IR AND UV-VISIBLE SPECTRA OF IRON(II) PHTHALOCYANINE COMPLEXES WITH PHOSPHINE OR PHOSPHITE

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ABSTRACT. We have prepared and studied by vibrational and electronic spectrometry of a series of ferrophthalocyanine complexes with phosphine or phosphite axial ligands [PMe_3, $P(OMe)_3$, PPh_3, $P(OPh)_3$, $PPh(OMe)_3$ and $POH(OEt)_2$]. With PMe_3, $P(OMe)_3$ as ligands, only hexacoordinated complexes are obtained but with PPh_3, $P(OPh)_3$ and $POH(OEt)_2$ as ligands, the coordination number depends on the FePc:ligand ratio in the reaction mixture. In the ratio 1:1 the complexes thus formed are pentacoordinated and in the ratio 1:2 hexacoordinated complexes are obtained. In the electronic spectra of hexacoordinated complexes, two charge-transfer transition bands, one at ~375 nm and the other at ~421 nm can be observed. We attribute the band at 375 nm to charge-transfer from axial ligand to macrocycle (CT $L_{ax} \rightarrow Pc$) and the band at 421 nm to charge-transfer from metal to axial ligand (CT $Fe \rightarrow L_{ax}$). In the IR spectra, the position of the ν_{FeN4} band is linked to the coordination number; in the spectra of pentacoordinated complexes, its frequency is almost the same as that in the FePc spectrum but in hexacoordinated complexes, it moves to high frequencies.

INTRODUCTION

Metallophthalocyanines [MPc] possesses a system of delocalised π-electrons. This delocalisation and the interactions of the π-electron with the central metal atom determine the redox properties of these complexes [1, 2]. These in turn led to the study of semi-conductivity, photoconductivity, photochemical reactions, photosynthetic and electrocatalytical activities, etc. [3-7]. An important theme has been to determine the influence of axial or equatorial ligands on the physico-chemical properties of the complexes [8-11]. Phthalocyaninato iron(II) is a widely investigated porphyrin-like molecule which exhibits a strong tendency to axial ligation. A former study of its adduct complexes with pyridine and substitued pyridines gave a consistent view of the axial and equatorial π-bonding in the series [8, 11]. There is, however, very little information concerning the compounds made by the reaction of FePc with phosphine or phosphite ligands [12-14].

In this paper, we present the results of the preparation and study by vibrational and electronic spectrometry of a series of FePc complexes containing axial phosphine or phosphite ligands. The ligands which are used are PMe_3, $P(OMe)_3$, PPh_3, $P(OPh)_3$, $PPh(OMe)_2$, and $POH(OEt)_2$.

EXPERIMENTAL

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Preparation of compounds

FePc. We have obtained this compound from a method developed in our Laboratory [15]. The pure product is obtained with a yield of 75 %.

FePcL pentacoordinated complexes. The pentacoordinated compounds were obtained by heating to 70 °C, with stiring, an equimolar mixture of FePc and the ligand in DMSO; the time of reaction varies with the ligand.

[FePc{POH(OEt)$_2$}]. A mixture of FePc (1 g, 1.760 mmol) and POH(OEt)$_2$ (0.245 g, 1.760 mmol) in 50 mL of DMSO was heated 70 °C with stirring. After 3 h the mixture was cooled, the solid was filtered off, washed with EtOH and dried in vacuum over P$_2$O$_5$. The yield (R) was 70%. The reaction lasts for 3 h for [FePc{PPh$_3$}] (the   yield, R, was 73%), 1½ h for [FePc{P(OPh)$_3$}] (yield 67 %) and 10 h for [FePc{PPh(OMe)$_2$}] (yield 75 %).

FePcL$_2$ hexacoordinated compounds

These compounds were obtained from the methods described in the literature [12, 13, 16].

[FePc{P(OMe)$_3$}$_2$]. A mixture of FePc (1 g, 1.760 mmol) and P(OMe)$_3$ (1.5 mL, 3.521 mmol) in DMSO was heated up to 70 °C with stirring. After 1½ h the mixture was cooled, the solid was filtered off, washed with EtOH, then dried in vacuum over P$_2$O$_5$. The yield (R) was 62%.

[FePc{PMe$_3$}$_2$]. A stirred mixture of FePc (1 g, 1.760 mmol) and PMe$_3$ (0.560 g, 3.521 mmol) in DMSO was heated to 70 °C for 10 h. After cooling, the solid was filtered off, washed with EtOH, then dried in vaccum over P$_2$O$_5$. (R = 57 %).

[FePc{PPh$_3$}$_2$], [FePc{P(OPh)$_3$}$_2$] and [FePc{POH(OEt)$_2$}$_2$]. These compounds were obtained in the same way as [FePc{PMe$_3$}$_2$] by use of the corresponding ligand. The reaction yields were 50% for [FePc{PPh$_3$}$_2$], 51% for [FePc{P(OPh)$_3$}$_2$] and 67 % for [FePc{POH(OEt)$_2$}$_2$] .

Reagents and apparatus

Phosphine and phosphite ligands were commercially grade (ACROS) and were used without purification.
    The IR absorption spectra were obtained on a PERKIN ELMER 843 spectrometer from KBr discs at 1% for the 700 – 1600 cm^{-1} domain and from CsI discs at 10% for the 200 – 650 cm^{-1} domain. The UV–visible spectra were obtained on a PHILIPS S-1000 spectrometer from saturated solutions of compounds in DMSO or benzene.

RESULTS AND DISCUSSION

Electronic absorption spectrometry of pentacoordinated complexes

For axially substituted compounds we noticed that the nature of the reaction product between FePc and phosphine or phosphite ligands depends on the quantity of ligand which is used. With FePc:L in 1:1 ratio, these ligands with FePc form pentacoordinated complexes [FePcL] and with FePc:L in 1:2 ratio the complex formed is hexacoordinated [FePcL$_2$].

As far as we know, this is the first time FePc pentacoordinated compounds with phosphine or phosphite ligands have been prepared and isolated in the solid form.

The wavelengths of the bands of FePc and pentacoordinated species of FePc having phosphine or phosphite in axial position in DMSO and in benzene are grouped in Table 1 below.

Table 1. Wavelengths of noticeable bands in DMSO and in benzene (nm).

Solvents	Compounds	λ^*_Q	λ^*_S	λ^*_B
DMSO	FePc	652	594	330
	[FePc{P(OPh)$_3$}]	678; 652	590	320
	[FePc{PPh$_3$}]	675; 645	587	327
	[FePc{POH(OEt)$_2$}]	675; 642	585	321
Benzene	FePc	704	651	330
	[FePc{POH(OEt)$_2$}]	678; 651	-	327

*Q = transition band $\pi \rightarrow \pi^*$, B = Soret band, S = shoulder.

The FePc spectrum in DMSO is similar to that of the literature with two main bands at 652 nm (Q band) and at 330 nm (Soret band or B band). The change of solvent results changes to the relative intensity and frequency of Q band but the Soret band is unchanged. The Q band at 652 nm in DMSO moves to 704 nm in benzene with a lower relative intensity. The same phenomena have already been observed in changing from DMSO to chloronaphthalene solution [17].

For the pentacoordinated compounds, the spectra in DMSO solution present a Soret band which is almost the same as that of the FePc spectrum and a Q band which possesses two maxima at 645 nm and 676 nm. Such a splitting of the Q band has been observed in the spectra of the [FePc(H$_2$O)] [18], [FePcPy] [19], [FePcSR] [17] and [FePcCl] [16]. This phenomenon is characteristic of FePc pendacoordinated complexes [16-19]. Some authors explain this by the molecule symmetry change from D$_{4h}$ for FePc to C$_{4v}$ for the pentacoordinated species. This symmetry change would leave some orbital degeneracies and result in splitting of the Q band in the spectra.

The very low solubility of the compounds in benzene made it possible for us to obtain spectra only for FePc and [FePc{POH(OEt)$_2$}]. The results obtained in benzene with [FePc{POH(OEt)$_2$}] confirm those which have been obtained in DMSO. The only one difference is the disappearance in the spectrum in benzene of the shoulder at 585 nm in DMSO.

Hexacoordinated compounds spectra

Table 2 shows the wavelengths of the maxima of the FePc bands and of the hexacoordinated derivatives.

Table 2. Wavelengths (nm) of the noticeable bands in DMSO and in benzene.

Solvent	Compounds	λ_Q	λ_S	λ_{CT} L$_{ax}\rightarrow$Pc	λ_{CT} Fe$\rightarrow$L$_{ax}$	λ_B

	FePc	704	651	-	-	330
	[FePc{PMe$_3$}$_2$]	663	600	376	430	321
Benzene	[FePc{P(OMe)$_3$}$_2$]	660	600	375	434	324
	[FePc{PPh$_3$}$_2$]	654	594	-	410	331
	[FePc{P(OPh)$_3$}$_2$]	660	600	-	419	324
	[FePc{POH(OEt)$_2$}$_2$]	652	593	-	412	327
	FePc	652	594	-	-	330
	[FePc{PMe$_3$}$_2$]	661	600	-	382	328
DMSO	[FePc{P(OMe)$_3$}$_2$]	655	594	-	410	330
	[FePc{PPh$_3$}$_2$]	654	593	-	-	324
	[FePc{P(OPh)$_3$}$_2$]	652	594	-	-	330
	[FePc{POH(OEt)$_2$}$_2$]	654	591	-	-	327

In general, the spectra of the hexacoordinated derivatives in benzene present additional bands which are not observed in that of FePc. Two groups can be observed: with PMe$_3$ and P(OMe)$_3$ ligands, two additional bands can be observed at about 375 and 432 nm and with the PPh$_3$, P(OPh)$_3$ and POH(OEt)$_2$ ligands only one band is visible around 414 nm (see Table 2). Similar results have been obtained by Swaigart [13] with [FePc{PBu$_3$}$_2$] and [FePc{P(OBu)$_3$}$_2$] in toluene solution, but the author did not make any comment concerning the origin of these new bands. Works in our Laboratory on [FePcL$_2$] complexes with nitrogen aromatic bases such as pyridine and substituted pyridines [8, 9] makes it possible for us to attribute the band at ~375 nm to a charge-transfer from the axial ligand towards the macrocycle through the central metal (CT L$_{ax} \to$ Pc) and the band at ~421 nm to charge-transfer from the metal towards the axial ligand (CT Fe$\to$ L$_{ax}$).

The phosphine and phosphite ligands are Lewis bases with empty d-π orbitals which are likely to receive electrons through back donation. That makes us think that these ligands have properties similar to those of the substituted pyridine. It is therefore not surprising that there can exist bands of CT L$_{ax} \to$ Pc type and Fe $\to$ L$_{ax}$ type in the spectra of the hexacoordinated derivatives we have obtained.

The fact that the energies of these transitions are lower with the pyridine and substituted pyridine ligands than with phosphines and phosphites can be explained by the fact that in pyridine, it is the donor power that dominates while in phosphines and phosphites, there are empty orbitals which are able to accept electrons; so that, in this laters there is a coexistence of the donating and attracting powers. It is also established that the nitrogen bases such as pyridine are more susceptible to inductive effects than are phosphine and phosphite [19]. That results in the formation of pyridine bases whose field is stronger than those of phosphines and phosphites.

In DMSO solution, the [FePc{PMe$_3$}$_2$] and [FePc{P(OMe)$_3$}$_2$] spectra are the only ones which differ from that of FePc. An additional band at about 400 nm, attributable to CT Fe $\to$ L$_{ax}$ can be observed. No additional band is visible in the spectra of compounds with PPh$_3$, P(OPh)$_3$ and POH(OEt)$_2$ ligands (see Table 2). We think that the absence of CT bands in the spectra of the compounds with these ligands can be explained by the failure of the ligands to displace DMSO from the Fe coordination sphere.

Comparison of the spectra of hexacoordinated and pentacoordinated derivatives makes it possible to observe the following:

i)   The Q band appears in spectra of the hexacoordinated derivatives at around 652 nm while in spectra of the pentacoordinated derivatives, this band shows maxima at around 676 and 645 nm.

ii) Charge-transfer bands appear in the hexacoordinated derivatives spectra which are not observed in either the FePc spectrum or in those of the pentacoordinated derivatives.

Infrared absorption spectra

The introduction of the phosphine or phosphite ligands in the axial position of FePc is shown in the spectra by a variation of relative intensities of bands in the 1000 – 1600 cm^{-1} domain and by the appearance of new bands.

The most notable modifications appear in the [FePc{P(OMe)$_3$}$_2$] spectrum. In the spectrum of this compound an increase of the intensities of the bands at 1490 and 1160 cm^{-1} can be observed while that of the band at 1330 cm^{-1} decreases. As the band at 1160 cm^{-1} is associated with the C-H vibrations of the macrocycle, it can be assumed that the presence of the CH$_3$ groups in the axial P(OMe)$_3$ ligand leads to the increase in intensity of this band. Two new bands appear at 1034 and 1014 cm^{-1} in the [FePc{P(OMe)$_3$}$_2$] spectrum. By analogy with the organic compounds of phosphorus [20], they can be attributed to the vibrations of the axial ligand.

Slight movements of bands between 700-800 cm^{-1} can be observed (see Table 3). This region, which shows the C-H out of plan vibrations, is sensitive to the modifications of the crystalline structure. Therefore, it is not unexpected that the bands of this region are perturbed by the axial ligand fixation. A new band ascribable to the distortion of the P-Ph link [20] appears at 700, 714 and 703 cm^{-1}, respectively, in the [FePc{PPh$_3$}$_2$], [FePc{PPh$_3$}] and [FePc{PPh(OMe)$_2$}] spectra. The presence of the bands of the vibrations ascribable to the axial ligands confirm the formation of these compounds.

Table 3. IR bands noticeable between 700 and 800 cm^{-1}.

	[FePc{PX$_3$}$_2$]					[FePc {PX$_3$}]			
FePc	PMe$_3$	P(OMe)$_3$	PPh$_3$	P(OPh)$_3$	POH(OEt)$_2$	PPh$_3$	P(OPh)$_3$	PPh(Ome)$_2$	POH(OEt)$_2$
-	-	797	775	-	-	790	-	-	796
770	777	775	770	772	778	780	783	774	780
748	752	757	750	748	752	750	753	752	750
724	728	740	730	724	728	728	734	728	730
			700	-	-	714	-	703	-

The 200 – 650 cm^{-1} domain is very sensitive to the symmetry around the central metal and to its formal state of oxidation [21]; it is therefore expected that phosphine and phosphite ligation fixation will result in modifications in the FePc spectrum.

We were particularly interested in the evolution of the ν_{FeN4} band [22] which is shown at 308 cm^{-1} in the FePc spectrum (see Table 4).

Table 4. Frequency of the ν_{FeN4} (cm^{-1}) band.

	[FePc{PX$_3$}$_2$]					[FePc {PX$_3$}]		
FePc	PMe$_3$	P(OMe)$_3$	PPh$_3$	P(OPh)$_3$	POH(OEt)$_2$	PPh$_3$	P(OPh)$_3$	POH(OEt)$_2$
308	328	320	337	330	330	310	308	308

In the spectra of the pentacoordinated species the frequency of the ν_{FeN4} band does not show much variation; such a phenomenon has already been observed with thiolate complexes of FePc

[17]. On the other hand, in the spectra of the hexacoordinated derivatives, the ν_{FeN4} band moves towards high frequencies (see Table 4).

Some authors have already suggested that the shift of this band towards high frequencies in the spectra of certain FePcL$_2$ complexes is closely related to the donating power of the axial ligand [8]. In the case when L is pyridine or a substituted pyridine, shift is greater the stronger the donor properties of the ligand. In our study, we could not show any correlation between the donating power of the axial ligand and the value of the ν_{FeN4} movement. However, as in the case when the ligand is a nitrogen aromatic base, we can assume that in the ligand series we have used, the donating power remains predominant.

CONCLUSION

In this work, we have prepared and isolated in a solid form the following complexes: [FePc{PMe$_3$}$_2$], [FePc{P(OMe)$_3$}$_2$], [FePc{PPh$_3$}$_2$], [FePc{P(OPh)$_3$}$_2$], [FePc{POH(OEt)$_2$}$_2$], [FePc{PPh$_3$}], [FePc{P(OPh)$_3$}], [FePc{POH(OEt)$_2$}] and [FePc{PPh(OMe)$_2$}].

For PPh$_3$, P(OPh)$_3$ and POH(OEt)$_2$, the nature of reaction product depends on the quantity of ligand used. For FePc:L 1:1, the compound obtained is pentacoordinated and for in FePc:L 1:2 ratio a hexacoordinated complex is obtained.

In electronic spectrometry we have observed charge transfer transitions at 375 nm and 421 nm. That at 375 nm is attributable to an axial ligand charge-transfer $\rightarrow$ macrocycle and that at 421 nm represents a metal charge transfer $\rightarrow$ axial ligand.

Vibrational spectrometry has made it possible for us to show that in the hexacoordinated complexes, the ν_{FeN4} frequency moves towards high values while in the pentacoordinated derivatives, its frequency remains almost constant.

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