

Synthesis, Physicochemical Characterization and Pyridine Binding to (2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-(2-pyridyl)-porphinato)cobalt(II)

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Dedicated to Prof. Oleg A. Golubchikov on the occasion of his 70th Birthday

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New (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) (Co^{II}P) was obtained in the reaction of 2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphyrin with Co(AcO)₂·4H₂O in boiling DMF. This porphyrin complex was characterized by UV-Vis, IR, ¹H NMR and mass spectra. Coordination of pyridine to Co^{II}P was studied by spectrophotometric titration. Cobalt(II) complex was found to react with pyridine forming 1:1 donor-acceptor complex in one-step reversible process. The obtained results are of interest for the creating of porphyrin-based donor-acceptor systems as components for photoactive materials.

Keywords: Cobalt porphyrins, pyridyl derivative, synthesis, spectroscopic properties, reaction with pyridine.

Синтез, физико-химическая характеристика и реакция координации (2,3,7,8,12,18-гексаметил-13,17-диэтил-5-(2-пиридил)порфинато)кобальта(II) с пиридином

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Новый комплекс кобальта(II) с 2,3,7,8,12,18-гексаметил-13,17-диэтил-5-(2-пиридил)порфирином получен реакцией свободного макроциклического лиганда с Co(AcO)₂·4H₂O в кипящем ДМФА. Комплекс охарактеризован методами УФ, видимой, ИК и ¹H ЯМР спектроскопии и масс-спектрометрии. Методом спектрофотометрического титрования изучена реакция между (2,3,7,8,12,18-гексаметил-13,17-диэтил-5-(2-пиридил)порфинато)кобальтом(II) и пиридином в среде толуола. Присоединение молекул пиридина к металлопорфиру проходит в одну стадию до состояния равновесия с образованием донорно-акцепторного комплекса состава 1:1. Определены спектральные характеристики и параметры устойчивости. Полученные результаты представляют интерес для создания на основе порфиринов донорно-акцепторных систем в качестве компонентов фотоактивных материалов.

Ключевые слова: Кобальт порфирилаты, пиридил производные, синтез, спектральные свойства, реакция с пиридином.

Introduction

Interest in cobalt porphyrins (CoPs) is maintained by their potential use in the design of electrochemical sensors, catalysts^[1-4] and other photoelectronic devices.^[5] Recent studies of the scientific group of Professor Oleg A. Golubchikov are proof of the growing interest in macroheterocyclic cobalt complexes.^[6-8] Divalent cobalt forms numerous complexes of various stereochemical types and Co(II) porphyrins can exist as the four-, five-, and six coordinate species.^[9,10] Co(II) is a d^7 system and readily forms five coordinate complexes but the formation of the six coordinate system is disfavoured due to destabilisation of the d_z^2 orbital.^[9] Co^{II}P (where P is 5,10,15,20-tetra(4*N*-carboxymethylenepyridyl)porphyrin dianion) was found to react with pyridine and piperidine releasing five coordinate complexes in one-step reversible process.^[6] Co^{II}P (where P is (2,3,12,13-tetrakis(trifluoromethyl)-5,10,15,20-tetraphenylporphyrin dianion)^[9] the first bonding constants (K_1) for pyridine bonding could be determined. Determination of the bonding constant for the second ligation (K_2) has been unsuccessful due to the extremely slow reaction from the five to the six coordinate species.^[9] However, values for the second axial bonding constants (K_2) are known for Co(II) complexes of electrondeficient porphyrins such as (2,3,12,13-tetracyano-5,10,15,20-tetraphenylporphinato)cobalt(II) (CoTPP(CN)₄),^[11] (2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphinato)cobalt(II) (CoTPPF₈) or (2,3,8,12,13,17,18-octafluoro-5,10,15,20-tetrakis(pentafluorophenyl)porphinato)cobalt(II) (CoTPFPF₈).^[12]

In the present work, we represent the synthesis of new cobalt(II) complex containing β -alkyl and *meso*-(2-pyridyl) groups, and donor-acceptor dyad based on it and pyridine.

Experimental

All reagents were of analytical grade. Co(AcO)₂·4H₂O was purchased from Sigma Aldrich. Chloroform was purchased from EKOS. Toluene was treated with potassium hydroxide and was distilled prior to use (bp 110.6 °C); the concentration of water therein was determined by Karl Fischer titration; it did not exceed 0.01 %. Pyridine was distilled prior to use also (bp 115.2 °C). (2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-(2-pyridyl)porphyrin was synthesized by reaction of 2,2'-methylene-bis(3-ethyl-4-methyl-1*H*-pyrrole) with 3,4-dimethyl-1*H*-pyrrole-2-carbaldehyde in butan-1-ol in the presence of hydrobromic acid at room temperature followed by boiling with pyridine-2-carbaldehyde.^[13]

The UV-Visible spectra were measured on Agilent 8453 UV-Visible spectrophotometers. IR and ¹H NMR spectra were recorded on a VERTEX 80v and a Bruker Avance III-500 NMR spectrometers, respectively. Elemental analysis was performed on a CHNSO Analyzer Flash EA 1112 Series. Mass spectra were performed on Shimadzu Confidence. All ¹H NMR measurements were carried out at room temperature in deuteriochloroform (CDCl₃).

Co(AcO)₂·4H₂O (47.0 mg, 0.19 mmol) and (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphyrin H₂P (20.0 mg, 0.04 mmol) were reacted in boiling dimethylformamide (10 ml) for 20–30 min. Completion of the reaction was monitored by TLC, until no traces of starting material were detected. The reaction mixture was cooled, after dilution with water the products were extracted into chloroform and purified by flash chromatography (Al₂O₃/CHCl₃). The red zone displays on the chromatogram corresponding to Co^{II}P.

(2,3,7,8,12,18-Hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II), Co^{II}P. Found, %: C 72.53, H 5.94, N 11.74. C₃₅H₃₅N₅Co requires C 71.91, H 6.03, N 11.98. m/z (MS MALDI-TOF) 584.22 [M]⁺. UV-Vis (toluene) λ_{\max} (lge) nm: 329 (4.19), 398 (5.25), 523 (4.00), 557 (4.27). IR (KBr) ν_{\max} cm⁻¹: 3062 ν (C-H_{meso}), 2962, 2928, 2867 ν (C-H) alkyl groups, 1730, 1668, 1585, 1445 vibrations of 2-pyridyl group, 1424 δ (C-H) alkyl groups, 1384, 1561, 1484, 1312, 1280, 1235, 1170, 1147, 1059 vibrations of macrocycle, 1013 ν (Co-N), 993, 978, 941 vibrations of pyrrole rings, 835 γ (C-H_{meso}), 765, 753 vibrations of 2-pyridyl group, 719, 664, 579 vibrations of macrocycle, 465 ν (Co-N). ¹H NMR (CDCl₃) δ_{H} ppm: 31.24 (br.s, 2H, H-*meso*), 24.81 (br.s, 1H, H-*meso*), 12.13 (br.m, 2H, H-pyridyl), 10.05 (br.s, 1H, H-pyridyl), 9.69 (s, 1H, H-pyridyl), 8.83 (s, 6H, CH₃), 8.24 (s, 6H, CH₃), 7.91 (s, 2H, -CH₂-), 7.67 (s, 2H, -CH₂-), 5.31 (s, 6H, CH₃), 5.20 (s, 6H, CH₃).

The reaction of Co^{II}P with pyridine at 298 K was studied in toluene by spectrophotometry. Series of toluene solutions with a constant concentration of the cobalt complex (4.1·10⁻⁵ M) and different concentrations of Py (from 0 to 10.5 M) were prepared. The overall volume of equilibrium mixtures was maintained using required amounts of Co^{II}P solution in toluene, a solution of pyridine in toluene, and pure toluene.

Results and Discussion

Synthesis and characterization

The formation of (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) was prepared by direct metallation of the corresponding macrocycle (Experimental). The UV-Vis spectrum of (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphyrin in DMF exhibits four typical bands in the visible region with the absorption maxima at 502, 537, 571 and 623 nm (Figure 1, solid line). This changes fundamentally when H₂P and Co(AcO)₂·4H₂O in molar ratio 1:5 are refluxed in DMF at 153 °C. The cobalt(II) porphyrin is the main product of the synthesis for 20 minutes. The reaction completion was detected by a disappearance of H₂P band and by termination of changes in the UV-Vis spectrum of the reaction mixture in chloroform. The reaction mixture was cooled and, after dilution with water, the products were extracted into chloroform. The solution was repeatedly washed with warm water to remove DMF. Its UV-Vis spectrum in CHCl₃ exhibits complicated Soret band and two bands with absorption maxima at 541 and 573 nm (Figure 1, dashed line) corresponding to the mixture of cobalt(II) and cobalt(III) porphyrins. The mixture obtained after isolation into chloroform was purified by flash chromatography on the column with Al₂O₃ (Brockman activity II) using CHCl₃. The red and red-orange zones display on the chromatogram.

The UV-Vis spectrum of the substance isolated from the first zone exhibits Soret band at 398 nm and band with absorption maxima at 556 nm. This spectrum being similar to those of cobalt(II) complexes (Table 1) describes the substance under consideration as compound Co^{II}P. The (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) in solid and in CHCl₃ solution is stable at ambient temperature for a long time. The UV-Vis spectrum of the substance isolated from the second zone with Soret band at 420 nm and with absorption maxima at 569 nm corresponds to cobalt(III) porphyrin (Table 1). It was determined that the synthesis time influenced on the ratio of Co^{II}

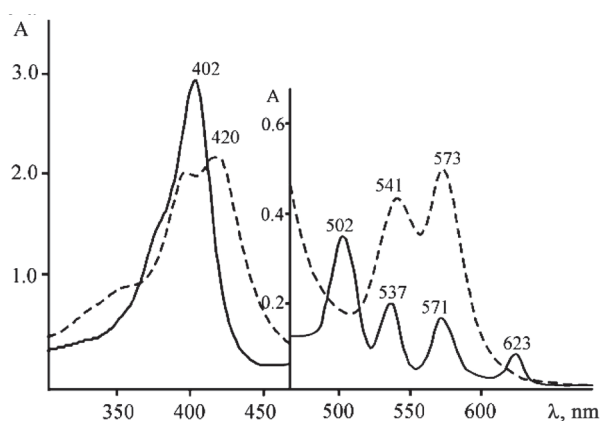


Figure 1. UV-Vis spectra of H_2P in DMF (solid line) and the reaction mixture (the synthesis time is 40–60 min) after washing with water (dashed line) in $CHCl_3$ at 298 K.

and Co^{III} porphyrins in the reaction mixture. The cobalt(III) porphyrin is probably formed resulting from the oxidation at the increase of synthesis time to 3 hours and will be described later in detail.

The structures of compounds $Co^{II}P$ were established by UV-Vis, 1H NMR and IR spectroscopy. The hypsochromic shift of bands in UV-Vis spectrum of $Co^{II}P$ (Table 1) as compared with $Zn^{II}OEP$ (λ_{max} (log ϵ) nm) in benzene: 400 (5.25), 535 (4.04), 568 (3.86)^[15] shows the strong π dative interaction of $d_{\pi}-e_g(\pi^*)$ type between Co^{II} and the porphyrin macrocycle. Cobalt(II) \rightarrow cobalt(III) oxidation in the (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato) complex leads to the bathochromic shift of absorption bands in UV-Vis spectrum (Table 1).

The IR spectra of H_2P and $Co^{II}P$ were obtained in the range of 4000–400 cm^{-1} . All the bands present in the IR spectrum of H_2P were also observed in the spectrum of cobalt(II) porphyrin. N-H stretching vibrations at

3269 (ν NH), 958 (δ NH) and 689 (γ NH) cm^{-1} in the H_2P IR spectrum are an exception. The disappearance of N-H vibration of H_2P in IR spectrum of $Co^{II}P$ predicated that the metalloporphyrin was successfully synthesized (Experimental). The bands of the cobalt(II) porphyrin in IR spectrum in the region of 1059–1280 and 941–993 cm^{-1} are caused by vibrations of the macrocycle skeleton. The intense bands at 2962, 2928, 2867 cm^{-1} are assigned to the stretching vibrations of $\nu(CH_3)$ and $\nu(CH_2)$ groups. The characteristic vibrations of 2-pyridyl group were observed at 1668, 1585, 1445 and 765 cm^{-1} . The frequencies of the $\gamma(C-H_{meso})$ and $\nu(C-H_{meso})$ are 835 and 3062 cm^{-1} , respectively. The weak band at 465 cm^{-1} in the IR spectrum of $Co^{II}P$ is observed in the range of stretching vibrations of Co–N bonds.^[16] This band is absent in the IR spectrum of H_2P .

The 1H NMR spectroscopy is very useful to determine the paramagnetic or the diamagnetic character of cobalt porphyrins. In Table 2 are summarized the chemical shifts of the Co^{II} and Co^{III} complexes with different substituted porphyrins.^[14,17–20] The paramagnetic complex $Co^{II}P$ (with the ground state configuration $3d^7$ of Co^{II}) exhibits down-field chemical shifts of the *meso*-protons, which appear as two broad singlets at 31.24 and 24.81 ppm (Figure 2). Four protons of 2-pyridyl group give three signals

Table 2. 1H NMR spectra of substituted CoP.

Complex	Solvent	δ_H ppm		
		<i>meso</i> -H	-CH ₂ -	-CH ₃
$Co^{II}OEP^a$ ^[14]	$CDCl_3$	29.60	8.80	5.10
$Co^{II}EtioI^b$ ^[17]	$CDCl_3$	29.50	8.84	5.95
$(Py)Co^{II}OEP^a$ ^[25]	C_6D_6	9.30	3.60	2.99
$(Cl)Co^{III}OEP^a$ ^[21]	$CDCl_3$	9.97	4.15	1.89
$(Br)Co^{III}OEP^a$ ^[21]	$CDCl_3$	10.65	4.06	1.88

^aOEP is octaethylporphyrin dianion

^bEtioI is etioporphyrin I dianion

Table 1. UV-Vis spectra of substituted CoP.

Complex	Solvent	λ_{max} (log ϵ) nm
$Co^{II}P$	toluene	398 (5.25), 523 (4.00), 557 (4.27)
$Co^{II}OEP^a$ ^[14]	chlorobenzene	391, 516, 551
$[(NO_2)_2Co^{III}OEP]^-$ ^[14]	chlorobenzene	425, 536, 569
$Co^{II}TPP$ ^[15]	dichloromethane	408 (5.37), 528 (4.24)
$(CN)(H_2O)Co^{III}TPP$ ^[15]	dichloromethane	433 (5.14), 548 (4.14), 582 (3.95)

^aOEP is octaethylporphyrin dianion.

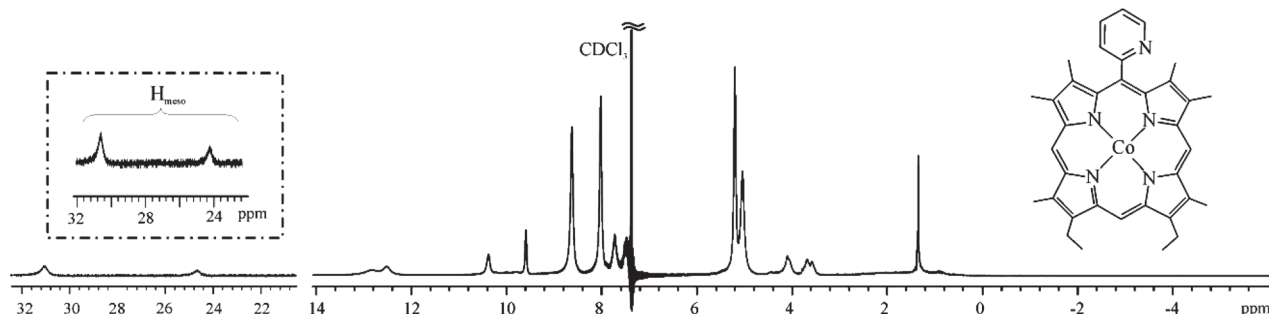


Figure 2. 1H NMR spectrum of (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) in $CDCl_3$.

in the range of 12.13 (2H, H-pyridyl), 10.05 (1H, H-pyridyl) and 9.69 (1H, H-pyridyl) ppm. Four singlets at 8.83, 8.24, 5.31 and 5.20 ppm correspond to 24 protons of β -methyl groups. Two singlets at 7.91 and 7.67 ppm are due to four protons of the $-\text{CH}_2-$ groups.

Coordination complex of cobalt(II) porphyrin with pyridine

The transformation of the UV-Vis spectrum of $\text{Co}^{\text{II}}\text{P}$ in toluene when the increasing amount of Py was added is shown in Figure 3. The addition of pyridine to solution of $\text{Co}^{\text{II}}\text{P}$ causes a gradual decrease in intensity and a small bathochromic shift (2 nm) of the Soret band at 398 nm. In the Q -band region, the peak at 558 nm decreases in intensity and the new peak appears at 548 nm. Isosbestic points are located at 410 and 551 nm, indicating only two absorbing species in solution, one of which is initial $\text{Co}^{\text{II}}\text{P}$. The spectrum of $\text{Co}^{\text{II}}\text{P}$ in toluene remains constant within a week upon addition of 1.5 M Py. Also, the spectrum does not change after addition of an excess amount of Py (10.5 M). The spectral changes occur as a result of conversion in time of $\text{Co}^{\text{II}}\text{P}$ to the six coordinate complex when the solvent is replaced by CH_2Cl_2 (Figure 4). The UV-Vis spectra in Figure 4 show the changes during two Py bonding to $\text{Co}^{\text{II}}\text{P}$ with clear isosbestic points.^[9] This is also confirmed by the ^1H NMR spectra analysis of the donor-acceptor complex with pyridine. $(\text{Py})_2\text{Co}^{\text{II}}\text{P}$ in CDCl_3 exhibits paramagnetic properties ($3d^7$ configuration), whereas (porphyrinato)cobalt(III) and donor-acceptor complexes based on them exhibit diamagnetic properties ($3d^6$ configuration).^[14]

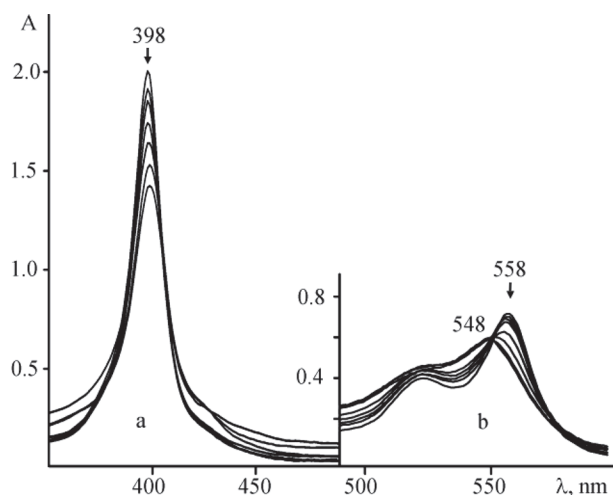


Figure 3. UV-Vis spectra of $\text{Co}^{\text{II}}\text{P}$ in toluene-pyridine mixtures ($C_{\text{Py}}=0-1.5$ M): a – $C_{\text{CoP}}=1.03 \cdot 10^{-5}$ M, b – $C_{\text{CoP}}=4.12 \cdot 10^{-5}$ M.

The equilibrium constant of the reaction of $\text{Co}^{\text{II}}\text{P}$ with Py (K) was obtained from spectrophotometric titration. The equilibrium was achieved instantly at all concentrations of Py. The complex $\text{Co}^{\text{II}}\text{P}$ binds one pyridine molecule, as followed from the slope of the $\log I - \lg C_{\text{Py}}$ dependence ($\text{tg}\alpha=0.95$) (Figure 5), where $I=(A_i - A_0)/(A_\infty - A_i)$ (A_0 , A_i , and A_∞ are the optical densities at a working wavelength at 558 nm of the initial cobalt complex, equilibrium mixture at

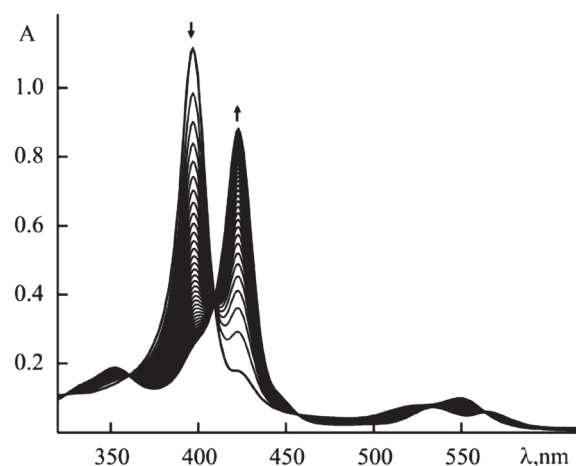


Figure 4. UV-Vis spectra of $\text{Co}^{\text{II}}\text{P}$ in CH_2Cl_2 -pyridine mixtures ($C_{\text{Py}}=0.024$ M, $C_{\text{CoP}}=6.86 \cdot 10^{-6}$ M), $\tau=0-6$ h.

a definite Py concentration, and coordination complex with Py). This indicates a simple bonding process with the formation of the 1:1 coordination complex. This result is in agreement with the fact of almost exclusively five coordinated state of cobalt in porphyrin complexes.

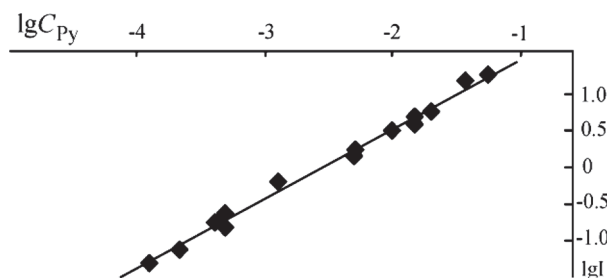


Figure 5. Plots of $\lg I$ vs $\lg C_{\text{Py}}$ for the reaction of pyridine with $\text{Co}^{\text{II}}\text{P}$ ($R^2=0.992$).

The numerical value of the equilibrium constant was calculated by the equation (1):

$$K = \frac{(A_i - A_0)/(A_\infty - A_0)}{1 - (A_i - A_0)/(A_\infty - A_0)} \cdot \frac{1}{(C_{\text{Py}}^0 - C_{\text{CoP}}^0) \cdot (A_i - A_0)/(A_\infty - A_0)} \quad (1)$$

Here, C_{Py}^0 and C_{CoP}^0 are, respectively, the initial concentrations of pyridine and $\text{Co}^{\text{II}}\text{P}$ in toluene. The K values were optimized by the least squares procedure using Microsoft Excel. The relative error in determination of K did not exceed 20 %. The constant of the coordination complex $(\text{Py})\text{Co}^{\text{II}}\text{P}$ formation is equal to $(3.56 \pm 0.72) \cdot 10^2$ $\text{L} \cdot \text{mol}^{-1}$. Thus, the reaction between $\text{Co}^{\text{II}}\text{P}$ and Py can be represented by equilibrium (2).



The formation of donor-acceptor complex between $\text{Co}^{\text{II}}\text{P}$ and Py was confirmed by analysis of IR spectra

of (porphyrinato)cobalt(II) and the equilibrium mixture in which the concentration of Py was equal to that in the equivalence point upon titration. New absorption bands in the IR spectrum of (Py)Co^{II}P appeared at 816, 704 and 581 cm⁻¹ due to vibrations of pyridine molecule coordinated; no such bands were observed in the spectrum of initial compound Co^{II}P. All vibration frequencies of Py coordinated are higher by 10–30 cm⁻¹ than those of free Py.^[22] The new signal with frequency at 452 cm⁻¹ due to vibrations of the Co–N_{py} was observed.^[23] The low-frequency shift of intensive signals of alkyl groups in the IR spectrum of (Py)Co^{II}P was monitored as a result of donor-acceptor complexation. The stretching vibrations of ν(CH₃) and ν(CH₂) groups are 2961, 2921 and 2862 cm⁻¹. The other vibration frequencies in the range 941–996 cm⁻¹ due to vibrations of macrocycle are shifted by 2–4 cm⁻¹ than those of Co^{II}P (Experimental). These spectral changes can be reasonably attributed to deformation of the macrocycle plane during the addition of axial ligand.

The formation of (Py)Co^{II}P was confirmed by ¹H NMR spectroscopy. The introduction of Py to the solution of the complex Co^{II}P in CDCl₃ is accompanied by the appearance of three new relatively narrow signals of Py ring at 9.88, 9.77 and 7.62 ppm, which have a small shift in a weak field compared with the signals of uncoordinated Py.^[24] The formation of donor-acceptor Py→Co bond leads to a change in the ring current in the macrocyclic ligand, appearing under an external electromagnetic field, and thus shifts the proton signals. This influence is more noticeable on the *meso*-proton signals of macrocycle.^[25] There are the *meso*-proton signals as two broad singlet at 31.24 and 24.81 ppm in the Co^{II}P spectrum (Figure 6a). Upon addition of 2, 3, 4 equiv. of Py, the *meso*-proton signals are located at 25.78 and 20.25, 21.94 and 14.23, 20.99 and 16.82 ppm, respectively. The increase of pyridine concentration in the mixture results to even greater upfield shifts of these two broad singlets at 19.05 and 14.32 ppm in the spectrum of (Py)Co^{II}P (Figure 6b). The proton signals of 2-pyridyl groups are also shifted upfield and are appeared as three singlets at 11.77 (2H, H-pyridyl), 10.22 (1H, H-pyridyl) and 9.11 (1H, H-pyridyl) ppm. Goff and co-workers noted that five-coordinated cobalt(II) complexes Co^{II}(OEP)(L) (L – monodentate neutral axial ligand) show hydrogens of alkyl groups in the region ~3–4 ppm (Table 2).^[25] The CH₃ proton signal migrated from 5.31 and 5.20 ppm (the value for Co^{II}P) to 3.52 and 3.40 ppm at formation of dyad (Py)Co^{II}P. The proton signals of –CH₂– groups are also shifted upfield and appear at 4.26 ppm.

The similar reaction of Co^{II}Pc (where Pc is octakis(3,5-di-*tert*-butylphenoxy)phthalocyanine dianion) with pyridine was studied in work.^[26] The addition of Py results in single-

stage equilibrium with formation of the donor-acceptor complex (Py)Co^{II}Pc. At keeping with the equilibrium constants, the stability of the Py complexes decreases from (Py)Co^{II}Pc ($K = (3.42 \pm 0.47) \cdot 10^3 \text{ L} \cdot \text{mol}^{-1}$) to (Py)Co^{II}P ($K = (3.56 \pm 0.72) \cdot 10^2 \text{ L} \cdot \text{mol}^{-1}$). It is seen that the stability constant of cobalt(II) phthalocyanine–pyridine coordination complex is higher by a factor of 10 than that of cobalt(II)porphyrin–pyridine dyad. This is likely to be related to the size of the coordination cavity of the macroring which decreases in going from porphyrin to phthalocyanine ligand.

Conclusions

We have described the synthesis of new cobalt(II) complex with 2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphyrin. The complex was characterized by UV-Vis, IR and ¹H NMR spectroscopy. The Co^{II}P is stable in solid state and exhibits paramagnetic properties. Co^{II}P gives the stable complex with Py in toluene formed in fast-established equilibrium that shows the self-assembly properties of the systems under consideration: $K = (3.56 \pm 0.72) \cdot 10^2 \text{ L} \cdot \text{mol}^{-1}$. The donor-acceptor type of the (Py)Co^{II}P dyad was established by UV-Vis, IR and ¹H NMR spectroscopy. It was found that the replacement of the solvent by CH₂Cl₂ results in the formation of six coordinated complex. Further work will be focused on quantitative studies of this reaction in CH₂Cl₂ and electrochemical studies of cobalt porphyrins using cyclic voltammetry and investigation of their photoactivity.

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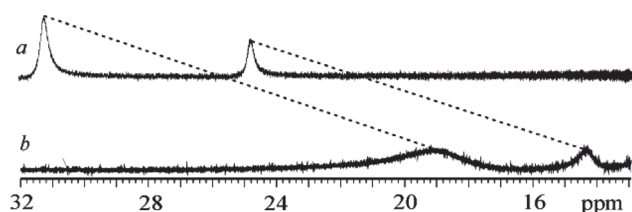


Figure 6. The informative fragment of the ¹H NMR spectra of Co^{II}P (a) and Co^{II}P/Py in ratio 1:40 (b) in CDCl₃.

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