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trans(*Cl*,N_{amino})-Chloro(dimethyl sulfoxide-κS)[tris(2-pyridylmethyl)-amine-$\kappa^4 N$]ruthenium(II) trichloro-tris(dimethyl sulfoxide-κS)ruthenate(II)

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.006 Å
R factor = 0.027
wR factor = 0.066
Data-to-parameter ratio = 12.6

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

In the title compound, $[RuCl(C_{18}H_{18}N_4)(C_2H_6OS)][RuCl_3(C_2H_6OS)_3]$, all the dimethyl sulfoxide (dmso) ligands coordinate through the S atom. In the anion, three chlorides and three dmso ligands form an octahedral coordination around the Ru atom in a facial coordination. In the cation, a chloride ligand is located *trans* to the amine–N atom and *cis* to the dmso ligand.

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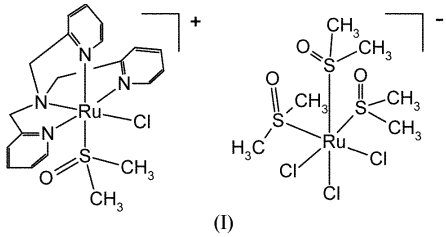
Comment

Due to the interest in oxidation by non-heam enzymes containing iron, which is a congener of ruthenium, ruthenium complexes with polypyridyl ligands have been extensively studied. Since polydentate polypyridyl ligands have been found to be useful biomimetic ligands (Yan *et al.*, 1989), tris(2-pyridylmethyl)amine (TPA) and modified TPA have been applied to the preparation of ruthenium complexes with a view to the production of redox and substrate-oxidizing agent by several groups including us (Kojima, 1996; Yamaguchi *et al.*, 1997; Kojima *et al.*, 1998; Kojima, Hayashi & Matsuda, 2000; Kojima, Matsuo & Matsuda 2000; Sugimoto *et al.*, 2001; Jitsukawa *et al.*, 2001).



(I)

In the course of constructing new ruthenium complexes for alkane-oxidation catalysis, we have already reported that the combination of TPA with chloride and dimethyl sulfoxide in the ruthenium complex affords two isomers, with Cl located *cis* and *trans* to the amine–N atom. The former complex was structurally determined by X-ray diffraction as a PF_6^- salt, but the structure of the latter, which showed higher oxidizing activity, has been confirmed only by the chemical shifts of ^{1}H NMR (Yamaguchi *et al.*, 1997). Fortunately, we have achieved *in situ* formation of the title compound, *trans*(N_{amino},Cl)-$[RuCl(dmso)(TPA)][RuCl_3(dmso)_3]$, (I), and the structure has been determined.

The structure of the cation of (I) shows that the four N atoms of TPA, a chloride ligand and the S atom of dmso form a distorted octahedral configuration around the atom Ru1 (Fig. 1 and Table 1). The Ru1—S1 distance of 2.2385 (10) Å is

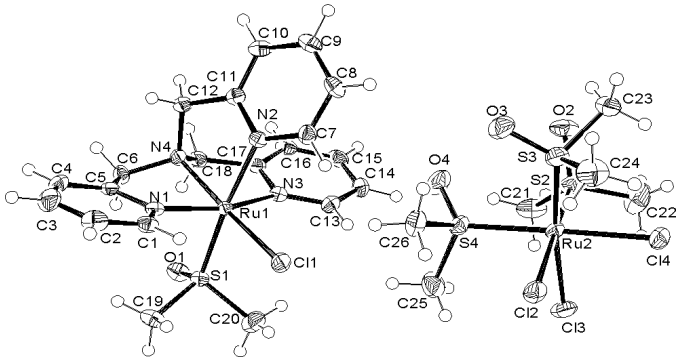


Figure 1
ORTEP-3 diagram (Farrugia, 1997) of the title compound, showing 50% displacement ellipsoids for non-H atoms.

slightly shorter than that in the *cis*-isomer, 2.264 (1) Å, whereas both isomers have similar Ru—Cl distances, *viz*. 2.4321 (9) and 2.433 (1) Å, respectively. The structure of the anion also shows an octahedral configuration, formed by three chlorides and three dmso S atoms, around the atom Ru2. The configuration is facial. The three Ru—Cl distances range from 2.4307 (11) to 2.4503 (10) Å, and the three Ru—S distances from 2.2643 (10) to 2.2707 (11) Å. These Ru—Cl distances are slightly longer than those already reported for the same anion [2.420 (2)–2.438 (2) Å; Yamamoto *et al.*, 1999], while the Ru—S distances are comparable [2.263 (2)-2.276 (2) Å].

Experimental

The mother liquor from the recrystallization of the *cis*(Cl,N_{amino}) and *trans*(Cl,N_{amino}) mixture of [RuCl(dimethyl sulfoxide){tris(2-pyridylmethyl)amine}]Cl (Yamaguchi *et al.*, 1997) was evaporated. The residue was redissolved in a mixture of methanol and ethyl acetate (1:9 *v*/*v*). The solution was stored at room temperature for a month. A deposited yellow crystal of (I) was used for X-ray crystallographic analysis.

Crystal data

$[RuCl(C_{18}H_{18}N_4)(C_2H_6OS)]$-$[RuCl_3(C_2H_6OS)_3]$
M_r = 946.82
Triclinic, $P\overline{1}$
a = 10.1817 (18) Å
b = 14.221 (2) Å
c = 14.664 (3) Å
α = 114.362 (3)°
β = 96.804 (3)°
γ = 105.610 (3)°
V = 1798.1 (5) Å^3
Z = 2
D_x = 1.749 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 965 reflections
θ = 3.0–23.3°
μ = 1.41 mm^{-1}
T = 173 (2) K
Block, yellow
0.20 × 0.10 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: none
8007 measured reflections
5113 independent reflections
4463 reflections with $I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 23.3°
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 14$
$l = -9 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.066
S = 0.98
5113 reflections
405 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—N3	2.060 (3)	Ru2—S2	2.2643 (10)
Ru1—N4	2.070 (3)	Ru2—S4	2.2668 (9)
Ru1—N1	2.078 (3)	Ru2—S3	2.2707 (11)
Ru1—N2	2.106 (3)	Ru2—Cl3	2.4307 (11)
Ru1—S1	2.2385 (10)	Ru2—Cl2	2.4341 (9)
Ru1—Cl1	2.4321 (9)	Ru2—Cl4	2.4503 (10)
N3—Ru1—N4	82.90 (11)	S2—Ru2—S4	91.39 (4)
N3—Ru1—N1	163.45 (10)	S2—Ru2—S3	95.66 (4)
N4—Ru1—N1	80.55 (10)	S4—Ru2—S3	93.37 (4)
N3—Ru1—N2	82.12 (10)	S2—Ru2—Cl3	86.94 (3)
N4—Ru1—N2	80.75 (10)	S4—Ru2—Cl3	93.32 (3)
N1—Ru1—N2	95.40 (10)	S3—Ru2—Cl3	172.76 (3)
N3—Ru1—S1	89.39 (8)	S2—Ru2—Cl2	173.93 (4)
N4—Ru1—S1	98.48 (8)	S4—Ru2—Cl2	87.57 (3)
N1—Ru1—S1	92.81 (7)	S3—Ru2—Cl2	90.37 (4)
N2—Ru1—S1	171.51 (8)	Cl3—Ru2—Cl2	87.15 (3)
N3—Ru1—Cl1	101.71 (8)	S2—Ru2—Cl4	91.61 (4)
N4—Ru1—Cl1	171.41 (8)	S4—Ru2—Cl4	176.96 (3)
N1—Ru1—Cl1	94.73 (7)	S3—Ru2—Cl4	85.81 (3)
N2—Ru1—Cl1	92.62 (7)	Cl3—Ru2—Cl4	87.37 (3)
S1—Ru1—Cl1	88.87 (3)	Cl2—Ru2—Cl4	89.51 (3)

All H atoms were included in calculated positions, with C—H distances of 0.95 Å for aromatic H atoms, 0.99 Å for benzyl (picolinic) H atoms, and 0.98 Å for methyl.

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

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