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Coordination-Induced Spin Crossover (CISCO) through Axial Bonding of Substituted Pyridines to Nickel–Porphyrins: σ-Donor versus π-Acceptor Effects

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Abstract: Nickel-porphyrins, with their rigid quadratic planar coordination framework, provide an excellent model to study the coordination-induced spin crossover (CISCO) effect because bonding of one or two axial ligands to the metal center leads to a spin transition from S=0 to S=1. Herein, both equilibrium constants K_{1S} and K_2 , and for the first time also the corresponding thermodynamic parameters ΔH_{18} , ΔH_2 , ΔS_{18} , and ΔS_2 , are determined for the reaction of a nickel-porphyrin (Nitetrakis(pentafluorophenyl)porphyrin) with different 4-substituted pyridines by temperature-dependent NMR spectroscopy. The association constants K_{1S} and K_2 are correlated with the basicity

of the 4-substituted pyridines (R: $OMe > H > CO_2Et > NO_2$) whereas the ΔH_{1S} values exhibit a completely different order ($OMe < H > CO_2Et > NO_2$). 4-Nitropyridine exhibits the largest binding enthalpy, which, however, is overcompensated by a large negative binding entropy. We attribute the large association enthalpy of nitropyridine with porphyrin to the back donation of electrons from the Ni d_{xz} and d_{yz} orbitals into the π orbitals of pyridine, and the negative association entropy to a

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decrease in vibrational and internal rotation entropy of the more rigid porphyrin-pyridine complex. Back donation for the nitro- and cyanopyridine complexes is also confirmed by IR spectroscopy, and shows a shift of the N-O and C-N vibrations, respectively, to lower wave numbers. X-ray structures of 2:1 complexes with nitro-, cyano-, and dimethylaminopyridine provide further indication of a back donation. A further trend has been observed: the more basic the pyridine the larger is K_{1S} relative to K_2 . For nitropyridine K_2 is 17 times larger than K_{1S} and in the case of methoxypyridine K_2 and K_{1S} are almost equal.

Introduction

The coordination of axial ligands to porphyrins is of fundamental importance in many areas of chemistry, biology, and materials science.^[1] The most prominent example is the

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bonding of O_2 to the heme group in hemoglobin and myoglobin, which proceeds under conversion of high-spin Fe^{II} (S=2) in the deoxy form to low-spin Fe^{III} (S=1/2) in the oxy form of these metalloproteins. In the nickel(II)-porphyrins, on the other hand, the metal center is diamagnetic (S=0) in the axially uncoordinated complexes and paramagnetic (S=1) in the five- and six-coordinated state. The spin change provides an opportunity to use these systems as molecular sensors, through monitoring the bonding of axial ligands by electro-optical methods. Alternatively, if the pyridine ligand is suitably tethered to the porphyrin backbone, the coordination and decoordination of this moiety induced by an external stimulus can be exploited for the fabrication of a molecular switch.^[2]

The association constants of Ni-porphyrins to a number of nitrogen donor ligands have been measured.^[3] The binding strength increases with the electron deficiency of the porphyrin and the basicity of the nitrogen donor. Electron-with-

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drawing substituents at the *meso* position of the porphyrin (substituents R in Scheme 1) favor the association of axial ligands.^[4] Walker et al. observed a Hammett relationship of β



 $\beta = K_{1S} \cdot K_2$

Scheme 1. Definition of the association constants of porphyrins with axial ligands (L).

 $(K_{1S}K_2)$ of piperidine with various porphyrins as a function of the *meso* substituent $(R = p - C_6 H_4 R')$.^[5] A closer look reveals that the increase of the association constant induced by the electron deficiency of the porphyrin and the donor strength of the axial ligand is more pronounced for K_{1S} than for K_2 . In most combinations of porphyrins and nitrogen donor ligands K_2 is considerably larger than K_{1S} . Even with an electron-deficient porphyrin such as tetra(4-cyanophenyl)porphyrin ($R = C_4H_5CN$) and the strong donor piperidine, the first equilibrium constant $(K_{1S} = 0.4 \text{ m}^{-1})$ is much smaller than the second $(K_2 = 2.5 \text{ M}^{-1})$.^[6] Hence, the concentration of the five-coordinate 1:1 complex in the equilibrium does not exceed 15% during titration of the porphyrin with piperidine.^[7] It needs the extremely electron-deficient porphyrin nickel tetrakis(2,3,5,6-tetrafluoro-N,N,N-trimethyl-4aniliniumyl)porphyrin ($[Ni(TF_4TMAP)]^{4+}$; $R = C_6F_4N(Me_3)$) and the very strong donor ligand methyl imidazole to reverse the order of association constants ($K_{18} = 550, K_2 =$ $110 \,\mathrm{m}^{-1}$) and to make the five-coordinate species the predominant complex in solution.^[8]

Another factor affecting the axial coordination is the degree of nonplanarity of the Ni-porphyrin in its four-coordinate S=0 low-spin state. Upon coordination to one or two axial ligands, the spin state changes to high spin (S=1) and induces a flattening of the porphyrin core. Large substituents in the *meso* position hinder this decrease in ruffling, and with it axial coordination.^[5] Steric hindrance at the donor ligand is also a very sensitive parameter. Pyrrolidine, for example, binds almost ten times more strongly to Ni-TPP (TPP: tetraphenyl porphyrin; $\beta=23$) than 2-methylpyrrolidine ($\beta=0.27$).^[9] Thermodynamic parameters of axial coordination have been determined by measuring association constants as a function of temperature, however, only for

the coordination of two ligands (β). Ni-TPP binds two piperidine molecules with an enthalpy $\Delta H_{\beta} = -5.6 \text{ kcal mol}^{-1}$ and an entropy $\Delta S_{\beta} = -21 \text{ cal mol}^{-1} \text{K}^{-1}$.^[5] The corresponding thermodynamic parameters for the system Ni-TPP/pyridine have also been determined.^[10]

For the design of a spin switch based on the coordinationinduced spin crossover (CISCO) effect, that is, by controlled coordination/decoordination of an axial ligand, we determined the thermodynamic parameters of both coordination stages by measuring the temperature dependence of K_{1S} and K_2 . In an ideal system K_{1S} should be considerably larger than K_2 to provide the possibility to switch the spin state by adding/removing a single ligand. To this end we developed a simple and reliable methodology to experimentally determine both association constants K_{1S} and K_2 (Scheme 1.) The coordination of 4-substituted pyridines (R=NO₂, CO₂Et, H, OMe) to Ni-tetrakis(pentafluorophenyl)porphyrin was investigated (Scheme 2).



Scheme 2. Ni^{II}-tetrakis(pentafluorophenyl)porphyrin 1 and 4-substituted pyridine derivatives 2a-f used as axial ligands.

In a somewhat simplified fashion, the bonding of the first ligand can be associated with a bonding constant K_{1S} and that of the second ligand with a bonding constant K_2 (see below). Herein, K_{1S} and K_2 are determined by means of NMR spectroscopy, by monitoring the paramagnetic shift of the pyrrole protons as a function of the concentration of added ligand. Through the temperature dependence of K_{1S} and K_2 , bonding enthalpies and entropies are evaluated, which provides the first experimental determination of these parameters for both individual stages of axial ligand coordination to a Ni-porphyrin. The influence of σ versus π effects on the bonding of the substituted pyridine ligands to Ni-porphyrins is discussed.

Results and Discussion

Determination of the association constants K_{1S} and K_2 : The most frequently used methods for the determination of association constants of porphyrins with axial ligands are UV and NMR titration. In preliminary experiments we recorded

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the UV spectra of porphyrin **1** as a function of the concentration of added pyridine. The Soret band of porphyrin **1** at 406 nm decreases and a new band at 429 nm appears. However, there is no clear isosbestic point, which indicates that there are more than two species involved in the equilibrium (Figure 1). This is attributed to the formation of a five- and six-coordinated complex.



Figure 1. UV/Vis spectra of 1 as a function of added pyridine 2d. The Soret band of pure 1 (406 nm) decreases and a new band arises at 429 nm upon addition of pyridine.

Unfortunately, the deviation from an isosbestic plot is not sufficient for an accurate and separate determination of both association constants (K_{1S} and K_2). However, assuming that the paramagnetic complexes **1·2d** and **1·(2d)**₂ have similar absorption maxima (λ_{max}) and extinction coefficients (ε), K_{1S} and K_2 can be estimated from the decrease of the Soret band of the uncoordinated porphyrin at 406 nm.^[11] By using this approximation the association constants of **2d** with **1** were determined at 305 K in toluene as: $K_{1S} = (5.9 \pm$ 0.3) Lmol⁻¹, $K_2 = (13.7 \pm 1.2)$ Lmol⁻¹, and $\beta = (81.1 \pm$ 2.1) L²mol⁻² (for details see the Supporting Information). These values are in good agreement with the binding constants evaluated by NMR spectroscopy (see Table 1.)

NMR titration turned out to provide a very accurate method for the evaluation of K_{1S} and K_2 . Upon addition of axial ligands the diamagnetic porphyrin forms the paramagnetic five- and six-coordinated axial complexes. The paramagnetic Ni^{II} induces a strong paramagnetic shift and a broadening of the NMR signal of the pyrrole protons in the

Table 1. Association constants $[Lmol^{-1}]$ of porphyrin **1** with pyridine derivatives **2a** and **2c–e** at different temperatures in $[D_8]$ toluene.

Association constant	2a	2 c	2 d	2 e
K _{1S}	0.68	2.90	8.20	30.40
K_2	11.60	19.80	22.40	22.70
K_{1S}	0.48	2.16	6.00	21.50
K_2	9.40	13.90	15.80	20.20
K_{1S}	0.34	1.61	4.50	15.80
K_2	6.60	10.40	11.60	14.00
K_{1S}	0.25	1.26	3.40	11.60
K_2	4.80	7.65	8.60	10.80
	Association constant K _{1S} K ₂ K _{1S} K ₂ K _{1S} K ₂ K _{1S} K ₂ K _{1S} K ₂	Association constant $2a$ K_{1S} 0.68 K_2 11.60 K_{1S} 0.48 K_2 9.40 K_{1S} 0.34 K_2 6.60 K_{1S} 0.25 K_2 4.80	Association constant $2a$ $2c$ K_{1S} 0.68 2.90 K_2 11.60 19.80 K_{1S} 0.48 2.16 K_2 9.40 13.90 K_{1S} 0.34 1.61 K_2 6.60 10.40 K_{1S} 0.25 1.26 K_2 4.80 7.65	Association constant2a2c2d K_{1S} 0.682.908.20 K_2 11.6019.8022.40 K_{1S} 0.482.166.00 K_2 9.4013.9015.80 K_{1S} 0.341.614.50 K_2 6.6010.4011.60 K_{1S} 0.251.263.40 K_2 4.807.658.60

porphyrin. In a fast equilibrium of complexation and decomplexation, the ratio of diamagnetic and paramagnetic species can be determined from the average chemical shift of the pyrrole protons. In free porphyrin **1** the pyrrole protons resonate at 8.79 ppm and upon addition of pyridine the chemical shift attains saturation at 57 ppm (Figure 2).



Figure 2. Plot of the chemical shift of the pyrrole protons of porphyrin **1** as a function of added pyridine in $[D_8]$ toluene at 298.03 K.

An Evans measurement of **1** in pure pyridine yielded a molar susceptibility of the six-coordinated paramagnetic complex of $\chi_m = 3.66 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ and a magnetic moment of $\mu = 2.9 \text{ B.M.}$ (Bohr magneton). This fits very well to an S = 1 state with two unpaired electrons $(3.5 < \mu < 2.8 \text{ B.M.}).^{[12-14]}$

The titration experiments (analogous to Figure 2) were performed with the 4-substituted pyridines **2a** and **2c–e** at four different temperatures (298, 308, 318, 328 K). Because of solubility problems, **2b** and **2f** could not be used in this study. K_{1S} as well as K_2 were calculated from the corresponding titration curves by linear fitting of Equation (7) (see below and Table 1).

As expected, the equilibrium constants decrease with increasing temperature (see below). Moreover, both log K_{1S} and log K_2 (and therefore also log β) exhibit linear relationships^[5] with respect to the pK_a values of the pyridines (**2a** 1.5, **2c** 3.5, **2d** 5.2, **2e** 6.6; see Figure 3, Figure 4, and Figure 5).^[15]

Electron-withdrawing substituents give rise to smaller association constants whereas electron-donating groups lead to a stronger binding to the porphyrin. With 4-nitropyridine **2a** as the axial ligand, K_{1S} and K_2 are significantly smaller (2 and 50%, respectively) relative to the most basic ligand used in our study, 4-methoxypyridine **2e**. However, the influence of the basicity of the pyridines on the association constant is more pronounced for K_{1S} than for K_2 : with ligand **2a** K_{1S} is considerably smaller than K_2 ($K_{1S}/K_2=0.06$ at 298 K) whereas for ligand **2e**, K_{1S} is larger than K_2 ($K_{1S}/K_2=1.34$ at 298 K).

Determination of thermodynamic parameters: From the temperature dependence of the association constants, the

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Figure 3. Association of **1** with **2a** and **2c–e** to form high-spin five-coordinated complexes (log K_{1S}) as a function of the basicity of the pyridines **2** (p K_a) in [D₈]toluene at 298 K.



Figure 4. Formation of high-spin six-coordinated complexes from the five-coordinated complex of **1** with **2a** and **2c–e** (log K_2) as a function of the basicity of the pyridines **2** (p K_a) in [D₈]toluene at 298 K.



Figure 5. Formation of high-spin six-coordinated complexes from porphyrin **1** with two equivalents of **2a** and **2c–e** (log β) as a function of the basicity of the pyridines **2** (p K_a) in [D₈]toluene at 298 K.

corresponding binding enthalpies (ΔH_{1s} , ΔH_2) and entropies (ΔS_{1s} , ΔS_2) were determined (Table 2).

The plots of $\ln K$ as a function of T^{-1} exhibit excellent linear relationships (0.998 < R < 0.9999), thus providing accu-

Table 2. Association enthalpies [kcal mol⁻¹] and entropies [cal mol⁻¹K⁻¹] calculated from the temperature dependence of the association constants K_{1s} , K_2 , and β (see Table 1).

	2 a	2 c	2 d	2e
ΔH_{1S}	-6.85 ± 0.06	-5.45 ± 0.07	-5.3 ± 0.1	-6.19 ± 0.06
ΔS_{1S}	-23.7 ± 0.2	-16.2 ± 0.2	-13.6 ± 0.3	-14.0 ± 0.06
ΔH_2	-6.2 ± 0.2	-6.1 ± 0.1	-5.97 ± 0.04	-6.1 ± 0.2
ΔS_2	-15.7 ± 0.9	-14.5 ± 0.4	-13.9 ± 0.1	-13.8 ± 0.6
ΔH_{β}	-13.1 ± 0.3	-11.5 ± 0.1	-11.2 ± 0.5	-12.2 ± 0.08
ΔS_{β}	-39.4 ± 0.8	-30.7 ± 0.3	-27.5 ± 0.4	-27.7 ± 0.3

rate values for the enthalpies and entropies. For **2c–e**, the entropies ΔS_{1S} and ΔS_2 range from -13.6 to -16.2 calmol⁻¹K⁻¹, whereas the formation of the five-coordinated complex with 4-nitropyridine (**2a**) is associated with an exceptionally large negative entropy ΔS_{1S} of -23.67 calmol⁻¹K⁻¹ (Table 2). The binding enthalpies, in contrast, exhibit a much smaller variation; that is, the ΔH_{1S} values range from -5.29 (**2d**) to -6.85 kcalmol⁻¹ (**2a**) and the ΔH_2 values from -5.97 (**2d**) to -6.18 kcalmol⁻¹ (**2a**). In spite of the large differences observed for K_{1S} and K_2 (see above), the associated binding enthalpies are thus quite similar.

Also surprising is the relationship of ΔH_{1S} and ΔH_2 with respect to the basicity of the para-substituted pyridines. For pure σ binding of the pyridine ligand to the nickel ion, a linear correlation of the basicity (pK_a) of the pyridines with the enthalpies (ΔH_{18} and ΔH_2) would be anticipated. However, we observe a V- or U-shaped relationship. As expected, the more basic 4-methoxypyridine (2e, R = OMe) binds more strongly than the parent pyridine (2d). However, the binding enthalpy increases again for electron-deficient 2c $(R = CO_2Et)$ and **2a** $(R = NO_2)$. The least basic pyridine $(2a, R = NO_2)$ binds more strongly $(\Delta H_{1S} = -6.85 \text{ kcal mol}^{-1})$ than the most basic pyridine (2e, R=OMe; ΔH_{1S} = $-6.19 \text{ kcal mol}^{-1}$) (see Figure 6). A similar trend was observed for ΔH_2 (and, as a consequence, for ΔH_β) as a function of the pK_a of the pyridine ligands (Figure 7 and Figure 8). Importantly, the influence of the binding entropy converts the V- or U-shaped characteristics of ΔH versus



Figure 6. Enthalpy ΔH_{1S} (**n**) and free enthalpy ΔG_{1S} (**A**) of complex formation of the *para*-substituted pyridines (**2a**, **2c**-**e**) with porphyrin **1** in $[D_8]$ toluene plotted as a function of the pK_a of the pyridines.

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Figure 7. Enthalpy ΔH_2 (**•**) and free enthalpy ΔG_2 (**•**) of complex formation of the 2:1 complex **1**-(**2**)₂ from the 1:1 complex **1**-2 by coordination of a second pyridine ligand (**2a**, **2c**-**e**) in [D₈]toluene plotted as a function of the p K_a of the pyridines.



Figure 8. Enthalpy ΔH_{β} ($\Delta H_{1S} + \Delta H_2$; •) and free enthalpy ΔG_{β} ($\Delta G_{1S} + \Delta G_2$; •) of complex formation of the *para*-substituted pyridines (**2a**, **2c**-**e**) with porphyrin **1** in [D₈]toluene plotted as a function of the *pK*_a of the pyridines.

 pK_a to the almost linear characteristics observed for ΔG or log K.

Obviously, the basicity of the pyridine nitrogen lone pair is not the exclusive factor determining the binding energy of the corresponding pyridine to the nickel ion. There must be an additional effect operating in the opposite direction. A straightforward explanation would be back donation of the d_{xz} and d_{yz} orbitals into the π orbitals of the nitro-, cyano-, and ester-substituted pyridines. Back donation of Ni^{II} to pyridines has been reported previously.^[16,17] Cole et al. determined the binding enthalpies of several pyridines to Fe^{II}porphyrins by optical spectroscopy.^[18] They also observed that pyridine (R = H) was the weakest axial ligand, and electron-donating (e.g., R=NH₂) as well as electron-deficient substituents (e.g., R = CN) in the 4-position of the pyridine ligands gave rise to larger binding enthalpies, which led to a V shape of the ΔH versus p K_a plot. These rather unusual results were explained by a back-donation effect. Although π acceptor interactions are expected to be weaker for $\mathrm{Ni}^{\mathrm{II}}$

than Fe^{II} ions due to an increased effective nuclear charge, such effects are clearly still present for Ni-porphyrins.

IR investigations on back donation: If back donation is the cause of the unexpected trend in binding energies, the π density of the electron-deficient pyridines should be larger in the Ni complexes relative to the free ligand. Electron transfer into π^* -type orbitals should lead to a weakening of bonds, which in turn should give rise to a decrease in force constants and thus a shift of normal-mode vibrations of suitable symmetry to lower wave numbers. Thus, back donation of electrons from the d_{xz} or d_{yz} orbital of Ni into the LUMO of 4-nitropyridine (**2a**) should give rise to lower wave numbers of the asymmetric and symmetric N–O stretching frequency of the nitro group (which has a node between N and O, see Figure 9).



Figure 9. Molecular orbital diagram for the back donation of the Ni d_{xz} orbital into the LUMO of 4-nitropyridine.

To obtain an idea about the magnitude of these σ -donor and π -acceptor effects, we compiled data from model compounds. A suitable model for back donation is the mesomeric (M+) effect of π -donor substituents in the *para* position to the electron-withdrawing nitro and cyano groups. Thus, *p*methoxynitrobenzene and *p*-methoxycyanobenzene should serve as model structures. Similar to the Ni d_{xz} orbital, the methoxy group donates electrons into the LUMO of the aromatic system including the nitro or cyano group (Figure 9). As expected the symmetric (ν_s) and asymmetric (ν_a) stretching frequencies of the nitro group as well as the CN stretching of the cyano group are shifted to lower wave numbers (Table 3).

The strongest effect is observed for the asymmetric stretching frequency of the nitro group ($\Delta \nu = -27 \text{ cm}^{-1}$), followed by the symmetric nitro N–O vibration ($\Delta \nu = -8 \text{ cm}^{-1}$) and the C=N stretch ($\Delta \nu = -5 \text{ cm}^{-1}$). Electron-withdrawing

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Table 3. Shift of the N-O and C=N stretching frequencies in nitro and cyano aromatics upon introduction of a π donor (methoxy) and σ acceptor (protonation of pyridine) in the para position. The methoxy group serves as a model for back donation and the protonated pyridine nitrogen 100 atom as the $\sigma\mbox{-acceptor}$ interaction of a coordinated metal center. Wave numbers are given in cm^{-1} .

R		<i>α</i> −− ⊥	R OMe	Δ	R		Δ
NO	$\nu_{\mathrm{a}}^{\mathrm{[a]}}$	1526 ^[19]	1499 ^[19]	-27	1539 ^[20]	1548 ^[d]	+9
NO_2	$\nu_{\rm s}^{[b]}$	1349 ^[19]	1341 ^[19]	$^{-8}$	1355 ^[20]	1359 ^[d]	+4
C≡N	$\nu^{[c]}$	2220 ^[21]	2215 ^[21]	-5	2245 ^[20]	2280 ^[d]	+35

[a] Asymmetric stretching vibration of the nitro group. [b] Symmetric stretching vibration of the nitro group. [c] Stretching vibration of the cyano group. [d] Experimental data from hydrochlorides.

groups in the 4-position (e.g., CN instead of OMe) exhibit a reverse effect. The σ -donor effect from the nitrogen lone pair of pyridine to the Ni^{II} ion can be modeled by protonation of the pyridine. For symmetry reasons there is no direct effect on the π system; however, by second-order perturbation the electron density of the π system is also decreased. Therefore, protonation (as well as σ donation) should lead to a shift of the nitro and cyano stretching frequencies to higher wave numbers, which is in fact observed $(\Delta v_a, \Delta v_s, \Delta v_s)$ $\Delta v = +9, +4, +35 \text{ cm}^{-1}$, respectively; Table 3). For the Niporphyrin–pyridine complexes, σ donation as well as π back donation are expected. In more basic pyridines such as 2e (R = OMe), the σ -donor effect is dominant and at the lower end of the p K_a scale (e.g., **2a**, R=NO₂) back donation should prevail. Unfortunately, both effects give rise to opposite shifts of the nitro and CN stretching modes. Because σ donation is operative in all complexes, a shift to lower wave numbers should be observed only if the influence of back donation on the stretching frequencies is stronger than the σ -donation effect.

To study the back-donation effect we measured the stretching frequencies of the nitro group in free 4-nitropyridine (2a) and 4-cyanopyridine (2b) and compared these data with those for the corresponding 2:1 complexes with porphyrin 1 in the solid state (Figure 10). Although the interpretation of the normal modes in the free pyridines is straightforward, the assignment of the stretching frequencies in the complexes is difficult because of interfering bands from the porphyrin 1. We therefore calculated the vibrational spectra (optimization including harmonic frequency calculations) at the PBE/DZP level of density functional theory. According to our calculations the asymmetric as well as the symmetric stretching frequencies of the nitro group split into two lines ($\Delta \nu \approx 1 \text{ cm}^{-1}$) by the coupling of these modes between the two nitropyridine ligands at the two axial positions. The frequencies of the calculated and the experimental spectra agree well ($< 10 \text{ cm}^{-1}$; for spectra and assignments see the Supporting Information). However, the measured splittings of the asymmetric (Δv_a) and symmetric (Δv_s) vibrational modes of the nitro group are larger (13



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Figure 10. Experimental (solid state) IR spectrum of the 2:1 complex of 4-nitropyridine (2a; top left) and 4-cyanopyridine (2b; top right) with porphyrin 1. The corresponding calculated spectra (PBE/DZP) are given below.

and 9 cm⁻¹, respectively), probably because of packing effects in the asymmetric unit cell (see crystal structure in the Supporting Information). We therefore use average values for ν_s and ν_a (Table 4).

By comparing the stretching frequencies of the free pyridines and the corresponding vibrations in the 2:1 complex

Table 4. Experimentally determined stretching frequencies of the nitro and cyano groups in the corresponding 4-substituted pyridines and in their 2:1 complexes with porphyrin 1. Wave numbers are given in cm⁻¹

R		Pyridine 2a	Complex $1 \cdot (2a)_2$	Δ
NO	$\nu_{a}^{[a]}$	1532	1525 ^[d]	-7
NO_2	$\nu_{\rm s}^{\rm [b]}$	1351	1346 ^[d]	-5
C≡N	$\nu^{[c]}$	2242	2239	-3

[a] Asymmetric stretching mode of the nitro group. [b] Symmetric stretching mode of the nitro group. [c] Stretching mode of the cyano group. [d] Bands are split into two in the crystal due to the asymmetric environment of the nitro groups in the unit cell, therefore the average value is given.

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with Ni-porphyrin, we observe a shift to lower wave numbers of -7 and -5 cm^{-1} for $\Delta \nu_a$, and $\Delta \nu_s$ of the nitro group, respectively, and a shift of -3 cm^{-1} for the C=N stretching mode (a shift of -4 cm^{-1} was found in the Raman spectra of the free and complexed ligand). Thus, the magnitude of the shift is about one third of the effect of the methoxy group in our model system (Table 3) for all three vibrational modes. If no back donation was involved in the complexes with the 4-nitro (**2a**) and 4-cyanopyridine (**2b**) the reverse shift to *higher* wave numbers would be expected, because σ donation is operative in all pyridine complexes (see above). Hence the effect of back donation on the vibrational modes investigated for **2a** and **2b** must exceed that of σ donation.

X-ray structures of Ni-tetrakis(pentafluorophenyl)porphyrin complexes with 4-nitro-, 4-cyano-, and 4-dimethylaminopyridine: Single crystals suitable for X-ray diffraction were obtained for the 2:1 complexes of 4-nitro- (2 a), 4-cyano- (2 b), and 4-dimethylaminopyridine (2 f) with porphyrin 1. A selection of geometry parameters is given in Table 5 and these parameters are defined in Figure 11. Figure 12 shows the crystal structures of the complexes.

Table 5. Selection of important bond lengths [Å], angles [°], and dihedral angles [°] of **2a**, **2b**, and **2f** determined by X-ray structure analysis. For definitions of the geometry parameters, see Figure 11.

R	NO ₂	CN	NMe ₂
a	2.230(2)	2.220(2)	2.192(2)
b_1	2.046(2)	2.046(2)	2.060(2)
b_2	2.050(2)	2.052(2)	2.054(2)
Θ	40.2(2)	44.1(2)	21.1(2)
Φ	86.8(1)	82.8(1)	76.8(1)



Figure 11. Definition of the geometry parameters listed in Table 5.

with pure σ coordination free rotation would be expected. Back donation, however, with the pyridine ligand breaks the degeneracy of the d_{xz} and d_{yz} orbitals (see Figure 13 c and d) and should thus induce a rotational barrier. According to PBE/DZP calculations including dispersion corrections, the activation barrier to rotation around the pyridine-N–Ni bond of 4-nitropyridine is predicted to be 1.76 kcalmol⁻¹. As expected, the barrier decreases with decreasing electron deficiency of the pyridine. The parent pyridine rotates with a barrier of 1.59 kcalmol⁻¹ and 4-aminopyridine with 1.41 kcalmol⁻¹.

Electron-rich dimethylaminopyridine (which is not expected to be susceptible to back donation) forms an angle of 21.1°. Obviously, in the latter case the orientation of the pyridine rings is influenced by packing effects, whereas in the electron-deficient pyridines back donation determines the

The bond lengths (a) of the two axial ligands to the Ni^{II} ion slightly decrease with increasing basicity of the pyridine ligands. The distance a is 0.04 Å shorter in dimethylaminopyridine 2f than in nitropyridine 2a. The two axial bond lengths in each complex are identical. The bond lengths b_1 and b_2 between the Ni^{II} ion and the pyrrole nitrogen atoms increase with increasing basicity. In all three complexes both axial pyridine ligands are coplanar. Interestingly, in the nitro- and cyanopyridine complexes the pyridine molecules are rotated by almost 45° (Θ) with respect to the pyrrole-N-Ni bond, and provide optimal overlap and back donation with the d_{xz} and d_{yz} orbitals of Ni (Figure 13). For a ligand



Figure 12. Crystal structures of complexes of **2a**, **2b**, and **2 f** with porphyrin **1**.



Figure 13. a,b) Molecular orbital plots of the degenerate nickel d_{xz} and d_{yz} orbitals in the triplet state of parent nickel-porphyrin (PBE/DZP). c,d) Molecular orbital plots of HOMO-3 and HOMO-4 of the five-coordinate complex of nickel-porphyrin with one axial pyridine ligand in the triplet state (PBE/DZP). HOMO-4 represents the back-donation effect (see also Figure 9; note the antibonding character of the N–O bonds in the nitro group).

orientation. Similar effects are observed for the coordination angle Φ of the pyridine ligands with respect to the porphyrin plane (Φ is the angle between the pyridine-N–R axis and porphyrin plane, see Figure 11). In the electron-rich 4dimethylaminopyridine **2f**, the deviation from orthogonal coordination is largest (Φ =76.8°) whereas the smallest deviation from perpendicular binding is observed for the most electron-deficient ligand nitropyridine (Φ =86.8°). The σ donation is less sensitive to a distortion from orthogonal coordination than π interaction (back donation). Therefore the electron-rich pyridine **2f** is more easily distorted by packing effects, whereas **2a** and **2b** are fixed in an upright position by back donation.

CCDC-766988 (2a), 766989 (2b), and 766990 (2f) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Conclusion

We have developed a new method for the determination of the association constants K_{1S} and K_2 in 2:1 Ni-porphyrin complexes based on paramagnetic NMR shift data. By evaluation of more than 400 NMR spectra, binding enthalpies $(\Delta H_{1S}, \Delta H_2)$ and entropies $(\Delta S_{1S}, \Delta S_2)$ of both coordination steps could be determined with high accuracy $(\Delta \Delta H_{1S} < (\pm 0.1), \Delta \Delta H_2 < (\pm 0.2)$ kcal mol⁻¹, $\Delta \Delta S_{1S} < (\pm 0.34), \Delta \Delta S_2 < (\pm 0.9)$ cal mol⁻¹K⁻¹). The free binding enthalpies $(\Delta G_{1S}$ and $\Delta G_2)$ exhibit a linear relationship with respect to the p K_a values of the axial *para*-substituted pyridine ligands. How-

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ever, this linear dependence is fortuitous. In contrast to ΔG_{1S} and ΔG_2 , the binding enthalpies (ΔH_{1S} , ΔH_2) are *not* a linear function of the pK_a. ΔH_{1S} and ΔH_2 are lowest in the pyridine complex (2d, R = H). Electron-donating (R =OMe) as well as electron-withdrawing substituents (R = CO_2Et , NO_2) at the 4-position of the pyridine give rise to larger binding enthalpies. We explain this unusual behavior by back donation of electrons from the occupied Ni d_{xz} orbital into the LUMO of the electron-deficient pyridines (R= CO₂Et, NO₂). The gain in binding enthalpy from back donation overcompensates the loss in σ donation (which should be a linear function of the pK_a). Unexpected as well is the large binding entropy, particularly ΔS_{1S} , of the nitropyridine complex $(-23.7 \text{ calmol}^{-1} \text{K}^{-1})$ relative to that of the electron-rich pyridine complexes (methoxypyridine: -14.0 calm $ol^{-1}K^{-1}$). This large negative binding entropy renders the coordination of nitropyridine comparatively unfavorable, in spite of the large binding enthalpy. A more rigid geometry and hindered rotation of the axial ligands could be an explanation. The X-ray structures of the nitro- (2a), cyano-(2b), and dimethylaminopyridine (2f) complexes are in agreement with this argument. DFT calculations also predict a larger rotational barrier for the electron-deficient nitropyridine (2a) than for pyridine (2d) and dimethylaminopyridine (2 f). Moreover, 2 f binds with a coordination angle that is inclined from perpendicular binding ($\Theta = 76.8^{\circ}$). This hardly affects the σ coordination but would be unfavorable for π back donation. Independent evidence for back donation comes from IR spectroscopy; that is, upon coordination to the Ni-porphyrin 1 the stretching frequencies of the nitro group in nitropyridine and the C=N stretching in cyanopyridine shift to lower wave numbers. This is expected for an electron transfer from occupied Ni orbitals into the LUMO of the electron-deficient pyridines.

Experimental Section

Spectroscopy: ¹H NMR spectra were measured on a 500 MHz FT NMR spectrometer DRX 500 (Bruker). IR spectra were recorded with a 1600 series FTIR spectrometer from Perkin–Elmer by using a golden-gate-diamond attenuated total reflection (ATR) unit A531-G.

Materials and solvents: $[D_8]$ Toluene, $[D_5]$ pyridine, 4-methoxypyridine, and ethyl 4-pyridinecarboxylate were commercially available and used as received.

Synthesis of starting materials: 4-Nitropyridine was synthesized by oxidation of 4-aminopyridine.^[22] 5,10,15,20-Tetrakis(pentafluorophenyl)porphyrin was prepared by the method of Iida et al.^[23]

Nickel-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (NiTPPF₂₀) (1): Nickel(II) acetylacetonate (7.00 g, 27.2 mmol) was added to a solution of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin (975 mg, 1.00 mmol) in toluene (100 mL) and the mixture was heated at reflux for 5 days. After removal of the solvent in vacuo, the crude solid was purified by column chromatography (silica gel 0.04–0.063 mesh) with CH₂Cl₂ as eluent to afford the product in 90% yield. ¹H NMR (500 MHz, [D]CHCl₃, 25 °C, TMS): δ = 8.79 ppm (s, 8H; pyrrole-*H*); ¹⁹F NMR (470 MHz, [D₈]toluene, 25 °C, CFCl₃): δ = -137.35 (d, ³*J*(F,F) = 21 Hz; F_{ortho}), -151.43 (t, ³*J*(F,F) = 20 Hz; F_{para}), -161.66 ppm (t, ³*J*(F,F) = 20 Hz; F_{meta}); ¹⁹F NMR data of paramagnetic complex of pyridine **2d** with porphyrin **1** (**1**-(**2d**)₂): ¹⁹F NMR (470 MHz, [D₈]toluene, 25 °C, CFCl₃): $\delta = -136.82$ (br, F_{ortho}), -152.97 (br, F_{para}), -163.21 ppm (br, F_{meta}).

Titration: The paramagnetism of the Ni²⁺ in the penta- and hexacoordinated complexes gave rise to a strong downfield shift and a broadening of the pyrrole proton resonance in porphyrins such as $NiTPPF_{20}$ (1). Due to the very rapid coordination/decoordination process, the time-averaged signal of the dia- and paramagnetic species was observed in the ¹H NMR spectra. The signal of the pyrrole protons was followed as a function of the axial ligand concentration (25 different ligand concentrations and four different pyridines: 2a, 2c-e). K_{1S} and K_2 were determined from these data by using the linear analysis outlined below. All titration experiments were performed at four different temperatures (298, 308, 318, and 328 K) to determine reaction enthalpies and entropies. More than 400 ¹H NMR spectra were measured with an automatic sampler. A different NMR tube was used for each ligand concentration. Each ¹H NMR tube was filled with 200 μL of a porphyrin solution (10.0 $\text{mmol}\,L^{\text{-1}})$ in [D8]toluene. Then different amounts of a solution of ligand in [D₈]toluene (10 vol%) were added and the tubes were filled up to $600 \,\mu\text{L}$ with [D₈]toluene and sealed. NMR titration experiments could not be performed for the pyridines 2b and 2f because of solubility problems.

Susceptibility measurements after Evans: To quantify the paramagnetic properties of our Ni^{II} complexes, we determined their magnetic susceptibility by using the "Evans method".^[11,24-26] A set of two coaxial NMR tubes consisting of an ordinary outer NMR tube and an inner tube with a smaller diameter was used. The inner tube contained the reference solvents [D₅]pyridine and 2 vol% tert-butanol. The outer tube was filled with the same mixture and additionally with paramagnetic complex. [D₅]Pyridine was used as the solvent as well as the axial ligand to make sure that the hexacoordinated 2:1 complex was formed. A concentration of $m = 0.0113 \text{ g cm}^{-3}$ of porphyrin 1 in [D₅]pyridine was applied for the actual Evans experiment. The mass susceptibility χ_g of the complex was calculated from the difference of the chemical shifts Δf of the *tert*-butanol proton signals in the inner and outer tubes. A downfield shift of 60.5 Hz was measured for the paramagnetic outer solution. The susceptibility was corrected by the diamagnetic susceptibility of the solvent and the Ni-porphyrin [Eq. (1)]:

$$\chi_{\rm g} = \frac{3\Delta f}{4\pi fm} + \chi_{\rm g,pyr} - \chi_{\rm g,Ni} \tag{1}$$

in which *f* is the frequency of the NMR instrument (Hz), Δf the frequency shift of *tert*-butanol (Hz), *m* the concentration of porphyrin **1** (gcm⁻¹), $\chi_{g,pyr}$ the mass susceptibility of solvent [D₃]pyridine (cm³g⁻¹), and $\chi_{g,Ni}$ the diamagnetic correction for porphyrin **1** (cm³g⁻¹).

The molar susceptibility of pyridine is known $(-49.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1})^{[27]}$ and the diamagnetic correction of porphyrin **1** was calculated from an increment system.^[28] The molar susceptibility $\chi_g = 3.14 \times 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ was calculated from the mass susceptibility and the molecular weight *M* of the complex [Eq. (2)]:

$$\chi_{\rm m} = \chi_{\rm g} M \tag{2}$$

The magnetic moment μ in Bohr magnetons (B.M.), with T=temperature, is defined as follows [Eq. (3)]:

$$\mu = 2.828 \sqrt{\chi_{\rm m} T} \tag{3}$$

The magnetic moment calculated from our data at 300 K of 2.9 B.M. is in good agreement with the literature values for two unpaired electrons in an octahedral ligand field. Depending on the contribution of the orbital moment, values of 2.8 to 3.5 B.M. were found for the magnetic moment μ .

The magnetic moment μ was also measured at 12 different temperatures (from 293 to 283 K in increments of 10 K) to make sure that the number of unpaired electrons was not temperature dependent. A plot of the observed shift difference Δf as a function of *T* does not exhibit any hystere-

sis, and the plot of χ_m (cm³mol⁻¹) versus T^{-1} (K⁻¹) exhibits a straight line with a slope of 1.15 ± 0.03 .^[13] According to Equation (4):

$$\chi_{\rm m} = \frac{N\mu_{\rm B}^2}{3k}\mu_{\rm eff}^2 \frac{1}{T} = \frac{N\mu_{\rm B}^2}{3k}g^2 S(S+1)\frac{1}{T}$$
(4)

in which N is the Avogadro constant ($6.022 \times 10^{23} \text{ mol}^{-1}$), $\mu_{\rm B}$ the Bohr magneton, $\mu_{\rm eff}$ the effective magnetic moment, k the Boltzmann constant, g the Landé factor, S the spin quantum number, and T the temperature (K), a slope of 1 is expected for two unpaired electrons. The observed slope of 1.15 corresponds to a magnetic moment of 3.0, in good agreement with the above room-temperature value of $\chi_{\rm m}$.

Single-crystal structure analysis: The investigation was performed with an imaging plate diffraction system (IPDS-1) with $Mo_{K\alpha}$ radiation from STOE & CIE. The structure solutions were carried out by direct methods with SHELXS-97. These refinements were performed against $|F|^2$ by using SHELXL-97.^[29] All non-hydrogen atoms except some of the disordered C atoms in compound 2b were refined with anisotropic displacement parameters. All hydrogen atoms were positioned with idealized geometry and were refined with fixed isotropic displacement parameters $[U_{eq}(H) = -1.2 \times U_{eq}(C)]$ by using a riding model with $d_{C-H} = 0.93$ Å. In compound 2a one of the two crystallographically independent toluene molecules is disordered and in compound 2b both molecules are disordered. They were refined by using a split model. Details of the structure determination are given in the Supporting Information. CCDC 766988 (2a), 766989 (2b) and 766990 (2f) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam. ac.uk/data_request/cif.

Derivation of Equation (7): We derived an equation for the determination of the equilibrium constants K_{1S} and K_2 from NMR and UV titration data. Usually the coordination of one ligand without spin change is described by K_1 , and if there is also a spin crossover during this process the equilibrium constant is denoted $K_{1S}^{[10]}$ Equilibrium constant K_2 describes coordination of a second ligand to the five-coordinate, high-spin (HS) nickel complex. The simultaneous coordination of two ligands to a fourcoordinate Ni center is described by β [Eqs. (a)–(d)]:

$$Ni + L \xrightarrow{K_1} NiL_{LS}$$
 (a)

$$Ni + L \xrightarrow{K_{IS}} NiL_{HS}$$
 (b)

 $NiL_{HS} + L \xrightarrow{K_2} NiL_2$ (c)

$$Ni + 2L \xrightarrow{\beta} NiL_{2HS}$$
 (d)

It is generally accepted that the quadratic pyramidal 1:1 complexes of Niporphyrins as well as the quadratic bipyramidal 2:1 complexes are high spin. Thus, the complexation of the first axial ligand is accompanied by a spin crossover from low to high spin. The validity of this approach is shown by the excellent regression coefficient obtained when fitting experimental data to equations based on these assumptions. La Mar and Walker derived an equation which describes the ratio between paramagnetic and diamagnetic species [Eq. (5)]:^[11]

$$\frac{[\text{para}]}{[\text{dia}]} = \frac{\delta - \delta_0}{\delta_{\text{max}} - \delta} = \frac{[\text{NiL}_{2\text{HS}}] + [\text{NiL}_{\text{HS}}]}{[\text{Ni}_{\text{LS}}] + [\text{NiL}_{\text{LS}}]}$$
(5)

in which δ_0 is the chemical shift of the pyrrole protons of the porphyrin in the absence of an axial ligand, δ is the chemical shift of the pyrrole protons at different ligand concentrations, δ_{max} is the chemical shift of the pyrrole protons of completely coordinated porphyrin, [NiL_{2HS}] is the concentration of the hexacoordinate high-spin complex, [NiL_{HS}] is the concentration of the pentacoordinate high-spin complex, [NiL_S] is the concentration of the low-spin porphyrin, [NiL_{LS}] is the concentration of the pentacoordinate low-spin complex, and [L] is the concentration of the ligand.

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We assume that [Ni_{LS}], [NiL_{LS}], [NiL_{HS}], and [NiL_{2HS}] exhibit similar chemical shifts of the pyrrole protons. By using $K_{1S} = \frac{[NiL_{HS}]}{[NiL_{HS}][L]}$ $K_2 = \frac{[NiL_{2HS}]}{[NiL_{HS}][L]}\beta = \frac{[NiL_{2HS}]}{[Ni_{LS}][L]^2} = K_{1S}K_2$, we obtain [Eq. (6)]:

$$\frac{[\text{para}]}{[\text{dia}]} = \frac{\delta - \delta_0}{\delta_{\text{max}} - \delta} = \frac{K_{1\text{S}}[L] + \beta_2[L]^2}{1 + K_1[L]} \tag{6}$$

With the assumption that $K_1[L] = 0$, we obtain [Eq. (7)]:

$$\frac{[\text{para}]}{[\text{dia}][L]} = \frac{\delta - \delta_0}{(\delta_{\text{max}} - \delta)[L]} = K_{1\text{S}} + K_2 K_{1\text{S}}[L]$$
(7)

A plot of $\frac{\delta - \delta_0}{(\delta_{\max} - \delta)[L]}$ versus [L] should give a straight line if the above preconditions are met. The intercept corresponds to $[K_{1S}]$ and the slope gives $\beta = K_{1S}K_2$. (At large concentrations of the ligand L deviations from the linear behavior are observed.)

Computational details: The geometries of the pyridines **2a** and **2b** ($C_{2\nu}$ symmetry) and of the complexes **1**-(**2a**)_{**2**} and **1**-(**2b**)_{**2**} (C_1 symmetry) were optimized at the DFT functional PBE^[30-33] with a double-zeta Ahlrichs basis DZP^[35] by using the TURBOMOLE program^[32] and the multipole accelerated resolution of identity method.^[34] Harmonic frequency analyses were performed at the same level of theory. The stretching frequencies of the nitro and cyano group could be unambiguously assigned in the free pyridines **2a** and **2b**. The calculated stretching frequencies of the complexes **1**-(**2a**)_{**2**} and **1**-(**2b**)_{**2**} were linearly scaled between 1300 and 1600 cm⁻¹ with the parameters determined by a linear fitting of the theoretical and experimental IR spectra of **2a** and **2b** within the same spectral region.

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