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# Protolytic Dissociation of Copper(II) and Nickel(II) Dipyrrolylmethenates in Benzene Solutions of Acetic Acid

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**Abstract**—Protolytic dissociation of copper(II) and nickel(II) dipyrrolylmethenates in benzene solutions of acetic acid has been studied. The results have completed the knowledge of kinetics of dipyrrolylmethene complexes dissociation in acidic medium. The effect of the nature of complex forming atom, ligand, and other factors on the complexes kinetic stability has been analyzed.

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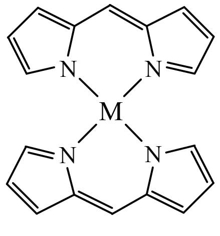
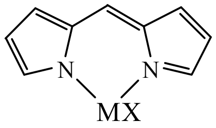
Coordination compounds of dipyrrolylmethenes and their derivatives are regarded as promising materials for optics, medicine, sensors development, and in other fields [1–3]. The optimization of the properties of such complexes in order to combine the desired photophysical features with chemical stability is of extreme importance. Practically interesting properties of the materials are those characterizing their photochemical reactivity, stability towards the action of solvent and acids (that is, towards solvolytic, protolytic, and solvoprotolytic dissociation), and stability towards termooxidative destruction and other impacts [4, 5]. For example, procedures to form mesoscopic and nanosized materials of dipyrrolylmethene complexes are based on their stability characteristics in acidic and alkaline solutions [6, 7]. Even though the physical and chemical properties of complexes of dipyrrolylmethenes and their derivatives have been extensively studied, to date there are only few works discussing their stability with variation of the medium acidity [3, 8–10].

In contrast to ions of other *d*-metals, copper(II) and nickel(II) can form both biligand dipyrrolylmethene complexes [M(dpm)$_2$] and heteroligand complexes [Mdpm(X)], the latter being highly stable (log $K_s$ 7–10 [11]). It may be assumed that the compounds with mixed coordination sphere, [Mdpm(X)], are intermediates of [M(dpm)$_2$] protolytic dissociation, as it was previously observed in the case of copper complex with butyl-substituted dipyrrolylmethene [8].

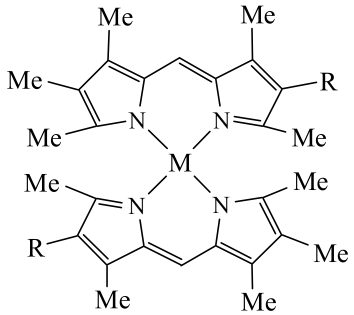


[M(dpm)$_2$]



[Mdpm(X)]

In this work, the protolytic dissociation of copper(II) and nickel(II) dipyrrolylmethenates in benzene solutions of acetic acid was studied. This allowed analyzing and comparing the kinetic stability of the complexes with respect to the acids action, taking into account the available data on dipyrrolylmethenates of other metals and fluoroboric complexes.



[Ni(dpm)$_2$]: M = Ni, R = Et; [Cu(dpm)$_2$]: M = Cu, R = Me.

The absorption spectra of [Cu(dpm)$_2$] and [Ni(dpm)$_2$] benzene solutions contained three absorption maxima:

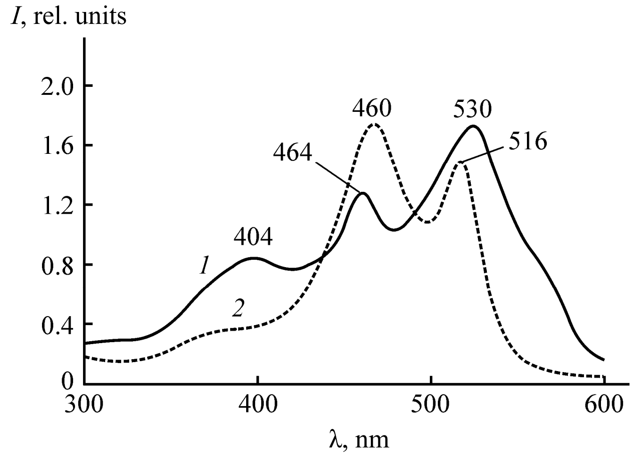


**Fig. 1.** Electronic absorption spectra of benzene solutions of (*1*) [Ni(dpm)$_2$] and (*2*) [Cu(dpm)$_2$].

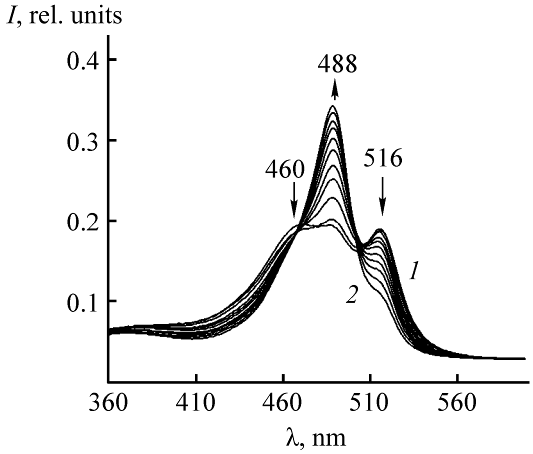


**Fig. 2.** Electron absorption spectra of [Cu(dpm)$_2$] benzene solution as function of $c_{\mathrm{AcOH}}$, mol L$^{-1}$: (*1*) 0.02 and (*2*) 0.12.

the most intense at 527–530 nm, at 460–464 nm, and at about 300 nm, the latter one corresponding to the charge transfer (Fig. 1). Addition of small amount of acetic acid ($c_{\mathrm{AcOH}}$ = 0.04 mol L$^{-1}$) to the [Cu(dpm)$_2$] solution induced instant spectral changes: the decrease of the complex absorption band and the appearance of the absorption band at 488 nm assigned to the protonated ligand $H_2dpm^+$ (Fig. 2). Addition of the strong base, triethylamine, reversed the process and led to formation of [Cu(dpm)$_2$]. Thus, the observed dissociation of [Cu(dpm)$_2$] was an equilibrium and reversible process, and the equilibrium constant of the reaction could be determined by means of spectrophotometry.

$$[\mathrm{Cu(dpm)_2}] + 4\mathrm{AcOH} = 2[\mathrm{H_2dpm}](\mathrm{AcO}) + \mathrm{Cu(AcO)_2}.$$

The average value of equilibrium constant $K$ was (7.55±0.4)×10$^{-7}$ L$^2$ mol$^{-2}$, being in line with the data on thermodynamic stability of copper(II) dipyrrolylmethenates [11, 12]. In contrast to the case of copper(II) complex with butyl-substituted dipyrrolylmethene (in that case the heteroligand complex was formed at low concentration of the acid [8]), the dissociation of the complex studied in this work was not accompanied with the formation of the mixed coordination sphere even with a tiny amount of the acid added.

In contrast with [Cu(dpm)$_2$], the protolytic dissociation of the corresponding nickel(II) complex occurred with a measurable rate at the acid concentration of 2.4×10$^{-4}$ to 0.2 mol L$^{-1}$. Upon addition of AcOH to the nickel(II) complex solution, the intensity of the absorption band at 530 nm decreased with time and the intensity of the protonated ligand absorption band at 493 nm increased (Fig. 3). At lower concentrations of the acid ($c_{\mathrm{AcOH}} < 2\times10^{-3}$ mol L$^{-1}$) the bands of the heteroligand complex absorption were observed [11]. However, at $c_{\mathrm{AcOH}} > 2\times10^{-3}$ mol L$^{-1}$ the heterocomplex was not observed, thus, [Ni(dpm)$_2$] was completely dissociated.

The kinetic curves in semilogarithmic coordinates revealed the first order reaction with respect to the complex (Fig. 4a), whereas the linear dependence of the observed reaction rate as a function of the acid concentration showed the first order reaction with respect to the acid (Fig. 4b), thus, the kinetic equation was as follows:

$$-dc[\mathrm{Ni(dpm)_2}]/d\tau = k_{\mathrm{obs}}c[\mathrm{Ni(dpm)_2}]c_{\mathrm{AcOH}}$$

with $c$[Ni(dpm)$_2$] being the complex concentration, $c_{\mathrm{AcOH}}$ being acetic acid concentration, and $k_{\mathrm{obs}}$ being the effective rate constant.

Thus, each of the two protolytic dissociation equilibria could be represented as a kinetic scheme describing the sequential protonation of the ligand nitrogen atoms. In the case of equilibrium formation of the heteroligand complex [Ni(dpm)$_2$] + 2AcOH ↔ [Ni(dpm)(AcO)] + [H$_2$dpm](AcO), the kinetic scheme is as follows.

$$[\mathrm{Ni(dpm)_2}] + \mathrm{AcOH} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \{\mathrm{Ni(dpm)_2(AcOH)}\}\ \text{(slowly)},$$

$$\{\mathrm{Ni(dpm)_2(AcOH)}\} \xrightarrow{k_2} [\mathrm{Ni(dpm)(AcO)}] + \mathrm{Hdpm}\ \text{(fast)},$$

$$\mathrm{Hdpm} + \mathrm{AcOH} \xrightarrow{k_3} [\mathrm{H_2dpm}](\mathrm{AcO})\ \text{(fast)}.$$

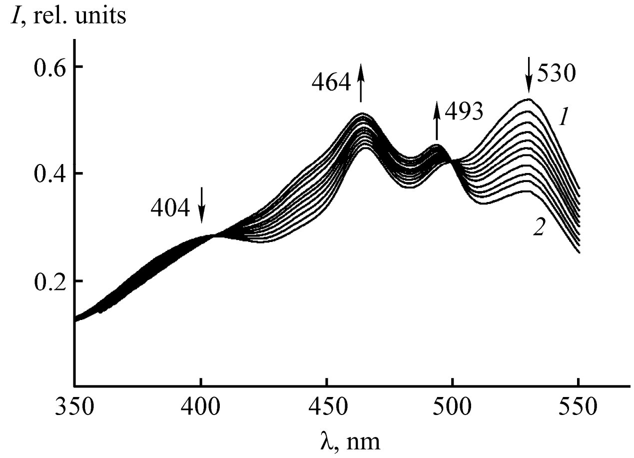


**Fig. 3.** Changes of electronic absorption spectra of [Ni(dpm)$_2$] benzene solution after addition of acetic acid: (*1*) initial state and (*2*) final state.

In the case of equilibrium of the heteroligand complex dissociation [Ni(dpm)(AcO)] + 2AcOH = Ni(AcO)$_2$ + [H$_2$dpm](AcO), the kinetic scheme is as follows.

$$[\mathrm{Ni(dpm)(AcO)}] + \mathrm{AcOH} \underset{k_{-1}^{*}}{\overset{k_1^{*}}{\rightleftarrows}} \{\mathrm{Ni(dpm)(AcO)(AcOH)}\}\ \text{(slow)}.$$

That the first order reaction was observed with respect to the acid, proved that the overall reaction was limited by the formation of the heteroligand complex, and thus its dissociation rate could be neglected. In the quasi-stationary state, the kinetic equation was as follows.

$$-dc[\mathrm{Ni(dpm)_2}]/d\tau = [(k_1k_2)/(k_{-1} + k_2)]c[\mathrm{Ni(dpm)_2}]c_{\mathrm{AcOH}}.$$

This was consistent with the experimentally found equation.

$$k_{\mathrm{obs}} = [(k_1k_2)/(k_{-1} + k_2)].$$

From the temperature dependences of the rate constants, the activation parameters were determined (see the table). As compared with the nickel complex of dibutyl-substituted dipyrrolylmethene [8], the activation energy of the complex studied in this work was higher. Thus, the kinetic stability of the complex was enhanced, likely due to the inductive effect of the methyl and ethyl groups and, consequently, higher electron donor ability of the pyrrole nitrogen atoms.

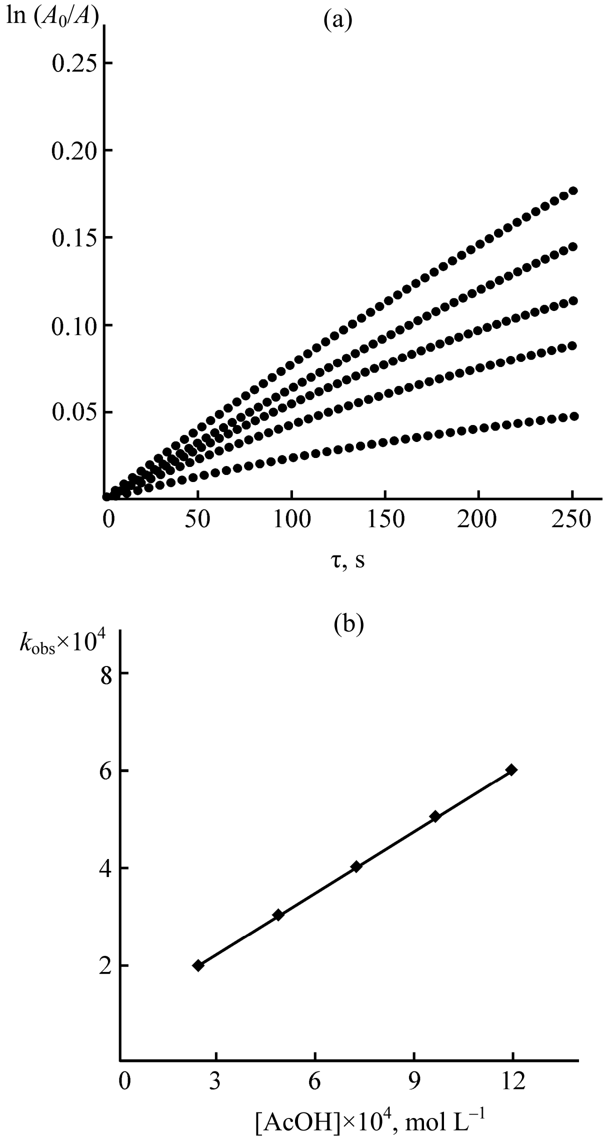


**Fig. 4.** Kinetics of (a) [Ni(dpm)$_2$] dissociation in semi-logarithmic coordinates and (b) the observed rate constant of [Ni(dpm)$_2$] protolytic dissociation as function of $c_{\mathrm{AcOH}}$.

The data obtained in this work added to the available knowledge on the kinetic stability of dipyrrolylmethene complexes in acidic media [3, 8–10]. The influence of the ligand substitution with alkyl was mainly due to the alkyls inductive effect that in turn determined the electron density on the coordinated nitrogen atoms. With longer alkyl chain, the +*I*-effect was diminished and, thus, the intermediate complex stability was decreased, as confirmed by results of this work and of [8–10]. The ability of the coordinated nitrogen atoms to interact with the acid strongly affected the kinetic stability of the complexes. The nature of the complexing metal ion not only governed the complex stability, but also the route of its

Kinetic and activation parameters of $[Ni(dpm)_2]$ protolytic dissociation in benzene solutions of acetic acid

| $T$, K | $k$ | $E_a$, kJ mol$^{-1}$ | $\Delta S^{\neq}$, J mol$^{-1}$ K$^{-1}$ | $\Delta H^{\neq}$, kJ mol$^{-1}$ |
|---|---|---|---|---|
| dpm$^-$ = anion of 3,3',4,5,5'-pentamethyl-4'-ethyl-2,2'-dipyrrolylmethene | | | | |
| 298 | 0.29±0.02 | 43.9±2.7 | –115.2±12.7 | 41.4±2.5 |
| 318 | 0.42±0.03 | | | |
| 328 | 0.83±0.05 | | | |
| dpm$^-$ = anion of 3,3',5,5'-tetramethyl-4,4'-dibutyl-2,2'-dipyrrolylmethene [8] | | | | |
| 298 | 2279±3 | 35±3 | –72.14±13 | 32.5±3.8 |
| 303 | 2660±3 | | | |
| 313 | 4541±5 | | | |
| 318 | 5272±11 | | | |

interaction with the acid. The complexes of zinc(II) and nickel(II) were relatively stable. The protolytic dissociation of the nickel(II) complex led to the formation of heteroligand complex. Cobalt(II) complexes were quite stable as well, and the respective kinetic data were obtained in [8]. Complexes of palladium(II) were much more stable, they only dissociated in the presence of trifluoroacetic acid [9]. Fluoroboric complexes of dipyrrolylmethenes were of unique kinetic stability towards protolytic and solvoprotolytic dissociation [10], in some cases superacid was needed to break the coordination bonds in those compounds. That was due to the covalent character of the B–N bond and to the chelate effect enhancing the stability of the coordination node. The quantum-chemical calculation revealed that the first stage of the protolytic dissociation was the F atom protonation with subsequent elimination of HF, this special feature distinguished such complexes from the complexes with *d*- and *f*-elements.

## EXPERIMENTAL

The complexes of 3,3',4,5,5'-pentamethyl-4'-ethyl-2,2'-dipyrrolylmethene with nickel(II) $[Ni(dpm)_2]$ and of 3,3',4,4',5,5'-hexamethyl-2,2'-dipyrrolylmethene with copper(II) $[Cu(dpm)_2]$ were prepared, purified, and identified as described in [13, 14]. Prior to the experiments, the solid samples were powdered and dried to constant mass in a vacuum at 40°C. Benzene (specially pure grade) and acetic acid (chemically pure grade) were purified according to standard procedures [15].

The electron absorption spectra were recorded at 350–600 nm with SF-104 spectrophotometer (Akvilon, Russia). The measurements were performed in quartz cells with the optical pathway of 10 mm, with temperature control using Peltier element.

The copper complex protolytic dissociation was studied at 298 K.

The protolytic dissociation kinetics was studied at 298, 318, and 328 K. The kinetic activation parameters: effective rate constant ($k_{obs}$), activation energy ($E_a$), and activation entropy ($\Delta S^{\neq}$) were determined according to equations (1–3).

$$k_{obs} = (1/\tau)\ln[(A_0 - A_\infty)/(A_\tau - A_\infty)]. \quad (1)$$

Here $A_0$, $A_\infty$, and $A_\tau$ are initial, final, and current ($t = \tau$) absorbances, respectively, at the band maximum.

$$E_a = 19.1\{T_1T_2/[(T_2 - T_1)]\}\log(k^{T2}/k^{T1}), \quad (2)$$

$$\Delta S^{\neq} = 19.1\log k^T + E_a/T - 19.1\log T - 205. \quad (3)$$

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