metal-organic compounds

mer-Trichloridotris(dimethyl sulfide-κS)-rhodium(III)

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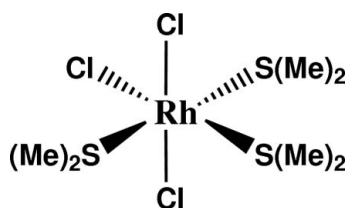Correspondence e-mail: aabbasi@khayam.ut.ac.ir

The title compound, $[RhCl_3(C_2H_6S)_3]$, exists as discrete molecules in which the Rh^{III} atom is coordinated by three S atoms from the dimethyl sulfide molecules and three Cl atoms in a *mer*-octahedral configuration.

Related literature

For the related dimethyl sulfoxide compound, see Abbasi *et al.* (2006). For related literature, see: Alessio (2004); Calligaris (2004); James *et al.* (1968).

Experimental

Crystal data

$[RhCl_3(C_2H_6S)_3]$	V = 1450.1 (3) Å^3
M_r = 395.64	Z = 4
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
a = 7.9835 (10) Å	μ = 2.12 mm^{-1}
b = 13.312 (2) Å	T = 290 (2) K
c = 13.6450 (18) Å	0.2 × 0.1 × 0.1 mm

Data collection

Stoe IPDSII diffractometer	7089 measured reflections
Absorption correction: numerical	3037 independent reflections
(X-RED; Stoe & Cie, 1997)	2965 reflections with $I > 2\sigma(I)$
T_{min} = 0.693, T_{max} = 0.793	R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.017	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$wR(F^2)$ = 0.039	$\Delta\rho_{min}$ = −0.24 e Å^{-3}
S = 1.08	Absolute structure: Flack (1983),
3037 reflections	with 1283 Friedel pairs
118 parameters	Flack parameter: −0.02 (3)
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

Rh1—S1	2.3283 (8)	S1—C11	1.782 (3)
Rh1—Cl3	2.3350 (7)	S1—C12	1.793 (4)
Rh1—S2	2.3422 (7)	S2—C22	1.785 (4)
Rh1—Cl1	2.3481 (7)	S2—C21	1.795 (4)
Rh1—Cl2	2.3609 (7)	S3—C32	1.790 (3)
Rh1—S3	2.3660 (7)	S3—C31	1.790 (3)

Data collection: *IPDS Software* (Stoe & Cie, 1997); cell refinement: *IPDS Software*; data reduction: *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2277).

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supplementary materials

mer-Trichloridotris(dimethyl sulfide-*κS*)rhodium(III)

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Comment

One aim of the current study is to investigate the nature of Rh—S bonds and to make a comparison with analogous compounds such as the sulfoxide complexes (Abbasi, *et al.*, 2006; Calligaris, 2004; Alessio, 2004). Interest in the use of the dimethyl sulfide ligand arises from its involvement in the homogeneous hydrogenation of olefinic substrates (James *et al.* 1968).

The rhodium(III) ion is octahedrally coordinated by the sulfur atoms of the three dimethyl sulfide molecules, and three chlorine atoms in a *mer* octahedral configuration (Fig. 1). The Rh—S bond distance in for the sulfur *trans* to the chlorine [2.328 (1) Å] is longer than that *cis* to the chlorine [2.283 (1) Å], which indicates strongr π-back bonding from metal to sulfur (Abbasi *et al.*, 2006).

Experimental

The compound was synthesized by dissolving rhodium(III) chloride (Aldrich, 98%) in excess of dimethyl sulfide (Merck, 99%) at 343 K followed by a 12 h reflux. The mixture was then cooled to room temperature. Crystals were obtained after the evaporation of the solvent.

Refinement

The Flack parameter was refined from 1283 Friedel pairs.

The H atoms are in calculated positions and constrained to ride on the parent C atoms with the C—H distance 0.96 Å and $U_{iso}(H) = 1.5 U_{eq}(C)$.

Figures

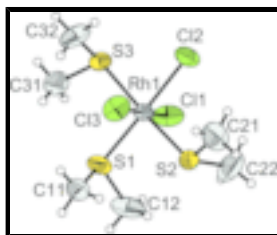Fig. 1. Molecular structure of (I), shown with 50% probability displacement ellipsoids. H atoms are shown with arbitrary radii.

supplementary materials

mer-Trichloridotris(dimethyl sulfide-*κS*)rhodium(III)

Crystal data

$[RhCl_3(C_2H_6S)_3]$	$F_{000} = 792$
$M_r = 395.64$	$D_x = 1.812$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 7089 reflections
$a = 7.9835$ (10) Å	$\theta = 2.1–26.7°$
$b = 13.312$ (2) Å	$\mu = 2.12$ mm^{-1}
$c = 13.6450$ (18) Å	$T = 290$ (2) K
$V = 1450.1$ (3) Å^3	Needle, brown
$Z = 4$	$0.2 \times 0.1 \times 0.1$ mm

Data collection

Stoe IPDS II diffractometer	3037 independent reflections
Radiation source: fine-focus sealed tube	2965 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.016$
$T = 290(2)$ K	$\theta_{max} = 26.7°$
Area detector, φ oscillation scans	$\theta_{min} = 2.1°$
Absorption correction: numerical (X-RED; Stoe & Cie, 1997)	$h = -8 \rightarrow 10$
$T_{min} = 0.693$, $T_{max} = 0.793$	$k = -16 \rightarrow 14$
7089 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.017$	$w = 1/[\sigma^2(F_o^2) + (0.0163P)^2 + 0.5475P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.039$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.08$	$\Delta\rho_{max} = 0.28$ e Å^{-3}
3037 reflections	$\Delta\rho_{min} = -0.24$ e Å^{-3}
118 parameters	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), with 1283 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: −0.02 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Rh1	0.27392 (2)	0.830500 (13)	0.232940 (12)	0.03469 (5)
S1	0.15639 (11)	0.67291 (6)	0.20553 (5)	0.05978 (18)
S2	0.15091 (10)	0.88897 (5)	0.08792 (5)	0.05395 (17)
S3	0.40313 (9)	0.78043 (5)	0.38115 (4)	0.04733 (15)
Cl1	0.04246 (9)	0.86245 (7)	0.33444 (5)	0.0681 (2)
Cl2	0.38670 (10)	0.98917 (5)	0.27322 (5)	0.06140 (18)
Cl3	0.50634 (10)	0.79376 (7)	0.13543 (5)	0.0654 (2)
C11	0.2440 (5)	0.6116 (2)	0.1013 (3)	0.0790 (10)
H11A	0.3600	0.5972	0.1134	0.095*
H11B	0.2343	0.6545	0.0451	0.095*
H11C	0.1848	0.5500	0.0894	0.095*
C12	−0.0530 (4)	0.6866 (3)	0.1598 (3)	0.0839 (12)
H12A	−0.1209	0.7194	0.2082	0.101*
H12B	−0.0988	0.6215	0.1456	0.101*
H12C	−0.0512	0.7263	0.1010	0.101*
C21	0.2849 (7)	0.9835 (2)	0.0363 (2)	0.0870 (13)
H21A	0.3885	0.9533	0.0161	0.104*
H21B	0.3070	1.0342	0.0846	0.104*
H21C	0.2308	1.0135	−0.0193	0.104*
C22	−0.0265 (6)	0.9645 (4)	0.1181 (3)	0.1057 (16)
H22A	−0.1115	0.9232	0.1472	0.127*
H22B	−0.0697	0.9952	0.0596	0.127*
H22C	0.0064	1.0159	0.1636	0.127*
C31	0.3508 (5)	0.6535 (3)	0.4118 (2)	0.0690 (9)
H31A	0.2335	0.6492	0.4268	0.083*
H31B	0.4149	0.6327	0.4678	0.083*
H31C	0.3760	0.6105	0.3573	0.083*
C32	0.6223 (4)	0.7626 (3)	0.3596 (3)	0.0796 (11)
H32A	0.6722	0.8255	0.3413	0.096*
H32B	0.6377	0.7148	0.3078	0.096*
H32C	0.6746	0.7381	0.4183	0.096*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Rh1	0.03557 (8)	0.04055 (8)	0.02795 (7)	−0.00209 (7)	0.00126 (6)	−0.00432 (6)
S1	0.0891 (5)	0.0511 (3)	0.0391 (3)	−0.0230 (4)	−0.0130 (3)	0.0006 (3)

S2	0.0735 (5)	0.0478 (3)	0.0406 (3)	0.0079 (3)	−0.0169 (3)	−0.0056 (3)
S3	0.0523 (4)	0.0567 (4)	0.0330 (3)	−0.0014 (3)	−0.0059 (3)	−0.0039 (3)
Cl1	0.0431 (4)	0.1089 (7)	0.0523 (4)	−0.0039 (4)	0.0116 (3)	−0.0301 (4)
Cl2	0.0819 (5)	0.0494 (3)	0.0530 (3)	−0.0191 (3)	−0.0068 (4)	−0.0064 (3)
Cl3	0.0523 (4)	0.0961 (6)	0.0478 (3)	0.0098 (4)	0.0156 (3)	−0.0042 (4)
C11	0.089 (3)	0.0612 (17)	0.087 (2)	0.0176 (19)	−0.029 (2)	−0.0321 (16)
C12	0.064 (2)	0.105 (3)	0.083 (2)	−0.036 (2)	0.0082 (17)	−0.033 (2)
C21	0.143 (4)	0.066 (2)	0.0520 (17)	−0.012 (2)	−0.005 (2)	0.0160 (14)
C22	0.101 (3)	0.123 (4)	0.094 (3)	0.060 (3)	−0.034 (3)	−0.019 (3)
C31	0.084 (2)	0.072 (2)	0.0515 (16)	−0.0090 (17)	−0.0111 (15)	0.0156 (15)
C32	0.0433 (16)	0.121 (3)	0.075 (2)	−0.0062 (18)	−0.0167 (16)	0.011 (2)

Geometric parameters (Å, °)

Rh1—S1	2.3283 (8)	C12—H12A	0.9600
Rh1—Cl3	2.3350 (7)	C12—H12B	0.9600
Rh1—S2	2.3422 (7)	C12—H12C	0.9600
Rh1—Cl1	2.3481 (7)	C21—H21A	0.9600
Rh1—Cl2	2.3609 (7)	C21—H21B	0.9600
Rh1—S3	2.3660 (7)	C21—H21C	0.9600
S1—C11	1.782 (3)	C22—H22A	0.9600
S1—C12	1.793 (4)	C22—H22B	0.9600
S2—C22	1.785 (4)	C22—H22C	0.9600
S2—C21	1.795 (4)	C31—H31A	0.9600
S3—C32	1.790 (3)	C31—H31B	0.9600
S3—C31	1.790 (3)	C31—H31C	0.9600
C11—H11A	0.9600	C32—H32A	0.9600
C11—H11B	0.9600	C32—H32B	0.9600
C11—H11C	0.9600	C32—H32C	0.9600
S1—Rh1—Cl3	92.29 (3)	S1—C12—H12A	109.5
S1—Rh1—S2	89.70 (3)	S1—C12—H12B	109.5
Cl3—Rh1—S2	85.49 (3)	H12A—C12—H12B	109.5
S1—Rh1—Cl1	86.60 (3)	S1—C12—H12C	109.5
Cl3—Rh1—Cl1	177.97 (3)	H12A—C12—H12C	109.5
S2—Rh1—Cl1	96.21 (3)	H12B—C12—H12C	109.5
S1—Rh1—Cl2	175.67 (3)	S2—C21—H21A	109.5
Cl3—Rh1—Cl2	90.97 (3)	S2—C21—H21B	109.5
S2—Rh1—Cl2	93.40 (3)	H21A—C21—H21B	109.5
Cl1—Rh1—Cl2	90.04 (3)	S2—C21—H21C	109.5
S1—Rh1—S3	93.40 (3)	H21A—C21—H21C	109.5
Cl3—Rh1—S3	94.68 (3)	H21B—C21—H21C	109.5
S2—Rh1—S3	176.89 (3)	S2—C22—H22A	109.5
Cl1—Rh1—S3	83.68 (3)	S2—C22—H22B	109.5
Cl2—Rh1—S3	83.50 (3)	H22A—C22—H22B	109.5
C11—S1—C12	97.72 (17)	S2—C22—H22C	109.5
C11—S1—Rh1	112.51 (13)	H22A—C22—H22C	109.5
C12—S1—Rh1	109.86 (14)	H22B—C22—H22C	109.5
C22—S2—C21	99.7 (2)	S3—C31—H31A	109.5
C22—S2—Rh1	108.98 (15)	S3—C31—H31B	109.5

C21—S2—Rh1	108.32 (13)	H31A—C31—H31B	109.5
C32—S3—C31	98.14 (19)	S3—C31—H31C	109.5
C32—S3—Rh1	108.87 (12)	H31A—C31—H31C	109.5
C31—S3—Rh1	111.35 (10)	H31B—C31—H31C	109.5
S1—C11—H11A	109.5	S3—C32—H32A	109.5
S1—C11—H11B	109.5	S3—C32—H32B	109.5
H11A—C11—H11B	109.5	H32A—C32—H32B	109.5
S1—C11—H11C	109.5	S3—C32—H32C	109.5
H11A—C11—H11C	109.5	H32A—C32—H32C	109.5
H11B—C11—H11C	109.5	H32B—C32—H32C	109.5

Fig. 1