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Coordination Reactions of 3,3'-Bis(dipyrrolylmethene) with Co(II), Cu(II), and Zn(II) Acetylacetonates, Valinates, and Dipyrrolylmethenates

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Abstract—Using spectrophotometry we found that ligand exchange in the systems of H_2L–$[MX_2]$–DMF, where M denotes Co^{2+}, Cu^{2+}, and Zn^{2+}; X means $Acac^-$, Val^-, dpm^-; $Hdpm^-$ is hexamethyldipyrrolylmethene, H_2L is bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)methane, proceeds through successive stages of formation of hetero- and homoleptic binuclear complexes. Conventional sensitivity of the spectrophotometric determination of Co^{2+}, Cu^{2+}, and Zn^{2+} reaches 10^{-9} M.

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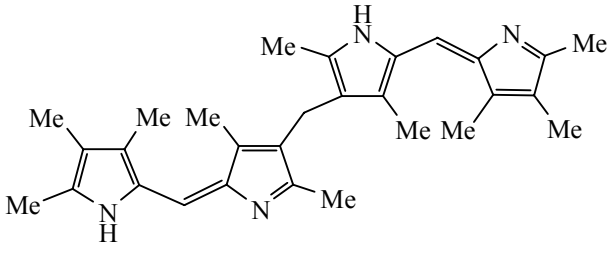
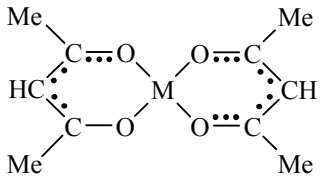
Increasing requirments to chemical analysis, environmental monitoring, and medical diagnostics make urgent the problem of creating a new generation of chromogenic chemosensors suitable for a fast and affordable determination of the *d*-metal ions in ultramicro amounts. Modern chemosensors based on the chromophore organic molecules [1] often have low selectivity and sensitivity, low photostability, and a number of other shortcomings that restrict their practical application. A successful outcome was reached in the modern research in this direction that have introduced 3,3'-bis(dipyrrolylmethenes), open-chain tetrapyrrole tetradentate N-helikands (H_2L), constructed of two chromophoric dipyrrolylmethene domains connected by a 3,3'-spacer [2–4]. Bis (dipyrrolylmethenes) do not interact with ions of alkali and alkaline earth metals, but are effectively coordinated by the doubly charged cations of a small group of *d*-metals due to covalent bonds [5]. Earlier studies [5] have shown that the products of coordination reactions of H_2L by Co(II), Cu(II), and Zn(II) acetates are stable binuclear double-stranded helicates $[M_2L_2]$ with intense chromophoric properties: the value of the logarithm of the extinction coefficient (log ε) of the strong bands in the electron absorption spectra (EAS) of the helicates is from 4.85 to 5.48. A significant (70–90 nm) difference in the positions of the maxima of the characteristic bands in slightly overlapping EAS ligands H_2L and helicates $[M_2L_2]$ as well as intense fluorescence of the complexes $[Zn_2L_2]$ in solution [6] provide the necessary conditions for the development of affordable and fast spectrophotometric determination methods of the *d*-metals in the respective helicates in ultramicro amount.

The purpose of this study was to investigate the chelating ability dekamethyl-3,3'-bis(dipyrrolyl-methene) relative to the Co(II), Cu(II) and Zn(II) intra-complex salts more stable than acetates: widely used in industry acetylacetonates $[M(Acac)_2]$, the biologically relevant valinates $[M(Val)_2]$, as well as structurally related dipyrrolylmethenates $[M(dpm)_2]$.

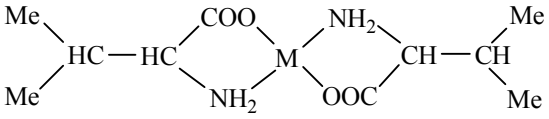
The choice of DMF as a medium for studying the interaction of simple and chelate salts with dipyrrolylmethenes and 3,3'-bis(dipyrrolylmethenes) has been substantiated earlier [4, 5] by the following reasons: the optimal combination of the polarity of the



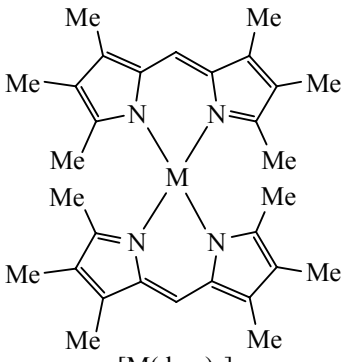
H_2L



[M(acac)$_2$]



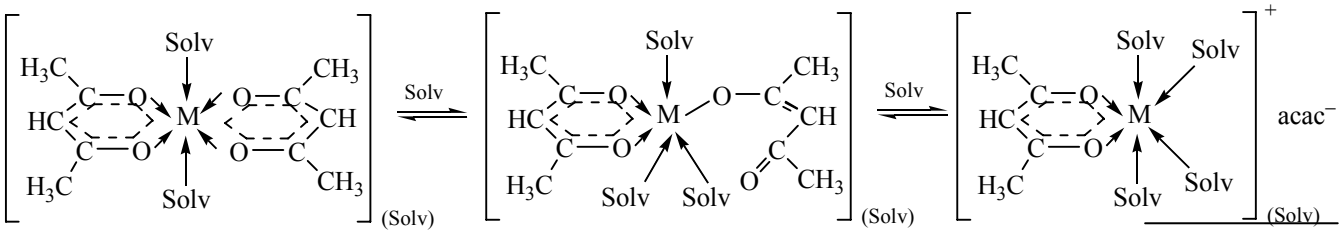
[M(Val)$_2$]



[M(dpm)$_2$]

M = Co^{2+}, Cu^{2+}, Zn^{2+}.

solvent dielectric constant, which ensures a satisfactory solubility in it of both electrolytes and nonelectrolytes; the availability of information on the state of ligand complexes of oligopyrroles [6–8] and salts of a number of *d*-metals [9–11] in this solvent. Dipyrrolylmethene and bis(dipyrrolylmethene) helicates are formed by covalent bonds and are a very stable intramolecular complexes, which do not suffer noticeable electrolytic dissociation in aprotic media [6–8, 12, 13]. The dissolution of the acetates and the chelate salts [MX_2] (where M = Co(II), Cu(II), Zn(II); X = $Acac^-$, Val^-) in DMF and binary solvents based on it [9–11] is accompanied by additional coordination of solvent molecules with the metal to form solvatocomplexes of the composition [$M(X)_2(Solv)_4$] in the case of acetate or [$M(X)_2(Solv)_2$] with acetylacetonates and valinates with octahedral configuration of the coordination site. Additional coordination of molecular ligands causes the displacement of one of the anions in the outer coordination sphere to form ionic solvatocomplexes [$M(X)(Solv)_5$](X) or [$M(X)(Solv)_4$](X):



By an example of the ligand exchange of porphyrin ligands and acetataes or acetylacetonates of *d*-metals it was shown [9, 10] that in the electron-donor solvent the process of ligand replacement in the coordination sphere of a *d*-metal proceeded more effectively, because the complex cation $[M(X)(Solv)_4]^+$ formed at the additional coordination was more reactive species compared to the molecular form of the salt due to an increase in the space open for the successful attack on the complexing agent by the chelating agent.

The results of spectrophotometric monitoring of reactions in the systems of H_2L–[MX_2]–DMF (M = Co(II), Cu(II), Zn(II); X = $Acac^-$, Val^-) showed the similarity in the transformations of the EAS of solutions in comparison with previously published data for the reactions of H_2L with acetates of the same metals [5]. The ligand exchange processes are accompanied by a transformation of the spectrum of H_2L (Fig. 1) in the spectra of its coordination compounds with significant red (65–79 nm) shift and hyperchromic effect of the most intense long-wave band of the spectrum, which is caused by the auxochromic effect of the metal ion on the aromatic π-system of dipyrrolylmethene domains H_2L. The curves of molar ratios (Fig. 2) include two inflection points, at the ratio of the concentrations of reactants $c(MX_2)$: $c(H_2L)$ = 1: 1 and 2: 1.

In view of these results and existing data [2, 6–8] on the EAS and XRD of the coordination compounds of Co(II), Cu(II), and Zn(II) with 3,3'-bis(dipyrrolylmethenes), we can conclude that the final product of the ligand exchange reactions in the studied systems

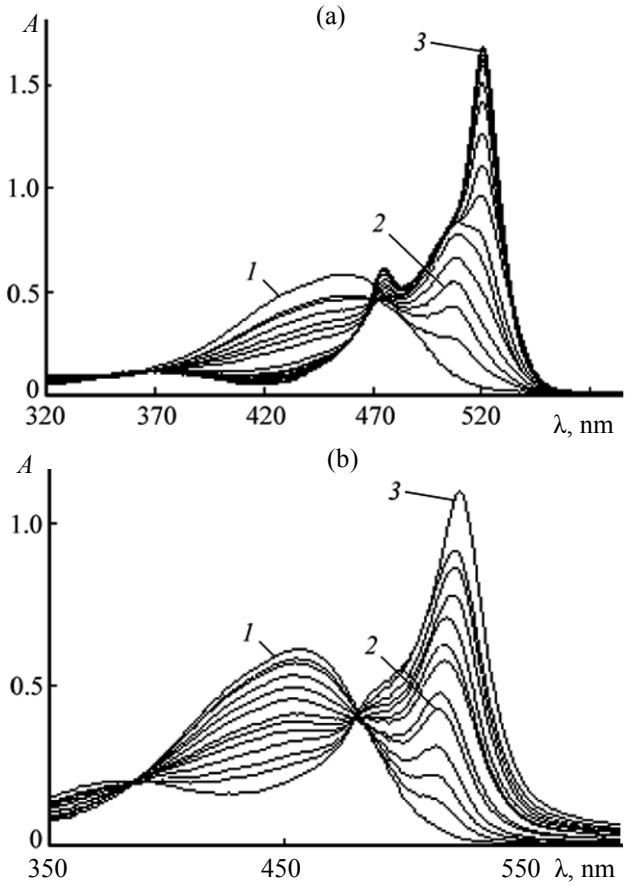


Fig. 1. EAS for the systems: (a) H_2L–$Zn(acac)_2$–DMF, $c^0(H_2L) = 1.2\times10^{-5}$ M; (*1*) H_2L, (*2*) $[Zn_2L(acac)_2]$, (*3*) $[Zn_2L_2]$; (b) H_2L–$Co(Val)_2$–DMF, $c^0(H_2L) = 9.1\times10^{-6}$ M; (*1*) H_2L, (*2*) $[Co_2L(Val)_2]$, (*3*) $[Co_2L_2]$.

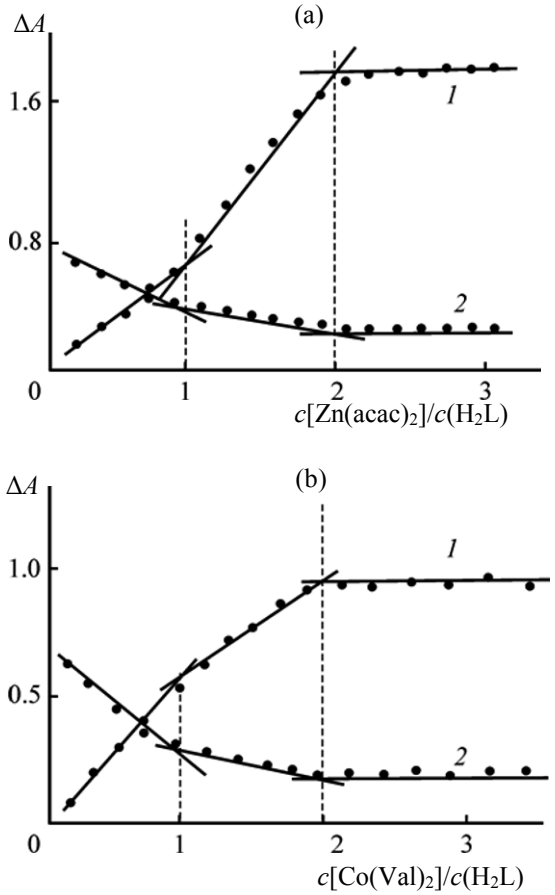


Fig. 2. Curves of molar ratios for the systems: (a) H_2L–$Zn(acac)_2$–DMF, $c^0(H_2L) = 1.2\times10^{-5}$ M, $\lambda_{max} = 521$ nm (*1*), $\lambda_{max} = 456$ nm (*2*); (b) H_2L–$Co(Val)_2$–DMF, $c^0(H_2L) = 9.1\times10^{-6}$ M, $\lambda_{max} = 527$ nm (*1*), $\lambda_{max} = 456$ nm (*2*).

are homoleptic helicates of binuclear structure $[M_2L_2]$ with the architecture of the double helix, which are formed through the stage of formation of binuclear complexes of heteroleptic mono-helix complexes $[M_2LX_2]$:

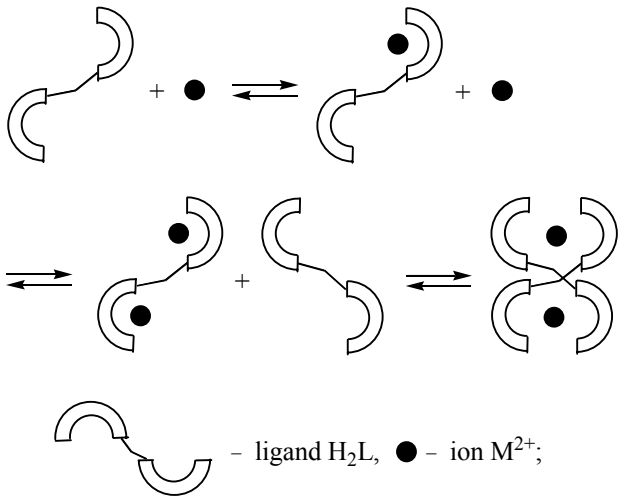
$$H_2L + 2[MX]^+ + 2X^- \rightleftarrows [M_2LX_2] + 2HX, \quad (1)$$

$$[M_2LX_2] + H_2L \rightleftarrows [M_2L_2] + 2HX. \quad (2)$$

In the reaction mixtures with $c(MX_2):c(H_2L) \geq 2$ only the helicates $[M_2L_2]$ are found. Equation (3) of the overall process of ligand exchange in the systems of H_2L–$[MH_2]$–DMF and an illustrative diagram of the individual stages are as follows:

$$2H_2L + 2[MX]^+ + 2X^- \rightleftarrows [M_2L_2] + 4HX. \quad (3)$$

Note that in contrast to the double-stranded homoleptic helicates $[M_2L_2]$, the attempts to synthesize binuclear heteroleptic complexes $[M_2LX_2]$ have not yet been successful, and only the data of spectrophotometric studies of the processes of coordination of



acido ligands are not shown for clarity.

3,3'-bis(dipyrrolylmethenes) by the salts of *d*-metals [5] indicate their formation in solution in the first stage of formation of double-stranded helicates $[M_2L_2]$.

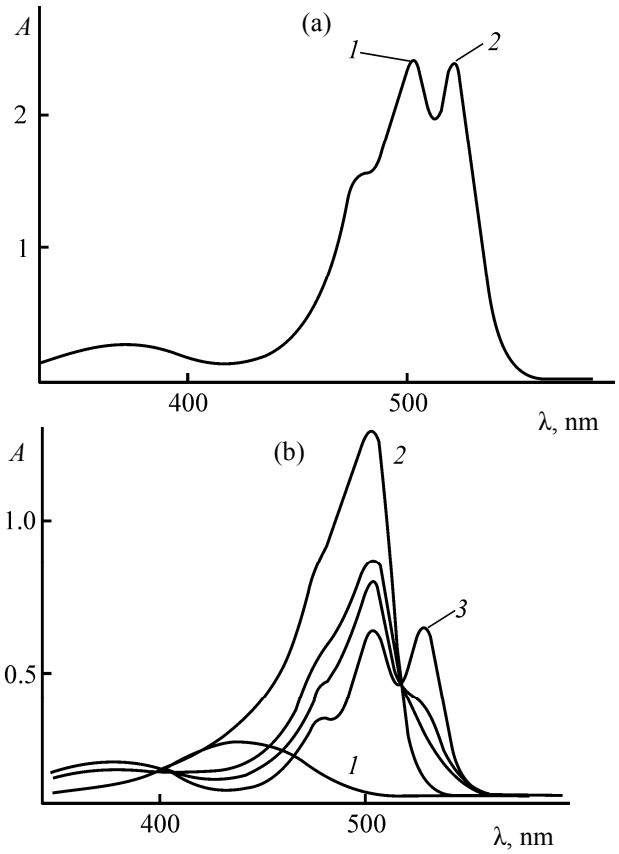


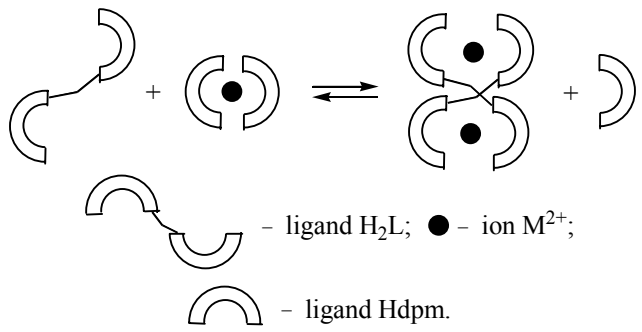
Fig. 3. EAS of solution in DMF: (a) with equimolar mixture ($c \sim 10^{-5}$ M) of H_2L and Hdpm ligands after the addition of a three-fold molar excess of $Zn(AcO)_2$, (*1*) $[Zn(dpm)_2]$, (*2*) $[Zn_2L_2]$; (b) H_2L ($c \sim 10^{-6}$ M) (*1*) and immediately after addition of three-fold molar excess $[Zn(dpm)_2]$ (*2*), in a week (*3*). The other spectra correspond to the intermediate time intervals. The wavelength maxima of the intensity bands in the spectra H_2L, $[Zn(dpm)_2]$ and $[Zn_2L_2]$ are 456, 501 and 521 nm, respectively.

As shown previously [2, 5], 3,3'-bis(dipyrrolylmethenes) have better structural pre-organization for the formation of binuclear homoleptic helicates com-pared with 2,2'-analogs, the biladienes-*a,c* [14]. The invariance of the conformational state of the latter results in a high probability of formation, along with the binuclear helicates, the porphyine-like mono-nuclear complexes [ML]. Nevertheless, the features of the processes of formation from the bimetallic biladiene helicands of the double helices are similar to those in the case of 3,3'-bis(dipyrrolylmethenes) [14]. Moreover, if the mononuclear [ML] and binuclear $[M_2L_2]$ biladiene complexes were obtained and identified [15, 16], the heteroleptic complexes $[M_2LX_2]$ were not yet identified.

On the other hand, both homoleptic and heteroleptic complexes of some *d*-metals with the dipyrrolylmethene ligands (Hdpm) so far obtained were characterized by XRD, EAS, and other methos [17, 18]. As shown in [19], the processes of ligand exchange involving Hdpm also take place in two successive stages: in the first the heteroleptic mononuclear helicates [M(dpm)X] ($X = AcO^-$, $Acac^-$) formed, in the second, the homoleptic mononuclear helicates $[M(dpm)_2]$.

It is known [19, p. 669] that for the formation of polymetallic spirals from the helicands of different lengths the effects of self-recognition are very important. Dipyrrolylmethenes and bis(dipyrrolylmethenes) are structurally related ligands forming coordination compounds with the same type of structure of the coordination site, a distorted tetrahedron. It is expectable that in the reactions of ligand exchange between the $[M(dpm)_2]$ and H_2L complexes, or, conversely, $[M_2L_2]$ helicates and Hdpm, there is a high probability of the formation of heteroleptic complexes of $[M_2L(dpm)_2]$ type. Our studies showed that the reaction of cobalt(II), copper(II), or zinc(II) acetates with an equimolar mixture of ligands H_2L and Hdpm in DMF leads only to the formation of respective homoleptic helicates $[M_2L_2]$ and $[M(dpm)_2]$ (Fig. 3a). The ratios of the equilibrium molar concentrations of the complexes formed in the mixtures are $[Zn_2L_2]/[Zn(dpm)_2] \sim 1.4$, $[Co_2L_2]/[Co(dpm)_2] \sim 1.2$ and $[Cu_2L_2]/[Cu(dpm)_2] \sim 0.4$. Spectrophotometric monitoring of the titration process of the ligand H_2L in DMF with a solution of $[M(dpm)_2]$ in the same solvent also showed that during the week in the system a stable equilibrium is established between the homoleptic complexes $[M_2L_2]$ and $[M(dpm)_2]$. Equation (4) and the reaction scheme of the ligand exchange in the system of H_2L–$[M(dpm)_2]$–DMF are as follows:

$$2H_2L + 2[M(dpm)_2] \rightleftarrows [M_2L_2] + 4\ Hdpm. \qquad (4)$$



Varying the molar ratio of reagents $c[M(dpm)_2]/c(H_2L)$ in the range from 1 to 3 cannot significantly shift the equilibrium towards $[M_2L_2]$, as has been

observed in reactions with acetates and other studied chelate salts (Fig. 3b). Apparently, this is due to the fact that chelating properties of dipyrrolylmethene and its bis-domain derivative are comparable and their respective coordination compounds $[M(dpm)_2]$ and $[M_2L_2]$ are similar in the stability. These results clearly demonstrate the manifestation of the principle of positive cooperativity, when, once begun, the subsequent assembly of 3,3'-bis(dipyrrolylmethene) helicates is facilitated by nonlinear process. Earlier experimental confirmation of the positive cooperativity was obtained by the example of Cu(I) complexes with the CO_2Et hexapyridine derivative [19].

In the comparative analysis of the thermodynamic constants (K^0) of the process of ligand exchange (see the table) with the studied chelate salts it is necessary to consider the effect of differences in the stability of the involved in reaction complex cations $[MAcO]^+$, $[MAcac]^+$, $[MVal]^+$ and molecules $[M(dpm)_2]$. Mononuclear complexes of 2,2'-dipyrrolylmethenes $[M(dpm)_2]$ and binuclear 3,3'-bis(dipyrrolylmethene) helicates, as noted above, are the most stable [5, 20]. Therefore, the lowest K^0 values are observed for the reactions of H_2L with dipyrrolylmethenes $[M(dpm)_2]$. The pattern of stability of the acetylacetonates is consistent with the well-known Irving–Williams series. So, according to [21], for $[Cu(Acac)]^+$ in water the logarithm of the stability constant ($\log \beta_2 = 15.05\pm0.10$) is maximal compared to the $[Co(Acac)]^+$ and $[Zn(Acac)]^+$ cations for which the corresponding values of $\log \beta_2$ are 9.5 ± 0.10 and 8.8 ± 0.10. On the other hand, according to [22], the stability of complex acetate cations $[MAcO]^+$ in similar environmental conditions differ slightly for different complexing agents.

For all the studied reactions the values of K^0 (see the table) increase slightly (within the same order) at replacing acetate by the metal acetylacetonate or valinate. A similar pattern of influence of the nature of anion was observed previously [23] for the reactions of Hdpm with $M(AcO)_2$, $[M(Acac)_2]$ and $[M(Val)_2]$.

A more significant effect on the equilibrium in the reactions (3) with the *d*-metal acetates, acetylacetonates, and valinates has the nature of the complexing agent. The value of K^0 increases by ~5 orders of magnitude in the series of cations: $Cu^{2+} < Co^{2+} < Zn^{2+}$.

On the other hand, the reverse pattern was found earlier for the reactions of 2,2'-dipyrrolylmethenates $[M(dpm)_2]$ from Hdpm and $M(AcO)_2$ or $[MX_2]$ (X = $Acac^-$, Val^-) in DMF [24]: the $\log K^0$ values increase

The values of the logarithms of the thermodynamic constants ($\log K^0$) for the reactions (3) and (4) of cobalt(II), copper(II), and zinc(II) dipyrrolylmethenates, acetates, acetylacetonates, and valinates with decamethyl-3,3'-bis(dipyrrolylmethene) in DMF at 298.15 K

$[MX_2]$	Zn^{2+}	Co^{2+}	Cu^{2+}
$[M(AcO)_2]$	13.73 [5]	12.58 [5]	8.56 [5]
$[M(acac)_2]$	13.34	12.35	8.07
$[M(Val)_2]$	–	12.07	7.81
$[M(dpm)_2]$	2.35	2.29	1.84

substantially in the series of complexing agents: $Co^{2+} < Zn^{2+} < Cu^{2+}$, that is, the most stable are the complexes of copper(II).

Thus, the main factor determining the difference in the observed regularities is the level of pre-organization of ligand for the formation of coordination compound with specific structure with the considered metal cations. Unlike dipyrrolylmethenes, in the molecules of bis(dipyrrolylmethenes) the central spacer limits the ability of the dpm-domains to the effective formation on the two Cu^{2+} ions of coordination sites with distorted tetrahedron geometry (Jahn–Teller effect). Therefore the biladienes-*a,c* in the *ridge-tile* conformation do not form binuclear complexes $[Cu_2L_2]$, and in the *helical* conformation form only mononuclear complexes [CuL] [14]. The transfer of the spacer from 2,2'- to 3,3'-positions greatly improves the pre-organization of the 3,3'-bis(dipyrrolylmethene) ligands to the formation of the helicates $[Cu_2L_2]$, however, yudging from the obtained results, the stability of these complexes is lower than that of the corresponding coordination compounds of Zn(II) and Co(II).

The experimental confirmation obtained in this paper of the high chelating ability of the 3,3'-bis(dipyrrolylmethene) ligands in reactions with cobalt(II), zinc(II), and copper(II) acetates and chelate salts, together with significant differences in the quantitative characteristics of EAS of the chromophores

$[M_2L_2]$, $[M(dpm)_2]$, and H_2L in the systems of H_2L–$[MX_2]$–DMF provide a good basis for the development of analytical methods of detecting *d*-metal ions in solution at ultramicro amounts. Conditional sensitivity of determination of Co^{2+}, Cu^{2+}, and Zn^{2+} calculated theoretically from the value of the molar absorption coefficient of $[M_2L_2]$ complexes on

the long-wavelength band at the optical density of the solution equal to 0.001, and cell thickness 1 cm reaches up to ~10^{-9} M.

EXPERIMENTAL

Bis(2,4,7,8,9-pentamethyldipyrrolylmethene-3-yl)-methane hydrobromide (H_2L·2HBr) was synthesized, isolated, and identified by IR, ESP, ^{1}H NMR spectra and elemental analysis according to [4]. The cobalt(II), copper(II), and zinc(II) acetylacetonates and valinates were synthesized, purified, and identified in accordance with the procedures [9, 10, 25]. The complexes of cobalt(II), copper(II), and zinc(II) with 2,2'-hexa-methyldipyrrolylmethene were synthesized, purified, and identified in accordance with [12, 13].

Dimethylformamide of the chemically pure grade used as a solvent was purified by standard methods [26], the H_2O content (by Fischer) was less than 0.02%.

EAS of the reaction mixtures H_2L–$[MX_2]$–DMF were recorded on an SF-103 (Aquilon) spectrophotometer in the wavelength range 300–650 nm using quartz cells with a thickness of absorbing layer 10 mm.

To determine the equilibrium concentrations of reactants and the thermodynamic constants of complexation reactions we used the method of molar ratios [27, 28]. Investigations were carried out at a constant concentration of the ligand H_2L (8×10^{-6} to 1.5×10^{-5} M) and varied from 0 to 7 molar excess of metal salt.

The values of the concentration constant (K^c) of the reactions of helicates $[M_2L_2]$ with acetylacetonates and valinates were calculated by the equation:

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

The dependence of K^c on the concentration of the metal salt is described by the equation $\log K^c = \log K^0 - ac^{1/2}$ based on the calculation of the mean ion activity coefficient of electrolyte in the Debye–Huckel first approximation [29, 30]. Typical values of the constants (K^0) in the equilibria of complexation in these systems were obtained by extrapolation to infinite dilution of the linear dependences in the coordinates $\log K^c - f(c^{1/2})$ at 2–5-fold molar excess of metal salt. At five times repetition of each spectrophotometric run the error in the determination of K^0 from the spectrophotometric data did not exceed 5%.

The values of K^c in the reaction mixtures H_2L–$[M(dpm)_2]$–DMF, where M = Co(II), Cu(II), or Zn(II), were calculated from the relation:

$$K^c = \frac{[M_2L_2][Hdpm]^4}{[M(dpm)_2]^2[H_2L]^2} = \frac{256x^5}{\{c^0[M(dpm)_2] - 2x\}^2\{c^0(H_2L) - 2x\}^2}.$$

Typical values of the constants of equilibria K^0 in mixtures of H_2L–$[M(dpm)_2]$–DMF were obtained as the average of the series (at least of 10) of measurements of the concentration constants obtained at different initial concentrations of reagents. To calculate the equilibrium concentrations of reactants and reaction products were used the previously published quantitative characteristics of the EAS of dipyrrolylmethenates [12, 13], bis(dipyrrolylmethenates) [6–8], the ligands H_2L [4] and Hdpm [31] and well-known mathematical technique was applied [32] .

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REFERENCES

1. Bren' V.A., *Usp. Khim*., 2001, vol. 70, no. 12, p. 1152.
2. Wood, E. and Thompson, A., *Chem. Rev*., 2007, vol. 107, no. 5, p. 1831.
3. Antina, E.V., Berezin, M.B., Dudina, N.A., Guseva, G.B., Antina, L.A., and V'yugin, A.I., *Zh. Obshch. Khim*., 2010, vol. 80, no. 6, p. 1048.
4. Guseva, G.B., Dudina, N.A., Antina, E.V., V'yugin, A.I., and Semeikin, A.S., *Zh. Obshch. Khim*., 2008, vol. 78, no. 6, p. 987.
5. Dudina, N.A., Antina, E.V., and Guseva, G.B., *Koord. Khim*., 2011, vol. 37, no. 5, p. 331.
6. Berezin, M.B., Antina, E.V., Dudina, N.A., Bushmarinov, I.S., Antipin, M.Yu., Antina, L.A., and Guseva, G.B., *Mendeleev Commun*., 2011, vol. 21, no. 3, p. 168.
7. Antina, L.A., Dudina, N.A., Guseva, G.B., Berezin, M.B., and V'yugin, A.I., *Zh. Obshch. Khim*., 2011, vol. 81, no. 11, p. 1898.
8. Antina, L.A., Dudina, N.A., Guseva, G.B., and Berezin, M.B., *Zh. Obshch. Khim*., 2011, vol. 81, no. 1, p. 164.
9. Berezin, B.D., Trofimenko, T.N., and Berezin, M.B., *Zh. Fiz. Khim*., 1995, vol. 69, no. 7, p. 1202.
10. Berezin B.D., Mamardashvili G.M., *Koord. Khim*., 2002, vol. 28, no. 11, p. 822.

11. Peshkov,a V.M. and Mel'chakova, N.V., *β-Diketonaty* (β-Diketonates), Moscow: Nauka, 1986.
12. Chernova, O.M., Antina, E.V., and Berezin, M.B., *Zh. Fiz. Khim*., 2003, vol. 77, no. 6, p. 1002.
13. Falk, Y., *The Chemistry of Linear Oligopyrroles and Bile Pigments*, New York: Springer, 1989.
14. Antina, E.V. and Rumyantsev, E.V., *Khimiya bilirubina i ego analogov* (Chemistry of Bilirubin and Its Analogues), Moscow: KRASAND, 2009.
15. Khoury, R.G., Jaquinod, L., and Smith, K.M., *Tetrahedron*., 1998, vol. 54, p. 2339.
16. Zhang, Y. and Thompson, A*., J. Am. Chem. Soc*., 1998, vol. 120, no. 51, p. 13537.
17. March, F.C., Couch, D.A., Emerson, K., Fergusson, J.E., and Robinson, W.T., *J. Chem. Soc. (A).,* 1971, no. 3, p. 440.
18. Guseva, G.B., Antina, E.V., Berezin, M.B., and V'yugin, A.I., *Zh. Obshch. Khim*., 2004, vol. 74, no. 8, p. 1383.
19. Stid, D.V. and Etwood, D.L., *Supramolekulyarnaya khimiya* (Supramolecilar Chemistry), Moscow: Akademkniga, 2007, vol. 2.
20. Guseva, G.B., Antina, E.V., V'yugin, A.I., and Loginova, A.E., *Koord. Khim*., 2008, vol. 34, no. 8, p. 606.
21. Stary, J. and Liljenzin, J.O., *Pure and Appl. Chem*., 1982, vol. 54, no. 12, p. 2557.
22. Golubchikov, O.A*., Makrogeterocikly*., 2009, vol. 2, no. 2, p. 92.
23. Guseva, G.B. and Antina, E.V., *Koord. Khim*., 2006, vol. 32, no. 7, p. 541.
24. Guseva, G.B., Antina, E.V., V'yugin, A.I., Mamardashvili, G.M., and Petrov, V.V., *Koord. Khim*., 2006, vol. 32, no. 2, p. 123.
25. Craddon, D.P. and Munday, L., *J. Inorg. Nucl. Chem*., 1961, vol. 23, nos. 3–4, p. 231.
26. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.
27. Bek, M. and Nad'pal, I., *Issledovanie kompleksoobrazovaniya noveishimi metodami* (The Study of Complex by Modern Methods), Moscow: Mir, 1989.
28. Bulatov, M.I. and Kalinkin, I.P., *Prakticheskoe rukovodstvo po fotokolorimetricheskim i spektrofotometricheskim metodam analiza* (A Practical Guide to Photocolorimetric and Spectrophotometric Methods of Analysis), Leningrad: Khimiya, 1968.
29. Mironov, I.V., *Vliyanie sredy i kompleksoobrazovanie v rastvorakh elektrolitov* (Influence of Environment and Complexation in Electrolytic Solutions), Belevantsev, V.I., Ed., Novosibirsk: INH SO RAN, 2003.
30. Durov, V.A. and Ageeva, E.P., *Termodinamicheskaya teoriya rastvorov neelektrolitov* (Thermodynamic Theory of Solutions of Nonelectrolytes), Moscow: Izd. Mosk. Univ., 1987.
31. Berezin, M.B., Semeikin, A.S., Antina, E.V., Pashanova, N.A., Lebedeva, N.Sh., and Bukushina, G.B., *Zh. Obshch. Khim*., 1999, vol. 69, no. 12. S., 2040.
32. Otto, M., *Sovremennye metody analiticheskoi khimii* (Modern Methods of Analytical Chemistry), Moscow: Tekhnosfera, 2008, p. 427.