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Transition metal complexes with sulfur ligands
Part LXVIII*. Side-on N_2H_3 and N_2HR_2 in metal sulfur complexes: $[M(NHNR_2)(NO)(\text{'}S_4\text{'})]$ ($M = Mo$, W; $R = H$, CH_3; $\text{'}S_4\text{'}^{2-} =$ 1,2-bis(2-mercaptophenylthio)ethane(2 −))

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Abstract

N_2H_3, a potential intermediate of N_2 reduction, has been stabilized by metal sulfur ligand fragments. The reaction of $[M(Cl)(NO)(\text{'}S_4\text{'})]$ ($M = Mo$ (**1**), W (**2**); $\text{'}S_4\text{'}^{2-} =$ 1.2-bis(2-mercaptophenylthio)ethane-(2 −)) with hydrazines yields the hydrazinyl complexes $[M(NHNR_2)(NO)(\text{'}S_4\text{'})]$ ($M = Mo$, $R = H$ (**3a**), Me (**3b**); $M = W$, $R = H$ (**4a**), Me (**4b**)). **3b** was characterized by X-ray structure analysis (monoclinic, $P2_1/c$, $Z = 4$, $a = 1162.3$, $b = 1228.4$, $c = 1476.3$ pm, $\beta = 98.47°$, $R(R_W) = 0.087(0.072)$). The molybdenum centre is surrounded by four sulfur and three nitrogen atoms in a distorted pentagonal pyramid. The ^{95}Mo NMR chemical shift of **3b** is compatible with a Mo(II) centre indicating that in the reaction between **1** and NH_2NMe_2 reduction of **1** takes place and the $NHNR_2$ ligands must be regarded as neutral hydrazinyl residues. The parent $[M(NHNH_2)(NO)(\text{'}S_4\text{'})]$ complexes are very labile. **3a** easily loses N_2H_3 and gives $[\underline{Mo}(NO)(\mu\text{-'}S_4\text{'})]_2$ (**5**). The structure of **5**·2DMF was determined by X-ray crystallography (triclinic, $P\bar{1}$, $Z = 1$, $a = 859.1$, $b = 1064.1$, $c = 1165.3$ pm, $\alpha = 70.18$, $\beta = 78.51$, $\gamma = 76.26°$, $R(R_w) = 0.066(0.053)$). The seven-coordinate Mo centres are surrounded by five sulfur, one molybdenum and one nitrogen atom. The Mo atoms of the two enantiomeric $[Mo(NO)(\text{'}S_4\text{'})]$ fragments are connected via two thiolato S atoms and a Mo–Mo single bond.

Introduction

The reduction of N_2 to NH_3 by way of enzymatic N_2 fixation in nitrogenases is still a rather ill understood chemical process. It probably takes place at iron and/or molybdenum centres whose coordination sites are dominated by sulfur donors [2]. Intermediates are suggested to be N_2H_x species where x ranges from 1–4 comprising the diazene as well as the hydrazine stage of N_2 reduction. N_2H_2 which is one of the key intermediates because of its extreme instability in the free state was proved to be stabilized by metal sulfur ligand fragments [3], but as yet no complex is known in which the likewise unstable N_2H_3 is stabilized by coordination to metal sulfur sites. N_2H_3 complexes are very rare and the only two examples in which the occurrence of N_2H_3 was proved by X-ray crystallography are $[W(\eta^5\text{-}C_5Me_5)Me_4(\eta^2\text{-}NHNH_2)]$ and $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)][SO_3CF_3]$ [4]. Further complexes that very probably contain the N_2H_3 ligand are $[Mo\{HB(Me_2pz)_3\}(NO)I(\eta^1\text{-}NHNH_2)]$($Me_2pz = 3,5$-dimethylpyrazolyl) and $[W\{HB(Me_2pz)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)Br(\eta^1\text{-}NHNH_2)]$ [5]. Complexes with N_2R_3 ligands are only slightly more common [6]. Examples are $[Re(Cl)_2(\eta^1\text{-}NHNHCOPh)(NNHCOPh)(PPh_3)_2]$ [7a], $[Tc(Br)_2(PPh_3)_2(NNPh)(\eta^1\text{-}NHNHPh)]Br$ [7b], $[CpTi(Cl)_2(\eta^2\text{-}NHNMe_2)]$ [7c], $[Mo(\eta^2\text{-}NHNHCO_2Me)(NNCO_2Me)(S_2CNMe_2)_2]$ [7d], $[Mo(Cp)(NO)I(\eta^2\text{-}NRNR'R'')]$ ($R = H$, alkyl; $R' = H$, alkyl, aryl; $R'' =$ alkyl, aryl) [7d] and $[W(Cp)_2(\eta^2\text{-}NRNH_2)]BF_4$ ($R = p\text{-}XC_6H_4$; $X = H$, F, Me, OMe) [7e]. In all complexes the site of coordination carries little or no resemblance to the active sites of nitrogenases with respect to metals and sulfur donors. In this paper the first complexes are described in which N_2H_3 and N_2HR_2 residues coordinate to molybdenum sulfur sites.

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*For Part LXVII see ref. 1.

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Experimental

General

All synthetic procedures were carried out under nitrogen atmosphere at room temperature using standard Schlenk techniques. Solvents were dried and distilled before use. Reactions were monitored by IR spectroscopy as far as possible. Spectra were recorded on the following instruments: IR (CaF_2 cuvettes or KBr discs): Zeiss IMR 16. NMR: Jeol JNM-GX 270. Mass spectra: Varian MAT 212 (EI and FD mode). [Mo(Cl)(NO)('S_4')] [8], [W(Cl)(NO)('S_4')] [9] and 'S_4'-H_2 [10] were prepared by literature methods.

X-ray data collection, structure determination and refinement of [Mo(η^2-NHNMe$_2$)(NO)('S_4')] (3b) and [Mo(NO)(μ-'S_4')]$_2$·2DMF (5·2DMF)

Single crystals of [Mo(η^2-NHNMe$_2$)(NO)('S_4')] (**3b**) were grown by covering a CH_2Cl_2 solution of **3b** with a layer of ether under ambient conditions. Single crystals of [Mo(NO)(μ-'S_4')]$_2$·2DMF (**5**·2DMF) were obtained from a saturated DMF solution of **3a** standing for some days at r.t.

The single crystals were sealed under N_2 in glass capillaries. The structures were solved by direct methods. Non-hydrogen atoms were refined anisotropically and the aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups. The H atoms of the methyl and methylene groups were placed in ideal tetrahedral positions and rotated around the central carbon atom during refinement. The atoms were refined with common isotropic temperature factors. Table 1 summarizes crystallographic data for **3b** and **5**·2DMF; the fractional atomic coordinates are listed in Table 2.

Syntheses

[Mo(NHNH$_2$)(NO)('S_4')] (3a)

Hydrazine (70 mg, 2.2 mmol) was added to a brown purple suspension of **1** (500 mg, 1.06 mmol) in 15 ml of THF and instantaneously a yellow solution resulted that was stirred for 1 h and evaporated to dryness. The orange residue was washed with 50 ml of H_2O, dried *in vacuo* for 1 h, and redissolved in 50 ml of THF at 40 °C. The solution was concentrated to 10 ml and cooled to 5 °C for 3 days. The precipitated orange microcrystals of **3a** were separated, washed with 30 ml of Et_2O, and dried *in vacuo*. Yield 290 mg (59%).

TABLE 1. Summary of crystallographic data and data collection procedures for [Mo(η^2-NHNMe$_2$)(NO)('S_4')] (**3b**) and [Mo(NO)(μ-'S_4')]$_2$·2DMF (**5**·2DMF)

Compound	[Mo(η^2-NHNMe$_2$)(NO)('S_4')]	[Mo(NO)(μ-'S_4')]$_2$·2DMF
Formula	$C_{16}H_{19}MoN_3OS_4$	$C_{34}H_{38}Mo_2N_4O_4S_8$
M_r	493.5	1015.1
Space group	$P2_1/c$	$P\bar{1}$
Crystal system	monoclinic	triclinic
a (pm)	1162.3(4)	859.5(1)
b (pm)	1228.4(4)	1064.1(3)
c (pm)	1476.3(5)	1165.3(4)
α (°)	90.00	70.18(2)
β (°)	98.47(2)	78.51(2)
γ (°)	90.00	76.26(2)
Cell volume (pm^3)	$2084(1)\times10^6$	$965(1)\times10^6$
Molecules unit cell	4	1
D_{calc} (g/cm^3)	1.566	1.75
μ (cm^{-1})	10.04	10.9
Diffractometer	Nicolet R3m/V	Nicolet R3m/V
Radiation (pm)	Mo Kα (71.073)	Mo Kα (71.073)
Temperature of measurement (K)	200	200
Crystal size (mm)	$0.30\times0.20\times0.05$	$0.30\times0.20\times0.05$
Scan technique	ω-scan	ω-scan
2θ range (°)	3–52	3–54
Scan speed (°/min)	3.0–15	3.0–15
Reflections measured	4034	4424
Independent reflections	3649	4026
Observed reflections	2432	3035
σ-criterion	$F>4\sigma(F)$	$F>6\sigma(F)$
Programm	SHELXTL-PLUS	SHELXTL-PLUS
R	0.087	0.066
R_w	0.072	0.053

TABLE 2. Fractional atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($pm^2 \times 10^{-1}$) of the non-hydrogen atoms for [Mo(η^2-NHNMe$_2$)(NO)('S$_4$')] and [Mo(NO)(μ-'S$_4$')]$_2$·2DMF

	x	y	z	U_{eq}[a]
[Mo(η^2-NHNMe$_2$)NO('S$_4$')]				
Mo(1)	3503(1)	1788(1)	4085(1)	19(1)
N(1)	3310(9)	705(8)	4844(7)	25(3)
O(1)	3107(8)	−9(8)	5354(8)	38(3)
N(2)	5310(8)	2034(9)	4286(7)	26(3)
N(3)	4896(10)	2512(8)	5037(7)	24(3)
C(1)	5292(13)	1958(13)	5936(9)	37(4)
C(2)	5040(14)	3683(13)	5104(11)	38(5)
S(1)	2141(3)	3009(2)	4723(2)	24(1)
S(2)	3416(2)	3363(3)	2891(2)	22(1)
S(3)	1586(3)	1282(3)	3129(2)	24(1)
S(4)	4217(3)	690(3)	2856(2)	26(1)
C(15)	2631(10)	4402(10)	3344(8)	21(3)
C(14)	2543(12)	5435(12)	2891(10)	36(4)
C(13)	1969(13)	6301(12)	3240(10)	36(5)
C(12)	1496(13)	6134(12)	4038(12)	37(4)
C(11)	1600(11)	5156(12)	4500(9)	28(4)
C(10)	2128(11)	4238(10)	4129(8)	22(3)
C(25)	1877(11)	125(10)	2443(8)	22(4)
C(24)	958(12)	−509(11)	2044(10)	30(4)
C(23)	1188(12)	−1389(11)	1544(9)	29(4)
C(22)	2298(11)	−1685(13)	1460(8)	29(4)
C(21)	3216(12)	−1046(11)	1875(8)	29(4)
C(20)	3029(11)	−101(11)	2349(8)	25(4)
C(16)	2352(11)	2848(10)	1957(8)	25(4)
C(26)	1299(11)	2390(11)	2284(9)	28(4)
[Mo(NO)(μ-'S$_4$')]$_2$·2DMF				
Mo(1)	6417(1)	−113(1)	4091(1)	19(1)
S(1)	8996(2)	725(2)	3582(2)	25(1)
S(2)	7964(2)	−1623(2)	2831(2)	23(1)
S(3)	7691(2)	−2114(2)	5862(2)	23(1)
S(4)	4304(2)	−1458(2)	4673(2)	21(1)
N(1)	5510(7)	981(6)	2776(5)	20(2)
O(1)	4928(6)	1624(5)	1848(5)	32(2)
C(15)	9750(9)	−930(7)	2058(7)	25(3)
C(14)	10684(9)	−1452(7)	1164(7)	28(3)
C(13)	12090(9)	−996(8)	594(7)	31(3)
C(12)	12526(10)	−27(8)	951(7)	36(3)
C(11)	11599(9)	490(7)	1831(7)	28(3)
C(10)	10163(8)	51(7)	2430(7)	24(3)
C(25)	6436(8)	−3369(7)	6237(7)	21(3)
C(24)	6938(9)	−4641(7)	7016(7)	28(3)
C(23)	6054(10)	−5654(7)	7293(7)	31(3)
C(22)	4620(10)	−5337(8)	6792(7)	32(3)
C(21)	4084(10)	−4078(7)	6023(7)	28(3)
C(20)	4998(9)	−3061(7)	5722(7)	22(3)
C(16)	8927(10)	−3169(7)	3926(7)	31(3)
C(26)	9401(9)	−2893(7)	4983(7)	28(3)
C(1)	9029(10)	4570(8)	1673(7)	34(3)
O(2)	9642(7)	5353(6)	1898(6)	46(3)
N(2)	7995(8)	4885(6)	865(6)	29(3)
C(2)	7274(11)	3862(9)	725(9)	48(4)
C(3)	7459(11)	6293(8)	179(8)	44(4)

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

Anal. Calc. for $C_{14}H_{15}MoN_3OS_4$ (465.47): C, 36.12; H, 3.25; N, 9.03; S, 27.55. Found: C, 36.27; H, 3.14; N, 8.82; S, 27.55%.

[Mo(NHNMe$_2$)(NO)('S$_4$')]·½CH$_2$Cl$_2$ (3b·½CH$_2$Cl$_2$)

When *N*,*N*-dimethyl hydrazine (145 mg, 2.4 mmol) was added to a brown-purple suspension of **1** (585 mg, 1.2 mmol) in 20 ml of THF, instantaneously a cloudy light red solution was obtained. It was stirred for 3 h and evaporated to dryness. The residue was washed with methanol, dried *in vacuo* for 0.5 h, and dissolved in 50 ml of CH_2Cl_2. The solution was filtered, its volume reduced to 5 ml, and stored at −30 °C for 2 days. The precipitated flesh-coloured microcrystals of **3b**·½CH_2Cl_2 were separated, washed with 30 ml of Et_2O, and dried *in vacuo*. Yield 380 mg (59%).

Anal. Calc. for $C_{16.5}H_{20}ClMoN_3OS_4$ (536.01) = **3b**·½CH_2Cl_2: C, 36.97; H, 3.76; N, 7.84. Found: C, 37.13; H, 3.85; N, 7.54%.

[W(NHNH$_2$)(NO)('S$_4$')] (4a)

A solution of hydrazine (260 mg, 2 mmol) in 10 ml of THF was added dropwise to a suspension of **2** (550 mg, 0.99 mmol) in 10 ml of THF whereupon the colour of the reaction mixture changed from orange to yellow. The solvent was removed *in vacuo*, the residue was washed with 40 ml of H_2O and 20 ml of CH_2Cl_2, and dried *in vacuo*. Yield 500 mg (91%).

Anal. Calc. for $C_{14}H_{15}N_3OS_4W$ (553.40): C, 30.39; H, 2.73; N, 7.59; S, 23.18. Found: C, 30.43; H, 2.71; N, 7.42; S, 22.58%.

[W(NHNMe$_2$)(NO)('S$_4$')]·½CH$_2$Cl$_2$, (4b·½CH$_2$Cl$_2$)

N,*N*-Dimethylhydrazine (125 mg, 2.08 mmol) was added to an orange suspension of **2** (580 mg, 1.04 mmol) in 20 ml of THF. A beige suspension resulted that was stirred for 30 min and evaporated to dryness. The residue was extracted with 50 ml of CH_2Cl_2, the CH_2Cl_2 extract was filtered, and covered with 60 ml of Et_2O. Yellow crystals of **4b**·½CH_2Cl_2 precipitated that were filtered off, washed with 20 ml of MeOH and dried in *vacuo*. Yield 470 mg (72%).

Anal. Calc. for $C_{16.5}H_{20}ClN_3OS_4W$ (623.92) = **4b**·½CH_2Cl_2: C, 31.76; H, 3.23; N, 6.73; Found: C, 31.63; H, 3.06; N, 6.53%.

[Mo(NO)(μ-'S$_4$')]$_2$ (5)

5·2DMF crystallized from a solution of **3a** (200 mg, 0.43 mmol) in 10 ml of DMF at r.t. After four days the orange crystals were separated, washed with 15 ml of MeOH, and dried *in vacuo*. Yield 130 mg (60%).

Anal. Calc. for $C_{34}H_{38}Mo_2N_4O_4S_8$ (1015.09) = **5**·2DMF: C, 40.23; H, 3.77; N 5.52. Found: C, 40.09; H, 3.84; N, 5.42%.

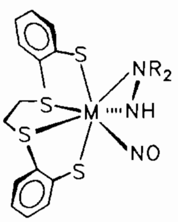
Results and discussion

Synthesis and properties of [M(NHNR$_2$)(NO)('S$_4$')] (M = Mo, R = H (3a), Me (3b); M = W, R = H (4a), Me (4b))

The chloro complexes **1** and **2** react instantaneously with hydrazine or 1,1-dimethyl hydrazine, according to eqn. (1).

$$[M(Cl)(NO)('S_4')] + 2NH_2NR_2 \xrightarrow[-NH_2NR_2\bullet HCl]{THF/RT}$$

M = Mo (**1**), W(**2**)



(1)

M = Mo; R = H(**3a**), Me(**3b**)
M = W; R = H(**4a**), Me(**4b**)

For a complete reaction two equivalents of the hydrazines are required. **3a** is soluble in THF, DMSO and DMF, **3b** is also soluble in CH_2Cl_2. **4a** is only soluble in DMSO and DMF, **4b** also in CH_2Cl_2.

X-ray structure determination of [Mo(η^2-NHNMe$_2$)(NO)('S$_4$')]

Single crystals of **3b** suitable for X-ray structure analysis could be grown. Its molecular structure is shown in Fig. 1; selected distances and angles are given in Table 3.

In **3b** the molybdenum is surrounded by four sulfur and three nitrogen atoms in a distorted pentagonal pyramid with the main axis going through S(2)–Mo(1)–N(1). The substitution of the chloride by a 'side-on' bonded $NHNMe_2$ ligand leads to a reduction of the S(1)–Mo(1)–S(4) angle in the [Mo('S$_4$')] core from 162.1° in **1** [8] to 155.0° in **3b**. The average Mo–S distance in the [Mo'S$_4$'] core of **3b** (253.0 pm) compares to the distances in other seven-coordinate molybdenum complexes such as [Mo(NH_2O)(NO)('S$_4$')] (253 pm) [11] and [Mo$(CO)_2$(PMe$_3$)('S$_4$')] (253 pm) [12]. The η^2 bonding mode of the $NHNMe_2$ ligand is concluded from the Mo(1)–N(2) and Mo(1)–N(3) distances of 209.9 and 217.2 pm that correspond to Mo–N single bonds. The N(2)–N(3) distance of 140.3 pm compares to reported N_2R_3 complexes and is slightly shorter than in N_2H_4 (147 pm) [13] (see Table 4).

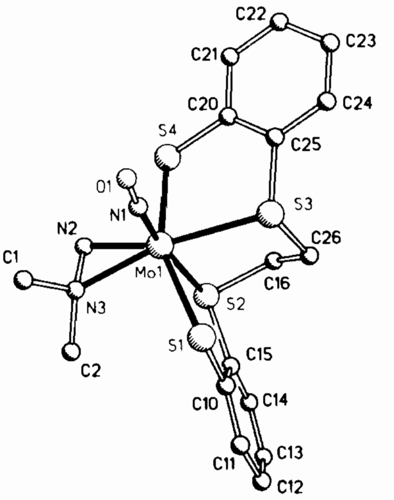


Fig. 1. Molecular structure of [Mo(η^2-NHNMe$_2$)(NO)('S$_4$')] (H atoms omitted).

TABLE 3. Selected interatomic distances (pm) and angles (°) of [Mo(NO)(η^2-NHNMe$_2$)('S$_4$')]

Distances		Angles	
Mo(1)–N(1)	177.9(11)	N(1)–Mo(1)–N(2)	103.7(5)
Mo(1)–N(2)	209.9(11)	N(1)–Mo(1)–N(3)	93.0(5)
Mo(1)–N(3)	217.2(12)	N(2)–Mo(1)–N(3)	38.3(4)
Mo(1)–S(1)	247.0(8)	N(2)–Mo(1)–S(1)	122.9(3)
Mo(1)–S(2)	261.5(8)	N(3)–Mo(1)–S(1)	87.8(3)
Mo(1)–S(3)	253.4(8)	N(2)–Mo(1)–S(2)	85.8(3)
Mo(1)–S(4)	250.1(8)	N(3)–Mo(1)–S(2)	94.7(3)
N(1)–O(1)	120.4(15)	S(1)–Mo(1)–S(2)	80.9(2)
N(2)–N(3)	140.3(16)	N(2)–Mo(1)–S(3)	153.3(3)
N(3)–C(1)	150.2(17)	S(1)–Mo(1)–S(3)	78.6(2)
N(3)–C(2)	145.6(19)	S(2)–Mo(1)–S(3)	82.2(2)
S(1)–C(10)	175.0(13)	N(2)–Mo(1)–S(4)	75.4(3)
S(2)–C(15)	176.1(13)	N(3)–Mo(1)–S(4)	113.3(4)
S(2)–C(16)	182.4(13)	S(1)–Mo(1)–S(4)	155.0(2)
S(3)–C(25)	178.4(13)	Mo(1)–N(1)–O(1)	175.9(10)
S(3)–C(26)	184.7(14)	Mo(1)–N(2)–N(3)	73.7(6)
S(4)–C(20)	176.5(14)	Mo(1)–N(3)–N(2)	68.0(6)

The N*H*NR$_2$ proton that could not be localized definitely by X-ray structure analysis follows from the diamagnetism and the neutral charge of **3b**. It was further confirmed by IR and ^1H NMR spectroscopy.

Spectroscopy

The KBr IR spectra of **3b** and **4b** each show one characteristic sharp ν(NH) band at 3240 and 3220 cm^{-1}. The KBr IR spectrum of **3a** displays three ν(NH) bands at 3340, 3250 and 3170 cm^{-1}; in this

TABLE 4. Corresponding distances (pm) and angles (°) for the [M(η^2-NRNR$_2$)] core of η^2-N$_2$R$_3$ complexes

Complex	Distances			Angles			Reference
	N–N	M–NR	M–NR$_2$	NR$_2$–M–NR	M–NR–NR$_2$	NR–NR$_2$–M	
[Ti(Cp)(Cl)$_2$(NHNMe$_2$]	141(2)	183(1)	222(1)	39.1(5)	85.7(8)	55.3(7)	7c
[Ti(Cp)(Cl)$_2$(NPhNH$_2$)]	141(2)	187.7(9)	214(1)	40.4(4)	80.0(6)	59.6(5)	7c
[Mo(NHNMePh)(NNMePh)(S$_2$CNMe$_2$)$_2$]BPh$_4$	139(2)	207.0(8)	217.6(9)	38.1(4)	75.1(6)	66.8(3)	7a
[Mo(NHNHCO$_2$Me)(NNCO$_2$Me)(S$_2$CNMe$_2$)$_2$]	140(2)	213(1)	210(1)	38.5(7)	72.0(12)	69.5(1)	7a
[Cp*WMe$_4$(NHNH$_2$)] (2 molecules/unit)	135(3)	216(2)	210.5(16)	36.8(9)	69.3(12)	73.8(11)	4
	139(1)	217(2)	212(2)	37.9(9)	69.2(15)	72.9(14)	
[Cp*WMe$_3$(NHNH$_2$)][SO$_3$CF$_3$]	139(3)	186(1)	215(1)	39.7(4)	81.5(6)	58.7(5)	4
[Mo(NHNMe$_2$)(NO)('S$_4$')]	140.3(16)	209.9(11)	217.2(12)	38.3(4)	73.7(6)	68.0(6)	this work

TABLE 5. Selected spectroscopic data for the NHNR$_2$ complexes **3a**, **3b**, **4a**, **4b** and **5**·2DMF

Complex	IR[a] (cm^{-1})	^{1}H NMR[b] (ppm)	^{14}N NMR[f] (ppm)	^{95}Mo NMR[i] (ppm)	MS (*m*/*e*)
[Mo(NHNH$_2$)(NO)('S$_4$')] (**3a**)	1627 ν(NO) 3340, 3250, 3170 ν(NH)	2.85 (s, NHN$\underline{H}_2$, 2H)[c] 3.2–3.7 (m, C$_2$H$_4$, 4H) 4.9 (broad, N$\underline{H}$NH$_2$, 1H) 6.9–7.7 (m, C$_6$H$_4$, 8H)	12(NO)[e] −355 (NHNH$_2$)	[g]	467 (FD)
[Mo(NHNMe$_2$)(NO)('S$_4$')]·$\frac{1}{2}$CH$_2$Cl$_2$ (**3b**)	1620 ν(NO) 3240 ν(NH)	2.65; 3.3 (s, NHN(C$\underline{H}_3$)$_2$, 6H)[d] 2.7–3.6 (m, C$_2$H$_4$, 4H) 4.0 (broad, N$\underline{H}$NMe$_2$, 1H) 6.9–7.7 (m, C$_6$H$_4$, 8H)	15 (NO)[d] −315 (broad, NHNMe$_2$)	−445[d]	495 (FD)
[W(NHNH$_2$)(NO)('S$_4$')] (**4a**)	1570 ν(NO) 3210 ν(NH) (broad)	2.9 (s, NHN$\underline{H}_2$, 2H)[c] 3.4–4.0 (m, C$_2$H$_4$; N$\underline{H}$NH$_2$, 5H) 6.9–7.8 (m, C$_6$H$_4$, 8H)	−10 (NO)[e] −352 (NHNH$_2$)		553 (FD)
[W(NHNMe$_2$)(NO)('S$_4$')]·$\frac{1}{2}$CH$_2$Cl$_2$ (**4b**)	1580 ν(NO) 3220 ν(NH)	2.65; 3.35 (s, NHN(C$\underline{H}_3$)$_2$, 6H)[d] 2.6–3.7 (m, C$_2$H$_4$; N$\underline{H}$NMe$_2$, 5H) 6.8–7.7 (m, C$_6$H$_4$, 8H)	−8 (NO)[d] [g]		581 (EI)
[Mo(NO)(μ-'S$_4$')]$_2$·2DMF (**5**·2DMF)	1665, 1605 ν(NO)	1.9–3.8 (m, C$_2$H$_4$, 8H)[e] 7.0–8.1 (m, C$_6$H$_4$, 16H)	[h]	[h]	870 (FD)

[a]In KBr. [b]Relative to TMS. [c]In DMF-d$_7$. [d]In CD$_2$Cl$_2$. [e]In DMSO-d$_6$. [f]Relative to NH$_4$NO$_3$. [g]Not observed due to the great broadness of the signal. [h]Not obtained due to the low solubility of the complex. [i]Relative to (NH$_4$)$_6$(Mo$_7$O$_{24}$). s = singlet; m = multiplet; EI = electron impact; FD = field desorption.

region **4a** shows only one broad band at 3210 cm^{-1} that could not be resolved. The molecular ions of all compounds could be observed in their mass spectra (Table 5).

The ^1H NMR spectra of both **3b** and **4b** display two methyl signals of the η^2 bonded $NHN(C\mathit{H}_3)_2$ ligand; the signal of the $N\mathit{H}N(CH_3)_2$ proton is either broad and could clearly be observed only at temperatures below −10 °C (**3b**) or overlapping with the multiplet of the C_2H_4 protons of the 'S_4'$^{2-}$ ligand (**4b**) (see Table 5). The $^{13}C\{^1H\}$ NMR spectra of both **3b** and **4b** show two signals for the $NHN(\mathit{C}H_3)_2$, two signals for the C_2H_4, and twelve signals for the aromatic carbon atoms (see Table 6).

The $^{13}C\{^1H\}$ NMR spectra of **3a** and **4a** are very similar with respect to the number of ^{13}C signals and display also exactly 14 signals for the 'S_4'$^{2-}$ ligands. The two $NHN\mathit{H}_2$ protons of **3a** and **4a** give rise to broad signals at 2.85 and 2.9 ppm. The $N\mathit{H}NH_2$ protons could be observed only at temperatures below −20 °C. Then **3a** shows a broad signal at 4.8 ppm (−40 °C) and **4a** a relatively sharp singlet at 3.8 ppm (−20 °C).

These NMR results prove that all four complexes do not form stereoisomers in solution as was observed for the closely related $[Mo(NH_2O)(NO)('S_4')]$ [11]. If isomers differing in the orientation of the $NHNR_2$ groups with respect to the $[M(NO)('S_4')]$ core were formed, the number of ^{13}C signals of the $[M('S_4')]$ core would be doubled.

The ^{14}N NMR spectra of both **3a** and **4a** exhibit only one relatively sharp signal at −355 or −352 ppm, respectively, for the two chirotopic N atoms of the $NHNH_2$ ligand. This may be taken as NMR spectroscopic evidence for the η^2 bonding mode of the N_2H_3 ligands, because 'end-on' bonding should make the two N atoms magnetically more different giving rise to two ^{14}N NMR signals. The ^{14}N NMR signal of **3b** at −315 ppm is very broad ($\Delta\nu_{1/2} \cong 60$ ppm).

A ^{95}Mo NMR spectrum could be obtained of **3b**. It displays a signal at −445 ppm that indicates a Mo(II) centre in **3b** when compared to Mo(II) complexes such as $[Mo(NO)_2('S_4')]$ (−512 ppm) [12] and Mo(III) complexes such as $[Mo(NMe_2)(NO)('S_4')]$ (+340 ppm) [8] and $[Mo(NPMePh_2)(NO)('S_4')]$ (+390 ppm) [12]. (Of the even more directly related $[Mo(Cl)(NO)('S_4')]$ we have not yet obtained a ^{95}Mo NMR spectrum [8]). Consequently, when **1** is reacted with hydrazines in order to form **3a** or **3b**, a reduction of Mo(III) to Mo(II) must take place simultaneously with the chloride substitution. The Mo(II) oxidation state then requires the $NHNR_2$ groups to be neutral hydrazinyl 3e$^-$ donor ligands.

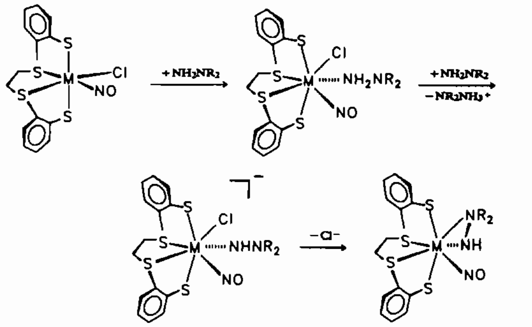
Reaction mechanism

The metal centre in $[M(Cl)(NO)('S_4')]$ can accommodate a seventh ligand as demonstrated by addition of PMe_3 when $[M(PMe_3)(Cl)(NO)('S_4')]$ (M = Mo, W) is formed [9]. Thus, the metal centre has a latently vacant site of coordination and an associative mechanism for the reaction according to eqn. (2) can be suggested.

TABLE 6. $^{13}C\{^1H\}$- NMR data for the $NHNR_2$ complexes **3a**, **3b**, **4a** and **4b** (ppm, relative to TMS)

Complex	C_2H_4	C_{Phenyl}	Other
$[Mo(NHNH_2)(NO)('S_4')]$[a] (**3a**)	42.0; 44.1	123.6; 123.8; 129.5; 130.3; 130.4; 131.1; 132.0; 133.0; 133.2; 135.1; 156.4; 157.4	
$[Mo(NHNMe_2)(NO)('S_4')]\cdot\frac{1}{2}CH_2Cl_2$[b] (**3b**)	42.1; 44.2	123.6; 124.4; 127.2; 130.2; 130.9; 131.1; 132.4; 132.5; 132.6; 134.6; 155.5; 156.4	41.5; 43.2 ($NHN(CH_3)_2$)
$[W(NHNH_2)(NO)('S_4')]$[a] (**4a**)	42.2; 44.3	123.8; 124.2; 129.4; 130.6 (2 signals); 131.5; 132.5; 132.9; 133.5; 135.4; 155.8; 156.4	
$[W(NHNMe_2)(NO)('S_4')]\cdot\frac{1}{2}CH_2Cl_2$[b] (**4b**)	42.4; 44.6	123.8; 124.8; 130.6; 131.2; 131.6; 132.8; 133.0; 133.1; 134.8; 135.2; 155.1; 155.7	42.0; 43.6 ($NHN(CH_3)_2$)

[a] In DMF-d_7. [b] In CD_2Cl_2.



(2)

In the primary step the hydrazine adds to **1** or **2**, respectively, and in the subsequent step H^+ is released that is trapped by the second hydrazine being necessary for the reaction. Intramolecular electron transfer from the hydrazido(1−) ligand to the metal(III) centre, expulsion of Cl^-, and filling of the resulting vacant site by the NR_2 group finally complete the reaction.

Reactions

In orienting experiments the reactivity of the hydrazinyl complexes towards acids and bases was investigated. **3a** yields with gaseous HCl in CH_2Cl_2 [Mo(Cl)(NO)('S_4')] (**1**) and $N_2H_4 \cdot 2HCl$ which were identified by IR and FD-MS spectroscopy. **3a** does not react with NEt_3, and with n-BuLi it yields species that have not yet been characterized. In solution at room temperature, **3a** and **4a** slowly decompose under loss of the $NHNH_2$ ligand. The species resulting from **3a** could be fully characterized as [Mo(NO)(μ-'S_4')]$_2$ (**5**). Its structure was elucidated by X-ray crystallography.

5 is only slightly soluble in DMSO. The KBr IR spectrum of **5** shows two sharp ν(NO) bands at 1665 and 1605 cm^{-1}. The molecular ion could be observed in the mass spectrum. The ^1H NMR spectrum of **5** displays multiplets for the C_2H_4 and the aromatic protons of the 'S_4'$^{2-}$ ligands (Table 5). The low solubility of **5** prevented the recording of $^{13}C\{^1H\}$ NMR and ^{14}N NMR spectra.

X-ray structure analysis of 5·2DMF

The molecular structure of **5**·2DMF is shown in Fig. 2; selected bond distances and angles are summarized in Table 7.

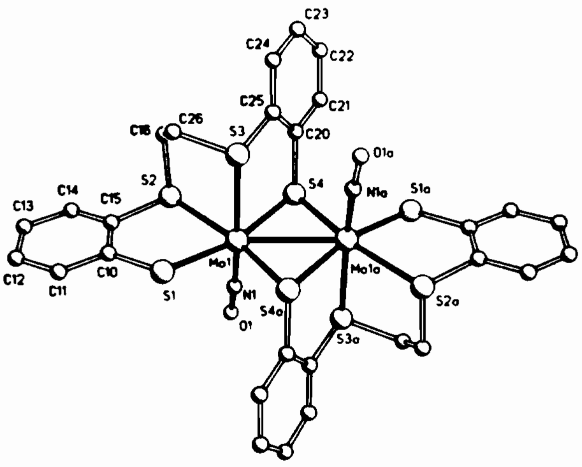


Fig. 2. Molecular structure of [Mo(NO)(μ-'S_4')]$_2$·2DMF (**5**·2DMF) (H atoms and DMF molecules are omitted).

TABLE 7. Selected interatomic distances (pm) and angles (°) of [Mo(NO)(μ-'S_4')]$_2$·2DMF (**5**·2DMF)

Mo(1)–S(1)	247.3(2)	S(3)–Mo(1)–N(1)	168.4(2)
Mo(1)–S(2)	251.2(2)	S(4)–Mo(1)–S(4A)	106.8(1)
Mo(1)–S(3)	260.9(2)	Mo(1)–S(4)–Mo(1A)	73.2(1)
Mo(1)–S(4)	242.7(2)	S(1)–Mo(1)–N(1)	98.0(2)
Mo(1)–N(1)	177.3(5)	S(1)–Mo(1)–S(2)	81.7(1)
Mo(1)–Mo(1A)	291.4(2)	S(2)–Mo(1)–S(3)	81.9(1)
Mo(1)–S(4A)	245.9(2)	S(1)–Mo(1)–S(3)	87.8(1)
S(1)–C(10)	176.0(8)	S(1)–Mo(1)–S(4)	166.4(1)
S(2)–C(15)	180.3(8)	S(2)–Mo(1)–S(4)	88.3(1)
S(2)–C(16)	183.6(7)	S(3)–Mo(1)–S(4)	81.7(1)
S(3)–C(26)	181.5(7)	S(2)–Mo(1)–N(1)	89.0(2)
S(3)–C(25)	180.0(8)	S(4)–Mo(1)–N(1)	90.9(2)
S(4)–C(20)	177.6(6)	S(1)–Mo(1)–Mo(1A)	134.0(1)

5 exhibits a crystallographically imposed centre of inversion. The Mo centres are each coordinated by five sulfur, one nitrogen and one molybdenum atom. The two [Mo(NO)('S_4')] fragments are connected by a Mo–Mo single bond being indicated by the Mo–Mo distance of 291.4 pm and bridged via two 'α'-thiolate S atoms.

As we have recently shown, the thiolate S atoms in [M(L)('S_4')] fragments are different and can be labeled by α and β. The suffix α indicates thiolato S atoms whose corresponding thioether S atoms in the *ortho* position at the respective benzene ring stand *trans* to the coligand L; the suffix β corresponds to the second thiolato S atoms in [M(L)('S_4')] fragments [14]. Bridging via α thiolato S atoms appears to be electronically favoured in binuclear [M(L)(μ-'S_4')]$_2$ complexes and is observed also in **5**·2DMF. When pseudooctahedral [M(L)('S_4')] fragments having *trans* thiolato S atoms dimerize, ten stereoisomers can theoretically form [14, 15]. The structure of **5**·2DMF represents one of the stereoisomers in which enantiomeric fragments are combined and the coligands L point in opposite directions. It differs from the structure of the isomeric [Mo(NO)(μ-'S_4')]$_2$·2DMF, that was recently reported [15], in several respects. In the latter two diastereomeric [Mo(NO)('S_4')] fragments are combined, one having *cis* and one having *trans* thiolato atoms, and the NO ligands point in the same direction. In spite of these quite considerable differences the distances and angles in both isomers are almost identical, including the Mo–Mo distances which differ only by 3 pm.

Conclusions

The hydrazinyl complexes [M($NHNH_2$)(NO)('S_4')] (M = Mo (**3a**), W (**4a**) have been synthesized. They are labile, but could be fully characterized by IR, NMR and mass spectroscopy. According to the NMR spectra their structure is analogous to that of [M($NHNMe_2$)(NO)('S_4')] (M = Mo, W). The molecular structure of [Mo($NHNMe_2$)(NO)('S_4')] (**3b**) was solved by X-ray structure analysis. **3b** exhibits a 'side-on' $NHNMe_2$ ligand coordinating to a metal site whose coordination sphere is dominated by sulfur donors. In that respect **3a** and **3b** represent structural and functional models for the active sites of nitrogenases. When the labile **3a** loses $NHNH_2$, the remaining complex fragments dimerize and form [Mo(NO)(μ-'S_4')]$_2$ (**5**). The molecular structure of **5**·2DMF was solved by X-ray structure determination.

Supplementary material

Further details of X-ray crystal structure analysis have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 by citing the deposition nos. CSD 320195 (**5**) and CSD 320196 (**3b**), the authors and reference.

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Note added in proof

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