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# The electronic and magnetic properties of iron(III) derivatives of selected substituted meso-tetraphenyl porphyrins: ESR spectroscopic study

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#### Abstract

The electronic and magnetic behaviour of the nonsolvated ferric complexes of: (a) meso-tetratolyl-, (b) meso-tetra-4-hydroxyphenyl-, (c) meso-tetra-4-carboxyphenyl-, and (d) 5-(4-carboxyphenyl)-10,15,20-tritolyl-porphyrins was studied by ESR spectroscopy in the temperature range between 300 and 4 K. The complexes exhibit predominant contribution from the low-spin iron species at high temperature and a drastic shift toward the high-spin iron species at the low-temperature limit. These paramagnetic species are in different proportions at different temperatures, as well as in porphyrins with different substituents. The examined porphyrins obtained as disordered solids contain iron complexes with continuous short-range disorder which is additionally sensitive to change of temperature.

## 1. Introduction

The iron porphyrins are important biological transients whose intermediacy has been demonstrated in numerous peroxidase and catalase enzymes. Therefore, they are the most intensively studied from among metalloporphyrins. A number of results of these investigations have been summarized in excellent papers by Ann Walker [1,2]. The ESR spectroscopy is a useful technique for determining electronic and magnetic properties of the paramagnetic complexes. It is considerably interesting for establishing which factors affect the electronic and magnetic properties and for understanding how these physical properties may relate to each other. The aim of this work is to analyse the influence of the porphyrin peripheral substituents and the temperature effect on the electronic structure of ferric: (a) meso-tetratolyl-, (b) meso-tetra-4-hydroxyphenyl-, (c) meso-tetra-4-carboxyphenyl-, and (d) 5-(4-carboxyphenyl)-10,15,20-tritolyl-porphyrins.

The above-mentioned free base tetraphenylporphyrins were chosen because they can be used as photosensitizers in

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PDT method. Meso-tetra-4-hydroxyphenylporphyrin is applied since several years as approved for clinical use photosensitizer [3]. We also decided to investigate these porphyrins as a result of their chemical properties. This kind of substituents linked with the phenyl rings makes them very convenient intermediate to synthesize derivative of porphyrins with compounds which show biological activity, e.g. amino acids [4]. Carboxylic group allows forming an amide bond which is very characteristic for proteins. Methoxy- and hydroxyl-groups allow forming ether bonds between a variety of compounds. The presence of such substituents open the possibility to design compounds with desired biochemical properties.

## 2. Experimental procedure

#### 2.1. Synthesis of compounds

Meso-tetraphenylporphyrins and 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin were prepared using the procedure of Adler and Longo [5]. Meso-tetratolylporphyrin (TTP) was synthesied by heating 4-methylbenzaldehyde with pyrrole (molar ratio 1:1) in boiling propionic acid.

Overnight cooling gave purple crystals of meso-tetratolylporphyrin which was separated from reaction mixture on Buchner funnel, washed twice with water and finally with hot water in order to remove traces of propionic acid and partially formed tars. The obtained porphyrin was purified on chromatography column ( $4 \times 40$  cm) filled with silica gel (60-230 mesh). Dry chloroform was used as an eluent. The same procedure was used for the preparation of meso-tetra-4hydroxyphenylporphyrin (THP) and meso-tetra-4-carboxyphenylporphyrin (TCP) using 4-hydroxybenzaldehyde and 4-carboxybenzaldehyde, respectively.

5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin (MCP) was prepared using 4-methylbenzaaldehyde, 4-carboxybenzaldehyde and pyrrole with molar ratio (1:3:4). The formed six possible derivatives of tolylporphyrin were separated on chromatography column ( $4 \times 50$  cm) filled with silica gel (60–230 mesh) when mixture of chloroform:methanol, v/v 9:1 was applied as an eluent. The second fraction was the desired product of 5-(4-carboxyphenyl)-10,15,20-tritolylporphyrin.

The Fe(III) porphyrins were obtained by standard method [6] of refluxing iron chloride (III) in DMF for 1 h. The metalloporphyrins were precipitated by adding water and then separated from solvent on Buchner funnel. The formed porphyrins were checked by spectroscopic methods. The XPS-technique confirmed the presence of Cl-species in compounds. The absorption spectra at a room temperature were measured by a JASCO UV-spectrometer using chloroform solutions (with exception of Fe(III)THP where the mixture of methanol/chloroform was used). In the visible region (Q bands) two characteristic bands for metal complexes of porphyrins are observed. Instead of the I, III and II, IV bands which are present in free base porphyrin,  $\alpha$ and  $\beta$  bands have appeared. Their intensities are 10 times smaller compared to Soret band. However, iron(III) ions produce abnormal spectral types for the porphyrin which belong to the 'hyper spectrum' class. This spectrum is defined as a 'shifted metalloporphyrin spectrum' with  $\alpha$ ,  $\beta$ , Soret and one more extra band. The 'hyper' type is caused by charge transfer and other metal-ligand interactions. The values of the optical parameters are summarized in Table 1. The results of electronic spectroscopy data can be explained by comparison with hemin studies in which the profile in the visible region near 500 nm is the usual marker of a high-spin ferric species [7]. On the other hand, the band shifted to approximately 570 nm is characteristic of low-spin ferric porphyrins.

Table 1 The optical parameters of studied iron-porphyrins

Compound	Soret band (nm)	Q bands (nm)		
Fe(III) TTP	418	511 576 695		
Fe(III) THP	421.5	504 630 740		
Fe(III) MCP	417.5	512 573 613		

MS spectra were measured on MAS Spectrometer TSQ 700 Finigan-Mat using ESI technique. Molecular peaks proved molecular mases of investigated metalloporphyrins: (a) Fe(III)TTP-M=760; (b) Fe(III)THP-M=768; (c) Fe(III)TCP-M=880; and (d) Fe(III)MCP-M=790.

IR spectra were recorded on IR 560 Magma Nicolet spectrometer as KBr pellets in the range  $450-4000 \text{ cm}^{-1}$ . Representative N-H stretching vibrations of free base porphyrins in the region of  $3300-3360 \text{ cm}^{-1}$  are absent in our spectra. This observation proves successful insertion of iron(III) to porphyrin ring. Typical absorption band for C-H, C-C stretching and deformation vibrations are in agreement with literature [8]. The presence of substituents of phenyl ring in p-position was observed. C-O stretching vibration of carboxylic group absorbs at  $1701 \text{ cm}^{-1}$  for TCP porphyrin and at 1723  $\text{cm}^{-1}$  for MCP porphyrin. O–H stretching mode of hydroxyl group occurring in the THP porphyrin is presented in the spectra as a broad peak at  $3413 \text{ cm}^{-1}$ . For TTP and TCP are observed typical stretching mode for aliphatic hydrocarbons around  $2925 \text{ cm}^{-1}$ .

The results obtained from TLC chromatography showed higher  $R_{\rm F}$  values of metalloporphyrins in comparison with free-base porphyrins.

The structural formula of iron(III) derivatives of mesotetra-phenylporphyrins is presented in Fig. 1.

#### 2.2. Methods

The electron spin resonance spectra were recorded with a standard EPR spectrometer operating at X-band (9 GHz) frequency, using 100 kHz field modulation. The microwave frequency was measured using Hewlett Packard 534 microwave frequency counter. The temperature dependence measurements were performed in the temperature range



Fig. 1. General structure of iron(III) derivatives of meso-tetra-phenylporphyrins. For samples: (a)  $R_{1,2,3,4}=CH_3$ ; (b)  $R_{1,2,3,4}=OH$ ; (c)  $R_{1,2,3,4}=$ COOH; and (d)  $R_{1,2,3}=CH_3$  and  $R_4=COOH$ .



Fig. 2. X-ray diffraction pattern of a ferric-meso-tetra-4-hydroxyphenylporphyrin.

from 4 to 300 K with an Oxford Instruments ESR-900 continuous-flow helium cryostat.

All complexes studied in this work were used in the form of solid samples.

The crystalline structure was studied by powder X-ray diffraction. The amorphous products were obtained by us, as can be seen in Fig. 2, when exemplary diffraction pattern for Fe(III)THP is shown. The diffraction patterns of the other products are similar.

Simulated spectra were calculated with Bruker-Symphonia program.

# 3. Results and discussion

Fig. 3(a)–(d) shows the ESR spectra of: (a) Fe(III)TTP, (b) Fe(III)THP, (c) Fe(III)MCP, and (d) Fe(III)TCP recorded at room temperature. For all compounds ESR spectra are complex and contain the group lines around g=2 (denoted as B) and low-field signal with gfactor near 6 (denoted as A). The appearance of these features suggested that two paramagnetic species were present: (i) A-type signals are due to the high-spin state (S =5/2) of Fe(III) ions in the tetragonal symmetry crystal field



Fig. 3. The comparison of the ESR spectra for: (a) Fe(III)TTP, (b) Fe(III)THP, (c) Fe(III)MCP, and (d) Fe(III)TCP recorded at T = 300 K. D-signal is the free radical signal originated from base porphyrin.



Fig. 4. (a) The low-temperature ESR spectrum of Fe(III)TTP observed at T=5 K. (Below) Simulated spectrum for the parameters which are listed in Table 2. (b) The ESR spectrum of Fe(III) MCP observed at a room temperature. (Below) Simulated spectrum for the parameters which are listed in Table 2 (A-type signal is not included).

and (ii) B-type signals are associated with the low-spin state (S=1/2) of Fe(III) complexes in the rhombic symmetry crystal field.

The spin Hamiltonian for a paramagnetic ion with S = 5/2in tetragonal symmetry may be written as:

$$H = D\{S_z^2 - 1/3S(S+1)\} + g_{\parallel}\mu_B B_z S_z \cos \theta$$
$$+ g_{\perp}\mu_B B_x S_x \sin \theta \tag{1}$$

where the magnetic field **B** forms an angle  $\theta$  with the *z*-tetragonal axis and *D* is zero-field splitting parameter.

For a large *D* value  $(D \gg h\nu)$ , the ESR signal that can be observed is the transition from  $m_{\rm S} = -1/2$  to +1/2states. The resonance condition for the ground-state doublet is described with an effective *g* value so that [9]

$$h\nu = g_{\rm eff}(\theta)\mu_{\rm B} {\rm B} \tag{2}$$

When the magnetic field is applied along the *z*-axis, one has

Table 2

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$\sigma_{\parallel cc} \equiv \sigma_{\parallel}$	( 5	1
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and when the magnetic field is applied perpendicularly to the *z*-axis

$$g_{\perp \text{eff}} = 3g_{\perp} [1 - 2(g_{\perp} \mu_{\text{B}} \text{B})^2 (2D)^{-2}]$$
(4)

From Eq. (4) we can see that when a zero-fieldparameter |2D| is much greater than the Zeeman splitting, the signal with effective g values  $g_{\perp eff} \cong 6$  is observed. The spin-Hamiltonian (1) with the assumption that  $D \gg h\nu$  was used to simulate the low-field part of the experimental spectrum. Fig. 4(a) shows the exemplary simulation obtained for Fe(III)TTP. The values of gfactors for all compounds are listed in Table 2.

The B-type signal may be described by the rhombic spin Hamiltonian including only the Zeeman interaction:

$$H = \mu_{\rm B}(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) \tag{5}$$

Compound	Low tem- perature g-factors	Room temperature spectra								
		g-Factors		$V(\mathrm{cm}^{-1})$	$\Delta (\mathrm{cm}^{-1})$	V/Δ	Mixing coefficient			
							a	b	С	
		(I)	(II)	(I)	(I)	(I)	(I)	(I)	(I)	
Fe(III)TTP	T=5  K	$g_z = 2.71$	$g_z = 2.39$	1353	2936	0.46	0.36	0.05	0.02	
	$g_{\perp} = 5.9$	$g_y = 2.27$	$g_y = 2.05$	(II)	(II)	(II)	(II)	(II)	(II)	
	$g_{  } = 1.99$	$g_x = 1.96$	$g_x = 1.85$	1658	4054	0.41	0.35	0.04	0.02	
Fe(III)THP	T=5  K	$g_z = 2.34$		1790	3016	0.60	0.35	0.04	0.02	
	$g_{\perp} = 5.8$	$g_{y} = 2.08$								
	$g_{  } = 1.99$	$g_x = 1.83$								
Fe(III)TCP	T=17 K	$g_z = 2.30$		1186	1077	1.10	0.37	0.07	0.05	
	$g_{\perp} = 5.75$	$g_{y} = 2.10$								
	$g_{  } = 1.99$	$g_x = 1.50$								
Fe(III)MCP	T = 16  K	$g_{z} = 2.35$		1475	3697	0.40	0.36	0.05	0.02	
	$g_{\perp} = 5.75$	$g_{y} = 1.97$								
	$g_{  } = 2.00$	$g_x = 1.75$								

g-Factors and crystal field parameters for Fe(III)TTP, Fe(III)THP, Fe(III)TCP, and Fe(III)MCP compounds

Crystal field parameters were estimated by using a method outlined by Taylor [10]. According to this method the electron configuration of low-spin is  $(d_{xy})^2(d_{xz}, d_{yz})^3$  and the energy separation between the doubly degenerate  $d_{xz}$  and  $d_{yz}$  orbitals and the nondegenerate  $d_{xy}$  orbital is a measure of the tetragonal splitting designated as  $\Delta$ . *V* is designated the energy separation between the  $d_{xz}$  and  $d_{yz}$  when lowering symmetry removes degeneracy. The wave functions of ferric ions are linear combination of the three states with mixing coefficients *a* (for  $d_{yz}$ ), *b* (for  $d_{xz}$ ) and *c* (for  $d_{xy}$ ). If the Zeeman operator is applied to these functions the relationship between mixing coefficients and the principal *g* values is as follows:

$$a = (g_z + g_y)/4p, \quad b = (g_z - g_x)/4p, \quad c$$
  
=  $(g_y - g_x)/4p$  (6)

with  $p = (g_x + g_y + g_z)/2$ .

The crystal field parameters V and  $\Delta$  may be expressed as:

$$V/\lambda = E_{yz} - E_{xz} = g_x/(g_z + g_y) + g_y/(g_z - g_x)$$
(7)



(energies are in units of  $\lambda = 400 \text{ cm}^{-1}$ , the spin-orbit coupling constant).

The ESR *g*-values, mixing coefficient, tetragonal and rhombic splitting parameters for all examined complexes are shown in Table 2.

The B-type signals of investigated porphyrins, presented in Fig. 3(a)–(d), are dissimilar. The B-type spectrum of Fe(III)TTP is interpreted as two overlapping rhombic spectra with g-factors whose values are listed in Table 2. A common feature of ESR in amorphous solids is the broadening of absorption lines. Because of the randomness in the local atomic surrounding of paramagnetic ions in disordered solids, the ESR spectra in these materials are explained by the statistical distribution of ESR parameters. The ESR spectrum of Fe(III)TTP is characterized by smaller linewidth in comparison with  $\Delta B$  for other obtained porphyrins. Under these conditions, the high-field ESR spectrum for meso-tetratolylporphyrin at a room temperature is characterized by two features with g-values of about



Fig. 5. The temperature evolution of the ESR spectra of: (a) Fe(III)TTP, (b) Fe(III)THP, (c) Fe(III)MCP, and (d) Fe(III)TCP.



Fig. 6. The relative spin susceptibility of: (a) Fe(III)TTP, (b) Fe(III)THP, (c) Fe(III)MCP, and (d) Fe(III)TCP versus temperature.

 $g_{av}$ =2.09 and 2.31. At the same time, more symmetric B-spectrum, characteristic for the others complexes, means that the features of rhombic spectrum are smeared out, as the amount of short-range disorder is increased [11]. The exemplary simulation referring only to B-type species is presented in Fig. 4(b).

The temperature evolution from the room temperature to T=4 K of ESR spectrum of ferric complexes is displayed in Fig. 5(a)–(d). The inspection of overlapping spectra shows a sequential build-up of the high-spin species with g-values present near g=6 (see Table 2). The two paramagnetic species are in different proportions at different temperatures. For Fe(III)TTP there was no evidence to support the existence of the lowspin component over the lowest temperature range, however, for remaining porphyrins the low-spin component is still present but much less intense than at room temperature.

When the temperature is lowered the ESR spectra of Fe(III)THP and Fe(III)TCP exhibit the signal with g=4.3 (denoted as C). The ESR features with  $g_{eff}=4.3$  have been observed for Fe<sup>3+</sup> in various disordered solids and were interpreted by Kliava [11] on the basis of the rhombic spin-Hamiltonian:

$$H = g\mu_{\rm B}\mathbf{B}S + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2)$$
(9)

where D and E are zero-field-splitting parameters and S=5/2.

Assuming  $|D| \ge h\nu$  and  $|D/E| \cong 3$ , the following expression was obtained for the middle Kramers doublet [11]:

$$g_{\text{eff}} = (30/7)[1 + (4/7)q(l_z^2 - l_y^2) + (4/49)(4p^2 + 15q^2)(l_y^2 + l_z^2) - (2/49)(5p^2 + 4q^2)(l_y^2 - l_z^2)^2 - (24/343)(4p^2 + 17q^2)]$$
(10)

where  $p = g\mu_{\rm B} \mathbf{B}/(D+E)$  and q = (D-3E)/(D+E).

The C-signal with g=4.3 implies the presence in examined compounds the high-spin ferric species in the rhombic symmetry crystal field.

Additionally, for explanation of the character of observed ESR spectra we estimated the temperature dependence of the spectrum intensity. In Fig. 6 temperature evolution of intensity of ESR spectrum (calculated as double integration of the spectrum—DI) is shown. This defined intensity should be proportional to the spin susceptibility of the sample.

(a) For Fe(III)TTP, susceptibility increases monotonically up to about T=50 K, below this temperature the rise is more rapid; (b) Fe(III)THP susceptibility increases up to

T=190 K, next in 40 K < T < 190 K range there is a plateau and below T=40 K rapid increase is observed; (c) for Fe(III)MCP DI-values monotonically increase as the temperature is reduced from 300 to 4 K; (d) at the same time, spin susceptibility of Fe(III)TCP does not change up to T=100 K and next increases to higher values.

It is known from the ferriheme protein investigations [1] that two different state ferric species arise from two sixcoordinated conformers, differing in the position of Fe with respect to the ligands and to the heme plane. According to the crystal field theory changing axial field strength leads low-spin to high-spin states. The characteristic features of disordered solids are distributions of the short-range order parameters, namely bond lengths and bond angles. We believe that the examined porphyrins obtained by us as disordered solids contain iron complexes with different axial ligands and the different local symmetry around them. As can be seen in Fig. 6, DI(T) curves exhibit influence of temperature on electronic and magnetic properties of obtained complexes. When temperature is lowered the ESR spectra exhibit predominant contribution of high-spin state of ferric ions. It means the change of ferric ion position and stiffness of Fe(III) complexes. For porphyrins with different substituents this process takes place with various rates in different temperature ranges. We assume therefore that the temperature sensitivity of the complexes is dependant upon the substituents.

## 4. Conclusions

The observed EPR spectra of iron-phenylporphyrin complexes with various substituents are complex; at

the high temperature the samples exhibit predominantly the presence of the low-spin ferric species in the rhombic local symmetry and the high-spin ferric species in the (i) tetragonal and (ii) rhombic symmetries when the temperature is lowered. These species are in different proportions at different temperatures, as well as in the porphyrins with various substituents. The examined porphyrins obtained as disordered solids contain iron complexes with continuous short-range disorder which is additionally sensitive to change of temperature. It is worth noting that observed effects appear under solvent-free conditions. Therefore, the ESR investigations provide convincing arguments to influence of the temperature on electronic and magnetic properties of iron-porphyrin complexes.

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