Electronic Structures of Porphyrinoid Complexes Bearing Paramagnetic Metal Ions

March 2018

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Summary

Recently, novel porphyrinoids of π-conjugated macrocycles such as modified hydroporphyrins (chlorin, bacteriochlorin, and isobacteriochlorin), porphyrin isomers (porphycene, corrole, and *N*-confused porphyrin), and expanded or contracted porphyrins (pentaphyrin and subporphyrin) have been synthesized by employing the exceptional reactions, reagents, and techniques. Although new porphyrinoid complexes containing paramagnetic metal ions attract an interest of many scientists, their investigated data are still insufficient due to the highly complex electron structure and some interaction between paramagnetic ions and/or free-radicals. In this dissertation, as the model compounds of active center in heme proteins, the author synthesized porphyrinoid complexes bearing the paramagnetic metal ions, confirmed the structure by X-ray crystal structure, and investigated the spectroscopic and magnetic properties both in solution and solid states by the UV-Vis, NMR, ESR, Mossbauer spectra, and SQUID measurements.

In first chapter, four-coordinate Ni(II) complex of pyrrolidine-fused pyrrocorphin was prepared by successive 1,3-dipolar cycloaddition reactions of an azomethine ylide to *meso*-tetra(pentafluorophenyl) porphyrin. The addition of excess pyridine to four-coordinate Ni(II) pyrrocorphin complex in toluene solution yielded five-coordinate Ni(II) pyrrocorphin complex with mono-pyridine molecule, which was then converted completely to six-coordinate Ni(II) pyrrocorphin complex with bis-pyridine molecules. The first oxidation potentials of four-coordinate Ni(II) complexes determined by Cyclic Voltammetry in CH_2Cl_2 solution were quite different; they showed a large decrease as the reduction of the porphyrin ring proceeds. In contrast, the first reduction potentials were not so sensitive to the difference in porphyrin structure. Consequently, the HOMO–LUMO gap (ΔE) was the smallest in four-coordinate Ni(II) pyrrocorphin complex, 1.45 V, as compared with Ni(II) porphyrin complex (2.34 V), Ni(II) chlorin complex (2.08 V), and Ni(II) isobacteriochlorin complex (1.88 V). The result was further verified by UV-Vis spectroscopy and DFT calculation. SQUID magnetometry for the microcrystalline sample revealed that six-coordinate Ni(II) pyrrocorphin complex with bis-pyridine molecules was paramagnetic with $S = 1$ spin state between 2 and 300 K. Correspondingly, ^{1}H NMR spectrum showed the *pyrrole* and *pyrroridine β*-proton signals extremely downfield and upfield positions, respectively, supporting the presence of unpaired electrons. Close inspection of the chemical shifts suggested that the spin densities on *pyrrocorphin α*-carbon and nitrogen atoms are quite different as is revealed from the large difference in chemical shifts of the *pyrroridine β*-proton signals at –21.0, –17.5, and –0.93 ppm. UV-Vis and NMR titration experiments have shown that the binding constant of pyridine to six-coordinate Ni(II) pyrrocorphin complex with bis-pyridine molecules is ca. 4 times as large as that of Ni(II) isobacteriochlorin complex. The difference was ascribed to the fact that four-coordinate Ni(II) pyrrocorphin complex has longer a

Fe–N(porphyrin) length than the other three complexes. Thus, the pyridine ligand prefers the electron deficient Ni(II) in six-coordinate Ni(II) pyrrocorphin complex, resulting in the larger binding constant as compared with other three complexes.

In second chapter, as an extension of our work on seeking for the new spin-crossover system, the author have examined the electronic, magnetic, and structural properties of iron(III) *meso*-tetramesitylporphyrin cation complexes $[Fe(TMP)L_2]^+$, *meso*-tetra(perfluorophenyl) porphyrin cation complex $[Fe(TPFPP)L_2]^+$, *meso*-tetraphenylporphyrin cation complex $[Fe(TPP)L_2]^+$, octaethylporphyrin cation complexes $[Fe(OEP)L_2]^+$ *para*- or *meta*-substituted pyridine *N*-oxides (L = 4-XPyNO or 3,5-Me_2PyNO; X = Cl, H, Me, OMe, NMe_2) as axial ligands. Among them, molecular structures of some sample were determined by X-ray crystallography at 100 K. In each complex, the porphyrin ring is almost planar and the iron(III) ion is located within the porphyrin plane perfectly. In the case of a series of $[Fe(TMP)L_2]^+$, stepwise decrease of both Fe-N_P and Fe-O bonds on going from $[Fe(TMP)(4\text{-}ClPyNO)_2]^+$ and $[Fe(TMP)(3,5\text{-}Me_2PyNO)_2]^+$ to $[Fe(TMP)(4\text{-}MePyNO)_2]^+$, and then to $[Fe(TMP)\ (4\text{-}NMe_2PyNO)_2]^+$ indicate the removal of an electron from both $d_{x^2-y^2}$ and d_{z^2} orbitals due to the destabilization of the corresponding d orbitals, which in turn indicates that $[Fe(TMP)(4\text{-}ClPyNO)_2]^+$ adopts the $S = 5/2$ state while $[Fe(TMP)(4\text{-}NMe_2PyNO)_2]^+$ adopt the $S = 1/2$ state at 100 K. In addition, both the average Fe–N_p and Fe–O lengths in $[Fe(TMP)(4\text{-}MePyNO)_2]^+$ have increased by 0.019 and 0.047 Å, respectively, when the temperature is raised to 300 K. As the models for the prosthetic group in heme proteins, structures of six-coordinate $[Fe(OEP)(4\text{-}MePyNO)_2]^+$ and $[Fe(OEP)(4\text{-}NMe_2PyNO)_2]^+$ were confirmed by the single-crystal X-ray analysis. Both the average Fe-N_p and Fe-O lengths are thought to be the cause of the difference of the field strength of axial ligands and the steric hindrance and the electron property of ring-periphery substituents. As the general tendency, the six-coordinate iron(III) porphyrin complexes with neutral oxygen ligands adopt a high-spin state in a wide range of temperature. By using of X-ray crystal structure, SQUID, Mössbauer, ESR, and NMR measurements results, however, the author has found that $[Fe(TPFPP)(4\text{-}NMe_2PyNO)_2]^+$ is the first example of six-coordinated iron(III) porphyrin that adopts the $S = 1/2$ state. Furthermore, some of these complexes have shown spin-crossover phenomenon between high-spin ($S = 5/2$) and low-spin ($S = 1/2$) with a $(d_{xy})^2(d_{xz}, d_{yz})^3$ electron configuration states both in solution and solid states. The difference in the magnetic behaviours in $[Fe(TMP)(4\text{-}NMe_2PyNO)_2]^+$ and $[Fe(TPFPP)(4\text{-}NMe_2PyNO)_2]^+$ as compared with those in $[Fe(TMP)L_2]^+$ (L = 4-XPyNO or 3,5-Me_2PyNO; X = Cl, H, Me, OMe, NMe_2), should be ascribed to the strong electron donating dimethylamino group in the former complexes, which should raise the energy level of the d_{z^2} orbital and consequently stabilize the low-spin state. In addition, the electron withdrawing group at the *meso* positions stabilizes the d_π-type rather than the d_{xy}-type low-spin state. It is expected that the coordination strength of the porphyrin ring is weakened by the electron withdrawing groups at the meso positions. Consequently, the axial coordination should be strengthened, which stabilizes the low-spin state.

In third chapter, the active centers in heme proteins such as cytochrome P450, peroxidase, and catalase have a very important function of electron transfer and enzyme by the difference of axial ligands. When the active site of peroxidase and catalase are activated by peroxides or peracids, they form an oxo iron(IV) porphyrin π-radical cation intermediate called Compound I. It is generally accepted that the diverse functions of compound I are controlled by heme environmental structures, such as porphyrin peripheral structures, heme axial ligands, and protein structures around heme. Therefore, elucidation of the electronic structures in a variety of iron porphyrin complexes as model compounds is quite important to understand the function and catalytic processes of naturally occurring heme proteins. The synthesis and characterization of five-coordinate iron(III) TMP complex with one 4-dimethylaminopyridine *N*-oxide ($4\text{-}NMe_2PyNO$) $[Fe^{III}(TMP)(4\text{-}NMe_2PyNO)]ClO_4$ as the precursor of high-valent oxo iron porphyrins in synthetic model systems were summarized. The molecular structure of five-coordinate iron(III) complex $[Fe^{III}(TMP)(4\text{-}NMe_2PyNO)]ClO_4$ was determined by X-ray crystallography at 100 K. The effective magnetic moments (μ_{eff}) values were showed the high spin $S = 5/2$ state in the range of 2–300 K. ^1H NMR spectrum at 298 K and Curie plots of some proton signals at 183-303 K for five-coordinate $[Fe^{III}TMP(4\text{-}NMe_2\text{-}PyNO)]ClO_4$ were taken in CD_2Cl_2 solution. The assignment of all proton signals was carried out on the basis of the relative integral intensities and the signal widths, which indicated the five-coordinate conformation. Curie plots of some proton signals at 183-303 K exhibited good linearity. The positive slope of pyrrole-H clearly indicates that five-coordinate $[Fe^{III}TMP(4\text{-}NMe_2\text{-}PyNO)]ClO_4$ adopts the high spin $S = 5/2$ state. The ESR spectra in solid and solution states exhibited both of axial type signals, which also indicated that five-coordinate $[Fe^{III}TMP(4\text{-}NMe_2PyNO)]ClO_4$ maintains a pure high spin $S = 5/2$ state. Under the low temperature, the solution of five-coordinate iron(III) porphyrin complex $[Fe^{III}(TMP)(4\text{-}NMe_2PyNO)]ClO_4$ in CH_2Cl_2 changed from the blown color to the green color by the oxidation reaction, resulting in the six-coordinate oxo iron(IV) porphyrin π-radical cation complex. The ESR spectrum of six-coordinate $[O{=}Fe^{IV}(TMP)^{\cdot}(4\text{-}NMe_2PyNO)]ClO_4$ exhibited axial type signals, which was typical of signals of $S = 3/2$ systems. Consequently, The auther confirmed the procedure and the spectroscopic property of six-coordinate oxo iron(IV) porphyrin π-radical cation complex bearing one $4\text{-}NMe_2PyNO$ as the model compound in catalase active center with tyrosine molecule.

Finally, owing to the fruitful development of the synthesis of porphyrinoids, porphyrinoids with paramagnetic properties have gained potent tools to create various types of porphyrin-based materials and to reveal a variety of reactivities and mechanism in heme and chromophore by spectroscopic and magnetic measurements. Consequently, porphyrinoid chemists can now focus on exploring the properties and functions of sophisticated porphyrinoid complexes. The important goal for chemists is to achieve intriguing and useful properties and functions of materials not the synthesis itself. To approach this goal, new design concepts of functional porphyrins are strongly awaited.