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(4,4′-Dimethoxy-2,2′-bipyridine-κ^2N,N')bis[2-(pyridin-2-yl)phenyl-κC^1]iridium(III) hexafluoridophosphate unknown solvate

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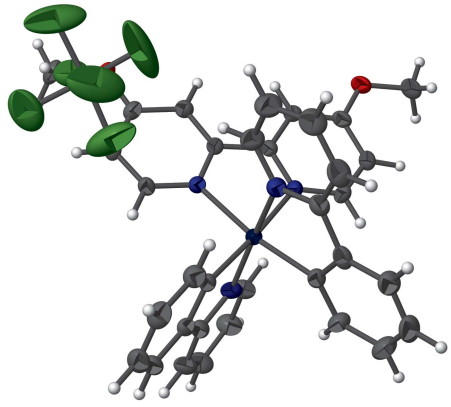
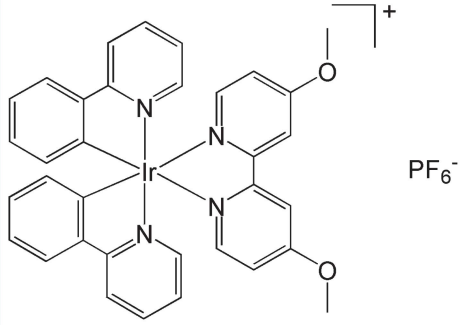
Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title complex, $[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2O_2)]PF_6$, comprises a $[Ir(ppy)_2(diMeO\text{-}bpy)]^+$ cation (Hppy = 2-phenylpyridine and diMeO-bpy = 4,4′-dimethoxy-2,2′-bipyridine) and a PF_6^- anion. The Ir^{III} atom is coordinated by two anionic ppy^- ligands, each coordinating in a $C\hat{}N$ cyclometalated mode, and one neutral diMeO-bpy ligand, leading to a distorted octahedral geometry defined by a *cis*-C_2N_4 donor set. Intermolecular C—F···H contacts lead to a three-dimensional architecture that define columns parallel to *a*. Unknown disordered solvent molecules reside in these columns with the electron density being treated with SQUEEZE [Spek (2015). *Acta Cryst.* C**71**, 9–18]. The unit-cell data do not reflect the presence of the unresolved solvent.

3D view



Chemical scheme



Structure description

Heteroleptic cyclometalated iridium complexes, $[Ir(C\hat{}N)_2(N\hat{}N)]^+$, which have long-lived and highly efficient phosphorescence emission, are of interest for applications such as dopants for organic light emitting diodes, phosphorescence sensors and photosensitizers for solar cells and for artificial photosynthesis (Lowry & Bernhard, 2006). Recently, it was reported that the counter-ions in these complexes greatly influence the performance of their applications in the solid state (Schneider *et al.*, 2014). One of the reasons for this may relate to the hydrogen-bonding interactions between the counter-ion and the $N\hat{}N$ ligand in the $[Ir(C\hat{}N)(N\hat{}N)]^+$ complexes. Thus, the crystal structure analyses of these complexes are considered to be important for providing insight into their applications.

As depicted in Fig. 1, the molecular structure of the title compound, $[Ir(ppy)_2(diMeO\text{-}bpy)](PF_6)$, reveals a distorted octahedral geometry for the Ir^{III} atom within a *cis*-C_2N_4

Table 1
Selected bond lengths (Å).

Ir1—C22	2.011 (4)	Ir1—N2	2.056 (3)
Ir1—C11	2.012 (4)	Ir1—N3	2.137 (3)
Ir1—N1	2.045 (3)	Ir1—N4	2.135 (3)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···F1^{i}	0.95	2.39	3.290 (6)	158
C26—H26···F5^{ii}	0.95	2.53	3.442 (5)	160
C29—H29···F1^{ii}	0.95	2.46	3.296 (6)	146
C29—H29···F5^{ii}	0.95	2.53	3.442 (5)	161
C33—H33*C*···F5	0.98	2.50	3.396 (5)	152

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $-x, -y+1, -z$.

donor set. The central Ir^{III} atom is cyclometalated by two ppy (*ĈN*) anions and further coordinated by a neutral diMeO-bpy (*N̂N*) ligand. The Ir—N bond lengths *trans* to the Ir—C bonds are longer than the remaining Ir—N bonds, Table 1. All three chelate ligands show small bite angles; range: 76.11 (12)–80.74 (14)°. Intermolecular C—F···H contacts between the ions lead to a three-dimensional architecture that defines columns parallel to *a*, Table 2.

Synthesis and crystallization

A mixture of $[IrCl(ppy)_2]_2$ (214.4 mg, 0.20 mmol) and diMeO-bpy (95.1 mg, 0.44 mmol) was refluxed in 60 ml MeOH/CH_2Cl_2 (1:1, *v*:*v*) for 24 h. The solvent was evaporated under reduced pressure. The yellow residue was collected and washed with diethyl ether. The residue was redissolved in water and then an aqueous solution of NH_4PF_6 (717.2 mg, 0.44 mol) added. The yellow precipitate was filtered off, washed with water and dried under vacuum at 353 K for 5 h to give the product $[Ir(ppy)_2(diMeO\text{-}bpy)](PF_6)$. Yield: 316.3 mg (0.37 mmol, 92.5%). The product was crystallized by vapour diffusion of $(C_2H_5)O$ into a CH_2Cl_2 solution of the salt. Analysis: calculated for $C_{34}H_{28}F_6IrN_4O_2P$ (861.81) C 47.39, H 3.27, N 6.50%; found C 47.43, H 3.42, N 6.54%. ^{1}H NMR (500 MHz, DMSO-d_6): δ = 8.44 (*d*, 2H), 8.24 (*d*, 2H), 7.88–7.94 (*m*, 4H), 7.66 (*d*, 2H), 7.60 (*d*, 2H), 7.29 (*dd*, 2H), 7.17 (*m*, 2H), 6.99 (*td*, 2H), 6.87 (*td*, 2H), 6.18 (*dd*, 2H), 3.98 (*s*, 6H).

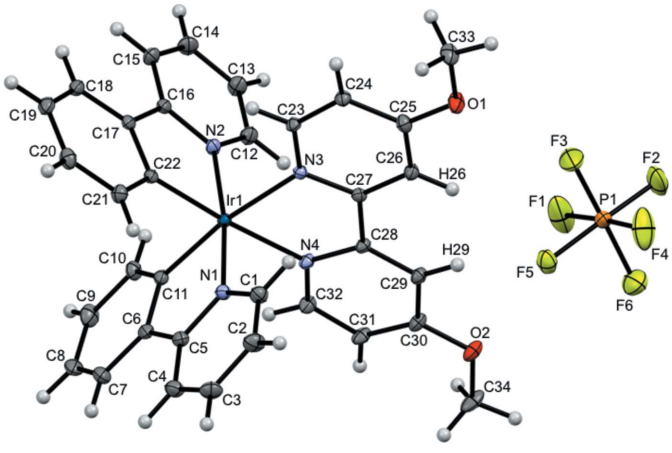


Figure 1
The molecular structure of the asymmetric unit in the title salt showing the atom labelling. Displacement ellipsoids are drawn at the 20% probability level.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2O_2)]PF_6$
M_r	861.77
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, *b*, *c* (Å)	9.4106 (12), 14.936 (2), 24.175 (4)
β (°)	90.290 (2)
V (Å^3)	3397.8 (9)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	4.05
Crystal size (mm)	0.24 × 0.10 × 0.08
Data collection	
Diffractometer	Rigaku Saturn724
Absorption correction	Multi-scan (*REQAB*; Rigaku, 1998)
T_{min}, T_{max}	0.541, 0.723
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26767, 7696, 6889
R_{int}	0.045
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.032, 0.083, 1.08
No. of reflections	7696
No. of parameters	433
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.05, −0.75

Computer programs: *CrystalClear* (Rigaku, 2008), *SIR2004* (Burla *et al.*, 2005), *SHELXL97* (Sheldrick, 2008) and *CrystalStructure* (Rigaku, 2014).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Guest solvents in the title salt could not be determined because of the severe disorder. Thus, the data were treated with SQUEEZE (Spek, 2015). The estimated void volume and residual electron count per unit cell are 395.2 Å^3 and 44 e, respectively. The unit-cell data do not reflect the presence of this feature of the structure.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x160487 [doi:10.1107/S2414314616004879]

(4,4′-Dimethoxy-2,2′-bipyridine-κ^2N,N')bis[2-(pyridin-2-yl)phenyl-κC^1]iridium(III) hexafluoridophosphate unknown solvate

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(4,4′-Dimethoxy-2,2′-bipyridine-κ^2N,N')bis[2-(pyridin-2-yl)phenyl-κC^1]iridium(III) hexafluoridophosphate

Crystal data

$[Ir(C_{11}H_8N)_2(C_{12}H_{12}N_2O_2)]PF_6$
M_r = 861.77
Monoclinic, $P2_1/c$
a = 9.4106 (12) Å
b = 14.936 (2) Å
c = 24.175 (4) Å
β = 90.290 (2)°
V = 3397.8 (9) Å^3
Z = 4
$F(000)$ = 1688
D_x = 1.685 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 10557 reflections
θ = 3.2–27.5°
μ = 4.05 mm^{-1}
T = 150 K
Block, yellow
0.24 × 0.10 × 0.08 mm

Data collection

Rigaku Saturn724 diffractometer
Radiation source: rotating anode
Detector resolution: 7.111 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*REQAB*; Rigaku, 1998)
T_{min} = 0.541, T_{max} = 0.723
26767 measured reflections
7696 independent reflections
6889 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 27.5°, θ_{min} = 3.2°
h = −12→9
k = −19→19
l = −29→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.083
S = 1.08
7696 reflections
433 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 5.431P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.05 e Å^{-3}
$\Delta\rho_{min}$ = −0.75 e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ir1	0.29982 (2)	0.59502 (2)	0.20275 (2)	0.02079 (6)
P1	−0.03812 (14)	0.78800 (9)	0.01015 (5)	0.0459 (3)
F1	−0.1028 (6)	0.7975 (3)	−0.05066 (15)	0.1163 (19)
F2	0.0467 (6)	0.8783 (3)	0.0019 (2)	0.1134 (19)
F3	0.0820 (5)	0.7333 (4)	−0.0143 (3)	0.171 (3)
F4	0.0156 (6)	0.7788 (3)	0.07105 (18)	0.1084 (17)
F5	−0.1341 (3)	0.6998 (2)	0.01565 (12)	0.0578 (8)
F6	−0.1660 (4)	0.8445 (3)	0.03404 (19)	0.0887 (12)
O1	−0.1882 (3)	0.4604 (2)	0.04687 (14)	0.0440 (8)
O2	0.4844 (3)	0.2444 (2)	0.08318 (12)	0.0393 (7)
N1	0.3942 (3)	0.6549 (2)	0.13632 (13)	0.0279 (7)
N2	0.2077 (3)	0.5505 (2)	0.27465 (13)	0.0279 (7)
N3	0.1204 (3)	0.5503 (2)	0.15575 (12)	0.0225 (6)
N4	0.3652 (3)	0.4682 (2)	0.17102 (13)	0.0259 (6)
C1	0.3360 (5)	0.6619 (3)	0.08563 (17)	0.0358 (9)
H1	0.2460	0.6351	0.0789	0.043*
C2	0.4016 (5)	0.7065 (3)	0.04331 (19)	0.0444 (11)
H2	0.3578	0.7106	0.0079	0.053*
C3	0.5321 (5)	0.7451 (3)	0.0530 (2)	0.0452 (11)
H3	0.5795	0.7762	0.0242	0.054*
C4	0.5935 (5)	0.7384 (3)	0.1045 (2)	0.0415 (10)
H4	0.6836	0.7649	0.1114	0.050*
C5	0.5235 (4)	0.6929 (3)	0.14636 (17)	0.0298 (8)
C6	0.5770 (4)	0.6784 (3)	0.20330 (18)	0.0317 (8)
C7	0.7082 (4)	0.7084 (3)	0.22131 (19)	0.0388 (10)
H7	0.7664	0.7426	0.1972	0.047*
C8	0.7541 (5)	0.6893 (4)	0.2731 (2)	0.0465 (12)
H8	0.8431	0.7118	0.2855	0.056*
C9	0.6709 (5)	0.6364 (4)	0.3088 (2)	0.0483 (12)
H9	0.7051	0.6213	0.3446	0.058*
C10	0.5374 (5)	0.6062 (3)	0.29088 (18)	0.0353 (9)
H10	0.4811	0.5701	0.3146	0.042*
C11	0.4865 (4)	0.6291 (3)	0.23786 (16)	0.0274 (8)
C12	0.2039 (4)	0.4656 (3)	0.29191 (17)	0.0354 (9)
H12	0.2441	0.4204	0.2692	0.042*
C13	0.1433 (5)	0.4415 (3)	0.34178 (19)	0.0410 (10)
H13	0.1435	0.3806	0.3532	0.049*
C14	0.0826 (5)	0.5061 (3)	0.37484 (19)	0.0438 (11)
H14	0.0412	0.4908	0.4093	0.053*
C15	0.0838 (5)	0.5935 (3)	0.35638 (18)	0.0370 (10)
H15	0.0419	0.6389	0.3785	0.044*
C16	0.1449 (4)	0.6164 (3)	0.30635 (16)	0.0285 (8)
C17	0.1532 (4)	0.7069 (3)	0.28270 (15)	0.0265 (8)
C18	0.0974 (4)	0.7831 (3)	0.30829 (17)	0.0332 (9)
H18	0.0522	0.7782	0.3432	0.040*

C19	0.1081 (5)	0.8654 (3)	0.28283 (19)	0.0379 (10)
H19	0.0703	0.9173	0.3001	0.045*
C20	0.1749 (5)	0.8724 (3)	0.2315 (2)	0.0386 (10)
H20	0.1815	0.9289	0.2137	0.046*
C21	0.2321 (4)	0.7961 (3)	0.20633 (17)	0.0332 (9)
H21	0.2785	0.8018	0.1717	0.040*
C22	0.2224 (4)	0.7117 (2)	0.23108 (15)	0.0239 (7)
C23	−0.0041 (4)	0.5937 (2)	0.15193 (16)	0.0249 (7)
H23	−0.0180	0.6450	0.1745	0.030*
C24	−0.1127 (4)	0.5679 (3)	0.11716 (17)	0.0285 (8)
H24	−0.1997	0.6002	0.1161	0.034*
C25	−0.0925 (4)	0.4936 (3)	0.08373 (16)	0.0290 (8)
C26	0.0371 (4)	0.4467 (3)	0.08738 (16)	0.0293 (8)
H26	0.0535	0.3954	0.0650	0.035*
C27	0.1396 (4)	0.4764 (2)	0.12398 (14)	0.0235 (7)
C28	0.2779 (4)	0.4304 (3)	0.13203 (15)	0.0243 (7)
C29	0.3185 (4)	0.3547 (3)	0.10299 (15)	0.0289 (8)
H29	0.2571	0.3295	0.0758	0.035*
C30	0.4498 (4)	0.3158 (3)	0.11396 (16)	0.0303 (8)
C31	0.5355 (4)	0.3513 (3)	0.15557 (17)	0.0338 (9)
H31	0.6234	0.3241	0.1653	0.041*
C32	0.4886 (4)	0.4273 (3)	0.18210 (17)	0.0324 (9)
H32	0.5477	0.4523	0.2101	0.039*
C33	−0.3191 (5)	0.5088 (3)	0.0402 (2)	0.0441 (11)
H33A	−0.3790	0.4785	0.0127	0.053*
H33B	−0.3690	0.5112	0.0756	0.053*
H33C	−0.2986	0.5698	0.0276	0.053*
C34	0.6225 (5)	0.2046 (4)	0.0921 (2)	0.0503 (13)
H34A	0.6342	0.1534	0.0672	0.060*
H34B	0.6965	0.2491	0.0846	0.060*
H34C	0.6305	0.1843	0.1305	0.060*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ir1	0.02019 (9)	0.02285 (8)	0.01933 (8)	0.00084 (5)	−0.00028 (5)	−0.00115 (5)
P1	0.0481 (7)	0.0470 (7)	0.0428 (7)	−0.0148 (6)	0.0160 (5)	−0.0147 (6)
F1	0.188 (5)	0.121 (4)	0.0394 (19)	−0.090 (4)	−0.004 (2)	0.014 (2)
F2	0.142 (4)	0.106 (3)	0.093 (3)	−0.089 (3)	0.039 (3)	−0.035 (3)
F3	0.060 (3)	0.162 (5)	0.293 (8)	−0.012 (3)	0.052 (4)	−0.154 (6)
F4	0.161 (4)	0.078 (3)	0.085 (3)	−0.006 (3)	−0.065 (3)	−0.008 (2)
F5	0.075 (2)	0.0509 (18)	0.0474 (17)	−0.0219 (15)	0.0047 (15)	0.0001 (14)
F6	0.081 (3)	0.067 (2)	0.119 (3)	0.007 (2)	0.020 (2)	−0.022 (2)
O1	0.0334 (16)	0.0473 (18)	0.0509 (19)	0.0081 (14)	−0.0193 (14)	−0.0176 (15)
O2	0.0467 (18)	0.0430 (17)	0.0281 (15)	0.0215 (14)	−0.0023 (13)	−0.0071 (13)
N1	0.0252 (16)	0.0324 (17)	0.0261 (16)	−0.0016 (13)	0.0013 (12)	−0.0006 (13)
N2	0.0330 (18)	0.0297 (17)	0.0209 (15)	−0.0053 (13)	0.0009 (12)	−0.0001 (13)
N3	0.0214 (15)	0.0246 (15)	0.0215 (14)	−0.0005 (12)	−0.0003 (11)	−0.0009 (12)

N4	0.0239 (16)	0.0300 (16)	0.0238 (15)	0.0066 (13)	−0.0025 (12)	−0.0033 (13)
C1	0.037 (2)	0.041 (2)	0.030 (2)	−0.0038 (18)	−0.0005 (17)	0.0021 (18)
C2	0.044 (3)	0.058 (3)	0.031 (2)	−0.005 (2)	0.0030 (19)	0.006 (2)
C3	0.045 (3)	0.055 (3)	0.036 (2)	−0.003 (2)	0.010 (2)	0.011 (2)
C4	0.032 (2)	0.043 (2)	0.049 (3)	−0.0041 (19)	0.0080 (19)	0.000 (2)
C5	0.027 (2)	0.031 (2)	0.031 (2)	0.0004 (15)	0.0046 (15)	−0.0031 (16)
C6	0.026 (2)	0.0281 (19)	0.041 (2)	0.0021 (15)	0.0046 (16)	−0.0069 (17)
C7	0.029 (2)	0.045 (2)	0.042 (2)	−0.0047 (18)	0.0003 (18)	−0.007 (2)
C8	0.024 (2)	0.057 (3)	0.058 (3)	−0.004 (2)	−0.003 (2)	−0.015 (2)
C9	0.046 (3)	0.057 (3)	0.042 (3)	0.006 (2)	−0.018 (2)	−0.008 (2)
C10	0.035 (2)	0.042 (2)	0.030 (2)	−0.0018 (18)	−0.0084 (17)	−0.0037 (17)
C11	0.0238 (18)	0.0286 (18)	0.0298 (19)	0.0024 (15)	−0.0019 (14)	−0.0059 (16)
C12	0.044 (3)	0.031 (2)	0.030 (2)	−0.0023 (17)	0.0054 (18)	−0.0001 (16)
C13	0.056 (3)	0.031 (2)	0.036 (2)	−0.004 (2)	0.007 (2)	0.0060 (18)
C14	0.051 (3)	0.048 (3)	0.033 (2)	−0.006 (2)	0.0114 (19)	0.005 (2)
C15	0.040 (2)	0.044 (3)	0.027 (2)	−0.0047 (18)	0.0048 (18)	−0.0066 (17)
C16	0.0222 (18)	0.035 (2)	0.0286 (19)	−0.0032 (15)	0.0004 (15)	−0.0066 (16)
C17	0.0204 (17)	0.0322 (19)	0.0267 (18)	−0.0031 (15)	−0.0024 (14)	−0.0066 (15)
C18	0.029 (2)	0.039 (2)	0.032 (2)	0.0006 (17)	0.0016 (16)	−0.0118 (18)
C19	0.035 (2)	0.035 (2)	0.044 (2)	0.0057 (18)	−0.0017 (18)	−0.0125 (19)
C20	0.039 (2)	0.028 (2)	0.048 (3)	0.0009 (18)	−0.0088 (19)	0.0018 (19)
C21	0.035 (2)	0.031 (2)	0.033 (2)	0.0005 (17)	−0.0012 (16)	0.0008 (17)
C22	0.0190 (17)	0.0272 (18)	0.0256 (17)	0.0002 (14)	−0.0028 (13)	−0.0050 (15)
C23	0.0233 (18)	0.0242 (18)	0.0271 (19)	0.0030 (14)	0.0008 (14)	−0.0038 (14)
C24	0.0231 (19)	0.0291 (19)	0.033 (2)	0.0031 (15)	−0.0023 (15)	0.0014 (16)
C25	0.0262 (19)	0.032 (2)	0.0288 (19)	−0.0013 (15)	−0.0063 (15)	−0.0008 (16)
C26	0.029 (2)	0.0293 (19)	0.0294 (19)	0.0036 (16)	−0.0023 (15)	−0.0075 (16)
C27	0.0222 (17)	0.0265 (17)	0.0217 (16)	0.0009 (14)	0.0009 (13)	0.0012 (14)
C28	0.0249 (18)	0.0265 (18)	0.0214 (17)	0.0043 (14)	0.0000 (14)	−0.0006 (14)
C29	0.030 (2)	0.034 (2)	0.0228 (18)	0.0053 (16)	−0.0021 (14)	−0.0029 (15)
C30	0.038 (2)	0.0292 (19)	0.0242 (18)	0.0112 (16)	0.0019 (15)	−0.0022 (15)
C31	0.030 (2)	0.041 (2)	0.031 (2)	0.0150 (17)	−0.0024 (16)	−0.0018 (17)
C32	0.029 (2)	0.040 (2)	0.028 (2)	0.0102 (17)	−0.0086 (16)	−0.0045 (17)
C33	0.032 (2)	0.047 (3)	0.052 (3)	0.0062 (19)	−0.019 (2)	−0.006 (2)
C34	0.056 (3)	0.058 (3)	0.037 (2)	0.035 (2)	−0.002 (2)	−0.006 (2)

Geometric parameters (Å, º)

Ir1—C22	2.011 (4)	C10—H10	0.9500
Ir1—C11	2.012 (4)	C12—C13	1.384 (6)
Ir1—N1	2.045 (3)	C12—H12	0.9500
Ir1—N2	2.056 (3)	C13—C14	1.379 (6)
Ir1—N3	2.137 (3)	C13—H13	0.9500
Ir1—N4	2.135 (3)	C14—C15	1.380 (6)
P1—F3	1.517 (4)	C14—H14	0.9500
P1—F4	1.560 (4)	C15—C16	1.385 (6)
P1—F2	1.580 (4)	C15—H15	0.9500
P1—F6	1.581 (4)	C16—C17	1.471 (6)

P1—F1	1.594 (4)	C17—C18	1.399 (5)
P1—F5	1.603 (3)	C17—C22	1.412 (5)
O1—C25	1.357 (5)	C18—C19	1.379 (6)
O1—C33	1.437 (5)	C18—H18	0.9500
O2—C30	1.341 (5)	C19—C20	1.398 (7)
O2—C34	1.445 (5)	C19—H19	0.9500
N1—C1	1.344 (5)	C20—C21	1.401 (6)
N1—C5	1.364 (5)	C20—H20	0.9500
N2—C12	1.336 (5)	C21—C22	1.398 (5)
N2—C16	1.381 (5)	C21—H21	0.9500
N3—C23	1.342 (5)	C23—C24	1.375 (5)
N3—C27	1.358 (5)	C23—H23	0.9500
N4—C32	1.338 (5)	C24—C25	1.387 (6)
N4—C28	1.369 (5)	C24—H24	0.9500
C1—C2	1.370 (6)	C25—C26	1.409 (5)
C1—H1	0.9500	C26—C27	1.379 (5)
C2—C3	1.375 (7)	C26—H26	0.9500
C2—H2	0.9500	C27—C28	1.483 (5)
C3—C4	1.373 (7)	C28—C29	1.386 (5)
C3—H3	0.9500	C29—C30	1.389 (5)
C4—C5	1.389 (6)	C29—H29	0.9500
C4—H4	0.9500	C30—C31	1.391 (6)
C5—C6	1.479 (6)	C31—C32	1.378 (6)
C6—C7	1.382 (6)	C31—H31	0.9500
C6—C11	1.405 (6)	C32—H32	0.9500
C7—C8	1.352 (7)	C33—H33A	0.9800
C7—H7	0.9500	C33—H33B	0.9800
C8—C9	1.411 (8)	C33—H33C	0.9800
C8—H8	0.9500	C34—H34A	0.9800
C9—C10	1.401 (6)	C34—H34B	0.9800
C9—H9	0.9500	C34—H34C	0.9800
C10—C11	1.408 (6)		

C22—Ir1—C11	87.40 (15)	C10—C11—Ir1	127.9 (3)
C22—Ir1—N1	92.75 (14)	N2—C12—C13	122.1 (4)
C11—Ir1—N1	80.74 (14)	N2—C12—H12	118.9
C22—Ir1—N2	80.62 (14)	C13—C12—H12	118.9
C11—Ir1—N2	95.51 (14)	C14—C13—C12	119.7 (4)
N1—Ir1—N2	172.57 (13)	C14—C13—H13	120.1
C22—Ir1—N4	175.44 (13)	C12—C13—H13	120.1
C11—Ir1—N4	97.08 (14)	C13—C14—C15	118.1 (4)
N1—Ir1—N4	88.79 (13)	C13—C14—H14	121.0
N2—Ir1—N4	98.07 (13)	C15—C14—H14	121.0
C22—Ir1—N3	99.50 (13)	C14—C15—C16	121.4 (4)
C11—Ir1—N3	171.37 (13)	C14—C15—H15	119.3
N1—Ir1—N3	93.67 (12)	C16—C15—H15	119.3
N2—Ir1—N3	90.76 (12)	N2—C16—C15	119.3 (4)
N4—Ir1—N3	76.11 (12)	N2—C16—C17	114.5 (3)

F3—P1—F4	94.7 (4)	C15—C16—C17	126.2 (4)
F3—P1—F2	91.8 (3)	C18—C17—C22	121.7 (4)
F4—P1—F2	91.9 (3)	C18—C17—C16	123.7 (4)
F3—P1—F6	178.3 (3)	C22—C17—C16	114.6 (3)
F4—P1—F6	86.9 (3)	C19—C18—C17	120.0 (4)
F2—P1—F6	88.7 (3)	C19—C18—H18	120.0
F3—P1—F1	88.3 (4)	C17—C18—H18	120.0
F4—P1—F1	176.5 (3)	C18—C19—C20	119.8 (4)
F2—P1—F1	89.9 (2)	C18—C19—H19	120.1
F6—P1—F1	90.1 (3)	C20—C19—H19	120.1
F3—P1—F5	90.7 (3)	C19—C20—C21	120.1 (4)
F4—P1—F5	91.7 (2)	C19—C20—H20	120.0
F2—P1—F5	175.4 (3)	C21—C20—H20	120.0
F6—P1—F5	88.7 (2)	C22—C21—C20	121.4 (4)
F1—P1—F5	86.38 (19)	C22—C21—H21	119.3
C25—O1—C33	117.1 (3)	C20—C21—H21	119.3
C30—O2—C34	117.7 (3)	C21—C22—C17	117.1 (3)
C1—N1—C5	119.3 (3)	C21—C22—Ir1	127.6 (3)
C1—N1—Ir1	125.0 (3)	C17—C22—Ir1	115.3 (3)
C5—N1—Ir1	115.7 (3)	N3—C23—C24	123.6 (3)
C12—N2—C16	119.4 (3)	N3—C23—H23	118.2
C12—N2—Ir1	125.7 (3)	C24—C23—H23	118.2
C16—N2—Ir1	115.0 (3)	C23—C24—C25	118.5 (3)
C23—N3—C27	118.2 (3)	C23—C24—H24	120.8
C23—N3—Ir1	125.0 (2)	C25—C24—H24	120.8
C27—N3—Ir1	116.6 (2)	O1—C25—C24	125.6 (4)
C32—N4—C28	117.8 (3)	O1—C25—C26	115.5 (3)
C32—N4—Ir1	125.8 (3)	C24—C25—C26	118.9 (3)
C28—N4—Ir1	116.1 (2)	C27—C26—C25	118.9 (3)
N1—C1—C2	122.4 (4)	C27—C26—H26	120.6
N1—C1—H1	118.8	C25—C26—H26	120.6
C2—C1—H1	118.8	N3—C27—C26	122.0 (3)
C1—C2—C3	118.8 (4)	N3—C27—C28	114.9 (3)
C1—C2—H2	120.6	C26—C27—C28	123.1 (3)
C3—C2—H2	120.6	N4—C28—C29	121.3 (3)
C4—C3—C2	119.7 (4)	N4—C28—C27	115.0 (3)
C4—C3—H3	120.2	C29—C28—C27	123.8 (3)
C2—C3—H3	120.2	C28—C29—C30	119.5 (4)
C3—C4—C5	119.8 (4)	C28—C29—H29	120.3
C3—C4—H4	120.1	C30—C29—H29	120.3
C5—C4—H4	120.1	O2—C30—C29	116.4 (4)
N1—C5—C4	120.0 (4)	O2—C30—C31	124.2 (4)
N1—C5—C6	113.8 (3)	C29—C30—C31	119.4 (3)
C4—C5—C6	126.2 (4)	C32—C31—C30	117.7 (4)
C7—C6—C11	121.7 (4)	C32—C31—H31	121.2
C7—C6—C5	123.0 (4)	C30—C31—H31	121.2
C11—C6—C5	115.2 (3)	N4—C32—C31	124.3 (4)
C8—C7—C6	120.3 (4)	N4—C32—H32	117.9

C8—C7—H7	119.9	C31—C32—H32	117.9
C6—C7—H7	119.9	O1—C33—H33A	109.5
C7—C8—C9	120.6 (4)	O1—C33—H33B	109.5
C7—C8—H8	119.7	H33A—C33—H33B	109.5
C9—C8—H8	119.7	O1—C33—H33C	109.5
C10—C9—C8	119.4 (4)	H33A—C33—H33C	109.5
C10—C9—H9	120.3	H33B—C33—H33C	109.5
C8—C9—H9	120.3	O2—C34—H34A	109.5
C9—C10—C11	120.2 (4)	O2—C34—H34B	109.5
C9—C10—H10	119.9	H34A—C34—H34B	109.5
C11—C10—H10	119.9	O2—C34—H34C	109.5
C6—C11—C10	117.7 (4)	H34A—C34—H34C	109.5
C6—C11—Ir1	114.3 (3)	H34B—C34—H34C	109.5

C5—N1—C1—C2	−0.3 (6)	C17—C18—C19—C20	0.0 (6)
Ir1—N1—C1—C2	176.9 (4)	C18—C19—C20—C21	−0.7 (7)
N1—C1—C2—C3	0.2 (7)	C19—C20—C21—C22	1.0 (6)
C1—C2—C3—C4	−0.1 (8)	C20—C21—C22—C17	−0.4 (6)
C2—C3—C4—C5	−0.1 (7)	C20—C21—C22—Ir1	−178.8 (3)
C1—N1—C5—C4	0.2 (6)	C18—C17—C22—C21	−0.3 (5)
Ir1—N1—C5—C4	−177.3 (3)	C16—C17—C22—C21	179.4 (3)
C1—N1—C5—C6	−178.6 (4)	C18—C17—C22—Ir1	178.2 (3)
Ir1—N1—C5—C6	3.9 (4)	C16—C17—C22—Ir1	−2.1 (4)
C3—C4—C5—N1	0.0 (7)	C27—N3—C23—C24	−0.7 (6)
C3—C4—C5—C6	178.6 (4)	Ir1—N3—C23—C24	173.4 (3)
N1—C5—C6—C7	177.5 (4)	N3—C23—C24—C25	−0.7 (6)
C4—C5—C6—C7	−1.2 (7)	C33—O1—C25—C24	3.0 (6)
N1—C5—C6—C11	−0.6 (5)	C33—O1—C25—C26	−177.2 (4)
C4—C5—C6—C11	−179.2 (4)	C23—C24—C25—O1	−179.1 (4)
C11—C6—C7—C8	1.1 (7)	C23—C24—C25—C26	1.1 (6)
C5—C6—C7—C8	−176.8 (4)	O1—C25—C26—C27	−180.0 (4)
C6—C7—C8—C9	2.0 (7)	C24—C25—C26—C27	−0.2 (6)
C7—C8—C9—C10	−2.3 (8)	C23—N3—C27—C26	1.7 (5)
C8—C9—C10—C11	−0.5 (7)	Ir1—N3—C27—C26	−172.9 (3)
C7—C6—C11—C10	−3.8 (6)	C23—N3—C27—C28	−177.9 (3)
C5—C6—C11—C10	174.3 (4)	Ir1—N3—C27—C28	7.5 (4)
C7—C6—C11—Ir1	178.9 (3)	C25—C26—C27—N3	−1.3 (6)
C5—C6—C11—Ir1	−3.1 (4)	C25—C26—C27—C28	178.3 (4)
C9—C10—C11—C6	3.4 (6)	C32—N4—C28—C29	−3.0 (6)
C9—C10—C11—Ir1	−179.7 (3)	Ir1—N4—C28—C29	171.0 (3)
C16—N2—C12—C13	−2.4 (6)	C32—N4—C28—C27	176.9 (3)
Ir1—N2—C12—C13	178.0 (3)	Ir1—N4—C28—C27	−9.1 (4)
N2—C12—C13—C14	1.0 (7)	N3—C27—C28—N4	1.1 (5)
C12—C13—C14—C15	0.5 (7)	C26—C27—C28—N4	−178.5 (4)
C13—C14—C15—C16	−0.5 (7)	N3—C27—C28—C29	−179.0 (4)
C12—N2—C16—C15	2.3 (6)	C26—C27—C28—C29	1.4 (6)
Ir1—N2—C16—C15	−178.0 (3)	N4—C28—C29—C30	0.6 (6)
C12—N2—C16—C17	−178.8 (3)	C27—C28—C29—C30	−179.3 (4)

Ir1—N2—C16—C17	0.8 (4)	C34—O2—C30—C29	177.6 (4)
C14—C15—C16—N2	−0.9 (7)	C34—O2—C30—C31	−3.1 (6)
C14—C15—C16—C17	−179.6 (4)	C28—C29—C30—O2	−178.0 (4)
N2—C16—C17—C18	−179.5 (3)	C28—C29—C30—C31	2.8 (6)
C15—C16—C17—C18	−0.7 (6)	O2—C30—C31—C32	177.2 (4)
N2—C16—C17—C22	0.8 (5)	C29—C30—C31—C32	−3.5 (6)
C15—C16—C17—C22	179.6 (4)	C28—N4—C32—C31	2.2 (6)
C22—C17—C18—C19	0.6 (6)	Ir1—N4—C32—C31	−171.2 (3)
C16—C17—C18—C19	−179.1 (4)	C30—C31—C32—N4	1.1 (7)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···F1^{i}	0.95	2.39	3.290 (6)	158
C26—H26···F5^{ii}	0.95	2.53	3.442 (5)	160
C29—H29···F1^{ii}	0.95	2.46	3.296 (6)	146
C29—H29···F5^{ii}	0.95	2.53	3.442 (5)	161
C33—H33*C*···F5	0.98	2.50	3.396 (5)	152

Symmetry codes: (i) *x*, −*y*+3/2, *z*+1/2; (ii) −*x*, −*y*+1, −*z*.