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Cyclopalladated Ethylenediamine Complexes on the Basis of 4-Phenylpyrimidine and 4,6-Diphenylpyrimidine

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Abstract—Mono- and binuclear cyclopalladated complexes $[Pd(ppm)En]ClO_4$, $[Pd(Hdphpm)En]ClO_4$, and $[(PdEn)_2(\mu\text{-dphpm})]ClO_4$ (ppm^- is the deprotonated form of 4-phenylpyridine, $Hdphpm^-$ and $dphpm^{2-}$ are the mono- and bisdeprotonated forms of 4,6-diphenylpyrimidine, En is 1,2-diaminoethane) were prepared and characterized by means of ^1H NMR and electronic absorption and emission spectroscopy, and cyclic voltammetry. It was shown that cyclopalladation leads to a bathochromic shift of intraligand absorption and phosphorescence bands, appearance of new absorption band associated with metal-to-ligand charge transfer, and an anodic potential shift of the ligand-centered electroreduction $Hppm \approx H_2dphpm < [Pd(ppm)En]^+ \approx [Pd(Hdphpm)En]^+ < [(PdEn)_2(\mu\text{-dphpm})]^{2+}$.

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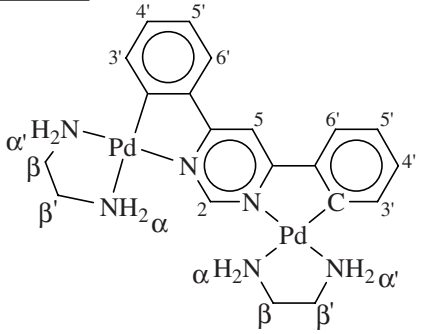
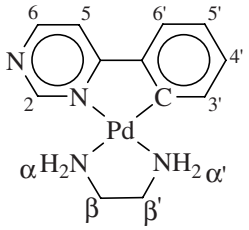
Cyclopalladated complexes with heterocyclic ligands are promising compounds for creation of photoactive molecularly organized metal complex systems and devices on their basis [1, 2]. Of special interest are polydentate bridging ligands capable of forming polynuclear complexes. Contrary to the previously studied complexes of 2,3-diphenyl-substituted 1,4-diazines, where steric interactions of phenyl rings predetermines preferential formation of mononuclear cyclopalladated complexes [3-5], using 4,6-diphenylpyrimidine one can expect formation not only of mono-, but also of binuclear complexes.

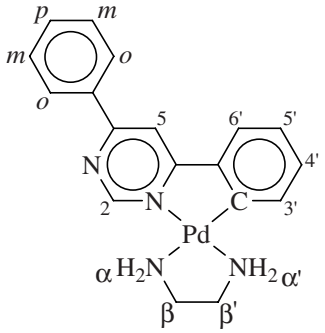
The present work deals with the synthesis, identification, and comparative spectroscopic and electrochemical study of mono- and biscyclopalladated complexes on the basis of 4-phenylpyrimidine and 4,6-diphenylpyrimidine, $[Pd(ppm)En]ClO_4$, $[Pd(Hdphpm)\cdot En]ClO_4$, and $[(PdEn)_2(\mu\text{-dphpm})](ClO_4)_2$ (see scheme).



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



$[Pd(ppm)En]^+$



$[Pd(Hdphpm)En]^+$

Mono- and biscyclopalladated complexes were obtained by the reaction of phenyl-substituted pyrimidine ligands with one or two equiv of $Li_2[PdCl_4]$, followed by substitutionof the bridging chloride ligands in $[Pd(ppm)(\mu\text{-Cl})]_2$, $[Pd(Hdphpm)(\mu\text{-Cl})]_2$ and $Pd(\mu\text{-dphpm})(\mu\text{-Cl})]_n$ by ethylenediamine.

The cationic complexes obtained are stable in the solid state and in various solvents (CH_3CN, DMSO, DMF).

The ^1H NMR spectra of the complexes confirm the structure and coordination mode of the ligands. The coordination-induced chemical shifts of ligand protons ($\Delta\delta = \delta_c - \delta_l$) reflect the trend in variation of the chemical shifts of the latter due to donor–acceptor interactions with the metal (Table 1) and show that, in response to the σ-donor effect of the latter, complex formation produces a significant and practically constant deshielding of ethylenediamine protons [$\Delta\delta(H^{\alpha}) = (3.01 \pm 0.06)$, $\Delta\delta(H)^{\beta} = (2.37 \pm 0.08)$ ppm] both in mono- and in binuclear complexes. The different *trans* effects of the carbanionic and pyrimidine parts of the cyclometallated ligands are responsible for the magnetic nonequivalence of the ethylenediamine protons H^{α} and H^{β}. The monocyclopalladated complex [Pd(Hdphpm)En]ClO_4 complex contains a free and a coordinated phenyl substituents in 4,6-diphenylpyrimidine; in agreement with this, the proton chemical shifts in the former ring change insignificantly ($\Delta\delta < 0.04$ ppm), whereas those in the latter ring change like in [Ph(ppm)En]ClO_4. The H^2 protons of the pyrimidine part of the cyclometallated ligands in [Pd(ppm)En]ClO_4 and [Pd(Hdphpm)En]·ClO_4, which are closest to palladium, too, undergo deshielding [$\Delta\delta(H^2)$ –0.41 ppm].

The binuclear symmetric structure of [$(PdEn)_2$(μ-dphpm)]$(ClO_4)_2$ predetermines magnetic equivalence both of two coordinated phenyl rings of 4,6-diphenylpyrimidine and of two ethylenediamine ligands; therewith, the coordination-induced chemical shifts of protons are close to those in the mononuclear complexes [Pd(ppm)En]ClO_4 and [Pd(Hdphpm)En]·ClO_4. At the same time, biscyclopalladation much enhances proton shielding in the pyrimidine part of the cyclopalladated ligand [$\Delta\delta(H^2)$ –0.90 and $\Delta\delta$ (H^5) –0.24 ppm].

The localized molecular orbitals model [7] treats electrochemical and optical properties of mixed-ligand complexes as metal- and ligands centers, taking into account preferred localization of participating orbitals. Therewith, provided the Koopmans theorem [7] is fulfilled, the orbital nature of redox and spectroscopic LUMOs and HOMOs of complexes is similar.

The voltammograms of one-electron electroreduction of cyclopalladated complexes and heterocyclic ligands (Table 2) give evidence showing that the process is ligand-centered and involves

Table 1. Coordination-induced chemical shifts ($\Delta\delta = \delta_c - \delta_l$, ppm) of cyclopalladated complexes in CD_3CN

H	$[Pd(ppm)En]^+$	$[Pd(Hdphpm)En]^+$	$[(PdEn)_2(\mu\text{-dphpm})]^{2+}$
2	–0.41	–0.41	–0.90
5	0.04	–0.06	–0.24
6	–0.06	–	–
3'	–0.52	–0.52	–0.52
4'	–0.32	–0.3	–0.24
5'	–0.34	–0.3	–0.24
6'	–0.31	–0.32	–0.36
2''	–	0.02	–
3''	–	0.04	–0.52
4''	–	0.04	–0.24
5''	–	0.04	–0.24
6''	–	0.02	–0.36
α	2.95	3.01	3.06
β	2.29	2.45	2.37
γ	0.48	0.34	0.37

electron transfer on the π* orbitals mainly localized on the pyrimidine part of the ligand. Cyclopalladation induces a regular anodic shift of the electroreduction potential in the series: Hppm ≈ H_2dphpm < [Pd(ppm)·En]$^+$ ≈ [Pd(Hdphpm)En]$^+$ < $[(PdEn)_2(\mu\text{-dphpm})]^{2+}$. Unlike Hppm, H_2dphpm, and $[Pd(ppm)En]^+$, which undergo irreversible electroreduction, the reduction voltammograms of $[Pd(Hdphpm)En]^+$ and $[(PdEn)_2(\mu\text{-dphpm})]^{2+}$ are reversible (Fig. 1). Consequently, the one-electron reduction products of these two complexes are relatively stable. The anodic shift of the half-wave reduction potential ($E_{1/2}$) of dimeric complexes as compared to monomeric shows that the energy of the LUMO localized mainly on the pyrimidine part of the cylcometallated ligand in these complexes decreases by 0.33 eV.

The irreversible waves of electrooxidation of complexes are attributed to the metal-centered character of the process, which is explained by a high rate of subsequent chemical reactions of primary electrooxidation products: highly reactive Pd(III) complexes.

Comparison of the electronic absorption spectra of free ligands and cyclopalladated complexes shows (Fig. 2) that, along with the batochromic shift of intraligand π–π* optical transitions in phenyl-substituted pyrimidine ligands, cyclopalladation gives rise to a new long-wave spin-allowed absorption band (Table 2) corresponding to the optical transition

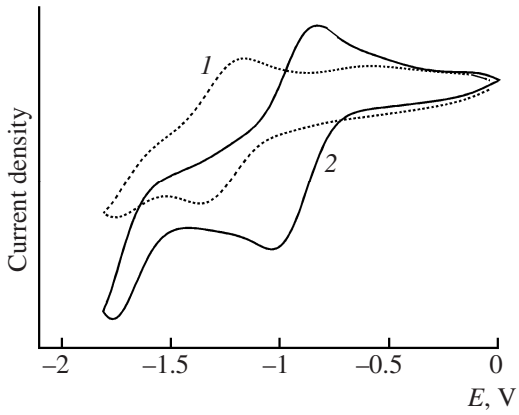


Fig. 1. Reduction voltammograms: (*1*) [Pd(Hdphpm)En] ClO_4 and (*2*) $[(PdEn)_2(\mu\text{-dphpm})](ClO_4)_2$.

between the metal-centered HOMO (d_{Pd}) and ligand-centered LUMO(π*) of complexes (d–π* charge transfer). In agreement with the electrochemical characteristics, the mononuclear $[Pd(Hphpm)En]^+$ and $[Pd(ppm)En]^+$ complexes have practically constant parameters of the new absorption band (λ ~354 nm, ε ~5×10^3 mol^{-1} cm^{-1}), whereas the formation of the binuclear $[(Pd(Hdphpm)En]^{2+}$ complex induces a batochromic shift and enhancement of the band (λ 389 nm, ε 11 × 10^3 mol^{-1} cm^{-1}). The energy of the HOMO–LUMO optical transition in $[(PdEn)_2(\mu\text{-dphpm})]^{2+}$ in lower by 0.31 eV than in $[Pd(Hdphpm)En]^+$, which agrees well with the decrease of 0.33 eV for the LUMO energy, established by electrochemical data.

The vibrationally structured (ν 1.4 kK) low temperature (77 K) luminescence spectra of cyclopalladated complexes (Fig. 3) are attributed to spin-forbidden intraligand optical transitions between LUMO and HOMO, localized mainly on the cyclometallated ligand. This is confirmed (Table 2) by

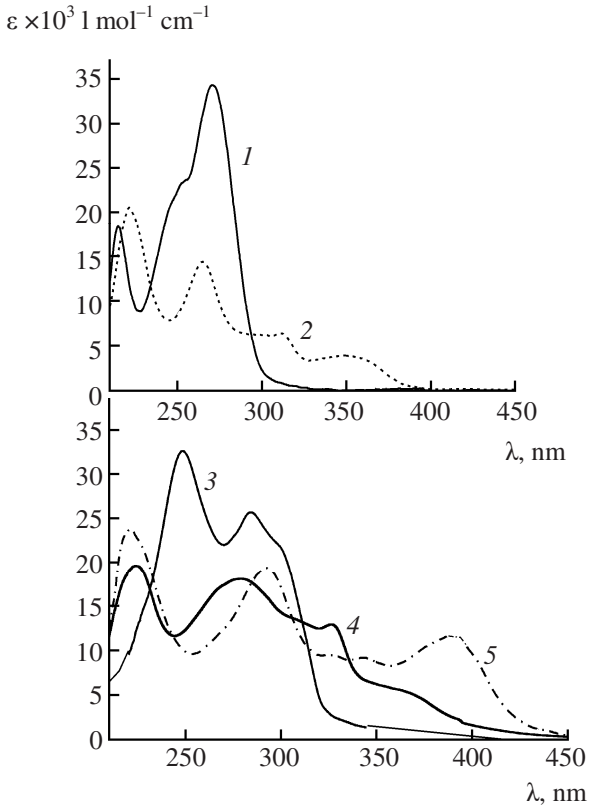


Fig. 2. Electronic absorption spectra: (*1*) Hppm, (*2*) [Pd(ppm)En]ClO_4, (*3*) H_2dphpm, (*4*) [Pd(Hdphpm)En]ClO_4, and (*5*) $[(PdEn)_2(\mu\text{-dphpm})](ClO_4)_2$.

the typical fluorescence extinguishment time (τ~10^{-4} s) and the relatively small bathochromic shift of the luminescence spectra of mononuclear complexes as compared to free pyrimidine ligands [Δλ (27 ± 4) nm]. Contrary to a 0.31-eV decrease in the energy of the spin-allowed transition between the metal-centered HOMO and ligand-centered LUMO in $[(PdEn)_2(\mu\text{-dphpm})^{2+}$ as compared to $[Pd(Hdphpm)En]^+$, the

Table 2. Optical and electrochemical parameters of cyclopalladated complexes

Compound	Absorption[a]	Luminescence[b]	Voltammogram	
	λ_{max}, nm (ε × 10^3, mol^{-1} cm^{-1})	λ_{max}, nm (τ, μs)	$-E_{1/2}^{red}$, V[c]	E_p, V[d]
Hppm	215 (18), 253 (24), 271 (34)	434, 465, 491, 512	2.40[e]	–
H_2dphpm	248 (33), 284 (26), 300 sh (21.6)	423, 452, 478, 508 sh	2.45[e]	–
$[Pd(ppm)En]^+$	222 (21), 265 (14), 304 sh (6.3), 312 (6.4), 353 (3.8)	457, 489, 517, 551 sh, 613 (140)	2.06[e]	0.31
$[Pd(Hdphpm)En]^+$	223 (19.6), 227 sh (18), 327 (13), 355 (6)	454, 490, 515, 550 sh (70)	1.85	0.15
$[(PdEn)_2(\mu\text{-dphpm})]^{2+}$	220 (23.6), 292 (19), 326 (9.5), 343 (9.1), 389 (11)	478, 512, 542 (43)	1.52	0.05

[a] Acetonitrile, 293 K. [b] DMF–toluene 1 : 1, 77 K. [c] DMF, 293 K. [d] .Acetonitrile, 293 K. [e] Peak current potential at the sweep rate 100 mV s^{-1}.

energy of spin-forbidden transitions responsible for phosphorescence decreases by only 0.14 eV. The difference in the orbital nature of the low-energy spin-allowed (d–π^*) and spin-forbidden (π–π^*) optical transitions responsible for the low-wave absorption and phosphorescence of cyclopalladated complexes is explained by the fact that the singlet–triplet splitting energy of intraligand (π–π^*) transitions is larger compared to (d–π^*) charge-transfer transitions [8].

The absence of luminescence of cyclopalladated complexes in solutions at room temperature suggests an effective thermally-activated process nonradiative degradation of photoexcitation energy, probably involving population of a high-energy metal-centered state of the $^3(d$–$d^*)$ type.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on a Bruker AC-200F spectrometer. The electronic absorption spectra were obtained on an SF-2001 spectrophotometer at 298 K. The luminescence parameters were measured at 77K in frozen glassy 1:1 DMF–toluene solutions on a KSVU-1 device with pulse photoexcitation [LGI-21 nitrogen laser (λ 337 nm, τ 10 ns)] [11]. The oxidation and reduction voltammograms were obtained at 293 K in DMF and acetonitrile solutions on a computerized SVA-1B device in a three-electrode cell with separated working (Pt), auxiliary (C), and reference (Ag) electrode compartments in the presence of 0.1 M [N$(C_4H_9)_4$]ClO_4 at the potential sweep rate 100 mV s^{-1}, according to the procedure in [12]. The potentials are presented against the ferrocenium–ferrocene redox system.

4,6-Diphenylpyrimidine was prepared by the reaction of dibenzoylmethane with formamide according to the procedure in [9]. Yield 35%, ^{1}H NMR spectrum, δ, ppm (J, Hz): 9.26 d (H^2, $^3J_{HH}$ 1.5), 8.38 s (H^5), 8.30 d ($4H^o$, $^3J_{HH}$ 6.5), 7.60 m ($6H^{o,m}$).

Cyclopalladated complexes were prepared by a common procedure, involving reaction of a methanolic suspension of prepared $[Pd(ppm)(\mu\text{-}Cl)]^2$, $[Pd(Hdphpm)(\mu\text{-}Cl)]_2$, and $[Pd(\mu\text{-}dphpm)(\mu\text{-}Cl)]_n$ [10] with an equivalent amount of ethylenediamine. The solution obtained was filtered, and the resulting complex was precipitated by treatment with saturated methanolic $NaClO_4$. The precipitate was filtered off, washed with methanol and ether, and dried in a vacuum.

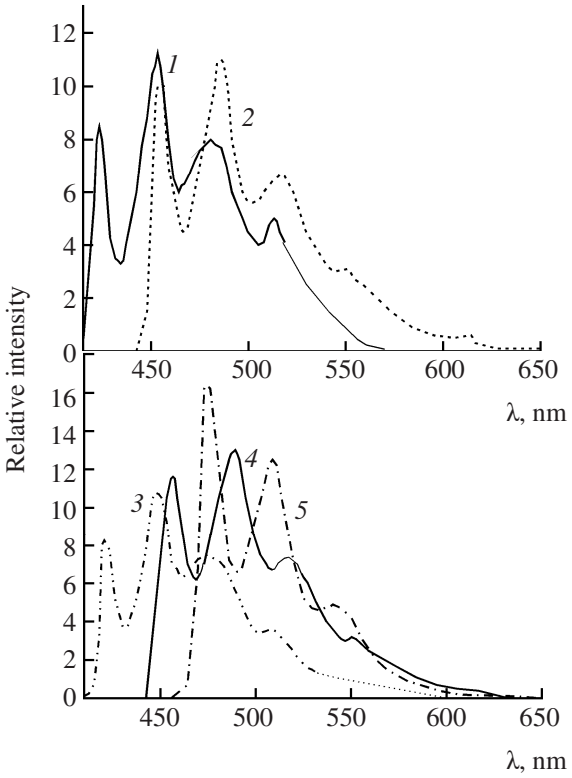


Fig. 3. Luminescence spectra: (*1*) Hppm, (*2*) [Pd(ppm)En]·ClO_4, (*3*) H_2dphpm, (*4*) [Pd(Hdphpm)En]$(ClO_4)_2$, and (*5*) $[(PdEn)_2(\mu\text{-dphpm})](ClO_4)_2$.

[(4-Phenyl-3-ido)pyrimidin](ethylenediamine)-palladium(II) perchlorate. Yield 60%. ^{1}H NMR spectrum (CD_3CN), δ, ppm (J, Hz): 8.84 d (H^5, $^3J_{HH}$ 5.5), 8.82 s (H^2), 7.85 d (H^4, $^1J_{HH}$ 5.5), 7.78 m ($H^{6'}$), 7.26 t.d ($H^{4'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.4), 7.24 t.d ($H^{5'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.4), 7.06 m ($H^{3'}$), 4.10 s ($2H^{\alpha}$), 3.44 s ($2H^{\beta}$), 3.05 s ($4H^{\gamma}$).

[(4-Phenyl-3-ido)(6-phenyl)pyrimidin](ethylenediamine)palladium(II) perchlorate. Yield 40%. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm (J, Hz): 8.85 s (H^2), 8.32 s (H^5), 8.31 m ($2H^o$), 7.98 d ($H^{6'}$, $^3J_{HH}$ 4.4), 7.28 m ($2H^{4',5'}$), 7.08 m ($H^{3'}$), 4.16 s ($2H^{\alpha}$), 3.50 s ($2H^{\beta}$), 2.91 s ($4H^{\gamma}$).

[(μ-4,6-Diphenyl-3,3'-ido)pyrimidin](bisethylenediamine)dipalladium(II) perchlorate. Yield 80%. ^{1}H NMR spectrum (CD_3CN), δ, ppm (J, Hz): 8.36 s (H^2), 8.14 s (H^5), 7.93 d ($2H^{6'}$, $^3J_{HH}$ 8.7), 7.34 m ($4H^{4',5'}$), 7.08 d ($H^{3'}$, $^3J_{HH}$ 8.7), 4.16 s ($4H^{\alpha}$), 3.50 s ($4H^{\beta}$), 2.91 s ($8H^{\gamma}$).

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