Inner C-cyanide addition and nucleophilic addition to Ni(II) N-confused porphyrins†

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Inner C-cyanide addition and subsequent addition of a methoxy group were observed in the reactions of Ni(II) N-confused tetra(p-tolyl)porphyrin with sodium methoxide and DDQ.

An N-confused porphyrin is a porphyrin isomer with an inverted pyrrolic ring. Since their first syntheses,[1,2] N-confused porphyrins have been extensively studied.[3–7] In our studies of the Diels–Alder reactions of Ni(II) N-confused porphyrins as dienophiles, it was postulated that the peripheral C–N bond of a Ni(II) N-confused porphyrin would have some iminium character.[8] Thus, it was expected that, similar to iminium compounds, Ni(II) N-confused porphyrins might be reactive towards nucleophiles, and their reactions with NaOCH$_3$ were studied. When Ni(II) N-confused tetra(p-tolyl)-porphyrin (**1**) was added to a solution of NaOCH$_3$ in 1:1 CH$_2$Cl$_2$/CH$_3$OH, no reaction was observed. It was postulated that the addition product, an N-confused chlorin (similar to **8**, Scheme 1), was not stable. The reaction, however, might be driven towards a more stable product, an N-confused porphyrin, with the addition of an oxidant. Thus, to a 1:1 CH$_2$Cl$_2$/CH$_3$OH (70 mL) solution of NaOCH$_3$ (200 mg) were added **1** (110 mg) and DDQ (400 mg). The solution was stirred for 24 h at rt and complexes **2** (27%) and **3** (9.9%) were obtained (Scheme 1).† ‡

The structures of complexes **2** and **3** were determined by X-ray diffraction analyses (Figure 1).§ Cyanide addition had been found to occur in both complexes on the inner C(21) site. Additionally, the anticipated methoxy addition on the peripheral C(3) site was observed in complex **3**. The porphyrin skeletons of complexes **2** and **3** are distorted from planarity. In the structure of complex **2**, the dihedral angles between the pyrrole planes and the plane defined by N(22)N(23)N(24) are as follows: C(21) 40.4(2)°, N(22) −21.0(3)°, N(23) 13.4(3)°, and N(24) −18.5(2)°. For complex **3**, the dihedral angles between the pyrrole planes and the plane defined by N(22)N(23)N(24) are as follows: C(21) 39.52(13)°, N(22) −21.01(14)°, N(23) 12.77(13)°, and N(24) −20.56(16)°. The degree of distortion for **2** and **3** is similar to that observed in the C(21)-methylated Ni(II) N-confused tetraphenylporphyrin, in which the inverted pyrrole plane deviates from the N(22)N(23)N(24) plane by 42.2°.[9] In the crystal structure of complex **2**, the bond distances of C(21)–C(1) and C(21)–C(4) are markedly longer than those of N(2)–C(1), N(2)–C(3), and C(3)–C(4) (Table 1), suggesting that the C(21) atom approaches sp^3 hybridization. The distance between Ni and C(25) is 2.402(6) Å, suggests a possible interaction between these two atoms. However, the bond lengths of C(25)–N(26) and C(21)–C(25) at 1.157(7) and 1.478(8) Å, and the bond angle of 179.4(6)° for C(21)–C(25)–N(26) are characteristic of N≡C–C bonding, suggesting no bonding between Ni and C(25). The same structural features were also observed for complex **3**.

In the ^{1}H NMR spectra of **2** and **3**, signals representative of the pyrrole protons, excluding C(3)H, are observed in the region of δ 8.54–8.78 and 8.29–8.51, respectively and are downfield
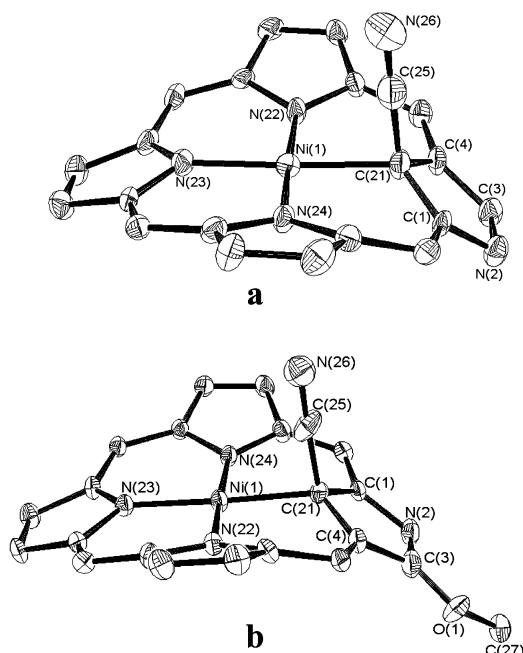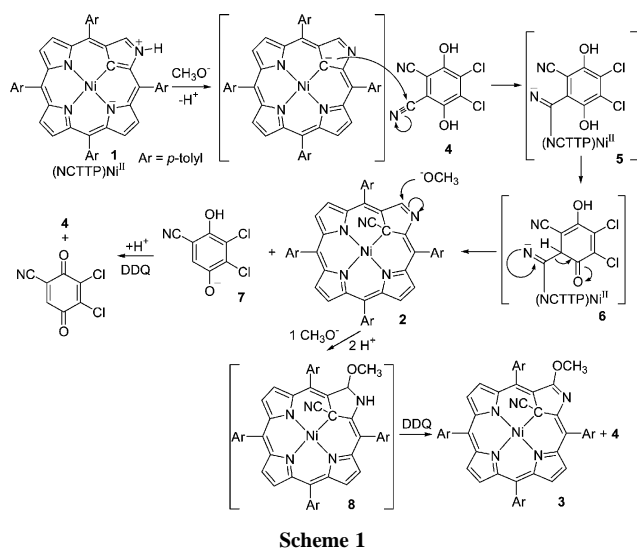

Scheme 1

Fig. 1 ORTEP representations of **2** (**a**) and **3** (**b**), showing atomic labeling and thermal ellipsoids at 50% probability. p-Tolyl groups, H atoms, solvent (0.5H$_2$O for **a**) and the disorder of the OCH$_3$ fragment (for **b**) have been removed for clarity.

Table 1 Selected bond lengths for complexes **2** and **3**.

Bond	Bond lengths in complex **2** (Å)	Bond lengths in complex **3** (Å)
N(2)–C(1)	1.378(6)	1.375(4)
N(2)–C(3)	1.332(5)	1.372(4)
C(3)–C(4)	1.396(6)	1.395(4)
C(21)–C(1)	1.459(5)	1.470(4)
C(21)–C(4)	1.454(6)	1.462(3)
C(21)–C(25)	1.478(8)	1.462(4)
C(25)–N(26)	1.157(7)	1.144(4)
Ni–C(25)	2.402(6)	2.429(3)

compared to those of **1** in the δ 7.65–8.12 region. Notably, the position of the C(3)H chemical shift at δ 10.03 for **2** is approximately 1.5 ppm downfield compared to that of **1**. Complexes **2** and **3** seem to favor π delocalization *via* the outer path C(1)–N(2)–C(3)–C(4) at the inverted pyrrole fragment, since C(21) atoms in both complexes approach sp³ hybridization and inner conjugation C(1)–C(21)–C(4) is not possible. The downfield signal of C(3)H may be the result of a closer ring current and a similar effect is observed in the case of inner C-methylated Ni(II) N-confused porphyrins.[9]

A possible mechanism for the generation of complexes **2** and **3** is shown in Scheme 1. Electrophilic addition of compound **4**, the reduction product of DDQ, to deprotonated **1**, results in **5**, which tautomerizes to **6**. Elimination of **7** from **6** gives complex **2**. Nucleophilic addition of CH_3O^- to **2** at C(3) followed by protonation gives Ni(II) N-confused chlorin **8**. Oxidation of **8** with DDQ results in compounds **3** and **4**. Compound **4** can also be generated through the reduction of DDQ by **7**. Deprotonation of **1** is suggested by the change of UV-vis spectra of **1** after adding NaOCH₃.

In conclusion, reaction of Ni(II) N-confused porphyrin **1** with NaOCH₃ and DDQ resulted in an inner C-cyanide addition product **2**. Subsequent nucleophilic addition of CH_3O^- to **2** followed by oxidation with DDQ gave complex **3**. Structures of both complexes **2** and **3** were determined by X-ray diffraction analyses. Nucleophilic addition of deprotonated **1** to a cyanide group was proposed as the critical step for the inner cyanide addition. The generality of the cyanide addition to other nucleophiles with DDQ and base is worthy of study in the future.

Notes and references

‡ *Characterization data for* **2** R_f (silica-CH₂Cl₂/hexanes 2:1) 0.37; ¹H-NMR (400 MHz, CD₂Cl₂) δ = 2.66 (m, 12H), 7.56 (d, J = 7.7 Hz, 4H), 7.63 (d, J = 7.7 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.78–8.43 (m, 8H), 8.56 (d, J = 4.8 Hz, 1H), 8.58–8.66 (m, 3H), 8.73 (d, J = 5.0 Hz, 1H), 8.76 (d, J = 5.0 Hz, 1H), 10.03 (s, 1H); UV-vis (CH₂Cl₂) λ_{max}/nm (log ε) 434 (5.14), 716 (3.65); MS (LSIMS) 752 (MH⁺, 100%); HRMS (LSIMS) m/z Calcd for $C_{49}H_{36}N_5Ni$: 752.23237, found 752.23242 (MH⁺); Anal. Calcd for $C_{49}H_{35}N_5Ni\cdot CH_3OH\cdot 0.5H_2O$: C, 75.68; H, 5.08; N, 8.83. Found: C, 75.97; H, 4.76; N, 9.09%.

3 R_f (silica-CH₂Cl₂/hexanes 2:1) 0.63; ¹H-NMR (400 MHz, CD₂Cl₂) δ = 2.63 (m, 12H), 4.21 (s, 3H), 7.41–7.62 (m, 9H), 7.65–8.20 (m, 7H), 8.32 (d, J = 4.8 Hz, 1H), 8.36 (s, 2H), 8.38–8.51 (m, 3H); UV-vis (CH₂Cl₂) λ_{max}/nm (log ε) 434 (5.12), 716 (3.96); MS (LSIMS) 782 (MH⁺, 100%); HRMS (LSIMS) m/z Calcd for $C_{50}H_{38}N_5NiO$: 782.24294, found 782.24344 (MH⁺); Anal. Calcd for $C_{50}H_{37}N_5NiO\cdot H_2O$: C, 75.02; H, 4.91; N, 8.75. Found: C, 74.74; H, 4.68; N, 8.68%.

§ *Crystal data for* **3**: $C_{49}H_{36}N_5NiO_{0.5}$, M = 761.54, triclinic, a = 9.7125(10), b = 14.3732(15), c = 14.0565(15) Å, α = 94.720(10)°, β = 77.440(10)°, γ = 76.150(10)°, V = 1840.9(3) Å³, T = 173(2) K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo–Kα) = 5.73 cm⁻¹, 44912 reflections measured, 10104 unique (R_{int} = 0.063) which were used in all calculations. The final $wR(F^2)$ was 0.159 (all data). The C(3) and N(2) atoms are disordered and not distinguishable in the X-ray structure.

Crystal data for **3**: $C_{50}H_{37}N_5NiO$, M = 782.56, triclinic, a = 9.8239(4), b = 12.7674(6), c = 15.3382(7) Å, α = 82.788(8)°, β = 81.698(7)°, γ = 82.301(8)°, V = 1875.39(15) Å³, T = 173(2) K, space group $P\bar{1}$ (No. 2), Z = 2, μ(Mo–Kα) = 5.65 cm⁻¹, 17139 reflections measured, 7723 unique (R_{int} = 0.066) which were used in all calculations. The final $wR(F^2)$ was 0.112 (all data). The structure of **3** displayed disorder in the locations of the methoxy fragment. The structure has been refined to give 63% occupancy with –OCH₃ as shown in Figure 1 and 37% occupancy with –OCH₃ attached to the C(3) which replaces N(2) of the major form.

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