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LETTERS TO THE EDITOR

Binuclear Cyclopalladated Benzo[*h*]quinoline and 2-Tolylpyridine Complexes with the Bridging 2-Mercaptopyridine Ligand

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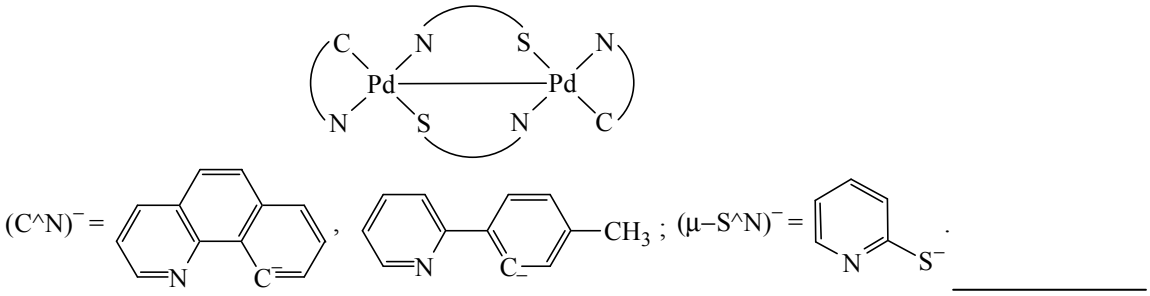
The planar binuclear cyclometalated Pt(II) and Pd(II) complexes with the metal–metal bonding are of wide interest due to the important role of such complexes in the metal catalysis [1], their anti-carcinogenic properties [2], and the possibility of their use as the components in light-emitting diodes [3, 4].

This work presents the results of a study of spectroscopic and electrochemical characteristics of the $[Pd(C^N)(\mu\text{-}S^N)]_2$ complexes, where $(C^N)^-$ denotes the deprotonated forms of benzo[*h*]quinolone and 2-tolylpyridine, and $(S^N)^-$ corresponds to that of 2-mercaptopyridine.



The obtained characteristics of the $[Pd(C^N)(\mu\text{-}S^N)]_2$ complexes indicate the presence of a metal–metal bond and their *anti*-symmetric structure. Similar to the cyclopalladated complexes with the bridging acetate ligands [5], the virtually parallel spatial position of two cyclopalladated ligands determines the mutual anisotropic effect of their circular currents, which leads to the upfield shift of the proton signals of the complexes ($\Delta\delta$ = –0.5 to –1.1 ppm). Unlike the cyclopalladated ligands, the downfield shift of the proton signals in the spectra of the bridging ligads ($\Delta\delta$ ~0.5 ppm) is consistent with their *trans*-*N*–*N* coordination.

The electron absorption spectra of the complexes, along with the metal-to-ligand charge transfer and intraligand optical transitions in the UV region, contain the specific [5] spin-allowed metal-to-metal-to-ligand charge transfer bands in the region of 450–480 nm. The spin-forbidden metal-to-metal-to-ligand charge transfer leads to a wide [$\Delta\nu_{1/2}$ (1.8–2.2) kK] low-temperature (77 K) phosphorescence band of the complexes in the red region (λ_{max} ~ 670 nm). Two one-electron irreversible oxidation waves of the complexes at 0.32–0.37 and 0.96–1.13 V reflect the successive formation of Pd^{III} in the $[Pd(C^N)(\mu\text{-}S^N)]_2$ complexes.

The complexes were prepared by reacting 1 mmol of $[Pd(C^N)(\mu\text{-}Cl)]_2$ [6] with 2 mmol of $AgNO_3$ in CH_3CN under stirring for 30 min at 50°C. After removal of the precipitated AgCl, 2.1 mmol of 2-mercaptopyridine and 1.05 mmol of $N(C_4H_9)_3$ was added to the filtrate at 0°C. After stirring for 30 min

the precipitated $[Pd(C^N)(\mu\text{-}S^N)]_2$ was filtered off and recrystallized from CH_2Cl_2. Yield 90–95%.

Bis(μ-2-mercaptopyridinato)(2-tolyl-3-ido)pyridinepalladium. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.63 d.d (2H, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.7), 7.60 d (2H, ^3J 5.5), 7.53 d.d. d (2H, $^3J_{HH}$ 8.1, 7.6, $^4J_{HH}$ 1.6), 7.29 d (2H, $^3J_{HH}$ 8.5), 7.11 d (2H, $^3J_{HH}$ 7.4), 7.10 m (2H), 7.07 s (2H), 6.88 t.d (2H, $^3J_{HH}$ 5.7, $^4J_{HH}$ 1.2), 6.84 d (2H, ^3J 7.8), 6.71 t.d (2H, $^3J_{HH}$ 5.6, $^4J_{HH}$ 1.2), 6.54 d.d (2H, ^3J 7.8, $^4J_{HH}$ 1.1), 1.91 s (6H). UV spectrum (CH_2Cl_2), λ_{max}, nm ($\varepsilon\times10^{-3}$, mol^{-1} 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). Phosphorescence spectrum (2-MeOEtOH–EtOH, 1:1), λ_{max}, nm ($\Delta\nu_{1/2}$, kK; τ, μs): 668 (1.8; 250). Oxidation voltammogram (CH_2Cl_2), E_p, V: 0.37, 0.96.

Bis(μ-2-mercaptopyridanato)(benzo[*h*]quinolin-10-ido)palladium. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 8.71 d.d (2H, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.0), 7.95 d.d (2H, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.3), 7.89 d.d (2H, $^3J_{HH}$ 5.4, $^4J_{HH}$ 1.4), 7.56 d (2H, $^3J_{HH}$ 8.3), 7.29 d.d (2H, $^3J_{HH}$ 5.2, 8.0), 7.19 m (2H), 7.15 d (2H, $^3J_{HH}$ 8.4), 7.13 d (2H, $^3J_{HH}$ 8.6), 7.12 d.d (2H, $^3J_{HH}$ 7.3, $^4J_{HH}$ 0.6), 6.79 t.d (2H, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.2), 6.76 d (2H, $^3J_{HH}$ 8.0), 6.44 t (2H, $^3J_{HH}$ 7.5). UV spectrum (CH_2Cl_2), λ_{max}, nm ($\varepsilon\times10^{-3}$, mol^{-1} cm^{-1}): 288 (52.6), 372 (20.3), 450 sh (2.5). Phosphorescence spectrum (2-MeOEtOH–EtOH, 1:1), λ_{max}, nm ($\Delta\nu_{1/2}$, kK; τ, μs): 670 (2.2; 250). Oxidation voltammogram (CH_2Cl_2), E_p, V: 0.32, 1.13.

The ^{1}H NMR spectra (293 K), electronic absorption spectra (293 K), and phosphorescence spectra (77 K) were obtained on a JNM-ECX400A, SF-2000-02 and Fluorat Panorama spectrometers, respectively. The voltammograms were recorded on a IPC-PRO instrument at 293 K in a cell with separate spaces of the working (GC), auxiliary (Pt) and reference (Ag) electrodes in the presence of 0.1 M of $[N(C_4H_9)]PF_6$ solution in CH_2Cl_2. The potentials peaks are given at a rate of 100 mV s^{-1} with respect to the ferrocene-ferrocenium redox system.

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