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# Mössbauer studies of the interaction of oxygen with solid $\beta$ -Fe<sup>II</sup>-phthalocyanine

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## Abstract

Oxygen has been diffused into the interplanar spacings of solid  $\beta$ -Fe<sup>II</sup>Pc at relatively low temperatures in the dry state and in aqueous suspensions. A variety of oxygen adducts are stabilized in the solid matrix, which do not exist in solution. Tentative assignment of species have been made with the help of Mössbauer and IR spectroscopy.

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## 1. Introduction

An oxygen ambient is known to greatly increase both the dark- and the photo-conductivity of phthalocyanines [1,2]. However, a more direct evidence of charge transfer was obtained by direct observation of O<sub>2</sub><sup>-</sup> in ESR studies [3,4]. In several cases, O<sub>2</sub> can be reversibly desorbed by thermal treatment in vacuum. For instance, it has been shown that O<sub>2</sub> diffuses into a single crystal of lead phthalocyanine (Pb<sup>II</sup>Pc) on thermal treatment at 230°C for 10 h. The dark conductivity of oxygenated Pb<sup>II</sup>Pc is observed to be three orders of magnitude higher than that for the untreated material. This was attributed to O<sub>2</sub> molecules accepting electrons from neighboring Pb<sup>II</sup>Pc molecules and thereby injecting holes. When the material was baked in vacuum, O<sub>2</sub> was desorbed and complete reversibility was observed [1,2].

Phthalocyanines can acquire several polymorphic forms of which  $\alpha$  and  $\beta$  are fairly well characterized [1,2,5]. The difference in the  $\alpha$ - and  $\beta$ -polymorph lies essentially in the orientation of the flat molecules with respect to the crystallographic axes, where the perpen-

dicular distance between the stacks of molecules remains approximately the same, viz., 3.38 Å. The inclination of the molecular stacks in the  $\alpha$ -form is much less than in the  $\beta$ -form. Therefore, the distance between the central metal atoms in the adjoining stacks is about 3.8 Å in the  $\alpha$ -form and about 4.8 Å in the  $\beta$ -form. In the  $\beta$ -polymorph, the nitrogen atoms of the neighboring molecules are present axially above and below the central metal atom at a distance of about 3.38 Å. In the  $\alpha$ -form, the nitrogens of the nearest molecules are not in axial positions. The Mössbauer isomer shifts ( $\delta$ ) and quadrupole splittings ( $\Delta$ ) for the  $\beta$ -polymorphs of Co<sup>II</sup>Pc and Fe<sup>II</sup>Pc are larger than the ones observed for the  $\alpha$ -form because of the interaction of the  $\pi$ -electrons of the aromatic rings of the neighboring molecules, through the nitrogens with the  $3d_{xz}$ ,  $3d_{yz}$  orbitals of the central Fe(Co) atom [6].

Grenoble and Drickamer [7] had reported formation of a single adduct with chemical shift  $\delta = 0.35$  mm/s and quadrupole splitting  $\Delta = 1.13$  mm/s on heating Fe<sup>II</sup>Pc in air at 150°C. This result could not be reproduced in our laboratory despite various thermal treatments of Fe<sup>II</sup>Pc in air and oxygen ambients at different temperatures [8]. Complex Mössbauer spectra were obtained which could be fit with not less than five different species. On closer inspection, it was also

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Table 1  
Mössbauer parameters for the different oxygen adducts formed by oxygenation of  $\beta$ -Fe<sup>II</sup>Pc

Sample: Conditions of oxygenation	Temperature	Species I		Species II		Species III		Species IV		Species V		Line Width	
		RT	80K	RT	80K	RT	80K	RT	80K	RT	80K	RT	80K
A: O <sub>2</sub> /H <sub>2</sub> O, at RT 14 days	$\delta$ (mm/s)	0.373	0.472			0.47	0.54			0.17	0.28	0.33	0.29
	$\Delta$ (mm/s)	2.544	2.625			0.80	0.68			0.72	0.58		
	Area fraction (%)	76.2	71.9			12.5	14.5			11.3	13.6		
B: O <sub>2</sub> /H <sub>2</sub> O, at 50°C 14 days	$\delta$ (mm/s)	0.379	0.476	0.41	0.62	0.39	0.55	0.12	0.19	0.13	0.30	0.31	0.28
	$\Delta$ (mm/s)	2.573	2.638	1.00	1.04	0.59	0.67	0.79	1.06	0.56	0.55		
	Area fraction (%)	53.5	50.4	7.4	6.1	24.1	18.5	2.9	8.8	12.1	16.2		
C: O <sub>2</sub> /H <sub>2</sub> O, at 50°C 44 days	$\delta$ (mm/s)	0.388	0.479	0.41	0.48	0.39	0.53	0.12	0.19	0.13	0.30	0.32	0.29
	$\Delta$ (mm/s)	2.634	2.655	0.96	1.05	0.59	0.61	0.84	1.09	0.46	0.46		
	Area fraction (%)	39.0	45.2	15.6	10.3	31.0	20.1	10.3	14.5	4.0	9.9		
D: O <sub>2</sub> /dry 50°C 92 days	$\delta$ (mm/s)	0.390	0.470	0.46	0.57	0.49	0.60	0.14	0.24	0.16	0.30	0.41	0.40
	$\Delta$ (mm/s)	2.556	2.631	1.25	1.42	0.74	0.85	1.13	1.21	0.64	0.64		
	Area fraction (%)	36.6	31.7	14.1	12.1	20.2	21.8	10.4	14.4	18.7	20.0		

observed that if the thermal treatment was carried out above 60°C,<sup>1</sup> it was associated with some decomposition products which condense in the cooler parts of the outlet.

Here, we report an amazingly rich solid-state chemistry of oxygen interaction with  $\beta$ -Fe<sup>II</sup>Pc. Most of the oxygen adducts stabilized in the solid matrix either do not exist at all in solution or constitute only transient intermediates.

## 2. Experimental

Commercial  $\beta$ -Fe<sup>II</sup>Pc was heated at 425°C under good vacuum. The residue and the sublimate were characterized by powder X-ray diffractometry (XRD), IR and Mössbauer spectroscopy [6] and found to be pure  $\beta$ -Fe<sup>II</sup>Pc. This pristine compound is denoted by P. These materials were oxygenated under O<sub>2</sub> flow in the dry state or suspended in water at different temperatures below 60°C.

The sample which was oxygenated by bubbling oxygen in aqueous suspension at room temperature (RT) for 14 days and then dried in vacuum chamber for 7 days is designated as A. Samples oxygenated in aqueous suspension at 50°C for 14 and 44 days are designated as B and C, respectively. The sample heated

in the dry state under O<sub>2</sub> flow at 60°C for 92 days is designated as D.

<sup>57</sup>Fe Mössbauer spectra of pristine  $\beta$ -Fe<sup>II</sup>Pc and its oxygen adducts were recorded in the regular constant acceleration mode in the temperature range of 78–300 K. A <sup>57</sup>Co(Rh) source was used. The isomer shifts are reported with respect to  $\alpha$ -iron. MOSSWIN program [9] was used for computer fitting of the complex Mössbauer spectra.

X-ray diffractograms of the pristine  $\beta$ -Fe<sup>II</sup>Pc and its oxygen adducts were recorded by a computer-assisted DRON-2 diffractometer using CoK $\alpha$  radiation and  $\beta$ -filter. IR measurements were also made on all samples.

## 3. Results and discussion

The Mössbauer spectra for samples oxygenated at room temperature (A) can be fit with three different species including the parent  $\beta$ -Fe<sup>II</sup>Pc. Only 24% of the compound is oxygenated. However, if the oxygenation is carried out at 50°C in aqueous suspension, or in the dry state, for prolonged periods, then two additional oxygen adducts are formed and a larger fraction of the compound is oxygenated (Table 1 and Fig. 1). It may be pointed out that the fraction of area for each species is only approximately related to the abundance of the species. For a complete equivalence, one has to assume that the fraction of recoil-free events for each species at any specified temperature are the same. The fraction of recoil-free events are determined by how strongly the iron atom and the molecule incorporating the iron atom

<sup>1</sup>Caution: Thermal treatments under oxygen flow above 100°C could be mildly explosive due to the exothermicity of the interaction. It is safer to carry out the thermal treatments in steps, gradually increasing the temperature.

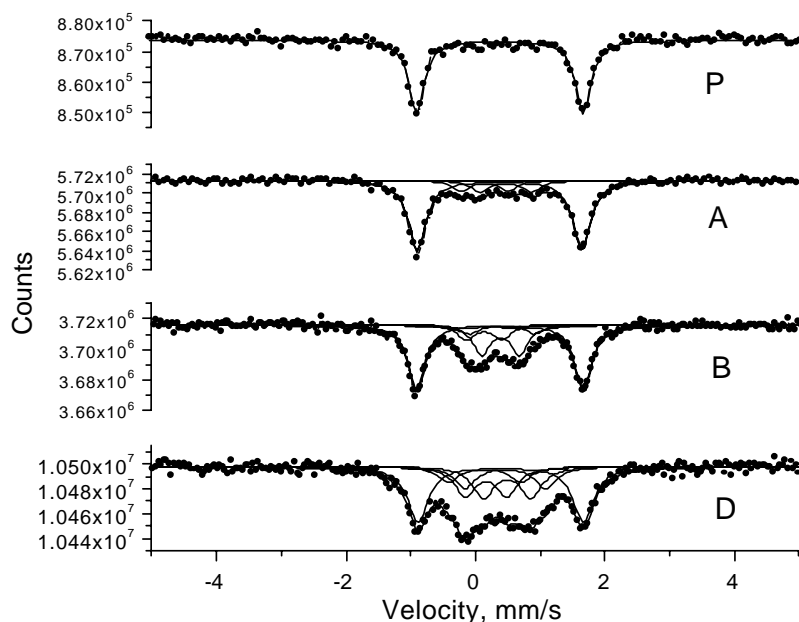


Fig. 1. Mössbauer spectra, recorded at 295 K, of pristine, P, and oxygenated phthalocyanine samples A, B, and D.

are bound to the neighbors. In a general way, one would expect that the five-coordinate domed iron atom would be somewhat less strongly bound than the four and six coordinate ones where the ring is planar. However, the higher the concentration of oxygen between the planes the more strongly would they be bound. It is interesting to note that the relative area of  $\beta$ -Fe<sup>II</sup>Pc is observed to be higher at room temperature (RT) as compared to 80 K for all samples except D (Table 1). It suggests that Fe<sup>II</sup>Pc has higher recoil-free events (i.e. higher Lamb-Mössbauer factor) as compared to the oxygen adducts, which manifest itself as an “apparent” increase in its relative abundance at RT. However, for sample D which has undergone very prolonged oxygenation, the situation changes presumably due to stronger interaction between the layers. The contraction of the cell volume on oxygenation is clearly evident from XRD measurements (Fig. 2). This is reminiscent of the contraction observed during oxygenation of the perovskite YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6</sub> to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> [10]. In principle, one could estimate the local Debye temperature (which is a measure of the recoil-free events) of iron located in each of the species by observing the change in their relative areas as a function of temperature, however, that possibility is frustrated by some interesting interconversions between the species with temperature. From Fig. 3 one can see quite clearly an evidence of interconversion of oxygen adducts as a function of temperature.

The XRD of pristine  $\beta$ -Fe<sup>II</sup>Pc and the oxygenated samples is shown in Fig. 4. For samples C and D which have undergone prolonged oxygenation, one can observe considerably increased background due to lack of

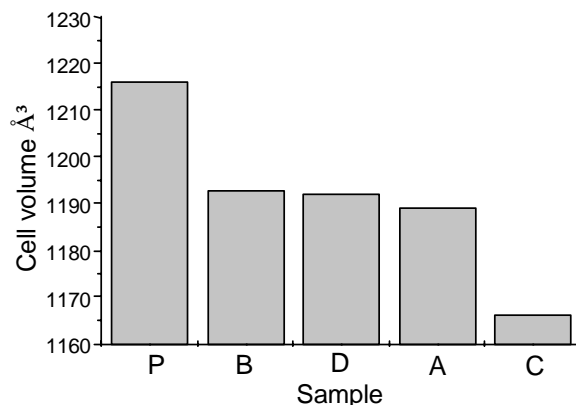


Fig. 2. Cell volume of pristine (P) and oxygenated (A–C) phthalocyanine samples. (See notation of the samples in Table 1.) The standard deviation of the cell parameters was 0.0006 Å.

coherence resulting from breakdown of long-range order presumably because of inhomogeneous distribution of oxygen. Some broadening of lines is also observed for the same reason.

Interestingly, species II and III have similar isomer shifts,  $\delta$ , but different quadrupole splittings  $\Delta$ ,  $\delta \cong 0.4$  and  $\Delta \cong 1.0$ – $1.2$  and  $0.6$ – $0.8$  mm/s, respectively at RT. Again species IV and V have the same  $\delta$  but different  $\Delta$ . Another intriguing observation is that species IV and V seem to convert reversibly to species II and III at higher temperatures, i.e. RT (Table 1).

In Fe<sup>II</sup>Pc and for most of its adducts, the electric field gradient (EFG) is generated mostly by the highly covalent in-plane bonding and is positive [11–14]. The major axis of the EFG lies along  $z$ , the molecular axis.

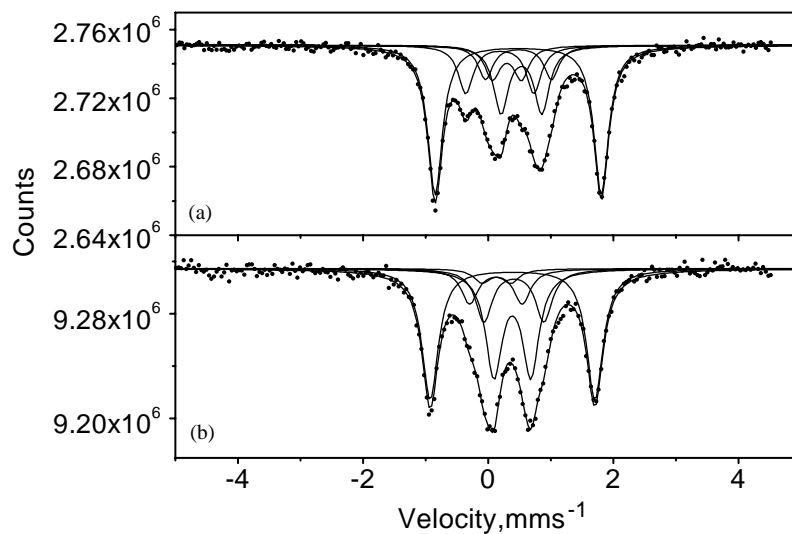


Fig. 3. Mössbauer spectra, of oxygenated phthalocyanine sample C, recorded at 78 K (a) and 295 K (b).

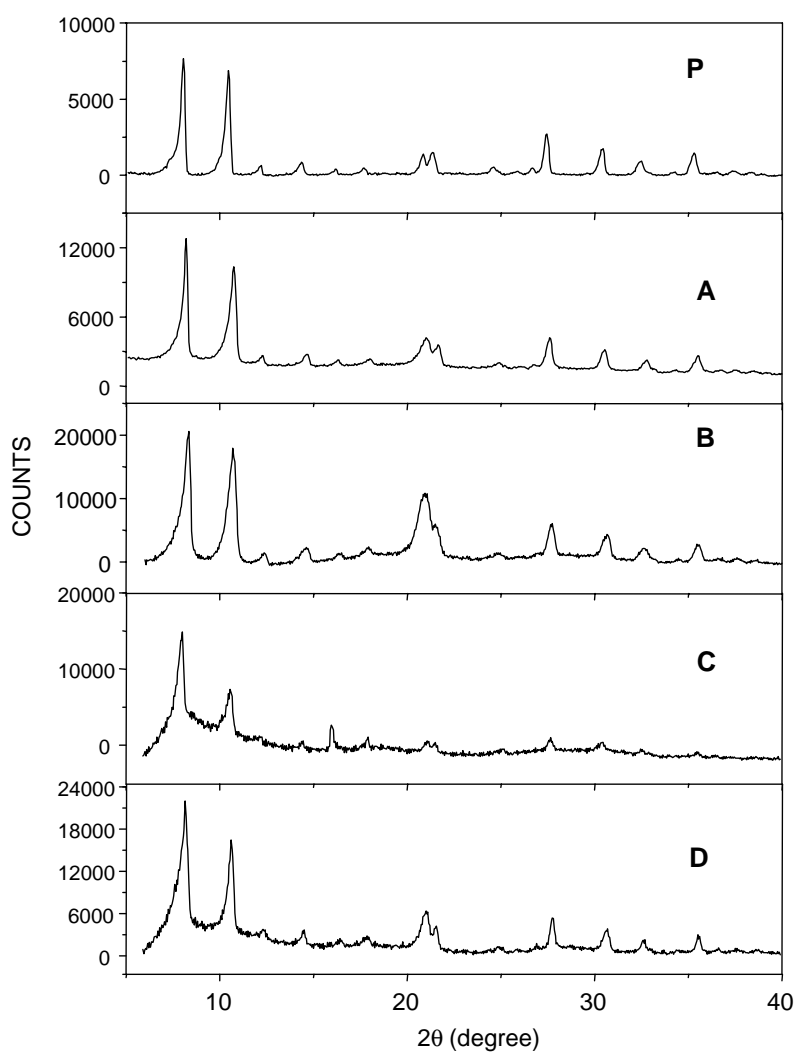


Fig. 4. XRD of the pristine (P) and oxygenated (A–D) phthalocyanine samples.

There is also considerable  $\pi$ -back donation from  $d_{xz}, d_{yz}$  into the macrocycle. The Mössbauer parameters of all the four oxygen adducts (Table 1) are consistent with  $\text{Fe}^{\text{III}}$  high spin configuration [13–15]. Species II and III are probably five-coordinate, however species IV and V having considerably smaller isomer shifts associated with not too large  $\Delta$  are indicative of sixfold coordination. Six coordinate  $\text{Fe}^{\text{III}}$  high spin compounds for phthalocyanine have not been reported earlier [13–15]. The solid matrix tends to stabilize species which would ordinarily be regarded as metastable. The possible configurations for the four oxygenated species are shown in Fig. 5.

Five coordinate  $\text{Fe}^{\text{III}}$  in species II and III is likely to be displaced from the plane of the ring. Despite the cell contraction and the out-of-plane displacement of the Fe atom, the Fe–O–Fe oxo-bridge formation would involve some stretching of bonds. However, species similar to III and V have been observed as an intermediate [16,17], as well as in a peroxy compound [18]. For species IV and V, interaction of  $\text{O}_2$  at the sixth coordination site to

form superoxo compound is rather weak. At higher temperatures (RT) the diatomic oxygen, either end-on or side-on, is detached from the sixth axial position and becomes free to migrate. On lowering the temperature, any  $\text{O}_2$  molecules floating in the vicinity of  $\text{Fe}^{\text{III}}$  of species II and III are captured. Chemical analysis shows that oxygen is present in great abundance indicating the presence of several  $\text{O}_2$  molecules unattached to Fe even at 80 K. The detachment of  $\text{O}_2$  is reflected in the decrease of abundance of species IV and V and corresponding increase in abundance of species II and III at RT. This interconversion is rather small in the oxygenated compound which has undergone dry thermal treatment, namely D. In principle, longer Fe–O–Fe (or Fe–O–O–Fe) chains are possible with the end members being five-coordinate. However, the ratio of the five- to six-coordinate species does not support this contention (Table 1).

The assignment of different species receives support from the IR spectra of the oxygenated compounds. In Fig. 6, by comparison of the two spectra, one can see

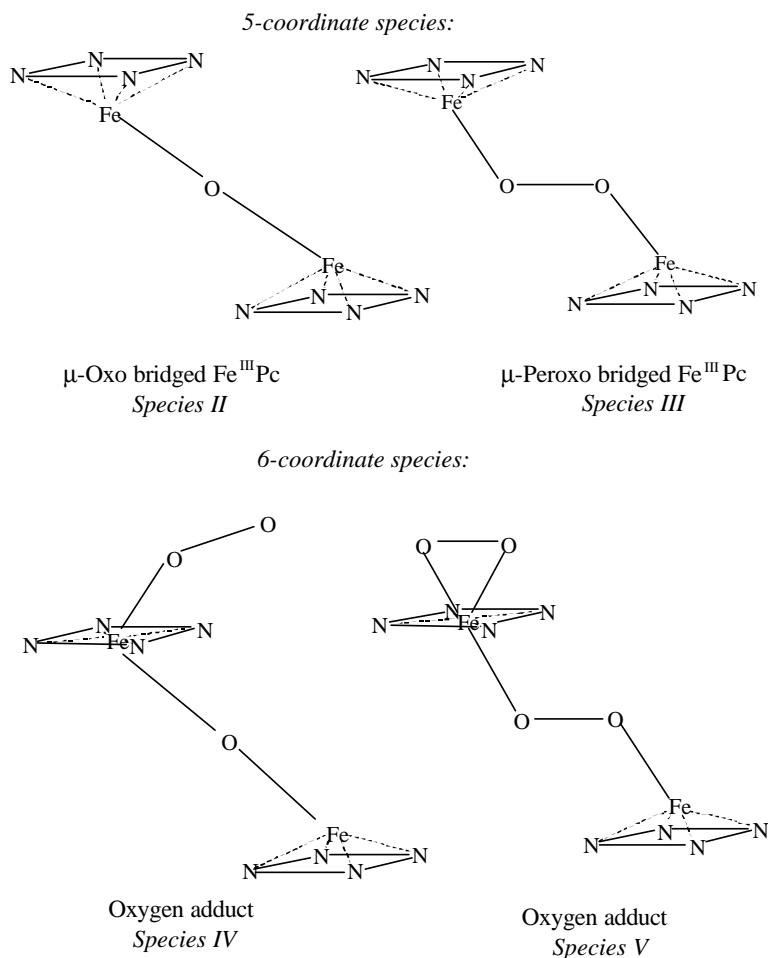


Fig. 5. Suggested structures of species found in oxygenated  $\beta\text{-Fe}^{\text{II}}\text{Pc}$ . In the six-coordinate species (upper Fe), end-on or side-on positions of the dioxygen ligand may be possible for both the  $\mu$ -oxo and the  $\mu$ -peroxo form. The domed structure of the  $[\text{FeN}_4]$  unit may be preserved to some extent after attachment of  $\text{O}_2$  (not shown in the figure).

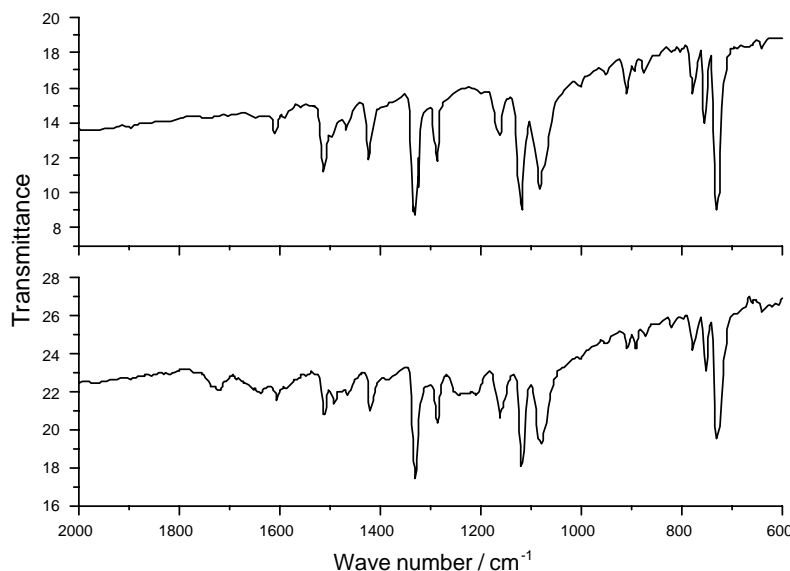


Fig. 6. Infra-red spectra of pristine  $\beta\text{-Fe}^{\text{II}}\text{Pc}$  (top) and oxygenated  $\beta\text{-Fe}^{\text{III}}\text{Pc}$  (bottom, sample C).

that noticeable changes occur in the 1600–1740, 1200 and the  $890\text{ cm}^{-1}$  region. The first region can be ascribed to diatomic oxygen physisorbed to the phthalocyanine rings, second to superoxo attachment in a coordinate position (either end-on or side-on) and the third region is due to Fe–O bridging [19].

In summary, we find novel oxygen adducts are stabilized in the solid matrix of  $\beta\text{-Fe}^{\text{II}}\text{Pc}$ . Some tentative assignments of the species are made on the basis of their Mössbauer parameters. The assignments receive support from IR spectra.

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