

A Mössbauer Study of the Low Spin-High Spin Transition of an Oxygen Adduct Formed in Solid β -Fe(II)Phthalocyanine

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Abstract: Several oxygen adducts are formed when oxygen is diffused into the interplanar spacings of solid β -Fe^{II}Pc suspended in water. The constraints imposed by the solid matrix induce formation of interesting oxygen adducts which cannot be synthesized by regular solution chemistry. One of the oxygen adducts exhibits low-spin to high-spin transition with considerable thermal hysteresis.

Keywords: Fe-phthalocyanine, oxygenation, Mössbauer spectroscopy, temperature dependence, oxygen adducts, spin crossover.

INTRODUCTION

Phthalocyanines have been widely used as electrochemical catalysts, photosensitizers of TiO₂ electrodes, gas sensors and as regular heterogeneous catalysts [1-6]. Exposure to oxygen, iodine, and bromine increases their conductivity by several orders of magnitude due to p-type doping. Similarly, lithium doping induces n-type conductivity. The two well characterized polymorphic forms of phthalocyanines are α - and β -. The main difference in the two forms is the orientation of the flat molecules with respect to the crystallographic axis, where the perpendicular distance between the stacks of molecules remains approximately the same, namely 0.338 nm. The inclination of the molecular stacks in the β -polymorph is much larger than that in the α -form. Consequently, the distance between the central metal atoms in the adjoining stacks is about 0.48 nm in the β -form versus 0.38 nm in the α -form. In the β -form, the nitrogen atoms in the neighboring molecules are present axially above and below the central metal atom at a distance of about 0.338 nm. The Mössbauer isomer shifts and quadrupole splittings for the β -polymorphs of Co^{II}Pc and Fe^{II}Pc are larger in magnitude than the ones observed for the α -form because of the interaction of the π -electrons of the aromatic rings of the neighboring molecules, through the nitrogens with the 3d_{xy}, 3d_{yz} orbitals of the central Fe(Co) atom [7].

There is considerable interest in the interaction of oxygen with phthalocyanines [4-6] partly, because of the use of oxygen adducts for the formation of Co and Fe nanoparticles

coated with carbon [8-10]. Recently, we reported formation of a variety of oxygen adducts with Fe^{II}Pc which are stabilized in the solid matrix and do not exist in solution [11].

EXPERIMENTAL

Needle shaped crystals of pure β -Fe^{II}Pc were obtained by sublimation of the commercial material. After grinding, the powder was suspended in water maintained at 50°C. Oxygen was bubbled through the suspension for more than 6 weeks. Part of the material was taken out and dried in vacuum. With the other, argon is bubbled for a few weeks while maintaining the suspension at 50°C, to check the stability of oxygen adducts and also to remove freely floating diatomic oxygen, if any is present. Both materials showed similar behavior, therefore, the presence of freely floating oxygen was not confirmed, and the stability of the oxygen adduct was affirmed.

⁵⁷Fe Mössbauer spectra of the samples were recorded with a conventional Mössbauer spectrometer (WISSEL) in transmission geometry between 78 K and 300 K, in a temperature-controlled cryostat (Leybold, Germany). Isomer shifts are relatively given to α -iron. A ⁵⁷Co/Rh γ -radiation source 3.6*10⁹ Bq activity was used. The Mössbauer spectra were analyzed by the least-squares, fitting of Lorentzian lines using the MOSSWINN code [12].

RESULTS AND DISCUSSION

The Mössbauer spectra showed very interesting changes with temperature. We attributed the spectral changes at low temperature to coordinate with a freely floating O₂ molecule in the sixth axial position of a five-coordinate μ -oxo bridged or μ -peroxo bridged Fe^{III}Pc. Such free O₂ molecules have

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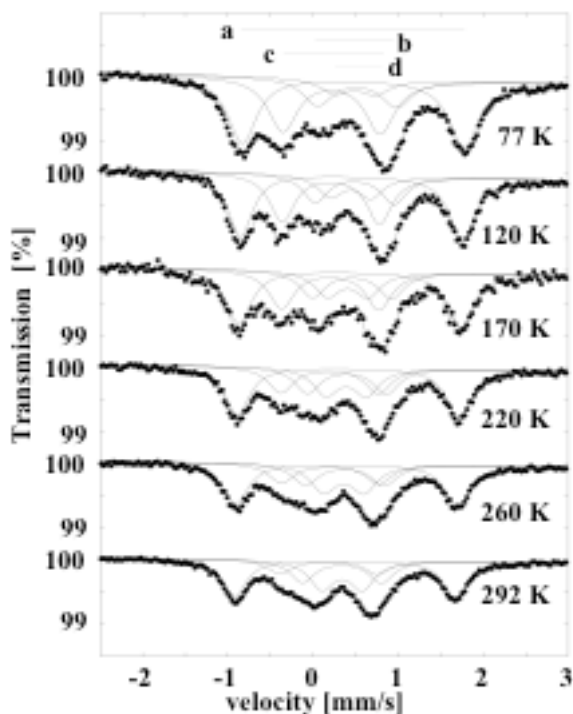


Fig. (1). Temperature dependence of the Mössbauer spectra of β -Fe-Phthalocyanine ($\text{Fe}^{\text{II}}\text{Pc}$), treated with bubbling oxygen in aqueous suspension at 50°C for more than 6 weeks. The interconversion of the LS species (c) to HS species (d) with increasing temperature is observed.

been reported for $\text{Pb}^{\text{II}}\text{Pc}$ and $\text{Zn}^{\text{II}}\text{Pc}$ [4,5,13]. We assumed that the bonding with O_2 , was weak due to constraints im-

posed in the solid matrix and that the bond ruptured at higher temperatures. Here we report that it is not necessary to assume free O_2 molecules in the channels between the stacks of $\text{Fe}^{\text{II}}\text{Pc}$ and the spectral changes can be interpreted as high-spin to low-spin transition in an unusual adduct of $\text{Fe}^{\text{II}}\text{Pc}$ formed with the help of constraints imposed by the solid matrix.

The Mössbauer spectra obtained at different temperatures are shown in Fig. (1). One can see clearly a dramatic change in the spectral envelope. The spectra were computer analyzed and fit with four species, the original pristine $\text{Fe}^{\text{II}}\text{Pc}$ with large quadrupole splitting (a) and three oxygen adducts (b, c, and d) formed with $\text{Fe}^{\text{II}}\text{Pc}$. The data obtained from the computer fit are shown in Table 1. One can see that the isomer shifts for each species, show a slight decrease in temperature as expected (see also in Fig. 2). The quadrupole splittings was constrained to be the same at all temperatures in a simultaneous fitting of the six spectra.

The abundances (normalized areas) of the different species are plotted as a function of temperature as shown in Fig. (3). The non-oxygenated pristine $\text{Fe}^{\text{II}}\text{Pc}$ is designated as (a) and one of the oxygen adducts (b) exhibit minor changes in the abundance with temperature. The minor variations for (a) and (b) probably arise from the differences in the Debye-Waller factors at different iron sites in the lattice. It is obvious from the plots that species (c) which is abundant at low temperatures is converted into species (d) as the temperature increases. The sum of their abundances is approximately the same, namely 42% units. The isomer shift of the high spin oxygen adduct (d) is significantly larger than that of the low spin (c). On the other hand, the quadrupole splitting changes the reverse order as expected for Fe^{III} compounds [14]. There

Table 1. Computer Evaluation Results of the Mössbauer Spectra of Oxygen-Treated $\text{Fe}^{\text{II}}\text{Pc}$. A = Abundance, δ = Chemical Shift and Δ = Quadrupole Splitting

T [K]	species (a)			species (b)		
	A [%]	δ [mm/s]	Δ [mm/s]	A [%]	δ [mm/s]	Δ [mm/s]
77	41.3(4)	0.473(2)	2.605(4)	17(4)	0.520(8)	0.93(7)
120	39.8(4)	0.451(2)	2.605(4)	17(4)	0.492(9)	0.93(6)
170	38(1)	0.432(4)	2.605(9)	19(4)	0.46(1)	0.93(4)
220	38.2(6)	0.412(2)	2.605(5)	20(2)	0.40(1)	0.93(2)
260	37.5(5)	0.396(2)	2.605(5)	20(2)	0.376(7)	0.93(4)
292	36.9(4)	0.377(2)	2.605(4)	22(1)	0.34(6)	0.93(3)
T [K]	species (c)			species (d)		
	A [%]	δ [mm/s]	Δ [mm/s]	A [%]	δ [mm/s]	Δ [mm/s]
77	33.1(2)	0.220(8)	1.14(2)	9(5)	0.50(1)	0.47(7)
120	29.7(9)	0.212(6)	1.14(1)	13(4)	0.444(8)	0.47(5)
170	27(1)	0.205(7)	1.14(2)	17(4)	0.41(1)	0.474(4)
220	20(1)	0.197(8)	1.14(2)	21(2)	0.391(6)	0.474(2)
260	18(1)	0.203(5)	1.14(1)	25(2)	0.363(4)	0.474(2)
292	13(1)	0.185(7)	1.14(1)	27(2)	0.343(3)	0.474(2)

is considerable thermal hysteresis, and therefore (d) and (c) coexist as has been reported earlier for some HS-LS transitions in Fe^{III} complexes [14]. The abundance of (c) and (d) also depends on the rate of cooling.

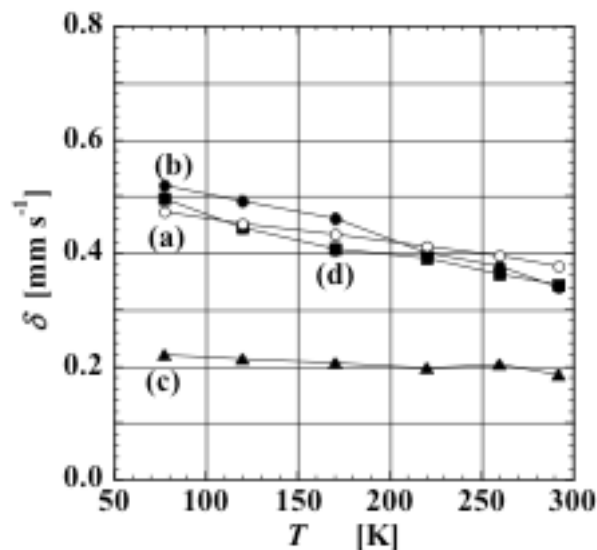


Fig. (2). Temperature dependence of the isomer shifts of doublets (a), (b), (c), and (d) obtained from the Mössbauer spectra of oxygen treated $\text{Fe}^{\text{II}}\text{Pc}$.

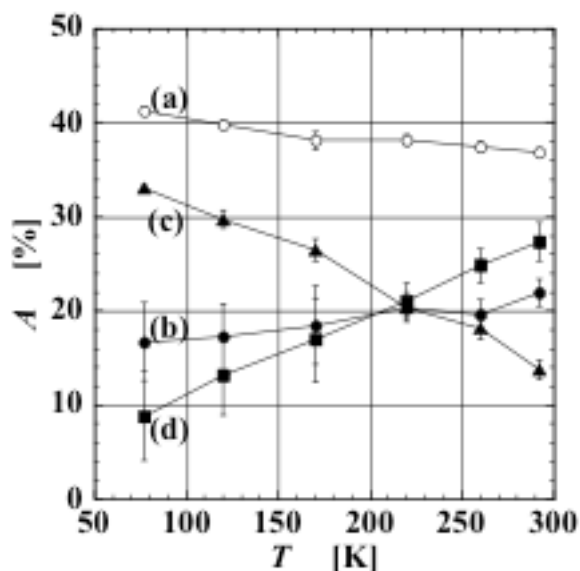


Fig. (3). Temperature dependence of the absorption area of doublets (a), (b), (c), and (d) obtained from the Mössbauer spectra of oxygen treated $\text{Fe}^{\text{II}}\text{Pc}$.

After reviewing the Mössbauer parameters of several μ -oxo bridged dimers of Fe^{III} and Fe^{II} phthalocyanines [15-17] and taking into account the distance between iron atoms in adjoining stacks, we propose formation of μ -peroxo bridge on one of the axial positions of $\text{Fe}^{\text{III}}\text{Pc}$ and a bond with O_2 (sideways or end-on) on the other axial position as shown in Fig. (4). Such bonding has been proposed earlier between iron atoms for a model compound of an enzyme [18] and also for an iron-copper complex [19]. It is likely that the iron atom in the high spin (d) is situated slightly out-of-plane

towards the peroxo bridge due to tension in the bridge. At lower temperatures, the channels between the stacks presumably shrink a little and the Fe^{III} atom flips in the Pc plane.

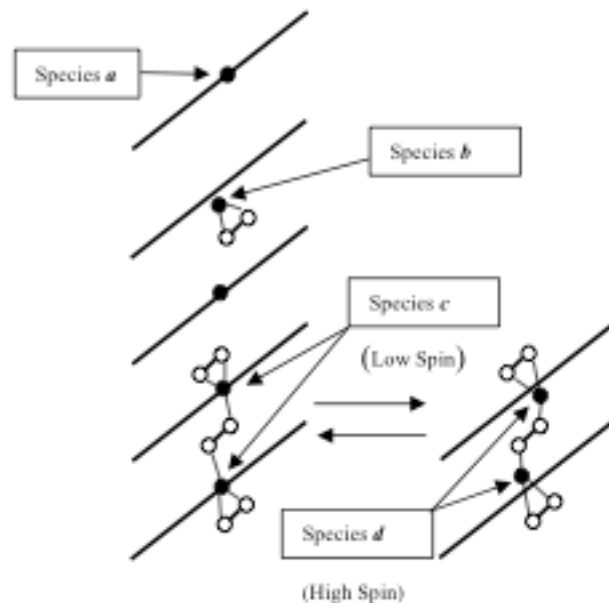


Fig. (4). Schematic presentation of the four species observed in oxygenated solid $\text{Fe}^{\text{II}}\text{Pc}$. The tilted bars show the plane of the Pc rings stacked in the lattice; black and white circles represent iron and oxygen atoms, respectively.

Oxygen is bonded pretty strongly as no differences were observed in the spectra of the material which was subjected to thermal treatment in an inert ambient. One can speculate that in the oxygen adduct (b), Fe^{III} is attached to O_2 on one of the axial positions, forming a high spin five-coordinate compound with Fe atom slightly out of the plane.

CONCLUSION

Based on the temperature dependent changes, observed in the Mössbauer parameters of subspectra belonging to oxygen adducts in oxygenated β -phthalocyanine a low spin-high spin crossover of one of the oxygen adducts has been shown.

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