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Journal of Organometallic Chemistry 514 (1996) 183–189

Journal of Organometallic Chemistry

Synthesis and molecular structures of di- and trinuclear molybdenum complexes containing pyridine-2-thiolato (pyS) ligand

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Received 8 September 1995

Abstract

Dinuclear complexes $[Mo_2(\mu\text{-pyS})_2(CO)_4(PPh_3)_2]$ (1), $[Mo_2(\mu\text{-pyS})_2(CO)_5(PPh_3)]$ (2) and a trace quality of trinuclear complex $[Mo_3(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2(CO)_6]$ (3) were obtained from the reaction of $[Mo(CO)_3(MeCN)_3]$ with pyridine-2-thione (pySH) and PPh_3 in THF. The crystal structures of $1 \cdot 2C_7H_8$ and $3 \cdot C_7H_8$ have been determined by X-ray diffraction studies. Crystals of $1 \cdot 2C_7H_8$ are monoclinic, space group $C2/c$ and $Z = 4$, with $a = 18.797(3)$, $b = 11.143(4)$, $c = 28.157(7)$ Å, $\beta = 101.23(2)°$. The structure was refined to $R = 0.050$ and $Rw = 0.057$ for 3146 observed reflections. Crystals of $3 \cdot C_7H_8$ are monoclinic, space group $P2_1/a$ and $Z = 4$, with $a = 13.912(2)$, $b = 17.161(2)$, $c = 15.577(3)$ Å, $\beta = 101.17(1)°$. The structure was refined to $R = 0.046$ and $Rw = 0.051$ for 4357 observed reflections. The molecule of 1 consists of two $Mo(CO)_2(PPh_3)$ fragments linked by an Mo–Mo bond (2.974(2) Å) and by two doubly-bridging pyS ligands. The compound 3 contains a bent open geometry of three molybdenum atoms (Mo(1)–Mo(2)–Mo(3) angle 122.99(3)°) linked by two Mo–Mo bonds (2.943(1) and 2.950(1) Å) and by two doubly- and two triply-bridging pyS ligands.

Keywords: Mo; Dinuclear complexes; Trinuclear complexes; Pyridene-2-thiolato complexes; X-ray structures

1. Introduction

The pyridine-2-thione (pySH) and its deprotonated derivative pyridine-2-thiolato (pyS) are potentically amibedente or multi-functional donors with either the exocyclic sulphur atom or heterocyclic nitrogen atom available for coordination to metals. By using these ligands, many transition metal, especially Group 8, complexes with different coordination modes of pySH and pyS ligands have been reported [1–6]. However, Group 6 metal complexes containing the ligands are relatively rare [7–10]. In this paper we report the synthesis and structures of di- and trinuclear molybdenum complexes with doubly- and triply-bridging pyS ligands.

2. Results and discussion

Treatment of $[Mo(CO)_3(MeCN)_3]$ with pySH and PPh_3 in THF solution at 50°C for 5 h yields dinuclear complexes $[Mo_2(\mu\text{-pyS})_2(CO)_4(PPh_3)_2]$ (1), $[Mo_2(\mu\text{-pyS})_2(CO)_5(PPh_3)]$ (2) and a trace quality of trinuclear complex $[Mo_3(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2(CO)_6]$ (3), which were separated by TLC on alumina. The complexes 1 and 2 were characterized by IR and ^1H NMR spectra. The ^1H NMR spectrum of 1 in CD_3COCD_3 reveals four types of pyridine proton. The IR spectrum shows two strong CO absorptions at 1915 and 1835 cm^{-1}, consistent with its crystal structure revealed by X-ray structure analysis. The IR spectrum of 2 reveals a three-band pattern, with bands at 2000, 1970 and 1875 cm^{-1}. All of the bands have shifted to higher frequencies relative to those in 1, which can be attributed to reduced metal-to-CO back-bonding due to only one PPh_3 donor ligand existing in 2. The complex 3 could only be characterized by obtaining a few crystals suitable for

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SSDI 0022-328X(95)06037-5

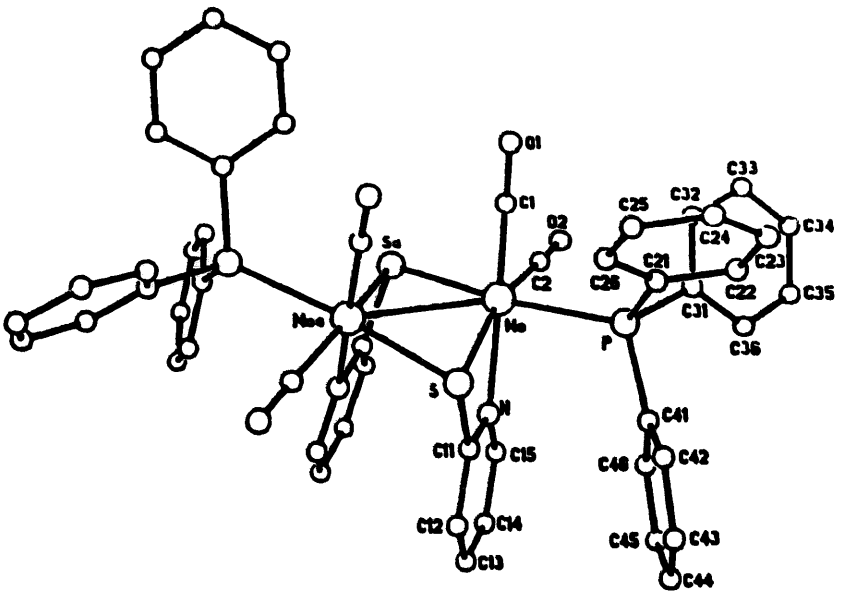

Fig. 1. Molecular structure of $[Mo_2(\mu\text{-pyS})_2(CO)_4(PPh_3)_2]$ (1).

determining X-ray structure and recording IR spectrum. The IR spectrum shows three bands at 1950, 1900 and 1848 cm^{-1}. Attempting to obtain **3** by the reaction of $[Mo(CO)_3(MeCN)_3]$ with pySH in a molar ratio of 3:4 in THF solution at 50°C was a failure.

Complexes **1** and **2** are air sensitive both in the solid state and in solution. They are soluble in polar solvents, such as CH_2Cl_2, THF and acetone, but insoluble in non-polar solvents. The compounds were formed in very low yield and a brown decomposition material

Table 1
Selected bond lengths (Å) and angles (°) of the complex 1

Mo–Mo(a)	2.974(1)	Mo–C(1)	1.934(6)
Mo–C(2)	1.992(7)	Mo–S	2.497(2)
Mo–N	2.261(5)	Mo–P	2.496(1)
Mo–S(a)	2.460(1)	C(1)–O(1)	1.172(8)
C(2)–O(2)	1.143(9)	S–C(11)	1.772(6)
N–C(11)	1.339(8)	N–C(15)	1.320(8)
C(11)–C(12)	1.394(9)	C(12)–C(13)	1.368(11)
C(13)–C(14)	1.369(12)	C(14)–C(15)	1.374(10)
P–C(21)	1.826(6)	P–C(31)	1.826(6)
P–C(41)	1.829(6)		
C(1)–Mo–C(2)	87.8(3)	C(1)–Mo–S	107.1(2)
C(2)–Mo–S	163.5(2)	C(1)–Mo–N	172.2(2)
C(2)–Mo–N	99.7(2)	S–Mo–N	65.2(1)
C(1)–Mo–P	89.0(2)	C(2)–Mo–P	88.0(2)
S–Mo–P	85.2(1)	N–Mo–P	89.1(1)
C(1)–Mo–Mo(a)	91.4(2)	C(2)–Mo–Mo(a)	136.2(2)
S–Mo–Mo(a)	52.6(1)	N–Mo–Mo(a)	84.7(1)
P–Mo–Mo(a)	135.7(1)	C(1)–Mo–S(a)	88.8(2)
C(2)–Mo–S(a)	82.5(2)	S–Mo–S(a)	104.4(1)
N–Mo–S(a)	94.2(1)	P–Mo–S(a)	170.4(1)
Mo–C(1)–O(1)	178.3(6)	Mo–C(2)–O(2)	177.6(5)
Mo–S–C(11)	82.1(2)	Mo–S–Mo(a)	73.7(1)
C(11)–S–Mo(a)	101.3(2)	Mo–N–C(11)	101.9(4)
Mo–N–C(15)	140.0(4)	C(11)–N–C(15)	118.1(5)
S–C(11)–N	110.7(4)	S–C(11)–C(12)	126.9(5)
N–C(11)–C(12)	122.3(6)	C(11)–C(12)–C(13)	118.2(7)
C(12)–C(13)–C(14)	119.4(7)	C(13)–C(14)–C(15)	119.0(7)
N–C(15)–C(14)	123.0(7)	Mo–P–C(21)	116.7(2)
Mo–P–C(31)	115.0(2)	Mo–P–C(41)	115.6(2)

accompanies their formation. A similar phenomenon has previously been observed in the reactions of $[M(CO)_3(MeCN)_3]$ (M = Mo, W) with pySH in acetonitrile. The reactions give low yields of mononuclear complexes of formulae $[M(CO)_3(pyS)_2]$ (M = Mo, W) and $[W(CO)_5(pySH)]$ [8].

The structure of **1** is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The molecule consists of two $Mo(CO)_2(PPh_3)$ fragments linked by an Mo–Mo bond and by two doubly-bridging pyridine-2-thiolato ligands. There is a crystallographically imposed two-fold axis of rotation through the middle point of the Mo–Mo bond and perpendicular to the Mo_2S_2 ring, which is non-planar with a dihedral angle of 161.9° between MoMo(a)S and MoMo(a)S(a) planes. The pyS ligand bridges two Mo atoms through an S atom and coordinates to one of the two Mo atoms through an N atom, forming a less common coordination mode which has only been observed in structurally determined complexes $[Re_2(\mu\text{-MepyS})_2(CO)_6]$ [11] and $[Et_4N][Mo_2(\mu\text{-pyS})(CO)_9]$ [10]. The pyS ligand in complex **1** is anionic and can be the donor of six electrons. Pyridine rings of the two pyS ligands are on the same side of the Mo_2S_2 skeleton. The geometry of the μ-pyS ligand does not seem to be distorted by the bridging sulphur atom (the S atom and the pyridine ring are in the same plane). The Mo atom completes its distorted octahedral coordination with 2S, N, 2CO and PPh_3 groups. The distortion is due to the small interligand angle S–Mo–N (65.2(1)°) and the large S–Mo–S(a) angle of 104.4(1)°. The Mo–S–Mo(a) angle is 73.7(1)°. The Mo–Mo bond length is 2.974(2) Å. The metal–metal bond results from the coupling of the unpaired spins of two Mo(I) ions (d^5). The bond distance Mo–S (2.497(2) Å) is longer than Mo–S(a) (2.460(1) Å). This might be partly due to the effect of the different *trans* ligands and partly due to the non-equivalence of the two sulphur P_π orbitals acting as donors; one of them is surely perturbed by the pyridine π-system, while the other is not. The bond lengths Mo–N (2.261(5) Å), Mo–S and Mo–S(a) in the complex are shorter than the corresponding bond distances (2.284(4), 2.617(1) and 2.582(1) Å respectively) in $[Et_4N][Mo_2(\mu\text{-pyS})(CO)_9]$ [10]. This is reasonable when considering that the two complexes have metals in two different oxidation states. The Mo atoms in $[Et_4N][Mo_2(\mu\text{-pyS})(CO)_9]$ are in a zero oxidation states.

The structure of **3** is shown in Fig. 2. Selected bond lengths and angles are listed in Table 2. The compound contains a bent open geometry of three molybdenum atoms (Mo(1)–Mo(2)–Mo(3) angle 122.99(3)°) linked by two Mo–Mo bonds and by two doubly- and two triply-bridging pyS ligands. Each μ-pyS ligand bridges two Mo atoms (Mo(1) and Mo(2) or Mo(3) and Mo(2)) through a sulphur atom and coordinates to the central Mo(2) atom through a nitrogen atom. Each μ_3-pyS

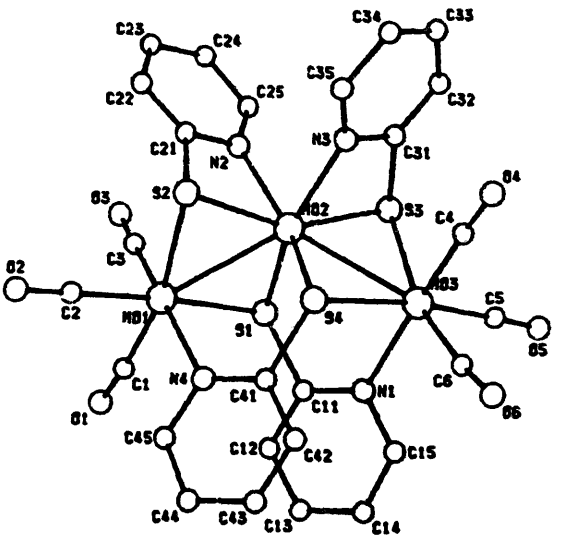

Fig. 2. Molecular structure of $[Mo_3(\mu\text{-pyS})_2(\mu_3\text{-pyS})_2(CO)_6]$ (3).

ligand also bridges two Mo atoms (Mo(1) and Mo(2) or Mo(3) and Mo(2)) through a sulphur atom, but coordinates to the third terminal Mo atom (Mo(1) or Mo(3)) through a nitrogen atom. The coordination mode of μ-pyS ligands in the complex is the same as that in complex **1**, whereas the coordination mode of μ_3-pyS ligands has not previously been found in Group 6 metal complexes, although it has often been observed in Group 8 transition metal trinuclear complexes or clusters containing pyS ligands [4–6]. The geometries of μ-pyridine-2-thiolato ligands do not seem to be substantially distorted by the bridging sulphur atoms (the sulphur atoms deviate from the mean planes through the pyridine rings by 0.03 Å for S(2) and 0.07 Å for S(3)), whereas those of the μ_3-pyridine-2-thiolato ligands are highly distorted by the bridging sulphur atoms (the sulphur atoms deviate from the mean planes through the pyridine rings by 0.12 Å for S(1) and 0.26 Å for S(4)).

The coordination environments of the three Mo atoms are different, but those of the two terminal Mo atoms (Mo(1) and Mo(3)) are similar. Both the Mo atoms complete their distorted octahedral coordination with 2S, N, and 3CO groups. The distortions are associated with the large angles S(1)–Mo(1)–S(2) (102.31(7)° for the Mo(1) atom) and S(3)–Mo(3)–S(4) (101.15(7)° for the Mo(3) atom). The coordination geometry of the central Mo(2) atom, which is coordinated by 4S and 2N atoms, cannot be described in terms of simple symmetry. At best the coordination (neglecting the terminal Mo atoms) may be approximated as intermediate between a trigonal antiprism (octahedron) and a trigonal prism.

Like the pyS ligand in complex **1**, both the μ-pyS and μ_3-pyS ligands in complex **3** are anionic and they are six electron donors. The two terminal metals and the central metal are in oxidation states of (I) and (II)

Table 2
Selected bond lengths (Å) and angles (°) of the complex 3

Mo(1)–Mo(2)	2.943(1)	Mo(2)–Mo(3)	2.950(1)
Mo(1)–S(1)	2.483(2)	Mo(1)–S(2)	2.542(2)
Mo(2)–S(1)	2.359(2)	Mo(2)–S(2)	2.438(2)
Mo(2)–S(3)	2.433(2)	Mo(2)–S(4)	2.344(2)
Mo(3)–S(3)	2.564(2)	Mo(3)–S(4)	2.496(2)
Mo(1)–C(1)	2.00(1)	Mo(1)–C(2)	1.99(1)
Mo(1)–C(3)	1.911(8)	Mo(3)–C(4)	1.95(1)
Mo(3)–C(5)	1.975(9)	Mo(3)–C(6)	1.983(9)
Mo(1)–N(4)	2.337(6)	Mo(2)–N(2)	2.191(6)
Mo(2)–N(3)	2.177(6)	Mo(3)–N(1)	2.315(6)
C(1)–O(1)	1.14(1)	C(2)–O(2)	1.15(1)
C(3)–O(3)	1.179(9)	C(4)–O(4)	1.16(1)
C(5)–O(5)	1.15(1)	C(6)–O(6)	1.16(1)
S(1)–C(11)	1.791(7)	S(2)–C(21)	1.771(8)
S(3)–C(31)	1.793(8)	S(4)–C(41)	1.804(8)
N(1)–C(11)	1.33(1)	N(2)–C(21)	1.36(1)
N(3)–C(31)	1.35(1)	N(4)–C(41)	1.34(1)
Mo(1)–Mo(2)–Mo(3)	122.99(3)	C(1)–Mo(1)–Mo(2)	138.1(3)
C(1)–Mo(1)–S(1)	87.4(3)	C(1)–Mo(1)–S(2)	167.6(3)
C(1)–Mo(1)–N(4)	93.2(3)	C(2)–Mo(1)–Mo(2)	136.1(2)
C(2)–Mo(1)–S(1)	173.2(2)	C(2)–Mo(1)–S(2)	84.3(2)
C(2)–Mo(1)–N(4)	94.6(3)	C(2)–Mo(1)–C(1)	85.8(3)
C(3)–Mo(1)–Mo(2)	95.2(2)	C(3)–Mo(1)–S(1)	87.2(2)
C(3)–Mo(1)–S(2)	91.7(2)	C(3)–Mo(1)–N(4)	171.7(3)
C(3)–Mo(1)–C(1)	81.0(4)	C(3)–Mo(1)–C(2)	90.9(3)
N(4)–Mo(1)–S(1)	86.6(2)	N(4)–Mo(1)–S(2)	95.0(2)
N(4)–Mo(1)–Mo(2)	85.2(2)	S(1)–Mo(1)–S(2)	102.31(7)
S(1)–Mo(1)–Mo(2)	50.68(5)	S(2)–Mo(1)–Mo(2)	52.15(5)
N(3)–Mo(2)–N(2)	79.5(2)	N(3)–Mo(2)–S(4)	94.9(2)
N(3)–Mo(2)–S(1)	154.5(2)	N(3)–Mo(2)–S(3)	67.4(2)
N(3)–Mo(2)–S(2)	93.0(2)	N(3)–Mo(2)–Mo(1)	148.2(2)
N(3)–Mo(2)–Mo(3)	83.3(2)	N(2)–Mo(2)–S(4)	153.6(2)
N(2)–Mo(2)–S(1)	97.7(2)	N(2)–Mo(2)–S(3)	92.0(2)
N(2)–Mo(2)–S(2)	66.8(2)	N(2)–Mo(2)–Mo(1)	83.7(2)
N(2)–Mo(2)–Mo(3)	147.6(2)	S(4)–Mo(2)–S(1)	97.90(7)
S(4)–Mo(2)–S(3)	109.83(7)	S(4)–Mo(2)–S(2)	88.02(7)
S(4)–Mo(2)–Mo(1)	88.25(6)	S(4)–Mo(2)–Mo(3)	54.82(5)
S(1)–Mo(2)–S(3)	87.49(7)	S(1)–Mo(2)–S(2)	109.34(7)
S(1)–Mo(2)–Mo(1)	54.52(5)	S(1)–Mo(2)–Mo(3)	86.21(5)
S(3)–Mo(2)–S(2)	153.95(7)	S(3)–Mo(2)–Mo(1)	140.43(6)
S(3)–Mo(2)–Mo(3)	55.90(5)	S(2)–Mo(2)–Mo(1)	55.42(5)
S(2)–Mo(2)–Mo(3)	141.92(6)	C(4)–Mo(3)–C(5)	93.4(4)
C(4)–Mo(3)–C(6)	80.7(4)	C(4)–Mo(3)–N(1)	172.1(3)
C(4)–Mo(3)–S(4)	91.5(3)	C(4)–Mo(3)–S(3)	88.1(3)
C(4)–Mo(3)–Mo(2)	97.0(3)	C(5)–Mo(3)–C(6)	86.3(4)
C(5)–Mo(3)–N(1)	89.9(3)	C(5)–Mo(3)–S(4)	171.4(3)
C(5)–Mo(3)–S(3)	86.0(3)	C(5)–Mo(3)–Mo(2)	135.8(3)
C(6)–Mo(3)–N(1)	92.3(3)	C(6)–Mo(3)–S(4)	87.6(3)
C(6)–Mo(3)–S(3)	166.0(3)	C(6)–Mo(3)–Mo(2)	137.8(3)
N(1)–Mo(3)–S(4)	84.4(2)	N(1)–Mo(3)–S(3)	99.4(1)
N(1)–Mo(3)–Mo(2)	85.6(1)	Mo(2)–S(3)–Mo(3)	72.32(6)
Mo(2)–S(4)–Mo(3)	75.04(6)	C(41)–S(4)–Mo(2)	112.5(3)
C(41)–S(4)–Mo(3)	114.1(3)	C(11)–N(1)–Mo(3)	127.4(5)
C(21)–N(2)–Mo(2)	102.3(5)	C(31)–N(3)–Mo(2)	102.0(5)
C(41)–N(4)–Mo(1)	127.7(5)	S(4)–Mo(3)–S(3)	101.15(7)
S(4)–Mo(3)–Mo(2)	50.14(5)	S(3)–Mo(3)–Mo(2)	51.78(5)
C(11)–S(1)–Mo(2)	112.1(3)	C(11)–S(1)–Mo(1)	111.4(2)
C(21)–S(2)–Mo(2)	82.4(3)	C(31)–S(3)–Mo(2)	81.2(3)
Mo(2)–S(1)–Mo(1)	74.81(6)	Mo(2)–S(2)–Mo(1)	72.44(6)
N(1)–C(11)–S(1)	108.4(5)	N(2)–C(21)–S(2)	118.4(5)
N(3)–C(31)–S(3)	108.6(5)	N(4)–C(41)–S(4)	118.4(6)

respectively. The bond lengths of the two Mo–Mo bonds which result from the coupling of the two unpaired electrons in the central Mo(II) ion, together with the single electrons of the two terminal Mo(I) ions, are 2.943(1) and 2.950(1) Å. They are comparable, but smaller than that (2.974(1) Å) in complex **1**. Unlike complex **1**, in which the Mo_2S_2 ring is non-planar, two Mo_2S_2 rings in complex **3** are planar. The mean deviations from the planes Mo(1)Mo(2)S(1)S(2) and Mo(2)Mo(3)S(3)S(4) are 0.09 and 0.10 Å respectively. The two planes (also containing that two Mo–Mo bonds) are nearly perpendicular to each other with a dihedral angle of 88.16°. This is consistent with the metal bonds being originated by two unpaired electrons of the central d^4 metal residing in two orthogonal orbitals (specifically, $x^2 - y^2$ and yz of the pseudo-octahedral t_{2g} set).

3. Experimental details

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen prior to use. $[Mo(CO)_6]$, PPh_3 and pySH were used as received.

IR spectra were recorded on a Perkin-Elmer 683 infrared spectrometer. ^1H NMR spectra were recorded on a Varian XL-400 or an FT-80 instrument. Elemental analyses were performed with a Carlo Erba elemental analyser MOD 1106.

3.1. Reaction of $[Mo(CO)_3(MeCN)_3]$ with pyridine-2-thione and triphenyl phosphine

A mixture of $[Mo(CO)_6]$ (0.200 g, 0.76 mmol) and acetonitrile (10 ml) was refluxed under nitrogen for 4 h to generate $[Mo(CO)_3(MeCN)_3]$ as a yellow solid after removal of volatiles under vacuum. pySH (0.084 g, 0.76 mmol), PPh_3 (0.200 g, 0.76 mmol) and THF (20 ml) were added to the yellow solid to give a red solution. The solution was allowed to stir at 50°C for 5 h. After evaporation of the solvent under reduced pressure, the residue was redissolved with toluene (6 ml) and separated by TLC (Al_2O_3, 20 × 1.5 cm). The first purple band eluted with toluene was concentrated and stood at room temperature for several days to give a trace quantity of complex **3** as black crystals suitable for X-ray study. The second band extracted with a mixture of toluene and dichloromethane was concentrated and cooled to −20°C overnight to give **1** as red crystals (0.05 g, 12.5%) suitable for X-ray studies. Futher reduction in volume and cooling of the mother liquor produced black crystals (**2**) (0.024 g, 7.7%). Complex $1 \cdot 2C_7H_8$. Anal. Found: C, 62.00; H, 4.40; N, 2.58.

Table 3
Summary of crystal data and intensity data

	Compound	
	$1 \cdot 2C_7H_8$	$3 \cdot C_7H_8$
Formula	$C_{64}H_{54}Mo_2N_2O_4P_2S_2$	$C_{33}H_{24}Mo_3N_4O_6S_4$
MW	1233.09	988.64
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/n$
a (Å)	18.797(3)	13.912(2)
b (Å)	11.143(4)	17.161(2)
c (Å)	28.157(7)	15.577(3)
β (°)	101.23(2)	101.17(1)
U (Å^3)	5790(2)	3648(2)
Z	4	4
$F(000)$	2520	1952
D_c (g cm^{-3})	1.41	1.80
μ(Mo K α)(cm^{-1})	5.9	12.59
Radiation	Mo K α graphite-monochromated	
Scan speed (° min^{-1})	4.88	7.00
Scan mode	ω	ω–2θ
2θ range (°)	3–50	3–50
Crystal size (mm^3)	0.12 × 0.24 × 0.36	0.40 × 0.30 × 0.30
Diffractometer	Nicolet R3m/E	Enraf-Nonius CAD4
Temperature (°C)	23	23
No. data with $I > 3\sigma(I_o)$	3146	4357
R	0.050	0.046
Rw	0.057	0.051
Goodness of fit	1.09	1.13
$(\Delta/\sigma)_{max}$	0.035	0.25
$(\Delta\rho)_{max}$(e Å^{-3})	0.71	0.83

$C_{60}H_{54}Mo_2N_2O_4P_2S_2$ Calc.: C, 62.28; H, 4.38; N, 2.27%. IR (KBr pallet, cm^{-1}) ν(CO): 1915(s),1835(s). ^1H NMR (CD_3COCD_3, 400 MHz 20°C), δ 7.72(d, 2H, pyS), 7.59(m, 2H, pyS), 7.41(d, 2H, pyS), 6.78(m, 2H, pyS), 7.55–7.30(m, 30H, PPh_3). Complex **2**. Anal. Found: C, 48.80; H, 2.71; N, 3.65. $C_{33}H_{23}Mo_2N_2O_5PS_2$ Calc. C, 48.65; H, 2.83; N, 3.44%. IR (KBr pallet, cm^{-1}) ν(CO): 2000(w), 1970(s), 1875(s). ^1H NMR (CD_3COCD_3, 80 MHz, 20°C), δ 7.70(m, 2H, pyS), 7.50–7.25(m, 19H, pyS and PPh_3), 6.79(m, 2H, pyS). Complex **3**. IR (KBr pallet, cm^{-1}) ν(CO): 1950(s), 1900(w), 1848(s).

3.2. Crystal structure determinations

Crystals of $\mathbf{1} \cdot 2C_7H_8$ and $\mathbf{3} \cdot C_7H_8$ suitable for X-ray diffraction studies were grown as described above. Crystal data and experimental details are collected in Table 3. Intensity data was collected for Lp factors and for empirical absorptions.

The structure of $\mathbf{1} \cdot 2C_7H_8$ was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All non-hydrogen atoms were assigned anisotropic thermal parameters. The hydrogen atoms were added at idealized positions with isotropic thermal parameters. The phenyl rings in co-crystallized toluene molecules were constrained to rigid groups with C–C 1.395 and C–H 0.96 Å, all angles 120°. The structure of $\mathbf{3} \cdot C_7H_8$ was solved by the direct method and refined by alternating cycles of full-matrix least-squares. Three molybdenum atoms were located from an E-map of the direct method MITHRIL program and the remaining non-hydrogen atoms were found from an E-map of the DIRDIF program. Hydrogen atoms were placed in calculated positions with isotropic thermal parameters.

Final coordinates for $\mathbf{1} \cdot 2C_7H_8$ and $\mathbf{3} \cdot C_7H_8$ are listed in Tables 4 and 5 respectively. All calculations

Table 4
Atomic coordinates ($\times 10^4$) for $\mathbf{1} \cdot 2C_7H_8$

Atom	x	y	z
Mo	5245(1)	5982(1)	3034(1)
C(1)	5053(3)	4282(6)	3066(2)
O(1)	4924(3)	3258(4)	3094(2)
C(2)	4781(3)	6191(6)	3607(2)
O(2)	4493(3)	6295(6)	3926(2)
S	6007(1)	6262(1)	2409(1)
N	5576(3)	7900(4)	2930(2)
C(11)	5985(3)	7779(5)	2594(2)
C(12)	6320(4)	8754(6)	2418(2)
C(13)	6212(5)	9871(7)	2593(3)
C(14)	5788(4)	9995(7)	2934(3)
C(15)	5485(3)	8988(5)	3094(2)
P	6422(1)	5668(1)	3607(1)
C(21)	6907(3)	4277(5)	3540(2)
C(22)	7428(4)	3828(6)	3919(3)
C(23)	7810(4)	2793(7)	3862(3)
C(24)	7681(4)	2199(6)	3434(3)
C(25)	7184(4)	2625(6)	3062(3)
C(26)	6792(3)	3642(6)	3112(3)
C(31)	6355(3)	5567(5)	4244(2)
C(32)	5193(3)	4682(6)	4373(2)
C(33)	5850(4)	4511(7)	4849(3)
C(34)	6200(4)	5248(8)	5195(3)
C(35)	6611(5)	6137(8)	5074(3)
C(36)	6177(4)	6289(7)	4609(2)
C(41)	7116(3)	6808(5)	3589(2)
C(42)	7737(3)	6558(6)	3403(2)
C(43)	8216(4)	7479(7)	3348(3)
C(44)	8099(4)	8616(6)	3574(3)
C(45)	7492(4)	8867(6)	3662(2)
C(46)	7005(4)	7975(5)	3717(2)
C(51)	4882(3)	8(9)	702(3)
C(52)	4396	−715	390
C(53)	3669	−382	260
C(54)	3427	673	442
C(55)	3913	1396	755
C(56)	4640	1063	885
C(57)	5632(7)	−374(17)	861(5)

Table 5
Atomic coordinates for $3 \cdot C_7H_8$

Atom	x	y	z
Mo(1)	0.15477(5)	0.37601(4)	0.68133(4)
Mo(2)	0.15619(5)	0.23435(4)	0.77816(4)
Mo(3)	0.19846(5)	0.07805(4)	0.72581(4)
S(1)	0.2871(1)	0.2783(1)	0.7246(1)
S(2)	0.0289(1)	0.3340(1)	0.7706(1)
S(3)	0.2706(1)	0.1427(1)	0.8725(1)
S(4)	0.0657(1)	0.1720(1)	0.6647(1)
O(1)	0.2984(6)	0.4697(5)	0.5878(5)
O(2)	0.0079(5)	0.5132(4)	0.6189(5)
O(3)	0.2686(5)	0.4771(4)	0.8311(4)
O(4)	0.0559(6)	−0.0163(4)	0.8164(5)
O(5)	0.3661(6)	−0.0449(5)	0.7697(5)
O(6)	0.1038(6)	−0.0420(5)	0.5830(5)
N(1)	0.2874(4)	0.1430(4)	0.6368(4)
N(2)	0.1745(4)	0.3170(4)	0.8972(4)
N(3)	0.0911(5)	0.1684(4)	0.8818(4)
N(4)	0.0995(5)	0.2946(4)	0.5626(4)
C(1)	0.2455(7)	0.4324(5)	0.6175(6)
C(2)	0.0602(7)	0.4618(5)	0.6407(5)
C(3)	0.2216(6)	0.4394(4)	0.7750(5)
C(4)	0.1108(7)	0.0202(5)	0.7858(6)
C(5)	0.3055(7)	0.0012(5)	0.7559(6)
C(6)	0.1409(7)	0.0055(5)	0.6306(6)
C(11)	0.3031(5)	0.2195(5)	0.6335(5)
C(12)	0.3368(6)	0.2564(5)	0.5646(5)
C(13)	0.3533(6)	0.2115(6)	0.4956(5)
C(14)	0.3406(7)	0.1324(6)	0.4987(6)
C(15)	0.3088(6)	0.1007(5)	0.5697(6)
C(21)	0.0939(6)	0.3635(4)	0.8747(5)
C(22)	0.0735(7)	0.4219(5)	0.9265(6)
C(23)	0.1362(8)	0.4362(6)	1.0063(6)
C(24)	0.2161(7)	0.3870(6)	1.0326(5)
C(25)	0.2329(6)	0.3280(5)	0.9763(5)
C(31)	0.1692(6)	0.1290(5)	0.9265(5)
C(32)	0.1675(7)	0.0864(5)	1.0003(5)
C(33)	0.0796(8)	0.0817(5)	1.0289(6)
C(34)	−0.0000(7)	0.1199(6)	0.9836(6)
C(35)	0.0063(6)	0.1631(5)	0.9100(5)
C(41)	0.0810(5)	0.2175(4)	0.5637(5)
C(42)	0.0674(7)	0.1713(5)	0.4897(5)
C(43)	0.0669(7)	0.2060(6)	0.4102(6)
C(44)	0.0764(7)	0.2848(6)	0.4055(5)
C(45)	0.0917(6)	0.3270(5)	0.4825(5)
C(51)	0.419(1)	0.2839(8)	0.1891(8)
C(52)	0.351(1)	0.293(1)	0.230(1)
C(53)	0.273(2)	0.246(1)	0.259(1)
C(54)	0.296(2)	0.178(1)	0.230(1)
C(55)	0.365(1)	0.150(1)	0.186(1)
C(56)	0.425(2)	0.200(2)	0.160(2)
C(57)	0.490(2)	0.192(2)	0.123(2)

were performed on an Eclipse S/140 computer using the SHELXTL program system [12] for $1 \cdot 2C_7H_8$ and on a MICRO VAX310 computer using the TEXSAN Vers. 2.0 program package [13] for $3 \cdot C_7H_8$. Atomic scattering factors and anomalous dispersion corrections were taken from Ref. [14]. Additional material available from the authors comprises thermal parameters and remaining bond lengths and angles.

Acknowledgement

This work was supported by grants from the National Natural Science Fund, People's Republic of China.

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