Assemblies of Mixed-metal Hexaporphyrins with an Oxo-bridged Iron(III) Porphyrin Dimer in the Center

Masamitsu Suzuki, Kiyoshi Tsuge, Yoichi Sasaki, and Taira Imamura*
Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810

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Four novel Fe-Ru mixed-metal hexaporphyrins having an Fe(III)-O-Fe(III) porphyrin dimer unit at the center and four surrounding ruthenium(II) porphyrin units were synthesized, characterized, and structurally analyzed by X-ray crystallography.

In construction of highly ordered porphyrin architectures, the use of non-covalent bonds is one of the powerful techniques.[1] In practice, many supramolecular porphyrin systems with elegant shapes have been self-assembled using coordination bonds such as metal-pyridyl interactions.[2,3] Especially, metal oligoporphyrins having different bond types of metal–ligand interactions and different metal ions are of prime interests.[4] These oligoporphyrins revealed that the physical properties are significantly affected by porphyrin geometry.

Herein we extend this methodology to discrete mixed-metal oligoporphyrins and present two types of novel Fe-Ru hexaporphyrins and their X-ray crystal structures. To construct these hexaporphyrins, we chose a μ-oxoiron(III) porphyrin dimer as a building core because of various coordination modes of iron porphyrins.[5] By the introduction of two pyridyl groups to the *trans-* or *cis-meso* positions of each porphyrin unit in the μ-oxoiron(III) porphyrin dimer, it is possible to construct versatile mixed-metal hexaporphyrins with an Fe-O-Fe moiety in the center. Respective treatments of [Fe(*trans*-4-Py_2T_2P)]$_2$O[6] and [Fe(*cis*-4-Py_2T_2P)]$_2$O with a stoichiometric amount of Ru(OEP)(CO)(MeOH) and Ru(TTP)(CO)(MeOH) led to the isolation of the corresponding hexaporphyrins, [Ru(OEP)(CO)]$_4$[Fe(*trans*-4-Py_2T_2P)]$_2$O (**1**), [Ru(OEP)(CO)]$_4$[Fe(*cis*-4-Py_2T_2P)]$_2$O (**2**), [Ru(TTP)(CO)]$_4$[Fe(*trans*-4-Py_2T_2P)]$_2$O (**3**), and [Ru(TTP)(CO)]$_4$[Fe(*cis*-4-Py_2T_2P)]$_2$O (**4**) as shown in Figure 1.[7]

Purple crystals of **1** suitable for X-ray analysis were obtained by diffusion of pentane into the dichloromethane solution of the compound.[8] **1** has an Fe(III)-O-Fe(III) porphyrin dimer unit at the center and four surrounding ruthenium porphyrin units (Figure 2a). The tolyl and pyridyl groups of the Fe2 porphyrin unit (the upper unit of the top view) and the Fe1 porphyrin unit (the lower unit) lie alternatively. Since the twist angle (29.8°) around the Fe1-O-Fe2 axis is not significantly different from those of μ-oxoiron(III) tetraarylporphyrin dimers without pyridyl groups (30–35°),[9] the twist angle of **1** must be mainly determined by interactions between aryl groups in the central iron porphyrin dimer unit. As the result, the bulky [Ru1(OEP)(CO)] and [Ru2(OEP)(CO)] are close to [Ru3(OEP)(CO)] and [Ru4(OEP)(CO)], respectively.

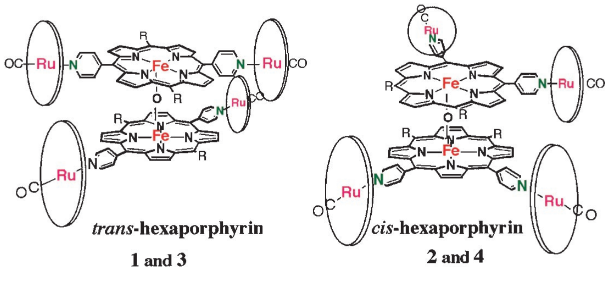

Figure 1. Fe-Ru hexaporphyrins. The ring of Ru units and R denote OEP or TTP and tolyl groups, respectively.

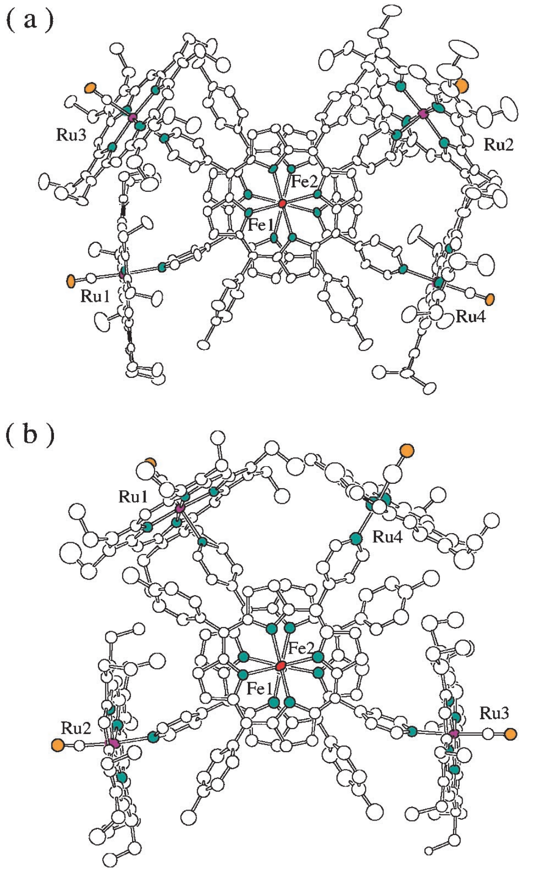

Figure 2. ORTEPs of the *trans*-hexaporphyrin **1** and the *cis*-hexaporphyrin **2**. In both the hexaporphyrins, the Ru1 and Ru2 units are linked to the Fe1 units (the lower units). Top view (a) of **1** showing 50% thermal ellipsoids. Selected distances (Å) and angles (deg): Fe(1)···Fe(2) 3.523(2); Ru(1)···Ru(2) 19.506(2); Ru(3)···Ru(4) 19.833(2) Å; Fe(1)-O-Fe(2) 177.2°. Top view (b) of **2** with 30% probability level. Selected distances (Å) and angles (deg): Fe(1)···Fe(2) 3.484(4); Ru(1)···Ru(2) 12.788(5); Ru(3)···Ru(4) 12.738(5); Ru(2)···Ru(3) 18.65(2) Å; Fe(1)-O-Fe(2) 171.5°.

Crystals of **2** were obtained by diffusion of pentane into the toluene solution containing a small amount of dichloromethane.

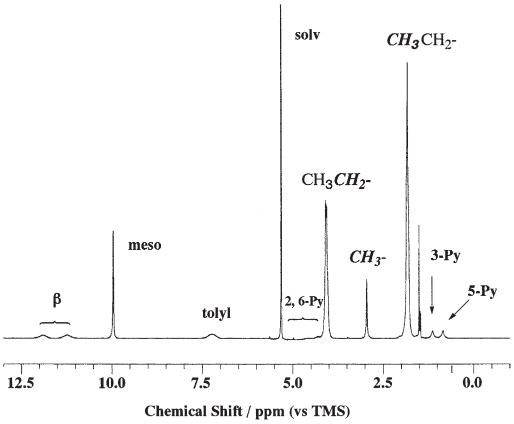

Figure 3. ^{1}H NMR spectrum of $[Ru(OEP)(CO)]_4[Fe($*trans*-4-$Py_2T_2P)]_2O$ (**1**) in CD_2Cl_2 at 18.9°.

The structure of **2** is shown in Figure 2b. Despite the large size of the ruthenium porphyrin units, [Ru1(OEP)(CO)] and [Ru4(OEP)(CO)] are again close to each other. However, in **2**, the smaller value (25.8°) of the twist angle suggests a little larger effect of steric hindrance of the peripheral ruthenium porphyrin units on the geometry.

In spite of the complicated structures in these hexaporphyrins, the UV–vis spectra in solution are offset of the constituent porphyrin units. ^{1}H NMR measurements revealed that these compounds are stable in solution. The ruthenium porphyrin units and the aryl groups gave ^{1}H NMR signals, though the central μ-oxoironporphyrin cores are paramagnetic. In the Ru-OEP hexaporphyrins of **1** and **2**, 3,5- and 2,6-pyridyl proton NMR signals of the μ-oxoiron(III) porphyrin dimer unit are up-field shifted to 0.8–1.4 and 4.3–4.5 ppm, respectively, from the peaks at around 9 ppm in the parent μ-oxo dimers without ruthenium porphyrins, which shows the coordination of the pyridyl groups of μ-oxo dimers to ruthenium porphyrins in solution (Figure 3). The meso-proton signal of ruthenium OEP porphyrin units gives a single peak, which suggests rotation of the ruthenium porphyrin units around the Ru-N(Py) bond. On the other hand, in the TTP ruthenium analog of **4**, each of the β protons and the tolyl protons of the four ruthenium porphyrins gave multiply-split signals at room temperature, suggesting no rotation of ruthenium porphyrin units at room temperature. The different dynamic behavior of **4** from **1** and **2** must result from the larger ring diameter (18.5 Å) of Ru(TTP)(CO) in comparison with Ru(OEP)(CO) (12.7 Å).[10] Detailed study on the behavior of these hexaporphyrins in solution is now underway.

References and Notes

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6 Abbreviations: TTP = 5,10,15,20-tetratolylporphyrinato dianion, OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion, *trans*-4-Py_2T_2P = 5,15-di(4-pyridyl)-10,20-ditolylporphyrinato dianion, *cis*-4-Py_2T_2P = 5,10-di(4-pyridyl)-15,20-ditolylporphyrinato dianion.

7 These hexaporphyrins were constructed from the corresponding ruthenium(II) porphyrin units and μ-oxoiron(III) porphyrin units. **1**: $[Fe($*trans*-4-$Py_2T_2P)]_2O$ (22.6 mg, 0.016 mmol) and Ru(OEP)(CO)(MeOH) (44 mg, 0.063 mmol) were dissolved in 50 mL of toluene and stirring overnight under Ar atmosphere. The solution was evaporated to dryness. The red product was recrystallized from toluene/pentane and washed with cold pentane and dried at 100 °C in vacuo for 3 h (yield : 53 mg, 82%). Anal. Calcd for $C_{236}H_{236}N_{28}O_5Fe_2Ru_4$: C, 69.81; H, 5.86; N, 9.66%. Found: C, 69.82; H, 6.05; N, 9.63%. UV–vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^4\ M^{-1}cm^{-1}$) 394 (95.6), 517 (6.38), 548 (10.3), 616 (1.08). IR (KBr): ν_{CO} 1946 cm^{-1} $\nu_{Fe\text{-}o\text{-}Fe}$ 876 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz): Fe units $H_{\beta\text{-pyrrol}}$ 11.2, 11.9, H_{tolyl} 7.23 (br), H_{py} 0.85, 1.14, 4.32, 4.54, H_{CH3} 2.96, Ru units H_{meso} 9.96, H_{CH2} 4.06, 4.08, H_{CH3} 1.82 ppm. **2**: Yield : 70%. Anal. Calcd for $C_{236}H_{236}N_{28}O_5Fe_2Ru_4$: C, 69.81; H, 5.86; N, 9.66%. Found: C, 69.84; H, 5.93; N, 9.93%. UV–vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^4\ M^{-1}cm^{-1}$): 394 (97.5), 517 (6.08), 549 (9.82), 612 (0.93). IR (KBr): ν_{CO} 1946 cm^{-1} $\nu_{Fe\text{-}o\text{-}Fe}$ 876 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz): Fe units $H_{\beta\text{-pyrrol}}$ 11.3, 12.2, H_{tolyl} 6.5–7.0, 7.34, H_{py} 0.93, 1.41, 4.54 (br),H_{CH3} 2.97, Ru units H_{meso} 10.0, H_{CH2} 4.12, 4.14, H_{CH3} 1.92 ppm. **3**: Yield : 78%. Anal. Calcd for $C_{284}H_{204}N_{28}O_5Fe_2Ru_4$: C, 74.08; H, 4.47; N, 8.52%. Found: C, 73.83; H, 4.60; N, 8.53%. UV–vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^4\ M^{-1}cm^{-1}$): 410 (103), 534 (7.64), 568 (3.85), 609 (1.04). IR (KBr): ν_{CO} 1950 cm^{-1} $\nu_{Fe\text{-}o\text{-}Fe}$ 870 cm^{-1}. **4**: Yield : 88%. Anal. Calcd for $C_{284}H_{204}N_{28}O_5Fe_2Ru_4$: C, 74.08; H, 4.47; N, 8.52%. Found: C, 74.11; H, 4.64; N, 8.61%. UV-vis (CH_2Cl_2) λ_{max}/nm ($\varepsilon/10^4\ M^{-1}cm^{-1}$): 411 (105), 533 (7.35), 567 (3.86), 609 (1.06). IR (KBr): ν_{CO} 1954 cm^{-1} $\nu_{Fe\text{-}o\text{-}Fe}$ 872 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 270 MHz): Fe units $H_{\beta\text{-pyrrol}}$ 11.4, H_{tolyl} 6.5–7.5, H_{py} 1.52, 1.71, 4.97 (br), H_{CH3} 2.80, Ru units $H_{\beta\text{-pyrrol}}$ 8.72, 8.76, H_{tolyl} 7.39, 7.64, 7.93, 8.21, H_{CH3} 2.68, 2.71 ppm.

8 X-ray diffraction data of **1** and **2** were collected on a Mercury CCD area detector with a Rigaku AFC-8S diffractometer using graphite monochromated Mo Kα ($\lambda = 0.7107$ Å) at 123 K. Data were collected and processed using CrystalClear (Rigaku Corp.; Tokyo, 1999). All calculations were performed using a teXan crystallographic software package from Molecular Science Corp. The structures were solved with direct method, successive Fourier and difference Fourier analyses, and refined by full matrix least-squares on F^2. In the crystal of **1**, two ethyl groups in OEP ruthenium porphyrin units (one group in each of Ru2 and Ru4) were disordered and refined isotropically. Other non-hydrogen atoms of hexamer units were refined anisotropically. Crystal solvents were refined with isotropic atomic displacement parameters. Crystallographic data for the *trans*-hexaporphyrin, **1**$\cdot 6C_5H_{12}\cdot 1.33CH_2Cl_2$: $C_{267.33}H_{310.67}N_{28}O_5Fe_2Ru_4Cl_{2.67}$, $M_r = 4606.84$; triclinic, space group P-1, $a = 21.1561(14)$ Å, $b = 26.566(3)$ Å, $c = 26.716(2)$ Å, $\alpha = 114.319\ (3)°$, $\beta = 102.808(4)°$, $\gamma = 93.146\ (7)°$, $V = 13240(2)$ Å^3; $Z = 2$; $D_{calcd} = 1.16$ g cm^{-3}; $\mu = 0.415$ mm^{-1}; 61249 measured reflections, an empirical absorption correction was applied (min./max. transmission factor 0.427/1.01), 48190 unique reflections ($R_{int} = 0.049$), of which 27197 were considered observed ($I > 2\sigma(I)$); $R1 = 0.098$, $wR2 = 0.217$. CCDC reference number CCDC-209045 (**1**). For **2**, ruthenium and iron atoms were refined anisotropically and other non-hydrogen atoms were refined isotropically. The porphyrin ring ligating to the Ru4 atom was disordered at two positions, which prevented the determination of the positions of four ethyl groups of the porphyrin. Electron densities among the oligomer units were assigned to disordered pentane and dichloromethane molecules. Crystallographic data for the *cis*-hexaporphyrin, **2**$\cdot 1.3C_5H_{12}\cdot 0.25CH_2Cl_2$: $C_{242.75}H_{252.1}N_{28}O_5Fe_2Ru_4Cl_{0.5}$, $M_r = 4175.65$; triclinic, space group P-1, $a = 14.637\ (6)$ Å, $b = 21.85\ (2)$ Å, $c = 37.84\ (1)$ Å, $\alpha = 85.944\ (9)°$, $\beta = 84.909\ (19)°$, $\gamma = 82.346\ (17)°$, $V = 11927\ (10)$ Å^3; $Z = 2$; $D_{calcd} = 116$ g cm^{-3}; $\mu = 0.428$ mm^{-1}; 31791 measured reflections, an empirical absorption correction was applied (min./max. transmission factor 0.485/1.091), 26102 unique reflections ($R_{int} = 0.045$), of which 13797 were considered observed ($I > 2\sigma(I)$); $R1 = 0.152$, $wR2 = 0.332$. CCDC reference number CCDC-209046 (**2**).

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