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meso-Spacer Influence on Properties of Zinc(II) Complexes with 2,3'- and 3,3'-Bis(Dipyrrolylmethenes)

L. A. Antina, G. B. Guseva, A. I. V'yugin, E. V. Antina, and M. B. Berezin

Krerstov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Alekseevskaya 1, Ivanovo, 153045 Russia
e-mail: ala@isc-ras.ru

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Abstract—The study and comparative analysis of spectral-luminescent characteristics (absorption and fluorescence spectra), of quantum yield, and fluorescence life time in solutions, of lability in proton-donor media, solid phase thermal stability in air oxygen and argon was carried out for binuclear zinc(II) helicates with decamethyl-substituted 2,3'- and 3,3'-bis(dipyrrolylmethenes). The influence of molecular structure features of the ligands on the physicochemical properties of helicates was discussed.

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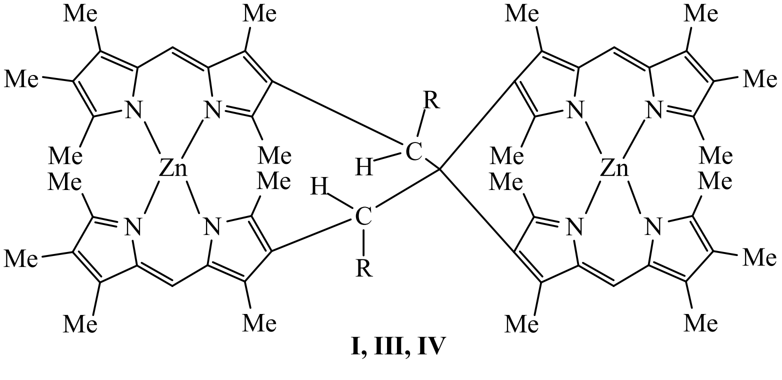
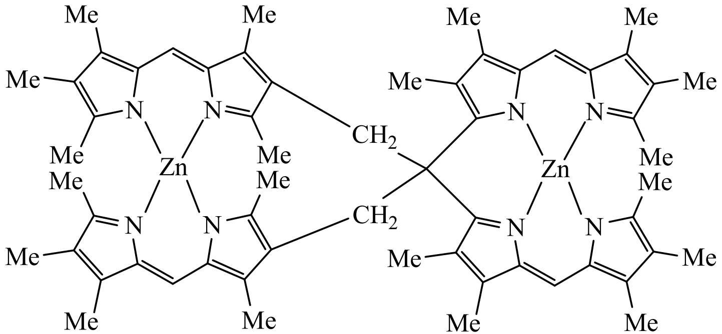
The interest to new coordination compounds of *d*-metals with tetradentate bis(dipyrrolylmethene ligands (H_2L), binuclear homoleptic two-spiral helicates, is connected with a possibility of wide variation of molecular structures of ligand systems, which essentially affects the physicochemical properties and structure of chelated compounds. The development of investigations on the coordination chemistry of bis(dipyrrolylmethenes) makes it possible to create directionally coordination compounds of practical interest. Among them we can mention the intensively fluorescent zinc(II) complexes with 3,3'-bis(dipyrrolylmethenes), which are characterized by a sufficient thermal stability in solid phases and a low lability in proton-donor media alongside with a high sensitivity of the fluorescence quantum yield to the polarity of medium and to temperature [1]. Practically significant properties of [Zn_2L_2] helicates should be mainly affected by structural features of tetrapyrrol ligands defined by differences in the nature of substituents, in the central spacer structure, and in the mode of its attachment to proximal pyrrol rings. Previously we have studied the effect of the structure of substituents in pyrrol rings, using [Zn_2L_2] helicates and a series of alkylated ligands 3,3'-bis(dipyrrolylmethenes) as examples [1].

The aim of the present work was to analyze the effects of attachment positions of a methylene *ms*-spacer and of the insertion of electron-donor substituents in it on the properties of [Zn_2L_2] helicates formed by decamethyl-substituted 2,3'- and 3,3'-bis(dipyrrolylmethenes)-3,3'-bis(dipyrrolylmethenates) (**I, III, IV**) and 2,3'-bis(dipyrrolylmethenate) (**II**).



I, III, IV



II

R = H (**I**), $PhOCH_3$ (**III**), CF_3 (**IV**).

Spectral-luminescent properties. Quantitative characteristics of electron absorption and fluorescence spectra of $[Zn_2L_2]$ helicates in various organic solvents are presented in Table 1. The ligand structure and the solvent nature do not influence the character of the electron absorption spectra of helicates **I–IV**: the absorption spectra in the visible and short-range UV regions contain three bands corresponding to the S_0–S_1, S_0–S_2 , and S_0–S_3 transitions. In contrast to helicate **I** the insertion of the $PhOCH_3$ group into the ligand 3,3'-spacer (helicate **III**) and the transfer of an *ms*-spacer from position 3,3' to the 2,3' position (helicate **II**) do not give rise to significant changes in the positions of bands maxima in the EAS: the most intensive absorption band S_0–S_1 is located in the range of 524–531 nm; an intermediate-intensity band of the S_0–S_2 electronic transition is present in the range of 475–482 nm, and the least intensive broadened S_0–S_3 band occupies the range from 364 up to 377 nm (see the figure). The insertion of the strong electron-acceptor substituent CF_3 in the *ms*-spacer gives rise to an appreciable (up to 7 nm) blue shift of the S_0–S_1 band maximum in EAS of helicate **IV**. As compared to helicates **I**, extinction coefficients of complexes **II–IV** are much lower. The values of log ε (5.34–5.48) for the S_0–S_1 band in EAS of compound **I** are comparable with those for the most intensive band (Soret band) in EAS of such strongest chromophores as porphyrins and metalloporphyrins [3], whereas the insertion of the CH_3OPh or CF_3 group in the *ms*-spacer and especially the transfer of the *ms*-spacer from 3,3'- to 2,3'-position causes a decrease in the extinction coefficients of the most intensive band by 100000 mol^{-1} l cm^{-1} (Table 1). When the polarity of solvents increases, EAS of all the compounds undergoes a slight (up to 6 nm) blue shift of maxima of intensive absorption bands.

In non-polar solvents (cyclohexane, hexane, and heptane) synthesized complexes **II–IV** intensively fluoresce with a high quantum yield (φ 0.4–0.6), which is however lower than that of helicate **I** (φ 0.6–0.9). The fluorescence intensity decreases in the series of complexes: **I** > **III** > **IV** > **II**, i.e. the position of the methylene *ms*-spacer stronger affects influence on the fluorescence of $[Zn_2L_2]$ helicates than the nature of substituents in the 3,3'-spacer in the bis(dipyrrolylmethene) ligand [1]. In aromatic solvents (benzene and toluene) the φ value for helicates **I, III, IV** (Table 1) is reduced by a factor of 2.5 at most, whereas for helicate **II** with the 2,3'-spacer in ligands (see the figure) a sharp fluorescence quenching (φ 0.06–0.08), an increase in the Stokes shift (twice), and a decrease in fluorescence life time (τ) are observed, which can be accounted for by stronger solvation of aromatic systems of dipyrrolylmethene domains of the helicate in an excited state by the π-stacking mode. Practically complete fluorescence quenching in investigated complexes **II–IV**, as well as in helicates **I** and other Zn(II) helicates with 3,3'-bis(dipyrrolylmethes) [1, 4–6], which we have studied earlier, is observed in polar electron-donor solvents (DMF, ethanol, etc.) due to the additional coordination of solvent molecules by complex-forming atoms. The Stokes shift for compounds **II–IV** in THF, 1-propanol, and ethanol increases from 8 up to 23 nm as compared to non-polar solvents, whereas for helicate **II** in DMF it reaches 34 nm. Values of the radiation constant k_{rad} (see Experimental) weakly depend on solvent, being 1.5–2 times lower for complex **II** as compared with other compounds under consideration.

Lability in proton-donor media. In this work we have estimated the effect of the location of *ms*-spacer

Table 1. Spectral-luminescent characteristics of complexes **I–IV** in organic solvents[a]

Comp. no.	Solvent	λ_{max}^{abs}, nm (log ε)	$\lambda_{max}^{fl}(\lambda^{exc})$, nm	$\Delta\nu_{st}$, cm^{-1}	φ	$k_{rad}\times10^{-8}$, s^{-1}	τ, ns
I	C_6H_{12}	(S_0–S_1) 530 (5.40) (S_0–S_2) 478 (4.96) (S_0–S_3) 370 (4.27)	543(495)	452	0.91	2.7	3.3
	C_6H_6	(S_0–S_1) 530 (5.48) (S_0–S_2) 478 (5.08) (S_0–S_3) 369 (4.31)	545(495)	519	0.56	3.2	1.7
	C_6H_{14}	(S_0–S_1) 527 (5.47) (S_0–S_2) 478 (5.07) (S_0–S_3) 367 (4.52)	541(495)	491	0.61	3.8	1.6
	Toluene	(S_0–S_1) 531 (5.46) (S_0–S_2) 481 (5.06) (S_0–S_3) 377 (4.33)	545(495)	484	0.64	3.2	2.0
	THF	(S_0–S_1) 528 (5.46) (S_0–S_2) 478 (5.05) (S_0–S_3) 365 (4.38)	542(495)	489	0.13	3.4	0.38
	PrOH	(S_0–S_1) 527 (5.40) (S_0–S_2) 477 (4.99) (S_0–S_3) 367 (4.25)	542(495)	525	0.010	3.3	0.027
	EtOH	(S_0–S_1) 525 (5.44) (S_0–S_2) 476 (5.04) (S_0–S_3) 370 (4.27)	542(495)	597	0.005	3.7	0.013
	DMF	(S_0–S_1) 526 (5.34) (S_0–S_2) 477 (4.94) (S_0–S_3) 367 (4.22)	543(495)	595	0.002	2.8	0.007
II	C_6H_{12}	(S_0–S_1) 529 (S_0–S_2) 476 (S_0–S_3) 367	537(490)	282	0.39	–	–
	C_6H_6	(S_0–S_1) 530 (5.24) (S_0–S_2) 479 (5.07) (S_0–S_3) 368 (4.32)	547(490)	586	0.060	2.0	0.30
	C_6H_{14}	(S_0–S_1) 527 (S_0–S_2) 475 (S_0–S_3) 373	537(490)	353	0.35	–	–
	Toluene	(S_0–S_1) 530 (5.23) (S_0–S_2) 479 (5.07) (S_0–S_3) 370 (4.30)	547(490)	586	0.080	2.0	0.40
	THF	(S_0–S_1) 527 (S_0–S_2) 477 (S_0–S_3) 368	548(490)	727	0.13	–	–
	PrOH	(S_0–S_1) 527 (S_0–S_2) 476 (S_0–S_3) 369	548(490)	727	0.007	–	–

Table 1. (Contd.)

Comp. no.	Solvent	λ_{max}^{abs}, nm (log ε)	$\lambda_{max}^{fl}(\lambda^{exc})$, nm	$\Delta\nu_{st}$, cm^{-1}	φ	$k_{rad}\times10^{-8}$, s^{-1}	τ, ns
II	EtOH	(S_0–S_1) 526 (S_0–S_2) 476 (S_0–S_3) 373	547(490)	730	0.001	–	–
	DMF	(S_0–S_1) 527 (5.20) (S_0–S_2) 476 (4.98) (S_0–S_3) 367 (4.27)	561(495)	1150	0.007	2.2	0.032
III	C_6H_{12}	(S_0–S_1) 531 (S_0–S_2) 480 (S_0–S_3) 365	547(495)	531	0.59	–	–
	C_6H_6	(S_0–S_1) 526 (5.29) (S_0–S_2) 482 (5.07) (S_0–S_3) 369 (4.32)	547(495)	730	0.13	5.8	0.23
	C_6H_{14}	(S_0–S_1) 528 (S_0–S_2) 479 (S_0–S_3) 365	546(495)	624	0.57	–	–
	Toluene	(S_0–S_1) 526 (S_0–S_2) 482 (S_0–S_3) 375	547(495)	730	0.20	–	–
	THF	(S_0–S_1) 524 (5.25) (S_0–S_2) 480 (5.01) (S_0–S_3) 371 (4.27)	546(495)	769	0.039	4.0	0.096
	PrOH	(S_0–S_1) 525 (S_0–S_2) 479 (S_0–S_3) 364	546(495)	733	0.013	–	–
	EtOH	(S_0–S_1) 524 (5.27) (S_0–S_2) 480 (5.04) (S_0–S_3) 371 (4.35)	546(495)	733	0.003	–	–
	DMF	(S_0–S_1) 525 (S_0–S_2) 478 (S_0–S_3) 365	545(495)	735	0.002	4.4	0.005
IV	C_6H_{12}	(S_0–S_1) 524 (S_0–S_2) 474 (S_0–S_3) 366	541(490)	600	0.43	–	–
	C_6H_6	(S_0–S_1) 523 (5.28) (S_0–S_2) 475 (5.02) (S_0–S_3) 369 (4.21)	544(490)	738	0.17	3.7	0.45
	C_6H_{14}	(S_0–S_1) 523 (S_0–S_2) 473 (S_0–S_3) 364	540(490)	539	0.52	–	–
	Toluene	(S_0–S_1) 524 (5.26) (S_0–S_2) 476 (5.00) (S_0–S_3) 375 (4.23)	544(490)	738	0.27	3.00	0.89

Table 1. (Contd.)

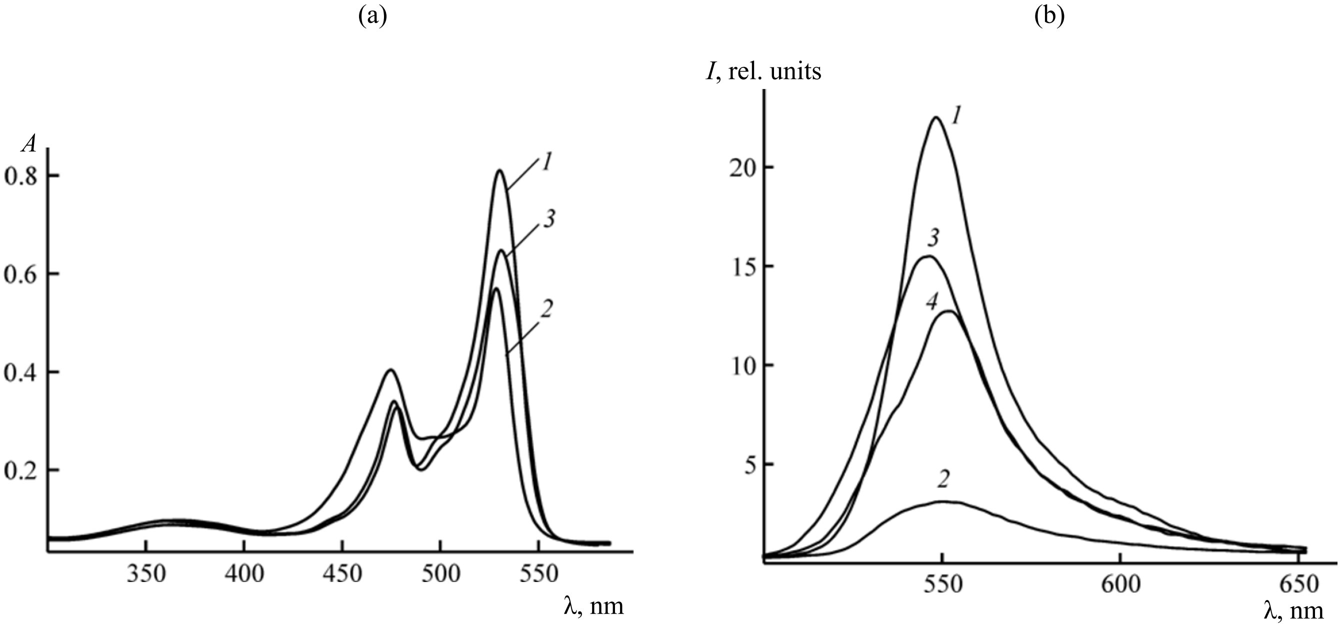
Comp. no.	Solvent	$\lambda_{\max}^{\text{abs}}$, nm (log ε)	$\lambda_{\max}^{\text{fl}}$ (λ^{exc}), nm	$\Delta\nu_{\text{st}}$, cm^{-1}	φ	$k_{\text{rad}}\times10^{-8}$, s^{-1}	τ, ns
IV	THF	(S_0–S_1) 520 (5.26) (S_0–S_2) 473 (4.99) (S_0–S_3) 364 (4.24)	542(490)	781	0.044	3.5	0.12
	PrOH	(S_0–S_1) 521 (S_0–S_2) 472 (S_0–S_3) 369	541(490)	710	0.015	–	–
	EtOH	(S_0–S_1) 519 (S_0–S_2) 471 (S_0–S_3) 365	541(490)	784	0.004	–	–
	DMF	(S_0–S_1) 519 (5.24) (S_0–S_2) 472 (4.97) (S_0–S_3) 369 (4.19)	539(485)	715	0.002	3.2	0.006

[a] $\lambda_{\max}^{\text{abs}}$, λ^{exc}, and $\lambda_{\max}^{\text{fl}}$ are maxima of absorption, excitation, and fluorescence; $\Delta\nu_{\text{st}}$ is Stokes shift, ε is molar absorption coefficient, φ is the fluorescence quantum yield; k_{rad} is the radiation constant; τ is the fluorescence life time.

attachment points and the effect of the CF_3 substituting group with the pronounced electron-acceptor properties inserted in the 3,3'-spacer on the lability of helicates **II** and **IV** in acetic acid-benzene mixtures in comparison with complex **I** studied earlier [7]. The dissociation rate of the complex **II** and its analog **I** [7] in acetic acid with concentrations lying in the range under consideration is described by the equation of third total order (1).

$$\frac{dc}{d\tau} = k_{\text{obs}} c_{\text{M}_2\text{L}_2} c^2_{\text{AcOH}}\,. \tag{1}$$

Comparative analysis of kinetic parameters of the helicate **II** dissociation reaction and earlier data [7] for compound **I** has shown that the replacement of 3,3'-bis-(dipyrrolylmethene) by its 2,3'-analog increases lability of [Zn_2L_2] helicates by ~25%.



(a)

(b)

Electron absorption spectra of solutions of complexes **I–III** in (a) cyclohexane (c 3.0×10^{-6} M) and (b) emission spectra of complexes **I–IV** in benzene (c 5.0×10^{-7} M).

Table 2. Thermal destruction of $[Zn_2L_2]$ helicates **I–IV** in air oxygen and argon[a]

Comp. no.	Argon	Air		
	t_b, °C	t_b, °C	Δ^{theor}, %	Δ^{exp}, %
I	409	202	16.2	16.3
II	376	197	16.2	16.8
III	362	192	23.0	23.2
IV	359	180	24.3	24.6

[a] t_b is the temperature of destruction beginning, Δ^{theor} and Δ^{exp} are theoretical and experimental values of zinc oxide weight.

The spectrally-controlled complex **IV** dissociation begins at the CH_3COOH concentration in C_6H_6 higher than 2.1 M, which is a little less than that for analog **I**. However it proved to be difficult to estimate the complete kinetic pattern of helicate **IV** dissociation, as in mix-tures with acid contents greater than 6.5 M (298.15 K) the helicate dissociates instantaneously, and when the CH_3COOH concentration is lowered an equilibrium between reagents and dissociation products is established in the system.

Thermogravimetric analysis. Thermal stability of $[Zn_2L_2]$ complexes is defined by the strength of M–N bonds, thermal activation of metal ions, and also by concomitant reactions of the organic component decomposition, and hence it essentially depends on the ligand nature. Earlier we have studied effects of features of the alkylation of pyrrol rings of the ligands 3,3'-bis(dipyrrolylmethenes) [8, 9] and features of the nature of the complex-forming agent (M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}) [6] on the thermostability of $[M_2L_2]$ helicates, including compound **I**. The characteristics of thermal conversions of compounds **II–IV** in argon and air oxygen determined in this work and the data published earlier for complex **I** are shown in Table 2. All investigated compounds have shown a good thermal stability, though it is slightly lower than that of 3,3'-bis(dipyrrolylmethenes) hydrobromides [8, 9]. The beginning of thermal decomposition of complexes **I–IV** is evident in thermograms as a sharp weight loss of a sample at temperatures higher than 180°C in the oxygen atmosphere and 359°C in argon. Thermal destruction of open-chain oligopyrrol ligands in oxygen medium includes the stages of oxidation of peripheral substituents and spacers and opening and oxidation of pyrrol cycles. It is completed by the formation of molecular nitrogen and hydrogen and carbon oxides [8, 9]. The thermal destruction of helicates **I–IV** in oxygen is accompanied by the formation of zinc(II) oxide along with gaseous oxides (Table 2). The destruction in argon is ended at the formation of a solid product, which contains concomitant carbon. The experiment has shown that at a higher rate of heating samples (>10 deg min^{-1}) complexes **I–IV** are capable to be sublimed with conservation of a molecular structure even at a normal pressure and temperatures much lower than the temperature of the beginning of destruction.

Temperature of the beginning of destruction of helicate **II** with 2,3'-bis(dipyrrolylmethene) ligands in argon is lower by ~33°C than that of helicate **I**. The presence of electron-acceptor (PhOMe and especially CF_3) substituents even more increases the thermal stability of corresponding complexes **III** and **IV** in comparison with unsubstituted analog **I**.

Thus, we can conclude that the variation of the *ms*-spacer attachment points and the nature of substituents in it is a rather effective way of adjusting physicochemical properties of $[Zn_2L_2]$ helicates to particular tasks of their practical application in various media.

In comparison with the variation of alkyl substituents in pyrrol rings of a ligand, the mode of incorporating the methylene *ms*-spacer into bis(dipyrrolylmethene) renders the strongest influence on spectral-fluorescent properties of $[Zn_2L_2]$ helicates without changing the sensitivity of their fluorescence to the solvent nature. It points to the promising practical application of such fluorophores as appropriate ON/OFF-sensors.

Alongside with it, the insertion of electron-acceptor substituents in the 3,3'-spacer and the replacement of a 3,3'-ligand by its 2,3'-analog results in increasing lability of $[M_2L_2]$ complexes in the presence of acids and in decreasing their thermal stability, but do not affect the ability of the investigated $[M_2L_2]$ complexes to the thermal sublimation in mild conditions, which, alongside with fluorescent properties, makes them rather promising objects for diverse practical applications.

EXPERIMENTAL

Chemically pure grade organic solvents were purified according to the known procedures [10]. 1-Propanol PAI (1-PrOH) (UV-IR-HPLC-HPLC preparative) and cyclohexane (Panreac, Barcelona) were used without additional purification. Pure grade acetic acid was frozen twice, boiled with a rated amount of acetic anhydride, and distilled. Chemically pure grade benzene was additionally purified [10]. Water content in individual solvents did not exceed 0.02% (according to Fischer's method).

The ^{1}H NMR spectra were recorded in deuterated chloroform on a Bruker 500 NMR spectrometer. The IR spectra of $[Zn_2L_2]$ complexes in KBr tablets were taken on an Avatar 360 FT-IR ESP device.

Electron absorption and fluorescence spectra of samples in organic solvents were recorded on an SF-103 spectrophotometer (“Akvilon,” Russia) and an SM 2203 (SOLAR) spectrofluorometer. The fluore-scence spectra were obtained in equal conditions at the exciting wave length corresponding to the optical density not exceeding 0.1 [11]. The experiments were carried out in quartz cells with absorbing layer thickness of 1 or 10 mm at the concentration of solutions under study 10^{-6}–10^{-4} M. Temperature (298.15 K) of solutions in the cell was maintained accurate to ±0.1°C by means of a Peltier cell. A solution of Rhodamine 6G in ethanol with the known φ value of 0.94 was used as the standard for the determination of fluorescence quantum yield (φ) [11]. On the basis of the spectral-luminescent characteristics we have estimated the fluorescence quantum yields and fluorescence life times (τ) [12].

The radiation constant (k_{rad}) was calculated by formula (2) [11].

$$k_{\text{rad}} = 2.9\times10^{-9}[(9n^2)/(n^2+2)^2]\nu^2_{\max}\varepsilon_{\max}\Delta\nu_{1/2}. \tag{2}$$

As $\varphi = k_{\text{rad}}/(k_{\text{rad}} + k_{\text{d}})$ and $\tau = 1/(k_{\text{rad}} + k_{\text{d}})$, the fluorescence life time (τ) was determined by formula (3).

$$\tau = \varphi/k_{\text{rad}}. \tag{3}$$

Here n is a refraction index of a solvent, ν is a wave number (cm^{-1}), ε is an extinction coefficient in an absorption band, k_{rad} is a rate of radiating processes, and k_{d} is a rate of non-radiative processes.

Kinetics of dissociation of complexes **II** and **IV** was studied by spectrophotometry in the temperature range 298.15–318.15 K at the concentration of complexes ~3.5×10^{-6} M and a significant molar excess of an acid in relation to a complex. The technique of kinetic experiments and the methodology of determination of kinetic parameters for the dissociation reaction of complexes and of the reaction orders with respect to a complex and an acid were described earlier [13, 14].

Thermogravimetric analysis in atmospheric oxygen was carried out on a 1000D derivatograph (MOM, Hungary) in the temperature range of 10–1000°C at the sample heating rate of 2.5 deg min^{-1} (sample weight 20–30 mg, a platinum crucible). Thermal analysis in argon atmosphere was carried out on a TG 209 F1 Netzsch microthermobalance in the temperature range of 10–950°C at a sample heating rate of 10 deg min^{-1}. The sample weight was 5–7 mg, the inaccuracy of the weight loss determination was less than 1×10^{-4} mg.

The determination of C, H, and N contents in the samples under study was carried out on a FlashEA 1112 elemental analyzer.

Complexes $[Zn_2L_2]$ (II–IV) were synthesized by the reaction of zinc acetate dihydrate $Zn(AcO)_2\cdot2H_2O$ with the corresponding decamethyl-substituted bis(dipyrrolylmethenes) dihydrobromides $H_2L\cdot2HBr$ in a medium of chloroform (methylene chloride)-methanol in the presence of triethylamine and(or) sodium acetate. The procedure of the synthesis, the X-ray data, and the characteristics of ^{1}H NMR and IR spectra of compound **I** are published in [1, 4, 5]. The composition and purity of synthesized compounds **II–IV** were confirmed by the data of mass spectrometry, elemental analysis, and ^{1}H NMR and IR spectroscopy. Solid samples of $[Zn_2L_2]$ complexes were crushed and dried to a constant weight in a vacuum drying cabinet at 70–120°C.

Complex II of Zn(II) with (1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl)(1,2,3,7,8-pentamethyldipyrrolylmethene-9-yl)methane. To a solution of 0.288 g (0.478 mmol) of the ligand in 10 ml of methanol 0.048 g (0.478 mmol) of triethylamine was added with heating and stirring, and then a solution of 0.524 g (2.39 mmol) of $Zn(Ac)_2\cdot2H_2O$ in 10 ml of methanol. The mixture was boiled for 1 h, cooled, the precipitate was filtered off, washed with water and methanol, and dried in air. The solid residue was dissolved in benzene and chromatographed on silica gel. The eluate was evaporated under a reduced pressure, and complex **II** was precipitated by methanol. Yield 71%. IR spectrum, ν, cm^{-1}: 2956, 2910, 2854, 1597, 1542, 1441, 1385, 1230, 1165, 1107, 1022, 933, 876, 785, 737, 673. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.24 s (6H, CH_3), 1.62 s (6H, CH_3), 1,72 s (6H, CH_3), 1.85 s (6H, CH_3), 1.95 s (6H, CH_3), 1.96 s (6H, CH_3), 2.03 s (6H, CH_3), 2.16 s (6H, CH_3), 2.18 s (6H, CH_3), 2.25 s (6H, CH_3), 3.34 d (2H, CH_2, spacer), 3.49 d (2H, CH_2, spacer), 6.66 s (2H, CH_{meso}), 6.92 s (2H, CH_{meso}). Found, %: C 69.06; H 6.72; N 11.05. $C_{58}H_{68}N_8Zn_2$. Calculated, %: C 69.11; H 6.80; N 11.12. M 1007.98.

Complex III of Zn(II) with bis(1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl)methoxyphenylmethane. Bis(1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl)-methoxyphenylmethane dihydrobromide, 0.200 g (0.28 mmol), was dissolved in 10 ml of methanol with heating and stirring, then 0.092 g (0.566 mmol) of triethylamine and a solution of 0.311 g (1.415 mmol) of $Zn(Ac)_2 \cdot 2H_2O$ in 15 ml of methanol were added successively. The mixture was boiled within 1 h and cooled, the precipitate was filtered off, washed with water and methanol, and dried in air. Yield 0.121 g (70.3%). IR spectrum, cm^{-1}: 2914, 2858, 1597, 1508, 1441, 1392, 1228, 1167, 1107, 1018, 943, 877, 789, 739, 675. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.95 s (12H, CH_3), 2.01 s (12H, CH_3), 2.08 s (12H, CH_3), 2.15 s (12H, CH_3), 2.20 s (12H, CH_3), 3.81 s (6H, OCH_3), 5.21 s (2H, CH, spacer), 5.21 (6H, OCH_3), 6.79 s (4H, H-Ph), 6.93 d (4H, CH_{meso}). Found, %: C 73.85; H 6.56; N 9.12; O 2.60. $C_{72}H_{80}N_8O_2Zn_2$. Calculated, %: C 70.87; H 6.61; N 9.18; O 2.62. M 1220.23.

Complex IV of Zn(II) with bis(1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl) trifluoromethylmethane. Bis(1,2,3,7,9-pentamethyldipyrrolylmethene-8-yl)dihydrobromide, 0.220 g (0.328 mmol), was dissolved in 10 ml of methanol with heating and stirring, 0.067 g (0.658 mmol) of triethylamine and at once a solution of 0.36 g (1.64 mmol) of $Zn(Ac)_2 \cdot 2H_2O$ in 10 ml methanol were added. The mixture was boiled within 1 h and cooled, the precipitate was filtered off, washed with water and methanol, and dried in air. The solid residue was dissolved in benzene and chromatographed on silicagel. The eluate was evaporated under a reduced pressure, and the complex was precipitated by methanol. Yield 61%. IR spectrum, cm^{-1}: 2920, 2854, 1594, 1520, 1500, 1441, 1383, 1228, 1149, 1109, 1007, 941, 877, 798, 739, 687. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.00 s (12H, CH_3), 2.07 s (12H, CH_3), 2.20 s (12H, CH_3), 2.56 s (12H, CH_3), 2.68 s (12H, CH_3), 4.64 d (2H, CH, spacer), 7.07 s (4H, CH_{meso}). Found, %: C 62.97; H 5.72; N 9.78. $C_{60}H_{66}F_6N_8Zn_2$. Calculated, %: C 63.00; H 5.82; N 9.80. M 1143.97.

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