Molybdenum–Nitrogen Multiple Bonds: The Crystal and Molecular Structures of Tris(*NN*-diethyldithiocarbamato)nitridomolybdenum and Tris(*NN*-dimethyldithiocarbamato)thionitrosylmolybdenum

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The crystal and molecular structures of the title compounds have been determined by single-crystal *X*-ray analyses. The nitride is monoclinic, space group $P2_1/c$, with a = 10.844, b = 13.253, c = 17.317 Å, β = 90.12°, and Z = 4. The structure has been refined to an R value of 0.054 5 using 1 695 observed intensity data measured on an automatic diffractometer. The thionitrosyl is triclinic, space group $P\bar{1}$, with a = 9.090, b = 9.327, c = 12.080 Å, α = 95.01, β = 91.95, γ = 96.16°, and Z = 2. Structure refinement using 1 907 observed data measured on a manual diffractometer has given an R value of 0.068. Both compounds have a pentagonal-bipyramidal molecular structure with the nitrogen ligands axial and with one axial/equatorial and two equatorial/equatorial chelating dithiocarbamates. The geometry of the thionitrosyl group (Mo–N 1.738, N–S 1.592 Å) suggests a close analogy with the linear nitrosyl $[NO]^+$ ligand. In the nitride, the Mo–N distance of 1.641 Å is consistent with its formulation as a triple bond. In both compounds, the axial Mo–S bond, *trans* to the π-bonding ligand, is lengthened with the nitride showing the largest effect. This particular feature, together with other aspects of the distortion of the pentagonal-bipyramidal co-ordination sphere, are discussed in relation to other systems with comparable structures.

IN a recent publication,[1] Chatt and Dilworth described the preparation for the first time, of a series of thionitrosyl complexes $[Mo(NS)(S_2CNR_2)_3]$ by reaction of elemental sulphur or propylene sulphide with the corresponding nitrido-complex. We have determined the crystal structure of the complex $[Mo(NS)(S_2CNMe_2)_3]$ in order to confirm the proposed pentagonal-bipyramidal geometry and to ascertain the bonding characteristics of the NS ligand. We have also determined the structure of a parent nitride $[MoN(S_2CNEt_2)_3]$ for comparison with the thionitrosyl and, in addition, to observe the bonding characteristics of the increasingly interesting nitride ligand.

EXPERIMENTAL

Crystal Data.—(*a*) $[MoN(S_2CNEt_2)_3]$. $C_{15}H_{40}MoN_4S_6$, M = 554.75, Monoclinic, a = 10.844(1), b = 13.253(2), c = 17.317(2) Å, β = 90.12(1)°, U = 2 488.7 Å^3, D_m = 1.56, Z = 4, D_c = 1.48 g cm^{-3}, $F(000)$ = 1 184, space group $P2_1/c$, Cu-K_α radiation (λ = 1.541 8 Å), μ(Cu-K_α) = 87.7 cm^{-1}.

The crystals are pale yellow transparent blocks and the specimen chosen for *X*-ray study measured 0.06 × 0.1 × 0.1 mm. The space group and preliminary cell dimensions were determined from oscillation and Weissenberg photographs. Accurate cell dimensions were calculated by least-squares refinement of setting angles for 15 reflections with $17 < \theta < 30°$ automatically centred on a Nonius CAD4 diffractometer. Intensity data were collected on the same instrument using Cu-K_α radiation and an ω–2θ scan mode, the ω scan width being given by the expression 1.5 × (0.8 + 0.2 tan θ)°. For each reflection in the range $1.5 < \theta < 55°$ and with $h \geqslant 0$, $k \geqslant 0$, and l positive and negative, an initial prescan was made at a speed of *ca*. 20° min^{-1} and all reflections for which $I_{net} < 5$ counts were rejected. The remainder were rescanned at variable speeds, calculated from the results of the prescan, such that attempts were made to achieve a total of 3 000 counts, subject to a maximum counting time of 120 s. The 206 and 116 reflections were used as intensity controls and remeasured every 50 reflections. Of the 3 227 independent reflections measured, 1 695 satisfied the condition $I > 2.5\sigma(I)$, where $\sigma(I)$ was calculated from the basic equation $\sigma(I) = |I_{net} + 2B|^{\frac{1}{2}}$, suitably modified to take account of the particular measuring process of the diffractometer. The observed intensities were corrected for absorption using a local version of the program ICABS.[2,3]

The structure was solved *via* the heavy-atom method and refined by least squares, using the SHELX[4] program. Hydrogen atoms on the ethyl groups were included in calculated positions with C–H 1.08 Å and the idealised CH_3 group orientated in a staggered configuration with respect to the bonds at the methylene carbons. The methylene and methyl hydrogen-atom groups were given two separate overall isotropic temperature factors which were refined. A weighting scheme of the form $w = 1/[\sigma^2(F) + gF^2]$ was used, with the value of $g = 0.001$ giving reasonably flat agreement analyses. With all non-hydrogen atoms assigned anisotropic temperature-factor coefficients, the final R values were 0.054 5 (unweighted) and 0.054 4 (weighted). The final atomic positional parameters for the non-hydrogen atoms are given in Table 1, and for hydrogen in the Supplementary Publication. The atomic scattering factor for molybdenum was taken from ref. 5, and corrected for both parts of anomalous dispersion using $\Delta F'$ and $\Delta F''$ values from ref. 6, and neutral-atom scattering factors were taken from refs. 7 (non-hydrogen atoms) and 8 (spherical bonded hydrogen atoms).

(*b*) $[Mo(NS)(S_2CNMe_2)_3]$. $C_9H_{18}MoN_4S_7$, M = 502.65, Triclinic, a = 9.090(6), b = 9.327(6), c = 12.080(8) Å, α = 95.010(2), β = 91.950(2), γ = 96.160(2)°, U = 1 013.72 Å^3, D_m = 1.66, Z = 2, D_c = 1.646 g cm^{-3}, $F(000)$ = 508, Cu-K_α radiation (λ = 1.541 8 Å), μ = 116.28 cm^{-1}.

The crystals are orange-yellow plates and the specimen chosen for the *X*-ray study measured 0.42 × 0.30 × 0.12 mm. Oscillation and Weissenberg photographs were used for preliminary determination of the cell dimensions and space group. Accurate values were determined by diffractometer measurement of 2θ, φ, and χ values for axial reflections. Intensities were measured on a General Electric XRD-6 manual diffractometer using the stationary-crystal–counter technique with a counting time of 10 s. Backgrounds were taken from a graph prepared by measurement of individual backgrounds for some 200 reflections spread over the 2θ range used. No significant variations

TABLE 1

Final positional parameters ($\times 10^4$) * for $[MoN(S_2CNEt_2)_3]$

Atom	*X*	*Y*	*Z*
Mo	3 196(1)	2 587(1)	989(1)
S(1)	3 784(3)	3 873(3)	1 993(2)
S(2)	3 691(3)	1 775(2)	2 281(2)
S(3)	711(3)	2 593(2)	1 525(2)
S(4)	2 166(3)	894(2)	931(2)
S(5)	2 052(3)	2 577(2)	−290(2)
S(6)	3 091(4)	4 309(2)	385(2)
N	4 544(8)	2 250(7)	646(5)
N(1)	4 846(9)	3 052(7)	3 244(5)
N(2)	−235(10)	780(8)	1 238(6)
N(3)	1 769(9)	4 408(7)	−914(5)
C(1)	4 181(11)	2 905(9)	2 619(6)
C(2)	754(11)	1 369(10)	1 241(6)
C(3)	2 260(11)	3 846(9)	−367(7)
C(11)	5 200(13)	2 179(13)	3 728(7)
C(12)	6 527(15)	1 900(12)	3 565(11)
C(13)	5 259(13)	4 082(10)	3 488(8)
C(14)	4 351(16)	4 572(10)	4 011(8)
C(21)	−178(14)	−294(9)	1 023(7)
C(22)	38(19)	−958(12)	1 725(9)
C(23)	−1 464(13)	1 159(12)	1 416(8)
C(24)	−2 138(14)	1 535(12)	692(10)
C(31)	997(11)	3 986(11)	−1 527(7)
C(32)	−334(13)	4 029(14)	−1 352(9)
C(33)	1 967(14)	5 508(10)	−940(7)
C(34)	3 023(17)	5 775(13)	−1 444(10)

* Estimated standard deviations are given in parentheses throughout this paper.

TABLE 2

Final positional parameters ($\times 10^4$) for $[Mo(NS)(S_2CNMe_2)_3]$

Atom	*X*	*Y*	*Z*
Mo	2 167(1)	1 878(1)	2 454(1)
S	724(4)	−1 389(4)	1 377(4)
S(1)	1 289(4)	1 894(5)	4 407(3)
S(2)	−134(4)	3 157(4)	2 701(3)
S(3)	3 622(4)	4 451(4)	2 706(3)
S(4)	1 882(4)	3 134(4)	739(3)
S(5)	4 341(4)	1 303(4)	1 328(3)
S(6)	4 119(4)	856(4)	3 596(3)
N	1 309(11)	183(11)	1 943(8)
N(1)	−1 214(15)	3 113(13)	4 763(12)
N(2)	3 342(13)	5 752(12)	827(10)
N(3)	6 443(13)	132(13)	2 419(10)
C(1)	−190(15)	2 800(15)	4 040(12)
C(2)	2 989(15)	4 605(15)	1 386(12)
C(3)	5 168(15)	665(15)	2 451(11)
C(11)	−2 442(17)	3 913(20)	4 359(15)
C(12)	−1 198(22)	2 734(20)	5 925(14)
C(21)	4 333(18)	7 017(17)	1 366(14)
C(22)	2 732(20)	5 848(17)	−289(13)
C(31)	7 316(15)	45(18)	1 387(12)
C(32)	7 103(18)	−432(18)	3 412(13)

in the intensities of four standard reflections occurred during the course of data collection. 2 154 Independent reflections (with $5 < 2\theta < 100°$) were measured, of which 1 907 had significant intensities. The structure was solved by the heavy-atom technique, and refined by least-squares using the '*X*-Ray '70' program system.[9] With isotropic temperature factors for all atoms, the *R* factor was reduced to 0.125. Correction of the data for absorption followed by further cycles of isotropic refinement gave an *R* factor of 0.112. Continuation of the least-squares refinement with anisotropic temperature factors for all atoms and a weighting scheme of the type $w = 1$ for $F < F^*$ and $w = F^*/F$ for $F > F^*$ gave a final weighted *R* factor of 0.068.. The value of F^* which gave most satisfactory agreement analysis was 24 on an absolute scale. Methyl-hydrogen atoms were not included in the structure refinement. The final atomic positional parameters are given in Table 2. Scattering factors for neutral atoms were taken from ref. 10, with those for Mo and S corrected for the real part of the anomalous dispersion.

Calculations for both structure analyses were made on the CDC7600 computer at the University of London. Tables of the anisotropic temperature factors and lists of $|F_o|$ and F_c for the two structures have been deposited as Supplementary Publication No. SUP 22527 (26 pp.).†

RESULTS AND DISCUSSION

These structure analyses have confirmed that the two complexes are monomeric and possess slightly distorted forms of the now familiar[11] MXL_3 (L = chelate) pentagonal-bipyramidal molecular geometry with the X ligand axial and one of the chelating ligands spanning one axial and one equatorial site. A molecule of the nitride is shown in Figure 1(*a*) and of the thionitrosyl in Figure 1(*b*).[12] The atomic numbering schemes have been chosen so that structurally equivalent atoms in each complex are similarly labelled. Bond lengths and angles

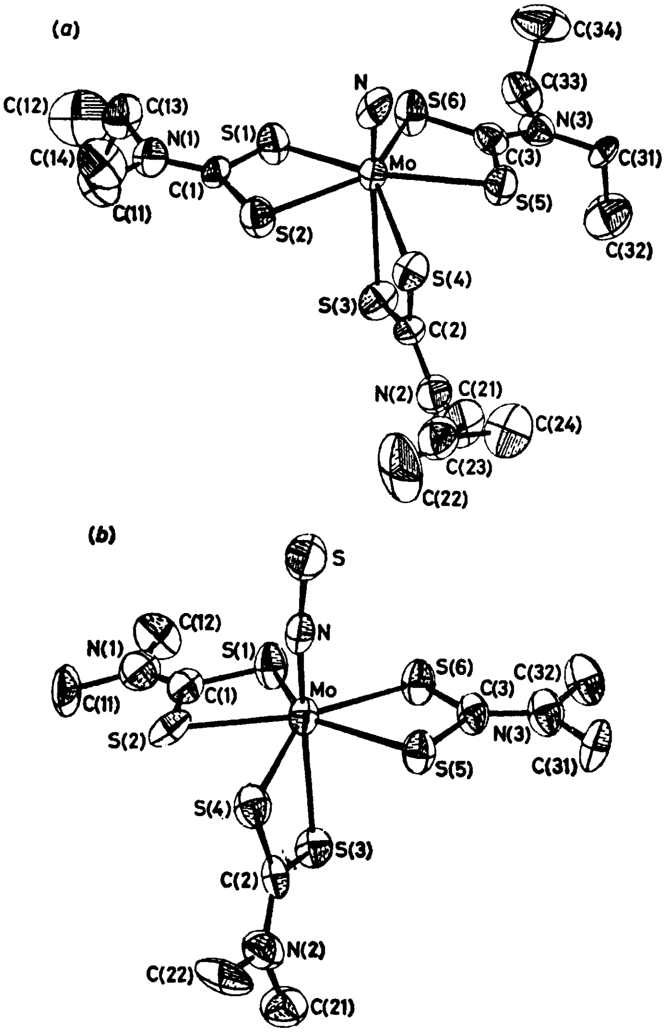

FIGURE 1 The molecular structures of (*a*) $[MoN(S_2CNEt_2)_3]$ and (*b*) $[Mo(NS)(S_2CNMe_2)_3]$

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

involving the co-ordination spheres in the two molecules are given in Table 3. Values for the S_2CN_2 ligands have been deposited in the Supplementary Publication. Results of various calculations for least-squares planes are given in Table 4.

TABLE 3

Selected bond lengths and angles in $[MoN(S_2CNEt_2)_3]$ and $[Mo(NS)(S_2CNMe_2)_3]$

	Nitride	Thionitrosyl
(*a*) Bond lengths (Å)		
Mo–S(1)	2.515(3)	2.515(4)
Mo–S(2)	2.538(3)	2.530(4)
Mo–S(3)	2.852(3)	2.602(4)
Mo–S(4)	2.509(3)	2.488(4)
Mo–S(5)	2.537(3)	2.515(4)
Mo–S(6)	2.512(3)	2.527(4)
Mo–N	1.641(9)	1.738(11)
N–S		1.592(11)
(*b*) Bond angles (°)		
S(1)–Mo–S(2)	68.0(1)	67.6(1)
S(3)–Mo–S(4)	66.1(4)	69.8(1)
S(5)–Mo–S(6)	67.6(1)	67.9(1)
S(1)–Mo–S(6)	71.5(1)	73.3(1)
S(2)–Mo–S(4)	75.5(1)	74.7(1)
S(4)–Mo–S(5)	75.1(1)	75.3(1)
N–Mo–S(1)	102.1(3)	98.1(4)
N–Mo–S(2)	91.2(3)	98.2(3)
N–Mo–S(3)	164.1(3)	165.7(3)
N–Mo–S(4)	98.0(3)	98.0(3)
N–Mo–S(5)	96.7(3)	87.0(3)
N–Mo–S(6)	97.8(3)	93.8(3)
S–N–Mo		172.0(7)

TABLE 4

Core atom deviations (Å) from the least-squares planes

	Plane				
Atom	1	2	3	4	5
Mo	0.30	0.23	0.04 *	−0.02 *	−0.01 *
	(−0.22)	(−0.15)	(−0.01)	(−0.00)	(0.01)
S(1)	−0.17 *	−0.12 *	−0.07 *	1.41	−0.60
	(0.00)	(−0.04)	(0.01)	(1.53)	(0.09)
S(2)	0.19 *	0.07 *	−0.07 *	2.45	−0.45
	(−0.08)	(0.02)	(0.01)	(2.44)	(0.32)
S(3)	−2.44	−2.55	−2.77	0.04 *	−2.75
	(2.32)	(2.41)	(2.56)	(0.00)	(2.56)
S(4)	−0.13 *	−0.36	−0.76	0.04 *	−0.53
	(0.12)	(0.33)	(0.47)	(0.00)	(0.58)
S(5)	0.04 *	−0.07 *	−0.40	−2.44	0.01 *
	(−0.13)	(−0.02)	(0.27)	(−2.43)	(0.01)
S(6)	0.08 *	0.12 *	0.07	−1.52	0.01 *
	(0.08)	(0.04)	(0.28)	(−1.47)	(0.01)
N	1.93	1.85	1.64	−0.04	1.60
	(−1.95)	(−1.87)	(−1.72)	(−0.23)	(−1.74)

Atoms defining the planes are indicated with asterisks. For planes 3—5 the carbon atoms attached to the two sulphur atoms were also included in the definition of the planes.

Having identified the basic molecular geometry for each complex, the two main points of interest are the Mo–X bonding and the nature of the distortions of the $MoNS_6$ pentagonal-bipyramidal core.

In the nitride, the Mo–N bond length of 1.64 Å lies at the lower end of the range for ' $M\overset{\leftarrow}{=}O$ ' and ' M≡N ' bond lengths for second- and third-row transition metals. In particular it compares with the values of 1.603(9), 1.614(13), and 1.656(8) Å found for $[ReNCl_2(PPh_3)_2]$,[13] $[OsNCl_5]^{2-}$,[14] and $[ReN(S_2CNEt_2)_2]$ [15] respectively, all of which have co-ordination number less than seven. These M≡N bond lengths may be especially compared with the $M\overset{\leftarrow}{=}O$ lengths of 1.74(1) and 1.684(6) Å in the two species $[NbO(S_2CNEt_2)_3]$ [16] and $[MoO(S_2CNEt_2)_3]^+$,[17] both of which are isoelectronic with our nitride (the niobium complex also being crystallographically isostructural). This relationship is discussed further below, but for the moment we can consider our result to be in keeping with the simple picture of a strong Mo≡N triple bond with good π overlap.

In the thionitrosyl complex the Mo–N bond length (1.74 Å) is longer than in the nitride, as would be expected especially if the thionitrosyl ligand behaves in a manner analogous to the $[NO]^+$ ligand, as the almost linear Mo–N–S system implies. This possibility can be usefully explored by comparing the thionitrosyl complex with the analogous molecule $[Mo(NO)(S_2CNBu^n{}_2)_3]$.[18] In fact the Mo–N distance and Mo–N–X angle in this molecule (1.73 Å and 173.2° respectively) are equal, within the limits of experimental error, to the corresponding values in the thionitrosyl. Thus, it would seem that the NS and NO ligands are quite similar, and indeed the N–S distance (1.59 Å) is consistent with a considerable degree of Mo→NS π-back bonding, since it is greater than that in the free ligand [19] or the value calculated from sums of covalent radii for an N=S double bond, or even values found in a variety of compounds purporting to contain N=S partially multiple bonds.[20]

The geometry of the pentagonal-bipyramidal $MoNS_6$ cores and distortions from regularity can be discussed in terms of four particular features. These can be summarised as: (*a*) repulsion of equatorial bonds by the high electron density in the Mo–N multiple bonds; (*b*) puckering of the S_5 equatorial girdle to accommodate the S · · · S interatomic repulsion; (*c*) the effect of the restricted bite of the dithiocarbamate ligand spanning the axial and equatorial sites; and (*d*) the relative strengths of the $Mo–S_{eq.}$ and $Mo–S_{ax.}$ bonds. Clearly the structures finally adopted will reflect compromises between all of these and none can really be discussed separately. For instance, the configuration of the five equatorial sulphur atoms will be particularly influenced by the first three effects. The $N–Mo–S_{eq.}$ angles in the nitride complex lie in the range 91—102° and in the thionitrosyl, 87—98°. They do not therefore all correspond to a significant bending down of the Mo–S bonds away from the MoN multiple bond. One obvious way of viewing the overall distortion would be to use the atoms C(1), S(2), S(5), and S(6) from the equatorially chelating dithiocarbamate ligands as a reference set. The N–Mo–S angles relating to these are 91.2—102.1° in the nitride and 87.0—98.2° in the thionitrosyl complex. The corresponding angles to S(4), the equatorial sulphur atom of the equatorial/axial dithiocarbamate, are 98.4 and 98.0°. This is not the largest angle in the nitride and in the thionitrosyl complex it is only just the largest; this is surprising since a large distortion here would help the restricted bite of this ligand and the equatorial crowding. In fact, for both compounds the deviation of S(3) from the line of the Mo–N bond is greater than the deviation of the N–Mo–S(4) angle from 90°. Thus, although the relief of the S · · · S contacts in the equatorial girdle results in its puckering, the metal–sulphur bonds seem to be strong and constrained near to the equatorial plane. However, it must be noted that, overall, the metal atom does lie above the plane of the equatorial sulphur atoms as can be seen in Table 4, where data for various least-squares planes are presented. Results similar to those discussed above are also found in the structures of [Mo(NO)($S_2CNBu^n{}_2)_3$],[18] [NbO($S_2CNEt_2)_3$],[16] and [MoO($S_2CNEt_2)_3$].[17] The final distortion, which to us is the most intriguing, concerns the length of the axial Mo–S bond compared to the equatorial values.

Lengthening of a single bond *trans* to a multiple bond in six- and seven-co-ordinated species is well known[11] and its occurrence could be explained in terms of two effects. Bright and Ibers[14] have suggested that the lengthening of the axial bond has its origin mainly in the steric repulsions set up as the equatorially bonded atoms are pushed down by the electron density of the multiple bond. An alternative explanation is that the origin of this *trans* influence could be mainly electronic. The two compounds described here together with the three other species already mentioned provide a useful opportunity to further investigate this feature. For convenience, some relevant parameters derived from the five structures are presented in Table 5 and a number of interesting features are apparent. First, we see that the lengthening of the *trans* Mo–S bond in the nitride, which has the shortest, and thus presumably strongest, M–X bond, is much greater than in any of the other species, but the bending down of the equatorial ligands is not greater and in two cases less. Although the bending down of the equatorial sulphur atoms will contribute to the repulsion of the axial sulphur atoms, there is no indication that it is the main cause. The $S_{eq.} \cdots S_{ax.}$ contacts in the nitride are larger than in any of the other compounds and are in fact equal to double the accepted value for the van der Waals radius of sulphur (1.85 Å). Examination of the data for the other compounds shows that much shorter contacts can be accommodated and so the most logical explanation is that, in the nitride complex, the *trans* Mo–S bond is so weakened that it can easily be 'stretched' to the normal van der Waals distance by the $S_{eq.} \cdots S_{ax.}$ contacts. The exact cause of this weakening is obscure. Since there is a reasonably good correlation between the lengthening of the M–S bond and the shortness of the M–X bond, it may be explained in terms of a kind of *trans* influence, where the increasing strength of the σ component in the M–X bonding simply reduces the potential for bonding of the metal σ orbital *trans* to it.

TABLE 5

Data relating to the lengthening of the M · · · S bonds *trans* to an M–X multiple bond in five [MX($S_2CNR_2)_3$] pentagonal-bipyramidal structures

Parameter	M = Mo, X = N [a]	M = Mo, X = NS [a]	M = Mo, X = NO [b]	M = Nb, X = O [c]	M = Mo, X = O [d]
M–$S_{eq.}$ (mean)/Å	2.522	2.515	2.509	2.575	2.486
M–$S_{ax.}$/Å	2.852	2.602	2.568	2.753	2.630
$\frac{M - S_{ax.}}{M - S_{eq.}(mean)}$	1.13	1.034	1.023	1.069	1.057
Mo–$X_{ax.}$/Å	1.641	1.738	1.731	1.739	1.684
X–M–$S_{eq.}$/°	91.0—102.1	87.0—98.2	90.2—97.7	91.1—106.1	91.0—106.9
Deviation of M out of S_5 equatorial plane towards X/Å	0.31	0.22	0.19	0.32	0.34
$S_{eq.} - S_{eq.}$ mean non-bonded contact/Å	3.035	3.037	3.140	3.106	2.963
$S_{eq.} - S_{ax.}$ mean non-bonded contact/Å	3.727	3.591	3.605	3.680	3.480
$\frac{S_{eq.} - S_{ax.}(mean)}{S_{eq.} - S_{eq.}(mean)}$	1.227	1.182	1.148	1.185	1.174
S–S mean bite of eq. ligands/Å	2.818	2.812	2.814	2.868	2.809
S–S bite of ax./eq. ligand/Å	2.937	2.912	2.933	2.925	2.902

[a] This work. [b] Ref. 18. [c] Ref. 16. [d] Ref. 17.

One other intriguing feature of these structures concerns the geometry of the dithiocarbamate ligands. As expected, the S · · · S bite of the axial/equatorial ligand is greater than for the equatorial/equatorial ligands. Rather unexpected, however, is the fact that the grossly asymmetric bonding of the former ligand does not seem to produce any equivalent asymmetry in the S–C bonds as found, for example, in As($S_2CNR_2)_3$.[21] Whilst the S–C distance for the axially bonded sulphur atom in the nitride complex is shorter than that for the equatorially bonded sulphur (1.69 *vs.* 1.74 Å) the difference is only 4σ and similar differences are found in the nitride and also in the other species, for ligands where both sulphur atoms are bonded equatorially.

In all other aspects, the dithiocarbamate ligand geometries must be considered normal, that is all apparent differences fall within the limits of experimental error. The ligands generally form planar chelate rings with the metal atom, with fold angles at the S · · · S vector in the range 0.1—2.6° for the thionitrosyl but 2.4—13.5° for the nitride complex. Whilst this last value might be due to the effect of intermolecular packing forces (the ligand is involved in two S · · · C contacts <3.7 Å, two of the shortest in the structure), it is some indication of the 'flexibility' (at the sulphur atoms) in the metal–dithiocarbamate bonding.

The packing of the molecules in the two structures can be seen in Figure 2(*a*) and (*b*).[22] The shortest inter-

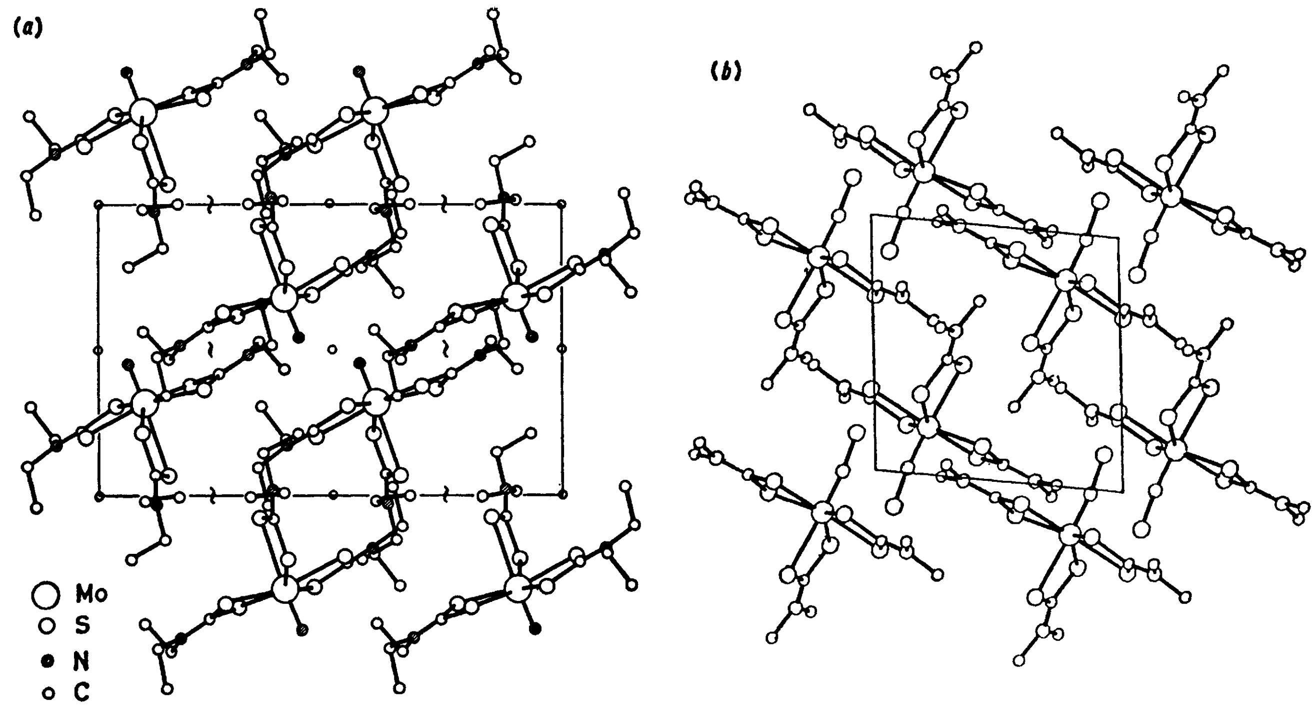

FIGURE 2 Packing diagrams of (*a*) [$MoN(S_2CNEt_2)_3$] molecules viewed along the *b* axis and (*b*) [$Mo(NS)(S_2CNMe_2)_3$] viewed along the *c* axis

molecular contacts are S · · · C and N · · · C *ca.* 3.4 Å and thus the structures are, in general, held together only by weak van der Waals forces.

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REFERENCES

[1] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 517.
[2] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.
[3] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.
[4] SHELX Crystallographic Calculation Program, G. M. Sheldrick, University of Cambridge.
[5] P. A. Doyle and P. S. Turner, *Acta Cryst.*, 1968, **A24**, 390.
[6] D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.
[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.
[8] R. F. Stewart, *J. Chem. Phys.*, 1965, **42**, 3175.
[9] 'X-Ray '70' System of Programs, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin, University of Maryland.
[10] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1962, vol. 3.
[11] M. G. B. Drew, *Progr. Inorg. Chem.*, 1977, **23**, 67.
[12] ORTEP, Thermal Ellipsoid Plotting Program, C. K. Johnson, Oak Ridge National Laboratory, Report ORNL 3794, 1965.
[13] R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 204.
[14] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 709.
[15] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 1079.
[16] J. C. Dewan, D. L. Kepert, C. L. Raston, D. Taylor, A. H. White, and E. N. Malsen, *J.C.S. Dalton*, 1973, 2082.
[17] J. Dirand, L. Ricard, and R. Weiss, *Transition Metal Chem.*, 1975, **1**, 2.
[18] T. F. Brennan and I. Bernal, *Inorg. Chim. Acta*, 1973, **7**, 283.
[19] *Special Publ.*, The Chemical Society, London, 1965, no. 18.
[20] See, for example, 'Molecular Structures by Diffraction Methods,' vol. 2, *Specialist Periodical Reports*, The Chemical Society, London, 1974.
[21] C. L. Ralston and A. H. White, *J.C.S. Dalton*, 1975, 2425.
[22] PLUTO, A program for Plotting Molecules and Crystal Structures, Dr. W. D. S. Motherwell, University of Cambridge.