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Luminescent Zinc(II) and Cadmium(II) Complexes Based on 2-(4,5-Dimethyl-1*H*-imidazol-2-yl)pyridine and 2-(1-Hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine

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Abstract—Complexes ZnL^1Cl_2, CdL^1Cl_2, $ZnL^1_2Cl_2\cdot1.5H_2O$, $CdL^1_2Cl_2\cdot2H_2O$, $CdL^1_2Cl_2\cdot MeOH\cdot H_2O$ [L^1 = 2-(4,5-dimethyl-1*H*-imidazol-2-yl)pyridine] and inner-complex compounds $ZnL^2_2\cdot2H_2O$, CdL^2_2 [HL^2 = 2-(1-hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine] were synthesized. The complexes exhibit bright photoluminescence in the blue region of the spectrum, with the intensity exceeding this characteristic of the compounds L^1 and HL^2. Compound L^1 in aqueous solution is a potential chemosensor for the determination of zinc and cadmium.

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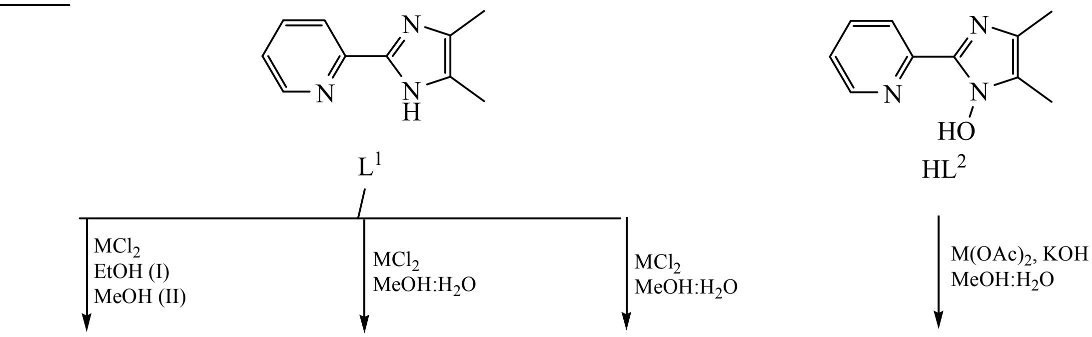
The synthesis of complex compounds of metals with organic ligands that exhibit electro- and photoluminescence is an important branch of the modern coordination chemistry. This is due to the prospects of using such systems in luminescent devices (OLED) [1–3]. Organic reagents capable of acting as ligands can be used as the chemosensors for the determination of metal ions [4, 5].

One of the major classes of compounds showing luminescence is metal complexes of 12th group of the periodic system with heteroaromatic nitrogen-containing ligands [6–10]. Typically, the complexes of these metals exhibit more bright photoluminescence than the heteroaromatic compounds that act as the ligands. This is due, firstly, to the fact that coordination of polyheteroatomic chelating ligands with non luminescent zinc(II) and cadmium(II) cations (electronic configuration d^{10}) results in the formation of a rigid closed ring systems. This increases the degree of conjugation of the heteroaromatic fragments in the molecules of the ligands and, thus, the probability of luminescent emission which is due to the subsystem of organic ligands [11–14]. Secondly, the unshared electron pairs of nitrogen atoms of heteroaromatic compounds are quenchers of the luminescence, and therefore their involvement in the formation of coordination bond also contributes to the luminescence intensity [13]. Note that certain role in the increasing the lumi-nescence intensity can also play a variety of intermolecular interactions like stacking interaction [15, 16].

Among the heteroaromatic ligands, a particular interest attract the compounds having in their composition the nitrogenous heterocycles that are parts of the natural nitrogen bases. We can expect that complexes with such ligands are not toxic. This fact is of great importance in designing electroluminescent devices and chemosensors.

As the ligands for the synthesis of the zinc(II) and cadmium(II) complexes, we chose 2-(4,5-dimethyl-1*H*-imidazol-2-yl)pyridine (L^1) and 2-(1-hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)pyridine (HL^2). A special feature of these reagents is the presence of the imidazole moiety that can be regarded as the core of some naturally occurring compounds [17]. The aim of this work was to synthesize the zinc(II) and cadmium(II) complexes with the compounds $\mathrm{L^1}$ and $\mathrm{HL^2}$ and to study their luminescent properties. A number of transition metal complexes with these ligands is known [18–23]. Moreover, some complexes with unsubstituted 2-(1*H*-imidazol-2-yl)pyridine and its derivatives are under study [24–30]. To our knowledge, luminescent zinc(II) and cadmium(II) complexes with the ligands $\mathrm{L^1}$ and $\mathrm{HL^2}$ have not been described in literature.

Taking into account that compound $\mathrm{L^1}$ probably possesses a function of a chelating ligand, and is capable of forming the complexes of stoichiometry M:L = 1:1 or 1:2, the synthesis of complexes was carried out using different molar ratios. The synthesis of complexes $\mathrm{ZnL^1Cl_2}$ (**I**) and $\mathrm{CdL^1Cl_2}$ (**II**) was performed in alcohol solution (EtOH for **I** and MeOH for **II**) at a ratio $\mathrm{M{:}L^1}$ = 1:1. Note that complex **II** is obtained with a yield close to quantitative. Reducing the ratio of reagents to 1:2 does not result in complexes with 1:2 stoichiometry: only the complexes **I** and **II** were isolated. Further reduction of the $\mathrm{M{:}L^1}$ ratio to 1:4 resulted in obtaining complexes $\mathrm{ZnL^1_2Cl_2{\cdot}1.5H_2O}$ (**III**) and $\mathrm{CdL^1_2Cl_2{\cdot}2H_2O}$ (**IV**). The synthesis was carried out in water-methanol solutions. Isolation of the complexes in the solid phase from the alcohol media failed. Single crystals of the complex $\mathrm{CdL^1_2Cl_2{\cdot}H_2O{\cdot}MeOH}$ (**V**) were obtained by slow crystallization from water-methanol solution when the reagents $\mathrm{CdCl_2{\cdot}2.5H_2O}$ and $\mathrm{L^1}$ were taken in a molar ratio of 1:4. For the synthesis of chelates $\mathrm{ZnL^2_2{\cdot}2H_2O}$ (**VI**) and $\mathrm{CdL^2_2}$ (**VII**) we used zinc(II) and cadmium(II) acetates, which reacted with $\mathrm{HL^2}$ in a water–methanol solution at a ratio of $\mathrm{M{:}HL^2}$ = 1:2, in the presence of stoichiometric amounts of KOH. All complexes are stable in air. Thus, the following transformations were performed:



$\mathrm{ML^1Cl_2}$ (**I, II**) $\mathrm{ML^1_2Cl_2{\cdot}}n\mathrm{H_2O}$ (**III, IV**) $\mathrm{CdL^2_2Cl_2{\cdot}H_2O{\cdot}MeOH}$ (**V**) $\mathrm{ML^2_2{\cdot}}n\mathrm{H_2O}$ (**VI, VII**)

M = Zn (**I**), Cd (**II**); M = Zn, n = 1.5 (**III**); M = Cd, n = 2 (**IV**); M = Zn, n = 2 (**VI**); M = Cd, n = 0 (**VII**).

The IR spectrum of compound $\mathrm{L^1}$ (Table 1) contains bands at 1587–1518 $\mathrm{cm^{-1}}$ that correspond to the stretching-deformation vibrations of the imidazole and pyridine fragments ($\mathrm{R_{ring}}$). In the spectra of the complexes **I–IV** the system of these bands varies considerably, indicating the coordination of $\mathrm{L^1}$ molecules to the metal ions. The broad structured band in the spectrum of compound $\mathrm{L^1}$ at 2300–3200 $\mathrm{cm^{-1}}$ is apparently due to the vibrations of NH group involved in the formation of an intramolecular hydrogen bond with the N atom of the pyridine ring. Vibrations of the NH group in the spectra of complexes **I** and **II** appear as a narrow band, whereas in the spectra of the complexes **III** and **IV** they are observed as broad bands (Table 1). The broadening of this band in the spectra of the complexes **III** and **IV** is presumably due to the formation of hydrogen bonds with water molecules included in the composition of these compounds. Analysis of the spectra of complexes in the low frequency region allowed us to identify the bands of stretching vibrations ν(M–N) and ν(M–Cl) (Table 1). In the high frequency region of the spectra of complexes **III** and **IV** there are the bands of OH group vibrations, ν(OH) at 3367 $\mathrm{cm^{-1}}$ for complex **III** and 3399 $\mathrm{cm^{-1}}$ for complex **IV**, broadened due to the formation of hydrogen bonds. This is consistent with the data of elemental analysis indicating the presence of water molecules in the composition of these compounds.

In the UV spectrum of complex **I** in EtOH there is a band with the absorption maximum at 324 nm (log ε 4.20) and a shoulder at 295 nm (log ε 3.91), which correspond to a small red shift of the absorption maximum in comparison with the UV spectrum of compound L^1 (λ_{max} 313 nm, log ε 4.21 in EtOH).

In the IR spectrum of the compound HL^2 there are broad bands at 3367, 2300, and 1850 cm^{-1} indicating the formation of a short intramolecular hydrogen bond OH···N. These bands disappear in the spectra of compounds **VI** and **VII**, indicating deprotonation of compound HL^2. The shift of the bands of stretching-deformation vibrations of rings in the spectra of complexes **VI** and **VII** with respect to their positions in the spectrum of the compound HL^2 confirms the coordination of the ligand (Table 1). In the low-frequency region of the spectra of complexes **VI** and **VII** there are the bands of ν(M–O) and ν(M–N) vibrations. In the high-frequency region of the spectrum of complex **VI** the vibration bands ν(OH) (3375 cm^{-1}) are observed broadened due to the formation of hydrogen bonds. Thus, the data of IR spectroscopy are consistent with the results of elemental analysis, according to which the compounds **VI** and **VII** are inner-complex compounds.

The UV spectrum of the complex **VI** in EtOH contains two bands with absorption maxima at 301 nm (log ε 4.09) and 350 nm (log ε 4.29), as does the UV spectrum of the initial ligand HL^2 (λ_{max} 285 nm, log ε 3.93 and λ_{max} 313 nm, log ε 4.18) in EtOH. The red shift of the absorption maxima in comparison with the spectra of compounds HL^2, L^1 and the complex **I** is probably due to the coordination of the deprotonated form of the compound HL^2 in the complex **VI**.

The crystal structure of complex **I** is molecular, the complex is built by molecules ZnL^{1}Cl$_2$, located in the *m* plane. The structure and the numbering of the atoms are shown in Fig. 1, the main bond lengths and bond angles of **I** are listed in Table 2. Molecule L^1 is coordinated to the Zn atom in a bidentate cyclic manner by the N atoms of pyridine and imidazole rings. The coordination polyhedron of Zn is supplemented with two chlorine atoms to nearly regular tetrahedron. Coordination of the ligand L^1 in the complex leads to the formation of a planar five-membered metallocycle ZnN$_2$C$_2$. The bond lengths in the molecule of the ligand are as follows: imidazole ring, N–C 1.337(8)–1.381(8) Å, C–C 1.367(9) Å, C–CMe 1.478(9), 1.492(9) Å; pyridine ring, N–C 1.340(8) and 1.351(8) Å, C–C 1.373(10)–1.385(10) Å, C–C$_{pyr}$ 1.454(9) Å. The imidazole and pyridine rings are planar, their bond lengths are in good agreement with published data [31]. The stacks of the ZnL^{1}Cl molecules extending along the *b* axis are connected by the hydrogen bonds between the Cl atoms and NH groups of imidazole rings (Cl^1···N$^{3'}$ 3.308 Å, Fig. 2). In the structure of the complex the stacking interactions were found between pyridine and imidazole rings of adjacent molecules (C^7···N^1 3.700 Å, C^8···C$^{4'}$ 3.666 Å, C^6···C$^{6'}$ 3.646 Å, Fig. 2), the distance between the rings centroids is 3.927 Å. In addition, the structure of the complex **I** includes the contacts Cl^1···Cl$^{1'}$ (3.489 and 3.790 Å).

Table 1. Main vibrational frequencies in the IR spectra of compounds, cm^{-1}.

Comp. no.	NH	R$_{ring}$	MCl	MN	MO
L^1	3200–2300	1587, 1564, 1518			
I	3263	1596, 1526	323	231	
II	3218	1593, 1526	323	224	
III	3200–2200	1591, 1525	274	212	
IV	3200–2200	1587, 1521	225	204	
HL^2		1585, 1521, 1488			
VI		1601, 1575, 1501		264	420, 373
VII		1594, 1579, 1499		264	405, 370

The crystal structure of complex **V** is molecular, formed by molecules CdL$^1_2$Cl$_2$, H$_2$O and CH$_3$OH. Molecular structure of CdL$^1_2$Cl$_2$ and numbering of atoms are shown in Fig. 3. The main bond lengths and bond angles of **V** are listed in Table 2. The ligand molecule L^1 is coordinated to the Cd atom in the

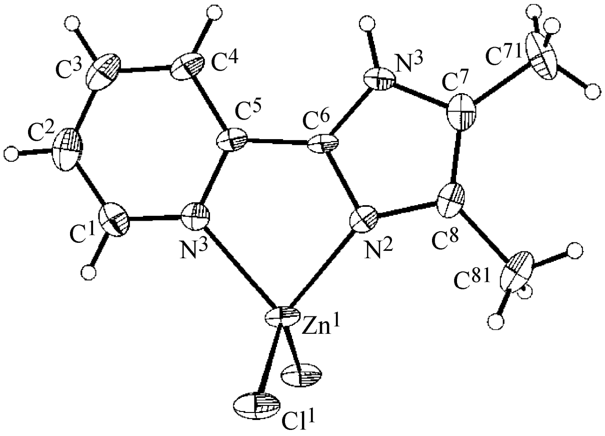


Fig. 1. General view of molecule of complex **I**.

Table 2. Main bond lengths (Å) and bond angles (deg) in compounds **I** and **V**

Bond	*d*	Angle	ω
		Compound **I**	
Zn^1–N^2	2.002(5)	$N^2Zn^1N^1$	81.4(2)
Zn^1–N^1	2.113(5)	$N^2Zn^1Cl^{1\#1}$	113.91(6)
Zn^1–$Cl^{1\#1}$	2.2114(12)	$N^1Zn^1Cl^{1\#1}$	112.03(6)
Zn^1–Cl^1	2.2114(12)	$N^2Zn^1Cl^1$	113.91(6)
		$N^1Zn^1Cl^1$	112.03(6)
		$Cl^{1\#1}Zn^1Cl^1$	117.97(6)
		Compound **V**[a]	
Cd^1–N^{22}	2.359(4)	$N^{22}Cd^1N^{12}$	88.36(12)
Cd^1–N^{12}	2.374(3)	$N^{22}Cd^1N^{11}$	98.32(13)
Cd^1–N^{11}	2.400(3)	$N^{12}Cd^1N^{11}$	71.03(12)
Cd^1–N^{21}	2.411(4)	$N^{22}Cd^1N^{21}$	71.46(14)
Cd^1–Cl^2	2.5786(11)	$N^{12}Cd^1N^{21}$	100.83(12)
Cd^1–Cl^1	2.6214(11)	$N^{11}Cd^1N^{21}$	167.49(12)
		$N^{22}Cd^1Cl^2$	161.78(10)
		$N^{12}Cd^1Cl^2$	91.04(9)
		$N^{11}Cd^1Cl^2$	98.70(8)
		$N^{21}Cd^1Cl^2$	90.80(10)
		$N^{22}Cd^1Cl^1$	90.11(9)
		$N^{12}Cd^1Cl^1$	161.39(9)
		$N^{11}Cd^1Cl^1$	90.87(9)
		$N^{21}Cd^1Cl^1$	96.24(9)
		$Cl^2Cd^1Cl^1$	96.10(4)

[a] Symmetry operators: # 1 *x*, –*y*+1/2, *z*.

bidentate cyclic manner through the N atoms of pyridine and imidazole rings. The coordination surrounding of Cd atoms is completed to octahedral by two Cl atoms. The coordination of the ligand L^1 leads to the formation of the flat five-membered metallocycle CdN_2C_2. The bond lengths in the coordinated molecule L^1 are as follows: imidazole ring, N–C 1.334(5) –1.383(5) Å, C–C 1.378(6) and 1.395(7) Å, C–CMe 1.467(7) –1,500(6) Å; pyridine ring, N–C 1.335(6)–1.401(6) Å, C–C 1.353(7)–1.417(8) Å, C–C_{im} 1.457(6) and 1.419(6) Å. Imidazole and pyridine rings are almost planar, the deviations of atoms from the least-mean-square planes of the rings do not exceed 0.02 Å, the bond lengths in them are in good agreement with published data [31]. The planes of pyridine rings are turned with respect to the planes of imidazole rings at 2.1° and 3.5°. In the structure of the complex **V** the molecules $CdL^1_2Cl_2$, H_2O and CH_3OH are connected in a network by the hydrogen bonds: $O^{1W}\cdots N^{23}$ 2.783 Å, $O^{1W}\cdots Cl^{1'}$ 3.220 and 3.205 Å, $O^{1S}\cdots N^{13'}$ 2.800 Å, $O^{1S}\cdots Cl^{2'}$ 3.080 Å (Fig. 4). The stacks of molecules $CdL^1_2Cl_2$ extending along the *b* axis are connected due to the stacking interaction between imidazole and pyridine rings of neighboring molecules ($N^{13}\cdots C^{12'}$ 3.402 Å, $C^{16}\cdots C^{13'}$ 3.442 Å, $C^{15}\cdots C^{14'}$ 3.449 Å, $N^{23}\cdots C^{22'}$ 3.326 Å, $C^{26}\cdots C^{23'}$ 3.393 Å, $C^{25}\cdots C^{24'}$ 3.392 Å, in Fig. 4), the distance between the rings centroids is 3,946 Å. The stoichiometry of complexes **III** and **IV** is the same as that of complex **V**, M:L^1 = 1:2. In addition, the IR spectra of compounds **III** and **IV** are similar. We can therefore assume that complexes **III** and **IV** also have octahedral structure.

Complexes **I–IV**, **VI**, and **VII** in the solid state exhibit bright luminescence in the visible spectral region. Position of the maxima in the emission spectra of the complexes are 412, 414, 456, 388, 482, and 468 nm, respectively. To compare the relative luminescence intensities, the emission spectra of all samples were recorded under identical conditions (Fig. 5a). The luminescence intensity of the complexes is much greater than the same characteristic of compounds L^1 and HL^2 (the spectra of compounds L^1 and HL^2 are omitted due to the extremely low intensity). Since the complexes differ by water content in their compositions, the comparison of the luminescence intensity is possible only for a series of compounds L^1, **I**, and **II**. The luminescence intensity increases in this series L^1 << **II** < **I**. The position of the emission maximum in the spectrum of complex **II** is practically the same as in the spectrum of compound **I**. It is interesting that on going from the complexes with the stoichiometry 1:1 to 1:2 the emission band position varies differently: in the case of complex **III** a shift is observed to longer wavelengths, while in the case of complex **IV**, to the shorter. When comparing the positions of the bands in the luminescence spectra of a series of complexes based on compounds L^1 and HL^2 it is noted that the bands of inner-complex compounds **VI** and **VII** are shifted significantly to longer wavelengths relative to the bands of the complexes containing L^1 molecule.

The fact of a significant increase of the luminescence intensity of complexes **I–IV** compared with L^1 in a solid state stipulated us to investigate the luminescence of aqueous solutions of MCl_2–L^1 (M = Zn, Cd). To investigate the dependence of the luminescence

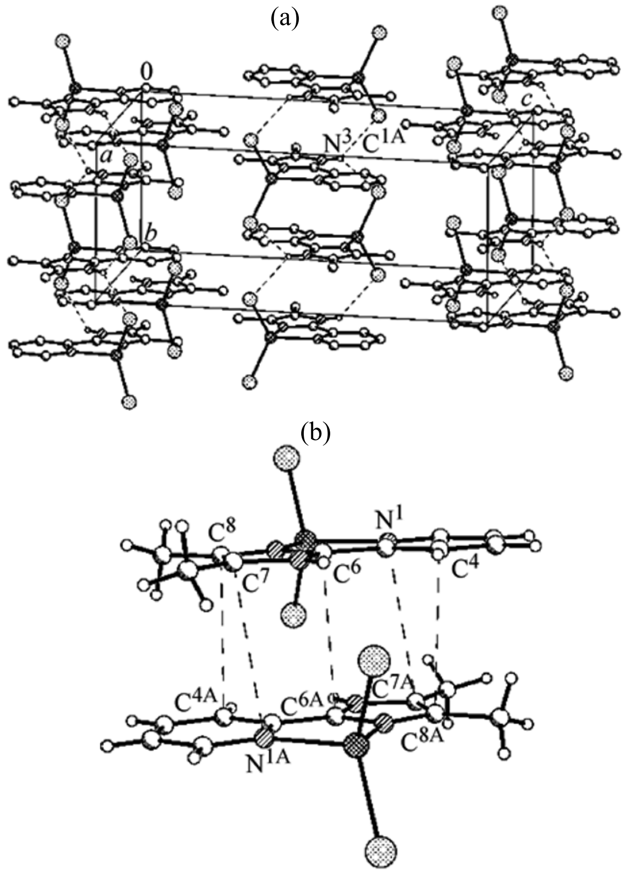


Fig. 2. (a) Hydrogen bonds and (b) stacking interactions in the structure of complex **I**.

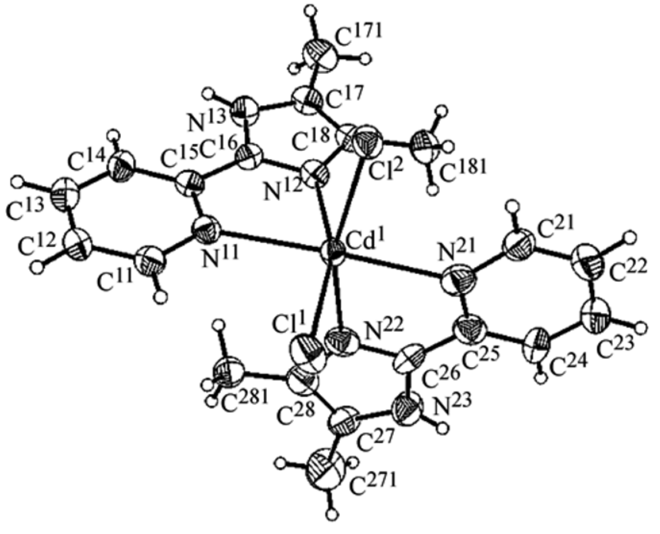


Fig. 3. General view of molecule of complex **V**.

intensity on the metal concentration, we prepared solutions with a fixed concentration of compound L^1 0.2 mM and varied concentrations of MCl_2 (M = Zn, Cd) 0, 0.1, 0.2 and 0.35 mM. To find the optimal conditions for recording the luminescence spectra, we recorded initially the excitation spectra. We found that the increase in the metal ions concentration in solution to 0.20 mM leads to a sharp increase in the luminescence intensity (Figs. 5b and 5c). This concentration corresponds to the molar ratio M:L = 1:1. Further increase in metal concentration up to 0.35 mM (corresponding to the molar ratio $M:L^1$ = 1.75:1) results only in slight increase in intensity. The maxima in the emission spectra of the systems MCl_2–L^1 are located at 419 nm (M = Zn) and 415 nm (M = Cd). Thus, the position of the maxima of emission spectra of the MCl_2–L^1 solutions differ little from the same of solid samples of complexes **I** and **II**. This indicates that in solutions of MCl_2–L^1 with different $M:L^1$ ratios dominate the chemical forms of the same stoichiometry, $M:L^1$ = 1:1. This fact is consistent indirectly with the fact that the inflection on the dependence of emission intensity of solutions MCl_2–L^1 on the metal concentration is also observed at the ratio of $M:L^1$ = 1:1. Under identical conditions, brighter luminescence is observed in the system of $ZnCl_2$–L^1 compared to $CdCl_2$–L^1. Thus, at the $M:L^1$ ratios 1:1 and 1.75:1 the luminescence intensity of $ZnCl_2$–L^1 is 1.5 times higher compared with $CdCl_2$–L^1. It is important that the photoluminescence of solution of L^1 is very weak. Since upon the addition of the salt MCl_2 (M = Zn, Cd) to a solution of compound L^1 the luminescence intensity increases for many times, the compound L^1 can be considered as potential chemosensor for the detection and determination of zinc(II) and cadmium(II).

An important result of this work is finding a significant increase in the luminescence intensity of complexes of zinc(II) and cadmium(II) compared with the weakly luminescenting compounds L^1 and HL^2 in solid form. This suggests that imidazolylpyridine ligands are promising for the synthesis of luminescent metal complexes. It is established that the zinc(II) and cadmium(II) complexes with imidazolylpyridine L^1 are appreciably stable in aqueous solutions. This fact seems essential for the practical application of compound L^1 as chemosensor. The problem of increasing selectivity of compound L^1 toward zinc or cadmium can be solved apparently by the modification of the imidazolylpyridine core by introducing additional functional groups.

EXPERIMENTAL

For the synthesis of the complexes we used $ZnCl_2$. (pure grade) and $CdCl_2{\cdot}2.5H_2O$ (chemically pure

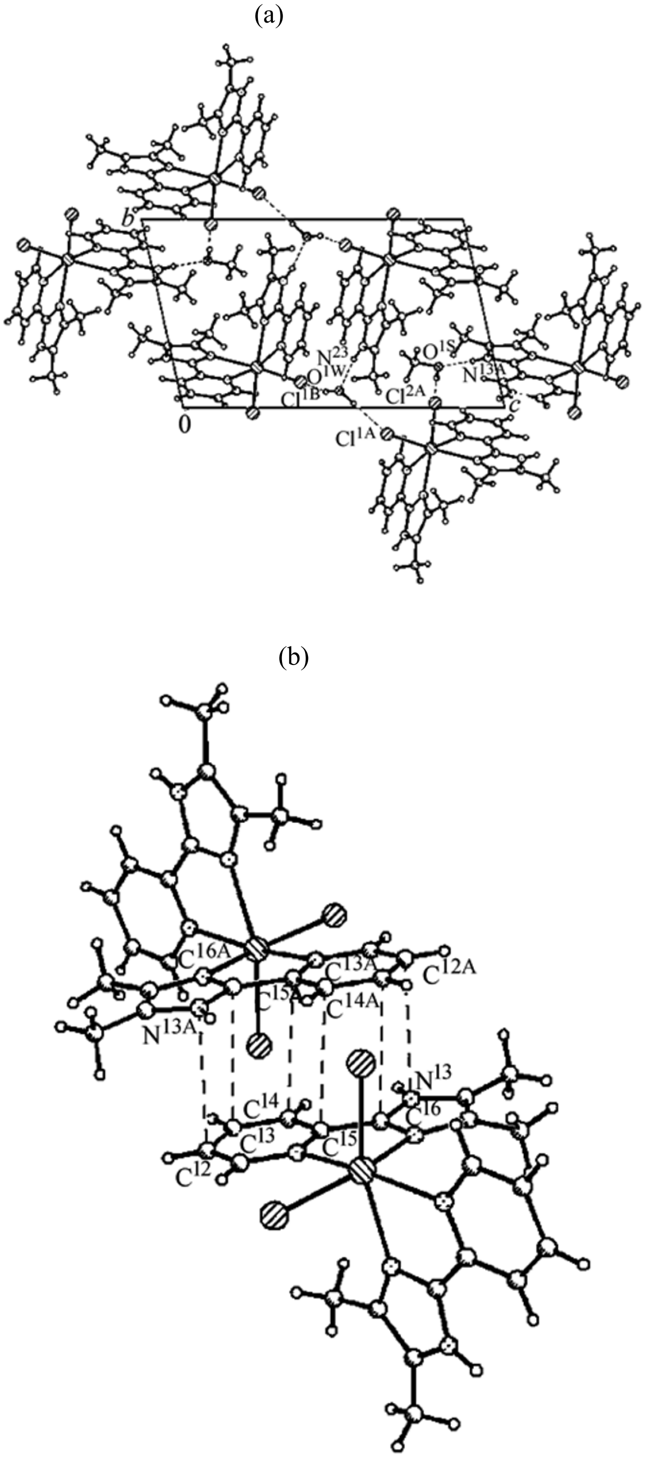


Fig. 4. (a) Hydrogen bonds and (b) stacking interactions in the structure of complex **V**.

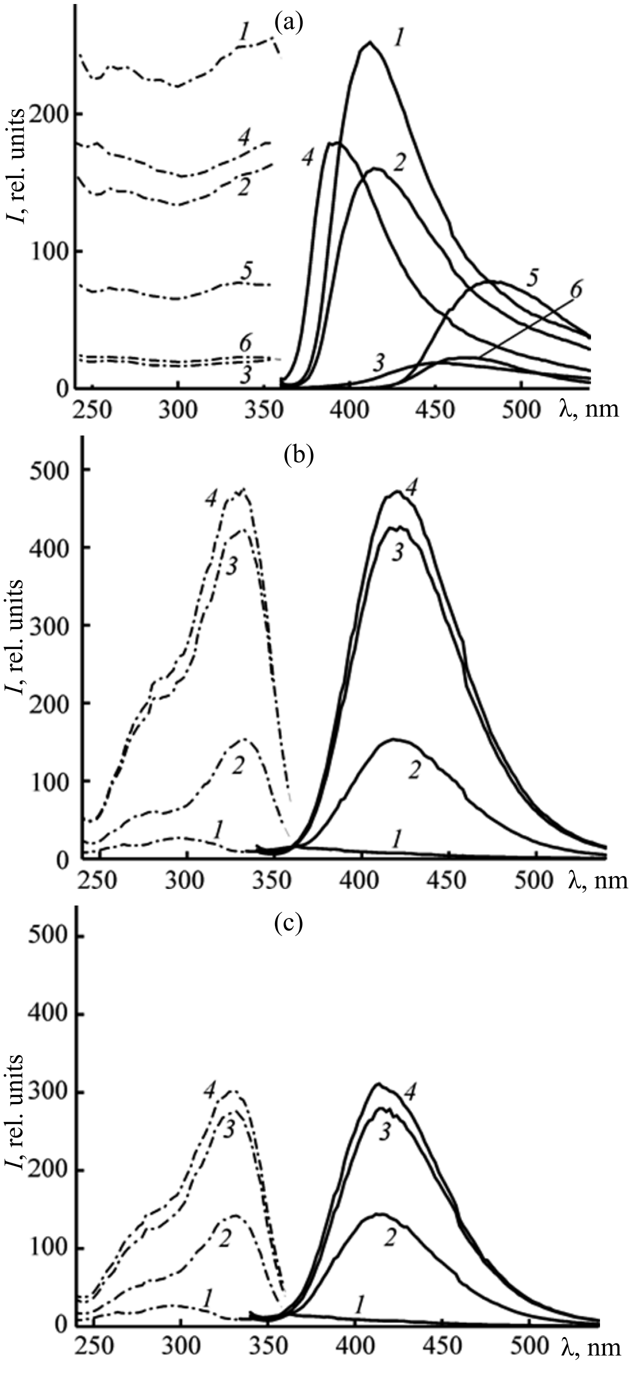


Fig. 5. The excitation spectra (dashed lines) and the luminescence of solids complexes: (a) (*1*) **I**, (*2*) **II**, (*3*) **III**, (*4*) **IV**, (*5*) **VI**, (*6*) **VII**; of solutions (b) $ZnCl_2$–L^1, and (c) $CdCl_2$–L^1, (*1*) L^1 (0.20 mM), (*2*) MCl_2: L^1 (0.10:0.20 mM), (*3*) MCl_2: L^1 (0.20:0.20 mM), and (*4*) MCl_2: L^1 (0.35:0.20 mM).

grade). The used organic solvents are MeOH (chemically pure) and EtOH (rectificate). The content of C, H, N were determined in the analytical laboratory at Institute of Inorganic Chemistry of Siberian Branch of Russian Academy of Sciences on a Euro EA 3000 analyzer. The IR spectra of the complexes were obtained on a Fourier spectrometer IR Scimitar FTS 2000 in the range of 400–4000 cm^{-1} and Vertex 80 in the range of 200–400 cm^{-1} from the mulls in mineral or fluorinated oil. The excitation and luminescence spectra were recorded on a Varian Cary Eclipse spectrophotometer at room temperature under the same conditions for all samples. The excitation and luminescence spectra of solid samples were recorded at a voltage of 450 **V** and λ_{exc} = 350 nm, the spectra of solutions MCl_2–L^1 (M = Zn, Cd) at 500 V and λ_{exc} = 330 nm. The IR spectra of organic compounds (KBr tablets with concentration 0.25%) were recorded on a Bruker Vector 22 FT–IR spectrometer. The ^{1}H NMR spectra were recorded on a Bruker AM–400 instrument with an operating frequency of 400.136 MHz, internal reference were the residual protons of the solvent ($CDCl_3$ 7.24 ppm, DMSO-d_6 2.50 ppm). Melting points were measured on a Mettler Toledo device and were reported without correction. UV spectra of compounds L^1, HL^2, **I**, and **VI** (solutions in ethanol) were recorded on a Hewlett Packard 8453 spectrophotometer. Monitoring the progress of reactions and checking the purity of organic compounds obtained was carried out by TLC on Silufol UV-254 plates, eluent chloroform–methanol 10:1, development under UV-irradiation. *N*-(2-Hyd-roxyimino-1-methylpropyl)hydroxylamine acetate was prepared according to the procedure [32].

2-(4,5-Dimethyl-1*H*-imidazol-2-yl)pyridine (L^1). To a suspension of 3.9 g of NH_4OAc in 20 ml of EtOH was added dropwise a solution of 2.68 g of pyridine-2-aldehyde and 2.15 g of diacetyl in 15 ml of EtOH . The resulting mixture was refluxed for 24 h, cooled, and then 50 ml of water and 30 ml of CH_2Cl_2 were added. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2×10 ml). To the aqueous layer was added while stirring a saturated solution of sodium hydrogen carbonate to pH 8. The mixture was stirred for 1 h. The precipitate was filtered off, washed on the filter with water (2×10 ml) and hexane (2×10 ml), and dried in air. The dried product (3.9 g) was purified by sublimation (145–150°C, 25 mm Hg). Yield 2.95 g (68%), light yellow crystals, mp 157°C. Found, %: C 69.5; H 6.3; N 24.3. $C_{10}H_{11}N_3$. Calculated, %: C 69.3; H 6.4; N 24.3. IR spectrum, ν, cm^{-1}: 3431, 3080, 3041, 2966, 2920, 2862, 2760, 2710, 1587, 1564, 1518, 1466, 1441, 1406, 1250, 1132, 997, 791, 744. 706. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm, *J*, Hz): 2.19 s (6H, CH_3); 7.15 d.d.d, (^{1}H, H^5, *J* = 1.2, 5.0, 7.5); 7.70 d.t (^{1}H, H^4, *J* = 8.1, 1.8); 8.06 d.t (^{1}H, H^6, *J* = 8.1, 1.8); 8.45 d (^{1}H, H^3, *J* = 5.0) 10.40 br.s (^{1}H, NH).

2-(1-Hydroxy-4,5-dimethyl-1*H*-imidazol-2-yl)-pyridine (HL^2). A solution of 1.78 g of *N*-(2-hydroxyimino-1-methylpropyl)hydroxylamine acetate and 1.7 g of pyridine-2-aldehyde in 25 ml of acetic acid was heated until complete consumption of the starting compounds (18 h, TLC monitoring). The solvent was distilled off in a vacuum of water-jet pump. The residue was dissolved in 50 ml of 5% hydrochloric acid at a gentle heating (50°C or below). The resulting solution was stirred at room temperature with 3 g of charcoal for 2 h. The charcoal was filtered off on a paper filter and washed with water (2×10 ml), the filtrate was concentrated to a half volume in a vacuum of water-jet pump and cooled with ice water, and then aqueous ammonia (concentration ~25%) was added to pH ~ 8. The precipitate formed was filtered off, washed on the filter with water (4×10 ml) and diethyl ether (2×5 ml), and dried in air. Yield 1.74 g (90%), white crystals, mp 163.2°C. Found, %: C 62.0; H 5.9; N 21.4. $C_{10}H_{11}N_3O\cdot 0.25H_2O$. Calculated, %: C 62.0; H 6.0; N 21.7. IR spectrum, ν, cm^{-1}: 3367, 3046, 2921, 2857, 1639, 1585, 1521, 1488, 1447, 1310, 1231, 1154, 1116, 991, 965, 815, 795, 744. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, *J,* Hz: 2.06 s (3H, CH_3); 2.15 s(3H, CH_3); 7.32 d.d.d (1H, H^5, *J* = 1.4, 4.8, 7.8); 7.88 d.t (1 H, H^4, *J* = 7.8, 1.4); 8.57 d (1H, H^6, *J* = 4.8); 9.05 br.s (1H, H^3), 12.62 br.s (1H, N–OH).

Dichlorido[2-(4,5-dimethyl-1*H*-imidazol-2-yl)pyridine]zinc, ZnL^{1}Cl$_2$ (I) A warm solution of 104 mg of L^1 in 3 ml of EtOH was added dropwise to a warm solution of 82 mg of $ZnCl_2$ in 3 ml of EtOH. A white precipitate formed. The reaction mixture was stirred at heating for 30 min, the precipitate was filtered off, washed with a small amount of EtOH, and dried in air. Yield 155 mg (83%). Found, %: C 39.0, H 3.7, N 13.5. $C_{10}H_{11}Cl_2N_3Zn$. Calculated, %: C 38.9; H 3.6; N 13.6.

Dichlorido[2-(4,5-dimethyl-1*H*-imidazol-2-yl)pyridine]cadmium, CdL^{1}Cl$_2$ (II). Hot solution of 29.0 mg of L^1 in 3 ml of MeOH was added dropwise to a warm solution of 34.3 mg of $CdCl_2\cdot 2.5H_2O$ in 1 ml of MeOH. White precipitate formed. The reaction mixture was stirred while heating for 30 min, the precipitate was filtered off, washed with a small amount of EtOH, and dried in air. Yield 51.7 mg (97%). Found, %: C 33.5; H 3.1; N 11.7. $C_{10}H_{11}\cdot CdCl_2N_3$. Calculated, %: C 33.7; H 3.1; N 11.8.

Dichloridobis[2-(4,5-dimethyl-1*H*-imidazol-2-yl)-pyridine]zinc–water (1/1.5), $ZnL^1_2Cl_2\cdot 1.5H_2O$ (III). A solution of 121 mg of L^1 and 23.8 mg of $ZnCl_2$ in 3 ml of MeOH:H_2O (1:3) was evaporated to a volume of 1 ml. On cooling the solution to room temperature a

Table 3. Crystallographic data, experimental details, and refinement of the structure of compounds **I** and **V**

Parameter	**I**	**V**
The stoichiometric formula	$C_{10}H_{11}Cl_2N_3Zn$	$C_{21}H_{28}CdCl_2N_6O_2$
Molecular weight	309.49	579.79
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma*	$P\bar{1}$
The unit cell parameters		
a, Å	9.6002(12)	8.6484(2)
b, Å	7.2797(7)	9.9707(3)
c, Å	17.765(2)	15.6699(6)
α, deg		99.508(2)
β, deg		96.120(2)
γ, deg		110.145(1)
Volume, Å^3	1241.5(2)	1231.47(7)
Z	4	2
d_{calc}, g cm^{-3}	1.656	1.564
$\mu(MoK_\alpha)$, mm^{-1}	2.383	1.133
F(000)	624	588
Crystal size, mm	0.25×0.22×0.15	0.18×0.07×0.06
The scanning area of θ, deg	2.29–26.37	1.34–26.36
Intervals of reflection indices	$-12 \le h \le 12$ $-5 \le k \le 8$ $-22 \le l \le 22$	$-10 \le h \le 10$ $-12 \le k \le 12$ $-19 \le l \le 19$
Number of measured reflections	7780	10310
Number of independent reflections	1309 (R_{int} 0.0524)	4999 (R_{int} 0.0186)
Number of reflections with $I > 2\sigma(I)$	1124	4337
Transmission, min/max	0.7163/0.5872	0.9351/0.8220
S-factor on F^2	1.258	1.082
R-factor on $I > 2\sigma(I)$	R_1 0.0469, wR_2 0.0979	R_1 0.0414, wR_2 0.0997
R-factor for all reflections	R_1 0.0576, wR_2 0.1003	R_1 0.0512, wR_2 0.1038
The residual electron density, e Å^{-3}	–0.863/0.710	–1.232/1.718

white precipitate separated. The precipitate was filtered off, washed with a little water, and dried in air. Yield 78.4 mg (85%). Found, %: C 46.8; H 5.1; N 16.4. $C_{20}H_{25}Cl_2N_6O_{1.5}Zn$. Calculated, %: C 47.1; H 4.9; N 16.5.

Dichloridobis[2-(4,5-dimethyl-1*H*-imidazol-2-yl)-pyridine]cadmium–water (1/2), $CdL^1_2Cl_2·2H_2O$ (IV). A solution of 104 mg of L^1 and 34.2 mg of $CdCl_2·2.5H_2O$ in 3 ml of MeOH–H_2O (1:1) was evaporated to a volume of 1 ml. This resulted in the formation of a white precipitate. The precipitate was filtered off, washed with a small amount of a mixture of MeOH–H_2O (1:1), and dried in air. Yield 49.7 mg (59%). Found, %: C 42.3; H 4.6; N 14.9. $C_{20}H_{26}CdCl_2N_6O_2$. Calculated, %: C 42.5; H 4.6; N 14.9.

Dichloridobis[2-(4,5-dimethyl-1*H*-imidazol-2-yl)-pyridine]cadmium–water–methanol (1/1/1), $CdL^1{}_2Cl_2·MeOH·H_2O$ (V). A solution of 34.6 mg of L^1 and 11.4 mg $CdCl_2·2.5H_2O$ in 1 ml of MeOH:H_2O (1:1) mixture was left for crystallization. Colourless crystals were obtained in a month. The compound composi-tion was identified by XRD of single crystals.

Bis[4,5-dimethyl-2-(pyridin-2-yl)-1*H*-imidazol-1-olato]zinc–water (1/2), $ZnL^2_2Cl_2·2H_2O$ (VI). A hot solution of 37.8 mg of HL^2 and 11.2 mg of KOH in 0.5 ml of MeOH was added to hot solution of 21.9 mg of $Zn(OAc)_2·2H_2O$ in 0.5 ml of MeOH. Yellowish solution formed. The reaction mixture was stirred at heating for 2 h, and then 5 ml of H_2O was added. Light yellow precipitate formed. The reaction mixture was evaporated to a volume of 1 ml, the precipitate was filtered off, washed with water, and dried in air. Yield 36.0 mg (75%). Found, %: C 49.6; H 5.2; N 17.6. $C_{20}H_{24}N_6O_4Zn$. Calculated, %: C 50.3; H 5.1; N 17.6.

Bis[4,5-dimethyl-2-(pyridin-2-yl)-1*H*-imidazol-1-olato]cadmium, CdL^2_2 (VII). Hot solution of 56.8 mg of HL^2 and 16.8 mg of KOH in 2 ml of MeOH was added to the solution of 40.0 mg of $Cd(OAc)_2·2H_2O$ in 1 ml of 1:1 MeOH–H_2O mixture. The yellow suspension formed was stirred at heating for 2 h. A bright yellow precipitate formed. To the reaction mixture 3 ml of H_2O was added, and it was heated for 2 h, then cooled, the precipitate was kept in contact with the mother liquor for 15 h. Then the precipitate was filtered off, washed with water, and dried in air. Yield 56.6 mg (88%). Found, %: C 48.4; H 4.3; N 16.7. $C_{20}H_{20}CdN_6O_2$. Calculated, %: C 49.1; H 4.1; N 17.2.

XRD analysis. Unit cell parameters for compounds **I** and **V** and arrays of the experimental intensities at 150 K were obtained on an automatic diffractometer Bruker Nonius X8 Apex with 4K CCD detector [33]. Diffraction data were obtained by standard methods (λMoK_α, graphite monochromator). Crystallographic data and details of diffraction experiment are shown in Table 3. The extinction is taken into account semiempirically, based on the intensity of equivalent reflections (SADABS) [33]. The structure was solved by the direct method and refined by full-matrix anisotropic approximation with respect to F^2 for non-hydrogen atoms using the program package SHELX97 [33]. Hydrogen atoms of organic ligands were localized geometrically and refined in the approximation of a *rigid body*. Atomic coordinates and thermal parameters are deposited in the Cambridge Structural Database (CCDC 848765 and 848766).

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