ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 12, pp. 2306–2308. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © N.A. Dudina, E.V. Antina, G.B. Guseva, A.I. V'yugin, 2013, published in Zhurnal Obshchei Khimii, 2013, Vol. 83, No. 12, pp. 2021–2024.

The Influence of *ms*-Substitution on the Properties of 3,3'-Bis(dipyrrolylmethenes) and Their Coordination Compounds

N. A. Dudina, E. V. Antina, G. B. Guseva, and A. I. V'yugin

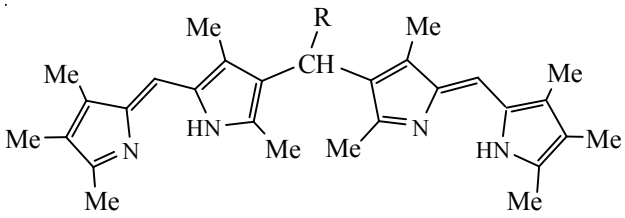
Krestov Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: nad@isc-ras.ru

Received January 14, 2013

Abstract—We have compared the coordination properties of decamethyl-substituted 3,3'-bis-(dipyrrolylmethenes) (H_2L) with different ms-spacers separating the dipyrrolylmethene domains: methylene $–CH_2–$, methoxyphenylmethylene $–CH(p\text{-}C_6H_4OMe)–$, and trifluoromethylmethylene $–CH(CF_3)–$. The stable binuclear homoligand complexes $[M_2L_2]$ are formed in reactions of the ligands with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) acetates. In the cases of all H_2L ligands the thermodynamic constants of the complex formation reactions increase in the following series: Cu(II) < Cd(II) < Hg(II) < Ni(II) < Co(II) < Zn(II). The change in $–CH_2–$ ms-spacer to $–CH(p\text{-}C_6H_4OMe)–$ or $–CH(CF_3)–$ results in a decrease in the constant of H_2L complex formation by 1–4 orders of magnitude, the cation being the same. The influence of ms-substitution on the stability and luminescence properties of $[M_2L_2]$ has been discussed.

DOI: 10.1134/S107036321312013X

Our studies [1–6] have shown that 3,3'-bis(dipyrrolylmethenes) H_2L with methylene *ms*-spacer form stable binuclear double helix helicates $[M_2L_2]$ possessing practically important spectral luminescent properties. It was found that at growing number more of methyl substituents in the pyrrole fragments, some utilitarian properties of the helicates can be improved; this is reflected in the red shift of the strong electron absorption and fluorescence bands, the enhancement of the fluorescence intensity, and the increase of the helicates stability [1, 3, 6]. In order to modify the chemical properties or thermal stability of the linear tetrapyrroles various substituents can be introduced in the *ms*-spacer of H_2L; simultaneously, the coordination properties of 3,3'-bis(dipyrrolylmethenes) are modified. In order to investigate these substitution effects we compared the coordination properties of decamethyl-substituted 3,3'-bis(dipyrrolylmethene) with methylene spacer **I** [3] and analogous compounds with *p*-methoxyphenyl and trifluoromethyl groups in the central spacer (**II** and **III**, respectively).



R = H (**I**), PhOMe (**II**), CF_3 (**III**).

The complex formation of ligands **I–III** with Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Hg(II) acetates in the electron-donor DMF medium was accompanied by typical spectral changes (see Fig. 1): red shift of the bands and the hyperchromic effect [3]. From comparison with the published absorption spectra and X-ray diffraction data of the *d*-metal complexes with 3,3'-bis(dipyrrolylmethenes) [3, 7–10] it followed that the spectra of the studied H_2L mixtures with more than two-fold excess of the Co(II), Ni(II), Cu(II), Zn(II), Cd(II), or Hg(II) salt corresponded to those of the binuclear double helix homoleptic helicates $[M_2L_2]$. The two isosbestic points observed in the absorption spectra (Fig. 1a) and the two inflection points in the spectral profiles {at $c[M(AcO)_2] : c(H_2L)$ of 1 : 1 and 2 : 1, Fig. 1b} confirmed the previously suggested mechanism of $[M_2L_2]$ formation through the intermediate binuclear heteroleptic complex $[M_2L(AcO)_2]$. At $c[M(AcO)_2] : c(H_2L) < 1 : 1$, those intermediates

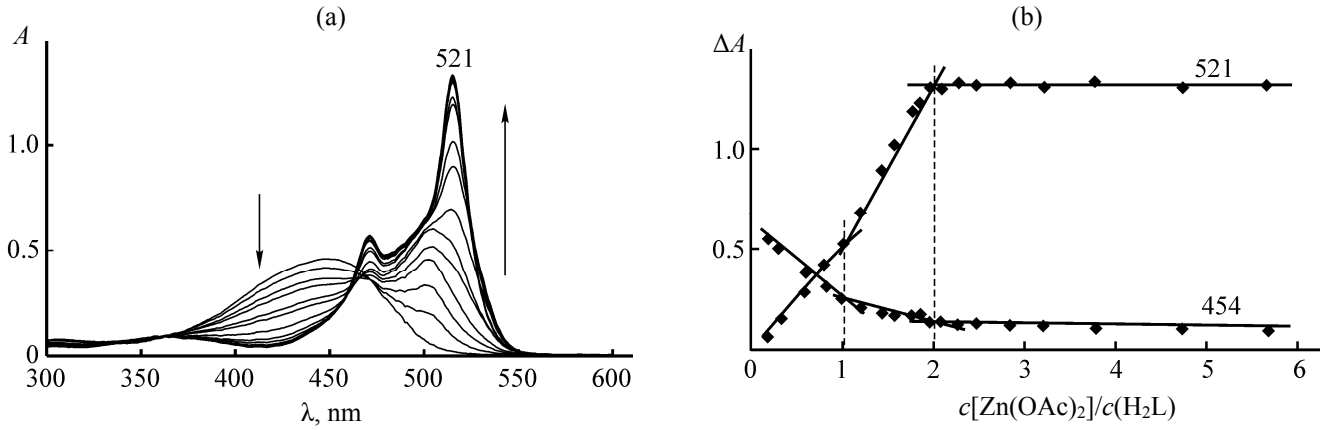


Fig. 1. The electron absorption spectra (a) and the slices at the representative wavelengths (b) of **II**–$Zn(AcO)_2$–DMF at various ratio of components [$c(H_2L) = 1.0\times10^{-5}$ mol/L].

were detected in the spectra (see Fig. 1). In the excess of metal acetate, the equilibrium was almost completely shifted towards homoleptic helicates $[M_2L_2]$.

The increase in the thermodynamic equilibrium constant of the complex formation K^0 in the series Cu(II) < Cd(II) < Hg(II) < Ni(II) < Co(II) < Zn(II), previously found in the cases of **I** and some other alkyl-substituted H_2L [3], was confirmed in the studied cases of *ms*-substituted analogs. In this cations series the K^0 values increased by about 5 orders of magnitude in the cases of **I–III** (see table).

On the other hand, the K^0 values of the complex formation between the certain cation and the helicands **II** and **III** were significantly lower than that in the case of **I**. The introduction of methoxyphenyl group at the 3,3'-spacer decreased K^0 by 1–2 orders of magnitude. The observed changes evidenced the decreased basicity of the ligand due to *–I* effect prevailing over the *+M* effect. The strong electron-acceptor properties of CF_3 group led to further decreased ligand basicity, therefore, K^0 was decreased by 2–4 orders of magnitude.

The auxochromic effect of the complex forming ion, characterized by the band shift $\Delta\lambda(M^{2+}) = \lambda^{[M_2L_2]} - \lambda^{[H_2L]}$, ranged from 62 to 89 nm and was increased in the ligands series **I** < **II** < **III** by up to 8 nm. The auxochromic effect induced by the cations followed the series of enhancing polarization of the chromophore π-system: $Cd^{2+} \le Hg^{2+} \le Zn^{2+} < Co^{2+} < Cu^{2+} < Ni^{2+}$.

As was previously demonstrated [11], the *ms*-spacer substitution, along with the slight auxochromic effect, strongly influenced the quantum yield of fluorescence (φ). In particular, in cyclohexane medium the highest quantum yield was observed in the case of $[Zn_2(\mathbf{I})_2]$ (φ 0.91), whereas the fluorescence of $[Zn_2(\mathbf{II})_2]$ and $[Zn_2(\mathbf{III})_2]$ was much weaker (φ = 0.59 and 0.43, respectively). A similar trend was found in the case of the cadmium(II) helicates. Thus, the probability of radiationless transitions increased in the series $[M_2(\mathbf{I})_2] < [M_2(\mathbf{II})_2] < [M_2(\mathbf{III})_2]$ likely due to two main reasons. Firstly, bulky substituents were present in the *ms*-spacers of **II** and **III**, their rotation being enhanced upon excitation. Secondly, the *–I* effect of those substituents led to the decrease in the coordination bond energy and thus to higher mobility of the excited molecules fragments.

Parameters of the reactions of helicates $[M_2L_2]$ formation in DMF at 298.15 K

H_2L	Parameter	Zn(II)	Co(II)	Ni(II)	Hg(II)	Cd(II)	Cu(II)
I[a]	λ_{max}	521	527	540	519	518	535
	Δλ	65	71	84	63	62	79
	log K^0	13.37	12.58	11.60	10.78	9.50	8.56
II	λ_{max}	521	526	537	520	518	536
	Δλ	67	72	83	66	64	82
	log K^0	12.13	11.00	10.29	9.69	8.38	7.80
III	λ_{max}	516	522	535	516	516	533
	Δλ	70	76	89	70	70	87
	log K^0	10.19	9.58	9.23	8.65	8.05	7.52

[a] Data from [3].

To conclude, the presence of bulky electron-donor substituents in the *ms*-spacer of the ligands **II** and **III** did not prevent the complex formation with the studied metal ions; however, the formed complexes were less stable, and their fluorescence intensity decreased.

EXPERIMENTAL

The preparation and spectral properties of bis-(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)methane (**I**), bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)-(4'-methoxyphenyl)methane (**II**), and bis(2,4,7,8,9-pentamethyldipyrrolylmethen-3-yl)trifluoromethyl-methane (**III**) in the form of hydrobromide were reported elsewhere [12–14].

The electron absorption and fluorescence spectra of the solutions of H_2L–$M(AcO)_2$ in DMF were recorded with SF-103 (Akvilon, Russia) spectrophotometer and SM 2203 (SOLAR, Belarus) spectrofluorimeter, respectively, at 300–650 nm. The measurements were performed in a quartz cell (l = 1 cm), at temperature control at 298.15 K using the Peltier element.

DMF (chemically pure grade) was purified by standard procedures [15]. The Fischer's titration showed the presence of less than 0.02 wt % of water in DMF. Zn(II), Cd(II), Cu(II), Co(II), and Ni(II) acetates (pure or chemically pure grade, Khimmed, Russia) were recrystallized from glacial acetic acid and dried; their composition was determined by TGA (MOM 1000D derivatograph, Hungary).

In order to determine the equilibrium concentrations of the components and the equilibrium constant of the complex formation K^0 between H_2L and the metal acetates, we studied the spectral properties of the solutions at the constant ligand concentration of 1×10^{-5} mol/L, the metal salt concentration being varied within $c[M(AcO)_2] : c(H_2L) =$ 0–8. To plot the absorption as a function of the components ratio, the ligand absorption was subtracted.

The standard thermodynamic equilibrium constant of the complex formation K^0 were determined as described in [3], by extrapolation of the concentration constant K^c to infinite dilution.

$$K^c = [M_2L_2][HAcO]^4/[MAcO^+]^2[AcO^-]^2[H_2L]^2.$$

All the measurements were repeated five times, the error of K^0 determination was below 5%.

ACKNOWLEDGMENTS

This work was financially supported by the Russian Foundation for Basic Research (project no. 12-03-97510-r_tsentr_a).

REFERENCES

1. Antina, E.V., Berezin, M.B., Dudina, N.A., Guseva, G.B., Antina, L.A., and V'yugin, A.I., *Russ. J. Gen. Chem.,* 2010, vol. 80, no. 6, p. 1214.
2. Antina, L.A., Dudina, N.A., Berezin, M.B., and Guseva, G.B., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 1, p. 162.
3. Dudina, N.A., Antina, E.V., and Guseva, G.B., *Russ. J. Coord. Chem*., 2011, vol. 37, no. 5, p. 333.
4. Antina, L.A., Dudina, N.A., Berezin, M.B., Guseva, G.B., and Antina, E.V., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 3, p. 591.
5. Antina, L.A., Dudina, N.A., Guseva, G.B., Berezin, M.B., and V'yugin, A.I., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 11, p. 2349.
6. Antina, L.A., Dudina, N.A., Guseva, G.B., Antina, E.V., Berezin, M.B., and V'yugin, A.I., *Russ. J. Inorg. Chem*., 2012, vol. 57, no. 2, p. 261.
7. Zang, Y., Thompson, A., Retting, S.J., and Dolphin, D., *J. Am. Chem. Soc*., 1998, vol. 120, no. 51, p. 13537.
8. Yang, L., Zhang, Y., Yang, G., Chen, Q., and Ma, J.S., *Dyes and Pigments*, 2004, vol. 62, p. 27.
9. Wood, T.E., Ross, A.C., Dalgleish, N.D., Power, E.D., Thompson, A., Chen, X., and Okamoto, Y., *J. Org. Chem*., 2005, vol. 70, no. 24, p. 9967.
10. 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.
11. Antina, L.A., Guseva, G.B., V'yugin, A.I., Antina, E.V., and Berezin, M.B., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 6, p. 1143.
12. Guseva, G.B., Dudina, N.A., Antina, E.V., V'yugin, A.I., and Semeikin A.S., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 6, p. 1215.
13. Dudina, N.A., Berezin, M.B., Antina, E.V., and Guseva, G.B., *Russ. J. Gen. Chem*., 2011, vol. 81, no. 11, p. 2352.
14. Berezin, M.B., Semeikin, A.S., Yutanova, S.L., Antina, E.V., Guseva, G.B., and V'yugin A.I., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 7, p. 1287.
15. Gordon, A.J. and Ford, R.A., *The Chemist's Companion. A Handbook of Practical Data, Techniques and References*, New York: Wiley, 1972.