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Spectral-luminescence properties of cyclometallated Pd(II) complexes based on cinchophen methyl ester

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A procedure of synthesis of Pd(II) complexes with 2-phenylquinoline-4-carboxylic acid methyl ester: PdMpqc(μ-Ac)]$_2$ and [PdEnMpqc]BF$_4$, where Mpqc is methyl 2-phenyl-4-quinolinecarboxylate ion, Ac — acetate ion, En — ethylenediamine, was developed. The composition and structure of the complexes obtained were established on the basis of IR and polynuclear NMR spectroscopy data, optical and physical properties were described on the basis of UV and fluorescence spectroscopy. The phosphorescence of Pd(II) complexes in the visible region was assigned to the radiative transition from the spin-forbidden intraligand electronically excited state $^3(\pi - \pi)$ that is localized on the aromatic Mpqc system.

Keywords: Pd(II) complexes, methyl 2-phenyl-4-quinolinecarboxylate, NMR spectroscopy, spectral-luminescence properties.

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Cinchophen (2-phenylcinchoninic acid) and its derivatives have been known since the end of the 19th century. The introduction of various substituents into the cinchophen molecule facilitates the reduction of toxicity, increasing the solubility, absorption capacity, transport through the bloodstream and, as a result, broadening of the spectrum of pharmacological action (painkillers, antipyretics, anti-gout, antimicrobial and anti-cancer agents) [1–4].

The presence of oxygen and nitrogen atoms in the cinchophen molecule facilitates its complex formation with some d-metals. Thus, the Zn(II) and Cd(II) cations are connected through the oxygen atoms of the carboxyl group [5,6], while Au(III) and the platinum group metals Pt(II), Pd(II), Rh(III), Ir(III) are coordinated through nitrogen and the deprotonated carbon of the phenyl ring [7–12]. However, photophysical characteristics have been studied in detail only for octahedral Ir(III), Rh(III) and square planar Pt(II) complexes [8,10–12]. Metallated cinchophens are part of a large community of cyclometallated complexes, whose intensive luminescence, combined with the feature of the electronic structure, attracts the attention of researchers in the development of light-inducing devices (like OLED) [13], sensors for molecular oxygen [14], ions of heavy elements [15], pH, luminescent markers of biomolecules [11], and are also used for photodynamic therapy [16].

However, for the electronic analogue of Pt(II) — complexes of Pd(II) with cinchophen, there are no luminescent studies [9]. This paper presents the results of spectral-luminescent studies of the compounds [PdMpqc(μ-Ac)]$_2$ (**2**) and [PdEnMpqc]BF$_4$ (**3**), where Mpqc is deprotonated form of methyl-2-phenyl-4-quinolinecarboxylate-ion, Ac is acetate-ion, En is ethylenediamine (Fig. 1).

Experimental part

Spectral studies were performed using the equipment of the Center for Collective Use of the Department of Chemistry of the Herzen State Pedagogical University of Russia. ^{1}H, ^{13}C{^{1}H} NMR, ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC and ^{1}H-^{15} N HMBC spectra were registered on Jeol ECX400A spectrometer with operating frequencies of 399.78 (^{1}H), 100.53 (^{13}C) and 40.52 MHz (^{15}N); solvent — DMSO-d_6. The residual proton signals of the non-deuterated solvent were used as internal standard. Chemical shifts ^{15}N were determined relative to CH$_3$NO$_2$. IR spectra were obtained on Shimadzu IR-Prestige-21 Fourier spectrometer in KBr pellets. Electronic absorption spectra were obtained at room temperature in 96% ethanol using SF-2000 („OKB Spektr“, St. Petersburg, Russia). Luminescence studies were carried out at 77 K on Fluorat-02-Panorama spectrofluorimeter (GC „Lumex“, St. Petersburg, Russia).

Methyl 2-phenylquinoline-4-carboxylate (HMpqc), ammonium tetrafluoroborate (NH$_4$BF$_4$) (commercial substances, Sigma-Aldrich, „Neva reagent“) were used without further purification. All solvents were purified using standard procedures [17].

The complex **2** was obtained by heating 89 mg (0.4 mmol) of palladium acetate Pd(Ac)$_2$ and 105 mg (0.4 mmol) **1** in glacial acetic acid (5.0 ml). The progress of the chemical reaction was discussed by the color change of the solution from brown to red and the precipitate formation upon evaporating the reaction mixture by half. The precipitate collected on the filter and washed with cold dichloromethane was dried in air to constant weight. The weight of the product was 150 mg, the yield was 90%.

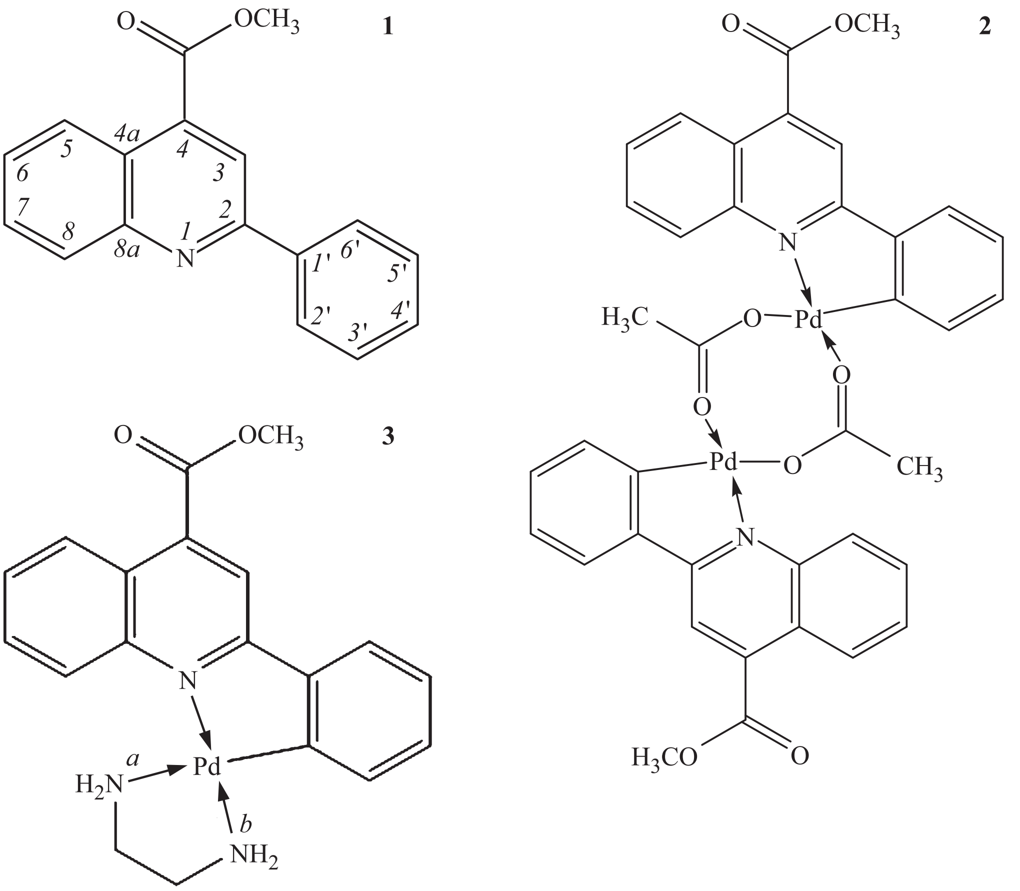

Figure 1. Structural formulas of methyl 2-phenylquinoline-4-carboxylate (**1**) and cyclopalladized complexes: [PdMpqc(μ-Ac)]$_2$ (**2**) and [PdEnMpqc]BF$_4$ (**3**).

The synthesis of the **3** complex consisted of two stages. First, to a suspension consisting of 20 mg (0.023 mmol) **2** and 8 ml of warm methanol (50°C) 0.2 ml of 0.24 mol/l aqueous solution of ethylenediamine was added. Dissolution of **2**, and color change of the solution from red to yellow were observed. Next, a saturated solution of ammonium tetrafluoroborate was added to the resulting warm solution until the precipitate began to form. After the suspension was cooled to room temperature, the precipitate was collected on the filter, washed with cold methanol, and dried in air to constant weight. The weight of the product was 20 mg, the yield was 81%.

Methyl 2-phenylquinoline-4-carboxylate (HMpqc, 1). ^{1}H NMR spectrum, δ, ppm: 3.97 s (3H, CH$_3$), 7.45–7.55 m (3H, H$^{3',4',5'}$), 7.64 d. d. d. (1H, H^6, $^3J_{5,6}$ 8.50, $^3J_{6,7}$ 6.95, $^4J_{6,8}$ 1.35 Hz), 7.79 d. d. d. (1H, H^7, $^3J_{7,8}$ 8.45, $^3J_{6,7}$ 6.95, $^4J_{5,7}$ 1.25 Hz), 8.10 d. d. d. (1H, H^8, $^3J_{7,8}$ 8.45, $^4J_{6,8}$ 1.35, $^5J_{5,8}$ 0.50 Hz), 8.19–8.24 m (2H, H$^{2',6'}$), 8.39 s (H^3), 8.51 d. d. d. (1H, H^5, $^3J_{5,6}$ 8.50, $^4J_{5,7}$ 1.25, $^5J_{5,8}$ 0.50 Hz). ^{13}C{^{1}H} NMR spectrum, δ, ppm: 53.43 (CH^3), 119.88 (C^3), 123.67 (C^4), 125.61 (C^5), 127.71 (C$^{2',6'}$), 128.48 (C^6), 129.48 (C$^{3',5'}$), 130.35 (C^8), 130.55 (C$^{4'}$), 130.83 (C^7), 136.60 (C^{4a}), 138.24 (C$^{1'}$), 148.85 (C^{8a}), 156.20 (C^2), 166.75 (C=O). ^{15}N NMR spectrum, δ, ppm: −62.65.

Bis-((μ-acetate)-methyl-2-phenyl-4-quinolinecarboxylatopalladium(II)) (2). Poorly soluble red powder. ^{1}H NMR spectrum, δ, ppm: 2.11 s (3H, acetate), 4.11 s (3H, CH$_3$), 6.11 t (1H, J 6.41 Hz), 6.24 d (1H, J 6.71 Hz), 6.50 t (1H, J 6.30 Hz), 7.03 d (1H, J 7.32 Hz), 7.53 t (1H, J 7.20 Hz), 7.64 t (1H, J 7.10 Hz), 8.17 d (1H, J 8.24 Hz), 8.37 d (1H, J 7.93 Hz) (total 8H, benzene and quinoline rings). The ^{13}C{^{1}H} NMR spectrum could not be measured due to the low solubility of the compound. IR spectrum (KBr), ν, cm^{-1}: 1725 (O-C=O), 1367, 1267, 1247 (C=N/C=C). $C_{38}H_{30}N_2O_8Pd_2$, identified (%) C 53.47; H 3.53; N 3.28, calculated (%) C 53.40; H 3.51; N 3.28.

Methyl-2-phenyl-4-quinolinecarboxylatoethylenediaminepalladium(II) tetrafluoroborate (3). ^{1}H NMR spectrum, δ ppm: 2.58–2.64 m (2H, CH$_2$), 2.68–2.75 m (2H, CH$_2$), 4.03 s (3H, CH$_3$), 4.43 br. s (NH$_2^a$), 5.40 br. s (NH$_2^b$), 7.13–7.16 m (1H, H$^{3'}$), 7.16–7.25 m (2H, H$^{4',5'}$), 7.94–7.98 m (1H, H$^{6'}$), 7.76 d. d. d. (1H, H^6, $^3J_{5,6}$ 8.30, $^3J_{6,7}$ 7.10, $^4J_{6,8}$ 1.00 Hz), 7.85 d. d. d. (1H, H^7, $^3J_{7,8}$ 8.54, $^3J_{6,7}$ 7.10, $^4J_{5,7}$ 1.30 Hz), 7.98 d (1H, H^8, $^3J_{7,8}$ 8.54), 8.44 d. d. (1H, H^5, $^3J_{5,6}$ 8.30, $^4J_{5,7}$ 1.30), 8.54 s (H^3). ^{13}C{^{1}H} NMR spectrum, δ, ppm: 44.47 (CH$_2$), 46.37 (CH$_2$), 53.95 (CH$_3$), 118.47 (C^3), 124.21 (C^4), 125.80 ($C^{5'}$), 126.36 (C^5), 126.65 (C^8), 127.17 ($C^{6'}$), 128.95 (C^6), 130.52 ($C^{4'}$), 132.54 (C^7), 134.08 ($C^{3'}$), 139.95 (C^{4a}), 146.55 ($C^{1'}$), 148.02 (C^{8a}), 156.39 (C^2), 16.12 (C=O), 166.61 ($C^{2'}$). ^{15}N NMR spectrum, δ, ppm: -142.06. IR spectrum (KBr), ν, cm^{-1}: 3335, 3278, 3258 (NH), 1728 (C-C=O), 1367, 1276, 1236 (C=N/C=C), 1122, 1109, 1080, 622 (B-F). $C_{19}H_{20}N_3O_2BF_4Pd$: identified (%) C 44.30; H 3.90; N 8.19, calculated (%) C 44.27; H 3.88; N 8.16.

Results and discussion

Complex compounds Pd(II) **2** and **3** were synthesized according to the following reactions:

$$2\,PdAc_2 + 2HMpqc = [PdMpqc(\mu\text{-}Ac)]_{2\downarrow} + 2CH_3COOH,$$

$$[PdMpqc(\mu\text{-}Ac)]_2 + 2En = 2[PdEnMpqc]Ac,$$

$$[PdEnMpqc]Ac + (NH_4)BF_4 = [PdEnMpqc]BF_4 + NH_4Ac.$$

The composition and structure of the compounds **2** and **3** were confirmed by IR and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopy involving homo- (^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY) and heteronuclear (^{1}H-^{13}C HMQC, ^{1}H-^{13}C HMBC and ^{1}H-^{15}N HMBC) experiments, as well as in comparison with the data of uncoordinated **1** (see supplementary materials).

In IR spectra **2, 3** there are characteristic frequencies of valence and deformation C=C-, C=N vibrations in the region of 1500−1200 cm^{-1}, N−H-vibrations in the region of 3350−3200 m^{-1}, vibrations of COO^--group — at 1720−1560 cm^{-1} and 1420−1240 cm^{-1}, as well as B-F vibrations of the tetrafluoroborate ion located in the outer sphere of the complex at 1100−1070 and 622 cm^{-1} [18] (see supplementary material).

The ^{1}H NMR spectrum of the compound **1** shows groups of phenyl proton signals ($H^{2'}$-$H^{6'}$) in the region 7.45−8.24 ppm, protons of the quinoline ring (H^1-H^8) in the region of 7.64-8.51 ppm, as well as protons of the methyl group (CH_3) at 3.97 ppm, which agrees with literature data [19–25]. The signal of H^3 proton of the quinoline ring in the *ortho*-position to the methylcarboxylate group, which manifests itself as a singlet at 8.39 ppm, is taken as a marker. In ^{1}H-^{1}H NOESY spectrum of the compound **1**, the cross-peaks between the signals of protons H^5/CH_3 and H^3/CH_3 indicate the conformational mobility of the ester fragment. Also attention is drawn to the cross-peak (also present in the spectrum of the compound **3**) between the signals of proton $H^3/H^{6'}$, which indicates their convergence in space — presence in the same plane.

The use of ^{1}H-^{13}C HMQC and ^{1}H-^{13}C HMBC spectroscopy made it possible to reliably identify protonated carbon atoms, and non-protonated carbon atoms — by analyzes of the cross-peaks (through 2−3 connections). In the ^{1}H-^{13}C HMBC spectrum of the compound **3**, the following cross-peaks important for identification should be noted:

– cross-peaks $H^{6'}/C^2$ ensure determination of C^2,

– cross-peaks $H^3/C^{1'}$, $H^{5'}/C^{1'}$, $H^{3'}/C^{1'}$ ensure determination of $C^{1'}$,

– cross-peaks H^3/C^4 ensure determination of C^4,

– cross-peaks H^3/C^{4a}, H^5/C^{4a} ensure determination of C^{4a},

– cross-peaks H^5/C^{8a}, H^7/C^{8a} ensure determination of C^{8a}.

– cross-peaks of protons and atoms of carbon of methylene groups of ethylendiamine (2.58-2.64/44.47 and 2.68-2.75/46.37 ppm).

Complex formation between **1** and Pd(II) was estimated by the coordination-induced shift of peaks ($CIS = \delta_{complex} - \delta_{ligand}$) of signals of hydrogen and carbon nuclei (Table 1). A positive CIS value indicates a downfield shift of the resonances, i.e. to the electron density decreasing on the atoms of Mpqc ligand. The highest CIS value was recorded for the $C^{2'}$ carbon atom, subjected to deprotonation and formed a chemical bond with palladium. The largest negative CIS value recorded for C^8 of quinoline ring indicates a high field shift of resonances and, consequently, the electron density increasing on the ligand atoms. This may be due to the π-dative interaction of palladium with the quinoline ring.

Also note the presence in the spectrum ^{1}H-^{1}H NOESY of complex **3** of cross-peaks between the signals of protons H^8/NH_2^a and $H^{3'}/NH_2^b$, which makes it possible to separate proton signals of non-equivalent amino groups. There is also a correlation between the signals of protons NH_2^a (4.43 ppm) and methylene protons at 2.58−2.64 ppm and the signals of protons NH_2^b (5.40 ppm) and methylene protons at 2.68−2.75 ppm. The spin-spin coupling of protons was proved by analysis of the spectra ^{1}H-^{1}H COSY by the presence of the corresponding cross-peaks. The totality of the data obtained allows us to state the planar location of the nitrogen atoms of ethylenediamine, the atoms of the phenyl and quinoline rings, and the central ion — Pd(II).

Using the method of ^{1}H-^{15}N HMBC-experiment (the presence cross-peak with proton H^8) permits to assign to nitrogen atoms of quinoline the chemical shift (δ_N) at -62.65 ppm in the free ligand (HMpqc) and -142.06 ppm in the compound **3**. Such values δ_N of signal of the nitrogen atom of the quinoline ring are in agreement with the literature data. For example, for unsubstituted quinoline -77.5 ppm [19], complex formation with a silver cation leads to high field shift by 23−30 ppm, -75 [20], -71.1 ppm [21], for 2-(4-methoxyphenyl)quinoline-4-carboxylic acid -68.23 ppm [22], 2-phenylquinoline -86.8 ppm [23]; for the palladium diacetate dimer obtained from 4-(2-bromophenoxy)-6-phenylquinoline, -191.3 ppm [24], for the dihydrobis(triphenylphosphine)rhodium(III), complex obtained from quinoline-2-carboxylic acid, -114.1 ppm [25]. Literature data relating nitromethane are given (if another standard was used in the article, then we recalculated the data, taking the chemical shift of nitromethane equal to 388 ppm relative to NH_3).

The electronic absorption and emission properties of compounds **1**−**3** can be considered within the framework

Table 1. Coordination-induced shifts (CIS, ppm) of carbon and hydrogen in the complex **3**; the numbering of atoms is shown in Fig. 1

Carbon	CH_3	$C^{1'}$	$C^{2/2'}$	$C^{3/3'}$	$C^{4/4a}$	C^5	C^6	C^7	$C^{8/8a}$	C=O
CIS	0.52	8.31	4.19/38.9	−0.96/3.6	0.54/3.35	0.75	0.47	1.67	−3.7/−0.63	−0.63

Hydrogen	CH_3	H^3	H^5	H^6	H^7	H^8
CIS	0.06	0.15	0.07	0.12	0.06	−0.12

Table 2. Spectral and luminescent characteristics of complexes and ligands

Compound	Absorption		Luminescence	
	λ_{max}, nm ($\varepsilon \cdot 10^3$, l/mol cm)	Assignment	λ_{max}, nm	τ, μs
1	337 (15.4)	$^1(\pi-\pi^*)$	400	–
2	350 (14.6)	$^1(\pi-\pi^*)$	556	100^{****}
	402 (7.3)	$^1(d-\pi^*)$	598^{***}	
	490 (1.4)	$^1(d-\pi^*)$		
3	352 (12.2)	$^1(\pi-\pi^*)$	556	135
	400 (7.0)	$^1(d-\pi^*)$	600^{***}	
$[IrDppb^*(Mpqc)_2]^+$ [11]	255^p (86)	$^1(\pi-\pi^*)$	620	0.43^{****}
	284 (31)	$^1(\pi-\pi^*)$		
	361 (14)	$^1(\pi-\pi^*)$		
$[PtDppb^*Mpqc]^+$ [11]	275^p (31)	$^1(\pi-\pi^*)$	620^p	0.38
	358 (8.3)	$^1(\pi-\pi^*)$	648	
	410^p (2.6)	$^1(d-\pi^*)$		
$[RhDppz^{**}(Mpqc)_2]^+$ [10]	278 (32.5)	$^1(\pi-\pi^*)$	576	0.128
	361 (12.0)	$^1(\pi-\pi^*)$		
	426 (1.8)	$^1(d-\pi^*)$		

Note. * Dppb — bis(diphenylphosphino)benzene, **Dppz — dipyrido[3,2-*a*:2',3'-*c*]phenazine, *** — magnitude of vibrational splitting ~ 1300 cm^{-1}, **** — non-monoexponential, ^{n} — shoulder.

of the theory of localized molecular orbitals [26], i. e. molecular orbitals are predominantly localized either on Pd(II) or on the Mpqc ligand (Table 2). Absorption spectra of compounds **1**–**3** in ethanol solution (Fig. 2) are characterized by a number of spin-allowed transitions of different intensity and orbital nature:

– in the short-wavelength region (below 360 nm), more intense ($\varepsilon > 10^4$ l/mol·cm) intraligand transitions (IL) are localized at aromatic system of the Mpqc fragment and are $^1(\pi-\pi^*)$-type transitions; in the spectra of complexes **2** and **3** due to complexation —deprotonation **1** and formation of C-Pd bond, the IL transitions are bathochromically shifted;

– in the longer wavelength region (more than 390 nm) less intense bands ($\varepsilon > 10^3$ l/mol·cm) of charge transfer from the metal to ligand (CTML) or $^1(d-\pi^*)$-type transitions, which are absent in the absorption spectrum **1**, appear.

The luminescence spectrum **1** at room temperature is symmetrical to the long-wavelength absorption band. The insignificant Stokes shift (~ 4700 cm^{-1}) and the nanosecond range of the luminescence lifetime allow us to state that the fluorescence **1** originates from the lowest spin-allowed IL state and is $^1(\pi-\pi^*)$-type transition.

All cyclometallated complexes Pd(II) are characterized by effective temperature decay of luminescence [27–29]. The **2** and **3** complexes luminesce only at 77 K and in a longer wavelength band than **1**. The agreement of the phosphorescence excitation spectra with the absorption spectra of the complexes and the exponential character of the phosphorescence decay indicate the occurrence of a radiative process of degradation of the photoexcitation energy from the lowest by energy electronically excited state of the complex **3**. Vibrational structure of low-temperature phosphorescence spectra of Pd(II) complexes with frequency of 1300 cm^{-1}, close to the frequency of stretching vibrations of bonds C=C/C=N Mpqc, and a relatively long decay time (135 μs) make it possible to attribute the phosphorescence of complexes to a spin-forbidden intraligand optical transition of $^3(\pi-\pi^*)$-type, predominantly localized on the aromatic system of Mpqc ligand.

The luminescence maximum of Pd(II) **2** and **3** complexes has a hypsochromic shift compared to the Rh(III), Pt(II), and Ir(III) complexes, which also contain the Mpqc ligand [8,10,11]. This is probably due to the influence of a number of factors: the nature and degree of metal oxidation, the difference in the donor-acceptor

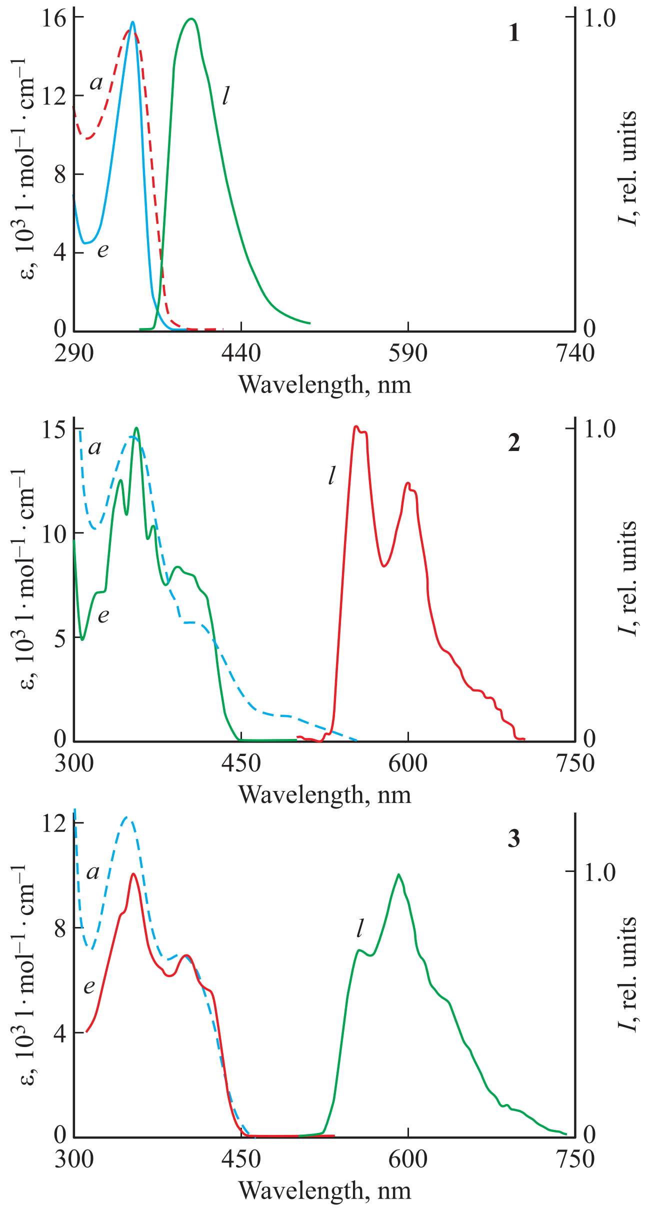

Figure 2. Absorption spectra (*a*) (at 290 K), normalized luminescence excitation spectra (*e*) and luminescence (*l*) of compounds **1**–**3** in ethanol at 77 K.

properties of the non-cinchofene ligand (ethylenediamine, bis(diphenylphosphino)benzene, dipyrido[3,2-*a*:2',3'-*c*]phenazine) [29].

Thus, complexation and the effect of the heavy atom Pd(II) led to the appearance of long-lived phosphorescence due to the aromatic system of Mpqc ligand.

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Conflict of interest

The authors declare that they have no conflict of interest.

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