In situ Infrared Spectroelectrochemical Studies of Tetraphenyl-porphyrin Complexes containing Manganese, Iron and Cobalt

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The difference spectra in the mid-infrared region associated with oxidation of the porphyrin ring in 5,10,15,20-tetraphenylporphyrin complexes of Mn^{III}, Fe^{III} and Co^{III} have been obtained by *in situ* Fourier-transform infrared spectroelectrochemistry, and are compared to those similarly observed for the corresponding metal(II)–metal(III) redox couples. Oxidation of the porphyrin ligand to the π-cation radical results in the appearance of three new bands near 1420, 1290 and 1230 cm^{-1}, as well as characteristic shifts and intensity changes of several bands present for the parent complex. In contrast, the difference spectra associated with the metal redox couple show less complex changes, the extent of which vary in the order Co < Fe < Mn. The spectral changes thus provide a means to differentiate between ligand- and metal-centred oxidation. In addition, the results provide insight into the nature of the infrared porphyrin ligand vibrations, as well as the character of the molecular orbitals associated with the oxidation processes.

Metalloporphyrins can undergo reversible redox reactions in which the site of electron transfer may be localized at either the porphyrin ring or the central metal. Both reaction types are important in natural processes such as photosynthesis, or the action of haem enzymes such as cytochrome P-450. For this reason, the differentiation between metal- and porphyrin ring-centred redox reactions of metalloporphyrins is a topic which has merited considerable attention.

On one-electron oxidation a metalloporphyrin may form either a π-cation radical or a complex in a higher metal oxidation state. In this regard a number of diagnostic criteria have been developed to allow the correct formulation of the oxidized product based on optical spectra, EPR, electrochemistry, magnetic moment or magnetic circular dichroism measurements.[1,2] More recently, criteria based on solid-state infrared spectra of the isolated products[3] and resonance Raman spectra obtained in solution following bulk electrolysis[4] have been suggested.

This laboratory recently applied the technique of *in situ* Fourier-transform infrared (FTIR) thin-layer reflectance spectroelectrochemistry to a study of this question.[5,6] In this method a thin layer (10–100 μm) of electrolyte solution is confined between the surface of a polished electrode (Pt in our studies) and an infrared-transparent window. Infrared radiation is directed through the thin layer onto the electrode. Analysis of the energy of the specularly reflected radiation prior to and following electrolysis of the thin-layer solution affords the difference in absorbance resulting from the electrolysis reaction.

Our previous studies involved the oxidation of a series of metal complexes of tetraphenylporphyrin which were all known to yield π-cation radicals upon one-electron oxidation.[6] This work confirmed the presence of a new strong infrared absorption near 1280 cm^{-1}, which had previously been observed in the solid-state spectra of isolated cation radicals[3] and suggested to be diagnostic of one-electron oxidation of the tetraphenylporphyrin ring. In addition, the *in situ* difference spectra revealed that a similar series of absorbance increases and decreases accompanied formation of each of the π-cation radicals investigated. However, since it is well known that a number of porphyrin ligand vibrations are sensitive to the oxidation state, as well as the spin state of the central metal atom,[7] it was not clear to what extent these additional features

of the difference spectra might be specifically characteristic of oxidation of the porphyrin ring, as opposed to metal oxidation.

In this paper we report on the *in situ* FTIR reflectance spectroelectrochemistry of 5,10,15,20-tetraphenylporphyrinato-cobalt(II), [Co(tpp)], (5,10,15,20-tetraphenylporphyrinato)-iron(III) chloride, [Fe(tpp)]Cl and (5,10,15,20-tetraphenyl-porphyrinato)manganese(III) perchlorate, [Mn(tpp)]ClO₄. The complex [Co(tpp)] can be oxidized in two successive one-electron transfer steps yielding first the metal(III) complex and then the metal(III) π-cation radical complex; [Fe(tpp)]Cl and [Mn(tpp)]ClO₄ can be reduced to the corresponding metal(II) species or oxidized to metal(III) π-cation radical complexes in independent one-electron transfer steps. These compounds thus afford the opportunity for direct comparison of the changes to the vibrational spectrum associated with the metal(II)–metal(III) redox couple with those accompanying oxidation of the porphyrin ring.

Experimental

Materials.—The complexes [Co(tpp)] and [Mn(tpp)]ClO₄ were prepared and purified according to literature methods;[8,9] [Fe(tpp)]Cl was used as received from Porphyrin Products. Tetra-*n*-butylammonium hexafluorophosphate was prepared by the addition of 1 mol equivalent of aqueous sodium hexafluorophosphate (Aldrich) to tetra-*n*-butylammonium bromide (Fluka) dissolved in the minimum volume of water. The white crystalline precipitate was filtered off, washed with water, recrystallized twice from isopropyl alcohol–water mixtures, and dried at 110 °C *in vacuo* for several days. Dibromomethane (Aldrich) was shaken with alumina prior to use. Acetonitrile (BDH Omnisolve) was distilled from CaH_2.

Instrumentation and Methodology.—The same cell was utilized for *in situ* FTIR spectroelectrochemistry, time-resolved thin-layer UV/VIS spectroelectrochemistry and thin-layer cyclic voltammetry. It employs a platinum-wire counter electrode, a platinum-disc working electrode (diameter 7 mm) polished to a mirror finish, and a CaF_2 optical window, which is transparent from the ultraviolet portion of the electromagnetic spectrum through to *ca.* 1000 cm^{-1} in the infrared. Thin-layer cavities of variable thickness are maintained between the surface of the electrode and the window. Details of the cell construction

Table 1 Half-wave potentials for the first metal- and ligand-centred redox reactions of the porphyrin complexes in CH_2Br_2-MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

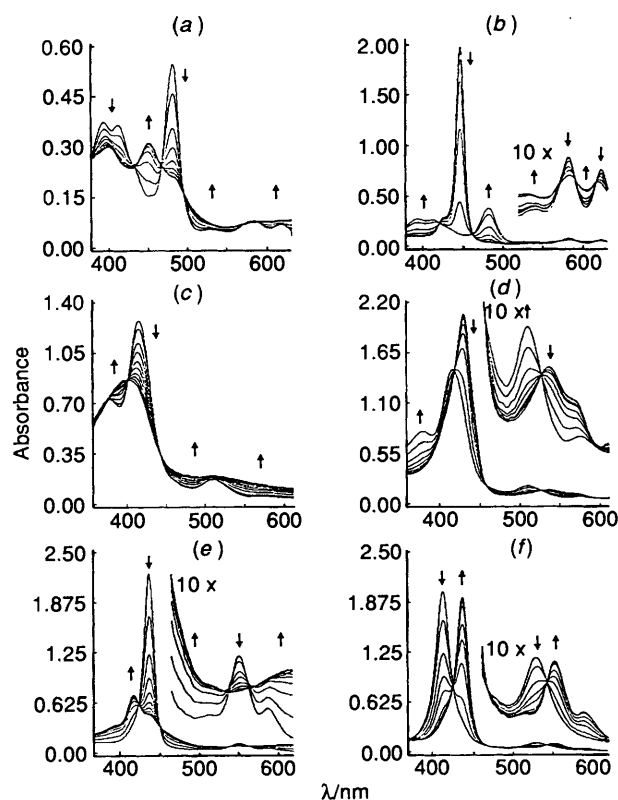|	$E_{\frac{1}{2}}$/V vs. SCE	
Compound	M^{III}–M^{II}	tpp$^-$–tpp^{2-}
[Mn(tpp)]ClO$_4$	−0.23	1.23
[Fe(tpp)]Cl	−0.30	1.09
[Co(tpp)]	0.33	1.06

Fig. 1 Time-resolved thin-layer UV/VIS spectroelectrochemistry of the one-electron oxidation of (a) [Mn(tpp)]ClO$_4$, (b) [Mn(tpp)], (c) [Fe(tpp)]Cl, (d) [Fe(tpp)], (e) [Co(tpp)]PF$_6$ and (f) [Co(tpp)] in CH_2Br_2-MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

are fully described elsewhere.[5] A description of the cell used for conventional cyclic voltammetry is contained in ref. 10. For all electrochemical experiments, potential control of the working electrode was achieved with a Hi-Tek DT2101 potentiostat operating in conjunction with a Hi-Tek PPR1 waveform generator. An aqueous saturated calomel electrode (SCE) was utilized as reference electrode for all experiments. All solutions employed 0.1 mol dm^{-3} NBu$_4$PF$_6$ as supporting electrolyte, and were purged with argon to remove O_2.

Infrared spectroelectrochemical measurements employed a Nicolet 8000 FTIR spectrometer and a liquid-nitrogen cooled narrow-range mercury cadmium telluride detector. Two front-surfaced gold mirrors were used to direct the infrared beam onto the platinum electrode and back to the detector, as described in ref. 5. The infrared difference spectra associated with the redox couples were determined by collecting and averaging a set of 128 interferograms at each of two potentials, E_1 and E_2, selected to lie 120 mV on either side of the observed half-wave potential for the couple. The potential was automatically switched under computer control on completing collection of the first set of spectra. To allow time for complete electrolysis, a 30 s delay was invoked before initiating acquisition of the second set of spectra. Fourier processing of the two resulting interferograms and taking the logarithm of the ratio of the resulting energy spectra

affords the difference in absorbance between the two forms of the redox couple.

The instrument utilized for time-resolved thin-layer UV/VIS spectroelectrochemistry employs a Rofin-Sinar model RSO 6101 spinning-grating monochromator. The details of its construction and implementation are fully described in ref. 11. The absorbances of the thin-layer solutions were determined at 83 ms intervals following the application of a potential step appropriately chosen to bring about the desired electrolysis reaction. Successive sets of 16 or 32 spectra were averaged in real time to provide a record of the spectral changes every 1.2 or 2.7 s.

Results and Discussion

Electrochemistry and UV/VIS Spectroelectrochemistry.—In order to ascertain that the electrode reactions could be carried out cleanly and reversibly on the time-scale required for *in situ* FTIR spectroelectrochemical characterization, the reactions were first investigated by cyclic voltammetry, thin-layer cyclic voltammetry and thin-layer UV/VIS spectroelectrochemistry. Initial studies were carried out in CH_2Br_2 containing 0.1 mol dm^{-3} NBu$_4$PF$_6$, since CH_2Br_2 has been shown in previous studies to be useful for FTIR characterization of metallo-porphyrin electrode reactions.[5] In this solvent the oxidation of [Co^{II}(tpp)] to [Co^{III}(tpp)]$^+$, and subsequent oxidation to the porphyrin π-cation radical, [Co^{III}(tpp$^•$)]$^{2+}$, could both be carried out cleanly and reversibly. Similarly, the oxidations of [Fe(tpp)]Cl and [Mn(tpp)]ClO$_4$ to the corresponding π-cation radicals occurred reversibly. The reductions of [Fe(tpp)]Cl and [Mn(tpp)]ClO$_4$ to the corresponding metal(II) species, however, were accompanied by an irreversible following reaction, as evidenced by reverse-to-forward peak current ratios of less than 1:1 in conventional and thin-layer cyclic voltammetry experiments, and the absence of isosbestic points in the time-resolved thin-layer UV/VIS spectroelectrochemistry. Both iron(II) and manganese(II) porphyrins are known to be highly unstable in the presence of dioxygen, so that reaction with trace O_2 is a likely explanation for the observed instability of these metal(II) complexes.

It was observed that the required stability of the iron(II) and manganese(II) species could readily be attained in 1:1 mixtures of CH_2Br_2-MeCN, which may be due to a competitive inhibition of O_2 binding by MeCN. Acetonitrile alone could also be used to study the manganese complex, but was not useful for the iron or cobalt complexes because of their limited solubility.

For the oxidation of [Mn(tpp)]ClO$_4$, [Fe(tpp)]Cl and [Co-(tpp)]$^+$ to the corresponding π-cation radicals and the metal-centred oxidation of [Co^{II}(tpp)] to [Co^{III}(tpp)]$^+$ it was possible to use both CH_2Br_2-MeCN (1:1) and dibromomethane alone as solvent for the infrared spectroelectrochemical experiments. In both cases the infrared difference spectra obtained were nearly identical.

Table 1 presents the reversible half-wave potentials for the various redox couples observed in CH_2Br_2-MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$, as measured by cyclic voltammetry. Fig. 1 illustrates the UV/VIS spectral changes associated with the redox processes identified in Table 1. In all cases clear isosbestic points are observed, indicating that the electrode reactions proceed in a quantitative fashion. The spectral changes are consistent with literature data for the indicated processes, confirming the electron-transfer sites as indicated.[12,13]

In situ FTIR Spectroelectrochemistry.—The mid-infrared difference spectra observed upon metal- and ligand-centred oxidation of the porphyrin complexes in CH_2Br_2-MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$ are shown in Figs. 2–4. The mid-infrared difference spectra observed upon metal- and ligand-centred oxidation of [Mn(tpp)]ClO$_4$ in MeCN contain-

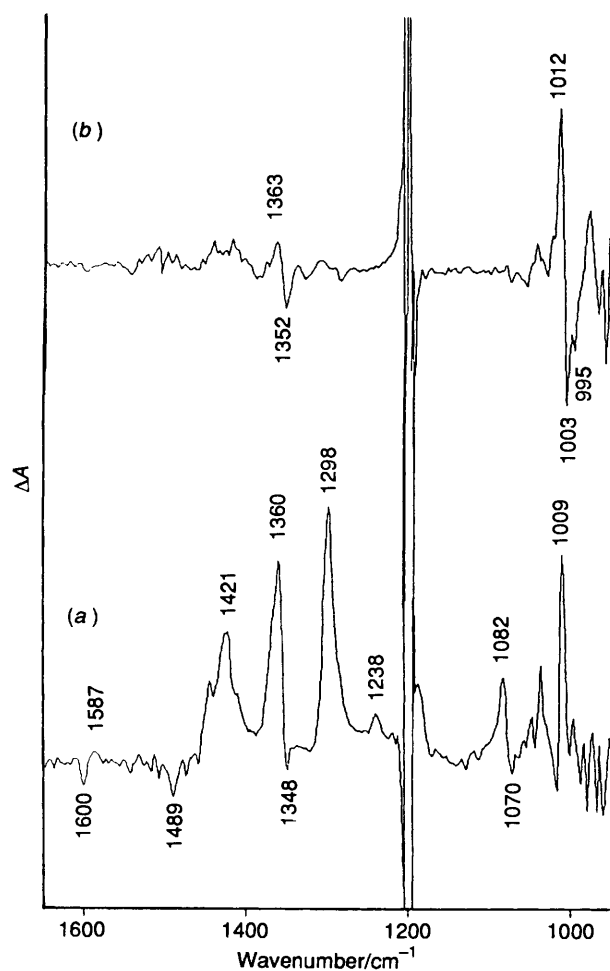**Fig. 2** *In situ* FTIR difference spectra observed for the one-electron oxidation of (*a*) [Co(tpp)]ClO$_4$ and (*b*) [Co(tpp)] in CH$_2$Br$_2$–MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

Fig. 3 *In situ* FTIR difference spectra observed for the one-electron oxidation of (*a*) [Fe(tpp)]Cl and (*b*) [Fe(tpp)] in CH$_2$Br$_2$–MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

ing 0.1 mol dm^{-3} NBu$_4$PF$_6$ are shown in Fig. 5. The positive absorbance (appearance) features indicate an increased absorption of the oxidized complex relative to the unoxidized system, whereas negative absorbance (disappearance) features indicate a corresponding decrease in absorption. The relatively high absorption due to the solvent mixture, as well as the tetra-*n*-butylammonium cation, acted to lower the signal-to-noise ratio in several regions of the spectra. Most notably, an intense band at 1192 cm^{-1} due to CH$_2$Br$_2$ absorbed practically all of the infrared beam energy near 1200 cm^{-1}.

The mid-infrared spectral changes associated with the metal- and ligand-centred oxidation of [Co(tpp)] in dibromomethane containing 0.1 mol dm^{-3} NBu$_4$ClO$_4$ have been previously reported.[6] However, co-ordination changes involving the perchlorate anion became manifest in the mid-infrared difference spectra because the anion absorbs near 1100 cm^{-1} in the infrared. Consequently, any changes to the porphyrin vibrations in the region around 1100 cm^{-1} were not observable. In the present study the use of the hexafluorophosphate anion, which has no strong bands in the mid-infrared region, avoided such effects.

The mid-infrared difference spectra associated with the ligand-centred oxidation of the porphyrin complexes are shown in Figs. 2(*a*), 3(*a*), 4(*a*) and 5(*a*). The general pattern of appearance and disappearance features is seen to be very similar for all three complexes. This pattern has been observed with all the tpp π-cation radicals studied to date, including that of the free base.[6]

The strong and medium intensity mid-infrared bands produced by the porphyrin complexes of Mn^{III}, Fe^{III} and Co^{II} are
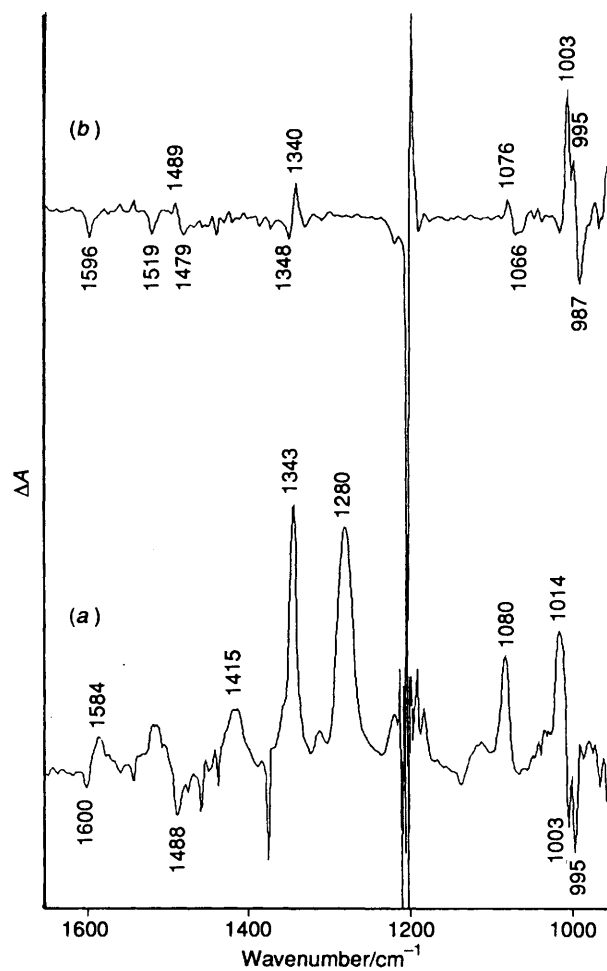
listed in Table 2, together with a tentative assignment. In this region of the spectrum the observed bands are due to in-plane vibrations of the porphyrin ring, as well as modes arising from the four phenyl substituents.[14] If the effective molecular symmetry is D_{4h} then the allowed infrared transitions in this region will have E$_u$ symmetry. On one-electron oxidation of the porphyrin ligand it is observed that a number of these modes undergo characteristic shifts in wavenumber (see Table 3). In most cases the magnitude of these shifts could be estimated from the separation between appearance and disappearance features in a bipolar difference band. In cases where intensity changes had masked the disappearance feature the shift was estimated from the difference in wavenumber between the appearance feature in the difference spectrum and the parent band in the solution-state spectrum of the unoxidized complex (Table 2). Thus, the phenyl mode, φ_4'', shifted to lower wavenumber by *ca.* 10–16 cm^{-1}. In contrast, there was a shift to higher wavenumber of the porphyrin ring modes v_{41} (*ca.* 4–12 cm^{-1}), v_{51} (*ca.* 7–12 cm^{-1}) and v_{44} (*ca.* 9–19 cm^{-1}). The v_{39} mode was seen to lose intensity, but apparently did not undergo any significant shift in wavenumber. The possibility that v_{39} shifts to lower wavenumber producing the appearance feature near 1420 cm^{-1} may be ruled out since both bands can be seen in the solid-state spectrum of the isolated π-cation radical derived from [Fe(tpp)]Cl.[3] The v_{41} mode underwent no apparent change in either wavenumber or intensity on ligand-centred oxidation.

The manganese complex could also be studied using acetonitrile as solvent [Fig. 5(*a*)] which avoided loss of information from the region near 1200 cm^{-1}. In this case it was observed that v_{52} lost intensity and φ_6'' gained intensity,

Table 2 Mid-infrared bands (cm^{-1}) of strong and medium intensity due to the porphyrin complexes[a]

Assignment[b]	[Mn(tpp)]ClO$_4$[c]	[Fe(tpp)]Cl	[Co(tpp)]$^+$
φ_4'', v(phenyl)	1597 (1599)	1597 (1599)	1599 (1599)
v_{39}, $v_{sym}(C_\alpha C_{meso})$	1487 (1489)	1485 (1487)	1491 (1492)
v_{40}, v(pyrrole quarter-ring)	1441 (1441)	1440 (1442)	1440 (1442)
v_{41}, v_{sym}(pyrrole half-ring)	1341 (1343)	1339 (1339)	1350 (1350)
		1334	
v_{52}, $\delta_{sym}(C_\beta H)$	1204	1200	1206
φ_6'', v(phenyl)	1179	1175	1177
v_{51}, $\delta_{asym}(C_\beta H)$	1073 (1076)	1070 (1073)	1072 (1071)
v_{44}, v_{asym}(pyrrole half-ring)	1013 (1011)	1003 (1003)	1005 (1005)
		995 (995)	997 (997)

[a] Samples in the form of KBr pellets. Numbers in parentheses refer to solution-state spectra measured in CH$_2$Br$_2$–MeCN (1:1) (pathlength 1 × 10^{-4} m). [b] Taken from ref. 14. [c] v(ClO$_4$) bands appear at 1122 and 1099 cm^{-1}.

Fig. 4 *In situ* FTIR difference spectra observed for the one-electron oxidation of (a) [Mn(tpp)]ClO$_4$ and (b) [Mn(tpp)] in CH$_2$Br$_2$–MeCN (1:1) containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

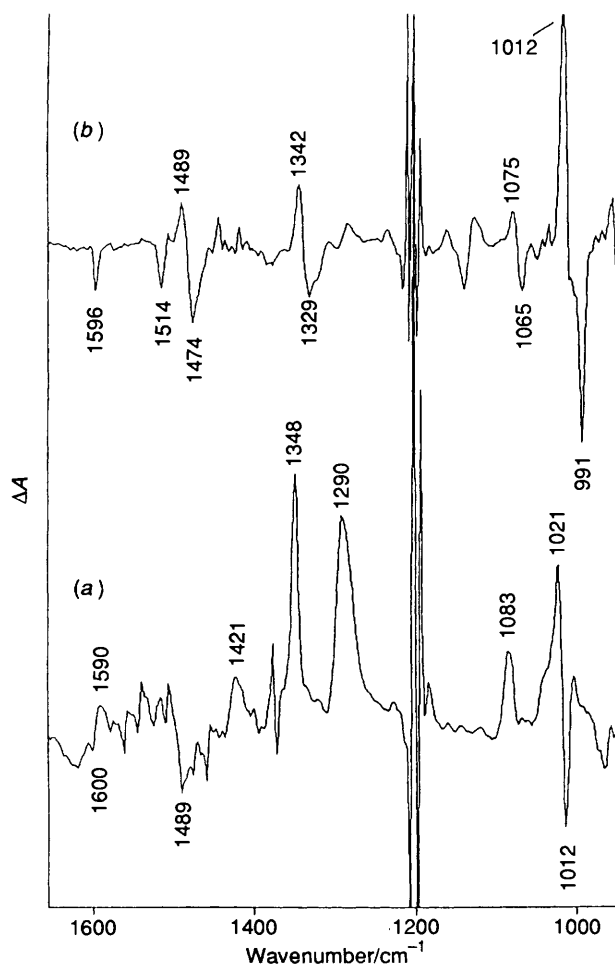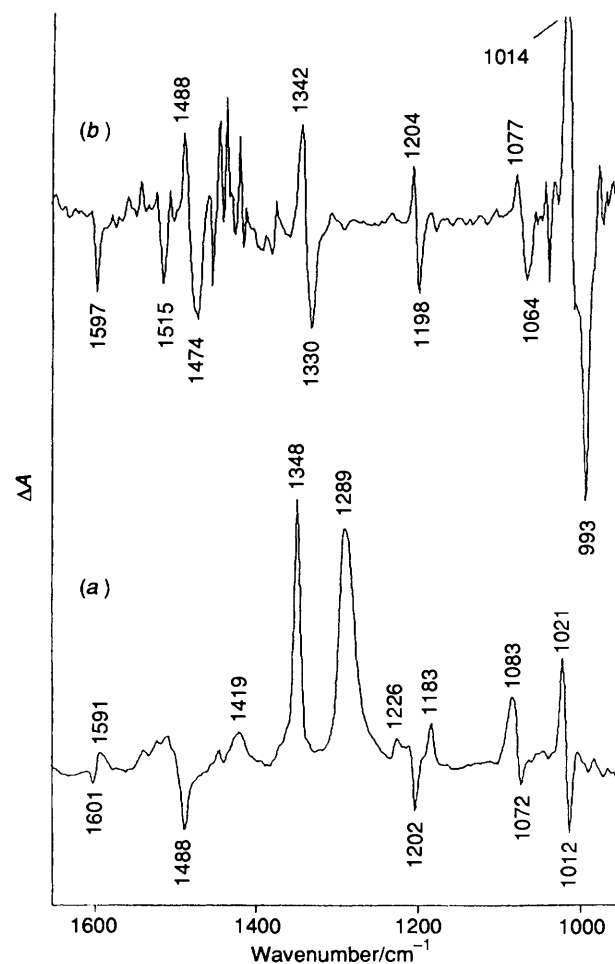**Fig. 5** *In situ* FTIR difference spectra observed for the one-electron oxidation of (a) [Mn(tpp)]ClO$_4$ and (b) [Mn(tpp)] in MeCN containing 0.1 mol dm^{-3} NBu$_4$PF$_6$

although neither underwent any appreciable shift in wavenumber. Again this interpretation is borne out by comparison with the solid-state infrared spectrum of an isolated tpp π-cation radical.[3]

It is believed that the ligand-centred oxidation of tpp metal complexes involves removal of an electron from an a$_{2u}$ molecular orbital to produce a π-cation radical with an A$_{2u}$ ground state.[15] The a$_{2u}$ orbital is predicted to have antibonding character between the N and C$_\alpha$ atoms, as well as the C$_\alpha$ and C$_\beta$ atoms.[16] Since calculations,[14,17] as well as spectroscopic measurements,[18] suggest that the porphyrin ring modes v_{41} and v_{44} contain significant v(C$_\alpha$N) and v(C$_\alpha$C$_\beta$) character, the shift

to higher wavenumber of these modes can be understood in terms of the increased bond strength between these centres, resulting from the removal of an electron from the a$_{2u}$ orbital. The relatively large shift of the v_{51} mode is less easily explained, since this mode is considered to arise from a δ(C$_\beta$H) asymmetric stretch.[14]

In addition to characterizing the perturbation to bands present for the unoxidized porphyrins, the difference spectra indicate the appearance of new bands near 1420 and 1290 cm^{-1} upon ligand-centred oxidation. Additionally, a band near 1230 cm^{-1} can be seen in the difference spectrum of the cobalt complex, and the manganese complex when studied in

Table 3 Wavenumber shifts to existing bands and new bands observed during ligand-centred oxidation of the porphyrin complexes in CH_2Br_2–MeCN (1:1) containing 0.1 mol dm^{-3} NBu_4PF_6

Assignment *	[Mn(tpp)]ClO$_4$	[Fe(tpp)]Cl	[Co(tpp)]$^+$
φ_4'', v(phenyl)	−10	−16	−13
v_{41}, v_{sym}(pyrrole half-ring)	+5	+4	+12
v_{51}, $\delta_{asym}(C_\beta H)$	+7	+7	+12
v_{44}, v_{asym}(pyrrole half-ring)	+9	+11	
		+19	
New bands:	1421	1415	1421
	1290	1280	1298
			1238

* Taken from ref. 14.

Table 4 Wavenumber shifts to existing bands and new bands observed during metal-centred oxidation of the porphyrin complexes in CH_2Br_2–MeCN (1:1) containing 0.1 mol dm^{-3} NBu_4PF_6

Assignment *	[Mn(tpp)]ClO$_4$	[Fe(tpp)]Cl	[Co(tpp)]$^+$
v_{39}, $v_{sym}(C_\alpha C_{meso})$	+15	+10	
v_{41}, v_{sym}(pyrrole half-ring)	+13	−8	+11
v_{51}, $\delta_{asym}(C_\beta H)$	+10	+10	
v_{44}, v_{asym}(pyrrole half-ring)	+21	+8	+9
		+16	+17
Lost bands:	1514	1519	

* Taken from ref. 14.

acetonitrile. One reason for the presence of extra bands in the π-cation radical spectra might be a distortion of the porphyrin ring resulting in a lowering of the effective molecular symmetry. It is known that the solid-state geometry of porphyrin π-cation radicals often shows a 'saddle' distortion which lowers the molecular symmetry from D_{4h} to D_{2d}.[19] Such a distortion might allow the in-plane B_{2g} modes to become infrared active. The v_{29}, v_{27} and v_{34} vibrational modes, which have B_{2g} symmetry, have been calculated to absorb in this wavenumber region.[14] Furthermore, the saddle distortion permits a decrease in the dihedral angle between the phenyl substituents and the plane of the porphyrin ring.[19] This effect might explain the observed perturbation of the phenyl modes φ_4'' and φ_6''. However, if tpp π-cation radicals do adopt a saddle conformation in the solution state, the reason for this remains unclear. Although an argument based on considerations of electronic structure has been advanced,[4] steric factors,[20] as well as solid-state effects,[19] are also considered to be important in determining the conformation of the porphyrin ring in metalloporphyrin complexes.

The mid-infrared difference spectra associated with the metal-centred oxidation of the porphyrin complexes are shown in Figs. 2(b), 3(b), 4(b) and 5(b). Since both metal- and ligand-centred redox reactions were performed using the same thin solution layer without any adjustment to the pathlength, it is possible to compare the difference spectra obtained for both reaction types directly. In general, the pattern of absorbance changes was distinct from those produced on ligand-centred oxidation. The difference spectra contained mainly bipolar features resulting from perturbations to existing vibrational modes (see Table 4). Thus, the oxidation of [Co^{II}(tpp)] to the cobalt(III) species resulted in shifts to higher wavenumber of the vibrational modes v_{41} (ca. 11 cm^{-1}) and v_{44} (ca. 9–17 cm^{-1}). Metal-centred oxidation of the iron(II) porphyrin produced considerably greater perturbation to the mid-infrared bands. In this case there was a shift to lower wavenumber of v_{41} (ca. 8 cm^{-1}). In addition there were shifts to higher wavenumber of v_{39} (ca. 10 cm^{-1}), v_{51} (ca. 10 cm^{-1}) and v_{44} (ca. 8–16 cm^{-1}). Also, the phenyl mode φ_4'' and a second band (possibly due to the phenyl mode φ_5'', ref. 14) lost intensity upon metal-centred oxidation.

The pattern observed for the oxidation of the manganese(II) species was similar to that seen for the iron system except that the wavenumber shifts were larger. Most notably, the v_{44} mode was seen to shift ca. 21 cm^{-1} to higher wavenumber. In addition, v_{41} shifted to higher wavenumber (ca. 13 cm^{-1}), as in the case of the cobalt system.

In relation to the magnitude of the absorbance changes produced upon ligand-centred oxidation, the porphyrin ring vibrational modes were seen to be increasingly perturbed by changes to the metal oxidation state in the order: Co < Fe < Mn. The removal of an electron from a molecular orbital with mainly d character is expected to cause a change in the mixing between the d orbitals and the ligand orbitals, which acts to transfer electron density back onto the metal.[21] Such a perturbation would be likely to have an impact upon the ligand vibrational modes. Oxidation of a manganese(II) porphyrin is considered to involve depopulation of the $d_{x^2-y^2}$ orbital, whereas oxidation of a cobalt(II) porphyrin involves depopulation of the d_{z^2} orbital.[13] Since the $d_{x^2-y^2}$ orbital should have greater overlap with the nitrogen centres of the porphyrin ring relative to that of the d_{z^2} orbital, it might be expected that a greater perturbation of the porphyrin ring vibrations would result from redox processes involving the $d_{x^2-y^2}$ orbital. Furthermore, the observed degree of perturbation decreases as the effective atomic number of the central metal increases. This is reasonable, since the size of the central metal should also be important in determining the degree of overlap between metal-and porphyrin ring-based molecular orbitals. Therefore, the observed trend is suggested to reflect an increase in the degree of mixing between the metal d orbitals and the porphyrin ring orbitals which arises from a reorganization of electron density during the electron-transfer reaction.

Acknowledgements

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