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PHYSICAL CHEMISTRY OF SOLUTIONS

Copper(II), Cobalt(II), Cobalt(III), and Tin(IV) 5,10,15,20-Tetraphenyl Tetrabenzoporphyrinates: Synthesis and Properties

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Abstract—The complexation reactions of 5,10,15,20-tetraphenyl tetrabenzoporphyrin and the metal exchange reactions of its cadmium(II) complex with copper(II), cobalt(II), and tin(II) acetates and chlorides in a chloroform–methanol mixture and dimethylformamide were studied spectrophotometrically. Corresponding copper(II), cobalt(II), cobalt(II), and tin(IV) porphyrinates were synthesized and identified.

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In recent years, metal porphyrins have been widely studied and applied as organic semiconductors, dyes, sensibilizers, and thermal and light stabilizers. Interest in the synthesis and study of porphyrin complexes with variable valency metals was provoked by the possibility of their application in catalysis and biomedicine [1].

Copper(II), cobalt(II), cobalt(III), tin(II), and tin(IV) tetraphenylporphirine complexes were described in [2–7]. Copper(II), cobalt(III), and tin(IV) tetrabenzoporphyrinates were synthesized in [8–10]. Galanin [11] showed shown that cobalt and tin *meso*-tetraphenyl tetrabenzoporphyrin complexes are formed under boiling of dimethylformamide (DMF) solutions of the corresponding tetraphenyl tetrabenzoporphyrin ligand with cobalt(II) and tin(II) chlorides for 2.5 and 3 h, respectively. The tin(IV) complex yield was 22% [11].

In this work, the coordination reactions of 5,10,15,20-tetraphenyl tetrabenzoporphyrin (**I**) and the metal exchange reactions of its cadmium complex (**II**) with copper(II), cobalt(II), and tin(II) acetates and chlorides in a chloroform–methanol mixture and DMF were studied spectrophotometrically.

EXPERIMENTAL

Electronic absorption spectra (EASs) were recorded on a Cary 100 spectrophotometer at room temperature. ^{1}H NMR spectra were taken on a Bruker AV III-500 spectrometer (internal standard was tetramethyl silane (TMS)). Mass spectra were obtained on a Maldi TOF Shimadzu Biotech Axima Confidence mass spectrometer (solvent was acetonitrile). Elemental analysis was performed on a Flash EA 1112 analyzer.

5,10,15,20-Tetraphenyl tetrabenzoporphyrin (I) was synthesized as described in [11]. DMF, $CHCl_3$, benzene, $Cd(OAc)_2$ of chemically pure grade, and methanol (Fisher Scientific) were used without additional purification. $CuCl_2$, $CoCl_2$, and $SnCl_2$ of chemically pure grade were calcined at 200°C for 4 h. $Cu(OAc)_2$ and $Co(OAc)_2$ of chemically pure grade were recrystallized from glacial acetic acid and dried at 80°C for 1 h.

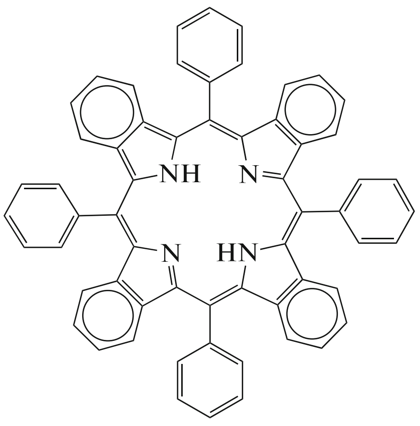
The complexation and metal exchange reactions were monitored spectrophotometrically: reaction mixture samples were taken in certain time intervals, dissolved in chloroform or DMF, and placed into an analytical cell. The obtained complexes were subjected to chromatography on alumina (Merck).

The synthesized complexes were characterized by electron absorption and ^{1}H NMR spectroscopy, mass spectrometry, and elemental analysis.

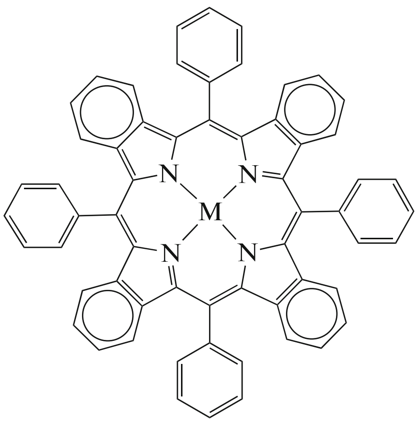
EAS of porphyrin **I** in chloroform, λ, nm ($\log(\varepsilon)$): 695 (3.72), 636 (4.18), 592 (3.82), 465 (5.06).

^{1}H NMR spectrum ($CDCl_3$) of porphyrin **I** (δ, ppm): 8.38 d (8H, *ortho*-C_6H_5), 7.95 t (4H, *para*-C_6H_5), 7.88 d (8H, *meta*-C_6H_5), 7.22–7.12 m (16H, benzene rings), −1.18 (2H, NH protons).

Mass spectrum, m/z (I_{rel}, %) of porphyrin **I**: 814 (89) $[M]^+$.



(I)



M = Cd(II) (II),
M = Cu(II) (III),
M = Co(II) (IV),
M = Co(III)OH (V),
M = Sn(IV)(OH)$_2$ (VI).

Synthesis of cadmium(II) 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (II). A mixture of porphyrin **I** (0.02 g, 0.02465 mmol) and Cd(OAc)$_2$ (0.057 g, 0.245 mmol) was dissolved in DMF (4 mL), heated to boiling, boiled in a refluxed flask for 1 min, cooled, and the precipitate settled after addition of water was filtered out, washed with water, dried, and subjected to chromatography on alumina (eluent was benzene). The yield was 0.017 g (0.0184 mmol) or 75%. For $C_{60}H_{36}N_4Cd$, anal. calcd. (%): C, 77.88; N, 6.05; H, 3.92. Found (%): C, 77.65; N, 6.15; H, 3.99.

^{1}H NMR spectrum (C_6D_6), δ, ppm: 8.37 d (8H, *ortho*-C_6H_5), 7.73 t (4H, *para*-C_6H_5), 7.63 d (8H, *meta*-C_6H_5), 7.15–7.08 m (16H, benzene rings).

Copper(II) 5,10,15,20-tetraphenyl tetrabenzoporphirinate (III). (a) A mixture of porphyrin **I** (0.02 g, 0.0245 mmol) and Cu(OAc)$_2$ (0.045 g, 0.245 mmol) was dissolved in a mixture of chloroform (5 mL) and methanol (3 mL), heated to boiling, boiled for 10 s, cooled, and the organic layer formed after addition of water was separated out, washed with water, dried with Na_2SO_4, evaporated to a minimum amount, and subjected to chromatography on alumina (eluent was chloroform). The yield was 0.018 g (0.0205 mmol) or 85%. (b) A mixture of porphyrin **I** (0.02 g, 0.0246 mmol) and Cu(OAc)$_2$ (0.045 g, 0.246 mmol) or $CuCl_2$ (0.033 g, 0.246 mmol) was dissolved in DMF (4 mL), heated to boiling, cooled, and the precipitate settled after addition of water was filtered out, washed with water, dried, and subjected to chromatography on alumina (eluent was chloroform). The yield of complex **III** was 0.017 g (0.0194 mmol) or 80%. (c) A mixture of complex **II** (0.02 g, 0.0215 mmol) and Cu(OAc)$_2$ (0.039 g, 0.215 mmol) or $CuCl_2$ (0.029 g, 0.215 mmol) was dissolved in DMF (4 mL), heated to boiling, and treated by method (b). The yield was 0.017 g (0.0194 mmol) or 89%.

Mass spectrum, *m/z* (I_{rel}, %): 875 (69) $[M]^+$.

Cobalt(II) 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (IV) was synthesized as described for complex **III**: (b) porphyrin **I** (0.02 g, 0.0245 mmol), Co(OAc)$_2$ (0.043 g, 0.245 mmol), and DMF (4 mL) were heated to boiling. The yield was 0.017 g (0.0197 mmol) or 82%.

^{1}H NMR spectrum ($CDCl_3$,), δ, ppm: 13.17 br s (8H, *ortho*-C_6H_5), 12.40 br s (4H, *para*-C_6H_5), 9.80 br s (8H, *meta*-C_6H_5), 9.50 br s (8H, benzene rings in positions 3 and 6), 8.72 br s (8H, benzene rings in positions 4 and 5).

Mass spectrum, *m/z* (I_{rel}, %): 870.9 (100) $[M]^+$.

Co(III)(OH) · H_2O 5,10,15,20-tetraphenyl tetrabenzoporpyirinate (V) was synthesized as described in [11]. A mixture of porphyrin **I** (0.02 g, 0.0246 mmol) and $CoCl_2$ (0.064 g, 0.492 mmol) was dissolved in DMF (4 mL), heated to boiling, boiled for 2.5 h, cooled, and settled in a 20-% NaOH solution (30 mL), and the precipitate was filtered out, washed with water, and dried. The yield was 0.016 g (0.0176 mmol) or 72%.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 8. 17 d (8H, *ortho*-C_6H_5), 7.76 t (4H, *para*-C_6H_5), 7.50 d (8H, *meta*-C_6H_5), 7.20–7.10 m (16H, benzene rings in positions 3 and 6, 4 and 5). For $C_{60}H_{36}N_4Co(OH) \cdot H_2O$ anal. calcd. (%): C, 79.46; N, 6.18; H, 4.00. Found (%): C, 79.54; N, 6.11; H, 3.91.

Sn(IV)(OH)$_2$ 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (VI). (a) A mixture of porphyrin **I** (0.02 g, 0.0246 mmol) and $SnCl_2$ (0.046 g, 0.246 mmol) was dissolved in DMF (4 mL), heated to boiling, boiled for 2 min, and treated as described for complex **III** in method (b). The yield was 0.017 g (0.017 mmol) or 70%. (b) A mixture of complex **II** (0.02 g, 0.0215 mmol) and $SnCl_2$ (0.041 g, 0.215 mmol) was dissolved in DMF (4 mL), heated to boiling, and treated as described for complex **III** in method (b). The yield was 0.018 g (0.018 mmol) or 82%.

^1H NMR spectrum ($CDCl_3$), δ, ppm: 8. 40 d (8H, *ortho*-C_6H_5), 8.04 t (4H, *para*-C_6H_5), 7.97 d (8H, *meta*-C_6H_5), 7.55–7.45 m (16H, benzene rings).

Mass spectrum, m/z (I_{rel}, %): 965 (74) $[M]^+$.

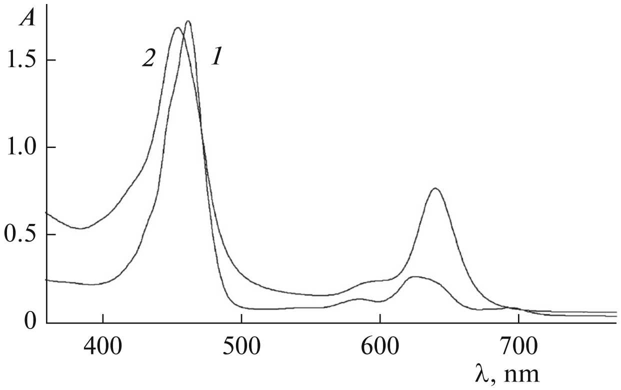


Fig. 1. EAS in DMF for (*1*) porphyrin **I** and (*2*) complex **IV**.

RESULTS AND DISCUSSION

Our studies show that the complexation of porphyrin **I** with $Cu(OAc)_2$ (molar ratio, 1 : 10) in a boiling chloroform–methanol mixture occurs in 10 s with the formation of copper(II) 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (**III**) as

$$H_2P + MX_2(solv)_{n-2} \rightleftharpoons (solv)_mMP + 2HX + (n-2-m)solv, \quad (1)$$

where H_2P is porphyrin, $MX_2(solv)_{n-2}$ is a solvate metal salt complex, solv is a solvent, and MP is metal porphyrin.

The EAS of a reaction mixture sample dissolved in chloroform contains bands with λ_{max} of 647, 598, 459, and 447 nm, but the initial compound bands with λ_{max} of 695, 636, 592, and 465 nm disappear. Complex **III** is readily formed in a strongly coordinating basic solvent, such as DMF: porphyrin I or its cadmium(II) complex with $Cu(OAc)_2$ or $CuCl_2$ must be heated to the solvent boiling temperature.

The heating of a DMF solution of porphyrin **I** and $Co(OAc)_2$ to the boiling temperature gives cobalt(II) 5,10,15,20-tenrqaphenyl tetrabenzoporphyrinate (**IV**) (Fig. 1). The EAS of the reaction mixture sample dissolved in DMF contains bands with λ_{max} of 638, 591, and 453 nm, but the initial compound bands with λ_{max} of 696, 626, 586, and 464 nm disappear. The reaction between tetrabenzoporphyrin and $Co(OAc)_2$ under similar conditions for 10 min gives cobalt(III) tetrabenzoporphyrinate [9]. An increase in the reactivity of porphyrin **I** with $Co(OAc)_2$ in DMF in comparison with tetrabenzoporphyrin can be explained by the transformation of the spatial macroring structure under the action of bulky phenyl substituents. Some X-ray diffraction data for a zinc(II) complex with porphyrin **I** were obtained in [12]. The zinc(II) porphyrin was shown to be in a saddle conformation with an average deviation of C_β atoms from the initial macroring plane a $\Delta C_\beta = 0.765$ Å. To obtain cobalt(III) 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (**V**), porphyrin **I** and $CoCl_2$ (molar ratio, 1 : 20) in DMF must be boiled for 2.5 h with further separation of the reaction mixture into an aqueous NaOH solution. EAS of complex V in benzene contains bands with λ_{max} of 652, 608, and 475 nm. The reaction between porphyrin **I** and $Co(OAc)_2$ in a boiling chloroform–methanol mixture for 2 min results in the formation of cobalt(II) and cobalt(III) tetraphenyl tetrabenzoporphyrinates. EAS (mixture of the synthesized complexes in benzene), λ_{max}, nm: 647, 600, 467.

In contrast to the manganese porphyrins [13], complex **IV** is oxidized to the cobalt(III) complex during shaking of a DMF solution with solid KOH in a sealed cell for 10–15 min. EAS of the reaction mixture contains bands with λ_{max} of 654, 605, and 475 nm, which correspond to complex **V**. An increase in the time of reaction with KOH to 1.5 h leads to the shift of EAS bands to 664, 622, and 493 nm (Fig. 2) probably due to additional extracoordination to the trivalent cobalt cation. The separation of the synthesized compound from an alkaline solution results in the formation of cobalt(III) tetraphenyl tetrabenzoporphyrinate (**V**).

The character of EAS of cobalt(II) porphyrinate in a DMF solution remains unchanged. Cobalt(II) porphyrinate (**IV**) is formed upon dissolution of a mixture of cobalt(II) and cobalt(III) tetraphenyl tetrabenzoporphyrinates or complex V in DMF for several minutes. In contrast to complex V, cobalt(III) tetrabenzoporphyrinate is not reduced in a DMF solution [9].

Some tin tetraphenyl porphine complexes [TPP-Sn(II), TPP-Sn(IV)] were described in [7]. Tin(II) and tin(IV) tetraphenylporphyrinates were synthesized by the reaction between tetraphenylporphine and tin(II) chloride, respectively, in a tetrahydrofurane–pyridine mixture and pyridine.

Studies show that the boiling of a solution of porphyrin **I** with tin(II) chloride in DMF for 2 min leads to the formation of $Sn(IV)(OH)_2$ 5,10,15,20-tetraphenyl tetrabenzoporphyrinate (**VI**). EAS of the sample dissolved in DMF contains bands with λ_{max} of 658, 612, and 463 nm. To synthesize $Sn(IV)(OH)_2$ tetrabenzoporphyrinate [TBP-Sn(IV)], a DMF solution of

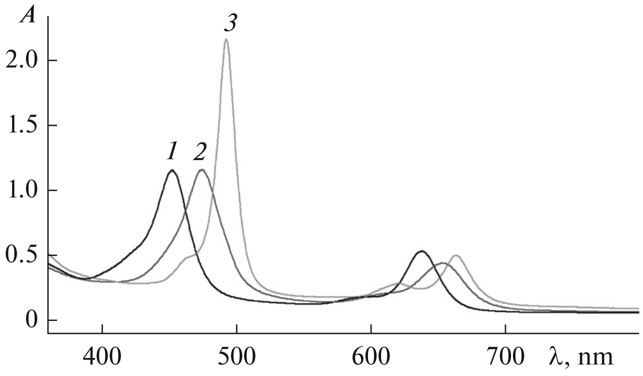


Fig. 2. EAS in DMF in the presence of KOH_{solid} (*1*) upon dissolution of complex **IV** and (*2*, *3*) in (*2*) 15 min and (*3*) 1.5 h.

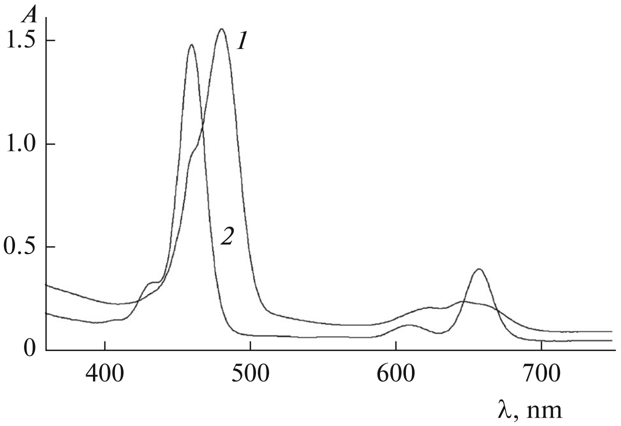


Fig. 3. EAS in DMF for (*1*) complex **II** and (*2*) complex **VI**.

porphyrin with tin(II) chloride must be boiled for 3 h under comparable conditions [10].

The heating of a DMF solution of complex II with tin(II) chloride to the boiling temperature also results in the formation of complex **VI** (Fig. 3) as

$$\begin{gathered} \mathrm{CdP} + \mathrm{MX_2(solv)}_{n-2} \\ \rightarrow \mathrm{CdX_2(solv)}_{n-2}\mathrm{M(P)(OH)_2}. \end{gathered} \tag{2}$$

An essential decrease in the time of the metal exchange reaction of the labile cadmium complex in comparison with complexation can be explained by the absence of need for the cleavage of NH bonds in the macrocycle.

The characteristics of EASs for the synthesized complexes are given in the table. The hypsochromic shift of the absorption bands of copper(II) and cobalt(II) porphyrinates in comparison with cadmium(II) and zinc(II) porphyrinates is explained by the existence of strong π-donating interaction between the metal ion and the porphyrin d_π-$e_g(\pi^*)$-type macroring. The oxidation Co(II) → Co(III) leads to the bathochromic shift of EAS bands. An essential bathochromic shift of EAS bands is observed when passing from tin(IV) tetraphenylporphyrinate to tin(IV) tetrabenzoporphyrinate and tin(IV) tetraphenyl tetrabenzoporphyrinate (table).

It is known that cobalt(II) porphyrinates exhibit paramagnetic properties ($3d^7$ configuration) [14]. This leads to that the proton signals in the ^{1}H NMR spectra of cobalt(II) porphyrins are considerably broadened and appear in a weak field. The spectrum of complex **IV** contains the signals from the *ortho*-, *para*-, and *meta*-protons of phenyl rings at 13.17, 12.40, and 9.8 ppm, and the signals from condensed benzene rings in the region of 9.5–8.7 ppm. In the spectrum of cobalt(III) porphyrinate, the signals from phenyl and benzene rings appear in a strong field in the region of 8.17–7.10 ppm. The ^{1}H NMR spectrum of $Sn(IV)(OH)_2$ porphyrinate (**VI**) contains the signals from phenyl rings at 8.40–7.97 ppm and the signals from benzene rings at 7.55–7.45 ppm.

Electronic absorption spectra of cadmium(II), zinc(II), copper(II), cobalt(II), cobalt(III), tin(II), and tin(IV) porphyrinates (λ, nm (logε))

Complex	Solvent	Band I	Band II	Soret band
I-Cd(II)	DMF	654 (4.20)	618 (4.13)	481 (5.08)
I-Cd(II)	Benzene	649 (4.19)	611 (3.96)	476 (4.87)
I-Zn(II)*	DMF	653 (4.34),	610 (4.04)	466 (5.09)
I-Cu(II)	DMF	646 (4.40)	598 (4.12)	447 (4.71), 458 (4.73)
I-Co(II)	DMF	638 (4.49),	591 (3.99)	453 (4.83)
I-Co(III)	Benzene	652 (4.42),	608 (4.07),	475 (4.84)
I-Sn(IV)*	Benzene	656 (4.21)	612 (4.06)	460 (4.97)
I-Sn(IV)	DMF	657 (4.48)	593	461 (5.05), 434 (4.43)
TBP-Sn(IV)**	DMF	638 (4.63)	560	430 (4.81), 413
TPP-Sn(IV)***	$CHCl_3$	600	488	426
TPP-Sn(II)***	THF	692		397

The data were taken from: * [11], ** [10], and *** [7].

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REFERENCES

1. *Porphyrins: Spectroscopy, Electrochemistry, Applications*, Ed. by N. S. Enikolopyan (Nauka, Moscow, 1987) [in Russian].
2. G. D. Dorough, J. R. Miller, and F. M. Huennekens, J. Am. Chem. Soc. **73**, 4315 (1951).
3. A. Shirazi and H. M. Goff, Inorg. Chem. **21**, 3420 (1982).
4. F. Shunichi, K. Hironori, S. Tomoyoshi, and O. Seiji, Chem. Commun. **17**, 1984 (2002).
5. D. Scherson, A. A. Tanaka, S. L. Gupta, et al., Electrochim. Acta **31**, 1247 (1986).
6. N. V. Chizhova, R. S. Kumeev, and N. Zh. Mamardashvili, Russ. J. Inorg. Chem. **58**, 740 (2013).
7. D. P. Arnold and J. Blok, Coord. Chem. Rev. **248**, 299 (2004).
8. E. B. Karavaeva, T. I. Potapova, and B. D. Berezin, Izv. Vyssh. Uchebn. Zaved., Ser.Khim. Khim. Tekhnol. **21** (8), 1099 (1978).
9. N. V. Chizhova and N. Zh. Mamardashvili, Proceedings of the 7th International Conference "Kinetics and Crystallization Mechanisms", Ivanovo, 2014 (Ivanovo, 2014), p. 195 [in Russian].
10. S. A. Vinogradov and D. F. Wilson, J. Chem. Soc., Perkin Trans. 2, 103 (1995).
11. N. E. Galanin, Extended Abstract of Candidate's Dissertation in Chemistry (IGKhTU, Ivanovo, 2002).
12. R. J. Cheng, Y. R. Chen, and S. L. Wang, Polyhedron **12**, 1353 (1993).
13. V. B. Sheinin, N. V. Chizhova, and A. O. Romanova, Russ. J. Gen. Chem. **80**, 351 (2010).
14. B. B. Ali, M. S. Belkhiria, M. Giorgi, and H. Nasri, Open J. Inorg. Chem. **1**, 39 (2011).

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