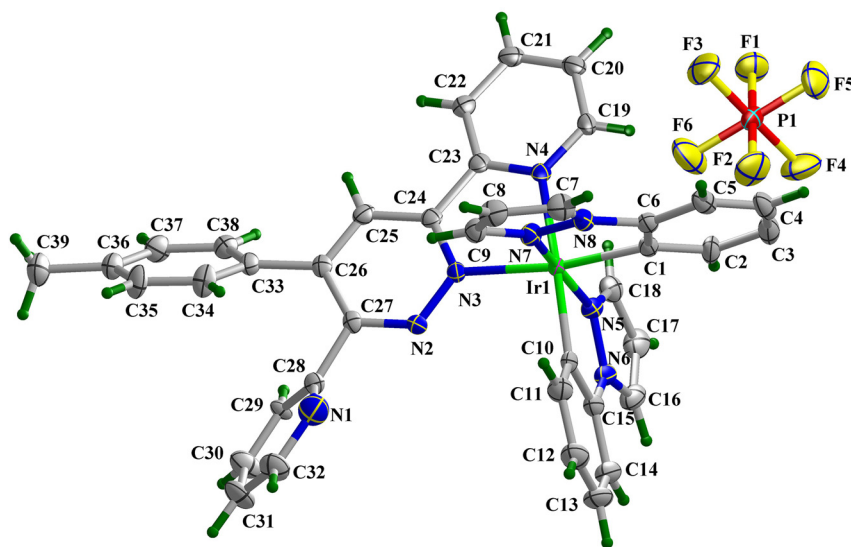


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Crystal structure of (3,6-di(2-pyridyl)-4-methylphenyl pyridazine- k^2N,N')-bis(1-phenylpyrazole- k^2C,N) iridium(III) hexafluorophosphate, $C_{39}H_{29}F_6IrN_8P$



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Abstract

$C_{39}H_{29}F_6IrN_8P$, orthorhombic, *Pbca* (no. 61), $a = 19.6205(7)$ Å, $b = 16.2026(6)$ Å, $c = 23.0700(8)$ Å, $V = 7334.0(5)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0258$, $wR_{ref}(F^2) = 0.0611$, $T = 293$ 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.

1 Source of materials

All the reagents were A. R. grade commercially available and used as received without any further purification. The

Table 1: Data collection and handling.

Crystal:	Red block
Size:	0.23 × 0.20 × 0.18 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ :	3.76 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	26.4°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	23365, 7498, 0.017
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6340
$N(param)_{refined}$:	497
Programs:	Bruker, ¹ Olex2, ² SHELX, ^{3,4} PLATON ⁵

cyclometalated chloro-bridged iridium(III) dimer, [(ppy)₂Ir(μ -Cl)]₂ (ppy = 1-phenyl-pyrazole), was synthesized following the reported literature procedures⁶ by heating IrCl₃ · 3H₂O (1 equiv) and 1-phenyl-pyrazole (2.5 equiv) in a mixed solution of water and ethylene glycol ether (v/v = 1/4) at 135 °C under the nitrogen atmosphere. Tetrazine (1 equiv) and 4-ethynyl toluene (1 equiv) were added into toluene with strong stirring at 140 °C to obtain 3,6-di(2-pyridyl)-4-methylphenyl pyridazine (DpTz-MPh) after 144 h. The iridium(III) dimer [(ppy)₂Ir(μ -Cl)]₂ (1 equiv) and DpTz-MPh ligand (1 equiv), as well as potassium hexafluorophosphate (1 equiv) were added together in a mixed solvent containing dichloromethane

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Ir1	0.37036 (2)	0.60189 (2)	0.29156 (2)	0.01751 (5)
N1	0.22406 (19)	0.4377 (2)	0.47339 (15)	0.0435 (9)
N2	0.26147 (13)	0.55758 (16)	0.38027 (11)	0.0206 (6)
N3	0.29082 (14)	0.62067 (17)	0.35161 (11)	0.0200 (6)
N4	0.36202 (13)	0.73302 (16)	0.29553 (11)	0.0192 (5)
N5	0.30704 (15)	0.59503 (18)	0.22326 (12)	0.0246 (6)
N6	0.29107 (15)	0.51631 (18)	0.20603 (12)	0.0264 (6)
N7	0.44084 (14)	0.59431 (17)	0.35469 (12)	0.0233 (6)
N8	0.50615 (14)	0.58543 (17)	0.33565 (13)	0.0240 (6)
C1	0.45581 (18)	0.5980 (2)	0.24255 (15)	0.0240 (7)
C2	0.4635 (2)	0.6041 (2)	0.18230 (16)	0.0327 (8)
H2	0.4249	0.6078	0.1590	0.039*
C3	0.5277 (2)	0.6047 (2)	0.15656 (18)	0.0380 (9)
C4	0.5854 (2)	0.5995 (2)	0.19105 (19)	0.0390 (10)
H4	0.6282	0.6005	0.1737	0.047*
C5	0.58060 (19)	0.5929 (2)	0.25060 (18)	0.0315 (8)
H5	0.6193	0.5894	0.2738	0.038*
C6	0.51565 (18)	0.5917 (2)	0.27446 (15)	0.0242 (7)
C7	0.54802 (19)	0.5704 (2)	0.38079 (17)	0.0322 (8)
H7	0.5948	0.5618	0.3788	0.039*
C8	0.5093 (2)	0.5699 (2)	0.42982 (16)	0.0332 (8)
H8	0.5246	0.5613	0.4675	0.040*
C9	0.44248 (19)	0.5849 (2)	0.41237 (15)	0.0275 (8)
H9	0.4049	0.5878	0.4369	0.033*
C10	0.36508 (17)	0.4778 (2)	0.28343 (14)	0.0236 (7)
C11	0.3988 (2)	0.4151 (2)	0.31383 (17)	0.0307 (8)
H11	0.4273	0.4292	0.3445	0.037*
C12	0.3907 (2)	0.3326 (2)	0.29943 (19)	0.0395 (10)
H12	0.4145	0.2923	0.3198	0.047*
C13	0.3470 (2)	0.3097 (2)	0.2545 (2)	0.0419 (10)
H13	0.3410	0.2541	0.2456	0.050*
C14	0.3124 (2)	0.3691 (2)	0.22313 (18)	0.0373 (9)
H14	0.2832	0.3546	0.1930	0.045*
C15	0.32264 (18)	0.4514 (2)	0.23812 (15)	0.0267 (7)
C16	0.2519 (2)	0.5182 (3)	0.15780 (16)	0.0347 (9)
H16	0.2348	0.4729	0.1378	0.042*
C17	0.2422 (2)	0.5992 (3)	0.14404 (16)	0.0367 (9)
H17	0.2171	0.6196	0.1130	0.044*
C18	0.27700 (19)	0.6453 (2)	0.18531 (15)	0.0295 (8)
H18	0.2790	0.7026	0.1863	0.035*
C19	0.39876 (18)	0.7875 (2)	0.26440 (14)	0.0232 (7)
H19	0.4329	0.7677	0.2401	0.028*
C20	0.38781 (19)	0.8713 (2)	0.26708 (15)	0.0274 (7)
H20	0.4145	0.9073	0.2453	0.033*
C21	0.33658 (19)	0.9014 (2)	0.30254 (16)	0.0291 (8)
H21	0.3283	0.9579	0.3050	0.035*
C22	0.29799 (19)	0.8463 (2)	0.33416 (16)	0.0272 (7)
H22	0.2629	0.8653	0.3577	0.033*
C23	0.31181 (17)	0.7628 (2)	0.33061 (14)	0.0215 (7)
C24	0.27447 (16)	0.6995 (2)	0.36371 (14)	0.0208 (6)
C25	0.22658 (17)	0.7179 (2)	0.40680 (15)	0.0243 (7)
H25	0.2147	0.7724	0.4142	0.029*
C26	0.19725 (16)	0.6554 (2)	0.43806 (13)	0.0209 (7)
C27	0.21670 (16)	0.5739 (2)	0.42189 (13)	0.0202 (6)
C28	0.18467 (17)	0.4999 (2)	0.44863 (14)	0.0232 (7)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
C29	0.11687 (15)	0.49932 (19)	0.44710 (14)	0.0189 (6)
H29	0.0927	0.5421	0.4298	0.023*
C30	0.0848 (2)	0.4357 (3)	0.47106 (19)	0.0405 (10)
H30	0.0375	0.4342	0.4696	0.049*
C31	0.1190 (2)	0.3709 (3)	0.49843 (19)	0.0431 (10)
H31	0.0950	0.3281	0.5159	0.052*
C32	0.1889 (2)	0.3720 (2)	0.49881 (17)	0.0370 (9)
H32	0.2129	0.3290	0.5160	0.044*
C33	0.14951 (17)	0.6708 (2)	0.48611 (15)	0.0250 (7)
C34	0.1577 (2)	0.6310 (3)	0.53894 (16)	0.0351 (9)
H34	0.1948	0.5962	0.5447	0.042*
C35	0.1113 (2)	0.6428 (3)	0.58280 (16)	0.0387 (9)
H35	0.1176	0.6157	0.6180	0.046*
C36	0.0554 (2)	0.6939 (2)	0.57585 (17)	0.0368 (9)
C37	0.0474 (2)	0.7342 (2)	0.52331 (18)	0.0365 (9)
H37	0.0101	0.7688	0.5178	0.044*
C38	0.09407 (19)	0.7240 (2)	0.47878 (16)	0.0303 (8)
H38	0.0885	0.7524	0.4441	0.036*
C39	0.0046 (2)	0.7035 (3)	0.6244 (2)	0.0517 (12)
H39A	−0.0355	0.7306	0.6101	0.078*
H39B	0.0243	0.7360	0.6549	0.078*
H39C	−0.0074	0.6501	0.6392	0.078*
P1	0.37136 (5)	0.64473 (6)	0.57764 (4)	0.0311 (2)
F1	0.34213 (15)	0.55658 (15)	0.55790 (11)	0.0517 (7)
F2	0.39947 (16)	0.73218 (15)	0.59746 (12)	0.0567 (7)
F3	0.39538 (18)	0.60476 (16)	0.63710 (10)	0.0628 (8)
F4	0.34645 (17)	0.68291 (16)	0.51755 (12)	0.0610 (8)
F5	0.44202 (14)	0.62210 (18)	0.54876 (12)	0.0574 (7)
F6	0.29975 (15)	0.66653 (18)	0.60624 (15)	0.0703 (9)

and methanol (v/v = 2/1). The mixture was heated to 85 °C, then refluxed in a dark N_2 atmosphere for 24 h to obtain reddish solid products. The obtained solid product (137.5143 mg, 0.1446 mmol) was dissolved in dichloromethane (1 mL), after filtration, 0.5 mL of buffer layer ($V_{\text{dichloromethane}}/V_{\text{n-hexane}} = 1/1$) was added, and finally 3 mL of n-hexane was added. Red block crystals were obtained after 11 days at room temperature in dark with a yield of 73.91 mg (54 % based Ir). **Anal. Calcd.** for $C_{39}H_{29}F_6IrN_8P$: C, 49.41 %; H, 3.19 %; N, 11.82 %. Found C, 49.23 %; H, 3.34 %; N, 11.71 %. **IR** (KBr, ν/cm^{-1}): 3434(m), 3048(s), 1580(s), 1479(m), 1395(vs), 1020(m)(pyridine: C=N), 985(m), 795(m).

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 of the hydrogen atoms were added by theoretical method and isotropic displacement parameters were given ($U_{iso} = 1.2$ (1.5 for methyl hydrogen) U_{eq} , U_{eq} is the equivalent isotropic displacement parameter of the parent atom).⁵

3 Comment

Under the impetus of potential applications as functional materials, such as organic light-emitting diodes (OLEDs), light-emitting electro-chemical cells (LECs), biosensing, photocatalysis, and nonlinear optics, cyclometalated iridium(III) complexes have received enormous interests.^{6–8} As a result, considerable efforts in crystal engineering have been devoted to the design and synthesis of various kinds of cyclometalated iridium(III) complexes with diverse physical functions.^{9,10} Up to now, several synthetic strategies have been successfully applied in the construction of cyclometalated iridium(III) complexes.^{11,12} Among these, the construction of cyclometalated iridium(III) complexes based on versatile iridium(III) dimers has been regarded as an applicable approach.¹³ In addition, the modification of structures 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.^{14,15}

The asymmetric unit of the title structure consists of one Ir^{3+} cation, one DpTz-MPh ligand, two ppya 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 both pyrazole and pyridine rings, forming an octahedral spatial configuration. Two chelated ppya ligands are arranged perpendicular to each other with two N atoms residing in trans positions, whereas the cyclometalated carbon atoms are in cis positions. The Ir–C bond length is 2.023(3) Å, while the distances of Ir–N range from 2.010(3) Å to 2.133(3) Å, which are comparable with similar structures.¹⁶ The adjacent metal-organic structural units can be further extended into a three-dimensional supramolecular structure by hydrogen bonding, where the hydrogen bonds are formed by the H atoms on the chelated ligand ppya and auxiliary ligand DpTz-MPh with the F atoms of the PF_6^- anion.

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