ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 3, pp. 552–557. © Pleiades Publishing, Ltd., 2013.
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Synthesis, Spectral Properties and Stability Towards Protolytic Dissociation of the Palladium(II) Complexes with Dipyrrolylmethene and Its Bis-Derivatives

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Received February 1, 2012

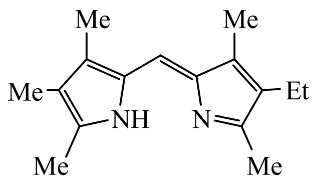
Abstract—Palladium(II) complexes with alkylated dipyrrolylmethene (Hdpm) and its bis-derivative, biladiene-*a,c* (H_2bd), of the composition [Pd(dpm)$_2$] and [Pd(bd)] were synthesized and were characterized by IR, UV-VIS, and NMR spectroscopy. It was shown that the nature of the solvent has almost no effect on the spectral characteristics of the complexes due to the square-planar configuration of the coordination nodes in them and, respectively, the impossibility of further coordination. From the results of the kinetic study of the complexes stability to the action of acids in the C_6H_6–CCl_3COOH mixtures it was concluded that the Pd(II) complexes are much more stable compared to the other *d*-metal dipyrrolylmethenates. Kinetic manifestation of polychelate effect was observed consisting in a sharp decrease in the dissociation rate of the palladium(II) complex with biladiene as compared to that with dipyrrolylmetene.

DOI: 10.1134/S1070363213030249

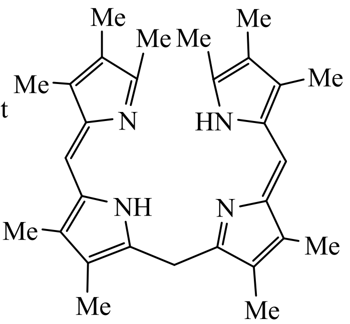
Coordination chemistry of linear oligopyrroles, where the chelating unit is a molecule of dipyrrolylmethene is currently undergoing a rapid development [1, 2]. The dipyrrolylmethenes are actively studied as promising compounds in different areas of science and technology: as the components of optical materials, photo-sensitizers, antioxidants, etc. In particular, the planar structure of the dipyrrolylmethene ligands combined with the high mobility in the conjugated`π-electron system are of interest when performing exploratory research of the dipyrrolylmethene metallocomplexes as anticancer drugs capable of intercalation of the DNA double helix [3]. World practice shows [4, 5] that the attention in this respect is focused on the platinum and palladium complexes with organic ligands due to strict square-planar structure of the coordination nodes that provides the greatest efficiency of incorporation of molecules of these compounds between the pairs of nitrogen bases in the DNA double helix. Despite this, in contrast to the relatively well-studied dipyrrolylmethene complexes with 3*d*-elements, the complexes of 4*d*-series did not attract proper attention.

In a fundamental aspect, a comparative study of the physicochemical properties of metal complexes with uniform coordination environment, but with different structure of the ligands is of great interest. For example, the replacement of dipyrrolylmethenates by the biladiene complexes is associated with the emergence of the third chelate metallocycle, and thus the appearance is possible of the differential polychelate effect [6].

In this paper we synthesized the Pd(II) complexes with the bialkylated pyrrolylmethene (Hdpm) and with



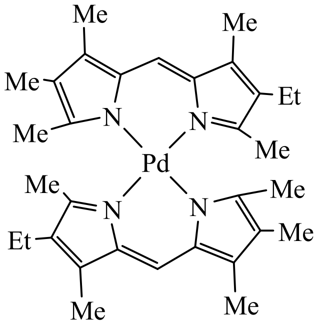
Hdpm



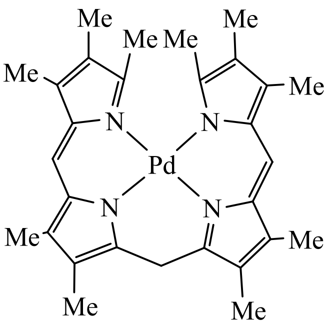
H_2bd

the related bis-derivative, the biladiene-*a,c* (H_2bd), studied their spectral properties and the kinetic resistance to acids (protolytic dissociation).

In the reaction of $PdCl_2$ with Hdpm and H_2bd in methanol the complexes [Pd(dpm)$_2$] and [Pd(bd)] were obtained in high yields. The progress in the synthesis was monitored by EAS of the reaction mixtures (Fig. 1). At the excess of $PdCl_2$ the reaction is completed on an average in 30 min. In the IR spectra of crystalline samples of compounds the bands of stretching and bending vibrations of NH bonds disappear evidencing the formation of coordination bonds. The same situation is observed in the ^{1}H NMR spectra: The proton signals belonging to NH groups specific to the ligands are absent in the spectra of the metal complexes. These observations suggest the formation of complexes of the following structure:



[Pd(dpm)$_2$]



[Pd(bd)]

The synthesized complexes and their solutions in organic solvents are of intense red color. The features of EAS of the complexes in various solvents are given in Table 1. The spectra contain a long-wavelength maximum (intra-ligand absorption band) at ~505 nm corresponding to π–π* transition, and a maximum in the near-UV region (~393 nm) corresponding to the charge transfer band (Fig. 1) It was established earlier [7–9] that the red shift of the absorption maximum of dipyrrolylmethene at its coordination with metal ions correlates with the stability of the complexes and points to a predominance of the ionic and/or covalent contributions to their stabilization. Values of the absorption maxima of the synthesized compounds show primarily a covalent type of the Pd–N bonds.

Effect of the nature of solvent on the spectral characteristics of [Pd(dpm)$_2$] appears to be rather weak, and the spectra of [Pd(bd)] are identical in all solvents. The weak solvent effect is the result of square-planar configuration of the coordination node in the analyzed complexes leading to unfavorable in energy additional coordination of the ligands to the central atom of palladium(II) at the axial positions [10].

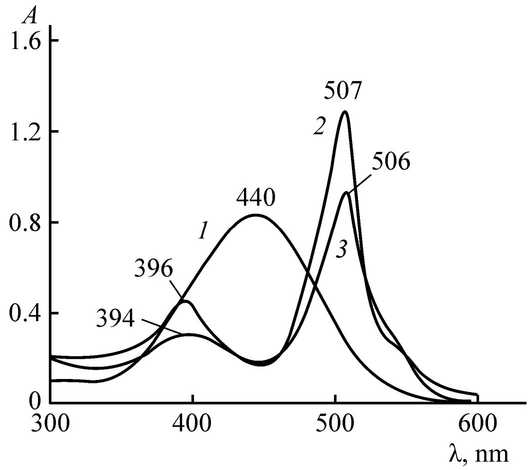


Fig. 1. EAS of solutions of (*1*) Hdpm, (*2*) [Pd(bd)], and (*3*) [Pd(dpm)$_2$] in benzene (c ~1×10^{-5} M).

Thus, the possibility of further polarization of the π-electron system of the dipyrrolylmethenes are limited to π–π interactions, rather than to changes in the effective charge on the metal due to the axial attachment of additional ligands, in contrast to the complexes of dipyrrolylmethenes with other *d*-metals. A stronger red shift of the absorption band is observed for solutions in benzene, which is caused, apparently, by the polarization of π–π interactions of the ligand aromatic system and the solvent.

The formation of palladium complexes is regulated by kinetic factors, in contrast to other *d*-metals,

Table 1. EAS of the complexes [Pd(dpm)$_2$] and [Pd(bd)] in various organic solvents at 298.15 K

Solvent	λ_{max}, nm (log ε)	
	[Pd(dpm)$_2$]	[Pd(bd)]
Cyclohexane	–[a]	394 (3.74), 506 (4.26)
Benzne	396 (3.78), 507 (4.27)	394 (3.91), 506 (4.36)
Chloroform	395 (3.97), 506 (4.42)	394 (3.90), 506 (4.28)
Ethanol	391 (3.87), 503 (4.25)	–
DMF	394 (4.00), 504 (4.46)	–
DMSO	392 (3.94), 503 (4.32)	–
Pyridine	396 (3.94), 506 (4.42)	394 (3.93), 506 (4.35)

[a] Data were not obtained due to insufficient solubility of the studied compounds.

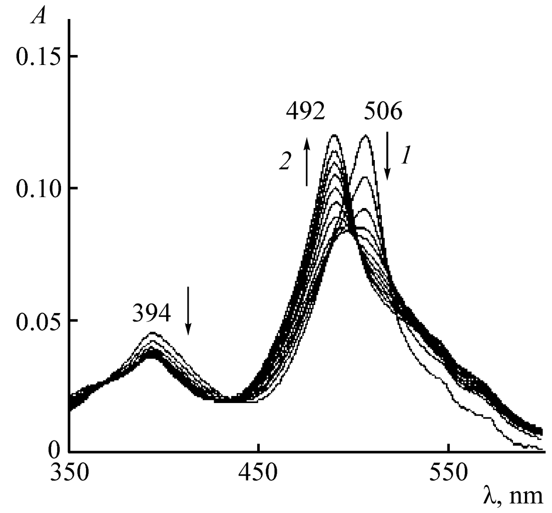


Fig. 2. Changes in EAS of solution of [Pd(bd)] at the protolytic dissociation at 298.15 K; τ, s: (*1*) 0, (*2*) 2820. The arrows indicate the direction of the change in intensity of the monitored absorption bands over time.

reaching the complexation equilibrium almost instantly. Preliminary experiments showed that the complexes are completely inert toward the protolytic dissociation in the C_6H_6–CH_3COOH. Thus, in contrast to similar complexes with 3*d*-metals [11], the palladium(II) complexes are much more resistant to protolytic dissociation. To study the reactions of protolytic dissociation of the complexes, and thus to determine the range and quantitative characteristics of their kinetic stability, we used a mixture based on benzene and trichloroacetic acid. The use of trichloroacetic acid as a protonating agent is due to the convenience of studying the kinetics of the reaction: The dissociation of complexes proceeds at a measurable rate even at 298 K. Changes in the EAS of the reaction mixtures in the course of the protolytic dissociation are shown in Fig. 2. The appearance of the absorption maximum at 485 nm followed by its regular growth indicates the destruction of the metal complex under the action of acids with the formation of protonated ligand. The linear dependence in semilog coordinates in Fig. 3 correspond to the first order with respect to metal complexes, and the dependence of the observed reaction rate constants (k_{obs}) on the acid concentration (Fig. 4) indicates a second order with respect to CCl_3COOH:

$$k_{obs} = kc^2(CCl_3COOH). \qquad (1)$$

Thus, the protolytic dissociation of the studied metallocomplexes occurs by the same type with the formation of protonated forms of ligands, and obeys the kinetic equation of the total third order

$$-\frac{dc[Pd(dpm)_2]}{d\tau} = kc[Pd(dpm)_2]c^2(CCl_3COOH), \qquad (2)$$

$$-\frac{dc[Pd(bd)]}{d\tau} = kc[Pd(bd)]c^2(CCl_3COOH). \qquad (3)$$

Tables 2 and 3 show the values of k_{obs} and k at different temperatures and the corresponding activation parameters of the reaction. The formation of protonated ligands H_2dpm^+ and H_4bd^{2+} at the dissociation of the complexes as well as the third order kinetic equations, makes it possible to consider the process of the protolytic dissociation of the complex as a combination of three stages involving sequential protonation of the ligand at the donor nitrogen atoms (for example, reaction with $[Pd(dpm)_2]$):

$$[Pd(dpm)_2] + 2H^+\cdots A^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \{[Pd(dpm)_2\cdot 2H]^{2+}\cdots 2A^-\}, \text{ slow}, \qquad (4)$$

$$\{[Pd(dpm)_2\cdot 2H]^{2+}\cdots 2A^-\} \xrightarrow[\text{fast}]{k_2} 2Hdpm + PdA_2, \qquad (5)$$

$$Hdpm + H^+\cdots A^- \xrightarrow[\text{fast}]{k_3} [H_2dpm^+\cdots A^-], \qquad (6)$$

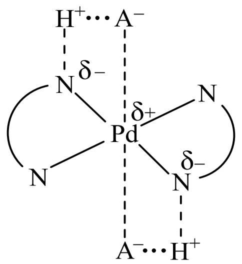
where $H^+\cdots A^-$ are the protonating acid particles. The kinetic equation for the reaction of the protolytic dissociation of $[Pd(dpm)_2]$ in the quasi-steady conditions is as follows:

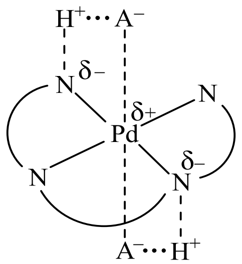
$$-\frac{dc[Pd(dpm)_2]}{d\tau} = \left(\frac{k_1k_2}{k_{-1} + k_2}\right)c[Pd(dpm)_2]c^2_{H^+\cdots A^-}, \qquad (7)$$

which corresponds to the experimentally found Eqs. (2), (3). Assuming that the reversible stage of the reaction (4) with a rate constant k_{-1} does not occur in the conditions of the experiment, that is, is kinetically insignificant, the Eq. (7) takes the form:

$$-\frac{dc[Pd(dpm)_2]}{d\tau} = k_1cdc[Pd(dpm)_2]c^2_{H^+\cdots A^-}. \qquad (8)$$

Thus, the limiting stage (4) contributes mainly to the overall reaction rate, and the resulting activation parameters belong to the formation of corresponding proposed transition state [taking into account the possible interaction of the central atom of Pd(II) with the acid anion]:





Comparative analysis of the kinetic and activation parameters (Tables 2, 3) in the reactions of protolytic dissociation of [Pd(dpm)$_2$] and [Pd(bd)] leads to the conclusion on the kinetic manifestation of the differential polychelating effect. The rate constant of the reaction of [Pd(dpm)$_2$] with the acid is 4.2 times larger ($T = 298$ K) than in the analogous reaction of the [Pd(bd)] complex. The activation energy required for the protolytic dissociation of [Pd(bd)] is about 1.3 times higher than that of [Pd(dpm)$_2$]. This is due to more rigid screening of the coordination node of the complex by the polychelating biladiene ligand, effecttively preventing interaction of protons of the acid with the coordinated nitrogen atoms. The obtained values of the activation entropy and enthalpy are in agreement with this conclusion.

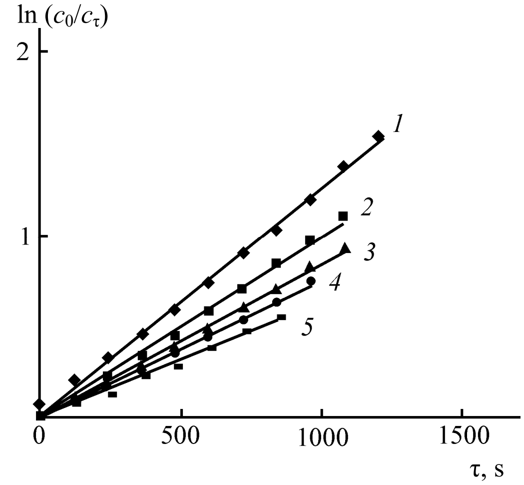


Fig. 3. Kinetic data for the reaction of protolytic dissociation of [Pd(bd)] at 298 K, M: (*1*) 6, (*2*) 5.3, (*3*) 4, (*4*) 2.8, and (*5*) 1.3.

It should be noted that earlier the studies of the kinetics of protolytic dissociation of the complex of platinum(III) with biliverdin, the natural bilatriene, were carried out [12]. It turned out that the complex is stable in solutions of AcOH in DMSO up to $c_{\mathrm{AcOH}} = 16.85$ M, but dissociates at replacing AcOH by H_2SO_4; the reaction is of an equilibrium nature. The kinetic data obtained, as well as the comparison of the medium acidity required for the dissociation of the complexes of biliverdin and protoporphyrin **IX** allowed us to estimate the macrocycle effect: the kinetic stability of the complex of protoporphyrin **IX** compared to biliverdine complex increases 10^4 times. Similar results were obtained for the complexes of manganese(III): the macrocycle effect stabilizes the manganese(III) protoporphyrinate complex 17.3× 10^7 times [13]. Thus, the results obtained in this study and the existing literature data allow us to draw the attention to the kinetic character of both polychelating and macrocycle effects as the most important factors of stabilization of coordination compounds. In the kinetics of protolytic dissociation of metal complexes

Table 2. The observed rate constants ($k_{\mathrm{obs}} \cdot 10^3$) of the reaction of protolytic dissociation of [Pd(dpm)$_2$] and [Pd(bd)] in a C_6H_6–CCl_3COOH mixture

$c(CCl_3COOH)\times10^4$, M	T, K		
	298	308	318
[Pd(dpm)$_2$]			
6.0	2.3	4.1	7.9
5.25	2.0	3.9	7.3
4.0	1.6	2.9	5.0
2.8	1.0	2.1	3.6
1.27	0.7	1.8	2.4
[Pd(bd)]			
6.0	1.0	2.6	4
5.25	0.9	2.2	3.5
4.0	0.8	1.5	3.3
2.8	0.7	1.2	2.4
1.27	0.6	0.8	1.9

Table 3. Kinetic and activation parameters of the protolytic dissociation reaction of [Pd(dpm)$_2$] and [Pd(bd)] in a C_6H_6–CCl_3COOH mixture

T, K	k	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}
[Pd(dpm)$_2$]				
298	4700±200	52.4±2.3	–6.0±0.3	44.8±2.2
308	7320±360			
318	18788±393			
[Pd(bd)]				
298	1120±50	65.8±3.2	25.7±0.5	65.3±3.2
308	5210±190			
318	5860±280			

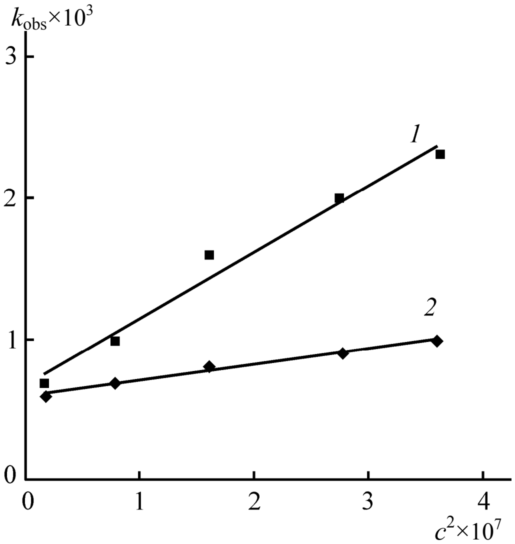


Fig. 4. Dependence of k_{obs} on $c^2(CCl_3COOH)$ (T = 298 K) for (*1*) [Pd(bd)] and (*2*) $[Pd(dpm)_2]$.

the polychelating and macrocycle effects are manifested in the sharp decrease in the reaction rate constants in the transition from complexes with chelate ligands to the compounds with multiple metal-chelate rings, and finally to the macrocyclic analogs.

EXPERIMENTAL

Benzene, methanol, acetic acid, trichloroacetic acid and trifluoroacetic acid of extra pure and chemically pure grade were purified by convential methods [14, 15].

EAS of solutions of the synthesized compounds were recorded in the range 350–800 nm on an SF-104 instrument (Akvilon, Russia) controlled by a PC, using the software package UVWin 5.1.0. Investigated solutions were charged in quartz cells with the absorbing layer thickness of 10 mm placed to a Peltier cell with controlled temperature, at fixed temperature with the accuracy ±0.1 deg.

The kinetics of protolytic dissociation of the complexes was studied by spectrophotometric method at the fixed values of temperature, 298, 308 and 318 K. The obtained kinetic and activation parameters: observed rate constants (k_{obs}), activation energy (E_a) and entropy ($\Delta S^{\neq}$) were calculated according to the equations:

$$k_{obs} = \frac{1}{\tau}\ln\frac{A_0 - A_\infty}{A_\tau - A_\infty}. \qquad (9)$$

Here A_0, A_∞, and A_τ are optical densities of solutions at the absorption maximum in the initial, final and intermediate time points, respectively.

$$E_a = 19.1\,\frac{T_1T_2}{T_2 - T_1}\log\frac{k^{T_2}}{k^{T_1}}. \qquad (10)$$

$$\Delta S^{\neq} = 19.1\log k^T + E_a/T - 19.1\log T - 205. \qquad (11)$$

Palladium(II) complex with 3,3',4,5,5'-pentamethyl-4'-ethyl-2,2'-dipyrrolylmethene. 3,3',4,5,5'-Tetramethyl-4'-ethyl-2,2'-dipyrrolylmethene hydrobromide (0.03 g, 2×10^{-3} mol) was preliminary deprotonated by triethylamine in methanol, and then to the reaction mixture was added 0.04 g (4×10^{-3} mol) of $PdCl_2$, and the mixture was boiled for 30 min. The reaction completion was fixed by the disappearance of the absorption band of the ligand in the EAS of the reaction mixture and by the reaching constant value of the intensity of the band of the complex. After synthesis, the reaction mixture was evaporated, the main product was isolated and purified by column chromatography on silica gel using benzene as an eluent. Then, the resulting complex was extracted with benzene, washed with water, and dried in a vacuum drying cabinet at 40ºC. Yield 0.041 g (70%). EAS, $\lambda_{\text{max}}^{\text{a bs}}$, nm (log ε): in C_6H_6, 396 (3.78), 507 (4.25); in $CHCl_3$, 395 (3.97), 506 (4.42); in ethanol, 391 (3.87), 503 (4.25). IR spectrum (tablets with KBr) ν, cm^{-1}: 3420 w, 3059 w, 3026 w, 2922 s, 2851 w, 1600 w, 1491 w, 1449 w, 1065 s. ^1H NMR spectrum ($CDCl_3$, δ, ppm), 6.73 s (2H, µs-CH), 2.67 s (12H, CH_3), 2.58 s (12H, CH_3), 2.52 q (4H,$C\underline{H}_2CH_3$) , 2.24 (6H, CH_3), 1.04 t (6H,$CH_2C\underline{H}_3$). Found, %: C 63.95, H 7.19, N 9.96. $C_{32}H_{42}N_4Pd$. Calculated, %: C 63.99, H 7.16, N 9.95.

Palladium(II) complex with 1,2,3,7,8,12,13,17,18,19-decamethylbiladiene-*a*,*c*. 1,2,3,7,8,12,13,17,18,19-Decamethylbiladiene-*a*,*c* dihydrobromide (0.04 g, 1.24×10^{-4} mol) was preliminary deprotonated with triethylamine in methanol. Then 0.064 g (2.5×10^{-4} mol) of $PdCl_2$ was added and the reaction mixture was boiled for 30 min. The reaction completion was fixed by the disappearance of the absorption band of the ligand in the EAS of the reaction mixture and by reaching a constant value of the intensity of the band of the complex. Then the resulting complex was extracted with benzene, washed with water, and dried in a vacuum in a drying cabinet at 40ºC. Yield 0.052 g (79%). EAS, nm (log ε): in C_6H_6, 394 (3.91), 506 (4.36); in $CHCl_3$, 394 (3.89), 506 (4.28). IR spectrum (tablets with KBr), ν, cm^{-1}: 3415 w, 3026 w, 2923 s, 2849 w, 1639 w, 1492 w, 1449 w, 1382 w, 1089 s. ^1H

NMR spectrum ($CDCl_3$, δ, ppm), 6.73 s (2H, μs-CH), 3.58 s (2H, CH_2-spacer), 2.67 s (6H, CH_3), 2.58 s (12H, CH_3), 2.24 (6H, CH_3), 1.98 s (6H, CH_3). Found, %: C 63.86, H 6.31, N 10.30. $C_{31}H_{42}N_4Pd$. Calculated, %: C 63.90, H 6.29, N 10.28.

ACKNOWLEDGMENTS

This work was supported by the grant of the President of the Russian Federation for young Russian scientists Candidates of sciences (no. MK-401.2011.3) and the Federal Program “Scientific and scientific-pedagogical personnel of innovative Russia” for 2009–2013 (state contract no. 14.740.11.0617).

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