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Synthesis and properties of copper(II)–lanthanide(III) complexes of N,N′-bis(3-formyl-5-methylsalicylidene)-1,3-propanediamine

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Abstract—Heteronuclear copper(II)–lanthanide(III) complexes of H_2(Fsal-3), CuLn(Fsal-3)$(NO_3)_3(CH_3OH)_{0.5}$ (Ln : La, Nd, Eu, Gd or Ho), were synthesized and characterized, where H_2(Fsal-3) denotes N,N′-bis(3-formyl-5-methylsalicylidene)-1,3-propanediamine, and Cu^{II} and Ln^{III} are located at the N_2O_2- and O_4-coordination sites of ligand, respectively. The bonding behavior of amino alcohols toward the Cu–Ln heterometal centre was discussed, based on the absorption spectra and circular dichroism. The fluorescence intensity of Eu^{III} decreased markedly in the Cu–Eu complex. Cryomagnetic measurements (4.2–260 K) for the Cu–Gd complex revealed that the spin coupling between Cu^{II} and Gd^{II} ions is ferromagnetic with coupling constant $J = +0.8\ cm^{-1}$, on the basis of the spin-Hamiltonian $\mathcal{H} = -2JS_{Cu} \cdot S_{Gd}$. © 1997 Elsevier Science Ltd

Keywords: heteronuclear complex; copper(II)–lanthanide(III) complex; electronic spectra; specific binding of amino alcohol; magnetic property; fluorescent property.

Heterometal dinuclear complexes have been numerously studied in order to develop the catalytic reactions associated with multi-electron transfer [1], to elucidate the mechanism of the spin-exchange interaction between paramagnetic metal ions [2], and to mimic the active sites of some metalloenzymes [3]. A general method for the preparation of heterometal dinuclear complexes is the use of dinucleating ligands which possess two dissimilar coordination sites. A number of such compartmental ligands have been synthesized and many heterometal dinuclear complexes with these ligands have been reported. However, few reports [4–22] are available on the heteronuclear complexes comprising a *d*-transition metal ion and a lanthanide ion (*d*–*f* heteronuclear complexes), compared with the heteronuclear complexes comprising only the *d*-transition metal ions (*d*–*d* heteronuclear com-

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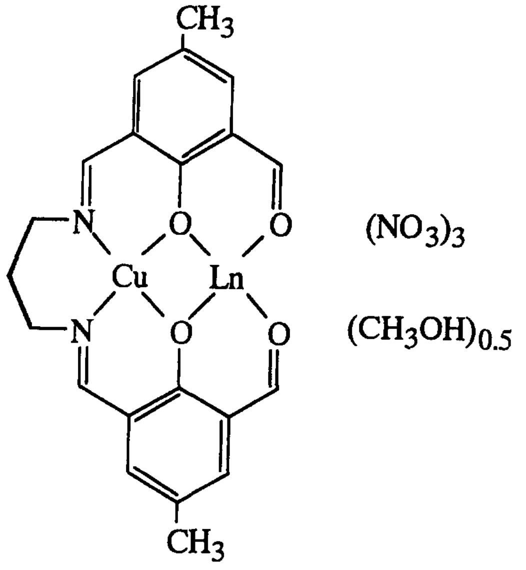

Fig. 1. Chemical structure of dinuclear complexes.

plexes), though some new unique properties which are not exhibited by the *d–d* heteronuclear complexes are expected.

In the present work, we have prepared and characterized the heteronuclear Cu^{II}–Ln^{III} complexes, $CuLn(Fsal\text{-}3)(NO_3)_3(CH_3OH)_{0.5}$ (abbreviated hereafter as Fsal-3-Cu,Ln : Ln = La, Nd, Eu, Gd or Ho), and their absorption, CD (circular dichroism) and fluorescence spectra and temperature dependence of magnetic susceptibilities have been investigated, where $H_2(Fsal\text{-}3)$ is N,N′-bis(3-formyl-5-methylsalicylidene)-1,3-propanediamine, (see Fig. 1).

EXPERIMENTAL

Elemental analyses of carbon, hydrogen and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University, Japan. The contents of copper and lanthanides were determined by the EDTA titration of aqueous solution of copper(II) nitrate and lanthanide(III) nitrate prepared by dissolving in HNO_3 after the complex was ignited. IR spectra were measured with a Hitachi 270-50 spectrophotometer on KBr disks. Electronic and CD (circular dichroism) spectra were obtained with a Shimadzu UV-240 spectrophotometer and a JASCO J-20 automatic recording spectropolarimeter, respectively. Fluorescence spectra were measured with a Shimadzu RF-540 fluorospectrophotometer. Magnetic susceptibilities were determined in the range of liquid helium temperature to *ca* 260 K by the Faraday method with an Oxford Magnetic Balance, at the Instrument Center, Institute for Molecular Science, Japan.

2,6-Diformyl-4-methylphenol was prepared according to the method reported by Ullmann and Brittners [23]. N,N′-Bis(3-formyl-5-methylsalicylidene)-1,3-propanediamine (H_2Fsal-3) was obtained by treating 2,6-diformyl-4-methylphenol with 1,3-diaminopropane in ethanol in the 1 : 1 molar ratio [24]. Mononuclear copper(II) complex of H_2Fsal-3 (abbreviated as Fsal-3-Cu) was synthesized by adding an aqueous solution of the equivalent amount of copper(II) acetate monohydrate to the H_2Fsal-3 in ethanol [24].

Synthesis of the heteronuclear Cu^{II}–Ln^{III} *complexes,* $CuLn(Fsal\text{-}3)(NO_3)_3(CH_3OH)_{0.5}$ (Fsal-3-Cu,Ln) (Ln = La, Nd, Eu, Gd or Ho)

A methanolic solution (4 cm^3) of lanthanide (III) nitrate hydrate (1.2 mmol) was added to a suspension of the mononuclear copper(II) complex, Fsal-3-Cu (1.2 mmol), in methanol (30 cm^3). Soon, the suspension became clear and then the greenish crystal began to be precipitated. After the mixture was stirred at room temperature for 0.5–1 h, the crystals were collected by suction filtration, washed with methanol and then dried over P_2O_5 under reduced pressure. The yields were 65–70% for Fsal-3-Cu,La, Fsal-3-Cu,Nd, Fsal-3-Cu,Eu and Fsal-3-Cu,Gd, and 50% for Fsal-3-Cu,Ho.

RESULTS AND DISCUSSION

General characterization

From the analytical results summarized in Table 1, it can be proposed that the composition of heteronuclear complexes, Fsal-3-Cu,Ln, obtained in this work is $CuLn(Fsal\text{-}3)(NO_3)_3(CH_3OH)_{0.5}$. The addition of Er(III) to the mononuclear copper(II) complex gave also the greenish crystals which seem to have the same composition as Fsal-3-Cu, Ln (Ln = La, Nd, Eu, Gd or Ho) from the analyses of Cu^{II} and Er^{III}, though the yield is very low. The

Table 1. Elemental analyses of complexes

	Found(%) (Calc.)[a]				
Complex	C	H	N	Cu	Ln
Fsal-3-Cu,La	33.8	2.9	9.2	8.2	17.8
	(33.6)	(2.9)	(9.1)	(8.3)	(18.1)
Fsal-3-Cu,Nd	33.2	2.8	9.0	8.1	18.4
	(33.4)	(2.9)	(9.1)	(8.2)	(18.6)
Fsal-3-Cu,Eu	32.8	2.9	9.0	7.8	19.5
	(33.0)	(2.8)	(9.0)	(8.1)	(19.4)
Fsal-3-Cu,Gd	32.7	2.8	8.9	7.8	19.4
	(32.8)	(2.8)	(8.9)	(8.1)	(20.0)
Fsal-3-Cu,Ho	32.2	2.7	8.9	7.4	20.8
	(32.5)	(2.8)	(8.8)	(8.0)	(20.8)

[a] Values for $CuLn(Fsal\text{-}3)(NO_3)_3(CH_3OH)_{0.5}$ ($C_{21.5}H_{22}N_5O_{13.5}CuLn$).

addition of Tm^{III}, Yb^{III} and Lu^{III} which are heavier than Er^{III} gave no crystals in the present condition, suggesting the possibility of the separation of these three lanthanides from others. The IR spectrum of Fsal-3-Cu shows the sharp ν(C=O) and ν(C=N) bands at about 1670 and 1630 cm^{-1}, respectively, as is previously reported [24]. On the other hand, all of Fsal-3-Cu,Ln show only a strong and broad band near 1645 cm^{-1}. This may result from the red-shift of the ν(C=O) by the coordination of carbonyl oxygens to the lanthanide ion. From these observations and by the analogy with the HSAB (Hard and Soft Acids and Bases) sense, it is suggested that the copper(II) and lanthanide(III) ions are located at the endogenous N_2O_2 site and the exogenous O_4 site of the ligand, respectively, as illustrated in Fig. 1.

Electronic spectra

Some of the electronic spectra determined on Nujol mulls are shown in Fig. 2. The mononuclear copper(II) complex, Fsal-3-Cu, gives the *d-d* absorption as a shoulder near 600 nm. However, the heteronuclear complexes, Fsal-3-Cu,Ln, exhibit their *d–d* bands as an apparent absorption maximum at 590 nm for Fsal-3-Cu,La, at 610 nm for Fsal-3-Cu,Eu and Fsal-3-Cu,Gd, and at 615 nm for Fsal-3-Cu,Ho. Such decreasing of *d–d* absorption energy with increasing the atomic number of lanthanide may be due to the decrease of the ligand field around copper(II) ion on forming a dinuclear complex with smaller lanthanide, i.e. the larger the effective nuclear charge of lanthanide(III) ion is, the stronger the coordinate bonds of the bridging phenolate oxygens to the lanthanide(III) become and hence the weaker the interaction between the phenolate oxygens and the copper(II) becomes. Figure 3 shows the absorption spectra in methanolic solution of Fsal-3-Cu,La and Fsal-3-Cu,Gd, together with the spectrum of methanolic solution containing equivalent amounts of Fsal-3-Cu and Lu(III). As described above, Fsal-3-Cu,Tm, Fsal-3-Cu,Yb and Fsal-3-Cu,Lu could not be isolated as crystals in the present condition. However, these three dinuclear complexes are probably formed in methanol, since the solubility of Fsal-3-Cu is very low and the transparent solution is obtained by the addition of an equivalent amount of Tm^{III}, Yb^{III}, or Lu^{III} to the suspension of Fsal-3-Cu in methanol. The energy of *d-d* absorption maximum of Cu^{II} is the following order: Fsal-3-Cu,La > Fsal-3-Cu,Gd > Fsal-3-Cu,Lu which may be explained in a similar discussion as that for the solid state.

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

The absorption spectra of Fsal-3-Cu,Gd in methanol were measured by adding 1,2-ethanediol, 1,3-propanediol or 3-amino-1-propanol as a substrate (see Fig. 4). In general, the axial coordination of a substrate to the copper centre results in a red-shift of the *d–d* band maximum. This is indeed the case when 3-amino-1-propanol is added. On the other hand, the shift of the *d–d* band is not seen when diols were added. These results obviously indicate that the amine nitrogen of amino alcohol coordinates at the axial site of the copper(II) centre whereas alcoholic oxygen(s) do not. However, it is unclear from the absorption

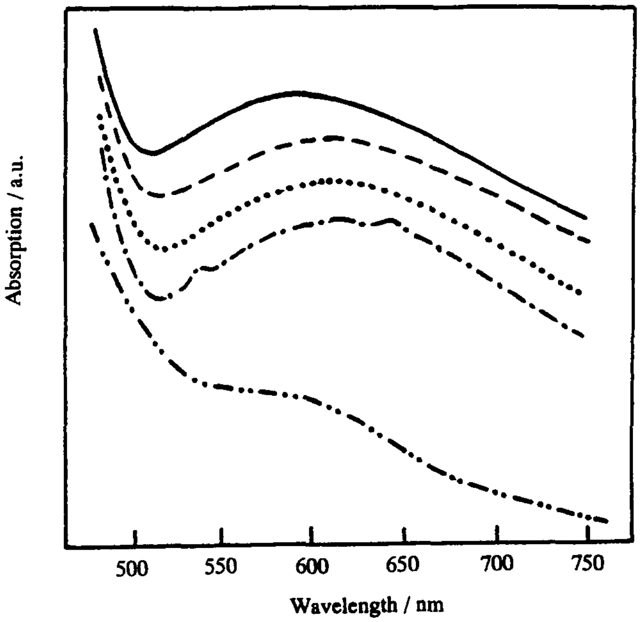

Fig. 2. Electronic spectra on Nujol mulls. (–··–): Fsal-3-Cu; (——): Fsal-3-Cu,La; (– – –): Fsal-3-Cu,Eu; (···): Fsal-3-Cu,Gd; (–·–): Fsal-3-Cu,Ho.

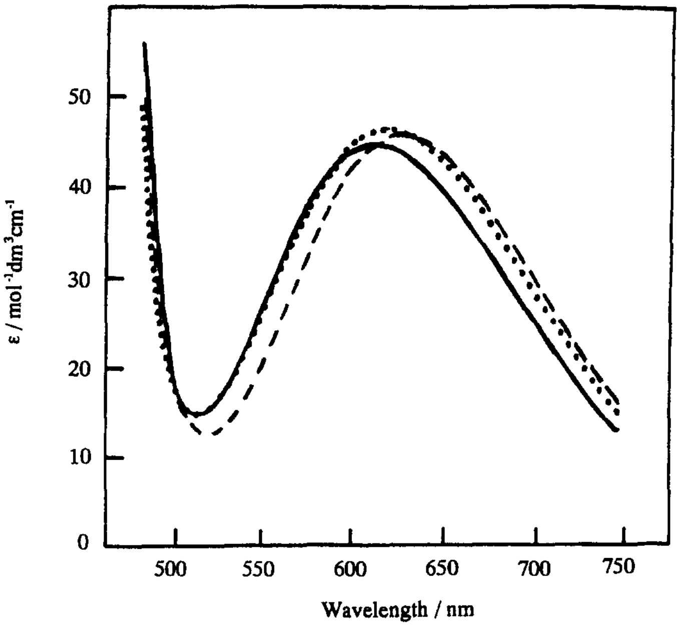

Fig. 3. Absorption spectra in methanol. (——) : Fsal-3-Cu,La (2.0×10^{-3} mol dm^{-3}) ; (···) : Fsal-3-Cu,Gd (2.0×10^{-3} mol dm^{-3}) ; (– – –) : Fsal-3-Cu (2.0×10^{-3} mol dm^{-3}) + Lu(NO_3)$_3$ (2.0×10^{-3} mol dm^{-3}).

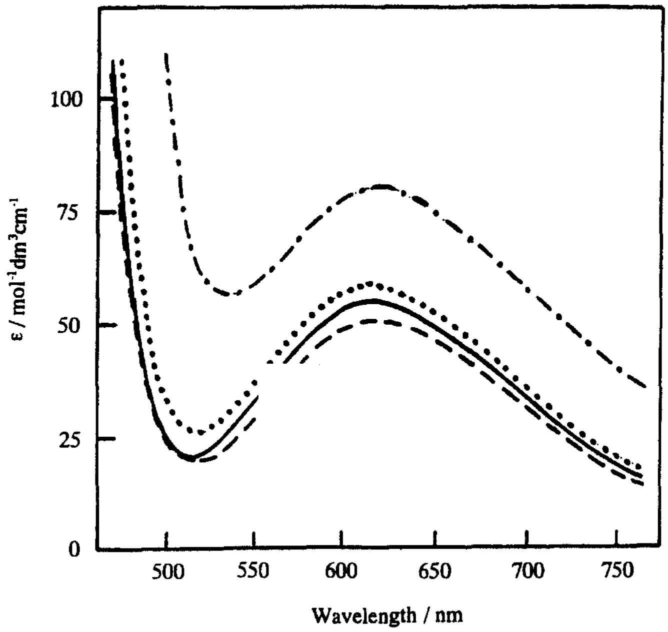

Fig. 4. Absorption spectra of Fsal-Cu,Gd in methanol with several additives. Fsal-3-Cu,Gd : 2.0×10^{-3} mol dm^{-3}. Additive : 1.1 mol dm^{-3}. (——) : without additive ; (···) : with 1,2-ethanediol ; (– – –) : with 1,3-propanediol ; (–·–) : with 3-amino-1-propanol.

spectra how the alcoholic oxygen of the amino alcohol is associated with the coordination to the Cu^{II}–Ln^{III} heterometal centre. In order to investigate the coordination behaviour of amino alcohols and diols in more detail, the CD spectra of Fsal-3-Cu,La were measured in methanol by adding chiral amino alcohols, alcohol or diol (Fig. 5). When (R)-(−)-2-amino-1-propanol or (R)-(−)-2-amino-1-butanol was added as the substrate, significant circular dichroism was induced in the *d*–*d* band region of Cu^{II}, whereas no CD activity occurred by the addition of (S)-(+)-2-butanol or (S)-(+)-1,2-propanediol. These observations clearly indicate that the amino nitrogen of amino alcohols coordinates to the copper(II) and the free rotation of the amino alcohols is hindered with respect to the Cu—N bond. Such difficulty of the free

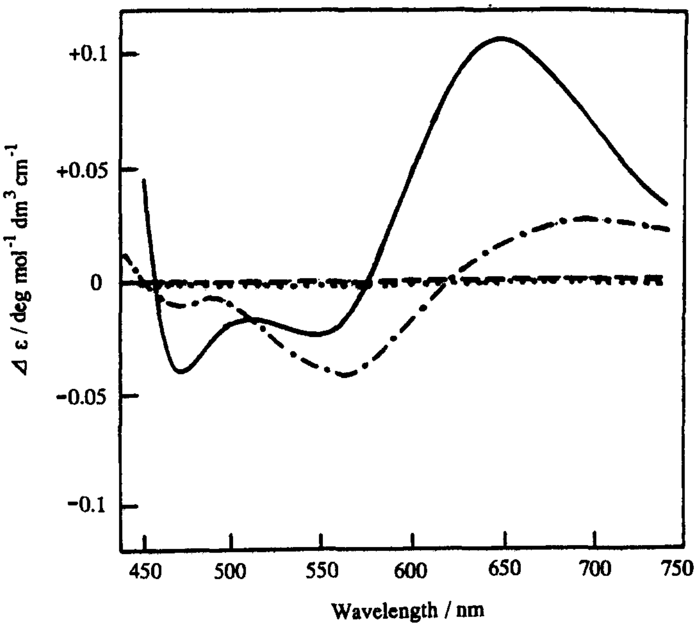

Fig. 5. CD spectra of Fsal-3-Cu,La in methanol with several chiral additives. Fsal-3-Cu,La : 2.0×10^{-3} mol dm^{-3}. Additive : 0.25 mol dm^{-3}. (– – –): with (S)-(+)-2-butanol ; (···): with (S)-(+)-1,2-propanediol ; (–·–): with (R)-(–)-2-amino-1-propanol ; (——): with (R)-(–)-2-amino-1-butanol.

rotation of amino alcohols will be accomplished by the following reasons [13,14,17,19,21,22]. (i) the hydroxyl group of amino alcohols may be directly bound to the lanthanum(III) ion or (ii) the hydroxyl group may interact with H_2O or CH_3OH molecule(s) coordinated to the lanthanum(III) ion through the hydrogen bonding. It cannot be decided at present which is the most plausible. (S)-(+)-2-butanol and (S)-(+)-1,2-propanediol may coordinate to the lanthanum(III) ion as a mono- or bidentate ligand and hence give little effect on the ligand field of copper(II), inducing no CD activity in the *d–d* band region of copper(II).

Consequently, it is concluded that the amino alcohols specifically interact with the Cu^{II}–Ln^{III} heterometal centre, through the nitrogen to the copper site and through the oxygen to the lanthanide site, as previously reported in some *d-f* heteronuclear complexes [11,13,14,17,19,21,22].

Magnetic properties

The magnetic properties of Fsal-3-Cu,Gd were investigated. The temperature dependences of the magnetic susceptibilities per CuGd unit (χ_M), the reciprocal magnetic susceptibilities ($1/\chi_M$) and the effective magnetic moment (μ_{eff}) are shown in Fig. 6. The plot of $1/\chi_M$ *vs* T follows the Curie–Weiss law with Weiss constant, $\theta = +1.0$ K, suggesting a weak ferromagnetic interaction. The effective magnetic moment at 260.5 K is 8.18 μ_B. This value is very close to the spin-only value (8.12 μ_B) calculated from the equation, $\mu_{eff} = (\mu_{Cu}^2 + \mu_{Gd}^2)^{1/2}$, in the absence of magnetic interaction for the present spin-system ($S_{Cu} = 1/2$, $S_{Gd} = 7/2$). Here, it should be noted 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, $\mu_{eff} = [4S(S+1)]^{1/2}$. As the temperature is lowered, the magnetic moment increases gradually and reaches the maximum value (8.75 μ_B) at 4.5 K. Such an increase in magnetic moment with lowering of temperature indicates the operation of a ferromagnetic spin-coupling between Cu^{II} and Gd^{III}, because the spin-only value for the spin-state $S = 4$ resulting from the ferromagnetic interaction between Cu^{II} ($S = 1/2$) and Gd^{III} ($S = 7/2$) is 8.94 μ_B. The analysis of magnetic data was tried on the basis of a spin-only expression (1), using the spin-Hamiltonian $\mathscr{H} = -2JS_{Cu} \cdot S_{Gd}$.

$$\chi_M = \frac{4Ng^2\beta^2}{kT} \frac{15+7\exp(-8J/kT)}{9+7\exp(-8J/kT)} \qquad (1)$$

The best fit was attained with parameters of g = 2.01 and J = +0.8 cm^{-1}, where the fit was sufficient without considering an impurity. Thus, the interaction between Cu^{II} and Gd^{III} is apparently ferromagnetic in the present complex, consistent with the positive Weiss constant, though the coupling is very small. Such ferromagnetic interaction has been recognized in some other Cu^{II}–Gd^{III} complexes [8,12,15,18,25–31].

Fluorescence spectra

The fluorescence spectrum of Fsal-3-Cu,Eu was measured in methanol in order to investigate the effect

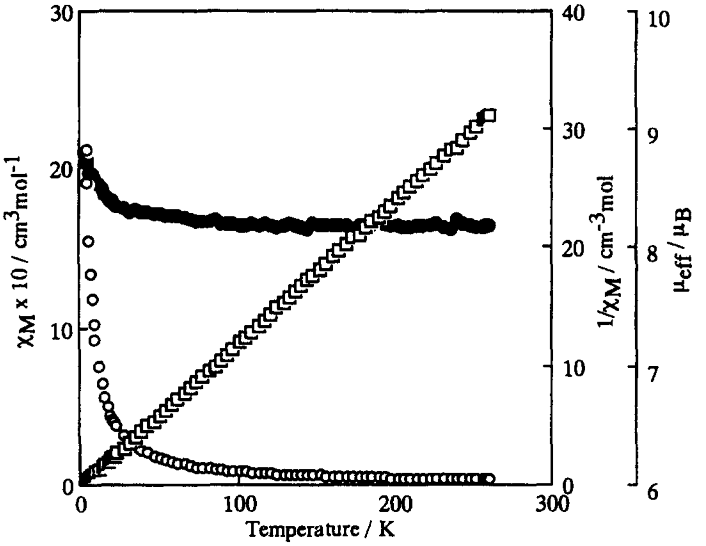

Fig. 6. Temperature dependences of χ_M(○), $1/\chi_M$ (□) and μ_{eff} (●) of Fsal-3-Cu,Gd. χ_M is the magnetic susceptibility per CuGd unit and μ_{eff} is the effective magnetic moment.

of an adjacent metal ion on the fluorescence of Eu^{III}. Fsal-3-Cu,Eu showed no significant fluorescence in the range 590–700 nm, whereas $Eu(NO_3)_3 \cdot 6H_2O$ gave the well-known fluorescence bands attributable to the $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$, $^5D_0 \rightarrow {}^7F_3$, and $^5D_0 \rightarrow {}^7F_4$ at 593, 618, 650, and 687 and 696 nm, respectively. As previously discussed [16,17,19,21,22,32–35], such a fluorescence decrease may be due to the energy transfer from the excited Eu(III) to the adjacent Cu(II) complex moiety (intramolecular energy transfer), followed by the radiationless energy loss through the Cu(II) complex moiety, though the absorption of exiting light (394 nm) by the Fsal-3-Cu,Eu itself and the intermolecular energy transfer cannot be neglected.

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