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

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The solution was stirred for 24 h at rt and complexes and dienophiles, it was postulated that the peripheral C
Ni(II) N-confused porphyrin would have some iminium character.

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

Thus, it was expected that, similar to iminium compounds, Ni(II) N-confused porphyrins might be reactive towards nucleophiles, and their reactions with NaOCH3 were studied. When Ni(II) N-confused tetra(p-toly)porphyrin (1) was added to a solution of NaOCH3 in 1:1 CH2Cl2/CH3OH, no reaction was observed. It was postulated that the addition product, an N-confused porphyrin, with the addition of an oxident, thus, to a 1:1 CH2Cl2/CH3OH (70 mL) solution of NaOCH3 (200 mg) were added 1 CH2Cl2/CH3OH, no reaction was observed. See http://www.rsc.org/suppdata/cc/b2/b211990k/

† Electronic supplementary information (ESI) available: UV-vis spectra of 1 with and without NaOCH3. See http://www.rsc.org/suppdata/cc/b2/b211990k/

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 crystal 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°.§ 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(22)–C(1), N(22)–C(3), and C(3)–C(4) (Table 1), suggesting that the C(21) atom approaches sp3 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 1H 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 from the aromatic protons. In 2, the aromatic protons are observed at δ 8.54–8.55 while in 3, the aromatic protons are observed at δ 8.39–8.78. The chemical shift of the pyrrole protons is dependent on the substituent at the C-pyrole site. The methoxy group was observed in the reactions of Ni(II) N-confused porphyrins with sodium methoxide and DDQ.

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Table 1 Selected bond lengths for complexes 2 and 3.

<table>
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<tr>
<th>Bond</th>
<th>Bond lengths in complex 2 (Å)</th>
<th>Bond lengths in complex 3 (Å)</th>
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<tr>
<td>N(2)–C(1)</td>
<td>1.378(6)</td>
<td>1.375(4)</td>
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<tr>
<td>N(2)–C(3)</td>
<td>1.332(5)</td>
<td>1.372(4)</td>
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<tr>
<td>C(3)–C(4)</td>
<td>1.396(6)</td>
<td>1.395(4)</td>
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<tr>
<td>C(21)–C(21)</td>
<td>1.489(5)</td>
<td>1.470(4)</td>
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<tr>
<td>C(21)–C(25)</td>
<td>1.484(6)</td>
<td>1.462(3)</td>
</tr>
<tr>
<td>C(25)–N(26)</td>
<td>1.157(7)</td>
<td>1.144(4)</td>
</tr>
<tr>
<td>Ni–C(25)</td>
<td>2.402(6)</td>
<td>2.429(3)</td>
</tr>
</tbody>
</table>

Notes and references

† Characterization data for 2, 3. (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), 8.76 (m, J = 10.03 (s, 3H), UV-vis (CH2Cl2) lam(ε) = 434 (5.14), 716 (3.65); MS (LSIMS) 752 (MH+, 100%); HRMS (LSIMS) m/z: Calcd for C38H32NiN4O2: 722.2337, found 722.2342 (MH+); Anal. Calcd for C38H32NiN4O2·CH2Cl2·H2O: C, 75.68; H, 5.08; N, 8.83. Found: C, 75.97; H, 4.76; N, 9.09%.

§ Crystal data for 2: C50H37N5NiO·CH2Cl2·H2O, 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 = 8.150(10), V = 1840.9(3) Å3, T = 173 K, space group P1 (No. 2), Z = 2, ρ(Mo-Kα) = 5.73 cm−1, 44912 reflections measured, 10104 unique (Rs = 0.063) which were used in all calculations. The final wR2(F2) 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: C49H36N5NiO·0.5H2O, M = 752.56, triclinic, a = 9.7125(10), b = 14.3732(15), c = 14.0565(15) Å, α = 94.720(10), β = 77.440(10), γ = 8.150(10), V = 1840.9(3) Å3, T = 173 K, space group P1 (No. 2), Z = 2, ρ(Mo-Kα) = 5.73 cm−1, 7723 unique (Rs = 0.066) which were used in all calculations. The final wR2(F2) was 0.112 (all data). The structure of 3 displayed disorder in the location of the methoxy group. The structure has been refined to give 63% occupancy with −OCCH3 as shown in Figure 1 and 37% occupancy with −OCH3 attached to the C(3) which replaces N(2) of the major form.


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 CH3O− 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 7 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 CH3O− 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.

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