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Two novel molybdenum complexes containing $[Mo_2O_2S_2]^{2+}$ fragment: synthesis, crystal structures and catalytic studies

Jun-Feng Wu[1], Dong-Mei Li[1,2]*, Li-Feng Cui[1], Chang-Fu Zhuang[1], Sai-Nan Song[1], Tie-Gang Wang[1], Ji-Qing Xu[1]*, Heng-Qing Jia[3] and Ning-Hai Hu[3]

[1]College of Chemistry, Jilin University, Jiefang Road 2509, Changchun, 130023, People's Republic of China
[2]Nanoscale Physics & Devices Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
[3]Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, People's Republic of China

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$Mo_2O_2S_2(HGly)(Gly)_2$ 1 and $K_6[Mo_2O_2S_2(nta)_2][Mo_2O_2S_2(ntaH)_2]\cdot 4H_2O$ 2 were synthesized by the reactions of $(NH_4)_2MoS_4$ and amino acids L (L = glycine, nitrilotriacetic acid) in ethanol–water medium at ambient temperature. The two complexes were characterized by elemental analysis, infrared spectra, UV–visible spectra, TG–DTA and XPS. X-ray crystallographic structural analyses revealed that compound 1 is a binuclear Mo–S–glycinate complex, a glycinate ligand is coordinated to each molybdenum atom through its amine nitrogen and carboxylato oxygen, respectively, and the third glycinate acts as a bridge through its two carboxylato oxygens linking the two molybdenum atoms. Compound 2 is also a binuclear Mo–S complex with two nitrilotriacetate ligands, each of which is coordinated to a molybdenum atom via its two β-carboxylato oxygens and a nitrogen atom. Simultaneously, each molybdenum atom in 1 and 2 is chelated to a terminal oxygen and two bridging sulfurs to complete the octahedral configuration. Their catalytic activities in the reduction from C_2H_2 to C_2H_4 as well as other binuclear Mo–S–polycarboxylate complexes, a $[Fe_4S_4]$ single cubane and a chainlike Mo–Fe–S compound were investigated and it was found that 1 exhibited relatively good catalytic activity.

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KEYWORDS: molybdenum complexes; glycine; nitrilotriacetic acid; crystal structure; catalytic activity

INTRODUCTION

Nitrogenase, one of the most fascinating transition metal catalysts in nature, has been studied for decades since it can reduce dinitrogen to ammonia at ambient pressure and mild temperature.[1–4] The most common form of these enzymes is Mo-dependent nitrogenase, which consists of Fe protein and MoFe protein. The Fe protein is considered as the electron donor to the MoFe protein. The active site of the substrate binding and reduction, FeMo–cofactor, which is composed of Mo/Fe/S cubanes with a bidentate homocitrate in the ratio 1:7:9:1, is within the MoFe protein.[5–8] Recently, a high-resolution 1.16 Å crystallographic analysis revealed that an atom, most likely nitrogen, was found to sit inside the FeMo–cofactor cage.[9–12] On the basis of experimental observation, the homocitrate has been supposed to participate in the conversion from N_2 to NH_3; however, it is still an enigma how homocitrate is involved in this catalytic process.[13–16] Thus, many groups have contributed to investigate the chemical bondings of the homocitrate and its analogs to the molybdenum atom. Some Mo/W–Fe–S complexes with (α-hydroxy)-polycarboxylates have been reported, such as $(Et_4N)_4\{[MoFe_3S_4Cl_4]_2(\mu\text{-}C_2O_4)\}$,

*Correspondence to: Dong-Mei Li, College of Chemistry, Jilin University, Jiefang Road 2509, Changchun, 130023, People's Republic of China.
E-mail: wujf0912@yahoo.com.cn
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$(Et_4N)_3[MoFe_3S_4Cl_4(C_2O_4)]$,[17] $[Mo_nW_{3-n}S_4(Hnta)_3]^{3-}$ (n = 0–3),[18] $[Mo_6S_6O_6(OH)_4(C_2O_4)_3]^{4-}$, $[M_2O_2S_2(edta)]^{2-}$ (M = Mo, W),[19,20] $Na_2[Mo_2O_3S(C_3H_5O_2NS)_2]\cdot 4H_2O$,[21] $K_2[Mo_2O_2S_2(C_6H_4O_7)]\cdot 5H_2O$.[22] We are currently investigating binuclear Mo/W-polycarboxylates with sulfur bridges, such as homocitrate, citrate, cysteine and benzilate.[23–26] In this paper, we report the synthesis and characterization of two μ-sulfide binuclear molybdenum (V) complexes with glycine and nitrilotriacetate ligands. Generally, specific activity for acetylene reduction is a common method to investigate the catalytic activity of altered MoFe protein or wild-type nitrogenases. Herein, this kind of reduction catalyzed by compounds **1** and **2** as well as other Mo–S–polycarboxylates, Mo–Fe–S cubanes and Fe–S cubanes is discussed.

EXPERIMENTAL SECTION

Preparation of $Mo_2O_2S_2(HGly)(Gly)_2$ (1) and $K_6[Mo_2O_2S_2(nta)_2][Mo_2O_2S_2(ntaH)_2]\cdot 4H_2O$ (2)

The ligand L (L = glycine and nitrilotriacetate acid; 1 mmol) was dissolved in water (6 ml) and ethanol (12 ml), and the solution was adjusted to pH 7.0 for **1** and pH 7.2 for **2** with potassium hydroxide. $(NH_4)_2MoS_4$ (0.5 mmol, 0.13 g) was subsequently added to the solution. The mixture was continuously stirred at room temperature for 24 h, then filtered to remove the precipitate. The filtrate was kept at room temperature for some time (one month for **1**, 20 days for **2**). Red rhombic crystals formed and were isolated by filtration. Complex **1**, yield: 0.040 g, 30% based on Mo. Anal. calcd for $C_6H_{13}Mo_2N_3O_8S_2$: C, 14.08; H, 2.54; N, 8.22%. Found: C, 13.96; H, 2.42; N, 8.17%. IR (KBr, cm^{-1}): 1675s, 1643vs, 1612s, 1587 m cm^{-1} (ν_{sCOO^-}); 1441s, 1373s, 1345 m cm^{-1} (ν_{asCOO^-}); 943s, 918 s cm^{-1} (ν_{Mo-O}); 459 w cm^{-1} ($\nu_{Mo-S-Mo}$). Complex **2,** yield: 0.10 g, 52% based on Mo. Anal. calcd for $C_{24}H_{34}K_6Mo_4N_4O_{32}S_4$: C, 17.59; H, 2.08; N, 3.42%. Found: C, 17.50; H, 2.14; N, 3.36%. IR (KBr, cm^{-1}): 1740s, 1636 vs cm^{-1} (ν_{sCOO^-}); 1441s, 1390 s cm^{-1} (ν_{asCOO^-}); 987s, 926s, 880 m cm^{-1} (ν_{Mo-O}); 469 w cm^{-1} ($\nu_{Mo-S-Mo}$).

Measurements and apparatus

$(NH_4)_2MoS_4$ was synthesized using a literature method.[27] Other chemicals were commercially available and used without further purification. Elemental analyses (C, H, N) were obtained on a Perkin–Elmer 2400 LS elemental analyzer. UV–visible spectra were performed in solid state with a UV-3100 spectrophotometer. Infrared spectra were performed in the solid state (KBr) using a Perkin–Elmer Spectrum One FT–IR in the region 4000–200 cm^{-1}. X-ray photoelectron spectroscopic analysis (XPS) was carried out on an EASY ESCA spectrometer using MgK_α radiation at a pressure of 10^{-7} Pa. Thermogravimetric analyses (TG) and differential thermal analyses (DTA) were performed on a DTG-60 Simultaneous DTA–TGA apparatus with a heating rate of 10 °C min^{-1} from room temperature to 800 °C under a nitrogen atmosphere (flow rate 20 ml min^{-1}). For the analyses of products in catalytic activity experiments, Shimadu GC-8A gas chromatography with a flame ionization detector (FID) fitted with a 30 × 0.3 cm Pozakak-N column was employed. Air was the carrier gas. The products were identified by comparison of retention times with those of authentic samples.

Structural characterization

Red single crystals of **1** and **2** were selected for X-ray diffraction analyses. Diffraction data were collected on a Bruker SMART-CCD diffractometer with graphite monochromated MoKα radiation at 273 K. A Lorenz polarization factor was applied. The structures were solved by direct methods with SHELXTL-PLUS program packages, refined by full-matrix least-squares technique and corrected for Lorenz-polarization factors. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement, and the locations of H atoms on methene were obtained by theoretical models. Crystallographic data for the compounds **1** and **2** are summarized in Table 1.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, no. 621 474 for **1** and CCDC no. 621 475 for **2**. Copies of the data may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Synthesis

$(NH_4)_2MoS_4$ reacted with the ligand (glycine or nitrilotriacetate) in aqueous ethanol to afford dark red solution, for which the pH value was near neutral. The mixture was allowed to crystallize slowly, and large, rhombic, good-quality crystals of **1** and **2** for X-ray diffraction studies were finally obtained. During the reactions, sulfur and a small amount of H_2S were generated. Hence, the title compounds may be described by the following equations:

$$2(NH_4)_2MoS_4 + 3NH_2CH_2COOH + 2H_2O \longrightarrow Mo_2O_2S_2(NH_3CH_2COO)(NH_2CH_2COO)_2 + S + H_2S + 4NH_4HS \quad (1)$$

$$4(NH_4)_2MoS_4 + 4N(CH_2COOH)_3 + 6KOH \longrightarrow K_4[Mo_2O_2S_2(nta)_2] + K_2[Mo_2O_2S_2(ntaH)_2] + 2S + 8NH_4HS + 2H_2S + 2H_2O \quad (2)$$

It was found that the formation of the final products was dependent on the molar ratio of $(NH_4)_2MoS_4$ and ligands as well as the pH value. The pH value was especially crucial. In our reactions, the optimal pH value was in the range 6.5–7.4. In these two compounds, the ligands were found to be partially protonated. In fact, binuclear deprotonated

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Table 1. Crystal data and structure refinement for complexes **1** and **2**

	1	**2**
Empirical formula	$C_6H_{13}Mo_2N_3O_8S_2$	$C_{24}H_{34}K_6Mo_4N_4O_{32}S_4$
Molecular weight	511.19	1637.15
Crystal size (mm)	0.715 × 0.147 × 0.087	0.179 × 0.141 × 0.136
Temperature (K)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	P2 (1)/c	C2/m
Cell constants		
a (Å)	13.074 (17)	16.163(3)
b (Å)	10.871 (6)	20.964(4)
c (Å)	10.586 (3)	17.366(4)
β (deg)	91.029 (5)	113.807(3)
V (Å^3)	1442.4 (11)	5383.7(19)
Z	4	4
D_c(g cm^{-3})	2.359	2.020
F(000)	1004	3232
Data collection (deg)	$2.48 < 2\theta < 26.05$	$1.75 < 2\theta < 25.88$
Reflns collected	7827	14 302
Reflns measured	2809	5200
Reflns observed [$I > 2\sigma(I)$]	6075	4770
$R_1[I > 2\sigma(I)]$	0.0230	0.0648
$wR_2[I > 2\sigma(I)]$	0.0619	0.1642
Data/restraints/parameters	2809/0/218	5200/0/347
GOOF/F^2	1.018	1.100

and protonated Mo–S–citrate complexes have also been reported by our group.[22,23,25,26] Thus, the protonation and deprotonation of the ligands are supposed to have less influence on their dimeric structure and H^+ ions may be transformed without destroying the sulfido-bridges, shown as follows:

$$[Mo_2O_2S_2(HL)_2]^{m-} \overset{-H^+}{\rightleftharpoons} [Mo_2O_2S_2L(HL)]^{(m-1)-} \overset{-H^+}{\rightleftharpoons} [Mo_2O_2S_2L_2]^{(m-2)-}$$

Thus, different protonated forms of Mo–S–polycarboxylate complexes could be theoretically obtained by controlling the pH value. Unfortunately, the pH value actually falls into a very narrow range and it is not easy to control and monitor the pH change during the reaction; it is therefore very hard to control the exact pH value when the crystal appears. However, it is yet to be confirmed that the solutions turned weakly acidic when **1** and **2** crystallized, which is in good agreement with the release of H_2S. Two kinds of compounds, polycarboxylato-molybdate and sulfido-bridge molybdenum–polycarboxylato complexes, could be obtained under very different reaction conditions. For example, molybdenum (VI) peroxo glycinate complex $MoO(O_2)_2(gly)(H_2O)$ (gly = glycinate ion) was reported to be crystallized at pH ~3.8 whereas another mononuclear complex $[MoO_2(gly)_2]$ appeared at even low pH values.[28,29] Different structures may strongly affect the acid-resistance ability of Mo/W–S complexes, i.e. incomplete cubane-type $[Mo_nW_{3-n}S_4(Hnta)_3]^{3-}$ ($n = 0$–3) was obtained under strongly acid conditions (0.1 M HCl) whereas **1** and **2** were unstable under these acidic conditions.

In addition, different molar ratios of $(NH_4)_2MoS_4$ and the ligands result in various stoichiometry compounds, e.g. $Mo_2O_2S_2(HGly)(Gly)_2$ **1** gives a 2:3 molar ratio of Mo/glycinate while $K_3[Mo_2O_2S_2(nta)(ntaH)]\cdot 2H_2O$ **2** gives a 1:1 molar ratio of Mo/nitrilotetraacetate. Other similar structure Mo–S complexes with different (poly)carboxylate ligands, e.g. citrate,[19] EDTA,[25,30] cysteine [31] and oxalate,[32] have already been reported.

Spectroscopic characterization

The IR spectra of compounds **1** and **2** are very useful not only for identifying the terminal oxomolybdenum and sulfido-bridged species, but also for establishing the coordination mode of the carboxylates. The Mo–O bands give two strong bands at 943 and 918 cm^{-1} for compound **1**, and broad strong bands at 987, 926 and 880 cm^{-1} for compound **2**. Medium-intensity vibrations at 546 cm^{-1} for **1** and 618 cm^{-1} for **2** are attributable to the Mo–O stretching.[33] They also exhibit characteristic C=O stretching frequencies. Complex **1** displays four intense asymmetric C=O vibrations at 1675,

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1643, 1612 and 1587 cm^{-1}, and three symmetric vibrations at 1441, 1373 and 1345 cm^{-1}. This gives rise to the separation between ν_{asym} (C═O) and ν_{sym} (C═O) of 298 and 146 cm^{-1}, indicating the presence of the bridging bidentate glycinate and unidentately coordinated carboxylates.[34–36] It is noted that **2** shows a medium shoulder vibration at 1740 cm^{-1}, which arises from the protonated, uncomplexed carboxylate. In addition, an intense broad band 1636 cm^{-1} attributable to ν_{asym} (C═O) is found in **2**, and strong symmetrical vibrations at 1441 and 1390 cm^{-1}. Its separation between ν_{asym} (C═O) and ν_{sym} (C═O) ranging from 350 to 195 cm^{-1}, is greater than the separation value of 150 cm^{-1} for an uncoordinated carboxylate, further verifying the presence of the uncoordinated carboxylate group in **2**. Involvement of the amines is shown by the δ(N–H) shift from 3166 cm^{-1} in uncomplexed glycine to 3277 and 3311 cm^{-1} in **1**, suggesting that the uncoordinated amido group is protonated.[37] The bands at 459 cm^{-1} for **1** and 469 cm^{-1} for **2** were assigned to Mo–S–Mo skeletal stretching vibrations, which are in good agreement with the values previously reported in the literature.[19]

Compounds **1** and **2** exhibited similar electronic absorption spectra. Three major electronic absorption bands were observed in these two complexes, λ_{max} (H_2O)/nm: 203 (ε/dm^3 mol^{-1} cm^{-1} 17 000), 282 (4800) and 356 (1500) for **1**, and 205 (13 000), 282 (3800) and 349 (1100) for **2**. The strong peak at ~204 nm in the ultra-violet range was derived from oxygen-to-metal transition, while the peak 282 nm was derived from charge-transfer bands of the (π) S → (d) Mo of the four-membered ring Mo_2S_2. A broad, weak peak at ~350 nm was due to d–d transition of the central metals, which is consistent with previous results.[19,38]

X-ray photoelectron spectrum (XPS) of **1** was performed. Its Mo $3d_{5/2}$ binding energy (eV) was 230.5 eV, suggesting that the oxidation state of Mo is +5, which is in accordance with the structural analysis.[39]

The thermal behavior of **1** was investigated. The TG study revealed that two main pyrolitic decomposition processes occurred. A slight weight increase in the range 20–120 °C was accompanied by the slow oxidation of S^{2-} to S while sulfido-bridge atoms were gradually replaced by oxygen atoms. Then the corresponding compound was stable up to 245 °C, beyond which decomposition started. The decomposition reached a maximum rate around 315 °C and completed at 450 °C, as revealed by the weight loss of about 40.7%, which is in accordance with the calculated value of 44.0%. In the DTA curve, an exothermic process centered at 330 °C occurred, which is mainly due to the decomposition of the glycinates without a stable intermediate product. Another sharp exothermic peak at 359 °C followed, which may be caused by the oxidation of molybdenum(V) to molybdenum(VI) during the primary decomposition process. The final product of decomposition was MoO_3, occurring at 500 °C. The weight loss during this step was found to be 26.9%, which is in good agreement with the calculated value of 28.1%.[40–42]

Crystal structure

The crystal structures of compounds **1** and **2** are illuminated in Figs 1 and 2, respectively, with selected bond distances and bond angles in Table 2.

Neutral complex **1** crystallized in P2(1)/c. In an asymmetric unit, this complex contains two octahedra sharing the sulfido-bridge line. Two coordination modes of the glycine ligands are involved: a glycinate is chelated to each Mo atom via its amine nitrogen atom and α-carboxylate oxygen atom. The third glycine ligand acts as a bridge to link the two molybdenum atoms by its two carboxylate oxygen atoms. In addition, two sulfur atoms and a terminal oxygen atom complete the octahedral moiety around the molybdenum atom. The Mo–O bond from the bridging glycinate [average 2.302 (2) Å] is longer than the Mo–O from the chelated glycinate [average 2.116 (2) Å], slightly longer than Mo–N (average 2.215 Å), and the bond angles C5–O1–Mo1 123.87(19)°, C5–O8–Mo2 123.37(18)° and O7–C5–O8 126.8(3)° are all more than 120°. Literally, these are caused by strong Mo–Mo interaction [2.8167(6) Å]. The C–O bond distances from the bridging carboxylate were the same, which tells us that it is deprotonated. The other C–O bonds in **1** are also deprotonated since the differences between C1–O3 and C1–O4, C3–O5 and C3–O6 are both less than 0.1 Å.[43] The amine group from the bridging glycinate, however, is protonated with relatively long C–N bond distance [C6–N3 1.484(4) Å], in comparison with C2–N1 1.459(4) Å and C4–N2 1.456(5) Å. The planes Mo1, O7, C5, O8, Mo2 and Mo1, O1, O2, Mo2 are almost coplanar, nearly perpendicular to the plane Mo1, S1, S2, Mo2 with dihedral angles 91.1° and 89.2°, respectively. Strong N–H–O hydrogen bonds involving the adjacent amines ($-NH_2$) and uncoordinated oxygen atoms (the distances ranging from 2.812 to 3.097 Å, angles ranging from 154.95° to 170.56°), lead to an overall three-dimensional structure.

Complex **2**, which is composed of two anions $[Mo_2O_2S_2(nta)_2]^{4-}$ and $[Mo_2O_2S_2(ntaH)_2]^{2-}$, six potassium

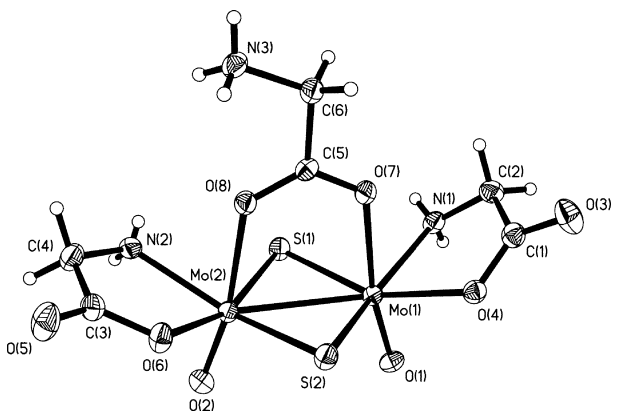

Figure 1. Perspective view of complex **1** showing the atom-labeling scheme. Thermal ellipsoids as drawn by ORTEP represent 30% probability surface.

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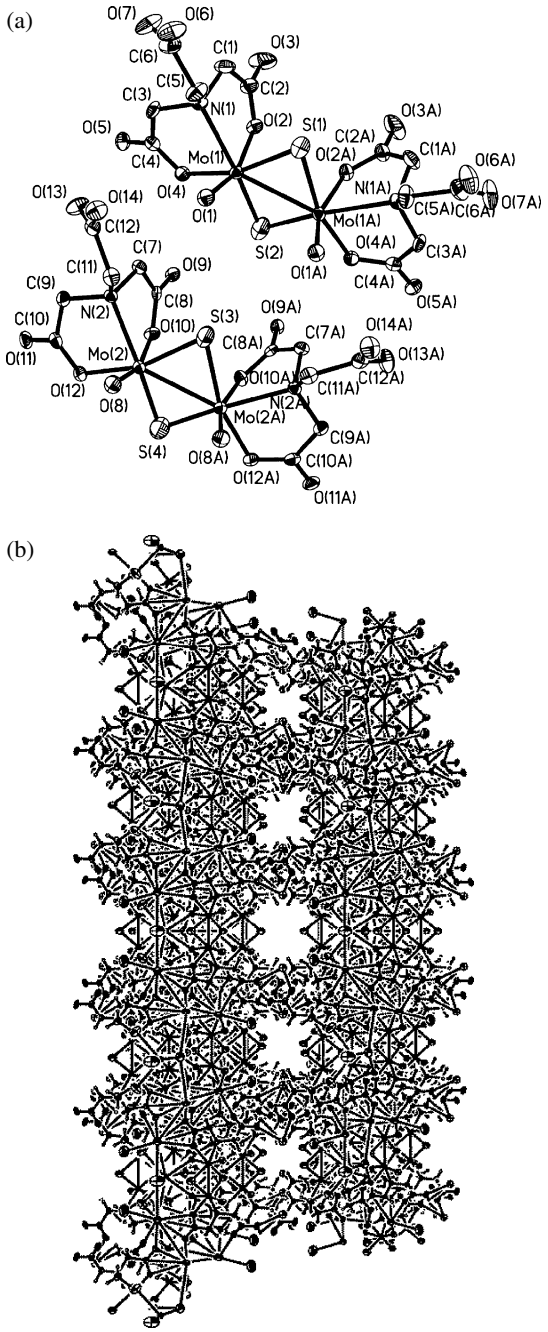

Figure 2. (a) Perspective view of $\{[Mo_2O_2S_2(nta)_2][Mo_2O_2S_2(ntaH)_2]\}^{6-}$ anion of complex **2** showing the atom-labeling scheme. (b) A view of the crystal packing along the *a*-axis. Thermal ellipsoids as drawn by ORTEP representing 30% probability.

ions and four water molecules, is the first binuclear Mo–S–nta complex possessing a crystallographically required symmetric plane. In an asymmetric unit, two anions are connected through strong interactions between the potassiums and the oxygen atoms. Three of the coordination sites on the Mo atom are occupied by a terminal oxygen atom and two sulfur atoms, and the other three by the nitrilotriacetate ligand through its two β-carboxylate oxygens and the nitrogen. One carboxylate group in nitrilotriacetate is uncoordinated. This kind of coordination mode for the ligand could be found in other nitrilotriacetato molybdates, i.e. $(pyH)_2[Mo_2O_5(ntaH)_2]$.[44] The average Mo–O distance to the ligand in **2** is 2.135(5) Å, which is similar to that found in $(pyH)_2[Mo_2O_5(ntaH)_2]$. Compared with Mo–O bonds, the Mo–N bond distances [average 2.316(5) Å] are longer, and even a little longer than Mo–S_b [S_b = bridging sulfur, average 2.240(4) Å]. This kind of difference can also be seen in $[Mo_2O_2S_2(edta)]^{2-}$ anion.[19,45] It seems that the electronic cloud density on N atom will result in the different Mo–N bond, for example, relatively high electron cloud density on the amine nitrogen will result in a stronger Mo–N bond in **1**, in comparison with the relatively weak Mo–N bond in **2**. It is very interesting to note that the differences between the C–O bonds on C2, C4, C6, C8 and C10 are less than 0.1 Å except the C12–O bonds, indicating that these carboxylates (C2, C4, C6, C8 and C10) are deprotonated while C(12)OOH is protonated. Another feature of compound **2** is that the potassium ions play an important role in the construction of the three-dimensional structure. For example, the key role of K4 is linkage of the two anions through the strong interations with S2 and O9 with the bond distances in the range 2.323–2.804 Å. In addition, K1, K2, K3 and K5 adopt six, nine, four and five coordination modes, respectively, with the carboxylate oxygen atoms and the water molecule, with K–O bond distances in the range 2.744–3.179 Å.

Catalytic study of the reduction from C_2H_2 to C_2H_4

The catalytic characterization of FeMo–cofactor has been investigated over three decades.[30,46–48] In addition to catalyzing the reduction of dinitrogen to ammonia, FeMo–cofactor can catalyze the reduction of a number of alternative substrates, such as acetylene (C_2H_2) to ethylene (C_2H_4) and hydrazine to ammonia.[49,50] In fact, the acetylene reduction is a common method for assessing nitrogen fixation, mainly due to acetylene combining with the FeMo–cofactor to less reduced levels than N_2 does, which experimentally simplifies the study of N_2 fixation [equation (3)]:[51,52]

$$C_2H_2 + 2\,e^- + 2\,H^+ \longrightarrow C_2H_4 \qquad (3)$$

Herein, we use this method to investigate the catalytic activity of the different molybdenum (iron)–sulfur compounds without any enzymatic assistance; ethylene is formed together with ethane as a by-product (see Table 3).[54] The acetylene reduction was carried out by employing a procedure which has been documented previously.[53,54] Several Mo/Fe–S compounds were chosen as the catalysts, which covered four binuclear Mo(V)–S–polycarboxylate compounds, **1, 2**, Mo–S–homocitrate $[Mo_2O_2S_2(C_7H_5O_7)_2]^{6-}$ compound and Mo–S–citrate $[Mo_2O_2S_2(C_6H_4O_7)_2]^{6-}$ compound,[19] a single cubane $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ and a chainlike compound $(Et_4N)_4[Mo_2Fe_2S_{10}] \cdot 2CH_3OH$. KBH_4 was selected as the

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Table 2. Selected bond distances and bond angles for complexes **1** and **2**

1		**2**[a]	
Mo(1)–O(1)	1.687(2)	Mo(1)–O(1)	1.679(5)
Mo(1)–N(1)	2.212(3)	Mo(1)–O(4)	2.111(5)
Mo(1)–S(2)	2.3209(8)	Mo(1)–O(2)	2.151(5)
Mo(1)–O(4)	2.131(2)	Mo(1)–S(2)	2.231(4)
Mo(1)–O(7)	2.281(2)	Mo(1)–S(1)	2.254(3)
Mo(1)–S(1)	2.3254(8)	Mo(1)–N(1)	2.337(5)
Mo(1)–Mo(2)	2.8157(6)	Mo(1)–Mo(1)[1]	2.7193(12)
Mo(2)–O(2)	1.681(2)	Mo(2)–O(8)	1.692(5)
Mo(2)–N(2)	2.218(3)	Mo(2)–O(12)	2.098(5)
Mo(2)–O(8)	2.322(2)	Mo(2)–O(10)	2.179(4)
Mo(2)–O(6)	2.100(2)	Mo(2)–S(4)	2.204(4)
Mo(2)–S(2)	2.3234(9)	Mo(2)–S(3)	2.269(3)
Mo(2)–S(1)	2.3317(8)	Mo(2)–N(2)	2.294(5)
C(1)–O(3)	1.234(4)	Mo(2)–Mo(2)[1]	2.7005(12)
C(1)–O(4)	1.284(4)	C(2)–O(3)	1.234(10)
C(3)–O(5)	1.220(4)	C(2)–O(2)	1.246(9)
C(3)–O(6)	1.298(4)	C(4)–O(5)	1.232(8)
C(5)–O(7)	1.258(3)	C(4)–O(4)	1.287(9)
C(5)–O(8)	1.258(3)	C(6)–O(7)	1.213(11)
O(1)–Mo(1)–O(7)	169.89(9)	C(6)–O(6)	1.278(10)
O(7)–Mo(1)–S(2)	84.85(6)	C(8)–O(9)	1.220(8)
O(7)–Mo(1)–S(1)	83.23(6)	C(8)–O(10)	1.274(8)
S(2)–Mo(1)–S(1)	105.46(3)	C(10)–O(11)	1.212(8)
S(2)–Mo(2)–O(8)	83.74(6)	C(10)–O(12)	1.291(9)
S(2)–Mo(2)–S(1)	105.18(3)	C(12)–O(13)	1.188(10)
O(8)–Mo(2)–S(1)	82.81(6)	C(12)–O(14)	1.296(9)
Mo(1)–S(1)–Mo(2)	74.40(3)	S(2)–Mo(1)–S(1)	104.54(10)
Mo(1)–S(2)–Mo(2)	74.64(3)	S(4)–Mo(2)–S(3)	104.40(11)
C(5)–O(7)–Mo(1)	123.87(19)	Mo(1)[1]–S(1)–Mo(1)	74.19(13)
C(5)–O(8)–Mo(2)	123.36(18)	Mo(1)–S(2)–Mo(1)[1]	75.10(15)
O(7)–C(5)–O(8)	126.8(3)	Mo(2)[1]–S(3)–Mo(2)	73.02(13)
O(7)–C(5)–C(6)	115.0(3)	Mo(2)–S(4)–Mo(2)[1]	75.56(16)
O(8)–C(5)–C(6)	118.2(2)	O(3)–C(2)–O(2)	124.7(8)
		O(5)–C(4)–O(4)	122.7(6)
		O(7)–C(6)–O(6)	125.0(8)
		O(9)–C(8)–O(10)	125.1(6)
		O(11)–C(10)–O(12)	123.1(7)
		O(13)–C(12)–O(14)	126.5(7)

[a] Symmetry transformations used to generate equivalent atoms: [1] $x, -y+1, z$.

reducing agent. A 3.0 ml aliquot of borate buffer solution (pH = 9.68) was initially injected into a sealed vial pre-flushed with N_2 gas. Then, 1 ml of acetylene gas and $\sim 8 \times 10^{-4}$ M stock solution prepared by dissolving 1.2 mmol of the selected complexes or combined systems in 1.5 ml of dimethylformamide (DMF) were successively added into the vial. Finally, 0.5 ml of a freshly prepared 1.2 M KBH_4 solution in pH 9.6 borate buffer was injected into the above solution, during which it started to set the time while half-addition of the solution was performed. The vials were gently shaken for 30 min while being kept at 25 °C. Ethylene produced was analyzed by gas chromatography. The combination system of $(NH_4)_2MoS_4$ and $FeCl_3$ in different ratios was also repeated (see Table 3). We found that the activity of the catalytic system reached a maximum when Mo/Fe = 1:6–1:7, similar to the previous result in our lab, which is in accordance with the Mo/Fe ratio of FeMo–cofactor.[8,11,54]

In this paper, catalytic activities are expressed by the turnover numbers (μmol) of C_2H_4 produced per min per μmol Mo in 30 min as well as total C_2H_4 conversion rate (%) in 30 min in the presence of given catalysts. Three features of the catalytic properties are summarized as follows:

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Table 3. Activities of different compounds (compositions) for catalytic reduction of C_2H_2

No.	Sample	Amount of M in system (μmol)		TN[a] C_2H_4	Conversion to C_2H_4[b] (%)	Selectivity to C_2H_4 (%)
		Mo	Fe			
1	Compound **1**	0.390	0	1.46	42.23	66.23
2	Compound **2**	0.552	0	1.36	55.96	88.07
3	Compound **3**[c]	0.446	0	0.31	10.39	70.28
4	Compound **4**[d]	0.410	0	0.80	24.48	82.53
5	Compound **5**[e]	0.459	0.459	0.30	10.16	85.69
6	Compound **6**[f]	0	0.872	0.10[g]	6.27[h]	93.35
		Combination systems				
7	$(NH_4)_2MoS_4$	0.462	0	1.72	58.31	90.97
	$FeCl_3$	0	0.455	0.012[g]	0.40[h]	100
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	1.366	1.41	47.64	86.64
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	1.820	1.34	45.47	85.19
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	2.277	2.15	72.72	85.12
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	2.732	2.24	75.84	87.84
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	3.188	2.20	74.69	87.44
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	3.643	2.12	71.91	83.96
	$(NH_4)_2MoS_4 + FeCl_3$	0.462	4.098	1.71	57.98	80.00
8	Compound **1** + $FeCl_3$	0.390	2.500	0.35	10.27	73.83
9	Compound **2** + $FeCl_3$	0.552	2.770	1.53	62.68	87.59
10	Compound **3** + $FeCl_3$	0.446	2.462	2.18	72.42	78.32
11	Compound **4** + $FeCl_3$	0.410	2.500	1.69	51.59	82.01
12	Compound **5** + homocitrate	0.459	0.459	0.18	6.06	89.79
13	Compound **5** + glycine	0.459	0.459	0.47	5.96	91.34
14	Compound **6** + $(NH_4)_2MoS_4$	0.718	2.560	0.17	8.96	95.09

[a] TN = turnover number (μmol) from C_2H_2 to C_2H_4 per min per μmol Mo in 30 min; [b] percentage conversion from C_2H_2 to C_2H_4 in 30 min; [c] compound **3** = $[Mo_2O_2S_2(cit)_2]^{6-}$; [d] compound **4** = $[Mo_2O_2S_2(homocit)_2]^{6-}$,[19]; [e] compound **5** = $(Et_4N)_4[Mo_2Fe_2S_{10}] \cdot 2CH_3OH$; [f] compound **6** = $(Bu_4N)_2[Fe_4S_4(sph)_4]$; [g] turnover number ($\mu$mol) from C_2H_2 to C_2H_4 per min per μmol Fe in 30 min; [h] percentage conversion from C_2H_2 to C_2H_4 per min per μmol Fe in 30 min.

(1) Remarkable specific activity of molybdenum is apparent in our established system. $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ exhibited lower catalytic activity than other Mo–S compounds no matter what the exact structures of these molybdenum compounds were. Its activity was slightly increased in the presence of $(NH_4)_2MoS_4$.

(2) The coordination environment of the molybdenum atom seems to have a great influence on the catalytic activity of the complexes. Among the four binuclear Mo–S complexes with homocitrate, citrate, glycine and nitrilotriacetate ligands, compound **1** gave relatively high activity and rapid initial rate; however, compound **2** gave better selectivity. In contrast, Mo–S–homocitrate and Mo–S–citrate complexes gave relatively lower activity. It is assumed that glycinate and nitrilotriacetate are more labile, resulting in lower stability and higher catalytic activity of compounds **1** and **2**.

(3) Under identical conditions, $FeCl_3$ almost does not give any catalytic activity, and the single cubane $(Bu_4N)_2[Fe_4S_4(SPh)_4]$ exhibited low activity as well. In the combination systems of $FeCl_3$ and binuclear Mo–S–polycarboxylate complexes, catalytic activity was slightly increased. Thus, it is supposed that iron may not be directly involved in the acetylene reduction reaction. Iron could have a cocatalyst effect, mainly facilitating the electron transfer to the molybdenum active site.[55] Thus, mixtures of $FeCl_3$ and the molybdenum complexes are supposed to generate some kind of Mo–Fe–S intermediates in the process of acetylene reduction. Especially for the $(NH_4)_2MoS_4$–$FeCl_3$ systems, this intermediate is much easier to form, leading to higher activities, which is consistent with previous results.[55]

The reduction of acetylene to ethylene is a two-electron process. A similar reaction was performed upon MoO_4^{2-} – Tg (Tg = 1-thioglycerol) and MoO_4^{2-} – Cys (Cys = cysteine) systems by Schrauzer.[55] According to their proposed mechanism and our experimental results, it is suggested that this catalytic reduction on Mo–S–polycarboxylate complexes most likely occurs via organomolybdenum intermediates.[55–57] The first stage is probably involved in the cleavage of the binuclear Mo–S–polycarboxylate compound into reactive molybdenum monomer.[56–59] Assuming the

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coordination mode of the ligand changed, a coordination site for the acetylene was provided, so-called organomolybdenum intermediates. Under the existence of $NaBH_4$, ethylene was finally released. Obviously, different ligands will significantly influence the catalytic activity, for example, when homocitrate or citrate are linked to the molybdenum atom, the coordination modes are quite stable and thus give lower activity whereas amino acids (glycinate and nitrilotriacetate) could labilize the sulfur bridges, thus resulting in less stability and higher catalytic activity of their molybdenum complexes. Further study of this system from kinetic studies is presently underway in our laboratory.

CONCLUSION

In summary, two sulfido-bridge binuclear molybdenum (V) complexes with glycinate and nitrilotriacetate ligands have been successfully synthesized. They were characterized by FT-IR, UV–visible spectra, XPS, TG–DTA and X-ray diffraction analysis. We also investigated their catalytic properties, and found that they exhibited good catalytic activity for the reduction of C_2H_2 to C_2H_4.

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