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Electronic Absorption Spectra and Acid–Base and Ligand Properties of Alkyl-Substituted Biladiene-*a,c*

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Abstract—The influence of the nature of a solvating medium on the chromophore properties and stability of alkyl-substituted biladiene-*a,c* dihydrobromide, a synthetic analogue of a bile pigment bilirubin, was analyzed. The results of the spectophotometric study of the protonation of a tetrapyrrol ligand and of the complex formation with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) acetates in DMF at 298.15 K were considered. Depending on the nature of a complex-forming cation and concentrations of reagents in solution the formation of complexes of three various types is possible: porphyrin-like (1 : 1), binuclear with different ligands (2 : 1), and binuclear biligand (2 : 2). The nature of metal cation renders essential influence on the formation of coordination polyhedra of the metal chelates with various structure.

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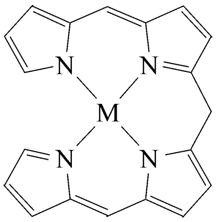
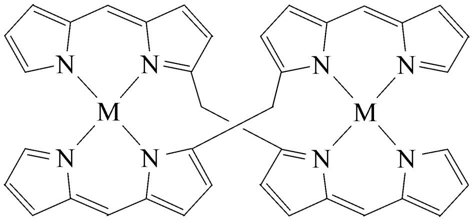
Natural predecessors of porphyrins, linear tetrapyrrol compounds, have a number of unique physical and chemical properties [1]. These substances forming a group of pigments perform the major role of prosthetic groups of phytochromes, participate in a metabolism of vital hemoproteins (hemoglobin of blood, myoglobin of muscles, oxidoreductases, etc.) [2]. Bile pigments: bilirubin, biliverdin, urobilinogen, and stercobilin [3] are most widespread in animal and human organisms. Earlier they were considered as ballast metabolism products, however, resent study [4] proved the major function of bilirubin as a natural antioxidant in a cardiac muscle and other tissues of an organism.

Furthermore, it was found [5, 6] that bile pigments, including bilirubin, and also their synthetic analogues are capable of acting as effective chelating ligands for heavy metal ions, including toxic [7–9], that has served as stimulus to the development of researches of coordination properties of natural and synthetic tetrapyrrols. It was shown on the basis of the spectral measurements [10] that bilirubin can be used as an effective carrier of mercury ions through cellular membranes. The study of coordination modes of synthetic tetrapyrrols has shown [11, 12] that, depending on conditions of a medium and the nature of reagents, reactions of Ni(II), Zn(II), Hg(II), and Co(II) acetates with biladiene-*a*,*c* alkyl-substituted can yield stable complexes of various composition or their mixture: porphyrin-like (ML), binuclear with different ligands [$M_2L(AcO)_2$], and complexes with equal ligands (M_2L_2)–“double stranded” structures.



ML



M_2L_2

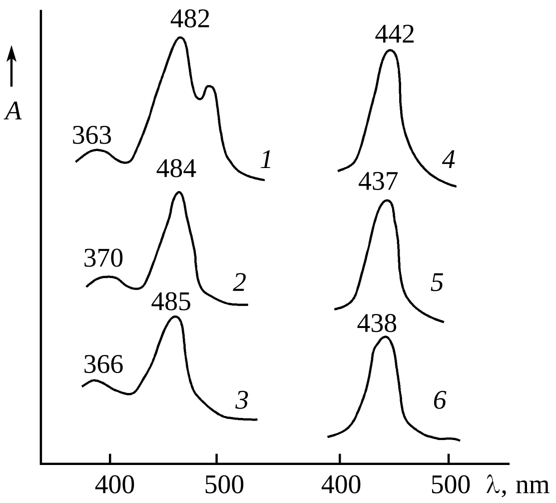
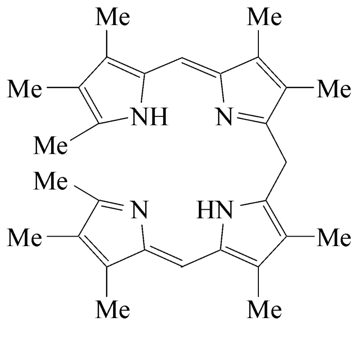


Fig. 1. Electronic absorption spectra of $H_2L \cdot 2HBr$ solutions in organic solvents. The spectra in DMF, DMSO, and pyridine correspond to the spectra of the free H_2L base. (*1*) $CHCl_3$, (*2*) CCl_4, (*3*) C_6H_6, (*4*) DMSO, (*5*) pyridine, (*6*) DMF.

In some cases it was noted that the formation of dinuclear complexes in a reaction mixture, in particular of rather stable M_2L_2, substantially reduces, efficiency of the template synthesis of porphyrins and corrines from di- and tetrapyrrols. As the template synthesis of macrocycles from linear predecessors includes the stages of deprotonation and coordination of di- or tetrapyrrol to a metal ion and is carried out at elevated temperatures, its efficiency in many respects is determined by acid–base, coordination, and redox properties of linear substrates [5].

The present research is directed on studying chromophore, acid–base, and ligand properties of symmetrically substituted linear tetratetrapyrrol, 1,2,3,7,8,-12,13,17,18,19-decamethylbila-dien-*a,c* (H_2L), in relation to the nature of the solvating medium and to electronic structure of a *d*-metal atom.



H_2L

Chromophore properties. As a rule, linear di- and tetrapyrrols are synthesized as salts with hydrobromic acid, in which chromophore molecules are much more stable against oxidation by molecular oxygen [13]. However, as it has been shown earlier [14], in electron-donor solvents and in the presence of nucleophilic reagents a dissociation of di- and tetrapyrrols hydrobromides proceeds. Its kinetic and thermodynamic characteristics depend on the donor power, polarity, and other properties of the solvent, concentration of salt in solution, and specific features of the oligopyrrol molecular structure. These characteristics can be determined from the changes in electronic absorp-tion spectra of solution. Therefore, in the first stage it was necessary to analyze influence of the nature of solvating medium on the electronic spectra of the $H_2L \cdot 2HBr$ salt in various organic solvents.

It is seen from Fig. 1 that the absorption spectra of $H_2L \cdot 2HBr$ solutions in inert solvents (C_6H_6 and CCl_4) have two absorption bands, one of which, low-intensive, lies in the near UV region (360–370 nm) and, according to the published data [15], is identified as a charge-transfer band. Thus, the salt $H_2L \cdot 2HBr$ can be related to charge-transfer complexes, in which Br^- ions fulfill the role of an electronic pair donor, and the $[H_4L]^{2+}$ cation with charges delocalized over the π-system of the chromophore is an acceptor. The long-wave absorption band at 485 nm (in C_6H_6) or 484 nm (in CCl_4) corresponds to the π–π* electronic transition [16]. Unlike non-polar solvents, the spectrum of the salt in chloroform contains an additional low-intensity long-wavelength band at 521–522 nm, which is connected with the activation of electronic states of the molecule due to strengthening its polarization as a result of solvation by polar proton-donor $CHCl_3$ molecules. This phenomenon was also observed earlier for certain alkyl-substituted derivatives of dipyrrolylmethene and biladiene-*a,c* [17].

Electronic spectra of solutions of the $H_2L \cdot 2HBr$ salt in electron-donor solvents (DMF, DMSO, Py) essentially change. First, the charge-transfer band disappears, second, the long-wave band undergoes an essential (by 20–30 nm) hypsochromic shift accompanied by a sharp hypochromic effect. These changes in the spectra point to occurring solvolytic dissociation of the $H_2L \cdot 2HBr$ salt in solutions in electron–donor solvents with the formation of a free H_2L base. In view of data obtained earlier [18] we can assert that the specific solvation of protons by electron-donor molecules of the solvents controlled by kinetic factors play a leading part in this process. Thus, in the case of solutions with concentrations exceeding the specified range, the transformation of a spectrum of the salt into a spectrum of the free base can be observed in time.

Protonation. The knowledge of quantitative characteristics of acid–base properties of di- and tetrapyrrol ligands allows us to compare equilibrium constants of protonation and complex formation. Therefore in the following stage of the work we studied for the first time the protonation of H_2L by hydrobromic acid in DMF using a spectrophotometric titration method (298.15 K). As is shown above, the positions of characteristic band vs. in the electronic spectra of protonated ($[H_4L]^{2+}$) and molecular (H_2L) forms of the ligand (by 44 nm) differ considerably from each other that allowed us to use the spectral data for the calculation of equilibrium concentrations and protonation constant.

The changes in the spectrum resulted from the addition of hydrobromic acid to H_2L solution are presented in Fig. 2. A significant bathochromic shift (by 44 nm) of the absorption bands in the spectrum of the solution and a sharp increase in its intensity (hyperchromic effect) point to the occurring of the ligand protonation. The character of the spectrophotometric titration curve allows us to conclude that the stoichiometric ratio of reagents in the reaction of biladiene-*a,c* protonation is 2 : 1, i.e. the reaction is described by Eq. (1).

$$H_2L + 2HBr \longrightarrow [H_4L]Br_2. \quad (1)$$

Concentration constants of protonation or constants of ligand basicity (K_b^c) were calculated by Eq. (2).

$$K_b^c = \frac{[H_2L \cdot 2HBr]}{[H_2L][HBr]^2} = \frac{x}{(c^0_{H_2L} - x)(c^0_{HBr} - 2x)}. \quad (2)$$

Here x is equilibrium concentration of $[H_4L]Br_2$ determined from the spectral data on the intensity of a characteristic band of the protonated ligand.

In the studied concentration range K_b^c is independent of the hydrobromic acid concentration in solution within the limits of the experimental error that allowed us to take the average value from the set of K_b^c values as the standard value of the basicity constant K_b^0. The average value of $\log K_b^0$ was 9.51 ± 0.38 l^2 mol^{-2}, which is higher by 4–5 orders of magnitude than the published data [2] for the average value of basicity constants of natural porphyrins under similar conditions, including electron–donor solvents with additions of chloric and other inorganic acids. One of principal causes for the higher basicity of the linear tetrapyrrol can be the absence of a macrocyclic effect.

The fact that the monocationic form of tetrapyrrol is not detected by spectrophotometry on the protonation of alkyl-substituted biladiene-*a,c* deserves special attention. In the case of the ligands of the majority of porphyrins mono- and dication forms generated on the protonation are also indistinguishable by spectral methods [19], and constants of their dissociation differ only slightly. Thus, the results of the present study point to identical basicity of tertiary nitrogen atoms of the both dipyrrolylmethene fragments of a biladiene-*a,c* molecule. The results of thermogravimetric analysis [20] of crystalline samples of a wide range of biladienes-*a,c* with various degree of alkyl substitution also support this conclusion: HBr molecules in the salts of linear tetrapyrrols are energetically equivalent.

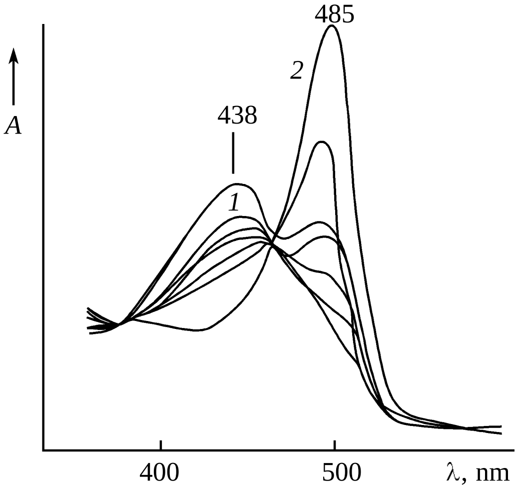


Fig. 2. Electronic absorption spectra of H_2L–HBr–DMF solutions at $c^0_{H_2L}$ 1.66×10^{-5} M. c^0_{HBr}: (*1*) 5.03×10^{-6}; (*2*) 5.03×10^{-5} M; other curves correspond to intermediate HBr concentrations.

It is necessary to note that a rather high value of $\log K_b^0$ for H_2L agrees with the earlier [21, 22] data on the dihydrobromide stability in crystals and on the proton affinity of free ligand in a gas phase. Compared to salts of other alkyl-substituted derivatives of biladiene-*a,c*, the dihydrobromide of the completely methylated analogue ($H_2L \cdot 2HBr$) is the most stable against deprotonation in solutions containing additions of nucleophilic reagents. A rather high stability of the $H_2L \cdot 2HBr$ salt has been confirmed also by the thermogravimetric analysis of the crystalline form of the compound and by the computer simulation of the molecular and protonated forms in a gas phase. The temperature of $H_2L \cdot 2HBr$ dissociation (150°C), the enthalpy of HBr evaporation from the crystal salt (145 kJ mol^{-1}), and the proton affinity in a gas phase calculated for the double protonated form (572 kcal mol^{-1}) are considerably higher than for biladiene-*a,c* substituted salts with a lower alkylation degree [23]. It suggests that the regular trend to increasing basicity of porphyrin ligands with increasing

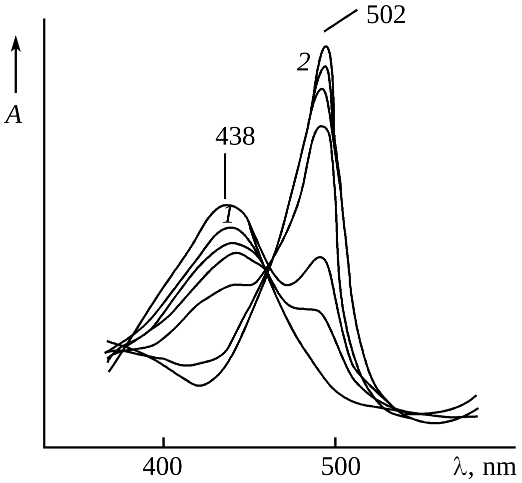


Fig. 3. Electronic spectra of H_2L–$Co(AcO)_2$–DMF solutions at $c^0_{H_2L}$ 2.38×10^{-5} M. $c^0_{Co(AcO)_2}$: (*1*) 0.8×10^{-5}, (*2*) 7.5×10^{-5} M; other curves correspond to intermediate $Co(AcO)_2$ concentrations.

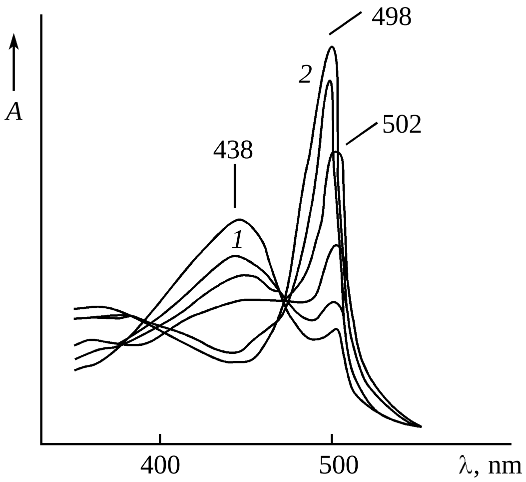


Fig. 4. Electronic spectra of H_2L–$Hg(AcO)_2$–DMF solutions at $c^0_{H_2L}$ 3.32×10^{-5} M. $c^0_{Hg(AcO)_2}$: (*1*) 8.12×10^{-6}, (*2*) 1.22×10^{-4} M; other curves correspond to intermediate $Hg(AcO)_2$ concentrations.

degree of alkyl substitution of a molecule periphery is preserved also for noncyclic pyrrol pigments.

Complex formation. To confirm a high basicity of tertiary nitrogen atoms in the H_2L molecule and to study its chelating ability, we investigated coordination interactions of H_2L with cobalt(II), nickel(II), coppers(II), zinc(II), cadmium(II), and mercury(II) acetates in DMF. The choice of DMF as a medium for studying the complex formation is caused by its satisfactory solvating ability in relation to the reagents and products of the reactions under study and also by availability of reliable published data on the state of transition metal acetates in this solvent [24, 25].

Quantitative characteristics of electronic absorption spectra and thermodynamic stability of M(II) complexes (M = Ni, Cu, Zn, Co, Cd, Hg) with H_2L in DMF

Complex	λ_{max}, nm	$\log\varepsilon_\lambda$	$\log K^{0\,a}$	$B\times10^8$, M[b]
NiL	500	4.45	4.34 ± 0.33^a	3.55
CuL	505	4.52	5.83 ± 0.35	3.02
ZnL	502	4.91	10.21 ± 0.37	1.23
$Co_2(OAc)_2L$	498	4.74	14.44 ± 0.39	1.82
Co_2L_2	502	5.03	11.04 ± 0.52	9.33
$Cd_2(OAc)_2L$	491	4.60	14.04 ± 0.51	2.51
$Hg_2(OAc)_2L$	502	4.66	19.64 ± 0.13	2.19

[a] The error in the determination of the constant was calculated by the least square method using the programs MicroCal Origin (version 6.1). [b] *B* is an arbitrary sensitivity of the determination of metal contents calculated from molar absorption coefficients of metal complexes at *A* 0.001 and *l* 1 cm.

Similarly to the H_2L protonation, the complex formation of the tetrapyrrol ligand is accompanied by the bathochromic displacement of its characteristic band and by the appearance of a charge-transfer band (Figs. 3, 4 and the table). The data on the electronic spectra of the ligand, its salt, and complexes presented in the table allow us to point out a stronger auxochromic effect of metal cations on the tetrapyrrol chromophore properties as compared to the effect of protons, which seems to be caused by two factors: (1) an effective action of a central metal atom on bonding, antibonding, and nonbonding orbitals of a ligand (electronic effect of coordination); (2) an increase in structural rigidity and planar structure of conjugated dipyrrol fragments of a ligand molecule in the composition of a coordination polyhedron (steric effect of coordination).

We determined composition of the complexes and thermodynamic constants of the complex formation from the spectral data, using a method of molar ratios (see the table). The results obtained show that depending on the nature of a complex forming cation various types of complexes can be formed in DMF: porphyrin-like ML (1 : 1, M = Ni, Cu, Zn), dinuclear with different ligands $M_2L(AcO)_2$ (2 : 1, M = Cd, Hg), and dinuclear biligand M_2L_2 (2 : 2, M = Co).

Taking into account the data [25, 26] on the features of the state (solvation and dissociation) of *d*-metal acetates in electron-donor solvents, we can describe the studied coordination processes by Eqs. (3)–(5).

$$[M(AcO))]^+_{(Solv)} + AcO^-_{(Solv)} + H_2L_{(Solv)} \rightleftarrows ML_{(Solv)} + 2AcOH_{(Solv)}, \quad (3)$$

$$2M(AcO))]^+_{(Solv)} + 2AcO^-_{(Solv)} + H_2L_{(Solv)} \rightleftarrows M_2(AcO)_2L_{(Solv)} + 2AcOH_{(Solv)}, \quad (4)$$

$$2[M(AcO))]^+_{(Solv)} + 2AcO^-_{(Solv)} + 2H_2L_{(Solv)} \rightleftarrows M_2L_{2(Solv)} + 4AcOH_{(Solv)}. \quad (5)$$

The corresponding concentration constants of Eqs. (3)–(5) and the concentrations of their participants are linked by Eqs. (6)–(8).

$$K_1^c = \frac{[ML][AcOH]}{[M(AcO)^+][AcO^-][H_2L]} = \frac{4x^3}{(c^0_{M(AcO)_2} - x)^2(c^0_{H_2L} - x)}, \quad (6)$$

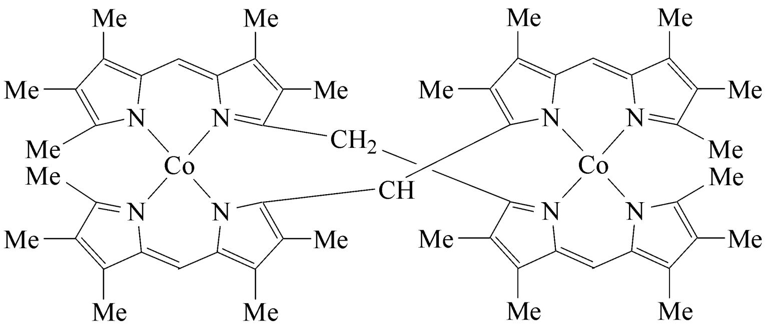
$$K_2^c = \frac{[ML(AcO)_2][AcOH]^2}{[M(AcO)^+][AcO^-]^2[H_2L]} = \frac{4x^3}{(c^0_{M(AcO)_2} - x)^2(c^0_{H_2L} - x)}, \quad (7)$$

$$K_3^c = \frac{[M_2L(AcO)_2][AcOH]^2}{[M(AcO)^+]^2[AcO^-]^2[H_2L]} = \frac{256x^3}{(c^0_{M(AcO)_2} - x)^2(c^0_{H_2L} - x)}. \quad (8)$$

Here x is equilibrium concentration of a metal complex; $c^0_{Hg(AcO)_2}$ and $c^0_{H_2L}$ are the starting concentrations of a metal acetate and a ligand, respectively.

Equilibrium constants determined at various concentrations of starting salt were standardized on the basis of the assumption of the full dissociation of solvato complexes of d-metal acetates by the first stage in dilute solutions (the range of operating concentrations $c^0_{Hg(AcO)2}$ was 10^{-4}–10^{-6} M). Accepting activity coefficients of H_2L molecular species, metal complexes, and acetic acid (for which pK_a in DMF is 13.3 [27]) to be equal to unity and also taking into consideration a low ionic strength of the medium ($I <$ 0.01) created due to dissociation of solvato complexes, we described concentration constants of Eqs. (3)–(5) by an equation based on the calculation of an average ionic activity coefficient of electrolytes within the limits of the first approximation of Debye–Huckel theory [28, 29].

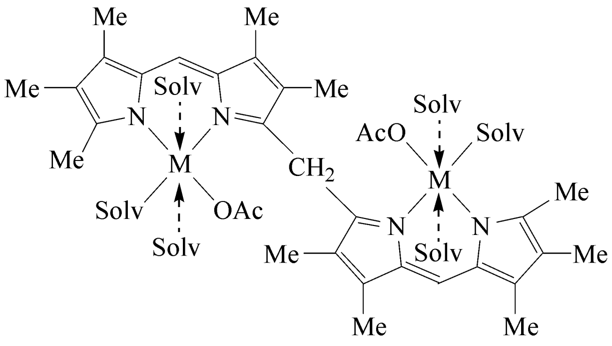
It follows from the data on $\log K^0$ of the complexes (see the table) that formation of the different-ligand complex $Co_2(AcO)_2L$ is more favorable thermodynamically than that of the Co_2L_2 complex with a “double interlacing” structure. A low value of $\log K_3^0$ is obviously connected with a considerable negative contribution of the reaction (5) entropy caused by a necessity of a strict spatial orientation of the second tetrapyrrol ligand relatively to the two coordination sites of $Co_2L(AcO)_2$ molecule required to reach optimal conditions for the formation of the complex Co_2L_2 geometric configuration [14].



Co_2L_2

However this is the high stability of the complex $Co_2L(AcO)_2$ which explains the existence of biladiene complexes with the “double interlacing” structure under conditions of a ligand excess in solution. As a result in many cases depending on synthesis conditions M_2L_2 complexes are obtained with a high yield on a background of the main reaction product, a complex with a porphyrinlike structure, and are precipitated as solids that essentially depresses the efficiency of the synthesis of porphyrins.

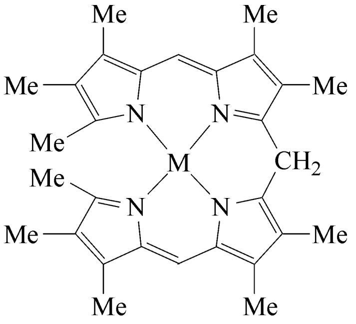
The results of our study showed that dinuclear different-ligand complexes $M_2(AcO)_2L$ can be formed as products of the biladiene-*a,c* reaction not only with Co(II) acetate, but also with Cd(II) and Hg(II) acetates. In view of the monodentate type of acetate anion coordination [30, 31] and of the possibility for an additional coordination of electron-donor molecules of DMF or other solvents, the structure of such metal complex can be described by the following formula.



$M_2L(AcO)_2$

M = Co, Cd, Hg.

The Ni(II), Cu(II), and Zn(II) acetates form with H_2L only porphyrin-like complexes ML (1 : 1).



ML

M = Ni, Cu.

The results of this work show that the nature of a salt cation essentially affects both composition of biladiene-*a,c* metal chelates and characteristics of their stability. A decrease in the ability of metal ions to form ML complexes correlates with the increase in ionic radii [32] in the sequence $Ni^{2+} < Cu^{2+} < Zn^{2+} < Cd^{2+} < Hg^{2+}$ (0.078, 0.082, 0.083, 0.103, and 0.112 nm, respectively). Thus, the increase in the size of a complexforming ion seems to create steric hindrances for effective closing tetrapyrrol cycle around the ion.

The analysis of the thermodynamic characteristics of the obtained H_2L metal complexes with Zn(II), Cd(II), and Hg(II) allows us to examine the influence of the nature of a complexing agent in the group of $(n - 1)d^{10}$ metals on the structure and stability of resulting chelates. The increase in numerical values of thermodynamic constants of the complex formation in the series ZnL–CdL–HgL agrees with a known trend for chelates of various bidentate O- and N-donor ligands: increase in the size of $(n - 1)d$ orbitals of metal ions results in an increasing stability of the complexes due to increase in the contribution of a covalent component of coordination M–L bonds [33, 34].

Electronic spectra of chelates can be used for the identification of products of template synthesis of porphyrins and for their chromatographic separation. Essential distinctions in spectral characteristics of the H_2L ligand and its metal complexes, and also in stability of these latter make it possible to use H_2L in analytical chemistry for the determination of contents of *d*-metal ions in organic solvents (conditional sensitivities of the determination of these ions by the spectrophotometric method are given in the table). The results of the present study evidently show an opportunity for the application of tetrapyrrol ligands, synthetic derivatives of bilirubin, as probes for the determination of heavy metal ions in lipidic layers of cellular membranes and micelle structures of type of blood plasma lipoproteins.

EXPERIMENTAL

The electronic absorption spectra of H_2L, its dihydrobromide, and metal complexes in DMF were recorded in the wavelength range of 350-750 nm on a Specord M-40 spectrophotometer in quartz cuvettes with the thickness of absorbing layer of 2 and 10 mm placed in a temperature-controlled (at 298.15 K) cell (accuracy of the temperature control ±0.01 deg).

1,2,3,7,8,12,13,17,18,19-Decamethylbiladiene-*a,c* dihydrobromide was prepared by the technique [35]. In 20 ml of methanol 1 g of 5,5'-dicarboxy-3,3',4,4'-tetramethyldipyrrolylmethane and 0.09 g of 2,3,4-trimethyl-5-formylpyrrol were dissolved. To the resulting solution 3 ml of concentrated HBr was added, and the mixture was stirred for 2 h. The precipitate formed was filtered off, washed by methanol with a drop of HBr added and by ether, and dried up. Yield 1 g (48%). IR spectrum (KBr), cm^{-1}: 3477 w, 3414 s, 2913 m, 2846 w, 1412 m, 1362 m, 1255 s, 1179 s, 1164 m, 1112 m, 1097 m, 931 m, 867 m, 821 m, 746 m, 668 m, 607 w. Electronic absorption spectrum, λ_{max}, nm: 366, 485 (in C_6H_6), 370, 484 (in CCl_4), 363, 482, 521 (in $CHCl_3$), 438 (in DMF), 432 (in DMSO), 435 (in C_5H_5N).

1,2,3,7,8,12,13,17,18,19-Decaamethylbiladiene-*a,c*. In 30 ml of methylene chloride 0.2 g of dihydrobromide was dissolved and shaked in a separatory funnel for 1 min with an equal amount of 10% aqueous solution of ammonia. The organic layer was separated, ammonia was washed off by water, the solution was boiled out, and a free ligand was precipitated with methanol. Electronic absorption spectrum, λ_{max}, nm: 438 (DMF), 440 ($CHCl_3$).

Metal acetates of chemically-pure grade were recrystallized from ice acetic acid, and then dehydrated by thermogravimetry [36]. Organic solvents of specialpurity grade were additionally refined and dehydrated according to the standard techniques [37–39]; residual water content (less than 0.02 wt%) was monitored by amperometric titration according to Fisher's procedure.

To determine the composition, equilibrium concentrations, and apparent molar absorption coefficients of metal complexes, we used the method of molar ratios [40]. Diagrams of the method of molar ratios were obtained by plotting a measured absorption of a formed metal complex minus an absorption of a ligand at a specified wavelength on the axis of ordinates: $\Delta A = A_{ML} - A_{H_2L}$. Concentrations of reagents were varied within the range 10^{-6}–10^{-4} M.

ACKNOWLEDGMENTS

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REFERENCES

1. Falk, H., *The Chemistry of Linear Oligopyrroles and Bile Pigments,* New York: Springer, 1989, p. 621.
2. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianinov* (Coordination Compounds of Porphyrins and Phthalocyanines), Moscow: Nauka, 1978.
3. *The Porphyrins and Metalloporphyrins,* Smith, K.M., Ed., New York: Elsevier, 1975.
4. Makarov, N.N., Rumyantsev, E.V., and Antina, E.V., Abstracts of Papers, *Mezhdunarodnaya konferentsiya po khimii geterotsiklicheskikh soedinenii* (Int. Conf. on the Chemistry of Heterocyclic Compounds), Moscow, 2005, p. 238.
5. Maravin, G.B. and Mironov, A.F., *Mendeleev Commun.,* 1993, no. 3, p. 104.
6. Velapoldi, R.A. and Menis, O., *Clin. Chem.,* 1971, vol. 17, no. 6, p. 1165.
7. Zakharova, S.P., Rumyantsev, E.V., and Antina, E.V., Abstracts of Papers, *XXII Mezhdunarodnaya Chugaevskaya konferentsiya po koordinatsionnoi khimii* (XXII Int. Chugaev Conf. on Coordination Chemistry), Kishinev, 2005, p. 366.
8. Van Norman, J.D. and Yatsko, E.T., *Bioinorg. Chem.,* 1978, vol. 17, no. 9, p. 349.
9. Yang Lanying, Zhang Yi, Cen Qingqi, and Ma Jin Shi, *Monatsh. Chem.,* 2004, vol. 135, no. 2, p. 223.
10. Falk, H., *Monatsh. Chem.,* 1988, vol. 119, no. 10, p. 1155.
11. Dolphin, D., Harris, R.L.N., and Happatz, J.L., *J. Chem. Soc., C,* 1966, vol. 30, no. 1, p. 30.
12. Badger, G.M., Harris, R.L.N., and Jones, R.A., *Austral. J. Chem.,* 1964, vol. 17, no. 1, p. 103.
13. Rumyantsev, E.V., Zakharova, S.P., Guseva, G.B., Antina, E.V., Berezin, M.B., and Semeikin, A.S., *Zh. Fiz. Khim.,* 2004, vol. 78, no. 12, p. 2167.
14. Zakharova, S.P., Rumyantsev, E.V., Antina, E.V., and Semeikin, A.S., *Koord. Khim.,* 2005, vol. 1, no. 1, p. 1.
15. Berezin, B.D. and Enikolopyan, N.S., *Metalporfiriny* (Metalporphyrins), Moscow: Nauka, 1988.
16. Semeikin, A.S. and Berezin, B.D., *Uspekhi khimii porfirinov* (Progress in the Chemistry of Porphyrins), Golubchikov, O.A., Ed., St. Petersburg: NIIKhimii St. Petersburg Gos. Univ., 2004, vol. 4, p. 7.
17. Guseva, G.B., *Cand. Sci. (Chem.) Dissertation,* Ivanovo, 2002.
18. Guseva, G.B., Antina, E.V., Berezin, M.B., and V'yugin, A.I., *Koord. Khim.,* 2004, vol. 30, no. 5, p. 396.
19. *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1985.
20. Rumyantsev, E.V., Antina E.V., and Gusev G.B., Available from VINITI, 2003, Moscow, no. 1463-B2003.
21. Rumyantsev, E.V., Sheinin, V.B., and Antina, E.V., Available from VINITI, 2003, Moscow, no. 1302-B2003.
22. Rumyantsev, E.V., Guseva, G.B., and Antina, E.V., *Zh. Fiz. Khim.,* 2005, vol. 79, no. 2, p. 219.
23. Rumyantsev, E.V. and Antina E.V., Abstracts of Papers, *XXII Mezhdunarodnaya Chugaevskaya konferentsiya po koordinatsionnoi khimii* (XXII Int. Chugaev Conf. on Coordination Chemistry), Kishinev, 2005, p. 479.
24. Golubchikov, O.A. and Berezin, B.D., *Zh. Fiz. Khim.,* 1986, vol. 60, no. 9, p. 2113.
25. Golubchikov, O.A., *Doctorate (Chem.) Dissertation,* Ivanovo, 1985.
26. Golubchikov, O.A., Berezin, B.D., Ageeva, T.A., Lipatova, I.M., and Kadykova, E.L., *Zh. Fiz. Khim.,* 1989, vol. 63, no. 1, p. 26.
27. Sidahmed, I.M. and Wells, C.F., *J. Chem. Soc., Faraday Trans.,* 1988, vol. 84, no. 2, p. 1153.
28. Mironov, I.V., *Vliyanie sredy i kompleksoobrazovanie v rastvorakh elektrolitov* (Influence of Medium and Complex Formation in Solutions of Electrolytes),

Novosibirsk: Inst. Neorg. Khim. Sibirsk. Otd. Ross. Akad. Nauk, 2003.

29. Durov, V.A. and Ageev, E.P., *Termodinamicheskaya teoriya rastvorov neelektrolitov: Uchebnoe posobie* (Thermodynamic Theory of Solutions of Non-Electrolytes: Handbook), Moscow: Mosk. Gos. Univ., 1987.
30. Darensbourg, D.J., Longridge, E.M., Atnip, E.V., and Reibenspies, J.H., *Inorg. Chem.*, 1992, vol. 31, no. 4, p. 3951.
31. Allmann, R., *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, 1973, vol. 138, no. 2, p. 366.
32. *Khimiya koordinatsionnykh soedinenii: Uchebnoe posobie* (Chemistry of Coordination Compounds: Handbook), Kostromina, N.A., Ed., Moscow: Vysshaya Shkola, 1990.
33. *Kompleksony i kompleksonaty metallov* (Complexones and Complexonates of Metals), Dyatlova, N.M., Temkina, V.Ya., and Popova, K.I., Eds., Moscow: Khimiya, 1988.
34. Sharma, V.S., Mathur, H.B., and Kulkarni, P.S., *Indian J. Chem.*, 1964, vol. 2, no. 7, p. 257.
35. Guseva, G.B., Antina, E.V., Berezin, M.B., Semeikin, A.S., and V'yugin, A.I., *Zh. Obshch. Khim.*, 2002, vol. 72, no. 1, p. 135.
36. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
37. Weissberger, A. and Proskauer, E.S., *Organic Solvents. Physical Properties and Methods of Purification*, Riddig, J.A. and Toops, E.E., Eds., New York: Interscience, 1955.
38. Voskresenskii, P.I., *Tekhika laboratornykh rabon* (Technics of Laboratory Works), Leningrad: Khimiya, 1970.
39. Yur'ev, Yu.K., *Prakticheskie raboty po organicheskoi khimii* (Practical Works on Organic Chemistry), Moscow: Mosk. Gos. Univ., 1961.
40. Beck, M. T. and Nagypal, I., *Chemistry of Complex Equilibria*, Budapest: Akad. Kiado, 1989.