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Additional Characterization of the two Oxygen-containing Compounds formed by the Interaction of Phthalocyaninatoiron(II) and Dioxygen. Reproducible Synthesis of the Species Isomorphic with the α Form of Fe(II)Pc

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Abstract

The two compounds obtained by the interaction in solution of Fe(II)Pc with O_2, presently considered two crystalline modifications of the μ-oxo dimer of Fe(III)Pc, are further characterized by visible absorption, XPS and Mössbauer spectra. The results stress the difference between the solid state properties of the two Fe(III) compounds.

The behaviour of Fe(II)Pc and the two oxidized compounds in some chlorinated and non-chlorinated solvents, at different temperatures in the presence and absence of O_2, is reported. It is seen that heating the two Fe(III) products in 1-chloronaphthalene, or dimethylformamide, in vacuum sealed tubes, gives as a final product βFe(II)Pc. However, the same procedure in chlorobenzene or nitrobenzene yields, in a reproducible way, the pure oxygen-containing species which is isomorphic with αFe(II)Pc. Until now this product was only obtained in a fortuitous manner.

Introduction

There have been several reports in the literature concerning the solid product obtained by the interaction of iron(II) phthalocyanine, FePc, with O_2 in solution. In 1979 this author identified two crystalline modifications, indicated as **S** and **B**, and proposed a μ-peroxo structure for both of them [1]. Even if the preparative conditions for **B** were found not to be reproducible, the two compounds were univocally characterized by visible and IR spectra and by X-ray powder patterns. Singularly, the IR spectrum and the X-ray powder pattern of **B** were found identical to those of the α form of Fe(II)Pc.

Afterwards μ-oxo structures were given to both compounds (μ-oxo 1 = **S**, μ-oxo 2 = **B**) and two reproducible methods were reported for obtaining the μ-oxo 2 form [2] Since then several authors have dealt with the μ-oxo 1 compound and in some cases have increased its characterization [3a–d].

In a very recent work Silver *et al.* [4] utilized both procedures previously reported [2] to obtain the form μ-oxo 2 (*i.e.* **B**). Following the first one they only obtained μ-oxo 1; following the second one they obtained a mixture containing μ-oxo 1 (~35%) and another product that, on the basis of the Mössbauer data and the preparative conditions the authors considered to be a sulphonated phthalocyanine Fe(II) species. They concluded that there was no evidence of a second μ-oxo compound.

This latest work prompted us to report here a new reproducible method for synthesizing the compound in question. Both solids are further characterized by visible absorption spectra, XPS and Mössbauer measurements. The two compounds will be indicated here as $FePcoxyg_1$ and $FePcoxyg_2$ while FePcoxyg will be a more generical indication.

Results

Let us recall some important properties, characteristic of the solid and solution states of $FePcoxyg_1$ and $FePcoxyg_2$ which are useful when working with Fe(II)phthalocyanine.

$FePcoxyg_1$ has an IR spectrum (IR_1) characterized by peculiar absorptions at 825, 855 and 895 cm^{-1}. An additional useful feature is the shift to 1490 cm^{-1} of the absorption peak generally found in Fe(II)Pc and derivatives above 1500 cm^{-1}. Its pyridine solution spectrum has the strongest band at 620 nm. Its X-ray powder pattern is hereafter indicated as R_{x1}. $FePcoxyg_2$ has an IR spectrum and X-ray powder pattern identical to those of αFe(II)Pc, and therefore they can be indicated with IR_α and $R_{x\alpha}$. Its absorption spectrum in py is identical to that of $FePcoxyg_1$ with the band at 620 nm. These data are shown in Table I, together with the corresponding data for β and αFe(II)Pc.

The possibility of identifying mixtures of βFePc + $FePcoxyg_1$, βFePc + $FePcoxyg_2$, αFePc + $FePcoxyg_2$, $FePcoxyg_1$ + $FePcoxyg_2$ is evident from Table I, examining both the IR and the pyridine

TABLE I. Iron Phthalocyanines Spectral Features

Compound	βFe(II)Pc	αFe(II)Pc	$FePcoxyg_1$	$FePcoxyg_2$
Colour of the ground compound	greenish-blue	greenish-blue	blue	blue
R_x	$R_{x\beta}$	$R_{x\alpha}$	R_{x1}	$R_{x\alpha}$
IR	IR_β	IR_α	IR_1	IR_α
λ_{max} in py	655 nm	655 nm	620 nm	620 nm

optical data. However in the presence of a αFePc + $FePcoxyg_1$ mixture it may not be easy to exclude $FePcoxyg_2$ since, qualitatively, αFePc + $FePcoxyg_1$ gives the same set of data of αFePc + $FePcoxyg_1$ + $FePcoxyg_2$.

For the above reasons care should be exercised in interpreting the results of experiments performed with FePc and, at least, both IR and visible data should be examined.

If chlorinated solvents are used, in which the iron phthalocyanines can be unstable to give Fe(III)PcCl, the properties of this recently described compound [3a] have also to be considered. Fe(III)PcCl when ground is greenish. Its IR spectrum is similar to that of βFe(II)Pc. In py, it readily reduces to the Fe(II) compound, giving the absorption spectrum with the maximum at 655 nm. The presence of Fe(III)PcCl, in a mixture containing Fe(II)Pc and FePcoxyg, can be established by halogen analysis; alternatively, it is useful to examine the visible absorption spectrum of a solution in non degased nitrobenzene. In this solvent, $FePcoxyg_1$ and $FePcoxyg_2$ are practically insoluble; Fe(II)Pc in solution interacts with O_2 giving the oxygenated species with absorptions at ~700 nm which slowly decrease as FePcoxyg precipitates (see below); Fe(III)PcCl dissolves and remains in solution, giving bands at 655 and 830 nm. The latter band, when it is no longer obscured by the absorptions tails of the oxygenated species, allows the identification of Fe(III)PcCl since only this compound shows maxima between 800–900 nm.

Reported Procedures to Obtain $FePcoxyg_2$

As verified by Silver *et al.* both procedures previously indicated [2] fail to give $FePcoxyg_2$ reproducibly and pure. This compound can be obtained in a variety of conditions, including dissolution and reprecipitation from 1-ClN and a volatile aliphatic N-base (procedure 1 [2]), but this result is fortuitous. Precipitation with H_2O from a solution of Fe(II)Pc in 96% H_2SO_4 in air (procedure 2 [2]) yields the compound but not in pure form.

Procedure 2 is the one generally used to prepare the α modification of M(II) phthalocyanines [5]. Fe(II)Pc reversibly interacts with O_2 when dissolved in 96% H_2SO_4 [6], therefore the result will depend on the working conditions. In rigorous absence of O_2 there will be αFe(II)Pc. In air, the result will depend on the oxygenation time before precipitation. A mixture of αFe(II)Pc and FePcoxyg or only FePcoxyg can therefore be obtained. The latter may consist of $FePcoxyg_2$ or of a mixture of $FePcoxyg_1$ and $FePcoxyg_2$.

Bearing in mind the properties of the compounds summarized in Table I, if the investigation of the precipitate is made only by the IR spectrum, it may lead to mistakes. This is probably what happened to some previous authors [4]. Also, it has been stated that αFe(II)Pc does not react with NO [7]. However the sample used, prepared following procedure 2 and identified by IR and Rx, was, as verified later by the author himself [2], pure $FePcoxyg_2$ instead of αFe(II)Pc.

Behaviour of Iron Phthalocyanines in some Chlorinated or Non-chlorinated Solvents. The Reproducible Synthesis of Pure $FePcoxyg_2$

Homborg *et al.* found that $FePcoxyg_1$ in solution of 1-chloronaphthalene, 1-ClN, is not stable and gives the species Fe(III)PcCl [3a]. They also noted that the absorption spectrum previously reported [8] for a solution of Fe(II)Pc in dichlorobenzene, and therefore assigned to the Fe(II) species, was to be attributed to the species Fe(III)PcCl.

Spectral data for $FePcoxyg_1$ in chlorobenzene, ClB, are reported in [3b] but nothing is said about the stability of the solution.

Some observations on the compounds Fe(II)Pc, $FePcoxyg_1$ and $FePcoxyg_2$, in solutions of chlorinated and non-chlorinated solvents, are reported below. The procedure of heating suspensions of the compounds in vacuum sealed tubes was also employed. At the end, the tube was left to cool and then opened, the solid and the solution were immediately separated and examined.

1-Chloronaphthalene

Fe(II)Pc. Suspensions of Fe(II)Pc (α or β) in 1-ClN, after 3 days heating at 130 °C in a tube, still contained Fe(II)Pc (β form). The absorption spectrum of the green solution separated from the solid was immediately recorded, and the spectra resulting from the interaction with ambient O_2 are shown in

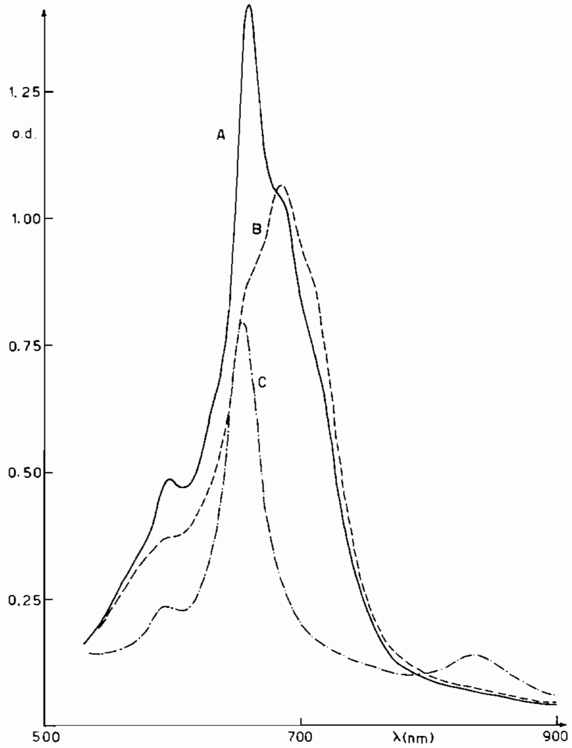

Fig. 1. Absorption spectra of 1-ClN solution of Fe(II)Pc (A), under oxygen (B and C, see text).

Fig. 1. The first spectrum (Fe(II) species) is characterized by a maximum at 660 nm (spectrum A, the shoulders appearing near 700 nm are clearly due to traces of oxygenation product). The contact with O_2 gives the spectrum B characterized by a new maximum at 690 nm, with a shoulder at 710 nm. While this spectrum B slowly modifies (~1 day) to give spectrum C (reported for Fe(III)PcCl [3a], λ_{max} = 655, 835 nm), the absorption intensity decreases because of the separation of a solid which deposits on the bottom of the cuvette.

After decanting the solution, it is proven that this solid is FePcoxyg by dissolution in py. In fact, the visible spectrum shows the maximum at 620 nm.

$FePcoxyg_1$ and $FePcoxyg_2$. After ~2 months heating of the pure solids in tubes at ~100 °C in 1-ClN, a mixture of solids $FePcoxyg_2$, Fe(III)PcCl and βFe(II)Pc is obtained. The green solution gives the spectrum C. A suspension of pure $FePcoxyg_1$, heated for over 7 days at 160 °C, after the same treatment, results in βFe(II)Pc, practically pure.

Therefore in the absence of O_2, Fe(II)Pc in 1-ClN is stable; $FePcoxyg_1$ and $FePcoxyg_2$ are not stable. In particular, by heating, $FePcoxyg_1$ converts first to $FePcoxyg_2$. The reaction with the solvent then produces Fe(III)PcCl which finally reduces to Fe(II)Pc.

Nitrobenzene

The absorption spectrum of Fe(II)Pc in degased NB is reported in Fig. 2, together with the changes caused by the interaction with gaseous O_2. The absorption spectra of both Fe(II)Pc (λ_{max} = 655 nm) and the species formed in solution by the interaction with O_2 (λ_{max} = 690 nm, shoulder at 710 nm) are similar to those observed in 1-ClN.

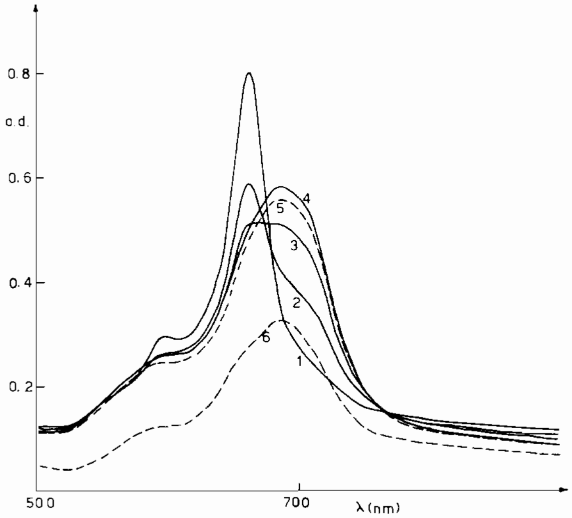

Fig. 2. Spectral changes of nitrobenzene solution of Fe(II)Pc (curve 1) under oxygen (curves 2, 3, 4, 5 and 6).

The spectral changes are not characterized by isosbestic points. This is due to the contemporary separation of a solid and it becomes evident by the decreasing intensity of the spectrum of the oxygenated species (curves 5 and 6). The solid on the bottom of the cuvette is FePcoxyg.

A suspension of Fe(II)Pc (α or β) in NB, after 3 days heating at 150 °C, in a tube, gives back unaltered Fe(II)Pc (β form).

Suspensions of $FePcoxyg_1$, heated for 15 days at 100–120 °C, in tubes, reproducibly give $FePcoxyg_2$.

Chlorobenzene

The spectrum of Fe(II)Pc in degased ClB is similar to that obtained in 1-ClN and NB (λ_{max} = 658 nm). As observed in the above solvents, the concentration of the species formed in solution with O_2 decreases while depositing FePcoxyg on the bottom of the cuvette.

Suspensions of $FePcoxyg_1$ in ClB in tubes, after 15 days heating at 120–130 °C become pure $FePcoxyg_2$. The same result is obtained after 5 months of heating at 100 °C, showing that, in these conditions, the Fe–O bond is not broken by the halogen of the solvent.

Dimethylformamide

Some experiments of heating in vacuum sealed tubes were carried out on $FePcoxyg_1$ and $FePcoxyg_2$ with DMF as solvent. It was seen that in this solvent, reduction to Fe(II) occurred to give βFe(II)Pc.

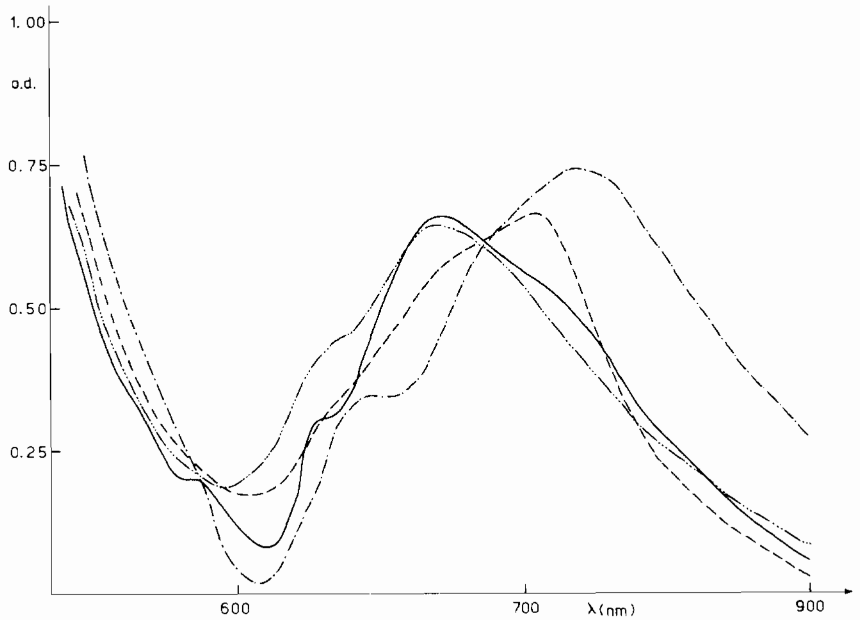

Fig. 3. Absorption spectra of βFe(II)Pc (———), αFe(II)Pc (– – –), FePcoxyg$_1$ (–·–·–) and FePcoxyg$_2$ (··–··–), as Nujol mulls.

The transformation FePcoxyg$_1$ → FePcoxyg$_2$ observed in ClB or NB was verified by several experiments varying the temperature in the range 100–170 °C. At the highest temperatures, in some cases, the FePcoxyg$_2$ obtained was accompanied by small quantities of βFe(II)Pc (<10%).

To check if the transformation also occurs without a solvent, samples of 3–4 mg of FePcoxyg$_1$ in vacuum sealed tubes were heated for 3–4 h at different temperatures. No transformation was observed: FePcoxyg$_1$ was unaltered up to ~320 °C, at which temperature its decomposition starts giving βFe(II)Pc. In the same conditions FePcoxyg$_2$ starts its direct decomposition into βFe(II)Pc at nearly 360 °C.

Absorption Spectra of Solids β and αFe(II)Pc, FePcoxyg$_1$ and FePcoxyg$_2$

The visible absorption spectra are shown in Fig. 3. The four compounds appear clearly differentiated. We note that the spectrum of FePcoxyg$_1$ does not agree with that previously obtained [3a] using KBr discs. The spectra of βFe(II)Pc and FePcoxyg$_2$ show broad absorptions centred at higher energies (650 and 640 nm); those of αFe(II)Pc and FePcoxyg$_1$, at lower energies (710–740 nm).

XPS Spectra

XPS spectra were performed on FePcoxyg$_1$ and FePcoxyg$_2$ to determine the binding energy (*BE*) of Fe 2p 3/2 electrons. This is reported as 708.8 eV in Fe(II)Pc [9] and a chemical shift of the order of 2 eV is expected between Fe^{2+} and Fe^{3+}.

The measured *BE* were of 711.3 eV in FePcoxyg$_1$ and 712.1 in FePcoxyg$_2$ (a C_{1S} energy of 285 eV was the internal reference). These values are fairly different but they appear to indicate an oxidation state 3+ for both compounds.

Mössbauer Spectra

As mentioned in the 'Introduction', recently [4] Mössbauer spectra have been measured on compounds prepared by other methods [2] to obtain the species indicated here as FePcoxyg$_1$ and FePcoxyg$_2$. The products obtained were examined only by IR spectra. The authors did not have problems with FePcoxyg$_1$; the Mössbauer analysis showed it to be a unique compound with $\delta = 0.34(2)$ and $\Delta E = 0.38(2)$. In the case of FePcoxyg$_2$, the sample obtained according to procedure 1 [2] was still FePcoxyg$_1$ from IR and Mössbauer data. The product obtained following procedure 2 [2], by Mössbauer analysis was a mixture of two compounds: FePcoxig$_1$ (35%) ($\delta = 0.34$, $\Delta E = 0.38$) and a compound (65%) with $\delta = 0.23(2)$ and $\Delta E = 1.28(2)$. The latter is considered by the authors to be an unknown low-spin Fe(II) species.

Mössbauer parameters determined on FePcoxyg$_1$ and FePcoxyg$_2$, prepared as described in 'Experimental', are reported in Table II. The values of δ and Δ*E* found for FePcoxyg$_1$ fully agree with those reported by Silver *et al.* for this compound. The values of δ and Δ*E* for FePcoxyg$_2$ are very close to those previously obtained [4] for the unknown component of the mixture.

TABLE II. Mössbauer Spectral Data

Compound	T (K)	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
$FePcoxyg_1$	78	0.343(3)	0.365(3)
$FePcoxyg_2$	298	0.166(3)	1.007(3)

Consistent with what we have described for procedure 2, we think that the second component obtained by Silver *et al.*, was $FePcoxyg_2$*. This could have been immediately confirmed by a visible spectrum in py: in fact, only one absorption at 620 nm would have resulted for $FePcoxyg_1$ + $FePcoxyg_2$. On the contrary, the mixture of $FePcoxyg_1$ + Fe(II)Pc species would have presented two peaks, at 620 and 655 nm.

Discussion

In 1979, a formulation as O_2 containing compounds was assigned to the FePc derivatives, $FePcoxyg_1$ and $FePcoxyg_2$ (then indicated as **S** and **B**), mainly due to the following observation**: the solution of the compounds in degased 96% H_2SO_4 shows the reversible spectrum observed when Fe(II)Pc and O_2 react in this medium [6]. This spectrum, by N_2 bubbling, reverses to that of Fe(II)Pc.

'Claims of reversible oxygenation which rely solely on the criterion of solution spectral change must be treated with utmost caution'; Collman gave this advice in 1973. Very often when O_2 is eliminated, the solvent or any reducing impurities may cause the reduction of the irreversibly formed Fe(III) species [10]. Even bearing this in mind, in the case under study it was difficult to consider: (i) 96% H_2SO_4 as a reducing agent or (ii) the presence, in this Suprapur grade Merck reagent, of reducing impurities, as probable.

On this basis, the more common formulation as μ-oxo compounds was excluded. In fact, it appeared well stated that the latter species are formed via an irreversible oxidation of Fe(II) compounds [11].† In agreement with the μ-peroxo formulation of the solids, in a kinetic study of the oxygenation reaction in 96% H_2SO_4, the above reversible spectrum was assigned to the $PcFe-O_2-FePc$ species [14].

More recently [15], a kinetic study of the interaction of Fe(II)Pc with O_2 in DMSO was carried out by the same authors as in ref. 14. The entire process leading to these FePcoxyg compounds, considered as Fe(III) μ-oxo derivatives, was presented as being reversible. This may appear surprising; however, if it is accepted also in concentrated H_2SO_4, then it appears to resolve all the questions.

The properties of the solid state of both compounds, already clearly different for what concerns IR spectra and X-ray powder patterns, appear even more differentiated by Mössbauer, XPS and optical data reported in this paper.

Russian authors [3d] have found in XPS data a valuable support to formulate the μ-oxo dimer of $(t\text{-}Bu)_4PcFe$ as a Fe(II) derivative $H_2[((t\text{-}Bu)_4PcFe)_2O]$. On this basis, they have proposed a similar structure for the FePc derivative, $FePcoxyg_1$. XPS measurement on $FePcoxyg_1$ and $FePcoxyg_2$ shows this is incorrect. The Fe 2p 3/2 levels of the two compounds show bonding energies fairly different, but indicative of the same oxidation state 3+.

Both pairs of δ and ΔE_Q values found for $FePcoxyg_1$ and $FePcoxyg_2$ are peculiar and the ones presented by the unidentified $FePcoxyg_2$ led the authors in ref. 4 to hypothesize a Fe(II) low-spin compound. In reality, Mössbauer data close to those determined here for $Fe(II)Pcoxyg_2$ may be found also for some Fe(III) porphyrins, when hexacoordinate in both high and low-spin state [16]. Obviously the reasons which determine such different Mössbauer parameters for the two compounds and what they mean in absolute terms are still unclear. Further work is clearly needed.

The observations here reported on the behaviour of iron phthalocyanines compounds in some solvents in the absence of O_2, increase the information on the redox properties of the couple Fe(II)Pc/Fe(III)Pc. The ability of FePcoxyg to give back the Fe(II) compound in strong N-bases, at room temperature, even in the presence of O_2, was immediately noted [1]. It has now been shown that the reduction Fe(III)Pc → Fe(II)Pc in the absence of O_2, occurs at higher temperatures, also in solvents like DMF and 1-ClN.

In conclusion, we confirm that from the interaction of Fe(II)Pc with O_2 in solution, two forms of an oxygen-containing Fe(III)Pc compound, with the same visible absorption spectrum in solution can be obtained. As far as the intriguing properties of reversibility of these compounds and their differences in the solid state properties (visible, IR, X-ray, XPS, Mössbauer), it is evident that definitive X-ray single

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*The IR spectrum previously reported [4] for the mixture appears to be of poor quality. Probably the product was not sufficiently washed. It is difficult, for example, to locate the band present in all iron phthalocyanines compounds near 1500 cm^{-1}.

**The statement [2] that such formulation was based only on the elemental analysis is not really correct.

†Some previous observations on solids αCuPc and αFePc, considered to have absorbed dioxygen, appeared to support the μ-peroxo formulation [12, 13]. As it occurs in $FePcoxyg_2$, no variation in the IR spectrum of the oxygenated form of CuPc with respect to the non oxygenated one, was noted. As concerns FePc, the X-ray powder pattern was found unchanged and a μ-peroxo structure was proposed.

crystal structures, would establish the real nature of these compounds.

Experimental

Preparation of Compounds

The solvents were purified by conventional methods.

βFe(II)Pc was obtained by sublimation of FePc Eastman Kodak Co. at 480 °C, 10^{-2} torr.

αFe(II)Pc was obtained by thermal decomposition of $Fe(II)Pc(DMSO)_2$ [17], in a pure N_2 stream at ~100 °C. The product was checked by CHNS analysis, IR spectrum and visible absorption spectrum in py.

$FePcoxyg_1$ was obtained, in a simple procedure, by heating in air at 80 °C for 40 min a suspension of Fe(II)Pc (500 mg) in DMF (8 ml). After cooling, the solid was filtered out, washed with DMF and CH_3OH and vacuum dried.

Pure $FePcoxyg_2$ was obtained reproducibly by heating a suspension of $FePcoxyg_1$ in chlorobenzene (10–15 mg/3 ml), for 2 days under N_2 at 100–110 °C. For the preparation of larger amounts, suspensions of 50 mg of $FePcoxyg_1$ in 5 ml of ClB or 2 ml of nitrobenzene, in vacuum sealed tubes, were heated for a long time (not less than 15 days) at 100–120 °C.

After cooling, the tubes were opened, the solid was filtered, washed with CH_3OH and vacuum dried.

Physical Measurements

IR and UV–Vis. spectra were recorded on Perkin Elmer Spectrophotometers 580B and 555 respectively. The best results for the visible absorption spectra of the solids were achieved in the following way: nujol mulls of the compounds were squashed between two quartz plates. The two plates were separated and put both in the spectrophotometer optical path.

Mössbauer spectra were recorded on the constant accelerator mode with a $^{57}Co(Rh)$ source held at room temperature. The velocity scale was calibrated using a thin metallic iron foil and all isomer shifts were referred to the centre of the spectrum of an α-Fe absorber. Lorentzian lineshapes were used for the least-squares fitting of the experimental data. For technical reasons, measurements on $FePcoxyg_2$ compound were possible only at room temperature.

XPS spectra were performed on a VG-ESCA3 spectrometer with an Alkα ($h\nu$ = 1486.6 eV) source.

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