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Organometallic chemistry of carbaporphyrinoids: synthesis and characterization of nickel(II) and palladium(II) azuliporphyrins†

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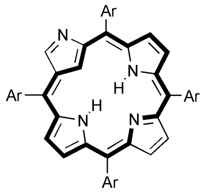
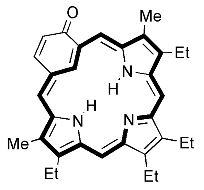
Brief treatment of azuliporphyrins 5 with nickel(II) or palladium(II) acetate in refluxing DMF afforded excellent yields of the related chelates; these novel organometallic compounds retain cross-conjugated borderline aromatic structures as judged by UV-Vis and NMR spectroscopy, and X-ray crystallography.

N-confused porphyrins (NCPs; **1**), a group of porphyrin isomers that have an inverted pyrrole subunit, were first reported in 1994.[1,2] NCPs were shown to form nickel(II) complexes[1,3,4] with a direct carbon–metal bond by simply heating the system with nickel(II) acetate, and organometallic derivatives of copper(II), palladium(II), nickel(III) and silver(III) were subsequently noted.[5] Soon after the initial discovery of N-confused porphyrins, a series of carbaporphyrinoids with carbocyclic rings in place of one of the usual pyrrole rings were reported,[6–8] including oxybenziporphyrin (**2**),[6] carbaporphyrins (*e.g.* **3**),[9] tropiporphyrin (**4**)[10] and azuliporphyrins **5**.[11] However, while these systems share the same inner core as **1**, with three internal nitrogen atoms and one carbon atom, initial attempts to generate organometallic complexes from carbaporphyrins **3** were unsuccessful.[12] NCP's have three internal hydrogens, but when M(II) complexes are generated two protons are displaced while the third is relocated to the external nitrogen atom.[1,3] This is not an option for carbaporphyrins **3** and this may well be a factor in limiting the coordination chemistry of this system.[13,14] On the other hand, azuliporphyrin only has two hydrogen atoms within the macrocyclic cavity and therefore holds greater promise in the generation of novel organometallic derivatives. We now report the first metallo-derivatives of the azuliporphyrins.

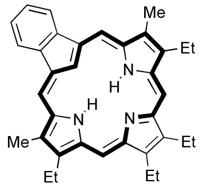
Azuliporphyrins **5a** and **5b** were treated with nickel(II) acetate in DMF at 80–90 °C for 10 min. Following chromatography on silica eluting with chloroform and recrystallization from chloroform–hexanes the nickel(II) complexes **6** were isolated in 64–73% yield. The UV-Vis spectra for the metal chelates were not particularly porphyrin-like, showing moderate bands for **6a** at 385, 454 and 546 nm while **6b** gave slightly red shifted absorptions at 392, 457 and 558 nm (Fig. 1A). The proton NMR spectra for these diamagnetic complexes were also consistent with cross-conjugated species that retain a degree of aromatic character.‡ In the case of **6a**, for instance, the *meso*-protons resonated at 8.51 and 9.13 ppm, considerably upfield of the values expected for fully aromatic porphyrinoids although the data are consistent with some contributions from dipolar canonical forms such as **7**. The plane of symmetry present in these chelates was confirmed by carbon-13 NMR spectroscopy, and the identity of **6a** and **6b** were further demonstrated by high resolution EI MS. In the case of the diphenyl derivative **6b**, dark green single crystal rods were grown by diffusion of hexanes into a CH_2Cl_2 solution, and the molecular structure confirmed by X-ray crystallographic analysis (Fig. 2).§ The nickel(II) atom is essentially situated over the center of the macrocyclic cavity and draws the macrocycle into a bowl (Fig. 2b) with the nickel atom slightly above the C(21), N(22), N(23), N(24) plane. The



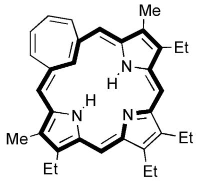
1 N-Confused Porphyrins



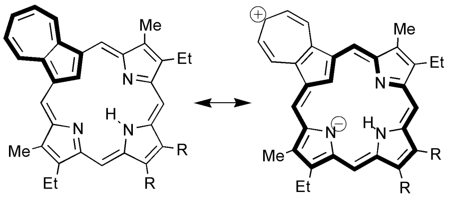
2 Oxybenziporphyrin



3 Carbaporphyrin

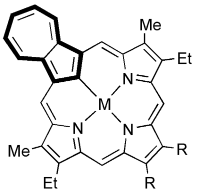


4 Tropiporphyrin



5 Azuliporphyrin **7**

a. R = Et; b. R = Ph



6 M = Ni(II)
8 M = Pd(II)

a. R = Et
b. R = Ph

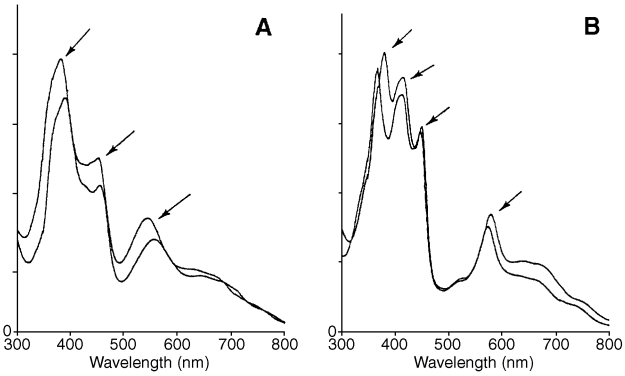


Fig. 1 A. UV-Vis spectra of nickel(II) chelates **6a** and **6b** in chloroform. The trace due to **6a** is indicated with arrows. B. UV-Vis spectra of palladium(II) chelates **8a** and **8b** in chloroform. In this case, the trace due to **8b** is indicated with arrows.

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metal is centered between the donor ligands with equivalent *trans*-N–N, 1.934(3) and 1.928(3) Å bond lengths, and a slightly distended *cis*-Ni(1)–N(23) bond length of 1.964(2) Å. The latter may be explained by the *trans*-effect of the more Lewis basic alkenyl, C(21), donor. The shorter Ni(1)–C(21) bond length of 1.897(3) Å is consistent with the smaller covalent bonding radius of carbon compared to nitrogen.

As the nickel(II) complexes **6** were formed under very mild conditions, the corresponding palladium chelates **8** were considered to be viable targets for synthesis. Indeed, reaction of **5a** or **5b** with palladium(II) acetate in DMF afforded **8a** and **8b** in 72–93% yield. The UV-Vis spectra showed three moderate bands in the Soret region (368, 412 and 447 nm for **8a** and slightly red shifted values for the diphenyl chelate **8b**) together with a broad band near 580 nm Fig. 1B). The system shows slightly downfield shifted *meso*-resonances compared to the nickel(II) chelates ($\Delta\delta \approx 0.15$ ppm) suggesting that the palladium chelates possess a larger diatropic ring current than the corresponding nickel derivatives.‡ In porphyrins, the methyl substituents commonly resonate near 3.6 ppm. In **6b**, the methyl unit appears at 3.09 ppm while the related palladium complex **8b** gave a value of 3.18 ppm. Again, these values suggest that the diatropic ring current for the palladium chelates **8** is significantly greater than in the nickel(II) derivatives **6**, although neither series of azuliporphyrin chelates show shifts that are comparable to fully aromatic porphyrinoid systems. The structures of the palladium complexes were confirmed by carbon-13 NMR spectroscopy and high resolution EI MS. At this time, it has not proven possible to obtain X-ray crystallographic data for **8a** or **8b**. Reaction of azuliporphyrins **5** with copper(II) acetate has been shown to afford stable derivatives but these paramagnetic derivatives have not yet been fully characterized.

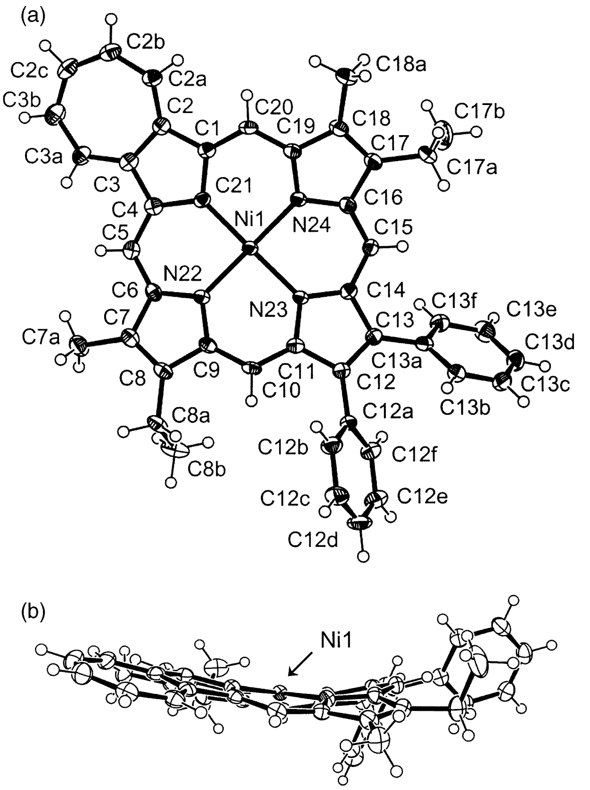

Fig. 2 (a) Arial view ORTEP drawing (50% probability level) of **6b**, with hydrogen atoms arbitrarily drawn small. Selected bond lengths (Å) and angles (°): Ni(1)–C(21) 1.897(3), Ni(1)–N(22) 1.934(3), Ni(1)–N(23) 1.964(2), Ni(1)–N(24) 1.928(3), C(1)–C(21) 1.417(5), C(4)–C(21) 1.426(5); C(1)–C(21)–C(4) 105.3(3), C(1)–C(21)–Ni(1) 127.5(2), C(4)–C(21)–Ni(1) 127.2(2), C(21)–Ni(1)–N(23) 177.2(1), C(21)–Ni(1)–N(24) 89.8(2), N(22)–Ni(1)–N(24) 176.2(2), N(22)–Ni(1)–C(21) 90.4(2). (b) Edge view ORTEP drawing of **6b**.

The preliminary results demonstrate that the CNNN cavity of azuliporphyrins is well suited for the synthesis of novel organometallic derivatives and this system will provide a valuable platform for coordination chemistry.

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Notes and references

‡ Selected spectroscopic data: **6b**: mp >300 °C; UV-Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 392 (4.72), 457 (4.52), 558 (4.32), 641 nm (4.10); ^1H NMR (d_5-pyridine): δ 1.51 (6H, t, J = 7.6 Hz), 3.09 (6H, s), 3.33 (4H, q, J = 7.6 Hz), 7.45–7.61 (9H, m), 7.76 (4H, d), 9.10 (2H, s), 9.23 (2H, d), 9.63 (2H, s); ^{13}C NMR (d_5-pyridine): δ 10.9, 16.6, 19.4, 99.5, 108.0, 127.9, 128.9, 129.6, 131.7, 132.1, 135.8, 136.5, 138.3, 138.9, 142.1, 143.3, 146.1, 147.4, 151.3, 153.9, 155.5; HRMS: calcd for $C_{44}H_{35}N_3Ni$: *m*/*z* 663.2184. Found: 663.2182. Anal. Calcd. for $C_{44}H_{35}N_3Ni$: C, 79.53; H, 5.31; N, 6.32. Found: C, 79.09; H, 5.17; N, 6.41%. **8b**: mp >300 °C; UV-Vis ($CHCl_3$): λ_{max} ($\log_{10}\varepsilon$) 380 (4.82), 415 (4.78), 450 (4.69), 580 (4.15), 638 nm (3.92); ^1H NMR (d_5-pyridine): δ 1.58 (6H, t), 3.18 (6H, s), 3.42 (4H, q), 7.45–7.58 (9H, m), 7.66 (2H, t), 8.03 (2H, d), 9.25 (2H, s), 9.80 (2H, s); ^{13}C NMR (d_5-pyridine): δ 10.9, 16.6, 19.5, 100.2, 110.2, 126.4, 127.9, 129.0, 132.2, 132.6, 137.2, 137.5, 139.3, 141.3, 142.8, 143.7, 143.8, 146.0, 148.8, 149.2, 155.5; HRMS: calcd for $C_{44}H_{35}N_3Pd$: *m*/*z* 711.1866. Found: 711.1882. Anal. Calcd. for $C_{44}H_{35}N_3Pd$: C, 73.89; H, 4.93; N, 5.87. Found: C, 73.28; H, 4.70; N, 5.72%.

§ *Crystal data* for **6b**: $C_{44}H_{35}N_3Ni$, M = 664.5, monoclinic space group $P2_{1/n}$ (no. 14), D_c = 1.378 g cm^{-3}, Z = 4, a = 31.028(2), b = 8.8409(6), c = 11.7434(8) Å, β = 96.166(2)°, V = 3202.8(4) Å^3, T = 193 K, μ = (Mo-Kα) = 0.644 mm^{-1}, 14860 reflections measured, 6534 unique, final R_1 = 0.052, $wR_2(F^2)$ = 0.116 for 433 parameters and 4718 data with $F_o^2 > 2\sigma(F_o^2)$. CCDC 179074. See http://www.rsc.org/suppdata/cc/b2/b200131b/ for crystallographic files in .cif or other electronic format.

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