Synthesis and Magnetic Properties of a Planar Binuclear Copper(II) Phthalocyanine Complex

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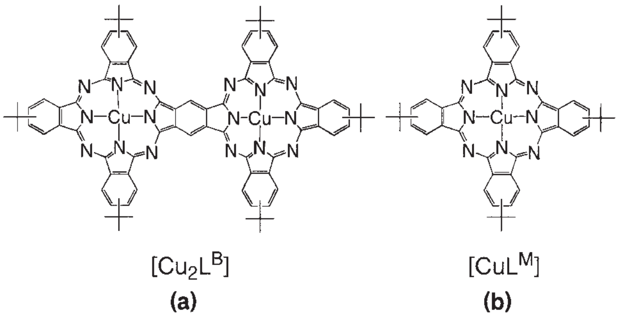
A binuclear copper(II) phthalocyanine complex, in which two Cu(II) phthalocyanine units are linked by their common benzene ring to give a planar structure, was prepared and investigated concerning its magnetic properties. No significant magnetic interaction was found between the copper(II) ions through the benzene ring.

One of the most remarkable properties of phthalocyanine (pc) complexes is their intensive bands (called Q-bands) in the visible region (around 680 nm).[1] It is well known that the band position and features are strongly affected by the pc–pc ring interaction; e.g., the Q-band is red-shifted when the pc rings are stacked by facing their planes with each other.[1,2] Recently, planar binuclear pc complexes, in which the pc rings are connected by their common benzene ring to make the pc planes arranged coplanarly, have been prepared and investigated concerning the effects on the spectral features coming from pc–pc interactions.[3] The binucleating pc ligands can accommodate two metal ions, and hence their magnetic interaction, through the common benzene ring, may be operative if the accommodated metal ions are paramagnetic. To our knowledge, there has been no report on the magnetic interaction within the binuclear complexes using variable-temperature (VT) magnetic susceptibility data, although ESR studies on the spin interactions between copper(II) ions of a binuclear phthalocyanine complex and between the pc rings for the excited triplet state of the binucleating pc ligands, themselves, have been reported.[3b,d] In this study, we prepared a binuclear copper(II) complex, $[\mathrm{Cu^{II}}_2\mathrm{L^B}]\cdot 0.5\mathrm{CHCl_3}$ (**1**) (Scheme 1(a)), and investigated the interaction between the paramagnetic ions within the dimer based on the VT susceptibility (5–300 K) as well as ESR and the absorption spectra, a mononuclear complex $[\mathrm{Cu^{II}L^M}]$ (**2**) (Scheme 1(b))[4] also being included in this report for a comparison of the ESR data.



Scheme 1.

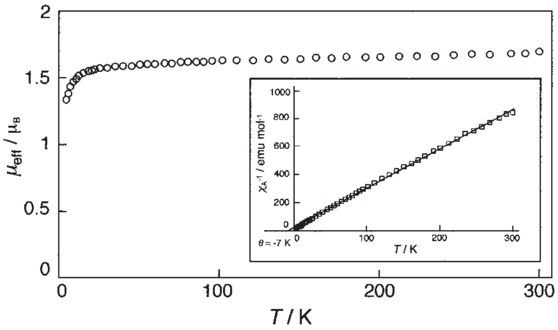


Fig. 1. Temperature dependence of magnetic moment per the $\mathrm{Cu^{II}}$(pc) unit for **1**. Reciprocal χ_A values are displayed in the inset.

The temperature dependence of the effective magnetic moment, μ_{eff} ($= \sqrt{8\chi_A T}$, where χ_A is the magnetic susceptibility per copper(II) ion), is shown for **1** in Fig. 1. The moment of **1** decreases very slightly from a value of $1.69\mu_B$ (μ_B = Bohr magneton), corresponding to that for one half spin per Cu(II) ion, while lowering the temperature until ca. 10 K. The decrease becomes steep below 10 K, which is considered to originate from an intermolecular interaction, which has been observed for many paramagnetic compounds.[5] The reciprocal values of χ_A are plotted at the measured temperatures in the inset of Fig. 1. They obey the Curie–Weiss law with a Weiss constant of $\theta = -7$ K, which is indicative of the existence of a weak antiferromagnetic interaction. The magnetic behavior of **1** could not be simulated by the Bleaney–Bowers equation for the $S_1 = S_2 = 1/2$ paramagnetic centers.[5] Hence, it is difficult to present a conclusive discussion concerning the origin of the weak interaction, although it is certain that there is no significant magnetic interaction between the Cu(II) ions within the dimer.

Figure 2 displays the ESR spectra of **1** and **2** in benzene at room temperature, where their Cu(pc) unit concentrations are the same at 6.0×10^{-4} M (1 M = 1 mol dm^{-3}). The spectral features are different from each other; **1** shows only a broad signal without the hyperfine structure, unlike the case of **2** ($A_0 = 98.9$ G; $A_N = 16.5$ G).[4] This seems to indicate that the intramolecular magnetic interaction operates in **1**. However, a careful investigation based on the spectral measurements while changing the concentration of **1** in benzene showed that the molecular aggregation could be the main reason to make the signal broaden, because the hyperfine structure became

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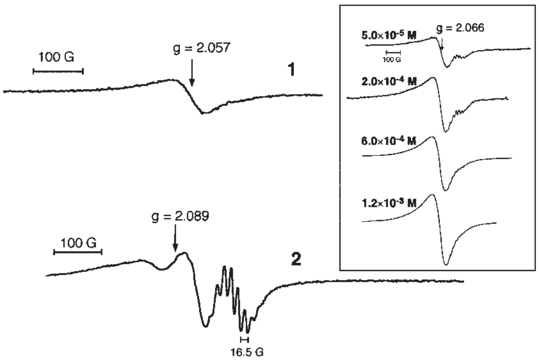

Fig. 2. ESR spectra of **1** and **2** in benzene at room temperature, of which concentration dependence is shown for **1** in the inset.

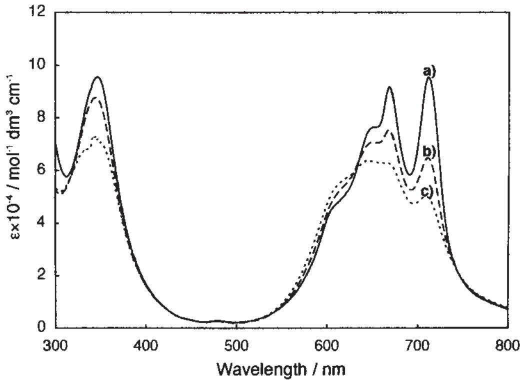

Fig. 3. Absorption spectra of **1**, measured in benzene at the concentrations of 5.0×10^{-5} (a), 2.0×10^{-4} (b), and 6.0×10^{-4} M (c).

clear when the concentration was decreased (in the inset of Fig. 2). The aggregating nature of **1** was confirmed by the absorption spectra in benzene; the shoulder band at the shorter wavelength region of the Q-band is more outstanding and the Q-band intensity is smaller at higher concentrations, which is diagnostic of aggregation (Fig. 3),[2] while such a large concentration dependence of the Q-band cannot be observed for **2** in this concentration region. The spectral feature of **1** is nearly the same as those of the previously reported cobalt(II) and zinc(II) complexes of a similar binucleating pc ligand when their measured concentrations are $\sim 10^{-5}$ M.[3c]

In this study, a planar binuclear Cu(II) phthalocyanine complex **1** was newly prepared, and no significant intramolecular magnetic interaction was found between the Cu(II) ions.

Experimental

Synthesis of Complex 1. The binuclear ligand H_4L^B was prepared according to a method described in the literature.[3c] The ligand H_4L^B (100 mg (0.078 mmol)) and $CuCl_2 \cdot 2H_2O$ (100 mg (0.59 mmol)) were reacted by refluxing for 20 h in a mixed solvent of 2-methoxyethanol and toluene (1:1). The solvent was removed by evaporation to give a blue powder. The crude sample obtained in this manner was employed for purification using a column chromatography technique (SiO_2 column, eluent: $CHCl_3$). The yield was 36 mg (32% based on the ligand). Anal. Found C, 67.68; H, 5.29; N, 14.88; Cu, 9.0%. Calcd for **1**: C, 67.39; H, 5.11; N, 15.24, Cu, 8.6%.

Measurements. Elemental analyses for carbon, hydrogen, and nitrogen were carried out using a Yanaco CHN CORDER MT-5. The analysis of copper ion was carried out with a Hitachi Atomic Absorption-Flame Spectrometer Model 508A. The magnetic susceptibilities were measured by the Faraday method over the 5–300 K temperature range, operating at a magnetic field of 0.5 T. The susceptibilities were corrected for any diamagnetism of the constituent atoms using Pascal's constant.[6] ESR and electronic spectra were measured with JEOL-1X and Shimadzu UV-3100 spectrometers, respectively.

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