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Ferromagnetic Hetero-Metal Assemblies, $\{NBu_4[CuCr(ox)_3]\}_x$ and $\{[\{Cu(bpy)\}_2Cr(ox)_3]NO_3\}_x$

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Two types of hetero-metal assemblies $\{NBu_4[CuCr(ox)_3]\}_x$ (**1**) and $\{[\{Cu(bpy)\}_2Cr(ox)_3]NO_3\}_x$ (**2**)(NBu_4=tetrabutylammonium ion, ox=oxalate ion, bpy=2,2'-bipyridine, x=infinite number) have been synthesized and their cryomagnetic properties (4.2-300 K) have been examined. The compound **1** has an oxalate-bridged three-dimensional lattice and show a ferromagnet-like property (Curie point 7 K): the moment (per CrCu) increases from 4.37 μ_B at 300 K to 14.80 μ_B at 9 K and diverges below 9 K. The compound **2** also shows a ferromagnetic interaction and its moment (per $CrCu_2$) increases from 4.82 μ_B at 300 K to 8.78 μ_B at 5 K.

The design of molecular-based ferromagnetic materials is one of the most stimulating challenges for chemists. In the latest few years several novel examples such as charge-transfer complexes exhibiting ferromagnetism,1) organic molecules with a large spin-multiplicity,2) and a ferromagnetic-like Mn(II)-Cu(II) chain complex with an irregularity of the spin-state structure3) have been reported. Our synthetic strategy to obtain ferromagnetic materials is to assemble paramagnetic metal ions ferromagnetically coupled with each other. We adopt oxalate-bridged Cr(III)-Cu(II) unit as a building block, because the magnetic interaction in such unit must be ferromagnetic owing to the strict orthogonality of the magnetic orbitals of the metal ions.4) Further, it is expected that the oxalate group of trioxalatochromate(III) ion $[Cr(ox)_3]^{3-}$ acts as a ligand to copper(II) ions to form a three-dimensional hetero-metal assemblies. We report here the synthesis and ferromagnetic property of two Cr(III)-Cu(II) hetero-metal assemblies $\{NBu_4[CuCr(ox)_3]\}_x$ **1** and $\{[\{Cu(bpy)\}_2Cr(ox)_3]NO_3\}_x$ **2** (NBu_4=tetrabutylammonium ion, ox=oxalate ion, bpy=2,2'-bipyridine, x=infinite number).

The compound **1** was prepared as follows. Aqueous solutions of $K_3[Cr(ox)_3]$-$3H_2O$ and $Cu(NO_3)_2\cdot 3H_2O$ (in 1:1 mole ratio) were mixed at ambient temperature. To the resulted violet solution was added an aqueous solution of tetrabutylammonium bromide (slight excess) to give a green precipitate. It was collected by filter suction and thoroughly washed with water.5) It was hardly soluble in most common solvents.

The compound **2** was obtained as green microcrystals by the reaction of $K_3[Cr(ox)_3]\cdot 3H_2O$ and $[Cu(bpy)(NO_3)_2]$6) in the 1:1 mole ratio in water. The reaction in the 1:2 mole ratio gave the same result.[7)]

It is presumed that in compounds **1** and **2** the inert chromium(III) ion retains the original six-coordinate environment with three oxalate groups and the $[Cr(ox)_3]^{3-}$ entity functions as a ligand to copper(II) ions through its outer oxalate oxygens. In the IR spectrum of **1** the antisymmetric $\nu(CO)$ vibrations of the oxalate groups appear at 1652 and 1610 cm^{-1} and the $\delta(CO)$ vibrations at 810 and 804 cm^{-1}. Chelated oxalate groups generally show the antisymmetric $\nu(CO)$ vibration at ca. 1700 cm^{-1} and the $\delta(CO)$ vibration at ca. 800 cm^{-1}.[8)] Thus, the IR data indicates that all the oxalate groups of **1** are concerned with bridging. In compound **1**, the coordination geometry of the copper is likely to be a tetragonal pyramidal configuration with two chelate bridging oxalate groups at the basal plane and an oxygen atom of one oxalate group at the axial position. Molecular model shows that the compound assumes a three-dimensional hetero-metal assembly. In compound **2** the coordination geometry of the copper is also likely to be tetragonal pyramid with a bridging oxalate group and a bpy molecule at the basal plane.[9)] Thus, two oxalate groups of the $[Cr(ox)_3]^{3-}$ entity acts as the bridge to $Cu(bpy)^{2+}$. The remaining oxalate group may coordinate to the axial site of a copper of neighboring $\{[\{Cu(bpy)\}_2Cr(ox)_3]NO_3\}$ to form a polynuclear structure. The antisymmetric $\nu(CO)$ vibrations of **2** appear at 1700, 1680, and 1640 cm^{-1}, indicating that there are different coordination modes of oxalate group. The nitrate group is free from coordination judging from its IR band at 1390 cm^{-1}. Recently Kahn et al.[10)] reported a related complex $[Cr(ox)_3\{Ni(Me_6[14]aneN_4)\}_3](ClO_4)_3$ ($Me_6[14]aneN_4$=5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in which the four coordination site of each nickel(II) ion are occupied by $Me_6[14]aneN_4$ as an "end-cap" ligand and the remaining two sites are linked to the outer oxalate oxygens of $[Cr(ox)_3]^{3-}$ to afford a discrete tetranuclear $CrNi_3$ core. There are essential differences between our compounds and Kahn's compound both in structure and magnetism as described below.

Magnetic susceptibilities of **1** and **2** were determined in the temperature range 4.2-100 K by the use of a SQUID magnetometer HOXAN HSM 2000 and in the temperature range 80-300 K by the use of a Faraday balance. Data were corrected for the magnetization of the sample holder and for the diamagnetism of the constituting atoms by the use of Pascal's constants.[11)] The cryomagnetic behaviors of **1** and **2** are shown in Figs. 1 and 2, respectively, in the forms of $1/\chi_M$ vs. T plots and μ_{eff} vs. T plots, where χ_M is the magnetic susceptibility per CrCu unit for **1** and per $CrCu_2$ unit for **2**, μ_{eff} is the effective magnetic moment calculated by the equation $\mu_{eff}=2.828(\chi_M T)^{1/2}$, and T is the absolute temperature.

The plots of inverse magnetic susceptibility against temperature of compound **1** form a linear line in the range 30-300 K but the line is curved significantly below 30 K. The Weiss constant determined from the plots in the 30-300 K range based on the equation $1/\chi_M=C(T-\theta)$ is +14 K, suggesting the operation of ferromagnetic interaction. The effective magnetic moment per CrCu unit is 4.37 μ_B at room temperature which is close to the spin-only value 4.24 μ_B for magnetically non-interacting binuclear Cr(III)-Cu(II) system. As the temperature is lowered, however, the magnetic moment increases gradually and shows a divergence at very

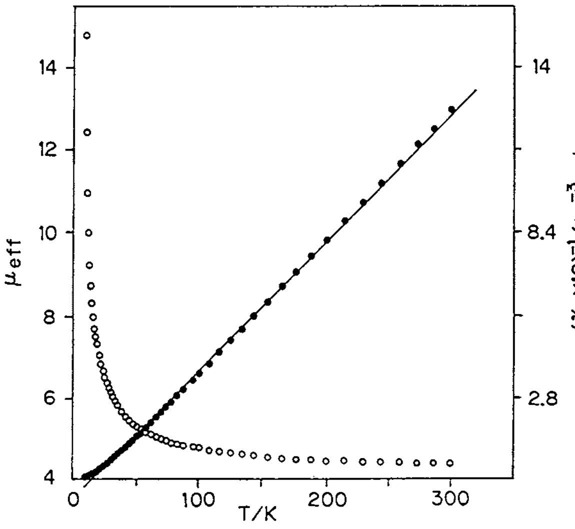

Fig. 1. $1/\chi_M$ vs. T (●) and μ_{eff} vs. T (○) plots of compound **1**.

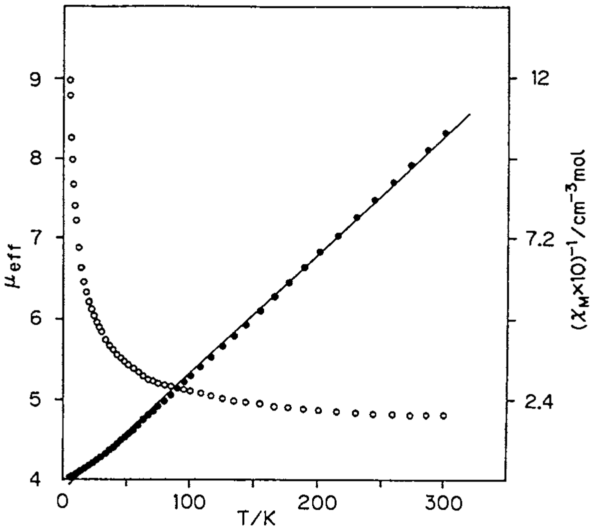

Fig. 2. $1/\chi_M$ vs. T (●) and μ_{eff} vs. T (○) plots of compound **2**.

low temperature. Because of this tendency the magnetic susceptibility near liquid helium temperature could not be determined with our SQUID magnetometer. The magnetic moment at 9 K is 14.80 μ_B. This value is unusually large compared with 4.90 μ_B, the spin-only value for the S=2 state generated by ferromagnetic coupling of Cr(III) and Cu(II) ions in the discrete binuclear system. Temperature dependence of the magnetization of **1** was measured by applying a weak magnetic field (2 G). The result indicated the Curie point of 7 K, as expected for a polycrystalline ferromagnet.3) Thus, the unusual magnetic behavior of **1** must be arising from the three-dimensional lattice comprised of ferromagnetically interacting chromium(III)-oxalate-copper(II) units.

The plots of $1/\chi_M$ vs. T of compound **2** form a linear line in the temperature range 4.5-300 K with a Weiss constant of +9 K, indicating the operation of a ferromagnetic interaction. The effective magnetic moment per $CrCu_2$ unit is 4.82 μ_B at room temperature. The moment gradually increases with lowering of temperature to 8.78 μ_B around 5 K and diverges below this temperature. The cryomagnetic result clearly demonstrates that this compound is not trinuclear, because the magnetic moment at 5 K (8.78 μ_B) is much larger than the spin-only value 5.92 μ_B expected for the largest total-spin state (S=5/2) in the trinuclear $Cr^{III}Cu^{II}_2$ system. The trend in the increase of the magnetic moment with lowering of temperature is not so pronounced as that of **1**, but the cryomagnetic behavior strongly suggests that **2** also has a three-dimensional lattice.

The detailed molecular structures of **1** and **2** are unknown. The present study, however, demonstrates that the use of chromium(III)-oxalate-copper(II) as a building block offers a promising way for the design of molecular-based ferromagnets. Further detailed investigations on temperature- and field-dependences of magnetization and magnetic hysterisis are now in progress.

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