

Mössbauer Spectroscopic Studies on some Low-spin Iron(II) and High-spin Iron(III) Complexes of *meso*-Tetrakis(2,4,6-trimethoxyphenyl)porphyrin

HUSAM M. ABU-SOUD* and J. SILVER**

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

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Abstract

Studies using Mössbauer spectroscopy indicate that bispiperidine and bispyridine complexes of (*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron(II) are the only complexes found in frozen solutions when this porphyrin iron(III) complex is dissolved in piperidine and pyridine solutions respectively.

High-spin iron(III) five-coordinate complexes containing porphyrin where the axial ligand is Γ^- , Br^- , Cl^- , OH^- or N_3^- have also been studied using Mössbauer spectroscopy. The magnitude of their quadrupole splittings is discussed.

Introduction

In their studies on 'fenced' porphyrinato(iron(II)/(III)) species Latos-Grazynski *et al.* [1] found that the reduction of (*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron(III) chloride $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ or (*meso*-tetrakis(2,4,6-triethoxyphenyl)porphyrinato)iron(III) chloride $[\text{T}(\text{EtO})_3\text{PPFeCl}]$ with either aqueous sodium dithionite or zinc amalgam in dichloromethane solution produced $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ and $[\text{T}(\text{EtO})_3\text{PPFe}(\text{II})]$ respectively. The previously reported reduction of these two porphyrins with piperidine [2] was re-examined by the same authors and it was shown that the bis(piperidine) adducts of the iron(II) porphyrins [1] were the end products.

In the preparation and characterization of some hydroxy complexes of iron(III) porphyrins, Cheng *et al.* [3] showed that the oxidation of $[(\text{TMP})\text{-Fe}(\text{II})]$ (TMP is the dianion of *meso*-tetramesitylporphyrin) or $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ yields $[(\text{TMP})\text{-FeOH}]$ or $[\text{T}(\text{MeO})_3\text{PPFeOH}]$. These same hydroxy complexes are obtained by treating the corresponding

$[\text{PPFeCl}]$ with aqueous sodium hydroxide. Cheng *et al.* [3] also demonstrated that these complexes of the type $[\text{PPFeOH}]$ are distinguished from the more common oxo-bridged dimers $[\text{PPe}-\text{O}-\text{FeP}]$ on the basis of ^1H NMR spectra, magnetic susceptibilities, UV-Vis and electron spin resonance spectroscopy. These hydroxy complexes behave as typical high-spin five-coordinate iron(III) compounds [3].

The aims of the work reported in this study were (a) to check if in concentrated solutions the piperidine reduced $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ to form an intermediate-spin iron(II) complex of four coordination or if the piperidine also reacts with $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ and forms a low-spin $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})(\text{Pip})_2]$; (b) to study the influence of axial ligands on the quadrupole splittings of $[\text{T}(\text{MeO})_3\text{PPFe}(\text{III})]$ complexes.

Experimental

All starting chemicals were purchased from Aldrich or Sigma and used without further purification. The free base $\text{T}(\text{MeO})_3\text{PPH}_2$ [4, 5] was synthesized by previously reported procedures starting with 2,4,6-trimethylbenzaldehyde. $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ was prepared by the literature method [6]. $[\text{T}(\text{MeO})_3\text{PPFeOH}]$ [3] was prepared by dissolving $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ in a minimal amount of toluene solution and stirring with aqueous sodium hydroxide for 2 days. The toluene solution was separated from the mixture and evaporated to dryness. The resulting solid was then redissolved in toluene and filtered, and the iron porphyrin was reprecipitated by the addition of heptane. UV-Vis spectra of the $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ and $[\text{T}(\text{MeO})_3\text{PPFeOH}]$ prepared in this study were in good agreement with the spectra of Cheng *et al.* [3]. The compounds $[\text{T}(\text{MeO})_3\text{PPFeX}]$ (where $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{N}_3$) were prepared by the reaction of CHCl_3 solutions of $[\text{T}(\text{MeO})_3\text{PPFeOH}]$ with excess of aqueous solution of the desired axial ligand sodium salt in the presence of H_2SO_4 . The aqueous layer was removed and the CHCl_3 solution was filtered and

*Present address: Department of Chemistry, Texas A & M University, College Station, TX 77843-3255, U.S.A.

**Author to whom correspondence should be addressed.

evaporated to dryness. These complexes were then placed in sample holders and transferred to the Mössbauer spectrometer.

One hundred mg of $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ were dissolved in 2 ml pyridine or piperidine solution. These solutions were frozen in perspex cells for the Mössbauer spectroscopic experiment. The Mössbauer data were collected at 78 K on an apparatus previously described [7]. All spectra are computer fitted. Chemical shifts are referred to natural iron foil as zero shift.

Results and Discussion

In the complex (*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato(iron(III))) $[\text{T}(\text{MeO})_3\text{PPFe}]^+$, only one isomeric form is possible. The *ortho*-alkoxy substituents are positioned above and below the porphyrinato core. This symmetrically 'fenced' species was designed to prevent two metal centres from forming a μ -oxo-bridge and thereby producing new types of dioxygen carriers [1–4].

Vaska *et al.* [2, 4] found that the reduction of $[(\text{T}(\text{MeO})_3\text{PP})\text{FeCl}]$ yields $[(\text{T}(\text{MeO})_3\text{PP})\text{Fe}(\text{II})]$, an insoluble four-coordinated, diamagnetic species which reacts readily with pyridine, forming $[(\text{T}(\text{MeO})_3\text{PP})\text{Fe}(\text{Py})_2]$ but not with piperidine, consistent with predictions based on molecular models. In contrast to the earlier studies, Latos-Grazynski *et al.* [1] using the ^1H NMR spectroscopy, demonstrated that piperidine does reduce these iron(III) porphyrins as expected, and contrary to previous expectations, is capable of coordination to both the iron(III) and iron(II) complexes [1].

The Mössbauer data of the iron porphyrin are presented in Tables 1 and 2. The Mössbauer spectra of $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Py})_2]$ and $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Pip})_2]$ have isomer shifts that are typical of low-spin iron(II) in hexacoordinate porphyrin complexes. The spectra of these two complexes are symmetric at 78 K and the Mössbauer parameters are similar to those observed for similar complexes by other workers [8–13] (Table 1). No evidence was found in the Mössbauer spectra for other species being present in the solution of $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ in pyridine or piperidine. So species such as $[\text{T}(\text{MeO})_3\text{Fe}(\text{Py})_2]^+$, $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Pip})_2]^+$ or unreacted $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ can be neglected.

The electronic absorption spectra of $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$, both in pyridine or piperidine are typical of those for other iron(II) low-spin hexacoordinate porphyrinato complexes.

It has been shown that most of the pyridine iron porphyrin complexes have isomer shifts and quadrupole splitting (at room temperature) around 0.35 and 1.2 mm/s, respectively [14], whereas for the piperidine iron porphyrin complexes all have the same isomer shift (within experimental error, Table 1), and the quadrupole splittings span the narrow range 1.48 ± 0.05 s [14].

It is therefore apparent that there is enough room to accommodate a pyridine or a piperidine ligand bound to the iron atom in the centre of (*meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato)iron-(II)/(III). Note the end complexes are iron(II) species but these resulted from iron(III) species, and to reduce the iron(III) species such ligands must first bind to the iron(III) centres.

TABLE 1. ^{57}Fe Mössbauer spectroscopic data for low-spin iron(II) porphyrin complexes ($S = 0$) with pyridine and piperidine as ligands

Compound	Temperature (K)	δ (mm s $^{-1}$)	Δ (mm s $^{-1}$)	Reference
$[\text{T}(\text{MeO})_3\text{PPFe}(\text{Pip})_2]$	78	0.47(1)	1.48(2)	this work
$[(\text{PP})\text{Fe}(\text{Pip})_2]$	77	0.49	1.42	8
	295	0.42	1.43	
$[(\text{ETIOP})\text{Fe}(\text{Pip})_2]$	298	0.40	1.45	9
$[(\text{TPP})\text{Fe}(\text{Pip})_2]$	4.2	0.51	1.44	10
	77	0.50	1.44	
$[(\text{PClPP})\text{Fe}(\text{Pip})_2]$	298	0.40	1.47	9
$[(\text{PMEPP})\text{Fe}(\text{Pip})_2]$	298	0.42	1.53	9
$[(\text{PMXPP})\text{Fe}(\text{Pip})_2]$	298	0.42	1.49	9
$[(\text{MeO})_3\text{PPFe}(\text{Py})_2]$	78	0.42(2)	1.21(3)	this work
$[(\text{PP})\text{Fe}(\text{Py})_2]$	77	0.45	1.21	8
$[(\text{PClPP})\text{Fe}(\text{Py})_2]$	298	0.36	1.27	9
$[(\text{PMXPP})\text{Fe}(\text{Py})_2]$	298	0.37	1.27	9
$[(\text{DP})\text{Fe}(\text{Py})_2]$	295	0.34	1.13	11
$[(\text{OEP})\text{Fe}(\text{Py})_2]$	4.2	0.46	1.13	12
	85	0.46	1.14	
	115	0.45	1.17	
	295	0.38	1.21	

TABLE 2. ^{57}Fe Mössbauer spectroscopic data of the high-spin $\text{T}(\text{MeO})_3\text{PPFe}(\text{III})$ complexes at 78 K

No.	Compound	δ (mm s^{-1})	Δ (mm s^{-1})	Γ_1 (mm s^{-1}) ^a	Γ_2 (mm s^{-1}) ^a
1	$[\text{T}(\text{MeO})_3\text{PPFeN}_3]$	0.34(8)	0.38(16)	0.48(14)	1.27(21)
2	$[\text{T}(\text{MeO})_3\text{PPFeOH}]$	0.35(5)	0.38(9)	0.25(12)	0.92(7)
3	$[\text{T}(\text{MeO})_3\text{PPFeCl}]$	0.32(6)	0.62(11)	0.31(6)	1.20(7)
4	$[\text{T}(\text{MeO})_3\text{PPFeBr}]$	0.36(4)	0.78(8)	0.26(3)	1.26(10)
5	$[\text{T}(\text{MeO})_3\text{PPFeI}]$	0.41(2)	0.92(6)	0.33(3)	0.53(8)
	site 1				
	$[\text{T}(\text{MeO})_3\text{PPFeI}_2]^-$	0.34(5)	2.79(13)	0.50(11)	
	site 2 ^b				

^aHalf width at half height.^bFitted as a simple doublet hence only one line half width tabulated.

We thus agree with Latos-Grazynski *et al.* [1] that the claim of the separation of diamagnetic $[\text{T}(\text{MeO})_3\text{PPFe}(\text{II})]$ [2] in the presence of piperidine was in error. The species formed is $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Pip})_2]$.

The Mössbauer data for compounds 1–5 (Table 2) are consistent with the presence of high-spin five-coordinate iron(III). The Mössbauer spectra of the compounds in Table 2 are all assigned to monomer species. These asymmetric spectra are typical of iron(III) porphyrin and are explained in the same way as those for haemin by Blume [15] (in terms of a temperature dependent spin–spin relaxation process).

The Mössbauer data available in Table 2 for $[\text{T}(\text{MeO})_3\text{PPFeX}]$ ($\text{X}^- = \text{I}^-, \text{Br}^-, \text{Cl}^-, \text{OH}^-$ and N_3^-) shows the order for the magnitude of the quadrupole splittings is $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{OH}^- \approx \text{N}_3^-$. It must be stressed that the data for these high-spin Fe(III) sites are fitted as two lines. These data manifest as asymmetric lines. Unfortunately, the fitted two lines are of very different areas but the appearance of the spectra are typical of high-spin Fe(III) porphyrin complexes. The spread in quadrupole splitting (Δ) in the series is from 0.92(6) to 0.38(9) mm s^{-1} , showing that the axial ligand influences the magnitude of Δ . Moreover, the stronger ligands N_3^- and OH^- cause smaller Δ s. A similar trend has previously been observed for $(\text{PMXPP})\text{FeX}$ [16] ($\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NCS}^-, \text{N}_3^-, \text{O}_2\text{CMe}^-$ and O_2CCF_3^-) and has been discussed by us recently [17]. In complex 5 (Table 2) two sites were observed in the Mössbauer spectrum. The first site is consistent with a high-spin iron(III) species as discussed above and is designated as $[\text{T}(\text{MeO})_3\text{PPFeI}]$ (site 1 in Table 2), the other site is likely to have two very weak I^- ligands bonded in the fifth and sixth positions. This site is similar to that assigned to $[\text{PPIXFe}(\text{III})\text{I}_2]^-$ and is likely to be indicative of a spin admixed 3/2, 5/2 species [18].

Conclusions

The axial ligand in the $[\text{T}(\text{MeO})_3\text{PPFeX}]$ complexes influences the magnitude of Δ . The stronger

ligands cause smaller Δ s for the five-coordinate complexes.

Pyridine and piperidine react with $[\text{T}(\text{MeO})_3\text{PPFeCl}]$ and form $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Py})_2]$ and $[\text{T}(\text{MeO})_3\text{PPFe}(\text{Pip})_2]$ respectively. This demonstrates that there is enough room to accommodate a pyridine ligand bound to the iron(II) or iron(III) in (*meso*-tetraakis(2,4,6-trimethoxyphenyl)porphyrinato)-iron(II)/(III) complexes.

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