Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Anthony L. Spek,[a]* Duncan M. Tooke,[a] Ariadna Garza-Ortiz[b] and Jan Reedijk[b]

[a]Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, and [b]Leiden institute of Chemistry, Gorlaeus Laboratories, PO Box 9502, 2300 RA Leiden, The Netherlands

Correspondence e-mail: a.l.spek@chem.uu.nl

Received 24 October 2005
Accepted 25 October 2005
Online 31 October 2005

Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.012 Å
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.

The title compound, $[RuCl_3(C_{12}H_8N_2)(C_2H_6OS)]\cdot CHCl_3$, 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).

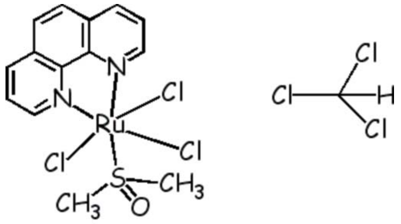
(I)

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 C—H···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*-$[RuCl_2(dmso)_4]$ (dmso = dimethyl sulfoxide) was prepared according to the literature procedure of Evans *et al.* (1973). Recrystallized *cis*-$[RuCl_2(dmso)_4]$ (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-

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-brown 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

$[RuCl_3(C_{12}H_8N_2)(C_2H_6OS)]\cdot CHCl_3$
$M_r = 585.12$
Triclinic, $P\overline{1}$
$a = 13.8023\ (16)$ Å
$b = 19.731\ (3)$ Å
$c = 25.597\ (3)$ Å
$\alpha = 75.823\ (9)°$
$\beta = 74.676\ (10)°$
$\gamma = 69.907\ (8)°$
$V = 6221.8\ (15)$ Å^3
$Z = 12$
$D_x = 1.874$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 290 reflections
$\theta = 4.0$–$25.0°$
$\mu = 1.64$ mm^{-1}
$T = 150$ K
Plate, orange–red
$0.30 \times 0.25 \times 0.07$ mm

Data collection

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

Refinement

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

Table 1
Selected bond lengths (Å).

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)

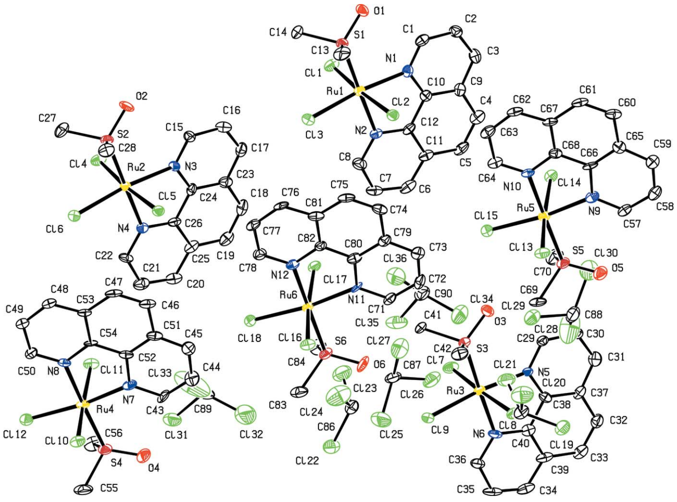

Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

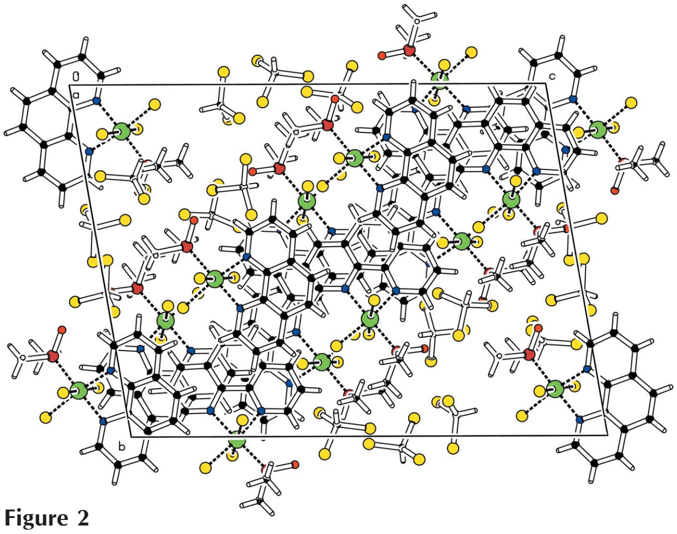

Figure 2
Projection of the unit-cell contents of (I) down the *a* axis, illustrating the layer-type structure.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—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 $[01\overline{1}]$. 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 *MERGEHKLF5* (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

Acta Cryst. (2005). E**61**, m2428–m2430 Spek *et al.* • $[RuCl_3(C_{12}H_8N_2)(C_2H_6OS)]\cdot CHCl_3$ **m2429**

calculated positions and refined riding on their carrier atoms (the CH_3 moiety as a rigid rotor), with C—H = 0.95 Å for aromatic, 0.98 Å for CH_3 and 1.00 Å for chloroform, and with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms and 1.2 $U_{eq}(C)$ 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*.

This work was supported in part (ALS and DMT) by the Council for the Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO) and in part by the Mexican Research Organization CONACYT (grant to AGO).

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