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cis-Dichlorobis(4,4′-dimethyl-2,2′-bipyridine)-iridium(III) hexafluorophosphate

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The crystal structure of the title compound, $[IrCl_2(C_{24}H_{24}N_4)_2]PF_6$, contains a monomeric $[IrCl_2(dmbpy)_2]^+$ cation (dmbpy is 4,4′-dimethyl-2,2′-bipyridine) and a hexafluorophosphate anion. The iridium(III) ion is coordinated by four N atoms from two dmbpy ligands [mean Ir—N distance = 2.052 (5) Å] and two Cl atoms [Ir—Cl = 2.360 (9) and 2.356 (2) Å], forming a distorted octahedral environment. Each 4,4′-dimethyl-2,2′-bipyridine ligand is planar, the mean deviations from the least-squares planes being 0.035 (4) and 0.013 (3) Å.

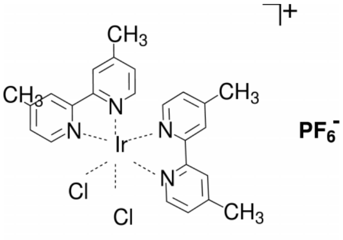
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.009 Å
R factor = 0.053
wR factor = 0.126
Data-to-parameter ratio = 18.3

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

Comment

Polypyridine complexes of transition metals, particularly of iridium, have received much interest on account of their intense emission properties. These iridium complexes exhibit a very intense emission at around 532 nm, originating from a ^{3}LC (ligand-centered charge transfer) state in acetonitrile solution, even at room temperature. Recent research in this area has been focused on trials to replace bipyridine ligands with other polypyridine ligands. However, the synthetic difficulties precluded further work along these lines. To our knowledge, no structure of an iridium complex with the 4,4′-dimethyl-2,2′-bipyridine ligand (dmbpy) has been reported previously.



(I)

In this paper, we report the synthesis and crystal structure of a mononuclear iridium compound, *viz*. $[IrCl_2(dmbpy)_2]PF_6$, (I), whose crystal structure consists of a discrete $[IrCl_2(dmbpy)_2]^+$ cation and a hexafluorophosphate anion. As illustrated in Fig. 1, the Ir^{III} atom is located in a distorted octahedral environment formed by two dmbpy ligands and two chloride anions. The Ir—N bond lengths are in the range 2.015 (5)–2.131 (5) Å. Three *trans* angles are in the range 175.1 (2)–175.9 (3) Å. Ir is coordinated by four N atoms from a pair of *cis*-related chelating dmbpy ligands and two Cl atoms [Ir—Cl1 2.360 (9) Å and Ir—Cl2 2.356 (2) Å]. An equatorial plane is formed by atoms Cl1, N1, N2 and N4, with the largest deviation from the mean plane being 0.035 (4) Å and the Ir atom being 0.013 (3) Å out of this plane. The axial positions are occupied by the fourth dmbpy N atom and another Cl atom. Atom Cl1 has particularly high anisotropic displace-

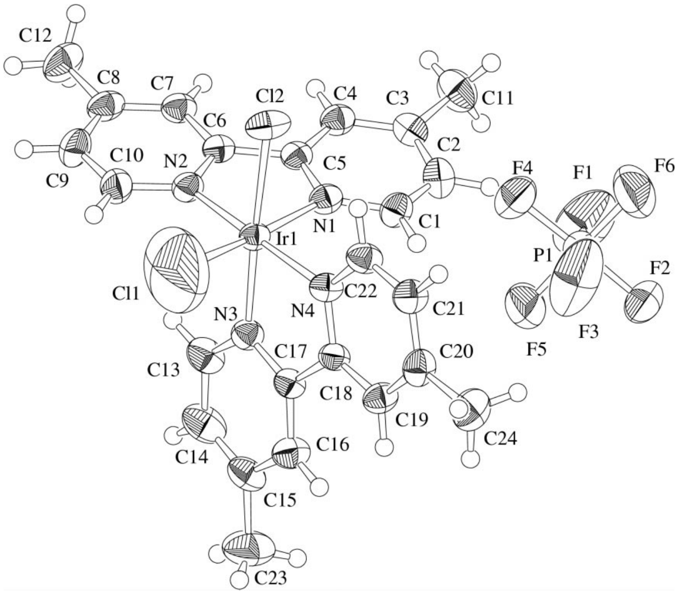


Figure 1
The molecular structure of (I), showing ellipsoids at the 50% probability level.

ment coefficients, probably indicative of some disorder. Each dmbpy ligand is planar, the mean deviation from the least-squares planes being 0.024 (6) Å. The dihedral angle between dmbpy planes is 79.7 (1) Å. The two Cl ligands are coordinated in a *cis* fashion, but PF_6^- is not coordinated to the iridium metal atom. The average length of the Ir—N bonds is 2.052 (5) Å and the average of the N1—Ir—N2 and N3—Ir—N4 ligand angles is 78.9 (2)°, which compare well with the values published for $Ir(bpy)_3(ClO_4)_3$ (bpy = 2,2′-bipyridine; Hazell & Grønbaek Hazell, 1984) of 2.026 Å and 79.1°. No hydrogen-bond interactions exist in the crystal structure.

Experimental

The precursor $(NH_4)_3[IrCl_6]H_2O$ and two equivalents of 4,4′-dimethyl-2,2′-bipyridine were suspended in ethylene glycol. Under a purging nitrogen atmosphere, the suspension was subjected to reflux for 15 min under microwave irradiation with a frequency of 2450 MHz to activate the OH group of ethylene glycol, and then cooled to room temperature. A saturated aqueous solution of KPF_6 was added to the brown solution. Air-stable yellow single crystals were obtained by recrystallization from acetonitrile (Yoshikawa *et al.*, 2000).

Crystal data

$[IrCl_2(C_{24}H_{24}N_4)_2]PF_6$
$M_r = 776.57$
Monoclinic, $P2_1/n$
$a = 7.8114$ (2) Å
$b = 21.6075$ (7) Å
$c = 16.6606$ (5) Å
$\beta = 91.4634$ (7)°
$V = 2811.1$ (1) Å^3
$Z = 4$
$D_x = 1.835$ Mg m^{-3}
Mo Kα radiation
Cell parameters from 25815 reflections
$\theta = 1.5$–30.5°
$\mu = 5.07$ mm^{-1}
$T = 296.2$ K
Platelet, yellow
0.80 × 0.10 × 0.02 mm

Data collection

Rigaku RAXIS-RAPID imaging plate diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.552$, $T_{max} = 0.904$
32401 measured reflections
8462 independent reflections
6274 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 30.5°$
$h = -9 \rightarrow 11$
$k = -30 \rightarrow 30$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.126$
$S = 1.41$
6274 reflections
343 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.003$
$\Delta\rho_{max} = 2.81$ e Å^{-3}
$\Delta\rho_{min} = -2.53$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir1—Cl1	2.360 (9)	Ir1—N2	2.036 (5)
Ir1—Cl2	2.356 (2)	Ir1—N3	2.015 (5)
Ir1—N1	2.131 (5)	Ir1—N4	2.024 (4)
Cl1—Ir1—Cl2	89.5 (2)	Cl2—Ir1—N4	96.2 (1)
Cl1—Ir1—N1	175.9 (3)	N1—Ir1—N2	78.1 (2)
Cl1—Ir1—N2	101.7 (3)	N1—Ir1—N3	94.8 (2)
Cl1—Ir1—N3	89.3 (3)	N1—Ir1—N4	97.7 (2)
Cl1—Ir1—N4	82.6 (3)	N2—Ir1—N3	98.1 (2)
Cl2—Ir1—N1	86.4 (1)	N2—Ir1—N4	175.1 (2)
Cl2—Ir1—N2	86.1 (1)	N3—Ir1—N4	79.6 (2)
Cl2—Ir1—N3	175.8 (1)		

All H atoms bonded to C atoms were placed at calculated positions, with isotropic displacement parameters. The maximum and minimum electron-density peaks are 0.24 and 0.47 Å, respectively, from atom Cl1.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); 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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