metal-organic papers

cis,cis-μ-2,3,5,6-Tetra-2-pyridylpyrazine-κ³*N*¹,*N*²,*N*⁶:κ³*N*³,*N*⁴,*N*⁵-bis[dichloro(dimethyl sulfoxide-κ*S*)ruthenium(II)] dihydrate acetone disolvate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.009 Å
Some non-H atoms missing
R factor = 0.066
wR factor = 0.176
Data-to-parameter ratio = 21.3

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

The reaction of 2,3,5,6-tetra-2-pyridylpyrazine (tppz) with dichlorotetrakis(dimethyl sulfoxide)ruthenium(II) in dimethyl sulfoxide (DMSO) yielded the title centrosymmetric dinuclear complex, $[Ru_2Cl_4(C_{24}H_{16}N_6)(C_3H_6OS)_2] \cdot 2C_2H_6OS \cdot 2H_2O$ or cis,cis-[{Ru(DMSO)Cl$_2$}$_2$(μ-tppz)]·2Me$_2$CO·2H$_2$O. Each ruthenium ion is in a distorted octahedral coordination in which the chloro ligands are cis to each other and DMSO is coordinated through sulfur. The asymmetric unit contains half of two independent molecules.

Comment

2,3,5,6-Tetra-2-pyridylpyrazine (tppz) has attracted a great deal of interest in supramolecular chemistry because it can function as a bis-tridentate bridging ligand (Fantacci *et al.*, 2004). Crystal structures of dinuclear tppz complexes are mainly those of first-row transition metal ions (Carranza *et al.*, 2003; Graf *et al.*, 1997; Hadadzadeh *et al.*, 2005; Campos-Fernandez *et al.*, 2001). The only dinuclear Ru[II] tppz crystal structure reported (Hartshorn *et al.*, 1999) is that of [{Ru(Me$_2$bpy)Cl}$_2$(μ-tppz)]$^{2+}$, where Me$_2$bpy is 4,4′-dimethyl-2,2′-bipyridine.

(I)
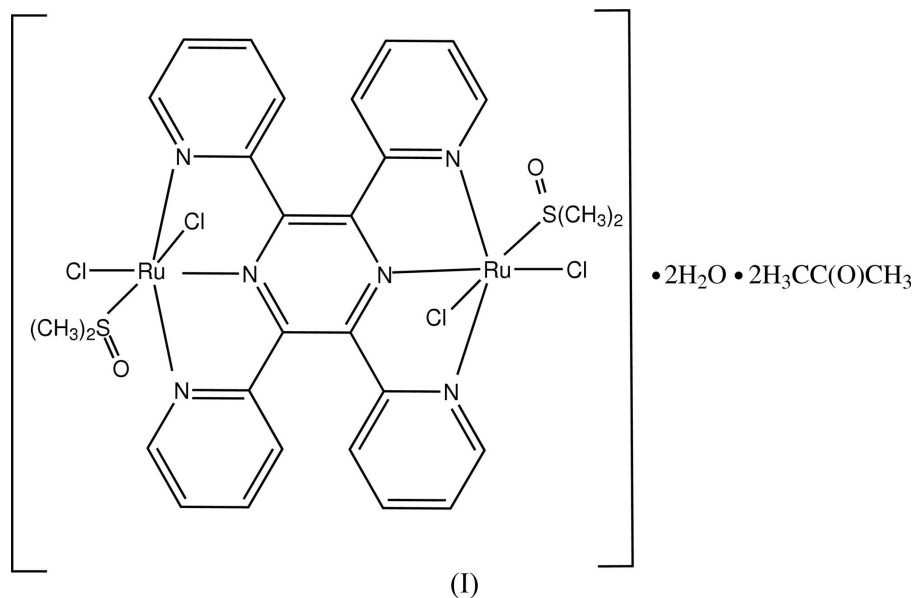
cis,cis-[{Ru(DMSO)Cl$_2$}$_2$(μ-tppz)] was synthesized by reacting two equivalents of Ru(DMSO)$_4$Cl$_2$ with one equivalent of tppz in DMSO solution. For the neutral complex to dissolve in water, it is suggested that aqua substitution of at least one of the chloro ligands must have occurred. The slow reformation of the complex and consequent slow crystal
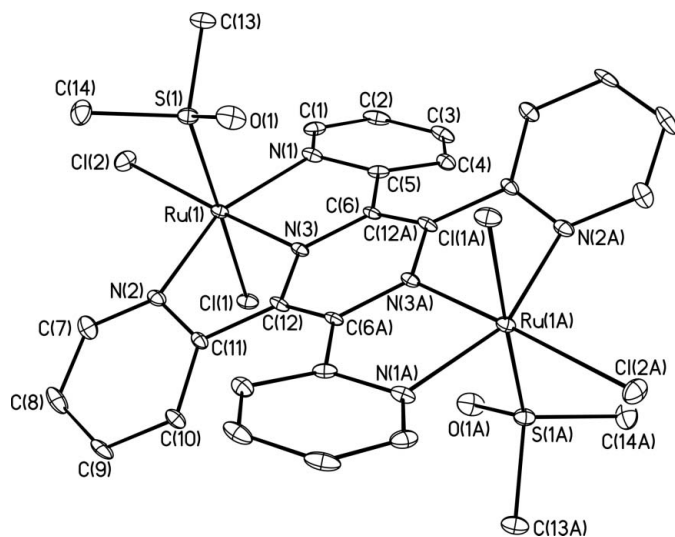
Figure 1
The structure of one of the independent complex molecules, with 50% probability displacement ellipsoids. H atoms have been omitted. [Symmetry code: (A) −1 − x, −y, 2 − z.]

growth occurred with the diffusion of acetone into the solution. Only the *cis* isomer was isolated and this is to be contrasted to the reaction of 2,2′:6′,2″-terpyridine (trpy) with Ru(DMSO)$_4$Cl$_2$, which gave both the *cis* and the *trans*-Ru(trpy)(DMSO)Cl$_2$ isomers, albeit in yields of 85 and 10%, respectively (Ziessel *et al.*, 2004).

Crystallography revealed two acetone and two water molecules per complex molecule in the crystal structure. Two independent centrosymmetric complexes are found, with half of each in the asymmetric unit. The ruthenium ions display distorted octahedral coordination in which DMSO is sulfur-bound and the chloro ligands are in a *cis* geometry. Fig. 1 shows one of the two complexes, and it clearly shows the distortion from planarity of the tppz ligand in which two pyridyl groups coordinated to the same Ru^{II} ion are tilted above the plane of the pyrazine ring, while the other two pyridyl groups coordinated to the second Ru^{II} ion are tilted below the plane of the pyrazine ring. This conformation probably minimizes steric strain while at the same time maximizing the bonding interaction of the tppz ligand with the ruthenium ions. The shortness of the Ru—N(pyrazine) bonds compared with the Ru—N(pyridine) bonds (Table 1) is suggested to be due to the stronger π-accepting properties of the pyrazine ring.

Experimental

Ru(DMSO)$_4$Cl$_2$ (1 mmol) was dissolved in DMSO (20 ml). To the yellow solution was added tppz (0.5 mmol). The stirred reaction solution was heated to 333 K and the temperature maintained for two days, during which time the solution became deep purple in color. Addition of 600 ml of diethyl ether precipitated the purple product, which was collected and washed with diethyl ether. The crude product was recrystallized by diffusion of acetone into an aqueous solution of the complex. After four weeks, purple crystals formed. The yield was 90% based on tppz.

Table 1
Selected bond lengths (Å).

Ru1—N3	1.944 (5)	Ru2—N6	1.946 (5)
Ru1—N2	2.068 (5)	Ru2—N4	2.061 (5)
Ru1—N1	2.068 (5)	Ru2—N5	2.061 (5)
Ru1—S1	2.2454 (18)	Ru2—S2	2.2450 (18)
Ru1—Cl2	2.4112 (19)	Ru2—Cl4	2.4201 (19)
Ru1—Cl1	2.4226 (18)	Ru2—Cl3	2.4242 (18)

Initial structural solution showed two severely disordered, cocrystallized acetone solvent molecules and two water molecules per complex molecule. The data set was treated with the SQUEEZE filter of *PLATON* (Spek, 2003) to model the solvent molecules as diffuse contributions to the electron density. H atoms were assigned calculated positions with C—H = 0.95–0.98 Å and U_{iso}(H) values of 1.2 or 1.5 times U_{eq}(C). The deepest electron density hole is located 0.90 Å from atom Ru2.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL*.

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