

Structure and Spectroscopic Property of Bis(1-(3',5'-difluorophenyl)isoquinolino-*C*^{2'},*N*)(1-methylimidazole-2-carboxylato-*N*³,*O*)Ir(III) Hydrate

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The luminescent cyclometalated Ir(III) complexes have received great interest in the development of organic light emitting diodes.^{1,2} Many bis- and tris-cyclometalated complexes of Ir(III) with relatively high quantum efficiency have been synthesized and characterized.³⁻⁸ The color of phosphorescent complexes used in light emitting devices are tuned by the variation of both cyclometalating and ancillary ligands. The purpose of the present study is the molecular design of a highly efficient phenylisoquinoline-based red-phosphorescent complex suitable for red organic light emitting diodes devices. Herein, we report the synthesis, electroluminescent properties and crystal structure of the phenylisoquinoline-based iridium complex, bis(1-(3',5'-difluorophenyl)isoquinolino-*C*^{2'},*N*)(1-methylimidazole-2-carboxylato-*N*³,*O*)Ir(III).

The title compound is a hydrated, neutral mononuclear complex. Bond lengths and angles for the coordination of Ir are summarized in Table 1. The Ir atom has a distorted octahedral geometry involving two difluorophenylisoquinoline ligands and a 1-methylimidazole-2-carboxylate ligand with *trans*-N1-N2 disposition. The Ir-N1(2.025(6) Å) and Ir-N2(2.055(6) Å) bond lengths are shorter than the Ir-N3 bond length of 2.121(6) Å. Similar observations were made concerning bond lengths in *mer*-bis[2-(6-fluoro-3-methylquinoxalin-2-yl- κ N¹)-phenyl] [3-phenyl-5-(2-pyridyl- κ N)-1,2,4-triazol-1-yl]-iridium.⁹ The three *trans* angles are in the range of 170.4(2)-177.6(3)°. The three five-membered, chelating rings are nearly planar and orthogonal to each

other; the r.m.s. deviations are 0.040, 0.075 and 0.025 Å for the rings involving Ir/N1/C15(ring A), Ir/N2/C30(B) and Ir/N3/O1(C), respectively, and the angles between rings are 86.5(2)(A/B), 78.7(2)(B/C) and 89.0(2)°(C/A), respectively. Within difluorophenylisoquinoline ligands, the difluorophenyl rings are inclined with respect to the isoquinoline ring systems, based on N1 and N2, by 14.5(2) and 30.3(2)°, respectively.

The crystal structure is stabilized by strong aromatic π - π stacking associations formed between adjacent isoquinoline[N2, C16-C24] rings from two centrosymmetric related molecules. The short C \cdots C contact includes C21 \cdots C21 ($-x, -y, -z+1$) = 3.315(12) and C17 \cdots C27 ($-x-1, -y, -z+1$) = 3.470(14) Å. Furthermore, there are cyclic, eight-membered, hydrogen-bonded rings involving two water molecules. The oxygen atom of the water molecule donates two hydrogen bonds of O2 \cdots H-O3w-H \cdots O2 ($-x, -y-1, -z+1$). Two

Table 1. Geometric parameters of Ir(III) octahedron (Å, °)

| | | | |
|------------|-----------|-----------|-----------|
| Ir-C15 | 1.992 (7) | Ir-N2 | 2.055 (6) |
| Ir-C30 | 2.007 (8) | Ir-N3 | 2.121 (6) |
| Ir-N1 | 2.024 (6) | Ir-O1 | 2.181 (5) |
| C15-Ir-C30 | 91.7 (3) | N1-Ir-N3 | 88.4 (2) |
| C15-Ir-N1 | 78.6 (3) | N2-Ir-N3 | 94.0 (2) |
| C30-Ir-N1 | 98.3 (3) | C15-Ir-O1 | 170.4 (2) |
| C15-Ir-N2 | 101.6 (3) | C30-Ir-O1 | 96.4 (3) |
| C30-Ir-N2 | 79.3 (3) | N1-Ir-O1 | 95.1 (2) |
| N1-Ir-N2 | 177.6 (3) | N2-Ir-O1 | 85.1 (2) |
| C15-Ir-N3 | 95.5 (3) | N3-Ir-O1 | 77.1 (2) |
| C30-Ir-N3 | 171.0 (3) | | |

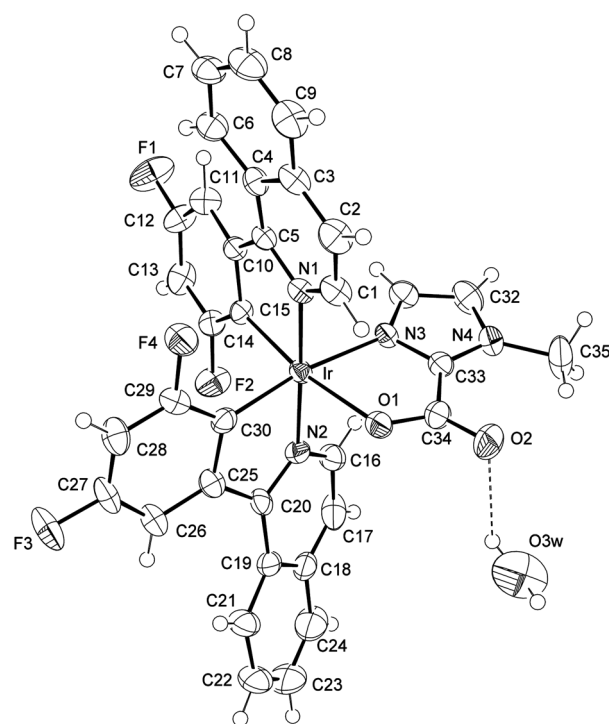


Figure 1. Molecular structure of **1**, with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level.

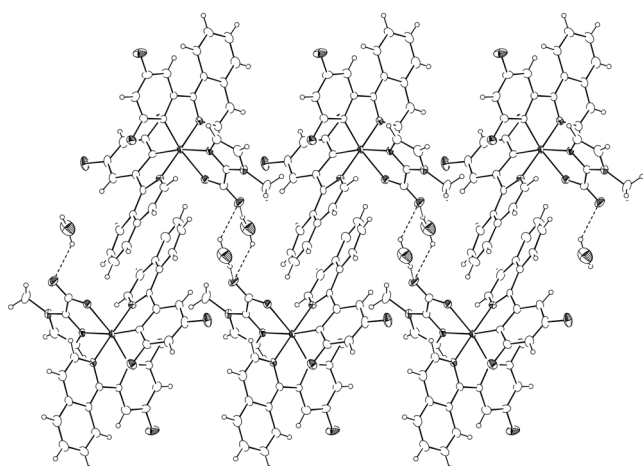


Figure 2. The packing diagram viewed down *a* axis showing the π - π interactions and hydrogen-bonded rings on **1**. The dotted lines indicate hydrogen bonds.

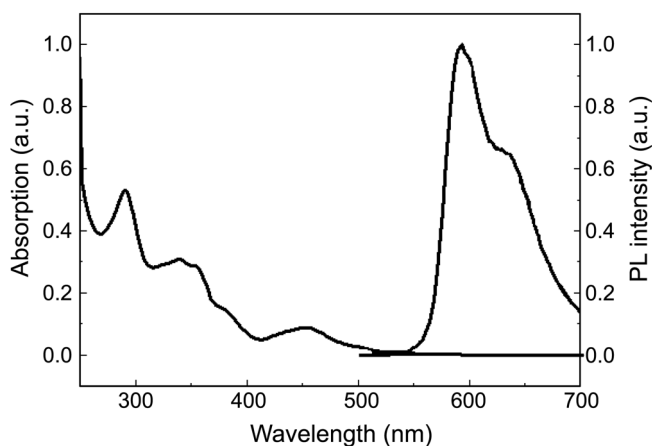


Figure 3. UV-vis and photoluminescence spectra of **1** in CHCl_3 solution.

hydrogen bond lengths are 3.023(13) and 2.997(13) Å. The O2 atom accepts two hydrogen bonds from the two water molecules. Therefore, the hydrogen bonded ring makes a centrosymmetric molecular dimer (see Figure 2).

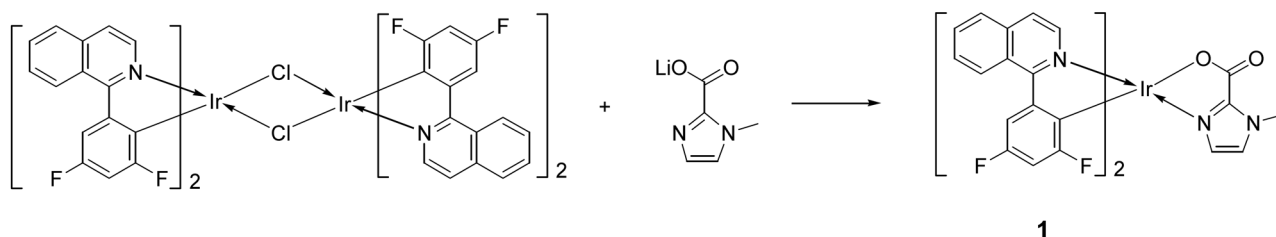
The UV-vis absorption and photoluminescence spectra of **1** were investigated in CHCl_3 solution (Figure 3). The UV-vis spectrum of the complex shows a metal-to-ligand charge-transfer band at 453 nm, in addition to the π - π^* transition at 290 and 340 nm. The complex exhibits a strong emission band with vibrational structure at around 592 nm. The emission should probably be assigned to the π - π^*

charge-transfer interaction. This observed emission wavelength of 592 nm is in range of those of other phenyl-isoquinoline-based red-phosphorescent complexes⁶ of 586 to 732 nm. Thus, this compound may be a candidate for red-light luminescent materials.

Experimental Section

The ligand, 1-(3,5-difluorophenyl)isoquinoline, was prepared from the reaction of 1-chloroisoquinoline with 3,5-difluorophenyl boronic acid in THF and water in the presence of $\text{Pd}(\text{PPh}_3)_4$ and Na_2CO_3 . After that, $(\text{piqF}_2)_2\text{Cl}_2\text{Ir}(\text{piqF}_2)_2$ (piq : phenylisoquinoline) was prepared by the reactions of $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$ with 1-(3,5-difluorophenyl)isoquinoline ligands as previously reported in the literature.¹⁰ The reaction of $(\text{piqF}_2)_2\text{Cl}_2\text{Ir}(\text{piqF}_2)_2$ (1.0 mmol, 1.416 g) and 1-methylimidazole-2-carboxylic acid lithium salt (2.5 mmol, 330 mg) was proceeded in CHCl_3 solvent at 50 °C for 12 hrs. After reaction completion, the mixture was poured into water and then extracted with chloroform (3×50 mL). The combined organic layer was dried with anhydrous MgSO_4 and concentrated to 10 mL. Column chromatography was carried out to isolate the major component using hexane + ethyl acetate (10:1 v/v) as eluents. The red solution was collected and dried under vacuum, to afford a red powder of 58% yield (925 mg). ¹H-NMR (Bruker spectrometer, 300 MHz, CD_2Cl_2 , ppm): 8.90 [m, 2H], 8.67 [d, 1H], 8.02-7.91 [m, 4H], 7.77 [m, 4H], 7.63 [d, 1H], 7.52 [d, 1H], 7.37 [d, 1H], 6.85 [d, 1H], 6.41 [d, 1H], 6.39-6.26 [m, 2H], 4.01 [s, 3H]. Anal. Calcd for $[\text{Ir}(\text{C}_{15}\text{H}_8\text{F}_2\text{N})_2(\text{C}_5\text{H}_5\text{N}_2\text{O}_2)] \cdot \text{H}_2\text{O}$: C, 51.53 H, 2.84 N, 6.87%, found: C, 51.71 H, 2.79 N, 6.91%.

Single crystals, suitable for X-ray diffraction analysis, were grown by layer diffusion of methanol into the CH_2Cl_2 solution of **1**. X-ray data were collected using a Nonius CAD-4 diffractometer with Mo $\text{K}\alpha$ graphite monochromated radiation at room temperature. The structure was solved by direct methods and the refinements were carried out with full-matrix least-squares methods. Water H atoms were located in a difference Fourier map and refined with a DFIX¹¹ restraint of O-H = 0.88(1) Å and with Uiso(H) = 1.5Ueq(O). The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C-H = 0.93 and 0.96 Å for aromatic and methyl H, respectively, and with Uiso(H) = 1.2Ueq(C) for aromatic and Uiso(H) = 1.5Ueq(C) for methyl H atoms. The following programs are used: Data collection: CAD-4-PC software,¹²



Scheme 1

Table 2. Summary of crystal data of Ir(III) complex

| Crystal data | |
|---|---|
| $[\text{Ir}(\text{C}_{15}\text{H}_8\text{F}_2\text{N})_2(\text{C}_5\text{H}_5\text{N}_2\text{O}_2)] \cdot \text{H}_2\text{O}$ | $V = 1451.4 (6) \text{ \AA}^3$ |
| $M_r = 815.77$ | $Z = 2$ |
| Triclinic, $P (-1)$ | $D_x = 1.867 \text{ Mg m}^{-3}$ |
| $a = 8.623 (3) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 9.485 (2) \text{ \AA}$ | $\mu = 4.67 \text{ mm}^{-1}$ |
| $c = 18.402 (3) \text{ \AA}$ | $T = 293 (2) \text{ K}$ |
| $\alpha = 87.41 (2)^\circ$ | Plate, red |
| $\beta = 88.18 (2)^\circ$ | $0.14 \times 0.13 \times 0.10 \text{ mm}$ |
| $\gamma = 74.92 (2)^\circ$ | |
| Data collection | |
| Nonius-CAD4 diffractometer | 4182 reflections with $I > 2\sigma(I)$ |
| ω scan | $R_{\text{int}} = 0.043$ |
| Absorption correction: Ψ scan ¹⁵ | $\theta_{\text{max}} = 25.0^\circ$ |
| $T_{\text{min}} = 0.876$, $T_{\text{max}} = 0.999$ | 3 standard reflections |
| 9793 measured reflections | every 60 min. |
| 5099 independent reflections | intensity decay: 3.6% |
| Refinement | |
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | $w = 1/[\sigma^2(\text{Fo}^2) + (0.0675\text{P})^2]$ where $\text{P} = (\text{Fo}^2 + 2\text{Fc}^2)/3$ |
| $wR(F^2) = 0.106$ | $(\Delta/\sigma)_{\text{max}} = 0.029$ |
| $S = 1.05$ | $\Delta\rho_{\text{max}} = 2.38 \text{ e \AA}^{-3}$ |
| 5099 reflections | $\Delta\rho_{\text{min}} = -2.97 \text{ e \AA}^{-3}$ |
| 430 parameters | Extinction correction: none |

Cell refinement: SET4¹² and CELDIM,¹² Data reduction: WinGX,¹³ Program(s) used to solve structure: SHELXS-97,¹¹ Program(s) used to refine structure: SHELXL-97,¹¹ Molecular graphics: ORTEP3.¹⁴ The crystal data and refinements were summarized in Table 2. Crystallographic data for **1** have been deposited at the Cambridge Crystallo-

graphic Data Centre (Deposition number CCDC 653772). The data can be obtained free of charge via <http://ccdc.cam.ac.uk/perl/catreq/catreq.cgi> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk).

UV-vis and photoluminescence spectra were measured by UV spectrometer (Reiken Co.) and by the photoluminescence spectrometer (PSSI Co.) in CHCl_3 solution, respectively.

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