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FERROMAGNETIC INTERACTION IN SOLID OCTABUTOXYPHTHALOCYANINATO COBALT

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Abstract We found a weak ferromagnetic interaction in solid (octabutoxyphthalocyaninato)cobalt $CoPc(OBu)_8$ at low temperature. It is conceivable that a dimer of $CoPc(OBu)_8$ having a triplet ground state is involved in the magnetic property of this material.

INTRODUCTION

We have studied on the conducting CoPc salt, concentrating on the magnetic interaction between the unpaired electrons on Co and Pc macrocyclic ligand. To estimate the magnetic exchange energy between them, we are performing the experiment on the cation radical of $CoPc(OBu)_8$ (see figure 1) that is soluble to organic solvents. In this study we unexpectedly found a ferromagnetic interaction in the neutral $CoPc(OBu)_8$ compound at low temperature. This property interests us from the viewpoint of the comparison with the antiferromagnetic property of the β polymorph of CoPc. Since the ferromagnetic interaction is rare even in the molecules involving transition metals, the study of this material may give an insight into the molecular ferromagnetism.

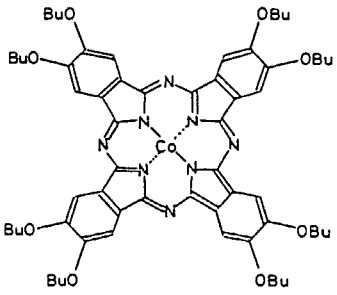

FIGURE 1 Molecular structure of $CoPc(OBu)_8$

SAMPLE PREPARATION

$CoPc(OBu)_8$ was synthesized by the following method. 500 mg of 1,2-dibutoxy-4,5-dicyanobenzene[1] and 1ml of *n*-amyl alcohol were refluxed for several minutes. After refluxing the solution with a little bit of lithium metal for two hours, a greenish blue lithium complex was obtained. 30 mg of anhydrous cobalt chloride(II) was added into this solution and was refluxed for more 2-3 hours. The residue of crude $CoPc(OBu)_8$ was washed with hot acetone and was purified by column chromatography on silica gel eluted with chloroform. Total yield was 20 %. (Found: C,66.90;H,6.89;N,9.82%. Calcd: C,66.94;H,7.02;N,9.76 %)

MAGNETIC PROPERTIES

The magnetic susceptibility $\chi(T)$ and mangetization $M(H/T)$ were measured with a Faraday magnetic balance[2] operating in the temperature range of 2.9-270 K and in the magnetic field of 0.2-5 T. 13.93 mg of powdered crystals were used in this experiment. The diamagnetic part of the magnetic susceptibility was estimated to be $\chi_D = -2.9\times10^{-4}$ emu mol^{-1} from the high-temperature part of the χT vs T plot. The temperature dependence of $\chi_P T$, the product of the paramagnetic part χ_P and T, is shown in figure 2(a). The increase of $\chi_P T$ at low temperature is evidence for the ferromagnetic interaction between $CoPc(OBu)_8$ molecules, in which the unpaired electrons are located on the central metals Co. Since the crystal structure of

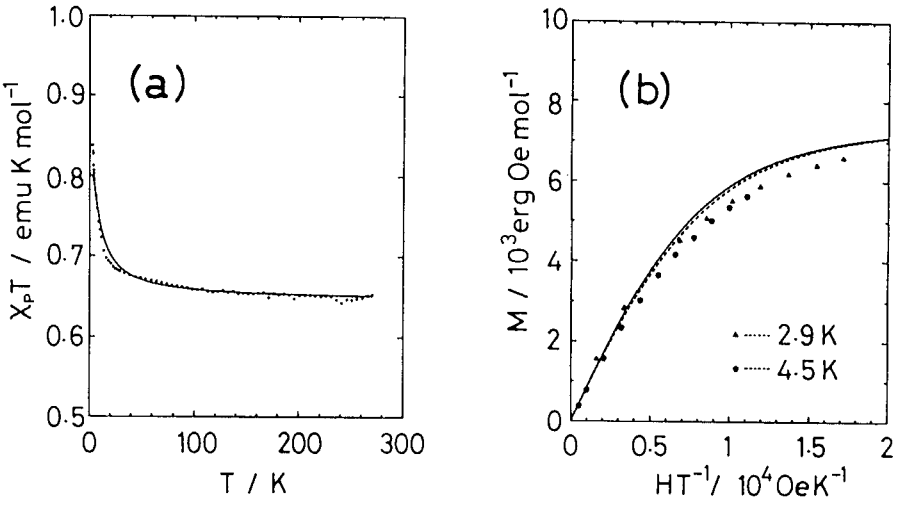

FIGURE 2 (a): Temperature dependence of the $\chi_P T$. Solid line is the theoretical line for the singlet-triplet model with g=2.63 and $2J/k_B$=7.7 K.

(b): Field dependence of Magnetization of CoPc(OBu)$_8$ at 2.9 and 4.5 K. Solid line is the theoretical curve for the singlet-triplet model with g=2.63, $2J/k_B$=7.7 K, and T=2.9 K. Broken line is the same one for T=4.5 K.

this material is not known, we analyze the $\chi_P T$ curve by two models. In the first model we use the Curie-Weiss relation, $\chi(T) = C/(T-\theta)$. The best-fit parameters are θ=0.74 K and C=0.66 emu K mol^{-1}. From this Curie constant ($C = N_A g^2 \mu_B^2 S(S+1)/3k_B$), g=2.64 is obtained when we assume the spin quantum number of S=1/2. The g-value of this molecule is reasonable as compared with the g-values of 2.28 for the α polymorph of CoPc[3] and 2.59 for β-CoPc[3]. Another model assume a dimer structure in solid state. If the ferromagnetic interaction within this dimer is predominant, the magnetic property is described by the singlet-triplet model with a triplet ground state. In this model the magnetic susceptibility is given by $\chi(T) = N_A g^2 \mu_B^2 (k_B T)^{-1}/[3+\exp(-2J/k_B T)]$, where $2J$ is the energy separation between singlet and triplet states. The parameters are g=2.63 and $2J/k_B$ = 7.7 K. A solid line in figure 2(a) shows the $\chi_P T$ curve calculated with these parameters. The experimental $\chi_P T$ curve

is intermediate between the first and second models.

The field dependences of the magnetization recorded at 2.9 K and 4.5 K are displayed in figure 2(b). Data at 2.9 K is slightly larger than that of 4.5 K. In the first model we use a Brillouin function to simulate the magnetization curve. Using g=2.64, the experimental data of magnetization is located between S=1 and S=1/2. In the singlet-triplet model, we take account of the four states, three Zeeman-split triplet states and one singlet state for the calculation of the magnetization curve, since the energy separation of singlet and triplet state is comparable with the Zeeman splitting. The magnetization curve used in this model is given by the following equation,

$$M(H/T) = \frac{2^{-1}N_A g\mu_B[\exp(g\mu_B H/k_B T)-\exp(-g\mu_B H/k_B T)]}{1+\exp(g\mu_B H/k_B T)+\exp(-g\mu_B H/k_B T)+\exp(-2J/k_B T)}$$

where H is the magnetic field. The simulated curves at 2.9 K (solid line) and 4.5 K (broken line) are shown in figure 2(b).

The slight disagreement between the experimental data of $\chi_P T$ and $M(H/T)$ and these two models may be related to the possible existence of a large amount of lattice defect or the ferromagnetic interaction between dimers. These hypotheses will be solved by the crystal structure analysis of this material which is going on now. Structural study will also clarify the different magnetic property of this compound from β-CoPc which is related to the structural change coming from the introduction of the long side chains.

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