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Spectroscopic and Electrochemical Properties of Cyclopalladated Complexes of 2,3-Diphenylquinoxaline and 2,2',3,3'-Tetraphenyl-6,6'-Biquinoline

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Abstract—Comparative study of cyclopalladated ethylenediamine complexes of 2,3-diphenylquinoxaline (Hdphqx) $[Pd(dphqx)En]ClO_4$ and 2,2',3,3'-tetraphenylbiquinoline (H_2tphbq) $[(PdEn)_2(\mu\text{-tphbq})](ClO_4)_2$, and the free heterocyclic ligands was performed by means of ^{1}H NMR spectroscopy, electronic absorption and emission spectroscopy, and cyclic voltammetry. It was shown that cyclopalladation gives rise to a long-wave absorption band in the visible spectrum, a batochromic shift of the vibrationally structured phosphorescence band, and an anodic shift of the ligand-centered reduction potential of the complexes com-pared to free ligands.

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Cyclometalated square-planar complexes of platimum metals have long-lived electronically excited states and characteristically undergo reversible one-electron electrochemical reduction. For this reason, they are promising candidates for the design of photoactive molecularly organized metal complex systems with directed charge and energy transfer [1–3]. Special attention is attached to coordinately unsaturated “ligand complexes” capable of coordinating additional metal complex fragments to form molecularly organized systems with spatially separated photoinduced charges [4, 5].

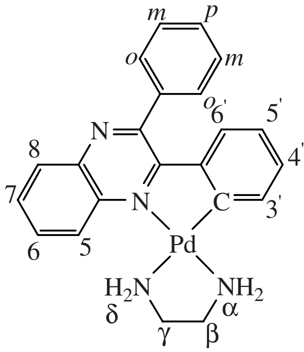
It was previously shown [6–10] that cyclometalated complexes of the general formula $[M(C\text{^}N)En]^{2+}$ [M = Pd(II), Pt(II), Au(III); $(C\text{^}N)^-$ are deprotonated forms of phenyl- and benzo-substituted imines and diazines; En is ethylenediamine] are convenient model compounds for tracing the effect of the heterocyclic ligand $(C\text{^}N)^-$ on the spectroscopic and electrochemical properties of the complexes as compared to the free compound H(C^N).

In the present work we present the results of a comparative study of properties of the free 2,3-diphenylquinoxaline (Hdphqx) and 2,2',3,3'-tetraphenyl-6,6'-biquinoline (H_2tphbq) and their cyclopalladated complexes $[Pd(dphqx)En]ClO_4$ and $[(PdEn)_2(\mu\text{-tphbq})]\cdot(ClO_4)_2$.

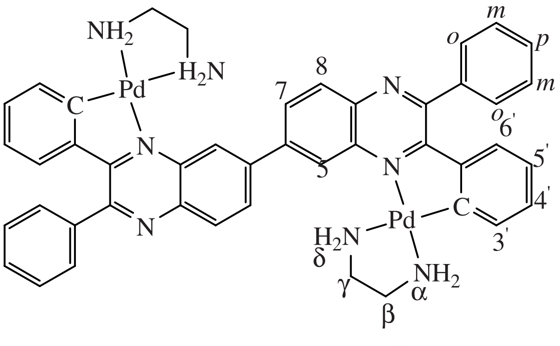
Heterocyclic ligands prepared by the reaction of benzil with phenylenediamine and biphenyl-3,3',4,4'-tetramine undergo facile cyclopalladation when reacted with an ethanolic solution of $Li_2[PdCl_4]$ to give poorly soluble complexes $[Pd(dphqx)(\mu\text{-Cl})]_2$ and $[(PdCl_2)_2(\mu\text{-tphbq})]$. Subsequent substitution of chloride ligands with ethylenediamine and precipitation of the reaction products as perchlorates leads to isolation of the complexes $[Pd(dphqx)En]ClO_4$ **I** and $[(PdEn)_2(\mu\text{-tphbq})](ClO_4)_2$ **II**.

The ^{1}H NMR spectra provide evidence for the composition and structure of the resulting complexes. The coordination-induced chemical shifts of protons (CIS = $\delta_c - \delta_l$) of the ligands, that reflect the changes in their structure, produced by complex formation, are listed in Table 1.

Comparison of the ^{1}H NMR spectra of $[Pd(dphqx)En]^+$ and $[(PdEn)_2(\mu\text{-tphbq})]^{2+}$ shows that cyclopalladation similarly affects the chemical shifts of ligand protons. In the dimeric complex $[(PdEn)_2(\mu\text{-tphdq})]^{2+}$, magnetic equivalence of protons in both quinoxaline constituents of the cyclometalated ligand, as well as in both



$[Pd(dphqx)En]^+$



$[(PdEn)_2(\mu\text{-}tphbq)]^{2+}$

ethylenediamine ligands is observed. The strongest cyclopalladation-affected is the H^5 shift (CIS = –0.43 ppm), whereas the H^7 and H^8 shifts change only slightly (CIS < 0.1). This result suggests selective formation of a steric isomer of $[(PdEn)_2(\mu\text{-}tphbq)]^{2-}$, in which palladium is coordinated to nitrogen atoms of 2,2',3,3'-tetraphenyl-6,6'-biquinoline, nearest just to the H^5 protons. It was previously shown [6] that the steric interaction of the $H^{6'}$ and H^0 protons of the palladated and uncoordinated phenyl rings in $[Pd(dphqx)]^-$ leads to their ortogonal location (the angle between the ring planes is 61°). This causes strong shielding of the $H^{6'}$ and $H^{5'}$ protons, resulting from the anisotropic effect of the circular current of the uncoordinated phenyl ring of the ligand. The analogous effect in $[(PdEn)_2(\mu\text{-}tphbq)]^{2+}$ can be also related to the ortogonal location of the palladated and uncoordinated phenyl rings of the ligand. In agreement with the different *trans*-effects of the diazine and carbanionic part of the cyclometalated ligands, both complexes exhibit magnetic nonequivalence of protons in the ethylenediamine ligand.

In terms of the localized MO model, the optical and electrochemical properties of mixed-ligand complexes are classed, in accordance with the prevailing character of orbitals [11], as metal- and ligand-centered. Therewith, provided the Koopmans theorem is fulfilled [12], optical and redox orbitals of complexes are similar in nature. The results of out study of the optical and electrochemical properties of the heterocyclic ligands and their cyclopalladated complexes are summarized in Table 2.

The reduction voltammorgam of Hdphqx shows a reversible one-electron wave assigned to electron transfer on π* orbitals mostly localized in the quinoxaline part of the ligand. In the case of H_2tphbq, two reversible one-electron waves related to consecutive electron transfer on π* orbitals of the two quinoxaline groups of the ligand (Fig. 1). The difference between the half-wave potentials ($\Delta E_{1/2}$ = 0.3 V) agrees with the expected weak interaction between π orbitals of the two σ-bonded free rotating quinoxaline parts of the ligand.

The reduction voltammorgam of $[Pd(dphqx)En]^+$, too, shows a reversible one-electron reduction wave attributed to ligand-centered electron transfer on p orbitals of the quinoxaline part [Pd(dphqx)] of the

Table 1. Coordination-induced shifts (CIS = $\delta_c - \delta_l$, ppm) of ligand protons in DMSO solutions of complexes

Complex	Proton no.										
	5	6	7	8	3'	4'	5'	6'	*o*	*m*	*p*
$[Pd(dphqx)En]ClO_4$	–0.14	0.05	0.00	0.01	–0.14	–0.29	–0.54	–0.81	0.2	0.2	0.2
	α 4.18	β 0.29	γ 0.22	δ 3.16							
$[(PdEn)_2(\mu\text{-}tphbq)] (ClO_4)_2$	–0.43	–	0.01	0.07	–0.12	–0.38	–0.56	–0.85	0.2	0.2	0.2
	α 4.21	β 0.33	γ 0.25	δ 3.22							

Table 2. Optical and electrochemical parameters of ligands and cyclopalladated complexes

Compound	Absorption[a]	Phosphorescence[b]	Reduction
	λ_{max}, nm ($\varepsilon \times 10^{-3}$ l mol^{-1} cm^{-1})	λ_{max}, nm (τ, μs)[c]	$-E_{1/2}$,V (ΔE, mV)[d]
Hdphqx	247 sh (33.6), 279 sh (11.1), 347 (8.6)[e]	483	2.06 (60)
H_2tphbq	270 (68.8), 290 sh (58.5), 382 (55.2)[e]	545	1.65 (70) 1.94 (80)
[Pd(dphqx)En]ClO_4	210 (27.3), 240 sh (26.9), 287 (9.5), 423 (2.1)[f]	584 (70)	1.48 (80)
[$(PdEn)_2$(μ-tphbq]$(ClO_4)_2$	240 (63.7), 273 (62.5), 290 (61.4), 380 (40.0), 440 sh (~14), 464 (16.8)[e]	585 sh (90)	1.31[g]

[a] 293 K. [b] 77 K, DMF–toluene (1 : 1). [c] Position of the short-wave phosphorescence maximum and the decay time. [d] Half-wave potential against Fe^+/Fe and the difference in the oxidation and reduction current peak potentials, DMF. [e] CH_2Cl_2. [f] CH_3OH. [g] Current peak potential at the potential sweep rate 100 mV s^{-1}

metal complex fragment. The broadened reduction wave observed for $[(PdEn)_2(\mu\text{-tphdq})]^{2+}$ at –1.3 V is evidently caused by overlap of two waves associated with consecutive electron transfer on π* orbitals of the two quinoxaline parts of the [Pd_2(μ-tphdq)] fragment. The anodic shift of the half-wave potential {0.6 V for $[Pd(dphqx)En]^+$} and peak current {~0.5 V for $[(PdEn)_2\cdot(\mu\text{-tphbq})]^{2+}$} reflect a decrease in the energy of quinoxaline π orbitals, induced by cyclopalladation. The oxidation voltammograms of the complexes have a typical [6] irreversible character and are on the electrochemical stability border of the solvent due to formation of highly reactive Pd(III) complexes that undergo subsequent fast chemical reactions. The oxidation peak current potentials depend on the potential sweep rate, which makes impossible assessment of the effect of cyclopalladation on the HOMO energy.

The absorption spectra of the free heterocyclic ligands show strong vibrationally structured bands (Fig. 2) related to spin-allowed π–π* optical transitions. In agreement with the electrochemical data showing that the energy of the free π* orbital of the quinoxaline part of the ligand in H_2tphbq is lower compared to Hdphqx, a batochromic shift of the long-wave optical transition (0.3 eV) is observed. Photoexcitation of frozen (77 K) glassy solutions of the ligands causes their vibrationally structured phosphorescence resulting from spin-forbidden π–π* optical transitions.

Comparison of the electronic absorption spectra of the complexes and free ligands (Figs. 2, 3) shows that, along with the expected batochromic shift of intra π–π * optical transitions (ΔE < 1 kK) localized in the heterocyclic ligands, cyclopalladation gives rise to

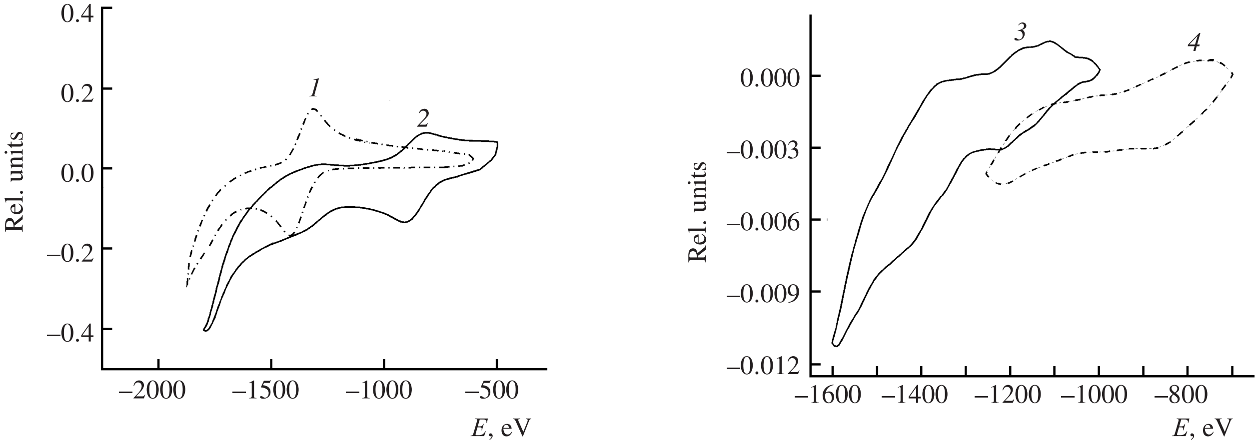


Fig. 1. Reduction voltammograms of (*1*) Hdphqx, (*2*) [Pd(dphqx)En]ClO_4, (*3*) H_2tphbq, and (*4*) [$(PdEn)_2$(μ-tphbq)]$(ClO_4)_2$ in DMF.

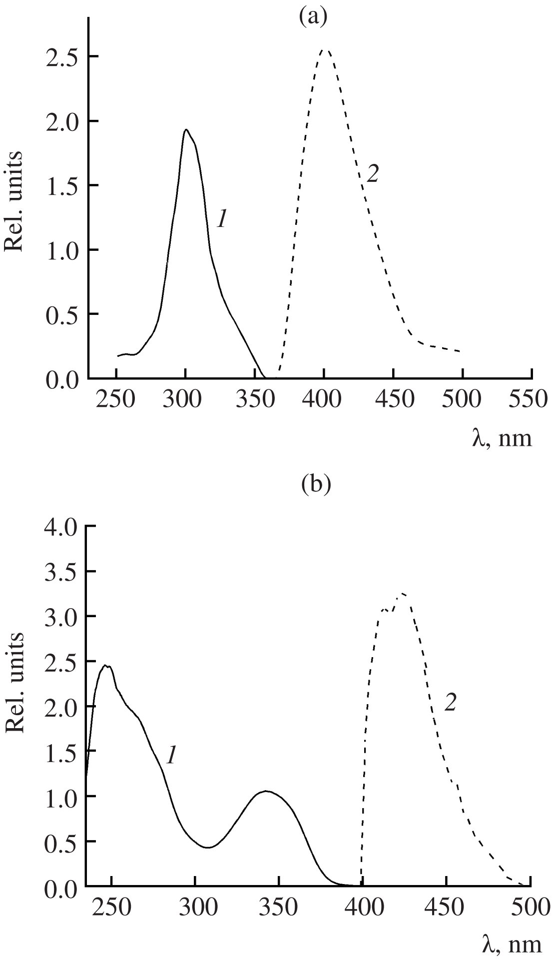


Fig. 2. Absorption and luminescence spectra of (a) Hdphqx and (b) H_2tphbq.

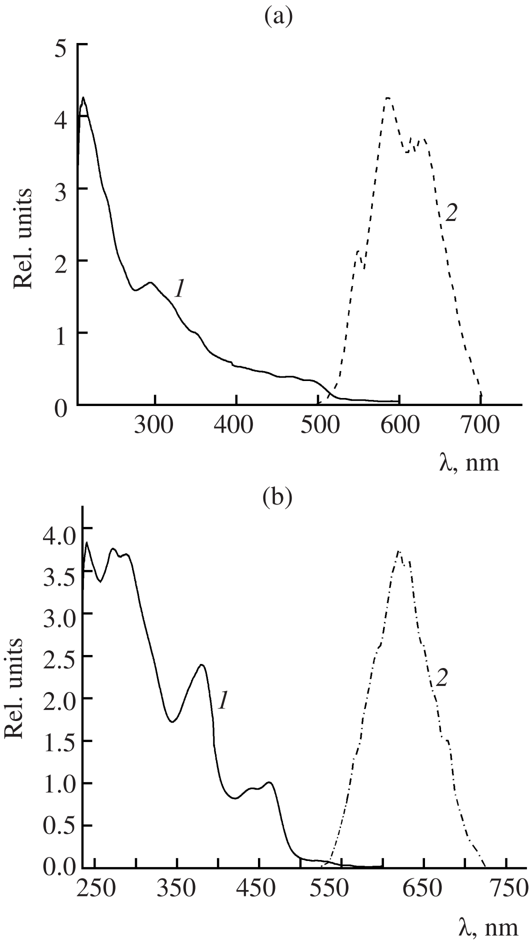


Fig. 3. Absorption and luminescence spectra of (a) [Pd (dphqx)En]ClO_4 and (b) [$(PdEn)_2$(μ-tphbq)]$(ClO_4)_2$.

new low-energy bands related to spin-allowed charge-transfer optical transitions from the HOMO to LUMO (π*) in the [Pd(dphqx)] and [Pd_2(μ-tphbq)] metal complex fragments. The spectral and kinetic characteristics of the vibrationally structured low-temperature luminescence of the complexes are determined by the spin-forbidden irradiative decay of the photoexcitation energy from the lowest electronically excited state of the metal complex fragments. This is confirmed by the exponential luminescence decay kinetics and by the independence of the spectrum on the excitation wavelength (λ 250–400 nm). The strong temperature quenching characteristic of spin-forbidden optical transitions localized in the cyclopalladated metal complex fragments [6–10] leads, together with the effective spin-orbital interaction characteristic of palladium complexes, leads to the absence of both phosphorescence and fluorescence on photoexcitation of the complexes in liquid (293 K) solutions.

The presence of long-lived electronically excited states and the ligand-centered character of the reduction of the complexes, together with their coordinational unsaturation, allows the cyclometalated "ligand complexes" on the basis of 2,3-diphenylquinoxaline and 2,2',3,3'-tetraphenyl-6,6'-biquinoline as possible structural components of photosensitive molecularly organized systems with directed charge and energy transfer.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker AC-200F spectrometer. The electronic absorption spectra were obtained on an SF-2000 spectrophotometer at 293 K. Luminescence studies were carried out on an

SDL-2 spectrometer and a KSVU-1 device with pulse laser excitation (LGI-21, λ 337 nm) in glassy 1 : 1 DMF–toluene matrices at 77 K and in acetonitrile solutions at 293 K [13]. The cyclic voltammograms were obtained on a modified SVA-1B device at 293 K in a three-electrode cell with separated compartments for the operating (Pt), auxiliary (Pt), and reference (Ag) electrodes, in presence of an 0.1 M $[N(C_4H_9)_4]ClO_4$ solution in DMF [14]. The half-wave potentials are presented against the ferrocenium–ferrocene redox system.

The heterocyclic ligands were prepared by condensation of benzil with phenylenediamine and biphenyl-3,3',4,4'-tetramine according to a modified procedure [15]. $[Pd(dphqx)En]ClO_4$ and $[(PdEn)_2(\mu\text{-}tphbq)](ClO_4)_2$ were synthesized by the procedure in [6].

2,3-Diphenylquinoxaline. Yield 90%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (^3J, Hz): 8.16 (H^{5,8}, 3.6, 6.5), 7.89 (H^{6,7}, 3.6, 6.5), 7.48 (4H^o), 7.37 (6H^{m,p}).

2,2'3,3'-Tetraphenylbiquinoline. Yield 70%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (^3J, Hz): 8.71 (2H^5), 8.33 (2H^8, 8.7), 8.26 (2H^7, 8.7), 7.54 (8H^o), 7.40 (12H^{m,p}).

Ethylenediamine[(2-phenyl)(3-phenyl-2-ido)quinoxalin]palladium(II) perchlorate [Pd(dphqz)En] ClO$_4$. Yield 80%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (^3J, Hz): 8.17 (H^8, 8.0), 8.02 (H^5, 8.0), 7.94 (H^6, 5.8, 8.0), 7.89 (H^7, 5.8, 8.0), 7.62-7.71 (H^{m,p}), 7.71 (H^o, 8.0), 7.23 (H$^{3'}$ 7.3), 7.08 (H$^{4'}$ 7.3), 6.82 (H$^{5'}$, 7.3, 8.0), 6.67 (H$^{6'}$, 8.0), 5.49 (2H$^\alpha$), 4.47 (2H$^\delta$), 2.77 (2H$^\beta$), 2.70 (2H$^\gamma$).

Bis[ethylenediaminopalladium(II)]{μ-(2,2'-diphenyl)[3,3'-di(phenyl-2-ido)]-6,6'-biquinoline} [(PdEn)$_2$ · (μ-tphbq)](ClO$_4$)$_2$. Yield 60%. ^{1}H NMR spectrum (DMSO-d_6),δ, ppm (^3J, Hz): 8.38 (2H^7, 8.7), 8.33 (H^8, 8.7), 8.28 (2H^5), 7.73 (4H^o), 7.56 (6H^{m,p}), 7.23 (2H$^{3'}$, 7.3), 7.01 (2H$^{4'}$, 8.0, 7.3), 6.83 (2H$^{5'}$, 8.0, 7.3) 6.71 (2H$^{6'}$, 8.0), 5.52 (4H$^\alpha$), 4.53 (4H$^\delta$), 2.81 (4H$^\beta$), 2.73 (4H$^\gamma$).

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