Inorganica Chimica Acta, *171* (1990) 247–249

A Frozen Solution Mössbauer Spectroscopic Study of Six-coordinated High Spin (S = 2) Bis(tetrahydrofuran)(protoporphyrinato IX)iron(II)

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(Received August 25, 1989)

Abstract

The Mössbauer spectrum of six-coordinated iron(II) bis(tetrahydrofuran)(protoporphyrinato IX), [(PPIX)Fe(II)(THF)$_2$], was recorded in frozen solutions of tetrahydrofuran, 5% aqueous cetyltrimethylammonium bromide (CTAB) and 5% aqeuous sodium dodecylsuphate (SDS) detergents. The bis(THF) adduct of [(PPIX)Fe(II)] was found to be high spin (S = 2) with a quadrupole splitting of 2.49 mm s^{-1}. In the absence of the detergents the formation of the compound was considerably suppressed by [(PPIX)Fe(II)] aggregation. The basicity of the porphyrin has an influence on the quadrupole splitting of the compound.

The high spin (S = 2) Fe(II) ion in haemoproteins, such as deoxy haemoglobins and deoxymyoglobins, is always found as a five-coordinated species and the iron atom is above the plane of porphyrin towards the fifth ligand [1, 2]. Binding of a sixth ligand, such as carbon monoxide, stabilizes the low spin (S = 0) state where the iron atom is pulled into the plane of the porphyrin [1, 2]. It was thought that high spin Fe(II) ions were too large to fit in the N$_4$ hole in the porphyrin plane [2] so that a high spin S = 2 ferrous state was equated with a displaced iron atom. This led to the general belief that high spin haems are always five-coordinated with the iron atom out of haem plane and that six-coordinated in-plane Fe(II) is always low spin.

Though there are many exceptions to this generality in the case of ferric porphyrins [3], the only well-characterized high spin six-coordinated ferrous porphyrin is [(TPP)Fe(II)(THF)$_2$]† where the Fe(II) atom was shown to be rigorously centred in the porphyrin plane [4, 5]. In this complex the high spin iron atom is accommodated inside the N$_4$ porphyrin core which undergoes a radial expansion generated both by the population of the Fe(II) $d_{x^2-y^2}$ orbital and by significant non-bonding repulsions of the axial ligands by the porphyrinato core [5].

Continuation of our interest in six-coordinated high spin complexes of natural porphyrins [6–8] led us to study bis(THF)(protoporphyrinato IX)-iron(II) [(PPIX)Fe(II)(THF)$_2$] which is analogous to the TPP complex [4, 5]. We believed that such a study would be significant, as from resonance Raman work [9] it is believed that the complex [(PPIX)Fe(II)(THF)$_2$] also has an expanded porphyrinato core with the high spin Fe(II) ion centred in the haem plane [9]. We report here the Mössbauer spectum of [(PPIX)Fe(II)(THF)$_2$] and compare it to the other six-coordinated high spin ferrous porphyrin analogues [4, 5].

[(PPIX)Fe(II)(THF)$_2$] in THF solvent was prepared according to the reported procedure [9], but was found by this Mössbauer study to contain about 53% of the bis(THF) adduct contaminated with aggregated [(PPIX)Fe(II)]$_n$ species (see below). We found that a better yield of the bis(THF) adduct can be obtained if the compound [(PPIX)Fe(III)-(H$_2$O)(OH)] [7] in 5% aqueous cetyltrimethylammonium bromide (CTAB) or 5% aqueous sodium dodecylsulphate (SDS) is equilibrated with excess THF for about 4–5 h prior to reduction of the complex by solid sodium dithionite. The electronic absorption spectrum [10] of the bis(THF) species shows that the compound is a typical six-coordinated Fe(II) species [5], and the proton NMR spectrum at room temperature also indicates the presence of a high spin species [10].

The Mössbauer spectrum in Fig. 1(a) and the data in Table 1 for the 9:1 (vol./vol.) THF:H$_2$O frozen solution contains two quadrupole doublets corresponding to two species being present in almost equal proportion. The inner pair of lines is due to the presence of aggregates of the type [(PPIX)Fe(II)]$_n$ [11, 12] which did not appear when the spectrum was recorded in the detergent solutions well equilibrated with THF. It is clear from the comparison of the Mössbauer data in Table 1 with those reported for aggregated ferrous proto-

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†Abbreviations: TPP = *meso* tetraphenyl porphyrin; THF = tetrahydrofuran, PPIX = protoporphyrin IX.

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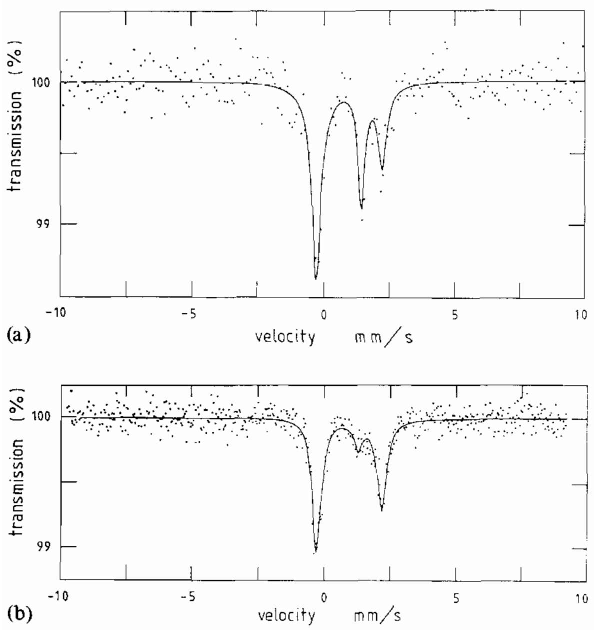

Fig. 1. Frozen solution ^{57}Fe Mössbauer spectra of [(PPIX)Fe(II)(THF)$_2$] at 78 K in (a) 9:1 (vol./vol.) THF:H_2O; (b) 5% aqueous CTAB at pH 10.0.

porphyrin IX [11, 12] that stacking of haems was prevented in the detergent solution. The frozen solution Mössbauer spectrum of the [(PPIX)Fe(II)(THF)$_2$] complex in CTAB which was not equilibrated with THF for a sufficiently long time contained an inner pair of lines (Fig. 1(b)). These are due to the presence of unreacted monomer [(PPIX)Fe(II)], which is an intermediate spin (S = 1) square planar (protoporphyrinato IX)iron(II) species [13, 14].

The isomer shift of the outer pair of lines in Fig. 1(a) and (b) correspond to that of a high spin (S = 2) iron(II) species. The quadrupole splitting, ΔE_Q, of 2.49(2) mm s^{-1} is similar, within experimental errors, in both the solvents. The ΔE_Q value is comparable to that in the well characterized six-coordinated high spin [4, 5] [(TPP)Fe(II)(THF)$_2$]. This together with the visible spectra in THF solution [9] and in the aqueous detergent [10] (that indicate six coordination at room temperature) confirms that the ΔE_Q value of 2.49 mm s^{-1} is due to the presence of [(PPIX)Fe(II)(THF)$_2$].

It is interesting to note that the basicity of the porphyrin has an influence on the ΔE_Q values for six-coordinated high spin Fe(II) porphyrins. The ΔE_Q in the PPIX derivative (even allowing for double the computer fitted errors to the experimental data) is smaller than in the TPP analogue (Table 1) (although unfortunately no errors in the fitting are quoted for the latter compound [5]). A recent low temperature electron density study [15] on the d-electron population in [(TPP)Fe(THF)$_2$] shows evidence for σ donation and π backbonding in this complex. Such backbonding is likely to be stronger in the PPIX complex, which contains electron deficient vinyl substituents on the pyrrole rings; these will withdraw electron density from the Fe(II) and influence the Fe d_π electron population and hence the ΔE_Q value [16]. The resonance Raman [9] spectrum of the bis(THF) complex was interpreted as being due to the iron atom in the haem plane and an expanded porphyrinato core. In the Fe in-plane position the iron → porphyrin π-backbonding is likely to be sensitive to porphyrin basicity.

There is considerable evidence in the literature that the binding of THF to a haem is very weak at room temperature [5, 17]. In this Mössbauer study the spectra were recorded in the presence of excess of THF and the data are for a frozen solution at 78 K. It is known that ethers [17] bind strongly at 77 K and that the Fe–O (THF) distances of [(TPP)Fe(THF)$_2$] decrease [15] by about 0.06 Å on cooling the crystals to 100 K.

Although this study does not provide proof that in [(PPIX)Fe(II)(THF)$_2$] the iron atom is in the plane of the porphyrin. The similarity of the Mössbauer data to those of [(TPP)Fe(II)(THF)$_2$], taken together with the work of refs. 9 and 10 strongly suggest that the complex is a six-coordinated high spin iron(II) species. Moreover, it is very likely that the iron(II) ion is in the porphyrin plane.

TABLE 1. Mössbauer data of high spin (S = 2) iron(II) porphyrins

Compound	Conditions	δ(Fe) (mm s^{-1})	ΔE_Q (mm s^{-1})	Γ^a (mm s^{-1})		A (%)	
[(PPIX)Fe(II)(THF)$_2$]	9:1 THF:H_2O^b	1.00(3)	2.48(5)	0.21(4)	0.38(5)	29.6(6.7)	23.0(6.2)
	5% CTAB^c	0.91(2)	2.49(2)	0.18(2)	0.24(2)	41.4(4.0)	39.3(4.2)
	SDS	0.87(9)	2.42(9)	0.21(5)	0.35(9)	48(13)	52(1)
[(TPP)Fe(II)(THF)$_2$]	solid^d	0.95	−2.64				

[a] Half width at half height. [b] 47% of another site (Fig. 1(a)) at δ = 0.60(2), ΔE_Q = 1.73(3), Γ = 0.16(3) mm s^{-1} is due to the presence of [(PPIX)Fe(II)]$_n$ aggregates. [c] 19% of another site (Fig. 1(b)) at δ = 0.58(3), ΔE_Q = 1.36(6), Γ = 0.19(5) mm s^{-1} is due to the presence of intermediate spin (S = 1) [(PPIX)Fe(II)] monomer uncomplexed in some micelles. [d] Ref. 5 – unfortunately no errors were quoted for this data.

Acknowledgement

We thank the Association of Commonwealth Universities, London, for support to one of us (O.K.M.).

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