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Key indicators

Single-crystal X-ray study
T = 100 K
Mean $\sigma(\text{C}-\text{C})$ = 0.006 Å
R factor = 0.033
wR factor = 0.084
Data-to-parameter ratio = 22.8For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis{tri- μ -chloro-bis[(η^6 -*p*-cymene)ruthenium(II)]}
di- μ -chloro-bis[dichloromercurate(II)]

The title compound, $[\text{Ru}_2\text{Cl}_3(\text{C}_{10}\text{H}_{14})_2]_2[\text{Hg}_2\text{Cl}_6]$, contains two $[\{\text{Ru}(\text{C}_{10}\text{H}_{14})\}_2(\mu\text{-Cl})_3]^+$ cations and one $[\text{Hg}_2\text{Cl}_6]^{2-}$ anion. In the cation, two $[\text{Ru}(\eta^6\text{-}p\text{-cymene})]$ fragments are linked by three bridging Cl atoms. The anion lies on a twofold rotation axis. The coordination geometry of ruthenium is pseudo-octahedral, while the coordination around mercury is highly distorted tetrahedral. The average Ru—Cl bond length is 2.435 Å. The average bridging and terminal Hg—Cl distances are 2.664 and 2.435 Å, respectively.

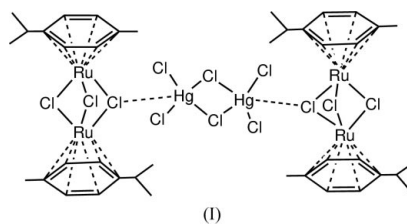
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Comment

(η^6 -Arene)ruthenium(II)-based catalytic systems are found to be effective in the hydrogenation of ketones for the synthesis of chiral alcohols (Bernard *et al.*, 2000). Yamakawa *et al.* (2000) have reported the transfer hydrogenation of prochiral ketones achieved in high enantiomeric excess by tailoring the chiral ruthenium catalysts. Thus, tridentate ligands based on (η^6 -arene)ruthenium(II) complexes have been extensively studied for the design and synthesis of new ruthenium catalysts (Pearson *et al.*, 1996). To this end, efforts have been made to investigate the coordination chemistry of half-sandwich (η^6 -arene)ruthenium(II) with some labile groups. In the course of our research on ruthenium complexes in a sulfur-rich coordination environment (Zhang *et al.*, 2001), we are still trying to find an active (η^6 -arene)ruthenium(II)-based intermediate for an efficient synthetic route to ruthenium sulfur complexes (Yao *et al.*, 2003). We report here the crystal structure of a ruthenium-cymene-chloro complex, *viz.* $[\{\text{Ru}(\text{C}_{10}\text{H}_{14})\}_2(\mu\text{-Cl})_3][\text{HgCl}_2(\mu\text{-Cl})_2]$, (I), enhancing the structural chemistry of the half-sandwich (η^6 -arene)ruthenium(II) fragment.



Compound (I) crystallizes in the centrosymmetric space group $C2/c$. The molecular structure, depicted in Fig. 1, consists of two $[\{\text{Ru}(\text{C}_{10}\text{H}_{14})\}_2(\mu\text{-Cl})_3]^+$ cations and one $[\text{Hg}_2\text{Cl}_6]^{2-}$ anion. The $[\text{Hg}_2\text{Cl}_6]^{2-}$ anion lies on a twofold rotation axis and is sandwiched between two $[\{\text{Ru}(\text{C}_{10}\text{H}_{14})\}_2(\mu\text{-Cl})_3]^+$ cations, with a close contact $[\text{Hg1}-\text{Cl1} = 3.847(3) \text{ \AA}]$ between mercury and one of the bridging Cl atoms in the cation. In the cation of (I), two $[\text{Ru}(\eta^6\text{-}p\text{-cymene})]$ fragments are linked by three bridging Cl atoms,

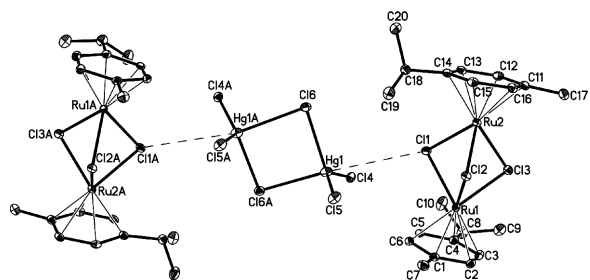


Figure 1
The structure of the title compound, showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level. The suffix *A* corresponds to symmetry code (i) in Table 1.

with an average Ru–Cl bond distance of 2.435 Å and an average Ru–Cl–Ru bond angle of 84.5°. Each Ru atom exhibits a distorted octahedral coordination with the benzene ring of the *p*-cymene ligand formally occupying three sites. The Cl–Ru–Cl angles are considerably reduced (average 79.7°) because of steric interactions. The separation between pairs of Ru atoms is 3.276 (4) Å, which is slightly shorter than that in [(C₅Me₄CH₂)RuCl(μ-Cl)]₂ (3.662 Å; Fan *et al.*, 1994), but still beyond direct metal–metal bond distances.

In the [Hg₂Cl₆]²⁻ anion, the four-membered Hg₂Cl₂ ring is non-planar. The ring contains pairs of long and short Hg–Cl bonds [Hg1–Cl6 = 2.5681 (12) Å and Hg1–Cl6A = 2.7605 (12) Å] and is almost rectangular, with angles close to 90°. The coordination about each Hg^{II} atom is highly distorted tetrahedral, the four sites being occupied by two bridging and two terminal Cl atoms. The terminal Hg–Cl bond lengths [Hg1–Cl4 = 2.3801 (11) Å and Hg1–Cl5 = 2.3807 (11) Å] are obviously shorter than the bridging Hg–Cl bond distances. The angle at mercury involving two terminal Cl atoms [Cl4–Hg1–Cl5 = 138.08 (4)°] is nearly 34° larger than those involving one bridging and one terminal Cl atoms (average 104.2°). The two Hg atoms are 3.680 (4) Å apart and thus are non-bonded.

Experimental

To a tetrahydrofuran solution (25 ml) of [(η⁶-*p*-cymene)RuCl(μ-Cl)]₂ (112 mg, 0.22 mmol) was added an excess (204 mg, 0.75 mmol) of HgCl₂ powder. The mixture was stirred under reflux for 6 h and then the solvent was pumped off and the residue was extracted with CH₂Cl₂. Recrystallization from CH₂Cl₂–Et₂O gave orange crystals. ¹H NMR (CDCl₃, p.p.m.): δ 1.32 [*d*, 7.4 Hz, CH(CH₃)₂], 2.95 [septet, 7.9 Hz, CH(CH₃)₂], 3.24 (*s*, PhCH₃), 5.53 and 5.79 (*dd*, each 6.4 Hz, C₆H₄). MS (FAB): *m/z* 577 {[[Ru(C₁₀H₁₄)₂(μ-Cl)₃]⁺ + 1}. Analysis calculated for C₄₀H₅₆Cl₁₂Hg₂Ru₄: C 27.15, H 3.17%; found: C 26.85, H 3.14%.

Crystal data

[Ru₂Cl₃(C₁₀H₁₄)₂]₂[Hg₂Cl₆]
M_r = 1767.71
Monoclinic, C2/c
a = 20.0879 (13) Å
b = 11.1018 (7) Å
c = 23.7560 (15) Å
β = 107.055 (1)°
V = 5064.9 (6) Å³
Z = 4

D_x = 2.318 Mg m⁻³
Mo Kα radiation
Cell parameters from 6323 reflections
θ = 2.3–28.2°
μ = 7.87 mm⁻¹
T = 100 (2) K
Needle, orange
0.40 × 0.08 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
5982 independent reflections
5361 reflections with *I* > 2σ(*I*)
R_{int} = 0.030
θ_{max} = 28.3°
φ and ω scans
h = -25 → 26
Absorption correction: multi-scan (SADABS; Sheldrick, 1997a)
k = -14 → 13
T_{min} = 0.245, T_{max} = 0.533
l = -18 → 31
15246 measured reflections

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.033
wR(F²) = 0.084
S = 1.04
5982 reflections
262 parameters
H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0484P)² + 1.6219P]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} = 0.001
Δρ_{max} = 1.81 e Å⁻³
Δρ_{min} = -1.06 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Hg1–Cl5	2.3801 (11)	Ru1–Cl3	2.4399 (11)
Hg1–Cl4	2.3807 (11)	Ru1–Cl2	2.4420 (10)
Hg1–Cl6	2.5681 (12)	Ru2–Cl5	2.148 (4)
Hg1–Cl6 ⁱ	2.7605 (12)	Ru2–Cl3	2.156 (4)
Ru1–C5	2.136 (4)	Ru2–Cl6	2.169 (4)
Ru1–C6	2.148 (4)	Ru2–Cl4	2.170 (4)
Ru1–C2	2.173 (4)	Ru2–Cl2	2.173 (4)
Ru1–C3	2.179 (5)	Ru2–Cl1	2.179 (4)
Ru1–Cl1	2.192 (4)	Ru2–Cl1	2.4151 (11)
Ru1–Cl4	2.200 (4)	Ru2–Cl2	2.4428 (10)
Ru1–Cl1	2.4253 (11)	Ru2–Cl3	2.4451 (12)
Cl5–Hg1–Cl4	138.08 (4)	Cl3–Ru1–Cl2	79.63 (3)
Cl5–Hg1–Cl6	106.44 (4)	Cl1–Ru2–Cl2	79.72 (4)
Cl4–Hg1–Cl6	109.27 (4)	Cl1–Ru2–Cl3	79.98 (4)
Cl5–Hg1–Cl6 ⁱ	104.42 (4)	Cl2–Ru2–Cl3	79.51 (3)
Cl4–Hg1–Cl6 ⁱ	96.70 (4)	Ru2–Cl1–Ru1	85.18 (3)
Cl6–Hg1–Cl6 ⁱ	90.27 (4)	Ru1–Cl2–Ru2	84.22 (3)
Cl1–Ru1–Cl3	79.89 (4)	Ru1–Cl3–Ru2	84.22 (3)
Cl1–Ru1–Cl2	79.54 (4)	Hg1–Cl6–Hg1 ⁱ	87.27 (4)

Symmetry code: (i) 1 – x, y, ½ – z.

All H atoms were found in a difference map, but were then placed in calculated positions (C–H = 0.95–1.00 Å) and included in the refinement using the riding-model approximation, with U_{iso}(H) = 1.2U_{eq}(C) [1.5U_{eq}(C) for alkyl H atoms. The largest peak in the final difference map is in the vicinity of the Hg atoms.

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

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