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Ferromagnetic Interaction in Oxalato Bridged Cu(II) Complex with Zigzag Chain Structure

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Magnetic susceptibility study on a zigzag chain complex $[Cu(ox)(bpy)]\cdot 2H_2O$ bridged by oxalates has revealed that the complex is a ferromagnetic S=1/2 Heisenberg linear chain (J = +1.22 cm^{-1} and g= 2.185), and magnetization experiment at 2.0 K has revealed that spin multiplicity (S) is greater than 3/2.

Molecular based ferromagnetic materials have been of continuing interest. An oxalato group has been proved to propagate a strong magnetic interaction1) and this anion is promising bridging ligand to built molecular assemblies which have interesting magnetic properties. Recently, heteronuclear oxalato bridged systems Cr(III)-Ni(II)2) and Cr(III)-Cu(II)3) have been reported to have a ferromagnetic interaction because the orthogonality of the magnetic orbitals (d_π spin for Cr(III), and d_σ spins for Ni(II) and Cu(II)). It is, however, expected that a homonuclear system with a low dimensional structure can also have the ferromagnetic interaction if each magnetic orbitals in adjacent metal ions are orthogonal. In this report, the intrachain magnetic interaction in a homonuclear complex $[Cu(ox)(bpy)]\cdot 2H_2O$4) with a zigzag chain structure is described and the origin of ferromagnetic interaction is discussed.

Samples of $[Cu(ox)(bpy)]\cdot 2H_2O$ were prepared by the procedure given by Hathaway et al.4) X-Ray structure analysis5) of the blue crystals revealed that the complex forms an infinite 'zigzag' chain structure along c-axis (Fig. 1) by the bridge of oxalate anion. The copper atom is coordinated by two nitrogen atoms of the bipyridine and four oxygen atoms of the two oxalate ligands and a coordination geometry of the copper atom is described as an elongated rhombic octahedron. The oxalate ligands are centrosymmetric and involved in an asymmetric bridges between centre-related copper atoms. According to the bond lengths and angles around Cu and coordinating atoms(Cu-O(1): 1.984(2), Cu-O(2): 1.993(1), Cu-N(1): 2.012(1), Cu-N(2): 1.998(2), Cu-O(3): 2.313, Cu-O(4): 2.314 Å, O(1)-Cu-O(2): 90.31(5), O(1)-Cu-N(1): 94.02(6), O(1)-Cu-N(2): 173.67(6), O(1)-Cu-O(3): 77.89(6), O(1)-Cu-O(4): 89.95(6), O(2)-Cu-N(1): 175.64(7), O(2)-Cu-N(2): 94.93(6), O(2)-Cu-O(3): 85.74(5), O(2)-Cu-O(4): 77.50(5), N(1)-Cu-N(2): 80.72(6), N(1)-Cu-O(3): 94.67(6), N(1)-Cu-O(4): 102.97(6), N(2)-Cu-O(3): 98.92(7) N(2)-Cu-O(4): 94.66(6)°), that is, four bonds with small bond distances and two bonds with large bond distances, the ground state of the copper atom can be expressed as the $d_{x^2-y^2}$ with a subtle mixing of d_{z^2} orbital. The basal plane for the octahedron is regarded as the plane defined by the O(1), O(2), N(1), and N(2) atoms.

Cryogenic magnetic susceptibilities were measured down to 1.9 K. $\chi_m T$ vs. Temperature plot (Fig. 2) shows a gradual increase starting from 60 K as the temperature decreased. This magnetic behavior does indicate the existence of the ferromagnetic interaction between metal centers. A small hump appearing in the temperature range from 30 to 50 K is due to the absorbed oxygen. The magnetic susceptibility data was analyzed based on ferromagnetic S=1/2 Heisenberg linear chain model.6,7) A least squares calculation gave the best fit parameters to be J = +1.29 cm^{-1} and g = 2.19 where Currie and Weiss constants are 0.4405 cm^3 mol^{-1} K^{-1} and 2.07 K,

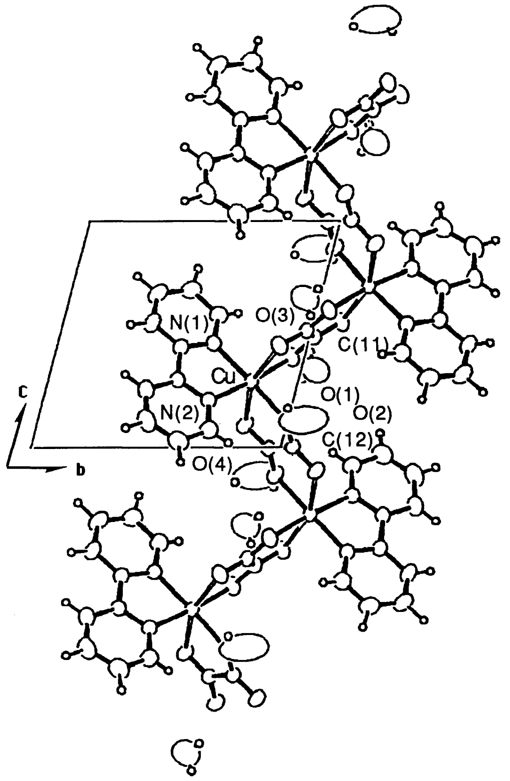

Fig. 1. Projection View on *bc*-plane.

respectively. The best fit g value is slightly higher than the g value obtained by Currie constant. The result of the magnetization as a function of applied field at 2 K (Fig. 3) also supports a ferromagnetic interaction, that is, the experimental magnetization values at 2 K were greater than predicted value by the Brillouin function for S = 1/2 system.8) From the data of the low magnetic field region, the spin multiplicity as the result of ferromagnetic interaction is greater than 3/2. It is reasonable to conclude that the ferromagnetic interaction is an intrachain interaction propagated by bridging oxalate because the copper atom is coordinated by six atoms and the closest copper atoms are adjacent each other in the chain.

Some mechanisms to explain the ferromagnetic interaction in multinuclear copper(II) complexes bridged by acetato- or caroboxylato groups have been proposed.9) The spin density on a copper atom is delocalized to the neighboring copper atom through bridging oxalato ligand. There are two types of the σ-pathways. First is a Cu-O(1)-C(11)-C(11)'-O(1)'-Cu' or Cu-O(2)-C(12)-C(12)'-O(2)'-Cu' and second is a Cu-O(1)-C(11)-O(3)'-Cu' or Cu-O(2)-C(12)-O(4)'-Cu', where Cu', C(11)', C(12)', O(1)', O(2)', O(3)', and O(4)' atoms belong to the adjacent unit. In the first pathway, O(1)'and O((2)' atoms, on which the spin density might be delocalized from Cu atoms, coordinate to Cu' atom from $d_{x^2-y^2}$ direction, this might result in the antiferromagnetic interaction because the copper atom is in the $d_{x^2-y^2}$ ground state. However , the two bonds (Cu-O(1) and Cu'-O(1)', or Cu-O(2) and Cu-O(2)') are separated by the C-C bonds, this long pathway makes the antiferromagnetic interaction

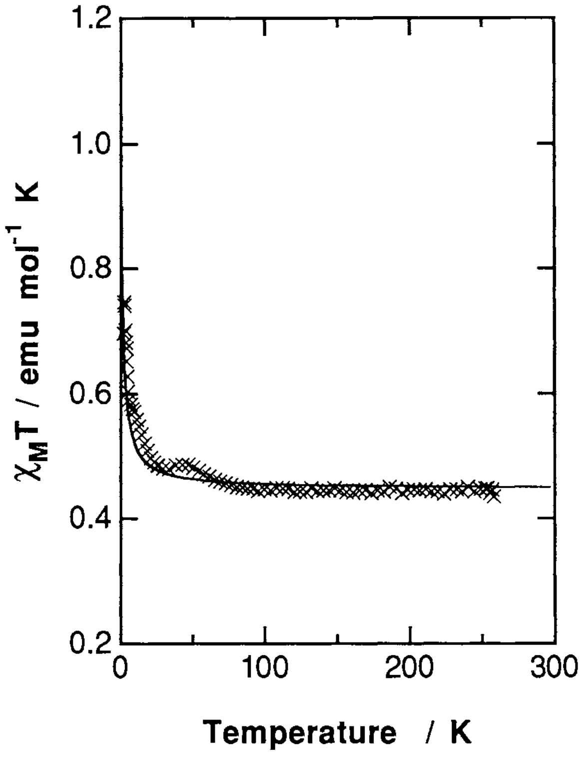

Fig. 2. χ_mT - T plot of $[Cu(ox)(bpy)]\cdot 2H_2O$.

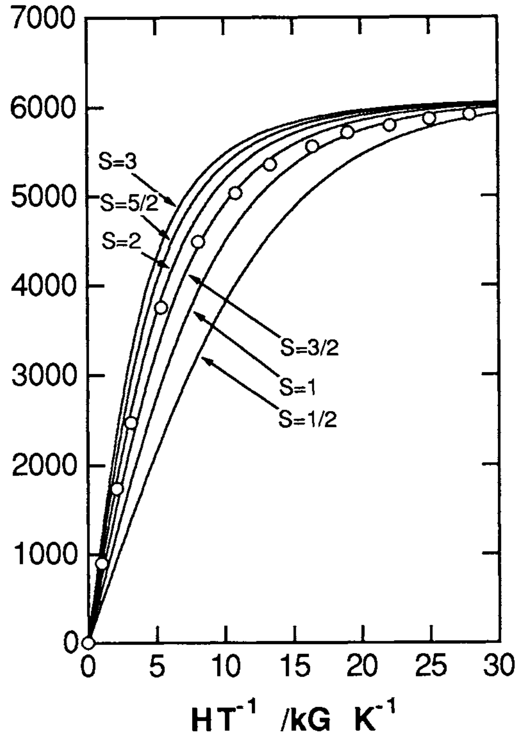

Fig. 3. Plots of magnetization (M)-field strength (H/T)of $[Cu(ox)(bpy)]\cdot 2H_2O$ at 2.0 K. Solod lines are given by the Brillouin fucnction with J=1/2, 1, 3/2, 2, 5/2, and 3.

weak. In the second pathway, the spin density of a copper atom is delocalized on the O(3)' or O(4)' atoms, which coordinates to the adjcacent copper atom from the d_{z^2} direction. The delocalized spin density on the O(3)' and O(4)' atoms can induce the spin on the d_{z^2} orbital of the adjacent copper atom, which is orthogonal to its $d_{x^2-y^2}$ orbital. This orthogonality of the induced spin and its own $d_{x^2-y^2}$ spin on the copper atom is responsible for the ferromagnetic intrachain interaction.

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4) W. Fitzgerald, J. Foley, D. McSweeney, N. Ray, D. Sheahan, S. Tyagi, and B. Hathaway, *J. Chem. Soc., Dalton Trans.*, **1982**, 1117.
5) *Crystal Data* :$C_{12}H_{12}CuN_2O_6$, M = 343.783, triclinic, space group P$\bar{1}$, a = 9.110(1), b = 9.675(1), c = 8.922(1) Å, α = 97.54(1), β = 105.80(1), γ = 110.26(1)°, U = 687.4(2)Å^3, Z = 2, D_c = 1.661 g cm^{-3}, crystal size = 0.40x0.18x0.22 mm^3, λ(Mo K$_\alpha$)= 0.71073 Å, F(000) = 350, μ(Mo K$_\alpha$) = 16.82 cm^{-1}, R =

0.037, $R_w = 0.052$ for 4161 reflections with $|F_0|>3\sigma(F_0)$. Intensity data were collected at room temperature on a Rigaku AFC-5 four-circle diffractometer by use of the ω-2θ scan technique($2° < 2\theta < 65°$). The intensities were corrected for Lorentz-polarization factors and the absorption effect, but not for extinction. The structure was solved by the conventional heavy atom method and refined by a block-diagonal least-squares technique with anisotropic thermal parameters for non-H atoms and isotropic for H atoms. In the refinement, a weighting scheme was chosen as $w=[\sigma_c^2 + (0.030|F_0|)^2]^{-1}$ where σ_c^2 was the standard deviation of $|F_0|$ calculated from counting statistics. All the calculations were carried out on HITAC M680 computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS-III.

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7) The solid line was generated from the best fit calculation using the Padé expansion series for the S=1/2 Heisenberg Model.

$$\chi_m T = Ng^2\mu_B{}^2 T\left[\frac{1+a_1K+a_2K^2+a_3K^3+a_4K^4+a_5K^5}{1+b_1K+b_2K^2+b_3K^3+b_4K^4}\right]^{2/3}$$

where $K = J/2k_BT$, a_i and b_i are expansion coefficient, g is g factor, μ_B is the Bohr magnetron, k_B is the Boltzmann constant, and J is the intrachain-exchange coupling constant.

8) Theoretical magnetization curves(solid lines) are given by the Brillouin function($B_J(x)$) with $J = S = 1/2$, 1, 3/2, 2, 5/2, and 3.

$$M = M_s B_J(x)$$

with $x = Jg\mu_B H/k_BT$, where M_S is the saturation magnetization, J is the quantum number of the total angular momentum and $B_J(x)$ is the Brillouin function for J. In this calculation, g value was estimated to be 2.176 from the Currie constant.

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