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cis-Dichlorobis(di-2-pyridylamine)iridium(III) hexafluorophosphate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.012 Å
R factor = 0.056
wR factor = 0.128
Data-to-parameter ratio = 18.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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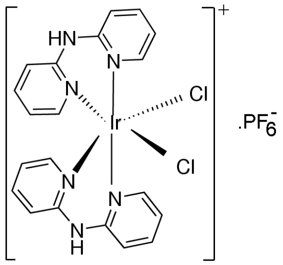
The crystal structure of the title compound, $[IrCl_2(C_{10}H_9N_3)_2]PF_6$, contains a monomeric $[IrCl_2(bpya)_2]^+$ cation (bpya is di-2-pyridylamine) and a hexafluorophosphate anion. The iridium(III) ion is coordinated by four N atoms from two bpya ligands [mean Ir—N distance = 2.049 (6) Å] and two Cl atoms [Ir—Cl = 2.344 (2) Å], forming a distorted octahedral environment.

Comment

Generally, iridium is regarded as a catalytic metal or as a useful metal center for reactivity. In particular, some of its complexes display promising photochemical properties. However, Ir^{III} is characterized by the great inertness of its coordination sphere, requiring harsh reaction conditions to substitute the chlorine ligands of$(NH_4)_3[IrCl_6]$. DeSimone & Drago (1969) reported the preparation of $[IrCl_2(bpy)_2]Cl$ by fusing K_3IrCl_6 at 543 K for 15 min. Yoshikawa *et al.* (2003) reported the preparation of $[IrCl_2(dmbpy)_2]PF_6$ using a microwave oven for 15 min (dmbpy is 4,4′-dimethyl-2,2′-bipyridine). However, no single-crystal structure of an iridium complex with the di-2-pyridylamine ligand has been reported previously. In this study, we have prepared and investigated the title iridium bis-dipyridylamine complex, (I).



(I)

The crystal structure of (I) consists of a discrete $[IrCl_2(bpya)_2]^+$ cation and a hexafluorophosphate anion. As illustrated in Fig. 1, the Ir^{III} atom is located in a distorted octahedral environment involving two bpya ligands and two chloride anions. The Ir—N bond lengths are in the range 2.034 (5)–2.059 (7) Å. The three *trans* angles are in the range 176.9 (2)–178.2 (2)°. Ir is coordinated by four N atoms from a pair of *cis*-related chelating bpya ligands and two Cl atoms [Ir—Cl1 = 2.337 (2) Å and Ir—Cl2 = 2.351 (2) Å]. The equatorial plane is formed by atoms Cl2/N1/N3/N4, with the largest deviation from the mean plane being 0.023 (2) Å. The axial positions are occupied by the fourth bpya N atom and another Cl atom. Each bpya ligand is planar and the maximum deviation from the mean planes is 0.335 Å. The two Cl ligands

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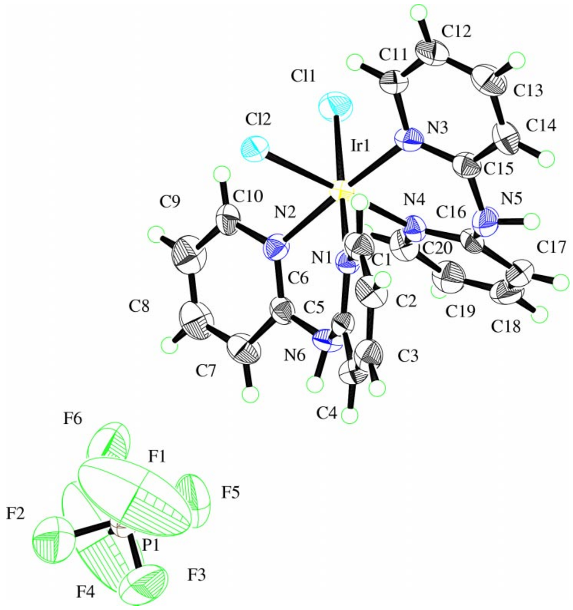

Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

are coordinated in a *cis* fashion, but $\mathrm{PF_6}^-$is not coordinated to the Ir atom. The average length of the Ir—N bonds [2.049 (6) Å] and the average of the N1—Ir—N2 and N3—Ir—N4 bite angles [87.7 (2)°] are larger than the values published for $[\mathrm{IrCl_2(dmbpy)_2}]\mathrm{PF_6}$ (Yoshikawa *et al.*, 2003), *viz*. 2.026 Å and 79.1°, respectively.

Experimental

The title complex, (I), was prepared by the ligand-replacement procedure. $\mathrm{(NH_4)_3[IrCl_6]\cdot H_2O}$ (0.5 mmol) and di-2-pyridylamine (1.0 mmol) were mixed in ethylene glycol (15 ml). The suspended mixture was refluxed for 15 min in a microwave oven under a purging nitrogen atmosphere. The mixture was cooled to room temperature. A saturated aqueous solution of $\mathrm{KPF_6}$ (20 ml) was added and a yellow product began to precipitate and was collected by vacuum filtration. The residue was dissolved in a minimum amount of acetone and flash precipitated in diethyl ether. The product was separated by vacuum filtration and dried under vacuum. Yellow single crystals were obtained by recrystallization from acetonitrile.

Crystal data

$[\mathrm{IrCl_2(C_{10}H_9N_3)_2}]\mathrm{PF_6}$
$M_r = 750.49$
Triclinic, $P\overline{1}$
$a = 7.6920$ (8) Å
$b = 12.940$ (1) Å
$c = 13.229$ (1) Å
$\alpha = 68.958$ (3)°
$\beta = 75.775$ (4)°
$\gamma = 79.760$ (6)°
$V = 1185.4$ (2) Å^3
$Z = 2$
$D_x = 2.102$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7910 reflections
$\theta = 2.0$–30.5°
$\mu = 6.01$ mm^{-1}
$T = 296.2$ K
Needle, yellow
0.20 × 0.10 × 0.08 mm

Data collection

Rigaku R-AXIS RAPID imaging-plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.220$, $T_{\max} = 0.618$
14 053 measured reflections
7054 independent reflections
6111 reflections with $I > 2.0\sigma(I)$
$R_{\mathrm{int}} = 0.066$
$\theta_{\max} = 30.5°$
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.128$
$S = 1.72$
7054 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 3.70$ e Å^{-3}
$\Delta\rho_{\min} = -1.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir1—Cl1	2.337 (2)	Ir1—N2	2.059 (7)
Ir1—Cl2	2.351 (2)	Ir1—N3	2.049 (7)
Ir1—N1	2.055 (5)	Ir1—N4	2.034 (5)
Cl1—Ir1—Cl2	91.09 (6)	Cl2—Ir1—N4	178.2 (2)
Cl1—Ir1—N1	177.5 (2)	N1—Ir1—N2	87.7 (2)
Cl1—Ir1—N2	94.4 (2)	N1—Ir1—N3	89.7 (2)
Cl1—Ir1—N3	88.3 (2)	N1—Ir1—N4	92.6 (2)
Cl1—Ir1—N4	88.7 (1)	N2—Ir1—N3	176.9 (2)
Cl2—Ir1—N1	87.7 (1)	N2—Ir1—N4	90.7 (2)
Cl2—Ir1—N2	87.5 (1)	N3—Ir1—N4	87.7 (2)
Cl2—Ir1—N3	94.1 (2)		

All H atoms bonded to carbon and nitrogen were placed at calculated positions (C—H and N—H = 0.95–0.97 Å) and fixed in position. The maximum and minimum electron-density peaks are 0.81 Å from Ir1 and 1.12 Å from N1, respectively.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation and Rigaku, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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