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***trans*-[Bis-2,6-(2-benzimidazolyl- κ N²)-pyridine- κ N]nitrobis(triphenylphosphine-*P*)ruthenium(II) Perchlorate Ethanol Solvate**

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Abstract

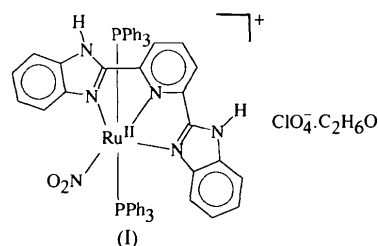
In the title compound, $[\text{Ru}(\text{NO}_2)(\text{C}_{19}\text{H}_{13}\text{N}_5)(\text{C}_{18}\text{H}_{15}\text{P})_2]\cdot\text{ClO}_4\cdot\text{C}_2\text{H}_6\text{O}$, the two phosphine ligands are in *trans* positions. The Ru atom and imidazolylpyridine moiety are almost coplanar, with the fused ring of the imidazolyl groups somewhat bent from the plane due to the steric hindrance of the phosphine phenyl groups. The nitro ligand is coordinated so that the NO_2 group is rotated $40.5(1)^\circ$ from the imidazolylpyridine plane.

Comment

There has been considerable interest in transition metal complexes containing a nitro ligand because of their capability to transfer oxygen to a number of organic and inorganic substrates (Leising & Takeuchi, 1987). Nitro-ruthenium complexes involving terpyridine (terpy) or bis(pyrazolyl)pyridine have been studied with respect to their reactivity and the coordination environment

around the central metal atom (Bailey & Drago, 1987; Bessel, See, Jameson, Churchill & Takeuchi, 1993; Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990). The orientation of the NO_2 plane is dependent on the meridional ligands. For example, the angles between the NO_2 and meridional coordination planes are almost 90° in the Ru–nitro complex containing 2,6-bis(3,5-dimethylpyrazol-1-yl)pyridine (Bessel, See, Jameson, Churchill & Takeuchi, 1993) and almost 0° in the complex containing 2,6-bis(pyrazol-1-yl)pyridine (Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990).

We report here the orientation of the NO_2 ligand in the title compound, (I), in which it is bound to the metal atom. The Ru atom is also coordinated by a pyridine ring carrying two benzimidazolyl groups rather



than substituted imidazole rings. An *ORTEP*II (Johnson, 1976) drawing of the molecule is shown in Fig. 1. The structure reveals that a bis(2-benzimidazolyl)pyridine (BIP) moiety, an NO_2 and two triphenylphosphine (PPh_3) groups are bound to the Ru atom, with ClO_4^- as anion. The two phosphine ligands are in an almost *trans* arrangement, with a P1—Ru—P2 angle of $178.79(8)^\circ$.

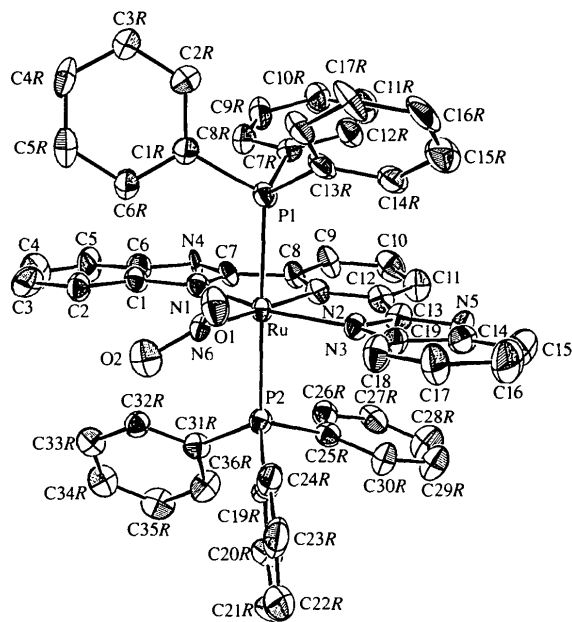


Fig. 1. The molecular structure of the title compound, with displacement ellipsoids drawn at the 40% probability level.

The Ru atom and the imidazolylpyridine moiety are coplanar within 0.077 (7) Å and the fused rings of the imidazolyl groups are somewhat bent from the plane due to the steric hindrance of the PPh₃ groups.

The nitro ligand is coordinated so that the O1—N—O2 plane is rotated 40.5 (1)° from the molecular plane defined by the Ru atom and the three heterocyclic rings. The contact distances of H18···O1, H6R···O1, H2···O2 and H32R···O2 are 2.474 (9), 2.773 (9), 2.709 (9) and 2.490 (9) Å, respectively. This means that the orientation of the NO₂ ligand is affected by the benzyl fragments of BIP and the PPh₃ groups. The rotating angle of the O1—N—O2 plane is in the midpoint of the range (0–88°) found in similar Ru complexes (Bessel, See, Jameson, Churchill & Takeuchi, 1993; Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990). The orientation of the NO₂ plane is dependent on the meridional. Other geometric parameters are close to expected values allowing for experimental error.

Experimental

The title compound was prepared by the method used to synthesize *trans*-[Ru(NO₂)(PPh₃)₂(terpy)]ClO₄ using BIP instead of terpy (Leising, Kubow, Churchill, Buttrey, Ziller & Takeuchi, 1990). *trans*-[Ru(BIP)(PPh₃)₂Cl]ClO₄ was produced by addition of an ethanol solution of Ru(BIP)Cl₃ in the presence of zinc powder. The title compound was prepared by reaction of NaNO₂ with *trans*-[Ru(BIP)(PPh₃)₂Cl]ClO₄. Crystals suitable for X-ray diffraction were obtained using a solvent pair of ethanol–acetone.

Crystal data

[Ru(NO₂)(C₁₉H₁₃N₅)-
(C₁₈H₁₅P)₂]ClO₄·C₂H₆O

M_r = 1128.48

Triclinic

P $\bar{1}$

a = 11.991 (2) Å

b = 13.951 (4) Å

c = 14.923 (4) Å

α = 96.02 (2)°

β = 94.49 (2)°

γ = 98.42 (2)°

V = 2445 (1) Å³

Z = 2

D_x = 1.533 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 10.0–16.0°

μ = 0.505 mm⁻¹

T = 293 (2) K

Tetragonal prism

0.50 × 0.50 × 0.45 mm

Red–brown

Data collection

Enraf-Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

empirical *via* four ψ scans (Fair, 1990)

T_{min} = 0.690, *T_{max}* = 0.797

5441 reflections with

I > 2σ(*I*)

R_{int} = 0.065

θ_{max} = 24.98°

h = 0 → 14

k = -16 → 16

l = -17 → 17

6933 measured reflections
5731 independent reflections

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.066

wR(*F*²) = 0.164

S = 1.069

5725 reflections

647 parameters

H atoms: see below

w = 1/[σ²(*F_o*²) + (0.0991*P*)² + 4.9903*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

3 standard reflections
frequency: 120 min
intensity decay: 0.03%

(Δ/σ)_{max} = 0.001

Δρ_{max} = 1.145 e Å⁻³

Δρ_{min} = -0.902 e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Ru—N2	2.011 (6)	N1—C7	1.299 (9)
Ru—N6	2.057 (6)	N1—C1	1.412 (9)
Ru—N3	2.116 (6)	N2—C8	1.337 (9)
Ru—N1	2.134 (6)	N2—C12	1.365 (9)
Ru—P1	2.407 (2)	N3—C13	1.318 (9)
Ru—P2	2.432 (2)	N3—C19	1.413 (9)
P1—C13R	1.826 (7)	N4—C7	1.326 (8)
P1—C7R	1.834 (8)	N4—C6	1.368 (10)
P1—C1R	1.839 (8)	N5—C13	1.347 (9)
P2—C31R	1.834 (7)	N5—C14	1.374 (10)
P2—C19R	1.836 (8)	N6—O1	1.229 (8)
P2—C25R	1.845 (8)	N6—O2	1.245 (8)
N2—Ru—N6	177.6 (3)	N1—Ru—P1	88.3 (2)
N2—Ru—N3	78.0 (2)	N2—Ru—P2	89.4 (2)
N6—Ru—N3	100.5 (2)	N6—Ru—P2	92.4 (2)
N2—Ru—N1	77.0 (2)	N3—Ru—P2	87.9 (2)
N6—Ru—N1	104.5 (2)	N1—Ru—P2	91.8 (2)
N3—Ru—N1	155.0 (2)	P1—Ru—P2	178.79 (8)
N2—Ru—P1	89.4 (2)	O1—N6—O2	118.2 (6)
N6—Ru—P1	88.8 (2)	O1—N6—Ru	120.3 (5)
N3—Ru—P1	91.5 (2)	O2—N6—Ru	121.5 (5)

The enclosed solvent molecule was highly disordered and ambiguous. The molecule was therefore refined isotropically as CH₃CH₂OH; H atoms on the solvent molecule were not located. The ClO₄ anion was also disordered and refined isotropically with occupancies of 0.7 and 0.3. The maximum residue had an electron density of 1.145 e Å⁻³ at 1.3 Å from the Ru atom.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: KH1147). Services for accessing these data are described at the back of the journal.

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Bis(piperidinium) Tetrachloromercurate

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Abstract

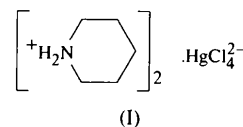
The title compound, (C₅H₁₂N)₂[HgCl₄], contains piperidinium cations and tetrachloromercurate anions, which are connected by N—H···Cl bonds *via* the Cl1, Cl2 and Cl3 atoms into a two-dimensional network in the (101) plane through the origin. The Hg—Cl bond lengths lie between 2.431 (3) and 2.515 (2) Å.

Comment

The reaction of substituted ammonium halides with metal halides leads to a series of compounds of the general formula (R_xNH_{4-x})₂MX₄, where R is an aliphatic or aromatic hydrocarbon, M is a divalent metal and X = Cl, Br or I.

These compounds show interesting structural and physical properties such as ferroelectricity, successive phase transitions and incommensurate phases, *e.g.* [N(CH₃)₄]₂[ZnCl₄] (*cf.* Mashiyama, 1980). An example of interesting physical properties is the compound [N(CH₃)₄]₂[MnCl₄], which was used by Dupas & Renard (1973) and Birgeneau, Shirane & Kitchens (1974) for studying low-dimensional magnetism.

Another point of interest is the investigation of the coordinative environment of Hg^{II} because of the closed shell and relatively large coordination distances. Coordination numbers can be three, four (tetrahedral) and five (trigonal bipyramidal); in the special case of (RNH₃)₂HgX₄, perovskite-like structures with MX₆ octahedra are found (Ben Salah, Daoud, Bats & Fuess, 1982).



The title compound, (I), contains two piperidinium cations and one tetrachloromercurate anion in the asymmetric unit (Fig. 1). The Hg atom is surrounded by four Cl atoms forming a slightly distorted tetrahedron. Three of the Cl atoms are connected to piperidinium cations by hydrogen contacts in the range from 2.27 to 2.47 Å, the Cl···N distances vary between 3.219 (4) and 3.395 (4) Å.

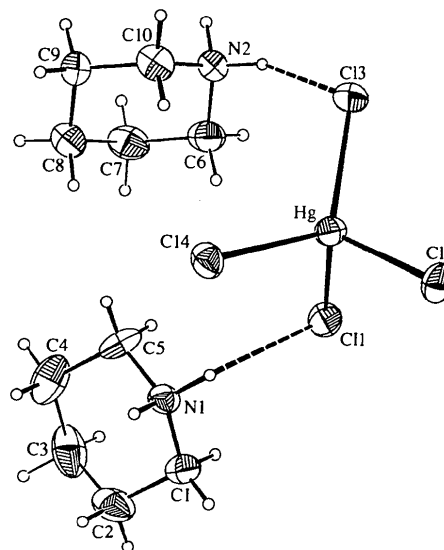


Fig. 1. Formula unit of the title compound in the crystal. Displacement ellipsoids correspond to 35% probability.

The base of the tetrahedron (Cl1, Cl2, Cl3) lies approximately in the glide plane *n*, *i.e.* ($x \frac{1}{4} y$), as do the atoms H3—N2—H4, setting up a zigzag chain in [101] direction: Cl3—Hg—Cl1—H4—N2—H3—Cl3—Hg—, and so on. The chain is augmented to a two-dimensional network close to the plane (101) by H1—N1—H2, which connects tetrahedra related by the centres of symmetry at (0 $\frac{1}{2}$ 0) and ($\frac{1}{2}$ $\frac{1}{2}$ 0), thus resulting in the translational repetition in the [010] direction (see Fig. 2 and Table 2). The hydrogen-bonding parameters are in good agreement with other experimental data (Ben