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Spectroscopic and Electrochemical Properties of Mixed-Ligand Cyclopalladinized Complexes of Deprotonated Forms of 2-(2-Thienyl)Pyridine and 2-Phenylpyridine with 1,10-Phenantroline and Its 1,4-Diazine Derivatives

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Abstract—A comparative study of $[Pd(N^\wedge C)(N^\wedge N)]^+$ complexes $\{(N^\wedge C)^-$ are deprotonated forms of 2-phenylpyridine and 2-(2-thienyl)pyridine and $(N^\wedge N)$ is 1,10-phenantroline, dipyrido[*f*,*h*]quinoxaline, dipyrido[*a*,*c*]phenazine or 6,7-dicyanodibenzo[*f*,*h*]quinoxaline$\}$ was carried out by the methods of ^{1}H NMR, electronic absorption and emission spectroscopy, and cyclic voltammetry. Optical and electrochemical properties of dipyrido-substituted 1,4-diazines are conditioned by the electron transfer involving π^* orbitals localized on weakly interacting phenantroline (π^*_{phen}) and diazne (π^*_{diaz}) components.

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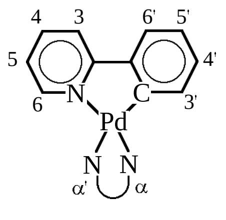
The advancement of the chemistry of molecular-organized metal-complex systems, capable of directed transport and accumulation of charge or energy on a reaction center owing to a spatial and structural organization of individual photo- and electroactive components determines interest to complexes characterized by long-living excited states and reversible processes of outer-sphere charge transfer. Such complexes can act as structural components of molecular-organized systems with variable optical and electrochemical properties [1, 2].

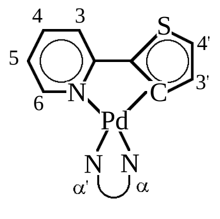
Ethylenediamine (en) cyclopalladinized complexes $[Pd(N^\wedge C)en]^+$ [$(N^\wedge C)$ are deprotonated forms of phenyl-, thienyl-, and benzo-substituted pyridine] are characterized by both the presence of long-living electron-excited states responsible for luminescence of the complexes and quasireversible one-electronic processes of their electrochemical reduction [3]. Variation in the nature of $(N^\wedge C)$ cyclometallated ligands allows obtaining complexes with variable optical and electrochemical properties. The replacement of aliphatic ethylenediamine by derivatives of 1,10-phenantroline characterized by low-energy delocalized π^*-orbitals expands the possibility for the modification of their optical and electrochemical parameters.

In this work we represented results of studying spectroscopic and electrochemical properties of the mixed-ligand cyclopalladinized $[Pd(N^\wedge C)(N^\wedge N)]^+$ complexes based on the deprotonated forms of 2-phenylpyridine (ppy) and 2-(2-thienyl)pyridine (tpy) with 1,10-phenantroline (phen) and its 1,4-diazine derivatives: dipyrido[*f*,*h*] quinoxaline (dpq), dipyrido[*a*,*c*]phenazine (dppz), and 6,7-dicyanodipyrido-[*f*,*h*]quinoxaline (dicnq) The proton chemical shifts (δ, ppm) in NMR spectra, maxima of absorption bands (λ_{max}), and their extinction coefficients (ε), maxima of luminescence bands (λ'_{max}), and also half-wave potentials ($E_{1/2}$) and differences between potentials of peak currents (ΔE) in voltammograms of electroreduction of chelated $(N^\wedge N)$ ligands are given in Table 1.

The specificity of the electronic structure of 1,4-diazine derivatives of 1,10-phenantroline (dpq, dppz, and dicnq) is determined by the presence of the two heterocycles, phenantroline and diazine, in their composition. The results of quantum-chemical calculations of the electronic structure of dipyrido[*a*,*c*]phenazine [4] point to a weak electronic interaction between phenantroline and diazine components of the ligand, which suggests substantially isolated character of electro- and photo-stimulated electron transfer involving low-energy π^* orbitals localized on these fragments. The ^{1}H NMR spectroscopy data illustrate a weak



[Pd(ppy)(N^N)]$^+$



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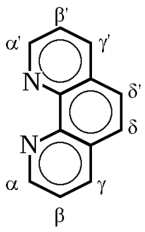
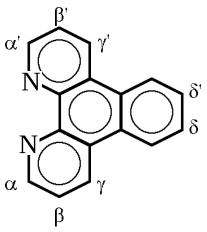
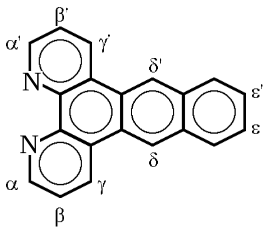


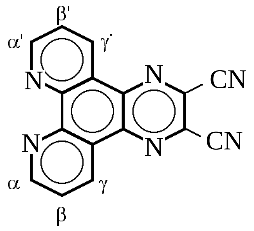
phen



dpq



dppz



dicnq

influence of the nature of diazine substituents on the proton chemical shifts of the phenantroline parts of dipyrido-substituted 1,4-diazines [$\delta(H^\alpha)$ 9.25±0.11, $\delta(H^\beta)$ 7.95±0.09, $\delta(H^\gamma)$ 9.43±0.02 ppm] and a closeness of the chemical shifts of H^α and H^β protons and similar signals for 1,10-phenantroline ($\Delta\delta < 0.2 \pm 0.1$ ppm). A decrease in the chemical shifts of H^α and H^β protons in the series dicnq > dpq > dppz > phen points to regular reduction in the basicity of phenantroline nitrogen atoms on the introduction of diazine substituents with acceptor properties.

Electroreduction voltammograms of 1,10-phenantroline and its diazine derivatives are characterized by one-electron reduction waves with practically constant values (–2.53±0.03 V) of the half-wave potential (phen and dppz) or the peak current (dpq and dicnq) assigned to the electron transfer on the π^*_{phen} redox orbitals of the ligands. At the same time for diazine derivatives of 1,10-phenantroline an additional one-electronic reversible reduction wave, which is anode-displaced, is characteristic. Its half-wave potential is displaced in the anodic region in the presence of acceptor substituents in the sequence: dicnq> dppz >> dpq. It allows us to assign this wave of the reduction of 1,10-diazine derivatives of phenantroline to the electron transfer on the lowest in energy π^*_{diaz} redox orbital of the ligand. In accordance with the electrochemical data on the localized π^*_{phen} and π^*_{diaz} redox orbitals, the electronic spectra of the (N^N) ligands contain vibration-structured absorption bands caused by spin-allowed optical π–π* electron transitions presumably localized on the phenantroline and diazine parts of the ligands. These transitions are the high-energy ones with close values of the both energy ($\nu_{\max}$ 37.1±0.6 kK) and extinction coefficient [ε (3±1)× 10^4 l mol^{-1} cm^{-1} and also the more longwavelength (λ > 330 nm) and less probable (ε ~10^3 l mol^{-1} cm^{-1})

Table 1. Spectroscopic and electrochemical parameters of 1,10-phenantroline and its 1,4-diazine derivatives

Compound	^{1}H NMR spectrum, δ, ppm^a (J_{HH}, Hz^a)				
	H^α, $H^{\alpha'}$	H^β	H^γ	H^δ, H^ε	$^3J_{HH}$
phen	9.08	7.71	8.43	7.91	$J_{\alpha\beta}$ 4.3, $\mathbf{J}_{\alpha\gamma}$ 1.9, $J_{\beta\gamma}$ 8.6
dppz	9.14	7.86	9.44	8.27/7.99	$J_{\alpha\beta}$ 4.3, $J_{\alpha\gamma}$ 1.5, $J_{\beta\gamma}$ 8.1, $J_{\delta\varepsilon}$ 6.7, $J_{\delta\varepsilon'}$ 3.7
dpq	9.24	7.96	9.45	9.17	$J_{\alpha\beta}$ 3.8, $J_{\alpha\gamma}$ 1.9, $J_{\beta\gamma}$ 8.1
dicnq	9.36	8.04	9.41	–	$J_{\alpha\beta}$ 4.4, $J_{\alpha\gamma}$ 1.9, $J_{\beta\gamma}$ 8.1

Table 1. (Contd.)

Compound	Electronic spectra				Voltammogram[d]	
	absorption[b]		luminescence[c]			
	λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	assignment	λ, nm (ν_{vib}, kK)	assignment	$-E_{1/2}$, V (ΔE, mV)	assignment
phen	270 [28.1]	$^1(\pi-\pi^*_{phen})$	459, 490, 531 (1.30)	$^3(\pi-\pi^*_{phen})$	2.51 (60)	π^*_{phen}
dppz	268 [27.3], 363 [10.4],	$^1(\pi-\pi^*_{phen})$	545, 559,[e] 589, 640[e]	$^3(\pi-\pi^*_{diaz})$	1.61 (60)	π^*_{diaz} π^*_{phen}
	378 [7.9]		(0.5, 1.36)		2.49 (60)	
dpq	276[e] [22.1]	$^1(\pi-\pi^*_{phen})$	429,[e] 455, 476, 518[f]	$^3(\pi-\pi^*_{diaz})$	2.00 (60)	π^*_{diaz}
	336 [13.2]	$^1(\pi-\pi^*_{diaz})$	(1.33)		2.53[f]	π^*_{phen}
dicnq	265 [33.6]	$^1(\pi-\pi^*_{phen})$	466,[e] 478, 517, 573[e]	$^3(\pi-\pi^*_{diaz})$	1.09 (70)	π^*_{diaz}
	307 [13.1]	$^1(\pi-\pi^*_{diaz})$	(0.5, 2.10)		2.57[f]	π^*_{phen}

[a] Dimethyl sulfoxide solutions (293 K), reference TMS. [b] Solutions in dimethyl formamide (293 K). [c] Solutions in a dimethyl formamide–toluene mixture, 1:1 (77 K). [d] Solutions in dimethyl formamide (293 K), $E_{1/2}$ relative to the Fc^+/Fc redox system. [e] Shoulder. [f] Peak-current potential at the potential scanning rate of 100 mV s^{-1}.

Table 2. Coordination-induced chemical shifts ($\Delta\delta = \delta_{comp} - \delta_{lig}$, ppm, relative to TMS) of protons of ligands in dimethyl sulfoxide solutions of $[Pd(N^\wedge C)(N^\wedge N)]^+$ complexes

Complex	Designation of hydrogen atoms of (C^N) and (N^N) ligands												
	3	4	5	6	3'	4'	5'	6'	α/α'	β/β'	γ/γ'	δ/δ'	ε/ε'
$[Pd(ppy)phen]^+$	0.3[a]	0.3[a]	0.05	0.14	–0.25	0.11	–0.3[a]	–0.39	0.31	0.5[a]	0.56	0.43	–
$[Pd(ppy)dppz]^+$	0.33	0.4[a]	–0.02	0.16	–0.15	0.15	–0.24	–0.39	0.33	0.50	0.38	0.17	0.18
$[Pd(ppy)dpq]^+$	–0.01	0.30	–0.26	–0.02	–0.37	0.10	–0.49	–0.79	0.13	0.26	0.13	0.17	–
$[Pd(ppy)dicnq]^+$	0.19	0.42	–0.12	0.13	–0.2[a]	0.1[a]	–0.3[a]	–0.5[a]	0.23	0.34	0.32	–	–
$[Pd(tpy)phen]^+$	0.0[a]	0.44	0.20	0.30	0.57	0.26	–	–	0.37	0.51	0.61	0.45	–
$[Pd(tpy)dppz]^+$	–0.16	0.38	0.14	0.19	0.46	0.12	–	–	0.24	0.44	0.28	0.09	0.13
$[Pd(tpy)dpq]^+$	–0.15	0.39	0.16	0.23	0.49	0.18	–	–	0.25	0.36	0.29	0.19	–
$[Pd(tpy)dicnq]^+$	–0.11	0.39	0.06	0.26	0.52	0.20	–	–	0.26	0.35	0.36	–	–

[a] Multiplet.

ones depending on the nature of a diazine substituent. The low-temperature (77 K) luminescent spectra of dipyrido-substitued 1,4-diazines also depend on the nature of substituents in the diazine part of the ligand and are caused by spin-forbidden π–π^*_{diaz} transitions.

Proton signals from both deprotonated forms of cyclometallated (N^C) and chelated (N^N) ligands are observed in the ^1H NMR spectra of the $[Pd(N^\wedge C)\cdot(N^\wedge N)]^+$ complexes. The values of coordination-induced proton chemical shifts of the ligands ($\Delta\delta = \delta_{comp} - \delta_{lig}$), reflecting changes in the electronic density of ligands due to donor-acceptor ligand → metal interaction, are given in Table 2.

Unlike $[Pt(N^\wedge C)(N^\wedge N)]^+$ complexes with similar chelated and cyclometallated ligands [5], and $[Pd(N^\wedge C)en]^+$ [3], Pd(II) complexes, the complexes under study are characterized by the magnetic equivalence of the protons of chelated (N^N) ligands located in the *trans*-position to the pyridine and carboanion parts of the (N^C) ligands, which points to the similarity in the efficiency of interaction of two pyridine nitrogen atoms with Pd(II). In accordance with the coordination mode, irrespective of the nature of phenantroline diazine derivatives, the complex formation results in deshieding of their protons due to a reduction in the electronic density mainly on the phenantroline part of the ligand [$\Delta\delta(H^{\alpha})$ 0.24 ± 0.06 ppm, $\Delta\delta(H^{\delta})$ 0.38?0.08, $\Delta\delta(H^{\gamma})$ 0.29 ± 0.09 ppm], whereas the electronic density on the diazine part of the ligands [$\Delta\delta(H^{\delta})$ 0.13?0.05 ppm] is much less changed. The decrease in the basicity of pyridine

Table 3. Parameters of electronic absorption and luminescent spectra and reduction voltammograms of $[Pd(N\text{^}C)(N\text{^}N)]^+$ complexes

Complex	Absorption, λ_{max}, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)			Reduction, $-E_{1/2}$, V (ΔE, mV)			Luminescence, λ_{max}, nm ($\tau_{1/2}$, μs)	
	$^1(\pi-\pi^*)$	$^1(d-\pi^*_{N\text{^}C})$	$^1(d-\pi^*_{phen})$	π^*_{diaz}	π^*_{phen}	$\pi^*_{N\text{^}C}$	$^3(\pi-\pi^*_{N\text{^}C})$	$^3(\pi-\pi^*_{diaz})$
$[Pd(ppy)phen]^+$	270 [27.8], 312 [5.9][a]	355 [3.4][a]	402 [1.0][a]	–	1.60[b]	1.93[b]	469, 504, 535 (200)	–
$[Pd(ppy)dpq]^+$	300 [24.6], 345 [11.2]	361 [9.1]	382 [0.9][a]	2.02 (0.10)	2.62[b]		465, 499	430[a]
$[Pd(ppy)dppz]^+$	291 [33.2], 360 [18.6]	377[c] [16.5]	390 [1.1][a]	1.61 (0.08)	1.81[b]	2.57[b]	472, 510	547,[a] 561[a]
$[Pd(ppy)dicnq]^+$	306 [24.9], 341[a] [10.8]	365[c] [11.5]	403 [1.0][a]	1.16 (0.06)	>2.7[d]		466,[e] 484,[e] 508[e]	
$[Pd(tpy)phen]^+$	275 [25.6][a], 316 [8.7][a]	373 [3.7][a]	405 [0.8][a]	–	1.55[b]	1.99[b]	532, 555, 582 (230)	–
$[Pd(tpy)dpq]^+$	281 [24.3], 341 [6.7][a]	375 [5.0]	408 [0.7][a]	2.02 (0.10)	2.40[b]		538, 582	431,[a] 455, 474
$[Pd(tpy)dppz]^+$	273 [37.0], 364 [13.5]	377[c] [13.5]	404 [0.6][a]	1.54 (0.10)	1.75[b]	2.45[b]	542,[c] 560,[c] 585[c]	
$[Pd(tpy)dicnq]^+$	302 [30.6], 351 [11.9][a]	365[c] [11.5]	409 [0.9][a]	1.16 (0.06)	>2.7[d]		540, 560[a]	466,[a] 474[a]

[a] Shoulder. [b] Potential of a peak current at the potential scanning rate of 100 $mV\,s^{-1}$. [c] Overlapping of $^1(\pi-\pi^*_{N\text{^}C})$ and $^1(d-\pi^*_{diaz})$ absorption bands. [d] Reduction outside electrochemical stability of the solvent. [e] Overlapping of $^3(\pi-\pi^*_{N\text{^}C})$ and $^3(d-\pi^*_{diaz})$ luminescent bands.

nitrogen atoms of diazine ligands compared to 1,10-phenantroline and the reduction in deshielding of H^{α} and H^{β} protons in the phenantroline part of the ligands are connected with a decrease in the efficiency of their donor–acceptor interaction with Pd(II). The change in the nature of (N^C) ligand in going from ppy to tpy results in the increase of deshielding of the protons of the both pyridine [$\Delta\delta(H^6$ ppy) $0.10 \pm 0.0.08$, $\Delta\delta(H^6$ tpy) 0.25 ± 0.05 ppm] and carboanion parts [$\Delta\delta(H^{3'}$ ppy) $0.24 \pm 0.0.09$, $\Delta\delta(H^{3'}$ tpy) 0.51 ± 0.05 ppm] of the ligands.

Within the framework of the model of localized molecular orbitals [6] electro- and photo-stimulated processes in cycloplatinated complexes are classified into metal- and ligand-centered, according to the nature of participating orbitals, a similarity in the nature of spectroscopic and redox orbitals of the complexes being observed when Koopmans theorem is obeyed [7]. The results of studying the influence of the nature of cyclometallated and chelated ligands on the electrochemical and optical properties of the $[Pd(N\text{^}C)phen]^+$ complexes are presented in Table 3.

Electroreduction voltammograms of the $[Pd(N\text{^}C)phen]^+$ complexes are characterized by two one-electron irreversible reduction waves with current peak potentials close ($\Delta E_p < 0.1$ V) to the half-wave potentials of quasireversible reduction waves of $[Pt(N\text{^}C)phen]^+$ complexes [5] assigned to the processes of consecutive electron transfer onto π* redox orbitals localized on {μphen} and {M(N^C)} metal-complex fragments. The irreversible character of the waves of Pd(II) complexes reduction corresponds to the expected decrease in the chemical stability of the ligand-centred electroreduction product, $[Pd^{II}(N\text{^}C)\cdot(phen)]$, owing to the reduction in the energy gap between vacant π* and σ*(4*d*) orbitals of a ligand and palladium, that favors thermally activated formation of highly reactive $[Pd^{I}(N\text{^}C)(phen)]$ complexes exposed to a fast chemical reaction [8].

The voltammograms of the reduction of $[Pd(N\text{^}C)\cdot(N\text{^}N)]^+$ complexes with diazine derivatives of phenantroline as (N^N)-chelated ligands alongside with irreversible waves of the reduction of the bound ligand contain (Fig. 1) also a quasireversible wave with a half-wave potential practically coinciding ($\Delta E_{1/2} << 0.07$ V) with the reduction potential of a free phenantroline derivative (Table 1). It allows us to assign this wave to the electron transfer on the π* redox orbital mainly localized on the diazine part of chelating ligand spatially distant and weakly interact-

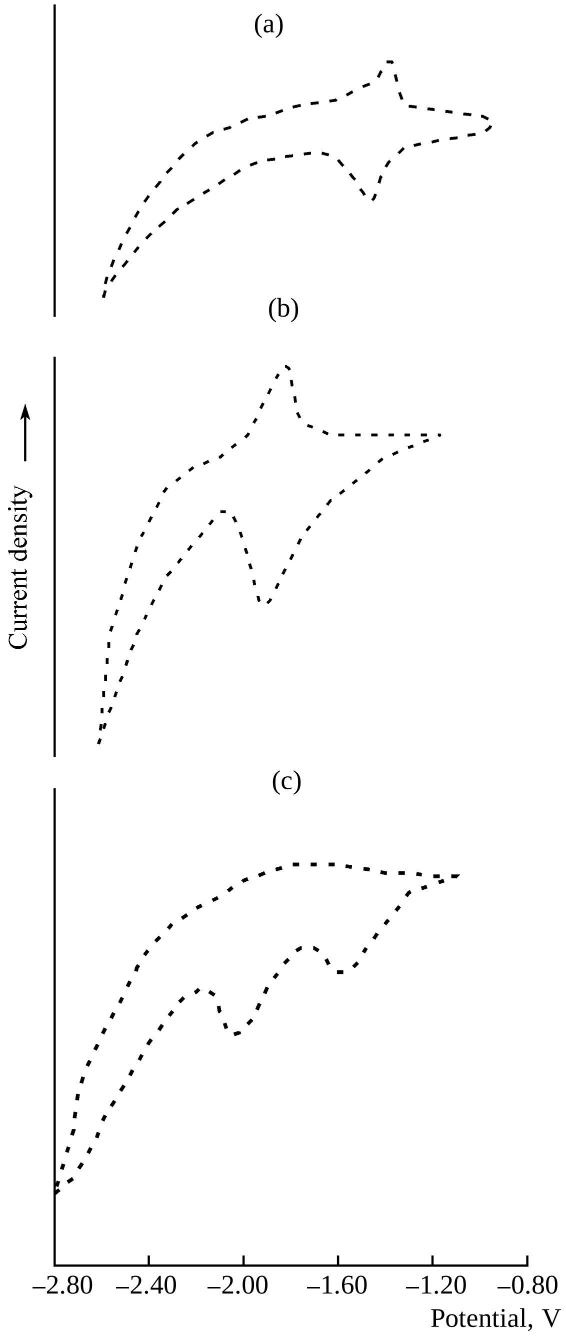


Fig. 1. Reduction voltammograms for complexes. (a) $[Pd(ppy)dicnq]^+$, (b) $[Pd(ppy)dpq]^+$, (c) $[Pd(ppy)phen]^+$

ing with the coordination center. The potential of the current peak of the second irreversible reduction wave of $[Pd(N^\wedge C)dppz]^+$ complexes slightly differs from the potential of the wave of the ligand-centred reduction of $[Pd(N^\wedge C)phen]^+$ complexes with the participation of the redox π* orbitals of the {Pd(phen)} fragment [ΔE_p (0.21 ± 0.01) V]. It agrees with insignificant distinctions of coordination-induced chemical shifts of $H^{\alpha/\alpha'}$ protons (ΔΔδ 0.08 ± 0.05 ppm), which points to practically equal character of donor-acceptor interactions of 1,10-phenantroline and the phenantroline part of ddpz with Pd(II) and to a close energy position of π^*_{phen} redox orbitals of the complexes. The irreversible reduction wave of the $[Pd(N^\wedge C)(N^\wedge N)]^+$ complexes [(N^N) = dpq, dppz], displaced to the cathode to the greatest degree, with the potential of peak current of (E_p –2.4 to –2.6 V] on the border of the electrochemical stability of the dimethyl formamide solvent can be caused by the electron transfer on π* redox orbitals of {M(N^C)} and {M(N^N)} metal-complex fragments.

The voltammograms of the oxidation of $[Pd(N^\wedge C)\cdot dpq]^+$ complexes have a typical [3] irreversible metal-centered character owing to the formation of such primary products of the electrochemical oxidation as highly reactive Pd(III) complexes exposed to a subsequent fast chemical reaction. The peak current potentials of the oxidation waves of these complexes [E_p 0.82 and 0.87 V for the complexes with the ligands (N^C) = ppy and tpy, respectively] are on the border of the electrochemical stability of the solvent, whereas the oxidation of the complexes with other diazine (N^N) ligands occurs at potentials lying outwards its stability ($ð_{®} > 1.0$ V), which does not allow studying the influence of ligands on the energy position of the highest occupied redox *d* orbitals of the complexes.

Alongside with the spin-allowed $\pi–\pi^*_{N^\wedge C}$ and $d–\pi^*_{N^\wedge C}$ optical electron transitions typical for $[Pd(N^\wedge C)en]^+$ complexes with orbitals localized on the {Pd(N^C)} fragment [3], the electronic absorption spectra of $[Pd(N^\wedge C)(N^\wedge N)]^+$ complexes contain additional bands caused by $\pi–\pi^*_{N^\wedge N}$ and $d–\pi^*_{N^\wedge N}$ transitions between the orbitals of the {Pd(N^N)} fragment. Unlike the $–\pi^*_{N^\wedge N}$ intraligand vibration-structured absorption bands, the position and extinction coefficient of the most long-wave metal → (N^N) ligand charge-transfer bands are almost independent (ν_{max} 25.0 ± 0.6 kK, ε $(0.9 \pm 0.2) \pm 10^3$ $l\,mol^{-1}\,cm^{-1}$) of the nature of cyclometallated and chelated ligands. In combination with the expected character of the variation of extinction coefficients of the metal-ligand charge transfer bands $\varepsilon(d–\pi^*_{N^\wedge C}) \sim \varepsilon(d–\pi^*_{phen}) >> \varepsilon(d–\pi^*_{dirs})$ it allows us to assign this absorption band of diazine derivatives of phenantroline to an optical transition involving π^*_{phen} orbitals mainly localized on the phenantroline part of the ligands. Comparison of parameters of the electronic absorption spectra and electrochemical characteristics of $[Pd(N^\wedge C)phen]^+$ complexes shows that, despite the overlapping of absorption bands and the irreversible character of reduction waves, a correspondence between energy difference of optical

[$\nu_{max}(d–\pi^*_{N\wedge C}) – \nu_{max}(d–\pi^*_{phen}) = 0.34 \pm 0.07$ eV] and redox- [$E_{1/2}(\pi^*_{N\wedge C}) – E_{1/2}(\pi^*_{phen}) = –0.39 \pm 0.06$ V] orbitals is observed. It confirms the applicability of the model of localized molecular orbitals and the validity of Koopmans theorem to a joint interpretation and forecasting of optical and electrochemical properties of [Pd(N^C)(N^N)]$^+$ complexes.

Spectral and kinetic characteristics of the luminescence of [Pd(N^C)phen]$^+$ complexes in frozen glassy solutions (77 K, dimethyl formamide–toluene, 1:1) are caused by the spin-forbidden radiation from the lowest energy electron-excited $^3(\pi–\pi^*)$ state of electrons localized on the {Pd(N^C)} fragment. It is evidenced by the similarity of the vibration-structured spectra and the time of the exponential luminescence decay ($\tau_{1/2}$) of [Pd(N^C)phen]$^+$ complexes and [Pd(N^C)en]$^+$ complexes [3]. The sequence of energy positions of singlet $^1(\pi–\pi^*) > {}^1(d–\pi^*)$ and triplet $^3(\pi–\pi^*) < {}^3(d–\pi^*)$ excited states of the complexes is connected with a greater energy of the singlet-triplet splitting for the intraligand $\pi–\pi^*$ transition in comparison with the $d–\pi^*$ metal-ligand charge transfer [9]. Thus, despite of a distinction between electron-excited states of the {Pd(N^C)} and {Pd(N^N)} metal-complex fragments, a strong electronic interaction results in the effective radiationless energy transfer in the lowest electron-excited state $^3(\pi–\pi^*)$. It is its deactivation that determines the luminescence of the [Pd(N^C)phen]$^+$ complexes.

The low-temperature luminescence of [Pd(N^C)·(N^N)]$^+$ complexes with diazine derivatives of phenantroline is characterized by a non-exponential decay kinetics, whereas the vibration-structured luminescent spectra (Fig. 2) are determined by a superposition of vibronic transitions from two excited electronic states, parameters of these states being close to those of the radiation transitions from the $^3(\pi–\pi^*_{N\wedge C})$ state of the [Pd(N^C)phen]$^+$ complexes, on the one hand, and of the transitions from the $^3(\pi–\pi^*_{diaz})$ state of electrons localized on the diazine part of free (N^N) ligands, on the other. Thus, despite of the thermodynamic favorableness of the energy transfer in the lowest in energy electronic excited state, the weak electronic interaction of electron-excited states of spatially separated (N^N) and {Pd(N^C)} fragments results in a low efficiency of energy transfer between them and in a presumably isolated character of energy radiation, which is the reason that determines the appearance of the low-temperature multiluminescence of [Pd(N^C)·(N^N)]$^+$ complexes. A strong temperature luminescence quenching characteristic of intraligand electron transitions from the $^3(\pi–\pi^*_{N\wedge C})$ and $^3(\pi–\pi^*_{diaz})$ states of [Pd(N^C)phen]$^+$ complexes results in its absence from liquid (293 K) solutions of [Pd(N^C)(N^N)]$^+$ complexes.

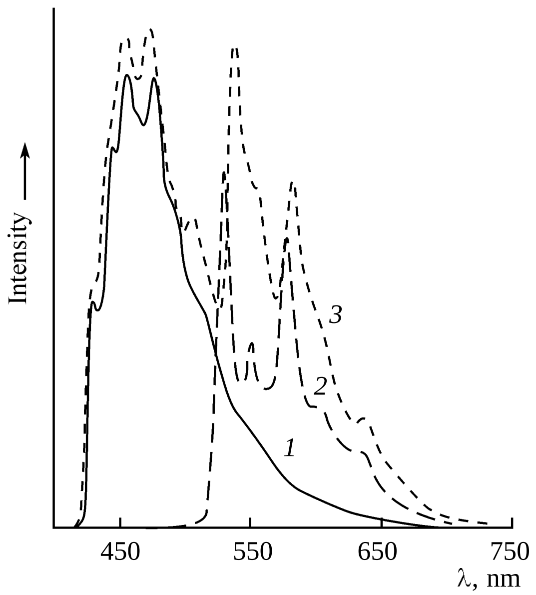


Fig. 2. Luminescent spectra (77 K, DMF–toluene, 1:1). (*1*) dpq, (*2*) [Pd(tpy)phen]$^+$, (*3*) [Pd(tpy)dpq]$^+$.

EXPERIMENTAL

The ^{1}H NMR spectra and the electronic absorption spectra were taken on a Bruker AC-200F spectrometer and an SF-2000 spectrophotometer at 298 K in $(CD_3)_2SO$ and DMF solutions, respectively. The luminescent experiments were carried out on an SDL-2 spectrometer and a KSVU-1 installation with a pulse photoexcitation laser (LGI-21, λ 337 nm) at 77 K in glassy DMF–toluene (1:1) matrixes and at 298 K in DMF solutions [10]. Parameters of cyclic voltammograms were determined on a modified SBA-1B installation at 298 K in a three-electrode cell with separated compartments of a working (Pt), an auxiliary (Pt), and a reference (Ag) electrodes in the presence of a 0.1 M $[N(C_4H_9)_4]ClO_4$ solution in DMF [8]. Half-wave and current peak potentials are given in relation to the ferrocenium-ferrocene redox system.

Dipyrido-substituted 1,4-diazines were obtained by the condensation of 1,10-phenantroline-5,6-dion with the corresponding diamines: ethylenediamine (dpq), orthophenylenediamine (dppz), and diaminomaleonitrile (dicnq) [11–13]. The complexes [Pd(N^C)·(N^N)]NO_3 [(N^C) = ppy, tpy; (N^N) = phen, dpq, dppz, dicnq] were synthesized by the modified technique [5] as a result of reactions of preliminarily obtained complexes [Pd(N^C)(μ-Cl)]$_2$ [3] with $AgNO_3$ in an acetonitrile solution after removal of an AgCl precipitate and addition of an (N^N) ligand to the resulting solution.

(1,10-Phenantroline)[2-(2-pyridyl)thiophene-3-ido]palladium(II) nitrate [Pd(tpy)phen]NO_3. Yield 58%. ^1H NMR spectrum (CD_3OD), δ, ppm (^3J, Hz): 9.45 ($H^{\alpha/\alpha'}$, *J* 3.5), 9.04 ($H^{\gamma,\gamma'}$ *J* 8.1), 8.81 (H^6, *J* 4.6), 8.36 ($H^{\delta}/H^{\delta'}$), 8.22 ($H^{\beta/\beta'}$), 8.12 (H^4, *J* 8.1), 7.80 (H^3), 7.83 ($H^{4'}$, *J* 5.8), 7.55 ($H^{3'}$, *J* 4.6), 7.41 (H^5, *J* 6.9).

(Dipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)thiophene-3-ido]palladium(II) nitrate [Pd(tpy)(dpq)]·NO_3. Yield 53%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.49 ($H^{\alpha/\alpha'}$, *J* 4.8), 9.74 ($H^{\gamma,\gamma'}$, *J* 8.6), 9.36 ($H^{\delta/\delta'}$), 8.74 (H^6, *J* 5.7), 8.32 ($H^{\beta/\beta'}$, *J* 5.0, 8.0), 8.07 (H^4, *J* 7.6), 7.75 ($H^{4'}$, *J* 4.8), 7.61 (H^3, *J* 7.6), 7.47 ($H^{3'}$, *J* 4.8) 7.37 (H^5, *J* 7.6, 5.7).

(Dipyrido[*a,c*]phenazine)[2-(2-pyridyl)-thiophene-3-ido]palladium(II) nitrate [Pd(tpy)(dppz)]·NO_3. Yield 56%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.72 ($H^{\gamma,\gamma'}$, *J* 7.9), 9.38 ($H^{\alpha/\alpha'}$, *J* 3.5), 8.70 (H^6, *J* 4.9), 8.36 ($H^{\delta/\delta'}$, *J* 3.5, 6.3), 8.30 ($H^{\delta/\delta'}$, *J* 7.1, 5.7), 8.35 ($H^{\beta/\beta'}$), 8.18 ($H^{\varepsilon/\varepsilon'}$, *J* 3.5, 6.6), 8.06 ($H^4$, *J* 7.1), 7.74 ($H^{4'}$, *J* 4.9), 7.60 ($H^3$, *J* 7.1), 7.44 ($H^{3'}$, *J* 4.4), 7.35 ($H^5$, *J* 5.7, 7.1).

(6,7-Dicyanodipyrido[*f,h*]quinoxaline)[2-(2-pyridyl)thiophene-3-ido]palladium(II) nitrate [Pd(tpy)(dicnq)]NO_3. Yield 40%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.77 ($H^{\gamma,\gamma'}$, *J* 8.6), 9.62 ($H^{\alpha/\alpha'}$, *J* 4.8), 8.77 (H^6, *J* 5.7), 8.39 ($H^{\beta/\beta'}$, *J* 5.7, 8.6), 8.07 (H^4, *J* 7.6), 7.78 ($H^{4'}$, *J* 4.8), 7.65 (H^3, *J* 7.6), 7.50 ($H^{3'}$, *J* 5.7), 7.37 (H^5, *J* 5.7, 7.6).

(1,10-Phenantroline)[2-pyridyl)phenyl-1-ido]palladium(II) nitrate [Pd(ppy)phen]NO_3. Yield 65%. ^1H NMR spectrum (CD_3OD), δ, ppm (^3J, Hz): 9.39 $H^{\alpha/\alpha'}$, 8.99 ($H^{\gamma,\gamma'}$, *J* 3.5), 8.84 (H^6, *J* 5.8), 8.34 ($H^{\delta/\delta'}$), 8.17 ($H^{\beta/\beta',4,3}$, 7.74 ($H^{6'}$, *J* 3.5), 7.53 ($H^{4'}$, *J* 7.6), 7.34 (H^5), 7.24 ($H^{3',5'}$).

(Dipyrido[*f,h*]quinoxaline)[(2-pyridyl)pheny-2-ido]palladium(II) nitrate [Pd(ppy)(dpq)]NO_3. Yield 55%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.58 ($H^{\gamma,\gamma'}$, *J* 7.6), 9.37 ($H^{\alpha/\alpha'}$, *J* 3.8), 9.34 ($H^{\delta/\delta'}$), 8.68 (H^6, *J* 5.7), 8.22 ($H^{\beta/\beta'}$, *J* 7.6, 4.8), 8.09 (H^4, *J* 7.6), 7.87 (H^3, *J* 7.6), 7.34 ($H^{6d'}$, *J* 6.7), 7.45 ($H^{4'}$, *J* 6.7), 7.12 ($H^{3'}$, *J* 7.6), 7.03 (H^5, *J* 7.6), 7.00 ($H^{5'}$, *J* 6.7).

(Dipyrido[*a,c*]phenazine)[2-pyridyl)-phenyl-2-ido]palladium(II) nitrate [Pd(ppy)(dppz)]NO_3. Yield 50%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.82 ($H^{\gamma,\gamma'}$, *J* 8.4), 9.47 ($H^{\alpha/\alpha'}$, *J* 4.8), 8.86 (H^6, *J* 6.0), 8.44 ($H^{\delta/\delta'}$, *J* 3.6, 6.0), 8.36 ($H^{\beta/\beta'}$, *J* 3.6, 8.4), 8.17 ($H^{\varepsilon/\varepsilon'}$), 8.21 ($H^3$, *J* 7.2), 7.74 ($H^{6'}$, *J* 7.2), 7.57 ($H^{4'}$, *J* 7.2, 6.0), 7.34 ($H^{3'}$, *J* 8.0), 7.27 ($H^5$, *J* 7.2), 7.25 ($H^{5'}$, *J* 7.2).

(6,7-Dicyanodipyrido[*f,h*]quinoxaline)[(2-pyridyl)phenyl-2-ido]palladium(II) nitrate [Pd(ppy)·(dicnq)]NO_3. Yield 40%. ^1H NMR spectrum, δ, ppm (^3J, Hz): 9.73 ($H^{\gamma,\gamma'}$, *J* 8.4), 9.59 ($H^{\alpha/\alpha'}$, *J* 3.2), 8.83 (H^6, *J* 4.8), 8.38 ($H^{\beta/\beta'}$), 8.21 (H^4, *J* 7.6), 8.07 (H^3, *J* 7.6), 7.61 ($H^{6'}$), 7.56 ($H^{4'}$), 7.26 ($H^{3'}$), 7.17 ($H^{5,5'}$).

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