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Complexes of Pd(II) and Zn(II) Chlorides with Anthracene-Containing α-Amino Oxime Derived from the Naturally Occurring Monoterpenoid (+)-3-Carene

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Abstract—The complex $Pd(HL)Cl_2$ (**I**) was obtained (HL is the anthracene-containing chiral α-amino oxime derived from the natural monoterpenoid (+)-3-carene). Single crystals of its solvate $[Pd(HL)Cl_2] \cdot 0.33EtOH$ (**II**) were grown. According to X-ray diffraction data (CIF file CCDC no. 1008947), the crystals are built from mononuclear molecules of complex **I** and uncoordinated EtOH molecules. The coordination environment of the Pd atom in complex **I** ($PdCl_2N_2$) makes up a distorted square (trapezoid). The compound HL acts as a chelating bidentate ligand. The $[Pd(HL)Cl_2]$ and EtOH molecules are united into chains through weak hydrogen bonds. The photoluminescence (PL) of HL and the system $ZnCl_2$–HL in acetonitrile was studied. The emission spectra show three bands at 394, 415, and 440 nm. The photoluminescence of the system $ZnCl_2$–HL in solution is more intense than that of HL. A study of the system $ZnCl_2$–HL by the molar ratio method in conjunction with emission spectroscopy suggests the formation of the complex $Zn(HL)Cl_2$ in acetonitrile.

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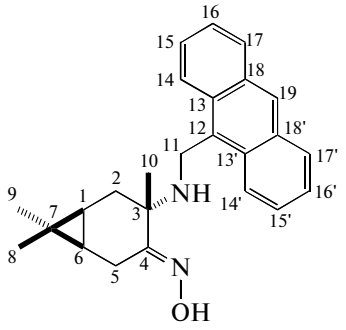
INTRODUCTION

The coordination chemistry of naturally occurring and hybrid chiral organic ligands (including those based on natural terpenoids) is currently under extensive development [1–4]. This is due to a variety of functional properties possessed by such optically active metal complexes. Photoluminescence (PL) is among those properties. Specifically, the emission of lanthanide complexes with chiral terpene ligands containing pinene [5] and camphor residues [5–10] as well as the emission of Zn(II) and Cd(II) complexes with chiral (+)-3-carene-containing pyrazolylquinoline have been studied [11, 12]. Various aromatic or heterocyclic fragments are used in organic ligands to impart intense photoluminescence to their metal complexes. For instance, Zn(II) and Cd(II) complexes with achiral N-donating ligands containing an anthracene residue (anthracene is a well-known fluorophore) show intense photoluminescence [13–20]. Such complexes are promising as fluorescent chemosensors [15, 16]. It is interesting to study transition metals complexes with anthracene-containing chiral terpenoid derivatives.

Earlier, complexes of $ZnCl_2$ and $PtCl_2$ with chiral 3-*N*,*N*-dimethylaminocaran-4-one oxime have been synthesized [21]. The goal of this work was to obtain chiral (1*S*,3*S*,6*R*)-3-((anthracen-9-ylmethyl)amino)caran-4-one *E*-oxime (HL) and study its complexation reactions with $ZnCl_2$ and $PdCl_2$.



HL
(the atomic numbering refers to the NMR spectra)

EXPERIMENTAL

The α-amino oxime of (+)-3-carene was prepared as described in [22]. Anthracene-9-carbaldehyde (reagent grade, Reakhim), $PdCl_2$ (high-purity grade), $ZnCl_2$ (analytical grade), rectified EtOH, concen-

trated HCl, CH_2Cl_2, and pentane (reagent grade) were used.

Synthesis of HL. Anthracene-9-carbaldehyde (10.0 mmol, 2.06 g) and acetic acid (10.0 mmol, 0.60 g) were added to a solution of α-amino oxime of (+)-3-carene (10.0 mmol, 1.82 g) in THF (30 mL). The reaction mixture was stirred at room temperature for 2 h. Then sodium triacetoxyborohydride (30.0 mmol, 6.3 g) was added, and stirring was continued at room temperature for 24 h. After completion of the reaction, the reaction mixture was poured into water and alkalified with aqueous ammonia to pH 9–10. The product was extracted with ethyl acetate (3 × 30 mL). The pooled organic extracts were washed with water (30 mL) and brine, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was purified by column chromatography on SiO_2 with light petroleum–ethyl acetate–ethanol or chloroform–ethanol as an eluent (gradient elution). The yield of HL was 57%, $[\alpha]_{589}^{26}$ + 173 (*c* 0.460, EtOH). IR (KBr; ν, cm^{-1}): 3430 (O–H), 3287 (N–H), 1622 (C=C), 940 (N–O). High-resolution MS: found, *m/z* 372.2196 [M^+]. $C_{25}H_{28}O_1N_2$. Calculated: *M* = 372.2198. MS, *m/z* (I_{rel}, %): 355 (5), 271 (13), 191 (100), 165 (4), 42 (3).

^{1}H NMR ($CDCl_3$–DMSO-d_6, 2 : 1, v/v), δ: 10.50 (br.s, 1H, =NO–H), 8.34 (s, 1H, H(19)), 8.19 (l, 2H, H(14), H(14'), *J* = 8.4 Hz), 7.93 (d, 2H, H(17), H(17'), *J* = 8.8 Hz), 7.47 (ddd, 2H, H(15), H(15'), *J* = 8.8 Hz, *J* = 8.4 Hz, *J* = 1.2 Hz), 7.37 (dd, 2H, H(16), H(16'), *J* = 8.8 Hz, *J* = 8.4 Hz), 4.46 and 4.32 (d, 2H, H(11), *J* = 12.2 Hz), 2.86 (dd, 1H, H(5 *pro-S*), *J* = 19.6 Hz, *J* = 1.8 Hz), 2.61 (dd, 1H, H(5 *pro-R*), *J* = 19.6 Hz, *J* = 9.2 Hz), 2.05 (dd, 1H, H(2 *pro-R*), *J* = 15.1 Hz, *J* = 9.6 Hz), 1.43 (s, 3H, H(9)), 1.29 (dd, 1H, H(2 *pro-S*), *J* = 15.1 Hz, *J* = 5.8 Hz), 0.88 (s, 3H, H(10)), 0.75 (s, 3H, H(8)), 0.69 (ddd, 1H, H(6), *J* = 9.2 Hz, *J* = 9.0 Hz, *J* = 1.8 Hz), 0.50 (ddd, 1H, H(1), *J* = 9.6 Hz, *J* = 9.0 Hz, *J* = 5.8 Hz).

^{13}C NMR (^{13}C ($CDCl_3$–Cl_4, 1 : 1, v/v), δ: 158.75 (C(4)), 131.23 (C(12)), 131.00 (C(13), C(13')), 129.71 (C(18), C(18')), 128.64 (C(17), C(17')), 126.48 (C(14), C(14')), 125.71 (C(15), C(15')), 124.64 (C(16), C(16')), 123.62 (C(19)), 54.67 (C(3)), 38.62 (C(11)), 34.09 (C(2)), 27.43 (C(6)), 22.20 (C(1)), 18.44 (C(7)), 17.86 (C(5)), 17.68 (C(9)), 15.92 (C(8)), 14.23 (C(10)).

Synthesis of Pd(HL)Cl_2 (I). A solution of $PdCl_2$ (0.036 g, 0.2 mmol) in three drops of concentrated HCl was evaporated almost to dryness. The residue was diluted with EtOH (1.5 mL). The ligand HL (0.075 g, 0.2 mmol) was dissolved with gentle heating in a mixture of EtOH (3 mL) and CH_2Cl_2 (6 mL), and this solution was added to the prepared solution of $PdCl_2$. The resulting solution was concentrated to a minimum volume at room temperature under a fan. After 2 h, the yellow precipitate that formed was filtered off by suction, washed with EtOH and pentane, and dried in air. The yield of complex **I** was 0.082 g (75%), $[\alpha]_{589}^{22}$ + 384 (*c* 0.394, $CHCl_3$).

For $C_{25}H_{28}N_2OCl_2Pd$				
anal. calcd., %:	C, 54.5;	H, 5.1;	N, 5.1;	Cl, 12.9.
Found, %:	C, 54.1;	H, 5.2;	N, 5.0;	Cl, 12.4.

Microanalyses for C, H, and N were performed on a EuroEA3000 analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument (500.13 and 125.75 MHz, respectively) for solutions with *c* = 5–10 mg/mL at 30°C. The signals of the solvent ($CDCl_3$): δ_H 7.24, δ_C 76.90) were used as the internal standards. Optical rotation was measured on a PolAAr polarimeter.

Storage of the mother liquor produced single crystals of the complex [Pd(HL)Cl_2] · 0.33EtOH (**II**) suitable for X-ray diffraction.

X-ray diffraction study of complex II. An experimental set of reflection intensities was collected on an X8 APEX automated diffractometer at 150 K according to a standard procedure. Structure **II** was solved by the direct method and refined anisotropically (for non-hydrogen atoms) by the full-matrix least-squares method with the SHELXL-97 program package [23]. The structure solution revealed not only the peaks due to the atoms of complex **I** but also a group of peaks corresponding to EtOH. It emerged from the refinement that for each EtOH molecule there are three complex molecules. The H atoms at the C atoms were located geometrically and refined using a riding model. Selected crystallographic parameters and the data collection and refinement statistics for structure **II** are given in Table 1. Bond lengths and bond angles in structure **I** are listed in Table 2. The comprehensive data on the atomic coordinates, bond lengths, and bond angles have been deposited with the Cambridge Structural Database (CCDC no. 1008947; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk) and can be made available from the authors upon request.

Study of the photoluminescence of the system $ZnCl_2$–HL in acetonitrile. The emission spectra of a solution of HL ($c = 0.5 \times 10^{-4}$ mol/L) in acetonitrile and a series of acetonitrile solutions containing HL ($c = 0.5 \times 10^{-4}$ mol/L) and $ZnCl_2$ in a concentration range from 1.0×10^{-5} to 1.0×10^{-4} mol/L were recorded. The excitation (*V* = 500 V, slit width 5 nm) and photoluminescence spectra (*V* = 500 V, slit width 5 nm, λ_{ex} = 250 nm) were acquired on a Cary Eclipse spectrophotometer (Varian) at room temperature under identical experimental conditions.

Table 1. Crystallographic parameters and the data collection and refinement statistics for structure **II**

Parameter	Value
Empirical formula	$C_{77}H_{30}N_6O_4Cl_6Pd_3$
M	1695.45
Temperature, K	150(2)
Crystal system	Hexagonal
Space group	$P6_1$
Unit cell parameters:	
a, Å	28.052(4)
b, Å	28.052(4)
c, Å	18.424(4)
γ, deg	120.00
V, Å^3	12556(4)
Z; ρ(calcd.), mg/cm^3	6; 1.345
μ, mm^{-1}	0.876
Crystal dimensions, mm	0.25 × 0.08 × 0.08
F(000)	5196
θ scan range, deg	1.68–26.37
Number of measured reflections	81205
Number of unique reflections	8819
R_{int}	0.0547
Number of reflections with $I > 2\sigma(I)$	7772
Number of parameters refined	871
GOOF for F^2	1.193
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0613$ $wR_2 = 0.1560$
R-factor (for all I_{hkl})	$R_1 = 0.0730$ $wR_2 = 0.1628$
Flack parameter	0(10)
Residual electron density (max/min), e/Å^3	3.030/–1.333

RESULTS AND DISCUSSION

A reaction of $PdCl_2$ with chiral dextrorotary HL in EtOH–CH_2Cl_2 gave dextrorotary complex **I**. Its structure was elucidated by the formation of single crystals of complex **II**. According to X-ray diffraction data, the crystal structure of complex **II** comprises acentric molecules of mononuclear complex **I** and uncoordinated EtOH molecules. Three crystallographically independent complex molecules have close geometrical parameters, so the structure of only one of them is visualized in Fig. 1. The Pd atom is coordinated by two N atoms of the chelating bidentate ligand HL and by two Cl atoms. The chelation produces the five-membered ring PdN_2C_2; the Pd–N bond lengths range from 1.967(7) to 2.080(7) Å (in three molecules). The distances between the Pd atom and the N atoms of the oxime group are shorter. The Pd–Cl bond lengths vary from 2.272(3) to 2.323(3) Å. The coordination units PdN_2Cl_2 can be regarded as distorted squares (trapezoids): N···N 2.598–2.605, N···Cl 3.017–3.226, Cl···Cl 3.398–3.411 Å. The chelate rings PdN_2C_2 adopt an envelope conformation; the N(2), N(4), and N(6) atoms deviate from the planes of the other four atoms of their own rings by 0.65(1), 0.63(1), and 0.67(1) Å, respectively. In all three molecules of complex **I**, the six-membered carbocycles adopt a distorted boat conformation. The idealized boat conformation in such systems is characterized by zero values of two endocyclic dihedral (torsion) angles. In structure **I**, the angle between the exocyclic bonds in the cyclopropane fragment is 1°–1.5°, and the other endocyclic torsion (dihedral) angle is 23°–25°. For instance, the torsion angle C(2)C(1)C(6)C(5) is 25.4°. In the other two crystallographically independent molecules, this angle is 23.9° (C(50)C(49)C(54)C(53) and C(26)C(25)C(30)C(29)).

The dimethylcyclopropane fragments share the C–C edges with the six-membered carbocycles, making dihedral angles of ~140.0(1)° with the planes of four C atoms. In addition, all three molecules of structure **I** are stabilized by intramolecular hydrogen bonds O–H···Cl (O···Cl 2.997(10), 3.001(7), and 3.045(9) Å) closing the five-membered H-rings PdNOHCl. The angles at the H atoms of the oxime groups are 119°, 128°, 124°, respectively.

The mutual arrangement of the molecules in the crystal structure of **II** is shown in Fig. 2 (as a projection onto the plane (001)). The molecules of complex **I** and ethanol molecules are linked by hydrogen bonds. The shortest bonds are N(4)···O(1S) 2.88(2), O(1S)···Cl(5) 3.18(2) Å). The chain-forming hydrogen bonds between the molecules of complex **I** and ethanol are indicated with dashed lines (Fig. 2).

We failed to isolate the complex of $ZnCl_2$ with HL in the solid state. Using luminescence spectroscopy, we studied an interaction between these reactants in acetonitrile. Figure 3 displays the excitation and photoluminescence spectra of both a solution of HL and solutions of the system $ZnCl_2$–HL for a constant concentration of HL and a variable concentration of $ZnCl_2$. The excitation spectra consist of a single band with an intense narrow peak at ~250 nm. That is why we recorded photoluminescence spectra using

Table 2. Selected bond lengths and bond angles in structure **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Pd(1)–N(1)	2.002(8)	Pd(2)–N(3)	1.967(7)	Pd(3)–N(5)	2.009(8)
Pd(1)–N(2)	2.066(8)	Pd(2)–N(4)	2.080(7)	Pd(3)–N(6)	2.066(8)
Pd(1)–Cl(1)	2.272(3)	Pd(2)–Cl(3)	2.277(2)	Pd(3)–Cl(5)	2.281(3)
Pd(1)–Cl(2)	2.315(3)	Pd(2)–Cl(4)	2.323(3)	Pd(3)–Cl(6)	2.306(3)
N(1)–C(1)	1.264(13)	N(3)–C(25)	1.291(12)	N(5)–C(49)	1.247(12)
N(1)–O(1)	1.353(11)	N(3)–O(2)	1.372(10)	N(5)–O(3)	1.372(10)
N(2)–C(6)	1.520(13)	N(4)–C(30)	1.515(12)	N(6)–C(54)	1.512(12)
N(2)–C(2N)	1.520(13)	N(4)–C(4N)	1.510(11)	N(6)–C(6N)	1.522(12)
C(2N)–C(24)	1.502(14)	C(4N)–C(48)	1.494(13)	C(6N)–C(72)	1.521(14)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
N(1) Pd(1)N(2)	79.7(3)	N(3)Pd(2)N(4)	80.1(3)	N(5)Pd(3)N(6)	79.2(3)
N(1)Pd(1)Cl(1)	172.9(3)	N(3)Pd(2)Cl(3)	174.9(2)	N(5)Pd(3)Cl(5)	171.8(2)
N(2)Pd(1)Cl(1)	95.4(2)	N(4)Pd(2)Cl(3)	95.4(2)	N(6)Pd(3)Cl(5)	94.3(2)
N(1)Pd(1)Cl(2)	89.4(3)	N(3)Pd(2)Cl(4)	89.0(2)	N(5)Pd(3)Cl(6)	91.1(3)
N(2)Pd(1)Cl(2)	168.6(2)	N(4)Pd(2)Cl(4)	168.9(2)	N(6)Pd(3)Cl(6)	169.9(3)

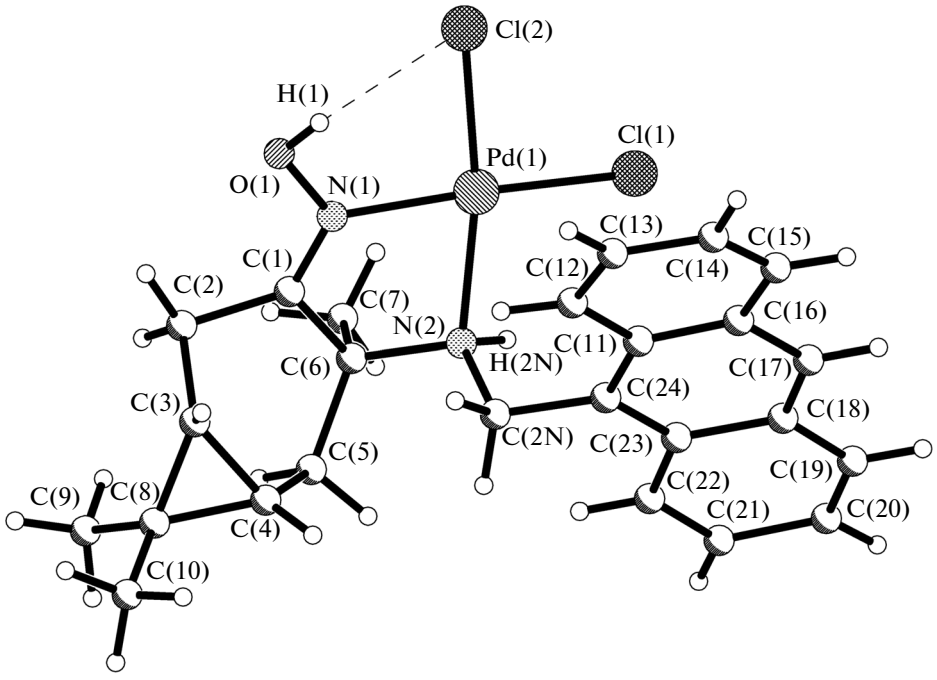


Fig. 1. Structure of mononuclear complex **I** in the crystal of complex **II**.

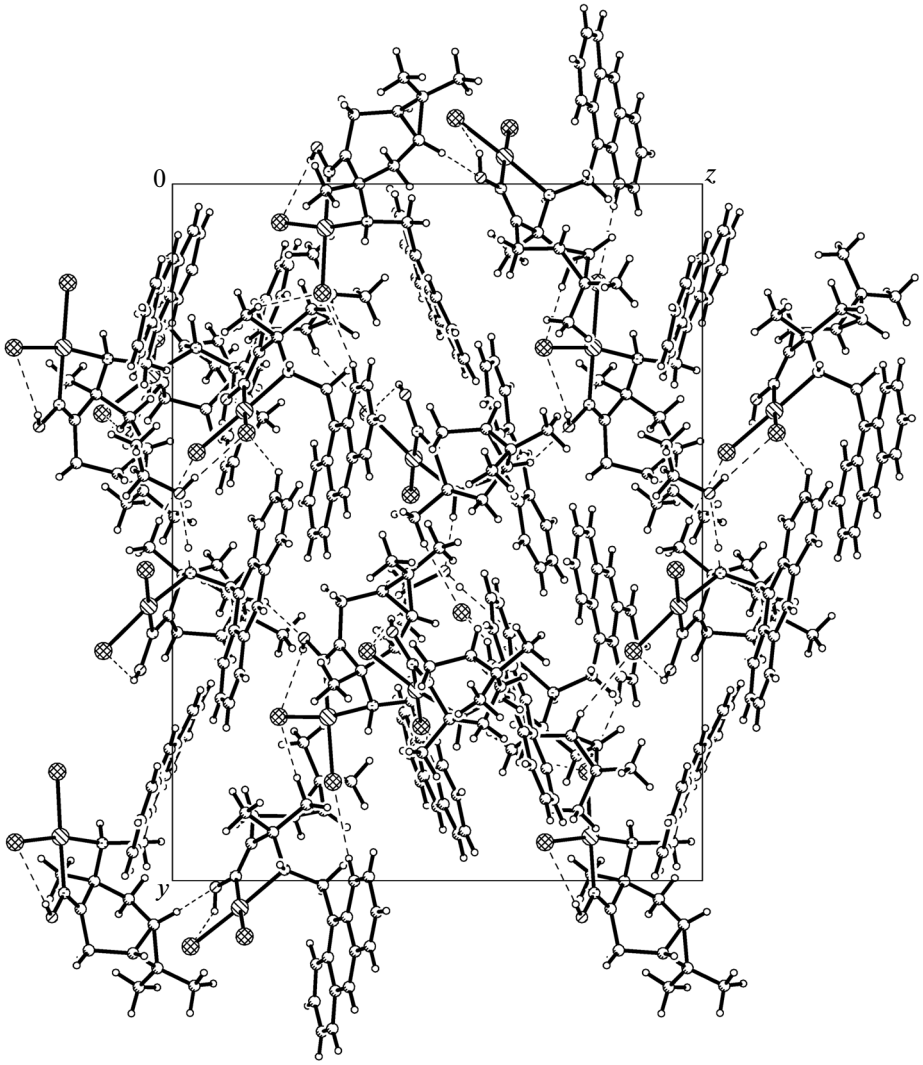


Fig. 2. Projection of the crystal structure of complex **II** onto the plane (100).

$\lambda_{exc} = 250$ nm. The emission spectra show three bands at 394, 415, and 440 nm; the band at 415 nm being most intense. The positions of the above bands are close to those of three bands in the PL spectrum of 9,10-dimethylanthracene [13]. Solutions of the system $ZnCl_2$–HL produce stronger photoluminescence than does a solution of HL. Obviously, this is due to complexation between $ZnCl_2$ and HL. Apparently, the way of HL coordination in the complex with $ZnCl_2$ is similar to that found in complex **I** (closure of the five-membered chelate ring ZnN_2C_2). The Zn–N bonds are formed by the lone electron pairs of the N atoms, which thus become incapable of quenching the photoluminescence. This accounts for the increased PL intensity of complex **I** compared to free HL (the CHEF effect) [13]. As the concentration of $ZnCl_2$ increases, the PL intensity increases and then remains constant (Fig. 3). The total relative error associated with preparation of solutions for measurements as well as with PL intensity measurements was estimated at ~5%. To determine the possible composition of the complex, we used the molar ratio method and plotted the intensity of the band at 415 nm in the emission spectra versus the $c_{ZnCl_2} : c_{HL}$ ratio (Fig. 4). It can be seen that the initial appreciable increase in the PL intensity slows down and virtually stops at ratios of 1.2 : 1 to 2 : 1, eventually making the PL intensity almost 4.5 times that of HL in solution. The pattern of this relationship suggests that $ZnCl_2$ reacts with HL in acetonitrile to give a complex of the formula $Zn(HL)Cl_2$.

The discovery of the intense photoluminescence of the Zn(II) complex with the chiral ligand derived from the natural monoterpenoid (+)-3-carene and containing an anthracene fluorophore opens new pros-

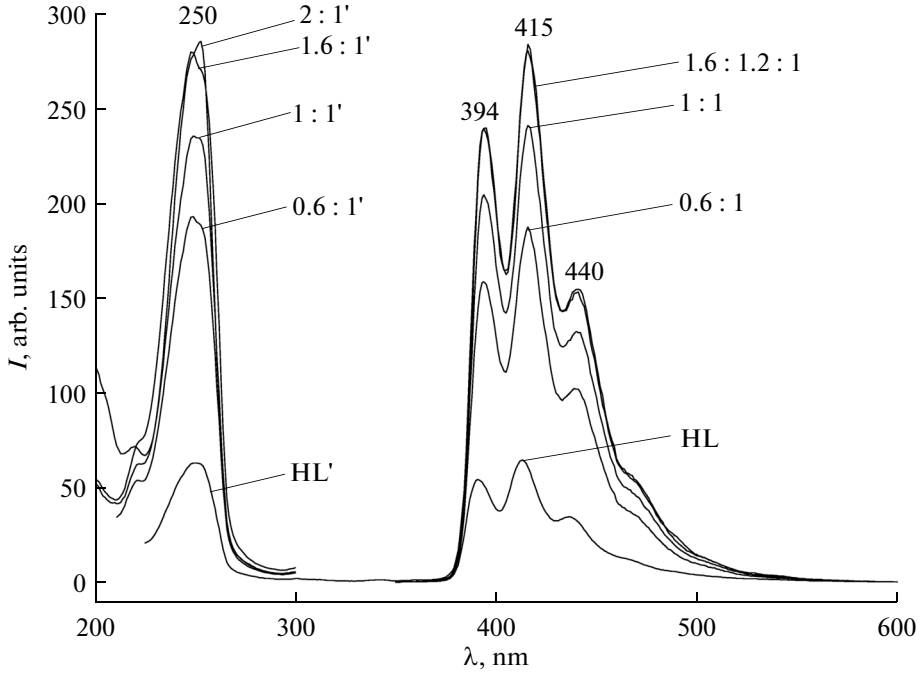


Fig. 3. Excitation (HL', 0.6 : 1', 1 : 1', 1.6 : 1', and 2 : 1') and emission spectra (HL, 0.6 : 1, 1 : 1, 1.6 : 1, and 2 : 1) of a solution of HL in acetonitrile ($c = 0.5 \times 10^{-4}$ mol/L) and solutions of the system HL–$ZnCl_2$ in acetonitrile for the $c_{ZnCl_2} : c_{HL}$ ratios specified above, respectively.

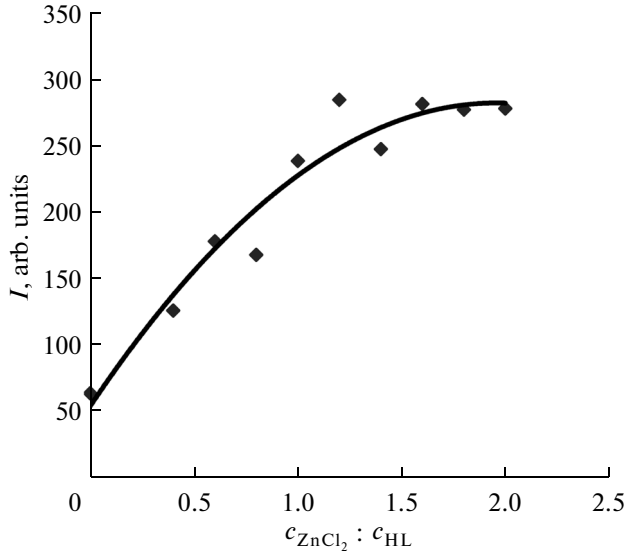


Fig. 4. Plot of the intensity of the band at 415 nm in the emission spectra vs. the $c_{ZnCl_2} : c_{HL}$ ratio.

pects for further investigations of the photoluminescence of complexes with such ligands.

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