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Interaction between molybdate and histidine and its reduction to molybdenum(V) dimer

Quan-Liang Chen [a,b], Zhao-Hui Zhou [b,*]

[a] College of Chemistry and Environmental Protection Engineering, Southwest University for Nationalities, Chengdu 610041, China
[b] College of Chemistry and Chemical Engineering, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China

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ABSTRACT

Temperature-dependent reactions of molybdates with histidine in weak acidic solution resulted in the isolations of coordinated and uncoordinated products $Na[Mo_{\Lambda}O_3(S\text{-His})]\cdot H_2O$ (**1**) (HHis = histidine, $C_6H_9N_3O_2$) and $K_4(S\text{-}H_2His)_2(Mo_7O_{24})\cdot 16H_2O$ (**2**) respectively. The former **1** can be reduced by hydrazine hydrochloride for the preparation of molybdenum(V) histidine $[Mo_2O_4(S\text{-His})_2]\cdot 3H_2O$ (**3**) with dinuclear $[Mo_2O_4]^{2+}$ core. The complex **2** shows strong hydrogen bonds between molybdate and histidine. The solution behaviors of the complexes were probed and compared between solid and solution ^1H and ^{13}C NMR spectra. Obvious dissociation of histidine in **1** has been observed for 35%, showing the equilibrium between the coordinated and free histidine groups. This may support the liability of coordinated imidazole in histidine with iron-molybdenum cofactor. Furthermore, solid CD spectra show **1** and **3** with positive and negative Cotton effects respectively.

1. Introduction

Histidine is a common coordinating ligand in metalloproteins and a part of catalytic site in certain enzyme. In the catalytic process, the basic nitrogen of histidine is used to abstract a proton from serine, threonine, or cysteine to activate it as a nucleophile [1–3]. Its interaction with molybdenum displays a monodentate coordination mode in iron-molybdenum cofactor [FeMo-co = $MoFe_7S_9C(R\text{-Hhomocit})$] of nitrogenase as shown in Fig. 1 and Mo_8^{VI} cluster in Mo storage protein [4–12]. There is also a model for the intramolecular hydrogen bonding in FeMo–co [13]. The histidine sidechain was found to be captured by the complete $[MoFe_7S_9C]$ core in the final biosynthesis process of FeMo–co [14–16], and also accompanied in the molybdopterin and pyranopterin [17–19]. The interaction between molybdenum and histidine causes much interest. Up to now, a variety of histidine molybdenum complexes have been reported, such as Mo^V histidine complexes $Mo_2O_4(S\text{-His})_2\cdot 3H_2O$ [20,21], $Mo_2S_2O_2(S\text{-His})_2\cdot 1.5H_2O$ [22], polyoxoanion $[P_2Mo_{18}O_{62}]^{6-}$ with *R,S*-histidine in aqueous solution [23], and low-valent complex $[Mo(S\text{-His})(allyl)(CO)_2]$ [24]. In the reported structures molybdenum histidines, the ligand chelates tridentately to the molybdenum atom with α-carboxy, α-amino and imidazole groups. However, molybdenum(VI) histidines and their re-dox properties were less investigated. For a better understanding the interaction between molybdenum and histidine, monomeric and dimeric molybdenum(VI/V) histidine complexes were studied and transformed for comparisons, including CD, FTIR, solid and solution NMR spectroscopies, and X-ray structural analyses. Their solution and solid behaviors are discussed.

2. Materials and instrumentation

Molybdates (99%) and histidine were purchased from Sigma. All chemicals were analytical reagents. Infrared spectra were recorded as Nujol mulls between KBr plates using Nicolet 200 FT-IR spectrometer. UV spectra were recorded in solid state on a Cary 5000 spectrophotometer. Elemental analyses were performed using EA 1110 elemental analyzers. Solid CD spectra were performed on a JASCO J-810 spectropolarimeter. The measurements were done by incorporating individual crystals with KCl pellets. Each pellet was prepared using a KCl matrix with 13 mm in diameter and 50 mg in weight. pH value was determined by PHB-8 digital pH meter. Solution ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV 500 NMR spectrometer in D_2O using DSS (sodium 2,2-dimethyl-2-silapentane-5-sulfornate) as an internal reference. Solid state ^{13}C NMR spectra were recorded on a Bruker AV 400 NMR spectrometer using cross polarization, magic angle spinning (13 kHz) and adamantane as reference.

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[*] Corresponding author. Tel.: +86 592 2184531; fax: +86 592 2183047.
E-mail address: zhzhou@xmu.edu.cn (Z.-H. Zhou).

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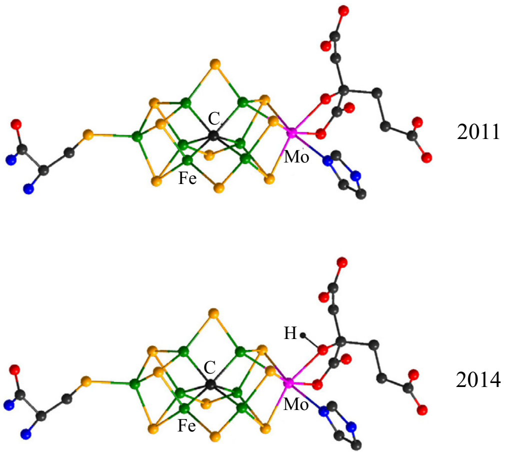


Fig. 1. Comparisons of X-ray crystal structure of FeMo-co in 2011 and the proposed in 2014 [9–11,29].

2.1. Preparation of $Na[Mo_{\wedge}O_3(S\text{-}His)]\cdot H_2O$ (**1**)

$Na_2MoO_4\cdot 2H_2O$ (0.24 g, 1.0 mmol) and histidine (1.09 g, 1.0 mmol) were dissolved in 5.0 mL water. The mixture was kept stirring for 2 h and the pH value of the solution was adjusted to 6.5. The solution was refluxed for about 17 h. After cooling to room temperature, the solution was filtered into 25 mL beaker. Slow evaporation at room temperature led to the block crystals of molybdenum(VI) histidine **1** for several days. The crystals were collected and washed with 95% ethanol and cold water. Yield: 0.25 g (73%). *Anal.* Calc. for $C_6H_9Mo_1Na_1N_3O_6$: C, 21.3; H, 2.7; N, 12.4. Found: C, 21.2; H, 2.6; N, 12.2%. IR (KBr, v, cm^{-1}): 3358_{vs}, 3237_{vs}, 2895_{s}, $1665_{vs,}$ 1566_{m}, 1491_{m}, 1471_{m}, 1436_{m}, 1395_{s}, 1328_{w}, 1267_{s}, 1174_{m}, 1138_{m}, 1019_{s}, 950_{vs}, 892_{m}, 842_{vs}, 837_{vs}, 622_{s}, 576_{s}, 473_{m}. Solution ^1H NMR (500 MHz, D_2O): δ_H (ppm) 8.19 (NC*H*NH), 6.99 (NC*H*CH), 4.18 (C*H*CO_2), 3.20 (C*H*$_2$); Solution ^{13}C NMR (500 MHz, D_2O): δ_C (D_2O, ppm) 184.29 (*C*O_2), 139.71 (N*C*HNH), 134.98 (*C*N), 117.49 (*C*NH), 56.81 (CO_2*C*HNH_2), 30.90 (*C*H_2).

2.2. Preparation of $K_4(S\text{-}H_2His)_2(Mo_7O_{24})\cdot 16H_2O$ (**2**)

Potassium molybdate pentahydrates (0.33 g, 1.0 mmol) and histidine (0.78 g, 0.5 mmol) were dissolved in 10 mL water. The solution was kept stirring about 4 h and the pH value of the solution was adjusted to 5.0 by the addition of 2.0 M hydrochloric acid. Slow evaporation at room temperature led to the light yellow crystals of **2** for several days. The crystals were collected and washed with cold water and 95% ethanol. Yield: 0.10 g (39% based on Mo). *Anal.* Calc. for $C_{12}H_{52}K_4Mo_7N_6O_{44}$: C, 8.0; H, 2.9; N, 4.6. Found: C, 8.2; H, 2.6; N, 4.6%. IR (KBr, v, cm^{-1}): 3421_{vs}, 1630_{vs}, 1494_{m}, 1401_{vs}, 1329_{vs}, 1254_{w}, 1170_{m}, 1111_{m}, 1060_{m}, 959_{s}, 889_{vs}, 695_{m}, 688_{w}, 623_{s}, 526_{s}, 461_{s}.

2.3. Preparation of $[Mo_2O_4(S\text{-}His)_2]\cdot 3H_2O$ (**3**) [20]

$[Mo_2O_4(S\text{-}His)_2]\cdot 3H_2O$ (**3**) was prepared in a slightly changed method as reported [20]. **1** (169 mg, 0.50 mmol) and hydrazine hydrochloride (53 mg, 0.50 mmol) were dissolved in 10 mL water to give a brown mixture. The mixture was kept stirring about 2 h and the pH value of the solution was adjusted to 6.5 with the addition of 1.0 M ammonium hydroxide. The mixture was kept in a refrigerator for one week to give deep yellow crystals, which were filtered and washed with ethanol and cold water to give **3**. Yield: 0.086 g (51% based on Mo). (KBr, v, cm^{-1}): 3440_{vs}, 2920_{s}, 1633_{vs}, 1439_{m}, 1388_{vs}, 1348_{m}, 1261_{s}, 1183_{m}, 1124_{s}, 1078_{s}, 949_{s}, 829_{s}, 760_{m}, 629_{m}, 454_{s}. Solid ^{13}C NMR (400 MHz): δ_C (ppm) 180.19 (*C*O_2), 136.64 (im), 118.73 (im), 57.97 (CO_2*C*HNH_2), 30.51 (*C*H_2).

2.4. X-ray data collections, structure solutions and refinements

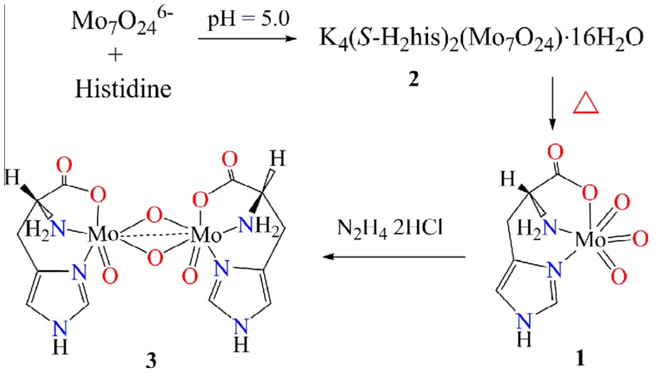
Crystallographic data for histidine molybdates **1** and **2** are summarized in Table S1. Diffraction data were collected on an Oxford Gemini diffractometer with graphite monochromated Mo-Kα radiation at 173 K. A Lorentz-polarization factor, anisotropic decay and empirical absorption corrections were applied. The structures were solved and refined by full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms [25]. H atoms were located from difference Fourier map and refined with use of a riding model.

3. Results and discussion

The preparations of histidine molybdenum(VI/V) complexes **1**–**3** mainly depend on the pH value and requisite proportions of molybdate and ligand, especially on the temperature of reactions as shown in Scheme 1. Weak acidic and neutral conditions are suitable for the preparations of molybdenum(VI) histidines. A mixture of molybdate and histidine at room temperature resulted in the formation of a mixed-salt of heptamolybdate $K_4(S\text{-}H_2His)_2(Mo_7O_{24})\cdot 16H_2O$ (**2**) with protonated histidine as counter cations, where no coordination of histidine is observed. Further prolonged heating condition drove the production of monomeric molybdenum(VI) histidine $Na[Mo_{\wedge}O_3(S\text{-}His)]\cdot H_2O$ (**1**). To the best of our knowledge, this is the first monomeric molybdenum(VI) histidine complex isolated so far. The suitable pH value was 5.0–7.0. Slight excess of histidine and heating drive the reaction completely. Although a recent solution study shows that the main product was dimeric molybdenum(VI) complexes $Mo_2O_4(OH)_4(aaH)$ (aaH = GlyH, PheH, LeuH, MetH) by the reaction of α-amino acids (aaH) with Na_2MoO_4 or $(NH_4)_6Mo_7O_{24}$, with Mo/aaH = 2:1 [26]. In our work, no dimeric molybdenum(VI) histidine $Mo_2O_4(OH)_4(HHis)$ or $Mo_2O_5(His)$ was isolated in strong acid solution. When a mixture of molybdate and histidine was reduced by hydrazine hydrochloride. Dimeric molybdenum(V) histidine $[Mo_2O_4(S\text{-}His)_2]\cdot 3H_2O$ (**3**) could be obtained at room temperature even with different molar ratio of metal and ligand [20,21]. It seems that strong acidic condition is not good for the coordination of histidine.

3.1. Crystal structure descriptions

Complex **1** consists of discrete sodium cations, trioxo molybdenum histidine anions and water molecules. As shown in Fig. 2, each



Scheme 1. Syntheses and transformations of molybdenum histidines.