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Oxidation chemistry of group 10 metal diphenoxide complexes

hemistry of redox active transition metal complexes with pro-radical ligands and their detailed electronic structures have been actively pursued in recent years. An "experimental" valence state in metal complexes is sometime different from the "formal" oxidation state, especially in the species having redox active ligands. This difference can be also seen in biological system, such as iron(IV)-porphyrin π -cation radical in some heme proteins and copper(II)-phenoxyl radical in galactose oxidase (GO). Many efforts for determination of the experimental oxidation number have been close to the goal of the "truth oxidation state" in various oxidized metal complexes with redox-active ligands. Depending on the relative energies of the redoxactive orbitals, metal complexes with the redox active ligands exist in two limiting descriptions, either a metal-ligand radical $(M^{n+}(L^{\cdot}))$ or a high valent metal $(M^{(n+1)}+(L^{-}))$ complex. The reaction mechanisms of artificial and biological catalysts depend on the electronic structures of the high valent intermediates. However, geometric and electronic structural characterizations of the high valent species have been rare due to their stability. Recently, some artificial metal-phenoxyl radical complexes as models of GO have been synthesized and successfully characterized by X-ray crystal structure. The one-electron oxidized metal-phenolate complexes showed various electronic structures depending on small perturbations, such as substitution of the phenolate ring and the chelate effect of the phenolate ligands and so on. In this presentation, I will focus on X-ray crystal structures of the oneand two-electron oxidized metal(II)-phenolate complexes (Ni(II), Pd(II), Pt(II) and Cu(II)) with Schiff base ligands of 2N,O donor sets. Especially electronic and geometric structure relationship such as differences of metal-phenoxyl radical and highvalent metal phenolate complexes, and the effect of different oxidation locus of the radical electron on the ligands in oxidized forms will be discussed ...

Biography

Yuichi Shimazaki has received his Doctorate degree in Science from Nagoya University in 2000 under the supervision of Professor Osamu Yamauchi. He joined Professor Yoshinori Naruta's group at Kyushu University as Assistant Professor and worked on the redox behavior of various metal porphyrin complexes as models of the active site of metalloenzymes. In 2008, he was promoted to Associate Professor at the College of Science, Ibaraki University. His research interests include the oxidation chemistry of the complexes of various metal ions, model studies of metalloenzymes, bioorganometallic chemistry, and weak interactions in metal-organic molecule systems.

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