Influence of Metal Cation on Chromophore Properties of Complexes of Some *d* Metals with α,α -Dipyrrolylmethene

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Received November 15, 2002

Abstract — In complexes of Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, and Hg²⁺ with 3,3',5,5'-tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene, the *d*-metal ion exerts an auxochromic effect on the π system of the ligand, manifested in a bathochromic shift of the first absorption band in the spectrum of the complex, compared to the free ligand. Polarization of the chromophore π system in the complexes increases in the order Zn²⁺ < Hg²⁺ < Co²⁺ < Ni²⁺ < Cu²⁺. The Hg²⁺ ion in the complex with dipyrrolylmethene participates in mercuration of benzene and chloroform; the reaction with chloroform is faster, with the rates of both reactions strongly depending on temperature.

Development of studies in the chemistry of polypyrrole compounds is mainly stimulated by their unique biological effect as photoreceptors in the structures of some chromoproteins and intermediate substrates of porphyrin metabolism, and also by their wide use in preparative organic chemistry for synthesis of various manmade and natural porphyrins [1, 2]. The efficiency of template synthesis of porphyrins from dipyrrolylmethenes on a metal ion matrix is largely determined by the chelating power of the dipyrrolyl ligand and by the physicochemical properties of the resulting chelates. Therefore, the search for new efficient procedures for template synthesis of porphyrins should be based on systematic data on the reactivity of linear polypyrrole compounds toward various metal ions and on physicochemical properties of the corresponding chelates. Such data are limited [2-4].

In this work we made a comparative analysis of the electronic absorption spectra of the free ligand, 3,3',5,5'-tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene **I**, and its complexes with Zn^{2+} (**II**), Hg^{2+} (**III**), Co^{2+} (**IV**), Ni^{2+} (**V**), and Cu^{2+} (**VI**) [5, 6] in various organic solvents: 1-propanol, benzene, DMF, pyridine, and chloroform.

The spectroscopic data are given in Table 1. Complexes V and VI have two, and II–IV, one absorption band in the visible range. All the complexes exhibit a relatively weak broad absorption band with a maximum at 366-398 nm. The spectrum of the free ligand in all the examined solvents has one strong absorption band at 440-446 nm, i.e., at shorter wavelength as compared to the stronger band in the spectra of the complexes.



 $M = Zn^{2+} (II), Hg^{2+} (III), Co^{2+} (IV), N^{2+} (V), Cu^{2+} (VI).$

It is known that the bathochromic shift of the first absorption band in the spectra of a complex relative to the free ligand, $\Delta\lambda^{I} = \lambda_{C}^{I} - \lambda_{L}^{I}$, where λ_{C}^{I} and λ_{L}^{I} are the wavelengths of the first absorption maximum of the complex and ligand, respectively, correlates not only with the extent of polarization of the chromophore with the metal ion, but also in many cases with the strength of the metal–ligand coordination bonds in the complexes. For phthalocyanines, the corresponding criterion of stability of the complexes was postulated by Linsted and thoroughly analyzed in [7, 8]. It should be noted that, in porphyrins, the combined effect of coordination and increase in the molecular symmetry upon complexation results in a decrease in the number of bands and in a hypsochromic shift of

the first absorption band relative to the free ligand, suggesting decreased polarization of the chromophore in the complex. Our experimental (Tables 1, 2) and published [2, 3] data show that, with dipyrrolylmethenes and their complexes, the trend is opposite: λ_C^I is considerably larger than λ_L^I . This suggests enhanced polarization of the π system of the dipyrrolylmethene molecule caused by an auxochromic effect of the metal ion on the chromophore, apparently determined by not only electronic but also structural and steric factors. The metal ion, becoming a partner of the conjugated system of dipyrrolylmethene π electrons, makes the pyrrole fragments more coplanar, which should enhance the conjugation between them [2]. As a result, in all the solvents (except $CHCl_3$), the first absorption band of complxes I-IV is shifted bathochromically by 50-75 nm relative to the free ligand (Table 2). In chloroform, the shift is considerably smaller and does not exceed 20-30 nm. This fact is due to specific solvation with chloroform of the heteroatom of the pyrrolenine ring $(\geq N \cdots HCCl_3)$ [5], causing $\lambda_{\rm I}^1$ of the free ligand I to increase relative to the other solvents. The chloroform proton acts as an auxochrome similar to metal ions in the complexes, but its polarizing effect on the chromophore is considerably weaker [9].

The structural features of metal dipyrrolylmethene complexes [2] are as follows. In cyclic tetrapyrrole porphyrin ligands, the structure of the coordination core is rigid, with a fixed void size, and formation of stable complexes requires matching of the void size and metal ionic radius. In going to open-chain dipyrrole ligands, this condition is lifted. Complexation should make the pyrrole rings in dipyrrolylmethene more coplanar. The electron density transfer from the ligands to the metal ion in dipyrrolylmethene complexes is determined by formation of mainly covalent and donor-acceptor metal-ligand σ bonds. In some cases, π backbonding takes place. The spectrum characteristics may be significantly affected by changes in the conformational state of the dipyrrolylmethene molecule upon complexation and by specific features of solvation in various solvents.

Thus, analysis of bathochromic shifts of the first absorption maximum in the electronic spectra of the complexes, compared to the free ligand, primarily allows estimation of the degree of ligand-to-metal electron density transfer. The average (for the series of the solvents tested) values of $\Delta\lambda^{\rm I}$ show that the polarization of the ligand chromophore in complexes with double-charged metal ions increases in the order ${\rm Zn}^{2+} < {\rm Hg}^{2+} < {\rm Co}^{2+} < {\rm Ni}^{2+} < {\rm Cu}^{2+}$. The well-known Irving–Williams series of double-charged ions characterizing the stability of complexes [10] is ${\rm Co}^{2+} <$

Table 1. Positions of maxima (nm) and intensities ($\log \varepsilon$ [$1 \mod^{-1} \operatorname{cm}^{-1}$]) of bands in the electronic absorption spectra of complexes of *d* metals with dipyrrolylmethene **I** in organic solvents

Comp.	<i>i</i> -PrOH	DMF	Ру	C ₆ H ₆	CHCl ₃
I	446(4.417)	440(4.440)	445	445	446
					484
Π	366 br	368 (4.260)	370	370	370
	500 (5.047)	498 (5.200)	502	502	502
III	366 (3.926)	368 (4.028)	374	368	372
	502 (4.745)	498 (4.957)	501	509	508
IV	372 (3.973)	371 (3.973)	374	374	375
	504 (4.740)	504 (5.187)	506	506	506
V	394 (4.245)	395 (4.495)	398	398	395
	458 (4.370)	458 (4.638)	459	459	459
	510 (4.488)	511 (4.757)	510	512	512
VI	395 br	395 br	395	395	397 br
	461 (4.679)	461 (4.831)	464	466	463
	512 (4.582)	512 (4.709)	515	516	516

Table 2. Shift of the first absorption band in the electronic spectra of dipyrrolylmethene complexes **II**–**VI** compared to the free ligand **I** ($\Delta\lambda^{I} = \lambda^{I}_{C} - \lambda^{I}_{L}$) in organic solvents

	$\Delta\lambda^{I}$, nm				Metals ranked in	
Solvent	п	III	IV	v	VI	order of increasing $\Delta \lambda^{I}$
DMF	58	58	64	71	72	Zn=Hg <co<ni<cu< td=""></co<ni<cu<>
Py	57	56	61	65	70	$Zn \approx Hg < Co < Ni < Cu$
1-PrOH	54	56	58	64	66	Zn <hg<co<ni<cu< td=""></hg<co<ni<cu<>
C ₆ H ₆	57	64	61	67	71	Zn <co<hg<ni<cu< td=""></co<hg<ni<cu<>
CHCl ₃	18	24	22	28	32	Zn <co<hg<ni<cu< td=""></co<hg<ni<cu<>
$\Delta \lambda_{av}^{I}, \tilde{a} nm$	57	59	61	67	70	Zn < Hg < Co < Ni < Cu

^a Average value for all the solvents except chloroform.

 $Ni^{2+} < Cu^{2+} > Zn^{2+}$. This order is followed in most cases, but the position of zinc is uncertain. It is only known that the zinc complexes are less stable than copper complexes. As a rule, zinc occupies the place between cobalt and nickel [11, 12]. However, this order is not obeyed with ligands coordinating through nitrogen atoms at double bonds (N=C). In this case, π backbonding becomes possible, and cobalt complexes become more stable than zinc complexes: $Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$.

This order is consistent with the stability order constructed for the dipyrrolylmethene complexes on the basis of the $\Delta\lambda^{I}$ values. The order is similar in all

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 74 No. 8 2004



Fig. 1. Electronic absorption spectrum of complex **III**: (a) in C_6H_6 at 298.15 K and (b) in $CHCl_3$ at 318.15 K. (A) Optical density. (1) Initial spectrum, (2) in 24 h, and (3) in 3 weeks. Arrows denote the direction of variation of the spectrum in successive recordings.

the solvents except benzene and chloroform, in which the position of Hg is different (Table 2). Note that the transfer of **II** and **IV–VI** from 1-PrOH to Py, C_6H_6 , and DMF is accompanied by an increase in $\Delta\lambda^I$, which suggests enhancement of the chromophore polarization, caused by solvation interaction with molecules of electron-donor and aromatic solvents.

For III, $\Delta \lambda^{I}$ is maximal in benzene, compared to the other solvents. Experiments show that prolonged storage (for more than a month) of solutions of **II** and **IV–VI** in the examined solvents causes no changes in the spectra, whereas in the spectrum of **III** in benzene (at 298.15 K) the absorption intensity at λ_C^I noticeably decreases even in 24 h (Fig. 1a). Upon storage of this solution for 3 weeks, the ligand absorption band appears and grows in intensity (λ_L^I 445 nm), whereas the band of the complex gradually decreases and disappeares. At 318.15 K, similar changes in the solution spectrum are complete in 10 days. The spectra show isobestic points suggesting the presence of two colored species: complex **III** and ligand **I**, which apparently indicates that benzene undergoes mercuration [13, 14]. Various agents are used for mercuration of aromatic compounds. Mercuration of benzene is usually performed with mecrucy(II) acetate in acetic acid; the reaction is catalyzed with perchloric acid. Mercuration shows characteristic features of electrophilic aromatic substitution; it involves initial formation of the π complex and is accelerated in the presence of bases which bind the proton displaced by mercury. With complex **III** as mercurating agent, the dipyrrolylmethene anion acts as such a base. The experimental data obtained in this study suggest the following mechanism of mercuration of benzene with **III** (HL denotes compound **I**):

Apparently, formation of a π complex in the initial step of the process enhances the polarization of the chromophore π system, which accounts for the largest bathochromic shift $\Delta \lambda^{I}$ of the mercury complex in benzene compared to the other solvents.

In chloroform, too, complex **III** has a larger $\Delta\lambda^1$ than the related Zn(II) and Co(II) complexes (Table 2). The spectrum of a solution of **III** in CHCl₃ also

changes with time. The transformation into the spectrum of the protonated ligand is complete in a week at 298 K and in 24 h at 318 K (Fig. 1b). In this solvent, mercuration can occur via formation of a σ complex to give the chloromethylmercury derivative (CCl₃)HgL or (CCl₃)₂Hg [13, 14]. Thus, our results show that complex **III** can be used as an agent for mercuration of benzene and chloroform.

EXPERIMENTAL

The electronic absorption spectra of pigment solutions were recorded on a Specord M-40 spectrophotometer in a temperature-controlled cell. The temperature was maintained with an accuracy of $\pm 0.1^{\circ}$ C.

3,3',5,5'-Tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene was synthesized, purified, and isolated according to [5]. Complexes **II–VI** were prepared according to [6] by reactions of **I** with metal acetates. The purity of the complexes was confirmed by TLC on Silufol UV-254 plates and by comparison of the spectral characteristics with published data [5, 6].

The organic solvents (chemically pure grade) were additionally purified by common procedures [15].

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