Copper(II)-Lanthanoid(III) Complexes of Binucleating Ligands Derived from 3-Formylsalicylic Acid and Diamines

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Heterometal binuclear complexes, $[CuLn(fsaen)(H_2O)_n](NO_3)$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu; n=4—5) and $[CuLn(fsapn)(H_2O)_4](NO_3)$ (Ln=La, Pr, Nd, Sm, Eu, Gd, Tb, or Dy) have been synthesized and characterized, where H_4fsaen and H_4fsapn denote N,N'-bis(3-carboxysalicylidene)ethylenediamine and N,N'-bis(3-carboxysalicylidene)-1,2-propanediamine, respectively. The ligand field band due to the copper(II) ion bound to the N_2O_2-site is at 18.5×10^3—19.5×10^3 cm^{-1} for $[CuLn(fsaen)(H_2O)_n](NO_3)$ and 18.4×10^3—19.2×10^3 cm^{-1} for $[CuLn(fsapn)(H_2O)_4](NO_3)$, which are higher frequencies than those of the mononuclear complexes, $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$ (18.3×10^3 and 18.4×10^3 cm^{-1}, respectively). When the complexes are dissolved in pyridine (Py), dimethyl sulfoxide (DMSO), or N,N-dimethylformamide (DMF), the d-d band frequency decreases in the order of the solvent DMSO>DMF>Py for the binuclear complexes, whereas it decreases in the order of DMF>DMSO>Py for the mononuclear complexes. These trends were discussed in terms of the different affinities of solvent molecules for copper(II) and lanthanoid(III) ions. No significant magnetic spin-exchange interaction occurred between metal ions.

Various rare earth perovskite or garnet type compounds have been widely studied because of their growing possible use as the magnetic material, electrical semiconductor, catalysis, and so on.[1] However, the role of rare earth metal ions in these materials seems not to be still well-defined. For the understanding of their interesting properties, heterometal binuclear complexes comprising a transition metal and a lanthanoid ions are presumed to be good simple models.

A general method for obtaining heterometal binuclear complexes is the stepwise addition of two different metal ions to a coordinatively selective binucleating ligand, in which two coordinating sites differ from each other in the ligand field strength or in the stereochemistry of coordination. A number of such compartmental ligands have been synthesized[2-8] and studies on binuclear complexes with dissimilar d-transition metal ions have been developed with these ligands.[3,5,6,9-15] On the other hand, very few reports[8] are available on the heterometal binuclear complexes containing a d-transition metal ion and a lanthanoid ion.

Since Okawa et al.[3] first used N,N'-bis(3-carboxysalicylidene)ethylenediamine (H_4fsaen) as an excellent binucleating ligand possessing dissimilar coordination sites, this ligand and its homologs have been extensively utilized for the syntheses of homo- and heterometal binuclear complexes to investigate their magnetic, optical, electrochemical, and structural properties.[3,5,9,10,13-16] In those studies, it was revealed that physicochemical properties of the metal ion bound at N_2O_2-site (inside coordination site) are very sensitive to the second metal ion at the O_4-site (outside coordination site).[5] Since the outside coordination site seems favorable for binding lanthanoid ions, these ligands are expected to be applicable to the syntheses of heterometal binuclear complexes comprising a d-transition metal and a lanthanoid metal ions.

In this work we have prepared copper(II)-lanthanoid(III) complexes of H_4fsaen and N,N'-bis(3-carboxysalicylidene)-1,2-propanediamine (H_4fsapn), in which copper(II) and lanthanoid(III) ions are bound at the inside and outside coordination sites, respectively (Fig. 1). The effect of the presence of a lanthanoid(III) ion at the outside site upon the ligand field around copper (II) ion at the inside site has been discussed mainly on the basis of electronic spectra. The IR, ESR, and magnetic data of these complexes are also reported.

Experimental

Syntheses. 3-Formylsalicylic acid was prepared after the method of Duff and Bills.[17] The mononuclear copper(II) complexes, $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O_{0.5}$, were obtained by the method of Okawa et al.[4]

$CuLn(fsaen)(NO_3)(H_2O)_4$ and $CuLn(fsapn)(NO_3)(H_2O)_4$ (Ln=La—Nd): The corresponding mononuclear copper(II) complex (1 mmol) was dissolved in a methanolic solution (50 cm^3) of lithium hydroxide monohydrate (2 mmol). To this solution was added a methanolic solution (50 cm^3) of lanthanoid nitrate hydrate (1 mmol) with stirring. After the mixture was refluxed for 2—3 h with stirring, the precipitate formed was filtered, washed with methanol and then with diethyl ether, and dried in the open air.

$CuLn(fsaen)(NO_3)(H_2O)_n$ (Ln=Sm—Ho, n=4—5): The procedure was the same in principle as that described above, except for the use of 25 cm^3 methanol for each treatment.

$CuLn(fsaen)(NO_3)(H_2O)_5$ (Ln=Er—Lu) and $CuLn(fsapn)(NO_3)(H_2O)_4$ (Ln=Sm—Dy): These binuclear complexes were synthesized in the same way as that for the above complexes, except that the mononuclear copper(II) complex (1 mmol) was dissolved in a methanolic solution (25 cm^3) of

Table 1. Elemental Analyses of Complexes

Complex	Found(%)(Calcd (%))				
	C	H	N	Cu	Ln
$\mathrm{CuLa(fsaen)(NO_3)(H_2O)_4}$	31.07	2.55	6.35	9.26	20.65
	(31.39)	(2.93)	(6.10)	(9.23)	(20.17)
$\mathrm{CuPr(fsaen)(NO_3)(H_2O)_4}$	30.96	2.56	6.13	9.14	19.93
	(31.30)	(2.92)	(6.08)	(9.20)	(20.40)
$\mathrm{CuNd(fsaen)(NO_3)(H_2O)_4}$	31.16	2.68	5.99	9.14	20.68
	(31.15)	(2.90)	(6.05)	(9.15)	(20.78)
$\mathrm{CuSm(fsaen)(NO_3)(H_2O)_4}$	31.12	2.65	5.63	9.15	21.80
	(30.87)	(2.88)	(6.00)	(9.07)	(21.47)
$\mathrm{CuEu(fsaen)(NO_3)(H_2O)_4}$	30.38	2.71	5.68	9.20	21.98
	(30.80)	(2.87)	(5.99)	(9.05)	(21.65)
$\mathrm{CuGd(fsaen)(NO_3)(H_2O)_4}$	30.33	2.71	5.60	8.93	22.63
	(30.57)	(2.85)	(5.94)	(8.99)	(22.24)
$\mathrm{CuTb(fsaen)(NO_3)(H_2O)_5}$	29.85	2.58	5.85	8.85	22.13
	(29.74)	(3.05)	(5.78)	(8.74)	(21.86)
$\mathrm{CuDy(fsaen)(NO_3)(H_2O)_5}$	29.37	2.65	5.89	8.56	22.65
	(29.60)	(3.04)	(5.75)	(8.70)	(22.25)
$\mathrm{CuHo(fsaen)(NO_3)(H_2O)_5}$	29.73	2.85	5.80	8.80	23.05
	(29.50)	(3.03)	(5.73)	(8.67)	(22.51)
$\mathrm{CuEr(fsaen)(NO_3)(H_2O)_5}$	29.11	2.55	5.47	9.06	23.20
	(29.40)	(3.02)	(5.72)	(8.64)	(22.75)
$\mathrm{CuTm(fsaen)(NO_3)(H_2O)_5}$	28.89	2.73	5.60	8.75	23.01
	(29.34)	(3.01)	(5.70)	(8.62)	(22.93)
$\mathrm{CuYb(fsaen)(NO_3)(H_2O)_5}$	28.58	2.78	5.61	8.72	23.38
	(29.18)	(2.99)	(5.67)	(8.58)	(23.35)
$\mathrm{CuLu(fsaen)(NO_3)(H_2O)_5}$	28.64	2.51	5.51	8.60	23.80
	(29.10)	(2.98)	(5.66)	(8.55)	(23.55)

Table 2. Elemental Analyses of Complexes

Complex	Found(%)(Calcd (%))				
	C	H	N	Cu	Ln
$\mathrm{CuLa(fsapn)(NO_3)(H_2O)_4}$	31.64	3.08	6.03	9.02	19.96
	(32.47)	(3.15)	(5.98)	(9.04)	(19.76)
$\mathrm{CuPr(fsapn)(NO_3)(H_2O)_4}$	31.38	3.11	6.12	8.61	20.34
	(32.38)	(3.14)	(5.96)	(9.02)	(19.99)
$\mathrm{CuNd(fsapn)(NO_3)(H_2O)_4}$	31.97	2.99	6.06	8.96	20.56
	(32.22)	(3.13)	(5.93)	(8.97)	(20.37)
$\mathrm{CuSm(fsapn)(NO_3)(H_2O)_4}$	31.37	3.05	5.76	8.73	21.10
	(31.95)	(3.10)	(5.88)	(8.90)	(21.15)
$\mathrm{CuEu(fsapn)(NO_3)(H_2O)_4}$	31.37	3.05	6.14	8.58	22.12
	(31.88)	(3.10)	(5.87)	(8.88)	(21.23)
$\mathrm{CuGd(fsapn)(NO_3)(H_2O)_4}$	31.24	3.04	5.84	8.63	21.86
	(31.64)	(3.07)	(5.83)	(8.81)	(21.80)
$\mathrm{CuTb(fsapn)(NO_3)(H_2O)_4}$	31.34	3.05	5.92	8.75	21.57
	(31.57)	(3.07)	(5.81)	(8.79)	(21.99)
$\mathrm{CuDy(fsapn)(NO_3)(H_2O)_4}$	30.95	3.01	5.87	8.35	22.17
	(31.41)	(3.05)	(5.78)	(8.75)	(22.37)

lithium hydroxide monohydrate (2 mmol), followed by the addition of methanolic solution (5 cm^3) of lanthanoid nitrate hydrate (1 mmol).

Elemental analyses for the complexes are given in Tables 1 and 2.

Measurements. Elemental analyses of carbon, hydrogen, and nitrogen were carried out at the Service Center of Elemental Analysis, Kyushu University or Advanced Instrumentation Center for Chemical Analysis, Ehime University. Metal contents were determined by EDTA titration. Infrared spectra were measured with a JASCO IR-G Spectrometer on KBr disks or on nujol mulls. Electronic spectra were obtained on nujol mulls and in dimethyl sulfoxide, *N*,*N*-dimethylformamide, or pyridine with a Shimadzu UV-VIS Recording Spectrophotometer Model 240. Magnetic susceptibilities were measured by the Gouy method or the Faraday method from liquid nitrogen temperature to room temperature. Diamagnetic correction was done using the Pascal's constants. Magnetic moments were calculated from the equation, $\mu_M=2.828\sqrt{\chi_M T}$, where χ_M is the susceptibility per molecule. The ESR spectra were recorded with a JES-ME-3X Spectrometer by the X-band in dimethyl sulfoxide, *N*,*N*-dimethylformamide, or pyridine at liquid nitrogen temperature.

Results and Discussion

Infrared spectra of the binuclear complexes are essentially similar to each other as far as the same ligand is concerned. The absorption band at 1630—1640 cm^{-1} is assignable to the C=N stretching mode. The band due to the free carboxyl group was reported to appear at 1705 cm^{-1} for both $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$.[4] However, this band disappeared in the spectra of $CuLn(fsaen)(NO_3)(H_2O)_n$ and $CuLn(fsapn)(NO_3)(H_2O)_4$. Instead a broad and strong band was observed around 1540 cm^{-1}. The binuclear d-transition metal complexes of 3-formylsalicylic acid[18] and its Schiff bases[3—5,9,19] are known to exhibit the absorption band at 1540—1580 cm^{-1} which is attributable to the C=O stretching vibration. Therefore, it seems reasonable to assign the band around 1540 cm^{-1} to the coordinated carboxylato group.

It is well-known that for the phenoxo-bridged binuclear complexes one of the skeletal vibrations (near 1540 cm^{-1}) is by 15—20 cm^{-1} higher than that of the corresponding mononuclear complexes.[2] For example, the mononuclear copper(II) complex of a macrocycle, 24,25-dihydroxy-10,22-dimethyl-3,6,14,18-tetraazatricyclo[$18.3.1.1^{8,12}$]pentacosa-1(24),2,6,8(25),9,11,13,18,20,22-decaene, shows the skeletal band at 1543 cm^{-1}, whereas its binuclear copper(II) complex shows the corresponding band at 1560 cm^{-1}.[2] For the present Cu(II)-Ln(III) complexes, however, such a marked shift of the skeletal band was not observed. That is, the band for the Cu(II)-Ln(III) complexes appeared around 1560 cm^{-1}, whereas the band for $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$ appeared around 1555 cm^{-1}.

For the nitrates of lanthanoid complexes it is reported that IR bands appear around 1450—1500, 1300, 1030, and 815 cm^{-1} if the nitrate ion functions as a bidentate ligand.[8,20] Such bands could not be clearly seen in the IR spectra of the present binuclear complexes. Instead the sharp bands appeared at 1380 and 805 cm^{-1} which are characteristic of free nitrate ion.[21] Furthermore, the splitting of combination bands in the region of 1700—1800 cm^{-1}, which has been often utilized as a diagnosis of the bonding mode of nitrate ion,[22] was not recognized for the complexes. These observations indicate that the nitrate ion does not coordinate to the metal ion. The spectra on nujol mulls for the binuclear complexes showed two bands at 3350 and 3250 cm^{-1} assignable to the asymmetric and symmetric stretching vibrations of H_2O molecule, respectively, whereas $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$ showed a band at 3400 cm^{-1} attributable to a lattice water. Judging from these facts, the present binuclear complexes can be formulated as $[CuLn(fsaen)(H_2O)_n](NO_3)$ and $[CuLn(fsapn)(H_2O)_4](NO_3)$ in which lanthanoid ions are presumably of eight or nine coordination with O_4-donor atoms of the Schiff base and four or five H_2O molecules, though the detailed structure is unclear at the present stage.

Some of the electronic spectra determined on nujol mulls are shown in Fig. 2. The absorption maxima of the complexes are summarized in Figs. 3 and 4. $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$ show the ligand field band due to the copper(II) ion at 18.25×10^3 and 18.38×10^3 cm^{-1}, respectively, which are very close to those determined by reflection on powder samples by Okawa et al.[4] The d-d band is shifted to higher frequency on binuclear complex formation. This is in accord with that $[Cu(H_2fsaen)](H_2O)_{0.5}$ and $[Cu(H_2fsapn)](H_2O)_{0.5}$ are purple while the Cu(II)-Ln(III) complexes are red-purple. Such a blue shift of the d-d band may be attributed to the enhanced

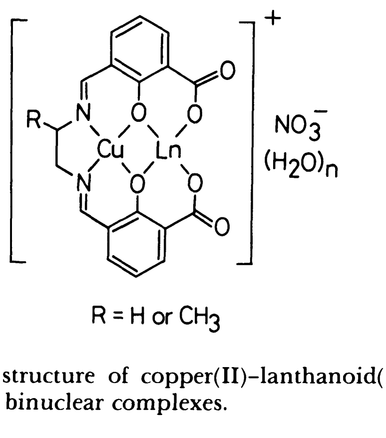

Fig. 1. The structure of copper(II)-lanthanoid(III) heterometal binuclear complexes.

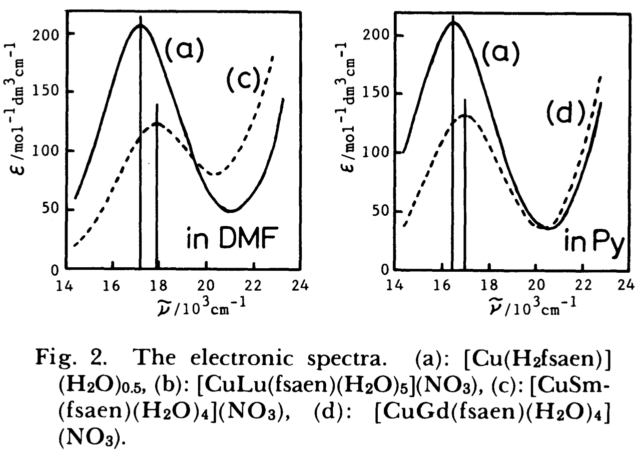

Fig. 2. The electronic spectra. (a): $[Cu(H_2fsaen)](H_2O)_{0.5}$, (b): $[CuLu(fsaen)(H_2O)_5](NO_3)$, (c): $[CuSm(fsaen)(H_2O)_4](NO_3)$, (d): $[CuGd(fsaen)(H_2O)_4](NO_3)$.

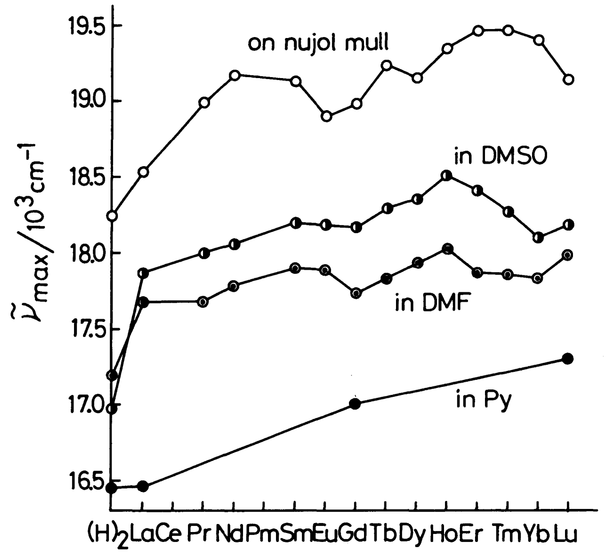

Fig. 3. The d-d band absorption maxima of [Cu(H$_2$fsaen)](H$_2$O)$_{0.5}$ and [CuLn(fsaen)(H$_2$O)$_n$](NO$_3$). (H)$_2$, La, Pr, ···, and Lu of abscissa denote the mononuclear copper(II), copper(II)-lanthanum(III), copper(II)-praseodymium(III), ···, and copper(II)-lutetium(III) binuclear complexes, respectively.

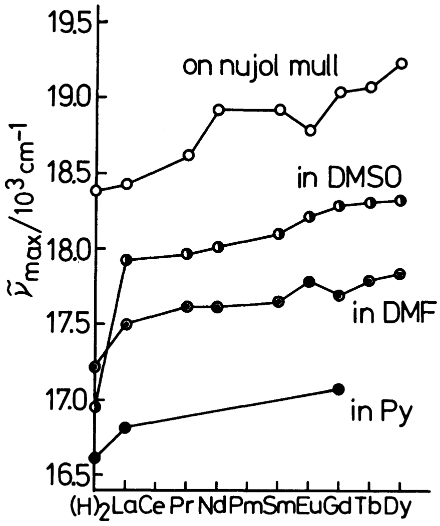

Fig. 4. The d-d band absorption maxima of [Cu(H$_2$fsapn)](H$_2$O)$_{0.5}$ and [CuLn(fsapn)(H$_2$O)$_4$](NO$_3$). (H)$_2$, La, ···, and Dy of abscissa denote the mononuclear copper(II), copper(II)-lanthanum(III), ···, and copper(II)-dysprosium(III) binuclear complexes, respectively.

planarity of the [CuN$_2$O$_2$] chromophore on forming a binuclear complex with a lanthanoid ion at the outside coordination site as was observed for Cu(II)-M(II) (M=Co,Ni,Cu,Zn,Mg) heterometal binuclear complexes of *N,N'*-bis(3-carboxysalicylidene)-1,1-dibenzylethylenediamine.[5] The relatively small shift of the band for the CuLa complexes suggests that large lanthanum ion cannot reside in the outside coordination site and causes more or less a distortion of the [CuN$_2$O$_2$] plane.

When the mononuclear copper(II) complexes were dissolved in pyridine (Py), dimethyl sulfoxide (DMSO), or *N,N*-dimethylformamide (DMF), the solutions were all blue. Their absorption spectra are given in Fig. 2. The frequency of the d-d band is in the following order of solvent: DMF>DMSO>Py(see also Figs. 3 and 4). This is quite understandable when one recalls the facts that the coordination at the apical site causes a red shift of the d-d band for planar copper(II) complexes and that the donating ability of the solvent increases in the order, DMF<DMSO<Py. On the other hand, solutions of the Cu(II)-Ln(III) complexes in Py are blue but those in DMSO or DMF purple. Accordingly, the spectra showed that the frequency of the d-d band is in the order, DMSO>DMF>Py. This may be explained by taking into consideration the difference in coordination affinity of a solvent molecule to copper(II) and lanthanoid(III) ions. Since pyridine has a higher affinity for copper(II) ion than for lanthanoid(III) ions, the pyridine molecule selectively coordinates to the copper(II) ion to result in the shift of the d-d band to lower frequency. On the other hand, DMSO and DMF have similar affinities for both copper(II) and lanthanoid(III) ions. If these solvents preferentially coordinate to the lanthanoid ion rather than the copper(II) ion to afford a high coordination number around the lanthanoid ion, then the coordinated solvent molecules block the apical part of the copper(II) ion and hence hinder the approach of other solvent molecules to the copper(II) ion. Such a shielding must be more effective in DMSO than in DMF because the former solvent generally coordinates more strongly to lanthanoid ions. Planar copper(II) complexes of *N,N'*-disalicylideneethylenediamine and its homologs show the d-d band at 17.8×10^3—18.2×10^3 cm^{-1} in nondonative solvents.[5,24—26] These frequencies are comparable to those of the present binuclear complexes in DMSO, indicating that the coordination geometry of copper is essentially planar even in DMSO. It is presumed that the situation is nearly the same in DMF, judging from the d-d band frequency.

We have measured the ESR spectra of [Cu(H$_2$fsaen)](H$_2$O)$_{0.5}$ and [CuLn(fsaen)(H$_2$O)$_n$](NO$_3$) (Ln=La, Lu) in Py, DMSO, or DMF at liquid nitrogen temperature and found that ESR parameters, $g_{//}$ and $A_{//}$, are essentially the same for the mononuclear and binuclear complexes irrespective of the change of the solvent. This may be explained by that the axial coordination of the solvents (Py, DMSO, DMF) to the mononuclear complexes and the axial coordination of Py to the binuclear CuLn-complexes may destabilize the d$_{z^2}$ orbital but this is not clearly detected by ESR because the d$_{z^2}$ orbital is EPR-innocent.

The magnetic moments of the Cu(II)-Ln(III)

Table 3. Magnetic Moments of Complexes[a)]

Complex	Magnetic moment		Complex	Magnetic moment	
	μ_M[b)]	μ_M^{calcd}[c)]		μ_M[b)]	μ_M^{calcd}[c)]
$CuLa(fsaen)(NO_3)(H_2O)_4$	1.85	1.85	$CuYb(fsaen)(NO_3)(H_2O)_5$	4.80	5.20
$CuPr(fsaen)(NO_3)(H_2O)_4$	3.81	3.87	$CuLu(fsaen)(NO_3)(H_2O)_5$	1.81	1.85
$CuNd(fsaen(NO_3)(H_2O)_4$	3.85	3.96	$CuLa(fsapn)(NO_3)(H_2O)_4$	1.85	1.84
$CuSm(fsaen)(NO_3)(H_2O)_4$	2.43	2.43	$CuPr(fsapn)(NO_3)(H_2O)_4$	3.83	3.87
$CuEu(fsaen)(NO_3)(H_2O)_4$	3.80	3.89	$CuNd(fsapn)(NO_3)(H_2O)_4$	3.84	3.95
$CuGd(fsaen)(NO_3)(H_2O)_4$	8.04	8.12	$CuSm(fsapn)(NO_3)(H_2O)_4$	2.35	2.43
$CuTb(fsaen)(NO_3)(H_2O)_5$	9.69	9.68	$CuEu(fsapn)(NO_3)(H_2O)_4$	3.82	3.88
$CuDy(fsaen)(NO_3)(H_2O)_5$	10.53	10.56	$CuGd(fsapn)(NO_3)(H_2O)_4$	8.11	8.12
$CuHo(fsaen)(NO_3)(H_2O)_5$	10.43	10.56	$CuTb(fsapn)(NO_3)(H_2O)_4$	9.74	9.68
$CuEr(fsaen)(NO_3)(H_2O)_5$	9.68	9.58	$CuDy(fsapn)(NO_3)(H_2O)_4$	10.43	10.56
$CuTm(fsaen)(NO_3)(H_2O)_5$	7.32	7.34			

a) Moments are given in Bohr magneton, $\mu_B(=9.274\times10^{-24}\,Am^2$ in SI units). b) Experimental values at 287 K. c) Calculated from the equation, $\mu_M^{calcd}=\sqrt{(\mu_{Cu})^2+(\mu_{Ln})^2}$, where μ_{Cu} denotes the values,[4)] 1.85 μ_B (294.3 K) and 1.84 μ_B (292.9 K) for $Cu(H_2fsaen)(H_2O)_{0.5}$ and $Cu(H_2fsapn)(H_2O)_{0.5}$, respectively and μ_{Ln} are those reported[27)] for the general lanthanoid(III) compounds.

complexes at room temperature are summarized in Table 3, together with the moments calculated from the equation, $\mu_M^2=\mu_{Cu}^2+\mu_{Ln}^2$ using the reported moments, μ_{Cu}, for the mononuclear complexes[4)] and the common values, μ_{Ln}, of tervalent lanthanoid ions.[27)] The moments observed coincide approximately with the calculated values. The cryomagnetic investigations down to liquid nitrogen temperature ruled out the possibility of the operation of a spin-exchange interaction in these complexes: That is, their magnetic moments were practically independent of temperature in the range 78—300 K (except for the case of Cu(II)-Sm(III) and Cu(II)-Eu(III) complexes). It is known that the magnetic spin-exchange interaction between lanthanoid ions is very weak because the 4f-electrons are shielded by the outer-shell electrons. The present work reveals that no significant magnetic spin-exchange interaction is operating also between copper(II) and lanthanoid(III) ions.

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