

Spectroscopic characteristics of Fe^I-phthalocyanine

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Abstract. Results of Mössbauer and EPR study of a univalent-iron phthalocyanine complex (Fe^IPc) are presented in this paper. Fe^IPc has been obtained from Fe^{II}Pc by the chemical reduction method in tetrahydrofuran (THF) and dimethoxyethan (DME) solutions. Like in the case of Fe^I-porphyrin complexes, Mössbauer and EPR data as well as quantum calculations of electronic absorption spectra confirm in this case a low-spin configuration of Fe^I ions with an unpaired electron located at d_{z^2} orbital. Interaction between Fe^IPc and THF molecules does not change significantly the electron configuration of Fe^I ions coordinated to phthalocyanine ligand.

Key words: iron phthalocyanine • reduction process • Mössbauer spectroscopy • EPR • DFT

Introduction

Phthalocyanines and their metallo-derivatives have attracted attention mainly from view of their practical applications. In contrast to metalloporphyrins, phthalocyanines take no part in biological processes important for life and they have not commanded such intense attention. Applications of phthalocyanines (Pc) in industrial technologies are usually connected with their functions as catalysts, dyes, sensitizers, photovoltaic materials, molecular semiconductors etc. [5, 9, 14]. Metal ions, placed at the centre of the phthalocyanine ligands effect significantly on physical and chemical properties of the whole complexes. Iron ions coordinated to tetrapyrrole ligands exhibit a variety of oxidation and spin states [19] and the background information on the relationship between their electronic configurations and ligand structures can be helpful for prediction of more extended applications of these complexes in the future. Iron phthalocyanine complexes have been studied intensively in their commonly occurring oxidation states such as Fe^{III} and Fe^{II}, e.g. [10, 11, 14]. Study of iron porphyrins (FeP) and phthalocyanines (FePc) with unusual oxidation states such as Fe^I, Fe⁰ or Fe^{IV} is at the very beginning stage, although it has almost a forty-year history [23]. Different papers dealing with porphyrins and phthalocyanines containing Fe^I, Fe⁰ and Fe^{IV} atoms present sometimes ambiguous data because of complexity of the redox processes involving iron. As far as Fe^I tetrapyrrole complexes are concerned, there is much more spectroscopic data for iron porphyrins, e.g. [4, 7–9, 13, 16, 17, 20, 24, 26] than for iron phthalocyanines [6, 12,

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15, 22, 23]. One of the strong limitations to an extensive study of $\text{Fe}^{\text{I}}\text{Pc}$ is the low solubility of $\text{Fe}^{\text{II}}\text{Pc}$ in the commonly used solvents in reduction processes [21].

In this paper, we discuss the results of Mössbauer and EPR study of the $\text{Fe}^{\text{I}}\text{Pc}$ complex. It is worth noticing that Mössbauer data dealing with an anionic product, generated in THF solution by transition of an electron from metallic lithium to iron(II)-phthalocyanine, are interpreted in paper [24] as obtained from a complex $[\text{Fe}^{\text{II}}\text{Pc}]^-$, with additional electron located at the π -orbital of the phthalocyanine ring, while the same data are attributed in paper [22] to a $\text{Fe}^{\text{I}}\text{Pc}$ complex with an additional electron occupied the $3d$ -orbital of the iron ion. In the case of EPR study of $\text{Fe}^{\text{I}}\text{Pc}$, different spectra have been obtained in papers [6, 12]. The main aim of this paper is to give unequivocal spectroscopic characteristic of the $\text{Fe}^{\text{I}}\text{Pc}$ complex.

Experimental

$\text{Fe}^{\text{I}}\text{Pc}$ complex (Fig. 1a) was obtained at the first step of the reduction process of $\text{Fe}^{\text{II}}\text{Pc}$ by contact of THF or DME solutions with a sodium mirror. $\text{Fe}^{\text{II}}\text{Pc}$ compound was purchased from Aldrich Chemical Co. and purified by sublimation. The solvents were carefully degassed by freeze-thaw cycles. The reduction process was controlled by means of electronic absorption spectra (Figs. 2a and 2d). The $\text{Fe}^{\text{I}}\text{Pc}$ reduction product is air sensitive and the reaction was run on a vacuum line. A special cuvette which contained a vessel where the reduction reaction was carried out, a cell for absorption and Mössbauer spectra and a quartz tube for EPR spectra, allowed to carry out the reaction in anaerobic conditions. ^{57}Fe Mössbauer spectra were obtained with a $^{57}\text{Co}(\text{Rh})$ source and powder absorbers in the horizontal transmission geometry 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. Layers prepared by evaporation of DME solvent were destroyed during registration of Mössbauer spectra and it was impossible to record their spectra in the horizontal transmission geometry of the spectrometer. The parameters of Mössbauer spectra were found by fitting the experimental spectra to Lorentzian lines using the NORMOS-90 program [1]. The results of Mössbauer spectra analysis were correlated with EPR data. EPR measurements were performed at liquid-nitrogen temperature using a conventional X-band spectrometer, equipped with an IBM PC data acquisition system. DFT calculations of electronic absorption spectra were carried out using the Amsterdam Density Functional (ADF) program package [25].

Results and discussion

The electronic absorption spectra of transition metal phthalocyanines are much more complex than the corresponding spectra of phthalocyanines coordinated to Mg or Zn. One of possible reasons of the complexity

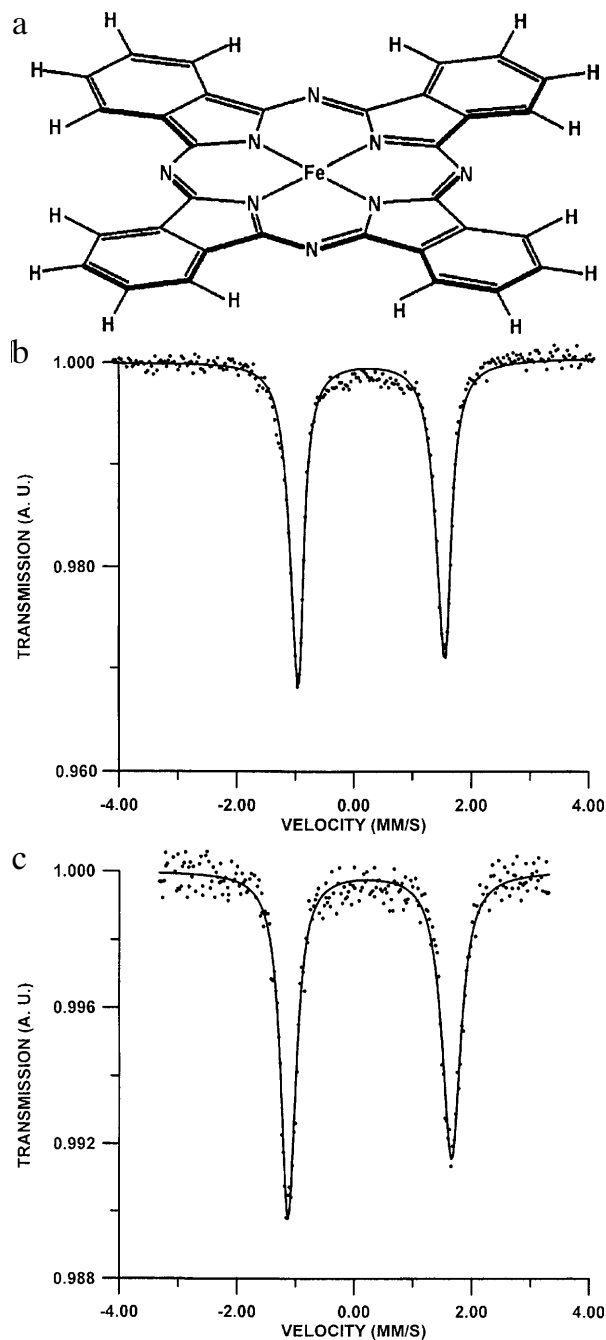


Fig. 1. Molecular structure of FePc complex (a), Mössbauer spectra of $\text{Fe}^{\text{II}}\text{Pc}$ (b) and $\text{Fe}^{\text{I}}\text{Pc}$ (c) at room temperature.

of these spectra can be the potential presence of metal \rightarrow ligand and ligand \rightarrow metal charge transfer bands [15]. The electronic absorption spectra of the $\text{Fe}^{\text{I}}\text{Pc}$ studied, presented as the insets in Fig. 2, coincide very well with the corresponding spectrum of the $\text{Fe}^{\text{I}}\text{Pc}$ complex generated by the electrochemical reduction in pyridine [12]. The spectrum recorded for $\text{Fe}^{\text{I}}\text{Pc}$ in THF solution (characteristic bands of the high intensity: 325, 399, 515, 598, 661 and 807 nm) is very close to that recorded for $\text{Fe}^{\text{I}}\text{Pc}$ in DME solution (323, 401, 516, 599, 664 and 807 nm). This can suggest that the interaction between $\text{Fe}^{\text{I}}\text{Pc}$ and THF molecules is rather weak and cannot change significantly the electronic structure of the univalent phthalocyanine complex. DFT calculations of

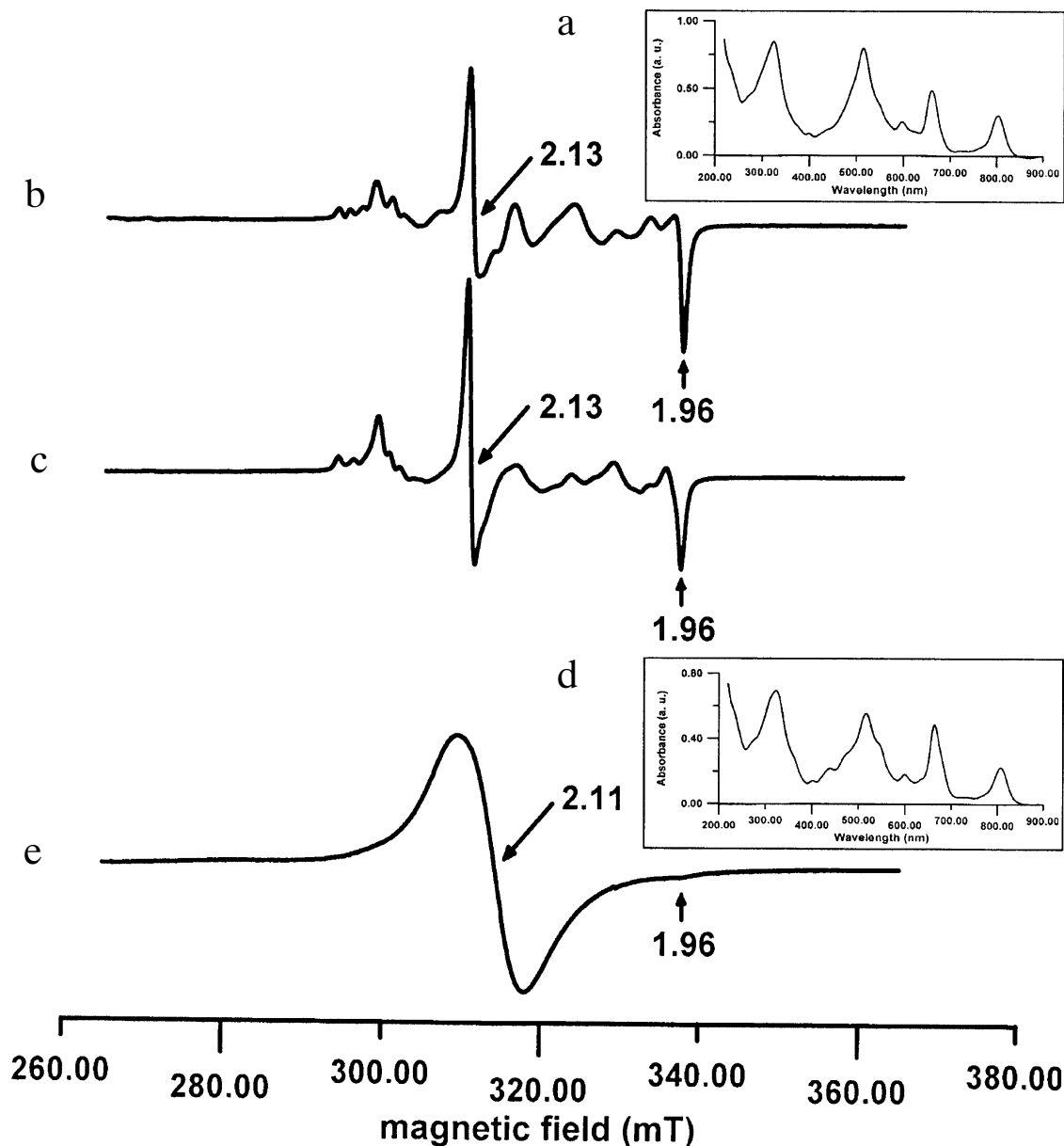


Fig. 2. EPR spectra of Fe^IPc in THF solution (b and c) and in DME solution (e) at 80 K. Insets show electronic absorption spectra of Fe^IPc in THF solution (a) and DME solution (d) at room temperature.

the electronic absorption spectra of Fe^IPc for $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z^2})^1$ electron configuration of Fe^I have shown many bands. The most intensive bands (oscillator strength $f > 0.05$) are the following: 221, 231, 232, 247, 263, 264, 316, 337, 343, 355, 456, 481, 541 and 641. The long-wave band 808 nm has a very low intensity ($f = 0.01$) in comparison with the experimental one. Relative intensities of the other bands in the theoretical spectrum are similar to those observed in the experimental spectra. Detailed results of Fe^IPc calculations will be published in a separate paper.

Mössbauer spectra of the Fe^IPc and Fe^{II}Pc complexes (Fig. 1) are similar in shape and parameter values (Table 1). Both are slightly asymmetrical. Such a kind of the asymmetry is characteristic of the electronic spin relaxation processes [18] and of positive sign of the V_{zz} component of electric field gradient (EFG) tensors. The positive sign of the V_{zz} indicates that Fe ion has a more

negative charge in the porphyrin plane than the perpendicular to it [2]. To describe the asymmetry we have introduced an asymmetry parameter W_{21} (Table 1) which is equal to the linewidth ratio of the higher energy absorption line of the doublet to the lower energy absorption line (Γ_2/Γ_1). This assignment is acceptable because of the equal areas under the components of the doublets. Comparing Mössbauer parameters collected in Table 1 one can notice that values obtained for Fe^{II}Pc in this paper are close to those from paper [22]. However, in the case of the Fe^IPc complex a significant difference in quadrupole splittings Q is observed. It should be noted that Mössbauer spectra considered in papers [22, 23] were recorded for frozen THF solution while the spectra discussed in the frame of this paper were recorded for powder samples which, however, contained a significant amount of THF molecules. Because parameter values of Fe^{II}Pc spectra

Table 1. Parameters of Mössbauer spectra of Fe-phthalocyanines at room temperature

Compound	Q (mm/s)	δ (mm/s)	Γ_1 (mm/s)	Γ_2 (mm/s)	W_{21}	Ref.
Fe ^{II} Pc	2.51 ± 0.02	0.37 ± 0.01	0.28 ± 0.01	0.31 ± 0.02	1.09 ± 0.02	this work
Fe ^{II} Pc	2.58 ± 0.02	0.38 ± 0.01	–	–	–	22
Fe ^I Pc	2.80 ± 0.02	0.38 ± 0.01	0.30 ± 0.02	0.36 ± 0.04	1.21 ± 0.04	this work
Fe ^I Pc	3.24 ± 0.03	0.35 ± 0.02	–	–	–	22

are close one another (Table 1), the sample preparation cannot explain the difference in the quadrupole splittings of the Fe^IPc spectra. It should be added that the quadrupole splittings of Fe^I-porphyrins show much lower values (e.g. 1.97 mm/s for Fe^I-octaethylporphyrin [3]) in comparison with those for Fe^IPc summarized in Table 1. It is well known that the value of the quadrupole splitting depends on the interaction between a nuclear quadrupole moment and a non-zero electric field gradient (EFG) at the nucleus. Because nuclear quadrupole moment is constant for a given Mössbauer nuclide (⁵⁷Fe), changes in the quadrupole interaction energy, under constant experimental conditions, can only arise from changes in the EFG at the nucleus. The total EFG depends on three main factors: (i) valence electron contribution which originates from anisotropic electron distribution in the valence *d*-shell of the ⁵⁷Fe ion, (ii) lattice contribution from charges on distant atoms which surround the ⁵⁷Fe ion and (iii) lattice contribution from charge distribution in the covalent bonds. If we assume the same electron configuration of Fe^I ions in porphyrins and phthalocyanines which corresponds to low spin state $S = 1/2$ (see EPR data in this paper and [3, 12]), and a similar symmetry of charge distribution around the Fe^I ion in porphyrin and phthalocyanine complexes, it is reasonable to expect that in this case the lattice contribution from charges on distant atoms and the covalency term have a more significant effect on the Q value than the valence electron contribution. Some differences in isomer shifts of Fe^I-porphyrins and phthalocyanines can be attributed to the slight changes in the population of *s* atomic orbitals of Fe^I ions.

EPR spectra of Fe^IPc in THF and DME (Fig. 2) are similar in shape and parameters to Fe^I-porphyrins and correspond to the electron configuration of Fe^I: $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z^2})^1$ [7, 13, 24]. A similar spectrum of Fe^IPc (with superhyperfine splitting from pyridine) was observed in the case of the electrochemical reduction [12] and quite different spectrum showing nine intensive lines was obtained in paper [6] in the case of chemical reduction by contact with Na in THF solution. In our opinion the later EPR spectrum can correspond to more highly reduced species, when the additional electron is taken up by the ligand. The EPR spectra obtained from THF solution (Figs. 2b, 2c) indicate a relatively intensive component close to $g_{\perp} = 2.13$, a less prominent absorption derivative near $g_{\parallel} = 1.96$ and a number of lower intensity lines. The low-intensity hyperfine structure has been observed earlier in EPR spectra of Fe(I)-porphyrin complexes in THF solutions [4, 13]. Identical low-intensity lines could be detected at the moment when the solution is frozen. If the sample is

thaw and next frozen again the relative intensity of the lines is significantly changed (compare Figs. 2b and 2c). This suggests that this kind of hyperfine splitting can be connected with the interaction of an unpaired electron with protons of THF molecules. The changeable form of this part of the EPR spectra indicates that the hyperfine-interaction lines correspond to some statistically average orientation of THF molecules with respect to the phthalocyanine ring. So, the observed lines are a result of the overlapping of a great number of spectra with somewhat different hyperfine splittings from local orientations of THF in relation to Fe^IPc. In such a case simulation of these spectra is rather impossible. The Fe^IPc EPR spectrum detected from DME solution (Fig. 2e) shows a significant line broadening in comparison with the spectra from THF solution. This suggests that the THF solvent, interacting with Fe^IPc molecules, prevents their aggregation in a higher degree than the DME solvent. The similar *g* values of both kinds of the spectra indicate that the interaction of THF and Fe^IPc molecules does not change the electron configuration of Fe^I ions coordinated to phthalocyanine ligands.

Conclusion

Summing up, we can conclude that the electronic and Mössbauer spectroscopies, EPR data as well as DFT calculations of the electronic absorption spectra confirm formation of the Fe^IPc complex at the first stage of the Fe^{II}Pc reduction. Interaction of the THF solvent with Fe^IPc does not influence the electronic structure of Fe^I ions coordinated to the phthalocyanine ligand. Electron configuration of Fe^I ions is the same as in the case of Fe^I-porphyrins, that is $(d_{xy})^2(d_{xz}, d_{yz})^4(d_{z^2})^1$. Reduction process of Fe-porphyrins and phthalocyanines is rather complex and needs further systematic investigations, especially of highly-reduced species.

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