

## A Mössbauer Study of Polymeric Iron(II)phthalocyanine

J. BLOMQUIST, L. C. MOBERG

*Institute of Physics, University of Stockholm, Vanadisvägen  
9, S-113 46 Stockholm, Sweden*

L. Y. JOHANSSON and R. LARSSON

*Division of Inorganic Chemistry 1, Chemical Center, University of Lund, Box 740, S-220 07 Lund, Sweden*

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### Introduction

The electrocatalytic properties of iron(II)phthalocyanine (FePc) have been subjects of several investigations previously [1–8]. The detailed mechanisms are not fully understood although there has been a great interest in the processes behind the catalytic activity. It is known that the electronic structure of the complex and in particular that of the metal ion of the chelate has a significant influence on the catalytic efficiency. The monomeric form of FePc is not very active as catalyst for the cathodic reduction of oxygen while the polymer is. Besides the degree of polymerisation, the support or substrate (*e.g.* active carbon) has a significant effect on the activity, in parts by its porosity, which makes the catalyst accessible, and by its conductivity. There is also evidence for a participation of the substrate in the catalytic process in some way. Other important concepts affecting the catalytic activity are the redox potential, orbital symmetries and energies and also the spin, *i.e.* properties which all represent different aspects of the electronic structure of the chelate and in particular of its metal ion. Our experimental technique to study this electronic structure has been Mössbauer spectroscopy, and the main interest has been to investigate the influence of the polymerisation on the charge distribution of the iron atom. The samples were prepared by a chromatographic procedure by which mono- and dimers could be excluded.

### Experimental

#### *Materials and Analysis*

The polymeric iron(II)phthalocyanine was prepared from pyromellitic acid dianhydride, urea, iron(II)sulphate and with ammonium molybdate as a catalyst in a melt at 570 K for five hours [9]. The product was purified by extraction with water

in a Soxhlet apparatus and recrystallized twice from concentrated sulphuric acid followed by careful rinsing of the precipitate with water and drying at 390 K. The polymer contains some peripheral COOH and CONH<sub>2</sub> end groups which are removed by heating in vacuum at 570 K.

For the chromatographic separation experiments the polymer was dissolved in dimethylformamide (DMF) giving a black solution which was eluted in a column with diameter 50 mm and length 250 mm. Sephadex LH 20\* which was used as column material swells in many organic solvents and separates molecules according to their molecular weights with an upper limit of 5000 so that smaller molecules are retarded more than bigger ones because the latter do not penetrate the gel particles to such a great extent. When eluted the polymer separated into one black-coloured high molecular weight fraction and one yellow, fluorescent fraction of low molecular weight. The molecular weight of the black fraction has been estimated earlier by thin layer chromatography to about 10000 which means that it consists of 16–18 monomeric units [10]. This fraction was collected, evaporated to near dryness and crystallized by adding an excess of diethylether.

#### *Mössbauer Measurements*

A constant acceleration Mössbauer spectrometer, horizontally mounted and with transmission geometry, was used together with a cryostat [11]. The spectrometer was calibrated with a foil of enriched metallic iron. The source, <sup>57</sup>Co in Pd, was kept at room temperature (300 K) during all runs, and the obtained isomer shifts are quoted with respect to Pd.

The fittings were performed by a least squares method. The lineshape was assumed to be Lorentzian, since the absorbers were considered thin, and the lines of each quadrupole doublet were constrained to the same width and intensity.

### Results

Mössbauer measurements were performed on (i) polymeric and (ii) chromatographed polymeric FePc at 77 K. The obtained rather complex spectra are shown in Fig. 1.

As a first step of the analysis the absorption of the spectra were normalized and the difference spectrum evaluated. As a result a single quadrupole doublet was obtained. Since this component occurs only in the non-chromatographed polymeric sample

\*Manufactured by Pharmacia Fine Chemicals, Sweden

TABLE I. Experimental Isomer Shifts ( $\delta$ ), Quadrupole Splittings ( $\Delta$ ), Relative Areas of Absorption Lines (A) and Linewidths ( $\Gamma$ ) of Samples of FePc. The isomer shifts are given relative to Pd at 300 K, and the absorber temperature is 77 K. C and P indicate the two proposed sites of polymeric FePc. M and O indicate monomeric and oxidized FePc, respectively. The errors in  $\delta$  and  $\Delta$  are of the order  $0.01 \text{ mm s}^{-1}$ .

Sample	$\delta$ ( $\text{mm s}^{-1}$ )	$\Delta$ ( $\text{mm s}^{-1}$ )	A	$\Gamma$ ( $\text{mm s}^{-1}$ )	Proposed interpretation
polymeric FePc (sample 1)	0.01	2.95	0.31	0.56	M
	0.28	2.66	0.22	0.48	C
	0.07	1.97	0.34	0.48	P
	0.30	0.83	0.13	0.58	O
chromatographed polymeric FePc (sample 2)	0.34	2.53	0.24	0.51	C
	0.08	1.99	0.63	0.51	P
	0.36	0.85	0.13	0.48	O
difference spectrum (sample 1 – sample 2)	0.08	2.99	1.00	0.50	M
polymeric FePc heated in vacuum at 570 K	0.32	2.73	1.00	0.42	M
monomeric FePc	0.31	2.59	1.00	0.22	
polymeric FePc heated in vacuum at 330 K (data from room temperature measurements)	-0.14	2.62	0.33	0.62	M
	0.18	2.73	0.25	0.52	C
	-0.05	1.84	0.24	0.52	P
	0.13	0.82	0.18	0.65	O

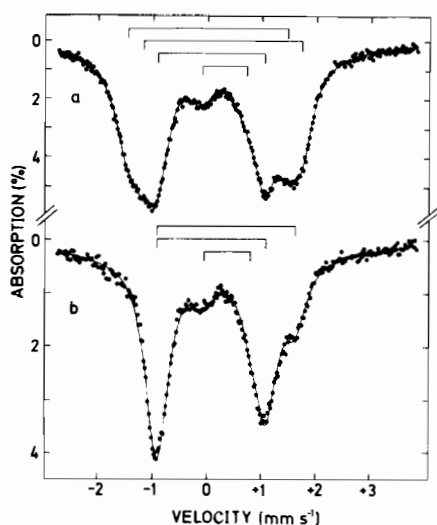


Fig. 1. Mössbauer spectra obtained at 77 K of a) polymeric FePc, b) chromatographed polymeric FePc. The bars indicate the positions of the absorption lines.

of FePc and hence is eliminated in the chromatographic procedure it should be due to a monomeric (possibly dimeric) form of FePc. The spectra in Figs. 1a and 1b are best interpreted in terms of four and three superimposed quadrupole doublets respectively (Table I). The additional doublet in Fig. 1a is thus attributed to monomeric FePc.

The many doublets in the observed spectrum of polymeric FePc (Fig. 1a) arose the question of adsorbed oxygen could influence the electron structure of the iron atom. However, after heat treatment at 330 K in vacuum ( $10^{-3}$  torr) and storage in nitrogen atmosphere (with no excess of oxygen) the obtained Mössbauer spectrum was not changed significantly from the spectrum in Fig. 1a (Table I).

After heat treatment for two hours in vacuum (1 torr) at 570 K the COOH and CONH<sub>2</sub> groups have been substituted by H atoms (decarboxylation) and the recorded Mössbauer spectrum only shows one quadrupole doublet. The isomer shift and quadrupole splitting of this doublet are almost in accord with the monomeric data [12] (Table I).

### Comments

The chromatographed sample only contains polymers with a high degree of polymerisation (16–18 monomeric units). The non-chromatographed sample on the other hand exhibits an additional doublet which accordingly has been attributed to monomeric FePc. The deviation of the isomer shift of this doublet from the typical monomeric value (a change from  $0.31$  to  $0.01 \text{ mm s}^{-1}$ ) could be due to the presence of COOH and CONH<sub>2</sub> groups in the sample preparation (see below). These groups are usually not

present in the monomeric form of FePc because of the extra purifying process involved in the preparation of such samples. (It is possible that also other byproducts present in the syntheses can give rise to such a doublet in the Mössbauer spectrum or being a part of it.)

The isomer shifts and quadrupole splittings of the remaining three doublets in the spectrum of the polymeric FePc (Fig. 1a) are in fairly good agreement with the corresponding doublets due to the chromatographed sample (Fig. 1b). The doublet with the smallest quadrupole splitting in these spectra (doublet O) probably originates from iron in an oxidized state [13]. Such a ferric state of (monomeric) FePc has been reported in the literature [14]. According to ref. 14 the oxidized state appears after heating FePc in air to 150 °C. Oxygen was shown to be necessary since heating in vacuum did not produce any change in the properties of FePc. This observation is in agreement with our high temperature measurements in vacuum on monomeric FePc [15] which did not show any oxidized form of FePc either. The isomer shift at room temperature is given in ref. 14 as 0.17 mm s<sup>-1</sup> and the quadrupole splitting as 1.13 mm s<sup>-1</sup>. These values are comparable to our values given in Table I for the room temperature measurement on polymeric FePc heated in vacuum to 330 K, 0.13 and 0.82 mm s<sup>-1</sup> respectively.

An interpretation of the inner doublet as due to an oxidized form of iron is also supported by the results of a series of measurements on heat treated polymeric FePc samples dispersed onto active carbon [13].

The existence of two remaining doublets indicates that iron atoms occur in (at least) two different sites in the polymer. The less intense component (Table I) has isomer shift and quadrupole splitting close to the corresponding data for the monomer. This indicates an electronic structure similar to that of the monomer. (Cooperative phenomena due to Fe-Fe interactions are not considered probable due to large Fe-Fe distances.) The isomer shift and quadrupole splitting of the last doublet differ significantly from the monomeric values, which points out another electronic structure. The relative occurrence of the two sites suggests that the weak component in the spectrum corresponds to central positions of the monomeric subunits in the polymer (C) while the

more abundant component then corresponds to peripheral positions (P) (of the individual monomeric units).

The side groups COOH and CONH<sub>2</sub> are attached to the peripheral units and the electron affinity of these groups causes an attenuation of the 3d-electron population of the iron atom of the peripheral unit. This is equivalent to a smaller isomer shift and explains the deviation of the Mössbauer parameters for the doublet originating from the P-positions. That this influence on the parameters originates from the side-groups is further supported by the fact that the Mössbauer spectrum of decarboxylized FePc only exhibits one doublet.

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