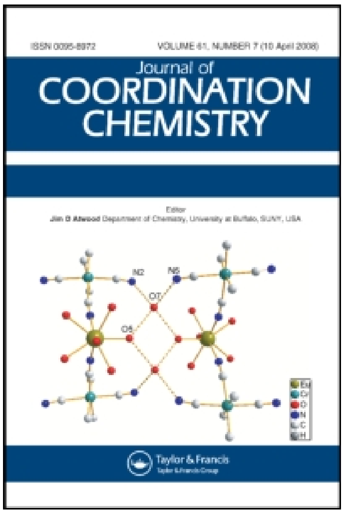

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THE CRYSTAL AND MOLECULAR STRUCTURE OF A SERIES OF OXO MOLYBDENUM DITHIOCARBAMATES

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THE CRYSTAL AND MOLECULAR STRUCTURE OF A SERIES OF OXO MOLYBDENUM DITHIOCARBAMATES

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The crystal and molecular structure of a series of oxo-molybdenun di-n-propyldithiocarbamates have been studied by X-ray diffraction methods. The compounds studied were di(oxo-di-n-propyldithiocarbamato) molybdenum VI (A), μ-oxo-bis-(di(oxo-di-n-propyldithiocarbamato) molybdenum V) (B), and oxo-bis-di-n-propyldithiocarbamato molybdenum IV (C). Compound A is orthorhombic, space group Pbca, with eight molecules in a unit cell having dimensions a = 16.577(3) Å, b = 18.771(3) Å and c = 13.702(2) Å. The molybdenum V compound (B) crystallizes in the orthorhombic non-centrosymmetric space group $Pca2_1$, with four molecules in a unit cell having parameters a = 19.605(6) Å, b = 13.491(3) Å and c = 16.342(4) Å. The last compound (C) is triclinic, space group $P\bar{1}$ with two molecules in the unit cell. Its crystal parameters are a = 10.183(6) Å, b = 13.012(9) Å, c = 9.208(5) Å' $\alpha = 71.57(5)^\circ$, $\beta = 105.81(5)^\circ$ and $\gamma = 81.82(5)^\circ$. The intensities were collected by counter techniques using MoKα radiation. All structures were refined by full matrix least-squares, using anisotropic temperature factors for all non-hydrogen atoms. For each compound, respectively, these refinements were conducted on 2795, 3216 and 2346 reflections and the corresponding R factors were 0.052, 0.052 and 0.063. The dioxo molybdenum VI compound contains two oxygen atoms in cis position, as it is usually observed in these compounds. The four sulfur atoms occupy the remaining four positions of an octahedron around molybdenum. This octahedron is deformed by steric interactions between the sulfur atoms. The molybdenum V complex possesses a similar geometry around each molybdenum. A common oxygen atom bridges the two metal atoms. This structure is similar to that of $Mo_2O_3(S_2COC_2H_5)_4$. The ligand around the molybdenum IV complex form a square pyramid. The four sulfur atoms occupy the basal plane and the oxygen is at the summit of the pyramid.

INTRODUCTION

The catalytic activation of molecular oxygen by transition metal complexes has recently drawn much attention.[2] The oxidation of tertiary phosphines at close to room temperature constitutes a good model for the study of the activation processes. Several reactions of this type, have been studied with dioxygen complexes of low valent metals.[3] Sajus and co-workers have recently found that oxo complexes of molybdenum behave the same way.[4] A particularly interesting system is that of the oxo molybdenum dithiocarbamates where these workers have shown the existence of an oxido-reduction cycle that is repeated until all the phosphine is oxidized. In order to elucidate some of the factors influencing this reaction, it was decided to study the molecular structure of some of the above mentioned products, namely the molybdenum V and molybdenum IV oxo-dithiocarbamates. In view of the recent report concerning oxidative addition by the latter compound,[5] knowledge of its structure takes on added interest. Because of the absence of precise structural data on molybdenum VI oxo-dithiocarbamates, and so as to have a coherent set of data, the study of the molecular structure of this compound was also undertaken.

EXPERIMENTAL SECTION

The complex $MoO_2(S_2CN(C_3H_7)_2)_2$ (A) was prepared following the method of Moore.[6] Crystals suitable for X-ray diffraction measurements were obtained by recrystallization from toluene-hexane. The crystals used for the structure determination of $Mo_2O_3(S_2CN(C_3H_7)_2)_4$ (B) and $MoO(S_2CN(C_3H_7)_2)_2$(C) were kindly supplied by the Institut Francais du Pétrole. These compounds were prepared by reacting in toluene the appropriate stoichiometric amounts of A and triphenylphosphine.[4]

TABLE I
Crystal data for the three oxomolybdenum complexes

	$MoO_2(S_2CN(C_3H_7)_2)_2$	$Mo_2O_3(S_2CN(C_3H_7)_2)_4$	$MoO(S_2CN(C_3H_7)_2)_2$
Space group	Pbca	Pbcmor $Pca2_1$	P_1 or $P_{\bar{1}}$
a(Å)	16.577(3)	19.605(6)	10.183(6)
b(Å)	18.771(3)	13.491(3)	13.012(9)
c(Å)	13.702(2)	16.342(4)	9.208(5)
α(°)			71.57(5)
β(°)			105.81(5)
γ(°)			81.82(5)
V(Å^3)	4264	4322	1078
d_{obs}(g/cm^3)	1.50	1.43	not measured
d_{calc}(g/cm^3)	1.49	1.45	1.43
Z	8	4	2
μ(cm^{-1})	9.83	9.61	9.69
M	480.57	945.14	464.57

Crystal Data

Precession photographs were used to determine the approximate crystallographic parameters of all three compounds and the possible space groups, listed in table I, were determined from the observed systematic extinctions. The refined unit cell dimensions and their estimated standard deviations were obtained at room temperature (20 ± 2°) with MoKα radiation (λ = 0.70926 Å) using the method outlined by Busing for four circle diffractometers.[7] The experimental densities were measured by flotation in mixtures of cyclohexane and bromoform .

Data Collection

The available crystals were shaped into cubes to record the intensities. In all cases, the edges of the cube were approximately 200 microns. The fragments were then sealed in Lindemann glass capillaries and mounted on a rotation free goniometer head. No special precautions were required except for compound C, which is very air sensitive and had to be cut and sealed under argon. All quantitative data were obtained from a four-circle Picker diffractometer controlled by a PDP-8I computer, using graphite monochromated MoKα radiation. The monochromator was set at a 2θ angle of 11.84° (θ = 5.57°). The refined parameters listed in Table I and the orientation matrices were obtained using standard Picker-supplied routines.

Intensity data were collected by use of the θ-2θ scan technique with a scan rate of 2°/min. The scan ranges used are listed in Table II. In all cases, stationary background counts were recorded for 20 sec. at each end of the scan. Attenuators were used

TABLE II
Summary of data collection and least-squares structure refinement parameters for the three oxomolybdenum complexes

	A	B	C
Scan range for data collection (°)	1.6	2.2	1.6
Total number of reflections recorded	6147	4245	4174
2θ maximum	60.0	50.0	50.0
$\sigma(I)/I$, acceptance criterion for data reduction	0.40	0.33	0.40
number of reflection with $I > \sigma(I)/I$	2796	2142	2346
Final p value	0.06	.05	0.10
$R_1 = \Sigma(\vert F_o\vert - \vert F_c\vert)/\Sigma\vert F_o\vert$	0.052	0.052	0.063
$R_2 = (\Sigma w(\vert F_o\vert - \vert F_c\vert)^2/\Sigma w\vert F_o\vert^2)^{1/2}$	0.074	0.065	0.089
Rejection limit n in the expression $\Delta F < n\sigma\vert F_o\vert$	4.0	5.0	5.0
Number of reflections with $\Delta F > n\sigma\vert F_o\vert$[a]	65	31	14
R_1 same as above excluding rejects	0.047	0.048	0.060
R_2 same as above excluding rejects	0.056	0.052	0.078
e.s.d. of a unit weight observation	1.185	1.194	1.279

[a] Low intensity reflections believed to be in error because of counting statistics.

whenever the scan count exceeded 7000 counts/sec. The intensities of three standard reflections were monitored at intervals of 70 measurements throughout the data collections for compounds A and B and 50 measurements for compound C. In the first two recordings the stability of the standard intensities was excellent and constant within two percent. In the case of compound C, however, these intensities dropped linearly by 20% in the time required to record all intensities and it was necessary to rescale them. This was done by least-squares using a local program.[8] A standard deviation was assigned to each measured intensity using the expression:

$$\sigma(I) = (C + (t_b)^2(B_1 + B_2) + (pI)^2)^{\frac{1}{2}}$$

where C is the scan count, B_1 and B_2 are background counts, t_c and t_b are respectively scan and background times and p is an empirical coefficient of the net count I.[9] The value of p and other relevant parameters of the data collections are listed in Table II. No absorption corrections were applied in view of the small crystal dimensions and small linear absorption coefficients (see Table I).

Structure Solution and Refinement

Three dimensional Patterson maps were computed for each compound. The interpretation of the vector map for compound A was straightforward. Similarly, for compound C, the vector map readily indicated that the correct space group was P$\bar{1}$. In the case of compound B, the interpretation of the Patterson map was a little more difficult. The existence of a strong Harker plane in the Patterson map however, indicated that the correct space group was Pca2_1. The vector map was successfully interpreted in this space group, yielding the position of the two independent molybdenum atoms. Since the intensities had been recorded with a choice of axis permitted in Pbcm, the h and k indices of all reflections were permuted to conform to the convention adopted in the 'International Tables for X-Ray Crystallography'.[10] The crystal parameters listed in Table I for compound B are then those required in the space group Pca2_1. The choice of this space group was confirmed by successful refinement of the structure. Fourier maps computed in each case using the coordinates so obtained for the molybdenum atoms revealed the positions of all other non-hydrogen atoms.

In all structure factor calculations, the atomic scattering factors used were those tabulated by Moore[11] using the development of Pepinsky.[12] The effects of anomalous dispersion were included for the molybdenum and sulfur atoms; the values of $\Delta f'$ and $\Delta f''$ are those given in the 'International Tables for X-Ray Crystallography'.[13] Atomic coordinates and individual anisotropic thermal parameters were refined by full-matrix least-squares using the program

TABLE IV

Fractional coordinates and anisotropic temperature factors for $MoO_2(S_2CN(C_3H_7)_2)_2$ (x10^5)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
MO	10350(2)	13625(2)	15135(2)	343(2)	291(2)	404(2)	-33(2)	72(2)	-42(2)
S1	10520(10)	1616(7)	8191(10)	524(7)	262(4)	411(7)	-53(5)	63(7)	8(5)
S2	16672(8)	25293(7)	17869(10)	325(5)	242(4)	618(9)	35(4)	28(6)	-41(5)
S3	26074(8)	12793(7)	13564(10)	375(6)	250(5)	601(9)	41(4)	17(6)	-26(5)
S4	11330(10)	13945(7)	-4369(10)	520(7)	258(4)	433(7)	54(5)	65(6)	2(5)
O1	10206(28)	9575(25)	26181(28)	618(23)	383(16)	373(21)	-116(17)	136(20)	-16(16)
O2	1304(25)	17765(23)	14055(29)	307(17)	401(17)	690(30)	5(14)	97(19)	-160(19)
C1	26258(31)	21691(28)	16640(34)	304(21)	247(16)	348(28)	10(16)	-13(20)	25(17)
C2	32766(40)	32914(29)	20969(43)	461(29)	221(17)	540(36)	-1(19)	-49(27)	-9(21)
C3	34301(56)	33571(39)	31899(50)	841(49)	326(23)	546(41)	-25(28)	-92(38)	-93(25)
C4	35192(45)	41386(39)	34986(54)	516(33)	357(24)	853(54)	-66(24)	-29(35)	-211(31)
C5	40927(30)	21942(34)	16638(40)	268(22)	359(21)	433(32)	41(17)	-22(21)	-4(21)
C6	43749(37)	22626(37)	6214(43)	343(25)	424(24)	471(33)	61(20)	40(25)	72(24)
C7	51693(43)	18772(43)	4838(56)	466(33)	455(29)	882(53)	147(26)	211(34)	15(33)
C8	11844(30)	4888(30)	-3478(37)	242(21)	287(18)	388(29)	-14(16)	28(20)	21(18)
C9	14492(34)	-7142(28)	-9439(41)	338(24)	218(16)	475(33)	-25(16)	-37(22)	-43(19)
C10	23220(39)	-8810(32)	-6923(46)	394(27)	265(19)	728(44)	33(19)	8(29)	-7(24)
C11	24489(45)	-16830(34)	-6347(50)	549(34)	289(21)	753(45)	5(23)	43(36)	32(26)
C12	14450(34)	3135(32)	-20935(40)	341(24)	328(21)	338(29)	-14(18)	-27(21)	-23(20)
C13	6750(43)	2160(44)	-27051(45)	432(30)	614(34)	458(38)	-40(27)	-120(29)	45(29)
C14	8449(52)	4020(48)	-37721(50)	728(45)	557(33)	436(37)	82(31)	-74(32)	30(29)
N1	32866(27)	25305(25)	17981(30)	294(17)	276(15)	409(24)	37(15)	-33(18)	0(16)
N2	13357(28)	547(22)	-10961(33)	302(18)	211(14)	433(26)	-10(13)	14(18)	-7(16)

SFLS-5.[14] The correlation matrix for compound B revealed the existence of strong correlation terms between the z coordinates of the $Mo_2O_3S_8$ skeleton. Since the number of parameters exceeded the maximum allowed by the program it was decided to continue the refinement using blocks as large as possible. To this end, the molecule was divided into three parts: all molybdenum, sulfur, oxygen, nitrogen and CS_2 carbon atoms were first refined for two cycles; the two ligands bonded to molybdenum Mo_1 were then refined for two cycles and, finally, the two ligands bonded to Mo_2 were refined in the same manner. This procedure was repeated until convergence occured. In all least-squares computations, the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factors. The weight w was taken as $1/\sigma^2(|F_o|)$. The final R factors and other relevant refinement parameters appear in Table II.

Fourier maps computed at this stage revealed the positions of some hydrogen atoms, but these were not included in the refinements. No other peaks higher than 0.5e/Å^3 were detected.

All computations were conducted on a Univac 1108 computer. Other programs used include ORTEP, by C. K. Johnson[15] for drawings and local programs for Fourier and least squares planes.[8]

Tables III, IV and V contain the observed and

TABLE VII
Fractional coordinates and anistropic temperature factors for $Mo_2O_3(S_2CN(C_3H_7)_2)_4$ (x10^5)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
MO1	36650(7)	20917(10)	65629(29)	211(4)	488(9)	223(5)	63(6)	-11(5)	-30(7)
MO2	50185(7)	17476(8)	49881(28)	232(4)	396(7)	211(5)	30(6)	11(5)	-19(7)
S1	27651(21)	29933(31)	73680(43)	252(14)	633(31)	534(23)	1(16)	52(15)	-63(23)
S2	39632(21)	38456(31)	66351(42)	310(13)	683(31)	462(23)	-52(17)	65(19)	-162(26)
S3	29469(25)	6329(32)	62019(40)	404(17)	582(31)	383(21)	5(20)	-41(15)	56(20)
S4	28437(22)	24468(31)	52935(40)	383(16)	520(28)	420(21)	-28(18)	-129(16)	56(20)
S5	45611(23)	34676(31)	43667(41)	333(16)	566(30)	419(21)	25(18)	-74(16)	-14(21)
S6	57148(22)	31906(31)	54423(41)	325(15)	547(32)	468(22)	15(17)	-80(16)	-17(22)
S7	55599(21)	15998(33)	35841(38)	263(13)	690(31)	338(19)	-50(18)	30(13)	-9(21)
S8	42283(21)	9154(34)	40616(39)	283(15)	809(35)	333(20)	-141(18)	80(14)	-127(22)
O1-2	43355(59)	19033(72)	57645(78)	300(34)	398(73)	348(45)	-21(39)	28(33)	-106(47)
O1	39927(59)	15144(80)	73737(72)	357(40)	676(84)	296(51)	105(48)	-36(38)	-138(55)
O2	55459(63)	9281(82)	54280(78)	397(44)	534(78)	420(58)	26(48)	-2(43)	26(58)
C1	32577(74)	40092(118)	72895(100)	244(51)	556(111)	385(77)	-3(61)	-72(54)	7(79)
C2	25679(87)	49596(136)	82524(110)	221(50)	884(126)	527(88)	101(72)	131(61)	14(101)
C3	28635(93)	47977(142)	91691(110)	307(58)	1153(166)	404(86)	47(83)	47(65)	-35(100)
C4	22776(105)	49535(142)	97168(114)	485(85)	797(136)	559(114)	-66(90)	143(70)	-177(101)
C5	36042(95)	57179(118)	75836(123)	474(67)	354(102)	670(113)	50(76)	-102(78)	165(83)
C6	33109(148)	65271(208)	72589(203)	878(123)	2108(249)	1659(189)	-836(149)	-516(134)	356(196)
C7	28266(183)	65201(203)	66131(195)	1321(187)	1665(279)	1165(170)	-52(185)	-482(172)	492(203)
C8	26271(71)	12277(104)	53886(97)	197(45)	487(99)	349(71)	76(57)	-13(49)	14(74)
C9	20020(89)	13182(123)	40856(113)	354(62)	878(140)	416(82)	-25(78)	-65(63)	65(90)
C10	13216(93)	19582(134)	42486(109)	339(59)	1012(140)	446(84)	112(87)	22(61)	-76(95)
C11	7036(109)	13636(178)	44203(143)	430(81)	1592(228)	722(129)	-100(109)	291(84)	-233(140)
C12	21203(78)	-3103(114)	48716(119)	247(48)	672(122)	637(103)	-84(62)	29(65)	-120(94)
C13	26272(95)	-8361(106)	43042(105)	476(74)	472(106)	427(94)	76(73)	148(68)	-131(80)
C14	24829(126)	-19949(109)	43817(131)	709(84)	333(95)	808(124)	7(89)	-76(99)	-39(92)
C15	51876(63)	39868(93)	40384(101)	242(49)	304(90)	309(59)	47(45)	-31(51)	-114(74)
C16	47879(97)	56843(119)	46926(103)	501(76)	499(118)	489(92)	50(74)	-21(65)	181(80)
C17	50357(97)	58692(139)	37390(118)	308(65)	947(148)	505(92)	-48(86)	61(71)	268(95)
C18	44782(113)	65037(145)	32649(131)	631(90)	954(159)	685(120)	331(100)	95(87)	492(115)
C19	57740(89)	54197(118)	55317(110)	382(65)	641(122)	489(93)	-155(72)	-7(64)	-150(88)
C20	54315(97)	57208(131)	63994(108)	498(71)	833(136)	403(92)	-301(84)	-38(70)	-109(90)
C21	59722(125)	62160(192)	69799(139)	543(83)	1705(239)	605(119)	0(123)	-197(86)	-194(138)
C22	48495(78)	10010(102)	33012(93)	346(62)	394(97)	320(70)	0(59)	-23(52)	-15(67)
C23	53130(80)	6021(113)	19631(89)	343(53)	617(113)	237(61)	-10(65)	16(51)	-49(68)
C24	52260(71)	15579(109)	14113(95)	266(45)	588(101)	328(71)	93(57)	43(46)	61(70)
C25	57795(100)	14816(134)	7318(109)	526(78)	959(153)	289(73)	61(89)	59(66)	89(86)
C26	40875(86)	1093(121)	23420(99)	388(58)	640(120)	346(82)	-126(75)	-76(58)	76(80)
C27	41056(101)	-10064(118)	25174(104)	552(76)	487(113)	369(79)	50(77)	-71(68)	-61(81)
C28	34701(105)	-15013(139)	21935(122)	562(82)	1011(155)	465(92)	-397(94)	-43(73)	-148(100)
N1	31306(63)	48721(97)	76715(82)	268(41)	481(91)	533(77)	74(55)	-50(46)	-136(70)
N2	22602(61)	7583(86)	48197(74)	291(43)	484(87)	310(64)	-73(49)	23(42)	80(56)
N3	52436(59)	49692(102)	50001(93)	317(46)	735(100)	391(57)	7(52)	117(54)	-100(84)
N4	47582(57)	6149(82)	25753(72)	240(38)	463(77)	266(57)	-60(44)	27(37)	-27(54)

TABLE VIII
Fractional coordinates and anisotropic temperature factors for $MoO(S_2CN(C_3H_7)_2)_2$ $(x10^5)$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
MO	10891(7)	23279(7)	41017(7)	971(10)	951(7)	1147(11)	-57(6)	317(7)	-378(7)
S1	15237(22)	34995(19)	17585(25)	1440(30)	913(19)	1636(34)	-307(18)	481(25)	-520(21)
S2	-4560(23)	21532(22)	17305(25)	1283(29)	1497(26)	1459(33)	-599(22)	456(25)	-444(24)
S3	16097(25)	3786(23)	58034(32)	1214(31)	1277(25)	2307(46)	-524(22)	125(29)	-6(27)
S4	35460(23)	17540(19)	57581(28)	1286(28)	875(19)	2012(39)	-297(18)	182(26)	-417(22)
O	1707(76)	31481(69)	47418(76)	1704(100)	1743(84)	1598(103)	247(72)	326(82)	-709(79)
C1	2511(84)	30750(69)	5614(89)	1112(101)	855(72)	1205(117)	-38(67)	284(89)	-313(75)
C2	6938(95)	40881(72)	-19010(101)	1457(123)	820(74)	1505(133)	-21(75)	728(107)	-135(82)
C3	20845(101)	33931(80)	-18451(113)	1445(125)	1011(84)	1875(158)	-245(82)	647(115)	-480(95)
C4	27188(148)	41953(117)	-29222(183)	2462(215)	1541(127)	4217(337)	-1136(140)	2257(235)	-1145(178)
C5	-10581(102)	29072(91)	-19395(105)	1439(129)	1414(106)	1381(137)	-453(94)	330(108)	-615(101)
C6	-25355(135)	38002(121)	-27158(175)	1561(169)	1691(152)	3243(288)	-422(127)	-373(171)	-163(164)
C7	-35718(185)	33649(195)	-37887(231)	2432(271)	3029(281)	3912(398)	-1290(225)	-390(255)	-708(274)
C8	33511(89)	4154(74)	64831(105)	1098(109)	797(73)	1756(144)	-222(73)	162(103)	-192(85)
C9	41310(139)	-16224(138)	82902(179)	1891(188)	2135(181)	3392(294)	-729(148)	856(193)	-1583(203)
C10	42949(169)	-21454(156)	71927(200)	2358(241)	2319(214)	3660(361)	-205(178)	1092(239)	-1097(237)
C11	42336(182)	-34797(104)	83522(276)	3093(302)	716(100)	7639(643)	-877(145)	1402(349)	-611(204)
C12	59048(108)	-3702(89)	76051(142)	1321(133)	1095(96)	2897(228)	-198(89)	320(136)	-799(123)
C13	64559(118)	-1558(95)	91589(149)	1630(155)	1141(104)	2841(229)	-215(101)	556(152)	-615(128)
C14	80238(113)	-1138(117)	94089(185)	1066(132)	1689(143)	4441(349)	-534(110)	302(167)	-1251(134)
N1	-330(69)	33477(59)	-10229(76)	1138(86)	942(62)	1207(99)	-151(58)	258(75)	-326(65)
N2	44127(82)	-4516(65)	73365(118)	1176(101)	696(62)	3451(200)	-383(66)	182(113)	-267(90)

computed structure factors for all reflections used in the refinement of compounds A, B and C respectively.[16] Final positional and thermal parameters are listed in Tables VI, VII and VIII.

DESCRIPTION OF THE STRUCTURES

I Bis-(oxo-di-n-propyldithiocarbamato) molybdenum VI and Oxo-bis-(di(oxo-di-n-propyldithiocarbamato) molybdenum V).

The structure of many dioxomolybdenum VI complexes are presently known.[17] Of particular interest in the present case is that of di(oxo-diethyldithiocarbamato) molybdenum VI.[18] Like all other molybdenum VI dioxo complexes, it presents a deformed octahedral structure, with two oxygen atoms in cis position. The present (A) complex possesses a similar geometry. The only noteworthy difference is the longer Mo–O bond length observed in this work. This discrepancy is attributed to imprecisions introduced by the smaller data set and different data collection method used by Kopwillem.

The structure of the molybdenum V complex (B) is similar to that previously reported by Cotton for $Mo_2O_3(S_2COC_2H_5)_4$.[19] The distances observed in

TABLE IX
Molecular dimensions in $MoO_2(S_2CN(C_3H_7)_2)_2$ (A)

a) *bond lengths* (Å)			
$Mo-S_1$	2.446(2)	C_3-C_4	1.533(10)
$Mo-S_2$	2.457(2)	C_5-C_6	1.510(8)
$Mo-S_3$	2.621(2)	C_6-C_7	1.515(9)
$Mo-S_4$	2.681(2)	C_8-S_1	1.728(5)
$Mo-O_1$	1.695(5)	C_8-S_4	1.706(5)
$Mo-O_2$	1.696(5)	C_8-N_2	1.334(6)
C_1-S_2	1.736(5)	C_9-N_2	1.470(6)
C_1-S_3	1.722(5)	$C_{12}-N_2$	1.463(7)
C_1-N_1	1.302(7)	C_9-C_{10}	1.520(8)
C_2-N_1	1.485(7)	$C_{10}-C_{11}$	1.521(9)
C_5-N_1	1.490(7)	$C_{12}-C_{13}$	1.538(9)
C_2-C_3	1.526(9)	$C_{13}-C_{14}$	1.530(9)
b) *bond angles* (°)			
S_1-Mo-S_2	151.1(1)	$S_3-C_1-N_1$	123.7(2)
S_1-Mo-S_3	84.4(1)	$C_1-N_1-C_2$	122.0(4)
S_1-Mo-S_4	68.4(1)	$C_1-N_1-C_5$	121.2(3)
S_2-Mo-S_3		$C_2-N_1-C_5$	116.8(3)
S_2-Mo-S_4	96.2(1)	$N_1-C_2-C_3$	110.3(4)
S_3-Mo-S_4	81.9(1)	$N_1-C_5-C_6$	111.1(3)
O_1-Mo-O_2	105.7(1)	$C_2-C_3-C_4$	111.4(4)
O_1-Mo-S_1	86.3(1)	$C_5-C_6-C_7$	110.3(4)
O_1-Mo-S_2	105.5(1)	$S_1-C_8-S_4$	114.5(2)
O_1-Mo-S_3	93.5(1)	$S_1-C_8-N_2$	121.3(2)
O_1-Mo-S_4	154.5(1)	$S_4-C_8-N_2$	124.2(2)
O_2-Mo-S_1	113.5(1)	$C_8-N_2-C_9$	120.9(3)
O_2-Mo-S_2	89.0(1)	$C_8-N_2-C_{12}$	122.7(3)
O_2-Mo-S_3	154.2(1)	$C_9-N_2-C_{12}$	116.3(3)
O_2-Mo-S_4	87.5(1)	$N_2-C_9-C_{10}$	110.9(3)
$S_2-C_1-S_3$	112.7(2)	$N_2-C_{12}-C_{13}$	111.6(3)
$S_2-C_1-N_1$	123.7(2)	$C_{12}-C_{13}-C_{14}$	110.0(4)
		$C_9-C_{10}-C_{11}$	110.3(4)

TABLE X
Molecular dimensions in $Mo_2O_3(S_2CN(C_3H_7)_2)_4$ (B)

a) *bond lengths* (Å)			
Mo_1-O_1	1.666(12)	N_2-C_9	1.505(22)
Mo_2-O_2	1.676(12)	N_2-C_{12}	1.470(19)
Mo_1-O_{1-2}	1.870(13)	C_9-C_{10}	1.611(25)
Mo_2-O_{1-2}	1.856(13)	$C_{10}-C_{11}$	1.480(29)
Mo_1-S_1	2.515(6)	$C_{12}-C_{13}$	1.533(24)
Mo_1-S_2	2.440(5)	$C_{13}-C_{14}$	1.594(21)
Mo_1-S_3	2.491(5)	S_5-C_{15}	1.695(15)
Mo_1-S_4	2.669(7)	S_6-C_{15}	1.703(15)
Mo_2-S_5	2.687(5)	$C_{15}-N_3$	1.334(18)
Mo_2-S_6	2.491(5)	N_3-C_{16}	1.467(22)
Mo_2-S_7	2.536(7)	N_3-C_{19}	1.485(22)
Mo_2-S_8	2.440(6)	$C_{16}-C_{17}$	1.513(26)
S_1-C_1	1.681(16)	$C_{17}-C_{18}$	1.590(28)
S_2-C_1	1.762(16)	$C_{19}-C_{20}$	1.621(25)
C_1-N_1	1.344(21)	$C_{20}-C_{21}$	1.571(30)
N_1-C_2	1.460(22)	S_7-C_{22}	1.677(16)
N_1-C_5	1.478(21)	S_8-C_{22}	1.742(16)
C_2-C_3	1.621(26)	$C_{22}-N_4$	1.308(19)
C_3-C_4	1.472(27)	N_4-C_{23}	1.478(19)
C_5-C_6	1.343(34)	N_4-C_{26}	1.530(20)
C_6-C_7	1.420(38)	$C_{23}-C_{24}$	1.583(21)
S_3-C_8	1.674(16)	$C_{24}-C_{25}$	1.556(23)
S_4-C_8	1.706(15)	$C_{26}-C_{27}$	1.533(22)
C_8-N_2	1.335(19)	$C_{27}-C_{28}$	1.509(27)
b) *bond angles* (°)			
$O_1-Mo_1-O_{1-}$	102.7(5)	$N_1-C_2-C_3$	108.6(1.4)
$O_2-Mo_2-O_{1-2}$	103.1(6)	$N_1-C_5-C_6$	113.4(1.9)
$Mo_1-O_{1-2}-Mo_2$	178.1(7)	$C_2-N_1-C_5$	118.4(1.3)
$S_1-Mo_1-S_2$	70.9(2)	$C_2-C_3-C_4$	105.3(1.5)
$S_1-Mo_1-S_3$	96.3(2)	$C_5-C_6-C_7$	125.1(2.7)
$S_1-Mo_1-S_4$	84.1(2)	$S_3-C_8-S_4$	116.2(9)
$S_2-Mo_1-S_3$	155.9(2)	$S_3-C_8-N_2$	121.8(1.1)
$S_2-Mo_1-S_4$	90.5(2)	$S_4-C_8-N_2$	121.9(1.1)
$S_3-Mo_1-S_4$	67.5(2)	$C_8-N_2-C_9$	119.9(1.2)
$S_5-Mo_2-S_6$	67.7(2)	$C_8-N_2-C_{12}$	121.7(1.2)
$S_5-Mo_2-S_7$	82.3(2)	$N_2-C_9-C_{10}$	114.4(1.3)
$S_5-Mo_2-S_8$	87.2(2)	$N_2-C_{12}-C_{13}$	107.3(1.3)
$S_6-Mo_2-S_7$	95.8(2)	$C_9-N_2-C_{12}$	118.4(1.2)
$S_6-Mo_2-S_8$	153.2(2)	$C_9-C_{10}-C_{11}$	114.8(1.6)
$S_7-Mo_2-S_7$	70.6(2)	$C_{12}-C_{13}-C_{14}$	106.9(1.4)
$O_1-Mo_1-S_1$	94.6(4)	$S_5-C_{15}-S_6$	116.5(8)
$O_1-Mo_1-S_2$	108.8(4)	$S_5-C_{15}-N_3$	120.8(1.1)
$O_1-Mo_1-S_3$	92.1(4)	$S_6-C_{15}-N_3$	122.7(1.1)
$O_1-Mo_1-S_4$	159.2(4)	$C_{15}-N_3-C_{16}$	124.7(1.0)
$O_2-Mo_2-S_5$	159.7(5)	$N_3-C_{16}-C_{17}$	109.0(9)
$O_2-Mo_2-S_6$	92.8(4)	$N_3-C_{19}-C_{20}$	108.9(9)
$O_2-Mo_2-S_7$	94.5(4)	$C_{16}-N_3-C_{19}$	114.6(1.0)
$O_2-Mo_2-S_8$	110.8(4)	$C_{19}-C_{20}-C_{21}$	110.8(1.1)
$O_{1-2}-Mo_1-S_1$	157.6(4)	$S_7-C_{22}-S_8$	114.6(9)
$O_{1-2}-Mo_1-S_2$	89.8(4)	$S_7-C_{22}-N_4$	123.7(1.1)
$O_{1-2}-Mo_1-S_3$	97.2(4)	$S_8-C_{22}-N_4$	121.8(1.1)
$O_{1-2}-Mo_1-S_4$	84.6(4)	$C_{22}-N_4-C_{23}$	121.3(9)
$O_{1-2}-Mo_2-S_5$	85.4(4)	$C_{22}-N_4-C_{26}$	121.3(1.0)
$O_{1-2}-Mo_2-S_6$	95.9(4)	$N_4-C_{23}-C_{24}$	107.3(7)
$O_{1-2}-Mo_2-S_7$	158.3(4)	$N_4-C_{26}-C_{27}$	111.8(8)
$O_{1-2}-Mo_2-S_8$	91.1(4)	$C_{23}-N_4-C_{26}$	117.3(9)
$S_1-C_1-S_2$	113.3(9)	$C_{23}-C_{24}-C_{25}$	106.1(9)
$S_1-C_1-N_1$	124.3(1.2)	$C_{26}-C_{27}-C_{28}$	110.5(1.0)
$S_2-C_1-N_1$	122.4(1.2)	$C_{15}-N_3-C_{19}$	120.6(1.0)
$C_1-N_1-C_2$	120.8(1.3)	$C_{16}-C_{17}-C_{18}$	108.8(1.1)
$C_1-N_1-C_5$	120.5(1.3)		

the $Mo_2O_3S_8$ skeleton are nearly identical in both compounds. The previously reported trend in a lengthening of the Mo–S bonds trans to oxygen atoms is still observed. Other distances observed in the ligands are similar in both dithiocarbamates. The C–S bond lengths are equal within three standard deviations and the short C–N bond indicates a high degree of double bond character. The C–C bond lengths and angles compare favourably with accepted values.

The geometries of the complexes are shown in Figure 1A and 1B for the molybdenum VI and V complexes, respectively. Significant bond lengths and angles in both molecules are listed in Tables IX and X. There are no important intermolecular contacts.

II *Oxo-bis-di-n-propyldithiocarbamato molybdenum IV*

The molecular geometry and numbering scheme adopted are shown in Figure 1C. Important bond lengths and angles are listed in Table XI. In the solid state, the complex adopts a square pyramidal

TABLE XI
Molecular dimensions in $MoO(S_2CN(C_3H_7)_2)_2$ (C)

a) *bond lengths* (Å)			
MO–O	1.664(8)	C_5-C_6	1.602(14)
$Mo-S_1$	2.412(2)	C_6-C_7	1.541(26)
$Mo-S_2$	2.418(2)	S_3-C_8	1.724(8)
$Mo-S_3$	2.413(2)	S_4-C_8	1.726(9)
$Mo-S_4$	2.410(2)	N_2-C_8	1.295(9)
S_1-C_1	1.729(8)	N_2-C_9	1.582(17)
S_2-C_1	1.732(8)	N_2-C_{12}	1.504(12)
N_1-C_1	1.312(9)	C_9-C_{10}	1.396(28)
N_1-C_2	1.474(11)	$C_{10}-C_{11}$	1.745(22)
N_1-C_5	1.474(13)	$C_{12}-C_{13}$	1.508(18)
$C2-C_3$	1.550(13)	$C_{13}-C_{14}$	1.560(16)
C_3-C_4	1.526(18)		
b) *bond angles* (°)			
$O-Mo-S_1$	108.3(2)	$N_1-C_2-C_3$	110.0(5)
$O-Mo-S_2$	109.6(2)	N_1-C-C_6	107.4(6)
$O-Mo-S_3$	111.7(2)	$C_2-N_1-C_5$	118.0(6)
$O-Mo-S_4$	110.3(2)	$C_2-C_3-C_4$	107.4(7)
S_1-Mo-S_2	72.4(1)	$C_5-C_6-C_7$	106.5(9)
S_1-Mo-S_3	139.9(1)	$S_3-C_8-S_4$	111.1(2)
S_1-Mo-S_4	93.0(1)	$S_3-C_8-N_2$	125.6(4)
S_2-Mo-S_3	95.0(1)	$S_4-C_8-N_2$	123.0(4)
S_2-Mo-S_4	140.1(1)	$C_8-N_2-C_9$	119.4(8)
S_3-Mo-S_4	72.3(1)	$C_8-N_2-C_{12}$	122.3(6)
$S_1-C_1-S_2$	111.1(2)	$N_2-C_9-C_{10}$	98.9(8)
$S_1-C_1-N_1$	124.1(3)	$N_2-C_{12}-C_{13}$	109.7(6)
$S_2-C_1-N_1$	124.6(3)	$C_9-N_2-C_{12}$	118.1(7)
$C_1-N_1-C_2$	121.0(5)	$C_9-C_{10}-C_{11}$	98.2(9)
$C_1-N_1-C_5$	120.9(6)	$C_{12}-C_{13}-C_{14}$	107.0(7)

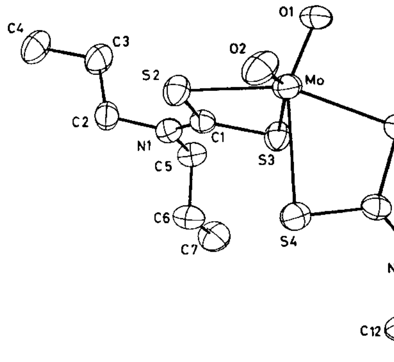


FIGURE 1a Molecular geometry of $MoO_2(S_2CN(C_3H_7)_2)_2$.

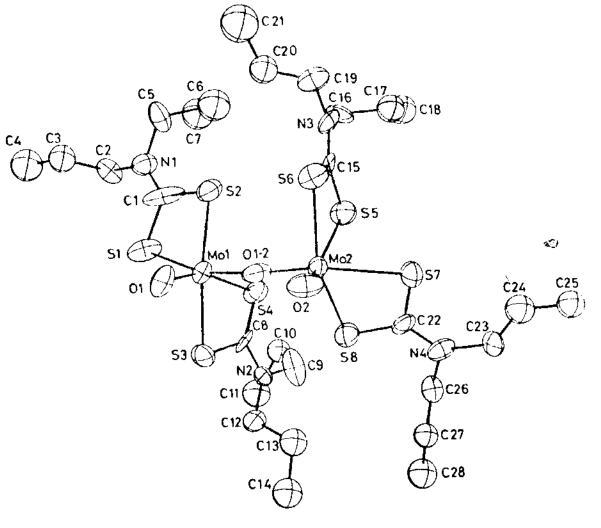


FIGURE 1b Molecular geometry of $Mo_2O_3(S_2CN(C_3H_7)_2)_4$.

geometry. The basal plane of the pyramid is formed by the four sulfur atoms. The molybdenum atom lies 0.83 Å above this plane and the oxygen atom occupies the summit. The Mo-O line is perpendicular to the least-squares plane formed by the four sulfur atoms. There are no steric interactions in this complex, so that the four Mo–S bond lengths are identical and slightly shorter than those observed for trans sulfur atoms in the two previous complexes. Similarly, the C–S and C–N bond lengths are respectively identical in both ligands. The C–C bond lengths compare favourably with accepted values.

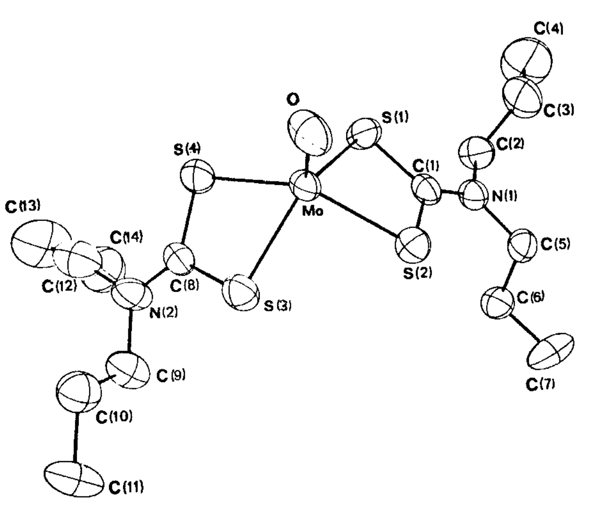


FIGURE 1c Molecular geometry of $MoO(S_2CN(CH_7)_2)_2$.

Finally the Mo–O bond is slightly shorter than that observed in the other complexes.

The only intermolecular contact shorter than 3.5 Å is between the oxygen atom and carbon C3 of a neighbouring molecule.

DISCUSSION

Average bond lengths and standard deviations for the three molecules are assembled in Table XII.

TABLE XII
Average bond lengths and deviation from the mean in the three complexes.

a) Environment of the metal atoms

	A	B	C
Mo–O_t	1.695(1)	1.671(4)	1.664(8)
Mo–O_b		1.863(7)	
Mo–S_{ct}	2.452(5)	2.465(14)	2.414(2)
Mo–S_{tt}	2.651(18)	2.678(5)	
Mo–S_{tb}		2.526(6)	

O_b = bridging oxygen
O_t = terminal oxygen
S_{ct} = sulfur cis to O_t
S_{tt} = sulfur trans to O_t
S_{tb} = sulfur trans to O_b

b) Intraligand bond lengths.

	A	B	C
S–C_1	1.723(6)	1.705(12)	1.728(2)
N–C_1	1.318(9)	1.33 (6)	1.303(5)
N–C_2	1.477(6)	1.484(8)	1.508(25)
C_2–C_3	1.524(4)	1.534(15)	1.553(14)

The values of the Mo–O bond lengths observed in the molybdenum VI dioxo complex (A) and molybdenum V complex (B) are in good agreement with previously reported values. The only structure of a mono-oxo molybdenum IV complex previously reported is that of oxo-dichloro-tris (dimethylphenylphosphine) molybdenum IV, in which a Mo–O bond length of 1.676(7) Å is reported.[20] This value does not differ significantly from the length of 1.664(8) Å we observe; the difference is about two standard deviations. However, the deviation is such that it is consistent with a shortening of the Mo–O bond due to a change of coordination from six to five: such a change would be expected to induce a slight shortening of the bond lengths.

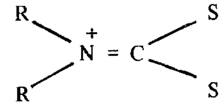
The usefulness of Cotton and Wing's[21] correlation between Mo–O bond lengths and bond orders in oxomolybdenum compounds has long been recognised.[22] In the present instance, it would be particularly interesting to determine the bond order for the molybdenum IV complex (C). It has recently been shown that oxomolybdenum IV complexes similar to (C) probably undergo oxidative addition with a number of unsaturated ligands.[5] According to Tolman's rules,[23] this requires the molybdenum IV oxo complex to be diamagnetic and to present a sixteen electrons configuration. Referring to Cotton and Wing's correlation, we find a bond order of approximately 3.0 for compound (C). In turn, this implies an electron configuration of sixteen for the molybdenum IV complex (C). It thus appears that this correlation can still give useful indications for oxo-molybdenum IV complexes.

Another point of interest is the possibility of trans influence to explain the lengthening of the Mo–S_{tt} bond lengths. Since there are large steric hindrances between the sulfur atoms, as shown by the short S–S contact distances (See Table XIII) and the deformation of the Mo-ligand angles from the ideal ninety degrees, it is not clear whether this is indeed the case. However, one notices that in the molybdenum V compound, the Mo–S_{tb} bond length has a value intermediate to that of Mo–S_{ct} and Mo–S_{tt}. Since the Mo–O_b bond is weaker than the Mo–O_t bond by a factor of about two, one would expect less trans influence by the former oxygen. Thus, despite the fact that there exist strong steric interactions between the sulfur atoms, one cannot entirely rule out the occurence of trans influence on the basis of the present data.

TABLE XIII
Intramolecular contact distances in the three complexes (Å)

A $MoO_2(S_2CN(C_3H_7)_2)_2$			
$O_1 \ldots O_2$	2.702	$O_2 \ldots S_2$	2.960
$O_1 \ldots S_1$	2.883	$O_2 \ldots S_4$	3.106
$O_1 \ldots S_2$	3.338	$S_1 \ldots S_3$	3.405
$O_1 \ldots S_3$	3.205	$S_2 \ldots S_4$	3.824
$O_2 \ldots S_1$	3.488	$S_3 \ldots S_4$	3.473
B $Mo_2O_3(S_2CN(C_3H_7)_2)_4$			
$O_1 \ldots O_{1-2}$	2.628	$O_2 \ldots O_{1-2}$	2.747
$O_1 \ldots S_1$	3.029	$O_2 \ldots S_6$	3.062
$O_1 \ldots S_2$	3.305	$O_2 \ldots S_7$	3.085
$O_1 \ldots S_3$	2.930	$O_2 \ldots S_8$	3.342
$O_{1-2} \ldots S_2$	3.091	$O_{1-2} \ldots S_5$	3.224
$O_{1-2} \ldots S_3$	3.213	$O_{1-2} \ldots S_6$	3.345
$O_{1-2} \ldots S_4$	3.121	$O_{1-2} \ldots S_8$	3.111
$S_1 \ldots S_3$	3.761	$S_5 \ldots S_7$	3.467
$S_1 \ldots S_4$	3.588	$S_5 \ldots S_8$	3.562
$S_2 \ldots S_4$	3.666	$S_6 \ldots S_7$	3.721
C $MoO(S_2CN(C_3H_7)_2)_2$			
$O \ldots S_1$	3.332	$O \ldots S_4$	3.374
$O \ldots S_2$	3.363	$S_1 \ldots S_4$	3.494
$O \ldots S_3$	3.403	$S_2 \ldots S_3$	3.559

Finally, one notices that the C_1–S and C_1–N bond lengths are equal in all complexes. The fact that both C–S bonds are identical within experimental errors along with the observation of the very short C_1–N bond confirms that the most important resonance form responsible for complex formation by the dithiocarbamates is



as it has previously been observed.

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