V-F Bioinorganic Studies on Structures and Functions of Non-Heme Metalloenzymes Using Model Complexes

Metal-containing enzymes have been widely distributed in both plants and animals and have been related to metabolic processes such as hydroxylation, oxygen transport, oxidative catalysis, electron transfer, and so on. In this project, their structural/functional models have been originally constructed and studied using physico-chemical methods.

V-F-1 Novel Phosphate Bond Formation in a Cobalt(III) Complex System

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[*Inorg. Chem.* submitted]

Reaction of an aqueous solution (pH 3) of $[Co^{III}(tpa)(CO_3)]Cl$ (**1**) (tpa = tris(2-pyridylmethyl)amine) with 2 equiv. of an active phosphate ester, disodium 4-nitrophenylphosphate (NPP), in the presence of a catalytic amount of active charcoal at 60 °C gave $[Co^{III}(tpa)(PO_4)]$ (**2**) (7.8% yield) and $[\{Co^{III}(tpa)\}_2(\mu\text{-}P_2O_7)]Cl_2$ (**3**) (50.7% yield). The structures of **2** and **3** were determined by X-ray crystallography. Complex **3** has a novel molecular structure with ligation of the two Co(III) centers *via* an NPP-derived bridging-diphosphate. The phosphate bond formation does not occur without active charcoal or under conditions of neutral pH. A proposed reaction mechanism involves initiation by hydrolysis of NPP to give **2** with the phosphate bond formed as an intermediate dimer structure.

V-F-2 Syntheses and Structures of Tetrakis(1-methyluracilato)palladium Complexes Capturing Alkali Metal Ions. A New Type of Metallo-Podand

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[*Inorg. Chim. Acta* in press]

Four tetrakis(1-methyluracilato)palladium complexes containing alkali metal ions, $[Li_2Pd(1\text{-}MeU^-)_4]$ (**1**), $[Na_2Pd(1\text{-}MeU^-)_4]$ (**2**), $[K_2Pd(1\text{-}MeU^-)_4]$ (**3**), and $[Cs_2Pd(1\text{-}MeU^-)_4]$ (**4**), have been prepared from M_2PdCl_4 ($M = Li^+, Na^+, K^+$, and Cs^+) and four equivalents of 1-methyluracil (1-MeUH). The X-ray crystal structure analyses of complexes **2**, **3** and **4** have revealed that each palladium atom is coordinated in a square-planar geometry with four 1-MeUH-derived N3-deprotonated imidato groups, upright-oriented with angles of 60 ~ 70° from the basal coordination plane. Interestingly, the carbonyl groups of the four imidato rings form two cavities above and below the Pd(II) atom, and two alkali metal ions are incorporated with Pd–*M* distances of 3.007(4) and 3.137(3) Å for **2**, 3.432(3) and 3.594(3) Å for **3**, and 3.746(1) and 3.999(1) Å for **4**, respectively. The cavity sizes of the three complexes are tunable according to the ionic radii of the alkali metal ions. ^1H-NMR spectra of complexes **1–4** indicate that all proton signals of the $1\text{-}MeU^-$ moiety shifted upfield relative to those of free $1\text{-}MeU^-$. The magnitude of the up-field shifts, **1** < **2** < **3** < **4**, corresponds well to the order of the ionic potentials of alkali metal ions. These up-field shifts are reduced by coordination of 5-fluoro-1-methyluracil in place of 1-MeUH, indicating that the electron-donating character of $1\text{-}MeU^-$ to Pd(II) is decreased by substitution with an electron-withdrawing fluoro group. These observations suggest that the up-field shifts may be rationalized in terms of π-back donation from Pd(II) $d\pi$-orbital to imidato π^*-orbital and the ionic potentials of alkali metals, which have also been investigated on the basis of the DFT calculation. On the basis of these characteristic features, the $[M_2Pd(1\text{-}MeU)_4]$ complexes may be classified as a new type of metallo-podand that captures alkali metal ions.

V-F-3 Investigations of the Effects of Intramolecular Hydrogen Bonding Networks on Tripodal Trihydroxamate-Type Artificial Siderophores

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[*Inorg. Chem.* submitted]

The solution behavior of the iron(III) complex with tris[2-{(*N*-acetyl-*N*-hydroxy)glycylamino}ethyl]amine (TAGE) has been investigated using ^1H NMR, UV-vis, and FAB mass spectroscopies and cyclic voltammetry in efforts to characterize the hydrogen bonding networks between the amide hydrogens and coordinating aminohydroxy oxygens of the complex. Temperature dependencies of ^1H-NMR spectra for Al(III) and Ga(III) complexes of TAGE indicate that hydrogen bonding networks are maintained even in polar solvents such as DMSO-d_6 and D_2O. The UV-vis spectra of the Fe(III)-TAGE complex in various pH conditions show that TAGE forms a tris(hydroxamato)iron(III) complex in an aqueous solution from pH 4–8. On the other hand, tris[2-{(*N*-acetyl-*N*-hydroxy)propylamido}ethyl]amine (TAPE; a TAGE analogue that does not form hydrogen bonds), does not form the tris(hydroxamato)iron(III) complex in the same pH range. Both the stability constant ($\log\beta_{FeTAGE} = 28.6$; $\beta_{FeTAGE} = [Fe^{III}TAGE]/$-

($[Fe^{3+}][TAGE^{3-}]$)) and pM (–log$[Fe^{3+}]$) value for Fe^{III}TAGE (pM 25) are comparable to those of ferrichrome, a natural siderophore (logβ = 29.1 and pM 25.2). The rate of the ligand exchange reaction between Fe^{III}TAGE and EDTA is 6.7×10^{-4} s^{-1}, a rate similar to those of the ferrichromes. The redox potential of Fe^{III}TAGE in aqueous solution is –227 mV (*vs.* NHE) at pH 7, about 200 mV higher than those of Fe^{III}TAPE and ferric natural trihydroxamates. The high redox potential of Fe^{III}TAGE is interpreted in terms of the intramolecular hydrogen bonding networks wherein both iron(III) and iron(II) complexes are tightly fixed and stabilized by the TAGE ligand. In a biological activity experiment, TAGE promotes the growth of the siderophore-auxotroph gram-positive bacterium *Microbacterium flavescens*, and thus mimics the activity of ferrichrome. These results indicate that the artificial siderophore TAGE is a good structural and functional model for ferrichrome and that the intramolecular hydrogen bonding networks provide stability for the complex and allow the redox potential to increase even in an aqueous solution.

V-F-4 The Role of the Zn(II) Site in Cu,Zn SOD (1). Synthesis and Characterization of Novel Hydroperoxo-Zinc(II) Intermediates

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[*J. Amer. Chem. Soc.* Submitted]

A novel Zn–OOH species has been prepared using an original ligand bis(6-neopentylamino-2-pyridylmethyl)(2-pyridylmethyl)amine (H_2BNPA), whose synthesis was determined by ^{1}H-NMR and ESI-mass spectroscopic methods. The formation of $[Zn(H_2BNPA)(OOH)]^+$ has been confirmed from the ESI-mass spectral measurements of the reactions of $[Zn(H_2BNPA)(OH)]^+$ with H_2O_2 and subsequent addition of CO_2 as well as the X-ray structure of the product crystal obtained from the reaction solution kept at 0 °C under CO_2, $[\{Zn(H_2BNPA)\}_2(CO_4{}^{2-})]^{2+}$. Comparisons of the reactivities of Zn(II)–OOH and Cu(II)–OOH species toward CO_2 have suggested that the hydroperoxide bound to Zn(II) ion exhibits a higher nucleophilicity/basicity than that of hydroperoxide bound to Cu(II). This implies that in the 2nd half of the reaction cycle of Cu,Zn SOD, the transformation of hydroperoxide to hydrogen peroxide tends to proceed within the coordination sphere of Zn(II) site instead of within the coordination sphere of Cu(II).

V-F-5 Epoxidation Activities of Mononuclear Ruthenium-oxo Complexes with a Square Planar 6,6'-Bis(benzoylamino)-2,2'-bipyridine and Axial Ligands

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[*Tetrahedron Lett.* **43**, 1491 (2002)]

Some ruthenium complexes with a square planar ligand, H_2BABP, ($[Ru^{II}(babp^{2-})(dmso)_2]$ (**1**), $[Ru^{II}(babp^{2-})(dmso)(im)]$ (**2**), $[Ru^{II}(babp^{2-})(dmso)\text{-}(py)]$ (**3**), and $[Ru^{II}(babp^{2-})(dmso)(Phpy)]$ (**4**)) have been prepared as a catalyst of oxygen transfer reaction. Catalytic activity of the metal-oxo species derived by the reaction of **1** ~ **4** with PhIO has been affected by the axial ligands of the complexes, whose oxidation active species has been interpreted in terms of contribution of both characters of Ru(V)=O and Ru(IV)–O·.

V-F-6 Reactivity of Hydroperoxide Bound to a Mononuclear Non-Heme Iron Site

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[*Inorg. Chem.* **41**, 616 (2002)]

The first isolation and spectroscopic characterization of the mononuclear hydroperoxo-iron(III) complex, $[Fe(bppa)(OOH)]^{2+}$ (**2**), and the stoichiometric oxidation of substrates by the mononuclear iron-oxo intermediate generated by its decomposition have been described. The purple species **2** obtained from reaction of $[Fe(bppa)(HCOO)](ClO_4)_2$ with H_2O_2 in acetone solution at –50 °C gave characteristic UV-vis (λ_{max} = 568 nm, ε = 1200 M^{-1} cm^{-1}), ESR (g = 7.54, 5.78 and 4.25 S = 5/2), and ESI mass spectra (m/z = 288.5 corresponding to the ion, $[Fe(bppa)(OOH)]^{2+}$), which revealed that the complex **2** is a high-spin mononuclear iron(III) complex with a hydroperoxide in an end-on fashion. The resonance Raman spectrum of **2** in d_6-acetone revealed two intense bands at 621 and 830 cm^{-1}, in which the former band shifted to 599 cm^{-1} when reacted with ^{18}O-labeled H_2O_2 and the latter band showed a small isotope shift to 813 and 826 cm^{-1} upon reaction with of $H_2{}^{18}O_2$ and D_2O_2, respectively. Reactions of the isolated (bppa)Fe^{III}–OOH (**2**) with various substrates (single turnover oxidations) exhibited that the iron-oxo intermediate generated by decomposion of complex **2** is a nucleophilic species formulated as [(bppa)Fe^{III}–O·].

V-F-7 Reactivity Control for Epoxidation of Olefins and Dehydrogenation of Alcohols Catalyzed by Ruthenium-oxo Complexes

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[*Shokubai* **43**, 440 (2001)]

Several ruthenium complexes with tripodal polypyridine or diamidobipyridine ligands were prepared for investigation of catalytic activity on the oxygen transfer reactions. Ruthenium(V)-oxo species generated through the reaction of low-valent ruthenium complex and PhIO was observed in the ESI-mass spectroscopy. Their catalytic activities for epoxidation of olefins, hydroxylation of alkanes and dehydrogenation of alcohols were affected by the coordination environment and redox property of the starting ruthenium complexes. These findings are explained by the hypothesis as follows: Ruthenium-oxo species generated on the complexes with non-porphine ligands show both characters of Ru(V)=O and Ru(IV)–O·. The former intermediate favors epoxidation pathway and the latter radical one.

V-F-8 Crystal Structure and Solution Behavior of the Iron(III) Complex of the Artificial Trihydroxamate Siderophore with Tris(3-aminopropyl)amine Backbone

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[*Eur. J. Inorg. Chem.* **10**, 2481 (2001)]

Microorganisms produce low molecular weight compounds called siderophores for an uptake of iron. A large number of siderophores have hydroxamates or catecholates as the iron binding site that exhibits very high affinity for iron(III) ion, and their siderophores form very stable iron(III) complexes. The high stability of Fe(III)-siderophore complexes is attributed to not only such chelating effect but also hydrogen bonding and van der Waals interactions and predisposition of ligands. Thus, the ligand backbones are quite important for the stabilization of iron(III) complexes. Many tripodal artificial siderophores were synthesized as ferrichrome and enterobactin analogues; the synthetic siderophores adopt various tripodal backbones as follows, *e.g.*, tris(2-aminoethyl)amine (TREN), tri-aminomethylbenzene, 1,5,9-triazacyclododecane, nitrilotriacetic acid, 1,1,1-tris{(2-carboxyethoxy)-methyl}propane. Among such tripodal backbones, TREN has been frequently used. Recently, we also have reported the synthesis of tris[2-{(N-acetyl-N-hydroxy)-glycylamino}ethyl] amine (TAGE) as the artificial siderophore with TREN anchor, whose iron(III) complex showed extremely high stability ($\log\beta = 28.7$). From the crystal structure of the iron(III) complex, this higher stability was revealed to be attributed to the intramolecular hydrogen bonding networks. However, the tripodal anchors such as TREN have been reported to make reduce the stability of iron(III) complexes than the natural siderophore-iron (III) complexes, which are presumed to be due to the small size of the anchor for an iron(III) chelation. On the other hand, tris(3-aminopropyl)amine (TRPN), whose alkyl chains are one methylene longer than TREN, has not been much used, and the details are little described, despite the similarity in these structures. At this stage, we newly synthesized tris[{3-(N-acetyl-N-hydroxy)-glycylamino}propyl]-amine (TAGP, Figure 1) as a trihydroxamate artificial siderophore with TRPN anchor in order to examine the efficiency of the size. Tris[{3-(N-acetyl-N-hydroxy)-glycylamino}propyl]amine (TAGP) forms the 1 : 1 tris(hydroxamato)-iron(III) complex even at a low pH (~2), which promotes the growth of the siderophore-auxotrophic mutant *Microbacterium flavescens*. Here, we described the crystal structure and solution behavior of its iron(III) complex.

V-F-9 Reverse Reactivity in Hydroxylation of Adamantane and Epoxidation of Cyclohexene Catalyzed by the Mononuclear Ruthenium-oxo Complexes with 6-Substituted Tripodal Polypyridine Ligands

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[*Tetrahedron Lett.* **42**, 3467 (2001)]

The electronic character of the ruthenium complexes with tripodal polypyridine ligands, which is controlled by the substituted groups at pyridine 6-position, gives rise to differences in the reactivity for the ruthenium catalyzed hydroxylation of adamantane and epoxidation of cyclohexene with PhIO as an oxidant; Ru complexes containing electron-withdrawing groups promote the epoxidation, while those containing electron-donating groups promote the hydroxylation.

V-F-10 Characterization of an NH-π Interaction in Co(III) Ternary Complexes with Aromatic Amino Acids

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[*Inorg. Chem.* **40**, 3936 (2001)]

The NH-π interaction has been detected in the crystal structures of Co(III) ternary complexes with N,N-bis(carboxymethyl)-(*S*)-phenylalanine (BCMPA) and aromatic amino acids including: (*S*)-phenylalanine ((*S*)-Phe), (*R*)-phenylalanine ((*R*)-Phe), and (*S*)-tryptophan ((*S*)-Trp)). Additionally, this interaction has been studied in solution for Co(III) ternary complexes with BCMPA or NTA (NTA = nitrilotriacetic acid) and several amino acids (AA) by means of electronic absorption, circular dichroism (CD), and ^{1}H NMR spectroscopies. The CD intensities of the Co(III) complexes with aromatic amino acids measured in the *d-d* region (~ 20.5×10^3 cm^{-1}) are significantly decreased in ethanol solutions relative to water. Analogous complexes with aliphatic amino acids do not exhibit this solvent effect. The ^{1}H NMR spectra of the Co(III) complexes with aromatic amino acids measured in DMSO-d_6 and D_2O exhibit up-field shifts of the N–H peaks compared with those with aliphatic amino acids for both cases, which suggest a shielding effect due to the aromaticity. The up-shift values coincide with those experimentally evaluated from the crystal structures. The magnitude of the upfield shifts observed in DMSO-d_6 agrees well with Hammett's rule and similar tendency is slightly characterized also in D_2O, indicating that the increase of π-electron densities on the aromatic rings exerts a larger shielding effect for the NH protons and it is reduced in aqueous solution. In ligand-substitution reactions of the carbonatocobalt(III) complexes with amino acids, the yields of those with aromatic amino acids are higher than the yields obtained for complexes with aliphatic amino acids. This observation is discussed in connection with the important contribution of the NH-π interaction as one of the promotion factors in the reaction.

V-F-11 The Role of the Zn(II) Site in Cu,Zn SOD. (2) Evidence of Superoxide Disproportionation Catalyzed by Sterically- and Electrostatically-Controlled Zinc(II) Complexes

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[*J. Amer. Chem. Soc.* submitted]

The role of the Zn(II) site in the disproportionation reaction of superoxide catalyzed by Cu,Zn superoxide dismutase (Cu,Zn SOD) has been systematically examined using sterically- and electrostatically-controlled Zn(II) complexes in an aprotic solvent (MeCN/-DMSO (9:1)) by cyclic voltammetry, ESI-mass spectroscopy and ESR spectroscopy. Interestingly, higher SOD activity was observed in the Zn(II) complexes with lower Lewis acidity and in Zn(II) complexes without a superoxide-accessible site. These findings clearly indicate that the efficient catalytic SOD reaction is due to efficient access of superoxide to the Zn(II) ion. Here we offer a new proposal for the role of Zn(II) site in Cu, Zn SOD and propose an alternate mechanism for the 2nd step of SOD reaction.

V-F-12 SOD Activities of the Copper Complexes with Tripodal Polypyridylamine Ligands Having a Hydrogen Bonding Site

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[*Inorg. Chim. Acta* **324**, 108 (2001)]

For investigation of the correlation with the coordination structures of the copper complexes and their superoxide dismutation activities, four mononuclear copper complexes with tris(2-pyridylmethyl)-amine derivatives containing pivalamido or neopentylamino groups at pyridine 6-position, [Cu(tnpa)(OH)]-ClO_4 (**1**), [Cu(tapa)Cl]ClO_4 (**2**), [Cu(tapa)(OH)}ClO_4 (**3**), and [Cu(bppa)]$(ClO_4)_2$ (**4**), and two dinuclear copper complexes, $[Cu_2(tppen)(H_2O)_2](ClO_4)_2$ (**5**) and $[Cu_2(tppen)Cl_4]$ (**6**), were prepared as single crystals suitable for X-ray analysis except the complex **3**. Such hydrogen bonding moiety at pyridine 6-position of these ligands is regarded as a Arg 141 residue around copper site in native bovine superoxide dismutase (SOD). Coordination geometry around copper ion in **1** ~ **3**, **5**, and **6** was determined to have 5-coordinate trigonal bipyramidal or square pyramidal structure both in crystal and solution phases on the basis of their X-ray analyses or spectroscopic results. However, that in **4** was 4-coordinate square planar structure. The redox potentials of the mononuclear complexes, **1** ~ **4**, (Cu(II)/Cu(I) couple) were within the range between -330 mV (*vs*. NHE at pH 7. $O_2/O_2^{\bullet -}$) and + 890 mV (*vs* NHE. $O_2^{\bullet -}/H_2O_2$), which were in good range for superoxide dismutation, so that these complexes were used for investigating their catalytic activity. Moderate dismutation activities were demonstrated in the cases of **1** ~ **3** in comparison with other mononuclear copper complexes previously reported, although **4** showed the lowest activity of all. The distorted structure around copper center, such as 5-coordinate trigonal bipyramidal or square pyramidal structure, is important for demonstrating SOD activity. In addition, the activities caused by the dinuclear complex, **5** and **6**, were higher than those by the mononuclear ones. 6-Neopentylamino or 6-amino group of the tripodal polypyridine ligands, which is designed as a hydrogen bonding moiety, plays an important role for acceleration of activity in the SOD mimics through stabilization of superoxide species binding to the metal center.

V-F-13 Site-Selective Recognition of Amino Acids by Co(III) Complexes Containing a $(N)(O)_3$-Type Tripodal Tetradentate Ligand

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[*Bull. Chem. Soc. Jpn.* **74**, 1035 (2001)]

The bis-*N*,*N*-carboxymethy-(*S*)-phenylalaninato carbonato cobalt(III) complex, $[Co(bcmpa)(CO_3)]^{2-}$, has been prepared as a simple model that enables the recognition of an amino acid (Haa) whose coordination behaviours in solution have been characterized by electronic absorption (AB), circular dichroism (CD) and ^{1}H-NMR spectroscopies. The reaction of the $K_2[Co(bcmpa)(CO_3)]$ complex with amino acids (Haa) has predominantly afforded the [Co(bcmpa)(aa)] complex in the *trans*(*N*)-configuration mode, rather than in the *cis*(*N*)-form. By using amino acid derivatives with bulky substituents at their amino or carboxylate sites under a neutral condition, the reactions have been demonstrated to be initiated by coordination of the amino nitrogen site. Interestingly, the *cis*(*N*)-complex, which is isolated as a minor product, isomerizes to the *trans*(*N*)-form in the presence of active charcoal under pH 7 in an aqueous solution. The site-selective coordination of Haa to the $[Co(bcmpa)(CO_3)]^{2-}$ complex and the stereoselective isomerization of the $[Co(bcmpa)(aa)]^-$ complex have been explained to be regulated by weak non-covalent interactions within the ligands, whose origin has been discussed based on a detailed examination of the crystal structures of the *trans*(*N*)- and *cis*(*N*)-K[Co(bcmpa)(aa)] complexes.