Crystal and Molecular Structure of the Square-pyramidal Complex Nitridobis(*NN*-diethyldithiocarbamato)rhenium(v)

By **S. R. Fletcher** and **A. C. Skapski,*** Chemical Crystallography Laboratory, Imperial College, London SW7 2AY

The crystal structure of the title compound has been determined from three-dimensional single-crystal *X*-ray data. The crystals are monoclinic, with unit-cell dimensions $a = 14{\cdot}782$, $b = 9{\cdot}153$, $c = 12{\cdot}829$ Å, $\beta = 108° 4'$, space-group $P2_1/c$ and $Z = 4$. Full-matrix least-squares refinement, using 1606 independent reflections, has reached *R* 0·034.

The complex is monomeric, and the rhenium atom has a square-pyramidal co-ordination, with nitrogen in the apical position and the four sulphur atoms from the two bidentate ligands forming the base. The co-ordination is distorted with rhenium almost 0·73 Å above the base of the pyramid and N–Re–S angles of *ca.* 108°. The Re≡N triple bond distance is 1·656 Å, while Re–S distances are in the range 2·381—2·391 Å.

A NUMBER of nitrido-complexes of rhenium(V) have been reported. Apart from $K_2[ReN(H_2O)(CN)_4]$,[1] they can all be placed in the category $ReNX_2(PR_3)_x$ ($x = 2$ or 3; X = halide).[2,3] The co-ordination number of rhenium in these complexes depends upon the nature of the phosphine substituents. Thus, it is found that with diethyl(phenyl)phosphine a six-co-ordinate complex $ReNCl_2(PPhEt_2)_3$ is obtained,[4] while only two of the more bulky triphenylphosphine ligands can be accommodated to give five-co-ordinate $ReNCl_2(PPh_3)_2$.[5] The possibility that these are in fact rhenium(VI) imido-complexes has been ruled out by the absence of N–H resonance in the n.m.r. spectra.

As part of a study on rhenium dithiocarbamate complexes, Rowbottom and Wilkinson[6,7] prepared a compound of stoicheiometry $ReN(S_2CNEt_2)_2$, obtained by the reaction of sodium diethyldithiocarbamate monohydrate with $ReNCl_2(PPh_3)_2$ in acetone. We have carried out an *X*-ray structure determination on this compound in order to compare it with the oxo-complex $Re_2O_3(S_2CNEt_2)_4$,[8] and to see whether the nitrogen atom was terminal or possibly bridging as found in $M[Ru_2NCl_8(H_2O)_2]$, (where M = K[9] or NH_4[10]). The complex has proved to be monomeric, the rhenium atoms having a square-pyramidal co-ordination with nitrogen in the apical position.

A preliminary account of this work has been published.[7]

EXPERIMENTAL

Nitridobis-(*NN*-diethyldithiocarbamato)rhenium(V) crystallises from acetone as thick bright yellow plates.

Crystal Data.—$C_{10}H_{20}S_4N_3Re$, $M = 496{\cdot}8$, Monoclinic, $a = 14{\cdot}782$, $b = 9{\cdot}153$, $c = 12{\cdot}829$ Å, $\beta = 108° 4'$, $U = 1650{\cdot}4$ Å^3, $D_m = 2{\cdot}00$ (by flotation), $Z = 4$, $D_c = 2{\cdot}00$, $F(000) = 960$. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 183{\cdot}7$ cm.$^{-1}$ Space-group $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$.

Intensity data were collected for a crystal of dimensions *ca.* $0{\cdot}36 \times 0{\cdot}29 \times 0{\cdot}16$ mm mounted about the *b* axis on a Siemens off-line automatic four-circle diffractometer. Cu-K_α radiation at a take-off angle of 4·5°, a nickel β filter and a Na(Tl)I scintillation counter were used. A total of 1616 independent reflections (to $\theta = 50°$) were measured, by use of the θ—2θ scan technique with a 'five-value' measuring procedure,[11] of which 36 were judged to be unobserved.[11] The net count of the 504 reflection, measured as a reference every 50 reflections did not alter significantly during the data collection (*ca.* 60 h). The data were scaled by use of this reflection and the Lorentz and polarisation corrections were applied.

Solution and Refinement of the Structure.—The structure was solved and refined using the crystal structure calculations system '*X*-Ray 63'.[12] The calculations were carried out on the Imperial College IBM 7094 and the University of London CDC 6600 computers.

A three-dimensional Patterson synthesis gave a straightforward solution for the position of the rhenium atom, and one cycle of least-squares refinement on this atom gave *R* 0·40. The resulting difference Fourier showed the positions of the four sulphur atoms bonded to rhenium and also two carbon atoms bonded to sulphur. *R* now dropped to 0·159 and all remaining non-hydrogen atoms were located. Three cycles of isotropic refinement of all atoms gave *R* 0·110.

At this stage an absorption correction was applied according to the method of Busing and Levy[13] using a $10 \times 8 \times 8$ grid, with crystal pathlengths determined by the vector-analysis procedure of Coppens *et al.*[14] Refinement as before reduced *R* to 0·071, and when all atoms were allowed to refine with anisotropic thermal parameters *R* dropped to 0·053. A difference Fourier now showed the positions of all 20 hydrogen atoms. Inclusion of these in refinement, as a 'fixed atom contribution' with isotropic thermal parameters of their parent carbon atoms, gave *R* 0·052. Examination of the observed and calculated structure-factors showed that two reflections at very low

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[3] J. Chatt, J. D. Garforth, N. P. Johnson, and G. A. Rowe, *J. Chem. Soc.*, 1964, 1012.

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

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

[8] S. R. Fletcher and A. C. Skapski, preceding paper.

[9] M. Ciechanowicz and A. C. Skapski, *Chem. Comm.*, 1969, 574; *J. Chem. Soc.* (*A*), 1971, 1792.

[10] R. J. D. Gee and H. M. Powell, *J. Chem. Soc.* (*A*), 1971, 1795.

[11] A. C. Skapski and P. G. H. Troughton, *Acta Cryst.*, 1970, **B26**, 716.

[12] '*X*-Ray '63' system of programs, J. M. Stewart, University of Maryland Report TR 64 6.

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

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

values of θ had been partially obscured by the backstop. These two and also eight strong reflections thought to be suffering from extinction were removed from refinement to give R 0·038.

Up to this point, in view of the nearly constant counting statistics in the data collection,[15] each reflection had been assigned a unit weight. In the final stages, however, a weighting scheme of the type suggested by Hughes[16] was used in the refinement, where $w = 1$ for $F < F^*$, $\sqrt{w} = F^*/F$ for $F \geq F^*$, with $F^* = 60$ found to be optimum. Application of the weighting scheme produced a significant reduction in the standard deviations, and also the more unusual feature of a sizeable reduction in R to a final value of 0·034. The final difference Fourier was featureless except for a few peaks of *ca.* 0·3—0·5 eÅ^{-3} in the immediate vicinity of the metal atom.

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Re	0·26791(3)	0·11337(4)	0·26451(3)
N(1)	0·2242(6)	−0·0543(9)	0·2569(7)
S(11)	0·36693(17)	0·12493(25)	0·14856(18)
S(12)	0·42858(17)	0·11193(26)	0·38066(18)
S(21)	0·14294(15)	0·26721(24)	0·15711(16)
S(22)	0·20776(15)	0·24568(23)	0·38936(16)
C(11)	0·4641(6)	0·1358(9)	0·2648(7)
C(21)	0·1305(6)	0·3341(9)	0·2790(7)
N(12)	0·5514(5)	0·1698(8)	0·2678(6)
N(22)	0·0724(5)	0·4420(8)	0·2856(5)
C(13)	0·5748(7)	0·1870(13)	0·1620(8)
C(14)	0·6052(11)	0·0367(16)	0·1308(11)
C(15)	0·6289(7)	0·1961(12)	0·3733(9)
C(16)	0·6810(9)	0·0581(14)	0·4158(9)
C(23)	0·0697(7)	0·4933(11)	0·3938(7)
C(24)	0·1388(11)	0·6138(12)	0·4392(10)
C(25)	0·0092(7)	0·5090(10)	0·1853(7)
C(26)	0·0560(9)	0·6318(12)	0·1422(10)

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 *

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	274(3)	705(7)	472(4)	66(2)	104(2)	−5(3)
	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
N(1)	44(5)	87(11)	108(1)	−22(6)	29(5)	−18(7)
S(11)	32(1)	129(4)	42(2)	11(2)	8(1)	−5(2)
S(12)	35(1)	156(4)	43(2)	23(2)	12(1)	11(2)
S(21)	29(1)	102(3)	36(1)	9(1)	7(1)	−5(3)
S(22)	31(1)	97(3)	37(1)	10(1)	10(1)	4(2)
C(11)	22(5)	100(12)	64(7)	6(6)	6(5)	−1(7)
C(21)	28(5)	94(12)	55(6)	−1(6)	16(4)	1(7)
N(12)	35(5)	113(11)	56(6)	−4(6)	6(4)	−15(7)
N(22)	33(4)	85(10)	56(6)	15(5)	15(4)	8(6)
C(13)	54(7)	178(18)	79(8)	−10(9)	31(6)	7(10)
C(14)	109(11)	240(25)	126(12)	13(13)	64(10)	−45(15)
C(15)	45(6)	155(17)	99(9)	−3(8)	13(6)	−2(10)
C(16)	82(9)	188(19)	90(10)	36(11)	16(7)	45(12)
C(23)	69(7)	140(15)	61(7)	29(8)	35(6)	−14(8)
C(24)	107(11)	166(20)	98(11)	2(10)	37(9)	−32(11)
C(25)	42(6)	121(14)	78(8)	28(7)	14(5)	23(8)
C(26)	84(9)	156(18)	105(11)	21(9)	33(8)	59(11)

* In the form: $f_0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Full-matrix least-squares refinement was used throughout. The atomic scattering factors were taken from ref. 17 and the real and the imaginary parts of the anomalous dispersion correction for rhenium were taken from ref. 18. Tables 1 and 2 give the final co-ordinates of the non-hydrogen atoms and the coefficients for the anisotropic temperature factors. The co-ordinates of the hydrogen atoms are listed in Table 3. The observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 20343 (4 pp., 1 microfiche).*

TABLE 3

Fractional co-ordinates of the hydrogen atoms

Atom	x	y	z
H(131)	0·644	0·100	0·155
H(132)	0·644	0·267	0·175
H(141)	0·638	0·040	0·040
H(142)	0·691	−0·015	0·125
H(143)	0·533	−0·067	0·125
H(151)	0·673	0·267	0·338
H(152)	0·577	0·233	0·426
H(161)	0·724	0·001	0·362
H(162)	0·667	−0·067	0·420
H(163)	0·713	0·086	0·502
H(231)	−0·004	0·530	0·390
H(232)	0·083	0·401	0·455
H(241)	0·121	0·703	0·383
H(242)	0·211	0·583	0·452
H(243)	0·134	0·650	0·519
H(251)	−0·013	0·427	0·119
H(252)	−0·054	0·550	0·200
H(261)	0·084	0·717	0·118
H(262)	0·125	0·595	0·191
H(263)	0·038	0·585	0·062

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

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

Figure 1 shows the molecular structure of the complex together with the thermal vibration ellipsoids[19] of the atoms. The complex is monomeric and the rhenium atom has a distorted square-pyramidal co-ordination with a nitrogen in the apical position and four sulphur atoms forming the base. The pyramid is distorted in two ways. Firstly the rhenium atom is almost 0·73 Å

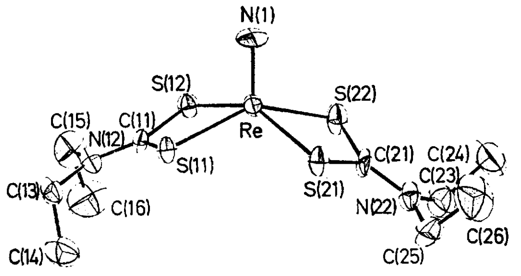

FIGURE 1 The molecular structure of $ReN(S_2CNEt_2)_2$. Thermal vibration ellipsoids scaled to enclose 50% probability

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* 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).

[15] P. G. H. Troughton, *Siemens Review*, 4th Special Issue, '*X*-Ray and Electron Microscopy News,' 1970, **37**, 22.

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

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TABLE 4

Selected bond lengths (Å) and bond angles (°) with standard deviations in parentheses

(*a*) Distances			
Re–N(1)	1·656(8)	Re–S(12)	2·381(2)
		Re–S(21)	2·391(2)
Re–S(11)	2·391(3)	Re–S(22)	2·389(2)
	Mean Re–S	2·388	
C(11)–S(11)	1·724(8)	C(21)–S(21)	1·740(9)
C(11)–S(12)	1·736(10)	C(21)–S(22)	1·721(8)
	Mean C–S	1·730	
	Mean C–N	1·323(12)	
	Mean N–CH_2	1·488(12)	
	Mean CH_2–CH_3	1·509(17)	
(*b*) Angles			
N(1)–Re–S(11)	107·9(3)	N(1)–Re–S(21)	107·1(3)
N(1)–Re–S(12)	109·1(3)	N(1)–Re–S(22)	106·8(3)
S(11)–Re–S(12)	72·87(8)	S(21)–Re–S(22)	72·91(7)
S(11)–Re–S(21)	97·36(8)	S(12)–Re–S(22)	95·14(8)
S(11)–Re–S(22)	145·25(8)	S(12)–Re–S(21)	143·78(8)
	Mean Re–S–C	88·4(4)	
	Mean S–C–S	110·2(5)	
	Mean S–C–N	124·9(7)	
	Mean C–N–CH_2	120·5(8)	
	Mean CH_2–N–CH_2	118·6(8)	
	Mean N–CH_2–CH_3	111·2(10)	

above the base of the pyramid such that the N–Re–S angles are *ca.* 108°. Secondly the base of the pyramid is rectangular; this necessarily arises from the presence of bidentate diethyldithiocarbamato-ligands (dtc), where the S–Re–S angles within the same ligand are *ca.* 73°. The more significant bond lengths and bond angles are given in Table 4. The four Re–S bond distances are in very close agreement with each other, with a mean value of 2·388 Å. This is shorter by 0·05 Å than the mean Re–S distance in the six-co-ordinate complex $Re_2O_3(S_2CNEt_2)_4$.[8] This shortening between similar five- and six-co-ordinate complexes is to be expected, and has also been noted [5] for other rhenium(V) complexes.

The only crystal-structure determination of a five-co-ordinate rhenium(V) complex so far reported is that of $ReNCl_2(PPh_3)_2$.[5] The Re–N bond distance found there was 1·602 Å, somewhat shorter than the 1·656 Å found in the title compound. In $ReNCl_2(PPh_3)_2$, however, although the co-ordination is closest to square-pyramidal, there is a distortion towards trigonal-bipyramidal geometry with the nitrogen in one of the equatorial positions. Since in a square-pyramidal co-ordination the apical bond tends to be comparatively longer, and no trigonal-bipyramidal distortion is observable in the title complex, this may explain the slight difference in bond length.

In the octahedral complexes $ReCl_3(NMe)(PPh_2Et)_2$ [20] and $ReCl_3(NPhCOMe)(PPh_2Et)_2$,[21] Re–N distances of 1·685 and 1·690 Å have been reported. These would seem rather short for what are, formally, double bonds, but Chatt *et al.*[22] have observed that Re⋮NR bonds are comparatively strong owing to a greater *s* contribution in the σ-bond formed by the co-ordinating nitrogen of an organo-imido-group. In $ReNCl_2(PPhEt_2)_3$ [4] the Re·N bond length is 1·788 Å, but this particularly long distance has been attributed to considerable steric strain imposed by the three bulky diethyl(phenyl)-phosphine groups, all of which are *cis* to the nitrogen atom.

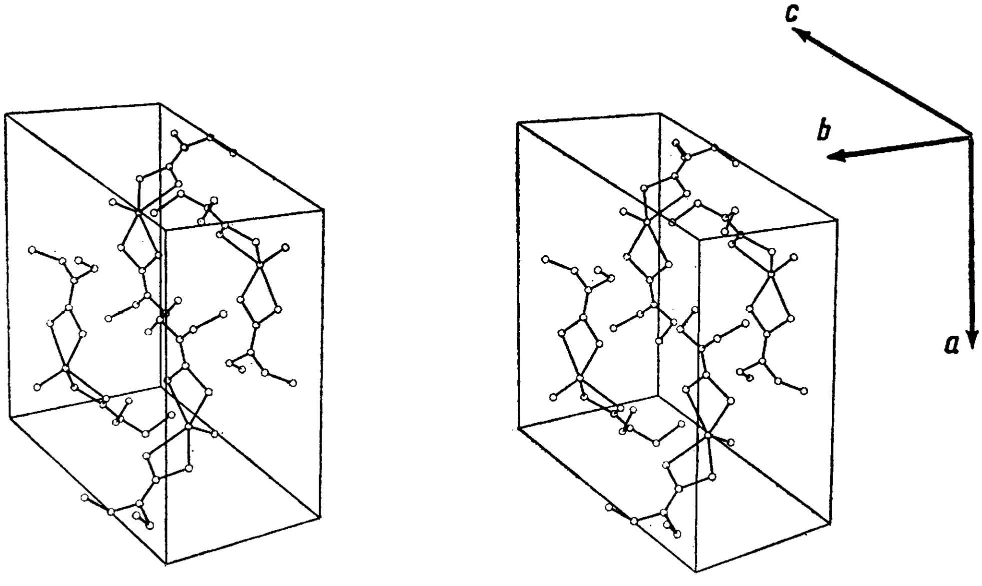

FIGURE 2 A stereoscopic view of the packing of $ReN(S_2CNEt_2)_2$ molecules

There is little doubt that the Re–N bond in the title complex is a triple bond. The rhenium atom uses $d_{x^2-y^2}sp^3$ hybrid orbitals to form σ-bonds with the five ligands. The vacant d_{yz} and d_{xz} orbitals are then suitably placed to form π-bonds with the donor *p* orbitals of the nitrogen, leaving the d_{xy} orbital to accommodate

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[20] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1969, **8**, 703.

[21] D. Bright and J. A. Ibers, *Inorg. Chem.*, 1968, **7**, 1099.

[22] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 2288.

the lone pair of 5*d* electrons. One would expect that an Re–N bond should be of approximately the same length as an Re–O bond of the same bond order. The Re–N distance of **1·656 Å** found here is somewhat shorter than the 1·72 Å which is the mean of Re–O triple-bond distances in octahedral environments in three structures.[8] The difference may be explained by the usual shortening observed in five-co-ordinate complexes and also by the absence of any π-donor ligand *trans* to the nitrogen.

TABLE 5

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 the plane (Å)
S(11), S(12), S(21), S(22)	0·014	0·014	Re	0·727
S(11), S(12), C(11), N(12), C(13), C(15)	0·042	0·066	Re	0·391
			C(14)	1·51
			C(16)	1·29
S(21), S(22), C(21), N(22), C(23), C(25)	0·011	0·017	Re	0·148
			C(24)	1·40
			C(26)	1·37

The bond lengths and bond angles in the dtc ligands are in good agreement with those found in other such complexes and also in the free ion found in sodium diethyldithiocarbamate.[23] An unusual feature, however, is the *syn*-configuration adopted by the terminal methyl groups (Figure 1). The dtc ligands almost invariably adopt the *anti*-configuration, although in the structure of $FeCl(S_2CNEt_2)_2$ [24] the *syn*-arrangement is also found. It may be that this unusual configuration is adopted because of packing considerations. Figure 2 shows a stereoscopic pair [19] of illustrations of the packing of molecules in the unit cell. It can be seen that a neat way of packing in which the methyl groups point into the empty underside of each molecule is adopted to give an interlocking pattern of molecules. A similar mode of packing is found in $FeCl(S_2CNEt_2)_2$. With an *anti*-configuration such an arrangement would have been impossible. The intermolecular non-bonded separations are not particularly noteworthy, with all distances between non-hydrogen atoms > 3·6 Å.

Table 5 shows the planarity of the dtc ligands (apart from the terminal methyl groups). Although dtc (2*n*) is quite planar the other dtc ligand has a slight twisting distortion which appears to be statistically significant. The angle between the two dtc planes is 60° and in both cases the rhenium atom is slightly out of the plane of the dtc ligands. Table 5 also shows that the four sulphur atoms attached to the rhenium atom form a good plane base for the pyramidal co-ordination.

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