

Biscopper Complexes of *meso*-Aryl-Substituted Hexaphyrin: Gable Structures and Varying Antiferromagnetic Coupling

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Recently, increasing attention has been focused on expanded porphyrins that have a conjugated pyrrolic macrocycle larger than porphyrins.¹ One of the promising potentials of expanded porphyrins relies on their rich metalation chemistry, which may allow formation of discrete dinuclear metal complexes with notable metal–metal interaction, as anticipated from their large cavities. This is in contrast to the metalation of porphyrins, in which metal ions are usually coordinated in a 1:1 fashion. Despite this promise, there are only limited examples of such dinuclear metal complexes in the literature.^{2–6} Gossauer et al. were the first to prepare β -dodecaalkyl-substituted [26]hexaphyrins and their dinuclear zinc(II) and palladium(II) complexes, though they never characterized them structurally.⁴ Recent structurally characterized examples include dinuclear metal complexes of amethyrin⁵ and doubly N-confused hexaphyrin.⁶

Here we report copper(II) metalation of *meso*-aryl-substituted hexaphyrins **1** and **2** (chart 1). Hexaphyrin **1** displays pronounced aromaticity along rectangular conjugated 26π -network,^{7a} while a thermally stable form of perfluorinated analogue **2** is nonaromatic [28]hexaphyrin with a figure eight conformation.^{7c} As such, these molecules occupy a central position of *meso*-aryl-expanded porphyrins that are real homologues of *meso*-tetraaryl porphyrins,⁷ but their metalation has not been reported yet.⁸

A solution of **1** in CH_2Cl_2 was stirred at room temperature in the presence of anhydrous CuCl_2 and NaOAc for 4 h. After usual workup, dinuclear copper complex **3** was isolated in 84% yield. Interestingly, the metalation with anhydrous $\text{Cu}(\text{OAc})_2$ led to isolation of a different dinuclear copper complex **4** in 90% yield. The high-resolution (HR) FAB-MS spectra of **3** and **4** indicated the presence of two copper ions and one oxygen atom; **3**: m/z : 1600.9256, calcd for $\text{C}_{66}\text{H}_{13}\text{F}_{30}\text{N}_6\text{OCu}_2$: 1600.9264 and **4**: m/z : 1599.9168, calcd for $\text{C}_{66}\text{H}_{12}\text{F}_{30}\text{N}_6\text{OCu}_2$: 1599.9186. The structures of **3** and **4** have been confirmed by X-ray crystallographic analysis. In **3** (Figure 1, left), the two copper ions are each bound to the bridging chloride atom, the oxygen atom attached at the *meso*-position, and three pyrrolic nitrogen atoms of the semi-planar tripyrrolic ligand attached in a square pyramidal fashion with the chloride atom as an apical ligand.⁹ Displacements of the copper ions from the mean plane defined by the three nitrogen atoms and oxygen atom are 0.23 and 0.24 Å. The gable structure of **3** is caused by addition of oxygen and hydrogen atoms at the opposite *meso*-positions and flipping of the two inverted pyrroles in **1** to constitute two semi-planar tripyrrolic units. The resulting rehybridization of the methene bridges, from sp^2 to sp^3 , serves to interrupt the conjugation of the ligand, which was also confirmed by its less

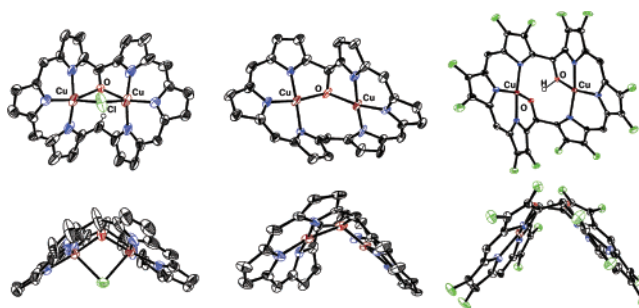


Figure 1. X-ray crystal structures of **3** (left), **4** (middle), and **6** (right). The thermal ellipsoids were scaled to the 50% probability level. *meso*-Pentafluorophenyl substituents, β -hydrogen atoms, and solvent molecules were omitted for clarity.

intense absorption spectrum (Supporting Information, SI). Complex **4** exhibits a similar gable structure (Figure 1, middle), in which the two copper ions are bound to the *meso*-attached bridging oxygen atom and three pyrrolic nitrogen atoms in a square-planar fashion with smaller displacements of the copper ions (0.08 and 0.05 Å).¹⁰

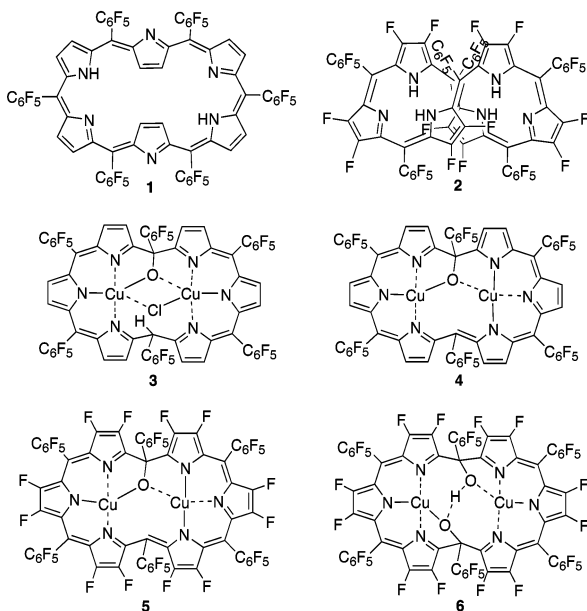
The perfluorinated hexaphyrin **2** gave complex **5** as a sole product (96%) upon treatment with CuCl_2 , while **5** and **6** were obtained in 26 and 56% from the reaction with $\text{Cu}(\text{OAc})_2$. The HR FAB-MS spectra displayed a molecular ion peak at $m/z = 1815.8092$ for **5** (calcd for $\text{C}_{66}\text{F}_{42}\text{N}_6\text{OCu}_2$: 1815.8055) and at $m/z = 1832.8089$ for **6** (calcd for $\text{C}_{66}\text{HF}_{42}\text{N}_6\text{O}_2\text{Cu}_2$: 1832.8082). The structures of **5** and **6** were also determined by X-ray crystallographic analysis. The structure of **5** is quite similar to that of **4** in respect of the square-planar coordination with the *meso*-attached bridging oxygen atom and three pyrrolic nitrogen atoms (SI).¹¹ Complex **6** takes a different structure (Figure 1, right), in which the two copper ions are not directly bridged by oxygen atom but rather separately bound to the different tripyrrolic ligand and *meso*-attached oxygen atom.¹² The oxygen ligands have been revealed to be tertiary alcohol and alkoxide, which are hydrogen-bonded with an O–O distance of 2.366(4) Å. The presence of a hydroxy group was shown by H–D exchange upon treatment with D_2O , which has been probed by the FAB-MS spectroscopy (SI). Importantly, this structure leads to the assignment of **6** as Cu(I)–Cu(II) mixed valence. Collectively, the biscopper complexes **3–6** take the similar gable structures, in which the symmetric two tripyrrolic semimacrocycles are obliquely arranged with varying dihedral angles (**3**, 118°; **4**, 108°; **5**, 109°; **6**, 79°) and Cu–Cu distances (**3**, 3.469(2) Å; **4**, 3.708(2) Å; **5**, 3.603(1) Å; **6**, 3.906(1) Å). The source of the *meso*-attached oxygen atoms has been assigned to adventitious water in the reaction mixture on the basis of the metalation experiments carried out in

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Chart 1. Structures of *meso*-Aryl Hexaphyrins **1** and **2** and Their Biscopper Complexes **3**, **4**, **5**, and **6**



the presence of a small amount of H_2^{18}O , which afforded ^{18}O -incorporated products as determined by the FAB-MS spectroscopy.¹³

Complexes **3**, **4**, and **5** exhibit magnetic behaviors typical of antiferromagnetically coupled biscopper(II) pairs in the variable-temperature magnetic susceptibility measurements (2–300 K), while complex **6** exhibits temperature-independent susceptibility $\chi_p T$ value ($0.4229 \text{ emu K mol}^{-1}$), which corresponds to $S = 1/2$ state in agreement with Cu(I)–Cu(II) mixed valence state (SI).¹⁴ The least-squares fit of the experimental data through the Bleaney–Bowers equation gave $-J$ values of 8.27 cm^{-1} for **3**, 87.6 cm^{-1} for **4**, and 42.1 cm^{-1} for **5**. Different $-J$ values for **4** and **5** are interesting despite the similar coordination environments and Cu–Cu distances. Provided that magnetic interaction propagates predominantly through the Cu–O–Cu bond for **4** and **5**, the larger $-J$ value in **4** compared with **5** may be explained in terms of more electron-withdrawing ligand in **5**. The small $-J$ value in **3** may be ascribed to the presence of the bridging chloride atom, which might act a mediator of superexchange ferromagnetic interaction through bridge.^{15,16} Alternatively, the square pyramidal coordination caused by the chloride bridge may influence the magnetic interaction.

As noted above, the absorption spectra of **3–6** are less intense compared with that of the aromatic hexaphyrin (**SI**). Curiously, very broad absorption bands around near-IR region are observed in the spectra of **4** ($\lambda_{\text{max}} = 1498 \text{ nm}$), **5** ($\lambda_{\text{max}} = 1475 \text{ nm}$), and **6** ($\lambda_{\text{max}} = 1842 \text{ nm}$) with molar absorption coefficients of ca. $10^4 \text{ cm}^{-1} \text{ M}^{-1}$. Though origins of these bands are not clear at this stage, preliminary spectroelectrochemical studies suggest that they may be ligand-derived absorptions.

In summary, the hexaphyrins **1** and **2** can serve as an effective ligand for two copper ions with unexpected but rather common large structural changes to provide the gable biscopper complexes **3–6** that exhibit varying antiferromagnetic couplings. This is a new mode of metalation of *meso*-aryl-expanded porphyrins. Relatively similar structures of **3–6** are remarkable, considering a large difference between **1** and **2** in respects of aromaticity, stable

conformation, electronic demands, and the number of NH available for the metalation. Metalation of *meso*-aryl-substituted hexaphyrins and other expanded porphyrins is an attractive subject and worthy of further investigation.

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Supporting Information Available: Synthetic procedures and spectral data of complexes **3**, **4**, **5**, and **6**, including magnetic susceptibility and ESR spectra (PDF). CIF files for the X-ray structural analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Reports (ref 3) on the metalation of octaphyrins encourage new potentials of expanded porphyrins.
- (9) Crystallographic data of **3**: $\text{C}_{68}\text{H}_{15}\text{N}_6\text{F}_{30}\text{Cu}_2\text{O}_{1.61}\text{Cl}_7$, $M_w = 1886.88$, monoclinic, space group $C2/c$ (No. 15), $a = 18.37(3)$, $b = 16.20(2)$, $c = 25.17(4)$ Å, $\beta = 113.52(9)^\circ$, $V = 6866(16)$ Å³, $D_c = 1.825 \text{ g/cm}^3$, $Z = 4$, $R = 0.095$, R_w ($I > 3.0\sigma(I)$) = 0.135, GOF = 1.070 ($I > 3.0\sigma(I)$).
- (10) Crystallographic data of **4**: $\text{C}_{67}\text{H}_{13}\text{N}_6\text{F}_{30}\text{Cu}_2\text{O}_4\text{Cl}_2$, $M_w = 1732.82$, triclinic, space group $P1$ (No. 2), $a = 13.979(3)$, $b = 15.646(3)$, $c = 15.932(4)$ Å, $\alpha = 78.753(4)$, $\beta = 73.062(4)$, $\gamma = 74.027(4)^\circ$, $V = 3179(1)$ Å³, $D_c = 1.810 \text{ g/cm}^3$, $Z = 2$, $R = 0.104$, R_w (all data) = 0.265, GOF = 1.097 ($I > 2.0\sigma(I)$).
- (11) Crystallographic data of **5**: $\text{C}_{69}\text{N}_6\text{F}_{42}\text{O}_2\text{Cu}_2\text{Cl}_6$, $M_w = 2066.54$, monoclinic, space group $P2_1/n$ (No. 14), $a = 22.60(1)$, $b = 13.063(5)$, $c = 25.05(1)$ Å, $\beta = 109.73(3)^\circ$, $V = 6960(5)$ Å³, $D_c = 1.972 \text{ g/cm}^3$, $Z = 4$, $R = 0.092$, R_w (all data) = 0.310, GOF = 1.269 ($I > 2.0\sigma(I)$).
- (12) Crystallographic data of **6**: $\text{C}_{69}\text{H}_3\text{N}_6\text{F}_{42}\text{Cu}_2\text{O}_3\text{Cl}_5$, $M_w = 2066.11$, triclinic, space group $P1$ (No. 2), $a = 13.964(6)$, $b = 16.264(7)$, $c = 16.295(8)$ Å, $\alpha = 86.66(4)$, $\beta = 74.89(4)$, $\gamma = 84.63(4)^\circ$, $V = 3554(2)$ Å³, $D_c = 1.930 \text{ g/cm}^3$, $Z = 2$, $R = 0.065$, R_w ($I > 3.0\sigma(I)$) = 0.076, GOF = 1.340 ($I > 3.0\sigma(I)$).
- (13) The biscopper complexes **3**, **4**, and **5** formed in the presence of H_2^{18}O exhibit a cluster of peaks that fit well with the respective formula with ^{18}O in the FAB-MS spectra. **3**: 1603, calcd for $\text{C}_{66}\text{H}_{13}\text{F}_{30}\text{N}_6^{18}\text{OCu}_2$: 1602.9307, **4**: 1602, calcd for $\text{C}_{66}\text{H}_{12}\text{F}_{30}\text{N}_6^{18}\text{OCu}_2$: 1601.9228, and **5**: 1818, calcd for $\text{C}_{66}\text{F}_{42}\text{N}_6^{18}\text{OCu}_2$: 1817.8098 (SI).
- (14) Consistent with this assignment, the ESR spectrum of **6** at 1.5 K can be simulated as a single-spin system, and the XPS measurements revealed that the satellite peak associated with Cu(II) ion in **6** was weaker in comparison to **3** and **5** (SI).
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- (16) Interestingly, a smaller antiferromagnetic interaction ($-J = 5 \text{ cm}^{-1}$) was reported for bis(μ -chloro)copper(II) amethyrin with a Cu–Cu distance of 2.76 Å (ref 5b).

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