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Kinetic Stability of Complexes of Some *d*-Metals with 3,3'-Bis(dipyrrolylmethene) in the Binary Proton-Donor Solvent Acetic Acid–Benzene

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Abstract—The kinetics of dissociation of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) binuclear homoleptic double-stranded helicates with bis(2,4,7,8,9-pentametyldipyrrolylmethen-3-yl)methane (H_2L) of the $[M_2L_2]$ composition in the binary proton-donor solvent acetic acid–benzene was studied. Protolytic dissociation of the helicates $[M_2L_2]$ proceeds in accordance with the third order kinetic equation. Effect of the complexing metal nature is manifested in increased kinetic inertness in the following series of the helicates: $[Cd_2L_2] < [Hg_2L_2] < [Cu_2L_2] < [Ni_2L_2] < [Zn_2L_2] < [Co_2L_2]$. By the lability in similar environmental conditions the helicates $[M_2L_2]$ are comparable to the metal complexes of distorted porphyrins and are much more inert than dipyrrolylmethenate mononuclear complexes.

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In the past two decades extensive data was accumulated on the synthetic chemistry of the chromophoric linear oligopyrroles [1–3], among which the bis (dipyrrolylmethenes) and their metallocomplexes are of particular interest. The limitless possibilities of varying molecular structure of bis(dipyrrolylmethenes) by varying functional substituents and spacers between pyrrole rings place this class of compounds among a group of the most promising ones for the creation of new materials with practically useful properties. Along with considerable success in the synthesis of bis (dipyrrolylmethenes) and their metal complexes, there is a global lag in the research of their most important physical and chemical properties. There are no available information on the lability of complexes of bis(dipyrrolylmethenes) in the proton-donor environment, which is necessary for solving a variety of problems at their preparation and practical application. In this connection, we studied for the first time the kinetics of dissociation of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) helicates with bis- (2,4,7,8,9-pentametildipyrrolylmethen-3-yl)methane of the $[M_2L_2]$ composition in binary proton-donor solvent $CH_3COOH–C_6H_6$ (298.15–318.15 K) with a large excess of the acid with respect to the complex.

The 3,3'-bis(dipyrrolylmethene) helicates of the $[M_2L_2]$ composition, like metalloporphyrins [4], are intramolecular complexes formed with the fragments connected through covalent and donor-acceptor bonds,

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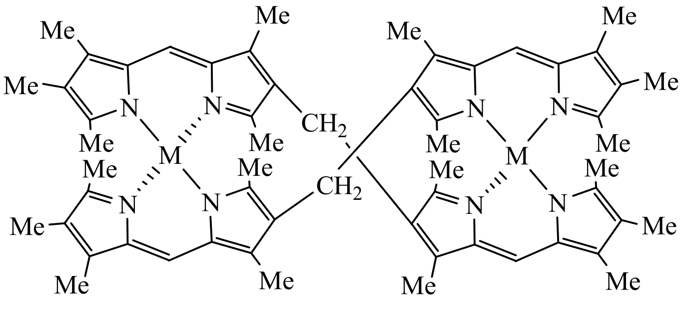

M = Co(II), Ni(II),Cu(II), Zn(II), Hg(II), Cd(II).

Table 1. Kinetic parameters of dissociation processes of the complexes $[Co_2L_2]$, $[Zn_2L_2]$, $[Ni_2L_2]$, and $[Cu_2L_2]$ in binary solvent acetic acid–benzene[a]

c^0_{AcOH}, M	$k_{obs} \times 10^3$, s^{-1}					E, kJ mol^{-1}	$-\Delta S^{\#}$, J mol^{-1} K^{-1}
	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K		
$[Co_2L_2]$							
4.523	0.13	0.21	0.32	0.47	0.65	61	122
5.915	0.23	0.35	0.53	0.76	1.05	60	124
7.307	0.37	0.54	0.82	1.17	1.65	60	126
8.699	0.52	0.78	1.20	1.72	2.37	60	124
10.439	0.74	1.14	1.73	2.49	3.47	62	118
$[Zn_2L_2]$							
2.610	0.11	0.21	0.29	0.42	0.54	75	75
3.914	0.26	0.49	0.66	0.87	1.22	72	79
5.219	0.45	0.79	1.14	1.57	2.20	71	80
6.524	0.69	1.32	1.77	2.54	3.48	75	61
7.829	1.04	1.91	2.66	3.84	5.17	73	64
$[Ni_2L_2]$							
3.131	0.2	0.31	0.5	0.75	0.99	64	107
3.914	0.33	0.5	0.76	1.17	1.62	64	109
5.219	0.57	0.85	1.36	2.12	2.82	65	106
6.524	0.90	1.37	2.18	3.31	4.38	64	109
7.829	1.28	1.96	3.09	4.63	6.27	64	109
$[Cu_2L_2]$							
0.190	2.10	2.50	2.83	3.14	3.58	22	231
0.253	3.81	4.19	4.89	5.70	6.24	18	237
0.291	4.87	5.80	6.43	7.47	8.20	23	221
0.316	5.75	6.83	7.72	8.78	9.66	23	219
0.342	6.80	8.10	9.20	10.34	11.44	23	217
0.380	8.44	9.82	11.33	12.53	14.26	22	220

[a] The errors in determining the values are: k_{obs} 3–5%, E and $\Delta S^{\neq}$ 10% or less.

They do not exhibit the ability to solvolytic dissociation into ions in neutral media. In the $[M_2L_2]$ molecules the tetrapyrrole chains of each of the two helicands braid two coordinated metal atoms. Each atom is coordinated to four nitrogen atoms of two dipyrrolylmethene domains of both ligands. Due to the presence of four dipyrrolylmethene domains in the $[M_2L_2]$ molecules the compounds possess pronounced chromophore properties.

The study showed that the kinetically controlled dissociation of the complexes $[Co_2L_2]$, $[Ni_2L_2]$, $[Cu_2L_2]$, and $[Zn_2L_2]$ in benzene solution proceeds in the presence of a large excess of acetic acid, from 0.19 to 10.4 M, depending on the nature of complexing agent (Table 1), and at lower concentrations of acid the reaction either does not occur, or is equilibrial. The process is accompanied by the transformation of the EAS of the $[M_2L_2]$ into the spectrum of the protonated ligand $H_2L{\cdot}2AcOH$ with retention of several isosbestic points (Fig. 1).

The dependence of the dissociation rate of $[M_2L_2]$ [M = Co(II), Ni(II), Cu(II), Zn(II)] on the initial helicate concentration (c^0, M) is described by a kinetic equation of first order, $dc/dt = k_{obs}c_{M2L2}$, which is confirmed by the linearity of the dependences in the coordinates $\ln (c^0/c_\tau)$–τ, $\rho = 0.998$–0.999 (Fig. 2), and permanency of the rate constants during the whole reaction. Table 1 lists the observed rate constants obtained by the treatment of linear dependences $\ln(c^0/c_\tau)$–τ and the values of the activation energy and entropy.

It was difficult to estimate the total kinetic pattern of dissociation for the helicates $[Cd_2L_2]$ and $[Hg_2L_2]$ on the following reasons. At 298.15 K the complexes $[Hg_2L_2]$ and $[Cd_2L_2]$ are stable in mixtures containing AcOH less than 5×10^{-3} and 5×10^{-4} M respectively. When the content of the acid in the mixed solvent was higher than 1×10^{-2} and 5×10^{-3} M, respectively, the dissociation of the complexes $[Hg_2L_2]$ and $[Cd_2L_2]$ proceeded immediately with the formation of the protonated ligand ($H_2L{\cdot}2AcOH$). At the intermediate concentration of the acid the dissociation of the helicates $[Hg_2L_2]$ and $[Cd_2L_2]$ proceeds with the simultaneous decomposition of the formed protonated ligand

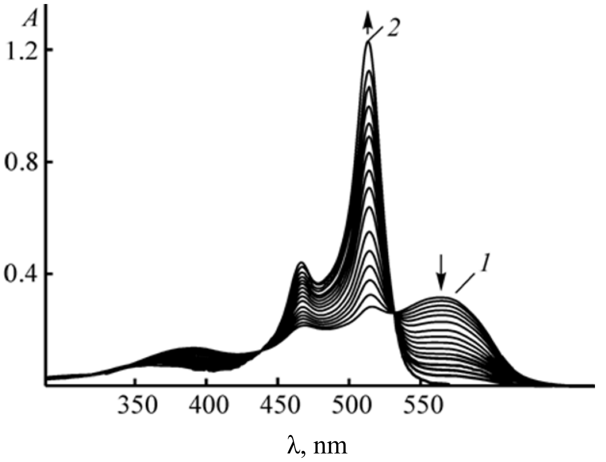

Fig. 1. Variation of the electron absorption spectrum of [Ni_2L_2] in a mixed solvent AcOH–C_6H_6 in the process of dissociation of the complex at 298.15 K, c^0_{AcOH} = 3.131 M, c^0([Ni_2L_2]) = 3.6×10^{-6} M; τ = 0 (*1*) and ∞ (*2*) (min), the remaining curves correspond to intermediate time points.

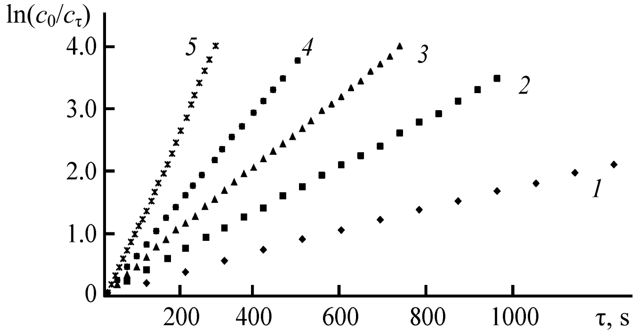

Fig. 2. The ln(c^0/$c_τ$)–τ dependences in the reaction of [Cu_2L_2] dissociation in proton donor binary solvent AcOH–C_6H_6, c^0_{AcOH} (M) and (*T*, K): (*1*) 0.190 (298.15), (*2*) 0.253 (303.15), (*3*) 0.291 (308.15), (*4*) 0.316 (313.15), (*5*) 0.380 (318.15).

to afford monopyrroles, as evidenced by discoloration of solutions and increased absorption in the EAS below 350 nm. According to the literature [5–8] the dissociation of helicate [Hg_2L_2] in benzene can also be accompanied with processes of mercuration. Nevertheless, the results obtained indicate the greatest lability of the complexes [Hg_2L_2] and [Cd_2L_2] in comparison with other studied helicates, due probably to the large ionic radii of Cd^{2+} and Hg^{2+} compared to Co^{2+}, Ni^{2+}, and Zn^{2+}, and in the case of the most labile complex [Cd_2L_2] due to a significant contribution of the ionic component in the coordination interaction. Similar pattern of influence of the nature of complexing agent has been observed previously for the chlorophyll complexes [HgCHL] and [CdCHL] in binary solvent AcOH–EtOH [9].

Considering the general order of dissociation of the complexes [Co_2L_2], [Ni_2L_2], [Cu_2L_2], and [Zn_2L_2] in the medium of the mixed solvent CH_3COOH–C_6H_6 we took into consideration the data of [4, 11–14] which showed that in solutions of acetic acid in benzene an equilibrium existed between the four forms: monomer, cyclic dimer, and two linear *cis*- and *trans*-dimers. In a dilute solution monomers and dimers dominate. The results of calculations performed using the data of [11] on the dependence of the activity coefficients on the concentration of the acid in C_6H_6 at 298.15–318.15 K showed that in the studied concentration range the activity coefficient of acetic acid in benzene was constant and within the error was equal to one. Low values of constants (10^{-10} to 10^{-18}) of the acetic acid autoprotolysis in benzene [12] and the value of benzene dielectric constant (2.284) [13] suggest that in solutions of AcOH in benzene the main agent serving as a carrier of proton is the molecular form of acetic acid [14, 8].

To determine the reaction order with respect to the acid we analyzed, according to [4], the dependence of the dissociation rate constant on the initial concentration of acetic acid in benzene (Fig. 3). This dependence for the complexes [Co_2L_2], [Zn_2L_2], [Ni_2L_2] and [Cu_2L_2] is not linear, and is well described by a second order power function: $k_{eff} = const_1(c^0_{AcOH})^{const2}$, where the constants $const_1$ and $const_2$ have the physical meaning of the true rate constant (k_V^T) and reaction order (*n*) with respect to the acid, respectively, which for all systems at all temperatures was equal to two (ρ = 0.998–0.999). Table 2 lists the true rate constant, reaction order with respect to the acid, the activation energy (E_v) and entropy ($\Delta S^{\neq}$) of the dissociation reaction of Zn(II), Co(II), Ni(II), and Cu(II) helicates in the proton-donor solvent acetic acid–benzene.

Given the first reaction order with respect to the complex and the second order on acetic acid, the rate of dissociation process of the helicates in the range of working concentrations of acetic acid can be expressed by the total third-order equation: $dc/dt = k_{obs}c(M_2L_2)\cdot c^2_{AcOH}$. Given the overall third order reaction and the facts that in the reaction product formed $H_2L\cdot 2AcOH$ and acetic acid reacted in the molecular form, the process of the [M_2L_2] acid dissociation could be regarded as a twofold protonation of the coordinated ligand at the donor nitrogen atoms in accordance with the scheme:

$$[M_2L_2] + 2AcOH \xrightarrow{\text{slow}} [M_2(AcOH{\cdot}L)_2] + 6AcOH$$

$$\xrightarrow{\text{fast}} 2(H_2L{\cdot}2AcOH) + 2M(AcO)_2.$$

Relatively low activation energy and the negative values of entropy $\Delta S^{\neq}$ allow us defining as the limiting the successive stages of attack on two nitrogen atoms of one of the coordination units $[M_2L_2]$ by the acetic acid molecules, which leads to the subsequent stages of the fast decomposition of the complex. The reaction of protonation of the formed ligand bis(dipyrrolylmethene) to afford $H_2L{\cdot}2AcOH$ is also very fast, as follows from the fact that the molecular form of the ligand is not detected by spectrophotometry. In view of these data and the fact that in an environment of nonpolar benzene the molecular form of acetic acid serves as protonating agent [10–13], the dissociation of the helicates Co(II), Zn(II), Ni(II), and Cu(II) in the proton-donor solvent benzene–acetic acid can be regarded as protolytic reaction.

Analysis of the data on the dissociation rate constant (Tables 1, 2) indicates that in the binary proton-donor solvent acetic acid–benzene the investigated helicates $[M_2L_2]$ can be arranged in the following series by the kinetic stability: $[Cd_2L_2] < [Hg_2L_2] < [Cu_2L_2] < [Ni_2L_2] < [Zn_2L_2] < [Co_2L_2]$. The activation energies E_v are comparable for the complexes $[Ni_2L_2]$, $[Co_2L_2]$, and $[Zn_2L_2]$ and about three times lower for the helicate $[Cu_2L_2]$. The values of activation entropy $\Delta S^{\neq}$ for the reactions of protolytic dissociation of all helicates are negative, and in the case of $[Cu_2L_2]$, the value $-\Delta S^{\neq}$ is almost two times higher than for the other three complexes, which indicate an increase in solvation of the reacting system in the transition state.

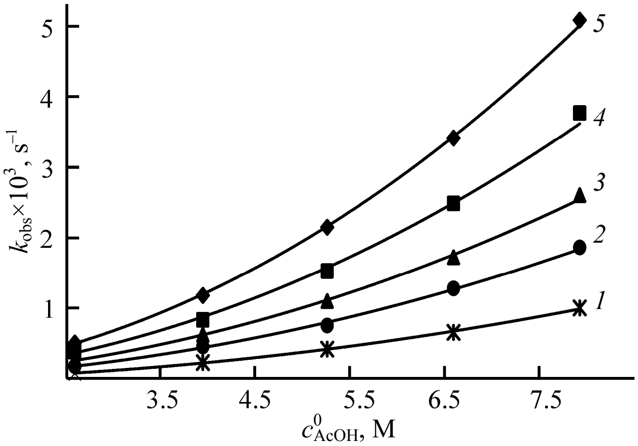

Fig. 3. Dependences of k_{obs} in the reaction of the $[Zn_2L_2]$ dissociation on the initial concentration of acetic acid in C_6H_6, at different temperatures, T, K: (*1*) 298.15, (*2*) 303.15, (*3*) 308.15, (*4*) 313.15, (*5*) 318.15.

Table 2. The true rate constants and activation parameters of the dissociation reaction of the complexes $[Co_2L_2]$, $[Zn_2L_2]$, $[Ni_2L_2]$, and $[Cu_2L_2]$ in a binary solvent acetic acid–benzene

T, K	k_v^T(const$_1$), l^2 mol^{-2} s^{-1}	n(const$_2$)	ρ	E_v, kJ mol^{-1}	$-\Delta S^{\#}$, J mol^{-1} K^{-1}
$[Co_2L_2]$					
298.15	6.00×10^{-6}	2.06	0.9996	69.1±7	128±15
303.15	1.02×10^{-5}	2.03	0.9992		
308.15	1.44×10^{-5}	2.04	0.9992		
313.15	2.18×10^{-5}	2.01	0.9985		
318.15	3.01×10^{-5}	2.02	0.9990		
$[Zn_2L_2]$					
298.15	1.57×10^{-5}	2.03	0.9995	75.5±8	109±12
303.15	3.03×10^{-5}	2.01	0.9985		
308.15	4.23×10^{-5}	2.00	0.9996		
313.15	5.69×10^{-5}	2.03	0.9978		
318.15	7.43×10^{-5}	2.05	0.9998		
$[Ni_2L_2]$					
298.15	2.05×10^{-5}	2.01	0.9996	66.7±6	121±13
303.15	3.20×10^{-5}	2.00	0.9995		
308.15	5.01×10^{-5}	2.00	0.9997		
313.15	7.68×10^{-5}	2.00	0.9997		
318.15	1.03×10^{-4}	2.00	0.9995		
$[Cu_2L_2]$					
298.15	5.85×10^{-3}	2.01	0.9991	23.1±2	221±25
303.15	6.96×10^{-3}	2.02	0.9988		
308.15	7.97×10^{-3}	2.02	0.9996		
313.15	9.00×10^{-3}	2.02	0.9996		
318.15	9.78×10^{-3}	2.00	0.9997		

The true reaction rate constants of dissociation and the lability of helicates $[M_2L_2]$ in the $AcOH–C_6H_6$ medium are close to those for the corresponding metallocomplexes with distorted (nonplanar) porphyrin ligands [14] and significantly lower than those of mononuclear analogs, the dipyrrolylmethene complexes, under the similar environmental conditions [8]. So, while for the cobalt(II) dipyrrolylmethenate of $[CoL_2]$ composition the true constant at 298.15 K in the acetic acid–C_6H_6 mixture is 5.7×10^{-4} l^2 mol^{-1} s^{-1}, then for the binuclear helicate $[Co_2L_2]$ the value of k_v^T decreases by two orders of magnitude (Table 2). Even greater differences are observed in the lability of the nickel(II) complexes: for dipyrrolylmethenate $[NiL_2]$, the value of k_v^T reaches 2279 l^2 mol^{-1} s^{-1}, while for bis(dipyrrolylmethenate) $[Ni_2L_2]$ the k_v^T is only 5.2×10^{-5} l^2 mol^{-1} s^{-1}, that is, decreases by eight orders of magnitude. These results indicate a much greater inertia toward the protolytic dissociation of the binuclear double-stranded bis(dipyrrolylmethene) helicates compared with mononuclear dipyrrolylmethenes, and expand the range of proton media for the solution of preparative (synthesis, purification and separation) and practical problems associated with the [M_2L_2] helicates.

EXPERIMENTAL

The features of synthesis of binuclear homoleptic Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) helicates with decametylated 3,3'-bis(dipyrrollylmethene) (H_2L), the results of XRD, ^{1}H NMR, IR, mass spectrometry and electronic spectroscopy were reported in detail earlier [15–17].

The electron absorption spectra of samples in organic solvents were obtained on a CM 2203 (Solar) spectrofluorimeter. Acetic acid of pure grade was twice frozen, boiled with the calculated amount of acetic anhydride, and distilled at 117.5–118°C. Benzene of chemically pure grade was additionally purified according to [18]. Water content in the individual solvents did not exceed 0.02% by Fischer.

The rate of dissociation reaction of the complexes [M_2L_2] was registered spectrophotometrically in the temperature range 298.15–318.15 K at a concentration of ~3.6×10^{-6} M with a significant (10000-fold or more) molar excess of acid with respect to the complex. The calculation of the observed dissociation rate constant (k_{obs}, s^{-1}) was carried out in accordance with the formal first-order equation (1):

$$k_{\text{obs}} = (1/\tau)\ln[(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (1)$$

The k_{obs} values were optimized by least-squares procedure using the Microsoft Excel program. The activation energy of the complexes dissociation reactions were calculated with the Arrhenius equation, activation entropy in a wide temperature range was obtained by the basic equation of the transition state transformed to Eq. (2) [4]:

$$\Delta S^{\neq} = 19.1\log k^T + (E + \Delta E)/T - 19.1\log T - 205. \quad (2)$$

Here k^T, E and ΔE are the rate constant at the temperature T, activation energy and average deviation of the latter, respectively. The numerical value of $\Delta S^{\neq}$ was calculated as the average $\Delta S^{\neq}$ value at all the studied temperatures.

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