Cyclometalated complexes of platinum metals – the new luminescent sensors

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Abstract. The influence of the environment on the cyclometalated Pt(II), Pd(II), Ir(III) complexes' optical properties in the presence of various organic and inorganic compounds in solution and the gas phase is studied. The feasibility of complexes' using as optical sensors for molecular oxygen, halides ions, hydrogen and Hg(II) cations in the liquid phase, as well as for water and some organic solvents' vapor in the immobilized state in the MF-4SK membrane.

1. Introduction
Heterocyclic luminophores with high quantum yield of fluorescence and photostability [1], biological and catalytic activity [2] are attracted the attention of researches to modification of their properties. Together with introducing different substituents the modification of properties of heterocyclic phosphors occurs by metalation of their aryl substituted derivatives. It has been shown [3–7] that metalation by platinum metals leads to a significant change in the optical properties of luminophores.

In contrast to fluorescence of free luminophores, metal-complex phosphors are characterized by intense and relatively long-lived phosphorescence in solutions and outer-sphere electron transfer reversible processes. The specific structure of the cyclometalated Pt(II), Pd(II), and Ir(III) complexes with heterocyclic ligands determines the possibility of developing of these complexes-based optical sensors and chemosensors for the presence of various organic and inorganic compounds in the liquid and the gas phase, including in biosystems [7–10].

This work is aimed at studying the effect of the environment on the optical properties and the photoexcitation energy degradation efficiency of the cyclometalated Pt(II), Pd(II), and Ir(III) complexes in homogeneous solutions and which immobilized on the surface of a MF-4SK cation-exchange membrane.

The investigation subjects are the mono- and binuclear Pt(II), Pd(II), and Ir(III) complexes with metalated phenyl-substituted \((C^N)\) imines:

\[
\{M(C^N)\} = \begin{array}{c}
\text{phenyl-pyridine (Ppy)} \\
\text{2-(2’-thienyl)pyridine (Tpy)} \\
\text{2-phenyl-benzothiazole (Bt)} \\
\text{4-phenyl-pyrimidine (Ppm)} \\
\text{1,7-phenanthroline (1,7-Phen)}
\end{array}
\]

where \((C^N)^-\):
chelating (N–N, S–S) ligands:

\[
\{M(N-N)\} = \begin{array}{c}
\text{NH}_2 \\
\text{M} \\
\text{NH}_2
\end{array}
\]

\[
\{M(S-S)\} = \begin{array}{c}
\text{N} \\
\text{S} \\
\text{S} \\
\text{N} \\
\text{M}
\end{array}
\]

N–N: ethylenediamine (En) S–S: diethyldithiocarbamate (Dtc) ethylxanthate (Exn)

and bridging 2-mercapto-derived (µ-N–S) ligands:

\[
\{\text{Pt}(\mu-N^S)\text{Pt}\} = \begin{array}{c}
\text{N} \\
\text{Pt} \\
\text{S} \\
\text{Pt}
\end{array}
\]

(µ-N^S):

2-mercaptop-pyridine (Pyt) 2-mercaptop-pyrimidine (Mpm) 2-mercaptop-benzothiazole (Mbt) 2-mercaptop-1-methylimidazole (Mim)

The cyclometalated complexes were synthesized by well-known methods and investigated by electronic absorption (SF-2000 spectrophotometer) and emission (Fluorat-02-Panorama spectrofluorimeter) spectroscopy, multinuclear one- and two-dimensional NMR spectroscopy (JEOL JNM-ECX400A spectrometer), X-ray crystallography (Agilent Technologies Xcalibur Eos single crystal X-ray diffractometer), and cyclic voltammetry (IPC-Pro MF potentiostat).

2. Sensor optical properties of cyclometalated complexes of platinum metals

2.1. Effect of halide ions on the luminescence of complexes

The luminescence quenching of complexes by halide ions (Cl^−, Br^−, I^−) was done in an argon-saturated ethanol solution at 298 K. In the absence of halide ions, the photoexcitation of solutions of [PtEnPpy]^+, [PtEnTpy]^+, and [PtEnBt]^+ complexes leads to an intense vibrationally structured luminescence in the visible spectral region (figure 1) with an exponential decay kinetics, which, within the model of localized molecular orbitals, is assigned to the spin-forbidden optical transition from the metal-to-ligand charge transfer state. The presence of halide ions (C ≤ 10^{-2} M) in solutions does not change the absorption spectra of complexes that points at the absence of the outer-sphere complexation of [PtEn(C^N)N]Hal. At the same time, the intensity (I) and decay time (τ) of the complexes' photoluminescence with increase of halide ions concentration decrease (figure 2) [11].

**Figure 1.** Luminescence spectra of (1) [PtEnPpy]^+, (2) [PtEnBt]^+, and (3) [PtEnTpy]^+ complexes in ethanol at 298 K.

**Figure 2.** Dependences of the luminescence intensity and decay time for (1) [PtEnPpy]^+, (2) [PtEnBt]^+, and (3) [PtEnTpy]^+ complexes on the concentration of iodide ions in ethanol at 298 K.
The phosphorescence quenching efficiency of Pt(II) complex solutions by halide ions (Cl\(^{-} < Br\(^{-} < I\(^{-}\)) is defined by external heavy atom effect due to increasing the spin-orbit interaction constant of halide ions.

Substitution of chelated En ligand for monodentate ammonium changes fundamentally the mechanism of quenching: an effective complete reaction of replacement of both ammonium for halogen. This is reflected in the absorption spectra and the absence of the luminescence of complex.

2.2. Effect of molecular oxygen on the luminescence of complexes

The luminescence quenching of complexes by molecular oxygen was done in an argon-deaerated water, acetonitrile, and methanol solution at 295 K. With the increase of oxygen amount in deaerated solutions of complexes, a reduction was observed in the luminescence intensity (figure 3) and lifetime. The absence of the association of oxygen molecules with complexes, as well as the dynamic character of quenching, are indicated by the absence of changes in the absorption spectra of complexes and by the coincidence of the linear dependences of \(I_0/I - 1\) and \(\tau_0/\tau - 1\) on the oxygen concentration (figure 4) \[12\].

![Figure 3. Luminescence intensity of [PtEnPpy]ClO\(_4\) in acetonitrile at molecular oxygen concentrations of (1) 0, (2) 1.49 \times 10^{-3}, (3) 2.98 \times 10^{-3}, (4) 4.47 \times 10^{-3}, and (5) 5.96 \times 10^{-3} \text{ mol/l}.

![Figure 4. Quenching of the luminescence of Pt(II) complexes in acetonitrile as a function of the oxygen concentration \(Q\) for (1) [PtEnBt]ClO\(_4\), (2) [PtEnPpy]ClO\(_4\), and (3) [PtEnTpy]ClO\(_4\).]

The dynamic character of phosphorescence quenching of the complexes by molecular oxygen in solutions with the near-diffusion rate constant determines the feasibility of complexes' using as luminescent sensors for the presence of molecular oxygen in solution.

Spectral changes of the ammonia cyclometalated Pt(II) complexes in water also have their specificity: molecular oxygen causes a complete chemical reaction in which the final substance is platinum blue, i.e. polynuclear Pt(II) complexes with bridging OH\(^{-}\)-ligand \[13\].

2.3. Effect of acidity on the luminescence of complexes

Protonation of nitrogen atom of cyclometalated ligands in the composition of [Pd(NH\(_3\))\(_2\)(Ppm)]ClO\(_4\) and [Pd(NH\(_3\))\(_2\)(1,7-Phen)]ClO\(_4\) complexes with the addition of perchloric acid to their ethanol solutions is shown. It leads to the phosphorescence quenching of complexes at 77 K (figure 5). The absorption spectra of complexes with the addition of acid remain almost unchanged.

The dependences of the first luminescence maximum on pH (pH = − \log [HClO\(_4\)]) (figure 6) point at the influence of perchloric acid concentration on the luminescence spectra. The observed changes in the spectra are reversible with addition of sodium carbonate to the ethanol solution, the luminescence spectra are restored completely to their initial shapes. \[14\].
Figure 5. Luminescence spectra of (a) [Pd(NH$_3$)$_2$Ppm]ClO$_4$ and (b) [Pd(NH$_3$)$_2$(1,7-Phen)]ClO$_4$ complexes in ethanol at 77 K with increasing (in the direction of the arrow) perchloric acid concentration. The dashed lines show the initial luminescence spectra of complexes.

Figure 6. Dependence of the intensity of the first luminescence maximum of (a) [Pd(NH$_3$)$_2$Ppm]ClO$_4$ and (b) [Pd(NH$_3$)$_2$(1,7-Phen)]ClO$_4$ complexes in ethanol at 77 K on pH.

2.4. Effect of Hg(II) cation on the luminescence of complexes

Development of optical sensors for the presence of mercury, which is one of the most toxic metals, in the environment is the number one problem [15].

Addition of acetonitrile Hg(ClO$_4$)$_2$ solution to dichloromethane solution of binuclear [PtBt(μ-(N^S))]$_2$ complexes with a Pt–Pt chemical bond leads to a change of the optical characteristics of complexes’ solutions, according to relationship between concentrations of Hg(II) and Pt(II) complex.

The optical density increase of solution in the 450–650 nm region and the phosphorescence quenching with the maximum at 670–694 nm (figure 7a), with increasing of Hg(ClO$_4$)$_2$ concentration to 1:1 ratio with platinum complex, result from interaction between Lewis Hg(II) acid and base – binuclear Pt(II) complex:

$$[\text{Pt(bt)(μ-(N^S))}]_2 + \text{Hg(ClO}_4)_2 = \{\text{Hg[Pt(bt)(μ-(N^S))]}_2\}(\text{ClO}_4)_2.$$  

Further Hg(II) concentration increase leads to a decrease of solution absorption in the 450–650 nm region and an appearance (figure 7b) of the typical bands of [Pt(bt)(CH$_3$CN)$_2$]$^+$ in the luminescence spectra, with the maxima at 530 and 568 nm [16], due to adduct destruction:

$$\{\text{Hg(ClO}_4)_2[\text{Pt(bt)(μ-(N^S))}]_2\} + \text{Hg(ClO}_4)_2 + 4 \text{CH}_3\text{CN} = 2 [\text{Pt(bt)(CH}_3\text{CN)}_2]\text{ClO}_4 + 2 \text{Hg(N^S)ClO}_4.$$

It has been shown that the presence of Hg(II) cations in solutions of cycloiridated [IrBt$_2$Dtc] and [IrBt$_2$Exn] complexes leads to a substitution reaction of chelating Dtc$^-$ or Exn$^-$ ligands for acetonitrile solvent and is accompanied by hypsochromic shift of 20–40 nm of the phosphorescence spectra and long wavelength bands of complexes’ absorption spectra.

The selective sensor optical properties of Ir(III) complex solutions as well as mono- and binuclear Pt(II) complexes with sulfur-containing donor atoms of chelating and bridging ligands are related to a specific complex formation of “soft” donor S atoms with “soft” Hg(II) ion.
Figure 7. Optical densities and phosphorescence intensities ($\lambda_{ex} = 400$ nm) of [PtBt($\mu$-Mbt)]$_2$ (C = 2 $\times$ 10$^{-5}$ mol/l) in acetonitrile at Hg(ClO$_4$)$_2$ concentrations of (0) 0, (1) 5 $\times$ 10$^{-6}$, (2) 1 $\times$ 10$^{-5}$, (3) 2 $\times$ 10$^{-5}$, (4) 2.5 $\times$ 10$^{-5}$, (5) 3 $\times$ 10$^{-5}$, and (6) 3.5 $\times$ 10$^{-5}$ mol/l.

3. Effect of vapors of water and organic solvents on the luminescence of cation-exchange MF-4SK membrane modified with Pt(II) complexes

Immobilization of cation-exchange membrane with Pt(II) complexes was done by immersing the membrane into acetonitrile solution of Pt(II) complex with concentration on the order of 10$^{-5}$ mol/l. The efficiency of immobilization was monitored by changing the optical densities of solutions before and after immersion of membrane (figure 8), by an increase in the optical density of the modified membrane with time, and by observing bright luminescence of modified membrane in the corresponding spectral region under photoexcitation (the unmodified membrane weakly luminesces in the blue region). The sorption properties of membranes modified by platinum complexes with respect to vapors of organic solvents and water were studied by the desiccator method.

The obtained data on the sorption of vapors of water, methanol, ethanol, isopropanol, n-butanol, acetonitrile, and acetone (table 1) show that the modification of the cation-exchange membrane by Pt(II) complexes leads to a decrease in the molar sorption of all solvents by up to 20%. This occurs because the adsorbed cations of Pt(II) complexes decrease the volume of the membrane pores and block its sulfo groups. It was found that the sorption efficiency also depends on the nature of solvents (table 1), namely, on the size and polarity of molecules and on the presence or absence of intermolecular hydrogen bonds.

Table 1. Effect of the solvent nature on the luminescence intensity ($I_0/I_{sol}$) and on the molar sorption (A) of the initial membrane and membranes modified with Pt(II) complexes

| Membrane     | H$_2$O | CH$_3$OH | C$_2$H$_5$OH | iso-C$_3$H$_7$OH | n-C$_4$H$_9$OH | CH$_3$CN | (CH$_3$)$_2$CO |
|--------------|--------|----------|--------------|-----------------|---------------|----------|---------------|
|              | $I_0/I_{sol}$ | A, mmol/g | $I_0/I_{sol}$ | A, mmol/g | $I_0/I_{sol}$ | A, mmol/g | $I_0/I_{sol}$ | A, mmol/g | $I_0/I_{sol}$ | A, mmol/g |
| Initial      | –      | 12.2     | –            | 14.2           | –             | 5.5      | –             | 3.2         | –            | 2.5       | –      | 2.2 | –   | 4.6 |
| [PtEnPpy]$^+$ | 2.6    | 10.7     | 8.6          | 13.7           | 4.5           | 2.7      | 3.1           | 2.2         | 2.1         | 3.3       | 2.1    | 4.0 | 4.4 |
| [PtEnBt]$^+$ | 2.0    | 6.7      | 7.7          | 13.5           | 3.7           | 4.5      | 1.8           | 3.1         | 1.8         | 2.1       | 2.1    | 3.1 | 4.3 |
| [PtEnTpy]$^+$ | 3.0    | 11.7     | 16.5         | 11.4           | 11.0          | 4.0      | 4.0           | 3.4         | 1.9         | 6.2       | 1.7    | 7.3 | 4.1 |

In the process of sorption of solvent vapors, a membrane immobilized with a Pt(II) complex sharply decreases the intensity of the vibrationally structured complex phosphorescence for the first hour spent in the atmosphere of organic solvents (figure 9). At a longer action of solvent vapors, the luminescence intensity smoothly decreases until dynamic equilibrium in the system is established. In a thermostat (up to 100°C), a membrane saturated with solvent vapors and immobilized with a Pt(II)
complex restores its initial luminescence intensity, which points to reversibility of the sorption of solvent vapors and to the chemical stability of the complex in the membrane [17].

Figure 8. Optical densities of acetonitrile solutions of [PtEnPpy]ClO₄ with MF-4SK membrane immersed in them for (1) 0, (2) 20, (3) 40, (4) 60, (5) 120, (6) 180, and (7) 1440 min.

Figure 9. Dependences of luminescence intensity of membrane immobilized with [PtEnPpy]⁺ on time of action of vapors of (1) acetonitrile, (2) acetone, (3) ethanol, and (4) methanol.

4. Conclusion
The results of this work show an application perspective of cyclometalated Pt(II), Pd(II), and Ir(III) complexes as optical sensors for the acidity and the presence of various organic and inorganic compounds, as well as for obtaining new complexes-luminophores based on reactions of coordinated ligands.

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