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Correlation between Spin-Coupling Constants of Oxalate-bridged Binuclear Cu(II)-Cr(III) Complexes and of Ferromagnetic Phase-Transition Temperature *Tc* of $\{NBu_4[CuCr(ox)_3]\}_x$

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Three oxalate-bridged binuclear Cu(II)-Cr(III) complexes [(salen)Cr(ox)-Cu(L^m)] (**1**, HL^1=N-salicylidene-N-(2-pyridylethyl)amine; **2**, HL^2=N-acetylacetonylidene-N-(2-pyridylethyl)amine; **3**, HL^3=N-salicylidene-N',N'-diethylethylenediamine) have been prepared and the cryomagnetic susceptibility measurements(4.2-300 K) revealed that the spin-coupling is ferromagnetic with the J values +2.8, +2.2, and +2.7 cm^{-1} for **1**, **2**, and **3**, respectively, based on $H=-2JS_{Cu}S_{Cr}$. The J values are well compatible with J=+2.9 cm^{-1} of $\{NBu_4[CuCr(ox)_3]\}_x$ evaluated from the equation $Tc=nJ/3k[S_{Cr}(S_{Cr}+1)S_{Cu}(S_{Cu}+1)]^{1/2}$ (Tc=7 K, n=3) based on Heisenberg's theory of ferromagnetism.

The design of molecular-based ferromagnets is one of the stimulating challenges for chemists.[1-3] In the previous paper, we have reported a novel type of ferromagnet $\{NBu_4[CuCr(ox)_3]\}_x$, which should be composed of three-dimensional networks constructed by Cr(III)-ox-Cu(II) linkages as shown in Fig. 1.[4] Thus, the ferromagnetic phase-transition temperature *Tc* should be simply correlated to the magnitude of the magnetic interaction of

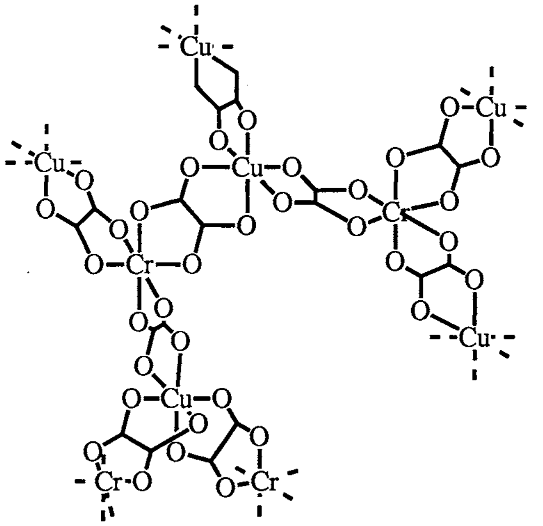
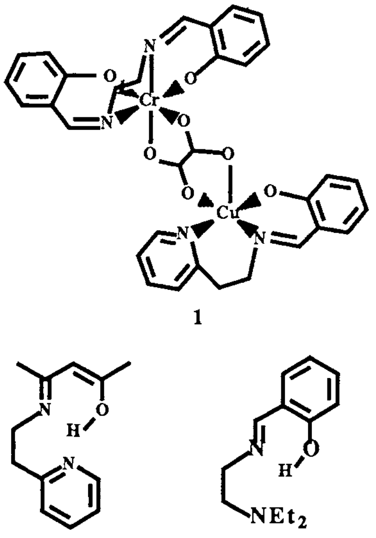


Fig. 1. Three-dimensional structure of $\{NBu_4[CuCr(ox)_3]\}_x$.



1

HL^2 HL^3

Schematic structures of **1** , HL^2, and HL^3

the constituting Cr(III)-ox-Cu(II) unit. However, oxalate-bridged Cr(III)-Cu(II) binuclear complexes which are essential to confirm the above mentioned view have not been reported.

In this study, three oxalate-bridged Cr(III)-Cu(II) complexes [(salen)Cr(ox)Cu(L^m)] (m=1, 2, 3) have been prepared and the magnetic properties of the complexes have been investigated in order to examine the correlation between the coupling constants and the *Tc* of $\{NBu_4[CuCr(ox)_3]\}_x$, where H_2salen=N,N'-bis(salicylidene)ethylenediamine, HL^1=N-salicylidene-N-(2-pyridylethyl)amine, HL^2=N-acetylacetonylidene-N-(2-pyridylethyl)amine, and HL^3=N-salicylidene-N',N'-diethylethylenediamine.

The Cr(III) component complex [Hpip][Cr(salen)(ox)] was prepared by the reaction of $[Cr(salen)(H_2O)_2]NO_3$ and $[Hpip]_2[ox]\cdot 2H_2O$ according to the method of literature[5]) ($Hpip^+$=piperidinium cation, ox^{2-}=oxalate anion). The copper(II) component complexes $[Cu(L^m)H_2O]ClO_4$ (m=1, 2, 3) were obtained as green crystals by the reaction of copper(II) acetate monohydrate, HL^m, triethylamine, and $NaClO_4$ in methanol with the mole ratio of 1:1:1:1.[6])

The complex **1** $[(salen)Cr(ox)Cu(L^1)]0.5H_2O$ was prepared as follows; To a methanol solution (30 cm^3) of $[Cu(L^1)H_2O]ClO_4$ (1 mmol) was added a mixed solution of methanol-water(150 cm^3) of [Hpip][Cr(salen)(ox)] (1 mmol) at room temperature to precipitate immediately dark green crystalline material. They were collected by suction filtration, washed with methanol, and dried in air. They were recrystallized from dichloromethane at room temperature. The synthesis was carried out without heating to avoid the contamination of biproducts such as Cu(ox). Anal. Found: C, 54.60; H, 3.93; N, 7.91; Cr, 7.09; Cu, 8.89%. Calcd for $C_{32}H_{27}N_4O_7CrCu\cdot 0.5H_2O$: C, 54.59; H, 4.01; N, 7.96; Cr, 7.38; Cu, 9.63%.

The complex **2** $[(salen)Cr(ox)Cu(L^2)]1.5H_2O$ was prepared in a way similar to that of **1**. Anal. Found: C, 51.71; H, 4.44; N, 8.09; Cr, 7.10; Cu, 8.79%. Calcd for $C_{30}H_{29}N_4O_7CrCu\cdot 1.5H_2O$: C, 51.47; H, 4.60; N, 8.00; Cr, 7.43; Cu, 9.08%.

The complex 3 $[(salen)Cr(ox)Cu(L^3)]0.5H_2O$ was prepared in a way similar to that of **1**. Anal. Found: C, 53.15; H, 4.67; N, 7.93; Cr, 7.21; Cu, 8.93%. Calcd for $C_{31}H_{33}N_4O_7CrCu\cdot 0.5H_2O$: C, 53.33; H, 4.91; N, 8.03; Cr, 7.45; Cu, 9.10%.

The elemental analyses are consistent with the chemical formulas of [(salen)Cr(ox)Cu(L^m)]. The infrared absorption bands attributable to ClO_4^- (1100 cm^{-1}) and piperidine(3000-3500 cm^{-1}) of the component complexes $[Cu(L^m)H_2O]ClO_4$ and [Hpip][Cr(salen)(ox)] are absent in the infrared spectra of **1**, **2**, and **3**. The electrical conductivity measurements in dichloromethane showed that the compounds are nonelectrolyte.

The magnetic susceptibilities were measured by a SQUID magnetometer in the temperature range 4.2-100 K and by a Faraday balance in the temperature range 80-300 K. The diamagnetic corrections were made with Pascal's constants.[7]) The magnetic behaviors of **1**, **2**, and **3** are similar to each other. The magnetic behavior of **2** is shown in Fig. 2, in the forms of plots of χ_M vs. T, $1/\chi_M$ vs.T, and μ_{eff} vs. T. The plots of $1/\chi_M$ vs. T is nearly linear and obey the Curie-Weiss law($1/\chi_M=(T-\theta)/C$) with a positive Weiss constant θ=1.4 K, suggesting a weak ferromagnetic interaction. The effective magnetic moment per molecule is 4.32 μ_B at 290 K which agrees with the spin-only value 4.24 μ_B of a spin-system (S_1, S_2)=(3/2, 1/2) assuming no magnetic interaction. As the temperature is lowered, the magnetic moment increases gradually from 4.32 μ_B at 290 K to the maximum value 4.66 μ_B at 6-8 K, and then decreases. The magnetic data were analyzed by Eq. 1 derived from the isotropic spin-Hamiltonian $H=-2JS_1S_2$,

$$\chi_M=(Ng^2\beta^2/kT)[(10+2\exp(-4J/kT))/(5+3\exp(-4J/kT))] + N\alpha \qquad (1)$$

where each symbol has its usual meaning.[8] In the least-squares calculation, the temperature-independent paramagnetism $N\alpha$ is fixed at 100×10^{-6} cm^3 mol^{-1} and the disagreement factor is defined as $R=[\Sigma(\mu_{obsd}-\mu_{calcd})^2/\Sigma\mu_{obsd}{}^2]^{1/2}$. The least-squares fits to the experimental data were attained using parameters g=2.03, J=2.2 cm^{-1}, and R=0.0271. The similar procedures were applied to **1** and **3**, and the best-fit parameters obtained are g=2.20, J=2.8 cm^{-1}, R=0.0343 for **1** and g=2.00, J=2.7 cm^{-1}, R= 0.0220 for **3**. The magnetic analysis revealed that a weak ferromagnetic spin-coupling is operating between Cr(III) and Cu(II) ions through oxalate bridge.

In the previous paper[4] we reported a ferromagnet $\{NBu_4[CuCr(ox)_3]\}_x$, which should be composed of three-dimensional networks constructed by Cr(III)-ox-Cu(II) linkages. The temperature dependence of magnetization under a weak magnetic field showed a ferromagnetic phase-transition at Tc=7 K. For this three-dimensional assembly the coupling constant of the constituting unit Cr(III)-ox-Cu(II) can be evaluated by the equation (2) based on the Heisenberg's theory on ferromagnetism,[9]

$$Tc=nJ/3k[S_{Cr}(S_{Cr}+1)S_{Cu}(S_{Cu}+1)]^{1/2} \qquad (2)$$

where Tc is ferromagnetic phase-transition temperature, k denotes Boltzman constant, and n is the number of neighboring metal ions of Cr(III). By introducing Tc=7 K and n=3 to Eq. 2, the J value of the constituting unit Cu(II)-ox-Cr(III) of $\{NBu_4[CuCr(ox)_3]\}_x$ is calculated at 2.9 cm^{-1}, which is well compatible with the J values of **1**, **2**, and **3**. This result demonstrates that $\{NBu_4[CuCr(ox)_3]\}_x$ assumes a three-dimensional network structure and the ferromagnetic phase-transition temperature is determined by the magnitude of coupling constant of the constituting unit Cr(III)-ox-Cu(II).

In the latest five years, three-types of molecular-based magnetic

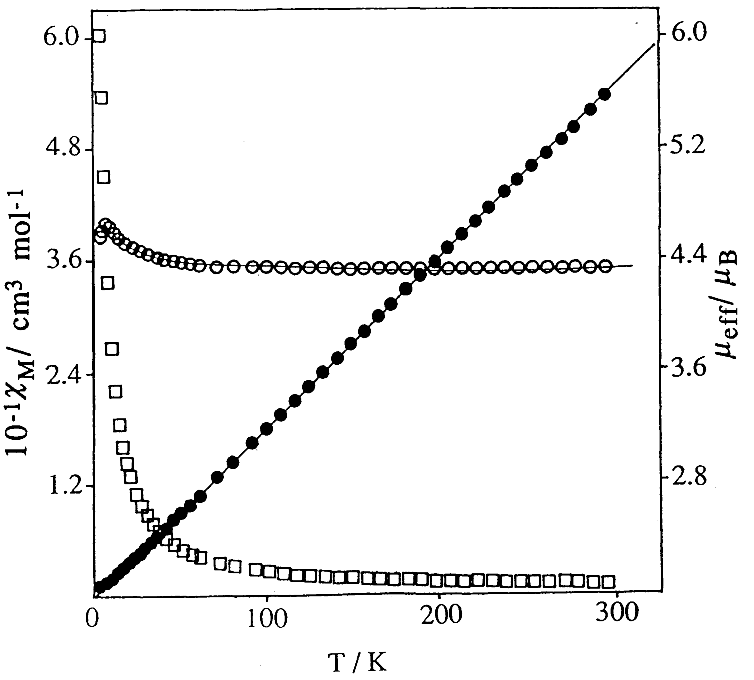


Fig. 2. Temperature dependences of χ_M(□), $1/\chi_M$(●), and μ_{eff}(○) for 2.

materials exhibiting ferromagnetic phase-transition have been fully characterized from both structural and magnetic viewpoints; (1) Miller's charge-transfer complex $[Fe(Me_5Cp)_2]^+[TCNE]^-$ (Me_5Cp=penta-methylcyclopentadienyl, TCNE=tetra-cyanoethylene),[1] (2) Kahn's hetero-metal one-dimensional complex $\{MnCu(pbaOH)(H_2O)_3\}_x$ ($pbaOH^{4-}$=2-hydroxy-1,3-propylenebis(oxamato) anion),[2] and (3) Gatteschi's Mn(II)-organic radical linear-chain complex $\{Mn(hfac)_2NITR\}_n$ ($hfac^-$=hexafluoroacetylacetonate ion, NITR=2-R-4,4,5,5-tetramethyl-4,5-dihydro-1H-imidazo-yl-1-oxy 3-oxide).[3] These molecular-based ferro- and ferri-magnets are essentially composed of one-dimensional chains where there are two distinct magnetic interactions, i.e. intrachain and inter-chain interactions. For example, in the case of $\{Mn(hfac)_2NITR\}_n$ (R=Me, Et, *n*-Pr)[3] the intrachain interaction is strongly antiferromagnetic (J = -105 - -165 cm^{-1}) whereas the interchain interaction is weakly ferromagnetic. The phase-transition temperatures of those ferri- and ferro-magnets based on one-dimensional chains are mainly determined by the weaker interchain magnetic interaction, hence are limited to a low temperature.

The present study has revealed that the Tc of ferromagnet with a three-dimensional network structure can be improved when the M_A-L-M_B building unit is properly chosen so as to cause a strong magnetic interaction. Along with this line the modifications of $\{NBu_4[CuCr(ox)_3]\}_x$ are in progress in our laboratory.

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