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Chloro(η^6-*p*-cymene)(diethyldithiocarbamato-$\kappa^2 S,S$)ruthenium(II)

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.003 Å
R factor = 0.024
wR factor = 0.061
Data-to-parameter ratio = 25.3

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

The structure of the title compound, $[Ru(C_5H_{10}NS_2)Cl(\eta^6\text{-}C_{10}H_{14})]$, consists of a ruthenium center bonded to an η^6-*p*-cymene, a chelating diethyldithiocarbamate and a terminal chloride. The Ru atom adopts an octahedral configuration. The metal–ligand distances are Ru—Cl = 2.4276 (5) Å, Ru—S = 2.3978 (5) Å and Ru—S = 2.3925 (5) Å.

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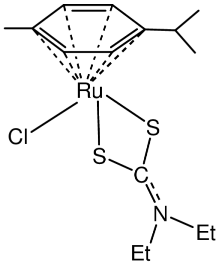
Comment

The chemistry of transition metal–sulfur compounds has attracted much interest for their importance in the field of metalloenzymes, materials precursors, and catalysts (Hidai *et al.*, 2000). In recent years there has been an increased interest in ruthenium complexes with sulfur-donor ligands, in part because of the high catalytic activity of RuS_2 in various hydrogenation processes (Vit & Zdrazil, 1989). As part of this development, many examples of ruthenium–thiolate complexes have been reported; however, ruthenium complexes with dithio ligands are rare (Sellmann *et al.*, 1999). As arene–ruthenium complexes, such as $[RuCl_2(arene)]_2$ and $[RuCl_2(PR_3)(arene)]$, have been used as homogeneous catalysts (Lavastre & Dixneuf, 1995), the [(arene)Ru] species may provide a means of expansion of reactivity and catalytic properties (Pearson *et al.*, 1996). In our research on the preparation of ruthenium complexes with sulfur- and selenium-donor ligands (Zhang *et al.*, 2001), we have synthesized arene–ruthenium complexes with bidentate dithiocarbamate ligands, and have attempted to establish the structural characterization of this typical complex. In this paper, the initial results of this work are reported.



(I)

The molecular structure of the title complex, (I), consists of discrete monomeric molecules with distorted octahedral configuration around the Ru atom, having a *p*-cymene ring at one face. The (η^6-*p*-cymene)Ru fragment is coordinated by S atoms of a symmetrically chelating diethyldithiocarbamate group and a terminal chloride ligand. The ruthenium atom is situated 1.749 (2) Å from the center of the planar aromatic in the *p*-cymene moiety. All Ru—C bond distances in (I) are in

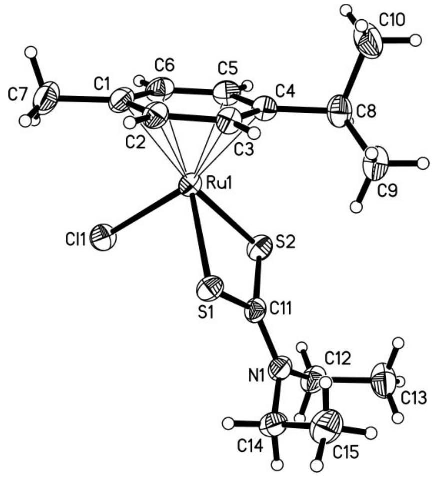


Figure 1
A perspective view of the title compound, showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

the range 2.1604 (17)–2.2319 (17) Å, in good agreement with values in other related complexes, such as [(η^6-*p*-cymene)-$RuCl_2(PH_2Cy)$] (Van der Maelen Uría *et al.*, 1994) and [(η^6-*p*-cymene)RuCl(μ-N_3)] (Bates *et al.*, 1990). The two Ru—S bond distances are essentially the same [2.3925 (5) and 2.3978 (5) Å], slightly shorter than those in [(η^6-*p*-cymene)Ru{$S_2P(OMe)_2$}(PPh_3)][BPh_4] [2.431 (2) and 2.4312 (14) Å] with a chelating dithiophosphate ligand (Jain & Jakkal, 1996). The Ru—Cl bond length of 2.4276 (5) Å in (I) is slightly longer than those reported in other complexes, such as in [(*p*-cymene)RuCl($Me_2PCH_2CH_2SMe$)][BPh_4] [2.389 (2) Å] (Suzuki *et al.*, 1996) and [(η^6-*p*-cymene)*Ru*Cl_2-(PH_2Cy)] [2.408 (1) and 2.411 (1) Å; Van der Maelen Uría *et al.*, 1994]. One of the angles around the ruthenium, S1—Ru1—S2, is considerably reduced [72.019 (17)°] due to the small bite of the dithio ligand. The four-membered chelate ring RuS_2C is approximately planar, with a mean deviation of 0.0262 Å from the least-squares plane. The short C11—N1 bond length of 1.325 (2) Å in (I) indicates considerable partial double-bond character, as is typical for chelating 1,1-dithiolate ligands (Eisenberg, 1970). The FT–IR spectrum of (I) shows a strong absorption at 1482 cm^{-1} due to the stretching vibration of the C═N bond with considerable double-bond character.

Experimental

To a THF solution (25 ml) of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (225 mg, 0.45 mmol) was added one equivalent of sodium diethyldithiocarbamate $Et_2NCS_2Na\cdot3H_2O$ (101 mg, 0.45 mmol). The mixture was stirred at room temperature for 6 h, during which time a brown solution was obtained. The solvent was pumped off and the residue was washed with diethyl ether and hexane. The dark orange solid was recrystallized from CH_2Cl_2/hexane to give red block crystals. ^1H NMR ($CDCl_3$, p.p.m.): δ 1.20 (*m*, CH_2CH_3), 1.30 [*d*, 7.2 Hz, $CH(CH_3)_2$], 2.98 [*septet*, 7.8 Hz, $CH(CH_3)_2$], 3.48 (*m*, CH_2CH_3), 5.47 and 5.78 (*dd*, each 6.2 Hz, C_6H_4). MS (FAB): *m*/*z* 420 (M^+ + 1). IR (KBr pellets, cm^{-1}): ν (C═N), 1482 (*s*); (C—S), 992 (*s*), 926 (*m*). Analysis calculated for $C_{15}H_{24}ClNRuS_2$: C 42.96, H 5.73, N 3.34%; found: C 42.58, H 5.71, N 3.33%.

Crystal data

[$Ru(C_5H_{10}NS_2)Cl(C_{10}H_{14})$]
M_r = 418.99
Triclinic, $P\overline{1}$
a = 9.8886 (5) Å
b = 10.0266 (5) Å
c = 10.9300 (5) Å
α = 100.548 (1)°
β = 111.312 (1)°
γ = 103.620 (1)°
V = 937.01 (8) Å^3
Z = 2
D_x = 1.485 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5443 reflections
θ = 2.2–28.3°
μ = 1.19 mm^{-1}
T = 294 (2) K
Block, red
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Apex CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.659, T_{max} = 0.787
9910 measured reflections
4582 independent reflections
4275 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 28.3°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.061
S = 1.08
4582 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 0.1488P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—C3	2.1638 (17)	Ru1—S1	2.3979 (5)
Ru1—C5	2.1846 (18)	Ru1—Cl1	2.4272 (5)
Ru1—C4	2.1857 (18)	S1—C11	1.7122 (19)
Ru1—C6	2.1999 (19)	S2—C11	1.717 (2)
Ru1—C2	2.2159 (18)	N1—C11	1.323 (2)
Ru1—C1	2.2318 (18)	N1—C14	1.467 (3)
Ru1—S2	2.3925 (5)	N1—C12	1.474 (3)
C3—Ru1—S2	120.86 (5)	C3—Ru1—Cl1	150.38 (5)
C5—Ru1—S2	95.52 (5)	C5—Ru1—Cl1	120.94 (5)
C4—Ru1—S2	94.66 (5)	C4—Ru1—Cl1	159.02 (5)
C6—Ru1—S2	120.60 (6)	C6—Ru1—Cl1	92.64 (6)
C2—Ru1—S2	158.55 (5)	C2—Ru1—Cl1	112.81 (5)
C1—Ru1—S2	157.66 (6)	C1—Ru1—Cl1	88.74 (5)
C3—Ru1—S1	93.58 (5)	S2—Ru1—Cl1	87.695 (18)
C5—Ru1—S1	148.83 (5)	S1—Ru1—Cl1	87.769 (18)
C4—Ru1—S1	112.81 (5)	C11—S1—Ru1	88.63 (7)
C6—Ru1—S1	167.38 (6)	C11—S2—Ru1	88.70 (6)
C2—Ru1—S1	101.39 (5)	C11—N1—C14	120.86 (17)
C1—Ru1—S1	129.86 (6)	C11—N1—C12	120.95 (18)
S2—Ru1—S1	72.023 (17)		

There is a void of 56 Å^3 in the unit cell, but, while the final difference map showed some fairly large ripples around the Ru atoms, there was nothing of any significance in the void.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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