Univalent iron monoazaetioporphyrin complexes studied by Mössbauer spectroscopy

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Abstract Results of Mössbauer and EPR studies of univalent-iron monoazaetioporphyrin complexes [Fe(I)(MAEP)] are presented in this paper. Fe(I)(MAEP) were generated using the chemical reduction method. Three forms of the univalent-iron monoazaetioporphyrin complexes were observed: (I) typical Fe(I)(MAEP), (II) with an additional electron on the porphyrin ligand [Fe(I)(MAEP$^\bullet$)]$^-$ and (III) the Fe(I)(MAEPh) phlorin structure. Electron configuration of Fe(I) ions in these complexes is $(d_{xy})^2(d_{xz},d_{yz})^4(d_z^2)^1$. The [Fe(I)(MAEP$^\bullet$)]$^-$ structure is stable only in solution and it is transferred into Fe(I)(MAEP) in the solid state. Mössbauer parameters for all products of the reduction reaction are given.

Key words EPR • iron porphyrins • Mössbauer spectroscopy • reduction reactions

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Introduction

Metalloporphyrins with a central iron ion in unusual oxidation states are of interest from the preparative point of view and their relationship to biological functions. Univalent iron porphyrins are of synthetic values for generating (σ-alkyl)iron porphyrin complexes and may be of importance for dioxygen activation [12]. Central position of the iron atom in tetrapyrrole structures corresponds to the significant influence of this atom on chemical and physical properties of these complexes. Electron configuration at the Fe atom is sensitive to molecular structure of the surrounding porphyrin and axial ligands [13, 14].

A main purpose of our study is to determine how the substitution of the methine bridges (CH) in the porphyrin ring (positions α, β, γ, δ in Fig. 1a) by nitrogen atoms (so--called *aza* substitution) affects the electron configurations of products obtained during the reduction process. In this paper we consider results of Mössbauer spectroscopy investigations of a Fe-monoazaetioporphyrin complex {Fe(MAEP)} with the porphyrin ring which contains one of four methine bridges substituted by a nitrogen atom (position α in Fig. 1a). We focused attention here on the complex with univalent iron ion at the center as species obtained by one electron reduction below the iron(II) oxidation level. Complexes with iron ions at other oxidation states (Fe(III), Fe(II) and Fe(0)) are also briefly characterized.

It was established earlier that the *aza* substitution at porphyrin rings 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 ($S = 5/2$) [15], while in the case of chloroiron tetraaza-octaethylporphyrin {Fe(Cl)(TAOEP)} (four methine

bridges α, β, γ, δ substituted by nitrogen atoms) the pure intermediate ($S = 3/2$) spin state of the Fe(III) ion has been found [7]. Reduction process of Fe-porphyrins is rather complex and has not been unambiguously explained.

Experimental

Univalent iron monoazaetioporphyrin complex {Fe(I)(MAEP)} was obtained during the reduction process where a chloroiron(III)-monoazaetioporphyrin {Fe(III)(Cl)(MAEP)} was used as the initial substrate. Fe(III)(Cl)(MAEP) was synthesized according to published procedures [8, 18]. Free-base monoazaetioporphyrin {H$_2$(MAEP)} compound was obtained at the first stage of the synthesis [8] and next iron was incorporated into the monoazaetioporphyrin molecules using FeCl$_3$ enriched (about 95%) with the ^{57}Fe isotope [18]. The reduction process was performed using the chemical method by contact of tetrahydrofuran (THF) solution with metallic sodium. Because reduction products are air sensitive, the reaction was carried out in a vacuum line (10^{-2} Pa), inside a special cuvette which contained a vessel, where reduction reaction was carried out, cells for electronic absorption and Mössbauer samples and a quartz tube for EPR measurements. The electronic absorption spectra as well as EPR spectra were examined during the reduction reaction. The concentration of iron porphyrins in solution for EPR samples was about 10^{-3} M and for electronic absorption measurements – about 10^{-4} M. Details of the reduction process are the same as in the case of NMR investigations of other iron porphyrins [8]. Samples for Mössbauer measurements were prepared as powder layers obtained after evaporation of THF solvent. The layers contained about 4×10^{-4} g/cm^2 of ^{57}Fe. Mössbauer spectra were recorded with a ^{57}Co(Rh) source at room temperature. Isomer shifts are given *vs.* metallic iron. The parameters of Mössbauer spectra were found by fitting the experimental spectra to Lorentzian lines using the NORMOS-90 program [3]. Mössbauer data were correlated with EPR spectra. EPR measurements were performed at liquid-nitrogen temperature using a conventional X-band spectrometer, equipped with an IBM PC data acquisition system. Electronic absorption spectra were recorded with a Specord UV-VIS spectrometer.

Results

Mössbauer studies of trivalent and divalent porphyrin complexes have been studied practically soon after the discovery of the Mössbauer effect [4]. Mössbauer spectrum of the Fe(III)(Cl)(MAEP) complex, which we have studied recently [6], exhibits an asymmetrical doublet with the following parameters: isomer shift δ = 0.31 mm/s, quadrupole splitting ΔE_Q = 1.03 mm/s. The corresponding Mössbauer parameters for Fe(III)(Cl)-octaethylporphyrin ($S = 5/2$) with CH methine bridges at all four α, β, γ, δ positions are the following: δ = 0.41 mm/s, ΔE_Q = 0.93 mm/s (values at 4.2 K) [5] and the parameters for Fe(III)(Cl)(TAOEP) ($S = 3/2$) are as follows (two doublets are assigned to two different local environments for iron, caused by differences

in solvation [7]): δ$_1$ = 0.28 mm/s, ΔE_{Q_1} = 2.98 mm/s, δ$_2$ = = 0.07 mm/s, ΔE_{Q_2} = 2.90 mm/s [7]. Characteristic values of *g*-factors in EPR spectra of high-spin ($S = 5/2$) iron porphyrins in axial symmetry of ligand fields are equal to: $g_\perp$ = 6.0 and $g_{//}$ = 2.0 [11] while *g*-factors in the same conditions for the pure intermediate spin state ($S = 3/2$) are equal to: $g_\perp$ = 3.98 and $g_{//}$ = 1.99 [7]. The *g*-factors in an EPR spectrum of Fe(III)(Cl)(MAEP) complex corresponding to $g_\perp$ value are somewhat deviated from 6.0 and are equal to g_x = 5.93, g_y = 5.86. Splitting of the $g_\perp$ component in the latter spectrum is caused by lowering of the porphyrin-ring symmetry as a result of the *aza* substitution. The value of $g_{//}$-factor remains unchanged and it is equal to 2.00. Characteristic bands in the electronic absorption spectrum of Fe(III)(Cl)(MAEP) are the following: 360, 552 and 640 nm.

At the first stage of the reduction process, the chloride axial ligand is removed from the Fe(III)(Cl)(MAEP) molecule and a divalent iron Fe(II)(MAEP) complex appears. A noticeable shoulder observed on the higher-energy component of Fe(II)(MAEP) Mössbauer spectrum (Fig. 1b) suggests that this spectrum should be fitted at least by two doublets. Previously [6], we assigned both doublets to two forms of Fe(II)MAEP complex. We supposed that existence of two forms of Fe(II)(MAEP) in the solid state can be connected with THF molecules bonded to Fe(II)(MAEP) macrocycles which were not removed during the solvent evaporation or with conformationally distorted macrocycles, as it was suggested in the case of Fe(II)(TAOEP) [7]. However, when we repeated the reduction process we have observed at this stage a low intensity EPR spectrum characteristic of univalent iron porphyrin complexes. The EPR spectrum indicates that one of the doublets in Mössbauer spectrum shown in Fig. 1b, may belong to the univalent iron Fe(I)(MAEP) complex and the other one should be assigned to Fe(II)(MAEP). Intensity of the doublet with the parameters: δ$_1$ = 0.16 mm/s, ΔE_{Q_1} = 1.76 mm/s increases during the further reduction and the second one with the parameters: δ$_2$ = 0.21 mm/s, ΔE_{Q_1} = 2.03 mm/s disappears in the same time and, therefore, the former doublet was assigned to Fe(I)(MAEP) and the latter to Fe(II)(MAEP). (Some deviations from the parameters values given in paper [6] can be caused by different fitting procedures.) The electronic absorption spectra of both complexes differ significantly. Characteristic bands for Fe(II)(MAEP) are: 365, 560, 665 nm and for Fe(I)(MAEP): 363, 385, 435, 490, 560, 600 and 680 nm.

EPR spectrum of the Fe(I)(MAEP) complex exhibits strong perpendicular (g_x = 2.35, g_y = 2.21) and parallel (g_z = 1.92) components [6]. It should be noted that numerical analysis of this EPR spectrum indicates existence of one type of paramagnetic species at this stage of the reduction process. After next contact of the solution with metallic sodium, an additional component characteristic of π-radicals appears in the EPR spectrum (g = 2.00) and only slight changes are observed in the corresponding Mössbauer spectrum. It means that successive electron in the reduction process localizes on the porphyrin ring and the [Fe(I)(MAEP$^\bullet$)]$^-$ complex is generated. This complex is stable only in solution and it is transferred into Fe(I)(MAEP) after evaporation of the solvent (in Mössbauer samples).

On higher reduction levels, Mössbauer spectra become more complex. Intensity of the component corresponding to Fe(I)(MAEP) decreases and numerical analysis indicates two additional components (Fig. 1c). Parameters which describe the Mössbauer spectrum, shown in Fig. 1c, are the following: first component (A): $\delta_1 = 0.13$ mm/s, $\Delta E_{Q_1} = 1.61$ mm/s; second component (B): $\delta_2 = 0.15$ mm/s and $\Delta E_{Q_2} = 1.38$ mm/s; third component (C): $\delta_3 = 0.76$ mm/s and $\Delta E_{Q_3} = 3.45$ mm/s. An additional signal appears in the EPR spectrum at this stage of the reaction and two distinct parallel components are observed while the shape of the perpendicular components is characteristic for Fe(I)(MAEP) complexes. It suggests that this spectrum belongs to two paramagnetic centres. Fitting of the theoretical EPR spectrum to the experimental one has shown that parameters corresponding to both paramagnetic species are close one another: $g_{x_1} = 2.34$, $g_{y_1} = 2.20$, $g_{z_1} = 1.92$ and $g_{x_2} = 2.41$, $g_{y_2} = 2.18$, $g_{z_2} = 1.79$.

The reduction process ran very slowly during further contact of the solution with a sodium mirror, no additional product was observed and the reaction was stopped at this stage.

Discussion

Comparison of Mössbauer and EPR data for the Fe(III)(Cl)(MAEP) complex containing partly substituted CH methine bridges by nitrogen with the corresponding data for the porphyrin analogues containing all the substituted and unsubsited methine bridges indicates a quantum-mechanically mixed spin state ($S = 5/2, 3/2$) of the iron in the former complex with predominant character of the high-spin state [6]. Asymmetry observed in the high-spin Fe(III)-porphyrin Mössbauer spectra are caused by magnetic relaxation processes [2].

Electrons transferred from the Na atoms into the iron porphyrin molecules during the chemical reduction process can be localized on the iron ion, on the porphyrin ring or on both. In the case of iron porphyrins, transformations of one product of the reduction into another can occur involving solvent molecules and counter ions. Thus, correct analysis of spectroscopic data is not a simple task.

The first product of the reduction obtained during this investigations is Fe(II)(MAEP). The Mössbauer parameters of this complex suggest the intermediate spin state ($S = 1$), as it was observed for other square planar Fe(II)-porphyrins {Fe(II)P} without solvent (THF) environment [4]. It is known that some Fe(II)P can be weakly coordinated with one or two THF molecules and in both cases Fe(II) ions are in the high spin ($S = 2$) state [4, 17]. It means that THF molecules were absent in the Fe(II)(MAEP) layer prepared for the Mössbauer measurements. Generation of π-radical anions of the type [Fe(II)(MAEP•)]⁻, suggested in paper [10], should be excluded because no EPR spectrum which could be assigned to π-radicals has been observed at this stage of the reduction. Fe(II)P complexes are EPR silent since the conventional EPR technique is generally not applicable to integer spins, non-Kramers systems.

A successive step of the reduction leads to the univalent Fe(I)(MAEP) complex. The Mössbauer and EPR results indicate the low spin state ($S = 1/2$) of iron in the complex
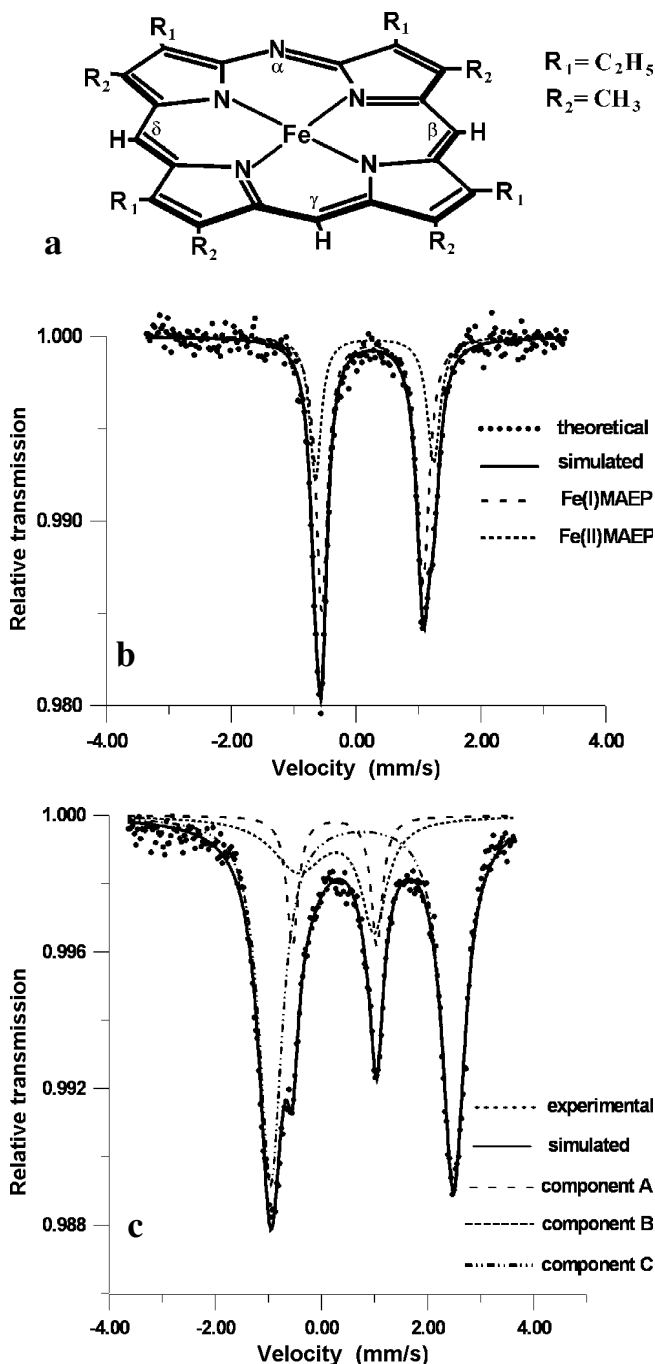
Fig. 1. a – Molecular structure of Fe(MAEP) complex. Experimental and simulated Mössbauer spectra; b – Fe(II) and Fe(I)MAEP; c – products at further reduction stages: component A – Fe(I)MAEP, component B – Fe(I)MAEPh, component C – Fe(0)MAEPh.

studied. Partly resolved hyperfine structure was observed in the $g_\perp$ component of the Fe(I)(MAEP) EPR spectrum, like in the case of other univalent-iron EPR spectra of porphyrin complexes in THF solutions [9, 19]. This hyperfine structure is observed only in the case of THF solutions and it is assigned to the interaction of the unpaired electron localized at d_z^2 orbital with four hydrogen atoms of THF molecules [9]. It indicates that the electron configuration of Fe(I) coordinated with the MAEP ligand is the following: $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z^2})^1$.

The further contact of the Fe(I)(MAEP) with Na gives [Fe(I)(MAEP•)]⁻ π-radical with localization of the unpaired electron on the MAEP ligand. It means that two unpaired electrons are present in such a species. Because each of the two unpaired electrons gives own EPR signal, the spin interaction between these electrons is rather weak. It confirms additionally the electron configuration of Fe(I) ions proposed for the complex studied.

The Mössbauer and EPR data for products obtained at the highly reduced stages suggest the existence of two forms (assigned to A and B) of complexes which contain Fe(I) ions and one complex (C) with Fe(0) in the centre. The form A is the same Fe(I)(MAEP) complex which was observed at the beginning of the reduction process and the structure of the form B is not clear now. We suppose that it can be a phlorin structure. It was shown earlier [16] that the reduction of Zn-monoazaporphyrins leads to such an electron distribution in porphyrin ring where relatively large negative charge is induced on the carbon atom of the methine bridge localized in front of the N bridge. The large negative charge favours binding of protons to the CH methine bridge and this leads to generation of Zn-phlorins. The phlorin structures (Ph) were also suggested in the case of the reduction of Fe-porphyrins [1]. Taking into account the above reasons we postulate that Fe(I)(MAEPh) structures are possible in this case. However, some complexes which contain THF molecules or Na⁺ ions cannot be excluded. Assignment of the form C to the complex coordinated to Fe(0) was done on the basis of electronic absorption spectra [17]. If one assumes that the phlorin structure is obtained at the previous stage of the reduction, then Fe(0)(MAEPh) should be generated at this stage. Characteristic feature of the Mössbauer doublet of this complex is the relatively large values of the isomer shift and quadrupole splitting. Bands in the electronic absorption spectra of the phlorin structures are the following: Fe(I)(MAEPh) – 354, 425, 580, 745 nm and Fe(0)(MAEPh) – 366, 496, 616, 663, 706, 700 and 783 nm.

Molecular structure of the complexes obtained at the two last stages of the reduction process remains open to further studies.

Conclusion

To summarize the problems considered in this paper we make the following statements:

– the chemical reduction process of Fe-monoazaetio-porphyrin complexes runs in the multi-stage way with localization of additional electrons both on the iron ions and on the porphyrin ring;

– Mössbauer and EPR data indicate three forms of the univalent-iron monoazaetioporphyrin complexes: first – typical Fe(I)(MAEP), second – with an additional electron on the porphyrin ligand [Fe(I)(MAEP•)]⁻ and third – the Fe(I)(MAEPh) phlorin structure. Electron configuration of Fe(I) ions in these complexes is $(d_{xy})^2(d_{xz},d_{yz})^4(d_{z^2})^1$;

– values of the isomer shifts and quadrupole splitting assigned to Fe(0)(MAEPh) are much greater than the corresponding parameters for the other products of the reduction process.

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