Crystal data

[$MnRh(C_5H_5)(C_{12}H_{22}P)$-
($CO)_5$]
$M_r = 560.26$
Monoclinic
$P2_1/n$
$a = 16.185\ (7)$ Å
$b = 9.110\ (3)$ Å
$c = 17.535\ (8)$ Å
$\beta = 116.85\ (2)°$
$V = 2306.7\ (16)$ Å^3
$Z = 4$
$D_x = 1.613$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 8–18°$
$\mu = 1.362$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.46 × 0.33 × 0.15 mm
Red

Data collection

Siemens *R*3 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.686$, $T_{max} = 0.815$
5491 measured reflections
5321 independent reflections
3397 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 27.56°$
$h = -21 \rightarrow 18$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 22$
3 standard reflections every 400 reflections intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.083$
$S = 1.072$
5321 reflections
264 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2 + 0.9739P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.439$ e Å^{-3}
$\Delta\rho_{min} = -0.403$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Rh1—P1	2.2937 (14)	Mn1—P1	2.2487 (15)
Rh1—Mn1	2.7632 (10)		
P1—Rh1—Mn1	51.80 (4)	Mn1—P1—Rh1	74.93 (4)
P1—Mn1—Rh1	53.28 (4)		

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1346). Services for accessing these data are described at the back of the journal.

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[2,6-Bis(*N*-*tert*-butyliminomethyl)pyridine-κ^3N](phenolato-κO)rhodium(I)

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Abstract

The title compound, [$Rh(C_6H_5O)(C_{15}H_{23}N_3)$], is the first Rh^I–phenoxide compound with a tridentate nitrogen ligand to be crystallographically characterized. The Rh^I atom shows an essentially undistorted square-planar conformation, unlike the corresponding chlorine compound, which displays significant non-planarity. The flexibility observed by NMR in solution is partly supported by the conformation found in the crystalline state.

Comment

Recently, a number of studies involving rhodium compounds with various tridentate nitrogen ligands (TNL) have reported the synthesis, properties and oxidation chemistry involving four-, five- and six-coordinate Rh compounds of the types (TNL)RhCl, (TNL)Rh(*R*)Cl_2

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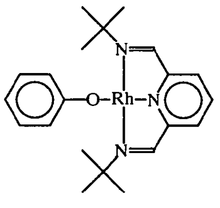
(R = $CHCl_2$, $PhCH_2$ and PhCHCl; Haarman, Ernsting *et al.*, 1997), (TNL)RhCl(diene) and $[(TNL)_2Rh]^+$ (Haarman, Bregman *et al.*, 1997). Special attention was given to the synthesis and reactivity of rhodium alkoxide and phenoxide compounds, (TNL)Rh(OR), examples of which are scarce (Haarman, Kaagman *et al.*, 1997; Kegley *et al.*, 1987). Only recently have we succeeded in obtaining suitable crystals of the air- and moisture-sensitive title compound, (I), which is one of the very few crystallographically authenticated Rh^I–phenoxide compounds and the only one with a tridentate nitrogen ligand.



(I)

There are no anomalies in the bond distances compared with compounds having similar chemical moieties reported in the Cambridge Structural Database (Version of October 1998; Allen & Kennard, 1993). With the exception of the methyl groups, the tridentate ligand is completely planar (maximum deviation of the least-squares plane through all relevant atoms is 0.015 Å).

The N2—Rh1—N3 angle of 158.0 (2)° is comparable to those observed for similar (TNL)Rh compounds (Haarman, Ernsting *et al.*, 1997; Haarman, Bregman *et al.*, 1997; Haarman, Kaagman *et al.*, 1997) and somewhat smaller than the value of 167° observed for the more flexible completely saturated TNL-type ligands (*e.g.* Ziolo *et al.*, 1974)

In the (TNL)RhCl compound reported earlier (Haarman, Ernsting *et al.*, 1997), the Rh—Cl bond makes an angle of approximately 15° with the plane defined by the three N atoms. In the title compound, atoms N1, N2, N3 and O1 are all within 0.003 (4) Å of the least-squares plane fitted through these atoms. The Rh atom is slightly out of this plane [0.0293 (4) Å]. The dihedral angle between the least-squares plane through the phenoxide group and the coordination plane is 86.2 (2)°, and the C—O—Rh angle is bent [127.6 (3)°].

On the basis of NMR measurements (Haarman, Kaagman *et al.*, 1997), it was concluded that the phenoxide moiety could rotate freely around the C—O and Rh—O bonds. The crystal structure shows there is no large steric hindrance in the conformation observed; the only intramolecular distance between the phenoxide and TNL ligands shorter than the sum of the van der Waals radii is C16···H(C9) [−0.17 Å]. This short contact can be easily relieved by a slight rotation of the C9-methyl or the complete C7-*tert*-butyl moieties around the C9—C7 and C7—N2 bonds, respectively. For a complete rotation around the C—O bond, the molecule has to be distorted somewhat. However, the completely free rotation around Rh—O observed in solution is not possible for the configuration observed in the crystal without major re-organization of the molecule.

The crystal packing displays tetramers of the title compound, arranged around a $\bar{4}$ axis. The molecules are linked by C2—H2···O1(y, $\frac{1}{2} - x$, $\frac{3}{2} - z$) hydrogen bonds [C2···O1 3.243 (7), H2···O1 2.32 Å and C2—H2···O1 172°].

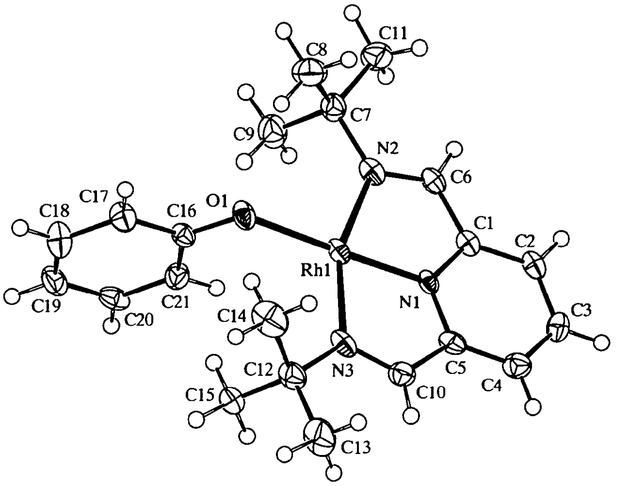


Fig. 1. Displacement ellipsoid plot of the title compound drawn at the 50% probability level (Spek, 1990). H atoms have an arbitrary radius.

Experimental

The preparation of the title compound has been described elsewhere (Haarman, Kaagman *et al.*, 1997). Crystals suitable from X-ray diffraction were grown from a toluene solution.

Crystal data

$[Rh(C_6H_5O)(C_{15}H_{23}N_3)]$
M_r = 441.38
Tetragonal
$P4_2/n$
a = 20.412 (3) Å
c = 10.482 (2) Å
V = 4367.1 (12) $Å^3$
Z = 8
D_x = 1.343 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 150 reflections
θ = 2–20°
μ = 0.80 mm^{-1}
T = 120 K
Block
0.20 × 0.15 × 0.15 mm
Dark red

Data collection

Nonius Kappa-CCD diffractometer
Area-detector φ and ω scans
Absorption correction: none
19 786 measured reflections
3848 independent reflections
3685 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.046
$\theta_{\rm max}$ = 25°
$h = -24 \rightarrow 24$
$k = -23 \rightarrow 23$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.123$
$S = 1.454$
3848 reflections
241 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0076P)^2 + 21.4166P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.62$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Rh1—O1	2.051 (4)	O1—C16	1.325 (6)
Rh1—N1	1.900 (4)	N2—C6	1.288 (7)
Rh1—N2	2.089 (4)	N3—C10	1.291 (8)
Rh1—N3	2.102 (5)		
O1—Rh1—N1	178.02 (16)	N2—Rh1—N3	157.99 (19)
O1—Rh1—N2	100.41 (17)	Rh1—O1—C16	127.6 (3)
O1—Rh1—N3	101.52 (17)	C6—N2—C7	119.2 (4)
N1—Rh1—N2	78.87 (19)	C10—N3—C12	118.4 (5)
N1—Rh1—N3	79.15 (18)		

The structure contains a solvent-accessible void, located on a 4_2 axis, with its centre at $(\frac{1}{4}, \frac{3}{4}, -0.024)$. Integration of the electron density in this area resulted in a total of zero electrons.

Data collection: *COLLECT* (Nonius, 1998). Cell refinement: *DirAx* (Duisenberg, 1992). Data reduction: *EVAL*14 (Duisenberg, 1998). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *PLATON* (Spek, 1990). Software used to prepare material for publication: *PLATON*.

This work was supported in part (ALS) by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW–NWO).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1325). Services for accessing these data are described at the back of the journal.

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A hydrated diclofenac salt of the hexaaquamagnesium ion

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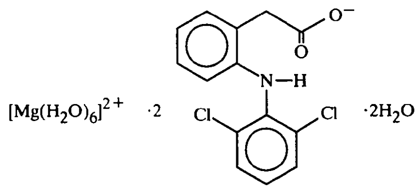
Abstract

In the title compound, hexaaquamagnesium bis{[2-(2,6-dichloroanilino)phenyl]acetate} dihydrate, $[Mg(H_2O)_6](C_{14}H_{10}Cl_2NO_2)_2\cdot 2H_2O$, the two centrosymmetric hexaaquamagnesium ions, the two [2-(2,6-dichloroanilino)phenyl]acetate anions and the two water molecules are tied into an elaborate network of hydrogen bonds.

Comment

In previous work, we investigated the structures of several diclofenac salts (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997). We report here the crystal structure of the dihydrated 1:2 salt of $[Mg(OH_2)_6]^{2+}$ with [2-(2,6-dichloroanilino)phenyl]acetate, hereinafter abbreviated as MgD_2.



MgD_2

Diclofenac sodium salt (NaD) is an effective drug used in rheumatology and magnesium is an essential cofactor in biology. The asymmetric unit of the MgD_2 salt consists of two anions in general positions, two cations located at the inversion centers $\frac{1}{2},0,0$ and $0,\frac{1}{2},0$, and two crystallization water molecules. Each cation is coordinated by six water molecules. The hexahydrated magnesium complex, the carboxylate ions and the water molecules are linked by a network of hydrogen bonds in which, as expected, $[Mg(OH_2)_6]^{2+}$ cations act as proton donors, carboxylate O atoms as proton acceptors and the two water molecules both