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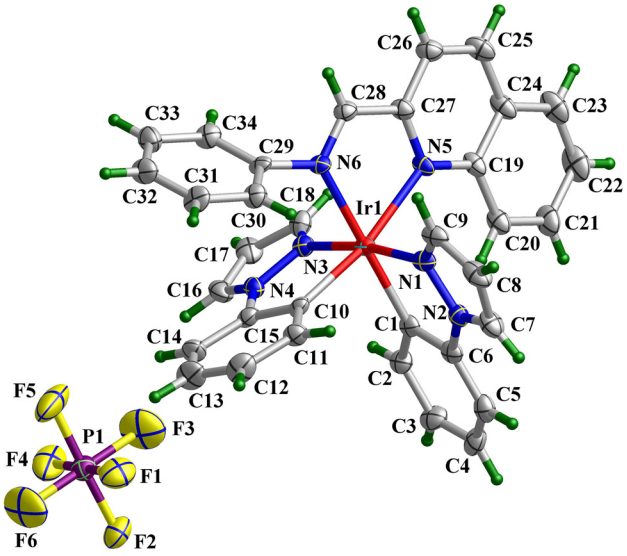
Crystal structure of (2-phenylimino methylquinoline-κ^2N,N')-bis(1–phenylpyrazole-κ^2C,N)-iridium(III) hexafluorophosphate, $C_{34}H_{26}F_6IrN_6P$



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Abstract

$C_{34}H_{26}F_6IrN_6P$, monoclinic, $P2_1/c$ (no. 4), a = 11.929(2) Å, b = 12.653(3) Å, c = 21.707(4) Å, β = 105.48(3)°, V = 3157.5(12) Å^3, Z = 4, $R_{gt}(F)$ = 0.0241, w$R_{ref}(F^2)$ = 0.0461, T = 293 K.

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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.

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Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.25 × 0.22 × 0.18 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	4.35 mm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
θ_{max}, completeness:	25.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	20,822, 5775, 0.027
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5448
N(param)$_{refined}$:	433
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4], PLATON [5]

1 Source of materials

All the reagents were A. R. grade commercially available and used as received without further purification. The cyclometalated chloro-bridged iridium(III) dimer, $[(ppz)_2Ir(m–Cl)]_2$ (ppz = 1–phenylpyrazole), was synthesized following the reported literature procedures [6] by heating $IrCl_3{\cdot}3H_2O$ (1 equiv) and 1–phenylpyrazole (2.3 equiv) in a mixed solution of 2-ethoxyethanol and water (v/v = 3/1) at 135 °C. 149.3 mg quinoline-2-formaldehyde (0.95 mmol) was added into dichloromethane (20 mL) with strong stirring, and then aniline (0.95 mmol) was added dropwise to obtain 2-phenylimino methylquinoline (pmmq). The synthesized iridium(III) dimer $[(ppz)_2Ir(m–Cl)]_2$ (200.0 mg, 0.19 mmol) and ligand 2-phenylimino methylquinoline (90.1 mg, 0.388 mmol) were added together to a mixed solvent containing methanol (8 mL) and dichloromethane (32 mL). Subsequently, potassium hexafluorophosphate powder (37.6 mg, 0.19 mmol) was added, heated to 135 °C, and refluxed in a dark N_2 atmosphere for 24 h. Dissolve the obtained solid product in dichloromethane (1 mL), after filtration, 0.5 mL of buffer layer ($V_{dichloromethane}/V_{n\text{-}hexane}$ = 1/1) was added, and finally 3 mL of n-hexane was added. Red crystals were obtained after a week at room temperature in dark with a yield of 40 mg (43 % based Ir). **Anal. Calcd**. for $C_{34}H_{26}F_6IrN_6P$: C, 47.72 %; H, 3.06 %; N, 9.82 %. Found C, 47.69 %; H, 3.01 %; N, 9.84 %. **IR** (KBr, cm^{-1}): 3057(W), 1662(s), 1592(s), 1547(s), 1514(s), 1492(s), 1411(s), 1020(m) (pyridine: C=N), 964(m), 845(w), 739(w), 692(w), 545(m).

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ir1	0.32696 (2)	0.71986 (2)	0.09915 (2)	0.01607 (4)
N1	0.4347 (2)	0.8041 (2)	0.16951 (12)	0.0203 (6)
N2	0.5384 (2)	0.7566 (2)	0.19722 (13)	0.0208 (6)
N3	0.2281 (2)	0.6153 (2)	0.03720 (12)	0.0198 (6)
N4	0.1854 (2)	0.5345 (2)	0.06583 (13)	0.0210 (6)
N5	0.3496 (2)	0.8318 (2)	0.02385 (12)	0.0189 (6)
N6	0.1826 (2)	0.8237 (2)	0.08551 (12)	0.0174 (6)
C1	0.4688 (3)	0.6248 (3)	0.11813 (15)	0.0189 (7)
C2	0.4868 (3)	0.5281 (3)	0.09188 (16)	0.0230 (7)
H2A	0.4291	0.5009	0.0579	0.028*
C3	0.5888 (3)	0.4709 (3)	0.11513 (17)	0.0297 (8)
H3A	0.5982	0.4067	0.0962	0.036*
C4	0.6760 (3)	0.5076 (3)	0.16554 (17)	0.0295 (8)
H4A	0.7441	0.4688	0.1803	0.035*
C5	0.6621 (3)	0.6028 (3)	0.19435 (16)	0.0256 (8)
H5A	0.7197	0.6284	0.2289	0.031*
C6	0.5597 (3)	0.6587 (3)	0.17020 (15)	0.0205 (7)
C7	0.5985 (3)	0.8146 (3)	0.24781 (16)	0.0293 (8)
H7A	0.6716	0.7989	0.2743	0.035*
C8	0.5319 (3)	0.9003 (3)	0.25272 (17)	0.0312 (9)
H8A	0.5506	0.9538	0.2831	0.037*
C9	0.4305 (3)	0.8915 (3)	0.20340 (16)	0.0241 (8)
H9A	0.3690	0.9393	0.1952	0.029*
C10	0.2748 (3)	0.6264 (2)	0.16138 (15)	0.0184 (7)
C11	0.2936 (3)	0.6386 (3)	0.22718 (16)	0.0238 (7)
H11A	0.3453	0.6900	0.2485	0.029*
C12	0.2363 (3)	0.5751 (3)	0.26139 (18)	0.0334 (9)
H12A	0.2480	0.5857	0.3050	0.040*
C13	0.1621 (3)	0.4961 (3)	0.23077 (19)	0.0362 (9)
H13A	0.1233	0.4547	0.2539	0.043*
C14	0.1449 (3)	0.4784 (3)	0.16627 (18)	0.0301 (9)
H14A	0.0966	0.4242	0.1456	0.036*
C15	0.2020 (3)	0.5436 (3)	0.13310 (16)	0.0212 (7)
C16	0.1357 (3)	0.4611 (3)	0.02180 (18)	0.0296 (8)
H16A	0.1013	0.3984	0.0296	0.036*
C17	0.1452 (3)	0.4958 (3)	−0.03634 (18)	0.0319 (9)
H17A	0.1183	0.4620	−0.0756	0.038*
C18	0.2034 (3)	0.5922 (3)	−0.02466 (16)	0.0247 (8)
H18A	0.2223	0.6342	−0.0556	0.030*
C19	0.4307 (3)	0.8339 (3)	−0.01116 (15)	0.0211 (7)
C20	0.5198 (3)	0.7575 (3)	−0.00041 (16)	0.0249 (8)
H20A	0.5255	0.7070	0.0314	0.030*
C21	0.5981 (3)	0.7572 (3)	−0.03649 (17)	0.0315 (9)
H21A	0.6560	0.7060	−0.0291	0.038*
C22	0.5922 (3)	0.8329 (3)	−0.08431 (18)	0.0384 (10)
H22A	0.6456	0.8312	−0.1086	0.046*
C23	0.5087 (3)	0.9087 (3)	−0.09527 (17)	0.0344 (9)
H23A	0.5058	0.9590	−0.1269	0.041*
C24	0.4255 (3)	0.9121 (3)	−0.05891 (16)	0.0258 (8)
C25	0.3377 (3)	0.9891 (3)	−0.06961 (17)	0.0300 (8)
H25A	0.3341	1.0418	−0.0999	0.036*
C26	0.2579 (3)	0.9858 (3)	−0.03506 (16)	0.0260 (8)
H26A	0.1988	1.0359	−0.0415	0.031*
C27	0.2660 (3)	0.9058 (3)	0.01035 (15)	0.0214 (7)
C28	0.1763 (3)	0.8979 (3)	0.04485 (15)	0.0210 (7)
H28A	0.1155	0.9463	0.0372	0.025*
C29	0.0874 (3)	0.8097 (2)	0.11386 (15)	0.0191 (7)
C30	0.1062 (3)	0.8151 (3)	0.17928 (16)	0.0246 (8)
H30A	0.1796	0.8322	0.2052	0.029*
C31	0.0159 (3)	0.7952 (3)	0.20621 (16)	0.0264 (8)
H31A	0.0287	0.7972	0.2504	0.032*
C32	−0.0928 (3)	0.7723 (3)	0.16789 (18)	0.0310 (8)
H32A	−0.1536	0.7593	0.1862	0.037*
C33	−0.1124 (3)	0.7682 (3)	0.10241 (18)	0.0316 (9)
H33A	−0.1865	0.7533	0.0767	0.038*
C34	−0.0217 (3)	0.7865 (3)	0.07464 (16)	0.0253 (8)
H34A	−0.0342	0.7832	0.0305	0.030*
P1	0.07162 (8)	0.15347 (8)	0.13115 (4)	0.0276 (2)
F1	0.1301 (2)	0.22754 (18)	0.19060 (10)	0.0464 (6)
F2	0.18255 (17)	0.07723 (17)	0.14869 (10)	0.0403 (5)
F3	0.1319 (3)	0.2219 (2)	0.08776 (12)	0.0666 (8)
F4	0.0124 (2)	0.0802 (2)	0.07213 (12)	0.0602 (8)
F5	−0.0365 (2)	0.2311 (2)	0.11262 (14)	0.0731 (9)
F6	0.0133 (3)	0.0864 (2)	0.17514 (15)	0.0731 (9)

2 Experimental details

The structure was solved by Direct Methods and refined using the SHELX software [3]. 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) [5].

3 Comment

Cyclometalated iridium(III) complexes have received enormous interests, due to their potential applications in multidisciplinary areas such as organic light-emitting diodes (OLEDs), light-emitting electro-chemical cells (LECs), biosensing, photocatalysis, and nonlinear optics, etc. [7–10]. The strong spin–orbit coupling induced by the Ir(III) ion results in efficient intersystem crossing (ISC) and promotes triplet excited-state formation, which are intrinsically related to aforementioned applications. Considerable efforts in this field are focused on the structural modifications of Ir(III) complexes to obtain desirable optical or electronic properties, especially for OLEDs and LECs applications [11, 12]. Recently, the design and synthesis of cyclometalated Ir(III) complexes with nonlinear optical properties has also been extensively developed [13]. For example, many researchers studied the second-order nonlinear optical properties [14],

the reverse saturable absorption (RSA) [15], the two-photon and three-photon absorption (TPA) of Ir(III) complexes [16]. In this context, iminoquinoline ligand with *p*-conjugation structure has been employed as ancillary ligand into the preparation of cyclometalated Ir(III) complex.

The crystal structure consists of a Ir^{3+} cation, one pmmq ligand, two ppz ligands, and one PF_6^- anion (see the Figure). The Ir(III) center is 6-coordinated by four N atoms and two C atoms from two ppz ligands and the ancillary pmmq ligand, forming an octahedral plane. The Ir–C bond lengths are 2.027(3) Å and 2.014(3) Å, respectively, while the bond lengths of Ir–N range from 2.018(3) Å to 2.233(3) Å. The bond angles of N–Ir–N range from 75.97(10)° to 171.0(1)°, while the value for C–Ir–N fall in the range of 80.25(12)° and 176.16(11)° [17]. Due to the semi-rigid structure of iminoquinoline ligand, it forms a five membered chelating ring with the Ir(III) center through the bidentate chelation of quinoline nitrogen and imino nitrogen.

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

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