Acta Crystallographica Section E
**Structure Reports**
**Online**
ISSN 1600-5368

# *trans*-Dichloro(*meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene-$\kappa^4N^{3,7,11,17}$)rhodium(III) hexafluorophosphate

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Received 24 August 2001
Accepted 6 September 2001
Online 20 September 2001

In the title compound, $[RhCl_2(C_{18}H_{32}N_4)]PF_6$, the $Rh^{III}$ ion lies at the centre of a distorted octahedron of two axial chloride and four equatorial aza ligands. Within estimated error, the complex cation possesses non-crystallographic mirror symmetry. The Rh—Cl distances of 2.345 (3) and 2.349 (3) Å are equivalent, as are the three Rh—N*sp*$^3$ distances [mean 2.145 (7) Å]. The Rh—N*sp*$^2$ distance is much shorter at 1.964 (7) Å, reflecting the different hybridization of this donor atom. The four N atoms are not coplanar, and the metal ion lies out of the $N_4$ plane by 0.013 (3) Å, suggesting that, with an ionic radius of 0.805 Å, the $Rh^{III}$ ion is somewhat large for the macrocyclic cavity.

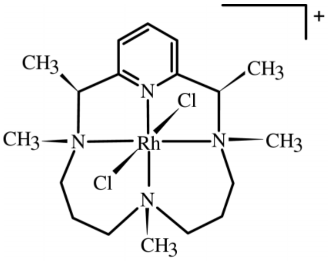
**Key indicators**

Single-crystal X-ray study
*T* = 293 K
Mean σ(C–C) = 0.016 Å
Disorder in solvent or counterion
*R* factor = 0.065
*wR* factor = 0.182
Data-to-parameter ratio = 9.5

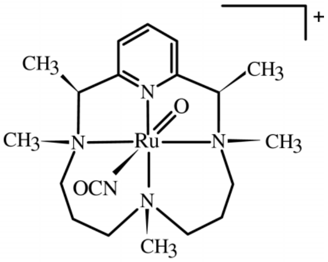
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

## Comment

The distortions from ideal octahedral coordination of the metal centre in the title complex, (1), are seen in the *cis* and *trans* angles subtended at that centre, which range from 82.3 (3) to 97.9 (3)° and from 164.5 (3) to 175.9 (3)°, respectively. The bonds to Rh formed by the two chloride ligands are equivalent, as are the three bonds from the *sp*$^3$ nitrogen donors N3, N7 and N11. The Rh—N17 distance is much shorter, reflecting the *sp*$^2$ hybridization of this donor atom. The four N atoms are not coplanar [mean r.m.s. deviation from the $N_4$ best plane is 0.065 (8) Å] and this effect is represented in the 29° twists of N3 and N11 from the plane of the pyridyl



(1)



(2)

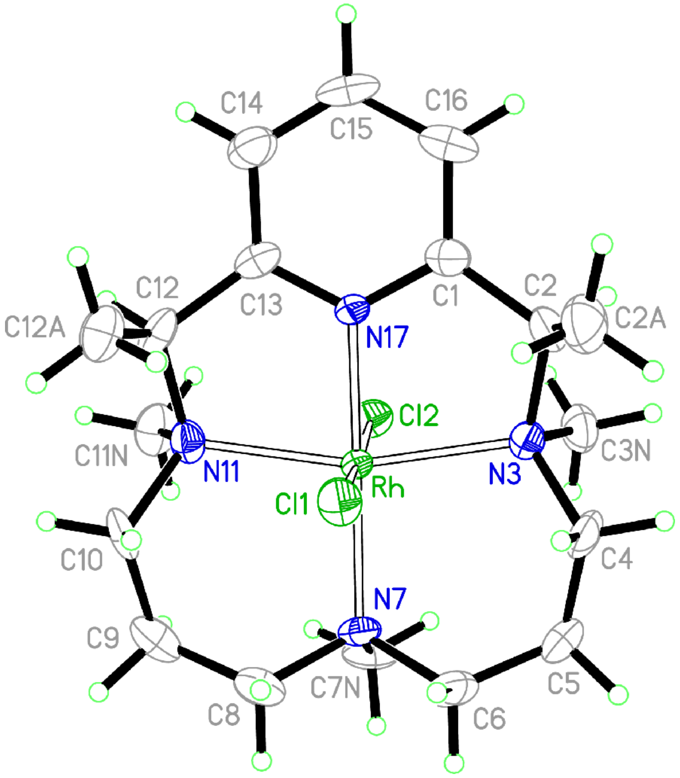


**Figure 1**
A view of the cation of (1) with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces. A non-crystallographic mirror plane bisects the cation, passing through atoms C15, N17, Rh, Cl1, Cl2, N7 and C7N.

ring. The metal ion lies 0.013 (3) Å out of the $N_4$ plane, in the direction of Cl2. These observations suggest that, with an ionic radius of 0.805 Å (Shannon, 1976), the $Rh^{III}$ ion is somewhat large for the macrocyclic cavity and the observed distortions are a mechanism to accommodate this misfit. A non-crystallographic mirror plane bisects the cation, passing through C15, N17, Rh, Cl1, Cl2, N7 and C7N (Fig. 1).

Complexes of second-row transition metals with the 2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene ligand are rare, the only structurally characterized example of which we are aware being the *trans*-isocyanatooxoruthenium(IV) complex, (2) (Che *et al.*, 1989). However, a number of complexes of first-row elements are known, for example with cobalt(II) (Che *et al.*, 1986) and nickel(II) (Che *et al.*, 1988) and there are a large number of complexes with ligands having different functionalization of the 3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene backbone, for example, carbonylchloro[*cis*-2,7,12-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,-15-triene-$\kappa^4N^{3,7,11,17}$]ruthenium(II) tetraphenylborate (Blake *et al.*, 1986).

## Experimental

Reaction of $RhCl_3$ with *meso*-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene in MeOH was followed by addition of $PF_6^-$. Crystals of (1) were grown from $CH_3NO_2$ solution. Elemental analysis, found: C 35.9, H 5.17, N 8.5%; calculated for $C_{18}H_{32}Cl_2F_6N_4PRh$: C 34.6, H 5.17, N 9.0%.

### *Crystal data*

$[RhCl_2(C_{18}H_{32}N_4)]PF_6$
$M_r = 623.26$
Triclinic, $P\overline{1}$
$a = 7.949$ (5) Å
$b = 11.067$ (5) Å
$c = 14.116$ (5) Å
$\alpha = 74.22$ (5)°
$\beta = 86.26$ (5)°
$\gamma = 84.67$ (5)°
$V = 1188.7$ (10) Å$^3$

$Z = 2$
$D_x = 1.741$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
$\theta = 12$–13°
$\mu = 1.07$ mm$^{-1}$
$T = 293$ (2) K
Lath, yellow
0.5 × 0.2 × 0.1 mm

### *Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega$–$2\theta$ scans
Absorption correction: $\psi$ scans; refined from $\Delta F$ (North *et al.*, 1968; Walker & Stuart, 1983)
$T_{\min} = 0.448$, $T_{\max} = 0.898$
3098 measured reflections
3098 independent reflections

2378 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 22.5°$
$h = -8 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 15$
2 standard reflections every 60 reflections intensity decay: 3%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.182$
$S = 1.00$
3094 reflections
325 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.149P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 1.92$ e Å$^{-3}$
$\Delta\rho_{\min} = -1.77$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Rh—Cl1 | 2.345 (3) | Rh—N7 | 2.140 (7) |
| Rh—Cl2 | 2.349 (3) | Rh—N11 | 2.150 (7) |
| Rh—N3 | 2.145 (7) | Rh—N17 | 1.964 (7) |
| | | | |
| Cl1—Rh—Cl2 | 175.61 (8) | Cl2—Rh—N17 | 88.7 (2) |
| Cl1—Rh—N3 | 91.1 (2) | N3—Rh—N7 | 97.9 (3) |
| Cl1—Rh—N7 | 88.9 (2) | N3—Rh—N11 | 164.5 (3) |
| Cl1—Rh—N11 | 91.3 (2) | N3—Rh—N17 | 82.5 (3) |
| Cl1—Rh—N17 | 86.9 (2) | N7—Rh—N11 | 97.5 (3) |
| Cl2—Rh—N3 | 88.3 (2) | N7—Rh—N17 | 175.9 (3) |
| Cl2—Rh—N7 | 95.4 (2) | N11—Rh—N17 | 82.3 (3) |
| Cl2—Rh—N11 | 88.2 (2) | | |

The primary absorption correction was semi-empirical (North *et al.*, 1968), supplemented by calculated corrections (Walker & Stuart, 1983). The largest residuals in the final $\Delta F$ synthesis lie near the metal atom. There is disorder in the equatorial F atoms of the anion, which was modelled by allowing two orientations for each of these four atoms, F2–F5. Extensive restraints were applied to P—F distances, F—P—F angles and anisotropic displacement parameters. The occupancies of these orientations refined to 0.50 (3), indicating that they are equally occupied, and so all were set equal to 0.5. H atoms were placed geometrically and refined riding on their parent C atoms at distances of 0.93, 0.96, 0.97 and 0.98 Å for aromatic, methine, methylene and methyl groups, respectively, with $U_{\rm iso}(H) = xU_{\rm eq}(C)$, where $x = 1.5$ for methyl H atoms and 1.2 for all others.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CADABS* (Gould & Smith, 1986); program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*/*PC* (Sheldrick,

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1994); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2001).

We thank EPSRC for support.

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