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LETTERS TO THE EDITOR

Binuclear Cyclometallated Complexes of 2-Phenylbenzothiazole with 2-Mercaptothiazole and 2-Mercaptobenzoxazole Bridging Ligands

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Phosphorescence of cyclometallated Pt(II) complexes at room temperature makes it possible to consider them as promising components for creating light-emitting diodes [1]. The square-planar structure of Pt(II) complexes defines the possibility of formation of both mononuclear and binuclear complexes, as a result of a metal–metal interaction, which considerably changes optical and electrochemical properties of the complexes [2, 3].

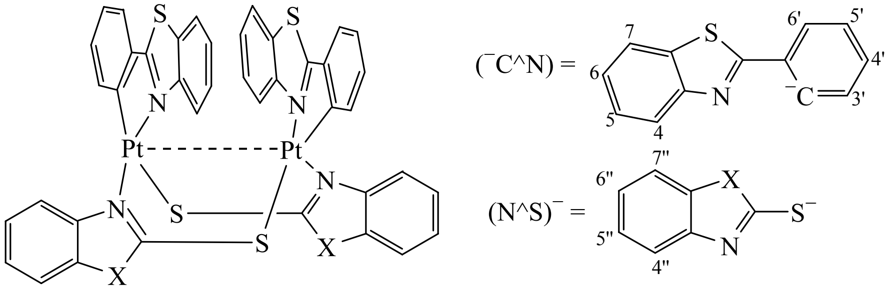
Results of studying complexes **I** and **II** [Pt(pbt)·(μ-S^N)]$_2$ [(pbt)$^-$ and (S^N)$^-$ are deprotonated forms of 2-phenylbenzothiazole, 2-mercaptobenzothiazole (mbt), and 2-mercaptobenzoxazole (mbo)] are presented in this work (Scheme 1).

Spectroscopic and electrochemical characteristics of complexes **I** and **II** are similar to those of the complex [Pt(bzq)(μ-S^N)]$_2$ [(bzq)$^-$ is benzo[*h*]quinoline] [4, 5], which points to the formation of a metal–metal bond and to the antisymmetric position of metallated and bridging ligands.

The ^{1}H NMR spectra of complexes **I** and **II** show the magnetic equivalence of two cyclometallated and bridging ligands. The close to parallel spatial position of two platinated ligands defines mutual anisotropic action of their circular currents, which leads to an upfield displacement of chemical shifts of protons of 2-phenylbenzothiazole bound in a complex with respect to the free 2-phenylbenzothiazole [$\Delta\delta(H^{4-7})$ (0.3–0.7), $\Delta\delta(H^{3'-6'})$ (0.6–1.2) ppm]. The magnetic equivalence and downfield shift of the proton signals of μ-N^S ligands [$\Delta\delta(H^{4''-7''})$ (0.3–1.3) ppm] agree with *trans*-coordination of their nitrogen atoms.

UV-vis absorption spectra of the complexes contain specific [3–5] spin-allowed charge-transfer metal-metal–ligand bands in the region of 425–540 nm along with intraligand optical transitions in the UV region

Scheme 1.



X = S (mbt) (**I**), O (mbo) (**II**).

(λ_{max} 233–337 nm) and a charge transfer metal-ligand band (λ_{max} 374–381 nm). A spin-forbidden metal–metal–ligand optical transition gives wide [$\Delta\nu_{1/2}$ (2.3–2.6) × 10^3 cm^{-1}] phosphorescence bands in the red (λ_{max} 670–678 nm) spectral region under photoexcitation of solutions of the complexes in CH_2Cl_2.

The overlap of two d_{z^2} orbitals of platinum atoms with the formation of a metal–metal bond and the occurrence of σ* higher occupied molecular orbital in complexes **I** and **II** lead to a characteristic [3, 4] two-electron wave of oxidation of the complexes with potentials 0.46–0.50 V.

The complexes were obtained by the reaction of 1 mmol of the chlorine-bridged dimer [Pt(pbt)(μ-Cl)]$_2$ with 2 mmol of $AgNO_3$ in CH_3CN. The mixture was stirred for 30 min at 50°C, and then AgCl was filtered out. To the filtrate 1.02 mmol of 2-merkapto-benzothiazole or 2-merkapto-benzoxazole sodium salt were added at 0°C, and the mixture was stirred at 5°C. A red precipitate separated. Then the solvent was distilled off at heating up to 50–60°C, the remainder was dissolved in CH_2Cl_2, the solution was filtered, and the complexes were salted out by pentane. Yield 60–70%.

Bis(μ-2-mercaptobenzothiazolato)(2-phenyl-3-ido)-benzothiazoleplatinum (I). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.71 d ($2H^{4''}$, ^3J 8.2), 7.59 d ($4H^{4,7''}$, ^3J 7.7), 7.43 d ($2H^7$, ^3J 7.7), 7.29–7.20 m ($4H^{5,6}$), 7.23 m ($2H^{6''}$), 7.10 m (2H), 7.11 d ($2H^{6'}$, ^3J 7.5), 7.09 m ($2H^{5''}$), 6.69 t ($2H^{5'}$, ^3J 7.4), 6.57 d ($2H^{3'}$, ^3J 8.4), 6.21 t ($2H^{4'}$, ^3J 7.6). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε × 10^{-3}, mol^{-1} cm^{-1}): 234 (72.9), 262 (52.1), 314 (52.5), 337 sh (37), 381 (15.1), 425 sh (5.8), 476 (3.41), 507 (3.18), 540 sh (1.7). Phosphorescence spectrum (CH_2Cl_2), λ_{max}, nm ($\Delta\nu_{1/2}$, cm^{-1}; τ, μs): 678 (2.3; 5). Oxidation voltammogram (CH_2Cl_2), E_p, V: 0.46.

Bis(μ-2-mercaptobenzoxazolato)(2-phenyl-3-ido)-benzothiazoleplatinum (II). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 7.90 m ($2H^{4''}$), 7.54 d ($2H^4$, ^3J 7.9), 7.50 d ($2H^7$, ^3J 7.7), 7.39 m ($2H^{7''}$), 7.20 m ($6H^{5,6,6''}$), 7.14 d ($2H^{5''}$, ^3J 7.5), 7.09 d.d ($2H^{5'}$, ^3J 8.0, 7.6), 6.77 d ($2H^{3'}$, ^3J 8.4), 6.65 t ($2H^{5'}$, ^3J 7.4), 6.23 t ($2H^{4'}$, ^3J 7.6). UV spectrum (CH_2Cl_2), λ_{max}, nm (ε × 10^{-3}, mol^{-1} cm^{-1}): 233 (53.1), 261 (44.3), 297 (51.6), 317 sh (41.0), 333 sh (25), 374 (11.1), 470 (3.82), 505 sh (2.5), 540 sh (0.88). Phosphorescence spectrum (CH_2Cl_2), λ_{max}, nm ($\Delta\nu_{1/2}$, cm^{-1}; τ, μs): 670 (2.6; 4). Oxidation voltammogram (CH_2Cl_2), E_p, V: 0.50.

^{1}H NMR spectra in $CDCl_3$ were obtained on a JNM-ECX400A spectrometer (Common use center of the chemical faculty of Herzen Russian State Pedagogical University). UV-Vis absorption and luminescence spectra were taken at 293 K on SF-2000 and Flyuorat-02 Panorama spectrometers in CH_2Cl_2. Voltammograms were recorded at 293 K on an IPC-PRO installation in a cell with separated spaces of working (Pt), auxiliary (Pt), and reference (Ag) electrodes in the presence of 0.1 M $[N(C_4H_9)_4]PF_6$ solution in CH_2Cl_2. Peak potentials are given with respect to the ferrocenium-ferrocene redox system at a potential scanning rate of 100 mV/s.

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