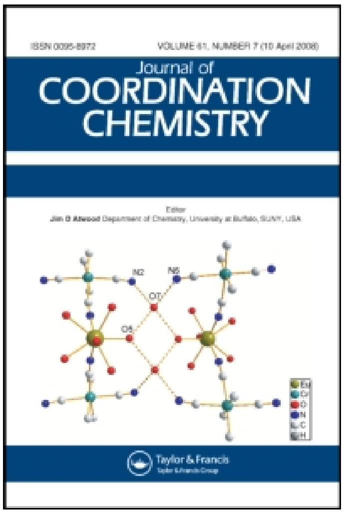

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NICKEL(II)-LANTHANIDE(III) COMPLEXES OF THE DINUCLEATING LIGAND *N,N'-BIS*(3-HYDROXYSALICYLIDENE)ETHYLENEDIAMINE

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NICKEL(II)-LANTHANIDE(III) COMPLEXES OF THE DINUCLEATING LIGAND *N,N'-BIS*(3-HYDROXYSALICYLIDENE)ETHYLENEDIAMINE

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Heteronuclear nickel(II)-lanthanide(III) complexes, NiLn(dhbaen)(NO_3)(H_2O)$_2$ (Ln = La, Eu or Gd), and a mononuclear Eu(III) complex, Eu(Hdhbaen)(H_2O)$_3$, were synthesized, where H_4dhbaen denotes *N,N'-bis*(3-hydroxysalicylidene) ethylenediamine. IR spectra shows that Ni(II) and Ln(III) ions are located at the endogenous N_2O_2- and exogenous O_4-coordination sites of ligand, respectively. Based on CD spectra, it was concluded that amino alcohols are specifically bound at the Ni(II)-Ln(III) heterometal centre, through the nitrogen to the Ni-site and through the oxygen to the Ln-site. The fluorescence intensity of the mononuclear Eu(III) complex is much greater than that of the heteronuclear Ni(II)-Eu(III) complex.

KEYWORDS: heteronuclear complex, lanthanide, nickel, fluorescence

INTRODUCTION

A great number of heteronuclear complexes comprising *d*-transition metal ions have been reported in view of magnetic spin-exchange interactions between paramagnetic ions[1] and catalytic functions associated with multi-electron transfer,[2] and as models

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for the active sites of some metalloenzymes.[3] On the other hand, the chemistry of heteronuclear complexes comprising *d*-transition metal and lanthanide ions (*d-f* heteronuclear complexes) is an attractive new area developed in the last decade.[4–8] We have synthesized some *d-f* heteronuclear complexes of dinucleating ligands obtained from 3-carboxysalicylaldehyde and several diamines, and have found that the complexes exhibit some interesting properties.[9–17] First M(II)-Ln(III) complexes (M = Cu or VO, Ln = lanthanides) show unique "selective solvation" associated with the heterometal centre depending upon the nature of the solvent.[9,10,17] That is, in pyridine, which contains a nitrogen as a donating atom, solvation takes place preferentially at the copper centre, whereas in an oxygen-containing solvent like *N,N*-dimethylformamide or dimethylsulfoxide, solvation takes place exclusively at the lanthanide centre. Secondly, this selective solvation was extended to the specific binding of substrates which possess both nitrogen and oxygen atoms in the donating groups.[11,13,14,17] 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) observed in the mononuclear Eu(III) complex is markedly decreased on forming the heteronuclear Cu(II)-Eu(III) or V(IV)O-Eu(III) complex.[16,17] These are new properties which have not been reported in the *d-d* systems. However, the *d*-transition metals investigated so far are Cu(II),[9–12,14–16] Co(II)[13] and V(IV)O.[17]

In the present work we have synthesized the hetronuclear Ni(II)-Ln(III) complexes, $NiLn(dhbaen)(NO_3)(H_2O)_2$ (Ln = La, Eu or Gd) and the mononuclear Eu(III) complex, $Eu(Hdhbaen)(H_2O)_3$, where $H_4dhbaen$ is *N,N'-bis*(3-hydroxysalicylidene)ethylenediamine, as reported by Vigato *et al.*,[7,8] in order to examine whether the interaction of the heteronuclear Ni(II)-Ln(III) complex with amino alcohols is similar to that of the heteronuclear Cu(II)-Ln(III) or V(IV)O-Ln(III) complex previously reported with amino alcohols or not. This is of interest because the Ni(II) complex of *N,N'-bis*(salicylidene)ethylenediamine, which is regarded as a Ni(II) complex moiety of the present complex, is known to maintain a square planar structure even in pyridine, without coordination of pyridine molecules at apical positions.[18,19] Another aim is to investigate the effect of the Ni(II) complex moiety on the fluorescence of Eu(III) in the complex.

EXPERIMENTAL

Elemental analyses were carried out at the Service Centre for Elemental Analysis, Kyushu University, Japan. Infrared spectra were measured with a Jasco IR-G spectrometer using KBr disks. Absorption spectra were obtained with a Hitachi 320 spectrophotometer. CD and fluorescence spectra were measured with a Jasco J-20 automatic recording spectropolarimeter and a Shimadzu RF-540 fluorospectrophotometer, respectively.

Synthesis of Ligand

The ligand, *N,N'-bis*(3-hydroxysalicylidene)ethylenediamine ($H_4dhbaen$), was synthesized using a similar method to that reported by Vigato *et al.*,[7] except for the use of ethanol as a solvent. To a solution of 2,3-dihydroxybenzaldehyde (10 mmol, 1.382 g) in ethanol (30 cm^3) was added a solution of ethylenediamine (5.5 mmol, 0.331 g) in ethanol (10 cm^3) with stirring. Soon, orange crystals formed. After the mixture was stirred at room temperature for 1 h, the crystals were collected by suction filtration, washed successively with ethanol and diethylether, and then dried under reduced pressure. The yield was 75% (1.13 g). Anal. calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33%. Found: C, 63.15; H, 5.73; N, 9.50%.

Mononuclear Nickel(II) Complex, [Ni(H_2dhbaen)]

To a solution of 2,3-dihydroxybenzaldehyde (20 mmol, 2.763 g) in methanol (60 cm^3) was added an aqueous solution (50 cm^3) of nickel(II) acetate tetrahydrate (10 mmol, 2.488 g) and then ethylenediamine (10 mmol, 0.601 g). After the mixture was stirred at room temperature for 2 h, brownish red crystals were collected by suction filtration, washed successively with water, methanol and diethylether, and then dried under reduced pressure. The yield was 80% (2.86 g).

Mononuclear Europium(III) Complex, Eu(Hdhbaen)(H_2O)$_3$

Lithium hydroxide monohydrate (4.5 mmol, 0.189 g) in methanol (10 cm^3) was added to a suspension of the ligand, H_4dhbaen, (1.5 mmol, 0.451 g) in methanol (30 cm^3). To the resulting clear solution was added hydrated europium(III) nitrate (1.5 mmol) in methanol (3 cm^3). Soon, orange crystals were deposited. After the mixture was warmed with stirring for 30 mins, the microcrystals were collected by suction filtration, washed with methanol and diethylether, and then dried under reduced pressure. The yield was 94% (0.17 g).

Heteronuclear Nickel(II)-Lanthanide(III) Complexes, NiLn(dhbaen)(NO_3)(H_2O)$_2$ (Ln = La, Eu or Gd)

To a suspension of the mononuclear Ni(II) complex (1.5 mmol, 0.536 g) in methanol (30 cm^3) was added a methanolic solution (6 cm^3) of lithium hydroxide monohydrate (3 mmol, 0.126 g). The mixture was stirred for 1 h at room temperature and hydrated lanthanide nitrate (1.5 mmol) in methanol (3 cm^3) was added. After the mixture was warmed with stirring for 3 h, brownish yellow microcrystals were collected by suction filtration, washed with methanol and diethylether, and then dried under reduced pressure. The yields were almost quantitative in all cases.

RESULTS AND DISCUSSION

Composition of Complexes

According to the method reported by Vigato *et al.*, the composition of Ni(II)-Ln(III) complexes are NiLn(dhbaen)(NO_3)(CH_3OH)$_2$.[8] However, analytical results summarized in Table I demonstrate the complexes obtained by the present method to be dihydrates, NiLn(dhbaen)(NO_3)(H_2O)$_2$.

IR Spectra

IR spectra of Ni(II)-Ln(III) complexes were similar. The ν(C=N) band at 1632 cm^{-1} observed in the free ligand (H_4dhbaen) is lowered to 1610 cm^{-1} in the mononuclear

Table I Elemental analyses for the complexes

Complex	Found(%)(Calcd(%)) C	H	N
Ni(H_2dhbaen)	53.64 (53.83)	3.99 (3.95)	7.81 (7.85)
Eu(Hdhbaen)(H_2O)$_3$	38.00 (38.18)	3.39 (3.81)	5.81 (5.57)
NiLa(dhbaen)(NO_3)(H_2O)$_2$	32.23 (32.47)	2.83 (2.72)	7.04 (7.10)
NiEu(dhbaen)(NO_3)(H_2O)$_2$	31.62 (31.77)	2.49 (2.67)	6.99 (6.95)
NiGd(dhbaen)(NO_3)(H_2O)$_2$	31.06 (31.49)	2.59 (2.64)	6.90 (6.89)

Ni(II) complex and does not shift further in the Ni(II)-Ln(III) complexes. Furthermore, the IR spectrum of the mononuclear Eu(III) complex exhibits the ν(C=N) at 1634 cm^{-1} which is close to the frequency (1632 cm^{-1}) of the free ligand. From these observation, it is suggested that the nickel(II) and lanthanide(III) ions are located at the endogenous N_2O_2-site and the exogenous O_4-site of ligand, respectively, as illustrated in Figure 1.

Specific Binding of Amino Alcohols

Absorption spectra of the Ni(II)-La(III) complex in *N,N*-dimethylformamide (DMF) were measured by adding 2-amino-1-ethanol, in order to investigate the interaction of the Ni(II)-Ln(III) heterometal centre with amino alcohols. As shown in Figure 2, the spectrum is very similar to that measured without additives (substrates). In both cases the *d-d* band of Ni(II) is observed around 18 × 10^3 cm^{-1} as a shoulder. Therefore, it is impossible to discuss the interaction between Ni(II) and amino alcohols from the absorption measurement. However, CD measurements using chiral substrates offer evidence of ligating interaction of amino alcohols with the

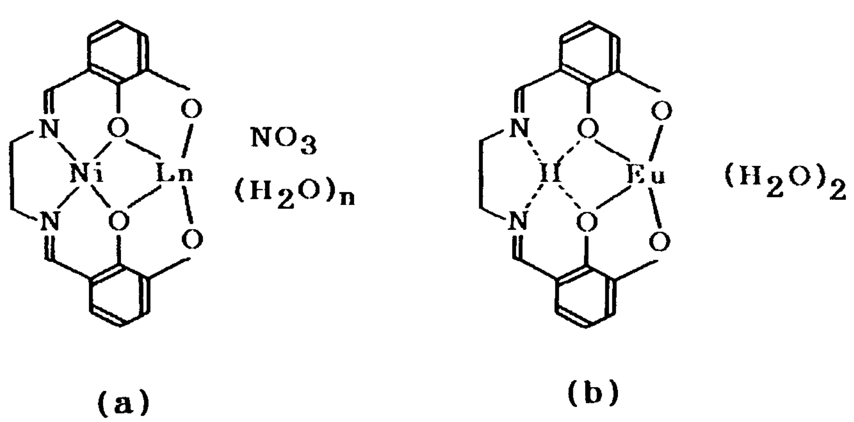

Figure 1 Structures of heteronuclear Ni(II)-Ln(III) (a) and mononuclear Eu(III) (b) complexes.

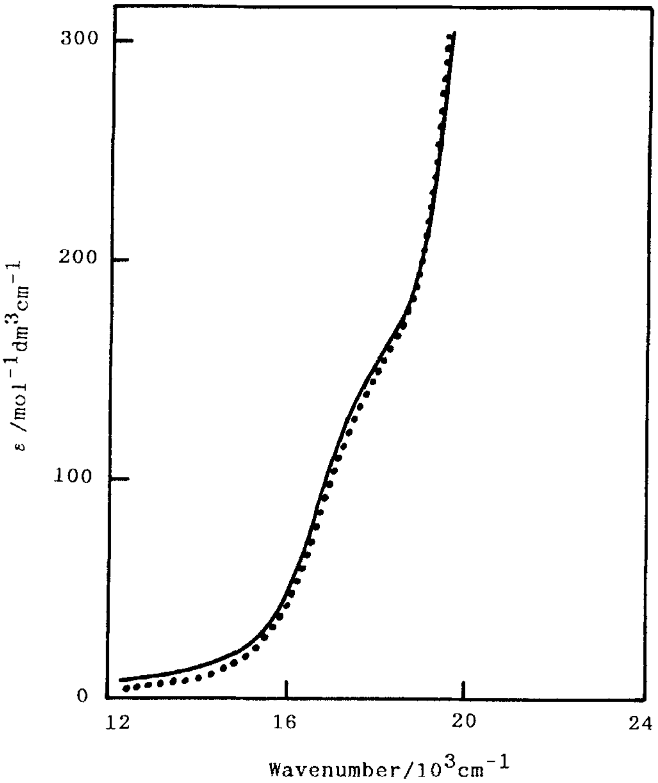

Figure 2 Absorption spectra of the heteronuclear Ni(II)-La(III) complex in DMF. Concentration of complex is 5 × 10^{-3} mol dm^{-3}; (——): with no additive; (····): with 2-amino-1-ethanol (2.5 × 10^{-1} mol dm^{-3}).

heterometal centre (see Figure 3). When (*R*)-(-)-2-amino-1-propanol was added, significant circular dichroism was induced in the *d-d* band region of Ni(II). Such CD activity was not observed when (*S*)-(+)-2-butanol or (*S*)-(+)-1,2-propanediol was added (see also Figure 3). These results indicate that the nitrogen atom of amino alcohols is bound at the Ni(II)-site and that free rotation of amino alcohols with respect to the Ni-N bond is fixed. Such fixation will be achieved by the direct co-ordination of the hydroxyl group of the amino alcohol to the La(III) ion or by the interaction of the hydroxyl group with La(III) centre through hydrogen bonding of the hydroxyl group to DMF or H_2O molecules sited on the La(III) ion, as previously discussed.[13,14,17] Thus, the heteronuclear Ni(II)-Ln(III) complexes were found also to exhibit specific binding of amino alcohols, as well as the previously reported Cu(II)-Ln(III) and V(IV)O-Ln(III) complexes.[11,13,14,17] Here, it should be noted that the Ni(II) complex of *N,N'*-*bis*(salicylidene)ethylenediamine, which is regarded as a Ni(II) complex moiety of the present complex, has a square planar structure without solvating at its apical positions even in a polar solvent like pyridine.[18,19]

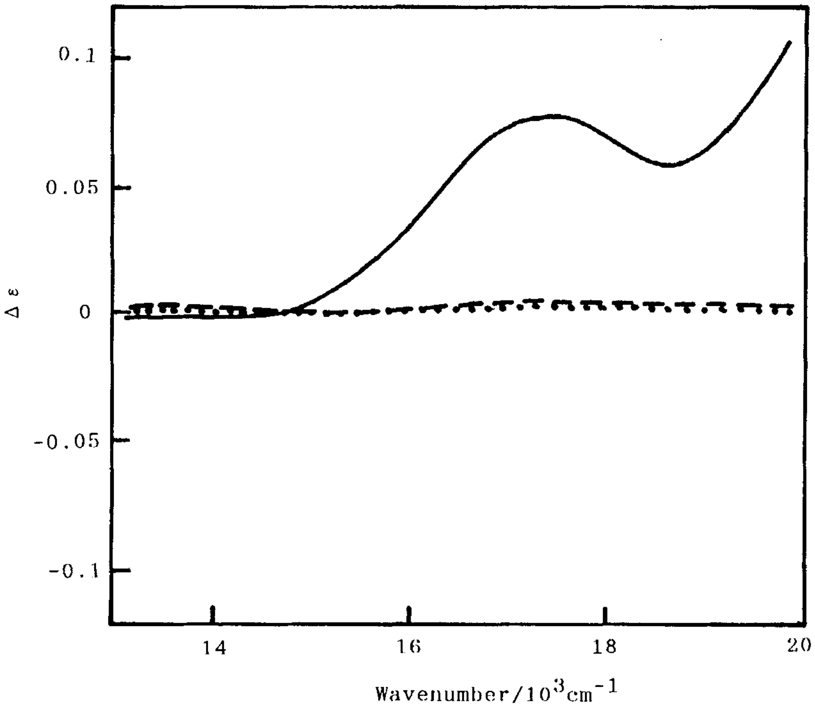

Figure 3 CD spectra of the heteronuclear Ni(II)-La(III) complex in DMF. Concentrations of complex and additives are 2.5 × 10^{-3} and 2.5 × 10^{-1} mol dm^{-3}; (——): with (*R*)-(–)-2-amino-1-propanol; (····): with (*S*)-(+)-2-butanol; (---): with (*S*)-(+)-1,2-propanediol.

Fluorescence Spectra

Figure 4 shows the fluorescence spectra of the mononuclear Eu(III) complex and the Ni(II)-Eu(III) complex in DMF. The spectrum of the mononuclear Eu(III) complex exhibits fluorescence bands attributable to $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$ and $^5D_0 \rightarrow {}^7F_4$ transitions at 586 and 594, 613, 653, and around 700 nm, respectively. The intensities of these bands are markedly decreased in the Ni(II)-Eu(III) complex. In relation to these results, we recently 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)] on 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.[20–22] From these investigations, it was found that the fluorescence intensities of both Eu(III) and Tb(III) are decreased by addition of the above complexes, whereas they are little affected by the addition of simple metal salts such as Cu(NO_3)$_2$·3H_2O, Ni(NO_3)$_2$·6H_2O or Cr(NO_3)$_3$·9H_2O. According to Fragala *et al.*[23,24] and Bencini *et al.*,[25,26] [M(salen)] and [M(saltn)] (M = Cu(II) or Ni(II)) function as bidentate ligands toward lanthanide(III) ions through the two phenolic oxygen atoms. Furthermore, it is generally accepted that the luminescence is decreased by radiationless energy loss through the excited state of other molecules

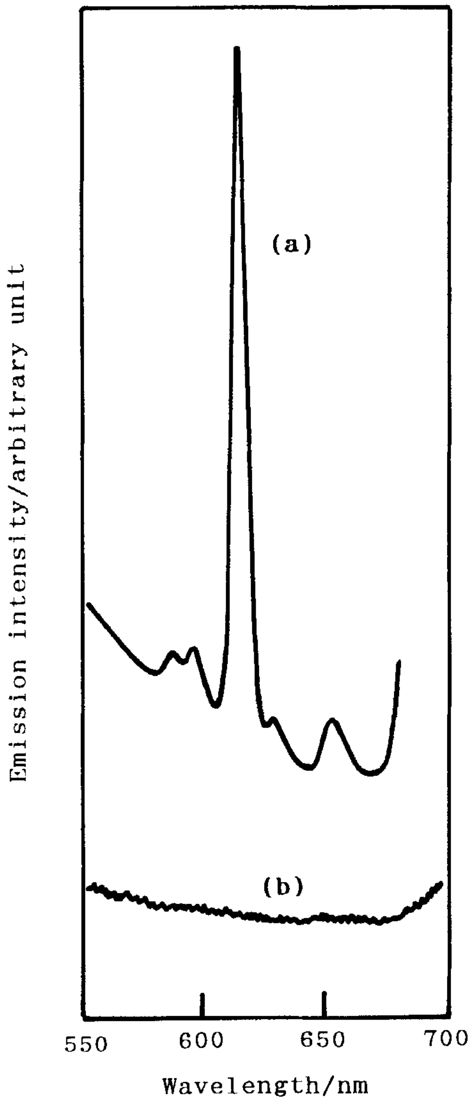

Figure 4 Fluorescence spectra of mononuclear Eu(III) (**a**) and heteronuclear Ni(II)-Eu(III) (**b**) complexes in DMF. The concentration of each complex is 2.5 × 10^{-4} mol dm^{-3}; exciting wavelength is 394 nm; slit widths of excitation and emission sides are 20 and 5 nm, respectively; ordinate scales are × 32 for (**a**) and × 1024 (**b**).

which are located near the exciting species.[27] From these considerations, it is presumed that the fluorescence intensity of the present Ni(II)-Eu(III) complex is quenched by energy transfer from Eu(III) to the Ni(II) centre through the bridging phenolic oxygen atoms, as previously discussed.[16,17]

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