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(2,2′-Bipyridine)chloro(4′-tolyl-2,2′:6′,2″-terpyridine)iridium(III) bis(hexafluorophosphate) acetonitrile disolvate

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.018
wR factor = 0.045
Data-to-parameter ratio = 16.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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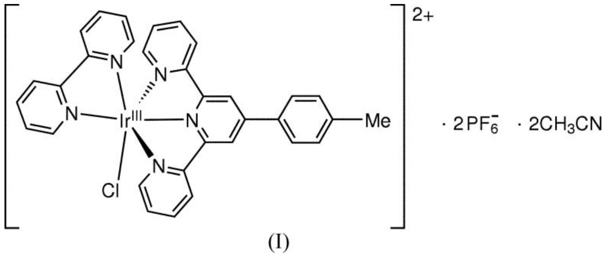
In the title compound, $[\mathrm{IrCl(C_{10}H_8N_2)(C_{22}H_{17}N_3)}]$-$(\mathrm{PF_6})_2\cdot 2\mathrm{C_2H_3N}$, the complex cation $[\mathrm{Ir^{III}Cl(bpy)(tterpy)}]^{2+}$ shows a deformed octahedral coordination geometry (tterpy = 4′-tolyl-2,2′:6′,2″-terpyridine and bpy = 2,2′-bipyridine). Due to the relatively strong intercationic tterpy–tterpy associations, the tolyl group deviates significantly from ideal geometry. The benzene ring of tterpy is inclined with respect to the central pyridyl ring at an angle of 24.7 (1)°.

Comment

Recently, iridium complexes have received considerable attention due to their attractive luminescence properties in respect of the fabrication of new electroluminescence devices. In this context, various new iridium(III) complexes ligated with polypyridyl-type ligands have been prepared in our research group to evaluate their potential as electroluminescent materials. The title $\mathrm{Ir^{III}}$ compound, (I), involving a π-conjugated planar tridentate ligand, namely 4′-tolyl-2,2′:6′,2″-terpyridine (abbreviated as tterpy), has been prepared and structurally analyzed by X-ray diffraction. It should be noted here that the synthesis and the spectroscopic properties of (I) have recently been reported by the same authors (Yutaka *et al.*, 2005).



(I)

The asymmetric unit of (I) consists of an $[\mathrm{Ir^{III}Cl(tterpy)(bpy)}]^{2+}$ cation (bpy = 2,2′-bipyridine), two $\mathrm{PF_6^-}$ anions, and two acetonitrile molecules (see Fig. 1). Bond distances and angles for the coordination of Ir are summarized in Table 1. The oxidation level of the metal centre has been unambiguously judged to be $\mathrm{Ir^{III}}$. The diamagnetic character of (I) is also obvious from the fact that the ^{1}H NMR spectrum of (I) does not suffer from any broadening factors due to the coexistence of paramagnetic species (Yutaka *et al.*, 2005). One of the two acetonitrile molecules has an association to the bpy ligand based on a π–π stacking interaction achieved between the nitrile group and one of the pyridyl rings of bpy involving atoms N5/C28–C32 (see Fig. 1); atoms N7 and C35 of the nitrile group are displaced out of the mean plane defined by atoms N5/C28–C32 by 3.235 (2) and 3.387 (3) Å, respectively.

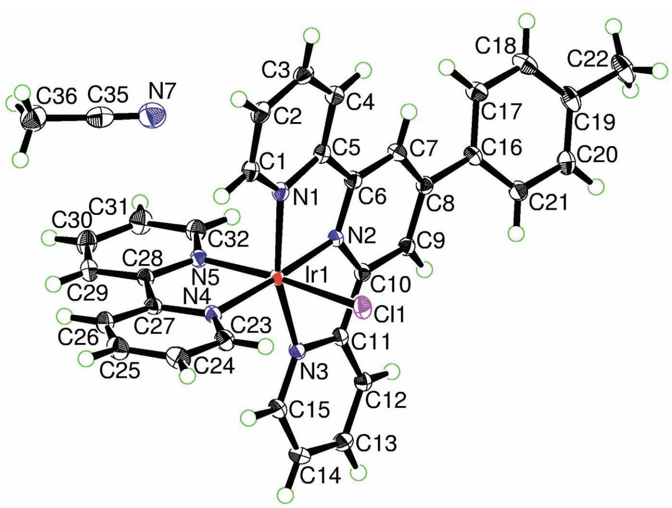


Figure 1
The structure of the complex cation, together with one of the two acetonitrile solvent molecules in the asymmetric unit of (I), showing the atom-labelling scheme and the manner in which the acetonitrile molecule has a π-stacking interaction with a 2,2′-bipyridine unit. Displacement ellipsoids are shown at the 50% probability level. The counter-ions and one of the two acetonitrile solvent molecules in the asymmetric unit of (I) have been omitted for clarity.

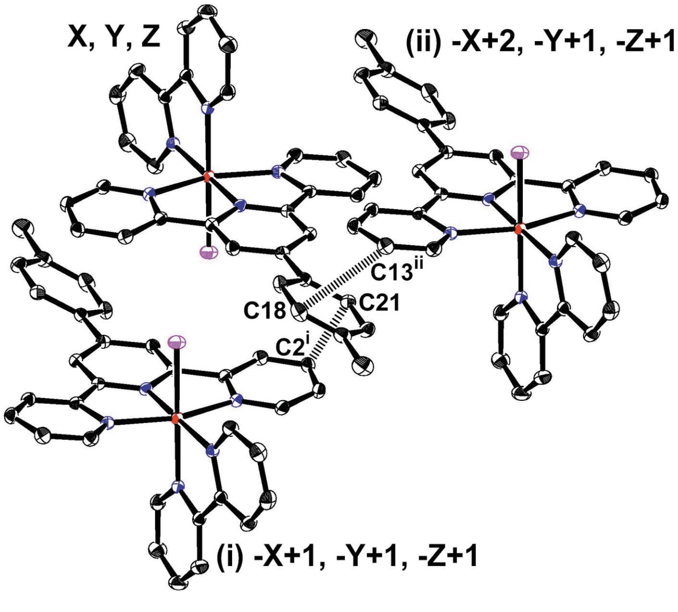


Figure 2
A view showing the manner in which the $[Ir^{III}Cl(bpy)(tterpy)]^{2+}$ cations are stacked along the *a* axis, based on π–π stacking interactions between the tterpy ligands. Counter-anions, acetonitrile molecules and H atoms have been omitted for clarity. Broken lines indicate short C—C contacts.

Relatively short contacts include C32···N7 = 3.362 (3) Å, C29···C35 = 3.489 (3) Å and C30···C35 = 3.551 (3) Å.

Furthermore, the intercationic interactions are partly stabilized by π–π associations formed between adjacent tterpy units (see Fig. 2). Although the dihedral angles between the tolyl and pyridyl planes of adjacent cations are relatively large [28.9 (1) and 19.3 (1)°], extremely short C···C contacts are observed [C21···C2($-x + 1, -y + 1, -z + 1$) = 3.251 (3) Å and C18···C13($-x + 2, -y + 1, -z + 1$) = 3.149 (3) Å]. As a result, an unusual structural strain is introduced in the tolyl group; thus atoms N2/C8/C16/C19 clearly deviate from ideal collinearity, with C16—C8···N2 = 178.32 (14)° and C8—C16···C19 = 176.05 (14)°.

Mean-plane calculations have been performed for the six aromatic rings in the ligands of (I). The six-atom r.m.s. deviations are calculated to be 0.008, 0.013, 0.004, 0.006, 0.008, and 0.006 Å for ring *A* (atoms N1/C1–C5), ring *B* (N2/C6–C10), ring *C* (N3/C11–C15), ring *D* (C16–C21), ring *E* (N4/C23–C27) and ring *F* (N5/C28–C32), respectively. The results reveal that only the central pyridyl ring *B* of tterpy is deformed from planarity, presumably due to the intercationic contacts described above in Fig. 2. The two pyridyl rings *A* and *C* are inclined with respect to the central pyridyl ring *B* by 4.2 (1) and 7.8 (1)°, respectively. The dihedral angle between rings *A* and *C* is 11.5 (1)°. The benzene ring *D* of the tolyl group is inclined to the central pyridyl ring *B* by 24.7 (1)°. It is quite reasonable to consider here that the tolyl ring is tilted with respect to the central pyridyl ring so as to avoid the steric contacts H(—C7)···H(—C17) and H(—C9)···H(—C21). As for the bpy geometry, the dihedral angle between rings *E* and *F* is 7.5 (1)°.

Experimental

The title compound, (I), was prepared as described elsewhere (Yutaka *et al.*, 2005). Single crystals of (I) suitable for X-ray diffraction were grown by slow diffusion of diethyl ether into an acetonitrile solution at 293 K. Since the crystals were found to be rather unstable upon exposure to air, a crystal together with the filtrate was rapidly mixed with an oil and placed in a nitrogen gas stream (100 K) for the X-ray measurements.

Crystal data

$[IrCl(C_{10}H_8N_2)(C_{22}H_{17}N_3)]$-
$(PF_6)_2(C_2H_3N)_2$
M_r = 1079.27
Monoclinic, $P2_1/c$
a = 11.3701 (5) Å
b = 19.4632 (8) Å
c = 17.7735 (7) Å
β = 103.338 (1)°
V = 3827.2 (3) Å^3
Z = 4
D_x = 1.873 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 9226 reflections
θ = 2.2–28.3°
μ = 3.74 mm^{-1}
T = 100 (2) K
Prism, yellow
0.28 × 0.26 × 0.2 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.373, T_{max} = 0.473
47376 measured reflections
8779 independent reflections
8138 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 27.5°
$h = -14 \rightarrow 14$
$k = -25 \rightarrow 25$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.045
S = 1.05
8779 reflections
535 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 2.5729P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.88 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Ir1—N2	1.9629 (15)	Ir1—N3	2.0513 (16)
Ir1—N5	2.0354 (16)	Ir1—N4	2.0605 (16)
Ir1—N1	2.0512 (17)	Ir1—Cl1	2.3343 (5)
C32···N7	3.362 (3)	C18···C13^{i}	3.149 (3)
C29···C35	3.489 (3)	C21···C2^{ii}	3.251 (3)
C30···C35	3.551 (3)		
N2—Ir1—N5	98.44 (7)	N1—Ir1—N4	96.93 (6)
N2—Ir1—N1	80.74 (6)	N3—Ir1—N4	102.33 (6)
N5—Ir1—N1	92.89 (6)	N2—Ir1—Cl1	86.69 (5)
N2—Ir1—N3	80.08 (6)	N5—Ir1—Cl1	174.41 (5)
N5—Ir1—N3	92.31 (6)	N1—Ir1—Cl1	90.09 (5)
N1—Ir1—N3	160.66 (6)	N3—Ir1—Cl1	86.39 (5)
N2—Ir1—N4	176.84 (6)	N4—Ir1—Cl1	95.47 (5)
N5—Ir1—N4	79.49 (7)		

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z+1$.

All H atoms were placed at their idealized positions [C—H(methyl) = 0.96 Å and C—H(aromatic) = 0.93 Å] and included in the refinement in the riding-model approximation, with $U_{\rm iso}$(methyl H) = $1.5U_{\rm eq}$(bonded C) and $U_{\rm iso}$(aromatic H) = $1.2U_{\rm eq}$(bonded C).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL97*, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEPII* (Johnson, 1976).

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References

Bruker (2001). *SAINT* (Version 6.22) and *SMART* (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (2001). *TEXSAN*. Version 1.11r1. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381-5209, USA.

Sakai, K. (2002). *KENX*. Graphical User Interface for *SHELXL97*. Tokyo University of Science, Japan.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Yutaka, T., Obara, S., Ogawa, S., Nozaki, K., Ikeda, N., Ohno, T., Ishii, Y., Sakai, K. & Haga, M. (2005). *Inorg. Chem.* In the press.

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