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Charge-Transfer and Mössbauer Spectra of Axially Substituted Iron Phthalocyanines

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Preparation of complexes of ferrophthalocyanine with imidazole, piperidine, pyridine, and several substituted pyridine derivatives (Rpy where py = pyridine and R = CH_3, OH, Cl, CN, CHO) is reported. A metal-to-macrocycle charge-transfer band is characterized in the optical spectra of all compounds in the series. An extra band is observed in complexes with electron-withdrawing substituents on the axial pyridine. Mössbauer measurements on all the compounds have been made, and correlation of Mössbauer parameters with optical data is proposed. $d_\pi \rightarrow \pi^*$ back-donation accounts for the experimental data.

Introduction

There is an increasing interest in nitrogen-ligand iron complexes as most of them could be good models for protein-active sites.[1] Thus, species such as $[Fe^{II}(CN)_5L]^{n-}$,[2] $Fe^{II}(CO)_4L$,[3] and $Pt^{II}Cl_2L_2$,[4] where L is a variety of nitrogen ligands, have been investigated as well as metallocomplexes of dimethylglyoxime (DMG),[5] porphyrins,[6] and phthalocyanine.[5,7] In the latter type of complexes the equatorial macrocycle imposes a rigid geometry and the main effects have been assumed to originate from axial ligands with constant metal-ligand bonds in the planar framework.[8] The study of the reactivity of iron porphyrin and phthalocyanine (FePc) with the axial nitrogen ligands is particularly justified as the presence of at least one imidazole from an histidine residue is confirmed or suspected as an axial ligand in most isolated and studied hemoproteins.[9] Another type of interest raises from the special nature of Pc complexes as organometallic conductors[10] and as complexes with particular magnetic and redox properties.[11]

Several authors have reported on optical and Mössbauer spectra of FePc complexes,[7,9,12] but data are scarce or remain rather inhomogeneous so that a few questions still remain unanswered. We have prepared 16 complexes of FePc with piperidine (pip), imidazole (Im), pyridine (py), and several derivatives of pyridine (Rpy with R = CH_3, OH, Cl, CN, CHO). Donor or withdrawing substitutents on one or two carbons of the pyridine ring modify appreciably the properties of the ligands.[13] Rather important effects are induced on both the metal- and macrocycle-delocalized electron atmosphere. Optical spectra and Mössbauer resonances reported in the present paper appear to be quite sensitive to the remote modification on pyridine. From the data we can reach a conclusion on the nature of the charge-transfer (CT) bands and discuss the correlation between structure and ^{57}Fe isomer shifts (δ) and quadrupole splittings (Δ).

Experimental Section

Physical Measurements. The optical spectra have been recorded on a Beckman Model 25 spectrophotometer.

The Mössbauer spectra of ^{57}Fe have been recorded on a Mössbauer Elscint spectrometer working in the constant-acceleration mode with a ^{57}Co source in a Pt matrix.

Preparation of Complexes. Compounds reported in Table I have been isolated as microcrystalline powders, by adapting the published methods, from iron(II) phthalocyanine ($Fe^{II}Pc$) and the considered ligand.

The β form of $Fe^{II}Pc$ has been prepared with high yield and purity from *o*-phthalonitrile and anhydrous iron(II) acetate in chloronaphthalene by an improved method already described in a previous paper.[14]

Pure imidazole (Im) (Koch light Laboratoire Ltd.), piperidine (pip), 3-methylpyridine (3-Mepy), 4-methylpyridine (4-Mepy), 3,4-dimethylpyridine (3,4-Me_2py), 3,5-dimethylpyridine (3,5-Me_2py), 3-hydroxypyridine (3-OHpy), 4-hydroxypyridine (4-OHpy), 3-chloropyridine (3-Cl-py), 4-chloropyridine hydrochloride (4-Cl-py(HCl)), 3,5-dichloropyridine (3,5-Cl_2py), 3-cyanopyridine (3-CNpy), 4-cyanopyridine (4-CNpy), 3-pyridinecarboxaldehyde (3-CHOpy), and 4-pyridinecarboxaldehyde (4-CHOpy) (Fulka A.G.) are chemical grade and used without further purification. Pyridine (py) (RPE, Carlo ERBA) has been dried on KOH and distilled according to the usual method.

Attempts to prepare complexes of iron phthalocyanine with ligands such as 2-methylpyridine, 2,4- and 2,6-dimethylpyridine, 2-chloropyridine, 2,6-dichloropyridine, and 2-cyanopyridine by direct reaction of the ligand on $Fe^{II}Pc$ were unsuccessful though such reactions have been reported by authors.[12]

The compounds have been identified by IR, visible, and Mössbauer spectra and elemental analysis from which the figures for FePc(3-Mepy)$_2$ are given here as a sample test. Anal. Calcd: C, 70.05; N, 18.56; Fe, 7.42. Found: C, 70.16; N, 18.09; Fe, 7.22.

Results

Optical Spectra. The optical absorptions of the different compounds $FePcL_2$ (complexes of FePc with ligands L) have been obtained from chloroform solutions containing an excess of the ligand for compounds **2**–**7**, **10**, **12**, **15**, and **16** and from Me_2SO (dimethyl sulfoxide) solutions containing an excess of the ligand for **1**, **8**, **9**, **11**, **13**, and **14**. Changing the solvent does not affect the frequencies of maximum absorption[7] though the relative intensities of the bands vary. When solutions with no excess ligand are used, we observe a fast modification of the spectra (Figure 1). A shoulder appears at ~690 nm, and its intensity increases with the time while the intensity of the main band at ~650 nm decreases. An equilibrium between FePcL and $FePcL_2$ species during the reaction of FePc with pyridine was postulated, and the band at ~690 nm has been attributed to the 1:1 complex. The band at ~650 nm attributed to the 2:1 complex is obtained only when pyridine is in large excess in the solution.[15] This was confirmed for all complexes in the series as excess ligand keeps the solutions stable for several days while **13** and **14** are degraded after a few hours even with excess pyridinecarboxaldehyde.

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Table I. Visible Spectral Data for $Fe^{II}Pc$ and $FePcL_2$ Complexes

no.	compd	pK_a	$\lambda_{\pi\rightarrow\pi}$[a]	λ_{sh}	λ_{sh}	$\lambda_{Fe\rightarrow L}$	$\lambda_{L\rightarrow Pc}$
	$Fe^{II}Pc$		655		595		
1	$FePc(pip)_2$	11.20[b]	663	642	602		434
2	$FePc(Im)_2$	6.65[c]	663	640	602		430
3	$FePc(py)_2$	5.29[d]	655	630	595		415
4	$FePc(3\text{-}Mepy)_2$	5.68[d]	655	630	595		415
5	$FePc(4\text{-}Mepy)_2$	6.00[d]	656	630	595		412.5
6	$FePc(3,4\text{-}Me_2py)_2$	6.46[d]	656	630	595		412.5
7	$FePc(3,5\text{-}Me_2py)_2$	6.15[d]	656	630	595		415
8	$FePc(3\text{-}OHpy)_2$	5.10[d]	656	630	595		412
9	$FePc(4\text{-}OHpy)_2$	11.12[d]	662	635	602		432
10	$FePc(3\text{-}Cl\text{-}py)_2$	2.84[d]	653	627	592	446	407
11	$FePc(4\text{-}Cl\text{-}py)_2$	3.84[d]	680	642	613		555
12	$FePc(3,5\text{-}Cl_2py)_2$	0.67[e]	650	625	591	465	397
13	$FePc(3\text{-}CHOpy)_2$	3.70[d]	655	630	595		410
14	$FePc(4\text{-}CHOpy)_2$	4.53[d]	654	630	595	520 sh	410
15	$FePc(3\text{-}CNpy)_2$	1.39[d]	651	625	591	482	402
16	$FePc(4\text{-}CNpy)_2$	1.90[d]	652.5	625	591	527 sh	405

[a] λ = maximum wavelength of the transition in nm. sh = shoulder. [b] D. D. Perin, "Organic Reagents", Interscience, New York, 1964. [c] A. Albert, *Phys. Methods Heterocycl. Chem.*, 1, 1 (1963). [d] D. D. Perin, "Dissociation Constants of Organic Bases in Aqueous Solutions", Pure Appl. Chem., Suppl., Butterworths, London, 1965. [e] K. Schoefield, "Hetero Aromatic Nitrogen Compounds", Plenum Press, New York, 1967.

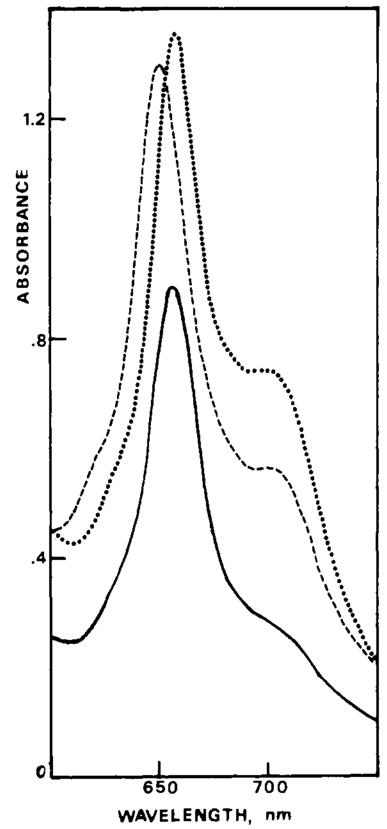

Figure 1. Optical absorption bands of 1:1 and 2:1 species in the visible region: **3** (—), **9** (···), **12** (- - -).

Wavelengths in nm of the maximum visible absorptions are reported in Table I. Typical spectra are presented in Figures 2 and 3. The trend of variation of absorption maxima around 650 nm separates the series into two groups. In group I (compounds **1–9** and **11**) where the axial ligands are Im, pip, py, and pyridine with donor substitutents, the main band moves up from the $Fe^{II}Pc$ wavelength while in group II (compounds **10** and **12–16**) with electron-withdrawing substituents resting on axial pyridine positions, the main band moves down. One or two bands with no equivalence in the spectrum of $Fe^{II}Pc$ appear in the 400–590-nm range in the $FePcL_2$ compounds. Group I compounds have one extra band, while group II compounds have two extra bands.

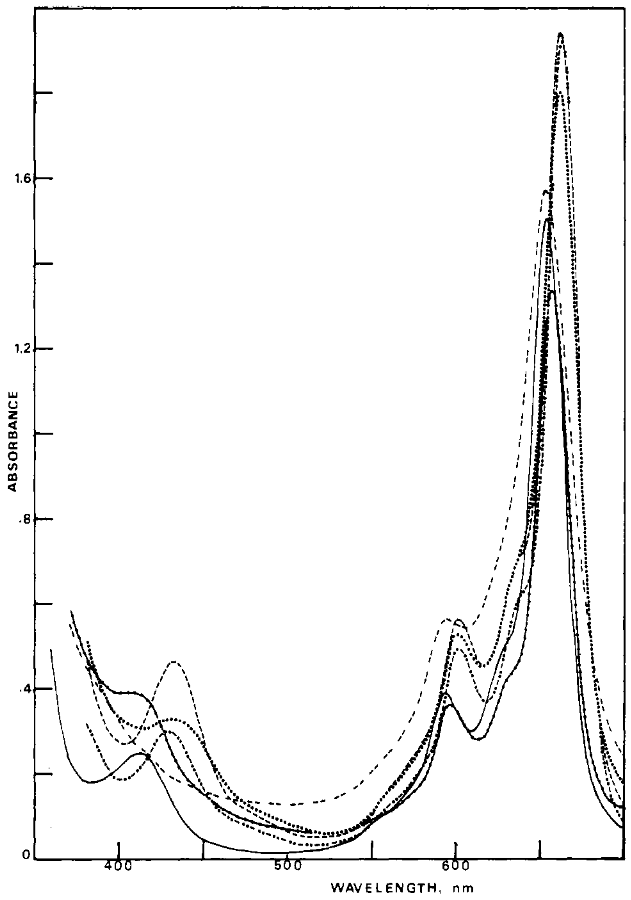

Figure 2. Optical absorption spectra of $Fe^{II}Pc$ and group I compounds in the visible region: $Fe^{II}Pc$ (- - - -), **1** (-··-··), **2** (- - -), **3** (—), **8** (-·-·-·-), **9** (···).

Mössbauer Resonances. The Mössbauer spectra have been recorded at 77 K on powder samples. Table II shows the values of δ and Δ. δ varies very little as reported by Taube,[16] who concludes that the s density is relatively independent of the nature of the bonds on nitrogen in the different axial amines. In $FePcL_2$ complexes, more variation is noticed for Δ values, which lay below the splitting for $Fe^{II}Pc$. This is

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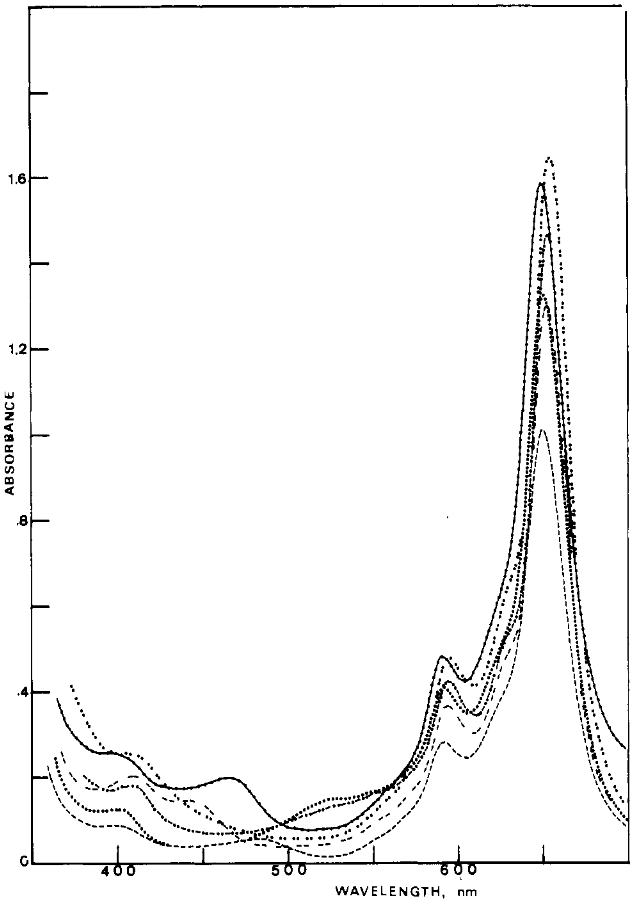

Figure 3. Optical absorption spectra of group II compounds: **10** (-- --), **12** (-•-•-•-), **13** (- - -), **14** (•••), **15** (•• ••), **16** (-••-••).

Table II. ^{57}Fe Mössbauer Parameters for FePcL$_2$ Complexes[a]

compd	δ, mm s^{-1}	Δ, mm s^{-1}
FePc(pip)$_2$	0.364	2.19
FePc(Im)$_2$	0.313	1.74
FePc(py)$_2$	0.322	1.94
FePc(3-Mepy)$_2$	0.321	1.87
FePc(4-Mepy)$_2$	0.347	1.97
FePc(3,4-Me$_2$py)$_2$	0.342	1.98
FePc(3,5-Me$_2$py)$_2$	0.338	1.95
FePc(3-OHpy)$_2$	0.355	1.90
FePc(4-OHpy)$_2$	0.265	1.80
FePc(3-Cl-py)$_2$	0.343	1.91
FePc(4-Cl-py)$_2$	0.389	2.45
FePc(3,5-Cl$_2$py)$_2$	0.360	2.05
FePc(3-CHOpy)$_2$	0.345	1.97
FePc(4-CHOpy)$_2$	0.325	1.84
FePc(3-CNpy)$_2$	0.355	2.17
FePc(4-CNpy)$_2$	0.340	1.90

[a] Isomer shifts are relative to metallic iron. Error limits for the Mössbauer parameters recorded at 77 K are estimated to be ±0.007 mm s^{-1}.

Table III. XPS Parameters of the N 1s, Fe 2p$_{3/2}$, and Fe 3s Levels in Fe^{II}Pc and FePcL$_2$ Complexes[a]

compd	BE (N 1s)[b]	BE (Fe 2p$_{3/2}$)	BE (Fe 3s)
Fe^{II}Pc	399.2	709.1	92.8
FePc(Im)$_2$	398.7	708.0	92.5
FePc(3-Mepy)$_2$	398.6	708.0	92.2
FePc(3-Cl-py)$_2$	398.6	708.1	92.3

[a] From ref 18. [b] BE denotes the binding energy at maximum intensity. All energies are in eV. Accuracy in determining BE values estimated to ±0.1 eV for N 1s and ±0.2 eV for Fe levels.

consistent with a model in which the positive electric field gradient created by the macrocycle is compensated by axial bonding.[16]

Discussion

Nature of the Charge Transfer. The band at ~410 nm has been observed by Dale[7] in the spectra of FePc derivatives with axial nitrogen ligands. By analogy with what is described for the complexes of divalent iron with diimines, dimethylglyoxime (DMG), and 1,2-cyclohexanedione dioxime (niox), this band has been attributed to a charge transfer (CT) as it is not observed in the spectrum of Fe^{II}Pc. Its higher energy is presented as resulting from the fact that in FePcL$_2$ the first CT transition is forbidden ($b_{2g} \rightarrow e_g$ or $e_g \rightarrow e_g$). The study by Dale is very short, with ligands having close properties, and the limited range of variation renders the assignment of the CT band rather uncertainly. However the pressure-modified optical spectra of compounds **1** and **3**–**5** support an electronic transfer from the iron d_π orbitals toward the π^* orbitals of the pyridine and the substituted pyridines.[12]

In our study the properties of the pyridine derivatives are modified by the donor or acceptor substituents on the aromatic ring in a more extended range of variation than in previous studies. Therefore it has been possible to follow the evolution of the band at ~410 nm, and our results suggest that its assignment to a metal-to-axial-ligand CT is erroneous on the following basis: (i) The trend of variation of the wavelength is 4-Cl-py < 4-OHpy < pip < Im < py ~ 3-Mepy ~ 3,5-Me$_2$py < 4-Mepy ~ 3,4-Me$_2$py < 3-OHpy < 3-Cl-py < 4-CHOpy < 3-CNpy < 4-CNpy < 3,5-Cl$_2$py with increasing energy. Most donor ligands have lower transition energies, and conversely, the more acceptor the ligand, the higher the energy. (ii) No π^* orbitals exist in piperidine or NH$_3$,[7] and we see no way of d_π(Fe) → π^*(axial) assignment for the CT band observed in those cases. (iii) Crystallographic results on FeP(4-Mepy)$_2$ show no geometric agreement, which makes probable a back-bonding.[17] On the other hand, a ligand-to-Pc CT is quite feasible either by direct overlap between the equatorial macrocycle π orbitals and those of the axial ligands or through intermediate iron orbitals. Then the observed trend of variation for the wavelengths is justified. This hypothesis is supported by our XPS measurements on the N 1s level of Fe^{II}Pc, FePc(Im)$_2$, FePc(3-Mepy)$_2$, and FePc(3-Cl-py)$_2$ (Table III).[18] A decrease of the N 1s BE (binding energy) characterizes an increase of charge on the nitrogen atom involved in the ionization, and we have observed that the BE (N 1s) values for FePcL$_2$ are below that of Fe^{II}Pc. We have showed moreover that the N 1s peaks of the axial ligand nitrogens are ~1.8 eV from the peak of the Pc ring nitrogens, giving a value of ~400.4 eV for the BE (N 1s) of the axial ligand nitrogens. As for free pyridine, the BE (N 1s) is 338.0 eV;[19] it is clear that the axial ligand nitrogen charge is decreased in FePcL$_2$. The same L → M type CT is shown in other pyridine complexes such as HgCl$_2$(py)$_2$ and *trans*-PtCl$_2$(py)$_2$ by BE (N 1s) measurements.[4] For FePc(4-Mepy)$_2$, IR absorption frequencies at ~300 cm^{-1} attributed to in-plane vibrations of FeN$_4$(Pc) bonds are strongly moved upward from Fe^{II}Pc; this confirms a reinforced d(Fe)–π^*(Pc) bond population in the case of axial donor substituted pyridines.[17]

In Figure 4 the $\lambda_{L\rightarrow Pc}$ (maximum wavelength of the CT band at ~410 nm) of the compounds **5**, **9**, **14**, and **16** have been plotted against the total densities of the Mulliken electronic population on the nitrogen of the free ligand[13] and evaluated by an ab initio calculation, and in Figure 5 $\lambda_{L\rightarrow Pc}$

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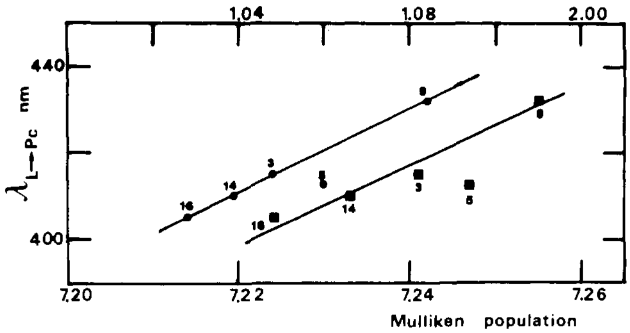

Figure 4. Plot of $\lambda_{L \rightarrow Pc}$ of compounds **5**, **9**, **14**, and **16** vs. Mulliken electronic population densities on the free ligand nitrogen: π densities (●), total densities (■).

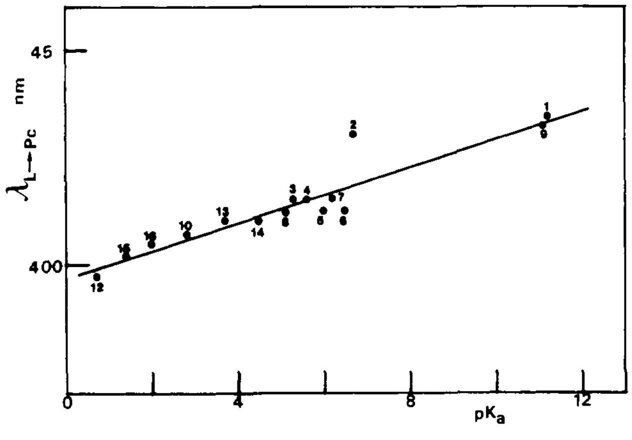

Figure 5. Plot of $\lambda_{L \rightarrow Pc}$ of $FePcL_2$ vs. free ligand pK_a.

of all the studied compounds are plotted against the pK_a of the free ligand. In both cases a good linear correlation is obtained. This confirms that the mechanism governing the L → Pc CT is clearly related to the charge on the ligand nitrogen and shows well that the energy of the CT band decreases as the ligand becomes more donor as a whole.

The Band at 440–530 nm. The group II compounds show a second band between 440 and 530 nm (Figure 3). The maximum wavelength of this band increases in the order 3-Cl-py < 3,5-Cl_2py < 3-CNpy < 4-CHOpy < 4-CNpy. This band is not detected in the spectra of $FePc(py)_2$ or complexes of FePc with the studied donor ligands. To our knowledge, it is the first time that this band is evidenced in the optical spectra of compounds of phthalocyanine. We attribute this band to a CT transition involving a Fe → L transfer (iron-to-axial-ligand charge transfer). The Fe → L CT band moves in the same way as in the case of $Fe(DMG)_2$[20] and $Fe(niox)_2$[21] with ternary ligands identical with those we have studied. The fact that the spectrum of $Fe(DMG)_2(Im)_2$[22] does not show a CT band in the visible region confirms that the band at 430 nm observed in the spectrum of $FePc(Im)_2$ is not attributable to a Fe → Im CT. Moreover the complexes of $Fe(DMG)_2L_2$ or $Fe(niox)_2L_2$ with acceptor ligands such as 3-CNpy, 4-CNpy, 3-CHOpy, or 4-CHOpy have only one CT band in the visible region.[20,21] The last two observations confirm the attribution of L → Pc CT for the band at ~410 nm and Fe → L CT for the second band between 440 and 530 nm for the group II compounds. In Figure 6 we have plotted $\lambda_{L \rightarrow Pc}$ and $\lambda_{Fe \rightarrow L}$ of the two CT bands of the group II compounds and of $FePc(py)_2$ against the excess of charge on the free ligand nitrogen, calculated from NQR measurements.[23] We notice that $FePc(py)_2$ resides at the crossing point of the two correlation lines as a proof of its medium position.

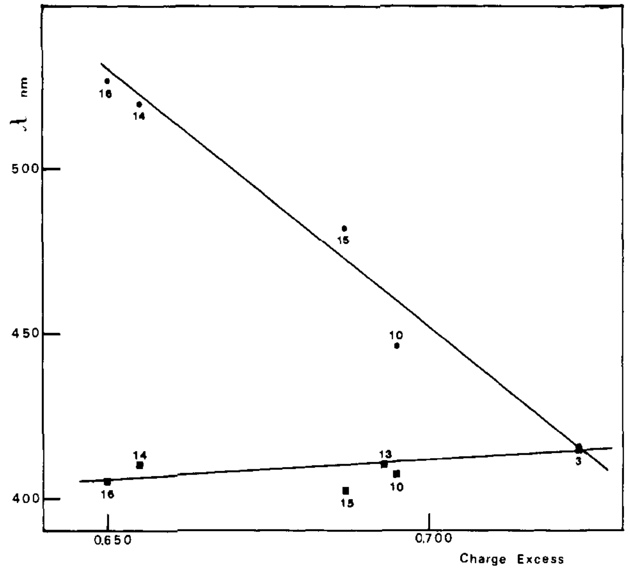

Figure 6. Plot of $\lambda_{L \rightarrow Pc}$ and $\lambda_{Fe \rightarrow L}$ of $FePc(py)_2$ and group II compounds vs. total charge excess on the free ligand nitrogen.

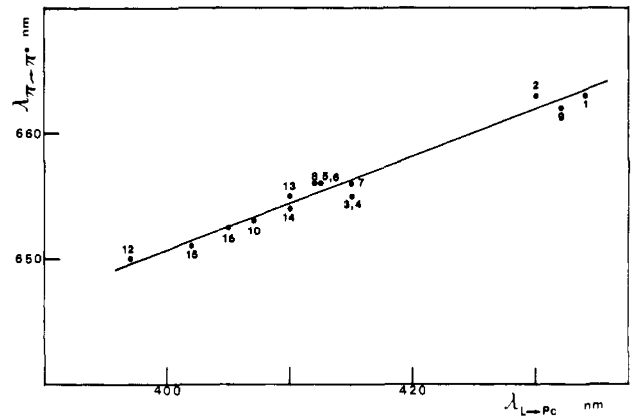

Figure 7. Plot of $\lambda_{\pi \rightarrow \pi^*}$ vs. $\lambda_{L \rightarrow Pc}$.

The Band at 650 nm. The calculations by Försterling and Kuhn[24] show that in the phthalocyanines, the highest occupied π orbital has a_{1u} symmetry and is followed by an a_{2u} orbital (D_{4h} symmetry). The wave function associated with a_{1u} has its maximum density on the pyrrolic carbons C(1), C(2), C(9), C(10), ...[25] A study by photoelectron spectroscopy on gaseous H_2Pc (free phthalocyanine) and MPc (metallophthalocyanines), where M = Mg, Fe, Co, Ni, Co, or Zn, reports that the highest energy occupied orbitals are macrocycle-ligand-like and not metal-3d-like orbitals.[26] These experimental data confirm that two of these orbitals have a_{1u} and a_{2u} symmetry. The a_{1u} orbital is delocalized on the carbons, and the a_{2u} orbital extends partly on the nitrogens.

Therefore the lowest $\pi \rightarrow \pi^*$ transition corresponds to $a_{1u} \rightarrow e_g^*$ and is materialized in the visible spectrum by an intense band at ~650 nm. The e_g^* wavefunctions have their density on the pyrrolic carbons C(3), C(8), C(11), C(16), ... and on the bridge nitrogens N(3), N(4), N(5), and N(6). The $a_{1u} \rightarrow e_g^*$ transition results in a CT from the center of the molecule toward the periphery. It is established that in the MPc there is a π back-donation of electrons from the metal

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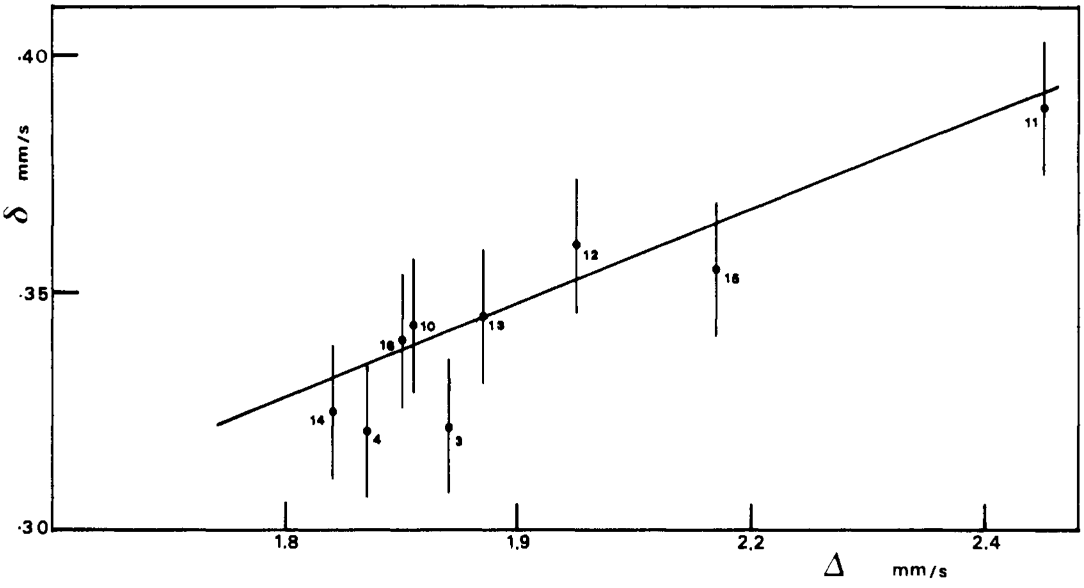

Figure 8. Plot of δ vs. Δ.

d orbitals to the macrocycle ligand π^* orbitals.[17] The $\pi \rightarrow \pi^*$ transition energy is strongly influenced by this π back-donation.[27] The introduction of the axial ligands in FePc leading to a CT L → Pc will modify the π back-donation to the macrocycle, and therefore the $\pi \rightarrow \pi^*$ transition energy will be affected. In Figure 7 the plot of $\lambda_{\pi \rightarrow \pi^*}$ against $\lambda_{L \rightarrow Pc}$ shows clearly this correlation. In the spectra of the complexes with donor ligands, the $\pi \rightarrow \pi^*$ wavelength is raised with increasing donor strength while with acceptor ligands the band moves toward the short wavelengths with increasing acceptor power.

It is interesting to note that the band at ~650 nm for the complexes of FePc with pyridine and pyridine derivatives with methyl groups is almost unchanged relative to that of Fe^{II}Pc, confirming that with these species the so-called donor and acceptor properties tend to cancel out.

Mössbauer Spectrometry. The isomer shift (δ) is a measure of the s density at the iron nucleus. For complexes like those we examine here, the interactions that determine the δ value can be classified as (i) ligand-to-metal donation (from a filled σ or from a filled π ligand orbital) or (ii) metal-to-ligand donation (into unfilled ligand orbitals).[28] In a series of similar compounds one will see smaller values of δ as a consequence of increased 4s population, and interactions that raise the 3d population will result in higher values for δ. A decrease of the 3d population may result from an increased delocalization of charges in more extended molecular orbitals.

The quadrupole splitting ($\Delta = e^2qQ$) denotes in these complexes the different occupation of the 3d orbitals (the contribution of the lattice is neglected). The expression of the field gradient $q = {}^2/_7(2n_{z^2} - 2n_{x^2-y^2} - 2n_{xy} + n_{xz} + n_{yz})(1 - R)\langle r^{-3}\rangle_d$ in which the n terms are the populations of d orbitals. If they contribute to delocalized molecular orbitals, this expression must be corrected by introducing some factors of covalency.

Now, we consider the case of FePc, and we suppose in first approximation that the local symmetry around the iron is D_{4h}. The valence orbitals of the iron have the symmetry a_{1g} (4s, $3d_{z^2}$), e_u ($4p_x$, $4p_y$), b_{1g} ($3d_{x^2-y^2}$), e_g ($3d_{xz}$, $3d_{yz}$), b_{2g} ($3d_{xy}$), a_{2u} ($4p_z$), while the orbitals of the equatorial ligand span the representations a_{1g}, e_u, b_{1g}, e_g, a_{2u}, and b_{2u} (notice that d_{xy} is nonbonding). Taube[16] shows that a strong d_π–p_π interaction exists between Fe and Pc through the e_g orbitals, which transmit every modification of charge. On this basis a value of $\Delta = 1.9$ mm s^{-1} (found 2.67 mm s^{-1}) has been calculated for the commonly adopted configuration $(xy)^2(xz, yz)^3(z^2)^1$.[29] This is a rough approximation as d_{xz} and d_{yz} are involved in equatorial π bonding and are delocalized (Δ's should be greater than observed).

The introduction of axial ligands modifies this configuration, because a pyridine (or substituted pyridine) cannot have an order of symmetry higher than 2 and bind axially with an a_{1g} type orbital. The π type bonds will be made by the orbitals of e_g type, and the two ligands are generally assumed to be in a perpendicular position. This is confirmed by X-ray data for FePc(4-Mepy)$_2$[17] and by Mössbauer data ($\eta = 0$) for FePc(py)$_2$.[30] Assuming that the D_{4h} symmetry is locally conserved around the iron, Dale et al.[8] have given an analysis of δ and Δ, which shows the following: (i) δ would be expected to decrease both with increasing σ-donor power and with increasing π-acceptor power of the axial ligands. (ii) Δ would be expected to decrease with increasing σ-donor power but to increase with increasing π-acceptor power of the axial ligands. Then, linear correlations between δ and Δ would only be expected for idealized ligands, those that can be considered to be either pure σ donors or pure π acceptors. In spite of the linear correlation between δ and Δ given by Dale et al.,[8] great discrepancies exist in the order of the various complexes on the plots either with "σ-donor power" or with "π-acceptor power" of the ligands.

Our results show at first that an attempt to correlate δ and Δ for all the studied compounds left the representative points grouped around an average value. Moreover if we examine in particular the ligands for which the "π-acceptor" character (group II) is already evidenced in the discussion of optical results, a linear correlation (Figure 8) is observed. In this series, we observe that Δ increases with the "π-acceptor" power. This confirms our proposal to attribute the absorption bands between 440 and 530 nm to Fe → L CT. The approximately linear plot of δ against Δ has a positive slope. This indicates that even in group II ligands the "σ-donor" power is still the major factor and δ and Δ decrease together when the "σ-donor" power of the ligand increases. This fact would

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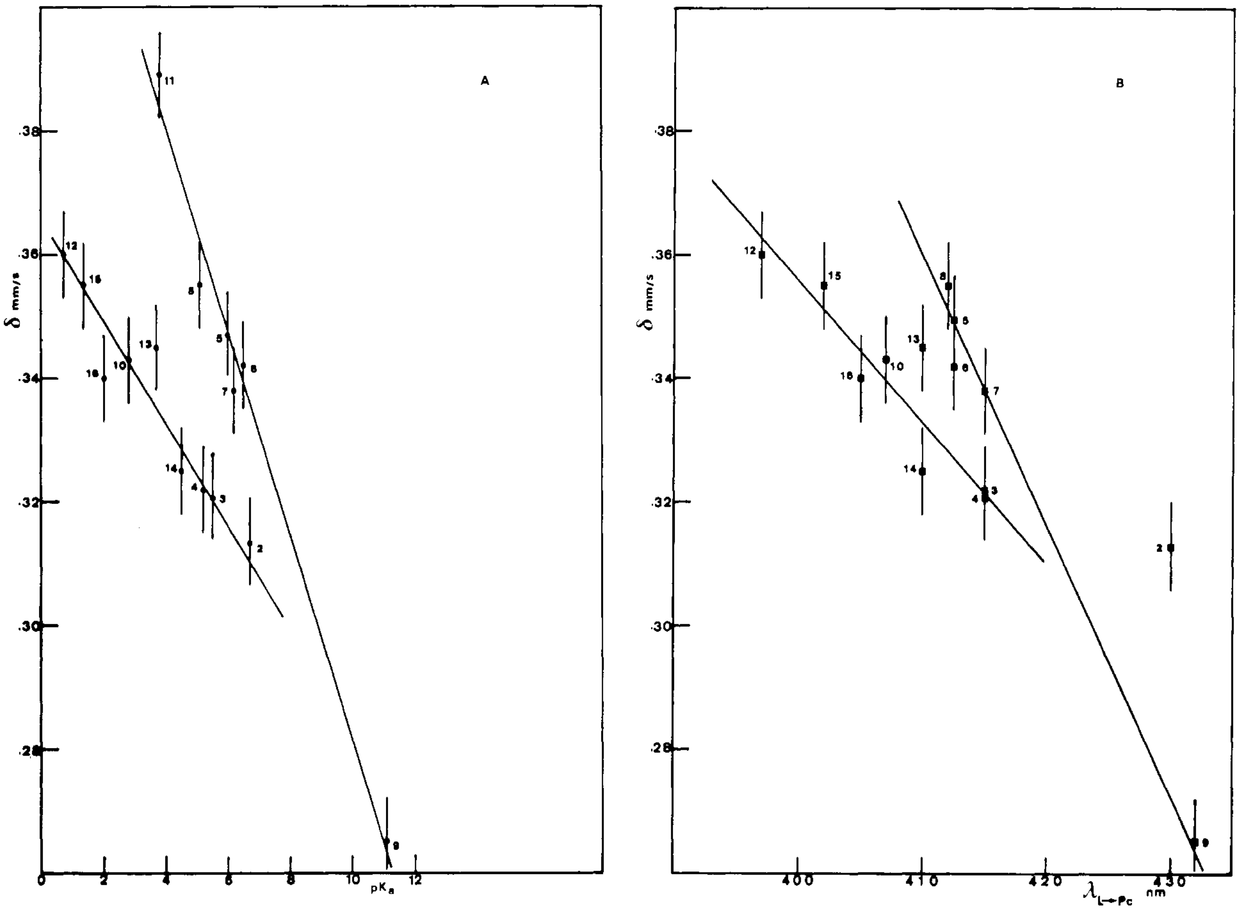

Figure 9. Plot of δ vs. (A) free ligand pK_a (●) and (B) $\lambda_{L\rightarrow Pc}$ (■).

be unexpected for complexes with strong "π-acceptor" ligands such as CO or NO directly bound to the metal, but no parallel is possible as no values are known for FePc(CO)$_2$ or FePc(NO)$_2$.

The δ values plotted against the pK_a of the axial base (Figure 9A) and against the $\lambda_{L\rightarrow Pc}$ (Figure 9B) are separated into two families (the two groups previously determined). Compounds **3** and **4** are classified with the group II complexes, confirming therefore the medium position attributed to FePc(py)$_2$ (Figure 6) and showing that almost no change in "π-acceptor" properties results from the substitution of 3-H by a methyl on the pyridine. The two groups are represented by lines with negative slopes, showing that δ decreases with increasing pK_a values, then with increasing σ donating power of the ligands. In each group the order of the plots agrees with our incremental series of substituents and Taube's results on the reduced species.[16] Moreover these correlations show that the "π-acceptor" character, though not being the major property of the ligands, is clearly reflected in the δ variation.

Donor-substituted pyridines induce lower Δ's than is the case for FePc(py)$_2$, while higher Δ's are induced by electron-withdrawing groups. Contrary effects are reported in the Fe(niox)$_2$L$_2$ series of complexes.[8]

The higher Δ value of FePcL$_2$ has been tentatively interpreted in comparison both with the much lower Δ values of homologous porphyrin complexes[31] and with what is expected for low-spin iron(II) complexes.[32] We summarize some of the contradictory statements on this question: (i) Hudson and Whitfield[32] have based their arguments for large Δ's on anisotropic covalent bonds from spliced d_{xz} and d_{yz} orbitals to differentiated axial pyridines, and data from hemoglobins bonded to dioxygen (one π bond, Δ = 2.2 mm s^{-1}) and carbon monoxide (two π bonds, Δ = 0.36 mm s^{-1}) support their view. They propose the π delocalization to axial ligands as the major factor of the EFG at the Fe nucleus. (ii) Conversely the Δ value of FePc(py)$_2$, higher than those of several porphyrin homologues,[31] was attributed to a larger σ overlap from Pc in the $d_{x^2-y^2}$ orbital. (iii) The electron-withdrawing power of peripheral groups fixed on heme has been put forward by Moss and Robinson[33] to justify large values of Δ resulting from larger in-plane delocalization. This assumption can explain the Δ values of 1.94 and 0.68 mm s^{-1}, respectively, for FePc(py)$_2$ and FeOTBP(py)$_2$ (OTBP is octamethyltetrabenzporphyrin),[31] since these two complexes differ mainly in the nature of the bridges in the cycle. At this point it is worth noticing that Pc complexes may have quite a different behavior as "aza" bridges will interfere in the bonding system. For instance, the d_{xy} (b_{2g}), which is 96% pure metallic in porphyrins, combines with the b_{2g} (N p_σ) of the bridge nitrogens to give a pair of split (b_{2g} – b_{2g}*) MO's.[34]

Our results are consistent with a model of bonding in which the Pc ring appears to be different from porphyrin ligands. The EFG at the Fe nucleus originates mainly from in-plane delocalization. This is supported (i) by XPS measurements, which show permanent electron transfers from axial to macrocycle nitrogens, (ii) by the presence of a L → Pc CT band throughout the whole FePcL$_2$ series due to in-plane delocalization from the center of the periphery, and (iii) by the trend of variation of Δ values as it decreases with the increasing donor power of the ligand (compounds **2**, **4**, **8**, and **9**) or as

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it increases when the σ-donor power is modified by electron-withdrawing groups (compounds **12**, **13**, and **15**).

Though the delocalization on the macrocycle can be a possible explanation of the high Δ value of FePcL$_2$ compared with the parameters of porphyrin homologues, it cannot account for its detailed variation along the series. The position of the substituent on the pyridine ring determines mainly the σ and π properties of the ligand;[13,23] this would explain the differences observed between complexes with meta- and para-substituted pyridines. We single out the Δ values of the species FePcXCO (X = piperidine, dimethylformamide, tetrahydrofuran, methanol, dimethyl sulfoxide, tetrahydrothiophene, or H$_2$O), which are lower than those of FePcX$_2$.[35] In that case, the authors assume that the reduction of d_{xz} and d_{yz} electron population by π bonding to CO is overcompensated by the strong σ component along the z axis, which increases the d_{z^2} population. This must be related to the Δ value of 0.51 mm s^{-1} for K$_2$FePc(CN)$_2$.[8] This shows that the question of the precise origin of Δ is still open; no absolute model is proposed, but our results give an example of useful comparisons of data along homogeneous families of compounds. No crystal structure exists for most of the examined complexes, but we assume a strictly constant geometry about iron when L varies. Changes in η values arising from distortions in the Fe–L region would not account for the changes in Δ, which are reasonably related to variations in π-overlap populations.

Conclusion

Our results concur to reveal that if the complexes of phthalocyanine, particularly FePc, can be taken as analogues of complexes of porphyrins or dimethylglyoxime in view of their planar and rigid structure, they are different enough to forbid hasty generalization of their properties.

We have shown the following: (i) The CT at ~410 nm is a L → Pc CT, and a Fe → L CT appears in the spectrum of FePcL$_2$ only when L has enough evident acceptor properties, as shown by correlation with pK_a values and electron population values. (ii) δ is almost constant along the series of studied compounds while Δ varies. δ values appear to be differently correlated with pK_as and CT optical absorptions for compounds with electron-withdrawing substituted pyridines and for complexes with donor substituents. No marked correlation is observed between δ and Δ for all the compounds. (iii) The high Δ value of FePcL$_2$ may be related to the L → Pc CT. More effective equatorial π type delocalization in the case of Pc complexes than for any other tetrapyrrolic macrocycle appears to be the main factor for EFG.

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Temperature Dependence of ^{63}Cu and ^{14}N Nuclear Quadrupole Resonance Frequencies in Potassium Dicyanocuprate(I)

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^{63}Cu and ^{14}N nuclear quadrupole resonance frequencies were measured as functions of temperature between 77 and 300 K for potassium dicyanocuprate(I), KCu(CN)$_2$. Four ^{14}N resonance frequencies at 3.1382, 2.9658, 2.5253, and 2.3947 MHz were observed at 77 K. These four resonance frequencies were assigned on the basis of the Zeeman effect on a powdered specimen. These four nitrogen lines showed normal temperature dependence, whereas the ^{63}Cu resonance frequency showed a large, positive temperature dependence. These experimental results were interpreted in terms of the vibrational effect on d–π^* bonds between Cu atom and C atoms. Electron distribution over various bond and lone-pair orbitals is discussed.

Introduction

Potassium dicyanocuprate(I), KCu(CN)$_2$, crystallizes in a monoclinic system with a space group $P2_1/c$ (C_{2h}^5), and its unit cell contains four formula units.[1] The complex anions form spiral polymer chains composed of [Cu(CN)$_2^-$]$_\infty$, in which a slightly distorted trigonal coordination of copper is recognized as shown in Figure 1. Each Cu atom forms three coordination bonds with two carbon atoms from two different cyanide ions (cyanide 1 and cyanide 2) and one nitrogen atom from another cyanide 2. This structure is entirely different from those of analogous silver and gold complexes, in which discrete linear 2-fold coordination has been found.

Krüger and Meyer-Berkhout[2] reported in 1952 that there is only one ^{63}Cu nuclear quadrupole resonance (NQR) line in polycrystalline KCu(CN)$_2$ and that the frequency is much higher at 300 K than at about 100 K. They ascribed the unusual, positive temperature coefficient to elongation of the bond in a discrete [NC–Cu–CN]$^-$ complex, which they assumed forms the anion. The crystal structure determined later did not substantiate their model.

McKown and Graybeal determined the directions of the principal axes of the electric field gradient (EFG) tensor and the asymmetry parameter at the Cu nucleus by a Zeeman study of the NQR.[3] They attempted to explain their experimental results on the basis of sp^2-hybrid σ bonds and d–π^* bonding between copper and ligands but did not explain the positive temperature coefficient of the ^{63}Cu resonance frequency.[6]

The present paper presents the experimental results of ^{63}Cu and ^{14}N NQR frequency measurements as functions of temperature. The ^{14}N data would not only supplement the ^{63}Cu

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