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Crystal structure of 1-[3-(trifluoromethyl)cinnamoyl]-3-(pyridin-2-yl- κN)pyrazole- $\kappa^2 N$ -bis(2-phenylpyridinato- $\kappa^2 C, N$)iridium(III) hexafluorophosphate complex, $[C_{40}H_{28}F_3IrN_5O]PF_6$

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Abstract

$[C_{40}H_{28}F_3IrN_5O]PF_6$, monoclinic, $P2_1/c$ (no. 14), $a = 20.2282(19)$ Å, $b = 14.5095(11)$ Å, $c = 12.6091(10)$ Å, $\beta = 96.937(3)^\circ$, $V = 3673.7(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0498$, $wR_{ref}(F^2) = 0.1250$, $T = 107(2)$ K.

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The crystal structure is shown in the figure (hydrogen atoms are omitted for clarity). Table 1 contains crystallographic data and Table 2 shows the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Orange plate
Size:	0.30 × 0.18 × 0.11 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	3.77 mm ^{−1}
Diffractometer, scan mode:	Bruker D8 QUEST PHOTON 100, φ and ω -scans
θ_{max} , completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	112848, 9126, 0.182
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 6926
$N(param)_{refined}$:	496
Programs:	Bruker programs [1], SHELX [2], SHELXT [3], SHELXL [4] and Olex2 [5]

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Source of material

3-(Dimethylamino)-1-(2-pyridyl)-2-propen-1-one, hydrazine hydrate, 3-(trifluoromethyl)cinnamoyl chloride, iridium

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Ir1	0.22452(2)	0.42037(2)	0.46589(2)	0.02025(8)
P1	0.10114(10)	0.78265(12)	0.43177(14)	0.0346(4)
F1	0.4711(3)	0.5441(4)	−0.1143(4)	0.0725(11)
F2	0.5112(2)	0.6570(4)	−0.0172(4)	0.0638(10)
F3	0.4420(3)	0.6840(4)	−0.1540(4)	0.0725(11)
F4	0.1493(2)	0.7922(4)	0.5429(4)	0.0638(10)
F5	0.1008(3)	0.8932(3)	0.4195(4)	0.0665(10)
F6	0.0532(3)	0.7725(3)	0.3191(4)	0.0665(10)
F7	0.1022(2)	0.6740(3)	0.4440(4)	0.0509(11)
F8	0.1649(3)	0.7771(4)	0.3704(4)	0.0704(16)
F9	0.0364(3)	0.7871(5)	0.4928(4)	0.0777(18)
O1	0.4095(2)	0.6461(4)	0.5037(4)	0.0459(12)
N1	0.1617(2)	0.4429(3)	0.3292(4)	0.0225(10)
N2	0.2915(2)	0.3892(4)	0.5963(4)	0.0260(10)
N3	0.1432(2)	0.4576(3)	0.5522(4)	0.0232(10)
N4	0.2473(2)	0.5635(3)	0.5201(4)	0.0231(10)
N5	0.3060(3)	0.6123(4)	0.5394(4)	0.0273(11)
C1	0.1477(3)	0.5262(5)	0.2859(5)	0.0294(13)
H1	0.1670(10)	0.5792(5)	0.3213(7)	0.035*
C2	0.1057(3)	0.5376(6)	0.1906(5)	0.0389(16)
H2	0.0963(23)	0.5971(6)	0.1611(6)	0.047*
C3	0.0784(3)	0.4599(6)	0.1407(5)	0.0435(18)
H3	0.0508(8)	0.4651(4)	0.0743(2)	0.052*
C4	0.0906(3)	0.3745(5)	0.1863(5)	0.0388(16)
H4	0.0706(5)	0.3212(7)	0.1522(2)	0.047*
C5	0.1319(3)	0.3659(4)	0.2817(5)	0.0280(13)
C6	0.1484(3)	0.2813(4)	0.3409(5)	0.0305(14)
C7	0.1947(3)	0.2910(4)	0.4335(5)	0.0268(12)
C8	0.2114(4)	0.2122(4)	0.4949(6)	0.0365(15)
H8	0.2427(6)	0.2166(3)	0.5571(6)	0.044*
C9	0.1827(4)	0.1275(5)	0.4657(7)	0.0445(18)
H9	0.1947(8)	0.0745(2)	0.5079(1)	0.053*
C10	0.1368(4)	0.1197(5)	0.3760(7)	0.051(2)
H10	0.1170(9)	0.0616(4)	0.3567(8)	0.061*
C11	0.1196(4)	0.1961(5)	0.3144(6)	0.0412(17)
H11	0.0876(8)	0.1906(3)	0.2530(1)	0.049*
C12	0.2755(3)	0.3808(5)	0.6968(5)	0.0325(14)
H12	0.2301(9)	0.3864(2)	0.7087(1)	0.039*
C13	0.3228(4)	0.3645(5)	0.7822(5)	0.0387(16)
H13	0.3103(6)	0.3582(9)	0.8521(8)	0.046*
C14	0.3886(4)	0.3572(6)	0.7648(6)	0.0487(19)
H14	0.4223(2)	0.3467(9)	0.8227(5)	0.058*
C15	0.4045(4)	0.3651(6)	0.6619(6)	0.0476(19)
H15	0.4496(4)	0.3600(1)	0.6487(1)	0.057*
C16	0.3553(3)	0.3805(4)	0.5780(5)	0.0315(14)
C17	0.3651(3)	0.3856(5)	0.4643(5)	0.0327(14)
C18	0.3059(3)	0.3957(4)	0.3930(5)	0.0256(12)
C19	0.3113(4)	0.3906(4)	0.2832(5)	0.0326(14)
H19	0.2721(4)	0.3934(8)	0.2334(6)	0.039*
C20	0.3726(4)	0.3813(5)	0.2461(6)	0.0452(18)
H20	0.3752(6)	0.3780(1)	0.1715(2)	0.054*
C21	0.4304(4)	0.3769(6)	0.3182(7)	0.053(2)
H21	0.4725(1)	0.3738(6)	0.2922(9)	0.064*
C22	0.4271(4)	0.3769(6)	0.4260(7)	0.0485(19)
H22	0.4665(7)	0.3710(2)	0.4746(5)	0.058*

Table 2 (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C23	0.0857(3)	0.4111(4)	0.5534(5)	0.0248(12)
H23	0.0798(9)	0.3546(8)	0.5153(7)	0.030*
C24	0.0349(3)	0.4422(5)	0.6077(5)	0.0342(15)
H24	−0.0048(5)	0.4072(6)	0.6077(9)	0.041*
C25	0.0425(3)	0.5248(5)	0.6618(5)	0.0361(15)
H25	0.0077(6)	0.5477(4)	0.6989(4)	0.043*
C26	0.1008(3)	0.5739(5)	0.6618(5)	0.0320(14)
H26	0.1068(9)	0.6307(4)	0.6990(7)	0.038*
C27	0.1502(3)	0.5393(4)	0.6068(4)	0.0247(12)
C28	0.2125(3)	0.5862(4)	0.5992(5)	0.0246(12)
C29	0.2475(3)	0.6510(4)	0.6686(5)	0.0317(14)
H29	0.2329(7)	0.6793(6)	0.7296(9)	0.038*
C30	0.3062(3)	0.6640(4)	0.6293(5)	0.0345(14)
H30	0.3415(3)	0.7026(2)	0.6594(5)	0.041*
C31	0.3547(3)	0.6205(4)	0.4665(5)	0.0313(14)
C32	0.3323(3)	0.6062(4)	0.3529(5)	0.0319(14)
H32	0.2872(8)	0.5906(2)	0.3301(9)	0.038*
C33	0.3752(3)	0.6149(4)	0.2821(5)	0.0319(13)
H33	0.4201(1)	0.6271(5)	0.3095(7)	0.038*
C34	0.3606(3)	0.6077(4)	0.1661(5)	0.0303(13)
C35	0.4135(3)	0.6175(5)	0.1033(5)	0.0347(14)
H35	0.4576(3)	0.6266(8)	0.1367(3)	0.042*
C36	0.4009(3)	0.6139(5)	−0.0062(5)	0.0352(14)
C37	0.3378(4)	0.5999(5)	−0.0565(6)	0.0411(16)
H37	0.3302(5)	0.5962(2)	−0.1321(8)	0.049*
C38	0.2852(4)	0.5913(5)	0.0030(7)	0.0440(17)
H38	0.2412(4)	0.5831(2)	−0.0317(2)	0.053*
C39	0.2966(3)	0.5945(5)	0.1137(6)	0.0348(15)
H39	0.2602(5)	0.5875(2)	0.1542(3)	0.042*
C40	0.4571(4)	0.6230(5)	−0.0728(6)	0.0429(17)

trichloride hydrate, 2-phenylpyridine, ammonium hexafluorophosphate and solvents were purchased and used without further purification.

The synthesis of the complex involves a total of four steps.

In the first step, 2-(1H-pyrazol-3-yl)pyridine (PyPzH) was synthesised according to the literature [5]. Subsequently, PyPzH was reacted with 3-(trifluoromethyl)cinnamoyl chloride to produce 1-[3-(trifluoromethyl)cinnamoyl]-3-(pyridin-2-yl)pyrazole (3-CF₃CnPyPz) [6–8].

Next, iridium trichloride hydrate (0.352 g, 1.0 mmol) with 2-phenylpyridine (0.388 g, 2.5 mmol) were dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and then refluxed for 24 h. The solution was cooled to room temperature, and the resulting yellow precipitate was collected by filtration through a Büchner funnel. The precipitate was washed with an excess of water and dried under vacuum. The crude cyclometalated chlorido-bridged dimer was directly used for the next step without purification.

In the final step, the aforementioned chlorido-bridged dimer (1.0 mmol) and 3-CF₃CnPyPz ligand (2.5 mmol) were

dissolved in dichloromethane (30 mL). The solution was refluxed under argon for 7 h. After cooling to room temperature, ammonium hexafluorophosphate (NH_4PF_6) in methanol (5 mL) was added and the mixture was stirred for 15 min. The solvent was then reduced under atmospheric pressure and the crude product was purified by column chromatography on silica gel with CH_2Cl_2/CH_3OH (98:2) as eluent. The complex was obtained as orange powders. Yield: 67%. **IR** (ATR, cm^{-1}): 1716 [$\nu(C=O)$], 1605 [$\nu(C=N_{pyridine})$], 1476 [$\nu(C=C_{pyridine})$], 832 [$\nu(PF_6)$]. **1H NMR** ($CDCl_3$, 400 MHz) δ (ppm): 8.35 (d, $J = 7.6$ Hz, 1H), 8.31 (d, $J = 3.2$ Hz, 1H), 8.16 (td, $J = 8.0$ Hz, 1H), 8.05 (d, $J = 5.6$ Hz, 1H), 8.02 (d, $J = 8.0$ Hz, 1H), 7.87–7.93 (m, 2H), 7.70–7.77 (m, 3H), 7.65 (d, $J = 7.6$ Hz, 1H), 7.59 (t, $J = 7.6$ Hz, 1H), 7.49–7.52 (m, 3H), 7.42–7.45 (m, 1H), 7.36–7.38 (m, 2H), 7.21–7.26 (m, 2H), 7.03–7.10 (m, 2H), 6.90 (td, $J = 7.6$ Hz, 1H), 6.82 (td, $J = 8.0$ Hz, 1H), 6.44–6.49 (m, 2H), 6.19 (d, $J = 7.6$ Hz, 1H), 6.12 (d, $J = 7.6$ Hz, 1H). **MS** (ESI): Found: 844.2006. $C_{40}H_{28}F_3IrN_5O$ requires 844.1880.

Experimental details

All hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms with C–H distances = 0.95 Å, and with $U_{iso}(H) = 1.2U_{eq}$ for aryl and alkene H atoms. The PF_6^- anion molecule was refined with geometrical constraints (SADI) and displacement parameter constraints (EADP). The large R(int) parameter results from a non-optimal data collection. The resulting R-factors however verifies the structure assignments.

Comment

Phosphorescent cyclometalated Ir(III) complexes have attracted extensive interest due to their broad range of emission colours and high phosphorescence quantum efficiencies [9, 10]. These unique properties are quintessential for a complex to be explored as a promising candidate in the applications of organic light-emitting diodes (OLEDs) [11, 12] and light-emitting electrochemical cells (LEECs) [13, 14]. The archetypal Ir(III) phenylpyridine based complexes are widely employed in OLEDs and LEECs due to their high quantum yields, stability and facile colour tunability [15, 16]. The photophysical properties of these Ir(III) complexes can be tuned by utilising different ancillary ligands [17, 18] and also by employing various substituents on the phenylpyridine moieties and ancillary ligands [19, 20]. The photophysical properties of Ir(III) phenylpyridine complex with pyridylpyrazole moieties as an ancillary ligand has been studied for LEECs application [21]. Herein, we tune the emission of the aforementioned Ir(III) complex by attaching a cinnamoyl group to the pyridylpyrazole moieties. The crystal structure and the photophysical properties of the title complex were investigated.

In the crystal structure of the title compound, the Ir(III) metal centre adopts a distorted octahedral geometry, and is coordinated by two 2-phenylpyridyl (PPy) ligands and one 3- CF_3 CnPyPz ligand. The PPy ligands are arranged in a *cis*-C,C and *trans*-N,N chelate dispositions, which resemble those of previously reported $[Ir(PPy)_2(N^N)]^+$ complexes (N^N = polypyridine chelating ligand) [9, 22]. The bond lengths and angles around the iridium centre are similar to those related structures of $[Ir(C^N)_2(N^N)]^+$ complexes (C^N = C-,N-donor cyclometalated ligand and N^N = polypyridine chelating ligand) [23, 24]. The Ir–N bond distances between the Ir centre and the pyridylpyrazole moiety, namely Ir(1)–N(3) and Ir(1)–N(4), are longer than those between the Ir centre and the PPy ligands, i.e. Ir(1)–N(1) and Ir(1)–N(2), which reflects the stronger *trans* influence of the phenyl groups of the PPy cyclometalated ligand [9, 25]. The pyridine and pyrazole moieties in the same ancillary ligand are slightly distorted from each other with an angle of $22.0(3)^\circ$. The trifluoromethyl-cinnamoyl fragment is tilted with respect to the pyridylpyrazole mean plane with a dihedral angle of $133.3(13)^\circ$. The vinyl hydrogens, $-CH=CH-$ showed a *trans* configuration, with the H(32)–C(32)=C(33)–H(33) torsion angle of $-176.6(6)^\circ$.

An extraordinary phenomenon is observed for the packing of the title complex, in which the PF_6^- counter ions play a crucial role to form the packing scheme of this structure. Two adjacent molecules form a centrosymmetric dimer *via* a non-classical C(22)–H(22)···O(1) hydrogen bond and these dimers are connected by five C–H···F contacts, generating a two-dimensional network when viewed along the *c* axis. Interestingly, there were no significant $\pi \cdots \pi$ interactions formed between the heterocyclic rings of the neighbouring complexes despite the presence of 7 heterocyclic rings. However, a weak $\pi \cdots \pi$ interaction (between the pyrazole and pyridine rings of the ancillary ligand) is observed.

The absorption and photoluminescence spectra of the titled complex in CH_3CN solution were investigated. Intense absorption bands between 210–300 nm was assigned to the spin allowed $\pi \rightarrow \pi^*$ intraligand transitions [26, 27]. The weaker and broad absorption band in the range of 350–500 nm were assigned to the mixture of metal-to-ligand charge transfer (spin allowed 1MLCT and spin forbidden 3MLCT) [22, 28] and ligand-centered (LC) transitions [23, 29]. The complex displayed a broad emission band at 493 nm. The broad and featureless photoluminescence spectrum indicates that the emissive excited states have predominantly 3MLCT characters [30, 31].

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