

Structural Studies in the Ruthenium–Dithiocarbamate System. Part II.¹ Crystal Structures of Two Salts of the $[\text{Ru}_2(\text{dtc})_5]^+$ Cation, One containing the $[\text{Ru}_2\text{Cl}_6]^{2-}$ Anion

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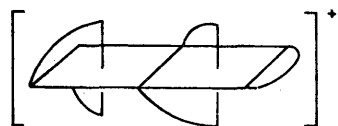
The crystal structures of two derivatives of ruthenium di-isopropylidithiocarbamate (dte) have been determined by X-ray diffraction: viz. (I) $[\text{Ru}_2(\text{dte})_5]\text{Cl}\cdot 2.5\text{C}_6\text{H}_6$ and (II) $[\text{Ru}_2(\text{dte})_5]_2[\text{Ru}_2\text{Cl}_6]\cdot 2\text{CHCl}_3\cdot (\text{C}_6\text{H}_{12}?)$. The structures were solved by the heavy-atom method and refined by least squares to R 0.084 [(I) 5 079 reflections] and 0.12 [(II) 4 714 reflections]. Crystals of both are monoclinic, space groups $P2_1/a$ (I), $P2_1/n$ (II); for (I) $a = 27.13(1)$, $b = 17.25(2)$, $c = 14.53(3)$ Å, $\beta = 97.82(4)^\circ$, $Z = 4$; for (II) $a = 33.83(1)$, $b = 12.527(2)$, $c = 15.825(2)$ Å, $\beta = 95.72(2)^\circ$, $Z = 2$. Within the $[\text{Ru}_2(\text{dte})_5]^+$ cation, a strong $\text{Ru} \cdots \text{Ru}$ interaction is found, the geometry of the bridging ligands being greatly compressed with a short $\text{Ru} \cdots \text{Ru}$ distance [2.789(4) Å]. The bridging dithiocarbamate groups are also unusual: the p_π orbital of one of the sulphur atoms is utilized for bonding so that there is an unusual disparity in the two $\text{C} \cdots \text{S}$ distances, the longer of which approximates to the single-bond value. (II) contains the novel $[\text{Ru}_2\text{Cl}_6]^{2-}$ centrosymmetric anion; the ruthenium atoms are pseudo-tetrahedral.

THE preceding paper describes the preparation of derivatives of the type $[\text{Ru}(\text{dte})_3]$ (dte = $\text{CS}_2\text{-NR}_2$, the disubstituted dithiocarbamate ligand), and their recrystalliz-

ation from chloroform.¹ In the course of this work, it was observed that a number of green $[\text{Ru}(\text{dte})_3]$ derivatives

¹ Part I, C. L. Raston and A. H. White, preceding paper.

in chloroform solution, notably those with branched substituents such as Pr^i_2 , often turned red quite rapidly, and during chromatographic purification of $[\text{Ru}(\text{dtc})_3]$ derivatives the appearance of red and brown bands on the column indicated the presence of a number of other species. It was not possible to isolate crystalline samples of the brown derivatives but eventually very small amounts of two distinct red derivatives were obtained as small crystals by allowing chloroform-cyclohexane (II) or benzene (I) solutions to evaporate over a period of weeks for the isopropyl derivatives only; although it was possible to obtain a number of the other derivatives in solution, attempts to obtain solid samples were unrewarding. Analysis of (I) showed the presence of Ru, dtc, and Cl but not in a ratio indicative of any simple stoichiometry; the quantity of (II) available permitted only carbon and hydrogen analyses which were similarly indeterminate. In view of the great difficulty of obtaining any appreciable quantity of these derivatives, crystal-structure determinations were carried out and showed the derivatives to be: (I) $[\text{Ru}_2(\text{dtc})_5]^+\text{Cl}^-$, *ca.* $2.5\text{C}_6\text{H}_6$, and (II) $[\text{Ru}_2(\text{dtc})_5]_2[\text{Ru}_2\text{Cl}_6] \cdot 2\text{CHCl}_3$ (*ca.* $2\text{C}_6\text{H}_{12}$?), the cation being the same in both cases.



Cation of (I) and (II)

Magnetic-moment determinations indicated a slight temperature-independent paramagnetism of *ca.* 1 B.M. per cationic ruthenium after application of suitable diamagnetic corrections and assuming a diamagnetic $[\text{Ru}_2\text{Cl}_6]^{2-}$ anion in (II). Electronic spectra (cm^{-1}) recorded for chloroform solution are ($\log \epsilon$ in parentheses) (I): 9 500 (2.35), 22 220 (4.02), 30 100 (4.69), 33 000sh (4.87), 37 500sh (5.01) [41 000 (5.05?)]; (II): 4 200 (2.32) 9 500 (2.40), 22 330 (4.08), 30 100 (4.73), 33 500sh (4.90), 37 500sh (5.07) [41 000 (5.12?)].

Throughout the remainder of this paper, the abbreviation dtc will be taken to refer specifically to the di-isopropyl substituted ligand, $[\text{CS}_2 \cdot \text{NPr}^i_2]$.

Analysis of (I) (found, calc. for $[\text{Ru}_2(\text{dtc})_5]^+\text{Cl}^-$, $2.5\text{C}_6\text{H}_6$): Ru, 14.80, 15.38; S, 23.20, 24.36; Cl, 2.50, 2.70; C, 42.28, 45.71; N, 5.16, 5.33; H, 6.33, 6.52.

EXPERIMENTAL

Structure determinations were carried out by use of data gathered by a Syntex PI four-circle diffractometer by a conventional 2θ - θ scan; unit cells were calibrated by a least-squares fit of the angular parameters of *ca.* 15 reflections with 2θ *ca.* 20° centred in the counter aperture in each case. For (I), a crystal $0.18 \times 0.36 \times 0.09$ mm was used and data were gathered within the limit $2\theta < 45^\circ$ to yield 6 613 reflections, of which 5 079 with $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement; because of the large cell and a wide mosaic spread, considerable difficulty was experienced in certain portions of the data in gathering backgrounds and profiles clearly without overlap from neighbouring reflections.

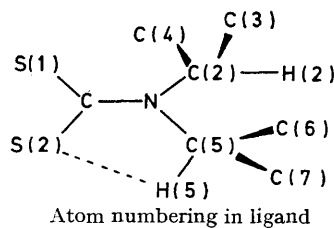
Accordingly for (II), with a larger cell dimension, copper radiation was used instead of the molybdenum used for (I), and data gathered in the range $2\theta < 100^\circ$ to yield 4 714 reflections, of which 4 531 were considered observed, as before, and used for structure solution and refinement. The crystal used for (II) was $0.04 \times 0.16 \times 0.09$ mm.

Crystal Data.—(I), $\text{C}_{50}\text{H}_{85}\text{Cl}_1\text{N}_5\text{Ru}_2\text{S}_{10}$, $\{[\text{Ru}_2(\text{dtc})_5]\text{Cl}\cdot 2.5\text{C}_6\text{H}_6\}$, $M = 1\ 314$, Monoclinic, $a = 27.13(1)$, $b = 17.25(2)$, $c = 14.53(3)$ Å, $\beta = 97.82(4)^\circ$, $U = 6\ 737$ Å³, $D_m = 1.33(1)$, $Z = 4$, $D_c = 1.30$ g cm⁻³, $F(000) = 2\ 728$. Monochromatic Mo- K_α radiation, $\lambda = 0.71069$ Å; μ (Mo- K_α) = 8.13 cm⁻¹. Space group $P2_1/a$ (C_{2h}^5 , No. 14).

(II) $2(\text{C}_{36}\text{H}_{71}\text{Cl}_6\text{N}_5\text{Ru}_3\text{S}_{10})$, $\{[\text{Ru}_2(\text{dtc})_5]_2[\text{Ru}_2\text{Cl}_6] \cdot 2\text{CHCl}_3\}$, $M = 2\ 822$, Monoclinic, $a = 33.83(1)$, $b = 12.527(2)$, $c = 15.825(2)$ Å, $\beta = 95.72(2)^\circ$, $U = 6\ 673(2)$ Å³, $D_m = 1.40(1)$, $Z = 2$, $D_c = 1.40$ g cm⁻³, $F(000) = 3\ 548$, Ni-filtered Cu- K_α radiation, $\lambda = 1.5418$ Å; μ (Cu- K_α) = 109 cm⁻¹. Space group $P2_1/n$ (C_{2h}^5 , No. 14).

Data for (II) were corrected for absorption. Both structures were solved by the heavy-atom method and refined by 9×9 block-diagonal least-squares, the parameters of the Ru_2S_{10} cationic cores and the Ru_2Cl_6 anion being refined as single blocks to approximate to a full-matrix procedure. Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}k lb^*c^*)]$ were used. Scattering factors were for the neutral atoms,² those for ruthenium, sulphur, and chlorine being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).³ At convergence, no parameter shift in either structure exceeded 0.2σ , except for those of solvent molecules; C_6H_6 carbon shifts were up to 0.8σ ; R was 0.084 (I) and 0.12 (II), and $R' = [(\sum w|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ was 0.087 (II) and 0.15 (I). A weighting scheme of the form $w = (\sigma^2(F_o) + 6 \times 10^{-4}(F_o)^2)^{-1}$ was found appropriate in both cases. In both structures disorder occurred. In (I), the one independent chlorine atom is disordered over three independent sites near the centre of symmetry $(0, \frac{1}{2}, 0)$; relative populations were established from a difference map. All benzene rings have very high thermal motion. In (II), the problem is more serious, a large disordered region occurring about $(0.4, 0, 0)$. It is suspected that a disordered C_6H_{12} molecule occupies this region, but it was not possible to locate any meaningful distribution of peaks in a difference map corresponding closely to this or any other species.

Within the di-isopropylthiocarbamate ligands, the atomic numbering is as shown. The isopropyl groups are directed



Atom numbering in ligand

so that the hydrogen atoms H(5) attached to C(5) are directed towards S(2), the other isopropyl group being rotated by 180° so that H(2) points away from S(1); C(3) and C(6) lie on the same side of the ligand plane with the parity implied in the diagram. In all cases, the ligand assumes a planar configuration with C(2) and S(1) on the same side of the ligand. Atom labels are denoted by a—e, where necessary, to indicate

² D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

³ D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

TABLE I

Atomic fractional cell parameters (x, y, z), with least-squares estimated standard deviations in parentheses. Decimal points are omitted from x, y, z . H atom positions are estimated

Compound (I)			
Atom	x	y	z
(a) The cation			
Ru(1)	34 777(5)	28 286(8)	5 273(1)
Ru(2)	31 826(5)	36 639(8)	6 748(1)
(i) Ligand (a)			
S(1)	4 195(2)	2 596(3)	4 528(3)
S(2)	3 246(1)	1 977(3)	3 971(3)
N	4 024(5)	1 628(8)	3 091(9)
C(1)	3 844(6)	2 023(9)	3 746(10)
C(2)	4 541(7)	169(1)	284(1)
C(3)	4 924(7)	134(2)	354(2)
C(4)	4 610(9)	253(1)	247(2)
C(5)	3 702(6)	106(1)	248(1)
C(6)	3 928(8)	023(1)	254(2)
C(7)	3 592(9)	139(2)	155(2)
H(5)	3 306	099	270
(ii) Ligand (b)			
S(1)	3 240(2)	3 915(3)	4 271(3)
S(2)	2 668(1)	3 126(2)	5 476(3)
N	2 257(4)	4 289(7)	4 300(9)
C(1)	2 666(6)	3 880(9)	461(1)
C(2)	2 274(6)	490(1)	355(1)
C(3)	2 323(7)	451(1)	259(1)
C(4)	2 613(7)	560(1)	387(1)
C(5)	1 790(6)	423(1)	476(1)
C(6)	1 358(6)	400(1)	398(1)
C(7)	1 715(7)	493(1)	533(1)
H(5)	1 846	371	522
(iii) Ligand (c)			
S(1)	3 663(2)	1 734(3)	6 264(3)
S(2)	3 981(2)	3 267(3)	6 549(3)
N	4 289(4)	2 081(8)	7 810(9)
C(1)	4 022(6)	2 267(9)	702(1)
C(2)	4 342(7)	124(1)	816(1)
C(3)	4 616(7)	075(1)	750(1)
C(4)	3 838(7)	091(1)	841(1)
C(5)	4 526(7)	271(1)	850(1)
C(6)	5 127(6)	255(1)	860(1)
C(7)	4 315(7)	270(1)	938(1)
H(5)	4 468	332	816
(iv) Ligand (d)			
S(1)	3 332(2)	4 929(3)	6 175(3)
S(2)	3 583(2)	4 425(3)	8 019(3)
N	3 663(5)	5 918(8)	758(1)
C(1)	3 551(6)	5 190(9)	728(1)
C(2)	3 594(8)	657(1)	689(2)
C(3)	3 082(7)	689(2)	669(2)
C(4)	3 973(9)	675(2)	633(2)
C(5)	3 875(9)	610(1)	860(2)
C(6)	3 471(9)	629(1)	912(1)
C(7)	4 389(8)	624(2)	875(1)
H(5)	3 840	543	853
(v) Ligand (e)			
S(1)	2 951(2)	2 607(3)	7 674(3)
S(2)	2 455(2)	4 045(3)	7 386(3)
N	2 220(5)	3 051(9)	8 696(9)
C(1)	2 506(6)	3 198(10)	800(1)
C(2)	2 311(8)	229(1)	926(1)
C(3)	2 794(8)	230(2)	987(2)
C(4)	2 101(11)	154(1)	865(2)
C(5)	1 844(6)	363(1)	894(1)
C(6)	2 043(8)	404(1)	982(1)
C(7)	1 315(6)	324(1)	891(1)
H(5)	1 811	405	836

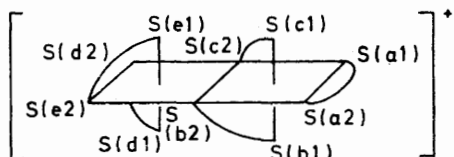
TABLE I (Continued)

Atom	x	y	z
(b) The disordered chloride anion (populations 0.4, 0.4, 0.2 respectively)			
Cl(1)	0 875(7)	3 518(6)	1 366(8)
Cl(2)	0 066(6)	3 877(8)	0 727(9)
Cl(3)	0 636(9)	477(2)	-041(2)
(c) The benzene solvent molecules			
(i) Benzene (a)			
C(1)	0 572(8)	183(1)	592(1)
C(2)	1 092(9)	172(2)	609(2)
C(3)	1 429(8)	230(1)	630(2)
C(4)	1 241(8)	301(1)	636(1)
C(5)	0 739(8)	322(1)	626(1)
C(6)	0 393(8)	258(1)	602(1)
(ii) Benzene (b)			
C(1)	415(1)	529(2)	214(2)
C(2)	455(1)	520(1)	150(2)
C(3)	437(1)	474(2)	072(2)
C(4)	391(1)	438(2)	069(2)
C(5)	360(1)	431(2)	132(2)
C(6)	377(1)	478(2)	205(2)
(iii) Benzene (c) (centrosymmetric)			
C(1)	4 757(8)	460(1)	416(2)
C(2)	4 557(8)	473(1)	499(1)
C(3)	4 760(9)	506(1)	584(2)
Compound (II)			
(a) The cation			
Ru(1)	21 647(7)	0 457(2)	4 922(1)
Ru(2)	29 920(7)	0 386(2)	5 081(1)
(i) Ligand (a)			
S(1)	1 599(2)	0 684(8)	5 693(5)
S(2)	1 573(2)	0 308(8)	3 943(5)
N	0 917(8)	053(2)	471(1)
C(1)	1 310(9)	053(3)	477(2)
C(2)	0 636(9)	066(3)	545(2)
C(3)	073(1)	-033(4)	602(3)
C(4)	068(1)	177(4)	582(3)
C(5)	069(1)	034(3)	381(2)
C(6)	051(1)	-082(4)	383(3)
C(7)	037(1)	130(4)	362(3)
H(5)	089	036	333
(ii) Ligand (b)			
S(1)	2 188(2)	2 328(7)	4 647(5)
S(2)	2 574(2)	0 658(6)	3 856(4)
N	2 653(8)	274(2)	338(1)
C(1)	2 504(8)	203(2)	390(2)
C(2)	2 554(9)	392(3)	330(2)
C(3)	2 130(9)	404(3)	302(2)
C(4)	270(1)	449(3)	419(2)
C(5)	2 973(9)	237(3)	280(2)
C(6)	282(1)	253(3)	199(2)
C(7)	336(1)	288(3)	309(2)
H(5)	301	152	291
(iii) Ligand (c)			
S(1)	2 152(3)	-1 435(7)	5 236(5)
S(2)	2 574(2)	0 194(6)	6 153(4)
N	2 607(8)	-188(2)	668(1)
C(1)	2 468(9)	-119(3)	610(2)
C(2)	251(1)	-304(3)	671(2)
C(3)	204(1)	-308(3)	683(2)
C(4)	259(1)	-367(3)	590(2)
C(5)	2 940(8)	-144(2)	734(2)
C(6)	278(1)	-163(4)	831(2)
C(7)	332(1)	-221(4)	728(2)
H(5)	302	-062	726

TABLE 1 (Continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
(iv) Ligand (d)			
S(1)	3 117(2)	2 187(7)	5 534(5)
S(2)	3 535(2)	0 348(7)	6 173(5)
N	3 838(7)	232(2)	652(1)
C(1)	353(1)	169(3)	616(2)
C(2)	387(1)	360(3)	641(2)
C(3)	391(1)	379(3)	546(2)
C(4)	354(2)	410(3)	684(3)
C(5)	420(1)	167(3)	700(3)
C(6)	452(1)	165(5)	649(4)
C(7)	428(2)	216(5)	790(3)
H(5)	410	086	708
(v) Ligand (e)			
S(1)	3 077(3)	-1 430(7)	4 652(5)
S(2)	3 528(2)	0 327(7)	4 194(5)
N	3 762(8)	-167(2)	388(2)
C(1)	3 487(9)	-104(2)	418(2)
C(2)	373(1)	-290(3)	394(3)
C(3)	378(1)	-322(3)	482(3)
C(4)	338(1)	-341(4)	341(4)
C(5)	409(1)	-114(3)	350(2)
C(6)	444(1)	-109(7)	426(5)
C(7)	412(2)	-181(5)	261(4)
H(5)	403	-032	332
(b) The anion			
Ru(3)	0 121(1)	-0 226(4)	1 009(3)
Cl(1)	0 008(3)	1 341(8)	0 201(5)
Cl(2)	0 731(3)	-0 319(9)	1 616(6)
Cl(3)	-0 350(3)	-0 499(8)	1 882(5)
(c) The chloroform			
C(1)	017(2)	324(9)	778(5)
Cl(11)	-003(1)	371(2)	688(2)
Cl(12)	-028(1)	337(2)	828(2)
Cl(13)	049(1)	380(2)	841(3)
H(1)	026	242	774

the ligand to which they belong. Disposition of the ligands within the cation is as follows:



i.e. all sulphur atoms of type 2 lie in the equatorial plane.

Computation was carried out on a CDC 6200 machine at this University by use of a local variant of the X-Ray program system.⁴ Structure-factor tables and thermal parameters are deposited as Supplementary Publication No. SUP 21441 (56 pp., 1 microfiche),* together with details of interligand and benzene geometries and ligand least-squares planes. Results are shown in Tables 1 and 2 and Figures 1-3.

DISCUSSION

Crystallographic investigation of (I) and (II) shows the presence in each case of $Ru_2(dtc)_5$ species with stereochemistries and geometries which differ only trivially; their similarity is confirmed by the close relationship of their electronic spectra in solution which differ only in respect of an additional band at 4200 cm^{-1} in (II)

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

⁴ 'X-Ray' System, Technical Report TR 192, Computer Science Centre, University of Maryland, June 1972.

(assigned to the accompanying complex anion). They are accompanied in their crystal lattices by other entities,

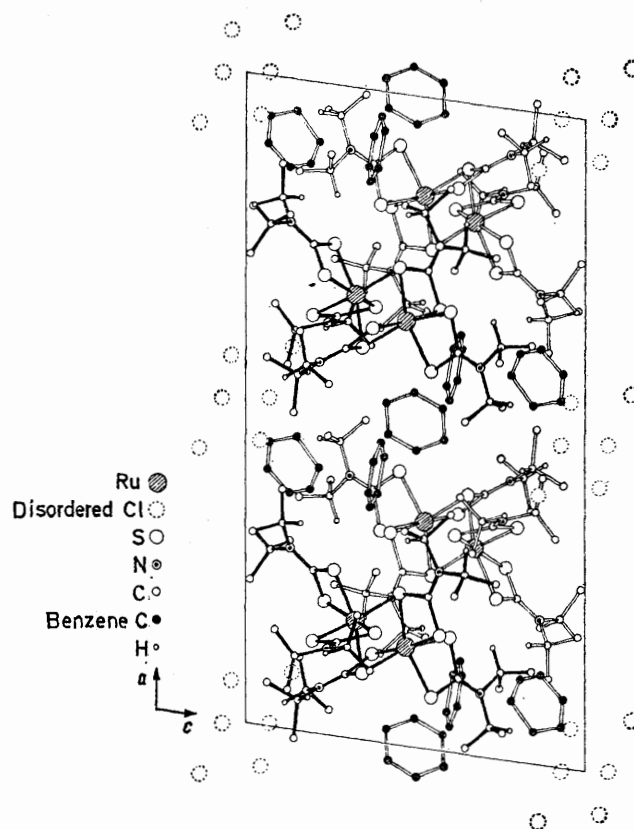


FIGURE 1 Unit cell contents of (I) viewed down *b*

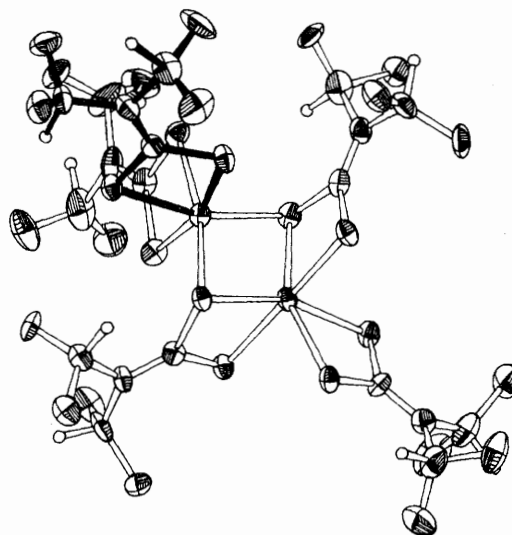


FIGURE 2 ORTEP diagram (20% ellipsoids) of the cation in (I)

including molecules of solvent, namely benzene, chloroform, and possibly cyclohexane. Identification of the valence state of the ruthenium atoms within the cation is

somewhat uncertain by virtue of the fact that in neither (I) nor (II) is the assignment of valence within the anion as clearcut as it might be. In (I), the species assigned as a chloride ion is disordered over three sites, and although its description as the sum of three partially occupied sites

unknown and there is no precedent for the present stoichiometry whereby meaningful comparison might be made. The ruthenium atoms in the cations have been assigned a valence of III formally, on the assumption of accompanying Cl^- and $[\text{Ru}_2\text{Cl}_6]^{2-}$ anions, supported by

TABLE 2

Interatomic distances (Å) and angles (°) with least squares estimated standard deviations in parentheses

(a) The cations; values for (II) follow those for (I)

(i) Intraligand	(a)	(b)	(c)	(d)	(e)
Ru(1)-S(1)	2.387(5), 2.388(9)	2.408(5), 2.387(9)	2.387(5), 2.422(9)		
Ru(1)-S(2)	2.411(6), 2.414(8)	2.314(4), 2.300(8)	2.278(5), 2.298(7)		
Ru(2)-S(1)				2.390(5), 2.392(9)	2.400(6), 2.400(9)
Ru(2)-S(2)		2.350(5), 2.309(7)	2.328(5), 2.327(8)	2.402(6), 2.394(8)	2.386(5), 2.401(9)
S(1)-Ru(1)-S(2)	71.5(2), 71.4(3)	73.9(2), 74.1(3)	73.6(2), 73.0(3)		
S(1)-Ru(2)-S(2)				71.8(2), 72.7(3)	72.4(2), 71.8(3)
S(1)···S(2)	2.803(6), 2.80(1)	2.840(7), 2.82(1)	2.795(7), 2.81(1)	2.811(8), 2.84(1)	2.827(7), 2.81(1)
S(1)-C(1)-S(2)	111(1), 113(2)	108(1), 110(1)	106(1), 109(2)	112(1), 112(2)	112(1), 110(2)
Ru(1)-S(1)-C(1)	89.1(6), 88(1)	88.6(5), 87(1)	91.1(6), 88(9)		
Ru(1)-S(2)-C(1)	88.2(5), 88(1)	89.1(5), 89(1)	89.6(5), 90(1)		
Ru(2)-S(1)-C(1)				88.1(6), 87(1)	87.3(6), 88(1)
Ru(2)-S(2)-C(1)				87.8(6), 88(1)	87.4(6), 88(1)
S(1)-C(1)-N	124(1), 123(2)	129(1), 125(2)	131(1), 128(2)	126(1), 123(2)	126(1), 127(2)
S(1)-C(1)-N	124(1), 123(2)	129(1), 125(2)	131(1), 128(2)	126(1), 123(2)	126(1), 127(2)
S(2)-C(1)-N	125(1), 123(2)	123(1), 125(2)	123(1), 123(2)	122(1), 125(2)	122(1), 122(2)
C(1)-N-C(2)	126(1), 128(2)	120(1), 127(2)	123(1), 126(3)	119(1), 126(2)	119(1), 121(3)
C(1)-N-C(5)	121(1), 118(2)	121(1), 119(2)	121(1), 115(2)	122(1), 114(3)	121(1), 117(3)
C(2)-N-C(5)	123(1), 114(2)	118(1), 114(2)	116(1), 119(2)	119(1), 120(2)	120(1), 122(3)
C(3)-C(2)-C(4)	121(2), 120(3)	119(2), 115(3)	117(2), 110(2)	123(2), 121(3)	124(2), 115(4)
C(3)-C(2)-N	113(2), 104(3)	111(1), 109(2)	110(1), 105(3)	115(2), 105(3)	112(2), 109(3)
C(4)-C(2)-N	108(2), 109(3)	113(1), 108(2)	112(1), 114(3)	120(2), 107(3)	111(1), 116(3)
C(6)-C(5)-C(7)	116(2), 115(3)	117(1), 116(3)	114(1), 107(2)	133(2), 117(4)	117(2), 123(4)
C(6)-C(5)-N	111(1), 107(3)	106(1), 109(2)	105(1), 106(2)	110(2), 109(4)	110(1), 104(4)
C(7)-C(5)-N	108(2), 108(3)	112(1), 109(2)	111(1), 106(2)	115(2), 107(4)	111(1), 103(3)
S(1)-C(1)	1.70(2), 1.69(3)	1.70(2), 1.71(3)	1.65(2), 1.67(3)	1.70(2), 1.75(3)	1.70(2), 1.71(3)
S(2)-C(1)	1.70(2), 1.67(3)	1.81(2), 1.74(3)	1.86(2), 1.78(4)	1.70(2), 1.67(4)	1.71(2), 1.71(3)
C(1)-N	1.32(2), 1.32(4)	1.34(2), 1.34(4)	1.31(2), 1.31(4)	1.35(2), 1.39(4)	1.38(2), 1.34(4)
C(2)-N	1.50(2), 1.59(4)	1.53(2), 1.51(4)	1.53(2), 1.49(4)	1.51(3), 1.60(5)	1.55(3), 1.55(4)
C(5)-N	1.50(2), 1.56(4)	1.52(2), 1.56(4)	1.56(2), 1.56(4)	1.54(3), 1.60(4)	1.50(2), 1.48(5)
C(3)-C(2)	1.48(3), 1.54(6)	1.57(3), 1.47(4)	1.55(3), 1.60(6)	1.48(3), 1.55(5)	1.48(3), 1.44(7)
C(4)-C(2)	1.56(3), 1.50(6)	1.54(3), 1.62(4)	1.67(3), 1.57(5)	1.42(4), 1.50(6)	1.63(3), 1.52(6)
C(6)-C(5)	1.55(3), 1.57(6)	1.57(2), 1.48(4)	1.64(2), 1.70(4)	1.46(3), 1.42(6)	1.50(3), 1.60(7)
C(7)-C(5)	1.46(3), 1.64(6)	1.49(3), 1.48(5)	1.47(3), 1.62(5)	1.40(3), 1.54(7)	1.58(3), 1.66(7)
S(2)···H(5)	2.53, 2.40	2.43, 2.45	2.53, 2.43	1.98, 2.37	2.39, 2.44

Also: S(d2)···H(b5) 3.40, 2.83 S(e2)···H(c5) 3.06, 2.96

(b) The anion in (II)

Ru(3)-Cl(1)	2.35(1)	Ru(3)-Ru(3 ^I)	3.264(6)	Cl(1)-Ru(3)-Cl(2)	112.2(4)	Cl(2)-Ru(3)-Cl(3)	114.7(4)
Ru(3)-Cl(2)	2.19(1)	Ru(3)-Cl(1 ^I)	2.37(1)	Cl(1)-Ru(3)-Cl(3)	112.1(4)	Cl(2)-Ru(3)-Cl(1 ^I)	114.3(4)
Ru(3)-Cl(3)	2.24(1)	Ru(3)-Cl(1)-Ru(3 ^I)	87.4(4)	Cl(1)-Ru(3)-Cl(1 ^I)	92.6(3)	Cl(3)-Ru(3)-Cl(1 ^I)	108.9(4)

Superscript I denotes transformation $\bar{x}, \bar{y}, \bar{z}$.

(c) The chloroform in (II)

C(1)-Cl(11)	1.63(9)	C(1)-Cl(13)	1.56(8)	Cl(11)-C(1)-Cl(12)	94(4)	Cl(12)-C(1)-Cl(13)	104(5)
C(1)-Cl(12)	1.77(8)	H(1)···Cl(3 ^{II})	2.50(—)	Cl(11)-C(1)-Cl(13)	127(7)		

Superscript II denotes transformation: $\bar{x}, \bar{y}, 1 - z$.

(d) Intermolecular H···Cl contacts

(I) H(c2) (0.4600, 0.130, 0.884)···Cl(2 ^{III})	2.88(—)	(II) H(d2) (0.4147, 0.388, 0.675)···Cl(3 ^V)	2.64(—)
H(a2) (0.4540, 0.131, 0.220)···Cl(2 ^{IV})	2.76(—)	H(e2) (0.3996, -0.312, 0.366)···Cl(2 ^{VI})	2.96(—)
		H(a5) (0.0894, 0.036, 0.333)···Cl(2)	2.84(—)

Superscripts denote the following positions: III $1/2 - x, y - 1/2, 1 - z$; IV $1/2 + x, 1/2 - y, z$; V $1/2 + x, y - 1/2, 1/2 + z$; VI $1/2 - x, y + 1/2, 1/2 - z$.

(e) Inter-chlorine distances in (I)

Cl(1)···Cl(2)	2.35(2)	Cl(2)···Cl(3)	2.85(3)	Cl(1)···Cl(3)	3.36(3)	Cl(2)···Cl(3 ^{VII})	3.01(3)
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Superscript VII denotes position: $\bar{x}, 1 - y, \bar{z}$.

is reasonable other plausible conjectures might also be made. (For example, the proximity of the three sites might be interpreted as a consequence of the presence of hydroxide ions.) In (II), the accompanying species is clearly an Ru_2Cl_6 entity but again difficulties arise by virtue of the fact that Ru_2Cl_6 species of any type are

the following more or less circumstantial evidence limited by the quantities of material available: (i) the analytical figures which are reasonably definitive for (I); (ii) *post facto* conductivity measurements on (I) in pure dry nitrobenzene solution (0.001 M) suggest it to be ionic with molar conductivity typical of a 1 : 1 electrolyte (Λ 24.0

S cm² mol⁻¹); (iii) whereas the metal-metal distance in the dimeric derivative [Ru₂(CS₂·NEt₂)₄(CO)₂] is 3.654(2) Å,⁵ and the molecular geometry is indicative of no metal-metal interaction, as might be expected for the octahedral d⁶ configuration, in the present case the metal-metal distance is contracted considerably and is indicative of the presence of a higher oxidation state; (iv) the geometry of the Ru₂Cl₆ species is consistent with an assignment of divalency to the metal atoms (see later); and (v) in the cations the non-bridging-sulphur-ruthenium geometries are in fair agreement with those reported previously for [Ru(CS₂·NEt₂)₃] and 2[Ru(CS₂·N[CH₂]₄O)₃],⁵CHCl₃, wherein Ru-S is typically 2.38 Å (cf. Table 2).^{1,6}

If we accept that the most likely description of the cation is [Ru₂(dtc)₅]⁺, then the stoichiometries of the

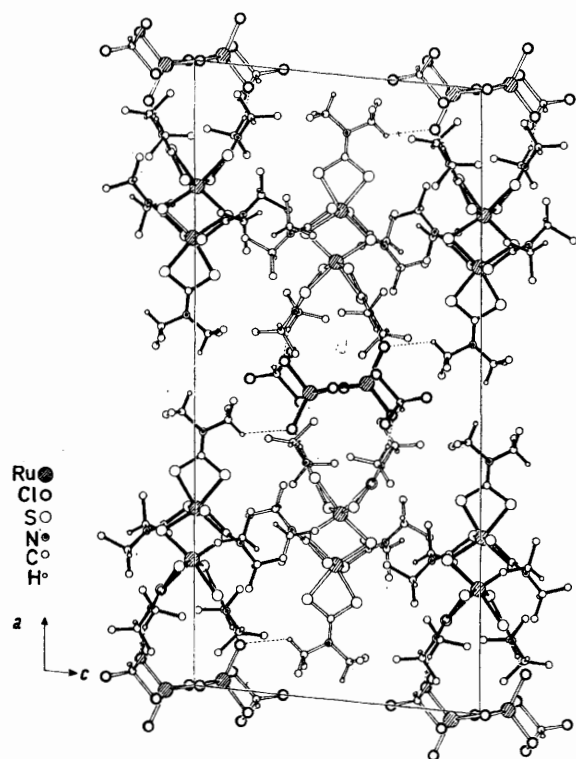


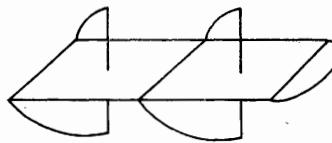
FIGURE 3 Unit cell contents of (II) viewed down *b*

two derivatives become: (I) [Ru₂(dtc)₅]⁺Cl⁻·2.5C₆H₆ with a chloride anion disordered over three sites; one of the benzene molecules is positioned about a centre of symmetry at (0.5,0.5,0.5) so that only half of it is independent crystallographically; and (II) [Ru₂(dtc)₅]⁺·2[Ru₂Cl₆]²⁻·2CHCl₃·(C₆H₁₂)₂. In this case only half the anion is crystallographically independent being centrosymmetric about (0,0,0) with a region of disorder described earlier. In spite of the disorder occurring in both structures and the difficulties of obtaining satisfactory data, the agreement in the two cation geometries is generally good and the accuracy of (I) acceptable.

⁵ C. L. Raston and A. H. White, following paper.

⁶ L. Pignolet, *Inorg. Chem.*, 1974, **9**, 2051.

The [Ru₂(dtc)₅]⁺ cation may be considered as a combination of [Ru(dtc)₃] with a *cis*-[Ru(dtc)₂]⁺ species, the [Ru(dtc)₃] molecule acting as a ligand to the [Ru(dtc)₂]⁺ by donation of the *p*_π electrons from each of a pair of bridging sulphur atoms mutually *cis* but from different ligands in the [Ru(dtc)₃] molecule. Given this mode of combination two isomers are possible, if the ligand substituents are identical, one being as described and as confirmed by the structure determinations, and the other being:



In addition, we note that these dimers may in turn act as ligands to further [Ru(dtc)₂]⁺ entities yielding polymeric species such as [Ru₃(dtc)₇]²⁺...[Ru_{*n*}(dtc)_{2*n*+1}]^{(*n*-1)⁺; the addition of each Ru(dtc)₂ unit adds two further combinations to the isomeric combinations possible in a linear chain. However, with the combination of three ruthenium-dithiocarbamate entities, bent as well as linear sequences become possible, and it is also feasible for a pair of sulphur atoms from adjoining ruthenium atoms to co-ordinate in the *cis*-positions of the third, as in [Ru₃(CS₂·NEt₂)₄(CO)₃Cl₂].⁷ The existence of the latter species clearly demonstrates the feasibility of preparing such oligomers, but the obstacles to their isolation as crystalline solids appear formidable.}

In the present case with di-isopropyl substituents on the ligand, the isomeric possibilities are multiplied further since the di-isopropylidithiocarbamate ligand at low temperatures in solution and in the solid state appears to adopt the minimum potential-energy configuration described in the Experimental section, in which the C₂ symmetry is destroyed, the ligand becoming entirely asymmetric in the disposition in which methyl crowding is least.⁸ In both the present structure determinations, the cation adopts a configuration in which all sulphur atoms of the type S(2) are equatorial, presumably to minimize the greater crowding occurring about the molecular equator in this type of derivative.

In view of the trivial nature of those differences which might be considered significant between the cations in (I) and (II) (Table 2), discussion of the cation geometry will be conducted in terms of the more accurate values determined for (I). Within the [Ru₂(dtc)₅]⁺ cation, a number of significantly different Ru-S distances are observed; those not associated with the bridging sulphur atoms are all similar (mean Ru-S 2.399 Å) and similar to values reported for simple monomeric [Ru(CS₂·NEt₂)₃] (Ru-S ca. 2.38 Å).⁶ In contrast, the geometry about the bridging sulphur atoms is considerably distorted and explicable in terms of an Ru...Ru interaction. The inter-metallic distance is very short [2.789(4) Å], and consistent with the presence of a metal-metal bond; it is

⁷ C. L. Raston and A. H. White, Part IV, see following papers.

⁸ P. W. G. Newman and A. H. White, *J.C.S. Dalton*, 1972, 2239.

considerably shorter than in $[\text{Ru}_2(\text{CS}_2\cdot\text{NEt}_2)_4(\text{CO})_2]$ [3.654(2) Å], in which the ruthenium is divalent and no such interaction is expected, the configuration of the ruthenium being d^6 .⁵ The Ru(1)–S(b,c2)–Ru(2) angles are $74.0 \pm 0.5^\circ$ [*cf.* $94.3(1)^\circ$ in the carbonyl derivative], and the corresponding Ru–S distances are abnormally short. In the present context we note that the electronic absorption spectrum differs considerably from that reported for $[\text{Ru}(\text{CS}_2\cdot\text{NR}_2)_3]$ in solution.¹ The magnetic moment (temperature independent) is low (*ca.* 0.7–1 B.M.) and probably originates in a T.I.P. contribution from low-lying energy levels generated by the Ru •• Ru interaction, as perhaps also does the spectrum.

TABLE 3

Comparison of ruthenium–ruthenium bonding distances

$[(\text{Me}_3\text{C}_{10}\text{H}_5)\text{Ru}_4(\text{CO})_9]^a$	2.702(5)—2.902(5)
$[(\text{C}_{10}\text{H}_9)\text{Ru}_3(\text{CO})_7]^b$	2.740(4), 2.944(5)
$[(\text{C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4]^c$	2.735(2)
$[\text{Ru}_3(\text{CO})_6\{\text{C}(\text{AsMe}_2)\text{CF}_2\}_2]^d$	2.785(4), 2.853(3)
$[(\text{C}_6\text{H}_5)_2\text{Ru}_2(\text{CO})_6]^e$	2.865(2)
$[(\text{C}_6\text{H}_5)_2\text{Ru}_2(\text{CO})_6]^f$	2.782(2)—2.947(2)
$[\text{Ru}_3(\text{CO})_{10}\{\text{C}(\text{AsMe}_2)\text{CF}_2\}_2]^g$	2.831(3)—2.858(6)
$[\text{HRu}_3(\text{CO})_9(\text{C}_{12}\text{H}_{15})]^h$	2.775(4)—2.929(4)
$[(\text{C}_{12}\text{H}_{15})\text{Ru}_4(\text{CO})_{10}]^i$	2.772(6)—2.816(3)
$[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_5\text{Me}_3)]^j$	2.853(7)—2.956(1)
$[\text{HRu}_3(\text{CO})_9(\text{C}_6\text{H}_5)]^k$	2.783(5)—2.964(6)
$[\text{Ru}_2(\text{dtc})_3]^l$	2.786(4), 2.789(4)

^a M. R. Churchill and P. H. Bird, *J. Amer. Chem. Soc.*, 1968, **90**, 800; M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, 1969, **8**, 1956. ^b M. R. Churchill, F. R. Scholer, and J. Wormald, *J. Organometallic Chem.*, 1971, **28**, C21. ^c O. S. Mills and J. P. Nice, *J. Organometallic Chem.*, 1967, **9**, 339. ^d P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1970, 3246. ^e F. A. Cotton and W. T. Edwards, *J. Amer. Chem. Soc.*, 1968, **90**, 5412. ^f M. J. Bennett, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 1968, **90**, 6335. ^g P. J. Roberts and J. Trotter, *J. Chem. Soc. (A)*, 1971, 1479. ^h A. Cox and P. Woodward, *J. Chem. Soc. (A)*, 1971, 3599. ⁱ R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Comm.*, 1970, 1159. ^j R. Mason and W. Robinson, *Chem. Comm.*, 1968, 468. ^k M. Evan, M. Hursthouse, E. W. Randall, E. Rosenberg, L. Milone, and M. Valle, *J.C.S. Chem. Comm.*, 1972, 545. ^l This work.

The magnetic moment might also be explained in terms of a partial quenching of the magnetic moment of the $[\text{Ru}(\text{dtc})_3]$ monomer (typically *ca.* 1.8 B.M.) by spin–spin or similar interaction, but such magnetic moments are typically temperature-dependent.

A small but significant asymmetry is found in the geometry about the bridging sulphur atoms, Ru(1)–S(b2) and Ru(1)–S(c2) being slightly shorter than Ru(2)–S(b2) and Ru–S(c2) (Table 2). The origin of this may lie in the constraints of ligand geometry and the fact that Ru(1) is chelated by the ligands involved whereas Ru(2) is not. It is also clear, however, that different orbitals from the sulphur atoms concerned are involved, those bonding to Ru(2) being unusual in that they are the p_π lone pairs normal to the ligand plane. That this is so is confirmed by the rather remarkable variations observed in ligand

geometry. In dithiocarbamate chelates, a wide variation is commonly observed in the C–S distances which, being conjugated with each other and the C–N system, lie in the partial double-bond region of 1.68–1.72 Å. [Typical C–S single- and double-bond distances are in the vicinity of 1.84 and 1.64 Å (*ref.* 9).] Variations in this region are often ascribed to ligand substituent or metal variation effects, hydrogen bonding, packing distortions, or more usually insufficient accuracy in structure determination. In the present case it is clear that the C–S distances associated with the bridging ligands are completely asymmetric. The non-bridging S–C distances lie at the lower end of the usual range, approaching values for a double bond, while those associated with the bridging sulphur in which the p_π orbital is now associated with the Ru(2)–S bond are very long, approaching the single-bond value.

The remainder of the ligand geometries are inaccurate and not significantly abnormal, although significant but trivial deviations of some of the defining S_2CNC_2 atoms occur in certain of the ligand least-squares planes. Of particular interest in this context is the pronounced deviation of Ru(2) from the planes of ligands d and e in both structures, the deviation generally being of the order of 0.45 Å and attributed to interaction with ligands b and c; planes c and d are not parallel (as would be expected for perfectly octahedral stereochemistries) but are inclined at angles of 16.2° (I) and 22.7° (II) and a similar situation is found for planes b and e [27.1° (I) and 20.1° (II)]. Significant deviations from planarity are also found from the best plane calculated through the two ruthenium atoms and the six equatorial sulphur atoms as follows:

0.11, 0.05	–0.35, –0.24	0.31, 0.27
(d 2)	(c 2)	(a 1)
2	1	
–0.01, 0.00	–0.01, 0.00	
(e 2)	(b 2)	(a 2)
0.33, –0.05	0.19, 0.25	–0.22, –0.27

Values for (I) precede those for (II)

Sufficient sample of (I) remained to permit determination of the 90 MHz ^1H n.m.r. spectrum in CDCl_3 in the temperature range -60 to 60° (Figure 4); the spectra at -60 and 60°C are compared with those of a variety of other Pr^1 substituted dithiocarbamates in Table 4. A structural study of $[\text{Ni}(\text{CS}_2\cdot\text{NHPr}^1)_2]$ ¹⁰ shows that in the solid the CH proton is directed towards rather than away from the nearby sulphur atoms and if, as seems likely, this is also the ligand configuration in derivatives such as $[\text{Co}(\text{CS}_2\cdot\text{NMePr}^1)_3]$ in low temperature in solution, then the CH proton signal at *ca.* 450 Hz for the derivatives tabulated may be ascribed to H(5) type protons while the multiplet of equal intensity at *ca.* -360 Hz may be ascribed to H(2) type protons. A similar argument for the methyl protons suggests that the C(6,7) proton multiplets are located at *ca.* -115 Hz and C(3,4) at -155 Hz

⁹ I. L. Karle, J. A. Estlins, and K. Britts, *Acta Cryst.*, 1967, **22**, 273. [This example $(\text{Et}_2\text{N}\cdot\text{CS}_2\cdot\text{NEt}_2)$ is particularly relevant to the present case.]

¹⁰ C. L. Raston and A. H. White, *J.C.S. Dalton*, 1974, 1791.

(see ref. 11 for a discussion of the spectra of $[\text{Co}(\text{CS}_2 \cdot \text{NPr}^i_2)_3]$).

Although the cation in (I) and (II) is slightly paramagnetic, the positions of the CH and CH_3 signals are not temperature-dependent (apart from structural changes in

and -364 Hz with intensities *ca.* 4 : 1 : 5; the CH_3 spectrum comprises two bands at *ca.* -167 and -126 Hz in the intensity ratio *ca.* 7 : 3. If at -60°C the solution conformation of the cation is the same as that of the solid, then it is probably that the -364 Hz multiplet

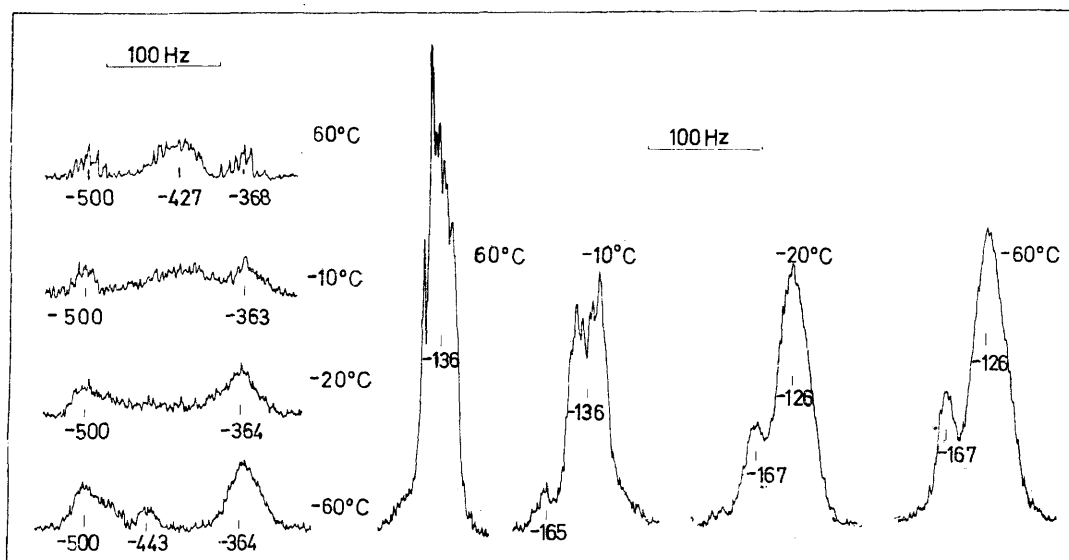


FIGURE 4 90 MHz ^1H n.m.r. spectrum of (I) in CDCl_3 at various temperatures; the left-hand section of the diagram shows the spectrum in the CH proton region, while the right-hand section gives the spectra of the methyl groups

the spectra) and it is likely that the order of the multiplets will be unchanged from those discussed. The CH

TABLE 4

Chemical shifts (Hz) from tetramethylsilane of the centres of the CH and CH_3 proton multiplets in a number of Pr^i substituted dithiocarbamate derivatives recorded at -60 and 60°C at 90 MHz in CDCl_3

Compound	CH		CH_3	
	60°C	-60°C	60°C	-60°C
$[\text{Co}(\text{CS}_2 \cdot \text{NMePr}^i)_3]$	-455	-454	108	110
$[\text{Co}(\text{CS}_2 \cdot \text{NEtPr}^i)_3]$	-453	-453	111	113
$[\text{Co}(\text{CS}_2 \cdot \text{NPr}^o)_3]$	-450	-450	110	112
$[\text{Co}(\text{CS}_2 \cdot \text{NPr}^i)_3]$	-407	-457, -356*	126	146, 111
$\text{MeCS}_2 \cdot \text{NiPr}^i_2$	-432	-563, -449, -362*	-130	-151, 116
$\text{Pr}^i_2\text{N} \cdot \text{CS}_2\text{CS}_2 \cdot \text{NiPr}^i_2$	-439	-543, -488, -363*	-137	-157, -122
$[\text{Ru}_2(\text{dte})_3]^+\text{Cl}^-$	-500, -427, -366	-500, -443, -364*	-136	-167, -126

* Intensity of *ca.* -360 Hz multiplet is *ca.* equal to the sum of the intensities of the remaining CH multiplets.

^1H n.m.r. spectrum of (I) at 60°C comprises three multiplets at *ca.* -500 , -427 , and -368 Hz, with intensity ratios *ca.* 1 : 3 : 1 and a complex multiplet for the CH_3 protons at *ca.* -136 Hz. As the temperature falls, the -427 Hz multiplet collapses and at -60°C the CH spectrum comprises three multiplets at *ca.* -500 , -443 ,

corresponds to the H(2) type protons, with the multiplet at -500 Hz corresponding to the H(5) protons, with the exception of H(a5) to which the signal at -443 Hz is ascribed.

H(b,c5) are unusual, being involved in interligand hydrogen bonding (Table 2). The high-temperature spectrum is consistent with the usual interpretation of relatively free rotation within the ligands yielding single intense CH and CH_3 multiplets at -427 and -136 Hz, but with remnant CH signals at -368 and -500 Hz indicating that this is not true of all ligands; the latter signals are assumed to arise from bridging ligands b and c, the rotation of these being strongly hindered even at elevated temperatures by the strong interaction of H(b,c5) with neighbouring ligands.

It is apparent from the chromatographic isolation of the derivatives that the present derivatives represent only two of a variety of dithiocarbamate species formed in the reaction mixture, while the unusual $[\text{Ru}_2\text{Cl}_6]^{2-}$ anion also exists in appreciable quantities. As a rule, the tetrahedral tetrahalogeno-anions of the first-transition series appear to have no analogues among the metals of the second and third series and it is surprising, in the present case, to find that the metal geometry is pseudo-tetrahedral. The only other well-authenticated parallel to this species appears to be the $[\text{Co}_2\text{Cl}_6]^{2-}$ species;¹² the geometries of the present anion and of the $[\text{Co}_2\text{Cl}_6]^{2-}$ analogue are remarkably similar, the angle subtended by the bridging chlorines at the metal atom being 92.6 and

¹¹ R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, 1972, **11**, 2435.

¹² W. Harrison, N. L. Paddock, J. Trotter, and J. N. Wingfield, *J.C.S. Chem. Comm.*, 1972, 23.

90.0° respectively, while the angle at the bridging chlorine is 87.4 and 89.1° and both anions are centrosymmetric in their respective complexes. The Ru...Ru distance in the anion [3.264(6) Å] is longer than that in the cation, but shorter than in [Ru₂(CS₂·NEt₂)₄(CO)₂] (3.654(2) Å) and this, together with the apparent diamagnetism of the anion, suggests the likelihood of metal-metal bond formation in the anion also. A number of MO schemes may be devised to account for this, but the present lack of useful diagnostic information renders the pastime futile.

The chloroform solvent molecule has a hydrogen-bonding interaction with the anionic Cl(3), in contrast to the interaction described in the previous paper, where hydrogen-bonding to the ligand sulphur atoms occurs; this preference in the present case is probably a consequence of the greater electronegativity of chlorine *vis-à-vis* sulphur. Although the level of significance is doubtful, it is possible that this interaction is reflected in the observation that Ru(3)-Cl(3) is longer than Ru(3)-Cl(2) [2.24(1) *cf.* 2.19(1) Å]. In (II), we also find contacts between the non-bridging chlorines of the anion and the hydrogens H(2,5) of the isopropyl groups of the cation (see Figure 3). In (I), similar intermolecular contacts are found between H(a2,c) and the disordered chloride ion. In both cations the H(2) hydrogens of the bridging ligands, as well as interacting in the usual way with the adjacent intraligand sulphur atoms, also have close con-

tacts to sulphur atoms on adjacent ligands (Table 2). The more accurate thermal ellipsoids of cation (I) show a pronounced anisotropy indicative of oscillation about the N-CH bond (Figure 2).*

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* *Note added at proof:* The structure of a dimeric ruthenium dithiocarbamate, [Ru₂(CS₂·NEt₂)₅]⁺BF₄⁻·CH₃COCH₃, formed by the reaction of a benzene solution of [Ru(CS₂·NEt₂)₃] with gaseous BF₃, has recently been determined by Pignolet and Mattson.¹³ Although the formula unit is the same as the di-isopropyl derivatives, the molecular structure differs significantly; one ligand bridges the pair of ruthenium atoms, two are bridging on the same side of the Ru₂S₂ plane, and the two remaining ligands are terminal. Unlike (I), the anion is not disordered and the ruthenium oxidation state is clearly III. The short Ru...Ru distance (2.74 Å), similar to that found in (I) and (II), is consistent with an [Ru₂(dthc)₅]⁺ cation in the di-isopropyl derivatives. Ru...S distances associated with non-bridging sulphur atoms (Ru-S, 2.41 Å) are similar to those found in (I) and (II) (2.40 Å). Those involved with the bridging sulphur atoms are short with an average of 2.31 Å compared with *ca.* 2.32 Å in (I) and (II). With the exception of certain terminal methyl groups, the symmetry of the [Ru₂(CS₂·NEt₂)₅]⁺ cation is C₂; the symmetry axis is collinear with the C::N bond of the ligand bridging the pair of ruthenium atoms. Unlike (I) and (II), the chirality of the ruthenium atoms is the same. Differences in the synthesis and/or ligand substituents of the dimers, [Ru₂(dthc)₅]⁺ and [Ru₂(CS₂·NEt₂)₅]⁺, may be the dominant factors in the type of stereochemistry obtained. However, more structural data are required before any decisive conclusions can be drawn.

¹³ L. H. Pignolet and B. M. Mattson, *J.C.S. Chem. Comm.*, 1975, 49.