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The Crystal and Molecular Structure of a Heptacoordinated Molybdenum Compound, Mononitrosylmolybdenum Tris(NN-di-n-butyldithiocarbamate)

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The crystal structure of tris(N,N-di-n-butyldithiocarbamato)molybdenum(II) nitrosyl has been determined from three dimensional X-ray data collected by precession methods and measured with a scanning microdensitometer. The material crystallizes in the space group $P2_1/c$ with four molecules per unit cell, $a = 15.078(9)$, $b = 27.590(7)$, $c = 9.502(4)$ Å, and $\beta = 92.33(8)^\circ$. Anisotropic refinement of all non-hydrogen atoms by block diagonal least-squares methods led to final residuals of $R_1 = 8.1\%$ and $R_2 = 10.3$ per cent for 2185 non-zero reflections for which $F \geqslant 2\sigma$. The structure consists of discrete monomers, each composed of three bidentate dithiocarbamato ligands and one nitrosyl group. The donor atoms surrounding the central metal are arranged in a pentagonal bipyramidal configuration which is somewhat distorted due to the small and rigid bite of the dithiocarbamato ligands, two of which occupy four of the basal plane positions while the third one spans an axial to equatorial pair of sites. The nitrosyl ligand coordinates through the nitrogen and ocupiecs the second axial position. The Mo-N and N-O distances, 1.731(8) and 1.154(9) Å respectiveiy, are relatively short and the Mo-N-O angle is slightly bent (173.2 (7)°). Adjacent S...S contacts in the equatorial plane are quite short, ranging from 2.809 to 3.080 Å, suggesting sizable non-bonded interactions. The molecule has the following mean bond lengths: Mo-S, 2.518; S-C, 1.715; C-N, 1.296 Å. The three S_2CNC_2 fragments are planar and the canonical form $(-)S_2CN(+)R_2$ makes an important contribution to the electronic structure of the dithiocarbamato ligands. There are weak intermolecular interactions between the nitrosyl oxygen atoms and alkyl hydrogen atoms.

Introduction

In 1966 Domenicano, *et al.*[1] reported the structure of $ONRu(S_2CNEt_2)_3$, which they found to contain a six-fold coordinated Ru atom and whose ligands were the nitrogen of the NO, four sulfurs of a pair of bidentate dithiocarbamate ligands and one sulfur of a third, monodentate, dithiocarbamate moiety. In 1968 Johnson and Al-Obaidi[2] reported the syntheses of the family of Mo derivatives $ONMo(S_2CNR_2)_3$, with R = Me, Et, Pr^n and Bu^n. Later Johnson, *et al.*[3] reported detailed spectral studies which led them to postulate a pentagonal bipyramidal configuration. For the complex in which the nitrosyl ligand occupies an axial position.

In view of the paucity of data on heptacoordination[4] it seemed interesting to determine the detailed geometrical characteristics of he molybdenum derivatives and to obtain accurate bonding parameters for the molecule. We have given preliminary reports[5,6] of the shape and some of the bonding characteristics of the di-Bu^n derivative; here, we give a detailed account of a three-dimensional X-ray study carried out at these Laboratories.

Experimental Section

Of the four derivatives prepared by Johnson and Al-Obaidi,[2,3] the only one which readily yields crystals of good crystallographic quality is the di-Bu^n salt. The substance crystallizes in the form of well developed yellow-orange rhombs which are stable to air and in the X-ray beam.

Crystal Data. The crystals used in this study were obtained by slow evaporation of a methanol solution and the one chosen for data collection measured 0.50×0.40×0.50 mm. Precession and cone axis photographs indicated that the crystals are monoclinic with the following unit cell dimensions:[7] a = 15.078 (9) Å, b = 27.590(7) Å, c = 9.502(4) Å, and β = 92.33(8), and a unit cell volume of 4001 Å^3. Precession photographs showed the following systematic absences: $h0\ell$: $\ell \neq 2n$ and $0k0$: $k \neq 2n$, which are consistent with the space group $P2_1/c$, whose fourfold set of general positions is $\pm(x,y,z;\ x,\tfrac{1}{2}-y,\ \tfrac{1}{2}+z)$. The measured density of 1.21 gm/cm^3 was obtained by flotation in an aqueous solution of zinc

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[1] A. Domenicano, A. Vaciago, L. Zambonelli, P.L. Loader, and L. Venanzi, *Chem. Comm.*, 476 (1966).

[2] B.F.G. Johnson and K.H. Al-Obaidi, *Chem. Comm.*, 876 (1968).

[3] B.F.G. Johnson, K.H. Al-Obaidi, and J.A. McCleverty, *J. Chem. Soc.*, (A), 1668 (1969).

[4] E.L. Muetterties and C.M. Wright, *Quart. Rev.*, *21*, 109 (1967).

[5] T.F. Brennan and I. Bernal, Abstract XIV-51, Eighth International Congress of Crystallography, Stony Brook, New York, 1969.

[6] T.F. Brennan and I. Bernal, *Chem. Comm.*, 138 (1970).

[7] Each cell parameter was obtained from averaging at least twenty independent observations taken from calibrated procession photographs. The values of the standard deviations quoted in the text are standard deviations from the mean.

chloride. The calculated density of 1.23 gm/cc for Z = 4 molecules per unit cell was in reasonable agreement with the observed density. The linear absorption coefficient was calculated[8a] to be 6.488 cm^{-1} for Mo radiation, with a mean μR value of 0.30.

Intensity Measurements

The X-ray intensities were measured from precession photographs using a Joyce-Loebl double-beam scanning microdensitometer. Each layer of precession data was exposed four different lengths of time, in such a way that all reflections available in that layer appeared in the region of linear response of the densitometer. Every single reflection appearing in each exposure was recorded; thus, the data was collected over both asymmetric sets and many reflections were measured several times in each layer. The following layers of data were recorded: $0k\ell$ through $3k\ell$; $\bar{h}k0$ through hk2; h,k,h and h,k2h; 2h,k,h; 3h, k,h; $\bar{h}$,k,h and $\bar{h}$,k,2h. The data were corrected for Lorentz and polarization factors and suitably averaged, when necessary. No absorption correction was made since the absorption coefficient is very small and the crystal was almost equi-dimensional. The observed structure amplitudes were placed on a common scale using the method of Hamilton, Rollet and Sparks[9] and a scale and overall temperature factor were computed using a Wilson plot.[10]

Solution and Refinement of the Structure

The structure was solved by the heavy-atom method using standard three-dimensional Patterson techniques. The position of the molybdenum atom was evident from the Harker lines and sections and the position of the six sulfur atoms were obtained from six vectors of length approximately 2.5 Å, which is the expected Mo-S distance. A series of observed Fourier and difference Fourier maps revealed the positions of the remaining atoms fairly quickly. When trial coordinates for all the atoms in the structure tropic thermal parameters gave a residual of R = 0.17. At this point, because of the size of the problem (39 non-hydrogen atoms) refinement with anisotropic thermal parameters had to be carried out using block diagonal methods. At the end of the refinement (when the values of the shifts in parameters were about 0.1 of the value of the estimated standard deviation in that same quantity) the residuals were $R_1 =$ 8.1% and R_2 = 10.3%. The function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes respectively and $w = 4F_o^2/\sigma^2(F_o^2)$. The weights used were derived from an analysis of variance of the data using program NANOVA. The scattering factor tables used are those of Cromer and Waber[10] and the anomalous dispersion corrections for Mo and S used were taken from the International Tables.[8b] At the end of the refinement the goodness of fit, $[\Sigma w\Delta^2/(NO\text{-}NV)]^{1/2}$ was 0.80, where NO is the number of observations, NV is the number of variables and Δ is the difference between the observed and calculated amplitudes. Table I is a list of the observed and calculated structure factors.

The programs used were: LPFPRE (a local version of Baur's program for the calculation of Lorentz and polairzation effects for precession data); INRSCALE (local version of the Hamilton, Rollet and Sparks[9] scaling program); XDATA (Brookhaven's version of the Wilson[10] plot calculation) JIMDAP (a Brookhaven modification of the Zalkin Fourier summation program, as modified by Ibers); LINUS (a local version of the Busing, Martin and Levy ORFLS least-squares program[11]); ORFFE (the function and error program[12]); ORTEP (Johnson's[13] molecular plotting program).

Description of the Structure and Discussion

The structure of $(Bu_2dtc)_3MoNo$ consists of discrete monomeric molecules, each composed of three bidentate Bu_2dtc ligands and a nitrosyl group with the donor atoms arranged in a pentagonal bipyramidal configuration around the molybdenum ion. The three Bu_2dtc ligands are coordinated to the molybdenum through both sulfur atoms, with two ligands in the equatorial plane and the third spanning an equatorial and an axial position. The nitrosyl group coordinates through the nitrogen and occupies the other axial position. If the outer $-CH_2-CH_2-CH_3$ fragments are

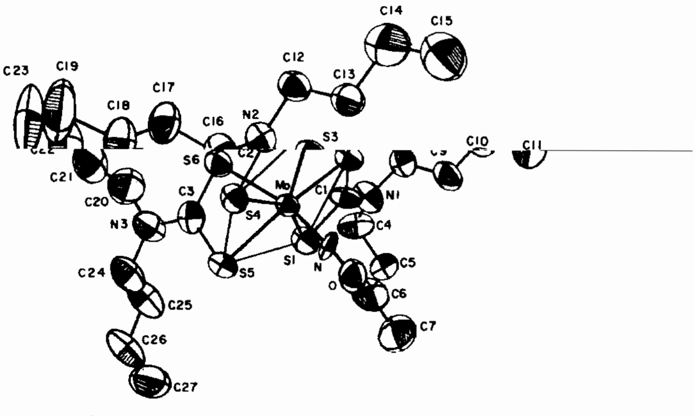

Figure 1. The molecular structure of the ONMO (n-butdtc)$_3$ molecule showing the labelling of the atoms used in this study. The thermal parameters used in this Figure are the final, refined values.

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(8) (a) The value of the linear absorption coefficient given is the sum of the individual atomic contributions, which were calculated from the values listed in the « International Tables for X-ray Crystallography », Vol. III, The Kynoch Press, Birmingham, England, 1967, p. 162. (b) p. 215.

(9) W.C. Hamilton, J.S. Rollet, and R.A. Sparks, *Acta Cryst., 18,* 129 (1965).

(10) A.J. Wilson, *Nature, 150,* 152 (1942).

(11) W.R. Busing, K.O. Martin, and H. Levy, «ORFLS, A Fortran Crystallographic Least Squares Program», ORNL-TM-305, Oak Ridge National Laboratory (1962).

(12) W.R. Busing, K.O. Martin, and H. Levy, «ORFFE, A Fortran Crystallographic Function and Error Program», ORNL-TM-306, Oak Ridge National Laboratory (1964).

(13) C.K. Johnson, «ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations», ORNL-3794-Revised, Oak Ridge National Laboratory (1965).

Table I. Observed and Final Calculated Structure Amplitudes.

[illegible]

Table II. Final Parameters[a] for Tris(N,N-di-n-butydithiocarbamate) Molybdenum(II) Nitrosyl.

	Fraction Coordinates			Anisotropic Temperature Factors					
Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	—2175(1)	0825(0)	2621(1)	0041(1)	0010(0)	0079(1)	—0001(0)	0011(1)	0000(0)
O	—0808(8)	0266(4)	4070(13)	0052(6)	0022(2)	0144(16)	0003(3)	0018(10)	0010(5)
N	—1324(7)	0491(4)	3422(12)	0024(5)	0014(2)	0093(14)	0010(3)	—0000(9)	0001(4)
S1	—2661(3)	1103(1)	5005(4)	0050(2)	0014(1)	0107(5)	—0003(1)	0015(3)	—0006(1)
S2	—1528(3)	1633(1)	3303(4)	0068(2)	0012(1)	0104(5)	—0003(1)	0032(3)	—0000(1)
S3	—1297(3)	1135(1)	0595(4)	0064(2)	0012(1)	0099(5)	—0004(1)	0016(3)	—0007(1)
S4	—2279(3)	0266(1)	0531(4)	0070(3)	0014(1)	0125(5)	—0005(1)	0033(3)	—0013(1)
S5	—3405(3)	0273(1)	3139(5)	0058(2)	0013(1)	0134(6)	—0006(1)	0007(4)	0004(1)
S6	—3652(3)	1191(1)	1687(5)	0057(2)	0017(1)	0138(6)	—0001(1)	0011(4)	0010(2)
C1	—2034(10)	1617(4)	4913(14)	0051(9)	0008(2)	0107(17)	0002(3)	0005(12)	0005(5)
N1	—1886(9)	1932(4)	5891(13)	0049(7)	0015(2)	0090(15)	—0004(3)	—0005(10)	—0008(4)
C4	—2286(13)	1893(6)	7293(16)	0071(12)	0023(3)	0125(19)	—0003(5)	0034(15)	—0018(6)
C5	—3153(14)	2175(7)	7317(20)	0069(12)	0023(3)	0174(25)	0005(5)	0034(18)	—0007(7)
C6	—3532(14)	2119(7)	8734(24)	0067(11)	0027(3)	0171(32)	0004(5)	0031(19)	—0010(8)
C7	—4435(19)	2386(12)	8882(35)	0091(17)	0057(7)	0365(61)	0026(9)	0092(31)	0014(18)
C8	—1293(11)	2362(4)	5707(18)	0068(9)	0013(2)	0143(24)	—0005(3)	0028(14)	—0009(5)
C9	—0362(12)	2245(5)	6133(22)	0056(9)	0015(2)	0191(32)	—0002(4)	—0006(16)	0009(7)
C10	0268(19)	2673(8)	5727(33)	0102(16)	0025(4)	0372(59)	—0002(6)	—0011(28)	0001(11)
C11	1180(20)	2566(9)	6091(31)	0103(20)	0032(5)	0328(51)	—0011(8)	0003(30)	0002(13)
C2	—1554(13)	0640(5)	—0367(16)	0100(12)	0008(2)	0108(20)	—0004(4)	0047(16)	—0007(5)
N2	—1291(11)	0540(5)	—1596(15)	0078(9)	0023(3)	0140(19)	—0011(4)	0015(14)	—0007(6)
C12	—0626(13)	0870(6)	—2280(16)	0064(12)	0022(3)	0091(18)	—0002(5)	0017(15)	0004(6)
C13	0330(15)	0747(7)	—1786(21)	0075(13)	0021(3)	0178(27)	—0007(5)	0046(19)	0001(8)
C14	0974(19)	1084(9)	—2525(34)	0095(17)	0029(4)	0441(62)	—0001(7)	0053(29)	0018(14)
C15	1964(21)	1010(12)	—2091(45)	0094(20)	0039(6)	0715(110)	0006(9)	0033(41)	0028(21)
C16	—1718(15)	0141(6)	—2512(21)	0116(14)	0018(3)	0202(29)	0003(5)	—0012(20)	0012(7)
C17	—1137(14)	—0319(6)	—2328(27)	0069(11)	0017(3)	0303(42)	0005(4)	0014(20)	0012(9)
C18	—1597(19)	—0745(6)	—3254(31)	0140(20)	0016(3)	0486(55)	—0011(5)	0074(30)	—0045(10)
C19	—1012(23)	—1179(10)	—2948(38)	0142(22)	0028(6)	0489(61)	0008(4)	0045(28)	—0030(15)
C3	—4131(13)	0689(6)	2325(17)	0057(11)	0021(3)	0086(20)	0000(4)	0007(15)	—0004(6)
N3	—4993(10)	0596(6)	2304(18)	0068(8)	0022(3)	0189(26)	—0009(4)	—0013(13)	0017(7)
C20	—5367(13)	0148(7)	2891(19)	0065(11)	0029(4)	0176(24)	—0021(5)	—0021(16)	0005(8)
C21	—5389(17)	—0245(8)	1689(23)	0096(16)	0033(4)	0116(30)	—0029(7)	—0010(21)	—0006(9)
C22	—5731(21)	—0719(9)	2361(25)	0125(21)	0037(5)	0224(35)	—0026(9)	0048(26)	0019(12)
C23	—5048(25)	—0964(9)	3239(32)	0149(28)	0027(4)	0290(49)	—0001(9)	0039(36)	0024(12)
C24	—5580(20)	0965(9)	1582(29)	0108(18)	0031(4)	0251(45)	0002(7)	0011(28)	0010(12)
C25	—5929(15)	1305(10)	2734(28)	0063(11)	0036(5)	0271(45)	—0005(7)	—0023(22)	0018(13)
C26	—6484(22)	1730(13)	2231(38)	0103(21)	0057(8)	0421(66)	0002(11)	0064(35)	—0010(20)
C27	—6748(21)	2067(13)	3556(41)	0068(17)	0089(10)	0516(75)	0005(10)	0069(35)	—0080(22)

[a] All values ×10^4.

omitted, there is a virtual non-crystallographic mirror plane bisecting the equatorial plane and which contains the axial-equatorial Bu_2dtc group, although all atoms lie in general positions of the space group $P2_1/c$.

The final positional and thermal parameters of the structure are given in Table II, and Figures 1 and 2 show a lebelled and a stereoscopic drawing of the molecule, respectively. Selected bond lengths and angles and their estimated standrad deviation, as calculated by the program ORFFE,[12] are listed in Table III. In general, the dimensions of the three Bu_2dtc are in good agreement with those of other dtc complexes (see Table V), and the three $S_2CN(CH_2)_2$ fragments are likewise planar (see Table IV). However, the spanning ligand differs in several respects from the two ligands in the equatorial plane. First, the "bite" and the S-Mo-S angle of the spanning ligand are larger by 0.077 Å and 3.5°, respectively, than the corresponding values of the equatorial dtc ligands. Secondly, the H_2C-N-CH_2 angle is larger (120.9° vs. 115.2° and 117.2°) in the spanning ligand than in the other two; concommitantly, the C-NR_2 bond distance of the spanning dtc ligand is longer, i.e., 1.324 vs. 1.279 and 1.286 Å. In addition, the Mo-S_{ax} and the Mo-S_{eq} bond distances of the spanning ligand are 0.05 Å longer and 0.05 Å shorter, respectively, than the other four essentially equivalent Mo-S distances for the two equatorial ligands. Thus, these differences may be ascribed to the attempt by the spanning Bu_2dtc ligand to have its two sulfur atoms more nearly occupy their ideal axial and equatorial sites despite the constraints imposed by the rigidity of the ligand and reasonable Mo-S distances. The average Mo-S value of 2.52 Å is similar to that of 2.53 Å found in $MoO_2(Et_2dtc)_2$.[14]

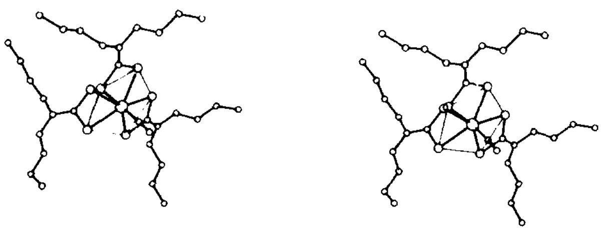


Figure 2. A stereoscopic view of the molecule. This stereo pair can best be appreciated if the observer uses a and-held stereo viewer. The thermal parameters used in this Figure were arbitrarily selected for minimizing overlap between atoms; all are the same and isotropic. The final, refined, anisotropic thermal parameters can best be appreciated in Figure 1.

Table III. Selected Interatomic Distances and Angles in Tris(N,N-di-n-butyldithiocarbamate) Molybdenum(II) Nitrosyl.

a) Core Atoms

Distance (Å)		Angles (°)	
Mo-S1	2.528(4)	S1-Mo-S2	67.8(0.2)
Mo-S2	2.507(4)	S3-Mo-S4	67.9(0.2)
Mo-S3	2.529(4)	S5-Mo-S6	70.3(0.2)
Mo-S4	2.513(4)	S1-Mo-S5	76.2(0.2)
Mo-S5	2.463(4)	S2-Mo-S3	71.7(0.2)
Mo-S6	2.568(4)	S4-Mo-S5	75.9(0.2)
Mo-N	1.731(8)	S6-Mo-N	167.9(0.3)
N-O	1.154(9)	Mo-N-O	173.2(0.7)
S1-C1	1.707(14)	Mo-S1-C1	91.4(0.6)
S2-C1	1.737(15)	Mo-S2-C1	91.4(0.5)
S3-C2	1.679(14)	Mo-S3-C2	91.3(0.7)
S4-C2	1.750(17)	Mo-S4-C2	90.2(0.6)
S5-C3	1.743(18)	Mo-S5-C3	88.2(0.8)
S6-C3	1.686(18)	Mo-S6-C3	86.0(0.8)
S1...S2	2.809(5)	S1-C1-S2	109.3(0.9)
S2...S3	2.950(5)	S3-C2-S4	110.4(1.1)
S3...S4	2.815(5)	S5-C3-S6	115.4(1.3)
S4...S5	3.059(5)	S1-C1-N1	127.2(1.4)
S1...S5	3.080(5)	S2-C1-N1	123.3(1.3)
S5...S6	2.899(5)	S3-C2-N2	126.8(1.6)
		S4-C2-N2	122.7(1.4)
		S5-C3-N3	118.6(1.6)
		S6-C3-N3	126.0(1.7)

b) Ligand Atoms

Distances (Å)

dtc 1		dtc 2		dtc 3	
C1-N1	1.286(17)	C2-N2	1.279(19)	C3-N3	1.324(24)
N1-C4	1.488(18)	N2-C12	1.520(14)	N3-C20	1.478(15)
N1-C8	1.500(18)	N2-C16	1.529(14)	N3-C24	1.497(16)
C4-C5	1.522(26)	C12-C13	1.536(30)	C20-C21	1.574(29)
C5-C6	1.491(29)	C13-C14	1.534(34)	C21-C22	1.553(33)
C6-C7	1.559(32)	C14-C15	1.547(47)	C22-C23	1.464(45)
C8-C9	1.480(26)	C16-C17	1.547(29)	C24-C25	1.550(38)
C9-C10	1.570(34)	C17-C18	1.609(35)	C25-C26	1.506(46)
C10-C11	1.435(49)	C18-C19	1.509(42)	C26-C27	1.627(53)

Angles (°)

dtc 1		dtc 2		dtc 3	
C1-N1-C4	122.2(1.5)	C2-N2-C12	119.7(1.7)	C3-N3-C20	123.0(2.0)
C1-N1-C8	122.6(1.5)	C2-N2-C16	122.5(1.9)	C3-N3-C24	116.0(2.0)
C4-N1-C8	115.2(1.4)	C12-N2-C16	117.2(1.8)	C20-N3-C24	120.9(2.1)
N1-C4-C5	110.9(1.5)	N2-C12-C13	111.4(1.3)	N3-C20-C21	107.4(1.5)
C4-C5-C6	108.8(1.8)	C12-C13-C14	109.2(1.9)	C20-C21-C22	106.2(1.9)
C5-C6-C7	113.6(2.3)	C13-C14-C15	114.8(2.8)	C21-C22-C23	112.7(2.7)
N1-C8-C9	111.0(1.4)	N2-C16-C17	107.6(1.7)	N3-C24-C25	107.5(2.1)
C8-C9-C10	110.2(1.7)	C16-C17-C18	107.9(2.0)	C24-C25-C26	116.6(2.9)
C9-C10-C11	111.7(2.3)	C17-C18-C19	103.8(2.9)	C25-C26-C27	110.4(3.9)

Intermolecular Contacts in $Mo(Bu_2dtc)_3NO$

O...O(i)	3.30 Å	C1...C12(iii)	3.93 Å
O...C17(ii)	3.43	N3...C21(vii)	3.98
O...C13(ii)	3.63	C4...C12(iii)	3.78
O...C17(iii)	3.83	C5...C7(v)	3.92
O...C12(iii)	3.85	C5...C6(v)	3.94
O...C19(ii)	3.91	C7...C27(viii)	3.80
O...C18(ii)	3.97	C9...C14(iii)	3.97
N...C17(ii)	3.92	C10...C19(ix)	3.94
S1...C22(iv)	3.71	C11...C19(ix)	3.90
S1...C23(iv)	3.91	C11...C27(x)	3.60
S2...C8(v)	3.74	C21...C21(vii)	3.72
S6...C6(vi)	3.81		

Where the atoms with the notation (i) - (x) are related to those in Table II (xyz) as follows

(i)	−x, −y, −1−z	(vi)	x, y, −1+z
(ii)	−x, −y, −z	(vii)	−1−x, −y, −z
(iii)	x, y, 1+z	(viii)	x, 1/2−y, 1/2+z
(iv)	−1−x, −y, 1−z	(ix)	−x, 1/2+y, 1/2−z
(v)	x, 1/2−y, −1/2+z	(x)	1+x, 1/2−y, 1/2+z

Table IV. Equations of the Best Least-Squares Planes. Distances (Å) of Atoms from Planes and Dihedral Angles between Planes in Mo(Bu$_2$dtc)$_3$NO

(1) The plane through S1,S2,S3,S4
$11.66x-13.54y+3.511z-2.833 = 0$
S1, −0.0008; S2, 0.0011; S3, −0.0012; S4, 0.0007; S5, −0.4135; Mo, 0.1024

(2) The plane through S1,S2,C1,N1,C4,C8
$11.7x-14.49y+3.195z-3.089 = 0$
S1, 0.0140; S2, 0.0138; C1, −0.0383; N1, −0.0071; C4, 0.0095; C8, 0.0082

(3) The plane through S3,S4,C2,N2,C12,C16
$11.25x-14.94y+3.383z-2.852 = 0$
S3, −0.0507; S4, 0.0410; C2, 0.0267; N2, 0.0361; C12, 0.0515; C16, −0.0640

(4) The plane through S5, S6, C3, N3, C20, C24
$1.805x-12.87y-8.368z-3.597 = 0$
S5, −0.0029; S6, −0.0009; C3, 0.0110; N3, −0.0158; C20, 0.0057; C24, 0.0029

(5) The plane through C4,C5,C6,C7
$7.198x+22.70y+2.746z+4.664 = 0$
C4, −0.0080; C5, 0.0100; C6, 0.0180; C7, −0.0535
Dihedral angle between plane (5) and plane (2) = 84.2°

(6) The plane through C8,C9,C10,C11
$2.330x-11.80y-8.515z-7.949 = 0$
C8, 0.0061; C9, −0.0096; C10, −0.0309; C11, 0.0298
Dihedral angle between plane (6) and plane (2) = 88.5°

(7) The plane through C12,C13,C14,C15
$1.481x-17.81y-7.229z+0.010 = 0$
C12, −0.0004; C13, 0.0005; C14, 0.0023; C15, −0.0035
Dihedral angle between plane (7) and plane (3) = 86.6°

(8) The plane through C16,C17,C18,C19
$8.194x+7.127y-7.793z+0.631 = 0$
C16, −0.0128; C17, 0.0177; C18, 0.0346; C19 −0.0466
Dihedral angle between plane (8) and plane (3) = 86.0°

(9) The plane through C20,C21,C22,C23
$14.62x+0.744y-2.670z-8.561 = 0$
C20, −0.0452; C21, 0.2354; C22, −0.4486; C23, 0.2606
Dihedral angle between plane (9) and plane (4) = 89.9°

(10) The plane through C24,C25,C26,C27
$12.56x+15.06y-1.179z-5.778 = 0$
C24, −0.0108; C25, 0.0090; C26, 0.0146; C27, −0.0192
Dihedral angle between plane (10) and plane (4) = 87.1°

Because of the geometrical contraints on the spanning dtc ligand the pentagonal base is puckered at the S(5) position, and the N-Mo-S(6) angle of 167.9° differs significantly from linearity. The S(5) atom is displaced 0.40 Å above the plane described by the four sulfur atoms (S(1), S(2), S(3) and S(4) of the two equatorial ligands. The molybdenum ion lies 0.10 Å below the same plane in the direction of the nitrosyl group (see Figure 3). The S-Mo-S angles in the pentagonal base differ from the ideal pentagonal angle of 72° by four or five degrees, the observed values ranging from 67.18° to 76.18°. The smaller S-Mo-S angles occur between intraligand sulfur atoms while the larger ones involve interligand sulfur atoms.

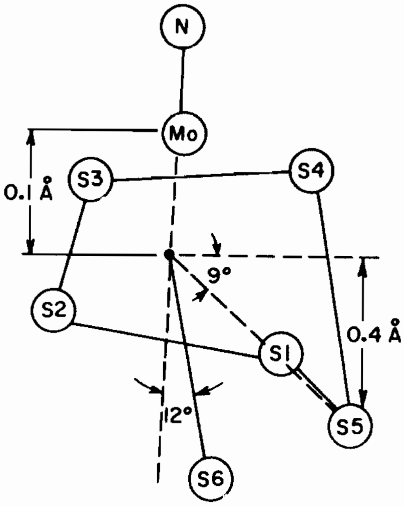
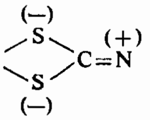


Figure 3. Schematic diagram showing the distortions from the ideal pentagonal bipyramidal geometry. Each of the distortions has been magnified so as to make it very obvious but the scale is not very realistic and was meant strictly in a qualitative sense to emphasize the effect.

The very short C-NR$_2$ bond distances (the average value is 1.296 Å) are close to that of a double bond (1.24 Å),[15] indicating that the canonical form



of the dithiocarbamate ligand contributes greatly to the electronic configuration of all three (Bu$_2$dtc) ligands. As a result, one might expect the S-C bond distances of each ligand to be nearly equal as is the case, for example, in Co(Et$_2$dtc)$_3$[31] (see Table V). However, such is not the case since, on the average, the two S-C bond distances in each (Bu$_2$dtc) ligand differ from each other by 0.05 Å, indicating that the two

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Table V. Comparison of Bond Distances in Various Bis and Tris 1,1-dithiolate Complexes

	Ionic radii of metal,[40] Å		Bond Distances,[a] Å			
		M-S	S-C	C-NR$_2$	N-C	Reference
Co^{III}[S$_2$CN(C$_2$H$_5$)$_2$]$_3$	0.63	2.267	1.718	1.309	1.466	30
Co^{III}[S$_2$COC$_2$H$_5$]$_3$	0.63	2.277	[b]	[b]	[b]	31
Fe^{III}[S$_2$CN(C$_4$H$_9$)$_2$]$_3$	0.64	2.417	[c]	1.41	[c]	32
Fe^{III}[S$_2$COC$_2$H$_5$]$_3$	0.64	2.317	[b]	[b]	[b]	33
Fe^{III}[S$_2$CC$_6$H$_4$CH$_3$)$_2$ [S$_2$CC$_6$H$_4$CH$_3$]	0.64	2.32[d]	1.69[d]	[b]	[b]	34
Ru^{III}[S$_2$CN(C$_2$H$_5$)$_2$]$_3$	0.67	2.382	[c]	[c]	[c]	1
Ni^{II}[S$_2$CN(C$_2$H$_5$)$_2$]$_2$	0.69	2.201	1.707	1.330	1.485	36
Cu^{II}[S$_2$CN(C$_2$H$_5$)$_2$]$_2$	0.72	2.312	1.717	1.333	1.470	37
Zn^{II}[S$_2$CN(C$_2$H$_5$)$_2$]$_2$	0.74	2.362	1.722	1.347	1.472	38
V^{III}[S$_2$P(OC$_2$H$_5$)$_2$]$_3$	0.74	2.45	[b]	[b]	[b]	39
Mo^{II}[S$_2$CN(C$_4$H$_9$)$_2$]$_3$NO	0.85	2.517	1.715	1.296	1.499	This study

[a] Average bond lengths are used; nonbridging M-S values were averaged. [b] Not applicable. [c] Not given. [d] Only values for (S$_2$CC$_6$H$_4$CH$_3$)$^-$ ligand are used.

Dithiocarbamato Complexes Having Unusual Bonding Charact eristics

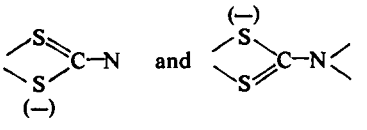
		Distances (Å)		
Complex	C-NR$_2$	S-C	S...S[a]	Reference
Mo(Bu$_2$dtc)$_3$NO	1.296[b]	1.715[b]	2.838[b]	This study
Fe(Bu$_2$dtc)$_3$	1.41	[c]	2.87[d]	32
Ni(H$_2$dtc)$_2$	1.38[b]	1.69[b]	2.80[d]	41
[Cu(Et$_2$dtc)]$_4$	1.408	1.71[b]	3.037	37
[Ag(Pr$_2$dtc)]$_6$	1.38[b]	1.71[b]	3.00[b]	34

[a] Intraligand distance. [b] Averaged values. [c] Not given. [d] Calculated values.

Comparison of Bond Distances in Various Dialkyldithiocarbamates Mean Values of the Bond Lengths (Å) in the dtc Groups.

Compound	S-C	C-NR$_2$	N-C	Reference
Fe(Me$_2$dtc)$_2$NO	1.71	1.34	1.48	42
Mo(Et$_2$dtc)$_2$O$_2$	1.71	1.29	1.52	14
[T1(Pr$_2$dtc)]$_2$	1.70	1.36	1.48	43
Sn(Et$_2$dtc)$_4$	1.72	1.32	1.50	28
Ni(Et$_2$dtc)$_2$	1.71	1.33	1.48	36
Cu(Et$_2$dtc)$_2$	1.72	1.33	1.47	37
Zn(Me$_2$dtc)$_2$	1.72	1.35	1.47	38
[Et$_2$dtc]$_2$	1.73	1.35	1.47	43
Co(Et$_2$dtc)$_3$	1.72	1.31	1.47	30
Mo(Bu$_2$dtc)$_3$NO	1.72	1.30	1.50	This study

remaining canonical structures,



do not contribute equally. These unequal S-C bond distances enable better donor atom packing around the molybdenum ion with reasonable molybdenum-sulfur bond distances and with a minimum of interligand contact. Thus the virtual regularity of the pentagonal plane is achieved at the expense of slight distortions in the coordination of the individual chelate ligands.

As can be seen from the contents of the unit cell, shown in Figure 4, the crystal structure of Mo(Bu$_2$dtc)$_3$NO consists of discrete monomers. The intermolecular contacts listed in Table III indicate that forces between molecules are of van der Waals type with some weak C-H . . O and C-H . . S hydrogen bonding. Morever, the close O . . O contacts may account for the slightly bent M-N-O angle.

Perhaps the most interesting feature of this molecule is the fact that the distances between adjacent sulfur atoms in the equatorial plane are nearly the same for all pairs of contacts, irrespective of wether the atoms in question belong to the same ligand or not. These S . . S contacts range from 2.809 to 3.080 Å (average value is 2.943 Å) and are all shorter than van der Waals' contacts (about 3.4 Å).[16] These short

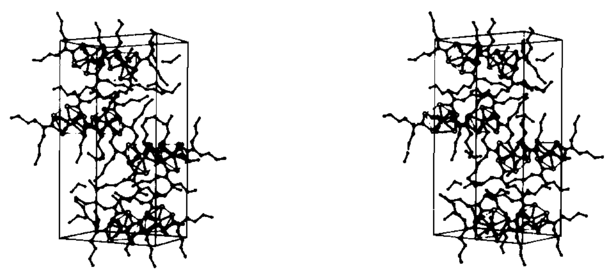


Figure 4. The packing of the molecules in the lattice. This is a stereo pair which should be studied with the aid of a hand-held stereo viewer.

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contacts indicate that ligand-ligand interactions are operative and that they help stabilize the equatorial pentagonal plane of this structure. Similar forces arising from short interligand S . . S contacts in Re$(S_2C_2(C_6H_5)_2)_3$,[17] $V(S_2C_2(C_6H_5)_2)_3$[18] and $Mo(S_2C_2H_2)_3$[19] (3.050, 3.064 and 3.11 Å respectively).have been invoked to help explain the stabilization of trigonal prismatic coordination in these 1,2-dithiolate complexes. The net effect of such interactions between adjacent sulfur atoms is to facilitate dispersal of electrons around the positively charged central metal ion presumably via overlap of the low lying sulfur 3d orbitals.

The short Mo-N and N-O bond distances (1.731 and 1.154 Å respectively) and the diamagnetism of the complex indicate that the nitric oxide ligand is present as the nitrosonium ion, NO^+, and that the molybdenum ion is formally in the plus two state, having a low spin d^4 electronic configuration. If C5v symmetry is assumed for the donor atoms around the molybdenum ion, then the metal orbitals can be shown to transform as

$$3A_1 + 1E_1 + 1E_2$$

The molybdenum orbitals which transform as these representations are:

A_1: $5s, 5p_z, 4d_{z^2}$
E_1: $(5p_x, 5p_y), (4d_{xz}, 4d_{yz})$
E_2: $(4d_{x^2-y^2}, 4d_{xy})$

In this case the $(5p_x, 5p_y)$ orbitals are more suitable for sigma bonding than the $(4d_{xy}, 4d_{yz})$ orbitals. Thus the most reasonable hydridization scheme for the molybdenum orbitals for this pentagonal bipyramidal geometry is $(5s)\ (5p_x)\ (5p_y)\ (5p_z)\ (4d_{z^2})\ (4d_{x^2-y^2})\ (4d_{xy})$ which is abbreviated sp^3d.[3] Since the d_{xz} and d_{yz} orbitals are directed between donor atoms and the d_{z^2} orbitals at donor atoms, the most likely ordering of the molybdenum d orbitals in increasing energy is

$$d_{xz}, d_{yz} < d_{x^2-y^2}, d_{xy} < d_{z^2}$$

Hence the four *d* electrons of the Mo^{II} ion occupy the d_{xz} and d_{yz} orbitals where they are in excellent position for back-bonding with the nitrosyl ion through the latter's empty π^* orbitals. Thus the Mo-NO bonding consists of the dative overlap of filled N σ orbitals with Mo σ orbitals (Mo σ NO^+) together with the dative overlap of filled Mo dπ orbitals with empty $NO^+\pi^*$ orbitals (Mo π NO^+).[20] This bonding mechanism accounts for the short Mo-N distance in Mo$(Bu_2dtc)_3NO$.

Furthermore, this simplified electronic scheme can be used to explain why the analogous ruthenium complex[1] is six, instead of seven-coordinated. The extra two electrons of the ruthenium(II) ion (d^6) occupy either the $d_{x^2-y^2}$ or d_{xy} orbitals in which they interact repulsively with the electrons of some of the sulfur atoms in the pentagonal plane. In order to relieve this uneven repulsive strain, an equatorial sulfur atom is expelled from the coordination sphere and the configuration of atoms around the ruthenium ion becomes octahedral. Although the configuration around the central ion has been changed in the Ru case, the M-NO bonding is essentially the same in both cases, this is strongly suggested by the very similar M-N and N-O distances and M-N-O angles for both the Mo(II) and Ru^{II} complexes: 1.731 Å, 1.154 Å and 173.2° vs. 1.72 Å, 1.17 Å and 172°, respectively. It would be interesting to study the analogous Tc^{II} (d^5) complex to determine whether the (*d*-electron)-(ligand) repulsion due to the addition of a single electron is enough to overcome the stabilization of the pentagonal plane by the sulfur-sulfur interactions.

Until recently few structures in which a transition metal is at the center of a pentagonal bipyramidal arrangement of donor atoms have been reported. In 1967 Fleicher and Hawkinson[21] reported the structures of two iron(II) complexes: $[FeB(NCS)_2]ClO_4$ and the dimer $[(H_2O)BFeOFeB(H_2O)]$. Here B represents a pentadentate macrocyclic ligand: 2,13-dimethyl-3,6,9,12,18-pentaza-bicyclo 12.3.1 -octadeca-1(18),2,12,14,16-pentane, in which five nitrogen atoms arranged in a pentagonal plane coordinate to the iron-(III) ion. The remaining two ligands occupy axial positions. However, it is clear that the occurrence of pentagonal bipyramidal coordination is a consequence of the conformation of the macrocyclic ligand. More recently the structure[22] of a dimer, μ-oxalatobis(oxalato)hexaquodititanium(III)tetrahydrate, was found to contain seven-coordinate(pentagonal dipyramidal) titanium(III) ions. Similarly, the zirconium in the three-dimensional polymeric zirconium molybdate,[23] $[ZrO_2(OH)OMo_2O_2(OH)_5]_n$, and the tin in the complex $(C_5H_5)Sn(AlCl_4)$. C_5H_6,[24] a linear chain structure, have been found to be at the center of a pentagonal bipyramidal coordination sphere. None of the above complexes, however, contain discrete monomeric pentagonal bipyramidal molecules.

In a recent review[25] on molecular polyhedra of high coordination number, Muetterties and Wright point out that for a complex of composition $(chel)_3MX$ which acquires a pentagonal bipyramidal configuration three isomers are possible: one in which X occupies an equatorial site. However, there seem to be no clear-cut factors which lead specifically to the formation of any of the three isomers. Only recently have such tris-chelate pentagonal bipymamidal structures been reported. Hoard[26] has reported pentagonal bipyramidal structures for tris-tropolono Sn^{IV} chloride and hydroxide. Also Elder[27] has determined the structure of tris(hexafluoroacetylacetonato)-π-cyclopentadienyl zirconium to be pentagonal bipyramidal, assuming the cyclopentadienyl group to occupy only

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one coordination site, while Morris and Schlemper[28] have found $Sn(Et_2dtc)_3CH_3$ to have a pentagonal arrangement of donor atoms around the tin ion.

In comparing $Mo(Bu_2dtc)_3NO$ with other $(chel)_3$-MX complexes it is interesting to note that these complexes have the following features in common: (a) only the isomer with the X group in an axial position has been found; (b) the four metal to donor atom bond distances of the two bidentate ligands in the equatorial plane are virtually identical, while the two metal to donor atom distances of the axial-equatorial ligand differ significantly from each other and from the mean value of the four equatorial distances; (c) the central metal atom is displaced from the pentagonal plante toward the X group; (d) the axial-equatorial group subtends a greater angle at the central metal atom and its intramolecular donor atom to donor atom distance (bite) is concommitantly longer.

The bonding charactetistics of $Sn(Et_2dtc)_3CH_3$ are very similar to those of $Mo(Bu_2dtc)_3NO$ with some interesting exceptions. Although the pentagonal arrangement of sulfur atoms about the tin ion is also slightly puckered, interligand S ... S interactions as in the molybdenum complex are precluded by the relatively large Sn-S distances averaging 2.67 Å. For the axial-equatorial ligand the axial Sn-S distance is 0.21 Å shorter and the equatorial Sn-S distance is 0.11 Å longer than the average value of the nearly equivalent Sn-S distances of the equatorial ligands. This effect is opposite in direction to that of the molybdenum complex. Moreover, the zirconium complex of Elder[27] also show an axial contraction and equatorial elongation of the Zr-O distances of the spanning ligand relative to those of the two equatorial ligands. This effect is due in part to the different trans effects of $C_6H_5^-$ and CH_3^- wih respect to NO^+. The former groups are electron donors while the latter is an electron acceptor. Differences in the electronic configuration of the metal ions are also important.

In $Sn(Et_2dtc)_3CH_3$, as in $Mo(Bu_2dtc)_3NO$, the $C\text{-}NR_2$ distance of the bridging ligand is significantly larger than the two corresponding distances of the equatorial ligands (1.38 vs. 1.24 and 1.29 Å). A similar difference in $C\text{-}NR_2$ distances exists in $(Et_4N)Np(Et_2dtc)_4$,[29] an eight coordinate complex whose coordination geometry, however, is similar to that about the molybdenum ion in $Mo(Bu_2dtc)_3NO$. It contains an almost plane pentagonal arrangement of five sulfur atoms, with one other sulfur atom located below and the remaining two above this plane. The bridging $C\text{-}NR_2$ distance is 1.41 Å while the two equatorial distances are 1.33 and 1.28 Å. Again the long Np-S distances preclude any interligand S ... S interactions.

More studies on the $(che)_3MX$ class of complexes are needed to understand what factors lead to the pentagonal bipyramidal geometry and why that isomer with X in the axial position seems to be more stable than either of the two with X accupying an equatorial site.

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