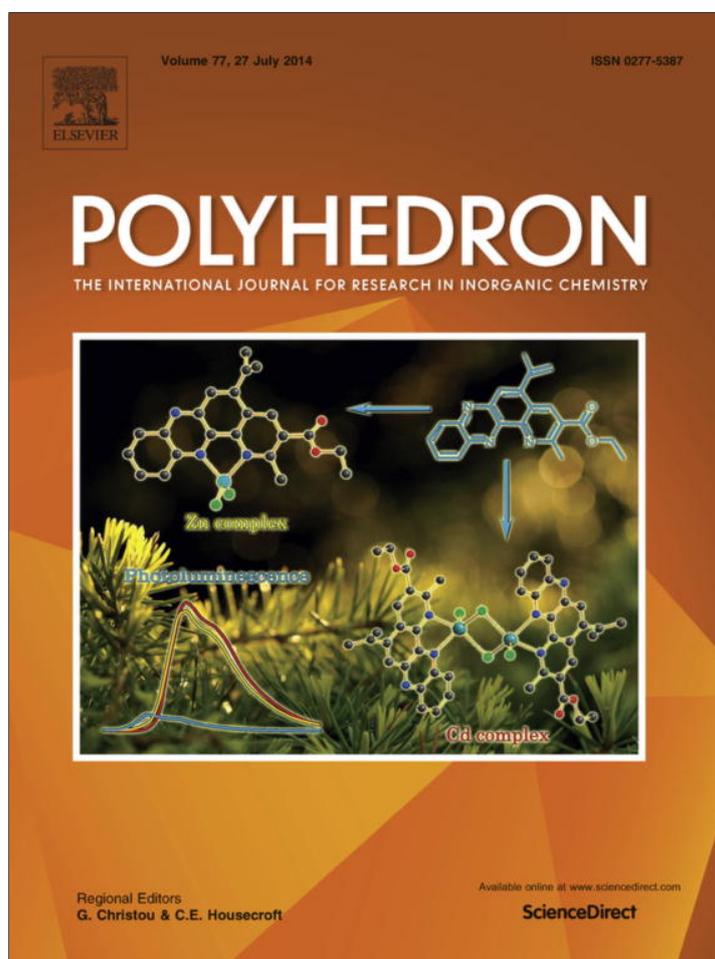


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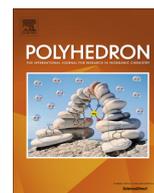
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Synthesis, structure and photoluminescence of Zn(II) and Cd(II) complexes with pyridophenazine derivative



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ABSTRACT

The [ZnLCl₂] (**1**) and Cd₂L₂Cl₄ (**2**) complexes, where L is ethyl 2-methyl-5-(prop-1-en-2-yl)pyrido[2,3-a]phenazine-3-carboxylate, were synthesized. The complexes were characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy, and X-ray powder diffraction. Single crystals of **1** and [Cd₂L₂Cl₄].4CH₂Cl₂ (**3**) have been grown. The structure of **1** consists of mononuclear molecules, while the structure of **3** is built up of centrosymmetrical binuclear [Cd₂L₂Cl₄] complex molecules and uncoordinated CH₂Cl₂ molecules. In **1** and **3**, L acts as a bidentate chelating ligand. There is five-membered ZnN₂C₂ chelate cycle in the [ZnLCl₂] molecule. There are two five-membered CdN₂C₂ chelate cycles and a Cd₂Cl₂ dinuclear unit in the molecule of [Cd₂L₂Cl₄]. The coordination polyhedra are distorted tetrahedron Cl₂N₂ (in the structure **1**) and distorted tetragonal pyramid Cl₃N₂ (in the structure of **3**). According to IR-spectroscopic data, complex **2** is binuclear. Complexes **1** and **2** display bright luminescence in CHCl₃ solutions ($\lambda_{\text{max}} = 477$ and 475 nm, respectively) and in the solid state ($\lambda_{\text{max}} = 510$ and 529 nm, respectively). The free L ligand shows weak luminescence intensity ($\lambda_{\text{max}} = 441$ and 467 nm in CHCl₃ and solid state, respectively).

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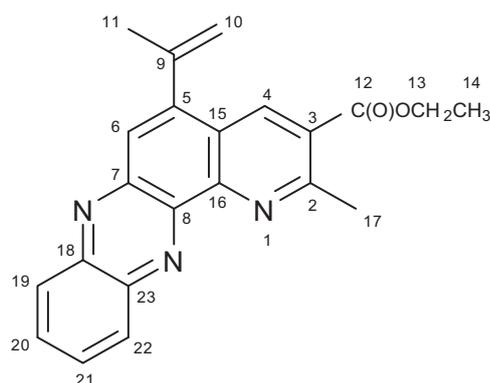
1. Introduction

The synthesis of luminescent metal complexes with organic ligands is a hot topic of modern coordination chemistry [1–11]. A great attention is focused on the study of luminescent Zn(II) complexes in the solid state and in solutions. Luminescent zinc(II) complexes are used for production of organic light-emitting diodes (OLED) [1,5,6,12–14]. The color of emission of Zn(II) compounds depends strongly on the nature of organic ligands [6]. Complexes showing white luminescence are of particular interest [5,13–15]. In solutions, some organic ligands can be used for recognition and sensing of Zn²⁺ ions [16,17]. Fluorescence intensity (*I*) of Zn(II) chelate complexes was found to increase significantly as compared to the intensity of free organic ligand. High intensity was observed for the complex of ZnCl₂ with 9,10-bis(((2-(dimethylamino)ethyl)methylamino)-methyl)anthracene in CH₃CN [18].

The increase of luminescence intensity is believed to be associated with chelation (the so-called CHEF effect, *i.e.*, chelation enhanced fluorescence) [18–25]. Luminescent Cd(II) complexes are also of interest for producing luminescent materials [19,22]. Many N-donor ligands coordinating Zn²⁺ and Cd²⁺ ions contain quinoline or 1,10-phenanthroline moieties [20–24]. Heteroaromatic compounds consisting of four fused aromatic rings are of interest as ligands-fluorophores. However, there are little data available on the synthesis and luminescence of these compounds [17,20]. Of particular interest is synthesizing the coordination compounds with derivatives of natural products. Upon functionalization of chiral pinopyridine prepared from natural (–)- α -pinene, tetracyclic ethyl 2-methyl-5-(prop-1-en-2-yl)pyrido[2,3-a]phenazine-3-carboxylate (L) was formed (Scheme 1) [26]. This compound exhibits dark blue photoluminescence. The crystal structure of L has been reported [26]. The structure of pyridophenazine derivative L is favorable for chelating coordination to metal ions to form luminescent complexes. Substituents in L represent a result of functionalization of pyridophenazine core. In our opinion, they must have no essential effect on the coordination ability of L. Of importance to

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Scheme 1. Structure of L ligand (atomic numeration is given for assigning NMR spectra).

potential further study is that using the additional functions (isopropenyl and/or ester) allows L to be chemically grafted to the polymeric matrix (fibers) to form chelating materials.

Our goal was to prepare Zn(II) and Cd(II) chloride complexes with a new tetracyclic compound L and to study their structures and photoluminescent properties.

2. Experimental

2.1. General

Reagent L was prepared by a technique reported in Ref. [26]. The following compounds were used for the synthesis: ZnCl₂ and CdCl₂ (pure for analysis), EtOH (rectified), CH₂Cl₂, CHCl₃, and hexane (chemically pure). Elemental analysis was performed on Euro EA 3000 analyzer. IR absorption spectra were recorded on a VERTEX-80 spectrophotometer at 100–600 cm⁻¹. Samples **1** and **2** were studied by powder X-ray diffraction method on an automated powder DRON-3M diffractometer (Cu K α radiation, Ni filter). NMR spectra were recorded at +30 °C for solutions in CDCl₃ (5–10 mg/ml) using a Bruker DRX-500 instrument (500.132 MHz for ¹H and 25.758 MHz for ¹³C) locked to the deuterium resonance of the solvent. The chemical shifts were calculated relative to the solvent signals used as the internal standard: δ_C 76.90 ppm and δ_H 7.24 ppm. Signal assignment was made using *J* modulated ¹³C NMR spectra (proton-noise-decoupling, the opposite phases for the signals of the atoms with the odd and even numbers of the attached protons, tuning to the constant *J* = 135 Hz) and 2D NMR spectra: (1) homonuclear ¹H–¹H correlation, (2) heteronuclear ¹³C–¹H correlation at the direct spin–spin coupling constants (*J* = 135 Hz), and (3) heteronuclear ¹³C–¹H correlation at the long-range spin–spin coupling constants (*J* = 10 Hz). The excitation and photoluminescence (PL) spectra of the compounds in CHCl₃ solutions and in the solid state were detected using an FLS920 spectrofluorimeter (Edinburg Instruments) at room temperature. The solid samples for recording PL spectra and PL kinetics were prepared by grinding the compounds to powder between two quartz glasses. The thin layer of powder between glasses was placed at 45° to the excitation light beam. For registration of PL in the solutions, the standard 1 cm cuvette and the spectral pure CHCl₃ were used. The xenon Xe900 lamp was employed as a light source to excite the steady-state PL spectra. To record PL kinetics, the laser diode EPLED-320 (λ_{ex} = 320 nm, pulse duration 600 ps) and the diode laser EPL-375 (λ_{ex} = 375 nm, pulse duration 60 ps) were applied. The PL kinetics were fitted by triexponential approximations using the FLS920 program or FAST program (Edinburgh Instruments). The anthracene was used as a standard to measure the quantum

yields. The optical absorption spectra were recorded on a HP 8453 spectrophotometer (Agilent Technologies).

2.2. Synthesis of [ZnLCl₂] (**1**)

A solution of L (0.036 g, 0.1 mmol) in a mixture of EtOH and CH₂Cl₂ (1:1 v/v, 4 mL) was added dropwise to a stirred solution of ZnCl₂ (0.027 g, 0.2 mmol) in EtOH (2 mL). The solution was kept at room temperature. Small yellow crystals formed when the volume of the solution became ca. 1–2 mL. The precipitate was filtered off, washed with cold *i*-PrOH, and dried *in vacuo* at room temperature. The crude product was recrystallized from a CHCl₃–hexane mixture. Yield 0.011 g (20%). *Anal. Calc.* for C₂₂H₁₉Cl₂N₃O₂·Zn (493.7): C, 53.5; H, 3.9; N, 8.5. Found: C, 53.4; H, 3.9; N, 8.6%. Single crystals of complex **1** were grown by slow evaporation of the solution of this compound in an acetone–EtOH (1:1) mixture.

2.3. Synthesis of Cd₂L₂Cl₄ (**2**)

A solution of L (0.036 g, 0.1 mmol) in 4 mL of CH₂Cl₂ was added to a stirred solution of CdCl₂·2.5H₂O (0.034 g, 0.15 mmol) in 3 mL of EtOH. The resulting solution was stirred for 40 min and evaporated to a minimal volume. After that, the precipitated yellow residue was filtered off. The product was recrystallized from CH₂Cl₂. Yield 0.033 g (30%). *Anal. Calc.* for C₄₄H₃₈Cl₄N₆O₄Cd₂ (1081.4): C, 48.9; H, 3.5; N, 7.8. Found: C, 47.0; H, 3.9; N, 7.3%.

2.4. Preparation of [Cd₂L₂Cl₄]·4CH₂Cl₂ (**3**)

Single crystals of **3** solvate were prepared by slow evaporation of the solution of complex **2** in CH₂Cl₂. Those were taken from the solution and poured with Vaseline oil.

2.5. X-ray crystallography

For single crystals of **1** and **3** compounds, the unit cell parameters and intensities of reflections were measured at 150 K on a Bruker X8 Apex CCD diffractometer equipped with a two-axis detector by a standard technique (Mo K α radiation, λ = 0.71073 Å, graphite monochromator). Crystallographic characteristics, X-ray diffraction data, and structure refinements are listed in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares method in *F*² in anisotropic approximation for non-hydrogen atoms using SHELXL-97 program package [27]. All hydrogen atoms were located from difference Fourier syntheses and included into the refinement in isotropic approximation along with non-hydrogen atoms. Selected interatomic distances and bond angles are given in Tables S1 and S2 (Supporting information).

3. Results and discussion

3.1. Synthetic aspects

The complexes **1** and **2** were synthesized by reacting corresponding metal salt with L in CH₂Cl₂–EtOH medium. The M:L = 2:1 and 1.5:1 M ratio was applied for the synthesis of the complexes, respectively. The complexes are slightly soluble in water and in DMSO. To recrystallize crude products, CHCl₃–hexane mixture and CH₂Cl₂ have been used. Complexes are stable in air.

3.2. Description of the crystal structures

3.2.1. [ZnLCl₂] (**1**)

The crystal structure of **1** complex is built of mononuclear molecules (Fig. 1). The Zn atom coordinates two N atoms of the

Table 1
Crystallographic characteristics, experimental data and structure refinement for **1** complex and **3** solvate.

Compound	1	3
Empirical formula	C ₂₂ H ₁₉ Cl ₂ N ₃ O ₂ Zn	C ₄₈ H ₄₆ Cd ₂ Cl ₁₂ N ₆ O ₄
Molecular mass	493.67	1421.11
Crystal system	monoclinic	triclinic
Space group	<i>P</i> 2 ₁	<i>P</i> 1̄
<i>a</i> (Å)	8.3902(4)	11.1261(3)
<i>b</i> (Å)	14.9988(6)	11.5834(3)
<i>c</i> (Å)	9.0185(4)	11.8419(3)
α (°)		94.622(1)
β (°)	108.224(1)	97.670(1)
γ (°)		110.213(1)
<i>V</i> (Å ³)	1077.99(8)	1406.11(6)
<i>Z</i>	2	1
ρ_{calc} (g cm ⁻³)	1.521	1.678
μ (mm ⁻¹)	1.411	1.347
Crystal sizes (mm)	0.25 × 0.13 × 0.05	0.15 × 0.13 × 0.04
Scan range, θ , degree	2.38–28.41	1.75–30.65
Number of measured reflections	7899	14579
Number of independent reflections	4688	8550
<i>R</i> _{int}	0.0275	0.0151
Number of reflections with $ I > 2\sigma(I)$	4174	7526
Number of refined parameters	275	328
Goodness-of-fit (GOF) on <i>F</i> ²	0.852	1.065
<i>R</i> -factor, $ I > 2\sigma(I)$		
<i>R</i> ₁	0.0275	0.0285
<i>wR</i> ₂	0.0531	0.0681
<i>R</i> -factor (for all <i>I</i> _{hkl})		
<i>R</i> ₁	0.0327	0.0356
<i>wR</i> ₂	0.0544	0.0707
Residual electron density (max/min) (e/Å ³)	0.375/−0.244	1.014/−0.951

bidentate chelating ligand L. This results in closure of five-membered chelate cycle ZnN₂C₂. The Zn–N distances differ only slightly (2.078(2) and 2.085(2) Å). The coordination sphere of the Zn atom involves two Cl atoms with the Zn–Cl distances of 2.1986(7) and 2.2016(6) Å, respectively (Table S1). The Cl₂N₂ polyhedron is a distorted tetrahedron. The moiety consisting of the chelate and four six-membered organic cycles have a virtually planar structure. An average deviation from the root-mean-square atomic plane of the cycles is 0.058(2) Å. The Cl(1) and Cl(2) atoms deviates from this plane by 2.203(2) and 1.609(2) Å, respectively, on different

sides. The intermolecular distances are within the range typical for van der Waals interactions and weak H bonds. The shortest Zn···Zn separation is 7.522(2) Å.

3.2.2. [Cd₂L₂Cl₄]·4CH₂Cl₂ (**3**)

The crystal structure of compound **3** consists of centrosymmetric binuclear molecules [Cd₂L₂Cl₄] and uncoordinated CH₂Cl₂ molecules. The molecular structure of [Cd₂L₂Cl₄] is shown in Fig 2. The coordination Cl₃N₂ polyhedron is a distorted tetragonal pyramid with two N atoms of the bidentate chelating ligand L (Cd–N 2.327(1) and 2.391(2) Å) and two bridging Cl atoms (Cd–Cl 2.548(1) and 2.609(1) Å) in its base (Table S2). The root-mean-square deviation of four atoms (2Cl + 2N) from the plane is 0.073 Å. The Cd atom deviates from the plane by 0.892(8) Å. The terminal Cl(2) atom occupies the axial pyramid vertex at the shorter distance of 2.417(1) Å. In the molecule, there are two five-membered chelate cycles CdN₂C₂ and a metal cycle Cd₂Cl₂. The CdN₂C₂ cycles adopt the envelope conformation. The root-mean-square deviation of four atoms of this cycle (2N + 2C) from the plane is 0.006(1) Å, and the Cd atom deviates by 0.651(3) Å. The Cd₂Cl₂ unit is planar and the Cd···Cd separation is 3.877(2) Å. Two Cl₃N₂ polyhedra share the Cl(1)···Cl(1)' edge with the distance of 3.401(2) Å. In the metal cycle, the angle at Cl(1) is 97.5°. The terminal Cl(2) and Cl(2)' atoms are situated in *trans*-positions relative to the metal cycle. The molecule of [Cd₂L₂Cl₄] has a ladder segment shape (Fig. 2). The five cycles of two mononuclear moieties have a virtually planar structure with the average atomic deviation of 0.093(2) Å.

The packing of the molecules along the (100) plane in the crystal structure of **3** is shown in Fig. S1. Translationally identical molecules of the binuclear [Cd₂L₂Cl₄] complex are not linked to each other. The neighboring molecules have only weak contacts with C(22)···C(22') distances of 3.602(5) Å. There are cavities (424 Å³) between the discrete molecules of the complexes. Each of them is occupied by four CH₂Cl₂ molecules. A minimum distance between Cl atoms of the complex and C atoms of the CH₂Cl₂ molecules (Cl(2)···C(24)) is 3.604(3) Å. This exceeds the sum of van der Waals radii of Cl and C (3.5 Å). The occupation of the cavities by CH₂Cl₂ molecules is probably favorable for the formation of single crystals of solvate **3**.

The identity of single crystals of **1** compound and the polycrystalline phase synthesized was evidenced by powder X-ray diffraction analysis. The observed X-ray diffraction pattern of compound **2** differs from those of mononuclear complex **1** and solvate **3**.

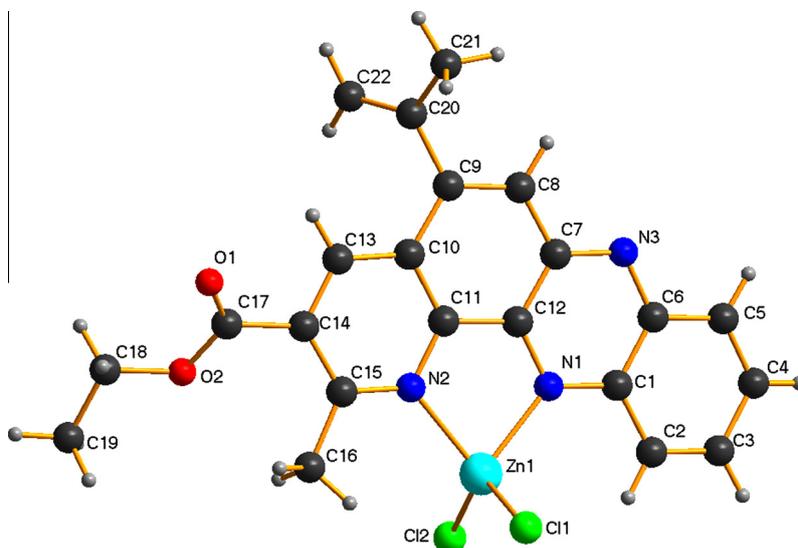


Fig. 1. Molecular structure of complex **1** with the numeration of non-hydrogen atoms.

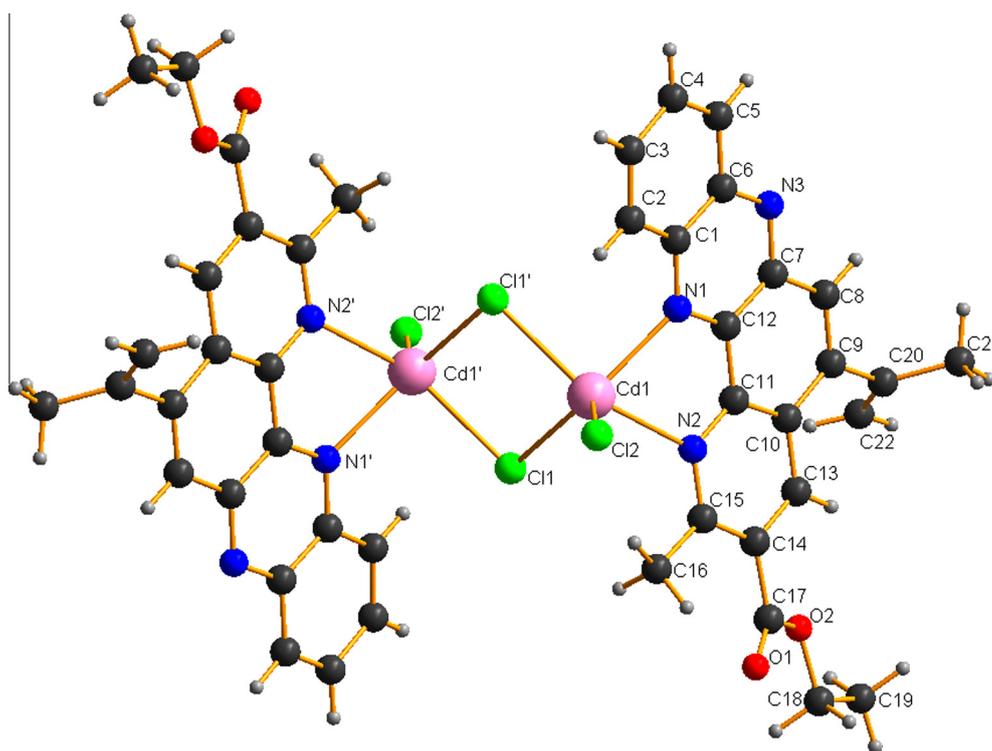


Fig. 2. Molecular structure of $[\text{Cd}_2\text{L}_2\text{Cl}_4]$ complex with the numeration of non-hydrogen atoms.

The split $\nu(\text{Zn}-\text{Cl})$ band with the intensive maximum at 346 cm^{-1} is observed at the IR-spectrum of mononuclear complex **1** in the range typical for metal–ligand bond vibrations. The IR-spectrum of complex **2** exhibits two intensive bands at 268 and 188 cm^{-1} which can be attributed to stretching vibrations of the terminal and bridging Cd–Cl bonds, respectively. These data and X-ray structure data for solvate **3** allow us to suggest complex **2** to be a dimer. It seems reasonable that the structure of compound **2** is similar to that of the $[\text{Cd}_2\text{L}_2\text{Cl}_4]$ complex in solvate **3**.

3.3. NMR study

NMR study shows both compounds **1** and **2** to exist as molecular complexes in CDCl_3 solution. The coordination of two nitrogens of the azaphenazine moiety to the metal atom is proved by changes in the chemical shifts of the ligand atoms in the immediate environment to the coordination site (Table S3). Noticeable changes in chemical shifts of the ester group and atom H-4 in compounds **1** and **2** in comparison with those of the free L ligand can be explained in terms of additional dynamic coordination of the ester oxygen atom to the metal. Formation of intermolecular associates seems to be reversible (like aggregate interchange) because carbon-13 NMR spectra of the compounds look like dynamic and contain broadened signals: some signals are quite narrow, some are broadened to different extent, and some are too broad to be visible.

3.4. UV–Vis spectra and spectra and kinetics of luminescence

Fig. 3a shows the optical absorption and PL spectra of the compounds L, **1** and **2** in CHCl_3 . The incorporation of L into the coordination spheres of Zn^{2+} or Cd^{2+} ions leads to the red shift of absorption bands. For the intensive band of L located at 310 nm the shift is ca. 500 cm^{-1} . For the long-wave bands at $\lambda > 350\text{ nm}$ the shift is close to $1300\text{--}1650\text{ cm}^{-1}$. The difference of spectra

(Fig. 3a) shows that complexes **1** and **2** do not dissociate in CHCl_3 . This agrees well with NMR data.

The emission bands of **1** and **2** complexes show a red shift of $1600\text{--}1700\text{ cm}^{-1}$ with respect to the emission band of the free ligand L (Fig. 3a). The free ligand displays blue fluorescence with a wide band at 441 nm [26]. The intensity of the band is less by an order of magnitude than the intensity of PL bands of complexes **1** and **2** (maxima at 477 and 474 nm , respectively) at the same registration conditions (the same absorption at the excitation wavelength). The red shift of emission bands of complexes **1** and **2** is due to the red displacement of long-wave absorption of these complexes relative to the free ligand band. The Stokes shifts for compounds L, **1**, and **2** in CHCl_3 are small enough ($1650\text{--}2200\text{ cm}^{-1}$). The excitation PL spectra for all three compounds coincide with the absorption spectra. The positions of absorption and PL bands maxima and the values of absorption coefficients are presented in Table S4.

The kinetics of PL in CHCl_3 attracts considerable interest because of its drastic difference for free L, **1**, and **2** (Fig. 3b). An EPL-375 diode laser with pulses at 375 nm (duration 60 ps) was used for excitation of PL. The convolution with the response function, which was registered with a scattering on quartz frosted glass, allowed to determine the PL times above 20 ps . To fit the kinetic curves, the triexponential approximation was used which agree best with the experimental curves

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}}$$

The percent of emitted quanta in every exponent is determined by the $A_i \tau_i$ product. The results of kinetic curves processing are presented in Table 2 (the times of exponents and the percent of emitted quanta). For the free L ligand the basic time of PL is 125 ps (92% of emitted quanta). The contribution of components with longer times (1.1 and 5.1 ns) does not exceed 4% for each. Complexes **1** and **2** display a longer lifetime of PL, 1.33 ns (98%) and 1.49 ns (96%), respectively. The presence of low intensity components in

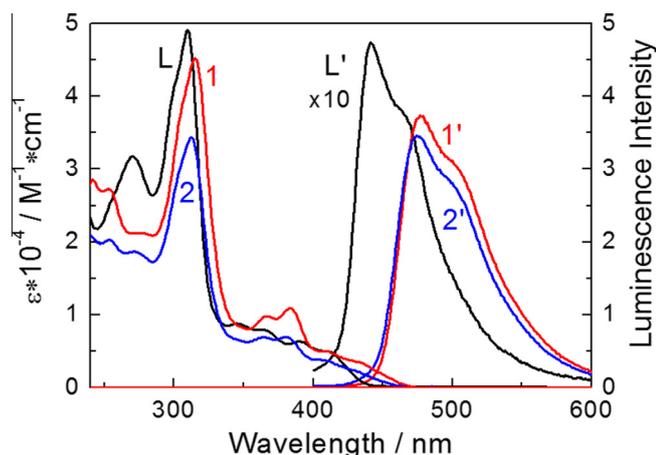


Fig. 3a. The optical absorption (L, 1, 2) and PL (L', 1', 2') spectra of compounds L, 1 and 2 in CHCl₃; (L' spectrum is enlarged by a factor of ten in comparison with 1' and 2' spectra).

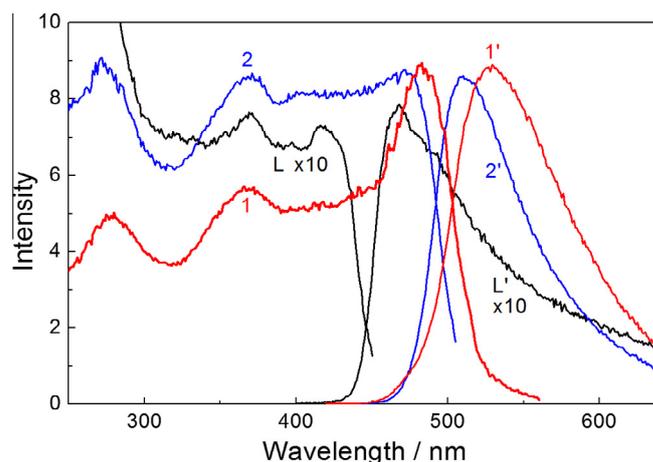


Fig. 4. The excitation (L, 1, 2) and PL (L', 1', 2') spectra of L, 1 and 2 powders. Spectra L and L' are enlarged by a factor of ten in comparison with 1, 1' and 2, 2' spectra. The excitation spectra were recorded at maxima of PL.

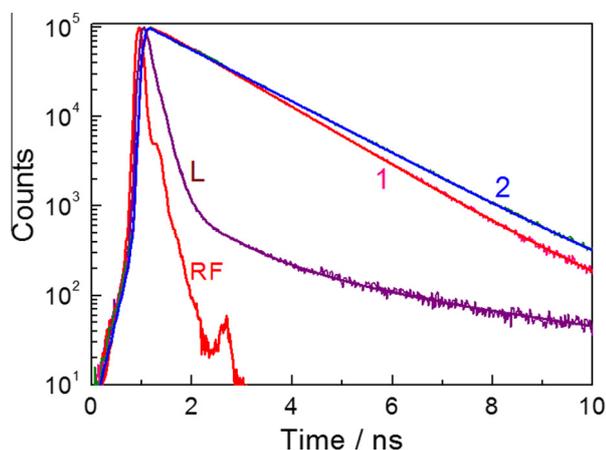


Fig. 3b. RF – the response function with an EPL-375 laser; L, 1, 2 – the luminescence kinetics of compounds L, 1, 2 in CHCl₃. The solid lines are the fitting in three-exponential approximation (the results of fitting are presented in Table 2).

luminescence kinetics can be explained by different reasons. It can be traces of uncontrolled impurities or the existence of small concentrations of other forms of complexes. We cannot also neglect the existence of other conformers of ligand L in the ground or excited states. For the further calculations we used the fastest times of components with the intensity above 92–98%.

The lifetime and quantum yield of PL are determined by the expressions:

$$\tau = \frac{1}{k_{nr} + k_r}, \phi = \frac{k_r}{k_{nr} + k_r} = k_r \tau,$$

Table 2

The maxima of bands, quantum yields and lifetimes of PL for compounds L, 1 and 2 in CHCl₃ and as powders. The fitting of kinetic curves is in three exponential approximation. In last two columns the rate constants of radiative k_r and radiationless k_{nr} transitions are presented.

Conditions	λ_{max}/nm	ϕ_f	τ_1/ns	$A_1\tau_1\%$	τ_2/ns	$A_2\tau_2\%$	τ_3/ns	$A_3\tau_3\%$	$k_r \times 10^{-7}/s^{-1}$	$k_{nr} \times 10^{-9}/s^{-1}$	
L	In CHCl ₃	441	0.01200	0.125	92	1.10	4	5.2	4	9.3	7.91
	Powder	467	~0.00034	0.073	89.2	0.82	8.1	4.4	1.7	0.47	14.0
1	In CHCl ₃	477	0.1000	0.145	1.35	1.33	98	6.5	0.7	7.5	0.675
	Powder	510	~0.0098	0.66	10.2	1.63	73.4	4.1	16.4	0.60	0.610
2	In CHCl ₃	475	0.096	0.139	3.2	1.49	96	4.9	0.8	6.4	0.616
	Powder	529	~0.014	0.21	5.6	1.31	34.3	5.1	60.1	1.07	0.750

where k_{nr} and k_r are the rate constants of radiationless and radiative transitions, respectively, from excited S_1 state to ground S_0 state. The times and quantum yields of PL (Table 2) show that the radiative rate constants (k_r) for the free L ligand and complexes 1 and 2 are closely related (for example, $k_r^L/k_r^{ZnCl_2} \approx 1.2$). So, the increase in quantum yield and excited state lifetimes for the complexes in comparison with free L is associated with the decrease in the rate constant of radiationless transitions by a factor of ten (Table 2). It is likely that the coordination of L ligand with Zn^{2+} or Cd^{2+} ions leads to increase of the molecular structure rigidity and to the disappearance of low frequency vibrations which take part in the fast radiationless relaxation of the free ligand. So, the CHEF effect can be determined by the decrease of the radiationless rate constants upon complex formation.

The excitation and PL spectra for the free L ligand and complexes 1 and 2 in the solid state are presented in Fig. 4. In this case, as for CHCl₃ solutions, the PL band of the free L ligand is multiplied by a factor of ten because its intensity is less than those of PL bands of the complexes. The maxima of PL bands in the solid state are red shifted in comparison with CHCl₃ solutions by 26, 33, and 54 nm for L, 1, and 2, respectively. These shifts are probably determined by the migration of excitation which emitted at the defective centers with lower energetic levels. The excitation spectra in solid state overlap practically all spectral ranges where the absorption spectra of L, 1, and 2 in CHCl₃ are located (Figs. 3a and 4). It is surely impossible to expect the accurate coincidence due to the scattering processes in solid state at the luminescence registration.

The fluorescence kinetics for the compounds L, 1, and 2 in solid state are more different from a monoexponential law in comparison with CHCl₃ solutions. The fitting of kinetic curves in this case was performed also in the triexponential approximation and the results of fitting are presented in Table 2. The fluorescence lifetime for the free L ligand, as in CHCl₃ solutions, is short enough (73 ps,

89.2%). The longer time components (0.82 and 4.4 ns) have the low contributions. The fluorescence lifetimes for the complexes **1** and **2** are greater and the kinetics displays the considerable nonexponential profile. For example, the lifetimes for the complex **1** are in the interval 0.66–4.1 ns. For the complex **2** they are in the range 0.21–5.1 ns (Table 2).

The nonexponential nature of kinetics is most likely determined by the heterogeneity of the emitting centers. Some of them can be located on the surface of polycrystals. The others are in the depth of crystal framework or close to different defects. Moreover, for the Cd(II) complex, the appearance of the intensive component with a lifetime of 5.1 ns (60%) may be due to the binuclear structure [Cd₂L₂Cl₄] with the relatively short Cd...Cd distance of 3.877(2) Å. For the mononuclear Zn(II) complex, the Zn...Zn distance is 7.522(2) Å. The such influence of the structure of the complexes on the fluorescence intensity was detected for the chloride Zn(II) and Cd(II) complexes with (+)-3-carene pyrazolylquinoline (L¹) [28,29], however, no CHEF effect was observed for these complexes.

The estimations of quantum yields for compounds L, **1** and **2** were carried out by comparison with the spectrum of anthracene in CHCl₃ solution and in the solid state (anthracene quantum yield is 0.93 [30]). The quantum yields for the solid samples (Table 2) are less by approximately an order of magnitude as compared to CHCl₃ solutions. These estimations show that the radiationless rate constants k_{nr} for the solid samples are close to those for solutions, and the quantum yield decrease is due to suppression of the radiative rate constant k_r by a factor of ten (Table 2).

4. Conclusions

The complexes [ZnLCl₂] (**1**), Cd₂L₂Cl₄ (**2**), and solvate [Cd₂L₂Cl₄]-4CH₂Cl₂ (**3**) were prepared by reacting the fused tetracyclic L ligand ethyl 2-methyl-5-(prop-1-en-2-yl)pyrido[2,3-a]phenazine-3-carboxylate with zinc(II) and cadmium(II) chlorides. It ought to note that **1** and **2** are the first complexes with pyridophenazine derivative. Compound **1** is a mononuclear complex with a distorted tetrahedral structure of the Cl₂N₂ polyhedron, while [Cd₂L₂Cl₄] in the structure of **3** is a binuclear complex with the distorted tetragonal pyramidal coordination polyhedron Cl₃N₂. Owing to the greater ionic radius, Cd(II) tends to increase its coordination number as compared to Zn(II) [31]. The similar tendency was observed for Zn(II) and Cd(II) chloride complexes with L¹, i.e., [ZnL¹Cl₂] is a mononuclear complex with the coordination number of four [28] while [Cd₂L¹Cl₄] is a binuclear complex with the coordination number of five [29]. Unlike L, complexes **1** and **2** show bright photoluminescence in the solid state.

The coordination of L ligand with Zn²⁺ and Cd²⁺ ions leads to increase of luminescence intensity in order of magnitude. Complexes **1** and **2** show bright photoluminescence both in the solid state and in CHCl₃ solutions due to the considerable reduction of radiationless rate constants k_{nr} in comparison with the free L ligand. Thus, the use of fused tetracyclic compound L as the ligand is promising for preparing other metal complexes with intensive photoluminescence.

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Appendix A. Supplementary data

CCDC 925313 and 925314 contain the supplementary crystallographic data for **1** and **3**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.04.011>.

References

- [1] A. Vogler, H. Kunkely, *Top. Curr. Chem.* 213 (2001) 143.
- [2] C.W. Tang, S.A. Van Slyke, *Appl. Phys. Lett.* 51 (1987) 913.
- [3] T.A. Hopkins, K. Meerholz, S. Shaheen, M.L. Anderson, A. Schmidt, B. Kippelen, A.B. Padias, H.K. Hall, N. Peighambarian, N.R. Armstrong, *Chem. Mater.* 8 (1996) 344.
- [4] L.S. Sapochak, A. Padmaperuma, N. Washton, F. Endrino, G.T. Schmett, J. Marshall, D. Fogarty, P.E. Burrows, S.R. Forrester, *J. Am. Chem. Soc.* 123 (2001) 6300.
- [5] M.N. Bochkarev, A.G. Vitukhnovski, M.A. Katkova, *Organic Light-Emitting Diodes*, DEKOM, Nizhnii Novgorod, 2011.
- [6] A.V. Metelitsa, A.S. Burlov, S.O. Bezuglyi, I.G. Borodkina, V.A. Bren', A.D. Garnovskii, V.I. Minkin, *Russ. J. Coord. Chem.* 32 (2006) 858.
- [7] L. Armelao, S. Quici, F. Barigelli, G. Accorsi, G. Bottaro, M. Cavazzini, E. Tondello, *Coord. Chem. Rev.* 254 (2010) 487.
- [8] M.A. Katkova, M.N. Bochkarev, *Dalton Trans.* 39 (2010) 6599.
- [9] P. Chakraborty, A. Guha, S. Das, E. Zangrando, D. Das, *Polyhedron* 49 (2013) 12.
- [10] B. Kupcewicz, A. Kaczmarek-Kedziera, K. Lux, P. Mayer, E. Budzisz, *Polyhedron* 55 (2013) 259.
- [11] B. Machura, I. Nawrot, R. Kruszynski, M. Dulski, *Polyhedron* 54 (2013) 272.
- [12] W. Yang, H. Schmider, Q. Wu, Y. Zhang, S. Wang, *Inorg. Chem.* 39 (2000) 2397.
- [13] T. Sano, Y. Nishio, Y. Hamada, H. Takahashi, T. Usuki, K. Shibata, *J. Mater. Chem.* 10 (2000) 157.
- [14] G. Yu, S. Yin, Y. Liu, Z. Shuai, D. Zhu, *J. Am. Chem. Soc.* 125 (2003) 14816.
- [15] S.V. Larionov, Z.A. Savel'eva, R.F. Klevtsova, L.A. Glinskaya, E.M. Uskov, S.A. Popov, A.V. Tkachev, *J. Struct. Chem.* 51 (2010) 519.
- [16] E. Kimura, T. Koike, *Chem. Soc. Rev.* 27 (1998) 179.
- [17] N.C. Lim, H.C. Freaake, C. Brückner, *Chem. Eur. J.* 11 (2005) 38.
- [18] M.E. Huston, K.W. Haider, A.W. Czarnik, *J. Am. Chem. Soc.* 110 (1988) 4460.
- [19] A.W. Czarnik, *Acc. Chem. Res.* 27 (1994) 302.
- [20] A.P. De Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher, T.E. Rice, *Chem. Rev.* 97 (1997) 1515.
- [21] A.P. De Silva, D.V. Fox, A.J.M. Huxley, T.S. Moody, *Coord. Chem. Rev.* 205 (2000) 41.
- [22] B. Valeur, I. Leray, *Coord. Chem. Rev.* 205 (2000) 3.
- [23] L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, *Coord. Chem. Rev.* 205 (2000) 59.
- [24] N.J. Williams, W. Gan, J.H. Reibenspies, R.D. Hancock, *Inorg. Chem.* 48 (2009) 1407.
- [25] M. Royzen, J.W. Canary, *Polyhedron* 58 (2013) 85.
- [26] E.S. Vasilyev, A.M. Agafontsev, V.D. Kolesnik, Y.V. Gatilov, A.V. Tkachev, *Mendeleev Commun.* 21 (2011) 253.
- [27] G.M. Sheldrick, *SHELXS97 and SHELXL97*, Programs for the Refinement of Crystal Structures, Göttingen University, Göttingen, Germany, 1997.
- [28] S.V. Larionov, Z.A. Savel'eva, R.F. Klevtsova, E.M. Uskov, L.A. Glinskaya, S.A. Popov, A.V. Tkachev, *Russ. J. Coord. Chem.* 37 (2011) 1.
- [29] S.V. Larionov, Z.A. Savel'eva, R.F. Klevtsova, L.A. Glinskaya, E.M. Uskov, M.I. Rakhmanova, S.A. Popov, A.V. Tkachev, *J. Struct. Chem.* 52 (2011) 531.
- [30] G.T. Wright, *Proc. Phys. Soc. B* (1955) 241.
- [31] S.S. Batsanov, *Zh. Neorg. Khim.* 36 (1991) 3015.