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The photodecomposition product μ-oxalato-$1\kappa^2O,O':2\kappa^2O'',O'''$-bis{bis[2-(2-pyridyl)phenyl-κ^2C,N]iridium(III)}–acetone (1/1.974)

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An attempt to grow crystals of [Ir(ppy)$_2$(vacac)], (I), from an acetone-d_6 solution formed instead crystals of [{Ir(ppy)$_2$}$_2$(μ-oxalato)] acetone solvate, (II), [Ir$_2$(C$_{11}$H$_8$N)$_4$(C$_2$O$_4$)]·1.974C$_3$H$_6$O, where ppy is the phenylpyridine anion and vacac is vinylacetylacetonate. Each Ir^{III} ion in (II) is in a pseudo-octahedral coordination environment, where the pyridine N atoms are *trans* to each other and the phenyl C atoms are *trans* to the O atoms of the oxalate bridging ligand. There are two crystallographically independent dimer molecules, each lying on an inversion centre. It is suggested that the oxalate ligand is formed in a series of steps initiated by the aldol condensation of acetone with vacac.

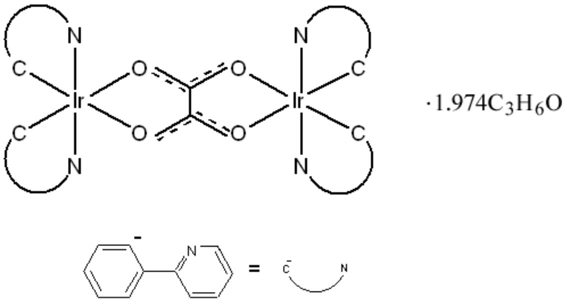
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.040
wR factor = 0.098
Data-to-parameter ratio = 21.9

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

Comment

The excited state of cyclometallated iridium(III) complexes is readily quenched by oxygen and this makes these complexes ideal for incorporation into oxygen-sensing devices. We recently published a study demonstrating their utility (DeRosa *et al.*, 2003), as well as a study describing the syntheses of a number of promising iridium complexes (DeRosa *et al.*, 2004).



(II)

In an attempt to grow crystals of [Ir(ppy)$_2$(vacac)], (I), where ppy is the phenylpyridine anion and vacac is vinyl acetylacetonate, from an acetone-d_6 solution of the complex, golden-yellow crystals of the dimer [{Ir(ppy)$_2$}$_2$(μ-oxalato)] acetone solvate (1/1.974), (II), were isolated. We present here the crystal structure of (II).

Crystallography revealed the space group of (II) to be triclinic, $P\overline{1}$, with both Ir dimers of the unit cell centred on inversion centres, and the presence of acetone in the crystal structure. The asymmetric unit consists of two half-dimers (both being completed across an inversion centre), one fully occupied ordered acetone site, one partially occupied acetone

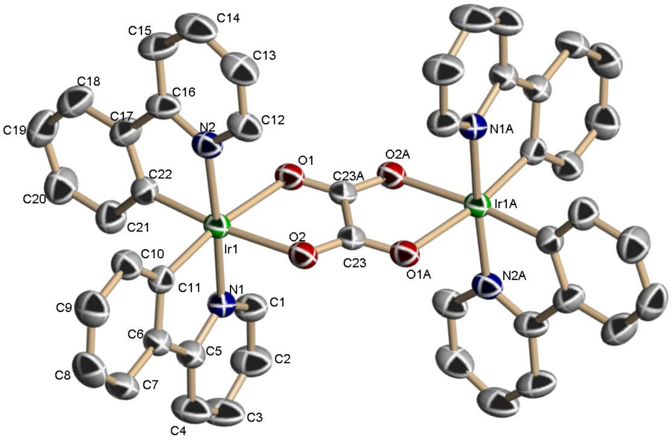


Figure 1
The molecular structure of (II). All acetone molecules and H atoms have been omitted for clarity. Only one of the two crystallographically independent molecules is depicted. Anisotropic displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: A, $1 - x$, $-y$, $1 - z$.]

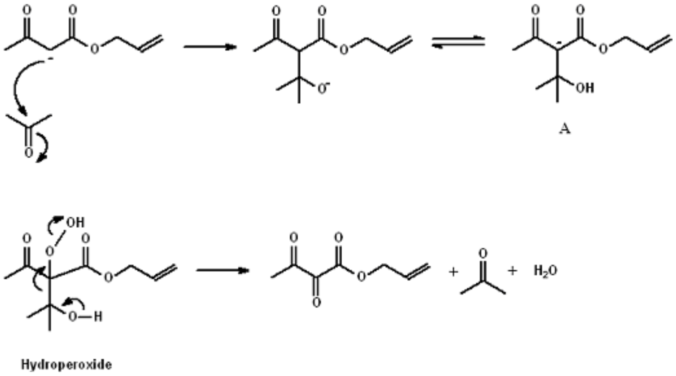


Figure 2
Aldol condensation between the vacac ligand and acetone, and the dehydration of the hydroperoxide that is formed from *A* reacting with singlet oxygen.

site [occupancy 0.234 (3)], and one partially occupied and disordered (overlapped) acetone site [occupancies of 0.531 (3) and 0.209 (3)]. The asymmetric unit thus contains the equivalent of one Ir dimer cluster and 1.974 acetone molecules.

Each Ir^{III} ion in (II) is in a pseudo-octahedral coordination environment, where the pyridine N atoms are *trans* to each other and the phenyl C atoms are *trans* to the O atoms of the oxalate bridging ligand. Fig. 1 shows the molecular structure of one of the iridium dimers, and selected structural data are compiled in Table 1.

The formation of complex (II) from (I) is unexpected. Oxalate was not added to the reaction mixture, nor is oxalate associated with the synthesis of (I). Complex (II) did not form in $CHCl_3$, CH_3CN or methanol, or if under an argon atmosphere, or if shielded from light. Because acetone is required for the formation of (II), it is suggested that the initial step involves an aldol condensation between the enolate vacac anion and acetone (Fig. 2) (Wasserman & Ives, 1981; Wasserman, 2004).

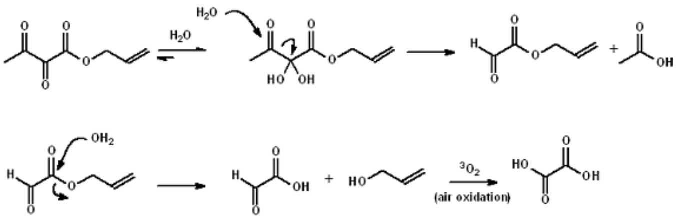


Figure 3
Cleavage of the tricarbonyl and formation of oxalic acid.

Dioxygen quenching of the excited state of (I) likely produces singlet oxygen which attacks the aldol condensation product *A* (Fig. 2), forming a hydroperoxide which can then dehydrate to form the tricarbonyl species. The tricarbonyl species can be easily hydrated to the geminal-diol and further hydrolysis can form the aldehydo ester (Rubin & Gleiter, 2000). Hydrolysis of the allyl ester and air oxidation of the aldehyde gives oxalic acid (Fig. 3).

The formation of (II) is indicative that $[Ir(ppy)_2(vacac)]$ is subject to decomposition and this may have implications in its use in oxygen-sensor applications.

Experimental

$[Ir(ppy)_2(vacac)]$ (10 mg) was dissolved in acetone-d_6 (1 ml) and placed in an NMR tube. No attempt was made to exclude air from the tube. The tube was left sealed, but unshielded from light, for four weeks. Small golden crystals of (II) were harvested from the NMR tube for X-ray crystallography. IR: ν(C═O) 1617 cm^{-1}. The complex could also be prepared by reacting oxalate with (μ-dichloro)tetrakis(phenylpyridine)diiridium(III).

Crystal data

$[Ir(C_{11}H_8N)_4(C_2O_4)]\cdot 1.974C_3H_6O$
$M_r = 1203.79$
Triclinic, $P\overline{1}$
$a = 9.9708$ (5) Å
$b = 13.0403$ (7) Å
$c = 19.3556$ (10) Å
$\alpha = 103.383$ (1)°
$\beta = 99.003$ (1)°
$\gamma = 98.203$ (1)°
$V = 2375.9$ (2) $Å^3$

$Z = 2$
$D_x = 1.683$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 1.7$–29.6°
$\mu = 5.65$ mm^{-1}
$T = 173$ (2) K
Block, gold
0.20 × 0.15 × 0.10 mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.430$, $T_{max} = 0.568$
30 150 measured reflections

13 184 independent reflections
9639 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 29.6°$
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -26 \rightarrow 26$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.098$
$S = 1.01$
13184 reflections
602 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 0.9043P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.040$
$\Delta\rho_{max} = 2.37$ e $Å^{-3}$
$\Delta\rho_{min} = -1.13$ e $Å^{-3}$

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Table 1
Selected geometric parameters (Å, °).

Ir1—C22	1.979 (2)	Ir1′—C11′	1.9876 (19)
Ir1—C11	1.9824 (19)	Ir1′—N1′	2.0191 (17)
Ir1—N1	2.0308 (13)	Ir1′—N2′	2.0303 (18)
Ir1—N2	2.0429 (14)	Ir1′—O1′	2.1931 (13)
Ir1—O2	2.1911 (14)	Ir1′—O2′	2.1969 (15)
Ir1—O1	2.1938 (13)	O1—C23$^{\rm i}$	1.238 (2)
Ir1′—C22′	1.980 (2)		
N1—Ir1—N2	175.79 (7)	C22′—Ir1′—C11′	89.48 (8)
N2—Ir1—O2	96.11 (6)	C22′—Ir1′—N1′	96.51 (8)
C22—Ir1—O1	98.03 (7)	C11′—Ir1′—N1′	80.88 (8)
C11—Ir1—O1	171.29 (7)	C22′—Ir1′—N2′	80.65 (8)
N1—Ir1—O1	94.75 (5)	C11′—Ir1′—N2′	94.79 (8)
N2—Ir1—O1	85.70 (5)	N1′—Ir1′—N2′	174.88 (7)
O2—Ir1—O1	76.18 (5)		

Symmetry code: (i) $-x+1, -y, -z+1$.

H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–0.98 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$, or $1.5U_{\rm eq}({\rm C})$ for methyl atoms. First- and second-neighbour distance restraints were applied to the disordered solvent molecules. Equal anisotropic displacement parameter restraints were applied to three pairs of disordered atoms of solvent molecules that almost overlap. The highest peak and the deepest hole in the final Fourier map are 0.80 and 1.36 Å, respectively, from the Ir atom.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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