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Cyclopalladated Complexes of 2-Phenylbenzothiazole with 4,4'-Bipyridyl

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Abstract—Complexes [Pd(bt)(4,4'-bpy)OOCCH$_3$], [Pd(bt)NO$_3$]$_2$(m-4,4'-bpy), [Pd(bt)(m-4,4'-bpy)]$_4$(NO$_3$)$_4$ (bt$^-$ is deprotonated form of 2-phenylbenzothiazole, bpy is 4,4'-bipyridyl) are prepared and characterized by ^{1}H NMR, electron absorption and emission spectroscopy, as well as by voltammetry. The upfield shift of the signal of proton in the *ortho*-position to the donor carbon atom of the cyclopalladated ligand in the complexes [($\Delta\delta$ = –(1.1–1.5) ppm] is assigned to the anisotropic effect of the ring current of the pyridine rings of the 4,4'-bipyridyl moiety, which are orthogonal to the coordination plane. Characteristic longwave absorption bands λ = (387±4) nm and the low-temperature phosphorescence bands λ = (512±3) nm in the complexes are assigned to the chromophore {Pd(bt)} metal complex fragment. The reduction waves in the complexes [$E_{1/2}$ = –(1.54±0.04) and E_p = –(1.83±0.03) V] are assigned to the ligand-centered processes of the successive electron transfer to the π* orbitals localized predominantly on the coordinated pyridine components of the 4,4'-bipyridyl moiety.

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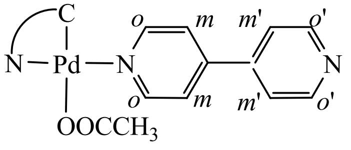
An important role of the cyclopalladated complexes in catalysis of various organic reactions and in the components of optoelectronic devices determines an increased attention to the investigation of their structure and properties [1]. Special attention is drawn to the mixed-ligand complexes of Pd(II) with potential bridging ligands capable of formation of polynuclear, in particular, macrocyclic, metal complex systems [2–5].

In the present work we report on the results of comparative study of spectroscopic and electrochemical properties of the mono [Pd(bt)(4,4'-bpy) OOCCH$_3$] (**I**), bi [(Pd(bt)NO$_3$)$_2$)(μ-4,4'-bpy)] (**II**), and tetranuclear [Pd(bt)(μ-4,4'-bpy)]$_4$(NO$_3$)$_4$ (**III**) complexes (bt$^-$ is deprotonated form of 2-phenylbenzothiazole, bpy is 4,4'-bipyridyl).

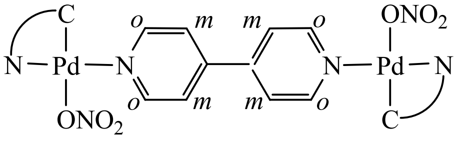
The results of the ^{1}H NMR spectroscopy study of the complexes prove their composition and the character of coordination of the ligands. The mononuclear complex **I** is characterized by the presence of four spin-coupled systems due to the presence in the coordination sphere of the benzothiazole (H^4–H^7), deprotonated phenyl (H$^{3'}$–H$^{6'}$) parts of the cyclopalladated 2-phenylbenzothiazole, and of two magnetically nonequivalent (H$^{o,o'}$, H$^{m,m'}$) pyridine rings of 4,4'-bipyridyl. The symmetrical character of binuclear complex **II** determines the magnetic equivalence of the protons of both two cyclopalladated ligands and the two pyridine moieties of the bridging 4,4'-bipyridyl. Tetranuclear complex **III** shows the presence in the coordination sphere of the bridging and cyclopalladated ligands in the ratio of 1:1. Note that as distinct from the four magnetically equivalent {Pd(bt)} of the metal complex components of complex **III**, the pyridine rings of the bridging ligand are characterized by magnetic nonequivalence.

Earlier it was shown [6] that the steric interaction of the *cis*-coordinated bridging ligand with the thienyl component of the cyclopalladated 2-(2'-thienyl)-pyridine (tpy$^-$) in the complex [Pd(tpy)NO$_3$]$_2$(μ-4,4'-bpy) resulted in the orientation of the pyridine rings of 4,4'-bipyridyl with respect to the palladium coordination planes at the angle of ~65°. Due to the anisotropic effect of the ring current of the pyridine ring orthogonal to the coordination plane a substantial upfield shift of the signals of the thienyl part of the cyclopalladated ligand was observed, which was indicative of their *cis*-position in the coordination sphere of the complex.



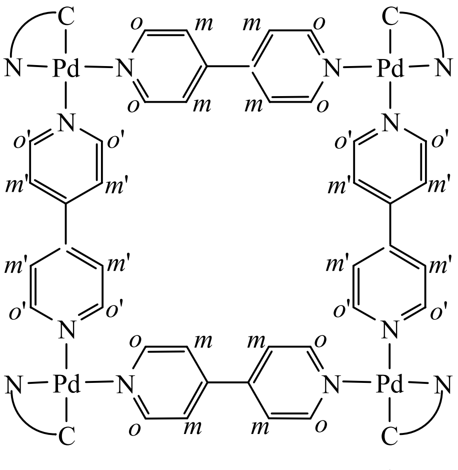
[Pd(bt)(4,4'-bpy)OOCCH$_3$]

I



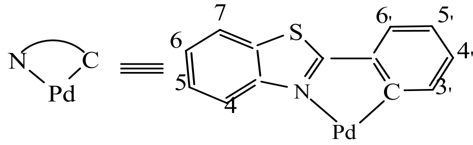
[(Pd(bt)NO$_3$)$_2$(μ-4,4'-bpy)]

II



[Pd(bt)(μ-4,4'-bpy)]$_4^{4+}$

III



{Pd(bt)}

The values of the coordination-induced chemical shifts ($\Delta\delta = \delta_{complex} - \delta_{ligand}$) of the protons of the heterocyclic ligands nearest to the metal demonstrate a substantial upfield shift of the signals of protons $H^{3'}$ of the cyclopalladated ligand in complexes **I–III** [Δδ –1.1 ppm (**I**), –1.5 ppm (**II**), –1.4 ppm (**III**)]. This shift is assigned to the anisotropic effect of the ring current of the pyridine ring of 4,4'-bipyridyl located *cis* to the phenyl part of {Pd(bt)} of the metal complex fragment.

The proton H^4 of the benzothiazole moiety of {Pd(bt)} spatially more distant from the bridge ligand shows small downfield shift [Δδ(H^4) 0.13 ppm] due to a decreased anisotropic effect of the *cis*-located pyridine ring.

The downfield shift of the H^o protons of the coordinated pyridine ring of 4,4'-bipyrodyl in complexes **I–III** [Δδ 0.4 (**I**), 0.7 (**II**), 0.7 ppm (**III**)] is indicative of the predominant donor effect of these rings that proved their spatial orthogonal orientation to the coordination plane impeding the manifestation of their π-acceptor properties. As distinct from the magnetic equivalence of the protons of the two pyridine rings of the 4,4'-bipyridyl ligand in complex **II**, the monocoordinated 4,4'-bipyridyl in complex **I** is charac-

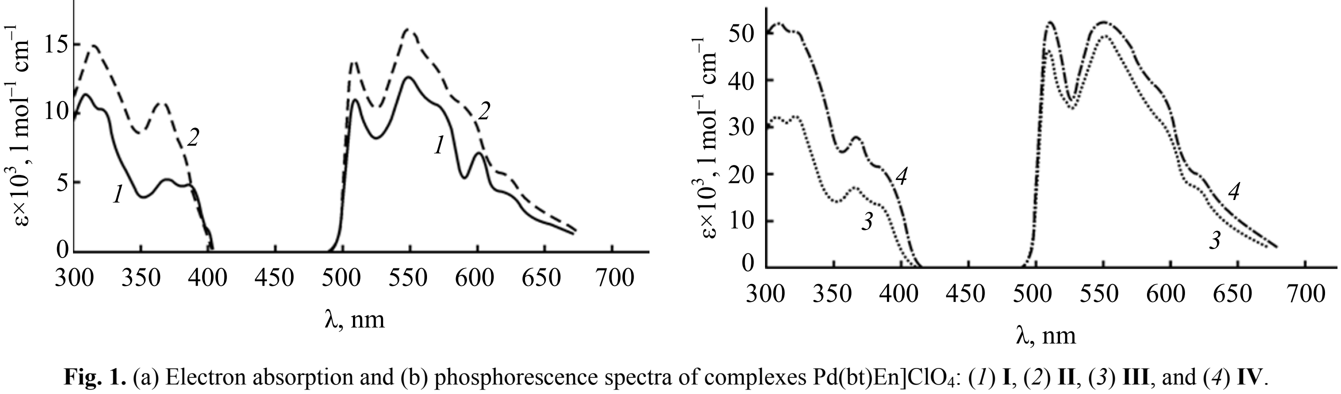


Fig. 1. (a) Electron absorption and (b) phosphorescence spectra of complexes Pd(bt)En]ClO$_4$: (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**.

terized by magnetic nonequivalence of the *ortho*-protons of the coordinated [$\Delta\delta(H^o)$ 0.4 ppm] and free [$\Delta\delta(H^{o'})$ 0.1 ppm] pyridine rings. The difference in the *trans*-effect of the donor atoms N and C of the cyclopalladated ligand results in the magnetic nonequivalence of the *ortho*-protons of the *trans*-N and *trans*-C arranged pyridine components of the bridge ligand [$\Delta\delta(H^o)$ 0.7 ppm, [$\Delta\delta(H^{o'})$ 0.14 ppm].

Within the model of the localized molecular orbitals [7], the optical and electrochemical properties of the mixed ligand complexes are classified according to the predominant localization of the participating molecular orbitals. The results of investigation of the electron absorption and luminescence spectra of complexes **I–III** (see the table) show small variation in the energy of optical transitions depending on the composition and structure of the complexes. The absorption spectra of complexes, along with red shift (<1 kK) of the spin-allowed (ε ~10^4 l mol^{-1} cm^{-1}) intraligand optical transitions in the UV region (λ < 320 nm) relative to the free 2-phenylbenzo-thiazole, are characterized by the presence of an additional longwave absorption having the form of a shoulder at (387±4) nm (Fig. 1), assigned {similar to [Pd(bt)En]$^+$ (En is ethylenediamine) [8]) to the optical transition of the charge-transfer from metal to ligand of the d–$\pi^*_{(bt)}$ type. In spite of the presence in the complexes of the heterocyclic 4,4'-bipyridyl ligand having its own low-energy π^* orbitals, no optical transitions of the metal–ligand charge transfer with their participation are observed in the spectra of the complexes. This may be due to the low extinction coefficient for these transitions as a result of the orthogonal arrangement of the pyridine rings of 4,4'-bipyridyl with respect to the coordination plane leading to small overlap of the d orbitals of Pd and the π^* orbitals of the ligand.

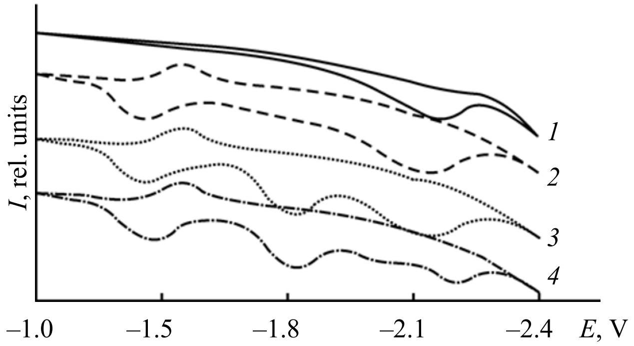


Fig. 2. Voltammograms of reduction: [Pd(bt)En]ClO$_4$ (*1*) **I**, (*2*) **II**, (*3*) **III**, and (*4*) **IV**.

The vibronically structured (ν ~1.4 kK) luminescence of the frozen (77 K) solutions of complexes **I–III** in the yellow region of the spectrum (Fig. 1) is characterized by practically constant position [λ_{max} = (512 ± 3) nm] and the time of decay [τ = (120 ± 15) μs (microseconds)], that, along with the closeness of its parameters to the intraligand phosphorescence of [Pd(bt)En]$^+$ [8], allows to assign it to the spin-forbidden intraligand exchange between the orbitals localized on the {Pd(bt)} metal complex fragment. The typical for cyclopalladated complexes temperature quenching of phosphorescence caused by the temperature-induced population of the low energy d–d^* excited states and their subsequent non-radiative deactivation [9] leads to the absence of luminescence of complexes **I–III** in solutions.

Comparison of voltammograms of reduction of complexes **I–III** and [Pd(bt)En]$^+$ [8] (see the table) shows that the presence in the inner sphere of the

Optical and electrochemical parameters of complexes

Complex	Absorption, λ_{max}, nm [$\varepsilon\times10^3$, l mol^{-1} cm^{-1}]^a	Luminescence, λ_{max}, nm (τ, μs)^b	Reduction, $-E_{1/2}$, V^a
Hbt [8]	222 (43.3), 227 (39.8), 248 sh (16.6), 255(16.6), 298 (35.4)^c	470 (290)	2.41^d
[Pd(bt)En]$^+$ [8]	221 (48.0), 226 sh (38.1), 258 (14.5), 268(10.7), 316 (14.9), 364 (10.7)^c	510 (140)	2.10^d
I	310 (11.4), 320 sh (10.6), 370 (5.3), 392 sh (3.9)	515 (120)	1.65, 2.15^e
II	312 (31.6), 320 (32.0), 365 (17.0), 385 sh (13.3)	512 (140)	1.68, 1.95^e, 2.10^e
III	312 (51.6), 320 (50.3), 365 (27.7), 385 sh (21.3)	510 (110)	1.58, 1.86^e, 2.10^e

[a] $(CH_3)_3NCO(H)$, 293 K. [b] $(CH_3)_3NCO(H):C_6H_5CH_3$ (1:1), 77 K. [c] CH_3CN. [d] The position of the shortwave maximum of the spectrum. [e] The position of the peak of the current of irreversible wave.

complexes, along with the cyclopalladated ligand, of the heterocyclic 4,4'-bipyridyl ligand with low energy π* orbitals leads to the appearance on voltammograms of not only the irreversible ligand-centered reduction wave of the cyclopalladated ligand (E_p ~ –2 V) but also of additional waves shifted to the anodic region (Fig. 2) related to the processes of successive electron transfer to the π* orbitals localized predominantly on each of the pyridine components of 4,4'-bipyridyl.

The obtained results demonstrate that similar to the earlier studied macrocyclic complexes of Pd(II) and Pt(II) [6, 10] with peripheral cyclometallated 2-phenylpyridine, 2-(2'-thienyl)-pyridine and bridging 4,4'-bipyridyl or benzimidazole, the optical properties of the cyclopalladated complexes of 2-phenylbenzothiazole are determined by the chromophore metal complex ligand {Pd(bt)}, whereas their electrochemical activity is determined by the bridging 4,4'-bipyridyl ligand. Taking into account the possibility to vary the size of the cavity of macrocyclic complexes depending on the bridging ligand and, as a result, to react selectively with substrates, this shows the prospects of their use in electrochemical sensor devices.

EXPERIMENTAL

^{1}H NMR spectra were obtained at 293 K from solutions in $(CD_3)_2SO$, $CDCl_3$, and $(CH_3)_3NCO(H)$ on a Bruker AC-200F spectrometer. Electron absorption spectra were obtained at 293 K in the same solvents on an SF-2000 spectrophotometer. The luminescence was measured on a FSVU-1 apparatus with pulse laser photoexcitation (LGI-21, λ 337 nm, τ_{pulse} 10 ns) at 77 K in glassy matrices $(CH_3)_3NCO(H):C_6H_5CH_3$ (1:1) [11]. 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 $(CH_3)_3NCO(H)$ [12]. The potentials are given with respect to the ferrocenium/ferrocene redox system with the potential sweep rate of 100 mV s^{-1}.

Complexes **I–III** were prepared by the earlier described procedure [13].

Acetato(2-phenyl-3-ydo)benzothiazole(4,4'-bipyridyl)palladium (I). Yield 25%. ^{1}H NMR spectrum, DMSO-d_6, δ, ppm (*J*, Hz): 9.23 m (2H, H^o), 8.78 m (2H, $H^{o'}$), 8.20 m (2H, $H^{4,7}$), 7.98 m (2H, H^m), 7.89 m (1H, $H^{m'}$), 7.77 d (1H, $H^{6'}$, $^3J_{HH}$ 8), 7.44 m (2H, $H^{5,6}$), 7.16 m (1H, $H^{4'}$), 6.97 m (1H, $H^{5'}$), 6.13 d (1H, $H^{3'}$, $^3J_{HH}$ ~7), 2.50–2.40 m (3H, CH_3COO).

(μ-4,4'-Bipyridyl)bis[nitrato(2-phenyl-3-ydo)-benzothiazolpalladium] (II). Yield 25%. ^{1}H NMR spectrum, DMSO-d_6, δ, ppm (*J*, Hz): 9.40 m (4H, H^o), 8.30 m (4H, $H^{4,7}$), 7.93 m (4H, H^m), 7.79 d (2H, $H^{6'}$, $^3J_{HH}$ 7), 7.55 m (4H, $H^{5,6}$), 7.25 t (2H, $H^{4'}$, $^3J_{HH}$ 8), 7.06 t (2H, $H^{5'}$, $^3J_{HH}$ 8), 6.09 d (2H, $H^{3'}$, $^3J_{HH}$ 8).

Tetrakis[(μ-4,4'-bipyridyl)(2-phenyl-3-ydo)benzothiazolpalladium(II)] nitrate (III). Yield 20%. ^{1}H NMR spectrum, DMSO-d_6, δ, ppm (*J*, Hz): 9.40 m (8H, H^o), 8.86 m (8H, $H^{o'}$), 8.35 m (8H, H^m), 8.29 d (8H, $H^{4,7}$, $^3J_{HH}$ 8), 8.03 m (8H, $H^{m'}$), 7.76 d (4H, $H^{6'}$, $^3J_{HH}$ 7), 7.65 t (4H, H^5, $^3J_{HH}$ 8), 7.58 t (4H, H^6, $^3J_{HH}$ 8), 7.24 t (4H, $H^{4'}$, $^3J_{HH}$ 7), 7.05 d.d (4H, $H^{5'}$, $^3J_{HH}$ 7, 8), 6.09 d (4H, $H^{3'}$, $^3J_{HH}$ 7).

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