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Transition metal complexes with sulfur ligands
Part LIII*. Binuclear molybdenum sulfur centers with CO and NO binding sites. Synthesis, structure and electrochemistry of $[Mo(CO)(\mu\text{-}`S_4')]_2\cdot THF$ and $[Mo(NO)(\mu\text{-}`S_4')]_2\cdot 2DMF$ ($`S_4'^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2−))

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Abstract

In order to investigate the coordination of CO and NO^+ or NO to oligonuclear transition metal sulfur complexes containing chirotopic and stereogenic metal centers $[Mo(CO)(\mu\text{-}`S_4')]_2$ (**1**) and $[Mo(NO)(\mu\text{-}`S_4')]_2$ (**2**) were synthesized ($`S_4'^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2−)). **1** was obtained from $[Mo(CO)_4nor]$ and $`S_4'\text{-}H_2$. Subsequent reaction with $NOBF_4$ or NO yielded **2**. **1**·THF crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$, $a=1108.2(2)$, $b=1962.1(4)$, $c=1742.9(5)$ pm, $\beta=104.64(2)°$, $R(R_w)=0.051$. **2**·2DMF crystallizes also in $P2_1/n$ with $Z=4$, $a=1761.0(6)$, $b=1082.6(4)$, $c=2415.1(10)$ pm, $\beta=110.64(3)°$, $R(R_w)=0.134(0.104)$. **1** and **2** possess seven-coordinate Mo centers surrounded by five sulfur, one molybdenum and one carbon or one nitrogen atom, respectively. The Mo atoms are connected via two thiolato-S atoms and a Mo–Mo double bond in **1** and a Mo–Mo single bond in **2**, respectively. The two 'S_4' ligands differently coordinate the respective Mo centers, one 'S_4' showing *cis* thiolato-S and the other *trans* thiolato-S donors. **1** and **2** are chiral and have a stereogenic Mo_2 center. In CH_2Cl_2, **1** undergoes two one-electron reductions and two one-electron oxidations, the first reduction and oxidation being reversible. The two-electron reduction product $[\mathbf{1}]^{2-}$ is isoelectronic with **2**.

Introduction

Polynuclear molybdenum complexes with sulfur dominated coordination spheres are of general interest in context with the search for model compounds of metal oxidoreductases [2] and homogeneous as well as heterogeneous catalysts [3]. In order to understand the molecular mechanisms of the catalytic reactions, basic knowledge of the characteristic properties of metal sulfur centers is required. In this respect the stereochemistry of the metal sulfur centers and its influence on asymmetric catalyses [4], cooperative effects between the centers, stabilization of vacant sites at the metals being necessary for the coordination of substrates, and the reactivity of these molecules in the metal sulfur coordination sphere are of major interest. Coordination of thiolate and sulfide ligands to metal centers usually creates polynuclear complexes [5]. Vacant or easily accessible coordination sites are rarely found in such complexes, and model compounds such as the 'single cubane' $[MoFe_3(S)_4(SR)_3(o\text{-catecholat})L]^{2-}$ (L = $p\text{-}ClC_6H_4S^-$, PhO^-, CN^-, PMe_3) [6] are the exception rather than the rule in this class of thiolate sulfide complexes.

On the other hand, in mononuclear complexes, bidentate dithiolate or multidentate thioether-thiolate ligands, e.g. $`S_2'^{2-}$ ($`S_2'^{2-}$ = 1,2-benzenedithiolate(2−)) or $`S_4'^{2-}$ ($`S_4'^{2-}$ = 2,3,8,9-dibenzo-1,4,7,10-tetrathiadecane(2−)) can very effectively stabilize vacant sites. This was shown, for example, by the isolation of $(N(CH_3)_4)_2[Cr(CO)_3(`S_2')]$ [7] and the substitution reactions of $[Ru(PPh_3)_2(`S_4')]$ [8] or $[Ru(PPh_3)_2(`N_{H2}S_2')]$ ($`N_{H2}S_2'^{2-}$ = 1,2-bis(2-mercapto-anilino)ethane(2−)) [9]. In our search for complexes modelling the active centers of metal oxidoreductases we have concentrated on multidentate ligands. They were expected to guarantee a high degree of sulfur coordination of the metal(s) and could possibly even mimic the protein environment

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*Dedicated to Professor Dr. H. P. Fritz on the occasion of his 60th birthday. For Part LII see ref. 1a.

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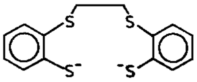
of the metals. Cysteine and methionine residues in the peptide chains of oxidoreductases provide the sulfur donors and constitute a polydentate ligand holding the metal(s) in fixed positions and generating a chiral environment of the metal center(s). In case of polynuclear enzyme centers this should lead to a different reactivity of the individual metal centers, or in the terms of Stack and Holm, to 'subsite specific' reactivity [10].

With transition metals the 'S_4' ligand forms

'S_4'$^{2-}$ =



mononuclear complexes of the type $[M(L)_2('S_4')]$ (M = transition metal, L = monodentate coligand, e.g. CO, NO or PPh_3) [8, 11] as well as binuclear complexes, e.g. $[Fe(CO)(\mu\text{-}'S_4')]_2$ [1] or $[\mu\text{-}'S_4'\{Mo(CO)_3\}_2]$ [12]. In $[Fe(CO)(\mu\text{-}'S_4')]_2$ one CO binding site can be occupied by NO^+; $[\mu\text{-}'S_4'\{Mo(CO)_3\}_2]$ possesses two latent coordination sites which reversibly open upon reduction and coordinate additionally CO and close upon oxidation under loss of CO.

Another important feature of binuclear complexes with $[M('S_4')]$ fragments is their stereoisomerism [1]. In chiral $[Fe(CO)(\mu\text{-}'S_4')]_2$, two homochiral $[Fe(CO)('S_4')]$ fragments with *trans* thiolato-S donor atoms are combined. In the systematic search for further binuclear complexes we have now obtained $[Mo(CO)(\mu\text{-}'S_4')]_2$ (**1**) and $[Mo(NO)(\mu\text{-}'S_4')]_2$ (**2**). **1** and **2** display a new stereochemistry, contain diastereomeric $[Mo(L)('S_4')]$ fragments (L = CO, NO) and are also chiral. The synthesis, properties and X-ray structure analysis of **1**·THF and **2**·2DMF will be described here.

Experimental

General

Unless otherwise noted all synthetic procedures were carried out under nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible the reactions were monitored by IR spectroscopy. Spectra were recorded on the following instruments: IR (CaF_2 cuvettes or KBr discs): Zeiss IMR 25 or Perkin-Elmer 983; solvent bands were compensated. Mass spectra: Varian MAT 212; NMR: Jeol FT-JNM-GX 270. Electronic spectra: Beckman DK 2A and Shimadzu UV-3100 UV-VIS-NIR spectrometers. Magnetic moments were obtained with a Johnson Matthey susceptibility balance. Cyclic voltammetry (CV) experiments were carried out with a PAR 264A potentiostat. The working electrode was a glassy carbon disk (ROTEL A) which was polished with 0.05 μm alumina before each use. Ag/AgCl and Pt were used as reference and counter electrodes, respectively. CH_2Cl_2 solutions were 0.1 mM in complex and 0.1 M in tetrabutylammoniumperchlorate as supporting electrolyte.

$NOBF_4$ was purchased from Merck and NO gas from Messer-Griesheim. $[Mo(CO)_4nor]$ (nor = norbornadien) [13] and 'S_4'-H_2 [14] were prepared by literature methods.

X-ray data collection, structure determination and refinement of $[Mo(CO)(\mu\text{-}'S_4')]_2$·THF (1·THF) and $[Mo(NO)(\mu\text{-}'S_4')]_2$·2DMF (2·2DMF)

Single crystals of $[Mo(CO)(\mu\text{-}'S_4')]_2$·THF (**1**·THF) were obtained from the reaction mixture as described below. Single crystals of $[Mo(NO)(\mu\text{-}'S_4')]_2$·2DMF (**2**·2DMF) were grown by covering a DMF solution of **2** with a layer of ether under ambient conditions. The single crystals were sealed under N_2 in glass capillaries. The structures were solved by direct methods. Non-hydrogen atoms of **1**·THF were refined anisotropically and the aromatic H atoms were placed at calculated positions and refined as rigid groups. The H atoms of the methylene groups were placed in ideal tetrahedron positions and rotated around their central C atom during refinement. The H atoms were refined with common isotropic temperature factors. The Mo and S atoms of **2**·2DMF were refined anisotropically; the N, O and C atoms isotropically. The H atoms were not considered. The structure of **1**·THF could be refined to conventional R factors. $[Mo(NO)(\mu\text{-}'S_4')]_2$·2DMF (**2**·2DMF) easily loses DMF and the DMF molecules in the crystal are partially disordered. This led to a poor quality of the crystal data set and the structure refinement stopped at R (R_w) = 13.4% (10.4%). The overall structure of **2**·2DMF, however, could be determined and $[Mo('S_4')]_2$ core angles and distances were obtained with sufficient accuracy to be able to compare them with bond distances and angles of **1**·THF. Table 1 summarizes crystallographic data for **1**·THF and **2**·2DMF; the fractional atomic coordinates are listed in Table 2.

Syntheses

$[Mo(CO)(\mu\text{-}'S_4')]_2$·THF (1·THF)

The colourless solution of 'S_4'-H_2 (780 mg, 2.5 mmol) in 15 ml of THF was added to a yellow solution of $[Mo(CO)_4nor]$ (1500 mg, 5 mmol) in 10 ml of THF. The reaction mixture slowly turned blue and within 3 to 7 days deep blue crystals of **1**·THF precipitated. They were collected, washed with 15 ml of THF and dried *in vacuo*. Yield: 420 mg (36% ref. to 'S_4'-H_2).

Anal. Calc. for $C_{34}H_{32}S_8O_3Mo_2$ (937.0) = **1**·THF: C, 43.58; H, 3.44; S, 27.38. Found: C, 43.80; H, 3.39; S, 27.20%.

TABLE 1. Summary of crystallographic data and data collection procedures for [Mo(CO)(μ-'S$_4$')]$_2$·THF (**1**·THF) and [Mo(NO)(μ-'S$_4$')]$_2$·2DMF (**2**·2DMF)

Compound	[Mo(CO)(μ-'S$_4$')]$_2$·THF	[Mo(NO)(μ-'S$_4$')]$_2$·2DMF
Formula	$C_{34}H_{32}S_8O_3Mo_2$	$C_{34}H_{38}S_8O_4N_4Mo_2$
M_r	937.0	1015.1
Space group	$P2_1/n$	$P2_1/n$
Crystal system	monoclinic	monoclinic
Crystal size (mm)	0.5×0.4×0.1	0.4×0.3×0.2
cell dimensions		
a (pm)	1108.2(2)	1761.0(6)
b (pm)	1962.1(4)	1082.6(4)
c (pm)	1742.9(5)	2415.1(10)
β (°)	104.64(2)	110.64(3)
Molecule unit cell	4	4
Cell volume (pm^3)	3667(2)×10^6	4309(3)×10^6
D_{calc} (g/cm^3)	1.70	1.56
μ (cm^{-1})	11.4	9.8
Radiation (pm)	Mo Kα (71.073)	Mo Kα (71.073)
Diffractometer	Nicolet R3m/V	Nicolet R3m/V
Scan technique	ω-scan	ω-scan
Scan speed (°/min)	3.0–15	3.0–15
$2\theta_{range}$ (°)	4–52	3–54
Reflections measured	8289	8815
Independent reflections	7217	6975
Observed reflections	5203	4757
σ-criterion	$F>4\sigma(F)$	$F>4\sigma(F)$
Temperature of measurement (K)	293	200
Programm	SHELXTL-PLUS	SHELXTL-PLUS
R	0.051	0.134
R_w	0.051	0.104

[Mo(CO)(μ-'S$_4$')]$_2$·CH$_2$Cl$_2$ (1·CH$_2$Cl$_2$)

The colourless solution of 'S$_4$'-H$_2$ (750 mg, 2.4 mmol) in 30 ml of CH_2Cl_2 was combined with the yellow solution of [Mo(CO)$_4$nor] (1000 mg, 3.3 mmol) in 30 ml of CH_2Cl_2. The reaction mixture slowly turned blue and after 3 days lustrous deep blue crystals had precipitated. They were isolated by filtration, showed only one ν(CO) band in the KBr IR spectrum at 1890 cm^{-1} and have not yet been further identified. Within another 5 days blue microcrystals of **1**·CH$_2$Cl$_2$ precipitated from the mother liquor. They were separated, washed with 15 ml of CH_2Cl_2 and dried *in vacuo*. Yield: 100 mg (9% ref. to 'S$_4$'-H$_2$).

Anal. Calc. for $C_{31}H_{26}S_8O_2Cl_2Mo_2$ (949.8) = **1**·CH$_2$Cl$_2$: C, 39.20; H, 2.76. Found: C, 39.07; H, 2.56%.

[Mo(NO)(μ-'S$_4$)']$_2$·0.5DMF (2·0.5DMF) from 1·THF and NOBF$_4$

To the blue suspension of **1**·THF (220 mg, 0.23 mmol) in 20 ml of CH_2Cl_2 a solution of NOBF$_4$ (55 mg, 0.47 mmol) in 10 ml of CH_3CN was added in small portions. The mixture was stirred at room temperature for 12 h during which time its colour turned deep red. It then contained a suspended yellow brown solid which was separated by filtration and washed with CH_2Cl_2. This solid was dissolved in 30 ml of DMF which was covered with a layer of methanol. Within 14 days orange crystals of **2**·0.5DMF precipitated which were separated, washed with 20 ml of methanol and dried *in vacuo* for 24 h. They analyzed for [Mo(NO)(μ-'S$_4$')]$_2$·0.5 DMF. Yield: 10 mg (5%).

Anal. Calc. for $C_{29.5}H_{27.5}S_8O_{2.5}N_{2.5}Mo_2$ (905.4) = **2**·0.5DMF: C, 39.13; H, 3.06; N, 3.85. Found: C, 39.14; H, 3.07; N, 3.84%.

[Mo(NO)(μ-'S$_4$')]$_2$·DMF (2·DMF) from 1·THF and NO gas

A suspension of **1**·THF (340 mg, 0.36 mmol) in 182 ml of CH_2Cl_2 was treated with NO gas (16.5 ml, 0.73 mmol) and stirred for 18 h in a closed Schlenk tube. During this time the colour of the reaction mixture turned to red–brown. After filtration the brown solution was evaporated to dryness *in vacuo* yielding a brown solid residue. It was stirred in 10 ml of THF for 1 h yielding a light brown powder which was separated, washed with 5 ml of THF and dried *in vacuo*. Yield: 80 mg (25%).

The crude product was dissolved in 30 ml of DMF, the solution was filtered and covered with a layer

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the non-hydrogen atoms for $[Mo(CO)(\mu\text{-'}S_4\text{'})]_2 \cdot THF$ (a) and $[Mo(NO)(\mu\text{-'}S_4\text{'})]_2 \cdot 2DMF$ (b)

	x	*y*	*z*	*U*(eq)[a]
(a)				
Mo(1)	1304(1)	6376(1)	8522(1)	38(1)
Mo(2)	637(1)	7625(1)	7993(1)	40(1)
C(1)	1284(7)	6651(4)	9610(5)	49(3)
O(1)	1358(7)	6791(4)	10260(3)	75(3)
C(2)	97(8)	7838(5)	8968(5)	56(3)
O(2)	−199(8)	7982(4)	9532(5)	97(4)
S(1)	−774(2)	6659(1)	7752(1)	46(1)
S(2)	1491(2)	5842(1)	7217(1)	54(1)
S(3)	262(2)	5264(1)	8636(1)	51(1)
S(4)	3182(2)	5731(1)	9179(1)	58(1)
S(5)	2744(2)	7330(1)	8636(1)	46(1)
S(6)	1402(2)	7491(1)	6763(1)	54(1)
S(7)	−1092(2)	8244(1)	7034(1)	58(1)
S(8)	1488(2)	8793(1)	8196(1)	58(1)
C(15)	7(8)	6009(4)	6535(5)	53(3)
C(14)	−133(10)	5795(6)	5742(5)	74(4)
C(13)	−1235(12)	5955(6)	5190(6)	86(5)
C(12)	−2152(11)	6294(7)	5415(6)	91(5)
C(11)	−2040(9)	6489(5)	6200(6)	68(4)
C(10)	−913(8)	6353(4)	6758(5)	52(3)
C(16)	1300(10)	4947(5)	7409(6)	66(4)
C(25)	2636(8)	4995(4)	9565(5)	54(3)
C(24)	3462(10)	4598(5)	10130(6)	72(4)
C(23)	3062(12)	4017(6)	10439(6)	78(5)
C(22)	1850(13)	3816(5)	10212(6)	83(5)
C(21)	1017(11)	4196(5)	9666(6)	70(4)
C(20)	1408(8)	4780(4)	9345(5)	54(3)
C(26)	213(10)	4797(5)	7751(6)	67(4)
C(35)	3049(8)	7559(4)	7096(5)	55(3)
C(34)	3783(10)	7679(6)	6577(6)	74(4)
C(33)	5039(10)	7668(6)	6839(7)	88(5)
C(32)	5611(10)	7520(6)	7610(8)	84(5)
C(31)	4883(8)	7403(5)	8137(6)	66(4)
C(30)	3606(7)	7417(4)	7895(5)	51(3)
C(36)	827(9)	8263(6)	6228(5)	67(4)
C(45)	261(9)	9343(4)	7786(5)	57(3)
C(44)	387(10)	10036(5)	7952(6)	75(4)
C(43)	−588(13)	10478(6)	7664(8)	90(6)
C(42)	−1687(13)	10250(6)	7206(8)	92(6)
C(41)	−1837(10)	9578(6)	6994(6)	76(4)
C(40)	−880(9)	9118(5)	7293(5)	61(3)
C(46)	−574(10)	8233(6)	6104(5)	69(4)
O(50)	2155(17)	1027(14)	−267(9)	246(13)
C(51)	3009(19)	1481(11)	344(14)	154(11)
C(52)	2324(29)	557(11)	903(12)	173(14)
C(53)	1581(25)	540(10)	95(16)	182(14)
C(54)	3297(25)	1004(14)	945(13)	200(14)
(b)				
Mo(1)	4228(1)	529(2)	2682(1)	17(1)
Mo(2)	5970(1)	928(2)	3255(1)	17(1)
N(1)	4007(9)	1298(14)	3252(7)	18(3)
O(1)	3828(9)	1783(15)	3644(7)	41(4)
N(2)	5901(10)	1519(17)	3907(8)	31(4)
O(2)	5840(11)	1843(17)	4376(8)	53(5)
S(1)	5207(3)	−936(5)	3333(2)	22(2)
S(2)	4354(3)	−1025(5)	1885(2)	25(2)
S(3)	3087(3)	−911(5)	2636(2)	24(2)
S(4)	3179(3)	1488(5)	1821(3)	27(2)
S(5)	5016(3)	2288(4)	2565(2)	20(2)
S(6)	6124(3)	121(4)	2305(2)	22(2)
S(7)	7282(3)	−238(4)	3713(2)	21(2)
S(8)	6926(3)	2623(5)	3236(3)	28(2)
C(15)	5002(10)	−2251(16)	2292(8)	13(4)
C(14)	5129(13)	−3250(20)	1986(10)	31(5)
C(13)	5669(14)	−4196(21)	2285(11)	39(6)
C(12)	6072(12)	−4052(21)	2880(9)	31(5)
C(11)	5937(13)	−3061(19)	3180(10)	28(5)
C(10)	5393(12)	−2160(19)	2896(10)	27(5)
C(25)	2202(14)	−140(22)	2157(11)	37(6)
C(24)	1437(12)	−526(20)	2185(10)	29(5)
C(23)	735(14)	−2(22)	1823(11)	38(6)
C(22)	765(14)	1024(24)	1465(11)	41(6)
C(21)	1536(13)	1398(21)	1466(10)	32(5)
C(20)	2244(12)	885(20)	1816(9)	27(5)
C(16)	3347(13)	−1773(21)	1637(10)	33(5)
C(26)	3120(12)	−2213(19)	2155(10)	26(5)
C(35)	5781(11)	1389(18)	1802(9)	23(5)
C(34)	6006(12)	1420(20)	1312(10)	28(5)
C(33)	5599(14)	2390(22)	853(11)	37(6)
C(32)	5015(14)	3144(22)	960(11)	39(6)
C(31)	4854(12)	3057(18)	1467(9)	24(5)
C(30)	5232(13)	2168(20)	1876(10)	29(5)
C(45)	8025(12)	935(20)	3938(9)	26(5)
C(44)	8827(13)	610(21)	4307(10)	34(5)
C(43)	9447(13)	1373(21)	4439(10)	35(5)
C(42)	9292(14)	2623(21)	4202(11)	36(5)
C(41)	8548(12)	2991(19)	3853(10)	26(5)
C(40)	7889(13)	2107(20)	3705(10)	28(5)
C(36)	7243(13)	−40(22)	2529(11)	34(5)
C(46)	7475(11)	−852(19)	3082(9)	25(5)
C(1)	2469(18)	52(30)	−514(14)	63(8)
C(2)	2810(19)	1851(28)	99(14)	63(8)
C(3)	3749(20)	116(33)	266(16)	74(9)
O(3)	2597(13)	−924(23)	−742(10)	81(6)
N(3)	2998(11)	616(18)	−52(9)	39(5)
C(4)	7073(26)	3486(38)	−245(19)	89(11)
C(5)	8473(26)	3895(43)	−105(20)	101(12)
C(6)	7439(36)	5044(57)	−789(28)	137(17)
O(4)	6320(22)	3686(33)	−525(17)	132(11)
N(4)	7604(15)	4112(26)	−381(11)	67(7)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

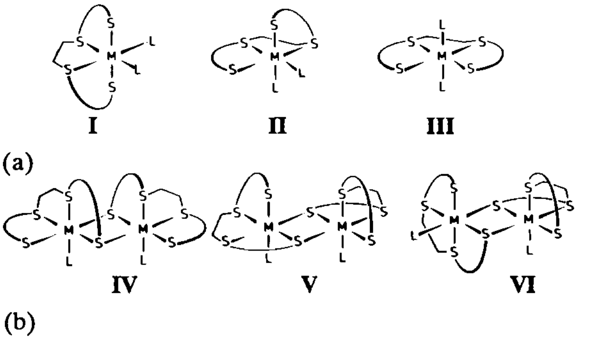
of ether. During 3 weeks orange–brown crystals precipitated. Single crystals from this charge analyzing for $[Mo(NO)(\mu\text{-'}S_4\text{'})]_2 \cdot 2DMF$ were used for X-ray structure determination. The remaining crystals were washed with ether, and prolonged drying *in vacuo* for 8 h removed the DMF solvate partially from the complex, which then analyzed for [Mo(NO)(μ-'S$_4$')]$_2$·DMF.

Anal. Calc. for $C_{31}H_{31}S_8O_3N_3Mo_2$ (942.0) = **2**·DMF: C, 39.53; H, 3.32; N, 4.46; S, 27.23. Found: C, 39.72; H, 3.52; N, 4.61; S, 27.80%.

Results and discussion

Stereoisomers of [M(L)('S$_4$')]$_2$ complexes

Hexacoordinate metal complexes [M(L)$_2$('S$_4$')] with the 'S$_4$' ligand and two identical coligands L of type **I** (Scheme 1(a)) are chiral and all atoms are chirotopic but none, including the M center, is stereogenic [15].



Scheme 1. (a) 'S$_4$' coordination in hexacoordinated complexes with thiolato-S atoms in *trans* (**I**) or *cis* positions (**II** and **III**); (b) three possible stereoisomers of [M(L)(μ-'S$_4$')]$_2$ with diastereoisomeric [M(L)('S$_4$')] fragments (M = transition metal, L = monodentate ligand), ⌒ = C_6H_4.

After loss of one coligand L the resulting coordinatively and electronically unsaturated [M(L)('S$_4$')] fragments can form binuclear [M(L)(μ-'S$_4$')]$_2$ complexes. This was previously described for [Fe(CO)$_2$('S$_4$')] which decarbonylates to give [Fe(CO)('S$_4$')] and subsequently [Fe(CO)(μ-'S$_4$')]$_2$. If the chiral [Fe(CO)('S$_4$')] fragments are configurationally stable, dimerization can theoretically lead to already ten stereoisomers [1].

In addition to type **I** (Scheme 1) where the thiolato donor atoms occupy *trans* positions at the metal center, two additional ligating modes for binding the 'S$_4$' ligand with *cis* thiolato atoms exist in a hexacoordinate metal complex (type **II** and **III** of Scheme 1(a)).

These structures may eventually be only kinetically stable, but when they lose one coligand L and combine not only with themselves but also with fragments of type **I**, they enhance the theoretically possible number of [M(L)(μ-'S$_4$')]$_2$ isomers quite drastically; Scheme 1(b) shows three of them (**IV**–**VI**). Type **IV** now has been found in the structures of [Mo(L)('S$_4$')]$_2$ (L = CO, NO).

Synthesis and spectroscopy of [Mo(CO)(μ-'S$_4$')]$_2$ (1)

Oxidative addition of thiols to molybdenum(0) compounds often yields thiolato complexes with Mo centers in higher oxidation states. [Mo(SR)$_3$]$_n$ [16], [Mo(SR)$_2$(dppe)$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane) [17] and [Mo(CO)$_3$(CH$_3$SC$_6$H$_4$S)]$_2$ [18, 12b] were prepared by such a route.

When we tried to improve the synthesis of [μ-'S$_4$'{Mo(CO)$_3$}$_2$] [12] by reacting labile [Mo(CO)$_4$nor], (nor = norbornadiene) with the neutral 'S$_4$'-H$_2$ligand, according to eqn. (1),

$$2[\mathrm{Mo(CO)_4nor}] + \text{'S}_4\text{'-H}_2 \xrightarrow[\text{3–7 days}/-\mathrm{CO}]{\text{THF/20 °C}} \underset{\mathbf{1}}{[\mathrm{Mo(CO)}(\mu\text{-'S}_4\text{'})]_2} + \text{other products} \qquad (1)$$

a smooth evolution of gas was observed and the reaction mixture immediately darkened. Within two days dark blue crystals precipitated from the solution which had changed colour to blue–green. Instead of [μ-'S$_4$'{Mo(CO)$_3$}$_2$], however, we obtained a mixture of different complexes including [Mo(CO)(μ-'S$_4$')]$_2$ (**1**). The simultaneous formation of large amounts of [Mo(CO)$_6$] was detected by IR spectroscopy. The separated dark blue crystals analyzed for [Mo(CO)(μ-'S$_4$')]$_2$·THF (**1**·THF). **1**·THF is only sparingly soluble in CH$_2$Cl$_2$, DMSO or DMF; it shows two strong ν(CO) bands of unequal intensity in the KBr IR spectrum at 1930 and 1870 cm^{-1} (Fig. 1).

The binuclearity of **1** could be concluded from the mass spectrum showing the **1**$^+$ ion at m/e = 864. The electronic spectrum of compound **1**·THF in the range of 200–1800 nm exhibits several bands (cf.

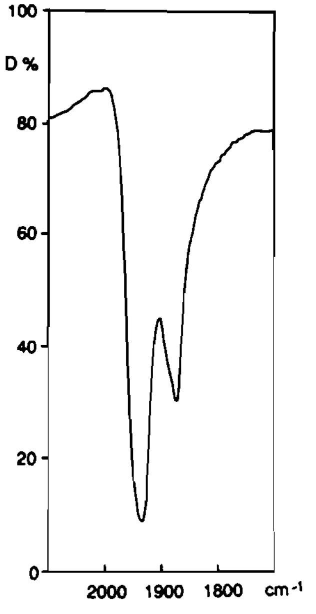


Fig. 1. ν(CO) IR region of **1**·THF in KBr.

Table 7), among them one intense band at 603 nm which is responsible for the bright blue colour of 1·THF. The ^1H NMR spectrum displays a very complex pattern of 'S$_4$' protons. It did not allow conclusions with regard to the structure of 1 but proved the presence of one THF molecule per [Mo(CO)(μ-'S$_4$')]$_2$ entity (see Table 7). The low solubility of 1·THF prevented recording of ^{13}C NMR spectra and in order to elucidate the structure of 1·THF an X-ray structure determination was carried out.

X-ray structure analysis of [Mo(CO)(μ-'S$_4$')]$_2$·THF (1·THF)

The molecular structure of 1 is shown in Fig. 2; selected interatomic distances and angles are given in Table 3.

1 contains two seven-coordinate molybdenum centers in distorted pentagonal bipyramids. Five sulfur, one carbon and the neighbour Mo atom form the coordination sphere of each Mo center. The short Mo–Mo distance of 265.7(1) pm indicates a direct interaction of the two Mo centers which are bridged via two thiolato-S atoms.

1 displays several remarkable features. The two CO ligands point into the same direction. The [Mo(CO)('S$_4$')] entities are connected via thiolato-S atoms whose corresponding thioether-S atoms in *ortho* position at the benzene ring stands *trans* to the CO ligands. This type of bridging termed 'α-bridging' for the sake of brevity was found and discussed in the structure of [Fe(CO)(μ-'S$_4$)']2 [1]. It indicates that electronic rather than steric factors determine the way in which [M(L)('S$_4$')] fragments dimerize. Like in [Fe(CO)(μ-'S$_4$')]$_2$, the metal coordination spheres of 1 are very unequally occupied such that the 'upper' half of 1 looks overcrowded and the 'lower' half almost empty. Unlike [Fe(CO)(μ-'S$_4$')]$_2$, however, two different types of 'S$_4$' ligating occur. Mo1 carries a 'S$_4$' ligand with *trans*, Mo2, however, a 'S$_4$' ligand with *cis* thiolato-S atoms. Hence 1 has only C_1 symmetry and is chiral. All atoms are chirotopic and, in contrast to chiral [Fe(CO)(μ-'S$_4$')]$_2$, the bimetallic entity is also prostereogenic [15]. Permutation of L and L′ in an as yet hypothetical complex [Mo(L)(L′)(μ-'S$_4$')]$_2$ gives rise to stereoisomers which are diastereomeric and, in consequence, a different chemical reactivity can be expected not only by these diastereomers but also of the two individual Mo centers in each of them.

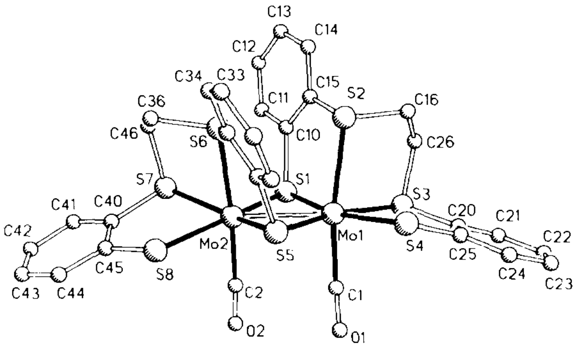


Fig. 2. Molecular structure of [Mo(CO)('S$_4$)]$_2$·THF (H atoms and THF molecules omitted).

1 formally contains 18 e$^-$ configurated Mo^{II} centers and is diamagnetic. The Mo–Mo distance (265.7(1) pm) is extremely short and indicates a double bond between the Mo^{II} centers. Mo–Mo single bonds which are assumed for [μ-'S$_4$'{Mo(CO)$_3$}$_2$] (291.9(1) pm) [12] or [Mo(μ-^{t}BuS)(CO)$_4$]$_2$ (298.4(2) pm) and related compounds [19] and even the triple bond in the Mo^{III} complex [Mo(μ-SEt)Cl(EtSC$_2$H$_4$SEt)]$_2$ (268.2(1) pm) [20] show larger bond distances.

The short Mo–Mo distance agrees with the large S1Mo1S5 and S1Mo2S5 angles of 112.4(1) and 113.7(1)°. In [Mo(μ-^{t}BuS)(CO)$_4$]$_2$ and [μ-'S$_4$'{Mo(CO)$_3$}$_2$] the corresponding angles are only 106° (i.e. closer to octahedral 90°). The Mo–S distances vary between 239.1(2) and 255.9(2) pm depending on whether the S atom belongs to a thiolato bridge, a thioether or a thiolate function; the mean Mo–S distance (246.9(2) pm) is slightly shorter than in mononuclear Mo^{II}'S$_4$' complexes, e.g. [Mo(CO)$_2$(PMe$_3$)('S$_4$')] (253.3 pm) [21] or [Mo(NO)$_2$('S$_4$')] (249.4 pm) [11b] which could be due to the Mo–Mo double bond in 1. This double bond and its 'distance compressing effect' could be also the reason for the mean Mo–S distance within the Mo$_2$S$_2$ ring of 241.8(2) pm which is shorter than the mean terminal Mo–S(thiolato) distance (246.3(2) pm). The [Mo1Mo2S1S5] ring itself is nearly planar showing a dihedral angle of 173.5°. Finally the strong coupling between the Mo centers revealed by the structure of 1 might be responsible for the unusual ν(CO) pattern of the IR spectrum (cf. Fig. 1).

Isomers of [Mo(CO)(μ-'S$_4$')]$_2$ and discussion of the mechanism of their formation

According to the discussion of stereoisomers above the structurally characterized 1 is not the only possible species when two [Mo(CO)('S$_4$')] fragments combine. This we noticed when we tried to improve the yield of 1 by varying the reaction conditions. Change of the solvent from THF to CH$_2$Cl$_2$ and of the [Mo(CO)$_4$nor]/'S$_4$'-H$_2$ ratio from 2:1 to 3:2, according to eqn. (2), in addition to 1·CH$_2$Cl$_2$, another isomer formed.

$$3[\mathrm{Mo(CO)_4nor}] + 2\text{'S}_4\text{'-H}_2 \xrightarrow[\text{3–7 days}]{\mathrm{CH_2Cl_2/r.t.}}$$

$$\text{other isomer of } \mathbf{1} + \mathbf{1}\cdot\mathrm{CH_2Cl_2} \quad (2)$$

TABLE 3. Selected interatomic distances (pm) and angles (°) for $[\mathrm{Mo(CO)}(\mu\text{-'S}_4\text{'})]_2\cdot\mathrm{THF}$[a]

Mo(1)–Mo(2)	265.7(1)	S(2)–C(15)	179.9(8)
Mo(1)–C(1)	197.7(8)	S(2)–C(16)	181.1(11)
Mo(1)–S(1)	241.9(2)	S(3)–C(20)	178.0(8)
Mo(1)–S(2)	255.9(2)	S(3)–C(26)	182.3(10)
Mo(1)–S(3)	250.9(2)	S(4)–C(25)	176.5(9)
Mo(1)–S(4)	245.7(2)	S(5)–C(30)	179.9(10)
Mo(1)–S(5)	243.6(2)	S(6)–C(35)	177.5(9)
Mo(2)–C(2)	198.2(10)	S(6)–C(36)	180.8(10)
Mo(2)–S(1)	242.6(2)	S(7)–C(40)	177.3(10)
Mo(2)–S(5)	239.1(2)	S(7)–C(46)	185.1(11)
Mo(2)–S(6)	251.2(2)	S(8)–C(45)	174.1(9)
Mo(2)–S(7)	251.5(2)	S(1)–C(10)	180.5(9)
Mo(1)–S(5)–Mo(2)	66.8(1)	Mo(1)–S(1)–Mo(2)	66.5(1)
C(1)–Mo(1)–S(1)	103.2(2)	S(1)–Mo(2)–S(5)	113.7(1)
C(1)–Mo(1)–S(2)	170.7(2)	C(2)–Mo(2)–S(6)	173.7(3)
S(1)–Mo(1)–S(2)	83.2(1)	S(1)–Mo(2)–S(6)	96.4(1)
C(1)–Mo(1)–S(3)	91.5(3)	S(5)–Mo(2)–S(6)	82.8(1)
S(1)–Mo(1)–S(3)	81.8(1)	C(2)–Mo(2)–S(7)	97.1(2)
S(2)–Mo(1)–S(3)	82.7(1)	S(1)–Mo(2)–S(7)	85.0(1)
C(1)–Mo(1)–S(4)	84.7(2)	S(5)–Mo(2)–S(7)	156.7(1)
S(1)–Mo(1)–S(4)	162.2(1)	S(6)–Mo(2)–S(7)	81.3(1)
S(2)–Mo(1)–S(4)	87.4(1)	C(2)–Mo(2)–S(8)	82.5(3)
S(3)–Mo(1)–S(4)	82.1(1)	S(1)–Mo(2)–S(8)	163.0(1)
S(1)–Mo(1)–S(5)	112.4(1)	S(6)–Mo(2)–S(8)	91.2(1)
S(2)–Mo(1)–S(5)	100.9(1)	S(7)–Mo(2)–S(8)	81.2(1)

[a] e.s.d.s are given in parentheses.

The originally light yellow solution again darkened to deep blue within 12 h, and after three days dark blue crystals had precipitated. These crystals also analyzed for $[\mathrm{Mo(CO)}(\mu\text{-'S}_4\text{'})]_x$, but showed only one ν(CO) band at 1890 $\mathrm{cm^{-1}}$ in the KBr IR spectrum and have not yet been further characterized. From the mother liquor crystals of $\mathbf{1}\cdot\mathrm{CH_2Cl_2}$ separated (for spectroscopic data see Table 6).

The formation of isomers of **1** is not unexpected. When the structures of $[\mathrm{Fe(CO)}(\mu\text{-'S}_4\text{'})]_2$ and the structurally characterized $[\mathrm{Mo(CO)}(\mu\text{-'S}_4\text{'})]_2$ isomer are compared, a major difference is the different ligation of the metal centers. $[\mathrm{Fe(CO)}(\mu\text{-'S}_4\text{'})]_2$ contains only '$\mathrm{S_4}$' ligands with *trans* thiolato-S atoms; in $[\mathrm{Mo(CO)}(\mu\text{-'S}_4\text{'})]_2$ (**1**), however, one '$\mathrm{S_4}$' ligand displays *trans*, the other *cis* thiolato-S atoms. This might be a direct consequence of the different syntheses of the complexes. $[\mathrm{Fe(CO)}(\mu\text{-'S}_4\text{'})]_2$ arises from $[\mathrm{Fe(CO)(\text{'S}_4\text{'})}]$ fragments presumably having the same fixed coordination geometry as the precursor $[\mathrm{Fe(CO)_2(\text{'S}_4\text{'})}]$. The $[\mathrm{Mo(CO)(\text{'S}_4\text{'})}]$ fragments, however, form only during the course of the synthesis which must definitely comprise several steps. It is as yet unclear at which stage complete coordination of the '$\mathrm{S_4}$' ligand is achieved. The primary steps probably involve the substitution of norbornadiene and oxidative addition of '$\mathrm{S_4}$'-$\mathrm{H_2}$ (eqn. (3)).

$$[\mathrm{Mo(CO)nor}] \xrightarrow[+\text{'S}_4\text{'-H}_2]{-\text{nor}} [\mathrm{Mo(CO)_4(H)(\text{'S}_4\text{'-H})}] \xrightarrow[-\mathrm{CO}]{-1/2\mathrm{H}_2} [\mathrm{Mo(CO)_3(\text{'S}_4\text{'-H})}] \rightarrow \rightarrow \rightarrow \mathbf{1} \qquad (3)$$

Reductive elimination of $\mathrm{H_2}$, loss of CO and reiteration of these steps yields coordinatively unsaturated fragments. Depending on whether these fragments immediately combine via thiolato bridges and then lose further CO ligands or whether they first lose more CO before dimerizing, the most diverse combinations can be easily imagined.

Electrochemistry and substitution reactions of 1·THF

In **1** the CO binding sites should be suited for binding other σ–π ligands instead of CO. In this sense, the $[\mathrm{Mo_2S_8}]$ core of **1** can be considered to have two potentially vacant coordination sites and it was of interest whether these sites react independently or cooperatively. When probing this question by cyclovoltammetry we observed two reduction and oxidation waves each (Fig. 3(a)). They may be assigned to the series of the five redox states of **1** given in eqn. (4).

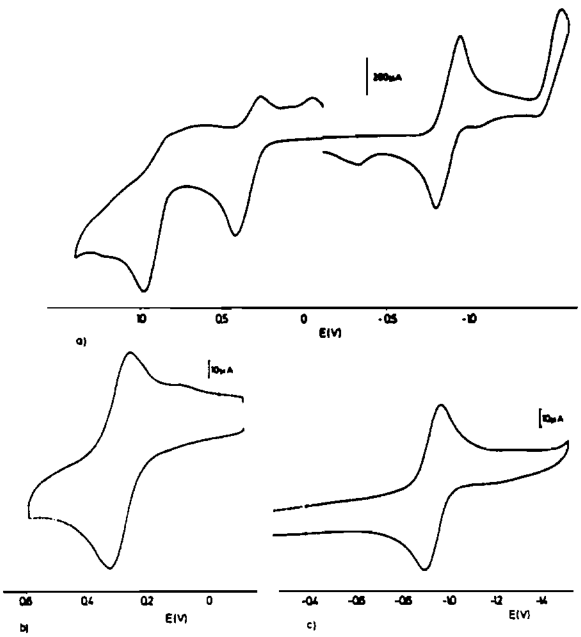


Fig. 3. (a) Cyclic voltammogram of **1** in CH_2Cl_2 ($v=50$ mV/s); (b) reversible oxidation at +0.29 V; (c) reversible reduction at −0.93 V (vs. NHE).

$$[1]^{2+} \xleftarrow{-e^-} [1]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [1]^0 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [1]^- \xrightarrow{+e^-} [1]^{2-} \qquad (4)$$

The oxidation at +0.29 V and reduction at −0.93 V leading to $[1]^+$ and $[1]^-$, respectively, are reversible one electron processes (Fig. 3(b) and 3(c)). This is indicated by the ΔE_p values and the constancy of ΔE_p as well as i_{pa}/i_{pc} ratios at variable scan rates up to 200 mV s^{-1} (cf. Table 4). The other two redox waves are irreversible and can be assigned to the formation of $[1]^{2-}$ and $[1]^{2+}$, both of which are unstable and undergo rapid chemical reactions.

Evidently, one electron can be reversibly added to or removed from the $Mo_2S_8(CO)_2$ core of **1**. But as soon as a second electron is involved, bonds in the $Mo_2S_8(CO)_2$ core break, and as the reactions of **1** with NO^+ or NO show, both Mo centers are simultaneously involved. This indicates again a strong coupling of the Mo centers which is already suggested by the Mo–Mo double bond.

A reaction of both Mo centers took place when **1** was treated with $NOBF_4$ according to eqn. (5),

$$1 + 2NOBF_4 \xrightarrow[12\ h/r.t.]{CH_2Cl_2/CH_3CN} [Mo(NO)(\mu\text{-}`S_4')]_2 + \text{other products} \qquad (5)$$

but contrary to our expectations, the CO substitution was accompanied by a redox reaction and not the isoelectronic $[Mo(NO)(\mu\text{-}`S_4')]_2(BF_4)_2$, but the neutral $[Mo(NO)(\mu\text{-}`S_4')]_2$ (**2**) formed in low yields. After recrystallization from DMF brown–orange crystals analyzing for **2**·0.5DMF were obtained. The KBr IR spectrum of **2**·0.5DMF shows two characteristic ν(NO) bands of unequal intensity at 1665 and 1605 cm^{-1}; ν(NO) and ν(CO) pattern of **2** and **1**, respectively, are nearly identical indicating very similar structures. In the mass spectrum the molecular ion 2^+ is observed at $m/e=868$. The unexpected redox reaction and the low yields **2** obtained according to eqn. (5) made us try the direct reaction of **1** with NO gas according to eqn. (6).

$$1 + 2NO \xrightarrow[18\ h]{CH_2Cl_2/r.t.} [Mo(NO)(\mu\text{-}`S_4')]_2 + \text{other products} \qquad (6)$$

Now, **2** formed in much higher yields and was isolated as **2**·2DMF after recrystallization from DMF. **2**·2DMF proved to be even more sparingly soluble than **1**·THF. It was characterized by the same methods as **2**·0.5DMF and, additionally, by cyclovoltammetric measurements and X-ray structure determination.

The cyclic voltammogram of **2** displays no redox peak between 0 and −1.70 V but one reversible and one irreversible oxidation wave at 0.80 and 1.20 V (cf. Table 4), respectively, which can be assigned

TABLE 4. Cyclic voltammetry data[a] of **1**·THF in CH_2Cl_2

	E_{pc}[b] (V)	E_{pa}[c] (V)	ΔE_p[d] (V)	E°[e] (V)	I_R[f]
$1^{\circ} \rightleftharpoons 1^-$	−0.96	−0.90	0.06	−0.93	0.93
$1^- \rightleftharpoons 1^{2-}$	−1.59	g			
$1^{\circ} \rightleftharpoons 1^+$	0.26	0.33	0.07	0.29	0.80
$1^+ \rightleftharpoons 1^{2+}$	g	0.80			
$2^{\circ} \rightleftharpoons 2^+$	0.77	0.83	0.06	0.80	0.80
$2^+ \rightleftharpoons 2^{2+}$	g	1.20			

[a] All potentials vs. NHE; scan rate 50 mV s^{-1} [b] CV, reduction peak. [c] CV, oxidation peak. [d] $\Delta Ep = |Ep_a - Ep_c|$. [e] $E^{\circ\prime}$ = formal redox potential. [f] Peak current ratio: $I_R = i_{pa}/i_{pc}$ for reduction process; $I_R = i_{pc}/i_{pa}$ for oxidation process. [g] Cyclovoltammetric wave not well developed.

to the formation of $[2]/[2]^+$ and $[2]^+/[2]^{2+}$, respectively. These results indicate a lower electronic flexibility of the $[Mo_2S_8N_2]$ entity compared with the $[Mo_2S_8C_2]$ fragment, since no reduction peak could be observed.

X-ray structure analysis of 2·2DMF

Due to the poor quality of the crystals and disorder of the DMF molecules the structure refinement stopped at unsatisfying R $(R_w) = 13.4\%$ (10.4%). The overall structure, however, could be unambiguously determined, and the distances and angles of the $[Mo_2S_8N_2]$ core were obtained with sufficient accuracy to enable cautious comparisons of **2** with **1** to be made. Figure 4 displays the molecular structure; selected bond distances and angles are summarized in Table 5.

2·2DMF possesses the same $[Mo_2(\mu\text{-'}S_4\text{'})_2]$ coordination geometry as **1**·THF. It differs from **1**·THF with respect to the NO ligands, distances and angles. The most notable difference is the increase of the Mo–Mo distance in **2** to 291.2(2) pm. It indicates a reduction of the Mo–Mo bond order of two in **1** to one in **2** and is easily rationalized: the $2e^-$ donors CO are substituted by the $3e^-$ donors NO. The Mo orbitals which form the MoMo π-bond in **1** become now fully occupied by two electrons each and change to non-bonding. In other words, the Mo centers try to maintain their $18e^-$ configuration. In accordance with the increased Mo–Mo distance the S1Mo1S5 and S1Mo2S5 angles decrease from 113.0(1)° (average) in **1** to 106.5(2)° (average) in **2**. Simultaneously the Mo_2S_2 ring having a dihedral angle of 175.5° further approaches planarity. The corresponding average Mo–S distances are slightly longer in **2** than in **1**. This effect may arise from the difference of two electrons in **1** and **2**. A comparison of selected distances and angles of **1**·THF and **2**·2DMF is given in Table 6.

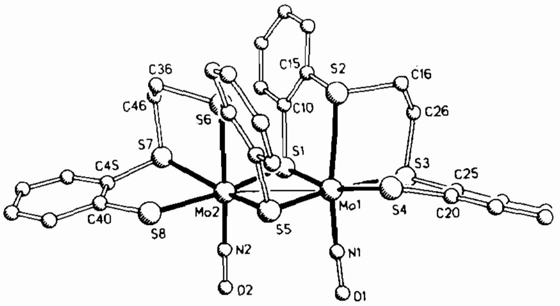


Fig. 4. Molecular structure of $[Mo(NO)(\mu\text{-'}S_4\text{'})]_2\cdot2DMF$ (**2**·2DMF) (H atoms and DMF molecules omitted).

The Mo–S distances in **2** lie between 243.4(5) and 263.2(6) pm and cover the range which was observed for other molybdenum nitrosyl complexes with the 'S$_4$' ligand, e.g. $[Mo(NO)_2(\text{'}S_4\text{'})]$ (244.6–253.8 pm) [11b], $[Mo(NO)NPMePh_2)(\text{'}S_4\text{'})]$ (237.5–263.8 pm) [21] and $[Mo(NO)(NH_2O)(\text{'}S_4\text{'})]$ (246.9–258.8 pm) [22]. Like in **1** the Mo–S(thioether) bonds *trans* to the σ–π ligands display the largest Mo–S distances (260.2(6) pm average), presumably due to the *trans* effect of the NO ligand. The Mo–NO distances in **2** (176.2(21) pm average) are very similar to the corresponding values in $[Mo(NO)(NPMePh_2)(\text{'}S_4\text{'})]$ (176.1(7) pm) and $[Mo(NO)(NH_2O)(\text{'}S_4\text{'})]$ (176.1(3) pm) but they are slightly shorter than in $[Mo(NO)_2(\text{'}S_4\text{'})]$ (183.7(7) pm average) indicating a higher electron density at the Mo^{II} centers carrying only one NO ligand.

Selected spectroscopic data is given in Table 7 .

Conclusions

$[Mo(CO)(\text{'}S_4\text{'})]_2$ (**1**) and $[Mo(NO)(\text{'}S_4\text{'})]_2$ (**2**) were synthesized and characterized by X-ray structure analysis. Both complexes have analogous $[Mo_2(\mu\text{-'}S_4\text{'})_2]$ coordination geometries and represent examples of a new type of $[M(L)(\text{'}S_4\text{'})]_2$ isomers (M = transition metal, L = monodentate ligand). In contrast to $[Fe(CO)(\text{'}S_4\text{'})]_2$ the 'S$_4$'-ligands in **1** ligate the Mo centers in the *cis* as well as the *trans* mode with respect to the thiolato-S atoms, a behavior observed here for the first time. As in $[Fe(CO)(\mu\text{-}$

TABLE 5. Selected interatomic distances (pm) and angles (°) for $[Mo(NO)(\mu\text{-'}S_4\text{'})]_2\cdot2DMF$[a]

Mo(1)–Mo(2)	291.2(2)	Mo(2)–S(1)	246.8(5)
Mo(1)–S(1)	245.4(5)	Mo(2)–S(5)	240.3(5)
Mo(1)–S(2)	263.2(6)	Mo(2)–S(6)	257.1(6)
Mo(1)–S(3)	251.6(6)	Mo(2)–S(7)	251.5(5)
Mo(1)–S(4)	246.6(5)	Mo(2)–S(8)	250.3(6)
Mo(1)–S(5)	243.4(5)	Mo(1)–N(1)	177.4(18)
Mo(2)–N(2)	175.1(21)		
Mo(1)–S(1)–Mo(2)	72.5(1)	Mo(1)–S(5)–Mo(2)	74.0(1)
S(1)–Mo(1)–S(5)	106.3(2)	S(1)–Mo(2)–S(5)	106.8(2)
N(1)–Mo(1)–S(2)	166.7(5)	N(2)–Mo(2)–S(6)	177.5(6)

[a] e.s.d.s are given in parentheses.

TABLE 6. Corresponding distances (pm) and angles (°) for 1·THF and 2·2DMF

		$[Mo(CO)(\mu\text{-}'S_4')]_2 \cdot THF$	$[Mo(NO)(\mu\text{-}'S_4')]_2 \cdot 2DMF$
$d_{Mo1-Mo2}$	(pm)	265.7(1)	291.2(2)
$d_{Mo-S\ (thiolato,\ terminal)}$	(pm)	246.3(2)	248.4(6)
$d_{Mo-S\ (thiolato,\ bridging)}$	(pm)	241.6(2)	244.0(5)
$d_{Mo-S\ (thioether\ trans\ to\ L,\ L=CO,\ NO)}$	(pm)	253.6(2)	260.1(6)
$d_{Mo-S\ (thioether,\ terminal)}$	(pm)	251.2(2)	251.5(6)
S1–Mo1–S5	(°)	112.4(1)	106.3(2)
S1–Mo2–S5	(°)	113.7(1)	106.8(2)
Mo1–Mo2–S1–S5	(°)	173.5	175.5

TABLE 7. Selected spectroscopic data

Complex	$[Mo(CO)(\mu\text{-}'S_4')]_2 \cdot THF$	$[Mo(CO)(\mu\text{-}'S_4')]_2 \cdot CH_2Cl_2$	$[Mo(NO)(\mu\text{-}'S_4')]_2 \cdot 2DMF$
IR[a] (cm^{-1})	1930 ν(CO) 1870 ν(CO)	1935 ν(CO) 1875 ν(CO)	1660 ν(NO) 1605 ν(NO)
^1H NMR[b] (ppm)	8.33–6.8 (m, C_6H_4) 3.71 (m, THF) 3.3–1.6 (m, C_2H_4) 1.85 (m, THF)	8.33–6.8 (m, C_6H_4) 5.33 (CH_2Cl_2) 3.3–1.6 (m, C_2H_4)	[d]
FD-MS (*m/e*)	864 (M^+)	864 (M^+)	868 (M^+)
UV[c] (nm) ε (l mol^{-1} cm^{-1}))	1070 (1150) 603 (10400) 340sh (15000) 270sh (30000) 220sh (83000)		

[a] In KBr. [b] In CD_2Cl_2; m = multiplet. [c] In CH_2Cl_2; sh = shoulder. [d] Not obtained due to low solubility.

'S_4')]$_2$ electronic factors evidently determine which thiolato atoms are used for bridging the Mo centers and connecting two [Mo(CO)('S_4')] fragments, respectively. As a consequence thereof 1 adopts a structure with a very unequal spatial filling of the coordination sphere. The Mo^{II} centers of 1 are electronically and structurally strongly coupled leading to cooperative reactivity of the metal centers and preservation of the $[Mo_2S_8]$ core during CO/NO substitution reactions. Cyclic voltammetry results prove the electronic flexibility of the $[Mo_2S_8]$ core in 1. 1 can take up and release two electrons, the one-electron reductions and oxidations, respectively, being reversible.

A first approximation of a multimetal center in an enzyme is a bimetallic center. In this respect the unusual structure of 1 reminds us of metals held in a fixed position by cysteinate and methionine residues of protein peptide chains.

As is to be expected for metals in proteins, the Mo centers of 1 are chirotopic and additionally the $[Mo_2S_8]$ core is prostereogenic. Thus 1 offers in principle the possibility to study asymmetric reactions at bimetallic centers as well as site specific reactions of polynuclear metal centers towards achiral molecules. The accessibility of vacant sites is demonstrated by the transformation 1 → 2, and the low valent Mo centers make the $[Mo(\mu\text{-}'S_4')]_2$ entity a potential model for enzymes reacting with soft substrates, e.g. CO, N_2, H_2 or NO. These investigations will be the subjects of further reports.

Supplementary material

Further details of X-ray crystal structure analyses have been deposited with the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 and can be obtained by quoting the deposition numbers CSD 320 086 (1·THF) and CSD 320 087 (2·2DMF), the authors' names and the reference.

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