ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 6, pp. 1470–1473. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © E.M. Kuvshinova, I.A. Vershinina, S.A. Syrbu, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 6, pp. 1004–1008.

# Coordination Properties of Trimeric Porphyrin in Acetic Acid

**E. M. Kuvshinova[a], I. A. Vershinina[b], and S. A. Syrbu[a]**

[a] *Ivanovo State University of Chemistry and Technology, Scientific Research Institute of Macroheterocyclic Compounds, Sheremetevskii pr. 7, Ivanovo, 153000 Russia*
*e-mail: kuvshinovae@isuct.ru*

[b] *Institute of Solutions Chemistry, Russian Academy of Sciences, Ivanovo, Russia*

Received November 20, 2014

**Abstract**—Trimeric porphyrin $H_6TP$ as well as its binuclear $Cu_2H_2TP$ and trinuclear $Cu_3TP$ copper complexes have been prepared. Kinetic features of $H_6TP$ and $Cu_2H_2TP$ complexes formation with copper(II) acetate in acetic acid as well as dissociation kinetics of $Cu_2H_2TP$ and $Cu_3TP$ in acetic acid medium in the presence of sulfuric acid have been studied.

**Keywords:** porphyrin, metal, complex formation, coordination

**DOI:** 10.1134/S1070363215060183

The earlier studies on formation and dissociation of metal complexes with mono- and dimeric porphyrins in organic solvents [1–6] have revealed that distortion of the porphyrin fragments planarity significantly affects the reactions kinetics. In extension of our studies of spatially distorted porphyrins, we have prepared the trimeric porphyrin-type ligand $H_6TP$ and the corresponding binuclear $Cu_2H_2TP$ (see Scheme 1) and trinuclear $Cu_3TP$ copper complexes [7]. Here we report on selected coordination properties of these compounds in acetic acid medium.

The reaction rate of the complexes formation and dissociation was studied by means of spectrophotometry. Spectral series recorded in the course of complex formation between $Cu_2H_2TP$ and copper(II) acetate in acetic acid medium clearly revealed the isosbestic points at 535 and 578 nm (Fig. 1). The final product spectrum was identical to that of the trinuclear complex $Cu_3TP$.

The rate of the complex formation reaction (1) could be expressed in the general form of Eq. (2).

$$Cu_2H_2TP + Cu(OAc)_2 = Cu_3TP + 2AcOH, \quad (1)$$

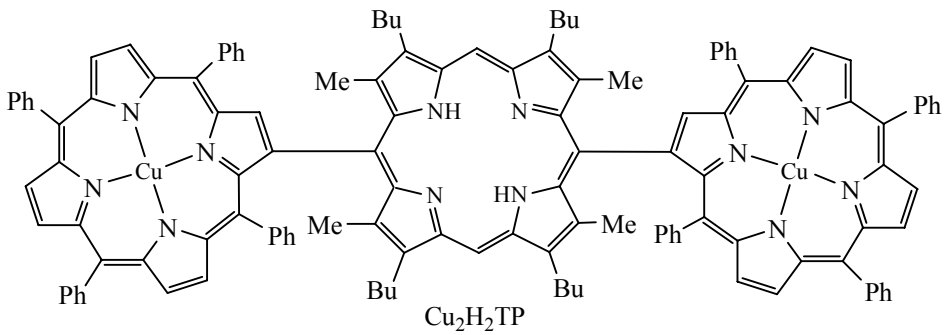
$$dc[Cu_2H_2TP]/dt = -k_v[Cu_2H_2TP]^m \cdot [Cu(OAc)_2]^n. \quad (2)$$

Since the 100-fold excess of copper(II) acetate with respect to the $Cu_2H_2TP$ porphyrin was used, the effective first-order rate constant $k_{eff}$ of the reaction (1) could be calculated using Eq. (3).

$$k_{eff} = 2.3/\tau \log [c^0(Cu_2H_2TP)/c(Cu_2H_2TP)]. \quad (3)$$

Indeed, the first reaction rate order with respect to the porphyrin ($m$ = 1) was evidenced by the linear

**Scheme 1.**




$Cu_2H_2TP$

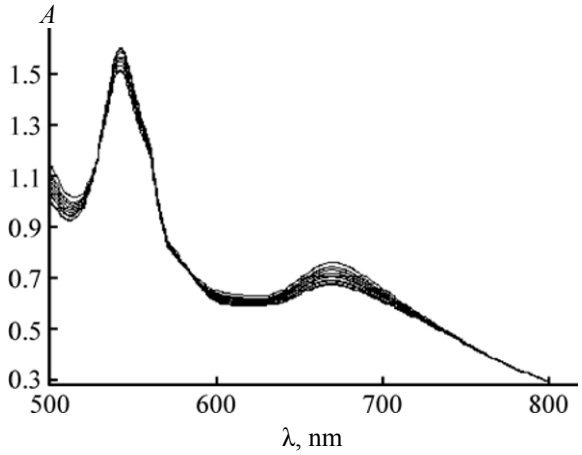



**Fig. 1.** Variation of the electron absorption spectrum in the course of coordination of $Cu_2H_2TP$ with $Cu(OAc)_2$ in acetic acid.

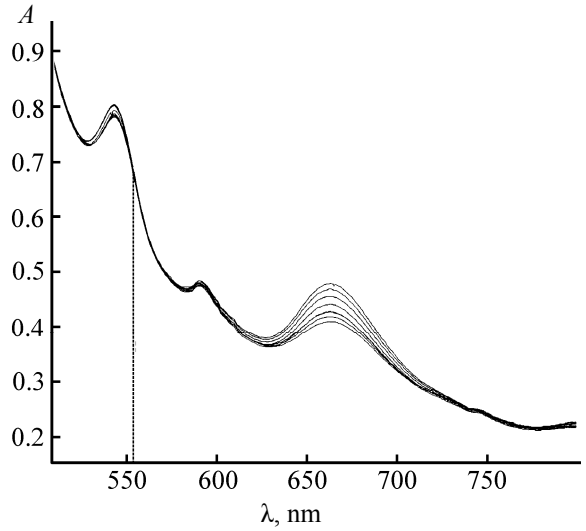



**Fig. 2.** Variation of the electron absorption spectrum in the course of dissociation of $Cu_2H_2TP$ in acetic acid in the presence of sulfuric acid.

kinetic curves when plotted as log $[c^0(Cu_2H_2TP)/c(Cu_2H_2TP)]$ versus the reaction time $\tau$, $c^0(Cu_2H_2TP)$ and $c(Cu_2H_2TP)$ being the starting and the current concentrations of the ligand. In turn, the $Cu_2H_2TP$ ligand concentration in the course of the reaction was determined from the spectrophotometry data using Eq. (4).

$$c(Cu_2H_2TP) = c^0(Cu_2H_2TP)\cdot(A - A_\infty)/(A_0 - A_\infty), \quad (4)$$

with $A_0$, $A$, and $A_\infty$ being the starting, the current, and the final absorbance of the reaction mixture.

The pseudo first-order reaction rate constant was then expressed with Eq. (5).

$$k_{eff} = 2.3/\tau \log [(A - A_\infty)/(A_0 - A_\infty)]. \quad (5)$$

The activation energy $E_a$ was calculated using the Arrhenius equation (6).

$$E_a = 19.1 T_1 T_2/(T_2 - T_1)\lg(k_2/k_1). \quad (6)$$

The activation entropy $\Delta S^{\neq}$ was calculated basing on the absolute reaction rates theory. Taking $\Delta H = E - RT$ and $\chi = 1$, Eq. (7) was derived.

$$\Delta S^{\neq} = 19.1 \log k_{298} + E_a/(298 - 253). \quad (7)$$

Transformation of the metal-free trimeric ligand $H_6TP$ into the trinuclear copper complex $Cu_3TP$ followed Eq. (8).

$$H_6TP + 3Cu(OAc)_2 = Cu_3TP + 6AcOH. \quad (8)$$

The complex formation involving the central porphyrin fragment of the ligand did not result in the mixture absorbance change at 535 and 578 nm, whereas the interaction of the side porphyrin rings with copper(II) ions significantly changed the absorbance at those wavelengths. Those features allowed determination of $k_{eff}$ values corresponding to coordination of the side cycles of the trimer.

The rate constant of the $(n + 1)$th order was calculated using Eq. (9).

$$k_{n+1} = k_{eff}/c^n[Cu(OAc)_2], \quad (9)$$

with $n$ being the reaction rate order with respect to the metal salt ($n = 0.5$ in the case of copper(II) acetate in acetic acid [8]).

Kinetic parameters of the reactions of copper complexes formation with the studied trimeric porphyrins are given in Table 1. For the sake of comparison the corresponding data for the spatially distorted 5,15-diphenyl-2,3,7,8,12,13,17,18-octaethylporphyrin ($H_2$DPOEP, its tetrapyrrole fragment was saddle-like [9, 10]) are given in the same table. The parameters of $Cu(OAc)_2$ reaction of the complex formation with the central tetrapyrrole cycle of the trimer were comparable to those of the reaction with $H_2$DPOEP. The bulky tetrapyrrole fragments in the *meso* positions should have induced strong distortion of the central cycle and influence kinetic parameters of reaction (1) more significantlyThe side tetrapyrrole fragments were likely located almost perpendicular to the plane of the central tetrapyrrole cycle, the latter being therefore nearly planar. The influence of the

**Table 1.** Kinetic parameters of coordination of $Cu_2H_2TP$, $H_6TP$, and $H_2DPOEP$ porphyrins with copper(II) acetate in acetic acid

| Porphyrin | λ, nm | $[Cu(OAc)_2] \times 10^3$, mol/L | $T$, K | $k_{eff} \times 10^3$, $s^{-1}$ | $k_{n+1} \times 10^2$, L $mol^{-1}$ $s^{-1}$ | $E_a$, kJ/mol | $\Delta S^{\neq}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|---|---|
| $Cu_2H_2TP$ | 670 | 5.0 | 298 | 0.98±0.05 | 1.39±0.07 | 71±2 | –50±10 |
| | | | 308 | 2.45±0.08 | 3.46±0.01 | | |
| | | | 318 | 6.0±0.40 | 8.48±0.50 | | |
| $H_6TP$ | 535 | 5.0 | 288 | 8.5±0.10 | 12±0.13 | 41±1 | –128±10 |
| | | | 298 | 15±0.30 | 21.2±0.42 | | |
| | | | 308 | 26±0.80 | 36.7±1.10 | | |
| $H_2DPOEP$ | 573 | 5.0 | 288 | 0.50±0.01 | 0.707±0.01 | 68±2 | –58±10 |
| | | | 298 | 1.3±0.10 | 1.84±0.12 | | |
| | | | 308 | 3.2±0.25 | 4.52±0.33 | | |

porphyrin fragments of the trimer was then barely reflected in the shielding of the central reactive site of the trimer with the side substituents. The phenyl groups hindered the contact with the copper(II) acetate existing in the form of bulky solvated complex $[Cu(OAc)_2Solv_4]$ [11–13], thus slowing down the reaction (1).

The major contribution to the activation energy is known to come from extension of the N–H porphyrin bonds [14]; therefore, the electron-donating substituents (Me or Bu) in the β positions of the central porphyrin fragment strengthening the N–H bond should have increased the $E_a$ value.

Dissociation of the binuclear and trinuclear copper complexes of the trimeric ligand could be described with Eqs. (10) and (11), respectively.

$$Cu_2H_2TP + 10H^+ = 2Cu^{2+} + H_{12}TP^{6+}, \quad (10)$$

$$Cu_3TP + 12H^+ = 3Cu^{2+} + H_{12}TP^{6+}. \quad (11)$$

Each tetrapyrrole fragment of the trimer after the dissociation existed in the twice deprotonated form $H_4P^{2+}$.

**Table 2.** Kinetic parameters of dissociation of $Cu_2H_2TP$ and $Cu_3TP$ in acetic acid in the presence of sulfuric acid (0.64 mol/L)

| Porphyrin | λ, nm | $T$, K | $k_{eff} \times 10^4$, $s^{-1}$ | $E$, kJ/mol |
|---|---|---|---|---|
| $Cu_2H_2TP$ | 665 | 318 | 0.26±0.02 | 83±1 |
| | | 328 | 0.69±0.03 | |
| | | 338 | 1.7±0.10 | |
| $Cu_3TP$ | 556 | 288 | 2.28±0.03 | 87±1 |
| | | 298 | 7.8±0.40 | |
| | | 308 | 25±1.00 | |

The dissociation kinetics was studied in acetic acid medium in the presence of sulfuric acid; the latter was taken in the higher than 100-fold excess with respect to the metal porphyrin, allowing for determination of the $k_{eff}$ value using Eq. (5).

The effective rate constants remained satisfactorily constant in the course of the experiment runs. The rate constant of dissociation of the copper complex with the central tetrapyrrole fragment was determined using the same method as described above for the complex formation. The transformation of $Cu_3TP$ into $(H_4P^{2+})_3$ did not result in the change of absorbance of the solution at the stage of the $Cu_2H_2TP$ complex dissociation (Fig. 2); hence, the absorbance change at that wavelength reflected the stability of the copper(II) complex with the central tetrapyrrole ring.

Results of kinetic studies of dissociation of $Cu_2H_2TP$ and $Cu_3TP$ in acetic acid in the presence of sulfuric acid (Table 2) revealed that the complex with the central tetrapyrrole fragment was 300 times more labile than that with the side tetrapyrrole fragments. The activation energy of the dissociation stages was practically the same. The effect of the reactive site shielding with phenyl groups seemed not significantly to affect the dissociation rate owing to the small size of the attacking particle ($H^+_{Solv}$).

In the course of $Cu_2H_2TP$ dissociation in acetic acid medium part of $H_2SO_4$ was consumed for protonation of the central metal-free porphyrin fragment. The rate of metal complexes with porphyrins dissociation is known to be proportional to the squared concentration of the solvated protons [15]. Therefore, the dissociation of copper(II) complexes with the side porphyrin fragments was slowed down. Another reason for the

higher stability of the copper(II) complex with the side groups of the trimeric ligand as compared to that with the central fragment was the deformation of the metal-free ring in $Cu_2H_2TP$ due to its protonation. The porphyrin ring deformation resulted in its lowered aromaticity and the increased basicity of the nitrogen atoms [16]. The non-uniform distribution of the electron density in the central porphyrin fragment of the trimer could facilitate the formation of the acceptor sites at the side fragments of $Cu_2H_2TP$, slowing down the dissociation. Hence, kinetic parameters of $Cu_2H_2P$ and $Cu_3P$ dissociation were mainly affected by the protonation of the central tetrapyrrole fragment of the trimer.

## EXPERIMENTAL

Copper(II) acetate ("analytically pure" grade) was recrystallized from aqueous acetic acid and dried at 117 °C. Acetic acid ("chemically pure" grade) was dried via fractional freezing and distillation. The water content (below 0.03 wt %) was determined by the Fischer titration. Sulfuric acid monohydrate was prepared by saturation of 95 wt % $H_2SO_4$ with oleum; water content was monitored by potentiometry.

The trimeric porphyrin $H_6TP$, its copper complexes $Cu_2H_2TP$ and $Cu_3TP$, and 5,15-diphenyl-2,3,7,8,12,-13,17,18-octaethylporphyrin $H_2DPOEP$ were prepared as described elsewhere [7, 9].

Electron absorption spectra of the solutions in closed cells were registered using a Hitachi U-2000 spectrophotometer at 288–338 K. The temperature was maintained constant with the accuracy of ±0.1 K.

Rates of the copper(II) acetate complexes formation with $H_6TP$, $Cu_2H_2TP$, and $H_2DPOEP$ in acetic acid medium as well as rates of $Cu_2H_2TP$ and $Cu_3TP$ dissociation in acetic acid medium in the presence of sulfuric acid were determined from the spectrophotometry data. The solution absorbance at the selected wavelength (see the main section for details) was measured 15–20 times at regular intervals in the course of the kinetic experiment. The root-mean-square error of the effective rate constants determination was 5–8% at the confidence probability of 95%.

The content of $Cu^{2+}$ in the solutions after the complexes dissociation was determined by atomic absorption with electrothermal atomization using an MGA-915 spectrometer.

## ACKNOWLEDGMENTS

This work was financially supported by the Russian Scientific Foundation (agreement 14-23-00204).

## REFERENCES

1. Takeda, I., Ohya, T., and Sato, M., *Inorg. Chem.,* 1992, vol. 31, p. 2877. DOI: 10.1021/ic00039a038.
2. Kuvshinova, E.M., Kuzmin, D.L., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A*., Russ. J. Gen. Chem*., 2003, vol. 73, no. 4, p. 652. DOI: 10.1023/A:1025673427341.
3. Kuvshinova, E.M., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A., *Russ. J. Gen. Chem*., 2004, vol. 74, no. 10, p. 1610. DOI: 10.1007/s11176-005-0066-8.
4. Kuvshinova, E.M., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov O.A., *Russ. J. Phys. Chem. (A),* 2005, vol. 79, no. 6, p. 871.
5. Kuvshinova, E.M., Semeikin, A.S., Syrbu, S.A., and Golubchikov, O.A., *Russ. J. Phys. Chem. (A),*2010, vol. 84, no. 9, p. 1516. DOI: 10.1134/S0036024410090128.
6. Kuvshinova, E.M., Semeikin, A.S., Kolodina, E.A., Syrbu, S.A., and Golubchikov, O.A., *Russ. J. Gen. Chem*., 2012, vol. 82, no. 3, p. 488. DOI: 10.1134/S1070363212030218.
7. Semeikin, A.S., Kuvshinova, E.M., Syrbu, S.A., and Golubchikov, O.A., *Izv. Vuzov, Ser. Khim. Khim. Tekhnol*., 2007, vol. 50, no. 6, p. 18.
8. Kuvshinova, E.M., Pukhovskaya, S.G., Guseva, L.Zh., Semeikin, A.S., and Golubchikov, O.A., *Zh. Fiz. Khim.*, 1998, vol. 72, no. 6, p. 1040.
9. Dudkina, N.S., Shatunov, P.A., Kuvshinova, E.M., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A., *Russ. J. Gen. Chem*., 1998, vol. 68, no. 12, p. 1955.
10. Kuvshinova, E.M., Kuzmin, D.L., Dudkina, N.S., Pukhovskaya, S.G., Semeikin, A.S., and Golubchikov, O.A., *Russ. J. Gen. Chem*., 2002, vol. 72, no. 1, p. 133. DOI: 10.1023/A:1015322118490.
11. Grasdalen, H. and Svare, I*., Acta Chem. Scand*., 1971, vol. 25, no. 3, p. 1089.
12. Sawada, K., Ohtaki, H., and Tanaka, M*., J. Inorg. Nucl. Chem*., 1972, vol. 34, no. 2, p. 625.
13. Golubchikov, O.A., Fgeeva, T.A., Ponamariva, E.L., and Berezin, B.D., *Koord. Khim*., 1987, vol. 13, no. 1, p. 37.
14. Golubchikov, O.A Kuvshinova, E.M., Koifman, O.I., and Berezin, B.D., *Mezhvuz. Sb.. "Problemy sol'vatatsii i kompleksoobrazovaniya"* (Problems of Solvation and Complexation), 1980, p. 9.
15. Berezin, B.D., *Teor. Eksp. Khim*., 1973, vol. 9, no. 10, p. 500.
16. Venediktov, E.A. and Golubchikov, O.A., *Zh. Fiz. Khim*., 1996, vol. 70, no. 1, p. 164.