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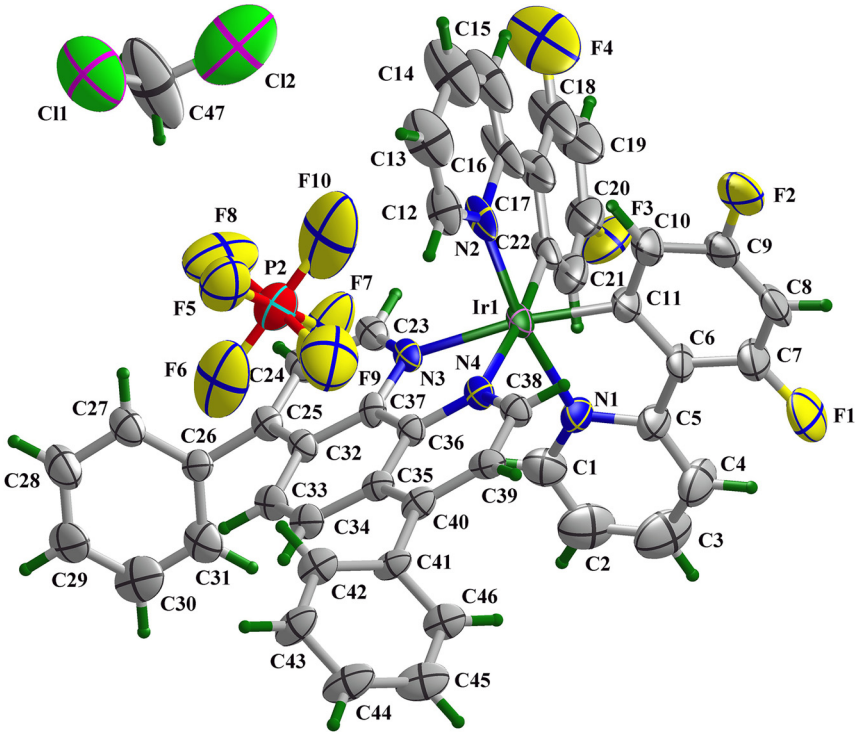
Crystal structure of 4,7-diphenyl-1,10-phenanthroline-κ²*N*,*N*′)-bis(2,4-di(fluorine)-1-phenylpyridine-κ²*C*,*N*)-iridium(III) hexafluorophosphate–dichloromethane (1/1), $C_{47}H_{30}Cl_2F_{10}IrN_4P$



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Abstract

$C_{47}H_{30}Cl_2F_{10}IrN_4P$, monoclinic, $P2_1/n$ (no. 14), a = 14.4048(8) Å, b = 19.8150(10) Å, c = 15.5151(8) Å, β = 106.018(2)°, V = 4256.6(4) Å^3, Z = 4, $R_{gt}(F)$ = 0.0451, $wR_{ref}(F^2)$ = 0.0921, T = 150(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.

1 Source of materials

All the reagents were A. R. grade commercially available and used as received without any further purification. The cyclometalated chloro-bridged iridium(III) dimer, $[(fpyd)_2Ir(\mu\text{–}Cl)]_2$ (fpyd = 2,4-di(fluorine)-1-phenylpyridine), was synthesized following the reported literature procedures[5] by heating $IrCl_3 \cdot 3H_2O$ (1 equiv) and 2,4-di(fluorine)-1-phenylpyridin (2 equiv) in a mixed solution of water and ethylene glycol ether (v/v = 1/5)

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.28 × 0.25 × 0.20 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	3.39 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
θ_{max}, completeness:	25.1°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	66477, 7514, 0.064
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5,960
$N(param)_{refined}$:	586
Programs:	Bruker,[1] Olex2,[2] SHELX[3, 4]

at 135 °C under nitrogen atmosphere. 1,10-Phenanthroline-5,6-dione (1 equiv), salicylaldehyde (2 equiv) and ammonium acetate (5 equiv) were added into glacial acetic acid with strong stirring at 140 °C to obtain the 4,7-diphenyl-1,10-phenanthroline (Ph_2Phen) ligand after 3 h. The above iridium(III) dimer $[(fpyd)_2Ir(\mu\text{–}Cl)]_2$ (1 equiv) and the pure ligand Ph_2Phen (2 equiv), as well as potassium hexafluorophosphate (1 equiv) were added together in a mixed solvent containing dichloromethane and methanol (v/v = 4/1). Next the mixture was refluxed at 85 °C in a dark N_2 atmosphere for 24 h. Subsequently, the reaction mixture was filtered, washed with the mixed solution of dichloromethane and ethanol, and then dryed with rotary evaporator. The obtained solid product (155.0 mg, 0.1366 mmol) was dissolved in dichloromethane (1 mL), after filtration, after that 1 mL of buffer layer ($V_{dichloromethane}/V_{n\text{-}hexane}$ = 1/1) was added, and finally 3 mL of n-hexane was added. And then yellow block crystals were obtained after one week at room temperature in dark with a yield of 74.4079 mg (48 % based Ir). **Anal. Calcd.** for $C_{47}H_{30}Cl_2F_{10}IrN_4P$: C, 49.70 %; H, 2.64 %; N, 4.93 %. Found C, 49.23 %; H, 2.54 %; N, 4.81 %.

2 Experimental details

The crystal structure determination was carried on a Bruker APEX–II diffractometer. The structure was solved by Direct Methods and refined using the SHELX software.[3] All the non-hydrogen atoms were determined with anisotropic thermal displacement coefficients. All of the hydrogen atoms were added by theoretical method and isotropic displacement parameters were given (U_{iso} = 1.2 U_{eq}, U_{eq} is the equivalent isotropic displacement parameter of the parent atom).[6]

3 Comment

Due to the unique luminescent properties, cyclometalated iridium(III) complexes have potential applications in several fields, such as organic light-emitting diodes (OLEDs), light-emitting electro-chemical cells (LECs), biosensing, photocatalysis, and nonlinear optics.[5,7,8] These findings greatly expand the boundaries of the application of cyclometalated iridium(III) complexes. It is known that the incorporation of different substituents on the chelating ligands and/or auxiliary ligands of cyclometalated iridium(III) complexes, could efficiently modify their properties and applications.[9–11] Previous research revealed that the π orbitals of C^N chelating ligands and the *d* orbitals of Ir(III) centers mainly affect the highest occupied molecular orbital (HOMO) of the complexes.[12] Therefore, the introduction of electron withdrawing groups on the chelating ligand will lower the HOMO energy level of the system. In addition, the modification of conjugation via the auxiliary N^N ligands helps to elaborate the influences of electron effects on the photophysical properties of the corresponding cyclometalated iridium(III) complexes.[13–15] Herein, Ph_2Phen with large π-conjugation structure has been employed as the auxiliary N^N ligand to synthesize cyclometalated iridium(III) complexes, while F substituents were introduced as electron withdrawing group of chelating ligand fpyd.

The synthesized iridium(III) complex crystallizes in the monoclinic crystal system. The asymmetric unit of the title structure is composed of one Ir^{3+} cation, one Ph_2Phen ligand, two fpyd ligands, one PF_6^- anion, and one dichloromethane solvent molecule (see the Figure). The Ir(III) center is 6-coordinated by four nitrogen atoms and two carbon atoms from the pyridine rings of both C^N and N^N ligands, forming an octahedral spatial configuration. The Ir–C bond lengths are 2.005(7) Å and 2.010(6) Å, while the distances of Ir–N range from 2.024(6) Å to 2.138(4) Å, which are comparable with similar structures.[16] The cationic main structures are further extended into a three-dimensional supramolecular structure by intermolecular hydrogen bonding, where the hydrogen bonds are formed by the H atoms on the chelating ligands fpyd with the F atoms of the PF_6^- anions.

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