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α-Dichlorobis(2-phenylazo-4,6-dimethylpyridine)ruthenium(II) chloroform solvate

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The crystal structure of $[RuCl_2(C_{13}H_{13}N_3)_2]$ contains complexes on general positions and complexes located on crystallographic twofold rotation axes. The three independent 2-phenylazo-4,6-dimethylpyridine ligands all have the same conformation.

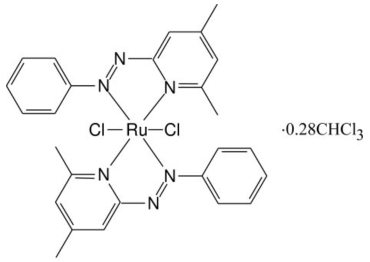
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.034
wR factor = 0.083
Data-to-parameter ratio = 19.6

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

Comment

Several ruthenium complexes are known for their cytotoxic, antitumor or antimetastatic activity (Clarke, 2002; Reedijk, 2003). The isomeric dichlorobis(2-phenylazopyridine)ruthenium(II) complexes $[Ru(azpy)_2Cl_2]$ are under renewed investigation due to their cytotoxic activity in human tumor cell lines (Hotze *et al.*, 2004; Velders *et al.*, 2000). In order to find structure–activity relationships for this type of ruthenium complexes, methylated azpy derivatives have also been synthesized and the corresponding ruthenium complexes have been subsequently tested for their cytotoxic behavior (Hotze *et al.*, 2004). Besides ligands with only one methyl substituent, a ligand with two methyl groups, 2-phenylazo-4,6-dimethylpyridine (dazpy), has been used in these studies. This ligand has been reported in the literature in the synthesis of molybdenum complexes (Ackermann *et al.*, 1996, 2003), but has not been studied in complexes with ruthenium. Crystal structures of transition metal complexes with dazpy or other azpy derivatives with two methyl substituents were not found in the Cambridge Structural Database (November 2003 release; Allen, 2002).



(I)

The asymmetric unit of the crystal structure of the title compound, (I), consists of one $Ru(dazpy)_2Cl_2$ complex located on a general position and one half of a complex, with Ru located on a crystallographic twofold rotation axis. Displacement ellipsoid plots of the complexes are given in Figs. 1 and 2, respectively. In both complexes, the dazpy ligand is coordinated to ruthenium in the so-called α configuration, meaning that the coordinating pairs of Cl, N_{py} and N_{azo} are in *cis, trans* and *cis* orientations, respectively. The Ru atoms adopt an octahedral geometry that is somewhat distorted due to the small bite angle of the dazpy ligand.

The three independent dazpy ligands are in the same conformation, as is indicated by the acute angles between the

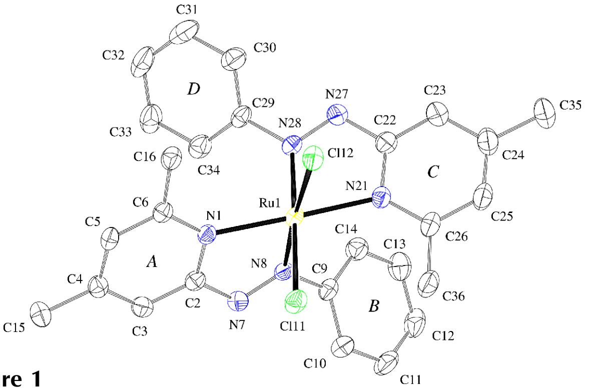


Figure 1
View of the Ru(dazpy)$_2$Cl$_2$ complex located on a general position, with the atom and ring numbering schemes. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity.

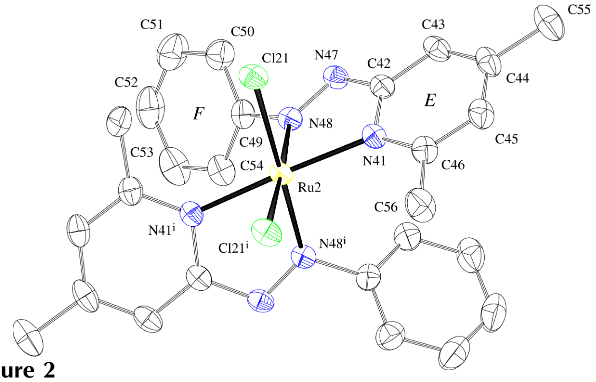


Figure 2
View of the Ru(dazpy)$_2$Cl$_2$ complex located on a crystallographic twofold rotation axis, with the atom and ring numbering schemes. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms have been omitted for clarity. [Symmetry code: (i) $-x,y,\frac{1}{2}-z$.]

least-squares planes through their six-membered rings: ∠(*A*,*B*) = 48.31 (12)°, ∠(*C*,*D*) = 41.22 (13)° and ∠(*E*,*F*) = 45.26 (13)° (capitals refer to the ring systems as labeled in Figs. 1 and 2).

The independent Ru complexes adopt the same overall conformation, as is illustrated by the superposition of the complexes shown in Fig. 3. The fit was carried out by the quaternion method (Mackay, 1984) applied to the non-H atoms of the complexes. An r.m.s. deviation of 0.140 Å was found.

Experimental

The dazpy ligand was synthesized according to a literature method for the synthesis of 2-phenylazopyridine (Krause & Krause, 1980), but where aminopyridine and nitrosobenzene were used in the literature synthesis, 4,6-dimethylaminopyridine and nitrosobenzene were used for the preparation of the title compound. Crystals of the title compound appeared after slow evaporation of the filtrate of the compound γ-[Ru(dazpy)$_2$Cl$_2$], synthesized according to the literature synthesis (Goswami *et al.*, 1981) of γ-[Ru(azpy)$_2$Cl$_2$]. It should be noted, however, that the title compound has also been obtained using the literature procedure (Bao *et al.*, 1988) for α-[Ru(azpy)$_2$Cl$_2$] and β-[Ru(azpy)$_2$Cl$_2$]. In the former case, a mixture of γ-[Ru(dazpy)$_2$Cl$_2$] and α-[Ru(dazpy)$_2$Cl$_2$] appeared, but in the latter case, strangely enough, almost pure α-[Ru(dazpy)$_2$Cl$_2$] was formed and hardly any β isomer. Recrystallization from CHCl$_3$ and diethyl ether resulted in pure α-[Ru(dazpy)$_2$Cl$_2$] (yield: 64%). ^{1}H NMR 300 MHz in CDCl$_3$ (numbering used as in crystal structure): δ 8.22 (*s*, 1H, H3), 7.30 (*t*, 1H, H12), 7.12 (*t*, 2H, H11/H13), 7.02 (*s*, 1H, H5), 6.82 (*d*, 2H, H10/H14), 2.64 [*s*, 3H, (C16)H$_3$], 2.55 [*s*, 3H, (C15)H$_3$].

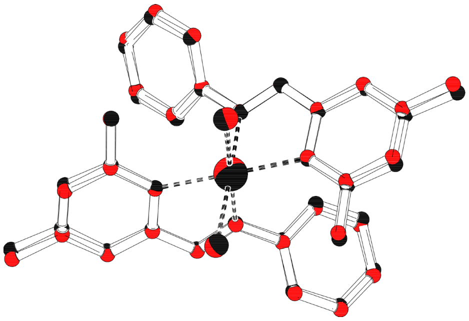


Figure 3
Superposition of the complex containing Ru1 (red) with the complex containing Ru2 (black).

Crystal data

[RuCl$_2$(C$_{13}$H$_{13}$N$_3$)$_2$] ignoring solvent; see following text
M_r = 594.50
Monoclinic, *C*2/*c*
a = 26.986 (3) Å
b = 18.412 (3) Å
c = 17.365 (2) Å
β = 107.295 (9)°
V = 8238.0 (19) Å^3
Z = 12

D_x = 1.438 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1772 reflections
θ = 2.0–25.0°
μ = 0.79 mm^{-1}
T = 150 K
Block, black
0.25 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: none
85875 measured reflections
9406 independent reflections
7787 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.051
$\theta_{\rm max}$ = 27.4°
$h = -34 \rightarrow 34$
$k = -23 \rightarrow 23$
$l = -22 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.083
S = 1.05
9406 reflections
480 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 9.95P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.72 e Å^{-3}
$\Delta\rho_{\rm min}$ = −2.31 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ru1—Cl11	2.4417 (7)	Ru1—N28	1.9712 (19)
Ru1—Cl12	2.4279 (8)	Ru2—Cl21	2.4139 (7)
Ru1—N1	2.0966 (19)	Ru2—N41	2.091 (2)
Ru1—N8	1.967 (2)	Ru2—N48	1.968 (2)
Ru1—N21	2.101 (2)		
Cl11—Ru1—Cl12	89.39 (2)	N8—Ru1—N21	99.27 (8)
Cl11—Ru1—N1	80.67 (5)	N8—Ru1—N28	99.06 (8)
Cl11—Ru1—N8	84.73 (6)	N21—Ru1—N28	76.85 (8)
Cl11—Ru1—N21	104.24 (5)	Cl21—Ru2—N41	82.34 (6)
Cl11—Ru1—N28	175.88 (6)	Cl21—Ru2—N48	86.79 (6)
Cl12—Ru1—N1	105.49 (5)	Cl21—Ru2—Cl21$^{\rm i}$	88.13 (2)
Cl12—Ru1—N8	173.50 (6)	Cl21—Ru2—N41$^{\rm i}$	103.20 (6)
Cl12—Ru1—N21	79.47 (6)	Cl21—Ru2—N48$^{\rm i}$	174.89 (6)
Cl12—Ru1—N28	86.90 (6)	N41—Ru2—N48	76.66 (8)
N1—Ru1—N8	76.33 (8)	N41—Ru2—N41$^{\rm i}$	172.41 (7)
N1—Ru1—N21	173.22 (7)	N41—Ru2—N48$^{\rm i}$	98.29 (8)
N1—Ru1—N28	98.58 (8)	N48—Ru2—N48$^{\rm i}$	98.30 (8)

Symmetry code: (i) $-x, y, \frac{1}{2}-z$.

m248 Huub Kooijman *et al.* • [RuCl$_2$(C$_{13}$H$_{13}$N$_3$)$_2$] *Acta Cryst.* (2004). E**60**, m247–m249

The methyl groups were refined as rigid groups, allowing for rotation around the C—C bonds. Aromatic H atoms were placed on idealized positions. Isotropic displacement parameters of H atoms were set to 1.5 or 1.2 times the equivalent isotropic displacement parameter of the carrier atom for methyl H atoms and other H atoms, respectively. The unit cell contains four symmetry-related cavities located on the crystallographic inversion centres at ($\frac{1}{4}$, $\frac{3}{4}$, 0), ($\frac{3}{4}$, $\frac{1}{4}$, 0), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{2}$) and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{1}{2}$). The cavities are filled with disordered solvent, probably chloroform. The volume of each cavity is 149.3 Å^3. Since disorder models gave unsatisfactory results, the contribution of the disordered solvent to the scattering factors has been taken into account with *PLATON*/*SQUEEZE* (Spek, 2003; van der Sluis & Spek, 1990). A total of 48 e was found in each cavity, corresponding to approximately 0.83 chloroform molecule per cavity. Where relevant, the crystal data reported earlier in this paper are without the contribution of the disordered solvent. Taking into account the partial occupation of each cavity with chloroform, the following values are obtained for those parameters: $C_{26}H_{26}Cl_2N_5Ru{\cdot}0.28CHCl_3$, M_r = 624.35 Mg m^{-3} μ = 0.853 mm^{-1}, $F(000)$ = 3798 and D_x = 1.51 Mg m^{-3}. The deepest hole in the difference Fourier is located at (0.177, 0.162, 0.290) in a small cavity between the Ru complexes which is not large enough to contain any solvent.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Acta Cryst. (2004). E**60**, m247–m249 Huub Kooijman *et al.* • $[RuCl_2(C_{13}H_{13}N_3)_2]$ **m249**