Structural Studies in the Ruthenium–Dithiocarbamate System. Part III.[1] Crystal Structure of Di-[μ-diethyldithiocarbamato-carbonyldiethyldithiocarbamatoruthenium(II)]

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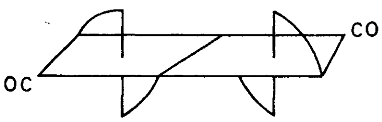
The crystal structure of the title complex has been determined by the heavy-atom method from *X*-ray diffractometer data and refined to R 0.052 for 2 997 independent reflections. Crystals are triclinic, space group $P\bar{1}$, $a = 16.08(1)$, $b = 11.907(5)$, $c = 9.693(3)$ Å, $\alpha = 103.04(3)$, $\beta = 77.80(4)$, $\gamma = 94.15(4)$°, $Z = 2$.

The complex, reported previously as $[Ru(dtc)_2CO]$ ($dtc^- = CS_2^- \cdot NEt_2$), is dimeric, the sixth co-ordination position in the pseudo-octahedral co-ordination sphere about each ruthenium being *trans* to the carbonyl (mean Ru–C 1.78 Å) and filled by a bridging sulphur atom from one of the ligands about the other ruthenium (mean Ru–S 2.55 Å); the remaining Ru–S distances are slightly longer than those usually found (mean 2.399 Å). The Ru ··· Ru distance [3.654(2) Å] indicates there is no metal–metal interaction. The molecule approximates to C_2 point-symmetry.

RECENT crystallographic studies have shown that the red species readily obtained from solutions of green $[Ru(dtc)_3]$ ($dtc^- = CS_2^- \cdot NR_2$) in chloroform solution contains the cation $[Ru_2(dtc)_5]^+$.[1] In view of the ease of formation of these derivatives, it seemed likely that derivatives reported earlier as being $[Ru(dtc)_2CO]$ and containing five-co-ordinate ruthenium[2] might be better described in terms of similar dimeric entities. This paper reports the structure determination of the complex '$[Ru(CS_2 \cdot NEt_2)_2CO]$', prepared according to the literature method and shown to be a dimeric complex (I) the bidentate ligands being $(CS_2 \cdot NEt_2)^-$. {A green impurity reported in the literature preparation was also shown crystallographically to be identical with the previously described $[Ru(CS_2 \cdot NEt_2)_3]$.} The electronic spectrum (cm^{-1}), demined for chloroform solution, has the following characteristics (log ε in parentheses): 26 000sh (3.82), 33 000 (4.46), 38 300 (4.83), and 42 750 (4.78)].



(I)

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[1] Part II, C. L. Raston and A. H. White, preceding paper.

[2] J. V. Kingston and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1966, **28**, 2709.

EXPERIMENTAL

A crystal 0.15 × 0.05 × 0.22 mm was used for the crystallographic work. The unit cell was calibrated by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique set of data in the range $2\theta < 40°$ gathered by a conventional 2θ—θ scan yielded 3 327 independent reflections of which 2 997 having $I > \sigma(I)$ were considered ' observed ' and used in the structure solution and refinement after correction for absorption.

TABLE 1

Atomic fractional cell parameters (x,y,z) and thermal parameters $(\times 10^3$ Å$^2)$, with least-squares estimated standard deviations in the final digit in parentheses (decimal points are omitted before x,y,z)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*a*) Part (1) of the molecule									
Ru	24 922(6)	16 287(8)	0 138(1)	48(1)	38(1)	34(1)	−5(0)	−17(1)	12(0)
C	3 302(8)	0 873(11)	−117(1)	52(9)	50(8)	67(10)	3(7)	−16(8)	24(7)
O	3 854(7)	0 353(9)	−201(1)	99(8)	104(9)	83(8)	35(7)	7(7)	32(7)
Ligand (a)									
S(1)	2 203(2)	0 043(3)	1 333(3)	70(2)	44(2)	59(2)	−10(2)	−34(2)	22(2)
S(2)	3 294(2)	1 984(3)	2 022(3)	54(2)	56(2)	57(2)	−16(2)	−28(2)	27(2)
C(1)	2 805(7)	0 764(10)	253(1)	50(8)	53(8)	59(8)	−7(6)	−21(6)	28(6)
N	2 854(6)	0 469(8)	377(1)	59(7)	67(7)	48(6)	−2(5)	−15(5)	31(5)
C(2)	2 338(9)	−051(1)	427(1)	103(11)	89(11)	62(9)	−19(9)	−32(8)	50(8)
C(3)	2 854(10)	−146(1)	428(2)	141(14)	60(10)	80(11)	16(9)	−5(10)	24(8)
C(4)	3 435(8)	116(1)	468(1)	91(10)	62(9)	47(8)	12(7)	−27(7)	18(7)
C(5)	4 305(9)	084(1)	419(2)	110(12)	81(11)	90(12)	13(9)	−57(9)	14(9)
Ligand (b)									
S(1)	2 633(2)	3 378(2)	−0 765(3)	50(2)	40(2)	32(2)	−8(1)	−13(1)	13(1)
S(2)	1 587(2)	1 403(2)	−1 584(3)	67(2)	41(2)	38(2)	−9(2)	−24(2)	10(1)
C(1)	1 877(6)	2 755(9)	−184(1)	42(7)	41(7)	35(7)	−3(5)	−11(6)	4(5)
N	1 619(6)	3 281(7)	−273(1)	65(7)	48(6)	38(6)	2(5)	−23(5)	12(5)
C(2)	1 873(9)	446(1)	−283(1)	120(11)	43(8)	49(8)	−1(7)	−32(8)	24(6)
C(3)	2 617(10)	452(1)	−403(2)	138(14)	64(10)	77(11)	−9(9)	−7(10)	37(8)
C(4)	1 028(8)	264(1)	−367(1)	90(9)	68(9)	35(7)	10(7)	−36(7)	7(6)
C(5)	0 121(9)	274(1)	−291(1)	92(11)	106(12)	68(10)	29(9)	−50(9)	−22(9)
(*b*) Part (2) of the molecule									
Ru	18 585(6)	46 154(8)	1 629(1)	46(1)	36(1)	32(1)	−8(0)	−16(1)	8(0)
C	1 420(8)	5 418(10)	344(2)	60(9)	45(8)	57(9)	6(7)	−28(8)	−3(7)
O	1 139(6)	5 910(8)	458(1)	112(8)	78(7)	48(6)	13(6)	−21(6)	−12(6)
Ligand (a)									
S(1)	2 390(2)	6 309(3)	0 772(4)	64(2)	44(2)	61(2)	−12(2)	−21(2)	20(2)
S(2)	3 293(2)	4 952(3)	1 997(3)	55(2)	50(2)	49(2)	−10(1)	23(2)	9(2)
C(1)	3 361(7)	6 075(9)	112(1)	42(7)	39(7)	44(7)	−5(5)	−2(6)	−9(6)
N	4 061(6)	6 689(8)	082(1)	49(6)	49(6)	70(7)	−14(5)	−2(5)	5(5)
C(2)	4 056(8)	763(1)	002(2)	65(9)	94(11)	131(14)	−53(9)	−21(9)	64(10)
C(3)	4 266(13)	718(2)	−154(2)	174(20)	208(24)	120(17)	−23(17)	9(15)	96(17)
C(4)	4 880(8)	644(1)	118(1)	58(9)	71(10)	76(10)	5(7)	6(7)	−17(8)
C(5)	4 972(9)	715(1)	264(2)	75(10)	107(13)	85(12)	3(9)	−23(9)	−37(10)
Ligand (b)									
S(1)	1 411(2)	2 773(2)	2 165(3)	48(2)	43(2)	31(2)	−10(1)	−17(1)	12(1)
S(2)	0 484(2)	4 171(2)	1 015(3)	50(2)	43(2)	45(2)	−4(1)	−21(2)	12(2)
C(1)	0 475(6)	2 899(9)	151(1)	40(7)	41(7)	20(6)	4(5)	−7(5)	−7(5)
N	−0 126(5)	2 087(7)	148(1)	48(6)	55(6)	29(5)	−11(5)	−11(5)	2(5)
C(2)	−0 008(8)	098(1)	181(1)	82(9)	39(7)	40(7)	−17(6)	−20(7)	8(6)
C(3)	−0 223(9)	101(1)	346(1)	89(10)	83(10)	60(9)	−28(8)	−30(8)	38(8)
C(4)	−0 905(7)	222(1)	093(1)	43(7)	65(8)	50(8)	−18(6)	−27(6)	13(6)
C(5)	−1 712(7)	216(1)	203(1)	34(7)	96(11)	66(9)	−14(7)	−4(7)	18(8)

Crystal Data.—$C_{22}H_{40}N_4O_2Ru_2S_8$, $M = 851$, Triclinic, $a = 16.08(1)$, $b = 11.907(5)$, $c = 9.693(3)$ Å, $\alpha = 103.04(3)$, $\beta = 77.80(4)$, $\gamma = 94.15(4)°$, $U = 1\,766(1)$ Å^3, $D_m = 1.60(1)$, $Z = 2$, $D_c = 1.60$ g cm^{-3}, $F(000) = 864$. Mo-$K_{\bar{\alpha}}$ monochromatic radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 13.1$ cm^{-1}. Space group $P\bar{1}$, (C_i^1, No. 2). Neutral atom scattering factors,[3] those for Ru and S being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[4]

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares; the parameters of the $Ru_2S_8(CO)_2$ molecular core were refined as a single block in order to approximate to a full-matrix procedure. Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were employed for all non-hydrogen atoms; all hydrogen atoms were clearly located in difference maps and included as invariants in the refinement with U 0.10 Å^2, except those on carbon atom C(2a3) which were set at U 0.15 Å^2. At convergence no parameter shift exceeded 0.1σ; R was 0.052 and R' $\{= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}\}$ being 0.056. The weighting scheme was of the form $w = (\sigma^2|F_o| + 3 \times 10^{-4}|F_o|^2)^{-1}$. Within a given ligand, atoms are labelled as shown: where necessary in the Discussion, the atom number is preceded by the ligand number (n = 1a, 1b, 2a, 2b). Hydrogen atoms are labelled according to the carbon atom to which they are attached.

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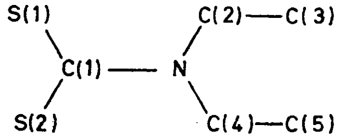
[3] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

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

[C(2) is on the same side of the ligand as S(1)]. The ligands are disposed within the molecule as follows: atom



1*mn* is related to atom 2*mn* by the intramolecular rotation (C_2) operation (approximate); the molecule has approximate C_2 symmetry and is labelled accordingly.

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) geometries about the Ru atoms; values for Part (2) of the molecule follow those for Part(1) (*i.e.* $l = 1$, $l = 2$)

Ru–S(a1)	2.399(4), 2.386(4)	S(a1)–Ru–C	91.1(5), 93.6(4)
Ru–S(a2)	2.396(4), 2.399(4)	S(a2)–Ru–S(b1)	105.6(1), 106.6(1)
Ru–S(b1)	2.414(3), 2.393(3)	S(a2)–Ru–S(b2)	174.3(1), 174.1(1)
Ru–S(b2)	2.397(4), 2.400(4)	S(a2)–Ru–S(b1′)	80.9(1), 81.1(1)
Ru–S(b1′)	2.535(4), 2.570(3)	S(a2)–Ru–C	94.4(5), 92.5(4)
Ru–C	1.75(1), 1.82(1)	S(b1)–Ru–S(b2)	72.7(1), 73.0(1)
C–O	1.17(2), 1.14(2)	S(b1)–Ru–S(b1′)	83.2(1), 82.8(1)
O–C–Ru	177(1), 179(1)	S(b1)–Ru–C	97.3(5), 94.2(4)
S(a1)–Ru–S(a2)	72.7(1), 72.8(1)	S(b2)–Ru–S(b1′)	93.4(1), 93.0(1)
S(a1)–Ru–S(b1)	171.5(1), 172.1(1)	S(b2)–Ru–C	93.1(5), 93.4(4)
S(a1)–Ru–S(b2)	108.1(1), 106.8(1)	S(b1)′–Ru–C	175.2(5), 171.9(5)
S(a1)–Ru–S(b1′)	88.3(1), 89.3(1)		
Ru(1)–S(1b1)–Ru(2)	94.3(1)	Ru(1)–S(2b1)–Ru(2)	95.7(1)
Ru(1) · · · Ru(2)	3.654(2)		

Atom (Sb1′) refers to S(2b1) in the co-ordination sphere of Ru(1) and *vice versa.*

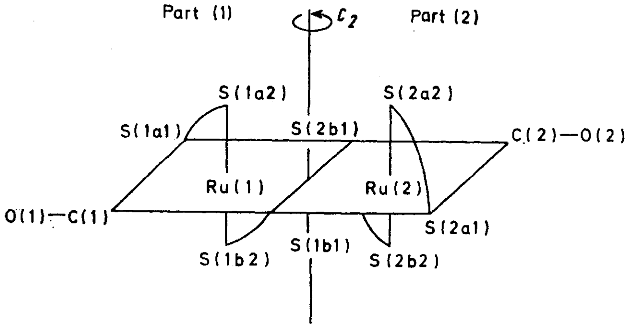
(*b*) Ligand geometries

Ligand *lm*	(1a)	(2a)	(1b)	(2b)
S(1)–C(1)	1.71(1)	1.73(1)	1.78(1)	1.78(1)
S(2)–C(1)	1.72(1)	1.72(1)	1.70(1)	1.69(1)
S(1)–C(1)–S(2)	111.7(8)	111.0(6)	110.0(7)	110.6(5)
S(1)–C(1)–N	124.8(0)	125.5(9)	123.2(8)	122.0(9)
S(2)–C(1)–N	123.4(9)	123.4(9)	126.7(8)	127.4(9)
C(1)–N	1.34(2)	1.32(2)	1.32(2)	1.32(1)
C(1)–N–C(2)	122(1)	119(1)	123(1)	121(1)
C(1)–N–C(4)	119(1)	122(1)	119(1)	120(1)
C(2)–N–C(4)	119(1)	118(1)	118(1)	118(1)
C(2)–C(3)	1.45(2)	1.49(2)	1.49(2)	1.55(2)
N–C(2)–C(3)	113(1)	111(1)	113(1)	113(1)
C(4)–C(5)	1.43(2)	1.51(2)	1.49(2)	1.51(1)
N–C(4)–C(5)	114(1)	110(1)	112(1)	113(1)
N–C(2)	1.49(2)	1.50(2)	1.45(1)	1.46(2)
N–C(4)	1.50(2)	1.49(2)	1.50(2)	1.50(2)

(*c*) H · · · S contacts (<3.0 Å)

S(2b2) · · · H(0.007, 0.638, 0.212) [attached to C(1b5) at $\bar{x}$, 1 − $\bar{y}$, $\bar{z}$]	2.68
S(1a1) · · · H(0.094, −0.158, 0.006) [attached to C(2b4) at $\bar{x}$, $\bar{y}$, $\bar{z}$]	2.97
S(1b2) · · · H(0.041, −0.030, −0.130) [attached to C(2b2) at $\bar{x}$, $\bar{y}$, $\bar{z}$]	2.67

Structure factor tables are deposited as Supplementary Publication No. SUP 21442 (15 pp., 1 microfiche).* All computation was carried out on the CDC 6200 machine at this University using a local variant of the '*X*-Ray' system.[5] Final positional and thermal parameters are listed in Table 1,



distances and angles in Table 2, and details of planes in Table 3.

TABLE 3

Equations of least-squares planes in the form $pX + qY + rZ = s$, with the estimated standard deviation of the defining atoms (σ/Å), and atomic deviations (Δ/Å). The orthogonal (Å) frame is defined by X parallel to *a*, and Z in the *ac* plane

(*a*) Ligand planes [defined by S(1), S(2), C(1), N, C(2), C(4)]

lm	(1a)	(2a)	(1b)	(2b)
10^4p	7 219	−0 911	6 490	−2 916
10^4q	−5 782	6 417	−3 627	4 015
10^4r	−3 802	7 616	−6 688	8 682
s	2.203	3.689	2.055	1.705
σ	0.05	0.02	0.04	0.04
χ^2 *	153.5	11.5	82.2	97.4
ΔRu	−0.37	−0.25	−0.02	−0.10
ΔS(1)	0.04	0.02	0.04	0.03
ΔS(2)	−0.07	−0.01	−0.03	−0.04
ΔC(1)	0.03	−0.01	−0.02	0.00
ΔN	0.01	0.02	0.00	0.04
ΔC(2)	−0.07	−0.02	−0.04	−0.05
ΔC(4)	0.05	0.01	0.05	0.02
ΔC(3)	1.12	−1.40	1.32	1.31
ΔC(5)	1.37	1.42	−1.31	1.22

(*b*) 'Plane' through Ru(1), Ru(2), C(1), C(2), S(1a1), S(2a1), S(1b1), S(2b1)

$$0.8925X + 0.1667Y + 0.4191Z = 3.752$$

σ = 0.303, χ^2 (7 degrees of freedom) 12 300

[Deviations: Ru(1) −0.08, Ru(2) −0.10, C(1) 0.32, C(2) 0.33, S(1a1) 0.18, S(1b1) −0.39, S(2a1) 0.18, S(2b1) −0.45]

* 5 degrees of freedom.

DISCUSSION

The asymmetric unit of the structure is the binuclear structure depicted in (I). The molecule is very near to point-symmetry C_2 and departs from that symmetry only in respect of the arrangement of certain of the terminal methyl groups on the dithiocarbamate ligands; comparison of the geometry of the two related parts of the molecule (Table 2) shows that although there are differences which are probably significant, they are trivial in nature. Unit-cell contents are illustrated in the Figure.

Each ruthenium atom is six-co-ordinate, but appreciably distorted from ideal octahedral geometry; it is

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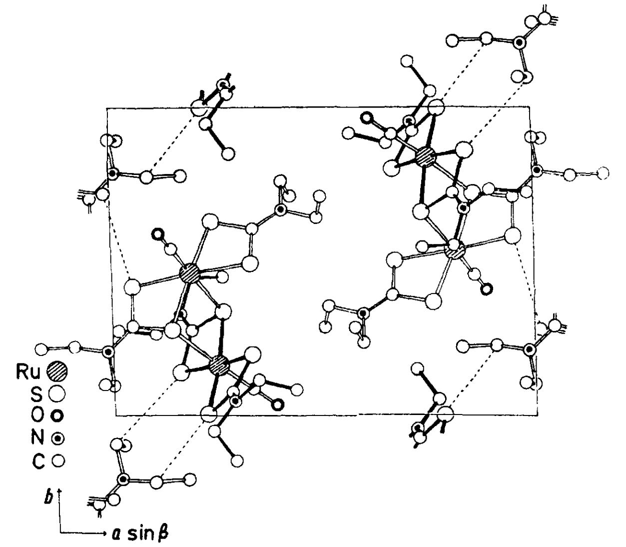
* For details, see Notice to Authors, No. 7, *J.C.S. Dalton*, 1974, Index issue.

[5] '*X*-Ray' System, Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

surrounded by two dithiocarbamate ligands, opposed to each other and each of which bridges axial and equatorial positions; all Ru–S distances are similar (mean 2.399 Å) and slightly longer than those in ruthenium(III) dithiocarbamate derivatives {*e.g.* [$Ru(CS_2{\cdot}NEt_2)_3$] 2.38 Å},[6] a consequence of the extra *d* electron associated with the ruthenium(II) valence state. The third equatorial position is occupied by the carbonyl groups. The disparity between the Ru–CO distances [1.75(1) and 1.82(1) Å] is surprising and appears to be the result of error in positioning C(1) since C(1)–O(1) [1.17(2) Å] is rather long; the value [1.14(1) Å] for C(2)–O(2) is closer to the usual carbonyl distance. If this is ' corrected ', then it seems that the Ru–CO distance in the present complex is probably somewhere in the vicinity of 1.80 Å; this value is considerably shorter than any Ru–CO distances hitherto reported and which are associated with (formally) zero-valent ruthenium (Table 4). Although the values of the Ru^0–CO distance tend to be generally inaccurate and with a wide scatter, the mean appears to lie in the vicinity of *ca.* 1.88 Å. Although many carbonyl groups have high thermal motion (and the present case is no exception) it is unlikely that the present distance, if corrected, would approach the corrected mean Ru^0–CO distance; the difference of *ca.* 0.08 Å between the present Ru^{II}–CO case and the mean Ru^0 case will probably be preserved. The sixth co-ordination position, in the equatorial plane *trans* to the carbonyl group, is filled by one of the equatorial sulphur atoms from the co-ordination sphere of the other ruthenium in such a way that the dimer is rotationally symmetric. Although this has no effect on the geometry of the Ru($CS_2{\cdot}NEt_2$) donor-system, the distance between the acceptor Ru and the bridging sulphur is much longer than the other Ru–S distances, mean 2.552 Å.



Unit-cell contents projected down *c*; dashed lines show S · · · H close contacts. Ligand bonds associated with one half of each dimeric molecule are shown solid for the sake of clarity

This disparity in distances about the bridging sulphur atoms is much greater than that observed in the [$Ru_2(CS_2{\cdot}NPr^i{}_2)_5$]$^+$ cation;[1] in the latter there is good evidence for a powerful metal–metal interaction, the result of which is to compress the geometry about the bridging sulphur so that both types of bridging-sulphur–ruthenium distance become shortened appreciably to *ca.* 2.30 and *ca.* 2.32 Å, the difference only being of the order of 0.02 Å compared with *ca.* 0.15 Å in the present case. However, somewhat similar bridging sulphur atoms are found in the trinuclear [$Ru_3(CO)_3(CS_2{\cdot}NEt_2)_4Cl_2$];[7] such a disparity in Ru–S distances about the bridging sulphur atoms is not found there, although the ruthenium atom valences are similar there is again an absence of metal–metal interaction. It seems likely that the difference between the two structures lies in the *trans*-effect of the donor opposite the p_π sulphur donor; in the present case, in which the Ru–S bond is abnormally long, the p_π sulphur atoms are opposed to the carbonyl groups in each of the co-ordination spheres about ruthenium, whereas in the trimeric derivative where the geometry is ' normal ' the opposed ligand is another dithiocarbamate sulphur atom. Clearly, the *trans*-effect of the carbonyl group differs greatly from that of the sulphur atom of the ligand; the ligand disposition, moreover, suggests that the effect originates in the σ component of the metal–ligand bonds.

TABLE 4

Comparison of ruthenium–carbon distances (Å)

Complex	
[$Ru_3(CO)_{10}\{{:}C(AsMe_2)CF_2{\cdot}\}_2$] [a]	1.83(3)—2.00(3)
[$Ru_3(CO)_8\{[{:}C(AsMe_2)CF_2{\cdot}]_2\}_2$] [b]	1.86(3)—1.92(2)
[$(Me_3C_{10}H_5)Ru_4(CO)_9$] [c]	1.76(4)—1.97(4)
[$(C_8H_8)Ru(CO)_3$] [d]	1.908(8)—1.924(6)
[$(C_8H_8)Ru_2(CO)_6$] [e]	1.86(2)—1.95(2)
[$(C_8H_8)_2Ru_3(CO)_4$] [f]	1.79(2)—1.83(2)
[$(C_5H_5)_2Ru_2(CO)_4$] [g]	1.98(1), 2.00(1) * 1.86(1)
[$HRu_3(CO)_9(C_{12}H_{15})$] [h]	1.79(4)—2.00(5)
[$Ru(C_8H_7CN)(CO)_3$] [i]	1.94 †
[$(C_{12}H_{16})Ru_4(CO)_{10}$] [j]	1.88 †
[$Ru_6C(CO)_4(C_6H_3Me_3)$] [k]	1.92 † 2.06 *
[$Ru_2(dtc)_4(CO)_2$] [l]	~1.80

* Bridging carbonyl; all others terminal. † Mean.

[a] P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1479. [b] P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1970, 3246. [c] M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1956; M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, 1968, **90**, 800. [d] F. A. Cotton and R. Eiss, *J. Amer. Chem. Soc.*, 1969, **91**, 6593. [e] F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412. [f] M .J. Bennet, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1968, **90**, 6335. [g] O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **9**, 339. [h] A. Cox and P. Woodward, *J. Chem. Soc. (A)*, 1971, 3599. [i] F. A. Cotton, M. D. LaPrade, B. F. G. Johnson, and J. Lewis, *J. Amer. Chem. Soc.*, 1971, **93**, 4626. [j] R. Belford, M. L. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159. [k] R. Mason and W. Robinson, *Chem. Comm.*, 1968, 468. [l] This work.

The carbon–sulphur distances in the ligand in the present derivative are asymmetric in the case of the bridging ligands in an analogous fashion to that observed in the [$Ru_2(CS_2{\cdot}NPr^i{}_2)_5$]$^+$ cation; although the non-

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[6] L. V. Pignolet, *Inorg. Chem.*, 1974, **13**, 2051.

[7] C. L. Raston and A. H. White, following paper.

bridging-sulphur–carbon distances in the present case are not noticeably shorter than usual, the bridging distances are very long [1.78(1) Å]. As before, this is ascribed to non-participation of the bridging-sulphur p_π electrons in the normal conjugation associated with the $CS_2^-\cdot NR_2$ system, because of its involvement in the Ru–S σ-bond. However, the distance [1.78(1) Å] is slightly shorter than in the $[Ru_2(CS_2\cdot NPr^i{}_2)_5]^+$ cation (>1.80 Å). This effect correlates with the longer Ru–S bond of 2.54 Å, suggesting that the p_π electrons of the bridging sulphur in the present case have a dual function, participating in both the Ru–S bond and (slightly) in the π-system of the ligand.

The remainder of the ligand geometry is normal although the terminal methyl groups of the ligands, which are usually on opposite sides of the ligand plane, are not invariably so in the present structure (see Figure).

The present structure is consistent with the i.r. data reported previously, which reported only one C–O stretching frequency. The ^1H n.m.r. spectrum has been determined at room temperature for CD_2Cl_2 solution and shows a pair of superimposed ethyl signals of equal intensity.

Crystal-packing forces in the present structure appear to be dominated as is usual in simple dithiocarbamate derivatives by hydrogen–sulphur interactions from the hydrogen atoms α to the nitrogen atom (Table 2); in the present case, there is also an unusually short contact from sulphur to a methyl hydrogen.

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