, H 3.28%, and N 6.36%).

2.2.2. $(H_2enMe)_4\{Cu^ICu^{II}[Mo^V{}_6O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\} \cdot 3H_2O$ (2). A mixture of MoO_3 (0.1535 g), 1,2-diaminopropane (0.3356 g), cuprous chloride (0.0528 g), and deionized water (10 mL) was stirred for 20 min in air, and 50% H_3PO_4 was added to the mixture giving final pH of 4. Then the solution was stirred for another 20 min and transferred to a 20 mL Teflon-lined autoclave and heated to 170°C for 7 days. After being cooled to room temperature, black block-like crystals were filtered, washed with deionized water, and dried in air (0.3527 g, yield 37% based on Mo). Elemental analysis: Found C 5.21%, H 5.42%, and N 3.98% (Calcd C 5.01%, H 5.35%, and N 3.89%).

Table 1. Crystal data and structure refinements for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{18}H_{104}CuMo_{12}N_{14}O_{69}P_8$	$C_{12}H_{54}Cu_2Mo_{12}N_8O_{65}P_8$
Formula weight	3083.73	2876.75
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions (Å, °)		
a	12.1739(17)	13.5331(10)
b	13.4642(19)	19.8548(15)
c	13.9696(19)	25.388(2)
α	85.797(2)	90
β	79.049(2)	101.824(10)
γ	65.195(10)	90
Volume (Å^3), Z	2040.6(5), 1	6677.0(9), 4
Calculated density (g cm^{-3})	2.509	2.862
Absorption coefficient (mm^{-1})	2.315	3.120
F(000)	1515	5536
Crystal size (mm^3)	$0.13 \times 0.12 \times 0.10$	$0.14 \times 0.12 \times 0.11$
Limiting indices	$-14 \le h \le 13$; $-16 \le k \le 16$; $-16 \le l \le 16$	$-16 \le h \le 14$; $-24 \le k \le 24$; $-31 \le l \le 31$
Reflections collected/unique	14,529/7108 [R(int) = 0.0297]	22,149/6494 [R(int) = 0.0304]
Max. and min. transmission	0.8015 and 0.7528	0.7253 and 0.6692
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	7108/580	6494/548
Goodness-of-fit on F^2	1.078	1.134
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0902$	$R_1 = 0.0392$, $wR_2 = 0.1113$
R indices (all data)	$R_1 = 0.0380$, $wR_2 = 0.0934$	$R_1 = 0.0468$, $wR_2 = 0.1155$

2.3. *X-ray crystallography*

The single crystals of **1** and **2** were selected by visual examination under a microscope and glued at the top of a thin glass fiber with epoxy in air for data collection; crystallographic data were collected on a Bruker Apex II CCD with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K using an ω–2θ scan method. The crystal structures were solved by direct methods and refined on $|F|^2$ by full-matrix least-squares using the SHELX97 program package [22]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organoamine were placed in calculated positions, while hydrogen atoms of water and OH were located from the difference map. Some disordered water molecules with the partial occupation factors and their hydrogen atoms are not located. The crystal data are presented in table 1.

3. Results and discussion

3.1. *Synthesis*

pH, temperature, and organoamine can influence the growth and final structures of the crystals. When the pH was 6, we obtained **1**, while **2** was obtained at pH 4. Organoamine play important roles in reaction system also.

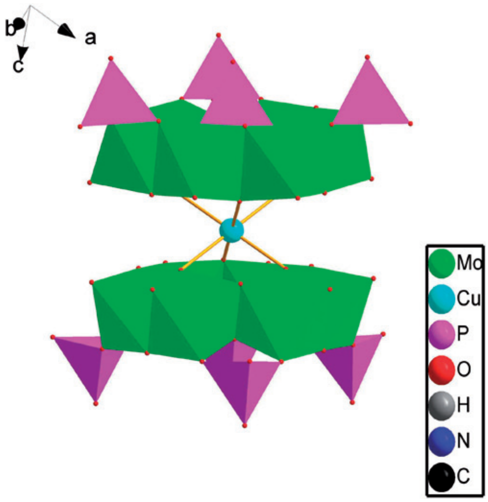

Figure 1. The classical sandwich-type anion in **1** and **2**.

3.2. *Crystal structure*

Compounds **1** and **2** have the same sandwich-type anion Cu[P_4Mo_6]$_2$ (figure 1). The [P_4Mo_6] unit can be described as a ring of six edge-sharing MoO_6 octahedra decorated by four PO_4 tetrahedra on one side, in which three are distributed around the edge of the ring and one is located in the center. Six MoO_6 groups from one ring are coplanar with alternating short Mo–Mo bonds (average 2.594 Å for **1**, 2.579 Å for **2**) and non-bonding Mo $\cdots$ Mo contacts (average 3.515 Å for **1**, 3.536 Å for **2**). The Mo–O distances are 1.676(3)–2.301(2) Å for **1** and 1.675(3)–2.294(3) Å for **2**, respectively, and the angles of O–Mo–O are between 72.55(8)° and 169.48(11)° for **1**, 71.13(10)° and 171.30(13)° for **2**. The central PO_4 tetrahedron provides three μ_3-O bridging the six molybdenums and three other peripheral PO_4 groups share two oxygen atoms to span the non-bonding Mo–Mo contacts. The P–O distances vary from 1.501(3) to 1.558(3) Å for **1**, 1.436(6) to 1.660(6) Å for **2** and the angles of O–P–O are between 106.66(15)° and 112.4(2)° for **1**, 105.35(17)° and 117.7(3)° for **2**. All the bond lengths and angles agree with reported compounds [23–27]. The assignment of the oxidation states of Mo and P for **1** and **2** are based on bond valence sum calculations [28], which gives the average value 4.817 and 4.814 for Mo and 4.992 and 4.969 for P, respectively. According to previously reported Mo–O cluster compounds [18–21, 23], Mo^{VI} can be reduced to Mo^{V} in the presence of organoamines under hydrothermal conditions. The calculation results confirm that both Mo and P have the oxidation state of +5.

Single-crystal X-ray diffraction analysis showed that **1** consists of $[Mo^{V}{}_6O_{12}(OH)_3(HPO_4)(PO_4)_3]^{8-}$, Cu^{I} cations, protonated organoamine cations (ethylenediamine and 1,2-diaminopropane), and water molecules. Terminal O(29) with longer P–O bonds [P(1)–O(29) (1.549(3) Å)] and μ_2-O atoms [O(10), O(11), O(14)] between two adjacent Mo atoms can be ascribed to OH^{-} groups due to their bond valence sum values of 0.899–1.199. Thus, the cluster anion can be formulated as

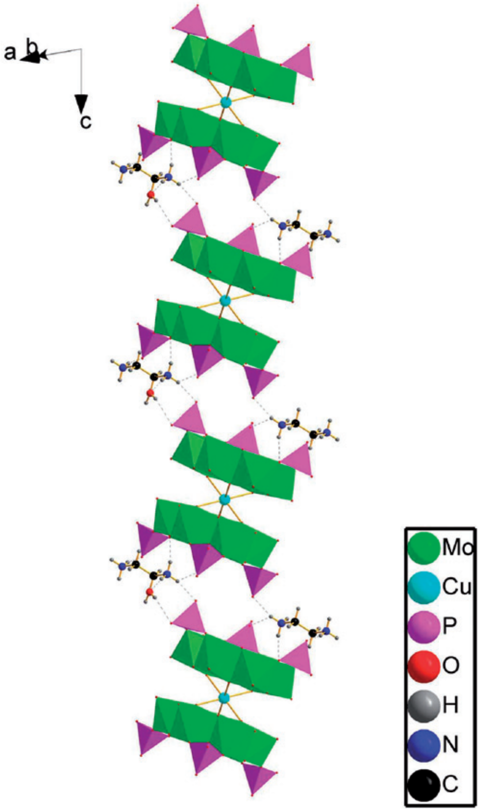

Figure 2. The infinite chain in **1**.

$[Mo^{V}_{6}O_{12}(OH)_3(HPO_4)(PO_4)_3]^{8-}$. For **1**, there exists only one coordination type of Cu, which bridges two $[P_4Mo_6]$ clusters by six μ_3-O to form a classical sandwich-type anion; the Cu–O distances are 2.208(2)–2.269(2) Å. Figure 2 shows that clusters in **1** are bridged through hydrogen bonds (N–H $\cdots$ O) from PO_4 tetrahedra and protonated organic amines to form an infinite chain. The N–H $\cdots$ O distances are 2.720(4)–3.234(5) Å. Protonated organoamines (ethylenediamine and 1,2-diaminopropane) fill into adjacent chains and each chain is linked by organoamines through hydrogen bonds (N–H $\cdots$ O) to generate a layer, exhibited in figure 3. Adjacent layers are also connected through hydrogen bonds to form a 3-D supermolecule (figure 4). Mixed organic amine-templated sandwich-type phosphomolybdates have not been reported. $[(H_3O)(H_2O)_6]^{+}$ water cluster is found in **1**. As shown in figure 5, the distances between adjacent water molecules vary from 2.975 to 3.303 Å.

When we use 1,2-diaminopropane alone, **2** was obtained, constructed by $\{Cu^{I}[Mo^{V}_{6}O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\}^{11-}$, Cu^{II} cations, 1,2-diaminopropane, and lattice water molecules. Some P–O bonds [P(1)–O(2), 1.550(4) Å; P(1)–O(7), 1.543(4) Å; P(2)–O(15), 1.550(5) Å; P(2)–O(26), 1.541(5) Å; P(3)–O(17), 1.543(5) Å; P(3)–O(20), 1.543(4) Å] are longer than other P–O bonds. The μ_2-O [O(10), O(11), O(16)] between adjacent Mo, O(2), O(7), O(15), O(17), O(20), and O(26), can be

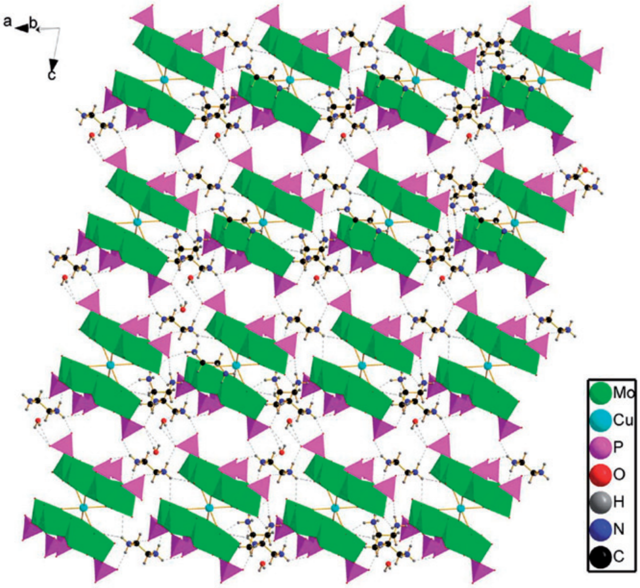

Figure 3. The 2-D layer of **1** *via* intermolecular hydrogen bonds.

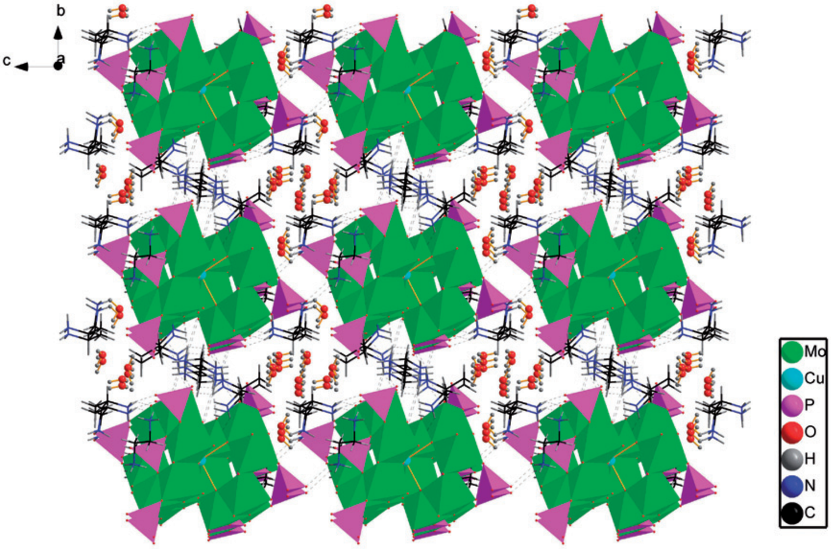

Figure 4. The 3-D supermolecular structure of **1**.

ascribed to OH^- sites due to their bond valence sum values of 1.140–1.221. So the $[P_4Mo_6]$ unit can be formulated as $\{Cu^I[Mo_6O_{12}(OH)_3(PO_4)(HPO_4)_2(H_2PO_4)]_2\}^{11-}$. There are two crystallographically different coppers, with two kinds of coordination environments in **2**. Cu(1) is four coordinate by O(1) and O(5) from two adjacent anion

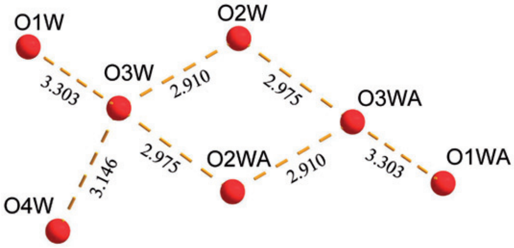

Figure 5. The $[(H_3O)(H_2O)_6]^+$ cluster in **1**.

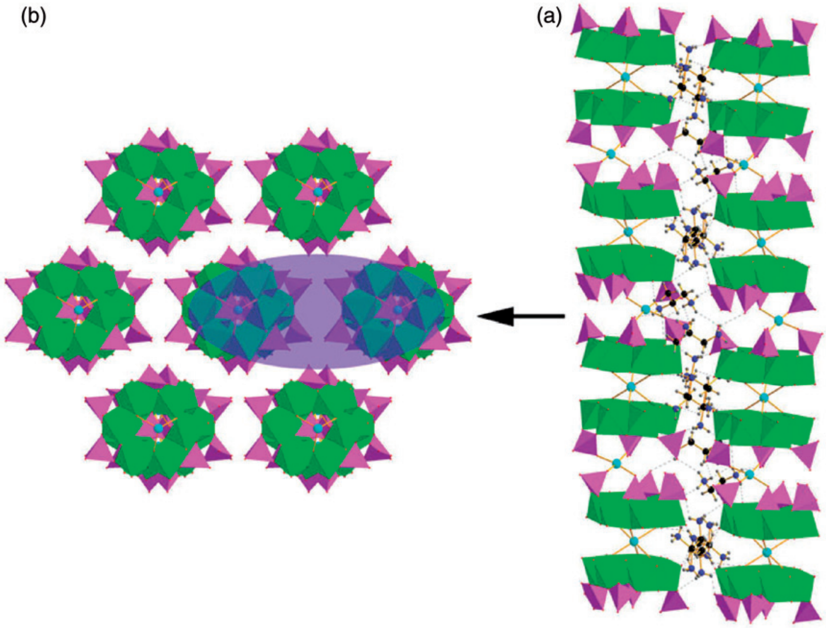

Figure 6. (a) Hydrogen-bond interactions between chains in **2** and (b) the 3-D supermolecular structure of **2**.

clusters (Cu(1)–O(1) is 1.964(3) Å, while Cu(1)–O(5) is 1.942(2) Å). Cu(2) bridges two $[P_4Mo_6]$ clusters *via* three groups of μ_3-O [O(3), O(4), O(9)] to form a classical sandwich-type anion; the bond lengths of Cu(2)–O are 2.214(3)–2.286(3) Å. The oxidation states of Cu(1) and Cu(2) in **2** are calculated by bond valence sum calculation, which are 1.808 and 0.9688, respectively. The bond valence sum results suggest that Cu(1) is +2 and Cu(2) is +1, different than reported [23]. In **2**, the sandwich-shaped $[Cu(Mo_6P_4)_2]$ clusters, as the basic building unit, are linked by four-coordinate copper to form an infinite chain. Each chain is linked by six other chains through hydrogen bonds (N–H···O) to form a 3-D supermolecule (figure 6). The N–H···O distances are from 2.702(2)–3.227(113) Å. This is the first example for mixed Cu(I)/Cu(II) sandwich phosphomolybdates.

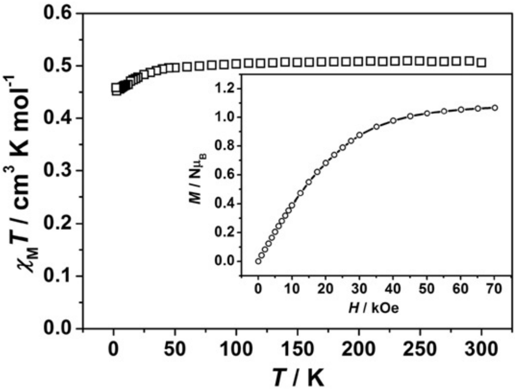

Figure 7. The variable-temperature magnetic properties under 2 kOe and the variable-field magnetization at 2 K for **2**.

3.3. *IR spectra*

The IR spectrum of **1** exhibits peaks at 611, 700, and 728 cm^{-1} associated with ν(Mo–O–Mo) and a strong band at 945 cm^{-1} due to ν(Mo=O). It also possesses bands from 1037 to 1097 cm^{-1} attributed to ν(P–O) and bands between 1383 and 1614 cm^{-1} are assigned to the C–C and C–N stretches of organoamines. Broad bands at 3219–3437 cm^{-1} are due to ν(O–H) and ν(N–H). For **2**, peaks at 3172–3427 cm^{-1} are attributed to ν(O–H) and ν(N–H). A series of bands at 1385–1629 cm^{-1} are associated with the organoamine. The ν(P–O) is 1009 cm^{-1} and strong peaks at 957, 614, 696, and 743 cm^{-1} are attributed to ν(Mo=O) and ν(Mo–O–Mo). The features are in agreement with reported compounds [29, 30].

3.4. *Magnetic properties*

Variable-temperature magnetic susceptibility measurements were carried out on crystalline samples of **2** from 300 to 2 K at an applied field of 2 kOe. As presented in figure 7, $\chi_M T$ is almost constant at 0.5 cm^3 K mol^{-1} above 50 K. After this temperature, $\chi_M T$ slightly decreases and reaches 0.45 cm^3 K mol^{-1} at 2 K. So, **2** is suggested as a paramagnet with $S = 1/2$. According to components of **2**, six Mo^{V} ions and one Cu^{II} ion will provide seven spins. However, the structure of **2** shows very short bond distance between Mo ions, Mo2–Mo5 = Mo3–Mo6 = 2.578, and Mo1–Mo4 = 2.583 Å, which should lead to very strong antiferromagetic coupling. So, the magnetic contribution of six Mo^{V} ions cannot be observed. Therefore, **2** only shows the magnetic properties of the mononuclear Cu^{II}. Further evidence can be obtained from the variable-field magnetization (inset of figure 7). With the increasing field, the magnetization slowly increases and reaches saturation above 50 kOe, then to 1.07 Nμ_B at 70 kOe, which is typical of a paramagnet and the ground state spin is 1/2 with $g = 2.14$.

3.5. *TG analysis*

The TG curve of **1** indicates that weight loss can be divided into two distinct stages. The first weight loss of 4.19% (Calcd 4.12%) at 40–260°C corresponds to loss of water.

From 260°C to 700°C, the second weight loss is attributed to decomposition of ethylenediamine and 1,2-diaminopropane (weight loss: exp. 19.03%, Calcd 19.28%).

The TG curve of **2** indicates that weight loss can be divided into two distinct stages. The first weight loss of 1.91% (Calcd 1.88%) at 40–270°C corresponds to loss of water. From 260°C to 600°C, the second weight loss is attributed to decomposition of 1,2-diaminopropane (weight loss: exp. 12.47%, Calcd 12.80%).

4. Conclusion

Two compounds based on reduced copper phosphomolybdates and organoamines are synthesized under hydrothermal conditions. Despite slight distinction of organoamines, these compounds have different structures and the dissimilar formation of **1** and **2** demonstrates that organic amine plays an important role during synthesis and crystallization.

Supplementary material

CCDC-882236 and 882235 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1E2, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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