

Reaction of Molybdenum Hexa-carbonyl with Mercapto-pyridine (PySH) or Mercapto-pyridine Oxide (PyS→O) and Crystal Structure of [Et₄N][Mo₂(PyS)₃(CO)₅]

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Mixed-valence dinuclear molybdenum complex [Et₄N][Mo₂(PyS)₃(CO)₅] (**1**) (PyS=C₅H₄NS) has been synthesized and characterized by crystallography. **1** crystallizes in monoclinic system with space group *P*2₁/*c* with *a*=1.5769(11) nm, *b*=1.3144(5) nm, *c*=1.6935(10) nm; β=111.20(4)°; *V*=3.2724 nm³; *Z*=4, *D*_c=1.61 g/cm³, μ=9.7 cm⁻¹ and *F*(000)=1600. The final *R*=0.054 and *wR*=0.073, for 1811 observed reflection with *I*>3σ(*I*). In compound **1**, one chelating PyS ligand and two bridging PyS ligands are 3-electron and 5-electron donors, respectively, and two molybdenum atoms are located in different coordination environments resulting in mixed-valence state. The reaction mechanism of Mo(CO)₆ with PySH and PyS→O (C₅H₅SN→O) was investigated and two reaction pathways were proposed.

Keywords mixed-valence Mo-PyS complex, synthesis, crystal structure, PyS→O

Introduction

Mercapto-pyridine, C₅H₄NS⁻(PyS), containing two active atoms, S and N, is a bidentate ligand, which may act as a 3-electron donor or a 5-electron donor and may be a bridging ligand to link two metal atoms to form polynuclear metal clusters or a chelating agent to coordinate to a metal atom by S and N atoms. So the mercapto-pyridine is a very important reagent and its reaction with metal compound is very useful for simulating the active center in metal enzymes and syntheses of novel metal clusters. Thus, the chemistry of mercapto-pyridine has been studied extensively.¹⁻¹⁵ As a part of our investigation on metal clusters containing low valence metal atoms and the modeling compound of the active center in nitrogenase, we reported several Mo-complexes containing PyS ligands such as [Et₄N][Mo(PyS)(CO)₄] (**2**),¹⁶ [Et₄N][Mo₂(PyS)(CO)₉] (**3**),¹⁷ [Et₄N]₂[Mo₂(PyS)₂(CO)₆] (**4**),¹⁸ which were synthesized by the reaction of PySH with Mo(CO)₆. Herein we report the synthesis and structure of a new mixed valence complex [Et₄N][Mo₂(PyS)₃(CO)₅] (**1**) and investigation on the reaction mechanism of Mo(CO)₆ with PySH and its oxide PyS→O.

Experimental

Materials and methods

All procedures were performed under N₂ atmosphere

using a Schlenk technique. PySH, PySNa, Mo(CO)₆ and Et₄NCl were purchased from Aldrich. All solvents and reagents were dried and deoxygenated prior to use. Elemental analyses were carried out on a Carlo Erba MOD 1106 analyzer. Infrared spectra were recorded on a Magna 750 spectrometer.

Synthesis of [Et₄N][Mo₂(PyS)₃(CO)₅] (**1**)

The mixture of PySH (0.22 g, 2 mmol), MeONa (0.12 g, 2 mmol), Et₄NCl (0.33 g, 2 mmol) and Mo(CO)₆ (0.53 g, 2 mmol) in 30 mL of CH₃CN was stirred at 30—35 °C under N₂ atmosphere for 24 h resulting in an orange solution with white solid in it. After filtering off the white precipitate, the filtrate was concentrated to about 15 mL. 7 mL of EtOH were dropped onto the surface of the filtrate and then the resulting solution was cooled at 4 °C for 7 d. 0.04 g of deep red crystals of **1** were collected, yield 7.5% (based on the PySH used). IR (KBr) ν: 1950, 1910, 1870, 1800, 1760 cm⁻¹. Anal. calcd for C₂₈H₃₂Mo₂N₄O₅S₃: C 42.42, H 4.04, N 7.07, Mo 24.24, S 12.12; found C 41.95, H 3.82, N 7.20, Mo 24.54, S 12.60.

Reaction of Mo(CO)₆ with mercapto-pyridine oxide (C₅H₅SN→O) (**2**)

A mixture of Mo(CO)₆ (0.53 g, 2 mmol), Et₄NCl (0.33 g, 2 mmol) and C₅H₄NOSNa (0.20 g, 1.34 mmol) in MeCN (40 mL) was stirred at 60 °C under N₂ for 24 h. After filtering off the insoluble solid, the red filtrate was

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concentrated to 30 mL and 45 mL of PrOH were added. The resulting solution was concentrated to about 35 mL. 0.48 g of yellow crystalline product, $[\text{Et}_4\text{N}][\text{MoPyS}(\text{CO})_4]$ (**2**),¹⁶ was obtained. Yield: 80% (based on the $\text{C}_5\text{H}_4\text{NOSNa}$ used). IR (KBr) ν : 2000, 1910, 1850, 1795 cm^{-1} . Anal. calcd for $\text{C}_{17}\text{H}_{24}\text{MoN}_2\text{O}_4\text{S}$: C 45.54, H 5.36, N 6.25, Mo 21.43, S 7.14; found C 45.80, H 5.36, N 6.30, Mo 21.80, S 7.20.

X-ray crystal structure determination

A single crystal of compound **1** with $0.05 \text{ mm} \times 0.20 \text{ mm} \times 0.40 \text{ mm}$ was mounted on a glass fiber in a random orientation. The data collection was performed with Mo $K\alpha$ radiation ($\lambda = 0.071069 \text{ nm}$) on an MSC/Rigaku diffractometer at a temperature of $(23 \pm 1)^\circ\text{C}$ using ω - 2θ scan technique, and scan rate is $8^\circ/\text{min}$ (in omega). The ω scan width is $1.10 + 0.35 \tan \theta$. The data were collected to a maximum 2θ of 50.0° . An anisotropy decay correction and Lp correction were applied to the data. Empirical absorption correction based on psi-scans using the program of DIFABS was also applied. A total of 6263 reflections were collected. Only 1811 reflections with $I > 3\sigma(I)$ were used for structure solution by direct method. A total of 5 heavy atoms were located from an E-map and the remaining atoms were located in

succeeding difference Fourier syntheses. Hydrogen atoms were not included in the calculations. The final cycle of refinement included 379 variable parameters resulted in $R = 0.054$, $wR = 0.073$, $w = [\sigma^2(F_o^2) + (0.010F_o)^2 + 1.000]^{-1}$. The max. and min. peaks in the final difference Fourier map are 800 and -760 e/nm^3 , respectively. Calculations were performed on a VAX computer using SDP/VAX.

Results and discussion

The structure of $[\text{Et}_4\text{N}][\text{Mo}_2(\text{PyS})_3(\text{CO})_5]$ (**1**)

The coordinates and thermal parameters of all non-hydrogen atoms of compound **1** are listed in Table 1. Selected bond lengths and bond angles are given in Table 2 and the structure of the anion of **1** is depicted in Figure 1. Compound **1** is composed of a cation Et_4N^+ and an anion $[\text{Mo}_2(\text{PyS})_3(\text{CO})_5]^-$ in an asymmetric unit. As shown in Figure 1 and Table 2, the anion of compound **1** possesses a bimetallic Mo_2S_2 core adopting a butterfly configuration with dihedral angle of 143.6° (between the two planes $\text{Mo}(1)\text{-S}(1)\text{-Mo}(2)$ and $\text{Mo}(1)\text{-S}(2)\text{-Mo}(2)$). Around the core, there are two pyridine rings, one PyS-ligand and five carbonyls con-

Table 1 Positional parameters and their estimated standard deviations for $[\text{Et}_4\text{N}][\text{Mo}_2(\text{PyS})_3(\text{CO})_5]$ (**1**)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (nm^2)	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (nm^2)
Mo(1)	0.7493(1)	0.0931(2)	0.0405(1)	0.0213(4)	C(22)	0.717(2)	0.490(2)	-0.046(1)	0.044(7)
Mo(2)	0.7682(1)	0.3798(2)	0.0324(1)	0.0264(4)	C(23)	0.663(2)	0.378(2)	0.071(2)	0.050(7)
S(1)	0.6991(4)	0.2301(6)	-0.0736(3)	0.031(2)	C(24)	0.932(1)	0.266(2)	0.057(1)	0.030(6)
S(2)	0.8705(4)	0.2250(5)	0.1173(3)	0.024(1)	C(25)	1.015(1)	0.222(2)	0.062(1)	0.039(7)
S(3)	0.7310(4)	-0.0958(5)	0.0068(4)	0.036(2)	C(26)	1.059(2)	0.271(2)	0.008(2)	0.057(8)
O(12)	0.540(1)	0.064(2)	-0.053(1)	0.060(6)	C(27)	1.020(2)	0.354(2)	-0.045(2)	0.049(8)
O(13)	0.667(1)	0.131(1)	0.1802(9)	0.047(5)	C(28)	0.939(2)	0.387(2)	-0.046(1)	0.035(6)
O(21)	0.845(1)	0.555(1)	0.169(1)	0.057(6)	C(34)	0.818(2)	-0.104(2)	0.111(1)	0.025(5)
O(22)	0.681(2)	0.554(2)	-0.097(2)	0.118(9)	C(35)	0.853(2)	-0.196(2)	0.155(2)	0.040(7)
O(23)	0.600(1)	0.384(2)	0.088(1)	0.076(6)	C(36)	0.923(2)	-0.180(2)	0.232(1)	0.038(7)
N(1)	0.817(1)	0.089(1)	-0.058(1)	0.030(5)	C(37)	0.941(2)	-0.084(2)	0.264(1)	0.032(6)
N(2)	0.896(1)	0.349(1)	0.007(1)	0.025(5)	C(38)	0.902(1)	0.002(2)	0.221(1)	0.028(6)
N(3)	0.842(1)	-0.012(1)	0.140(1)	0.020(4)	N(5)	0.594(1)	0.685(1)	0.219(1)	0.030(5)
C(12)	0.616(2)	0.071(2)	-0.021(1)	0.038(7)	C(51)	0.516(2)	0.720(2)	0.246(1)	0.030(6)
C(13)	0.699(2)	0.118(2)	0.131(1)	0.038(7)	C(52)	0.544(2)	0.726(2)	0.340(1)	0.038(7)
C(14)	0.778(1)	0.170(2)	-0.109(1)	0.028(6)	C(53)	0.677(2)	0.749(2)	0.249(1)	0.038(7)
C(15)	0.801(2)	0.198(2)	-0.180(2)	0.043(7)	C(54)	0.661(2)	0.859(2)	0.221(2)	0.062(9)
C(16)	0.868(2)	0.141(2)	-0.195(2)	0.056(9)	C(55)	0.631(2)	0.578(2)	0.254(1)	0.045(7)
C(17)	0.905(2)	0.052(2)	-0.147(2)	0.057(8)	C(56)	0.577(2)	0.498(2)	0.243(2)	0.051(8)
C(18)	0.879(2)	0.031(2)	-0.080(2)	0.035(7)	C(57)	0.550(2)	0.678(2)	0.126(2)	0.042(7)
C(21)	0.820(2)	0.488(2)	0.119(1)	0.032(6)	C(58)	0.614(2)	0.655(2)	0.081(2)	0.049(8)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) \times [a^2 \times \beta(1,1) + b^2 \times \beta(2,2) + c^2 \times \beta(3,3) + ab(\cos \gamma) \times \beta(1,2) + ac(\cos \beta) \times \beta(1,3) + bc(\cos \alpha) \times \beta(2,3)]$.

necting with the Mo and S atoms resulted in 6 and 7 coordination of Mo atoms. The two pyridine rings are not exactly parallel with each other with dihedral angle being about 20° , and locate at the same side of the Mo_2S_2 ring like Re-PyS complex, $[\text{Re}_2(\text{PyS})_2(\text{CO})_6]$.¹ The dihedral angles between the two pyridine rings and Mo_2S_2 ring are about 99° and 79° , respectively. The pyridine ring of PyS-ligand chelating to Mo(1) atom is nearly parallel with the Mo_2S_2 ring (dihedral angle is about 8°). In the anion of compound **1**, there are three PyS ligands, two of which, as a 5-electron donor, respectively chelate one Mo atom and simultaneously bridge the second Mo atom via the S atom, and the third one as a 3-electron donor coordinates to one of the two Mo atoms (Mo(1)), which results in two Mo atoms in different coordination environments. Three PyS ligands of compound **1** have almost same dimension (bond lengths and bond angles) as those in other complexes containing PyS ligands¹⁻³ and each S atom is coplanar with its parent pyridine ring. $\text{Mo}\cdots\text{Mo}$ distance is 0.3687(3) nm, indicating no significant metal-metal interaction. The Mo(1)—S and Mo(2)—S bond lengths are 0.254 and 0.265 nm (av.). The different coordination environments of the two Mo atoms and two different Mo—S bond lengths observed in compound **1** may imply that the two Mo atoms possess different electron density.

The reactions of $\text{Mo}(\text{CO})_6$ with PySH or $\text{PyS}\rightarrow\text{O}$ and two reaction pathways

Four different products were isolated from the reaction of $\text{Mo}(\text{CO})_6$ with PySH: $[\text{Et}_4\text{N}][\text{Mo}(\text{PyS})(\text{CO})_4]$ (**2**),¹⁶ $[\text{Et}_4\text{N}][\text{Mo}_2(\mu\text{-PyS})(\text{CO})_9]$ (**3**),¹⁷ $[\text{Et}_4\text{N}]_2[\text{Mo}_2(\mu\text{-PyS})_2(\text{CO})_6]$ (**4**)¹⁸ and $[\text{Et}_4\text{N}][\text{Mo}_2(\mu\text{-PyS})_2(\text{PyS})(\text{CO})_5]$ (**1**). Their anions are **a**, **b**, **c** and **d**, respectively (Scheme 1). X-ray crystal determination indicated that there are two kinds of PyS-ligands in these products. One kind is a three-electron donor ligand, which chelates to one Mo atom by its S and N atoms (for example in **a**, **d**) and the other is a five-electron donor, which bridges two Mo atoms (in **b**, **c**, **d**). **d** contains both two kinds of PyS

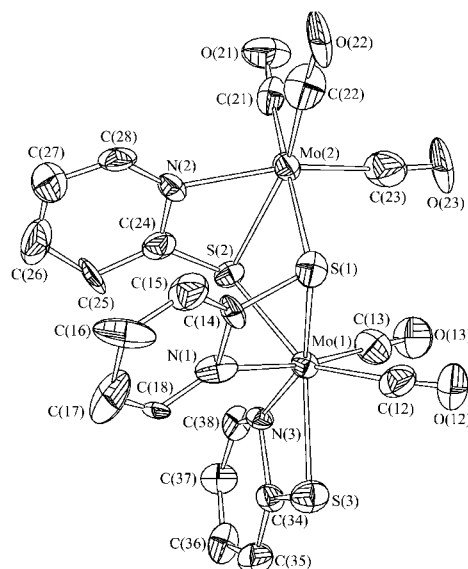
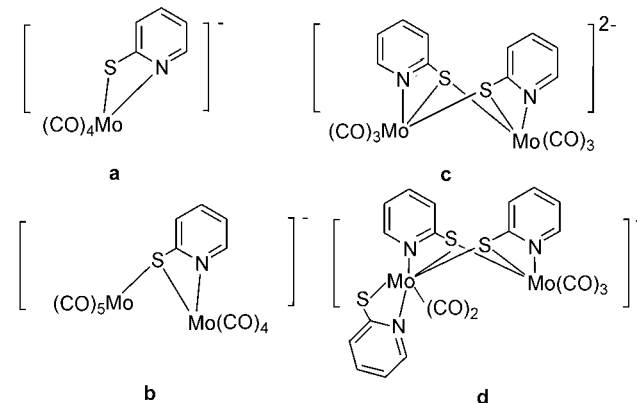


Figure 1 Structure of the anion of complex **1**.

Scheme 1



ligands and **c** and **d** possess two Mo atoms in different coordination environments forming mixed valence metal clusters. It is worth pointing out that in **c** and **d**, the two bridging PyS ligands are in *cis*-arrangement which was observed in Re-PyS analog.¹

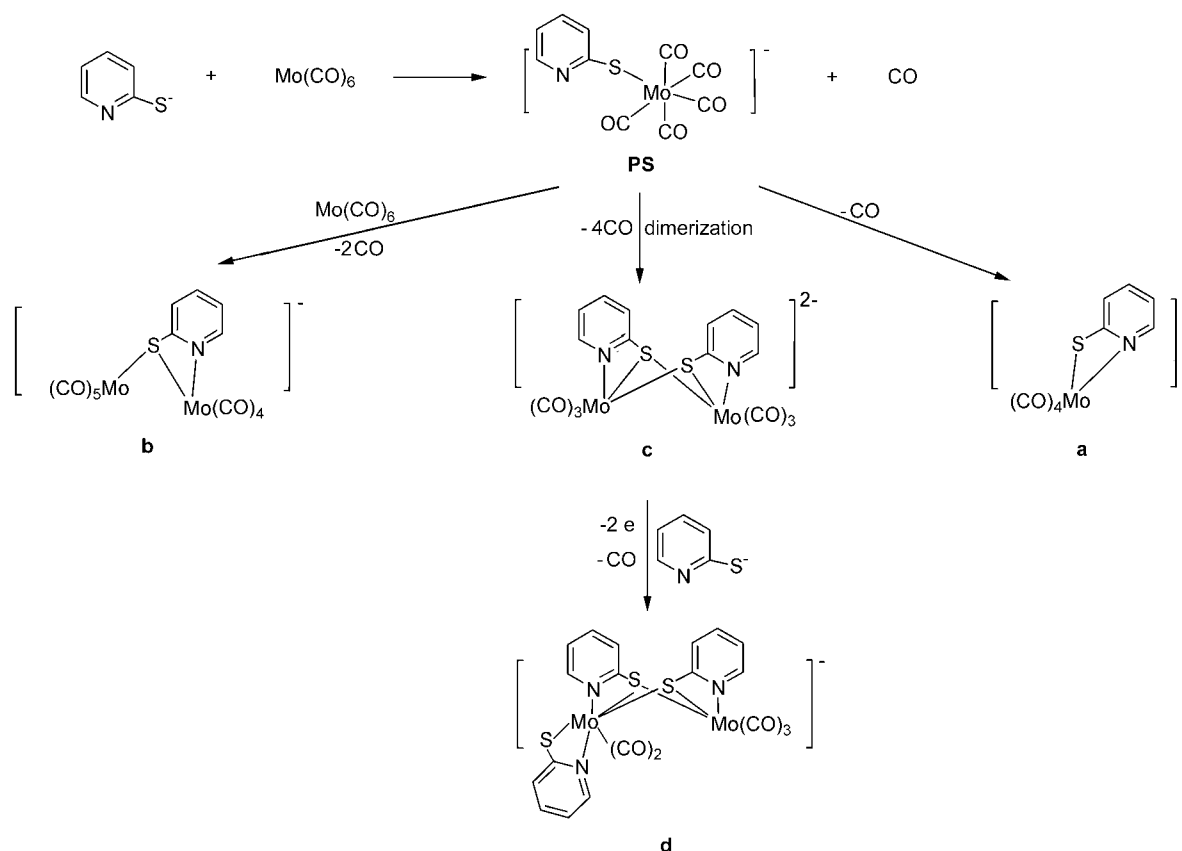
Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) for $[\text{Et}_4\text{N}][\text{Mo}_2(\text{PyS})_3(\text{CO})_5]$ (**1**)

Mo(1)—Mo(2)	0.3786(3)	Mo(2)—C(24)	0.289(2)
Mo(1)—S(1)	0.2549(6)	S(1)—C(14)	0.175(3)
Mo(1)—S(2)	0.2559(6)	S(2)—C(24)	0.174(2)
Mo(1)—S(3)	0.2541(7)	S(3)—C(34)	0.180(3)
Mo(1)—N(1)	0.228(2)	O(12)—C(12)	0.113(3)
Mo(1)—N(3)	0.226(2)	O(13)—C(13)	0.113(2)
Mo(1)—C(12)	0.201(3)	O(21)—C(21)	0.118(3)
Mo(1)—C(13)	0.200(2)	O(22)—C(22)	0.119(3)
Mo(1)—C(14)	0.290(2)	O(23)—C(23)	0.112(3)
Mo(1)—C(34)	0.289(2)	N(1)—C(14)	0.136(3)
Mo(2)—S(1)	0.2619(8)	N(1)—C(18)	0.140(3)
Mo(2)—S(2)	0.2671(6)	N(2)—C(24)	0.137(3)

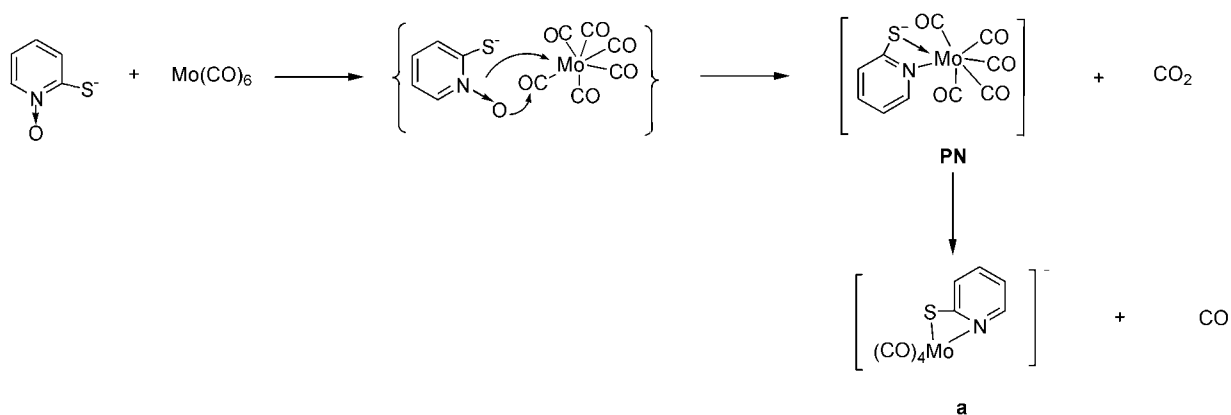
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Mo(2)—N(2)	0.226(2)	N(2)—C(28)	0.140(3)
Mo(2)—C(21)	0.199(3)	N(3)—C(34)	0.131(3)
Mo(2)—C(22)	0.193(3)	N(3)—C(38)	0.136(2)
Mo(2)—C(23)	0.200(3)		
Mo(2)-Mo(1)-S(1)	43.6(2)	S(1)-Mo(2)-C(21)	176.5(7)
Mo(2)-Mo(1)-S(2)	44.8(1)	S(1)-Mo(2)-C(22)	97.2(9)
Mo(2)-Mo(1)-S(3)	165.5(2)	S(1)-Mo(2)-C(23)	91.8(9)
Mo(2)-Mo(1)-N(1)	86.1(5)	S(2)-Mo(2)-N(2)	63.5(5)
Mo(2)-Mo(1)-N(3)	126.7(5)	S(2)-Mo(2)-C(21)	98.1(8)
Mo(2)-Mo(1)-C(12)	102.0(7)	S(2)-Mo(2)-C(22)	164.0(8)
Mo(2)-Mo(1)-C(13)	85.6(8)	S(2)-Mo(2)-C(23)	103.2(8)
S(1)-Mo(1)-S(2)	83.0(2)	N(2)-Mo(2)-C(21)	96.4(9)
S(1)-Mo(1)-S(3)	122.8(3)	N(2)-Mo(2)-C(22)	100.6(9)
S(1)-Mo(1)-N(1)	64.0(6)	N(2)-Mo(2)-C(23)	167(1)
S(1)-Mo(1)-N(3)	159.8(5)	C(21)-Mo(2)-C(22)	86(2)
S(1)-Mo(1)-C(12)	74.2(8)	C(21)-Mo(2)-C(23)	86(2)
S(1)-Mo(1)-C(13)	111.4(7)	C(22)-Mo(2)-C(23)	93(1)
S(2)-Mo(1)-S(3)	141.2(3)	Mo(1)-S(1)-Mo(2)	94.2(2)
S(2)-Mo(1)-N(1)	85.7(5)	Mo(1)-S(1)-C(14)	82.6(8)
S(2)-Mo(1)-N(3)	82.7(5)	Mo(1)-S(2)-Mo(2)	92.7(2)
S(2)-Mo(1)-C(12)	144.6(7)	Mo(1)-S(2)-C(24)	112.7(7)
S(2)-Mo(1)-C(13)	86.1(8)	Mo(2)-S(2)-C(24)	78.9(8)
S(3)-Mo(1)-N(1)	81.9(5)	Mo(1)-S(3)-C(34)	81.6(8)
S(3)-Mo(1)-N(3)	64.0(5)	Mo(1)-N(1)-C(14)	103(1)
S(3)-Mo(1)-C(12)	74.2(7)	Mo(1)-N(1)-C(18)	140(2)
S(3)-Mo(1)-C(13)	106.9(8)	C(14)-N(1)-C(18)	117(2)
N(1)-Mo(1)-N(3)	100.8(6)	Mo(2)-N(2)-C(24)	103(1)
N(1)-Mo(1)-C(12)	107.2(9)	Mo(2)-N(2)-C(28)	138(1)
N(1)-Mo(1)-C(13)	171.0(9)	C(24)-N(2)-C(28)	120(2)
N(3)-Mo(1)-C(12)	124.9(8)	Mo(1)-N(3)-C(34)	105(1)
N(3)-Mo(1)-C(13)	81.6(8)	Mo(1)-N(3)-C(38)	134(1)
C(12)-Mo(1)-C(13)	78(1)	C(34)-N(3)-C(38)	120(2)
Mo(1)-Mo(2)-S(1)	42.2(1)	Mo(1)-C(12)-O(12)	176(2)
Mo(1)-Mo(2)-S(2)	42.5(1)	Mo(1)-C(13)-O(13)	178(2)
Mo(1)-Mo(2)-N(2)	85.0(5)	S(1)-C(14)-N(1)	111(2)
Mo(1)-Mo(2)-C(21)	134.6(7)	S(1)-C(14)-C(15)	126(2)
Mo(1)-Mo(2)-C(22)	138.9(7)	Mo(2)-C(21)-O(21)	175(2)
Mo(1)-Mo(2)-C(23)	83.9(9)	Mo(2)-C(22)-O(22)	176(3)
S(1)-Mo(2)-S(2)	79.5(2)	Mo(2)-C(23)-O(23)	174(3)
S(1)-Mo(2)-N(2)	84.9(4)	S(2)-C(24)-N(2)	114(2)
S(3)-C(34)-N(3)	109(2)	S(2)-C(24)-C(25)	123(3)
S(3)-C(34)-C(35)	125(2)		

Scheme 2



Scheme 3



Interestingly, reaction of Mo(CO)_6 with $\text{PyS} \rightarrow \text{O}$ only produced compound **2** in high yield.

According to the reactivity of the —SH in PySH and the decarbonylation ability of $\text{N} \rightarrow \text{O}$ group in $\text{PyS} \rightarrow \text{O}$, the reaction of Mo(CO)_6 with PySH and $\text{PyS} \rightarrow \text{O}$ maybe form a precursor compound $[\text{Mo(CO)}_5\text{SC}_5\text{H}_4\text{N}]$ (PS) with Mo—S bond and $[\text{Mo(CO)}_5\text{NC}_5\text{H}_4\text{S}]$ (PN) with Mo—N bond, respectively. Therefore, two different reaction pathways may be proposed as follows, for the reaction of PySH with Mo(CO)_6 (Scheme 2) and for the reaction of $\text{PyS} \rightarrow \text{O}$ with Mo(CO)_6 (Scheme 3).

For the reaction of PySH with Mo(CO)_6 , it may form a precursor $[\text{Mo(CO)}_5\text{SC}_5\text{H}_4\text{N}]^-$ (PS) with Mo—S bond. PS turns into **a** by the coordination of the lone pair electron on N atom to Mo atom with loss of one carbonyl. PS further reacts with Mo(CO)_6 to afford **b**. PS undergoes dimerization with loss of four CO, yielding **c**. **c** further reacts with PySH in the presence of certain amount of oxygen, affording **d** via substitution of carbonyl by PyS -ligand and oxidation of Mo atoms. The presence of certain amount of oxygen should be an accident, hence there was no any oxidant in the synthetic reaction system and the reaction was carried out using a

Schlenk technique. This is the reason why the yield was so low for compound **1**. It is possible to enhance the yield if a proper air entrance can be controlled or certain oxidant is used.

For the reaction of PyS→O with Mo(CO)₆, the reaction pathway is different (Scheme 3). PyS→O as a decarbonylation reagent reacts with Mo(CO)₆ by its NO group, affording a reactive precursor [Mo(CO)₅NC₅H₄S]⁻ (PN) possessing Mo—N bond. At almost the same time, PN turns into stable **a** by its reactive S atom replacing a carbonyl of the Mo atom.

Both PySNa and PyS→O provide the same PyS-ligand when they react with Mo(CO)₆, but give different resulting products due to their different reaction pathways.

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