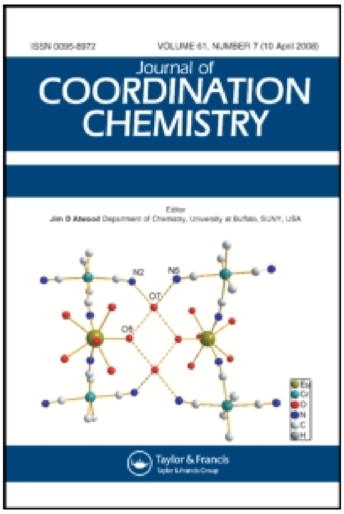

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TEMPLATE SYNTHESES AND PROPERTIES OF COPPER(II)-LANTHANIDE(III) COMPLEXES OF PHENOL-BASED SYMMETRIC AND UNSYMMETRIC DINUCLEATING MACROCYCLES

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TEMPLATE SYNTHESES AND PROPERTIES OF COPPER(II)–LANTHANIDE(III) COMPLEXES OF PHENOL-BASED SYMMETRIC AND UNSYMMETRIC DINUCLEATING MACROCYCLES

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Cu(II)–Ln(III) complexes of H_2(fsal-n,m) ((n,m = (2,3), (3,2) (3,3); Ln = Lanthanide), fsal-n,m-Cu,Ln, have been synthesized by a template reaction, where fsal-n,m^{2-} denotes dinucleating macrocycles with two 2,6-*bis*(iminomethyl)-4-methylphenolate entities combined through two lateral chains, $-(CH_2)_n-$ and $-(CH_2)_m-$, at the imino nitrogens. Temperature dependences of magnetic susceptibilities for the Cu(II)–Gd(III) complexes showed that an intramolecular ferromagnetic interaction operates between Cu(II) and Gd(III) ions in fsal-2,3-Cu,Gd and fsal-3,2-Cu,Gd. Absorption spectra suggested that substrates possessing N- and O-donor groups such

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[*] Corresponding author.

as amino alcohols are specifically bound at the Cu–Ln centre of fsal-2,3-Cu,Ln, through the nitrogen to the copper site and through the oxygen to the lanthanide site. The fluorescence intensity of Eu(III) decreased drastically on forming the Cu–Eu complex.

Keywords: Heteronuclear complex; lanthanide complex; dinucleating ligand; Schiff base

INTRODUCTION

Macrocycles derived from two 2,6-diformyl-4-methylphenol units and two diamines have been widely used for the syntheses of heteronuclear complexes, since such types of ligand were first reported by Pilkington and Robson[1] and by one of the present authors.[2] Heteronuclear complexes of these macrocycles with various lateral methylene chain lengths (Figure 1(b)) are generally synthesized by the reaction of a diamine with the corresponding mononuclear complex precursors of acyclic ligands (Figure 1(a)) prepared in advance, in the presence of a second metal ion as a template. Such a stepwise template reaction makes it possible to obtain the heteronuclear complexes even when macrocycles are symmetric ($n = m$ in Figure 1(b)) in their chemical structures. However, heteronuclear complexes of 2,6-diformyl-4-methylphenol-based macrocycles reported so far have been limited to those composed of only d-transition metal ions[3,4a,b] or d-transition metal and lead(II) ions.[4]

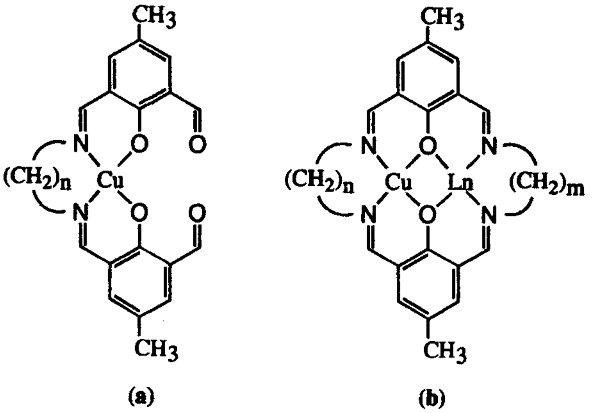

FIGURE 1 Chemical structures of fsal-*n*-Cu (a) and fsal-*n*,*m*-Cu,Ln (b).

Recently, we obtained the Cu(II)–Ln(III) complexes of the acyclic ligand, H_2(fsal-3), by the reaction of Ln(III) ions with the mononuclear copper(II) complex, fsal-3-Cu ($n = 3$ in Figure 1(a)), where lanthanide(III) ions are expressed as Ln(III) and located at the outer O_4-coordination site.[5] This suggests that the lanthanides may function as template ions, as well as d-transition metal ions and lead(II) ion. Thus, we tried to prepare the Cu(II)–Ln(III) complexes (fsal-2,2-Cu,Ln in Figure 1(b)) of a symmetric macrocycle, H_2(fsal-2,2), and were successful in isolating Cu(II)–Ln(III) complexes.[6] Except for this, reports are not available on the template syntheses of d–f heteronuclear complexes of dinucleating macrocycles, to the best of our knowledge, though it is meaningful for the further development of synthetic methods for new d–f heteronuclear complexes to challenge systematic studies of template syntheses by a series of lanthanides.

In the present work Cu(II)–Ln(III) complexes (fsal-2,3-Cu,Ln, fsal-3,2-Cu,Ln and fsal-3,3-Cu,Ln in Figure 1(b)) of symmetric and unsymmetric macrocycles were synthesized by the stepwise template reaction and characterized. Some properties arising from the co-operative effect of Cu(II) and lanthanide(III) ions were investigated.

EXPERIMENTAL

Elemental analyses of C, H, and N were carried out at the Service Centre for Elemental Analysis, Kyushu University, Japan. Infrared spectra were measured with a Hitachi 270-50 spectrophotometer. Absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer. Magnetic susceptibility measurements for fsal-2,3-Cu,Gd and fsal-3,2-Cu,Gd were carried out in the range of liquid helium temperature to room temperature with a HOXAN HSM-D SQUID Magnetometer at Kyushu University, Japan. The magnetic susceptibilities of fsal-3,3-Cu,Gd were measured in the range of liquid helium temperature to 260 K by the Faraday method with an Oxford Magnetic Balance at the Instrument Centre, Institute for Molecular Science, Japan. Fluorescence spectra were measured with a Shimadzu RF-540 fluorospectrophotometer.

2,6-Diformyl-4-methylphenol was prepared according to the method reported by Ullmann and Brittners.[7] *N,N′-Bis*(3-formyl-5-methylsalicylidene)ethylenediaminato-copper(II) (fsal-2-Cu) and *N,N′-bis*(3-formyl-5-methylsalicylidene)-1,3-propanediaminato-copper(II) (fsal-3-Cu) were synthesized by the method previously reported.[2b] All chemicals were of reagent grade and used as purchased.

Synthesis of Cu(II)–Ln(III) Complexes of H_2(fsal-2,3), fsal-2,3-Cu,Ln (Ln = La, Nd, Eu, Gd, Tb)

A methanolic solution (1.5–4 cm^3) of hydrated lanthanide(III) nitrate (1 mmol) was added with stirring at room temperature to a suspension of mononuclear copper(II) complex, fsal-2-Cu (1 mmol), in methanol (30 cm^3). After the mixture was stirred at room temperature for 2 h, a methanolic solution (1 cm^3) of 1,3-propanediamine (1 mmol) was added. The mixture was warmed at about 40°C with stirring for 2 h. Yellowish-brown crystals thus obtained were collected by suction filtration, washed successively with methanol and diethyl ether, and then dried in the open air. The yields were ~90% for all of the fsal-2,3-Cu,Ln. Elemental analyses are summarized in Table I.

Synthesis of Cu(II)–Ln(III) Complexes of H_2(fsal-3,2), fsal-3,2-Cu,Ln (Ln = La, Ce, Nd, Eu, Gd, Dy, Ho, Er, Tm)

A methanolic solution (1.5–6 cm^3) of hydrated lanthanide(III) nitrate (1 mmol) was added with stirring at room temperature to a suspension of mononuclear copper(II) complex, fsal-3-Cu (1 mmol), in methanol (25 cm^3). Soon, the suspension became clear. Then, greenish crystals began to precipitate except for the addition of Er(III) and Tm(III). Only a very small amount of crystals was precipitated after the formation of the clear solution when Er(III) was added and no crystals precipitated when Tm(III) was added. After the mixture was stirred at room temperature for 1 h, a methanolic solution (2 cm^3) of ethylenediamine (1 mmol) was added. The mixture was warmed at about 40°C with stirring for 3 h. Crystals thus obtained were collected by suction filtration, washed with methanol and then dried over P_2O_5 under reduced pressure. The yields were ~90% for fsal-3,2-Cu,La, fsal-3,2-Cu,Ce, fsal-3,2-Cu,Nd, fsal-3,2-Cu,Eu and fsal-3,2-Gd, ~75% for fsal-3,2-Cu,Dy and fsal-3,2-Cu,Ho, ~45% for fsal-3,2-Cu,Er, and ~30% for fsal-3,2-Cu,Tm. Elemental analyses are summarized in Table II.

TABLE I Elemental analyses for fsal-2,3-Cu,Ln complexes

Complex	*Found* (%) (*Calcd* (%))		
	C	*H*	*N*
fsal-2,3-Cu,La[a]	35.30 (35.56)	3.22 (3.11)	12.21 (12.62)
fsal-2,3-Cu,Nd[b]	33.93 (33.76)	3.19 (3.45)	11.67 (11.98)
fsal-2,3-Cu,Eu[b]	33.21 (33.44)	3.14 (3.42)	11.44 (11.87)
fsal-2,3-Cu,Gd[c]	34.28 (34.35)	3.34 (3.88)	10.66 (10.45)
fsal-2,3-Cu,Tb[c]	34.13 (34.27)	3.35 (3.88)	10.61 (10.43)

[a] Values in parentheses are those calculated for anhydrate, $C_{23}H_{24}N_4O_2CuLa(NO_3)_3$. [b] Values in parentheses are those calculated for dihydrate, $C_{23}H_{24}N_4O_2CuLn(NO_3)_3(H_2O)_2$. [c] Values in parentheses are those calculated for trihydrate, $C_{23}H_{24}N_4O_2CuLn(NO_3)_2(OH)(H_2O)_3$.

Synthesis of Cu(II)-Ln(III) Complexes of H_2(fsal-3,3), fsal-3,3-Cu,Ln (Ln = La, Ce, Eu, Gd, Dy, Ho)

A methanolic solution (1.5–6 cm^3) of hydrated lanthanide(III) nitrate (1 mmol) was added with stirring at room temperature to a suspension of mononuclear copper(II) complex, fsal-3-Cu (1 mmol), in methanol (25 cm^3). Soon, the suspension became clear and greenish crystals began to precipitate. After the mixture was stirred at room temperature for 1 h, a methanolic solution (2 cm^3) of 1,3-propanediamine (1 mmol) was added. The mixture was warmed at about 40°C with stirring for 3 h. Crystals thus obtained were collected by suction filtration, washed with methanol and then dried over P_2O_5 under reduced pressure. The yields were ~90% for fsal-3,3-Cu,La, fsal-3,3-Cu,Ce, fsal-3,3-Cu,Eu and fsal-3,3-Gd, ~35% for fsal-3,3-Cu,Dy, and ~5% for fsal-3,3-Cu,Ho. Elemental analyses are summarized in Table III.

TABLE II Elemental analyses for fsal-3,2-Cu,Ln complexes

Complex	*Found* (%) (*Calcd* (%))		
	C	*H*	*N*
fsal-3,2-Cu,La[a]	35.18 (35.56)	3.13 (3.11)	12.45 (12.62)
fsal-3,2-Cu,Ce[b]	35.20 (35.58)	3.47 (3.48)	12.00 (12.10)
fsal-3,2-Cu,Nd[b]	34.50 (35.40)	3.42 (3.47)	11.81 (12.04)
fsal-3,2-Cu,Eu[b]	34.37 (35.07)	3.39 (3.43)	11.68 (11.93)
fsal-3,2-Cu,Gd[c]	34.25 (34.10)	3.47 (3.58)	11.51 (11.60)
fsal-3,2-Cu,Dy[c]	34.09 (33.89)	3.51 (3.55)	11.33 (11.53)
fsal-3,2-Cu,Ho[c]	34.06 (33.79)	3.51 (3.54)	11.34 (11.49)
fsal-3,2-Cu,Er[c]	33.67 (33.70)	3.43 (3.54)	11.43 (11.46)
fsal-3,2-Cu,Tm[b]	34.01 (34.36)	3.41 (3.36)	11.61 (11.69)

[a] Values in parentheses are those calculated for anhydrate, $C_{23}H_{24}N_4O_2CuLa(NO_3)_3$. [b] Values in parentheses are those calculated for monomethanolate, $C_{23}H_{24}N_4O_2CuLn(NO_3)_3(CH_3OH)$. [c] Values in parentheses are those calculated for monohydratemonomethanolate, $C_{23}H_{24}N_4O_2CuLn(NO_3)_3(H_2O)(CH_3OH)$.

TABLE III Elemental analyses for fsal-3,3-Cu,Ln complexes

Complex	*Found* (%) (*Calcd* (%)[a])		
	C	*H*	*N*
fsal-3,3-Cu,La	35.86 (35.63)	3.38 (3.49)	12.08 (12.12)
fsal-3,3-Cu,Ce	35.33 (35.58)	3.29 (3.48)	11.83 (12.10)
fsal-3,3-Cu,Eu	35.25 (35.07)	3.45 (3.43)	11.85 (11.93)
fsal-3,3-Cu,Gd	35.03 (34.84)	3.34 (3.41)	11.77 (11.85)
fsal-3,3-Cu,Dy	35.32 (34.62)	3.33 (3.39)	11.77 (11.78)
fsal-3,3-Cu,Ho	35.39 (34.52)	3.31 (3.38)	11.79 (11.74)

[a] Values for monohydrate, $C_{24}H_{26}N_4O_2CuLn(NO_3)_3(H_2O)$.

RESULTS AND DISCUSSION

General Characterization

In the present synthetic condition, the yields of fsal-2,3-Cu,Ln were extremely low when a lanthanide(III) ion heavier than Tb(III) was used as a template ion. Crystals of fsal-3,2-Cu,Ln were not isolated when Yb(III) or Lu(III) was used as the template ion. This was also the case for fsal-3,3-Cu,Ln when the template ion was Er(III), Tm(III), Yb(III) or Lu(III). Both mononuclear copper(II) complexes, fsal-2-Cu and fsal-3-Cu, of acyclic ligands, H_2(fsal-2) and H_2(fsal-3), showed two strong and sharp bands attributable to ν(C=O) and the ν(C=N) around 1670 and 1630 cm^{-1}, respectively, as reported previously.[2b,5] In the Cu(II)–Ln(III) complexes, the band due to ν(C=O) disappeared, and only a strong and relatively broad band was observed at 1630–1640 cm^{-1} due to ν(C=N), indicating the formation of macrocyclic Schiff bases. From these observations and elemental analyses, the compositions of complexes given in Tables I–III can be proposed. Here, the colours of fsal-2,3-Cu,Ln and fsal-3,2-Cu,Ln are yellowish-brown and green, respectively, similar to those of fsal-2,2-Cu,Ln[6] and fsal-3,3-Cu,Ln. Indeed, the absorption spectra of fsal-2,3-Cu,Ln and fsal-3,2-Cu,Ln in DMF showed d–d bands around 18.0×10^3 and $16.0 \times 10^3\,cm^{-1}$, respectively, very similar in energy to those of fsal-2,2-Cu,Ln ($18.0–18.5 \times 10^3\,cm^{-1}$)[6] and fsal-3,3-Cu,Ln (around $16.0 \times 10^3\,cm^{-1}$, respectively). These observations suggest that the Cu(II) ion in fsal-2,3-Cu,Ln is located in the coordination-sphere of a 6-5-6 membered ring system with a lateral $-(CH_2)_2-$ chain and that the Cu(II) ion in fsal-3,2-Cu,Ln is located in the coordination-sphere of a 6-6-6 membered ring system with a lateral $-(CH_2)_3-$ chain; that is, trans-metallation does not occur during the template reactions. This is different from the fact[2b] that the Cu(II) ion of mononuclear Cu(II) complex, fsal-3-Cu, of acyclic ligand, fsal-3^{2-}, migrates from the coordination sphere with the 6-6-6 membered ring system to that with the 6-5-6 ring system when fsal-3-Cu reacts with ethylenediamine to form the mononuclear Cu(II) complex of macrocycle, fsal-$3,2^{2-}$.

Magnetic Properties

Magnetic properties were investigated for fsal-2,3-Cu,Gd, fsal-3,2-Cu,Gd and fsal-3,3-Cu,Gd. Figure 2 shows the temperature dependences of the magnetic susceptibilities per CuGd unit (χ_M), the reciprocal magnetic

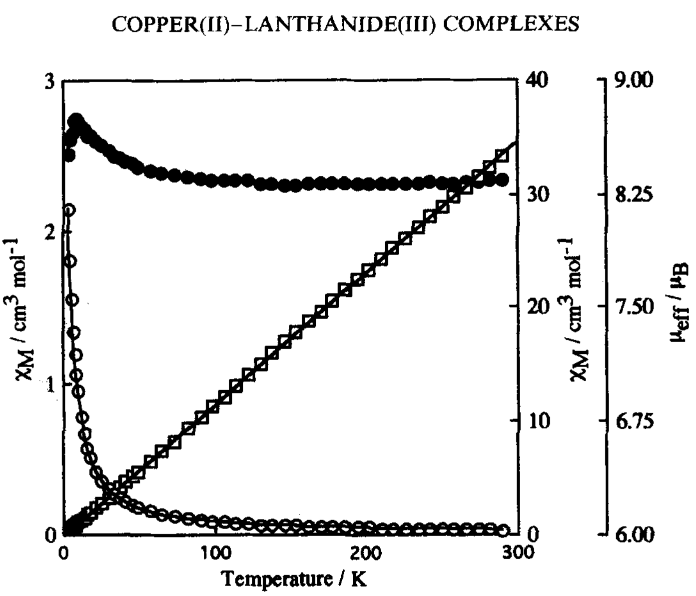

FIGURE 2 Temperature dependences of χ_M (○), $1/\chi_M$ (□) and μ_{eff} (●) of fsal-2,3-Cu,Gd; χ_M is the magnetic susceptibility per CuGd unit and μ_{eff} is the effective magnetic moment.

susceptibilities ($1/\chi_M$) and the effective magnetic moments (μ_{eff}) of fsal-2,3-Cu,Gd. The plot of $1/\chi_M$ *vs* T obeys the Curie–Weiss law ($\chi_M = C/(T-\theta)$) with Weiss constant, $\theta = +0.97$ K, suggesting the existence of a weak ferromagnetic interaction. The effective magnetic moment at 290.2 K is 8.34μ_B which is somewhat higher than the spin-only value (8.12μ_B) in the absence of the magnetic interaction of the present spin-system ($S_{Cu} = \frac{1}{2}$, $S_{Gd} = \frac{7}{2}$). It should be noted here that the ground state of Gd(III) is $^8S_{7/2}$ and that the next excited state is well separated in energy, so that μ_{eff} value of Gd(III) can be approximated by the spin-only equation, $\mu_{eff} = [4S(S+1)]^{1/2}$, without considering the contribution of orbital angular momentum. As the temperature is lowered, the magnetic moment increases gradually from 8.34μ_B at 290.2 K, reaches a maximum value of 8.74μ_B at 8 K and then decreases to 8.51μ_B at 4.2 K. Such an increase in magnetic moment with lowering of temperature suggests the operation of an intramolecular ferromagnetic spin–spin interaction between Cu(II) and Gd(III) ions, because the spin-only value for the spin state $S = 4$ resulting from the ferromagnetic interaction between Cu(II) and Gd(III) is 8.94μ_B. A decrease in the magnetic moment below 8 K may be attributed to an intermolecular antiferromagnetic interaction. The analyses of magnetic data were carried out using a spin-only expression (1) which includes a correction term (θ) of intermolecular interaction, where a spin-Hamiltonian is defined as $\mathcal{H} = -2JS_{\mathrm{Cu}} \cdot S_{\mathrm{Gd}}$.

$$\chi_{\mathrm{M}} = \frac{4Ng^2\beta^2}{k(T-\theta)} \frac{15 + 7\exp(-8J/kT)}{9 + 7\exp(-8J/kT)}. \tag{1}$$

The magnetic data were well reproduced by the best-fit parameters $g = 2.04$, $J = +1.9\,\mathrm{cm}^{-1}$ and $\theta = -0.6\,\mathrm{K}$. Theoretical curves using the best-fit parameters are represented by solid lines in Figure 2. The positive J value is consistent with the intramolecular ferromagnetic interaction inferred from the temperature dependence of μ_{eff}.

As shown in Figure 3, the magnetic behaviour of fsal-3,2-Cu,Gd is essentially similar to that of fsal-2,3-Cu,Gd, where the Curie–Weiss plot gave Weiss constant of +1.19 K and the magnetic moment, increasing from $8.19\mu_{\mathrm{B}}$ at 290.2 K to the maximum value of $8.80\mu_{\mathrm{B}}$ at 7.9 K, decreased to $8.67\mu_{\mathrm{B}}$ at 4.2 K. The experimental data are best-fitted using equation (1) with parameters $g = 2.00$, $J = 1.8\,\mathrm{cm}^{-1}$ and $\theta = -0.3\,\mathrm{K}$. Theoretical curves using these parameters are shown as solid lines.

The observations concerning fsal-3,3-Cu,Gd are different from those for fsal-2,3-Cu,Gd and fsal-3,2-Cu,Gd (see Figure 4). Only a decrease in

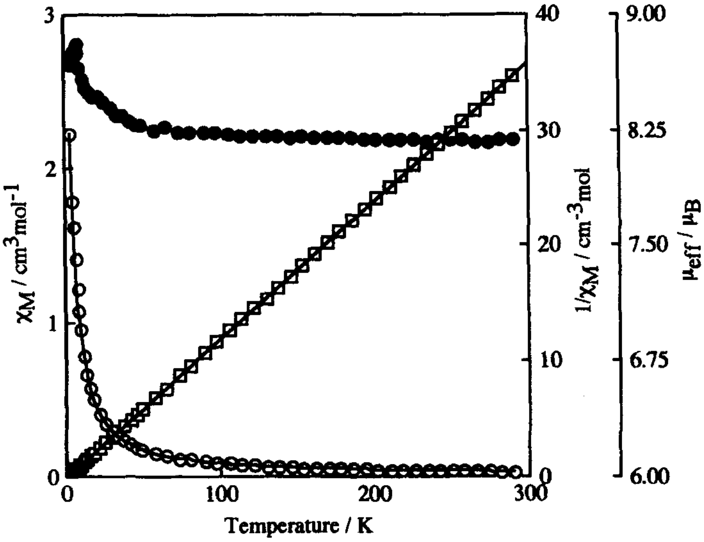

FIGURE 3 Temperature dependences of χ_{M} (○), $1/\chi_{\mathrm{M}}$ (□) and μ_{eff} (●) of fsal-3,2-Cu,Gd; χ_{M} is the magnetic susceptibility per CuGd unit and μ_{eff} is the effective magnetic moment.

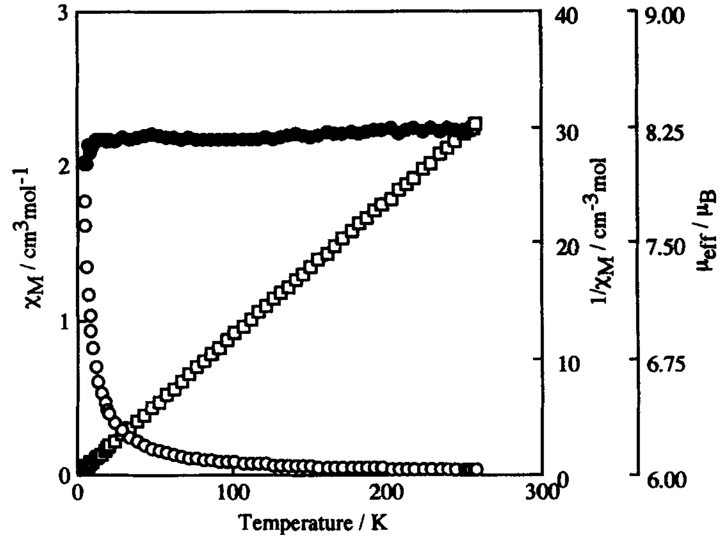

FIGURE 4 Temperature dependences of χ_M (○), $1/\chi_M$ (□) and μ_{eff} (●) of fsal-3,3-Cu,Gd; χ_M is the magnetic susceptibility per CuGd unit and μ_{eff} is the effective magnetic moment.

magnetic moment was observed from $8.25\mu_B$ at 257.3 K to $8.02\mu_B$ at 4.5 K. This may be attributed to the relatively larger contribution of an intermolecular antiferromagnetic interaction, on the basis of the previous studies[8–12] that the interaction between Cu(II) and Gd(III) ions is always ferromagnetic.

Specific Binding of Organic Compounds toward the Cu(II)–Ln(III) Heterometal Centre

The absorption spectra of fsal-2,3-Cu,La in DMF were measured in the d–d band region by adding various amino alcohols, diols or amines as substrate. Some typical spectra are shown in Figure 5 and the numerical data of absorption maxima are summarized in Table IV; fsal-2,3-Cu,La showed its d–d absorption maximum at $18.14 \times 10^3\,\mathrm{cm}^{-1}$ when no substrate was added. The addition of 1,2-ethanediol or 1,3-propanediol as a substrate did not change the spectrum, whereas the addition of 2-aminoethanol or 3-amino-1-propanol shifts the d–d band toward lower frequency. These results suggest that the aminoalcohols coordinate to the copper at the nitrogen atom. In order to confirm such coordination, the spectrum was measured by adding *N*,*N*-dimethylethanolamine as substrate, the nitrogen of which will not easily interact with copper because of the steric effect of

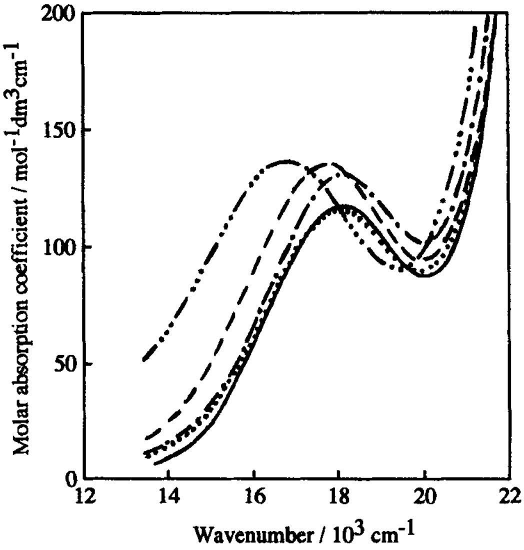

FIGURE 5 Typical absorption spectra of fsal-2,3-Cu,La in DMF solution of various additives. Concentrations of fsal-2,3-Cu,La and each additive are 2×10^{-3} and 0.1 mol dm^{-3}, respectively; (—): without additive; (- - -): with 1,2-ethanediol; (– · · · –): with 2-aminoethanol; (---): with 3-aminopropane; (· · ·): with *N*,*N*-dimethylaminoethanol.

TABLE IV D–d absorption band maxima for fsal-2,3-Cu,La in DMF solutions of various additives[a]

Additive	$\nu_{max}/10^3\,cm^{-1}$ (ε/mol^{-1} dm^3 cm^{-1})
None	18.14 (119)
1,2-Ethanediol	18.13 (132)
1,3-Propanediol	18.14 (134)
2-Aminoethanol	16.80 (136)
3-Amino-1-propanol	17.61 (140)
3-Aminopropane	17.86 (134)
N,*N*-Dimethylaminoethanol	18.01 (117)

[a] Concentrations of complex and each additive are 2.0×10^{-3} and 0.1 mol dm^{-3}, respectively.

two methyl groups. As expected, the d–d band absorption maximum was little influenced. Similar changes by the addition of substrates were also observed for fsal-2,3-Cu,Gd. These results support the specific coordination of the nitrogen atom of amino alcohols to the copper. It is plausible that the alcoholic oxygen of amino alcohols interacts with the lanthanide site, though the absorption data give no information about the behaviour of such alcoholic oxygen atoms.[5,6,13]

On the contrary, the addition of 2-aminoethanol or 3-amino-1-propanol to DMF solutions of fsal-3,2-Cu,Ln and fsal-3,3-Cu,Ln sometimes shifted the d–d band toward higher frequency, though the addition of 1,2-ethanediol or 1,3-propanediol did not. These somewhat different observations from fsal-2,2-Cu,Ln[6] and fsal-2,3-Cu,Ln may be due to structural differences; fsal-2,2-Cu,Ln and fsal-2,3-Cu,Ln possess a 6-5-6 membered ring system around Cu(II), whereas fsal-3,2-Cu,Ln and fsal-3,3-Cu,Ln possess a 6-6-6 membered ring system. In order to interpret this observation, further investigations are in progress.

Fluorescence Property

Some lanthanide ions and their complexes exhibit a characteristic fluorescence. Also in this work the fluorescence spectra of fsal-2,3-Cu,Eu, fsal-3,2-Cu,Eu and fsal-3,3-Cu,Eu in DMF were measured in order to investigate the effect of an adjacent metal ion on the fluorescence of Eu(III), where the wavelength of exciting light was 394 nm (which elevates the energy level of Eu(III) from the ground state, $^7F_0$, to one of the excited states, $^5L_6$). As shown in Figure 6, Eu(III) nitrate gives well-known 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

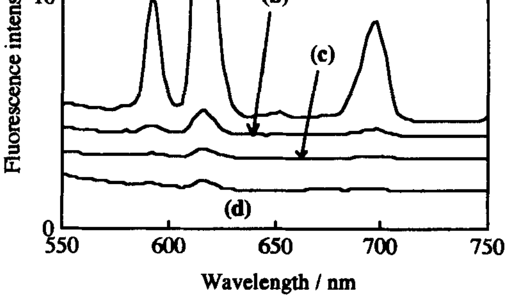

FIGURE 6 Fluorescence spectra of $Eu(NO_3)_3 \cdot 6H_2O$ (a), fsal-2,3-Cu,Eu (b), fsal-3,2-Cu,Eu (c), and fsal-3,3-Cu,Eu (d) in DMF. Concentration of $Eu(NO_3)_3 \cdot 6H_2O$ and each complex is 2×10^{-4} mol dm^{-3}. Exciting wavelength is 394 nm. Slit widths of excitation side and emission side are 20 and 5 nm, respectively. Ordinate scale of data processor is ×32 for all measurements.

around 590, 615, 650 and 700 nm, respectively. These bands are almost quenched when Cu(II)–Eu(III) complexes are formed. From the generally accepted view that luminescence decreases by the radiationless energy loss from other molecules located near to the exciting species,[14] such fluorescence decrease may be attributable to the radiationless energy loss after the intramolecular energy transfer from the excited Eu(III) to the adjacent Cu(II) complex moieties. We have reported similar fluorescence quenching of other M-Eu and M-Tb complexes (M=Cu(II), Ni(II), V(IV)O, Fe(III) and Co(III)).[5,6,13d–g,15]

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