MAGNETIC STUDY OF HIGHLY CONDUCTIVE TCNQ⁻ SALTS OF Cu(II) COMPLEXES WITH 2,2'-BIPYRIDINE, 1,10-PHENANTHROLINE AND ETHYLENEDIAMINE

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The magnetic susceptibility has been determined for $CuL_n(TCNQ^-)_2$ (L = 2,2'-bipyridine, 1,10-phenanthroline, or ethylenediamine; n = 1 or 2), having high electric conductivity. The results show that the $Cu^{2+}L_n$ chelates are partially reduced to Cu^+L_n in the complexes. The equilibrium $Cu^{2+}L_n(TCNQ^-)_2 \rightleftharpoons Cu^+L_n(TCNQ^-)(TCNQ^0)$ produces conduction electrons in TCNQ columns.

1. Introduction

We reported [1] that some Cu(II) complexes of 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) form a new class of highly conductive tetracyanoquinodimethalides, $CuL(TCNQ^-)_2$ and $CuL_2(TCNQ^-)_2$ (L = bpy or phen). The electric conductivities determined on compressed pellets at 300 K amount to 0.04–1.9 Ω^{-1} cm^{-1}, comparable to those of crystalline powders of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ [2] and partially oxidized phthalocyanine complexes [3]. Some chemical and structural features required for highly conductive materials have been pointed out [4]. One of them is the existence of unpaired electrons within molecular units. In the abovementioned Cu(II) complexes, which formally have three unpaired electrons in the chemical units, interaction between the unpaired electrons is suspected of playing an important role in the electric conduction. With this point of view, we have determined the magnetic susceptibilities of the Cu(II) complexes in the present investigation. Another important feature for high electric conduction is the potential capacity of constituent molecules as donors or acceptors [4]. A redox-potential study [5] has shown that $[Cu(bpy)_2]^{2+}$ and $[Cu(phen)_2]^{2+}$ are easily reduced to the corresponding Cu(I) chelates. This suggests that the following equilibrium can easily take place in the Cu(II)–$TCNQ^-$ complexes:

$$Cu^{2+}L_n(TCNQ^-)_2 \rightleftharpoons Cu^+L_n(TCNQ^-)(TCNQ^0). \quad (1)$$

This means that the Cu(II) chelates are capable of functioning as electron acceptors against $TCNQ^-$ ions (on the other hand, Cu^+L_n acts as an electron donor against $TCNQ^0$). This charge-transfer effect can enhance the electric conduction to a great extent. If this is correct, the corresponding ethylenediamine (en) complexes are expected to exhibit electric properties differing markedly from the bpy and phen complexes, because $[Cu(en)_2]^{2+}$ is reduced to $[Cu(en)_2]^+$ with much difficulty compared with the bpy and phen chelates [5]. Therefore, we prepared $Cu(en)(TCNQ^-)_2$ and $Cu(en)_2(TCNQ^-)_2$, and extended the electric and magnetic studies to them.

2. Experimental

The en complexes were prepared by essentially the same method as reported previously for the bpy and phen complexes [1]: to an aqueous solution of Li(TCNQ) was added an aqueous solution of Cu(en) or $Cu(en)_2$ nitrate in 10% excess. The preparations were carried out by use of deaerated water under a nitrogen atmosphere. Calculated for $Cu(C_2H_4N_2)(C_{12}H_4N_4)_2$: C, 58.7; H, 3.0; N, 26.3; Cu, 11.9%. Found: C, 59.1; H, 2.5; N, 24.7; Cu, 11.6%. Calculated

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for $Cu(C_2H_4N_2)_2(C_{12}H_4N_4)_2$: C, 56.8; H, 4.1; N, 28.4; Cu, 10.7%. Found: C, 56.5; H, 4.0; N, 27.6; Cu, 10.8%.

The electric conductivity was determined on compressed pellets by van der Pauw's four-probe method [6] at temperatures between 200 and 300 K. The thermoelectric power against Cu metal was measured also on compressed pellets at 300 K. Although the absolute value of the thermoelectric power determined on pellets is not reliable, its sign is significant for assigning the carriers of electric current

The magnetic susceptibility was determined by a Faraday balance in the temperature range 100–300 K. The molar magnetic susceptibility ‡ was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from bpy (−105), phen (−128), en (−46), and TCNQ (−121) [7,8].

3. Results

In the temperature range investigated, the conductivities σ obeyed the equation characteristic of semiconductors:

$$\sigma = \sigma_0 \exp(-E_a/kT). \tag{2}$$

The activation energy E_a of the en complexes is large compared with the bpy and phen complexes (table 1). The sign of the thermoelectric power (table 1) indicates that the en complexes are p-type semiconductors, whereas the bpy and phen complexes are n-type The en complexes exhibit electric properties quite different from those of the corresponding bpy and phen complexes, as expected.

Fig. 1 shows the reciprocal magnetic susceptibility plotted against temperature. The magnetic susceptibility χ of $Cu(en)_2(TCNQ^-)_2$ obeys the Curie–Weiss law $\chi = C/(T-\theta)$ with the Curie constant $C = 0.452$ emu K mol^{-1} and the Weiss constant $\theta = -32$ K. The Curie constant yields a magnetic moment of 1.90 μ_B, which falls in the range normally observed for Cu(II) complexes. This indicates that the observed paramagnetism is due to unpaired electrons each localized on a Cu atom. The unpaired electrons of the $TCNQ^-$ radicals are coupled almost completely, and no marked magnetic interaction is operative between Cu(II) and $TCNQ^-$. The magnetic susceptibilities of the other complexes deviated from the Curie–Weiss law (fig. 1). Except for $Cu(en)_2(TCNQ^-)_2$, the effective magnetic moments $\mu_{eff} = (8\chi T)^{1/2}$ per chemical unit are much lower than 1.73 μ_B of one odd electron, indicating that the unpaired electrons on the Cu atoms as well as on the $TCNQ^-$ radicals are subject to magnetic interaction. Fig. 2 shows that the magnetic susceptibilities can be reproduced by

$$\chi = \alpha + \gamma/T; \tag{3}$$

the paramagnetism arises from the temperature-independent term α and the Curie term γ/T. The α values (table 1) are too large to attribute to the temperature-independent paramagnetism due to the second-order Zeeman term of the Cu(II) ions (the order of its magnitude is 60×10^{-6} emu mol^{-1} [9]), and are nearly equal to the temperature-independent paramagnetic susceptibility 5×10^{-4} emu mol^{-1} attributable to the

Table 1
Conductivities σ (Ω^{-1} cm^{-1}) at 300 K and σ_0 (Ω^{-1} cm^{-1}) at infinite temperature, activation energy E_a (eV) for electric conduction, thermoelectric power S (μV K^{-1}), effective magnetic moment μ_{eff} (μ_B), magnetic parameters α (emu mol^{-1}) and γ (emu K mol^{-1}) in $\chi = \alpha + \gamma/T$, and unpaired electron density ρ_{Cu} on Cu of Cu(II)–$TCNQ^-$ complexes

Complex	σ	σ_0	E_a	S	μ_{eff}	$10^4\alpha$	γ	ρ_{Cu}
$Cu(bpy)_2(TCNQ^-)_2$	0.04 a)	0.36 a)	0.054 a)	−45	1.59	6.1	0.126	0.3
$Cu(phen)_2(TCNQ^-)_2$	0.23 a)	2.2 a)	0.057 a)	−60	1.43	5.5	0.088	0.2
$Cu(en)_2(TCNQ^-)_2$	7×10^{-4}	2.3	0.20	620	1.81	– b)	– b)	1
$Cu(bpy)(TCNQ^-)_2$	1.6 a)	6.3 a)	0.036 a)	−55	1.23	4.6	0.052	0.1
$Cu(phen)(TCNQ^-)_2$	1.9 a)	7.9 a)	0.039 a)	−30	0.48	0.77	0.0067	0.02
$Cu(en)(TCNQ^-)_2$	0.026	2.4	0.12	190	1.13	2.15	0.093	0.2

a) Ref. [1]. b) The susceptibility obeys the Curie–Weiss law with $C = 0.452$ emu K mol^{-1} and $\theta = -32$ K.

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‡ Given in cgs emu in this paper. Multiplication with $4\pi \times 10^{-6}$ yields the corresponding value in SI.

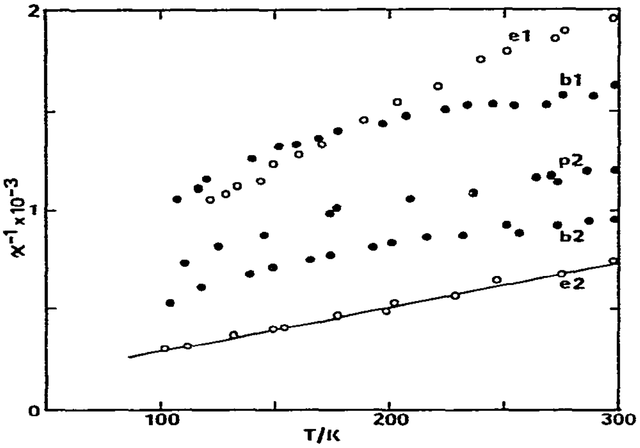

Fig. 1. Reciprocal molar magnetic susceptibilities χ^{-1} (in emu) of Cu(bpy) $(TCNQ^-)_2$ (b1), Cu(en) $(TCNQ^-)_2$ (e1), $Cu(bpy)_2$ $(TCNQ^-)_2$ (b2), $Cu(phen)_2$ $(TCNQ^-)_2$ (p2), and $Cu(en)_2$ $(TCNQ^-)_2$ (e2).

conduction electrons of the quinolinium–TCNQ complex $Q^+(TCNQ^-)(TCNQ^0)$ [10] which have a metallic nature [11]. This suggests that the α term is attributable to the paramagnetism of the conduction electrons. The γ term can be ascribed to localized unpaired electrons, although contributions of impurities cannot be entirely discarded.

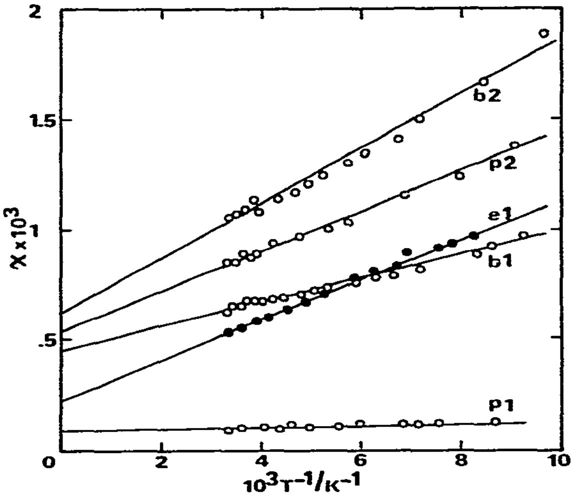

Fig. 2. Molar magnetic susceptibilities χ (in emu) plotted against reciprocal temperature for Cu(bpy) $(TCNQ^-)_2$ (b1), Cu(phen) $(TCNQ^-)_2$ (p1), Cu(en) $(TCNQ^-)_2$ (e1), $Cu(bpy)_2$ $(TCNQ^-)_2$ (b2), and $Cu(phen)_2$ $(TCNQ^-)_2$ (p2). The straight lines show $\chi = \alpha + \gamma/T$ with the parameters listed in table 1.

4. Discussion

The Cu(II) complexes investigated are very difficult to obtain as single crystals amenable to X-ray study. However, there are some structural resemblances among highly conductive materials involving $TCNQ^-$ and other flat molecules [4]: (1) $TCNQ^-$ ions are stacked face-to-face in linear chains separated by similar chains of cations, and (2) $A^{2+}(TCNQ^-)_2$ type crystals contain alternating linear chains of $TCNQ^-$. Planar Cu(II) chelates can also be stacked face-to-face to construct linear arrays as in $(TMPD^+)_2[Cu(mnt)_2]$ [12] (TMPD: N,N,N′,N′-tetramethyl-p-phenylenediamine, mnt. maleonitrildithiolato). From this, we can reasonably propose the molecular arrangement schematically shown in fig. 3 for CuL_2 $(TCNQ^-)_2$. The same type of molecular arrangement has been found in crystals of $[Pt(NH_3)_4]$ $(TCNQ^-)_2$ [13]. Alternating $TCNQ^-$ chains form intrinsic-semiconductor crystals, because each chain constructs an occupied valence band and a vacant band separated in energy from the former. In the Cu(II)–$TCNQ^-$ complexes, however, $[CuL_2]^{2+}$ can draw out electrons from an adjacent $TCNQ^-$ column by attaining the equilibrium of eq. (1), so that the valence band of the $TCNQ^-$ column is altered to a conduction band. Consequently, conduction electrons are produced in the otherwise occupied valence band of the $TCNQ^-$ columns and fractional unpaired electrons are localized on the Cu atoms. The former electrons exhibit temperature-independent paramagnetism and the latter Curie-type paramagnetism. This explains the magnetic susceptibilities observed for the bpy and phen complexes. The Curie constant corre-

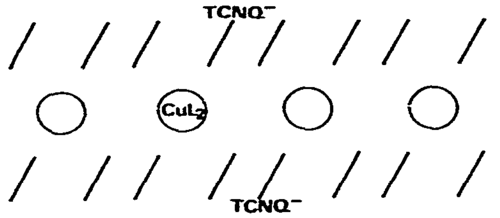

Fig. 3. Molecular arrangement proposed for CuL_2 $(TCNQ^-)_2$.

sponding to a free electron is equal to 0.375 emu K mol^{-1}. From the ratio $\gamma/0.375$, the density of unpaired electrons localized on the Cu atoms can be approximately evaluated as 0.3 for $Cu(bpy)_2(TCNQ^-)_2$ and 0.2 for $Cu(phen)_2(TCNQ^-)_2$. This suggests that the Cu atoms are in the incomplete oxidation state 1.2–1.3, and hence that each Cu atom draws out 0.7–0.8 electron on the average from the otherwise valence band of the $TCNQ^-$ columns. The incomplete electron transfer between the donors and acceptors results in the high electric conduction of the complexes. The $TCNQ^-$ columns also possibly exhibit Curie-type paramagnetism attributable to the chain-end effect [14], in addition to the intrinsic paramagnetism. This effect, however, contributes only at very low temperatures; for example, quinolinium$(TCNQ)_2$ and N-methylquinolinium$(TCNQ)_2$ show Curie-type paramagnetism below 50 K [14] In the Cu(II)–$TCNQ^-$ complexes, the Curie-type paramagnetism of the $TCNQ^-$ columns, even though it exists, is masked by the large temperature-dependent susceptibility contributed from the Cu atoms. The magnetic susceptibility of $Cu(en)_2(TCNQ^-)_2$ indicates that interaction between Cu(II) and $TCNQ^-$ ions is very weak. Therefore, the contribution of $Cu(en)_2(TCNQ^-)(TCNQ^0)$ to the equilibrium of eq. (1) is very small, in line with the result of the redox-potential study [5]. Accordingly, $[Cu(en)_2]^{2+}$ draws out only a few electrons from the valence band of $TCNQ^-$ to yield positive holes in it; the chelate forms an impurity level corresponding to that in doped p-type semiconductors. The resulting positive holes can carry electric current in line with the positive sign of the thermoelectric power observed for the complex.

In the $CuL(TCNQ^-)_2$ type complexes, $TCNQ^-$ ions should coordinate to Cu atoms, because a Cu(II) ion normally forms four or more coordination bonds. The coordination of $TCNQ^-$ facilitates electron transfer from $TCNQ^-$ to Cu(II) ions; the contribution of $CuL(TCNQ^-)(TCNQ^0)$ is enhanced in the equilibrium of eq. (1). This is the reason why the $CuL(TCNQ^-)_2$ complexes exhibit higher electric conductivities than those of the corresponding $CuL_2(TCNQ^-)_2$. This is supported by the present magnetic study indicating that the unpaired electron density on Cu is lower in the former complexes than in the latter (table 1).

In the new class of highly conductive Cu(II)–$TCNQ^-$ complexes, the partial reduction of the Cu(II) chelates results in electric conduction. This mechanism consistently explains the electric and magnetic properties of the complexes.

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