Structural Studies in the Ruthenium–Dithiocarbamate System. Part I. Crystal Structure of Tris(morpholyldithiocarbamato)ruthenium(III)–2.5 Chloroform

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The crystal structure of the title compound has been determined by the heavy-atom method from *X*-ray diffractometer data and refined by least-squares to *R* 0.11 for 6 499 reflections. Crystals are triclinic, space group $P\bar{1}$, a = 17.630(2), b = 17.893(2), c = 13.955(2) Å, α = 94.25(1), β = 108.68(1), γ = 120.31(1)°, Z = 2. The geometry of the complex molecule is conventional; the structure is of interest in establishing the nature of chloroform–dithiocarbamate interactions, the hydrogen atom of each chloroform being hydrogen-bonded to the sulphur atoms of various ligands.

STUDIES on the ruthenium–dithiocarbamate system ($CS_2^-\cdot NR_2 \equiv dtc^-$) have been relatively few[1-4] since the initial preparation and characterisation of the $[Ru(dtc)_3]$ and $[Ru(dtc)_3NO]$ series;[5,6] the structures of representative members of the two series have been reported briefly,[7] and recently that of $[Ru(CS_2\cdot NEt_2)_3]$ in more detail,[8] together with solution studies of the n.m.r. spectra of the $[Ru(dtc)_3]$ series over a temperature range.[9]

Aqueous solutions of 'ruthenium trichloride trihydrate' react with aqueous solutions of sodium dialkyldithiocarbamate to give a product which is primarily $[Ru(dtc)_3]$; green $[Ru(dtc)_3]$, purified by column chromatography (alumina–chloroform), were generally obtained as crystals with a red dichroism from chloroform–ethanol. (In the cases of the pyrrolidyl and methyl- and ethyl-phenyl derivatives, benzene–ethanol was found desirable to eliminate decomposition.) The complexes gave satisfactory analyses corresponding to $[Ru(dtc)_3]$, with the exception of the present morpholyl derivative which appeared to contain two molecules of chloroform of crystallization. During the preparation of a wide variety of $M(dtc)_n$ complexes, we have frequently observed that chloroform solvates are formed, usually as crystals which crumble rapidly as solvent is lost to the atmosphere; the present derivative was unusual in its stability under these conditions. Previous studies of the proton n.m.r. spectra of the cobalt(III) derivatives and their temperature dependence in chloroform solution have suggested anomalously strong solvent–complex interactions,[10] and it has been suggested that interaction with the solvent occurs at the ligand nitrogen atom;[11] alternatively, a charge-transfer complex might be a possibility. The crystal structure of the present complex was studied to give an insight into the nature of this interaction, at least in the solid state, with the possibility of extrapolation to the solution, and the derivative was subsequently shown to be $2[Ru(CS_2\cdot N[CH_2]_4O)_3],5CHCl_3$, the discrepancy in the analytical figures perhaps being due to loss of chloroform from the solvent-containing tunnels in the lattice.

Analytical figures for the $[Ru(dtc)_3]$ derivatives studied are given in Supplementary Publication No. SUP 21440, (30 pp., 1 microfiche);† the analytical figures for the present derivative are (in the order = found, calc. for $[Ru(CS_2\cdot N[CH_2]_4O)_3],2CHCl_3$, and calc. for $2[Ru(CS_2\cdot N[CH_2]_4O)_3],5CHCl_3$): Ru, 12.43, 12.23, 11.40; S, 24.50, 23.27, 21.71; Cl, 25.75, 25.74, 30.00; C, 24.61, 24.70, 23.72; N, 4.97, 5.08, 4.74; H, 3.22; 3.17, 3.01%. Repeated preparations and analyses gave no better agreement with the structure determination.

Magnetic moments were also determined by the Faraday method at 298 K and lie in the range 1.75—1.95 B.M.; a selection was run over the temperature range 80—300 K and showed no unusual features. Electronic spectra, determined for acetone and chloroform solutions showed only minor variations with solvent or ligand substituents: for $[Ru(CS_2\cdot NPr^i_2)_3]$ (10^3 cm^{-1}, with log ε in parentheses): 17.700 (3.26), 21.700 (3.49), 27.000 (4.03), 34.500sh (4.28), 38.000sh (4.46), 42.000 (4.60). (Detailed magnetic-moment data are deposited in the Supplementary Publication.)

Unlike the other unsolvated $[Ru(dtc)_3]$ species, which exist as green crystals with a red dichroism, the present complex is black, and when crushed is a dark brown powder. The solution spectrum does not differ significantly from those of the other $[Ru(dtc)_3]$ derivatives; attempts to obtain a reflectance spectrum for the powdered derivative were unenlightening.

EXPERIMENTAL

A crystal 0.16 × 0.09 × 0.20 mm was used. Cell constants were determined by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 40° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set in the range $2\theta < 100°$ was gathered by a

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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Table 1

Atomic fractional cell and thermal parameters ($\times 10^3 Å^2$), with least-squares estimated standard deviations in parentheses (decimal points omitted before x, y, z). H positions of chloroform solvent molecules are estimated

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*a*) Molecule (1)									
Ru	1 071(1)	3 024(1)	0 006(1)	73(1)	51(1)	47(1)	40(1)	20(1)	18(1)
(i) Ligand (1a)									
S(1)	2 035(4)	4 601(3)	0 245(4)	85(4)	54(3)	66(3)	42(3)	42(3)	25(3)
S(2)	0 430(4)	3 689(3)	0 763(4)	78(4)	53(3)	64(3)	39(3)	35(3)	26(3)
N	142(1)	5 494(9)	105(1)	75(11)	59(10)	55(11)	30(9)	30(9)	21(8)
C(1)	133(1)	468(1)	074(1)	72(14)	69(13)	43(12)	42(12)	24(11)	23(10)
C(2)	213(2)	634(1)	092(2)	99(18)	66(14)	92(17)	41(14)	56(15)	39(13)
C(3)	267(2)	710(1)	194(2)	88(17)	56(13)	111(20)	24(13)	52(16)	6(13)
C(4)	0 75(2)	554(1)	146(2)	94(17)	67(14)	83(16)	49(13)	41(14)	5(12)
C(5)	133(2)	628(1)	246(2)	118(20)	59(14)	127(22)	42(14)	81(18)	38(14)
O	199(1)	711(1)	228(1)	117(13)	78(10)	89(11)	61(10)	34(10)	11(8)
(ii) Ligand (1b)									
S(1)	2 066(4)	3 048(3)	1 658(4)	89(4)	59(3)	63(3)	45(3)	19(3)	23(3)
S(2)	0 154(4)	1 588(3)	0 279(5)	94(4)	53(3)	79(4)	42(3)	28(3)	25(3)
N	144(2)	148(1)	215(2)	141(19)	84(14)	138(19)	64(14)	59(16)	71(14)
C(1)	110(2)	195(1)	143(2)	116(18)	64(13)	60(14)	52(14)	29(14)	35(11)
C(2)	200(2)	185(1)	315(2)	134(24)	142(25)	98(21)	85(21)	−29(18)	51(19)
C(3)	215(2)	117(1)	338(2)	158(28)	110(22)	147(28)	69(21)	−7(23)	66(21)
C(4)	023(2)	058(2)	198(3)	116(24)	91(21)	241(40)	15(19)	−9(26)	85(24)
C(5)	056(2)	−002(2)	227(3)	192(33)	76(19)	184(34)	59(22)	16(28)	54(21)
O	133(2)	033(1)	327(1)	245(24)	111(14)	98(14)	97(16)	38(15)	65(12)
(iii) Ligand (1c)									
S(1)	1 752(4)	2 658(3)	−1 006(4)	75(4)	73(3)	53(3)	49(3)	14(3)	12(3)
S(2)	0 003(4)	2 558(3)	−1 810(4)	80(4)	70(3)	51(3)	53(3)	20(3)	17(3)
N	064(1)	205(1)	−309(1)	74(11)	57(10)	41(9)	34(9)	18(9)	6(8)
C(1)	078(1)	240(1)	−214(1)	74(14)	70(13)	54(23)	47(12)	18(11)	31(11)
C(2)	141(1)	203(2)	−329(2)	72(15)	119(19)	67(15)	58(15)	26(13)	−10(14)
C(3)	092(2)	116(2)	−414(2)	86(17)	119(20)	72(16)	67(16)	4(14)	−11(15)
C(4)	−018(2)	193(2)	−403(2)	94(18)	134(21)	59(15)	82(18)	3(13)	15(15)
C(5)	−056(2)	105(2)	−487(2)	80(17)	125(21)	59(15)	44(16)	26(13)	−21(14)
O	021(1)	112(1)	−508(1)	99(11)	78(10)	66(10)	37(9)	35(8)	−4(8)
(*b*) Molecule (2)									
Ru	6 127(1)	8 939(1)	3 047(1)	63(1)	57(1)	42(1)	37(1)	19(1)	20(1)
(i) Ligand (2a)									
S(1)	5 689(4)	9 775(3)	2 024(4)	73(4)	70(3)	58(3)	42(3)	22(3)	27(3)
S(2)	7 303(4)	9 665(3)	2 362(4)	70(3)	76(3)	51(3)	44(3)	26(3)	24(3)
N	639(1)	1.065(1)	144(1)	68(11)	62(11)	74(12)	24(10)	27(10)	23(9)
C(1)	664(1)	1.011(1)	177(1)	55(12)	44(11)	29(10)	8(10)	16(9)	−4(8)
C(2)	628(2)	1.089(2)	052(2)	108(20)	89(17)	138(24)	60(16)	37(18)	73(17)
C(3)	688(2)	1.188(2)	056(3)	143(26)	139(26)	266(41)	91(23)	145(29)	150(28)
C(4)	778(1)	1.089(1)	089(17)	81(17)	103(19)	128(22)	33(16)	66(17)	71(17)
C(5)	833(2)	1.186(2)	093(2)	90(19)	149(25)	179(29)	77(19)	58(20)	108(23)
O	767(1)	1.205(1)	026(1)	139(15)	75(11)	136(15)	39(11)	84(113)	53(11)
(ii) Ligand (2b)									
S(1)	4 987(4)	7 547(3)	1 684(4)	77(3)	61(3)	52(3)	43(3)	13(3)	12(3)
S(2)	6 549(4)	7 896(4)	3 531(4)	80(4)	71(3)	53(3)	50(3)	15(3)	19(3)
N	542(1)	631(1)	198(1)	80(12)	71(11)	73(12)	42(10)	34(10)	14(10)
C(1)	562(1)	713(1)	234(1)	49(12)	37(10)	53(12)	14(9)	7(10)	−16(9)
C(2)	467(2)	575(1)	090(2)	102(18)	46(12)	66(15)	27(13)	10(14)	4(10)
C(3)	418(2)	474(2)	090(2)	74(16)	89(17)	139(23)	55(15)	34(16)	19(16)
C(4)	611(2)	607(1)	254(2)	82(16)	69(15)	129(22)	61(14)	6(15)	27(14)
C(5)	546(2)	504(1)	240(2)	115(20)	72(15)	72(19)	63(15)	16(15)	6(13)
O	488(1)	453(1)	134(1)	111(12)	71(12)	104(12)	62(10)	37(10)	15(9)
(iii) Ligand (2c)									
S(1)	5 155(4)	8 659(3)	4 021(4)	65(3)	56(3)	64(3)	33(3)	26(3)	16(3)
S(2)	7 129(4)	1.0072(3)	4 691(4)	75(4)	66(3)	55(3)	33(3)	27(3)	19(3)
N	620(1)	988(1)	593(1)	88(13)	50(10)	49(10)	22(9)	26(10)	1(9)
C(1)	618(1)	961(1)	504(1)	75(14)	38(10)	38(11)	26(10)	14(10)	−1(9)
C(2)	534(1)	946(1)	620(2)	87(16)	79(15)	52(13)	46(13)	34(12)	19(11)
C(3)	570(2)	936(1)	734(2)	132(22)	76(16)	84(18)	53(16)	45(17)	34(14)
C(4)	701(2)	1.088(2)	668(2)	131(21)	109(19)	44(14)	56(17)	37(14)	33(13)
C(5)	731(2)	1.058(2)	784(2)	127(21)	102(18)	39(13)	45(17)	26(14)	22(13)
O	647(1)	1.021(1)	805(1)	152(15)	122(13)	67(10)	82(12)	61(11)	46(10)

TABLE 1 (*Continued*)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*c*) Chloroform solvent molecules									
(i) Chloroform (1)									
C	356(3)	231(2)	082(2)	246(37)	139(26)	77(20)	127(28)	38(23)	28(19)
H	336	277	060						
Cl(1)	409(1)	211(1)	022(1)	412(23)	332(20)	321(20)	−46(18)	294(19)	−104(16)
Cl(2)	2 461(7)	1 160(6)	0 543(7)	203(9)	147(7)	129(7)	103(7)	46(7)	45(6)
Cl(3)	4 236(9)	2 641(6)	2 222(7)	310(13)	123(6)	126(7)	125(8)	51(8)	40(6)
(ii) Chloroform (2)									
C	740(2)	212(2)	396(2)	119(21)	138(23)	63(16)	73(19)	41(15)	34(16)
H	700	238	348						
Cl(1)	6 758(7)	2 578(7)	3 154(8)	216(10)	222(10)	170(9)	162(9)	112(8)	124(8)
Cl(2)	8 440(7)	2 544(9)	3 891(8)	160(9)	296(14)	174(9)	136(10)	76(8)	113(10)
Cl(3)	7 403(8)	2 321(6)	5 153(7)	262(11)	164(8)	126(7)	136(8)	85(8)	53(6)
(iii) Chloroform (3)									
C	459(2)	647(2)	436(2)	129(21)	117(20)	87(18)	87(18)	55(17)	49(16)
H	501	709	418						
Cl(1)	3 681(6)	5 629(5)	3 187(6)	170(7)	146(7)	105(6)	91(6)	58(6)	28(8)
Cl(2)	5 327(7)	6 138(6)	5 058(7)	180(8)	150(7)	164(8)	112(7)	64(7)	65(6)
Cl(3)	4 046(7)	6 647(5)	5 139(7)	211(9)	125(6)	158(8)	103(7)	107(7)	40(6)
(iv) Chloroform (4)									
C	188(2)	458(2)	−234(3)	159(31)	122(25)	133(28)	−19(23)	−35(24)	51(22)
H	165	433	−195						
Cl(1)	300(1)	574(1)	−164(1)	309(16)	531(28)	297(17)	301(19)	207(15)	294(19)
Cl(2)	134(1)	562(1)	−216(1)	233(12)	231(12)	345(17)	170(10)	188(12)	188(12)
Cl(3)	136(2)	439(1)	−344(1)	902(47)	155(11)	216(14)	123(19)	317(23)	20(10)
(v) Chloroform (5)									
C	136(2)	373(2)	363(2)	192(31)	214(34)	91(21)	155(29)	54(21)	85(22)
H	146	377	290						
Cl(1)	0 451(7)	2 657(6)	3 468(8)	162(8)	155(8)	196(10)	88(7)	85(7)	66(7)
Cl(2)	109(1)	451(1)	394(1)	352(15)	249(12)	173(9)	245(12)	141(10)	124(9)
Cl(3)	2 442(7)	4 016(7)	4 718(7)	183(9)	187(9)	126(7)	105(8)	162(6)	38(7)

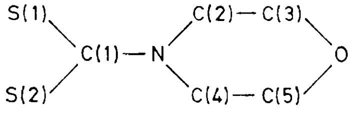
conventional 2θ—θ scan, yielding 7 083 independent reflections of which 6 499 having $I > 2\sigma(I)$ were considered observed and used in the structure solution and refinement after correction for absorption.

Crystal Data.—$C_{35}H_{53}Cl_{15}N_6O_6Ru_2S_{12}$, $M = 1\,773$, Triclinic, $a = 17.630(2)$, $b = 17.893(2)$, $c = 13.955(2)$ Å, $\alpha = 94.25(1)$, $\beta = 108.68(1)$, $\gamma = 120.31(1)°$, $U = 3\,447(1)$ Å^3, $D_m = 1.71(2)$, $Z = 2$, $D_c = 1.71$, $F(000) = 1\,776$. Cu-K_α radiation (Ni-filtered), $\lambda = 1.5418$ Å; μ (Cu-K_α) $= 126$ cm^{-1}. Space group $P\bar{1}$ (C_i^1, No. 2).

The structure was solved by conventional Patterson and Fourier methods and refined by 9 × 9 block-diagonal least-squares; 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 atoms. [Because of the size of the problem, no attempt was made to use a full-matrix refinement or to locate hydrogen atoms; the accuracy overall (which was limited) rendered the latter futile anyway.] At convergence no parameter shift exceeded 0.2σ, the residual R was 0.11, and R' was 0.131 $[R'(\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$. The weighting scheme was of the form $w = (\sigma^2(F_o) + 6 \times 10^{-4}(F_o)^2)^{-1}$. Neutral atom scattering factors were used,[12] those for ruthenium, sulphur, and chlorine being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[13] The rather high R value appears to be a consequence of the very high thermal motion on the chloroform molecules, coupled with the possibility of partial occupancy of sites by the latter; in view of the latter possibility, suggested by the analytical discrepancy, an attempt was made to refine the population of the solvent molecules, but the values obtained did not differ significantly from 1 and the attempt was abandoned. In addition, no change was observed in the standards during data collection and the discrepancies (together with the good value obtained for the density!) remain unresolved.

All data processing and computation was carried out on a CDC 6200 machine at this University, with a local adaptation of the '*X*-Ray' system.[14] Structure-factor tables are deposited in the Supplementary Publication. Results are shown in Tables 1—3.

Atomic numbering within the ligands is as follows: where necessary in the Discussion or Tables preceding digits *lm* denote the number of the ligand, where $l = 1$ or 2 is the number of the molecule, and m = a, b, or c the number of the ligand within the molecule. Within each molecule, sulphur atoms *lm*1 form an upper triangle of the D_3 molecular core and *lm*2 the lower triangle; C(2) is on the same side of the ligand as S(1).



DISCUSSION

The asymmetric unit of the crystal comprises two $[Ru(CS_2{\cdot}N[CH_2]_4O)_3]$ molecules together with five molecules of chloroform solvent. Within the complex, the familiar D_3 configuration of three symmetrically bidentate dithiocarbamate ligands chelated to the central metal

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

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

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

atom in a disposition midway between the octahedron and trigonal prism is found, closely resembling the structure established for the diethyl analogue [Ru(CS$_2$·NEt$_2$)$_3$].[7,8] In spite of the comprehensive data set, the present structure determination is less accurate than that of the diethyl derivative for reasons discussed earlier, and since the difference in the geometries of the [Ru(S$_2$)$_3$] molecular cores is only trivial, no further consideration will be given here to that aspect. The remainder of the ligand geometries are also unexceptionable; the configuration of the morpholyl rings in each case is a ' chair '. The chloroform molecular geometries are also conventional and of very low accuracy because of their very high thermal motion and the possibility of partial occupancy.

TABLE 2

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

(*a*) Intraligand geometries

Ligand *lm*	(1a)	(1b)	(1c)	(2a)	(2b)	(2c)	Mean
Ru–S(1)	2.370(5)	2.389(6)	2.368(6)	2.375(7)	2.379(5)	2.366(5)	2.383
Ru–S(2)	2.396(8)	2.389(6)	2.388(5)	2.374(7)	2.397(8)	2.399(7)	
S(1) · · · S(2)	2.829(9)	2.846(6)	2.826(10)	2.842(10)	2.843(8)	2.839(7)	2.824
S(1)–Ru–S(2)	72.8(2)	73.1(2)	72.9(2)	73.5(3)	73.0(2)	73.1(2)	73.1
Ru–S(1)–C(1)	86.9(7)	86.4(8)	88.5(9)	87.7(5)	87.8(5)	87.2(8)	87.3
Ru–S(2)–C(1)	85.3(10)	87.7(8)	88.5(7)	85.3(7)	86.8(4)	89.6(5)	
S(1)–C(1)–S(2)	115(1)	113(1)	110(1)	113(1)	112(1)	110(1)	112
S(1)–C(1)	1.66(3)	1.74(2)	1.74(2)	1.65(2)	1.70(2)	1.76(1)	1.71
S(2)–C(1)	1.69(2)	1.68(2)	1.71(3)	1.75(3)	1.72(1)	1.70(2)	
C(1)–N	1.40(3)	1.37(4)	1.31(3)	1.37(3)	1.34(3)	1.28(3)	1.35
S(1)–C(1)–N(1)	124(1)	122(1)	123(2)	127(2)	124(1)	123(2)	124
S(2)–C(1)–N(1)	121(2)	126(1)	127(2)	119(2)	123(2)	126(1)	
N–C(2)	1.48(3)	1.48(3)	1.49(4)	1.48(4)	1.48(2)	1.50(3)	1.49
N–C(4)	1.49(4)	1.52(3)	1.51(3)	1.51(4)	1.50(4)	1.48(2)	
C(1)–N–C(2)	121(2)	123(2)	122(2)	118(2)	119(2)	124(1)	121
C(1)–N–C(4)	122(2)	120(2)	118(2)	125(2)	119(1)	120(2)	
C(2)–N–C(4)	116(2)	117(3)	117(2)	116(2)	119(2)	114(2)	117
C(2)–C(3)	1.53(3)	1.42(6)	1.52(4)	1.52(1)	1.55(3)	1.58(4)	1.53
C(4)–C(5)	1.49(3)	1.48(6)	1.56(4)	1.48(4)	1.56(3)	1.66(4)	
N–C(2)–C(3)	109(2)	110(2)	107(2)	108(2)	108(2)	106(2)	107
N–C(4)–C(5)	109(2)	106$_6$3)	106(3)	110(3)	105(2)	105(2)	
C(3)–O	1.43(4)	1.41(3)	1.46(3)	1.47(5)	1.44(4)	1.40(2)	1.43
C(5)–O	1.46(3)	1.40(4)	1.43(4)	1.44(4)	1.39(3)	1.44(4)	
C(2)–C(3)–O	109(2)	116(3)	109(3)	110(3)	111(2)	110(2)	111
C(4)–C(5)–O	109(2)	115(3)	111(2)	109(2)	113(2)	106(2)	
C(3)–O–C(5)	117(2)	113(2)	111(2)	115(3)	110(2)	112(2)	111

(*b*) Other RuS$_6$ core angles; values for $l = 2$ follow those for $l = 1$

S(*a*1)–Ru–S(*b*1)	95.9(2), 93.6(2)	S(*a*1)–Ru–S(*b*2)	163.0(2), 160.8(2)
S(*a*1)–Ru–S(*c*1)	94.9(2), 99.3(3)	S(*b*1)–Ru–S(*c*2)	162.2(3), 164.7(2)
S(*b*1)–Ru–S(*c*1)	96.1(3), 95.5(2)	S(*c*1)–Ru–S(*a*2)	164.3(2), 163.0(2)
S(*a*2)–Ru–S(*b*2)	94.8(2), 94.8(2)	S(*a*1)–Ru–S(*c*2)	99.0(2), 98.3(3)
S(*a*2)–Ru–S(*c*2)	98.9(2), 98.3(2)	S(*b*1)–Ru–S(*a*2)	94.9(2), 100.3(2)
S(*b*2)–Ru–S(*c*2)	94.4(2), 97.5(2)	S(*c*1)–Ru–S(*b*2)	99.1(3), 95.9(2)
	Mean 96.3		Mean 163.0, 97.9

(*c*) Chloroform geometries

	(1)	(2)	(3)	(4)	(5)	Mean
C–Cl(1)	1.58(6)	1.87(4)	1.74(2)	1.66(3)	1.71(3)	1.74
C–Cl(2)	1.87(3)	1.63(3)	1.75(4)	2.02(6)	1.76(5)	
C–Cl(3)	1.79(3)	1.67(3)	1.76(4)	1.44(4)	1.81(4)	
Cl(1)–C–Cl(2)	103(2)	108(2)	110(2)	92(2)	111(2)	108
Cl(1)–C–Cl(3)	110(3)	106(2)	109(2)	130(3)	108(2)	
Cl(2)–C–Cl(3)	104(2)	110(2)	109(2)	103(3)	108(2)	

(*d*) Chloroform-hydrogen–sulphur contacts (<3.00 Å)

S(2*c*2) · · · H(2$^{\mathrm{I}}$)	2.94	S(2*a*1) · · · H(2$^{\mathrm{I}}$)	2.79
S(2*b*2) · · · H(3)	2.84	S(1*c*1) · · · H(1)	2.89
S(2*c*1) · · · H(3)	2.72	S(1*a*1) · · · H(4)	2.87
S(1*a*2) · · · H(5)	2.91	S(1*b*1) · · · H(5)	2.84

Transformation of the asymmetric unit: I x, $1 + y$. z.

The interesting feature of the structure lies in the disposition of the complex molecules and the solvent. Figure 1 clearly shows that the complex molecules form a cage-like structure through which pass tunnels containing the chloroform solvent molecules, the tunnels lying through the cell centre (as defined here) parallel to *a* with the complex molecules lying along the cell periphery. The hydrogen atoms of the chloroform molecules are directed away from the centre of the tunnels, which are largely filled with the chlorine atoms, while the hydrogen atoms interact with the complex molecules at the periphery. Although the complex did not appreciably deteriorate during data collection, the possibility of solvent molecules escaping from the tunnels is probably quite real and explains the poor analytical results and the rather low accuracy of the structure, and is consistent with the very high thermal motion found for the chloroform molecules. The possibility that this phenomenon is reversible at a suitable combination of temperature and pressure in a chloroform atmosphere has not been examined. (The high thermal motion of the solvent in some cases also appears to be a consequence of a tendency for the chloroform molecule to rotate about the C–H bond as an axis.)

TABLE 3

Equations of least-squares planes, defined by the S_2CNC_2 section of each ligand, in the form $pX + qY + rZ = s$, where in the orthogonal (Å) frame X is parallel to a, and Z is in the ac plane. Atomic deviations (Δ) and the standard deviation of the defining atoms (σ) are in Å

Ligand *lm*	(1a)	(1b)	(1c)	(2a)	(2b)	(2c)
10^4p	3 636	8 425	0 628	−0 777	6 835	−5 741
10^4q	1 751	−4 083	9 486	8 230	4 248	5 444
10^4r	9 150	−3 513	−3 102	5 627	−5 936	−6 116
s	−0.634	−1.953	4.576	10.93	6.205	6.308
σ	0.04	0.05	0.05	0.05	0.06	0.07
ΔS(1)	0.01	−0.06	0.00	0.02	0.04	0.07
ΔS(2)	−0.04	0.03	0.01	−0.06	0.00	−0.04
ΔC(1)	0.04	0.03	0.01	0.03	−0.03	−0.01
ΔN	0.04	0.05	−0.10	0.07	−0.09	−0.08
ΔC(2)	−0.05	0.03	0.04	−0.07	0.02	−0.03
ΔC(4)	0.01	−0.07	0.03	0.01	0.06	0.10
ΔRu	−0.11	−0.12	0.03	−0.11	0.31	0.07
ΔC(3)	1.00	0.89	−0.94	0.90	−0.85	−1.20
ΔC(5)	1.08	0.90	−0.94	0.97	−0.85	−1.15
ΔO	0.92	0.78	−0.67	0.74	−0.55	−1.01
χ^2 *	20.0	19.2	34.0	34.7	42.6	65.3

* Five degrees of freedom.

The strong interaction of chloroform solvent with a number of dithiocarbamate molecules in solution has been noted elsewhere.[10,11] This is demonstrated most spectacularly in those $[Co(dtc)_3]$ derivatives which have symmetrically substituted ligands. Thus, whereas $[Co(CS_2{\cdot}NEt_2)_3]$ gives an n.m.r. proton spectrum which is the typical quartet–triplet over a wide temperature range in all other common solvents, in chloroform solution a strongly temperature-dependent and complex pair of multiplets is observed (Figure 2). A mechanism has been suggested for this in terms of the methylene proton pairs being transposed between site pairs of different energy, the activation energy for the process being relatively low, leading *via* a density-matrix treatment to a series of expressions which reproduce the temperature dependence and multiplet composition exactly; a physical interpretation of this model has been lacking, however. It has been suggested elsewhere that chloroform–dithiocarbamate interaction occurs at the nitrogen atom.

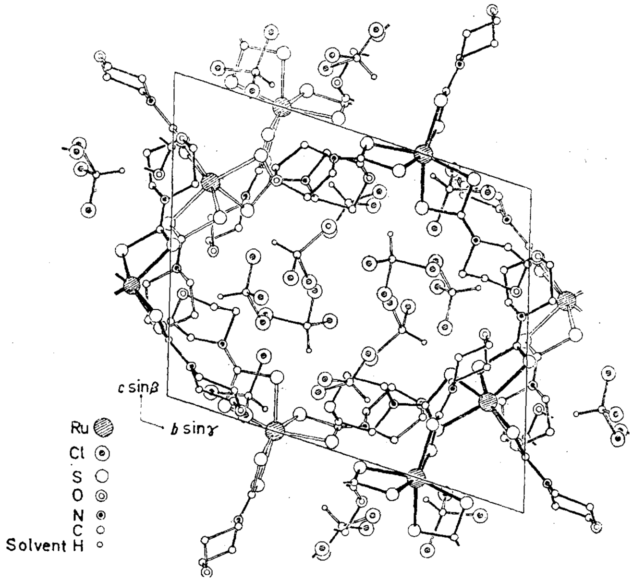

FIGURE 1 Unit cell contents, projected down *a*

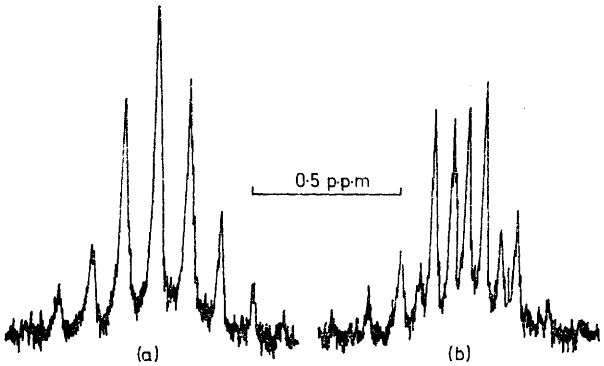

FIGURE 2 The 60 MHz methylene ^{1}H n.m.r. spectrum of $[Co(CS_2{\cdot}NEt_2)_3]$ in chloroform at (a) 10 and (b) 50 °C

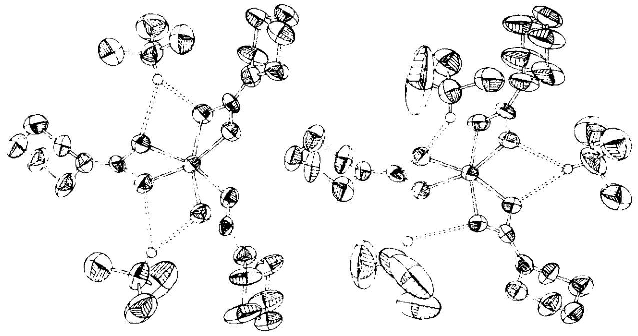

FIGURE 3 The molecules, projected down the pseudo-three-fold axes, showing 50% thermal ellipsoids and associated hydrogen-bonded solvent molecules

The present structure determination resolves the nature of the interaction; the solid state quite clearly can be plausibly extrapolated to the solution. Figure **3** shows that each chloroform proton is strongly hydrogen bonded to the ligand sulphur atoms, all S ••• H distances being <3.0 Å^2. It has been shown clearly in a series of structure determinations carried out for a variety of nickel(II) dithiocarbamates that the dominant intermolecular force within the crystal lattices of dithiocarbamate derivatives originates in S ••• H interactions, the usual distance being *ca.* 2.7—2.8 Å as here, although in cases where the hydrogen atom is attached to the more electronegative nitrogen atom, the interaction appears to be stronger.[15-18] A further consequence of such interactions may be distortions of the sulphur co-ordination sphere about the metal atom; this possibility does not warrant pursuing in the present case because of the lack of significant deviations from uniformity in the Ru–S distances, although some irregularity is observed in the angular geometry.

Inspection of Figure 3 shows that the S ··· H interactions are of two kinds: either the hydrogen atom is associated with one adjacent sulphur atom only, as is the case with H(1) and H(4) where the solvent molecule approaches the complex from above or below, or, as with the remainder, it bridges a pair of sulphur atoms, one from each of the upper and lower triangles of the D_3 co-ordination sphere, and from different ligands. The S ··· H distances associated with the two types are comparable and it thus appears likely that the bridging type of interaction, in which the approach of the solvent molecule is essentially from the side, with the C–H axis along the C_2 axis of the RuS_6 core, is at least as stable as the other type. If so, and if this array persists in solution, then a plausible mechanism for the anomalous n.m.r. spectra of the symmetrically substituted diethyldithiocarbamate cobalt(III) (and related) derivatives emerges. It has been shown elsewhere, by use of asymmetric substituents, that the CoS_6 inversion by a trigonal twist mechanism, S_2C–N bond rotation, and $S_2CN(-C)_2$ bond rotations, are all dynamic possibilities on the n.m.r. time-scale at easily accessible temperatures.[19] If the bulky chloroform solvent molecules solvate the complex by approach along the two-fold axis, so that the hydrogen interacts with two sulphur atoms, then a number of these molecular relaxation processes may be effectively retarded or jammed on the n.m.r. time-scale, depending on the strength of the interaction, either by the CH end of the solvent molecule or further out by the bulky chlorine atoms. Depending on the relative importance and effect of these interactions, it may easily be that the nature of the n.m.r. spectrum under this type of interaction could be determined by libration of the terminal ethyl groups between a pair of limiting positions of different energy defined by the bulk of the associated chloroform molecules.

[There seems no good reason why a similar hydrogen-bonding paproach along the more vulnerable and sulphur-rich molecular three-fold axis should not also be a feasible mode of association; it is however, much less likely that such an interaction would have any observable consequences leading to definitive diagnosis. If the interaction of the hydrogen atoms is with the sulphur p_π orbitals, however, this mode of association seems less likely, since they are directed away from the three-fold axis.]

A recent report [20] of the structures of $[Fe,Co(CS_2{\cdot}N[CH_2]_4O)_3],CH_2Cl_2$ show similar sulphur–solvent hydrogen bonding interactions, although the ^1H n.m.r. spectrum of $[Co(CS_2{\cdot}NEt_2)_3]$ in that solvent is a single quartet–triplet. However, whereas the ^1H n.m.r. spectrum of the methylene protons of $[Co(CS_2{\cdot}N[CH_2Ph]_2)_3]$ in CH_2Cl_2 is uncomplicated (unlike that in $CHCl_3$), the spectrum of the methylene protons in $PhNO_2$ solution is of the AB type up to 190 °C, suggesting that a strong solvent interaction also occurs in that case.[3]

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