$a = 21.331\,(4)$ Å
$b = 12.203\,(2)$ Å
$c = 20.881\,(4)$ Å
$\beta = 92.26\,(3)°$
$V = 5431.1\,(17)$ Å^3
$Z = 4$
$D_x = 1.625$ Mg m^{-3}
D_m not measured

$\mu = 1.509$ mm^{-1}
$T = 293\,(2)$ K
Cube
$0.4 \times 0.4 \times 0.3$ mm
Colorless

Data collection

Enraf–Nonius CAD-4
  diffractometer
ω–2θ scans
Absorption correction:
  empirical ψ scan (North
  et al., 1968)
$T_{min} = 0.485$, $T_{max} = 0.636$
5459 measured reflections
5312 independent reflections

4121 reflections with
  $I > 2\sigma(I)$
$R_{int} = 0.043$
$\theta_{max} = 25.99°$
$h = 0 \rightarrow 26$
$k = -15 \rightarrow 0$
$l = -25 \rightarrow 25$
2 standard reflections
  frequency: 60 min
  intensity decay: 2.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.107$
$S = 1.046$
5312 reflections
325 parameters
H atoms treated by a
  mixture of independent
  and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0582P)^2$
  $+ 9.4283P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.982$ e Å^{-3}
$\Delta\rho_{min} = -0.596$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

Refinement of the crystal structure in the non-centrosymmetric space group Cc did not lead to reasonable results, and in accordance with the $C2$ (twofold axis) molecular symmetry, the centrosymmetric setting $C2/c$ was therefore considered correct. Data reduction and decay correction used CADFOR/CADSEX (Keller, 1993).

Data collection: TURBOMOLE in CAD-4 EXPRESS (Enraf–Nonius, 1993). Cell refinement: TURBOMOLE in CAD-4 EXPRESS. Data reduction: CADFOR/CADSEX. Program(s) used to solve structure: SHELX97 (Sheldrick, 1997). Program(s) used to refine structure: SHELX97. Molecular graphics: SCHAKAL (Keller, 1995). Software used to prepare material for publication: CIFTAB in SHELX97.

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Bis(terpyridine)ruthenium(II) bis(hexafluorophosphate) diacetonitrile solvate

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Abstract

The crystal structure of the title compound, bis(2,2':-6',2''-terpyridine)ruthenium(II) bis(hexafluorophosphate) diacetonitrile solvate, with the composition $[Ru(C_{15}H_{11}-N_3)_2](PF_6)_2 \cdot 2C_2H_3N$ is described. The pseudo–octahedral Ru complex has a C_{2v} point symmetry, imposed by the geometry constraints of the two identical tridentate ligands. The tetragonal unit cell, with its remarkably long c axis [49.306(3) Å], contains two symmetry-independent formula units.

Comment

The coordination compounds formed by ruthenium(II) with polypyridine ligands such as 2,2'-bipyridine (bpy) or 2,2':6',2''-terpyridine (terpy) are among the most commonly used photoactive substances in artificial photosynthesis and photoinduced electron-transfer studies (Kalayanasundaram, 1992; Roundhill, 1994). Recent attempts to utilize Ru complexes of this type as photosensitizers in different applications, such as Grätzel-type solar-cell devices, have been successful in many aspects (Zakeeruddin et al., 1997). Ru–polypyridine complexes can also act as photoactive synthons in nanometer-sized

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supramolecular units (Balzani *et al.*, 1998, and references therein).

At room temperature, the [Ru(terpy)$_2$]$^{2+}$-type complexes usually show a weaker degree of luminescence than the [Ru(bpy)$_3$]$^{2+}$-type complexes (Norrby *et al.*, 1997), which have been intensively studied for their photochemical properties in recent decades (Juris *et al.*, 1988). Nevertheless, the geometrical properties of [Ru(terpy)$_2$]$^{2+}$-type complexes (Maestri *et al.*, 1995) have some advantages compared with [Ru(bpy)$_3$]$^{2+}$-type complexes that make them relevant in ruthenium supramolecular photochemistry and related fields. The molecular symmetry of [Ru(terpy)$_2$]$^{2+}$ complexes gives rise to the possibility of synthesizing highly symmetrical arrangements of bridged bis(terpy) complexes, *e.g.* by linking the 4' positions of the terpy ligands on adjacent complexes (Constable *et al.*, 1998).

This paper presents the first known structural report on the simplest [Ru(terpy)$_2$]$^{2+}$ complex, (I), which consists of an Ru^{II} ion and two unsubstituted terpy ligands (Fig. 1). Several structural studies

(I)
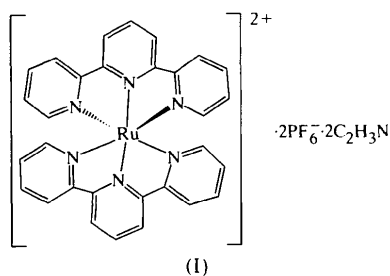
have been performed on 4'-substituted [Ru(terpy)$_2$]$^{2+}$ complexes (Constable *et al.*, 1992; Whittle *et al.*, 1996). The present study of the unsubstituted terpy complex enables a detailed study of the effects of 4'-substitution on the conformation of [Ru(terpy)$_2$]$^{2+}$ complexes. The molecular geometry of the present compound has been compared with the geometries of three previous investigations of 4'-substituted [Ru(terpy)$_2$]$^{2+}$-type complexes stored in the Cambridge Structural Database (Allen & Kennard, 1993), namely, bis[4'-(*N*,*N*-dimethylamino)-2,2':6',2''-terpyridine]ruthenium(II) bis(hexafluorophosphate) (reference code PATFIZ) by Constable *et al.* (1992), and [μ$_2$-1,4,-10,13-tetraoxa-7-(terpyridine-4'-yl)-7,16-diazacyclooctadecane](2,2':6',2''-terpyridine)bis(tetrafluoroborato-*F*)-ruthenium(II)sodium hexafluorophosphate (RADMUE) and {μ$_2$-1,4,10,13-tetraoxa-7,16-bis[4'-(4-methylene)-phenylterpyridine]-7,16-diazacyclooctadecane}bis(2,2':-6',2''-terpyridine)diruthenium(II) hexafluorophosphate (RADNAL) by Whittle *et al.* (1996).

As expected, the 4'-substitution will distort the geometry of the central pyridine ring, following the general patterns of effects of aromatic substitution (Domenicano & Murray-Rust, 1979; Norrestam & Schepper, 1978,
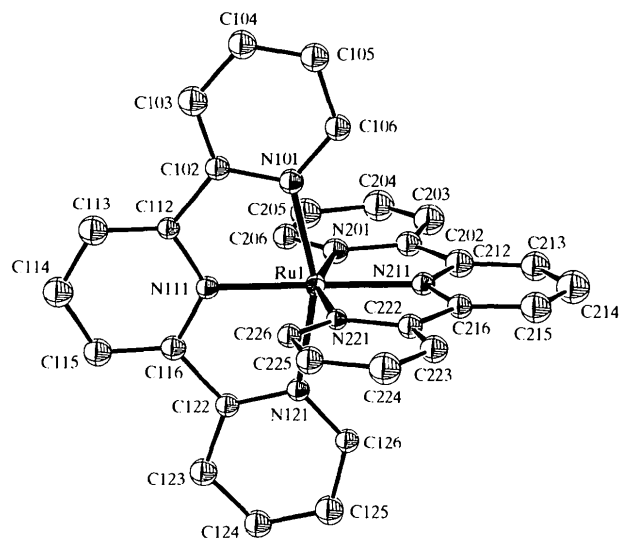
Fig. 1. One of the [Ru(terpy)$_2$]$^{2+}$ molecules in the asymmetric unit. The last number in the atomic labels specifies the position of each atom in its aromatic ring and the first two numbers specify to which ring the atom belongs. The ligand atoms around the second Ru atom, Ru2, are labeled in analogy to those of Ru1 by simply adding 200 to the numbers in the figure above. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms, hexafluorophosphate anions and acetonitrile solvent molecules have been omitted.

1981). Thus, the largest effect is observed for the endocyclic C—C—C angles at the 4'-position, while the planarity of the ring is preserved within 0.03 Å. The average endocyclic angle, which is 117.7 (7)° in the substituted terpy ligands of the PATFIZ, RADMUE and RADNAL structures, is increased to 120.9 (9)° in the present study.

The effects of aromatic substitution on endocyclic bond distances are expected to be small (Norrestam & Schepper, 1981) and no statistically relevant effects could be observed in the present case. The effects on the bite gap (~4.06 Å), as reflected by the distance between the N atoms of the outer rings, and the effects on the Ru—N bond lengths (about 1.97–2.00 Å to the N atom of the central ring and 2.06–2.08 Å to those of the outer rings) are negligible.

The [Ru(terpy)$_2$]$^{2+}$ cation and the hexafluorophosphate anions form alternating layers along the long *c* axis [49.306 (3) Å]. The acetonitrile solvent molecules are located in the voids formed between adjacent layers. The layers are held together by several short interactions between F atoms of the anions and the aromatic H atoms of the terpy ligands of the cations. The weak forces to the solvent molecules are consistent with the low stability of the crystals under ambient conditions.

Experimental

Detailed descriptions of the synthetic procedure, electro- and photochemical measurements, and NMR and UV/VIS

spectroscopic measurements are reported elsewhere (Norrby et al., 1997). Crystals suitable for single-crystal X-ray diffraction measurements were obtained through recrystallization by slow diffusion of diethyl ether into a moderately concentrated acetonitrile solution of [Ru(terpy)$_2$](PF$_6$)$_2$. These crystals are extremely unstable in air at room temperature due to evaporation of the acetonitrile solvent which stabilizes the crystal packing. After rapid mounting of a selected crystal with grease on top of a glass rod, it was placed under a nitrogen cryostream (100 K) and reflection data could be collected without noticeable change in the diffracting power of the crystal. Due to the pronounced crystal instability, the whole procedure from mounting to placing the crystal into the cryostream has to be completed within 25 s.

Crystal data

[Ru(C$_{15}$H$_{11}$N$_3$)$_2$](PF$_6$)$_2$·2C$_2$H$_3$N	Mo $K\alpha$ radiation
M_r = 939.65	λ = 0.71073 Å
Tetragonal	Cell parameters from 5000
$P4_1$	reflections
a = 12.3698 (5) Å	θ = 1.65–20.91°
c = 49.306 (3) Å	μ = 0.598 mm^{-1}
V = 7544.5 (6) Å^3	T = 100 (2) K
Z = 8	Thin plate
D_x = 1.655 Mg m^{-3}	0.45 × 0.22 × 0.05 mm
D_m not measured	Red

Data collection

Stoe IPDS diffractometer	7363 reflections with
Stoe IPDS image-plate scans	$I > 2\sigma(I)$
Absorption correction:	R_{int} = 0.092
numerical (*X-RED*; Stoe	θ_{max} = 20.91°
& Cie, 1995)	h = −12 → 12
T_{min} = 0.810, T_{max} = 0.930	k = −12 → 12
33 324 measured reflections	l = −49 → 49
7952 independent reflections	Intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.002
$R(F)$ = 0.054	$\Delta\rho_{max}$ = 0.944 e Å^{-3}
$wR(F^2)$ = 0.148	$\Delta\rho_{min}$ = −1.056 e Å^{-3}
S = 1.064	Extinction correction: none
7952 reflections	Scattering factors from
580 parameters	*International Tables for*
H atoms: see below	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.1072P)^2$	
$+ 7.9616P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

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

Ru1—N211	1.974 (7)	Ru2—N311	1.983 (7)
Ru1—N111	1.981 (7)	Ru2—N411	2.001 (7)
Ru1—N201	2.065 (7)	Ru2—N301	2.059 (6)
Ru1—N221	2.065 (6)	Ru2—N401	2.066 (6)
Ru1—N101	2.067 (7)	Ru2—N421	2.066 (7)
Ru1—N121	2.076 (6)	Ru2—N321	2.069 (6)
N211—Ru1—N111	178.8 (3)	N311—Ru2—N411	177.8 (3)
N201—Ru1—N221	159.1 (2)	N401—Ru2—N421	158.3 (3)
N101—Ru1—N121	158.4 (3)	N301—Ru2—N321	157.7 (3)

The crystal structure of the title compound was refined as a racemic twin. However, the absolute structure of the

compound cannot be unambiguously determined. Refining the structure in the selected space group gives a value of 0.42 (4) for the Flack parameter (Flack, 1983). A detailed examination of the distribution of the normalized E values and the distribution of the Ru atoms in the crystal structure offers an explanation for the failure to determine the absolute structure. Despite the non-centrosymmetric space-group symmetry, the statistics of the E values indicate a tendency towards a centrosymmetrical distribution of the electron density. By examination of the layered packing of the Ru atoms along [001] in the structure, the presence of pseudo-inversion centers within about 1 Å from $x = y = 0$ is noticed (Fig. 2).
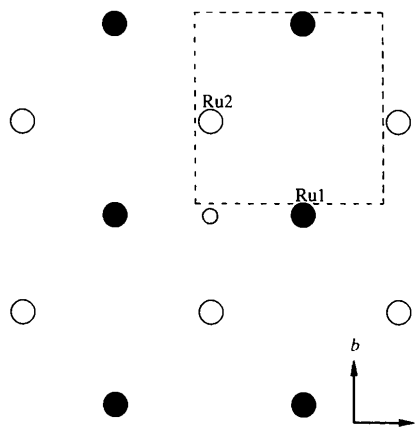

Fig. 2. A drawing of the section at $z \simeq -0.07$ showing the pseudo-inversion symmetry (at $x = 0.079$ and $y = -0.067$) when considering only the Ru atoms. The dashed lines represent the unit cell and the unfilled circle represents the pseudo-inversion center.

With Mo $K\alpha$ X-ray radiation, it is mainly the Ru atoms which will act as anomalous scatterers. Due to the presence of pseudo-inversion centers, the anomalous dispersion contribution to the structure factors will become very small, *i.e.* $F(hkl) \simeq F(\bar{h}\bar{k}\bar{l})$. Hence, there will be a lack of necessary information in the reflection data to determine the absolute configuration using Mo $K\alpha$ radiation. On the other hand, this will ensure that the anomalous-dispersion effects on the relative structural parameters obtained in the present study are negligible. Due to experimental limitations, the data collection could not be performed with radiation of a wavelength that would permit an unambiguous determination of the absolute configuration.

Two of the four octahedral hexafluorophosphate anions (P2 and P3) in the asymmetric unit were axially disordered. The disordered F atoms were refined with site-occupation factors fixed to 0.5. The four acetonitrile solvent molecules located in the asymmetric unit were also slightly disordered. No H atoms were located for the methyl group of these molecules. All H atoms were placed in calculated positions (C—H 0.95 Å) and were refined by applying the same shift to their coordinates as the shift of the parent C atoms. The displacement parameters for the H atoms were fixed to a value 1.3 times higher than the displacement parameters of the parent C atoms.

Due to the remarkably long c axis of the unit cell, a very large crystal-to-detector distance (100 mm) had to be used, in order to obtain enough separation between adjacent diffraction

spots. With an image-plate detector of diameter 180 mm, only reflections with $\theta < 20.9°$ could be observed.

Data collection: *EXPOSE* in *Stoe IPDS* (Stoe & Cie, 1997). Cell refinement: *SELECT* in *Stoe IPDS*. Data reduction: *INTEGRATE* in *Stoe IPDS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *PLATON98* (Spek, 1990) and *ATOMS* (Dowty, 1997). Software used to prepare material for publication: *PLATON98*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1037). Services for accessing these data are described at the back of the journal.

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trans-Carbonylchlorobis(tri-p-tolyl-phosphine)rhodium(I)

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Abstract

The crystal structure of the square-planar title compound, $[RhCl(C_{21}H_{21}P)_2(CO)]$, describes another of the Vaska-type complexes. It is isomorphous with selected Ir^I and even Pt^{II} structures. Important bond lengths include Rh—P1 2.3344 (11), Rh—P2 2.3305 (11), Rh—Cl 2.3581 (12), Rh—Cl 1.798 (5) and Cl—O1 1.139 (6) Å.

Comment

The original Vaska complex, $[Ir(CO)(Cl)(PPh_3)_2]$, was first reported in 1959 (Angoletta, 1959), but was later correctly formulated by Vaska in 1961 (Vaska & Di Luzio, 1961). Complexes of this type have since been established as catalysts in a variety of processes and have been extensively studied within this context (Douek & Wilkinson, 1969; Vastag *et al.*, 1979; Rankin *et al.*, 1997).

In this paper, we report the rhodium analogue, (I), with tri-p-tolylphosphine as another complex in this range. The compound is one of the few crystallographic examples of these complexes which does not show disorder along the carbonyl/chloro axis. A further interesting feature is the P—Rh—P bond angle of 175.67 (4)°, which is significantly smaller than 180°.

(I)
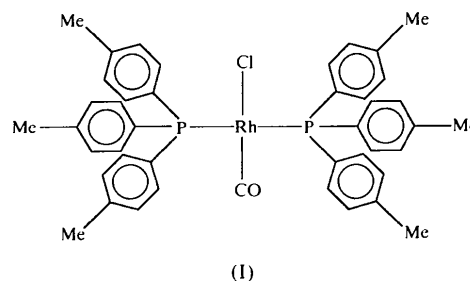
The rhodium Vaska analogue, $[Rh(CO)(Cl)(PPh_3)_2]$, is only slightly soluble in solvents such as acetone, but by incorporating the p-CH$_3$ substituents on the phenyl rings, this problem was overcome, enabling a wider range of solution studies (Table 2).