

Effect of nitrogen substitution in porphyrin ring on Mössbauer parameters of iron ions

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Abstract Electron configuration changes of Fe(III) ions in porphyrin complexes with chloride axial ligands caused by the successive nitrogen substitution of CH methine bridges at *meso* positions of the porphyrin ring is discussed on the basis of Mössbauer spectroscopy results. It was shown that increase of a number of nitrogen atoms at the *meso* positions changes the character of quantum-mechanically mixed spin state of Fe(III) ions ($S = 5/2 + 3/2$) by the increase of the intermediate-spin ($S = 3/2$) contribution. This feature is reflected in Mössbauer spectra by an increase of quadrupole splitting values and the decrease of the asymmetry of quadrupole doublets, when the number of nitrogen atoms at the *meso* positions increases. Isomer shifts remain practically unchanged. These peculiarities are discussed in the light of spin relaxation mechanisms and the occupancy of *d* orbitals in Fe(III) ions coordinated to the porphyrin ring and chloride ligand. It has been noticed that Mössbauer parameters correlate qualitatively with EPR data.

Key words Mössbauer spectroscopy • iron porphyrins • azaporphyrins • trivalent-iron spin states

Introduction

Iron porphyrins participate in the biological cycles as the heme prosthetic groups such hemoproteins as hemoglobin and myoglobin as well as some cytochromes, peroxidases and catalases [9]. Iron ions, placed at the centre of the prosthetic groups, play a key role in biological processes which involve hemoproteins. Sufficient background information on the relationship between a porphyrin ligand structure and an electronic configuration of the iron ions is provided to form a basis for discussion on the complex bioprocesses. Apart from the biological aspects, the molecular structure and physical properties of iron porphyrins promote these complexes for application in such contemporary technologies as non-linear optics, molecular semiconductors, liquid crystals and so on [8]. The substitution of the methine bridges CH (*meso* positions) by nitrogen atoms (*aza* substitution) is one of possible modifications of the porphyrin ring. It has been established that the *aza* substitution causes changes of trivalent-iron electron configurations. In particular, the electron configuration of Fe(III) ion in chloroiron porphyrins with unsubstituted methine bridges corresponds to the pure high spin state ($S = 5/2$) [14], while in the case of chloroiron tetraazaporphyrin (four methine bridges α , β , γ , δ substituted by nitrogen atoms) the pure intermediate spin state ($S = 3/2$) of the Fe(III) ion has been found [7]. The *aza* substitution of one of four *meso* positions leads to the unusual, quantum-mechanically mixed spin state ($S = 5/2, 3/2$) of Fe(III) ions [6]. So, partly substituted *aza*-porphyrins can be used as model systems for the study of subtle effects of the unusual spin state of the iron ions. In this paper, we report results obtained from Mössbauer spectroscopy for

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partly substituted Fe(III)Cl-monoazaethioporphyrin {Fe(III)(Cl)(MAEP)} (α methine bridge) and Fe(III)(Cl)-diazaoctaethylporphyrin {Fe(III)(Cl)(DAOEP)} (α and γ bridges) and compare them with the corresponding data for the unsubstituted Fe(III)Cl-octaethylporphyrin {Fe(III)(Cl)(OEP)} and completely substituted (α , β , γ , δ) Fe(III)Cl-tetrazaoctaethylporphyrin {Fe(III)(Cl)(TAOEP)} complexes. The nearest surrounding of the Fe ions is the same in the complexes studied and it is expected that the effect of *meso*-nitrogen atoms on their electron configuration is achieved through the delocalized π -electrons interaction with orbitals of the iron.

Experimental

The Fe(Cl)(OEP) complex was synthesized in the same way as described in paper [12]. Fe(Cl)(MAEP) and Fe(Cl)(DAOEP) were synthesized according to the procedures described in [10]. Mössbauer spectra were obtained with a $^{57}\text{Co}(\text{Rh})$ source at room temperature. A metallic iron foil absorber was used to calibrate the velocity scale, and isomer shifts are given vs. metallic Fe. Samples for Mössbauer measurements were prepared as layers obtained after evaporation of THF solvent. The layers contained about $4 \times 10^{-4} \text{ g/cm}^2$ of ^{57}Fe . The parameters of Mössbauer spectra were found by fitting the experimental spectra to Lorentzian lines using the NORMOS-90 program [2].

Results and discussion

There are two characteristic features observed in Mössbauer spectra of the complexes studied (Fig. 1) which are successively changing with an increasing number of the nitrogen atoms at the *meso* positions: (i) doublets in the spectra become more symmetrical and (ii) quadrupole splitting values (ΔE_Q) increase. Isomer shifts (δ) show similar values for the complexes studied (Table 1). To consider the asymmetry in the Mössbauer spectra, we have introduced an asymmetry parameter W_{21} which is equal to the linewidth ratio of the higher energy absorption line of the doublet (the right-side component) to the lower energy absorption line (the left-side component of the doublet). This assignment is acceptable because of the equal areas under the components of the doublets. Such a kind of the asymmetry is characteristic for the electronic spin relaxation processes [13] and positive sign of the V_{zz} component

Table 1. Mössbauer parameters of selected Fe(III)(Cl)-porphyrins at room temperature.

Molecule	Fe-spin state	δ [mm/s]	ΔE_Q [mm/s]	W_{21}
Fe(III)(Cl)(OEP)	5/2	0.27	0.70	3.49
Fe(III)(Cl)(MAEP)	5/2 + 3/2	0.26	1.06	2.04
Fe(III)(Cl)(DAOEP)	5/2 + 3/2	0.28	1.54	1.58
Fe(III)(Cl)(TAOEP)	3/2	0.28, 0.07	2.98, 2.90	1.00
Fe(III)(Cl)(Pc)	3/2 + 5/2	0.28	2.94	1.14

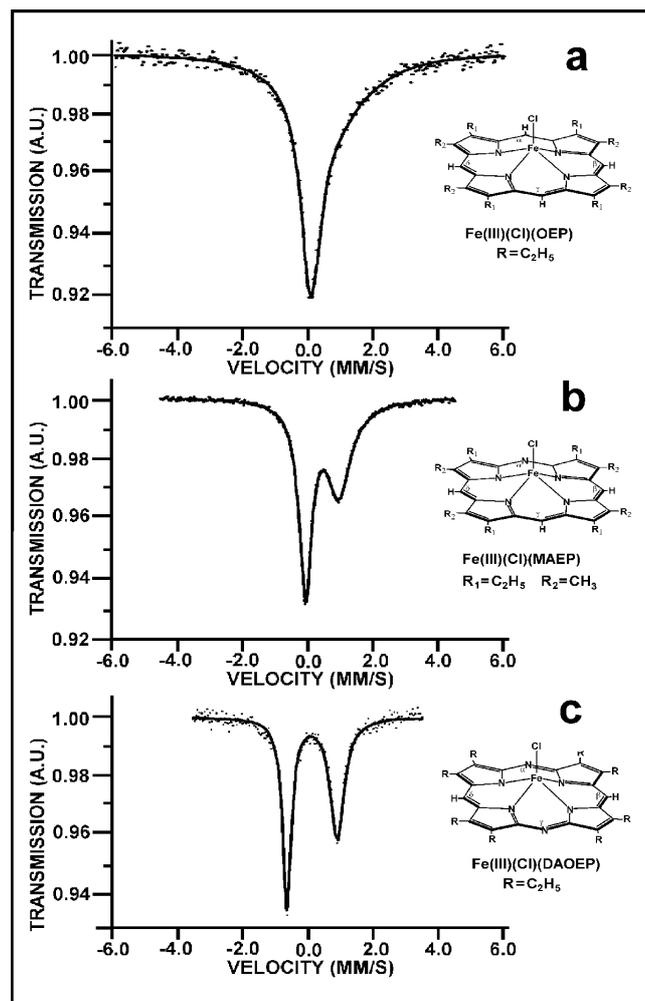


Fig. 1. Molecular structures and Mössbauer spectra of unsubstituted (a) and *aza*-substituted (b, c) Fe(III)(Cl)-porphyrins.

of electric field gradient (EFG) tensors. The positive sign of the V_{zz} indicates that Fe ion has more negative charge in the porphyrin plane than perpendicular to it [4]. The V_{zz} sign is the same for all the complexes studied because they have identical chloride axial ligands, although theoretically it could be changed by a significant charge change in the porphyrin plane. Substitution of the methine bridge CH by a nitrogen atom leads to deformation of the whole porphyrin ring. In particular, the iron-binding cavity, determined by the distance between transannular pyrrolic nitrogen atoms (Fig. 1), becomes smaller during the successive *aza* substitution because of (i) shorter bond distances between the pyrrolic carbon and the bridging nitrogen atoms and (ii) the smaller bond angle about the bridging nitrogen atom. Despite the smaller cavity size, the iron ion is displaced less from the macroring plane in *aza*-substituted than unsubstituted complexes [7]. It was shown for a number of five-coordinate iron porphyrins [14] that there is a relationship between the displacement of iron from the porphyrin plane and the iron spin state, in particular the occupancy of the $d_{x^2-y^2}$ orbital which is half-filled at the pure high-spin state ($S = 5/2$) and empty at the pure intermediate spin state ($S = 3/2$) [11]. The relatively large displacement is observed in the case of pure high-spin complexes which have one electron in each of the five d

orbitals and the orbital angular momentum is zero, so only the spin-spin relaxation mechanism is possible between the adjacent iron ions [1]. A characteristic feature of this relaxation is a special temperature dependence of the doublet asymmetry. As the temperature is raised, the spectrum becomes more asymmetric with one of the two doublet components considerably broadened. A Mössbauer spectrum of the Fe(Cl)(OEP) complex exhibits a symmetrical doublet at 4.2 K with the isomer shift $\delta = 0.41$ mm/s and quadrupole splitting $\Delta E_Q = 0.93$ mm/s [13], while at room temperature only the broad line is observed (Fig. 1). It should be noted that δ increases by about 0.13 mm/s between room and liquid helium temperatures [13]. It is expected in the case of the *aza*-substituted complexes with Fe(III) at admixed spin state ($S = 5/2 + 3/2$) that the $d_{x^2-y^2}$ orbital is occupied in a smaller degree than in the pure high-spin state. Then, the orbital angular momentum is not longer equal to zero and the electronic spin-lattice relaxation becomes more important. The increase of temperature in this relaxation mechanism leads to more symmetrical spectra. So, the shape of the Mössbauer spectrum depends on the effect of the spin-lattice and spin-spin competitive relaxation mechanisms on the asymmetry. We believe that temperature-dependent studies of the Fe(III)(Cl)-azaporphyrins which we are planning to perform, could confirm the increase of the spin-lattice contribution to the relaxation mechanism in these complexes.

Let us consider now the changes of the quadrupole splitting. The quadrupole splitting is a result of the splitting of the nuclear energy levels by interaction of the nuclear quadrupole moment with the EFG tensor. Distortion of the spherically symmetric half-filled shell caused by lowering of the $d_{x^2-y^2}$ orbital occupancy during the successive *aza* substitution leads to the increase of the valence contribution to the EFG, resulting from an asymmetric distribution of electrons in bonding and nonbonding orbitals. The lattice contribution to the EFG, resulting from changes on the porphyrin ligand can be also significant. The EFG changes indicate the stronger quadrupole interaction and this leads to an increase of the ΔE_Q values (Table 1).

The isomer shift, the last of the Mössbauer parameters under consideration in this paper, reflects the effect of the electronic charge density on the mean values of the nuclear ground- and excited-state energy levels. For the ^{57}Fe nuclei, an increase in *s*-electron density results in a decrease in the isomer shift δ [13]. Relatively small spread of the δ values (Table 1) suggests that the *aza* substitution in the complexes studied does not lead to significant changes in the 4*s*-orbital occupancy or to changes in shielding effects owing to electrons in the 3*d* orbitals. An additional example, which confirms the effect of the *aza* substitution on the Fe(III)-ion electron configuration and changes of the corresponding Mössbauer parameters, is an Fe(Cl)-phthalocyanine complex {Fe(Cl)(Pc)}. The Fe(III) ion in this complex is at the quantum-mechanically mixed spin state, but with the intermediate spin as a dominant contribution ($S = 3/2 + 5/2$) [4]. An expected asymmetry of the spectrum and values of the parameters (Table 1) are within the range characteristic of the *aza*-substituted complexes considered in this paper.

The above Mössbauer data correlate qualitatively with EPR results [5]. Intensive low-field components

corresponding to the g_{\perp} -factors equal to 5.93 and 5.86 for Fe(Cl)(MAEP) and g_{\perp} equal to 5.93 and 5.76 for Fe(Cl)(DAOEP) confirm the quantum-mechanically mixed spin state rather than the relaxation between the $S = 5/2$ and $S = 3/2$ states. The splitting of the g_{\perp} components indicates slight distortion of the axial symmetry in the nearest surrounding of the Fe(III) ions caused by the *aza* substitution in these complexes. The shifts of the above g_{\perp} values from $g_{\perp} = 6$ in the EPR spectra as a result of the *aza* substitution, which characterize the quantum-mechanically mixed spin state, are smaller as compared to the changes of the W_{21} and ΔE_Q parameters in the Mössbauer spectra. It should be noted that in the case of aggregated iron porphyrins, mixed Fe(III) \leftrightarrow Fe(II) valence states are also possible within the wide range of temperature [3], but Mössbauer spectra characteristic of them at room temperature differ from those observed for the Fe-azaporphyrins.

In conclusion, we have shown that the quantum-mechanically mixed spin ($S = 5/2 + 3/2$) states of Fe(III) ions in the *aza*-porphyrins change significantly with the increase of a number of nitrogen atoms at the *meso* positions of the porphyrin ring. The asymmetry and values of the quadrupole splitting in Mössbauer spectra can be used as parameters sensitive to the components of these spin states.

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