

Nonplanar Distortions of Bis-Base Low-Spin Iron(II)–Porphyrinates: Absorption and Resonance Raman Investigations of Cross-*Trans*-Linked Iron(II)–Basket-Handle Porphyrin Complexes

Thierry Picaud,[†] Carole Le Moigne,[†] Bernard Looek,[‡] Michel Momenteau,^{‡,§} and Alain Desbois^{*†}

Contribution from the Département de Biologie Joliot-Curie, SBFM, CEA et URA CNRS 2096, CEA/Saclay, F-91191 Gif-sur-Yvette Cedex, France, and the Institut Curie, Centre Universitaire, F-91405 Orsay Cedex, France

Received February 17, 2003; E-mail: desbois@dsvifd.cea.fr

Abstract: Electronic absorption and Soret-excited resonance Raman (RR) spectra are reported for bis-*N*-alkylimidazole and bis-pyridine complexes of various cross-*trans*-linked iron(II)–“basket-handle” porphyrins (Fe(II)–BHP) in methylene chloride. These compounds enable us to characterize the spectroscopic properties of ruffled six-coordinated low-spin Fe(II)–porphyrin complexes. The visible absorption spectra show that the Q and B bands are progressively red-shifted when the handles are shortened and/or when the steric hindrance of the axial ligands is increased. This effect is accompanied by both a decrease in RR frequency of the ν_2 mode and an increase in frequency of the ν_8 and ν_9 (Fe–ligand₂) modes. More precisely, an inverse linear correlation is found between the frequencies of the ν_2 and ν_8 modes. For each ligation state, the positions of the absorption bands are also linearly correlated with the frequency of the ν_2 or ν_8 mode. All of these spectroscopic data reveal that the degree of ruffling of the Fe(II)–BHP complexes is increased by the *N*-methylimidazole → pyridine axial substitutions, presumably because the mutual steric strains between the axial ligand rings, the porphyrin macrocycle and the porphyrin handles are increased. The present study provides a first basis for discerning ruffled conformations from planar and other nonplanar structures in ferrous heme proteins.

Introduction

Crystallographic structures of a large variety of hemoproteins show that the heme can be distorted from planarity.¹ The type of distortion differs for proteins with different functional activities, but is often conserved for proteins belonging to the same class.¹ For example, ruffled conformations are stabilized in mitochondrial c-type cytochromes and saddled conformations are generally observed for peroxidases (Figure 1). Studies on model compounds show that the nonplanar structures of the hemes have important chemical and biochemical consequences in terms of changes in redox potentials, ligand affinities, electron-transfer rates, and/or excited-state energetics.² All of these observations have led to the suggestion that out-of-plane

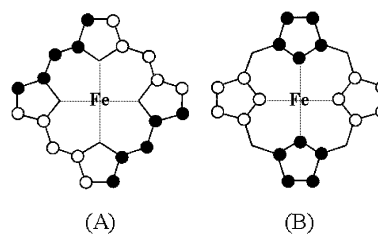


Figure 1. Schematic representation of ruffled (A) and saddled (B) conformations. The filled and open circles indicate displacements above and below the mean porphyrin plane, respectively.

(oop) distortions imposed by the protein matrix may control the functional properties of the hemes.^{1,2}

Resonance Raman (RR)³ spectroscopy is a very sensitive technique to detect nonplanar distortions of the hemes embedded in proteins.⁴ In particular, studies on membrane cytochrome bc₁/b₆f complexes recently showed its two bis-histidyl-coordinated b-type hemes have different conformations in both the oxidized and reduced states.^{4d,e} Unfortunately, in the absence of relevant model compounds, neither the form nor the extent of the

[†] CEA/Saclay.

[‡] Institut Curie, Orsay.

[§] Deceased.

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- (3) Abbreviations used: *N*-MeIm, *N*-methylimidazole; HIm, imidazole; Py, pyridine; LS: low-spin; 4c: four-coordinate; 6c: six-coordinate; TPP, tetraphenylporphyrinate; BHP, “basket-handle” porphyrinates; [(Piv₂)(C_n)], “bis(picket)-mono(handle)” porphyrinates; T pivPP, tetrakis(*o*-pivalamidophenyl)porphyrinates; CT, cross-*trans*; AC, adjacent-*cis*; RR, resonance Raman; oop, out-of-plane.

structural deformation can be predicted. Systematic investigations on a large variety of four-coordinate (4c) Ni(II)–porphyrins have revealed the influence of the peripheral substituents on the porphyrin deformation,⁵ but suitable spectroscopic studies on distorted low-spin (LS) six-coordinate (6c) iron-porphyrinate complexes, in particular in the reduced state, are lacking. It is therefore of main interest to gain more insight into model systems relevant to the bis-ligated ferrous hemes of hemoproteins.

In the past decades, many efforts have been done to mimic the active sites of hemoproteins.⁶ Due to chemical conveniences, most of the model compounds were built from 5,10,15,20-mesotetraphenylporphyrin (TPP). In the proteins, the amino acid residues of the heme binding sites determine the heme structure. In analogy with the stereochemical constraints imposed by the side chains of the protein matrix, the heme conformation may be modulated by the adjunction of various substituents on the phenyl rings of Fe-TPP, forming “superstructured” Fe-porphyrins.^{6c} These models offer numerous possibilities of changing the orientations and structures of the peripheral phenyl groups and, therefore, represent an opportunity to establish a reliable interpretative framework for the analysis of the spectroscopic and structural properties of the bis-ligated hemes in hemoproteins. In this paper, we describe the absorption and resonance Raman spectra of bis-base LS complexes of the so-called cross-trans-linked (CT) Fe(II)–“basket-handle” porphyrins (Fe(II)–BHP). In these compounds, two aliphatic chains constituting the “handles” are attached through ether or amide linkages to the ortho positions of two opposite phenyl groups of Fe-TPP (Figure 2). When at least one short handle is present in the CT Fe-BHP, a steric constraint is created and mainly released by a pronounced ruffling of the tetrapyrrole macrocycle.⁷ The handles of the investigated CT Fe(II)–BHP compounds provide a space sufficient to accommodate the binding of heterocyclic bases. We have thus varied the coordination of the axial rings in changing the bulkyness of the ligands. For this purpose, the *N*-methylimidazole (*N*-MeIm) and pyridine (Py) complexes of Fe(II)–BHP were investigated. Therefore, these systems provide the first interesting testing ground for the characterization of specific spectroscopic properties induced by nonplanar distortions of bis-base Fe(II)–porphyrin complexes.

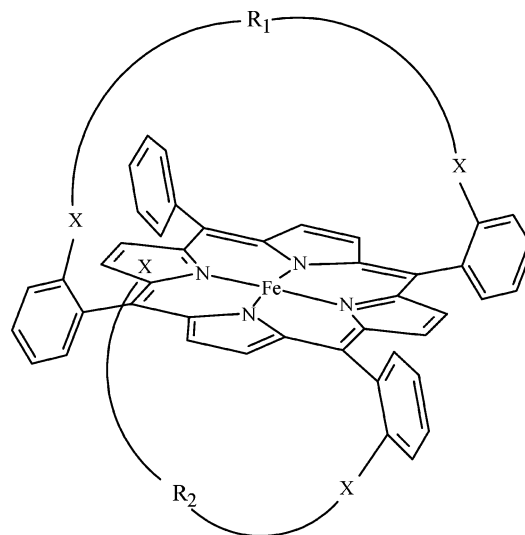


Figure 2. Schematic structure of the cross-trans-linked iron(II)–“basket-handle” porphyrins used in this study.

Experimental Section

The complexes of four CT Fe–BHP were studied (Figure 2, Table 1). The 5,15:10,20-bis(2,2′-(5-imidazol-1-ylnonane-1,9-diamido)diphenyl)porphyrin [(C₁₁Im)₂] is an amide-linked BHP with identical handles in which one imidazole ring is inserted in a central position (Table 1). The 5,15:10,20-bis(2,2′-[3,3′-(*p*-phenylene)dibutoxy]diphenyl)porphyrin [(C₄)₂φ]₂ is an ether-linked BHP with identical handles constituted by two (*p*-phenylene)dibutoxy groups. The α-5,15-[2,2′-(dodecanediamido)diphenyl]–β-10,20-[2,2′(3,3′-(*p*-phenylene) dipropionamido)diphenyl]porphyrin [(C₃)₂φ(C₁₂)] is an amide-linked BHP with two handles of different length and composition. The shortest handle is a (*p*-phenylene)dipropionamido group while the longest handle is formed by a dodecanediamino chain. The 5,15:10,20-bis(2,2′-[3,3′-(*p*-phenylene)dipropoxy]diphenyl)porphyrin [(C₃)₂φ]₂ is an ether-linked BHP with two identical (*p*-phenylene)dipropoxy handles. To measure the influence of the binding mode of the handles on the porphyrin structure, the adjacent-cis (AC) isomers of [(C₄)₂φ]₂ and [(C₃)₂φ]₂ were also investigated. The syntheses, purifications and characterizations of the CT and AC Fe(III)–BHP used in this study have been reported previously.⁸ *N*-methylimidazole (*N*-MeIm) (Sigma), pyridine (Py), and methylene chloride (Merck) were of spectroscopic grade. Perdeuterated imidazole (Im-*d*₄, isotopic enrichment: 98.8%) was purchased from the Bureau des Isotopes Stables of the Centre d’Etudes de Saclay. Pyridine-*d*₅ (Py-*d*₅, isotopic enrichment: 99.8%) was purchased from Merck.

The ferrous complexes were obtained by reduction of the chloride Fe(III) derivatives in a two-phases system consisting of methylene chloride and aqueous dithionite under vacuum.^{9,10} The absorption and RR measurements of the Fe(II)–BHP compounds were performed under anaerobic conditions.¹⁰ The ligand was present in a large excess (0.1–1 M) in order to warrant complete hemochrome formation. However, titrations showed that Py has a very low affinity for Fe(II)–[(C₃)₂φ]₂ (see Results). The ligand binding was also checked by absorption and RR spectroscopies.^{9–11}

The electronic absorption spectra were measured by using a Cary 5E (Varian) spectrometer. The resonance Raman (RR) spectra were

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Table 1. Molecular Structures of the Cross-Trans-linked Iron-“Basket-Handle” Porphyrins Studied in This Work

Fe-BHP	X	R ₁	R ₂
Fe[(C ₁₁ Im) ₂]	NH	CO-(CH ₂) ₄ -CH(Im)-(CH ₂) ₄ -CO	CO-(CH ₂) ₄ -CH(Im)-(CH ₂) ₄ -CO
Fe[((C ₄) ₂ φ) ₂]	O	(CH ₂) ₄ -C ₆ H ₄ -(CH ₂) ₄	(CH ₂) ₄ -C ₆ H ₄ -(CH ₂) ₄
Fe[((C ₃) ₂ φ)(C ₁₂)]	NH	CO-(CH ₂) ₂ -C ₆ H ₄ -(CH ₂) ₂ -CO	CO-(CH ₂) ₁₀ -CO
Fe[((C ₃) ₂ φ) ₂]	O	(CH ₂) ₃ -C ₆ H ₄ -(CH ₂) ₃	(CH ₂) ₃ -C ₆ H ₄ -(CH ₂) ₃

Table 2. Absorption Maxima (nm) and RR Frequencies and Bandwidths (cm⁻¹) of the ν₂, ν₄, and ν₈ Modes of Bis-*N*-Alkylimidazole Complexes of CT and AC Fe(II)-BHP and of Fe(II)-TPP

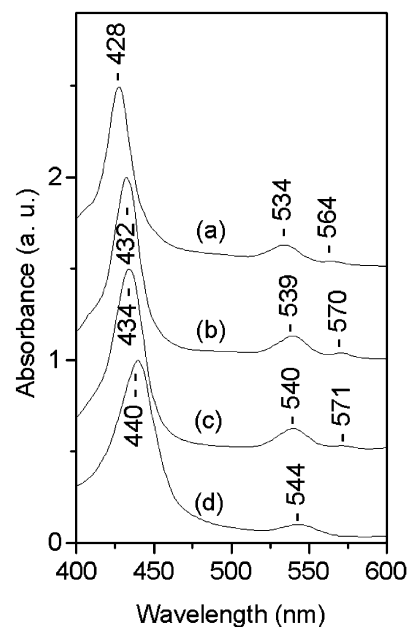
Fe(II)-porphyrin complex	absorption (nm)	ν ₂ (Γ) (cm ⁻¹)	ν ₄ (Γ) (cm ⁻¹)	ν ₈ (Γ) (cm ⁻¹)
CT Fe[(C ₁₁ Im) ₂]	428, 534, 564	1560 (13.0)	1355 (9.5)	381 (11.0)
CT Fe[((C ₄) ₂ φ) ₂](<i>N</i> -MeIm) ₂	432, 539, 570	1558 (12.0)	1355 (9.0)	383 (10.5)
CT Fe[((C ₃) ₂ φ)(C ₁₂)](<i>N</i> -MeIm) ₂	434, 540, 571	1556 (13.5)	1355 (9.5)	384 (13.5)
CT Fe[((C ₃) ₂ φ) ₂](<i>N</i> -MeIm) ₂	440, 544	1553 (13.5)	1355 (10.5)	389 (20.5)
FeTPP(<i>N</i> -MeIm) ₂	427, 533, 566	1558 (13.5)	1355 (9.5)	383 (11.0)
AC Fe[((C ₄) ₂ φ) ₂](<i>N</i> -MeIm) ₂	428, 535, 564	1559 (17.0)	1355 (11.0)	384 (17.0)
AC Fe[((C ₃) ₂ φ) ₂](<i>N</i> -MeIm) ₂	428, 535, 565	1559 (14.0)	1355 (11.0)	383 (20.5)

recorded at 20 ± 1 °C on a Jobin-Yvon spectrometer (HG2S-UV) with the 441.6 nm excitation of a He-Cd laser (Liconix model 4050) and the 413.1 and 406.7 nm excitations of a Kr⁺ ion laser (Coherent Innova). Using radiant powers of 10–50 mW, the RR spectra (6–12 scans) were independently collected and averaged. The spectral analysis was achieved using a Grams 32 software (Galactic Industries).^{4d,e,10} A mixture of benzene and methylene chloride (1/1 (v/v)) was used to calibrate the RR spectra. The frequencies of the RR bands of the Fe(II)-BHP complexes were also internally calibrated against the solvent bands. The frequency precision was ± 0.5 cm⁻¹ for the strongest RR bands (ν₂, ν₄, ν₈) and ± 1 cm⁻¹ for the weakest bands. The full width at half-height (Γ) of the ν₂, ν₄, and ν₈ bands was determined with an accuracy of ± 0.5 cm⁻¹.

Results

Electronic Absorption Spectra of the Bis-*N*-alkylimidazole Complexes. The Soret, β and α absorption bands of the bis-*N*-MeIm complex of CT Fe(II)[((C₄)₂φ)₂] are observed at 432, 539, and 570 nm, respectively (Figure 3). These bands are shifted toward the red by 4–6 nm with respect to those of the Fe(II)[(C₁₁Im)₂] derivative (Figure 3, spectra a and b; Table 2). When the length of at least one handle is decreased, the extent of the red shift is increased with bands peaking at 434, 540, and 571 nm for CT Fe(II)[((C₃)₂φ)(C₁₂)](*N*-MeIm)₂ and at 440 and 544 nm for CT Fe(II)[((C₃)₂φ)₂](*N*-MeIm)₂ (Figure 3, spectra c and d; Table 2). In the spectra of the latter complex, the Soret band is significantly broadened and the α band is too weak to be determined (Figure 3, spectrum d). The absorption spectra of the bis(*N*-MeIm) complexes of Fe(II)-TPP, AC Fe(II)[((C₄)₂φ)₂], and AC Fe(II)[((C₃)₂φ)₂] show small variations in the position of the visible absorption bands (427–428, 533–535, and 564–566 nm) (Spectra not shown; Table 2).

Electronic Absorption Spectra of the Bis-pyridine Complexes. The absorption spectra of the bis-Py complex of Fe(II)-[((C₄)₂φ)₂] exhibit Soret, β, and α bands at 429, 535, and 567 nm, respectively (Figure 4, spectrum a). These maxima are slightly red shifted to 431, 536, and 568 nm in the spectra of Fe(II)[((C₃)₂φ)(C₁₂)](Py)₂. Larger spectral modifications are seen for the Fe(II)[((C₃)₂φ)₂](Py)₂ complex with two bands at 441 and 543 nm, which are broadened (Figure 4, spectrum c; Table 3nn). It is worth mentioning that the absorption bands of the

**Figure 3.** Visible absorption spectra (400–600 nm) of bis-*N*-alkylimidazole complexes of Fe(II)-BHP in methylene chloride: (a): Fe(II)[(C₁₁Im)₂]; (b): Fe(II)[((C₄)₂φ)₂](*N*-MeIm)₂; (c): Fe(II)[((C₃)₂φ)(C₁₂)](*N*-MeIm)₂; (d): Fe(II)[((C₃)₂φ)₂](*N*-MeIm)₂.

Fe(II)TPP(Py)₂ complex are observed at 423, 530 and 562 nm (spectra not shown; Table 3). Those of the bis-Py complexes of AC Fe(II)[((C₄)₂φ)₂] are slightly blue-shifted to 422, 529, and 561 nm. On the contrary, the Soret, β, and α bands of AC Fe(II)[((C₃)₂φ)₂](Py)₂ are red-shifted to 425, 532, and 564 nm, respectively (spectra not shown; Table 3).

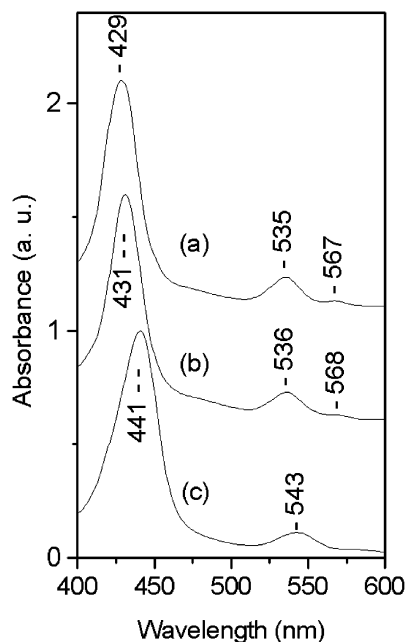
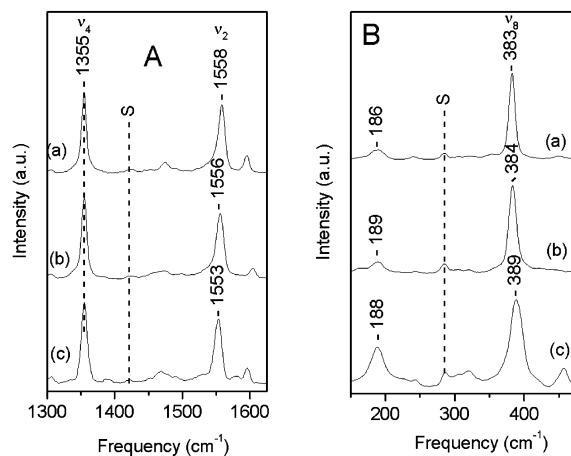
Resonance Raman Spectra of the Bis-*N*-alkylimidazole complexes. The RR spectra of the bis-*N*-MeIm complex of CT Fe(II)[((C₄)₂φ)₂] show the ν₂, ν₄ and ν₈ modes at 1558, 1355, and 383 cm⁻¹, respectively (Figure 5A,B, Table 2).

This set of frequencies slightly differs from that determined for Fe(II)TPP(*N*-MeIm)₂ and Fe(II)[C₁₁Im]₂ (Figure 5, Table 2). When the RR spectra of the bis-*N*-MeIm complexes of CT Fe(II)[((C₄)₂φ)₂] and CT Fe(II)[(C₃)₂φ)(C₁₂)] are compared, a downshift of ν₂ from 1558 to 1556 cm⁻¹ as well as an upshift of ν₈ from 383 to 384 cm⁻¹ are observed (Figure 5A,B, Table 2). The ν₂ and ν₈ modes are further shifted to 1553 and 389

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Table 3. Absorption Maxima (nm) and RR Frequencies and Bandwidths (cm^{-1}) of the ν_2 , ν_4 and ν_8 Modes of the Bis-pyridine Complexes of CT and AC Fe(II)–BHP and of Fe(II)–TPP

Fe(II)–porphyrin complex	absorption (nm)	ν_2 (Γ) (cm^{-1})	ν_4 (Γ) (cm^{-1})	ν_8 (Γ) (cm^{-1})
CT Fe[$((\text{C}_4)_2\phi)_2$](Py) $_2$	429, 535, 567	1557 (18.0)	1356 (10.0)	384 (12.5)
CT Fe[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py) $_2$	431, 536, 568	1552 (12.5)	1355 (9.0)	388 (12.0)
CT Fe[$((\text{C}_3)_2\phi)_2$](Py) $_2$	441, 543	1545 (16.0)	1354 (11.0)	400 (19.5)
FeTPP(Py) $_2$	423, 530, 562	1557 (17.0)	1357 (9.5)	386 (15.0)
AC Fe[$((\text{C}_4)_2\phi)_2$](Py) $_2$	422, 529, 561	1559 (16.5)	1358 (10.0)	387 (18.0)
AC Fe[$((\text{C}_3)_2\phi)_2$](Py) $_2$	425, 532, 564	1558 (16.0)	1358 (11.0)	384 (18.0)

**Figure 4.** Visible absorption spectra (400–600 nm) of bis-pyridine complexes of Fe(II)–BHP in methylene chloride: (a): Fe(II)[$((\text{C}_4)_2\phi)_2$](Py) $_2$; (b): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py) $_2$; (c): Fe(II)[$((\text{C}_3)_2\phi)_2$](Py) $_2$.**Figure 5.** High- (1300–1620 cm^{-1}) (A) and low- (150–460 cm^{-1}) (B) frequency regions of RR spectra of bis(*N*-methylimidazole) complexes of Fe(II)–BHP in methylene chloride: (a): Fe(II)[$((\text{C}_4)_2\phi)_2$](*N*-MeIm) $_2$; (b): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](*N*-MeIm) $_2$; (c): Fe(II)[$((\text{C}_3)_2\phi)_2$](*N*-MeIm) $_2$; excitation: 441.6 nm; summations of 6–8 scans; S indicates solvent bands at 1422 and 285 cm^{-1} .

cm^{-1} , respectively, in the RR spectra of CT Fe(II)[$((\text{C}_3)_2\phi)_2$](*N*-MeIm) $_2$ (Figure 5A,B, Table 2). In addition, a measure of the bandwidth at half-height (Γ) reveals a significant broadening for these two latter bands (Table 2). The ν_4 band exhibits a constant frequency (1355 cm^{-1}) in the RR spectra of the four bis-*N*-alkylimidazole derivatives (Figure 5A, Table 2).

Modes involving symmetric stretching of the axial bonds [ν_s -(Fe-L $_2$)] were previously detected in the 190–200 cm^{-1} regions of the RR spectra of bis-imidazole complexes of Fe(II)–porphyrins.¹² Unfortunately, the ν_s (Fe-*N*-MeIm $_2$) mode of the Fe(II)–BHP complexes is in great part hidden by a phenyl mode (ϕ_{10}) at 185–191 cm^{-1} ,¹³ contributing as a weak shoulder at 190 and 200 cm^{-1} in the RR spectra of the bis-*N*-MeIm complexes of Fe(II)[$((\text{C}_4)_2\phi)_2$] and Fe(II)[$((\text{C}_3)_2\phi)_2$], respectively (Figure 5B). To characterize more precisely the influence of the handle length on the ν_s (Fe-L $_2$) mode, we have thus investigated the RR spectra of the imidazole (HIm) complexes of the CT Fe(II)–BHP compounds. The decreased ligand mass produced by the *N*-MeIm \rightarrow HIm axial substitutions is expected to upshift the frequencies of the ν_s (Fe-L $_2$) modes.¹⁴ For the Fe(II)[$((\text{C}_4)_2\phi)_2$](HIm) $_2$ complex, a specific band observed at 200 cm^{-1} is downshifted at 195 cm^{-1} upon perdeuteriation of the axial ligands (Im-*h* $_4$ \rightarrow Im-*d* $_4$) (Figure 6, spectra (a) and (b)). Similarly, the 203 cm^{-1} band of the Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](HIm) $_2$ complex as well as the 209 cm^{-1} band of the Fe(II)[$((\text{C}_3)_2\phi)_2$](HIm) $_2$ complex are sensitive to the same isotopic substitution, respectively shifting to 198 and 203 cm^{-1} (Figure 6, spectra (c–f)).

Resonance Raman Spectra of the Bis-pyridine Complexes.

The ν_2 , ν_4 , and ν_8 modes of the bis-Py complex of CT Fe(II)[$((\text{C}_4)_2\phi)_2$] are observed at 1557, 1356, and 384 cm^{-1} (Figure 7A,B). The frequency of ν_8 differs significantly from that determined for Fe(II)TPP(Py) $_2$ (386 cm^{-1}) (Table 3). The RR spectra obtained for the bis-Py complex of Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py) $_2$ show ν_2 and ν_8 modes at 1552 and 388 cm^{-1} , respectively (Figure 7, Table 3). The affinity of Py with CT Fe(II)[$((\text{C}_3)_2\phi)_2$] is very low since the full 6c complex is not attained in net pyridine. In fact, the RR spectra exhibit a very small contribution of this five-coordinated species (spectra not shown). By varying the Py concentration and using a difference technique,¹⁰ we have however characterized the individual RR spectra of the mono-Py (not shown) and of the bis-Py species (Figure 7A,B). The RR spectra of Fe(II)[$((\text{C}_3)_2\phi)_2$](Py) $_2$ exhibit broad ν_2 and ν_8 bands at 1545 and 400 cm^{-1} , respectively ($\Gamma = 16$ and 19.5

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(14) (a) Assuming a linear symmetric oscillator for an axial L–Fe–L grouping,^{14b} the frequency of the symmetric stretching mode of the axial bonds (ν_s) is expressed as: $\nu_s = (2\pi c)^{-1}(K/m_L)^{1/2}$, where K is the force constant of the Fe–L bond, and m_L , the mass of the axial ligand. Therefore, a change in ligand mass (from m to m') can be related with a change in frequency of the axial mode (from ν_s to ν'_s) by the equation: $\nu'_s/\nu_s = (m/m')^{1/2}$. Taking full masses of 82 (m) and 68 (m') a.m.u for *N*-MeIm and HIm, respectively,¹² this calculation gives $\nu'_s = 0.911\nu_s$. (b) Herzberg, G. In *Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1945; p 173–175.

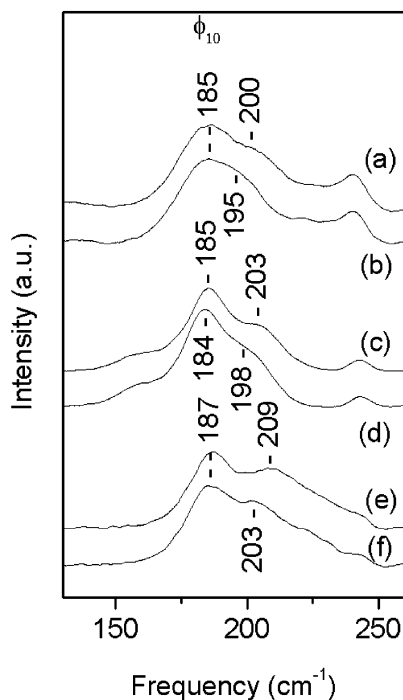


Figure 6. Low-frequency regions (130–260 cm^{-1}) of RR spectra of bis-imidazole complexes of Fe(II)–BHP in methylene chloride: (a): Fe(II)-[$((\text{C}_4)_2\phi)_2$](Im- h_4) $_2$; (b): Fe(II)[$((\text{C}_4)_2\phi)_2$](Im- d_4) $_2$; (c): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Im- h_4) $_2$; (d): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Im- d_4) $_2$; (e): Fe(II)[$((\text{C}_3)_2\phi)_2$](Im- h_4) $_2$; (f): Fe(II)[$((\text{C}_3)_2\phi)_2$](Im- d_4) $_2$; excitation: 441.6 nm; summations of 10–12 scans.

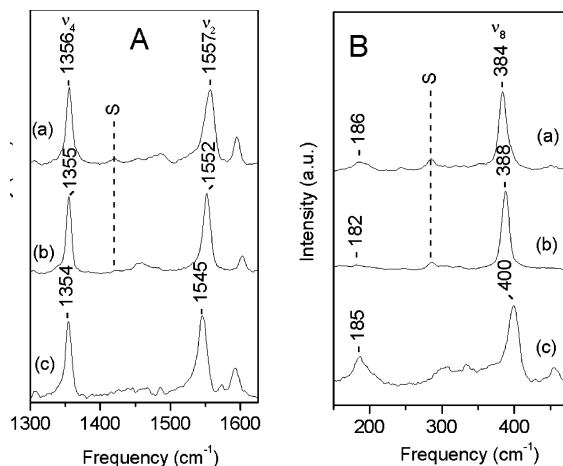


Figure 7. High- (1300–1620 cm^{-1}) (A) and low- (150–460 cm^{-1}) (B) frequency regions of RR spectra of the bis-pyridine complexes of Fe(II)–BHP in methylene chloride: (a): Fe(II)[$((\text{C}_4)_2\phi)_2$](Py) $_2$; (b): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py) $_2$; (c): Fe(II)[$((\text{C}_3)_2\phi)_2$](Py) $_2$; excitation: 441.6 nm; summations of 6–8 scans; S indicates solvent bands at 1422 and 285 cm^{-1} .

cm^{-1} , respectively) (Figure 7, Table 3). The frequency of ν_4 is slightly decreased from 1357 cm^{-1} for the Fe(II)TPP complex to 1354 cm^{-1} for the CT Fe(II)[$((\text{C}_3)_2\phi)_2$] complex (Figure 7, Table 3).

In the 150–200 cm^{-1} regions of the RR spectra of CT Fe(II)-[$((\text{C}_4)_2\phi)_2$](Py) $_2$, the Py- $h_5 \rightarrow$ Py- d_5 substitutions provoke the downshift of a 186 cm^{-1} band to 181 cm^{-1} (Figure 8, spectra a and b). In the spectra of Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py) $_2$, two bands observed at 182 and 158 cm^{-1} are sensitive to the ligand mass shifting to 176 and 153 cm^{-1} , respectively (Figure 8, spectra c and d). Finally, the RR spectra of CT Fe(II)[$((\text{C}_3)_2\phi)_2$](Py) $_2$ show a 205 cm^{-1} band that is downshifted to 198 cm^{-1} upon ligand

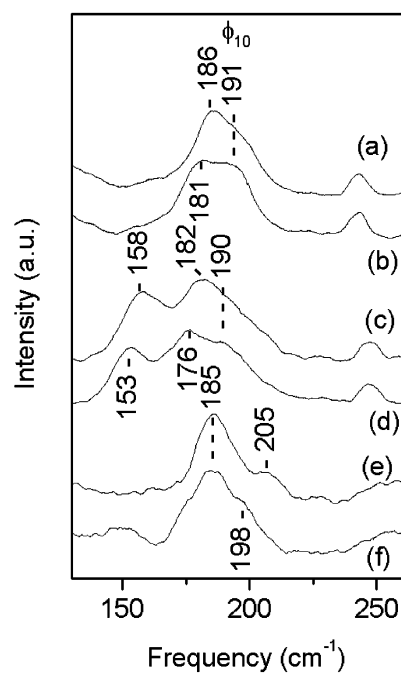


Figure 8. Low-frequency regions (130–260 cm^{-1}) of RR spectra of bis-pyridine complexes of Fe(II)–BHP in methylene chloride: (a): Fe(II)-[$((\text{C}_4)_2\phi)_2$](Py- h_5) $_2$; (b): Fe(II)[$((\text{C}_4)_2\phi)_2$](Py- d_5) $_2$; (c): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py- h_5) $_2$; (d): Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$](Py- d_5) $_2$; (e): Fe(II)[$((\text{C}_3)_2\phi)_2$](Py- h_5) $_2$; (f): Fe(II)[$((\text{C}_3)_2\phi)_2$](Py- d_5) $_2$; excitation: 441.6 nm; summations of 10–12 scans.

Table 4. Frequencies of $\nu_5(\text{Fe}-\text{L}_2)$ for the Bis-imidazole and Bis-pyridine Complexes of CT and AC Fe(II)–BHP and of Fe(II)–TPP^a

Fe(II)–porphyrin complex	$\nu_5(\text{Fe}-\text{HIm}_2)$ (cm^{-1})	$\nu_5(\text{Fe}-\text{Py}_2)$ (cm^{-1})
CT Fe[$((\text{C}_4)_2\phi)_2$](L) $_2$	200 (195) ^a	186 (181) ^a
CT Fe[$((\text{C}_3)_2\phi)(\text{C}_{12})$](L) $_2$	203 (198) ^a	182 (176) ^a
CT Fe[$((\text{C}_3)_2\phi)_2$](L) $_2$	209 (203) ^a	205 (198) ^a
FeTPP(L) $_2$		184 (178) ^a
AC Fe[$((\text{C}_4)_2\phi)_2$](L) $_2$		184 (179) ^a
AC Fe[$((\text{C}_3)_2\phi)_2$](L) $_2$		182 (176) ^a

^a Observed Frequency with Perdeuterated Ligands.

perdeuteration (Figure 8, spectra e and f). As far as the Fe(II)–TPP, AC Fe(II)[$((\text{C}_4)_2\phi)_2$], and AC Fe(II)[$((\text{C}_3)_2\phi)_2$] complexes are concerned, the corresponding ligand-sensitive mode is confined in the 182–184 cm^{-1} region (spectra not shown; Table 4).

Discussion

Visible Absorption Spectra of the Bis-Base Complexes of Fe(II)–BHP. Most of the bis-imidazole complexes of Fe(II)–tetraarylporphyrins have visible absorption bands at 426–430, 534–536, and 562–566 nm.¹⁵ Table 2 summarizes the positions of the α (Q_{00}), β (Q_{01}) and γ (Soret or B_{00}) bands of the bis-*N*-alkylimidazole complexes of Fe(II)–TPP and Fe(II)–BHP. The spectra of the bis-*N*-MeIm complexes of CT Fe(II)-[$((\text{C}_4)_2\phi)_2$], CT Fe(II)[$((\text{C}_3)_2\phi)(\text{C}_{12})$] and CT Fe(II)[$((\text{C}_3)_2\phi)_2$] are very significantly red-shifted when compared to those of Fe(II)–TPP(*N*-MeIm) $_2$, CT Fe(II)[$((\text{C}_{11}\text{Im})_2)$], AC Fe(II)[$((\text{C}_4)_2\phi)_2$](*N*-MeIm) $_2$, and AC Fe(II)[$((\text{C}_3)_2\phi)_2$](*N*-MeIm) $_2$. Shifts of 4–13

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(Soret band) and 4–11 (Q-bands) nm are clearly identified, their sizes depending on the handle length (Table 2). This spectral alteration is not due to an electronic effect of the ortho-phenyl substituents of Fe(II)–BHP, because the AC isomers of Fe(II)– $[(C_4)_2\phi]_2(N-MeIm)_2$ and Fe(II)– $[(C_3)_2\phi]_2(N-MeIm)_2$ exhibit absorption spectra very similar to that of the Fe(II)TPP($N-MeIm$)₂ complex (Table 2).

The visible absorption spectra of the bis-Py complexes of Fe(II)–tetraarylporphyrin usually display bands at 421–423, 527–530, and 558–562 nm.¹⁶ Table 3 shows that the absorption bands of the bis-Py complexes of CT Fe(II)– $[(C_4)_2\phi]_2$, CT Fe(II)– $[(C_3)_2\phi](C_{12})_2$, and CT Fe(II)– $[(C_3)_2\phi]_2$ are red-shifted when compared to those of Fe(II)TPP(Py)₂. The different σ - and π -bonding properties of the $N-MeIm$ and Py ligands shift by 3–4 cm⁻¹ toward the blue the peak positions of Fe(II)TPP(Py)₂ relative to those of Fe(II)TPP($N-MeIm$)₂ (Tables 2 and 3). Thus, considering the different ligand properties, the maximal red shifts observed for the β and Soret absorption bands of the Fe(II)TPP and Fe(II)–BHP compounds are more elevated for the bis-Py complexes (+13–18 nm) than for the bis- $N-MeIm$ complexes (+11–13 nm) (Tables 2 and 3).

In recent years, a controversy has raised about the origin of the red-shifted absorption spectra observed for sterically crowded nonplanar porphyrins.¹⁷ A first interpretation has associated the spectral shifts to nonplanar distortions of the porphyrin macrocycle.^{5c,d} For Ni(II)–porphyrins, the extent of the Soret shift was related to the magnitude of the porphyrin deformation.^{5c,d} On the contrary, DiMaggio et al.^{17a,c} proposed that the band shifts are related to substituent effects, termed in-plane nuclear reorganization. A recent paper has verified that red-shifted absorption spectra are the result of ruffling for a series of Ni(II)–porphyrins.^{17d} Our investigation on bis-base complexes of AC and CT Fe(II)–BHP (Tables 2 and 3) clearly demonstrates that porphyrin ruffling produces red-shifted absorption bands and extends the interpretation of absorption data to the 6c LS Fe(II)–porphyrin complexes and thus the corresponding heme proteins.

Skeletal Porphyrin Modes of the Bis-Base Complexes of Fe(II)–BHP. Three polarized bands dominate the RR spectra of the 6c LS Fe(II)–tetraarylporphyrinates, excited in the Soret regions.^{11a} In the high-frequency regions, two bands corresponding to the ν_2 and ν_4 modes are respectively detected at 1555–1560 and 1354–1358 cm⁻¹ (Tables 2 and 3). On the basis of a normal-mode vibrational analysis on Ni(II)TPP,¹³ the ν_4 mode was assigned to a “half-ring” pyrrole breathing mode, in which the C_aC_b and C_aN bond stretches largely contribute. For the Fe(II)– and Fe(III)–porphyrins, the ν_4 frequency constitutes a good indicator of the oxidation and coordination states of the iron atom.¹¹ The ν_2 mode involves primarily stretching of the C_bC_b and C_aC_m bonds.¹³ This mode mixing suggests that ν_2 is sensitive to different types of structural perturbations that may affect the C_bC_b and C_aC_m bond lengths

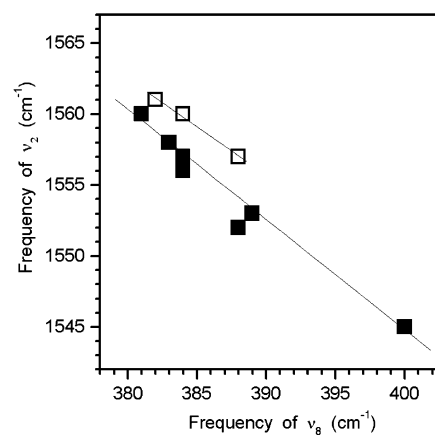


Figure 9. ν_2/ν_8 correlations for the bis-base complexes of CT Fe(II)–BHP (black squares) and the $N-MeIm/CO$ complexes of Fe(II)–“bis(picket)-mono(handle)” porphyrins (open squares).

differently. The most intense band in the low-frequency regions of Soret-excited RR spectra of 6c LS Fe(II)TPP derivatives corresponds to the ν_8 mode.^{11a} This mode consists primarily of the metal-N(pyrrole) and C_aC_m stretching motion and methine bridge bending ($\delta(C_aC_mC_a)$).¹³ The ν_8 mode is thus expected to be sensitive to changes in Fe–N(pyrrole) bond distances and/or in angular deformation of the methine bridges.

Tables 2 and 3 list the frequencies of the ν_2 , ν_4 , and ν_8 modes of the bis-base complexes of CT Fe(II)–BHP. For each type of axial ligation, we observe general trends as the strain generated by the handles increases. As far as the porphyrin modes are concerned, the frequency of ν_2 is decreased and that of ν_8 is increased upon handle shortening. The frequency of ν_4 remains unaffected for the bis- $N-MeIm$ complexes or is slightly decreased for the bis-Py complexes (Tables 2 and 3). When the ν_2 and ν_8 frequencies of the five complexes of the CT Fe(II)–BHP having symmetric handles are plotted, a remarkable inverse linear correlation is seen (Figure 9). The equation of this line can be expressed as

$$\nu_2 = 1856 - 0.78\nu_8$$

with a correlation coefficient (r^2) of 0.999. Small but significant deviations from this linear relationship are observed for the bis-base complexes of Fe(II)– $[(C_3)_2\phi](C_{12})_2$ in which the handles are asymmetrical. The linear correlation does not hold for the corresponding complexes of AC Fe(II)–BHP, Fe(II)TPP, and Fe(II)–“picket fence” porphyrins (Fe(II)–TpiVPP).¹⁸ The high sensitivity of ν_2 to porphyrin ruffling compared to saddling has been demonstrated for various Ni(II)–porphyrins.^{4c} The frequency dependence on ruffling was associated with the significant contribution of C_a–C_m stretching in the potential energy distribution of ν_2 . Ruffling causes considerable twisting about the C_a–C_m bonds, whereas saddling does not.^{4c} Because ruffling is the porphyrin deformation that allows the shortest Fe–N(pyrrole) bonds, a geometric relation is expected between C_a–C_m twisting and Fe–N(pyrrole) contraction when the ruffling is increased. Recalling that ν_8 involves a strong contribution of $\nu(Fe-N(pyrrole))$, a relationship between the ν_2 and ν_8 frequencies cannot be excluded for ruffled porphyrins. For the moderate ruffled deformations expected for Fe(II)–porphyrin complexes,

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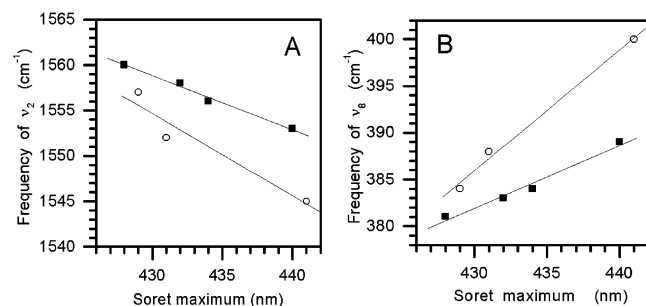


Figure 10. Correlations between the ν_2 (A) and ν_8 (B) frequencies and the Soret maxima of the bis-*N*-alkylimidazole (black squares) and the bis-pyridine (open circles) complexes of Fe(II)-BHP.

our experimental data clearly show a linear correlation between the two frequencies. When compared to the CT Fe(II)-BHP compounds, the peripheral strains are different in the AC Fe(II)-BHP and Fe(II)-TpivPP complexes. In particular, differences in the symmetry of the strains likely lead to the stabilization of saddled and/or waved deformation that affect differently the ν_2 and ν_8 frequencies. Moreover, the potential energy distribution of these modes could be slightly dependent on the porphyrin structure.

Finally, when the frequencies of the ν_2 or ν_8 mode are plotted against the positions of the α , β , or Soret absorption band, linear relationships are observed for a given type of axial ligation. To illustrate this trend, Figure 10 displays the ν_2 (A) and ν_8 (B) frequencies versus the Soret positions. A red shift of the absorption bands was identified as a marker of nonplanar distortions of the tetrapyrrole macrocycle.^{2a-c,5c,d,17e,19} It is clear that the macrocycle ruffling influences in different manner the absorption properties of the bis-*N*-alkylimidazole and bis-Py complexes of the CT Fe(II)-BHP compounds.

In addition to the broadening of the B and Q absorption bands, a line broadening is observed for the ν_2 and ν_8 RR modes of the bis-base complexes of Fe(II)[((C₃)₂φ)₂] (Tables 2 and 3). These observations indicate an equilibrium between different ruffled conformers, likely related to a conformational mobility of the handles.

Axial Modes of the Bis-Base Complexes of Fe(II)-BHP. Weak specific bands observed in the 170–240 cm⁻¹ regions and assigned to $\nu_s(\text{Fe-L}_2)$ were previously characterized for bis-Py and bis-HIm complexes of various Fe(II)-porphyrins.^{12,20} The determination of the frequency of this axial mode provides key information on the ligand-porphyrin interaction.

The $\nu_s(\text{Fe-HIm}_2)$ mode of bis-HIm complexes of Fe(II)-protoporphyrin IX has been previously assigned to a band at 199–203 cm⁻¹.¹² In the RR spectra of the Fe(II)-BHP(HIm)₂ complexes, we have identified a band at 200–209 cm⁻¹ that is sensitive to the Im-*h*₄ → Im-*d*₄ isotopic substitutions (Table 4). Moreover, the experimental downshifts that occur upon ligand perdeuteration (5–6 cm⁻¹) are in good agreement with the calculated shifts (5.6–5.9 cm⁻¹) using a linear oscillator and full masses of 68 and 72 amu for Im-*h*₄ and Im-*d*₄, respectively.^{14a}

Therefore, the bands observed at 200–209 cm⁻¹ are assigned to the $\nu_s(\text{Fe-HIm}_2)$ modes of the Fe(II)-BHP complexes (Table 4).

The $\nu_s(\text{Fe-Py}_2)$ mode of the bis-Py complexes of Fe(II)-mesoporphyrin and Fe(II)-protoporphyrin was previously assigned at 176–179 cm⁻¹.^{11a,12a,19} The low-frequency RR spectra of the Fe(II)-BHP(Py)₂ complexes show at least one band sensitive to the Py-*h*₅ → Py-*d*₅ substitutions. A band at 182–205 cm⁻¹ is observed in the RR spectra of the Fe(II)-BHP(Py)₂ and Fe(II)-TPP(Py)₂ complexes (Table 4). This band is downshifted by 5–6 cm⁻¹ upon ligand perdeuteration. The 182–205 cm⁻¹ bands are therefore assigned to the $\nu_s(\text{Fe-Py}_2)$ mode considering a theoretical shift of 5.5–6.2 cm⁻¹ for a linear symmetric Py-Fe-Py oscillator with masses of 79 and 56 amu for Py and Fe, respectively.^{14a} The origin of the additional isotopic-sensitive band seen at 158 cm⁻¹ in the RR spectra of Fe(II)[((C₃)₂φ)(C₁₂)](Py)₂ is not clear. The asymmetry of this complex could activate a deformation mode of the axial bonds.

Table 4 summarizes the $\nu_s(\text{Fe-L}_2)$ frequencies of the bis-HIm and bis-Py complexes of Fe(II)-BHP. Taking into account the symmetric porphyrins, the frequencies of the $\nu_s(\text{Fe-HIm}_2)$ and $\nu(\text{Fe-Py}_2)$ modes of the CT Fe(II)[((C₃)₂φ)₂] complexes are systematically higher than those of the corresponding CT Fe(II)[((C₄)₂φ)₂] complexes (Table 4). These shifts are indicative of a shortening of the axial bonds when the handle lengths are shortened by two methylene units. Using a linear symmetric L-Fe-L oscillator,¹⁴ a change in frequency of the axial mode (from ν_s to ν'_s) can be correlated with a change in force constant (from K to K') following: $\nu/\nu' = (K/K')^{1/2}$. Empirical relations can be used to describe a change in force constant (K) in relation to a change in bond length (r). One of the most simple is the exponential relation of Herschbach and Laurie²¹

$$K = 10^{-(r-a)/b}$$

where a and b are constants depending on the atoms involved in the bond. For the Fe and N atoms, they are equal to 2.15 and 0.60, respectively.²¹ Therefore, variations in frequency of the axial mode can be directly related to changes in axial bond length (from r to r') according to

$$\nu_s/\nu'_s = (K/K')^{1/2} = 10^{(r'-r)/1.2}$$

with ν and ν' in cm⁻¹, K and K' in mdyne Å⁻¹, and r and r' in Å. From this relationship, the upshift of the $\nu_s(\text{Fe-HIm}_2)$ mode from 200 cm⁻¹ for CT Fe(II)[((C₄)₂φ)₂](HIm)₂ to 209 cm⁻¹ for CT Fe(II)[((C₃)₂φ)₂](HIm)₂ is calculated to correspond to a shortening of the Fe-N(HIm) axial bonds of 0.023 Å. Taking an Fe(II)-N(HIm) distance of 2.014 Å,²² one can estimate an axial bond length of 1.991 Å in the bis-HIm complex of CT Fe(II)[((C₃)₂φ)₂]. Using the same type of calculation for the bis-Py compounds, a shift from 184 to 205 cm⁻¹ is found to correspond to an axial bond shortening of 0.056 Å. With an Fe(II)-N(Py) distance of 2.038 Å determined for Fe(II)TPP(Py)₂,²³ an axial bond length of 1.982 Å is calculated in CT

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Fe(II)[((C₃)₂φ)₂](Py)₂. For the Fe(II)TPP complexes, the Fe–N(axial ligand) distances are longer for Py than for HIm or *N*-MeIm. With nearly planar macrocycle, this difference in bond length was attributed to a steric effect of the six-membered ring of Py. For the CT Fe(II)[((C₃)₂φ)₂] compounds, the calculated Fe–N(ligand) distance is longer for HIm than for Py. However, these axial bond lengths cannot be directly compared since the extents of porphyrin distortion are very different. We have estimated that the porphyrin ruffling of the bis-Py complex is about twice that of the bis-*N*-MeIm complex (vide infra). A very strong porphyrin ruffling in CT Fe(II)[((C₃)₂φ)₂](Py)₂ likely creates two deep cavities in which the ligand rings can closely approach the porphyrin core. In the absence of crystallographic data on a ruffled Fe(II)[porphyrin](Py)₂ complex, a distance of 1.982 Å could appear to be very short for an Fe(II)–N(Py) bond. Nevertheless, this estimate does not seem unrealistic if we consider X-ray data obtained for bis-4-(dimethylamino)pyridine complexes of strongly saddled and/or ruffled Fe(III)–porphyrins.^{24d,e} In these determinations, Fe(III)–N(Py) distances of 1.978–1.989 Å have been measured.

In conclusion, the handle shortening in passing from the CT Fe(II)[((C₄)₂φ)₂] complexes to the CT Fe(II)[((C₃)₂φ)₂] complexes is expected to increase the porphyrin ruffling. Together with the shortening of the Fe–N(pyrrole) indicated by the upshift of the ν₈ mode, the calculated contractions of the axial L–Fe–L bonds are in agreement with the drawing of the axial and pyrrole rings toward the porphyrin center when the macrocycle ruffling is increased. A positioning of the axial rings between the Fe–N(pyrrole) bonds permits a contraction of the coordination sphere.

Ruffling of the Bis-Base Complexes of Fe(II)–“Basket Handle” Porphyrins Bearing Symmetrical Handles. Ni(II)–porphyrins undergoing different nonplanar deformations were investigated using RR spectroscopy.⁵ Increased nonplanarity of the porphyrin has been shown to correlate with downshifts of the ν₂, ν₃, and ν₄ modes.^{5b–d} Moreover, the data obtained on these four-coordinate systems indicate different sensitivities of these structure-sensitive bands to the magnitude of a particular distortion.²⁵ For example, the ν₂ frequency was found to be 8.4 times higher sensitive to ruffling than saddling.²⁵ Although Ni(II)–TPP exhibits both a downshift of ν₂ and an upshift of ν₈ upon change from planar to ruffled conformation,^{5c} no systematic trend was identified for the ν₈ frequency of a large series of ruffled Ni(II)–porphyrins.^{5c}

For Fe–porphyrin complexes, the nature of the axial ligands influence the oop porphyrin distortions. The natural trend of the *N*-MeIm/CO ligation is to stabilize a major saddling in Fe(II)TPP.²⁶ In the *N*-MeIm/CO complexes of the “mono(handle)-bis(picket)” Fe(II)–porphyrins, the addition of one short handle produces a major ruffling.^{7a,d} Minor doming and/or saddling was observed and can be associated with a residual effect of the mixed axial ligation. Moreover, a lateral mobility of the two

pickets has to be considered in the stabilization of a minor saddling component.^{24a} The linkage of two symmetric CT handles in the bis-strapped Fe(II)–BHP compounds is expected to enrich the ruffled component to the detriment of the other oop deformations. Short handles likely generate oop positions of opposite C_m atoms and block phenyl rotations, the combination of these two structural effects destabilizing porphyrin saddling.^{24a} The identity and the symmetry of the handles eliminate the possibility of waving. The binding of two identical ligands is suspected to totally remove porphyrin doming. It is difficult to quantify the percentage of porphyrin ruffling in the total oop distortions of the Fe(II)–BHP complexes. However, the symmetry elements in the porphyrin structure as well as in the ligation state of the iron atom strongly support very small or negligible contributions of doming, saddling or waving in the bis-base complexes of the symmetric CT Fe(II)–BHP compounds.

For these complexes, i.e., the CT Fe(II)[(C₁₁Im)₂], CT Fe(II)[((C₄)₂φ)₂], and CT Fe(II)[((C₃)₂φ)₂] complexes, we observe mutual relationships between the red shifts of the Soret and Q-bands, the decreases in frequency of the ν₂ mode, and the increases in frequency of the ν₈ and ν₈(Fe–L₂) modes (Tables 2–4). All of these spectral changes are consistent with an increased porphyrin ruffling as the strain of the handles is increased. Moreover, for the bis-base complexes of the symmetric Fe(II)–BHP compounds, the ruffling distortion that occurs is expected to be itself symmetric, its extent depending not only on the handle length, but also on the axial bases. The data listed in Tables 2–4 are clearly indicative that the *N*-MeIm → Py axial substitutions increase the extent of porphyrin ruffling of the CT Fe(II)–BHP compounds. The increased deformation can be associated with the steric hindrance of the six-membered Py ring that requires more distortion of the porphyrin core than the five-membered imidazole ring. This observation is similar to that made for LS 6c Fe(III)–porphyrins which show an increased porphyrin deformation for bis-Py complexes when compared to bis-HIm or bis-*N*-MeIm complexes.^{24c,27}

Ruffling of the Bis-Base Complexes of the Fe(II)–“Basket Handle” Porphyrin Bearing Unsymmetrical Handles. The Fe(II)[((C₃)₂φ)(C₁₂)] porphyrin contains a short and relatively rigid (C₃)₂φ handle and a long and loose C₁₂ handle (Table 1). The alterations observed in both absorption and RR spectra (Tables 2 and 3) clearly confirm that a single short (C₃)₂φ handle is sufficient to generate a macrocycle ruffling. However, in the plot of the ν₂/ν₈ frequencies of the Fe(II)–BHP complexes, we observe small but significant deviations for the two bis-base complexes of Fe(II)[((C₃)₂φ)(C₁₂)], the drift being more marked for the bis-Py derivative (Figure 9). Moreover, the frequency of the ν₈(Fe–L₂) mode of the Fe(II)[((C₃)₂φ)(C₁₂)](Py)₂ complex seems too low for an Fe(II)–BHP bearing a short (C₃)₂φ handle (Table 4). To explain the particularities of the Fe(II)[((C₃)₂φ)(C₁₂)] complexes, we suspect that the large difference in length and composition of the handles modulate different shapes of the steric pockets around the Fe center and could allow the porphyrin ruffling to be mixed with other oop deformations. In particular, the strain generated by the Py binding toward the

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(C₃)₂φ handle could be dissipated by a slight doming toward the C₁₂ handle. All these porphyrin rearrangements could allow the axial bond length of the bis-Py complex of Fe(II)[((C₃)₂φ)-(C₁₂)] to be similar to that of the Fe(II)TPP(Py)₂.

Frequencies of the ν₂ and ν₈ Modes and Porphyrin Ruffling of *N*-MeIm/CO Complexes of Fe(II)–“Bis(picket-Mono(handle))” Porphyrins. A number of RR investigations performed on Ni(II)–porphyrins showed frequency variations for several skeletal modes (ν₂, ν₃, ν₄, ν₁₀) upon nonplanar macrocycle deformations.⁵ Unfortunately, no investigation was performed on LS 6c Fe(II)–porphyrins, which are more relevant to the heme coordination of ferrocyclochromes. To determine relationships between the frequency of RR modes and the heme structure, one needs both structural and RR data on appropriate compounds. A previous RR study on the *N*-MeIm/CO complexes of Fe(II)–“bis(picket-mono(handle))” porphyrins (Fe(II)-[(Piv)₂(C_{*n*})] concluded to an increase in porphyrin distortion when the number of methylene units forming the amide handle was gradually decreased from 10 to 8 and 6 ((C₁₀) → (C₈) → (C₆)).^{2d} On one hand, the RR frequencies of the ν₂ mode were characterized at 1561, 1560, and 1557 cm⁻¹, respectively. On the other hand, the frequencies for the ν₈ mode were found to increase from 382 to 384 and 388 cm⁻¹ for the same complexes.^{2d} Crystallographic determinations have more precisely evaluated the type of distortion with a major porphyrin ruffling that is increased as the handle length is decreased.^{7a,d} The average absolute perpendicular displacement of the porphyrin meso carbons from the 24-atom mean porphyrin plane (|C_m|) is generally a measure of the degree of ruffling.^{24a} For the (C₁₀), (C₈), and (C₆) handles, this structural parameter was determined to be 0.155, 0.29, and 0.44 Å, respectively.^{7a,d} Therefore, the RR and crystallographic data on the Fe(II)-[(Piv)₂(C_{*n*})] compounds show that an increase in porphyrin ruffling induces both a decreased ν₂ frequency and an increased ν₈ frequency. When the ν₂ frequencies are plotted against the ν₈ frequencies, a negative linear correlation is again observed (Figure 9), which can be expressed as

$$\nu_2 = 1820 - 0.68\nu_8$$

with $r^2 = 0.996$. It is worth noting that the ν₂/ν₈ relationships of the Fe(II)-[(Piv)₂(C_{*n*})] and Fe(II)–BHP complexes are very similar in terms of slope (0.73 ± 0.05) (Figure 9). The shift observed between the two lines can be related to the difference in bonding (σ and π) and nonbonding properties of the sixth axial ligand (CO versus *N*-MeIm). Interestingly, the ν₂ and ν₈ frequencies of the Fe(II)-[(Piv)₂(C_{*n*})](*N*-MeIm)(CO) complexes are each linearly correlated with the average displacement of the meso carbon atoms (|δC_m|) (Figures not shown).²⁴

From the linear relationships shown in Figure 9, it is evident that the porphyrin ruffling affects both the ν₂ and ν₈ frequencies in a concerted fashion that is related to the normal composition of the two RR modes. Both the decreased ν₂ frequencies and the increased ν₈ frequencies of the CT Fe(II)–BHP derivatives are thus consistent with an increased porphyrin ruffling when the handles of Fe(II)–BHP are shortened.

Magnitude of the Porphyrin Ruffling in the Bis-Base Complexes of CT Fe(II)–BHP. The ruffling of the Ni(II)–porphyrins is favored by the small metal ion allowing short

metal-N(pyrrole) bonds.^{24a,29} The degree of core contraction is dependent on the metal size,^{24a} and therefore, the oop deformation of the porphyrin macrocycle is also metal-dependent.³⁰ For most of the crystallized 6c LS Fe(II)–porphyrin complexes, the macrocycle is nearly planar and the center-N(pyrrole) distance confined to a narrow range between 1.96 and 2.02 Å.^{17c,21a,23} This observation suggests that the maximal core contraction of a LS 6c Fe(II)–porphyrin upon porphyrin distortion is about 0.05–0.06 Å, the 2.01–2.02 Å distance likely representing a threshold between planar and nonplanar conformations.³¹ With such a restrained core size, nonplanar distortions of the Fe(II)–porphyrins can occur only under important environmental perturbations.

To evaluate the extent of porphyrin ruffling in the CT Fe(II)–BHP complexes, we have used the RR and X-ray data previously obtained for the *N*-MeIm/CO hemochromes of Fe(II)-[(Piv)₂(C_{*n*})] (vide supra). The ν₂ and ν₈ frequencies of these compounds are each linearly correlated with |C_m|.²⁸ From these relationships, we have first deduced that the frequency variations of ν₂ and ν₈ as a function of |C_m| variations are –14 cm⁻¹/Å for ν₂ and +21 cm⁻¹/Å for ν₈.²⁸ Using these values and assuming that the porphyrin macrocycle of the Fe(II)-[(C₁₁Im)₂] derivative adopts a planar conformation (Figure 9), the distortion of the C_m atoms in the bis-*N*-MeIm and bis-Py complexes of Fe(II)–BHP can be evaluated. For the Fe(II)-[(C₃)₂φ]₂ complexes that exhibit the most important frequency shifts for the ν₂ and ν₈ modes (Tables 2 and 3), |C_m| is calculated to be 0.38–0.50 Å for its bis-*N*-MeIm derivative and 0.90–1.07 Å for its bis-Py derivative. These estimations are crude since it is not certain that the linear relations used are valid for C_m deformations largely higher than 0.44 Å. However, they provide sufficient evidence for a molecular flexibility of the macrocycle of 6c LS Fe(II)–porphyrins. They also indicate that the degree of porphyrin ruffling can reach important values for the CT Fe(II)–BHP complexes.

Orientation of the Ligands Rings in the CT Fe(II)–BHP Complexes. Most of the bis-imidazole and bis-Py complexes of Fe(II)TPP have nearly planar porphyrin with parallel ligand rings.^{24a} The only known exception concerns a halogenated Fe(II)–porphyrin which adopts a saddled structure with axial Py ligands in nearly perpendicular planes and nearly eclipsing the Fe–N(pyrrole) bonds.^{19c} For the bis-base complexes of CT Fe(II)–BHP, the ruffled conformation is the result of mutual intramolecular interactions between the porphyrin macrocycle, the ligands and the handles. Among these, the bonding and steric effects of the axial ligands on the porphyrin core and the strains produced by the handles on the ligand rings appear to be critical for the determination of the ligand orientations. From the present

(28) The equations of the two lines can be expressed as: ν₂ = 1563.5 – 14.14|C_m| (r² = 0.969) and ν₈ = 378.4 + 21.16|C_m| (r² = 0.987) with ν₂ and ν₈ in cm⁻¹, and |C_m| in Å.

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(31) The average Fe–N(pyrrole) bond lengths (d(Fe–N_p)) of the Fe(II)-[(Piv)₂(C_{*n*})](*N*-MeIm)(CO) complexes are 1.999, 1.991, and 1.981 Å for the (C₁₂), (C₁₀), and (C₈) handles, respectively.^{7a,d} When d(Fe–N_p) is plotted against |C_m|, a linear relationship is observed and can be expressed as: d(Fe–N_p) = 2.009 – 0.063|C_m|, with r² = 0.999. For the Fe(II)-[(Piv)₂(C_{*n*})] derivatives, the threshold between ruffled and planar conformation (|C_m| = 0) is thus deduced to be 2.009 Å.

study, it is clear that the porphyrin macrocycle of the CT Fe(II)–BHP complexes bearing the shortest handles is strongly ruffled. This nonplanar distortion creates perpendicular cavities above and below the macrocycle plane and, thus, can orient the ligand rings in a perpendicular arrangement for the most strained CT Fe(II)–BHP compounds.

Nonplanar Deformations of Heme in Proteins. A number of RR studies has identified nonplanar distortions of heme in proteins.⁴ Various directions and degrees of band shifts were observed for the ν_2 , ν_{10} , ν_3 , and ν_8 modes, but these spectral alterations were difficult to interpret in terms of type and extent of heme distortion. The 6c LS hemes in crystallized hemoproteins adopt either planar, or ruffled, or saddled conformations.¹ The present spectroscopic study on Fe(II)–BHP complexes has allowed the distinction of planar and ruffled conformations. An upcoming publication¹⁸ extending the database to strained 6c LS complexes of Fe(II)–TpivPP confirms that the ν_2/ν_8 inverse linear correlation determined in this paper is specific to ruffled Fe(II)–porphyrins.

As far as the membrane bc-type complexes are concerned, they contain two hemes b, each axially coordinated by two histidylimidazole rings.³² Recent RR studies on a bacterial bc₁ complex and a plant b₆f complex showed that one of these b-type hemes exhibits ν_2 and ν_8 frequencies similar to those observed for the bis-HIm complex of Fe(II)–protoporphyrin.^{4d,e} On the contrary, the other b-type heme shows both a downshift

of the ν_2 mode by 4–6 cm⁻¹ and an upshift of the ν_8 mode by 7–10 cm⁻¹.^{4d,e} Although the uncertainties on the ν_2 and ν_8 frequencies are relatively elevated, these shifts quantitatively represent a $\Delta\nu_2/\Delta\nu_8$ ratio of -0.6 ± 0.2 that is closed to that detected for the bis-*N*-MeIm complexes of CT Fe(II)–BHP. It seems reasonable to conclude that the distorted heme b in the cytochrome bc₁/b₆f complexes most likely contains a major ruffled contribution.

Conclusion

In this study, we have used differently substituted CT Fe(II)–BHP compounds to obtain a better understanding of the correlations between absorption properties, RR frequencies, bis-base coordination, and porphyrin ruffling.

The absorption and RR data show a series of qualitative and quantitative relationships between the positions of the absorption bands and the RR frequencies of the ν_2 , ν_8 , and $\nu_8(\text{Fe-L}_2)$ modes. In relation to a handle shortening, a gradual red shift of the electronic transitions was found to be accompanied by both an increased downshift of the ν_2 mode and an increased upshift of the ν_8 mode. All of this information indicates that the Fe(II)–porphyrin has a flexible macrocycle, adopting different degree of tetrapyrrole ruffling depending on both the handle lengths and the steric hindrance of the axial ligands. Moreover, the RR data show inverse linear correlations between the ν_2 and ν_8 frequencies for two series of 6c LS Fe(II)–porphyrin complexes. With a slope of -0.73 ± 0.05 , the ν_2/ν_8 relationship is proposed to be a specific marker for porphyrin ruffling, a means to differentiate ruffling from other nonplanar conformations in biological bis-histidyl Fe(II)–porphyrin systems.

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