

Asymmetry in Mössbauer spectra of Fe^{III}-azaporphyrin complexes

Tomasz Kaczmarzyk,
Tomasz Jackowski,
Kazimierz Dziliński,
Gennadij N. Sinyakov

Abstract. Temperature dependence of asymmetry as well as isomer shift and quadrupole splitting values of Mössbauer spectra of trivalent iron complexes coordinated to porphyrin ligands such as octaethylporphyrin, monoazaethioporphyrin, diazaoctaethylporphyrin and phthalocyanine is discussed in this paper. All the above mentioned complexes have the chloride axial ligand at the fifth coordination site. Different temperature changes of asymmetry and other parameters of Mössbauer spectra of these complexes can be correlated with a number of methine bridges *CH* substituted by nitrogen atoms in the porphyrin macrocycle. The form of this asymmetry is such that the higher-energy component of the doublet is more broadened than the lower-energy one, while the areas (intensities) under each of two components are the same. The most distinct asymmetry is observed at room temperature. When temperature is decreasing, the spectrum becomes successively more symmetrical and at liquid helium temperature linewidths of both components of the quadrupole splitting are very close one another. The Mössbauer spectrum of the FeCl-monoazaethioporphyrin complex exhibits reversed asymmetry at liquid helium temperature in comparison with the spectra of the remaining complexes i.e. the lower-energy component of the doublet is slightly more broadened than the higher-energy one. The spin-spin and spin-lattice relaxation mechanisms in the context of quantum mechanically mixed spin states $S = 5/2 + 3/2$ of Fe^{III} ions are considered as a source of the observed asymmetry.

Key words: Mössbauer spectroscopy • iron porphyrins • azaporphyrins • asymmetry in Mössbauer spectra • spin-spin and spin-lattice relaxation

Introduction

Mössbauer spectroscopy in association with numerical analysis of spectra is a very effective tool in molecular and electronic structure investigations of chemical compounds or materials which contain Mössbauer-sensitive elements. Besides the main spectral Mössbauer parameters such as the isomer shift, quadrupole splitting and distribution of internal magnetic field also some important data of interaction between atoms sensitive to Mössbauer effect and their environment can be obtained from linewidth and symmetry of the spectra [10]. We have observed recently [12] that asymmetric line broadening in the ⁵⁷Fe Mössbauer spectra can be correlated with a molecular structure of trivalent iron porphyrins. It was shown that at room temperature the most distinct asymmetry is observed in a Mössbauer spectrum of Fe^{III}Cl-octaethylporphyrin [Fe(OEP)Cl] which contains four methine bridges (*CH*) in the *meso* positions of the porphyrin ring (Fig. 1). If the *CH* bridges are successively substituting by nitrogen atoms (*aza*-substitution), the corresponding Mössbauer spectra become more symmetrical at the same temperature. It should be noticed that the nearest surrounding of the Fe ions is the same in all the complexes studied and the *aza*-substitution involves the methine bridges

T. Kaczmarzyk, T. Jackowski, K. Dziliński✉
Institute of Physics,
Częstochowa University of Technology,
19 Armii Krajowej Str., 42-200 Częstochowa, Poland,
Tel./Fax: +48 34 3250795,
E-mail: dzil@mim.pcz.czyst.pl

G. N. Sinyakov
Institute of Molecular and Atomic Physics,
Belarus Academy of Sciences,
Prosp. F. Skoryny 70, 220 072 Minsk, Belarus

Received: 20 June 2006

Accepted: 14 December 2006

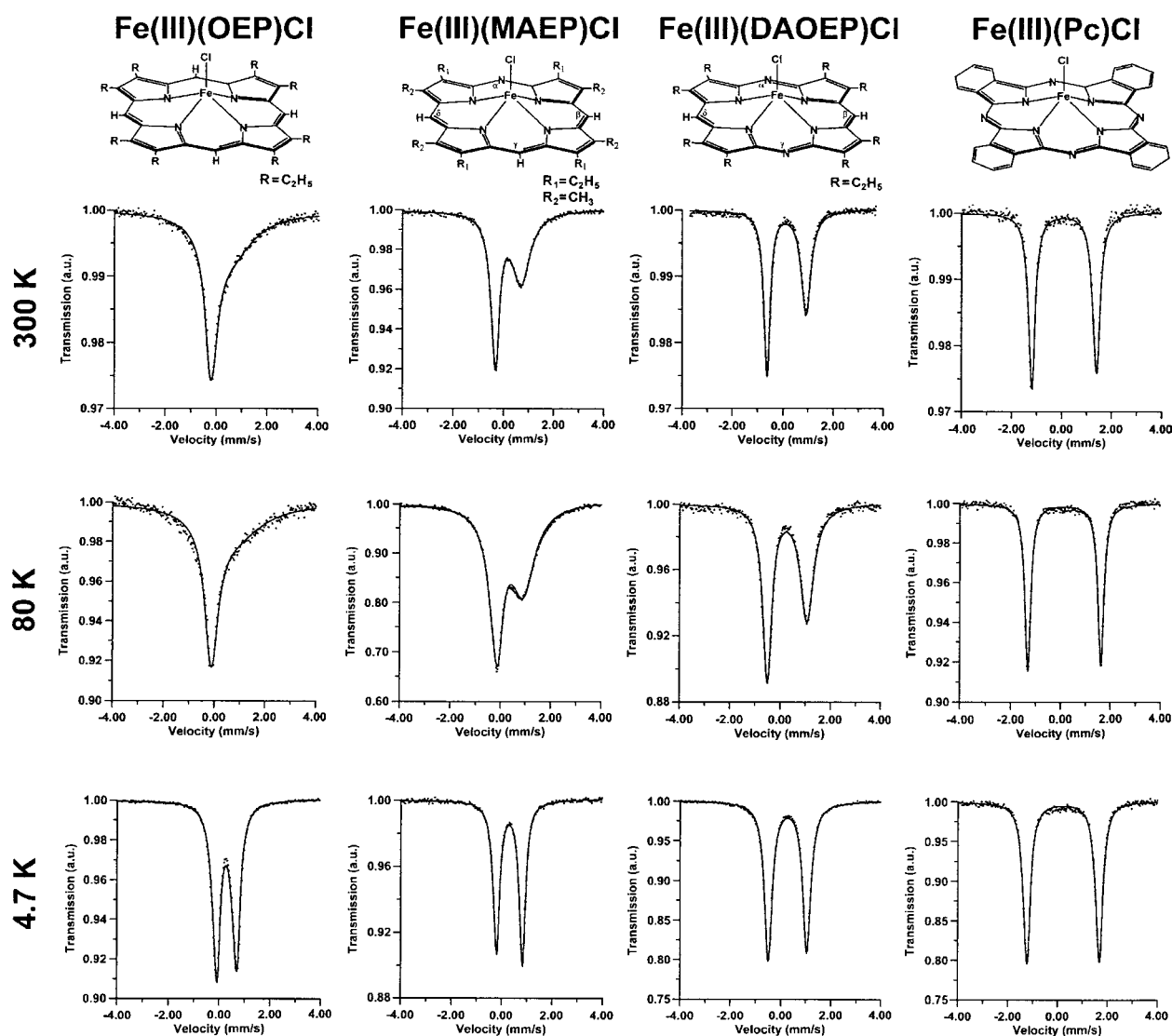


Fig. 1. Molecular structures and Mössbauer spectra of the Fe^{III}-porphyrins and phthalocyanine.

placed in the porphyrin macrocycle at a relatively long distance from the central iron ion (Fig. 1). The increase of quadrupole splitting values (ΔE_Q) with an increasing number of nitrogen atoms at *meso* positions suggests changes of the trivalent-iron electron configuration from 'pure' high-spin state ($S = 5/2$) for the Fe(OEP)Cl complex, through quantum-mechanically mixed spin states ($S = 5/2 + 3/2$) for the FeCl-mono- and diazaporphyrins, to 'pure' intermediate-spin state ($S = 3/2$) for FeCl-terazaporphyrins [12]. In this paper, we consider temperature dependence of the shape and parameter values of Mössbauer spectra of the trivalent iron porphyrin, monoazaporphyrin, diazaporphyrin and phthalocyanine complexes and we analyze the relaxation processes as possible mechanisms of the observed asymmetry. This study is going towards explanation, at the molecular level, of the effect of distant parts of the porphyrin ring on electron configuration of the central iron ion which determines biological activity as well as physical and chemical properties of this kind of complexes [13]. Iron porphyrins, because of their molecular structure, can be considered as model systems of the heme which is a main component of the

hemoproteins such as hemoglobin, myoglobin and some enzymes [17]. 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 others [13].

Experimental

Fe(MAEP)Cl and Fe(DAOEP)Cl complexes were prepared according to standard procedures described in [14]. Fe(OEP)Cl, H₂(OEP) and Fe(Pc)Cl compounds were purchased from Aldrich Chemical Co. and used as reagents of commercial quality. Mössbauer spectra were obtained with a ⁵⁷Co(Rh) source at room, liquid nitrogen and liquid helium temperatures. A metallic iron foil absorber was used to calibrate the velocity scale, and isomer shifts were given vs. metallic Fe. Samples for Mössbauer measurements were prepared as layers obtained after evaporation of the tetrahydrofuran or dimethoxyethane solvents. The layers contained about 4×10^{-4} g/cm² of ⁵⁷Fe. The parameters of Mössbauer

Table 1. Parameters of the Mössbauer spectra of the Fe^{III}-porphyrins and phthalocyanine^a

Compound	Fe(III)(OEP)Cl			Fe(III)(MAEP)Cl			Fe(III)(DAOEP)Cl			Fe(III)(Pc)Cl		
	300	80	4.2	300	80	4.2	300	80	4.2	300	80	4.2
ΔE_Q (mm/s)	0.75 (0.02)	0.85 (0.03)	0.82 (0.01)	1.04 (0.01)	1.08 (0.01)	1.04 (0.01)	1.55 (0.01)	1.58 (0.01)	1.54 (0.01)	2.59 (0.01)	2.92 (0.01)	2.90 (0.01)
δ (mm/s)	0.28 (0.01)	0.41 (0.02)	0.42 (0.01)	0.28 (0.01)	0.40 (0.01)	0.41 (0.01)	0.24 (0.01)	0.36 (0.01)	0.37 (0.01)	0.19 (0.01)	0.27 (0.01)	0.30 (0.01)
Γ_1 (mm/s)	0.60 (0.02)	0.65 (0.01)	0.37 (0.01)	0.41 (0.01)	0.65 (0.01)	0.36 (0.01)	0.29 (0.01)	0.43 (0.01)	0.36 (0.01)	0.31 (0.01)	0.31 (0.01)	0.35 (0.01)
Γ_2 (mm/s)	2.14 (0.10)	2.10 (0.11)	0.39 (0.02)	0.87 (0.02)	1.13 (0.01)	0.34 (0.01)	0.47 (0.02)	0.66 (0.02)	0.38 (0.01)	0.36 (0.01)	0.32 (0.02)	0.35 (0.01)
W_{21}	3.54 (0.08)	3.22 (0.10)	1.06 (0.01)	2.13 (0.01)	1.74 (0.01)	0.95 (0.01)	1.59 (0.02)	1.51 (0.02)	1.06 (0.01)	1.10 (0.01)	1.02 (0.01)	1.00 (0.01)

^a Errors in parentheses.

spectra were found by fitting the experimental spectra to Lorentzian lines using the NORMOS-90 program [3].

Results and discussion

We have mentioned earlier [12] that the correlation between molecular structure and Mössbauer parameters of the trivalent Fe-porphyrins and their azaporphyrin analogues should be considered in the context of the quantum mechanically spin states of the Fe^{III} ions. According to Maltempo's model [16], mixing of the ⁶A₁ sextet with ⁴A₂ quartet occurs via spin-orbit coupling, $\lambda \vec{L} \cdot \vec{S}$, in which the splitting between the two multiplets in units of λ (Δ/λ) is varied from negative to positive value giving the continuous ground-state changes from ⁶A₁ ($d_{xy}^1, d_{xz}^1, d_{yz}^1, d_{z^2}^1, d_{x^2-y^2}^1$) to ⁴A₂ ($d_{xy}^2, d_{xz}^1, d_{yz}^1, d_{z^2}^1$). Mössbauer and EPR data indicate the presence of a single quantum-mechanically mixed ground-state and rule out a thermal mixture of high- and low-spin states as a possible explanation of the unusual magnetic moments of Fe^{III} ions in some Fe-porphyrins [6, 18, 20]. On the basis of these data, one can conclude that the mixing of the ⁶A₁ sextet with ⁴A₂ quartet is induced by axial ligands bonded directly to Fe^{III} ions. We have shown [12] that such a mixing can be caused by the *aza*-substitution, too.

Mössbauer spectra of Fe^{III}Cl-porphyrins measured at room temperature as well as at liquid nitrogen and helium temperatures are shown in Fig. 1. Parameter values of these spectra are listed in Table 1. At first, we will discuss briefly the questions due to temperature dependence of the isomer shifts (δ) and quadrupole splittings (ΔE_Q) and next we will consider the temperature changes asymmetry observed in the Mössbauer spectra of the Fe^{III}Cl-porphyrins under study.

Isomer shift

A slight increasing of the isomer shift values δ with decreasing temperature in the range 300–5 K is

observed for all the complexes. Because of lack of phase transitions in these compounds, the temperature change of the observed isomer shifts should be attributed to the second order Doppler shift δ_{SOD} . An experimentally observed isomer shift contains contribution of δ_{SOD} which depends on lattice dynamics [21]. Because the sign of δ_{SOD} is negative, so the smaller absolute value of the δ_{SOD} the greater positive value of the experimentally observed isomer shift. The temperature dependence of the δ_{SOD} is assigned to decreasing of the mean square velocity $\langle v^2 \rangle$ of the Mössbauer atom induced by lattice vibrations with temperature decreasing and the value of the observed isomer shift δ becomes somewhat higher. The temperature changes of $\Delta\delta$ is equal approximately to 0.10–0.14 mm/s can be considered as a correction of the spectrum-centre shift characterized by the 'pure' isomer shift. Rearrangement effect resulting from changes in $3d$ population of the Fe^{III} ions during transformation of the high spin state $S = 5/2$ [Fe(OEP)Cl] into $S = 3/2 + 5/2$ [Fe(Pc)Cl], with predominant contribution of the intermediate spin state ($S = 3/2$), leads to a slight decreasing of the isomer shifts, assuming that the population of s atomic orbitals remains unchanged.

Quadrupole splitting

It can readily be seen from Table 1 that significant variation of the quadrupole splitting value with temperature is observed for the Fe(Pc)Cl complex, rather weak dependence exhibits the Fe(OEP)Cl compound and completely temperature independent are quadrupole splittings of the Fe(MAEP)Cl and Fe(DAOEP)Cl azaporphyrins. To our knowledge, the temperature dependence of the quadrupole splitting has not been explained quantitatively so far. Thermal electronic population of states which are energetically close to each other was suggested as a possible explanation [6], but other reasons should be considered as well. Molecular orbital (MO) calculations of the fifth coordinate Fe^{III}Cl-porphine [Fe(P)Cl] carried out using the

semiempirical INDO-SCF/CI method [8] and later [15] using the density-function theory (DFT) approach done with the Amsterdam Density Functional (ADF) program package developed by Baerends and co-workers [22], predict the intermediate-spin quartet 4A_2 as a ground state and the high-spin sextet 6A_1 as a first excited state for Fe(Pc)Cl and FeCl-porphine [15]. Experimental data indicate quantum mechanically mixed spin state $S = 3/2 + 5/2$, with a predominant contribution of the intermediate $S = 3/2$ component and a small admixture of the high spin $S = 5/2$ one for the Fe(Pc)Cl complex and reversed order of the ground and first excited states for FeCl-porphyrins with unsubstituted *meso*-bridges [18, 20]. Ethyl peripheral substituents (C_2H_5) taken into account in MO calculations of the Fe(OEP)Cl lead to reduction of energy gap between the 4A_2 and 6A_1 states by about 0.1 eV, but the 4A_2 state remains lower than 6A_1 [15]. Results of our calculations carried out with the ADF method and the exchange correlation potential based on the parameterization from [11, 19] have shown correct order of the ground and excited states. The calculations were performed for the Fe-porphyrins such as Fe(P)Cl, Fe(III)Cl-monoazaporphine [Fe(MAP)Cl] and Fe(III)Cl-diazaporphine [Fe(DAP)Cl] without the peripheral substituents as well as for the Fe(Pc)Cl complex. The sextet state was found to be about 0.15 eV below the quartet excited state for the Fe(P)Cl complex and 0.10 eV for Fe(MAP)Cl. For Fe(DAP)Cl and for Fe(Pc)Cl the quartet was determined as a ground state localized below the sextet excited state about 0.01 eV and 0.12 eV, respectively. If it is assumed that the thermal electronic population is the only possible reason of the quadrupole-splitting temperature dependence, then the most noticeable temperature dispersion of the quadrupole-splitting values should be observed in the Fe(DAOEP)Cl spectra while the experimental data indicate the Fe(Pc)Cl spectrum. This means that this problem cannot be explained only on the basis of the thermal electronic population.

The comparison of the quadrupole splitting values summarized in Table 1 has shown that the ΔE_Q increases with increasing number of nitrogen atoms at the bridge positions. It is well known that the value of the quadrupole splitting depends on the interaction between the nuclear quadrupole moment Q and the non-zero electric field gradient (EFG) at the nucleus. Because Q is constant for a given Mössbauer nuclide (for ^{57}Fe in nuclear excited state $Q \cong 0.18 \times 10^{-24} \text{ cm}^2$ [9]) 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 [10]: (i) valence electron contribution which originates from anisotropic electron distribution in the valence d -shell of the ^{57}Fe ion, (ii) lattice contribution from charges on distant atoms which surround the ^{57}Fe ion and (iii) lattice contribution from charge distribution in the covalent bonds. Redistribution of d -electrons in the $^{57}\text{Fe}^{\text{III}}$ ion during transformation from $S = 5/2$ spin state [Fe(OEP)Cl] to the spin state close to $S = 3/2$ [Fe(Pc)Cl] ($d_{x^2-y^2} \rightarrow d_{xy}$) and similar symmetry of charge distribution around the ^{57}Fe ion in both complexes confirm the state that the valence

electron contribution has a more significant effect on the ΔE_Q value than the lattice contribution from charges on distant atoms. The covalency term is also important in iron porphyrins and phthalocyanines because of the relatively large difference in strength of the in-plane and out-of-plane bonds.

Asymmetry of the Mössbauer spectra

Asymmetry of Mössbauer spectra has different forms and has been discussed in a few papers, for example [5, 9, 10]. In the case of Fe-porphyrins and their biological analogues, the asymmetry is usually limited to the inhomogeneous broadening of the doublets [2, 4, 6, 7, 20]. Considering the temperature dependent changes in the shape of the spectra analyzed in the frame of this paper (Fig. 1), one can find that the most noticeable asymmetry changes are observed for the Fe(OEP)Cl complex with pure high-spin ground state. Characteristic feature of this asymmetry is that the higher-energy (higher-velocity) component of the doublet is more broadened than the lower-energy one. Such a kind of the asymmetry is characteristic of the electronic spin relaxation processes [10] and positive sign of the V_{zz} component of the 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 [20]. To describe the observed asymmetry numerically we have introduced an asymmetry parameter W_{21} which is equal to the linewidth ratio of the higher energy absorption line of the doublet to the lower energy absorption line. For the FeCl-azacomplexes, which contain substituted *CH* methine bridges by one (α position) or two ($\alpha\gamma$ positions) nitrogen atoms and four nitrogens in the case of the Fe(Pc)Cl, the asymmetry changes of Mössbauer spectra become successively less pronounced as temperature is decreased and for Fe(Pc)Cl they are negligible. To our knowledge there are two mechanisms which can lead to the increase of the asymmetry as the temperature is raised, excluding effects connected with the sample preparation and the inappropriate geometric arrangement in a transmission spectrometer: (i) Goldanskii-Karayagin effect [9] and (ii) temperature dependent spin-spin relaxation [2]. The Goldanskii-Karayagin effect is based on the anisotropy of the Debye-Waller factor for a nucleus in a site with lower than cubic symmetry. This effect predicts different intensities (areas under the spectrum lines) each of the two doublet components. Because the asymmetry arises from the considerable line broadening of one of the two doublet components with conservation of their equal intensities, the Goldanskii-Karyagin effect cannot explain the asymmetry observed in our Mössbauer spectra.

Let us consider the effect of relaxation processes on the asymmetry of Mössbauer spectra. The spin-lattice relaxation lessens the asymmetry of Mössbauer spectra with temperature increasing. Fe^{III} ions in spin-lattice relaxation interact with the lattice by spin-orbit and orbital-phonon coupling which is related to fluctuation in the electrostatic crystal field potential or to lattice vibrations [10]. Since the matrix elements of

the orbital angular momentum vanish for the high-spin state of Fe^{III}Cl-porphyrins, the influence of the spin-lattice relaxation on the asymmetry of the spectra is not expected to be important in comparison with the spin-spin relaxation, although some spin-lattice relaxation involving the one-phonon direct process (at low temperatures) and two-phonons indirect process (at higher temperatures) has been found to be possible [1]. In the case of spin-spin relaxation, the energy transfer occurs between interacting Fe^{III} ions via dipole (or exchange) coupling. This suggests that one should observe concentration dependence of the spin-spin relaxation instead of temperature dependence. However, if different spin-spin relaxation rate for different Kramers doublets $|\pm 1/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$, resulting from the splitting of the 6A_1 state in crystalline field has been assumed, temperature-dependent spin-spin relaxation can become possible [2]. It was shown theoretically by Blume [2] that spin-spin relaxation for the $|\pm 1/2\rangle$ state is faster than for the $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$ states. Since the $|\pm 1/2\rangle$ state is appreciably occupied at liquid helium temperature, a symmetric spectrum is observed. At considerably higher temperatures, all the Kramers doublets are occupied equally and the spectrum becomes asymmetrically broadened because of the slowly relaxing $|\pm 3/2\rangle$ and $|\pm 5/2\rangle$ states. In the case of the *aza* substituted complexes such as Fe(MAP)Cl, Fe(DAOEP)Cl and Fe(Pc)Cl, with Fe^{III} at admixed spin state ($S = 5/2 + 3/2$), the orbital angular momentum is not longer close to zero and the electronic spin-lattice relaxation becomes more important. In our opinion it is reasonable to assume that the shape of the Mössbauer spectra of these complexes depends on the competitive mechanisms of the spin-lattice and spin-spin relaxations. The increase of the intermediate-spin component ($S = 3/2$) in the quantum-mechanically mixed spin state ($S = 5/2 + 3/2$) leads to the more essential effect of the spin-lattice relaxation on the asymmetry which becomes temperature dependent in a smaller degree. Such a picture of the asymmetry changes is observed in the experimental spectra.

It should be noticed that the Mössbauer spectrum of the Fe(MAEP)Cl complex (Fig. 1) exhibits reversed asymmetry at liquid helium temperature in comparison with the spectra of this complex at 80 K and room temperatures, i.e. the lower-energy component of the doublet is slightly more broadened than the higher-energy one. This rather unexpected feature is difficult to unequivocal explanation. At first sight, it can suggest the sign changing of the V_{zz} component of the EFG tensors from positive to negative values, but the physical background for such a temperature dependence is problematical. Although, if one assumes that the V_{zz} direction is strongly sensitive to the covalency term of the lattice contribution, this temperature dependence of the asymmetry seems to be possible, but it is not clear why this strange feature is observed only for the low-symmetry Fe(MAEP)Cl complex.

To estimate the influence of the spin-spin relaxation mechanism on the shape of the Mössbauer spectrum we prepared the sample which contained a mixture of the Fe(OEP)Cl and iron-free octaethylporphyrin [H₂(OEP)] compounds in the ratio 1:1, to reduce the

spin-spin relaxation rate by increasing Fe-Fe separation. The temperature changes of the parameter values and the asymmetry in Mössbauer spectra of this sample was found to be very similar to those for the pure Fe(OEP)Cl complex ($\delta = 0.27$ mm/s, $\Delta E_Q = 0.72$ mm/s and $W_{21} = 3.44$ at room temperature and $\delta = 0.42$ mm/s, $\Delta E_Q = 0.81$ mm/s and $W_{21} = 1.05$ at 4.2 K), although EPR spectrum of the mixed sample indicates noticeable decreasing of the dipole-dipole interaction. It means that the EPR spectroscopy appeared in this case to be more sensitive to spin relaxation processes than the Mössbauer spectroscopy.

Conclusion

We have discussed briefly the temperature dependence of the isomer shifts and quadrupole splittings as well as in detail the asymmetry of Mössbauer spectra of the iron tetrapyrrole complexes containing different number of the substituted methine *CH* bridges by nitrogen atoms. It has been shown that the ΔE_Q values and the temperature changes of the asymmetry of the Mössbauer doublets are quantitatively correlated with the high-spin ($S = 5/2$) and intermediate-spin ($S = 3/2$) components of the quantum-mechanically mixed spin state ($S = 5/2 + 3/2$). The higher contribution of the intermediate-spin component the larger ΔE_Q value and the less pronounced temperature dependence of the asymmetry. The asymmetry of the Mössbauer spectra is analyzed in the light of the spin-spin and spin-lattice relaxations considered as the competitive mechanisms determining the shape of the spectra of the complexes studied.

Acknowledgment The authors would like to thank Dr A. M. Shulga from the Institute of Molecular and Atomic Physics Belarus Academy of Sciences for Fe(MAEP)Cl and Fe(DAOEP)Cl syntheses and Dr J. Żukrowski from the University of Mining and Metallurgy in Cracow for recording of the Mössbauer spectra at helium temperatures.

References

1. Bizzari AR, Iakovleva OA, Parak F (1995) Spin-lattice relaxation in Mössbauer spectra of metmyoglobin: investigation of crystals, water and water-glycerol solutions. *Chem Phys* 191:185–194
2. Blume M (1967) Temperature-dependent relaxation times: application to the Mössbauer spectra of ferric hemin. *Phys Rev Lett* 18:305–308
3. Brand RA, <http://www.wissel-instruments.de/produkte/software.html>
4. Burda K, Hryniewicz A, Kołoczek H, Stanek J, Strzałka K (1995) Mixed valence state in ironporphyrin aggregates. *Biochim Biophys Acta* 1244:345–350
5. Clauser MJ, Mössbauer RL (1969) Pseudoquadrupole shift and asymmetric line broadening of recoilless nuclear resonance spectra. *Phys Rev* 178:559–567
6. Debrunner PG (1989) Mössbauer spectroscopy of iron porphyrins. In: Lever ABP, Gray HB (eds) *Iron porphyrins*. Part III. VCH Publishers, New York, pp 140–234

7. Dzilinski K (2000) Unusual linewidth in Mössbauer spectra of methoxy-Fe^{III}-octaethylporphyrin complex. *Mol Phys Rep* 30:38–43
8. Edwards WD, Weiner B, Zerner MC (1988) Electronic structure and spectra of various spin states of (porphinato)iron(III)chloride. *J Phys Chem* 92:6188–6197
9. Goldanskii VI, Herber RH (eds) (1968) Chemical applications of Mössbauer spectroscopy. Academic Press, New York-London
10. Gutlich P, Link R, Trautwein A (eds) (1978) Mössbauer spectroscopy and transition metal chemistry. Springer-Verlag, Berlin-Heidelberg-New York
11. Handy NC, Cohen RJ (2001) Left-right correlation energy. *Mol Phys* 99:403–412
12. Kaczmarzyk T, Jackowski T, Dzilinski K, Sinyakov GN (2004) Effect of nitrogen substitution in porphyrin ring on Mössbauer parameters of iron ions. *Nukleonika* 49;Suppl 3:S13–S16
13. Kadish KM, Smith KM, Guillard G (eds) (2000) The porphyrin handbook. Vol. 6. Academic Press, San Diego
14. Kobayashi N (2000) Meso-azaporphyrins and their analogues. In: Kadish KM, Smith KM, Guillard R (eds) The porphyrin handbook. Academic Press, San Diego. Vol. 3, pp 301–321
15. Liao M-S, Scheiner S (2002) Comparative study of metal-porphyrins, -porphyrazines and -phthalocyanines. *J Comput Chem* 23:1391–1403
16. Maltempo MM, Moss TH (1976) The spin 3/2 state and quantum spin mixture in haem proteins. *Quarterly Rev Biophys* 9:181–215
17. Milgrom LR (1997) The colours of life. Oxford University Press, Oxford-New York
18. Palmer G (1983) Electron paramagnetic resonance of hemoproteins. In: Lever ABP, Gray HB (eds) Iron porphyrins. Part II. Addison-Wesley Publishing Company, London-Amsterdam-Tokyo, pp 69–77
19. Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation. *Phys Rev Lett* 77:3865–3868
20. Sams JR, Tsin TB (1979) Mössbauer spectroscopy of iron porphyrins. In: Dolphin D (ed) The porphyrins. Academic Press, New York-San Francisco-London. Vol. 4, pp 425–475
21. Shenoy GK, Wagner FE, Kalvius GM (1978) The measurement of the isomer shift. In: Shenoy GK, Wagner FE (eds) Mössbauer isomer shifts. North-Holland Publishing Company, Amsterdam-New York-Oxford, pp 49–110
22. te Velde G, Bickelhaupt FM, Baerends EJ *et al.* (2001) Chemistry with ADF. *J Comput Chem* 22:931–967