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Synthesis, Characterization and Crystal Structure of Iridium(III)bis(2-*p*-tolyl-benzothiazolato-N,C²) (acetylacetonate)

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Abstract A novel thiazole-based iridium (III) complex (iridium(III)bis(2-*p*-tolyl-benzothiazolato-N,C²)(acetylace-tonate)) has been prepared and fully characterized by EA, IR, ¹H-NMR and MS. The molecular structure of the complex has been determined by single crystal X-ray diffraction analysis. The iridium (III) center adopts a distorted octahedral geometry with *cis*-O–O, *cis*-C–C, and *trans*-N–N chelate disposition. The complex crystallizes in the orthorhombic *P*bca space group with cell parameters *a* = 10.1388(7) Å, *b* = 18.3565(12) Å, *c* = 31.021(2) Å, $\alpha = \beta = \gamma = 90^{\circ}$ and *Z* = 8. The electronic absorption and emission spectra of this complex have been investigated.

Keywords Iridium complex \cdot Iridium(III)bis (2-*p*-tolyl-benzothiazolato-N,C²)(acetylacetonate) \cdot Crystal structure \cdot Photophysical properties

Introduction

Recently the long lived excited state and highly efficient solid-state emissions of d^6 and d^8 metal complexes have made them of interest as potential components in organic light emitting diodes (OLEDs) [1]. Especially, the iridium (III) complexes with cyclometalated ligands show intense phosphorescence at room temperature and behavior as very promising phosphor dye in OLEDs [2].

Generally, both the luminescent efficiency and emission wavelength of iridium complexes are greatly affected by the heterocyclic ligands [3]. The emission frequency of the iridium complexes can usually be tuned by the introduction of different heterocyclic ligands [4]. However, there is very little work to study iridium (III) complexes with thiazole-based heterocyclic ligands [5].

Herein we report the synthesis, characterization and crystal structure analysis of a novel thiazole-based iridium (III) complex (iridium(III)bis(2-p-tolyl-benzothiazolato-N,C²)(acetylacetonate)). The absorption and emission spectra of this complex will be presented.

Experimental

General Information

The reactions and manipulations involving iridium (III) complexes were carried out under argon atmosphere. Chemicals were used without further purification unless otherwise stated. Elemental analysis of carbon, hydrogen, and nitrogen was performed on a Carlorerba-1106 micro-analyzer. Infrared spectra were obtained on a Nicolet SX Fourier transform spectrometer. Mass Spectra (FAB-MS) was determined by VJ-ZAB-3F Mass Spectrometer. ¹H NMR spectra were recorded on Varian Mercury VX-300 MHz spectrometer. UV–Vis absorption spectra were recorded on Schimadzu 160A UV–Vis recording spectro-photometer. PL spectra were performed on Perkin-Elmer LS 55 luminescence spectrophotometer.

Synthesis of 2-p-tolyl-benzothiazole (TBT)

2-Aminothiophenol (1.25 g, 10 mmol) and 4-methylbenzaldehyde (1.20 g, 10 mmol) were dissolved to 20 mL of DMSO under argon atmosphere. The mixture

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was heated at 200 °C for 0.5 h. After cooling, the solution was poured into ice water, and then adjusted the solution to pH 8–9 with 1 N NaHCO₃ solution. The precipitate was filtered, washed with a great deal of water several times. After dried under vacuum, the crude product was recrystallized with ethanol. White crystal, yield: 89%. ¹H NMR (CDCl₃, 300 MHz) δ : 8.02 (d, J = 8.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.2 Hz, 1H) 7.26 (d, J = 8.1 Hz, 2H), 2.42 (s, 3H). mp = 85–86 °C. Anal.Calcd for C₁₄H₁₁NS: C, 74.63; H, 4.92; N, 6.22. Found: C, 74.55; H, 4.87; N, 6.24%. MS (FAB): m/e, 225 (M⁺).

Synthesis of Ir(III) Complexes

Cyclometalated chloride-bridged dimer: iridium trichloride hydrate (0.352 g, 1.0 mmol), combined with 2-*p*-tolylbenzothiazole (0.563 g, 2.5 mmol), were dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL), and then refluxed for 24 h. The solution was cooled to room temperature, and the resulting orange red precipitate was collected on by filtration and washed with water and ethanol. After dried, the crude product was directly used for next step without further purification [6].

Iridium(III)bis(2-p-tolyl-benzothiazolato-N,C²)(acetylacetonate) Ir(TBT)₂(acac): 0.1 mmol of chloride-bridged dimer, 0.25 mmol of acetylacetone and 1.0 mmol anhydrous sodium carbonate were dissolved in 2-ethoxyethanol. The solution was refluxed under argon for 15 h. After cooling to room temperature, small quantity water was added. The resulting orange precipitate was collected by filtration, washed with water, ethanol and hexane, and dried in vacuum. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (1:1-1:3) as eluent. Orange powders, yield: 88%. IR (KBr, cm^{-1}): 3030, 2987, 1720, 1604, 1503, 852. ¹H NMR (CDCl₃, 300 MHz): δ (ppm) 8.02 (m, 2H), 7.86 (m, 2H), 7.54 (d, J = 7.5 Hz, 2H),7.39 (m, J = 4.5 Hz, 4H), 6.65 (d, J = 7.8 Hz, 2H), 6.20 (s, J = 7.8 Hz, 2H), 7.2 Hz, 7.2H), 5.09 (s, 1H), 2.01 (s, 6H), 1.74 (s, 6H). Anal. Calcd for C₃₃H₂₇O₂N₂S₂Ir: C, 53.57; H, 3.79; N, 3.68. Found: C, 53.53; H, 3.74; N, 3.65%. MS (FAB): m/e, 740 (M⁺).

X-ray Crystallography Analysis

An orange-red crystal of $Ir(TBT)_2(acac)$ (dimensions $0.20 \times 0.20 \times 0.06 \text{ mm}^3$) suitable for X-ray diffraction studies was mounted in inert oil on a glass fiber for the cell determination, and data was collected using a Bruker SMART CCD detector diffractometer with graphite-mono chromatic Mo K α (0.71073 Å) radiation. The unit cell

parameters were determined from a least-squares fit of 4977 carefully centred reflections $(2.62^{\circ} < 2\theta < 56.56^{\circ})$. Heavy-atom method was employed to locate Ir atom and the remaining non-hydrogen atoms were refined by full-matrix least squares on F^2 using SHELXL-97 program [7]. An empirical absorption correction using the program SADABS [8] was applied. All non-hydrogen atoms were described with anisotropic thermal parameters. Hydrogen atoms were introduced at calculated positions. All figures were prepared using the program ORTEP-3 for windows [9]. A summary of the refinement details for the complex are given in Table 1.

Results and Discussion

Synthesis and Characterization

The synthetic route of the complex was outlined in Scheme 1. The heterocyclic ligand was prepared by the

Table 1 Crystal data and structure refinement for $Ir(TBT)_2(acac)\ \mbox{complex}$

Empirical formula	$C_{33}H_{27}O_2N_2S_2Ir$
CCDC deposit no	CCDC-271360
Color/shape	Orange, block
Formula weight	739.89
Crystal system	Orthorhombic
space group	Pbca
a	10.1388(7) Å
b	18.3565(12) Å
С	31.021(2) Å
$\alpha = \beta = \gamma$	90°
Volume	5773.4(7) Å ³
Ζ	8
Calculated density	1.702 Mg/m ³
Temperature	293(2) K
Wavelength (Mo-Ka)	0.71073 Å
Theta range	$1.31^\circ < \theta < 28.00^\circ$
Limiting indices	$ \begin{array}{l} -13 \leq h \leq 9, -23 \leq k \leq 24, \\ -39 \leq l \leq 40 \end{array} $
Crystal size	0.20 \times 0.20 \times 0.06 mm
Absorption coefficient	4.803 mm^{-1}
<i>F</i> (000)	2,912
Completeness to $\theta = 28.28$	99.2%
Reflections collected/unique	39,926/6,923 [R(int) = 0.0841]
Goodness-of-fit on F^2	1.191
Final <i>R</i> indices $[I > 2 \text{sigma}(I)]$	$R_1 = 0.0658^{\rm a}, wR_2 = 0.1248^{\rm b}$
R indices (F^2)	$R_1 = 0.1006^{\rm a}, wR_2 = 0.1413^{\rm b}$

^a $R_1 = \sum [|Fo| - |Fc|] / \sum |Fo|$

^b $wR_2 = \{\sum [w(Fo_2 - Fc_2)]/\sum (wFo_2)\}_{1/2}$

Scheme 1 Synthesis of Ir(TBT)₂(acac) complex



cyclomerization reaction of *o*-aminobenzenethiol with 4methylbenzaldehyde. Cyclometalated Ir (III) μ -chlorobridged dimer was synthesized by iridium trichloride hydrate with heterocyclic ligands according to the similar method reported by Nonoyama [10]. The chloride-bridged diiridium complex can be converted to mononuclear iridium complexes by replacing the two bridging chlorides with bidentate monoanionic acetylacetone ligand in high yield.

Elemental analysis of the complex is consistent with the expected formulation of their structures. The mass spectra of complex give corresponding molecular ion peak at 740. In addition, the mass spectra all show a peak at 641 for the complex, which arises from the $Ir(TBT)_2^+$ fragment. The FIT-IR spectrum (KBr) of this complex exhibits a sharp intense absorption peaks at 1,720 cm⁻¹ are corresponding to the stretch vibration of C=O group, which belongs to the characteristic absorption bonds of ketone group. ¹H-NMR spectrum shows well-resolved multiplets for the cyclometalated ligand parts of the complex. The maximum high-field



Fig. 1 ORTEP diagram of $Ir(TBT)_2(acac)$ with the thermal ellipsoids representing at 30% probability level. Hydrogen atoms are omitted for clarity

chemical shift in the aromatic region appears at 6.20 ppm, assigned for the proton *ortho* to the metalated carbon atom. The chemical shift for –CH– moiety in **acac** ancillary ligand is 5.09 ppm, which is similar to other analogues [5].

Table 2 Selected bond lengths (Å) and angles (°) for $Ir(TBT)_2(acac)$ complex

Bond lengths (Å)		Bond angles (°)		
Ir(1)–C(6)	1.998(8)	C(6)-Ir(1)-C(20)	92.1(3)	
Ir(1)-C(20)	1.998(7)	C(6)-Ir(1)-N(2)	95.6(3)	
Ir(1)–N(1)	2.053(6)	C(20)-Ir(1)-N(2)	80.3(3)	
Ir(1)-N(2)	2.053(6)	C(6)–Ir(1)–N(1)	80.4(3)	
Ir(1)–O(1)	2.163(5)	C(20)-Ir(1)-N(1)	95.1(3)	
Ir(1)–O(2)	2.139(5)	N(2)–Ir(1)–N(1)	173.9(2)	
O(1)-C(30)	1.272(9)	C(6)-Ir(1)-O(2)	87.5(3)	
O(2)–C(32)	1.296(10)	C(20)-Ir(1)-O(2)	179.0(3)	
		N(2)-Ir(1)-O(2)	98.8(2)	
		N(1)-Ir(1)-O(2)	85.7(2)	
		C(6)–Ir(1)–O(1)	175.2(3)	
		O(2)–Ir(1)–O(1)	87.7(2)	



Fig. 2 Absorption and PL spectra of $Ir(TBT)_2(acac)$ complex in CH_2Cl_2 solution at 298 K

Complex	λ_{\max} Abs(log ε) nm		$\lambda_{\rm max} \ {\rm Em} \ ({\rm nm})$		$\Phi_{\rm f}^{\ \rm c}$ (%)
	solution ^a	Film ^b	Solution ^a	Film ^b	
Ir(TBT) ₂ (acac)	245(3.9), 335(4.0), 412(3.2) 449(3.2), 479(3.1), 534(2.3)	256, 339, 398 450, 483, 535	555, 586	558, 590	39.6

Table 3 Photophysical data for Ir(TBT)2(acac) complex

^a In CH₂Cl₂ solution at 298 K

^b In PMMA film (5% weight ratio)

^c Quantum yield was measured in CH₂Cl₂ solution relative to quinine bisulfate (10⁻⁵ M in 1.0 N H₂SO₄)

Crystal Structure of Ir(TBT)₂(acac)

Single crystal of $Ir(TBT)_2(acac)$ suitable for X-ray diffraction studies was obtained by slow diffusion of diethylether to a dilute dichloromethane solution of the complex. The ORTEP drawing of $Ir(TBT)_2(acac)$ is shown in Fig. 1. The selected bond lengths (Å) and angles (deg) are collected in Table 2.

In general, the iridium (III) center adopts a distorted octahedral geometry with cis-O-O, cis-C-C, and trans-N-N chelate disposition. The bond distances of Ir-C (1.998(8), 1.998(7) Å) are shorter than the Ir-N bond distances (2.053(6), 2.053(6) Å). These values are very similar to those in the analogous complexes reported [11]. The Ir–O bond distances of 2.163(5) Å for O(1) and 2.139(5) Å for O(2) indicate a slight structural *trans* effect of the phenyl groups, while the similarity of O(1)-C(30) and O(2)-C(32)bond lengths indicate that the -1 charge of the acetylacetone is delocalized over both oxygen atoms. The C-Ir-C angle for the complex is 92.1(3)° and the N-Ir-N angle is 173.9(2)°, which are almost equal to the idealized value and well accorded with their cis-C-C and trans-N-N dispositions, respectively. The acac chelate results in O(1)-Ir(1)-O(2) bond angle of 87.7(2)° appreciably less than the idealized 90° value. The benzothiazole and phenyl moieties in the same cyclometalated ligand are approximately coplanar.

Absorption and Photoluminescent Spectra

Figure 2 shows the absorption and emission spectra of complex $Ir(TBT)_2(acac)$ in CH_2Cl_2 solution. As shown in Fig. 2, intense absorptions between 250 and 350 nm can be assigned to the spin allowed π - π * transitions from cyclometalated ligands. The weaker absorption bands in the range of 350–450 nm were clearly resolved, ascribing to a spin-allowed metal-to-ligand charge transfer (¹MLCT) transition. The long tail extended to lower energies (in the range of 420–550 nm) can be likely associated with both ³MLCT and ${}^{3}\pi$ - π * transitions. The photophysical data are listed in Table 3.

The complex shows strong orange luminescence both in solid state and in organic solutions upon irradiation by

UV-light at ambient temperature. As shown in Fig. 2, the complex displays a broad emission at 555 nm, which has good fluorescence quantum yield, and large Stoke's shifts (Table 3). The vibronic fine structures in the PL spectra imply that the emissions result predominantly from the ligand-based ${}^{3}\pi-\pi^{*}$ transitions [12].

Conclusions

In summary, we have presented the synthesis and detailed characterization of a novel thiazole-based iridium (III) complex (iridium(III)bis(2-*p*-tolyl-benzothiazolato-N,C²) (acetylacetonate)) based on analytical, spectrometric, spectroscopic and X-ray diffraction methods. The electronic absorption and emission spectra of this complex have been investigated. This provides some clue to design and develop new phosphorescent materials.

Supplementary Material

CCDC-271360 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving. html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0)1223–336033; email: deposit@ccdc.cam.ac.uk).

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