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FTIR and carbon-13 NMR spectra of chalcocarbonyl(5,10,15,20-tetraphenylporphinato)iron(II) complexes

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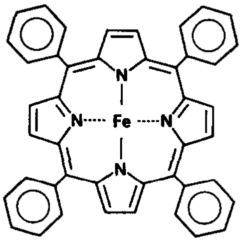
Abstract—The room-temperature, FTIR difference spectra of the solid chalcocarbonyl(5,20,15,20-tetraphenylporphinato)iron(II) derivatives, FeTPP(CX) and FeTPP(CX)L (X = S, Se; L = pyridine, EtOH), have been recorded (in CsI disks) in order to examine the influence of the axially bound CX and L ligands on the vibrations of the metal–porphyrin ring. The ^{13}C NMR spectra of these complexes in CD_2Cl_2 have been measured at room temperature for a similar reason. The vibrations and ^{13}C resonances of the metal–porphyrin ring are only slightly affected by the presence of the axial ligands. The positions of the ^{13}CX NMR resonances and the ν(CX) modes in the i.r. are dependent on the nature of L.

INTRODUCTION

Many metal–porphyrin derivatives have been synthesized as model compounds for the study of the binding of oxygen and other small diatomic molecules to hemoglobin and myoglobin, as well as to further the understanding of the detoxification mechanisms of porphyrin-containing cytochrome P-450 [1]. Among these porphyrin derivatives, (5,10,15,20-tetraphenylporphinato)iron(II) (FeTPP)§ is often used because of its stability and convenient synthesis [2, 3]. The structure of FeTPP is shown below. Four nitrogens bind the iron in the equatorial plane through σ-donation, and two ligands can be introduced at the axial positions to complete a pseudo-octahedral structure. The bonding between the iron and the porphyrin also involves π-donation from the filled metal $d\pi$ orbitals to the vacant π^* orbitals delocalized over the porphyrin ring. The extent of the π-backbonding component of the metal–porphyrin interaction varies with the π-accepting properties of the axial ligands.



Complexes of the form FeTPP(CO)L with axially bound CO *trans* to various ligands L [e.g. py, EtOH, methylimidazole (MeIm)] are especially well-known synthetic models for the study of the binding of CO to hemoglobin [4]. Recently, analogous complexes in which the CO ligand is replaced by a thiocarbonyl or selenocarbonyl ligand have been prepared [5–7]. In addition, the pentacoordinated species FeTPP(CX) (X = S, Se) have been obtained [6, 7]. Although other metalloporphyrin complexes containing a CS ligand have been synthesized [8], Fe(TPP)(CSe) and Fe(TPP)(CSe)L (L = py, EtOH, MeIm) represent the only examples of the incorporation of a CSe group into a metalloporphyrin system. The bonding properties of both the CS and CSe ligands have been reviewed elsewhere [9] and the better σ-donor and π-acceptor capabilities of CS and CSe compared to CO, giving rise to a stronger bonding to low-oxidation state metals, are now well recognized. The CS and CSe ligands may also act as π-donors [10] and a greater flexibility in the bonding properties of these ligands relative to those of CO has been demonstrated [11].

The dramatic effect of the differences between the CS and CSe ligands, on the one hand, and CO, on the other, in the porphyrin complexes studied in the present work is illustrated by the stability of FeTPP(CX) (X = S, Se). Whereas the corresponding FeTPP(CO) derivative is stable only under partial CO pressure [12], the thio- and selenocarbonyl complexes can be heated up to 150°C in vacuum without decomposition [6]. The strength of the Fe–C(X) bond is shown by the stability of the thiocarbonyl and selenocarbonyl complexes towards oxidation in aerated benzene—the half-life of FeTPP(CO)(py) is ~ 5 min [5], while the corresponding selenocarbonyl complex is stable for hours [7], and FeTPP(CS)(py) and FeTPP(CS) are stable to oxidation even after oxygen has been bubbled through the solution for 20 h [5]. The remarkable strength of the Fe–C(S) bond is also indicated by the two-electron oxidation of FeTPP(CS), which occurs without loss of the CS ligand, to form $[Fe(III)TPP(CS)]^+$, whereas FeTPP(CO) loses CO during the removal of the first electron [13].

The effects on metalloporphyrins of substituents on the porphyrin ring and of axially bound ligands have been studied by a variety of spectroscopic techniques [14, 15]. The use of i.r. spectroscopy has been fairly

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§Unless otherwise stated, FeTTP in the various complexes discussed in this paper will represent low-spin Fe(II).

limited, presumably due to the complexity of the porphyrin spectra. The i.r. spectra of tetraphenylporphyrin and several tetraphenylporphyrin metal complexes have been reported and partially assigned by ALBEN *et al.* [16, 17]. The metal–nitrogen stretching vibrations of such complexes, which appear in the far i.r., have also been assigned [18]. In a recent study of the i.r. spectra of a series of iron tetraphenylporphyrin complexes [19], bands sensitive to spin state and oxidation state were identified. In this present paper, the results of a study of the FTIR difference spectra of FeTPP(CX) (X = S, Se) and FeTPP(CX)L (X = S, Se; L = py, EtOH) will be presented. This investigation was undertaken in order to determine the perturbations induced by the axially bound ligands on the metal–porphyrin interactions. Some ^{13}C NMR results are also reported.

EXPERIMENTAL

Sources of materials

Fe(III)TPPCl was purchased from Strem Chemicals. Samples of FeTPP(CX)L (X = S, Se; L = EtOH, py) were synthesized utilizing the literature procedures [6, 7]. The FeTPP(CX) (X = S, Se) complexes were prepared by heating FeTPP(CX)(EtOH) at 160°C for 4 h [6]. FeTPP(CO)(py) was synthesized as described previously [4]. CsI (99.999%) was obtained from Aldrich Chemical Co.

Spectroscopic measurements

The i.r. spectra of the FeTPP derivatives were recorded for samples pressed into CsI pellets, which had been prepared in an argon-purged glove bag. FTIR spectra were obtained on a Nicolet 6000 Fourier-transform i.r. spectrometer (resolution 0.5 cm^{-1}). ^{13}C NMR spectra were measured on a Varian XL-200 spectrometer equipped with a broad-band probe. The chemical shifts reported are relative to TMS.

RESULTS AND DISCUSSION

FeTPP(CO)L complexes are quite unstable with half-lives in aerated solution of the order of minutes [5]. The pentacoordinated complex, FeTPP(CO), decomposes virtually instantly on exposure to air [12]. In contrast, the compounds described here are remarkably stable; their half-lives in solution are of the order of hours [FeTPP(CX)L] or days [FeTPP(CX)] (X = S, Se; L = py, EtOH) [5–7]. The pentacoordinated FeTPP(CX) (X = S, Se) species are stable in air for years in the solid state. The difference in stability between these complexes and their carbonyl analogs indicates a decreasing susceptibility of the metal towards oxidation and accordingly decreasing electron density at the metal in the order CO > CS $\simeq$ CSe. This trend may be interpreted in terms of a greater extent of π-back-donation from the metal to the CS or CSe ligand than to CO [20].

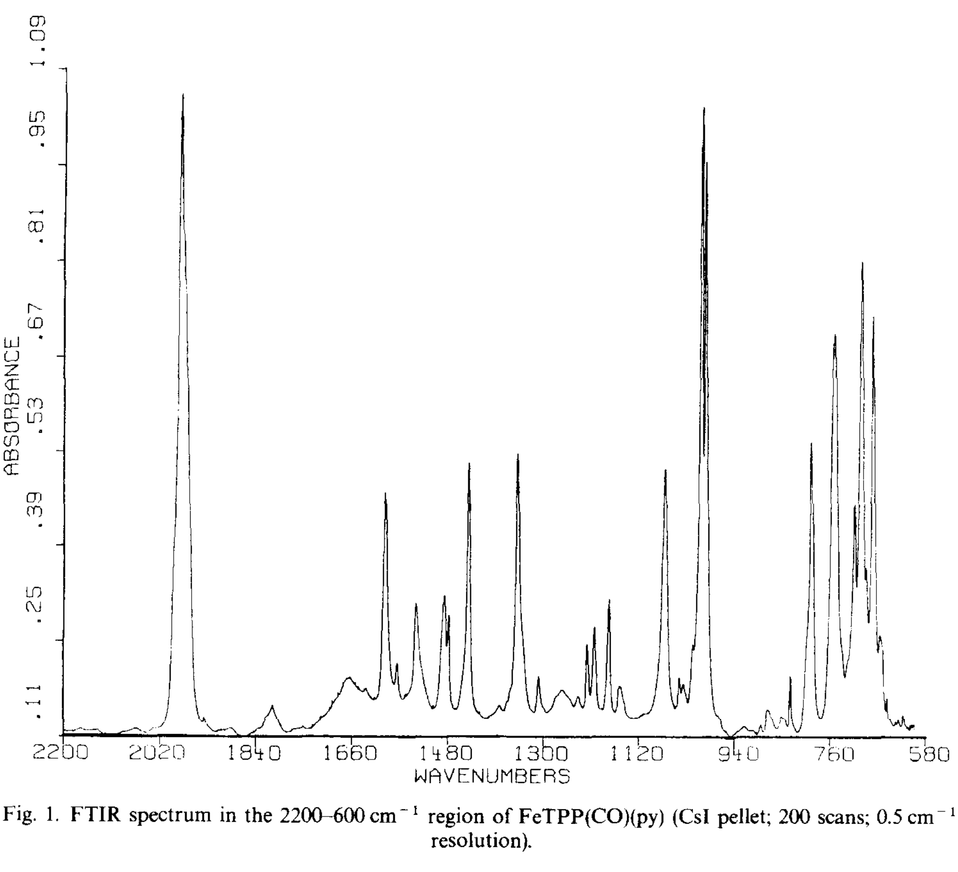

Fig. 1. FTIR spectrum in the 2200–600 cm^{-1} region of FeTPP(CO)(py) (CsI pellet; 200 scans; 0.5 cm^{-1} resolution).

Table 1. Selected frequencies (cm^{-1}) from the FTIR spectra of FeTPP(CX) and FeTPP(CX)(L) derivatives and Fe(III)TPPCl

CX	CO	CS	CS	CS	CSe	CSe	CSe	—
L	py	—	EtOH	py	—	EtOH	py	Cl
Oxidation state	II	II	II	II	II	II	II	III
Spin	0	0	0	0	0	0	0	5/2
ν(CX)	1983.6	1312.4	1294.1	1282.7	1164.7	1137.9	1121.6	—
Aromatic ring vibrations*	1598.4 1441.1	1598.6 1440.6	1598.8 1440.7	1598.8 1440.9	1598.2 1440.6	1598.8 1440.5	1598.6 1440.8	1596.9 1440.3
Spin state marker†	1349.9	1350.8	1350.4	1350.0	1350.3	1350.0	1350.0	1340.2 1334.1
Split in $TPPH_2$*	1176.3	1175.0	1175.7	1176.2	1175.5	1176.7	1176.9	1175.1
Unassigned	1071.2	1072.4	1072.6	1072.3	1072.3	1072.5	1072.1	1069.7
Porphyrin ring vibration*	1002.4	1001.2	1003.1	1003.7	1001.6	1002.9	1004.0	1002.2
Found at 1002 in $TPPH_2$*	995.3	995.3	995.7	996.4	995.5	995.7	996.5	995.5
β-Pyrrole out-of-plane C–H deformation*	796.9	802.6	799.8	795.2	802.6	799.4	795.3	806.5
Split in $TPPH_2$*	752.7	753.2	753.5	752.3	752.7	752.7	752.5	750.5
Porphyrin ring deformation (split in $TPPH_2$)*	714.9	720.7	717.8	713.9	720.5	717.2	713.7	720.3
Unassigned	701.3	704.3	702.1	701.0	703.9	701.4	700.7	703.4

*See Ref. [16].
†See Ref. [19].

The FTIR spectra of these complexes were obtained to assess the effects of the differences in the bonding properties of the ligands on the metal–porphyrin interaction. Some representative spectra of the porphyrin derivatives studied are shown in Figs. 1–3, and the positions of the most important peaks, together with assignments originally proposed by ALBEN *et al.* [16, 17], are listed in Table 1. The first row of this table lists the ν(CX) vibrations, while the remaining frequencies correspond to peaks characteristic of the FeTPP moiety.

Difference spectroscopy provides the simplest

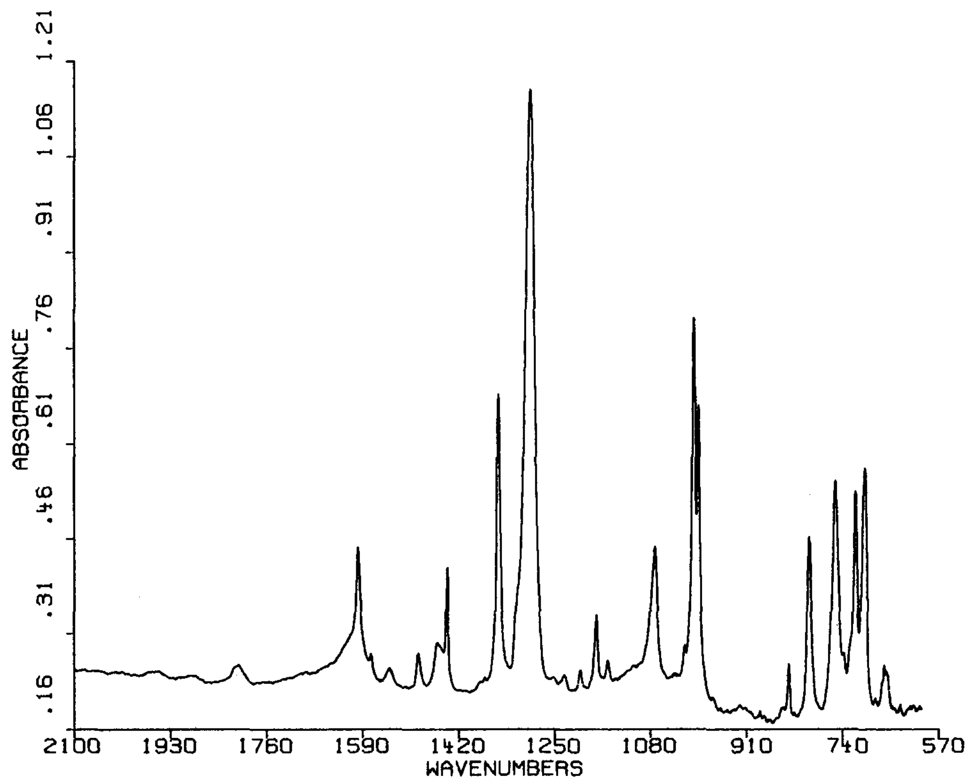

Fig. 2. FTIR spectrum in the 2100–600 cm^{-1} region of FeTPP(CS)(EtOH) (CsI pellet; 200 scans; 0.5 cm^{-1} resolution).

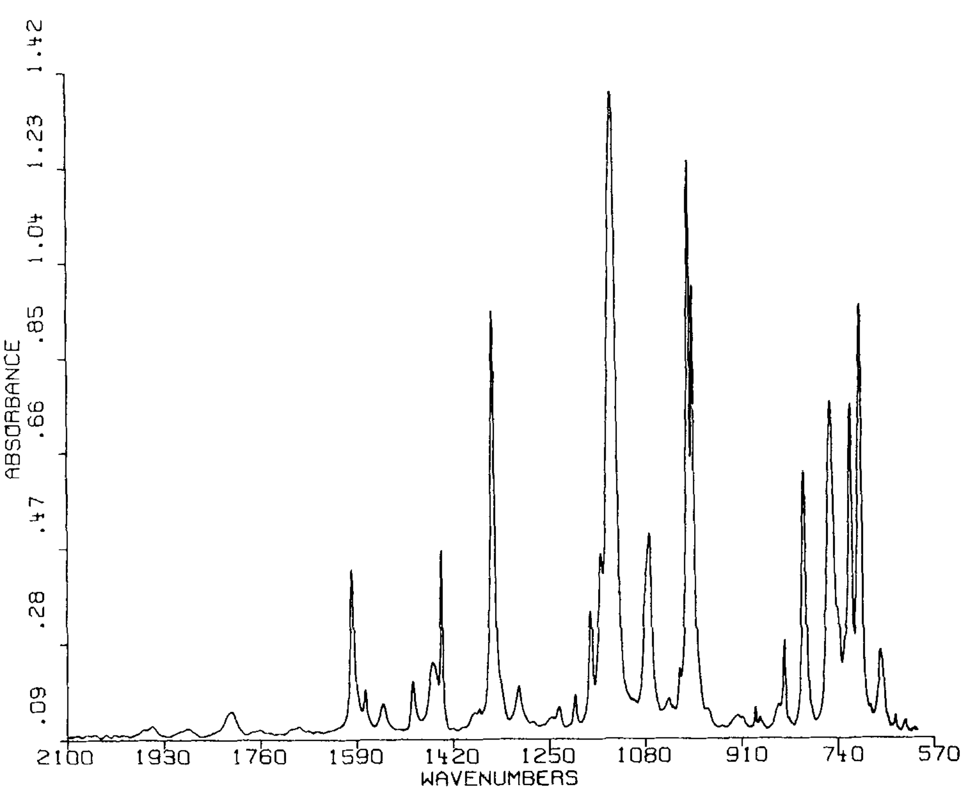

Fig. 3. FTIR spectrum in the 2100–600 cm^{-1} region of FeTPP(CSe)(EtOH) (CsI pellet; 200 scans; 0.5 cm^{-1} resolution).

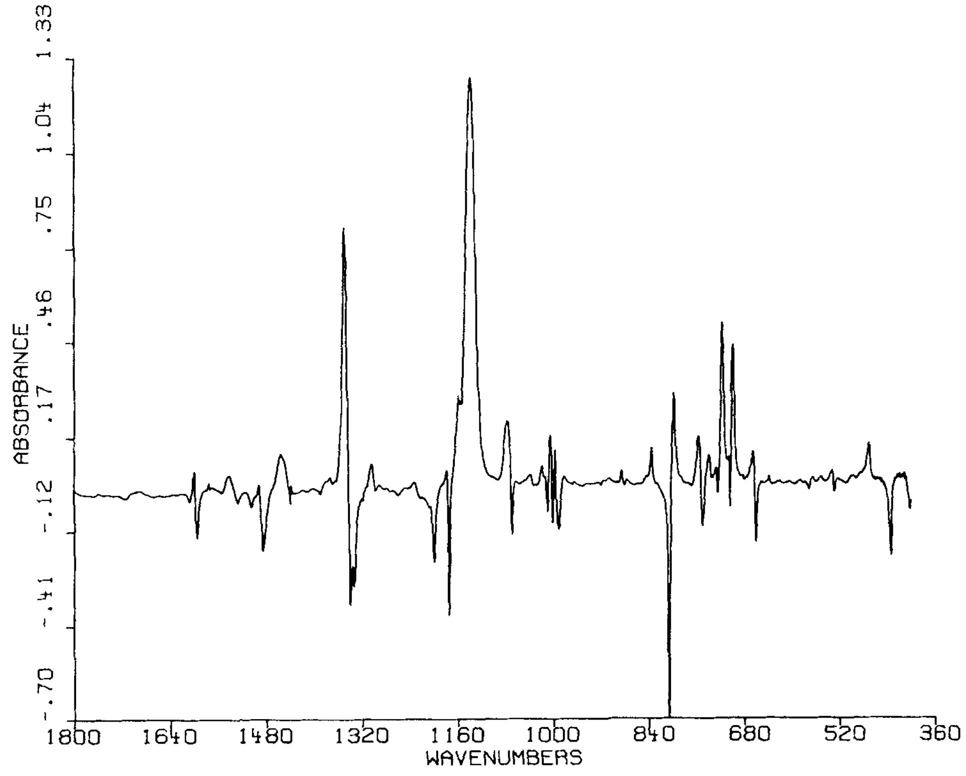

Fig. 4. Difference spectrum obtained by the subtraction of the FTIR spectrum of Fe(III)TPPCl from that of FeTPP(CSe)(EtOH).

method of establishing empirically any perturbations induced by the axial ligands on the porphyrin ring vibrations. In order to illustrate the utility of difference spectra in assessing changes in metal–porphyrin bonding, the spectrum obtained by subtracting the spectrum of Fe(III)TPPCl from that of FeTPP(CSe)(EtOH) is presented in Fig. 4. The features in this spectrum are the result of a number of factors: the different oxidation and spin states of the iron atom in the two complexes; the lower symmetry of Fe(III)TPPCl due to ring puckering [21]; and the absence of axial π-backbonding in the chloride complex.

The difference spectrum obtained by the subtraction of the spectrum of FeTPP(CS)(py) from that of FeTPP(CSe)(py) is shown in Fig. 5. The elimination of all prophyrin vibrations in the difference spectrum indicates that the interactions of the CS and CSe ligands with the metal in these systems are similar. Specifically, the comparable extent of metal $d\pi \rightarrow$ CX π^* back-bonding in these complexes is demonstrated by this result in that the availability of metal $d\pi$ electron density for donation to the π^* orbitals of the prophyrin is a function of the amount of $d\pi$ electron density transferred to the axial ligands [20]. Therefore, any variation in this amount should be reflected in the frequencies of the porphyrin vibrational modes. The difference spectra obtained for the FeTPP(CX)(EtOH) (X = S, Se) pair and the pentacoordinated species, FeTPP(CX), also did not exhibit any features due to the vibrational modes of FeTPP.

Figure 6 displays the FeTPP(CSe)(py)–FeTPP(CO)(py) difference spectrum. The most significant features are the ν(CX) modes at 1984 (X = O) and 1122 (X = Se) cm^{-1} and a peak at 680 cm^{-1} present in the carbonyl complex only due to a Fe–C–O bending mode [22]. The Fe–C–X bending modes are expected below 600 cm^{-1} [23], and this spectral region was not examined. Figure 6 and the data in Table 1 reveal some small shifts (< 2 cm^{-1}) in the positions of porphyrin vibrational modes in the spectrum of FeTPP(CSe)(py) as compared to that of the carbonyl analog. The small magnitudes of these shifts suggest a much greater similarity between the selenocarbonyl (or thiocarbonyl) and the carbonyl complex than do the relative stabilities described earlier. It thus appears that the differences in M–C(X) bond strengths among the carbonyl, thiocarbonyl and selenocarbonyl FeTPP complexes do not induce sufficient changes in the extensively delocalized π-framework of the porphyrin to give rise to significant shifts in vibrational frequencies.

The subtraction of the spectrum of FeTPP(CSe)(EtOH) from that of the corresponding pyridine derivative (Fig. 7) reveals several shifts in peaks due to porphyrin vibrational modes. Similar changes

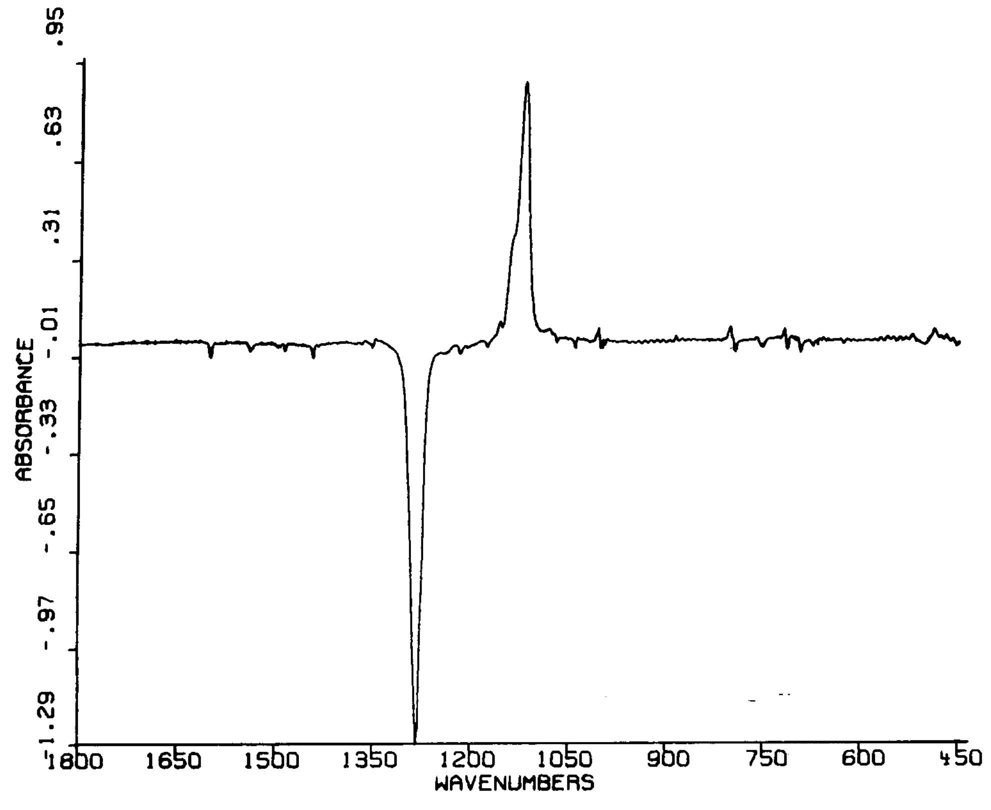

Fig. 5. Difference spectrum obtained by the subtraction of the FTIR spectrum of FeTPP(CS)(py) from that of FeTPP(CSe)(py).

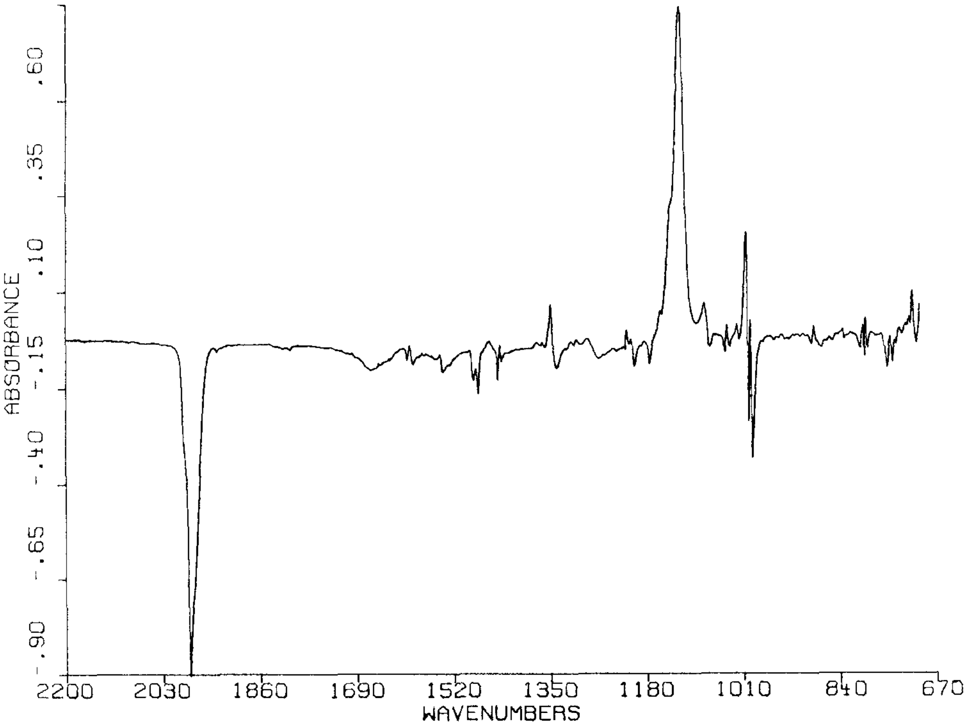

Fig. 6. Difference spectrum obtained by the subtraction of the FTIR spectrum of FeTPP(CO)(py) from that of FeTPP(CSe)(py).

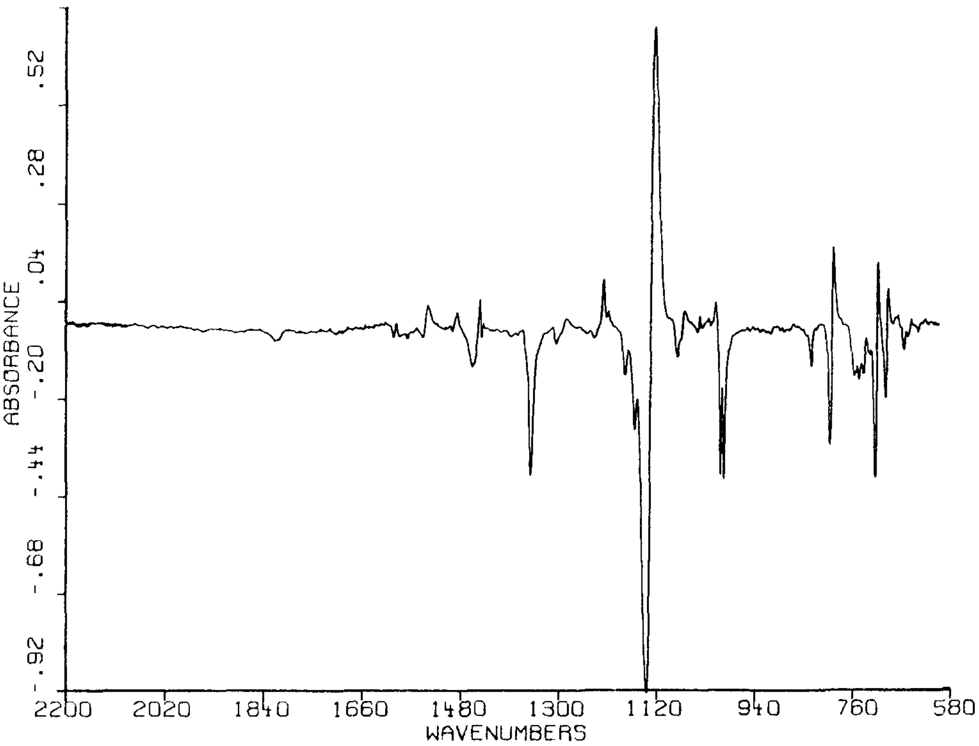

Fig. 7. Difference spectrum obtained by the subtraction of the FTIR spectrum of FeTPP(CSe)(EtOH) from that of FeTPP(CSe)(py).

are observed in Fig. 8 where the spectrum of FeTPP(CS)(EtOH) has been subtracted from that of FeTPP(CS). The positive peak in this spectrum at 1175 cm^{-1} represents a peak which appears in the spectra of both complexes but with an enhanced intensity in the spectrum of FeTPP(CS). This increased intensity may be attributed to reduced symmetry of the porphyrin ring in the pentacoordinated complex: an X-ray crystallographic study of FeOEP(CS) (OEP = octaethylporphyrin) has revealed a 0.23 Å displacement of the iron atom out of the porphyrin plane towards the CS ligand [24]. The data in Table 1 indicate that the shifts observed in the difference spectra with variation in, or removal of, the axial ligand L generally follow a consistent trend. The magnitude of the shift of a given peak relative to its position in the spectrum of FeTPP(CX)(py) (X = S or Se) increases in the order FeTPP(CX)(EtOH) < Fe(III)TPPCl < FeTPP(CX), while the direction of the shift may be towards higher or lower frequencies. This order appears to parallel the extent of displacement of the iron atom out of the porphyrin plane. For instance, FeTPP(CS)(py) exhibits planarity of the FeTPP core [25], while 0.23 and 0.38 Å displacements of the iron atom out of the porphyrin plane have been reported for FeOEP(CS) [24] and Fe(III)TPPCl [21], respectively. It is of interest to note that the 1350 cm^{-1} peak remains unshifted in the spectra of all the Fe(II) complexes. This peak is sensitive to the spin state of the metal [19], and this observation is corroborated in the present study by the appearance of this peak as a shifted doublet in the spectrum of Fe(III)TPPCl at 1340.2 and 1334.1 cm^{-1}. A second peak identified in previous work [19] as oxidation-state sensitive and slightly spin-state sensitive is observed in the 803–795 cm^{-1} range in the spectra of all the Fe(II) complexes studied here and at 807 cm^{-1} in the spectrum of Fe(III)TPPCl. Among the Fe(II) complexes, this peak shifts to higher energy on going from FeTPP(CX)(py) to FeTPP(CX)(EtOH) and is further shifted to higher wavenumber in the spectrum of the pentacoordinated species. Since the shifts of peaks sensitive to oxidation state are generally interpreted in terms of changes in the amount of metal $d\pi$ electron density transferred to the porphyrin π^* orbitals [19], the above data indicate that the extent of metal-to-porphyrin π-back-donation in the complexes studied here increases in the order FeTPP(CX) < FeTPP(CX)(EtOH) < FeTPP(CX)(py).

The resonance Raman spectra of FeTPP(CS) and FeTPP(CS)(py) have been reported as part of a resonance Raman investigation of a series of iron tetraphenylporphyrin complexes [25]. Spectra were obtained with excitation into both of the characteristic visible absorption bands of porphyrins—the Soret and α, β bands. From the data obtained for the entire series

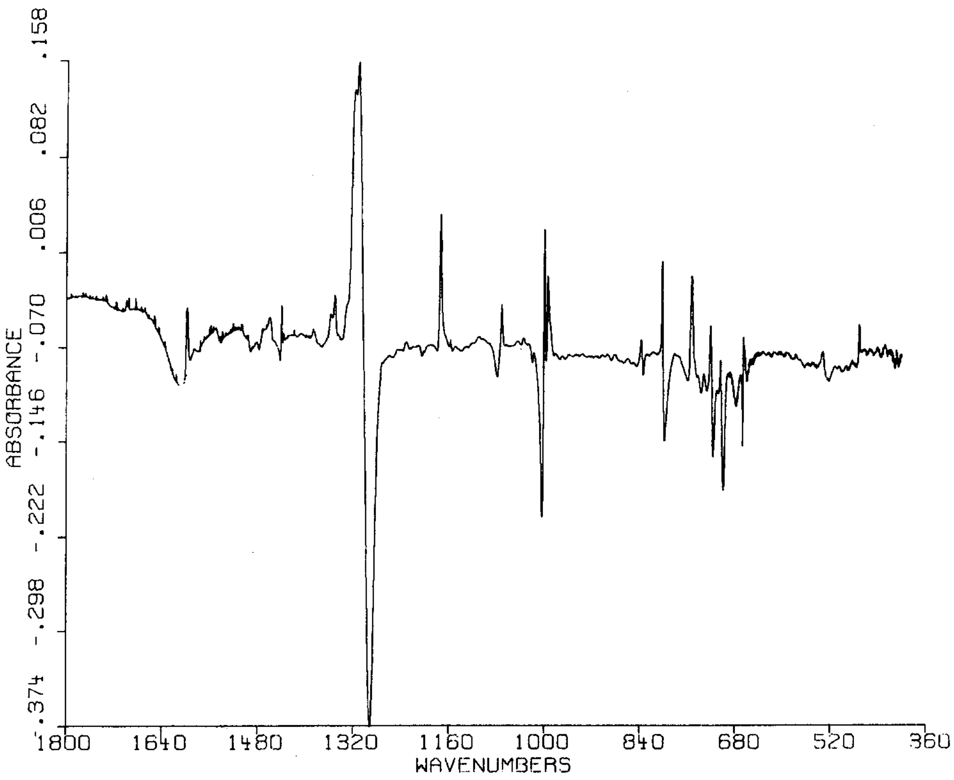

Fig. 8. Difference spectrum obtained by the subtraction of the FTIR spectrum of FeTPP(CS)(EtOH) from that of FeTPP(CS).

Table 2. ^{13}C NMR chemical shifts of FeTPP(CX) and FeTPP(CX)(L) complexes (X = S, Se)*†

Complex	α	β	meso	$C_{1''}$	$C_{2''},C_{6''}$	$C_{3''},C_{5''}$	$C_{4''}$	CX
FeTPP(CS)‡	146.5	133.1	122.7	141.9	134.2	127.3	128.2	308.1
FeTPP(CS)(EtOH)§	145.7	132.5	121.8	141.7	133.6	126.7	127.6	313.5
FeTPP(CS)(py)||	145.6	132.0	121.2	142.3	133.6	126.6	127.3	315.4
FeTPP(CSe)‡	146.3	133.0	122.7	141.9	134.0	127.3	128.2	305.1
FeTPP(CSe)(EtOH)¶	145.8	132.5	122.1	141.6	133.6	126.9	127.8	320.1

*Chemical shifts in ppm (±0.1 ppm) relative to TMS.
†Assignments adopted from Ref. [15], Ch. 1, p. 43.
‡In CD_2Cl_2 solution.
§Data from Ref. [6]; $CDCl_3$ solution.
||In CD_2Cl_2 solution containing 10% (v/v) pyridine-d_5.
¶Data from Ref. [7]; $CDCl_3$ solution.

of complexes studied, two bands sensitive to the extent of metal-to-porphyrin π-back-donation were identified. Both of these bands shift to a higher wavenumber on going from FeTPP(CS)(py) to FeTPP(CS), indicating that less electron density is transferred from the metal to the porphyrin in the pentacoordinated complex, in agreement with the present study. This result was attributed to the displacement of the iron atom out of the porphyrin plane in FeTPP(CS), leading to less favorable overlap of the Fe $d\pi$ orbitals and the porphyrin π^* orbitals than is the case in planar species such as FeTPP(CS)(py) [25].

In view of the frequency variations observed between the i.r. spectra of FeTPP(CX), FeTPP(CX)(py) and FeTPP(CX)(EtOH) for a given X, it is of interest to assess the extent of metal → CX π-back-donation in these various complexes. While differences in carbonyl frequencies can be related to changes in the CO bond order [i.e. the energy-factored force field approximation is valid for ν(CO) modes] [26], the CS and CSe stretching frequencies cannot serve as direct measures of bond order due to increased mixing of M–C(X) and C–X stretching modes with increase in the mass of X [27]. This effect was noted in a study of M(II)OEP(CS)(py) (M = Fe, Ru, Os) [8], and data for FeOEP(CS) do not fit the relationship between ν(CS) and the C–S bond distance established for a series of metal thiocarbonyl derivatives [24]. However, a trend in ν(CX) values among a series of related compounds can generally be considered to reflect variations in M → CX π-back-bonding. It can be seen from Table 1 that replacement of a pyridine ligand by an ethanol ligand results in an increase in ν(CX) (X = S, Se), indicating that when the *trans* ligand is ethanol less electron density is donated to the metal. The higher ν(CX) for the pentacoordinated complexes is indicative of a further decrease in the net electron density at the metal. The trend in ν(CX) frequencies thus suggests that the availability of metal electron density for π-back-donation to the porphyrin decreases in the order FeTPP(CX)(py) > FeTPP(CX)(EtOH) > FeTPP(CX). This finding is consistent with the conclusions reached after examination of the porphyrin vibrational modes in both the i.r. and resonance Raman spectra.

Attempts were made to coordinate a CO ligand *trans* to CX (X = S, Se) in the pentacoordinated FeTPP(CX) complexes [Eq. (1)], since the frequencies of the ν(CO) modes of the FeTPP(CO)(CX) complexes would provide a quantitative measure of the extent of $d\pi$ electron density transferred to the CX ligands*

$$\mathrm{FeTPP(CX) + CO} \overset{K_1}{\rightleftharpoons} \mathrm{FeTPP(CO)(CX)}\ (\mathrm{X = S, Se}). \tag{1}$$

The reactions represented by Eq. (1) did not take place even at CO pressures of 20 atm, while the corresponding reaction of FeTPP(CO) under less than 1 atm CO pressure yields $FeTPP(CO)_2$ [12]. However, the latter complex undergoes facile CO loss. The equilibrium constants for the formation of the monocarbonyl and dicarbonyl complexes by the following reactions:

$$\mathrm{FeTPP + CO} \overset{K_1}{\rightleftharpoons} \mathrm{FeTPP(CO)} \tag{2}$$

$$\mathrm{FeTPP(CO) + CO} \overset{K_2}{\rightleftharpoons} \mathrm{FeTPP(CO)_2} \tag{3}$$

have been reported [12]. K_1 [$(6.6 \pm 0.3) \times 10^4$] was found to be much greater than K_2 (140 ± 3) in direct contrast with the corresponding reaction of deuteroheme (H) with pyridine where K_1 for the formation of H(py) is substantially smaller than K_2 for the formation of $H(py)_2$ [28]. The lower affinity of the iron atom for CO after binding of one CO ligand has been attributed to the decreased availability of Fe $d\pi$ electron density for π-back-donation to CO after formation of the first Fe–CO bond [12]. This is manifested in the substantially higher ν(CO) value for $FeTPP(CO)_2$ as compared to that of FeTPP(CO) [12]. The lack of CO incorporation into the

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*FeTPP(CX) (X = S, Se) (20 mg) was dissolved in deaerated spectrograde benzene (10 ml) under argon. The solution was transferred to a high-pressure reactor and degassed in three freeze–thaw cycles. The reaction compartment of the vessel was then pressurized with CO (20 atm). After periods of 6–24 h, CO gas was removed by adsorption on charcoal in a second compartment. The FTIR spectra of the solutions did not exhibit any peaks in the ν(CO) region.

FeTPP(CX) complexes (i.e. $K_t < K_2$) provides further experimental evidence of the stronger π-acceptor capacities of CS and CSe compared to CO.

As part of the present study, the ^{13}C NMR spectra of FeTPP(CX) (X = S, Se) and FeTPP(CS)(py) were recorded. The positions of the resonances are listed in Table 2, together with the corresponding values from the literature for FeTPP(CX)(EtOH) [6, 7]. Comparison of the chemical shifts for the CX resonance of FeTPP(CX) with that for FeTPP(CX)(EtOH) reveals an upfield shift in the pentacoordinated species. The CS resonance of FeTPP(CS)(EtOH) is in turn upfield from that of FeTPP(CS)(py). It has been established in studies of the ^{13}C NMR spectra of metal chalcocarbonyl complexes that an upfield shift in the position of a CX (X = O, S, Se) resonance is indicative of a decrease in the extent of metal-to-chalcocarbonyl π-back-donation [29, 30]. Accordingly, the trends observed for the ^{13}CX resonances are consistent with those for the ν(CX) modes in the i.r. spectra. The other peaks listed in Table 2 exhibit very small shifts with variation in the axial ligands. In particular, it may be noted that replacement of a CS ligand by CSe in a given complex has virtually no effect on the ^{13}C NMR spectrum of the FeTPP moiety.

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