

## Synthesis and Characterization of Phosphorescent Platinum and Iridium Complexes of 6-Chloro-3-phenylpyridazine

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The preparation and the photophysics of organometallic Pt(II) and Ir(III) complexes with 6-chloro-3-phenylpyridazine (H6Clppdz) are reported.  $K_2PtCl_4$  and  $IrCl_3 \cdot nH_2O$  cleanly cyclometalate with H6Clppdz, forming the corresponding chloro-bridged dimers,  $(6Clppdz)Pt(\mu-Cl)_2Pt(6Clppdz)$  and  $(6Clppdz)_2Ir(\mu-Cl)_2Ir(6Clppdz)_2$  in good yield. These chloro-bridged dimers are cleaved with acetylacetonate (Hacac) to give the corresponding monomer,  $(6Clppdz)Pt(acac)$  and  $(6Clppdz)_2Ir(acac)$ , respectively. Both complexes show bright orange luminescence at room temperature and the emission wavelengths are different depending on the metal and the structure of complexes.  $(6Clppdz)Pt(acac)$  shows two sharp emission bands in shorter wavelength ( $\lambda_{em}=541$  and 580 nm), while  $(6Clppdz)_2Ir(acac)$  shows a broad emission band in longer wavelength ( $\lambda_{em}=615$  nm). Strong spin-orbit coupling due to the heavy metal atom allows for the formally forbidden mixing of the <sup>1</sup>MLCT with the <sup>3</sup>MLCT and <sup>3</sup> $\pi-\pi^*$  states.

**key words:** phosphorescence, platinum complex, iridium complex, 6-chloro-3-phenylpyridazine, emission, MLCT.

### INTRODUCTION

Recently, platinum and iridium complexes get a lot of attention owing to their possibility of phosphorescence at room temperature. It implies its practical use in organic light-emitting diodes (OLEDs) [1-4]. Fluorescent materials used in the emitting layer luminate via photophysically-allowed singlet-singlet transitions. However, electrically generated states are in either singlet or triplet states with the ratio of 1 to 3 [5,6]. Therefore quantum yield of photophysically-allowed fluorescence is only 25% at most in theory. In order to improve the effectiveness of OLED, transitions through the triplet states must be considered, which may result in phosphorescence. Phosphorescence is known to get via spin-orbit coupling usually by heavy atom effect [7,8].

Since Thompson group reported the use of  $Ir(ppy)_3$  ( $ppy=2$ -phenylpyridine) as a phosphore in OLED, a lot of luminescent Ir(III) complexes have been reported [10]. However, Pt(II), which is heavier than Ir(III) and has simpler structured complexes, usually planar geometry, and fewer ligand coordination number than the latter, has not been focused as much as Ir(III). Only Pt(OEP) (OEP=octaethylporphyrin) is attracted as an emitting material in OLED [5]. Therefore it is worth to explore Pt(II) complex which is phosphorescent at room temperature.

In this work, cyclometalated platinum and iridium

complexes of the structure,  $(6Clppdz)Pt(acac)$  and  $(6Clppdz)_2Ir(acac)$ , have been explored, where 6Clppdz is anion of 6-chloro-3-phenylpyridazine and acac is acetylacetonate.

### MATERIALS AND METHODS

#### Synthesis

$K_2PtCl_4$ ,  $IrCl_3 \cdot nH_2O$ , 3-chloro-6-phenylpyridazine, and 2-ethoxyethanol were purchased from Aldrich Chemical Co. and used without further purification. Methylene chloride, hexane, ether, and methanol were purchased from Oriental Chemical Ind. and distilled by usual methods. The National Center for Inter-university Facilities at Seoul National University performed the elemental analyses.

#### $(6Clppdz)Pt(acac)$

(Platinum(II) 6-chloro-3-phenylpyridazinato acetylacetonate, 1). The Pt(II)  $\mu$ -dichloro-bridged dimers were prepared by a modified method of Thompson et al [5]. This involves heating  $K_2PtCl_4$  (2.4 mmol) and 6-chloro-3-phenylpyridazine (6.0 mmol) in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL) to 80°C for 16h. The dimer was isolated in water and subsequently reacted with acetylacetonate (7.2 mmol) and  $Na_2CO_3$  (24 mmol) in 2-ethoxyethanol at 100°C for 16 h. The solvent was removed under reduced pressure and the compound was purified by flash chromatography using  $CH_2Cl_2$ . The product 1 was recrystallized in  $CH_2Cl_2/MeOH$ . <sup>1</sup>H-NMR ( $CDCl_3$ ):  $\delta$  (ppm), 2.06 (s, 3H), 2.13 (s, 3H), 5.53 (s, 1H), 7.13~7.21 (m, 1H), 7.27~7.48 (m, 2H), 7.68~7.78 (m, 3H). Anal. for  $C_{15}H_{13}ClN_2O_2Pt$ : found C 37.28, H 2.70, N 5.70, calcd. C 37.24, H 2.71, N 5.79.

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*(6Clppdz)2Ir(acac)*

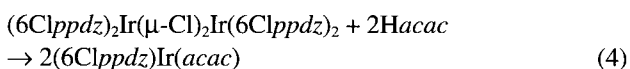
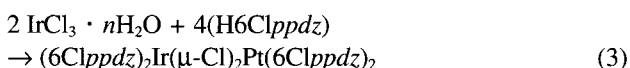
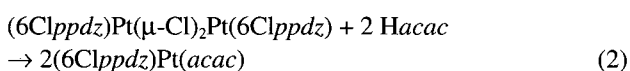
*(Iridium(III) bis(6-chloro-3-phenylpyridazinato) acetylacetonate, 2)* The Ir(III) complexes were prepared by the modified method of previous literature [10].  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  (1.0 g) and 6-chloro-3-phenylpyridazine (13.6 mmol) were dissolved in a mixture of 2-ethoxyethanol (40 ml) and water (10 ml) and refluxed for 24 h. The solution was cooled down to room temperature resulting in the dark red precipitate of the dimer, which was filtered and washed with ethanol and acetone. The dimer (0.078 mmol), acetylacetonate (0.2 mmol), and  $\text{Na}_2\text{CO}_3$  (85-90 mg) are refluxed under inert gas atmosphere in 2-ethoxyethanol for 12-15 h. After cooling down to room temperature, the red precipitate is filtered and washed with water and mixture of hexane and ether. The crude product is flash chromatographed using  $\text{CH}_2\text{Cl}_2$  to give ca. 75% of **2**.  $^1\text{H-NMR}$  (DMSO):  $\delta$  (ppm), 1.66 (6H, s), 5.10 (1H, s), 6.13 (d, 2H), 6.68-6.89 (m, 4H), 7.82 (d, 2H), 8.03 (d, 2H), 8.61 (d, 2H). Anal. for  $\text{C}_{25}\text{H}_{19}\text{Cl}_2\text{IrN}_4\text{O}_2$ : found C 44.81, H 2.85, N 8.40, calcd. C 44.78, H 2.86, N 8.36.

*Spectroscopy*

The UV-visible and the photoluminescence spectra were recorded on Shimadzu UV-2101PC spectrophotometer and Varian Cary Eclipse Fluorescence spectrometer, respectively.  $^1\text{H}$  NMR spectra were recorded on Varian 200 MHz spectrometer.

**RESULTS AND DISCUSSION**

**Synthesis and Structure.** Dichloro-bridged dimers of the structure  $(6\text{Clppdz})\text{Pt}(\mu\text{-Cl})_2\text{Pt}(6\text{Clppdz})$  and  $(6\text{Clppdz})_2\text{Ir}(\mu\text{-Cl})_2\text{Ir}(6\text{Clppdz})_2$  were prepared by the reaction of  $\text{K}_2\text{PtCl}_4$  and  $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$  with 6-chloro-3-phenylpyridazine in 2-ethoxyethanol (eq. 1 and 3).  $\text{H}6\text{Clppdz}$  is deprotonated by Pt(II) and Ir(III) ions resulting in cyclometalation without any base. The dimers were isolated as solids in color of orange and red, respectively. Since related dimers have been well characterized in the literature [11], in most instances the dimers were not further characterized and used directly in subsequent reactions. The dimers were dissociated into the monomers in the presence of a base,  $\text{Na}_2\text{CO}_3$ , and an ancillary ligand, Hacac (eq. 2 and 4). The isolated yields for these complexes were 33% and 40%, respectively.



The structures of the dimers and the monomers are expected as shown in Figure 1. Since according to the MO

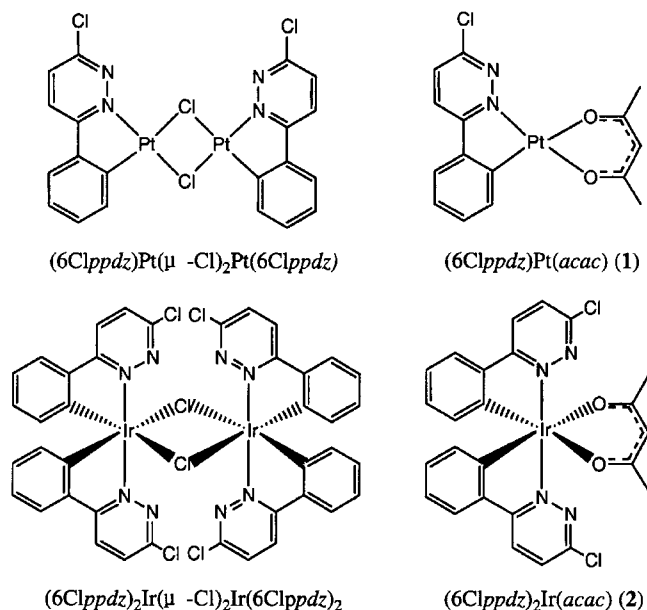


Figure 1. Structure of Pt(II)- and Ir(III)-dimer and monomer containing 6Clppdz and acac as ligands.

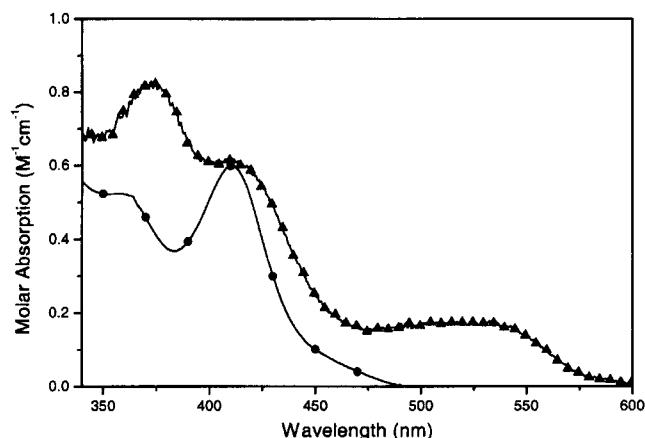


Figure 2. Absorption spectra for  $(6\text{Clppdz})\text{Pt}(\text{acac})$  (**1**, ●) and  $(6\text{Clppdz})_2\text{Ir}(\text{acac})$  (**2**, ▲) complexes in  $\text{CH}_2\text{Cl}_2$  solution.

calculation (N. K. Park, in personal communication), LUMO (lowest unoccupied molecular orbital) of complex **2** consists mostly of pyridazine ring and HOMO (highest occupied molecular orbital) consists mostly of phenyl ring, 6Clppdz is coordinated to Ir(III) with carbon in the phenyl ring trans to the nitrogen in the pyridazine ring of the different ligand. In the monomers, Pt(II) complex is planar and Ir(III) complex is octahedral which has only one isomer.

*Spectroscopy*

Absorption and emission spectra were recorded for both of the complexes as shown in Figure 2 and 3, respectively. The data are summarized in Table 1. Low energy transitions in the range of 407-525 nm, with extinction coefficients of 1,200 to 6,000  $\text{M}^{-1}\text{cm}^{-1}$ , are assigned to metal-to-ligand charge

Table 1. Wavelength maxima in absorption, excitation, and emission spectra of (6Clppdz)Pt(acac) (1) and (6Clppdz)<sub>2</sub>Ir(acac) (2) at room temperature.

Complexes	Absorption	Excitation	Emission
	$\lambda_{\max}$ (nm) [ $\epsilon$ ( $10^3 \text{ cm}^{-1} \text{ M}^{-1}$ )]	$\lambda$ (nm) <sup>1</sup>	$\lambda_{\text{em}}$ (nm) <sup>1</sup>
(6Clppdz)Pt(acac) (1)	300 (12.5), 360 (5.2), 410 (6), 450 (sh, 1.2)	363, 425, 470 (sh)	541, 580 <sup>2</sup>
(6Clppdz) <sub>2</sub> Ir(acac) (2)	274 (36.4), 370 (8.3), 407 (6.0), 525 (1.8)	370, 418, 508-537(br)	615 <sup>3</sup>

<sup>1</sup>in CH<sub>2</sub>Cl<sub>2</sub> soln. <sup>2</sup>excited at 424 nm. <sup>3</sup>excited at 410 nm.

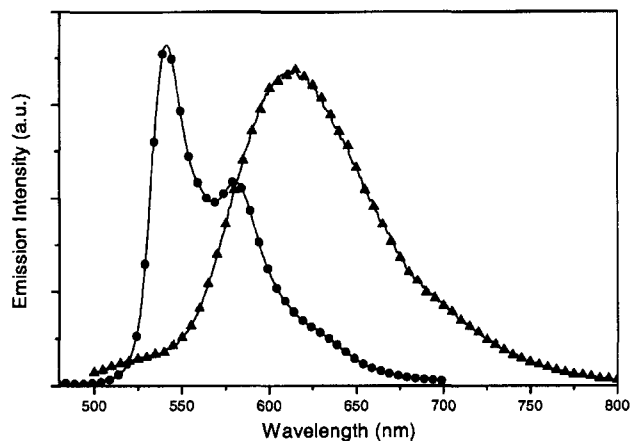


Figure 3. Emission spectra for (6Clppdz)Pt(acac) (1, ●) and (6Clppdz)<sub>2</sub>Ir(acac) (2, ▲) complexes in CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature.

transfer (MLCT) transitions. The intense absorption bands at higher energy are assigned to  $\pi$ - $\pi^*$  ligand-centered (LC) transitions.

In the emission spectra (Figure 3), excitation wavelengths ( $\lambda_{\text{ex}}$ ) are set at 424 nm for Pt(II) and 410 nm for Ir(III) complex and variations in  $\lambda_{\text{ex}}$  doesn't show any difference in emission band. Pt(II) complex shows two bands of emission which is similar to other Pt(II) complexes with 2-phenylpyridine (ppy) [5] or pppdz derivatives [12]. This is quite different from the Ir(III) complexes which shows only one band in emission spectra. Further study of MO's will make the band assignment possible.

In conclusion, Pt(II) and Ir(III) complexes containing 6Clppdz are intensely emissive in fluid solution (298 K). While Pt(ppy)<sub>2</sub> shows green colored emission with wavelength ( $\lambda_{\text{em}}$ ) of 489 and 517 nm similar to Ir(ppy)<sub>3</sub> (517 nm) [10], 6-chloro-3-phenylpyridazine complex shows different  $\lambda_{\text{em}}$  (541 to 615 nm) depending on the central metal ion. Variation of metal center as well as derivatization of the ligands must be explored in order to tune the emission color.

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