Crystal and Molecular Structure of Carbonyltris(*NN*-diethyldithiocarbamato)rhenium(III): a Complex of Seven-co-ordinate Rhenium

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The structure of the title compound has been determined from single-crystal *X*-ray diffractometer data. Crystals are triclinic, with unit-cell dimensions a = 15·666(1), b = 9·933(1), c = 9·507(1) Å, α = 107·61(1), β = 93·04(1), γ = 114·63(1)°, space group $P\bar{1}$, Z = 2. The structure was solved by Patterson and Fourier methods and least-squares refinement, using 2660 independent reflections, has reached R 0·0275.

The complex is monomeric and the rhenium atom is seven-co-ordinate, with a distorted pentagonal-bipyramidal geometry. The carbonyl group occupies an axial position, with Re–C 1·852 Å. The sulphur atoms of two bidentate *NN*-diethyldithiocarbamato-ligands (dtc) are in the equatorial plane with similar Re–S distances, in the range 2·474—2·489 Å. The third dtc ligand has one equatorial and one axial sulphur atom and the two Re–S distances are significantly different: 2·433 and 2·518 Å.

A CONSIDERABLE number of dithiocarbamate complexes of rhenium have been reported by Wilkinson and his co-workers.[1-3] In a recent preliminary note [4] a complex is described for which a formula $Re(S_2CNEt_2)_3(CO)_2$ was suggested, the evidence for the presence of two carbonyl groups being the oxygen analysis. As part of a structural study of rhenium dithiocarbamate complexes [5,6] we have determined the *X*-ray crystal structure of this compound. We find that it contains only one carbonyl group and has the stoicheiometry $Re(S_2CNEt_2)_3(CO)$. (We are satisfied that the crystal used for the structure determination was representative of the specimens.)

The complex is monomeric, and all three *NN*-diethyldithiocarbamato-ligands (dtc) are bidentate. The metal atom is therefore seven-co-ordinate, and the co-ordination geometry can best be described as distorted pentagonal bipyramidal. This is the first clear-cut example of seven-co-ordinate rhenium(III), since other examples either involve metal–metal bonds (cluster compounds such as Re_3Cl_9 [7]) or in the case of $(\eta\text{-}C_5H_5)_2ReH$ [8] require the assumption that $\eta\text{-}C_5H_5$ occupies three co-ordination sites.

EXPERIMENTAL

Carbonyltris(*NN*-diethyldithiocarbamato)rhenium(III) crystallises from acetone as wine-red plates. Accurate unit-cell dimensions were obtained by measuring 30 high-angle reflections on a diffractometer and performing a least-squares calculation.

Crystal Data.—$C_{16}H_{30}N_3OReS_6$, M = 659·0, Triclinic, a = 15·666(1), b = 9·933(1), c = 9·507(1) Å, α = 107·61(1), β = 93·04(1), γ = 114·63(1)°, U = 1254·1 Å^3, D_m = 1·74 (by flotation), Z = 2, D_c = 1·74, $F(000)$ = 652. Space group $P\bar{1}$. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 135·3 cm^{-1}.

The crystal selected for data collection was *ca.* 0·30 × 0·20 × 0·06 mm. It was mounted about the c axis on a Siemens off-line automatic four-circle diffractometer, and a total of 2665 independent reflections (to θ 52°) were measured. Cu-K_α radiation at a take-off angle of 3·0°, a nickel β filter, and a Na(Tl)I scintillation counter were used. The intensity measurement was carried out with a θ—2θ scan technique using a 'five-value' procedure (one side of peak, background, full peak, background on other side of peak, other side of peak). Of the reflections measured 47 were judged unobserved, having a net count $<2·58\sigma$. The net count of the 520 reflection, measured as a reference every 50 reflections, did not alter significantly during the period of data collection (*ca.* 5 days). Data were scaled by use of the reference reflection and Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The structure was solved by Patterson and Fourier methods. The computer programs used were those in the Crystal Structure Calculations System '*X*-Ray '63' [9] and its updated version of July, 1970.[10] Calculations were carried out mainly on the Imperial College IBM 7094 and CDC 6400 and the University of London CDC 7600 computers.

The position of the rhenium atom was obtained from a three-dimensional Patterson synthesis, and a few cycles of isotropic least-squares refinement gave R 0·38. The 26 remaining non-hydrogen atoms were located from subsequent difference-Fourier syntheses. Least-squares refinement with anisotropic thermal parameters for rhenium and isotropic parameters for the other atoms gave R 0·129. Data were now corrected for absorption by use of the Gaussian integration method,[11] with a 10 × 10 × 10 grid, with crystal pathlengths determined by the vector analysis procedure.[12] Refinement as previously reduced R to 0·051. All atoms were now allowed to refine with anisotropic thermal parameters to give R 0·037. At this stage five strong low-angle reflections thought to be suffering from extinction were removed from refinement (R 0·034). All 30 hydrogen atoms could now be clearly located in the resulting difference-Fourier synthesis, and when they were included in the refinement, as a fixed-atom contribution with isotropic temperature factors of their parent carbon atoms, R dropped to its final value of 0·0275.

Full-matrix least-squares refinement was used throughout. Towards the end of refinement a weighting scheme of the type suggested by Hughes [13] was applied, where

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[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] J. F. Rowbottom and G. Wilkinson, *J.C.S. Dalton*, in the press.

[4] J. F. Rowbottom and G. Wilkinson, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 675.

[5] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 1073.

[6] S. R. Fletcher and A. C. Skapski, *J.C.S. Dalton*, 1972, 1079.

[7] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, 1964, **3**, 1402.

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[10] Ref. 9, version of July 1970, eds. J. M. Stewart, F. A. Kundell, and J. C. Baldwin.

[11] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1957, **10**, 180.

[12] P. Coppens, L. Leiserowitz, and D. Rabinovich, *Acta Cryst.*, 1965, **18**, 1035.

[13] E. W. Hughes, *J. Amer. Chem. Soc.*, 1941, **63**, 1737.

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Re(1)	0·24128(2)	0·14224(3)	0·19902(3)
S(11)	0·20898(11)	0·32746(18)	0·40291(17)
S(12)	0·07017(11)	0·02844(18)	0·21892(18)
S(21)	0·38006(12)	0·12114(19)	0·09742(19)
S(22)	0·38872(11)	0·40137(18)	0·29323(19)
S(31)	0·18655(12)	−0·14213(18)	0·08498(17)
S(32)	0·28570(12)	0·04452(18)	0·39305(17)
C(11)	0·0907(4)	0·1951(7)	0·3667(7)
C(21)	0·4522(4)	0·3187(8)	0·1942(7)
C(31)	0·2396(4)	−0·1391(7)	0·2527(7)
N(12)	0·0259(4)	0·2191(6)	0·4409(6)
N(22)	0·5447(4)	0·3973(7)	0·1911(6)
N(32)	0·2445(4)	−0·2620(7)	0·2683(6)
C(13)	0·0535(5)	0·3694(8)	0·5659(7)
C(14)	−0·0758(5)	0·1009(8)	0·4000(8)
C(15)	0·0876(6)	0·3669(10)	0·7161(8)
C(16)	−0·1346(6)	0·1404(11)	0·3049(11)
C(23)	0·5982(5)	0·5713(9)	0·2772(8)
C(24)	0·5957(5)	0·3195(10)	0·1068(8)
C(25)	0·5920(6)	0·6670(10)	0·1832(10)
C(26)	0·6462(7)	0·2676(12)	0·2050(11)
C(33)	0·3014(6)	−0·2470(9)	0·4049(9)
C(34)	0·2010(5)	−0·4183(7)	0·1454(8)
C(35)	0·4033(7)	−0·2029(11)	0·3927(12)
C(36)	0·0993(5)	−0·5205(8)	0·1490(8)
C(1)	0·2060(4)	0·1913(7)	0·0394(7)
O(1)	0·1873(4)	0·2260(6)	−0·0611(5)

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

TABLE 2

Anisotropic thermal parameters and root-mean-square amplitudes of vibration (Å)

Atom	$10^5\beta_{11}$	$10^5\beta_{22}$	$10^5\beta_{33}$	$10^5\beta_{12}$	$10^5\beta_{13}$	$10^5\beta_{23}$	Min.	Inter.	Max.
Re(1)	421(2)	789(6)	1005(5)	246(3)	158(2)	365(4)	0·164	0·197	0·209
S(11)	411(9)	870(24)	1125(22)	235(12)	156(11)	230(18)	0·176	0·201	0·227
S(12)	418(9)	919(25)	1313(24)	151(12)	181(12)	197(20)	0·175	0·211	0·257
S(21)	530(10)	1133(27)	1345(24)	388(13)	319(12)	445(20)	0·195	0·207	0·250
S(22)	450(9)	889(24)	1468(25)	195(12)	259(12)	385(20)	0·174	0·213	0·256
S(31)	564(10)	852(24)	1004(22)	308(12)	102(11)	263(18)	0·172	0·205	0·241
S(32)	611(10)	819(24)	997(22)	325(13)	107(12)	292(18)	0·168	0·202	0·252
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$			
C(11)	52(4)	111(10)	117(9)	37(5)	17(5)	54(8)	0·182	0·218	0·226
C(21)	47(4)	137(11)	131(9)	31(5)	26(5)	71(8)	0·185	0·227	0·240
C(31)	49(4)	98(11)	118(9)	25(5)	23(4)	61(8)	0·160	0·221	0·232
N(12)	46(3)	124(9)	118(8)	38(4)	24(4)	35(7)	0·190	0·215	0·232
N(22)	44(3)	167(10)	133(8)	28(5)	20(4)	60(7)	0·202	0·230	0·262
N(32)	72(4)	97(10)	126(8)	41(5)	19(4)	52(9)	0·171	0·224	0·270
C(13)	62(4)	161(12)	143(11)	51(6)	34(5)	54(9)	0·214	0·241	0·260
C(14)	50(4)	147(12)	162(11)	33(6)	32(5)	61(9)	0·205	0·238	0·262
C(15)	90(6)	234(16)	127(11)	60(8)	16(6)	48(11)	0·225	0·296	0·305
C(16)	55(4)	277(19)	247(16)	63(8)	−9(7)	15(14)	0·216	0·287	0·382
C(23)	47(4)	189(15)	155(12)	1(6)	−1(6)	78(11)	0·193	0·234	0·328
C(24)	56(5)	261(17)	161(12)	52(7)	43(6)	60(11)	0·201	0·268	0·327
C(25)	87(6)	185(15)	196(14)	18(7)	22(7)	94(12)	0·223	0·279	0·349
C(26)	92(7)	307(21)	246(17)	112(10)	9(8)	35(15)	0·246	0·295	0·386
C(33)	100(7)	130(12)	182(13)	53(7)	0(7)	65(10)	0·197	0·258	0·338
C(34)	69(5)	73(10)	160(11)	32(6)	26(6)	18(8)	0·156	0·252	0·282
C(35)	102(8)	192(17)	303(20)	67(9)	−20(9)	69(14)	0·251	0·283	0·396
C(36)	69(5)	134(12)	174(12)	32(6)	10(6)	46(9)	0·219	0·264	0·282
C(1)	51(4)	131(11)	112(9)	48(5)	22(5)	45(8)	0·189	0·210	0·231
O(1)	89(4)	196(9)	131(7)	70(5)	16(4)	74(7)	0·208	0·258	0·298

$w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geqslant F^*$, with $F^* = 40$ found to be optimum. In the last cycle the largest parameter shift was $0{\cdot}02\sigma$, and the final value of the standard deviation of an observation of unit weight [*] was 1·46.

Atomic scattering factors were taken from ref. 14, except those for hydrogen which were from ref. 15. The real and the imaginary parts of the anomalous dispersion correction for rhenium were those quoted by Cromer.[16] Table 1 lists the final fractional co-ordinates of the non-hydrogen atoms together with their estimated standard deviations. The coefficients in the expression for the anisotropic temperature factor $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, and the root-mean-square amplitudes of vibration along the principal axes of the thermal ellipsoid are listed in Table 2. The unrefined co-ordinates of the hydrogen atoms are in Table 3, and the observed and the calculated structure amplitudes are listed in Supplementary Publication No. SUP 20901 (16 pp., 1 microfiche).[†]

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The complex is monomeric, and the presence of three bidentate dtc groups and only one carbonyl group gives the rhenium atom a seven-co-ordinate geometry. Figure 1 shows the molecular structure of the complex together with the thermal vibration ellipsoids[17] of the non-hydrogen atoms. The more important bond lengths and bond angles are given in Tables 4 and 5 respectively.

The immediate environment of the metal atom is shown in Figure 2. The co-ordination geometry does not fit any of the idealised models exactly, but can best be described as distorted pentagonal bipyramidal. Thus the carbonyl group occupies an axial position, two dtc groups are in equatorial positions, while in the third dtc

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[*] Defined as $[\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, where w is weight, $\Delta = (F_o - F_c)$, N_o = no. of observations, and N_v = no. of variables.

[†] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue.

[14] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[16] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[17] C. K. Johnson, ORTEP thermal ellipsoid plotting program, Oak Ridge National Laboratory, 1965, Report ORNL 3794.

group one sulphur atom is equatorial and the other is axial. Such a disposition is not what would be expected *a priori* for an ML(chelate)$_3$ complex.[18] The fact that the axial–equatorial dtc group is in several ways the odd one out compared to the two equatorial dtc groups is consistent with the pentagonal-bipyramidal description. A similar structure has been suggested on the basis of i.r. and n.m.r. evidence for Mo(S$_2$CNR$_2$)$_3$(NO) (R = Me or Et).[19,20]

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	*x*	*y*	*z*
H(131)	0·111	0·445	0·540
H(132)	−0·005	0·407	0·573
H(141)	−0·099	0·103	0·507
H(142)	−0·076	0·001	0·340
H(151)	0·019	0·283	0·750
H(152)	0·112	0·483	0·800
H(153)	0·150	0·340	0·710
H(161)	−0·104	0·130	0·203
H(162)	−0·136	0·237	0·367
H(163)	−0·198	0·070	0·283
H(231)	0·666	0·607	0·333
H(232)	0·562	0·580	0·380
H(241)	0·644	0·400	0·067
H(242)	0·550	0·233	0·003
H(251)	0·614	0·633	0·083
H(252)	0·622	0·780	0·243
H(253)	0·520	0·660	0·167
H(261)	0·578	0·167	0·233
H(262)	0·680	0·200	0·127
H(263)	0·694	0·353	0·288
H(331)	0·268	−0·197	0·503
H(332)	0·268	−0·342	0·415
H(341)	0·201	−0·417	0·029
H(342)	0·242	−0·496	0·141
H(351)	0·440	−0·167	0·517
H(352)	0·418	−0·267	0·290
H(353)	0·434	−0·107	0·353
H(361)	0·098	−0·533	0·260
H(362)	0·064	−0·620	0·067
H(363)	0·056	−0·460	0·130

The hydrogen atoms are numbered so that the first two digits correspond to the numbering of the carbon atoms to which they are bonded.

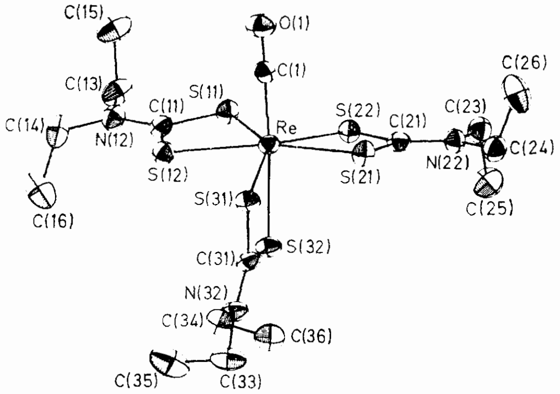

FIGURE 1 Molecular structure of Re(S$_2$CNEt$_2$)$_3$(CO). Thermal vibration ellipsoids scaled to enclose 50% probability

TABLE 4

Selected bond lengths (Å), with standard deviations in parentheses

Re(1)–S(11)	2·474(2)	Re(1)–S(12)	2·481(2)
Re(1)–S(21)	2·487(2)	Re(1)–S(22)	2·489(2)
Re(1)–S(31)	2·433(2)	Re(1)–S(32)	2·518(2)
Mean Re–S	2·480		
Re(1)–C(1)	1·852(8)	C(1)–O(1)	1·171(10)
C(11)–S(11)	1·706(6)	C(11)–S(12)	1·708(6)
C(21)–S(21)	1·710(6)	C(21)–S(22)	1·692(8)
C(31)–S(31)	1·745(7)	C(31)–S(32)	1·719(6)
Mean C–S	1·713		
C(11)–N(12)	1·327(9)	C(21)–N(22)	1·335(8)
C(31)–N(32)	1·305(11)		
Mean C–N	1·322		
Mean N–CH$_2$	1·470(10)		
Mean CH$_2$–CH$_3$	1·505(14)		

TABLE 5

Selected bond angles (°), with standard deviations in parentheses

S(11)–Re(1)–S(12)	68·01(5)	S(32)–Re(1)–S(22)	94·42(6)
S(12)–Re(1)–S(31)	76·87(6)	S(32)–Re(1)–S(31)	70·95(5)
S(31)–Re(1)–S(21)	76·16(6)	C(1)–Re(1)–S(11)	98·3(2)
S(21)–Re(1)–S(22)	68·07(6)	C(1)–Re(1)–S(12)	87·9(2)
S(22)–Re(1)–S(11)	72·48(5)	C(1)–Re(1)–S(21)	91·7(2)
S(32)–Re(1)–S(11)	87·98(6)	C(1)–Re(1)–S(22)	90·0(2)
S(32)–Re(1)–S(12)	92·15(6)	C(1)–Re(1)–S(31)	102·5(2)
S(32)–Re(1)–S(21)	85·13(7)	C(1)–Re(1)–S(32)	173·2(2)
Re(1)–C(1)–O(1)	177·4(5)		
S(11)–C(11)–S(12)	108·6(4)	S(21)–C(21)–S(22)	109·9(4)
S(31)–C(31)–S(32)	112·1(5)		
Mean S–C–N	124·9(5)		
Mean C–N–CH$_2$	121·3(6)		
Mean CH$_2$–N–CH$_2$	117·4(7)		
Mean N–CH$_2$–CH$_3$	112·0(7)		

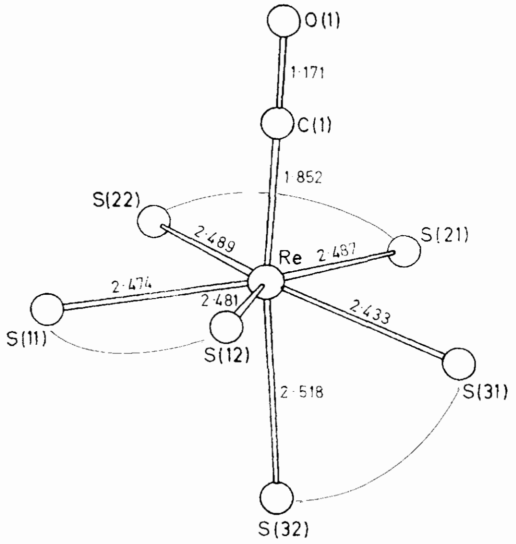

FIGURE 2 Co-ordination about the rhenium atom

The six Re–S distances lie in the range 2·433—2·518 Å, mean 2·480 Å. This may be compared with mean values of 2·388 in the five-co-ordinate complex ReN(S$_2$CNEt$_2$)$_2$[6] and 2·438 Å in the octahedral complex Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$.[5] Thus the observed lengthening in Re–S is consistent with the higher co-ordination number and lower oxidation state of the rhenium atom. Much

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

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

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

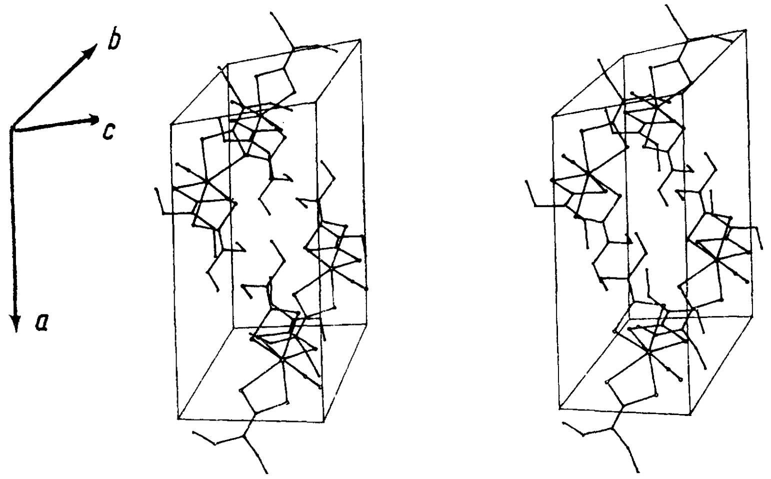

FIGURE 3 Stereoscopic view showing packing of $Re(S_2CNEt_2)_3(CO)$ molecules

shorter Re–S distances (mean 2·32 Å) are found in another Re^{III} complex, $Re(S_2C_2Ph_2)_3$,[21] which has a trigonal prismatic co-ordination, as do the vanadium[22] and molybdenum[23] analogues. However, in these compounds a degree of S–S interaction has been postulated to explain the co-ordination geometry and the short Re–S bond lengths are accounted for by metal–sulphur π-bonding in the plane of the ligand, in addition to normal σ bonding.[24]

TABLE 6

Equations of least-squares planes, in the form $Px + Qy + Rz = S$ in direct space. Deviations (Å) of atoms from the planes are given in square brackets

	P	*Q*	*R*	*S*
Plane (1): Re(1), S(11), S(12), S(21), S(22), S(31)	5·77	−6·00	8·47	2·37
[Re(1) −0·146, S(11) 0·283, S(12) −0·283, S(21) −0·079, S(22) −0·051, S(31) 0·277, S(32) 2·340, C(1) −1·996]				
Plane (2): S(11), S(12), C(11), N(12), C(13), C(14)	5·97	−7·60	7·75	1·89
[S(11) −0·012, S(12) 0·005, C(11) 0·006, N(12) 0·012, C(13) 0·004, C(14) −0·015, Re(1) 0·008, C(15) 1·390, C(16) −1·403]				
Plane (3): S(21), S(22), C(21), N(22), C (23), C(24)	5·34	−6·01	8·56	2·16
[S(21) −0·021, S(22) 0·017, C(21) 0·006, N(22) 0·001, C(23) −0·022, C(24) 0·020, Re(1) −0·019, C(25) −1·435, C(26) 1·441]				
Plane (4): S(31), S(32), C(31), N(32), C(33), C(34)	13·38	0·09	−4·73	2·02
[S(31) 0·067, S(32) −0·047, C(31) −0·016, N(32) −0·036, C(33) 0·081, C(34) −0·049, Re(1) 0·284, C(35) 1·506, C(36) −1·436]				

While the four Re–S distances to the equatorial dtc(1*n*) and dtc(2*n*) groups are probably not different from each other, for the dtc(3*n*) ligand the equatorial Re–S distance is markedly shorter (2·433 Å) and the axial distance longer (2·518 Å) than the mean. The equatorial dtc groups subtend angles of 68° at the metal atom, while for dtc(3*n*) this angle is 71°. The carbonyl ligand is linear and the Re–C distance of 1·852 Å is unexceptional. Similarly, the bond lengths found in the dtc ligands show good agreement with those in other complexes and with the free ion in sodium diethyldithiocarbamate.[25] The minor differences observed between the three groups, although individually not statistically significant, are what one would expect: thus, the slightly shorter S–C distances in dtc(1*n*) and dtc(2*n*) compared to those in dtc(3*n*) are matched by fractionally longer C–N distances.

Table 6 contains details of the various least-squares planes calculated for this structure. The equatorial dtc groups form much better planes (ignoring the terminal methyl groups) than dtc(3*n*). For this ligand the departure from planarity is quite marked, such that the two vectors S(31) · · · S(32) and C(33) · · · C(34) are twisted out of the least-squares plane in opposite senses so that the angular difference between them, relative to the plane, is *ca.* 5°. The metal atom is *ca.* 0·3 Å out of this plane whereas for dtc(1*n*) and dtc(2*n*) it is almost exactly in the least-squares planes. In all three bidentate ligands the terminal methyl groups adopt the *anti*-configuration found in most dtc complexes; two exceptions with a *syn*-configuration are the square-pyramidal complexes $FeCl(S_2CNEt_2)_2$[26] and $ReN(S_2CNEt_2)_2$.[6]

Figure 3 shows the packing of the molecules within the unit cell as a stereoscopic pair of illustrations.[17] Intermolecular non-bonded separations are not particularly noteworthy. The two nearest approaches between non-hydrogen atoms are *ca.* 3·39 Å and both involve the oxygen atom of the carbonyl group and an ethyl carbon atom.

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