Electrical and Magnetic Properties of a New Complex Cu-TCNQ Salt [Cu(Ethylenediamine)$_2$]$^{2+}$(TCNQ)$^{2-}$ $_3$

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Electrical and Magnetic Properties of a New Complex Cu-TCNQ Salt [Cu(Ethylenediamine)$_2$]$^{2+}$(TCNQ)$_3^{2-}$

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Electrical conductivity and magnetic susceptibility were determined for a new conductive TCNQ salt [Cu(ethylenediamine)$_2$]$^{2+}$(TCNQ)$_3^{2-}$. The powder conductivity was equal to 0.09 Ω^{-1}cm^{-1} at 300 K, and showed a semiconductor property with an activation energy equal to 0.25 eV. The susceptibility was resolved into two terms: 1) a Curie-Weiss para-magnetism attributed to unpaired electrons localized on Cu atoms, and 2) a thermally activated magnetism due to TCNQ. The latter magnetism can be explained by a delocalized electron model.

INTRODUCTION

Some Cu(II) chelates with bidentate ligands form highly conducting tetracyanoquinodimethanides [CuL$_2$](TCNQ)$_2$ (L: ethylenediamine, 2,2′-bipyridine or 1,10-phenanthroline), whose powder conductivity amounts to 0.0007 − 0.2 Ω^{-1}cm^{-1} at 300 K depending on the coordinating ligands.[1-3] Our previous magnetic study of the compounds indicated that a partial electron transfer between Cu(II) and TCNQ$^-$ ions gives rise to the high electrical conduction in TCNQ columns.[2] Usually, complex TCNQ salts R^{n+}(TCNQ)$_m$ involving TCNQ^0 as well as TCNQ$^-$ exhibit a higher electrical conductivity than that of the corresponding simple salts R^{n+}(TCNQ)$_n$. In the present investigation, we have prepared a new complex TCNQ salt of bis(ethylenediamine)copper(II), [Cu(en)$_2$]$^{2+}$(TCNQ)$_3^{2-}$, which shows electrical and magnetic properties markedly different from those of the corresponding simple salt [Cu(en)$_2$]$^{2+}$(TCNQ)$_2^{2-}$.

EXPERIMENTAL

The material was prepared by adding 23 mg of $Cu(en)_2Cl_2 \cdot 2H_2O$ dissolved in 2.5 ml of acetonitrile-water (3:2) to an acetonitrile-methanol (3:1) solution (6 ml) dissolving LiTCNQ (32 mg) and TCNQ (16 mg). Black precipitates were collected on a glass filter, washed successively with an acetonitrile-methanol mixture and water, and dried in vacuum. Materials prepared in different molar TCNQ/LiTCNQ ratios of 0.5–1.2 had the same chemical composition and also the same magnetic and electrical properties. Anal. Calcd. for $Cu(C_2H_8N_2)_2(C_{12}H_4N_4)_3$: C, 60.34; H, 3.53; N, 28.14. Found: C, 60.14; H, 3.48; N, 27.54. The material was characterized by infrared and electron spin resonance spectra. The IR spectrum of $Cu(en)_2(TCNQ)_3$ was quite different from that of $Cu(en)_2(TCNQ)_2$ as shown in Appendix. The polycrystalline powders of $Cu(en)_2(TCNQ)_2$ exhibited an ESR spectrum characteristic of Cu(II) complexes having an axial-symmetric ligand field ($g_{\parallel} = 2.204$ and $g_{\perp} = 2.047$),[3] whereas the $g_{\parallel}$ component signal was smeared out in the spectrum of $Cu(en)_2(TCNQ)_3$. These spectroscopic results demonstrated that the present samples were not contaminated by $Cu(en)_2(TCNQ)_2$.

The electrical conductivity of the compressed pellets was determined by van der Pauw's 4-probe method[4] between 250 and 300 K. The thermoelectric power of the pellets was measured against Cu metal at 300 K. The magnetic susceptibility was determined in a temperature range of 100–300 K by means of a Faraday balance constructed with a self-made electronic torsion balance and an electromagnet capable of producing magnetic field up to 5000 G. It was calibrated with $CuSO_4 \cdot 5H_2O$ (5.84×10^{-6} emu g^{-1} at 293 K) and NaCl (-0.52×10^{-6} emu g^{-1}). The torsion balance was so sensitive that it detected the susceptibility of NaCl with an error less than $\pm 2\%$ using 90 mg of the sample. A very small amount of specimen (*ca.* 15 mg) was enough for the present magnetic measurement of the compounds. The molar susceptibility was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from ethylenediamine (-46) and TCNQ (-121).[5,6]

RESULTS AND DISCUSSION

The electrical conductivity of $Cu(en)_2(TCNQ)_3$ exhibited 9×10^{-2} $\Omega^{-1}cm^{-1}$ at 300 K, and its temperature dependence obeyed the equation $\sigma = \sigma_\infty \exp(-E/kT)$ with the activation energy of electrical conduction $E = 0.25$ eV and the infinite temperature conductivity $\sigma_\infty = 1.4 \times 10^3$ $\Omega^{-1}cm^{-1}$. The thermoelectric power S was equal to -60 μV K^{-1} at

300 K. These electrical properties differ markedly from those of the corre-sponding simple salt ($\sigma = 7 \times 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$ at 300 K, $E = 0.20$ eV, and $S = +620\ \mu$V K^{-1});[2] the thermoelectric powers are especially differ-ent from each other in both sign and magnitude. The IR spectrum of the better conductor Cu(en)$_2$(TCNQ)$_3$ was very broad compared with that of the poorer conductor Cu(en)$_2$(TCNQ)$_2$ as mentioned above, in line with the correlation reported for many conductive TCNQ salts.[7]

Figure 1 shows the reciprocal magnetic susceptibility χ plotted against temperature. It obeyed the Curie-Weiss law $\chi = C/(T - \theta)$ with the Curie constant $C = 0.482$ emu K mol^{-1} and the Weiss constant $\theta = 8.2$ K be-
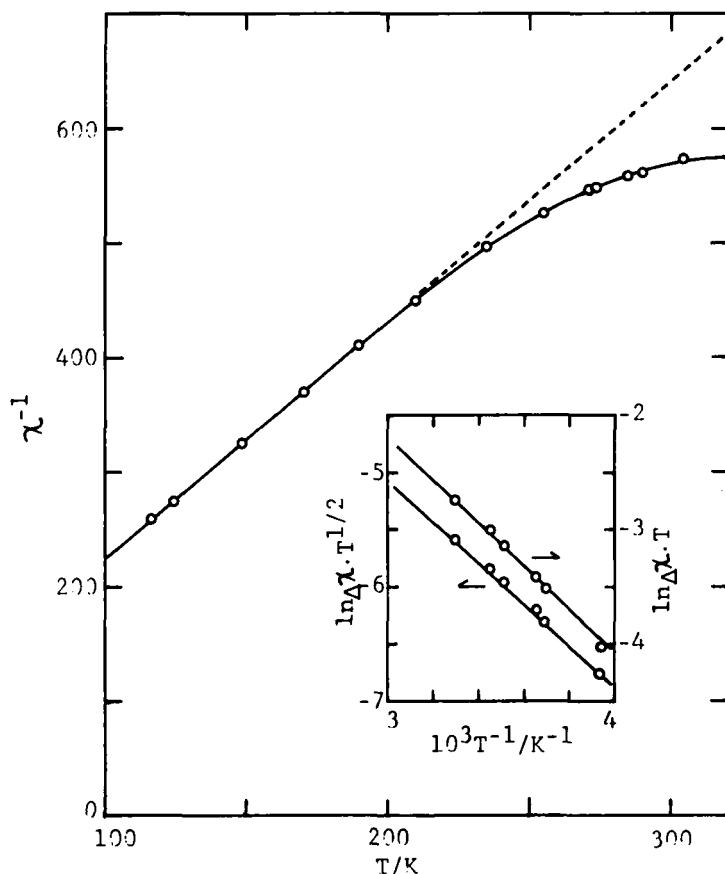

FIGURE 1 Reciprocal molar susceptibility χ (in emu) plotted against temperature. The broken line and the solid curve show susceptibilities calculated with the Curie-Weiss law and Eq. 1 of the text, respectively. The inset indicates that the susceptibility difference $\Delta\chi = \chi_{obs} - \chi_{Curie-Weiss}$ is attributable to a thermally activated paramagnetism.

low 200 K. Above this temperature, it deviated from the Curie-Weiss law. The Curie constant gives the magnetic moment 1.96 B.M., which falls in the range 1.8–2.0 B.M. normally observed for Cu(II) compounds. Accordingly, the Curie-Weiss paramagnetism is ascribable to Cu(II) ions. The broken line in Figure 1 shows the magnetic susceptibility evaluated on the assumption of the validity of the Curie-Weiss law in the high temperature range. This χ_{CW} was subtracted from the observed susceptibility χ_{obs}, and the logarithm of the susceptibility difference multiplied by temperature, $\ln[(\chi_{obs} - \chi_{CW})T]$, was plotted against reciprocal temperature as shown in the inset of Figure 1. The resulting straight line indicates that the difference susceptibility $\Delta\chi = \chi_{obs} - \chi_{CW}$ is thermally activated, and hence, that the observed susceptibility can be reproduced by the sum of two terms:

$$\chi = \frac{C}{T - \theta} + \frac{A}{T} \exp(-\varepsilon/kT) \qquad (1)$$

The parameters were evaluated from the semilogarithmic plot as $A = 32$ emu K mol^{-1} and $\varepsilon = 0.16$ eV. The solid curve in Figure 1 shows Eq. 1 calculated with the abovementioned parameters, reproducing well the observed data. The first term of Eq. 1 arises from unpaired electrons localized on Cu atoms as mentioned above, and the second term is obviously attributable to TCNQ radicals. The validity of Eq. 1 implies that respective unpaired electrons of Cu and TCNQ contribute independently to the magnetism of the present complex: the magnetic interaction between them is very weak compared with the thermal energy in the temperature range investigated.

When the two unpaired electrons of each $(TCNQ)_3^{2-}$ trimer in the chemical unit are localized within each trimer, the TCNQ susceptibility per unit can be given by

$$\chi = \frac{2Ng^2\mu_B^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1}, \qquad (2)$$

where, apart from obvious notations, J is the exchange integral between coupled unpaired electrons within each unit. When $J < 0$ and $|J| \gg kT$, the equation leads to

$$\chi = \frac{2Ng^2\mu_B^2}{kT}\exp(2J/kT). \qquad (3)$$

This has the same functional form as the second terms of Eq. 1. The evaluated constant $A = 32$ of Eq. 1, however, is much larger than the corresponding parameter $2Ng^2\mu_B^2/k = 3$ of Eq. 3, suggesting that the dimeric spin model is inadequate to the TCNQ susceptibility of the present

compound. Any theoretical curves proposed for interacting dimeric spins[8] cannot explain the large A value. This suggests that the unpaired electrons of TCNQ are extensively delocalized in crystal lattices.

The present magnetic study provides the following information: 1) the Cu(II) and TCNQ$^-$ ions are magnetically isolated from each other; 2) each Cu atom carries an unpaired electron localized on it; and 3) the unpaired electrons of the TCNQ$^-$ ions are extensively delocalized over TCNQ lattices. These suggest a molecular arrangement in which the TCNQ$^-$ ions construct columns separately from the Cu(II) chelates, although the single crystals of the compound were not obtained. Probably, centrosymmetric (TCNQ)$_3^{2-}$ trimers stack facet to face to construct columns isolated from one another by linear arrays of the Cu(II) chelates, as found in the crystals of [Pt(bipyridine)$_2$](TCNQ)$_3$.[9] The columns of the (TCNQ)$_3^{2-}$ trimers each having two unpaired electrons can construct some bands, although their band widths are thought to be narrow. The thermally activated magnetism observed for the present compound suggests that the highest occupied band is the singlet spin state, and that the paramagnetism arises from electrons activated thermally from the singlet state to the lowest vacant band. When these activated electrons behave in a group as highly-correlated electron gas, the susceptibility of the electron system at sufficiently high temperatures is given by[10]

$$\chi = \frac{ng^2\mu_B^2}{3\xi kT} \tag{4}$$

where n is the number of the correlated electrons, and $1/\xi$ is the enhancement parameter. The positive holes produced in the occupied band can be assumed to exhibit also the magnetism of the correlated electron gas. The number of the activated electrons n_e and that of the resulting positive holes n_p are given by

$$n_e = n_p = 2N \exp(-\Delta/kT), \tag{5}$$

where Δ is the excitation energy. The factor $2N$ comes from the number of electrons per mole existing in the TCNQ band. Substituting $n = n_e + n_p$ into Eq. 4, we obtain

$$\chi = \frac{4Ng^2\mu_B^2}{3\xi kT} \exp(-\Delta/kT). \tag{6}$$

This has the same functional form as the second term of Eq. 1. Comparison of the A value with the corresponding parameters of Eq. 6 yields $1/\xi$ equal to 16. This value is reasonable, since $1/\xi$ has been pointed out to have the order of 10 for conducting oxides such as V_2O_3.[10]

The susceptibility of a one-dimensional tight-binding band has been proposed to be given by an alternative expression of thermal activation:[11]

$$\chi = \frac{c}{T^{1/2}} \exp(-\delta/kT). \tag{7}$$

This also can reproduce the TCNQ susceptibility with $\delta = 0.15$ eV and $c = 1.3$ emu $K^{1/2}$ mol^{-1} as seen in the inset of Figure 1. Since the physical meaning of c is not clearly given, we cannot conclude if this equation is adequate to the susceptibility of the present compound.

The spin activation energies Δ and δ evaluated from the two different equations are nearly equal to each other. Thus, the observed susceptibility can be explained by the delocalized electron models.

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Appendix

Figure shows IR spectra recorded for $Cu(en)_2(TCNQ)_2$ and $Cu(en)_2(TCNQ)_3$ with a Perkin Elmer model-1420 spectrometer. In each chart, x marks the absorption peaks of nujol. The spectrum of $Cu(en)_2(TCNQ)_3$ is very broad compared with that of $Cu(en)_2(TCNQ)_2$, and the former has additional characteristics: 1) a very broad signal over a range of 1700-4000 cm^{-1}; and 2) sharp hollows in the $-C\equiv N$ stretching frequency region. The detailed analysis will be published elsewhere along with the IR spectrum data of other conductive Cu-TCNQ complexes.