A New Resonance Raman Band Characteristic of Pentaco-ordination in Iron Tetraphenylporphyrin Complexes

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Summary A new resonance Raman band is observed at *ca.* 1375 cm^{-1} which appears to be characteristic of pentaco-ordination in iron tetraphenylporphyrin complexes having different spin and oxidation states.

A LARGE amount of structural information can be obtained from the resonance Raman (RR) spectra of haemoproteins, based on correlations between the frequencies of distinct prominent Raman bands and the oxidation and/or spin states of the iron atom;[1] this leads mainly to the definition of an oxidation-state marker band (band I) at *ca.* 1350—1375 cm^{-1} and a spin-state marker band (band IV) at *ca.* 1550—1580 cm^{-1}.[2]

Many of the correlations have been extended to iron porphyrins such as iron mesoporphyrin dimethyl ester[2] and iron octaethyl porphyrin (OEP)[3] complexes. Structural implications for other metalloporphyrins have not been developed to such an extent, though an interesting correlation has been established between a Raman frequency of OEP derivatives of different metals and the core radius of the porphyrin.[4] Within the field of iron porphyrins, although a large number of iron tetraphenylporphyrin (TPP) complexes have been synthesized that mimic some of the properties of haemoproteins,[5] they have not been studied thoroughly by the RR technique. Recently, it has been shown that three RR bands of Fe(TPP) complexes (at 390, 1360, and 1560 cm^{-1}) all show frequency shifts responsive to both spin and oxidation changes of the iron atom;[6] despite its sensitivity to spin changes the 1360 cm^{-1} polarized band (hereafter called A) is considered as analogous to band I of physiological haems.[6]

We report here new RR results on a series of Fe(TPP) complexes, leading us to propose a new marker band characteristic of pentaco-ordination.

Upon irradiation at 514·5 nm, spectra are obtained[7] showing, besides the three bands already mentioned, an extra and previously unobserved band (called band B) at *ca.* 1375 cm^{-1} for the following complexes Fe^{II}(TPP)(L) with L = CS,[8] CCl$_2$,[9] C=C(p-ClC$_6$H$_4$)$_2$,[10] Pr^{i}NO, and 2-MeIm;[12] and Fe^{III}(TPP)(L) with L = Cl[12] and -O- (μ-oxo dimer).[12]

The frequencies of band B are given in the Table (together with the oxidation and spin states of the iron in the corresponding complexes); they have been measured in CHCl$_3$ and C$_6$H$_6$ solutions, with an estimated accuracy of (±) 1·5 cm^{-1}.

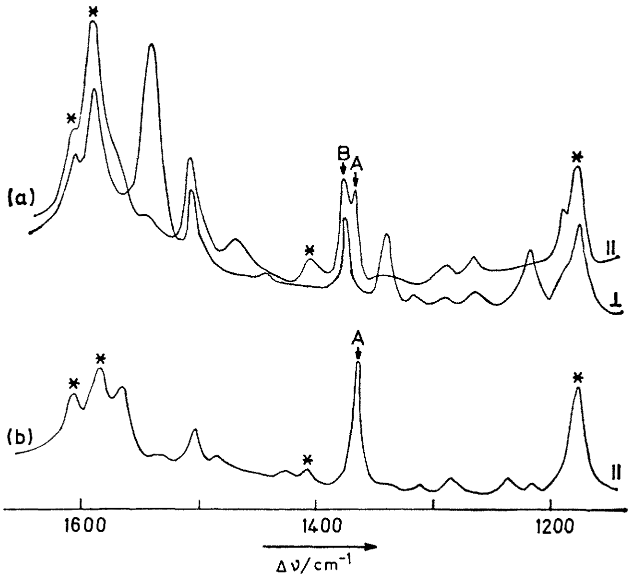

FIGURE 1. RR spectra of (a) Fe(TPP)(CS) with polarization || and ⊥ to the incident polarisation; (b) Fe(TPP)(CS)(py) with polarization || to the incident polarization. Excitation wavelength 514·5 nm, 60 mW; conc. 1 mg ml^{-1} in C$_6$H$_6$ (solvent bands indicated by *); rotating cell.

Band B shows polarization and intensity properties different from band A at 1360 cm^{-1} which allows a clear distinction. Band B is depolarized whereas band A is polarized (Figure 1). Its intensity decreases markedly when the exciting line frequency comes close to the Soret frequency, so that it is no longer observable (Figure 2); this explains why band B was not observed by Spiro *et al.* for complexes such as Fe^{II}(TPP)(2-Me-Im), Fe^{III}(TPP)(Cl), and [Fe^{III}(TPP)]$_2$O.[6]

TABLE Frequencies of band B in Fe(TPP)(L)(L′) complexes

L^a	L	Oxidation state	Spin state	Co ordination number	Band B /cm^{-1}
Cl		III	5/2	5	1369
O(μ oxo)		III	5/2	5	1368
Me$_2$SO	Me$_2$SO	III	5/2	6	—
None		II	1	4	—
2 Me Im		II	2	5	1365
CS		II	0	5	1375
CCl$_2$		II	0	5	1377
C C(p ClC$_6$H$_4$)$_2$		II	0	5	1379
Pr^i–NO		II	0	5	1376
py	py	II	0	6	—
CS	py	II	0	6	—
C=C(p ClC$_6$H$_4$)$_2$	py	II	0	6	—
Pr^{i}NO	py	II	0	6	—

^{a} Abbreviations py = pyridine 2 Me Im = 2 methylimidazole

Those characteristics allow us to rule out the hypothesis that band B results from a splitting of band A due to the occurrence of a new species formed upon photodecomposition of the complex with a different A frequency

The occurrence of band B is not related to a specific oxidation or spin state of the iron as exemplified in the Table but seems distinctive of five co ordinated species In fact we were not able to observe band B for hexaco ordinated derivatives such as Fe^{II}(TPP)(py)$_2$ Fe^{III}(TPP)-(Me$_2$SO)$_2$ and tetraco ordinated derivatives such as Fe^{II} (TPP) For the former complexes even with a 2 cm^{-1} resolution band A remains symmetrical and no shoulder assignable to band B could be characterized Moreover comparison of the spectra of Fe(TPP)(CS) and Fe(TPP)(CS)(py) (Figure 1) shows that they are similar except that the band at 1375 cm^{-1} has disappeared for the hexaco-ordinated species The same result is obtained with C–C(p ClC$_6$H$_4$)$_2$ or Pr^{i}NO instead of CS

We suggest that the Raman activity of band B is due to the lowering of the molecular symmetry from D_{4h} in hexa and tetra co ordinated species to C_{4v} in five co ordinated species [actually the molecular symmetry in Fe(TPP) is intermediate being D_{2d} owing to core ruffling[12]] *X* Ray structures[12] are available for Fe(TPP)(Cl) [Fe(TPP)]$_2$O and Fe(TPP)(2 Me Im) showing an important out of plane displacement of the iron atom so that the occurrence of band B might be linked to this displacement

Whatever may be the origin of band B it is the first reported RR band of iron porphyrin complexes distinctive of pentaco ordination

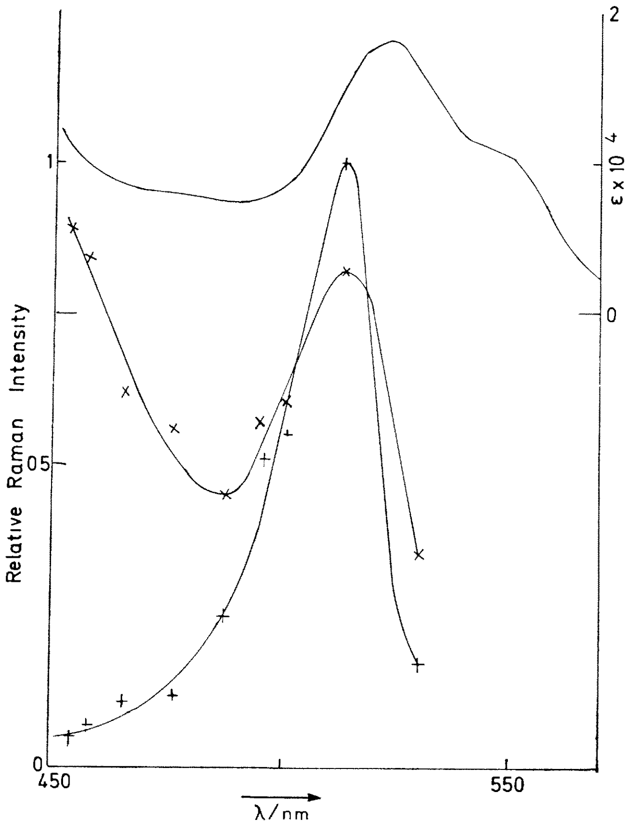

FIGURE 2 Fe(TPP)(CS) in C$_6$H$_6$ solution top absorption spectrum bottom relative Raman intensities of band A (×) and B (+) *vs* excitation wavelength

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