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(4,4′-Dimethyl-2,2′-bipyridine)chloro-(2,2′:6′,2″-terpyridine)-iridium(III) hexafluorophosphate

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.014 Å
R factor = 0.071
wR factor = 0.156
Data-to-parameter ratio = 16.3

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

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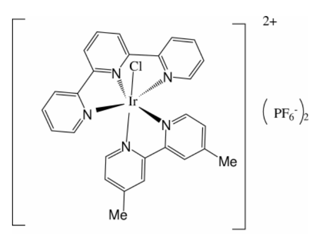
In the title compound, $[IrCl(C_{12}H_{12}N_2)(C_{15}H_{11}N_3)](PF_6)_2$, the ligand environment about the Ir atom is distorted octahedral. The 2,2′:6′,2″-terpyridine (terpy) ligand is coordinated in a meridional fashion, the 4,4′-dimethyl-2,2′-bipyridine (dmbpy) ligand coordinated in a *cis* fashion and the Cl atom is *trans* to one of the dmbpy N atoms. Ir—N bond distances are 1.971 (5)–2.065 (6) Å and the Ir—Cl distance is 2.357 (2) Å.

Comment

Extensive studies of the photophysics of octahedral [4d^6] and [5d^6] complexes have attracted a lot of attention with regard to their photochemical applications, on account of their long-lived excited states and good photoluminescence efficiencies (Volgler & Brewer, 1996). The studies have been focused mainly on the photophysical properties of octahedral diimine Ru^{III} and Os^{III} complexes with ligands such as 2,2′-bipyridine or 1,10-phenanthroline. Recently, a number of groups involving tris-chelate complexes of Rh and Ir with diimine and cyclometalated ligands have been investigated. Tris-chelate complexes of Rh and Ir show excited-state lifetimes in the microsecond region. The Ir complexes have intensive phosphorescence states at room temperature, while the Rh complexes give measurable emission states only at low temperatures. The stronger spin–orbit coupling mixes singlet and triplet excited states for Ir, leading to efficient phosphorescence (Yoshikawa & Matsumura-Inoue, 2003). From a structural point of view, the terpyridine ligand is superior to the bidentate one. However, along with this structural advantage, terpyridine complexes have the serious drawback of a relatively short-lived ^{3}MLCT with weak emitters. For the design of Ir^{III} terpyridine complexes with intense emission, we aimed to obtain monoterpyridine complexes using the ancillary ligands. As a first step toward this goal, we tried to synthesize several Ir^{III} complexes with matrixes of a terpyridine ligand and a polypyridine ligand because these ligands, with both electron-donor and/or electron-acceptor substituents, resulted in a decrease of the energy of the ^{3}MLCT state. In this paper, the structure of the title compound, (I), is reported.



(I)

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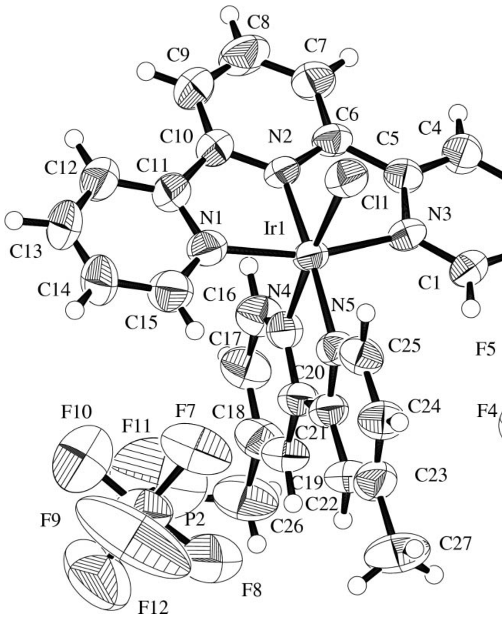

Figure 1
Molecular structure of (I), showing 50% probability displacement ellipsoids.

The ligand environment about the Ir atom is distorted octahedral; the terpy ligand is coordinated in a meridional fashion, the dmbpy ligand is coordinated in a *cis* fashion and the Cl atom is *trans* to one of the dmbpy N atoms (Fig. 1). The largest distortion of the octahedral geometry is due to the geometrical constraints of the terpy ligand, which exhibits small N—Ir—N chelate angles [80.5 (3)° and 81.2 (2)°] and an Ir—N distance for the central pyridyl ring fragment of 1.971 (5) Å, shorter than those for the outer two (Table 1). These values are in good agreement with those for other Ir^{III} and Ru^{II} complexes with the terpy ligand (Spek *et al.*, 1994; Collin *et al.*, 1999). The Ir—N distances of 2.057 (7)–2.065 (6) Å for the dmbpy ligand and 2.036 (8)–2.062 (7) Å for the two terminal terpy ring fragments are in the range found for other Ru^{II} complexes with polypirdyl ligands (Spek *et al.*, 1994; Mosher *et al.*, 2001). The two Ir—N (dmbpy) bond lengths are not significantly different, although N5 is *trans* to the sterically hindered atom N2, and N4 is *trans* to the chloride ion. Similarly, no *trans* influence associated with the opposite N atom of the terpy ligand has been observed in other mixed-ligand complexes involving terpy and Ru^{II} (Spek *et al.*, 1994).

Experimental

The complex was prepared by a sequential procedure involving ligand replacement. $(NH_4)_3[IrCl_6]$ (0.5 mmol) and 2,2′:6′,2″-terpyridine (0.5 mmol) were mixed in ethylene glycol (15 ml). The suspended mixture was refluxed for 5 min in a microwave oven under a purging nitrogen atmosphere. 4,4′-Dimethyl-2,2′-bipyridine (0.5 mmol) was added to the refluxing brown solution for 10 min. The mixture was then cooled to room temperature. A saturated aqueous solution of KPF_6 (20 ml) was added to provide a counter ion, and a yellow product began to precipitate; this was collected by vacuum filtration. Yellow single crystals were obtained by recrystallization from acetonitrile and water.

Crystal data

$[IrCl(C_{12}H_{12}N_2)(C_{15}H_{11}N_3)](PF_6)_2$	$Z = 2$
$M_r = 935.11$	$D_x = 1.634$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 10.9819 (1)$ Å	Cell parameters from 16650 reflections
$b = 13.5905 (2)$ Å	$\theta = 2.0–30.5°$
$c = 14.0636 (3)$ Å	$\mu = 3.76$ mm^{-1}
$\alpha = 77.320 (3)°$	$T = 296.2$ K
$\beta = 79.481 (3)°$	Prism, yellow
$\gamma = 69.137 (1)°$	0.30 × 0.15 × 0.10 mm
$V = 1900.96 (6)$ Å^3	

Data collection

Rigaku RAXIS-RAPID Imaging Plate diffractometer	11117 independent reflections
ω scans	7417 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)	$R_{int} = 0.069$
$T_{min} = 0.513$, $T_{max} = 0.687$	$\theta_{max} = 30.5°$
21482 measured reflections	$h = -15 \rightarrow 15$
	$k = -19 \rightarrow 19$
	$l = -20 \rightarrow 19$

Refinement

Refinement on F^2	Only H-atom U's refined
$R[F^2 > 2\sigma(F^2)] = 0.071$	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.156$	$(\Delta/\sigma)_{max} = 0.024$
$S = 1.50$	$\Delta\rho_{max} = 2.17$ e Å^{-3}
7417 reflections	$\Delta\rho_{min} = -1.06$ e Å^{-3}
456 parameters	

Table 1
Selected geometric parameters (Å, °).

Ir1—Cl1	2.357 (2)	Ir1—N3	2.062 (7)
Ir1—N1	2.036 (8)	Ir1—N4	2.057 (7)
Ir1—N2	1.971 (5)	Ir1—N5	2.065 (6)
Cl1—Ir1—N1	90.9 (2)	N1—Ir1—N5	98.1 (3)
Cl1—Ir1—N2	88.8 (2)	N2—Ir1—N3	81.2 (2)
Cl1—Ir1—N3	87.9 (2)	N2—Ir1—N4	95.8 (2)
Cl1—Ir1—N4	175.2 (2)	N2—Ir1—N5	175.2 (3)
Cl1—Ir1—N5	95.8 (2)	N3—Ir1—N4	91.4 (3)
N1—Ir1—N2	80.5 (3)	N3—Ir1—N5	100.3 (3)
N1—Ir1—N3	161.6 (2)	N4—Ir1—N5	79.6 (2)
N1—Ir1—N4	91.3 (3)		

All the H atoms bonded to carbon were placed at calculated positions, and fixed (C—H = 0.95–0.97 Å). The maximum and minimum residual-density peaks are at 2.17 and 1.06 Å from atoms Ir and N3, respectively. *PLATON*/*SQUEEZE* (Spek, 2002) indicated large voids in the structure, maximum volume of 420 Å^3, which may accommodate water and/or acetonitrile molecules. However, we could not detect any residual density peaks in the voids.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 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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