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Copper(II)-Rare Earth(III) (Ln=La, Gd, Lu) Binuclear Complexes of Bis[2-(3-carboxysalicylidene)aminoethyl]amine: Characterization and Specific Binding of Amino Alcohols

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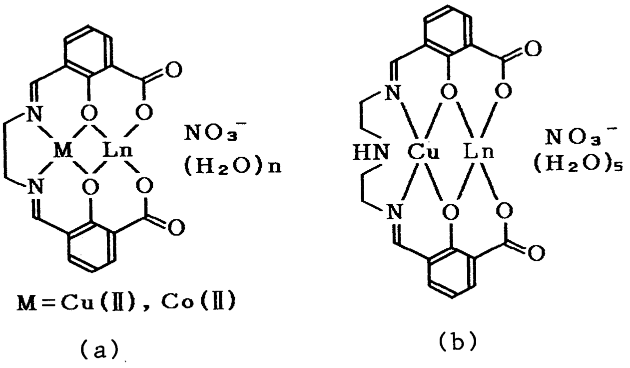
Synopsis. Heterometal complexes, [CuLn(fsadien)(NO_3)(H_2O)$_n$]·(H_2O)$_{5-n}$ (Ln=La, Gd, or Lu), have been synthesized and characterized, where H_4fsadien denotes bis[2-(3-carboxysalicylidene)aminoethyl]amine. Based on electronic absorption and CD spectra, it was suggested that amino alcohols were specifically bound to the Cu(II)–Ln(III) heterometal center, through the nitrogen to the copper(II) ion and through the oxygen to the rare earth(III) ion.

Recently we have reported that the copper(II)–rare earth(III) and cobalt(II)–rare earth(III) heterometal complexes of *N,N′*-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen, Fig. 1a)[1,2] show a unique "selective solvations" associated with copper or rare earth ion, depending upon the the nature of the solvent. That is, in pyridine the solvation occurs at the copper site, whereas in dimethyl sulfoxide or *N,N*-dimethylformamide the solvation occurs exclusively at the rare earth site. This selective solvation has been extended to specific binding of amino alcohols on the copper(II)–rare earth(III) or the cobalt(II)–rare earth(III) heterometal center.[2,3]



(a) (b)

Fig. 1. Chemical structures of copper(II)- or cobalt(II)–rare earth(III) complexes of H_4fsaen (a) and copper(II)–rare earth(III) complexes of H_4fsadien (b).

In this work we have synthesized and characterized copper(II)–rare earth(III) complexes of bis[2-(3-carboxysalicylidene)aminoethyl]amine (H_4fsadien, Fig. 1b), in which copper(II) and rare earth(III) ions are bound at the inside coordination site (N_3O_2-site) and the outside coordination site (O_4-site), respectively. The specific binding of amino alcohols on the Cu(II)–Ln(III) center has been investigated on the basis of electronic absorption and CD spectra.

Experimental

Syntheses. 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[4] Mononuclear copper(II) complex, [Cu(H_2 fsadien)]·H_2O was synthesized according to the method reported by Casellato et al.[5]

Binuclear Complexes, [CuLn(fsadien)(NO_3)(H_2O)$_n$]·(H_2O)$_{5-n}$(Ln=La, Gd, or Lu): A methanol solution (10 cm³) of lithium hydroxide monohydrate (2 mmol) was added to a suspension of the mononuclear copper(II) complex, [Cu(H_2 fsadien)]·H_2O (1 mmol), in methanol (50 cm³). Further addition of methanol (240 cm³) and heating gave a clear solution. To the resulting solution was added a methanol solution (5 cm³) of a rare earth(III) nitrate hydrate (1 mmol), and the mixture was refluxed under stirring for 3 h. After the solution was concentrated to 50 cm³ under reduced pressure, resulted greenish crystals were collected on a glass filter, washed with methanol and then diethyl ether, and dried in the open air. the yield was about 60 %.

Analytical results are given in Table 1.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were obtained at the Advanced Instrumentation Center for Chemical Analysis of Ehime University. Metal contents were determined by the EDTA titration of mixed nitrates, which were prepared by dissolving the ignition residue

Table 1. Elemental Analyses of Complexes

Complex	Found/% (Calcd/%)				
	C	H	N	Cu	Ln
CuLa(fsadien)(NO_3)(H_2O)$_5$	31.90	3.17	7.49	8.45	18.38
	(32.03)	(3.63)	(7.47)	(8.47)	(18.52)
CuGd(fsadien)(NO_3)(H_2O)$_5$	31.29	3.22	7.38	8.28	21.30
	(31.27)	(3.54)	(7.29)	(8.27)	(20.47)
CuLu(fsadien)(NO_3)(H_2O)$_5$	29.88	3.20	7.30	8.66	23.31
	(30.46)	(3.45)	(7,10)	(8.06)	(22.19)

(mixed oxides) of the complex in HNO_3. Infrared spectra were measured with a JASCO IR-G Spectrometer on KBr disks, nujol mulls, or hexachlorobutadiene mulls. Absorption and reflectance spectra were obtained with a Hewlett–Packard 8452A Spectrophotometer and an Otsuka Electronics MCPD 1000 Spectrophotometer, respectively. The CD spectra were recorded on a JASCO J-20 Automatic Recording Spectropolarimeter.

Results and Discussion

Infrared spectra of the Cu(II)–Ln(III) complexes are similar to each other. The ν (C=O) vibration (ca. 1670 cm^{-1}) and ν (O–H) vibration (3000—2000 cm^{-1}) of the chelated carboxyl groups are observed for H_4fsadien and [Cu(H_2fsadien)]·H_2O, but those bands disappear on the Cu(II)–Ln(III) complex formation. Instead, the Cu(II)–Ln(III) complexes show the carboxylate vibration at 1535—1550 cm^{-1}. These observations suggest the incorporation of a rare earth(III) ion at the O_4-site. The vibrations due to the nitrate ion are observed as split bands at ca. 1430 and 1380 cm^{-1}, suggesting the bidentate coordination of the nitrate ion.[6] The ν (O–H) vibration of the water molecules appears as a broad band at 3300—3400 cm^{-1} when measured on nujol mulls or hexachlorobutadiene mulls. It is presumed that the water molecules coordinate to the rare earth ion to afford a coordination number larger than six.

Reflectance spectra are shown in Fig. 2. The spectrum of [Cu(H_2fsadien)]·H_2O exhibits a band maximum at ca. 14.3×10^3 cm^{-1} and a shoulder at ca. 17.5×10^3 cm^{-1}, suggesting a trigonal-bipyramidal surrounding about the copper(II) ion[7] with the three nitrogen atoms of the diethylenetriamine moiety and the two phenolic oxygen atoms. On the other hand, the Cu(II)–La(III), Cu(II)–Gd(III), and Cu(II)–Lu(III) complexes show an unresolved broad band at ca. 17.1×10^3, ca. 16.7×10^3, and ca. 16.5×10^3 cm^{-1}, respectively, suggesting no coordination of the central nitrogen of the lateral bridge to the copper(II) to give a square planar configuration around the copper. The model considerations support that the coordination of central nitrogen of the lateral bridge to the copper is difficult when the two carboxylate groups coordinate to a rare earth ion.

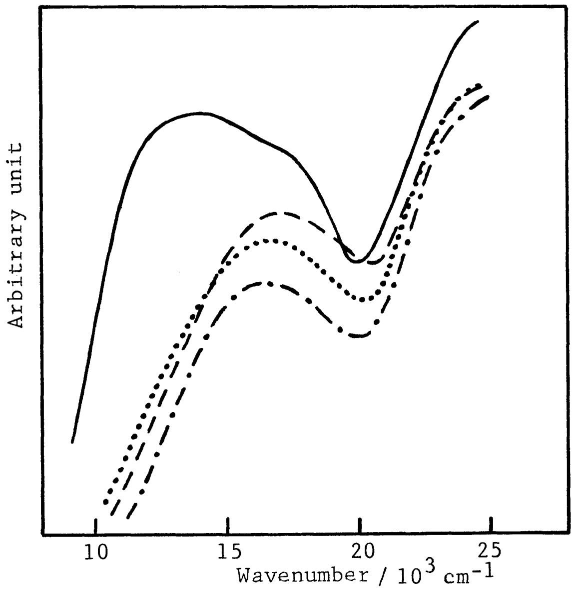


Fig. 2. Electronic spectra in solid state. (——): [Cu(H_2fsadien)]·H_2O; (– – –): [CuLa(fsadien)(NO_3)(H_2O)$_n$]·(H_2O)$_{5-n}$; (·····): [CuGd(fsadien)(NO_3)(H_2O)$_n$]·(H_2O)$_{5-n}$; (—·—): [CuLu(fsadien)(NO_3)(H_2O)$_n$]·(H_2O)$_{5-n}$.

The interaction of substrates on the heteronuclear center has been studied spectroscopically by adding various substrates to a DMF solution of the Cu(II)–La(III) complex. Typical absorption spectra are given in Fig. 3 and the numerical data are summarized in Table 2.

In general, the axial coordination of a substrate to planar copper(II) results in a red shift of the d–d band

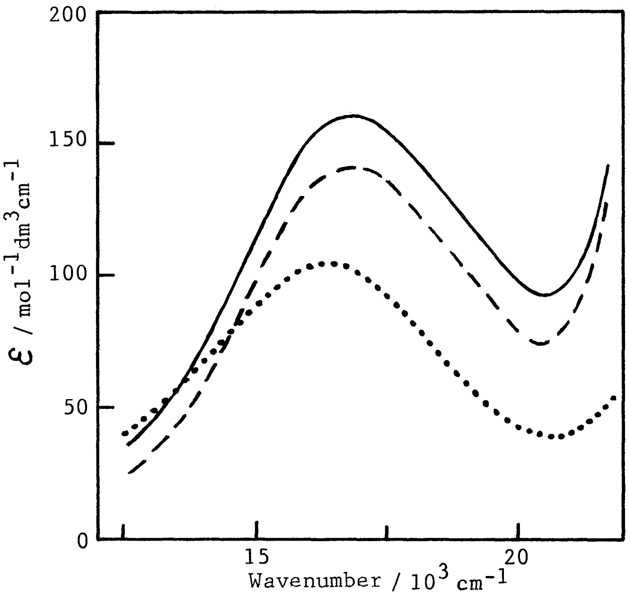


Fig. 3. Absorption spectra in DMF. Concentration of the Cu(II)–La(III) binuclear complex is 5×10^{-3} mol dm^{-3}. (——): with no substrate; (– – –): with 1,2-ethanediol (1 mol dm^{-3}); (·····): with 2-aminoethanol (1 mol dm^{-3}).

Table 2. The d–d Band Absorption Maxima of Cu(II)–La(III) Binuclear Complex in DMF Solution of Various Substrates[a]

Substrate	$\nu_{max}/10^3$ cm^{-1}
No substrate	16.72
Methanol[b]	16.72
Ethanol[b]	16.72
1,2-Ethanediol[c]	16.72
2-Aminoethanol[c]	16.29
3-Amino-1-propanol[c]	16.29
1-Aminopropane[c]	16.08

a) Concentration of the Cu(II)–La(III) complex is 5×10^{-3} mol dm^{-3}. b) Concentration is 5 mol dm^{-3}. c) Concentration is 1 mol dm^{-3}.

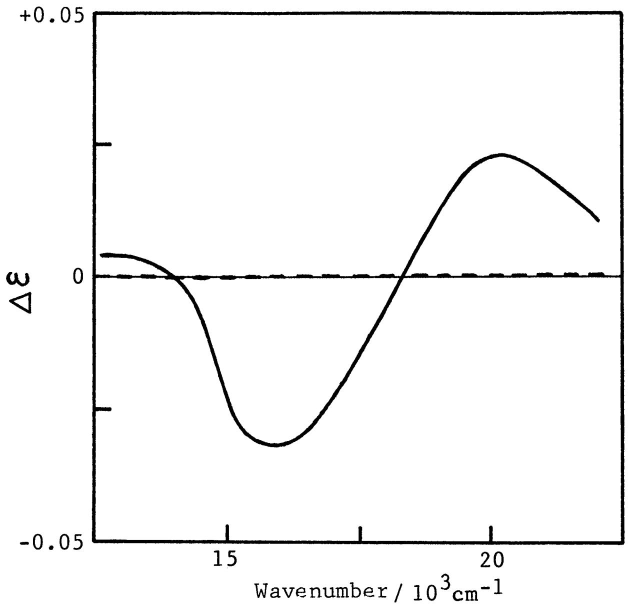


Fig. 4. The CD spectra in DMF. Concentration of the Cu(II)–La(III) binuclear complex is 5×10^{-3} mol dm^{-3}. (——): with (*R*)-(−)-1-amino-2-propanol (1 mol dm^{-3}); (– – – –): with (*S*)-(+)-1,2-propanediol (1 mol dm^{-3}).

maximum. This is indeed the case when 1-aminopropane is added to a DMF solution of the Cu(II)–La(III) complex. A similar red shift of the d–d band was observed when 2-aminoethanol or 3-amino-1-propanol was added as the substrate. On the other hand, such a spectral change was not seen when alcohols (methanol, ethanol, or 1,2-ethanediol) were added as substrates. Obviously amines coordinate to the axial site of the copper(II) center whereas alcohols do not.

It is unclear from the above results if alcohols are bound at the lanthanum(III) center or not, but our CD spectral investigations using a chiral amino alcohol as the substrate has revealed the ligating interaction of alcohols with the lanthanum(III) center. Figure 4 shows the CD spectrum of the Cu(II)–La(III) complex when (*R*)-(−)-1-amino-2-propanol was added as the substrate. The significant circular dichroism induced at the d–d band of the copper(II) clearly demonstrates that the free rotation of the amino alcohol is hindered with respect to the Cu–N bond owing to the following reasons; (i)the hydroxyl group of the amino alcohol may be directly bound to the lanthanum(III) ion or (ii)the hydroxyl group may be involved in hydrogen bonding with DMF or H_2O molecules coordinated to the lanthanum(III) ion discussed previously.[2] Such a CD activity was not observed in the visible region when (*S*)-(+)-1,2-propanediol was added as the substrate (see Fig. 4). This is quite understandable since the chiral diol is captured on the lanthanum(III) center probably as a bidentate ligand. Thus, the present work is another illustration of specific binding of amino alcohols on d–f heterodinuclear center.

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