coordination number of 4, contact is obtained between the Se^{4+} ion and Cl$^-$ ions in contrast to the case when the coordination number is 6). The formation of SeCl$_3^+$ rather than SeCl$_4$ is probably due to the presence of the stereochemically active lone pair.[28]

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Registry No. AlCl$_3$, 7446-70-0; NaCl, 7647-14-5; SeCl$_4$, 10026-03-6; Na$_2$O, 1313-59-3; SeCl$_3^+$, 21687-08-1; SeOCl$_2$, 7791-23-3; AlCl$_4^-$, 17611-22-2; Al$_2$Cl$_7^-$, 27893-52-3.

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Resonance Raman Spectra of Iron Tetraphenylporphyrin Complexes: Characterization of Structure and Bonding Sensitive Bands

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Resonance Raman spectra of iron–TPP complexes of general formula Fe^n(TPP)(L)(L′) with n = II or III are reported. The use of two different exciting lines allows the observation of totally and non totally symmetric modes. The frequencies of four structurally significant Raman bands, A (ca. 1360 cm^{-1}, p), B (ca. 1375 cm^{-1}, dp), C (ca. 1520 cm^{-1}, ap), and D (ca. 1560 cm^{-1}, p), are discussed: all of them are dependent on the spin of the iron atom. Among the non totally symmetric modes the occurrence of band B is characteristic of pentacoordinated derivatives, and the frequency of band C which appears as equivalent to band IV of physiological porphyrins is a sensitive spin indicator. Within the low-spin Fe$^{\mathrm{II}}$ derivatives, the frequencies of the totally symmetric modes A and D are both sensitive to $d\pi(\mathrm{Fe})$–$\pi^*(\mathrm{TPP})$ interactions: band A frequency is more specifically dependent on the π acidity of the axial ligand, and band D frequency reflects the stereochemistry around the iron atom. Finally, the vibrational pattern of pentacoordinated complexes is very distinctive.

During the last years, resonance Raman (RR) spectroscopy has been increasingly used to characterize hemoproteins and physiological porphyrin derivatives.[1] Correlations have been established between the frequencies of some prominent Raman bands and the spin and oxidation states of the iron atom in protoporphyrin IX and in mesoporphyrin: for example band I is considered as an oxidation-state marker band, while band IV is a spin marker band (nomenclature according to ref 2). Meanwhile, due to the convenient synthesis of iron tetraphenylprophyrin (hereafter TPP), a great number of Fe(TPP) derivatives have been prepared, as models for various hemoproteins complexes.[3,4] Usually X-ray structural studies have been carried out, and some of the data have been used to get a better insight into the heme structure, as the measurements on the proteins are of much lower accuracy. As far as the optical properties are concerned, the comparisons between Fe(TPP) complexes and hemoproteins derivatives have not been carried out to such an extent. And indeed significant differences exist in the visible spectra of Fe(TPP) derivatives compared to that of physiological porphyrins such as shifts on band positions and absence of $\alpha\beta$ splittings.[5] Recently a resonance Raman study has been devoted to some Fe(TPP) derivatives, showing a vibrational pattern poorer than that of physiological porphyrins: with use of blue excitation, only totally symmetric modes were observed, and three prominent bands were characterized, whose frequencies are altogether dependent on both the spin and oxidation states of the iron.[6]

As new derivatives have been described and structurally characterized,[7-9] including pentacoordinated low-spin Fe$^{\mathrm{II}}$ complexes, we think it worthwhile to investigate their Raman spectra, using both Soret and β excitations, and reinvestigate some of the previously examined derivatives, with β excitation. Thus the frequency changes of the totally symmetric modes, already described in ref 6, have been studied as a function of various electronic and structural parameters; non totally symmetric modes have been characterized, mainly band B (dp, ca. 1370 cm^{-1}) which only occurs in pentaccordinated species and band C (ap, ca. 1500–1550 cm^{-1}), whose frequency is dependent on the spin state of the iron and thus appears as the equivalent of band IV of physiological porphyrins. Finally a vibrational pattern characteristic of pentacoordination is proposed.

Experimental Section

In the Fe$^{\mathrm{III}}$ series, the complex [Fe(TPP)(Me$_2$SO)$_2$]$^+$[10] was obtained by dissolution in Me$_2$SO of [Fe(TPP)(C$_2$H$_5$OH)$_2$]BF$_4$, which was

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(10) Abbreviations: Me$_2$SO = dimethyl sulfoxide; Im = imidazole; py = pyridine; pip = piperidine; *i*-PrNO = isopropylnitroso; TPP = dianion of tetraphenylporphyrin; TpClPP = diianion of tetrakis(*p*-chlorophenyl)porphyrin; TpivPP = dianion of *meso*-5,5,5,5-tetrakis(*o*-(pivaloylamido)phenyl)porphyrin; MS = dianion of mesoporphyrin; PP$_{\mathrm{IX}}$ = dianion of protoporphyrin IX; Hb = hemoglobin.

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Table I. Resonance Raman Frequencies (cm^{-1}) of Fe(TPP)(L)(L′) Complexes

		L									
band no.		CS	CS L′ = py	CCl_2	$C{=}C(p\text{-}ClC_6H_4)_2$	$C{=}C(p\text{-}ClC_6H_4)_2$ L′ = py	=C= (carbene dimer)	CH_3NO	CH_3NO L′ = py	NO	Me_2SO L′ = Me_2SO
1	p	1602			1598		1599		1599		1602
2	dp	1591		1593	1592		1588				
3	p	1572	1563	1571	1572	1566	1569	1570	1560	1567	1545
4	p			1556			1555	1552			
5	ap	1543	1540	1545	1543	1539	1540	1542	1539	1538	1507
6	dp	1509	1504	1508	1508	1505	1502	1503	1499	1505	1499
7	p	1469			1469	1462		1473		1470	1442
8	p	1409	1405	1407	1404	1407		1407	1407	1408	
9	dp	1376		1377	1379		1377	1376			
10	p	1368	1366	1369	1369	1367	1365	1365	1366	1368	1360
11	ap	1342		1347	1342	1344		1340	1345		1335
12	dp	1297	1288								1290
13	dp	1269			1267			1265	1268		1269
14	p	1237	1236	1237	1232	1236	1234	1240	1235	1237	1239
15	ap	1221	1218	1221	1220			1211	1217		
16	dp	1189			1189				1184		1183
17		1081	1078	1079	1077		1081		1077	1078	
18		1031	1028		1029		1034		1028		
19		1019									
20		1011		1011							
21		1002	1001	1004	1003				1004		
22		887	886	869	885	884					
23		835	837		837	834			829		825
24		787									
25	p	668									
26	p	638	638		639	636	635		636		
27	p	393	391	390	391	393	392		389	388	385
28	p	366								373	
29	p	333	335	338	334	337	334		334		
30	p	260									
31	p	200	202	203	200	203			202		201

prepared according to ref 11. In the Fe^{II} series the synthesis of the pentacoordinated complexes Fe(TPP)(L) with carbenic axial ligands L = CS, CCl_2, C = $C(p\text{-}ClC_6H_4)_2$ and $(Fe(TPP))_2C$ have been already described.[7] The corresponding hexacoordinated complexes Fe(TPP)(L)(L′) with L′ = amine were obtained by dissolution of Fe(TPP)(L) in a solvent containing 1% of the appropriate amine. The complexes with L = alkylnitroso and L′ = amine were synthesized according to ref 8; when L′ = CH_3OH, the pentacoordinated alkylnitroso complex is generated in dilute solution.[12] The compounds Fe(TPP) and Fe(TPP)(2-CH_3Im) were obtained by reduction of Fe(TPP)Cl by sodium dithionite, using a bilayer technique.[13] All other compounds were obtained following classical procedures already described.[14]

The Raman spectra were measured in C_6H_6 and $CHCl_3$ solutions at 10^{-3} M concentration, using a rotating cell. The same cell was used to record the visible absorption, before and after the Raman measurements. A Coderg double monochromator was used, with Ar^+ and Kr^+ laser excitation. The laser power on the sample was kept ca. 50–60 mW for $\lambda_0 > 500$ nm and ca. 30 mW for $\lambda_0 < 500$ nm. The detection used a dc amplifier and a cooled RCA C31034 PM tube. The slit width is usually 5 cm^{-1}, and the frequencies are accurate within ± 1.5 cm^{-1}.

The Raman data on the hemoglobin derivatives were recorded in phosphate buffer at pH 7.4. HbCO was obtained from stripped human Hb by CO bubbling; HbC_6H_5NO and HbC_2H_5NC were obtained from deoxyhemoglobin by addition of the corresponding ligands,[15] and HbNO and $HbCH_3NO$ were prepared from HbO_2, by addition of $NaNO_2$ and CH_3NO_2, respectively, in the presence of $Na_2S_2O_4$.[16]

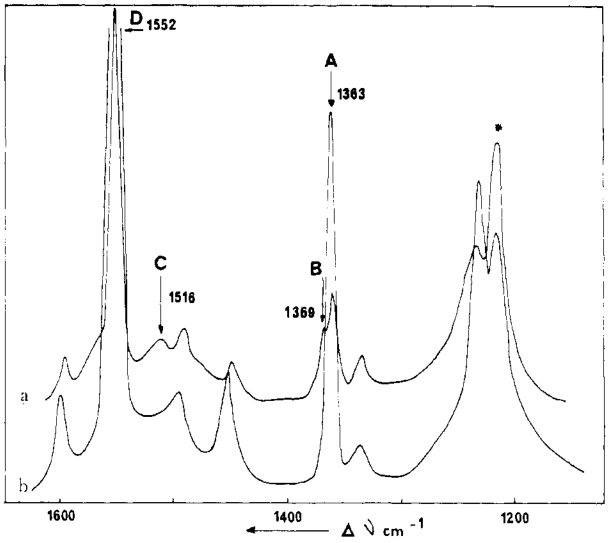

Figure 1. Raman spectrum of Fe(TPP)(Cl) in $CHCl_3$ (concentration 1 mg/mL). Excitation wavelength: a, 514.5 nm (60 mW); b, 457.9 nm (30 mW). The solvent band is indicated by an asterisk.

Results and Discussion

The Fe^{III} complexes Fe(TPP)(L) with L = Cl, O (μ-oxo), and Fe(TPP)(L)(L′) with L = L′ = Im and the Fe^{II} complexes Fe(TPP)(L) with L = 2-CH_3Im and Fe(TPP)(L)(L′) with L = L′ = pip or py already studied with 457.9-nm excitation by Burke et al.[6] were reinvestigated with use of both Soret (mainly 457.9 nm) and β excitation (mainly 514.5 and 530.8 nm). With blue excitation no significant discrepancies were observed between our results and the previous ones. As we worked with two sets of exciting lines, we observed some extra bands, in the high frequency region, mainly around 1410 (p), 1375 (dp),

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Table II. Structurally Significant Frequencies of Fe(TPP)(L)(L′) Complexes

L	L′	oxidn state	spin	$C_t \cdots N$,[a] Å	$Fe \cdots C_t$,[a] Å	A (p), cm^{-1}	B (dp), cm^{-1}	C (ap), cm^{-1}	D (p), cm^{-1}
Cl		III	$5/2$	2.012	0.38	1363	1369	1516	1552
O		III	$5/2$	2.027	0.5	1360	1368	1511	1554
Me_2SO	Me_2SO	III	$5/2$	2.045	0	1360		1507	1545
Im	Im	III	$1/2$	1.989	0.01	1370		1540	1568
		II	1	1.972	0	1367		1540	1565
$2\text{-}CH_3Im$		II	2	2.044	0.42	1345	1365	1500	1542
pip	pip	II	0	2.004	0	1355		1540	1560
py	py	II	0			1359		1543	1560
CO	py	II	0			1365		not observed	
NO		II	0	1.990	0.211	1368		1538	1567
O_2[b]	1-MeIm	II	0	1.98	0.03	1366			1563
i-PrNO		II	0			1365	1376	1542	1567
CH_3NO	py	II	0			1366		1539	1560
CS		II	0			1368	1376	1543	1572
CS	py	II	0	1.988	0	1366		1540	1563
CCl_2		II	0			1369	1377	1545	1571
$C{=}C(p\text{-}ClC_6H_4)_2$		II	0	1.97	0.2	1369	1379	1543	1572
$C{=}C(p\text{-}ClC_6H_4)_2$	py	II	0			1367		1539	1566
=C= (carbene dimer)		II	0			1365	1377	1540	1569

[a] X-ray data from ref 11, except for L = L′ = Me_2SO,[9] L = CS, L′ = py,[20] and L = $C{=}C(p\text{-}ClC_6H_4)_2$.[21] [b] Raman data for Fe(TpivPP)(1-CH_3Im)(O_2).[6] This complex can be also considered as an $Fe^{III}O_2^-$ complex.[6] The use of either formalism is still a matter of controversy.[26]

1300 (dp), and 1190 (dp) cm^{-1}, all showing maximum intensity within the β absorption region.

The Raman frequencies of the high-spin Fe^{III} complex with L = L′ = Me_2SO (some of which are already given in ref 17), of the low-spin Fe^{II} pentacoordinate complexes with L = NO, CH_3NO, CS, CCl_2, $C{=}C(p\text{-}ClC_6H_4)_2$, or =C= (carbene dimer), and of the low-spin Fe^{II} hexacoordinate complexes with L = CH_3NO, CS, $C{=}C(p\text{-}ClC_6H_4)_2$ and L′ = py are given in Table I. The three prominent polarized Raman bands mentioned by Burke et al.[6] are easily identified on the spectra. The assignment proposed in ref 18 may be used to describe some of the vibrational modes: thus bands numbered 1, 18, 21, and 22 are phenyl modes; the newly observed band 7 at 1410 cm^{-1} may also be a phenyl band as it is slightly shifted in Fe(TpClPP)(*i*-PrNO)(py) when compared to Fe(TPP)(*i*-PrNO)(py).

Due to the low concentration of the complexes, axial ligand vibrations would show up in the Raman spectra only if they are resonance enhanced; selection rules preclude such an enhancement. However, in the case of $Fe(MP)(py)_2$ strong axial ligand modes have been observed.[2] Careful examination of the whole series of spectra under study allows elimination of any significant contribution of axial ligand modes: for instance spectra of Fe(TPP)CS and Fe(TPP)[$C{=}C(p\text{-}ClC_6H_4)_2$] are very similar in the 1200–1600-cm^{-1} region; so are the spectra of Fe(TPP)CCl_2 and Fe(TPP)CH_3NO.

Most of the porphyrin bands exhibit frequency changes dependent on the nature and number of axial ligands and the spin and oxidation states of the iron atom. Among them, a few are easily characterized either by their strong intensity or their polarization properties. Therefore our interest is focussed on bands we call A (p, ca. 1365 cm^{-1}), B (dp, ca. 1375 cm^{-1}), C (ap, ca. 1500–1540 cm^{-1}), and D (p, ca. 1550–1570 cm^{-1}). Bands A and D belong to the set of three polarized bands mentioned previously.[6] The third band of this set ca. 380 cm^{-1} is easily characterized in all the spectra we have studied: its frequency varies within 8 cm^{-1}, and in this narrow range no correlation with electronic and structural factors is obvious.

Band A (p, ca. 1365 cm^{-1}). Considering its frequency and polarization, it is quite analogous to band I, or the oxidation-state marker band, of physiological porphyrins. If we consider the overall frequency variations of band A (Table II), their dependency on the oxidation state of the iron is not obvious at first, as the frequencies lie in the 1360–1370-cm^{-1} range for Fe^{III} derivatives and in the 1345–1369-cm^{-1} range for Fe^{II} derivatives. A dependency on the spin state is noticed more clearly, as among the Fe^{II} pentacoordinate complexes band A is at 1345 cm^{-1} for the high-spin Fe(TPP)(2-CH_3Im) complex and at 1364–69 cm^{-1} for the low-spin Fe(TPP)(L) complexes with L = CH_3NO, CS, CCl_2, $C{=}C(p\text{-}ClC_6H_4)_2$, =C=, or NO, and among the Fe^{III} hexacoordinate complexes, band A is at 1360 cm^{-1} for the high-spin $[Fe(TPP)(Me_2SO)_2]^+$ complex and 1370 cm^{-1} for the low-spin $[Fe(TPP)(Im)_2]^+$ complex. Considering the data of ref 2 and 18, a quite similar dependency on spin state is indeed noticeable on band I of physiological porphyrins for Fe^{II} derivatives but not for Fe^{III} derivatives. So it is this absence of sensitivity of Fe^{III} frequencies to spin effect that has allowed one to consider band I as an oxidation-state marker band (Figure 2).

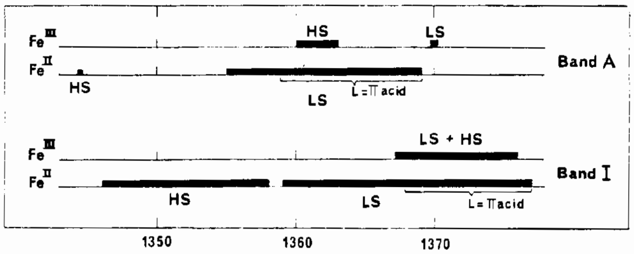

Figure 2. Comparison of the frequencies of bands A and I. Band A data are from this work, and band I data are from ref 19: HS = high spin; LS = low spin.

Keeping this in mind, if we select low-spin hexacoordinate complexes, band A shows an oxidation-state dependency as it occurs at 1355 cm^{-1} for $Fe(TPP)(pip)_2$ and 1370 cm^{-1} for $Fe^{III}(TPP)(Im)_2$, as already noticed by Burke et al.[6] Among the low-spin Fe^{II} complexes Fe(TPP)(L)(py), a sensitivity of the A frequency to the π-acceptor character of ligand L is noticeable: it changes from 1359 cm^{-1} for L = py to 1366 cm^{-1} for L = CH_3NO, CO, or CS and 1367 cm^{-1} for L = $C{=}C(p\text{-}ClC_6H_4)_2$; accordingly the $Fe(TPP)(pip)_2$ complex with axial donor ligands exhibits an even lower frequency. As a comparison we have measured the frequency of band I for low-spin Fe^{II} derivatives of hemoglobin $HbFe^{II}L$ at 1368 cm^{-1} for L = C_2H_5NC: 1372 cm^{-1} for L = CO; 1375 cm^{-1} for L

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= C_6H_5NO; 1376 cm^{-1} for L = NO, or CH_3NO; 1377 cm^{-1} for L = O_2. We see that for low-spin Fe^{II} derivatives the sensitivity to π-donor–π-acceptor ability of the axial ligand is similar in the Fe(TPP) and in the Fe(PP$_{IX}$) series. From the variations of the frequencies of band I in a series of Fe-(MP) derivatives, it has been suggested[2] that the sensitivity of this frequency to π acidity of the axial ligands may be rationalized by considering the back-donation from the iron dπ electrons to the π* orbitals of the porphyrin ring: π-acid axial ligands compete for those electrons, thus decreasing the π* population of the ring and allowing a concomittant strengthening of the bonds of the ring. Thus in the two low-spin Fe^{II} series Fe(TPP)(L)(L′) and HbFe^{II}L, the A and I frequencies allow a distinction between strong π-acceptor axial ligands such as CO, NO, O_2, RNO, C_6H_5NO, and CR_2 and poor π-acceptor ligands such as amines and isocyanides.

From Figure 2, it is clear that bands A and I show an overall similar behavior, the main difference being that the mean frequency of A is smaller than the mean frequency of I. It comes out also that both bands are not good marker lines of the formal oxidation state of the iron (for band I this point is also discussed in ref 19).

In the hemoproteins and Fe(MP) series, two other bands, band III (dp, ca. 1550 cm^{-1}) and band V (dp, ca. 1620 cm^{-1}), follow band I behavior.[2] In the Fe(TPP) series the depolarized band (numbered 6 in Table I) at ca. 1500 cm^{-1} follows quite well band A variations. Due to its lower intensity it is not as convenient a marker as band A.

Band C (ap, 1500–1550 cm^{-1}). This band is anomalously polarized and detectable only by β excitation. It shows the largest frequency shift (1500–1545 cm^{-1}) that we have observed during this study. Its polarization properties make it analogous to band IV of physiological porphyrins. Like band IV, its frequency is spin-state dependent, being 1500 cm^{-1} for high-spin Fe^{II}(TPP)(2-CH_3Im), varying from 1508 to 1516 cm^{-1} for high-spin Fe^{III} derivatives, and varying from 1538 to 1545 cm^{-1} for the low-spin Fe^{III} and Fe^{II} derivatives. No distinction is obvious between the low-spin (S = 0) and the intermediate-spin (S = 1) Fe^{II} cases.

First in a series of OEP metallo derivatives a strong correlation was found between the frequency of band IV and the core radius $\rho_{C_t\cdots N}$ of the porphyrin.[20] Later on, a linear relationship was proposed between these quantities.[21] Within the Fe(TPP) series the frequency of band C is almost 40 cm^{-1} lower than that of band IV of pyrrole-substituted iron porphyrins, both for high-spin and low-spin compounds. As the core radius is fairly insensitive to the presence of substituents either on the pyrrole or on the methine bridge, the proposed linear equation cannot be used right away in the Fe(TPP) series.

On Figure 3 we have plotted $\rho_{C_t\cdots N}$ vs. band C frequency; our data fit a best line of equation $\rho_{C_t\cdots N} = 0.0014\nu_C + 4.198$, determined by linear regression. For one value of ν_C, the scattering on the experimental X-ray data may be as large as 0.025 Å, so it does not seem reasonable to use this equation to get $\rho_{C_t\cdots N}$ values with a better accuracy than ±0.01 Å in this series.

With the data at hand, a large gap is noticeable in the ν_C values, allowing definition of two distinct frequency regions corresponding to low-spin (ca. 1540 cm^{-1}) and high-spin compounds (1500–1516 cm^{-1}). It is already known that the occupancy of the $d_{x^2-y^2}$ orbital is accompanied by an expansion of the core radius of the porphyrin.[14] Core expansion is considered as an important contribution to the lowering of the frequency of band IV of physiological porphyrins.[17] Our data emphasize the role of the occupancy of the $d_{x^2-y^2}$ orbital, and the concomittant core expansion, as the main factor governing the ν_C frequency.

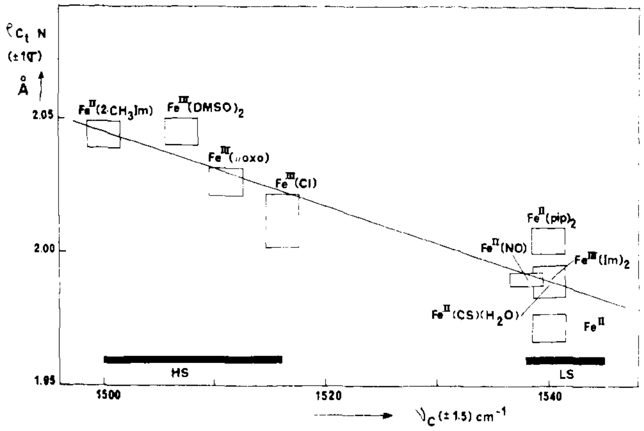

Figure 3. Frequency of band C vs. porphyrin core radius $\rho_{C_t\cdots N}$ (Å).

Band D (p, 1540–1575 cm^{-1}). This polarized band is located ca. 1560 cm^{-1} and is intense when observed with Soret excitation. It has been assigned previously to a C_β–C_β stretch.[17] Its frequency, alike that of the other bands, shows a dependency on the spin state of the iron atom, being in the 1542–1554-cm^{-1} range for high-spin complexes and in the 1560–1572-cm^{-1} range for low-spin complexes. This band is analogous to band D of physiological porphyrins, first proposed as a spin marker band[22] and then discarded, due to interference of a nearby vinyl band.[2]

Vibrational Pattern Associated with Pentacoordination. We have already described the depolarized Raman band B, observable only upon β excitation, at ca. 1370 cm^{-1}.[23] Its occurrence is not related to a specific spin or oxidation state of the iron, as exemplified in Table II, but is distinctive of pentacoordinate complexes. Its frequency shows some sensitivity to the spin state of the iron ranging from 1365 to 1369 cm^{-1} for high-spin derivatives and from 1376 to 1379 cm^{-1} for low-spin derivatives.

But this is not the only feature associated with pentacoordination: within the low-spin Fe^{II} series the frequency of band D is also sensitive to the coordination number; it is 1572 cm^{-1} for Fe(TPP)(CS) and 1563 cm^{-1} for Fe(TPP)(CS)(py) and 1567 cm^{-1} for Fe(TPP)[$(CH_3)_2CHNO$] and 1562 cm^{-1} for Fe(TPP)[$(CH_3)_2CHNO$](py).

Indeed a quite remarkable variation of the D frequency is noticeable: the lowest values correspond to symmetrical hexacoordinated species, intermediate values to nonsymmetrical hexacoordinated species, and the highest values to pentacoordinated species. Such a trend could be rationalized by considering the variations of the Fe dπ and ring π* interactions with the distance of the iron atom to the porphyrin plane: it seems reasonable to consider that the overlap of the $d_{xz}d_{yz}$ Fe orbitals with the e_g π* orbitals of the porphyin is maximum for the planar geometry and weakens as the iron moves out of the plane. So the π conjugation within the porphyrin ring is stronger for nonplanar species, and therefore the corresponding stretching frequencies are higher. With the present data, it appears that the frequency of band D may be

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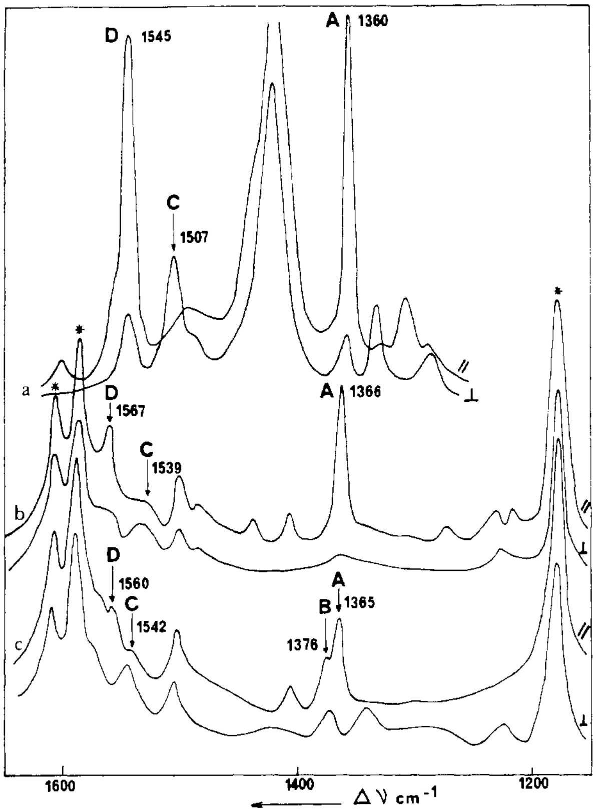

Figure 4. Raman spectra of (a) $Fe(TPP)(Me_2SO)_2$ in Me_2SO, (b) $Fe(TPP)(CH_3NO)(py)$ in C_6H_6, and (c) $Fe(TPP)(\textit{i}\text{-}PrNO)$ in C_6H_6 with polarization $\|$ and $\perp$ to the incident polarization (excitation wavelength 514.5 nm, power 60 mW, concentration 1 mg/mL). Solvent bands are indicated by asterisks.

correlated with the out of plane displacement of the iron atom, at least qualitatively. And we conclude that in the low-spin Fe^{II} series pentacoordinated complexes are characterized by higher D frequencies than hexacoordinated complexes.

Conclusion. From the shifts of the Raman frequencies in the Fe(TPP)(L)(L′) series, it is clear that the spin number of the iron is the main factor influencing those shifts.

With use of exciting lines within the β-absorption region, nontotally symmetric modes are observable among which band B (ca. 1375 cm^{-1}, dp) is specific of pentacoordination and band C (ca. 1500–1550 cm^{-1}, ap) is analogous to band IV of physiological porphyrins. This last band, due to the sensitivity of its frequency to the spin number, may be considered as a spin marker, via the influence of the spin on the core radius.

With use of exciting lines close to the Soret absorption region, totally symmetric modes are observed, mainly band A (ca. 1360 cm^{-1}, p) and band D (ca. 1560 cm^{-1}, p), as already mentioned.[6] Within the series of low-spin Fe^{II} complexes, the frequencies of these two bands are mainly dependent on $d\pi(Fe)-\pi^*(TPP)$ interactions and more specifically on the π-donor–π-acceptor ability of the axial ligands and the importance of the $d\pi-\pi^*$ overlap, which in turn is dependent on the stereochemistry around the iron atom and particularly the coordination number. The balance between these two factors is different for bands A and D; band A is more responsive to the π-donor–π-acceptor character of the axial ligands, since among hexacoordinated derivatives it shifts from 1355 cm^{-1} for $Fe(TPP)(pip)_2$ to 1367 cm^{-1} for $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2](py)$, whereas band D shifts from 1560 to 1566 cm^{-1}, along the same set of derivatives. On the other hand, band D is more sensitive to the coordination number of the iron as it shows, for example, a 9-cm^{-1} shift by addition of the sixth ligand to Fe(TPP)(CS), while the shift of the A frequency is only 2 cm^{-1}.

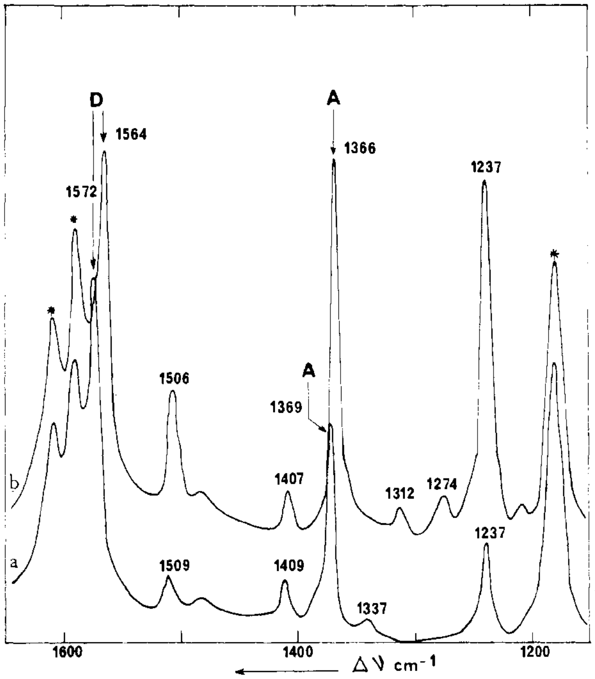

Figure 5. Raman spectra of (a) $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2]$ and (b) $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2](1\text{-}CH_3Im)$ (excitation wavelength 457.9 nm, power 30 mW, concentration 1 mg/mL in C_6H_6). Solvent bands are indicated by asterisks.

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Registry No. Fe(TPP)(CS), 67583-11-3; Fe(TPP)(CS)(py), 67670-43-3; $Fe(TPP)(CCl_2)$, 65979-89-7; $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2]$, 72042-21-8; $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2](py)$, 76807-87-9; $(Fe(TPP))_2C$, 75249-87-5; $Fe(TPP)(CH_3NO)$, 76807-88-0; $Fe(TPP)(CH_3NO)(py)$, 76807-89-1; Fe(TPP)(NO), 52674-29-0; $Fe(TPP)(Me_2SO)_2^+$, 68179-07-7; Fe(TPP)Cl, 16456-81-8; $(Fe(TPP))_2O$, 12582-61-5; $Fe(TPP)(Im)_2^+$, 52155-41-6; Fe(TPP), 16591-56-3; Fe(TPP)(2-MeIm), 48243-44-3; $Fe(TPP)(pip)_2$, 17845-65-7; $Fe(TPP)(py)_2$, 16999-25-0; Fe(TPP)(CO)(py), 53470-09-0; $Fe(TPP)(\textit{i}\text{-}PrNO)$, 74463-17-5; $Fe(TPP)[C{=}C(\textit{p}\text{-}ClC_6H_4)_2](1\text{-}CH_3Im)$, 76807-90-4; $Fe(TPP)[(CH_3)_2CHNO](py)$, 64479-14-7.