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Transition metal complexes with sulfur ligands Part XCIII*. Synthesis, structure and reactivity of [Mo^{IV}(μ-S)(‘^{bu}S$_4$’)]$_2$ (‘^{bu}S$_4$’$^{2-}$ = 1.2-bis(di(t-butyl)-2-mercaptophenylthio)ethane(2 −))

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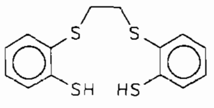
Abstract

In search for model compounds of the active centers of enzymes containing Mo we obtained in DMF the binuclear complexes [MoS(‘S$_4$’)]$_2$ (**1**) (‘S$_4$’$^{2-}$ = 1.2-bis(2-mercaptophenylthio)ethane(2 −)) and [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (**2**) (‘^{bu}S$_4$’$^{2-}$ = 1.2-bis(3.5-di(t-butyl)-2-mercaptophenylthio)ethane(2 −)) from either (a) H_2S and [MoCl$_2$(L)] or (b) H_2S, [MoCl$_4$(MeCN)$_2$] and L-H$_2$ (L = ‘S$_4$’, ‘^{bu}S$_4$’). According to method (b) [MoS(‘N$_2$H$_2$S$_2$’)]$_2$ (**3**) (‘N$_2$H$_2$S$_2$’$^{2-}$ = 1.2-bis(2-mercaptoanilino)ethane(2 −)) could also be prepared, being isolated as the solvate **3**·2DMF. [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$·6CD$_2$Cl$_2$ (**2**·6CD$_2$Cl$_2$) was obtained as single crystals and characterized by X-ray structure analysis (monoclinic space group $P2_1/c$, $Z = 2$, a = 1607.4(16), b = 1540.3(14), c = 1836.6(14) pm, β = 111.43(6)°, R (R_w) = 0.065 (0.056)). **2** contains two enantiochiral [Mo(‘^{bu}S$_4$’)] fragments which are connected via two sulfido bridges and one Mo–Mo bond such that the Mo centers become seven-coordinate. **2** is electrochemically redox active, showing two oxidation and reduction waves each in the cyclic voltammogram (CH$_2$Cl$_2$), but does not react with either N_2H_4 and O_2 or CO and PMe$_3$. Attempts to prepare anionic [Mo(‘N$_2$H$_2$S$_2$’)] complexes with sulfido ligands led to NBu$_4$Cl·(NBu$_4$)$_2$[Mo$_3$(μ_3-S)(μ_2-S$_2$)$_3$S$_6$] (**4**) as the minor by-product. **4** was characterized by X-ray structure analysis (monoclinic space group $P2_1/c$, $Z = 4$, a = 1274.4(7), b = 1322.6(6), c = 4143.8(15) pm, β = 97.30(4)°, R (R_w) = 0.098 (0.078)).

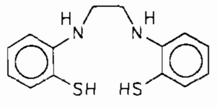
Introduction

Polynuclear Mo and Fe complexes with coordination spheres dominated by sulfur are being intensively investigated because of their model character for the active centers of nitrogenases. Such complexes have been obtained preferably by ‘self-assembly reactions’ of suitable Mo and Fe starting compounds in the presence of sulfide and thiolate ions [2]. The resulting complexes were predominantly clusters of the cubane type and contained only in a few special cases coordination sites that could bind substrates relevant to nitrogenases, e.g. CO or N_2H_4 [3].

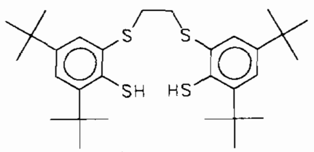
We have been trying to obtain polynuclear Fe and Mo complexes with polydentate thioether thiolate and thiolate amine ligands such as ‘S$_4$’$^{2-}$ (‘S$_4$’$^{2-}$ = 1.2-bis(2-mercaptophenylthio)ethane-2 −)), ‘^{bu}S$_4$’$^{2-}$ (‘^{bu}S$_4$’$^{2-}$ = 1.2-bis(3.5-di(t-butyl)-2-mercaptophenylthio)ethane-(2 −)) and ‘N$_2$H$_2$S$_2$’$^{2-}$ (‘N$_2$H$_2$S$_2$’$^{2-}$ = 1.2-bis(2-mercaptoanilino)ethane(2 −)).



‘S$_4$’-H$_2$



‘N$_2$H$_2$S$_2$’-H$_2$



‘^{bu}S$_4$’-H$_2$

These ligands were intended to model the peptide chains of the protein, which are likely to coordinate the Fe–Mo clusters in nitrogenases as polydentate ligands via their cysteine, methionine and imidazole residues [4].

In the course of these investigations we obtained, *inter alia*, [Fe^{II}(CO)(μ-‘S$_4$’)]$_2$ [5] by thermal decarbonylation of [Fe(CO)$_2$(‘S$_4$’)] and [(μ-S$_2$){Fe^{II}(μ-‘S$_4$’)}$_2$] [6] from FeCl$_2$, ‘S$_4$’$^{2-}$ and elemental sulfur. Both complexes contain chiral [Fe(μ-‘S$_4$’)]$_2$ cores. Similar efforts to prepare chiral Mo complexes with sulfido and ‘S$_4$’$^{2-}$

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*For Part XCII see ref. 1.

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ligands according to eqn. (1) yielded $[Mo^{IV}S(‘S_4’)]_2$ (**1**). **1** proved to be very insoluble, yielded no single crystals and could not be characterized by X-ray structure analysis [7].

$$2[MoCl_2(‘S_4’)] + 2Na_2S \xrightarrow[-4NaCl]{THF/20\,°C} [MoS(‘S_4’)]_2 \qquad (1)$$

The aim of the work reported here was to systematically investigate different reaction conditions for the synthesis of **1** in order to obtain single crystals, and also to react other suitable Mo(IV) precursor complexes with H_2S and ‘S_4’-H_2, ‘$^{bu}S_4$’-H_2 and ‘$N_2H_2S_2$’-H_2.

Experimental

General

All synthetic procedures were carried out under a nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were dried and distilled before use. Spectra were recorded on the following instruments: IR: Zeiss Perkin-Elmer 983; mass spectra: Varian MAT 212 (EI and FD mode). NMR: Jeol FT-JNM-GX 270; UV–Vis: Shimadzu UV-3100 PC. Diffuse reflectance spectra were measured on solid samples on corundum plates (Hoechst Ceram Tec). Magnetic moments were obtained with a Johnson Matthey susceptibility balance. Cyclic voltammograms were recorded on a PAR 264 A potentiostat with ROTEL A equipped with a glassy carbon working electrode, Ag/AgCl reference electrode and Pt counter electrode. Redox potentials were referred to NHE via ferrocene as internal standard. H_2S was purchased from Gerling Holz & Co, CD_2Cl_2 from Aldrich, NBu_4OH (12.5% sol. in MeOH) from Merck; ‘S_4’-H_2 [8], ‘$N_2H_2S_2$’-H_2 [9], ‘$^{bu}S_4$’-H_2 [10], $[MoCl_4(MeCN)_2]$ [11], $[MoCl_2(‘S_4’)]$ [7], $[MoCl_2(‘^{bu}S_4’)]$ [12] and $[MoCl_2(‘N_2H_2S_2’)]$ [13] were prepared by literature methods.

X-ray structure determinations of $[Mo(\mu\text{-}S)(‘^{bu}S_4’)]_2 \cdot 6CD_2Cl_2$ (2·6CD$_2$Cl$_2$) and $NBu_4Cl \cdot (NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (4)

Single crystals of $NBu_4Cl \cdot (NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (**4**) were obtained from the reaction solution; single crystals of $[Mo(\mu\text{-}S)(‘^{bu}S_4’)]_2 \cdot 6CD_2Cl_2$ (**2**·$6CD_2Cl_2$) from a saturated CD_2Cl_2 solution in a NMR tube cooled at −30 °C. Suitable crystals were sealed under N_2 in glass capillaries. The structures were solved by direct methods. Non-hydrogen atoms of **4** were refined anisotropically, the positions of the hydrogen atoms were not determined due to disorder of the n-butyl groups. Non-hydrogen atoms of **2**·$6CD_2Cl_2$ were refined anisotropically; the positions of the phenyl hydrogen atoms were calculated for ideal geometry and restricted during refinement. The methyl and methylene hydrogen atoms were calculated for ideal tetrahedra and rotated around their central carbon atoms during refinement. All hydrogen atoms were refined with common isotropic thermal parameters. Crystallographic data of **2**·$6CD_2Cl_2$ and **4** are summarized in Table 1, the fractional atomic coordinates and isotropic thermal parameters are listed in Table 2.

Syntheses

$[Mo^{IV}S(‘S_4’)]_2$ (1)

(a) A solution of ‘S_4’-H_2 (382 mg, 1.23 mmol) in 30 ml of DMF was saturated with H_2S and added dropwise to a light brown solution of $[MoCl_4(MeCN)_2]$ (393 mg, 1.23 mmol) in 30 ml of DMF. The resulting brown suspension was stirred for 2 days, the insoluble precipitate was separated, washed with 50 ml of MeOH (50 °C), 30 ml of n-pentane, and dried *in vacuo* for 1 day. Recrystallization was not possible. Yield 170 mg (32%).

Anal. Calc. for $C_{28}H_{24}Mo_2S_{10}$ (872.98): C, 38.5; H, 2.8. Found: C, 38.7; H, 3.0%.

(b) A violet–brown suspension of $[MoCl_2(‘S_4’)]$ (512 mg, 1.08 mmol) in 50 ml of DMF was saturated with H_2S. The resulting brown suspension was stirred for 2 days, the insoluble precipitate was filtered off and treated according to method (a). Yield 205 mg (44%).

Anal. Calc. for $C_{28}H_{24}Mo_2S_{10}$ (872.98): C, 38.5; H, 2.8; S, 36.7. Found: C, 38.3; H, 2.8; S, 36.2%.

$[Mo^{IV}(\mu\text{-}S)(‘^{bu}S_4’)]_2$ (2)

(a) A solution of ‘$^{bu}S_4$’-H_2 (685 mg, 1.28 mmol) in 15 ml of DMF was saturated with H_2S and added dropwise to a light brown solution of $[MoCl_4(MeCN)_2]$ (409 mg, 1.28 mmol) in 20 ml of DMF. The resulting brown reaction mixture was stirred for 2 h and cooled to −30 °C for 2 days. The brown precipitate was separated and recrystallized from CS_2 (20 → −78 °C) yielding reddish brown microcrystals. When dried *in vacuo*, they weathered to give a brown powder. Yield 415 mg (49%).

Anal. Calc. for $C_{66}H_{80}Mo_2S_{10}$ (1321.84): C, 54.5; H, 6.7; S, 24.2. Found: C, 54.5; H, 7.0; S, 23.8%.

(b) When a dark violet solution of $[MoCl_2(‘^{bu}S_4’)]$ (472 mg, 0.67 mmol) in 15 ml of DMF was saturated with H_2S, its colour changed to brown. The solution was stirred for 90 min and cooled to −30 °C for 2 days. The brown precipitate was separated and treated according to method (a). Yield 320 mg (72%).

Anal. Calc. for $C_{66}H_{80}Mo_2S_{10}$ (1321.84): C, 54.5; H, 6.7; S, 24.2. Found: C, 54.5; H, 6.9; S, 23.9%.

^1H NMR (270 MHz, CD_2Cl_2:CS_2 = 1:2, ppm relative to TMS): 7.93 (d, C_6H_2, 2H), 7.84 (d, C_6H_2, 2H), 7.28 (d, C_6H_2, 2H), 7.16 (d, C_6H_2, 2H); 3.62 (m, C_2H_4, 8H); 1.44 (s, C_4H_9, 18H), 1.35 (s, C_4H_9, 18H), 1.05 (s, C_4H_9, 18H), 1.03 (s, C_4H_9, 18H). $^{13}C\{^1H\}$ NMR (67.94 MHz,

TABLE 1. Summary of crystallographic data and data collection procedures of $[Mo(\mu\text{-}S)(\text{'}^{bu}S_4\text{'})]_2\cdot 6CD_2Cl_2$ (**2**·$6CD_2Cl_2$) and $NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (**4**)

Compound	$[Mo(\mu\text{-}S)(\text{'}^{bu}S_4\text{'})]_2\cdot 6CD_2Cl_2$	$NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$
Formula	$C_{66}H_{88}Cl_{12}D_{12}Mo_2S_{10}$	$C_{48}H_{108}ClMo_3N_3S_{13}$
M_r	1843.5	1467.52
Crystal size (mm)	0.8×0.4×0.4	0.4×0.3×0.2
Space group	$P2_1/c$	$P2_1/c$
Crystal system	monoclinic	monoclinic
a (pm)	1607.4(16)	1274.4(7)
b (pm)	1540.3(14)	1322.6(6)
c (pm)	1836.6(14)	4143.8(15)
β (°)	111.43(6)	97.30(4)
Cell volume (pm^3)	4231(6)×10^6	6928(5)×10^6
Molecules/unit cell	2	4
ρ_{calc} (g cm^{-3})	1.45	1.41
μ (cm^{-1})	9.62	9.7
Diffractometer	Siemens P4	Nicolet R3m/V
Radiation (pm)	Mo Kα (71.073)	Mo Kα (71.073)
Temperature of measurement (K)	173	200
Scan technique	ω scan	ω scan
2Θ Range (°)	3–48	3–54
Scan speed (° min^{-1})	3–29	3–15
Reflections collected	8201	10017
Independent reflections	6614	8416
Observed reflections	4072	4905
σ-Criterion	$F > 4\sigma(F)$	$F > 6\sigma(F)$
Program	SHELXTL-PLUS	SHELXTL-PLUS
R; R_w	0.065; 0.056	0.098; 0.078
Refined parameters	407	307

CD_2Cl_2:CS_2 = 1:2, ppm relative to TMS): 155.0, 153.6, 149.0, 148.9, 147.8, 147.5, 133.6, 133.0, 127.7, 127.1, 125.6, 125.4 (C_6H_2); 45.1, 44.6 (C_2H_4); 37.3, 37.0, 34.7, 34.6 ($C(CH_3)_3$); 31.8, 31.6, 30.1 ($C(CH_3)_3$).

$[Mo^{IV}S(\text{'}N_2H_2S_2\text{'})]_2\cdot 2DMF$ (3·2DMF)

A yellow solution of '$N_2H_2S_2$'-H_2 (456 mg, 1.65 mmol) in 30 ml of DMF was saturated with H_2S and added dropwise to a light brown solution of $[MoCl_4(MeCN)_2]$ (529 mg, 1.65 mmol) in 30 ml of DMF. The colour of the mixture changed to black and a solid precipitated. The suspension was stirred for 3 days, the insoluble brownish black precipitate was separated, washed with 1 ml of DMF, 10 ml of MeOH, and dried *in vacuo* for 1 day. It could not be recrystallized and was identified as the solvate **3**·2DMF by elementary analysis and IR spectroscopy. Yield 170 mg (18%).

Anal. Calc. for $C_{34}H_{42}Mo_2N_6O_2S_6$ (950.98): C, 42.9; H, 4.5; N, 8.8; S, 20.2. Found: C, 43.0; H, 4.6; N, 8.7; S, 20.0%.

$NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (4)

A violet–black suspension of $[MoCl_2(\text{'}N_2H_2S_2\text{'})]$ (428 mg, 0.97 mmol) in 50 ml of THF was saturated with H_2S, stirred for 1 day, and combined with 2.4 ml (0.97 mmol) of NBuOH/MeOH, whereupon its colour gradually turned to light brown. After 2 days the mixture was filtered, the brown filtrate was reduced to 15 ml in volume and cooled to −30 °C for 28 days. The small amount of deep brown crystals which precipitated was separated, washed with 4 ml of Et_2O, and dried *in vacuo* for 1 day. Yield 5 mg.

Results and discussion

Syntheses of $[Mo^{IV}S(L)]_2$ (L = 'S$_4$' (1), '$^{bu}S_4$' (2), '$N_2H_2S_2$' (3)

Diamagnetic, brown $[Mo^{IV}S(\text{'}S_4\text{'})]_2$ (**1**) formed according to eqn. (2) as well as eqn. (3) though in lower yields.

$$2[MoCl_2(\text{'}S_4\text{'})] + H_2S_{exc.} \xrightarrow[-4HCl]{DMF/20\ °C} \underset{\mathbf{1}}{[MoS(S_4\text{'})]_2} \qquad (2)$$

$$2[MoCl_4(MeCN)_2] + H_2S_{exc.} + 2\text{'}S_4\text{'}\text{-}H_2 \xrightarrow[-8HCl]{DMF/20\ °C} \underset{\mathbf{1}}{[MoS(\text{'}S_4\text{'})]_2} \qquad (3)$$

While the syntheses of **1** according to eqns. (1) and (2) take place in the heterogeneous phase, the reaction according to eqn. (3) proceeds in the homogeneous phase. The resulting **1** obtained by the three different methods of preparation, however, proved to be equally insoluble and could be neither recrystallized nor completely characterized.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\mathrm{pm}^2 \times 10^{-1}$) of $[\mathrm{Mo}(\mu\text{-S})(\text{‘}^{\mathrm{bu}}\mathrm{S}_4\text{’})]_2\cdot 6\mathrm{CD_2Cl_2}$ (**2**$\cdot 6\mathrm{CD_2Cl_2}$) (a) and $\mathrm{NBu_4Cl}\cdot(\mathrm{NBu_4})_2[\mathrm{Mo_3}(\mu_3\text{-S})(\mu_2\text{-S}_2)_3\mathrm{S_6}]$ (**4**) (b)

Atom	x	y	z	U_{eq}[a]
(a)				
Mo1	9738(1)	870(1)	4926(1)	20(1)
S1	8878(2)	1022(2)	5753(1)	26(1)
S2	8466(2)	1784(2)	4055(1)	23(1)
S3	10316(2)	2296(2)	5590(1)	26(1)
S4	10409(2)	1465(2)	4055(1)	24(1)
S5	10890(2)	237(2)	5929(1)	23(1)
C15	7633(6)	1791(6)	4484(5)	25(4)
C14	6824(6)	2165(6)	4032(6)	27(4)
C13	6141(6)	2230(7)	4307(6)	29(4)
C12	6340(6)	1954(6)	5084(6)	34(4)
C11	7151(6)	1602(6)	5565(6)	25(4)
C10	7823(6)	1490(6)	5234(6)	25(4)
C110	7299(7)	1383(7)	6427(6)	32(4)
C111	8042(7)	1936(8)	6978(6)	47(5)
C112	7497(7)	425(7)	6584(6)	50(5)
C113	6466(7)	1584(8)	6629(6)	54(5)
C130	5211(6)	2573(7)	3826(6)	37(4)
C131	5164(7)	2996(9)	3066(6)	66(6)
C132	4565(7)	1798(8)	3636(7)	58(6)
C133	4906(7)	3239(8)	4287(7)	66(6)
C25	11067(6)	2712(6)	5178(5)	25(4)
C24	11630(6)	3384(6)	5573(5)	27(4)
C23	12213(6)	3757(6)	5289(5)	26(4)
C22	12166(6)	3500(6)	4537(5)	28(4)
C21	11603(5)	2827(5)	4123(5)	17(3)
C20	11069(5)	2393(6)	4470(5)	23(4)
C210	11566(6)	2625(6)	3272(5)	26(4)
C211	11936(6)	1736(6)	3251(6)	36(4)
C212	10594(6)	2700(7)	2697(5)	38(4)
C213	12107(7)	3269(7)	2995(6)	37(4)
C230	12886(7)	4467(7)	5717(6)	37(5)
C231	13809(7)	4263(8)	5740(7)	65(6)
C232	12578(8)	5327(7)	5293(8)	68(6)
C233	12930(10)	4593(10)	6545(7)	116(9)
C16	8900(6)	2890(6)	4281(5)	27(4)
C26	9384(6)	3025(6)	5147(5)	32(4)
C1	9927(9)	249(9)	2193(7)	78(7)
Cl1	8900(2)	703(3)	1879(2)	77(2)
Cl2	10267(3)	−123(3)	1445(2)	90(2)
C2	3224(10)	5398(12)	2695(8)	135(10)
Cl3	3537(3)	5659(4)	3678(2)	117(3)
Cl4	4031(3)	5429(3)	2351(2)	110(2)
C3	2991(9)	4261(12)	494(8)	102(8)
Cl5	4005(3)	4461(4)	395(3)	146(3)
Cl6	3052(3)	3451(3)	1152(3)	144(3)
(b)				
Mo1	−889(1)	5413(1)	1301(1)	39(1)
Mo2	347(1)	6798(1)	1677(1)	38(1)
Mo3	42(1)	7007(2)	1009(1)	40(1)
S1	−359(4)	3635(4)	1262(1)	47(2)
S2	−2671(3)	4599(4)	1269(1)	49(2)
S3	2103(3)	6514(4)	1971(1)	46(2)
S4	245(4)	7817(4)	2173(1)	48(2)
S5	1496(3)	6792(4)	673(1)	48(2)
S6	−497(4)	8325(4)	583(1)	50(2)
S7	−458(3)	5289(4)	1904(1)	47(2)
S8	−1459(3)	6412(4)	1728(1)	43(2)
S9	1194(3)	8130(4)	1380(1)	48(2)
S10	−398(3)	8254(4)	1389(1)	44(2)
S11	−1015(4)	5666(4)	702(1)	48(2)
S12	−1814(3)	6659(4)	956(1)	45(2)
S13	925(3)	5671(4)	1299(1)	42(2)
Cl1	−2672(3)	8157(4)	1397(1)	58(2)
N100	5468(12)	1465(15)	3669(4)	65(8)
C111	6225(14)	599(20)	3706(5)	60(10)
C112	5718(18)	−454(22)	3746(7)	109(14)
C113	6541(32)	−1407(41)	3823(9)	208(26)
C114	6675(29)	−1430(33)	3527(11)	187(26)
C121	4818(13)	1537(20)	3955(5)	75(11)
C122	5490(15)	1618(24)	4296(5)	107(14)
C123	4633(23)	1612(28)	4548(7)	128(17)
C124	4300(25)	2694(30)	4544(8)	151(19)
C131	4606(13)	1380(19)	3369(5)	70(10)
C132	5110(15)	1262(21)	3057(6)	91(12)
C133	4210(15)	1439(23)	2770(5)	102(13)
C134	4701(20)	1283(32)	2457(6)	183(21)
C141	6146(16)	2400(21)	3644(6)	82(11)
C142	5531(18)	3405(21)	3602(8)	101(14)
C143	6178(27)	4222(28)	3450(16)	256(36)
C144	5687(32)	5054(44)	3372(12)	271(37)
N200	1718(14)	6193(16)	3091(5)	76(9)
C211	2002(19)	5134(20)	2996(6)	86(12)
C212	1615(18)	4834(18)	2638(7)	77(12)
C213	2460(45)	4005(34)	2552(10)	204(30)
C214	1942(28)	3658(28)	2338(15)	261(36)
C221	560(19)	6418(20)	2999(6)	89(12)
C222	−168(24)	5614(24)	3141(8)	135(17)
C223	−1382(37)	5836(32)	3054(9)	187(25)
C224	−1523(21)	5785(32)	2731(9)	166(21)
C231	2353(17)	6909(19)	2896(5)	63(10)
C232	2164(17)	7973(22)	2981(6)	84(12)
C233	3408(56)	8613(36)	2892(7)	160(41)
C234	3033(31)	8599(31)	2627(13)	260(29)
C241	1967(21)	6272(20)	3468(5)	92(12)
C242	3125(23)	6104(23)	3604(7)	134(16)
C243	2854(44)	5807(55)	4006(7)	207(62)
C244	4248(32)	6061(34)	4085(7)	254(27)
N300	959(13)	7252(13)	4679(4)	61(8)
C311	122(16)	7859(17)	4831(5)	62(10)
C312	−500(16)	8554(17)	4587(5)	64(10)
C313	−1357(16)	9121(17)	4756(5)	64(10)
C314	−2258(17)	8374(22)	4825(6)	100(13)
C321	1853(15)	7921(16)	4561(5)	54(9)
C322	2491(16)	8509(17)	4854(5)	70(10)
C323	3329(16)	9172(19)	4717(6)	82(11)
C324	4154(16)	8569(21)	4551(6)	98(12)
C331	516(17)	6648(16)	4368(4)	59(9)
C332	−409(20)	5953(20)	4434(5)	95(12)
C333	−908(22)	5544(21)	4096(7)	102(14)
C334	−1633(25)	6241(30)	3958(8)	167(21)
C341	1415(17)	6473(18)	4950(5)	76(10)
C342	2331(20)	5811(21)	4844(6)	109(14)
C343	2606(23)	5049(32)	5118(9)	149(20)
C344	3287(37)	5033(47)	5242(16)	472(49)

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

Efforts to obtain a sulfido complex with the isoelectronic '$N_2H_2S_2$' ligand provided dark brown, diamagnetic $[Mo^{IV}S('N_2H_2S_2')]_2$ (**3**) as the solvate **3**·2DMF according to eqn. (4).

$$2[MoCl_4(MeCN)_2] + H_2S_{exc.} + 2'N_2H_2S_2'\text{-}H_2 \xrightarrow[-8HCl]{DMF/20\,°C}$$

$$\underset{\mathbf{3}\cdot 2DMF}{[MoS('N_2H_2S_2')]_2\cdot 2DMF} + \text{other products} \qquad (4)$$

The DMF solvate molecules could not be removed, even when **3**·2DMF was heated in boiling MeOH. **3**·2DMF is as insoluble as **1** in all common solvents.

Only when the t-butyl derivative of the 'S_4' ligand, '$^{bu}S_4$'-H_2, was used, could a soluble complex be obtained. $[Mo(\mu\text{-}S)('^{bu}S_4')]_2$ (**2**) formed according to eqns. (5) or (6).

$$2[MoCl_4(MeCN)_2] + H_2S_{exc.} + 2'^{bu}S_4'\text{-}H_2 \xrightarrow[-8HCl]{DMF/20\,°C}$$

$$\underset{\mathbf{2}}{[Mo(\mu\text{-}S)('^{bu}S_4')]_2} \qquad (5)$$

$$2[MoCl_2('^{bu}S_4')] + H_2S_{exc.} \xrightarrow[-4HCL]{DMF/20\,°C}$$

$$\underset{\mathbf{2}}{[Mo(\mu\text{-}S)('^{bu}S_4')]_2} \qquad (6)$$

Brown **2** is diamagnetic and soluble in CS_2, CH_2Cl_2 and DMF. From a CD_2Cl_2 solution, which had been used for recording NMR spectra, reddish brown single crystals of the solvate **2**·$6CD_2Cl_2$ were obtained allowing its X-ray structure determination.

When we tried to convert $[MoCl_2('N_2H_2S_2')]$ into anionic sulfido complexes by addition of NBu_4OH according to eqn. (7), we did not obtain any $[Mo('N_2H_2S_2')]$ complexes, but in minor amounts single crystals of $NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (**4**), which was characterized by X-ray structure analysis.

$$[MoCl_2('N_2H_2S_2')] + H_2S_{exc.} + NBu_4OH \xrightarrow{THF/20\,°C}$$

$$\text{viscous products} +$$

$$\underset{\mathbf{4}}{NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]} \qquad (7)$$

X-ray structure determinations of $NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (4) and $[Mo(\mu\text{-}S)('^{bu}S_4')]_2\cdot 6CD_2Cl_2$ (2·$6CD_2Cl_2$)

Figure 1 shows the molecular structure, Table 3 summarizes selected distances and angles of the $[Mo_3S_{13}]^{2-}$ cluster of $NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2S_2)_3S_6]$ (**4**).

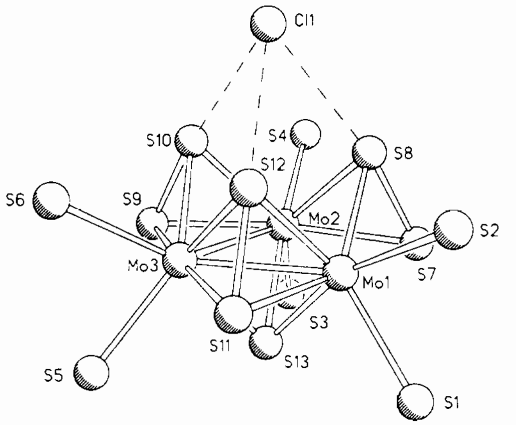

Fig. 1. Molecular structure of the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]^{2-}$ cluster of **4** including the external Cl^- ion.

TABLE 3. Selected interatomic distances (pm) and angles (°) for $NBu_4Cl\cdot(NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (**4**)[a]

Mo1–Mo2	276.3(3)	Mo1–Mo3	277.2(3)
Mo2–Mo3	275.9(3)	Mo1–S13	233.9(5)
Mo1–S1	245.8(6)	Mo1–S2	250.2(5)
Mo1–S7	249.2(5)	Mo1–S11	248.9(5)
Mo1–S8	239.4(6)	Mo1–S12	239.1(5)
S7–S8	203.1(7)	S1–S2	322.0
Cl1–S8	301.2	Cl1–S10	290.6
Cl1–S12	299.4		
Mo2–Mo1–Mo3	59.8(1)	Mo1–Mo3–Mo2	59.9(1)
Mo1–Mo2–Mo3	60.3(1)	Mo1–S13–Mo2	72.3(2)
Mo2–Mo1–S1	122.0(1)	Mo3–Mo1–S1	124.2(1)
Mo2–Mo1–S2	139.8(1)	Mo3–Mo1–S2	137.8(1)
Mo2–Mo1–S7	56.1(1)	Mo3–Mo1–S11	55.9(1)
Mo2–Mo1–S11	115.6(1)	Mo3–Mo1–S7	115.8(1)
Mo2–Mo1–S12	94.7(1)	Mo3–Mo1–S8	95.2(2)
Mo2–Mo1–S13	54.0(1)	Mo3–Mo1–S13	53.7(1)
Mo2–Mo1–S8	54.7(1)	Mo3–Mo1–S12	54.6(1)
S1–Mo1–S2	80.8(2)	S1–Mo1–S13	81.9(2)
S7–Mo1–S8	49.1(2)	S11–Mo1–S12	49.2(2)
S8–Mo1–S12	83.6(2)	S7–Mo1–S11	170.2(2)
S1–Mo1–S7	88.6(2)	S1–Mo1–S11	92.6(2)
S1–Mo1–S8	133.5(2)	S1–Mo1–S12	137.6(2)
S2–Mo1–S7	96.2(2)	S2–Mo1–S11	93.6(2)
S2–Mo1–S8	85.3(2)	S2–Mo1–S12	83.7(2)
S8–Mo1–S11	132.5(2)	S7–Mo1–S12	132.3(2)
S1–Mo1–S13	81.9(2)	S2–Mo1–S13	162.6(2)
S7–Mo1–S13	85.5(2)	S11–Mo1–S13	85.1(2)
S8–Mo1–S13	108.4(2)	S12–Mo1–S13	108.0(2)
Mo1–S7–Mo2	67.5(1)	Mo1–S8–Mo2	70.5(1)
Mo1–S7–S8	62.9(2)	Mo1–S8–S7	68.0(2)
S8–Cl1–S10	65.4	S10–Cl1–S12	65.2
S8–Cl1–S12	64.2		

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

The $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]^{2-}$ dianion of **4** possesses C_1 symmetry; corresponding distances and angles of the three $[Mo(\mu_2\text{-}S_2)S_2]$ fragments, however, are so similar that approximately C_{3v} symmetry results.

In a first approximation, the $[Mo_3S_{13}]^{2-}$ dianion of **4** exhibits a structure identical to that of the $[Mo^{IV}_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3]^{2-}$ dianion described by Müller *et al.* [14]. Unlike the latter, however, **4** contains a Cl^- ion that asymmetrically caps three of the S atoms, and in addition, **4** does not contain terminal non-bridging S_2^{2-} ligands.

Each Mo atom of $NBu_4Cl \cdot (NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$ (**4**) is coordinated by seven S and two Mo atoms. The Mo centers form the base of a trigonal pyramid topped by S13. The mean Mo–Mo distance (276.5 pm) is consistent with Mo–Mo single bonds and the mean Mo–S13 distance (234.3 pm) with Mo–S double bonds. Apart from the Mo–Mo bonds, two Mo centers are each bridged via one S_2 unit, the S7, S9 and S11 atoms of these S_2 units lying in the Mo_3 plane, the S8, S10 and S12 atoms above it. The average S–S distance of the S_2 units (203.5 pm) indicates S–S single bonds, i.e. disulfido bridges. The mean Mo–S distances of the resulting Mo_2S_2 units are 248.3 and 239.4 pm, consistent with Mo–S single bonds and partial Mo–S double bonds, respectively.

The most important distinction between the cluster anion of **4** and the $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3]^{2-}$ cluster, described by Müller *et al.* is the S^{2-} character of the six terminal S ligands in **4**. The average Mo–S(term.) distance in **4** (248.1 pm) indicates Mo–S single bonds. The mean S–S distance of S1–S2, S3–S4 and S5–S6 (322.0 pm) is so large that bonds between the respective S atoms can be ruled out. In contrast, the corresponding S–S distances in the cluster described by Müller are *c.* 206 pm indicating S–S bonds and S_2^{2-} entities. Accordingly, the cluster anion of **4** and Müller's anion formally contain Mo(VI) and Mo(IV) centers, respectively, and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]^{2-}$ and $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(S_2)_3]^{2-}$ can be considered as redox isomers [15]. The mean distance between the Cl atom and S8, S10 and S12, respectively (297.1 pm), is larger than the sum of the van der Waals radii of Cl and S (265 pm) [16]. Therefore, the most appropriate formulation of **4** is the double salt $NBu_4Cl \cdot (NBu_4)_2[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3S_6]$.

Figure 2 shows the molecular structure of $[Mo(\mu\text{-}S)(‘^{bu}S_4’)]_2$ (**2**); selected distances and angles are summarized in Table 4. **2** possesses crystallographically imposed C_i symmetry and contains two enantiochiral $[Mo(‘^{bu}S_4’)]$ fragments connected via two sulfido bridges. The corresponding distances and angles of the two $[Mo(‘^{bu}S_4’)]$ fragments are so similar that approximately C_{2h} symmetry results, the C_2 axis running through the Mo centers.

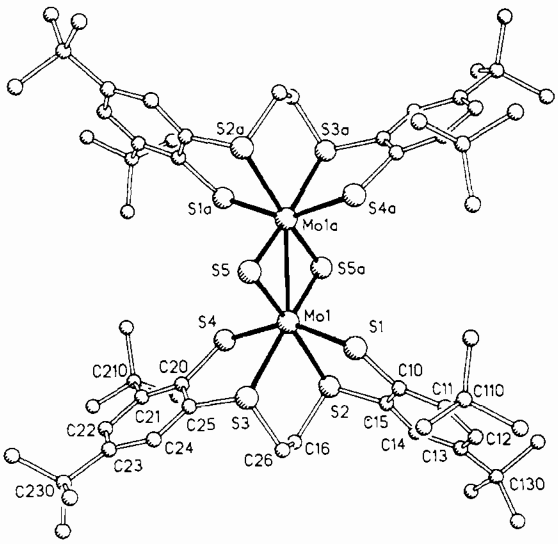

Fig. 2. Molecular structure of $[Mo(\mu\text{-}S)(‘^{bu}S_4’)]_2 \cdot 6CD_2Cl_2$ ($\mathbf{2} \cdot 6CD_2Cl_2$) (H atoms and CD_2Cl_2 omitted).

TABLE 4. Selected interatomic distances (pm) and angles (°) for $[Mo(\mu\text{-}S)(‘^{bu}S_4’)]_2 \cdot 6CD_2Cl_2$ ($\mathbf{2} \cdot 6CD_2Cl_2$)[a]

Mo1–Mo1a	279.2(3)	S5–S5a	363.9
Mo1–S1	240.9(4)	Mo1–S4	241.3(4)
Mo1–S2	251.6(3)	Mo1–S3	252.0(4)
Mo1–S5	229.8(3)	Mo1–S5a	228.7(3)
S1–C10	176.7(9)	S4–C20	177.7(9)
S2–C15	178.4(11)	S3–C25	176.3(11)
S2–C16	183.1(10)	S3–C26	181.0(10)
C10–C15	137.8(14)	C20–C25	139.1(14)
C16–C26	150.8(12)		
S5–Mo1–S5a	105.0(1)	Mo1–S5–Mo1a	75.0(1)
Mo1a–Mo1–S1	104.8(1)	Mo1a–Mo1–S4	103.7(1)
Mo1a–Mo1–S2	138.2(1)	Mo1a–Mo1–S3	138.1(1)
S1–Mo1–S2	80.0(1)	S3–Mo1–S4	79.3(1)
S1–Mo1–S3	78.8(1)	S2–Mo1–S4	79.7(1)
S1–Mo1–S4	151.5(1)	S2–Mo1–S3	83.7(1)
S2–Mo1–S5	167.6(1)	S3–Mo1–S5a	166.9(1)
S1–Mo1–S5	90.9(1)	S4–Mo1–S5	105.5(1)
S1–Mo1–S5a	107.2(1)	S4–Mo1–S5a	91.1(1)
Mo1–S1–C10	111.0(4)	Mo1–S4–C20	111.3(4)
Mo1–S2–C15	106.8(3)	Mo1–S3–C25	107.4(3)
Mo1–S2–C16	102.9(3)	Mo1–S3–C26	103.0(3)
S2–C16–C26	112.0(7)	S3–C26–C16	114.4(7)

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

The Mo centers are each pseudooctahedrally surrounded by two S(thioether), two S(thiolate) and two S(sulfide) atoms. Since the Mo–Mo distance of 279.2(3) pm indicates an Mo–Mo single bond, the coordination geometry of the Mo centers may be alternatively described as distorted pentagonal bipyramidal. Seven-coordinate Mo centers have also been found in the related Mo(II) complexes $[Mo(CO)_2(PMe_3)(‘S_4’)]$ [17] and $[Mo(NO)(\mu\text{-}‘S_4’)]_2$ [18]. The planar Mo_2S_2 ring in **2** is typical of μ-sulfido complexes containing Mo_2S_2 units [19]. The dihedral angle between the $[Mo_2(\mu\text{-}S)_2]$ plane and the [Mo1–S2–S3] plane is 9°.

The interatomic distances within the ‘$^{bu}S_4$’ ligands do not exhibit anomalies. The mean Mo–S(sulfide) and Mo–S(thiolate) distances (239.2 and 241.1 pm) indicate partial Mo–S double bond character due to sulfur π-donor effects as in $[(\mu\text{-}S)_2\{Mo(S_2C_2(CO_2Me)_2)_2\}_2]^{2-}$ [20] and $[(\mu\text{-}S)_2\{Mo(CN)_4\}_2]^{4-}$ [21]. On the other hand, the average Mo–S(thioether) distances in **2** (251.8 pm) are clearly larger and indicate Mo–S single bonds. Such differences between Mo–S(thiolate) and Mo–S(thioether) distances have also been found in other ‘S$_4$’ or ‘^{bu}S$_4$’ complexes, e.g. [Mo(NO)$_2$(‘S$_4$’)] [22], and attributed to *trans* effects of the σ-donor π-acceptor coligands. The results obtained here with [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (**2**) and previously with the related [(μ-O){MoO(‘^{bu}S$_4$’)}$_2$] [23] indicate that *trans* effects of σ-donor π-donor coligands may also be responsible for these different Mo–S(thiolate) and Mo–S(thioether) distances.

Spectra and electrochemistry of [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (2)

2 only exhibits the typical ‘^{bu}S$_4$’ bands in the KBr-IR spectrum and, unlike [(μ-S$_2$){Fe(μ-‘S$_4$’)}$_2$] [6] and [(μ-S$_2$){Ru(PPh$_3$)(‘S$_4$’)}$_2$] [24], does not show any intense NIR absorption bands in the UV–Vis–NIR spectrum. The two [MoS(‘^{bu}S$_4$’)] fragments which form **2** are enantiochiral and possess C_1 symmetry only. Accordingly, the t-butyl groups give rise to four singlets in the ^{1}H NMR spectrum (Fig. 3).

Like [(μ-S$_2$){Fe(μ-‘S$_4$’)}$_2$ [6], [Mo(NO)(‘S$_4$’)]$_2$ [18] and numerous metal sulfur clusters [2], [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (**2**) is electrochemically redox active. The cyclic voltammogram of **2** exhibits two oxidation and reduction waves each (Fig. 4). The oxidations at +0.82 as well as at +0.20 and the reduction at −1.12 V are quasi-reversible one-electron processes leading to [**2**]$^{2+}$, [**2**]$^+$ and [**2**]$^-$, respectively. The irreversible reduction at −1.81 V is consistent with the formation of unstable [**2**]$^{2-}$, whose decomposition product is oxidized at −1.24 V.

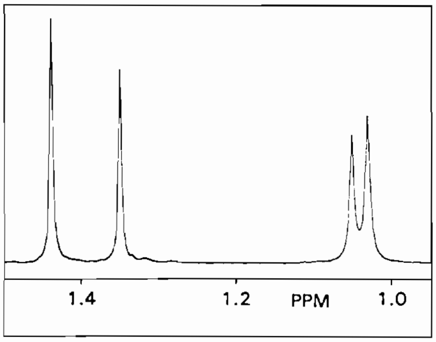

Fig. 3. t-Butyl region of the ^{1}H NMR spectrum of **2** (270 MHz; in CD$_2$Cl$_2$:CS$_2$ = 1:2).

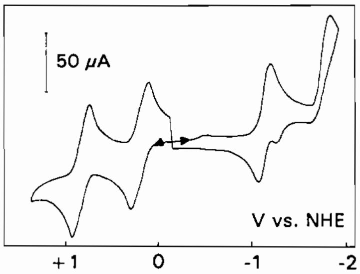

Fig. 4. Cyclic voltammogram of **2** (CH$_2$Cl$_2$, 10^{-3} M in complex, 10^{-1} M in NBu$_4$ClO$_4$; scan rate 200 mV s^{-1}).

Reactivity of [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (2)

Although **2** is easily oxidized electrochemically, it does not react with oxygen. It is also unreactive towards diluted mineral acids, CO, PMe$_3$ and N$_2$H$_4$, and thermally so stable that it withstands heating in boiling toluene for 3 days. A very slow reaction was observed between **2** and the 3*e*$^-$ donor NO, but the products could not be characterized further.

The chemical inertness of [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (**2**) may be traced back to the commonly high stability of the Mo$_2$S$_2$ rings, the coordinative saturation of the Mo centers, and their shielding by the sterically demanding ‘^{bu}S$_4$’ ligands.

Conclusions

Reactions of [MoCl$_4$(MeCN)$_2$] with H$_2$S and the tetradentate ligands L-H$_2$ (L = ‘S$_4$’ (**1**), ‘^{bu}S$_4$’ (**2**), ‘N$_2$H$_2$S$_2$’ (**3**)) afforded the binuclear [MoS(L)]$_2$ complexes. The syntheses could be carried out stepwise by isolating first the [MoCl$_2$(L)] complexes (L = ‘S$_4$’ (**1**), ‘^{bu}S$_4$’ (**2**)). Attempts to synthesize anionic [Mo(‘N$_2$H$_2$S$_2$’)] sulfido complexes yielded in minor amounts NBu$_4$Cl·(NBu$_4$)$_2$[Mo$_3$(μ_3-S)(μ_2-S$_2$)$_3$S$_6$] (**4**), which was characterized by X-ray structure analysis. The cluster anion of **4** was identified as a redox isomer of the previously reported [Mo$_3$(μ_3-S)(μ_2-S$_2$)$_3$(S$_2$)$_3$]$^{2-}$ dianion.

Well soluble [Mo(μ-S)(‘^{bu}S$_4$’)]$_2$ (**2**) could be completely characterized by spectra and X-ray structure analysis. **2** is electrochemically redox active, but chemically nearly inert towards oxidizing and reducing small molecules or 2*e*$^-$ donor ligands, e.g. O$_2$, N$_2$H$_4$, CO or PMe$_3$. **2** formally contains 16-electron Mo centers, whose electron deficit might be reduced by sulfur–metal p$_\pi$–d$_\pi$ donor bonds. The inertness of **2** can further be traced back to coordinative saturation of the Mo centers and their sterical shielding by the bulky ‘^{bu}S$_4$’ ligands.

Supplementary material

Further details of the X-ray crystal structure analyses can be obtained from the Fachinformationszentrum Karlsruhe GmbH, W-7514 Eggenstein-Leopoldshafen 2, by citing the deposition Nos. CSD 320437 ([Mo(μ-S)(‘^{bu}S$_4$’)]$_2$·6CD$_2$Cl$_2$, **2**·6CD$_2$Cl$_2$), CSD 320438 (NBu$_4$Cl·(NBu$_4$)$_2$[Mo$_3$(μ_3S)(μ_2-S$_2$)$_3$S$_6$], **4**), the authors, and the reference.

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