

Synthesis, structures, and properties of iridium(III) bis-cyclometallated complexes containing three-atom chelates

Wu-Sian Sie^a, Jing-Yu Jian^a, Tzu-Chih Su^a, Gene-Hsiang Lee^b, Hon Man Lee^c,
Kom-Bei Shiu^{a,*}

^a Department of Chemistry, National Cheng Kung University, Tainan 701, Taiwan, ROC

^b Instrument Center, National Taiwan University, Taipei 106, Taiwan, ROC

^c Department of Chemistry, National Chung Hua University, Chuang-Hua, Taiwan, ROC

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Dedicated to the memory of the late Professor F. Albert Cotton

Abstract

Heating of $[\text{Ir}(\eta^2\text{-ppy})_2(\text{MeCN})_2]\text{NO}_3$ (**1**, ppy = 2-phenylpyridine) in MeCN under reflux afforded $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-NO}_3)]$ (**2**). Treatment of **1** with 2-mercaptopyridine (Hmp), 6-methyl-2-hydroxypyridine (Hmhp), 6-chloro-2-hydroxypyridine (Hchp), trimethylacetic acid (Htma), benzoic acid (Hbz), 2-methylacrylic acid (Hma), and acetic acid (Hac) in the presence of excess Et_3N produced $[\text{Ir}(\eta^2\text{-ppy})_2(\eta^2\text{-XZY})]$ ($\text{XZY}^- = \text{mp}^-$ (**3**), mhp^- (**4**), chp^- (**5**), ac^- (**6**), bz^- (**7**), ma^- (**8**), tma^- (**9**)). Crystal structures of **2**, **3**, **7**, **8**, and **9** have been characterized by X-ray diffraction. The inherent strain contained in the four-member rings, $\{\text{Ir}(\eta^2\text{-XZY})\}$, is apparently reflected in the long Ir–X and Ir–Y distances. The absorption and emission properties of nearly all the new complexes except **2** show small variations. © 2007 Elsevier B.V. All rights reserved.

Keywords: Iridium(III); Cyclometallated complexes; Chelate

1. Introduction

Recently, luminescent cyclometallated d^6 transition metal complexes have been shown to exhibit an enormous potential for a range of photonic applications. In particular, organic light emitting devices (OLEDs) [1] based on the triplet emitters such as Ir(III) [2], Ru(II) [2c,2d,3], and Os(II) [2c,2d,4] as the organic dopants have been demonstrated with high efficiency. While extensive works have been done on a series of bis-cyclometallated Ir(III) complexes with 4- or 5-atom chelates [5,6], $[(\eta^2\text{-C}^{\wedge}\text{N})_2\text{Ir}(\eta^2\text{-chelate})]$, the isoelectronic Ir(III) analogues with 3-atom chelates (XZY^-) have received relatively less attention [7]. Note the contrasting feature whereby all the 4- and 5-atom

chelates used in the complexes are hard (N, N), (N, O), and (O, O) donors, whereas all the reported 3-atom chelates are soft (S, S) and (Se, Se) ligands. This feature is understandable in terms of the inherent, much higher, strain contained in four-member rings (i.e., $\{\text{Ir}(\eta^2\text{-XZY})\}$), relative to those in five- or six-member rings, if all rings contain hard (N, N), (N, O), and (O, O) chelates [8]. Hence, the reported four-member examples containing only softer (S, S) and (Se, Se) chelates (ligands, Lewis bases) and soft 5d transition-metal atom (Lewis acid) are obviously stabilized in terms of the soft-base–soft-acid interaction according to the Pearson HSAB (hard and soft acids and bases) theory [9]. In this paper, however, we wish to report on the facile syntheses and crystal structures of bis-cyclometallated Ir(III) complexes with 3-atom (N, O), (N, S), and (O, O) chelates. Both photophysical and electrochemical properties of these apparently thermally stable complexes are also described.

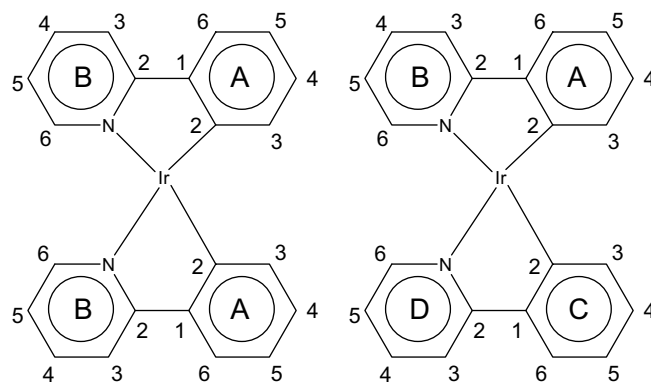
* Corresponding author. Tel.: +886 6 2080473; fax: +886 6 2740552.
E-mail address: kbshiu@mail.ncku.edu.tw (K.-B. Shiu).

2. Experimental

2.1. General information

All operations were carried out under prepurified N_2 by means of standard Schlenk and vacuum-line techniques. Solvents were purified by standard procedures and distilled prior to use. All organic reagents, including 2-mercapto-pyridine (Hmp), 6-methyl-2-hydroxypyridine (Hmhp), 6-chloro-2-hydroxypyridine (Hchp), 1,1,1-trimethylacetic acid (Htma), benzoic acid (Hbz), 2-methylacrylic acid (Hma), and acetic acid (Hac) were purchased from Aldrich and used without further purification. The bis-cyclometalated iridium precursor complex, $[Ir(\eta^2\text{-ppy})_2(\text{MeCN})_2]\text{-NO}_3$ (**1**, ppy = 2-phenylpyridine), was synthesized by the method reported by Watts et al. [10]. Two different atom labeling schemes for assignment of ^1H NMR spectral signals for ppy are shown below for complexes with the presence or absence of a molecular C_2 axis. ^1H NMR spectra were acquired on a Bruker AVANCE 300 (300 MHz) spectrometer using the deuterated solvent as the lock and the residual solvent as the internal reference. IR spectra were recorded on a Perkin–Elmer Spectrum-One or Bruker TENSOR 27 FT-IR spectrophotometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Heraeus CHN-OS rapid elemental analyzer by the staff of the Instrument Center, National Cheng Kung University. The ESI–MS spectra of the iridium complexes dissolved in MeCN, mixed with some drops of aqueous NH_3 , were measured on a Micromass Quattro Ultima mass spectrometer by the staff of the Instrument Center, National Chung Cheng University. UV–vis spectra were recorded with a Hewlett Packard 8453 instrument at room temperature using 1-cm path length quartz cell. Cyclic voltammetry (CV) was carried out in nitrogen-purged anhydrous 10^{-3} M dichloromethane solution at room temperature with a CHI 600a voltammetric analyzer. Tetramethylammonium tetrafluoroborate (TBABF_4) (0.1 M) was used as a supporting electrolyte. The conventional three-electrode configuration consists of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag/AgNO_3 (MeCN) reference electrode with ferrocenium/ferrocene ($\text{Fc}^{+/0}$) as the internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV/s. Photoluminescence (PL) spectra were performed on Hitachi F-4500 luminescence spectrophotometer. Excited-state lifetimes were measured by a home-constructed time-resolved Laser spectrometer. The instrument consists a Quanta Ray GCR-170, pulsed Nd:YAG Laser, and used the third harmonic (355 nm, FWHM = 10 ns) as an excitation source. Emission signals were focused into an ARC SpectraPro-500 monochromator. The monochromator output was sent into a PMT (Hamamatsu, R928). The signal was then further amplified by a home made fast amplifier before being sent into a digitizer (LeCory 9350A). Decay traces were transferred to a personal computer loaded with the commercial software Origin 3.5. All experimental data

were fitted by a single exponential decay. Analytical TLC was carried out using Merck glass-backed 0.2 mm silica gel 60 F254 plates. Flash column chromatography was conducted using Merck silica gel 60 (230–400 mesh).



2.2. $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-NO}_3)]$ (**2**)

A solution of **1** (0.0505 g, 0.078 mmol) in MeCN (25 ml) was refluxed for 3 h. The solvent was then pumped off. Recrystallization from CH_2Cl_2 at room temperature afforded the yellow product. Yield: 37 mg (84%). Anal. Calc. for $\text{C}_{22}\text{H}_{16}\text{IrN}_3\text{O}_3$: C, 46.97; H, 2.87; N, 7.47. Found: C, 46.87; H, 3.87; N, 8.34%. ^1H NMR (CD_2Cl_2): δ 8.80 (d, 2H, $J = 5.8$ Hz, $\text{H}^{6\text{B}}$), 7.96 (br, 4H, $\text{H}^{3\text{B}}$ and $\text{H}^{4\text{B}}$), 7.60 (d, 2H, $J = 7.8$ Hz, $\text{H}^{6\text{A}}$), 7.37 (br, 2H, $\text{H}^{5\text{B}}$), 6.91 (d, $\text{H}^{5\text{A}}$), 6.72 (br, 2H, $\text{H}^{4\text{A}}$), 6.12 (d, 2H, $J = 7.6$ Hz, $\text{H}^{3\text{A}}$). IR (KBr, cm^{-1}): 1549 ($\nu(\text{N}=\text{O})$), 1284 ($\nu_a(\text{NO}_2)$), 1010 ($\nu_s(\text{NO}_2)$).

2.3. $[Ir(\eta^2\text{-ppy})_2(\eta^2\text{-chelate})]$ (*chelate* $^- = \text{mp}^-$ (**3**), *mhp* $^-$ (**4**), *chp* $^-$ (**5**))

To a solution of **1** (ca. 0.16 mmol) in MeCN (15 ml) was added Hmp, Hmhp, or Hchp (ca. 0.4 mmol) and Et_3N (ca. 0.5 ml) stirred at room temperature for 30 min. The resulting solution was then heated under reflux overnight (ca. 8 h). The solvent was pumped off to produce the crude product. The crude product was further purified with a flash column chromatography and eluted with CH_2Cl_2 . A clear yellow band was then collected and evaporated to dryness, affording the yellow crystalline product.

3. Yield: 79 mg (81%). Anal. Calc. for $\text{C}_{27}\text{H}_{20}\text{IrN}_3\text{S}$: C, 53.10; H, 3.30; N, 6.88. Found: C, 53.27; H, 3.35; N, 6.86%. ^1H NMR (CD_2Cl_2): δ 9.86 (d, 1H, $J = 5.4$ Hz, $\text{H}^{6\text{B}}$ or $\text{H}^{6\text{D}}$), 8.03 (d, 1H, $J = 5.7$ Hz, $\text{H}^{6\text{D}}$ or $\text{H}^{6\text{B}}$), 7.94 (m, 2H, $\text{H}^{4\text{B}}$ and $\text{H}^{4\text{D}}$), 7.79 (m, 2H, $\text{H}^{3\text{B}}$ and $\text{H}^{3\text{D}}$), 7.65 (m, 2H, mp), 7.20 (m, 2H, $\text{H}^{6\text{A}}$ and $\text{H}^{6\text{C}}$), 7.16 (t, 1H, $J = 7.2$ Hz, $\text{H}^{5\text{B}}$ or $\text{H}^{5\text{D}}$), 7.12 (t, 1H, $J = 7.1$ Hz, $\text{H}^{5\text{D}}$ or $\text{H}^{5\text{B}}$), 6.95 (t, 1H, $J = 7.4$ Hz, $\text{H}^{5\text{A}}$ or $\text{H}^{5\text{C}}$), 6.79 (m, 4H with 2H from mp, 1H as $\text{H}^{5\text{C}}$ or $\text{H}^{5\text{A}}$, and 1H as $\text{H}^{4\text{A}}$ or $\text{H}^{4\text{C}}$), 6.66 (t, 1H, $J = 7.5$ Hz, $\text{H}^{4\text{C}}$ or $\text{H}^{4\text{A}}$), 6.35 (d, 1H, $J = 7.3$ Hz, $\text{H}^{3\text{A}}$ or $\text{H}^{3\text{C}}$), 6.33 (d, 1H, $J = 7.4$ Hz, $\text{H}^{3\text{C}}$ or $\text{H}^{3\text{A}}$). ESI–MS: m/z 612 ($(\text{M}+1)^+$).

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