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New tridentate cyclometalated platinum(II) and palladium(II) complexes of N,2-diphenyl-8-quinolinamine: syntheses, crystal structures, and photophysical properties

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Abstract—A new tridentate cyclometalated platinum(II) complex derived from N,2-diphenyl-8-quinolinamine, which consists of two crystallographic independent molecules with two intermolecular N–H–Cl–Pt hydrogen bonds forming a dimer, exhibited a low-energy luminescence at ca. 740 nm in a 1×10^{-3} M dichloromethane solution and a strong emission centered at 670 nm in a solid state, but the analogous palladium(II) complex was nonemissive at room temperature. © 2005 Elsevier Ltd. All rights reserved.

Square-planar d⁸ transition metal complexes have received considerable attention due to their intriguing photophysical and photochemical properties.¹ In particular, luminescent platinum(II) complexes with oligopyridines and cyclometalating ligands have been extensively investigated over the past years.^{2–5} Generally, square-planar d⁸ complexes stack in a solid state via metal-metal and/or ligand-ligand interactions, forming dimer or linear-chain structures.^{2,3a,b} Such stacking interactions result in interesting low-energy triplet emissions in the 600-750 nm region.^{3a,b,5c} In order to account for these phenomena, Miskowski et al. proposed oligomeric metal-metal-to-ligand charge transfer (MMLCT: $d\sigma^* \rightarrow \pi^*$) and excimeric ligandto-ligand $(\pi \rightarrow \pi^*)$ excited states.^{2b} Furthermore, a series of binuclear d⁸-d⁸ complexes have also been prepared to model the low-energy MMLCT or excimeric ligand–ligand emissions.^{3c,d,4b,5b} In view of the pronounced effect of metal-metal and ligand-ligand interactions on the photophysical properties, it appears to be interesting if the electronic structures of these com-

plexes can be affected by other weak interactions. With these considerations in mind, we designed and synthesized a new C^NN^N cyclometalating ligand, N,2-diphenyl-8-quinolinamine. This new ligand contains two different types of nitrogen atoms and one phenyl carbon atom for metalation. More importantly, the presence of one NH group in the phenylamino moiety may permit an intermolecular hydrogen bonding in cyclometalated complexes. Herein their syntheses, crystal structures, and photophysical properties are described.

The syntheses of the ligand 4 and its cyclometalated platinum(II) and palladium(II) complexes, 5 and 6, are shown in Scheme 1. A starting material, 8-bromo-2(1H)-quinolinone (1),⁶ was treated with POBr₃ to afford a key intermediate 2 in a high yield. Subsequent selective Suzuki–Miyaura mono-coupling was achieved in 84% yield owing to different reactivities of two bromine atoms at the 2- and 8-positions. Thus, further conversion to the desired ligand 4 was readily carried out by the reaction of 3 with 1.2 equiv of aniline under standard Buchwald coupling conditions. It is noteworthy that the present synthetic method provides a new route to 2-phenyl-8-quinolinamine derivatives. After the successful isolation of 4, the syntheses of cyclometalated platinum(II) and palladium(II) complexes were studied. According to the general procedures,⁷ a mixture

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Scheme 1. Reagents and conditions: (a) 2.0 equiv POBr₃, 140 °C, 3 h; (b) 1.1 equiv PhB(OH)₂, 3 mol % Pd(PPh₃)₄, 2 M K₂CO₃, toluene-ethanol, 80 °C, 22 h; (c) 1.2 equiv aniline, 3 mol % Pd₂(dba)₃, 7.2 mol % *rac*-Binap, 1.4 equiv NaOBu^t, toluene, 100 °C, 19 h; (d) 1.0 equiv K₂MCl₄ (M = Pt, Pd), H₂O/MeCN, reflux, 24 h; (e) 1.0 equiv *cis*-PtCl₂(DMSO)₂, 1.0 equiv NaOAc, methanol, reflux, 5 h.

of 4 and K_2PtCl_4 in acetonitrile–water was refluxed for 24 h under argon. After work-up, however, the complex 5 was isolated only in 32% yield. In order to improve the yield, another method by using *cis*-PtCl₂(DMSO)₂ as a metalating reagent and sodium acetate as a base was attempted. As a result, the desired product 5 was obtained in 72% yield after refluxing in methanol for 5 h. Thus, the use of *cis*-PtCl₂(DMSO)₂ as a precursor for the cycloplatinated product 5 proved superior to that of K₂PtCl₄ due to a shorter reaction time and a higher yield. In contrast, the analogous palladium complex 6 was easily prepared in 90% yield from K₂PdCl₄ (Scheme 1).

All these compounds were well characterized by ¹H NMR, ¹³C NMR, MS, and elemental analyses. Furthermore, the molecular structures of both **5** and **6** were determined by single-crystal X-ray analysis.

As shown in Figure 1, the crystal structure of 5 consists of two crystallographic independent molecules.⁸ Both Pt atoms exhibited a distorted square planar geometry similar to the tridentate Pt(II) complexes reported in the literatures.^{5,7a,9} All the bond lengths and angles are also comparable to those of the related Pt(II) complexes, ^{5,7a,9} except that Pt1-N2 and Pt2-N102 are longer. These longer Pt-N bonds may be attributed to strong trans influence of the phenyl carbon C(11) or C(111). An interesting structural feature for 5 depends on the formation of two N-H-Cl-Pt hydrogen bonds between two independent molecules (N(2)-Cl(2) 3.230(9) Å, N(102)-Cl(1) 3.332(9) Å; N(2)-H(10)-Cl(2) 171(2)°, N(102)-H(25)-Cl(1) 172(2)°). Each Cl atom bonded to the Pt center has a short contact with the NH group of the other Pt complex. All the distances and angles are present within a range of N-H-Cl-Pt hydrogen bonds observed in the literatures.¹⁰ In addition, two intermolecular N-H-Cl-Pt hydrogen bonds resulted in a dimeric aggregation of 5 in the crystal packing diagram. Within a dimeric unit, Pt(1)-Pt(2) distance of 3.41 A indicates a weak metal-metal interaction. The interplanar separation of ca. 3.60 Å between two $C^{\wedge}N^{\wedge}N$ ligands are sufficiently close for $\pi-\pi$ interaction as observed in the similar reported structures.^{5a,b,9}



Figure 1. A perspective view of the two independent molecules with selected atom numbering found in the crystal structure of 5. Selected bond lengths (Å) and angles (°): Pt(1)-Cl(1) 2.321(3), Pt(2)-Cl(2) 2.326(2), Pt(1)-C(11) 1.99(1), Pt(2)-C(111) 1.99(1), Pt(1)-N(1) 1.939(8), Pt(2)-N(101) 1.934(9), Pt(1)-N(2) 2.211(9), Pt(2)-N(102) 2.234(9); C(11)-Pt(1)-N(2) 163.1(4), C(111)-Pt(2)-N(102) 162.8(4).

However, there are no metal–metal and π – π interactions between two dimeric units. The crystal structure of the palladium complex **6** is similar to the structure of **5**. It also consists of two crystallographic independent molecules, in which two intermolecular hydrogen bonds were also formed to give the dimer.¹¹

The room-temperature absorption spectra of **5** and **6** were measured in a 1×10^{-5} M dichloromethane solution. The platinum complex **5** showed an intense absorption in the range 250–400 nm ($\varepsilon > 10^4$ M⁻¹ cm⁻¹), which is considered to be assigned to the intraligand transitions of the quinolinamine ligand. In addition, a broad absorption appeared at around 410 nm ($\varepsilon = 3800$ M⁻¹ cm⁻¹), which is likely due to the ¹MLCT transition (Pt $\rightarrow \pi^*$), similar to those identified in the spectra of the related cyclometalated platinum(II) complexes.^{5a,b} No

absorptions were found in the region beyond 500 nm. Since the X-ray crystal structure of **5** indicates strong intermolecular hydrogen bonding interactions, the effect of the concentration on the absorption spectrum was further investigated. When a 1×10^{-3} M dichloromethane solution was measured by using a thin cell (1 mm), a shoulder at ca. 570 nm was observed at room temperature. The absorption spectrum of the palladium complex **6** showed two intense bands in the range 250–380 nm ($\varepsilon > 10^4$ M⁻¹ cm⁻¹), accompanied by a weak shoulder at around 400 nm. These bands are considered to be mainly attributed to intraligand transitions. No low-energy absorption was observed for **6** at concentrations higher than 1×10^{-3} M.

The platinum complex **5** exhibited a strong emission at room temperature both in solution and solid states. However, its emissive behavior changed dramatically depending on the concentration and excitation wavelength as shown in Figure 2. In the 1×10^{-5} M dichloromethane solution, excitation of **5** at 410 nm resulted in a strong emission around 600 nm. As the concentration increased to 1×10^{-3} M, excitation at 500 nm produced a broad low-energy luminescence at around 740 nm. Besides, a microcrystalline sample of **5** also showed a strong emission centered at 672 nm when excited at 500 nm. In contrast to the strong luminescent platinum complex **5**, the analogous palladium complex **6** showed no emission at room temperature both in solution and solid states as reported in the literatures.¹²

In summary, we designed and synthesized the new tridentate C^N^N ligand *N*,2-diphenyl-8-quinolinamine and its cyclometalated platinum(II) and palladium(II) complexes. The crystal structures of both complexes revealed strong intermolecular hydrogen bonding interactions. In addition, the platinum complex exhibited unique room-temperature emissive behavior in diluted



Figure 2. The room-temperature emission spectra of 5 (a) in 1×10^{-5} M dichloromethane solution (λ_{ex} 410 nm), (b) in 1×10^{-3} M dichloromethane solution (λ_{ex} 500 nm), and (c) in solid state (λ_{ex} 500 nm).

and concentrated dichloromethane solutions as well as in a solid state. Further investigation is now in progress.

Acknowledgments

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Supplementary data

Electronic supplementary data: general experimental procedures for the syntheses of **2–6**, X-ray crystal data including selected bond lengths and angles for **5** and **6**, crystal packing diagram for **5** and crystal structure of **6**, and the room-temperature absorption spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.09.120.

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- 8. Crystal data for 5: $C_{21}H_{15}N_2ClPt$, M = 525.91, monoclinic, space group $P2_1/c$ (#14), a = 10.8156(3) Å, b = 14.6206(4) Å, c = 23.3398(6) Å, $\beta = 93.9063(6)^\circ$, V = 3606.6(2) Å³, Z = 8, $D_c = 1.973$ g cm⁻³, μ (Mo-K α) = 79.03 cm⁻¹, Mo-K α radiation ($\lambda = 0.71069$ Å), R1 =0.055, wR2 = 0.158.

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- 11. Crystal data for **6**: C₂₁H₁₅N₂ClPd, M = 437.22, monoclinic, space group $P2_1/c$ (#14), a = 10.7847(2) Å, b = 14.1411(4) Å, c = 23.6112(5) Å, $\beta = 94.3154(4)^\circ$, V = 3590.7(1) Å³, Z = 8, $D_c = 1.617$ g cm⁻³, μ (Mo-K α) = 11.88 cm⁻¹, Mo-K α radiation ($\lambda = 0.71069$ Å), R1 =0.054, wR2 = 0.195.
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