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Preparation, Spectral and Thermal Properties of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) Complexes with Iodosubstituted 2,2'-Dipyrrolylmethene

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Abstract—Complexes $[ML_2]$ of cobalt(II), nickel(II), copper(II), zinc(II), and cadmium(II) with asymmetrically substituted (*E*)-3-ethyl-5-[(4-iodo-3,5-dimethyl-2*H*-pyrrol-2-ylidene)methyl]-2,4-dimethyl-1*H*-pyrrole (HL) have been prepared and characterized for the first time. The spectral properties, stability in solutions and in the solid phase at elevated temperature of the complexes have been studied. The effects of complexing metal ion and the reaction medium on the spectral luminescent properties (absorptivity, quantum yield, fluorescence lifetime, and the radiation constant) and on thermal destruction of the $[ML_2]$ complexes have been discussed.

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Molecular design is one of the priority topics in the chemistry of acyclic oligopyrroles containing dipyrrole chromophores. Bidental dipyrrolylmethene N2helicands and their stable intramolecular complexes with d- and f-metals are of particular interest [1–4]. Due to combination of easily polarized dipyrrolylmethene aromatic system and the coordination center in the metal complex structure, the intensive intramolecular charge transfer occurs. This leads to a set of spectral and photophysical properties essential for the practical application of the complexes in medicine and technique; the potential uses are fluorescent labels, high-sensitive sensors, intensive laser radiation restrictors, active media of adjustable lasers, etc [1-5]. One of the topical tasks in the photonics of oligopyrrole coordination compounds is the study of the effect of ligand substitution with heavy atom on the spectral and fluorescent properties of the respective complexes, in order to efficiently control the properties

[6, 7]. This work is an extension of recently performed studies [8-11] on the structural and medium effects on the physicochemical properties of acyclic oligopyrroles. The effects of the nature of the complexing metal ion, of solvent, and of the introduction of a heavy atom into 2,2'-dipyrrolylmethene structure on the spectral luminescence properties and stability in solution as well as in the solid phase have been studied by means of electronic, NMR ¹H, IR spectroscopy, mass spectrometry, elemental analysis, and thermogravimetry. The examined objects were Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes with the asymmetrically substituted (E)-3-ethyl-5-[(4-iodo-3,5-dimethyl-2H-pyrrol-2-ylidene)methyl]-2,4-dimethyl-1Hpyrrole (also referred to as 3,3',5,5'-tetramethyl-4ethyl-4'-iodo-2,2'-dipyrrolylmethene, HL) as ligand.

Precursors for HL preparation were synthesized according to the following scheme.



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The ligand hydrobromide (HL·HBr) was prepared according to the Scheme 1.

The studied complexes $[ML_2]$ were prepared via reaction of the corresponding metal acetate $M(AcO)_2$ · nH_2O with the ligand hydrobromide HL·HBr in methanol in the presence of triethylamine (Scheme 2).

The composition and purity of thus prepared complexes was confirmed by ¹H NMR and IR spectroscopy, mass spectrometry, and elemental analysis.

Structure of the molecules. The PM6 quantumchemical simulation of the $[ML_2]$ complexes molecular structure was performed in GAUSSIAN 09W software [12]. The M–N bonds length, bond angles of the coordination bonds N–M–N, and dihedral angles between the dipyrrolylmethene planes φ are collected in Table 1. According to the simulation results, in [ML₂] molecules the metal atom coordinated two ligand anions L⁻ via two donor nitrogen atoms of each ligand, thus forming the MN₄ coordination center with geometry of a distorted tetrahedron. The M–N bond lengths in [ML₂] were 1.714–2.021 Å which corresponded well to the ordinary range (1.879–1.96 Å) of the bond lengths observed in the crystals of respective metals dipyrrolylmethenates [ML₂] [13–15]. The length of M–N bond increased with increasing ionic radius of the complex forming metal. In the cases of nickel(II) and copper(II) complexes, the Yahn-Teller effect led to a significant distortion of the tetrahedral geometry of the coordination center as compared to



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other complexes. For instance, whereas in the case of $[ZnL_2]$ complex the bond angles of the coordination bonds were of close value (N¹MN³ 113.52°, N³MN⁴ 101.07°), in the cases of [NiL₂] and [CuL₂] complexes they were significantly different: (145.38°, 94.46°) and (142.19°, 97.58°), respectively. The smallest dihedral angles between the dipyrrolylmethene planes were observed in the molecules of [NiL₂] (φ = 55.4°) and [CuL₂] (φ = 64.2°), whereas in the cases of [CdL₂], [ZnL₂], and [CoL₂] complexes the respective φ values were much larger: 89.2, 89.6, and 89.9°.

Electron absorption spectra. Quantitative parameters of the electron absorption spectra of [ML₂] complexes in various organic solvents are given in Tables 2, 3. The $[ML_2]$ spectrum shape was similar to that of other dipyrrolylmethenates of the corresponding metals [16, 17]. In the near UV and visible ranges of the [ML₂] spectra three bands were observed; following the reference data, they were assigned to the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$ electron transitions [18]. The $S_0 \rightarrow S_3$ band, weak and broad, was located in the near UV range and was not sensitive to the structural and solvation effects. According to the intensities ratio of $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ bands, the spectra could be divided into three groups (Figs. 1, 2). The first type of the electron absorption spectra was characteristic of $[ZnL_2]$, $[CdL_2]$, and $[CoL_2]$ helicates (Fig. 1): the first most intensive band at 497-510 nm was strongly overlapping with the second band at 480-485 nm of lower intensity. In the spectrum of [NiL₂] complex (Fig. 2), the overlap of the first and the second bands was less pronounced, and the bands intensities were close, log $\epsilon^1/\log \epsilon^2 \sim 1.03$. In the spectrum of [CuL₂] complex the two bands were nicely resolved, with the $\log \epsilon^{1}/\log \epsilon^{2}$ ratio of ~0.97 (Fig. 2), thus the second band was the most intensive. The ligand substitution with iodine did not influence significantly the intensity of the [ML₂] electron absorption as compared with the previously studied alkyl derivatives of dipyrrolylmethenates [16, 17].

The first band position (λ_{max}^{I}) was the most sensitive to the structural and solvation effects. The solvation effect was reflected (Table 2) in the noticeable, up to 6 nm, red shift of λ_{max}^{I} in the absorption spectra of [ML₂] solutions in nonpolar cyclohexane, benzene, and toluene as compared with those in polar coordinated solvents (dimethylformamide DMF and 1-propanol).

The auxochromous effect of the complex forming ion, calculated as the difference of the wavelengths of the first band maxima in the electronic spectra of

 Table 1. Geometry characteristics of dipyrrolylmethenates

 [ML₂]molecules

Compound	Bond	<i>d</i> , Å	Angle	ω, deg
[CoL ₂]	M-N ¹	1.747(3)	N^1MN^2	103.63(1)
	M-N ²	1.731(8)	N^1MN^3	111.01(7)
	M-N ³	1.714(6)	N^1MN^4	109.60(3)
	$M-N^4$	1.725(9)	N^2MN^3	112.96(7)
			N^2MN^4	111.25(9)
			N ³ MN ⁴	108.30(5)
[CuL ₂]	$M-N^1$	1.819(6)	N^1MN^2	97.52(7)
	M-N ²	1.833(9)	N^1MN^3	142.19(1)
	M-N ³	1.834(8)	N^1MN^4	94.75(9)
	M-N ⁴	1.819(3)	N^2MN^3	94.32(2)
			N^2MN^4	142.06(2)
			N ³ MN ⁴	97.58(1)
[NiL ₂]	$M-N^1$	1.902(5)	N^1MN^2	95.34(2)
	M-N ²	1.908(7)	N^1MN^3	145.38(1)
	M-N ³	1.908(3)	N^1MN^4	95.15(7)
	$M-N^4$	1.902(5)	N^2MN^3	95.12(8)
			N^2MN^4	144.01(7)
			N ³ MN ⁴	95.46(5)
$[ZnL_2]$	$M-N^1$	1.905(1)	N^1MN^2	101.08(9)
	$M-N^2$	1.910(4)	N^1MN^3	113.52(1)
	M-N ³	1.910(4)	N^1MN^4	115.61(1)
	$M-N^4$	1.905(1)	N^2MN^3	112.57(3)
			N^2MN^4	113.53(6)
			N ³ MN ⁴	101.07(9)
[CdL ₂]	$M-N^1$	1.997(7)	N^1MN^2	93.87(3)
	M-N ²	2.021(0)	N^1MN^3	117.26(9)
	M-N ³	2.021(1)	N^1MN^4	120.81(3)
	M-N ⁴	1.997(6)	N ² MN ³	115.63(6)
			N^2MN^4	117.30(6)
			N ³ MN ⁴	93.87(9)

 $[ML_2]$ complexes (Table 2) and the ligand HL in DMF $(\Delta \lambda_{M2^+} = \lambda_{[ML2]} - \lambda_{HL})$ increased from 39 to 58 nm in the following complexing ions series: Cd(II) < Zn(II) < Co(II) << Cu(II) < Ni(II). This order was in satisfactory agreement with the row of the stabilities as determined for majority of dipyrrolylmethenates [16, 17].

Fluorescence spectra. Our studies revealed no fluorescence in the cases of $[CoL_2]$, $[NiL_2]$, and $[CuL_2]$ complexes. Noticeable fluorescence was observed in the cases of $[ZnL_2]$ and $[CdL_2]$ solutions in nonpolar saturated and aromatic hydrocarbons (Table 3). The

Compound	C ₆ H ₆	C ₆ H ₅ –CH ₃	<i>cyclo</i> -C ₆ H ₁₂	CHCl ₃	1-PrOH	DMF
[CoL ₂]	373–374 (4.26)	372-373 (4.13)	372-373 (4.20)	372-374 (4.09)	372-374 (4.28)	372-374 (4.26)
	481–485	482–484	482–485	482-484	482–484	482–485
	510 (5.16)	509 (5.02)	509 (5.03)	506 (5.04)	506 (5.10)	506 (5.08)
[NiL ₂]	373 (4.23)	373 (4.28)	373–374 (4.31)	373 (4.20)	373–374 (4.37)	373–374 (4.27)
	459 (4.52)	459 (4.57)	458 (4.58)	458 (4.48)	458 (4.60)	455 (4.53)
	524 (6.64)	517 (4.70)	519 (4.71)	521 (4.60)	520 (4.71)	519 (4.64)
[CuL ₂]	373 (4.14)	373-374 (4.04)	372-373 (4.06)	373-374 (4.12)	372-374 (4.09)	372-373 (4.09)
	500 (4.88)	500 (4.81)	469 (4.81)	469 (4.80)	464 (4.80)	464 (4.81)
	518 (4.76)	518 (4.67)	519 (4.68)	516 (4.68)	515 (4.63)	512 (4.64)

Table 2. Quantitative parameters $[\lambda_{max}, nm (log \epsilon)]$ of electron absorption spectra of $[ML_2]$ complexes solutions in organic solvents

Table 3. Luminescence spectra parameters of [ML₂] in organic solvents

Solvent	λ_{max} , nm (log ϵ)	$\lambda_{\max}^{\text{lum}}$ nm ($\lambda^{\text{ex}} = 480 \text{ nm}$)	Δv_{st} , cm ⁻¹	$k_{\rm rad} \times 10^{-8}, {\rm s}^{-1}$	τ, ns	Φ	
[ZnL ₂]							
$C_{6}H_{12}$	$(S_0 - S_1)$ 506 (5.16) $(S_0 - S_2)$ 482–484 $(S_0 - S_3)$ 372–374 (4.03)	519	495	3.01	0.2161	0.065	
C_6H_{14}	$(S_0 - S_1)$ 506 $(S_0 - S_2)$ 480–484 $(S_0 - S_3)$ 370–372	518	497	_	_	0.057	
$C_{7}H_{16}$	$(S_0 - S_1)$ 506 $(S_0 - S_2)$ 480–484 $(S_0 - S_3)$ 370–372	518	458	_	_	0.056	
C ₆ H ₅ CH ₃	$(S_0 - S_1)$ 507 (5.15) $(S_0 - S_2)$ 481–484 $(S_0 - S_3)$ 372–374 (4.04)	521	530	2.86	0.0699	0.02	
C_6H_6	$(S_0 - S_1)$ 507 (5.15) $(S_0 - S_2)$ 482–484 $(S_0 - S_3)$ 372–374 (4.07)	520	493	3.77	0.0344	0.013	
1-PrOH	$(S_0 - S_1)$ 503 (5.15) $(S_0 - S_2)$ 480–484 $(S_0 - S_3)$ 373–374 (4.17)	517	538	3.16	0.0032	0.001	
CHCl ₃	$(S_0 - S_1)$ 505 (5.06) $(S_0 - S_2)$ 480–484 $(S_0 - S_3)$ 373–374 (3.95)	518	497	2.49	0.0040	0.001	
DMF	(S_0-S_1) 501 (5.02) (S_0-S_2) 481–484 (S_0-S_3) 372–373 (3.99)	_	_	_	_	-	

Table 3. (Contd.)

Solvent	λ_{max} , nm (log ϵ)	$\lambda_{\max}^{\text{lum}}, \text{nm}$ ($\lambda^{\text{ex}} = 480 \text{ nm}$)	Δv_{st} , cm ⁻¹	$k_{\rm rad} \times 10^{-8}, {\rm s}^{-1}$	τ, ns	Φ		
[CdL ₂]								
C_6H_{12}	$(S_0 - S_1)$ 501 (5.05) $(S_0 - S_2)$ 482–485 $(S_0 - S_3)$ 373–374 (4.08)	517	618	2.46	0.0284	0.007		
C_6H_{14}	$(S_0 - S_1)$ 501 $(S_0 - S_2)$ 476–479 $(S_0 - S_3)$ 372–373	516	580	_	-	0.005		
$C_{7}H_{16}$	$(S_0 - S_1) 501$ $(S_0 - S_2) 476 - 479$ $(S_0 - S_3) 372 - 373$	516	580	_	_	0.005		
C ₆ H ₅ CH ₃	$(S_0 - S_1) 501 (5.10)$ $(S_0 - S_2) 483 - 485$ $(S_0 - S_3) 372 - 373 (4.04)$	518	615	3.39	0.0147	0.005		
C_6H_6	$(S_0 - S_1)$ 502 (4.92) $(S_0 - S_2)$ 482–484 $(S_0 - S_3)$ 373–374 (4.03)	517	578	2.15	0.0233	0.005		
1-PrOH	$(S_0 - S_1)$ 496 (5.02) $(S_0 - S_2)$ 482–484 $(S_0 - S_3)$ 373 (3.99)	514	706	3.25	0.0061	0.002		
CHCl ₃	$(S_0 - S_1)$ 497 (5.08) $(S_0 - S_2)$ 483–484 $(S_0 - S_3)$ 373 (4.07)	518	816	4.59	0.0022	0.001		
DMF	(S_0-S_1) 494 (4.95) (S_0-S_2) 483–484 (S_0-S_3) 373–374(3.99)	_	_	_	_	-		

emission spectrum of the complexes solutions was a mirror transformation of their absorption spectra with a small (13–21 nm) Stokes shift (Fig. 1). In the nonpolar solvents, the quantum yield Φ of the [ZnL₂] complex fluorescence reached ~0.065, its intensity being comparable with that of gallium(III) and indium(III) dipyrrolylmethenates [2] and tetraphenylporphyrinates [19, 20]. In 1-propanol and chloroform, the quantum yield of [ZnL₂] fluorescence decreased ~65 times. The [CdL₂] complex also exhibited fluorescence in nonpolar organic solvents (cyclohexane, hexane, heptanes, benzene, and toluene), however, the quantum yield was 10 times lower than that in the case of

 $[ZnL_2]$. In 1-propanol and chloroform the quantum yield of the $[CdL_2]$ complex fluorescence was lower, close to that in the case of $[ZnL_2]$.

In general, the increase in the solvent polarity led to the increase in the Stokes shift and disturbed the rows arranged according to the position and (especially) intensity of the fluorescence (Tables 2, 3), thus presuming specific interactions in some of the solvents [21]. This assumption was confirmed by the distortion of the linear dependence of the Stokes shift on the function of universal interactions Δf in the cases of proton-donor and proton-acceptor solvents (Fig. 3). A



Fig. 1. (1) Electron absorption and (2) transmittance spectra of $[ZnL_2]$ in cyclohexane.



Fig. 2. Electron absorption spectra of (1) [CuL₂] and (2) [NiL₂] solutions in DMF.



Fig. 3. The Stokes shift as function of universal solvents interaction (Δf) in the case of [ZnL₂] complex: (1) hexane, (2) benzene, (3) cyclohexane, (4) heptane, (5) toluene, (6) chloroform, and (7) 1-propanol.

partial fluorescence quenching in the cases of $[ZnL_2]$ and $[CdL_2]$ helicates in benzene and toluene as compared to that in the saturated hydrocarbons (hexane, heptane, cyclohexane) was likely due to enhanced solvation of the chromophore in its excited state via the π -stacking mechanism. The steep or full fluorescence quenching in polar solvents (1-propanol, DMF) was likely due to additional coordination of the molecular ligands to the complex forming metal atom.

Even though the solvation shell was involved in the excitation energy deactivation, the values of radiation constant (showing the radiation emission probability in the absence of radiationless processes) were quite high, 2.15×10^8 to 3.77×10^8 s⁻¹, and weakly dependent on the solvent nature. The fluorescence lifetimes for the zinc(II) and cadmium(II) helicates increased with increasing solvent polarity, from $\tau \sim 2.2 \times 10^{-3}$ to ~ 0.21 ns.

Experimental conditions being the same, the fluorescence efficiency of $[ZnL_2]$ was about 14 times lower than that of the stronger fluorophore, binuclear homoleptic zinc(II) 3,3'-bis(dipyrrolylmethenate) $[Zn_2(bis$ $dpm)_2]$ (for the latter complex, $\Phi \sim 0.91$ [9] in cyclohexane). However, similarly to that observed in the $[Zn_2(bis-dpm)_2]$ case, the fluorescence of $[ZnL_2]$ was sensitive to the polarity and electron-donor ability of the solvent, oppositely to the majority of the Bodypy complexes [22, 23]; thus, the studied $[ZnL_2]$ complex could potentially be applied in construction of sensors capable of detecting the presence of specific molecules in the solvate shell.

Stability in solutions. Most of the prepared complexes [ML₂] were stable in the studied solvents, as confirmed by the invariance of their electron absorption spectra during 1 month. The exception was the $[CdL_2]$ complex that was unstable in the electrondonor DMF. During 1 week of incubation of the $[CdL_2]$ -DMF solution, the λ'_{max} intensity decreased, whereas the 450 nm band intensity increased. It could be assumed that the relatively long coordination M-N bonds (Table 1) and their relatively high ionic character (the latter being a known feature of Cd²⁺ oligopyrrole complexes [24]) made the $[CdL_2]$ complex significantly coordination-unsaturated. Additional coordination of DMF molecules initiated in turn the processes of ionic solvolitic dissociation of the complex and photodestruction of the labile L^{-} anion.

Thermal stability of the crystalline samples of the dipyrrolylmethenates $[ML_2]$ was studied under inert atmosphere (argon). The decomposition of individual

[ML₂] complexes included several stages of the sample mass loss (see the thermogravimetry and differential thermogravimetry curves), and ended up with the solid product consisting primarily of carbon (99 wt %) (Fig. 4). The thermal stability of chromophores $[ML_2]$ was determined by the M-N bonds strength, and by thermal activation rate and redox properties of the complex forming ion in the intramolecular ligand thermooxidation reactions [25, 26]. All the studied compounds showed relatively good thermal stability. The temperature of destruction start increased in the following series: $[NiL_2] = [CuL_2] < [CoL_2] < [ZnL_2] <$ [CdL₂] and equaled 201, 201, 213, 229, and 261°C, respectively. The ligand substitution with a heavy iodine atom significantly decreased the thermal stability of the prepared complexes as compared with the alkyl-substituted dipyrrolylmethenates [25] and bis-(dipyrrolylmethenates) [26]. For example, experimental conditions being the same, the thermal decomposition of bis(dipyrrolylmethenates) $[M_2(bis-dpm)_2]$ started by 129–181°C higher than that of [ML₂] with the corresponding complex-forming ion.

Thus, the analysis of the properties of prepared complexes revealed that the iodosubstituted dipyrrolylmethenates $[ZnL_2]$ were interesting fluorophores showing the set of practically important properties, similar to the homoleptic binuclear 3,3'-bis(dipyrrolylmethenes) $[Zn_2(bis-dpm)_2]$.

EXPERIMENTAL

¹H NMR spectra were recorded in deuterated chloroform solutions using Bruker 500 spectrometer. IR spectra of the $[ML_2]$ complexes in the form of KBr pellets were recorded using Avatar 360 FT-IR ESP spectrometer. Elemental analysis (C, H, and N) was performed using the elemental analyzer FlashEA 1112. Mass spectra (MALDI) were recorded with the use of Ultraflex III spectrometer (Bruker) in the mode of positive ions registration at the metal target (matrix: *p*-nitroaniline, 100:1) in the Laboratory of Physico-Chemical Analysis, A.E. Arbuzov Institute of Organic and Physical Chemistry (Kazan).

Electron absorption spectra and fluorescence spectra in the organic solvents were recorded using SF-103 spectrophotometer (Akvilon, Russia) and SM 2203 spectrofluorimeter (SOLAR), respectively. The radiation constants and the fluorescence lifetimes were estimated basing on the spectral luminescence parameters and the fluorescence quantum yields [23, 28]. Rhodamine 6G in ethanol was used as a standard for





Fig. 4. Thermogram of dipyrrolylmethanate [CdL₂] under argon.

 Φ measurement ($\Phi = 0.94$) [29]. The measurements were performed in the quartz cells with the optical path length of 1 or 10 mm; temperature was maintained at 298.15±0.1 K by means of Peltier element. When recording the electron absorption spectra, the chromophore concentration was 10^{-6} – 10^{-4} mol 1^{-1} , emission spectra were recorded at 10^{-7} – 10^{-6} mol 1^{-1} of fluorophore.

Thermal analysis was performed in argon atomsphere using the TG 209 F1 Netzsch microbalance, at 10–950°C. The heating rate was of 2.5 deg min⁻¹. The sample mass was of 5–7 mg, the mass loss measurement accuracy was 1×10^{-4} mg.

Quantum-chemical simulation (PM6 semiempirical method) was performed using GAUSSIAN W09 software [12] run on PC Athlon under GaussView 5.0 management; in analysis and visualizing of the data Chemcraft 1.6 software was used.

Organic solvents (benzene, toluene, hexane, heptanes, chloroform, dimethylformamide), all of chemically pure grade, were purified according to the procedures described in [27], water content was determined by Fischer method and was below 0.02%. 1-propanol (UV-IR-HPLC-HPLC) and cyclohexane (Panreac) were used as received.

(*E*)-3-ethyl-5-[(4-iodo-3,5-dimethyl-2*H*-pyrrol-2ylidene)methyl]-2,4-dimethyl-1*H*-pyrrole, hydrobromide (HL·HBr) [6]. At room temperature, under stirring, 2 ml of concentrated hydrobromic acid was added to the solution of 3.2 g (12.8 mmol) of 2-formyl-4-iodo-3,5-dimethylpyrrole and 1.58 g (12.8 mmol) of 2,4-dimethyl-3-ethylpyrrole in 20 ml of methanol. The mixture was stirred for 2 hours; the precipitate was filtered off, washed with methanol, ether, and dried in air at room temperature. Yield 2.1 g (67%). ¹H NMR spectrum (CDCl₃), δ , ppm: 1.08 t (3H, CH₃-Et, *J* 8 Hz), 2.29 s (3H, CH₃), 2.32 s (3H, CH₃), 2.43 q (2H, CH₂-Et, *J* 8 Hz), 2.71 s (6H, CH₃), 7.06 s (CH_{meso}), 13.30 br. s (NH). IR spectrum (KBr), v, cm⁻¹: 3448 (NH). Electron absorption spectrum, λ_{max} , nm (log ε): HL·HBr, 489 (4.91) (CHCl₃), 493 (4.97) (C₆H₆); HL, 460 (4.44) (DMF). Found, %: C 23.01; H 2.61; N 3.62. C₁₅H₂₀N₂IBr. Calculated, %: C 22.85; H 2.56; N 3.55.

[ML₂] complexes were obtained via reaction of the corresponding metal acetate $M(AcO)_2 \cdot nH_2O$ with HL·HBr in methanol medium, in the presence of triethylamine. The solution was boiled during 1 hour, and then cooled. The precipitate formed was filtered off, washed with excess of hot water and methanol, and dried in air at room temperature. The residue was dissolved in dichloromethane and applied to the silica gel column (100/250). The eluent was evaporated, and the complex was precipitated from methanol and dried under reduced pressure. The solid samples of the prepared [ML₂] complexes were crushed and dried in a vacuum in a drying cabinet at 100°C to the constant mass. The composition and purity of the complexes were confirmed by ¹H NMR, IR spectroscopy, elemental analysis, and mass spectrometry studies.¹H NMR signals from paramagnetic cobalt(II), copper(II), and nickel (II) complexes could not be recorded.

[**ZnL**₂] **complex.** Yield 71.5%, orange crystals with green metallic shine. IR spectrum (KBr), v, cm⁻¹: 2962, 2923, 2853, 2208, 1597, 1499, 1450, 1392, 1234, 1169, 1109, 1046, 967, 890, 791, 734, 665, 596. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.04 t (6H, CH₂CH₃, *J* 7 Hz), 1.94 s (6H, CH₃), 1.96 s (6H, CH₃), 2.24 s (6H, CH₃), 2.30 s (6H, CH₃), 2.36 q (4H, CH₂CH₃, *J* 7 Hz), 7.03 s (2H, CH_{meso}). Mass spectrum, *m/z*: 773.1 [*M* + H]⁺. Found, %: C 46.82; H 4.78; N 7.31. C₃₀H₃₆N₄I₂Zn. Calculated, %: C 46.69; H 4.70; N 7.26. *M* 771.83.

[CoL₂] complex. Yield 89%, green crystals. IR spectrum (KBr), v, cm⁻¹: 2960, 2920, 2856, 2362, 1595, 1489, 1443, 1387, 1225, 1165, 1103, 1041, 958, 893, 783, 733, 598. Mass spectrum, m/z: 766.5 $[M + H]^+$. Found, %: C 47.14; H 4.83; N 7.47. C₃₀H₃₆N₄I₂Co. Calculated, %: C 47.08; H 4.74; N 7.32. *M* 765.39.

[CuL₂] complex. Yield 80.5%, wine red-brown crystals. IR spectrum (KBr), v, cm⁻¹: 2962, 2921, 2856, 2208, 1600, 1487, 1441, 1358, 1227, 1169, 1103, 1038 960, 893, 785, 731, 698, 596. Mass spectrum, m/z: 771.1 [M + H]⁺. Found, %: C 46.97; H 4.88; N 7.36. C₃₀H₃₆N₄I₂Cu. Calculated, %: C 46.80; H 4.71; N 7.28. M 769.99.

[NiL₂] complex. Yield 89.8%, dark wine red crystals. IR spectrum (KBr), v, cm⁻¹: 2960, 2926, 2858, 2208, 1599, 1485, 1444, 1381, 1223, 1165, 1103, 1039, 958, 893, 783, 731, 702, 600. Mass spectrum, m/z: 766.3 $[M + H]^+$. Found, %: C 47.26; H 4.91; N 7.45. C₃₀H₃₆N₄I₂Ni. Calculated, %: C 47.09; H 4.74; N 7.32. *M* 765.14.

[CdL₂] complex. Yield 56.9%, green-brown crystals with metallic shine. IR spectrum (KBr), v, cm⁻¹: 2960, 2924, 2862, 2208, 1595, 1492, 1439, 1388, 1232, 1169, 1105, 1038, 960, 890, 781, 727, 700, 596. ¹H NMR spectrum (CDCl₃), δ , ppm: 1.06 t (6H, CH₂CH₃, *J* 7 Hz), 2.06 s (6H, CH₃), 2.13 s (6H, CH₃), 2.25 s (6H, CH₃), 2.31 s (6H, CH₃), 2.38 q (4H, CH₂CH₃, *J* 7 Hz), 7.02 s (2H, CH_{meso}). Mass spectrum, *m/z*: 819.8 [*M* + H]⁺. Found, %: C 44.13; H 4.59; N 6.96. C₃₀H₃₆N₄I₂Cd. Calculated, %: C 44.00; H 4.43; N 6.84. *M* 818.86.

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