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Four-Coordinate, Low-Spin ($S = 0$) and Six-Coordinate, High-Spin ($S = 1$) Nickel(II) Complexes of Tetraphenylporphyrins with β-Pyrrole Electron-Withdrawing Substituents: Porphyrin-Core Expansion and Conformation

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To examine the porphyrin-core expansion and the conformational variations induced by a change in the coordination sphere of nickel(II) from four-coordinate, low-spin ($S = 0$) to six-coordinate, high-spin ($S = 1$), several nickel(II) derivatives of tetraphenylporphyrins, substituted in their β-pyrrole positions with electron-withdrawing groups, were isolated and studied by X-ray crystallography. The four-coordinate nickel(II) complex studied, Ni(TPP(Br)$_4$(CN)$_4$) (**1**), is a derivative of the antipodal β-pyrrole brominated and cyanated macrocycle, 2,3,12,13-tetrabromo-7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrin. One of the six-coordinate species is the bis-pyridine nickel(II) adduct, Ni(TPP(Br)$_4$(CN)$_4$)(py)$_2$ (**2**), of this antipodal β-pyrrole brominated and cyanated ring, whereas the second six-coordinate complex is the bis-1-methylimidazole nickel(II) adduct, Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**), of the antipodal tetracyanated macrocycle, 7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrin. This study confirms that, upon conversion of a four-coordinate, low-spin nickel(II) derivative of a β-pyrrole-substituted tetraphenylporphyrin into a six-coordinate, high-spin complex, a radial expansion of the porphyrin core also takes place. This radial expansion flattens the porphyrin core, inducing more planarity in the conformations of the six-coordinate nickel(II) porphyrin species. The X-ray structure of **1** reveals an average Ni−N$_p$ bond distance of 1.920(2) Å, similar to that present in tetragonal Ni(OEP) [(Ni−N$_p$)$_{av}$ = 1.929(3) Å], the ruffled low-spin nickel(II) ($S = 0$) porphyrin derivative, and many other low-spin nickel(II) complexes of distorted porphyrins. The conformation of the macrocycle present in **1** is severely saddle-shaped with a small ruffling and a minor doming. The structures of **2** and **3** indicate a clear expansion of the porphyrin cores with two sets of (Ni−N$_p$)$_{av}$ bond lengths of 2.040(2) and 2.073(2) Å in **2** and 2.037(2) and 2.068(2) Å in **3**, which differ significantly from the average Ni−N$_p$ distance occurring in **1**. Relative to the conformation of the porphyrin ring present in **1**, the high-spin complex **2** is less saddle-shaped, but more ruffled. In **3**, in which only two opposite pyrrole rings of the porphyrin are substituted by cyano groups, the macrocycle adopts a slightly waved conformation. Crystal data: Ni(TPP(Br)$_4$(CN)$_4$)·2.5(1,2-Cl$_2$C$_2$H$_4$), [**1**·2.5(1,2-Cl$_2$C$_2$H$_4$)], triclinic, space group $P\bar{1}$, $a = 13.741(1)$ Å, $b = 14.029(2)$ Å, $c = 15.201(2)$ Å, $\alpha = 89.037(9)°$, $\beta = 70.829(8)°$, $\gamma = 67.607(8)°$, $V = 2539.4(5)$ Å^3, $T = 20$ °C, $Z = 2$, $R_F = 0.047$ and $R_{wF} = 0.067$ based on 5341 reflections with $I > 3\sigma(I)$; Ni(TPP(Br)$_4$(CN)$_4$)(py)$_2$·2.5(1,2-Cl$_2$C$_2$H$_4$), [**2**·2.5(1,2-Cl$_2$C$_2$H$_4$)], triclinic, space group $P\bar{1}$, $a = 11.9472(9)$ Å, $b = 14.3651(7)$ Å, $c = 19.556(1)$ Å, $\alpha = 87.049(5)°$, $\beta = 73.181(6)°$, $\gamma = 70.613(5)°$, $V = 3026.8(4)$ Å^3, $T = 173$ K, $Z = 2$, $R_F = 0.036$, $R_{wF} = 0.041$ based on 6846 reflections with $I > 3\sigma(I)$; Ni(TPP(CN)$_4$)(1-MeIm)$_2$·2CH$_2$Cl$_2$, [**3**·2(CH$_2$Cl$_2$)], monoclinic, space group $C2/c$, $a = 26.804(8)$ Å, $b = 10.948(3)$ Å, $c = 19.453(5)$ Å, $\beta = 113.13(2)°$, $V = 5251.5$ Å^3, $T = 20$ °C, $Z = 4$, $R_F = 0.047$, $R_{wF} = 0.067$ based on 4384 reflections with $I > 3\sigma(I)$.

Introduction

Cofactor 430 (F$_{430}$) present in *S*-methyl-coenzyme M reductase (methyl reductase) and tunichlorin are the only known tetrapyrrole rings from living systems containing nickel as the central metal.[1] Methyl reductase is a complex enzyme of molecular weight of approximately 300 kDa, with an $\alpha_2\beta_2\gamma_2$ subunit structure.[2,3] Each α subunit contains a tightly bound cofactor F$_{430}$, shown to be a nickel(II) tetrapyrrole (hydrocorphin) derivative.[4] The structure of F$_{430}$ containing a six-coordinate nickel(II) atom with a pseudo-octahedral environment has been deduced by a variety of spectroscopic techniques applied to the enzyme and to model compounds.[5−8] This environment has been confirmed by the X-ray structure of methyl-reductase published recently.[9,10] The occurrence of six-

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[‡] This article is dedicated to Professor John Osborn, an excellent friend, on the occasion of his 60th birthday.

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coordinate, pseudo-octahedral, nickel(II) atoms located in a tetrapyrrole ring is quite rare.[8] To date, most known nickel(II) porphyrins contain a four-coordinate metal atom;[11−14] only a few nickel(II) porphyrins in which the metal atom is six-coordinate have been investigated.[15−20] Moreover, almost all of the porphyrins present in these known six-coordinate nickel(II) complexes have mostly planar conformations. Six-coordinate, pseudo-octahedral nickel(II) environments in porphyrins can be generated, in the presence of an excess of axial base, when using porphyrin macrocycles which are substituted in their β-pyrrole positions by electron-withdrawing groups. We show here that the electron-withdrawing properties of the bromo and/or cyano substituents present in the 2,3,12,13-tetrabromo-7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrin, TPP-$(Br)_4(CN)_4$, and 7,8,17,18-tetracyano-5,10,15,20-tetraphenylporphyrin, $(TPP(CN)_4)$, dianions and, consequently, the electron-deficiency of the porphyrin and the nickel center enhance sufficiently the complexing power toward axial ligation of nickel(II) in $Ni(TPP(Br)_4(CN)_4)$ and $Ni(TPP(CN)_4)$. In noncoordinating solvents the nickel(II) centers of these porphyrins remain four-coordinate with a slightly distorted square-planar coordination polyhedron. However, addition of an excess of a nitrogen base leads to the binding of two axial nitrogen-donating ligands by the nickel(II) cation, lying now in a pseudo-octahedral environment.

However, since four-coordinate square-planar or almost square-planar nickel(II) complexes are low-spin, and six-coordinate octahedral or pseudo-octahedral nickel(II) derivatives are high-spin,[21] the $3d_{x^2-y^2}$ orbital which is unpopulated in $Ni(TPP(Br)_4(CN)_4)$ (**1**) will be singly populated in $Ni(TPP(Br)_4(CN)_4)(py)_2$ (**2**) and $Ni(TPP(CN)_4)(1\text{-MeIm})_2$ (**3**). Since this $3d_{x^2-y^2}$ unpaired electron is antibonding, the change in the spin state of nickel(II) between **1** and **2** and between **1** and **3** will affect the $Ni-N_p$ (N_p = pyrrole nitrogen) bond lengths. Moreover, these bond lengths are also affected by the nonplanar conformations of the porphyrin cores and by the reduced basicity of the pyrrole nitrogens belonging to the pyrrole rings which are substituted with electron-withdrawing groups. To assess the effects of axial ligation on nonplanar tetraphenylporphyrins, substituted in their β-pyrrole positions by eletron-withdrawing groups, we have characterized spectroscopically and determined the structures of the four-coordinate, low-spin ($S = 0$), nickel(II) porphyrin, $Ni(TPP(Br)_4(CN)_4)$ (**1**) and of the six-coordinate, high-spin ($S = 1$), bis-pyridine and bis-1MeIm adducts $Ni(TPP(Br)_4(CN)_4)(py)_2$ (**2**) and $Ni(TPP(CN)_4)(1\text{-MeIm})_2$ (**3**). We present here the results of these studies.

Experimental Section

All syntheses were performed using distilled and degassed solvents. Pyrrole and benzaldehyde were distilled before use. *N*-Bromosuccinimide (NBS) was purified by a published procedure to remove traces of bromine.[22] ^1H NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz. Chemical shifts of ^1H NMR resonances are given in parts per million relative to TMS. Electronic spectra were obtained on a Varian Cary 05E UV−vis−near-IR spectrometer. IR spectra were measured on a Perkin-Elmer FTIR 1600. The starting metal-free 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin, $H_2TPP(Br)_4$, its nickel(II) complex, $Ni(TPP(Br)_4)$, and the nickel(II) derivative of 2,3,12,13-tetracyano-5,10,15−20-tetraphenylporphyrin, $Ni(TPP(CN)_4)$, were prepared according to published procedures.[23] They were characterized in solution by UV−vis and ^1H NMR spectroscopy. The CN stretching vibrations of the cyano-β-pyrrole porphyrin substituents of $Ni(TPP(CN)_4)$ were measured in the solid state by FTIR spectroscopy.

$H_2TPP(Br)_4$. UV−vis (CH_2Cl_2); λ_{max} 436.5 (Soret), 534, 548, 683 nm. ^1H NMR ($CDCl_3$): δ (ppm) −2.81 (s, 2H, NH_{pyrr}), 7.79 (m, 12H, phenyl *p*- and *o*-H), 8.16 (m, 8H, phenyl *m*-H), 8.69 (s, 4H, β-*pyrr*-H).

$Ni(TPP(Br)_4)$. UV−vis (CH_2Cl_2): λ_{max} 430 (Soret), 546.5, 587 nm. ^1H NMR ($CDCl_3$): δ (ppm) 7.64 (m, 12H, phenyl *p*- and *o*-H), 7.85 (m, 8H, phenyl *m*-H), 8.54 (s, 4H, β-*pyrr*-H).

$Ni(TPP(CN)_4)$. UV−vis (CH_2Cl_2): λ_{max} 439 (Soret), 632 nm. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)/TMS = 7.74 (m, 12H, phenyl *p*- and *o*-H), 7.86 (m, 8H, phenyl *m*-H), 8.74 (s, 4H, β-*pyrr*-H). FTIR (KBr): $\nu_{CN} = 2216\ cm^{-1}$.

Preparation of $Ni(TPP(Br)_4(CN)_4)$ (1). To a refluxing solution containing 200 mg of $Ni(TPP(CN)_4)$ and 462 mg (10 equiv) of *N*-bromosuccinimide (NBS) in chloroform (150 mL) was added 50 mL of methanol. The reaction was monitored by UV−vis spectroscopy and taken to dryness when the Soret band, which is located at 439 nm in $Ni(TPP(CN)_4)$, reached 476 nm. The solid so obtained was dissolved in CH_2Cl_2 and washed twice with water, and the organic layer was dried over $MgSO_4$ and evaporated. Column chromatography over silica gel (Geduran Si6O, 0.040−0.063, Merck-1567) with CH_2Cl_2 as eluant yielded, after recrystallization in $CHCl_3$/MeOH, 60 mg (21%) of $Ni(TPP(Br)_4(CN)_4)$, containing the β-pyrrole octasubstituted tetraphenylporphyrin. Single crystals of composition $Ni(TPP(Br)_4(CN)_4)\cdot 2.5(1,2\text{-}Cl_2C_2H_4)$ [$\mathbf{1}\cdot 2.5(1,2\text{-}Cl_2C_2H_4)$] suitable for X-ray analysis were obtained by slow diffusion of decane into a solution of $Ni(TPP(Br)_4(CN)_4)$ in 1,2-dichloroethane.

UV−visible (CH_2Cl_2, room temperature): λ_{max} (ϵ, $mM^{-1}\ cm^{-1}$): 458 (215), 638 (39) nm. ^1H NMR ($CDCl_3$): δ (ppm) 7.8 (m, 8H, phenyl *m*-H), 7.9 (m, 12H, phenyl *o*- and *p*-H).

Preparation of $Ni(TPP(Br)_4(CN)_4)(py)_2$ (2). Slow diffusion of hexane into a solution of $Ni(TPP(Br)_4(CN)_4)$ in 1,2-dichloroethane/pyridine (10/1) led to the formation of single crystals of composition $Ni(TPP(Br)_4(CN)_4)(py)_2\cdot 2.5(1,2\text{-}Cl_2C_2H_4)$ [$\mathbf{2}\cdot 2.5(1,2\text{-}Cl_2C_2H_4)$] suitable for X-ray analysis. Dichloromethane solutions of these crystals displayed, at 195 K, a UV−vis spectrum with bands at λ_{max} (ϵ, $mM^{-1}\ cm^{-1}$) 390 (5), 460 (151), 478 (145), 712 (9), 775 (16) nm. This spectrum remains unchanged by addition of a large excess of pyridine. The presence of a six-coordinate nickel(II) center in **2** has been ascertained by X-ray crystallography (vide infra).

Preparation of $Ni(TPP(CN)_4)(1\text{-MeIm})_2$ (3). The bis-1-MeIm adduct $Ni(TPP(CN)_4)(1\text{-MeIm})_2$ was prepared by adding at room temperature 1000 equiv of 1-MeIm to a solution of $Ni(TPP(CN)_4)$ in dichloromethane. The X-ray structure of the bis-pyridine adduct

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Table 1. Crystallographic Data for **1**−**3**[a]

	1	**2**	**3**
empirical formula	$C_{48}H_{20}N_8NiBr_4 \cdot 2.5(C_2H_4Cl_2)$	$C_{58}H_{30}N_9NiBr_4 \cdot 2.5(C_2H_4Cl_2)$	$C_{56}H_{36}N_{12}Ni \cdot 2(CH_2Cl_2)$
fw	1334.49	1492.70	1105.57
space group	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	13.741(1)	11.9472(9)	26.804(3)
b, Å	14.029(2)	14.3651(7)	10.948(1)
c, Å	15.201(2)	19.556(1)	19.459(2)
α, deg	89.037(9)	87.049(5)	90
β, deg	70.829(8)	73.181(6)	113.13(2)
γ, deg	67.607(8)	70.613(5)	90
V, Å^3	2539.4(5)	3026.8(4)	5251(2)
Z	2	2	4
ρ_{calcd}, g cm^{-3}	1.745	1.637	1.398
μ, mm^{-1}	3.812	3.208	0.625
T (K)	293	173	293
no. of obsd reflns	5341 ($I > 3\sigma(I)$)	6846 ($I > 3\sigma(I)$)	4384 ($I > 3\sigma(I)$)
$R(F)$[b]	0.047	0.036	0.047
$R_w(F)$[c]	0.064	0.041	0.067

[a] In common: $\lambda = 0.710\ 73$ Å. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum wF_o^2]^{1/2}$.

$Ni(TPP(CN)_4)(py)_2$ has been established recently.[18] The UV−vis spectrum of **3** displayed bands at λ_{max} (ϵ, mM^{-1} cm^{-1}) 447 (sh, 79), 470 (122), 672 (38), 712 (32). The presence of a six-coordinate nickel(II) center in $Ni(TPP(CN)_4)(1\text{-}MeIm)_2$ (**3**) was ascertained by its X-ray structure (vide infra). Slow diffusion of hexane into dichloromethane/1-MeIm (10/1) solutions of $Ni(TPP(CN)_4)$ led to single crystals of composition $Ni(TPP(CN)_4)(1\text{-}MeIm)_2 \cdot 2CH_2Cl_2$[**3**·$2(CH_2Cl_2)$], suitable for X-ray analysis.

X-ray Data Collection and Processing. Crystal data and details of the diffraction data collections are given in Table 1. Systematic searches in reciprocal space using a Nonius CAD4-F diffractometer showed that the crystals of composition **1**·$2.5(1,2\text{-}Cl_2C_2H_4)$ and **2**·$2.5(1,2\text{-}Cl_2C_2H_4)$ belong to the triclinic system, space group $P\bar{1}$, whereas those of **3**·$2(CH_2Cl_2)$ are monoclinic, space group $C2/c$. Unit cell parameters were determined from 25 high-angle reflections. Quantitative data were obtained in the $\theta/2\theta$ mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The resulting data sets were transferred to a Digital Alpha computer, and for all subsequent calculations the OpenMoleN package[24] was used. The raw data were converted to intensities and corrected for Lorentz, polarization, and absorption factors, the latter derived from ψ scans of seven reflections. Three standard reflections measured every 2 h during the entire data collection periods showed no significant trends. The structures were solved using direct methods. After refinement of the heavy atoms, difference Fourier maps revealed maxima of residual electronic density close to the positions expected for hydrogen atoms. They were introduced into structure factor calculations as fixed contributors by their computed coordinates (C−H = 0.95 Å) with isotropic temperature factors such as $B(H) = 1.3B_{eqv}(C)$ Å^2. Final solutions were obtained using full-matrix least-squares refinements against F with weighting schemes $w = 4F_o^2/(\sigma^2(F_o^2) + 0.0064F_o^4)$. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from ref 25.

Results and Discussion

The molecular structures of the nickel(II) porphyrins $Ni(TPP(Br)_4(CN)_4)$ (**1**), $Ni(TPP(Br)_4(CN)_4)(py)_2$ (**2**), and $Ni(TPP(CN)_4)(1\text{-}MeIm)_2$ (**3**) together with the labeling schemes used are displayed in Figure 1, parts a, b, and c, respectively. Figure 2a−c shows in Å × 10^{-2} units the perpendicular displacements of all of the independent porphyrin-core and nickel atoms of the three complexes, relative to the 24-atom-core mean planes of their rings. Figure 3 displays an edge-on view of the porphyrin-core skeleton of **3**. Parts a, b, and c of Figure 4 are linear displays of the skeletal deviations from the planes defined by the 24-atom-core mean planes of **1**, **2**, and **3** in Å units, respectively. Table 2 lists selected bond distances and angles as well as some averages. The asymmetric units of the triclinic crystals of **1**·$2.5(1,2\text{-}Cl_2C_2H_4)$ and **2**·$2.5(1,2\text{-}Cl_2C_2H_4)$ (space groups $P\bar{1}$) each contain one independent molecule of $Ni(TPP(Br)_4(CN)_4)$ (**1**) or $NiTPP(Br)_4(CN)_4(py)_2$ (**2**), together with 2.5 molecules of 1,2-dichloroethane of solvation, respectively. Accordingly, one molecule of 1,2-dichloroethane lies on a crystallographic inversion center in both crystals. The asymmetric unit of the monoclinic crystals of **3**·$2(CH_2Cl_2)$ (space group $C2/c$) contains $^1/_2$ independent molecule, $Ni(TPP(CN)_4(1\text{-}MeIm)_2$ (**3**), together with one independent molecule of dichloromethane. Each nickel(II) porphyrin $NiTPP(CN)_4(1\text{-}MeIm)_2$ (**3**) lies on a crystallographic inversion center and, consequently, has $\bar{1}$ crystallographic symmetry. As indicated earlier, the bis-1-MeIm adduct $Ni(TPP(CN)_4)(1\text{-}MeIm)_2$ was obtained by adding at room temperature 1000 equiv of 1-MeIm to a solution of $Ni(TPP(CN)_4)$ in dichloromethane. Axial binding of pyridine to $Ni(TPP(CN)_4)$ was already observed in 1981 by Callot et al.,[26] by addition of pyridine to dichloromethane solutions of the four-coordinate, low-spin ($S = 0$), nickel(II) porphyrin. We have confirmed recently the structure of this bis-pyridine adduct.[18]

Since the displacement of nickel(II) in $Ni(TPP(Br)_4(CN)_4)$ (**1**) and $NiTPP(Br)_4(CN)_4)(py)_2$ (**2**) relative to the porphyrin-core mean planes is either zero or not significant, one can assume that the metal atom lies, in both complexes, in the porphyrin-core mean plane. Moreover, the nickel(II) atom of $Ni(TPP(CN)_4(1\text{-}MeIm)_2$ (**3**) occupies a crystallographic center of symmetry and, thus, is required by symmetry to lie in the porphyrin-core mean plane.

Nickel(II) is four coordinate, low-spin, in **1** and six-coordinate, high-spin, in **2** and **3**. In high-spin nickel(II) species, the $3d_{x^2-y^2}$ orbital is singly populated and this electron is antibonding. Accordingly, an expansion of the porphyrin core must take place, leading to $Ni-N_p$ bond distances which become longer in **2** and **3** than in **1**. Furthermore, two supplementary effects affect the $Ni-N_p$ bond lengths of nickel(II) porphyrins when this ring is substituted by electron-withdrawing groups and when its core conformation is nonplanar. These two effects

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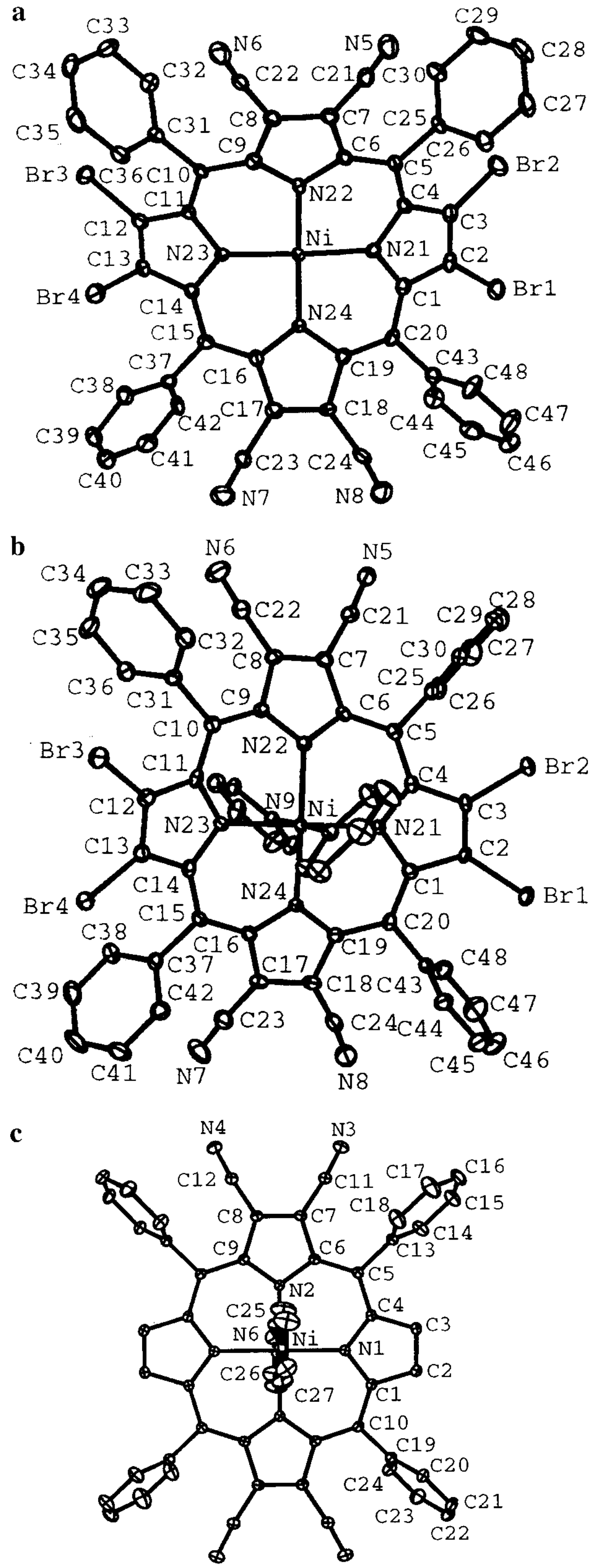

Figure 1. ORTEP diagrams of (a) Ni(TPP(Br)$_4$(CN)$_4$) (**1**), (b) Ni(TPP)(Br)$_4$(CN)$_4$)(py)$_2$ (**2**), and (c) Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**). Ellipsoids are drawn to illustrate 30% probability surfaces.

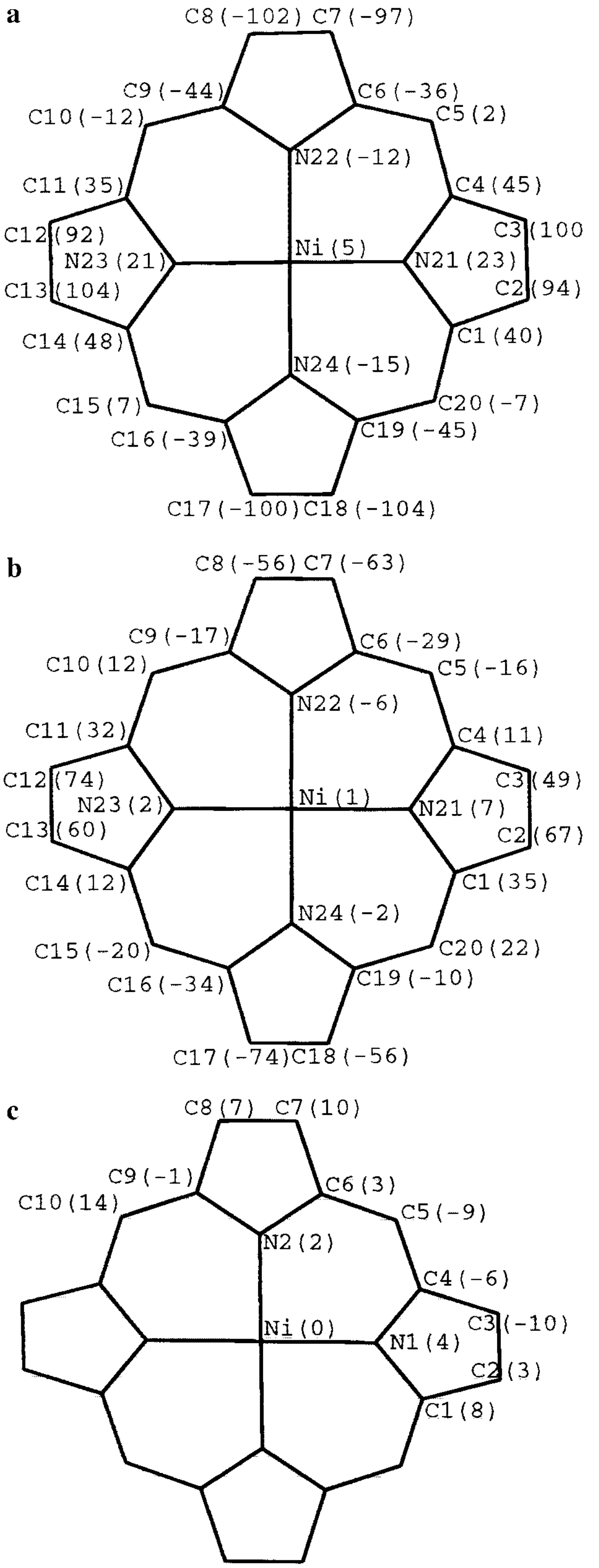

Figure 2. Displacements of the porphyrin-core, β-pyrrole substituent, and nickel atoms relative to the porphyrin-core mean plane of (a) Ni(TPP(Br)$_4$(CN)$_4$) (**1**), (b) Ni(TPP)(Br)$_4$(CN)$_4$)(py)$_2$ (**2**), and (c) Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**), in Å × 10^{-2} units.

are opposite because (i) nonplanar porphyrin cores tend to shorten the Ni$-$N$_p$ bond distances,[27,28] and (ii) when porphyrin pyrrole rings are substituted by electron-withdrawing groups the basicity of the nitrogen atoms belonging to these pyrroles

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Figure 3. Edge-on view of the porphyrin-core skeleton of Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**).

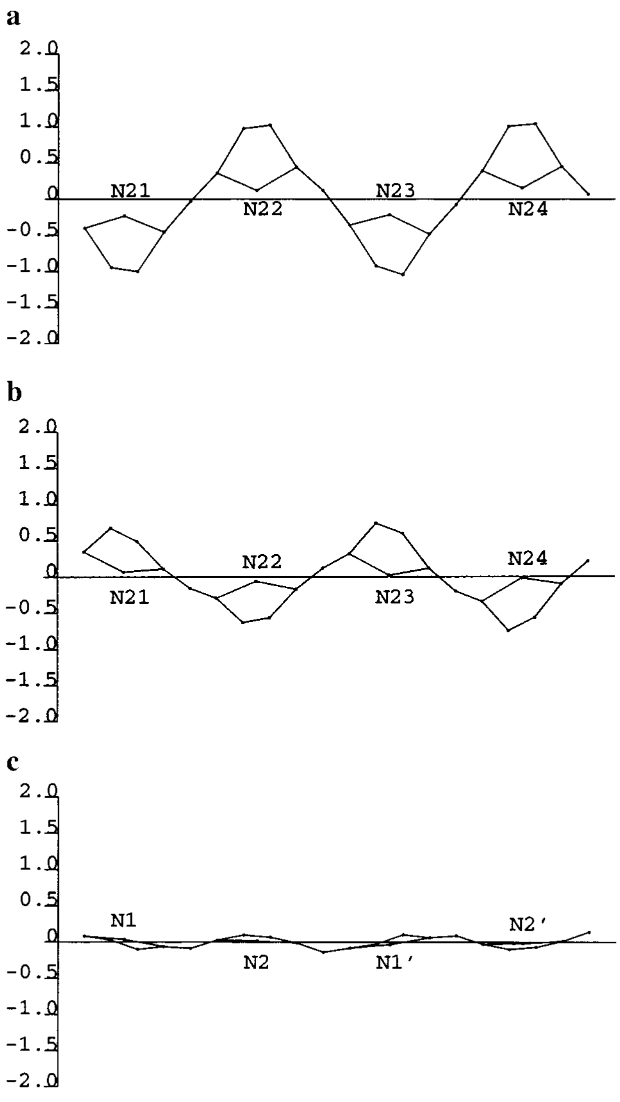

Figure 4. Linear display of the skeletal deviations from the porphyrin-core mean plane of (a) Ni(TPP(Br)$_4$(CN)$_4$) (**1**), (b) Ni(TPP)(Br)$_4$(CN)$_4$)(py)$_2$ (**2**), and (c) Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**), in Å units.

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Averages for **1**−**3**

	1	2	3
$(Ni-N_p(H))_{av}$			2.037(2)
$(Ni-N_p(Br))_{av}$	1.911(4)	2.073(2)	
$(Ni-N_p(CN))_{av}$	1.929(4)	2.040(2)	2.068(2)
$(N_p(H)-C_\alpha)_{av}$			1.364(2)
$(N_p(Br)-C_\alpha)_{av}$	1.385(4)	1.375(3)	
$(N_p(CN)-C_\alpha)_{av}$	1.383(4)	1.367(3)	1.366(2)
$(C_\alpha-C_m)_{av}$	1.381(8)	1.405(8)	1.405(9)
$(C_\alpha-N_p(H)-C_\alpha)_{av}$			106.6(2)
$(C_\alpha-N_p(Br)-C_\alpha)_{av}$	106.3(4)	108.2(2)	
$(C_\alpha-N_p(CN)-C_\alpha)_{av}$	106.7(4)	108.4(2)	108.2(2)
$(C_\alpha(H)-C_m-C_{Phe})_{av}$			117.1(1)
$(C_\alpha(Br)-C_m-C_{Phe})_{av}$	121.0(3)	119.2(2)	
$(C_\alpha(CN)-C_m-C_{Phe})_{av}$	118.9(3)	116.1(2)	117.7(1)
$(N_p(H)-C_\alpha-C_m)_{av}$			123.6(1)
$(N_p(Br)-C_\alpha-C_m)_{av}$	123.3(3)	124.6(2)	
$(N_p(CN)-C_\alpha-C_m)_{av}$	124.4(3)	126.0(2)	125.7(1)
$(C_\alpha-C_\beta)(H)_{av}$			1.454(2)
$(C_\alpha-C_\beta)(Br)_{av}$	1.450(5)	1.463(3)	
$(C_\alpha-C_\beta)(CN)_{av}$	1.438(5)	1.441(3)	1.438(2)
$(C_\beta-C_\beta)(H)$			1.338(4)
$(C_\beta-C_\beta)(Br)_{av}$	1.342(7)	1.341(4)	
$(C_\beta-C_\beta)(CN)_{av}$	1.368(7)	1.371(4)	1.374(4)
$(N_p(H)-C_\alpha-C_\beta)_{av}$			109.6(1)
$(N_p(Br)-C_\alpha-C_\beta)_{av}$	108.7(3)	108.1(2)	
$(N_p(CN)-C_\alpha-C_\beta)_{av}$	109.2(3)	108.6(2)	108.8(1)
$(C_\alpha-C_\beta-C_\beta)(H)_{av}$			107.0(1)
$(C_\alpha-C_\beta-C_\beta)(Br)_{av}$	107.5(3)	107.6(2)	
$(C_\alpha-C_\beta-C_\beta)(CN)_{av}$	107.2(3)	107.1(2)	106.9(1)
$(C_\alpha-C_m-C_\alpha)_{av}$	121.1(3)	124.6(2)	124.9(1)
$(C_\beta-Br)_{av}$	1.870(5)	1.870(4)	
$(C_\beta-C(CN))_{av}$	1.458(18)	1.433(7)	1.430(2)
$(C(CN)-N(CN))_{av}$	1.064(15)	1.147(7)	1.139(3)

decreases relative to that of the nonsubstituted pyrroles and, consequently, the Ni−N$_p$ bond distances tend to increase.[27] The Ni−N$_p$ bond lengths occurring in **1**, **2**, and **3** follow these trends. The major effect is the spin-state change of nickel(II) from $S = 0$ in **1** to $S = 1$ in **2** and **3**. Indeed, the average Ni−N$_p$ bond distances are significantly shorter in **1** (1.920(2) Å) than in **2** (2.056(2) Å) and **3** (2.052(2) Å). Moreover, if we denote by N$_p$(CN) the nitrogens belonging to the pyrrole rings which are substituted by cyano groups, by N$_p$(Br) the nitrogens of the brominated pyrrole rings, and by N$_p$(H) the nitrogen belonging to the nonsubstituted pyrroles, the average (Ni−N$_p$(CN))$_{av}$ and (Ni−N$_p$(Br))$_{av}$ bond distances in the low-spin species **1** are 1.911(1) and 1.929(4) Å, respectively. In contrast, in the high-spin complexes **2** and **3**, (Ni−N$_p$(CN))$_{av}$ = 2.040(2), (Ni−N$_p$(Br))$_{av}$ = 2.073(2) Å and (Ni−N$_p$(CN))$_{av}$ = 2.068(2), (Ni−N$_p$(H))$_{av}$ = 2.037(2) Å, respectively. These values indicate that the shortening of the bond lengths due to nonplanarity of the porphyrin core is larger than the lengthening of the bond distances due to reduction in basicity of the pyrrole nitrogens induced by the electron-withdrawing substituents. In low-spin Ni(TPP(Br)$_4$(CN)$_4$) (**1**) in which the ring is severely saddle shaped (vide infra), the (Ni−N$_p$)$_{av}$ bond distances are shorter than in the low-spin nickel(II) porphyrin complexes in which the porphyrin cores are planar, as in triclinic Ni(OEP) (1.958 Å),[29] Ni(DeuP) (1.960 Å) and in Ni(EtioP) (1.957 Å),[30,31] but similar to or longer than in the nickel(II) derivatives of porphyrins having similar or more strongly distorted cores as in tetragonal Ni(OEP) (1.929(3) Å),[32] Ni(DETPP) (1.923(6) Å), Ni(cTETPP) (1.923(4) Å), Ni(HETPP) (1.921(3) Å),[33] Ni(OETPP) (1.906(2) Å), Ni(OPrTPP) (1.902(2) Å), Ni(TC$_6$TPP) (1.914(9) Å),[28] Ni(TMOBP) (1.916(12) Å), Ni(TPFPOBP) (1.898(10) Å)[27] (1.903(1) Å).[34] In the high-spin complex, Ni(TPP(Br$_4$)(CN)$_4$)(py)$_2$ (**2**) in which the porphyrin ring is less planar than in the high-spin species Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**), the (Ni−N$_p$(CN))$_{av}$ distance of 2.040(2) Å present in **2** is shorter than that present in **3** (2.068(2) Å). In this last complex (**3**), in which the porphyrin core is not severely nonplanar, the (Ni−N$_p$(H))$_{av}$ bond length of 2.037(2) Å is not significantly different from that of 2.038 Å, occurring in the nickel(II) derivative, Ni(TMPyP)(ImH)$_2$ (TMPyP = *meso*-tetra(4-*N*-methylpyridinyl)porphyrin dianion) in which the porphyrin ring is

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almost planar.[15] It is well-known that, in planar porphyrins, the N−Cα and Cα−Cm bond distances and Cα−N−Cα, N−Cα−Cm, and N−Cα−Cβ bond angles are sensitive to a radial expansion of the porphyrin core.[35−37] An expansion of the porphyrin cores present in $Ni(TPP(Br)_4(CN)_4)(py)_2$ (**2**) and $Ni(TPP(CN)_4)(1\text{-}MeIm)_2$ (**3**) is also indicated by the average values of these bond distances and bond angles occurring in the β-cyanated pyrrole rings of these complexes: $(N-C\alpha)_{av}$ = 1.367(3) Å (**2**), 1.366(2) Å (**3**), and 1.383(4) Å (**1**); $(C\alpha-Cm)_{av}$ = 1.405(8) (**2**), 1.405(9) (**3**), and 1.381(8) (**1**); $(C\alpha-N-C\alpha)_{av}$ = 108.4(2)° (**2**), 108.2(2)° (**3**), and 106.7(4)° (**1**); $(N-C\alpha-Cm)_{av}$ = 126.0(2)° (**2**), 125.7(1)° (**3**), and 124.4(3)° (**1**); $(N-C\alpha-C\beta)_{av}$ = 108.6(2)° (**2**), 108.8(1)° (**3**), and 109.2(1)° (**1**).

Moreover, the axial average Ni−N(pyridine) bond length of 2.153(3) Å occurring in **2** is shorter than the corresponding value of 2.242(2) Å arising in the structure of $Ni(TPP(CN)_4)(py)_2$.[18] The observed difference can be attributed to a stronger σ-bond between pyridine and nickel(II) in complex **2** in which the electron deficiency of the porphyrin and, hence, of the nickel atom is larger than in $Ni(TPP(CN)_4)(py)_2$. The porphyrin present in **2** is β-substituted by four bromines and four cyano groups, whereas in $Ni(TPP(CN)_4)(py)_2$ the porphyrin ring is β-substituted by only four cyano groups. The average Ni−N(1-MeIm) axial bond distance of 2.174(2) Å present in $Ni(TPP(CN)_4(1\text{-}MeIm)_2$ (**3**) is similar to the $(Ni-N)_{av}$ axial bond distances observed in the six-coordinate nickel(II) derivative $[Ni^{II}(TMPyP)(ImH)_2]^{4+}$ (2.160 Å).[15] However, these two $(Ni-N)_{av}$ axial bond distances observed in **3** and in $[Ni^{II}(TMPyP)(ImH)_2]^{4+}$ are longer than the $(Ni-N)_{av}$ bond length of 2.08 Å observed in octahedral high-spin $Ni^{II}N_6$ complexes with nitrogen-donating ligands,[38] but shorter than the $(M-N_p)_{av}$ bond lengths observed in other metalloporphyrins in which the metal has, as in high-spin nickel(II), a singly occupied d_{z^2} orbital. Such a singly occupied d_{z^2} orbital occurs in the low-spin $3d^7$ cobalt(II) complexes, $Co(TPP)(piperidine)_2$ (2.436(2) Å) and $Co(OEP)(3\text{-}picoline)_2$ (2.386(2) Å),[39] and in the high-spin $3d^4$ manganese(III) derivative, Mn(TPP)(py)(Cl) (2.444(2) Å).[15] The shorter axial $(Ni-N)_{av}$ bond lengths present in the high-spin nickel(II) porphyrin species **3** and $[Ni^{II}(TMPyP)(ImH)_2]^{4+}$ can be ascribed to π-back-donation of the filled nickel d_π (d_{xz}, d_{yz}) orbitals into the antibonding π^*-orbitals of the imidazole axial ligands, back-donation which seems stronger in high-spin nickel(II) species than in low-spin cobalt(II) porphyrin complexes.[15]

A convenient measure of the pyridine or imidazole axial ligand orientations relative to the porphyrinato nitrogens is the dihedral angle formed by the coordinate plane containing opposite pyrrole nitrogens and the axial ligand mean plane. This dihedral angle is in general denoted by ϕ. A value of $\phi = 0°$ corresponds to an eclipsed orientation and a value of 45° to a staggered orientation.[40] In **2**, both ϕ values are close to 45° ($\phi_1 = 42.0(1)°$ and $\phi_2 = 50.0(1)°$); thus the axial ligands are mutually almost perpendicular and lie in a staggered conformation. This mutual perpendicular orientation of the axial ligand mean planes, making dihedral angles ϕ close to 45° with the closest $Ni-N_p$ axis, is probably related to the ruffled porphyrin core conformation present in **2**. The β-pyrrole tetracyanated and tetrabrominated porphyrin present in this compound is not planar, but less saddle shaped and more ruffled than in the tetracoordinated nickel(II) species **1** (vide infra). Studies of the axial ligand orientations of iron(II),[41] and iron(III),[42,43] porphyrinates with two axial nitrogen donating ligands in relation with the porphyrin-core conformations have shown that when the ring is planar the axial ligand mean planes are parallel, when the porphyrin is ruffled the ligand mean planes are perpendicular and staggered relative to the $Fe-N_p$ bonds, and when the ring is saddle-shaped the axial ligand mean planes are perpendicular and eclipsed relative to the $Fe-N_p$ bonds. Thus, most probably in **2** the ruffling of the ring imposes a perpendicular orientation of the axial pyridine mean planes with ϕ angles close to 45°. Moreover, this staggered conformation favors back-donation from the filled $d\pi$ (d_{xz}, d_{yz}) orbitals of high-spin nickel(II) and the empty π^* orbitals of the pyridines and minimizes the nonbonding interactions between the two axial ligands and the porphyrin ring. In contrast, in **3** the two axial 1-MeIm mean planes are parallel. This axial ligand orientation is related to the sligthly waved, almost planar, porphyrin-core conformation occurring in this compound due to the crystallographic required inversion center present at the nickel(II) atom. The near eclipsed conformation of the two axial ligands relative to the $Ni-N_p$ bonds ($\phi \approx 0°$) is probably the result of a competition between π-bonding and steric interactions. It favors π-donor interactions between the filled $p\pi$ orbitals of the axial ligands and the empty 4p orbitals of the nickel(II) atom.[44] These π-bonding interactions are quite strong with good π-donors such as 1-MeIm. However, these interactions, which are strong and stabilizing at small ϕ angles, but are negligible or destabilizing when these ϕ angles become larger, are counteracted by steric effects favoring larger values of ϕ. In **3**, in which ϕ is close to 0°, the steric effects are probably weak. The shortest nonbonding contact distances between the axial ligands and the porphyrin macrocycle are all larger than 2.6 Å.

Figure 1 indicates that the porphyrin present in **1** displays a more distorted nonplanar conformation than that present in **2** and **3**. The geometry of the $TPP(Br)_4(CN)_4$ dianion present in **1** is almost a pure saddle. Only small ruffling and doming distortions are superimposed on the larger saddle. A pure S_4 saddle distortion of a porphyrin core can be characterized by the average displacements of all of the geminal β-carbons of the four pyrrole rings above and below the porphyrin mean plane. Since in **1** the cyanated pyrroles alternate with brominated ones, the symmetry of the distortion is closer to C_2. However, the average values of the displacements of the geminal β-carbons corresponding to the cyanated and brominated pyrroles above and below the porphyrin-core mean plane of 1.010(6) and 0.975(6) Å, respectively, are not significantly different. Moreover, the ruffling of the $TPP(Br)_4(CN)_4$ dianion present in **1** is small as indicated by the average displacements of the meso

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carbons above and below the porphyrin mean plane of 0.0515(60) and 0.094(6) Å, respectively. Furthermore, the mean plane of the four pyrrole nitrogens lies 0.042(1) Å below the porphyrin mean plane, indicating that a small doming is also present. The structural decomposition method (NSD)[45] indicates also a strong saddling (sad = 3.068 Å) and a small ruffling (ruf = 0.205 Å) and doming (dom = 0.090 Å) for a total out-of-plane distortion $D_{\mathrm{oop}} = 3.080$ Å. Hexacoordination of nickel(II) in **2** reduces the out-of-plane distortions of the macrocyclic TPP(Br)$_4$(CN)$_4$ ring, as shown by the average displacement, above and below the porphyrin mean plane, of the geminal β-carbons of 0.625(4) Å belonging to the cyanated and brominated pyrroles. The saddling of the macrocycle is less important than in the four-coordinate, low-spin complex **1**. However, the ruffling is now more important, as indicated by the displacements of the meso carbons above and below the porphyrin mean plane of 0.167(4) and 0.176(4) Å, respectively. The separation between the 4N$_p$ and the porphyrin mean planes is not significant; thus in **2** there is no doming of the ring. The structural decomposition analysis (NSD)[45] confirms that, relative to **1**, a significant reduction of the saddle shape (*sad* = 1.866 Å), a significant increase in ruffling (*ruf* = 0.489 Å), and no doming (*dom* = 0.00 Å) occur in **2** for a total out-of-plane distortion $D_{\mathrm{oop}} = 1.950$ Å. Ni(TPP(CN)$_4$(1-MeIm)$_2$ (**3**) lies on a center of symmetry; thus the porphyrin is not saddle shaped, but shows a slightly waved conformation (Figure 3). In this waved conformation one pair of opposite cyanated pyrrole rings are tilted up and down by 4.64(8)°, while the other opposing nonsubstituted rings are only twisted by 2.46(7)° relative to the porphyrin mean plane. Moreover, a maximum deviation of 0.140(3) Å (meso carbon) and an average deviation of 0.063(2) Å are observed relative to the 24-atom mean plane. Again, the structural decomposition analysis (NSD)[45] is in total agreement with these qualitative observations: *sad* = 0.000, *ruf* = 0.000, *dom* = 0.000, but *wav(x)* = 0.119, *wav(y)* = 0.291, and *pro* = 0.000 for a total out-plane-distortion D_{oop} of 0.363. This waved conformation is due to the presence in **3** of a porphyrin ring with two opposite β-substituted and two opposite β-nonsubstituted pyrrole rings. The small steric strain arising between the cyano substituents and the *meso*-phenyl groups is released by a simple opening of the $C_\alpha(CN)-C_m-C_{Phe}$ bond angles relative to their counterparts $C_\alpha(H)-C_m-C_{Phe}$ [$C_\alpha(CN)$ = α-carbons belonging to the cyanated and $C_\alpha(H)$ to the nonsubstituted pyrrole rings, C_m = *meso* carbons, C_{Phe} = phenyl carbon atom attached to the porphine ring] as indicated by the mean values of these angles of 118.7(1)° ($C_\alpha(CN)-C_m-C_{Phe}$) and 116.6(1)° ($C_\alpha(H)-C_m-C_{Phe}$). A linear display of the skeletal deviations from the porphyrin mean planes occurring in these nickel(II) complexes **1**−**3** is shown in Figure 4.

The gradual decrease in the saddle distortion of the porphyrin rings when moving from **1** to **2** and **3** is accompanied by a gradual increase in the dihedral angles arising between the phenyl ring and the porphyrin-core mean planes. It is well-known that, in tetraarylporphyrins with saddle distortions, the phenyl rings rotate into the porphyrin mean plane to minimize unfavorable contact distances with the β-pyrrole substituents.[27,28,40,46] The average dihedral angles between the phenyl ring and porphyrin mean planes are 51.53(21)° in **1**, 63.30(10)° in **2**, and 74.61(6)° in **3**. Table 2 shows that, in the four-coordinate complex **1**, the inner pyrrole Cα−N−Cα, N−Cα−Cβ, and Cα−Cβ−Cβ angles of the brominated and cyanated rings do not differ significantly and have mean values similar to those present in the nonplanar saddle distorted nickel(II) porphyrins, Ni(OETPP), Ni(OPrTPP), and Ni(TC$_6$TPP), and Hoard's "average" porphyrin.[28,36] In contrast, in the six-coordinate derivatives **2** and **3**, the Cα−N−Cα angles become significantly larger except for the two unsubstituted pyrrole rings present in **3**. In **2**, the Cα−N−Cα bond angles of the brominated and cyanated rings are not significantly different, their mean value being 108.4(2)°. In contrast, in **3**, the Cα−N−Cα bond angles corresponding to the nonsubstituted and cyanated pyrroles are significantly different. The mean values in the two opposite unsubstituted and cyanated rings are 106.7(2)° and 108.2(2)°, respectively.

As usual, the nitrogen and carbon atoms of the substituted or nonsubstituted pyrrole rings are nearly planar, whereas the β-substituents of these rings are displaced out of the pyrrole mean planes. Relative to these mean planes, the average values of the displacements of the bromine substituents are 0.2193(9) and 0.1735(5) Å in **1** and **2**, respectively. Those of the carbon and nitrogen atoms forming the cyano substituents are 0.112(7) and 0.221(6) Å in **1**, 0.108(5) and 0.235(5) Å in **2**, and 0.0854(3) and 0.169(3) Å in **3**.

In summary, to assess the effects of axial ligation on nonplanar tetraphenylporphyrins, substituted in their β-pyrrole positions by electron-withdrawing groups, we have studied the structures of a four-coordinate, low-spin ($S = 0$), nickel(II) porphyrin and of two six-coordinate, high-spin ($S = 1$), bis-pyridine and bis-1MeIm adducts. β-Pyrrole substitution of tetraarylporphyrins by electron-withdrawing groups increases the electron deficiency of the nickel(II) atom, which allows the binding of two axial ligands and the formation of six-coordinate, pseudo-octahedral, high-spin nickel(II) ($S = 1$) porphyrin derivatives. The porphyrin ring present in the four-coordinate, low-spin ($S = 0$), nickel(II) complex of the tetrabrominated and tetracyanated tetraphenylporphyrin Ni(TPP(Br)$_4$(CN)$_4$) (**1**) displays a severely saddle-distorted, slightly ruffled conformation with (Ni−N$_p$)$_{av}$ bond distances of 1.929(4) [Ni−N$_p$(Br)] and 1.911(1) Å [Ni−N$_p$(CN)]. Upon conversion of this four-coordinate derivative into the six-coordinate species, a clear expansion of the porphyrin core takes place. In Ni(TPP(Br)$_4$(CN)$_4$)(py)$_2$ (**2**), the (Ni−N$_p$)$_{av}$ bond distances are now 2.073(2) ([Ni−N$_p$(Br)]) and 2.040(2) Å ([Ni−N$_p$(CN)]). In Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**), these (Ni−N$_p$)$_{av}$ bond distances are 2.068(2) ([Ni−N$_p$(CN)]) and 2.037(2) Å ([Ni−N$_p$(H)]. This expansion is accompanied by a significant decrease of the saddle distortion and a clear increase of the ruffling of the porphyrin present in Ni(TPP(Br)$_4$(CN)$_4$)(py)$_2$ (**2**). The macrocycle present in Ni(TPP(CN)$_4$)(1-MeIm)$_2$ (**3**) displays a waved conformation with a porphyrin core which is only slightly nonplanar.

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Supporting Information Available: Listings of positional parameters, anisotropic thermal parameters, selected bond lengths, and selected bond angles for crystals containing **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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