A Tricopper Complex Supported by a Cage-type Ligand as a Biomimetic Model for Thiocyanate Dehydrogenase

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A copper-containing enzyme, thiocyanate dehydrogenase (TcDH) found from the haloalkaliphilic sulfur-oxidizing bacterium is able to catalyze two-electron oxidation of thiocyanate ion providing cyanate ion and elemental sulfur under ambient conditions.[1] The active center of TcDH contains three copper centers in a triangle configuration, and a proposed mechanism exhibited that the tricopper center works cooperatively to assist nucleophilic attack of hydroxide ion to thiocyanate ion resulting in C-S bond cleavage. While examples of syntheses and reactions of artificial biomimetic models for the active sites of enzymes containing tricopper centers are still limited, we have successfully synthesized a trinuclear copper complex **1** (Figure 1, left) by using a cage-type ligand. In this study, we utilized the complex **1** as a model complex of TcDH, and examined the reactions with thiocyanate ion.

Depending on equivalents of potassium thiocyanate to be added, the solutions of complex **1** were found to show different behavior in UV-Vis absorption. When the ratio of complex to substrate was 1:1 or 1:2, the UV-Vis spectral change showed two isosbestic points, indicating at least two-step reactions. Because of difficulty in crystallization of the reaction intermediate, we examined independent synthesis by treatment of $Cu(ClO_4)_2 \cdot 6H_2O$ with KSCN with addition of the cage-type ligand. Consequently, we successfully obtained the complex **2** (Figure 1, right) as large green crystals. X-ray crystallography showed that the complex **2** contains two thiocyanate ligands and one of these ligands is bridging between two copper centers. By comparing the UV-Vis spectra, we confirmed that the complex **2** would be the reaction intermediate observed in the above tracing experiment.

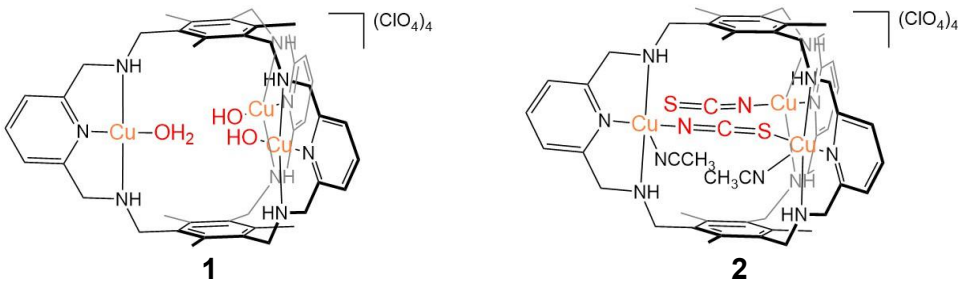

Figure 1. Structures of the tricopper complexes **1** and **2**.

1) Tamara, V. T. *et al.*, *PNAS*, **2020,** *117,* 5280-5290.