

Mono- and bis-tolylterpyridine iridium(III) complexes

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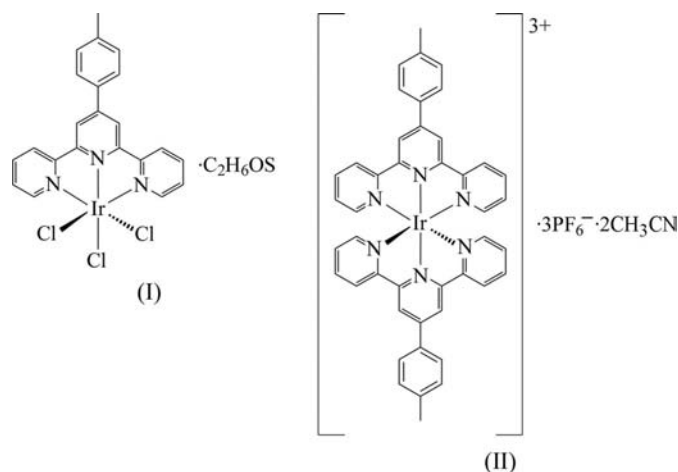
The first structure report of trichlorido[4'-(*p*-tolyl)-2,2':6',2''-terpyridine]iridium(III) dimethyl sulfoxide solvate, $[\text{IrCl}_3(\text{C}_{22}\text{H}_{17}\text{N}_3)] \cdot \text{C}_2\text{H}_6\text{OS}$, (I), is presented, along with a higher-symmetry setting of previously reported bis[4'-(*p*-tolyl)-2,2':6',2''-terpyridine]iridium(III) tris(hexafluoridophosphate) acetonitrile disolvate, $[\text{Ir}(\text{C}_{22}\text{H}_{17}\text{N}_3)_2](\text{PF}_6)_3 \cdot 2\text{C}_2\text{H}_3\text{N}$, (II) [Yoshikawa, Yamabe, Kanehisa, Kai, Takashima & Tsukahara (2007). *Eur. J. Inorg. Chem.* pp. 1911–1919]. For (I), the data were collected with synchrotron radiation and the dimethyl sulfoxide solvent molecule is disordered over three positions, one of which is an inversion center. The previously reported structure of (II) is presented in the more appropriate $C2/c$ space group. The iridium complex and one PF_6^- anion lie on twofold axes in this structure, making half of the molecule unique.

Comment

To our knowledge, before the publication of this paper only seven structures of terpyridine iridium(III) complexes were present in the Cambridge Structural Database (CSD, Version 5.30 of May 2009; Allen, 2002). The lack of both mono- and bis-terpyridine-based iridium(III) structures may be due in part to the inertness of the metal center or the difficulty of making tricationic iridium(III) species in considerable yield (Cusanelli *et al.*, 1996; Collin *et al.*, 1999). In an attempt to synthesize a tricationic bis-ttpy [ttpy is 4'-(*p*-tolyl)-2,2':6',2''-terpyridine] species, we were able to isolate the neutral trichlorido species. We present here the structures of both trichlorido[4'-(*p*-tolyl)-2,2':6',2''-terpyridine]iridium(III) dimethyl sulfoxide solvate, (I), and bis[4'-(*p*-tolyl)-2,2':6',2''-terpyridine]iridium(III) tris(hexafluoridophosphate) acetonitrile disolvate, (II).

Structure (I), or $[\text{Ir}(\text{ttpy})\text{Cl}_3] \cdot \text{DMSO}$ (DMSO is dimethyl sulfoxide), is shown in Fig. 1. The DMSO solvent molecule is disordered over three positions, one of which is $\bar{1}$. The tolyl group at the 4'-position of the terpyridine ligand is positionally disordered over two positions [0.64 (4):0.37 (4)]. The plane formed by the Ir metal center and the atoms of the three

chelating rings (N1/C1–C5, N2/C6–C10 and N3/C11–C15) of the ttpy ligand is planar, with an r.m.s. deviation of 0.0673 Å. This plane is twisted by 89.84 (5)° relative to the plane formed by the Ir atom and the three Cl ligands, which has an r.m.s. deviation of 0.0054 Å. Due to the bite angle of the ttpy ligand, the bond distance from Ir1 to the central N2 atom is 1.947 (4) Å, which is significantly shorter than those for the two outer atoms, *viz.* N1 and N3 of 2.037 (5) and 2.041 (4) Å, respectively. The chloride ligand (Cl2) *trans* to the central N atom of the ttpy ligand exhibits the longest bond distance of the three chlorides [Ir1–Cl2 = 2.3856 (13) Å]. All of the Ir–N and Ir–Cl bond distances in (I) fall within the expected ranges based on a CSD search.



The data for structure (II), or $[\text{Ir}(\text{ttpy})_2](\text{PF}_6)_3 \cdot 2\text{CH}_3\text{CN}$, were collected initially to aid in the identification of the products from a reaction between $\text{Ir}(\text{ttpy})\text{Cl}_3$ and ttpy. While

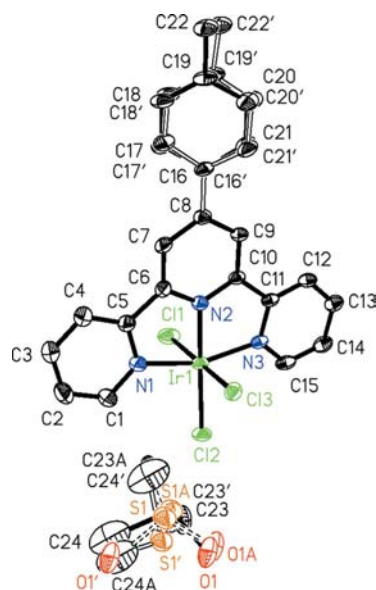
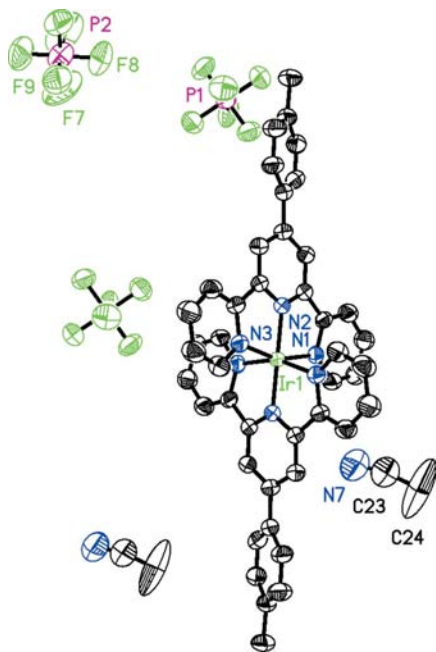


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Within the Ir-containing molecule, solid bonds represent the main disorder component. DMSO modeling is also shown and the molecule represented with dashed bonds is over the inversion center.


Figure 2

The symmetry-generated molecule of (II). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity, selected atoms have been labeled, and the ligand labeling scheme is identical to that used in Fig. 1.

the data collection temperature for (II) was lower, at 173 K, the initial unit-cell parameters and cell volume were similar to a room-temperature structure reported by Yoshikawa *et al.* (2007) for the same compound (CSD refcode YIDGAU). The previously reported structure was solved in space group *Cc*. However, closer examination of the bond distances within this structure led us to believe that the structure had been solved in the incorrect space group.

A comparison of the chemically equivalent bond distances between the two independent ttpy ligands in structure YIDGAU revealed many that were more than five standard deviations apart. This result was surprising considering the inherent D_{2d} symmetry of the molecule. Marsh (1997) reports that the space group *Cc* is often misassigned when a twofold axis has been overlooked. It appears that many structures in *Cc* are often revised to be *C2/c* after this missing symmetry element is found (Herbstein & Marsh, 1998; Marsh, 1997). Furthermore, this space group change leads to more reasonable bond lengths and angles within the structure. The ADDSYM routine in *PLATON* (Spek, 2009) was conducted on the YIDGAU CIF and conclusively found missing symmetry in the structure. The addition of $\bar{1}$ and twofold symmetry to the structure leads to a solution in space group *C2/c*. Solving the structure of (II) in the centrosymmetric space group *C2/c* gave bond lengths and angles comparable to those reported for a bis(2,2':6',2''-terpyridine)iridium(III) structure (CSD refcode FOHQAU; Collin *et al.*, 1999), leading us to believe that *C2/c* is indeed the correct space group setting for (II).

In (II), one P atom (P1) is in a general position, while the second (P2) lies on a twofold axis. The Ir atom also lies on this

twofold axis, making half of the cation unique. The acetonitrile solvent molecule is located on a general position as well (Fig. 2). Bond distances from the N atoms to the Ir atom are 2.052 (6) (N1), 1.966 (6) (N2) and 2.047 (6) Å (N3), following the similar long–short–long pattern found in the mono-ttpy derivative, (I), and are within the expected range for Ir–N bond distances. The Ir atom and the atoms of the three chelating rings of the ttpy ligand are planar, with an r.m.s. deviation from the plane of 0.0457 Å.

Experimental

Ir(ttpy)Cl₃ was synthesized following the method of Collin *et al.* (1999) and single crystals of (I) were grown by slow cooling of a hot DMSO solution. X-ray data were collected at the APS synchrotron sector 15-ID-C at Argonne National Laboratory, due to the extremely small size of at least one of the crystal dimensions. [Ir(ttpy)₂](PF₆)₃ was synthesized according to the method of Collin *et al.* (1999) and crystals of (II) were grown by slow evaporation of an acetonitrile solution after separation of the compound with dichloromethane and acetone on a neutral alumina column.

Compound (I)

Crystal data

[IrCl ₃ (C ₂₂ H ₁₇ N ₃)]·C ₂ H ₆ OS	$V = 2488.9 (9) \text{ \AA}^3$
$M_r = 700.06$	$Z = 4$
Monoclinic, $P2_1/c$	Synchrotron radiation
$a = 10.377 (2) \text{ \AA}$	$\lambda = 0.41328 \text{ \AA}$
$b = 23.166 (5) \text{ \AA}$	$\mu = 3.08 \text{ mm}^{-1}$
$c = 10.370 (2) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 93.22 (3)^\circ$	$0.08 \times 0.01 \times 0.01 \text{ mm}$

Data collection

Bruker SMART APEXII diffractometer	68215 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	7484 independent reflections
$T_{\min} = 0.791, T_{\max} = 0.985$	6292 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$	61 restraints
$wR(F^2) = 0.101$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 3.32 \text{ e \AA}^{-3}$
7484 reflections	$\Delta\rho_{\min} = -2.40 \text{ e \AA}^{-3}$
346 parameters	

Compound (II)

Crystal data

[Ir(C ₂₂ H ₁₇ N ₃) ₂](PF ₆) ₃ ·2C ₂ H ₃ N	$V = 4964.0 (8) \text{ \AA}^3$
$M_r = 1355.99$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.6977 (14) \text{ \AA}$	$\mu = 2.90 \text{ mm}^{-1}$
$b = 16.3737 (16) \text{ \AA}$	$T = 173 \text{ K}$
$c = 21.420 (2) \text{ \AA}$	$0.25 \times 0.25 \times 0.12 \text{ mm}$
$\beta = 105.639 (2)^\circ$	

Data collection

Bruker SMART Platform CCD area-detector diffractometer	13655 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2008a)	4995 independent reflections
$T_{\min} = 0.531, T_{\max} = 0.722$	3790 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$	355 parameters
$wR(F^2) = 0.146$	H-atom parameters constrained
$S = 1.11$	$\Delta\rho_{\max} = 1.69 \text{ e } \text{\AA}^{-3}$
4995 reflections	$\Delta\rho_{\min} = -1.22 \text{ e } \text{\AA}^{-3}$

In structure (I), the DMSO molecule was modeled over three positions whose site-occupation factors were restrained to sum to 1.00 [actual occupation factors of the three orientations = 0.500 (3), 0.328 (3) and 0.173 (2)]. Similarity restraints were applied to the chemically equivalent bond lengths and angles across the three orientations, while the distances between the S and O atoms and between the S and C atoms were restrained to 1.678 (5) and 1.862 (5) Å, respectively. The atomic displacement parameters of the corresponding atom in each of the three orientations were constrained to be identical. The tolyl substituent was also disordered over two orientations, with C16 serving as the anchor atom. The atomic displacement parameters of corresponding atoms in the two orientations were also constrained to be identical, while similarity restraints were applied to the chemically equivalent bond lengths and angles.

In structure (II), a direct methods solution was attempted but did not yield the correct position of the heavy atom. When a Patterson map solution was used, the correct position of the Ir atom was chosen as that on the C_2 axis. Refinement of the remaining atoms proceeded without incident. No disorder was modeled within this structure.

In both structures, all aromatic H atoms were placed in ideal positions and refined as riding, with C–H = 0.95 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Methyl H atoms were placed in ideal positions and refined as riding, with C–H = 0.98 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: *APEX2* (Bruker, 2008) for (I); *SMART* (Bruker, 2003) for (II). Cell refinement: *APEX2* for (I); *SAINT* (Bruker, 2003) for (II). For both compounds, data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008b); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008b); molecular

graphics: *SHELXTL* (Sheldrick, 2008b); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3173). Services for accessing these data are described at the back of the journal.

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