Crystal and Molecular Structure of μ-Oxo-bis[oxobis-(*NN*-diethyldithiocarbamato)rhenium(v)]; A Complex with a Linear O–Re–O–Re–O System

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The crystal and molecular structure of the title compound have been determined from single-crystal *X*-ray diffractometer data. The crystals are monoclinic with unit-cell dimensions: $a = 16{\cdot}343$, $b = 14{\cdot}128$, $c = 15{\cdot}346$ Å, $\beta = 93° 56'$; space-group $P2_1/n$, and $Z = 4$. The structure was solved by Patterson and Fourier methods, and least-squares refinement, using 3523 independent reflections, has reached R 0·037.

The molecule contains a linear O–Re–O–Re–O system. Each rhenium atom is also bonded to two bidentate *NN*-diethyldithiocarbamato-ligands (dtc) to give a slightly distorted octahedral co-ordination. The dtc ligands attached to the two rhenium atoms are staggered *ca.* 40° relative to each other. The eight Re–S distances have a mean value of 2·438 Å, while the mean Re–O(bridging) and Re–O(terminal) distances are 1·910 and 1·722 Å respectively. Bonding in the O–Re–O–Re–O system is discussed.

UNTIL recently the only known dithiocarbamate complexes of rhenium in any oxidation state were of the type $ReCl_2(S_2CNR_2)$.[1] The crystal structures of these compounds were not determined, but from spectroscopic evidence the dithiocarbamato-ligands were deduced to be bidentate and the co-ordination about rhenium tetrahedral. Rowbottom and Wilkinson [2,3] have now prepared a series of oxo-, nitrido-, and imido-complexes of rhenium with dialkyldithiocarbamato-ligands. One of these was prepared by the reaction between $ReOCl_3(PPh_3)_2$ and sodium diethyldithiocarbamate monohydrate in acetone. While there was little doubt that the diethyldithiocarbamato-ligands (dtc) in this complex were bidentate, there was some uncertainty about the amount of oxygen in the complex. An *X*-ray structure determination has shown that the formula of the complex is $Re_2O_3(S_2CNEt_2)_4$ and that the molecule contains a novel linear O–Re–O–Re–O system.

A preliminary account of this work has already been published [3] and an independent preliminary communication has subsequently confirmed the result.[4]

EXPERIMENTAL

μ-Oxo-bis[oxobis-(*NN*-diethyldithiocarbamato)rhenium-(v)] crystallises from acetone as dark brown polyhedra.

Crystal Data.—$C_{20}H_{40}S_8N_4O_3Re_2$, $M = 1013{\cdot}5$, Monoclinic, $a = 16{\cdot}343$, $b = 14{\cdot}128$, $c = 15{\cdot}346$ Å, $\beta = 93° 56'$,* $U = 3534{\cdot}9$ Å^3, $D_m = 1{\cdot}90$ (by flotation), $Z = 4$, $D_c = 1{\cdot}91$ g cm^{-3}, $F(000) = 1960$. Space-group $P2_1/n$ (No. 14) from systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$. Cu-K_α *X*-radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 172·2 cm^{-1}.

The crystal chosen for intensity-data collection was a polyhedron with opposite faces 0·35—0·6 mm apart. Data were measured on a Siemens off-line automatic four-circle diffractometer, with Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter and a Na(Tl)I scintillation counter. A total of 3531 independent reflections (to $\theta = 50°$) were measured by use of the θ—2θ scan technique with a 'five-value' measuring procedure.[5a] Of these, 198 reflections were judged to be unobserved.[5a] The net count of the 507 reflection, measured as a reference every 50 reflections, did not vary significantly during the data collection (*ca.* 6 days). The data were scaled using the reference reflection and the Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The Crystal Structure Calculations System '*X*-ray '63', was used to solve and refine the structure.[5b] The calculations were carried out on the Imperial College IBM 7094 and the University of London CDC 6600 computers.

A three-dimensional Patterson synthesis revealed the positions of the two independent rhenium atoms, refinement of which gave R 0·31. The eight sulphur atoms were located from the resulting difference Fourier to reduce R to 0·174. Successive difference Fouriers showed the positions of all remaining non-hydrogen atoms, and block-diagonal least-squares refinement with isotropic thermal parameters gave $R = 0{\cdot}109$. When all atoms were refined with anisotropic thermal parameters R dropped to 0·079,

* The β value was incorrectly printed in the preliminary account [3] as 96° 56′.

[1] R. Colton, R. Levitus, and G. Wilkinson, *J. Chem. Soc.*, 1960, 5275.

[2] J. F. Rowbottom and G. Wilkinson, *J.C.S. Dalton*, 1972, 826.

[3] S. R. Fletcher, J. F. Rowbottom, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1970, 1572.

[4] D. G. Tisley, R. A. Walton, and D. L. Wills, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 523.

[5] (*a*) A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716; (*b*) '*X*-Ray '63' system of programs, J. M. Stewart, University of Maryland Technical Report TR-64-6.

but for several atoms the thermal parameters became 'non-positive definite'. An absorption correction was now applied since, although the crystal was not particularly anisotropic in shape, it was fairly large and its linear absorption coefficient was quite high. The correction was made according to the method of Busing and Levy [6] using a 12 × 12 × 12 grid, with crystal path-lengths determined by the vector-analysis procedure of Coppens *et al.*[7]

Refinement as previously reduced R to 0·043 and all atoms now had reasonable thermal parameters. A

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Re(1)	0·35759(2)	0·22594(3)	0·08114(2)
Re(2)	0·19123(2)	0·11252(3)	−0·07160(3)
O(1)	0·4329(4)	0·2769(5)	0·1499(5)
O(2)	0·2709(3)	0·1718(4)	0·0066(3)
O(3)	0·1279(4)	0·0550(5)	−0·1487(5)
S(11)	0·43012(15)	0·07988(17)	0·05927(15)
S(12)	0·32074(15)	0·11321(17)	0·19344(17)
S(21)	0·26799(16)	0·36461(18)	0·08460(16)
S(22)	0·38633(15)	0·32928(16)	−0·04022(15)
S(31)	0·10068(16)	0·10550(18)	0·04573(19)
S(32)	0·22037(15)	−0·03408(16)	0·00990(15)
S(41)	0·29315(15)	0·13568(16)	−0·18116(15)
S(42)	0·16783(16)	0·26646(16)	−0·13814(16)
C(11)	0·3885(5)	0·0358(7)	0·1516(6)
C(21)	0·3139(6)	0·4071(6)	−0·0044(6)
C(31)	0·1438(6)	−0·0029(7)	0·0774(6)
C(41)	0·2453(6)	0·2412(6)	−0·2050(6)
N(12)	0·4073(5)	−0·0491(6)	0·1848(5)
N(22)	0·2980(5)	0·4894(6)	−0·0421(5)
N(32)	0·1215(5)	−0·0535(6)	0·1413(5)
N(42)	0·2629(5)	0·2953(6)	−0·2707(5)
C(13)	0·3788(7)	−0·0772(9)	0·2681(8)
C(14)	0·4390(10)	−0·0628(16)	0·4313(9)
C(15)	0·4637(8)	−0·1148(8)	0·1425(8)
C(16)	0·4186(10)	−0·1936(10)	0·0991(10)
C(23)	0·2351(8)	0·5555(8)	−0·0057(8)
C(24)	0·1517(8)	0·5333(9)	−0·0518(10)
C(25)	0·3395(8)	0·5243(8)	−0·1184(7)
C(26)	0·4097(9)	0·5887(11)	−0·0921(11)
C(33)	0·0577(7)	−0·0210(10)	0·1978(8)
C(34)	0·0927(9)	0·0393(10)	0·2719(8)
C(35)	0·1542(8)	−0·1506(8)	0·1606(7)
C(36)	0·1017(14)	−0·2219(11)	0·1142(11)
C(43)	0·3254(8)	0·2725(7)	−0·3324(7)
C(44)	0·4076(8)	0·3166(9)	−0·3039(9)
C(45)	0·2177(7)	0·3888(6)	−0·2877(7)
C(46)	0·1443(9)	0·3765(10)	−0·3464(9)

The diethyldithiocarbamato-ligands are composed of atoms with suffixes of the type (*mn*), where *m* is constant within the same ligand.

difference Fourier now showed the positions of all 40 hydrogen atoms, and these were assigned the isotropic temperature factors of their parent atoms. When these were included in least-squares refinement as a 'fixed contribution' R was reduced to 0·042. At this point, eight strong reflections thought to be suffering from extinction were removed from refinement which converged to give $R = 0{\cdot}037$. In the final stages of refinement a weighting scheme of the type suggested by Hughes [8] was used, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 70$ found to be optimum. Application of the weighting scheme left R unchanged at 0·037 but the standard deviations were reduced by *ca.* 20%. The function minimised in the least-squares refinement was $\Sigma w(F_o - F_c)^2$. The atomic scattering factors were taken from ref. 9 and the real and imaginary parts of the anomalous dispersion correction for rhenium from ref. 10. A final difference Fourier was featureless except for a few peaks of *ca.* 0·6—0·7 e Å^{-3} in the immediate vicinity of the rhenium atoms.

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

Tables 1 and 2 list the final co-ordinates of the non-hydrogen atoms and the coefficients for the anisotropic temperature factors. The standard deviations have been estimated from block-diagonal matrix refinement and are, therefore, a slight underestimate of the true deviations. The co-ordinates of the hydrogen atoms are given in Table 3. The observed and calculated structure-amplitudes are listed in Supplementary Publication No. SUP 20341 (6 pp., 1 microfiche).*

TABLE 2

Anisotropic thermal parameters *

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$
Re(1)	255(2)	317(2)	224(2)	−5(1)	7(1)	−37(2)
Re(2)	265(2)	269(2)	273(2)	−32(1)	−23(2)	28(2)
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^9\beta_{23}$
O(1)	42(3)	51(4)	44(4)	−8(3)	−17(3)	−5(3)
O(2)	26(3)	41(4)	23(3)	−12(2)	−10(2)	−5(3)
O(3)	43(3)	62(5)	47(4)	−17(3)	−13(3)	−4(3)
S(11)	29(1)	39(1)	29(1)	9(1)	11(1)	3(1)
S(12)	29(1)	42(1)	23(1)	5(1)	7(1)	0(1)
S(21)	40(1)	36(1)	32(1)	6(1)	8(1)	−3(1)
S(22)	29(1)	32(1)	31(1)	−1(1)	5(1)	2(1)
S(31)	31(1)	43(2)	51(1)	6(1)	12(1)	17(1)
S(32)	37(1)	26(1)	29(1)	0(1)	5(1)	4(1)
S(41)	37(1)	25(1)	26(1)	3(1)	1(1)	3(1)
S(42)	32(1)	31(1)	36(1)	3(1)	1(1)	9(1)
C(11)	26(4)	43(5)	28(4)	1(4)	−1(3)	3(4)
C(21)	34(4)	25(5)	41(5)	−2(4)	−2(4)	−8(4)
C(31)	28(4)	52(6)	32(5)	1(4)	0(3)	2(4)
C(41)	36(4)	19(5)	32(4)	−6(4)	−3(3)	4(4)
N(12)	41(4)	48(5)	32(4)	7(4)	14(3)	8(4)
N(22)	38(4)	36(5)	38(4)	−4(3)	3(3)	3(4)
N(32)	38(4)	41(5)	42(4)	−9(3)	6(3)	16(4)
N(42)	42(4)	30(4)	36(4)	−4(3)	5(3)	5(3)
C(13)	53(6)	66(8)	50(6)	12(5)	−1(5)	20(6)
C(14)	62(8)	195(19)	48(7)	−3(10)	2(6)	15(10)
C(15)	49(6)	53(7)	70(7)	19(5)	18(5)	19(6)
C(16)	83(9)	65(8)	78(9)	25(7)	16(7)	−18(7)
C(23)	58(6)	56(7)	64(7)	−18(5)	7(5)	−18(6)
C(24)	47(6)	63(8)	93(9)	−15(6)	8(6)	−6(7)
C(25)	60(6)	52(7)	43(6)	1(5)	−5(5)	−14(5)
C(26)	65(8)	82(10)	101(11)	27(7)	12(7)	−1(8)
C(33)	40(6)	95(10)	64(7)	3(6)	26(5)	23(7)
C(34)	62(7)	95(10)	52(7)	27(7)	20(5)	−8(7)
C(35)	56(6)	59(7)	45(6)	16(5)	4(5)	15(5)
C(36)	147(15)	69(10)	76(10)	−45(10)	−31(10)	27(8)
C(43)	62(6)	41(6)	43(6)	3(5)	16(5)	12(5)
C(44)	49(6)	62(8)	79(8)	6(5)	12(5)	4(6)
C(45)	46(5)	29(5)	45(6)	3(4)	−13(4)	5(4)
C(46)	59(7)	79(9)	70(8)	15(6)	−3(6)	36(7)

* In the form: $f_o \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The molecular structure, of which a novel feature is a linear O–Re–O–Re–O system, is shown in Figure 1. The two rhenium atoms have a distorted octahedral

[6] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.
[7] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.
[8] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.
[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.
[10] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

co-ordination, each being bonded to sulphur atoms of two bidentate dtc ligands as well as to one terminal and one bridging oxygen atom. The most significant bond lengths and bond angles are given in Tables 4 and 5 respectively.

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	*x*	*y*	*z*
H(131)	0·320	−0·043	0·280
H(132)	0·364	−0·155	0·266
H(141)	0·500	−0·069	0·340
H(142)	0·435	0·013	0·360
H(143)	0·425	−0·103	0·398
H(151)	0·498	−0·077	0·093
H(152)	0·510	−0·144	0·190
H(161)	0·448	−0·250	0·067
H(162)	0·385	−0·227	0·145
H(163)	0·379	−0·164	0·047
H(231)	0·271	0·587	−0·052
H(232)	0·262	0·487	−0·015
H(241)	0·115	0·570	−0·005
H(242)	0·145	0·561	−0·115
H(243)	0·138	0·452	−0·051
H(251)	0·355	0·448	−0·113
H(252)	0·305	0·537	−0·179
H(261)	0·448	0·522	−0·065
H(262)	0·387	0·659	−0·077
H(263)	0·445	0·563	−0·035
H(331)	0·010	0·018	0·155
H(332)	0·025	−0·084	0·220
H(341)	0·155	0·005	0·300
H(342)	0·106	0·109	0·248
H(343)	0·053	0·043	0·323
H(351)	0·218	−0·151	0·141
H(352)	0·158	−0·161	0·231
H(361)	0·104	−0·203	0·043
H(362)	0·073	−0·217	0·049
H(363)	0·093	−0·295	0·136
H(431)	0·277	0·312	−0·306
H(432)	0·324	0·200	−0·309
H(441)	0·408	0·336	−0·375
H(442)	0·405	0·378	−0·262
H(443)	0·454	0·269	−0·277
H(451)	0·240	0·332	−0·244
H(452)	0·231	0·455	−0·255
H(461)	0·106	0·339	−0·302
H(462)	0·114	0·440	−0·369
H(463)	0·151	0·332	−0·405

TABLE 4

Selected bond lengths (Å) with standard deviations in parentheses

Re(1)–S(11)	2·415(3)	Re(2)–S(31)	2·410(3)
Re(1)–S(12)	2·452(2)	Re(2)–S(32)	2·449(2)
Re(1)–S(21)	2·449(3)	Re(2)–S(41)	2·468(3)
Re(1)–S(22)	2·437(2)	Re(2)–S(42)	2·422(2)
	Mean Re–S	2·438	
Re(1)–O(1)	1·723(7)	Re(2)–O(3)	1·721(7)
Re(1)–O(2)	1·917(5)	Re(2)–O(2)	1·903(5)
C(11)–S(11)	1·729(9)	C(31)–S(31)	1·740(10)
C(11)–S(12)	1·713(10)	C(31)–S(32)	1·736(10)
C(21)–S(21)	1·712(10)	C(41)–S(41)	1·712(9)
C(21)–S(22)	1·732(10)	C(41)–S(42)	1·720(10)
	Mean C–S	1·724	
	Mean C–N	1·313(12)	
	Mean N–CH_2	1·488(15)	
	Mean CH_2–CH_3	1·488(19)	

The main distortion in the octahedral co-ordination of the metal atoms arises from the necessarily acute S–Re–S angles of *ca.* 72° within the same ligand caused by the small ' bite ' of the dtc entity. A further distortion is that the dtc ligands tend to incline slightly away from the terminal oxygen atoms and towards the bridging one, such that the mean O(terminal)–Re–S

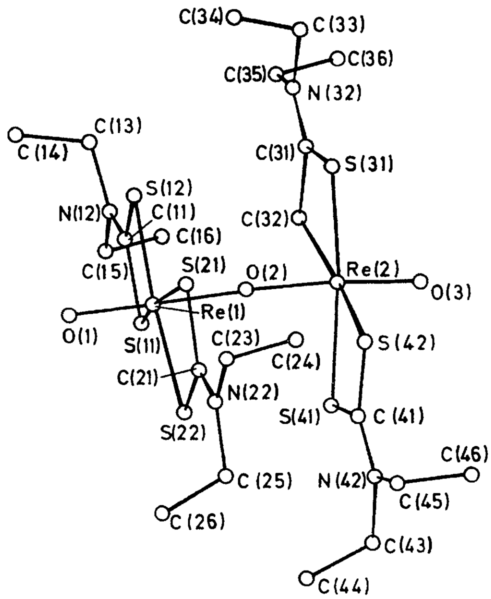

FIGURE 1 The molecular structure of $Re_2O_3(S_2CNEt_2)_4$

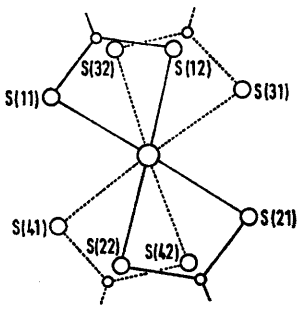

FIGURE 2 A schematic view down the Re · · · Re vector showing the degree of staggering of the diethyldithiocarbamato-ligands

TABLE 5

Selected bond angles (°) with standard deviations in parentheses

S(11)–Re(1)–S(12)	71·90(8)	S(31)–Re(2)–S(32)	72·03(9)
S(21)–Re(1)–S(22)	71·60(8)	S(41)–Re(2)–S(42)	71·83(8)
S(11)–Re(1)–S(22)	106·46(8)	S(31)–Re(2)–S(42)	105·35(9)
S(12)–Re(1)–S(21)	109·16(8)	S(32)–Re(2)–S(41)	110·08(8)
O(1)–Re(1)–S(11)	96·1(2)	O(3)–Re(2)–S(31)	97·1(3)
O(1)–Re(1)–S(12)	92·3(2)	O(3)–Re(2)–S(32)	92·2(3)
O(1)–Re(1)–S(21)	93·2(2)	O(3)–Re(2)–S(41)	89·8(3)
O(1)–Re(1)–S(22)	92·9(2)	O(3)–Re(2)–S(42)	93·7(3)
	Mean O(terminal)–Re–S	93·4	
O(2)–Re(1)–S(11)	85·8(2)	O(2)–Re(2)–S(31)	88·6(2)
O(2)–Re(1)–S(12)	87·3(2)	O(2)–Re(2)–S(32)	87·1(2)
O(2)–Re(1)–S(21)	85·1(2)	O(2)–Re(2)–S(41)	84·7(2)
O(2)–Re(1)–S(22)	87·5(2)	O(2)–Re(2)–S(42)	87·3(2)
	Mean O(bridging)–Re–S	86·7	
O(1)–Re(1)–O(2)	177·9(3)	O(2)–Re(2)–O(3)	173·8(3)
	Re(1)–O(2)–Re(2)	175·5(3)	
	Mean S–C–S	112·1(5)	
	Mean S–C–N	123·9(7)	
	Mean C–N–CH_2	121·9(9)	
	Mean CH_2–N–CH_2	116·1(9)	
	Mean N–CH_2–CH_3	111·2(1·1)	

angle is 93·4°. Within each molecule the dtc ligands attached to the two metal atoms are staggered by *ca.* 40° relative to each other (Figure 2).

The eight Re–S distances range between 2·410 and 2·468 Å, and are what would be predicted for a single bond in an octahedral Re^{V} complex. Structural data for similar bonds are not available, but an expected value may be derived using Pauling's covalent radius [11] for sulphur of 1·04 Å, and that for rhenium(V) which was evaluated as 1·38 Å from the structure of (Ph_4As)-$ReBr_4O(MeCN)$.[12] This gives an Re–S distance of 2·42 Å, which is very close to the mean value of 2·438 Å found in this structure. As would be expected, this is slightly longer (by *ca.* 0·05 Å) than the average Re–S distance of 2·388 Å found in the five-co-ordinate complex $ReN(S_2CNEt_2)_2$.[3,13]

The small differences in the Re–S distances in the oxo-complex would appear to be real, even if one takes account of the fact that the standard deviations of the bond lengths are slightly underestimated. This variation is not unusual in dithiocarbamato-complexes; for instance in $Cu(S_2CNEt_2)_2$ [14] a similar variation (*ca.* 20σ) is observed. Possibly the departure from octahedral co-ordination at the rhenium atoms may result in slightly varying degrees of overlap with the sulphur orbitals, although it is difficult to rationalise such small differences in bond length.

The mode of packing of the molecules in the unit cell is shown by the stereoscopic [15] pair of illustrations in Figure 3. The packing is such that the dtc ligands protrude into spaces between adjacent molecules. Some of the shorter non-bonded inter- and intra-molecular distances are quoted in Table 6. One should perhaps now consider the linearity of the O–Re–O–Re–O system in the light of these distances. The three angles O(1)–Re(1)–O(2), Re(1)–O(2)–Re(2), and O(2)–Re(2)–O(3) are 177·9, 175·5, and 173·8° respectively (σ 0·3°). Although the departure from linearity is small, in its cumulative effect it is almost certainly real. This view is reinforced by the fact that the distances between dtc(2*n*) and dtc(4*n*) atoms are in general shorter than those between equivalent atoms of dtc(1*n*) and dtc(3*n*), which is consistent with the direction of bending. This effect is magnified for the ethyl groups, for instance the distance C(25) ··· C(45) is appreciably shorter than the equivalent one C(13) ··· C(35) (see Table 6). The slight bending probably arises not for electronic reasons but because of steric pressure of a neighbouring molecule C(33) atom on the terminal O(3) atom, at which end of the molecule the distortion is most marked.

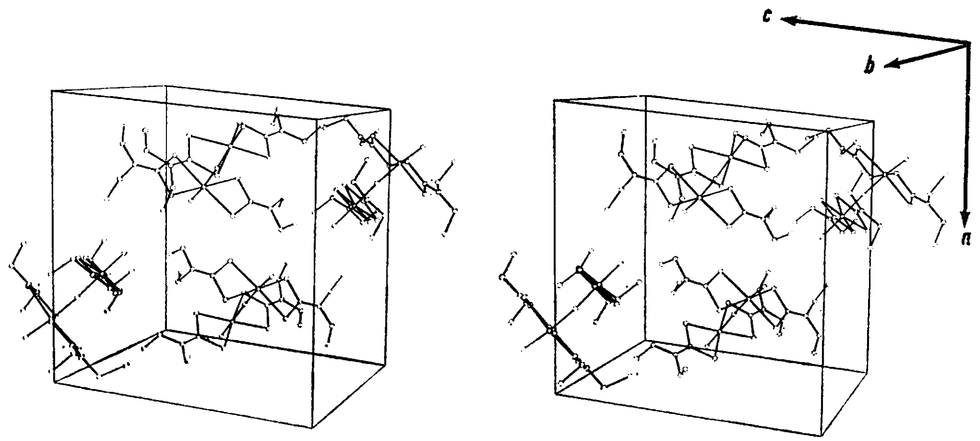

FIGURE 3 A stereoscopic view showing the packing of $Re_2O_3(S_2CNEt_2)_4$ molecules

TABLE 6

Selected non-bonded distances (Å)

(*a*) Intramolecular			
S(12) ··· S(32)	3·78	S(32) ··· C(11)	3·53
S(22) ··· S(41)	3·75	S(42) ··· C(21)	3·63
S(12) ··· C(31)	3·67	C(25) ··· C(45)	3·70
S(22) ··· C(41)	3·53	C(13) ··· C(35)	4·06
(*b*) Intermolecular			
O(3) ··· $C(33^{I})$	3·11	$H(163) \cdots H(463^{II})$	2·22
O(3) ··· $C(44^{II})$	3·49	$H(152) \cdots H(443^{IV})$	2·28
O(1) ··· $C(35^{III})$	3·48	$H(242) \cdots H(432^{V})$	2·36
S(21) ··· $C(13^{III})$	3·51		

Superscripts refer to atoms in the following positions:

I $-x, -y, -z$ IV $1 - x, -y, -z$
II $\frac{1}{2} - x, y - \frac{1}{2}, -\frac{1}{2} - z$ V $\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$
III $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$

The bond lengths and angles found in the dtc ligands show good agreement with those found in many such complexes and also with the free-ion value determined for sodium diethyldithiocarbamate.[16] The ligands are essentially planar, apart from the terminal methyl groups which adopt the *anti*-configuration found in

[11] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithaca, New York, 3rd edn., 1960, p. 246.
[12] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1966, **5**, 416.
[13] S. R. Fletcher and A. C. Skapski, following paper.
[14] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886.
[15] C. K. Johnson, ORTEP, thermal ellipsoid plotting program, Oak Ridge National Laboratory Report, 1965, ORNL 3794.
[16] M. Colapietro, A. Domenicano, and A. Vaciago, *Chem. Comm.*, 1968, 572.

most dtc complexes. The planarity of the ligands is summarised in Table 7. It can be seen that for two of the ligands, dtc(1*n*) and dtc(3*n*), the departure from planarity is rather more than would be expected in view of the standard deviations of the atomic parameters. This slight buckling may well be the result of packing forces. The Table also shows the planarity of the four sulphur atoms about each metal atom, and the fact that in both cases the latter is *ca.* 0·15 Å out of plane towards the terminal oxygen.

Bonding in the O–Re–O–Re–O *System*.—There have been no *X*-ray structural data reported on a linear O–M–O–M–O system, although the complex $Re_2O_3Cl_4(py)_4$ (py = pyridine), which may contain this unit, has been isolated.[17] A molybdenum dithiocarbamate complex of similar stoicheiometry to the title compound, $Mo_2O_3(S_2CNEt_2)_4$, has been prepared but, although its crystal structure has not been determined, the corresponding dithiocarbonate has the terminal and bridging Mo–O bonds in *cis*-positions.[18]

There have been many attempts to correlate Re^{V}–O bond lengths with bond order. In the structure of $ReOCl_3(PPhEt_2)_2$ Ehrlich and Owston [19] found an Re–O distance of 1·60 Å, the shortest reported. Cotton and Lippard subsequently investigated compounds containing anions of the type $(ReOBr_4L)^-$, L being a donor ligand. In (Ph_4As) $ReOBr_4(MeCN)$ [12] the Re–O distance is 1·73 Å and in $(Et_4N)ReOBr_4(H_2O)$ [20] it is 1·71 Å. These bonds were all suggested to be of the triple-bond variety. The accuracy of the Re–O distance in $ReOCl_3(PPhEt_2)_2$ is rather suspect since only two-dimensional visually estimated data were used, refinement was largely isotropic and no absorption correction was applied. For comparison, in the present investigation the terminal Re–O bond distances were 1·61 before anisotropic refinement, 1·65 before the absorption correction was applied, while the final value was 1·722 Å.

A number of dioxo-complexes of rhenium(V) have also been prepared, and the crystal structure of $K_3ReO_2(CN)_4$ has recently been redetermined.[21,22] The two oxo-ligands in the anion are mutually *trans*, and Re–O is 1·773 Å. It had been suggested [21] that these must be double bonds, but it now seems likely that some further multiple-bond character is present.

The only crystal-structure data available for a linear Re–O–Re system is that of the $(Re_2OCl_{10})^{4-}$ ion.[23] In contrast to the title structure, the chloride ligands bonded to different rhenium atoms are eclipsed, which suggests that the two Re–O bridging bonds are double bonds, with Re–O 1·86 Å.

A non-linear Re–O–Re bridge has been reported in $Re_2OCl_3(PPh_3)_2(EtCO_2)_2$ [24] where the two rhenium atoms are bridged by an oxygen, a chlorine, and two bidentate propionato-ligands. Here the Re–O distance of 1·916 Å is in excellent agreement with the value in the title compound, but a degree of Re–Re bonding has been suggested.

There are no compounds yet reported in which an Re–O single bond has been shown to exist. The expected length of such a bond can, however, be predicted by use of Pauling's covalent radius for oxygen, and Cotton and Lippard's value (1·38 Å) for the octahedral covalent radius of rhenium(V). On this basis it seems that an ideal Re–O single-bond length should be *ca.* 2·04 Å.

In the title compound the Re–O terminal bonds, mean 1·722 Å, appear therefore to be normal triple bonds, agreeing well with other reported values. The triple bonding may be justified on the following grounds. Assuming that rhenium uses its six valence orbitals, $5d_{z^2}$, $5d_{x^2-y^2}$, 6*s*, $6p_x$, $6p_y$, and $6p_z$ to form σ-bonds with the six ligands, empty d_{yz} and d_{xz} orbitals are then available to overlap with p_y and p_x orbitals on the terminal oxygen to form an effective triple bond. This leaves

TABLE 7

Planarity of groups of atoms within the molecule and distances from least-squares planes

Atoms defining plane	Mean |devn.| of atoms in plane (Å)	Maximum |devn.| of atoms in plane (Å)	Atom out of the plane	Perp. distance from from the plane (Å)
S(11), S(12), S(21), S(22)	0·042	0·043	Re(1)	0·153
S(31), S(32), S(41), S(42)	0·011	0·012	Re(2)	0·133
S(11), S(12), C(11), N(12), C(13), C(15)	0·047	0·082	Re(1)	0·215
			C(14)	1·43
			C(16)	1·38
S(21), S(22), C(21), N(22), C(23), C(25)	0·007	0·011	Re(1)	0·115
			C(24)	1·43
			C(26)	1·38
S(31), S(32), C(31), N(32), C(33), C(35)	0·038	0·062	Re(2)	0·078
			C(34)	1·44
			C(36)	1·47
S(41), S(42), C(41), N(42), C(43), C(45)	0·022	0·033	Re(2)	0·256
			C(44)	1·37
			C(46)	1·33

[17] N. P. Johnson, F. I. M. Taha, and G. Wilkinson, *J. Chem. Soc.*, 1964, 2614.
[18] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 1702.
[19] H. W. W. Ehrlich and P. G. Owston, *J. Chem. Soc.*, 1963, 4368.
[20] F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, 1965, **4**, 1621.
[21] K. Lukaszewicz and T. Glowiak, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1961, **9**, 613.
[22] R. H. Fenn, A. J. Graham, and N. P. Johnson, *J. Chem. Soc.* (*A*), 1971, 2880.
[23] J. C. Morrow, *Acta Cryst.*, 1962, **15**, 851.
[24] F. A. Cotton, R. Eiss, and B. M. Foxman, *Inorg. Chem.*, 1969, **8**, 950.

the d_{xy} orbital free to accommodate the remaining two d electrons, thus explaining the diamagnetism of the compound.

One should now consider why the title compund has a linear M_2O_3 system, whereas all similar known molybdenum(V) complexes have the bridging and terminal oxygen atoms mutually *cis*. These include $Mo_2O_3(S_2COEt)_4$,[18,25] $K_2[Mo_2O_5ox_2(H_2O)_2]$,[26] and almost certainly $Mo_2O_3(S_2CNEt_2)_4$.[18] In all these a similar bonding scheme can take place. However, the triple bond is completed by d_{xy}–p_y and d_{xz}–p_z overlap, leaving the d_{yx} orbital to accommodate the one d electron of Mo^V. These orbitals on the two molybdenum atoms can then combine with the p_y orbital on the bridging oxygen to form a three-centre π-bond. It might be expected that such a structure would be preferable in the rhenium compound, avoiding steric interactions between the diethyldithiocarbamato-ligands. However, since Re^V has a d^2 configuration, the d_{yz} orbitals would be filled and would therefore present an antibonding arrangement. In the linear system found, however, no such unfavourable orbital interactions exist.

It is interesting to consider the various configurations which the dtc ligands might possibly adopt in this compound. If the ligands bonded to different rhenium atoms were exactly eclipsed, the S···S distances would be very short at *ca.* 3·5 Å. In addition, the separations between methyl and methylene carbon atoms on different ligands [*e.g.* C(24)···C(45)] would be impossibly small if the *anti*-configuration was retained. Also in this situation the rhenium d_{yz} and d_{xz} orbitals would be suitably placed to accept π-electrons from the p orbitals of the bridging oxygen atom to give double bonding with a concomitant shortening of the Re–O(bridging) bonds and an even smaller S···S separation. Another possibility might be for the dtc ligands to be completely staggered at 90° to each other. Here there would be no steric interactions involving the terminal ethyl groups and the rhenium and oxygen orbitals would again be suitably placed for full overlap. The S···S distances, however, would again be too short as in the previous case.

Since the actual structure has the dtc ligands staggered *ca.* 40° relative to each other it seems that there is a strong tendency for the S···S separations between ligands bonded to different rhenium atoms to have the maximum possible values. In this equilibrium position the S···S separations are comfortable at >3·75 Å, despite the fact that the terminal triple-bonded oxygens repel the dtc ligands to give mean O(terminal)–Re–S angles of 93·4°. Although fairly short S···C distances of *ca.* 3·5 Å result from this arrangement one would expect electrostatic repulsion between residual negative charges to be less than for S···S. In addition the 40° staggering allows the terminal ethyl groups to arrange themselves so that intramolecular steric interactions are negligible.

As a result of this staggering the d_{yz} and d_{xz} orbitals of the two rhenium atoms are clearly placed at 40° relative to each other, so that ideal overlap with the bridging oxygen p-orbitals is not possible. The Re–O bond distance of 1·910 Å, however, suggests a bond order >1 and <2. It seems likely, therefore, that a small amount of overlap may still occur between these orbitals. The p_x and p_y orbitals may arrange themselves so that each is staggered 20° to the relevant orbitals of the two rhenium atoms. This amount of twisting probably results in the formation of weak π-bonds between the bridging oxygen and the rhenium atoms [Figure 4(a) and (b)].

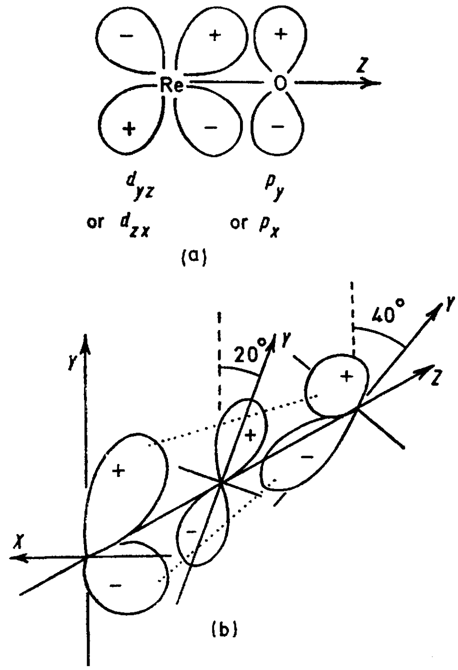

FIGURE 4 (a) A schematic representation of the orbitals used in π-bonding between rhenium atoms and both the bridging and the terminal oxygen atoms. (b) Staggering of the rhenium d_{yz} and oxygen p_y π-bonding orbitals in the Re–O–Re bridge. For sake of clarity the lobes pointing towards the terminal oxygens have been omitted, together with the d_{xz} and p_x orbitals

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[25] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Amer. Chem. Soc.*, 1964, **86**, 3024.

[26] F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, 1964, **3**, 1603.