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Spectroscopic and Electrochemical Properties of Dichlorodiimine Complexes of Au(III) and Pt(II) with 1,4-Diazine Derivatives of *o*-Phenanthroline

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Abstract—A series of dichlorodiimine complexes $[M(N^\wedge N)Cl_2]^z$ of Au(III) and Pt(II) with 1,4-derivatives of *o*-phenanthroline [(N^N) = *o*-phenanthroline (phen), dipyrido[*f*,*h*]quinoxaline (dpq), dipyrido[*a*,*c*]phenazine (dppz), 6,7-dicyanodipyrido[*f*,*h*]quinoxaline (dicnq)] were prepared and characterized by ^{1}H NMR, electronic absorption, and emission spectroscopy and by cyclic voltammetry. In all the complexes, the $^3(\pi–\pi^*)$-type transition is the spin-forbidden transition of the lowest energy, responsible for the luminescence. The longest wave bands in the absorption spectra of the Au(III) and Pd(II) complexes were assigned in accordance with the results of the electrochemical studies to the $^1(\pi–d^*)$- and $^1(d–\pi^*)$-type transitions, respectively.

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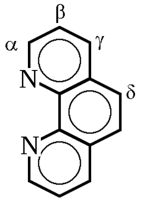
Coordination-unsaturated complexes of platinum metals with heterocyclic ligands are characterized, on the one hand, by long-lived electronically excited states and reversible outer-sphere electron transfer processes and, on the other hand, by the capability to form metal complex systems organized on the molecular level. These features make such complexes promising as structural components of artificial photosystems with directional transport of charge and energy [1–3]. Most of the data concerning the effect of the ligands and metal center on the optical and electrochemical properties of the complexes were obtained for octahedral polypyridine complexes of Ru(II), Os(II), Rh(III), and Ir(III), whereas the square-planar complexes of Au(III) and Pt(II), whose intercalation with nucleic acids [4–7] alters the optical and electrochemical properties of the complexes, were studied insufficiently.

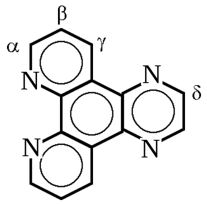
In this study we examined the spectroscopic and electrochemical properties of dichlorodiimine complexes $[M(N^\wedge N)Cl_2]^z$ [M = Au(III), Pt(II)] with 1,4-diazine derivatives of *o*-phenanthroline [(N^N) = *o*-phenanthroline (phen), dipyrido[*f*,*h*]quinoxaline (dpq), dipyrido[*a*,*c*]phenazine (dppz), 6,7-dicyanodipyrido[*f*,*h*]quinoxaline (dicnq)] in comparison with the properties of the free diimines (N^N) and dibenzo-substituted 1,4-diazines {dibenzo[*f*,*h*]quinoxaline (dbq), dibenzo[*a*,*c*]phenazine (dbpz), 6,7-dicyanodibenzo[*f*,*h*]quinoxaline (dicbq)}.

The electronic structure of dipyrido-substituted 1,4-diazines is determined by their two heterocyclic fragments: phenanthroline and diazine. In agreement with the results of quantum-chemical calculations of dppz [8], comparison of the spectroscopic and electrochemical characteristics (Tables 1, 2) of dipyrido-substituted 1,4-diazines with those of *o*-phenanthroline and dibenzo-substituted 1,4-diazines shows that the electronic interaction between the phenanthroline and diazine moieties of the (N^N) ligands is weak. The chemical shifts of the H^α and H^β protons in the phenanthroline moiety of the dipyrido-substituted ligands only slightly depend on the structure of diazine substituents and are close to those in *o*-phenanthroline ($\Delta\delta < 0.2 \pm 0.1$ ppm).

The optical and electrochemical properties of the (N^N) ligands are determined by the photo- and electrostimulated processes involving low-lying π* orbitals mainly localized on the phenanthroline (π^*_{phen}) and diazine (π^*_{diaz}) moieties. The voltammograms of the reduction of *o*-phenanthroline and its 1,4-diazine derivatives exhibit one-electron waves with virtually equal half-wave potentials (E -2.53 ± 0.03 V) (phen, dppz) or current peak potentials (dpq, dicnq), assigned to the electron transfer to the π^*_{phen} redox orbitals. At the same time, diazine derivatives of *o*-phenanthroline are characterized by additional anodically shifted reversible one-electron reduction waves with the half-wave potentials close to those of the one-electron reduction waves of the corresponding dibenzo derivatives of 1,4-diazines. This fact allows this reduction wave to be assigned to the electron transfer to the lowest energy π^*_{diaz} redox orbitals of the ligands. The π-acceptor benzo (dppz) and cyano (dicnq) substituents decrease the energy of the π^*_{diaz} redox orbitals and cause an anodic shift of the first reduction wave of the ligands in the series dicnq > dppz > dpq.



phen



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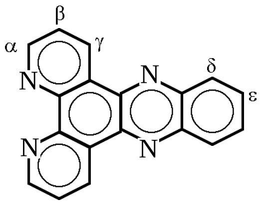

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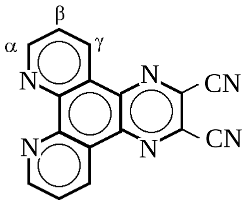

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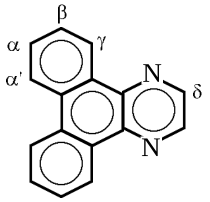
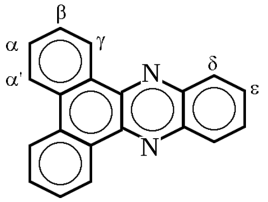


dbq



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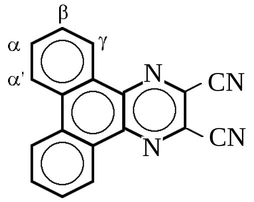

dicbq

The electronic absorption and luminescence spectra of the ligands confirm the conclusion that the electronic interaction between the phenanthroline and diazine moieties of the (N^N) ligands is weak. First, the energy [$\nu_{\max}$ (37.1 ± 0.6) × 10^3 cm^{-1}] and efficiency [ε (30.0 ± 0.9) × 10^3 l mol^{-1} cm^{-1}] of the high-energy spin-allowed optical transitions of the $^1(\pi\text{–}\pi^*)$ type localized on the phenanthroline moiety of the (N^N) ligands vary insignificantly. Second, the location of the long-wave (λ > 300 nm) absorption bands of the

Table 1. Proton chemical shifts δ, ppm [$(CD_3)_2SO$, relative to $(CH_3)_4Si$] (J_{HH}, Hz) in the ^1H NMR spectra of dibenzo- and dipyrido-substituted 1,4-diazines, *o*-phenanthroline, and diimine complexes of Au(III) and Pt(II)

Compound	$H^{\alpha}/H^{\alpha'}$	H^{β}	H^{γ}	H^{δ}	H^{ε}
phen	9.08 ($J_{\alpha-\beta}$ 4.3, $J_{\alpha-\gamma}$ 1.9)	7.71 ($J_{\beta-\alpha}$ 4.3, $J_{\beta-\gamma}$ 8.6)	8.43 ($J_{\gamma-\beta}$ 8.6, $J_{\gamma-\alpha}$ 1.9)	7.81	–
dpq	9.24 ($J_{\alpha-\beta}$ 3.8, $J_{\alpha-\gamma}$ 1.9)	7.96 ($J_{\beta-\alpha}$ 3.8, $J_{\beta-\gamma}$ 8.1)	9.45 ($J_{\gamma-\beta}$ 8.1, $J_{\gamma-\alpha}$ 1.9)	9.17	–
dppz	9.14 ($J_{\alpha-\beta}$ 4.2, $J_{\alpha-\gamma}$ 1.5)	7.86 ($J_{\beta-\alpha}$ 4.3, $J_{\beta-\gamma}$ 8.1)	9.44 ($J_{\gamma-\beta}$ 8.1, $J_{\gamma-\alpha}$ 1.5)	8.27 ($J_{\delta-\varepsilon}$ 6.7, $J_{\delta-\varepsilon'}$ 3.7)	7.99 ($J_{\varepsilon-\delta}$ 6.7, $J_{\varepsilon-\varepsilon'}$ 3.7)
dicnq	9.36 ($J_{\alpha-\beta}$ 4.4, $J_{\alpha-\gamma}$ 1.9)	8.04 ($J_{\beta-\alpha}$ 4.4, $J_{\beta-\gamma}$ 8.1)	9.41 ($J_{\gamma-\beta}$ 8.1, $J_{\gamma-\alpha}$ 1.9)	–	–
dbq	7.87 ($J_{\alpha-\beta}$ 7.7)/ 8.83 ($J_{\alpha'-\alpha}$ 7.7)	7.82 ($J_{\beta-\alpha\,\beta-\gamma}$ 7.6)	9.13 ($J_{\gamma-\beta}$ 7.6)	9.04	–
dbpz	7.91 ($J_{\alpha-\beta}$ 7.6)/ 8.80 ($J_{\alpha'-\alpha}$ 7.6)	7.83 ($J_{\beta-\alpha,\beta-\gamma}$ 7.6)	9.32 ($J_{\gamma-\beta}$ 7.6)	8.36 ($J_{\delta-\varepsilon}$ 6.7, $J_{\delta-\varepsilon'}$ 3.3)	8.00 ($J_{\varepsilon-\delta}$ 6.7, $J_{\varepsilon-\varepsilon'}$ 3.3)
dicbq	8.05 ($J_{\alpha-\beta}$ 8.2)/ 8.92 ($J_{\alpha'-\alpha}$ 8.2)	7.93 ($J_{\beta-\alpha,\beta-\gamma}$ 8.0)	9.08 ($J_{\gamma-\beta}$ 8.2)	–	–
$[Pt(phen)Cl_2]$	9.68 ($J_{\alpha-\beta}$ 5.0)	8.16 ($J_{\beta-\alpha}$ 5.0, $J_{\beta-\gamma}$ 8.1)	9.03 ($J_{\gamma-\beta}$ 8.1)	8.28	–

Table 1. (Contd.)

Compound	$H^{\alpha}/H^{\alpha'}$	H^{β}	H^{γ}	H^{δ}	H^{ε}
$[Pt(dpq)Cl_2]$	9.30 ($J_{\alpha-\beta}$ 4.9)	8.09 ($J_{\beta-\alpha}$ 4.9, $J_{\beta-\gamma}$ 8.4)	9.59 ($J_{\gamma-\beta}$ 8.4)	9.23	–
$[Pt(dppz)Cl_2]$	9.37 ($J_{\alpha-\beta}$ 4.9)	8.33 ($J_{\beta-\alpha}$ 4.9, $J_{\beta-\gamma}$ 8.5)	9.90 ($J_{\gamma-\beta}$ 8.5)	8.46 m	8.15 m
$[Pt(dicnq)Cl_2]$	9.29 ($J_{\alpha-\beta}$ 4.1)	8.01 ($J_{\beta-\alpha}$ 4.1, $J_{\beta-\gamma}$ 8.0)	9.87 ($J_{\gamma-\beta}$ 8.0)	–	–
$[Au(phen)Cl_2]Cl^a$	9.82 ($J_{\alpha-\beta}$ 5.6)	8.45 ($J_{\beta-\alpha}$ 5.6, $J_{\beta-\gamma}$ 8.4)	9.29 ($J_{\gamma-\beta}$ 8.4)	8.49	–
$[Au(dpq)Cl_2]Cl^b$	9.79 ($J_{\alpha-\beta}$ 5.4)	8.50 ($J_{\beta-\alpha}$ 5.4, $J_{\beta-\gamma}$ 7.3)	10.02 ($J_{\gamma-\beta}$ 7.3)	9.35	–
$[Au(dppz)Cl_2]Cl^b$	9.82 ($J_{\alpha-\beta}$ 5.8)	8.54 ($J_{\beta-\alpha}$ 5.8, $J_{\beta-\gamma}$ 8.0)	10.18 ($J_{\gamma-\beta}$ 8.0)	8.58 ($J_{\delta-\varepsilon}$ 8.0, $J_{\delta-\varepsilon'}$ 3.6)	8.26 ($J_{\varepsilon-\delta}$ 8.0, $J_{\varepsilon-\varepsilon'}$ 3.6)
$[Au(dicnq)Cl_2]Cl^b$	9.91 ($J_{\alpha-\beta}$ 5.8)	8.59 ($J_{\beta-\alpha}$ 5.8, $J_{\beta-\gamma}$ 8.0)	9.99 ($J_{\gamma-\beta}$ 8.0)		

[a] CD_3OD. [b] CD_3CN.

Table 2. Optical and electrochemical properties of dibenzo- and dipyrido-substituted 1,4-diazines, *p*-phenanthroline, and diimine complexes of Au(III) and Pt(II)

Compound	Absorption,[a] 298 K		Luminescence,[b] 77 K		Electroreduction[c]	
	λ, nm ($\varepsilon \times 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$)	assignment	λ, nm ($\nu_{vib} \times 10^3$, cm^{-1})	assignment	$-E_{1/2}$, V	assignment
phen	226 (15.8), 262 (10.0)	$^1(\pi-\pi^*)_{phen}$	459, 488, 521 (1.30)	$^3(\pi-\pi^*)_{phen}$	2.51	π^*
dpq	232 (13.6), 252 (19.8), 302 sh (5.1), 323 sh (2.3), 340 sh (1.8)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi-\pi^*)_{diaz}$	428, 444, 454, 464 sh, 474, 489 sh, 506 sh) (0.84, 1.34)	$^3(\pi-\pi^*)_{diaz}$	2.00 2.53	π^*_{diaz} π^*_{phen}
dppz	240 (19.6), 268 (33.4), 293 sh (11.6), 358 (7.4), 377 (7.3)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi-\pi^*)_{diaz}$	507 sh, 545, 559 sh, 589, 640 (0.46, 1.37)	$^3(\pi-\pi^*)_{diaz}$	1.61 2.49	π^*_{diaz} π^*_{phen}
dicnq	264 (40.5), 305 (24.9), 347 (8.5), 365 (6.8)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi-\pi^*)_{diaz}$	466, 478, 499, 509, 533, 549 sh (0.47, 1.35)	$^3(\pi-\pi^*)_{diaz}$	1.09 2.57	π^*_{diaz} π^*_{phen}
dbq[c]	305 (12.0), 338 (9.5), 353 (8.7)	$^1(\pi-\pi^*)_{diaz}$	444, 459, 469, 492 (0.74, 1.20)	$^3(\pi-\pi^*)_{diaz}$	2.12	π^*_{diaz}
dbpz[c]	306 (9.3), 374 (14.0), 392 (14.9)	$^1(\pi-\pi^*)_{diaz}$	551, 563, 594 (0.39, 1.31)	$^3(\pi-\pi^*)_{diaz}$	1.57	π^*_{diaz}
dicbq[c]	318 (14.4), 368 (6.7)	$^1(\pi-\pi^*)_{diaz}$	469, 489 sh, 500, 529 (0.87, 1.32)	$^3(\pi-\pi^*)_{diaz}$	1.03	π^*_{diaz}
$[Au(phen)Cl_2]^+$	225 (32.7), 276 (24.4), 318 (4.6)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi_{phen}-d^*)$	463, 497, 532, 588 sh (1.37)	$^3(\pi-\pi^*)_{phen}$	0.01[d]	d^*_{Au}
$Pt(phen)Cl_2$	254 (39.5), 274 (39.5), 328 (7.4), 387 (4.4)	$^1(\pi-\pi^*)_{phen}$ $^1(d-\pi^*_{phen})$	611 ($\Delta\nu_{1/2}$ 2.8)[e]	$^3(d-d^*)$	0.97[d]	d^*_{Pt}
$[Au(dpq)Cl_2]^+$	228 (41.6), 252 (37.4), 299 sh (12.3), 324 sh (7.4), 339 (5.4), 370 (1.5)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi-\pi^*)_{diaz}$ $^1(\pi_{phen}-d^*)$	437, 464, 478, (0.63, 1.33)	$^3(\pi-\pi^*)_{diaz}$	0.48[d]	d^*_{Au}
$Pt(dpq)Cl_2$	231 (30.0), 252 (42.6), 277 (16.9), 322 sh (6.7), 339 (5.7), 391 (2.2)	$^1(\pi-\pi^*)_{phen}$ $^1(\pi-\pi^*)_{diaz}$ $^1(d-\pi^*_{phen})$	431 sh, 457, 477, 514, 548 (0.92, 1.32)	$^3(\pi-\pi^*)_{diaz}$	2.01	π^*_{diaz}

Table 2. (Contd.)

Compound	Absorption,[a] 298 K		Luminescence,[b] 77 K		Electroreduction[c]	
	λ, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1})	assignment	λ, nm ($\nu_{vib} \times 10^3$, cm^{-1})	assignment	$-E_{1/2}$, V	assignment
$[Au(dppz)Cl_2]^+$	227 (46.3), 283 (32.1), 357 (8.7), 375 (7.6)	$^1(\pi–\pi^*)_{phen}$ $^1(\pi–\pi^*)_{diaz}$	546, 557, 588 (0.36, 1.31)	$^3(\pi–\pi^*)_{diaz}$	0.46[d]	d^*_{Au}
$Pt(dppz)Cl_2$	240 (13.0), 270 (23.6), 349 (4.4), 358 (4.9), 378 (4.8), 410 (1.8)	$^1(\pi–\pi^*)_{phen}$ $^1(\pi–\pi^*)_{diaz}$ $^1(d–\pi^*_{phen})$	552, 594, 645 (1.31)	$^3(\pi–\pi^*)_{diaz}$	1.37	π^*_{diaz}
$[Au(dicnq)Cl_2]^+$	227 (48.3), 265 (34.8), 307 (21.2), 344 (8.6), 365 (6.8)	$^1(\pi–\pi^*)_{phen}$ $^1(\pi–\pi^*)_{diaz}$	472, 485, 513, 546 (0.57, 1.70)	$^3(\pi–\pi^*)_{diaz}$	0.61[d]	d^*_{Au}
$Pt(dicnq)Cl_2$	264 (30.5), 290 (24.1), 384 (4.2)	$^1(\pi–\pi^*)_{phen}$ $^1(\pi–\pi^*)_{diaz}/$ $^1(d–\pi^*_{phen})$[f]	451, 489, 510, 531 (1.67)	$^3(\pi–\pi^*)_{diaz}$	0.96	π^*_{diaz}

[a] CH_3CN. [b] Dimethylformamide–toluene, 1 : 1. [c] Dimethylformamide. [d] Current peak potential at a potential sweep rate of 50 mV s^{-1}. [e] Polycrystal; $\Delta\nu_{1/2}$ is the luminescence band width at half-height. [f] Overlap of two bands.

dipyrido- and dibenzo-substituted 1,4-diazines and the shape of their vibronically structured low-temperature (T 77 K) luminescence spectra caused by the spin-forbidden optical transitions of the $^3(\pi–\pi^*)$ type localized on the diazine moiety are similar.

In accordance with the coordination mode, the complexation of dipyrido-substituted 1,4-diazines leads to a decrease in the electron density mainly on the phenanthroline moiety, which is reflected in the positive coordination-induced chemical shifts (*CIS* = $\delta_{comp} - \delta_{lig}$) of the H^{α}, H^{β}, and H^{γ} protons, whereas the electron density on the diazine moiety, remote from the coordination center, changes to a considerably lesser extent (Table 1). A decrease in *CIS* for the Pt(II) complexes in the series phen > dppz > dpq > dicnq is consistent with the decrease in the basicity of the imine nitrogen atoms of the ligands; it indicates that the efficiency of the donor–acceptor interaction (N^N)$\rightarrow$Pt(II) decreases in this series. A regular increase in the efficiency of the donor–acceptor interaction of the ligands with Au(III), compared to Pt(II), levels off the effect of substituents in the diazine moiety on *CIS* of the H^{α} protons (Δ*CIS* 0.55 ± 0.02).

A characteristic feature of the ^1H NMR spectra of the Pt(II) complexes with dipyrido-substituted 1,4-diazines is the absence of the characteristic platinum satellites originating form the coupling of the ^{195}Pt nucleus with ligand protons. This is caused by the strong anisotropy of the electric field gradient on Pt in the square-planar surrounding and by the related factor of second-kind scalar relaxation of the protons coupled with ^{195}Pt [9]. The short relaxation time of the diazine ligands leads to broadening of the platinum satellites and their apparent "absence" in the ^1H NMR spectra.

The voltammograms of the reduction of the Pt(II) complexes with dipyrido-substituted 1,4-diazines are characterized by the presence of one-electron reversible waves suggesting a ligand-centered character of the redox process (electron transfer to the π^* redox orbitals localized on the diazine moiety). Comparison of the electrochemical parameters of the electroreduction of the Pt(II) complexes and free ligands (Table 2) shows that the position of the reduction wave assigned to the electron transfer to the π^* redox orbital of the diazine moiety is essentially the same. The voltammograms of the oxidation of the platinum complexes are characterized by the chemical and electrochemical irreversibility, suggesting the metal-centered d_{Pt} nature of the highest occupied molecular redox orbital in the complexes. The oxidation current peak potential of the Pt(II) complexes is essentially independent of the structure of the diazine ligands: E_p 0.29 ± 0.02 V. The voltammograms of the reduction and oxidation of the Au(III) complexes are characterized by chemical and electrochemical irreversibility, with the current peak potentials essentially independent of the structure of the diazine ligands (E_p^{red} -0.58 ± 0.09, E_p^{ox} 0.54 ± 0.08 V), which is indicative of a metal-centered nature of both the highest occupied and the lowest unoccupied molecular redox orbitals.

Comparison of the electronic absorption spectra of the Pt(II) and Au(III) complexes (Fig. 1) with those of the ligands (Table 2) shows that, along with the intraligand optical transitions of the $^1(\pi–\pi^*)$ type localized on the phenanthroline and diazine moieties of the lig-

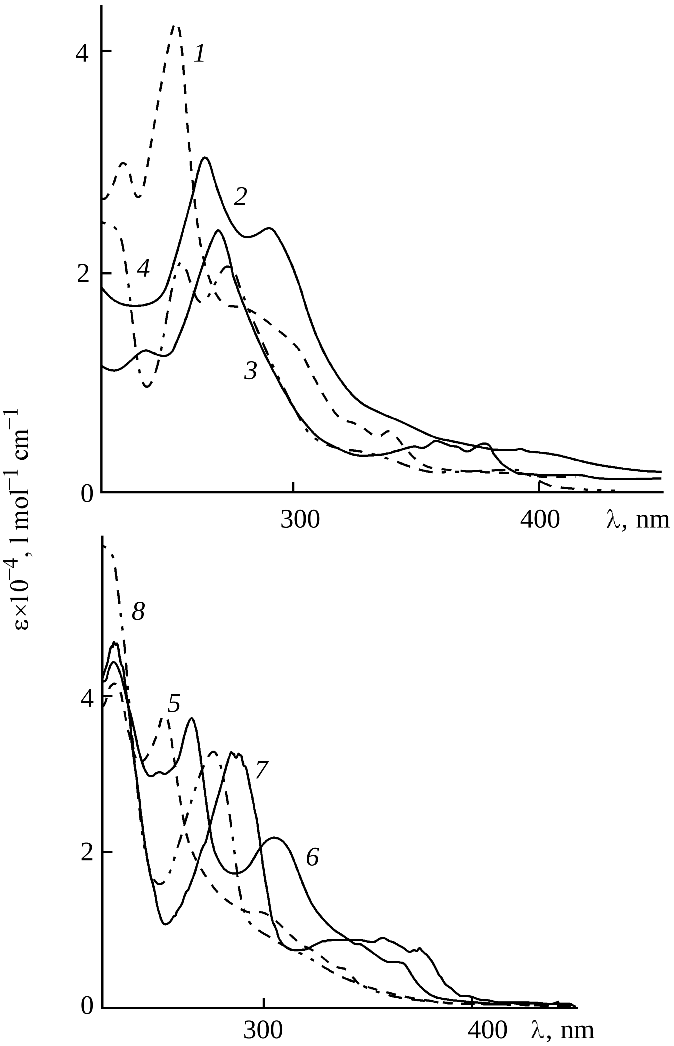

Fig. 1. Absorption spectra: (*1*) [Pt(dpq)Cl_2], (*2*) [Pt(dicnq)Cl_2], (*3*) [Pt(dppz)Cl_2], (*4*) [Pt(phen)Cl_2], (*5*) [Au(dpq)Cl_2]Cl, (*6*) [Au(dicnq)Cl_2]Cl, (*7*) [Au(dppz)Cl_2]Cl, and (*8*) [Au(phen)Cl_2]Cl.

ands, the complexation gives rise to new low-energy charge-transfer transitions assigned, in accordance with the results of the electrochemical studies, to the spin-allowed metal-to-ligand charge transfer transitions of the $^1(d–\pi_{phen})$ type for the Pt(II) complexes and ligand-to-metal charge-transfer transitions of the $^1(\pi_{phen}–d^*)$ type for the Au(III) complexes. In agreement with the NMR data, a decrease in the efficiency of the (N^N)→M donor–acceptor interaction in the order phen > dppz > dpq > dicnq results in a regular short-wave shift of the metal-to-ligand charge-transfer bands of the Pt(II) complexes and long-wave shifts of both the ligand-to-metal charge-transfer bands of the Au(III) and intraligand $^1(\pi–\pi^*)$-type intraligand bands localized on the phenanthroline moiety. At the same time, because of the weak electronic interaction between the phenanthroline and diazine moieties of the ligands, the intraligand absorption bands of the $^1(\pi–\pi^*)$ type localized on the diazine moiety are not noticeably shifted in the complexes relative to the free ligands.

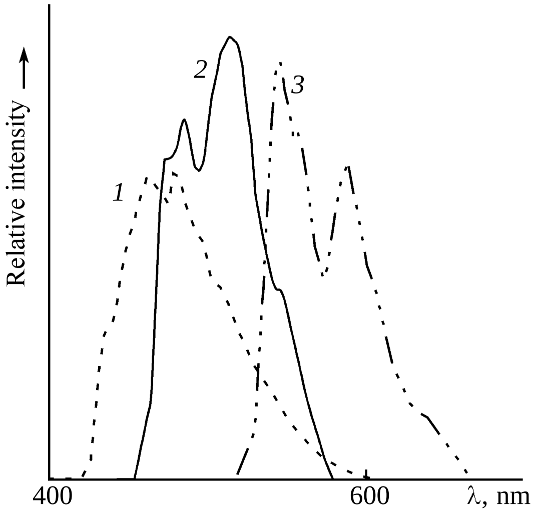

Fig. 2. Luminescence spectra: (*1*) [Au(dpq)Cl_2]Cl, (*2*) [Au(dicnq)Cl_2]Cl, and (*3*) [Au(dppz)Cl_2]Cl.

The vibronically structured (ν 1300 cm^{-1}) low-temperature luminescence spectra of the complexes (Fig. 2) and free diazine ligands (Table 2), assigned to spin-forbidden optical transitions of the $^3(\pi–\pi^*)$ type localized on the diazine moiety, are not noticeably affected by the complexation either, which confirms the conclusion that the electronic interaction of the diazine moiety with the phenanthroline moiety and coordination center is weak.

The lack of the luminescence of the Au(III) and Pt(II) complexes in solution and in the polycrystalline state at room temperature suggests occurrence of efficient thermally activated nonradiative energy decay, apparently through population of the higher lying state of the $^3(d–d^*)$ type.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on a Bruker DPX-300 Avance spectrometer at 298 K. The electronic absorption spectra were measured on an SF-2000 spectrometer at 298 K in acetonitrile. The luminescence characteristics were obtained at 77 K in frozen glass-forming DMF–toluene mixtures (1 : 1) on a previously described [10] KSVU-1 installation with pulse photoexcitation (LGI-21 nitrogen laser, λ 337 nm, τ_{pulse} 10 ns). The luminescence quantum efficiency was determined relative to fluorescein (Φ 0.85) [11].

Dipyrido and dibenzo derivatives of 1,4-diazines were prepared by a standard procedure [12–14] involving oxidation of *o*-phenanthroline and phenanthrene to 1,10-phenanthroline-5,6-dione and 9,10-phenanthroquinone, respectively, followed by the condensation with appropriate diamines: ethylenediamine (dpq, dbq), *o*-phenylenediamine (dppz, dpbz), and diaminomaleonitrile (dicnq, dicbq).

The synthesis of Pt(phen)Cl_2 [15], Pt(dppz)Cl_2 [16], and [Au(phen)Cl_2]ClO_4 [7] was described previously; Pt(dpq)Cl_2 and Pt(dicnq)Cl_2 were prepared in ~70% yield by a procedure similar to that in [16].

Complexes [Au(N^N)Cl_2]Cl *(general procedure).* A 10% excess of diimine ligand in acetonitrile was added to aqueous solution of H[$AuCl_4$], which led to precipitation of light yellow dichlorodiimine complexes. The suspension was stirred for 30 min, and the precipitate was filtered off, washed with acetonitrile and ether, and vacuum-dried. Yield ~60%.

Electrochemical studies were performed at 293 K in acetonitrile and dimethylformamide (DMF) on a computer-controlled SVA-1B installation in a three-electrode cell with separated compartments of the working (Pt), auxiliary (Pt), and reference (Ag) electrodes in the presence of 0.1 M [$N(C_4H_9)_4$]ClO_4 at a potential sweep rate of 100 mV s^{-1}. The potentials are given vs. ferrocenium/ferrocene redox system.

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