trans-Dichlorotetrakis(4-methylpyri-midine-*N*¹)ruthenium(II)

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The title compound, *trans*-[Ru^{II}Cl$_2$(N^1-mepym)$_4$] (mepym is 4-methylpyrimidine, C$_5$H$_6$N$_2$), obtained from the reaction of *trans,cis,cis*-[Ru^{II}Cl$_2$(N^1-mepym)$_2$(SbPh$_3$)$_2$] (Ph is phenyl) with excess mepym in ethanol, has fourfold crystallographic symmetry and has the four pyrimidine bases coordinated through N^1 and arranged in a propeller-like orientation. The Ru—N and Ru—Cl bond distances are 2.082 (2) and 2.400 (4) Å, respectively. The methyl group, and the N^3 and Cl atoms are involved in intermolecular C—H···N and C—H···Cl hydrogen-bond interactions.

Comment

The structural characterization of ruthenium complexes with pyrimidine and purine bases is an important preliminary step in understanding the molecular mechanism of the cytostatic effects exerted by certain ruthenium compounds (Clarke *et al.*, 1999, and references therein).

As part of a project devoted to the synthesis and structural characterization of new ruthenium complexes containing pyrimidine and purine bases (see previously published papers by this group: Cini & Pifferi, 2000; Bellucci & Cini, 1999; Pifferi & Cini, 1998; Cini *et al.*, 1993), we wish to report here the X-ray diffraction analysis of the crystal and molecular structure of *trans*-[RuCl$_2$(mepym)$_4$] (mepym is 4-methyl-pyrimidine), (I).

(I)
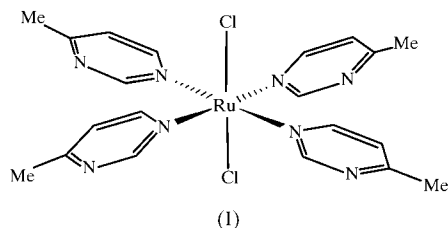
The complex molecule contains the 4-methylpyrimidine ligand, which can be considered as a model of the nucleic acid pyrimidine bases. It has a pseudo-octahedral coordination sphere (see Fig. 1) in which the metal atom is linked to two Cl⁻ anions (at apical positions) and to four N¹ atoms of the mepym

ligands. The Ru and Cl atoms are located on the fourfold crystallographic axis.

The Ru—Cl bond distances [average 2.400 (4) Å] are in agreement with the corresponding values for other Ru^{II} complexes (Bellucci & Cini, 1999; Pifferi & Cini, 1998). The Ru—N bond distances are 2.082 (2) Å, a value somewhat shorter than the Ru—N(mepym) lengths [2.131 (5) Å] found for *trans,cis,cis*-[RuCl$_2$(mepym)$_2$(SbPh$_3$)$_2$] (Cini *et al.*, 2001). This is understandable when considering the larger *trans* influence exerted by triphenylstibine compared with mepyn, as well as the high steric hindrance due to two *cis* SbPh$_3$ ligands. Other Ru—N bond lengths for substituted pyrimidine agree well with the value found in this work and examples are 2.036 (3) Å (average) for *cis,trans,cis*-dichlorobis[(2-phenyl-azo)pyrimidine]ruthenium(II) (Santra *et al.*, 1999) and 2.081 (2) Å (average) for *trans,cis,cis*-dichlorobis[(2-phenyl-azo)pyrimidine]ruthenium(II) (Santra *et al.*, 1999). The bond angles around the metal centre have almost the idealized values of 90 and 180°.

The bond distances and angles within the mepym ligand have normal values when compared with other metal complexes; see, for instance, *trans*-dichloro(phenyl)bis-(pyridine)(N^1-4-methyl-1,3-pyrimidine)rhodium(III) (Cini *et al.*, 1999) and *catena*-[(μ^2-*N,S*-thiocyanato)-(*N*-4-methyl-pyrimidine)copper(I)] (Teichert & Sheldrick, 1999). The orientation of the mepym planes with respect to the Ru—Cl vectors is almost exactly staggered, the C2—N1—Ru—Cl2 torsion angle being −39.3 (3)°. As a consequence, the arrangement of the four mepym ligands in the equatorial plane of the complex molecule can be described as propeller-like.

The existence of two intramolecular C—H···Cl hydrogen-bond interactions per mepym ligand is not excluded on the basis of the contact distances and angles (see Table 2), even
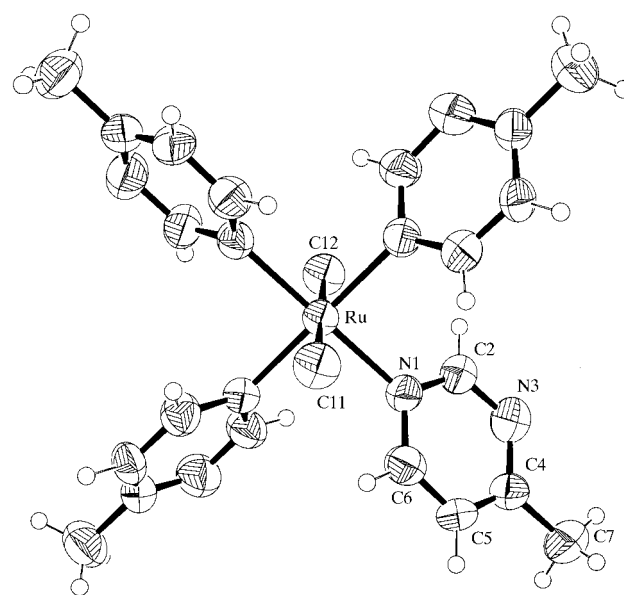
Figure 1
The molecular structure of the title compound showing 30% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

metal-organic compounds

though an eclipsed conformation would lead to stronger C—H···Cl interactions.

Analysis of the crystal packing shows the existence of short intermolecular C—H···Cl and C—H···N contacts involving the methyl group, the chloride ligands and the N3 atoms. Selected contact distances and angles are quoted in Table 2. It should be emphasized that interactions of the type C—H···X (X = O, N or halogen) are attracting increased interest in the community of structural and bioinorganic chemists (see, for instance: Taylor & Kennard, 1982; Sigel *et al.*, 1998; Lüth *et al.*, 2001; Huang *et al.*, 1998; Cini & Cavaglioni, 1999).

Experimental

Crystals of the title compound were obtained as red prisms on mixing a suspension of *trans,cis,cis*-[Ru^{II}Cl$_2$(N^1-mepym)$_2$(SbPh$_3$)$_2$] (Cini *et al.*, 2001) in absolute ethanol with a *ca* 100-fold excess of mepym and refluxing the mixture under an atmosphere of ultra-pure nitrogen for 30 min. The deaerated clear solution was then stored at 278 K and single crystals formed within 48 h.

Crystal data

[RuCl$_2$(C$_5$H$_6$N$_2$)$_4$]	Mo $K\alpha$ radiation
$M_r = 548.44$	Cell parameters from 24
Tetragonal, $I4$	reflections
$a = 11.295\,(1)$ Å	$\theta = 6$–$16°$
$c = 9.200\,(1)$ Å	$\mu = 0.92$ mm^{-1}
$V = 1173.7\,(2)$ Å^3	$T = 293\,(2)$ K
$Z = 2$	Prism, red
$D_x = 1.552$ Mg m^{-3}	$0.30 \times 0.20 \times 0.10$ mm

Data collection

Siemens *P*4 diffractometer	$R_{int} = 0.028$
ω scans	$\theta_{max} = 25.0°$
Absorption correction: empirical	$h = -10 \rightarrow 12$
via ψ scan (North *et al.*, 1968)	$k = -13 \rightarrow 11$
using *XEMP* (Siemens, 1994)	$l = -9 \rightarrow 10$
$T_{min} = 0.872$, $T_{max} = 0.912$	3 standard reflections
2354 measured reflections	every 97 reflections
990 independent reflections	intensity decay: none
898 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.29$ e Å^{-3}
990 reflections	$\Delta\rho_{min} = -0.17$ e Å^{-3}
73 parameters	Absolute structure: Flack, 1983
H-atom parameters constrained	Flack parameter = 0.19 (5)

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-32 (Farrugia, 1998); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

Table 1
Selected geometric parameters (Å, °).

Ru—N1	2.082 (2)	C2—N3	1.349 (5)
Ru—Cl1	2.398 (4)	N3—C4	1.371 (10)
Ru—Cl2	2.400 (4)	C4—C5	1.356 (11)
N1—C2	1.337 (6)	C4—C7	1.492 (5)
N1—C6	1.343 (7)	C5—C6	1.333 (5)
N1^i—Ru—N1	89.997 (3)	N1—C2—N3	125.0 (4)
N1—Ru—N1^{ii}	179.2 (4)	C2—N3—C4	117.0 (4)
N1—Ru—Cl1	90.4 (2)	C5—C4—N3	120.0 (3)
N1—Ru—Cl2	89.6 (2)	C5—C4—C7	121.8 (7)
Cl1—Ru—Cl2	180.0	N3—C4—C7	118.3 (8)
C2—N1—C6	115.1 (3)	C6—C5—C4	118.8 (4)
C2—N1—Ru	122.1 (4)	C5—C6—N1	124.1 (4)
C6—N1—Ru	122.8 (4)		

Symmetry codes: (i) $-y, x, z$; (ii) $-x, -y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2···Cl2	0.93	2.78	3.247 (5)	112
C6—H6···Cl1	0.93	2.83	3.300 (5)	113
C7—H7C···Cl1^i	0.96	2.92	3.772 (6)	149

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1526). Services for accessing these data are described at the back of the journal.

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