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Cyclopalladated Complexes Based on 2-Phenylbenzothiazole and 1,4-(Benzothiazol-2-yl)benzene with Acetate Ligands and Ethylenediamine

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Abstract—Complexes [Pd(bt)En]ClO$_4$, [Pd(bt)(μ-OOCCH$_3$)]$_2$, [(PdEn)$_2$(μ-dbt)](CH$_3$COO)$_2$, and [Pd$_2$(μ-dbt)·(μ-OOCCH$_3$)$_2$]$_2$ (bt$^-$ and dbt^{2-} are the mono- and bisdeprotonated forms of 2-phenylbenzothiazole and 1,4-bis-(benzthiazol-2-yl)benzene, En is ethylenediamine) are characterized by ^{1}H NMR, electron absorption spectroscopy, and voltammetry. The upfield shift of the signal of protons of heterocyclic ligands in complexes with acetate ligands is assigned to anisotropic effect of the ring current of the two fragments {Pd(bt)} and {Pd(dbt)} in the complexes. The red shift of the optical transition of the metal–ligand charge transfer as well as the anodic shift of the ligand-centered reduction of [(PdEn)$_2$(μ-dbt)](CH$_3$COO)$_2$ relative to [Pd(bt)En]ClO$_4$ is due to the decrease in the LUMO energy of the complexes. The cathodic shift of the oxidation potential and the long wavelength absorption in complexes with acetate ligands is assigned to variation in the HOMO nature due to the metal–metal bond formation.

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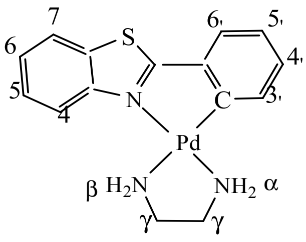
Specific electronic structure of the cyclopalladated complexes with heterocyclic ligands determines wide prospects of their use not only as catalysts of various organic reactions, but also as the components of optoelectronic devices [1]. As distinct from the mononuclear complexes, there are only few studies of the effect of ligands on optical and electrochemical properties of polynuclear cyclopalladated complexes [2–4].

In the present work we report on the results of a comparative study of the ^{1}H NMR spectra, optical and electrochemical properties of mono- [Pd(bt)En]ClO$_4$ (**I**), [Pd(bt)(μ-OOCCH$_3$)]$_2$ (**II**) and biscyclopalladated {[(En)Pd]$_2$(μ-dbt)}(ClO$_4$)$_2$ (**III**), {[Pd$_2$(μ-dbt)](μ-OOCCH$_3$)$_2$}$_2$ (**IV**) complexes (bt$^-$ and dbt^{2-} are the mono- and bisdeprotonated forms of 2-phenylbenzothiazole and 1,4-bis(benzthiazol-2-yl)benzene, En is ethylenediamine) with the chelating ethylenediamine (En) and bridging acetate ligands.

The distance between the palladium atoms in complexes **II** and **IV** is 2.871 Å [5] or 2.881 Å [6], which is less than the sum of their van der Waals radii equal to 3.26 Å [7], and it allows to assume the presence of the metal–metal bond in the complexes due to the overlap of the d_{z^2} orbitals and the formation of the $d\sigma^*_{\mathrm{Pd}2}$ as the HOMO [2].

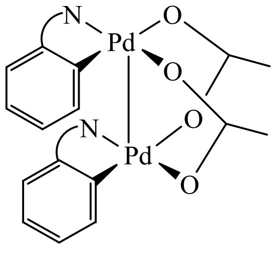
The results of the ^{1}H NMR spectroscopy prove the composition and the structure of complexes **I–IV**. Comparison of the ^{1}H NMR spectra of complexes **I, II** reveals both the magnetic equivalence of the two fragments {Pd(bt)} in complex **II** and a substantial upfield shift of the resonance of their protons as a result of mutual anisotropic effect of the ring current of the two heterocyclic ligands. This is consistent with practically parallel spatial arrangement of the two {Pd(bt)} fragments linked by the acetate bridge ligands in complex **II** [5].

The magnetic equivalence of the two benzothiazolyl moieties and the H$^{3'}$, H$^{5'}$ protons of the benzene part of the cyclopalladated 1,4-bis(benzothiazol-2-yl)benzene, as well as of the protons of the two ethylenediamine ligands is indicative of the symmetrical structure of complex **III**. Similar to complex **I**, due to the difference in the *trans*-effects of the donor atoms N and C of the heterocyclic ligand, the ethylenediamine ligands in complex **III** are characterized



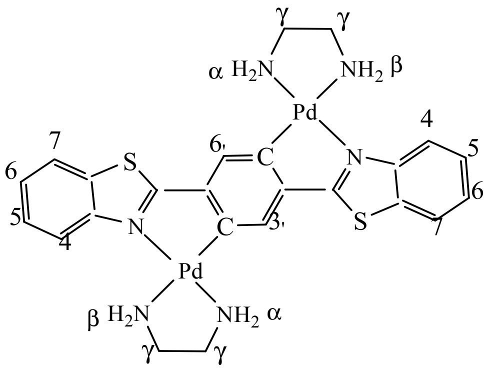
$[Pd(bt)En]^+$

I



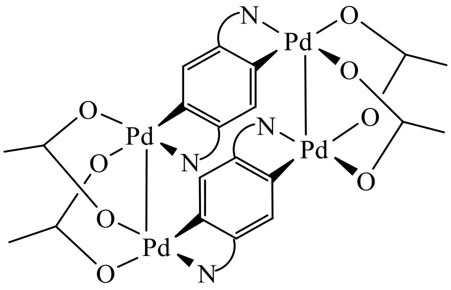
$[Pd(bt)(\mu\text{-}OOCCH_3)]_2$

II



$\{[(En)Pd]_2(\mu\text{-dbt})\}^{2+}$

III



$[Pd_2(\mu\text{-dbt})(\mu\text{-}OOCCH_3)_2]_2$

IV

by magnetic nonequivalence of the amine protons H^α and H^β [$\delta(H^\alpha)$ 5.69, $\delta(H^\beta)$ 4.96 ppm]. Relative to complex **III**, the ^1H NMR spectrum of complex **IV** is shifted upfield due to the anisotropic effect of the ring currents of the two {Pd(μ-dbt)Pd} components, which are practically parallel to each other [6].

Within the model of the localized molecular orbitals [8] the optical and electrochemical properties of complexes are considered from the viewpoint of predominant localization of the participating MO on the metal or ligand. The electron absorption spectra of complexes **I** and **III** (Fig. 1) are characterized, along with the intraligand absorption bands at < 350 and < 400 nm, by the presence of a longwave optical transition of the metal–ligand charge transfer as an unresolved band at 364 nm for complex **I** and vibronic components at 423 and 450 nm for complex **III**.

The investigation of voltammograms of reduction and oxidation of complexes **I** and **III** shows (Figs. 2, 3) that, while the potentials of the metal-centered

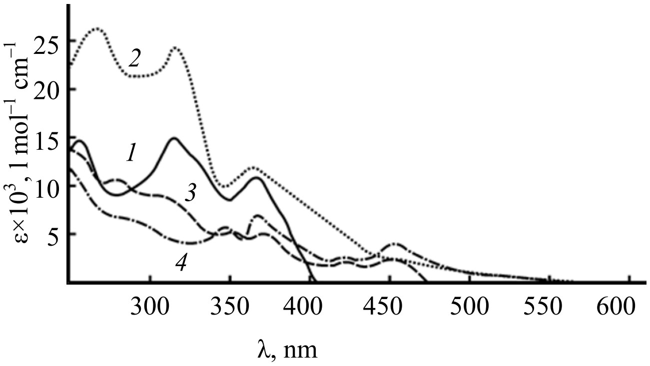


Fig. 1. Electron absorption spectra of complexes: (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**.

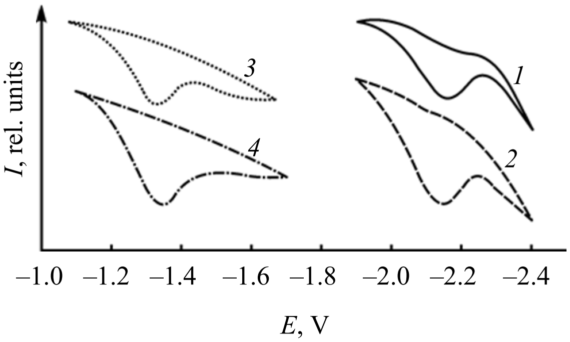


Fig. 2. Voltammograms of reduction of complexes: (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**.

oxidation wave for complexes **I** and **III** are similar, the ligand-centered one-electron reduction wave of complex **III** is shifted to the anode region by 0.83 V relative to complex **I** . This is indicative of a decrease in the LUMO energy of the biscyclopalladated complex **III** relative to the monocyclopalladated complex **I** that results in a red shift of the optical transition of the metal–ligand charge transfer in complex **III** . Earlier, a similar decrease in the LUMO energy leading to a red shift of the metal–ligand charge transfer band in the biscyclometallated complex relative to the monocyclometallated one was reported for the Ir(III) complex based on 1,4-bis(pyridin-2-yl)-benzene [9].

A specific feature of absorption spectra of complexes **II, IV** (Fig. 2) is the presence, along with the longwave optical transitions at 362 nm for complex **II** and 423, 450 nm for complex **IV**, of an additional absorption as shoulders at ~430 and ~500 nm, which is indicative of a decrease in the energy gap between the HOMO and LUMO of complexes.

Voltammograms of reduction of complexes **II, IV** with acetate bridge ligands are similar to those of complexes **I, III** with ethylenediamine (one-electron reduction wave of complex **IV** is anodically shifted by 0.85 V as compared with complex **II**) suggesting practically the same energy and the nature of their ligand-centered LUMOs. At the same time, voltammograms of oxidation of complexes **II, IV** and **I, III** are different (Fig. 2). As compared to the metal-centered oxidation wave of complexes **I, III** (E_p ~0.6 V), the voltammograms of oxidation of complexes **II** and **IV** are characterized by the presence of the cathodically shifted waves (Fig. 3) suggesting the increase in the HOMO energy in complexes **II, IV** relative to complexes **I, III**. Therefore, an additional longwave absorption appearing as shoulders at ~430 and ~500 nm for complexes **II** and **IV** can be assigned to the optical transition between the $d\sigma^*_{Pd_2}$ HOMO of complexes (formed due to the metal–metal interaction of the d_{z^2} orbitals) and the π^* LUMO localized predominantly on the heterocyclic cyclometallated ligand.

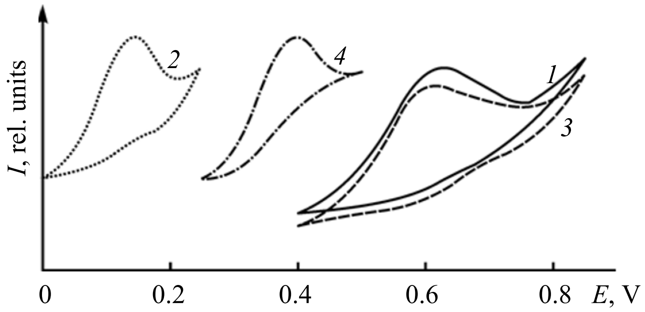


Fig. 3. Voltammograms of oxidation of complexes: (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**.

The results of the present study demonstrate the possibility of a purposeful variation of optical and electrochemical parameters of the cyclopalladated complexes both by lowering the energy of the LUMO of complexes by the use of a biscyclopalladated bridge

Optical and electrochemical characteristics of complexes

Comp. no.	Absorption, λ_{max}, nm ($\varepsilon\times10^3$, l mol^{-1} cm^{-1})	Oxidation, E_p, V^a	Reduction, $-E_p$, V^a
I	258 (14.5), 268 (10.7), 316 (14.9), 364 (10.7)^b	0.63^b	2.10^c
II	314 (24.0), 362 (11.8), 437 sh (2.8)^d	0.14^b	2.15^c
III	247 (15.1), 279 (10.7), 299 sh (9.1), 352 (5.3), 369 (4.8), 423 (2.1), 450 (2.4)^b	0.59^b	1.27^b
IV	247 (12.6), 276 sh (6.8), 348 (5.8), 365 (6.7), 423 (2.6), 450 (3.9), 500 sh (0.8)^d	0.40^b	1.30^b

[a] Peak potential at the potential sweep rate 100 mV s^{-1}. [b] CH_3CN. [c] $(CH_3)_3NCO(H)$. [d] CH_2Cl_2.

ligand and by increasing the energy of the HOMO of complexes with acetate bridge ligands, whose angular structure favors the formation of the metal–metal chemical bond.

EXPERIMENTAL

^{1}H NMR spectra were obtained at 293 K on a Bruker AC-200F spectrometer. Electron absorption spectra were obtained at 293 K on an SF-2000 spectrophotometer. Voltammograms were obtained on SVA-1B instrument at 293 K in a three-electrode cell with separated spaces of the working (Pt), auxiliary (glass carbon), and reference (Ag) electrodes in the presence of 0.1 M $[N(C_4H_9)_4]BF_4$ in solutions in DMF and acetonitrile [10]. The potentials are given with respect to the ferrocenium/ferrocene redox system with the potential sweep rate of 100 mV s^{-1}.

1,4-Bis(benzothiazol-2-yl)benzene [11] and complexes **I** [12], **II** [13], **IV** [6] were prepared by the known procedures. Complex **III** was obtained by substitution of the bridge acetate ligands by the chelating ethylenediamine as follows: 0.5 mmol of complex **IV** was dissloved in 5 ml of 30% solution of ethylenediamine, 20 ml of the mixture CH_2Cl_2:CH_3OH (1:1) was added, and the mixture was refluxed for 1 h. After cooling to room temperature and evaporation of the solvents ~15 ml of water was added to the jelly residue and the suspension formed was filtered. The precipitate was washed with diethyl ether and dried in air.

1,4-Bis(benzothiazol-2-yl)benzene, yield 40%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (*J*, Hz): 8.31 s (4H, $H^{2',3'5',6'}$), 8.21 d (2H, H^4,$^3J_{HH}$ 7), 8.13 d (2H, H^7, $^3J_{HH}$ 8), 7.60 d.d (2H, H^5, $^3J_{HH}$ 7, 8), 7.52 m (2H, H^6, $^3J_{HH}$ 7, 8).

(2-Phenyl-3-ydo)benzothiazoleethylenediamine-palladium(II) perchlorate (I), yield 70%. ^{1}H NMR spectrum (DMSO-d_6), δ , ppm (*J*, Hz): 8.27 d (1H, H^4, $^3J_{HH}$ 8), 7.74 m, 7.67–7.57 m (3H, $H^{6',5,6}$), 7.26–7.23 m (2H, $H^{3',4'}$), 7.18 m (1H, $H^{5'}$), 5.50 s (2H, NH_2^{α}), 4.88 s (2H, NH_2^{β}), 2.74 m (4H, C_2H_4).

Bis[(μ-acetato)(2-phenyl-3-ydo)benzothiazole-palladium](II) (II), yield 60%. ^{1}H NMR spectrum coincides with the earlier obtained data [13], $CDCl_3$, δ, ppm (*J*, Hz): 7.90 d (2H, H^4, $^3J_{HH}$ 8), 7.47 d (2H, H^7, $^3J_{HH}$ 8), 7.26 m (4H, $H^{5,6}$), 6.85 d.d (2H, $H^{6'}$,$^3J_{HH}$ 8, $^4J_{HH}$ 1), 6.55 d.d (2H, $H^{3'}$, $^3J_{HH}$ 8, $^4J_{HH}$ 1), 6.41 t.d (2H, $H^{5'}$, $^3J_{HH}$ 8, $^4J_{HH}$ 1), 6.16 t.d (2H, $H^{4'}$, $^3J_{HH}$ 8, $^4J_{HH}$ 1), 2.33 s (6H, CH_3).

(μ-1,4-Bis(benzothiazol-2-yl)benzen-2,5-ydo)bis-(ethylenediaminepalladium(II) perchlorate (III), yield 5%. ^{1}H NMR spectrum, $(CD_3)_2SO$, δ, ppm (*J*, Hz): 8.33 d (2H, H^4, $^3J_{HH}$ 8), 7.69–7.59 m (6H, $H^{5,6,7}$), 7.50 s (2H, $H^{3',5'}$), 5.69 s (4H, NH_2^{α}), 4.96 s (4H, NH_2^{β}), 2.77 m (8H, CH_2).

Bis[(μ-1,4-bis(benzothiazol-2-yl)benzen-2,5-ydo)-(μ-bisacetato)dipalladium] (IV), yield 80%. ^{1}H NMR spectrum, $CDCl_3$, δ , ppm (*J*, Hz): 7.81 d (4H, H^4, $^3J_{HH}$ 8), 7.38 d (4H, H^7, $^3J_{HH}$ 8), 7.04 t.d (4H, H^5, $^3J_{HH}$ 7, $^4J_{HH}$ 1), 7.00 t (4H, H^6, $^3J_{HH}$ 7), 6.82 s (4H, $H^{3',6'}$), 2.51 s (6H, CH_3), 2.30 s (6H, CH_3).

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