Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Charge Transfer Compounds with Copper(II) Halides: $(BEDT\text{-}TTF)_{1.5}CuX_2$ (X = Cl, Br)

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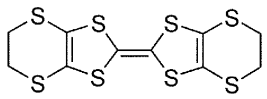
Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is an excellent electron donor to form a charge transfer compound which shows a wide range of electrical conductivity from insulators and semiconductors to metals and superconductors.[1,2,3]



BEDT - TTF

Halides, pseudohalides and some transition metal complexes have been used as electron acceptors in BEDT-TTF salts. Copper(II) complexes, among them, are good oxidants for BEDT-TTF to form charge transfer compounds because copper(II) is readily reduced to copper(I) ($Cu(II) \rightarrow Cu(I)$, $E_{1/2} = 0.158$ V *vs* SHE in aqueous solution) depending on the chemical circumstances. When copper(II) complexes are used as the oxidants, the extent of the charge transfer from BEDT-TTF to copper(II) per formular unit is dependent on reaction conditions such as the ratio of reactants, the solvents used, the reaction methods and so on. For example, Tanaka *et al.*[4] achieved 1 : 1 salt of BEDT-TTF with the formular of $(BEDT\text{-}TTF)_{1.0}Cu^{II/I}Cl_2$ by the diffusion method in 1,1,2-trichloroethane using BEDT-TTF and $CuCl_2$, in which some of the copper(II) metals were reduced to copper(I) being in a mixed-valence copper(II/I) state. Meanwhile, 1:2 salt, $(BEDT\text{-}TTF)_{2.0}CuCl_2$[5] was achieved by electrocrystallization method in 1,1,2-trichloroethane using BEDT-TTF and $[N(n\text{-}C_4H_9)_4]CuCl_2$. In this reported compound, copper(II) was completely reduced to copper(I) in $(BEDT\text{-}TTF)_{2.0}Cu^{I}Cl_2$ with behaviors of a semiconductor with $Ea = 0.15$ eV and $\sigma_{rt} = 3 \times 10^{-3}$ S·cm^{-1}.

In order to investigate a composite system composed of BEDT-TTF and copper halides in this study, we prepared $(BEDT\text{-}TTF)_{1.5}CuX_2$ (X = Cl, Br) compounds in acetonitrile and examined the oxidation state of the copper metal ion since the complete reduction from copper(II) to copper(I) leads to a high electrical conductivity. The prepared charge transfer compounds were characterized using spectroscopic (vibrational, optical), magnetic and electrochemical methods.

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Experimental Section

All of the reagents and solvents were purchased from either Aldrich or Sigma chemical companies and used without further purification. All of the reactions were carried out under a nitrogen atmosphere in a glove box.

$(BEDT\text{-}TTF)_{1.5}CuCl_2$ was obtained from the direct reaction of BEDT-TTF with $CuCl_2$. Anhydrous $CuCl_2$ (3.3×10^{-4} M) was dissolved in 20 mL of acetonitrile. $CuCl_2$ solution was added dropwise to a BEDT-TTF (9.8×10^{-4} M) solution dissolved in 10 mL of acetonitrile with constant stirring under a nitrogen atmosphere. The solution was changed to a dark green color immediately. The reaction solution was stirred for approximately 3 hours, and refrigerated overnight. The resultant precipitates were collected by filtration and washed several times with acetonitrile. The precipitates were dried under vacuum at room temperature. $(BEDT\text{-}TTF)_{1.5}CuBr_2$ was prepared by an analogous method using anhydrous $CuBr_2$ in acetonitrile.

Elemental analyses were performed at the Korean Basic Science Center, and the results are listed below.

Anal. (%) Calcd. for $(BEDT\text{-}TTF)_{1.5}CuCl_2$: C, 25.32; H, 1.70; S, 54.08. Found: C, 25.81; H, 1.83; S, 53.60. Calcd. for $(BEDT\text{-}TTF)_{1.5}CuBr_2$: C, 22.51; H, 1.51; S, 48.07. Found: C, 22.85; H, 1.60; S, 48.56.

The powdered electrical conductivities were measured by compressing the bulk sample between two graphite rods (5 mm in diameter) surrounded by a glass tube sheath with a EG & G Model 362 potentiostat in two electrodes configuration at room temperature.[6] Infrared (IR) spectra (400-4000 cm^{-1}) were obtained using KBr pellets with a Polaris FT-IR spectrophotometer, and electronic absorption spectra (200-1100 nm) were recorded on a Shimadzu 1601 PC spectrophotometer in DMF. $(BEDT\text{-}TTF)_{1.5}CuCl_2$: IR (KBr); 2960 (w), 2911 (w), 1420 (sh), 1406 (s), 1332 (vs), 1284 (sh), 1276 (s), 1174 (w), 1126 (vw), 1008 (w), 933 (w), 880 (w), 806 (w), 490 (w). λ_{max} (DMF); 270, 322, 441, 973 nm. $(BEDT\text{-}TTF)_{1.5}CuBr_2$: IR (KBr); 2962 (w), 2910 (w), 1399 (s), 1338 (vs), 1281 (sh), 1275 (s), 1174 (w), 1124 (vw), 1001 (w), 918 (w), 771 (w), 497 (w). λ_{max} (DMF); 268, 323, 444, 585, 969 nm.

EPR spectra measurements were carried out for the solution samples ($DMF/CH_2Cl = 50/50$) at 77 K using a ESP-300S EPR spectrometer at the X-band frequency. The field modulation frequency was 100 kHz and DPPH was

used as a reference. Magnetic susceptibility data was collected from 4 K to 300 K using the MPMS7 (Magnetic Property Measurement System) of the U.S.A. Quantum Design by the SQUID method. The data was corrected for temperature-independent paramagnetism and for the diamagnetism of the constituent atoms using Pascal's constants. Cyclic voltammograms were recorded on a BAS CV-50W Voltammetric Analyzer in a three electrode system at 0.1 M tetraethylammonium perchlorate (TEAP) in DMF.

Results and Discussion

The direct reaction of BEDT-TTF with CuX_2 (X = Cl, Br) produces the charge transfer $(BEDT\text{-}TTF)_{1.5}CuX_2$ (X = Cl, Br) compounds in acetonitrile. The ratio of BEDT-TTF to CuX_2 was found to be 1.5 when excess BEDT-TTF was used, and BEDT-TTF was ionized and mixed-valence copper(II/I) metal ions were present in the obtained compounds. Inoue *et al.*[7] reported TTF (tetrathiafulvalene) charge transfer compounds with copper(II) halides. They obtained $(TTF)_{4/3\text{-}7/3}Cu^{I}X_2$ under similar conditions in acetonitrile, and reported that copper metal was fully reduced from Cu(II) to Cu(I) in the reaction. This difference between the composition of TTF and that of BEDT-TTF could result from the difference of the π-donor capability of electron donors. The π-donor capability of BEDT-TTF is smaller than that of TTF as seen from comparing the half wave potential of BEDT-TTF ($E^1_{1/2} = -0.20$, $E^2_{1/2} = +0.32$ V)[8] to that of TTF ($E^1_{1/2} = -0.01$, $E^2_{1/2} = -0.23$ V)[9] in DMF *vs* Ag/Ag^+. Furthermore, the stronger π-donor TTF can reduce copper(II) readily, and copper(II) is fully reduced to copper (I) in TTF charge transfer compounds.

The IR spectra of $(BEDT\text{-}TTF)_{1.5}CuX_2$ consist of broad bands extending from 1000 cm^{-1}~2000 cm^{-1}, which arise from the interaction between the electronic structure of these charge transfer compounds and intramolecular vibrations. This vibronic interaction activates some of the A_{1g} modes in BEDT-TTF. Among the totally symmetric (A_{1g}) vibrations of the ring and central C=C bond in the TTF ring (ν_2, ν_3), the A_{1g}-ν_3 mode which is otherwise IR-inactive in BEDT-TTF molecule appears in the ionized $BEDT\text{-}TTF^{\delta+}$ compounds. Kozlov M. E. *et al.*[10] reported that a pair of vibronic transitions appeared at 1401 cm^{-1} and 1331 cm^{-1} in $(BEDT\text{-}TTF)I_3$ and assigned them to the A_{1g}-ν_2 and A_{1g}-ν_3 modes, respectively. A pair of vibronic bands was observed at 1406 cm^{-1} and 1332 cm^{-1} in $(BEDT\text{-}TTF)_{1.5}CuCl_2$, and at 1399 cm^{-1} and 1338 cm^{-1} in $(BEDT\text{-}TTF)_{1.5}CuBr_2$. This appearance of the vibronic bands strengthens the ionized $BEDT\text{-}TTF^{\delta+}$ state in the titled compounds. The observed characteristic broad absorptions at around 970 nm (973 nm for $(BEDT\text{-}TTF)_{1.5}CuCl_2$ and 969 nm for $(BEDT\text{-}TTF)_{1.5}CuBr_2$) in optical spectra, which is not appeared in BEDT-TTF molecule, may cause these vibronic interactions.[10]

The EPR spectra were obtained for frozen glass samples (DMF/CH_2Cl_2 = 50/50) at 77 K. A typical copper(II) EPR pattern as well as the radical $BEDT\text{-}TTF^{\delta+}$ peak were examined as shown in Figure 1. The singlet peaks at around

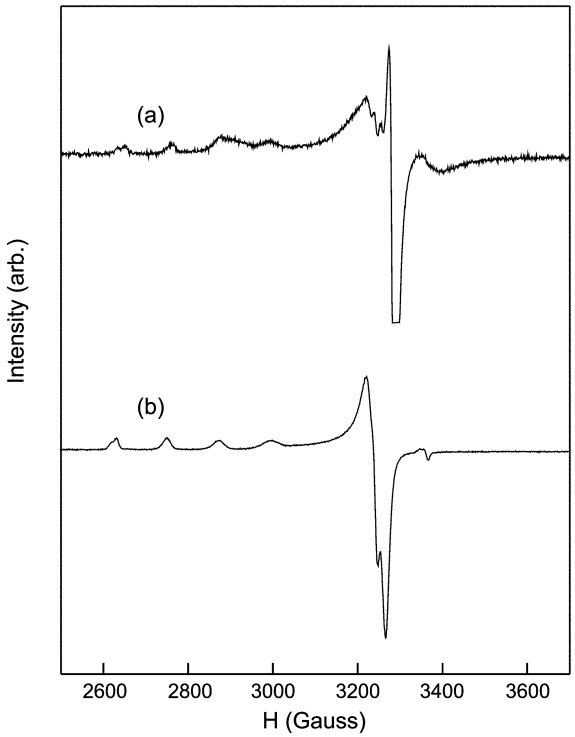

Figure 1. X-band EPR spectra (CH_2Cl_2/DMF) at 77 K (a) $(BEDT\text{-}TTF)_{1.5}CuCl_2$, (b) $(BEDT\text{-}TTF)_{1.5}CuBr_2$.

$\langle g \rangle = 2.07$ for both compounds were determined to arise from the $BEDT\text{-}TTF^{+}$ radical since the g values are similar to that of a free electron or TTF^{+} radical in solution ($\langle g \rangle$ = 2.00838).[11] The peaks from copper(II) metal exhibit a good resolution of parallel ($g_{\parallel}$) and perpendicular ($g_{\perp}$) components with a hyperfine splitting. This observation leads to the conclusion that the BEDT-TTF is partially ionized and that the copper metals are in the mixed valence Cu(II/I) states. The resultant EPR parameters are listed in Table 1.

The powdered electrical conductivities are 10^{-5}~10^{-6} $S{\cdot}cm^{-1}$ which are in the range of an insulator. These observed values are lower than that of $(BEDT\text{-}TTF)_2Cu^{I}Cl_2$ (~10^{-3} $S{\cdot}cm^{-1}$)[5] and that of $(BEDT\text{-}TTF)_2Cu^{II}Cl_4$ (~10^{-4} $S{\cdot}cm^{-1}$).[12] This means that the ionized BEDT-TTFs in $(BEDT\text{-}TTF)_{1.5}Cu^{I}Cl_2$ are not stacked effectively in the solid state. It is worth to note that the intensity of the Cu(II) peak relative to the $BEDT\text{-}TTF^{\delta+}$ radical in $(BEDT\text{-}TTF)_{1.5}CuBr_2$ in the EPR spectra is higher than that in $(BEDT\text{-}TTF)_{1.5}CuCl_2$, indicating that more copper(II) metal ions are present in the former compound. This result was caused from the lower electron inductive effect of Br^- comparing to that of Cl^-. The powdered electrical conductivity of $(BEDT\text{-}TTF)_{1.5}CuBr_2$ was lower than that of $(BEDT\text{-}TTF)_{1.5}CuCl_2$ at room temperature. This result can be explained on the basis of the fact that the existence of copper(II) metal decreases the conductivity due to the Coulomb interaction between the conductive electrons resident in the $BEDT\text{-}TTF^{\delta+}$ radical and the localized electrons in copper(II) metal ions.[13] Similar results are found in the $(TTF)_4CuX_2$ (X = NCS, NO_3, Cl, Br,

Table 1. EPR Parameters, Magnetic Properties, and Electrical Conductivities of $(BEDT\text{-}TTF)_{1.5}CuX_2$

Compounds	EPR Parameters (g(A[a]))		Magnetic Properties		Electrical Conductivities[d] (σ_{rt}, S·cm^{-1})
	Cu(I)	BEDT-TTF radical	Curie-Weiss Parameters C (Θ)	μ_{eff}[c] (BM)	
$(BEDT\text{-}TTF)_{1.5}CuCl_2$	$g_\perp$ = ~2.09[b] (23) $g_\parallel$ = 2.390 (120)	2.061 (16)	0.39 (−0.9)	1.26	9.4×10^{-5}
$(BEDT\text{-}TTF)_{1.5}CuBr_2$	$g_\perp$ = 2.163 (15) $g_\parallel$ = 2.480 (125)	2.08 (5)	0.53 (+0.9)	1.22	8.5×10^{-6}

[a]peak to peak EPR linewidth (gauss). [b]The exact $g_\perp$ value of Cu(II) was not obtained due to the strong BEDT-TTF radical peak in the similar region. [c]The effective magnetic moment was calculated by $\mu_{eff} = 2.828(\chi \cdot T)^{1/2}$ at room temperature. [d]The electrical conductivity was obtained at room temperature.

NCO, NO_2 and OAc) series, in which the extent of the reduction from copper(II) to copper(I) is strongly dependent on both the reduction potential of CuX_2 and the electron transfer rate from TTF to the CuX_2 entity in the reaction.[13] It was found that the electrical conductivity of $(TTF)_1CuX_2$ decreases as the amount of copper(II) metal ion present in $(TTF)_1CuX_2$ increases.

The magnetic susceptibility of both compounds was examined from room temperature to 4 K using the SQUID method. The typical temperature dependence of the magnetic susceptibility for $(BEDT\text{-}TTF)_{1.5}CuCl_2$ is shown in Figure 2. The magnetic susceptibility increases as the temperature decrease like a Curie-like tail, and the data follows the Curie-Weiss law, $\mu_{eff} = C/(T-\theta)$, from 4 K to 50 K. But the data deviated from the Curie-Weiss law above 50 K. The parameters of Curie-Weiss fit (4-50 K) are shown in Table 1.

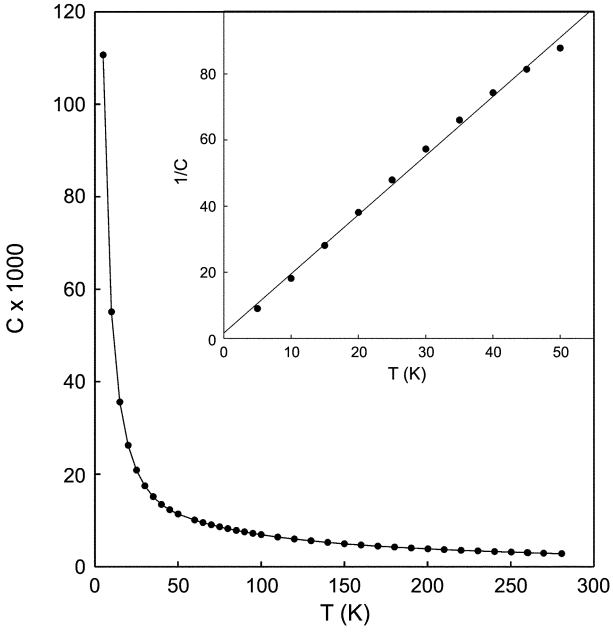

Figure 2. Temperature Dependence of Magnetic Susceptibility of $(BEDT\text{-}TTF)_{1.5}CuCl_2$.

The total magnetic susceptibility can be expressed as the following equation: $\chi(T) = \chi_{Cu(II)} + \chi_{TTF+\cdot} + \delta(T)$, which contains the contributions from the localized electrons on the copper(II) ion ($\chi_{Cu(II)}$), from the unpaired electrons on the BEDT-TTF radicals ($\chi_{TTF^{+\cdot}}$) and from an unprescribed temperature-dependent term that account for the exchange interactions ($\delta(T)$). The diamagnetic copper(I) metal ions present did not influence the magnetic properties. The observation that the Curie-Weiss law fit the data well indicates that the localized electrons in the copper(II) ions dominate the magnetic properties at low temperatures since the delocalized electrons in the BEDT-TTFs usually exhibit a small paramagnetism[14] or strong antiferromagnetic interactions[15] between BEDT-TTF radical cations. However, the magnetic susceptibility data is more complicated at higher temperatures, and we did not attempt to correlate the data in the above equation because of the difficulty in choosing the $\delta(T)$ term. The effective magnetic moments (μ_{eff}) calculated from $\mu_{eff} = 2.828\ (\chi \cdot T)^{-1/2}$ are 1.22-1.26 BM at room temperature. The values are less than the spin-only value of 1.73 BM for one unpaired electron. This low magnetic moment is additional evidence for the mixed valence copper(II/I) states.

Cyclovoltammograms were recorded in DMF/0.10 M TEAP *vs* the Ag/Ag+ electrode, and four reversible redox

Table 2. The Peak Potential Values (Ep, V) of $(BEDT\text{-}TTF)_{1.5}CuX_2$

Compounds	BEDT-TTF				Cu			
	E_{pc}	$E_{1/2}$	E_{pa}	process	E_{pc}	$E_{1/2}$	E_{pa}	process
BEDT-TTF	0.17	0.20	0.22	ET^-/ET	–	–	–	–
	0.29	0.32	0.35	ET^{2-}/ET^-	–	–	–	–
$(BEDT\text{-}TTF)_{1.5}CuCl_2$	0.09	0.12	0.14	ET^-/ET	−0.22	0.04	0.29	Cu^+/Cu
	0.23	0.25	0.28	ET^{2-}/ET^-	0.54	0.61	0.67	Cu^{2+}/Cu^+
$(BEDT\text{-}TTF)_{1.5}CuBr_2$	0.09	0.13	0.16	ET^-/ET	−0.16	−0.06	0.04	Cu^+/Cu
	0.22	0.24	0.27	ET^{2-}/ET	0.52	0.60	0.67	Cu^{2+}/Cu^+

potentials were examined. The waves were assigned tentatively by comparing the reported values, and the results are summarized in Table 2. The redox potentials of (BEDT-TTF)$_{1.5}$CuCl$_2$ were shifted to lower values compared to those of the BEDT-TTF molecule, supporting the conclusion that BEDT-TTFs in (BEDT-TTF)$_{1.5}$CuCl$_2$ were oxidized. A similar result was examined in (BEDT-TTF)$_{1.5}$CuBr$_2$.

Conclusions

We prepared the charge transfer (BEDT-TTF)$_{1.5}$CuX$_2$ (X = Cl, Br) compounds from the direct reaction of BEDT-TTF with the corresponding copper halides in acetonitrile, and found that the BEDT-TTFs were partially oxidized and that the copper metal ions were in the mixed-valence copper(II/I) state. More paramagnetic copper(II) ions are present in (BEDT-TTF)$_{1.5}$CuBr$_2$ than in (BEDT-TTF)$_{1.5}$CuCl$_2$ as shown in the EPR spectra, and the existence of the copper(II) ions is reflected in the electrical conductivity properties with the conductivity of (BEDT-TTF)$_{1.5}$CuCl$_2$ being much greater than that of (BEDT-TTF)$_{1.5}$CuBr$_2$. Furthermore, it can be concluded that the ratio of BEDT-TTF to CuX$_2$ should be more than 2 per formular unit to reduce copper (II) completely to copper(I), leading to a high electrical conductivity.

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