

Investigation of iron(III) complex with crown-porphyrin

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Abstract Iron complex of 5-(4-(((4'-hydroxy-benzo-15-crown-5)-5'-yl)diazo)phenyl)-10,15,20-triphenylporphyrin was investigated by ^{57}Fe Mössbauer spectroscopy and EPR. Two Fe sites were identified; they give two differing signals, doublet and wide absorption in a large velocity interval. EPR spectra of solutions of the complex in chloroform at room temperature also show two signals with $g = 2.064$, $A_{\text{Fe}} = 0.032 \text{ cm}^{-1}$; $g = 2.015$, $A_{\text{Fe}} = 0.0034 \text{ cm}^{-1}$. The doublet asymmetry is studied vs. temperature and normal angle to the sample plane and gamma-beam. The isomer shift δ in the doublet varies from 0.25 to 0.41 mm/s in the 360–5 K temperature range, whereas quadruple splitting value is constant, $\Delta \sim 0.65 \text{ mm/s}$. The relax absorption may be described as a wide singlet ($\delta = 0.30\text{--}0.44 \text{ mm/s}$ and $\Gamma = 2.83\text{--}3.38 \text{ mm/s}$); its relative area strongly depends on temperature. According to δ , both signals are assigned to Fe(III).

Keywords Iron(III) complex · Crown-porphyrin · Mössbauer spectroscopy · EPR

1 Introduction

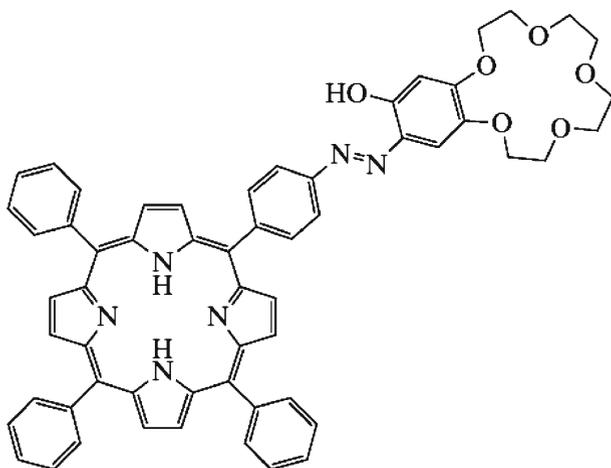
Structures and properties of metal porphyrins (MPs) (hemoglobin, chlorophyll, vitamin B₁₂, etc.) participating in vital processes depend on a central metal and periph-

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Fig. 1 The 5-(4-(((4'-hydroxy-benzo-15-crown-5)-5'-yl)diazo)phenyl)-10,15,20-triphenylporphyrin molecule [9]



eral substituents. Most MPs possess chemical and thermal stability, high extinctions coefficients in UV, visible and near IR ranges and reversible red-ox transitions. Therefore, detail study of their properties with the use of various physicochemical methods is of interest [1–3].

Varying peripheral substituents and central metal give unusual stable supramolecular assemblies with channels for electronic and ionic conductivity which are sensitive to weak effects. This is a new way for creating new materials, e.g. luminescent, which can be used in modern equipments [3, 4].

An actual direction of the MP chemistry is introduction of additional fragments, e.g. crown ethers (which can assume various metal atoms), into porphyrin molecules. It increases possibilities of formation of supramolecular metal-complex systems with specified properties [5, 6]. Stabilization of peroxy- and superoxy-derivatives in an iron complex of a crown-porphyrin was shown by Mössbauer spectroscopy [7, 8].

This work considers properties of the iron complex with a benzo-15-crown-5-substituted *meso*-tetraphenylporphyrin.

2 Experimental

The iron complex of 5-(4-(((4'-hydroxy-benzo-15-crown-5)-5'-yl)diazo)phenyl)-10,15,20-triphenylporphyrin (Fig. 1) (**1**), was prepared from the metallic iron, 98% enriched in ^{57}Fe , which contained $\text{Mn} \approx 0.003\%$, $\text{Cr} < 0.005\%$, $\text{Ni} < 0.005\%$, $\text{Cu} < 0.01\%$, $\text{Pb} < 0.005\%$, other metal sum 0.2% (analyzed by atomic emission spectroscopy). The metal was preliminarily dissolved in acetic acid [9].

Mössbauer absorption spectra were recorded using a VS1104EM express Mössbauer spectrometer (MosTek, Rostov-on-Don) with ^{57}Co in a rhodium matrix as the radiation source, activity 3.5 mCi (Cyclotron, Obninsk), in the 5–360 K temperature range. Chemical shifts were measured using $\alpha\text{-Fe}$ as a standard. Temperature was maintained within ± 1 K. After heating or cooling samples, their spectra were reproduced at room temperature.

EPR spectra were recorded using a Varian E-4 spectrometer (X-band)

Fig. 2 Mössbauer spectra of **1** in wide velocity range at 360 K (**a**), 298 K (**b**), 78 K (**c**), 5 K (**d**)

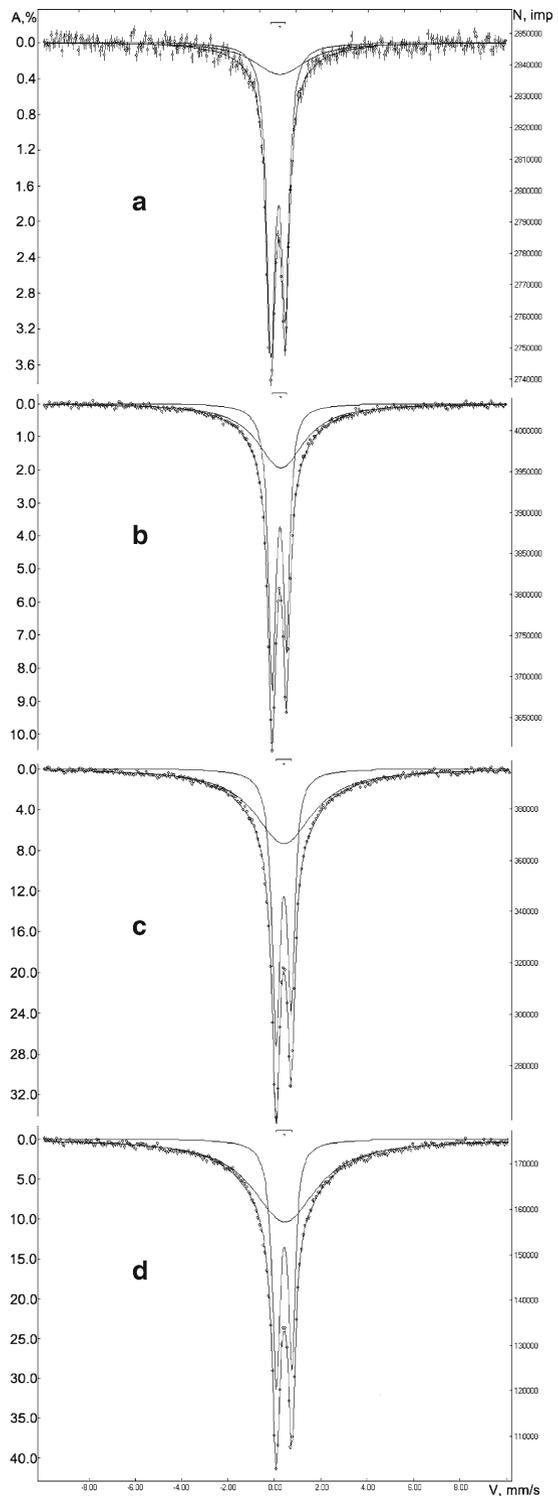
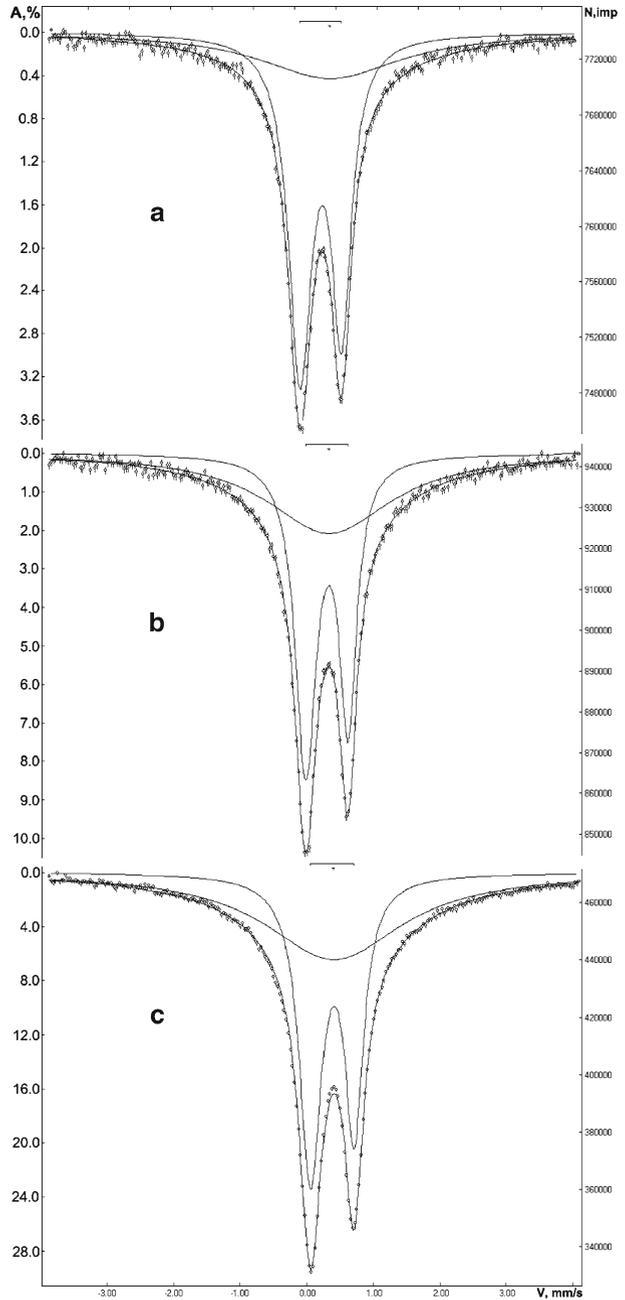


Fig. 3 Mössbauer spectra of **1** in narrow velocity range at 360 K (**a**), 298 K (**b**), 78 K (**c**)



3 Results and discussion

Mössbauer absorption spectra of **1** show a well resolved asymmetric doublet against a wide absorption band (Figs. 2 and 3).

Table 1 Mössbauer spectra of **1**

<i>T</i> , K	δ , mm/s	Δ , mm/s	$\Gamma\%_{\text{exp}}$, mm/s	I_1 , %	S/S_0 , %
Doublet ^a					
360	0.25 ± 0.01	0.63 ± 0.01	0.42 ± 0.01	3.1	73
298	0.30 ± 0.01	0.64 ± 0.01	0.39 ± 0.01	8.1	54
78	0.39 ± 0.01	0.66 ± 0.01	0.40 ± 0.01	22.3	47
5 ^b	0.41 ± 0.01	0.67 ± 0.01	0.41 ± 0.01	29.8	40
Wide band ^b					
360	0.3 ± 0.1		2.8 ± 1.0	0.36	27
298	0.36 ± 0.01		2.50 ± 0.03	1.95	46
78	0.40 ± 0.01		3.07 ± 0.07	7.3	53
5	0.44 ± 0.02		3.38 ± 0.08	10.3	60

^aParameters were refined for the spectra measured in narrow velocity ranges (Fig. 3)

^bParameters were refined for the spectra measured in wide velocity ranges (Fig. 2)

Table 2 Doublet asymmetry vs. temperature

<i>T</i> , K	Band	δ_i , mm/s	Γ_i , mm/s	Γ_2/Γ_1	I_i , %	I_2/I_1	S_2/S_1
360	1	-0.07	0.42	0.85	3.1	0.86	0.73
	2	0.56	0.36		2.7		
298	1	-0.01	0.39	0.80	8.1	0.84	0.68
	2	0.62	0.31		6.8		
78	1	0.06	0.40	0.83	22.3	0.85	0.71
	2	0.71	0.34		18.6		
5	1	0.07	0.41	0.82	29.8	0.90	0.74
	2	0.75	0.34		26.9		

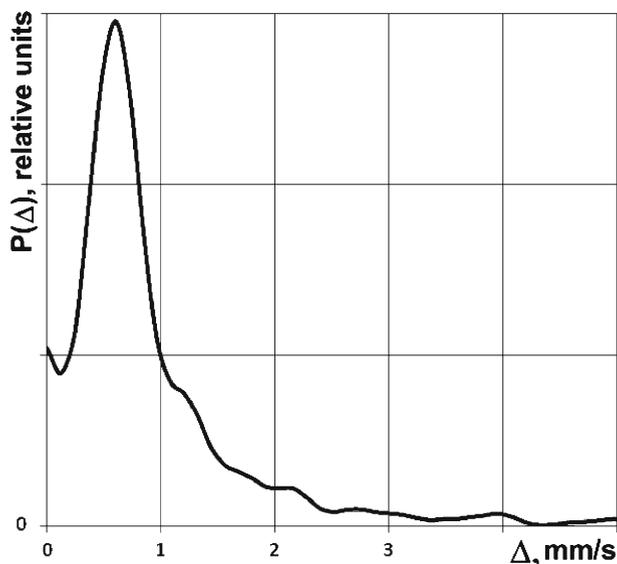
The values of isomer shift ($\delta = 0.30$ mm/s) and quadrupole splitting ($\Delta = 0.64$ mm/s) for the doublet at room temperature agree with the data for high-spin Fe(III) ions in nitrogen surrounding in metal porphyrins or phthalocyanines [10–13]. In Fe(II) phthalocyanines, the value of isomer shift for iron-porphyrin monomers and aggregates changes from in the 0.45–0.47 at 25 K to 0.33–0.37 mm/s at 305 K [13].

Intensities of the corresponding allowed resonance signals (I_i), as expected for organometal complex compounds, strongly depend on temperature and increase by more than nine times when lowering temperature from 360 to 5 K (Table 1), while ratios of intensities, linewidths and areas (S_i) of doublet resonance signals remain unchanged (Table 2).

The nature of the doublet asymmetry is of special interest.

First, the doublet may be represented as a superposition of two singlets, assigned to Fe(IV) and Fe(II) [10, 11]. In this case, area ratio (S_2/S_1) for the signals (with similar f -factors, proportional to contents) must be 7 : 3. Formation of Fe(IV) and Fe(II) porphyrins may be supposed as a low-probable disproportioning of the initial Fe(III) porphyrin. However, in this case the ratio of the resulting Fe(IV) and Fe(II) compounds and the areas of the corresponding singlets must be 1 : 1. In addition, symbate change of various Mössbauer parameters (isomer shift, band width, intensity) for different compounds seems improbable (Table 2).

Fig. 4 Function of probability distribution for quadruple split at 78 K



Second, the asymmetry may hardly be interpreted in terms of superposition of two doublets. From one hand, more intense left band has larger half-width (Table 2). From the other hand, the function of probability distribution for the quadrupole splitting is one-mode and symmetric (Fig. 4).

Third, the doublet asymmetry may be caused by texture effects in the anisotropic sample of **1**. In this case, relative probability of σ - and π -transitions can depend on the angle between directions of the γ -beam and electric field gradient [14]. Technique of sampling can cause texture of cylindrical symmetry with the symmetry axis perpendicular to the sample plane. For studying texture effect, Mössbauer spectra were recorded not only with traditional orientation of the sample plane at 90° to γ -beam, but also with orientation at magic angle $\approx 54.7^\circ$ [15], along with complement angle $\approx 35.3^\circ$ [16] (Fig. 5). However, intensities of resonance signals showed no leveling (Table 3); this excludes texture effects.

At last, independence of the doublet asymmetry on temperature prevents its interpretation in terms of Goldansky–Karyagin effect [17] or Blume relaxation mechanism [18]. However, small doublet asymmetry caused by relaxation effects of the Goldansky–Karyagin type along with its temperature independence against significant temperature dependence of probability of recoilless resonance absorption may prove isotropy of the entire complex (with doubtless local intramolecular anisotropy of iron surrounding inside porphyrin ring). This is in agreement with amorphous state of the compound. We suppose weak dependence on temperature for the intramolecular component of the Mössbauer factor and strong dependence for the intermolecular component.

The wide absorption band may be described as a singlet with parameters $\delta = 0.30\text{--}0.44$ mm/s and $\Gamma_{\text{exp}} = 2.8\text{--}3.38$ mm/s (Table 1) depending on temperature. With the temperature increase, its intensity, similar to the main doublet signal, noticeably decreases. The relative area of the wide absorption band increases on

Fig. 5 Mössbauer spectra of **1** at different normal angles to the sample plane and γ -beam

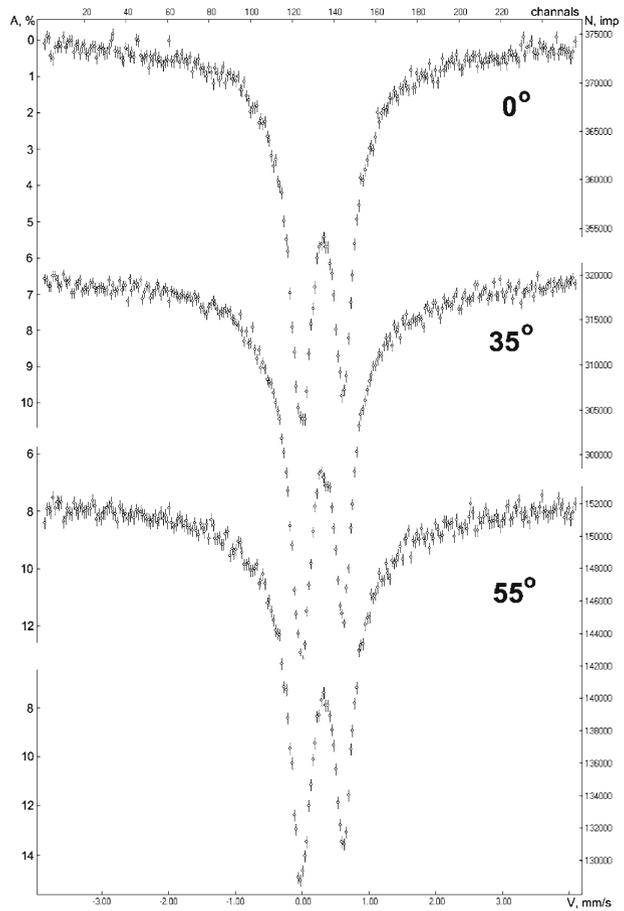


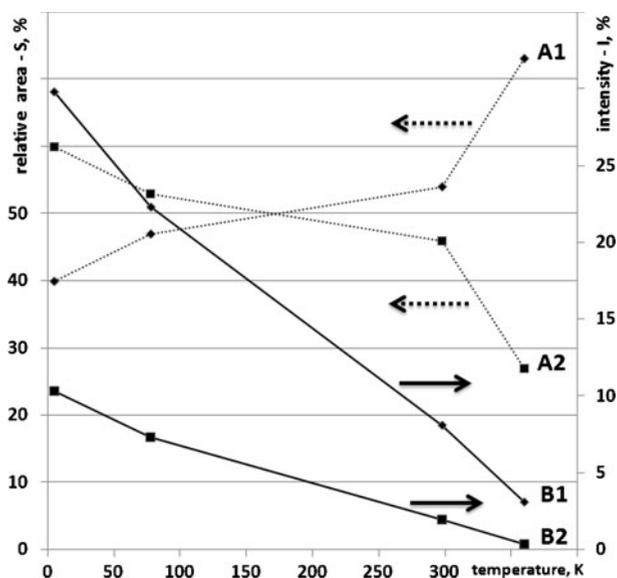
Table 3 Doublet asymmetry vs. normal angle to sample plane and γ -beam (room temperature)

Angle	Band	δ_i ,mm/s	Γ_i ,mm/s	Γ_2/Γ_1	I_i ,%	I_2/I_1	S_2/S_1
0	1	-0.02	0.39	0.81	8.2	0.85	0.69
	2	0.62	0.32		7.0		
35	1	-0.02	0.36	0.83	9.4	0.84	0.69
	2	0.62	0.29		7.9		
55	1	-0.02	0.37	0.82	11.4	0.85	0.69
	2	0.62	0.30		9.6		

temperature decrease (Table 1). The absorption seems to be caused by unresolved magnetic interaction of iron atoms; it has a relaxation origin. Despite spectral changes, lowering temperature down to 5 K did not allow to see magnetic superfine splitting of the Mössbauer spectrum.

Relaxation effects for iron porphyrins were observed earlier [12, 13]; they were assigned to spin–spin relaxation [13]. However, we saw no magnetic splitting even at

Fig. 6 Temperature dependences of relative areas and intensities of the doublet (1) and wide absorption band (2)



5 K (in [12], it was found at 5–20 K) and reversible extinction of the signal above room temperature.

The analysis of temperature dependence of intensities for partial spectra and their relative areas (Fig. 6) shows that the doublet and wide absorption band can be assigned to iron atoms in different surroundings. If the wide absorption band appearing at low temperatures would be responsible for relaxation effects for iron atoms, which give the doublet at high temperature, their intensities should change in opposite directions on temperature change, since increase of number of atoms in magnetically split state should decrease the number of atoms in quadruple-resolved state. However, with the temperature decrease, intensity of the doublet lines increases faster than of the band, which is responsible for relaxation effects (Fig. 6). It is possible if the partial spectra are assigned to iron atoms with absence of exchange between their states, i.e. they have different surroundings.

Since the doublet should be assigned to the iron atoms located in the porphyrin ring, it may be concluded that the wide absorption band is caused by the iron atoms coordinated by the crown-ether fragment. In contrast to [7, 8], they can be either solvated [19] or directly bonded [20]. Since the crown-ether ring is larger than the porphyrin ring, the iron atom is mobile at high temperature and delocalized at low temperature. In addition, the crown-ether complex can possess conformation isomerism increasing variability of the iron surrounding. This must lead to broadening resonance bands as well as decrease of probability of recoilless resonance absorption for the atoms, especially at high temperature. The value of the isomer shift agrees with the data for iron(III) complexes with crown-ethers [21].

EPR spectra of the **1** solution in chloroform (Fig. 7) at room temperature show two well-resolved signals ($g = 2.064$, $A_{\text{Fe}} = 0.032 \text{ cm}^{-1}$; $g = 2.015$, $A_{\text{Fe}} = 0.0034 \text{ cm}^{-1}$). No additional signals were found in higher and lower fields. The absence of

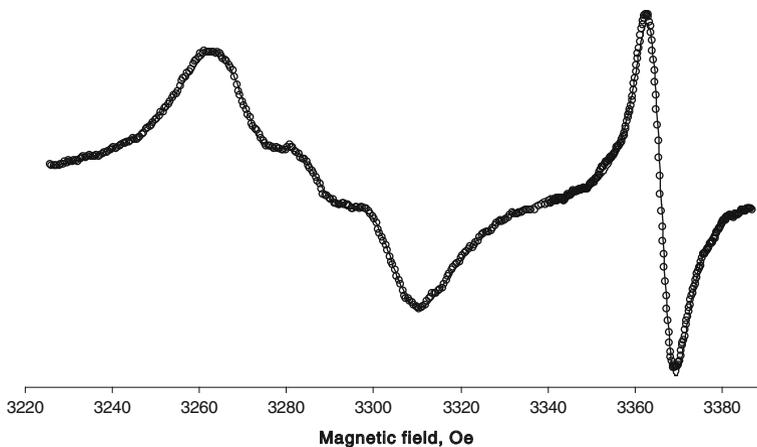


Fig. 7 EPR spectrum of the **1** solution in chloroform at room temperature (dots: experimental data; solid line: simulation)

signal anisotropy prevents obtaining information on the symmetry of the nearest coordination surrounding. At 77 K, the spectral lines/bands broaden.

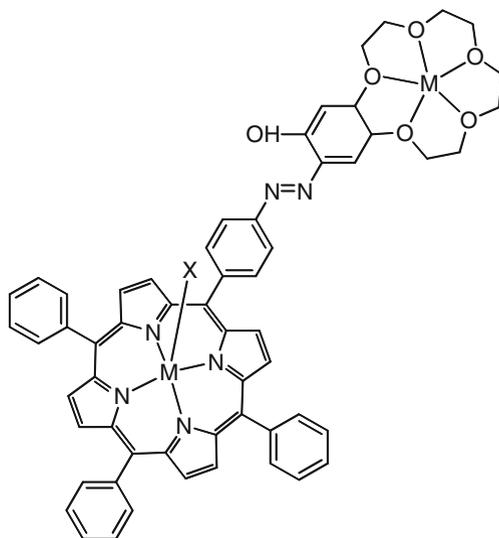
The sample contains iron enriched with ^{57}Fe ($I = 1/2$). Therefore, hyperfine splitting from the ^{57}Fe nucleus is found in the spectra; it overlaps with the non-split signal of ^{56}Fe . Band widths of the two signals differ noteworthy. Broadening of the signal with $g = 2.064$ may be caused by unresolved HFS from nitrogen atoms of the porphyrin ring. The narrow signal with relative intensity of 9% may be assigned to the iron atom in the surrounding of the crown-ether oxygen atoms. The HFS constants (Fe) for the two signals differ noticeably; this may be caused by strong delocalization of a lone electron in the 4s orbital of the metal atom in the iron complex with the porphyrin ring. Since HFS for the metal–nitrogen and metal–oxygen bonds must differ strongly, distribution of iron atoms between porphyrin and crown-ether fragments of the ligand seems grounded and consistent with the Mössbauer data.

4 Conclusion

According to the Mössbauer and EPR spectroscopy, the amorphous ^{57}Fe complex of 5-(4-(((4'-hydroxy-benzo-15-crown-5)-5'-yl)diazo)phenyl)-10,15,20-triphenylporphyrin contains iron atoms in two sites, porphyrin and crown-ether rings. In the Mössbauer spectra, iron atoms in hard porphyrin surrounding show the asymmetric doublet line with the parameters corresponding to the high-spin Fe(III).

The iron(III) atoms in the large crown-ether ring show the wide absorption band of relaxation origin.

The Mössbauer spectra of **1** show unusual features, such as absence of temperature dependence for doublet asymmetry and extremely low temperature of locking relaxation effects. These features of the Mössbauer spectra were not found yet [7, 21].

Fig. 8 Supposed structure of **1**

According to the EPR data, iron atoms are also distributed between porphyrin and crown-ether fragments of the ligand, since HFS for the metal–nitrogen and metal–oxygen bonds must differ strongly as observed in the corresponding EPR spectrum.

Therefore, the structure of the complex may be described by the formula shown in Fig. 8.

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