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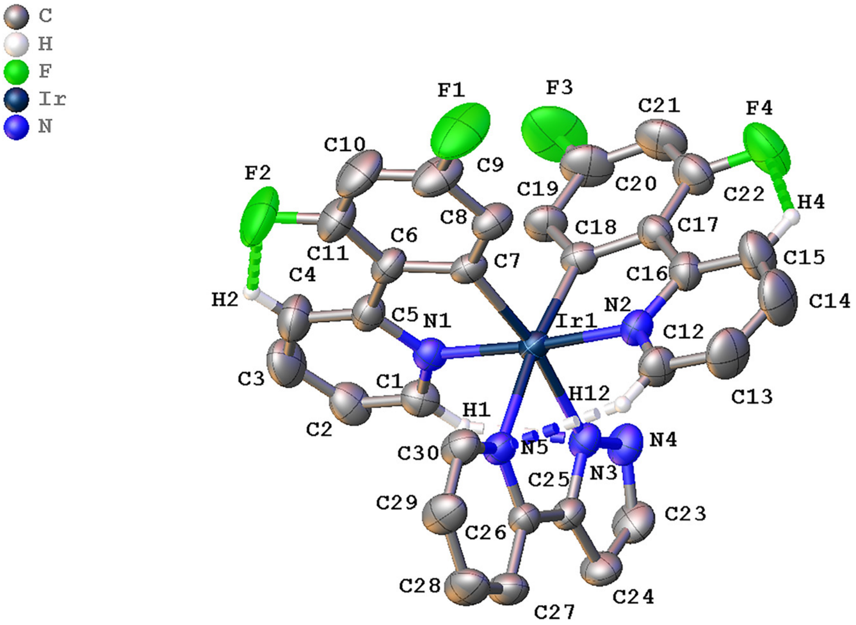
Crystal structure of 2-(1*H*-pyrazol-3-yl-κ*N*)pyridine-κ*N*-bis(2-(2,4-difluorophenyl)pyridinato-κ^2*C*,*N*)iridium(III) sesquihydrate, $C_{30}H_{18}F_4IrN_5\cdot1.5[H_2O]$



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Abstract

$C_{30}H_{18}F_4IrN_5\cdot1.5[H_2O]$, tetragonal, $I4_1/a$ (no. 88), a = 37.5562(5) Å, b = 37.5562(5) Å, c = 9.2031(2) Å, $V = 12980.7(4)$ Å^3, $Z = 16$, $R_{gt}(F) = 0.0312$, $wR_{ref}(F^2) = 0.1166$, $T = 300(2)$ K.

CCDC no.: 2169203

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.17 × 0.10 × 0.10 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	6.0 mm^{-1}
Diffractometer, scan mode:	Bruker APEXII, φ and ω
θ_{max}, completeness:	56.6°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13,239, 9148, 0.025
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7183
$N(param)_{refined}$:	686
Programs:	Bruker [1], SHELX [2–4], OLEX2 [5]

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	$U_{iso}*/U_{eq}$
Ir1	0.64748 (2)	0.29196 (2)	0.03393 (2)	0.03014 (9)
C1	0.65569 (13)	0.22476 (13)	0.2093 (5)	0.0424 (9)
H1	0.631831	0.228325	0.232043	0.051*
F1	0.75746 (11)	0.35698 (13)	−0.2427 (5)	0.0954 (15)
F2	0.77911 (9)	0.24709 (12)	−0.0291 (5)	0.0877 (13)
C2	0.67257 (16)	0.19575 (14)	0.2657 (6)	0.0532 (12)
H2	0.660575	0.180003	0.326451	0.064*
F3	0.68777 (15)	0.33183 (13)	0.5719 (4)	0.1024 (16)
C3	0.70777 (18)	0.19030 (16)	0.2307 (7)	0.0659 (16)
H3	0.719884	0.170681	0.267520	0.079*
F4	0.63174 (13)	0.41718 (10)	0.2821 (5)	0.0847 (12)
C4	0.72486 (15)	0.21384 (16)	0.1415 (7)	0.0607 (14)
H4	0.748551	0.209951	0.116722	0.073*
N1	0.67198 (9)	0.24840 (9)	0.1225 (4)	0.0348 (7)
N2	0.62643 (9)	0.33781 (10)	−0.0490 (4)	0.0363 (7)
N3	0.59654 (9)	0.27379 (10)	0.0923 (4)	0.0357 (7)
N4	0.57685 (11)	0.27745 (12)	0.2147 (4)	0.0445 (9)
N5	0.63172 (9)	0.25913 (9)	−0.1479 (4)	0.0347 (7)
C5	0.70696 (11)	0.24395 (12)	0.0866 (5)	0.0409 (9)
C7	0.69758 (11)	0.30045 (12)	−0.0351 (4)	0.0359 (8)
C8	0.71044 (12)	0.32917 (14)	−0.1166 (5)	0.0461 (10)
H8	0.695571	0.348211	−0.138808	0.055*
C9	0.74513 (14)	0.32907 (18)	−0.1637 (7)	0.0622 (15)
C10	0.76857 (14)	0.30188 (19)	−0.1371 (7)	0.0682 (17)
H10	0.791865	0.302443	−0.171265	0.082*
C11	0.75579 (13)	0.27377 (17)	−0.0572 (7)	0.0568 (13)
C6	0.72136 (11)	0.27235 (13)	−0.0028 (5)	0.0410 (9)
C18	0.65564 (11)	0.32442 (12)	0.2028 (4)	0.0367 (8)
C12	0.61342 (13)	0.34102 (14)	−0.1837 (5)	0.0470 (10)
H12	0.614090	0.321299	−0.244806	0.056*
C19	0.67119 (14)	0.31548 (14)	0.3362 (5)	0.0480 (10)
H19	0.680073	0.292693	0.352109	0.058*
C13	0.59899 (18)	0.37248 (18)	−0.2362 (7)	0.0672 (16)
H13	0.589790	0.373741	−0.329876	0.081*
C20	0.67312 (19)	0.34091 (18)	0.4433 (6)	0.0649 (16)
C14	0.5986 (2)	0.40149 (17)	−0.1474 (8)	0.0736 (18)
H14	0.589105	0.422896	−0.180209	0.088*
C21	0.66007 (19)	0.37524 (18)	0.4280 (7)	0.0677 (16)
H21	0.661624	0.391802	0.502903	0.081*
C15	0.61235 (18)	0.39910 (15)	−0.0087 (7)	0.0635 (15)
H15	0.612183	0.418883	0.052084	0.076*
C22	0.64488 (16)	0.38352 (15)	0.2981 (6)	0.0563 (13)
C16	0.62659 (13)	0.36662 (12)	0.0405 (5)	0.0431 (10)
C17	0.64213 (12)	0.35950 (12)	0.1826 (5)	0.0411 (9)
C23	0.54855 (14)	0.25609 (16)	0.1942 (6)	0.0542 (12)
H23	0.530536	0.253044	0.262395	0.065*
C24	0.54912 (13)	0.23919 (14)	0.0613 (6)	0.0492 (11)
H24	0.532243	0.223814	0.022174	0.059*
C25	0.58086 (11)	0.25059 (11)	−0.0001 (5)	0.0366 (8)
C26	0.59935 (10)	0.24331 (11)	−0.1348 (5)	0.0360 (8)
C27	0.58567 (13)	0.22247 (14)	−0.2467 (6)	0.0484 (11)
H27	0.563581	0.211562	−0.236529	0.058*
C28	0.60511 (15)	0.21806 (16)	−0.3729 (6)	0.0595 (14)
H28	0.596573	0.203823	−0.447892	0.071*
C29	0.63769 (14)	0.23538 (16)	−0.3855 (6)	0.0562 (13)
H29	0.650870	0.233614	−0.470719	0.067*
C30	0.65008 (12)	0.25491 (14)	−0.2719 (5)	0.0454 (10)
H30	0.672215	0.265821	−0.280451	0.055*

Source of material

The chemicals iridium(III) trichloride hydrate (99.9%, Sigma-Aldrich), 2-(2,4-difluorophenylpyridine) (97%, Sigma-Aldrich), 3-(dimethylamino)-1-(2-pyridyl)-2-propen-1-one (95%, Sigma-Aldrich) and hydrazine hydrate (50–60%, Sigma-Aldrich) were used without further purification.

The ancillary ligand pyridylpyrazole (PyPz) was obtained by mixing 3-(dimethylamino)-1-(2-pyridyl)-2-propen-1-one (30 mmol, 5.50 g) and hydrazine hydrate (5 ml) in ethanol (7 ml). The solution was heated to 60 °C and stirred for 30 min. Next, distilled water (37.5 ml) was added into the solution and left at temperatures 4–6 °C overnight. A white precipitate was formed. The solid was filtered with Büchner filter and washed with distilled water to give a white powder (2.85 g, 63%) [6].

The precursor complex $[Ir(dfppy)_2Cl]_2$ (Di-μ-chloro-bis {bis[2-(2,4-difluorophenyl)pyridinato-κ^2C, N)iridium(III)) was synthesized using Nonoyama's reaction [7], where iridium(III) trichloride hydrate (1 mmol, 0.30 g) and 2-(2,4-difluorophenylpyridine) (2.5 mmol, 0.48 g) were poured into a round bottom flask containing 2-ethoxyethanol (30 ml) and distilled water (10 ml). The solution was brought to refluxing temperature and was heated for 24 h under inert conditions. A yellow precipitate ($[Ir(dfppy)_2Cl]_2$) was formed and collected using Büchner filtration and used for the next step.

2-(1*H*-pyrazol-3-yl-κ*N*)pyridine-κ^2N-bis(2-(2,4-difluorophenyl)pyridinato-κ^2C,N)iridium(III), $[Ir(dfppy)_2PyPz]$ was obtained by adding PyPz into$[Ir(dfppy)_2Cl]_2$ in 30 ml dichloromethane under inert condition. The mixture was stirred and refluxed for 7 h. Crystals of the title compound were obtained through slow evaporation in a mixture of dichloromethane and acetone solvents.

Experimental details

All hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms with C–H distances = 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}$ for aryl H atoms. The diffuse electron density of part of the water molecule was removed with the solvent-mask procedure implemented in OLEX2 [5]. There were 240 electrons found in a volume of 3620 Å^3 in two voids per unit cell. This is consistent with the presence of 1.5$[H_2O]$ per formula unit which accounts for 252 electrons per unit cell.

Comment

Iridium(III) complexes are well known that some of them are light-emitting and were used for various applications such as organic light-emitting diodes (OLEDs) [8], light-emitting electrochemical cells (LECs) [9] and sensors [10]. Previous work has demonstrated that choosing the right ancillary or cyclometalating ligand is very crucial in determining the desired photophysical properties [11] and these can be done by modifying the ligand structures [12]. Over the years, extensive studies have been made on iridium(III) complexes with various conjugated aromatic compounds especially phenylpyridyl derivatives for tuning the emission color of the complexes [13]. In the present work, the synthesis and crystal structure of 2-(1*H*-pyrazol-3-yl-κ*N*)pyridine-κ^2N-bis(2-(2,4-difluorophenyl)pyridinato-κ^2C,N) iridium(III), $[Ir(dfppy)_2PyPz]$ is described.

The title compound shows an octahedral geometry where the iridium metal is coordinated with two difluorophenylpyridine (dfppy) groups and a PyPz ring *via* C, N and N, N atoms, respectively (Figure 1). The octahedral geometry of this complex is similar to the geometry of archetypal iridium(III) complexes [14]. The complex crystallizes in the tetragonal $I4_1/a$ space group whereby a similar complex was reported to crystallize in the monoclinic $P2_1/c$ space group [15]. The coordination of the iridium metal center with nitrogen atoms of PyPz moiety gives slightly longer Ir–N distances, ca 2.1 Å than that of dfppy moiety [Ir1–N1 = 2.046(4) Å; Ir1–N2 = 2.043(4) Å]. This observation is also associated with a smaller bite angle for the former with Ir(III) center [N3–Ir1–N5 = 76.31(14)°] compared to the latter chelating ligands [N2–Ir1–C18 = 80.54(16)°; N1–Ir1–C7 = 80.32(16)°] [16–18]. The PyPz ring is essentially planar, with a distortion of 4.24° between the two mean planes. The dfppy and PyPz moieties are twisted with a dihedral angles of 85.6–92.5°. The observed bond distances for Ir–C and Ir–N of dfppy are similar to the corresponding bond lengths of related structures [19, 21].

The packing of the title compound is dominated by weak intramolecular interactions and exhibits a column along *c*-axis. Two C–H···F interactions (C4–H4···F2 and C15–H15···F4) between fluorine atom of the phenyl ring and hydrogen atom of the pyridine ring from the same moiety, dfppy are observed (Figure). Besides, another two C–H···N interactions involving the dfppy moieties and pypz (C1–H1···N4 and C12–H12···N5) help to stabilize the structure. The hydrogen bonds involving the electronegative F atoms engendering two intramolecular S(6) motifs whereas the C–H···N interactions gave the S(6) and S(5) motifs. The presence of the electronegative F atom has influenced the X-ray structure. This hypothesis was further corroborated when an analogous crystal (2-(1*H*-pyrazol-1-yl-κ*N*)pyridine-κ^2N-bis(2-(2,4-difluorophenyl)πyridinato-κ^2C,N) iridium(III) hexafluorophosphate), $[Ir(dfppy)_2(PzPy)]PF_6$ exhibited similar intramolecular interactions between fluorine of difluorophenyl and hydrogen atom from the adjacent pyridine rings [20]. In addition, no observable π···π interaction is exhibited by the complex, albeit with the presence of six heterocyclic rings. A previously study also reported no discernable π···π interactions for Ir(III) complex consisting of seven heterocyclic rings [18].

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

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