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Coordination and photoisomerizaiton of Azobenzene-amino acid Schiff base copper(II) complexes to lysozyme

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We exhibited an amino acid (arginine and threonine) derivative Schiff base copper(II) complexes incorporating photochromic azobenzene moiety as a photoresponsive site and conjugates it to egg white lysozyme. Spectroscopic and crystallographic facts showed that the nitrogen atom of the amino acid residue of lysozyme bound to the paramagnetic copper(II) ion of the complex, and UV light irradiation confirmed photoisomerization of the ligand to cis-form.

1 Introduction

Azobenzene is one of the most famous photocromic dyes due to its high quantum yield, stability, and ease of synthesis and derivatization. Since the wavelength of photoisomeriza-tion is in the ultraviolet-visible (UV-vis) region (E → Z: 380 nm, Z → E: > 400 nm). In this study, by incorporating an azobenzene moiety into the ligand as a photoresponsive site into a Schiff base copper(II) complex containing an amino acid, the photo-responsiveness and switching of a protein (egg white lysozyme) was investigated with spectroscopic as well as crystallographic measurements.

2 Experiment

For example, azobenzene-salicylaldehyde [1] (226 mg, 1.00 mmol) and L-threonine (or other amio acids) (119 mg, 1.00 mmol) were dissolved in methanol (100 mL) and stirred at 313 K for 1.5 hr to give a red solution. Copper(II) acetate-hydrate (199 mg, 1.00 mmol) was added and stirred for 1 hr, and imidazole (68 mg, 1.0 mmol) was added and stirred for another hour to give a dark green solution. The reaction solution was allowed to stand at 298 K for 4 days to obtain green needle crystals. Commercially available chicken egg white lysozyme was used. After adjusting phosphate buffer solutions of copper(II) complexes and Lysozyme, we confirmed conventional spectra and grown the binding single crystals [2]. X-ray crystallography was carried out at KEK-PF BL-5A

3 Results and Discussion

Spectroscopically, absorption wavelength corresponding to the d-d transition of copper in a copper(II) complex shifts from 666 nm to 652 nm as the lysozyme concentration increases, short-wavelength shift similar to a copper(II) complex. This indicates that the copper(II) ion of a copper(II) complex is bound to the imidazole group of the histidine (or nitrogen atom containing) residue of lysozyme. Single crystals were grown in a conventional way (Fig. 1), though most of them were binging copper(II) ions only. However, crystallographic verification of binding features are under analyzing at present (Fig. 2), therefore, experimental details of the coordination geometry of a copper(II) complex will be presented elsewhere soon.

References

[1] K. Kashiwagi and T. Akitsu *et al.*, *Symmetry.* **12**, 808 (2020).
[2] T. Akitsu and M. Unno *et al.*, *Key Engineering Materials* **888**, 105 (2021).

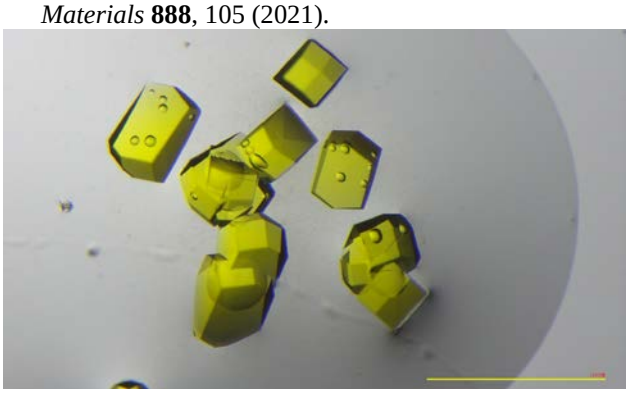

Fig. 1: Pale yellow single crystals of lysozyme containing a copper(II) complex.

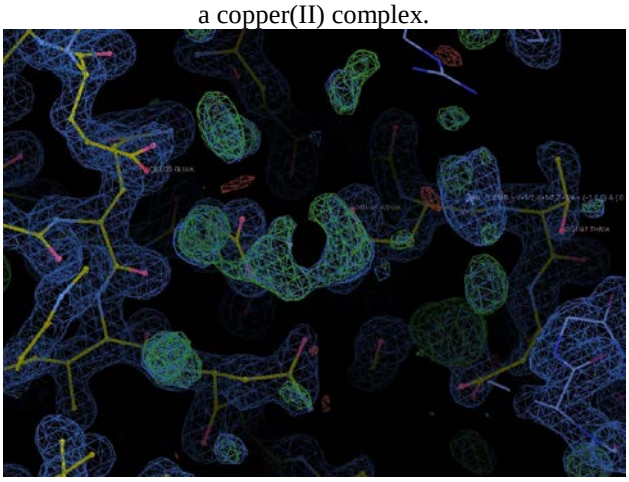

Fig. 2: Electron density of crystals of lysozyme including a copper(II) complex.

Research Achievements

1. We obtained pale yellow single crystals of lysozyme containing a copper(II) complex.
2. We could have confirmed that electron density suggested as the whole copper(II) complex or copper(II) ion in lysozyme under a certain condition.

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