

## 两个新的 Dowson 结构硫钼多酸盐合成, 表征以及催化性质

孙月霞<sup>1</sup> 张志斌<sup>2</sup> 孙 琪<sup>\*,1</sup> 许 岩<sup>\*,1,2</sup>

(<sup>1</sup> 辽宁师范大学化学化工学院, 化学功能材料研究所, 大连 116029)

(<sup>2</sup> 南京工业大学化学化工学院, 材料化学工程国家重点实验室, 南京 210009)

**摘要:** 通过水热技术合成了两种新的 Dowson 结构硫钼多酸盐  $[\text{C}_5\text{N}_2\text{H}_{14}]_2[\text{S}_2\text{Mo}^{\text{VI}}_{18}\text{O}_{62}] \cdot 8\text{H}_2\text{O}$  (**1**) 和  $[\text{C}_5\text{N}_2\text{H}_{14}]_8(\text{H}_3\text{O})_2[\text{S}_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{62}]_3 \cdot (\text{C}_5\text{H}_5\text{N})_2$  (**2**), 并通过 X 射线分析、红外光谱和元素分析其进行了表征。X 射线晶体结果分析, 化合物 **1** 结晶于正交晶系,  $Pmmn$  空间群,  $a=1.799\,29(17)\text{ nm}$ ,  $b=1.358\,04(13)\text{ nm}$ ,  $c=1.419\,26(13)\text{ nm}$ ,  $V=3.468\,0(6)\text{ nm}^3$ ,  $Z=2$ 。化合物 **2** 结晶于单斜晶系,  $C2/m$  空间群,  $a=2.266\,5(3)\text{ nm}$ ,  $b=1.374\,9(2)\text{ nm}$ ,  $c=3.291\,2(5)\text{ nm}$ ,  $\beta=104.31(0)^\circ$ ,  $V=9.938(2)\text{ nm}^3$ ,  $Z=4$ 。化合物 **1** 和 **2** 都含有 Dawson 结构的硫钼多酸阴离子和质子化的 *N*-甲基哌嗪阳离子。并且由苯乙烯的氧化催化结果中看出混价钼的化合物 **2** 的催化活性要比化合物 **1** 略高。

**关键词:** 硫钼酸盐; 晶体结构; 水热合成; 催化

中图分类号: O614.61<sup>2</sup>

文献标识码: A

文章编号: 1001-4861(2011)03-0556-05

## Syntheses, Characterization and Catalytic Properties of Two New Wells-Dawson Molybdosulfates

SUN Yue-Xia<sup>1</sup> ZHANG Zhi-Bin<sup>2</sup> SUN Qi<sup>\*,1</sup> XU Yan<sup>\*,1,2</sup>

(<sup>1</sup>Institute of Functionalized Chemistry Materials, Faculty of Chemistry and Chemical Engineering,  
Liaoning Normal University, Dalian, Liaoning 116029, China)

(<sup>2</sup>College of Chemistry and Chemical Engineering, State Key Laboratory of Materials-oriented  
Chemical Engineering, Nanjing University of Technology, Nanjing 210009, China)

**Abstract:** Two new wells-Dawson compounds  $[\text{C}_5\text{N}_2\text{H}_{14}]_2[\text{S}_2\text{Mo}^{\text{VI}}_{18}\text{O}_{62}] \cdot 8\text{H}_2\text{O}$  (**1**) and  $[\text{C}_5\text{N}_2\text{H}_{14}]_8(\text{H}_3\text{O})_2[\text{S}_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{62}]_3 \cdot (\text{C}_5\text{H}_5\text{N})_2$  (**2**) have been synthesized and characterized by single crystal X-ray analysis, IR spectra and elemental analysis. Single crystal X-ray diffraction confirms that compound **1** crystallizes in orthorhombic,  $a=1.799\,29(17)\text{ nm}$ ,  $b=1.358\,04(13)\text{ nm}$ ,  $c=1.419\,26(13)\text{ nm}$ ,  $V=3.468\,0(6)\text{ nm}^3$ ,  $Z=2$ . Compound **2**, monoclinic,  $a=2.266\,5(3)\text{ nm}$ ,  $b=1.374\,9(2)\text{ nm}$ ,  $c=3.291\,2(5)\text{ nm}$ ,  $\beta=104.31(0)^\circ$ ,  $V=9.938(2)\text{ nm}^3$ ,  $Z=4$ . Both compound **1** and **2** are built up of the Dawson-type molybdosulfate anions, full protonated *N*-methylpiperazine cations. The catalytic result in the oxidation of styrene indicates that the mixed  $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$  compound **2** has higher catalytic activity than **1**. CCDC: 783378, **1**; 783379, **2**.

**Key words:** molybdosulfate; crystal structure; hydrothermal synthesis; catalysis

Many researchers are endeavoring to study the structural chemistry of vanadium phosphates, polyoxomolybdenum and silicomolybdenum, and have

paid a great deal of attention to heteropolyanions containing organic-inorganic cationic ligands in recent years<sup>[1-2]</sup>, which is not only because of diverse structures,

收稿日期: 2010-09-20。收修改稿日期: 2010-12-02。

国家自然科学基金(No.20771050、20971068), 辽宁省教育厅基金(No.2008T106)资助项目。

\*通讯联系人。E-mail: yanxu@lnnu.edu.cn

but also the potential applications, such as medicine, as well as electrochemistry, magnetism, and catalysis in particular<sup>[3-11]</sup>. Compared with lots of reported molybdoarsenates and molybdophosphates<sup>[12-21]</sup>, molybdosulfates are much less developed. Among these polyoxoanions, Dawson polyoxoanions of the molybdenum-sulfate chemistry has not been reported extensively, which may be caused because it has the large size to decrease the electronic density and the oxygen coordination on its surface<sup>[22-23]</sup>. However, in view of the environmental problem, it has potential for fixing and absorbing Sulfur dioxides<sup>[24]</sup>, and exploring the possibility of the frameworks with pyramidal sulfate anions, which could result in novel structural features and unprecedented properties for these frameworks<sup>[25-28]</sup>. Here, we report the synthesis, structure, and catalytic property of two new molybosulfates  $[\text{C}_5\text{N}_2\text{H}_{14}]_2[\text{S}_2\text{Mo}^{\text{VI}}_{18}\text{O}_{62}] \cdot 8\text{H}_2\text{O}$  (**1**) and  $[\text{C}_5\text{N}_2\text{H}_{14}]_8(\text{H}_3\text{O})_2[\text{S}_2\text{Mo}^{\text{V}}_2\text{Mo}^{\text{VI}}_{16}\text{O}_{60}]_3 \cdot (\text{C}_5\text{H}_5\text{N})_2$  (**2**). Both compounds contain Dawson Mo-S anions, but with different oxidation states of Mo.

## 1 Experimental section

### 1.1 Materials and methods

All chemicals purchased were of reagent grade and used without further purification. Element analyses (C, H and N) were performed on a Perkin-Elmer 2400 elemental analyzer. IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets in the 4 000~400  $\text{cm}^{-1}$  region.

#### 1.2.1 Synthesis and characterization of compound 1

A mixture of  $\text{MoO}_3$  (0.288 0 g),  $\text{Fe}_2\text{O}_3$  (0.159 9 g),  $\text{NaHSO}_3$  (0.107 2 g), *N*-methylpiperazine (0.102 0 g),  $\text{H}_2\text{SO}_4$  (50%) (0.632 5 g) was dissolved in distilled water (10 mL), and was stirred for 5 h. The resulting solution was sealed into Teflon-lined steel autoclave and heated at 160  $^\circ\text{C}$  for 7 d. After cooling to room temperature in

air, brown crystals were washed and filtered by distilled water and dried in air, yield: 35% based on Mo. The elemental analysis calcd. for  $\text{C}_{10}\text{H}_{44}\text{Mo}_{18}\text{N}_4\text{O}_{70}\text{S}_2$  (%): C, 3.83; H, 1.41; N, 1.79. Found (%): C, 3.80; H, 1.34; N, 1.72.

#### 1.2.2 Synthesis and characterization compound 2

A mixture of  $\text{MoO}_3$  (0.289 2 g),  $\text{NaHSO}_3$  (0.107 8 g), *N*-methylpiperazine (0.106 6 g),  $\text{H}_2\text{SO}_4$  (50%) (0.584 9 g) and pyridine (0.201 2 g) was dissolved in distilled water (10 mL), and was stirred for 5 h. The resulting solution was sealed into Teflon-lined steel autoclave and heated at 160  $^\circ\text{C}$  for 7 d. After cooling to room temperature in air, black-rod crystals were washed and filtered by distilled water and dried in air, yield: 42% based on Mo. The elemental analysis calcd. for  $\text{C}_{50}\text{H}_{128}\text{Mo}_{54}\text{N}_{18}\text{O}_{188}\text{S}_6$  (%): C, 6.41; H, 1.37; N, 2.63. Found(%): C, 6.45; H, 1.40; N, 2.67.

### 1.3 Determination of crystal structure

The crystals of both compound **1** and **2** were carefully singled out under a microscope and glued at the tip of a thin glass fiber with cyanoacrylate adhesive. Single-crystal structure determination was performed on a Bruker Smart Apex II CCD diffractometer at 293(2) K, with a sealed tube X-ray source  $\text{Mo K}\alpha$  ( $\lambda = 0.071\ 073\ \text{nm}$ ) operating at 50 kV and 30 mA. The crystal structure was solved by the direct method and refined on  $F^2$  by full-matrix least-squares using the SHELX97 program package<sup>[29]</sup>. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms for organic molecules were placed in the calculation position. While the H atoms of water (or  $\text{H}_3\text{O}^+$ ) were located from the different Fourier maps. Further details of the X-ray structural analyses for compound **1** and **2** are given in Table 1.

CCDC: 783378, **1**; 783379, **2**.

Table 1 Crystallographic data for **1** and **2**

Compound	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{10}\text{H}_{44}\text{Mo}_{18}\text{N}_4\text{O}_{70}\text{S}_2$	$\text{C}_{50}\text{H}_{128}\text{Mo}_{54}\text{N}_{18}\text{O}_{188}\text{S}_6$
Formula weight	3 131.53	9 362.82
$T / \text{K}$	293(2)	293(2)
$\lambda / \text{nm}$	0.071 073	0.071 073
Crystal system	Orthorhombic	Monoclinic

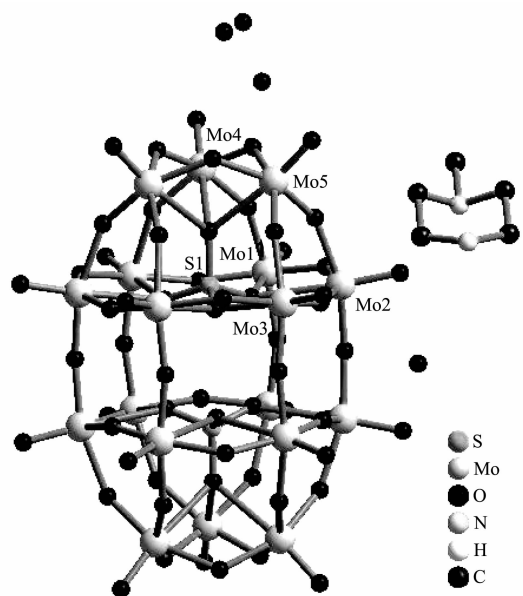
Continued Table 1

Space group	<i>Pmmn</i>	<i>C2/m</i>
<i>a</i> / nm	1.799 29(17)	2.266 5(3)
<i>b</i> / nm	1.358 04(13)	1.374 9(2)
<i>c</i> / nm	1.419 26(13)	3.291 2(5)
$\beta$ / (°)		104.314(2)
<i>V</i> / nm <sup>3</sup>	3.468 0(6)	9.938(2)
<i>Z</i>	2	2
<i>D<sub>c</sub></i> / (Mg·m <sup>-3</sup> )	2.999	3.129
Absorption coefficient / mm <sup>-1</sup>	3.32	3.468
<i>F</i> (000)	2 960	8 844
Crystal size / mm	0.14×0.13×0.12	0.13×0.12×0.10
Limiting indices	-20≤ <i>h</i> ≤22, -16≤ <i>k</i> ≤12, -17≤ <i>l</i> ≤12	-24≤ <i>h</i> ≤27, -16≤ <i>k</i> ≤16, -37≤ <i>l</i> ≤39
Reflections collected	18 283	25 331
Independent reflections ( <i>R<sub>int</sub></i> )	3 671 (0.031 1)	9 442 (0.083 2)
Data	3 671	9 442
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.195	0.993
Final <i>R</i> indices ( <i>I</i> >2σ( <i>I</i> ))	<i>R</i> <sub>1</sub> =0.048 4, <i>wR</i> <sub>2</sub> =0.183 0	<i>R</i> <sub>1</sub> =0.061 2, <i>wR</i> <sub>2</sub> =0.137 6
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> =0.058 6, <i>wR</i> <sub>2</sub> =0.193 7	<i>R</i> <sub>1</sub> =0.118 2, <i>wR</i> <sub>2</sub> =0.161 9

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

## 2 Description of structures

The IR spectrum of compound **1** shows intense absorption at 945, 793, 668 and 559 cm<sup>-1</sup> are attributed to  $\nu(\text{Mo}-\text{O}_i)$  or  $\nu(\text{Mo}-\text{O}_b)$ , the band at 1 149 cm<sup>-1</sup> can be attributed to  $\nu(\text{S}-\text{O}_a)$ . The wild band at 3 432 cm<sup>-1</sup> is featured of  $\nu$  (O-H) in water, 3 083, 1 601, 1 450, 1 383, 450 cm<sup>-1</sup> are characteristic bands for *N*-methylpiperazine. As shown in Fig.1, the polyanion of compound **1** is

Fig.1 Molecular structure of **1**

the well-known Dawson-type structure  $[\text{X}_2\text{Mo}_{18}\text{O}_{62}]^{n-}$ <sup>[28]</sup>, consisting of eighteen octahedral MoO<sub>6</sub> and two SO<sub>4</sub> pyramid. The Mo-O distances range from 0.168 1(3) to 0.250 7(3) nm, and the central SO<sub>4</sub> is a pyramid with S-O bond distances of 0.145 5(3)~0.150 3(4) nm and O-S-O angles ranging from 108.1(2)° to 110.62(15)°. All the bond angles and lengths above are consistent with the reported Dawson-type polyanions. The SO<sub>4</sub> pyramid and nine MoO<sub>6</sub> octahedra from three capped molybdenum atoms and six equatorial belt molybdenum atoms are linked together by  $\mu_4$ -O atom and  $\mu_3$ -O atom, and further joint the other hemisphere. The most interesting aspect of compound **1** is that there is complex hydrogen bonding between protonated *N*-methylpiperazine cations and the Dawson structural molybdosulfate anions. As shown in Fig.2, each *N*-methylpiperazine links two polyanions by using N-H...O hydrogen bonding interactions to generate a 1D chain (Table 2). The distance of N...O is 0.294 4(10)~0.308 3(15) nm, while the angle of N-H...O is from 131° to 134°. The water molecules are located between the chains, and making the chains are more stable. Although Fe<sub>2</sub>O<sub>3</sub> was not included in the final product, it is necessary as the oxidant of S<sup>IV</sup>→S<sup>VI</sup>.

Table 2 Hydrogen bonds lengths and bonds angles

D-H...A	D-H / nm	H...A / nm	D...A / nm	$\angle$ D-H...A / ( $^{\circ}$ )
Compound 1				
N1-H1E...O12 <sup>i</sup>	0.900 0	0.239 00	0.308 3(15)	134.00
N1-H1E...O12 <sup>ii</sup>	0.900 0	0.239 00	0.308 3(15)	134.00
N2-H2C...O14	0.910 0	0.227 00	0.294 4(10)	131.00
N2-H2C...O14 <sup>iii</sup>	0.910 0	0.227 00	0.294 4(10)	131.00
C1-H1A...O13 <sup>iv</sup>	0.960 0	0.245 00	0.317 2(15)	132.00
C3-H3A...O20	0.970 0	0.257 00	0.325 2(10)	138.00
Compound 2				
N2-H2C...O56	0.900 0	0.211 00	0.290 9(17)	148.00
N3-H3A...O41	0.900 0	0.199 00	0.286 0(14)	162.00
N6-H6B...O17	0.900 0	0.229 00	0.294 4(12)	129.00

Symmetry transformations used to generate equivalent atoms: <sup>i</sup>  $1-x, -1/2+y, -z$ ; <sup>ii</sup>  $1-x, -y, -z$ ; <sup>iii</sup>  $x, -1/2-y, z$ ; <sup>iv</sup>  $1-x, -1/2+y, 1-z$ .

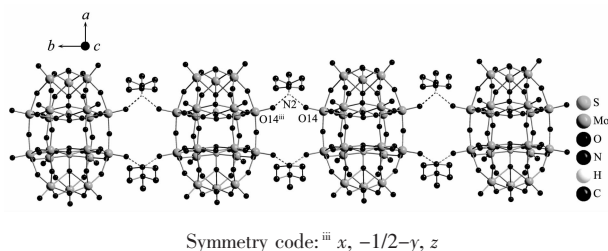


Fig.2 *N*-methylpiperazine molecules link polyanions by using N-H...O hydrogen bonding interactions to generate a 1D chain in **1**

When we replaced  $\text{Fe}_2\text{O}_3$  with pyridine, the mixed  $\text{Mo}^{\text{V}}/\text{Mo}^{\text{VI}}$  molibdosulfate **2** was obtained. The IR spectra of compound **2** shows intense absorption at 952, 801 and 685  $\text{cm}^{-1}$  are attributed to  $\nu(\text{Mo}-\text{O}_i)$  or  $\nu(\text{Mo}-\text{O}_b)$ , the band at 1146  $\text{cm}^{-1}$  can be attributed to  $\nu(\text{S}-\text{O}_a)$ . The wide band at 3427  $\text{cm}^{-1}$  is featured of  $\nu(\text{O}-\text{H})$  in water, 3083, 1619, 1451, 1382, 450  $\text{cm}^{-1}$  are characteristic bands for *N*-methylpiperazine and bipy. As shown in Fig.3, the asymmetric unit of **2** contains 103 non-hydrogen atoms. 15 Mo, 3 S and 56 O atoms belong to the two crystallographic independent Dawson structural molybdosulfate polyanions. The most significant aspect of compound **2** is that the polyanions are linked by protonated water  $\text{H}_3\text{O}^+$  and *N*-methylpiperazine cations by using hydrogen bonding interactions to form a soft 3D framework along the *c* axis (Table 2), as shown in Fig.4. The guest pyridine molecules are located in the channels. The assignment of the oxidation state of Mo atoms is based on the bond valence sum calculations<sup>[30]</sup>, which gives the average

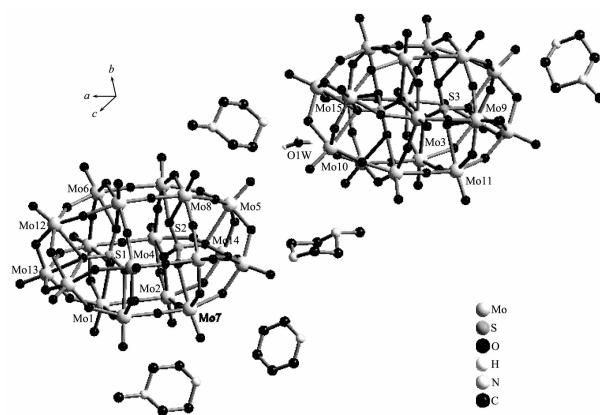


Fig.3 Molecular structure of **2**

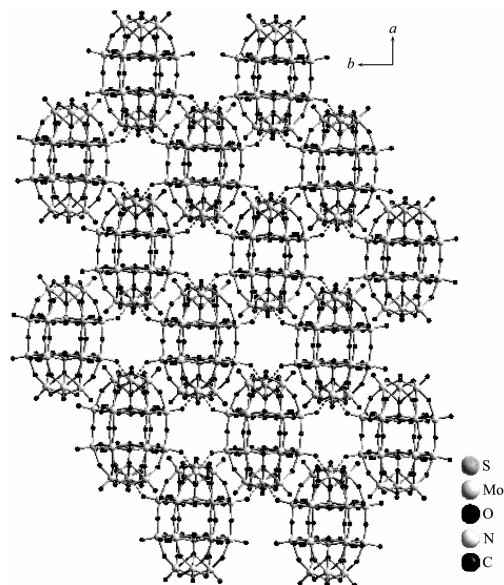


Fig.4 Polyanions are linked by protonated water  $\text{H}_3\text{O}^+$  and *N*-methylpiperazine cations by using hydrogen bonding interactions to form a soft 3D framework along the *c* axis

value 5.895 for oxidation state of Mo (expected value for **2** is 5.889), and the calculation result is consistent with the formula of **2**.

### 3 Catalytic properties

According to our previous work, compounds **1**, **2** (100 mg) and styrene (0.75 mL, 6.4 mmol) were stirred respectively and reacted in the 50 mL two-neck reaction flask with 7.5 mL acetonitrile as the solvent. The oxidation was performed in water constant reflux, and heated at 60 °C by adding 2.1 mL hydrogen peroxide (30%) under the conditions of constant temperature in water bath. After 3 h, we sampled and used gas chromatography (GC-6890, FID; 30 m×0.32 mm capillary column) to analyze products distribution, and the yields of epoxides were determined by GC analysis using internal standards, based on the Nitrobenzene. Under the same conditions, we did the blank compared test. The results showed the main products are benzaldehyde, and a small amount of benzoic acid. The conversions of styrene oxidation were represented in Table 3. The catalytic result indicates that the mixed Mo<sup>V</sup>/Mo<sup>VI</sup> compound **2** has higher catalytic activity than **1**.

**Table 3** Catalytic activity of compound **1** and **2** in the oxidation of styrene

Compound	Conversion / %	Selectivity / %	
		Benzaldehyde	Benzoic acid
<b>1</b>	7.78	74.55	25.45
<b>2</b>	9.29	87.66	12.34

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