

cis-Dichlorobis(2,2'-biquinoline)iridium(III) hexafluorophosphate

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Key indicators

Single-crystal X-ray study

$T = 223\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.009\text{ \AA}$

R factor = 0.036

wR factor = 0.097

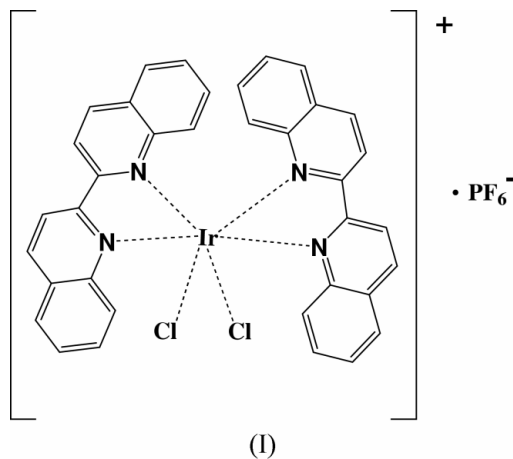
Data-to-parameter ratio = 13.1

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

The crystal structure of the title compound, $[\text{IrCl}_2(\text{bqn})_2]\text{PF}_6$, (bqn is 2,2'-biquinoline, $\text{C}_{18}\text{H}_{12}\text{N}_2$), contains a monomeric $[\text{IrCl}_2(\text{bqn})_2]^+$ cation and a hexafluorophosphate anion. The iridium(III) ion is coordinated by four N atoms from two bqn ligands [mean Ir–N distance $2.065(5)\text{ \AA}$] and two Cl atoms [Ir–Cl = $2.342(2)$ and $2.353(2)\text{ \AA}$], forming a distorted octahedral environment. Each 2,2'-biquinoline ligand is planar, the mean deviations from the least-squares planes being $0.2431(6)$ and $0.1665(6)\text{ \AA}$.

Comment

Extensive studies of the photophysics of octahedral $[4d^6]$ and $[5d^6]$ complexes have been attracting much attention to the photochemical applications of the complexes on account of their long-lived excited states and good photoluminescence efficiencies. The studies have been focused mainly on the photophysical properties of octahedral metal–diimine complexes of iridium(III) having such ligands as 2,2'-bipyridine and 1,10-phenanthroline. To our knowledge, no structure of an iridium complex with the 2,2'-biquinoline ligand (bqn) has been reported previously. We have prepared and investigated an iridium bis-polypyridine complex, (I).



The asymmetric unit of the crystal structure of (I) consists of a discrete $[\text{IrCl}_2(\text{bqn})_2]^+$ cation and a hexafluorophosphate anion. As illustrated in Fig. 1, the Ir^{III} atom is located in a distorted octahedral environment, coordinated by two bqn ligands and two chloride anions. The Ir–N bond lengths are in the range $2.056(5)$ – $2.071(5)\text{ \AA}$. The three *trans* angles are in the range $168.3(2)$ – $174.4(1)^\circ$. Ir is coordinated by four N atoms from a pair of *cis*-related chelating bqn ligands and two Cl atoms [Ir–Cl1 = $2.342(2)\text{ \AA}$ and Ir–Cl2 = $2.353(2)\text{ \AA}$]. The equatorial plane is formed by atoms Cl1, N1, N2 and N4,

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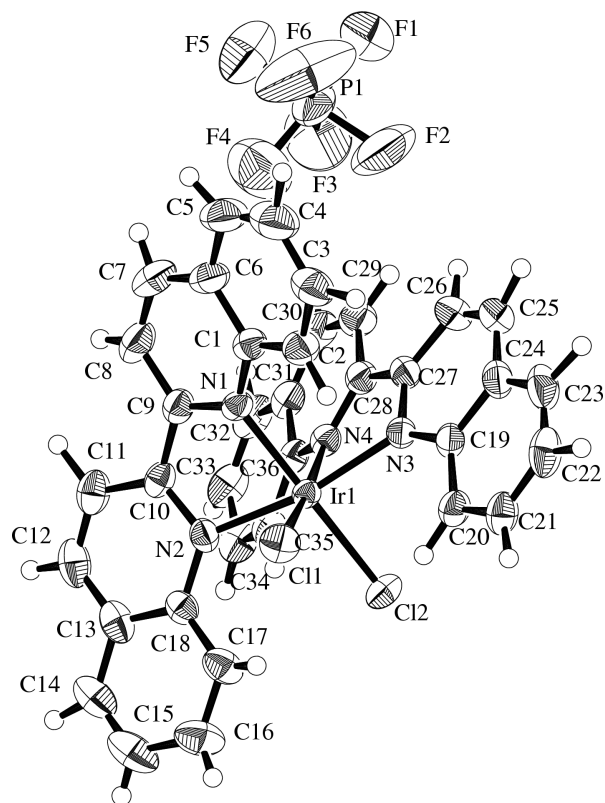


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

with the largest deviation from the mean plane being 0.023 (2) Å and the Ir atom lying 0.126 (2) Å out of this plane. The axial positions are occupied by the fourth bqn N atom and another Cl atom. Each bqn ligand is planar; the maximum mean deviation from the mean planes is 0.205 (6) Å. The dihedral angle between the bqn planes is 26.90 (9)°. The two Cl ligands coordinate in a *cis* fashion, but PF₆[−] is not coordinated to the Ir atom. The average Ir–N bond length of 2.065 (5) Å and the average N1–Ir–N2 and N3–Ir–N4 angles of 78.0 (2)° compare well with the values published for [IrCl₂(dmbpy)₂]₂PF₆ (Yoshikawa *et al.*, 2003; dmbpy is 4,4'-dimethyl-2,2'-bipyridine) of 2.026 Å and 79.1°, respectively. No hydrogen-bonding interactions exist in the crystal structure.

Experimental

The title complex was prepared by a ligand replacement procedure. (NH₄)₃[IrCl₆]·H₂O (0.5 mmol) and 2,2'-biquinoline (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 KPF₆ (20 ml) was added, and a brown product began to precipitate and was collected by vacuum filtration. The residue was dissolved in the minimum amount of acetone and flash precipitated by diethyl ether. The product was separated by vacuum filtration and dried under a vacuum. Brown single crystals were obtained by recrystallization from acetonitrile.

Crystal data

[IrCl₂(C₁₈H₁₂N₂)₂]₂PF₆
M_r = 920.70
 Monoclinic, *P*2₁/*n*
a = 10.5127 (2) Å
b = 23.6279 (5) Å
c = 13.7750 (2) Å
 β = 108.0188 (3)°
V = 3253.8 (1) Å³
Z = 4

D_x = 1.879 Mg m^{−3}
 Mo *K*α radiation
 Cell parameters from 27 860 reflections
 θ = 1.8–27.4°
 μ = 4.40 mm^{−1}
T = 223.2 K
 Prism, brown
 0.30 × 0.20 × 0.10 mm

Data collection

Rigaku R-Axis-RAPID Imaging
 Plate diffractometer
 ω scans
 Absorption correction: multi-scan
 (ABSCOR; Higashi, 1995)
T_{min} = 0.419, *T_{max}* = 0.644
 27 860 measured reflections

7310 independent reflections
 6212 reflections with *I* > 2σ(*I*)
R_{int} = 0.045
 θ_{max} = 27.4°
h = −13 → 13
k = −30 → 30
l = −17 → 17

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.036
wR (*F*²) = 0.097
S = 1.30
 6212 reflections
 475 parameters

Only H-atom *U*'s refined
w = 1/[σ²(*F_o*²) + (0.1*P*)²]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.003
 Δρ_{max} = 0.90 e Å^{−3}
 Δρ_{min} = −1.17 e Å^{−3}

Table 1

Selected geometric parameters (Å, °).

Ir1–Cl1	2.340 (1)	Ir1–N2	2.070 (4)
Ir1–Cl2	2.353 (1)	Ir1–N3	2.068 (4)
Ir1–N1	2.058 (4)	Ir1–N4	2.070 (4)
Cl1–Ir1–Cl2	96.15 (5)	Cl2–Ir1–N4	89.3 (1)
Cl1–Ir1–N1	89.8 (1)	N1–Ir1–N2	78.2 (2)
Cl1–Ir1–N2	86.6 (1)	N1–Ir1–N3	92.8 (2)
Cl1–Ir1–N3	101.1 (1)	N1–Ir1–N4	84.9 (1)
Cl1–Ir1–N4	174.4 (1)	N2–Ir1–N3	168.2 (2)
Cl2–Ir1–N1	173.6 (1)	N2–Ir1–N4	93.9 (2)
Cl2–Ir1–N2	99.7 (1)	N3–Ir1–N4	77.7 (2)
Cl2–Ir1–N3	88.5 (1)		

All H atoms bonded to C atoms were placed in calculated positions (C–H = 0.933–0.955 Å) with isotropic displacement parameters. The deepest hole in the difference map was located 0.38 Å from atom Cl1.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 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.
 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 (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381, USA.
 Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Yoshikawa, N., Sakamoto, J., Kanehisa, N., Kai, Y. & Matsumura-Inoue, T. (2003). *Acta Cryst.* **E59**, m155–m156.