Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

Di-μ-chloro-bis{bis[2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole-$\kappa^2C^{2'},N$]iridium(III)] dichloromethane disolvate

Lian-Qing Chen, Chu-Luo Yang* and Jin-Gui Qin

Department of Chemistry, Wuhan University, Wuhan 430072, People's Republic of China
Correspondence e-mail: clyang@whu.edu.cn

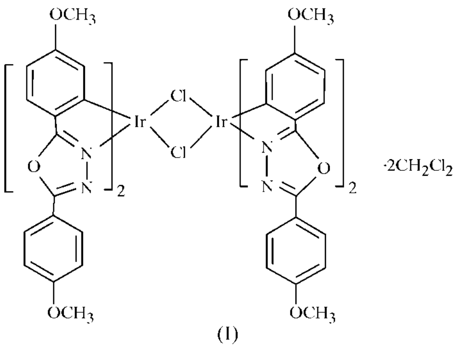
Received 7 September 2005
Accepted 6 October 2005
Online 11 November 2005

In the title compound, $[Ir_2(C_{16}H_{13}N_2O_3)_4Cl_2]\cdot 2CH_2Cl_2$, the two Ir atoms, 3.7075 (6) Å apart, are bridged by two Cl atoms which straddle a twofold axis of rotation through the two Ir atoms. Each Ir centre resides in a distorted octahedral environment completed by two chelating 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole ligands, with *trans*-N—N and *cis*-C—C dispositions. In the stacking structure, there are two types of hydrogen bonds, involving the methoxy substitutent, an N atom of the oxadiazole ring and the dichloromethane solvent molecules.

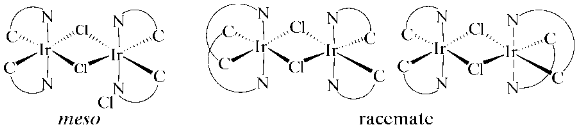
Comment

In recent decades, luminescent metal complexes have attracted considerable attention due to their intriguing photophysical, photochemical and excited-state redox properties, and their potential applications in photonic and photoelectronic devices (King *et al.*, 1985; King & Watts, 1987). In particular, iridium(III) complexes with cyclometallated ligands show intense phosphorescence at room temperature and very promising behaviour as phosphor dyes in OLEDs (organic light-emitting diodes) (Baldo *et al.*, 1998; Lamansky *et al.*, 2001). On the other hand, oxadiazole derivatives have played a very important role in the field of electroactive and photoactive materials, due to their high electron affinities which make them good candidates for electron injection and transportation (Gregory & Martin, 2005). However, oxadiazole-based metal complexes are very scarce. To our knowledge, there have not been any reports of oxadiazole-based cyclometallated iridium complexes. In addition, although many structures of mononuclear cyclometallated iridium complexes have been determined (Lamansky *et al.*, 2001), there are very limited reports on the structures of dinuclear iridium complexes. In this paper, a new dinuclear iridium complex, (I), with 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole as the cyclometallated ligand, is presented.

In compound (I), which is a dichloromethane solvate, the Ir atoms, 3.7075 (6) Å apart on a twofold axis of rotation, are bridged by two Cl atoms. The Ir—C bond exerts a significant *trans* effect which favours the formation of bridged Ir—Cl bonds *trans* to the Ir—C bonds. Each Ir centre sits in a distorted octahedral environment formed by two chelating ligands with *trans*-N—N and *cis*-C—C dispositions. The molecules take the racemate form, rather than the *meso* form, owing to the interligand steric interactions (see scheme). This conformation is consistent with a similar dirhodium complex (Sprouse *et al.*, 1984).



(I)



The Ir1—Cl, Ir1—C and Ir1—N bond distances are slightly different from the corresponding distances involving Ir2 (Table 1). These values are, in general, similar to those in the analogous complex $[Ir(ppy)_2Cl]_2$ (ppy = phenylpridine) [Ir—Cl = 2.500 (10) Å, Ir—C = 2.020 (2) Å and Ir—N = 2.090 (10) Å; Garces *et al.*, 1993]. The oxadiazole plane and metallated 4-methoxyphenyl ring are coplanar due to the

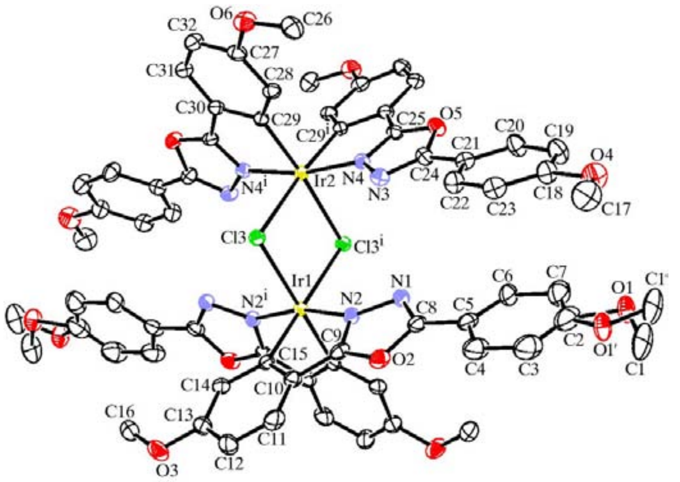


Figure 1
A view of the molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms and solvent molecules have been omitted for clarity. Primed atom labels indicate the minor disorder component. [Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.]

DOI: 10.1107/S0108270105031951

formation of a five-membered chelate ring by the coordination of Ir with a C atom of the 4-methoxyphenyl and an N atom of the oxadiazole. Each free 4-methoxyphenyl ring is twisted out of the oxadiazole plane by rotation of the C—C single bond; the dihedral angles between these planes are 10.3 (12)° with respect to Ir1 and 13.7 (11)° with respect to Ir2.

In the stacking structure of compound (I), there are two types of weak hydrogen bonds (Table 2), between atom O3 of the methoxy substitute and an H atom on C26, and between atom N4 of the oxadiazole ring and H atoms of the CH_2Cl_2 solvent molecule (Fig. 2).

The absorption and photoluminescence (PL) spectra of the dimer in CH_2Cl_2 solution were investigated (Fig. 3). In the absorption spectrum, intense absorptions are observed in the UV region of the spectrum, between 250 and 320 nm, which can be assigned to the spin-allowed π–π^* transition from the cyclometallated ligands. The weaker absorption bands in the range 320–450 nm can probably be assigned to metal-to-ligand charge transfer (MLCT) and $^3\pi$–π^* transition (Sprouse *et al.*, 1984). The PL spectrum of the dimer shows two major peaks at 503 and 540 nm. The vibronic fine structures in the PL spectrum imply that the emissions predominantly result from ligand-based $^3\pi$–π^* transition.

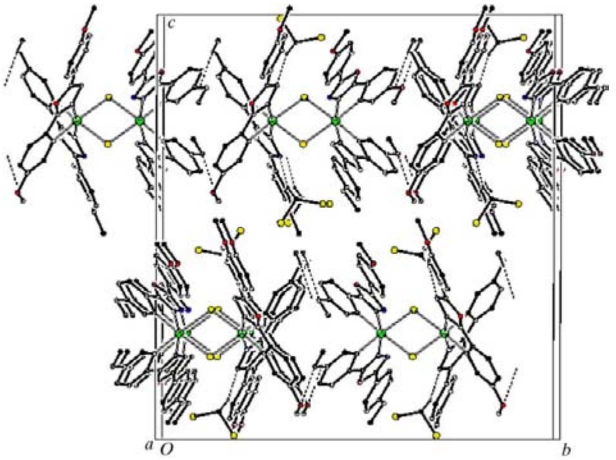


Figure 2
The packing structure of compound (I). Hydrogen bonds are indicated by dashed lines.

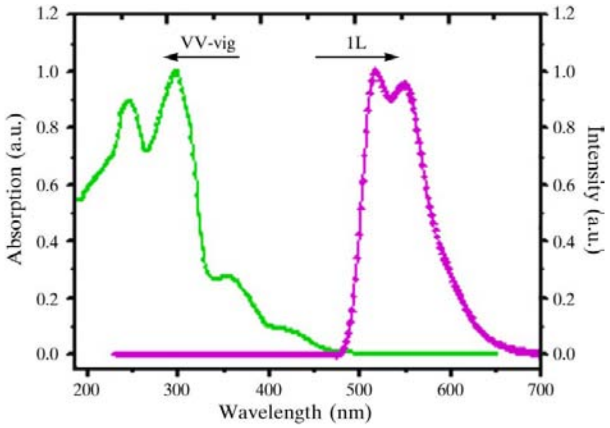


Figure 3
The absorption and photoluminescence spectra of the dimer in CH_2Cl_2 solution.

Experimental

Iridium trichloride hydrate (0.352 g, 1.0 mmol), purchased and used without further purification, was combined with 2.5 equivalents of the cyclometallating ligand 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole [0.705 g, 2.5 mmol; prepared according to Sun & Wang (2001)] dissolved in a mixture of 2-ethoxyethanol (30 ml) and water (10 ml). The resulting solution was refluxed for 24 h, cooled to room temperature and the yellow precipitate collected on a glass filter frit. The product was washed with water, ethanol and hexane, dried under vacuum and recrystallized from dichloromethane–hexane (1:1 *v*/*v*) (yield 0.515 g, 65.2%). ^{1}H NMR ($CDCl_3$): δ 7.84 (*d*, *J* = 8.4 Hz, 8H), 7.43 (*d*, *J* = 8.4 Hz, 4H), 6.64 (*d*, *J* = 8.4 Hz, 8H), 6.42 (*d*, *J* = 8.1 Hz, 4H), 6.01 (*s*, 4H), 3.84 (*s*, 12H), 3.50 (*s*, 12H). Analysis calculated for $C_{64}H_{52}Cl_2IrN_8O_{12}\cdot 2CH_2Cl_2$: C 45.29, H 3.22, N 6.40%; found: C 45.23, H 3.10, N 6.21%.

Crystal data

$[Ir_2(C_{16}H_{13}N_2O_3)_4Cl_2]\cdot 2CH_2Cl_2$
$M_r = 1750.29$
Monoclinic, $C2/c$
$a = 11.5352$ (10) Å
$b = 23.390$ (2) Å
$c = 25.239$ (2) Å
$\beta = 98.423$ (2)°
$V = 6736.4$ (10) Å^3
$Z = 4$
$D_x = 1.726$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3335 reflections
$\theta = 2.2$–20.4°
$\mu = 4.25$ mm^{-1}
$T = 292$ (2) K
Plate, yellow
0.28 × 0.20 × 0.08 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.321$, $T_{max} = 0.712$
17436 measured reflections
6526 independent reflections
4696 reflections with $I > 2\sigma(I)$
$R_{int} = 0.056$
$\theta_{max} = 26.0°$
$h = -13 \rightarrow 14$
$k = -28 \rightarrow 28$
$l = -31 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.122$
$S = 1.03$
6526 reflections
437 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.017$
$\Delta\rho_{max} = 1.84$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir1—C15	2.010 (7)	Ir2—C29	2.001 (7)
Ir1—N2	2.043 (6)	Ir2—N3	2.042 (6)
Ir1—Cl3	2.4974 (18)	Ir2—Cl3	2.4854 (17)
C15—Ir1—N2	79.4 (3)	C29—Ir2—Cl3	174.55 (19)
C15—Ir1—Cl3	176.4 (2)	N3—Ir2—Cl3	89.77 (16)
N2—Ir1—Cl3	97.78 (18)	Ir2—Cl3—Ir1	96.16 (6)
C29—Ir2—N3	93.0 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
C33—H33A···N4^{i}	0.97	2.53	3.456 (16)	160
C26—H26A···O3^{ii}	0.96	2.49	3.419 (12)	163

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

Atoms O1 and C1 of the 2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazole ligand were found to be disordered over two positions (O1/O1′ and C1/C1′), with refined occupancies of 0.623 (9) and 0.377 (9) and anisotropic displacement parameters. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for aromatic H atoms, C—H = 0.96 Å and $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C) for methyl H atoms, and C—H = 0.97 Å and $U_{\rm iso}$(H) = 0.183 Å^2 for the dichloromethane solvent H atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

The authors thank the National Natural Science Foundation of China (grant Nos. 20371036 and 20474047), the Program for New Century Excellent Talents in University of the Ministry of Education of China, and the Hubei Province Science Fund for Distinguished Young Scholars (No. 2003ABB008) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1229). Services for accessing these data are described at the back of the journal.

References

Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E. & Forrest, S. R. (1998). *Nature*, **395**, 151–152.

Garces, F. O., Dedeian, K., Keger, N. L. & Watts, R. J. (1993). *Acta Cryst.* C**49**, 1117–1120.

Gregory, H. & Martin, R. B. (2005). *J. Mater. Chem.* **15**, 94–107.

King, K. A., Spellane, P. J. & Watts, R. J. (1985). *J. Am. Chem. Soc.* **107**, 1431–1434.

King, K. A. & Watts, R. J. (1987). *J. Am. Chem. Soc.* **109**, 1589–1592.

Lamansky, S., Djurovich, P., Murphy, D., Abdel-Razzaq, F., Lee, H.-F., Adachj, C., Burrows, P. E., Forrest, S. R. & Thompson, M. E. (2001). *J. Am. Chem. Soc.* **123**, 4304–4309.

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

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

Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sprouse, S., King, K. A., Spellane, P. J. & Watts, R. J. (1984). *J. Am. Chem. Soc.* **106**, 6647–6653.

Sun, Y. M. & Wang, C. S. (2001). *Polymer*, **42**, 1035–1046.