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Binuclear Metal Complexes. LIV.[1] Strongly Spin-coupled Copper(II)-Iron(III) Complex of a Salen Homolog Containing Pendant Phenolic Group

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Synopsis. A copper(II)–iron(III) binuclear complex of *N*,*N*′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine has been prepared and characterized. Cryomagnetic measurements revealed the presence of an antiferromagnetic spin-exchange interaction of $J=-70\,\text{cm}^{-1}$ between the metal ions.

Magnetical investigations of copper(II)–iron(III) complexes are of current interest in connection with the models for the active site of cytochrome oxidase where the iron(III) center of cytochrome a_3 and copper(II) are strongly spin-coupled.[2,3] However, only few copper(II)–iron(III) complexes are magnetically characterized.[4–6]

N,*N*′-Disalicylideneethylenediaminatocopper(II) and its congeners can act as bidentate chelating agents through the phenolic oxygens. Sinn and coworkers have used these complexes to synthesize a number of binuclear and trinuclear metal complexes.[7] However, no polynuclear complexes of salen analogues containing iron(III) have been obtained, mainly because of their low stability. Recently, we synthesized a new salen analogue containing a pendant phenolic group, *N*,*N*′-disalicylidene-2-methyl-4-(2-hydroxy-5-methylphenyl)-1,2-butanediamine (abbreviated as H_2(sal-Hpen)).[8] Its iron(III) complex Fe(sal-pen) was shown to be of five-coordination with the pendant phenolic oxygen at the apical position.[7] In this study we report the synthesis, characterization, and magnetism of the copper(II)–iron(III) complex Fe(sal-pen)$CuCl_2$.

Experimental

Preparations. H_2(sal-Hpen) and Fe(sal-pen) were prepared by the method in the preceding paper.[8]

Fe(sal-pen)$CuCl_2$. A suspention of Fe(sal-pen) (0.10 g) and anhydrous $CuCl_2$ (0.33 g) in an ethanol–dichloromethane mixture (1:1, 30 cm³) was refluxed with stirring for 2 d. Reddish purple solution thus obtained was slowly condensed in a vacuum desiccator to give purple brown crystals.

Found: C, 49.41; H, 4.39; N, 4.43%. Calcd for Fe(sal-pen)$CuCl_2\cdot 3/2H_2O$: C, 49.59; H, 4.47; N, 4.44%.

Magnetic Measurements. Magnetic susceptibilities were measured in the temperature range 80—300 K by the Faraday method, the apparatus being calibrated with $[Ni(en)_3]S_2O_3$.[9] Magnetic moments were calculated by the equation, $\mu_{\text{eff}}=2.828(\chi_M\times T)^{1/2}$, where χ_M is the molar susceptibility per iron and copper atoms corrected for diamagnetism by the use of Pascal's constants.

Results and Discussion

The analytical results demonstrate the stoichiometry of the complex to be Fe(sal-pen)$CuCl_2$. However, this does not rule out the possibility of coprecipitation of Fe(sal-pen) and $CuCl_2$. The complexes obtained, however, appeared uniform prismatic crystals under microscopic observation. The color of the dichloromethane solution gradually changed from purple-brown to dark brown, suggesting the decomposition of the complex. Thus, the investigations were carried out on solid samples.

The infrared spectrum of Fe(sal-pen)$CuCl_2$ showed appreciable band shifts compared with that of Fe(sal-pen); the C=N stretching and skeletal bands were shifted from 1610 and 1540 cm⁻¹ to 1630 and 1550 cm⁻¹, respectively. The shift of the skeletal band to the higher frequency suggests the binuclear structure bridged by the phenolic oxygens.[10] The magnetic moment of Fe(sal-pen)$CuCl_2$ is 5.2 BM at room temperature, which is lower than that of Fe(sal-pen) (5.8 BM[†]). The ESR spectrum of Fe(sal-pen)$CuCl_2$ exhibited a very weak signal near $g=2$ and differs from the spectrum of Fe(sal-pen) which exhibits a strong signal near $g=3.7$. All these facts clearly demonstrate that Fe(sal-pen)$CuCl_2$ is a new heteronuclear complex, bridged by the phenolic oxygens of the salen skeleton (Fig. 1).

The magnetic moment of the complex (5.2 BM) is much lower than the spin-only value (6.2 BM) for the high-spin iron(III)–copper(II) system. Further, the moment decreased to 4.7 BM when the temperature was lowered to the liquid nitrogen temperature. These facts suggest the operation of the intramolecular spin-exchange interaction. The magnetic behavior is best understandable by assuming a high-spin iron(III) coupled with copper(II). Such a spin-coupling results in two total spin states $S_T=3$ and $S_T=2$ with an energy gap of $|6J|$ based on the Heisenberg model ($H=-2JS_1\cdot S_2$). The molar susceptibility can be calculated using the simplified Van Vleck's equation,[11]

$$\chi_M=\frac{Ng^2\beta^2}{kT}\times\frac{5\exp(-6J/kT)+14}{5\exp(-6J/kT)+7}+N\alpha,$$

where β is the Bohr magneton, N Avogadro's constant, k the Boltzmann constant, g the Landé splitting factor,

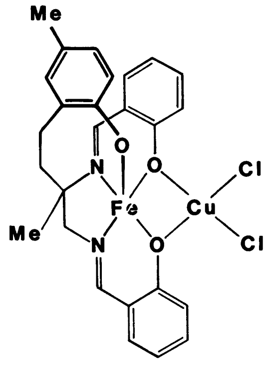

Fig. 1. Possible structure of Fe(sal-pen)$CuCl_2$.

[†] 1 BM=0.9273×10^{-23} J T^{-1}.

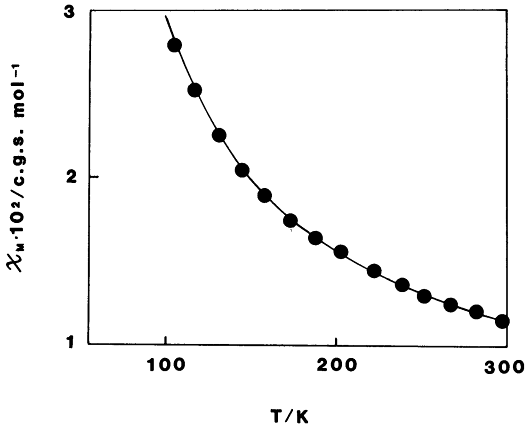

Fig. 2. Temperature-variation of magnetic susceptibility of Fe(sal-pen)CuCl$_2$. The solid curve is drawn based on the theoretical susceptibility equation for the (S=5/2)-(S=1/2) system with the parameters g= 1.98, $-J$=70 cm^{-1}, and $N\alpha$=0.

J the exchange integral, and $N\alpha$ the temperature-independent paramagnetism. The experimental χ_M *vs.* T plot was best reproduced by the theoretical curve by assuming $-J$=70 cm^{-1}, g=1.98, and $N\alpha$=0. Thus, the existence of a strong antiferromagnetic spin-exchange interaction between the metal ions in Fe(sal-pen)CuCl$_2$ has been established through the present study.

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