Pergamon

0277-5387(95)00051-8

Polyhedron Vol. 14, No. 17–18, pp. 2505–2509, 1995
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0277-5387/95 $9.50+0.00

COPPER(II)–LANTHANIDE(III) COMPLEXES OF COMPARTMENTAL LIGAND, N,N′-BIS(3-HYDROXYSALICYLIDENE)ETHYLENEDIAMINE

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(*Received* 30 *November* 1994; *accepted* 9 *January* 1995)

Abstract—Mononuclear copper(II) and europium(III) complexes, $[Cu(H_2dhbaen)]$ and $[Eu(Hdhbaen)(H_2O)_n]\cdot(2-n)H_2O$, and heteronuclear copper(II)–lanthanide(III) complexes, $[CuLn(dhbaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (Ln = La, Eu or Lu), have been synthesized [where $H_4dhbaen$ = N,N′-bis(3-hydroxysalicylidene)ethylenediamine]. Based on the CD spectra, it is suggested that amino alcohols are specifically bound at the Cu^{II}–Ln^{III} centre, through the nitrogen to the copper site and through the oxygen to the lanthanide site. The strong fluorescence of Eu^{III} for the monuclear Eu^{III} complex was markedly quenched on forming the heteronuclear Cu^{II}–Eu^{III} complex.

Since Abid and Fenton[1] and Vidali and co-workers[2] reported, in 1984, the synthesis of heteronuclear complexes comprising a *d*-transition metal ion and a lanthanide ion (*d*–*f* heteronuclear complexes) using compartmental ligands, attention has been increasingly attracted to such complexes.[3–14] Very recently, Vigato and co-workers[4,5] reported the syntheses, crystal structures and magnetic properties of the *d*–*f* heteronuclear complexes of dinucleating ligands derived from 2,3-dihydroxybenzaldehyde and diamines, and proposed that these hetero-

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nuclear complexes are very useful for the preparation of the fine and homogeneous mixed oxides. We have also synthesized *d–f* heteronuclear complexes for several years[6–14] and found the following interesting properties. First, M^{II}–Ln^{III} complexes (M = Cu or VO; Ln = lanthanides) show unique "selective solvation" associated with the heteronuclear centre depending upon the nature of the solvent.[6,7,14] That is, with a nitrogen-containing solvent such as pyridine, the solvation occurs preferentially at the copper centre, whereas with an oxygen-containing solvent such as N,N-dimethylformamide (dmf) or dimethyl sulphoxide (dmso) the solvation occurs exclusively at the lanthanide centre. Secondly, this selective solvation was extended to the specific binding of substrates that possess both nitrogen and oxygen atoms in the donating groups.[8,10,11,14] Such substrates coordinate specifically to the *d–f* heterometal centre, through the nitrogen to the *d*-transition metal site and through the oxygen to the lanthanide site. Thirdly, the intense fluorescence of Eu^{III} for the mononuclear Eu^{III} complex is markedly quenched on forming the dinuclear M^{II}–Eu^{III} complexes (M = Cu or VO).[13,14] Thus, the *d–f* heteronuclear complexes are promising compounds for the development of complexes with new functions.

In the present work we have prepared the heteronuclear Cu^{II}–Ln^{III} complexes $[CuLn(dhbaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (Ln = La, Eu or Lu) and the mononuclear Eu^{III} complex $[Eu(Hdhbaen)(H_2O)_n]\cdot(2-n)H_2O$, where H_4dhbaen is N,N′-bis(3-hydroxysalicylidene)ethylenediamine, previously reported by Vigato and co-workers[4,5] and their specific binding to amino alcohols and fluorescent property have been investigated.

EXPERIMENTAL

Elemental analyses of carbon, hydrogen and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University, Japan. IR spectra were measured with a JASCO IR-G spectrometer on KBr disks. Absorption spectra were obtained with a Hitachi 320 spectrophotometer. The CD and fluorescence spectra were measured with a JASCO J-20 automatic recording spectropolarimeter and a Shimadzu RF-540 fluorospectrophotometer, respectively.

Synthesis of the ligand

The ligand, N,N′-bis(3-hydroxysalicylidene) ethylenediamine (H_4dhbaen), was synthesized in a similar manner to that previously reported by Vigato and co-workers[4] but using ethanol as a solvent. Found: C, 64.0; H, 5.5; N, 9.2. Calc. for $C_{16}H_{16}N_2O_4$: C, 64.0; H, 5.4; N, 9.3%.

Synthesis of the mononuclear copper(II) *complex*, $[Cu(H_2dhbaen]$

This complex has been synthesized by the reaction of copper(II) acetate monohydrate with H_4dhbaen in methanol.[4] In the present work the following procedure was also employed. To a methanolic solution (60 cm^3) of 2,3-dihydroxybenzaldehyde (abbreviated as H_2dhba: 20 mmol) was added an aqueous solution (50 cm^3) of copper(II) actate monohydrate (10 mmol). After the mixture was stirred at room temperature for 1 h, the greenish brown crystals were collected by suction filtration, washed successively with water, methanol and diethyl ether, and dried under reduced pressure. The crystals, bis(3-hydroxysalicylaldehydato)copper(II) monohydrate ($[Cu(Hdhba)_2]\cdot H_2O$), thus obtained in advance were suspended in ethanol (150 cm^3). To this suspension was added ethylenediamine (35 mmol). After the mixture was warmed with stirring for 2 h and cooled to room temperature, brownish violet crystals were collected by suction filtration, washed successively with ethanol and diethyl ether and then dried under reduced pressure.

Synthesis of the heteronuclear Cu^{II}–Ln^{III} *complexes*, $[CuLn(dhbaen)(NO_3)(H_2O)_n]\cdot(m-n)H_2O$ (Ln = La, Eu *or* Lu)

The synthetic procedure was similar to the literature method.[4] A methanolic solution (10 cm^3) of lithium hydroxide monohydrate (4 mmol) was added to a suspension of the mononuclear copper(II) complex (2 mmol) in methanol (50 cm^3). To the resulting transparent solution was added lanthanide(III) nitrate hydrate (2 mmol) in methanol (5 cm^3). Soon, brownish crystals were precipitated. After the mixture was warmed with stirring for 3 h, the crystals were collected by suction filtration, washed with methanol and diethyl ether and then dried under reduced pressure.

Synthesis of the mononuclear europium(III) *complex*, $[Eu(Hdhbaen)(H_2O)_n]\cdot(2-n)H_2O$

A methanolic solution (10 cm^3) of lithium hydroxide monohydrate (4.5 mmol) was added to a suspension of the ligand, H_4dhbaen (1.5 mmol), in methanol (30 cm^3). To the resulting transparent solution was added europium(III) nitrate hydrate (1.5 mmol) in methanol (3 cm^3). Soon, orange crystals were precipitated. After the mixture was

Table 1. Elemental analyses of complexes

Complex	Found (%) (Calc.)		
	C	H	N
Cu(H_2dhbaen)	53.1	3.7	7.8
	(53.1)	(3.9)	(7.7)
Eu(Hdhbaen)(H_2O)$_2$	39.0	3.4	5.8
	(39.6)	(3.5)	(5.8)
CuLa(dhbaen)(NO_3)(H_2O)$_3$	31.8	2.7	6.8
	(31.3)	(2.9)	(6.8)
CuEu(dhbaen)(NO_3)(H_2O)$_3$	31.1	2.5	6.9
	(30.6)	(2.9)	(6.7)
CuLu(dhbaen)(NO_3)(H_2O)$_2$	30.0	2.6	6.5
	(30.4)	(2.5)	(6.6)

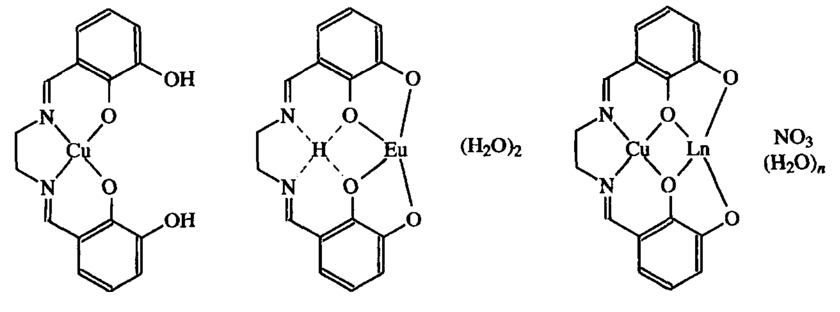
warmed with stirring for 30 min, the crystals were collected by suction filtration, washed with methanol and diethyl ether and then dried under reduced pressure.

RESULTS AND DISCUSSION

The analytical results in Table 1 demonstrate the compositions of heteronuclear Cu^{II}–Ln^{III} and mononuclear Eu^{III} complexes obtained in this work to be [CuLn(dhbaen)(NO_3)(H_2O)$_n$]·$(m-n)H_2O$ ($m = 3$ for Ln = La or Eu; $m = 2$ for Ln = Lu) and [Eu(Hdhbaen)(H_2O)$_n$]·$(2-n)H_2O$, respectively. As was reported by Vigato and co-workers,[4,5] the band assignable to ν(C=N) at 1632 cm^{-1} in the free ligand is lowered to 1622 cm^{-1} on forming the mononuclear Cu^{II} complex [Cu(H_2dhbaen)], and the band position for the mononuclear Cu^{II} complex is not significantly changed in the Cu^{II}–Ln^{III} complexes, suggesting that copper(II) and lanthanide (III) ions are located at the endogeneous N_2O_2 site and the exogeneous O_4 site of the ligand, respectively [see Figs 1a and c]. It should be noted here that the crystal structure of the heteronuclear Cu^{II}–Y^{III} complex of H_4dhbaen isolated from dmso was determined as a tetranuclear complex, [{CuY(dhbaen)(NO_3)(dmso)}$_2$]·2dmso.[4] By analogy with this complex, the present Cu^{II}–Ln^{III} complexes may be also tetranuclear. The ν(C=N) vibration for the mononuclear Eu^{III} complex [Eu(Hdhbaen)(H_2O)$_n$]·$(2-n)H_2O$ is observed at 1634 cm^{-1}, suggesting that in the mononuclear Eu^{III} complex the europium(III) ion is located at the O_4 site [see Fig. 1b].

Specific binding of amino alcohols towards the Cu^{II}–Ln^{III} *centre*

In order to investigate the interaction of substrates with the heteronuclear centre, we measured absorption spectra of the Cu^{II}–La^{III} complex in dmf by adding 1-propanol, 1,2-ethanediol or 2-amino-1-ethanol. Unfortunately, as shown in Fig. 2, these spectra give the *d–d* absorption band around 16 500 cm^{-1} as a shoulder. Therefore, it is impossible to discuss "specific binding of substrates" based on the absorption spectra as previously reported.[8,11,14] However, we have found that the CD spectral measurement is another useful method for these investigations.[8,10,11,14] When (*R*)-(−)-2-aminopropanol was added as the substrate to a dmf solution of the Cu^{II}–La^{III} complex, the solution showed significant CD in the *d–d* transition region of the Cu^{II} ion, as can be seen in Fig. 3. On the other hand, the addition of (*S*)-(+)-2-butanol or (*S*)-(+)-1,2-propanediol showed no CD activity in the *d–d* band region. From these observations, it is suggested that the amino alcohols are specifically bound to the Cu^{II}–Ln^{III} heterometal centre, with nitrogen to the Cu^{II} site and with oxygen to the Ln^{III} site, as illustrated in Fig. 4. Here, two types of interaction between Ln^{III} and the hydroxyl group of amino alcohols are considered.[10,11] One is a direct binding of the hydroxyl oxygen to Ln^{III} and another is an



(a) (b) (c)

Fig. 1. Chemical structures of (a) [Cu(H_2dhbaen)], (b) [Eu(Hdhbaen)(H_2O)$_n$]·$(2-n)H_2O$ and (c) [CuLn(dhbaen)(NO_3)(H_2O)$_n$]·$(m-n)H_2O$; Ln denotes lanthanide(III) ions.

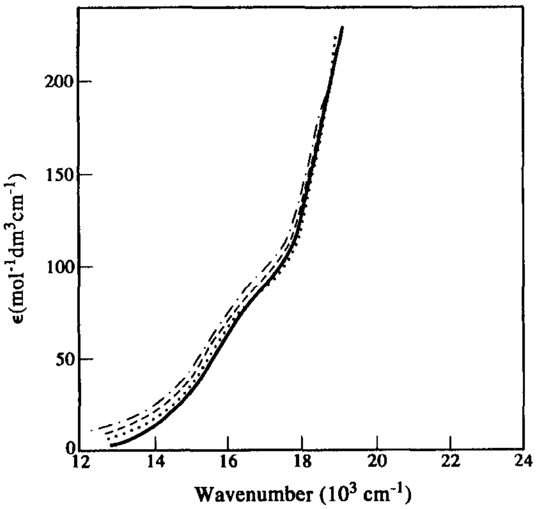


Fig. 2. Absorption spectra of the Cu^{II}–La^{III} complex in dmf. Concentration of the complex is 5×10^{-3} mol dm^{-3}. (——): without additive; (—·—): with 1-propanol (2.5×10^{-1} mol dm^{-3}); (– – –): with 1,2-ethanediol (2.5×10^{-1} mol dm^{-3}); (·····): with 2-amino-1-ethanol (2.5×10^{-1} mol dm^{-3}).

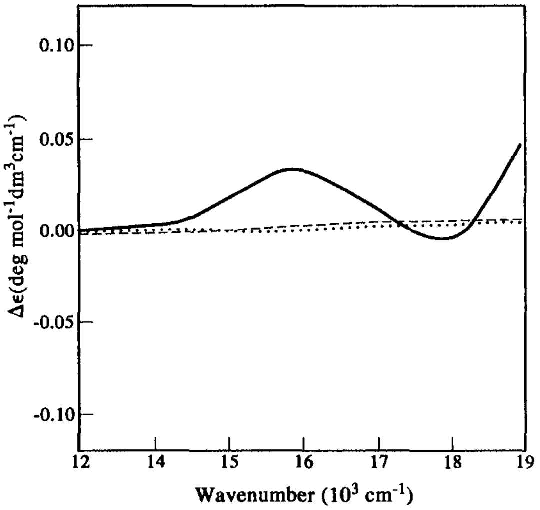


Fig. 3. CD spectra of the Cu^{II}–La^{III} complex in dmf. Concentration of the complex is 2.5×10^{-3} mol dm^{-3}. (——): with (*R*)-(−)-2-amino-1-propanol (2.5×10^{-1} mol dm^{-3}); (— — —): with (*S*)-(+)-1,2-propanediol (2.5×10^{-1} mol dm^{-3}); (·····): with (*S*)-(+)-2-butanol (2.5×10^{-1} mol dm^{-3}).

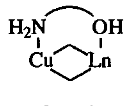


Fig. 4. Specific binding of amino alcohols to the Cu^{II}–Ln^{III} centre.

interaction through the hydrogen bonding of the hydroxyl group with dmf or H_2O molecules coordinated to the lanthanide(III) ion. It is not clear at present which interaction operates.

Fluorescence spectra

The fluorescence spectrum of the mononuclear Eu^{III} complex was compared with that of the Cu^{II}–Eu^{III} complex. The spectra are shown in Fig. 5. The mononuclear Eu^{III} complex shows the fluorescence bands attributable to the $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions at 586, 594, 613, 653 and around 700 nm, respectively. The intensities of these bands are drastically decreased in the Cu^{II}–Eu^{III} complex. Recently, we investigated the effects of [M(salen)] (M = Cu^{II} or Ni^{II}), [Cr(salen)$(H_2O)_2$]Cl, [M(saltn)] (M = Cu^{II} or Ni^{II}) and [Cu(acacen)] upon the fluorescence properties of Eu^{III} and Tb^{III} in methanol [where H_2salen, H_2saltn and H_2acacen are N,N′-bis(salicylidene)ethylenediamine, N,N′-bis(salicylidene)-1,3-propanediamine and N,N′-bis(1-methyl-3-oxobutylidene)ethylenediamine, respectively].[15–17]

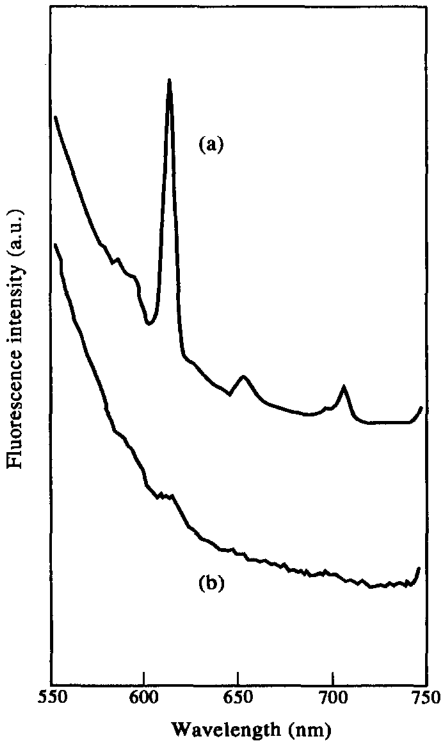


Fig. 5. Fluorescence spectra of (a) mononuclear Eu^{III} and (b) heteronuclear Cu^{II}–Eu^{III} complexes in dmf. Concentration of the complex is 2.5×10^{-4} mol dm^{-3}. Exciting wavelength is 394 nm. Slit widths of excitation and emission sides are 20 and 5 nm, respectively. Ordinate scales are × 32 for (a) and × 1024 for (b).

These investigations revealed that the fluorescence intensities of both Eu^{III} and Tb^{III} are decreased by the addition of the above complexes, but little affected by the addition of a simple metal salt such as $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ or $Cr(NO_3)_3 \cdot 9H_2O$. It is generally accepted that the luminescence decreases by the radiationless energy loss through the excited state of other molecules that are near the exciting species.[18] It is also known that [M(salen)] and [M(saltn)] (M = Cu^{II} or Ni^{II}) function as bidentate ligands through the two phenolic oxygens towards lanthanide(III) ions.[19–22] From these considerations, we presume that the fluorescence intensity of the present Cu^{II}–Eu^{III} complex is effectively quenched by the energy transfer from the excited Eu^{III} to the Cu^{II} centre through the bridging oxygen atoms, although the fluorescence decrease resulting from the absorption of exciting light by the Cu^{II}–Eu^{III} complex itself also cannot be ruled out.

Acknowledgements—The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes", Nos. 06241106 and 06241257, and a Grant-in-Aid for Scientific Research, No. 05640655, from The Ministry of Education, Science and Culture.

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