N2—C3	1.351 (3)	N10—O11	1.188 (3)
C3—C4	1.310 (4)	N10—O12	1.249 (3)
C4—N5	1.292 (4)		
N2—Cu1—N7	91.5 (1)	C8—N9—N10	116.8 (2)
N2—Cu1—O11$^{\rm i}$	90.1 (1)	O11—N10—O12	119.0 (3)
N7—Cu1—O11$^{\rm i}$	105.8 (1)	O11—N10—N9	120.6 (2)
C8—N7—Cu1	165.5 (2)	N10—O11—Cu1$^{\rm ii}$	123.9 (2)
N7—C8—N9	172.3 (3)		

Symmetry codes: (i) $x, y, z - 1$; (ii) $x, y, 1 + z$.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990) (Patterson methods). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: MU1302). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Λ-Tris(1,10-phenanthroline-*N*,*N*′)-ruthenium(II) Bis(hexafluorophosphate)–Acetonitrile–Diethyl Ether (1/1/0.5)

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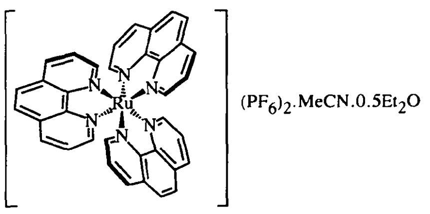
Abstract

The title compound was obtained from a solution of the resolved compound as an acetonitrile 0.5-diethyl ether solvate, $[\mathrm{Ru(C_{12}H_8N_2)_3](PF_6)_2.CH_3CN.0.5(CH_3CH_2)_2O}$. The cations possess idealized D_3 symmetry with three bidentate phenanthroline ligands arranged about each $\mathrm{Ru^{II}}$ center in a propeller-like fashion. Assignment of the appropriate polar space group corroborates the absolute configuration of the compound with chemical and circular dichroism data.

Comment

The chemistry of tris-chelated compounds of ruthenium(II) with bidentate nitrogen-donor ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy) has been studied for many years (Seddon & Seddon, 1984). Interest in these compounds continues unabated, due largely to their rich photophysical properties (Fox & Channon, 1988) and the interaction of these chiral transition metal complexes with DNA (Hiort, Lincoln & Nordén, 1993; Barton, Goldberg, Kumar & Turro, 1986). It is surprising, therefore, that while a structural report exists for $\mathrm{Ru(bpy)_3}^{2+}$ (Rillema, Jones & Levy, 1979), no analogous data have been reported for $\mathrm{Ru(phen)_3}^{2+}$, nor has the absolute configuration of one of its enantiomers been confirmed until now.

There are two molecules in the asymmetric unit of the title compound, (I). Each Ru center exists in a distorted octahedral environment, as demonstrated by the values of the 30 N—Ru—N angles, all of which would have values of either 90 or 180° in an ideal octahedral arrangement. The 12 independent Ru—N bond lengths range from 2.058 (8) to 2.082 (6) Å, with an average value of 2.067 Å. These values compare well with the average Ru—$\mathrm{N_{bpy}}$ bond length of 2.056 (6) Å in $\mathrm{Ru(bpy)_3(PF_6)_2}$ and the calculated Ru—$\mathrm{N_{phen}}$ bond length of 2.054 Å in $\mathrm{Ru(phen)_3}^{2+}$ (Lincoln, Broo & Nordén, 1996). The C—C bond lengths in the cations range from 1.33 to 1.46 Å, with an average e.s.d. of 0.01 Å. The idealized D_3 symmetry of the molecule is evidenced by the angles formed by the least-squares planes of the three ligands of each cation, which are approximately 80, 86 and 90° for those associated with Ru1, and 86, 90 and 87° for those associated with Ru2. For each cation, the ligands form a 'pitch' angle with the pseudo-threefold axis of the molecule of between 35.0 and 37.4°.



(I)

Most importantly, successful assignment of the absolute structure of this compound permits unambiguous assignment of the crystal used for this investigation

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as the Λ enantiomer. This is consistent with both the manner in which the compound was resolved (Gillard & Hill, 1974; Dwyer & Gyarfas, 1947) and its circular dichroism spectrum. For the Λ enantiomer in acetone, the wavelengths (nm) and magnitudes of peaks ($\Delta\varepsilon/M^{-1}\,cm^{-1}$) in the visible region are 466 (+22), 422 (−14). These values are consistent with its assigned stereochemistry and circular dichroism data as reported by Gillard & Hill (1974), and closely resemble data reported for aqueous solutions of its dichloride salt (Lincoln, Broo & Nordén, 1996).

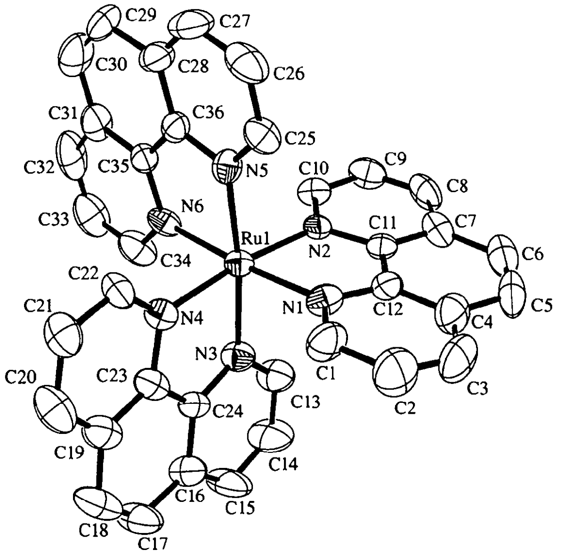

Fig. 1. The structure of one of the metal complexes in the asymmetric unit (containing Ru1) showing 50% probability ellipsoids. The cation associated with Ru2 is numbered sequentially starting from C37 in the same manner.

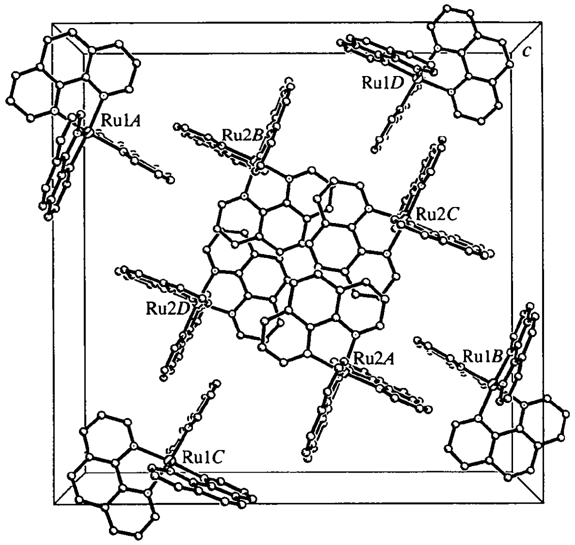

Fig. 2. Unit-cell packing diagram (cations only) viewed down the c axis.

Experimental

The synthesis of the racemic compound was effected by a modification of a previously published procedure (Burstall, 1936). Isolation of the Λ enantiomer was achieved *via* a modification of the procedure of Dwyer & Gyarfas (1947). Crystals of diffraction quality were obtained through vapor diffusion of diethyl ether into an acetonitrile solution of the Λ enantiomer. The density of a crystal of the compound was not measured due to facile loss of interstitial solvent.

Crystal data

$[Ru(C_{12}H_8N_2)_3](PF_6)_2$.-
$CH_3CN.0.5C_4H_{10}O$
$M_r = 1009.74$
Tetragonal
$P4_3$
$a = 25.372\,(1)$ Å
$c = 12.726\,(2)$ Å
$V = 8192.2\,(2)$ Å^3
$Z = 8$
$D_x = 1.637$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 59 reflections
$\theta = 5.08$–$16.48°$
$\mu = 0.558$ mm^{-1}
$T = 183\,(2)$ K
Parallelepiped
$0.50 \times 0.37 \times 0.25$ mm
Orange

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction:
ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.695$, $T_{max} = 0.774$
15 846 measured reflections
14 413 independent reflections

10 478 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25°$
$h = -30 \rightarrow 30$
$k = -30 \rightarrow 30$
$l = -15 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 6.8%

Refinement

Refinement on F^2
$R(F) = 0.063$
$wR(F^2) = 0.160$
$S = 1.04$
14 413 reflections
1124 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 6.4295P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.008$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.06 (4)

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

Ru1—N1	2.066 (6)	Ru2—N7	2.058 (8)
Ru1—N2	2.063 (7)	Ru2—N8	2.082 (6)
Ru1—N3	2.068 (6)	Ru2—N9	2.061 (6)
Ru1—N4	2.061 (8)	Ru2—N10	2.067 (8)
Ru1—N5	2.079 (6)	Ru2—N11	2.068 (6)
Ru1—N6	2.061 (6)	Ru2—N12	2.070 (6)
N1—Ru1—N2	79.8 (3)	N7—Ru2—N8	79.8 (3)
N1—Ru1—N3	87.3 (3)	N7—Ru2—N9	95.9 (3)
N1—Ru1—N4	95.8 (3)	N7—Ru2—N10	173.9 (3)
N1—Ru1—N5	97.3 (2)	N7—Ru2—N11	94.6 (3)
N1—Ru1—N6	174.7 (3)	N7—Ru2—N12	88.5 (3)
N2—Ru1—N3	94.8 (3)	N8—Ru2—N9	88.0 (3)
N2—Ru1—N4	173.1 (3)	N8—Ru2—N10	95.4 (3)
N2—Ru1—N5	90.8 (3)	N8—Ru2—N11	173.3 (3)
N2—Ru1—N6	95.6 (3)	N8—Ru2—N12	96.1 (3)

N3—Ru1—N4	79.6 (3)	N9—Ru2—N10	80.1 (3)
N3—Ru1—N5	173.4 (3)	N9—Ru2—N11	96.3 (2)
N3—Ru1—N6	95.9 (3)	N9—Ru2—N12	174.5 (3)
N4—Ru1—N6	89.0 (3)	N10—Ru2—N11	90.5 (3)
N4—Ru1—N5	95.1 (3)	N10—Ru2—N12	95.8 (3)
N5—Ru1—N6	79.9 (2)	N11—Ru2—N12	80.0 (2)

H atoms were placed at geometrically idealized coordinates for all expected locations. In the case of methyl C atoms, the torsion angle was set so as to maximize the sum of the electron density at the three calculated positions. The coordinates of all H atoms were then allowed to 'ride' on those of the attached C atoms, with isotropic displacement parameters fixed at 1.2 times (1.5 for methyl) the equivalent isotropic displacement parameters of their attached C atoms. In the final refinement cycles, the U^{ij} values of the C301 and C302 atoms (belonging to the diethyl ether solvate molecule) were constrained to be equal. Polar axis restraints were generated by the method of Flack & Schwarzenbach (1988). During the course of the cell determination, an initial tetragonal unit cell with a = 17.89 and c = 12.79 Å was obtained. Subsequent location of a sufficiently large number of strong reflections gave the larger tetragonal unit cell with a = 25.372 (1) and c = 12.726 (2) Å. Solution of the structure using the larger unit cell gave two independent molecules in the asymmetric unit in which the two cations are pseudosymmetrically related by a screw axis, as can be seen in the unit-cell packing diagram (Fig. 2). However, only 92 of 125 heavy atoms map fairly closely to their 'symmetry equivalents', indicating that no symmetry has been ignored in describing the overall structure and that the larger cell is required. Furthermore, refinement of the structure with the smaller unit cell resulted in a poorer structure with regard to both displacement parameters and the constancy of bond distances and angles. These factors were especially apparent during treatment of the anions and solvent molecules.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL/PC*. Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: BK1256). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(di-2-pyridylmethanediol-*N*,*N*′)-palladium(II) Dichloride Tetrahydrate and Dichloro(di-2-pyridylmethanediol-*N*,*N*′)-gold(III) Chloride

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Abstract

Structural analyses of $[Pd(C_{11}H_{10}N_2O_2)_2]Cl_2.4H_2O$, (I), and $[Au(C_{11}H_{10}N_2O_2)Cl_2]Cl$, (II), revealed that both metals are in square-planar coordination environments. The Pd atom in (I) is coordinated equatorially by four N-atom donors and has two long-range Pd···O interactions which lead to approximate pseudo-octahedral geometry. The Au complex achieves a coordination number of four with two N and two Cl donors, however, a weak long-range intramolecular axial interaction accounts for the fifth coordination site to make the species pseudo-square pyramidal.