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A NOVEL HIGH-SPIN NICKEL(II)-COPPER(II) BINUCLEAR COMPLEX[1)]

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The novel binuclear hetero-metal complex, CuNi(fsacen)·$3H_2O$, was synthesized, where H_4fsacen denotes N,N'-ethylenebis(3-carboxysalicylaldimine). This complex has $[CuN_2O_2]$- and $[NiO_6]$-chromophores and two metal ions are connected by the phenolic oxygens. The magnetic susceptibility was well explained in terms of the equation for the high-spin nickel(II)-copper(II) cluster.

Many binuclear metal complexes have been synthesized and characterized. However, most of these complexes are concerned with the complexes of the same metal ions and there have been few complexes with different paramagnetic ions in spite of the interest in the magnetic exchange interaction.

Previously we reported that 3-formylsalicylic acid[2)] and its Schiff bases[3)] form binuclear copper(II) and nickel(II) complexes. In the present study a novel binuclear metal complex possessing a paramagnetic nickel(II) ion and a copper(II) ion was synthesized by the use of N,N'-ethylenebis(3-carboxysalicylaldimine), which will be abbreviated to H_4fsacen.

By the reaction of H_4fsacen and copper(II) acetate monohydrate, N,N'-ethylenebis(3-carboxysalicylaldimino)copper(II) (Cu(H_2fsacen)) was prepared. When Cu(H_2fsacen), lithium hydroxide monohydrate and nickel(II) chloride hexahydrate were treated in water in the mole ratio of 1 : 2 : 1, reddish purple prisms were obtained. This complex is abbreviated to CuNi(fsacen)·$3H_2O$. Found: C, 40.65; H, 3.47; N, 5.27; Cu, 12.27; Ni, 10.74 %. Calcd for CuNi(fsacen)·$3H_2O$: C, 40.90; H, 3.43; N, 5.30; Cu, 12.02; Ni, 11.10 %.

The color of CuNi(fsacen)·$3H_2O$ is quite different from that of Cu_2(fsacen)-$2H_2O$ (yellowish brown) and that of Ni_2(fsacen)·$3H_2O$ (red).[4)] In the infrared spectrum of Cu(H_2fsacen) the band due to the free carboxyl group was found at 1705 cm^{-1}. On the other hand, this band could not be seen in the spectrum of CuNi(fsacen)·$3H_2O$. Instead, a new band was observed at 1550 cm^{-1}, which may be attributed to the carboxylate group.

The reflectance spectrum of CuNi(fsacen)·$3H_3O$ shows bands at 9.3, 14.5 and 17-19 kK. The band around 17-19 kK may be assigned to the $[CuN_2O_2]$-chromophore, since the reflectance spectrum of Cu(H_2fsacen) shows a d-d band at 18.1 kK. The bands at 9.3 and 14.5 kK may be assigned to the d-d bands of the octahedral

nickel(II) ion. Therefore, it is likely that CuNi(fsacen)·$3H_2O$ has a structure given in Fig. 1.

Based on the Heisenberg model, two spin-states, S=1/2 and 3/2, occur for the high-spin nickel(II)-copper(II) system. The energies of the S=1/2 and 3/2 states are 0 and -3J respectively. Based on the Van Vleck equation the magnetic susceptibility can be expressed as follows:

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \cdot \frac{10 + \exp(-3J/kT)}{2 + \exp(-3J/kT)} + N\alpha \quad .$$

As shown in Fig. 2, the χ_M values and $1/(\chi_M - N\alpha)$ values of CuNi(fsacen)·$3H_2O$, determined by the Faraday method in the temperature range 77.4-300 K, well fit to the theoreticl curves, when the magnetic parameters, J, g and $N\alpha$, are estimated at -75 cm^{-1}, 2.19 and 200×10^{-6} e.s.u./mol respectively.

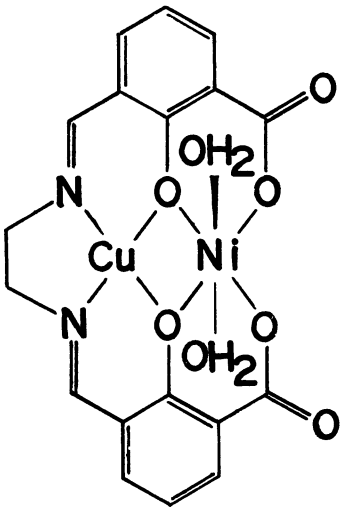

Fig. 1.

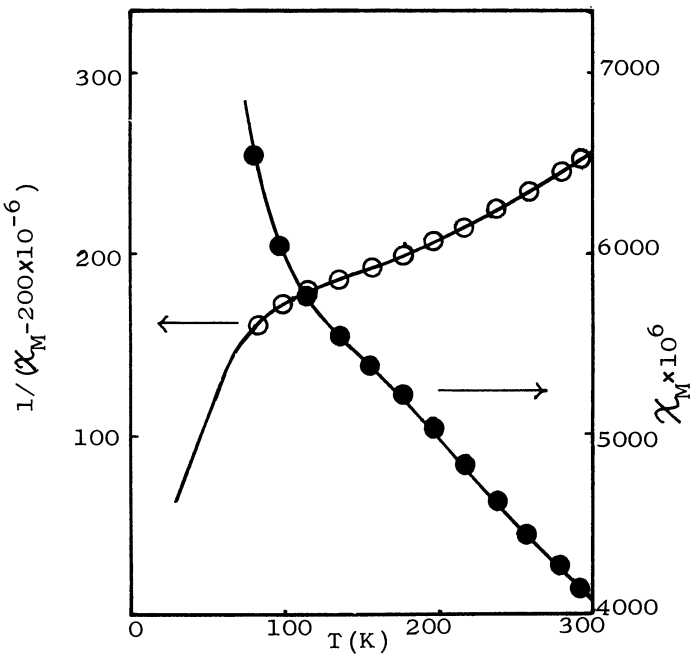

Fig. 2. Variations of molar susceptibility (●) and inverse susceptibility (○) of CuNi(fsacen)·$3H_2O$ as a function of temperature.

Accordingly it is evident that CuNi(fsacen)·$3H_2O$ is a novel binuclear complex containig copper(II) and high-spin nickel(II) ions. The energy separation between the ground spin-doublet and the spin-qualtet states is estimated at 225 cm^{-1}.

References

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4) To be published shortly.

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