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Magnetic Susceptibility and ESR Studies of Highly Conductive CuL(TCNQ)$_2$ Incorporating 2,2′-Bipyridine or Ethylenediamine as Ligand

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Electron spin resonance spectra were recorded on highly conducting CuL(TCNQ)$_2$ (L: 2,2′-bipyridine or ethylenediamine) at different temperatures. The observed g values increased with decreasing temperature. On the basis of the g shift and the static susceptibility observed, a local magnetic susceptibility contributed from Cu and that from TCNQ were evaluated individually. The local Cu susceptibility is of the Curie type. The Curie constant indicates that each Cu atom carries 0.05 umpaired electron on the average in Cu(bpy)(TCNQ)$_2$ and 0.07 in Cu(en)(TCNQ)$_2$: the average oxidation number of copper is equal to 1.05 in the former and 1.07 in the latter. The local susceptibility of TCNQ can be interpreted by a narrow band model in which the susceptibility is given by the sum of the Curie term and a temperature-independent paramagnetic term. This suggests that the TCNQ arrays have inherently metallic nature.

High electrical conductivity has been observed for a series of CuL(TCNQ)$_2$ (L:ethylenediamine, 2,2′-bipyridine, 1,10-phenanthroline, or their derivatives; TCNQ: 7,7,8,8-tetracyanoquinodimethan).[1,2] The powder conductivity amounts to 0.004—1.9 Ω^{-1} cm^{-1} at 300 K depending on the coordinating ligand.[1–3] These values are comparable to the powder conductivities observed for quinolinium(TCNQ)$_2$ and I$_2$-doped Ni-phthalocyanine whose single crystals exhibit metallic properties.[4–6] The presence of unpaired electrons has been pointed out to be required for the so-called synthetic metals.[7] Therefore, the magnetic study of conducting materials is essential to clarify the mechanism of the electrical conduction. Recently, we have briefly reported the magnetic susceptibilities of some typical CuL(TCNQ)$_2$ complexes.[2] The results suggested that the copper atoms have an intermediate oxidation state due to the so-called equilibrium in solids:

$$\dot{\mathrm{Cu}}^{2+}\mathrm{L(TCNQ)}_2{}^{2\dot{-}} \rightleftarrows \ddot{\mathrm{Cu}}^{+}\mathrm{L(TCNQ)}_2{}^{\dot{-}}. \qquad (1)$$

The resulting incomplete electron transfer yields conduction electrons in TCNQ arrays. The purpose of the present investigation is to obtain further information about the role of unpaired electrons in the electrical conduction. In this point of view, we have recorded the ESR spectra of the Cu complexes at different temperatures, and analyzed the magnetic susceptibilities in detail by taking the ESR results into account.

Experimental

The materials were prepared by the same method as reported previously.[1,2] The ESR spectra were recorded by means of a JEOL SCXA X-band spectrometer in a temperature range of 90—300 K. The temperature of the samples was controlled within ±1 K by a cold-gas flow method, and it was determined by two copper-constantan thermocouples placed near either side of the specimen along the gas flow. Mn^{2+}/MgO was employed as a marker.

Results and Discussion

ESR Spectra. Figure 1 shows ESR spectra observed for Cu(en)(TCNQ)$_2$ and Cu(bpy)(TCNQ)$_2$ at different temperatures. A sharp signal observed at g=2.00 in each spectrum is attributed to free TCNQ$^-$ ions involved as impurities in the samples. The intrinsic spectrum of each compound consists of a simple derivative curve with a g value intermediate between 2.003 of Li(TCNQ) and 2.1 of normal Cu(II) complexes. This indicates that Cu(II) and TCNQ$^-$ ions interact magnetically with a spin-exchange energy

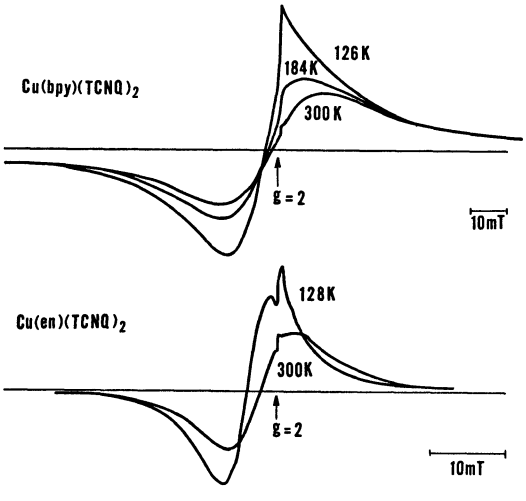

Fig. 1. ESR spectra observed for Cu(bpy)(TCNQ)$_2$ and Cu(en)(TCNQ)$_2$ at different temperatures. They were recorded in the same spectrum condition for each compound.

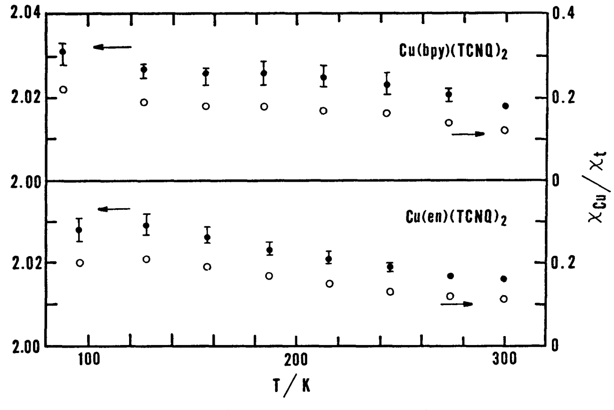

Fig. 2. g factor and the ratio of the local Cu susceptibility to the total susceptibility $\chi_{\mathrm{Cu}}/\chi_{\mathrm{t}}$.

much larger than that of the g value difference mentioned above. The g value of each compound fluctuated from sample to sample at low temperatures. This is probably due to the fluctuation of the impurity-signal strength. Figure 2, however, shows that the g value obviously increases with decreasing temperature.

Cu(phen)(TCNQ)$_2$ exhibited a spectrum resembling that of Cu(bpy)(TCNQ)$_2$, but an impurity signal at $g=2.00$ was too strong to determine the g value of the intrinsic signal.

Static Magnetic Susceptibility. The magnetic susceptibilities[8)] χ of the complexes deviated from the Curie-Weiss law[2)] and obeyed the following experimental equation as shown in Figs. 3 and 4:

$$\chi = \gamma/T + \alpha. \tag{2}$$

The parameters[8)] were evaluated as $\gamma=0.052$ emu K mol^{-1} and $\alpha=4.6\times10^{-4}$ emu mol^{-1} for Cu(bpy)(TCNQ)$_2$ and $\gamma=0.093$ emu K mol^{-1} and $\alpha=2.2\times10^{-4}$ emu mol^{-1} for Cu(en)(TCNQ)$_2$. These large α values of the temperature-independent paramagnetic term result in the deviation of the susceptibilities from the Curie-Weiss law. The uncertainty of diamagnetic correction may give an error in determining small spin susceptibility. The α values, however, are comparable to the employed diamagnetic corrections:[2)] 3.47×10^{-4} emu mol^{-1} for Cu(bpy)(TCNQ)$_2$ and 2.88×10^{-4} emu mol^{-1} for Cu(en)(TCNQ)$_2$. These values of the corrections were based on diamagnetic susceptibilities observed for the constituent molecules,[9,10)] and the uncertainty is estimated to be equal to at most 10%. Therefore, the large α values are not caused by the uncertainty of the diamagnetic corrections, but are ascribed to the intrinsic nature of the complexes. The following ESR results show that the γ/T term also is intrinsic to the complexes. 1) In each spectrum, the integrated intensity of the impurity signal due to isolated TCNQ$^-$ ions was very small compared with that of the intrinsic signal. 2) Every spectrum showed no appreciable impurity signal assignable to isolated Cu(II) ions. 3) The intrinsic signal became strong with decreasing temperature similarly to the temperature dependence of the static susceptibility, although its integrated intensity was difficult to evaluate accurately owing to the impurity signal at $g=2.00$.

g Value and Local Susceptibility. The g value of a spin system in which Cu(II) ions interact with TCNQ$^-$ radical ions is given by an average of the individual g values, g_{Cu} and g_{TQ} (TQ stands for TCNQ), in a strong coupling approximation:[11)]

$$g = (\chi_{\mathrm{Cu}}g_{\mathrm{Cu}}+2\chi_{\mathrm{TQ}}g_{\mathrm{TQ}})/\chi_{\mathrm{t}}, \tag{3}$$

where χ_{Cu} and χ_{TQ} are local magnetic susceptibilities contributed from Cu and TCNQ, respectively. The total susceptibility χ_{t} given by

$$\chi_{\mathrm{t}} = \chi_{\mathrm{Cu}} + 2\chi_{\mathrm{TQ}} \tag{4}$$

can be equated with the observed static susceptibility. The factor 2 comes from the number of TCNQ radicals involved in the chemical unit. If g_{Cu} and g_{TQ} are reasonably assumed, χ_{Cu} and χ_{TQ} can be determined individually from the g factor and the static susceptibility. g_{TQ} can be assumed to be equal to the g value 2.003 of Li(TCNQ). Cu(bpy)(NO$_3$)$_2\cdot$3H$_2$O exhibited an ESR spectrum characteristic of Cu(II) complexes having an axial symmetry: $g_{\parallel}=2.260$ and $g_{\perp}=2.067$. The averaged g factor $g_{\mathrm{av}}=[(g_{\parallel}^2+2g_{\perp}^2)/3]^{1/2}=2.133$ can be employed as g_{Cu}. Thus, χ_{Cu} and χ_{TQ} of Cu(bpy)(TCNQ)$_2$ were determined as plotted against $1/T$ in Fig. 3. In the same procedure, χ_{Cu} and χ_{TQ} were determined for Cu(en)(TCNQ)$_2$ by use of $g_{\mathrm{av}}=2.125$ (calculated with $g_{\parallel}=2.257$ and $g_{\perp}=2.056$ observed for Cu(en)SO$_4\cdot$3H$_2$O) as g_{Cu}. Figure 4 shows the resulting χ_{Cu} and χ_{TQ} as functions of $1/T$.

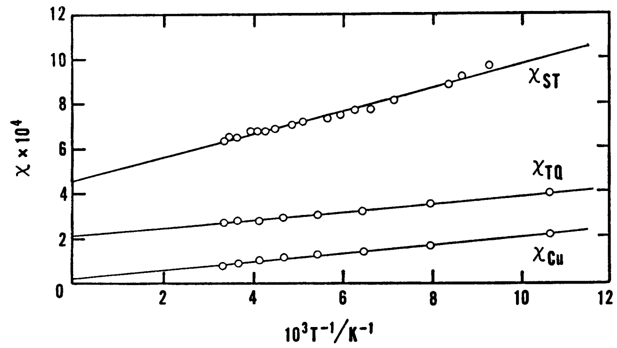

Fig. 3. Static magnetic susceptibility χ_{st}, the local Cu susceptibility χ_{Cu}, and the local TCNQ susceptibility χ_{TQ} (in emu) of Cu(bpy)(TCNQ)$_2$.

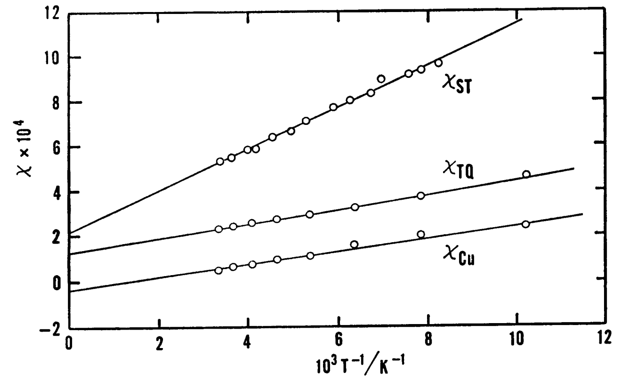

Fig. 4. Static magnetic susceptibility χ_{st}, the local Cu susceptibility χ_{Cu}, and the local TCNQ susceptibility χ_{TQ} (in emu) of Cu(en)(TCNQ)$_2$.

Figure 2 shows that the ratio $\chi_{\mathrm{Cu}}/\chi_{\mathrm{t}}$ signifying the Cu(II) spin contribution to the ESR signal increases with decreasing temperature. If the ratio is temperature independent, it gives the unpaired electron density of Cu atoms.[3)] On the contrary, the observed temperature-dependent ratio suggests that more detailed interpretation is required for the local susceptibility.

Local Cu Susceptibility. Figures 3 and 4 show that the local Cu susceptibility changes linearly to $1/T$. The temperature dependence of χ_{Cu} is reproduced by Eq. 2 employed for the interpretation of the static susceptibility. The parameters of Eq. 2 related to χ_{Cu} were determined as $\gamma_{\mathrm{Cu}}=0.018$ emu K mol^{-1} and $\alpha_{\mathrm{Cu}}=0.3\times10^{-4}$ emu mol^{-1} for Cu(bpy)(TCNQ)$_2$ and $\gamma_{\mathrm{Cu}}=0.028$ emu K mol^{-1} and $\alpha_{\mathrm{Cu}}=-0.3\times10^{-4}$ emu mol^{-1} for Cu(en)(TCNQ)$_2$. The Cu(II) contribution to the ESR spectrum increases with decreasing temperature as mentioned above. This shows that the paramagnetism expressed by γ_{Cu}/T is inherent to the complexes, although the γ_{Cu} values are very small. The absolute values of α_{Cu} fall in the range of the uncertainty (*ca.* 10%) of the diamagnetic corrections made for the static susceptibilities: the α_{Cu} negative in sign may be caused by an underestimation of the correction and the positive α_{Cu} by an overestimation. The α_{Cu} term probably arises from the uncertainty of the corrections and/or the experimental errors. Therefore, the local Cu susceptibilities of the complexes are thought to be of the Curie type intrinsically. Magnetic interaction between a copper atom and its neighboring paramagnetic ions is very weak as compared with the thermal energy in the temperature range investigated.

Local TCNQ Susceptibility. Figures 3 and 4 show that χ_{TQ} can be reproduced with an equation having the same functional form as Eq. 2. The parameters corresponding to χ_{TQ} were evaluated as $\gamma_{TQ}=0.017$ emu K mol^{-1} and $\alpha_{TQ}=2.2\times10^{-4}$ emu mol^{-1} for $Cu(bpy)(TCNQ)_2$, and $\gamma_{TQ}=0.032$ emu K mol^{-1} and $\alpha_{TQ}=1.2\times10^{-4}$ emu mol^{-1} for $Cu(en)(TCNQ)_2$. The α values of the static susceptibilities observed for the complexes agree very well with the respective $2\alpha_{TQ}$ values. Accordingly, the large temperature-independent paramagnetism is ascribed to electrons delocalized extensively in the TCNQ arrays. This supports the previous presumption that TCNQ carries conduction electrons.[2)]

The γ_{TQ}/T term shows that the local susceptibility of TCNQ conduction electrons cannot be interpreted simply in terms of the Pauli paramagnetism. As has been pointed out,[7)] TCNQ columns hardly form a wide conduction band having a large Fermi energy E_F. If the band has so narrow width that $E_F \gg kT$ does not hold, the paramagnetic susceptibility is temperature-dependent with an effective magnetic moment smaller than that predicted for localized electrons.[12)] At high temperatures, χT approaches asymptotically a constant predicted for localized electrons with increasing temperature.[13)] No exact expression has been given for the susceptibility. However, a qualitative plot of χT against T suggests that the temperature dependence can be approximated with the following equation in a given narrow temperature range:[13)]

$$\chi T = A(T+B). \tag{5}$$

In the expression, the parameters A and B should be temperature-dependent, but they can be presumed to be practically temperature-independent in a very narrow temperature range. The equation is rewritten by the same functional form as Eq. 2 reproducing χ_{TQ}:

$$\chi = AB/T + A. \tag{6}$$

The AB value is equated with γ_{TQ}, which is smaller than the Curie constant of a localized electron system. This shows that Eq. 6 holds for χ_{TQ}, and hence that the narrow band model explains χ_{TQ} satisfactorily.

Other possible explanation may be suggested for the γ_{TQ}/T term: for example, 1) a chain-end effect arising from crystal imperfections, and 2) a thermally activated electron transfer between Cu and TCNQ. If the end effect dominates the paramagnetic increase, the ratio of γ_{TQ} to the Curie constant 0.375 emu K mol^{-1} of a free electron system gives approximately the concentration of the crystal imperfection. It yields an improbable concentration equal to 5% for $Cu(bpy)(TCNQ)_2$ and 9% for $Cu(en)(TCNQ)_2$. If the electron transfer accompanying the equilibrium Eq. 1 is thermally activated, χ_{TQ} exhibits a temperature dependence of thermal activation. The semilogarithmic plot of $\chi_{TQ}\,T$ against $1/T$ (the simplest model of thermal activation) did not yield any straight line. We attempted computer analysis about the observed g shift assuming various models of thermal activation. However, we have obtained no satisfactory result. No conclusive evidence has been obtained for thermally activated electron transfer between Cu and TCNQ.

Electrical Conduction. In $CuL(TCNQ)_2$, two nitrogen atoms from an ethylenediamine or 2,2′-bipyridine molecule are thought to coordinate on a copper atom occupying *cis* positions around the copper atom. Probably, $TCNQ^-$ ions also coordinate to a copper atom to occupy the otherwise vacant positions around the central metal, because the first coordination sphere of copper scarecely has vacant *cis* positions. In spite of the plausible Cu–TCNQ bonding, the magnetic interaction between Cu and TCNQ is very weak. The ratio $\gamma_{Cu}/0.375$ gives an unpaired electron density ρ_{Cu} carried by each copper atom on the average: $\rho_{Cu}=0.05$ for $Cu(bpy)(TCNQ)_2$ and $\rho_{Cu}=0.07$ for $Cu(en)(TCNQ)_2$. The small ρ_{Cu} values are obviously caused by an incomplete electron transfer between Cu and TCNQ accompanying the equilibrium in solids (Eq. 1), in which Cu(II) ions act as electron acceptors against $TCNQ^-$ (on the contrary, Cu(I) ions do as electron donors against $TCNQ^0$). The average oxidation number of copper is equated with $1+\rho_{Cu}$: 1.05 in $Cu(bpy)(TCNQ)_2$ and 1.07 in $Cu(en)(TCNQ)_2$. In our previous paper,[2)] the unpaired electron densities were evaluated on the assumption that the paramagnetic term γ/T of the static susceptibility arises only from the copper atoms. The densities reported previously were overestimated. However, the present investigation supports the preceding conclusion that the equilibrium given by Eq. 1 lies so far to the right.[2,3)]

The electrical conductivities σ observed for the compressed pellets of the complexes obey

$$\sigma = \sigma_\infty \exp(-E/kT). \tag{7}$$

The activation energy E was determined as 0.036 eV for the bpy complex and 0.12 eV for the en complex.[1)] The energy of the former complex is of the order of an energy barrier predicted for contact resistance between powder particles. Possibly, the electrical conduction within the particles is inherently metallic. This is supported by the present magnetic study showing that the local TCNQ susceptibility involving the large temperature-independent paramagnetic term can be interpreted in terms of the narrow band model.

In conclusion, electric current in the $CuL(TCNQ)_2$ complexes flows through a narrow band formed by the TCNQ arrays, and the Cu(II) ions act as electron acceptors against $TCNQ^-$ ions to yield conduction electrons in the band.

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