

Syntheses, Characterization, and Reactivity of Co(III) Complexes with N2S3 Coordination Environment: As Models for Co-Containing Nitrile Hydratase

Satoshi Fujii, Shozo Kitamura, and Hiroshi Sakai

Department of Chemistry, Faculty of Science and Engineering, Konan University.

Cobalt-containing nitrile hydratases (NHases) are bacterial metalloenzymes that catalyze the hydrolysis of nitriles to their corresponding amides. Their active site has an unusual coordination environment that consists of two amide nitrogen atoms provided by the main chain of peptide and three sulfur atoms from cysteine residues. In addition, two of the metal-bound sulfur atoms are post-translationally modified to sulfenate and sulfinate groups.

To clarify how such unusual coordination environment affect the electronic state of Co(III) center and the reactivity, we have synthesized three ligands that afford two carboxamido nitrogen and three thiols (Figure). Co(III) complexes with these ligands and two thiol-oxidized $L\{Et(SO_2)\}$ were prepared and investigated by UV-Vis absorption, FT-IR spectroscopy and cyclic voltammetry. UV-Vis titration clearly showed water can bind the vacant sixth site of $[Co(III)L(Et)]^-$ (**1**) and $[Co(III)L\{Et(SO_2)\}]^-$ (**2**) with $pK_a = 7.2$ and 6.0 , respectively. Catalytic activity study showed that the activity of **1** is higher than that of **2**. Correlation between electronic state of Co(III) center and reactivity will be discussed.

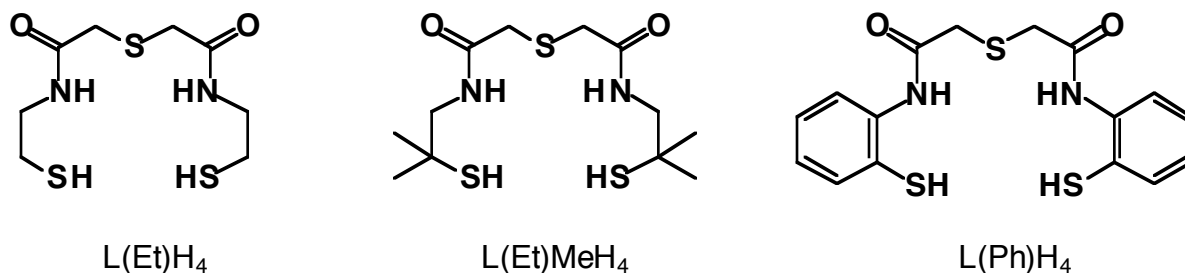


Figure Ligands synthesized