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Key indicators

Single-crystal X-ray study

T = 293 K

Mean $\sigma(S-C) = 0.005 \text{ \AA}$

R factor = 0.034

wR factor = 0.086

Data-to-parameter ratio = 26.7

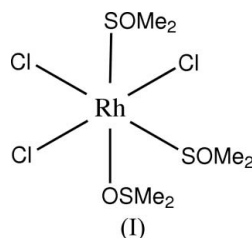
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.A new polymorph of *mer,cis*-trichlorotrakis(dimethyl sulfoxide)rhodium(III)

In the structure of *mer,cis*-[RhCl₃(C₂H₆OS)₃], the Rh^{III} ion is coordinated by one O and two S atoms, the latter in a *cis* position, from three dimethyl sulfoxide molecules and three chloride ions in a *mer* configuration in a distorted octahedral coordination.

Received 4 September 2006
Accepted 13 September 2006

Comment

The title compound, (I), has been studied with the aim of investigating the nature of Rh–S/O bonds and the *trans* influence by comparison with analogous compounds. Rhodium chloride–dimethyl sulfoxide complexes have been extensively studied in recent years (Calligaris, 2004; Alessio, 2004). Dimethyl sulfoxide is an ambidentate ligand, usually coordinating *via* oxygen. Coordination *via* the S atom takes place only for some soft metal ions (Calligaris, 2004). The rhodium(III) ion is classified as borderline (Pearson, 1967) and can bind to both the S and O atoms of sulfoxides (Calligaris, 2004). The structure of (I) had been reported earlier with very low precision ($R = 0.125$) and with a different space group and unit cell (Sokol & Porai-Koshits, 1975).



In the crystal structure of the new polymorph of (I), the rhodium(III) ion is octahedrally coordinated by one O and two S atoms from dimethyl sulfoxide molecules and three chloride ions in a *mer,cis* configuration (Fig. 1). Three non-classical hydrogen bonds are present in the structure (Table 2).

Previously, *mer,trans*-RhCl₃(C₂H₆SO)₃, (II), an isomer of (I), has been studied (Alessio *et al.*, 1993). The Rh–S bond distances in (I) for S *trans* to Cl [2.283 (1) Å] are shorter than the Rh–S bond in (II) to the *trans* S atom [2.311 (6) Å], indicating that S has a stronger *trans* influence than Cl. The Rh–O bond distance in (I) for O *trans* to S [2.106 (3) Å] is also longer than for the Rh–O bond in (II) *trans* to the Cl atom [2.067 (4) Å]. This effect can also be seen by comparing the Ru–S bond distances in *mer*-[RuCl₃(C₂H₆S)₃], which are shorter for S *trans* to Cl [2.380 (1) Å] than the Ru–S bonds to the *trans* S atom [2.388 (1) Å] (Bolton *et al.*, 2004).

The Rh–Cl bond distance in (I) for Cl *trans* to S [2.355 (1) Å] is longer than the corresponding bond distance

in (II) [2.231 (1) Å] for Cl *trans* to O, which is an indication of stronger *trans* influence of S compared to O. Also, the longer Rh—S bond distance in (I) *trans* to Cl than that *trans* to O [2.283 (1) and 2.242 (1) Å, respectively] shows the stronger *trans* influence of Cl. We can conclude that the order of *trans* influence is S > Cl > O.

Experimental

Compound (I) was synthesized by dissolving approximately 0.2 g of rhodium(III) chloride hydrate (Aldrich, 99.98%) in an excess of dimethyl sulfoxide (Merck, 99%) at 343 K. Crystals suitable for crystallography were obtained after recrystallization from ethanol.

Crystal data

[RhCl ₃ (C ₂ H ₆ OS) ₃]	Z = 8
<i>M_r</i> = 443.64	<i>D_x</i> = 1.821 Mg m ⁻³
Orthorhombic, <i>Pbca</i>	Mo Kα radiation
<i>a</i> = 10.0230 (4) Å	<i>μ</i> = 1.93 mm ⁻¹
<i>b</i> = 11.2803 (5) Å	<i>T</i> = 293 (2) K
<i>c</i> = 28.6327 (14) Å	Block, yellow
<i>V</i> = 3237.3 (2) Å ³	0.5 × 0.4 × 0.2 mm

Data collection

Oxford Diffraction Xcalibur-3 CCD detector diffractometer	23874 measured reflections
<i>ω</i> scans	3896 independent reflections
Absorption correction: numerical (<i>X-RED</i> ; Stoe & Cie, 1997)	2918 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T_{min}</i> = 0.382, <i>T_{max}</i> = 0.680	<i>R_{int}</i> = 0.026
	<i>θ_{max}</i> = 28.0°

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0384P)^2 + 3.6685P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.06	$\Delta\rho_{max} = 0.58 \text{ e \AA}^{-3}$
3896 reflections	$\Delta\rho_{min} = -0.87 \text{ e \AA}^{-3}$
146 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.00141 (14)

Table 1

Selected bond lengths (Å).

Rh1—O3	2.106 (3)	S1—C11	1.770 (4)
Rh1—S1	2.2414 (9)	S2—O2	1.463 (3)
Rh1—S2	2.2826 (9)	S2—C22	1.764 (4)
Rh1—Cl2	2.3363 (9)	S2—C21	1.766 (4)
Rh1—Cl1	2.3416 (9)	S3—O3	1.523 (3)
Rh1—Cl3	2.3545 (10)	S3—C31	1.752 (5)
S1—O1	1.463 (3)	S3—C32	1.799 (5)
S1—C12	1.759 (4)		

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C12—H12 <i>B</i> ...O2 ⁱ	0.96	2.30	3.171 (5)	151
C22—H22 <i>B</i> ...O1 ⁱⁱ	0.96	2.51	3.357 (5)	147
C31—H31 <i>B</i> ...Cl3 ⁱⁱⁱ	0.96	2.83	3.580 (6)	136

Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (iii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z$.

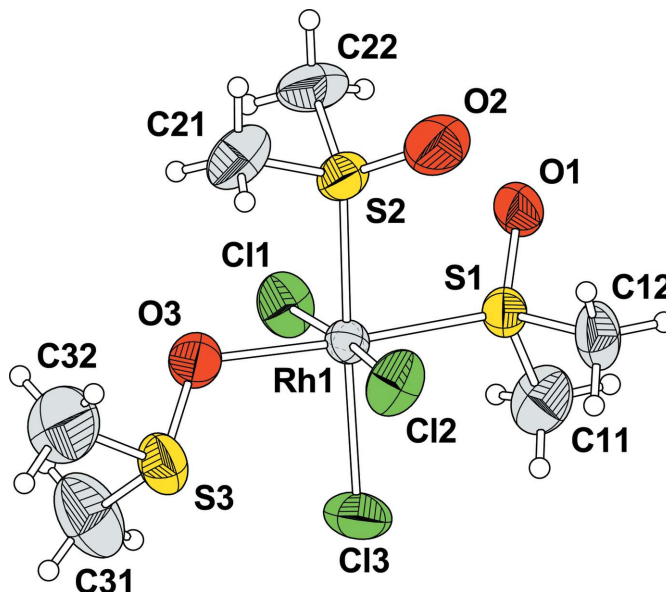


Figure 1

The molecular structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown with arbitrary radii.

The H atoms were placed in calculated positions and constrained to ride on the parent C atoms, with C—H = 0.96 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *PLATON* (Spek, 2003).

This work was supported by a grant from Tehran University and the Swedish Research Council.

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