DOI: 10.1002/anie.200902901

T-Shaped Three-Coordinate Copper(II) Heptaphyrin Complexes[**]

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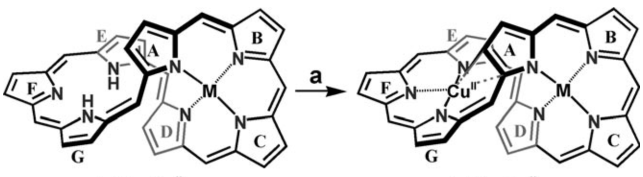
Copper proteins, in which copper ions are bound to proteins through the side-chain residues of histidine, cysteine, or methionine, have been a central focus in bioinorganic chemistry. A current topic in this field is the crystal structure of a bacterial copper-tolerance protein, which reveals the favorable copper(I)–tryptophan interaction as well as three normal coordination bonds.[1] Copper(I)–arene interactions have been reported for some small complexes in the context of their possible roles in natural systems.[2] These situations contrast those of copper(II) ions, since the direct observation of copper(II)–arene interactions has been very limited.[3] Copper(II), which has a d^9 electronic configuration, has been known to form four-, five-, and six-coordinate species with various shapes. In addition, three-coordinate copper(II) has been a unique focus in connection with the type 1 class of copper protein active sites.[4] In 1999, Holland and Tolman synthesized the first three-coordinate copper(II) complexes by using a small but hindered β-diketiminate ligand.[5a,b] These results suggest that the use of a bulky ligand can be effective to produce a low-coordinate copper(II) complex, which is easily further coordinated in order to overcome its coordination deficiency.

On the other hand, increasing attention has been focused on the unique coordination chemistry of expanded porphyrins, which are conjugated pyrrolic macrocycles.[6] Among these compounds, dicopper(II) complexes of amethyrin and hexaphyrin have been reported. In these complexes, copper(II) ions are bound to three pyrrolic nitrogen atoms and an additional ligand, either a chloride ion or an oxygen atom, to constitute total formal four and/or five coordination.[7] Herein, we report T-shaped three-coordinate copper(II) heptaphyrin complexes that exhibit attractive copper(II)–arene interactions. To the best of our knowledge, this complex shows the first example of a structurally characterized copper(II)–arene interaction. We have shown that such a three-coordinate copper(II) complex undergoes a regioselective oxygenation at the fourth coordinating pyrrolic double bond. We also report the first T-shaped three-coordinate copper(II) complex, which was synthesized by using a more rigid, quadruply N-fused heptaphyrin ligand, and does not contain any supplementary interactions.

We have recently reported *meso*-aryl-substituted [32]heptaphyrin(1.1.1.1.1.1.1) as a versatile scaffold that displays chemical, physical, structural, and coordination properties.[8] During these studies, monocopper(II) and monozinc(II) heptaphyrin complexes **1** and **2** with figure-of-eight conformations were prepared.[8b] In these complexes, the metal ions are accommodated by a hemiporphyrin tetrapyrrolic subunit, thus leaving the tripyrrolic moiety free. We discovered that dinuclear metal complexes **3** and **4** could be synthesized almost quantitatively by further treatment of **1** and **2** with five equivalents of $Cu(OAc)_2$ under basic conditions (Scheme 1).



1: M = Cu^{II}
2: M = Zn^{II}

3: M = Cu^{II}
4: M = Zn^{II}

Scheme 1. Insertion of copper into **1** and **2**. a) $Cu(OAc)_2$, NEt_3, CH_2Cl_2, MeOH, 25 °C, 1 h, 95 % for **3**, 98 % for **4**. *meso*-C_6F_5 substituents are omitted for clarity.

The figure-of-eight structures of **3** and **4** were elucidated by X-ray diffraction analysis, and the newly introduced Cu1 ion shows a novel coordination mode (Figure 1).[9] Curiously, in both cases, the Cu1 ion is bound to N5, N6, and N7 in the tripyrrolic moiety in a T-shaped manner, without other ligands such as an anion or a coordinating molecule. This coordination mode is obviously different from those of other reported copper(II) complexes.[3,7,10,15,16] Magnetic susceptibility measurements of **3** and **4** revealed that the oxidation state of the Cu1 ion is +2 and that there is a weak antiferromagnetic interaction between the two Cu^{II} ions in **3** (Figure 4 b and the Supporting Information). Notably, Cu1 is displaced from the N5-N6-N7 plane toward the pyrrolic C···C bond by 0.20–0.22 Å. The distances of Cu1···C2 and Cu1···C1 are 2.51 and 2.76–2.83 Å, respectively. These distances are significantly shorter than the sum of the van der Waals radii (3.10 Å) but longer than the covalent bond distance of 1.94 Å for $Cu^{II}\cdots C(sp^2)$ or 2.00–2.04 Å for $Cu^{II}\cdots C(sp^3)$.[10] These short distances possibly arise from some structural constraints of the figure-of-eight ligand or some attractive interaction between the low-coordinate copper(II) ion and the pyrrole ring, such as the copper(II)–arene interaction (such as η^2-coordination from C2···C1 to Cu1) or an agostic C2···H2···Cu1 interaction.[11]

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[**] This work was supported by Grants-in-Aid (nos. 19205006 (A) and 20108001 "pi-Space") from MEXT. S.S. acknowledges a JSPS Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200902901.

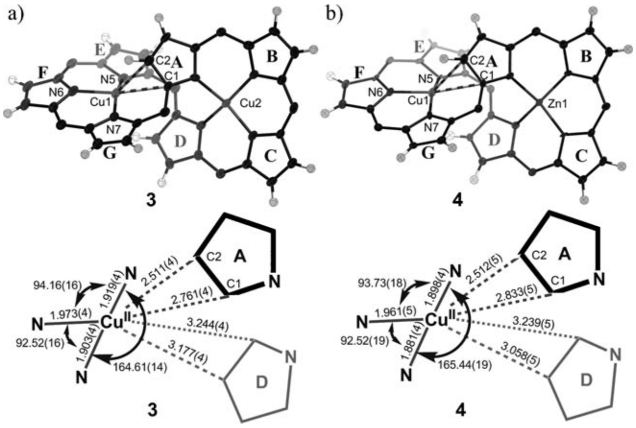


Figure 1. X-ray crystal structures of a) **3** and b) **4**. Thermal ellipsoids are set at 50% probability (top). *meso*-C_6F_5 substituents are omitted for clarity. Selected bond distances [Å] and angles [°] are displayed (bottom).

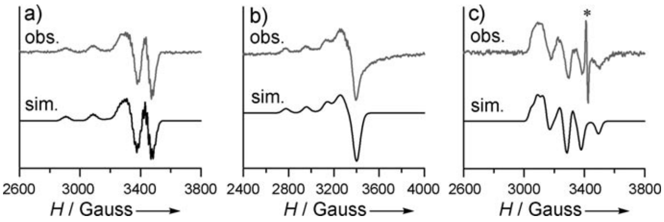


Figure 2. The observed (top) and simulated (bottom) ESR spectra of a) **1** in frozen toluene at 20 K, and b) **4** and c) **7** in the solid state at 20 K with simulated spectra (bottom). * denotes signals that arises from an impurity.

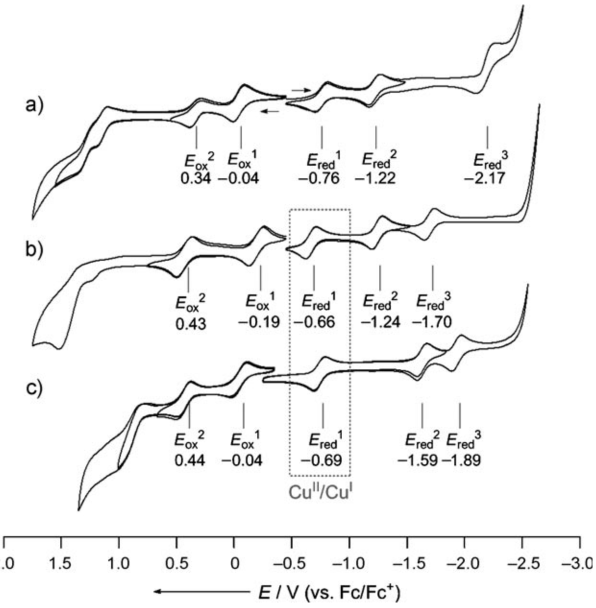
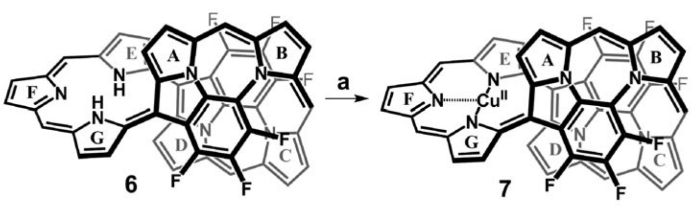


Figure 3. Cyclic voltammograms of a) **1**, b) **3**, and c) **7**. Solvent: CH_2Cl_2; scan rate: 50 mV s^{-1}; working electrode: glassy carbon; reference electrode: $Ag/AgClO_4$; electrolyte: Bu_4NClO_4. Fc/Fc$^+$ = ferrocene/ferrocenium.

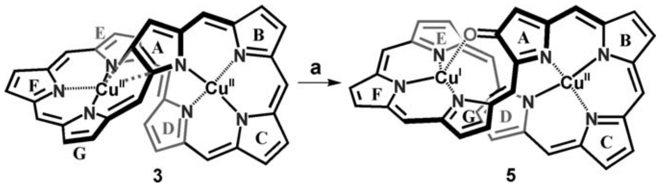
The DFT-optimized (UB3LYP/6-31G(d,p)) structure of **4** shows an even shorter Cu1⋯C2 distance (2.41 Å) than that in the crystal structure. This result strongly suggests an attractive interaction rather than structural constraints.[12] Analysis of selected molecular orbitals (MOs) shows orbital overlap between Cu1 d(x^2−y^2) and C1⋯C2 π orbitals, thus supporting the presence of d–π interactions, as seen in the case of copper(I)–arene complexes (see the Supporting Information).[2] The ^{1}H NMR spectrum of **3** in CD_2Cl_2 at 298 K displays seven paramagnetically shifted signals, which correspond to the fourteen β protons from $\delta = -26.69$ to 39.97 ppm. These signals indicate that **3** has an averaged C_2 symmetric structure around the Cu1⋯Cu2 axis in solution on the NMR timescale. Variable-temperature ^{1}H NMR measurements on **3** did not reveal any particular signal splitting or exceptional chemical shift, even at 183 K (see the Supporting Information). The lack of signal splitting means that the averaged C_2 symmetric structure is preserved in solution, and the lack of any particular signal shift indicates that no agostic proton with direct spin density transfer from the copper(II) ions is present.[11]

ESR measurements of **4** show that Cu1 has a 3d(x^2−y^2) ground state. The observed spectrum is in good agreement with the simulated spectrum with the following spin Hamiltonian parameters: $g_{xx} = 2.041$, $g_{yy} = 2.047$, $g_{zz} = 2.225$; $A_{xx} = 10\times10^{-4}$, $A_{yy} = 10\times10^{-4}$, $A_{zz} = 181\times10^{-4}$ cm^{-1}. These values are not largely different from those of **1** (simulated with the parameters $g_{xx} = 2.025$, $g_{yy} = 2.055$, $g_{zz} = 2.155$; $A_{xx} = 25\times10^{-4}$, $A_{yy} = 20\times10^{-4}$, $A_{zz} = 181\times10^{-4}$ cm^{-1}), despite the apparently different copper(II) coordination modes (Figure 2). The ESR spectra of **3** show only weak intensities, which probably arise from the antiferromagnetic interaction between two copper(II) ions (see the Supporting Information). Although it is difficult to distinguish coordination modes by ESR measurements, these data suggest that the copper(II)–arene interactions may compensate for the lack of a fourth coordination site, and gives rise to a ligand field with approximate tetrahedral shape. Cyclic voltammograms of **1**, **3**, and **7** are shown in Figure 3. The redox potentials of **1** and **2**, and those of **3** and **4** are essentially the same (see the Supporting Information). Spectroelectrochemistry of **1** and **3** revealed that the reduction waves at −0.76 and −1.22 V (versus Fc/Fc$^+$) of **1** and at −1.24 and −1.70 of **3** are ligand-centered processes, since the absorption spectral changes are each quite similar (see the Supporting Information) and the potential differences are also the same (0.46 V). On the other hand, almost no spectral change was observed for the reduction wave at −0.66 V for **3**, thus suggesting the occurrence of a metal-centered Cu^{II}/Cu^{I} process (see the Supporting Information).[13] This reduction potential is consistent with the high reduction potentials of copper(II) proteins that have a coordination geometry similar to that of copper(I).[5a] On the other hand, the first oxidation potential of **3** (−0.19 V) is negatively shifted from that of **1** (−0.04 V), which may result in the enhanced air sensitivity of **3** discussed below.[14]

Complex **3** is fairly stable toward heating and hydrolysis under an inert atmosphere. However, the blue color of **3** faded in air over a few weeks. In connection with the oxygen susceptibility, we confirmed the oxygenation reactivity of **3**. Treatment of **3** with MCPBA or H_2O_2 caused smooth regioselective oxygenation to produce **5** (Scheme 2). The X-ray crystal structure of **5** shows that the C2 atom is oxygenated and the resulting carbonyl group is coordinated to the Cu1 ion (Figure 4a).[9,15] Curiously, the magnetic susceptibility measurements, ESR measurements, and charge-balance consideration of **5** revealed that the oxidation state of the Cu1 ion changed from +2 to +1 during the oxygenation reaction (Figure 4b and the Supporting Information). This regioselective oxygenation reaction of **3** is interesting in view of its relevance to reactions of natural copper proteins and related arene hydroxylation chemistry, although it is difficult to determine the involvement of a copper hydroperoxo species.[16]



Scheme 3. Insertion of copper into **6**. a) $Cu(OAc)_2$, NEt_3, CH_2Cl_2, MeOH, 25 °C, 1 h, 84%. *meso*-C_6F_5 substituents are omitted for clarity.



Scheme 2. Regioselective oxygenation of **3** a) *meta*-chloroperoxybenzoic acid (MCPBA; 4 equiv), CH_2Cl_2, room temperature, 15 min, 33%; or aqueous H_2O_2, triethylamine, acetone, −78 °C to room temperature, 30%.

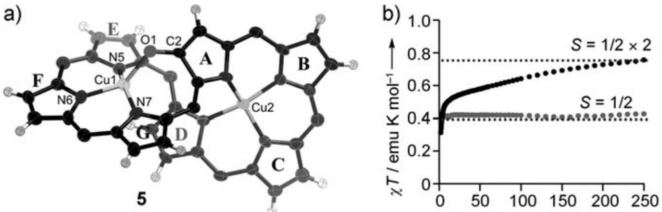


Figure 4. a) X-ray crystal structure of **5** (thermal ellipsoids set at 30% probability; *meso*-C_6F_5 substituents are omitted for clarity). Selected bond distances [Å]: Cu1–O1 1.927(9), Cu1–C2 2.778(12), C2–O1 1.290(14). b) Temperature-dependent magnetic susceptibilities of **3** (black) and **5** (gray) measured from powder samples.

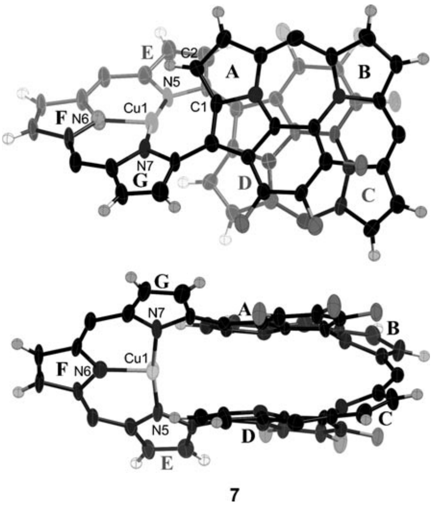


Figure 5. X-ray crystal structures of **7**; top view (top) and side view (bottom; thermal ellipsoids represent 50% probability). *meso*-C_6F_5 substituents are omitted for clarity). Selected bond distances [Å] and angles [°]: Cu1–N5 1.851(4), Cu1–N6 1.892(6), Cu1–N7 1.851(4), Cu1–C2 3.043(5), Cu1–C1 3.055(5); N5-Cu1-N6 95.05(13), N6-Cu1-N7 95.05(13), N5-Cu1-N7 169.9(3).

Finally, we obtained monocopper complex **7** by copper(II) complexation of quadruply N-fused heptaphyrin **6**[8a] in 84% yield (Scheme 3). The oxidation state of copper(II) was further confirmed by temperature-dependent magnetic susceptibility measurements and charge consideration (see the Supporting Information). Unlike **3** and **4**, the structure of **7** shows crystallographic C_2 symmetry. The tripyrrolic nitrogen atoms N5, N6, and N7 are closer to Cu1 (1.851(4) and 1.892(6) Å) than those in **3** and **4** (Figure 5). The distances of Cu1⋯C2 and Cu1⋯C1 are 3.043(5) and 3.055(5) Å, which are approximately the sum of van der Waals radii of those atoms. These data indicate that **7** has a T-shaped planar three-coordination of Cu1, and does not contain copper(II)–arene interactions.[17] These unique structural features of **7** probably arise from the highly rigid C_2 symmetric structure of **6**.[8a] The ESR spectrum of **7** is drastically different from those of typical octahedral or tetrahedral coordination compounds (Figure 2). Given the genuine T-shaped three-coordination, the ***A*** tensor is expected to deviate from the ***g*** tensor (see the Supporting Information). Hence, the spectral simulation was performed using the following spin Hamiltonian parameters: $g_{xx} = 2.061$, $g_{yy} = 2.065$, $g_{zz} = 2.201$; $A_{xx} = 111 \times 10^{-4}$, $A_{xz} = 12 \times 10^{-4}$, $A_{yy} = 34 \times 10^{-4}$, and $A_{zz} = 21 \times 10^{-4}\,\mathrm{cm}^{-1}$, to provide a simulated spectrum which is in good agreement with the observed spectrum. This result supports the hypothesis that the copper(II) ion in **7** is three-coordinate. The first reduction potential of **7** (−0.69 V (versus Fc/Fc^+)), which is assigned to the metal-centered Cu^{II}/Cu^{I} process, is almost the same as those of **3** and **4**. These high reduction potentials are likely characteristic of these T-shaped tricoordinate copper(II) complexes.

In summary, T-shaped three-coordinate copper(II) heptaphyrin complexes **3** and **4** were synthesized from the monometalated complexes **1** and **2**, in which the attractive copper(II)–arene interaction counteracts the coordination deficiency of copper(II). Complex **3** underwent regioselective oxygenation at the fourth coordination site to give **5** with concurrent reduction of copper(II) to copper(I). The first genuine T-shaped three-coordinated copper(II) complex **7**, which does not contain any supplementary ligands was obtained from a more rigid quadruply N-fused heptaphyrin **6**.

Received: May 30, 2009
Revised: August 29, 2009

Keywords: copper · macrocycles · metal–arene interactions · oxygenation · porphyrinoids

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[9] a) Crystallographic data for **3**: $\mathrm{C_{85}H_{22}N_7OF_{35}Cu_2}$, $M_w = 1949.18$, triclinic, space group $P\bar{1}$ (no.2), $a = 14.601(5)$, $b = 14.753(5)$, $c = 18.867(5)$ Å, $\alpha = 98.072(5)$, $\beta = 103.714(5)$, $\gamma = 111.053(5)°$, $V = 3569(2)$ Å^3, $\rho_{\mathrm{calcd}} = 1.814\ \mathrm{g\,cm^3}$, $Z = 2$, $R1 = 0.0483$ $[I > 2.0\sigma(I)]$, $Rw = 0.1398$ (all data), GOF = 0.985 $[I > 2.0\sigma(I)]$. For **4**: $\mathrm{C_{108.5}H_{46}N_7F_{35}CuZn}$, $M_w = 2241.43$, triclinic, space group $P\bar{1}$ (No.2), $a = 15.329(5)$, $b = 17.307(5)$, $c = 17.777(5)$ Å, $\alpha = 89.805(5)$, $\beta = 78.258(5)$, $\gamma = 73.359(5)°$, $V = 4417(2)$ Å^3, $\rho_{\mathrm{calcd}} = 1.685\ \mathrm{g\,cm^3}$, $Z = 2$, $R_1 = 0.0689$ $[I > 2.0\sigma(I)]$, $R_w = 0.1885$ (all data), GOF = 1.076 $[I > 2.0\sigma(I)]$. For **5**: $\mathrm{C_{78.38}H_{14.38}N_7OF_{35}Cl_{4.13}Cu_2}$, $M_w = 2008.38$, monoclinic, space group $P2_1/a$ (No.14), $a = 14.167(6)$, $b = 34.215(10)$, $c = 16.465(5)$ Å, $\beta = 103.233(13)°$, $V = 7769(5)$ Å^3, $\rho_{\mathrm{calcd}} = 1.717\ \mathrm{g\,cm^3}$, $Z = 4$, $R1 = 0.1080$ $[I > 2.0\sigma(I)]$, $Rw = 0.3701$ (all data), GOF = 0.968 $[I > 2.0\sigma(I)]$. For **7**: $\mathrm{C_{77}H_{14}N_7F_{31}Cu}$, $M_w = 1689.49$, monoclinic, space group $C2/c$ (no.15), $a = 21.206(10)$, $b = 21.618(8)$, $c = 22.041(8)$ Å, $\beta = 107.728(15)°$, $V = 9624(7)$ Å^3, $\rho_{\mathrm{calcd}} = 1.166\ \mathrm{g\,cm^3}$, $Z = 4$, $R1 = 0.0931$ $[I > 2.0\sigma(I)]$, $Rw = 0.2747$ (all data), GOF = 1.008 $[I > 2.0\sigma(I)]$. Values for **7** were obtained by removal of solvent molecules using the PLATON SQUEEZE program. CCDC 727381 (**3**), 727383 (**4**), 727382 (**5**), 731675 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[13] a) It is not reasonable to assign the first reduction potential of **3**, as a ligand-centered process as such an assignment would mean too small a potential gap (0.47 V) between the first reduction and the first oxidation of the heptaphyrin ligand; b) one of the referees suggested that the reduction of **3** might yield a copper(I) state, which may lead to the demetalation of copper(I). We thus attempted the reduction of **3** with $\mathrm{NaBH_4}$ and actually confirmed the demetalation of copper ion(s) (see the Supporting Information).

[14] It was difficult to assign $\mathrm{Cu^{II}}$ d–d or MLCT transitions in the UV/Vis absorption spectra because of large absorption coefficients of the heptaphyrin ligands, the absorption bands of which reach the near-IR region (see the Supporting Information).

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[17] The DFT-optimized structure of **7** loses C_2 symmetry, with Cu1···C2 and Cu1···C1 distances of 2.81 and 2.93 Å. The d–π orbital overlap in the selected MOs is smaller than that in **4** (see the Supporting Information).