Disulfur-bridged Complexes of Molybdenum. Crystal Structure of the Dimolybdenum(IV) Complex $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ and of the $Mo^{IV}Mo^{V}$ Complex $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$†

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Treatment of $[Mo(CO)_6]$ with S_2Cl_2 gave a very dark green material of empirical formula $Mo_2S_2Cl_6{\cdot}CH_2Cl_2$ **1** which, on reaction with L, gave green $[\{MoCl_3(L)\}_2(\mu\text{-}S_2)(\mu\text{-}L)]$ (L = C_4H_8S **2a**, $PhCH_2SMe$ **2b** or C_4H_8O **2c**), and with SMe_2 gave the novel, brown, unsymmetrical, mixed-oxidation-state complex $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**. The structures of **2a** and **3** have been established by X-ray crystallography. Compounds **2a**–**2c** are diamagnetic and NMR data have been obtained, whereas **3** is paramagnetic and shows, in a CH_2Cl_2 glass at 40 K, a broad, roughly axial EPR resonance with g_{max} at 1.94.

A family of disulfur-bridged complexes of molybdenum is known.[1] These include $[Cl_4Mo(\mu\text{-}S_2)_2MoCl_4]^{2-}$,[2] $[Mo_2(\mu\text{-}S_2)(\mu\text{-}SO_2)(CN)_8]^{2-}$,[3] and $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$.[4] The last complex was reported briefly by us[4] as formed from the reaction of C_4H_8S with the product of the reaction of $[Mo(CO)_6]$ with S_2Cl_2 in CH_2Cl_2, and formulated as $Mo_2S_2Cl_6{\cdot}CH_2Cl_2$ **1**. We prepared this material during our studies of compounds of sulfur-ligated molybdenum and tungsten which relate to important catalytic processes, particularly nitrogen fixation and hydrodesulfurisation.[4] Here we give full details of the synthesis of **1**, the structure and properties of $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a**, and the preparation of its analogues in which the C_4H_8S ligand is replaced by $PhCH_2SMe$ (**2b**) or C_4H_8O (**2c**). We also report the preparation and structure of the novel, co-ordinatively unsymmetrical, mixed-oxidation-state complex $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**, which is also obtained from **1**.

Results and Discussion

Reaction of $[Mo(CO)_6]$ *with* S_2Cl_2.—Our original aim in carrying out this reaction was to find an alternative, convenient route to the potential starting material, $MoSCl_3$. Published routes[5] to this compound often require long reaction times and high temperatures. We found that upon reflux in CH_2Cl_2, $[Mo(CO)_6]$ and S_2Cl_2 gave high yields of a very dark green, oxygen- and water-sensitive compound that analysed inconsistently, but close to the empirical composition $Mo_2S_2Cl_6{\cdot}CH_2Cl_2$ **1**. The presence of CH_2Cl_2 in this material was demonstrated by elemental analysis and IR spectra; details are in Table 1 and the Experimental section. This material also appears to contain the disulfide ligand since its reactions, described below, give products containing the disulfide group; also a band at 608 cm^{-1} in its IR spectrum is in the range associated with ν(S–S) for this ligand.[1] Synthesis of complexes of the disulfide ligand from S_2Cl_2 is well known, *e.g.* with S_2Cl_2, Nb gives $[Nb_2(S_2)_2Cl_4]$[6] and $MoCl_3$ gives $[Mo_3S(S_2)_3Cl_4]$ and $[Mo_2(S_2)_2Cl_6]$.[7] However, the situation cannot be completely clear in the absence of an X-ray crystal structure, because of the ability of terminal sulfide to be converted to disulfide in redox reactions.[5] Despite repeated attempts, the sensitivity of **1** prevented its further purification and crystallisation. Nevertheless, we were able to use it to produce a series of novel disulfide complexes in good yield, as described below.

Preparation of $[\{MoCl_3(L)\}_2(\mu\text{-}S_2)(\mu\text{-}L)]$ (L = C_4H_8S **2a** $PhCH_2SMe$ **2b** *or* C_4H_8O **2c**) *and X-Ray Crystal Structure of* **2a**.—Treatment of compound **1** with ligands L in CH_2Cl_2 gave the green, crystalline compounds **2** which are diamagnetic, poorly soluble in common solvents and moderately air-sensitive in solution. Their properties are given in Table 1. They show characteristic[1] S–S bands in their IR spectra at around 600 cm^{-1}. They are diamagnetic and for L = C_4H_8X (X = O or S) show two sets of ^1H NMR resonances in the ratio 2:1 (assignments are in Table 1, complex **2b** was insufficiently soluble for NMR spectroscopic measurements). The origin of this spectral pattern was shown to be due to the presence of one terminal and one bridging ligand in these complexes by determining the structure of **2a** by X-ray crystallography. We have already reported this structure, shown in Fig. 1, in a preliminary communication[4] and here we report additional features for completeness. Atomic coordinates and bond dimensions are in Tables 2 and 3.

The structure shows that the molecule has a μ-S_2 ligand between two molybdenum centres, and that each molybdenum has distorted pentagonal-bipyramidal co-ordination; the two co-ordination polyhedra share a common face. In addition to the μ-S_2 ligand, each molybdenum carries terminal C_4H_8S and Cl ligands and the relatively rare μ-C_4H_8S ligand; the bridging S atom of this ligand, S(3), is in an apical co-ordination site of each Mo atom, with Cl atoms, Cl(13) and Cl(23), in the opposite apical positions. Complexes with bridging thioether ligands are known, in particular a related series of C_4H_8S-bridged compounds exists for niobium and tantalum[8] and the complex $[(Me_2S)Cl_2Mo(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)MoCl_2(SMe_2)]$[9] is closely related to **2a**. The complex[3] $[(CN)_4Mo(\mu\text{-}S_2)(\mu\text{-}SO_2)\text{-}Mo(CN)_4]^{2-}$ also has a closely related structure in which, formally, CN^- replaces Cl^- and the terminal C_4H_8S ligands, and SO_2 replaces the bridging C_4H_8S. In the last complex, **2a**, the anion[2] $[Cl_4Mo(\mu\text{-}S_2)_2MoCl_4]^{2-}$ and the polymer $[\{MoCl_3S_2\}_n]$ the S–S distances are in the range (1.98–2.00 Å) generally found for μ-S_2 complexes and are shorter than that of free $S_2{}^{2-}$ (2.13 Å).[1,2] The μ-C_4H_8S ligand is symmetrically

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

Table 1 Physical properties of molybdenum complexes

Complex	Analysis[a] (%) C	H	S	λ_{max}[b]/nm	IR[c]/cm^{-1}	NMR[d] (δ_H)
1[e,f]	2.1	0.3	12.4		608, 378	
	(2.2)	(0.4)	(13.6)			
2a	19.7	3.0	21.8	686, 582	608, 367	2.83 (t, 8 H)[g]
	(19.6)	(3.2)	(21.8)		346	1.93 (t, 8 H)[h]
						1.60 (br, 4 H),[i] 1.25 (br, 4 H)[i]
2b	33.3	3.6		702	600, 385	
	(33.3)	(3.6)		362		
2c[j]	21.2	3.5		750	597, 396	1.9 (12 H)[k]
	(21.0)	(3.5)				3.8 (8 H)[l]
						4.55 (4 H)[m]
3[n]	10.8	2.5	28.5	686	611, 376	2.19 (12 H)[o]
		(2.8)	(29.5)		356	2.32 (6 H)[p]

[a] Calculated values in parentheses. [b] UV/VIS spectra as approximately 10^{-4} molar solutions in $CHCl_3$. [c] As KBr discs. [d] In $C^2H_2Cl_2$, relative to $SiMe_4$; t = triplet, qnt = quintet, br = broad multiplet. [e] Analytical values variable, but close to that for $Mo_2S_2Cl_6 \cdot CH_2Cl_2$, see text. [f] Cl 44.1 (45.4)%. [g] α-CH_2 of terminal C_4H_8S. [h] β-CH_2 of terminal C_4H_8S. [i] CH_2 of bridging C_4H_8S. [j] Cl 30.0 (28.4)%. [k] β-CH_2 of terminal and bridging C_4H_8O. [l] α-CH_2 of terminal C_4H_8O. [m] β-CH_2 of terminal C_4H_8O. [n] g_{max} = 1.94. [o] *trans* SMe_2. [p] unique SMe_2.

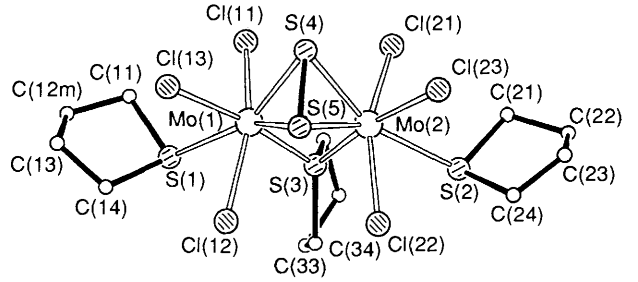


Fig. 1 Molecular structure of $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a**

Table 2 Final atomic coordinates (fractional × 10^4) for $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Mo(1)	614.0(1)	1208.2(1)	1789.8(2)
Cl(11)	334.8(4)	718.2(5)	3439.0(6)
Cl(12)	834.9(4)	2201.3(5)	611.1(7)
Cl(13)	−511.7(4)	1156.6(5)	1215.1(7)
S(1)	232.6(4)	2400.3(5)	2777.8(7)
C(11)	−390(2)	2198(3)	3750(3)
C(12m)*	−907(3)	2785(3)	3649(5)
C(12s)*	−970(12)	2329(16)	3335(20)
C(13)	−999(2)	2900(3)	2535(5)
C(14)	−328(2)	2953(2)	2001(4)
Mo(2)	1747.6(1)	387.9(1)	1504.5(2)
Cl(21)	1729.9(4)	−274.8(4)	3078.4(6)
Cl(22)	2280.6(4)	1152.7(4)	251.7(5)
Cl(23)	2050.1(4)	−716.7(4)	611.8(7)
S(2)	3005.7(4)	465.9(4)	2010.5(6)
C(21)	3276(2)	−253(3)	2880(3)
C(22)	3911(2)	−552(2)	2430(3)
C(23)	3825(2)	−576(3)	1302(3)
C(24)	3530(2)	138(2)	951(3)
S(3)	1666.5(3)	1480.7(4)	2512.1(5)
C(31)	1818(2)	1507(2)	3891(2)
C(32)	2353(2)	2086(2)	4007(3)
C(33)	2220(2)	2686(2)	3245(3)
C(34)	2126(2)	2320(2)	2219(3)
S(4)	643.0(4)	−91.2(4)	1466.8(6)
S(5)	876.3(4)	529.2(5)	268.0(6)

* The site occupancies for C(12m) and C(12s) are 0.8 and 0.2 respectively.

disposed between the two Mo atoms and the bridging Mo–S distance [mean 2.391(1) Å] (*trans* to Cl) is much less than that of the Mo to the terminal C_4H_8S ligands [mean 2.643(2) Å] (*trans* to S_2^{2-}). The Mo–Cl distances span the range 2.405(1)–2.418(1) Å.

The Mo–Mo distance [2.769(1) Å] is in the range (2.70–2.85 Å) generally observed in μ-S_2-dimolybdenum complexes[1,3,4] and a molybdenum–molybdenum bonding interaction is a possible, but inessential, reason for the diamagnetism of these Mo^{IV} compounds.

Because the physical properties of complexes **2b** and **2c** (Table 1) are so similar to those of **2a**, we assume that they have the same structure, with C_4H_8O and $PhCH_2SMe$ replacing C_4H_8S.

Preparation, X-Ray Crystal Structure and Properties of $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**.—Treatment of compound **1** with SMe_2 in CH_2Cl_2 did not give a green complex analogous to **2** but rather a brown, crystalline compound **3**. Analytical and physical properties of **3** are given in Table 1. The X-ray crystal structure of **3** has been determined (Fig. 2) and shows it to be dinuclear with the two molybdenum atoms joined by a μ-S_2–μ-S linkage, which as far as we are aware has no structural precedent for molybdenum, but analogues having the {Nb(μ-S)(μ-S_2)Nb}[5c] and {W(μ-S)(μ-S_2)W}[10] units have been structurally characterised. Atomic coordinates and dimensions for **3** are in Tables 4 and 5.

The seven-co-ordinate molybdenums of **3** have distorted pentagonal-bipyramidal geometry with a shared face as seen for **2a**; here also, the bridging sulfide atom, S(15), occupies an apical site to both Mo atoms, with Cl(11) and Cl(21) in the opposite apical positions. However, unlike **2a**, the molecule is co-ordinatively asymmetric with two molybdenum bonding to three Cl and one SMe_2, similar to **2a**, whereas the other is bonded to two Cl and two SMe_2 ligands. Thus the compound formally has one Mo^{IV} atom, Mo(1), and one Mo^V atom, Mo(2), neglecting any formal Mo–Mo bond, and is paramagnetic.

The S–S distance of the μ-S_2 group is, at 1.983(2) Å, close to the corresponding distance in **2a** and in the usual range for these ligands.[1,2] The mean Mo–μ-S_2 distance to Mo(1) and approximately *trans* to Cl(12) is 2.427(6) Å and is slightly longer than the mean distance to Mo(2) and approximately *trans* to S(24) at 2.407(12) Å. The Mo–μ-S bonds, both *trans* to Cl atoms, are similar, with mean value 2.433(3) Å; it is noticeable that these distances are longer than the Mo–μ-S_2 distances. This is unusual in the related family of compounds shown in Table 6, where in general for the metals Mo, Nb and W which have the M(μ-S_2)(μ-SR)M motif, the M–μ-S_2 distance is longer than the

Table 3 Molecular dimensions (bond lengths in Å, angles in °) in $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a** with e.s.d.s in parentheses; angles marked with an asterisk have e.s.d.s of less than 0.05°

(*a*) About the Mo atoms

Mo(1)–Mo(2)	2.769(0.3)	Mo(1)–S(1)	2.641(1)	Mo(2)–Cl(21)	2.389(1)	Mo(2)–S(3)	2.391(1)
Mo(1)–Cl(11)	2.405(1)	Mo(1)–S(3)	2.390(1)	Mo(2)–Cl(22)	2.408(1)	Mo(2)–S(4)	2.408(1)
Mo(1)–Cl(12)	2.418(1)	Mo(1)–S(4)	2.401(1)	Mo(2)–Cl(23)	2.404(1)	Mo(2)–S(5)	2.414(1)
Mo(1)–Cl(13)	2.410(1)	Mo(1)–S(5)	2.405(1)	Mo(2)–S(2)	2.644(1)		

Cl(11)–Mo(1)–Cl(12)	153.4*	Cl(12)–Mo(1)–S(4)	128.1*	Cl(21)–Mo(2)–Cl(22)	152.4*	Cl(22)–Mo(2)–S(4)	127.9*
Cl(11)–Mo(1)–Cl(13)	92.4*	Cl(13)–Mo(1)–S(4)	86.0*	Cl(21)–Mo(2)–Cl(23)	90.2*	Cl(23)–Mo(2)–S(4)	85.8*
Cl(12)–Mo(1)–Cl(13)	90.3*	S(1)–Mo(1)–S(4)	154.3*	Cl(22)–Mo(2)–Cl(23)	92.0*	S(2)–Mo(2)–S(4)	157.7*
Cl(11)–Mo(1)–S(1)	78.1*	S(3)–Mo(1)–S(4)	104.6*	Cl(21)–Mo(2)–S(2)	79.9*	S(3)–Mo(2)–S(4)	104.3*
Cl(12)–Mo(1)–S(1)	75.8*	Cl(11)–Mo(1)–S(5)	127.4*	Cl(22)–Mo(2)–S(2)	72.9*	Cl(21)–Mo(2)–S(5)	128.5*
Cl(13)–Mo(1)–S(1)	84.6*	Cl(12)–Mo(1)–S(5)	79.2*	Cl(23)–Mo(2)–S(2)	85.4*	Cl(22)–Mo(2)–S(5)	79.1*
Cl(11)–Mo(1)–S(3)	86.1*	Cl(13)–Mo(1)–S(5)	86.1*	Cl(21)–Mo(2)–S(3)	86.6*	Cl(23)–Mo(2)–S(5)	87.1*
Cl(12)–Mo(1)–S(3)	86.1*	S(1)–Mo(1)–S(5)	153.2*	Cl(22)–Mo(2)–S(3)	85.9*	S(2)–Mo(2)–S(5)	150.6*
Cl(13)–Mo(1)–S(3)	168.8*	S(3)–Mo(1)–S(5)	103.7*	Cl(23)–Mo(2)–S(3)	168.6*	S(3)–Mo(2)–S(5)	103.4*
S(1)–Mo(1)–S(3)	84.2*	S(4)–Mo(1)–S(5)	49.0*	S(2)–Mo(2)–S(3)	83.3*	S(4)–Mo(2)–S(5)	48.8*
Cl(11)–Mo(1)–S(4)	78.5*			Cl(21)–Mo(2)–S(4)	79.7*		

(*b*) In the tetrahydrothiophene ligands

S(1)–C(11)	1.831(4)	C(12s)–C(13)	1.476(25)	C(21)–C(22)	1.520(5)	S(3)–C(34)	1.829(3)
S(1)–C(14)	1.828(4)	C(13)–C(14)	1.536(6)	C(22)–C(23)	1.490(6)	C(31)–C(32)	1.520(5)
C(11)–C(12m)	1.503(7)	S(2)–C(21)	1.818(4)	C(23)–C(24)	1.502(6)	C(32)–C(33)	1.502(5)
C(11)–C(12s)	1.320(24)	S(2)–C(24)	1.849(3)	S(3)–C(31)	1.833(3)	C(33)–C(34)	1.511(5)
C(12m)–C(13)	1.486(7)						

Mo(1)–S(1)–C(11)	112.3(2)	C(12m)–C(13)–C(14)	110.2(4)	C(21)–C(22)–C(23)	107.1(3)	Mo(2)–S(3)–C(34)	122.8(1)
Mo(1)–S(1)–C(14)	111.1(1)	C(12s)–C(13)–C(14)	109.4(10)	C(22)–C(23)–C(24)	109.1(3)	C(31)–S(3)–C(34)	95.7(2)
C(11)–S(1)–C(14)	93.9(2)	S(1)–C(14)–C(13)	105.4(3)	S(2)–C(24)–C(23)	106.1(3)	S(3)–C(31)–C(32)	103.7(2)
S(1)–C(11)–C(12m)	106.2(4)	Mo(2)–S(2)–C(21)	114.2(1)	Mo(1)–S(3)–Mo(2)	70.8 *	C(31)–C(32)–C(33)	107.9(3)
S(1)–C(11)–C(12s)	107.1(11)	Mo(2)–S(2)–C(24)	110.6(1)	Mo(1)–S(3)–C(31)	123.1(1)	C(32)–C(33)–C(34)	107.2(3)
C(11)–C(12m)–C(13)	105.9(4)	C(21)–S(2)–C(24)	93.8(2)	Mo(1)–S(3)–C(34)	123.1(1)	S(3)–C(34)–C(33)	104.2(2)
C(11)–C(12s)–C(13)	117.1(18)	S(2)–C(21)–C(22)	105.7(3)	Mo(2)–S(3)–C(31)	123.6(1)		

(*c*) In the bridging disulfide ligand

S(4)–S(5)	1.991(1)						

Mo(1)–S(4)–Mo(2)	70.3*	S(5)–S(4)–Mo(2)	65.8*	Mo(1)–S(5)–Mo(2)	70.1*	S(4)–S(5)–Mo(2)	65.5*
Mo(1)–S(4)–S(5)	65.6*			Mo(1)–S(5)–S(4)	65.4*		

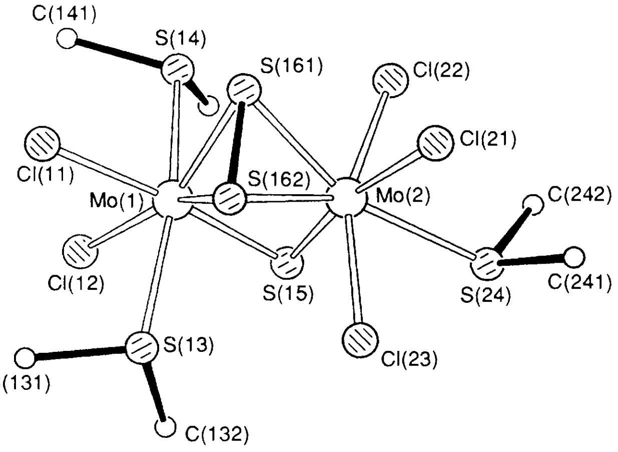


Fig. 2 Molecular structure of $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**

Table 4 Final atomic coordinates (fractional × 10^4) for $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Mo(1)	3124.8(5)	3166.8(3)	4900.1(4)
Cl(11)	2467(2)	4366.4(9)	4107(1)
Cl(12)	4500(2)	3856.2(9)	6305(1)
S(13)	5610(2)	3201.3(9)	4115(1)
C(131)	6138(10)	4168(4)	4030(7)
C(132)	7021(10)	2863(7)	5086(9)
S(14)	1084(2)	3327(1)	6157(1)
C(141)	938(13)	4309(6)	6450(10)
C(142)	1794(10)	2997(6)	7469(6)
S(15)	4005(2)	2090.2(8)	5989(1)
S(161)	893(2)	2749.8(9)	3867(1)
S(162)	2660(2)	2703.6(9)	3079(1)
Mo(2)	2472.7(5)	1706.3(3)	4380.4(4)
Cl(21)	1068(2)	1054.3(9)	2961(1)
Cl(22)	510(2)	1516.0(9)	5487(2)
Cl(23)	4734(2)	1366.6(9)	3675(1)
S(24)	3297(2)	405.7(9)	5256(1)
C(241)	2778(10)	−306(4)	4296(8)
C(242)	2298(13)	110(6)	6330(9)

M–μ-SR distance (SR = SO_2, SC_4H_8 or S^{2-}). Although a detailed comparison of distances is inappropriate because of the variety of metals, ligands and oxidation states involved, compound **3** is the only example to date involving a mixed oxidation state, paramagnetic system. Further structural studies of redox partners of the diamagnetic compounds included in Table 6 will be of interest in determining whether this metal–μ-SR bond lengthening has an electronic origin.

The unique Mo–S(24) distance of the terminal SMe_2 ligand *trans* to the μ-S_2 group is 2.631(2) Å and is similar to the corresponding distances in **2a**. In contrast, the mutually *trans* Mo(1)–SMe_2 distances are much shorter, mean 2.577(7) Å. The Mo–Cl distances to both Mo atoms lie in the range 2.395(2)–2.413(2) Å, *i.e.* very similar to those in **2a**.

Table 5 Molecular dimensions (bond lengths in Å, angles in °) in $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3** with e.s.d.s in parentheses; angles marked * have e.s.d.s of less than 0.05°

(*a*) About the Mo atoms

Mo(1)-Mo(2)	2.742(1)	Mo(1)-S(14)	2.583(2)	Mo(2)-Cl(21)	2.395(2)	Mo(2)-S(15)	2.436(1)
Mo(1)-Cl(11)	2.398(2)	Mo(1)-S(15)	2.430(2)	Mo(2)-Cl(22)	2.403(2)	Mo(2)-S(161)	2.395(2)
Mo(1)-Cl(12)	2.403(2)	Mo(1)-S(161)	2.421(2)	Mo(2)-Cl(23)	2.413(2)	Mo(2)-S(162)	2.419(2)
Mo(1)-S(13)	2.570(2)	Mo(1)-S(162)	2.432(2)	Mo(2)-S(24)	2.631(2)		
Cl(11)-Mo(1)-Cl(12)	86.1(1)	Cl(11)-Mo(1)-S(162)	84.8(1)	Cl(21)-Mo(2)-Cl(22)	89.3(1)	S(162)-Mo(2)-Cl(21)	85.9(1)
Cl(11)-Mo(1)-S(13)	90.9(1)	Cl(12)-Mo(1)-S(162)	153.7(1)	Cl(21)-Mo(2)-Cl(23)	90.9(1)	S(162)-Mo(2)-Cl(22)	126.7(1)
Cl(12)-Mo(1)-S(13)	81.7(1)	S(13)-Mo(1)-S(162)	73.8(1)	Cl(22)-Mo(2)-Cl(23)	153.9(1)	S(162)-Mo(2)-Cl(23)	79.3(1)
Cl(11)-Mo(1)-S(14)	89.1(1)	S(14)-Mo(1)-S(162)	123.2(1)	Cl(21)-Mo(2)-S(24)	89.1(1)	S(162)-Mo(2)-S(24)	151.9(1)
Cl(12)-Mo(1)-S(14)	81.3(1)	S(15)-Mo(1)-S(162)	105.5(1)	Cl(22)-Mo(2)-S(24)	80.7(1)	S(15)-Mo(2)-S(162)	105.8(1)
S(13)-Mo(1)-S(14)	162.9(1)	S(161)-Mo(1)-S(162)	48.2(1)	Cl(23)-Mo(2)-S(24)	73.2(1)	S(161)-Mo(2)-S(162)	48.6(1)
Cl(11)-Mo(1)-S(15)	169.1(1)	Cl(11)-Mo(1)-Mo(2)	135.1*	S(15)-Mo(2)-Cl(21)	167.2(1)	Mo(1)-Mo(2)-Cl(21)	137.2*
Cl(12)-Mo(1)-S(15)	83.1(1)	Cl(12)-Mo(1)-Mo(2)	138.9*	S(15)-Mo(2)-Cl(22)	87.8(1)	Mo(1)-Mo(2)-Cl(22)	98.6*
S(13)-Mo(1)-S(15)	88.7(1)	S(13)-Mo(1)-Mo(2)	96.1*	S(15)-Mo(2)-Cl(23)	86.4(1)	Mo(1)-Mo(2)-Cl(23)	99.0*
S(14)-Mo(1)-S(15)	88.1(1)	S(14)-Mo(1)-Mo(2)	95.9*	S(15)-Mo(2)-S(24)	78.2(1)	Mo(1)-Mo(2)-S(24)	133.7*
Cl(11)-Mo(1)-S(161)	84.0(1)	S(15)-Mo(1)-Mo(2)	55.8*	S(161)-Mo(2)-Cl(21)	85.5(1)	Mo(1)-Mo(2)-S(15)	55.6*
Cl(12)-Mo(1)-S(161)	154.3(1)	S(161)-Mo(1)-Mo(2)	54.9*	S(161)-Mo(2)-Cl(22)	78.1(1)	Mo(1)-Mo(2)-S(161)	55.7*
S(13)-Mo(1)-S(161)	122.1(1)	S(162)-Mo(1)-Mo(2)	55.3*	S(161)-Mo(2)-Cl(23)	127.9(1)	Mo(1)—Mo(2)-S(162)	55.8*
S(14)-Mo(1)-S(161)	75.0(1)			S(161)-Mo(2)-S(24)	158.2(1)		
S(15)-Mo(1)-S(161)	105.4(1)			S(15)-Mo(2)-S(161)	106.0(1)		

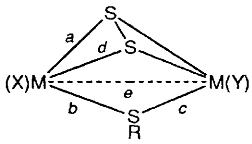
(*b*) In the bridging ligands

S(161)-S(162)	1.983(2)						
Mo(1)-S(15)-Mo(2)	68.6*	Mo(1)-S(161)-S(162)	66.2(1)	Mo(1)-S(162)-Mo(2)	68.9*	Mo(2)-S(162)-S(161)	65.1(1)
Mo(1)-S(161)-Mo(2)	69.4*	Mo(2)-S(161)-S(162)	66.3(1)	Mo(1)-S(162)-S(161)	65.6(1)		

(*c*) In the thioether ligands

S(13)-C(131)	1.795(8)	S(14)-C(141)	1.802(10)	S(14)-C(142)	1.796(8)	S(24)-C(242)	1.780(12)
S(13)-C(132)	1.778(10)			S(24)-C(241)	1.789(8)		
Mo(1)-S(13)-C(131)	107.2(3)	Mo(1)-S(14)-C(141)	108.2(4)	C(141)-S(14)-C(142)	98.6(5)	Mo(2)-S(24)-C(242)	114.9(4)
Mo(1)-S(13)-C(132)	109.8(3)	Mo(1)-S(14)-C(142)	107.9(3)	Mo(2)-S(24)-C(241)	107.7(3)	C(241)-S(24)-C(242)	100.4(5)
C(131)-S(13)-C(132)	100.3(5)						

Table 6 Bond distances (Å) in $(\mu\text{-}S_2)(\mu\text{-}SR)$ complexes. The complexes have the common motif illustrated below



M	X	Y	SR	*a*(mean)	*b*	*c*	*d*	*e*	M^{n+}	d^n	Ref.
Mo	$(CN)_4$	$(CN)_4$	SO_2	2.433(3)	2.369(8)	2.363(8)	2.00(1)	2.730(4)	3	3	3
Mo	$Cl_3(SC_4H_8)$	$Cl_3(SC_4H_8)$	SC_4H_8	2.407(3)	2.390(1)	2.391(1)	1.991(1)	2.769(0.3)	4	2	4, This work complex **2a**
Mo	$Cl_2(SMe_2)_2$	$Cl_3(SMe_2)$	S^{2-}	2.417(8)	2.430(2)	2.436(1)	1.983(2)	2.742(1)	4/5	2/1	This work complex **3**
Mo	Cl_4	Cl_4	$S_2{}^{2-}$	2.425(2)	2.425(2)	2.425(2)	1.981(1)	2.857(1)	5	1	2
Mo	Br_4	Br_4	$S_2{}^{2-}$	2.415(3)	2.415(3)	2.415(3)	1.983(15)*	2.853(2)*	5	1	2
W	Br_4	Br_4	S^{2-}	2.43(1)	2.27(2)	2.24(2)	2.02(2)	2.813(3)	5	1	10
Nb	$Cl_2(SC_4H_8)_2$	$Cl_2(SC_4H_8)_2$	S^{2-}	2.541(8)	2.292(6)	2.282(6)	2.013(11)	2.844(2)	4	1	5(*c*)
Nb	$Br_2(SC_4H_8)_2$	$Br_2(SC_4H_8)_2$	S^{2-}	2.487(4)	2.336(10)	2.329(10)	2.014(14)	2.830(5)	4	1	5(*c*)

* Mean values for two independent anions.

In the crystals of both **2a** and **3**, the dimolybdenum complex molecules are discrete moieties, and separated from neighbours by normal van der Waals interactions.

The room-temperature magnetic moment of **3** shows the presence of one unpaired electron per molecule, consequently **3** shows, in a CH_2Cl_2 glass at 40 K, a broad, roughly axial EPR resonance; this is about 50 mT in width and has g_{max} at 1.94 with unresolved ^{97}Mo and ^{95}Mo satellites at the extremes of the spectrum (Fig. 3). Complex **3** is a member of a family of related mixed-oxidation-state complexes, *e.g.* other members are the tungsten complexes $[(Me_2S)Cl_2W(SEt)_3WCl_2(SMe_2)]$[11] and $[(Me_2S)Cl_2W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_2(SMe_2)]$.[12] As might be expected from its d^2–d^1 formal electronic configuration (neglecting an Mo–Mo bond), an unpaired electron is likely to be delocalised over the bridging ligand system,[12] and complex **3** shows a rather broad ^1H NMR spectrum in $C^2H_2Cl_2$ at room temperature with SMe_2 resonances at δ 2.19 and 2.32 in the expected 2 : 1 ratio. The related complex $[(Me_2S)Cl_2W(\mu\text{-}Cl)$-

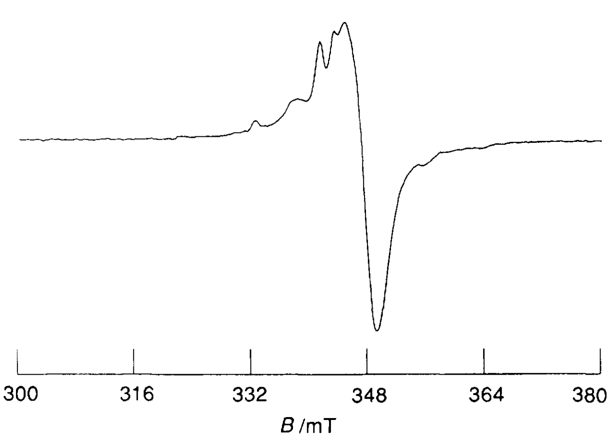


Fig. 3 EPR spectrum of $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**

$(\mu\text{-}SPh)_2WCl_2(SMe_2)]$ (formally d^3–d^2 configuration) similarly has a ^1H NMR spectrum at room temperature and an EPR spectrum at temperatures below 77 K.[12]

Conclusion

We have shown that a starting material for the preparation of $\mu\text{-}S_2^{2-}$ complexes can be conveniently prepared by the simple reaction of S_2Cl_2 and $[Mo(CO)_6]$. However, the exact nature of this material, **1**, is unclear. It is most likely a mixture of predominantly $Mo_2Cl_6S_2$ together with other S_2 species in up to 20% contamination (see Table 1). Treatment of **1** with thioethers and tetrahydrofuran gives $\mu\text{-}S_2$- and $(\mu\text{-}S_2)(\mu\text{-}S)$-species according to the conditions employed, as illustrated above. A variety of other related compounds has also been obtained[3,13] by variation of ligand and reaction conditions. They require further X-ray structural work for complete characterisation and will be reported in detail at a later date. Such complexity of reaction pathway is common in sulfur chemistry[5] and is further illustrated by the reaction of $[W(CO)_6]$ with S_2Cl_2, which gives $[WSCl_4{\cdot}S_8]$ rather than an analogue of **1**.[14]

Experimental

The reagents $[M(CO)_6]$, SMe_2, C_4H_8S, C_4H_8O, $PhCH_2SMe$ and S_2Cl_2 were used as purchased from Aldrich. Reaction solvents were dried and distilled under dinitrogen before use and all air-sensitive materials were manipulated by standard Schlenk or glove-box techniques. Infrared spectra were determined with a Perkin Elmer SP3-200 spectrometer, NMR spectra with a JEOL FX 270 spectrometer and EPR spectra with a Bruker ER-300SH spectrometer fitted with an ESR-9 cryostat and interfaced to an ESP 1600 computer. Magnetic moments were measured at 20 °C with a recording Faraday balance. Microanalyses were by Mr. C. Macdonald of this Laboratory or Butterworth Microanalytical Laboratory Ltd.

Preparations.—$Mo_2S_2Cl_6{\cdot}CH_2Cl_2$ **1**. Disulfur dichloride (2 cm^3, 0.025 mol) was added to $[Mo(CO)_6]$ (3.9 g, 0.015 mol) suspended in CH_2Cl_2 (100 cm^3). The mixture was heated to reflux and irradiated with a 150 W tungsten-filament bulb; CO was rapidly evolved. After 3.5 h the resulting dark suspension was left to cool to room temperature and the black precipitate was filtered off, washed with CH_2Cl_2 (2 × 10 cm^3), Et_2O (2 × 10 cm^3) and dried in a vacuum (3.7 g, 98% yield).

Hexachloro(μ-disulfido)(μ-tetrahydrothiophene)bis(tetrahydrothiophene)dimolybdenum(IV), $[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a**. Tetrahydrothiophene (0.3 cm^3, 3.3 equivalents) was added to compound **1** (0.3 g) suspended in CH_2Cl_2 (20 cm^3) and the resulting solution was stirred for 16 h. The green solid precipitate was filtered off, washed with ether and dried in a vacuum (0.24 g, 60% yield). Recrystallisation from CH_2Cl_2 gave green *crystals* which were analytically pure and were used for X-ray crystallography as described below.

The preparation of **2b** followed the same method as above and gave the green *crystalline* product in 50–60% yield.

Hexachloro(μ-disulfido)(μ-tetrahydrofuran)bis(tetrahydrofuran)dimolybdenum(IV), $[\{MoCl_3(C_4H_8O)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8O)]$ **2c**. Compound **1** (0.4 g) was dissolved in tetrahydrofuran (thf) (20 cm^3) to give a dark green solution. This solution was stirred for 1 h whereupon a green, microcrystalline *solid* precipitated, which was filtered off, washed with thf (2 × 10 cm^3), and dried in a vacuum (0.25 g, 60% yield).

Pentachlorotris(dimethyl sulfide)(μ-disulfido)(μ-sulfido)dimolybdenum(IV/V), $[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**. Dimethyl sulfide (1 cm^3) was added to compound **1** (0.4 g) suspended in CH_2Cl_2 (25 cm^3) and the resulting solution was stirred for 16 h to give a green-brown solution. This was concentrated to about one-third volume in a vacuum, then diethyl ether (15 cm^3) was added. After standing overnight the solution deposited dark brown *crystals* which were filtered off, washed with ether and dried in a vacuum (0.28 g, 50%). These crystals were analytically pure and were used for all subsequent measurements; μ_{eff} (293 K) = 1.4 μ_B per molecule.

The EPR spectrum of **3** was determined in an anaerobically loaded quartz tube using an approximately 10^{-3} molar solution as a CH_2Cl_2 glass at 40 K. The microwave power was 1.8 mW at 9.458 GHz. Field modulation was 0.48 mT at 100 kHz.

Crystal Structure Analyses.—$[\{MoCl_3(C_4H_8S)\}_2(\mu\text{-}S_2)(\mu\text{-}C_4H_8S)]$ **2a**. *Crystal data.* $C_{12}H_{24}Cl_6Mo_2S_5$, M = 733.2, orthorhombic, space group *Pbca* (no. 61), a = 20.315(7), b = 18.179(6), c = 13.105(4) Å, U = 4839.6 $Å^3$, Z = 8, D_c = 2.012 g cm^{-3}, $F(000)$ = 2896, $\mu(Mo\text{-}K\alpha)$ = 21.0 cm^{-1}, $\lambda(Mo\text{-}K\bar{\alpha})$ = 0.71069 Å.

The procedure of the X-ray analysis followed closely that described below for **3**; details were recorded in ref. 4.

$[(Me_2S)_2Cl_2Mo(\mu\text{-}S_2)(\mu\text{-}S)MoCl_3(SMe_2)]$ **3**.

Crystal data. $C_6H_{18}Cl_5Mo_2S_6$, M = 651.7, triclinic, space group $A\bar{1}$ (equivalent to no. 2), a = 9.142(1), b = 17.834(4), c = 12.535(2) Å, α = 89.37(2), β = 96.06(1), γ = 89.96(1)°, U = 2032.1 $Å^3$, Z = 4, D_c = 2.130 g cm^{-3}, $F(000)$ = 1276, $\mu(Mo\text{-}K\alpha)$ = 24.5 cm^{-1}, $\lambda(Mo\text{-}K\bar{\alpha})$ = 0.71069 Å.

Crystals are very dark, moisture-sensitive and have no regular morphology. Several were sealed, under N_2, in capillaries and trial photographs taken. The selected sample, *ca.* 0.50 × 0.60 × 0.80 mm (with additional, smaller fragments attached) was mounted on our Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of cell parameters (from 25 reflections, with θ = 10–10.5°, each centred in four orientations) and measurement of diffraction intensities (to θ_{max} = 23°).

Intensities were corrected for Lorentz–polarisation effects, slight deterioration (4% overall), absorption (by semi-empirical, ψ-scan methods) and to eliminate negative intensities (by Bayesian statistical methods). 2790 Unique data were entered into the SHELX program system,[15] where the structure was determined by a combination of heavy-atom and trial-and-error methods, principally in the non-centrosymmetric space group $A1$. Refinement of the molecule in $A\bar{1}$ proceeded smoothly to convergence at R = 0.037 and R_g = 0.057[15] for the 2447 'observed' reflections (having $I > 2\sigma_I$) weighted $w = (\sigma_F^2 + 0.002\,45F^2)^{-1}$. The Mo, S, Cl and C atoms were allowed anisotropic thermal parameters. Hydrogen atoms on three of the methyl groups were located in difference maps and refined independently; in the remaining methyl groups, H atoms were included in idealised, staggered arrangements and refined with geometrical restraints. In the final difference map, the only peaks of significance were four at *ca.* 0.74–0.87 e $Å^{-3}$, close to the two Mo atoms.

Scattering factor curves for neutral atoms were taken from ref. 16. Computer programs used in this analysis have been noted above and in Table 4 of ref. 17, and were run on the DEC MicroVax II machine in this Laboratory.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Dr. D. J. Lowe for measuring EPR spectra and the AFRC for studentships to J. D. L. and C. S.

References

1 T. Shibahara, *Coord. Chem. Rev.*, 1993, **123**, 73.
2 D. Fenske, B. Czeska, C. Schumaker, R. E. Schmidt and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1985, **520**, 7.
3 C. Potvin, J-M. Bregeault and J-M. Manoli, *J. Chem. Soc., Chem. Commun.*, 1980, 664; J-M. Manoli, J-M. Bregeault, C. Potvin and G. Chottard, *Inorg. Chim. Acta*, 1984, **88**, 75.
4 D. L. Hughes, R. L. Richards and C. Shortman, *J. Chem. Soc., Chem. Commun.*, 1986, 1731.
5 (*a*) D. Britnell, G. W. A. Fowles and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1974, 2191; (*b*) G. W. A. Fowles, R. J. Hobson, D. A. Rice and K. J. Shanton, *J. Chem. Soc., Chem. Commun.*, 1976, 552; (*c*) M. G. B. Drew, D. A. Rice and D. M. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 2251.
6 H. Schäffer and W. Beckmann, *Z. Anorg. Allg. Chem.*, 1966, **347**, 225.
7 J. Marcoll, A. Rabenau, D. Mootz and H. Wünderlich, *Rev. Chim. Miner.*, 1974, **11**, 607.
8 J. L. Templeton and R. E. McCarley, *Inorg. Chem.*, 1978, **17**, 2293.
9 P. M. Boorman, K. J. Moynihan and R. T. Oakley, *J. Chem. Soc., Chem. Commun.*, 1982, 899.
10 P. Klingelhöfer and U. Müller, *Z. Anorg. Allg. Chem.*, 1986, **542**, 7.
11 P. M. Boorman, V. D. Patel, K. A. Kerr, P. W. Codding and P. V. Roey, *Inorg. Chem.*, 1980, **19**, 3508.
12 J. M. Ball, P. M. Boorman, K. J. Moynihan, V. D. Patel, J. F. Richardson, D. Collison and F. E. Mabbs, *J. Chem. Soc., Dalton Trans.*, 1983, 2479.
13 J. D. Lane, D. Phil. Thesis, University of Sussex, 1990.
14 D. L. Hughes, J. D. Lane and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1991, 1627.
15 G. M. Sheldrick, SHELX 76, Program for crystal structure determination, University of Cambridge, 1976.
16 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99 and 149.
17 S. N. Anderson, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Dalton Trans.*, 1986, 245.

Received 15*th September* 1993; *Paper* 3/05567A