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Absorption and Resonance Raman Investigations of Ligand Rotation and Nonplanar Heme Distortion in Bis-Base Low-Spin Iron(II)–Tetrakis(*o*-pivalamidophenyl)porphyrin Complexes

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The absorption and resonance Raman (RR) spectra of the bis-*N*-methylimidazole, bis-1,5-dicyclohexylimidazole, and bis-pyridine complexes of the meso-$\alpha\alpha\beta\beta$ and meso-$\alpha\beta\alpha\beta$ atropisomers of Fe(II)–tetrakis(*o*-pivalamidophenyl)-porphyrins (Fe(II)TpivPP) were obtained in methylene chloride. The different spatial arrangements of the *o*-pivalamide pickets in these two Fe(II)TpivPP compounds are expected to control the absolute and relative positions of the axial ligand rings with respect to the Fe–N(pyrrole) bonds. In particular, the spectroscopic data obtained for the bis-*N*-methylimidazole and bis-dicyclohexylimidazole complexes of the Fe(II)[$\alpha\beta\alpha\beta$-TpivPP] derivative showed the most important differences. Redshifts of the B and Q absorption bands (+ 4–5 nm) as well as an upshift of the low frequency ν_8 RR mode (+ 5 cm^{-1}) were observed. No shift of the skeletal high frequency modes was detected. These spectral effects were associated with a change in relative position of the axial imidazole rings from nearly parallel in the bis-*N*-methylimidazole complex to nearly perpendicular in the bis-dicyclohexylimidazole complex. On the basis of stereochemical considerations as well as previous spectroscopic investigations, the data were interpreted in terms of change in porphyrin structure from planar to saddled. Complementing to a parallel study on bis-base Fe(II) "basket handle" porphyrin complexes, this spectroscopic investigation provides an additional means to distinguish planar, ruffled, and saddled conformations for ferrous hemes included in proteins.

Introduction

Bis-histidine-coordinated cytochromes (cyt's)[1] are involved in a large number of electron-transfer pathways and exhibit variable midpoint potentials ranging from ca. −400 mV for bacterial cyt c_3 to ca. + 100 mV for membrane cyt b.[2] Structural and environmental factors have been invoked to account for the 500 mV variation in heme redox potential.[2a] The coordination geometry of the axial histidylimidazole rings, the nonplanar distortion of the porphyrin macrocycle, and their plausible mutual interactions constitute structural parameters expected to play an important role in the control of the functional properties of heme in proteins.[3] The absolute and relative positions of the imidazole rings as well as the nonplanar distortions of the porphyrin are determined by the amino acid residues forming the heme pockets and, thus, can influence the electronic structure and the oxidation−reduction properties of the Fe−porphyrin(His)$_2$ complex.[2a,3a,4] Crystallographic investigations showed that the ligand rings

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(1) Abbreviations used: cyt, cytochrome; *N*-MeIm, *N*-methylimidazole; HIm, imidazole; DCHIm, 1,5-dicyclohexylimidazole; 2MeHIm, 2-methylimidazole; Py, pyridine; LS, low-spin; 6c, six-coordinate; TPP, tetraphenylporphyrinate; TpivPP, tetrakis(*o*-pivalamidophenyl)porphyrinates; PFP, "picket fence" porphyrinates; BHP, "basket handle" porphyrinates; CT, cross-*trans*; RR, resonance Raman.

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of the b-type hemes can be either parallel like in cyt b_5 or flavocytochrome b_2 or nearly perpendicular in mitochondrial cyt b.[5] In these hemoproteins, the heme macrocycle can be distorted by the polypeptide chain, but the available crystallographic structures do not indicate a clear correlation between the coordination geometry of the axial ligands and the porphyrin structure.[5c−e]

Various Fe(II)− and Fe(III)−porphyrins complexed with imidazole (HIm), *N*-methylimidazole (*N*-MeIm), 2-methylimidazole (2MeHIm), or pyridine (Py) have been prepared in order to model various situations of bis-His coordination in cytochromes. The tridimensional structure of a number of these complexes has been solved.[6,7] On one hand, bis-HIm and bis-*N*-MeIm complexes of simple Fe(III)−porphyrins have a slightly distorted macrocycle with ligand rings in a nearly parallel orientation.[6] On the other hand, model complexes with two axial rings arranged in perpendicular planes have 2MeHIm or Py derivatives as axial ligands. The porphyrin macrocycle of these compounds is almost invariably distorted from planarity.[6] The positioning of the ligand planes arises from the need to accommodate the bulkiness of the ligands by forcing the porphyrin macrocycle to be either ruffled or saddled. Considering the tridimensional structures of ferric model compounds, a relationship between ligand coordination and porphyrin distortion may be apparent. However, the histidylimidazole ligands of the natural hemes have no particular steric encrumbrance. Therefore, the fact that a perpendicular orientation of the axial imidazole ligands could induce a porphyrin distortion is not quite certain in hemoproteins. As far as the ferrous compounds are concerned, the tetrapyrrole ring is nearly planar, and the ligand rings are parallel for most crystallized bis-base Fe(II)−porphyrin complexes. Only the bis-Py complex of a halogenated Fe(II)−porphyrin was found to be saddled with axial rings nearly perpendicular.[7e]

In the frame of systematic studies on six-coordinated (6c) low-spin (LS) complexes of "superstructured" Fe(II)−tetraarylporphyrins, this study presents spectroscopic data obtained for bis-base complexes of Fe(II)−tetrakis(*o*-pivalamidophenyl)porphyrins (Fe(II)TpivPP). These "picket fence" porphyrin (PFP) systems provide new testing grounds to characterize distorted Fe(II)−porphyrin complexes. The meso-$\alpha\alpha\beta\beta$ and meso-$\alpha\beta\alpha\beta$ atropisomers of Fe(II)−PFP (Fe(II)[$\alpha\alpha\beta\beta$-TpivPP] and Fe(II)[$\alpha\beta\alpha\beta$-TpivPP], respectively) represent interesting compounds for the identification of molecular features that control the coordination geometry of the axial ligand rings and the porphyrin structure. The pivalamide substituents are arranged in adjacent up−up and down−down positions for the $\alpha\alpha\beta\beta$ atropisomer while they adopt alternated up and down positions for the $\alpha\beta\alpha\beta$ form (Figure 1). With respect to the Fe−N_4(pyrrole) coordinates, these different steric barriers can provide different relative and absolute positions for the axial rings.[9] To vary the coordination geometry of the axial rings, the *N*-MeIm, Py, and 1,5-dicyclohexylimidazole (DCHIm) ligands have been investigated. In particular, the chair-shaped cyclohexyl groups of DCHIm are expected to exert important steric repulsions with the pivalamide groups of the porphyrin, thus restricting the rotations of the axial imidazole rings. Therefore, parameters affecting the coordination sphere of the heme iron can be approached by structural modifications of the Fe(II)TpivPP complexes.

Experimental Section

The chloride derivatives of Fe(III)TpivPP were synthesized following the procedure of Collman et al.[10] The $\alpha\alpha\beta\beta$ and $\alpha\beta\alpha\beta$ atropisomers were purified and controlled according to standard methods.[9,10] *N*-Methylimidazole (Sigma) and methylene chloride (Merck) were of spectroscopic grade. 1,5-Dicyclohexylimidazole was synthesized, purified, and controlled as previously described by Traylor et al.[11] The perdeuterated *N*-methylimidazole (*N*-MeIm-d_6, 98% enrichment) was purchased from the Bureau des Isotopes Stables (CEA/Saclay). The perdeuterated pyridine (Py-d_5, 99.8%

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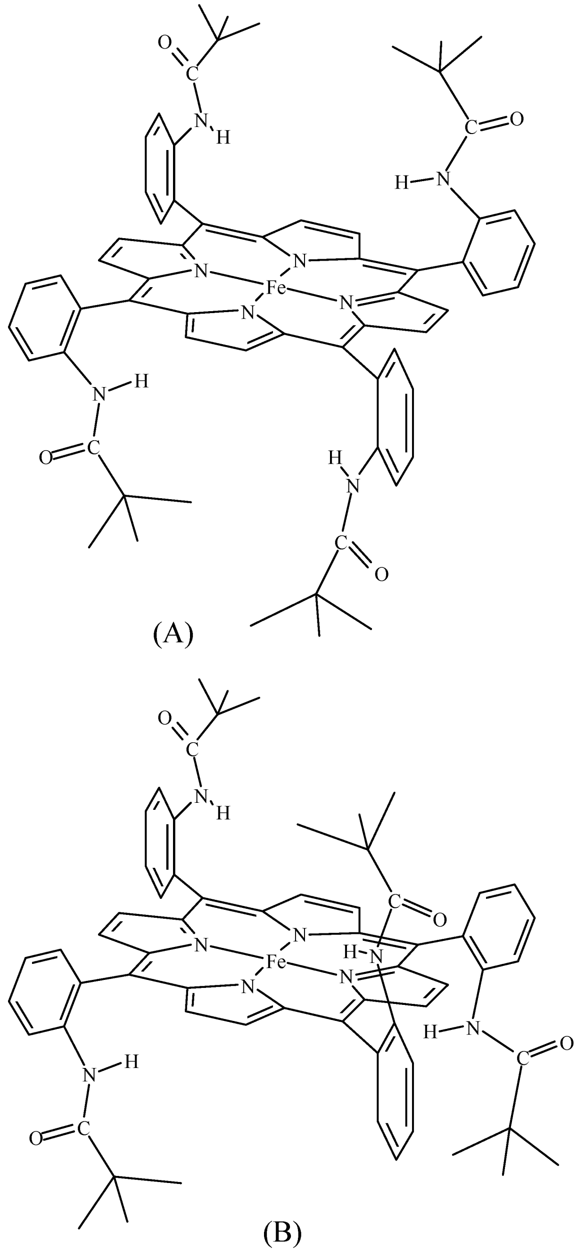

Figure 1. Schematic structures of the $\alpha\alpha\beta\beta$ (A) and $\alpha\beta\alpha\beta$ (B) atropisomers of Fe(II)−tetrakis(*o*-pivalamidophenyl)porphyrin.

enrichment) was from Merck. The ferrous complexes were obtained by reduction of the Fe(III) derivatives in a two-phase system consisting of methylene chloride and aqueous dithionite under vacuum.[8,12] The absorption and RR measurements of the Fe(II) compounds were performed under anaerobic conditions.[8] The ligand binding was checked by absorption and RR spectroscopies. For most of the investigated Fe(II)TpivPP complexes, the ligand concentrations were 0.1−1 mM. Preliminary titrations, however, showed that DCHIm has a low affinity for the four-coordinate Fe(II)TpivPP compounds ($\beta_2 \sim 1-2\ 10^3\ M^2$). A large ligand excess (1−4.3 M) was therefore used to form the bis-DCHIm complexes. The formation of the bis-base complexes was also checked by RR spectroscopy.[8,12]

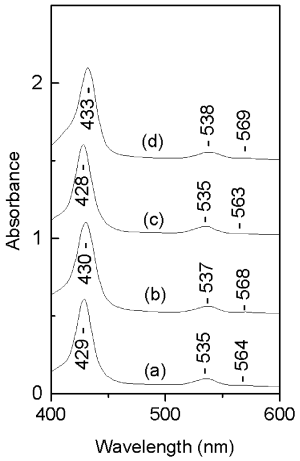

Figure 2. Visible absorption spectra (400−600 nm) of the bis-*N*-methylimidazole and bis-1,5-dicyclohexylimidazole complexes of Fe(II)[$\alpha\alpha\beta\beta$-TpivPP] and of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP] in methylene chloride: (a) Fe(II)[$\alpha\alpha\beta\beta$-TpivPP](*N*-MeIm)$_2$; (b) Fe(II)[$\alpha\alpha\beta\beta$-TpivPP](DCHIm)$_2$; (c) Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](*N*-MeIm)$_2$; (d) Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$.

The electronic absorption spectra were measured by using a Cary 5E (Varian) spectrometer. The RR spectra were recorded at 20 ± 1 °C on a Jobin-Yvon spectrometer (HG2S-UV) with the 441.6 nm excitation of a He−Cd laser (Liconix) and the 413.1 and 406.7 nm excitations of a Kr$^+$ ion laser (Coherent). Using radiant powers of 10−50 mW, the RR spectra (4−8 scans) were independently collected and averaged. The spectral analysis was achieved using Grams 32 software (Galactic Industries). The frequency precision was ±0.5 cm^{-1} for the strongest RR bands (ν_2, ν_4, ν_8) and ± 1 cm^{-1} for the other bands. The full bandwidth at half-height (Γ) of the ν_2, ν_4, and ν_8 bands was measured with an accuracy of ±0.5 cm^{-1}.

Results

Absorption Spectra of the Bis-Base Complexes of Fe(II)TpivPP. The absorption spectra of the bis-*N*-MeIm complexes of Fe(II)[$\alpha\alpha\beta\beta$-TpivPP] and Fe(II)[$\alpha\beta\alpha\beta$-TpivPP] in CH_2Cl_2 closely resemble the spectrum of the Fe(II)TPP(*N*-MeIm)$_2$ complex with Soret, β, and α bands peaking at 427−429, 533−536, and 563−566 nm, respectively (Figure 2, Table 1).

When the bulky DCHIm ligands are coordinated, the visible absorption bands are significantly red-shifted for the $\alpha\alpha\beta\beta$ and $\alpha\beta\alpha\beta$ atropisomers of Fe(II)TpivPP, but not for Fe(II)TPP (Figure 2 and spectra not shown, Table 1). The most pronounced effect is observed for the Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$ complex with band maxima observed at 433, 538, and 569 nm (Figure 2, Table 1). These bands are, respectively, detected at 430, 537, and 568 nm in the absorption spectra of Fe(II)[$\alpha\alpha\beta\beta$-TpivPP](DCHIm)$_2$ (Figure 2, Table 1). The bis-Py complexes of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP], Fe(II)[$\alpha\alpha\beta\beta$-TpivPP], and Fe(II)TPP have very similar absorption spectra with bands peaking at 423, 430−431, and 561−564 nm (spectra not shown, Table 1).

Resonance Raman Spectra of the Bis-Base Complexes of Fe(II)TpivPP. The assignment of the RR bands of the metallo-tetraphenylporphyrin derivatives is based on isotopic data and normal-mode vibrational analysis.[13] The RR spectra of the bis-*N*-MeIm complex of Fe(II)[$\alpha\alpha\beta\beta$-TpivPP] exhibit

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Table 1. Absorption Maxima (nm) and RR Frequencies (cm^{-1}) of the ν_2, ν_4, ν_8 and ν(Fe−L$_2$) Modes of the Bis-*N*-methylimidazole, Bis-dicyclohexylimidazole, and Bis-pyridine Complexes of Fe(II)TPP and Fe(II)PFP[a]

Fe(II) complex	absorption, nm	ν_2 (Γ), cm^{-1}	ν_4 (Γ), cm^{-1}	ν_8 (Γ), cm^{-1}	ν(Fe−L$_2$), cm^{-1}
FeTPP(N-MeIm)$_2$	427, 533, 566	1558 (13.5)	1355 (9.5)	383 (11.0)	192 (186)[a]
Fe[αα$\beta\beta$-TpivPP](N-MeIm)$_2$	428, 535, 564	1558 (12.0)	1355 (9.0)	381 (11.5)	190 (184)[a]
Fe[αβαβ-TpivPP](N-MeIm)$_2$	428, 535, 564	1558 (11.5)	1355 (9.5)	383 (10.5)	188 (181)[a]
FeTPP(DCHIm)$_2$	427, 534, 566	1558 (14.0)	1355 (9.0)	383 (10.0)	187
Fe[αα$\beta\beta$-TpivPP](DCHIm)$_2$	431, 536, 565	1558 (13.5)	1355 (9.5)	383 (13.5)	178
Fe[αβαβ-TpivPP](DCHIm)$_2$	433, 539, 568	1558 (12.5)	1355 (9.5)	388 (12.0)	168
FeTPP(Py)$_2$	423, 530, 562	1557 (17.0)	1357 (9.5)	386 (15.0)	184 (178)[a]
Fe[αα$\beta\beta$-TpivPP](Py)$_2$	423, 530, 561	1556 (13.5)	1356 (9.0)	383 (13.5)	181 (176)[a]
Fe[αβαβ-TpivPP](Py)$_2$	423, 531, 564	1558 (11.5)	1356 (9.0)	381 (9.0)	177 (171)[a]

[a] Observed frequency for perdeuterated ligands.

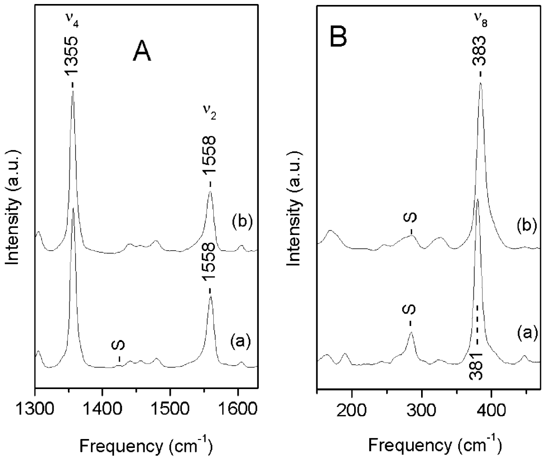

Figure 3. High (1300−1620 cm^{-1}) (A) and low (150−470 cm^{-1}) (B) frequency regions of RR spectra of the bis-*N*-methylimidazole and bis-1,5-dicyclohexylimidazole complexes of Fe(II)[αα$\beta\beta$-TpivPP] in methylene chloride: (a) Fe(II)[αα$\beta\beta$-TpivPP](*N*-MeIm)$_2$; (b) Fe(II)[αα$\beta\beta$-TpivPP]-(DCHIm)$_2$. Excitation: 441.6 nm; summations of 6−8 scans; S indicates solvent bands at 1422 and 285 cm^{-1}.

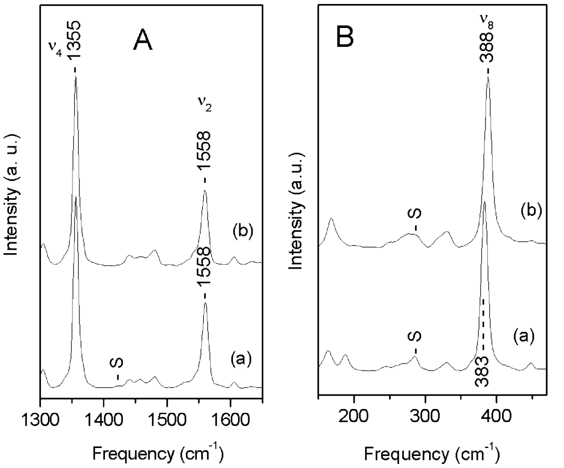

Figure 4. High (1300−1620 cm^{-1}) (A) and low (150−470 cm^{-1}) (B) frequency regions of RR spectra of the bis-*N*-methylimidazole and bis-1,5-dicyclohexylimidazole complexes of Fe(II)[αβαβ-TpivPP] in methylene chloride: (a) Fe(II)[αβαβ-TpivPP](*N*-MeIm)$_2$; (b) Fe(II)[αβαβ-TpivPP]-(DCHIm)$_2$. Excitation: 441.6 nm; summations of 6−8 scans; S indicates solvent bands at 1422 and 285 cm^{-1}.

the ν_2, ν_4, and ν_8 bands at 1558, 1355, and 381 cm^{-1}, respectively (Figure 3A,B, Table 1). The corresponding bands in the RR spectra of the homologous Fe(II)[αβαβ-TpivPP](*N*-MeIm)$_2$ complex are slightly different with frequencies observed at 1558, 1355, and 383 cm^{-1}, respectively (Figure 4A,B, Table 1). The substitution of *N*-MeIm by DCHIm in the Fe(II)[αα$\beta\beta$-TpivPP](L)$_2$ complexes does not influence the frequencies of the ν_2 and ν_4 bands but slightly upshifts the ν_8 band from 381 to 383 cm^{-1} (Figure 3A,B, Table 1). A small broadening of the ν_2 and ν_8 bands is also detected (Table 1). The same change in axial ligation in the Fe(II)[αβαβ-TpivPP](L)$_2$ complexes has again no effect on the frequencies of the ν_2 and ν_4 bands (Figure 4A). However, this ligand substitution produces a more important shift of the ν_8 band from 383 cm^{-1} for the bis-*N*-MeIm complex to 388 cm^{-1} for the bis-DCHIm complex (Figure 4B, Table 1). A broadening of the ν_2 and ν_8 bands is also measured (Table 1).

The *N*-MeIm complexes of natural Fe(II)−porphyrins exhibit a specific RR band at 189−194 cm^{-1}, which was assigned to the symmetric stretching mode of the axial Fe(II)-*N*-MeIm bonds.[14] The ν_s(Fe-*N*-MeIm$_2$) mode of the Fe(II)[αα$\beta\beta$-TpivPP](N-MeIm)$_2$ and Fe(II)[αβαβ-TpivPP]-(*N*-MeIm)$_2$ complexes is observed at 188 and 190 cm^{-1}, respectively (Figure 5A,B, Table 1). This assignment is based on the 6−7 cm^{-1} downshift detected upon *N*-MeIm-h_6 → *N*-MeIm-d_6 substitution (Figure 5A,B, Table 1).[14] In the RR spectra of the bis-DCHIm complexes, the 188−190 cm^{-1} band disappears (Figure 5A,B). It is replaced by a specific shoulder at 178 cm^{-1} for the αα$\beta\beta$ isomer (Figure 5A). When the intensities of the low frequency bands of the RR spectra of Fe(II)[αα$\beta\beta$-TpivPP](DCHIm)$_2$ excited at 406.7, 413.1, and 441.6 nm are compared, one can observed that the 178 cm^{-1} feature has an intensity profile identical to those of the ν_s(Fe-*N*-MeIm$_2$) modes (spectra not shown). Taking into account all these observations, the band observed at 178 cm^{-1} is tentatively assigned to the ν_s(Fe-DCHIm$_2$) mode of the bis-DCHIm complex of Fe(II)[αα$\beta\beta$-TpivPP] (Table 1). In the spectra of the Fe(II)[αβαβ-TpivPP](DCHIm)$_2$ complex, we observe no specific band in the 175−190 cm^{-1}

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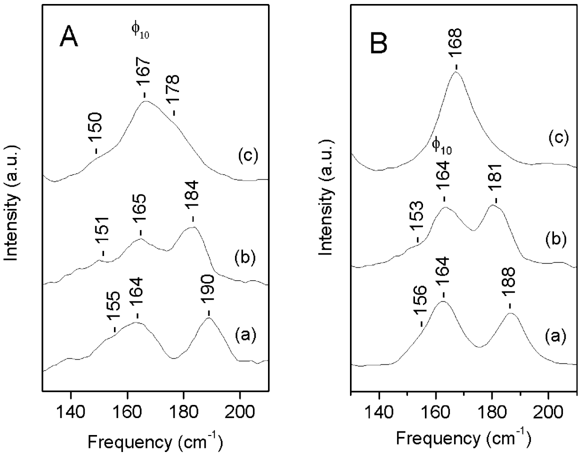

Figure 5. Low frequency regions (130−210 cm^{-1}) of RR spectra of the bis-*N*-methylimidazole and bis-1,5-dicyclohexylimidazole complexes of Fe(II)[αα*ββ*-TpivPP] (A) and of Fe(II)[α*β*α*β*-TpivPP] (B) in methylene chloride. In each panel, spectra (a) *N*-MeIm; (b) *N*-MeIm-d_6; (c) DCHIm.

region, but the intensity of a 168 cm^{-1} band becomes stronger when compared to that detected in the spectra of the αα*ββ* isomer (Figure 5A,B, spectra c). The ν_s(Fe-DCHIm$_2$) mode of Fe(II)[α*β*α*β*-TpivPP](DCHIm)$_2$ complex thus appears to be accidentally degenerated with the ϕ_{10} phenyl mode observed at 164−167 cm^{-1} for the other bis-base complexes.

The low frequency RR spectra of Fe(II)[αα*ββ*-TpivPP](Py)$_2$ and Fe(II)[α*β*α*β*-TpivPP](Py)$_2$ exhibit a ligand-specific band at 181 and 177 cm^{-1}, respectively (spectra not shown). These bands are assigned to ν_s(Fe−Py$_2$) modes considering the 5−6 cm^{-1} downshift observed after Py-h_5 → Py-d_5 substitution in the complexes (Table 1).[8,13a,15]

In passing from Fe(II)TPP to Fe(II)[αα*ββ*-TpivPP] and Fe(II)[α*β*α*β*-TpivPP], the general trend for the three series of axial ligation is thus to decrease markedly the frequency of the ν_s(Fe-L$_2$) modes (Table 1).

Discussion

The different spatial orientations of the *o*-pivalamide groups of Fe(II)[α*β*α*β*-TpivPP] and Fe(II)[αα*ββ*-TpivPP] constitute a preorganization of the Fe−porphyrin binding site. These atropisomers were designed to restrict the rotation of planar axial ligands and to determine the influence of the coordination geometry of the ligand rings on the porphyrin structure.

Bis-*N*-MeIm and Bis-DCHIm Complexes of Fe(II)[αα*ββ*-TpivPP]. In the Fe(II)[αα*ββ*-TpivPP] compound, the alternative up−up and down−down arrangement of the pivalamide pickets are expected to hold the imidazole rings in parallel planes, over two opposite N(pyrrole) atoms.[9] From the absorption and RR spectra, we have no clear indication concerning the absolute and relative positions of the ligand rings in 6c LS Fe(II)−porphyrin complexes. However, the EPR spectra of the homologous Fe(III) complexes supply relevant information on the coordination geometry.[16] The EPR spectrum of the bis-*N*-MeIm complex of Fe(III)[αα*ββ*-TpivPP] exhibits a rhombicity in agreement with a parallel arrangement of the axial imidazoles.[17a,b] That of the Fe(III)[αα*ββ*-TpivPP](DCHIm)$_2$ complex shows a mixture of two signals.[17c] This observation suggests that the imidazole rings of DCHIm adopt parallel orientations with distinguishable positions relative to the N(pyrrole)−Fe−N(pyrrole) axes.[16] In metalloporphyrin complexes, the orientation of the ligand rings is defined from crystallographic coordinates by the angle ϕ between the projection of the ring plane onto the porphyrin core and the closest N(pyrrole)−Fe−N(pyrrole) axis.[3a,4a] The small changes observed in the EPR parameters of the Fe(III)[αα*ββ*-TpivPP] complexes in fact reflect discrete effects of the orientation of parallel ligands.[6a,16]

In the Fe(III)[αα*ββ*-TpivPP](DCHIm)$_2$ complex, the strong steric interactions of the *o*-pivalamide groups with the 1,5-substituents of DCHIm thus lead to parallel alignments of the ligand rings. Since these steric interactions are not expected to be oxidation-dependent, this positioning is presumably similar for the corresponding ferrous complex. The *N*-MeIm → DCHIm substitution in the Fe(II)[αα*ββ*-TpivPP](L)$_2$ complexes produces a red-shift of the Soret band (428 → 431 nm) as well as an upshift of the ν_8 mode (381→ 383 cm^{-1}). All these spectral changes can be attributed to a small distortion of the porphyrin core. The modest spectral alterations do not, however, allow a safe attribution of the distortion type. The absence of shift of ν_2, however, excludes a porphyrin ruffling.[8] In the Fe(II)[αα*ββ*-TpivPP](DCHIm)$_2$ complex, the spatial distribution of the pivalamide arms as well the expected maintenance of parallel imidazole rings close to one of the N(pyrrole)−Fe−N(pyrrole) vector would favor a small porphyrin saddling and/or waving.[3a,18] The E$_g$ symmetry of the substituent orientation makes probable a significant component of wave deformation.

Bis-*N*-MeIm and Bis-DCHIm Complexes of Fe(II)[α*β*α*β*-TpivPP]. The steric interactions between the two cyclohexyl groups of DCHIm and the alternated up and down positions of the *o*-pivalamide groups of Fe(II)[α*β*α*β*-TpivPP] are expected to force the axial ligand rings to take a perpendicular arrangement.[9] The EPR spectrum of the bis-*N*-MeIm complex of Fe(III)[α*β*α*β*-TpivPP] exhibits a rhombic signal.[16,17a,19a] That of the bis-DCHIm ferric complex shows a different type of paramagnetic center with a "high $g_{\max}$ spectrum".[16,19b] This spectral transition clearly reflects a change in the geometry of the axial rings from parallel for

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(17) (a) Le Moigne, C.; Boussac, A.; Loock, B.; Momenteau, M.; Desbois, A. Unpublished spectra. (b) The EPR spectrum of the Fe(III)(αα*ββ*-TpivPP)(1MeIm)$_2$ complex in frozen CH$_2$Cl$_2$ has EPR parameters at 2.88, 2.30, and 1.57. (c) The g_z region of the EPR spectrum of Fe(III)[αα*ββ*-TpivPP](DCHIm)$_2$ exhibits two lines of nearly equal intensity at 3.08 and 2.91. Resonances are also detected at 2.29 in the g_y region and at 1.57 in the g_x region.

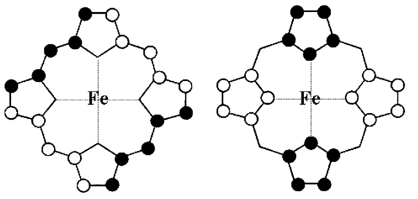
(18) Jentzen, W.; Simpson, M. C.; Hobbs, J. D.; Song, X.; Ema, T.; Nelson, N. Y.; Medforth, C. J.; Smith, K. M.; Veyrat, M.; Mazzanti, M.; Ramasseul, R.; Marchon, J.-C.; Takeuchi, T.; Goddard, W. A.; Shelnutt, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11085.

(19) (a) The EPR spectrum of Fe(III)(α*β*α*β*-TpivPP)(*N*-MeIm)$_2$ in frozen CH$_2$Cl$_2$ shows three lines at 2.95, 2.29, and 1.52. (b) The EPR spectrum of the Fe(III)[α*β*α*β*-TpivPP](DCHIm)$_2$ complex exhibits g values at 3.31, 2.30, and 1.54.

the bis-*N*-MeIm ferric complex to near perpendicular for the bis-DCHIm ferric complex.[16] Although the porphyrin structure could be slightly dependent on the oxidation state of the iron atom,[3a,6,7,20] the steric interactions between the pivalamide groups and the ligands appear to be sufficiently strong to assume a similar change in the arrangement of the axial rings in the homologous Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](*N*-MeIm)$_2$ and Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$ complexes.

The absorption spectra of the bis-*N*-MeIm and bis-DCHIm complexes of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP] show redshifts of the B- and Q-bands when the axial *N*-MeIm ligands are replaced by DCHIm (Table 1). These shifts are indicative of a change in porphyrin structure from a planar to a nonplanar conformation.[21] As far as the RR spectra are concerned, the frequencies of the ν_2 and ν_8 modes of the Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](*N*-MeIm)$_2$ complex are very similar to those obtained for Fe(II)TPP(*N*-MeIm)$_2$. The crystal structure of Fe(II)TPP(*N*-MeIm)$_2$ shows a flat porphyrin and parallel imidazole rings forming a ϕ angle of 10° with the nearest N(pyrrole)−Fe−N(pyrrole) axis.[7a] The absorption and RR data are thus in agreement with a very similar planar conformation for the porphyrin ring of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](*N*-MeIm)$_2$. The comparison of the RR spectra of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](*N*-MeIm)$_2$ and Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$ shows changes localized in the low frequency regions. While the ν_2 and ν_4 bands are not affected by the axial *N*-MeIm → DCHIm substitutions, the ν_8 band exhibits an upshift of 5 cm^{-1} (Table 1). Considering the ν_8 assignment,[13c,d] this shift represents a significant shortening of the Fe−N(pyrrole) bonds.

For 6c LS complexes of Fe(II) "bis(picket)−mono(handle)" porphyrins[8a] and of cross-*trans* (CT) Fe(II) "basket handle" porphyrins[8b] (Fe(II)BHP), planar → ruffled structural transitions cause upshifts of the ν_8 frequency as well as downshifts of the ν_2 frequency. Linear correlations were established between the frequencies of the two modes.[8] The bis-*N*-MeIm and bis-DCHIm complexes of the $\alpha\beta\alpha\beta$ isomer of Fe(II)TpivPP behave differently with an upshift of ν_8, but no shift of ν_2. Previous investigations on free-base porphyrins as well as on Cu− and Ni−porphyrins showed that porphyrin ring distortions produce bathochromic shifts for both the Q and Soret bands.[21] From the redshift of the visible absorption bands, one can conclude that the axial N-MeIm → DCHIm substitutions induce a nonplanar distortion of the tetrapyrrole macrocycle of Fe(II)[$\alpha\beta\alpha\beta$-TpivPP]. As far as the RR data of the bis-*N*-MeIm and bis-DCHIm complexes of Fe(II)-[$\alpha\beta\alpha\beta$-TpivPP] are concerned, a frequency upshift of ν_8 observed in the absence of ν_2 shift cannot be attributed to a ruffled porphyrin in Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$.[8]



(A) (B)

Figure 6. Schematic representation of ruffled (A) and saddled (B) conformations. The filled (●) and open (○) circles indicate displacements above and below the mean porphyrin plane, respectively.

In the FeTPP derivatives, the coordination geometry of the axial ligands as well as the porphyrin conformation are the result of an energetic compromise between steric and electronic effects of the ligands, the porphyrin macrocycle, and the peripheral *o*-substituted phenyl rings. On one hand, the coordination geometry of the axial rings is expected to be mainly conditioned by the steric interactions between the porphyrin pickets and the ligand substituents. On the other hand, the nonplanar distortions of the TPP derivatives are coupled with rotations and/or tilting of the phenyl rings.[3a] In particular, NiTPP exists in solution as two or three conformers, i.e., planar, ruffled, and saddled.[22] The two nonplanar conformers have different phenyl rotations.[22] A destabilization of a ruffled macrocycle in Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$ likely originates from favorable nonbonding interactions and/or unfavorable DCHIm−picket interactions. The phenyl rings of the ruffled FeTPP derivatives are perpendicular to the $C_aC_mC_a$ planes, and the C_m atoms are alternatively above and below the porphyrin plane. This structural effect promotes a concerted tilting of the *o*-pivalamidophenyl groups in which the terminal *tert*-butyl groups of each pair of opposite pickets are brought closer. The tilting of the *o*-pivalamidophenyl groups consequently decreases the size, and modifies the shape, of the ligand pockets and thus can destabilize the binding of the bulky DCHIm ligands.

Beside ruffling (Figure 6), crystallographic studies showed that the most frequent alternative distortion for 6c LS Fe(II)−porphyrin complexes is saddling.[6,7,23] Like ruffling, saddling in the Fe(II)[$\alpha\beta\alpha\beta$-TpivPP](DCHIm)$_2$ complex can accommodate a perpendicular orientation of two identical rings axially coordinated by a superstructured porphyrin possessing two axes of symmetry in its mean plane.[6m,7e] However, the phenyl−porphyrin interactions differ for the ruffled and saddled distortions. Indeed, the phenyl groups of saddled TPP derivatives are alternately tilted left or right with respect to the $C_aC_mC_a$ planes. This distortion allows small rotations about the C_m−C(phenyl) bonds of the aryl groups, and subsequently of the rigid pickets, toward the porphyrin plane.[3a] This rotation of the phenyl rings stabilizes the saddled structure in decreasing the steric strain between the pyrrole C_b−H groups and the *o*-substituents of the phenyl

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(20) Due to a strong photoreduction under laser illumination, the bis-DCHIm complexes of Fe(III)[$\alpha\alpha\beta\beta$-TpivPP] and of Fe(III)[$\alpha\beta\alpha\beta$-TpivPP] were not accessible to RR investigations.

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(22) Jentzen, W.; Unger, E.; Song, X.-Z.; Jia, S.-L.; Turowska-Tyrk, I.; Schweitzer-Stenner, R.; Dreybrodt, W.; Scheidt, W. R.; Shelnutt, J. A. *J. Phys. Chem. A* **1997**, *101*, 5789.

(23) Salzmann, R.; Ziegler, C. J.; Godbout, N.; McMahon, M. T.; Suslick, K. S.; Oldfield, E. *J. Am. Chem. Soc.* **1998**, *120*, 11323.

rings. In the Fe(II)[αβαβ-TpivPP](DCHIm)$_2$ complex, this movement likely decreases the steric interactions between the cyclohexyl groups of DCHIm and the *tert*-butyl groups of the pivalamide groups. Therefore, porphyrin saddling is expected to favor the DCHIm binding through slight rotations of the *o*-pivalamidophenyl groups. Moreover, the fact that ν_2 is insensitive to the axial N-MeIm → DCHIm substitutions in Fe(II)[αβαβ-TpivPP](L)$_2$ is similar to spectral distinctions made for variously distorted Ni(II)−porphyrins. Ruffled Ni(II)−porphyrins showed strongly downshifted ν_2 frequencies.[18] On the contrary, the downshift of ν_2 for Ni(II)−porphyrins combining ruffled and saddled distortions is relatively small. [21e,24]

The different vibrational origins of ν_2 and ν_8 easily explain their different sensitivities to different types of nonplanar distortions of the porphyrin macrocycle. The ν_2 mode was assigned to a mixing of $\nu(C_aC_m)$ and $\nu(C_bC_b)$ stretching.[13c] Ruffling causes important twisting about the C_aC_m bonds, whereas saddling does not.[3] The ν_2 frequency decreases with increasing ruffling. For saddling, the absence of effect on ν_2 is understandable considering that pyrrole tilting does not affect the C_aC_m bonds.[3] The ν_8 mode consists primarily of FeN(pyrrole) and C_aC_m bond stretching motion and $C_aC_mC_a$ bending.[13c] Both the FeN(pyrrole) bonds and the methine bridges are affected by the porphyrin distortions. The ruffled and saddled distortions shorten the FeN(pyrrole) bonds.[3] With respect to a planar structure, these two out-of-plane deformations are thus expected to increase the ν_8 frequency.

Finally, one could envisage a porphyrin waving for the Fe(II)[αβαβ-TpivPP](DCHIm)$_2$ complex. It is difficult to support this hypothesis since we have no structural information on a waved TPP compound as well as on the phenyl orientations for such a porphyrin structure. However, the symmetry elements generated by both the alternative positioning of the pickets and the perpendicular orientation of the axial rings are not expected to stabilize a significant waved component in the total out-of-plane distortions of the porphyrin.

In conclusion, the changes in orientation of the axial imidazole rings in the bis-*N*-MeIm and bis(DCHIm) complexes of Fe(II)[αβαβ-TpivPP] produce changes in absorption and RR spectra. The data obtained cannot be interpreted in the frame of a change in porphyrin conformation from planar to ruffled or waved when the axial *N*-MeIm ligands are substituted by DCHIm. The absence of effect on ν_2 is in agreement with a saddled porphyrin structure in Fe(II)[αβαβ-TpivPP](DCHIm)$_2$.

Bis-Pyridine complexes of Fe(II)[αα$\beta\beta$-TpivPP] and Fe(II)[αβαβ-TpivPP]. The porphyrin macrocycle of Fe(II)-TPP(Py)$_2$ complex is nearly planar.[7c] With two pyridine molecules of solvation, irregular out-of-plane displacements were observed.[7b] The absorption spectra of the bis-Py complexes of Fe(II)TPP, Fe(II)[αα$\beta\beta$-TpivPP], and Fe(II)[αβαβ-TpivPP] are very similar (Table 1). The absence of shift in Soret band position may indicate that the Py binding to either Fe(II)[αα$\beta\beta$-TpivPP] or Fe(II)[αβαβ-TpivPP] does not induce any additional out-of-plane distortion of the tetrapyrrole macrocycle. Ruffling and saddling promote red-shifts of the absorption bands,[8b,21] but we cannot exclude that other types of nonplanar motifs (doming, waving, or pyrrole propellering) or combinations of nonplanar distortion modes do not influence the electronic properties of the porphyrin. In this line, frequency changes in several RR modes have been observed (Table 1). In particular, the parallel downshift of the ν_8 and $\nu_s(Fe-L_2)$ frequencies indicates an expansion of the coordination sphere of the iron atom in passing from Fe(II)TPP to Fe(II)[αα$\beta\beta$-TpivPP] and Fe(II)[αβαβ-TpivPP] (Table 1). This effect is likely due to changes in position of the Py rings relative to the N(pyrrole)−Fe−N(pyrrole) coordinates. In Fe(III)−porphyrin complexes, a lengthening of the axial Fe−N(Py) bonds generally reflects increased nonbonded repulsions between the 2,6-hydrogens of the Py ligands and the porphyrinato nitrogens as the ϕ angle tends to be small.[3a]

The tridimensional structures of Fe(II)TPP(*N*-MeIm)$_2$ and Fe(II)TPP(Py)$_2$ show similar Fe−N(porphyrin) bonds, but the Fe−N(axial) bonds are significantly longer for the bis-Py complex than for the bis-N-MeIm complex.[3a] The ϕ angle has a value of 34−43° for the bis-Py complexes relative to 10° for the bis-*N*-MeIm complex.[7a−c] It indicates increased nonbonded ligand−porphyrin interactions in the bis-Py complexes.

In the bis-Py complexes of CT Fe(II)−BHP, RR data indicate that ruffling tends to contract the coordination sphere of the iron atom.[8b] In the bis-Py complexes of Fe(II)[αα$\beta\beta$-TpivPP] and Fe(II)[αβαβ-TpivPP], long Fe−N(Py) and Fe−N(pyrrole) bonds appear to accommodate mutual interactions between the Py rings, the porphyrin macrocycle, and the pivalamide substituents. From the presently available spectroscopic data, we cannot conclude about the type of porphyrin distortion, i.e., either in-plane core deformations, or out-of-plane doming, waving, and/or propellering deformations.

Porphyrin Structure in Bis-Base Complexes of Fe(II)−Porphyrins. The ruffled structures in CT Fe(II)−BHP were primarily associated with steric effects due to the tight linkage of opposite phenyl rings.[25] In the absence of introduced external effects, we observe no change in both the ligand coordination and the porphyrin structure for the Fe(II)TPP-(*N*-MeIm)$_2$ and Fe(II)TPP(DCHIm)$_2$ complexes (Table 1). The present investigation strongly suggests that a saddled conformation can be stabilized in the Fe(II)[αβαβ-TpivPP]-(DCHIm)$_2$ complex. One cannot, however, generalize the fact that all the Fe(II) "picket fence" compounds are not able to stabilize a ruffled conformation. Indeed, a previous RR study on a bis-*N*-MeIm complex of the Fe(II)−tetrakis(*N*-*tert*-butylcarbamoyl)phenyl)porphyrin ([αααα-TtButPP]), in

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[24] (a) Ma, J.-G.; Zhang, J.; Franco, R.; Jia, S.-L.; Moura, I.; Moura, J. G.; Kroneck, P. M. H.; Shelnutt, J. A. *Biochemistry* **1998**, *37*, 12431. (b) Franco, R.; Ma, J.-G.; Lu, Y.; Ferreira, G. C.; Shelnutt, J. A. *Biochemistry* **2000**, *39*, 2517.

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which the picket amide groups have been reversed in comparison with the homologous Fe(II)[αααα-TpivPP](*N*-MeIm)$_2$ complex, showed clear opposite shifts of the ν_2 and ν_8 modes.[8,12b,13a] In this case, an electronic effect of the *o*-phenyl substituents decreases the electron density of the porphyrin.[26] This effect appears to stabilize a ruffled conformation for the ferrous macrocycle.

Different investigations indicate the influence of nonplanar distortions on the chemical and physical properties of metalloporphyrins.[3d] The various behaviors of the absorption bands and of the RR modes open the possibility to diagnose the structure of the Fe(II)−porphyrins in model compounds or in hemoproteins. From the comparisons of the spectral data presently accumulated for various bis-base complexes of Fe(II)−tetraarylporphyrins, we can deduce that the B and Q absorption bands as well as the ν_2, ν_8, and ν_s(Fe−L$_2$) RR modes are sensitive to different types of structural perturbations of the Fe(II)−porphyrin macrocycle. Both a red-shift of the absorption bands and an upshift of the ν_8 mode constitute good criteria to diagnose a ruffled or saddled distortion in a bis-base Fe(II)−porphyrin complex.[27] The ruffled or saddled distortion can be subsequently differentiated from the sensitivity of the ν_2 mode. For ruffled porphyrins, a downshift of ν_2 is linearly correlated with the ν_8 upshift.[8] On the contrary, the ν_2 frequency appears to be insensitive to saddling of Fe(II)−porphyrins. As far as the other nonplanar distortions are concerned, the spectroscopic data obtained for adjacent-*cis* Fe(II)−BHP complexes as well as for the Fe(II)[αα*ββ*-TpivPP] complexes indicate behaviors different from those detected for either planar Fe(II)−TPP complexes, or ruffled CT Fe(II)−BHP complexes, or the saddled Fe(II)[α*β*α*β*-TpivPP](DCHIm)$_2$ complex. We are currently exploring the parameters along with variations in porphyrin peripheral substituents to further delineate their structural characteristics.

Conclusion

In this study, we have investigated different bis-base complexes of Fe(II)TpivPP atropisomers to obtain better understanding of the influence of restricted ligand rotations on the porphyrin structure. In particular, this spectroscopy study indicates that the Fe(II)[αα*ββ*-TpivPP](DCHIm)$_2$ complex is most likely saddled with its axial ligands arranged in a near perpendicular arrangement. This observation provides a basis to discern ruffled from saddled conformation in bis-base LS ferrous complexes.

RR and absorption spectroscopies of a number of b- and c-type cyt showed different patterns suggesting different types of nonplanar distortions of the porphyrin macrocycle. From our investigations on 6c LS Fe(II)−BHP and Fe(II)−PFP complexes, the behaviors of the absorption bands, as well as those of the ν_2, ν_8, and ν_s(Fe−L$_2$) RR modes, presently provide a convenient way to predict the planar, ruffled, or saddled structures of the ferrous hemes in 6c LS hemoproteins. Further investigations are in progress to develop predictive spectroscopic methods for determining other nonplanar porphyrin distortions in proteins.

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