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Di-μ-chloro-bis{bis[4-(2-pyridyl)benzaldehyde-κ^2C^2,N']iridium} dichloromethane sesquisolvate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.011 Å
Disorder in solvent or counterion
R factor = 0.042
wR factor = 0.088
Data-to-parameter ratio = 16.5

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

The title compound, $[Ir_2Cl_2(C_{12}H_8NO)_4]\cdot 1.5CH_2Cl_2$ or $[Ir(fppy)_2Cl]_2\cdot 1.5CH_2Cl_2$ [where fppy is 4-(2-pyridyl)benzaldehyde], is a dinuclear iridium(III) complex containing two six-coordinate iridium centres connected by two bridging chlorides, which has crystallized with the solvent dichloromethane.

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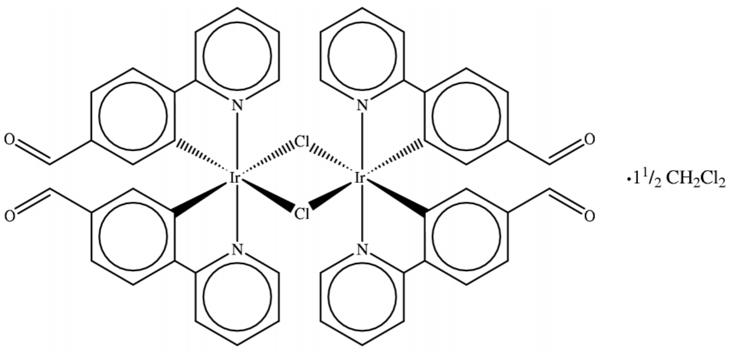
Comment

Electrophosphorescent complexes that are capable of generating pure red, green and blue light are in high demand due to their potential use as dopants in full-colour organic light-emitting displays. Triply *ortho*-metallated iridium(III) complexes containing cyclometalating ligands, such as 2-phenylpyridine, have already been exploited in these kinds of devices with a great deal of success (Baldo *et al.*, 1999; Adachi *et al.*, 2000; Beeby *et al.*, 2003). These monomeric cyclometallated iridium(III) complexes may be synthesized by a variety of synthetic pathways, which include those that utilize dichloro-bridged species as precursors (Dedeian *et al.*, 1991; Grushin *et al.*, 2001; Lamansky *et al.*, 2001; Tamayo *et al.*, 2003). These dinuclear species are generally produced in high yield from the reactions of iridium(III) chloride and the corresponding cyclometallating ligand (Sprouse *et al.*, 1984).

A number of novel dichloro-bridged species of this nature have been reported, where they have primarily been used as precursors for the preparation of monomeric *ortho*-metallated iridium(III) and rhodium(III) complexes (Garces *et al.*, 1988; Tamayo *et al.*, 2003). Despite this, they have received little or no detailed structural attention.



(I)

The title compound, (I) (Fig. 1), consists of two octahedral iridium(III) centres, each ligated by two 4-(2-pyridyl)benzaldehyde (fppy) and two bridging chloride ions, together with one and a half molecules of disordered dichloromethane solvent per asymmetric unit. The chloride ligands reside in the

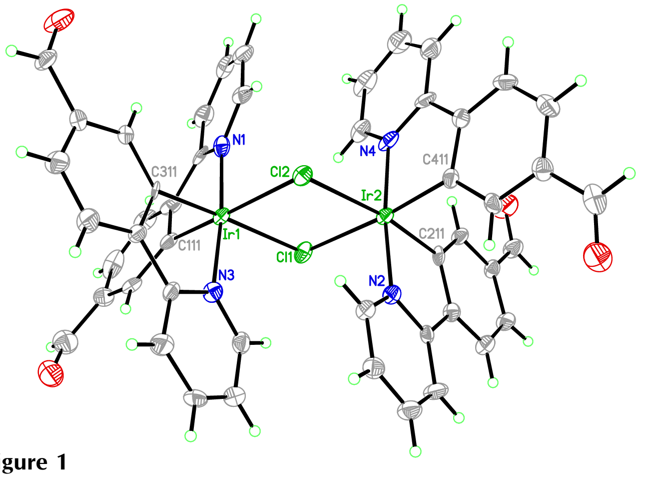


Figure 1
View of (I), with selected atoms labelled. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The solvent has been omitted.

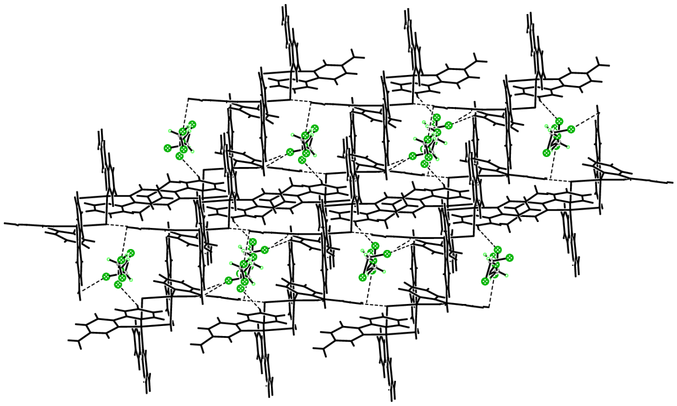


Figure 2
The crystal packing in the title compound, viewed down the channels occupied by the disordered dichloromethane, with selected C—H···Cl hydrogen bonds shown as dashed lines. The $[Ir(fppy)_2Cl]_2$ molecules are depicted in black for clarity.

equatorial plane *trans* to the fppy C atoms and the fppy N atoms occupy the apical sites with *trans* geometry. This is consistent with other dinuclear iridium(III) and rhodium(III) complexes of this type (Fronczek *et al.*, 1982; Steel, 1991; Garces *et al.*, 1993; Ghisdavu *et al.*, 1999). However, the Ir—Cl bond lengths fall into two groups, differing by approximately 0.1 Å, with both Ir—Cl1 bonds shorter than the Ir—Cl2 bonds (Table 1). This effect is also seen in the Ir—Cl—Ir angle, which is larger for Cl1 than Cl2. Some degree of asymmetry is seen in the other examples of chloride-bridged iridium(III) or rhodium(III) dimers, but in most cases pairs of Ir—Cl distances are constrained by crystal symmetry.

The disordered dichloromethane occupies channels within the structure (Fig. 2), with weak C—H···Cl interactions between the iridium dimer and the solvent, which limits the disorder to three components (see below).

Experimental

$IrCl_3 \cdot 3H_2O$ (0.35 g, 1.0 mmol), 4-(2-pyridyl)benzaldehyde (0.92 g, 5.0 mmol), 2-ethoxyethanol (15 ml) and water (7 ml) were placed in a reaction vessel and heated to 383 K for 8 h with continuous stirring. The initial dark-brown solution became lighter in colour and an orange precipitate formed. The solution was cooled to room temperature and was filtered. The resulting solid was washed with ethanol (2 × 10 ml) and acetone (2 × 10 ml). The product was dissolved in dichloromethane and column chromatography (silica gel, dichloromethane) yielded a bright-orange solid (0.44 g, 73%). ^1H NMR (300 MHz, $CDCl_3$): δ 9.53 (4H, *s*), 9.27 (4H, *d*, $J = 4.8$ Hz), 8.07 (4H, *d*, $J = 7.8$ Hz), 7.94 (4H, *td*, $J = 8.0$ Hz), 7.68 (4H, *d*, $J = 8.4$ Hz), 7.32 (4H, *dd*, $J = 1.5$ Hz), 6.91 (4H, *td*, $J = 6.0$ Hz), 6.29 (4H, *d*, $J = 1.5$ Hz). MS (EI$^+$): *m*/*z* 1184 (M^+), 592 $[(M - IrC_{24}H_{16}N_2O_2 - Cl)^+]$, 557 $[(M - IrC_{24}H_{16}N_2O_2 - Cl_2)^+]$. Crystals of (I) were grown from dichloromethane.

Crystal data

$[Ir_2Cl_2(C_{12}H_8NO)_4] \cdot 1.5CH_2Cl_2$
$M_r = 1311.46$
Triclinic, $P\overline{1}$
$a = 10.577$ (2) Å
$b = 12.779$ (2) Å
$c = 17.924$ (3) Å
$\alpha = 75.562$ (4)°
$\beta = 88.993$ (3)°
$\gamma = 71.629$ (3)°
$V = 2221.7$ (7) Å^3

$Z = 2$
$D_x = 1.96$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 999 reflections
$\theta = 3.1$–27.4°
$\mu = 6.34$ mm^{-1}
$T = 120$ (2) K
Block, clear intense orange
0.15 × 0.10 × 0.10 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
$T_{min} = 0.419$, $T_{max} = 0.531$
23 666 measured reflections

10 151 independent reflections
7329 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -22 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.088$
$S = 1.03$
10 151 reflections
614 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 1.83$ e Å^{-3}
$\Delta\rho_{min} = -2.60$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir1—C111	1.976 (7)	Ir2—C411	1.974 (7)
Ir1—C311	1.990 (6)	Ir2—C211	2.000 (6)
Ir1—N1	2.034 (6)	Ir2—N2	2.040 (6)
Ir1—N3	2.046 (6)	Ir2—N4	2.040 (6)
Ir1—Cl1	2.5020 (17)	Ir2—Cl1	2.5075 (19)
Ir1—Cl2	2.5187 (18)	Ir2—Cl2	2.5260 (16)
C111—Ir1—C311	92.9 (3)	C411—Ir2—N2	93.5 (3)
C111—Ir1—N1	80.8 (3)	C211—Ir2—N2	81.2 (2)
C311—Ir1—N1	96.6 (2)	C411—Ir2—N4	80.5 (3)
C111—Ir1—N3	94.7 (3)	C211—Ir2—N4	95.4 (2)
C311—Ir1—N3	80.5 (2)	N2—Ir2—N4	173.1 (2)
N1—Ir1—N3	174.5 (2)	C411—Ir2—Cl1	174.7 (2)
C111—Ir1—Cl1	92.0 (2)	C211—Ir2—Cl1	91.39 (19)
C311—Ir1—Cl1	172.9 (2)	N2—Ir2—Cl1	91.22 (17)
N1—Ir1—Cl1	89.34 (16)	N4—Ir2—Cl1	94.88 (19)
N3—Ir1—Cl1	93.94 (16)	C411—Ir2—Cl2	95.29 (19)
C111—Ir1—Cl2	171.5 (2)	C211—Ir2—Cl2	171.86 (19)
C311—Ir1—Cl2	93.32 (19)	N2—Ir2—Cl2	93.90 (16)
N1—Ir1—Cl2	92.77 (17)	N4—Ir2—Cl2	90.17 (16)
N3—Ir1—Cl2	92.00 (17)	Cl1—Ir2—Cl2	82.17 (5)
Cl1—Ir1—Cl2	82.43 (5)	Ir1—Cl1—Ir2	98.16 (6)
C411—Ir2—C211	91.5 (3)	Ir1—Cl2—Ir2	97.24 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
C14—H14A···Cl52	0.93	2.89	3.715 (10)	148
C33—H33A···Cl71$^{\text{i}}$	0.93	2.78	3.557 (10)	142
C43—H43A···Cl72$^{\text{ii}}$	0.93	2.56	3.205 (11)	127

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

All H atoms were positioned geometrically (C—H = 0.93 or 0.97 Å) and refined using a riding model, with $U_{\rm iso}$ = 1.2 or 1.5 times $U_{\rm eq}$(parent C atom). The solvent, dichloromethane, was modelled as disordered in three components, all partially occupied. One molecule of dichloromethane is rotationally disordered about the central C atom and the partial occupancies of the two components were refined (0.57/0.43) and then fixed. The remaining solvent molecule is located close to an inversion centre and was assigned 50% occupancy. Anisotropic displacement parameters were refined for all non-H atoms (including the solvent). Although there is a small amount of electron density unaccounted for in this disordered solvent model, all peaks larger than 1 e Å are within 1 Å of an Ir atom. The deepest hole is located 1.37 Å from atom H17A.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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