

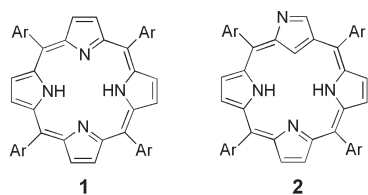
# Making Sense of *N*-Confused Porphyrins

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Porphyrins (**1**, Chart 1) are organic molecules that act as macrocyclic ligands and are comprised of four pyrrole rings connected by methine bridges. They are most familiarly known as the red pigment in hemoglobin where they serve as oxygen carriers. In this role, the porphyrin coordinates an iron atom in the central cavity in place of the two internal *N*-bound protons, and O<sub>2</sub> is bound to a vacant position on the iron. In the laboratory, tetra-arylporphyrins (**1**, Chart 1) can be easily prepared by a self-assembly reaction involving condensation of four equivalents each of pyrrole and an aldehyde (ArCHO) with subsequent oxidation to the 18  $\pi$ -electron aromatic macrocycle. Synthetic modifications of porphyrin ligands for a range of different applications in catalysis, medicine, and materials science are well-established, and most elements from the periodic table can be inserted into the porphyrins to form an ever-expanding range of coordination complexes. Most modifications of the porphyrin itself are concerned with different substituents at the *meso*-positions (those occupied by an aryl ring in **1**) or at the  $\beta$ -pyrrolic positions (occupied by H in the five-membered rings of **1**). However, over the last decade, interest in the special properties of porphyrin ligands has extended beyond these simple modifications to a growing family of *porphyrinoid* molecules, which share the essential features of porphyrin, namely pyrrole building blocks and an unsaturated macrocyclic framework. This extended family comprises expanded, contracted and isomeric porphyrins. It is the last of these, structural isomers of the familiar porphyrin ring, that are described below with a focus, in particular, on the isomer of regular porphyrin known as the *N*-confused porphyrins **2** (Chart 1).

Chart 1. Porphyrin (**1**) and *N*-confused porphyrin (**2**).



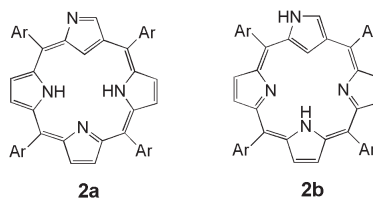
In *N*-confused porphyrin **2** the connectivity, and hence orientation of one of the pyrrole rings is different from porphyrin itself. Normally, each pyrrole is connected into the macrocycle through positions 2 and 5, whereas in *N*-confused porphyrin one pyrrole ring is, instead, connected through positions 2 and 4. This small change causes one of the nitrogen atoms to be located on the periphery of the macrocycle and a carbon atom to be located inside. This has a big influence on the ligand properties, not surprising as instead of the four *N*-donor atoms that occur in porphyrin **1**, the *N*-confused porphyrin **2** has three *N*-donors and a carbon available to coordinate to a central element.

The first example of an *N*-confused porphyrin (5,10,15,20-tetraaryl-2-aza-21-carbaporphyrin, **2**) was published simultaneously by two research groups, Furuta *et al.*<sup>1</sup> in Japan

and Latos-Grażyński *et al.*<sup>2</sup> in Poland. They discovered that *N*-confused porphyrin is produced in very low yield (4–7 %) as a by-product in the pyrrole/aldehyde condensation reaction used to form regular porphyrin.<sup>3</sup> An optimized synthetic route subsequently was published by Lindsey.<sup>4</sup>

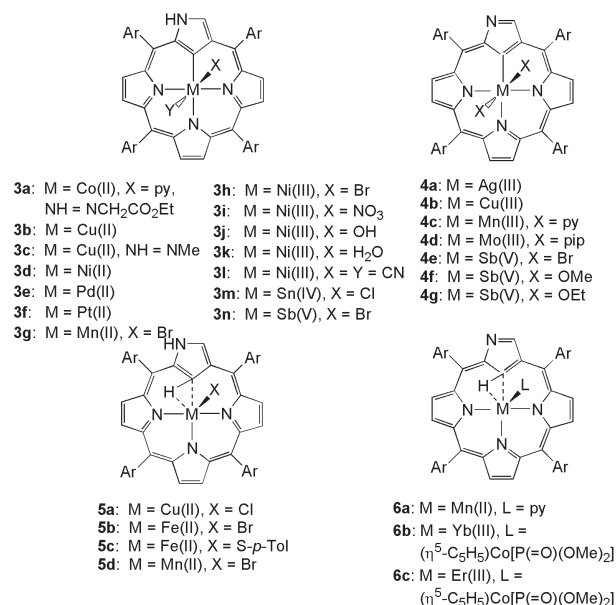
*N*-confused porphyrin can exist as two tautomers, depending on the solvent (Chart 2). Tautomer **2a**, observed in dichloromethane, has three inner protons, two NH and one CH. The second tautomer **2b**, which occurs in *N,N*-dimethylformamide, has one CH and one NH proton inside the macrocycle and one NH proton located outside. These tautomers are readily distinguished by their significantly different UV-visible and NMR spectra, as well as from the colours of the compound in different solvents.<sup>5</sup> From experimental observation, tautomer **2a** was found to be the most stable and this was confirmed by DFT studies.<sup>6,7</sup>

Chart 2. Tautomeric forms of *N*-confused porphyrin.



The proton NMR spectrum of *N*-confused porphyrin **2** is very different from that of regular porphyrin **1** that has idealized *D*<sub>4h</sub> symmetry and so a very simple spectrum in which, for example, the resonance for the eight  $\beta$ -pyrrole protons appears as a singlet. *N*-confused porphyrin has no symmetry (*C*<sub>1</sub>), so that a unique signal is observed for each  $\beta$ -pyrrole proton and the inner CH and NH protons.

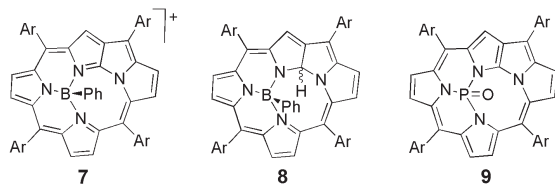
Depending upon which tautomer is involved in metal coordination, *N*-confused porphyrin can be a dianionic or trianionic ligand and can form different types of metal complexes. The first group of complexes comprises compounds containing a covalent M–C(21) bond between the metal and the inner [C(21)] carbon, in which the *N*-confused porphyrin is a dianion based on tautomer **2b** and bears an external NH. For example, these types of metal complexes are observed for all three of the group 10 metals Ni(II) **3d**, Pd(II) **3e** and Pt(II) **3f** as well as a range of other main group and transition metal ions **3a–n** as shown in Chart 3.<sup>8–17</sup> The second class of complexes also contains a covalent M–C(21) bond, but the external nitrogen on the ligand is not protonated, and the ligand coordinates as a trianion in the tautomer **2a** form, *e.g.* Ag(III) **4a**, Cu(III) **4b**, as well as **4a–g** in Chart 3.<sup>9,10,17–22</sup> The third and fourth group of metal complexes contain an agostic bond between M and H–C(21), in which C(21) retains its H substituent and the metal centre interacts with the C–H bond, occurring in the **2a** dianionic forms **5a–d**,<sup>9,15,23</sup> or the **2b** trianionic forms **6a–c**,<sup>24–26</sup> (Chart 3).

Chart 3. Metal complexes of *N*-confused porphyrin.

The examples given above primarily involve transition metals as well as two examples each of lanthanides Yb and Er,<sup>25,26</sup> and the heavier main group elements Sn and Sb.<sup>16,17,22</sup>

The smaller, lighter main group elements boron and phosphorus yield further unusual structural types of porphyrin-like complexes. The reaction of PhBCl<sub>2</sub> with *N*-confused porphyrin yields two types of monoboron complexes, **7** and **8**. Both of them have *N*-fused rather than *N*-confused porphyrin skeletons.<sup>27</sup> The *N*-fused porphyrin skeleton features one pyrrole  $\alpha$ -carbon, which has bonds to two pyrrole nitrogens. The addition of PCl<sub>3</sub> to *N*-confused porphyrin yields phosphorus(V) complex **9**, also containing the *N*-fused porphyrin skeleton.<sup>28</sup> Compounds **7-9** have subtle differences, including their charge, and the ligands occur as monoanion, dianion and trianion, respectively. The ligand in complex **7** is a true *N*-fused porphyrin, which is two oxidation levels higher than a porphyrin. The ligands in **8** and **9** are tautomers, but are formally at the same oxidation level as porphyrin, which means they are further examples of structural isomers of porphyrin and *N*-confused porphyrin.

Chart 4. Boron(III) and phosphorus(V) complexes.



What is the outlook for these new members of the porphyrin family? In fact, they are not all that new as they comprise by-products from porphyrin syntheses, but the recent focus on their chemistry has opened up some new possibilities. Firstly, the notion of a porphyrin isomer capable of forming a trianionic ligand has proved useful for stabilizing complexes of transition metals in higher oxidation states and also in unusual coordination geometries.<sup>29,30</sup> Examples of less common high oxidation states stabilized by coordination to *N*-confused porphyrin are the Ni(III) **3h-I**, Ag(III) **4a** and Cu(III) **4b** complexes listed in Chart 3.<sup>10-12,18,19</sup> Porphyrins and their expanded and contracted isomers are being widely used in supramolecular architectures of all

kinds, and the isomeric analogues are also being explored for these applications. Materials science applications utilize their strong light-absorbing properties and the *N*-confused and *N*-fused porphyrins add further members with different symmetries and electronic excited states to this family of chromophores. Last but not least, they are adding to our fundamental knowledge of the chemistry of the porphyrin core itself, which despite being familiar and widely utilized now has structural isomers established as an integral part of its chemistry, along with many new metal complexes.<sup>31</sup>

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