



Mössbauer study of a tetrakis (pentafluorophenyl) porphyrin iron (III) chloride in comparison with the fluorine unsubstituted analogue

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Abstract. Mössbauer investigations, in association with density functional theory (DFT) calculations, have been conducted for the molecular and electronic structures of iron (III) [tetrakis (pentafluorophenyl)] porphyrin chloride [(F₂₀TPP)Fe:Cl], as a Fe(III)-tetraphenylporphyrin complex containing chloride axial ligand and substituted hydrogen atoms by fluorine ones in the four phenyl rings, in comparison with its fluorine unsubstituted analogue [(TPP)Fe:Cl]. It was found that the parameters of Mössbauer spectra of both complexes are close to one another, and correspond to the high-spin state of Fe(III) ions, but they show the different temperature dependence and the quadrupole doublets in Mössbauer spectra show different asymmetry at low temperatures. Results of DFT calculations are analyzed in the light of catalytic activity of the halogenated complex.

Key words: catalytic activity • DFT calculations • electronic structure • iron(III)-[tetrakis (pentafluorophenyl)] • Mössbauer spectroscopy • porphyrin chloride

Introduction

Metalloporphyrins belong to complexes which are often used as model systems in investigations of catalytic mechanisms in many chemical and biological reactions [1, 2]. Iron porphyrins play an important role in oxidation–reduction reactions as effective catalysts, especially in those which involve hemo-proteins [3]. 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 [4]. Such a wide application of the iron porphyrins is connected, among other things, with their interesting feature to modify relatively easily molecular and electronic structures. Tetraphenylporphyrin compounds, including iron complexes, have been relatively intensively investigated both experimentally [5–8] and theoretically [9–12], but they are yet far from being determined with certainty, especially with reference to the relationships between molecular and electronic structures. Iron porphyrins containing halogenated substituents attached to porphyrin rings are particularly efficient for epoxidation and hydroxylation reactions [13–15]. The epoxidation and hydroxylation reactions are oxidative processes which usually require some catalysts to accelerate the pace of these reactions.

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Combination of experimental data with theoretical calculations is a very effective approach to study electronic structure, even in the case of relatively complex systems like iron porphyrins. We consider in this paper, results of Mössbauer study of an iron (III) [tetrakis (pentafluorophenyl)] porphyrin chloride complex $[(F_{20}TPP)Fe:Cl]$, containing fluorine atoms instead of hydrogen atoms in the four phenyl rings, in association with results of DFT calculations. Comparison of the results for $(F_{20}TPP)Fe:Cl$, which is a relatively effective catalyst with results for less chemically active unsubstituted analogue, $(TPP)Fe:Cl$, in epoxidation and hydroxylation reactions, creates some possibility to understand, at molecular level, catalytic mechanisms of important chemical and biological reactions. The results are analyzed in the light of correlation between catalytic properties and the electronic structure of the complexes studied.

Experimental and calculation procedures

Unsubstituted $(TPP)Fe:Cl$ and fluorine substituted $(F_{20}TPP)Fe:Cl$ compounds were purchased from Sigma Aldrich Chemical Co. and used as reagents of commercial quality. Tetrahydrofuran (THF) solvent was carefully degassed by freeze-thaw cycles with the use of a metallic potassium and sodium (KNa) alloy. Mössbauer spectra of powdered unenriched samples were recorded in horizontal transmission geometry using a constant acceleration spectrometer. The source $^{57}Co(Rh)$ was kept at room temperature and samples were detected in the 6–295 K temperature range. A metallic iron foil absorber was used to calibrate the velocity scale, and zero velocity was taken as the centroid of its room temperature Mössbauer spectrum. The samples for Mössbauer measurements

were prepared as powder layers obtained after evaporation of the 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 program package as previously [16]. DFT calculations of Mössbauer parameters were carried out using the Amsterdam Density Functional (ADF) program package [17].

Results and discussion

Molecular structures

Molecular structures of the complexes studied are shown in Fig. 1. Molecular geometry of both complexes was optimized by using DFT methods with OLYP functional (Hartree exchange and Lee–Young–Parr correlation potentials) and TZP (triple dzeta plus polarization) Slater type orbitals as basic functions, including the scalar relativistic ZORA treatment [17, 18]. The calculations were done for the ground state 6A corresponding to high-spin Fe(III) ions in the $((d_{xy})^1(d_{xz})^2(d_{yz})^1(d_{x^2-y^2})^1)$ electronic configuration. The coordination bond distances are collected in Table 1. Results obtained in this paper are in good correlation with experimental data [19, 20] and other theoretical calculations obtained with the use of the Gaussian-98 [21] and Gaussian-09 [9] program packages. The experimental [20] and our results of the theoretical calculations, as well as other theoretical data [9, 21], indicate the displacement of the iron atom out of the four-nitrogen-atoms plane equal to about 0.5 Å. Comparison of the theoretical and experimental data shows good precision of the geometry calculations. Changes of the bond lengths in the phenyl rings induced by the fluorine substitu-

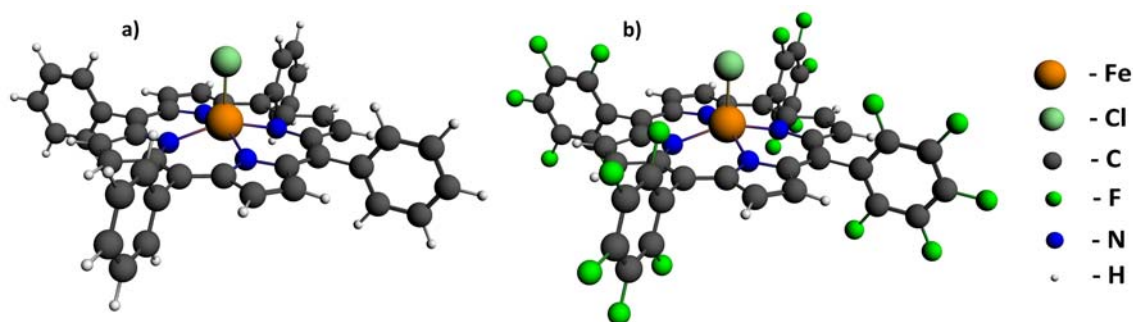


Fig. 1. Molecular structures: a) $(TPP)Fe:Cl$, b) $(F_{20}TPP)Fe:Cl$.

Table 1. Geometry parameters of $(TPP)Fe:Cl$ and $(F_{20}TPP)Fe:Cl$ complexes around Fe(III) ions obtained from DFT calculations

Complex	Fe-N [Å]	Fe-Cl [Å]	Fe-C _{14N} [Å]	Reference
$(TPP)Fe:Cl$	2.110	2.213	0.547	this paper
	2.070 ¹⁾	2.211	0.480	exp. [19, 26]
	2.081	1.977	0.500	theor. [21]
$(F_{20}TPP)Fe:Cl$	2.088	2.237	0.500	theor. [9]
	2.106	2.190	0.543	this paper
	2.082	1.975	–	theor. [21]

¹⁾Averaged bond distances.

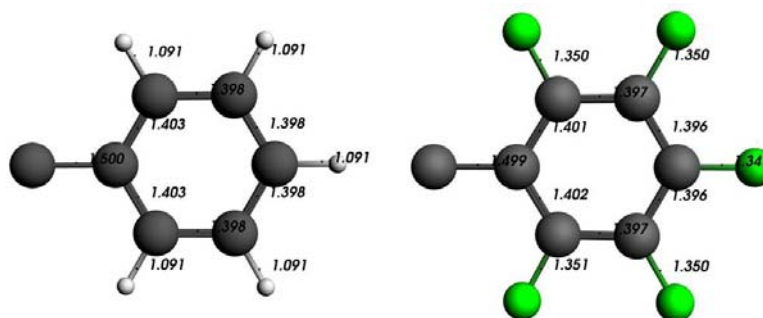


Fig. 2. Bond length in the phenyl rings: a) unsubstituted, b) fluorine substituted.

tion can be estimated from Fig. 2. The difference of the C-C bond lengths in the substituted and unsubstituted phenyl rings is rather small. The optimized molecular structures were used in the theoretical study of the electronic structure and quadrupole splittings QS in Mössbauer spectra.

Mössbauer investigation

Mössbauer spectra of both complexes are shown in Fig. 3 and the parameters of these spectra are given in Table 2. One can notice that the values of these parameters are close to one another for both complexes, but the shape of the quadrupole doublet shows different kinds of asymmetry at 6 K. In the case of (TPP)Fe:Cl complex lower-energy (lower-velocity)

component of the doublet has higher intensity than the higher-energy one and in the case of (F₂₀TPP)FeCl the intensity ratio of the doublet components is reversed. It suggests that the V_{zz} component of EFG tensors at Fe nuclei in these complexes can have opposite signs at low temperature. The positive sign of the V_{zz} indicates that Fe ion has more negative charge in the porphyrin plane than in the perpendicular direction to it [22]. The reason for such difference is unclear at the moment. One of the possible reasons can be the different deformation of the porphyrin rings in solid state induced, for instance, by the interaction of fluorine substitutes with THF solvent in the course of the evaporation process.

Another difference between both complexes is the temperature dependence of the isomer shifts (IS) and quadrupole splittings (QS) (see Table 2). As for the

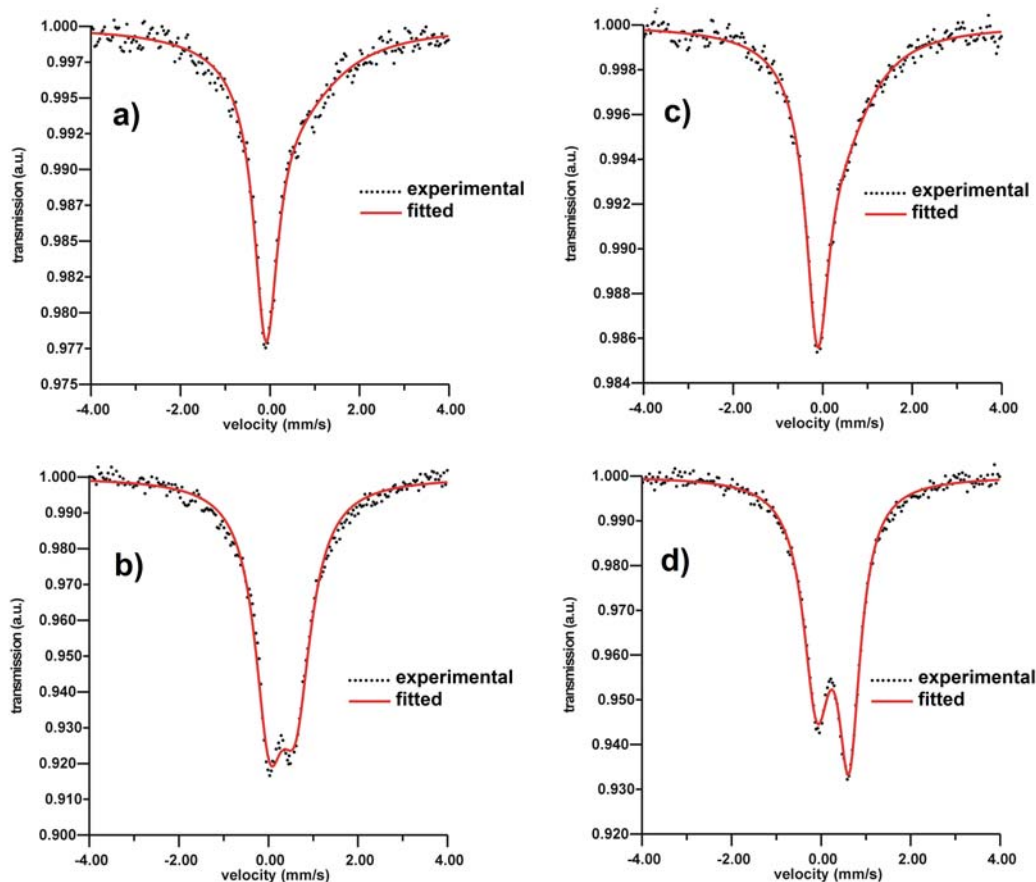


Fig. 3. Mössbauer spectra: a) (TPP)Fe:Cl at 293 K, b) (TPP)Fe:Cl at 6 K, c) (F₂₀TPP)Fe:Cl at 293 K, d) (F₂₀TPP)Fe:Cl at 6 K.

Table 2. Mössbauer parameters and charge distributions around Fe-nuclei in (TPP)Fe:Cl and (F₂₀TPP)Fe:Cl complexes

Compound and temperature	IS [mm/s]	QS [mm/s]	Charge	Electron occupation of s-orbitals	Theoretical QS [mm/s]
(TPP)Fe:Cl, 6 K	0.48	0.60	0.8038	6.1904	0.52
(TPP)Fe:Cl, 293 K	0.44	0.60			
(F ₂₀ TPP)Fe:Cl, 6 K	0.42	0.74	0.7925	6.1897	0.54
(F ₂₀ TPP)Fe:Cl, 293 K	0.27	0.51			

Table 3. Energy values of HOMO and LUMO for the complexes studied

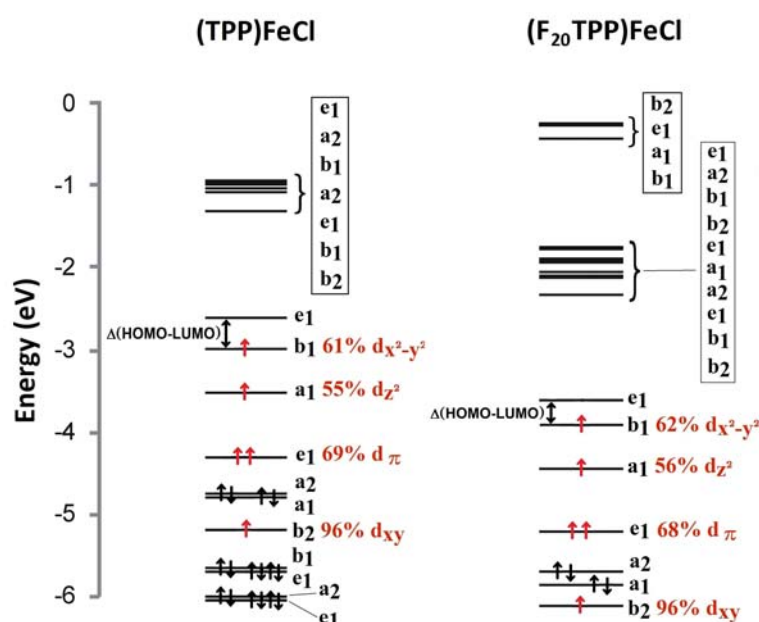
Orbitals	Energy [eV]	
	(TPP)Fe:Cl	(F ₂₀ TPP)Fe:Cl
LUMO e ₁	−2.988	−3.870
HOMO b ₁ (d _{x²−y²})	−3.136	−3.977
Δ(HOMO-LUMO)	0.148	0.107

isomer shift, if a phase transition in a compound does not occur, 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 [23]. Because the sign of δ_{SOD} is negative, hence the smaller absolute value of the δ_{SOD} the greater is the 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.

Temperature dependence of the quadrupole splitting, to our knowledge, has not been explained quantitatively so far. Thermal electronic population of states which are energetically close to each other can be one of the possible explanations [8], but other reasons can occur as well. To explain more accurately the observed difference in the temperature dependence of the Mössbauer parameters, additional investigations are necessary.

Electronic structure

It has been established earlier, that halogenated iron porphyrins are more active as catalysts in comparison with the non-halogenated ones [24]. So, it is interesting to compare electronic structures of halogenated compounds and their non-halogenated analogues to get to know catalytic mechanism as interaction between the catalyst and the substrate at the molecular level. One of the important features of the electronic structure are, so-called, frontier molecular orbitals, localized in the energy scale close to an energy gap where they meet the highest occupied (HOMO) and the lowest unoccupied (LUMO) molecular orbitals. It is widely assumed that the energy of HOMO corresponds to the ionization potential and the energy of LUMO is used to estimate the electron affinity [25]. The energy gap between LUMO and HOMO is correlated with the chemical activity, the smaller gap the higher activity. It should be noted also that if LUMO has low energy value in a porphyrin complex, an electron density transfer between the iron porphyrin and HOMO

**Fig. 4.** High occupied and low unoccupied molecular orbitals. Red color denotes the molecular orbitals containing majority components of iron *d*-orbitals. ΔE corresponds to the gaps between LUMO and HOMO.

of an oxidant can occur easily. The data listed in Table 3 and shown in Fig. 4 indicates the higher activity of the fluorine substituted complex in comparison with the unsubstituted analogue.

Conclusion

Mössbauer spectroscopy data are in good agreement with results of the DFT calculations. The latter confirm higher catalytic activity of the fluorine substituted (F_{20} TPP)Fe:Cl complex in comparison with its unsubstituted analogue. Combination of the experimental and theoretical investigations of halogenated metalloporphyrins is a promising approach to get the knowledge at molecular level about the course of catalytic processes in a number of chemically and biologically important reactions.

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