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THE CRYSTAL AND MOLECULAR STRUCTURES OF *TRANS*-DI-μ-THIOETHYLDINITROSYLBIS(*PENTAHAPTO*CYCLOPENTADIENYL)DIMOLYBDENUM, $[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$, AND *CIS*-DI-μ-THIOISOPROPYLDINITROSYLBIS(*PENTAHAPTO*CYCLOPENTADIENYL)DIMOLYBDENUM, $[(\eta^5\text{-}C_5H_5)\text{-}Mo(NO)(SCH(CH_3)_2]$

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Summary

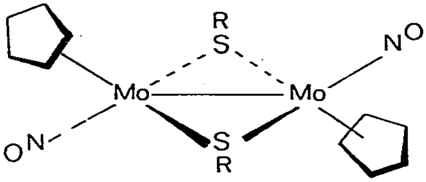
Structures of the title compounds have been determined from three-dimensional X-ray analyses using diffractometer data. Crystals of *trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$ are monoclinic, space group $P2_1/c$ with $Z = 2$ in a unit cell of dimensions $a = 7.924(1)$, $b = 12.692(1)$, $c = 9.510(1)$ Å, $\beta = 109.06(1)°$. Full matrix least squares refinement has returned a final R factor of 0.034 for 1120 reflections for which $I > 3\sigma(I)$. The analysis confirms that the molecule is a dimer, with molybdenum atoms bridged by sulphur atoms. The molecule is situated about a crystallographic centre of symmetry and thus the $(MoS)_2$ core is planar and the cyclopentadiene and nitrosyl ligands are in the *trans* configuration. The Mo-S distances are 2.398(2) and 2.400(2) Å; the Mo-Mo' distance is 2.923(1) Å.

Crystals of *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$ are orthorhombic, space group *Im2a*, with $Z = 16$ in a unit cell of dimensions $a = 30.874(2)$,

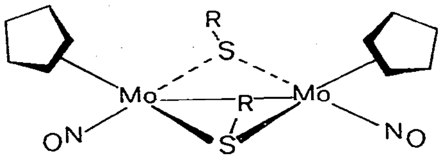
b = 14.849(3), c = 18.260(2) Å. The structure is based on a clearly defined subcell for which $c' = c/2$ and $Z' = 8$. The structure has been solved in terms of this subcell only, and therefore is described as the average of the two halves of the cell. Refinement was terminated with $R = 0.067$ for 1487 reflections having $I > 3\sigma(I)$. Within the subcell there are two independent molecules, one of which has space group required diad symmetry, and the other mirror symmetry. The two molecules are nevertheless very similar in geometry. In contrast to the ethyl complex, the disposition of ligands with regard to the planar $(MoS)_2$ core is *cis*.

Introduction

The chemistry of cyclopentadienylnitrosylmolybdenum complexes has been studied extensively by McCleverty and co-workers [1]. When $(\eta^5\text{-}C_5H_5)Mo(NO)(CO)_2$ was treated with I_2 the compound $[(\eta^5\text{-}C_5H_5)Mo(NO)\text{-}I_2]_2$ was formed but with CF_3I only the mono-iodide dimer $[(\eta^5\text{-}C_5H_5)Mo\text{-}(NO)I]_2$ resulted. The related series of μ-sulphide complexes $[(\eta^5\text{-}C_5H_5)Mo(NO)(SR)_2]_2$ and $[(\eta^5\text{-}C_5H_5)Mo(NO)(SR)]_2$ were also prepared. We have investigated the single crystal X-ray structures of $[(\eta^5\text{-}C_5H_5)Mo(NO)(SR)]_2$, R = $-CH_2CH_3$, $-CH(CH_3)_2$ to verify (i) that the nitrosyl groups are terminally bound with the linear Mo-N-O geometry [1a, 1d], (ii) the bridging nature of the sulphur ligands and (iii) the extent of direct Mo-Mo bonding. The available spectroscopic and electrochemical data do not differentiate between the possible *cis* and *trans* isomers shown below and therefore their specific configurations will also be established by the X-ray analysis.



TRANS



CIS

Experimental

Crystals of $[\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$ and $[\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$ were generously supplied by Dr. J.A. McCleverty of the University of Sheffield, U.K. Preliminary Weisenberg photography established the crystal systems, space groups, and approximate unit cell dimensions. Accurate cell constants for each compound were derived by a least-squares fit to the diffractometer setting angles [2] of 12 reflections carefully located on a Hilger and Watts Y290 computer controlled 4-circle diffractometer. Relevant crystal data are given in Table 1.

Intensity data were collected for $\theta \leqslant 56.5°$ using an $2\theta/\omega$ scan of width 0.60° in θ at a scan rate of 0.01° s^{-1}. The background was counted for 15 s at each end of the scan. The standard deviation in intensity was calculated as $\sigma(I) = [T + t^2B + (pI)^2]^{\frac{1}{2}}$, where T = integrated peak count, B = average background count, t = ratio of scan to background times, p = a factor to down-weight the more intense reflections during least squares refinement [3]. The value initially assigned to 'p', 0.04, for *trans*-$[\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$ was increased to 0.06 during the final stages of refinement to keep $\langle\Sigma\omega(|Fo|-|Fc|)^2\rangle$ approximately constant throughout the data. For *cis*-$[\eta^5\text{-}C_5H_5)Mo(NO)\text{-}(SCH(CH_3)_2)]_2$ the trial value of 0.06 did not require alteration. During data collections the intensities of three standard reflections were remeasured periodically to monitor crystal stability and alignment but no non-statistical variations were encountered. Any reflection whose count rate exceeded 8000 c s^{-1} was automatically remeasured after insertion of an aluminium foil attenuator. The data sets were processed for Lorentz and polarisation effects, and equivalent reflections were averaged. The data for *trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$ were corrected for absorption [4].

Structure determination and refinement

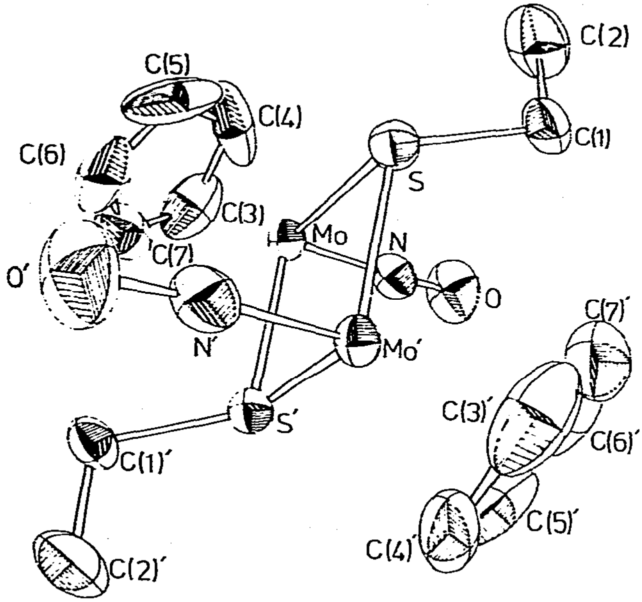
(a) *trans*-$[\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$

The unit cell contains four molybdenum atoms. These were found, from a Patterson synthesis, to occupy general positions in the cell.

TABLE 1. CRYSTAL DATA

Compound	*trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$	*cis*-$[\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$
Formula weight	504.4	532.4
Colour and habit	orange-brown plates	yellow needles
Forms developed	$\{010\}$ (100) $(\bar{1}\bar{2}0)$ $(0\bar{1}\bar{1})$ $(0\bar{1}1)$	$\{100\}$ $\{011\}$
Crystal system	monoclinic	orthorhombic
Systematically absent reflections	$h0l$ when $l = 2n+1$ $0k0$ when $k = 2n+1$	hkl when $h+k+l = 2n+1$ $hk0$ when $h = 2n+1$
Space group	$P2_1/c$ (No. 14)	$Im2a$ (No. 46 with b and c axes interchanged
a	7.924(1) Å	30.874(2) Å
b	12.692(1)	14.849(3)
c	9.510(1)	18.260(2)
β	109.06(1)°	
V	903.8 Å^3	8371 Å^3
Z	2	16
D(obs)(by flotation in aqueous $ZnBr_2$)	1.835 g cm^{-3}	1.682 g cm^{-3}
D(calc)	1.850	1.689
$\mu(CuK_\alpha)$	136.94 cm^{-1}	123.49 cm^{-1}
$F(000)$	500	4256
Max. $\sin\theta/\lambda$	0.5409	0.5409
No. observed reflections ($I>3\sigma(I)$)	1120	2974
Crystal size	0.03 x 0.20 x 0.16 mm	0.08 x 0.07 x 0.36 mm
Mosaic spread	0.11°	0.13°

It was noted that they were grouped into two pairs, as would be required if the molecule were to be dimeric. Two electron density maps enabled the S, N, O and C atoms to be located, and the dimeric formulation was confirmed. Refinement of atomic parameters was undertaken using the full least squares matrix [5]. Atomic scattering factors used were from standard listings with those for Mo corrected for real dispersion effects [6]. The function minimised was $\Sigma\omega(|Fo|-|Fc|)^2$, with weights $\omega = 4Fo^2/\sigma^2(F^2)$. The residuals quoted are $R = \Sigma(|Fo|-|Fc|)/\Sigma|Fo|$, $R_\omega = [\Sigma\omega(|Fo|-|Fc|)^2/\Sigma\omega Fo^2]^{\frac{1}{2}}$. Atoms were assigned initial isotropic temperature factors of 3.0 Å^2 for Mo and S and 4.0 Å^2 for O, N and C. For the second cycle the Mo and S atoms were given anisotropic thermal parameters. At this stage R was 0.106. A difference Fourier synthesis displayed two distinct peaks, one on each side of atom C(4) of the cyclopentadiene ring, and the next few cycles tested a model in which C(4) was split into two half-weighted atoms. However, a weighting and agreement analysis showed that the more intense reflections were dominating the calculated shifts, and the 'p' factor in the calculation of $\sigma(I)$ was increased to 0.06. In addition, there were some anomalies in the reflections which had required attenuation, and these were assigned zero weight. At the same time the data was corrected for absorption. A difference Fourier map was then computed and atom C(4), which had been omitted from the structure factor calculation, reappeared as a single peak and thereafter gave no problems. The nine hydrogen atoms were located and included in the refinement with variable positions but with fixed isotropic temperature factors of 5.0 Å^2. After four cycles the average parameter shift of the non-hydrogen atoms was less than 0.1 of its standard deviation and refinement was terminated with $R = 0.034$ and $R\omega = 0.046$. Final atomic positions are listed in Table 2. The atomic numbering scheme is shown in Fig. 1. Bond lengths and angles are given in Table 3. All standard deviations listed are derived from the least squares inverse matrix. Tables of observed and calculated structure factors and lists of anisotropic thermal parameters, are available on request from the authors (G.R.C.).



1. Molecular geometry of *trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$ Anisotropic thermal ellipses represent 50% probability boundaries.

(b) *cis*-$[\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$

It was known from the density that the unit cell contained 32 Mo atoms. The two possible space groups which were consistent with the systematically absent reflections were *Imma* and *Im2a*. *Imma* has 16 general positions and would require at least two independent Mo atoms. *Im2a* has only 8 general positions, and would require at least four independent Mo atoms. A Patterson synthesis was therefore computed. The vector distribution could not be reconciled with that expected for two independent Mo atoms in space group *Imma*.

The Patterson synthesis was therefore examined for a plausible model consisting of four independent Mo atoms in the non-centrosymmetric space group. The vector peaks observed, together with their relative height and final assignments are listed on p.418.

TABLE 2

ATOMIC POSITIONS FOR *trans*-$[(\eta^5\text{-}C_5H)Mo(NO)(SC_2H_5)]_2$

Atom	*x/a*	*y/b*	*z/c*
Mo	.0578(1)	.0358(0)	.1545(1)
S	-.1048(2)	.1341(1)	-.0629(2)
O	-.2493(8)	-.0324(4)	.2496(8)
N	-.1285(7)	-.0078(4)	.2030(6)
C(1)	-.3348(9)	.1572(5)	-.0635(8)
C(2)	-.337(1)	.2491(8)	.035(1)
C(3)	.254(2)	.066(1)	.394(1)
C(4)	.171(1)	.163(1)	.338(2)
C(5)	.247(2)	.1836(8)	.221(1)
C(6)	.354(1)	.102(1)	.217(1)
C(7)	.353(1)	.0377(7)	.318(1)
H(1)	-.420(9)	.174(5)	.815(9)
H(2)	-.38(1)	.083(6)	-.038(8)
H(3)	.70(1)	.233(7)	.11(1)
H(4)	.70(1)	.177(6)	.454(9)
H(5)	.51(1)	.229(5)	.504(9)
H(6)	.24(1)	.025(7)	.42(1)
H(7)	.09(1)	.131(6)	.151(8)
H(8)	.21(1)	.224(6)	.17(1)
H(9)	.48(1)	.083(6)	.218(9)
H(10)	.60(1)	-.001(8)	.69(1)

TABLE 3

BOND DISTANCES AND ANGLES FOR *trans*-[(η^5-C_5H_5)Mo(NO)(SC_2H_5)]$_2$

Mo – Mo'	2.923(1) Å	Mo – Mo' – S	52.50(4)°
Mo – S	2.398(2)	Mo – Mo – S'	52.45(4)
Mo – S'	2.400(2)	Mo – Mo – N	98.6(2)
Mo – N	1.773(5)	S – Mo – S'	104.94(7)
Mo – C(3)	2.33(1)	S – Mo – N	93.2(3)
Mo – C(4)	2.36(1)	Mo – S – Mo'	75.06(3)
Mo – C(5)	2.378(9)	Mo – S – C(1)	109.7(2)
Mo – C(6)	2.33(1)	Mo' – S – C(1)	114.3(2)
Mo – C(7)	2.348(8)	Mo – N – O	173.5(3)
S – C(1)	1.844(6)	S – C(1) – C(2)	109.6(3)
O – N	1.219(7)	C(4) – C(3) – C(7)	109.1(8)
C(1) – C(2)	1.50(1)	C(3) – C(4) – C(5)	100.8(6)
C(3) – C(4)	1.42(2)	C(4) – C(5) – C(6)	107.8(9)
C(3) – C(7)	1.28(1)	C(5) – C(6) – C(7)	108.4(8)
C(4) – C(5)	1.45(2)	C(3) – C(7) – C(6)	113.9(9)
C(5) – C(6)	1.35(1)		
C(6) – C(7)	1.26(1)		

	u	*v*	*w*	height	assignment
1.	0.000	0.000	0.000	999	origin
2.	0.000	0.000	0.500	903	$Mo_1 \rightarrow Mo_2$ and $Mo_3 \rightarrow Mo_4$
3.	0.000	0.500	0.130	386	0 ½ 2z + ½
4.	0.500	0.000	0.130	380	½ 0 2z + ½
5.	0.090	0.000	0.000	275	½ + 2x 0 0
6.	0.260	0.240	0.250	268	Mo_1 – Mo_3 vector

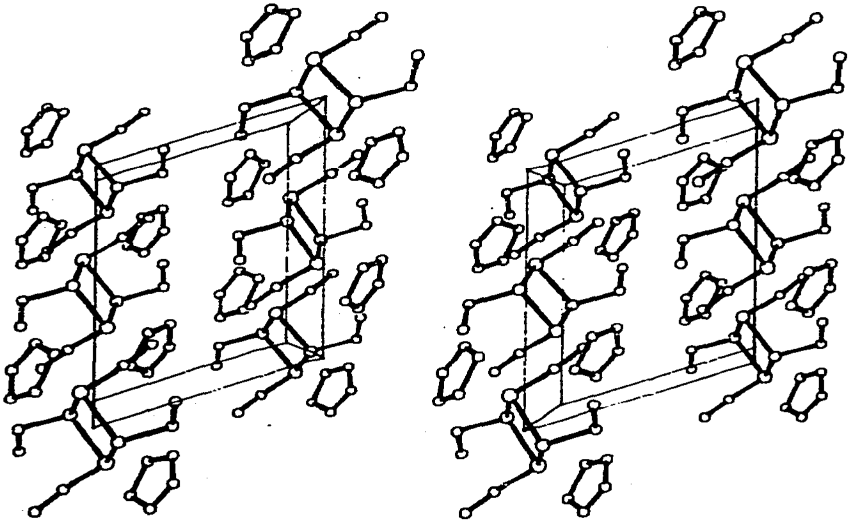
The large peak appearing on the line $(w,0,0)$ implies that there is a mirror plane perpendicular to the a axis. Thus the space group must be *Im2a*, i.e. *Ima2* with the b and c axes interchanged. Assuming that to each Mo at (x,y,z) there is a space group independent Mo at $(x,y,z+\frac{1}{2})$ and also a further independent Mo at approximately $(x+\frac{1}{4},\ y+\frac{1}{4},\ z+\frac{1}{4})$ the major peaks can be interpreted in *Im2a* in terms of Mo atoms at $(0.205,\ y,\ 0.315)$; $(0.205,\ y,\ 0.815)$; $(0.470,\ y+\frac{1}{4},\ 0.555)$; $(0.470,\ y+\frac{1}{4},\ 0.055)$. The actual interpretation is given in the above table of Patterson peaks. In order to define the origin, y may arbitrarily be assumed to be zero.

Because to each Mo atom at (x,y,z) there is another at $(x,y,z+\frac{1}{2})$, all structure factors with l odd must calculate to zero amplitude. These terms which were of small amplitude were therefore temporarily removed from the data set. The effect of this was that the analysis would now be incapable of distinguishing between these two pairs of molecules, (i.e. the pair with Mo at (0.205, 0, 0.315) and (0.204, 0, 0.815) and the pair with Mo at (0.470, 0.250, 0.055) and (0.470, 0.250, 0.055)), but until the nature of the differences became clear it would not be possible to phase the l odd terms correctly.

A structure factor calculation and an ensuing Fourier synthesis enabled the two S atoms which are independent in terms of the above assumptions to be located. One (near the fourth Mo atom) was on a general position, whereas near the first Mo atom were two S atoms situated on the mirror plane at $X = 0.25$. This is a special symmetry position and these two S atoms must be half-weighted in subsequent structure factor calculations.

In terms of these atom positions there are two independent $(\mathrm{MoS})_2$ groups, one having mirror plane symmetry with the S atoms on the plane, the other having diad symmetry with a two-fold axis $(\frac{1}{2},y,\frac{1}{2})$ at the centre of the group. At this stage neither group gave any indication of the possible difference between the pairs related by the vector $(0,0,\frac{1}{2})$.

The majority of the remaining non-hydrogen atoms were located, with some difficulty, from a series of difference electron density maps interspersed by trial least-squares refinement cycles. The residual R refined to 0.074, but the temperature factors of several atoms were unrealistically high. The molecule with the diad symmetry appeared to be posing no problems. All atoms associated with it had been located and all were refining with sensible temperature factors. On the other hand, the molecule with mirror symmetry was much less definite. The cyclopentadienyl ring had been located but the atoms had very high temperature factors. The oxygen of the nitrosyl had appeared as two diffuse half-atoms. The isopropyl groups were difficult to define and only the tertiary atoms had been allocated coordinates. It appeared clear that the pseudo-vector between molecules of $(0,0,\frac{1}{2})$ must apply fairly well to the diad symmetry molecules but not to the molecule having mirror symmetry. In particular, the two 'equivalent' molecules of this type almost certainly showed different orientations of the isopropyl groups, different positions for the nitrosyl oxygen, and slightly different positions for the cyclopentadienyl atoms.



2. Stereoscopic diagrams showing the molecular packing in *trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SC_2H_5)]_2$.

Because it remains essential to describe the differences explicitly and fairly accurately, in order that the initial phases of the reflections with *l* odd would be approximately correct, the previous refinement steps were repeated in a cautious manner.

Initially the isopropyl groups associated with the mirror symmetry molecule were omitted from the calculation. All other atoms described above were included, but the temperature factors of the light atoms of the mirror symmetry molecule were held constant at rather high values throughout the refinement. From successive difference Fourier syntheses interspersed with least-square cycles the remaining atoms were located, as weighted part atoms if appropriate. The above features remained and the possible methyl carbons of the isopropyl groups were also now located. In the case of the isopropyl group associated with diad symmetry there were two possibilities with sensible geometries which could constitute a possible difference between the pair of molecules separated by a vector $(0,0,\frac{1}{2})$, that is, the difference giving rise to the weak *l* odd reflections. The situation with regard to the molecule having mirror plane symmetry was more complex as the distribution of peaks in the difference map indicated a considerable disorder of the methyl groups. After investigating several trial models for these isopropyl groups, the most likely ones were adopted.

A structure factor calculation computed using the best available model returned an *R* factor of 0.072. Attempts were then made to unravel the differences which gave rise to the *l* odd terms, but none of the possibilities investigated were at all consistent with those observed data. It was reluctantly concluded that despite the fact that the broad features of the structure had been ascertained, it would be extremely difficult

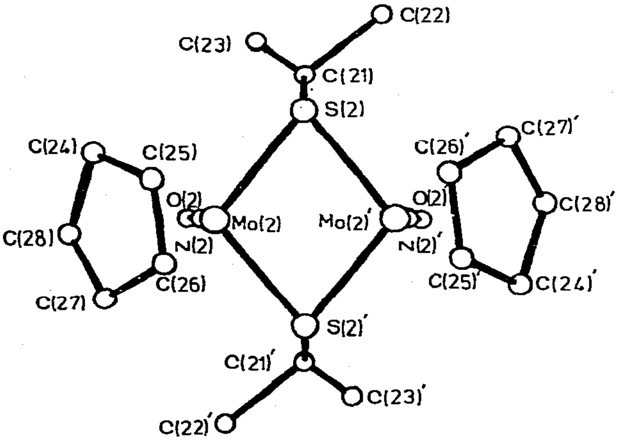
TABLE 4

ATOMIC POSITIONS FOR *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$

Atom	*x/a*	*y/b*	*z/c*
Mo(1)	0.2023(1)	0.0000	0.8217(1)
Mo(2)	0.4670(1)	0.2301(2)	0.5575(1)
S(1A)	0.2500	-0.0586(9)	0.9115(6)
S(1B)	0.2500	0.059(1)	0.7326(8)
S(2)	0.5441(2)	0.2305(5)	0.4277(3)
N(1)	0.1917(9)	-0.100(2)	0.787(2)
N(2)	0.4601(7)	0.348(2)	0.571(1)
O(1)	0.1824(7)	-0.152(1)	0.733(1)
O(2)	0.4537(6)	0.425(1)	0.5846(9)
C(1A1)	0.2500	-0.151(5)	0.938(3)
C(1A2)	0.292(3)	-0.186(7)	0.978(5)
C(1A3)	0.2500	-0.194(4)	0.886(3)
C(1B1)	0.2500	0.037(5)	0.655(4)
C(1B2)	0.293(4)	0.064(9)	0.598(7)
C(1B3)	0.298(3)	-0.025(7)	0.611(4)
C(1B4)	0.2500	-0.08(2)	0.67(1)
C(14)	0.177(1)	0.152(3)	0.851(2)
C(15A)	0.181(3)	0.125(7)	0.900(5)
C(15B)	0.177(3)	0.078(7)	0.922(5)
C(16)	0.148(1)	0.032(3)	0.904(3)
C(17)	0.131(1)	0.043(3)	0.840(2)
C(18)	0.156(1)	0.125(3)	0.798(2)
C(21)	0.5635(8)	0.346(2)	0.603(1)
C(22A)	0.623(4)	0.378(8)	0.595(6)
C(23A)	0.560(6)	0.34(1)	0.66(1)
C(22B)	0.608(3)	0.352(7)	0.570(4)
C(23B)	0.553(5)	0.35(1)	0.192(9)
C(24)	0.453(1)	0.153(3)	0.672(2)
C(25)	0.4642(8)	0.084(2)	0.614(2)
C(26)	0.437(1)	0.080(2)	0.556(2)
C(27)	0.4005(9)	0.147(2)	0.572(1)
C(28)	0.4110(9)	0.188(2)	0.639(2)

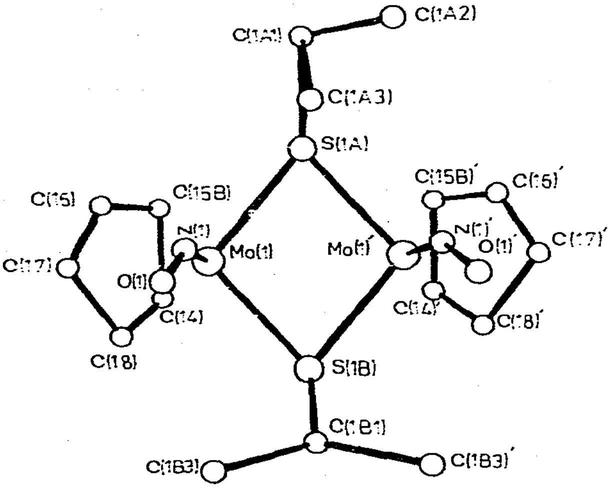
to determine those features which defined the difference between the molecules, and this avenue of investigation was discontinued.

Finally, using the original data set having only l even terms, and using all the atomic positions as deduced, and appropriately weighted for the average model, two least-squares cycles were computed on the positional coordinates only. One or two atoms were observed to move quite markedly in the first cycle but seemed to settle down in the second. An *R* factor of 0.067 was obtained.



3. Geometry of the molecule of *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$ having diad symmetry. Only one of the possible isopropyl arrangements has been shown.

The final atomic coordinates are listed in Table 4. The atomic numbering scheme is given in Figs. 3 and 4. Bond distances and angles are listed in Tables 5 and 6. Tables of observed and calculated structure factors, and a list of thermal parameters, are available on request from the authors (G.R.C.).



4. Geometry of the molecule of *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$ having mirror symmetry. Only one of the possible isopropyl arrangements has been shown.

Molecular structure of *trans*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH_2CH_3)]_2$

The complex is dimeric, with the overall molecular geometry shown in Fig. 1. If the cyclopentadienyl ring is considered to occupy three coordination sites, then each metal atom sits at the centre of a distorted octahedron composed of a cyclopentadienyl ring, two sulphurs, and one nitrogen. The central $(MoS)_2$ core is required to be planar by crystallographic symmetry

The average Mo-S distance is 2.399(2) Å which is somewhat longer than the Mo-S distances of 2.317(3) in $[(\eta^5\text{-}C_5H_5)Mo(O)(S)]_2$ [7]; 2.323 and 2.314 Å in $[MoSO(L\text{-histidine})]_2$ [8]; 2.343 and 2.340 Å in $Mo_2[NC(CH_3)_3]_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}S)_2$ [9]; 2.318(4), 2.299(4), 2.307(4) and 2.316(4) Å in di-μ-sulphido-bis[oxo-n-butyldithiocarbamato]molybdenum [10], but shorter than the distances of 2.455(5) and 2.451 Å in bis$(\eta^5\text{-}C_5H_5)MoS_4$ [11]; 2.437(3) Å in

TABLE 5

BOND DISTANCES AND ANGLES FOR THE MOLECULE OF *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)SCH(CH_3)_2)]_2$ POSSESSING DIAD SYMMETRY

Atom		Atom	Bond Distance	Atom		Atom		Atom	Angle
Mo(2)	-	Mo(2)'	2.926(4)	Mo(2)	-	Mo(2)'	-	S(2)	52.3(2)
Mo(2)	-	S(2)	2.396(7)	Mo(2)	-	Mo(2)'	-	S(2)'	52.4(2)
Mo(2)	-	S(2)'	2.395(7)	Mo(2)	-	Mo(2)'	-	N(2)	100.5(8)
Mo(2)	-	C(24)	2.42(4)	S(2)	-	Mo(2)	-	S(2)'	104.7(2)
Mo(2)	-	C(25)	2.41(3)	S(2)	-	Mo(2)	-	N(2)	95.8(8)
Mo(2)	-	C(26)	2.40(3)	Mo(2)	-	S(2)	-	Mo(2)'	75.3(1)
Mo(2)	-	C(27)	2.41(3)	Mo(2)	-	S(2)	-	C(21)	110.4(8)
Mo(2)	-	C(28)	2.37(3)	Mo(2)'	-	S(2)	-	C(21)	109.8(8)
Mo(2)	-	N(2)	1.78(2)	S(2)	-	C(21)	-	C(22A)	120(4)
S(2)	-	C(21)	1.90(3)	S(2)	-	C(21)	-	C(23A)	101(9)
N(2)	-	O(2)	1.19(3)	S(2)	-	C(21)	--	C(22B)	103(3)
C(24)	-	C(25)	1.51(5)	S(2)	-	C(21)	-	C(23B)	105(5)
C(24)	-	C(28)	1.52(5)	C(25)	-	C(24)	-	C(28)	99(2)
C(25)	-	C(26)	1.35(5)	C(24)	-	C(25)	-	C(26)	116(2)
C(26)	-	C(27)	1.53(4)	C(25)	-	C(26)	-	C(27)	106(2)
C(27)	-	C(28)	1.40(4)	C(26)	-	C(27)	-	C(28)	106(2)
C(21)	-	C(22A)	1.9(1)	Mo(2)	-	N(2)	-	O(2)	175.0(8)
C(21)	-	C(23A)	1.1(2)						
C(21)	-	C(22B)	1.50(9)						
C(21)	-	C(23B)	1.7(2)						

$(\eta^5\text{-}C_5H_5)_2MoS_2(C_6H_4)$ [12]; and 2.64 Å in $[(\eta^5\text{-}C_5H_5)Mo(SCH)_3)_2]_n$ [13]. The Mo-S distance in MoS_2 [14] is 2.35 Å and in Mo_2S_3 there are three sulphur atoms at a distance of 2.36 Å from the molybdenum and three at 2.57 Å [15]. These data would suggest that the longer molybdenum-sulphur distance is

TABLE 6

BOND DISTANCES AND ANGLES FOR THE MOLECULE OF *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)\{SCH(CH_3)_2\}]_2$ POSSESSING MIRROR SYMMETRY

Atom		Atom	Bond Distance	Atom		Atom		Atom	Angle
Mo(1)	-	Mo(1)'	2.945(3)	Mo(1)	-	Mo(1)'	-	S(1A)	51.6(3)
Mo(1)	-	S(1A)	2.37(1)	Mo(1)	-	Mo(1)'	-	S(1B)	51.5(3)
Mo(1)	-	S(1B)	2.36(1)	Mo(1)'	-	Mo(1)	-	N(1)	101(1)
Mo(1)	-	C(14)	2.45(4)	S(1A)	-	Mo(1)	-	S(1B)	103.0(4)
Mo(1)	-	C(15A)	2.4(1)	S(1A)	-	Mo(1)	-	N(1)	93(1)
Mo(1)	-	C(15B)	2.3(1)	S(1B)	-	Mo(1)	-	N(1)	101(1)
Mo(1)	-	C(16)	2.30(5)	Mo(1)	-	S(1A)	-	Mo(1)'	76.85(9)
Mo(1)	-	C(17)	2.32(4)	Mo(1)	-	S(1B)	-	Mo(1)'	77.11(9)
Mo(1)	-	C(18)	2.38(4)	Mo(1)	-	S(1A)	-	C(1A1)	125(2)
Mo(1)	-	N(1)	1.65(3)	Mo(1)	-	S(1B)	-	C(1B1)	126(2)
S(1A)	-	C(1A1)	1.46(5)	S(1A)	-	C(1A1)	-	C(1A2)	118(4)
S(1B)	-	C(1B1)	1/45(6)	S(1A)	-	C(1A1)	-	C(1A3)	104(2)
N(1)	-	O(1)	1.29(4)	S(1B)	-	C(1B1)	-	C(1B2)	122(4)
C(14)	-	C(15A)	1.0(1)	S(1B)	-	C(1B1)	-	C(1B3)	121(3)
C(14)	-	C(15B)	1.7(1)	S(1B)	-	C(1B1)	-	C(1B4)	94(7)
C(14)	-	C(18)	1.23(5)	C(18)	-	C(14)	-	C(15A)	130(6)
C(15A)	-	C(16)	1.7(1)	C(18)	-	C(14)	-	C(15B)	113(4)
C(15B)	-	C(16)	1.2(1)	C(14)	-	C(15A)	-	C(16)	107(3)
C(16)	-	C(17)	1.29(6)	C(14)	-	C(15B)	-	C(16)	99(3)
C(17)	-	C(18)	1.63(5)	C(15A)	-	C(16)	-	C(17)	96(4)
C(1A1)	-	C(1A2)	1.6(1)	C(15B)	-	C(16)	-	C(17)	119(5)
C(1A1)	-	C(1A3)	1.14(7)	C(16)	-	C(17)	-	C(18)	109(3)
C(1B1)	-	C(1B2)	1.7(1)	C(17)	-	C(18)	-	C(14)	97(2)
C(1B1)	-	C(1B3)	1.9(1)	Mo(1)	-	N(1)	-	O(1)	151.8(8)
C(1B1)	-	C(1B4)	1.8(2)						

associated with complexes in which the sulphur is also bonded to other atoms, whereas the shorter distances occur when the sulphur is bonded solely to the molybdenums.

The angles associated with the $(MoS)_2$ moiety are listed in Table 3. The S-Mo-S' angle of 104.94(7)° and the Mo-S-Mo' angle of 75.06(3)° compare with 102.7(1)° and 77.3(1)° for $[\eta^5-C_5H_5)Mo(O)(S)]_2$ [7]; 102.86° and 77.14° for $Mo_2[NC(CH_3)_3]_2(\eta^5-C_5H_5)_2(S)_2$ [9] and 101.9° and 75.1° for di-μ-sulphido-bis[oxo-n-butyldithiocarbamato]-molybdenum(V) [10]. Here again the angles associated with $[\eta^5-C_5H_5)Mo(NO)(SCH_2CH_3)]_2$ could arise from increased bulkiness due to the attachment of the ethyl group.

The Mo-Mo distance of 2.923(1) Å is similar to values of 2.894(5) Å found in $[\eta^5-C_5H_5)Mo(O)(S)]_2$ [7]; 2.8 Å in $[Mo(OC_6H_5)_3Cl_2]_2$ [16]; 3.06 Å in $[Mo(CO)_4(PEt_2)]_2$ [17] and 2.920 Å in $Mo_2[NC(CH_3)_3]_2$-$(\eta^5-C_5H_5)_2(\mu S)_2$ [9]. Many bridged Mo-Mo single bond distances in neutral complexes are in the range 2.50 - 2.90 Å.
This distance is, however, shorter than that of 3.253 Å found in $[\eta^5-C_5H_5)Mo(CO)_3]_2$ [18] in which there is no carbonyl bridging and a definite metal-metal bond, but longer than the 2.73 Å found in molybdenum metal [19] or 2.799 Å in $[Mo_2S_2O_2EDTA]^{2-}$ [20]. This would indicate that in the complex being studied there is definitely some metal-metal single bond character.

The average Mo-C (cyclopentadienyl) distance of 2.348 Å lies in the range for such bonds. Compare this with a value of 2.41 Å found in $[\eta^5-C_5H_5)Mo(O)(S)]_2$ [7]; 2.30 Å in $[Mo(\eta^5-C_5H_5)(SCH_3)_2]_2$ [13]; 2.34 Å in $[\eta^5-C_5H_5)Mo(CO)_3]_2$ [18] 2.38(2) Å in $[\eta^5-C_5H_5)Mo(CO)_3C_2H_5]$ [21]; 2.36 Å in $(\eta^5-C_5H_5)Mo(CO)_3C_3F_7$ [22] and $[C_{10}H_8Mo(CO)_3Me]_2$ [23]; and 2.383 Å in $Mo_2[NC(CH_3)_3]_2(\eta^5-C_5H_5)_2(\mu-S)_2$ [9]. The mean Mo-C bond length of 2.29 Å in $(\eta^5-C_5H_5)_2MoH_2$ [17] is somewhat shorter than these distances, but in the absence of strongly π-bonding ligands such as CO, back-donation from metal d_π orbitals to the antibonding π* orbitals of the hydrocarbon should become more important.

A least squares plane calculation was made to determine the distance from the molybdenum to the plane of the cyclopentadienyl ring. The equation of the plane is

$$-0.5912\ X + 0.4826\ Y - 0.6462\ Z + 2.0736 = 0.0$$

Displacements of atoms from the plane are C(3) -0.006, C(4) 0.010, C(5) -0.011, C(6) 0.008, C(7) -0.001, and Mo 2.046 Å. This value of 2.046 Å is in close agreement with those found for similar molybdenum cyclopentadienyl complexes. For example 2.00 Å in bis(η^5-C_5H_5)MoS_4 [11]; 2.01(2) Å in (η^5-C_5H_5)$_2$$MoS_2C_6H_4$ [12]; 2.04 Å in [(η^5-C_5H_5)Mo(CO)$_3$$C_2H_5$] [21] and 2.08 Å in Mo_2[NC(CH_3)$_3$]$_2$(η^5-C_5H_5)$_2$(μ-S)$_2$ [9].

The carbon-carbon bond lengths in the cyclopentadienyl ring vary from 1.262(12) Å to 1.451(17) Å. Distortions of complexed cyclopentadienyl rings are common [11, 17, 21, 24-26] and are generally rationalised in terms of the lack of cylindrical symmetry around the metal atom removing the degeneracy of the e_1 molecular orbitals of the cyclopentadienyl ring [27].

The Mo-N bond length of 1.773(5) Å is comparable with that of 1.780(6) Å found in [(η^5-C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4] [28]; 1.75(1) Å in bis-cyclopentadienylmethylnitrosylmolybdenum [29] and 1.765(12) Å in [(η^5-C_5H_5)Mo(NO)I]$_2$(μ-NNMe$_2$) [30].

The metal-nitrosyl grouping departs from linearity by a significant amount, the Mo-N-O angle being 173.5(3)°. In view of the proximity of the nitrosyl to the ethyl group of the SCH_2CH_3 bridge it is not possible to exclude a steric mechanism for the departure from 180° of the Mo-N-O angle. An angle of 170.6(3)° was found for the metal-nitrosyl in [(η^5-C_5H_5)Mo(NO)I(NH_2NHPh)][BF_4] [28], but the angle was 178(2)° in bis-cyclopentadienylmethylnitrosylmolybdenum [29] and

179.2° in tris-cyclopentadienylnitrosylmolybdenum [24]. A departure from linearity was, however, observed in $[(\eta^5\text{-}C_5H_5)Cr(NO)SPh]_2$ [31] where the Cr-NO angle was 170° as compared with 175.6° in $[Cr(NO)_2\text{-}(\eta^5\text{-}C_5H_5)]_2$ [25]. In the former the nitrogen of the nitrosyl was found to be close to the phenyl ring attached to the sulphur. This also would indicate that the bending of the nitrosyl was due to a steric effect.

The N-O distance is 1.219(7) Å which is comparable with 1.21 Å in bis-cyclopentadienylnitrosylmethylmolybdenum [29] and 1.207(4) Å in tris-cyclopentadienylnitrosylmolybdenum [24].

The sulphur-carbon (ethyl) distance was found to be 1.844(6) Å, and the ethyl carbon-carbon distance 1.50(1) Å.

The arrangement of molecules in the crystal is shown in the stereopair diagrams of Fig. 2.

Molecular structure of *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$

In describing the molecular structure of *cis*-di-μ-isopropylthio-dinitrosylbis(η^5-cyclopentadienyl)dimolybdenum it should be remembered that within the subcell there are two distinct molecules, and that only the subcell structure has been solved. This means that each molecule is described as the average of two slightly different molecules and that the exact nature of the differences is not known. Thus the apparent molecular dimensions must be regarded with some caution. From the behaviour during refinement it is thought that the molecule with diad symmetry is more precisely described than is the molecule with mirror symmetry.

In spite of these difficulties the general features of the molecular geometry are clear. As with the ethyl complex each molecule is a dimer, the molybdenums being bridged by the sulphur atoms, and with a nitrosyl group and a cyclopentadienyl ring co-ordinated to each molybdenum. As with the ethyl complex each molybdenum atom is therefore at the centre of a distorted octahedron (if one considers the cyclopentadienyl ring to occupy three co-ordination sites).

The most significant feature of difference is that because the isopropyl complexes have two-fold or mirror symmetry respectively, the dispositions of the nitrosyl group and cyclopentadienyl ring are *cis* with regard to the $(MoS)_2$ ring, whereas in the centrosymmetric ethyl complex they were *trans*. The two independent molecules are very similar in shape, in spite of having different required point group symmetries since, in fact, each molecule closely approximates to mm2 symmetry.

(a) The molecule possessing diad symmetry

The arrangement of atoms in the molecule having diad symmetry and the numbering system used are shown in Figure 3. In this molecule the $(MoS)_2$ system is planar, as shown by the calculation of a least squares plane for this ring.

The plane defined by Mo(2), Mo(2)', S(2), S(2)' is

$$X - Y + Z - 3.420 = 0$$

with atomic displacements of 0.003 Å.

The average Mo-S distance of 2.395 Å is comparable with that of 2.399(2) Å found in *trans*-$[(\eta^5-C_5H_5)Mo(NO)(SEt)]_2$.

The Mo-S-Mo' angle of 75.3(1)° and the S-Mo-S' angle of 104.7(2)° compare with those of 75.06(3)° and 104.94(7)° found in the ethyl complex. Any narrowing of the S-Mo-S' angle and widening of the Mo-S-Mo' angle could arise from the different spatial requirements of the ethyl and isopropyl groups.

The Mo-Mo distance of 2.926(4) Å is similar to that of 2.923(1) Å found in the ethyl complex. Again, we conclude that there must be some metal-metal single bond character.

The average Mo-C (cyclopentadienyl) distance of 2.403 Å lies in the upper range of such bonds. The distance from the molybdenum to the plane of the cyclopentadienyl ring was determined using a least squares plane calculation. The equation of the plane is

$$0.4184\ X + 0.7050\ Y - 0.4840\ Z - 2.9014 = 0.0$$

with displacements, C(4) 0.012, C(25) 0.017, C(26) -0.019, C(27) -0.007, C(28) -0.002, and Mo 2.055 Å. This value of 2.055 Å is in close agreement with those found for similar molybdenum cyclopentadienyl complexes.

The C-C bond lengths in the cyclopentadienyl ring vary from 1.35(5) Å to 1.53(4) Å. These are somewhat longer than those usually found, but whether this is due to some definite structural feature or to the poor refinement is uncertain.

The Mo-N (nitrosyl) bond length of 1.78(2) Å is comparable with that of 1.773(5) Å found in the ethyl complex and other similar compounds [28–30]. The metal-nitrosyl grouping does not depart from linearity as much as it did in the ethyl complex. Here the M-N-O angle is 175.0(8)°. This could be due to decreased interaction with the cyclopentadienyl ligand since here they are related *trans* whereas in the ethyl complex they were in *cis* positions relative to each other. The N-O distance is 1.19(3) Å as compared with that of 1.219(7) Å found in $[(\eta^5\text{-}C_5H_5)Mo(NO)(SEt)]_2$.

(b) The molecule possessing mirror symmetry

The molecule situated on a mirror plane is illustrated in Fig. 4. The bond lengths and angles associated with this molecule are listed in Table 6.

As in the previous case, the $(MoS)_2$ ring is planar. The least squares plane for the ring defined by Mo(1), Mo(1)', S(1A), S(1B) is

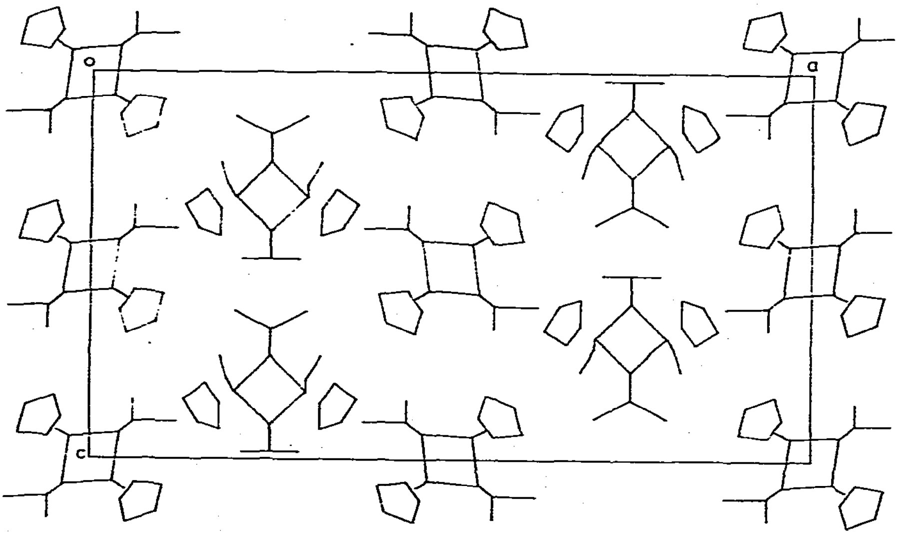
$$-0.8819\ Y - 0.4714\ Z + 7.0762 = 0.0$$

with atomic displacements of 0.003 Å.

The Mo-Mo distance is somewhat longer than the distances found in the previous molecule, being 2.945(3) Å as compared with 2.926(4) Å. Although the difference between these is greater than the estimated standard deviation, we cannot conclude that it is a real difference because of the poor resolution of this molecule. The average Mo-S-Mo' and S-Mo-S' angles here are 76.98(9)° and 103.0(4)° which are consistent with the lengthening in the Mo-Mo bond.

The Mo-S average distance is 2.37(1) Å which is shorter than that found in either the diad molecule or the ethyl complex.

The average Mo-C (cyclopentadienyl) distance is 2.364 Å which lies within the range of such bonds. As the cyclopentadienyl ring was poorly defined it was thought unsuitable to calculate the Mo-cyclopentadienyl plane distances. Furthermore, the cyclopentadienyl ring is greatly distorted as can be seen from the range of C-C distances (1.2(1) - 1.7(a) Å) and angles (113(4)° - 97(2)°) within the ring.



5. The packing of the molecules of *cis*-$[(\eta^5\text{-}C_5H_5)Mo(NO)(SCH(CH_3)_2)]_2$: (0 1 0) projection of the unit cell, from *y* = -0.1 to 0.4.

Similarly, the Mo-NO distance of 1.65(3) Å is not considered reliable since the nitrogen moved markedly in the final refinement cycles.

The arrangement of molecules in the crystal is shown in projection along the *b* axis in Fig. 5.

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