Preparation and Molecular Structure of Oxodihalogenobis(dialkyldithiocarbamato)molybdenum(VI) Complexes

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Bis(oxodialkyldithiocarbamato)molybdenum(VI) complexes react with concentrated hydrohalogenic acids to yield the novel compounds $[MoOX_2(S_2CNR_2)_2]$ (where X = F, Cl, or Br; R = Me, Et, or Pr^n). The crystal structure of the complex (I) $[MoOCl_2(S_2CNEt_2)_2]$ confirms that the compounds are seven-co-ordinate. Crystals are monoclinic, space group $P2_1/c$ with a = 8.900(2), b = 17.500(4), c = 12.703(3) Å, β = 110.16(3)°. The structure was refined to R 0.040 by use of 2 350 independent reflections measured by diffractometer. In order to establish the generality of the *cis–mer* configuration, the structure of the compound (II) $[MoOBr_2(S_2CNEt_2)_2]$ was also studied. Crystals are triclinic, space group $P\bar{1}$, with a = 9.952(3), b = 13.974(5), c = 7.548(3) Å, α = 75.69(3), β = 108.23(3), γ = 99.70(3)°. Its geometry is essentially the same as that of (I) and its structure was refined to R 0.056 by use of 3 081 independent reflections. I.r. and far-i.r. spectra are discussed.

DIALKYLDITHIOCARBAMATO(OXO)MOLYBDENUM complexes are known for a wide variety of oxidation states and environments. The molybdenum(VI) dioxo-complex has been known since 1939 [1] and good preparations have recently become available for the molybdenum(V) $Mo_2O_3L_4$ and the molybdenum(IV) $MoOL_2$ complexes.[2] Until recently, however, the chemistry of these species was almost nonexistent and it is only in the past few years that molybdenum(IV) compounds were shown to react with activated organic molecules,[3] or to dismute into $Mo_2O_4L_2$ molybdenum(V) and Mo_2L_6 molybdenum(III) complexes.[4] Similarly, molybdenum(V) complexes were shown to react with water to yield $Mo_2O_4L_2$ complexes and the dismutation of the former complexes into MoO_2L_2 and $MoOL_2$ species was demonstrated.[5] During the same period, Chatt and co-workers used the molybdenum(VI) complexes to prepare nitrido-complexes [6] and showed that one oxygen in the dioxo-compounds could be replaced by a hydrazo-group.[7] We now report the unexpected reactivity of the MoO_2^{2+} group towards the hydrohalogenic acids to yield $MoOX_2(dtc)_2$ compounds (dtc = dithiocarbamato). The compound $[MoOBr_2(S_2CNEt_2)_2]$ has already been mentioned in the literature.[8a]

RESULTS AND DISCUSSION

Molecular Structure of (I) $[MoOCl_2(S_2CNEt_2)_2]$.—The geometry of the complex is shown in Figure 1 and

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[1] L. Malatesta, *Gazzetta*, 1939, **69**, 752.

[2] (*a*) F. W. Moore and M. L. Larson, *Inorg. Chem.*, 1967, **6**, 998; (*b*) R. N. Jowitt and J. Mitchell, *J. Chem. Soc.* (*A*), 1969, 2632; 1970, 1702; (*c*) R. Barral, D. Bocard, I. Sereede Roch, and L. Sajus, *Tetrahedron Letters*, 1972, **17**, 1693.

[3] P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Amer. Chem. Soc.*, 1972, **94**, 8640.

[4] P. C. H. Mitchell and R. D. Scarle, *J.C.S. Dalton*, 1975, 110.

[5] W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, 1974, **13**, 1100.

[6] J. Chatt and J. R. Dilworth, *J.C.S. Chem. Comm.*, 1974, 517.

[7] M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Organometallic Chem.*, 1974, **73**, C59.

[8] (*a*) A. Nieuwpoort, Paper presented at 1st. Internat. Conf. Chem. Uses Molybdenum, 1973, Reading; (b) L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Co-ordination Chem.*, 1974, **3**, 227.

TABLE 1

Fractional atomic co-ordinates and anisotropic temperature factors * for $[MoOCl_2(S_2CNEt_2)_2]$, (I). Heavy atom co-ordinates are $\times 10^5$ and H atom co-ordinates $\times 10^3$

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	19 555(5)	13 416(2)	23 628(3)	885(7)	198(1)	359(3)	−31(2)	134(3)	−5(1)
S(1)	14 783(17)	−285(8)	18 607(13)	1 225(23)	218(5)	398(10)	−145(8)	209(13)	−60(5)
S(2)	26 891(19)	5 079(8)	40 823(11)	1 393(25)	185(5)	357(10)	−105(8)	176(12)	−27(5)
S(3)	33 273(19)	21 488(7)	40 576(11)	1 396(25)	175(5)	349(10)	−53(8)	229(13)	−24(5)
S(4)	24 829(16)	26 519(7)	18 234(11)	1 003(21)	201(5)	388(10)	2(7)	130(11)	39(5)
Cl(1)	10 930(19)	13 175(10)	3 390(11)	1 324(25)	378(7)	345(10)	−143(10)	38(13)	−3(7)
Cl(2)	47 481(15)	10 821(8)	24 197(11)	884(21)	276(5)	527(10)	58(7)	236(11)	−25(6)
O	1 142(43)	15 299(22)	24 245(35)	725(54)	283(14)	612(32)	79(22)	258(32)	28(17)
N(1)	20 521(54)	−9 795(28)	36 216(40)	976(71)	193(15)	560(40)	−23(28)	217(43)	−6(21)
N(2)	39 880(56)	35 727(26)	35 636(43)	1 018(71)	175(15)	610(41)	16(28)	266(43)	2(20)
C(1)	20 750(63)	−2 849(32)	32 453(48)	757(78)	238(21)	495(43)	−61(31)	216(45)	−41(23)
C(2)	15 108(82)	−16 313(37)	28 422(65)	1 332(108)	174(21)	807(61)	−200(38)	333(65)	−62(28)
C(3)	28 896(109)	−20 498(50)	26 598(87)	2 052(158)	324(30)	1 319(97)	−29(54)	936(99)	−170(44)
C(4)	25 606(80)	−11 461(39)	48 269(61)	1 049(100)	221(23)	698(56)	−7(37)	73(59)	25(28)
C(5)	11 819(109)	−12 276(56)	52 424(67)	1 872(145)	523(42)	528(57)	−227(57)	209(74)	39(39)
C(6)	33 684(63)	29 086(29)	32 004(47)	811(78)	181(19)	513(43)	32(30)	295(46)	23(22)
C(7)	47 794(87)	37 326(41)	47 615(59)	1 600(117)	242(23)	605(52)	−104(42)	376(63)	−115(28)
C(8)	65 651(95)	36 933(63)	51 095(74)	1 219(113)	676(47)	607(61)	−278(59)	90(65)	−69(44)
C(9)	38 677(82)	42 010(39)	27 610(65)	1 254(105)	213(22)	875(61)	−72(39)	346(65)	51(30)
C(10)	23 296(100)	46 510(48)	25 723(86)	1 369(126)	276(28)	1 388(104)	55(45)	240(91)	164(44)

	x/a	y/b	z/c	$B/Å^2$		x/a	y/b	z/c	$B/Å^2$
H(1,2) †	100(11)	−193(5)	317(7)	4.30	H(1,7)	439(10)	418(5)	490(7)	4.46
H(2,2)	41(11)	−140(4)	224(8)	4.30	H(2,7)	457(10)	341(5)	535(7)	4.46
H(1,3)	324(13)	−161(7)	216(9)	7.41	H(1,8)	698(15)	392(7)	464(10)	7.18
H(2,3)	256(14)	−238(7)	229(9)	7.41	H(2,8)	665(13)	308(7)	496(9)	7.18
H(3,3)	372(13)	−213(7)	341(9)	7.41	H(3,8)	694(14)	385(6)	577(11)	7.18
H(1,4)	317(11)	−153(5)	487(8)	4.20	H(1,9)	469(11)	461(5)	310(7)	4.82
H(2,4)	334(11)	−76(5)	519(7)	4.20	H(2,9)	412(11)	400(5)	205(8)	4.82
H(1,5)	61(13)	−160(6)	493(9)	6.73	H(1,10)	162(14)	434(6)	205(10)	7.32
H(2,5)	49(13)	−73(6)	507(8)	6.73	H(2,10)	230(14)	499(7)	217(9)	7.32
H(3,5)	157(14)	−135(6)	596(11)	6.73	H(3,10)	236(15)	468(7)	328(10)	7.32

* In the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$. † The second number is that of the C atom to which H is attached.

positional parameters in Table 1. The molybdenum atom is seven-co-ordinate. The apices of the deformed pentagonal bipyramid surrounding the metal are occupied by the oxygen atom and the chlorine atom Cl(2). The remaining chlorine and the two dithiocarbamato-ligands are roughly coplanar.

The Mo–O bond length [1.701(4) Å] is similar to that [1.695(5) Å] in the parent dioxo-compound.[8b] However, there are large *trans*-effects in the molecule as evidenced by the Mo–Cl bond lengths: the planar Mo–Cl(1) bond is 0.09 Å shorter than the axial Mo–Cl(2) bond, a result which parallels that obtained for $[MoOCl_2(PMe_2Ph)_3]$.[9]

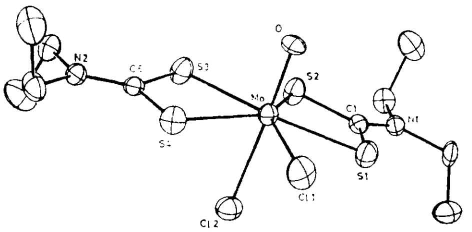

FIGURE 1 Molecular geometry of $[MoOCl_2(S_2CNEt_2)_2]$, (I)

Finally one may notice that the molecule is remarkably symmetric. There are two pairs of Mo–S distances: Mo–S(1) 2.481(1) and Mo–S(4) 2.483(1) Å, and Mo–S(2) 2.519(1) and Mo–S(3) 2.511(1) Å. Since the oxygen, molybdenum, and the two chlorine atoms are nearly coplanar, the virtual symmetry of the molecule appears close to C_s.

Distances and angles in the dithiocarbamato-ligands (Table 2) are similar to those reported previously.

TABLE 2

Molecular dimensions in (I), with standard deviations in parentheses

(*a*) Bond lengths (Å)

Mo–O	1.701(4)	N(1)–C(4)	1.469(7)
Mo–Cl(1)	2.417(1)	C(2)–C(3)	1.511(13)
Mo–Cl(2)	2.504(1)	C(4)–C(5)	1.511(13)
Mo–S(1)	2.481(1)	S(3)–C(6)	1.727(6)
Mo–S(2)	2.519(1)	S(4)–C(6)	1.713(6)
Mo–S(3)	2.511(1)	C(6)–N(2)	1.302(7)
Mo–S(4)	2.483(1)	N(2)–C(7)	1.463(8)
S(1)–C(1)	1.710(6)	N(2)–C(9)	1.480(9)
S(2)–C(1)	1.720(6)	C(7)–C(8)	1.506(11)
C(1)–N(1)	1.310(8)	C(9)–C(10)	1.525(11)
N(1)–C(2)	1.473(8)	Mean C–H	0.93 ± 0.20 *

(*b*) Important angles (°)

O–Mo–Cl(1)	95.4(1)	Cl(1)–Mo–Cl(2)	88.6(1)
O–Mo–Cl(2)	175.9(1)	Cl(2)–Mo–S(1)	85.0(1)
O–Mo–S(1)	96.7(1)	Cl(2)–Mo–S(2)	84.9(1)
O–Mo–S(2)	92.2(1)	Cl(2)–Mo–S(3)	83.8(1)
O–Mo–S(3)	92.5(1)	Cl(2)–Mo–S(4)	84.0(1)
O–Mo–S(4)	96.4(1)	S(1)–Mo–S(2)	68.5(1)
Cl(1)–Mo–S(1)	75.3(1)	S(2)–Mo–S(3)	71.2(1)
Cl(1)–Mo–S(4)	75.1(1)	S(3)–Mo–S(4)	68.6(1)

* Maximum deviation from the mean.

Structures of the Other Compounds.—The presence of an axial oxygen atom facilitates the formation of multiple

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[9] L. Manojlović-Muir, *J. Chem. Soc.* (*A*), 1971, 2796; A. V. Butcher and J. Chatt, *ibid.*, 1970, 2652.

Mo–O bonds.[10] For this reason, isomers containing the oxygen in the plane of the bipyramid are not considered.

There are three possible isomers [(A)—(C)] for axial oxygen in a seven-co-ordinate species of the type [$MoOX_2(S_2CNR_2)_2$]. Species (B) and (C) are not favoured for steric reasons. Species (A) is probably more stable since it reduces steric hindrance between the two halogens as well as between the sulphur and halogen atoms. All compounds would thus be expected to have structure (A).

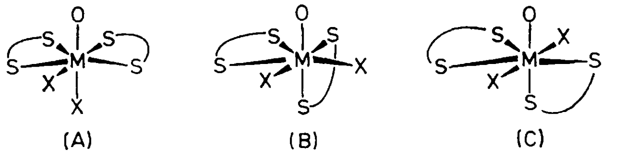

Table 3

Fractional atomic co-ordinates and anisotropic temperature factors * for [$MoOBr_2(S_2CNEt_2)_2$], (II). Heavy-atom co-ordinates are × 10^5, and the H atom co-ordinates × 10^3

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	10 841(7)	31 747(5)	10 716(8)	562(7)	286(3)	1 102(14)	−34(3)	315(7)	−148(5)
O	−3 165(61)	37 594(44)	−2 957(91)	741(71)	455(35)	2 017(148)	112(40)	208(80)	−67(57)
Br(1)	18 346(10)	29 471(7)	−17 212(14)	1 384(14)	567(5)	1 602(20)	−187(7)	1 000(14)	−413(8)
Br(2)	33 424(8)	21 818(5)	34 100(14)	624(10)	337(5)	2 305(23)	25(5)	103(11)	−94(7)
S(1)	−175(22)	14 937(14)	5 427(30)	809(23)	401(10)	1 752(45)	−138(13)	575(27)	−407(19)
S(2)	−1 410(22)	22 973(14)	35 361(30)	919(26)	404(11)	1 663(45)	−175(14)	739(28)	−327(17)
S(3)	16 399(25)	41 686(14)	35 633(30)	1 104(27)	386(10)	1 517(43)	−198(14)	724(28)	−335(17)
S(4)	28 834(22)	45 885(14)	5 802(30)	953(27)	347(10)	1 691(45)	−131(13)	722(28)	−202(17)
N(1)	−14 562(69)	5 057(45)	30 231(104)	439(69)	194(31)	1 546(149)	−21(37)	396(82)	−78(54)
N(2)	35 713(78)	57 285(52)	32 130(109)	686(80)	278(37)	1 439(158)	−93(42)	310(89)	−284(61)
C(1)	−6 783(69)	13 187(52)	24 545(109)	598(76)	493(43)	2 236(179)	−41(44)	399(93)	−359(71)
C(2)	−19 933(99)	4 149(71)	46 941(138)	1 286(118)	692(57)	2 886(234)	−120(65)	1 139(139)	−164(93)
C(3)	−34 609(135)	7 199(122)	40 889(198)	1 445(179)	1 485(123)	4 036(380)	389(119)	1 173(216)	−120(165)
C(4)	−18 101(97)	−3 403(61)	20 356(144)	1 078(113)	460(46)	3 416(262)	−111(56)	499(140)	−484(89)
C(5)	−30 431(125)	−2 372(97)	3 501(239)	1 338(149)	1 034(95)	6 287(501)	57(91)	−136(213)	−1 420(182)
C(6)	28 106(76)	49 656(50)	25 215(102)	980(91)	383(38)	1 787(168)	21(46)	374(101)	−204(63)
C(7)	35 114(110)	59 253(78)	50 360(148)	1 370(135)	789(69)	3 014(260)	10(76)	175(148)	−710(109)
C(8)	23 751(170)	65 566(134)	46 864(224)	3 163(297)	1 583(147)	4 555(440)	1 077(175)	−274(279)	−1 209(203)
C(9)	45 604(91)	63 753(65)	22 463(156)	916(104)	587(54)	3 626(278)	−208(59)	612(138)	−323(100)
C(10)	39 019(148)	72 661(101)	8 472(273)	2 154(213)	889(95)	7 418(669)	117(109)	1 538(302)	1 195(210)

	x/a	y/b	z/c	B/Å^2		x/a	y/b	z/c	B/Å^2
H(1,2)	−222(13)	−39(9)	491(18)	4.30	H(2,5)	−324(19)	−93(15)	−46(27)	9.20
H(2,2)	−115(14)	83(9)	562(18)	4.30	H(1,7)	287(15)	532(10)	557(19)	5.10
H(1,3)	−399(20)	−8(14)	343(27)	8.00	H(2,7)	465(15)	622(10)	543(19)	5.10
H(2,3)	−360(19)	131(14)	330(27)	8.00	H(1,8)	209(22)	731(16)	361(32)	11.10
H(3,3)	−351(18)	71(12)	591(25)	8.00	H(2,8)	242(21)	623(15)	691(31)	11.10
H(1,4)	−105(13)	−28(8)	156(17)	3.90	H(1,9)	536(14)	643(9)	354(18)	4.30
H(2,4)	−233(13)	−97(9)	312(17)	3.90	H(2,9)	483(13)	587(10)	174(18)	4.30
H(1,5)	−368(21)	−36(13)	120(26)	9.20	H(1,10)	421(26)	783(18)	−17(36)	12.60

* See footnote to Table 1.

Powder photographs did not permit us to establish the isomorphism of the diethyldithiocarbamato(dihalogeno)-complexes: the powder spectra of the fluoride is not rigorously identical to that of the chloride and that of the bromide is obviously different. In an attempt to show the generality of the *cis–mer* configuration, the structure of a bromo-complex (II) was studied, and final positional parameters are listed in Table 3.

The structure of [$MoOBr_2(S_2CNEt_2)_2$] (II) is indeed very similar to that of the chloride (I). The *trans*-effect is more pronounced than in (I): the axial and equatorial Mo–Br bond lengths differ by 0.18 Å. The Mo–O bond length is much shorter, being 1.648(5) *vs.* 1.701(4) Å in (I). This is the only compound showing an Mo–O absorption at 960 cm^{-1}, all the others being near 948 cm^{-1}. It is thus reasonable to expect a shorter Mo–O bond in (II), although there seems to be no obvious reasons for this behaviour. Distances and angles for the bromo-complex (II) are listed in Table 4.

Table 4

Molecular dimensions in (II), with estimated standard deviations in parentheses

(*a*) Bond lengths (Å)

Mo–O	1.656(5)	N(1)–C(4)	1.486(12)
Mo–Br(1)	2.550(1)	C(2)–C(3)	1.490(17)
Mo–Br(2)	2.729(1)	C(4)–C(5)	1.462(15)
Mo–S(1)	2.490(2)	S(3)–C(6)	1.709(7)
Mo–S(2)	2.498(2)	S(4)–C(6)	1.700(9)
Mo–S(3)	2.481(2)	C(6)–N(2)	1.318(10)
Mo–S(4)	2.472(2)	N(2)–C(7)	1.489(15)
S(1)–Cl	1.715(9)	N(2)–C(9)	1.464(12)
S(2)–Cl	1.689(8)	C(7)–C(8)	1.470(22)
C(1)–N(1)	1.321(9)	C(9)–C(10)	1.512(16)
N(1)–C(2)	1.487(14)	Mean C–H	1.0 ± 0.3 *

(*b*) Important bond angles (°)

O–Mo–Br(1)	94.4(3)	Br(1)–Mo–Br(2)	87.1(1)
O–Mo–Br(2)	178.1(4)	Br(2)–Mo–S(1)	83.9(1)
O–Mo–S(1)	95.4(3)	Br(2)–Mo–S(2)	84.8(1)
O–Mo–S(2)	93.3(3)	Br(2)–Mo–S(3)	85.2(1)
O–Mo–S(3)	94.2(3)	Br(2)–Mo–S(4)	85.2(1)
O–Mo–S(4)	96.2(3)	S(1)–Mo–S(2)	68.4(1)
Br(1)–Mo–S(1)	75.1(1)	S(2)–Mo–S(3)	71.3(1)
Br(1)–Mo–S(4)	75.2(1)	S(3)–Mo–S(4)	68.6(1)

* Maximum deviation for the mean.

The similarity of the i.r. spectra and, more conclusively, the ^{19}F n.m.r. spectrum of the difluoro-complex (III)

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[10] F. A. Cotton, Paper presented at 1st Internat. Conf. Chem. Uses Molybdenum, 1973, Reading.

shows that the most probable structure for the fluoro-compounds is the same as that of the chloride and bromide. This spectrum shows two resonances at 12.96 and 12.11 p.p.m. downfield from trifluoroacetic acid. Since all isomers described above would have symmetry close to C_s, only isomer (A) would provide different electronic environments for the two fluorine atoms and thus give rise to two signals in the n.m.r. spectrum.

Spectroscopic Data.—The assignment of Mo–F stretching frequencies is straightforward, all compounds exhibiting two strong absorptions near 500 and 540 cm^{-1}. The intensity of these bands is nearly as large as that of the Mo–O absorption. Details of spectra and assignments are in Table 5.

Typical far-i.r. spectra are shown in Figure 2. The chlorides display a medium strong absorption near 295 cm^{-1}, in a region commonly associated with Mo–Cl stretch.[11] All compounds show a weak or medium intensity band near 350 cm^{-1}. This absorption is stronger in the chlorides and could be the second expected absorption. Good Raman spectra of the chlorides could not be obtained and it was not possible to assign unambiguously the second Mo–Cl stretch.

TABLE 5

I.r. and far-i.r. spectroscopic data and tentative band assignments for the [$MoOX_2(S_2CNR_2)_2$] complexes. Frequencies are in cm^{-1}

X	R	ν(Mo–O)	ν(Mo–X)	ν(Mo–S)	Other bands
F	Me	956vs	534vs, 492vs	375s	355sh, 178s
	Et	945s	548vs, 506vs	365s, 360s	350sh, 152s
	Pr^n	948vs	543vs, 503vs	370s	152s
Cl	Me	950vs	296s	370s	355vs, 248vs, 236vs, 163m, 135sh
	Et	947vs	294s	368s	355vs, 248s, 230vs, 145ms, 133s
	Pr^n	947vs	294s	372s	358s, 245sh, 232s, 153ms, 124ms
Br	Me	948vs	225s, 204m	368s	354m, 181m, 150vs
	Et	960vs	226s, 204ms	368s	352sh, 180sh, 139vs,
	Pr^n	945vs	228vs, 195ms	370vs	353sh, 182m 148s

s = strong, m = medium, v = very, sh = shoulder.

In the spectra of the fluorides, the low-frequency absorption has somewhat lower intensity than the high-frequency band and similar features were sought in the spectra of the bromides. A strong band is thus found near 225 cm^{-1} and a medium absorption near 200 cm^{-1}. In order to confirm this interpretation, the Raman spectrum of the ethyl bromide was obtained. For a C_s symmetry molecule, two A' symmetry absorptions are expected, one corresponding to in-phase elongation of the Mo–X bond, the other to out-of-phase stretch. The Raman spectrum is thus expected to show higher intensity for the former, whereas the reverse is true in the i.r. The fact that the Raman spectrum indeed exhibits a strong absorption at 206 and a medium intensity band at 229 cm^{-1} confirms our interpretation for the far-i.r. spectrum. This is also in good agreement with Nieuwpoort's interpretation.[8a] In view of the foregoing discussion, the low-frequency absorptions are assigned to the in-phase Mo–X elongation and the high-frequency band, to the out-of-phase Mo–X vibration.

Figure 2 shows that all complexes exhibit common bands near 375 and 150 cm^{-1}, the first assigned to Mo–S stretch,[12] the second to a ligand deformation mode.

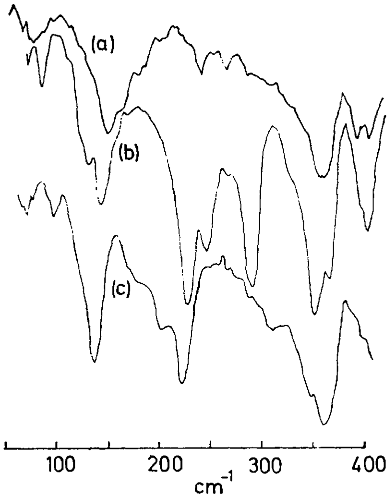

FIGURE 2 Typical far-i.r. spectra of the oxodihalogeno-complexes. Spectra of the diethyldithiocarbamato-complexes are shown: (*a*) fluoro-, (*b*) chloro-, and (*c*) bromo-complex

The origin of two strong bands near 215 cm^{-1} in the spectra of the chlorides is unknown. They could be linked to Cl–Mo–Cl [11] or, as has been suggested, O–Mo–Cl deformation modes.[12] Similar absorptions could be masked by the Mo–S stretch in the spectra of the fluorides. No attempts were made to assign similar bands in the spectra of the bromides.

The present work has extended knowledge of the reactivity of dioxomolybdenum(VI) complexes, and the importance of resonance forms such as Mo$^+$–O$^-$ in describing the dioxo-species [10] is clearly demonstrated. The reaction, however, is so far limited to the dithiocarbamates: all attempts to prepare similar complexes from the acetylacetonate or the L-cysteinate have failed. The high basicity of the terminal oxygen atoms may thus depend on the high electron-density available on the metal from the electron-rich dithiocarbamato-ligands.

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[11] K. Nakamoto, in 'Co-ordination Chemistry,' ed. A. E. Martell, A.C.S. Monograph 168, Van Nostrand–Reinhold, New York, 1971, p. 165; D. M. Adams, in 'Metal–Ligand and Related Vibrations,' Arnold, London, 1967, p. 61; J. R. Ferraro, in 'Low-frequency Vibrations of Inorganic and Coordination Compounds,' Plenum, New York, 1971.

[12] R. Kergoat and J. E. Guerchais, *Rev. Chim. minérale*, 1973, **10**, 585.

EXPERIMENTAL

The ^{19}F n.m.r. spectrum was obtained on a Varian XL 100 spectrometer, with trifluoroacetic acid as external standard. I.r. spectra (4 000—400 cm^{-1}) were measured on a Beckman IR 12 spectrometer by use of KBr pellets. Far-i.r. spectra were recorded (50—420 cm^{-1}) with a Polytec FIR 30 Fourier-transform apparatus in polyethylene discs using 3 mg of each compound. The spectrum of polyethylene itself was subtracted by use of an identical polyethylene pellet. The Raman spectrum of [$MoOBr_2(S_2CNEt_2)_2$] was recorded on a Phi Coderg apparatus, by use of a 150 mW helium–neon laser.

All chemicals were analytical grade and used without further purification. The molybdenum dioxodithiocarbamates were prepared following published procedures.[2a]

Preparation of the Complexes.—(*a*) *Diethyl- and di-n-propyl-dithiocarbamato chloro and bromo complexes.* Addition of concentrated acid (1.0 cm^3) to a solution of 2.0 g of the appropriate dioxo-complex caused an immediate colour change from orange to light yellow. The complexes crystallized when the solution was set aside and were recrystallized from dichloromethane–diethyl ether to remove some co-crystallized acetone.

(*b*) *Diethyl- and di-n-propyl-dithiocarbamato fluoro complexes.* Attempted preparation of the fluorides in a similar manner gave poor yields. These were improved by stirring a suspension of the desired oxo-complex in 4 : 1 hexane–diethyl ether previously saturated with concentrated hydrogen fluoride, until all the dioxo complex had reacted (24—48 h).

(*c*) *Dioxobis(dimethyldithiocarbamato)-derivatives.* Because of the insolubility of the methyldithiocarbamato-product, all complexes were prepared by prolonged stirring (up to 72 h) of the dioxo-complex suspended in CH_2Cl_2 containing the desired hydrohalogenic acid (1 ml). The removal of dioxo-complex was controlled by i.r. and stirring was continued for 24 h after no residual dioxo-complex was shown to remain.

Analytical Results.—These are listed in Table 6, and are compatible with the formulation of the complexes as [$MoOX_2(S_2CNR_2)_2$]. The low values obtained for the propyl and ethyl fluoro-compounds probably arise from their instability. This is also true for some of the methyl derivatives, whose insolubility prevented further purification.

TABLE 6

Analytical results (%) for the compounds $MoOX_2(S_2CNR_2)_2$

Compound No.	X	R	C	H	N	X
(III)	F	Me	17.5(18.4)	3.1(3.1)	7.5(7.2)	9.9(9.7)
	F	Et	27.6(26.9)	4.2(4.5)	6.2(6.3)	7.5(8.5)
	F	Pr^n	33.2(33.5)	5.6(5.6)	5.6(5.6)	5.4(7.6)
(I)	Cl	Me	17.0(16.8)	2.9(2.9)	6.7(6.6)	18.8(16.8)
	Cl	Et	25.6(25.0)	4.1(4.2)	5.8(5.9)	15.1(14.8)
	Cl	Pr^n	31.4(31.4)	5.1(5.3)	5.2(5.2)	13.2(13.2)
(II)	Br	Me	14.2(14.1)	2.4(2.4)	5.9(5.5)	28.4(31.2)
	Br	Et	21.6(21.1)	3.6(3.6)	4.7(4.9)	28.1(28.1)
	Br	Pr^n	27.0(26.9)	4.5(4.5)	4.7(4.5)	25.6(25.6)

Crystal Structure Determinations of (I) *and* (II)

Suitable crystals were obtained by slow evaporation of dichloromethane solutions of the complexes.

(*a*) *Oxodichlorobis(diethyldithiocarbamato)molybdenum.*—*Crystal Data.* $C_{10}H_{20}Cl_2MoN_2OS_2$, Monoclinic, $M = 479$, $a = 8.900(2)$, $b = 17.500(4)$, $c = 12.703(3)$ Å, $\beta = 110.16(3)°$, $U = 1\,978.5$ Å^3, $F(000) = 968$. $D_m = 1.61$ g cm^{-3}, $Z = 4$, $D_c = 1.608$ g cm^{-3}. Space group $P2_1/c$. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; μ(Mo-K_α) = 13.18 cm^{-1}.

Preliminary precession photographs enabled determination of the space group. Data collection and structure refinement were conducted as described previously by use of a Picker diffractometer and Mo-K_α radiation.[8] A spherical crystal fragment of radius *ca.* 110 μm was used for measurement of the intensities of 3 645 reflections in the range $6° < 2\theta < 50°$, with a scan range 1.6° and a 2θ scan speed 2.0° min^{-1}. Backgrounds were measured for 10 s at each end of the scan. 2 350 Of the recorded intensities having $I > 3\sigma(I)$ were used to solve the structure by conventional Patterson and Fourier methods and for the least-squares refinement. All heavy atoms were refined with anisotropic temperature factors and hydrogen atoms were included in the final least-squares cycles to yield R 0.040. The corresponding weighted factor R' was 0.060. A p value of 0.08 was employed in the weighting scheme [13] and the standard deviation of a unit weight observation was 1.14. Observed and computed structure factor amplitudes for both compounds are listed in Supplementary Publication No. SUP 21542 (15 pp., 1 microfiche).* No absorption corrections were applied in view of the small crystal dimensions and linear absorption coefficient.

(*b*) *Oxodibromobis(diethyldithiocarbamato)molybdenum*, (II). The crystal structure of (II) was similarly determined by use of a Philips PW 1 100 diffractometer and an approximately cubic crystal fragment (120 × 120 × 120 μm). Mo-K_α radiation was used since absorption effects would be less severe than fluorescence of the bromide.

Crystal Data. $C_{10}H_{20}Br_2MoN_2OS_2$, Triclinic, $M = 568$, $a = 9.952(3)$, $b = 13.974(5)$, $c = 7.548(3)$ Å, $\alpha = 75.69(3)$, $\beta = 108.23(3)$, $\gamma = 99.70(3)$ °, $\mu = 952.2$ Å^3, $F(000) = 556$. $D_m = 1.94$ g cm^{-3}, $Z = 2$, $D_c = 1.98$ g cm^{-3}. Space group $P\bar{1}$. μ(Mo-K_α) = 55.32 cm^{-1}.

3 081 Reflections having $I > 3\sigma(I)$ were collected in the range $4° < 2\theta < 60°$ with an ω scan speed of 2.5° min^{-1} and scan range of 2.0°. The structure was solved similarly and refined to R 0.056, and R' 0.073. A p value of 0.08 was used and the standard deviation of a unit weight observation was 1.19. No absorption corrections were applied.

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

[13] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.