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LETTERS TO THE EDITOR

Preparation and Properties of Cyclopalladated Complexes of Dibenzo[*a,c*]phenazine and Dibenzo[*f,h*]quinoxaline with Ethylenediamine

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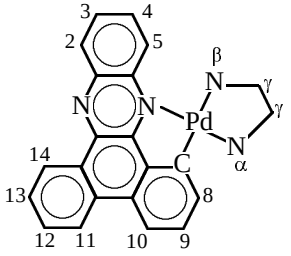
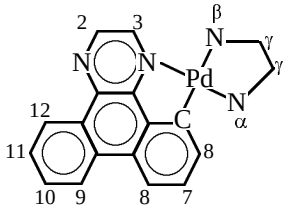
Coordination-unsaturated cyclopalladated complexes with polydentate heterocyclic ligands attract researchers' attention due to the prospects of using them as structural units in creation of molecular-organized metal complex systems with directed photo- and electrostimulated transfer of charge and energy [1, 2].

In this work we prepared the coordination-unsaturated complexes $[Pd(dbp)en]ClO_4$ (**I**) and $[Pd(dbq)en]\cdot ClO_4$ (**II**) (dbp^- and dbq^- are deprotonated forms of dibenzo[*a,c*]phenazine and dibenzo[*f,h*]quinoxaline, en is ethylenediamine) and characterized them by ^1H NMR and electronic spectroscopy and by cyclic voltammetry.



I



II

The complexes obtained are stable in solid state and solutions [$(CH_3)_2SO$, CH_3CN, and DMF]. Our spectroscopic and electrochemical studies of **I** and **II** show that they have a mononuclear structure and that changes in the properties of the ligands Hdbp and Hdbq, occurring upon complex formation, are similar. The formation of palladium-containing rings results in considerable shielding of protons adjacent to palladium, i.e., H^8, H^9, and H^{10} (**I**) and H^6, H^7, and H^8 (**II**): The coordination-induced chemical shift ($\Delta\delta = \delta_{com} - \delta_{lig}$) for both complexes is –0.4, –0.3, and –0.4 ppm, respectively. On the contrary, $\Delta\delta$ for remote protons H^{11-14} (**I**) and H^{9-12} (**II**) does not exceed ±0.1 ppm.

The optical and electrochemical properties of the complexes are determined by the fact that their highest occupied molecular orbital has predominantly the metal-centered d_{Pd} character, and the lowest unoccupied molecular orbital, the $\pi^*_{dbp/dbq}$ character. In accordance with the characteristics of the Hdbp and Hdbq ligands, this fact determines a regular decrease in the energy of the lowest optical transition of the d–π^* type ($\Delta\nu$ 2900 cm^{-1}) and the anodic shift of the ligand-centered reduction (ΔE 0.47 V) in going from **II** to **I**.

Dibenzo[*a,c*]phenazine and dibenzo[*f,h*]quinoxaline were prepared by condensation of 9,10-phenanthroquinone with *o*-phenylenediamine and ethylenediamine [3]. The procedure of the spectrophotometric and electrochemical studies was described previously [4].

Dibenzo[*a,c*]phenazine. ^1H NMR spectrum

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[$(CD_3)_2SO$], δ, ppm (*J*, Hz): 9.32 ($H^{7,14}$, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.4), 8.80 ($H^{10,11}$, $^3J_{HH}$ 7.4), 8.36 ($H^{2,5}$, $^3J_{HH}$ 6.7, $^4J_{HH}$ 3.3), 8.00 ($H^{3,4}$, $^3J_{HH}$ 6.4, $^4J_{HH}$ 3.3), 7.91 ($H^{9,12}$, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.6) 7.83, ($H^{8,13}$, $^3J_{HH}$ 7.6, $^4J_{HH}$ 1.2). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 279 (33.9), 309 (9.3), 374 (14.0), 392 (15.0). Luminescence characteristics (77 K, DMF–toluene, 1 : 1), λ_{max}, nm: 550, 563, 594, 641. Cyclic voltammogram [DMF, vs. ferricenium/ferrocene (Fc^+/Fc) redox system], $E_{1/2}$, V (difference between potentials of reduction and oxidation peaks Δ*E*, mV): –1.57 (60).

Dibenzo[*f,h*]quinoxaline. ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 9.13 ($H^{5,12}$, $^3J_{HH}$ 7.6), 9.04 ($H^{2,3}$), 8.83 ($H^{8,9}$, $^3J_{HH}$ 8.6), 7.87, ($H^{7,10}$, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.9), 7.82 ($H^{9,12}$, $^3J_{HH}$ 7.6). Electronic absorption spectrum (CH_2Cl_2), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 246 (35.8), 305 (12.0), 338 (9.5), 353 (8.8). Luminescence characteristics (77 K, DMF–toluene, 1 : 1), λ_{max}, nm: 442, 459, 470, 492, 506. Cyclic voltammogram [DMF, vs. (Fc^+/Fc)], $E_{1/2}$, V (Δ*E*, mV): –2.12 (70).

Cyclopalladated complexes [Pd(dbp)en]ClO_4 and [Pd(dbq)en]ClO_4 were prepared by a common procedure involving addition of a saturated solution of 1 equiv of the cyclometallating ligand in CH_2Cl_2 to a saturated methanolic solution of 1 equiv of $[N(C_4H_9)_4][PdCl_4]$, followed by refluxing of the reaction mixture for 1 h. After filtration, washing (CH_3OH, CH_2Cl_2, and ether), and drying in a vacuum of the precipitated $[Pd(dbp)(\mu\text{-}Cl)]_2$ (yield 47%) and $[Pd(dbq)(\mu\text{-}Cl)]_2$ (yield 96%), 1 equiv of ethylenediamine was added to the suspension of the dimeric complexes, and the mixture was stirred at room temperature for 30 min. Then the solution was filtered and cooled on an ice bath, and a saturated methanolic solution of $NaClO_4$ was added. The resulting precipitate was filtered off, washed with CH_3OH and ether, and dried in a vacuum.

(Dibenzo[*a,c*]phenazin-7-ido)ethylenediaminepalladium(II) perchlorate. Yield 30%. ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 9.17 (H^{14}, $^3J_{HH}$ 7.7), 8.70 (H^{11}, $^3J_{HH}$ 7.7), 8.44 (H^5), 8.39 (H^{10}, $^3J_{HH}$ 7.6), 8.0 (H^{2-4}), 7.91 (H^2, $^3J_{HH}$ 7.0, $^4J_{HH}$ 1.3), 7.83 (H^{13}, $^3J_{HH}$ 7.7, 7.0), 7.37 ($H^{8,3}$, $^3J_{HH}$ 5.6), 5.72 ($2H^{\alpha}$), 4.88 ($2H^{\beta}$), 2.79 ($4H^{\gamma}$). Electronic absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 221 (9.40), 262 (17.1), 393 (2.7), 426 (3.2). Luminescence characteristics (77 K, DMF–toluene, 1 : 1), λ_{max}, nm (lifetime τ, μs, quantum yield Φ): 590, 640 (230, 0.13). Cyclic voltammogram [DMF, vs. (Fc^+/Fc)], $E_{1/2}$, V (Δ*E*, mV): –1.26 (120); E_p, V: 1.13.

(Dibenzo[*f,h*]quinoxalin-5-ido)ethylenediaminepalladium(II) perchlorate. Yield 87%. ^{1}H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 9.13 (H^3), 9.04 (H^{12}, $^3J_{HH}$ 7.6), 8.78 (H^9, $^3J_{HH}$ 8.6), 8.77 (H^2), 8.42, (H^8, $^3J_{HH}$ 8.6), 7.92 (H^{10}, $^3J_{HH}$ 7.6), 7.84 (H^{11}, $^3J_{HH}$ 7.6), 7.60 (H^7, $^3J_{HH}$ 7.6), 7.38 (H^6, $^3J_{HH}$ 7.6), 5.56 ($2H^{\alpha}$), 4.67 ($2H^{\beta}$), 2.85 ($4H^{\gamma}$). Electronic absorption spectrum (CH_3CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 224 (15.0), 253 (22.2), 307 (4.0), 379 (1.9). Luminescence characteristics (77 K, DMF–toluene, 1 : 1), λ_{max}, nm (τ, μs, Φ): 497, 532 (130, 0.9). Cyclic voltammogram [DMF, vs. (Fc^+/Fc)], E_p, V: –1.73; 0.73.

The ^{1}H NMR spectra, electronic absorption spectra, and cyclic voltammograms were obtained at 293 K on a Bruker AM-400WB spectrometer, an SF-2001 spectrophotometer, and an SBA-1B electrochemical installation, respectively. The luminescence parameters were determined at 77 K on an SDL-2 spectrometer and a KSVU-1 installation with a laser (LGI-21) pulse photoexcitation.

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REFERENCES

1. Balzani, V., Juris, A., Venturi, M., Campagna, S., and Serroni, S., *Chem. Rev.*, 1996, vol. 96, no. 5, pp. 759–833.

2. Kulikova, M.V., Balashev, K.P., Kvam, P.-I., and Songstad, J., *Zh. Obsch. Khim.*, 2000, vol. 70, no. 2, p. 177.

3. Steel, P.J. and Caygill, G.B., *J. Organomet. Chem.*, 1990, vol. 395, no. 3, p. 359.

4. Kvam, P.-I., Puzyk, M.V., Cotlyr, V.S., Balashev, K.P., and Songstad, J., *Acta Chem. Scand.*, 1995, vol. 49, no. 9, p. 645.