Studies on the binding of nitrogenous bases to protoporphyrin IX iron(II) in aqueous solution at high pH values
Part II. Aliphatic nitrogen ligands

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Abstract

The first complimentary studies using Mossbauer spectroscopy and ligand titrations on protoporphyrin IX iron(II) with a series of aliphatic nitrogenous ligands are reported. Binding constants have been determined by titration of the metal complex with these ligands. The adduct formation was monitored through optical spectroscopy. Parallel Mossbauer spectroscopic experiments were conducted to monitor the electronic environment around the central iron atom in these adducts. Both spectroscopic methods indicated that all the aliphatic nitrogen bases yielded low spin octahedral complexes. The magnitude of the overall binding constants (log β_2 values which varied from 1.7 for ethanolamine to 4.26 for n-octylamine) are discussed and related to (i) the pK_a values of the free ligands and (ii) to the quadrupole splitting, ΔE_Q, of the haem iron. The aliphatic nitrogenous ligands studied here exhibited cooperative binding (except ethanolamine) with Hill coefficients close to 2 for protoporphyrin IX iron(II), but with significantly lower (~1000-fold) affinity than pyridine and imidazole ligands (which we have studied previously). However, these aliphatic and aromatic ligands displayed comparable ΔE_Q values (~1.00 to 1.20 mm s^{-1}). The β_2 and ΔE_Q values are also discussed in terms of the structure of the ligand.

Introduction

We have reported studies on the binding of pyridine, substituted pyridines and imidazole to protoporphyrin IX iron(II) in aqueous solution [1]. In the introduction to that paper we summarised the known literature and we refer the reader to it. In particular, attention was drawn to the manner in which the immediate environment of the iron was influenced by electron delocalisation on the macrocycles and the nature and size of the axial ligands in the iron porphyrin complexes [1]. Here we extend our earlier studies and report the preparation and characterisation of a number of low spin protoporphyrin IX iron(II) (PPIXFe(II)) complexes with a variety of aliphatic nitrogenous and related ligands. This work is part of a continuing programme to understand why histidine ligation to haem is so widespread in natural systems. The current investigation was aimed at examining σ and π bonding between the axial ligands and iron and in the iron porphyrin plane, as well as steric effects in the bonding of axial ligands. PPIX was the porphyrin selected for this study as it is the most widespread found in natural proteins. From the work of others [2, 3] and our own data [4–8] it appears that different porphyrins contribute different amounts of electron density to the iron centre depending on the nature and number of substituent groups on the periphery of the porphyrins. The main drawbacks to this approach have been pointed out [1].

Results and discussion

In all, ten aliphatic amine ligands were studied. Their structures and electronic absorption spectra of their PPIXFe(II) complexes in the visible region are presented in Table 1.

Visible spectra

In the known iron(II) porphyrins crystal structures the porphyrin ring is effectively planar and it has D_{4h} symmetry. Iron(II) porphyrins in the $S=0$ case have hypso spectra [9]. The spectral

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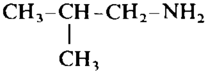
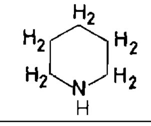
TABLE 1 The electronic absorption spectra of the complexes PPIXFe(II)(L_2) or (L), (where L = nitrogenous ligands) at pH 12, λ_{max} show Soret, β and α bands

Nitrogenous ligands	Structure	Band maxima		
		Soret band (nm)	β band (nm)	α band (nm)
1 Methylamine	CH_3NH_2	421	526	556
2 Ethylamine	$CH_3CH_2NH_2$	420	526	555
3 Diethylamine	$(CH_3CH_2)_2NH$	418	526	555
4 Ethanolamine	$OHCH_2CH_2NH_2$	421	525	555
5 1,2-Diamino-ethane	$NH_2{-}CH_2{-}CH_2{-}NH_2$	421	526	556
6 n-Propylamine	$CH_3(CH_2)_2{-}NH_2$	421	525	556
7 n-Butylamine	$CH_3(CH_2)_3{-}NH_2$	420	526	556
8 *sec*-Butylamine	 $CH_3{-}\underset{\substack{\vert\\CH_3}}{CH}{-}CH_2{-}NH_2$	420	525	555
9 n-Octylamine	$CH_3(CH_2)_7{-}NH_2$	420	526	556
10 Piperidine		421	528	557

bands in the visible region result from π–π* transitions on the porphyrin We have discussed their origin and shown typical spectra [1] The spectra reported here (Table 1) are similar in appearance to those and so additional figures are not necessary

It has been observed in this work (Table 1) and by others [10] that the position of the Soret band in porphyrin Fe(II) complexes, coordinated to aliphatic ligands, is unaffected or shifts slightly to longer wavelengths With unsaturated ligands (π-bonded systems) the Soret band moves to shorter wavelengths [1] The explanation of this movement of the Soret band is that as the π-electron density of the metal t_{2g} orbitals moves towards the periphery of the planar porphyrin nucleus, absorption occurs at longer wavelength Thus as the electron density donated to the iron by the saturated ligands is accumulated in the z direction, this will have only a slight effect on the spectrum [11] and will not affect the π electrons of the porphyrin nitrogen atoms in the xy plane However, when unsaturated ligands bind to the iron, the metal t_{2g} orbitals (d_{yz}, d_{xz}) are involved in π bonding to them This leads to a decrease in the overlap of metal t_{2g} orbitals with the π orbitals of the porphyrin ring (via the porphyrin N atoms) and results in the shift of the Soret band to shorter wavelength [1, 9, 10, 12]

We have established that some of the unsaturated ligand complexes have spectra where the Soret band appears at longer wavelength, viz substituted imidazoles [1] We suggested for imidazole that the reason is that it has better σ-donating abilities than the other aromatic ligands In addition, imidazole ligands are able to approach the iron closer than six-membered rings as they experience less steric hindrance [1]

Spectrophotometric titrations

We previously presented a typical spectrophotometric titration of PPIXFe(II) (reduced by dithionite and in the presence of dithionite) with imidazole [1] The ligands reported here behaved similarly and isosbestic points were observed in all cases in the visible region For ethanolamine the Soret band had no isosbestic on the shorter wavelength side This will be discussed below At very high ligand concentrations (for instance for *sec*-butylamine ~ 1 M) a second process was observed which is unrelated to ligand binding This process appears to be due to changes in the physical properties of the aqueous phase as the ligand concentration becomes very high A process of this type was not encountered in our earlier work [1] as the binding constants reported there were much higher and lower ligand concentrations were thus required For the weaker binding ligands reported here this second process is found when the log β_2 values are less than ~3 0 (Table 2) This second process can be distinguished from the binding of ligand to the central iron atom by comparison of the visible and Soret regions of the titration spectra For example, the formation of the α and β bands characteristic of low spin ferrous porphyrin (Table 1) occurs only in the first process at relatively low ligand concentrations The second process induces little change in these bands which are fully formed at the lower ligand concentration whilst enhancing and sharpening the Soret band The equilibrium constants for the PPIXFe(II) moiety with these nitrogenous

TABLE 2 Hill coefficient, ligand concentration at 50% saturation, stability constant of the haemochromes and the pK_a of free nitrogenous ligand involved

Nitrogenous ligands	Hill coefficient h	50% Saturation (M)	Stability constant $\log \beta_2$ (M^{-2})	pK_a[a]
1 Methylamine	2.0(2)	0.035(3)	2.9(1)	10.68
2 Ethylamine	2.0(2)	0.035(3)	2.9(1)	10.79(2)
3 Diethylamine	1.6(2)	0.090(5)	2.09(5)	10.05
4 Ethanolamine	1.2(1)	0.140(5)	1.71(3)	9.5
5 1,2-Diamino-ethane	2.0(1)	0.020(2)	3.4(1)	10.03[b]
6 n-Propylamine	1.6(2)	0.050(4)	2.6(1)	10.74(3)
7 n-Butylamine	2.0(1)	0.020(2)	3.4(1)	10.71
8 *sec*-Butylamine	2.0(2)	0.110(5)	1.90(5)	
9 n-Octylamine	1.5(1)	$7.2(3) \times 10^{-3}$	4.26(6)	10.66[b]
10 Piperidine	2.5(1)	0.021(2)	3.36(8)	11.07

[a]These data are taken from ref. 13. These are 20 °C data or as near to 20 °C as possible. The μ values are 0 or as near 0 as available, in keeping with a μ value of 0 used in this work. [b]This compound has two pK_a values (7.22 and 10.03), the higher of which is taken to be the appropriate one for experiments at pH 12 (see Fig. 3). In our experiments we are never dealing with the doubly protonated species.

ligands, along with their Hill coefficients (h), the ligand concentration at 50% saturation, and the pK_as of the free ligand involved are given in Table 2.

The Hill coefficients (h) were found from Hill plots of the type illustrated in Fig. 1 and took values between 1 and 2.5. Apart from ethanolamine all the titrations exhibit a strongly sigmoidal binding curve indicating Hill coefficients significantly in excess of unity. Precise values of h are critically dependent on accurate determination of the end point of the titration. Where a second process obscures the endpoint at high ligand concentration, the confidence in the reported value is diminished. Values of h close to unity indicate independent binding of ligands in a stepwise manner. Ethanolamine was the only ligand found for which h took a value close to unity and thus the PPIXFe(II) binds this ligand in a stepwise manner. Confirmation of this was seen in the fact that there is no isosbestic on the shorter wavelength side of the Soret band. Values of h greater than unity indicate cooperative binding of the ligands. Thus, for a system in which two ligands may bind to a central iron atom a value for h of 2 is indicative that the ligands bind in such a fashion that, throughout the titration, no complex with a single ligand bound exists. The value of h cannot exceed the number of incoming ligand molecules. Therefore values of h greater than 2 indicate cooperative binding of ligands not only to the 2 coordination positions of the iron but also to either the porphyrin ring [14–16] or, through hydrogen bonding, to already bound ligands (i.e. ligand self association [17]). The enhanced value of h for piperidine is surprising. Obviously, it cannot be explained using either of the preceding mechanisms. Recently we suggested that the propionate carboxylate group of the porphyrin and a NH_2 group of histidine might interact via an N–H···O hydrogen bond [18]. Such a bond could also form to piperidine and would explain the enhanced h value. It would also be in keeping with the high pK_a of piperidine (see Table 2). Hill coefficients can also be affected by the nature of the solvent as illustrated by the effect of water (as a polar solvent) upon the equilibrium constant, and h values found by McLees and Caughey [19] for complexes of Ni porphyrin with piperidine. It appears that polar solvents may participate via solute–solvent interactions lowering the apparent value of h [19].

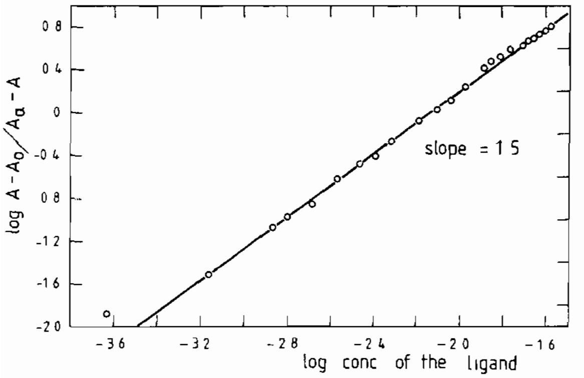


Fig. 1 Hill plot for the titration of PPIXFe(II) with n-octylamine

The results we obtained for the $\log \beta_2$ values in Table 2 are all lower than those for the analogous iron(II) porphyrin complexes (with, for example, imidazole and pyridine) in organic solvents. We have discussed the reasons for this [1]. We have previously studied PPIXFe(II) solutions in the pH range 7–14 [5] and established that three species predominate, a four-coordinate aggregated species which is present over the entire range and two monomers which are present at higher pH values

The presence of the polymer in polar solvents will certainly depress the β_2 values However, Mossbauer data [5, 7] indicate that the proportion of this aggregated species decreases rapidly with porphyrin concentration Recently we showed that the PPIXFe(II) monomer (four-coordinate, no axial ligands) can exist in cetyltrimethylammonium bromide frozen solutions [8] The Mossbauer data for such monomers [8] are similar to those for 5 mg of PPIXFe(II) in 3 ml reported previously [7b] by us as the 'polymer' site Clearly at concentrations around 3 × 10^{-3} M or less, most (or all) of the PPIXFe(II) is present as monomers at pH 12 0 Under the condition of our titration experiments, therefore, ~10 μM porphyrin, the large majority of the porphyrin Fe(II) is in the monomeric form A third effect that has been suggested to depress the value of K_{eq} is the presence in aqueous solution of OH^- and H_2O moieties which themselves will bind [5, 6, 20] to PPIXFe(II) (yet another solute–solvent interaction) We have found that the two monomeric PPIXFe(II) species at high pH contain OH^- and H_2O ligands [5, 6, 8]

Mossbauer spectroscopy

To aid in the understanding of the electronic environments around Fe(II) centres, and how these are affected by the binding of ligands, Mossbauer spectra were collected on frozen solutions at 78 K The spectra all consisted of sharp doublets and the parameters are presented in Table 3 A representative spectrum is shown in Fig 2 The range found for the isomer shifts for the purely σ-bonding ligands is 0 45–0 52 mm s^{-1}, and that for the quadrupole splittings (ΔE_Q) was 1 03–1 15 mm s^{-1} (except for piperidine, 1 4 mm s^{-1}) In comparison the isomer shift range for the unsaturated ligands which was 0 45–0 48 mm s^{-1} and the quadrupole splitting ΔE_Q range was 0 94–1 23 mm s^{-1} [1] These values agree well with previously reported data [21]

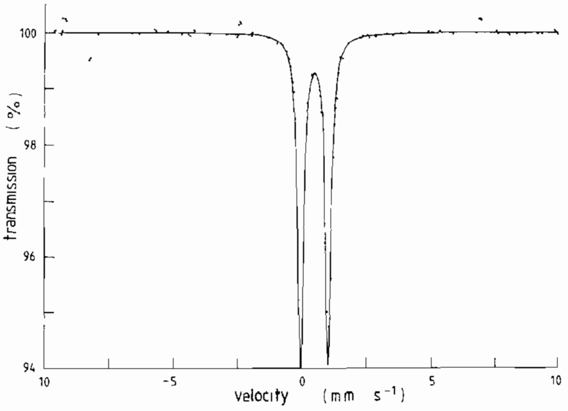


Fig 2 The ^{57}Fe Mossbauer spectrum of a frozen aqueous solution of PPIXFe(II)(n-propylamine)$_2$

It can be observed both in this work and that reported previously [1, 21] that there is little difference in the isomer shifts of these complexes, all values are similar with a slight trend to smaller values for the imidazole rings and larger for piperidine However, significant changes are observed in the ΔE_Q values For example, for the five-membered unsaturated ring (imidazole) a small ΔE_Q value is observed, whereas for the aliphatic six-membered ring (piperidine) a larger value is observed, and the six-membered unsaturated rings lie in between these extremes [1]

Only two of the known low spin ferrous porphyrin structures are five-coordinate [22, 23], all the rest are hexacoordinate and for these in every case where magnetic perturbation measurements have been made, V_{zz} is positive and the asymmetry parameter, η, is nearly or exactly zero It is accepted that the major contribution to V_{zz} in these diamagnetic complexes arises from an imbalance in electron densities in the iron $d_{x^2-y^2}$ and d_{z^2} orbitals, and the positive signs observed show that the covalent bonding to the planar porphyrin

TABLE 3 ^{57}Fe Mossbauer spectra parameters for the haemochrome frozen solution at 78 K

Nitrogenous ligand	δ (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ (mm s^{-1})^a
1 Methylamine	0 47(1)	1 08(1)	0 17(1)
2 Ethylamine	0 47(3)	1 09(1)	0 17(1)
3 Diethylamine	0 45(2)	1 07(1)	0 18(1)
4 Ethanolamine	0 47(1)	1 09(1)	0 18(1)
5 1,2-Diamino-ethane	0 52(1)	1 15(1)	0 15(1)
6 n-Propylamine	0 49(1)	1 09(1)	0 22(1)
7 n-Butylamine	0 48(1)	1 03(1)	0 17(1)
8 *sec*-Butylamine	0 48(1)	1 09(1)	0 13(1)
9 n-Octylamine	0 48(2)	1 09(1)	0 13(2)
10 Piperidine	0 52(1)	1 40(2)	0 16(1)

^{a}Half width at half height

is stronger than that to the axial ligands [24, 25] We have discussed the orbital population in relation to the bonding and geometry [1]

As stated, the aliphatic ligands generate ΔE_Qs in the range 1 03–1 15 mm s^{-1}, and bond with iron via an sp^3 hybrid orbital in a σ bond The fact that this ΔE_Q range is small and the absolute magnitude is less than that for cyclic aliphatic compounds (e g piperidine) can be interpreted to indicate that these ligands show no evidence of steric repulsions with PPIXFe(II) Evidence in support of this comes from [Fe(OEP)(NH$_3$)$_2$] where the measured ΔE_Q (1 10 mm s^{-1}, at 115 K) [26], is similar to those of the aliphatic ligands reported here Ammonia cannot be said to cause steric repulsion

Collman *et al* [27] have determined the structure of [Fe(II)TPP(pip)$_2$] and found that the axial Fe–N bonds to the piperidine nitrogen atoms are stretched to a length of 2 127 Å as a consequence of the severe steric interactions between piperidine hydrogen and porphyrin nitrogen atoms The value of 1 40(2) mm s^{-1} for the ΔE_Q for [Fe(II)PPIX(pip)$_2$] would be in keeping with a σ bond weakened by such steric effects This compound has been studied previously [3, 28] However, our data are obtained from frozen solution and are included to contrast to the other aliphatic nitrogen ligands which have not been studied in depth previously

Conclusions

The visible spectra of these PPIXFe(II)L$_2$ complexes have been characterised and provide insight into the electron density distribution of the σ bonding in the z direction Low spin octahedral complexes are indicated in all cases

The general conclusions that may be drawn from the data presented above are best appreciated by examination of Figs 3 and 4 In these the overall binding constant, β_2 is related either to a property of the free ligand, here the pK_a value (Fig 3), or to a property of the iron in the haem, here the quadrupole splitting, ΔE_Q (Fig 4)

In Fig 3 the aliphatic compounds studied are all in one group, included for comparison in this Figure are the pyridines Where steric constraints do not greatly hinder binding, we note the trend within each group is that the higher the pK_a of the amine the higher is the binding constant In other words increasing the affinity of a compound for protons increases its affinity for iron, presumably because each bears a positive charge

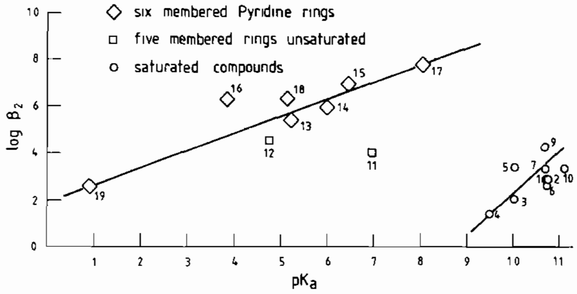


Fig 3 A plot of log β_2 values against the pK_a values of the free ligands The numbers refer to compounds listed in Tables 1 and 2 11 = imidazole, 12 = 5 chloro-1-methylimidazole, 13 = pyridine, 14 = 4-methylpyridine, 15 = 3,4-dimethylpyridine, 16 = 4-chloropyridine, 17 = 3-aminomethylpyridine, 18 = isoquinoline, 19 = pyridine-N-oxide The lines are not best fits of data, but simply show trends

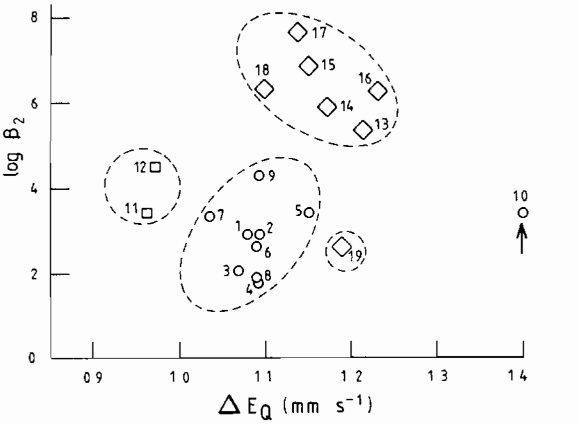


Fig 4 A plot of log β_2 against quadrupole splitting for the haemochromes The numbers refer to compounds listed in Tables 1 and 2 and the legend of Fig 3 The key for the symbols is included in Fig 3

Figure 4 shows the relationship between log β_2 and the quadrupole splitting (ΔE_Q) The ΔE_Q in this context gives an estimate of the electron imbalance between the four nitrogens of the porphyrin on the one hand and the two nitrogens of the axial ligands on the other The major factor which affects ΔE_Q is the distance of the axial nitrogen ligands from the iron, this in turn will reflect the orbital composition of the bond (and bond strength) and also steric interactions The compounds may be grouped into rough regions The aliphatic amines which show little or no steric hindrance have $\Delta E_Q \sim 1$ 1 mm s^{-1} (showing the above imbalance) These compounds bind to iron solely via σ bonding and their binding constants are low

The five-membered rings show the smallest orbital imbalance Therefore they can (i) get close to the iron, and (ii) accept some iron 3d electron density into their π^* orbitals As a result they have higher binding constants

The six-membered rings experience greater steric hindrance than the five-membered rings and although they are better π acceptors, which elevates their binding constants, they cannot approach the iron so closely Thus they have greater electron imbalance than the five-membered rings and hence exhibit greater ΔE_Qs

A striking feature of all the nitrogen ligands (except 19 which bonds through oxygen), irrespective of whether they are aliphatic, or aromatic, or indeed whatever the value of log β_2, is that the Hill coefficient is significantly greater than unity The finding of cooperative nitrogen binding ($h > 1$) reported here may have implications in the biological role of nitrogen ligands in haem proteins A nitrogen ligand is almost invariably one of the axial ligands and in many cases, (for example in electron transfer proteins), two axial nitrogen ligands are present

Very recently the structures of two new substituted imidazole complexes of Fe(II)TPP have been reported In these haemochromes the Fe–N_{Im} distances are 2 017(4) and 2 014(5) Å, respectively [29] These small distances reinforce our earlier findings [1] and our above statements It is likely that such distances are similar to those found in natural systems and this is the reason for the widespread use of histidine as axial ligands to iron porphyrins

Experimental

Electronic absorption spectra were obtained using a DU-7 spectrophotometer (Beckman)

Haematin was purchased from Sigma and used without further purification All the nitrogenous ligands were purchased from Aldrich Haematin was dissolved in NaOH (0 1 M) and diluted to the desired concentration ($\sim 10^{-5}$ M) with NaOH to give a solution of final pH = 12 The haematin was reduced to PPIXFe(II) with a slight excess of solid sodium dithionite As discussed in the text of this paper at pH 12 most of the PPIXFe(II) is present as monomer, thus investigations were carried out at high pH where we have previously shown a significant proportion of the PPIXFe(II) is monomeric in the absence of nitrogenous bases [7b, 8]

Spectrophotometric titrations (at 293 K) were carried out anaerobially by serial addition of degassed solutions of the various ligands Small volumes (~ 20 μl) of a stock solution (either neat compound or suitably diluted solution) of ligand were serially added to ~ 3 ml of PPIXFe(II) solution, the precise volume being determined by weight assuming a solution density of unity All experimental absorbance values were corrected for dilution effects on addition of ligand solution Spectra were recorded some 3 min after each addition to allow equilibrium to be established The spectroscopic data were analysed by transforming the ligand binding curve utilising a Hill plot from which both the Hill coefficient and the log β_2 values could be obtained The values of these parameters quoted are the average of three experiments

Mossbauer spectra were recorded on concentrated frozen solutions at 78 K The Mossbauer spectrometer and experimental details have been previously described [30]

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