The Crystal Structure of a Heptaco-ordinated Molybdenum Compound, Mononitrosylmolybdenum Tris-(*NN*-di-n-butyldithiocarbamate)

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Summary The crystal structure of the title compound has been determined from three-dimensional *X*-ray diffraction data collected by precession methods; the co-ordination around the central Mo atom is pentagonal bipyramidal.

MUETTERTIES AND WRIGHT[1] have stated that three isomers can exist for a heptaco-ordinated complex of composition chel$_3$MX, if the complex acquires pentagonal bipyramidal geometry. However, there seem to be no clear-cut factors which lead specifically to the formation of any one of the three isomers with this geometry. The structure of a complex of this compositional class, ONRu(S$_2$CNR$_2$)$_3$ (R = Et), has been reported;[2] the ruthenium ion is six-fold co-ordinated by five sulphurs and the nitrosyl nitrogen. Johnson and Al-Obaidi[3] have reported the syntheses of the compounds ONMo(S$_2$CNR$_2$)$_3$, with R = Me, Et, Pr^n, Bu^n. Physical measurements, particularly n.m.r. spectroscopy, suggested a pentagonal bipyramidal configuration of the ligands around the Mo atom, with the nitrosyl nitrogen occupying an axial position. We now report the structure of mononitrosylmolybdenum tris-(*NN*-di-n-butyldithiocarbamate) (Figure), and thus confirm the predicitions of Johnson and Al-Obaidi.[3]

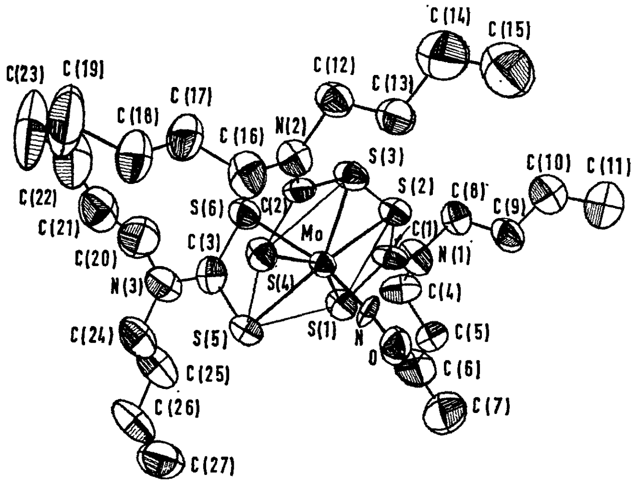


FIGURE. *The pentagonal base of the bipyramid is defined by sulphur atoms* 1—5. *The light line joining these atoms is illustrative only and no bonding is implied, even though these atoms are closer to one another than van der Waals contacts* (*see text*).

Crystal data. Yellow rhombs which crystallize in the monoclinic system: $a = 15{\cdot}078$ (9), $b = 27{\cdot}590$ (7), $c = 9{\cdot}502$ (4) Å, $\beta = 92{\cdot}33$ (8)°; $V = 3949$; $D_m = 1{\cdot}19$ (2); $D_c = 1{\cdot}23$ g.cm.$^{-3}$, for $Z = 4$; space group: $P2_1/c$, from systematic absences and refinement. Data from precession photographs were read with a Joyce-Loebl scanning microdensitometer (λ = Mo-K_α; four differently timed exposures for each layer; all reflections appearing on each film were scanned and recorded). The structure was solved by standard Patterson methods and Fourier and difference-Fourier maps revealed the positions of the missing light atoms. The co-ordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares methods to the present discrepancy factor of $R_F = 8{\cdot}1\%$, using 2184 non-zero, independent reflections. The relevant details of the bonding in the molecules are summarized in the Table.

The distances between adjacent sulphur atoms in the equatorial plane are approximately the same for all pairs of contacts, irrespective of whether the atoms in question belong to the same dithiocarbamate ligand or not. In either case, the S $\cdots\cdot$ S distances are shorter than van der Waals contacts (about 3·4 Å).[4] The pentagonal base is slightly puckered at the S(5) position due to the rigid "bite" of the ligand. This is the ligand which spans an axial and an equatorial position and, therefore, S(5) and S(6) occupy positions which are compromises between reasonable Mo–S distances, ligand constraints, *etc.* The interatomic distances and angles given in the Table demonstrate the uniqueness of this ligand; *e.g.* the S–C–S and H$_2$C–N–CH$_2$ angles are larger for this ligand than for the other two; concomitantly, the C=N bond is longer (1·32 *vs* 1·28, and 1·29). Atoms S(1), S(2), S(3), and S(4) lie in a very good least-squares plane, above which lies the Mo atom. The displacement of the Mo from this plane is approximately 0·10 Å in the direction of the NO ligand. The short C=N distances (the average C=N distance is 1·296 Å, *vide supra*) are close to double

Interatomic distances (Å)*

Mo–S(1)	= 2·528	S(5)–C(3)	= 1·743
Mo–S(2)	= 2·507	S(6)–C(3)	= 1·686
Mo–S(3)	= 2·529	C(1)–N(1)	= 1·286
Mo–S(4)	= 2·513	C(2)–N(2)	= 1·279
Mo–S(5)	= 2·463	C(3)–N(3)	= 1·324
Mo–S(6)	= 2·568	S(1)–S(2)	= 2·809
Mo–N	= 1·731	S(2)–S(3)	= 2·950
N–O	= 1·154	S(3)–S(4)	= 2·816
S(1)–C(1)	= 1·707	S(4)–S(5)	= 3·059
S(2)–C(1)	= 1·737	S(1)–S(5)	= 3·080
S(3)–C(2)	= 1·679	C–N	= 1·499†
S(4)–C(2)	= 1·750	C–C	= 1·534‡

Selected angles

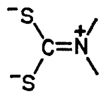
Mo–N–O	= 173·2°	S(5)–C(3)–S(6)	= 115·4
N–Mo–S(6)	= 167·9	C(1)–N(1)–C(5)	= 115·2
S(1)–C(1)–S(2)	= 109·3	C(12)–N(2)–C(16)	= 117·2
S(3)–C(2)–S(4)	= 110·4	C(20)–N(3)–C(24)	= 120·9

† Average value of the H_2C–N–CH_2 C–N bonds.

‡ Average value of the aliphatic C–C bond.

* Estimated standard deviations on bond lengths at this stage of the refinement: Mo–S = 0·003 Å, S–S = 0·005 Å, others = 0·010 Å.

bonds (1·24 Å),[5] indicating that the contribution of the canonical form :



is very high for all three dithiocarbamate ligands. The nitrosyl ligand is strongly bound to the Mo atom as evidenced by the short Mo–N distance of 1·731 Å; the corresponding distance in the Ru complex[2] was given as 1·72 Å. The N–O distance and Mo–N–O angle in the Mo compound are 1·154 Å and 173·2°, respectively, while for the Ru compound Vaciago *et al.*[2] found values of 1·17 Å and 172° for these parameters.

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