Magnetic interactions in frozen solutions of ironporphyrins

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Abstract. The powder samples of *meso*-tetraphenyloporphyrin iron(III) chloride and ferriprotoporphyrin IX chloride and their frozen in solutions *N,N*-dimethylformamide were studied by Mössbauer spectroscopy. The variation of the outer ligands of the porphyrin rings modifies their magnetic properties but the major influence on the magnetic relaxation process exerts the intermolecular magnetic interactions, which are eliminated in dilute solutions.

Key words: Fe-porphyrin • intermolecular interactions • magnetic relaxation • Mössbauer spectroscopy

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Introduction

The correspondence between the structural and electronic properties of the soft matter and their biological activity in life processes is the leading topic in molecular biophysics and medical physics. The solid state researches use usually dense, solid, lyophilized samples where intermolecular interactions may not be neglected. Thus, the question if the obtained results are relevant to *in vivo* situation, where these molecular systems are in the form of well dilute liquid solutions, is quite fundamental. Here this aspect is studied in a particular case of the magnetic interactions in ironporphyrins.

The ironporphyrins as naturally occurring compounds as well as their synthetic derivatives consist of macrocyclic porphyrins ring containing four subunits interconnected by the methane bridges. Porphyrins have a high ability to aggregation. Long-term studies of porphyrins lead to their diverse applications in science or medicine. For example, porphyrin derivatives are used both in the therapy and medical diagnostics as photosensitizers as well as a contrast in the magnetic resonance imaging. Moreover, due to their exceptional properties, porphyrins found application in industry as catalyst materials, semiconductors, colorants and sensors of volatile organic compounds.

Samples

The samples of iron-porphyrins complexes, namely *meso*-tetraphenyloporphyrin iron(III) chloride (FeTPPCl) and ferriprotoporhyrin IX chloride (FePPPIXCl) (Alfa Aesar) were studied by transmission Mössbauer spectroscopy. In both compounds iron Fe^{3+} occupies the centre of the identical porphyrin ring, but they differ in the external ligands, since the hydrocarbon chains in FePPIXCl have been replaced by four phenyl groups in FeTPPCl. The samples were studied in the powder form and in their frozen solution in DMF *(N,N-dimethylformamide)*.

Experimental and results

Powder samples

The Mössbauer spectra of FeTPPCl in the powder form were taken at 6 K in the external magnetic field, *B*, of 4.5 T and 9 T given by a superconducting magnet. The field was parallel to the gamma radiation. The 100 mCi $^{57}Co(Rh)$ source was kept at zero-field point at 6 K.

The spectra obtained in the external magnetic field at 6 K are shown in Fig. 1. In the residual field of 0.05 T the spectrum exhibits a relaxation pattern. The field of 4.5 T blocks significantly a spatial fluctuation of the Fe^{3+} atomic magnetic moments; at 9 T the spectrum is in the form of the static Zeeman pattern. Obtained from the fit the value of the effective magnetic field at ^{57}Fe nuclei, B_{eff}, is 36 T which means that the saturated internal hyperfine field, B_o, $B_o = B + B_{eff}$, is 45 T, the value typical of the Fe^{3+} state. The residual 2nd and 5th line in the spectrum are due to the poor collimation of the gamma beam and mixed quadrupole electric and magnetic interactions.

Next, the spectra of the powder sample of FeTPPCl were measured in the zero field in the temperature range between 80 and 300 K with the use of a bath cryostat with a 25 mCi $^{57}Co(Rh)$ source at room temperature.
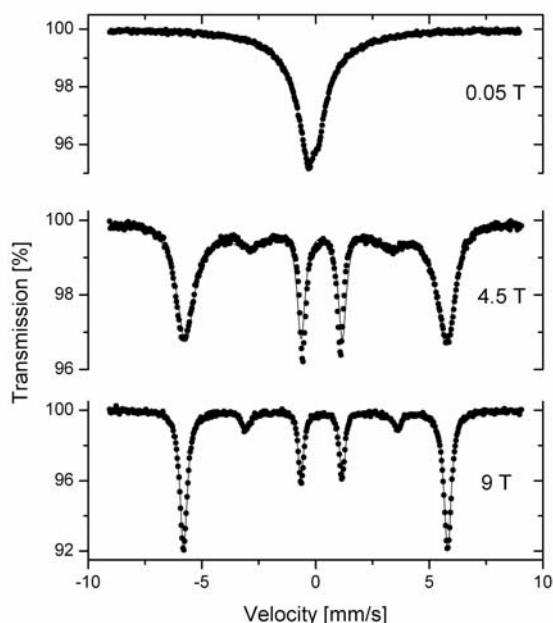

Fig. 1. Mössbauer spectra of ironporphyrin (FeTPPCl) at a temperature of 6 K in external magnetic fields as marked.
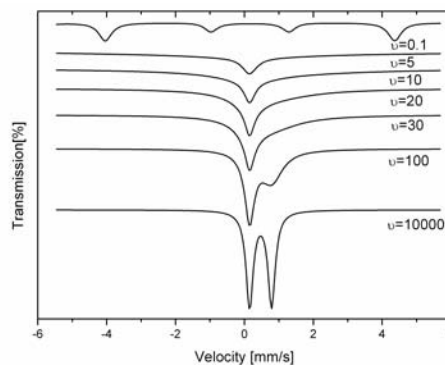

Fig. 2. The simulation of the relaxation spectra for the different frequency fluctuation, ν, of the hyperfine magnetic field $B_o = 45$ T. The frequency fluctuation is in the units of $1/\tau_{1/2}$, where $\tau_{1/2}$ is 141 ns, the lifetime of ^{57}Fe excited nuclear level. For ν = 0.1 (static case) only four inner lines are shown.

They have been numerically evaluated by Rancourt's MOSMOD program [4], which uses the Blume-Tjon model of relaxations [1]. Some examples of the simulated relaxation spectra for different values of the frequency fluctuations rate, ν, of the hyperfine field are shown in Fig. 2. The chosen experimental spectra are shown in Fig. 3. The fitted parameters, especially the magnetic field and the relaxation rate are strongly correlated. However, in the studied case the value of B_o could be fixed as 45 T. Thus, the obtained values of the fluctuation rates appear reliable. The temperature dependence of the relaxation time, τ, is shown in Fig. 4 and compared with the data obtained previously [2, 5].

Frozen solutions

The Mössbauer spectra of the frozen solution were measured subsequently at 80, 180 and 250 K (above the freezing point of DMF) and next again at 80 K using a Wissel spectrometer with the helium bath cryostat, as in the case of the powder samples. Because of the small solubility of the porphyrins in DMF, the resonance effect was well below 1%. However, due to the compact geometry of the cryostat and the fast electronics, it was
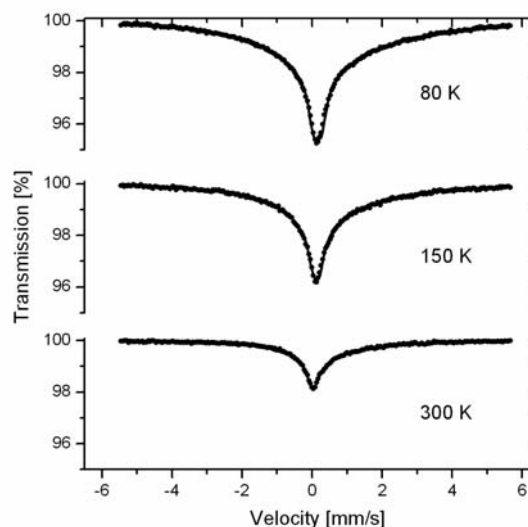

Fig. 3. The chosen Mössbauer spectra of powder FeTPPCl samples at temperatures as marked.
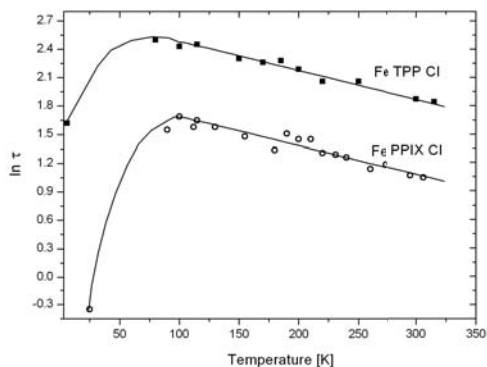
Fig. 4. A comparison of the temperature dependence of the relaxation time, τ (ns) of the magnetic moments of Fe^{3+} for powder FeTPPCl and FePPIXCl samples. The data for FePPIXCl were taken from [2].

possible to reach count rate of 15 000 counts/s in the Mössbauer line for the 25 mCi source. The measuring time was typically 48 h and the final statistics was 10^7 counts, with the relative statistical error of $3*10^{-4}$, 10 times smaller than the observed resonance effect. The obtained spectra are shown in Figs. 5 and 6. At 250 K, no resonant absorption has been detected after 48 h measurement which is the evidence that there was no measurable pollution by iron in the counter and/or cryostat windows. Surprisingly, the FeTPPCl spectrum re-measured at 80 K (after leaving the samples in the liquid form at 250 K) differed from the primary one. We explain this by the sedimentation of the porphyrin aggregates. This rather accidental observation allowed interpretation of the spectra, which are composed of the relaxation pattern arising from the porphyrin aggregates and of the symmetric quadrupole doublet which should be assigned to the isolated molecules, remaining in the solution after aggregates sedimentation. The difference in the relative contribution to the total spectrum at 80
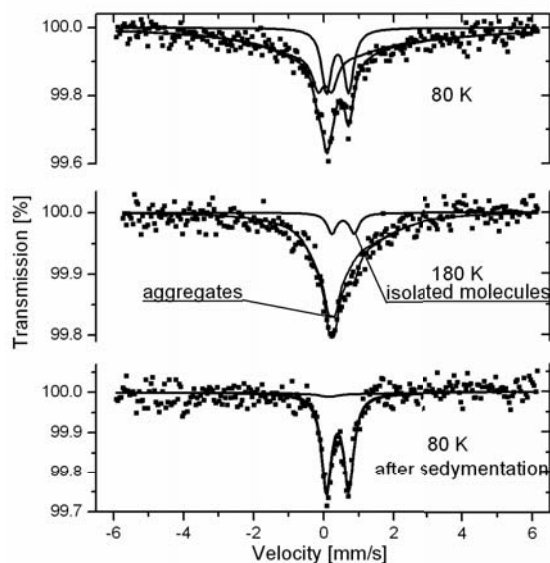

Fig. 5. Mössbauer spectra of the frozen FeTPPCl solution at a temperature of 80 and 180 K. The lowest spectrum (80 K) were taken after sedimentation of the small aggregates. The solid lines are the fits assuming two components: the paramagnetic doublet for isolated molecules and the relaxation pattern for small aggregates.

Fig. 6. Mössbauer spectra of the frozen FePPIXCl solution at a temperature of 80 and 180 K. The solid lines are the fits assuming two components: the paramagnetic doublet for isolated molecules and the relaxation pattern for small aggregates.
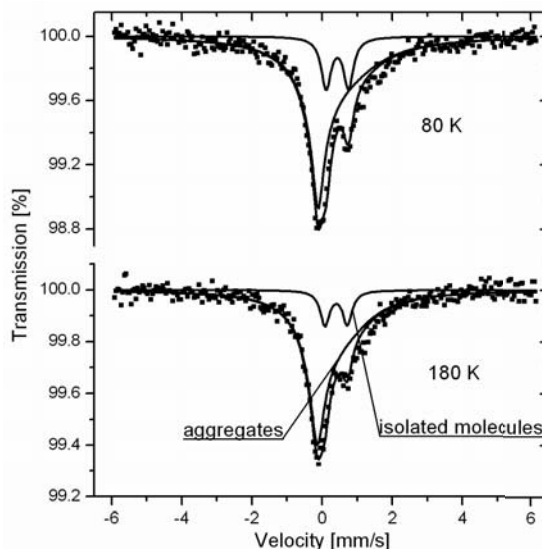
and 180 K is caused by the significant difference in the recoil free fraction for monomers in the solution and for aggregates. The sedimentation of FePPIXCl was negligible, probably because of its higher solubility in the DMF.

Discussion

A comparison of the temperature dependence of the relaxation time for FePPIXCl and FeTPPCl shows that the modification of the external ligands of the porphyrins, namely replacing the hydrocarbon chains in FePPIXCl by four phenyl groups in FeTPPCl slows down the magnetic relaxation of the central Fe^{3+} ions. Moreover, both specimens exhibit the surprising speeding up of the relaxation at low temperature, which used to be assigned to the preferential population of the low lying fast relaxing electronic states, determined by the crystal field [1]. This might suggest that the magnetic properties of the porphyrins are their inframolecular feature.

However, the previous magnetic susceptibility measurements [5] showed a weak antiferromagnetic coupling between Fe^{3+} ions, characterized be the g-factor of 1.99(1) and $zJ = -0.6(1)$ cm^{-1} value, where z is a number of the nearest neighbors and J is the exchange integral. Thus, the average antiferromagnetic interaction energy, $zJS(S + 1)$ is $\sim10^{-22}$ J. In the external magnetic field, B, the energy of ion with magnetic moment μ is μB. Estimating the magnetic movement of Fe^{3+} as $\mu = 4.6*10^{-23}$ JT^{-1}, one may conclude, that at $B \sim 2$ T the energy of internal antiferromagnetic coupling between Fe^{3+} ions becomes comparable with the energy of its interaction with external magnetic field. Indeed, the Mössbauer spectrum of FePPPIXCl at 4.5 T shows a strong alignment of the Fe^{3+} magnetic moments. This result is consistent with our previous conclusions [5]. The significant broadening of the resonant absorption lines may be caused by the still existing relaxation with the relaxation time comparable to the lifetime of the

14.4 keV excited state of the probe ^{57}Fe nucleus and/or may be related to the thermal population of the excited atomic states (Kramer doublets). For the field of $B = 9$ T, the energy of the magnetic interaction, μB, where μ is the magnetic moment of the Fe^{3+}, is about 30 K. Thus, at 6 K only one atomic level is occupied, that of the spin oriented parallel to the field. Consequently, all nuclei in the sample experience the same hyperfine field and the Mössbauer spectrum is in the form of one Zeeman pattern, perturbed only by the random distribution of the orientation of the main axis of the electric field gradient vs. magnetic field. Such an effect has been observed for Fe^{3+} in fluorohemoglobin [3].

For the final elucidation of the nature of the magnetic interactions in porphyrin powders, the experiments on the frozen solution samples were fundamental. The Mössbauer spectra of the individual well separated porphyrin molecules are in the form of the symmetric quadrupole doublet which is the evidence of the paramagnetic state. This means that the magnetic properties of the porphyrins powders are due to the antiferromagnetic intermolecular interactions.

Conclusions

By the adjustment of the outer ligands, one may slightly modify the inframolecular magnetic properties of the ironporphyrins. The major magnetic interactions are related to the intermolecular iron-iron coupling which are absent in the dilute systems. Thus, in the biological systems, the magnetic interactions between iron atoms might be taken into account only if the porphyrin-related centres form complexes, e.g. in hemoglobin. However, even in this case, the iron-iron separation is about four porphyrin subunits and probably the magnetic interactions are negligible.

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