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#### Key indicators

Single-crystal X-ray study  
T = 200 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.009 \text{ \AA}$   
R factor = 0.040  
wR factor = 0.091  
Data-to-parameter ratio = 13.0

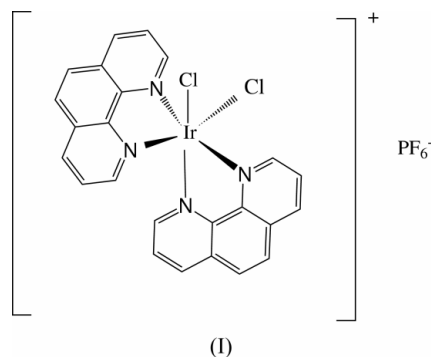
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## *cis*-Dichlorobis(1,10-phenanthroline)-iridium(III) hexafluorophosphate

The crystal structure of the title compound,  $[\text{IrCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{PF}_6$ , contains a monomeric  $[\text{IrCl}_2(\text{phen})_2]^+$  cation (phen is 1,10-phenanthroline) and a hexafluorophosphate anion. The iridium(III) ion is coordinated by four N atoms from two phen ligands [mean Ir–N distance 2.050 (5) Å] and two Cl atoms [Ir–Cl = 2.343 (1) Å], forming a distorted octahedral environment.

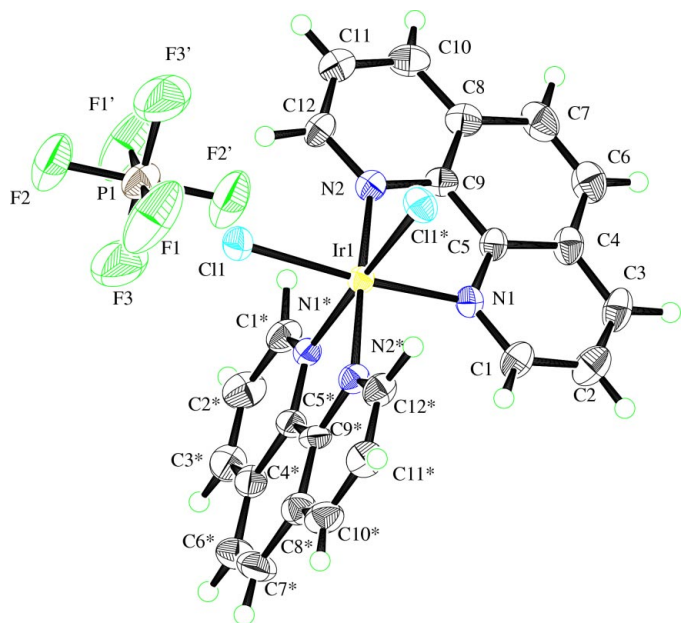
#### Comment

As a third-row transition metal,  $\text{Ir}^{\text{III}}$  is characterized by the great inertness of its coordination sphere, requiring harsh reaction conditions to substitute the chlorine ligands of  $(\text{NH}_4)_3[\text{IrCl}_6]\cdot\text{H}_2\text{O}$ . In 1964, Chiswell *et al.* reported the preparation of  $[\text{IrCl}_2(\text{phen})_2]\text{Cl}$  by heating  $\text{K}_3\text{IrCl}_6$  at 493 K for 14 h. In 2000, Yoshikawa *et al.* reported the preparation of  $[\text{IrCl}_2(\text{phen})_2]\text{PF}_6$  by using a microwave oven for 15 min. However, no single-crystal structure of an iridium complex with the 1,10-phenanthroline ligand has been reported previously. In this study, we have prepared and investigated the iridium bis-phenanthroline complex, (I).

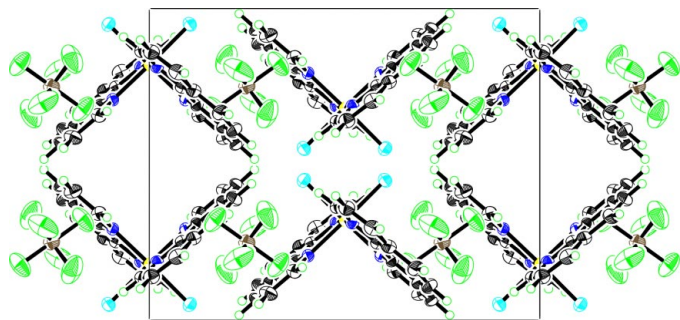


The crystal structure of (I) consists of a discrete  $[\text{IrCl}_2(\text{phen})_2]^+$  cation and a hexafluorophosphate anion. As illustrated in Fig. 1, the  $\text{Ir}^{\text{III}}$  atom is located in a distorted octahedral environment by two phen ligands and two chloride anions. The Ir–N bond lengths are in the range 2.046 (4)–2.053 (5) Å. Three *trans* angles are in the range 174.9 (1)–175.8 (2)°. It is coordinated by four N atoms from a pair of *cis*-related chelating phen ligands and two Cl atoms [Ir–Cl = 2.343 (1) Å]. The equatorial plane is formed by atoms Cl1/N1/N2/N4, with the largest deviation from the mean plane being 0.023 (2) Å and the Ir atom being 0.126 (2) Å out of this plane. The axial positions are occupied by the fourth phen N atom and another Cl atom. Each phen ligand is planar and the maximum deviation from the mean plane is 0.205 (6) Å. The

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



**Figure 2**  
The molecular packing diagram of (I), projected down the *c* axis.

two Cl ligands are coordinated in a *cis* fashion, but  $\text{PF}_6^-$  is not coordinated to the iridium atom. The average length of the Ir–N bonds [2.050 (5) Å] and the average of the N1–Ir–N2 and N3–Ir–N4 ligand angles [80.6 (2)°] compare well with the values published for  $[\text{IrCl}_2(\text{dmbpy})_2]\text{PF}_6$  (Yoshikawa *et al.*, 2003) (dmbpy = 4,4'-dimethyl-2,2'-bipyridine), *viz.* 2.026 Å and 79.1°, respectively. The structure contains a channel down the *c* axis (Fig. 2). However, no hydrogen-bonding interactions exist in the crystal structure.

## Experimental

The desired complex was prepared by the ligand replacement procedure.  $(\text{NH}_4)_3[\text{IrCl}_6]\cdot\text{H}_2\text{O}$  (0.5 mmol) and 1,10-phenanthroline (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 then cooled to room temperature. A saturated aqueous solution of  $\text{KPF}_6$  (20 ml) was added and a yellow product began to precipitate and was collected by vacuum filtration. The residue was dissolved in a minimal amount of acetone and flash precipitated in diethyl ether. The product was

separated by vacuum filtration and dried under a vacuum. Yellow single crystals were obtained by recrystallization from acetonitrile and water.

## Crystal data

$[\text{IrCl}_2(\text{C}_{12}\text{H}_8\text{N}_2)_2]\text{PF}_6$   
 $M_r = 768.51$   
 Monoclinic,  $C2/c$   
 $a = 16.340$  (1) Å  
 $b = 12.679$  (1) Å  
 $c = 12.9870$  (8) Å  
 $\beta = 103.321$  (2)°  
 $V = 2618.2$  (4) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.949$  Mg m<sup>-3</sup>

Mo K $\alpha$  radiation

Cell parameters from 13893

reflections

$\theta = 1.6$ – $27.5^\circ$

$\mu = 5.44$  mm<sup>-1</sup>

$T = 200.2$  K

Prism, yellow

0.13 × 0.12 × 0.10 mm

## Data collection

Rigaku RAXIS-RAPID Imaging

Plate diffractometer

$\omega$  scans

Absorption correction: multi-scan

ABSCOR (Higashi, 1995)

$T_{\min} = 0.426$ ,  $T_{\max} = 0.580$

11793 measured reflections

3007 independent reflections

2675 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.061$

$\theta_{\max} = 27.5^\circ$

$h = -21 \rightarrow 20$

$k = -16 \rightarrow 16$

$l = -14 \rightarrow 16$

## Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.091$

$S = 1.20$

2675 reflections

206 parameters

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.032$

$\Delta\rho_{\max} = 0.96$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.37$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ir1–Cl1	2.343 (1)	Ir1–N1 <sup>1</sup>	2.046 (4)
Ir1–Cl1 <sup>1</sup>	2.343 (1)	Ir1–N2	2.053 (5)
Ir1–N1	2.046 (4)	Ir1–N2 <sup>1</sup>	2.053 (5)
Cl1–Ir1–Cl1 <sup>1</sup>	90.02 (7)	Cl1 <sup>1</sup> –Ir1–N2 <sup>1</sup>	94.4 (1)
Cl1–Ir1–N1	174.9 (1)	N1–Ir1–N1 <sup>1</sup>	92.9 (2)
Cl1–Ir1–N1 <sup>1</sup>	88.7 (1)	N1–Ir1–N2	80.6 (2)
Cl1–Ir1–N2	94.4 (1)	N1–Ir1–N2 <sup>1</sup>	96.4 (2)
Cl1–Ir1–N2 <sup>1</sup>	88.5 (1)	N1 <sup>1</sup> –Ir1–N2	96.4 (2)
Cl1 <sup>1</sup> –Ir1–N1	88.7 (1)	N1 <sup>1</sup> –Ir1–N2 <sup>1</sup>	80.6 (2)
Cl1 <sup>1</sup> –Ir1–N1 <sup>1</sup>	174.9 (1)	N2–Ir1–N2 <sup>1</sup>	175.8 (2)
Cl1 <sup>1</sup> –Ir1–N2	88.5 (1)		

Symmetry code: (i) 2 – *x*, *y*,  $\frac{1}{2}$  – *z*.

All the H atoms were placed at calculated positions (C–H = 0.946–0.952 Å) and refined isotropically. The maximum and minimum electron-density peaks are 1.67 and 1.33 Å<sup>-3</sup>, respectively, from atoms F10 and Ir1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *teXsan* (Molecular Structure Corporation/Rigaku, 2000); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *teXsan*.

## References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.  
 Chiswell, B. & Livingstone, S. E. J. (1964). *Inorg. Nucl. Chem.* **26**, 47–51.  
 Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.  
Molecular Structure Corporation/Rigaku (2000). *teXsan*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.  
Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
Yoshikawa, N., Masuda, Y. & Matsumura-Inoue, T. (2000). *Chem. Lett.* pp. 1206-1207.  
Yoshikawa, N., Sakamoto, J., Kanehisa, N., Kai, Y. & Matsumura-Inoue, T. (2003). *Acta Cryst.* **E59**, m155-m156.