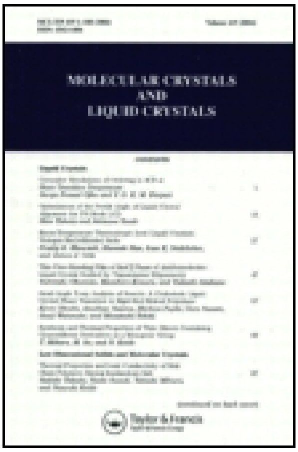

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# Ferromagnetic Spin-Coupling of Several Homo- and Mixed-Metal Complexes

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# FERROMAGNETIC SPIN-COUPLING OF SEVERAL HOMO- AND MIXED-METAL COMPLEXES

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Abstract Our studies on polynuclear metal complexes with ferromagnetic spin-coupling are described; (1) Tetranuclear Cu(II) and Ni(II) complexes with cubane structure, (2) mixed-metal complexes with imidazolate bridge, and (3) mixed-metal complexes with oxalate or dithiooxalate bridge.

## INTRODUCTION

Studies on discrete binuclear and oligonuclear metal complexes with ferromagnetic spin-coupling are fundamental requirement not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers[1,2] but also for developing ferromagnetic materials.[2] However, such complexes are relatively rare, while a large number of complexes with antiferromagnetic spin-coupling have been known. We describe here our studies on polynuclear metal complexes with ferromagnetic spin-coupling; (1) tetranuclear Cu(II) and Ni(II) complexes with cubane structure, (2) mixed-metal complexes with imidazolate bridge, and (3) mixed-metal complexes with oxalate or dithiooxalate bridge.

(1) Tetranuclear Cu(II) and Ni(II) Complexes with Cubane Structure. Figures 1 and 2 show the crystal structure and magnetic behavior of a Ni(II) complex with a tridentate ligand derived from salicylaldehyde and 2-aminoethanol with the 1:1 mole ratio. The magnetic behavior is represented in the forms of the $\chi_A$ vs. T, $1/\chi_A$ vs. T and the $\mu_{eff}$ vs. T plots, where $\chi_A$ is the magnetic susceptibility per Ni atom and $\mu_{eff}$ is the effective magnetic moment. On lowering the temperature, the $\mu_{eff}$ value per cubane molecule increases gradually and reaches 8.8 $\mu_B$ that is compatible with the spin-only value 8.94 $\mu_B$ of $S_T=4$. The magnetic data demonstrated that the eight unpaired electrons of the four nickel(II) ions are ferromagnetically coupled, the ground spin-state of the cubane molecule being S=4. The X-ray structural analysis confirmed several structural features; the distorted $Ni_4O_4$ cubane structure, the tetragonal bipyramidal coordination geometry

around each nickel(II) ion, and nearly perpendicular arrangement between adjacent basal coordination planes. The copper(II) complex with similar cubane structure exhibits a ferromagnetic spin-coupling, where the four unpaired electrons of the four copper(II) ions are ferromagnetically coupled and the ground spin-state is S=2.[4]

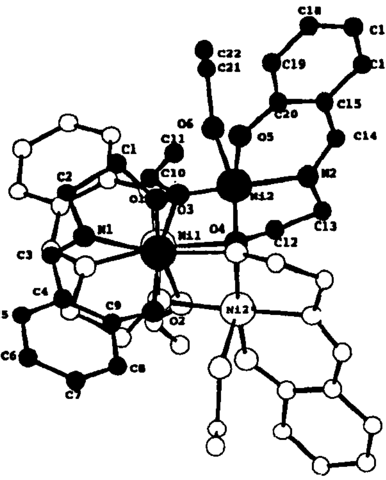


FIGURE 1 Crystal structure of tetranuclear Ni(II) complex with tridentate ligand derived from salicylaldehyde and 2-aminoethanol

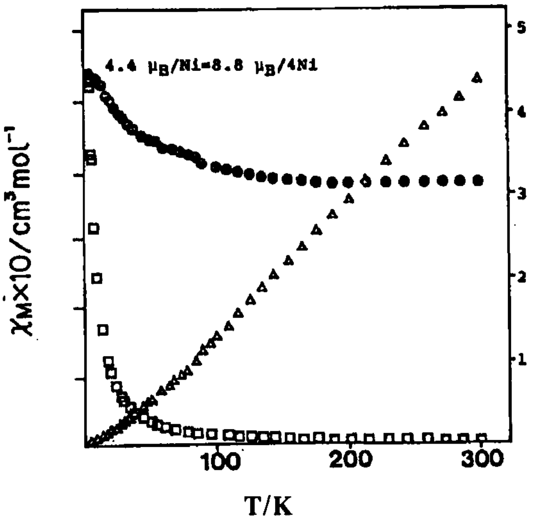
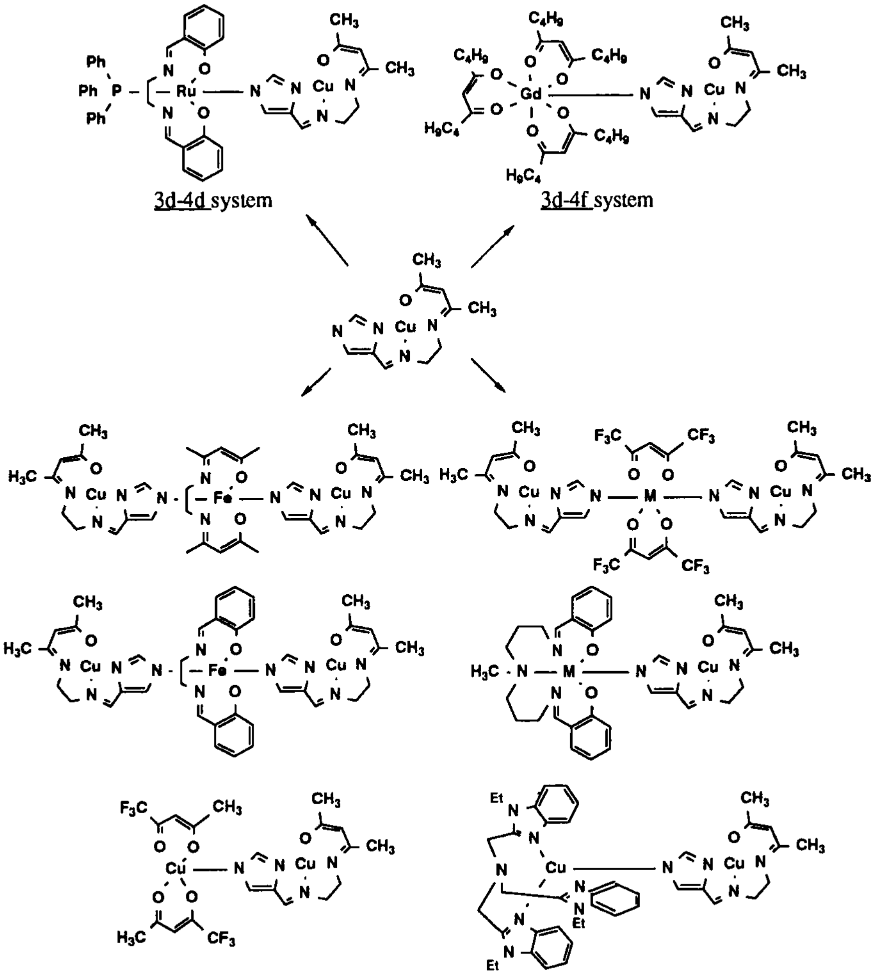


FIGURE 2 Plots of the $\chi_A$ vs. T, $1/\chi_A$ vs. T and $\mu_{eff}$ vs. T, where $\chi_A$ is the magnetic susceptibility per Ni atom and $\mu_{eff}$ is the effective magnetic moment

(2) Mixed-Metal Complexes with Imidazolate Bridge. Two synthetic strategies for mixed-metal polynuclear complexes have been developed; (a) the use of a binucleating ligand exhibiting inequivalent coordination sites with respect to the ligand field or the stereochemistry[5] and (b) the use of a ligand complex involving coordination ability to other metal ions.[6] We synthesized a copper(II) complex [Cu(HA)]$ClO_4$ and found that the deprotonated form [Cu(A)] is an effective "ligand-complex", where HA is a quadridentate ligand derived from the condensation reaction of acetylacetone, ethylenediamine, and 4-formylimidazole with the mole ratio of 1:1:1.[7]



Synthetic Scheme of Homo- and Mixed-Metal Complexes from "Ligand Complex" [Cu(A)]

As shown in the synthetic scheme, mixed-metal complexes with various combinations of metal ions (3d-3d, 3d-4d and 3d-4f systems) as well as homo-metal complexes exhibiting inequivalent coordination environments can be prepared. Several mixed-metal complexes with ferromagnetic spin-coupling are briefly described.

Cr(III)-Cu(II). A series of trinuclear Cu(II)-M(II)-Cu(II) and Cu(II)-M(III)-Cu(II) complexes are easily obtained by mixing [Cu(A)] and a metal complex exhibiting vacant coordination sites or exchangeable ligands.[8] Among them [Cu(A)Cr(salen)Cu(A)]$ClO_4$ shows a ferromagnetic character.[9] Three unpaired electrons of the Cr(III) ion occupy the $\delta$ and $\pi$ character orbitals with respect to the Cr-N(imidazolate) bond, while an unpaired electron of Cu(II) occupies the $\sigma$ character orbital with respect to Cu-N(imidazolate) bond. The $\delta/\sigma$ and $\pi/\sigma$ orthgonalities are preserved in this system and a ferromagnetic spin-coupling is expected. Figure 3 shows the magnetic behavior. The plots of $1/\chi_A$ vs T obey the Curie-Weiss law with a positive Weiss constant and the $\mu_{eff}$ increases gradually on lowering the temperature, demonstrating ferromagnetic spin-coupling. The magnetic susceptibility data were analyzed on the basis of the spin-only expression and the best-fit parameters g=1.95 and J=+8.0 $cm^{-1}$ were obtained, where the spin-Hamiltonian in the form of $H=-2J(S_{Cr}S_{Cu1}+S_{Cr}S_{Cu2})$ is used.

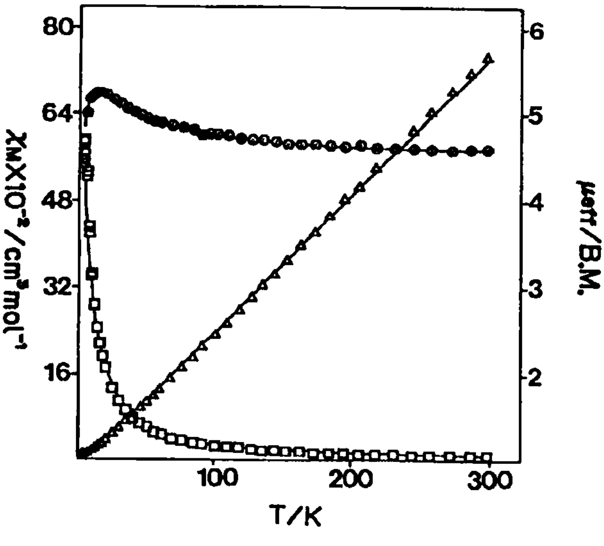


FIGURE 3 Temperature dependency of the magnetic susceptibility, reciprocal magnetic susceptibility, and effective magnetic moment of [Cu(A)Cr(salen)Cu(A)]-$ClO_4$, where the solid lines represent theoretical curves

Fe(III)-Cu(II). Two types of Cu(II)-Fe(III)-Cu(II) complexes, [Cu(A)Fe(acen)-Cu(A)]$ClO_4$ **1** and [Cu(A)Fe(salen)Cu(A)]$ClO_4$ **2** were prepared, where Fe(III) ion of **1** is in low-spin state and Fe(III) of **2** is high-spin state.[10] Figure 4 shows the temperature dependencies of the effective magnetic moment of **1** and **2**, demonstrating that the magnetic interaction between Fe(III) and Cu(II) ions is ferromagnetic for **1** and antiferromagnetic for **2**. ESR investigations on **1** showed that the Fe(III) and Cu(II) ions have an unpaired electron on $\delta$ and $\sigma$ character orbitals with respect to the Fe-N(imidazolate) and Cu-N(imidazolate) bonds, respectively. Therefore, the ferromagnetic spin-coupling in **1** can be explained in terms of the $\delta/\sigma$ orthogonality of the interacting magnetic orbitals. On the other hand, the Fe(III) of **2** is in high-spin state of a $d^5$ electronic configuration, and no strict orthogonality can be realized because at least one of the five magnetic orbitals of Fe(III) brings about a finite overlap integral with that of the Cu(II) ion and this provides an antiferromagnetic contribution that is usually dominant.

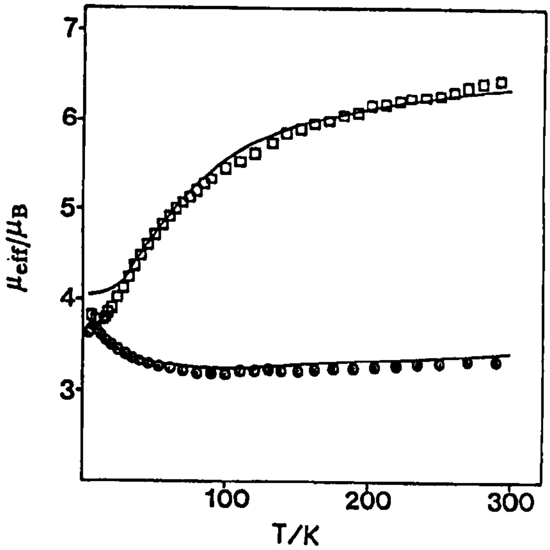


FIGURE 4 Temperature dependency of the effective magnetic moments for Cu(II)-Fe(III)-Cu(II) complexes; **1** (square) and **2** (circle).

Ru(III)-Cu(II). The magnetic susceptibility of Cu(II)-Ru(III) complex, [Ru(salen)($PPh_3$)Cu(A)]$ClO_4$, was measured. The Curie plot of $1/\chi_A$ vs. $T$ is nearly linear in the temperature range 5-300 K and obeys the Curie-Weiss law $1/\chi_A=(T-\theta)/C$ with a positive Weiss constant 1.9 K, suggesting a ferromagnetic interaction. The effective magnetic moment per molecule is 2.60 $\mu_B$ at room temperature which is slightly larger than the spin-only value 2.45 $\mu_B$ of binuclear Cu(A)-Ru(III) ($S_{Cu}$=1/2, $S_{Ru}$=1/2) system assuming no magnetic interaction between the metal ions. Below 50 K the moment increases gradually from 2.63 $\mu_B$ at 50 K to the maximum value 2.91 $\mu_B$ at 6 K and then decreases to 2.85 $\mu_B$ at 4.1 K. The maximum value 2.91 $\mu_B$ at 6 K is compatible with the spin-only value 2.83 $\mu_B$ expected for the spin ground state $S_T$=1 derived from ferromagnetic coupling of binuclear system ($S_{Ru}$=1/2, $S_{Cu}$=1/2). The magnetic susceptibility data were analyzed and the best-fit parameters $J$=+6.5 cm$^{-1}$ and $g$ = 2.04 were obtained. The coupling constant $J$=+6.5 cm$^{-1}$ is compatible with that (+9.0 cm$^{-1}$) of Cu(II)-Fe(III)(low spin)-Cu(II) trinuclear complex with imidazolate bridge **1**. The ESR spectra of [Cu(A)], [Ru(salen)(PPh$_3$)]Cl, and [Ru(salen)(PPh$_3$)Cu(A)]ClO$_4$ on frozen solutions at liquid nitrogen temperature were measured. Using the ESR spectra, the magnetic orbitals of the Cu(II) and Ru(III) ions were determined, as shown in Figure 5. As illustrated the magnetic orbitals of the Ru(III) and Cu(II) ions have δ and σ symmetries with respect to the Ru-N(imidazolate nitrogen) and Cu-N(imidazolate nitrogen) bonds, respectively. Therefore, the ferromagnetic coupling is explained in terms of the δ/σ orthogonality of the magnetic orbitals, indicating that the concept of the orthogonality of the magnetic orbitals is also applicable to 3d-4d system.

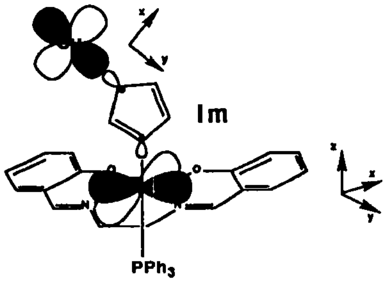


FIGURE 5 Magnetic orbitals of Ru(III) and Cu(II) ions

Gd(III)-Cu(II). The reaction of [Gd(pvm)$_3$] and [Cu(A)] in chloroform gave a 1:1 adduct [Gd(pvm)$_3$Cu(A)]. The magnetic behavior shows a ferromagnetic spin-coupling between the Gd(III) and Cu(II) ions.[11]

(3) Mixed-Metal Complexes with Oxalate or Dithiooxalate Bridge. We have reported a series of mixed-metal assemblies with the formula of $\{NBu_4[MCr(ox)_3]\}_x$ ($NBu_4^+$=tetra($n$-butyl)ammonium ion, ox$^{2-}$=oxalate ion, M$^{2+}$=Mn, Fe, Co, Ni, Cu, Zn).[12] In order to correlate the magnetic and structural properties of the mixed-metal

assemblies with the corresponding building unit, discrete oxalate-bridged Cr(III)-M(II) complexes were synthesized and their magnetic properties were investigated.[13]

Cr(III)-Cu(II). A "ligand complex", [Hpip][Cr(salen)(ox)] ($Hpip^+$=piperidinum ion, $H_2salen$=N,N-bis(salicylidene)ethylenediamine), reacts with several metal(II) complexes exhibiting a vacant coordination site or a substitutable ligand to give oxalate-bridged Cr(III)-M(II) complexes, where as metal(II) complexes ([Cu([9]ane$N_3$)Cl]+, [Ni([9]ane$N_3$)$Cl_2$], [ Mn(tea)$Cl_2$] (tea=tris(2-aminoethyl)amine), and etc were used.

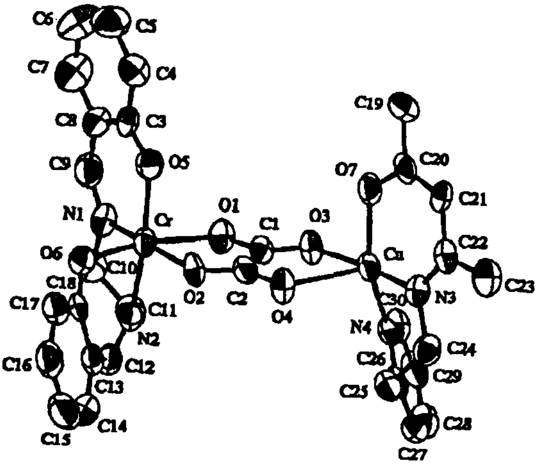


FIGURE 6 Structure of [(salen)Cr(ox)Cu(L)].

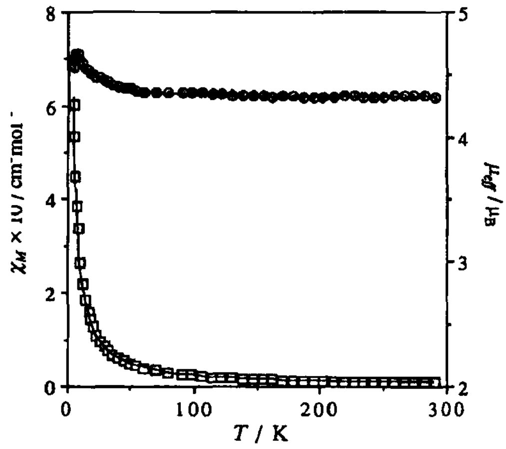


FIGURE 7 Temperature dependency of the magnetic susceptibility and effective magnetic moment of [(salen)Cr(ox)Cu(L)], where the solid lines represent theoretical curves.

Figures 6 and 7 show the crystal structure and magnetic behavior of a Cr(III)-Cu(II) complex [(salen)Cr(ox)Cu(L)] (HL=N-acetylacetonylidene-N-(2-pyridylethyl)amine), respectively. The magnetic interaction between Cr(III) and Cu(II) ions is ferromagnetic with the J value of +2.2 $cm^{-1}$.

Cr(III)-Ni(II). From the viewpoint of the strict orthogonality of the two interacting magnetic orbitals, most preferable mixed-metal ions pair both in octahedral surroundings is Cr(III)-Ni(II), because Cr(III) has three unpaired electrons occupying the three $t_{2g}$ orbitals and Ni(II) has two unpaired electron occupying the two $e_g$ orbitals. Kahn et al reported the first compound of this kind, {Cr[(dto)Ni($Me_6$[14]ane$N_4$]$_3$}-($ClO_4$)$_3$.[14] However, the structure has not been determined. We synthesized the corresponding dithiooxalate bridged $CrNi_3$ complex and obtained both the magnetic and structural properties. Figures 8 and 9 show the crystal structure and magnetic behavior, respectively. The magnetic interaction between Cr(III) and Ni(II) ions is ferromagnetic and the J-value is evaluated at +7.2 $cm^{-1}$ that is three times larger than that of the corresponding oxalate-bridged $CrNi_3$ complex.

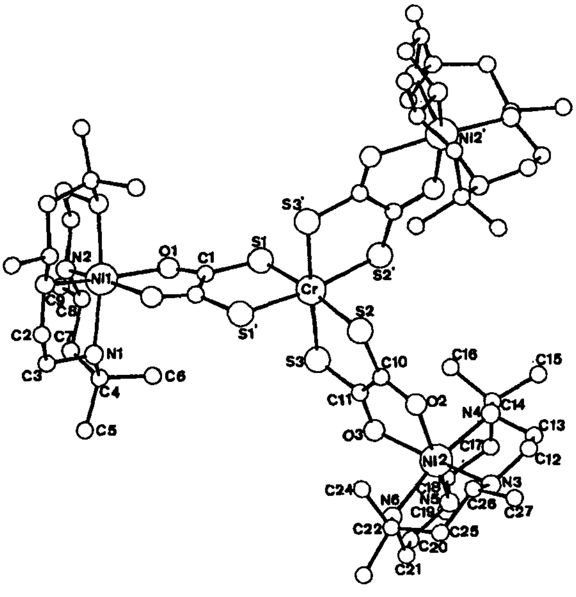


FIGURE 8 Crystal structure of the cation {Cr[(dto)Ni($Me_6$[14]ane$N_4$]$_3$}$^{3+}$, where dto=dithiooxalate and $Me_6$[14]ane$N_4$=racemic-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. There is a $C_2$ axis running through the atoms of Cr and Ni1.

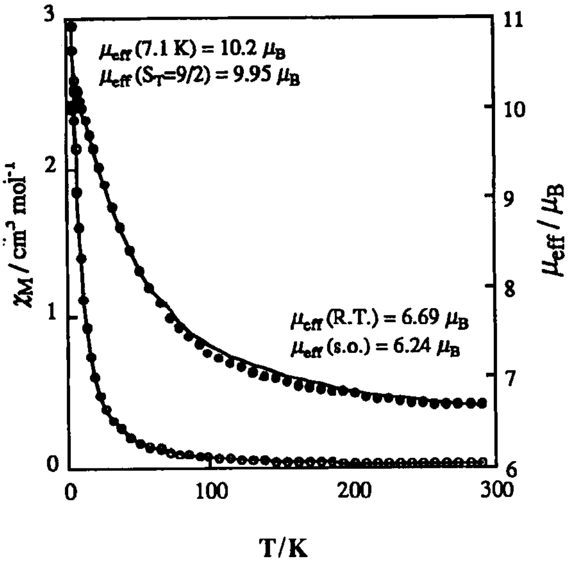


FIGURE 9 Temperature dependency of the magnetic susceptibility and effective magnetic moment of $CrNi_3$, where the solid lines represent theoretical curves.

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