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Formation of clusters by oxidative addition of organic and inorganic disulfides. Molecular structures of $(MeCN)_2(CO)_6Mo_2(\mu\text{-}SPh)_2$ and $Mo_2Fe_7S_8(CO)_{22}$

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Abstract

Reactions of the disulfides Ph_2S_2 and $(CO)_6Fe_2S_2$ with $(MeCN)_3Mo(CO)_3$ (I) leading to the splitting of S–S bonds have been studied. Binuclear $(MeCN)_2(CO)_6Mo_2(\mu\text{-}SPh)_2$ (II) is obtained from the reaction of I with Ph_2S_2. The X-ray diffraction data for II (space group $P2_1$, a 9.262(4), b 9.343(10), c 15.494(6), β 105.85(3), $Z = 2$, $R = 0.037$) show the Mo–Mo bond of length (2.982(1) Å), to be supported by thiolate bridges (Mo–S 2.468(1) Å). Interaction of I with the ferrosulfide dimer breaks the S–S and Fe–Fe bonds to give an antiferromagnetic nonanuclear cluster $Mo_2Fe_7S_8(CO)_{22}$ (III) (μ_{eff} 2.61(298 K) – 1.92(78 K) BM). An X-ray diffraction study (space group $P\bar{1}$, a 13.003(2), b 14.278(1), c 16.019(2) Å, $\alpha = 109.555(8)$, β 97.187(10), γ 113.006(7)°, $Z = 2$, $R = 0.045$) has revealed that molecule III consists of two fragments $(CO)_9Fe_3(S)_4Mo(CO)_2$ (Mo–Fe 2.750(2) Å, Fe–S 2.260(3) Å, Mo–S 2.406(3) Å) linked via the Fe atom (Mo–Fe 2.900(2) Å, Fe–S 2.242(3) and 2.529(3) Å), but without Fe–Fe bonds.

Introduction

Clusters having Mo–Fe bonds, in particular with the cubane-like fragments $MoFe_3S_4$ have been the focus of attention as models of the active center of the nitrogenase MoFe-cofactor. The designing of such clusters is of special interest. As a rule they are built of $[MoS_4]^{2-}$ units; recently the stepwise extension of the cluster core up to $[(S)_2Mo(\mu_3\text{-}S)_2Fe(\mu_3\text{-}S)_2Fe_2(CO)_6]^{2-}$ involving the Mo–Fe and Fe–Fe

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bonds has been demonstrated. Treatment of such a cluster with Ph_2S_2 readily converts it into the bis-cubane thiolate-sulfide cluster $[(PhS)_3Fe_3S_4Mo(\mu\text{-}S_2)]_2^{4-}$ [1]. A trinuclear cluster containing $Fe(SR)_2Mo(SR)_2Fe$ fragment with Mo–Fe bonds can be obtained by treatment of $Mo(SR)_4$ with iron carbonyl [2], and carbonylation of $Mo(SR)_4$ (where $R = CMe_3$) by carbon monoxide under pressure leads to a diamagnetic complex $Mo_2(CO)_8(\mu\text{-}SR)_2$ with the Mo–Mo bond [3]. Here we present the results of a comparative study of the reactions of $Mo(CO)_3(MeCN)_3$ with organic Ph_2S_2 or inorganic $Fe_2S_2(CO)_6$ disulfide.

Results and discussion

The reaction of $(MeCN)_3Mo(CO)_3$ with Ph_2S_2 in MeCN at 20 °C reduces the disulfide with formation of the binuclear diagmagnetic complex $(MeCN)_2(CO)_6Mo_2(\mu\text{-}SPh)_2$ (I) which has been previously obtained from the reaction of $(CO)_8Mo_2(\mu\text{-}SPh)_2$ with MeCN [4] (see Scheme 1).

The X-ray data for molecule I (Tables 1, 2, Fig.1) reveal that the two Mo atoms, having a short Mo–Mo bond of 2.982(1) Å and linked by two thiolate bridges (Mo–S 2.468(1) Å), comprise the inversion center. Each metal atom is bonded to three carbonyl groups and an acetonitrile molecule which is located in a *cis*-arrangement relative to the sulfur atom (Mo–N 2.223(2) Å). It is noteworthy that similar Mo–Mo (2.984(2) Å) and Mo–S (2.48 Å) bonds have been found by means of X-ray structural analysis in the well-known complex $Mo_2(CO)_8(SCMe_3)_2$ [3]. Similarly the inorganic disulfide $Fe_2S_2(CO)_6$ adds oxidatively thereby undergoing rupture of its S–S bond (2.007 Å) [5] to become a chelate-forming ligand. It can add $(PPh_3)_2Pd$ or $(PPh_3)_2Pt$ fragments [6,7] or bind with two wedge-like sandwich monomers $(MeC_5H_4)_2V$ via V–S bonds [8]. In some reactions with carbonyl metal complexes such as $Cp_2Mo_2(CO)_4$, not only the S–S bond but also the Fe–Fe bond (2.552 Å)

Table 1

Crystallographic data for the clusters I and II

	$(CO)_6(MeCN)_2Mo_2(\mu\text{-}SPh)_2$ (I)	$Mo_2Fe_7S_8(CO)_{22}$ (II)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.262(4)	13.003(2)
b (Å)	9.343(10)	14.278(1)
c (Å)	15.494(6)	16.019(2)
α (°)	90	109.555(8)
β (°)	105.85(3)	97.187(10)
γ (°)	90	113.006(7)
V (Å^3)	1289.9	2464.8
Z	2	2
Number of observed reflections	2792	7164
Number of reflections with $I > 3\sigma(I)$	2082	5512
$2\theta_{max}$	60	56
R_1	0.037	0.045
R_w	0.046	0.035

Table 2

Atomic coordinates and isotropic equivalent thermal parameters for the complex $(CO)_6(MeCN)_2Mo_2(\mu\text{-}SPh)_2$ (I)

Atom	x	y	z	B_{eq} [a]
Mo	0.09756(3)	0.38226(3)	0.98320(2)	2.949(6)
S	0.0185(1)	0.59842(9)	0.89084(6)	3.16(2)
O(1)	0.1797(4)	0.0686(3)	1.0549(3)	7.09(9)
O(2)	0.3144(4)	0.3333(4)	0.8614(2)	7.29(9)
O(3)	0.3861(3)	0.4773(4)	1.1276(2)	5.76(8)
N	−0.1086(3)	0.2905(3)	0.8906(2)	3.56(8)
C(1)	−0.2134(4)	0.2386(4)	0.8473(2)	3.89(8)
C(2)	−0.3511(5)	0.1759(6)	0.7909(3)	6.1(1)
C(3)	0.1480(4)	0.1813(4)	1.0279(3)	4.26(9)
C(4)	0.2333(4)	0.3480(4)	0.9043(3)	4.25(9)
C(5)	0.2767(4)	0.4482(4)	1.0721(3)	3.88(8)
C(6)	0.1569(4)	0.7343(4)	0.8939(2)	3.25(1)
C(7)	0.3056(4)	0.7243(4)	0.9406(2)	3.99(8)
C(8)	0.4027(5)	0.8345(5)	0.9374(3)	4.8(1)
C(9)	0.3535(5)	0.9532(4)	0.8854(3)	4.81(9)
C(10)	0.2067(5)	0.9638(4)	0.8366(3)	5.0(1)
C(11)	0.1063(4)	0.8536(4)	0.8399(2)	3.98(8)
H(21) [a]	−0.341(6)	0.138(6)	0.716(4)	9(2)
H(22)	−0.336(7)	0.075(6)	0.796(4)	10(2)
H(23)	−0.415(6)	0.235(9)	0.778(5)	13(2)
H(7)	0.333(4)	0.642(4)	0.979(3)	4.1(8)
H(8)	0.501(4)	0.830(4)	0.974(2)	4.5(9)
H(9)	0.437(4)	1.022(5)	0.888(2)	5.1
H(10)	0.164(5)	1.056(5)	0.811(3)	6(1)
H(11)	−0.012(4)	0.857(3)	0.803(2)	3.7(8)

[a] Hydrogen atoms were refined isotropically. [b] Anisotropically refined atoms are expressed in terms of the isotropic equivalent thermal parameter defined as:

$4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$

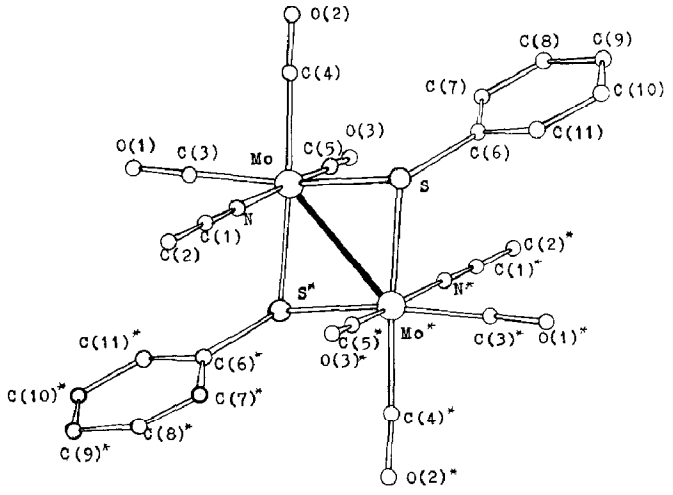
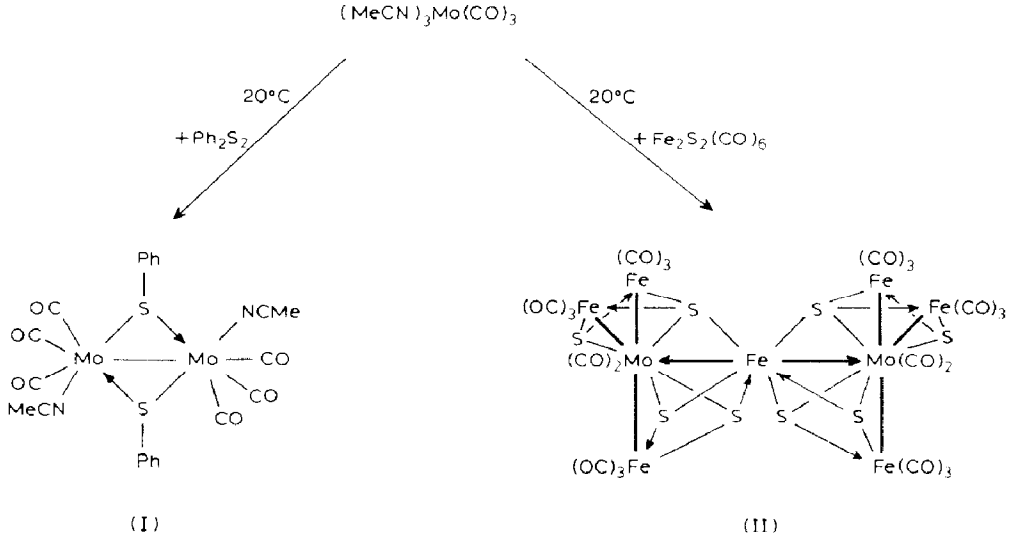


Fig. 1. The structure of $(MeCN)_2(CO)_6Mo_2(\mu\text{-}SPh)_2$.

are split with formation of $Cp_2Mo_2(\mu\text{-}CO)_2(\mu_3\text{-}S)_2[Fe(CO)_3]_2$ [9]. An analogous phenomenon is observed in the almost instantaneous reaction of $Fe_2S_2(CO)_6$ with $(MeCN)_3Mo(CO)_3$ in MeCN/THF (1/1) at 20 °C which in one step to give the nonanuclear cluster $Mo_2Fe_7S_8(CO)_{22}$ (II); after recrystallization from the benzene/hexane mixture dark-brown prisms of the solvate of II containing 1.5 molecules of benzene per molecule of II were isolated:



(I) (II)

Scheme 1.

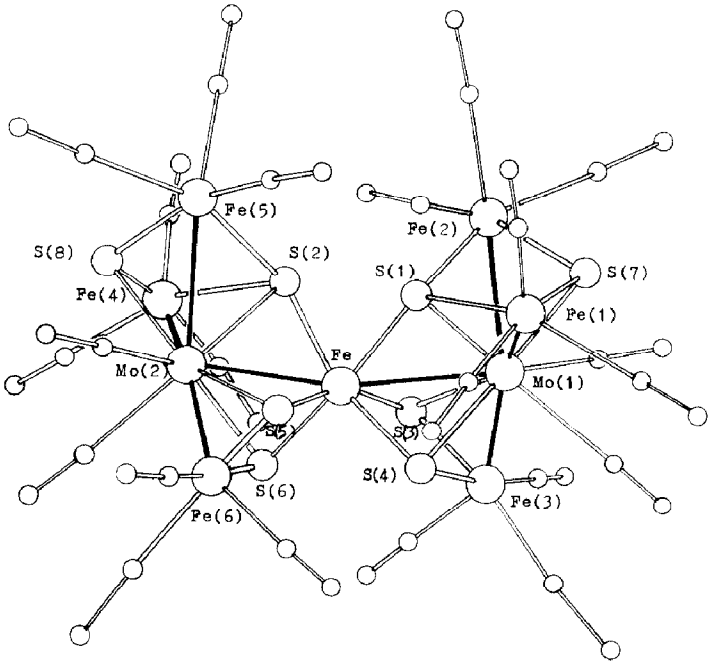


Fig. 2. The structure of $Mo_2Fe_7S_8(CO)_{22}$.

The structure II (Fig. 2) consists of the two fragments, $(CO)_9Fe_3S_4Mo(CO)_2$, in which each Fe atom has three terminal CO groups, and each Mo atom is bonded to two CO groups. Each of the iron tricarbonyl fragments is bonded to the molybdenum atom via the bridging sulfur atoms (Mo–S_{mean} 2.432(3) Å, Fe–S_{mean} 2.260(3) Å) and the three short bonds Mo–Fe (mean 2.762(2) Å). The molybdenum atoms in the tetranuclear fragments are bonded with each other via the central Fe by two elongated Mo–Fe (2.900(2) Å) bonds. It is also bonded to the six sulfur atoms by four short Fe–μ_3-S bonds (mean 2.268(3) Å) and two long Fe–μ_4-S bonds (mean 2.529(3) Å). There are no Fe–Fe bonds in the cluster. Each of the two parts of cluster II is thus expected to contain at least one unpaired electron thus accounting for the antiferromagnetic behaviour of II (μ_{eff} 2.61(298 K) – 1.92(78 K) MB). Unlike the core of $[S_2MoS_2FeS_2Fe_2(CO)_6]^{2-}$ [1] the metal framework of II has only Mo–Fe bonds (apart from the sulfide bridges).

Careful study of the reactions and structures of the complexes shows the molybdenum atoms to be active in the oxidative addition of the disulfide groups and to play the role of matrix in the formation of the $MoFe_3$ core, which is of interest because it is present in natural nitrogen fixers.

Experimental

All operations were carried out in absolute solvents under a stream of pure argon. The initial $(CO)_3Mo(NCMe)_3$ and $(CO)_6Fe_2S_2$ were prepared by published proce-

Table 3

Bond distances in $(CO)_6(MeCN)_3Mo_2(\mu\text{-SPh})_2$ (I)

Bond	d (Å)	Bond	d (Å)
Mo–Mo′	2.982(1)	Mo–C(5)	1.945(3)
Mo–S	2.468(1)	S–C(6)	1.796(2)
Mo–S′	2.478(1)	O(1)–C(3)	1.142(3)
Mo–N	2.223(2)	O(2)–C(4)	1.138(4)
Mo–C(3)	2.012(3)	O(3)–C(5)	1.168(3)
Mo–C(4)	2.005(3)	N–C(1)	1.128(3)
		C(1)–C(2)	1.457(4)

Table 4

Bond angles in $(CO)_6(MeCN)_3Mo_2(\mu\text{-SPh})_2$ (I)

Angle	ω (°)	Angle	ω (°)	Angle	ω (°)
Mo′MoS	53.09(2)	SMoC(3)	165.41(9)	NMoC(4)	96.7(1)
Mo′MoS′	52.77(2)	SMoC(4)	85.02(8)	NMoC(5)	174.58(9)
Mo′MoN	86.70(6)	SMoC(5)	102.24(8)	C(3)MoC(4)	86.3(1)
MoMoC(3)	136.34(8)	SMoN	93.17(6)	C(3)MoC(4)	88.8(1)
MoMoC(4)	137.33(8)	S′MoC(3)	84.65(9)	C(4)MoC(5)	85.8(1)
Mo′MoC(5)	94.77(9)	S′MoC(4)	166.20(9)	Mo′SMo	74.15(2)
S′MoS	105.85(2)	S′MoC(5)	83.62(9)	MoSC(6)	117.81(9)
SMoN	82.82(6)	NMoC(3)	86.6(1)	Mo′SC(6)	112.81(8)
MoNC(1)	176.2(2)	NC(1)C(2)	178.2(4)	MoC(3)O(1)	178.3(3)
MoC(4)O(2)	117.0(3)	MoC(5)O(3)	174.9(2)	SC(6)C(7)	124.9(2)

Table 5

Atomic coordinates of $Mo_2Fe_7S_8(CO)_{22}$ ($\times 10^4$; for Mo and Fe $\times 10^5$)

Atom	x	y	z	B_{eq}
Mo(1)	29129(6)	73250(5)	34824(5)	2.50(2)
Mo(2)	14140(6)	25881(6)	18575(5)	2.62(3)
Fe	19011(120)	49067(9)	27973(8)	2.00(4)
Fe(1)	20581(11)	71226(10)	17219(8)	2.47(5)
Fe(2)	47570(11)	75296(10)	27520(9)	2.63(5)
Fe(3)	21033(11)	67870(10)	48502(8)	2.31(5)
Fe(4)	34113(11)	29688(10)	30657(9)	2.81(5)
Fe(5)	30955(11)	30446(10)	9508(9)	2.76(5)
Fe(6)	−7111(10)	25566(9)	18763(8)	2.36(4)
S(1)	2903(2)	6099(2)	2013(1)	2.22(8)
S(2)	3339(2)	4157(2)	2437(1)	2.34(8)
S(3)	3285(2)	6164(2)	4194(1)	2.26(8)
S(4)	997(2)	5926(2)	3353(1)	2.29(8)
S(5)	586(2)	3659(2)	1366(1)	2.26(8)
S(6)	841(2)	3515(2)	3166(1)	2.48(8)
S(7)	3783(2)	8512(2)	2700(2)	2.72(8)
S(8)	2758(2)	1794(2)	1569(2)	3.11(9)
O(1)	1728(6)	8932(5)	3997(5)	4.7(3)
O(2)	5185(5)	9115(5)	5177(4)	4.4(3)
O(3)	57(6)	931(5)	−257(4)	4.4(3)
O(4)	309(6)	575(5)	2444(5)	5.4(3)
O(5)	−380(6)	5370(5)	1015(5)	5.3(3)
O(6)	2601(6)	6837(6)	−40(5)	5.3(3)
O(7)	1205(7)	8772(6)	1829(5)	6.3(4)
O(8)	5786(5)	6404(6)	3562(6)	6.4(4)
O(9)	6791(6)	9714(6)	3863(5)	5.5(3)
O(10)	5410(7)	7059(8)	1041(6)	8.3(5)
O(11)	1179(6)	5036(5)	5524(5)	4.8(3)
O(12)	657(6)	7871(6)	5440(5)	5.4(3)
O(13)	4012(6)	8420(6)	6579(4)	5.1(3)
O(14)	2933(7)	1101(6)	3591(6)	8.4(4)
O(15)	5883(6)	3695(6)	3300(5)	6.0(4)
O(16)	3447(7)	4307(6)	4915(5)	6.4(4)
O(17)	2347(7)	1161(6)	−849(5)	6.4(3)
O(18)	5601(7)	3966(7)	1210(6)	7.6(4)
O(19)	2639(8)	4336(6)	−3(5)	7.5(4)
O(20)	−2214(5)	1033(5)	−45(4)	4.7(3)
O(21)	−2025(6)	900(5)	2538(5)	5.2(3)
O(22)	−2044(6)	3815(6)	2275(5)	5.6(3)
C(1)	2154(8)	8359(7)	3814(6)	3.1(4)
C(2)	4376(7)	8489(6)	4558(6)	3.1(3)
C(3)	552(8)	1515(7)	485(6)	3.2(4)
C(4)	686(8)	1292(7)	2237(7)	3.9(4)
C(5)	590(8)	6035(7)	1298(6)	3.2(4)
C(6)	2377(8)	6966(7)	646(7)	3.7(4)
C(7)	1516(8)	8129(8)	1787(6)	3.9(4)
C(8)	5356(7)	6801(7)	3222(7)	4.1(4)
C(9)	6025(8)	8838(8)	3435(7)	3.8(4)
C(10)	5179(8)	7273(8)	1732(7)	4.3(4)
C(11)	1526(7)	5717(7)	5253(6)	3.4(4)
C(12)	1220(8)	7458(7)	5199(6)	3.6(4)
C(13)	3273(8)	7779(7)	5901(6)	3.3(4)
C(14)	3114(9)	1812(8)	3398(7)	5.2(5)
C(15)	4912(8)	3413(8)	3243(7)	4.0(4)

Table 5 (continued)

Atom	x	y	z	B_{eq}
C(16)	3448(9)	3819(8)	4202(6)	4.1(4)
C(17)	2639(9)	1908(8)	−165(7)	4.3(4)
C(18)	4627(8)	3620(8)	1101(7)	4.4(4)
C(19)	2822(9)	3872(8)	395(7)	4.6(5)
C(20)	−1634(7)	1616(7)	699(6)	3.2(4)
C(21)	−1494(8)	1555(7)	2302(6)	3.8(4)
C(22)	−1521(7)	3335(7)	2140(6)	3.3(3)
CB(1)	1652(10)	3294(12)	6614(12)	9.5(8)
CB(2)	1494(11)	2395(14)	5853(11)	10.3(9)
CB(3)	1274(10)	1392(12)	5885(10)	10.0(7)
CB(4)	1289(12)	1314(12)	6717(13)	11.1(9)
CB(5)	1461(15)	2175(17)	7458(13)	13(1)
CB(6)	1629(14)	3181(13)	7417(12)	10.7(9)
CBX(1)	4809(9)	10110(12)	9191(10)	8.3(7)
CBX(2)	4790(10)	9143(11)	9188(10)	8.3(6)
CBX(3)	5046(10)	10979(10)	10021(11)	7.8(7)

dures [10,11]. IR spectra were recorded with a Specord IR-75 spectrometer in KBr pellets. The magnetic susceptibilities of I and II were measured by Faraday method by means of a device designed at the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR [12]. X-ray reflection intensities were measured with CAD-4 and Hilger & Watts automatic diffracometers for I and II respectively (λ(Mo-K_α), graphite monochromator). Crystal data are given in Table 1. Structures I and II were solved by direct methods and refined anisotropically by full-matrix least squares for all non-hydrogen atoms (Tables 2–7). Hydrogen atoms for I were located in the difference Fourier synthesis and refined isotropically.

$(CO)_6(MeCN)_2Mo_2(\mu\text{-}SPh)_2$ (I)

A colourless solution of Ph_2S_2 (0.3 g, 1.3 mmol) in MeCN (15 ml) was added to the yellow-green solution of $(MeCN)_3Mo(CO)_3$ (obtained from 0.7 g (2.65 mmol) of $Mo(CO)_6$ in 25 ml of MeCN) and black-green prisms precipitated from the reaction mixture after 15 min stirring. They were separated by decantation, washed with pentane and dried in vacuo. Yield 0.14 g (15.8%). IR spectrum (ν(cm^{-1}): 470m, 500w, 515m, 595m, 615w, 680m, 740m, 940w, 1000w, 1020m, 1060w, 1175m, 1360w, 1450m, 1465m, 1475m, 1565m, 1625m, 1865vs, 1915vs, 1955vs, 2930br.w, 3055w.

$Mo_2Fe_7S_8(CO)_{22}$ (II)

A solution of $Mo(CO)_6$ (0.5 g, 1.9 mmol) in MeCN (20 ml) was refluxed for 5 h until the band characteristic of $Mo(CO)_6$ (2000 cm^{-1}) had disappeared. After filtration of the $(MeCN)_3Mo(CO)_3$ solution, and addition at room temperature of the orange-red solution of $(CO)_6Fe_2S_2$ (0.65 g, 1.9 mmol) in THF (20 ml) fine dark-brown crystals separated, they were isolated and extracted with 40 ml of benzene. The extract was concentrated to 15 ml, 2 ml of heptane was added, and the mixture was cooled up to −5 °C. The single crystals (dark-brown prisms) were washed with hexane and dried in vacuo. Yield 0.5 g (58%). IR spectrum (ν, cm^{-1}): 1970s, 1985w, 2015v.w, 2030s, 2060w, 2085m.

Table 6

Bond lengths d (Å) in $Mo_2Fe_7S_8(CO)_{22}$ (II)

Bond	d	Bond	d
Mo(1)–Fe	2.900(2)	Fe(3)–C(13)	1.798(9)
Mo(1)–Fe(1)	2.773(1)	Fe(4)–S(2)	2.269(3)
Mo(1)–Fe(2)	2.755(2)	Fe(4)–S(8)	2.229(3)
Mo(1)–Fe(3)	2.751(2)	Fe(4)–C(14)	1.82(1)
Mo(1)–S(1)	2.413(2)	Fe(4)–C(15)	1.75(1)
Mo(1)–S(3)	2.455(2)	Fe(4)–C(16)	1.801(9)
Mo(1)–S(4)	2.438(3)	Fe(5)–S(2)	2.275(3)
Mo(1)–S(7)	2.450(3)	Fe(5)–S(8)	2.244(3)
Mo(1)–C(1)	2.04(1)	Fe(5)–C(17)	1.79(1)
Mo(1)–C(2)	2.035(9)	Fe(5)–C(18)	1.78(1)
Mo(2)–Fe	2.901(2)	Fe(5)–C(19)	1.81(1)
Mo(2)–Fe(4)	2.779(2)	Fe(6)–S(5)	2.263(3)
Mo(2)–Fe(5)	2.762(2)	Fe(6)–S(6)	2.262(3)
Mo(2)–Fe(6)	2.750(2)	Fe(6)–C(20)	1.811(9)
Mo(2)–S(2)	2.406(3)	Fe(6)–C(21)	1.80(1)
Mo(2)–S(5)	2.449(3)	Fe(6)–C(22)	1.80(1)
Mo(2)–S(6)	2.450(2)	O(1)–C(1)	1.14(1)
Mo(2)–S(8)	2.440(3)	O(2)–C(2)	1.14(1)
Mo(2)–C(3)	2.056(9)	O(3)–C(3)	1.12(1)
Mo(2)–C(4)	2.05(1)	O(4)–C(4)	1.13(1)
Fe–S(3)	2.290(2)	O(5)–C(5)	1.15(1)
Fe–S(4)	2.242(3)	O(6)–C(6)	1.15(1)
Fe–S(5)	2.293(2)	O(7)–C(7)	1.13(1)
Fe–S(6)	2.246(3)	O(8)–C(8)	1.14(1)
Fe(1)–S(1)	2.267(3)	O(9)–C(9)	1.14(1)
Fe(1)–S(7)	2.232(3)	O(10)–C(10)	1.16(1)
Fe(1)–C(5)	1.78(1)	O(11)–C(11)	1.15(1)
Fe(1)–C(6)	1.78(1)	O(12)–C(12)	1.14(1)
Fe(1)–C(7)	1.81(1)	O(13)–C(13)	1.15(1)
Fe(2)–S(1)	2.282(3)	O(14)–C(14)	1.11(1)
Fe(2)–S(7)	2.241(3)	O(15)–C(15)	1.15(1)
Fe(2)–C(8)	1.81(1)	O(16)–C(16)	1.12(1)
Fe(2)–C(9)	1.78(1)	O(17)–C(17)	1.13(1)
Fe(2)–C(10)	1.76(1)	O(18)–C(18)	1.13(2)
Fe(3)–S(3)	2.259(3)	O(19)–C(19)	1.13(1)
Fe(3)–S(4)	2.261(2)	O(20)–C(20)	1.14(1)
Fe(3)–C(11)	1.79(1)	O(21)–C(21)	1.14(1)
Fe(3)–C(12)	1.79(1)	O(22)–C(22)	1.13(1)

Table 7

Bond angles (degrees) in $Mo_2Fe_7S_8(CO)_{22}$

Angle	ω	Angle	ω
FeMo(1)Fe(1)	90.54(4)	S(3)FeS(5)	177.3(1)
FeMo(1)Fe(2)	94.32(5)	S(3)FeS(6)	100.96(9)
FeMo(1)Fe(3)	73.37(4)	S(4)FeS(5)	100.85(9)
FeMo(1)S(1)	55.38(6)	S(4)FeS(6)	93.75(9)
FeMo(1)S(3)	49.78(6)	S(5)FeS(6)	80.89(9)
FeMo(1)S(4)	48.72(6)	Mo(1)Fe(1)S(1)	56.12(7)
FeMo(1)S(7)	128.72(7)	Mo(1)Fe(1)S(7)	57.40(7)
FeMo(1)C(1)	130.5(3)	Mo(1)Fe(1)C(5)	105.2(3)
FeMo(1)C(2)	127.2(3)	Mo(1)Fe(1)C(6)	142.8(3)
Fe(1)Mo(1)Fe(2)	76.42(5)	Mo(1)Fe(1)C(7)	110.4(3)
Fe(1)Mo(1)Fe(3)	139.70(5)	S(1)Fe(1)S(7)	80.51(9)
Fe(1)Mo(1)S(1)	51.28(6)	S(1)Fe(1)C(5)	96.4(3)
Fe(1)Mo(1)S(3)	138.01(7)	S(1)Fe(1)C(6)	94.0(3)
Fe(1)Mo(1)S(4)	90.27(7)	S(1)Fe(1)C(7)	166.3(3)
Fe(1)Mo(1)S(7)	50.13(7)	S(7)Fe(1)C(5)	160.9(3)
Fe(1)Mo(1)C(1)	81.1(3)	S(7)Fe(1)C(6)	99.8(3)
Fe(1)Mo(1)C(2)	133.3(3)	S(7)Fe(1)C(7)	89.9(3)
Fe(2)Mo(1)Fe(3)	139.91(5)	C(5)Fe(1)C(6)	99.3(5)
Fe(2)Mo(1)S(1)	51.89(6)	C(5)Fe(1)C(7)	89.4(5)
Fe(2)Mo(1)S(3)	91.62(7)	C(6)Fe(1)C(7)	97.3(5)
Fe(2)Mo(1)S(4)	141.06(7)	Mo(1)Fe(2)S(1)	56.31(7)
Fe(2)Mo(1)S(7)	50.58(7)	Mo(1)Fe(2)S(7)	57.65(7)
Fe(2)Mo(1)C(1)	129.8(3)	Mo(1)Fe(2)C(8)	101.3(3)
Fe(2)Mo(1)C(2)	74.5(3)	Mo(1)Fe(2)C(9)	111.7(3)
Fe(3)Mo(1)S(1)	128.71(7)	Mo(1)Fe(2)C(10)	145.5(4)
Fe(3)Mo(1)S(3)	51.03(6)	S(1)Fe(2)S(7)	80.03(9)
Fe(3)Mo(1)S(4)	51.22(6)	S(1)Fe(2)C(8)	97.8(3)
Fe(3)Mo(1)S(7)	157.84(7)	S(1)Fe(2)C(9)	166.0(4)
Fe(3)Mo(1)C(1)	82.1(3)	S(1)Fe(2)C(10)	93.2(4)
Fe(3)Mo(1)C(2)	83.0(3)	S(7)Fe(2)C(8)	156.2(4)
S(1)Mo(1)S(3)	89.61(8)	S(7)Fe(2)C(9)	87.2(4)
S(1)Mo(1)S(4)	91.24(8)	S(7)Fe(2)C(10)	105.5(4)
S(1)Mo(1)S(7)	73.45(8)	C(8)Fe(2)C(9)	91.6(5)
S(1)Mo(1)C(1)	132.1(3)	C(8)Fe(2)C(10)	98.2(5)
S(1)Mo(1)C(2)	124.7(3)	C(9)Fe(2)C(10)	95.8(5)
S(3)Mo(1)S(4)	74.02(8)	Mo(1)Fe(3)S(3)	57.69(7)
S(3)Mo(1)S(7)	141.45(9)	Mo(1)Fe(3)S(4)	57.21(7)
S(3)Mo(1)C(1)	132.6(3)	Mo(1)Fe(3)C(11)	146.5(3)
S(3)Mo(1)C(2)	78.5(3)	Mo(1)Fe(3)C(12)	108.6(3)
S(4)Mo(1)S(7)	138.78(9)	Mo(1)Fe(3)C(13)	104.5(3)
S(4)Mo(1)C(1)	82.4(3)	S(3)Fe(3)S(4)	81.34(9)
S(4)Mo(1)C(2)	134.2(3)	S(3)Fe(3)C(11)	95.5(3)
S(7)Mo(1)C(1)	80.7(3)	S(3)Fe(3)C(12)	166.3(3)
S(7)Mo(1)C(2)	83.2(3)	S(3)Fe(3)C(13)	91.9(3)
C(1)Mo(1)C(2)	90.3(4)	S(4)Fe(3)C(11)	102.5(3)
FeMo(2)Fe(4)	91.41(5)	S(4)Fe(3)C(12)	91.7(3)
FeMo(2)Fe(5)	94.65(5)	S(4)Fe(3)C(13)	161.3(3)
FeMo(2)Fe(6)	73.69(4)	C(11)Fe(3)C(12)	97.5(5)
FeMo(2)S(2)	55.99(6)	C(11)Fe(3)C(13)	95.5(4)
FeMo(2)S(5)	49.89(6)	C(12)Fe(3)C(13)	91.0(5)
FeMo(2)S(6)	48.74(6)	Mo(2)Fe(4)S(2)	55.83(7)
FeMo(2)S(8)	129.81(7)	Mo(2)Fe(4)S(8)	57.06(8)
FeMo(2)C(3)	128.0(3)	Mo(2)Fe(4)C(14)	110.7(4)
FeMo(2)C(4)	128.9(3)	Mo(2)Fe(4)C(15)	142.8(4)

Table 7 (continued)

Angle	ω	Angle	ω
Fe(4)Mo(2)Fe(5)	75.82(5)	Mo(2)Fe(4)C(16)	105.6(3)
Fe(4)Mo(2)Fe(6)	139.69(5)	S(2)Fe(4)S(8)	80.7(1)
Fe(4)Mo(2)S(2)	51.30(7)	S(2)Fe(4)C(14)	166.5(4)
Fe(4)Mo(2)S(5)	139.10(7)	S(2)Fe(4)C(15)	95.2(4)
Fe(4)Mo(2)S(6)	90.71(7)	S(2)Fe(4)C(16)	95.1(4)
Fe(4)Mo(2)S(8)	50.06(7)	S(8)Fe(4)C(14)	90.9(4)
Fe(4)Mo(2)C(3)	132.1(3)	S(8)Fe(4)C(15)	99.2(4)
Fe(4)Mo(2)C(4)	80.8(3)	S(8)Fe(4)C(16)	161.3(4)
Fe(5)Mo(2)Fe(6)	141.09(5)	C(14)Fe(4)C(15)	96.6(5)
Fe(5)Mo(2)S(2)	51.68(7)	C(14)Fe(4)C(16)	89.4(5)
Fe(5)Mo(2)S(5)	92.65(7)	C(15)Fe(4)C(16)	99.2(5)
Fe(5)Mo(2)S(6)	141.19(7)	Mo(2)Fe(5)S(2)	56.06(7)
Fe(5)Mo(2)S(8)	50.66(7)	Mo(2)Fe(5)S(8)	57.21(8)
Fe(5)Mo(2)C(3)	75.0(3)	Mo(2)Fe(5)C(17)	110.8(4)
Fe(5)Mo(2)C(4)	130.8(3)	Mo(2)Fe(5)C(18)	144.0(4)
Fe(6)Mo(2)S(2)	129.66(7)	Mo(2)Fe(5)C(19)	105.3(4)
Fe(6)Mo(2)S(5)	51.19(6)	S(2)Fe(5)S(8)	80.3(1)
Fe(6)Mo(2)S(6)	51.18(6)	S(2)Fe(5)C(17)	165.9(4)
Fe(6)Mo(2)S(8)	156.39(8)	S(2)Fe(5)C(18)	83.1(4)
Fe(6)Mo(2)C(3)	80.4(3)	S(2)Fe(5)C(19)	98.5(4)
Fe(6)Mo(2)C(4)	80.4(3)	S(8)Fe(5)C(17)	88.0(4)
S(2)Mo(2)S(5)	90.65(8)	S(8)Fe(5)C(18)	103.5(4)
S(2)Mo(2)S(6)	91.45(8)	S(8)Fe(5)C(19)	159.8(4)
S(2)Mo(2)S(8)	73.92(9)	C(17)Fe(5)C(18)	97.3(5)
S(2)Mo(2)C(3)	125.3(3)	C(17)Fe(5)C(19)	89.8(5)
S(2)Mo(2)C(4)	131.5(3)	C(18)Fe(5)C(19)	96.7(5)
S(5)Mo(2)S(6)	73.90(8)	Mo(2)Fe(6)S(5)	57.51(7)
S(5)Mo(2)S(8)	142.24(9)	Mo(2)Fe(6)S(6)	57.53(7)
S(5)Mo(2)C(3)	79.3(3)	Mo(2)Fe(6)C(20)	103.8(3)
S(5)Mo(2)C(4)	131.2(3)	Mo(2)Fe(6)C(21)	108.9(3)
S(6)Mo(2)S(8)	138.94(9)	Mo(2)Fe(6)C(22)	148.1(3)
S(6)Mo(2)C(3)	134.5(3)	S(5)Fe(6)S(6)	81.20(9)
S(6)Mo(2)C(4)	80.7(3)	S(5)Fe(6)C(20)	91.0(3)
S(8)Mo(2)C(3)	82.1(3)	S(5)Fe(6)C(21)	166.3(3)
S(8)Mo(2)C(4)	81.2(3)	S(5)Fe(6)C(22)	98.1(3)
C(3)Mo(2)C(4)	90.6(4)	S(6)Fe(6)C(20)	161.1(3)
Mo(1)FeMo(2)	163.60(6)	S(6)Fe(6)C(21)	92.3(3)
Mo(1)FeS(3)	54.97(7)	S(6)Fe(6)C(22)	102.0(3)
Mo(1)FeS(4)	54.83(7)	C(20)Fe(6)C(21)	91.5(5)
Mo(1)FeS(5)	124.62(8)	C(20)Fe(6)C(22)	96.2(4)
Mo(1)FeS(6)	140.22(8)	C(21)Fe(6)C(22)	95.0(4)
Mo(2)FeS(3)	124.69(8)	Mo(1)S(1)Fe(1)	72.60(8)
Mo(2)FeS(4)	140.33(8)	Mo(1)S(1)Fe(2)	71.80(8)
Mo(2)FeS(5)	54.77(7)	Fe(1)S(1)Fe(2)	97.5(1)
Mo(2)FeS(6)	55.09(7)	Mo(2)S(2)Fe(4)	72.87(8)
S(3)FeS(4)	81.08(9)	Mo(2)S(2)Fe(5)	72.27(8)
Fe(4)S(2)Fe(5)	97.0(1)	Fe(1)C(7)O(7)	178.3(9)
Mo(1)S(3)Fe	75.25(8)	Fe(2)C(8)O(8)	175.7(9)
Mo(1)S(3)Fe(3)	71.28(8)	Fe(2)C(9)O(9)	175.1(9)
FeS(3)Fe(3)	95.93(9)	Fe(2)C(10)O(10)	177(1)
Mo(1)S(4)Fe	76.44(8)	Fe(3)C(11)O(11)	178.5(9)
Mo(1)S(4)Fe(3)	71.56(8)	Fe(3)C(12)O(12)	177.9(9)
FeS(4)Fe(3)	97.2(1)	Fe(3)C(13)O(13)	179.0(9)
Mo(2)S(5)Fe	75.34(8)	Fe(4)C(14)O(14)	179(1)
Mo(2)S(5)Fe(6)	71.30(8)	Fe(4)C(15)O(15)	175.6(9)

Table 7 (continued)

Angle	ω	Angle	ω
FeS(5)Fe(6)	96.19(9)	Fe(4)C(16)O(16)	177(1)
Mo(2)S(6)Fe	76.16(8)	Fe(5)C(17)O(17)	177(1)
Mo(2)S(6)Fe(6)	71.29(8)	Fe(5)C(18)O(18)	178(1)
FeS(6)Fe(6)	97.5(1)	Fe(5)C(19)O(19)	176(1)
Mo(1)S(7)Fe(1)	72.48(8)	Fe(6)C(20)O(20)	179.2(9)
Mo(1)S(7)Fe(2)	71.77(8)	Fe(6)C(21)O(21)	177.2(9)
Fe(1)S(7)Fe(2)	99.7(1)	Fe(6)C(22)O(22)	177.7(9)
Mo(2)S(8)Fe(4)	72.88(9)	CB(2)CB(1)CB(6)	118(2)
Mo(2)S(8)Fe(5)	72.13(9)	CB(1)CB(2)CB(3)	121(2)
Fe(4)S(8)Fe(5)	99.1(1)	CB(2)CB(3)CB(4)	119(2)
Mo(1)C(1)O(1)	179.8(9)	CB(3)CB(4)CB(5)	120(2)
Mo(1)C(2)O(2)	177.4(8)	CB(4)CB(5)CB(6)	121(2)
Mo(2)C(3)O(3)	178.2(9)	CB(1)CB(6)CB(5)	120(2)
Mo(2)C(4)O(4)	178.4(9)	CBX(2)CBX(1)CBX(3)	120(1)
Fe(1)C(5)O(5)	176.3(9)	CBX(1)CBX(2)CBX(3)	121(1)
Fe(1)C(6)O(6)	177.1(9)	CBX(1)CBX(3)CBX(2)	120(1)

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