Structural Studies in the Ruthenium–Dithiocarbamate System. Part IV.[1] Crystal Structure of a Trinuclear Ruthenium(II) Carbonyl Dithiocarbamate Chloride

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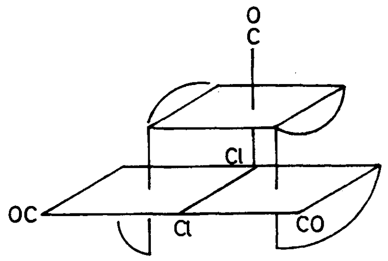
The crystal structure of the title complex $[Ru_3(CS_2{\cdot}NEt_2)_4(CO)_3Cl_2]$ has been determined by the heavy-atom method from *X*-ray diffractometer data and refined to *R* 0.068 for 1 407 reflections. Crystals are triclinic, space group $P\bar{1}$, $a = 13.964(5)$, $b = 13.919(9)$, $c = 11.073(5)$ Å, $\alpha = 102.09(4)$, $\beta = 109.91(3)$, $\gamma = 95.51(4)°$, $Z = 2$. The complex is trinuclear with ruthenium(II) atoms linked by bridging sulphur and bi- and ter-dentate chlorine atoms.

CARBONYLATED 'ruthenium trichloride' solution in methanol was allowed to react with the ester $MeCS_2{\cdot}NEt_2$. After a week, a minute quantity of tiny golden brown crystals appeared, too small for identification by conventional means. A tiny flake was shown to be a single crystal; its structure was determined and shown to be (I) (in which bidentate ligands are diethyldithiocarbamate).



(I)

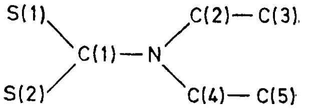
EXPERIMENTAL

A small flake, considered negligible in size for absorption correction purposes, was used. 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 $2\theta < 30°$, gathered by conventional 2θ—θ scan, yielded 1 583 independent reflections, of which 1 407 with $I > \sigma(I)$ were considered observed and used in the structure solution and refinement.

Crystal Data:—$C_{23}H_{40}Cl_2N_4O_3Ru_3S_8$, $M = 1\,051$, Triclinic, $a = 13.964(5)$, $b = 13.919(9)$, $c = 11.073(5)$ Å, $\alpha = 102.09(4)$, $\beta = 109.91(3)$, $\gamma = 95.51(4)°$, $U = 1\,945(1)$ Å^3, $D_m = 1.78$, $Z = 2$, $D_c = 1.79$ g cm^{-3}, $F(000) = 1\,048$. Mo-K_α radiation, $\lambda = 0.7107$ Å; $\mu = 17.0$ cm^{-1}. Space group $P\bar{1}$, (C_i, No. 2).

The structure was solved by the heavy-atom method and refined by 9 × 9 block-diagonal least-squares; in the final cycles, the parameters of the $Ru_3(CO)_3Cl_2S_8$ molecular core were refined as a single matrix, with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Neutral atom scattering factors were used,[2] those for ruthenium, sulphur, and chlorine being corrected for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$).[3] At convergence, no parameter shift exceeded 0.2σ; *R* was 0.068 and R' $[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ was 0.062, where $w = (\sigma^2(F_o) + 4 \times 10^{-4}|F_o|^2)^{-1}$.

Within a given ligand atoms are labelled as follows, C(2) being on the same side of the ligand as S(1).



The ligands are disposed within the molecule as shown; C(2b5) is disordered between two sites and was refined with

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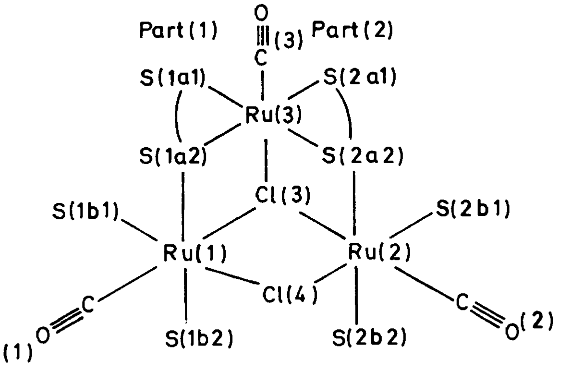
[1] Part III, C. L. Raston and A. H. White, preceding paper.

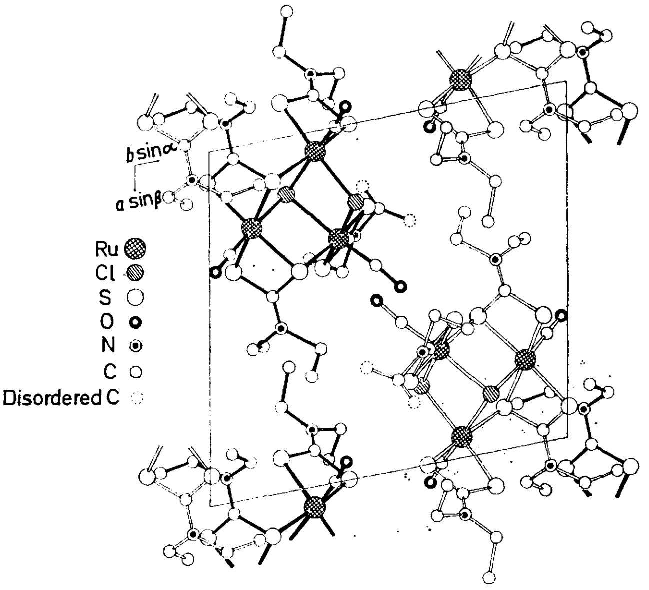
[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

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

fixed population parameters of 0.5. The molecule has approximate C_s symmetry and is labelled accordingly, ligand atom 1*mn* being related to 2*mn* by the pseudo-mirror operation.



Computation was carried out on our CDC 6 200 machine with a local variant of the '*X*-Ray' program system.[4] Structure factor tables and anisotropic thermal parameters are deposited as Supplementary Publication No.SUP 21443 (8 pp., 1 microfiche).* Results are shown in Tables 1—3. Unit-cell contents are illustrated in the Figure.



Unit-cell contents projected down *c*

DISCUSSION

The asymmetric unit in the present complex comprises discrete oligomeric molecules which are a new and interesting variation on the theme of the equilateral triangular arrangement of pseudo-octahedral ruthenium atoms; the system of bridges in the present case comprises ter- and bi-dentate chlorine and bridging sulphur atoms drawn from distinct dithiocarbamate ligands. The molecular symmetry is a close approximation to C_s; the ideal symmetry is destroyed by the disposition of certain of the terminal methyl groups on the ethyl ligand substituents. In spite of the fact that the bridging coordination about Ru(3) differs from that about Ru(1) and Ru(2), the approximation to an equilateral triangle is very close, the three Ru . . . Ru distances lying within the range 3.70 ± 0.04 Å; these distances are too long for significant metal–metal interaction to occur even if

TABLE 1

Atomic positional and isotropic thermal parameters ($\times 10^2$ Å^2), with least-squares estimated standard deviations in parentheses (decimal points are omitted before *x*,*y*,*z*)

Atom	*x*	*y*	*z*	*U*
Ru(3)	2 407(2)	1 185(2)	2 910(3)	*
Ru(1)	0 577(2)	2 955(2)	2 556(3)	*
Ru(2)	3 168(2)	3 591(2)	2 329(3)	*
Cl(3)	1 629(6)	2 151(6)	1 207(8)	*
Cl(4)	2 235(7)	4 093(6)	3 835(8)	*
C(3)	297(3)	062(3)	410(4)	8(1)
O(3)	342(2)	019(2)	492(3)	10(1)
C(1)	−001(3)	350(3)	355(3)	7(1)
O(1)	−051(2)	382(2)	425(2)	9(1)
C(2)	407(3)	458(3)	313(3)	8(1)
C(2)	484(2)	531(2)	369(2)	9(1)
Ligand (1a)				
S(1)	0 859(7)	−0 051(7)	1 912(9)	*
S(2)	1 181(7)	1 783(6)	3 829(9)	*
C(1)	035(2)	069(2)	281(3)	4(1)
N	−067(2)	047(2)	279(2)	5(1)
C(2)	−137(2)	−049(2)	177(3)	6(1)
C(3)	−121(2)	−142(2)	225(3)	6(1)
C(4)	−105(2)	114(2)	369(2)	3(1)
C(5)	−138(2)	063(2)	456(3)	5(1)
Ligand (2a)				
S(1)	3 544(7)	0 668(6)	1 799(9)	*
S(2)	3 876(7)	2 500(7)	3 742(8)	*
C(1)	440(2)	174(2)	281(3)	6(1)
N	537(2)	199(2)	275(2)	5(1)
C(2)	582(3)	119(3)	205(3)	10(1)
C(3)	578(3)	147(3)	088(4)	15(2)
C(4)	615(3)	305(3)	366(4)	12(1)
C(5)	688(4)	286(4)	478(6)	22(3)
Ligand (1b)				
S(1)	−0 985(7)	2 006(6)	0 934(9)	*
S(2)	−0 029(7)	3 910(7)	1 006(9)	*
C(1)	−099(2)	291(2)	012(3)	5(1)
N	−161(2)	286(2)	−111(2)	5(1)
C(2)	−240(2)	201(2)	−187(3)	6(1)
C(3)	−351(3)	222(3)	−198(4)	11(1)
C(4)	−150(2)	364(2)	−188(3)	7(1)
C(5)	−069(2)	334(2)	−248(3)	7(1)
Ligand (2b)				
S(1)	3 908(7)	3 149(7)	0 710(9)	*
S(2)	2 427(8)	4 404(7)	0 622(10)	*
C(1)	324(3)	388(2)	−008(3)	9(1)
N	321(2)	405(2)	−125(3)	10(1)
C(2)	412(2)	368(2)	−170(3)	7(1)
C(3)	358(4)	278(3)	−279(5)	16(2)
C(4)	255(3)	474(3)	−120(4)	14(2)
C(5) †	306(7)	563(7)	−151(9)	15(4)
C(5′) †	183(7)	429(6)	−276(8)	14(3)

* Anisotropic thermal parameters; see Supplementary Publication. † Population 0.5.

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* For details, see Notices to Authors No. 7, *J.C.S. Dalton*, Index issue, 1974 (items less than 10 pp. are supplied as full-size copies).

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

TABLE 2

Interatomic distances (Å) and angles (°)

(*a*) Ruthenium environments

(i) Unique geometry about Ru(3), C(3), Cl(3), Cl(4)

Ru–C	1.68(4)	C–Ru–Cl	176(1)
C–O	1.22(5)	S(a1)–Ru–S(a1′)	106.7(3)
Ru–Cl	2.55(1)	S(a2)–Ru–S(a2′)	106.6(3)
Ru–C–O	176(4)		
Ru(1)–Cl(3)–Ru(2)	99.0(3)	Ru(1)–Cl(4)–Ru(2)	99.0(3)
Ru(1) · · · Ru(2)	3.743(5)	Ru(1) · · · Ru(3) · · · Ru(2)	61.1(1)

(ii) Duplicated geometry; values appropriate to part (2) follow those for part (1). Primes indicate that the atom is drawn from the alternate part of the molecule

Ru(3)–S(a1)	2.39(1), 2.39(1)	Cl(3)–Ru(3)–S(a2)	83.5(3), 84.9(3)
Ru(3)–S(a2)	2.40(1), 2.38(1)	S(a1)–Ru(3)–S(a2)	72.8(3), 73.3(3)
C(3)–Ru(3)–S(a1)	94(1), 90(2)	S(a1)–Ru(3)–S(a2′)	174.4(4), 173.7(4)
Cl(3)–Ru(3)–S(a1)	89.5(3), 90.3(3)	Ru(3)–Cl(3)–Ru	91.9(3), 92.0(2)
C(3)–Ru(3)–S(a2)	96(2), 92(1)	Ru(3) · · · Ru	3.700(5), 3.667(5)
Ru(3)–S(a2)–Ru	100.7(4), 98.8(3)	Ru(3) · · · Ru · · · Ru	59.0(1), 59.9(1)
Ru–Cl(3)	2.60(1), 2.55(1)	Cl(3)–Ru–S(a2)	82.4(3), 83.8(3)
Ru–Cl(4)	2.45(1), 2.47(1)	Cl(3)–Ru–S(b1)	91.3(3), 94.5(3)
Cl(3)–Ru–Cl(4)	82.5(3), 83.0(3)	Cl(3)–Ru–S(b2)	90.1(4), 89.8(3)
Ru–S(a2)	2.40(1), 2.44(1)	Cl(4)–Ru–S(a2)	89.1(3), 85.9(3)
Ru–S(b1)	2.35(1), 2.36(1)	Cl(4)–Ru–S(b1)	167.1(4), 173.8(4)
Ru–S(b2)	2.37(1), 2.39(1)	Cl(4)–Ru–S(b2)	95.1(3), 101.4(3)
Ru–C	1.69(4), 1.63(4)	Cl(4)–Ru–C	93(1), 91(2)
C–O	1.25(5), 1.28(4)	S(a2)–Ru–S(b1)	101.4(3), 99.5(3)
Ru–C–O	174(3), 174(4)	S(a2)–Ru–S(b2)	170.9(3), 169.7(4)
Cl(3)–Ru–C	175(1), 173(2)	S(a2)–Ru–C	95(1), 98(1)
C–Ru–S(b1)	93(1), 91(1)	S(b1)–Ru–S(b2)	73.5(3), 72.9(4)
C–Ru–S(b2)	93(1), 89(2)	Ru–S(a2)–C(a2)	101(1), 102(1)

(*b*) The dithiocarbamate ligands; the Ru is enclosed by the chelate

Ligand *lm*	(1a)	(2a)	(1b)	(2b)
Ru–S(1)–C(1)	87(1)	86(1)	87(1)	88(1)
Ru–S(2)–C(1)	86(1)	87(1)	86(1)	85(1)
S(1)–C(1)–S(2)	114(2)	113(2)	113(1)	115(2)
S(1)–C(1)–N	125(2)	122(2)	126(2)	127(3)
S(2)–C(1)–N	121(2)	125(2)	121(2)	118(3)
S(1)–C(1)	1.66(3)	1.72(3)	1.69(3)	1.63(4)
S(2)–C(1)	1.73(2)	1.70(3)	1.70(3)	1.72(4)
C(1)–N	1.42(4)	1.40(4)	1.32(3)	1.35(5)
C(1)–N–C(2)	116(2)	119(2)	121(3)	114(3)
C(1)–N–C(4)	122(2)	121(3)	125(2)	126(3)
C(2)–N–C(4)	122(2)	118(3)	114(2)	118(3)
N–C(2)	1.55(3)	1.53(5)	1.43(3)	1.60(5)
N–C(4)	1.48(4)	1.63(4)	1.56(4)	1.57(6)
C(2)–C(3)	1.50(5)	1.42(3)	1.58(5)	1.47(5)
C(4)–C(5)	1.48(5)	1.41(7)	1.54(5)	1.27(9) *
N–C(2)–C(3)	113(2)	104(3)	112(3)	103(3)
N–C(4)–C(5)	113(2)	108(4)	105(2)	108(5) *
S(1) · · · S(2)	2.84(1)	2.85(1)	2.82(1)	2.82(1)

* C(4)–C(5′) 1.10(8), N–C(4)–C(5) 109(6), C(5)–C(4)–C(5) 143(8).

the electron configuration permitted it and there is no evidence for it in the geometry about the bridging atoms. The Ru–S distances lie between 2.35(1) and 2.44(1) Å; the two longest distances are Ru(1)–S(1a2) and Ru(2)–S(2a2) (2.40 and 2.44 Å) as might be expected, but unfortunately the rather low accuracy of the structure limited by the crystal size does not permit us to conclude that the difference between these distances and the remainder, in which the Ru is enclosed by the chelate, is significant. The Ru–CO distances are very short (1.63–1.69 Å) and it is clear in spite of the low accuracy that these distances are more akin to the Ru^{II}–CO distances of *ca.* 1.78 Å reported in $[Ru_2(dtc)_4(CO)_2]$ than the more usual value approaching 1.90 Å typical of the Ru^0 carbonyl derivatives.[1] The Ru–Cl distances found for the

TABLE 3

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

(*a*) Plane of three Ru atoms

$$0.0207X + 0.4100Y + 0.9119Z = 2.039$$

[Deviations: C(3) 1.01, C(1) 1.04, C(2) 0.99, Cl(3) −1.42, Cl(4) 1.50, S(1a1) −1.25, S(1a2) 0.96, S(2a1) −1.12, S(2a2) 1.11, S(1b1) −1.78, S(1b2) −1.27, S(2b1) −1.60, S(2b2) −1.45]

(*b*) Ligand planes

lm	(1a)	(2a)	(1b)	(2b)
10^4p	−1 321	−1 353	8 617	4 698
10^4q	4 832	4 104	−4 431	8 096
10^4r	− 8655	−9 018	−2 473	3 519
s	−1.786	−1.750	−3.024	5.573
$10^2\sigma$	5	8	4	8
χ^2 *	20.2	40.8	16.0	30.1
ΔS(1)	−5	8	5	−6
ΔS(2)	5	−8	−2	8
ΔC(1)		−2	−4	1
ΔN		7	−3	−9
ΔC(2)	5	−11	−2	10
ΔC(4)	−5	6	6	−4
Ru	2	−23	40	16
ΔC(3)	−129	119	−143	−127
ΔC(5)	−123	−124	156	118, −106

Angles (°) between ligand planes: (1a)–(2a) 4.7, (1a)–(1b) 83.5, (1a)–(2b) 88.6, (1b)–(2a) 85.7, (1b)–(2b) 87.2, (2a)–(2b) 87.7.

* Five degrees of freedom.

TABLE 4

Ruthenium(II)–chlorine distances (Å) in different bonding situations

Complex	
$[RuClH(PPh_3)_3]$ [a]	2.421
$[RuCl_2(PPh_3)_3]$ [b]	2.388(3)
$[RuCl_2(P_2C_{16}H_{20})_2]$ [c]	2.438
$[Ru_2Cl_3(PEt_2Ph)_3]^-$ [d]	2.446—2.513
$[Ru_2Cl_4(PEt_2Ph)_5]$ [e]	2.395 2.426—2.535 *
$[Ru_2Cl_3(PPhEt_2)_6]^+$ [d]	2.458—2.599 *

* Bridging Cl; others terminal.

[a] A. C. Skapski and P. G. H. Troughton, *Chem. Comm.*, 1968, 1230. [b] S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, 1965, **4**, 778. [c] I. Kawada, *Tetrahedron Letters*, 1969, 793. [d] K. A. Raspin, *J. Chem. Soc.* (*A*), 1969, 461. [e] N. W. Alcock and K. A. Raspin, *J. Chem. Soc.* (*A*), 1968, 2108.

bidentate bridging chlorine [2.45(1) and 2.47(1) Å)] are quite usual for that situation, but the distances from the three ruthenium atoms to the unusual terdentate bridging chlorine are long (2.55—2.60 Å) (Table 4); the only value comparable is in $[Ru_2Cl(O_2CC_3H_7)_4]$. These distances are all *trans* to the carbonyl groups.

The ligand geometries do not differ significantly either between themselves or in comparison to the normal Ru^{II} $(CS_2{\cdot}NR_2)$ geometry found in $[Ru_2(dtc)_4(CO)_2]$. Most ligands adopt C_2 symmetry with respect to the C–N ligand axis. In the present case, two of the ligands adopt the much less common C_s symmetry with the terminal methyl groups projecting on the one side of the ligand plane (Table 3); in ligand (2b), C(5) is disordered between the two possibilities. Unlike the derivatives $[Ru_2(CO)_2(CS_2{\cdot}NEt_2)_4]$ and $[Ru_2(CS_2{\cdot}NPr^i{}_2)_5]^+$,[5] there appear to be no asymmetric CS_2 geometries associated with bridging dithiocarbamate groups.

[5/040 *Received, 8th January,* 1975]

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[5] C. L. Raston and A. H. White, *J.C.S. Dalton,* Parts II and III, see preceding papers.