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Synthesis and Properties of Fe^{III} Complexes with Deuteroporphyrin and Hematoporphyrin

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Abstract—Deuteroporphyrin and hematoporphyrin as complete methyl esters and their complexes with iron(III) were synthesized and characterized by NMR and electronic spectroscopy. For the first time the changes of the specific heat capacity of these solid biological objects with temperature were investigated by the method of differential scanning calorimetry. These parameters are shown to be smooth functions of temperature in the range 290–360 K, indicating the absence of the phase transitions in these systems.

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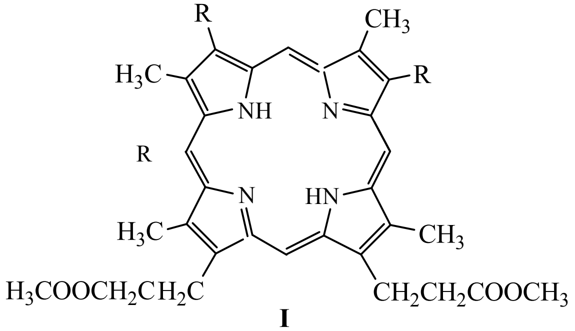
The blood group porphyrins and their derivatives are widely used in various fields of science and technology, including medicine and nanotechnology [1, 2]. For the objective assessment of the porphyrins reactivity in different types of chemical processes it is very important to know their thermodynamic characteristics of solvation. A considerable practical and theoretical interest in this regard presents the thermochemical method of study allowing collect the information on the intermolecular interactions of biological objects in solutions. Therefore at the analysis of polythermal dependence of the interaction enthalpy in order to obtain correct calculations of the changes of heat capacity and entropy of dissolution and transport with temperature, it is necessary to be sure of the absence of phase transitions in the solid phase and the resulting abrupt changes in the lattice energy of the macroheterocycles.

In this connection we synthesized complete methyl esters of deuteroporphyrin and hematoporphyrin and their complexes with iron (III). By differential scanning calorimetry at 290–360 K changes in temperature specific heat of solid samples of the synthesized compounds were investigated for the first time.

As in previous studies carried out by an example of (Cl)Fe^{III}DP dme [5,6], we were not able to identify completely all the signals of the compounds only on the basis of ^{1}H NMR spectrum. However, the spectra contain characteristic signals of the *meso*-protons in the region –58.5 ppm in the case of (Cl)Fe^{III}DP dme and –57.5 ppm in the spectrum of (Cl)Fe^{III}HP tme, as well as the signals of aromatic CH protons in the range of chemical shifts 42.2–48.7 ppm for the deuteronporphyrin complex and 40.8–44.9 ppm in the spectrum of (Cl)Fe^{III}HP tme. The proton signals of methyl groups in positions 2, 7, 12 and 18 of the aromatic macrocycle are located at 52.6–55.0 ppm in the spectrum of (Cl)Fe^{III}DP dme and at 50.7–53.5 ppm in the case of (Cl) Fe^{III}HP tme. In addition, the spectrum of (Cl)Fe^{III}DP dme is characterized by a strong downfield signal at 80.1 ppm corresponding to the aryl



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R= H (H_2DP, dme); CH(OCH_3)CH_3 (H_2HP, tme).

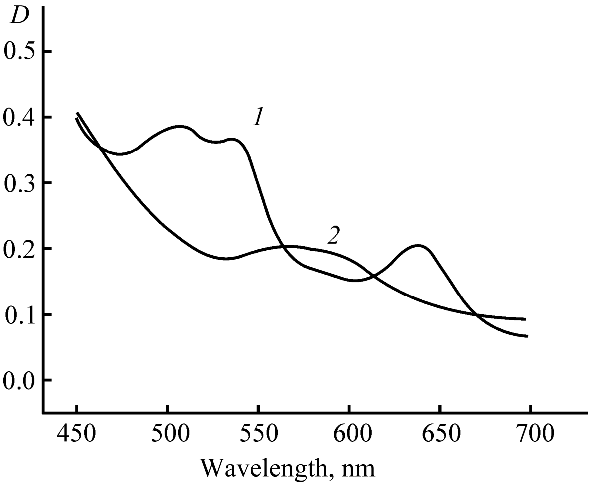

Fig. 1. Electron absorption spectrum of $Fe^{III}HP$ in methylene chloride (the Soret band is not shown): (*1*) (Cl)FeHP (tme) and (*2*) μ-oxo-dimer $O(FeHP)_2$ (tme).

protons at positions 3 and 8 of the macrocycle, in the spectrum of (Cl) $Fe^{III}HP$ tme signals in this region are absent. The ^1H NMR spectra of this type are characteristic of the iron(III) paramagnetic porphyrinate complexes with pentacoordinated metal atom [(X) FeP] in the high spin (5/2) state. It also follows from the values of the isotropic shifts (δ_{iso}, ppm) of the proton signals in the spectra of the complexes in comparison with diamagnetic ligands (see the table).

The resulting iron(III) chloride complexes exhibited high stability, especially when dried in vacuum at 100°C. However, it was found that if the extra-ligands X are acetate ions, the stability of the compounds is dramatically reduced, which is typical of the iron(III) porphyrinate complexes with weakly coordinating ligands [5]. Thus, after heating $(Ac)Fe^{III}P$ to 100°C the observed EAS spectrum of the complex is transformed in that characteristic of μ-oxo-dimer $\{O(Fe^{III}P)_2\}$ [7] (Fig. 1), and a sharp decrease occurs of the isotropic shifts of proton signals in the ^1H NMR spectrum (signals in the range 0.8–14.0 ppm). Apparently, this is due to the process of formation of the ferroprotoporphyrin μ-oxo-dimer, accompanied with a decrease in the spin state of the cation to the intermediate value 3/2 [5].

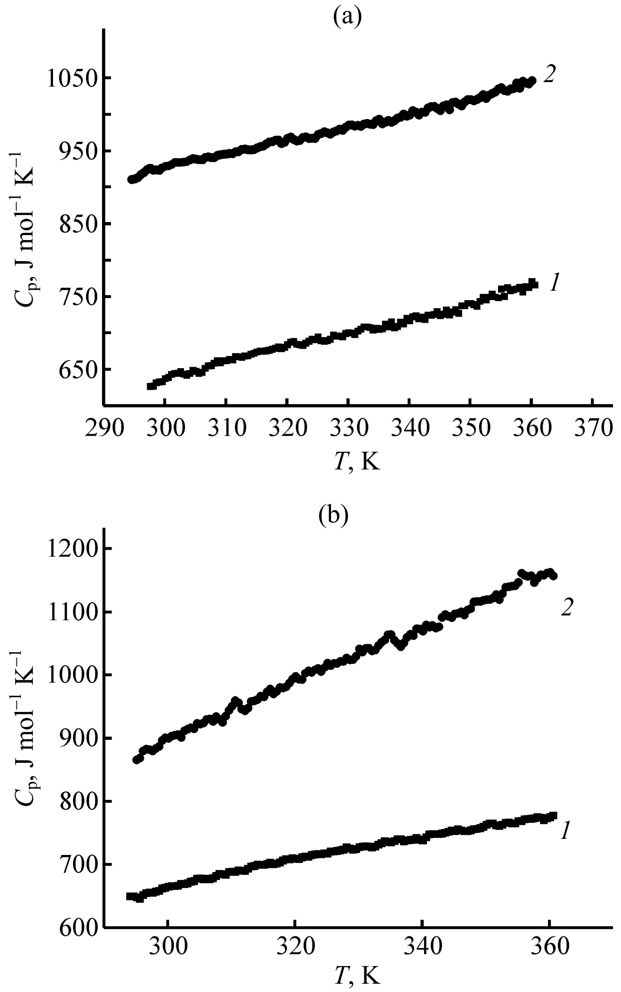

Fig. 2. Variation in the molar heat capacity of (a) solid samples of porphyrin ligands and (b) their complexes with Fe(III).

Figure 2 shows the temperature dependence of the specific heat capacity of solid samples of deuteronporphyrin, hematoporphyrin, and their complexes with Fe^{III} in the temperature range 290–360 K. The variation of the molar heat capacity with temperature for the ligands of deuteroporphyrin and hematoporphyrin within the experimental error is described by polynomials of third degree:

$$C_p(H_2DP\ dme) = -20199(1923) + 187.58(18)T$$
$$- 0.56628(0.05)T^2 + 5.750210^{-4}(5.4\times10^{-5})T^3,$$
$$s_f\ 2.9\ J\ mol^{-1}\ K^{-1}$$

$$C_p(H_2HP\ tme) = -9559.1(1376) + 94.277(8)T$$
$$- 0.28622(0.04)T^2 + 2.948810^{-4}\ (3.9\times10^{-5})T^3,$$
$$s_f\ 2.5\ J\ mol^{-1}\ K^{-1}.$$

In the case of iron complexes it is quite sufficient to the use of polynomials of the second degree:

$$C_p = -934.46(58) + 8.2301(0.35)T - 0.009690(5.4\times10^{-4})T^2,$$
$$s_f\ 2.1\ J\ mol^{-1}\ K^{-1}\ [(Cl)FeDP\ dme],$$

$$C_p = -850.84(162) + 7.0052(0.99)T - 0.003930(1.4\times10^{-3})T^2,$$
$$s_f\ 5.7\ J\ mol^{-1}\ K^{-1}\ [(Cl)FeHP\ tme].$$

Figure 2 shows that dependence of the heat capacity on the temperature is monotonic for all the

Assignment of the signals in the ^{1}H NMR spectra of paramagnetic complexes (Cl)Fe^{III}DP dme and (Cl)Fe^{III}HP tme

Compound	Chemical shift δ, ppm	Isotropic shift δ_{iso}, ppm	Assignment of the signals
(Cl)Fe^{III}DP	80.1	71.0	$H^{3,8}$
	55.01	51.31	$CH_3^{2,7,12,18}$
	54.06	50.46	
	52.65	49.05	
	48.67	44.27	$CH_2^{13\text{-}1,17\text{-}1}$
	46.4	42.0	
	42.77	38.37	
	42.2	37.8	
	–53.46	–63.66	$H^{5,10,15,20}$
	–55.53	–65.53	
	–58.57	–68.57	
(Cl)Fe^{III}HP	53.51	49.81	$CH_3^{2,7,12,18}$
	50.67	47.07	
	44.87	40.47	$CH_2^{13\text{-}1,17\text{-}1}$, $CH^{3\text{-}1,8\text{-}1}$
	43.72	39.32	
	43.28	38.88	
	40.82	34.82	
	–57.55	–67.0	$H^{5,10,15,20}$

objects, which indicates the absence of the *order–disorder* phase transitions in this temperature range. Perhaps the heating of the hematoporphyrin complex with iron is accompanied by some orientational disordering in the packing of terminal functional fragments, as evidenced by a slight deviation from the monotonic behavior of the specific heat capacity at 310 and 335 K. However, these changes are actually at the level of error, so we cannot say with certainty of the restructuring of the object. Much more important is the fact that while the difference in values of the heat capacity of deuteroporphyrin and hematoporphyrin methyl esters is practically independent of temperature being about 300 J mol^{-1} K^{-1}, for the corresponding complexes it increases with increasing temperature from 200 to almost 400 J mol^{-1} K^{-1}, indicating a difference in the molecular packing of the objects.

EXPERIMENTAL

Deuteroporfirin dimethyl ester was prepared by the procedure described in [3]. The ^{1}H NMR spectrum ($CDCl_3$, internal reference TMS) δ, ppm: 10.06 s (1H), 10.04 s (2H), 9.99 s (1H,) $H^{5,10,15,20}$; 9.07 s (2H, $H^{3,8}$); 4.41 br.t (4H, J = 6 Hz, $H^{13-2,7-2}$); 3.74 s (6H , $COOCH_3$); 3.70, 3.69 two s (3H each, $CH_3^{2,3}$); 3.62 s (6H, $CH_3^{12,18}$); 3.31 t (4H, J = 3.6 Hz, $H^{13-1,17-1}$); –3.98 br s (2H, NH). Electron absorption spectrum (EAS, λ_{max}, nm, benzene): I, 623; II, 568; III, 529; IV, 498; Soret, 401.

Hematoporphyrin, tetramethyl ether, was obtained according to [3]. ^{1}H NMR spectrum ($CDCl_3$, interal refrence TMS) δ, ppm: 10.60, 10.56, 10.17, 10.13 4s (1H each, $H^{5,10,15,20}$); 6.09 br.q (2H, J = 6.2 Hz, $H^{3-1,8-1}$); 4.47 t (4H, J = 7.2 Hz, $H^{13-2,17-2}$); 3.75 s (6H, $COOCH_3$); 3.69–3.71 br s (12H, $CH_3^{2,7,12,18}$); 3.66 s (6H, $OCH_3^{3-1,8-1}$); 3.34 t (4H, J = 7.2 Hz, $H^{13-1,17-1}$); 2.31 br.m (6H, $CH_3^{3-2,8-2}$); –3.65 br.s (2H, NH). EAS (λ_{max}, nm, benzene): I, 626; II, 570; III, 533; IV, 499; Soret, 403.

Complexes (Cl)Fe^{III}DP and (Cl)Fe^{III}HP were prepared according to [4].

Porphyrins ligands and their iron(III) complexes before the study were dried at 100°C under reduced pressure. All solvents used in this work were prepared according to [8]. The ^{1}H NMR spectra of the synthesized compounds were recorded on a Bruker Avance-500 spectrometer, solvent $CDCl_3$, internal reference TMS. The EAS were recorded on a spectrophotometer SF-56. The studies of heat capacity were performed on a NETZSCH differential scanning calorimeter with heat flux DSC 204 F1 Phoenix (Germany) with a highly sensitive μ-sensor. Scanning was carried out at a rate of 10 K min^{-1} with cooling by gaseous nitrogen, in an argon atmosphere using a standard aluminum crucible with a lid. The reference substance was a sapphire with a diameter of 0.25 mm (12.47 mg). To calculate the heat capacity the method of relations was used. The error in determining the heat capacity is about 1%. Reagents were loaded in air into aluminum crucibles within 15–20 seconds and then hermetically sealed. Measurement of heat capacity was carried out in three stages in an automatic mode according to a predetermined standard program.

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