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Crystal structure of 1-[3-(trifluoromethyl)cinnamoyl]-3-(pyridin-2-yl-κN)
pyrazole-κ²N-bis(2-phenylpyridinato-κ²C,N)iridium(III)
hexafluorophosphate complex, [C₄₀H₂₈F₃IrN₅O]PF₆

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Abstract
[C₄₀H₂₈F₃IrN₅O]PF₆, monoclinic, P2₁/c (no. 14),
a = 20.2282(19) Å, b = 14.5095(11) Å, c = 12.6091(10) Å,
β = 96.937(3)°, V = 3673.7(5) Å³, Z = 4, Rgt(F) = 0.0498,
wRref(F²) = 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 Kα radiation (0.71073 Å) |
| μ: | 3.77 mm⁻¹ |
| Diffractometer, scan mode: | Bruker D8 QUEST PHOTON 100, φ and ω-scans |
| θmax, completeness: | 28.3°, >99% |
| N(hkl)measured, N(hkl)unique, Rint: | 112848, 9126, 0.182 |
| Criterion for Iobs, N(hkl)gt: | Iobs > 2σ(Iobs), 6926 |
| N(param)refined: | 496 |
| Programs: | Bruker programs [1], SHELX [2],
SHELXT [3], SHELXL [4] and
Olex2 [5] |

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      | Ueq*    |
|----------|--------|--------|--------|---------|
| H1       | 0.2600 | 0.5045 | 0.6976 | 0.1010  |
| H2       | 0.3626 | 0.4570 | 0.7307 | 0.0772  |
| H3       | 0.4096 | 0.4875 | 0.7402 | 0.0705  |
| H4       | 0.4462 | 0.5175 | 0.7158 | 0.0694  |
| H5       | 0.4611 | 0.5296 | 0.6779 | 0.0686  |
| H6       | 0.4668 | 0.5005 | 0.6402 | 0.0627  |

Table 2 (continued)

| Atom     | x      | y      | z      | Ueq*    |
|----------|--------|--------|--------|---------|
| H2       | 0.6887 | 0.6175 | 0.7008 | 0.0612  |
| H3       | 0.7276 | 0.6575 | 0.6750 | 0.0586  |
| H4       | 0.7656 | 0.7045 | 0.6550 | 0.0557  |

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 [v(C=O)], 1605 [v(C=N)], 1476 [v(C=N)], 832 [v(PF_6)]. \(^1\)H NMR (CDCl_3, 400 MHz) \(\delta\) (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: 844.006. \(C_{40}H_{28}F_3IrN_3O\) 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 verify 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_3CNPyPz 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)(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)(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)°. The trifluoromethyl-cinnamoyl fragment is tilted with respect to the pyridylpyrazole mean plane with a dihedral angle of 133.3(13)°. 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)°.

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 π···π interactions formed between the heterocyclic rings of the neighbouring complexes despite the presence of 7 heterocyclic rings. However, a weak π···π interaction (between the pyrazole and pyridine rings of the ancillary ligand) is observed.

The absorption and photoluminescence spectra of the titled complex in CH_2CN solution were investigated. Intense absorption bands between 210–300 nm was assigned to the spin allowed π···π* 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 3MLCT) 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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References

1. Bruker. APEX3, SAINT and SADABS. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. A64 (2008) 112–122.
3. Sheldrick, G. M.: SHEXL – Integrated space-group and crystal-structure determination. Acta Crystallogr. A71 (2015) 3–8.
4. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. C71 (2015) 3–8.
5. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.: OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Crystallogr. 42 (2009) 339–341.
6. Mark-Lee, W. F.; Chong, Y. Y.; Law, K. P.; Ahmad, I.; Kassim, M. B.: Synthesis, structure and density functional theory (DFT) study of a rhodium(I) pyridylpyrazol complex as a potential photocatalyst for CO2 reduction. Sains Malaysiana. 47 (2018) 1491–1499.
7. Mark-Lee, W. F.; Chong, Y. Y.; Kassim, M. B.: Supramolecular structures of rhodium(I) complexes mediated by ligand planarity via the interplay of substituents. Acta Cryst. C 74 (2018) 997–1006.
8. Shelton, A. H.; Stephenson, A.; Ward, M. D.; Kassim, M. B.: 1-Benzoyl-3-(pyridin-2-yl)-1H-pyrazole. Acta Crystallogr. E67 (2011) o2445.
9. Zhang, F.; Li, W.; Wei, D.; Dong, X.; Li, S.; Li, Z.; Zhang, F.; Wei, X.; Wei, B.; Cao, G.; Zhai, B.: Solution-processed organic light-emitting diodes based on a blue-emitting cyclometalated cationic iridium(III) complex using 2-(1H-pyrazol-1-yl)pyridine as ancillary ligand. Inorg. Chem. Acta 453 (2016) 115–121.
10. Tang, M.; Zhu, S.; Liu, R.; Wang, J.; Zhang, Z.; Zhu, H.: Synthesis, characterization and optical properties of novel Ir(III) complexes bearing N-heterocycle substituents. J. Organomet. Chem. 880 (2019) 363–367.
11. Bolink, H. J.; Coronado, E.; Garcia Santamaria, S.; Sessolo, M.; Evans, N.; Klein, C.; Baranoff, E.; Kalyanasundaram, K.; Gräetzel, M.; Nazeeruddin, M. K.: Highly phosphorescent perfect green emitting iridium(III) complex for application in OLEDs. ChemComm. 31 (2007) 3276–3278.
12. Yang, C.-H.; Fang, K.-H.; Chen, C.-H.; Sun, I.: High efficiency mer-iridium complexes for organic light-emitting diodes. ChemComm. 19 (2004) 2232–2233.
13. Sunesh, C. D.; Shamugasundaram, K.; Subeeesh, M. S.; Chitumalla, R. K.; Jang, J.; Choe, Y.: Blue and blue-green light-emitting cationic iridium complexes: Synthesis, characterization, and optoelectronic properties. ACS Appl. Mater. Interfaces 7 (2015) 7741–7751.
14. Costa, R. D.; Orti, E.; Bolink, H. J.; Graber, S.; Housecroft, C. E.; Constable, E. C.: Intramolecular π-stacking in a phenylpyrazole-based iridium complex and its use in light-emitting electrochemical cells. J. Am. Chem. Soc. 132 (2010) 5978–5980.
15. Coppo, P.; Plummer, E. A.; De Cola, L.; Tuning iridium(III) phenylpyridine complexes in the “almost blue” region. ChemComm. 15 (2004) 1774–1775.
16. He, L.; Duan, L.; Qiao, J.; Zhang, D.; Wang, L.; Qiu, Y.: Enhanced stability of blue-green light-emitting electrochemical cells based on a cationic iridium complex with 2-(1-phenyl-1H-pyrazol-3-yl)pyridine as the ancillary ligand. ChemComm. 47 (2011) 6467–6469.
17. Shang, X.; Han, D.; Li, D.; Guan, S.; Wu, Z.: Theoretical study on the electronic structures and photophysical properties of a series of Ir(III) complexes based on substituted 2-(pyrazol-3-yl)pyridine ligand. Chem. Phys. Lett. 588 (2013) 68–75.
18. Chen, L.; Wu, Z.; Yang, J.; Zhang, S.: The synthesis and crystal structure of bis(2-(benzo[d]thiazol-2-yl)-5-methylbenzen-1-ido-k2,C,N)-(N,N′-diethylthiocarbamato-k2,S5)iridium(III), C23H24N2S4Ir. Z. Kristallogr. NCS 234 (2019) 1173–1176.
19. Ho, C.-L.; Lam, C.-S.; Sun, N.; Ma, D.; Liu, L.; Yu, Z.-Q.; Xue, L.; Lin, Z.; Li, H.; Lo, Y. H.; Wong, W.-Y.: Synthesis, characterization, and electroluminescent properties of iridium(III) 2-phenylpyridine-type complexes containing trifluoromethyl substituents and various main-group moieties. Isr. J. Chem. 54 (2016) 999–1014.
20. Zanoni, K. P. S.; Kariyazaki, B. K.; Ito, A.; Brennan, M. K.; Meyer, T. J.; Murakami Iha, N. Y.: Blue-green iridium(III) emitter and comprehensive photophysical elucidation of heteroleptic cyclometalated iridium(III) complexes. Inorg. Chem. 53 (2014) 4089–4099.
21. He, L.; Duan, L.; Qiao, J.; Wang, R.; Wei, P.; Wang, L.; Qiu, Y.: Blue-emitting cationic iridium complexes with 2-(1H-pyrazol-1-yl)pyridine as the ancillary ligand for efficient light-emitting electrochemical cells. Adv. Funct. Mater. 18 (2008) 2123–2131.
22. Stagni, S.; Colella, S.; Palazzi, A.; Valenti, G.; Zacchini, S.; Paolucci, F.; Marcaccio, M.; Albuquerque, R. Q.; De Cola, L.: Essential role of the ancillary ligand in the color tuning of iridium tetracarbene complexes. Inorg. Chem. 47 (2008) 10509–10521.
23. He, L.; Ma, D.; Duan, L.; Wei, Y.; Qiao, J.; Zhang, D.; Dong, G.; Wang, L.; Qiu, Y.: Control of intramolecular π–n stacking interaction in cationic iridium complexes via fluorination of pendant phenyl rings. Inorg. Chem. 51 (2012) 4502–4510.
24. Zubaidi, Z. N.; Metherell, A. J.; Baggaley, E.; Ward, M. D.: Ir(III) and Ir(III)/Re(I) complexes of a new bis(pyrazolyl-π -pyridine) bridging ligand containing a naphthalene-2,7-diyl spacer: Structural and photophysical properties. Polyhedron 133 (2017) 68–74.
25. Orselli, E.; Kottas, G. S.; Konradsson, A. E.; Coppo, P.; Fröhlich, R.; De Cola, L.; van Dijken, A.; Büchel, M.; Börner, H.: Blue-emitting iridium complexes with substituted 1,2,4-triazole ligands: Synthesis, photophysics, and devices. Inorg. Chem. 46 (2007) 11082–11093.
26. Sykes, D.; Parker, S. C.; Sazanovich, I. V.; Stephenson, A.; Weinstein, J. A.; Ward, M. D.: dF Energy transfer in Ir(III)/Eu(III) dyads: Use of a naphthyl spacer as a spatial and energetic “stepping stone”. Inorg. Chem. 52 (2013) 10500–10511.
27. Zhang, K. Y.; Lo, K. K.-W.: Synthesis, properties, and live-cell imaging studies of luminescent cyclometalated iridium...
(III) polypyridine complexes containing two or three biotin pendants. Inorg. Chem. 48 (2009) 6011–6025.
28. Connell, T. U.; White, J. M.; Smith, T. A.; Donnelly, P. S.: Luminous iridium(III) cyclometalated complexes with 1,2,3-triazole “click” ligands. Inorg. Chem. 55 (2016) 2776–2790.
29. Song, Y.-H.; Chiu, Y.-C.; Chi, Y.; Cheng, Y.-M.; Lai, C.-H.; Chou, P.-T.; Wong, K.-T.; Tsai, M.-H.; Wu, C.-C.: Phosphorescent iridium(III) complexes with nonconjugated cyclometalated ligands. Chem. Eur. J. 14 (2008) 5423–5434.
30. Jayabharathi, J.; Thanikachalam, V.; Srinivasan, N.; Perumal, M. V.: Evidence for strong mixing between the LC and MLCT excited states in some heteroleptic iridium(III) complexes. J. Fluoresc. 21 (2011) 1585–1597.
31. Jayabharathi, J.; Thanikachalam, V.; Sathishkumar, R.: Highly phosphorescent green emitting iridium(III) complex for application in OLEDs. New J. Chem. 39 (2015) 235–245.