

Molybdenum and tungsten complexes of the $\text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$ (NS_3) ligand with oxide, sulfide, diazenide, hydrazide and nitrosyl co-ligands

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Received 3rd November 1999, Accepted 4th January 2000

Published on the Web 7th February 2000

Reaction of $[\text{MoO}_2(\text{acac})_2]$ with $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ in CH_2Cl_2 gave an insoluble, red, diamagnetic complex formulated as $[\{\text{MoO}(\text{NS}_3)\}_2]$ **1** [$\text{NS}_3 = \text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$] together with a small amount of dark red, diamagnetic $[\{\text{Mo}(\text{NS}_3)\}_2-(\mu\text{-S})]$ **2**. The linear, sulfur-bridged structure of **2** was confirmed by a crystal structure determination. With NH_2NHR ($\text{R} = \text{Me}$ or Ph) in CH_2Cl_2 , **1** gave soluble, red, diamagnetic diazenides $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{R})]$ ($\text{R} = \text{Me}$ **3** or Ph **4**) whereas with N_2H_4 it gave a dark brown, insoluble compound formulated as $[\{\text{Mo}(\text{NS}_3)(\text{N}_2\text{H})\}_n]$ **5**. The crystal structures of **3** and **4** have been obtained. Both **3** and **4** react with mineral acids HX ($\text{X} = \text{BF}_4$ or Cl) in CH_2Cl_2 to give the yellow-brown, diamagnetic hydrazides $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{HR})]\text{X}$ (**6**, $\text{R} = \text{Me}$, $\text{X} = \text{BF}_4$; **7**, $\text{R} = \text{Me}$, $\text{X} = \text{Cl}$; **8**, $\text{R} = \text{Ph}$, $\text{X} = \text{BF}_4$), which deprotonate in more basic solvents to regenerate the parent complexes. Compound **3** reacted with $[\text{Me}_3\text{O}]\text{BF}_4$ to give yellow, diamagnetic $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{Me}_2)]\text{BF}_4$ **9** and with NO to give yellow, diamagnetic $[\text{Mo}(\text{NS}_3)(\text{NO})]$ **10**, whose crystal structure shows it to have a linear MoNO system. Reaction of $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ with $[\{\text{Mo}(\mu\text{-Br})\text{Br}(\text{CO})_4\}_2]$ and $[\text{W}(\text{CO})_3(\text{MeCN})_2]$ gave the poorly soluble, diamagnetic complexes $[\{\text{M}(\text{NS}_3)\}_2-(\mu\text{-SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})_2\text{-S})_2]$ ($\text{M} = \text{Mo}$ **11** or W **12**) whose structures have been established by determination of the crystal structure of **12**.

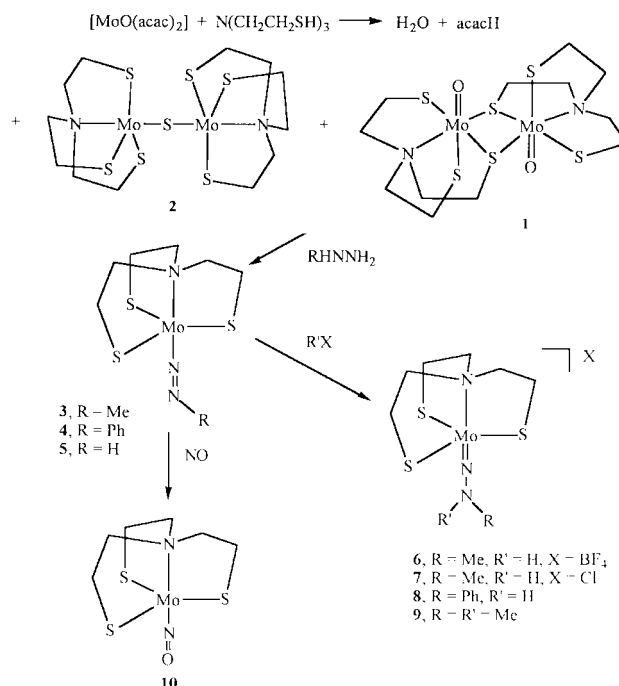
The Mo atom in the FeMoco cofactor of the iron–molybdenum nitrogenase is co-ordinated by three sulfides as well as two oxygens from homocitrate $[\text{O}_2\text{CCH}_2\text{C}(\text{O}^-)(\text{CO}_2^-)\text{CH}_2\text{CH}_2\text{CO}_2^-]$ and one histidine nitrogen¹ and it is thought that the vanadium atom in vanadium nitrogenase² and one iron atom in the “iron-only” nitrogenase³ are in similar environments. The chemistry of Mo, V and Fe which carry three sulfurs (plus other ligands) (MS_3 sites) is therefore of importance in understanding the mode of action of these enzymes.

Recently a rich chemistry of the tripodal nitrogen-donor ligand $[\text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_3]^{3-}$ (NN_3) and its analogues has been developed, including the preparation of the tris- $(\mu\text{-dinitrogen})$ complex, $[\text{Fe}\{\text{N}_2\text{Mo}(\text{NN}_3)\}_3]$, as well as the monomer $[\text{Mo}(\text{NN}_3)(\text{N}_2)]$.^{4,5} In addition, tripodal sulfur-donor ligands such as $\text{P}(\text{C}_6\text{H}_4\text{S-2})_3^{3-}$ and $\text{N}(\text{CH}_2\text{CH}_2\text{S})_3^{3-}$ (NS_3) feature in chemistry which aims to model the Fe–S structural units of hydrogenases and of nitrile hydratase.^{6,7}

This prompted us to explore the chemistry of Mo, V and Fe with the tripodal NS_3 ligand, our aim being to investigate the ability of metal sites carrying this ligand to bind species on the route from N_2 to NH_3 such as N_2H , N_2H_2 and N_2H_4 and their derivatives. We have already communicated some of our results for V⁸ and Fe⁹ and this paper presents data for Mo and W.

Results and discussion

The starting point of our investigation was to synthesize suitable precursor complexes containing the intact NS_3 ligand which would allow introduction of the desired ligands into the co-ordination sphere. In our vanadium chemistry we have used the precursor $[\text{VO}(\text{NS}_3)]^8$ and our initial aim was to prepare the molybdenum analogue of this compound. This was attempted by treatment of $[\text{MoO}_2(\text{acac})_2]$ ($\text{acac} = \text{pentane-2,4-dionate}$) with $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ in CH_2Cl_2 as in Scheme 1. An orange-red



Scheme 1

compound **1** precipitated over several hours; it is insoluble in common organic solvents and is stable to air for several days. It has a strong absorption in its IR spectrum at 937 cm^{-1} , in the region expected for a terminal $\text{Mo}=\text{O}$ group¹⁰ but we were unable to identify clearly a non- NS_3 band at lower frequency. This diagnostic IR frequency and microanalyses are consistent with the empirical formula $\text{MoO}(\text{NS}_3)$ for **1** and its chemistry detailed below confirms that it contains an intact NS_3 ligand. Evidently the $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ reagent, as well as removing one oxide ligand and the acac ligands from the starting material, has acted as a reducing agent in the reaction to produce the

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Table 1 Selected bond dimensions in the $M(NS_3)$ complexes. Bond lengths are in Å, angles in °. E.s.d.s are in parentheses

Complex	M–N	M–S	N–M–S	Z, M–Z	Other dimensions
2 [$\{Mo(NS_3)_2(\mu-S)\}$]	2.251(4)	2.2986(10)	83.93(3)	S(5), 2.1429(5)	Mo–S(5)–Mo' 180.0
3 [$\{Mo(NS_3)(NNMe)\}$]	2.256(2)	2.3117(9)	83.30(6)	N(5), 1.809(3)	N(5)–N(51) 1.213(4), N(51)–C(52) 1.405(5), N(51)–N(5)–Mo 177.4(3), N(5)–N(51)–C(52) 120.3
4 [$\{Mo(NS_3)(NNPh)\}$]	2.257(4)	2.285(2)	84.6(2)	N(5), 1.801(4)	N(5)–N(51) 1.232(6), N(51)–N(5)–Mo 174.1(5), N(51)–C(511) 1.468(9), N(51)–C(521) 1.40(3), N(5)–N(51)–C(511) 118.4(6), N(5)–N(51)–C(521) 118(2)
10 [$\{Mo(NS_3)(NO)\}$] Molecule A	2.257(2)	2.2900(7)	84.52(5)	N(5), 1.782(2)	N(5)–O(5) 1.191(3), O(5)–N(5)–Mo(1) 176.4(2)
Molecule B	2.257(2)	2.3063(8)	84.05(5)		
		2.3058(8)	84.75(6)		
		2.2890(8)	84.54(5)	N(10), 1.782(2)	N(10)–O(10) 1.188(3), O(10)–N(10)–Mo(2) 176.1(2)
		2.3099(7)	84.79(5)		
		2.3036(8)	84.10(6)		
12 [$\{W(NS_3)_2\}_2\{\mu-SCH_2CH_2N-(CH_2CH_2SH)_2-S\}_2\}$]	2.329(9)	2.397(4)	81.1(3)	S(5), 2.459(3)	N(4)–W–S(5) 88.4(3), W–S(5)–C(51) 118.2(5), N(4)–W–S(5') 159.7(3), W'–S(5)–C(51) 107.1(5), S(5)–W–S(5') 111.84(9), W–S(5)–W' 68.16(9), W...W' 2.7185(9)
		2.391(3)	79.0(3)	S(5'), 2.391(3)	
		2.349(3)	80.7(3)		

molybdenum(v) product **1**, which is diamagnetic and therefore cannot be monomeric.

It should be pointed out that reaction of $[MoO_2(acac)_2]$ with $N(CH_2CH_2SH)_3$ had been studied by Barbaro *et al.*¹¹ However, they used warm dmf as solvent and did not appear to obtain **1** under these conditions, but instead isolated very air-sensitive, brown-red dichroic crystals, which they could not completely characterise. They considered a possible formulation $[MoO(NS_3)_2(\mu-O)]$ on the basis of microanalysis and an IR band at 780 cm^{-1} . No band at 937 cm^{-1} was reported for their product, which would be expected to be diamagnetic, but showed some paramagnetism in that it gave broadened NMR absorptions, perhaps due to paramagnetic impurities.¹¹

We note that the analytical data obtained by the above authors and by ourselves are similar and give a better fit to our formulation for complex **1** than for $[MoO(NS_3)_2(\mu-O)]$. Although on the available data we cannot exclude the possibility that **1** could be the same as that reported by Barbaro *et al.* and therefore be $[MoO(NS_3)_2(\mu-O)]$, the variation in the properties of the two compounds suggests that they are different and we prefer the empirical formulation $MoO(NS_3)_2$ for **1**; consequently it has most probably an S-bridged dimeric structure as shown in Scheme 1 to account for its diamagnetism, since the molybdenum oxidation state is +5. The formulation as a six-co-ordinate dimer also helps to explain the relative stability of **1** in air, in contrast to the product reported in reference 11. S-Bridged structures are common in tripodal thiolate chemistry, for example in $[Ni(\mu-SCH_2CH_2N(CH_2CH_2S)-(CH_2CH_2SMe)-S,S')]_2$ ¹² and the thiolate-bridged complexes **11** and **12** described below. Compound **1** therefore appears to be a member of the general class of diamagnetic molybdenum(v) complexes containing the $[MoO\{(\mu-X)_2\}]^{2+}$ ($X = S$ or O) unit.¹⁰ Unfortunately the very poor solubility of **1** has prevented preparation of crystals for a definitive X-ray study. Although our formulation of **1** is therefore somewhat tentative, nevertheless **1** has proved to be a useful starting material for the development of non-oxide $Mo(NS_3)$ chemistry as described below.

After the filtration of **1**, addition of diethyl ether to the resulting deep red mother liquor gave on two occasions very dark red crystals of complex **2** in very low yield. A number of further attempts to repeat the preparation of **2** were unsuccessful. The amount of **2** obtained was sufficient to show that it is diamagnetic and to determine its crystal structure, which is shown in Fig. 1; relevant bond dimensions are in Table 1.

The mechanism of the formation of complex **2** is obscure. It has a linear structure with two formally molybdenum(IV), d^2 , $Mo(NS_3)_2$ units linked in a staggered conformation by a $(\mu-S)$ atom. It is therefore a member of a family of complexes containing the linear $[Mo-S-Mo]^n$ unit ($n = 2$ or 6) whose bonding consists of¹³ two σ -bonding orbitals and three pairs of π -type

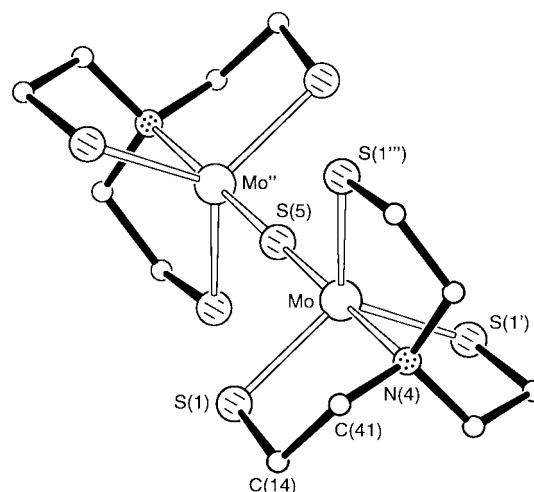


Fig. 1 A molecule of $[Mo(NS_3)_2(\mu-S)]$ in crystals of **2**. A threefold symmetry axis passes through the length of the molecule and the bridging sulfur atom S(5) lies on a centre of symmetry. For clarity, hydrogen atoms have been omitted in all the figures.

orbitals, one bonding, one non-bonding and one anti-bonding. For complexes such as **2** and the anion $[Mo(CN)_6(\mu-S)]^{6-}$,¹³ which contain the $[Mo-S-Mo]^{6+}$ unit, the 12 valence electrons of this unit fill the two σ -bonding orbitals and the four bonding and non-bonding π -type orbitals described above.

This bonding scheme explains why the Mo–($\mu-S$) distance in **2**, 2.143(1) Å, is close to those found in related complexes containing the linear $[Mo-S-Mo]^{2+}$ unit, *e.g.* $[Mo(CO)_2[BH-(C_3N_2H_3)_2]_2(\mu-S)]$ [2.180(1) Å],¹³ and $[Mo(CO)_2[BH-(C_3N_2Me_2H)_2]_2(\mu-S)]$ [2.200(2) Å],¹³ as well as the $[Mo-S-Mo]^{6+}$ -type complex $[Mo(Et_2NCS_2)_3]_2(\mu-S)$ [2.191(2) Å (mean)].¹⁴ This is because in the 16-electron $[Mo-S-Mo]^{2+}$ systems the σ -bonding orbitals and the four bonding and non-bonding π -type orbitals are filled as for the $[Mo-S-Mo]^{6+}$ systems and the extra two valence electrons provided by each Mo occupy non-bonding orbitals (in the plane normal to the Mo–S–Mo axis).¹³

The variation of co-ordination number at Mo in the above series (5, 6 and 7) appears to have little effect on the Mo–S distance, although the distance for **2**, with the lowest co-ordination number at Mo, lies at the shorter limit. The Mo–thiolate distance in **2** [2.299(1) Å] is close to the range of Mo–thiolate distances found for the related series of molybdenum(IV) $(\mu-S)_2$ -bridged complexes $[Mo(SR)(XR')(L)]_2(\mu-S)_2$ ($R = C_6H_5$, Pr^i , $2,4,6$ or Bu^t ; $X = O$ or S , $R' = Me$, Et or Bu^t ; $L = PMePh_2$, $PEtPh_2$, PMe_2Ph or $NHMe_2$) (2.31–2.35 Å).¹⁵

Upon treatment with NH_2NHR ($R = Me$ or Ph) in CH_2Cl_2 , complex **1** gives the soluble, red, diamagnetic diazenides

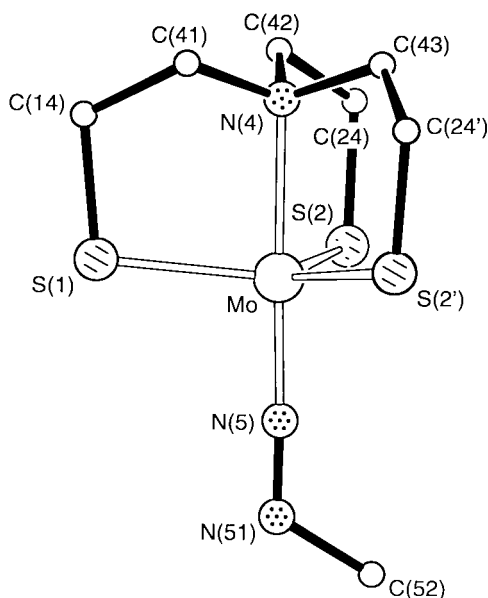


Fig. 2 A molecule of $[\text{Mo}(\text{NS}_3)(\text{NNMe})]$, **3**, which lies across a mirror plane; only one of the disordered NS_3 ligands is shown.

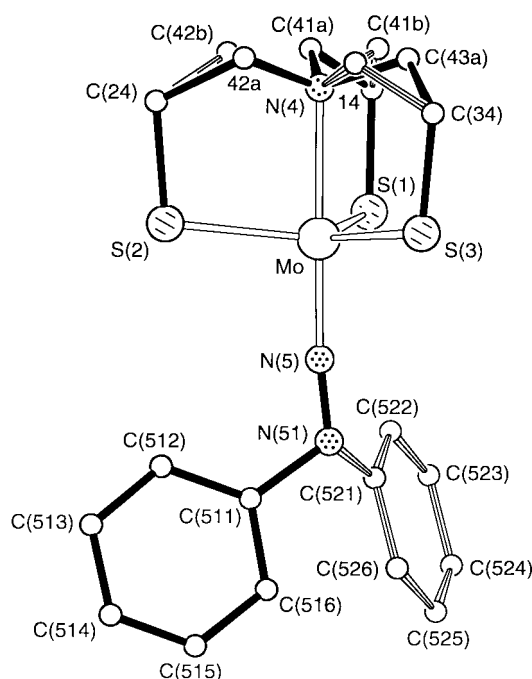


Fig. 3 A molecule of $[\text{Mo}(\text{NS}_3)(\text{NNPh})]$, **4**. The two orientations of both the disordered NS_3 ligand and the phenyl group of the NNPh ligand are shown.

$[\text{Mo}(\text{NS}_3)(\text{N}_2\text{R})]$ ($\text{R} = \text{Me}$ **3** or Ph **4**) in reasonable yield. Both complexes gave X-ray quality crystals from CH_2Cl_2 and have closely related structures as shown in Figs. 2 and 3; molecular dimensions are in Table 1. Both **3** and **4** have essentially trigonal bipyramidal geometry with the three sulfur ligands in the trigonal plane and the diazenide group *trans* to the apical nitrogen of the NS_3 ligand. In both compounds also the $\text{Mo}-\text{N}-\text{N}$ angle is essentially linear [$177.4(3)^\circ$ for **3** and $174.1(5)^\circ$ for **4**] and the $\text{N}-\text{N}-\text{C}$ angle is trigonal [$120.3(3)^\circ$ for **3** and $118.4(6)^\circ$ for **4**]. These dimensions and the $\text{N}-\text{N}$ distances [$1.213(4)$ Å for **3** and $1.232(6)$ Å for **4**] are in the normal range for diazenide complexes of this type, e.g. $[\text{Mo}(\text{NNPh})_2\{(\text{SCH}_2\text{CH}_2)_2\text{NCH}_2\text{CH}_2\text{NMe}_2\}]^{16}$ has $\text{Mo}-\text{N}-\text{N}$ angles of $173.0(15)$ and $162.7(15)^\circ$, $\text{N}-\text{N}$ distances of $1.23(2)$ and $1.22(2)$ Å plus trigonal $\text{N}-\text{N}-\text{C}$ angles, and $[\text{Mo}(\text{NNPh})(\text{SC}_6\text{H}_2\text{Pr}^1_3-2,4,6)_3(\text{MeCN})]^{17}$ has an $\text{Mo}-\text{N}-\text{N}$ angle of $171.2(11)^\circ$ and $\text{N}-\text{N}$ distance of $1.211(17)$ Å. The linearity of the $\text{Mo}-\text{N}-\text{N}$ units is consistent with exten-

sive delocalised multiple bonding throughout this grouping and with the diazenide ligands acting as three-electron donors to the Mo atoms.

The IR spectrum of complex **3** shows an absorption at 1610 cm^{-1} characteristic of the diazenide $\text{N}=\text{N}$ stretching vibration, but **4** shows two absorptions at 1601 and 1542 cm^{-1} indicative of coupling between the $\text{N}=\text{N}$ and phenyl vibrations, as has been observed in the related complexes $[\text{Mo}(\text{NNPh})(\text{SC}_6\text{H}_2\text{Pr}^1_3-2,4,6)_3(\text{MeCN})]$ (1645 and 1673 cm^{-1})¹⁷ and $[\text{Ru}(\text{NNPh})(\text{CO})_2(\text{PPh}_3)_2]\text{PF}_6$ (1680 and 1592 cm^{-1}).¹⁸

In its ^1H NMR spectrum, complex **3** shows two triplet resonances for the CH_2 groups at δ 3.50 and 3.43 and a singlet for the Me group at δ 3.8; there is no evidence for the occurrence of isomers under the conditions of measurement (see Experimental section). Compound **4** shows CH_2 triplets at δ 3.54 and 3.27 and a broad Ph absorption at δ 7.5–7.2.

With N_2H_4 , **1** gives a dark green-brown, diamagnetic, insoluble compound formulated as $[\{\text{Mo}(\text{NS}_3)(\text{N}_2\text{H})\}_n]$ **5**, on the basis of its microanalysis and broad IR absorptions centred at 1602 cm^{-1} , close to the values for $\nu(\text{N}=\text{N})$ observed for **3** and **4**, and at 3200 cm^{-1} , which is most likely associated with an $\text{N}-\text{H}$ stretching vibration. The broadness of its IR bands and its insolubility are consistent with an extended solid-state structure for **5** involving hydrogen bonding and/or bridging sulfur interactions. Attempts to deprotonate **5** to give a dinitrogen complex using LiBu^t , KOBU^t or Na gave dark brown, intractable materials which could not be characterised and showed no IR absorption characteristic of an N_2 ligand.

Both complexes **3** and **4** react with mineral acids HX ($\text{X} = \text{BF}_4$ or Cl) in CH_2Cl_2 to give the yellow-brown, diamagnetic hydrazides $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{HR})]\text{X}$ (**6**, $\text{R} = \text{Me}$, $\text{X} = \text{BF}_4$; **7**, $\text{R} = \text{Me}$, $\text{X} = \text{Cl}$; **8**, $\text{R} = \text{Ph}$, $\text{X} = \text{BF}_4$) as precipitates, which easily deprotonate in more basic solvents in which they are soluble to regenerate the red parent complexes. In the solid state they show $\text{N}-\text{H}$ stretching absorptions in their IR spectra (at 3180 cm^{-1} for **7** and **8**, and 3260 cm^{-1} for **6**). The facile deprotonation in solvents such as acetone, in which they are soluble, precluded reliable NMR measurements for **6**, **7** and **8** and production of crystals for X-ray study. In the absence of definitive structural study, it is assumed that **6**, **7** and **8** result from protonation of the terminal nitrogen atom of the diazenides **3** and **4**, and are thus terminal hydrazides, since this is the most usual pattern for such reactions^{19,20} and also appears to be the case for the NNMe_2 analogue of **6**, described as follows.

Compound **3** reacts with $[\text{Me}_3\text{O}]\text{BF}_4$ in CH_2Cl_2 to precipitate diamagnetic, yellow $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{Me}_2)]\text{BF}_4$ **9**. This complex does not show a band in the $\text{N}=\text{N}$ region of its IR spectrum and is sufficiently stable in acetone- d_6 to allow ^1H NMR study, which shows triplet CH_2 resonances at δ 4.03 and 3.82 and a singlet at δ 4.15, which is assigned to equivalent terminal NMe_2 groups of the hydrazide ligand. The ^{19}F NMR resonance assigned to BF_4^- is at $\delta -151.3$ and **9** dealkylates and reverts to **3** on standing in acetone for a few hours (see Experimental section).

As pointed out above and by others,²¹ NNR ligands are three-electron donors and therefore would be expected to have similar bonding properties to those of NO. We therefore treated complex **3** with NO gas and this caused displacement of the N_2Me ligand (its fate was not determined) to give yellow, diamagnetic $[\text{Mo}(\text{NS}_3)(\text{NO})]$ **10**, whose crystal structure (Fig. 4; two independent molecules with similar parameters, see Table 1 and Experimental section) shows it to have a similar geometry to **3** with a linear MoNO system replacing the MoN_2Me grouping. Its molecular dimensions [$d(\text{Mo}-\text{NO})$, $1.782(2)$; $d(\text{N}-\text{O})$, $1.190(3)$ (mean) Å] and $\nu(\text{NO})$ value (1644 cm^{-1}) are close to those of the analogue $[\text{Mo}(\text{SC}_6\text{H}_2\text{Pr}^1_3-2,4,6)_3(\text{NH}_3)(\text{NO})]$ [$d(\text{Mo}-\text{NO})$, $1.775(29)$; $d(\text{N}-\text{O})$, $1.14(4)$ Å; $\nu(\text{NO})$ 1680 cm^{-1}].²¹

In an attempt to obtain CO complexes of Mo and W with the NS_3 ligand, we treated $[\{\text{Mo}(\mu\text{-Br})\text{Br}(\text{CO})_4\}_2]$ and $[\text{W}_2(\text{CO})_3(\text{MeCN})_2]$ with $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ in the presence of NEt_3

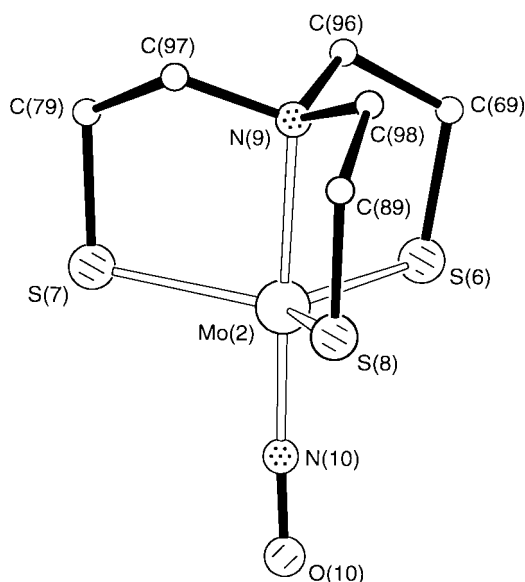


Fig. 4 One of two virtually identical molecules of $[\text{Mo}(\text{NS}_3)(\text{NO})]$ **10**.

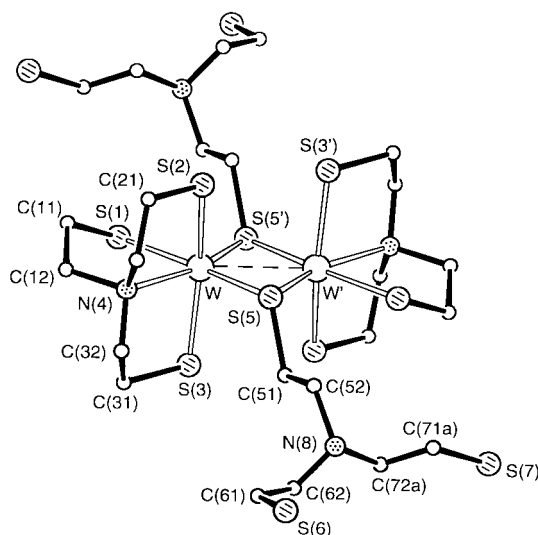
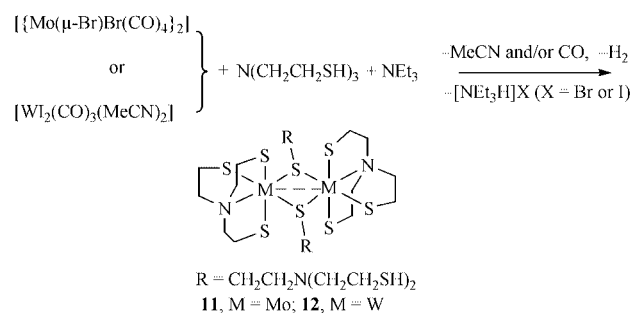


Fig. 5 A molecule of $[\{\text{W}(\text{NS}_3)\}_2\{\mu\text{-SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})_2\}_2]$ **12**. There is disorder in the S(7) arm of the bridging ligand; only the atoms of the major component are shown.



Scheme 2

(Scheme 2). However, these reactions gave mixtures of products, from which the only characterisable complexes were the poorly soluble, diamagnetic compounds $[\{\text{M}(\text{NS}_3)\}_2\{\mu\text{-SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})_2\}_2]$ ($\text{M} = \text{Mo}$ **11** or W **12**) whose structures have been established by a crystal structure determination of **12**. The structure of **12** (Fig. 5, Table 1) consists of two rather distorted octahedral $\text{W}(\text{NS}_3)$ units which share an edge formed by the bridging sulfur atoms of two monodentate $\text{SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})_2$ ligands. In the tetra-

dentate NS_3 ligands the three thiolate sulfur atoms are bound meridionally, and the pseudo-trigonal symmetry of this ligand noted in the previous structures has been lost. This asymmetry is reflected in the torsion angles of the N-C-S arms of the ligands; instead of three similar values of the same sign, the sign of one in this complex is opposed to that of the other two.

Formally, compounds **11** and **12** contain metal(IV) units. Thus, as well as elimination of halide (presumably as HBr and HI), CO and MeCN from the metal(II) starting materials, an oxidation process has occurred. It seems most likely that the latter process involved elimination of H_2 from the thiol and some H_2 was detected in the gas emitted from the reactions, but it was not quantified. Both **11** and **12** proved too insoluble for reliable NMR measurements and their IR spectra did not show clear S-H bands assignable to the $\mu\text{-SCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{SH})_2$ ligands.

In the structure of **12** the bridging W-S distances [2.391(3) and 2.459(3) Å] are slightly longer than the non-bridging W-S distances [mean 2.379(15) Å]. The $\text{W}\cdots\text{W}$ distance of 2.719(1) Å and the acute W-S-W angles [68.2(1)°] indicate multiple metal-metal bonding as would be expected for a diamagnetic $d^2\text{-}d^2$ metal(IV) system.¹⁵ The two co-ordination octahedra are essentially eclipsed and share a good 'equatorial' plane which includes the central W_2S_2 unit. The apical W-S(2) and W-S(3) bonds are, however, displaced from the normal to that plane; the S(2)-W-S(3) angle is 155.3(1)° and the S(2)-W-S(3') torsion angle is -23.4(1)°. These distortions arise from constraints in the NS_3 ligand geometry and, more importantly, from the proximity of the adjoining octahedra; the interligand $\text{S(2)}\cdots\text{S(3')}$ distance is still very short at 3.190(5) Å. The thiol hydrogen atoms on the pendant arms of the bridging ligands were not located, but intermolecular $\text{S(6)}\cdots\text{S(7'')}$ and $\text{S(7)}\cdots\text{S(3'')}$ distances of 3.981(12) and 3.865(8) Å suggest that molecules are linked through hydrogen bonds in a three-dimensional network.

Conclusion

The ability of $\text{N}(\text{CH}_2\text{CH}_2\text{SH})_3$ to act as a reducing or an oxidising agent, and as a precursor to mono-, di- or tri-dentate ligands which can also bridge metals, can lead to complicated co-ordination chemistry, as illustrated by this work. Nevertheless, the reaction of the Mo=O unit in complex **1** with hydrazines has allowed access to a range of monomeric complexes with N_2R and N_2HR ligands at $\text{Mo}(\text{NS}_3)$ sites. The diazenide compounds appear to be soluble, monomeric starting materials from which to prepare other complexes of interest. This has proved effective here in the preparation of $[\text{Mo}(\text{NS}_3)(\text{NO})]$ from $[\text{Mo}(\text{NS}_3)(\text{N}_2\text{Me})]$ and will be extended in future work.

Experimental

General

All operations were carried out under a dry dinitrogen atmosphere, using standard Schlenk techniques. All the solvents were distilled under dinitrogen from the appropriate drying agents prior to use. The compounds $[\{\text{Mo}(\mu\text{-Br})\text{Br}(\text{CO})_4\}_2]$ and $[\text{W}_2(\text{CO})_3(\text{MeCN})_2]$ were prepared by literature methods.²² All other starting materials were obtained from the Aldrich Chemical Co. and used without further purification unless stated otherwise. Infrared spectra were recorded on Perkin-Elmer 180, 883 or Shimadzu FTIR-8101M instruments in Nujol mulls, NMR spectra on JEOL GSX 270 or JNM-LA400 spectrometers (^1H and ^{19}F , reference SiMe_4 or CFCl_3 respectively). Magnetic moment determinations were in the solid state, using a Johnson-Matthey Gouy balance and mass spectra were determined with a VG Masstorr DX instrument. Microanalyses were by Mr A. Saunders of the University of East Anglia, UK.

Preparations

N(CH₂CH₂SH)₃ [NS₃H₃]. A modification of the literature method was used. Batches of tris(chloroethyl)amine hydrochloride²³ (**CAUTION:** vesicant) were made from 60 g batches of triethanolamine and converted the same day into tris[2-(isothioureido)ethyl]amine tetrahydrochloride.²⁴ This work was carried out in an enclosed Schlenk apparatus while wearing heavy duty gloves and a face mask. The tetrahydrochloride was treated in 0.05 or 0.1 mol batches with sodium hydroxide¹¹ giving tris(2-sulfonylethyl)amine NS₃H₃. The crude product was not purified by distillation nor by conversion into its hydrochloride, but rather it was dissolved in diethyl ether, filtered to remove a white solid, and the ether removed from the filtrate *in vacuo*. The overall yield of NS₃H₃ from triethanolamine was 30–40%.

[{MoO(NS₃)₂}]₂ **1.** To a stirred solution/suspension of [MoO₂-(acac)₂] (2.0 g, 6.1 mmol) in CH₂Cl₂ (60 cm³) was added NS₃H₃ (2.0 g, 15.0 mmol) and the resulting mixture stirred for 16 h to give an orange-red suspension in a brown solution. The precipitate was filtered off, washed with CH₂Cl₂ (3 × 4 cm³) and dried in a vacuum to give complex **1** as an orange-red solid. Yield 1.8 g, 92%. Found: C, 23.4; H, 3.9; N, 5.0; S, 28.9. C₆H₁₂MoNOS₃ requires C, 23.5; H, 3.9; N, 4.6; S, 31.4%. IR: 937s cm⁻¹ [ν(μMoO)], diamagnetic.

[{Mo(NS₃)₂(μ-S)}]₂ **2.** Diethyl ether (20 cm³) was added to the brown mother liquor resulting from the preparation of complex **1** above and the resulting solution allowed to stand for 7 d at room temperature, during which time deep red crystals deposited on the side of the containing flask. After decanting the mother liquor, these were carefully removed by hand in a glove box. Yield 0.05 g, 1.9%. Only one of a number of attempts to repeat this synthesis was successful, in similar yield. There were sufficient crystals for IR measurement (no notable bands), magnetic moment determination (diamagnetic) and structural characterisation by X-ray crystallography as described below.

[Mo(NS₃)(N₂Me)] **3.** The compound H₂NNHMe (2.8 g, 51.1 mmol) was added dropwise to a stirred suspension of complex **1** (1.5 g, 4.91 mmol) in CH₂Cl₂ (75 cm³) and the mixture stirred for 13 h. The resulting mixture was filtered from a sticky brown solid, which was not characterised, to give a burgundy-red solution. This was concentrated to about 20 cm³ in a vacuum then allowed to stand overnight at 4 °C, whereupon dark red crystals of **3** deposited. Yield 0.85 g, 52%. Recrystallisation from CH₂Cl₂–Et₂O gave diamagnetic, analytically pure red crystals which were suitable for X-ray studies. Found: C, 25.4; H, 4.4; N, 12.7. C₇H₁₅MoN₃S₃ requires C, 25.2; H, 4.5; N, 12.6%. IR: 1610s cm⁻¹ [ν(N=N)]. ¹H NMR (CD₂Cl₂): δ 3.50 (t, 2 H, ³J_{H-H} 5.7, CH₂), 3.43 (t, 2 H, ³J_{H-H} 5.7 Hz, CH₂) and 3.8 (s, 3H, NCH₃).

[Mo(NS₃)(N₂Ph)] **4.** The compound H₂NNHPh (0.22 g, 2.0 mmol) was added dropwise to a stirred suspension of complex **1** (0.12 g, 0.36 mmol) in CH₂Cl₂ (20 cm³) and the mixture stirred for 24 h. The resulting mixture was filtered from an air-sensitive, oily black solid which was not characterised, to give a burgundy-red solution which was concentrated to about 7 cm³ in a vacuum, then Et₂O (10 cm³) was added and the resulting red solution allowed to stand at room temperature overnight, whereupon dark red crystals of **4** deposited. Yield 0.07 g, 46%. Recrystallisation from CH₂Cl₂–Et₂O gave analytically pure red crystals which were suitable for X-ray studies. Found: C, 36.8; H, 4.4; N, 10.8. C₁₂H₁₇MoN₃S₃ requires C, 36.5; H, 4.3; N, 10.6%. IR: 1601s, 1542s cm⁻¹ [ν(N=N)], diamagnetic. ¹H NMR (CD₂Cl₂): δ 3.54 (t, 2 H, ³J_{H-H} 5.6, CH₂), 3.27 (t, 2 H, ³J_{H-H} 5.7, CH₂) and 7.5–7.2 (m, 5 H, NC₆H₅).

[{Mo(NS₃)(N₂H)}]_n **5.** Anhydrous N₂H₄ (0.1 g, 3.1 mmol) was added dropwise to a stirred suspension of complex **1** (0.1 g, 0.3 mmol) in MeCN (30 cm³) and the mixture stirred for 24 h. The resulting mixture was filtered to give **5** as a dark green-brown solid which was washed with Et₂O and dried in a vacuum. Yield 0.06 g, 60%. Compound **5** is insoluble in common solvents and diamagnetic in the solid. Found: C, 21.4; H, 4.3; N, 12.8. C₆H₁₃MoN₃S₃ requires C, 22.6; H, 4.1; N, 13.2%. IR: 3200s(br) [ν(NH)], 1602s(br) cm⁻¹ [ν(N=N)]. Attempts to deprotonate **5** to give a dinitrogen complex using LiBu^t, KOBu^t or Na in thf gave dark brown, intractable materials which could not be characterised and showed no IR absorption characteristic of an N₂ ligand.

[Mo(NS₃)(N₂HMe)]BF₄ **6.** The compound HBF₄·Et₂O (8.2 mmol, 1.3 cm³ of a solution containing 6.3 mmol cm⁻³ of HBF₄ in Et₂O) was added dropwise to a stirred suspension of complex **3** (0.2 g, 0.66 mmol) in CH₂Cl₂ (70 cm³). The solution changed immediately from burgundy-red to yellow and a brown-yellow precipitate began to form. It was stirred for 15 min then allowed to stand overnight, during which time fine brown-yellow needles of **6** had formed which were filtered off, washed with CH₂Cl₂ (5 cm³), then a small amount of Et₂O and dried in a vacuum. The crystals contained one CH₂Cl₂, probably held by hydrogen bonding with the BF₄⁻. Yield 0.17 g, 52%. Found: C, 18.7; H, 3.6; N, 8.8. C₈H₁₈BCl₂F₄MoN₃S₃ requires C, 19.0; H, 3.6; N, 8.3%. IR: 3260s [ν(NH)], 1161–1080s(br) cm⁻¹ [ν(BF₄)], diamagnetic. Attempts to obtain NMR spectra or to recrystallise **6** were frustrated by the ready loss of HBF₄ in solvents such as acetone in which **6** is soluble, regenerating the starting material **3**.

[Mo(NS₃)(N₂HMe)]Cl **7.** Anhydrous HCl (0.5 mmol, 0.5 cm³ of a molar solution in Et₂O) was added dropwise to a stirred suspension of complex **3** (0.1 g, 0.33 mmol) in CH₂Cl₂ (30 cm³). The solution changed immediately from burgundy-red to yellow and a brown-yellow precipitate deposited over 5 min which was filtered off, washed with CH₂Cl₂ (5 cm³), then Et₂O (2 × 5 cm³) and dried in a vacuum to give **7** as yellow-brown microcrystals. The crystals contained CH₂Cl₂ (0.25 mol). Yield 0.06 g, 50%. Found: C, 22.3; H, 4.3; Cl, 13.0; N, 11.0. C_{7.25}H_{16.5}Cl_{1.5}MoN₃S₃ requires C, 22.3; H, 4.3; Cl, 13.6; N, 10.7%. IR: 3180 cm⁻¹ [ν(NH)], diamagnetic. Attempts to obtain NMR spectra or recrystallise **7** were frustrated by the ready loss of HCl in solvents such as acetone in which **7** is soluble, regenerating **3**.

[Mo(NS₃)(N₂HPh)]BF₄ **8.** This complex was prepared in a similar manner to **6** from **3** (0.02 g, 0.07 mmol) and HBF₄·Et₂O (0.15 mmol, 0.3 cm³ of a solution containing 0.5 mmol cm⁻³ of HBF₄ in Et₂O) in CH₂Cl₂ (20 cm³). Yield 0.02 g, 52%. It easily loses HBF₄ as for **6** and is diamagnetic. Found: C, 28.8; H, 3.6; N, 8.6. C₁₂H₁₈BF₄MoN₃S₃ requires C, 29.8; H, 3.8; N, 8.7%. IR: 3180s [ν(NH)], 1161–1080s(br) cm⁻¹ [ν(BF₄)].

[Mo(NS₃)(N₂Me₂)]BF₄ **9.** The salt [Me₃O]BF₄ (0.7 g, 4.7 mmol) was added dropwise to a stirred solution of complex **3** (0.12 g, 0.36 mmol) in CH₂Cl₂ (30 cm³) and the mixture stirred for 24 h. The burgundy-red solution slowly became yellow and deposited a yellow precipitate which was filtered off, washed with CH₂Cl₂ (3 cm³) and dried in a vacuum to give **9** as yellow microcrystals. Compound **9** reverted to **3** only slowly on standing in acetone solution, so that NMR data could be obtained. Yield 0.07 g, 54%. Found: C, 22.1; H, 4.1; N, 9.3. C₈H₁₈BF₄MoN₃S₃ requires C, 22.1; H, 4.2; N, 9.7%. IR: 1100–1048s cm⁻¹ [ν(BF₄)]. ¹H NMR (acetone-d₆): δ 4.03 (t, 2 H, ³J_{H-H} 5.6, CH₂), 3.82 (t, 2 H, ³J_{H-H} 5.7 Hz, CH₂) and 4.15 (s, 6 H, NCH₃). ¹⁹F NMR (acetone-d₆): δ –151.3.

[Mo(NS₃)(NO)] **10.** Compound **3** (0.17 g, 0.53 mmol) was

Table 2 Crystallographic and refinement data at 298 K for the (NS₃) complexes of Mo and W

	[{Mo(NS ₃) ₂ (μ-S)}·0.3H ₂ O] 2	[Mo(NS ₃) ₂ (NNMe)] 3	[Mo(NS ₃) ₂ (NNPh)] 4	[Mo(NS ₃) ₂ (NO)] 10	[{W(NS ₃) ₂ {μ-SCH ₂ CH ₂ -N(CH ₂ CH ₂ SH) ₂ } ₂ }] 12
Elemental formula	C ₁₂ H ₂₄ Mo ₂ N ₂ S ₇ ·0.3H ₂ O	C ₇ H ₁₅ MoN ₃ S ₃	C ₁₂ H ₁₇ MoN ₃ S ₃	C ₆ H ₁₂ MoN ₂ OS ₃	C ₂₄ H ₅₂ N ₄ S ₁₂ W ₂
<i>M</i>	618.0	333.3	395.4	320.3	1149.1
Crystal system	Rhombohedral	Orthorhombic	Orthorhombic	Triclinic	Monoclinic
Space group (no.)	<i>R</i> $\bar{3}$ (no. 148)	<i>Pmcn</i> (equiv. to no. 62)	<i>Pcab</i> (equiv. to no. 61)	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> 2 ₁ / <i>a</i> (equiv. to no. 14)
<i>a</i> /Å	8.3292(5)	8.4093(7)	15.1833(14)	10.5200(13)	12.2952(14)
<i>b</i> /Å	8.3292(5)	10.5438(10)	12.2873(14)	13.435(2)	13.9137(15)
<i>c</i> /Å	8.3292(5)	14.0272(13)	16.861(2)	7.9567(8)	11.6072(14)
<i>α</i> /°	77.833(7)			90.410(9)	
<i>β</i> /°	77.833(7)			101.230(10)	107.072(10)
<i>γ</i> /°	77.833(7)			96.569(10)	
<i>V</i> /Å ³	543.74(7)	1243.7(2)	3145.6(6)	1095.3(2)	1898.2(4)
<i>Z</i>	1	4	8	4	2
<i>μ</i> (Mo-Kα)/cm ⁻¹	18.3	15.3	12.2	17.3	67.4
Total no. reflections measured (not including absences)	3814	1604	3168	6811	3076
<i>R</i> _{int} for equivalents	0.030	0.009	0.036	0.022	0.048
Total no. unique reflections	641	1168	2759	6366	2636
No. 'observed' reflections (<i>I</i> > 2σ _{<i>I</i>})	573	1064	1266	5078	1853
Structure determined by	Direct methods	Direct methods	Automated Patterson	Automated Patterson	Heavy atom method
Final <i>R</i> ₁	0.028	0.021	0.103	0.040	0.071
<i>wR</i> ₂	0.074	0.050	0.114	0.077	0.130

dissolved in CH₂Cl₂ (30 cm³) and NO bubbled through the solution for a few minutes to replace the N₂ atmosphere with NO (50 cm³ capacity flask). Upon stirring the solution darkened and stirring was continued for 16 h. Yellow-brown crystals of **10** precipitated and were filtered off, washed with Et₂O (2 × 3 cm³) and vacuum dried. Yield 0.14 g, 88%. Recrystallisation from dmf–Et₂O gave analytically pure yellow crystals which were suitable for X-ray study. Found: C, 22.9; H, 3.7; N, 8.9. C₆H₁₂MoN₂OS₃ requires C, 22.5; H, 3.8; N, 8.7%. IR: 1644s cm⁻¹ [ν(NO)]. ¹H NMR (CD₂Cl₂): δ 3.62 (t, 2 H, ³*J*_{H-H} 5.6, CH₂) and 3.44 (t, 2 H, ³*J*_{H-H} 5.6 Hz, CH₂).

[{Mo(NS₃)₂{μ-SCH₂CH₂N(CH₂CH₂SH)₂-S₂}] **11**. The complex [{Mo(μ-Br)Br(CO)₄}]₂ (0.4 g, 1.08 mmol) was dissolved in MeCN (some gas was evolved) then NS₃H₃ (0.2 g, 1.04 mmol) was added dropwise with stirring. Triethylamine (0.38 g, 3.9 mmol) was added immediately, more gas was evolved and a cloudy purple-brown solution formed during 1 h. The solution was then stirred for 16 h to give a brown solid precipitate in a purple solution. The solid was filtered off, washed with Et₂O and vacuum dried. It contained CO bands in its IR spectrum at 1996, 1946, 1876 and 1815 cm⁻¹ together with broad bands in the 2300–2800 cm⁻¹ range characteristic of [NEt₃H]⁺. It appeared to be a mixture, since the ratio and intensity of the IR bands varied between preparations, but its poor solubility prevented satisfactory purification and further characterisation was not attempted. The mother liquor was taken to dryness and MeOH (25 cm³) added to give **11** as a brown solid which was filtered off, washed with MeOH until the washings were clear (4 × 3 cm³) then dried in a vacuum. Complex **11** is diamagnetic, very poorly soluble in common solvents and has a very similar IR spectrum to that of structurally characterised **12** below. Yield 0.15 g, 29%. Found: C, 29.5; H, 5.0; N, 5.7. C₁₂H₂₆MoN₂S₆ requires C, 29.6; H, 5.4; N, 5.8%. In an experiment in which the reaction flask was closed by a septum a gas sample was removed by use of a syringe and some H₂ was detected by mass spectrometry, but not quantified.

[{W(NS₃)₂{μ-SCH₂CH₂N(CH₂CH₂SH)₂-S₂}] **12**. The complex [W₂(CO)₃(MeCN)₂] (0.4 g, 0.66 mmol) was dissolved in MeOH (25 cm³) giving an orange solution. The amine NS₃H₃ (0.13 g, 0.67 mmol) was added dropwise with stirring, followed

immediately by NEt₃ (0.38 g, 3.9 mmol). A brown solid deposited and the mixture was stirred for 3 h, after which the solid was filtered off, washed with MeOH (3 × 5 cm³) and vacuum dried. It had CO bands at 1966, 1936, 1901, 1839 and 1826 cm⁻¹ in its IR spectrum, but their intensity varied between different preparations and because its insolubility prevented satisfactory purification further characterisation was not attempted. The above washings were combined with the brown mother liquor from the filtration and the resulting solution deposited brown crystals of **12** on standing for 6 weeks. These were filtered off and after vacuum drying were suitable for X-ray analysis. Yield 0.1 g, 26%. Found: C, 25.4; H, 4.4; N, 5.3. C₁₂H₂₆N₂S₆W requires C, 25.1; H, 4.6; N, 4.9%. Compound **12** has no CO bands in its IR spectrum, is very poorly soluble in common solvents and is diamagnetic. Evolution of H₂ from the reaction was shown as in the preparation of **11**.

Crystal structure analyses

The X-ray crystallographic analysis of one complex, **2**, is described here; the other samples were examined similarly and some features of difference are noted below. Crystallographic data from all the analyses are collated in Table 2.

Crystal structure analysis of [{Mo(NS₃)₂(μ-S)}·0.3H₂O] **2.** A small crystal was mounted on a glass fibre. After preliminary photographic examination this was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters (from the settings of 25 reflections, each centred in four orientations) and for measurement of diffraction intensities.

The structure was determined by the direct methods routines in the SHELXS program²⁵ and refined by full-matrix least-squares methods, on *F*², in SHELXL.²⁶ Hydrogen atoms were included in idealised positions. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the isotropic temperature factors of the hydrogen atoms set to ride on the *U*_{eq} values of the parent carbon atoms. A persistent difference peak on a centre of symmetry was thought to be an adventitious water molecule and was included with partial occupancy. In the final difference map, the two highest peaks (*ca.* 1.2 and 0.6 e Å⁻³) were within the complex molecule; all other peaks were less than 0.4 e Å⁻³.

Scattering factors for neutral atoms were taken from reference 27. Computer programs used in this analysis have been noted above or in Table 4 of reference 28, and were run on a DEC-Alpha Station 200 4/100 in the Department of Biological Chemistry, John Innes Centre.

In complex **3** the molecule lies across a mirror plane; the NS₃ ligand is therefore disordered in two mirror-related orientations, and the NNMe ligand lies in the symmetry plane. There is orientational disorder, too, in approximately equal proportions, in the NS₃ ligand of **4**, and the phenyl group lies in one of two orientations in the ratio of *ca.* 4:1. Only those atoms with site occupancies greater than 0.5 were refined anisotropically. In crystals of **10** there are two virtually identical molecules in the asymmetric unit. In one of the two pendant NCH₂CH₂SH arms of the bridging ligands in **12**, alternative sites, with occupancy ratio of 68:32(5), were identified for the methylene groups.

CCDC reference number 186/1784.

See <http://www.rsc.org/suppdata/dt/a9/a908777j/> for crystallographic files in .cif format.

Acknowledgements

We thank the BBSRC for support.

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Paper a908777j