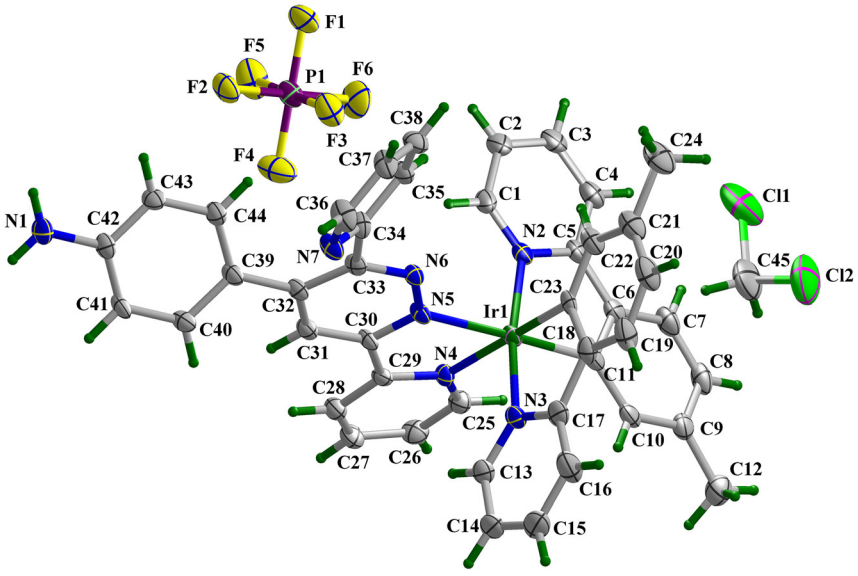
Jun Qian*, Liang Ma and Yida Wang

# Crystal structure of (3,6-di(2-pyridyl)-4-phenylaminopyridazine-κ$^2$N,N′)-bis(2-(p-toluene) pyridinyl-κ$^2$C,N)-iridium(III) hexafluorophosphate –dichloromethane (1/1), $C_{45}H_{37}Cl_2F_6IrN_7P$




https://doi.org/10.1515/ncrs-2024-0356
Received September 4, 2024; accepted October 18, 2024;
published online October 29, 2024

**Abstract**

$C_{45}H_{37}Cl_2F_6IrN_7P$, monoclinic, $P2_1/c$ (no. 14), $a$ = 23.518(5) Å, $b$ = 11.702(2) Å, $c$ = 15.426(3) Å, $\beta$ = 101.44(3)°, $V$ = 4161.0(15) Å$^3$, $Z$ = 4, $R_{gt}(F)$ = 0.0474, $wR_{ref}(F^2)$ = 0.0924, T = 293 K.

**CCDC no.:** 1869608

Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

**Table 1:** Data collection and handling.

| | |
|---|---|
| Crystal: | Red needle |
| Size: | 0.23 × 0.20 × 0.18 mm |
| Wavelength: | Mo *K*α radiation (0.71073 Å) |
| $\mu$: | 3.45 mm$^{-1}$ |
| Diffractometer, scan mode: | Bruker APEX-II, $\varphi$ and $\omega$ |
| $\theta_{max}$, completeness: | 25.0°, >99 % |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$, $R_{int}$: | 35810, 7324, 0.062 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs}$ > 2 $\sigma(I_{obs})$, 6,899 |
| $N(param)_{refined}$: | 559 |
| Programs: | Bruker,[1] Olex2,[2] SHELX,[3,4] PLATON[5] |

## 1 Source of materials

All commercially available reactants and solvents, unless otherwise noted, can be used immediately without pre-treatment. The cyclometalated chloro-bridged iridium(III) dimer, $[(mppy)_2Ir(\mu_2\text{–}Cl)]_2$ (mppy = 2-(p-toluene) pyridine), was synthesized following the reported literature procedures.[6] 1 Equiv. of $IrCl_3{\cdot}3H_2O$ and 2.5 equiv. of 1-phenyl-pyrazole are heated in a mixed solution of water and ethylene glycol ether ($v/v$ = 1/4) at 135 °C under the nitrogen atmosphere to obtain corresponding product. Tetrazine (1 equiv.) and 4-ethynylaniline (1 equiv.) were added into toluene with strong stirring at 140 °C to obtain 3,6-di(2-pyridyl)-4-phenylamino pyridazine (DpTz–PhA) after 120 h. The target cyclometalated Ir(III) complexes were finally synthesized by the obtained iridium(III) dimer $[(mppy)_2Ir(\mu_2\text{–}Cl)]_2$ (1 equiv.)

***Corresponding author: Jun Qian**, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu, 212013, P.R. China, E-mail: junqian8203@ujs.edu.cn. https://orcid.org/0000-0003-1538-6068
**Liang Ma and Yida Wang,** School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu, 212013, P.R. China

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

| Atom | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ir1 | 0.26085 (2) | 0.04989 (2) | 0.36158 (2) | 0.02633 (9) |
| N1 | −0.0972 (2) | 0.5869 (5) | 0.3799 (3) | 0.0390 (13) |
| H30A | −0.1261 | 0.5609 | 0.4002 | 0.047* |
| H30B | −0.0987 | 0.6543 | 0.3573 | 0.047* |
| N2 | 0.2644 (2) | 0.0834 (4) | 0.2329 (3) | 0.0292 (11) |
| N3 | 0.2703 (2) | 0.0166 (4) | 0.4943 (3) | 0.0317 (12) |
| N4 | 0.1835 (2) | −0.0493 (4) | 0.3234 (3) | 0.0272 (11) |
| N5 | 0.19247 (19) | 0.1650 (4) | 0.3689 (3) | 0.0270 (11) |
| N6 | 0.20207 (19) | 0.2767 (4) | 0.3847 (3) | 0.0255 (10) |
| N7 | 0.1656 (2) | 0.5134 (4) | 0.4861 (3) | 0.0356 (12) |
| C34 | 0.1803 (3) | 0.4633 (5) | 0.4163 (4) | 0.0339 (15) |
| C30 | 0.1385 (2) | 0.1216 (5) | 0.3608 (4) | 0.0259 (13) |
| C33 | 0.1587 (2) | 0.3452 (5) | 0.3928 (4) | 0.0282 (13) |
| C25 | 0.1808 (3) | −0.1577 (5) | 0.2932 (4) | 0.0326 (14) |
| H25A | 0.2144 | −0.1913 | 0.2820 | 0.039* |
| C29 | 0.1338 (2) | −0.0005 (5) | 0.3379 (4) | 0.0267 (13) |
| C18 | 0.3519 (3) | 0.1405 (5) | 0.4999 (4) | 0.0346 (14) |
| C26 | 0.1307 (3) | −0.2206 (5) | 0.2785 (4) | 0.0390 (16) |
| H26A | 0.1302 | −0.2944 | 0.2561 | 0.047* |
| C43 | −0.0018 (3) | 0.5596 (5) | 0.3478 (4) | 0.0322 (14) |
| H43A | −0.0036 | 0.6318 | 0.3223 | 0.039* |
| C39 | 0.0505 (2) | 0.3829 (5) | 0.3854 (4) | 0.0301 (13) |
| C17 | 0.3191 (3) | 0.0631 (6) | 0.5463 (4) | 0.0385 (16) |
| C32 | 0.1003 (2) | 0.3079 (5) | 0.3839 (4) | 0.0279 (13) |
| C28 | 0.0825 (3) | −0.0613 (5) | 0.3279 (4) | 0.0343 (14) |
| H28A | 0.0494 | −0.0277 | 0.3414 | 0.041* |
| C35 | 0.2217 (3) | 0.5096 (5) | 0.3724 (4) | 0.0348 (15) |
| H35A | 0.2311 | 0.4727 | 0.3238 | 0.042* |
| C11 | 0.3181 (2) | −0.0719 (5) | 0.3434 (4) | 0.0317 (14) |
| C42 | −0.0480 (2) | 0.5203 (5) | 0.3838 (4) | 0.0316 (14) |
| C1 | 0.2382 (3) | 0.1696 (5) | 0.1853 (4) | 0.0325 (14) |
| H1A | 0.2120 | 0.2136 | 0.2088 | 0.039* |
| C23 | 0.3292 (2) | 0.1513 (5) | 0.4078 (4) | 0.0272 (13) |
| C13 | 0.2356 (3) | −0.0470 (5) | 0.5334 (4) | 0.0373 (15) |
| H13A | 0.2015 | −0.0751 | 0.4988 | 0.045* |
| C40 | 0.0036 (2) | 0.3424 (5) | 0.4206 (4) | 0.0319 (14) |
| H40A | 0.0048 | 0.2692 | 0.4443 | 0.038* |
| C38 | 0.2483 (3) | 0.6112 (5) | 0.4029 (4) | 0.0387 (16) |
| H38A | 0.2759 | 0.6442 | 0.3751 | 0.046* |
| C6 | 0.3296 (2) | −0.0753 (5) | 0.2568 (4) | 0.0311 (14) |
| C4 | 0.3130 (3) | 0.0409 (6) | 0.1154 (4) | 0.0383 (16) |
| H4A | 0.3388 | −0.0040 | 0.0918 | 0.046* |
| C44 | 0.0466 (3) | 0.4926 (5) | 0.3497 (4) | 0.0333 (14) |
| H44A | 0.0774 | 0.5214 | 0.3267 | 0.040* |
| C31 | 0.0924 (2) | 0.1913 (5) | 0.3685 (4) | 0.0294 (13) |
| H31A | 0.0555 | 0.1599 | 0.3635 | 0.035* |
| C8 | 0.3910 (3) | −0.2397 (6) | 0.2938 (5) | 0.0444 (17) |
| H8A | 0.4148 | −0.2956 | 0.2772 | 0.053* |
| C41 | −0.0449 (2) | 0.4119 (5) | 0.4200 (4) | 0.0317 (14) |
| H41A | −0.0755 | 0.3848 | 0.4443 | 0.038* |
| C3 | 0.2861 (3) | 0.1309 (6) | 0.0675 (4) | 0.0382 (15) |
| H3A | 0.2935 | 0.1474 | 0.0118 | 0.046* |
| C10 | 0.3453 (2) | −0.1537 (5) | 0.4037 (4) | 0.0365 (15) |
| H10A | 0.3393 | −0.1516 | 0.4615 | 0.044* |
| C21 | 0.4051 (3) | 0.2935 (6) | 0.4048 (5) | 0.0475 (18) |
| C2 | 0.2478 (3) | 0.1970 (6) | 0.1032 (4) | 0.0376 (15) |
| H2A | 0.2289 | 0.2587 | 0.0720 | 0.045* |
| C19 | 0.3989 (3) | 0.2054 (6) | 0.5412 (5) | 0.0498 (19) |
| H19A | 0.4128 | 0.1974 | 0.6017 | 0.060* |
| C37 | 0.2332 (3) | 0.6621 (5) | 0.4744 (5) | 0.0466 (18) |
| H37A | 0.2509 | 0.7299 | 0.4967 | 0.056* |
| C5 | 0.3025 (2) | 0.0156 (5) | 0.1983 (4) | 0.0316 (14) |
| C36 | 0.1915 (3) | 0.6120 (6) | 0.5133 (5) | 0.0442 (17) |
| H36A | 0.1809 | 0.6489 | 0.5611 | 0.053* |
| C7 | 0.3658 (3) | −0.1594 (6) | 0.2334 (5) | 0.0430 (17) |
| H7A | 0.3730 | −0.1611 | 0.1763 | 0.052* |
| C9 | 0.3810 (3) | −0.2382 (6) | 0.3800 (5) | 0.0422 (17) |
| C27 | 0.0810 (3) | −0.1726 (5) | 0.2976 (4) | 0.0410 (16) |
| H27A | 0.0468 | −0.2147 | 0.2901 | 0.049* |
| C14 | 0.2472 (3) | −0.0734 (6) | 0.6216 (4) | 0.0446 (17) |
| H14A | 0.2217 | −0.1182 | 0.6460 | 0.054* |
| C20 | 0.4248 (3) | 0.2802 (7) | 0.4943 (5) | 0.0528 (19) |
| H20A | 0.4563 | 0.3230 | 0.5230 | 0.063* |
| C12 | 0.4070 (3) | −0.3275 (6) | 0.4474 (5) | 0.059 (2) |
| H12A | 0.4304 | −0.3793 | 0.4212 | 0.088* |
| H12B | 0.4307 | −0.2906 | 0.4975 | 0.088* |
| H12C | 0.3764 | −0.3691 | 0.4663 | 0.088* |
| C15 | 0.2973 (3) | −0.0324 (7) | 0.6734 (5) | 0.055 (2) |
| H15A | 0.3072 | −0.0517 | 0.7330 | 0.065* |
| C22 | 0.3572 (3) | 0.2292 (5) | 0.3627 (5) | 0.0401 (16) |
| H22A | 0.3437 | 0.2390 | 0.3023 | 0.048* |
| C24 | 0.4360 (3) | 0.3742 (6) | 0.3518 (5) | 0.060 (2) |
| H24A | 0.4166 | 0.3731 | 0.2908 | 0.091* |
| H24B | 0.4354 | 0.4504 | 0.3747 | 0.091* |
| H24C | 0.4755 | 0.3499 | 0.3564 | 0.091* |
| C16 | 0.3331 (3) | 0.0386 (7) | 0.6354 (5) | 0.052 (2) |
| H16A | 0.3664 | 0.0694 | 0.6701 | 0.063* |
| P1 | 0.09037 (8) | 0.44829 (15) | 0.11387 (12) | 0.0393 (4) |
| F1 | 0.11036 (18) | 0.5460 (4) | 0.0550 (3) | 0.0609 (12) |
| F2 | 0.04478 (16) | 0.5333 (3) | 0.1426 (3) | 0.0486 (10) |
| F3 | 0.13769 (17) | 0.4897 (4) | 0.1969 (3) | 0.0582 (11) |
| F4 | 0.0703 (2) | 0.3493 (4) | 0.1727 (3) | 0.0678 (13) |
| F5 | 0.04360 (18) | 0.4074 (4) | 0.0320 (3) | 0.0694 (13) |
| F6 | 0.13717 (19) | 0.3639 (4) | 0.0862 (3) | 0.0697 (13) |
| C45 | 0.4724 (3) | 0.0342 (8) | 0.3497 (7) | 0.082 (3) |
| H45A | 0.4401 | 0.0624 | 0.3741 | 0.099* |
| H45B | 0.4711 | −0.0487 | 0.3505 | 0.099* |
| Cl1 | 0.46439 (12) | 0.0817 (2) | 0.2385 (2) | 0.0986 (9) |
| Cl2 | 0.53608 (10) | 0.0795 (2) | 0.4146 (2) | 0.1160 (11) |

and DpTz–PhA ligand (1 equiv.), as well as potassium hexafluorophosphate (1 equiv.) in a mixed solvent containing dichloromethane and methanol (*v*/*v* = 2/1) at 85 °C in a dark $N_2$ atmosphere for 24 h. The above reddish solid product (164.70 mg, 0.15 mmol) was dissolved in dichloromethane (1 mL), after filtration, 1 mL of buffer layer ($V_{dichloromethane}/V_{n\text{-}hexane}$ = 1/1) and 3 mL of n-hexane was added successively. Red needle crystals were obtained after 12 days at room

temperature in dark with a yield of 79.0590 mg (48 % based Ir). **Anal. Calcd.** for $C_{45}H_{37}Cl_2F_6IrN_7P$: C, 49.82 %; H, 3.41 %; N, 9.04 %. Found C, 49.71 %; H, 3.44 %; N, 9.07 %. **IR** (KBr, $cm^{-1}$): 3324 (m), 3212 (s), 1579 (s), 1510 (m), 1386 (vs), 1039 (m) (pyridine: C=N), 776 (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), $U_{eq}$ is the equivalent isotropic displacement parameter of the parent atom).[5]

## 3 Comment

In recent years, cyclometalated iridium(III) complexes, have received many interests due to the potential applications, such as organic light-emitting diodes (OLEDs), light-emitting electro-chemical cells (LECs), biosensing, photocatalysis, and nonlinear optics.[6–8] The strong spin–orbit coupling induced by the heavy Ir(III) ion results in efficient intersystem crossing (ISC) and promotes triplet excited-state formation, which are intrinsically related to aforementioned applications.[9,10] Among the diverse classes of cyclometalated Ir(III) complexes, the heteroleptic systems containing a combination of diimine ($N^N$) ligands and cyclometalating ($^CN$) ligands have gained special attention due to their photophysical properties can be tuned by altering the ligands separately.[11–13] From the synthesis point of view, the judicious choice of auxiliary ligands, for example conjugacy and substituents, plays an important role in the construction of cyclometalated iridium(III) complexes.[14,15]

The title compound crystallizes in the monoclinic space group $P2_1/c$. As displayed in the figure, the asymmetric unit of the title structure consists of one $Ir^{3+}$ cation, one DpTz–PhA ligand, two mppy ligands, one $PF_6^-$ anion and one dichloromethane solvent molecule. The average Ir–C bond length is 2.015(6) Å, while the distances of Ir–N range from 2.042(5) to 2.140(5) Å, which are within the normal range and are consistent with those previously reported in similar structures.[16,17] The main skeleton of the title structure 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 mppy and auxiliary ligand DpTz–PhA with the F atoms of the $PF_6^-$ anion.

**Acknowledgments:** This work was funded by the funding for this research was provided by: National Natural Science Foundation of China (grant No. 51602130).

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

**Research funding:** National Natural Science Foundation of China (grant No. 51602130).

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

## 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. Adamovich, V.; Boudreault, P. L. T.; Esteruelas, M. A.; Gómez–Bautista, D.; López, A. M.; Onñate, E.; Tsai, J. Y. Preparation via a NHC Dimer Complex, Photophysical Properties, and Device Performance of Heteroleptic Bis(tridentate) Iridium(III) Emitters. *Organometallics* **2019**, *38*, 2738–2747.
7. 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.
8. Liu, B. Q.; Lystrom, L.; Kilina, S.; Sun, W. F. Effects of Varying the Benzannulation Site and P Conjugation of the Cyclometalating Ligand on the Photophysics and Reverse Saturable Absorption of Monocationic Iridium(III) Complexes. *Inorg. Chem.* **2019**, *58*, 476–488.
9. Lee, S.; Kim, S. O.; Shin, H.; Yun, H. J.; Yang, K.; Kwon, S. K.; Kim, J. J.; Kim, Y. H. Deep-Blue Phosphorescence from Perfluoro Carbonyl-Substituted Iridium Complexes. *J. Am. Chem. Soc.* **2013**, *135*, 14321–14328.
10. Fan, C.; Zhu, L.; Jiang, B.; Li, Y.; Zhao, F.; Ma, D.; Qin, J.; Yang, C. J. High Power Efficiency Yellow Phosphorescent OLEDs by Using New Iridium Complexes with Halogen-Substituted 2-Phenylbenzo[*d*]thiazole Ligands. *Phys. Chem. C* **2013**, *117*, 19134–19141.
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. Zhao, Q.; Liu, S.; Shi, M.; Wang, C.; Yu, M.; Li, L.; Li, F.; Yi, T.; Huang, C. Highly Phosphorescent Cyclometalated Iridium(III) Complexes for Optoelectronic Applications: Fine Tuning of the Emission Wavelength through Ancillary Ligands. *Inorg. Chem.* **2006**, *45*, 6152–6160.
13. 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.

14. Takizawa, S. Y.; Ikuta, N.; Zeng, F.; Komaru, S.; Sebata, S.; Murata, S. Impact of Substituents on Excited-State and Photosensitizing Properties in Cationic Iridium(III) Complexes with Ligands of Coumarin 6. *Inorg. Chem.* **2016**, *55*, 8723–8735.
15. Zaarour, M.; Singh, A.; Latouche, C.; Williams, J. A. G.; Ledoux-Rak, I.; Zyss, J.; Boucekkine, A.; Bozec, H. L.; Guerchais, V.; Dragonetti, C.; Colombo, A.; Roberto, D.; Valore, A. Linear and Nonlinear Optical Properties of Tris-cyclometalated Phenylpyridine Ir(III) Complexes Incorporating P-Conjugated Substituents. *Inorg. Chem.* **2013**, *52*, 7987–7994.
16. Qian, J.; Chen, C. J.; Ma, L.; Wang, Y. D. Crystal Structure of (2-Phenylimino Methylquinoline-k$^2$N,N′)-Bis(1-Phenylpyrazole-k$^2$C,N′)-Iridium(III) Hexafluorophosphate, $C_{34}H_{26}F_6IrN_6P$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 1165–1167.
17. Qian, J.; Chen, C. J.; Ma, L.; Wang, Y. D. Crystal Structure of (2-(2-Pyridine)-benzimidazole-*K*$^2$N,N′)-bis(1-phenylpyrazole-*κ*$^2$C,N′) Iridium(III) Hexafluorophosphate, $C_{30}H_{22}F_6IrN_7P$. *Z. Kristallogr. N. Cryst. Struct.* **2023**, *238*, 1229–1231.