

LETTERS TO THE EDITOR

Cyclometallated Pt(II) and Pd(II) Complexes of 2-Phenylbenzothiazole with Acetate Ligands

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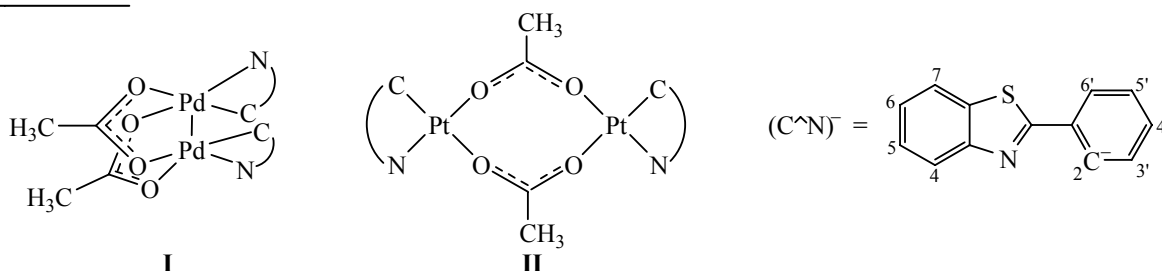
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Aryl-substituted benzothiazoles are effective fluorophores used as activating additives in scintillators [1]. The cyclometallation of luminophores in the acetic acid medium leads to the formation of complexes with bridging acetate ligands, which makes it possible to modify considerably their optical properties [2, 3].

In the present work the complexes $[M(C^{\wedge}N)(\mu-OAc)_2]$ (**I**, **II**) [$M = Pt(II)$, $Pd(II)$; $(C^{\wedge}N)^-$ is the deprotonated form of 2-phenylbenzothiazole, OAc^- is acetate ion] have been obtained and characterized by the NMR, IR, and electronic spectroscopy and by the voltammetry method.



The results of spectroscopic and electrochemical studies show that ligands in compounds **I**, **II** are coordinated similarly and that binuclear Pd(II) and Pt(II) cyclometallated complexes with bridging acetate ligands are formed. The metallation leads to the disappearance from the 1H NMR spectra of the complexes of the ortho-proton resonance of the phenyl substituent of benzothiazole, to the characteristic [4] change in the bands of nonplanar bending C–H vibrations, and to a decrease in the frequency ($\sim 30\text{ cm}^{-1}$) of stretching C=N vibrations in the IR spectra. The bridging nature of the coordination of acetate ligands in both complexes defines the characteristic value [4] of the difference in the frequencies ($\sim 170\text{ cm}^{-1}$) of asymmetric and symmetric vibrations of acetate ligands.

The results of comparative study of Pd(II) and Pt(II) complexes point to their different spatial

structures. The displacement of the resonances of protons of the cyclometallated ligand in the 1H NMR spectrum of complex **I** [$\Delta\delta(H^{3'}-H^{6'})$ from -1.0 to -1.2 and $\Delta\delta(H^4-H^7)$ from -0.2 to -0.4 ppm] to the strong field as compared with free 2-phenylbenzothiazole points [5] to the mutual anisotropic action of circular currents of the benzothiazole and phenyl components of two spatially parallel cyclometallated ligands. Unlike protons of cyclometallated ligands, the value of the chemical shift of the methyl group protons of bridging acetate ligands varies only slightly ($\Delta\delta < 0.1$ ppm). Owing to the presence of a metal-metal bond, weak optical transitions of the metal-metal-ligand charge transfer ($d\sigma^*-\pi^*$) are observed in the absorption and fluorescence electronic spectra of complex **I** [2] in the ranges of 400–480 and 490–520 nm alongside the intraligand ($\pi-\pi^*$) optical transition of the heterocyclic ligand in the regions of

315 and 398 nm, respectively. The presence of a metal–metal bond defines the presence of two one-electron waves in the voltammogram of the complex oxidation corresponding to the consecutive oxidation of each palladium center [3].

In contrast to complex **I**, the spectroscopic and electrochemical characteristics of binuclear complex **II** [a weak-field displacement ($\Delta\delta$ 1.4–0.13 ppm) of chemical shifts of protons of cyclometallated ligands, the lack in the absorption and fluorescence spectra of the complex of the optical transitions from the metal–metal–ligand charge transfer ($d\sigma^*-\pi^*$), the presence of one multielectron irreversible oxidation wave] point to the absence of both a mutual anisotropic action of circular currents of two cyclometallated ligands and a metal–metal bond. Photoexcitation of a solution of the Pt(II) complex at room temperature causes not only a weak intraligand ($\pi-\pi^*$) fluorescence at 398 nm, but also a more long-wave vibrationally structured ($d-\pi^*$) phosphorescence in the range of 530–600 nm. The presence of a phosphorescence of complex **II** agrees [6] with the influence of a 5d-metal on the increase in the efficiency of the intercombinatory conversion of singlet excited states of the complex to the energy-lowest triplet state of the metal–ligand charge transfer.

The results obtained show that unlike binuclear complex **I** characterized by the spatially parallel arrangement of two cyclometallated ligands and by the presence of a metal–metal bond, cyclometallated ligands in similar complex **II** are spatially separated, which prevents the formation of a metal–metal bond.

The synthesis of complex **I** was described earlier [7]. Complex **II** was prepared by the reaction of a suspension of 1 mmol of the chlorine-bridged dimer $[\text{Pt}(\text{C}^{\wedge}\text{N})(\mu\text{-Cl})_2]$ [8] in 5 ml of 2-methoxyethanol with 2 mmol of silver acetate; an AgCl precipitate was filtered off, and the solvent was removed on a rotary evaporator.

Bis(μ -acetato)(2-phenyl-3-ido)benzothiazolepalladium (I). Yield 70%. ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 7.90 d (2H^4 , 3J 8.2), 7.50 d (2H^7 , 3J 7.9), 7.32 d.d (2H^5 , 3J 7.4, 7.9), 7.24 d.d (2H^6 , 3J 7.4, 7.8), 6.88 d ($2\text{H}^{6'}$, 3J 7.4), 6.55 d ($2\text{H}^{3'}$, 3J 7.8), 6.43 t ($2\text{H}^{5'}$, 3J 7.4), 6.17 d.d ($2\text{H}^{4'}$, 3J 7.4, 7.8), 2.08 s (6H). IR spectrum (KBr), cm^{-1} : 1580, 1415 (CH_3COO^-), 1447 ($\text{C}=\text{N}$), 717, 751 ($\text{C}-\text{H}$). EAS (CH_2Cl_2), λ_{max} , nm ($\epsilon \times 10^{-3}$, $\text{mol}^{-1} \text{cm}^{-1}$): 235 (16.1), 255 sh (14.9), 266 (21.4), 315 (21.6), 362 (10.5), 444 sh (2.2), 480 sh (1.1). Fluorescence spectrum (CH_2Cl_2 λ_{exc} 320 nm)

λ_{max} , nm: 398, 494, 514. Oxidation voltammogram (CH_3CN), E_p , V: –0.08, 0.14.

Bis(μ -acetato)(2-phenyl-3-ido)benzothiazole-platinum (II). Yield 30%. ^1H NMR spectrum (CDCl_3), δ , ppm (J , Hz): 9.55 d (2H^4 , 3J 8.0), 8.33 m (2H^7), 8.24 d.d ($2\text{H}^{6'}$, 3J 8.0, 4J 1.1), 7.75 m ($2\text{H}^{3'}$), 7.60 t.d ($2\text{H}^{4'}$, 3J 7.3, 4J 1.4), 7.54 d.d.d ($2\text{H}^{5'}$, 3J 8.2, 7.3, 4J 1.2), 7.26 m ($4\text{H}^{5,6}$), 2.08 s (6H). IR spectrum (KBr), cm^{-1} : 1582, 1411 (CH_3COO^-), 1450 ($\text{C}=\text{N}$), 718, 749 ($\text{C}-\text{H}$). EAS (CH_2Cl_2), λ_{max} , nm ($\epsilon \times 10^{-3}$, $\text{mol}^{-1} \text{cm}^{-1}$): 234 (7.06), 267 (11.5), 305 sh (9.3), 317 (10.3), 331 sh (9.1), 371 (4.1), 406 sh (2.8), 431 sh (2.2). Fluorescence spectrum (CH_2Cl_2 , λ_{exc} 320 nm) λ_{max} , nm: 398. Phosphorescence spectrum (CH_2Cl_2 , λ_{exc} 396 nm) λ_{max} , nm: 534, 543 sh, 575, 598 sh. Oxidation voltammogram (CH_2Cl_2), E_p , V: 2.0.

The ^1H NMR, IR, electronic absorption and fluorescence spectra were obtained on JNM-ECX400A, Shimadzu IR Prestige, SF-2000, and Flyurat-Panorama spectrometers at 293 K in CDCl_3 and $(\text{CD}_3)_2\text{SO}$ solutions, KBr tablets, and CH_2Cl_2 solutions. The voltammograms were recorded on an IPC-2000 installation at 293 K in a three-electrode cell with separated spaces of the main (GC), auxiliary (Pt), and reference (Ag) electrodes in the presence of 0.1 M $[\text{N}(\text{C}_4\text{H}_9)_4] \cdot \text{PF}_6$ solutions in CH_3CN and CH_2Cl_2 . The potentials are given in relation to the ferrocenium-ferrocene redox system at a potential scanning rate of 100 mV/s.

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