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Expanded Porphyrins

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Lucky Seven: Characterization of Stable T-Shaped Copper(II) Complexes of [32]Heptaphyrins**

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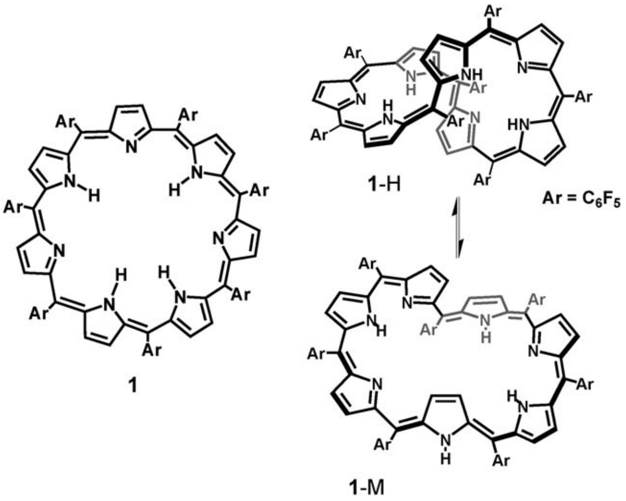
Dedicated to Professor Alan L. Balch

copper · expanded porphyrins · macrocycles · porphyrinoids

Apart from their versatile usefulness, porphyrins and their analogues and homologues can serve as laboratory systems developed just for the purpose of modeling a certain type of structure or reactivity. Their optical properties, including luminescence and two-photon absorption, multimodal coordinating ability, redox processes involving either the macrocyclic ring or a coordinated metal center, chirality, and aromaticity can be adjusted over a broad range or fine-tuned by a tailored synthesis. Thus it is not surprising that the universe of porphyrinoids expands continuously and from time to time gives birth to new systems, which from a distance all look alike; their diversity, however, is apparent after closer inspection.

A group of expanded porphyrins includes a set of porphyrin homologues comprising macrocycles which have more than four conjugated pyrrolic moieties in the ring. Among the expanded porphyrins, a system consisting of seven pyrroles, meso-heptaaryl[32]heptaphyrin(1.1.1.1.1.1.1) (**1**), seems to be one of the most versatile and intriguing. This macrocycle was originally obtained as one of the products of a stochastic condensation of pyrrole and pentafluorobenzaldehyde,[1] but a much better yield has been achieved in a rational synthesis involving predefined three- and four-pyrrolic fragments.[2] The heptaphyrins are nonplanar, but the actual geometry of the molecule has been shown to depend on several factors, such as the meso substituent type, solvent, temperature, and protonation.[3] The ring shape affects aromaticity of the conjugated system, which can thus show weak paratropic current effects when the ring adopts the form of an unsymmetrical figure eight or Hückel conformation **1**-H with all nitrogen atoms pointing towards the macrocyclic interior, or a distinct diatropic current upon forming a one-sided Möbius strip **1**-M (Scheme 1).[3] The latter ring conformation appears to be more stable for the meso-heptakis(2,6-dichlorophenyl) derivative and can be fixed by coordination of a palladium(II) ion to the three nitrogen atoms and one pyrrolic β-carbon atom of the macrocycle.[4] In the figure-eight conformation **1**-H, heptaphyrins feature two inequivalent coordination sites. One of them consists of four pyrroles forming a porphyrin-like donor set, and the other comprises three pyrrole nitrogen donors.[2] This situation clearly implies the formation of unsymmetrical metal complexes, even upon insertion of the same type of ion into both sites. On the other hand, considering the flexibility of the macrocyclic ring and the ability of the pyrrolic β-carbon atoms to form σ bonds with metal ions, other coordination modes are feasible as well. Apparently, the properties of the incoming metal determine the coordination mode of the macrocycle.



Scheme 1. Conformational equilibrium of heptaphyrin **1**.

A unique characteristic of the heptaphyrin bearing pentafluorophenyl substituents in the meso positions is the extremely facile nucleophilic displacement of fluorine atoms by pyrrolic nitrogen atoms, thus leading to mono-, di-, or tetra-N-fused systems. This reactivity, which was initially problematic because of the difficulties with crystallization of the unaltered heptaphyrin, provides access to the rigid fourfold-fused chiral system **2** that possesses only a tripyrrolic donor set.[2]

The insertion of zinc(II) or copper(II) ions into the tetrapyrrole fragment of the unaltered heptaphyrin **1** in the figure-eight conformation takes place quantitatively at room temperature, while no metalation of the tripyrrolic fragment

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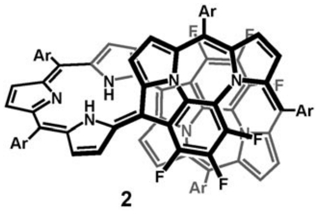


2

Ar = C_6F_5

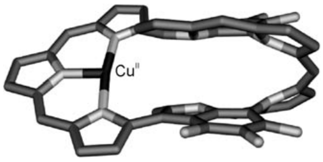
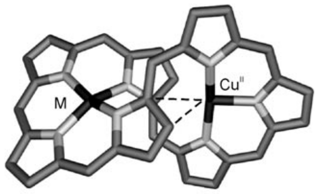


Figure 2. Stick representation of the molecular structure of the copper(II) complex of tetra-N-fused heptaphyrin. Only fused aryl substituents are shown. All hydrogen atoms are omitted.

is observed under these conditions.[5] Involvement of four consecutive pyrroles in coordination clearly stabilizes the figure-eight conformation of the macrocycle and prevents formation of the fused systems. Remarkably, an attempt to introduce boron(III) into the copper(II) complex of heptaphyrin resulted in a ring fission into an annular tripyrrolic system of subporphyrinatoboron(III) and a copper(II) complex of a regular tetrapyrrolic porphyrin.[5]

Nevertheless, bimetallic complexes with copper(II) in the tripyrrolic site of the unaltered heptaphyrin are readily obtainable.[6] Those systems, with zinc or copper(II) in the tetrapyrrolic site, are stable despite the extremely unusual coordination environment offered to Cu^{II} by the tripyrrolic segment. Owing to the constraints introduced by the remaining parts of the macrocycle, the NNN donor set is organized in such a way that it binds the metal ion in a T-shaped coordination environment. Tricoordinate complexes of copper(II) are very rare, and to date, in all of them a regular trigonal geometry of the metal environment has been determined.[7–9] In contrast, tricoordinate complexes of monovalent copper are quite common,[10] but still, with very few exceptions,[11] they adopt a regular trigonal rather than a T-shaped structure. It appears that the copper(II) ion in the heptaphyrin complexes is highly coordinatively unsaturated and is starving for a fourth donor. In the solid-state structures of bis(copper(II)) and copper(II) zinc complexes of heptaphyrin (Figure 1), two pyrrole β-carbon atoms are situated over the copper(II) ion within a distance shorter than the sum of van der Waals radii (2.5–2.8 Å).[6] The attractive $\mathrm{Cu{-}(C{=}C)}$ interaction is also indicated by DFT calculations. No such supporting copper–arene interaction occurs in the solid state for the complex of tetra-N-fused heptaphyrin **2**, which should then be considered as a genuine case of T-shaped copper(II) coordination (Figure 2). Note that the T-shaped geometry is not the only one which the coordination core can adopt in the complexes of **2**. Distorted tetrahedral boron(III) complexes with a supplementary hydroxy or alkoxy ligand have been characterized previously for this macrocycle.[2]



M = Cu^{2+}, Zn^{2+}

Figure 1. Stick representation of the molecular structure of the bimetallic heptaphyrin complexes comprising T-shaped copper(II). The supplementary interactions of one of the pyrrole carbon atoms with the copper ion are marked with dashed lines. All hydrogen atoms and all pentafluorophenyl substituents are omitted.

Although these novel tricoordinated copper(II) complexes are isolable, it seems that, to a large extent, their stability relies on the ligand construction reinforced by coordination of metal or fusion in the tetrapyrrole segment. However, the metal center in the T-shaped environment is prone to reduction, which is reflected by the remarkably high value of its reduction potential,[6] implying the relative stabilization of monovalent copper.[9]

The systems comprising d-block elements with T-shaped geometry of the coordination environment are expected to be highly reactive. There are, however, examples of structurally characterized complexes of late transition metals such as silver(I),[12] cobalt(I),[13] palladium(II),[14,15] or platinum(II)[16] with various ligands in which the central ion environment adopts a T-shaped geometry, but some of them are stabilized by agostic interactions with C–H fragments of distal parts of the ligand. All these complexes are diamagnetic, 14- or 16-electron species, except for one paramagnetic d^9 nickel(I) carbonyl complex.[17]

Paramagnetism of the heptaphyrin complexes, crucial for their formulation as copper(II)-containing systems, has been shown by magnetic susceptibility measurements and EPR spectra in the solid state. The most valuable, from a spectroscopic point of view, are spin Hamiltonian data extracted from the EPR spectrum of the "genuine case" system, that is, the copper complex of tetra-N-fused heptaphyrin. The parameters, which are clearly distinct from those obtained for octahedral, square-planar, tetrahedral, or trigonal environments, may be useful as a reference for identification of the T-shaped structure in other systems, such as T2 sites of multicopper oxidases[18] or transient species of similar characteristics of the coordination sphere. However, it seems that, because the **g** and **A** tensors are non-coaxial in the system with a T-shaped copper environment, high-frequency EPR measurements allowing better separation of Zeeman and hyperfine tensor components are required for the full interpretation of the magnetic behavior and for identifying the ground state of the metal center.

Although magnetic properties of the bis(copper(II))heptaphyrin complex observed in the solid state suggest magnetic exchange in line with the presence of antiferromagnetically interacting centers, in solution the magnetism of this system is not as clear. The antiferromagnetic coupling of the paramagnetic centers is expected to give reverse, "anti-Curie" dependencies of the chemical shifts on temperature for the solution ^1H NMR spectra, which means that paramagnetically shifted proton signals should approach their diamagnetic limits at low temperature, while for the bis(copper)heptaphyrin complex a "normal" Curie behavior is observed. It suggests no antiferromagnetic coupling in solution. The signals in the solution ^{1}H NMR spectrum are impressively narrow and spread over the range of $\delta = -27$–40 ppm at room temperature. If the spin density is delocalized from the metal ion onto the ligand mainly through the σ framework (as it is for the metal $(d_{x^2-y^2})^1$ ground state), only downfield isotropic shift is anticipated for pyrrole protons.[19,20] The alternation of chemical shift may suggest contribution of a radical electronic structure similar to that observed previously for oxidized copper(II) complexes of porphyrins or biliverdin analogues.[21] Such a metal radical species may be formed here by an intramolecular redox process involving tricoordinate copper and the heptaphyrin ring. The structure comprising Cu^{II} in the four- and Cu^{I} in the three-pyrrolic segments of the one-electron oxidized heptaphyrin may be investigated once the mixed-valence copper(I) copper(II) oxo heptaphyrin complex formation is elucidated (Figure 3), which occurs in the presence of peroxides.[6]

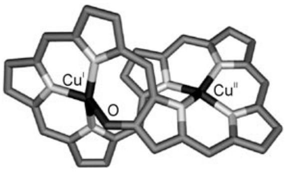


Figure 3. Stick representation of the molecular structure of the mixed-valence copper oxo heptaphyrin complex. All hydrogen atoms and all pentafluorophenyl substituents are omitted.

Clearly, a system comprising such an unusual structural feature like the one observed for the heptaphyrin copper(II) complexes merits further comprehensive exploration, and that makes it even more fascinating.

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