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Complexation between Decamethyl-3,3'-Bis(dipyrrolylmethene) and Zinc(II), Copper(II), and Cobalt(II) Acetates

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Abstract—Decamethyl-3,3'-bis(dipyrrolylmethene) dihydrobromide $H_2L \cdot 2HBr$ (H_2L is bis(3,4,7,8,9-pentamethylpyrrol-3-yl)methane), which is the simplest representative of a novel class of oligo(dipyrrolylmethenes) belonging to chromophore chelating nonmacrocyclic ligands, were examined by ^1H NMR, IR, and electronic absorption spectroscopy. Complexation reactions of $H_2L \cdot 2HBr$ with $M(AcO)_2$ (M = Zn(II), Cu(II), and Co(II)) in DMF at 298.15 K were monitored by electronic absorption spectroscopy and studied by the molar ratio method. The thermodynamic constants K^0 of these reactions were estimated. The *d* metal ions coordinate H_2L to give the binuclear homoleptic complexes $[M_2L_2]$. The reactions proceed through the intermediate binuclear heteroleptic complex $[M_2L(AcO)_2]$ detected by spectroscopic methods. The thermodynamic stabilities of $[M_2L_2]$ and $[M_2L(AcO)_2]$ increase when moving from Cu(II) to Zn(II) and Co(II). The probability of formation and stability of $[M_2L_2]$ containing 3,3'-bis(dipyrrolylmethene) are substantially higher than those of analogous complexes with the 2,2'-isomer (decamethyl-2,2'-biladiene-*a,c*). The low K^0 values for the complexation between H_2L and $Cu(AcO)_2$ are due to slow oxidation of the biladiene ligand into a bilatriene with participation of Cu^{2+} ions.

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First reports on the synthesis of Co(II) and Zn(II) complexes with bis(dipyrrolylmethenes) [1] have aroused an active interest in a novel class of linear oligopyrroles composed of dipyrrolylmethene fragments linked by an alkyl or pseudoalkyl spacer and especially in their chelate complexes as promising objects of supramolecular chemistry [2, 3]. The use of dipyrrolylmethenes in chelation reactions has a number of advantages. First, these ligands and their complexes are chromophores with individual characteristics of electronic absorption spectra. Depending on the ligand structure, the metal ion, and the solvent, the resulting complexes can vary in composition and structure (mono-, bi-, and trinuclear; homo- and heteroleptic; mono-, bi-, and higher helical complexes). Second, complexes of linear oligopyrroles mostly need no counterion because the ligand in the complex is charged and the ligand is bound to the metal mainly by covalent and donor–acceptor bonds. As the result, the complexes are highly stable and can be easily purified by standard chromatographic techniques, in contrast to complexes with oligopyridine and other popular ligands that are made up only by noncovalent donor–acceptor interactions. Third, metal dipyrrolylmethenes have ordered crystal structures, which facilitates their X-ray diffraction analysis [4]. It has been already shown to date that dipyrrolylmethene complexes are promising for use as basic components of catalytic materials and semiconductors [5]. Complexes with high fluorescent quantum yields and minimum triplet–triplet absorptions at the excitation wavelength have already found application as efficient laser dyes [6] and the ligands themselves are very promising as analytical reagents for detection and extraction of microamounts of the ions of *d* metals, including toxic (cadmium, mercury, etc.) and radioactive isotopes [7, 8]. In organic solvents, Ni^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, and Hg^{2+} ions in their complexes with dipyrrolylmethenes and biladienes can be detected in concentrations from 6.0×10^{-9} to 3.6×10^{-8} mol/l [7–9].

Our first investigations in the field of linear oligopyrroles were intended to determine the dominant structural and solvation factors that control the complexation between *d* metals (Zn(II), Cd(II), Cu(II), Co(II), Ni(II), Pb(II), Hg(II), etc.) and alkylated 2,2'-, 2,3'-, and 3,3'-dipyrrolylmethenes (**HL**) and 2,2'-biladiene-*a,c* (**H_2L**), which is the parent group of 2,2'-bis(dipyrrolylmethenes) [7–9]. We found that a structural variety of complexes of 2,2'-biladiene-*a,c* with a particular metal ion is due to the invariance of the conformational state of the ligand. The conformational analysis [10] showed that even the most stable [11, 12] ridge-tile and helical conformations of the ligand (Fig. 1) are separated by a potential barrier of only 2.1 kJ/mol, which accounts for the ease of conformational transitions caused by structural factors and environmental conditions [7–9, 13].

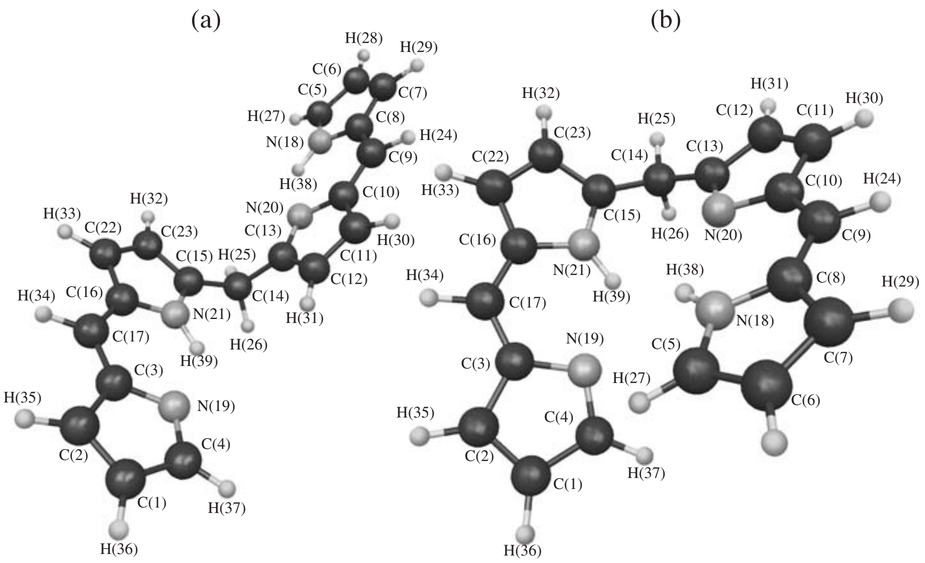


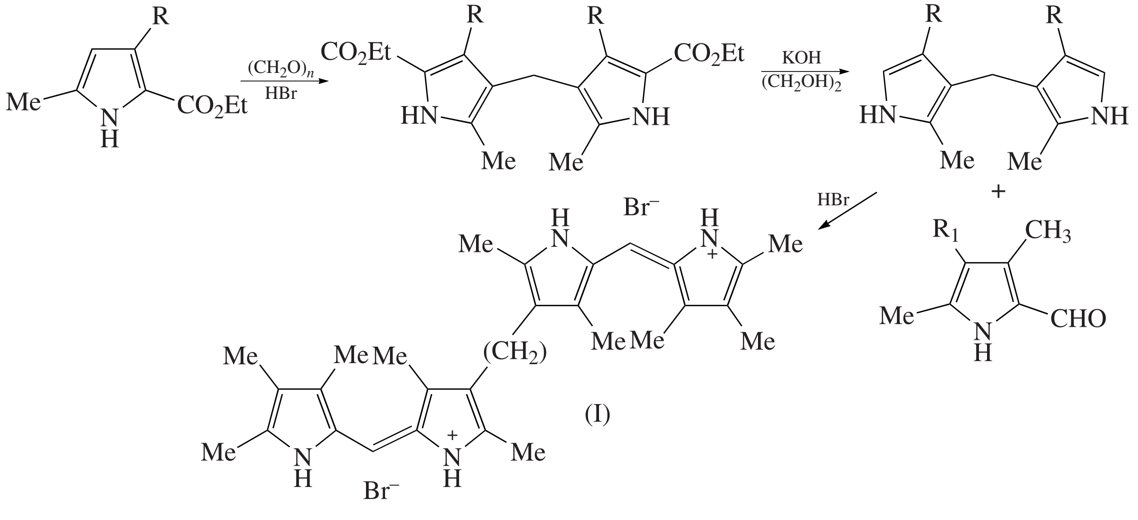
Fig. 1. (a) Ridge-tile and (b) helical conformations of unsubstituted 2,2'-biladiene-*a,c*.

Because of this, the resulting product is often a mixture of mononuclear ([**ML**]) and binuclear heteroleptic (**M_2LX_2**) and homoleptic complexes [**M_2L_2**]. The latter complexes are of the greatest interest for analytical and supramolecular chemistry. On the other hand, it have been demonstrated in [1, 3–5] that 3,3'-bis(dipyrrolylmethenes) with a short spacer are coordinated by doubly charged *d*-metal ions (Zn(II), Co(II), and Cu(II)) to give only the complexes [M_2L_2], which substantially simplifies the use of such ligands in supramolecular chemistry.

The goal of this study was to find out how the variation in the structure and insertion position of an alkyl spacer (at 2,2'-, 3,3'-, or 2,3'-carbon atoms of the dipyrrolylmethene fragments) affects the composition, structure, and stability of the resulting metal chelate complexes with bis(dipyrrolylmethenes). In this communication, we report spectroscopic data on the complexation between bis(3,4,7,8,9-pentamethylpyrrol-3-yl)methane dihydrobromide (**$H_2L \cdot 2HBr$**) (**I**), the simplest representative of 3,3'-bis(dipyrrolylmethenes)) and zinc(II), copper(II), and cobalt(II) acetates.

EXPERIMENTAL

Complex **I** (M = 602.46) was obtained as described in [2] according to the scheme:



The yield of complex **I** was 1.12 g (74%).

UV-VIS (DMF, $c < 5 \times 10^{-5}$ mol/l), λ_{max} ((logε)): 504 (5.08), 464 (4.83), 362 (4.29) (CH_2Cl_2), 502 (5.43), 461 (5.01), 364 (4.22) ($CHCl_3$), 457 nm (4.67).

^{1}H NMR ($CDCl_3$, Me_4Si), δ: 13.11 (s, 2H, NH), 12.99 (s, 2H, NH), 7.02 (s, 2H, *ms*-CH), 3.55 (s, 2H, *ms*-CH_2), 2.67 (s, 6H, 1-CH_3), 2.59 (s, 6H, 3-CH_3), 2.25 (s, 6H, 9-CH_3), 2.15 (s, 6H, 7-CH_3), 1.98 (s, 6H, 2-CH_3).

For $C_{29}H_{38}Br_2N_4$			
anal. calcd. %:	C, 57.82;	H, 6.36;	N, 9.30.
Found (%):	C, 57.96;	H, 6.40;	N, 9.35.

IR (KBr, cm^{-1}): 3480 (ν(N–H)), 1611 δ(N–H)).

Measurements were performed on a Bruker 200 NMR spectrometer, an Avatar 360 FTIR spectrometer, and SF-103 and Cary100 spectrophotometers.

The contents of water of crystallization in zinc(II), copper(II), and cobalt(II) acetates (reagent grade) were confirmed by TGA data (an MOM 1000D derivatograph). The water content of DMF (reagent grade) determined by the Fischer titration did not exceed 0.02%.

RESULTS AND DISCUSSION

The coordination chemistry of linear oligopyrroles had been in its infancy for a long period of time. Current investigations in this field [1–9] cover complexes of a particular metal, groups of structurally related ligands and their complexes with various metals, and specific solvents or processes (synthesis, reactivity, coordination thermodynamics, kinetics, and mechanism, etc.). That is why the development of kinetic and thermodynamic approaches to the study and quantitative description of complexation with metal ions in solutions becomes of particular interest for the experimental coordination chemistry of oligopyrroles.

Previously, it has been shown that the use of electron-donating solvents provides some advantages in the study of complexation between *d*-metal salts and linear oligopyrroles [7–9]. First, because of the irreversible solvolytic dissociation of tetrapyrrole hydrobromides in highly basic solvents [14]

$$[H_4L]Br_{2(Solv)} + 2B_{(Solv)} \longrightarrow H_2L_{(Solv)} + 2[B \cdot HBr]_{(Solv)} \quad (1)$$

(where B is an electron-donating solvent or a cosolvent), unprotonated ligands become more reactive than the initial protonated species [15, 16]. Second, in contrast to the alcohols employed in [15, 17], DMF shows an optimum combination of the dielectric constant ($\varepsilon^{298} = 36.71$), the electron-donating properties (*DN* = 26.6), and the low associativity [18, 19]. As the result, the chemical species of the reagents and the products (H_2L, $M(AcO)_2$), and AcOH) are more soluble and more reactive in this solvent. For instance, the acetates of doubly charged metal ions [20, 21] form the outer-sphere solvate complexes $[M(X)(Solv)_4](AcO)$ in DMF because of the extra coordination of solvent molecules. The above complexes have a tendency toward primary electrolytic dissociation to the cations $[M(AcO)(DMF)_4]^+$ according to the reactions

$$[M(AcO)_2(DMF)_4] \rightleftharpoons [M(AcO)(DMF)_4](AcO), \quad (2)$$

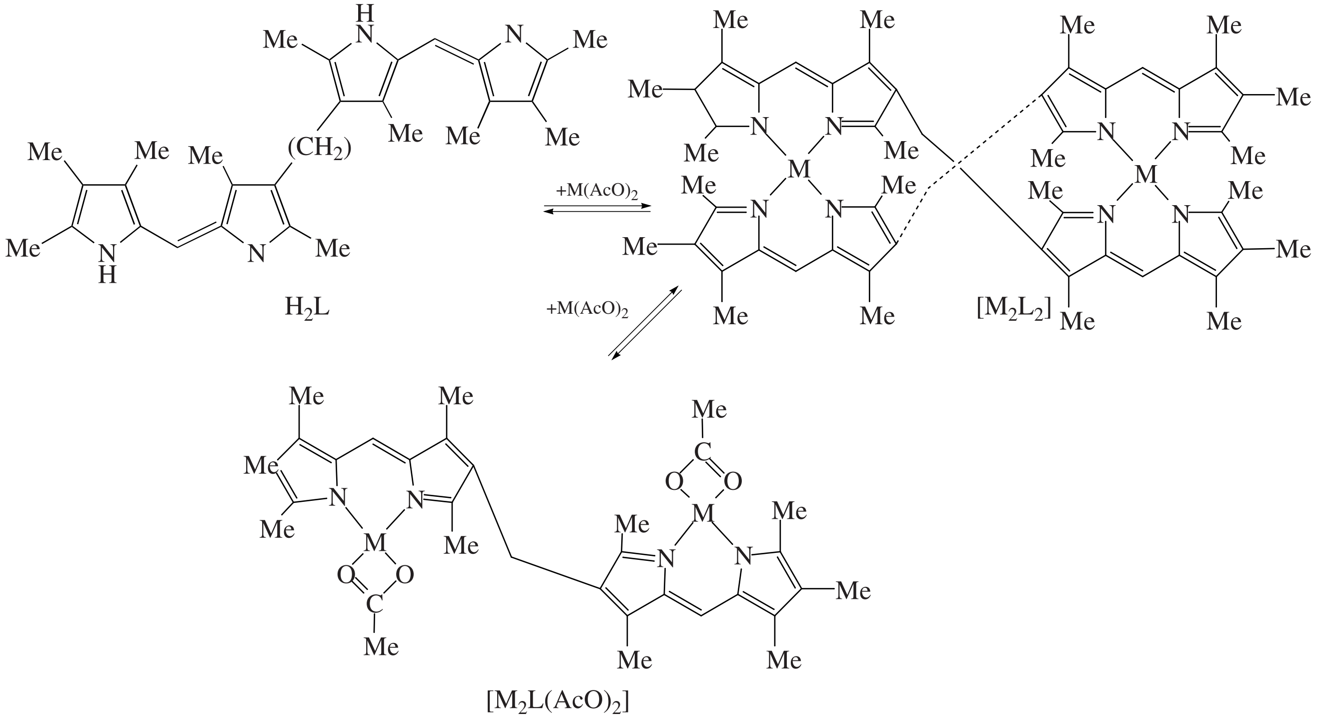
$$[M(AcO)(DMF)_4](AcO) \rightleftharpoons [M(AcO)(DMF)_4]^+ + AcO^-. \quad (3)$$

The resulting cations are much more reactive than the neutral solvate complexes [20, 21].

The typical spectral patterns for the complexation between H_2L and zinc(II), copper(II), and cobalt(II) acetates are shown in Fig. 2. Because of the irreversible solvolytic dissociation of $H_2L \cdot 2HBr$ (Eq. (1)) in the working concentration range (5×10^{-5} mol/l), the electronic absorption spectra of the solutions contain a band due to the unprotonated ligand ($\lambda_{max} = 457$ nm), which experiences a hypsochromic shift by 37–48 nm compared to the λ_{max} value of the starting salt in nonpolar and proton-donating solvents. In the general case, the complexation changes the single-band spectrum of the ligand into a spectrum in which the long-wavelength absorption band shows a large bathochromic shift (by 53–71 nm) because of the auxochromic effect of the metal ion on the conjugated π-systems of the dipyrrolylmethene fragments of the chromophore.

Such differences in band positions make it possible to use the spectrophotometric techniques of molar ratios and isomolar series for determination of the equilibrium concentrations of chromophore reagents and reaction products, the stoichiometric compositions of the resulting complexes, and the concentration constants of the complexation. For all the systems $M(AcO)_2$–H_2L–DMF we studied at $c_{M(AcO)_2} : c_{H_2L} \le 1$, the spectrum of the resulting complex exhibits an absorption band at $\lambda_{max} = 509$–520 nm. With an increase in the salt concentration, the intense band shifts to the longer wavelengths with a hyperchromic effect. The molar ratios curves show an intersection point at $c_{M(AcO)_2} : c_{H_2L} = 1 : 1$ for both c_{H_2L} = const and $c_{M(AcO)_2}$ = const (Fig. 3). According to the literature data on the spectral characteristics and compositions of the complexes of bis(dipyrrolylmethenes) [1, 3], this suggests the formation of the complexes $[M_2L_2]$ with a double-helix structure (Fig. 4). In addition, the molar ratios curves (Figs. 3a–3c) show another intersection point at $c_{M(AcO)_2} : c_{H_2L} = 2 : 1$ (for c_{H_2L} = const) or 0.5 : 1 (for $c_{M(AcO)_2}$ = const) and the spectral diagrams contain a second family of isosbestic points, which is attributable to the presence of the third chromophore complex $[M_2L(X)_2]$ in solution. Such binuclear heteroleptic complexes have been found earlier for 3,3'-bis(dipyrrolylmethenes) [8, 9]. The increased intensity of the longer-wavelength band is due to the double number of chromophore species in solution (Fig. 2). These changes are most pronounced in the spectrum of the $Zn(AcO)_2$–H_2L–DMF system: with an increase in the salt concentration, the absorption band of the complex $[Zn_2L_2]$ at λ_{max} = 509 nm transforms into the band of $[Zn_2L(AcO)_2]$ at λ_{max} = 521 nm (Fig. 2a).

Thus, the reaction mixture mainly contains the binuclear homoleptic complexes $[M_2L_2]$ when the ligand is used in excess and the binuclear heteroleptic complexes $[M_2L(AcO)_2]$ when the salt is used in excess. The complexation between $M(AcO)_2$ and 3,3'-bis(dipyrrolylmethene) can be represented as the following scheme:



The bathochromic shift of λ_{max} for the complexes $[M_2L(X)_2]$ and $[M_2L_2]$ ($X = AcO^-$) ranges from 65 to 71 nm and from 53 to 64 nm, respectively. This suggests the reduced auxochromic effect of the metal ions on the π-system of the chromophore when moving from the single- to double-helix structure of the chelate complex, probably because of steric hindrances. The electronic structure of the *d*-metal ion influences in such a way that the bathochromic shift of the absorption band increases considerably in the order $Zn^{2+} < Cu^{2+} < Co^{2+}$. For the complexes $[M_2L(X)_2]$ and $[M_2L_2]$, these shifts are 6 and 11 nm, respectively; this suggests the enhanced polarization effect of the auxochrome on the aromatic π-system of the chromophore.

It should be noted that a tenfold excess of the metal salt is required to substantially shift equilibrium (4) to the complex $[M_2L(X)_2]$ in the complexation with $Cu(AcO)_2$, while in the reactions with cobalt and zinc acetates, the ligand is almost completely bound in the heteroleptic complex $[M_2L(X)_2]$ even at $c_{M(AcO)_2} : c_{H_2L} < 4$. However, according to our spectroscopic observations, the equilibrium $[Cu_2L(X)_2] \rightleftarrows [Cu_2L_2]$ at the above molar ratios of the reagents shifted again to the right in 2 weeks (Fig. 5). Over the same period of time, the spectra of the systems containing zinc and cobalt acetates showed no noticeable changes. All this suggests that the differences in the thermodynamic constants of reactions (4) and (5) with copper acetate are smaller than those for analogous reactions with zinc and cobalt acetates. It should be emphasized that in the copper-containing system, along with the conversion $[Cu_2L(X)_2]$ to Cu_2L_2, an absorption band at 600 nm becomes more intense with time. This band is characteristic of bilatriene, which can form through the oxidation of the methylene bridge (between the dipyrrolylmethene moieties of the ligand) into a methine one by Cu^{2+} ions with a high oxidative potential [22]. Similar redox processes involving linear oligopyrroles and copper(II) have been observed earlier in macrocyclization reactions of biladienes [23].

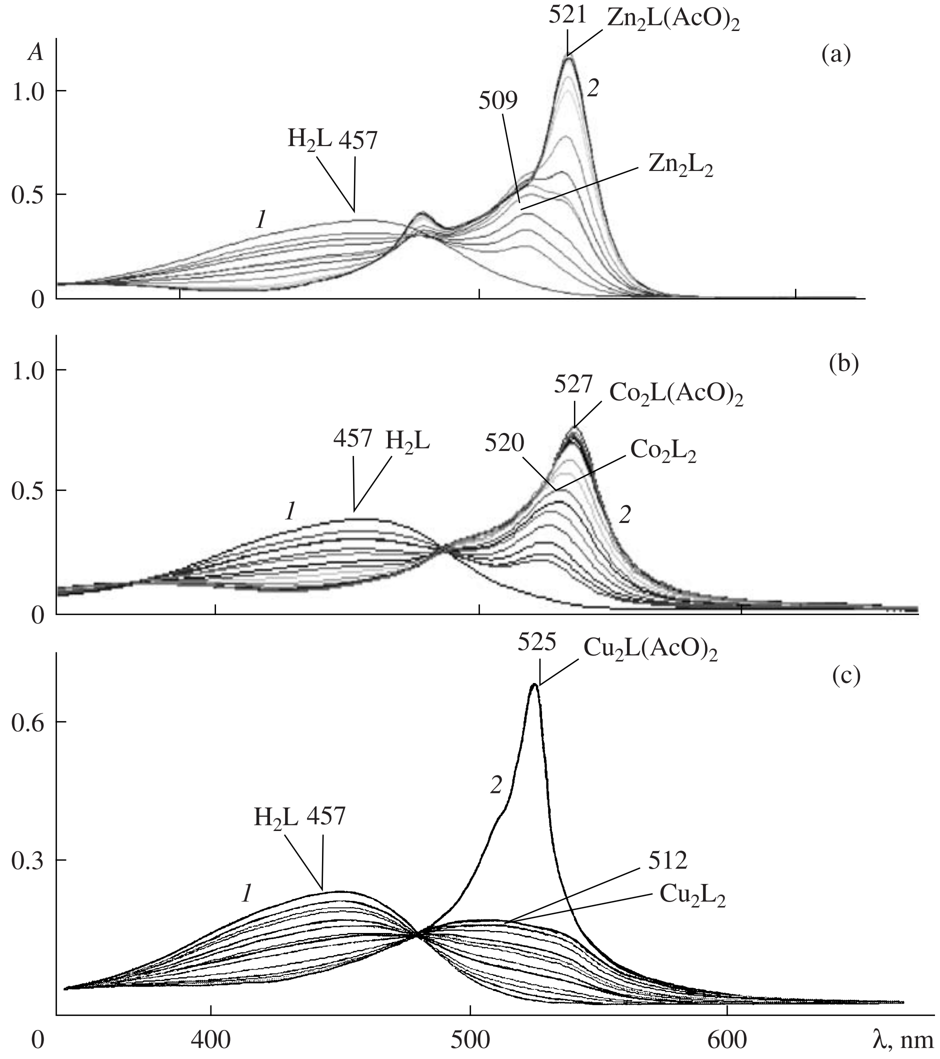


Fig. 2. Electronic absorption spectra (298.15 K) at a constant ligand concentration and a variable salt concentration for the systems: (a) $Zn(AcO)_2$–H_2L–DMF, (*1*) $c^0_{H_2L} = 7 \times 10^{-6}$ mol/l, (*2*) $c^0_{Zn(AcO)_2}/c^0_{H_2L} = 3.3$; (b) $Co(AcO)_2$–H_2L–DMF, (*1*) $c^0_{H_2L} = 8.5 \times 10^{-6}$ mol/l, (*2*) (*1*), $c^0_{Co(AcO)_2}/c^0_{H_2L} = 4.0$; (c) $Cu(AcO)_2$–H_2L–DMF, (*1*) $c^0_{H_2L} = 7 \times 10^{-6}$ mol/l, (*2*) $c^0_{Cu(AcO)_2}/c^0_{H_2L} = 10$.

To estimate the thermodynamic stabilities of the complexes from the quantitative spectral characteristics of the solutions of the ligand and the chelate complexes in DMF (table), we calculated the concentration constants $\boldsymbol{K^c}$ of formation of the complexes $[M_2L(X)_2]$ and $[M_2L_2]$ from the ligand H_2L and the metal salt according to reactions (4) and (5), respectively:

$$H_2L + 2[MX]^+ + 2X^- \rightleftarrows [M_2L(X)_2] + 2HX, \quad (4)$$

$$2H_2L + 2[MX]^+ + 2X^- \rightleftarrows [M_2L_2] + 4HX. \quad (5)$$

The corresponding equations for the calculation of K^c have the forms

$$K^c = \frac{[M_2L_2][HX]^4}{[MX^+]^2[X^-]^2[H_2L]^2} = \frac{256x^5}{(c^0_{MX_2} - 2x)^4(c^0_{H_2L} - 2x)^2},$$

$$K^c_1 = \frac{[M_2L(AcO)_2][HX]^2}{[MX^+]^2[X^-]^2[H_2L]} = \frac{4x^3}{(c^0_{MX_2} - 2x)^4(c^0_{H_2L} - x)},$$

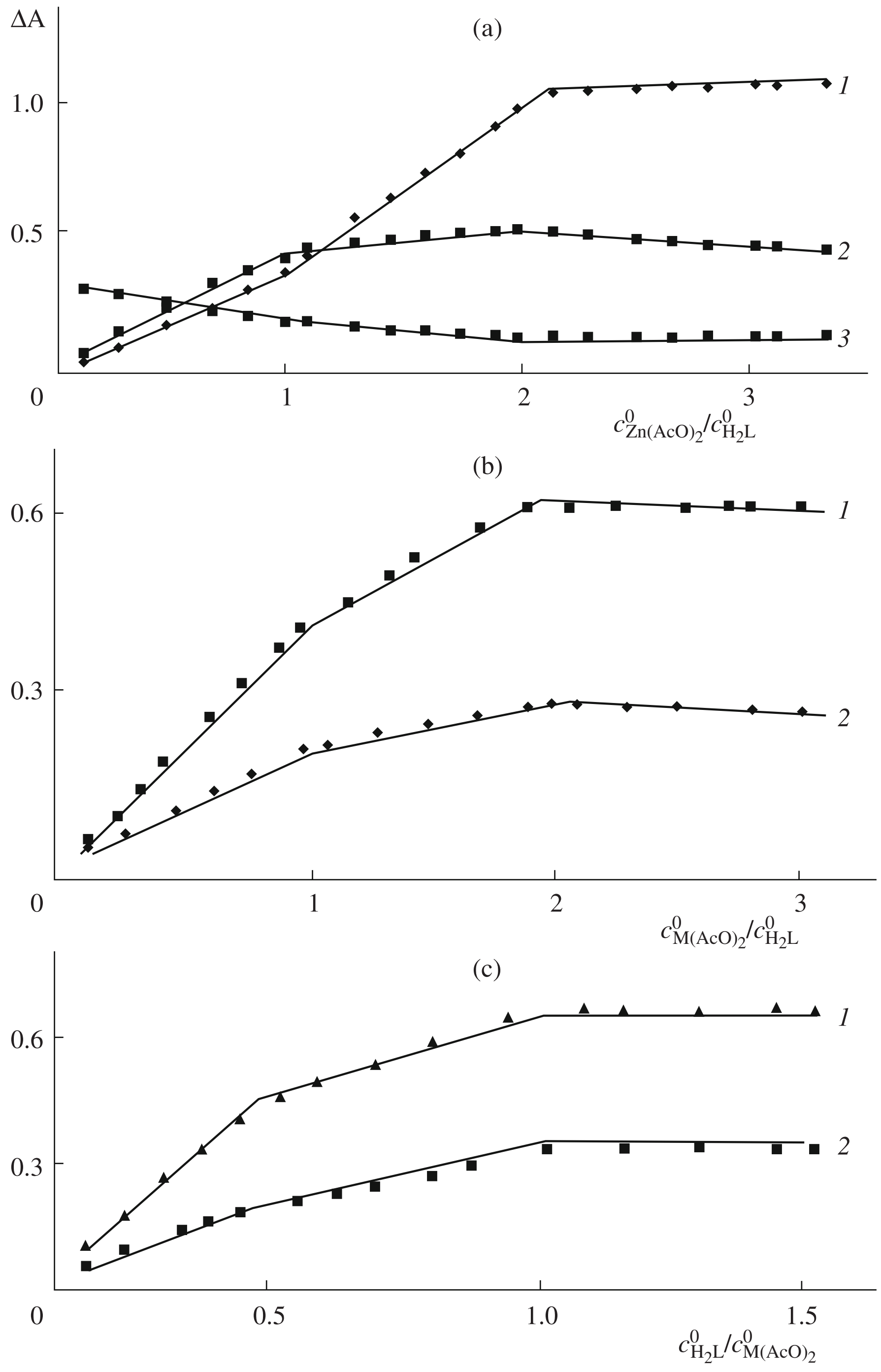


Fig. 3. Curves of spectrophotometric titration at the wavelength with the most intense absorption peak for the systems: (a) $Zn(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 7 \times 10^{-6}$ mol/l): (*1*) $[Zn_2L(AcO)_2]$ ($\lambda = 521$ nm), (*2*) $[Zn_2L_2]$ ($\lambda = 509$ nm), and (*3*) the ligand ($\lambda = 457$ nm); (b) (*1*) $Co(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 7 \times 10^{-6}$ mol/l, $\lambda = 520$ nm) and (*2*) $Cu(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 8.5 \times 10^{-6}$ mol/l, $\lambda = 512$ nm); (c) (*1*) $Co(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 8.5 \times 10^{-6}$ mol/l, $\lambda = 527$ nm) and (*2*) $Cu(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 8.5 \times 10^{-6}$ mol/l, $\lambda = 525$ nm).

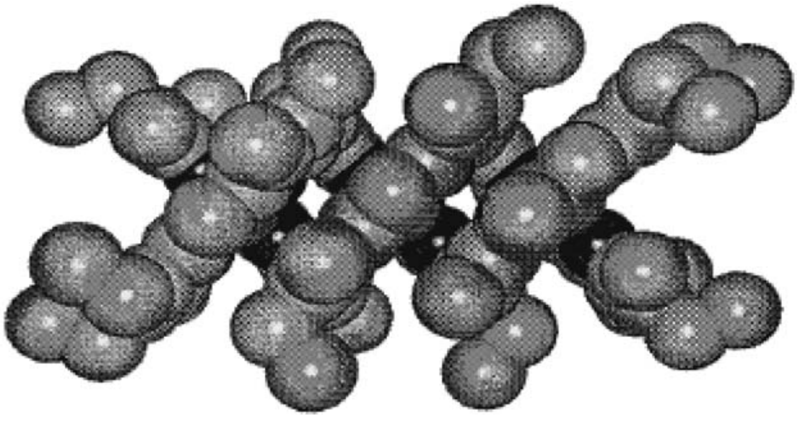


Fig. 4. HyperChem-modeled [1] molecular structure of the trinuclear zinc complex Zn_3L_2 with tris(dipyrrolylmethene).

where *x* is the equilibrium concentration of the complex.

We found experimentally that the K^c values are independent (to within the experimental error) of the ligand concentration for $4 \times 10^{-6} < c_{H_2L} < 8.5 \times 10^{-6}$ mol/l. Extrapolation of the linear plots of $\log K^c$ vs. $(c_{M(AcO)_2})^{1/2}$ in the salt concentration range (5–8.5) × 10^{-6} mol/l (Fig. 6) gave the correlation equations used to calculate the thermodynamic stability constant $\boldsymbol{K^0}$. The data obtained are tabulated together with data for the 2,2'-isomer (decamethyl-2,2'-biladiene-*a,c*) [24]. An analysis of the data revealed some distinctive features of the coordination of 3,3'-bis(dipyrrolylmethene) and allowed estimating the selectivity of its chelating power against the 2,2'-isomer.

In the series of complexing metals (Cu(II), Zn(II), and Co(II)), 3,3'-bis(dipyrrolylmethene) chelate complexes (both $[M_2L_2]$ and $[M_2L(X)_2]$) become much more stable: the stability constants increase by four to five orders of magnitude. It should be, however, noted that K^0 and K_1^0 for $[Cu_2L_2]$ and $[Cu_2L(X)_2]$ can be underestimated because of a parallel redox process. The differences between K^0 and K_1^0 become substantially larger when moving from the copper complexes to the cobalt and especially zinc ones; this confirms the assumption made from the spectral patterns of the complexation (Fig. 3).

By comparing the data for the cobalt and zinc complexes (table), one can conclude that the binuclear chelate complexes with 3,3'-bis(dipyrrolylmethene) are appreciably easier to form and much more stable than those with its 2,2'-isomer. For instance, the K^0 values for $[Co_2L_2]$ and $[Co_2L(AcO)_2]$ with 3,3'-bis(dipyrrolylmethene) are more than two orders of magnitude higher than the corresponding values for analogous complexes

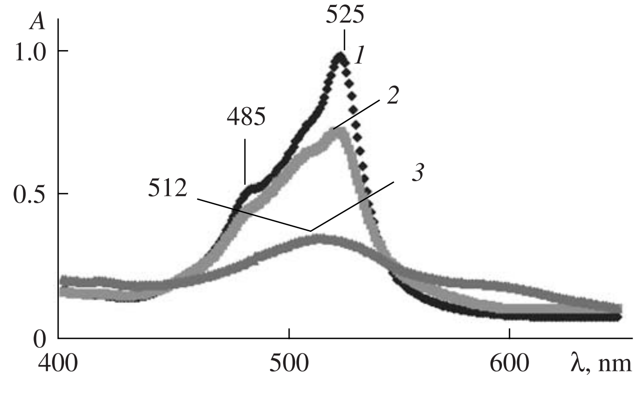


Fig. 5. Electronic absorption spectra of the system $Cu(AcO)_2$–H_2L–DMF ($c^0_{H_2L} = 1 \times 10^{-5}$ mol/l, $c^0_{Cu(AcO)_2} = 1 \times 10^{-4}$ mol/l): (*1*) a freshly prepared solution, (*2*) 2 hours after the heating to 323 K, and (*3*) after 2 weeks.

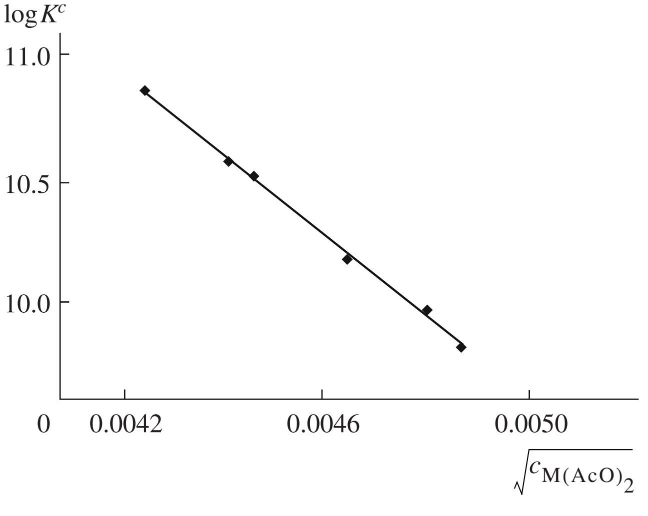


Fig. 6. Plot of $\log K^c$ vs. $\sqrt{c_{M(AcO)_2}}$ for equilibrium (5) in the system $Co(AcO)_2$–H_2L–DMF.

Quantitative characteristics of the electronic absorption spectra of the complexes (λ_{max}, nm ($\log\varepsilon$)) and the constants of the complexation between *d*-metal acetates and decamethylbis(dipyrrolylmethenes) in DMF

Complex	$\log K^0$	λ_{max}, nm ($\log\varepsilon$) in DMF
$[Co_2L_2]$	13.44 ± 0.35	520(5.08)
$[Co_2L_2^*]$	11.04 ± 0.51	498(4.74)
$[Zn_2L_2]$	10.14 ± 0.21	509(5.16)
$[Cu_2L_2]$	9.34 ± 0.22	512(4.62)
$[Co_2L(AcO)_2]$	16.60 ± 0.45	527(4.93)
$[Co_2L^*(AcO)_2]$	14.44 ± 0.39	502(5.03)
$[Zn_2L(AcO)_2]$	14.46 ± 0.34	521(5.22)
$[Cu_2L(AcO)_2]$	11.43 ± 0.23	525(5.00)

* L = 2,2'-bis(dipyrrolylmethene) [8, 24].

with 2,2'-biladiene-*a,c*. The data we obtained on the spectroscopic properties and stabilities of the complexes, as well as on the molecular mechanism of the complexation, will be useful for optimization of the reaction conditions and efficient synthesis of desired chelate complexes.

The high stabilities of the complexes and the large differences between their quantitative spectral characteristics (λ_{max}, ε) and K^0 values make 3,3'-bis(dipyrrolylmethene) a promising analytical reagent and a useful agent for extraction of microamounts of the *d*-metal ions studied from physiological and aqueous organic solutions. The lowest concentrations in which Zn^{2+}, Cu^{2+}, and Co^{2+} ions can be determined by this method were theoretically calculated from the molar absorption coefficient of the complex at the longer-wavelength band in the spectrum of its solution (0.001, cell thickness 1 cm); the concentrations are 6.9×10^{-9}, 2.4×10^{-8}, and 8.3×10^{-9} mol/l, respectively.

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