

Proposed Mechanism of Photo-Induced Reactions of Chiral Threonine Schiff Base Cu(II) Complexes with Imidazole by TiO₂

Makiha Kurata, Naoki Yoshida, Saori Fukunaga and Takashiro Akitsu*

Department of Chemistry, Faculty of Science, Tokyo University of Science
1-3 Kagurazaka, Shunjuku-ku, Tokyo 162-8601, Japan
* akitsu@rs.kagu.tus.ac.jp

Copyright © Makiha Kurata et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Abstract. We prepared hybrid systems of chiral Schiff base Cu(II) complexes incorporating threonine derivatives Schiff base and micro particles of TiO₂. Under N₂ atmosphere, it has been known UV light irradiation resulting in photo-induced reduction reaction of Cu(II) species to Cu(I) ones. In this study, we have investigated conditions of redox reactions in view of concentration of reactive species and reversible or irreversible exchanging ligands. We could summarize proposed reaction mechanism by present information.

Keywords: Copper(II), Schiff base, Threonine, Imidazole, TiO₂

Introduction

Recently, bioinorganic photochemistry is an attractive research area based on both photochemistry and inorganic chemistry [1]. In previous papers, we reported that some copper(II) complexes [2-6] especially Schiff base having L-amino acid moieties [7, 8] showed photo-induced electron transfer reactions with TiO₂ [9, 10] after UV light irradiation. Although limited spectral and electrochemical data could be obtained, reaction conditions as well as tuning redox properties by molecular design did not clear because of complimentary systems [11]. Herein, we prepared two new related Cu(II) complexes of threonine moiety (Fig. 1)

having imidazole ligands at the fourth coordination site, and examined photo-induced reaction with TiO_2 from several aspects in order to understand their reaction mechanism.

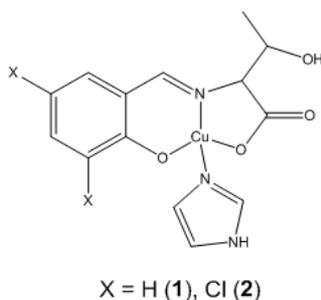


Fig. 1. Structures of Cu(II) complexes (**1** and **2**).

Experimental Sections

Preparations. Chemicals of the highest commercial grade available were used as received without further purification. Complexes were prepared according to the literature procedures replacing aldehyde and threonine [7, 8].

Complex 1. Yield 6.8 %. Anal. Found: C, 47.42; H, 4.11; N, 11.74 %. Calc. for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{CuO}_4$: C, 47.66; H, 4.29; N, 11.91 %. IR (KBr) 1631 cm^{-1} (C=N). UV-Vis (diffuse reflectance) 290, 400, 600 nm. UV-Vis (1 mM methanol, 298 K) 290, 390, 600 nm. CD (1 mM methanol, 298 K) 300 (-), 400 (-), 600 (+) nm. ESR (X-band, 1 mM methanol, 77 K) $g = 2.037$, $A = 176.9\text{ G}$. CV (1 mM in pH 5.1(sodium citrate buffer)) $E = 0.098\text{ V}$.

Complex 2. Yield 31.6 %. Anal. Found: C, 39.76; H, 2.81; N, 9.75 %. Calc. for $\text{C}_{14}\text{H}_{13}\text{N}_3\text{Cl}_2\text{CuO}_4$: C, 39.87; H, 3.11; N, 9.66 %. IR (KBr) 1628 cm^{-1} (C=N). UV-Vis (diffuse reflectance) 300, 410, 600 nm. UV-Vis (1 mM methanol, 298 K) 270, 400, 600 nm. CD (1 mM methanol, 298 K) 290 (-), 410 (-), 610 (+) nm. ESR (X-band, 1 mM methanol, 77 K) $g = 2.038$, $A = 177.2\text{ G}$. CV (1 mM in pH 5.1(sodium citrate buffer)) $E = 0.165\text{ V}$.

Physical measurements. Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400II CHNS/O analyzer at Tokyo University of Science. Infrared spectra were recorded a JASCO FT-IR 4200 spectrophotometer in the range of $4000\text{-}400\text{ cm}^{-1}$ at 298 K. Electronic spectra were measured on a JASCO V-570 spectrophotometer (equipped with an integrating sphere) in the range of $900\text{-}200\text{ nm}$ at 298 K. Circular dichroism (CD) spectra were measured on a JASCO J-725 spectropolarimeter in the range of $800\text{-}200\text{ nm}$ at 298 K. X-band ESR spectra of solutions were measured with a JEOL JES-FA200 spectrometer at 77K. Electrochemical (cyclic voltammetry, CV) measurements were carried out on a BAS SEC2000-UV/CVIS and ALS2323 system with Ag/AgCl electrodes. UV and visible light source used was Hayashi LA-310UV and LA-251Xe, respectively with visible ($\lambda > 350\text{ nm}$) or UV ($\lambda < 350\text{ nm}$) cut filters.

Results and Discussion

The present Cu(II) complexes of threonine derivatives (Fig. 1) have been prepared and characterized as summarized in Experimental Section. Changes of UV-vis spectra in the solid state (which is typical features for distorted square planar $[\text{CuN}_2\text{O}_2]$) and in solutions suggested that structural changes when they were dissolved in solvents. Which was also supported by ESR spectra of $s=1/2$. Positive shift of redox potential by CV exhibited that **1** is easy to be reduced than **2**, which is ascribed to electron withdrawing effect of Cl-groups. Reversible redox reaction of Cu(II) and Cu(I) moieties could be confirmed and the reversible reaction was also observed for reactions with oxygen.

Fig. 2 shows spectral changes of hybrid systems of **1** or **2** and TiO_2 before and after UV light irradiation. Due to photo-induced electron transfer reaction between Cu(II) complexes and TiO_2 , Cu(II) complexes were reduced to be Cu(I) complexes in the case of previous systems, which were exhibited by these spectra. Before UV light irradiation (0 min), no reaction occurred by mixing them immediately. After irradiation for 20 min, however, intensity of $\pi-\pi^*$ bands as well as d-d band increased, which suggested dissociation of imidazole and exchanging to methanol. After irradiation for 40 min, intensity of d-d bands increased, which suggested reaction with imidazole to yield Cu(II) species and irreversible exchanging of ligands.

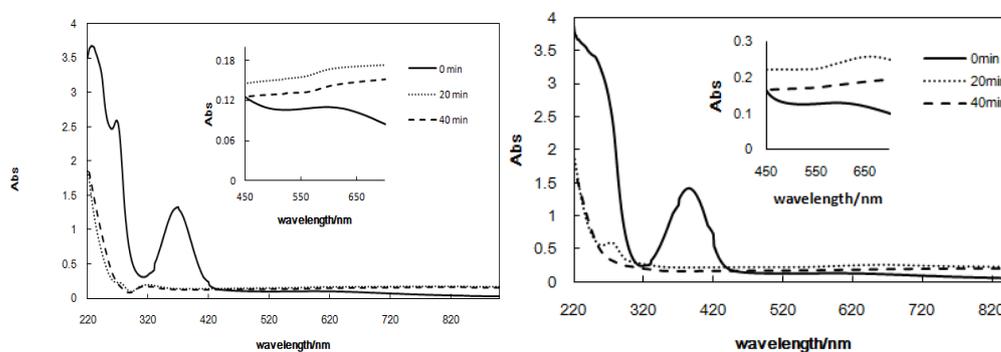


Fig. 2. UV-Vis spectra of 0.2 mM Cu(II) complexes (**1** left; **2** right) and 0.05 mM TiO_2 in methanol under N_2 atmosphere after UV light irradiation for 0, 20, and 40 min.

As for changes of d-d band intensity, concentration dependency of methanol solutions was also observed for Cu(II) complexes : $\text{TiO}_2 = 0.25 \text{ mM} : 0.125 \text{ mM}$, $0.5 \text{ mM} : 0.125 \text{ mM}$, and $1.0 \text{ mM} : 0.25 \text{ mM}$. The results elucidated that diluted solutions exhibited decreasing d-d band intensity (reduction of Cu(II) to Cu(I)), whereas concentrated solutions exhibited increasing d-d band intensity (reaction with imidazole to yield Cu(II) species) after UV light irradiation. In this way, there are appropriate conditions for commonly observed examples [7, 8] of Cu(II) species to Cu(I) ones in view of sufficient amounts of TiO_2 or dissociation of

imidazole ligands. In addition, Fig. 3 exhibits color changes of solutions before and after UV light irradiation. Regardless of concentration of solutes, it was confirmed that reduction Cu(II) to Cu(I) by TiO₂ and UV light and oxidation of Cu(I) to Cu(II) by oxygen were reversible reactions. These color changes are in agreement with changes of spectral intensity, namely decreasing d-d band (and increasing $\pi-\pi^*$ band) for (1) to (2), while increasing d-d band (and decreasing $\pi-\pi^*$ band) for (2) to (3) under appropriate conditions.

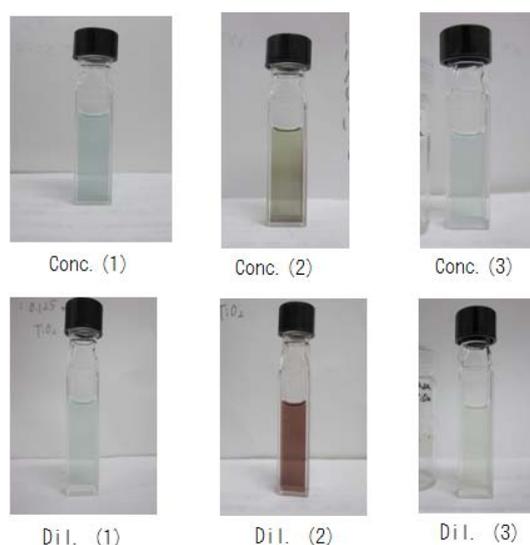


Fig. 3. Color changes during photo-induced reactions of **1** and TiO₂ in methanol under N₂ atmosphere. (Above; Conc.) 1 mM **1** and 0.25 mM TiO₂ (1) before UV irradiation, (2) after UV light irradiation for 19 min, and (3) after oxidation exposed by oxygen. (Below; Dil.) 0.5 mM **1** and 0.125 mM TiO₂ (1) before UV irradiation, (2) after UV light irradiation for 5 min, and (3) after oxidation exposed by oxygen in air.

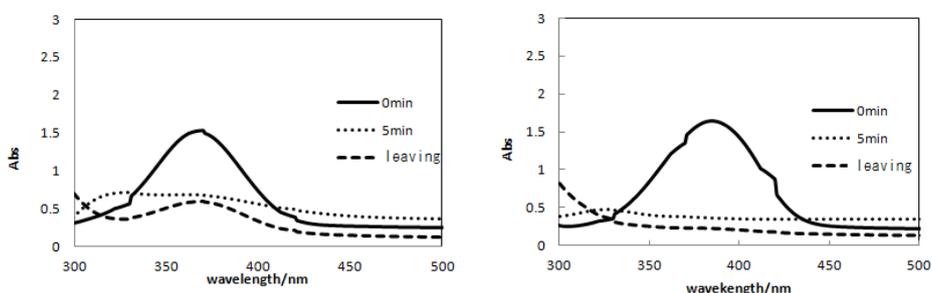


Fig. 4. UV-Vis spectra of 0.25 mM Cu(II) complexes (**1** left; **2** right) and 0.125 mM TiO₂ in methanol under N₂ atmosphere before and after UV light irradiation for 5min and leaving for 2h (allowed to stand after exposing oxygen).

As for changes of $\pi-\pi^*$ band intensity, irreversible dissociation of imidazole ligands was also suggested by Fig. 4. After UV light irradiation for 5 min,

intensity of $\pi-\pi^*$ band decreased, which suggested dissociation of imidazole ligands. Moreover, although d-d bands changed due to reversible changes from Cu(I) species to Cu(II) ones, after exposing oxygen in air for 2 h, intensity of $\pi-\pi^*$ bands was kept weak, which is irreversible exchanging of imidazole ligands into methanol ligands.

Conclusions

In summary, we synthesized new Cu(II) complexes having threonine moieties **1** and **2** and investigate their photo-induced reactions with TiO₂. Substitution of Cl-groups affected on shifts of spectral peaks as well as redox potentials. Reaction conditions with TiO₂ detected by $\pi-\pi^*$ bands depends on concentration of solutes, in other words, irreversible dissociation of imidazole ligands. Electrochemical features and reaction with oxygen elucidated that only redox reactions between Cu(II) and Cu(I) species were reversible nevertheless of exchanging ligands. According to the present information, tentative proposed reaction mechanism can be summarized as Fig. 5 consequently.

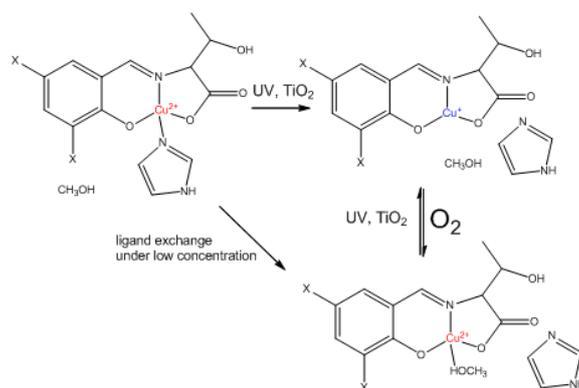


Fig. 5. Proposed reaction mechanism of the hybrid systems of Cu(II) complexes and TiO₂ affected by UV light and exposing oxygen.

Acknowledgements

This work was supported by The Cosmetology Research Foundation. This work was performed under the Cooperative Research Program of “Network Joint Research Centre for Materials and Devices”.

References

- [1] G. Stochel, M. Brindell, W. Macyk, Z. Stasicka, K. Szacilowski, *Bioinorganic Photochemistry*, Wiley, Sussex, 2009.

- [2] T. Akitsu T, Y. Ishiguro, S. Yamamoto, H. Nishizuru, Tuning Electronic States of Some Copper Complexes by Titanium Dioxide Photocatalyst, *Asian Chem. Lett.*, 14 (2010) 63-74.
- [3] T. Akitsu, H. Nishizuru, Tuning of electronic states of copper(II) complexes showing equilibrium of coordination in solutions, *Asian Chem. Lett.*, 14 (2010) 261-266.
- [4] Y. Watanabe, H. Nishizuru, T. Akitsu, Crystal structure of Bis((1*S*,2*S*)-*N,N'*-dimethylcyclohexanediamine- κ^2 -*N,N'*)bis(perchlorato- κ -O) copper(II), *Asian Chem. Lett.*, 15 (2011) 211-214.
- [5] T. Akitsu T, S. Yamamoto, Photofunctional supramolecular solution system of several copper(II) complexes and photochromic fluorescent indicators, *Asian Chem. Lett.*, 14 (2010) 29-36.
- [6] T. Akitsu, S. Yamamoto, Spectroscopic detection of photofunctional systems of copper(II) complexes, Azo-dye, and TiO₂, *Asian Chem. Lett.*, 14 (2010) 255-260.
- [7] T. Nakayama, M. Minemoto, H. Nishizuru, T. Akitsu, Spectroelectrochemistry of photoinduced electron transfer reactions between leucine and serine derivative Schiff base copper(II) complexes and titanium Oxide, *Asian Chem. Lett.*, 15 (2011) 215-219.
- [8] S. Yamamoto, T. Akitsu, Fluorescence detection by photochromic dye of photoinduced electron transfer reactions between lysine and methionine derivative Schiff base copper(II) complexes and titanium oxide, *Asian Chem. Lett.*, 15 (2011) 203-209.
- [9] I. Grenthe, P. Paoletti, M. Sandstorm, S. Gillberg, Thermochromism in copper(II) complexes. Structures of the red and blue-violet forms of bis(*N,N*-diethylethylenediamine)copper(II) perchlorate and the nonthermochromic violet bis(*N*-ethylethylenediamine)copper(II) perchlorate, *Inorg. Chem.*, 18 (1979) 2687-2692.
- [10] P. Chandi, K. Panneerselvan, C.-S. Chung, T.-H. Lu, Syntheses, crystal structures and solid state thermochromic conversion of trans-1,2-diaminocyclohexane complexes of copper (II) perchlorate, *Polyhedron*, 17 (1988) 2555-2561.
- [11] T. Akitsu (ed.) Integrating Approach to Photofunctional Hybrid Materials for Energy and the Environment, Nova Science Publishers, Inc., New York, 2013.

Received: June 26, 2013