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

Ekaterina N. Ovchenkova,a@ Nataliya G. Bichan,a Alexander S. Semeikin,b and Tatyana N. Lomovaa

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

aG.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, 153045 Ivanovo, Russian Federation
bIvanovo State University of Chemistry and Technology, Research Institute of Macroheterocyclic Compounds, 153000 Ivanovo, Russian Federation
@Corresponding author E-mail: enk@isc-ras.ru

New (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) (CoIIP) 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 CoIIP 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.
Introduction

Interest in cobalt porphyrins (CoPs) is maintained by their potential use in the design of electrochemical sensors, catalysts [5-6] and other photoelectronic devices. Recent studies of the scientific group of Professor Oleg A. Golubchikov are proof of the growing interest in macroheterocyclic cobalt complexes. Divalent cobalt forms numerous complexes of various stereochemical types and Co(II) porphyrins can exist as the four-, five-, and six coordinate species. [7,8] Co(II) is a d^8 system and readily forms five coordinate complexes but the formation of the six coordinate system is disfavoured due to destabilisation of the d^7 orbital. Co^6P (where P is 5,10,15,20-tetrasubstituted porphyrin dianion) was found to react with pyridine and piperidine releasing five coordinate complexes in one-step reversible process. [9] Co^6P (where P is 2,3,12,13-tetraakis(trifluoromethyl)-5,10,15,20-tetraphenylporphin dianion) is the first bonding constants (K) for pyridine bonding could be determined. Determination of the bonding constant for the second ligation (K') has been unsuccessful due to the extremely slow reaction from the five to the six coordinate species. However, values for the second axial bonding constants (K') are known for Co(II) complexes of electrondeficient porphyrins such as (2,3,12,13-tetracyano-5,10,15,20-tetraphenylporphino)cobalt(II) (CoTPP(CN)_4) [10], (2,3,7,8,12,13,17,18-octafluoro-5,10,15,20-tetraphenylporphino)cobalt(II) (CoTPPF_7) [11], or (2,3,8,12,13,17,18-octafluoro-5,10,15,20-tetraakis(pentafluorophenyl)porphino)cobalt(II) (CoTPFPFPF_7) [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 4H_2O 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). 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′-methylenebis(3,4-dimethyl-1-pyrrole) with 3,4-dimethyl-1-pyrrole. Elemental analysis was performed on a CHNSO elemental analyzer. All UV-Vis spectra were measured on a VERTEX 80v and a Bruker Avance III-500 NMR spectrometers, respectively. Absorption maxima at 502, 537, 571 and 623 nm (Figure 1, solid line). This changes fundamentally when H_2P is replaced by a pyridine molecule (Figure 1, dashed line). The UV-Vis spectrum of the mixture of cobalt(II) and cobalt(III) porphyrins exhibits four typical bands in the visible region with absorption maxima at 502, 537, 571 and 623 nm (Figure 1, solid line). This changes fundamentally when H_2P is replaced by a pyridine molecule (Figure 1, dashed line).

Results and Discussion

Synthesis and characterization

The formation of (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphino)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 spectrum being similar to that of the substance isolated from the second zone with Soret band at 420 nm and with absorption maxima at 569 nm corresponds to cobalt(II) porphyrin (Table 1). The reaction completion was detected by a disappearance of H_2P band and by terminal concentrations of cobalt complexes (4:10^5 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^6P solution in toluene, a solution of pyridine in toluene, and pure toluene.

Synthesis and Characterization of Co(II) Octaalkylpyridylporphyrin
and CoIII 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 CoIIIP were established by UV-Vis, 1H NMR and IR spectroscopy. The hypsochromic shift of bands in UV-Vis spectrum of CoIIIP (Table 1) as compared with ZnII OEP (λmax (logε) nm) in benzene: 400 (5.25), 535 (4.04), 568 (3.86)\,[15\] shows the strong π dative interaction of dπ–e\(^{\pi*}\) type between CoII and the porphyrin macrocycle. Cobalt(II) → 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\(^2\)P and CoIIIP were obtained in the range of 4000–400 cm\(^{-1}\). All the bands present in the IR spectrum of H\(^2\)P 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\(^2\)P IR spectrum are an exception. The disappearance of N-H vibration of H\(^2\)P in IR spectrum of CoIIIP predicted that the metallorporphyrin 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 v(CH\(_3\)) and v(CH\(_2\)) groups. The characteristic vibrations of 2-pyridyl group were observed at 1668, 1585, 1445 and 765 cm\(^{-1}\). The frequencies of the γ(C-H\(_{\text{meso}}\)) and ν(C-H\(_{\text{meso}}\)) are 835 and 3062 cm\(^{-1}\), respectively. The weak band at 465 cm\(^{-1}\) in the IR spectrum of CoIIIP is observed in the range of stretching vibrations of Co–N bonds\,[10\] This band is absent in the IR spectrum of H\(^2\)P.

The \(^1\)H 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 CoII and CoIII complexes with different substituted porphyrins.\,[14,17-20\] The paramagnetic complex CoIIIP (with the ground state configuration 3d\(^7\) of CoII) exhibits downfield 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

![Figure 1. UV-Vis spectra of H\(^2\)P 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.](image1)

![Figure 2. \(^1\)H NMR spectrum of (2,3,7,8,12,18-hexamethyl-13,17-diethyl-5-(2-pyridyl)porphinato)cobalt(II) in CDCl\(_3\).](image2)

**Table 1.** UV-Vis spectra of substituted CoP.

| Complex | Solvent | λ max (log ε) nm |
|---------|---------|-----------------|
| CoIIIP | toluene | 398 (5.25), 523 (4.00), 557 (4.27) |
| CoIIIP | chlorobenzene | 391, 516, 551 |
| [(NO\(_2\)]_2 CoIIIP | chlorobenzene | 425, 536, 569 |
| CoIIITPP | dichloromethane | 408 (5.37), 528 (4.24) |
| (CN)(H\(_2\)O)CoIIITPP | dichloromethane | 433 (5.14), 548 (4.14), 582 (3.95) |

\(^{\text{a}}\)OEP is octaethylporphyrin dianion

| Complex | Solvent | δ ppm |
|---------|---------|-------|
| CoIIIP\,[14\] | CDCl\(_3\) | 29.60, 8.80, 5.10 |
| CoIIEtioI\,[17\] | CDCl\(_3\) | 29.50, 8.84, 5.95 |
| (Py)CoIIIP\,[25\] | C\(_6\)D\(_6\) | 9.30, 3.60, 2.99 |
| (Cl)CoIIIP\,[21\] | CDCl\(_3\) | 9.97, 4.15, 1.89 |
| (Br)CoIIIP\,[21\] | CDCl\(_3\) | 10.65, 4.06, 1.88 |

\(^{\text{a}}\)OEP is octaethylporphyrin dianion

**Table 2.** \(^1\)H NMR spectra of substituted CoP.
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 -CH₂- groups.

**Coordination complex of cobalt(II) porphyrin with pyridine**

The transformation of the UV-Vis spectrum of Co²⁺P in toluene when the increasing amount of Py was added is shown in Figure 3. The addition of pyridine to solution of Co²⁺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 Co²⁺P. The spectrum of Co²⁺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 Co²⁺P to the six coordinate complex when the solvent is replaced by CH₂Cl₂ (Figure 4). The UV-Vis spectra in Figure 4 show the changes during two Py bonding to Co²⁺P with clear isosbestic points. This is also confirmed by the ¹H NMR spectra analysis of the donor-acceptor complex with pyridine. (Py)²Co²⁺P in CDCl₃ exhibits paramagnetic properties (3d⁷ configuration), whereas (porphyrinato)cobalt(III) and donor-acceptor complexes based on them exhibit diamagnetic properties (3d⁶ configuration).

The equilibrium constant of the reaction of Co²⁺P with Py (K) was obtained from spectrophotometric titration. The equilibrium was achieved instantly at all concentrations of Py. The complex Co²⁺P binds one pyridine molecule, as followed from the slope of the logI-lgC₀Py dependence (tgα=0.95) (Figure 5), where I=(A₀–A) (A₀, A are the optical densities at a working wavelength at 558 nm of the initial cobalt complex, equilibrium mixture at 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 3. UV-Vis spectra of Co²⁺P in toluene-pyridine mixtures (C₀Py=0–1.5 M): a – C₀CoP=1.03·10⁻⁵ M, b – C₀CoP=4.12·10⁻⁵ M.](image)

![Figure 4. UV-Vis spectra of Co²⁺P in CH₂Cl₂–pyridine mixtures (C₀Py=0.024 M, C₀CoP=6.86·10⁻⁶ M), τ=0–6 h.](image)

![Figure 5. Plots of lgI vs lgC₀Py for the reaction of pyridine with Co²⁺P (R²=0.992).](image)

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

$$K = \frac{(A_0 - A_y)(A_0 - A_y)}{1 - (A_0 - A_y)(A_0 - A_y)} \cdot \frac{1}{(C_0^{Py} - C_0^{CoP})(A_0 - A_y)(A_0 - A_y)}$$

(1)

Here, C₀Py and C₀CoP are, respectively, the initial concentrations of pyridine and Co²⁺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 (Py)Co²⁺P formation is equal to (3.56±0.72)·10² L·mol⁻¹. Thus, the reaction between Co²⁺P and Py can be represented by equilibrium (2).

$$Co²⁺P + Py \leftrightharpoons (Py)Co²⁺P$$

(2)

The formation of donor–acceptor complex between Co²⁺P and Py was confirmed by analysis of IR spectra.
of (porphyrinate)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)CoII(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 CoII(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\(_p\) was observed.\(^{[23]}\) The low-frequency shift of intensive signals of alkyl groups in the IR spectrum of (Py)CoII(P was monitored as a result of donor-acceptor complexation. The stretching vibrations of ν(CH\(_2\)) and ν(CH\(_3\)) 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 CoII(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)CoII(P was confirmed by \(^1\)H NMR spectroscopy. The introduction of Py to the solution of the complex CoII(P in CDCl\(_3\) is accompanied by the appearance of three new relatively narrow signals of Py ring at 9.88, 7.51 and 7.42 ppm (the value for CoII(P) to 3.52 and 3.40 ppm due to vibrations of macrocycle.\(^{[25]}\) There are the 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 CoII(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 higher shift of intensive signals of alkyl groups are also shifted upfield and are appeared as three singlets at 11.77 (2H, H-pyridyl) and 9.11 (1H, H-pyridyl) ppm. Goff and co-workers noted that five-coordinated cobalt(II) complexes CoII(OEP)\(_2\)(L) (L = monodentate neutral axial ligand) show hydrogens of alkyl groups in the region 3–4 ppm (Table 2).\(^{[23]}\) The CH\(_3\) proton signal migrated from 5.31 and 5.20 ppm (the value for CoII(P) to 3.52 and 3.40 ppm at formation of dyad (Py)CoII(P. The proton signals of -CH\(_2\)-groups are also shifted upfield and appear at 4.26 ppm.

The similar reaction of CoII(Pc (where Pc is octakis(3,5-di-tert-butlyphenoxo)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)CoII(Pc. At keeping with the equilibrium constants, the stability of the Py complexes decreases from (Py)CoII(Pc (K = (3.42±0.47)\times10^3 L\cdot mol\(^{-1}\)) to (Py)CoII(P (K=(3.56±0.72)\times10^2 L\cdot 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 \(^1\)H NMR spectroscopy. The CoII(P is stable in solid state and exhibits paramagnetic properties. CoII(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±0.72)\times10^2 L\cdot mol\(^{-1}\). The donor-acceptor type of the (Py)CoII(P dyad was established by UV-Vis, IR and \(^1\)H NMR spectroscopy. It was found that the replacement of the solvent by CH\(_2\)Cl\(_2\) results in the formation of six coordinated complex. Further work will be focused on quantitative studies of this reaction in CH\(_2\)Cl\(_2\) and electrochemical studies of cobalt porphyrins using cyclic voltammetry and investigation of their photoactivity.

Acknowledgements. This work was carried out with the help of the centre of the scientific equipment collective use «The upper Volga region centre of physicochemical research» and with the financial support from grants of the Russian Foundation for Basic Research (project no. 16-03-00631-a).

References

1. Swavey S., Eder A. Inorg. Chem. Commun. 2013, 29, 14–17.
2. Du Y.X., Zhang Z.Q., Yao Y.H., Li J. Inorg. Chem. Commun. 2016, 64, 19–22.
3. Zagal J., Bedioui F., Dodelet J.P. N4-Macrocyclic Metal Complexes. New York: Springer, 2006.
4. Kurmaz S.V., Perrepetitsina E.O., Bubnova M.L., Estrina G.A., Roshchupkin V.P. Mendeleev Commun. 2002, 12, 21–23.
5. Phthalocyanines: Properties and Applications (Leznoff C.C., Lever A.B.P., Eds.), Vols. 1–4, New York: VCH, 1989, 1992, 1993, 1996.
6. Guseva L.Zh., Pukhovskaya S.G., Golubchikov O.A. Russ. J. Inorg. Chem. 2010, 55, 552–555.
7. Vashurin A.S., Pukhovskaya S.G., Semeikin A.S., Golubchikov O.A. Macroheterocycles 2012, 5, 72–75.
8. Voronina A.A., Filippova A.A., Vashurin A.S., Pukhovskaya S.G., Shaposhnikov G.P., Golubchikov O.A. Russ. J. Gen. Chem. 2015, 85, 1713–1720.
9. Terazono Y., Patrick B.O., Dolphin D.H. Inorg. Chim. Acta 2003, 346, 265–269.
10. Kurtikyan T.S., Hovhannisyan A.A., Lyubimtsev A.V., Ageeva T.A., Ugarov V.S., Koifman O.I. Macroheterocycles 2016, 9, 156–162.

Figure 6. The informative fragment of the \(^1\)H NMR spectra of CoII(P (a) and CoII(P/Py in ratio 1:40 (b) in CDCl\(_3\).
11. Lin X.Q., Cocolios B.B., Kadish K.M. Inorg. Chem. 1986, 25, 3242–3248.
12. Smirnov V.V., Woller E.K., DiMaggio S.G. Inorg. Chem. 1998, 37, 4971–4978.
13. Ivanova Yu.B., Semeikin A.S., Glazunov A.V., Mamardashvili N.Zh. Russ. J. Org. Chem. 2010, 46, 144–149.
14. Ali B.B., Belkhiria M.S., Giorgi M., Nasri H. Open J. Inorg. Chem. 2011, 1, 39–46.
15. Chizhova N.V., Kumeev R.S., Mamardashvili N.Zh. Russ. J. Inorg. Chem. 2013, 58, 740–743.
16. Mabbs F.E. Chem. Soc. Rev. 1993, 22, 313–324.
17. Abraham R.J., Marsden I., Xiujing L. Magn. Reson. Chem. 1990, 28, 1051–1057.
18. Jimenez H.R., Moratala J.M., Loock B. New J. Chem. 2002, 26, 323–329.
19. Walker F.A. In: Handbook of Porphyrin Science, Vol. 6 (Kadish K.M., Smith K.M., Guilard R., Eds.) World Scientific Publishing, 2010. Ch. 29, p. 7–337.
20. Walker F.A. In: The Porphyrin Handbook, Vol. 5 (Kadish K.M., Smith K.M., Guilard R., Eds.) San Diego: Academic Press, CA, 2000. Ch. 36, p. 81–183.
21. Cao Y., Petersen J.L., Stolzenberg A.M. Inorg. Chem. 1998, 37, 5173–5179.
22. Gordon A.J., Ford R.A. The Chemist's Companion. NY-London-Sydney-Toronto, 1972.
23. Sacconi L., Sabatini A., Gans P. Inorg. Chem. 1964, 3, 1772–1774.
24. Katek M., Urbanski T. Bull. Acad. Polonaise Sci. Serie: Sci. Chim. 1968, 16, 347–350.
25. Shirazi A., Goff H.M. Inorg. Chem. 1982, 21, 3420–3425.
26. Ovchenkova E.N., Bichan N.G., Lomova T.N. Dyes Pigm. 2016, 128, 263–270.

Received 15.03.2017
Accepted 14.02.2018