Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction:
  ψ scan (North *et al.*, 1968)
  $T_{\min}$ = 0.723, $T_{\max}$ = 0.897
1919 measured reflections
1786 independent reflections
1231 reflections with $I > 3\sigma(I)$
$R_{\rm int}$ = 0.023
$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 12$
$l = -14 \rightarrow 14$
3 standard reflections
  every 150 reflections
  intensity decay: 0.85%

Refinement

Refinement on *F*
R = 0.043
wR = 0.045
S = 1.674
1231 reflections
111 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 0.42 e Å^{-3}
$\Delta\rho_{\min}$ = −0.62 e Å^{-3}
Extinction correction: Zachariasen (1967) type 2, Gaussian isotropic
Extinction coefficient: 0.0335
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 2. *Selected geometric parameters (Å, °) for (II)*

Ni—N1	1.911 (3)	N2—C6	1.326 (5)
Ni—N2	1.862 (3)	N2—C7	1.468 (5)
N1—Ni—N1^{i}	98.7 (2)	N1—Ni—N2^{i}	168.0 (1)
N1—Ni—N2	83.9 (1)	N2—Ni—N2^{i}	96.0 (2)

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

The positions of the H atoms were idealized (C—H 0.95 Å), assigned isotropic displacement parameters B(H) = $1.2B_{\rm eq}$(C), and allowed to ride on their parent C atoms. The water H atoms were refined isotropically.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *TEXSAN*; program(s) used to refine structures: *TEXSAN*; molecular graphics: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OA1076). Services for accessing these data are described at the back of the journal.

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Dichloro(2,6-diisopropylaniline-*N*)(η^5-pentamethylcyclopentadienyl)rhodium(III)

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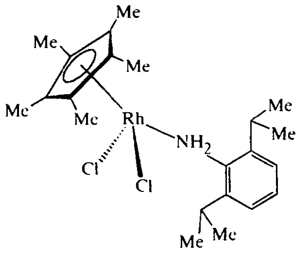
Abstract

The title compound, [RhCp*Cl_2(H_2N–C_6H_3-2,6-^{i}Pr_2)] (where Cp* is pentamethylcyclopentadienyl) or [RhCl_2($C_{10}H_{15}$)($C_{12}H_{19}N$)], was prepared from the reaction of di-μ-chloro-dichlorobis(pentamethylcyclopentadienyl)dirhodium(III), [Cp*RhCl_2]$_2$ [White, Yates & Maitlis (1992). *Inorg. Synth.* **29**, 228–234], with 2,6-diisopropylaniline in acetonitrile. This compound has a three-legged piano-stool structure. The ring is almost parallel to the phenyl ring of the 2,6-diisopropylaniline ligand.

Comment

The iridium analogue of the title compound, [IrCp*Cl_2(H_2N–C_6H_3-2,6-^{i}Pr_2)], was prepared by Bergman's group (Gluek *et al.*, 1991). Using the same methodology, we isolated the title compound, (I), which is stable both in the solid state and in solution.



(I)

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The unit-cell parameters and systematic absences indicated two possible space groups: *Pna*2$_1$ (non-centrosymmetric) and *Pnma* (centrosymmetric). A statistical analysis of the intensities suggested a non-centrosymmetric space group and the structure analysis converged only in *Pna*2$_1$. There is a local pseudo-mirror running through the C1, C6, Rh, N1, C11 and C14 atoms. This mirror is parallel to the *xy* plane at z = 0.846 (1). There are two intramolecular hydrogen bonds in which N1 acts as a donor to Cl1 and Cl2 [N1···Cl1 = 3.007 (9), H1*A*···Cl1 = 2.56 Å and N1—H1*A*···Cl1 = 112°; N1···Cl2 = 3.018 (9), H1*B*···Cl2 = 2.58 Å and N1—H1*B*···Cl2 = 111°].

The coordination sphere of the Rh atom can be described as a distorted octahedron, assuming that the pentamethylcyclopentadienyl (Cp*) ligand occupies three out of the six octahedral sites. This complex can also be referred to as a three-legged piano-stool compound. The Cp* ring (C1–C5) is almost parallel to the phenyl ring of the 2,6-diisopropylaniline ligand (C11–C16), with a dihedral angle of 2.12 (3)°. The plane defined by Rh, Cl1, and Cl2 is at a dihedral angle of 56.71 (9)° with respect to the Cp* ring and 57.51 (8)° with respect to the phenyl ring.

The Rh—N1 bond distance of 2.214 (2) Å indicates an Rh—N single bond (expected range 1.95–2.15 Å; Davis *et al.*, 1969). The two chemically equivalent Rh—Cl bonds [2.419 (3) and 2.420 (3) Å] are slightly longer than the terminal Rh—Cl bonds in the starting compound [2.397 (1) Å; Churchill *et al.*, 1977].

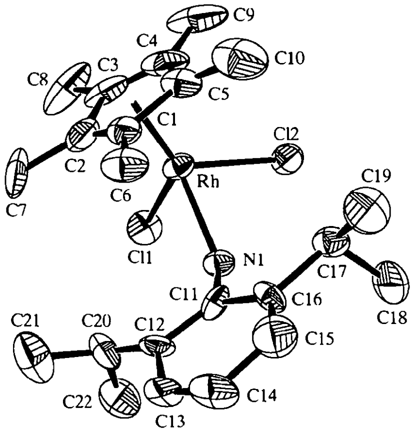

Fig. 1. The molecular structure of (I) with displacement ellipsoids drawn at the 50% level. H atoms have been omitted for clarity.

Experimental

2,6-Diisopropylaniline (0.11 ml, 0.6 mmol) was added to a solution of [Cp*RhCl$_2$]$_2$ (0.062 g, 0.1 mmol) in acetonitrile (20 ml) and the resulting solution stirred for 5 h. The solvent was removed under vacuum and the residue washed with hexane (2 × 20 ml) to give a mixture that contained the starting and title compounds. Recrystallization was from dichloromethane–hexane. ^{1}H NMR (CDCl$_3$): δ = 7.122 (2H, *d*, J = 7.5 Hz, Ph), 6.998 (1H, *t*, J = 7.5 Hz, Ph), 4.617 (2H, *br*, NH$_2$), 3.162 (2H, *br*, CH), 1.381 (15H, *s*, Cp*), 1.285 (12H, *d*, J = 6.5 Hz, CMe$_2$); ^{13}C{^{1}H} NMR (CDCl$_3$): δ = 137.973 (Ph), 137.127 (Ph), 123.730 (Ph), 122.959 (Ph), 94.556 (C$_5$ in C$_5$Me$_5$), 28.338 (CH in CHMe$_2$), 23.535 (Me$_2$ in CHMe$_2$), 9.264 (Me$_5$ in C$_5$Me$_5$); IR (KBr): 3304 (N—H), 3253 (N—H), 1459 cm^{-1} (Cp*).

Crystal data

[RhCl$_2$(C$_{10}$H$_{15}$)(C$_{12}$H$_{19}$N)]
M_r = 486.31
Orthorhombic
*Pna*2$_1$
a = 13.556 (1) Å
b = 9.8241 (9) Å
c = 17.604 (2) Å
V = 2344.4 (4) Å^3
Z = 4
D_x = 1.378 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 58 reflections
θ = 2.34–25.70°
μ = 0.962 mm^{-1}
T = 295 (2) K
Prism
0.58 × 0.42 × 0.24 mm
Orange–red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.671, $T_{\max}$ = 0.794
3063 measured reflections
2783 independent reflections
2277 reflections with $F > 4\sigma(F)$

$R_{\rm int}$ = 0.019
$\theta_{\max}$ = 25°
$h = -1 \rightarrow 16$
$k = -1 \rightarrow 11$
$l = -20 \rightarrow 1$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F)$ = 0.023
$wR(F^2)$ = 0.061
S = 1.083
2265 reflections
244 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.2111P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.205 e Å^{-3}
$\Delta\rho_{\min}$ = −0.455 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Rh—C2	2.144 (11)	Rh—N1	2.214 (2)
Rh—C4	2.142 (10)	Rh—Cl2	2.419 (3)
Rh—C5	2.141 (11)	Rh—Cl1	2.420 (3)
Rh—C1	2.152 (3)	N1—C11	1.451 (4)
Rh—C3	2.149 (9)		
N1—Rh—Cl2	81.2 (3)	Cl2—Rh—Cl1	92.74 (3)
N1—Rh—Cl1	80.8 (3)	C11—N1—Rh	131.5 (2)

All non-H atoms were refined anisotropically. All the H atoms were generated in ideal positions and refined using a riding model.

Data collection: *XSCANS* (Siemens, 1995). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Bruker, 1997). Program(s) used to solve structure: *SHELXTL*. Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1385). Services for accessing these data are described at the back of the journal.

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cis-(Nitrato-*O*,*O*′)[(1*RS*,4*SR*,5*SR*,8*RS*,11*SR*,12*SR*)-*C*-*rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) nitrate

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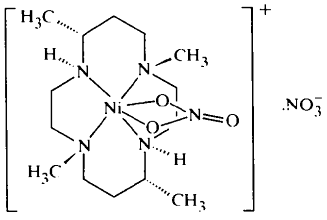
Abstract

The crystal structure of the title compound, $[Ni(NO_3)(C_{14}H_{32}N_4)]NO_3$, was determined by X-ray diffraction. The Ni^{II} ion is six-coordinate in a distorted octahedral arrangement, with the tetradentate macrocyclic ligand in a folded conformation. The two five-membered rings of the macrocyclic ligand have skew conformations, while the two six-membered rings adopt chair conformations. The four chiral N-atom centers are 1*RS*, 4*SR*, 8*RS* and 11*SR*, and the chiral C-atom centers are 5*SR* and 12*SR*.

Comment

The macrocyclic ligand 1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane exists as two isomers, *i.e.* *C-meso* and *C-rac* (Miyamura *et al.*, 1987). The crystal structure of the nickel(II) complex of the *C-meso* isomer has been reported previously (Miyamura *et al.*, 1987). This paper reports the crystal structure of the nickel(II) complex, (I), of the *C-rac* isomer.



(I)

The title complex cation has a distorted octahedral geometry, with the coordination formed by the tetradentate macrocyclic ligand in a folded conformation and the two O atoms of the bidentate nitrato group. The Ni1, N3 and O2 atoms lie on a crystallographic twofold axis. The four Ni—N bonds can be classified into two groups, *i.e.* the Ni1—N2 secondary amine bonds and the Ni1—N1 tertiary amine bonds. The Ni—N bond lengths are similar to those of the six-coordinate Ni^{II} complexes in related macrocyclic ligands (Lu *et al.*, 1991). The Ni—O bond is 2.154 (2) Å, which is longer than those found in *cis*-diaqua(1,4,8,11-tetraazacyclotetradecane)nickel(II) (2.140 and 2.130 Å; Barefield *et al.*, 1986), but shorter

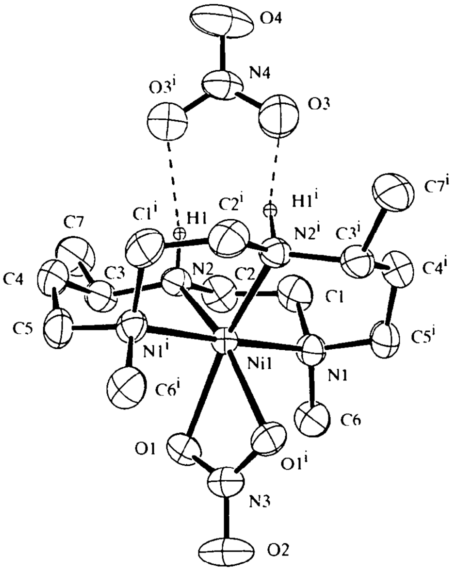


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. H atoms have been excluded, except for that on N2. The dotted lines represent N—H···O hydrogen bonds [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$].

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