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Group 12 Metal Complexes of [26]Hexaphyrin(1.1.1.1.1.1)

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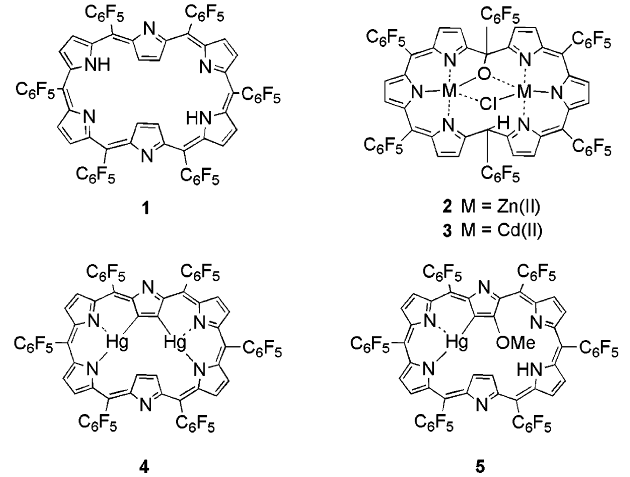
Metalation of *meso*-hexakis(pentafluorophenyl)-substituted [26]-hexaphyrin(1.1.1.1.1.1) (**1**) has been explored with group 12 metal ions Zn(II), Cd(II), and Hg(II). Zn(II) and Cd(II) ions afforded dinuclear gable-shaped complexes **2** and **3** in good yields, while Hg(II) ion provided bis-Hg(II) and mono-Hg(II) planar complexes (**4** and **5**) via C–H bond cleavage.

A recent surge in the development of various expanded porphyrins is owed largely to their attractive optical, electrochemical, and coordination properties arising from their larger π conjugation than that of porphyrins.[1] In particular, expanded porphyrins are highly promising as multi-metal coordinating ligands, allowing formation of polynuclear complexes with notable metal−metal interaction or catalytic activity.[2,3] *meso*-Hexakis(pentafluorophenyl)-substituted [26]hexaphyrin(1.1.1.1.1.1) (**1**) first synthesized by Cavaleiro et al. possesses an important and unique position that connects porphyrin and higher expanded porphyrin congeners in view of its flat structure and strong aromaticity.[4] Independently, we reported the improved synthesis of **1** via modified Rothemund−Lindsey protocol and the related reaction using dipyrromethane and tripyrrane precursors.[5,6]

Chart 1



1

2 M = Zn(II)
3 M = Cd(II)

4

5

With an efficient synthetic procedure of **1** in hand, we started our own studies on its metalation behaviors toward Cu(II), Cu(I), Ni(II), Pd(II), Pt(II), and Au(III) ions.[7] Gable bis-Cu(II) complexes with variable anti-ferromagnetic interactions were obtained with Cu(II) ion,[7a] while Cu(I) metalation induced double pyrrolic rearrangement to provide a bis-Cu(II) complex of doubly *N*-confused hexaphyrin.[7b] In the case with Ni(II), Pd(II), and Pt(II),[7c] mono- or bis-metal complexes with a C−metal bond were obtained. Remarkably, planar mono- and bis-Au(III) complexes were obtained from the metalation with Au(III) ion, both of which exhibit facile aromatic−antiaromatic switching upon two-electron redox process.[7d] These results indicate that at the present stage the metalation behaviors of **1** are somewhat

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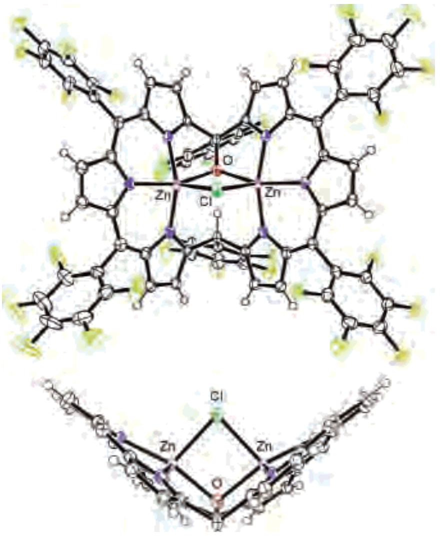

Figure 1. X-ray crystal structure of **2**. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

unpredictable, varying upon metal ions and metalation conditions, in sharp contrast to those of porphyrins. In this paper, we report on the metalation of **1** toward Zn(II), Cd(II), and Hg(II) ions.

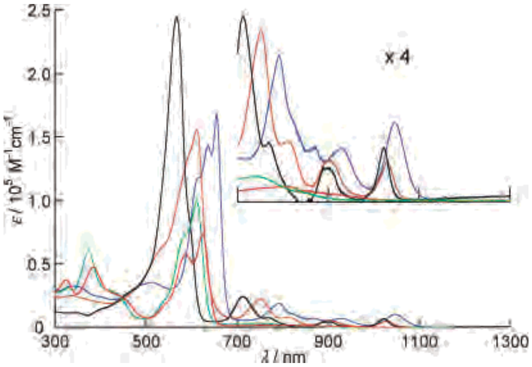

Figure 2. Absorption spectra of **1** (black), **2** (red), **3** (green), **4** (blue), and **5** (orange) in CH_2Cl_2.

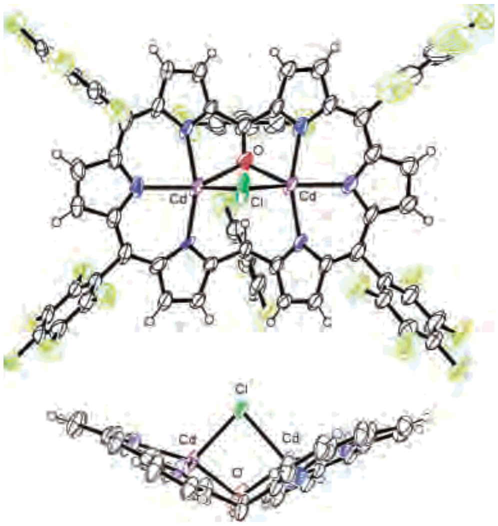

Figure 3. X-ray crystal structure of **3**. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

A solution of **1** and $Zn(OAc)_2{\cdot}2H_2O$ in a 4:1 mixture of $CHCl_3$ and methanol was refluxed in the presence of sodium acetate for 24 h. Aqueous workup including washing with brine gave bis-Zn(II) complex **2** in 91% yield. High-resolution electrospray ionization time-of-flight (HR-ESI-TOF) mass measurement reveals the parent ion peak of **2** at $m/z = 1640.8879$ ($[M - H]^-$), calcd for $C_{66}H_{12}N_6F_{30}OZn_2Cl$: 1640.8840 (Supporting Information). A single-crystal X-ray diffraction analysis revealed a gable bis-Zn(II) structure, where the two zinc ions are similarly bound to the three pyrrolic nitrogen atoms of the semi-planar tripyrrolic ligand and are bridged by the chloride atom and the oxygen atom attached at the meso position in a square pyramidal fashion (Figure 1).[8] The zinc ions are displaced by 0.420 and 0.396 Å from the mean plane defined by three nitrogen atoms of pyrrole rings and the oxygen bridge. The Zn−Cl lengths are 2.3777(10) and 2.3941(9) Å, the Zn−O distances are 2.151(2) and 2.167(2) Å, and the Zn−Zn distance is 3.24 Å. This gable structure is essentially the same as that of a bis-Cu(II) complex of **1**.[7a] The ^1H NMR spectrum of **2** exhibits signals due to the pyrrolic β-protons in the range of 6.56−6.06 ppm and a signal due to the meso proton at 10.75 ppm that has no correlation with other peaks in the HH COSY spectrum. This large downfield shift can be explained by the strong hydrogen bonding with the bridging oxygen atom, as is evident from the short distance of 2.91 Å between the meso sp^3 carbon and the oxygen atom. In the ^{13}C NMR spectrum, a peak due to the sp^3 carbon at meso position is observed at 41.0 ppm, which has a correlation with the meso proton in the CH-hetero COSY spectrum. Reflecting the disruption of cyclic full conjugation, complex **2** features an ill-defined absorption spectrum with attenuated absorbance (Figure 2), which is similar to that of the bis-Cu (II) complex.

Cd(II) metalation of **1** was conduted with $Cd(OAc)_2{\cdot}2H_2O$. By the use of the same procedure as for **2**, bis-Cd(II) complex **3** was isolated in 62% yield. HR-ESI-TOF mass spectroscopy exhibits the parent ion peak at $m/z = 1734.8319$ ($[M - H]^-$) (calcd for $C_{66}H_{12}N_6F_{30}OCd_2Cl$, 1734.8369). The single-crystal X-ray structure revealed a gable structure with two Cd(II) ions, which are bound with the tripyrrolic ligand and bridged by the chloride and meso-attached oxygen atom in a square pyramidal fashion (Figure 3),[9] These structural features are similar to those of **2**. The Cd−N distances are in the range 2.202−2.250 Å, the Cd−Cl distances are 2.578(2) and 2.5731(17) Å, the Cd−O distances are 2.336(5) and

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(8) Crystallographic data of **2**: $C_{66}H_{13}N_6F_{30}O_1Zn_2Cl_1{\cdot}4(CH_3CN){\cdot}2(O)$, $M_w = 1838.23$, triclinic, $P\bar{1}$ (No. 2), $a = 12.159(3)$ Å, $b = 14.350(3)$ Å, $c = 22.245(5)$ Å, $\alpha = 97.110(4)°$, $\beta = 97.185(4)°$, $\gamma = 110.593(3)°$, $V = 3545.5(14)$ Å^3, $D_c = 1.722$ g/cm^3, $Z = 2$, R1 = 0.0543 ($I > 2.0\sigma(I)$), wR2 = 0.1686 (all data), GOF = 1.037 ($I > 2.0\sigma(I)$).

(9) Crystallographic data of **3**: $C_{66}H_{13}N_6F_{30}O_1Cd_2Cl_1{\cdot}2(CHCl_3)$, $M_w = 1855.46$, monoclinic, $P2_1/c$ (No. 14), $a = 18.2170(18)$ Å, $b = 32.707(3)$ Å, $c = 12.5752(13)$ Å, $\beta = 101.453(2)°$, $V = 7343.4(12)$ Å^3, $D_c = 1.678$ g/cm^3, $Z = 4$, R1 = 0.0929 ($I > 2.0\sigma(I)$), wR2 = 0.2123 (all data), GOF = 1.104 ($I > 2.0\sigma(I)$). Some unassigned electron density due to severely disordered solvents was removed by use of the utility SQUEEZE in PLATON software package.; SQUEESE-PLATON: (a) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 2005. (b) Sluis, P. V. D.; Spek, A. L. *Acta Crystallogr. A* **1990**, *46*, 194.

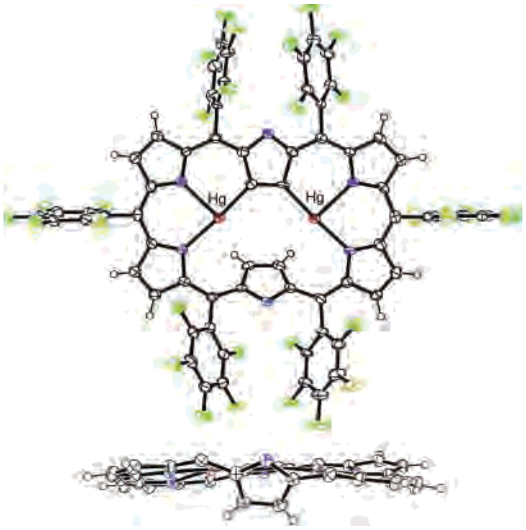

Figure 4. X-ray crystal structure of **4**. The thermal ellipsoids are scaled to the 50% probability level. In the side view, *meso*-pentafluorophenyl substituents are omitted for clarity.

2.300(6) Å, and the Cd−Cd distance is 3.47 Å. The ^{1}H NMR spectrum shows signals due to the pyrrolic β-protons in the range of 6.53−6.15 ppm similarly to those of **2**, but a singlet due to the meso proton is observed at 7.75 ppm, which is considerably upfield-shifted by 3 ppm as compared with **2**. This suggests weaker hydrogen-bonding interaction with the bridging oxygen atom, which is supported by a longer distance (3.31 Å) between the sp^3 carbon and the oxygen atom. The absorption spectrum of **3** is similar to that of **2** (Figure 2).

Finally, Hg(II) metalation of **1** was investigated with Hg(OAc)$_2$ in a toluene−methanol mixture. After being stirred for 1 h at room temperature, the solution color changed from violet to green, and the usual workup gave bis-Hg(II) complex **4** and mono-Hg(II) complex **5** in 27% and 29% yields, respectively. Complex **4** exhibits the parent ion peak at m/z = 1858.9973 ([M + H]$^+$), (calcd for $C_{66}H_{11}N_6F_{30}Hg_2$, 1858.9970). The structure of **4** was determined by X-ray diffraction analysis, as shown in Figure 4.[10] Interestingly, the two inner pyrrolic C−H bonds of the same pyrrole are cleaved to form Hg−C bonds.[11] Each Hg(II) ion is additionally bound with the two pyrrolic nitrogen atoms and fitted in a flat tridentate cavity. The distances between the Hg ions and β-carbon atoms of the unbound pyrrole are 2.82 and 2.95 Å, being shorter than the sum of van der Waals radii (3.32 Å). This suggests favorable mercury−sp^2 carbon interaction. The mean plane deviation defined by the three pyrrolic units is 0.043 and 0.139 Å. On the other hand, the opposite pyrrole is significantly tilted at 48.8° with respect to the mean plane of 36 atoms of macrocycle, probably to escape the steric repulsion. The Hg−N distances are 2.343(4), 2.142(4), 2.331(4), and 2.132(4) Å, and the Hg−C distances are 2.045(5) and 2.033(5) Å. In accord with the C_s-symmetric structure, **4** displays a simple ^{1}H NMR spectrum consisting of a singlet at 0.26 ppm for the inner pyrrolic β-protons, two sets of doublets at 9.95 and 9.70 ppm and 9.56 and 9.22 ppm for the outer pyrrolic β-protons (Supporting Information), indicating a strong diatropic ring current. Mono-Hg(II) complex **5** exhibits the parent ion peak at m/z = 1691.0535 ([M + H]$^+$) (calcd for $C_{67}H_{15}N_6F_{30}OHg$, 1691.0542), hence suggesting an addition of a methoxy group to the molecule. The ^{1}H NMR spectrum exhibits eight outer β-proton signals in the range 9.78−9.03 ppm, a set of mutually coupled doublets at −0.70 and −1.28 ppm due to the inner β-protons, and a broad NH proton singlet at −1.76 ppm. In addition, a singlet at −4.51 ppm due to the methoxy group is observed. These data support again a diatropic ring current for **5** as similar to **1** and **4**. In accord with this structural assignment, the absorption spectrum of **5** is similar to those of **1** and **4** in respect of a strong Soret-like band and several Q-like bands (Figure 2). The Soret-like bands are observed at 636 and 655 nm for **4** and 611 nm for **5**.

In summary, the metalation of **1** with Zn(II) and Cd(II) led to the formation of the gable-shaped bis-metalated complexes **2** and **3**, while the metalation with Hg(II) provided bis-Hg(II) complex **4** and mono-Hg(II) complex **5** via C−H bond cleavage, both of which preserve planar rectangular shapes and strong aromaticity. Currently, further work is underway to explore other metal complexes of **1** and utility as reaction catalysts.

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Supporting Information Available: Synthetic procedures, absorption spectra, HR-ESI-TOF mass spectra, ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, and ^{13}C−^{1}H COSY spectra of **2**−**5**, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystallographic data of **4**: $C_{66}H_{13}N_6F_{30}Hg_2 \cdot 2(C_7H_8)$, M_w = 2042.25, monoclinic, $P2_1/n$ (No. 14), a = 13.475(3) Å, b = 18.844(3) Å, c = 26.843(5) Å, β = 101.689(9)°, V = 6675(2) Å^3, D_c = 2.032 g/cm^3, Z = 4, R1 = 0.0396 ($I > 2.0\sigma(I)$), wR2 = 0.0995 (all data), GOF = 1.030 ($I > 2.0\sigma(I)$).

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