# Synthesis and *X*-Ray Structure of Tris(*N*,*N*-diethyldithiocarbamato)-hydrogensulphidomolybdenum(IV)–Tetrahydrofuran (1/1) †

**Nadine Dupré, Hugo M. J. Hendriks, and Jeanne Jordanov** *
*Laboratoires de Chimie (LA CNRS n° 321), Département de Recherche Fondamentale, Centre d'Etudes Nucléaires de Grenoble, 85 X, F-38041 Grenoble Cedex, France*

The complex $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$ (thf = tetrahydrofuran) has been prepared by the reaction of $[Mo(CO)_2(S_2CNEt_2)_2]$ with $[Fe_4(cp)_4S_6]$ (cp = $\eta^5$-cyclopentadienyl). The compound crystallizes in the space group $P\bar{1}$ with $a = 10.148(5)$, $b = 14.104(4)$, $c = 10.759(6)$ Å, $\alpha = 72.39(3)$, $\beta = 89.04(6)$, $\gamma = 97.84(3)°$, and $Z = 2$. The structure was solved by Patterson and Fourier-difference techniques and refined to $R = 0.070$ and $R' = 0.066$ for 2 774 independent reflections. The molybdenum atom is surrounded by seven sulphur atoms in a distorted pentagonal-bipyramidal co-ordination.

For several molybdenum-containing enzymes (nitrate reductase, sulphite oxidase, and xanthine oxidase), EXAFS (extended *X*-ray absorption fine structure) analyses have shown that sulphur atoms play an important role in the co-ordination sphere of the molybdenum atom.[1] The same also applies to nitrogenase,[1a,b] for which it has been pointed out that an Mo–S–Fe cluster is probably present at the active site, with the immediate environment of the Mo consisting exclusively of sulphur atoms. However, few monomeric molybdenum complexes with purely sulphur ligation are known at present.[2,3]

As part of a study aimed at the synthesis of model compounds for the iron–molybdenum cofactor of nitrogenase, we are currently investigating the reactivity of the iron–sulphur cluster $[Fe_4(cp)_4S_6]$[4] (cp = $\eta^5$-cyclopentadienyl) with respect to molybdenum compounds. Here we report the *X*-ray analysis of one of the products of the reaction of $[Fe_4(cp)_4S_6]$ with $[Mo(CO)_2(S_2CNEt_2)_2]$, the monomeric complex $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$ (thf = tetrahydrofuran), in which the $Mo^{IV}$ is exclusively co-ordinated by sulphur atoms,[5] and which is one of the few structurally characterized compounds with $SH^-$ as a ligand.[6] This molecule can be considered as an interesting model for the functional xanthine oxidase active site, for which recent biochemical data seem consistent with an Mo–SH structure.[7]

## Experimental

The synthesis was carried out under pure argon. Reagent grade solvents were distilled from $CaH_2$ or $LiAlH_4$. The complexes $[Fe_4(cp)_4S_6]$[4] and $[Mo(CO)_2(S_2CNEt_2)_2]$[8] were prepared by literature methods. I.r. spectra were obtained on a Beckman 4250 spectrophotometer (KBr pellets). Magnetic measurements (at 0.5 T) were made with a SQUID susceptometer.

*Synthesis of* $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$.—A filtered solution of $[Fe_4(cp)_4S_6]\cdot 0.25CH_2Cl_2$ (1.04 g, 1.5 mmol) in dichloromethane (30 cm$^3$) was added to a solution of $[Mo(CO)_2(S_2CNEt_2)_2]$ (2.64 g, 6 mmol) in dichloromethane (70 cm$^3$). The mixture was stirred for 1 week at room temperature. The complex $[Fe_4(cp)_4S_4]$ (identified by its i.r. and $^1H$ n.m.r. spectra[9]) slowly crystallized and was filtered off (500 mg). Hexane (15 cm$^3$) was added and a black powder, tentatively formulated as $[Mo_2S_2(S_2CNEt_2)_3]$, was isolated (500 mg). The resulting solution was evaporated to dryness and the residue was recrystallized from acetonitrile–thf–hexane (1 : 1 : 1). The complex $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$ was obtained as a green powder, mixed with black crystals; when crushed the crystals were also green.

*Crystallography.—Data collection, solution, and refinement.* Measurements were carried out on a crystal (0.55 × 0.28 × 0.14 mm) sealed under argon in a thin-walled capillary, using a Nonius CAD-4 diffractometer. Least-squares refinement of the angular settings of 22 reflections with $7 < \theta < 16°$ established the lattice constants. The $\omega$-scan technique was used to collect all reflections with $h \geqslant 0$ and $7.0 \leqslant 2\theta \leqslant 60.0°$. The scanning rate was adjusted to give the required precision of $\sigma(I)/I < 0.02$ with a maximum scan time of 150 s per reflection. During the data collection, two standard reflections, measured every 3 h, showed a decay of 29% due to loss of thf. The data were corrected for this decomposition and for Lorentz–polarization, but not for absorption or extinction. 5 774 Reflections were measured, of which 2 774, having $I > 2\sigma(I)$, were used in the structure analysis.

*Crystal data.* $C_{19}H_{39}MoN_3OS_7$,‡ $M = 645.9$, triclinic, space group $P\bar{1}$, $a = 10.148(5)$, $b = 14.104(4)$, $c = 10.759(6)$ Å, $\alpha = 72.39(3)$, $\beta = 89.04(6)$, $\gamma = 97.84(3)°$, $U = 1\,451$ Å$^3$, $Z = 2$, $D_c$‡ $= 1.48$ g cm$^{-3}$, graphite monochromated Mo-$K_\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 9.4$ cm$^{-1}$.

The structure was solved by conventional Patterson and Fourier methods. After several 'large-block' refinement cycles, the non-hydrogen atoms of the $Mo(SH)(S_2CNEt_2)_3$ unit were assigned anisotropic thermal parameters. The high thermal parameters of the thf atoms as well as the high residual electron density in the thf region in a Fourier-difference map suggested that the thf molecules are disordered. The five thf atoms were given occupancies of 0.5 and the eleven highest residual peaks in the thf region were included in the

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† *Supplementary data available* (No. SUP 23899, 19 pp.): structure factors, thermal parameters, co-ordinates of H atoms and thf, complete interatomic distances and interbond angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

*Non-S.I. unit employed*: B.M. = $9.27 \times 10^{-24}$ J T$^{-1}$.

‡ Assuming the presence of one lattice thf molecule per asymmetric unit.

**Table 1.** Fractional atomic co-ordinates for the non-hydrogen atoms of $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$ with estimated standard deviations in parentheses

| Atom | $X/a$ | $Y/b$ | $Z/c$ | Atom | $X/a$ | $Y/b$ | $Z/c$ |
|---|---|---|---|---|---|---|---|
| Mo | −0.785 2(2) | 0.203 5(1) | 0.656 8(2) | C(12) | −1.290 4(15) | 0.159 9(13) | 0.964 7(17) |
| S(10) | −0.828 9(4) | 0.289 7(3) | 0.824 0(4) | C(13) | −1.007 3(16) | 0.261 4(10) | 1.071 2(15) |
| S(11) | −0.989 3(4) | 0.118 1(3) | 0.799 1(4) | C(14) | −0.929 7(19) | 0.215 3(12) | 1.189 2(15) |
| S(20) | −0.650 3(4) | 0.184 2(3) | 0.469 1(4) | C(20) | −0.736 2(12) | 0.065 0(9) | 0.496 6(12) |
| S(21) | −0.863 4(4) | 0.041 8(3) | 0.612 2(4) | C(21) | −0.786 5(13) | −0.104 2(11) | 0.479 5(14) |
| S(30) | −0.660 5(4) | 0.376 2(3) | 0.553 5(4) | C(22) | −0.739 9(14) | −0.176 9(10) | 0.591 9(17) |
| S(31) | −0.926 2(4) | 0.306 5(3) | 0.503 1(4) | C(23) | −0.601 4(13) | 0.021 4(11) | 0.337 7(17) |
| S(40) | −0.618 9(4) | 0.131 9(3) | 0.796 1(4) | C(24) | −0.644 1(16) | 0.041 6(12) | 0.202 8(14) |
| N(10) | −1.043 1(12) | 0.193 3(8) | 0.991 2(11) | C(30) | −0.797 4(12) | 0.403 3(9) | 0.470 4(13) |
| N(20) | −0.709 5(10) | −0.003 6(8) | 0.441 4(11) | C(31) | −0.691 6(16) | 0.572 5(11) | 0.351 0(15) |
| N(30) | −0.804 2(11) | 0.492 6(8) | 0.383 8(11) | C(32) | −0.699 3(15) | 0.655 1(10) | 0.409 6(16) |
| C(10) | −0.962 9(13) | 0.202 5(9) | 0.886 7(12) | C(33) | −0.925 7(13) | 0.518 1(10) | 0.309 7(16) |
| C(11) | −1.171 8(19) | 0.122 4(10) | 1.023 9(13) | C(34) | −0.920 6(17) | 0.497 4(12) | 0.176 0(15) |

refinement as carbon atoms with occupancies of 0.20—0.25. Of the five original thf atoms, the one with the lowest isotropic thermal parameter was further refined as oxygen. The bond distances and angles of the eleven additional atoms make no chemical sense and are not reported in the tables. In fact these atoms could also well be part of disordered hexane molecules, occupying the holes where thf is absent. Fourier-difference maps revealed the positions of 21 (of the 30) ethyl hydrogen atoms and of the SH hydrogen atom. Attempts to refine their positions failed, and they were included as fixed contributions with isotropic thermal parameters of 5.0 Å$^2$. The atomic scattering factors for Mo were corrected for anomalous scattering. In a full-matrix refinement, all parameters of the $Mo(SH)(S_2CNEt_2)_3$ unit shifted by < 15% of their estimated standard deviations (e.s.d.s), while those of the thf atoms shifted by up to 40% of their e.s.d.s. The final values of the residuals are $R' = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{\frac{1}{2}} = 0.066$ and $R = 0.070$; $w = \sigma^{-2}(F_o)$. The fractional co-ordinates of the non-hydrogen atoms of $[Mo(SH)(S_2CNEt_2)_3]$ are listed in Table 1.

**Table 2.** Variation with temperature of the magnetic moment and of the reciprocal of the molecular magnetic susceptibility of $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$

| $T$/K | $\mu_{eff.}$/B.M. | $1/\chi$ * | $T$/K | $\mu_{eff.}$/B.M. | $1/\chi$ * |
|---|---|---|---|---|---|
| 4.4 | 0.965 5 | 37.92 | 20.0 | 1.332 2 | 90.13 |
| 5.5 | 0.993 9 | 40.48 | 25.0 | 1.392 9 | 103.1 |
| 6.0 | 1.033 8 | 44.90 | 30.0 | 1.442 8 | 115.3 |
| 7.0 | 1.065 2 | 49.34 | 35.0 | 1.486 7 | 126.6 |
| 8.0 | 1.093 4 | 53.52 | 40.0 | 1.542 2 | 134.5 |
| 9.0 | 1.121 1 | 57.27 | 50.0 | 1.594 0 | 157.4 |
| 10.0 | 1.146 8 | 60.81 | 60.0 | 1.657 1 | 174.8 |
| 11.0 | 1.169 9 | 64.28 | 80.0 | 1.763 8 | 205.7 |
| 12.0 | 1.192 5 | 67.49 | 100.0 | 1.866 4 | 229.6 |
| 14.0 | 1.232 5 | 73.70 | 140.0 | 2.049 2 | 266.6 |
| 16.0 | 1.269 5 | 79.40 | 179.5 | 2.206 3 | 294.9 |
| 18.0 | 1.302 9 | 84.81 | 250.0 | 2.452 0 | 332.5 |

* Corrected for diamagnetism.

## Results and Discussion

The bridging sulphur atoms of $[Fe_4(cp)_4S_6]$ are known to be relatively reactive.[4,10] This complex can thus be considered as an oxidizing agent which is reduced to $[Fe_4(cp)_4S_4]$ while generating 'active' $2S^{2-}$. This is indeed the first product isolated from the reaction of $[Fe_4(cp)_4S_6]$ with $[Mo(CO)_2(S_2CNEt_2)_2]$ in $CH_2Cl_2$. The resulting solution successively yielded two different products containing Mo, after loss of CO and generation of molybdenum-sulphide and -hydrogensulphide cores. The first is tentatively formulated as $[Mo_2S_2(S_2CNEt_2)_3]$ on the basis of elemental analysis, and formally contains one $Mo^{III}$ and one $Mo^{IV}$. Its i.r. spectrum shows two bands at 1 560m and 1 500s cm$^{-1}$, assigned to ν(C–N) of the ligands, and indicates that $S_2CNEt_2$ is present in chelating and bridging forms.[11,12] A medium-strong absorption at 558 cm$^{-1}$ is assigned to ν(Mo=S).[13]

The second compound is $[Mo(SH)(S_2CNEt_2)_3]\cdot thf$ and is isolated only after treatment with acetonitrile (see Experimental section). The hydrogen atom of the SH ligand is therefore believed to be provided by deprotonation of the $CH_3CN$ solvent by a nucleophilic species, possibly $S^{2-}$. The i.r. spectrum has a weak band at 2 480 cm$^{-1}$, which is comparable with the S–H frequency (2 498 cm$^{-1}$) reported for an Mo–SH compound.[14] Furthermore, a peak at 485 cm$^{-1}$ can be attributed to an Mo–S single bond. The magnetic susceptibility was investigated in the 4.4—250 K temperature range, and the data for a Curie–Weiss plot are in Table 2. When the temperature is lowered, the magnetic moment approaches 0, indicating a singlet ground state. At room temperature, the maximum value of μ remains somewhat lower than the spin-only value (2.83 B.M.) for $d^2$ systems ($S = 1$), presumably because of some spin–orbit coupling. The μ value is in good agreement with literature data for $\mu_{eff.}$ values of other molybdenum(IV) compounds.[15,16]

The crystal structure shows the seven-co-ordinate, distorted pentagonal-bipyramidal geometry of the molybdenum, with an unco-ordinated, disordered, lattice thf molecule. The Mo atom is exclusively surrounded by sulphur atoms; the SH group is in an axial position, two dithiocarbamate groups occupy four of the five equatorial positions, while the third dithiocarbamate group spans an axial and an equatorial position (see Figure). Some pertinent bond distances and angles are in Table 3.

The present geometry can be compared with those of similar seven-co-ordinated species such as $[Mo^{II}(NO)(S_2CNBu_2)_3]$,[17] $[Mo_2^{IV,V}O(S_2CNEt_2)_6]^-$,[12] $[Mo^VO(S_2CNEt_2)_3]$,[18] $[Nb^VO(S_2CNEt_2)_3]$,[19] and $[Mo^{VI}O(S_2CNEt_2)_3]^-$.[20] {According to $X$-ray powder diffraction measurements [18] $[Mo^VO(S_2CNEt_2)_3]$ is isomorphous with its niobium analogue, and is believed to have a similar geometry.}

Our assumption that one of the axial ligands is SH and not terminal =S is based on the following evidence. (1) The Mo–S distance of 2.398(4) Å is out of the usual range for terminal Mo=S bonds (2.085—2.129 Å [21]) (an Mo=S distance of 1.93 Å has also been reported[22]) and suggests instead a single bond. (2) In comparable compounds with a metal–oxygen double bond [18–20] the metal atom lies out of the equatorial plane in the direction of the double-bonded oxygen and the M–S

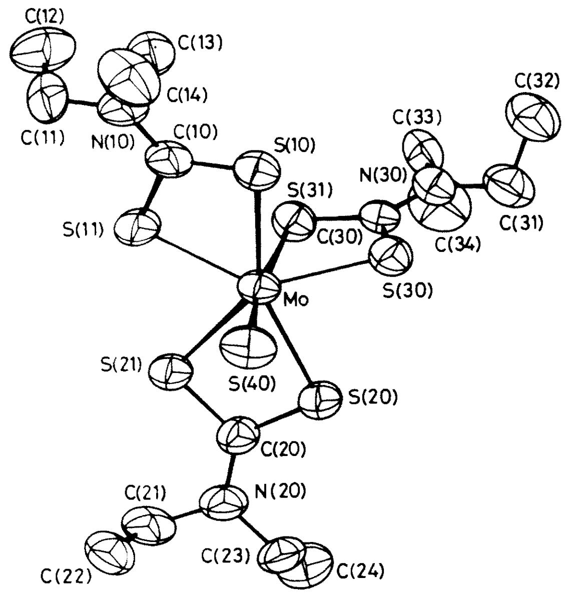

**Figure.** ORTEP drawing of $[Mo(SH)(S_2CNEt_2)_3]$. Thermal ellipsoids are plotted at the 50% level and hydrogen atoms are omitted for clarity

**Table 3.** Selected interatomic distances (Å) and interbond angles (°) for $[Mo(SH)(S_2CNEt_2)_3]\cdot$thf with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Mo–S(10) | 2.520(4) | S(10)–C(10) | 1.681(13) |
| Mo–S(11) | 2.487(4) | S(11)–C(10) | 1.726(12) |
| Mo–S(20) | 2.524(4) | C(10)–N(10) | 1.340(14) |
| Mo–S(21) | 2.499(4) | S(20)–C(20) | 1.722(12) |
| Mo–S(30) | 2.498(4) | S(21)–C(20) | 1.705(12) |
| Mo–S(31) | 2.467(4) | C(20)–N(20) | 1.333(13) |
| Mo–S(40) | 2.398(4) | S(30)–C(30) | 1.689(14) |
| S(40)–H(S40) | 0.72 | S(31)–C(30) | 1.704(12) |
| | | C(30)–N(30) | 1.333(14) |

| | | | |
|---|---|---|---|
| S(10)–Mo–S(11) | 68.4(2) | S(20)–Mo–S(21) | 68.1(2) |
| S(10)–Mo–S(20) | 152.6(2) | S(20)–Mo–S(30) | 76.8(2) |
| S(10)–Mo–S(21) | 138.6(2) | S(20)–Mo–S(31) | 90.8(2) |
| S(10)–Mo–S(30) | 78.1(2) | S(20)–Mo–S(40) | 87.3(2) |
| S(10)–Mo–S(31) | 90.9(2) | S(21)–Mo–S(30) | 142.5(2) |
| S(10)–Mo–S(40) | 86.0(2) | S(21)–Mo–S(31) | 96.6(2) |
| S(11)–Mo–S(20) | 139.0(2) | S(21)–Mo–S(40) | 92.5(2) |
| S(11)–Mo–S(21) | 71.2(2) | S(30)–Mo–S(31) | 70.3(2) |
| S(11)–Mo–S(30) | 140.0(2) | S(30)–Mo–S(40) | 99.0(2) |
| S(11)–Mo–S(31) | 88.6(2) | S(31)–Mo–S(40) | 169.3(2) |
| S(11)–Mo–S(40) | 99.8(2) | Mo–S(40)–H(S40) | 108.0 |

distance *trans* to M–O is significantly longer than the other metal–sulphur distances. In a compound with a metal–oxygen single bond [12] these effects have not been found. In the present case, the Mo atom does not lie significantly out of the best plane of the equatorial sulphur atoms of the $S_2CNEt_2$ ligands. Also, the Mo–S(31) distance *trans* to SH is not larger than the Mo–S(eq.) distances, and it is in fact the shortest of the six Mo–S($S_2CNEt_2$) distances; it has been suggested that a double-bonded S atom has a larger *trans* influence than a double-bonded O.[23] (3) In a Fourier-difference map some electron density was found at a distance of 0.72 Å from S(40); this peak is of similar magnitude to those of the other hydrogen atoms which were identified and the value of the Mo–S–H angle is acceptable (108°). Although this position could not be refined, we consider this peak as representing the S–H hydrogen atom. The relatively high anisotropy of the thermal motion of the sulphur atom could explain the shorter than expected S–H distance (1.3 Å based on covalent radii). (4) The i.r. band at 2 480 $cm^{-1}$ can only be explained by an SH stretching vibration. Although none of these arguments is conclusive evidence on its own, we consider that, taken together, they prove the presence of a hydrogensulphide ligand.

The presence of such a terminal SH group in the $Mo^{IV}$ co-ordination sphere is unusual, and only two other examples have been reported.[6c,d]

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