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LETTERS TO THE EDITOR

Cyclometalated Pd(II) and Rh(III) Complexes with Ethylenediamine Based on 2-(4-Biphenyl)-5-phenylbenzoxazole Luminophore

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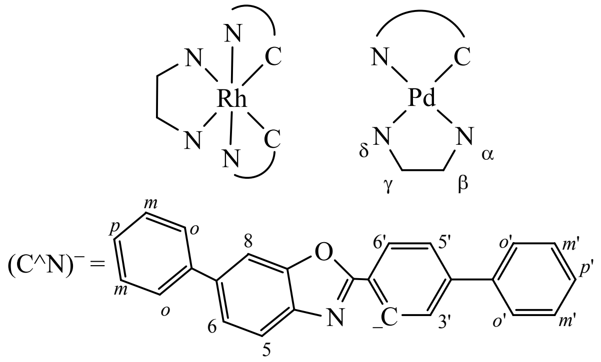
Arylsubstituted oxazoles are effective organic luminophores used as activating additives in scintillators [1]. However, formation of cycloiridiated and cycloplatinated complexes based on them [2, 3] leads to a change in their optical properties.

This report concerns the results of studying the complexes [Rh(C^N)$_2$En]Cl and [Pd(C^N)En]OOCCH$_3$] [(C^N)$^-$ is the 2-(4-biphenyl)-5-phenyloxazole deprotonated form, En is ethylenediamine].



The results of ^{1}H NMR and IR spectroscopy confirm the complexes composition in solution and solid state. Metalation of biphenyl substituent of the benzoxazoline ligand leads to an upfield shift of the protons H$^{3',5',6'}$ resonance. The *cis*-C,C-location of te cyclometalated ligands in the rhodium complex defines the mutual anisotropic effect of the circular currents of biphenyl substituents, which leads to an upfield shift of the signals of H$^{3',5',6'}$ and H$^{o',m',p'}$ protons. The difference in *trans*-influence of the donor C and N atoms of cyclopalladated ligand in the palladium complex and the difference in the anisotropic effects of benzoxazole ligands in the rhodium complex lead to the magnetic nonequivalence of the amine protons of ethylenediamine.

The IR spectra of the complexes are characterized by the low-frequency shift ($\Delta\nu$ ~17 cm^{-1}) of the stretching vibrations of C=N bond of the benzoxazole component of the ligand and characteristic [4] changing the bands of out-of-plane deformation vibrations of the C–H bond owing to the metalated biphenyl substituent of oxazole ligand. The characteristic frequencies of the CH$_2$ scissor and NH$_2$ stretching vibrations [5] indicate the presence of ethylenediamine in the inner sphere of the complexes.

The electronic absorption spectra of the complexes, along with the inner ligand optical π–π^* transition in the region < 340 nm, are characterized by the presence of long-wave metal–ligand charge transfer band: λ_{max} 369 nm for [Pd(C^N)En]$^+$ and 391 nm for [Rh(C^N)$_2$En]$^+$. Photoexcitation (λ_{em} 337 nm) of the complexes acetonitrile solutions leads to their inner ligand fluorescence. Compared with 2-(4-biphenyl)-5-phenylbenzoxazole, the complexes are characterized by a decrease (~50 times for [Pd(C^N)En]$^+$ and ~20 times for [Rh(C^N)$_2$En]$^+$) in the fluorescence intensity and by a bathochromic shift (λ ~20 nm). The absence of fluorescence of the complexes with excitation in the range of the metal–ligand charge transfer band confirms its π–π^* inner ligand character.

Thus, unlike the cyclometalated Pt(II) and Ir(III) complexes with oxazole ligands [2, 3] phosphorescenting intensively in solution, the Pd(II) and Rh(III) complexes are characterized by only weak inner ligand fluorescence.

Complexes of Pd(II) and Rh(III) were obtained at refluxing $Pd(OOCCH_3)_2$ and $RhCl_3 \cdot 3H_2O$ with 2-(4-biphenyl)-5-phenylbenzoxazole in acetic acid and 2-methoxyethanol medium, respectively, that led to the precipitation of $[Pd(C^\wedge N)(\mu\text{-}OOCCH_3)]_2$ and $[Rh(C^\wedge N)_2(\mu\text{-}Cl)]_2$ dimer complexes. Adding ethylenediamine to the solution of $[Pd(C^\wedge N)(\mu\text{-}OOCCH_3)]$ in CH_2Cl_2 led to the substitution of acetate ligands with chelating ethylenediamine and formation of $[Pd(C^\wedge N)En] \cdot OOCCH_3$ precipitate in 40% yield. The substitution of bridging chlorine ligands in the rhodium complex was performed by adding ethylenediamine to $[Rh(C^\wedge N)_2 \cdot (\mu\text{-}Cl)]_2$ suspension in 2-methoxyethanol and precipitating $[Rh(C^\wedge N)_2En]Cl$ from the solution with diethyl ether, yield 56%.

2-(4-Biphenyl-3-ido)-5-phenylbenzoxazole(ethylenediamine)palladium(II) acetate. ^1H NMR spectrum $[(CD_3)_2SO]$, δ, ppm (*J*, Hz): 8.19 s (H^8), 7.84 d (H^5, $^3J_{HH}$ 8.4), 7.77 m ($4H^{o,o'}$), 7.67 d ($H^{6'}$, $^3J_{HH}$ 8.2), 7.54 m ($5H^{6,m,m'}$), 7.42 m ($2H^{p,p'}$), 7.23 s ($H^{3'}$), 5.66 s ($2H^{\alpha}$), 4.91 s ($2H^{\delta}$), 2.80 m ($4H^{\beta,\gamma}$), 1.18 s (CH_3). IR spectrum (KBr), ν, cm^{-1}: 3370, 3289 (NH_2), 1607 (C=N), 1586 (C_2H_4), 1577, 1449 (COO), 858, 830 (C_6H_3, biphenyl metalated ring). Absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, $mol^{-1}\ cm^{-1}$): 230 (15.3), 262.8 (11.9), 302 sh (6.9), 315 sh (8.9), 329 (10.4), 369 (12.4). Fluorescence spectrum (CH_3CN, λ_{em} 337 nm), λ_{max} 419, 432 nm. Fluorescence excitation spectrum (CH_3CN, λ_{lum} 420 nm), λ_{max} 312, 326, 338, 343 nm.

Bis[2-(4-biphenyl-3-ido)-5-phenylbenzoxazol]-(ethylenediamine)rhodium(III) chloride. ^1H NMR spectrum $[(CD_3)_2SO]$, δ, ppm (*J*, Hz): 8.29 d ($2H^8$, $^3J_{HH}$ 1.4), 8.17 d ($2H^5$, $^3J_{HH}$ 8.3), 7.90 d ($2H^o$, $^3J_{HH}$ 8.0), 7.85 d ($2H^{6'}$, $^3J_{HH}$ 7.4), 7.55 d.d ($2H^m$, $^3J_{HH}$ 7.4, 7.5), 7.45 d. d ($2H^p$, $^3J_{HH}$ 7.3, 7.5), 7.32 d. d ($2H^6$, $^3J_{HH}$ 8.4, $^4J_{HH}$ 1.5), 7.22 m ($6H^{5',m',p'}$), 6.81 d ($2H^{3'}$, $^4J_{HH}$ 0.4), 4.88 d ($2H^{\alpha}$, $^3J_{HH}$ 10.5), 4.28 m ($2H^{\delta}$), 2.72 d ($2H^{\beta}$, $^3J_{HH}$ 10.5), 2.69 d ($2H^{\gamma}$, $^3J_{HH}$ 12.3). IR spectrum (KBr), ν, cm^{-1}: 3356, 3296 (NH_2), 1600 (C=N), 1587 (C_2H_4), 844, 868 (C_6H_3, biphenyl metalated ring). Absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, $mol^{-1}\ cm^{-1}$): 231 (36.3), 240 sh (31.1), 276 (25.5), 316 (37.1), 337 (33.3), 391 (20.9). Fluorescence spectrum (CH_3CN, λ_{em} 337 nm), λ_{max} 423 nm. Fluorescence excitation spectrum (CH_3CN, λ_{lum} 420 nm), λ_{max}, 311, 329 nm.

The ^1H NMR, absorption, fluorescence and fluorescence excitation spectra were obtained on JNM-ECX400A, SF-2000 and Fluorat Panorama spectrometers at 293 K in $(CD_3)SO$ and CH_3CN solutions. The IR spectra of the complexes were taken on a Shimadzu IR Prestige-21 spectrometer from KBr pellets.

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