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Homo- and Heterobismetal Complexes of 5-Hydroxy-10,15,25,30-tetrakis-(pentafluorophenyl)-Substituted [26]Hexaphyrin(1.1.1.1.1.1)

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Metalation of *meso*-free 5,10,20,25-tetrakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**4**) with Cu^{II} and Zn^{II} ions afforded homodinuclear complexes **6** and **7**, respectively. A demetalation−remetalation protocol provided monozinc(II) complex **9** selectively, from which copper(II)−zinc(II) heterodinuclear complex **10** was prepared effectively.

Recently, increasing attention has been focused on expanded porphyrins that have conjugated macrocycles consisting of more than five pyrrolic subunits.[1] Expanded porphyrins show attractive optical, electrochemical, and structural properties. Besides these, expanded porphyrins have rich coordination chemistry, providing various discrete multinuclear metal complexes by virtue of their large cavities.[2] Among these, hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**1**) occupies a key position in terms of a planar rectangular conformation and strong aromaticity.[3] Hexaphyrin **1** serves as a metal-coordinating ligand to produce mono- and dinuclear metal complexes with interesting properties.[4] Its bisgold(III) complex exhibits a distinct aromatic−antiaromatic switch upon a two-electron-redox process[4] and nickel(II), palladium(II), and platinum(II) complexes are all Möbius aromatic molecules with twisted topologies.[4,5] In both cases, the C−metal bond serves as an important structural element to maintain either a planar or twisted conformation. Upon metalation with Cu^{II} and Zn^{II} ions, both of which have virtually no C−H bond activation reactivity, hexaphyrin **1** gave gable-shaped dinuclear complexes **2**[4] and **3**.[4] Probably because of the need to accommodate two metal ions, the pyrrolic subunits are all inward-oriented and one *meso* position is oxygenated and, consequently, the overall macrocyclic conjugation is disrupted. Therefore, the exploration of a more convenient hexapyrrolic macrocyclic ligand that can accommodate two metal ions in a more general manner and preferably with preservation of macrocyclic 26π electronic conjugation is highly desirable.

Here we report zinc(II) and copper(II) metalation of *meso*-free hexaphyrin **4** and *meso*-oxygenated hexaphyrin **5** (Chart 1). Recently, we reported the synthesis of hexaphyrin **4** as the first example of *meso*-free variants,[6,7] which displays pronounced aromaticity along a spectacles-like conjugated 26π network. Interestingly, **4** undergoes smooth oxygenation at the free *meso* position to provide **5**, which is an exceptionally stable neutral radical.[6] It occurred to us that the *meso*-oxygenated hexaphyrin framework of **5** may be suitable for metalation of Cu^{II} and Zn^{II} ions with preservation of the macrocyclic 26π aromaticity.

A solution of **4** in CH_2Cl_2/MeOH was stirred in the presence of $CuCl_2$ and NaOAc at room temperature for 3 h. After aqueous workup including washing with brine, dinuclear copper(II) complex **6** was isolated in 75% yield. The high-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass spectrum of **6** indicated the presence of two copper ions and one oxygen atom by showing the

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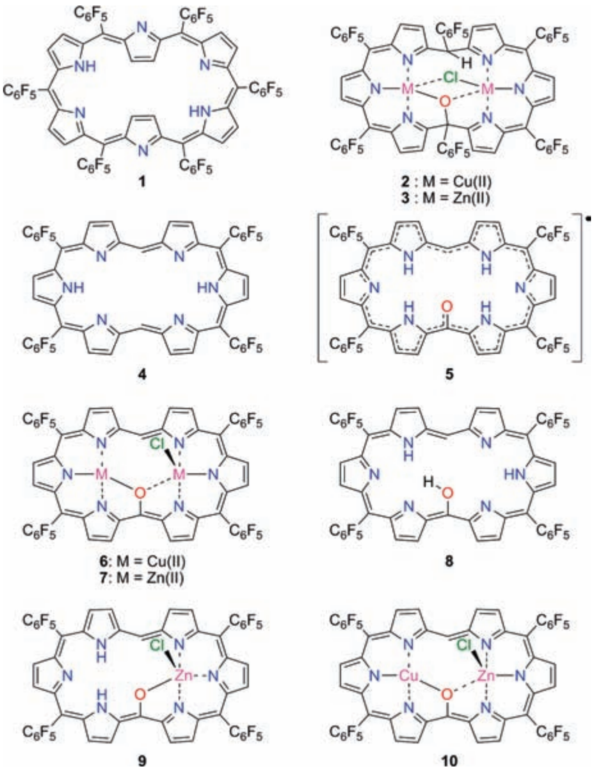
Chart 1. Hexaphyrins and Their Metal Complexes



parent ion peak at *m*/*z* 1268.9404 ([M − Cl]$^+$) (calcd for $C_{54}H_{13}F_{20}N_6OCu_2$: *m*/*z* 1268.9414). The structure of **6** has been revealed by X-ray crystallographic analysis to a spectacles-like planar conformation (Figure 1a), in which one of *meso* positions is oxygenated.[8−10] Coordination features are not identical for two Cu^{II} atoms; namely, Cu(1) is bound to NNNO atoms with distances of 1.996, 2.027, 2.012, and 2.528 Å, respectively, and Cu(2) is bound to NNNCl atoms with distances of 2.014, 2.034, 2.008, and 2.283 Å, respectively. The distance between Cu(2) and the *meso*-oxygen atom is 2.597 Å, thus suggesting some interaction. The mean-plane deviation of **6** defined by the 36 atoms of the pyrrolic rings and methine carbons constructing the hexaphyrin macrocycle is only 0.300 Å. Displacements of Cu(1) and Cu(2) from the mean plane are 0.348 and 0.444 Å, and the Cu(1)−Cu(2) distance is shown to be 4.769 Å. As expected, the metalation of *meso*-oxygenated hexaphyrin **5** gave **6** in 79% yield under comparable conditions.

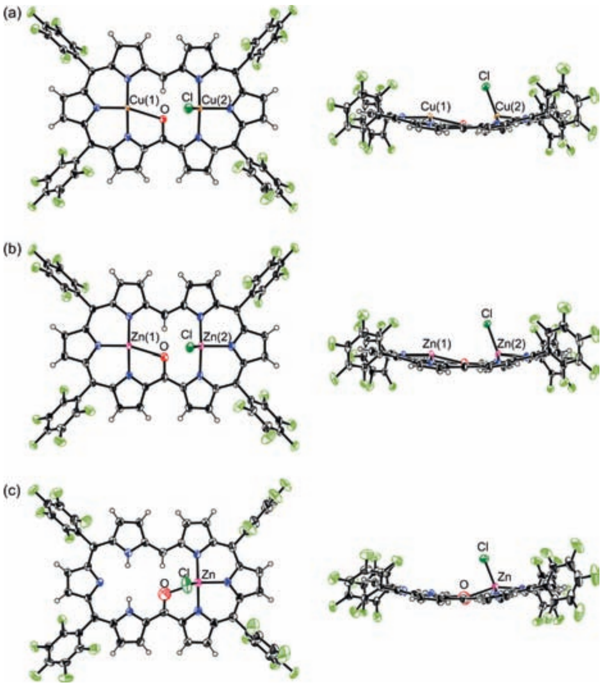


Figure 1. X-ray crystal structures of **6** (a), **7** (b), and **9** (c). The thermal ellipsoids are scaled to the 50% probability level. Solvent molecules are omitted for clarity.

The structure of **6** is interesting, in that two Cu^{II} ions are well accommodated within a hexaphyrin framework that preserves an aromatic 26π network. The conjugated electronic network of **6** is seen in its absorption spectrum, which shows a Soret-like band at 573 nm and a Q-like band at 934 nm (see the Supporting Information, SI).

The ^1H NMR spectrum of **6** is merely broad, showing signals very downfield (25−35 ppm) because of the unpaired electron of Cu^{II} ions. The mean *g* value was determined to be 2.1003 by electron spin resonance (ESR) spectroscopy in the solid state. The temperature-dependent magnetic susceptibility χ revealed a rather constant value of χT = 0.836 emu K mol^{-1} in the range of 10−300 K, indicating the presence of only two weakly interacting Cu^{II} ions in **6**. The observed decrease of the χT value at low temperature indicated a weak antiferromagnetic interaction between the two Cu^{II} ions. Using the Bleaney−Bowers equation, the exchange interaction J/kB was estimated to be −0.59 K.

In the next step, the metalation of **4** with $ZnCl_2$ was examined under similar conditions, which led to isolation of biszinc(II) complex **7** in 75% yield. The parent ion peak of **7** was detected at *m*/*z* 1272.9382 ([M − Cl]$^+$) (calcd for $C_{54}H_{13}F_{20}N_6OZn_2$: *m*/*z* 1272.9377). The structure of **7** has been revealed by X-ray crystallographic analysis to be a spectacles-like planar conformation that is essentially similar to that of **6** (Figure 1b).[10] Zn(1) is bound to NNNO atoms in a roughly square-planar geometry, while Zn(2) is bound to NNNCl atoms. The mean-plane deviation of **7** is also small, 0.298 Å. Displacements of Zn(1) and Zn(2) from the mean plane are 0.348 and 0.447 Å, and the Zn(1)−Zn(2) distance is 4.773 Å. The ^1H NMR spectrum of **7** in THF-d_8 exhibits 12 doublet signals in the range of 11.06−8.83 ppm due to the β protons and a singlet signal due to the inner *meso*-hydrogen atom at −2.34 ppm (see the SI), clearly indicating its nonsymmetric structure and strong diatropic ring current.

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(9) The mechanism of oxygenation has not been clarified yet, but the reaction of **4** with molecular oxygen is probable because no ^{18}O atom incorporation was detected in the experiment in the presence of a small amount of $H_2^{18}O$.

(10) Crystallographic data of **6**: $C_{54}H_{13}N_6F_{20}O_1Cu_2Cl_1\cdot(CCl_{2.4}, 2(CCl_3))$, M_w = 1638.04, monoclinic, $P2_1/n$ (No. 14), a = 19.952(5) Å, b = 11.640(3) Å, c = 26.043(6) Å, β = 104.898(2)°, V = 5845(2) g cm^{-3}, D_c = 1.862 g cm^{-3}, Z = 4, R1 = 0.722 [I > 2.0σ(I)], wR2 = 0.2229 (all data), GOF = 1.028 [I > 2.0σ(I)], CCDC-716607. Crystallographic data of 7: $C_{54}H_{13}N_6F_{20}O_1Zn_2Cl_1(C_3C_{19})$, M_w = 1663.02, monoclinic, $P2_1/n$ (No. 14), a = 19.946(2) Å, b = 11.5872(14) Å, c = 26.101(3) Å, β = 104.959(2)°, V = 5828.0(12) g cm^{-3}, D_c = 1.895 g cm^{-3}, Z = 4, R1 = 0.807 [I > 2.0σ(I)], wR2 = 0.2428 (all data), GOF = 1.079 [I > 2.0σ(I)], CCDC-716608. Crystallographic data of 9: $C_{54}H_{15}N_6F_{20}O_1Zn_1Cl_1\cdot C_{4.53}H_{10.46}Cl_{10.59}\cdot 0.7C_6H_{14}$, M_w = 1391.16, monoclinic, $P2_1/c$ (No. 14), a = 17.727(3) Å, b = 15.508(4) Å, c = 23.462(5) Å, β = 111.345(8)°, V = 6008 (2) g cm^{-3}, D_c = 1.538 g cm^{-3}, Z = 4, R1 = 0.0992 [I > 2.0σ(I)], wR2 = 0.2865 (all data), GOF = 1.036 [I > 2.0σ(I)], CCDC-716609.

These data are in contrast to the spectral feature of nonaromatic **3** that exhibits the β-proton signals in the range of 6.56−6.06 ppm.[4]

Interestingly, the treatment of **7** with 10 equiv of $CuCl_2$ in a 9:1 mixture of CH_2Cl_2/MeOH at room temperature resulted in smooth metal exchange within 1 h to provide **6** in 80%, whereas the reverse metal exchange from **6** to **7** did not proceed. These results indicated a higher affinity of this hexaphyrin ligand toward the Cu^{II} ion.

Demetalation of **7** was achieved upon treatment with trifluoroacetic acid in $CHCl_3$. After 15 h, almost complete demetalation was confirmed by thin-layer chromatography (TLC) and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (MS) analyses. The usual aqueous workup of this demetalated solution provided *meso*-hydroxyhexaphyrin (**8**)[6] in 79% yield. We also found that neutralization of the demetalated solution with triethylamine caused remetalation of one Zn^{II} ion to **8**. This process was carefully monitored by TLC and MALDI-TOF MS analyses. Indeed, this procedure allowed the selective formation of **9**. After the same workup as that for **6**, the complex **9** was obtained as brown solids in 88% yield. The HR-ESI-TOF mass spectrum of **9** indicated the parent ion peak at m/z 1207.0272 ($[M - Cl]^+$) (calcd for $C_{54}H_{15}F_{20}N_6OZn$: m/z 1207.0274). Final confirmation of the structure of **9** is coming from X-ray crystallographic analysis (Figure 1c).[10] A spectacles-like type I conformation is well preserved, where the Zn^{II} ion is bound to a chloride atom, the oxygen atom is attached at the *meso* position, and three pyrrolic nitrogen atoms of the semiplanar tripyrrolic ligand are attached in a square-pyramidal fashion with the chloride atom as an apical ligand. The ^{1}H NMR spectrum of **9** exhibits 12 doublet signals in the range of 9.87−8.04 ppm due to the β protons, a singlet at 0.34 ppm due to the inner *meso* proton, and two broad signals at 2.82 and 2.32 ppm due to the inner NH protons, showing a spectacles-like conformation and a diatropic ring current. Judging from the chemical shifts of the outer β and inner *meso* protons, the diatropic ring current along the hexaphyrin periphery decreases in the order of **7** > **9** > **8**.

The complex **9** may serve as a precursor of heterodinuclear metal complexes of hexaphyrins. In order to explore this possibility, we examined the metalation of **9** with a Cu^{II} ion. Copper(II)−zinc(II) heterodinuclear complex **10** was readily prepared by the treatment of **9** with an equimolar amount of $CuCl_2$ and 2 equiv of sodium acetate in CH_2Cl_2. After the usual workup, complex **10** was obtained as brown solids in 71% yield. The parent ion peak was detected at m/z 1269.9389 ($[M - Cl]^+$) (calcd for $C_{54}H_{13}F_{20}N_6OCuZn$: m/z 1269.9401) in the HR-ESI-TOF mass spectrum. The mean g value was determined to be 2.1002 by ESR spectroscopy in the solid state. Temperature-dependent magnetic susceptibility of **10** exhibits χT = 0.414 emu K mol^{-1} in the range of 10−300 K due to the unpaired electron of the Cu^{II} ion. The observed χT values were reproduced by the Curie−Weiss model with the Weiss temperature $\theta = -0.25$ K.

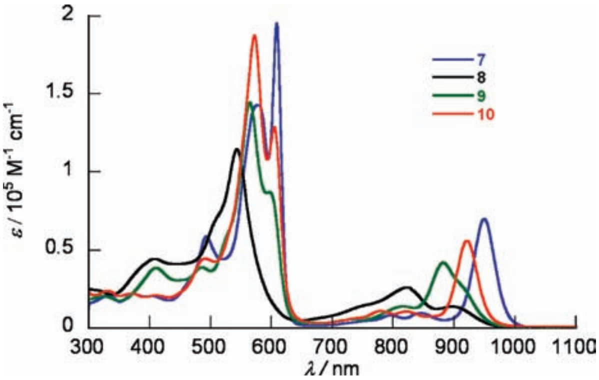

Figure 2. UV−vis absorption spectra of **7** (blue), **8** (black), **9** (green), and **10** (red) in CH_2Cl_2.

Figure 2 shows the absorption spectra of **7**−**10** in CH_2Cl_2. Free-base hexaphyrin **8**, monozinc(II) complex **9**, and biszinc(II) complex **7** exhibit systematic spectral changes. Soret bands are red-shifted in the order of **8** (544 nm), **9** (565 nm), and **7** (576 and 609 nm), and Q bands are similarly red-shifted in this order: **8** (823 and 898 nm), **9** (882 and 920 nm), and **7** (950 nm). The Soret and Q bands of heterodinuclear copper(II)−zinc(II) complex **10** are observed at 605, 572, and 921 nm, respectively. These spectral data are consistent with the fully conjugated π-electronic circuits.

In summary, the *meso*-hydroxyhexaphyrin framework represented by **5** and **8**, which are readily formed from the hexaphyrin **4**, has been demonstrated to serve as a useful ligand for copper(II) and zinc(II) metals with the preservation of full conjugation of the macrocycle. A demetalation−remetalation protocol has been developed for the preparation of monozinc(II) complex **9**, from which the copper(II)−zinc(II) heterodinuclear metal complex **10** was prepared. Exploration of other metal complexes with this hexapyrrolic ligand is currently underway in our group.

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Supporting Information Available: General procedures for **6**−**10**, spectral data for compounds **6** and **7**, absorption spectra for **6**−**10**, and CIF files for the X-ray analysis of **6**, **7**, and **9**. This material is available free of charge via the Internet at http://pubs.acs.org.