

The Mössbauer Spectrum of an Intermediate Spin ($S = 1$) Four-co-ordinated (Protoporphyrinato IX)iron(II) Complex in a Frozen Aqueous Solution of Cetyltrimethylammonium Bromide

Okhil K. Medhi and Jack Silver*

Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, U.K.

The Mössbauer spectrum of the four-co-ordinated haem, (protoporphyrinato IX)iron(II) monodispersed in an aqueous detergent solution of 5% cetyltrimethylammonium bromide (CTAB), is that of a typical intermediate spin ($S = 1$) system [the isomer shift is $0.57(2) \text{ mm s}^{-1}$ and the quadrupole splitting (ΔE_Q) is $1.44(2) \text{ mm s}^{-1}$]; the results are comparable to those found in synthetic (porphyrinato)iron(II) analogues, the ΔE_Q values follow the σ donating ability (basicity) of the porphyrin ligands and the two lines of the quadrupole doublet are of unequal intensity at 78 K.

Four-co-ordinated (porphyrinato)iron(II) complexes are rare, they contain the d^6 iron(II) ion stabilised in a square planar geometry and in an unusually stable intermediate spin $S = 1$ state.^{1–3} The theoretical requirements for such a spin state are that the $d_{x^2-y^2}$ orbital must be higher in energy than the rest of the 3d orbitals and that it is empty. It is the absence of an odd electron in the latter orbital that determines the $S = 1$ state.^{1,2}

Several papers have recently appeared that have considered the nature of four-co-ordinated iron(II) porphyrins.^{4–7} These papers confirm the triplet ground state for four-co-ordinated iron(II) porphyrins such as [(TPP)Fe^{II}]^{1,2} and [(OEP)Fe^{II}]³ (TPP = tetraphenylporphyrinato, OEP = octaethylporphyrinato), but the exact electronic configuration of the triplet ground state still remains controversial.

Electron density distribution studies in crystals of [(TPP)Fe^{II}] at 120 K show a significant population of electrons in the $d_{x^2-y^2}$ orbital of the Fe^{II} centre, that has been mainly attributed to a donation of electrons from the porphyrin ligand.⁵ However, Sontum *et al.*⁶ showed that inclusion of this orbital in their $X\alpha$ multiple scattering calculations gave a value of -2.4 mms^{-1} for the quadrupole splitting (ΔE_Q), which is very different from the experimental value of $+1.5 \text{ mm s}^{-1}$ for [(TPP)Fe^{II}].¹ They pointed out that in a low symmetry environment, crystal field models that involve only d orbitals² are inappropriate for interpreting quadrupole splittings for iron compounds, and suggested that a large asymmetry in the occupation of the three iron 4p orbitals would make a significant contribution to ΔE_Q . The in-plane iron 4p orbitals (p_x and p_y) can participate in σ bonds to the porphyrin ligand.⁶

We have previously published Mössbauer data on frozen solutions (78 K) of ⁵⁷Fe enriched (protoporphyrinato IX)-iron(II), [(PPIX)Fe^{II}], in the pH range 7.7 to > 14 .⁸ We found the presence of a site that had a chemical shift of $0.54(3) \text{ mm s}^{-1}$ and a ΔE_Q of $1.41(2)$ in every solution. We ascribed this site to be a four-co-ordinate [(PPIX)Fe^{II}] ($S = 1$) species from the similarity of the Mössbauer parameters to those of [(TPP)Fe^{II}],¹ though the room temperature electronic absorption spectrum showed only a broad Soret band at 384 nm and two similar small bands around 553 and 574 nm. Interestingly, when we later studied frozen solutions of [(PPIX)Fe^{II}] (containing only natural abundance ⁵⁷Fe), the ΔE_Q values were larger and concentration dependent, we ascribed this behaviour to aggregation.⁹

As a result of the current interest in four-co-ordinate (porphyrinato)iron(II) species^{4–7} and because one of us has recently found that [(PPIX)Fe^{II}] can be obtained as a four-co-ordinated monomer in an aqueous solution of cetyltrimethylammonium bromide (CTAB),¹⁰ we report here the Mössbauer spectrum of this interesting compound. Aquo-(monohydroxo)(protoporphyrinato IX)iron(III)^{11,12} in a 5% solution of CTAB at pH 10.0 was reduced by dissolving solid sodium dithionite under strictly anaerobic conditions. The visible spectrum¹⁰ shows that the Soret band splits into four components as is expected for a square planar haem.¹³ The ¹H n.m.r. spectrum and a magnetic moment of $3.8 \mu_B$ indicate a triplet ground state.¹⁰ It is worth noting that solutions of haemin in CTAB also only contain one haemin molecule per micelle.^{12b}

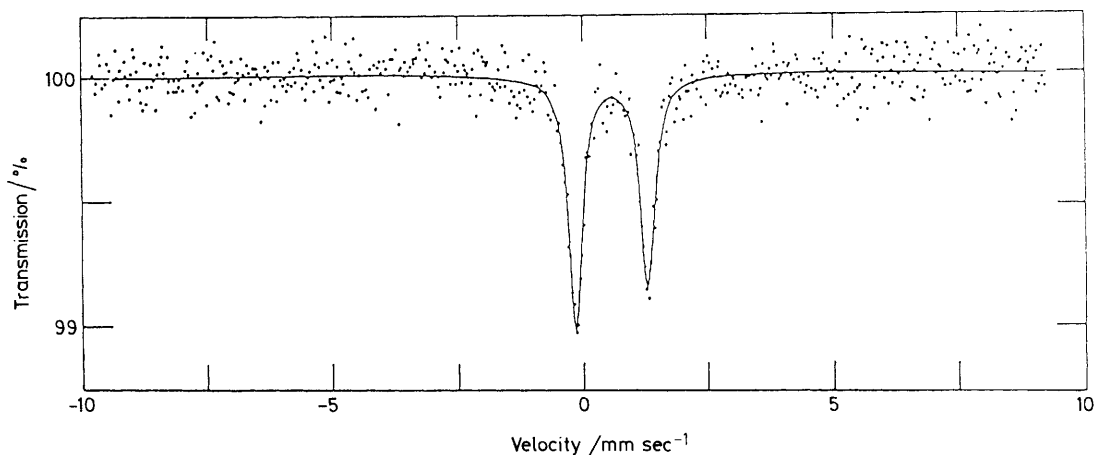


Figure 1. Mössbauer spectrum of [(PPIX)Fe^{II}] in frozen aqueous CTAB at pH 10.0 and 78 K.

Table 1. Mössbauer data of intermediate spin ($S = 1$) iron(II) porphyrins.

Compound	Conditions	$\delta(\text{Fe})$ mm s ⁻¹	ΔE_Q mm s ⁻¹	Γ^a mm s ⁻¹	Refs.
[(PPIX)Fe ^{II}]	5% CTAB pH 10.0, 78 K	0.57(2)	1.44(2)	0.17(2)	This work
[(TPP)Fe ^{II}]	Solid, 77 K	0.50	+1.51		2
[(OEP)Fe ^{II}]	Solid, 83 K	0.59	+1.60		3

^a Half width at half height.

The Mössbauer spectrum (Figure 1) of [(PPIX)Fe^{II}] in aqueous CTAB micelles was recorded using an instrument and technique previously described by us.^{9,14} The haematin starting materials contained only natural iron and a concentrated solution (*ca.* 30 mM in haem) was prepared in CTAB after the method outlined above.^{10,11} The isomer shift and quadrupole splitting are similar to those of other well characterised intermediate spin ferrous porphyrins and are thus consistent with an $S = 1$ ground state.

Comparison of the data found for [(PPIX)Fe^{II}] in the detergent solution with those reported previously by us for the ⁵⁷Fe enriched [(PPIX)Fe^{II}] in dilute solutions⁸ show close agreement and justify our original suggestion. Moreover, the facts (1) that more concentrated [(PPIX)Fe^{II}] solutions show somewhat wider ΔE_Q 's 1.47(2)—1.65(2) mm s⁻¹ and (2) that as the concentration increased the ΔE_Q increased,⁹ clearly demonstrate that aggregation of four-co-ordinate [(PPIX)-Fe^{II}] complexes in aqueous solution strongly influences the Mössbauer parameters. Aggregation of ferrous porphyrins in water is well established.¹⁵

The data for the three (porphyrinato)iron(II) complexes in Table 1 also indicate that the ΔE_Q values appear to follow the σ donating ability (basicity) of the porphyrin ligands. Dolphin *et al.*³ has suggested that the σ donor strengths of the porphyrins are in the order OEP > TPP > PPIX. It can be seen from this work that the change in ΔE_Q with donor power of the ligands follows from the extent of population of $d_{x^2-y^2}$ by sigma donation.

It may be pointed out that the two lines of the quadrupole doublet have the same line-width but different relative area ratios of the higher velocity line ($A_h = 46.5 \pm 4.1$) to the lower velocity line ($A_l = 53.5 \pm 4.0$), less than unity. Similar spectral features are apparent in the figures in our earlier papers^{8,9} and resemble those found for the mineral gillespite BaSi₄O₁₀, where the Fe²⁺ ion is high spin and is in a square

planar four-fold co-ordination of oxygen atoms.¹⁶ The imbalance of the areas in the spectra of gillespite was attributed to an anisotropic recoil free fraction,¹⁶ and slow electron spin lattice relaxation¹⁷ of the square planar iron. However, as no similar observations have been commented on for the other square planar ferrous porphyrins, further work on [(PPIX)-Fe^{II}] is necessary in order to comment on the asymmetry of the quadrupole doublet. We do note, however, that the earliest Mössbauer data for [(TPP)Fe^{II}],¹⁸ though inaccurate compared to latter work² and though wrongly ascribed to an $S = 2$ state, clearly show similar asymmetry of the quadrupole doublet to that found in this work.

One of us (O. K. M.), who is on leave from the Department of Chemistry, Gauhati University, Gauhatti 781014, Assam, India, thanks the Association of Commonwealth Universities, London, for support.

Received, 7th April 1989; Com. 9/01441A

References

- J. P. Collman, J. L. Hoard, N. Kim, G. Lang, and C. A. Reed, *J. Am. Chem. Soc.*, 1975, **97**, 2676.
- G. Lang, K. Spartalian, C. A. Reed, and J. P. Collman, *J. Chem. Phys.*, 1978, **69**, 5424.
- D. Dolphin, J. R. Sams, T. B. Tsin, and K. L. Wong, *J. Am. Chem. Soc.*, 1976, **98**, 6970.
- B. R. McGarvey, *Inorg. Chem.*, 1988, **27**, 4691.
- K. Tanaka, E. Elkaim, Liang Li, Zhu Nai Jue, P. Coppens, and J. Landrum, *J. Chem. Phys.*, 1986, **84**, 6969.
- S. F. Sontum, D. A. Case, and M. Karplus, *J. Chem. Phys.*, 1983, **79**, 2881.
- S. Obara and H. Kashiwagi, *J. Chem. Phys.*, 1982, **77**, 3155.
- J. Silver and B. Lukas, *Inorg. Chim. Acta*, 1983, **80**, 107.
- J. Silver, G. Al-Jaff, and J. A. Taies, *Inorg. Chim. Acta*, 1987, **135**, 151.
- O. K. Medhi, S. Mazumdar, and S. Mitra, to be published.
- S. Mazumdar, O. K. Medhi, and S. Mitra, *Inorg. Chem.*, 1988, **27**, 2541.
- (a) J. Simplicio and K. Schwenzer, *Biochemistry*, 1973, **12**, 1923; (b) J. Simplicio, K. Schwenzer, and F. Maenpa, *J. Am. Chem. Soc.*, 1975, **97**, 7319.
- D. Brault and M. Rougee, *Nature New Biol.*, 1973, **241**, 19.
- M. Y. Hamed, R. C. Hider, and J. Silver, *Inorg. Chim. Acta*, 1982, **66**, 13.
- W. I. White, in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1979, vol. 5, p. 303.
- M. G. Clark, G. M. Bancroft, and A. J. Stone, *J. Chem. Phys.*, 1967, **47**, 4250.
- M. G. Clark, *J. Chem. Phys.*, 1968, **48**, 3246.
- H. Kobayashi, Y. Maeda, and Y. Yanagawa, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2342.