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Synthesis and characterization of two new polyoxomolybdate compounds: $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ and $[Himi]_3[H_3O][SiMo_{12}O_{40}] \cdot H_2O$

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Abstract

Two new compounds, $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ (**1**) and $[Himi]_3[H_3O][SiMo_{12}O_{40}] \cdot H_2O$ (**2**) (imi = imidazole), have been synthesized and characterized by single crystal X-ray analysis, IR spectra and elemental analysis. Compound **1** consists of an imidazole-coordinated octamolybdate anion, two protonated imidazole cations and one imidazole and water coordinating copper cation per unit cell. Compound **2** is built up of the Keggin-type $[SiMo_{12}O_{40}]^{4-}$ anions, protonated imidazole cations, hydroxonium ions and lattice water molecules. Both compounds **1** and **2** are three-dimensional frameworks held together by complex hydrogen bonding.

Keywords: Polyoxometallates; Octamolybdates; Keggin-type anions; Imidazole ligands; Copper

1. Introduction

Polyoxometallates, a rich class of inorganic compounds with remarkable degrees of molecular and electronic tunabilities, have attracted great attention from researchers in many fields such as catalysis, material science, medicine and magnetochemistry [1–4]. It has been found that the compounds containing molybdenum atoms, especially polyoxomolybdates containing organic molecules, are good catalysts for oxidation reactions, because they can be applied as models for the interaction between organic substrates and catalytic metal oxide surfaces in heterogeneous catalysis employing solid molybdenum oxides [5,6]. Moreover, certain polyoxomolybdates have been recognized as potential anti-tumor agents [7]. One of the most challenging tasks is to synthesize chiral structures containing molybdenum atoms, since enantioselective oxidation catalysis and biological activity are fascinating fields of studies. Although various preparation methods had been proposed to obtain such polynuclear complexes, the development of a "rational" synthesis method for new compounds is still one of the major challenges in polyoxometallic chemistry [8].

During our investigations on compounds having asymmetric architectures, we have realized that almost all polyoxomolybdate units, for example, $\{Mo_8O_{26}\}$ [9], $\{XMo_{12}O_{40}\}$ (X = S, Si, P, V, etc.) [1], $\{Mo_6O_{19}\}$ [10] and $\{Mo_{36}O_{112}\}$ [11], are central symmetric in most cases. We have adopted an alternative strategy for the design of asymmetric compounds through modification of the outer parts of the cluster anions. Herein we report the rational synthesis and crystal structure characterization of two new compounds, $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ (**1**) and $[Himi]_3[H_3O][SiMo_{12}O_{40}] \cdot H_2O$ (**2**) (imi = imidazole), which provide examples of an effective and rational synthetic method in polyoxometallic chemistry.

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2. Experimental

2.1. Materials and measurements

All chemicals were of reagent grade and used as received. Elemental analyses were performed with a Vario EL III CHNOS Element Analyzer. Infrared spectra were recorded on an FTS-40 spectrophotometer using pressed KBr pellets.

2.2. Synthesis

2.2.1. $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ (**1**)

A mixture of H_2MoO_4 (1.62 g, 10 mmol) and imidazole (0.34 g, 5 mmol) in 120 ml H_2O was heated at 60 °C under stirring. After the color of the reaction solution turned clear, $Cu(OCOCH_3)_2 \cdot H_2O$ (0.5 g, 2.5 mmol) was added. The resultant was filtered off to give a light blue filtrate. Blue crystals of **1** were formed after 2 days, which were filtered off and washed with ethanol and diethyl ether, and finally dried in air (Yield about 65%). *Anal.* Calc. for **1**: C, 12.5; H, 1.98; N, 9.72. Found: C, 12.9; H, 1.93; N, 9.61%. IR (KBr pellet, cm^{-1}): 1630m, 1683s, 1543m, 1498m, 1448m, 1321m, 1267m, 1184m, 1132m, 1093s, 1074s, 1051m, 935s, 893s, 854sh, 939m, 756m, 677s, 638m, 557m, 530m, 482m, 440m, 417m.

2.2.2. $[Himi]_3[H_3O][SiMo_{12}O_{40}] \cdot H_2O$ (**2**)

A mixture of H_2MoO_4 (4.86 g, 30 mmol) and imidazole (0.51 g, 7.5 mmol) in 120 ml H_2O was heated at 60 °C under stirring. After the color of the reaction solution turned clear, $Cu(OCOCH_3)_2 \cdot H_2O$ (0.8 g, 4 mmol) was added to give a light-blue reaction mixture, which was then filtered. Light yellow crystals of **2** were isolated from the filtrate after several weeks in very low yield. However, when copper acetate was replaced by Na_2SiO_3 (0.35 g, 2.9 mmol), compound **2** was produced in higher yield within a few days, which was filtered off and washed with ethanol and diethyl ether, and finally dried in air (Yield about 89% based on Mo). *Anal.* Calc. for **2**: C, 5.2; H, 0.98; N, 4.1; Si, 1.36. Found: C, 5.4; H, 1.03; N, 4.0; Si, 1.33%. IR (KBr pellet, cm^{-1}): 1697s, 1579s, 1502s, 1441m, 1412s, 1294s, 1252m, 1165m, 1128m, 1092m, 1068m, 953s, 906s, 862m, 793s, 692m, 660m, 623m, 598m, 534m, 507m.

2.3. Crystal structure determination

Intensity data were measured on a Siemens SMART CCD with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K and corrected for adsorption by the SADABS [12] program. The structures were solved by direct methods and refined by full-matrix least-squares method with the SHELXL-97 [13] program package. All atoms except hydrogen atoms were refined anisotropically. All the hydrogen atoms were located from difference Fourier maps. Crystallographic data for compounds **1** and **2** are summarized in Table 1.

3. Result and discussion

It has been known that the reactivity of H_2MoO_4 is enhanced compared to MoO_3 [14,15]. In this case, the imidazole ligand easily coordinates to the molybdenum atom through one nitrogen atom to form $[(imi)_2Mo_8O_{26}]^{4-}$. Consequently, the protonated imidazole ligands are employed as cations for charge balance in the absence of additional cations. The uncoordinated

Table 1
Crystal data and structure refinements for $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ (imi = imidazole) (**1**) and $[Himi]_3[H_3O][SiMo_{12}O_{40}]H_2O$ (**2**)

Compound	**1**	**2**
Formula	$C_{18}H_{34}CuMo_8N_{12}O_{30}$	$C_9H_2OMo_{12}N_6O_{42}Si$
Formula weight	1729.63	2063.68
Crystal system	triclinic	orthogonal
Space group	$P\bar{1}$	*P*2(1)2(1)2(1)
a (Å)	10.0335(1)	13.8172(2)
b (Å)	11.5110(1)	14.5808(1)
c (Å)	11.8170(1)	21.1081(2)
α (°)	87.392(1)	90
β (°)	68.979(1)	90
γ (°)	65.936(1)	90
V ($Å^3$)	1155.10(2)	4252.56(8)
Z	1	4
$D_{Calc.}$ (g cm^{-3})	2.486	3.223
μ (Mo Kα) (mm^{-1})	2.651	3.566
λ (Å)	0.71073	0.71073
T (K)	293(2)	293(2)
$R1, wR2$ $[I > 2\sigma(I)]$	$R1 = 0.0274, wR2 = 0.0640$	$R1 = 0.0598, wR2 = 0.1212$
$R1, wR2$ (all data)	$R1 = 0.0308, wR2 = 0.0672$	$R1 = 0.0851, wR2 = 0.1431$

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

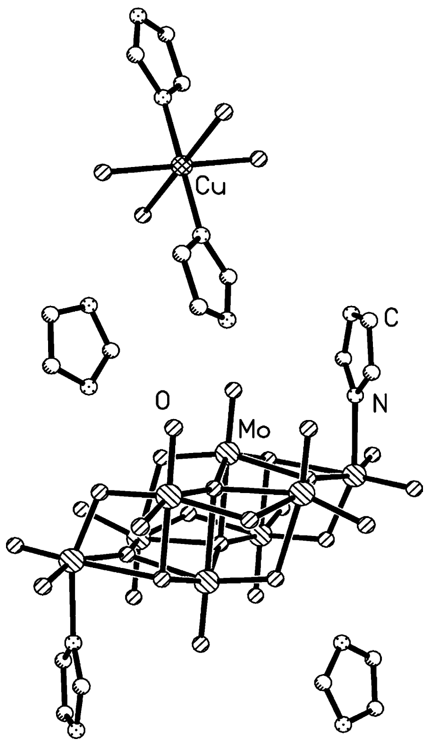

Fig. 1. The molecular structure of **1**.

ligands have potential coordination ability to coordinate to transition metal cations. Based on this finding, we have succeeded in the isolation of a new complex, $[Cu(imi)_2(H_2O)_4][Himi]_2[(imi)_2Mo_8O_{26}]$ (**1**).

The IR spectrum of compound **1** exhibits broad bands from 1051 to 1630 cm^{-1}, which can be assigned to the bending vibrations of the CH, NH and OH, or the ring stretching frequency of the imidazole ligand. The strong bands from 935 and 893 cm^{-1} are attributed to Mo–O stretching, while those from 638 to 854 cm^{-1} are assigned to Mo–O–Mo bending vibrations. As shown in Fig. 1, compound **1** consists of an imidazole coordinating octamolybdate anion, two protonated imidazole cations, one imidazole and water coordinating copper cation per unit cell. The centrosymmetric anion $[(imi)_2Mo_8O_{26}]^{4-}$ is built up of two $\{C_3H_4N_2MoO_5\}$ units and six $\{MoO_6\}$ edge-shared octahedra. It can also be described as two centrosymmetric related cyclic $\{(imi)\text{-}Mo_4O_{13}\}$ units that are cross-linked by bridging oxygen atoms. The two symmetry related molybdenum atoms are coordinated directly by two imidazole ligands with a Mo–N distance of 2.186(4) Å, which is comparable to those in $[(pyridine)_2Mo_8O_{26}]^{4-}$, $[(pyrazole)_2Mo_8O_{26}]^{4-}$, $[Mo_8O_{26}(NCS)_2]^{6-}$, $[(methylimidazole)_2Mo_8O_{26}]^{4-}$ and $[(imidazole)_2Mo_8O_{26}]^{4-}$ [15–18]. The coordination environment of each molybdenum atom is a distorted octahedron with Mo–O/N distances ranging from 1.696(3) to 2.455(3) Å. According to the coordinating mode, the oxygen atoms in the anion can be divided into four different groups: terminal oxygen atoms (Mo–O = 1.696(3)–1.728(3) Å), μ_2-O atoms (Mo–O = 1.756(3)–2.393(3) Å), μ_3-O atoms (Mo–O = 1.875(3)–2.292(3) Å) and μ_4-O atoms (Mo–O = 1.952(3)–2.455(3) Å).

Each copper atom in the $[Cu(imi)_2(H_2O)_4]^{2+}$ unit is coordinated by two nitrogen donors of imidazole ligands with a mean Cu–N distance of 1.979(4) Å, and four aqua ligands to complete the octahedral coordination environment with Cu–O distances in the 2.002(3)–2.498(4) Å range.

All the anions and cations are joined together through complex hydrogen bonding to form a three-dimensional architecture (Fig. 2). The distances between aqua ligands and the oxygen atoms of octamolybdate vary from 2.673(5) to 3.009(5) Å, while the distances between the nitrogen atoms of imidazole ligands and the oxygen atoms of octamolybdate or aqua ligands are also within the hydrogen bonding range (2.760(5)–3.281(6) Å).

It has been known that the molybdenum atoms can be further condensed when the acidity of the reaction mixture is lowered, when units like $\{Mo_{36}\}$ or other olimers $\{Mo_2O_7\}$ [19], $\{Mo_3O_{10}\}$ [20], $\{Mo_7O_{22}\}$ [21] and $\{Mo_8O_{27}\}$ [22] can be formed. Unfortunately, upon the addition of excess molybdenic acid, only a Keggin-type compound, $[Himi]_3[H_3O][SiMo_{12}O_{40}]\cdot H_2O$ (**2**), was obtained after several weeks. As previously mentioned, undesired compounds might result when the system contains an abundant amount of sodium silicate in the glass vessel [23]. After a large amount of sodium silicate was added to the reaction solution, a high yield of compound **2** was achieved.

In the IR spectrum of **2**, the strong bands at 953, 906, 862, 793 and 692 cm^{-1} are due to the Mo–O stretching or Mo–O–Mo bending vibrations. Bands in the 1697–1051 cm^{-1} region are attributed to extending vibrations

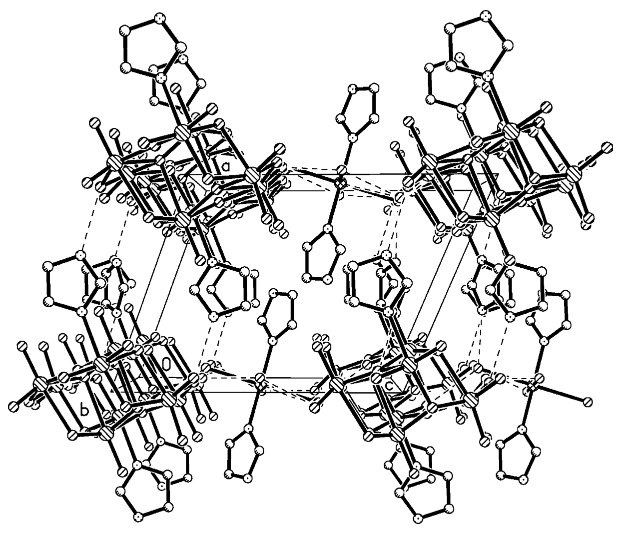

Fig. 2. The packing diagram of **1** viewed down the *b* axis.

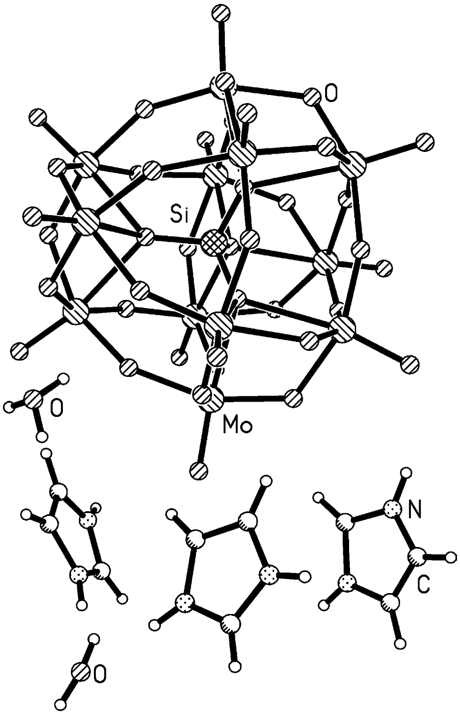

Fig. 3. The molecular structure of **2**.

of the imidazole ligands or O–H groups. As shown in Fig. 3, the central $[SiMo_{12}O_{40}]^{4-}$ anion is a typical Keggin-type structure [24] consisting of one $\{SiO_4\}$ tetrahedron and twelve $\{MoO_6\}$ octahedra. The central $\{SiO_4\}$ is a tetrahedron with Si–O distances ranging from 1.532(12) to 1.557(13) Å and O–Si–O angles ranging from 107.9(7)° to 111.1(8)°. The coordination environment for each molybdenum atom is a distorted octahedron with Mo–O distances ranging from 1.650(13) to 2.454(13) Å. The $\{SiO_4\}$ tetrahedron and twelve $\{MoO_6\}$ octahedra are linked together through μ_4-O atoms. As no distortion is observed and the central Si atom comprises tetrahedral coordination, it suggests that the $[SiMo_{12}O_{40}]^{4-}$ anion is noncentrosymmetric.

The most interesting aspect of compound **2** is that there exists complex hydrogen bonding between the central anions, lattice water molecules and protonated imidazole cations. The water molecules and hydroxonium cations link up the acentric polyanions to build up entangled helical chains along the *a*, *b* and *c* screw 2_1 axes, which are further fused into a three-dimensional framework through hydrogen bonding. The distances between the water molecules and the oxygen atoms of the polyanion are in the 3.145–3.186 Å range. The protonated imidazole cations, occupying the pseudo cavities, are connected with the cavities through multi-hydrogen bonding. The distances between the nitrogen atoms and water molecules lie in the range from 2.787 to 2.980 Å, while the $N–H \cdots O$ distances between nitrogen atoms and oxygen atoms of the polyanion are in the 3.003–3.177 Å range.

4. Conclusions

The traditional solution synthesis products are easily controlled compared with the hydrothermal synthetic method. The differences might result from the different mechanisms in generating the target complexes, which are still not fully understood and only described as self-assembly in the hydrothermal reaction chemistry. The successful isolation of complexes **1** and **2** provides some useful information for the synthesis of new heteropolyoxometallates. By taking advantage of suitable organic ligands and H_2MoO_4 in the designed synthesis of organic–inorganic hybrid materials, more and more interesting new materials with some desired architectures and useful properties may be obtained and studied.

5. Supplementary material

Crystallographic data for compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 202190 and 202191, respectively. 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 www: http://www.ccdc.cam.ac.uk).

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