Novel Two-dimensional Network Based on Amino-acid-octamolybdate Bridged by Second Metals: {M(H$_2$O)$_3$(pro)Mo$_4$O$_{13}$}$_2$·2H$_2$O (pro = proline, M = Co, Ni, Cu, Zn)

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Four isostructural amino-acid-based polyoxomolybdates, {M(H$_2$O)$_3$(pro)Mo$_4$O$_{13}$}$_2$·2H$_2$O (pro = proline, M = Co (**1**), Ni (**2**), Cu (**3**), Zn (**4**)), have been synthesized and structurally characterized by single crystal X-ray diffraction, elemental analysis, IR spectrum, TG analysis. The structures of **1-4** are layered networks built up from {Mo$_8$O$_{26}$(pro)$_2$}$^{4-}$ units and {M(H$_2$O)$_3$O$_3$} octahedra, the uncoordinated water molecules occupying the interlayer regions.

Key Words : Amino acid, Polyoxomolybdate, Hybrid materials, Crystal structure, Magnetism

Introduction

Inorganic-organic hybrid materials are of growing interest owing to their intriguing topological structures as well as applicable properties during the last decades.[1] Polyoxometalates, as an important class of inorganic clusters for the construction of interesting 1D chain, 2D layer, and even 3D inorganic-organic hybrid materials, have become one of the most important aspects in the recent developments.[2] To date, a number of hybrid materials based on polyoxometalates (POMs) clusters, such as the Lindquist, Keggin, Dawson type and six isomers of octamolybdates, have been widely studied and exhibited potential applications in catalysis, electrical conductivity, and biological chemistry. Generally, there are two routes to prepare such POMs-based hybrid materials: (a) organic ligands engraft onto POMs directly;[3] (b) organic ligands and second metal ions form complex subunits which link POMs through M-O bonds.[4] Among these materials, amino-acid-based POMs have drawn tremendous attentions as a model for researches on POMs-protein interactions.[5] Most of the researches were focused on the amino acid ligands covalently coordinating to POMs directly,[6] however, very rare compounds constructed from POMs and amino-acid-metal subunits have been reported.[7] Here, we introduced a second metal atom into the system of amino acid and POMs, and obtained a series of compounds: {M(H$_2$O)$_3$(pro)Mo$_4$O$_{13}$}$_2$·2H$_2$O [M = Co (**1**), Ni (**2**), Cu (**3**), Zn (**4**)] in an unusual layered network. To the best of our knowledge, this is the first report that amino acid ligands not only engraft into polyoxomolybdates directly, but also coordinate to the bridged metal ions.

Experimental Section

General Procedures. All chemicals were of reagent grade and used without further purification. The elemental analysis was performed with German Elementary Vario EL III instrument. IR spectrum was recorded on a FTS-40 spectrophotometer. The thermogravimetric analysis was carried out with a NETZSCH STA449C unit, at a heating rate of 10 °C/min under N$_2$ atmosphere from 30 to 600 °C. X-ray powder diffraction data were collected on an X-pert Pro diffractometer using Cu-Kα radiation (λ = 1.5406 Å).

Synthesis of {M(H$_2$O)$_3$(pro)Mo$_4$O$_{13}$}$_2$·2H$_2$O [M = Co (1), Ni (2), Cu (3), Zn (4)]. A mixture of MoO$_3$ (1 mmol), Co(Ac)$_2$·4H$_2$O (1 mmol), proline (1 mmol) and H$_2$O (10 mL) was stirred under ambient conditions, the pH value of which was adjusted to 3.6 by glacial acetic acid. The resultant mixture was sealed in a Teflon-line steel autoclave and heated at 100 °C for three days. After slow cooling to room temperature, red crystals of **1** were isolated in yield 46% based on Mo. Element analysis for **1**, Calcd. (%): H, 2.05; C, 7.17; N, 1.67; Co, 7.03; Mo, 45.80; Found (%): H, 2.15; C, 7.20; N, 1.65; Co, 7.00; Mo, 45.80; IR (cm^{-1}, KBr): 3414 (s), 1619 (s), 1559 (m), 1435 (m), 1417 (m), 1368 (m), 1333 (m), 1168 (m), 938 (s), 900 (s), 838 (m), 695 (s), 635 (s). Other compounds (**2-4**) were obtained with the same procedure for **1**. Element analysis for **2**, Calcd. (%): H, 2.05; C, 7.17; N, 1.67; Ni, 7.01; Mo, 45.81; Found (%): H, 2.10; C, 7.15; N, 1.68; Ni, 7.00; Mo, 45.80; Element analysis for **3**, Calcd. (%): H, 2.03; C, 7.13; N, 1.66; Cu, 7.54; Mo, 45.55; Found (%): H, 2.12; C, 7.18; N, 1.65; Cu, 7.52; Mo, 45.55; Element analysis for **4**, Calcd. (%): H, 2.03; C, 7.11; N, 1.66; Zn, 7.74; Mo, 45.45; Found (%): H, 2.14; C, 7.10; N, 1.65; Zn, 7.70; Mo, 45.44.

X-ray Crystallography. The diffraction data of compounds **1-4** were collected at 298 K on a Mercury CCD diffractometer equipped with a graphite monochromator with MoKα zradiation (λ = 0.71073). Empirical absorption correction was applied by using the CrystalClear program.[8] The structures were solved with direct methods and all calculations were performed using the SHELXTL package.[9] The structures

Table 1. Crystallographical data for compounds **1-4**

Empirical formula	$C_{10}H_{34}Co_2Mo_8N_2O_{38}$ (1)	$C_{10}H_{34}Mo_8N_2Ni_2O_{38}$ (2)	$C_{10}H_{34}Cu_2Mo_8N_2O_{38}$ (3)	$C_{10}H_{34}Mo_8N_2O_{38}Zn_2$ (4)
Formula weight	1675.77	1675.33	1684.99	1688.65
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)/n
Unit cell dimensions	a = 11.8078 (5) Å	a = 11.720 (2) Å	a = 11.7855 (6) Å	a = 11.8289 (7) Å
	b = 13.3392 (4) Å	b = 13.308 (1) Å	b = 13.3940 (7) Å	b = 13.3161 (8) Å
	c = 12.7242 (5) Å	c = 12.687 (2) Å	c = 12.6477 (8) Å	c = 12.7108 (9) Å
	beta = 103.947 (2) °	beta = 103.653 (8) °	beta = 103.472 (2) °	beta = 103.871 (3) °
Volume	1945.06(13) Å^3	1922.9(4) Å^3	1941.57(19) Å^3	1943.8(2) Å^3
Z	2	2	2	2
Calculated density	2.861 Mg/m^3	2.894 Mg/m^3	2.882 Mg/m^3	2.885 Mg/m^3
Absorption coefficient	3.437 mm^{-1}	3.594 mm^{-1}	3.685 mm^{-1}	3.820 mm^{-1}
F(000)	1604	1608	1612	1616
Crystal size	0.24 × 0.12 × 0.08 mm	0.12 × 0.10 × 0.06 mm	0.25 × 0.1 × 0.10 mm	0.28 × 0.28 × 0.13 mm
Theta range for data collection	3.05 to 27.48°	3.06 to 25.03°	3.04 to 27.48°	3.06 to 27.48°
Limiting indices	−15 ≤ h ≤ 13, −16 ≤ k ≤ 17, −16 ≤ l ≤ 16	−8 ≤ h ≤ 13, −15 ≤ k ≤ 15, −15 ≤ l ≤ 15	−15 ≤ h ≤ 13, −13 ≤ k ≤ 17, −16 ≤ l ≤ 16	−15 ≤ h ≤ 13, −11 ≤ k ≤ 17, −16 ≤ l ≤ 16
Reflections collected / unique	14681 / 4443 [R(int) = 0.0169]	11995 / 3378 [R(int) = 0.0602]	14686 / 4442 [R(int) = 0.0294]	14700 / 4454 [R(int) = 0.0261]
Max. and min. transmission	0.7705 and 0.4926	0.8133 and 0.6723	0.7095 and 0.4594	0.6365 and 0.4143
Data / restraints / parameters	4443 / 34 / 317	3378 / 46 / 308	4442 / 78 / 317	4454 / 46 / 317
Goodness-of-fit on F^2	1.041	1.047	1.034	1.062
Final R indices [I>2sigma(I)]	R1 = 0.0769, wR2 = 0.2076	R1 = 0.0796, wR2 = 0.1601	R1 = 0.0867, wR2 = 0.2212	R1 = 0.0794, wR2 = 0.2061
R indices (all data)	R1 = 0.0775, wR2 = 0.2078	R1 = 0.0902, wR2 = 0.1673	R1 = 0.0891, wR2 = 0.2223	R1 = 0.0813, wR2 = 0.2069
Largest diff. peak and hole	1.823 and −1.660 e·Å^{-3}	1.184 and −1.032 e·Å^{-3}	1.759 and −1.638 e·Å^{-3}	1.736 and −1.563 e·Å^{-3}

$R1 = \Sigma(\ |F_o| - |F_c|\ ) / \Sigma|F_o| \cdot wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2. Selected bond lengths for compound **1** (Å)

Bond	Distant (Å)	Bond	Distant (Å)	Bond	Distant (Å)
Mo(1)-O(1)	1.69(1)	Mo(3)-O(5)#1	2.40(1)	O(6)-Mo(4)#1	2.28(1)
Mo(1)-O(2)	1.72(1)	Mo(4)-O(12)	1.70(1)	O(10)-Mo(3)#1	1.76(1)
Mo(1)-O(3)	1.93(1)	Mo(4)-O(13)	1.74(1)	O(14)-C(1)	1.27(2)
Mo(1)-O(4)	1.98(1)	Mo(4)-O(4)#1	1.87(1)	O(15)-C(1)	1.23(3)
Mo(1)-O(5)	2.247(9)	Mo(4)-O(9)	2.04(1)	C(1)-C(2B)	1.53(4)
Mo(1)-O(6)	2.25(1)	Mo(4)-O(14)	2.15(1)	C(1)-C(2A)	1.60(4)
Mo(2)-O(7)	1.71(1)	Mo(4)-O(6)#1	2.28(1)	C(2A)-N(6A)	1.47(4)
Mo(2)-O(8)	1.72(1)	Co(5)-O(15)	2.03(2)	C(2A)-C(5A)	1.50(5)
Mo(2)-O(9)	1.93(1)	Co(5)-O(16)	2.05(1)	C(3A)-N(6A)	1.46(5)
Mo(2)-O(3)	1.94(1)	Co(5)-O(17)	2.07(1)	C(3A)-C(4A)	1.56(6)
Mo(2)-O(5)	2.247(9)	Co(5)-O(13)	2.09(1)	C(4A)-C(5A)	1.38(6)
Mo(2)-O(10)	2.37(1)	Co(5)-O(2)#2	2.09(1)	C(2B)-N(6B)	1.48(4)
Mo(3)-O(11)	1.70(1)	Co(5)-O(18)	2.13(1)	C(2B)-C(3B)	1.55(5)
Mo(3)-O(10)#1	1.76(1)	O(2)-Co(5)#3	2.09(1)	C(3B)-C(4B)	1.43(5)
Mo(3)-O(6)#1	1.91(1)	O(4)-Mo(4)#1	1.87(1)	C(4B)-C(5B)	1.46(6)
Mo(3)-O(5)	1.94(1)	O(5)-Mo(3)#1	2.40(1)	C(5B)-N(6B)	1.50(5)
Mo(3)-O(9)	2.17(1)	O(6)-Mo(3)#1	1.91(1)		

Symmetry transformations used to generate equivalent atoms: #1 −x+1, −y+1, −z; #2 x−1/2, −y+3/2, z+1/2; #3 x+1/2, −y+3/2, z−1/2

were refined by full-matrix least squares with anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were generated geometrically with C-H = 0.97 Å, N-H = 0.90 Å, O-H = 0.85 Å, and $U_{iso} = 1.2U_{eq}$. Details of the crystal data are listed in Table 1. Selected bond lengths for compound **1** are listed in Table 2.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Center {(Deposition No. CCDC 297746(1)-297749(4)). The data can be obtained free of charge via *www.ccdc.cam. ac.uk/conts/retrieving.html* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

The title compounds were obtained from hydrothermal reactions of MoO_3, $M(Ac)_2 \cdot xH_2O$ (M = Co, Ni, Cu, Zn), proline and H_2O in a mole ratio of 1 : 1 : 1 : 555 at 100 °C, with pH *ca.* 3.6. Of the four compounds, compound **3** was difficult to isolate and the yield was very low. It may be because the proline ligand and the copper ions easily form the {Cu(pro)$_2$} complex. Compounds **1**, **2** and **4**, can also be obtained from the solution of $M(Ac)_2 \cdot xH_2O$ (M = Co, Ni, Zn), $NaMoO_4 \cdot 2H_2O$, proline and H_2O by stirring at 60-100 °C.

Single crystal X-ray diffraction analyses reveal that compounds **1-4** are isostructural. Therefore, only the structure of compound **1** is here described. The structure of compound **1** consists of layered covalent networks formed by {Mo$_8$O$_{26}$(pro)$_2$}$^{4-}$ units and {Co(H$_2$O)$_3$O$_3$} octahedra, with the uncoordinated water molecules occupying the interlayer regions. The basic building block is shown in Fig. 1. In compound **1**, there exist four crystallographically independent Mo atoms and one cobalt atom. The environment around each Mo atom is a distorted {MoO$_6$} octahedron with Mo-O distances of 1.69(1)-2.40(1) Å, O-Mo-O angles of 70.6(4)-175.4(5)° and Mo-O-Mo angles of 91.9(4)-153.1(5)°. Four asymmetric {MoO$_6$} octahedra form a {Mo$_4$O$_{13}$} unit via edge-sharing, while two centrosymmetric

tetramolybdate units link together through edge-sharing to form a well known octamolybdate cluster. Two proline ligands engraft into the octamolybdate cluster via Mo(1)-O bonds to form a {Mo$_8$O$_{26}$(pro)$_2$}$^{4-}$ cluster, which displays a similar configuration to the reported {Mo$_8$O$_{26}$(L)$_2$}$^{4-}$ cluster (L = nic,[10] glycine,[6e] lysine[6d]). As depicted before, the oxygen atoms of the octamolybdate cluster can be classified into four types: two μ_4-O atoms with Mo-O distances varying from 1.94(1) to 2.40(1) Å, four μ_3-O atoms with Mo-O distances in the range of 1.91(1)-2.28(1) Å, six μ_2-O atoms with Mo-O distances in the range of 1.76(1)-2.37(1) Å, and fourteen terminal oxygen atoms with Mo-O distances of 1.69(1)-1.74(1) Å. Extensive bond valence sum calculations[11] indicated that the valence of each of the four Mo atoms is +6, which is in agreement with that in the common octamolybdate cluster. The crystallographically unique cobalt atom is coordinated in a distorted {CoO$_6$} octahedron to six oxygen atoms from one proline ligand, two adjacent octamolybdate clusters and three water molecules, respectively. Extensive bond valence sum calculations indicated that the valences of all the M atom are +2 (Co = 2.138, Ni = 2.139, Cu = 2.175, Zn = 2.181). The two oxygen atoms of the proline ligand coordinate to molybdate and cobalt atoms, respectively. The five-membered ring of the proline ligand is slight disordered. Alternatively, the structure of the layer framework may be described as a {Co$_2$Mo$_8$O$_{29}$} metal oxide network, the proline ligands engrafting into the network and occupying the cavities (shown in Fig. 2). The parallel layers are further connected by hydrogen bonds (shown in Fig. 3). There are three types of hydrogen bonding interactions: (i) $O_{(-Co)} \cdots O_{(-Mo)}$ bond distances of 2.74(2) and 2.85(2) Å; (ii) $O_{(-Co)} \cdots O_{(uncoord.)}$ bond distances of 2.70(2) and 2.93(3) Å; (iii) $O_{(uncoord.)} \cdots O_{(-Mo)}$ bond distances of 2.89(2) Å (listed in Table 3).

It should be noted that the amino acid ligands in the title compounds may play a new structural role different from the previous reports, such as (i) simple counterions interact to polyoxomolybdate anions through hydrogen bonding, *e.g.* in
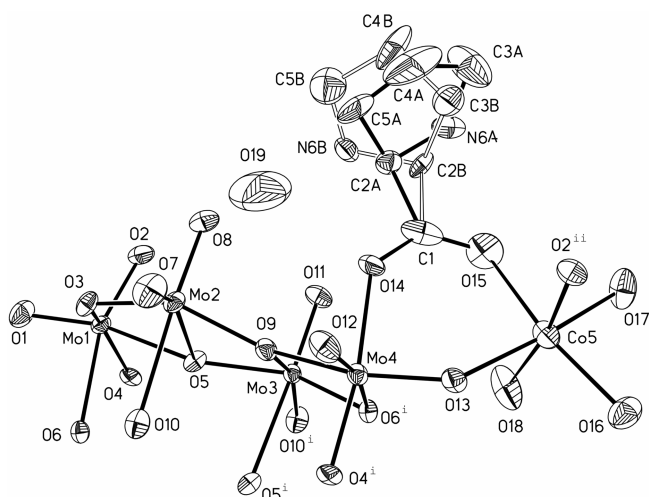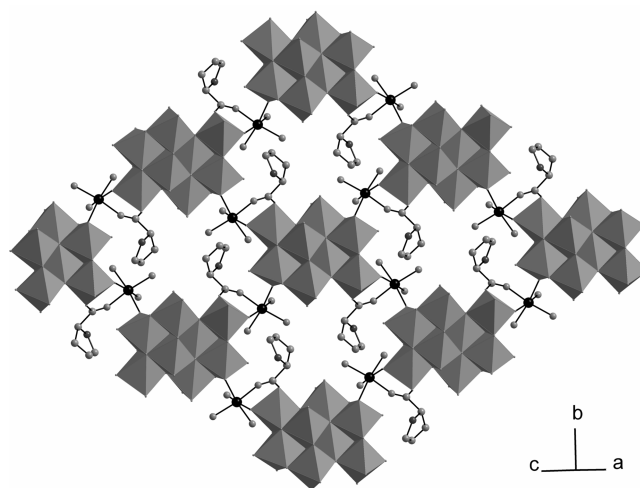

Figure 1. The asymmetry unit of compound **1** that shows the coordination environment around Co and Mo atoms. Displacement ellipsoids are drawn at the 50% probability level and the hydrogen atoms are omitted for clarity. The five-member ring of the proline is disordered, and treated as two parts; the part 1 is of C2A, N6A, C3A, C4A, and C5A; the part 2 is of C2B, N6B, C3B, C4B, and C5B. The symmetry codes are: (i) −x+1, −y+1, −z; (ii) −1/2+x, −1/2−y, −1/2+z.

Figure 2. A View of the layer structure of compound **1**. Polyhedra represent octamolybdate clusters.
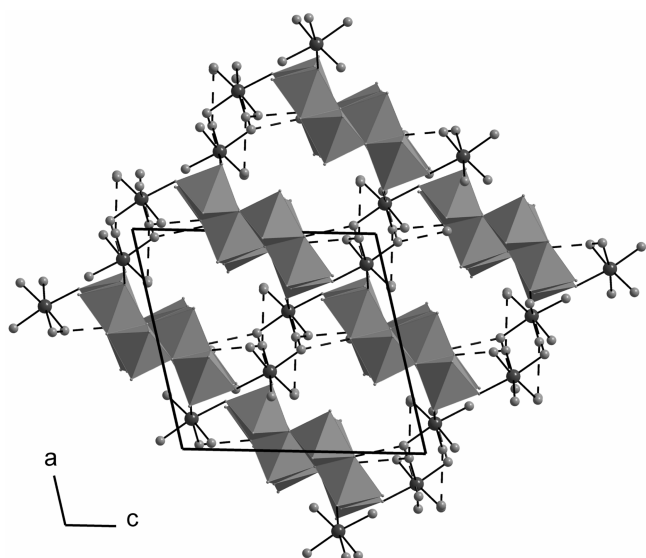
Figure 3. Three-dimensional network formed via the hydrogen-bonding interactions in compound **1**. Polyhedra represent octamolybdate clusters. All of the H, C, and N atoms are omitted for clarity.

Table 3. Hydrogen-bonding geometry for compound **1** (Å, °)

D — H···A	D—H	H···A	D···A	<(DHA)
O16 — H16A···O8(i)	0.85	1.98	2.83(2)	173.8
O16 — H16B···O19(ii)	0.85	1.85	2.70(2)	174.0
O17 — H17A···O3(iii)	0.85	1.91	2.75(2)	172.3
O17 — H17B···O12(iv)	0.85	2.01	2.85(2)	172.4
O18 — H18A···O6(v)	0.85	1.89	2.74(2)	171.7
O18 — H18B···O19(iv)	0.85	2.08	2.93(3)	172.6
O19 — H19A···O12	0.86	2.05	2.89(2)	167.1

Symmetry codes: (i): x−1/2, −y+3/2, z+1/2; (ii): −x+1/2, y−1/2, −z+1/2; (iii): x, y, z+1; (iv): x+1/2, −y+3/2, z+1/2; (v): −x+1, −y+1, −z.

Figure 4. Experimental and simulated X-ray powder diffraction pattern of compound **1**.
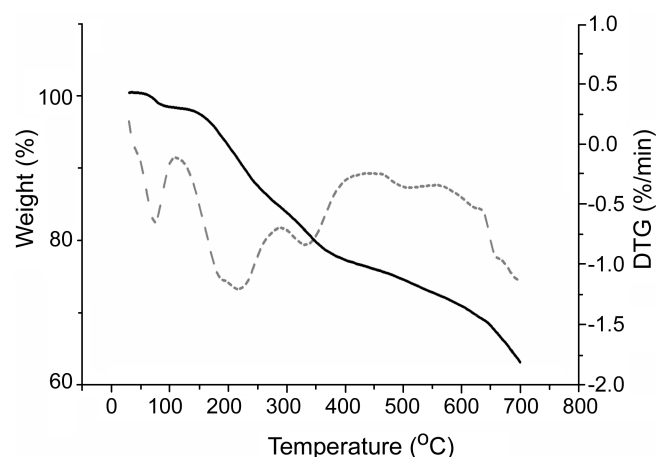
Figure 5. TGA-DTG of $\{Co(H_2O)_3(pro)Mo_4O_{13}\}_2 \cdot 2H_2O$ in flowing N_2 at 10 °C·min^{-1}.

$(Gly)_2H_4SiW_{12}O_{40} \cdot 5.5H_2O$;[5b] (ii) ligands incorporate a second-metal to form a part of a bimetallic molybdenum oxide backbone, e.g. in $[(Gly)_2Cu][Na(H_2O)_4Cr(OH)_6Mo_6O_{18}]\cdot 9.5H_2O$;[7a] and (iii) ligands covalently bind to the molybdenum oxide skeleton, *e.g.* in $[Mo_8O_{26}(L\text{-}lysH_2)_2]^{2-}$ [6d] and $[SeMo_6O_{21}(glyH)_3]^{2-}$.[6a] In the title compounds, one carboxyl oxygen atoms of the proline ligand is bound to octamolybdate center directly to form a $\{Mo_8O_{26}(pro)_2\}^{4-}$ cluster as the third mode, while the other one is bound to the second metal center to form a $\{M(H_2O)_3O_3\}$ octahedron as the second mode. Coupling such two modes, proline ligand exhibits a new structural role in construction of polyoxomolybdate-based compounds. It suggests that in the presence of a second metal, amino acids are excellent candidates for the construction of various structural motifs of polyoxomolybdate-based hybrid compounds.

The experimental XRD pattern and the simulated pattern on the basis of single crystal structure are shown in Figure 4. The diffraction peaks of both patterns correspond well in position, suggesting the phase purity of the sample. The IR spectra of compound **1** shows that the stretching vibrations
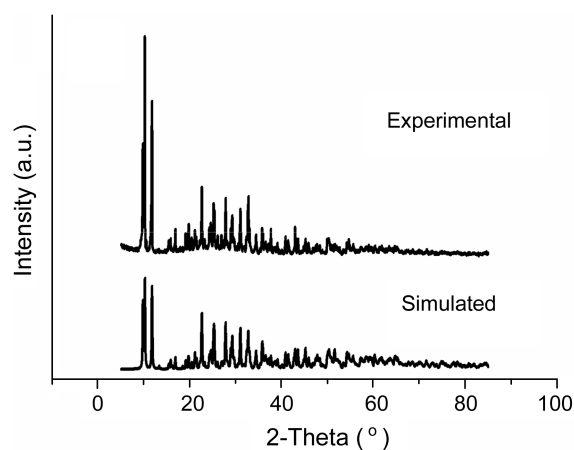
of C-H, N-H and O-H are in the 2851-3492 cm^{-1} region and the stretching vibrations of the proline ligand are in between 1000 and 1610 cm^{-1}. The strong bands in the region of 700-950 cm^{-1} may be assigned to the stretching vibrations of the Mo-O and Mo-O-Mo bonds.

TGA measurement was performed on a NETZSCH STA 449C system. As shown in Figure 5, the weight loss of compound **1** in the ranges of 50-110 °C (cal. 2.15%, found 2.02%) is in agreement with the removal of the lattice water molecules, in 110-290 °C (cal. 13.75%, found 13.87%) is in agreement with the removal of proline ligands, and in 290-380 °C (cal. 6.46%, found 6.49%) is in agreement with the removal of coordination water molecules.

Conclusion

In this work, four isostructural inorganic-organic hybrid molybdates with the amino acid (proline) have been reported. The compounds display a unique layer structure based on $\{Mo_8O_{26}(pro)_2\}^{4-}$ clusters bridged by second metal coordination centers. The successful preparations of **1-4** indicate that by introducing second metal into the system of amino acid and

POMs may be useful for constructing POMs-based hybrid materials with versatile structures. Further research will be focused on the study of the effects of all kinds of amino acid and second metals on the reaction systems.

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