

Solvent Effect of Co(III) Complexes with N₂S₂-type Ligands as Co(III)-type Nitrily Hydratase Model: Biological Implication of Hydrogen Bonding Interaction of Amide Carbonyl Oxygens of the Active Site with water molecules.

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Nitrile Hydratase (NHase) catalyzes the hydration of nitrile compounds to the corresponding amides. Recent X-ray analyses for the NHases revealed that two deprotonated amide nitrogens and three cystein sulfurs coordinated to a Fe(III) or a Co(III) center. Interestingly, three sulfurs were in different oxidation states (a thiolate, a sulfenate, and a sulfinate), as shown in Fig. 1. The relationship with the hydration mechanism and the unique coordination feature has been remained unknown.

Recent studies using mutants of NHases have demonstrated that interactions of coordinated functional groups with the second coordination sphere are one of the most important factors for the NHase activity.¹⁾ Therefore, we prepared Co(III) complexes of an N₂S₂-type ligand (H₂L) with amide groups in order to understand the influence to the metal center.

A Co(III) complex with H₂L (**1**) showed a square planar structure as schematically depicted in Fig. 2. Addition of ⁴BuNC into a solution including **1** afforded an octahedral complex. The formation equilibrium interestingly depended on the solvent. Solvent dependence of the equilibrium constant, redox potentials, and IR spectra of **1** indicated that the attractive interaction of amide carbonyl oxygens with solvent molecules increased the Lewis acidity of the Co(III) ion. We also prepared Co(III) complexes with oxidized sulfur atoms, and will discuss the interaction of the oxygen atoms on sulfurs with solvent molecules.

1) For example: Endo, I. et al. *J. Inorg. Biochem.*, **2000**, *80*, 283-288; Fushinobu, S. et al. *Eur. J. Biochem.*, **2004**, *271*, 429-438.

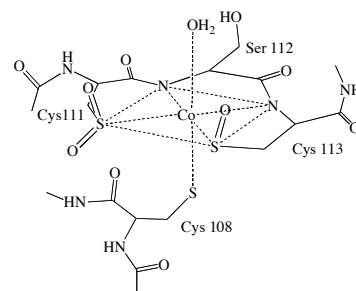


Fig. 1. Schematic structure of Co-type NHase.

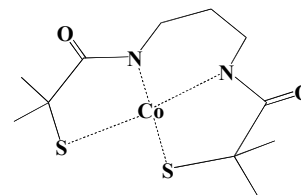


Fig. 2. Schematic structure of a [Co(H₂L)]⁻ anion (**1**).