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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
R factor = 0.046
wR factor = 0.134
Data-to-parameter ratio = 15.5

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Non-merohedrally twinned *mer*-trichloro(dimethyl sulfoxide- κS)(1,10-phenanthroline)ruthenium(III) chloroform solvate, with $Z' = 6$

The title compound, $[\text{RuCl}_3(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_2\text{H}_6\text{OS})]\cdot\text{CHCl}_3$, contains six crystallographically independent formula units in the asymmetric cell. The structure features alternating layers of the main molecule and CHCl_3 arranged parallel to (011).

Comment

The crystal structure of *mer*-trichloro(dimethyl sulfoxide- κS)(1,10-phenanthroline)ruthenium(III), crystallized from CHCl_3 /toluene, with toluene included in the structure, has been reported previously (van der Drift *et al.*, 2002). This structure contains one formula unit per asymmetric unit (*i.e.* $Z' = 1$). We now report the structure of the title compound, (I), containing the same main molecule, obtained by crystallization from CHCl_3 only. The asymmetric unit of (I) contains six molecules of the main complex along with six chloroform molecules of crystallization (*i.e.* $Z' = 6$) (Fig. 1). The geometries of the six main molecules are essentially the same (Table 1).

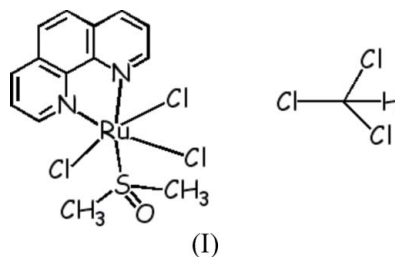


Fig. 2 illustrates the packing of the main molecules in layers parallel to (011), with the dimethyl sulfoxide molecules sticking out on both sides into an adjacent CHCl_3 layer. Each of the CHCl_3 molecules makes a $\text{C}-\text{H}\cdots\text{Cl}$ bond (Table 2) to an acceptor atom in an adjacent ruthenium complex molecule.

The unit cell features pseudo-translation symmetry $(0, \frac{1}{3}, \frac{2}{3})$ for the main molecules, but this is not supported by the CHCl_3 solvent molecules. This pseudosymmetry is also expressed as a pseudo-extinction rule of the form $k + 2l = 3n$.

Experimental

Commercially available analytical grade dimethyl sulfoxide (Biosolve BV), chloroform, hexane and acetone (Sigma-Aldrich), diethyl ether and 1,10-phenanthroline were used without further purification. *cis*- $[\text{RuCl}_2(\text{dmsO})_4]$ (dmsO = dimethyl sulfoxide) was prepared according to the literature procedure of Evans *et al.* (1973). Recrystallized *cis*- $[\text{RuCl}_2(\text{dmsO})_4]$ (0.3 g, 0.618 mmol) was dissolved in CHCl_3 (10 ml). The solution was placed in a round-bottomed flask containing 1,10-

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phenanthroline (0.1125 g, 0.625 mmol) dissolved in CHCl_3 (2 ml) with stirring. The reaction mixture was refluxed for 1 h. The dark-orange solution was subsequently concentrated to 1 ml. The dark-orange solid was redissolved in acetone (1 ml) whereupon a yellow solid appeared. The suspension was filtered and an orange solution recovered. To this solution was added diethyl ether until an orange solid was formed. The suspension was kept in a freezer overnight. The recovered solid was washed with diethyl ether. This solid was transferred, previously dissolved, into an alumina column for further purification by chromatography, using a 2:8 hexane–acetone mixture as eluent. The recovered orange fraction was dried using a rotary evaporator and dissolved in chloroform. On standing for several days, orange crystals of (I) were formed, filtered off, washed with diethyl ether and vacuum-dried at room temperature (yield 40%).

Crystal data

$[\text{RuCl}_3(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_2\text{H}_6\text{OS})]\cdot\text{CHCl}_3$	$Z = 12$
$M_r = 585.12$	$D_x = 1.874 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 13.8023 (16) \text{ \AA}$	Cell parameters from 290 reflections
$b = 19.731 (3) \text{ \AA}$	$\theta = 4.0\text{--}25.0^\circ$
$c = 25.597 (3) \text{ \AA}$	$\mu = 1.64 \text{ mm}^{-1}$
$\alpha = 75.823 (9)^\circ$	$T = 150 \text{ K}$
$\beta = 74.676 (10)^\circ$	Plate, orange-red
$\gamma = 69.907 (8)^\circ$	$0.30 \times 0.25 \times 0.07 \text{ mm}$
$V = 6221.8 (15) \text{ \AA}^3$	

Data collection

Nonius KappaCCD diffractometer	14784 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.086$
Absorption correction: analytical (de Meulenaer & Tompa, 1965)	$\theta_{\text{max}} = 25.0^\circ$
$T_{\text{min}} = 0.490$, $T_{\text{max}} = 0.850$	$h = -16 \rightarrow 16$
125300 measured reflections	$k = -23 \rightarrow 23$
21950 independent reflections	$l = -30 \rightarrow 30$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0508P)^2 + 19.2712P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.134$	$(\Delta\rho)_{\text{max}} = 0.003$
$S = 1.02$	$\Delta\rho_{\text{max}} = 2.10 \text{ e \AA}^{-3}$
21950 reflections	$\Delta\rho_{\text{min}} = -1.49 \text{ e \AA}^{-3}$
1418 parameters	
H-atom parameters constrained	

Table 1

Selected bond lengths (\AA).

Ru1—N1	2.109 (7)	Ru4—N7	2.068 (7)
Ru1—N2	2.106 (6)	Ru4—N8	2.100 (6)
Ru1—Cl1	2.335 (3)	Ru4—Cl10	2.343 (2)
Ru1—Cl2	2.345 (2)	Ru4—Cl11	2.338 (2)
Ru1—Cl3	2.338 (2)	Ru4—Cl12	2.351 (2)
Ru1—S1	2.302 (2)	Ru4—S4	2.303 (2)
Ru2—N3	2.114 (7)	Ru5—N9	2.080 (7)
Ru2—N4	2.100 (6)	Ru5—N10	2.107 (6)
Ru2—Cl4	2.343 (2)	Ru5—Cl13	2.334 (3)
Ru2—Cl5	2.342 (2)	Ru5—Cl14	2.346 (2)
Ru2—Cl6	2.332 (2)	Ru5—Cl15	2.341 (2)
Ru2—S2	2.295 (2)	Ru5—S5	2.300 (2)
Ru3—N5	2.096 (5)	Ru6—N11	2.085 (5)
Ru3—N6	2.105 (6)	Ru6—N12	2.106 (6)
Ru3—Cl7	2.339 (2)	Ru6—Cl16	2.342 (2)
Ru3—Cl8	2.340 (2)	Ru6—Cl17	2.342 (2)
Ru3—Cl9	2.355 (2)	Ru6—Cl18	2.333 (2)
Ru3—S3	2.302 (2)	Ru6—S6	2.299 (2)

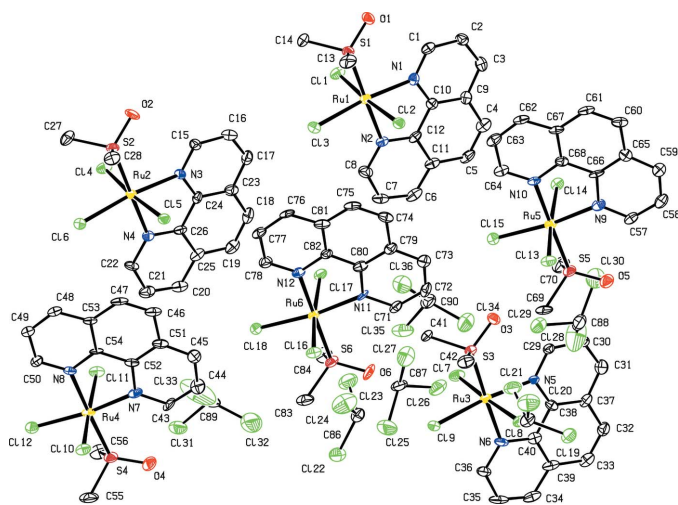


Figure 1

The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

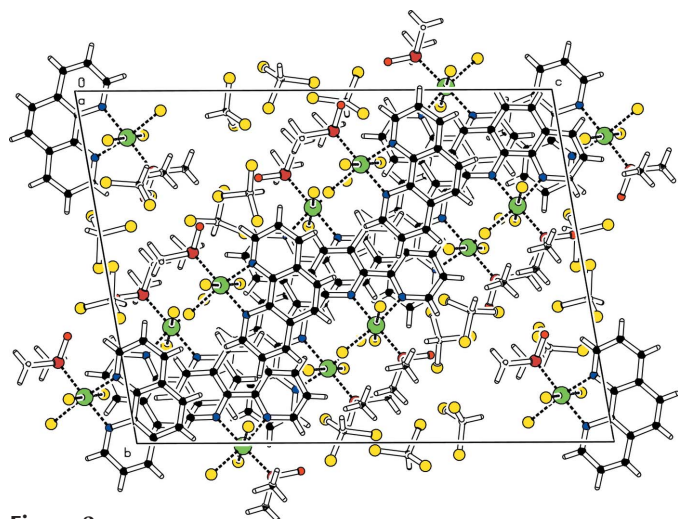


Figure 2

Projection of the unit-cell contents of (I) down the a axis, illustrating the layer-type structure.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C85—H85 \cdots Cl7 ⁱ	1.00	2.63	3.383 (10)	132
C86—H86 \cdots Cl10 ⁱⁱ	1.00	2.60	3.397 (10)	136
C87—H87 \cdots Cl16	1.00	2.69	3.470 (10)	135
C88—H88 \cdots Cl13 ⁱⁱⁱ	1.00	2.62	3.466 (10)	142
C89—H89 \cdots Cl1 ^{iv}	1.00	2.60	3.441 (10)	141
C90—H90 \cdots Cl4 ^{iv}	1.00	2.68	3.478 (10)	137

Symmetry codes: (i) $x + 1, y, z$; (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x, -y + 1, -z + 1$.

The twinning of the crystal was analysed with the program *DIRAX* (Duisenberg, 1992) in terms of a 180° degree rotation about $[01\bar{1}]$. The corresponding approximate twin matrix is given by $(-1 \ 0 \ 0 / 0 \ -\frac{1}{3} \ -\frac{2}{3} / 0 \ -\frac{4}{3} \ \frac{1}{3})$. The program *MERGEHKL5* (Schreurs, 2004) was used to generate the twinned data file used in the refinement. The twin ratio refined to 0.714 (1):0.286. H atoms were introduced at

calculated positions and refined riding on their carrier atoms (the CH₃ moiety as a rigid rotor), with C—H = 0.95 Å for aromatic, 0.98 Å for CH₃ and 1.00 Å for chloroform, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms and 1.2 $U_{\text{eq}}(\text{C})$ for all other H atoms. The structure was checked for missing higher symmetry with *PLATON/ADDSYM* (Spek, 2003). The highest peak is located 1.00 Å from Cl32 and the deepest hole is located 0.66 Å from Ru3.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DIRAX* (Duisenberg, 1992); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *DIRDIF99* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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