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Crystal structure of (2-(2-pyridine)-benzimidazole- κ^2 N,N')-bis(1-phenylpyrazole- κ^2 C,N)iridium(III) hexafluorophosphate, $C_{30}H_{22}F_6IrN_7P$

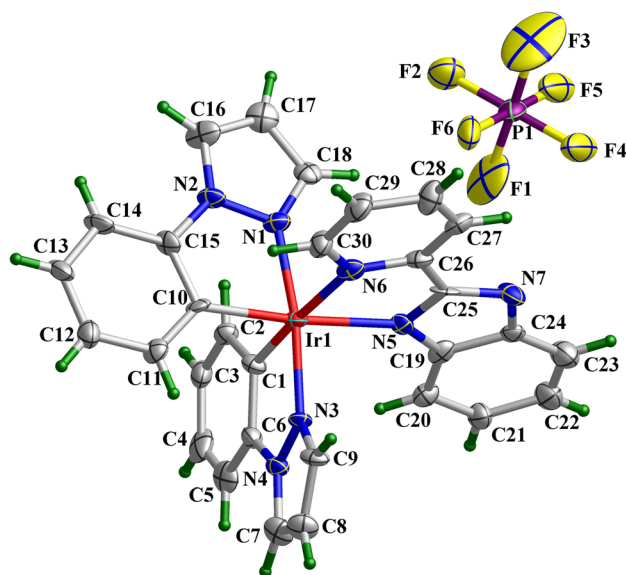


Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.23 × 0.20 × 0.18 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	9.97 mm ⁻¹
Diffractometer, scan mode:	Bruker P4, ω
θ_{max} , completeness:	66.6°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	27100, 5184, 0.175
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3683
$N(param)_{refined}$:	406
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, $[(ppz)_2Ir(\mu-Cl)]_2$ (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. 540.70 mg *o*-phenylenediamine was dissolved in 30 mL of ethanol with the help of sonication. After that, 0.48 mL of pyridine-2-formaldehyde was added to the above solution and reacted at 80 °C for 2 h to obtain 839.41 mg 2-(2-pyridine)-benzimidazole (bzip). The synthesized iridium(III) dimer $[(ppz)_2Ir(\mu-Cl)]_2$ (103.00 mg, 0.1 mmol), auxiliary ligand 2-(2-pyridine)-benzimidazole (39.04 mg, 0.2 mmol), and potassium hexafluorophosphate (36.81 mg, 0.2 mmol) were added together to a mixed solvent containing dichloromethane (50 mL) and methanol (10 mL). Subsequently, the mixture was heated to 85 °C and refluxed in a dark N_2 atmosphere for 24 h to obtain the target compound. After filtration, the obtained solid product was dissolved in chloroform (10 mL), and then 10 mL of buffer solution ($V_{chloroform}/V_{n-hexane} = 1/1$) and 20 mL of *n*-hexane were added successively. Under the diffusion effect of solution, bright yellow block crystals were obtained after a week at room temperature in the dark with a yield of

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Abstract

$C_{30}H_{22}F_6IrN_7P$, monoclinic, $P2_1/c$ (no. 4), $a = 8.8876(3)$ Å, $b = 32.8428(9)$ Å, $c = 10.5010(3)$ Å, $\beta = 106.623(2)^\circ$, $V = 2937.07(16)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0572$, $wR_{ref}(F^2) = 0.1171$, $T = 293$ 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 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ir1	0.62974 (5)	0.14409 (2)	0.94445 (4)	0.02000 (13)
N1	0.5291 (10)	0.1719 (2)	0.7693 (8)	0.0266 (19)
N2	0.5735 (10)	0.2118 (2)	0.7644 (8)	0.027 (2)
N3	0.7214 (9)	0.1238 (2)	1.1326 (8)	0.0211 (18)
N4	0.6309 (10)	0.1313 (2)	1.2157 (8)	0.0227 (18)
N5	0.5353 (9)	0.0851 (2)	0.8864 (8)	0.0229 (18)
N6	0.7945 (10)	0.1173 (2)	0.8476 (8)	0.0267 (19)
N7	0.5458 (11)	0.0275 (2)	0.7781 (9)	0.031 (2)
C1	0.4662 (12)	0.1638 (3)	1.0255 (9)	0.024 (2)
C2	0.3305 (11)	0.1871 (3)	0.9693 (10)	0.024 (2)
H2	0.3094	0.1961	0.8820	0.029*
C3	0.2283 (12)	0.1968 (3)	1.0416 (11)	0.033 (3)
H3	0.1382	0.2116	1.0009	0.040*
C4	0.2554 (13)	0.1852 (4)	1.1721 (12)	0.043 (3)
H4	0.1843	0.1918	1.2189	0.052*
C5	0.3892 (13)	0.1637 (3)	1.2317 (11)	0.033 (3)
H5	0.4122	0.1565	1.3208	0.040*
C6	0.4879 (12)	0.1532 (3)	1.1598 (10)	0.026 (2)
C7	0.7073 (13)	0.1189 (3)	1.3391 (10)	0.032 (3)
H7	0.6709	0.1209	1.4136	0.038*
C8	0.8461 (14)	0.1033 (3)	1.3358 (10)	0.035 (3)
H8	0.9226	0.0920	1.4068	0.042*
C9	0.8531 (13)	0.1071 (3)	1.2068 (9)	0.026 (2)
H9	0.9373	0.0993	1.1765	0.031*
C10	0.7326 (11)	0.1993 (3)	0.9822 (9)	0.022 (2)
C11	0.8407 (12)	0.2141 (3)	1.0974 (10)	0.026 (2)
H11	0.8795	0.1966	1.1688	0.031*
C12	0.8908 (13)	0.2537 (3)	1.1079 (11)	0.034 (3)
H12	0.9597	0.2627	1.1872	0.041*
C13	0.8411 (13)	0.2803 (3)	1.0032 (11)	0.035 (3)
H13	0.8810	0.3067	1.0104	0.042*
C14	0.7324 (14)	0.2680 (3)	0.8877 (11)	0.035 (3)
H14	0.6935	0.2860	0.8175	0.042*
C15	0.6825 (12)	0.2272 (3)	0.8800 (9)	0.025 (2)
C16	0.4929 (14)	0.2281 (3)	0.6456 (10)	0.035 (3)
H16	0.5018	0.2548	0.6184	0.043*
C17	0.3981 (14)	0.1992 (3)	0.5737 (10)	0.037 (3)
H17	0.3289	0.2021	0.4889	0.045*
C18	0.4250 (12)	0.1642 (3)	0.6525 (10)	0.029 (2)
H18	0.3772	0.1391	0.6270	0.034*
C19	0.4173 (12)	0.0606 (3)	0.9013 (9)	0.026 (2)
C20	0.3108 (12)	0.0650 (3)	0.9730 (9)	0.028 (2)
H20	0.3075	0.0887	1.0209	0.033*
C21	0.2087 (13)	0.0331 (3)	0.9712 (11)	0.034 (3)
H21	0.1364	0.0356	1.0196	0.041*
C22	0.2094 (15)	−0.0027 (4)	0.8999 (12)	0.043 (3)
H22	0.1371	−0.0232	0.8994	0.051*
C23	0.3168 (14)	−0.0074 (4)	0.8308 (12)	0.042 (3)
H23	0.3186	−0.0312	0.7833	0.050*
C24	0.4225 (12)	0.0233 (3)	0.8320 (10)	0.025 (2)
C25	0.6120 (12)	0.0643 (3)	0.8141 (9)	0.023 (2)
C26	0.7501 (12)	0.0812 (3)	0.7880 (10)	0.027 (2)
C27	0.8353 (12)	0.0625 (3)	0.7150 (10)	0.031 (2)
H27	0.8022	0.0375	0.6758	0.037*
C28	0.9691 (13)	0.0801 (4)	0.6984 (11)	0.038 (3)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
H28	1.0275	0.0673	0.6494	0.045*
C29	1.0139 (14)	0.1182 (4)	0.7586 (12)	0.038 (3)
H29	1.1026	0.1314	0.7494	0.046*
C30	0.9225 (12)	0.1357 (3)	0.8323 (10)	0.031 (2)
H30	0.9514	0.1609	0.8719	0.037*
P1	0.2901 (3)	0.06098 (9)	0.4193 (3)	0.0358 (7)
F1	0.2325 (10)	0.0651 (3)	0.5470 (9)	0.085 (3)
F2	0.2244 (9)	0.1054 (2)	0.3800 (8)	0.059 (2)
F3	0.3549 (14)	0.0581 (4)	0.2948 (9)	0.127 (5)
F4	0.3559 (9)	0.0162 (2)	0.4594 (11)	0.091 (3)
F5	0.1287 (10)	0.0428 (2)	0.3375 (12)	0.106 (4)
F6	0.4545 (7)	0.0787 (2)	0.5011 (7)	0.0501 (18)

65.40 mg (49 % based Ir). Anal. Calcd. for $\text{C}_{30}\text{H}_{22}\text{F}_6\text{IrN}_7\text{P}$: C, 44.06 %; H, 2.71 %; N, 11.99 %. Found C, 44.35 %; H, 2.92 %; N, 11.46 %. IR (KBr, cm^{-1}): 3049(m), 2924(s), 1661(m), 1595(m), 1468(s), 1433(s), 1259(m), 1053(m), 844(vs), 747(s), 552(s).

2 Experimental details

The structure was solved by Direct Methods and refined using the SHELX software [3]. All the hydrogen atoms were added by theoretical method and isotropic displacement parameters were given ($U_{\text{iso}} = 1.2 U_{\text{eq}}$, U_{eq} is the equivalent isotropic displacement parameter of the parent atom) [5].

3 Comment

The design and construction of cyclometalated iridium(III) complexes, which were assembled from iridium ions and organic conjugate ligands, have attracted much attention because of their favorable properties arising from strong spin-orbit coupling induced by the Ir(III) ion [7–10]. The cyclometalated Ir(III) complex is usually formed by the coordination of C–N chelate ligand and N–N auxiliary ligand with Ir(III) atom, and has a hexahedral spatial configuration [11, 12]. The p^* orbital of the N–N auxiliary ligand in the cyclometalated Ir(III) complex is the main contributor to the lowest unoccupied molecular orbital (LUMO), while the p orbital of the C–N chelate ligand and the d orbital of the Ir(III) center mainly affect the highest occupied molecular orbital (HOMO) [13, 14]. The conjugation adjustment of N–N auxiliary ligands or the introduction of electron withdrawing substituents can reduce the LUMO energy level of the system, while the introduction of electron donating substituents can increase the LUMO energy level [15]. Among the N–N auxiliary ligands, the Schiff base

ligands which contain --RC=N-- characteristic groups with lone pair electrons on the N atoms have strong ability of coordination with the metal ions and p -conjugation structure. In this context, we selected the 2-(2-pyridine)-benzimidazole (bzip) as the auxiliary ligand in the preparation of cyclometalated Ir(III) complex.

The crystal structure consists of one Ir^{3+} cation, two ppz chelate ligands, one bzip auxiliary ligand, and one $[\text{PF}_6]^-$ counter anion (see the Figure). The Ir(III) center is 6-coordinated by four N atoms and two C atoms, in which two N atoms and two C atoms come from the ppz chelate ligands while the rest two N atoms from the bzip ancillary ligand, forming an octahedral plane. The metal-carbon bond lengths (Ir–C) are 1.991(10) Å and 2.017(10) Å, respectively, while the distances of Ir–N bonds range from 2.019(8) Å to 2.192(9) Å. The bond angles about the Ir(III) ion range from $76.3(3)^\circ$ to $174.4(4)^\circ$, and these values match with the previously reported cyclometalated Ir(III) complexes [16]. There are C–H ... F hydrogen bonding interactions.

Author contribution: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

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References

1. BRUKER. *SAINT, APEX2 and SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2009.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, 42, 339–341.
3. Sheldrick G. M. SHELXT-integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, A71, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, C71, 3–8.
5. Spek A. L. Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.* 2003, 36, 7–13.
6. Kwon T. H., Cho H. S., Kim M. K., Kim J. W., Kim J. J., Lee K. H., Park S. J., Shin I. S., Kim H., Shin D. M., Chung Y. K., Hong J. I. Color tuning of cyclometalated iridium complexes through modification of phenylpyrazole derivatives and ancillary ligand based on ab initio calculations. *Organometallics* 2005, 24, 1578–1585.
7. Zhao Q., Huang C. H., Li F. Y. Phosphorescent heavy-metal complexes for bioimaging. *Chem. Soc. Rev.* 2011, 40, 2508–2524.
8. Liu J. L., Liu Y., Liu Q., Li C. Y., Sun L. N., Li F. Y. Iridium(III) complex-coated nanosystem for ratiometric upconversion luminescence bioimaging of cyanide anions. *J. Am. Chem. Soc.* 2011, 133, 15276–15279.
9. Sarma M., Chatterjee T., Bodapati R., Krishnakanth K. N., Hamad S., Rao V., Das S. K. Cyclometalated iridium(III) complexes containing $\kappa^2,4,4'$ -p-conjugated $\kappa^2,2,2'$ -bipyridine derivatives as the ancillary ligands: synthesis, photophysics, and computational studies. *Inorg. Chem.* 2016, 55, 3530–3540.
10. Sun W. F., Pei C., Lu T., Cui P., Li Z., McCleese C., Fang Y., Kilina S., Song Y., Burda C. Reverse saturable absorbing cationic iridium(III) complexes bearing the 2-(2-quinolinyl)quinoxaline ligand: effects of different cyclometalating ligands on linear and nonlinear absorption. *J. Mater. Chem. C* 2016, 4, 5059–5072.
11. Neve F., Deda M. L., Crispini A., Bellusci A., Puntoriero F., Campagna S. Cationic cyclometalated iridium luminophores: photophysical, redox, and structural characterization. *Organometallics* 2004, 23, 5856–5863.
12. Costa R. D., Monti F., Accorsi G., Barbieri A., Bolink H. J., Orti E., Armaroli N. Photophysical properties of charged cyclometalated Ir(III) complexes: a joint theoretical and experimental study. *Inorg. Chem.* 2011, 50, 7229–7238.
13. Nazeeruddin M. K., Wehrg R. T., Zhou Z., Klein C., Wang Q., De Angelis F., Fantacci S., Gratzel M. Efficient green-blue-light-emitting cationic iridium complex for light-emitting electrochemical cells. *Inorg. Chem.* 2006, 45, 9245–9250.
14. Sunesh C. D., Mathai G., Choe Y. Constructive effects of long alkyl chains on the electroluminescent properties of cationic iridium complex-based light-emitting electrochemical cells. *ACS Appl. Mater. Interfaces* 2014, 6, 17416–17425.
15. Skorka L., Filapek M., Zur L., Malecki J. G., Pisarski W., Olejnik M., Danikiewicz W., Krompiec S. Highly phosphorescent cyclometalated iridium(III) complexes for optoelectronic applications: fine tuning of the emission wavelength through ancillary ligands. *J. Phys. Chem. C* 2016, 120, 7284–7294.
16. Liu B. Q., Lystrom L., Brown S. L., Hobbie E. K., Kilina S., Sun W. F. Impact of benzannulation site at the diimine (NN) ligand on the excited-state properties and reverse saturable absorption of biscyclometalated iridium(III) complexes. *Inorg. Chem.* 2019, 58, 5483–5493.