Self-Assembly of Cyclic Ruthenium Porphyrin Tetramer

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A novel cyclic ruthenium porphyrin tetramer was synthesized and characterized by spectral methods.

Recent studies of metalloporphyrin oligomers cover versatile and important fields such as enzymatic catalysts,[1] model systems for photo-induced electron transfer,[2] and interactions of metal centers.[3] A key point to propagate these fields of chemistry is undoubtedly preparation of new porphyrin oligomers. Arylporphyrins having pyridyl groups such as H_2PyP_3P [4] are very attractive species because they act simultaneously as ligands and usual porphyrins to self-assemble or to bridge functional units to build up new oligomers. Hitherto, a ruthenium ternary complex has been prepared by linking two ruthenium porphyrins using trans-$H_2Py_2P_2P$ as a bridging ligand and used to prove coordination aspects in the cavity of polymacrocyclic zinc porphyrins.[5] Another ternary ruthenium porphyrin, Ru(OEP)(H_2PyP_3P)$_2$, was also constructed and showed an intriguing electronic interaction, i.e., metal to ligand charge transfer (MLCT) bands.[6] In addition, the arylporphyrins gave self-assembly of novel square multiporphyrins.[7] However, none of metalloporphyrin oligomers built up by only these arylporphyrins have been discretely synthesized so far. The complex of $ZnPyP_3P$ has only been known to exist in the solid state as long chain polymers and equilibrated in solutions.[8]

In the present study, we aimed to synthesize a discrete vertically linked cyclic ruthenium porphyrin tetramer by introducing ruthenium ions to the parent arylporphyrin of H_2PyP_3P, and succeeded self-assembly of the ruthenium(II) porphyrin tetramer [Ru^{II}(PyP_3P)(CO)]$_4$. The tetramer was synthesized by the reaction of $Ru_3(CO)_{12}$ with H_2PyP_3P [9] and characterized by UV-vis, IR, FAB-MAS, and ^1H NMR spectral measurements and by the reaction with pyridine in solutions. These data confirmed the formation of the cyclic porphyrin tetramer illustrated in Figure 1.

FAB-MAS (matrix : NBA) measurements gave a fragment peak corresponding to the molecular weight of the aimed oligomer [Ru(PyP_3P)(CO)]$_4$ at 2973 (m/z$^+$). Other peaks observed at 2203, 2102, 743, and 716 (m/z$^+$) were ascribed to those of [{Ru(PyP_3P)(CO)}$_2$Ru(PyP_3P)]$^+$, [{Ru(PyP_3P)(CO)}$_2$(PyP_3P)]$^+$, [Ru(PyP_3P)(CO)]$^+$, and [Ru(PyP_3P)]$^+$ respectively. IR (KBr mull) measurements gave the ν(CO) streching at 1955 cm^{-1}.

The ^1H NMR spectrum ($C_6D_5CD_3$, 270 MHz, 25 °C) is consistent with the structure (Figure 2). No inner NH proton signals were observed. The two sets of signals for 2,6- and 3,5-protons of pyridyl groups appeared around 1 ~ 2 and 5 ~ 6 ppm in the magnetic fields significantly higher than those of free H_2PyP_3P at 8.98 and 8.15 ppm respectively.[10] The upfield shifts indicated the coordination by the pyridyl groups to the central metal of ruthenium.[5,8,11] Further, the appearance of four signals of β-protons observed at 6.79 (d, J = 4.95), 8.27 (d, J = 4.95), 8.71 (d, J = 4.95), and 8.83 (d, J = 4.95 Hz) ppm supported the structure of the oligomer shown in Figure 1, i.e., each ruthenium porphyrin units are equivalent. The reason is that the oligomer should give more than five signals of β-protons provided porphyrin units are not equivalent each other like a chain compound of [$ZnPyP_3P$]$_n$.[8] The integrated intensity of those signals for the solutions containing a standard amount of a free porphyrin of H_2TPP confirmed that the number of porphyrin rings constructing the oligomer is 4, i.e., the oligomer synthesized is undoubtedly composed of four ruthenium porphyrin units.

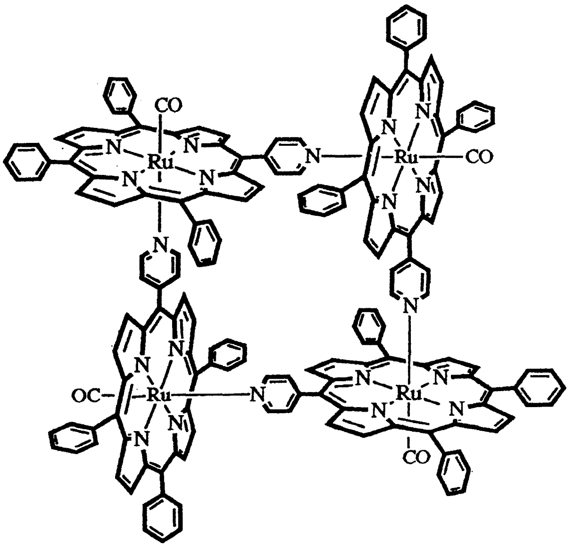

Figure 1. Predicted structure of the new ruthenium porphyrin tetramer [Ru(PyP_3P)(CO)]$_4$.

With temperature rise, the ^1H NMR signals of the pyridyl protons became singlet fashions as shown in Figure 2. Multiple phenyl proton signals observed at 7.38 ~ 7.52 (*m*-,*p*-, m), 7.90 (*o*-, d), 7.97 (*o*-, d), 8.03 (*o*-, d), and 8.40 (*o*-, d) ppm also coalesced. These spectral behavior indicated that the pyridyl and phenyl groups are rotating at high temperatures.[12] However, the chemical shifts due to β-position of the porphyrin rings showed essentially no change against the temperature rise. This results revealed that the framework of the tetramer does not change in the solutions even at high temperatures.

When pyridine (C_5D_5N) was added to the solution by one hundred times in concentration against the tetramer at 25 °C those signals due to β-protons and pyridyl protons diminished with time with concomitant appearance of the signal profile of Ru(PyP_3P)(CO)py in low magnetic fields. This result revealed that the cyclic tetramer cleaved to form a porphyrin monomer of Ru(PyP_3P)(CO)py in the presence of pyridine.

$$[Ru(PyP_3P)(CO)]_4 + 4py \rightarrow 4Ru(PyP_3P)(CO)py \qquad (1)$$

The dichloromethane solution of the tetramer showed a very

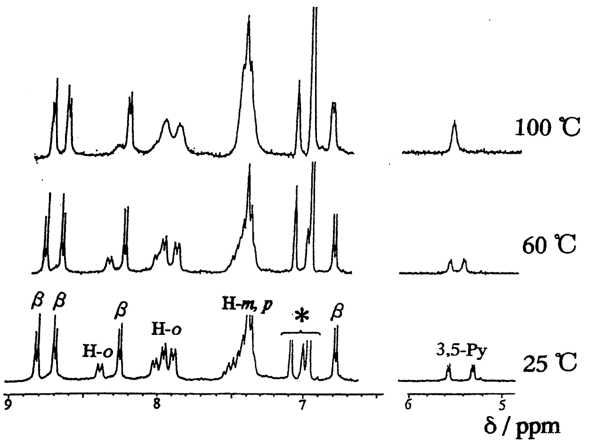

Figure 2. ^{1}H NMR spectra of $[Ru(PyP_3P)(CO)]_4$ in $C_6D_5CD_3$ at variable temperatures. * : solvent.

simple UV-vis spectrum having the bands of λmax/nm (ε/10^4 dm^3 mol^{-1} cm^{-1}) at 412 (78), 532 (6.0), and 569 (sh) as shown in Figure 3. The progress of the reaction of eq.1 by the addition of a small amount of pyridine increased the absorbance at 412 nm of the Soret band without change in those bands. The spectrum of $Ru(PyP_3P)(CO)py$ thus observed is very similar to that of a monomeric complex Ru(TPP)(CO)py with bands at 413 (28) and 532 (1.8) in chloroform.[13] This result supported that the complex synthesized exists as a cyclic tetramer constructed from the same units. Furthermore, in neat dichloromethane the absorptivity and absorption maxima of the tetramer did not change in the concentration range from 1.0×10^{-5} to 1.0×10^{-3} mol dm^{-3}. This revealed that there are no dissociation equilibria in neat dichloromethane.

The study for analogous tetramers composed by ruthenium porphyrin units having different valences each other or by heterometallporphyrins are now in progress.

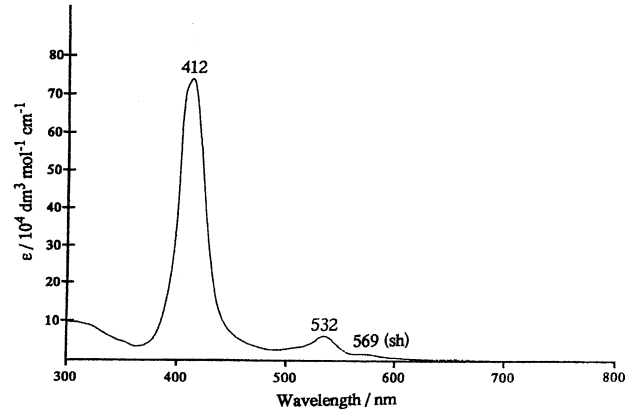

Figure 3. UV-vis spectrum of $[Ru(PyP_3P)(CO)]_4$ in dichloromethane at 25 °C.

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9 $[Ru(PyP_3P)(CO)]_4$: A 200 mg of $Ru_3(CO)_{12}$ and a 200 mg of H_2PyP_3P were dissolved in benzonitrile which was bubbled with argon before use. The solution was refluxed for 12 h and filtered through a sintered glass followed by evaporation to dryness. The resulting solid was dissolved in a small amount of dichloromethane and chromatographed using a silica gel column with dichloromethane as an eluent. The first eluted band was collected and evaporated to dryness. The complex thus obtained was recrystallized from dichloromethane-methanol. The elemental analysis was thoroughly satisfied (yield ; 20%).

10 The signals of 2,6- and 3,5-protons of pyridyl groups observed respectively at 0.91 (d, J = 5.94), 1.91 (d, J = 5.94) and 5.31 (d, J = 5.94), 5.57 (d, J = 5.94 Hz) ppm were grouped to two sets of peaks. Since the meso pyridyl groups might locate perpendicularly to the porphyrin plane of a unit molecule as well as a situation of the meso phenyl groups of the tetraphenylporphyrin, the peaks appeared at 1.91 and 5.57 ppm should be ascribed respectively to the 2,6- and 3,5-protons facing to the outer sphere of the cyclic tetramer. The signals observed in the upfield at 0.91 and 5.31 ppm were ascribed to the 2,6- and 3,5-protons directed toward the center of the tetramer.

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