

PHYSICAL CHEMISTRY
OF SOLUTIONS

Synthesis and Spectral Properties of Cobalt(II) and Cobalt(III) Tetraarylporphyrinates

N. V. Chizhova, R. S. Kumeev, and N. Zh. Mamardashvili

Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Akademicheskaya ul. 1, Ivanovo, 153045 Russia

Received March 15, 2012

Abstract—Reactions of 5,10,15,20-tetraphenylporphin, 5,10,15,20-tetra(4'-methoxyphenyl)porphyrin, and 5,10,15,20-tetra(4'-chlorophenyl)porphyrin with cobalt(II) acetate in dimethylformamide were studied by spectrophotometry. The corresponding cobalt(II) porphyrinates were synthesized and identified. The corresponding cobalt porphyrinates in +3 oxidation state were obtained by reaction of cobalt(II) 5,10,15,20-tetraphenylporphyrinate and cobalt(II) 5,10,15,20-tetra(4'-methoxyphenyl)porphyrinate with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in chloroform. The oxidation of cobalt(II) 5,10,15,20-tetra(4'-chlorophenyl)porphyrinate with hydrochloric acid in dimethylformamide leads to cobalt(III) porphyrinate.

DOI: 10.1134/S0036023613060089

Interest in the synthesis and study of porphyrin complexes with variable valence metals results from their possible application as chemical sensors, photochromic materials, and redox catalysts.

The kinetics of Co^{2+} complexation with tetraphenylporphin and its derivatives was studied in [1–3]. However, there are no synthesis and spectral characteristics of cobalt(II) and cobalt(III) complexes based on tetraphenylporphin in the cited works. ^1H and ^{13}C NMR spectra of cobalt(II) tetraphenylporphyrinate and its derivatives were studied in [4]. The authors [5] prepared and identified cobalt(II) and cobalt(III) complexes with octaethylporphyrin.

With the aim to obtain cobalt(II) and cobalt(III)E (E is an extra ligand) complexes with tetraphenylpor-

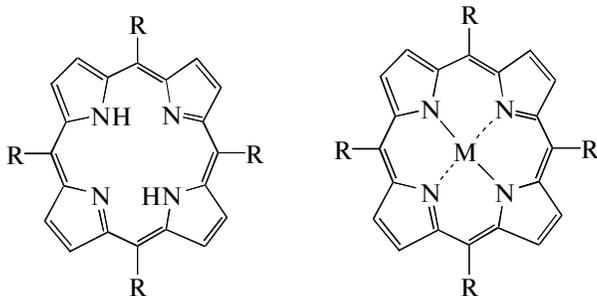
phin, its *para*-methoxy, and *para*-chloro derivatives, in this work we have studied the complexation of 5,10,15,20-tetraphenylporphin (**I**), 5,10,15,20-tetra(4'-methoxyphenyl)porphyrin (**II**), and 5,10,15,20-tetra(4'-chlorophenyl)porphyrin (**III**) with cobalt(II) acetate in dimethylformamide (DMF). Dimethylformamide is a universal medium for the complexation of metal ions with porphyrins of different structure [6].

Considerable difference in the electronic absorption spectra and ^1H NMR spectra of initial porphyrins and resulting cobalt porphyrinates (table, Experimental) enabled us to use spectrophotometry and ^1H NMR spectroscopy to study the complexation of compounds **I–III** and to identify porphyrinates **IV–VIII**.

Electronic absorption spectra of porphyrin ligands (**I–III**), cobalt(II) porphyrinates (**IV, VI, VIII**), cobalt(III)E porphyrinates (**V, VII, IX**), and Zn(II) porphyrinate (**X**)

Compound	Solvent	Band I λ , nm (log ϵ)	Band II λ , nm (log ϵ)	Bands III, IV λ , nm (log ϵ)	Soret peak λ , nm (log ϵ)
I	CHCl_3	647 (3.89)	591 (3.96)	549 (4.08), 514 (4.40)	417 (5.61)
II	CHCl_3	651 (3.92)	594 (3.88)	555 (4.10), 519 (4.25)	419 (5.58)
III	CHCl_3	645 (3.76)	590 (3.83)	550 (4.05), 515 (4.36)	417 (5.60)
IV	CH_2Cl_2	528 (4.24)			408 (5.37)
V	CH_2Cl_2	582 (3.95)	548 (4.14)		433 (5.14)
VI	CH_2Cl_2	530 (4.26)			412 (5.35)
VII	CH_2Cl_2	591 (4.01)	552 (4.11)		437 (5.19)
VIII	CH_2Cl_2	528 (4.23)			410 (5.32)
IX	CHCl_3	587 (3.93)	549 (4.15)		435 (5.17)
X*	CHCl_3	597 (3.99)	558 (4.36)		420 (5.19)

* Data from work [7].



R = C₆H₅ (I),

R = C₆H₄-4-OCH₃ (II),

R = C₆H₄-4-Cl (III),

M = cobalt(II), R = C₆H₅ (IV),

M = cobalt(III), E = (CN⁻, H₂O), R = C₆H₅ (V),

M = cobalt(II), R = C₆H₅-4OCH₃ (VI),

M = cobalt(III), E = (CN⁻, H₂O), R = C₆H₅-4-OCH₃ (VII),

M = cobalt(II), R = C₆H₄-4-Cl (VIII),

M = cobalt(III), E = (Cl⁻, H₂O), R = C₆H₄-4-Cl (IX),

M = Zn(II), R = C₆H₅ (X).

EXPERIMENTAL

Porphyrin ligands were obtained by procedures [7, 8]. Dimethylformamide, CHCl₃, and CH₂Cl₂ of reagent grade were used without additional purification. Cobalt diacetate of reagent grade was recrystallized from glacial acetic acid (reagent grade) and dried at 80°C for 1 h. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone was purchased from Merck. Hydrochloric acid (37%) of high purity grade was used.

The complexation of metal cation with porphyrin ligand was monitored by spectrophotometry of samples. The procedure of spectrophotometric study was as follows: samples of equal volumes were taken from reaction mixtures at preset time intervals, diluted with the same amount of DMF, and placed in an optical cuvette.

Electronic absorption spectra were recorded on a Cary-100 spectrophotometer at ambient temperature. ¹H NMR spectra were recorded on a Bruker AV III-500 spectrometer. IR spectra were obtained on an Avatar 360-FT-IR-ESP spectrometer as KBr pellets. Elemental analysis was carried out with a Flash EA 1112 analyzer. Thin layer chromatography was performed on Silufol plates.

Synthesis of cobalt(II) 5,10,15,20-tetraphenylporphyrinate (IV). Porphyrin I (0.05 g) was dissolved in 70 mL of dimethylformamide, 0.14 g of cobalt(OAc)₂ was added (molar ratio 1 : 10), the mixture was heated under reflux for 20 s. The mixture was cooled and poured into water. The precipitate was separated by filtration, washed with water, dried, and chromatographed on aluminum oxide (Merck) using methylene chloride as an eluent. Yield 0.035 g (0.0514 mmol), 63%. *R_f* = 0.77 (hexane–chloroform, 1 : 1, as eluent).

For C₄₄H₂₈CoN₄ anal. calcd. (%): C, 78.69; N, 8.34; H, 4.20.

Found (%): C, 78.58; N, 8.30; H, 4.15.

IR (ν, cm⁻¹): 2917, 2849 ν(C–H, Ph), 1694, 1599 ν(C=C, Ph), 1437 ν(C=N), 1350 ν(C–N), 1150, 1073 δ(C–H, Ph), 1004 ν(Co–N), 796 γ(C–H, pyrrole ring), 752, 702 γ(C–H, Ph), 470 ν(Co–N).

¹H NMR (CDCl₃, δ, ppm): 16.05 (br s, 8H, pyrrole ring), 13.20 (br s, 8H, *ortho*-C₆H₅), 8.20 (t, 8H, *meta*-C₆H₅), 8.01 (br s, 4H, *para*-C₆H₅).

For tetraphenylporphyrin (I) ¹H NMR (CDCl₃, δ, ppm): 8.87 (s, 8H, pyrrole ring), 8.25 (d, 8H, *ortho*-CDCl₃): 7.82 (m, 8H, *meta*-C₆H₅ and 4H, *para*-C₆H₅), –2.65 (s, 2H, NH).

Synthesis of cobalt(III) 5,10,15,20-tetraphenylporphyrinate (V) (E = CN⁻, H₂O). A mixture of 0.025 g of complex IV and 0.042 g of DDQ (molar ratio 1 : 5) was dissolved in 30 mL of CHCl₃ and kept at ambient temperature for 4 h. The reaction mixture was filtered, carefully washed with water, the organic layer was separated, the solvent was evaporated. Yield 0.021 g (0.0294 mmol), 80%. Chromatography on silica gel with chloroform as an eluent afforded 0.016 g (0.0224 mmol), 60% of compound V. *R_f* = 0.69 (hexane–chloroform, 1 : 1, as eluent).

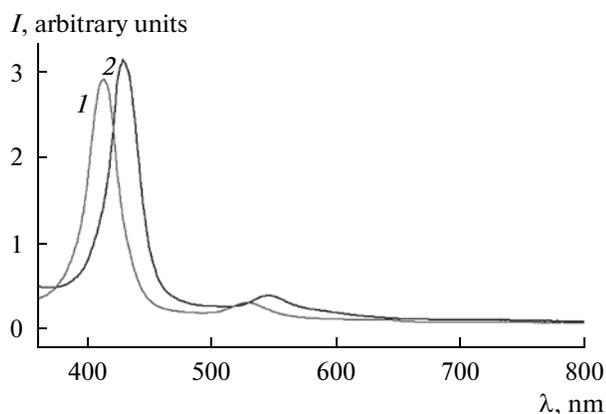
For C₄₅H₃₀CoN₅O anal. calcd. (%): C, 75.52; N, 9.79; H, 4.23.

Found (%): C, 75.43; N, 9.70; H, 4.18.

¹H NMR (CDCl₃, δ, ppm): 9.18 (s, 8H, pyrrole ring), 8.23 (d, 8H, *ortho*-C₆H₅), 7.78 (m, 8H, *meta*-C₆H₅, 4H, *para*-C₆H₅).

Cobalt(II) 5,10,15,20-tetra(4'-methoxyphenyl)porphyrinate (VI) and cobalt(II) 5,10,15,20-tetra(4'-chlorophenyl)porphyrinate (VIII) were obtained similarly to compound IV.

Cobalt(II) 5,10,15,20-tetra(4'-methoxyphenyl)porphyrinate (VI). Porphyrin II (0.05 g) and 0.12 g of cobalt(OAc)₂ in 30 mL of DMF were heated to boil-



Electron absorption spectra in DMF: 1, IV; 2, V.

ing temperature. Yield 0.036 g (0.0451 mmol), 67%. $R_f = 0.80$ (hexane–chloroform, 1 : 1, as eluent).

For $C_{48}H_{36}CoN_4O_4$ anal. calcd. (%): C, 72.82; N, 7.08; H, 4.58.

Found (%): C, 71.90; N, 6.65; H, 4.47.

1H NMR ($CDCl_3$, δ , ppm): 16.14 (br s, 8H, pyrrole ring), 13.24 (br s, 8H, *ortho*- C_6H_4), 8.11 (d, 8H, *meta*- C_6H_4), 4.10 (s, 12H, *para*- OCH_3).

IR (ν , cm^{-1}): 2920, 2851 (ν (C–H, Ph)), 1607, 1507 (ν (C=C, Ph)), 1462 (ν (C=N)), 1351 (ν (C–N)), 1288, 1248 (δ (CH_3O)), 1175 (δ (C–H, Ph)), 1001 (ν (C–C)), 800 (γ (C–H, pyrrole ring)), 717, 608 (γ (C–H, Ph)), 500 (ν (Co–N)).

Cobalt(III)E 5,10,15,20-tetra(4'-methoxyphenyl)porphyrinate (VII) ($E = CN^-$, H_2O) was obtained similarly to compound V. Molar ratio VI : DDQ = 1 : 3. Reaction time was 2 h. Complex VI (0.025 g) was converted into compound VII (0.022 g, 0.0263 mmol, 82%). Chromatography on silica gel using chloroform as an eluent gave VII in ~60% yield. $R_f = 0.74$ (hexane–chloroform, 1 : 1, as eluent).

For $C_{49}H_{38}CoN_5O_5$ anal. calcd. (%): C, 70.42; N, 8.38; H, 4.58.

Found (%): C, 70.33; N, 8.30; H, 4.52.

1H NMR ($CDCl_3$, δ , ppm): 9.14 (s, 8H, pyrrole ring), 8.52 (d, 8H, *ortho*- C_6H_4), 8.11 (d, 8H, *meta*- C_6H_4), 4.11 (s, 12H, *para*- OCH_3).

Cobalt(II) 5,10,15,20-tetra(4'-chlorophenyl)porphyrinate (VIII). Porphyrin III (0.05 g) and 0.12 g of cobalt(OAc)₂ in 20 mL of DMF were heated to boiling temperature. Yield 0.035 g (0.0433 mmol), 65%. $R_f = 0.86$ (hexane–chloroform, 1 : 1, as eluent).

For $C_{44}H_{24}Cl_4CoN_4$ anal. calcd. (%): C, 65.29; N, 6.92; H, 2.71.

Found (%): C, 65.11; N, 6.87; H, 2.65.

1H NMR ($CDCl_3$, δ , ppm): 15.82 (br s, 8H, pyrrole ring), 13.00 (br s, 8H, *ortho*- C_6H_4), 8.15 (d, 8H, *meta*- C_6H_4).

IR (ν , cm^{-1}): 2918, 2847 (ν (C–H, Ph)), 1640, 1488 (ν (C=C, Ph)), 1448 (ν (C=N)), 1350 (ν (C–N)), 1092

δ (C–H, Ph), 1002 (ν (C–C)), 891 (ν (C–Cl)), 806 (γ (C–H, pyrrole ring)), 718 (γ (C–H, Ph)), 505 (ν (Co–N)).

Cobalt(III)E 5,10,15,20-tetra(4'-chlorophenyl)porphyrinate (IX) ($E = Cl^-$, H_2O). Complex VIII (0.025 g), was dissolved in 10 mL of DMF, 1.5 mL of hydrochloric acid was added, the mixture was stirred, kept at ambient temperature for 15 min. Chloroform (30 mL) and water (100 mL) were added to the reaction mixture, the organic layer was separated, washed with water, the solvent was evaporated to minimal volume, the residue was precipitated from hexane to give 0.02 g (0.0235 mmol) of complex IX, 76%. $R_f = 0.79$ (hexane–chloroform, 1 : 1, as eluent).

For $C_{44}H_{26}Cl_5CoN_4O$ anal. calcd. (%): C, 61.25; N, 6.49; H, 3.04.

Found (%): C, 61.14; N, 6.38; H, 2.97.

1H NMR ($CDCl_3$, δ , ppm): 9.15 (s, 8H, pyrrole ring), 8.63 (d, 8H, *ortho*- C_6H_4), 8.05 (d, 8H, *meta*- C_6H_4).

RESULTS AND DISCUSSION

Cobalt complexes of simple porphyrin derivatives are known to show low redox potential $E_{(Co^{2+}/Co^{3+})}$ of the central ion. The magnitude of this potential is determined mainly by the donor-acceptor properties of tetrapyrrole ligands and can vary in a wide range. Electron-donating substituents in the tetrapyrrole macrocycle cause anode shift of redox potential and stabilize (X)Co^{III}P complexes, while electron-withdrawing groups produce cathode shift and stabilize Co^{II}P complexes (where P is porphyrin) [10, 11]. Therefore cobalt complexes with the majority of porphyrin ligands are characterized by oxidation state +3, while those with phthalocyanines have oxidation state +2 [10, 11].

Studies showed that the complexation of porphyrin I with cobalt(OAc)₂ (molar ratio 1 : 10) in boiling DMF proceeds over 20 s. Electron absorption spectrum of a sample taken from reaction mixture and dissolved in DMF shows a band at $\lambda_1 = 528$ nm and no bands of initial compound I with maxima at 647, 590, 547, and 513 nm (figure). The hypsochromic shift of Soret peak in the electron absorption spectrum of complex IV as compared with porphyrin I in DMF is 8 nm. The character of electron absorption spectra of complex IV does not change on increase in reaction time up to 1 min in boiling DMF. Compound IV is stable in solid state at ambient temperature for a long time (~120 days). The complexation of porphyrin I with Co(OAc)₂ (molar ratio 1 : 10) in DMF at ambient temperature proceeds slowly. The electronic absorption spectra of reaction mixture after 7 days shows the bands of initial porphyrin I at 647, 590, 547, 513, and 415 nm and emerging bands of complex IV with maxima at 528 and 407 nm. Forty days later, the electronic absorption spectra of reaction mixture exhibits two Soret peaks: from initial compound I at $\lambda_{max} = 416$ nm and from cobalt(III) complex with $\lambda_{max} = 429$ nm. Absorption

maxima in electronic absorption spectra due to formation of $\text{Co}^{\text{III}}\text{P}$ complex are observed in DMF at 578, 544, and 429 nm and reached over 50 days at ambient temperature. However, the obtained $\text{Co}^{\text{III}}\text{P}$ complex undergoes partial reduction to initial $\text{Co}^{\text{II}}\text{P}$ (**IV**) during isolation from reaction mixture. When 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) was used as oxidizing agent [12], the oxidation of cobalt(II) tetraphenylporphinate into $\text{Co}^{\text{III}}\text{E}$ tetraphenylporphinate (compound **V**) proceeds at reactants molar ratio of 1 : 5 in chloroform for ~4 h at ambient temperature. After isolation from reaction mixture, compound **V** is stable in solid state and solution (CHCl_3).

The introduction of methoxy groups (+J effect) and chlorine atoms (+C effect) in the *para* position of the benzene rings of tetraphenylporphin enhances the rate of **II** and **III** complexation with $\text{Co}(\text{OAc})_2$ in DMF in comparison with the parent compound. According to literature data [13], electron-donating substituents increase electron density on the tertiary nitrogen atoms of the macrocycle thus enhancing the coordination interaction of the cation of solvate complex $[\text{MX}_2(\text{Sol})_{n-2}]$ with porphyrin in transition state. Thus, the corresponding cobalt(II) porphyrinates (**VI**, **VIII**) form under conditions similar to those for **IV** on heating of reaction mixture to boiling point. $\text{Co}^{\text{III}}\text{E}$ porphyrinate (E = CN^- , H_2O) (**VII**) forms upon dissolution of compound **VI** and DDQ (in molar ratio 1 : 3) in CHCl_3 during 2 h. Cobalt(II) porphyrinate (**VIII**) containing electron-withdrawing chlorine atoms in the benzene rings undergoes only partial oxidation to cobalt(III) porphyrinate under conditions similar to those for **IV** and **VI**. Compound **VIII** can be oxidized to $\text{Co}^{\text{III}}\text{P}$ upon the use of tenfold excess of DDQ and increase in reaction time to ~20 h, however a mixture of cobalt(II) and cobalt(III) complexes forms on isolation from reaction mixture. The oxidation of compound **VIII** with hydrochloric acid in DMF solution for ~15 min at ambient temperature leads to formation of $\text{Co}^{\text{III}}\text{E}$ porphyrinate (E = Cl^- , H_2O) (**IX**). Compound **IX** is stable in solid state and CHCl_3 solution.

The data of elemental analysis, electron absorption, ^1H NMR, and IR spectroscopy agree well with the structure of prepared compounds. The hypsochromic shift of bands in electronic absorption spectra for cobalt(II) tetraphenylporphyrinate (**IV**) as compared with Zn(II) porphyrinate (**X**) is explained by the strong π dative interaction of $d_{\pi}-e_{\sigma}(\pi^*)$ type between the metal ion and the porphyrin macrocycle. The cobalt(II) \rightarrow cobalt(III) oxidation of tetraarylporphyrinates leads to the bathochromic shift of absorption bands in electronic absorption spectra (the figure, table). cobalt(II) tetraphenylporphyrinate like cobalt(II) octaethylporphyrinate [5] exhibits paramagnetic properties ($3d^7$ configuration). The ^1H NMR spectrum of cobalt(II) tetraphenylporphyrinate in CDCl_3 shows the signals of β pyrrole protons and *ortho*

protons at 16.05 and 13.20 ppm and signals of *meta* and *para* protons at 8.20 and 8.01 ppm. The cobalt(II) \rightarrow cobalt(III) oxidation of tetraphenylporphyrinate ($3d^6$ configuration) brings about the considerable upfield shift of signals of β pyrrole and *ortho* protons approximately by 7 and 5 ppm, respectively. The signals of *meta* and *para* protons of the oxidized form (cobalt(III)) are shifted upfield by ~0.4 ppm as compared with the reduced form (cobalt(II)).

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 11–03–00003-a), the Seventh Framework Program of the European Community for Research, Technological Development, and Demonstration Activities, IRSES-GA-2009-247260), and the Federal Targeted Program “Research and Research-Training Resources of the Innovative Russia” for 2009–2013 (State Contract 02.740.11.0857).

REFERENCES

1. B. D. Berezin, O. A. Golubchikov, L. V. Klopova, and A. V. Sviridov, *Zh. Fiz. Khim.* **56**, 1639 (1982).
2. O. A. Golubchikov, L. V. Klopova, A. V. Sviridov, and B. D. Berezin, *Zh. Fiz. Khim.* **57**, 603 (1983).
3. D. B. Berezin and O. V. Toldina, *Koord. Khim.* **30**, 616 (2004).
4. A. Shirazi and H. M. Goff, *Inorg. Chem.* **21**, 3420 (1982).
5. B. B. Ali, M. S. Belkhiria, M. Giorgi, and H. Nasri, *Open J. Inorg. Chem.* **1**, 39 (2011).
6. A. D. Adler, F. R. Longo, et al., *J. Inorg. Nucl. Chem.* **32**, 2443 (1970).
7. N. Zh. Mamardashvili and O. I. Koifman, *Abstracts of Papers, International Conference on Physicochemical Principles of the Newest Technologies of the 21st Century*, 275 (2005).
8. N. Zh. Mamardashvili and W. Dehaen, *Abstracts of the 5th Sigma–Aldrich Organic Synthesis Conference, Sol Cress Spa (Belgium)*, 43 (2001).
9. C. K. Mann and K. K. Barnes, *Electrochemical Reactions in Nonaqueous Systems* (Khimiya, Moscow, 1970) [in Russian].
10. *Porphyryns: Spectroscopy, Electrochemistry, and Application*, Ed. by N. S. Enikolopyan (Nauka, Moscow, 1987) [in Russian].
11. G. P. Shaposhnikov, V. P. Kulinich, and V. E. Maizlish, in *Advances in Porphyrin Chemistry*, Ed. by O. A. Golubchikov (NII khimii SPbGU, St. Petersburg, 1999), Vol. 2, p. 190 [in Russian].
12. E. A. Kokareva, Candidate’s Dissertation in Chemistry (Ivanovo State Chemical Engineering Univ., Ivanovo, 2011).
13. B. D. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanines* (Nauka, Moscow, 1978) [in Russian].

Translated by I. Kudryavtsev