Cyclometalated complexes of platinum metals – the new luminescent activators of OLED

M V Nikolaeva, E A Katlenok, M S Khakhalina, M V Puzyk and K P Balashev
Department of Chemistry, Herzen State Pedagogical University, St. Petersburg, 191186, Russia

E-mail: nikolaeva.mr@gmail.com

Abstract. Systematic investigations of the spectral and luminescent properties of the mixed-ligand cyclometalated Pd(II), Pt(II), Rh(III) and Ir(III) complexes are carried out. Based on these investigations some complexes may be recommended as activators of OLED.

1. Introduction

Aromatic heterocyclic molecules are characterized by intense luminescence, photostability and electrochemical reversible electron transfer processes. For this reason they are widely used in Organometallic Light Emitting Devices (OLED) [1–5]. It is possible to modify them in two ways: by introducing different substituents or by cyclometalating their aryl substituted derivatives [6–14].

The main problem of producing metal complex luminescent activators of OLED is nonradiative process behavior of the low-energy metal-centered electronically excited (d-d*)-type states. Therefore, many researchers started to pay attention to cyclometalated complexes of platinum metals to solve this problem. Energy in their electronically excited (d-d*) states increases due to metal–carbon bond formation.

There are several papers which show the wide application of cyclometalated complexes of platinum metals as OLED activators, biomaterial luminescent labels, optical sensors, materials with liquid-crystalline and photoreactive properties and photocatalytic system components for solar energy conversion to chemical or electrical one [1–5]. The aim of the present paper is to study the influence of ligand and metal structure, composition and nature on the spectral and luminescent characteristics of the cyclometalated square-planar Pt(II) and Pd(II) and octahedral Rh(III) and Ir(III) complexes. They contain the deprotonated form of the cyclometalating (C^N) ligand (2-phenylpyridine (Hppy), 7,8-benzo(h)quinolone (Hbzq), 2-tolylpyridine (Htlp), 4-phenylpyrimidine (Hppm), 1,7-phenanthroline (1,7-Hphen), 2-phenylbenzothiazole (Hbt), 2-phenylbenzoxazole (Hpbo) and 1-phenylpyrazole (Hppz)) and the noncyclometalating ligand (ethylenediamine (En), ammonium (NH3), acetate (OAc–), trifluoroacetate (OTF–), diethylthiocarbamate (dtc–), 2-mercaptopyrindinate (pyt–), 2-hydroxypyridinate (pyo–), acetyladonate (acac–), 2-mercaptopbenzothiazolate (mbt–) and 2-mercaptopbenzoxazolate (mbo–) ion).

The synthesis of these complexes was based on the substitution reactions of the chloride ligands with the corresponding cyclometalating and other ligands. The electronic absorption spectra were measured on an SF-2000 spectrophotometer (LOMO, St. Petersburg, Russia), and the luminescence was studied using a Fluorat-02-Panorama spectrofluorimeter (Lumeks, St. Petersburg, Russia).
2. Electronic absorption spectra of ligands and mononuclear complexes

Photo- and electrostimulated processes with complexes are classified within the model of localized molecular orbitals according to the preferred localization of involved orbitals on the metal or ligand [2]. The investigation results of the electronic absorption spectra of complexes and free heterocyclic ligands [6–14] demonstrate:

- a bathochromic shift of the long-wavelength (π-π*) optical transitions in a row (in nm) Hppz (255), Hptpy (301sh.), Hbt (312sh.), Hbzq (346) free heterocyclic ligands (sh. – shoulder);
- together with a bathochromic shift (< 1000 cm⁻¹) of the intraligand (IL) (π–π*) optical transitions complexes are characterized by a bathochromic shift of vibrationally structured long-wavelength absorption caused by both cyclometalated ligand and noncyclometalating ligand nature as well as metal nature (Pd(II) < Rh(III) < Pt(II) < Ir(III));
- in accordance with the increase of the spin-orbit coupling efficiency of Ir(III) compared to Rh(III) [3–5] together with the spin-allowed there also exists the spin-forbidden optical transitions for octahedral Ir(III) complexes in the long-wavelength region;
- substitution of σ-donor ethylenediamine or ammonium with π-donor chelated ligands results in a small (Δν ~ 1000 cm⁻¹) bathochromic shift of the long-wavelength absorption bands of Ir(III) complexes;
- the absorption of complexes at the longest wavelengths is assigned to the metal-to-ligand charge transfer (MLCT) optical transition between the mainly metal-centered HOMO and the LUMO mainly localized on the imine component of the cyclometalated ligand.

3. Electrochemical properties of mononuclear complexes

Reduction and oxidation voltammograms of cyclometalated complexes are characterized by one-electron processes of electron transfer on the cyclometalated ligand unoccupied π*-orbitals and electron removal from metal-centered d-orbitals of complexes. In accordance with the presence of one or two cyclometalated ligands in the inner sphere of square-planar and octahedral complexes their reduction voltammograms are marked by one and two waves:

1) [M(C^N)(L^L)]Z⁺ + e⁻ = [M(C^N–)(L^L)]Z⁻ (M = Pd(II), Pt(II));
2) [M(C^N)(C^N)(L^L)]Z⁺ + e⁻ = [M(C^N)(C^N–)(L^L)]Z⁻ (M = Rh(III), Ir(III)).

Metal-centered nature of one-electron oxidation processes of complexes:

1) [M^II(C^N)(L^L)]Z⁻ – e⁻ = [M^III(C^N)(L^L)]Z⁺ (M = Pd(II), Pt(II));
2) [M^III(C^N)(C^N)(L^L)]Z⁻ – e⁻ = [M^IV(C^N)(C^N)(L^L)]Z⁺ (M = Rh(III), Ir(III)), is supported by cathode bias of wave potential according to metal nature (for octahedral complexes [Ir(bzq)₂pyt] 0.39 V and [Rh(bzq)₂pyt] 0.75 V, for square-planar complexes [PtEn(tp)]PF₆ 0.89 V and [PdEn(tp)]PF₆ 1.07 V).

Thus the electrochemical data point to metal-centered nature of the HOMO and ligand-centered nature of the LOMO of complexes that is consistent with the assignment of their long-wavelength band in absorption spectra to the metal-to-cyclometalated-ligand charge transfer optical transition.

4. Spectral and luminescent properties of ligands and mononuclear complexes

Heterocyclic ligands’ metalation results in their fluorescence quenching in the ultraviolet region due to metal spin-orbital coupling. Complexes’ photoexcitation in glassy solutions leads to their phosphorescence in the visible region (luminescence maximum is from 418 to 530 nm for [PtEn(ppz)]Cl and [Pt(bt)(acac)] respectively) (table 1). Phosphorescence excitation spectra of complexes agree with their absorption spectra.

Like the bathochromic shift of free ligands’ fluorescence, complexes’ phosphorescence has also a bathochromic shift in the visible region during a change of ligand nature. For square-planar and octahedral complexes with ammine ligands substitution of Pd(II) and Rh(III) with Pt(II) and Ir(III) results in a bathochromic shift of spectra (Δν = (900±100) cm⁻¹) while luminescence spectra of Pd(II) and Rh(III) as also Pt(II) and Ir(III) complexes are similar [14].
Table 1. Luminescent characteristics of mono- (square-planar and octahedral) and binuclear Pd(II), Rh(III), Pt(II) and Ir(III) complexes (at 77 K, in CH$_3$OCH$_2$CH$_2$OH-C$_2$H$_5$OH (1:1) solution).

| Square-planar complexes | $\lambda_{\text{max}}$, nm | $\tau$, $\mu$s | Octahedral complexes | $\lambda_{\text{max}}$, nm | $\tau$, $\mu$s |
|-------------------------|--------------------------|----------------|---------------------|--------------------------|----------------|
| [PtEn(ppz)]$^+$         | 416                      | 40             | [RhEn(tlp)$_2$]     | 462                      | 114            |
| [Pd(NH$_3$)$_2$ppm]$^+$ | 455                      | 150            | [RhEn(bo)]$^+$      | 482                      | 90             |
| [Pd(NH$_3$)$_2$ppy]$^+$ | 455                      | 150            | [RhEn(bzq)$_2$]$^+$ | 491                      | 1720           |
| [Pd(NH$_3$)$_2$tlp]$^+$ | 467                      | 420            | [IrEn(tlp)$_2$]$^+$ | 485                      | 6              |
| [PdEn(tlp)]$^+$         | 469                      | 410            | [IrEn(bo)$_2$]$^+$  | 508                      | 5              |
| [PtEn(tlp)]$^+$         | 489                      | 20             | [IrEn(bzq)$_2$]$^+$ | 524                      | 25             |
| [PtEn(bzq)]$^+$         | 484                      | 307            | Binuclear complexes | $\lambda_{\text{max}}$, nm |
| [PdEn(bzq)]$^+$         | 476                      | 8600           | [Pt(tlp)(μ-mbo)$_2$] | 481/574                  | 9/2            |
| [Pd(NH$_3$)$_2$(bzq)]$^+$| 476                      | 7200           | [Pt(tlp)(μ-mbt)$_2$] | 482/588                  | 18/8           |
| [Pd(NH$_3$)$_2$(1,7-phen)]$^+$ | 453          | 3600           | [Pt(bo)(μ- pyt)$_2$]  | 625                      | 6              |
| [PdEn(bo)]$^+$          | 486                      | 130            | [Pt(bo)(μ-mbo)$_2$]  | 531/631                  | not exp        |
| [PtEn(bo)]$^+$          | 506                      | 16             | [Pt(bo)(μ-mbt)$_2$]  | 678                      | 5              |
| [PdEn(bt)]$^+$          | 510                      | 150            | [Pd(bzq)(μ-mbt)$_2$] | 673                      | 274            |
| [PtEn(bt)]$^+$          | 528                      | 10             | [Pd(bzq)(μ-mbt)$_2$] | 683                      | 306            |
| [Pt(bt)(acac)]$^+$      | 530                      | 9              | [Pd(tlp)(μ-OAc)$_2$] | 476/740                  | 392            |

As against Pt(II) and Ir(III) complexes which luminesce in glassy (77 K) and liquid (293 K) solutions, Pd(II) and Rh(III) complex luminescence is quenched in liquid solutions. The temperature quenching the luminescence of Pd(II) and Rh(III) complexes in liquid solutions (293 K) is assigned to the thermally activated population of the relative low-energy metal-centered excited (d-d*) states undergoing rapid nonradiative deactivation [9–12].

The energy increasing of metal-centered excited states of Pt(II) and Ir(III) complexes determines their luminescence in the visible region in glassy and liquid solutions. In agreement with an increased 5d-orbitals splitting of octahedral complexes (in comparison with square-planar complexes) [2–5, 11–14], the temperature quenching the luminescence of Ir(III) complexes is less than Pt(II).

In agreement with the luminescence quenching of the complexes as a result of the thermally activated population excited (d-d*) states for complexes with 1-phenylpyrazole, the temperature quenching the luminescence leads to its absence for [PdEn(ppz)]ClO$_4$ and [RhEn(ppz)$_2$]ClO$_4$ not only in liquid but in glassy solutions. Relative energy increase of excited (d-d*) states for [PtEn(ppz)]Cl determines the low-temperature luminescence and its quenching in liquid solutions. Further energy increase of excited (d-d*)-type states of Ir(III) complexes based on 1-phenylpyrazole determines their luminescence [8] both in glassy and in liquid solutions.

The relatively long luminescence decay time of the complexes (from 3 to 8600 $\mu$s) and its sensibility to oxygen presence in solution indicate on the spin-forbidden character of radiative process as a result of phosphorescence [2–4, 6, 11].

Monoexponential phosphorescence decay kinetics and the phosphorescence excitation spectrum agreement with the absorption spectrum of complexes show the occurrence of radiative decay of photoexcitation energy from the lowest energy electronically excited triplet state of complexes. Increasing the efficiency of singlet-triplet intersystem crossing of the complexes’ excited states (in comparison with free luminophore) points to the effective interaction of luminophore with platinum metals characterized by significant spin-orbital coupling.

Independently of the metal and the cyclometalating ligand nature, the low-temperature phosphorescence spectra of complexes are characterized by a main progression with frequency $\nu = (1460±50)$ cm$^{-1}$ corresponding to the C=C/C=N stretching vibrations of the cyclometalated ligand. As against the bathochromic shift of long-wavelength MLCT bands in the excitation spectra of Rh(III) complexes in comparison with Pd(II) ($\Delta\nu$ 1400 cm$^{-1}$) and Pt(II) complexes in comparison with Ir(III) ($\Delta\nu$ 2000 cm$^{-1}$), the phosphorescence spectra are virtually unchanged (figures 1 and 2). The Huang–
Rhys parameter (S) estimation from intensity ratio of the vibrational components in the low-temperature phosphorescence spectrum [14] and the singlet-triplet splitting energy (E_{ST}) for the intraligand (π-π*) excited state of complexes show their practical independence from the metal nature (S = (0.8±0.1), E_{ST} ~ 11600 cm\(^{-1}\)). The obtained estimations allowed us to classify complexes' phosphorescence to the intraligand optical transition. At the same time the bathochromic shift of phosphorescence spectra of Ir(III) and Pt(II) complexes in comparison with Rh(III) and Pd(II) complexes at (900±100) cm\(^{-1}\) as well as tenfold cutting phosphorescence decay time indicate on the mixed IL/MLCT character of complexes' excited state responsible for phosphorescence.

Figure 1. Phosphorescence (curves to the left) and excitation of emission (curves to the right) spectra at 77 K: (a) [PdEn(pbo)]PF\(_6\) (1) and [PtEn(pbo)]PF\(_6\) (2), (b) [RhEn(bt)]\(_2\)PF\(_6\) (1) and [IrEn(bt)]\(_2\)PF\(_6\) (2).

Figure 2. Electronic absorption (curves to the left) and luminescence (293 K) (curves to the right) spectra: (a) [PtEn(tp)]PF\(_6\) (1) and [IrEn(tp)]\(_2\)PF\(_6\) (2), (b) [PtEn(bzq)]PF\(_6\) (1) and [IrEn(bzq)]\(_2\)PF\(_6\) (2).

Thus spectral and luminescent properties of cyclometalated complexes of platinum metals with σ-donor ethylenediamine or ammonium ligands are defined by phosphorescence from the energy lowest mainly intraligand triplet state. At the same time π-donor chelated ligands enhance mixing degree of intraligand electronically excited state with charge transfer state due to interaction with d_π-metal orbitals. It results in the bathochromic shift of phosphorescence spectrum.

5. Optical and electrochemical properties of binuclear cyclometalated Pd (II) and Pt (II) complexes

In comparison with mononuclear complexes, the presence of metal–metal bond in binuclear cyclometalated complexes leads to a nature change of the HOMO due to formation of dσ*-molecular orbital. This determines, together with the IL (π-π*) and the MLCT (d-π*) spin-allowed optical transitions, additional absorption in the the long-wavelength region (405–512 nm) related to the metal–metal-to-cyclometalated-ligand charge transfer (MMLCT) (dσ*-π*) optical transition [10].
In agreement with the energy increase of Pt(II) 5d-orbitals (in comparison with Pd(II) 4d-orbitals) de* MO also have higher energy that leads to a bathochromic shift of their optical MMLCT-type bands in contrast with Pd(II) complexes.

Change of nature and energy of the HOMO during the formation metal–metal chemical bond in binuclear \[\text{[Pd(C}^\text{N})(\mu-\text{OAc})]_2\] and \[\text{[M(C}^\text{N})(\mu-\text{N}^\text{L})]_2\] complexes is reflected in cathode bias of electrooxidation wave potentials of binuclear complexes in comparison with mononuclear complexes.

Oxidation voltammograms of binuclear Pt(II) complexes are characterized by two one-electron waves corresponding to the sequent oxidation process behaviour of two palladium centres with the formation binuclear Pd(III) complex. Electrooxidation of binuclear Pt(II) complexes proceed as a result of two-electron process of binuclear Pt(III) complexes' formation:

\[
\text{[Pt}^{\text{II}}(\text{C}^\text{N})(\mu-\text{N}^\text{L})]_2 - 2e^- = \text{[Pt}^{\text{III}}(\text{C}^\text{N})(\mu-\text{N}^\text{L})]_2^{2+}. 
\]

6. Luminescent properties of binuclear complexes with metal–metal chemical bond
Photoexcitation of glassy solutions (77 K) of binuclear Pd(II) complexes in the absorption bands' region results in intraligand vibrationally (\(\pi-\pi^*\)) phosphorescence similar to the phosphorescence of \[\text{[Pd(C}^\text{N})\text{En}]PF_6\] complexes. At the same time together with intraligand phosphorescence in the red region there is a weak structureless band (figure 3) classified to MMLCT-type phosphorescence [10]. The phosphorescence excitation spectrum in the blue and red region is the same and agree with the absorption spectrum of complex. Phosphorescence decay kinetics is nonexponential that agree with radiative process behaviour from two thermally non-equilibrium electronically excited IL and MLCT states (table 1).

Photoexcitation of binuclear Pt(II) complexes both in glassy (77 K) and in liquid (293 K) solutions leads to complexes' phosphorescence only in the red region (figure 4). The phosphorescence excitation spectrum of complexes agree with the absorption spectrum. Exponential phosphorescence decay kinetics confirms radiative process behaviour of photoexcitation energy degradation from one electronically MMLCT excited state.

7. Conclusion
Thus mixed-ligand square-planar \[\text{[M(C}^\text{N})(\text{L}–\text{L})]X}\ (M = \text{Pt(II), Pd(II); X = ClO}_4^-, \text{PF}_6^-, \text{Cl}^-) and octahedral \[\text{[M(C}^\text{N})_2(\text{L}–\text{L})]X}\ (M = \text{Rh(III), Ir(III)}) complexes with heterocyclic cyclometalated \((\text{C}^\text{N})^\gamma = \text{ppz, pbo, bt, tlp, bzo, ppy, ppm, 1,7-phen}) and noncyclometalated \((\text{L}–\text{L}) = \text{En, NH}_3, \text{acac}^-, \text{dtc}^-, \text{OAc}^-, \text{OTF}^-, \text{pyt}^-, \text{mbt}^-, \text{pyo}^-, \text{mbo}^-)\) ligands are synthesized and classified by the composition, structure and optical properties.

Obtained results of this study demonstrate that mixed-ligand cyclometalated mono- and binuclear complexes of platinum metals form a family of complexes with long-lived electronically excited states. Localization of electronically excited states on the metal complex fragments in complex composition, together with the control and regulation ability of their optical parameter as a result of

![](figure3.png)

**Figure 3.** Absorption (293 K) (curves to the left) and low-temperature (77 K) luminescence (curves to the right) spectra of \[\text{[Pd(tlp)(\mu-OAc)]}_2\].

![](figure4.png)

**Figure 4.** Low-temperature (77 K) phosphorescence spectrum of \[\text{[Pt(bq)\mu-pyt]}_2\] in \(\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}:\text{C}_2\text{H}_5\text{OH}\) (1:1) solution.
change of heterocyclic ligands' nature and metal coordination centres in a wide range, determines their application perspectiveness as activators of organic light-emitting systems.

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