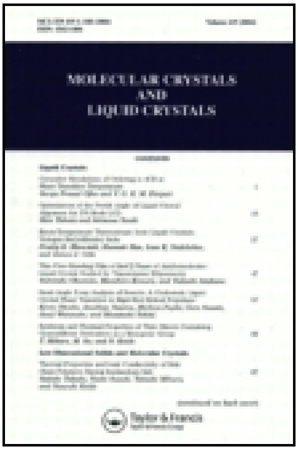

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Highly Conductive TCNQ Salts of Cu Chelates

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HIGHLY CONDUCTIVE TCNQ SALTS OF Cu CHELATES

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Cu(II) chelates with ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline and their analogues form highly conductive TCNQ salts $\mathrm{CuL_n(TCNQ)_2}$. The powder conductivity at room temperature amounts to 7×10^{-4}-1.9 $\Omega^{-1}\mathrm{cm}^{-1}$, depending on the coordinating ligands. The ESR and magnetic susceptibility studies indicate that the Cu atoms of the complexes have incomplete oxidation states.

INTRODUCTION

In our preceding papers,[1,2] we have reported that Cu(II) chelates with ethylenediamine (hereafter en), 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) form a new class of highly conducting TCNQ salts having the formula $\mathrm{CuL_n(TCNQ)_2}$. For example, the powder conductivity of $\mathrm{Cu(phen)(TCNQ)_2}$ amounts to 1.9 $\Omega^{-1}\mathrm{cm}^{-1}$ at 300 K. Our previous magnetic study has indicated that the Cu atoms of the complexes take incomplete oxidation states caused by the following equilibrium in solids:

$$[\mathrm{C\dot{u}L_n}]^{2+}[(\mathrm{TCNQ})_2^{\cdot\cdot}]^{2-} \rightleftharpoons [\mathrm{C\ddot{u}L_n}]^{+}(\mathrm{TCNQ}^{\cdot-})(\mathrm{TCNQ}^{0}) \qquad (1)$$

This suggests that the high electrical conductivities of the complexes are originated from an incomplete charge transfer between Cu^{2+} and $TCNQ^-$ ions. In the present investigation, we have recorded the ESR spectra of the TCNQ salts, in order to confirm the equilibrium in solids and the important role of unpaired electrons in the electric conduction.

In the aforementioned equilibrium, the Cu(II) chelates act as electron acceptors against $TCNQ^-$; the Cu(I) chelates function as electron donors against $TCNQ^0$. A redox potential study[3] of Cu(II) complexes with substituted bpy and phen ligands has shown that the stability of $Cu^{2+}L_n$ with respect to Cu^+L_n changes to great extent depending on the coordinating ligands. This suggests that the conductivity of the Cu-TCNQ complexes can be easily controlled by changing the coordinating ligands. The correlation between the redox potential and the electrical conductivity, if it exists, gives another experimental evidence for the presence of the equilibrium in solids. In this point of view, we have prepared the TCNQ salts of Cu(II) chelates with substituted bpy and phen ligands and have determined the electrical conductivity and the thermoelectric power.

EXPERIMENTAL

The materials $CuL(TCNQ)_2$ were prepared from the deaurated aqueous solutions of Li(TCNQ) and of the appropriate $CuL(NO_3)_2$ with ligands listed in Table 2 (hereafter, the ligands are abbreviated as shown in Table 2). Satisfactory carbon, hydrogen and nitrogen analyses were obtained. We attempted to prepare the $CuL_2(TCNQ)_2$ type complexes with the substituted ligands in a manner similar to that for the corresponding $CuL(TCNQ)_2$. However, the obtained materials were fluctuated in their chemical compositions.

The electrical conductivity was determined by van der Pauw's four-probe method on the compressed pellets between 200 and 300 K. The thermoelectric power was measured on the pellets against Cu metal at 300 K. The ESR spectrum was recorded by means of a JEOL SCXA X band spectrometer. Mn^{2+}/MgO and DPPH were employed as markers.

RESULTS

ESR Spectrum

Figure 1 shows ESR spctra observed for the powders of the en and bpy complexes at ambient temperature. Each spectrum involved a sharp signal attributed to unavoidable impurities at g = 2.00 except that of $Cu(en)_2(TCNQ)_2$.

The intrinsic signal of $Cu(en)(TCNQ)_2$ is symmetric, and its g factor 2.015 is larger than 2.003 of Li(TCNQ) and smaller than the averaged g factor $g_{av} = [(g_{\parallel}{}^2 + 2g_{\perp}{}^2)/3]^{1/2} = 2.125$ determined for $Cu(en)SO_4 \cdot 3H_2O$. These indicate that some magnetic interaction operates between Cu^{2+} and $TCNQ^-$ ions with an energy greater than the ESR frequency. This interaction probably originates from the aforementioned equilibrium. Since each equilibriated species in Eq. 1 involves one odd electron, the g factor of the spin system is given by

$$g = \rho_{Cu}g_{Cu} + (1 - \rho_{Cu})g_T \qquad (2)$$

in the strong coupling limit. In the equation, g_{Cu} and g_T are the g factors of isolated Cu and TCNQ spins, respectively, and ρ_{Cu} is unpaired electron density distributed on a Cu atom. Using $g_{Cu} = 2.125$ and $g_T = 2.003$, we can evaluate ρ_{Cu} as shown in Table 1. In the same manner, ρ_{Cu} of $Cu(bpy)(TCNQ)_2$ was evaluated (Table 1) by use of $g_{Cu} = 2.133$ equated to g_{av} of $Cu(bpy)(NO_3)_2 \cdot 3H_2O$.

$Cu(en)_2(TCNQ)_2$ exhibited an ESR spectrum characteristic of Cu(II) complexes having an axially symmetric ligand field. The principal g factors $g_{\parallel} = 2.204$ and $g_{\perp} = 2.047$ are nearly equal to $g_{\parallel} = 2.226$ and $g_{\perp} = 2.046$ of $Cu(en)_2Cl_2 \cdot 2H_2O$, respectively. These indicate that an unpaired electron is practically localized on each Cu atom: the equilibrium Eq. 1 lies so far to the left in this complex. The g anisotropy of $Cu(bpy)_2(TCNQ)_2$ is very small compared with those of usual Cu(II) complexes, suggesting the presence of magnetic interaction between Cu and TCNQ spins. Strictly speaking, Eq. 2 cannot be applied to this system, because its g anisotropy is not completely smeared out. We tentatively evaluated ρ_{Cu}, using the averaged g factor ($g_{av} = 2.143$ of $Cu(bpy)_2(NO_3)_2$-

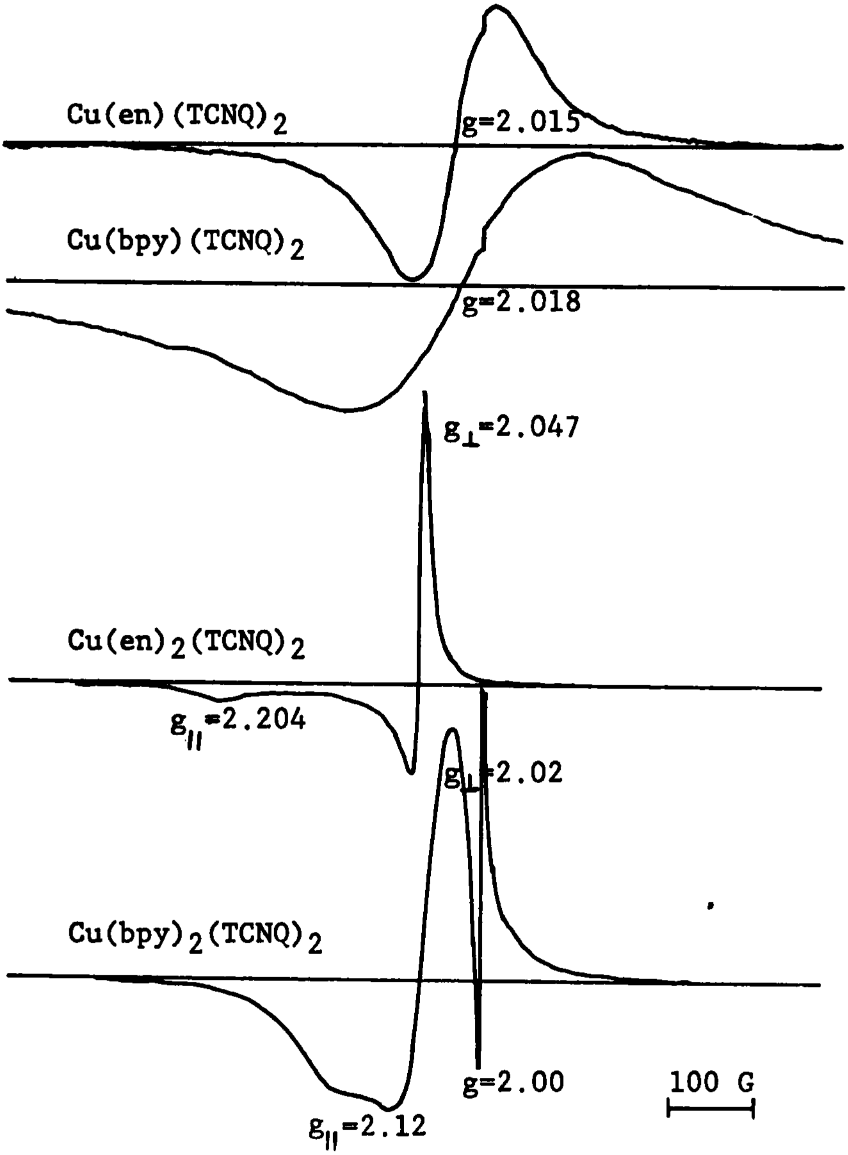


FIGURE 1 ESR spectra observed for $CuL_n(TCNQ)_2$ at ambient temperature

Table 1 g Factor of ESR, Unpaired Electron Densities ρ_{Cu} of a Cu Atom Evaluated by ESR and Magnetic Susceptibility Studies, Electrical Conductivity σ at 300 K, and Thermoelectric Power S

	g	ρ_{Cu}		σ^a $\Omega^{-1}cm^{-1}$	S^a μVK^{-1}
		ESR	Magn[a]		
$Cu(en)(TCNQ)_2$	2.015	0.1	0.2	0.026	+190
$Cu(bpy)(TCNQ)_2$	2.018	0.1	0.1	1.6	-55
$Cu(phen)(TCNQ)_2$	2.01	0.1	0.02	1.9	-30
$Cu(en)_2(TCNQ)_2$	2.101	1	1	$7x10^{-4}$	+620
$Cu(bpy)_2(TCNQ)_2$	2.05	0.4	0.3	0.04	-45
$Cu(phen)_2(TCNQ)_2$	2.03	0.3	0.2	0.23	-60

[a] ref. 2.

H_2O was employed as g_{Cu}).

Each ESR spectrum of the phen complexes involved a strong signal due to impurities at g = 2.00 in addition to the intrinsic signal, which resembled that of the corresponding bpy complex. Although accurate measurements were unsuccessful, the g factors were approximately determined, and the ρ_{Cu} values were evaluated in the same manner as for the bpy complexes (g_{av} = 2.079 of $Cu(phen)(NO_3)_2 \cdot H_2O$ and 2.095 of $Cu(phen)_2(NO_3)_2 \cdot H_2O$ were used as g_{Cu} for $Cu(phen)(TCNQ)_2$ and $Cu(phen)_2(TCNQ)_2$, respectively).

The ρ_{Cu} values evaluated in the present ESR experiment agree well with the corresponding values determined in our previous magnetic study.[2] The oxidation number of Cu atoms can be equated to 1 + ρ_{Cu}.

Electric Properties of Substituted Complexes

Figure 2 shows that the electrical conductivity of every substituted complexes can be explained by

$$\sigma = \sigma_0 \exp(-E/kT) \qquad (3)$$

The activation energy E for electric conduction is shown in Table 2 along with the electrical conductivity and the thermoelectric power determined at

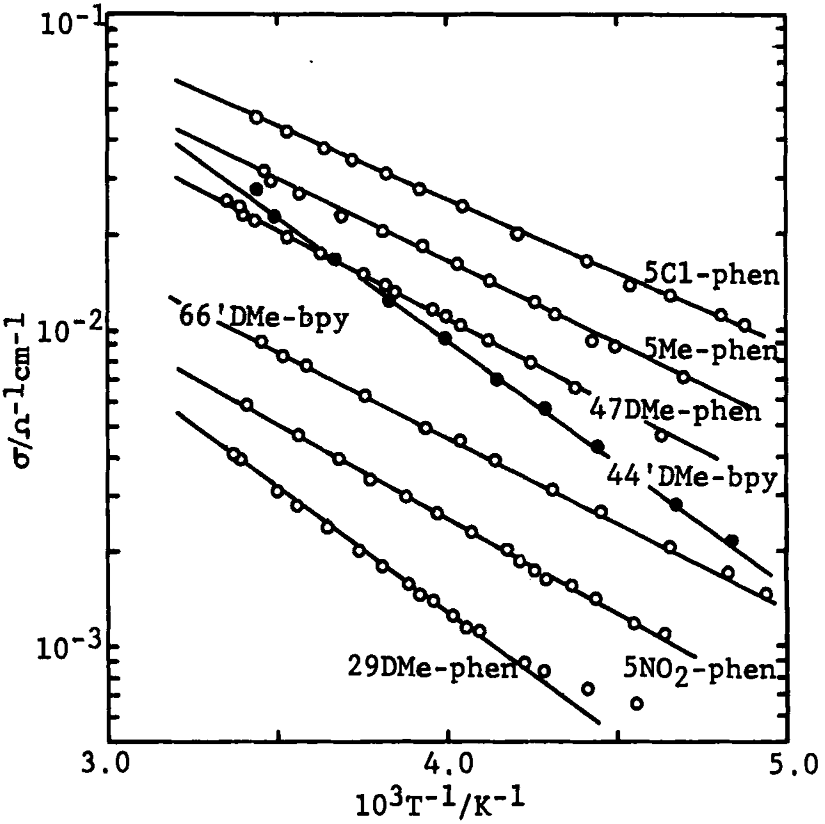


FIGURE 2 Electrical conductivity of $CuL(TCNQ)_2$ with substituted bpy and phen ligands

ambient temperature. The electrical conductivity of the series of the complexes can be controlled easily by changing the coordinating ligand, as has been expected.

DISCUSSION

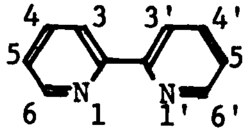
The present ESR investigation along with our previous magnetic study indicates that the Cu atoms of the Cu-TCNQ complexes have incomplete oxidation states. The high electrical conductivity originates from an incomplete "redox reaction" accompanying the equilibrium Eq. 1 in solids. In

Table 2 Electrical Conductivity σ at Ambient Temperature, Activation Energy E for Electric Conduction, and Thermoelectric Power S of $CuL(TCNQ)_2$.

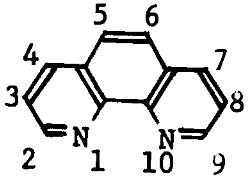
L	$\sigma/\Omega^{-1}cm^{-1}$(T/K)	E/eV	S/μV K^{-1}
bpy[a]	1.6 (300)	0.036	-55
44'DMe-bpy	0.028 (292)	0.15	-10
66'DMe-bpy	0.009 (290)	0.11	+30
phen[a]	1.9 (300)	0.039	-30
5Me-phen	0.032 (289)	0.10	-20
5Cl-phen	0.047 (290)	0.09	-5
$5NO_2$-phen	0.006 (292)	0.12	+15
47DMe-phen	0.023 (292)	0.11	-20
29DMe-phen	0.0038 (295)	0.16	-30
en[a]	0.026 (300)	0.12	+190

[a] refs. 1 and 2.

bpy



phen



this sense, the Cu-TCNQ complexes belong to the category of mixed valent complexes in spite of their stoiquiometric compositions.

In the crystals of $R(TCNQ)_2$ type salts, $TCNQ^-$ ions stack alternately in a linear array. The resulting alternating linear chain constructs an occupied valence band and a vacant band. Relative relation between the energy level of $Cu^{2+}L_n$ and that of the occupied TCNQ band yields various types of conducting materials. The redox potential study[3] has shown that the stability of $Cu^{2+}L_n$ with respect to Cu^+L_n decreases in the following respective orders: 1) en $\gg$ bpy, phen, 2) 4,4'DMe-bpy $>$ bpy $>$ 66'DMe-bpy, 3) 47DMe-phen $>$ phen $>$ 5Me-phen $>$ 5Cl-phen $>$ $5NO_2$-phen $\gg$ 29DMe-phen. $Cu^{2+}(en)_2$ is a very weak electron acceptor against $TCNQ^-$, because it is hardly reduced to the corresponding Cu(I) chelate. Hence, the equilibrium lies so far to the left in line with its ρ_{Cu} value. This means that the energy level of $Cu(en)_2$ lies much higher

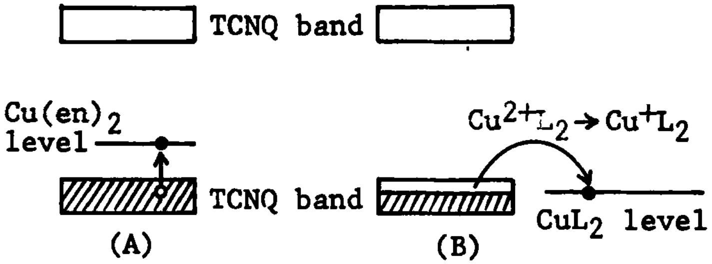


FIGURE 3 Band structure of $CuL_2(TCNQ)_2$ (A: L = en; B: L = bpy, phen)

than the occupied TCNQ band (Fig. 3). Therefore, $Cu(en)_2(TCNQ)_2$ exhibits the low conductivity and behaves as a p type semiconductor (Table 1). The coordination of bpy or phen lowers the CuL_2 level, so that the electrons of $TCNQ^-$ ions are easily transferred to the Cu chelates (Fig. 3). The ρ_{Cu} values of $Cu(bpy)_2(TCNQ)_2$ and $Cu(phen)_2(TCNQ)_2$ show that each Cu atom of the complexes draws out 0.6-0.8 electron on the average from the otherwise occupied TCNQ band. For this reason, these complexes exhibit much higher conductivities than that of $Cu(en)_2(TCNQ)_2$. Cu^{2+}(66'DMe-bpy) and Cu^{2+}(29-DMe-phen) are very easily reduced to Cu^+L. Accordingly, the equilibrium Eq. 1 lies so far to the right. These Cu(II) chelates have too large electron-accepting capacity to yield highly conducting TCNQ salts. Their conductivities are lowest in the respective analogues (Table 2). A "moderate" electron-accepting capacity of $Cu^{2+}L_n$ against $TCNQ^-$ is required for high electric conduction.

The complexes of unsubstituted bpy and phen exhibit higher conductivities than those of the substituted complexes. This is probably due to the higher symmetry of the unsubstituted ligands.

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