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Mössbauer Studies on Protoporphyrin IX Iron(II) Solutions

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Mössbauer spectroscopic studies on frozen solutions of protoporphyrin IX iron(II) in the pH range 7–14 reveal evidence for three different species. The species dominant over the pH range 7–13 is a polymeric species (A) made up of bare protoporphyrin IX iron(II) moieties, the number of moieties in the polymer is discussed relative to concentration and pH. This species is assigned an $S = 1$ spin state. Above pH 13 a high spin iron(II) species (C) is present. The quadrupole splitting associated with this species is discussed and is the largest yet reported for an iron(II) propoporphyrin. This species (C) is a five coordinate protoporphyrin IX iron(II) with a hydroxide ion as the fifth ligand. The third species (B) is a minor constituent of this system and also has a high spin iron(II) structure, though the Mössbauer parameters for this site are more in keeping with a distorted octahedral environment.

Introduction

As part of our continuing study on the chemical and physical properties of protoporphyrin IX with iron we have recently discussed the chemistry of protoporphyrin IX iron(III) in aqueous solution over the pH range 6–14.4 [1]. In this study, we reported Mössbauer spectra of 'frozen' solutions and demonstrated evidence for only two major components in the system; namely a monomeric protoporphyrin IX iron(III) species and a μ-oxo bridge-oligomer of protoporphyrin IX iron(III) containing two protoporphyrin IX iron(III) units previously known as the μ-oxo-dimer.

The natural extension of this work is a study of the iron(II) aqueous chemistry of protoporphyrin IX.

There have been some reports of dimers for Fe(II) protoporphyrin IX. Shack and Clark [2], and Davies [3], found evidence for such a dimer but the work was not 'convincing'. Gallagher and Elliott [4] provided good evidence for the existence of such a species in 0.02 M NaOH, though they did not provide evidence of its thermodynamic stability.

Bednarski and Jordan [5] have studied the electron transfer characteristics of the Fe(II) and Fe(III) protoporphyrin IX in aqueous solution. White [6] suggests the interpretation of polarographic data presented seems generally reasonable, but was questionable in one respect when compared to the work of Walter [7]. Above pH 12.5, they found Fe(II) protoporphyrin was monomeric in agreement with Walter's finding with Fe(II) deuteroporphyrin dimethyl ester disulfonic acid, which was found to be dimeric below pH 13 and monomeric above pH 13. Bednarski and Jordan find the Fe(II) protoporphyrin behaves as a dimer between pH 9 and 12.5, again in concurrence with Walter's work. However, they say that the Fe(II) protoporphyrin IX is a monomer between pH 7 and 9 (solubility presents studies at lower pH). White suggests that this is in disagreement with logic which dictates that aggregation should increase as the pH of precipitation is approached. White does provide a reasonable explanation that it is the Tris buffer used in their work [5] that disperses the Fe(II) protoporphyrins to give monomers.

White further states that the whole area of the behaviour of Fe(II) water-soluble porphyrins seems to have been little studied [6].

In the recent literature there has been a series of Mössbauer studies on Fe(II) porphyrins, though no Mössbauer studies on protoporphyrin IX iron(II) are yet reported [8–18]. These Mössbauer studies along with studies of other physical properties have provided evidence for Fe(II) porphyrins in the $S = 0$, 1 and 2 states. Mössbauer spectroscopy is a useful probe for Fe(II) chemistry in that it is easy to distinguish between high and low spin Fe(II). Though it is not no simple to distinguish Fe(II) in an $S = 1$ state by Mössbauer parameters alone. We report here the results of a Mössbauer spectroscopic study on frozen solution of protoporphyrin IX

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TABLE 1. Mössbauer Parameters of Solid Isolated Form and Frozen Solutions of Protoporphyrin IX Iron(II) Solution.

pH	δ/mm s^{-1}	Δ/mm s^{-1}	Γ/mm s^{-1}	%Absn. Area
5.8	0.56(2)	1.43(2)	0.22(2)	100(4)
solid				
7.7	0.52(2)	1.43(2)	0.18(2)	100(6)
frozen solution				
9	0.514(2)	1.41(2)	0.17(2)	100(7)
frozen solution				
10.3	0.54(2)	1.39(2)	0.22(2)	72(3)
frozen solution	0.92(7)	2.27(1)	0.27(7)	28(2)
11.95	0.52(2)	1.41(2)	0.20(2)	67(3)
frozen solution	0.93(7)	2.27(13)	0.27(7)	11(3)
	0.98(2)	4.15(3)	0.20(2)	22(2)
14	0.56(2)	1.41(3)	0.23(1)	59(4)
frozen solution	0.89(9)	2.20(18)	0.26(7)	13(4)
	1.03(2)	4.11(3)	0.18(2)	28(3)
>14	0.52(2)	1.40(4)	0.24(1)	43(2)
frozen solution containing	1.01(3)	2.25(4)	0.18(3)	15(2)
25% $(CH_3)_4N^+$	1.01(1)	3.97(1)	0.18(1)	43(1)

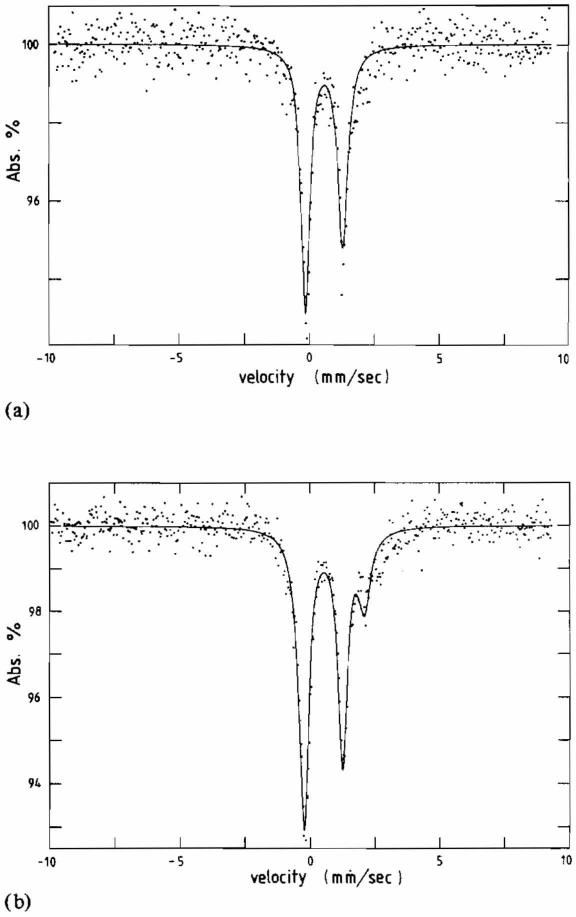


Fig. 1. Mössbauer spectra of protoporphyrin IX iron(II): a) solid from pH 5.8, b) frozen solution pH 10.3.

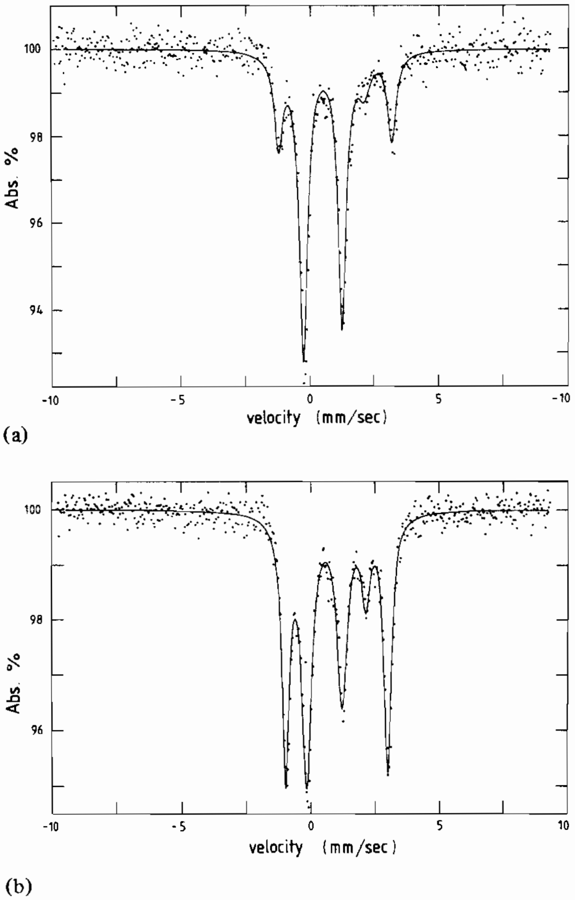


Fig. 2. Mössbauer spectra of protoporphyrin IX iron(II): a) frozen solution from pH 11.95, b) frozen solution from pH greater than 14 using $(CH_3)_4NOH$ as base.

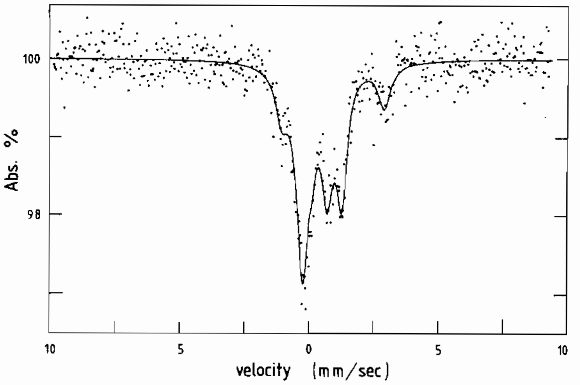


Fig. 3. Mössbauer spectrum of partially reduced protoporphyrin IX iron(III)/iron(II) solution from pH ~ 13.

iron(II), together with details of the UV–visible spectra of the ambient solutions.

Results and Discussion

The Mössbauer data obtained from both the frozen solutions and solids obtained from solutions of protoporphyrin IX iron(II) are presented in Table I, and Figs. 1, 2 and 3.

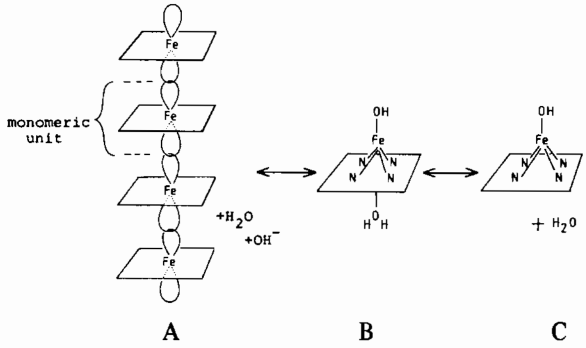
There are three distinct Mössbauer sites found in this system. Two of these are major sites and one from the proportion of the total Mössbauer spectrum contributed to is a minor site (Figs. 1–3).

The first site (which is a major site) reflects the only species present over the pH range 7–14. This is the only site found in this pH range 7–9. At pH 10.2 there are two iron environments found in the Mössbauer spectrum; the dominant site is that found in the lower pH range, and this site remains dominant to near pH 14. The second site, which is a minor site, has the Mössbauer parameters of a high spin iron(II). This site represents a very small amount of the total Mössbauer spectrum.

Above pH 11.95 a third site in addition to the two present at pH 10.3 is present. This site also has the Mössbauer parameters of a high spin iron(II) electronic environment, and also represents the second major site, though at pH 10.3 it is only a proportion of the total Mössbauer spectrum. These three sites all persist to pH 14.

To explain the Mössbauer data and understand the protoporphyrin IX iron(II) solution behaviour, Scheme A is suggested.

The stable form at pH 7–9 is form A. This species may be either a bare protoporphyrin IX iron(II) species or a polymer containing two or more protoporphyrin IX iron(II) units. The Mössbauer parameters for this species (Table I) are not too different from those found by other workers for FeTPP [17]. FeTPP exists in the solid form in the unusual spectroscopic state of intermediate spin (S = 1) [17]. FeTPP in the solid form has no axial ligands and the nearest Fe•••Fe distance is about 3.8 Å. We are in agreement with the hypothesis of White [6]. Aggregation of the protoporphyrin IX iron(II) should increase near the precipitation pH and we would expect such aggregation to cause interactions of the d_{z^2} orbitals of the protoporphyrin IX iron(III) units as shown below:



Species A; exists in solid and is dominant in solutions over the pH range 7–14. Species B; exists from pH 10.3 to above pH 14 (but only in small amounts). Species C; exists from pH 1 to 14 and is dominant above pH 14.

Scheme A

allowing no axial ligands and an intermediate spin (S = 1) spectroscopic state. Such aggregation would be solubilized by the presence of the charged propionic acid groups. Precipitation would occur when these groups protonate.

Studies on ferrous porphyrins in organic solvents [19, 20] have shown that in benzene, the hemes are free of axial ligands, though these authors do not conclude a definite answer for the spin state. Their magnetic moment of 4.52 B.M. for FeTPP in benzene is similar to that (4.4 B.M.) in the solid form [17].

In fact the Mössbauer data for site A persist until pH 14 suggesting some of the polymeric moieties exist even at very high pH. The Mössbauer data for this site are also similar to those found for $(Pip)_2Fe(TPP)$ [17] (Table II). In the latter material the two piperidine ligands are *trans* and the Fe–N axial distances are 2.127(3) Å [21]. The latter compound is an S = 0 state low spin Fe(II) complex. There are no known low spin ligands in our system, hence it is unlikely that the Mössbauer data of our species A is that of an S = 0 state complex.

No pK_a is found in this system in the pH range 8 to 11. Species B exists at pH 10.3 and above. The Mössbauer parameters are those of a high spin iron(II) in a distorted octahedral environment, which we have formulated to contain either one hydroxide and one water molecule as ligands, or two water

TABLE II. Mössbauer Parameters of Iron(II) Porphyrin Complexes.

Compound	T K	δ/mm s^{-1}	Δ/mm s^{-1}	Spin state	Ref.
$(Pip)_2Fe(TPP)$	77	0.75	1.42	s = 0	17
FP(1-MeIm)[a]	77	0.88	2.32	s = 2	16
Fe(TPP)(2-MeIm)[b]	77	0.92	2.26	s = 2	16
Deoxyhaemoglobin	4.2	0.91	2.26	s = 2	8

[a] P = meso-tetra($\alpha,\alpha,\alpha,\alpha$-pivaloylphenyl)porphyrin. [b] TPP = meso-tetraphenylporphyrin.

molecules as ligands. As the Mössbauer data are typical of a high spin iron(II) and such environments usually involve iron(II) sitting above the protoporphyrin plane [22, 48], we favour the two ligands being one water and one hydroxide.

Such an Fe(II) environment has been found in the crystal structure of $FeTPP \cdot OH \cdot H_2O$ where the Fe–OH distance is 2.18 Å and the Fe–H_2O distance is 2.95 Å [22]. The Fe(II) ion sits above the protoporphyrin plane towards the OH^- ligand. The Mössbauer parameters for site B are similar to those reported for FeP(1-MeIm) and Fe(TPP)(2-MeIm) [16]. Both of these compounds contain five coordinate high-spin Fe(II) in the S = 2 spin state. Indeed similar parameters to those for site B are also found in deoxy-haemoglobin [8].

Water molecules and hydroxide ions are the only ligands (other than N2 molecules) available to break up the polymers of species A.

The final species in the protoporphyrin IX iron(II) system is C. This is the environment we assign to the high spin Fe(II) site (S = 2) with a quadrupole splitting of 4.15 mm s^{-1}. This is a very large quadrupole splitting and is much larger than any previously recorded for an Fe(II) porphyrin compound. However, we would expect such a five coordinate structure to exhibit a more distorted environment than that of B and hence a larger quadrupole splitting. Species C is the dominant one at high pH, and although we found no evidence for a pK_a in pH titrations (using either NaOH, $(CH_3)_4NOH$ or KOH as the alkali). It is known that pH meters using glass electrodes are not reliable in this range. There is confirmatory evidence of a new species from the electronic spectra (see below).

The formation of species B is probably tied up with breakdown of species A as discusssed above, and it must then act as a precursor for species C. The structure of $FeTPP \cdot OH \cdot H_2O$ [22] would suggest that the Fe–OH_2 bond is weak, so if species B is similar we would except C to form at higher pH by preference as the Fe(II) ion moves further out of the protoporphyrin plane.

Evidence in support of our assignment for species C in the Mössbauer literature is common [23–28]. The large quadrupole splittings observed for iron(II) bis(dithiocarbamates) have been explained to constitute a case wherein the lattice and valence contributions to V_{zz} act in the same sense [28].

Vries *et al.* [23] advanced a level scheme of the type

$$(d_{x^2-y^2})^2(d_{zx}, d_{zy})^2(d_{z^2})^1(d_{xy})^1$$

for such molecules. The presence of the sixth electron in a $d_{x^2-y^2}$ orbital brings a strong positive contribution to V_{zz}, whilst the tetragonal perturbation generated by the square-pyramidal geometry contributes positively to V_{zz} also [28].

From our Mössbauer data for species C and its similarity to other data [23–28] we conclude that it corresponds to a square pyramidal five coordinate structure.

To investigate the presence of any possible dimeric intermediate in one Mössbauer spectroscopy experiment insufficient dithionite to reduce all the μ-oxo protoporphyrin IX iron(III) was used in a frozen solution at pH 13.

This spectrum could be fitted to three Mössbauer sites (Fig. 3). The first one is a high spin iron(III) species which we have previously assigned to the μ-oxo oligomer of protoporphyrin IX iron(II) [1]. The other two sites are both identified as iron(II) species, A and C respectively. There is therefore no evidence from our work of either a new μ-oxo-bridged protoporphyrin IX iron(II) species or a mixed μ-oxo bridged iron(II) iron(III) species.

Electronic Spectra

Only two major components are identified from a pH study of the electronic spectra of the protoporphyrin IX iron(II) system (Figs. 4, 5). The first change in this system is at pH 12.7 (Fig. 4), this indicates the presence of a high pK_a between species A and C. Figure 5 shows the bands associated with species C predominating.

The bands associated with species A are found over the pH range 7–14. The spectra are summarised in Table III along with those for species C. There are no bands that can be specifically assigned to species

TABLE III. Electronic Spectra.[a]

pH	λ_1 (nm)	ϵ m*M*	λ_2 (nm)	ϵ m*M*	λ_3	ϵ m*M*	λ_4 (nm)	ϵ m*M*	λ_5 (nm)	ϵ m*M*
6.2	383.0	42.02			555.0	6.37	576.0	6.42		
7.4	384.5	42.95			553.0	6.79	574.0	6.42		
8.5	385.5	44.07			550.0	6.08	574.5	6.16		
10.3	386.0	45.83			549.0	6.43	573.0	6.87		
11.0	385.5	47.80			556.5	6.71	574.0	7.05		
11.7	386.5	48.42			556.0	6.85	574.0	7.20		
12.7	383.5	47.33	π		555.5	6.95	575.0	6.38		
					λ_3' (nm)					
14.0	383.5	46.75	428.5	37.30	555.5	7.87	*		+	
>14.0†	383.0	46.70	428.5	43.51	555.5	9.07	*		+	
>14.0†	382.5	46.04	429.0	50.00	555.5	10.10	*		584.0	8.23
>14.0†	382.5	43.32	430.0	55.06	555.5	10.10			586.0	7.92
>14.0†	382.5	40.81	430.5	59.22	555.5	10.26	*		586.5	7.78

[a] See experimental section for details of solutions used. λ_1 and λ_2 are Soret bands. λ_1, λ_2 and λ_4 are due to species A. λ_2, λ_3, and λ_5 are due to species C. $^{\pi}$There is a component due to λ_2 whose intensity increases as the pH increases. *There is a component due to λ_4 whose intensity diminishes as the pH increases. $^{+}$There is a component due to λ_5 whose intensity increases as the pH increases. †These solutions contained increasing amounts of 25% $(CH_3)_4NOH$ (1 ml solution added progressively) for each solution after pH 14.

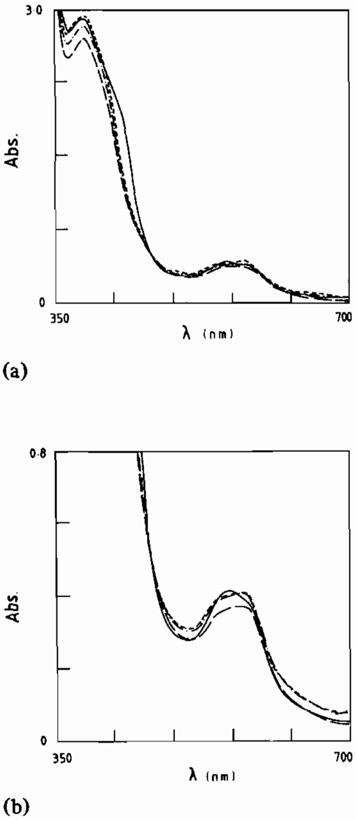


Fig. 4. Electronic absorption spectra of protoporphyrin IX iron(II) solutions of 60 *μM* at pH's – – – 8.15, –·–·– 10.3, ········ 11.0, ——— 12.7.

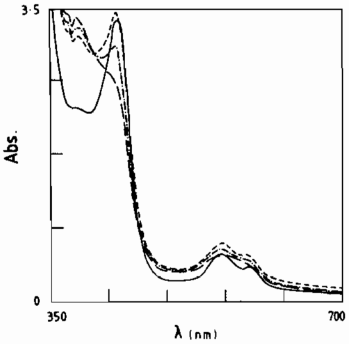
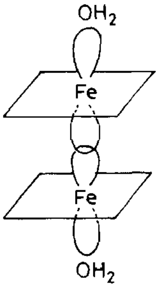


Fig. 5. Electronic absorption spectra of protoporphyrin IX iron(II) solutions of ~60 *μM* at pH's – – – 14, –·–·– 14†, ······ 14†, ——— 14† as explained in the footnote to Table III.

B possibly because it is never present in sufficient quantity relative to species A and C.

Conclusions

Whilst other workers [5, 7] agree that only monomeric Fe(II) protoporphyrin species exist above pH 12.5, we have found evidence for a polymeric species (species A) across the entire pH range 7–14. We note that Gallagher and Elliott [4] show stacking (for high ionic strength) of iron(II) porphyrins in their study, similar to that we suggest in the pH range 7–9. They also postulate an Fe(II) dimer, but their lack of specification to the presence or absence of a μ-oxo bridging ligand in this species is unfortunate. The structure they depict without a μ-oxo bridge:



could replace species A in our scheme or could be an intermediate between A and B, as water molecules would solvate the aggregates as the pH is raised. However, we found no evidence for the presence of such an intermediate species.

We find no evidence for any μ-oxo oligomer of protoporphyrin IX iron(II) and indeed such a species is unlikely to exist as a more polarising metal valence state would be needed to sustain such bonding. To date, only metal ions with a valence of 3+ or greater have been found to contain μ-oxo bridges in porphyrin chemistry [29–39].

Finally, we note that studies on aggregation of other metal(II) porphyrins have yielded much evidence in favour of aggregation through stacking the porphyrins [40–46].

The only question remaining is in regard to the nature of species A in solution in the pH range 7–9. It must be recognised that the charged carboxylate groups must be scattered around the resulting polymers (from monomer aggegation) to 1) enable the polymers to remain in solution and 2) not to break up the polymers via mutual repulsions between protoporphyrin IX moieties so that the resulting polymers are still soluble until a pH of just below pH 7, depending on concentration (the pH of precipitation of these arguments will depend on solution concentration). At higher pH values water molecules and hydroxide ions are responsible for the breakup of the polymers and the production of species B.

This hypothesis would pose a question in the protoporphyrin IX iron chemistry which is: what is the true pK_a of the propionic acid groups. In view of the findings of this paper and our previous work [1, 47, 48] in this field, the pKas generally assigned to protoporphyrin IX iron(III) for the propionic acid groups of 4.9 may be in question. Obviously from the precipitation pH they are higher or in some way modified in the protoporphyrin iron(II) system.

An interesting point arising from the Mössbauer data for species C (Table I) is that at very high pH in the presence of $(CH_3)_4N^+$ the quadrupole splitting is smaller than in the presence of Na^+. This means that the electronic environment of this species is affected by the cation present. It is likely that the Na^+ ions bind the propionic acid groups, the $(CH_3)_4N^+$ ions cannot bind in the usual way of a metal cation.

Experimental

Preparation of ^{57}Iron-PPIX Solution for Mössbauer Experiments

5 mg of enriched ^{57}Fe-PPIX prepared according to the method of Caughey [9] was dissolved in 0.5 ml 1 N NaOH solution and then diluted to 3 ml with distilled water.

The solution was centrifuged to remove the insoluble particles. The solution was then put under an N_2 atmosphere. A frew drops of concentrated sodium dithionite were then added to the solution. The pH of the solution was adjusted as required by adding 1 N HCl for pH $<$ 12 or by adding 2 N NaOH for pH $>$ 12. For the solution of pH 14, 3 ml 1 N NaOH was used to dissolve the compound. For solution pH 14, the compound was dissolved in 3 ml of 25% $(CH_3)_4$ NOH.

Electronic Absorption Experiments

20 mg hematin (Sigma) were dissolved in 2.5 ml 0.5 N $(CH_3)_4NOH$ and then diluted to 0.5 N $(CH_3)_4$-NOH with distilled water in a 100 ml two-neck flask connected to N_2 atmosphere. A few drops of concentrated sodium dithionite solution were added. The spectra were taken after the pH of the solution was adjusted to 6.2 by adding 1 N HCl. Higher pHs were obtained by adding 0.5 N $(CH_3)_4NOH$ solution. For pH $>$ 14, 1 ml of 25% $(CH_3)_4NOH$ was added progressively to the solution.

Instrumentation

Electronic spectra were recorded on a Beckman DU 7 spectrophotometer in 1 cm^2 cells.

The Mössbauer spectra were recorded on an instrument previously described [49]. The source was ^{57}Co (10 mCi) in rhodium (Radiochemical centre, Amersham), at 20 °C. The spectrometer was operated in a saw tooth mode and the spectra computer fitted. The spectrometer was calibrated with a 25 μM thick natural iron reference absorber. All isomer shifts are referred to this as zero shift.

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