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Mössbauer Spectroscopic Studies on Protoporphyrin IX Iron(III) Cyanide Complexes

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Abstract

The Mössbauer and other spectral data of a dicyanoprotoporphyrin IX iron(III) complex are reported. The low quadrupole splitting is discussed in relation to known low-spin iron(III) porphyrin structures and their Mössbauer parameters.

Introduction

There have been a great many studies on the binding of cyanide ion to haemoproteins [1] and porphinato-iron(III) complexes [2–6] as model compounds. Such binding of the strong field cyano ligands leads to low-spin ferric derivatives. The latter fact has been used in a number of NMR studies on haemoproteins [7, 8] and porphinato-iron(III) derivatives [4, 5, 9–11]. Equilibrium studies have demonstrated the stepwise binding of cyanide ions [4, 5]. We have studied binding of cyanide ions to protoporphyrin IX iron(III) using conductiometric titrations [3]. In these studies we found evidence in Mössbauer spectra on frozen solutions for species of the type [Fe(PP)CN(X)] where PP = protoporphyrin IX and X = OH$^-$ or CN. Recently the structure of potassium dicyano (*meso*-tetraphenylporphinato)iron(III) bis(acetone) has appeared [12]. The [Fe(TPP)(CN)$_2$]$^-$ ion has Ci-1 symmetry. The Fe–C–N group is essentially linear with Fe–C = 1.975(2) Å. As no Mössbauer data have been reported for this complex we have prepared the sodium dicyano(protoporphyrinato)iron(III) bis(dimethylformamide) and discuss here its Mössbauer spectrum in relation to known crystal structures and our previous Mössbauer study [3]

Results and Discussion

The Mössbauer data for Na(Fe(PP)(CN)$_2$) are presented in Table I and Fig. 1. The quadrupole splitting is very small for a low spin Fe(III) porphyrin complex (*cf.* nitrogen ligands, Table I). To understand this low quadrupole splitting it is useful to consider some literature extended Hückel calculations [13]. For Fe(III)P(CN)$_2^-$ (P = porphyrin) the ground state is a ^2E_g state with $(d_{xy})^2(d\pi)^3$. This is only one of two possible ground states for tetragonal D$_4$h symmetry. It has been pointed out that of the known low-spin haemichromes most have quadrupole splitting (*QS*) values around 1.90–2.35 mm s^{-1} (e.g. FeTPP(Im)$_2$Cl, Δ = 2.23 mm s^{-1}), the exception is FeTPP(Py)$_2$Cl (Δ = 1.25 mm s^{-1}) The most interesting possibility is that these compounds have different orbital ground states, if the ground

TABLE I. Mössbauer Parameters for Low-spin Iron(III) Complexes (S = ½)

Complex	T (K)	δ (mm s^{-1})	Δ (mm s^{-1})	Γ (mm s^{-1})[a]	Reference
Na[Fe(PP)(CN)$_2$]	80	0.20(1)	0.53(1)	0.24(1)	This work
	298	0.10(1)	0.40(1)	0.14(1)	This work
[Fe(PP)(Im)$_2$]Cl	77	0.13	2.27		18
	77	0.24	2.30		19
	298	0.14	2.17		
[Fe(TPP)(Im)$_2$]Cl	77	0.23	2.23		19
	298	0.13	2.11		
[Fe(PMXPP)(Im)$_2$]Cl[b]	298	0.17	2.06		20
[Fe(PMXPP)(Im)$_2$]Br[b]	298	0.16	2.05		20
[Fe(PClPP)(Im)$_2$]Cl[c]	298	0.15	2.01		20

[a] Half width at half height. [b] PMXPP = tetra(*p*-methoxyphenyl)porphin [c] PClPP = tetra(*p*-chlorophenyl)porphin.

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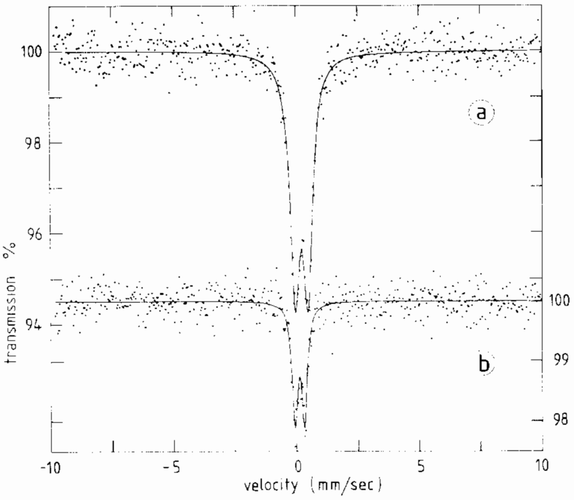

Fig. 1. Mössbauer spectra of sodium dicyano(protoporphyrinato)iron(III) bis(dimethylformamide): (a) at 80 K; (b) at 298 K.

state is $(d_{xz}d_{yz})^4(d_{xy})^1$ (that is $^2B_{2g}$), then the Townes–Daily formulation gives $eq_{\text{val}} = -\frac{4}{7}\langle r^{-3}\rangle d$, whereas for the $(d_{xy})^2(d_{xz}, d_{yz})^3$ state (^2E_g) then $eq_{\text{val}} = +\frac{2}{7}\langle r^{-3}\rangle d$. As in this case, effects of covalency can be neglected to first order, as the contributions from electrons in bonding orbitals formed from d_{z^2} and $d_{x^2-y^2}$ will effectively cancel. Thus the magnitudes of the quadrupole splitting for these ground states must be in the approximate ratio of 2:1 as observed. But to verify this the sign of e^2qQ in both complexes must be established. Also in these cases there is no obvious cause for such a difference in orbital ground state. The case for the orbital singlet (d_{xy} lowest) arises from a tetragonal compression along the C_4 axis of the haem complex, the doublet arises from an elongation along this axis. Scheidt and Gauterman appear to have ruled out a $^2B_{2g}$ state on the grounds that the Fe–CN bond is smaller than the Fe–Np (Np = porphyrin pyrole nitrogen) and so this is a compression along the C_4 axis and thus a ^2E_g state. However, a carbon atom is not exactly equivalent to a nitrogen and thus this may not be a totally correct stand. If the *QS* of our cyanide complex (0.5 mm s^{-2}) is considered, it could be explained in two ways. The first arising from a marked ground state where the 5 electrons are equally spread across the three orbitals. (Such a state could arise from spin orbital coupling of the $^2B_{2g}$ and ^2E_g states.) This would be seen by a large temperature dependence of the quadrupole splitting.

The alternative explanation is that it is a ^2E_g ground state but the difference in energy between the (d_{xy}) and (d_{xy}, d_{yz}) orbitals being very small so that it is only a slightly distorted octahedral environment and thus only a small quadrupole splitting with little temperature dependence will be observed.

As the temperature dependence of the quadrupole splitting is relatively large, 20% in this cyanide complex compared to around 5% in $Fe(TPP)(Im)_2Cl$, it might appear that the former description that the ground state is a mixed $^2B_{2g}$ and ^2E_g state is the best description. However, as the overall splitting is so small, the latter explanation cannot be ruled out.

This small quadrupole splitting is primarily due to the presence of the strong field CN^- ligands that act as both sigma donors and π-acceptors (better than nitrogen ligands), there is greater stabilization along the Fe–L (L = CN) coordinate due to π-backbonding from metal to ligand. This is reflected in the Fe–CN bond lengths (1.975(2) Å) in the known structure.

This compares to other known structural data [14–17] which appears in Table II. These are for imidazole ligands and can be compared to Mössbauer data for similar compounds [18–20] in Table I. These have much larger quadrupole splittings (the d_{xy}, d_{yz} and d_{xz} are not identical in energy) as is obvious in the structures where $Fe–L_1$ is not equal to $Fe–L_2$. Thus only very strong ligands will give small quadrupole splitting in low spin porphyrin

TABLE II. Structural Details of Low-spin Iron(III) Complexes

Complex[a]	Distance (Å)			Δ Core[e]	Reference
	Fe–Np[b]	Fe–L$_1$[c]	Fe–L$_2$[d]		
$[Fe(TPP)(Im)_2]Cl$	1.989(8)	1.957(4)	1.991(5)	0.009[f]	14
$[Fe(OEP)(Im)_2]ClO_4$	2.01[g]			0[h]	15
$[Fe(PP)(1\text{-}MeIm)_2]$	1.990(16)	1.996(5)	1.998(5)	0.03[f]	16
$[Fe(TPP)(2\text{-}MeIm)_2]ClO_4$	1.971(5)	2.013(4)		0	17
$K[Fe(TPP)(CN)_2]$	2.000(6)	1.975(2)		0[h]	12

[a] Im = imidazole; 1-MeIm = 1-methyl imidazole; 2-MeIm = 2-methyl imidazole; OEP = octaethylporphyrin [b] Fe–NP = Fe to N of porphyrin. [c] Fe–L$_1$ = Fe to axial ligand 1. [d] Fe–L$_2$ = Fe to axial ligand 2 (if same as 1 not given). [e] Δ core = displacement of Fe from porphinato plane. [f] Displacement towards more distant ligand. [g] Complete details not in literature. [h] Required by crystallographic symmetry.

iron(III) complexes. It is worth noting that this is reflected in met-haemoglobin where CN as the sixth ligand produces the smallest splitting [21].

The Mössbauer data we previously presented taken from frozen solutions of PPIXFe(III) containing CN^- ions we stated [3] is likely to be caused by the presence of $[Fe(PP)(CN)_2]^{2-}$ (δ = 0.20(1), Δ = 0.73(3) pH 12), and the second minor component we ascribed to $[Fe(PP)(CN)(OH)]^-$. With the result reported here there is possible conflict with our earlier studies. The obvious explanation is that our earlier suggestions are erronous and the most likely species present in aqueous solution are $[Fe(PP)(CN)(OH)]^-$ and $[Fe(PP)(CN)(H_2O)]^0$ with the latter being assigned the small quadrupole splitting. However as our previous work was carried out in a hundred-fold excess of CN^- it may have been correctly assigned, but then the Mössbauer spectrum in frozen solution is perturbed by solvent molecules.

A final point of interest on the Mössbauer spectra of the sodium complex is the temperature dependence of the line width; we are unable to suggest a reasonable explanation for the large decrease at this time.

The infrared spectrum of our material showed the presence of the sodium cyanide impurity at 2180 cm^{-1} and DMF at 1665 cm^{-1} (CO stretch). The CN stretching frequency for the iron bound CN was at 2120 cm^{-1}. This is in exactly the same position as that found in the potassium salt [12]. The UV–Visible spectrum (Fig. 2) shows two Soret bands at 358 cm^{-1} (ϵ = 38.2 mM) and 434 cm^{-1} (ϵ = 67.9 mM) and a broad band at 554 cm^{-1} (ϵ = 10.8 mM), our spectrum is quite different to that reported for the potassium salt [12], and we suggest that the latter which appears to have too many bands in the α and β positions is in error (possibly wet as addition of water to our sample moves the Soret band to 424 nm).

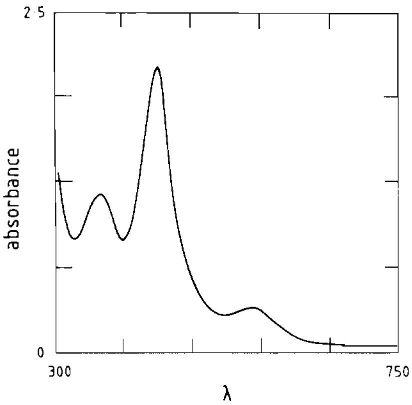

Fig. 2. Electronic absorption spectrum of a protoporphyrin IX iron(III) in DMF solution containing NaCN in excess.

Experimental

Preparation of Sodium Dicyano Protoporphyrinato)-iron(III) Bis(dimethylformamide)

200 mg hemin (Sigma) was dissolved in 100 ml DMF (Aldrich) with the aid of stirring. The insoluble particles were separated by filtration. 10 ml of a saturated solution (at 20 °C) of sodium cyanide in DMF was added to the hemin solution and mixed. Solid product was obtained by adding 100 ml of diethylether and filtered. No further purification was carried out as a note in the preparation of the potassium salt [12] says that the complex loses solvent. The final product was contaminated with sodium cyanide, but when three molecules of NaCN were allowed for in the analysis along with six molecules of water (the compound is hydroscopic) good analytical agreement was found. *Anal.* Calc: C, 48.00; H, 4.35; N, 13.69; Fe, 4.96; Na, 12.26. Found: C, 48.0; H, 4.3; N, 13.5; Fe, 4.95; Na, 13.95%.

Instrumentation

The solid used for Mössbauer spectroscopy was as formed, details of the spectrometer have been published previously [22]. The spectrometer was calibrated with a 25 μm thick natural iron reference absorber. The isomer shifts are referred to this as zero shift.

Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer spectrophotometer.

The UV–Vis spectrum was recorded in DMF on a Beckman DU-7 spectrometer at 21 °C.

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