# Specific Binding of Substrates Containing Nitrogen and Oxygen Donor Groups to Copper(II)-Gadolinium(III) Hetero-Metal Center

Masatomi SAKAMOTO,* Tomitaro ISHIMORI, and Hisashi ŌKAWA†
Department of Industrial Chemistry, Faculty of Engineering, Ehime University, Bunkyo-cho, Matsuyama 790
†Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812
(Received April 15, 1988)

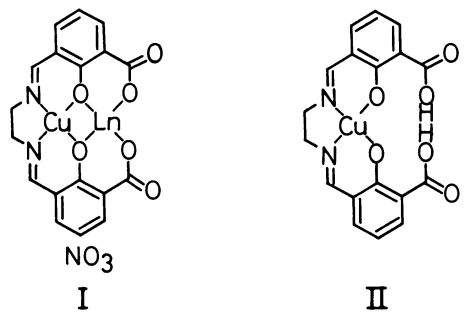
**Synopsis.** Substrate binding to the Cu(II)–Gd(III) hetero-metal complex of *N,N'*-bis(3-carboxysalicylidene)ethylenediamine was studied in *N,N*-dimethylformamide. It was suggested that substrates with a nitrogenous and an oxygenous groups (amino alcohols, 8-quinolinol, amino acids, and amino acid esters) were specifically bound to the Cu(II)–Gd(III) center, with the nitrogen to the copper and with the oxygen to the gadolinium.

Recently we have reported[1] that the copper(II)–lanthanoid(III) hetero-metal complexes (Fig. 1, I) of *N,N'*-bis(3-carboxysalicylidene)ethylenediamine ($H_4$-fsaen) show "solvation selectivity" associated with the copper or lanthanoid center depending upon the nature of solvents. That is, in pyridine solution the solvation occurs at the copper center to afford a pentacoordination around the metal, whereas in dimethyl sulfoxide or *N,N*-dimethylformamide solutions the solvation occurs exclusively at the lanthanoid center while maintaining the planar configuration around the copper ion. It should be emphasized that the mononuclear precursor complex (Fig. 1, II) takes a pentacoordination with a solvent molecule at an apical site in all of these solvents. The above findings prompted us to examine if the Cu(II)–Ln(III) center functions as a specific binding site for substrates containing both nitrogenous and oxygenous donating groups. In this study the Cu(II)–Gd(III) complex of $H_4$fsaen, in which gadolinium is located at the center of lanthanoid series, was adopted and the binding of various substrates (amino alcohols, 8-quinolinol, amino acids, and amino acid esters) to the complex was investigated in *N,N*-dimethylformamide (DMF).

## Experimental

**Materials.** The Cu(II)–Gd(III) complex of $H_4$fsaen was synthesized according to the method reported previously.[1] 2-Amino-1-butanol was purchased from Tokyo Kasei Co. Other reagents used as substrates were purchased from Wako Pure Chemical Industries. Methyl esters of the amino acids were obtained as hydrochloride after the literature method[3] and used for the following experiments without neutralization.

**Methods.** A solution of the Cu(II)–Gd(III) complex in DMF ($2.5\times10^{-2}$ mol·dm$^{-3}$) was prepared. To 2 cm$^3$ of this solution was added a weighed amount of a substrate (except for amino acids), and the total volume was made up to 10 cm$^3$ with DMF. Visible spectra of the mixture were determined with a HP 8452A Spectrophotometer. For amino acids as substrates, a suspension of an amino acid in the complex solution was stirred for 2 h, and the supernatant solution was submitted to the spectral measurements. The CD spectra were determined with a JASCO J-20 Automatic Recording Spectropolarimeter.




I II

Fig. 1. Chemical structures of copper(II)–lanthanoid(III) hetero-metal complexes(I) and copper(II) mononuclear complex(II) of *N,N'*-bis(3-carboxysalicylidene)ethylenediamine.

## Results and Discussion

In general the axial coordination of a substrate to the copper center results in a red shift of the d–d band maximum, along with a color change from purple to green or blue. For example, when an amino alcohol (2-aminoethanol, 3-amino-1-propanol, 1-amino-2-propanol, 2-amino-1-butanol) was added as the substrate to the complex solution, the d–d band maximum shifted by $1\times10^3$—$2\times10^3$ cm$^{-1}$ to lower frequency.

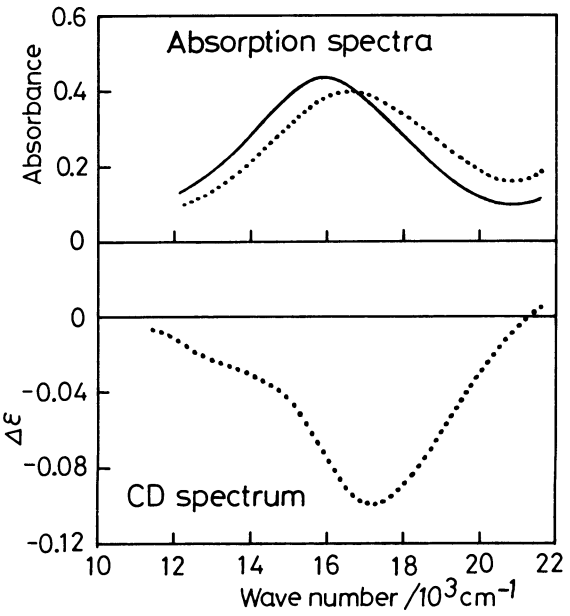



Fig. 2. Absorption and CD spectra in DMF. Concentration of the binuclear complex is $5\times10^{-3}$ mol dm$^{-3}$. (——): with 2-aminoethanol (10 mol dm$^{-3}$); (……): with (*R*)-(−)-2-amino-1-butanol (10 mol dm$^{-3}$).

Table 1. The d-d Band Maxima of Cu(II)-Gd(III) Binuclear Complex in DMF Solution of Various Substrates[a]

| Substrate | $\tilde{\nu}_{max}/10^3$ cm$^{-1}$ |
|---|---|
| No substrate | 17.86 |
| 1,2-Ethanediol[b] | 18.08 |
| 1,3-Propanediol[b] | 17.89 |
| 2-Aminoethanol[b] | 15.97 |
| 3-Amino-1-propanol[b] | 16.50 |
| 1-Amino-2-propanol[b] | 16.19 |
| (*R*)-(−)-2-Amino-1-butanol[b] | 16.67 |
| 8-Quinolinol[c] | 17.33 |
| Glycine[d] | 17.86 |
| β-Alanine[d] | 17.67 |
| 4-Aminobutyric acid[d] | 17.48 |
| Glycine methyl ester[e] | 17.64 |
| β-Alanine methyl ester[e] | 17.73 |
| Methyl 4-aminobutyrate[e] | 17.67 |

a) Concentration of binuclear complex is $5\times10^{-3}$ mol·dm$^{-3}$. b) Concentration is 10 mol·dm$^{-3}$. c) Concentration is 1 mol·dm$^{-3}$. d) Spectra were measured for the supernatant solution after these substrates were suspended with stirring for 2 h. e) Hydrochlorides were used. Concentration of glycinate, alaninate, and butyrate are $5.26\times10^{-3}$, $5.01\times10^{-3}$, and $5.40\times10^{-3}$ mol·dm$^{-3}$, respectively.

Typical spectra are shown in Fig. 2 and the numerical data are given in Table 1. The largest red shift of the d-d band is observed for 2-aminoethanol and the shift tends to decrease when the alkane chain is lengthened or a substituent is introduced on the ethylene chain. When (*R*)-(−)-2-amino-1-butanol was added as the substrate, the solution showed significant circular dichroism at the d-d transitions of the copper(II) ion (Fig. 2). The addition of 1,2-ethanediol or 1,3-propanediol as the substrate, on the other hand, showed no indication of the coordination to the copper center (see Table 1). All these facts indicate that the amino alcohols coordinate to the copper center at the nitrogen atom. The coordination at the lanthanoid center, however, cannot be monitored spectroscopically, because electronic structures of lanthanoid ions are little affected by the change in the coordination geometry or the ligand field strength.[4] However, it is expected that oxygenous substrates such as alcohols, phenols, carboxylic acids, or esters have a high affinity towards lanthanoid ions compared with DMF (amide) used as the solvent. This is probably the case of 1,2-ethanediol and 1,3-propanediol; these substrates may exclusively coordinate to the gadolinium ion at both oxygen atoms. Therefore, we presumed that the amino alcohols are bound to the Cu(II)-Gd(III) center, with the nitrogen to the copper and with the oxygen to the gadolinium.

The addition of quinoline as the substrate showed no indication of the coordination to the copper(II) ion, whereas the addition of 8-quinolinol caused a significant red shift of the d-d band. This is rationalized in terms of that the binding of quinoline to the copper center is sterically hindered but the binding of 8-quinolinol to the Cu(II)-Gd(III) center is not subjected to any steric hindrance when the hydroxyl group is concerned with the coordination to the gadolinium(III) ion. This adds a support to our presumption that amino alcohols are bound as bidentate bridge to the Cu(II)-Gd(III) center.

Somewhat different feature of binding was recognized for amino acids. When glycine was added to the complex solution, no indication of the nitrogen coordination to the copper was observed from its electronic spectrum. When β-alanine was added, no apparent color change occurred but its electronic spectrum showed a slight red shift of the d-d band. When 4-aminobutyric acid was the substrate, apparent color change occurred and its spectrum showed a larger red shift of the d-d band. Therefore, the nitrogen coordination to the copper center becomes feasible on lengthening the alkane chain of amino acid. This trend differs from that found for amino alcohols. Conceivably carboxylate group of amino acids coordinate bidentately to the gadolinium center. Such bidentate carboxylates were reported for some lanthanoid(III) acetate hydrates.[5] If this is the case, the coordination of the terminal nitrogen to the copper should be difficult for glycine but is easier for amino acids with a longer methylene chain.

In order to gain an insight into the binding mode of amino acids, we also examined the binding of amino acid esters (methyl aminoacetate, methyl 3-aminopropionate, methyl 4-aminobutyrate) to the Cu(II)-Gd(III) center. As seen in Table 1, the substrate binding to the copper center was evidenced spectroscopically for all the cases. We assume that in these cases, the ester group functions as a unidentate donor so that the amino acid esters are bound to the Cu(II)-Gd(III) center in the essentially the same way as that of amino alcohols.

From the above discussions it is suggested that the substrates possessing a nitrogenous and an oxygenous donor groups are specifically bound to the Cu(II)-Gd(III) center, though their binding constants have not yet been determined.

**References**

1) M. Sakamoto, M. Takagi, T. Ishimori, and H. Ōkawa, *Bull. Chem. Soc. Jpn.*, **61**, 1613 (1988).

2) M. Tanaka, M. Kitaoka, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **49**, 2469 (1976).

3) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," John Wiley & Sons, New York (1961), Vol. 2, pp. 925—928.

4) G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals," Interscience, New York (1968), p. 249.

5) S. Ganapathy, V. P. Chacko, R. G. Bryant, and M. C. Etter, *J. Am. Chem. Soc.*, **108**, 3159 (1986).