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# Ferromagnetic Spin-Coupling between Gadolinium(III) and Copper(II) Ions in Discrete Binuclear Gd(III)-Cu(II) Complexes

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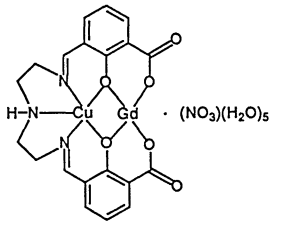
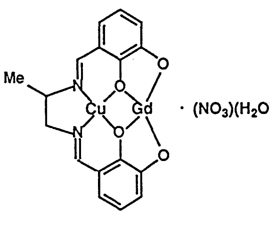
Three discrete binuclear gadolinium(III)-copper(II) complexes (CuGd(fsadien)$NO_3 \cdot 5H_2O$ (**1**), CuGd(hsapn)$NO_3 \cdot 3H_2O$ (**2**), and [Gd(pvm)$_3$Cu(A)] (**3**)) have been synthesized; we use the notation $H_4$fsadien=*N,N'*-bis(3-carboxysalicylidene)diethylenetriamine, $H_4$hsapn=*N,N'*-bis(3-hydroxysalicylidene)-1,2-propanediamine, Hpvm=dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione), and $H_2A$=4-(6-methyl-8-oxo-2,5-diazanona-1,5,7-trienyl)imidazole. Magnetic susceptibility measurements (4.2—300 K) have revealed that the spin coupling between the Gd(III) and Cu(II) ions is ferromagnetic with coupling constants $J=+2.3$ cm$^{-1}$ for (**1**), $+5.7$ cm$^{-1}$ for (**2**), and $+0.5$ cm$^{-1}$ for (**3**), on the basis of the spin-Hamiltonian $H=-2JS_{Gd} \cdot S_{Cu}$.

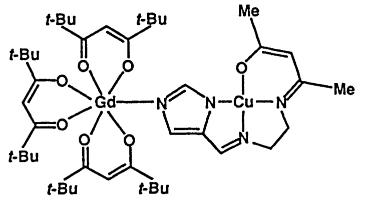
Magnetic studies on the d-transition metal polynuclear complexes have shown tremendous progress during the latest decade regarding experimental and theoretical fields.[1,2] Procedures have become fairly well established for predicting the magnetic properties of polynuclear d-transition metal complexes.[1,2] On the other hand, magnetic investigations concerning mixed-metal complexes comprising d- and f-transition metal ions have been overlooked until recently due to the very weak interaction and the large anisotropic effect of lanthanoid ions. Characterization of the magnetic interaction between d- and f-transition metal ions is our next target for elucidation. In particular, the synthesis of ferromagnetic complexes is among the stimulating subjects. Recently, Gatteschi and his co-workers reported on the ferromagnetic interaction operating between Gd(III) and Cu(II) ions in a trinuclear $GdCu_2$ system {Cu(saltn)}$_2$Gd($H_2O$)($NO_3$)$_3 \cdot 2C_2H_5NO_2$ ($H_2$saltn=*N,N'*-di(salicylidene)-1,3-propanediamine)[3] and its related complexes[4] as well as a tetranuclear $Gd_2Cu_2$ system [Gd(hfac)$_3$Cu(satn)(OH)]$_2$ (hfac=hexafluoroacetylacetonate, Hsatn=*N*-(3-aminopropyl)-salicylideneamine).[5] However, in these complexes the antiferromagnetic interaction operating between the terminal copper ions makes it difficult to evaluate the magnetic interaction between the Cu(II) and Gd(III) ions. In order to establish the magnetic interaction between Cu(II) and Gd(III) ions, it is desirable to synthesize discrete binuclear Gd(III)–Cu(II) complexes and to investigate their magnetic properties. Recently, in a communication, we reported on the synthesis and ferromagnetic property of a discrete Gd(III)–Cu(II) complex, CuGd(fsaen)$NO_3 \cdot 4H_2O$($H_4$fsaen=*N,N'*-bis(3-carboxysalicylidene)ethylenediamine).[6] In order to provide more examples of discrete binuclear Gd(III)–Cu(II) complexes and to investigate the structural variation effects (bridging mode and coordination geometry) upon spin-coupling, we prepared in the present study complexes (**1**), (**2**), and (**3**) and investigated their magnetic properties.



**1**



**2**



**3**

## Experimental

**Physical Measurements.** Elemental analyses for C, H, and N were carried out at the Service Center of Elemental Analysis, Kyushu University. Copper and Gadolinium were determined by titration against EDTA, where $NH_4F$ and thiourea were used as masking reagents for Gd and Cu, respectively. The magnetic susceptibilities were measured with a HOXAN HSM-D SQUID magnetometer over the temperature range 4.2—300 K under the applied magnetic field 500 G. The magnetic susceptibilities were calibrated by the use of $(NH_4)_2Mn(SO_4)_2 \cdot 6H_2O$. Data were corrected for magnetization of the sample holder and for diamagnetism contributions with Pascal's constants. The effective magnetic moments were calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$, where $\chi_M$ is the magnetic susceptibility per CuGd.

**Synthesis.** Starting complexes Cu($H_2$fsadien),[7] [Gd(pvm)$_3$],[8] and [Cu(A)]·0.5 $CHCl_3$[9] were prepared according to methods described in the literature; where $H_4$fsadien=*N,N'*-bis(3-carboxysalicylidene)diethylenetriamine, Hpvm=dipivaloylmethane (2,2,6,6-tetramethyl-3,5-heptanedione), and $H_2A$= 4-(6-methyl-8-oxo-2,5-diazanona-1,5,7-trienyl)imidazole.

**CuGd(fsadien)$NO_3 \cdot 5H_2O$ (1).** To a suspension of

$Cu(H_2fsadien)$ (1 mmol) in 50 $cm^3$ of methanol was added a methanol solution (10 $cm^3$) of $LiOH\cdot H_2O$ (2 mmol) followed by 240 $cm^3$ of methanol. The mixture was then heated until it became clear. To this solution was added a methanol solution (5 $cm^3$) of $Gd(NO_3)_3\cdot 6H_2O$ (1 mmol). After refluxing for 2 h, the solution volume was reduced to 50 $cm^3$ by a rotary evaporator. Green microcrystals precipitated were collected by suction filtration, washed with methanol and diethyl ether, and dried in air. Yield 60 %. Anal. Calcd for $C_{20}H_{27}N_4O_{14}CuGd$: C, 31.27; H,3.54; N, 7.29; Cu, 8.27; Gd, 21.32%. Found: C, 31.29; H, 3.22; N, 7.38; Cu, 8.28, Gd, 21.30%.

**Bis(2-formyl-6-hydroxyphenoxy)copper(II) Monohydrate (2a).** To a methanol solution (60 $cm^3$) of 2,3-dihydroxybenzaldehyde (20 mmol) was added an aqueous solution (50 $cm^3$) of copper(II) acetate monohydrate (10 mmol) in order to immediately precipitate a yellow-brown powder. After stirring for 1 h at room temperature, the precipitate was collected by suction filtration, washed with water, methanol, and diethyl ether, and dried in air. The yield was 90 %. Anal. Calcd for $C_{14}H_{10}O_6Cu\cdot H_2O$: C, 47.26; H, 3.40%. Found: C, 47.57; H, 3.5%.

**[*N,N′*-Bis(3-hydroxysalicylidene)-1,2-propanediaminato-copper(II) Monohydrate $Cu(H_2sapn)\cdot H_2O$ (2b).** To a suspension of **2a** (40 mmol) in ethanol (150 $cm^3$) was added 1,2-propanediamine (20 mmol). The mixture was first warmed on a hot plate for 2 h under stirring, and then cooled to room temperature, resulting in a brown precipitate which was collected by suction filtration, washed with water, ethanol, and diethyl ether, and finally dried in air. Yield 85—90%. Anal. Calcd for $C_{17}H_{16}N_2O_4Cu\cdot H_2O$: C, 51.84; H, 4.61; N, 7.11; Cu, 16.13%. Found: C, 52.33; H, 4.56; N, 7.08; Cu, 15.97%.

**$CuGd(hsapn)NO_3\cdot 3H_2O$ (2).** To a suspension of **2b** (2.5 mmol) in 20 $cm^3$ of methanol was added a methanol solution (25 $cm^3$) of $LiOH\cdot H_2O$ (5 mmol). To the resulting clear solution was added a methanol solution (10 $cm^3$) of $Gd(NO_3)_2\cdot 6H_2O$; the mixture was subsequently refluxed for 2 h. After cooling to room temperature, a brown precipitate was collected by suction filtration, washed with methanol and diethyl ether, and dried in air. Yield 95%. Anal. Calcd for $C_{17}H_{14}N_3O_7CuGd\cdot 3H_2O$:C, 31.55; H, 3.11; N, 6.49; Cu, 9.82; Gd, 24.30%. Found: C, 31.69; H, 3.05; N, 6.86; Cu, 9.48; Gd, 24.10%.

**$[Gd(pvm)_3Cu(A)]$ (3).** To a chloroform solution (20 $cm^3$) of $[Gd(pvm)_3]$ (0.5 mmol) was added a chloroform solution (30 $cm^3$) of $[Cu(A)]\cdot 0.5CHCl_3$ (0.5 mmol). The mixture was warmed on a hot plate for 10 min and filtered. To the filtrate was added diethyl ether dropwise until the solution became cloudy. After standing overnight, silky red crystals were collected by suction filtration, washed with ether, and dried in air. Recrystallization was carried out from the mixed solution of chloroform–diethyl ether. The yield was 10 %. Anal. Calcd for $C_{44}H_{71}N_4O_7CuGd$: C, 53.44; H, 7.24; N, 5.67; Cu, 6.43; Gd, 15.89%. Found: C, 53.50; H, 7.23; N, 5.69; Cu, 6.30; Gd, 15.75%.

## Results and Discussion

The temperature dependence of the magnetic susceptibility per CuGd unit ($\chi_M$), the reciprocal magnetic susceptibility ($1/\chi_M$), and the effective magnetic moment ($\mu_{eff}$) of $CuGd(fsadien)NO_3\cdot 5H_2O$ (**1**) are shown in Fig. 1. The numerical magnetic data of (**1**)—(**3**) and the plots of $\chi_M$ vs. $T$, $1/\chi_M$ vs. $T$, and $\mu_{eff}$ vs. $T$ for (**2**) and (**3**) are reported as supplementary materials (Tables SI—SIII, Figs. S1 and S2) as Document No. 8970 at the office of the Editor of Bull. Chem. Soc. Jpn. The $1/\chi_M$ vs. $T$ plot of (**1**) follows the Curie–Weiss law ($\chi_M=C/(T-\theta)$) with a Weiss constant $\theta=1.1$ K, suggesting a weak ferromagnetic interaction. The effective magnetic moment at room temperature is 8.27 $\mu_B$, which is slightly larger than the spin-only value (8.12 $\mu_B$) in the absence of the magnetic interaction of this spin-system ($S_{Cu}=1/2$, $S_{Gd}=7/2$). 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 its $\mu_{eff}$ value can be approximated by the spin-only equation, $\mu_{eff}=[4S(S+1)]^{1/2}$. As the temperature is lowered, the magnetic moment increasing gradually from 8.27 $\mu_B$ at 300 K, reaches a maximum value of 9.10 $\mu_B$ at 10.0 K, and then decreases to 8.73 $\mu_B$ at 4.8 K. The maximum value (9.10 $\mu_B$) is comparable to the spin-only value (8.94 $\mu_B$) for the spin-state $S=4$, which should arise from a ferromagnetic spin-coupling of the spin-system Gd(III)-Cu(II) ($S_{Gd}=7/2$, $S_{Cu}=1/2$). Thus, the observed magnetic behavior clearly demonstrates the operation of an intramolecular ferromagnetic spin-coupling between Gd(III) and Cu(II) ions. A decrease in the magnetic moment below 10 K may be attributed to an intermolecular antiferromagnetic interaction. The magnetic behaviors of (**2**) and (**3**) are essentially similar to that of (**1**). The magnetic data could be reproduced on the basis of a spin-only expression including a correction

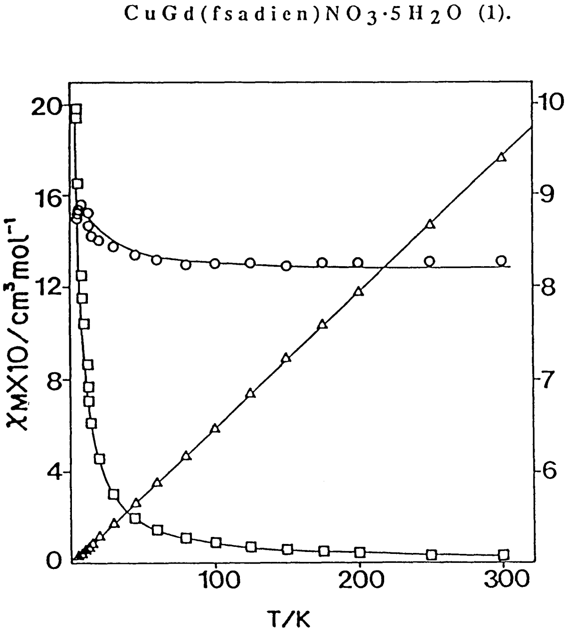


Fig. 1. Plots of $\chi_M$ vs. $T$(△), $1/\chi_M$ vs. $T$(△), and $\mu_{eff}$ vs. $T$(○) for (**1**), where $\chi_M$ is the magnetic susceptibility per GdCu unit, $\mu_{eff}$ the effective magnetic moment. The theoretical curve is drawn with the fitting parameters $g=2.01$, $J=+2.3$ $cm^{-1}$, $\theta=-0.12$ K as solid lines.

Table 1. Coupling Constants in Gd(III)-Cu(II) Complexes

| Compound | System | $J_{GdCu}$ | $\theta$ | $J_{CuCu}$ | Ref. |
|---|---|---|---|---|---|
| $CuGd(fsaen)NO_3 \cdot 3H_2O$ | GdCu | +2.1 | — | — | 6 |
| $CuGd(fsadien)NO_3 \cdot 5H_2O$ (**1**) | GdCu | $+2.3^{a)}$ | −0.12 | — | This work |
| $CuGd(hsapn)NO_3 \cdot 3H_2O$ (**2**) | GdCu | $+5.7^{b)}$ | −1.5 | — | This work |
| $Gd(pvm)_3Cu(A)$ (**3**) | GdCu | $+0.5^{c)}$ | — | — | This work |
| $[Cu(hapen)_2Gd(H_2O)_3](ClO_4)_3$ | $GdCu_2$ | +2.7 | — | −2.1 | 4 |
| $[Cu(salen)_2Gd(H_2O)_3](ClO_4)_3$ | $GdCu_2$ | +3.7 | — | −6.1 | 4 |
| $[Cu(saltn)_2Gd(H_2O)(NO_3)_2]$ | $GdCu_2$ | +0.61 | — | −1.8 | 3 |
| $[Gd(hfac)_3Cu(satn)OH]_2$ | $Gd_2Cu_2$ | +1.42 | — | −1.73 | 5 |

The spin-Hamiltonian is taken as the form $H=-2JS_{Gd} \cdot S_{Cu}$ for all the complexes. Cu(hapen) $=N,N'$-ethylenebis[1-(*o*-hydroxyphenyl)ethaniminato]copper(II). Cu(salen)=[$N,N'$-di(salicylidene)ethylenediaminato]copper(II). Cu(saltn)=[$N,N'$-di(salicylidene)-1,3-propanediaminato]-copper(II). $H_4$fsaen=$N,N'$-bis(3-carboxysalicylidene)ethylenediamine. a), b), c). The agreement factors $R=[\sum(\mu_{obsd}-\mu_{cald})^2/\sum\mu_{obsd}^2]^{1/2}$; a), 0.014; b), 0.015; c), 0.0068.

term of intermolecular interaction (1), where a spin-Hamiltonian is defined as $H=-2JS_{Cu} \cdot S_{Gd}$.

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

Theoretical curves using the best-fit parameters are represented as solid lines in Fig. 1. The best-fit parameters of (**1**)—(**3**) and the agreement factors $R=[\sum(\mu_{obsd}-\mu_{cald})^2/\sum\mu_{obsd}^2]^{1/2}$, along with the parameters of Gd(III)-Cu(II) oligomers reported so far are given in Table 1. The coupling between Gd(III) and Cu(II) ions are all ferromagnetic, in spite of the differences among the complexes in coordination numbers, coordination geometries, and bridging ligands (phenoxo, hydroxo, imidazolato). The coupling constants ($J_{GdCu}$) are small and similar to each other. The magnetic behaviors of the present discrete binuclear complexes (**1**)—(**3**) have demonstrated undoubtedly a ferromagnetic spin-coupling between the Gd(III) and Cu(II) ions.

In a superexchange mechanism which is successfully applicable to d-transition metal polynuclear complexes, a weak antiferromagnetic interaction would be expected, since the magnetic orbital of Cu(II) can overlap at least one of the seven f orbitals of Gd(III) ion and the antiferomagnetic contribution is dominat. Accidental orthogonality is also not probable due to the fact that ferromagnetic coupling is always observed in complexes with different coordination numbers, geometries, and bridging groups. One plausible mechanism that can cause a ferromagnetic coupling between Gd(III) and Cu(II) proposed by Benelli et al.[5] is the spin-polarization that occurs when the magnetic orbital of Cu(II) overlaps the empty 6s orbital of Gd(III) through a filled bridging orbital. The fraction of unpaired electron thus polarized from Cu to Gd is parallel to the f electrons due to Hund's rule, affording ferromagnetic coupling between Cu(II) and Gd(III). The fact that the 4 f orbital is shielded by the outer filled 5s and 5p orbitals, and lanthanoid ions generally form complexes using 6s, 6p, and/or 5d orbitals supports the spin-polarization mechanism.

**Supplementary Material Available:** Tables SI, SII, and SIII (temperatures, magnetic susceptibilities per CuGd unit, and effective magnetic moments per CuGd unit for (**1**), (**2**) and (**3**)), and Figures S1 and S2 (temperature dependence of the magnetic susceptibilities, reciprocal magnetic susceptibilities, and effective magnetic moments for (**2**) and (**3**)).

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