

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) Charge Transfer Compounds with Copper(II) Halides: (BEDT-TTF)_{1.5}CuX₂ (X = Cl, Br)

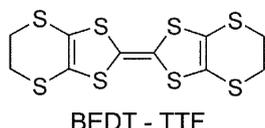
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Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) is an excellent electron donor to form a charge transfer compound which shows a wide range of electrical conductivity from insulators and semiconductors to metals and superconductors.^{1,2,3}



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) → 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-TTF)_{1.0}Cu^{II}Cl₂ by the diffusion method in 1,1,2-trichloroethane using BEDT-TTF and CuCl₂, 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-TTF)_{2.0}CuCl₂⁵ was achieved by electrocrystallization method in 1,1,2-trichloroethane using BEDT-TTF and [N(n-C₄H₉)₄]CuCl₂. In this reported compound, copper(II) was completely reduced to copper(I) in (BEDT-TTF)_{2.0}Cu^ICl₂ with behaviors of a semiconductor with $E_a = 0.15$ eV and $\sigma_T = 3 \times 10^{-3}$ S·cm⁻¹.

In order to investigate a composite system composed of BEDT-TTF and copper halides in this study, we prepared (BEDT-TTF)_{1.5}CuX₂ (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.

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-TTF)_{1.5}CuCl₂ was obtained from the direct reaction of BEDT-TTF with CuCl₂. Anhydrous CuCl₂ (3.3×10^{-4} M) was dissolved in 20 mL of acetonitrile. CuCl₂ 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-TTF)_{1.5}CuBr₂ was prepared by an analogous method using anhydrous CuBr₂ in acetonitrile.

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

Anal. (%) Calcd. for (BEDT-TTF)_{1.5}CuCl₂: C, 25.32; H, 1.70; S, 54.08. Found: C, 25.81; H, 1.83; S, 53.60. Calcd. for (BEDT-TTF)_{1.5}CuBr₂: 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-TTF)_{1.5}CuCl₂: 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-TTF)_{1.5}CuBr₂: 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/CH₂Cl = 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

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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 ($\text{X} = \text{Cl}, \text{Br}$) produces the charge transfer $(\text{BEDT-TTF})_{1.5}\text{CuX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) 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 $(\text{TTF})_{4/3-7/3}\text{Cu}^{\text{I}}\text{X}_2$ 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 $(\text{BEDT-TTF})_{1.5}\text{CuX}_2$ 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 $\text{A}_{1g}-\nu_3$ mode which is otherwise IR-inactive in BEDT-TTF molecule appears in the ionized $\text{BEDT-TTF}^{\delta+}$ compounds. Kozlov M. E. *et al.*¹⁰ reported that a pair of vibronic transitions appeared at 1401 cm^{-1} and 1331 cm^{-1} in $(\text{BEDT-TTF})\text{I}_3$ and assigned them to the $\text{A}_{1g}-\nu_2$ and $\text{A}_{1g}-\nu_3$ modes, respectively. A pair of vibronic bands was observed at 1406 cm^{-1} and 1332 cm^{-1} in $(\text{BEDT-TTF})_{1.5}\text{CuCl}_2$, and at 1399 cm^{-1} and 1338 cm^{-1} in $(\text{BEDT-TTF})_{1.5}\text{CuBr}_2$. This appearance of the vibronic bands strengthens the ionized $\text{BEDT-TTF}^{\delta+}$ state in the titled compounds. The observed characteristic broad absorptions at around 970 nm (973 nm for $(\text{BEDT-TTF})_{1.5}\text{CuCl}_2$ and 969 nm for $(\text{BEDT-TTF})_{1.5}\text{CuBr}_2$) 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/ $\text{CH}_2\text{Cl}_2 = 50/50$) at 77 K. A typical copper(II) EPR pattern as well as the radical $\text{BEDT-TTF}^{\delta+}$ peak were examined as shown in Figure 1. The singlet peaks at around

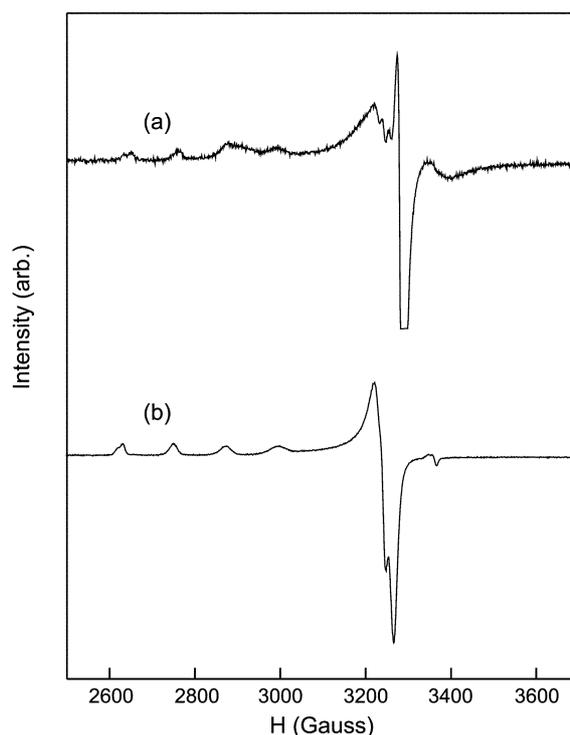


Figure 1. X-band EPR spectra ($\text{CH}_2\text{Cl}_2/\text{DMF}$) at 77 K (a) $(\text{BEDT-TTF})_{1.5}\text{CuCl}_2$, (b) $(\text{BEDT-TTF})_{1.5}\text{CuBr}_2$.

$\langle g \rangle = 2.07$ for both compounds were determined to arise from the BEDT-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} $\text{S}\cdot\text{cm}^{-1}$ which are in the range of an insulator. These observed values are lower than that of $(\text{BEDT-TTF})_2\text{Cu}^{\text{I}}\text{Cl}_2$ ($\sim 10^{-3}$ $\text{S}\cdot\text{cm}^{-1}$)⁵ and that of $(\text{BEDT-TTF})_2\text{Cu}^{\text{II}}\text{Cl}_4$ ($\sim 10^{-4}$ $\text{S}\cdot\text{cm}^{-1}$).¹² This means that the ionized BEDT-TTFs in $(\text{BEDT-TTF})_{1.5}\text{Cu}^{\text{I}}\text{Cl}_2$ are not stacked effectively in the solid state. It is worth to note that the intensity of the Cu(II) peak relative to the $\text{BEDT-TTF}^{\delta+}$ radical in $(\text{BEDT-TTF})_{1.5}\text{CuBr}_2$ in the EPR spectra is higher than that in $(\text{BEDT-TTF})_{1.5}\text{CuCl}_2$, 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 $(\text{BEDT-TTF})_{1.5}\text{CuBr}_2$ was lower than that of $(\text{BEDT-TTF})_{1.5}\text{CuCl}_2$ 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 $\text{BEDT-TTF}^{\delta+}$ radical and the localized electrons in copper(II) metal ions.¹³ Similar results are found in the $(\text{TTF})_4\text{CuX}_2$ ($\text{X} = \text{NCS}, \text{NO}_3, \text{Cl}, \text{Br}$,

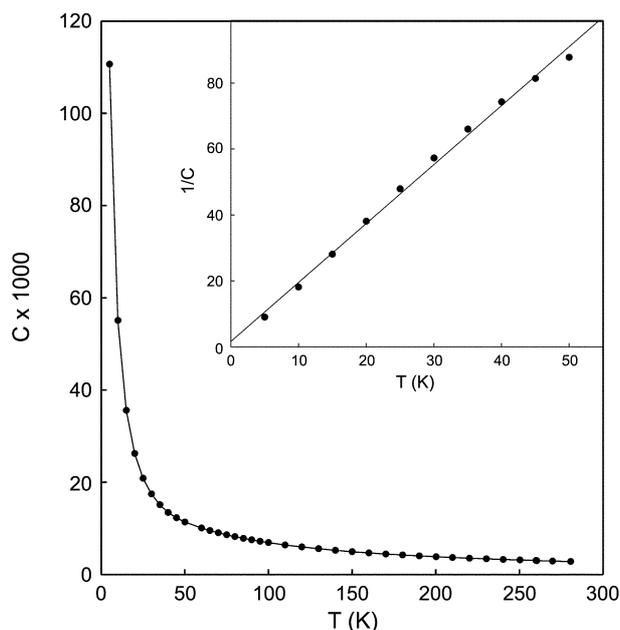
Table 1. EPR Parameters, Magnetic Properties, and Electrical Conductivities of (BEDT-TTF)_{1.5}CuX₂

Compounds	EPR Parameters (g(A ^a))		Magnetic Properties		Electrical Conductivities ^d (σ _{rt} , S·cm ⁻¹)
	Cu()	BEDT-TTF radical	Curie-Weiss Parameters C (Θ)	μ _{eff} ^c (BM)	
(BEDT-TTF) _{1.5} CuCl ₂	g _⊥ = ~2.09 ^b (23) g _∥ = 2.390 (120)	2.061 (16)	0.39 (-0.9)	1.26	9.4 × 10 ⁻⁵
(BEDT-TTF) _{1.5} CuBr ₂	g _⊥ = 2.163 (15) g _∥ = 2.480 (125)	2.08 (5)	0.53 (+0.9)	1.22	8.5 × 10 ⁻⁶

^apeak to peak EPR linewidth (gauss). ^bThe exact g_⊥ value of Cu(II) was not obtained due to the strong BEDT-TTF radical peak in the similar region. ^cThe effective magnetic moment was calculated by μ_{eff} = 2.828(χ · T)^{1/2} at room temperature. ^dThe electrical conductivity was obtained at room temperature.

NCO, NO₂ 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 CuX₂ and the electron transfer rate from TTF to the CuX₂ entity in the reaction.¹³ It was found that the electrical conductivity of (TTF)₄CuX₂ decreases as the amount of copper(II) metal ion present in (TTF)₄CuX₂ increases.

The magnetic susceptibility of both compounds was examined from room temperature to 4 K using the SQUID

**Figure 2.** Temperature Dependence of Magnetic Susceptibility of (BEDT-TTF)_{1.5}CuCl₂.

method. The typical temperature dependence of the magnetic susceptibility for (BEDT-TTF)_{1.5}CuCl₂ 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, μ_{eff} = C/(T-θ), 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.

The total magnetic susceptibility can be expressed as the following equation: χ(T) = χ_{Cu(II)} + χ_{TTF⁺} + δ(T), which contains the contributions from the localized electrons on the copper(II) ion (χ_{Cu(II)}), from the unpaired electrons on the BEDT-TTF radicals (χ_{TTF⁺}) and from an unprescribed temperature-dependent term that account for the exchange interactions (δ(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 paramagnetism¹⁴ or strong antiferromagnetic interactions¹⁵ 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 δ(T) term. The effective magnetic moments (μ_{eff}) calculated from μ_{eff} = 2.828 (χ · 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 (E_p, V) of (BEDT-TTF)_{1.5}CuX₂

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-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-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}CuCl₂ were shifted to lower values compared to those of the BEDT-TTF molecule, supporting the conclusion that BEDT-TTFs in (BEDT-TTF)_{1.5}CuCl₂ were oxidized. A similar result was examined in (BEDT-TTF)_{1.5}CuBr₂.

Conclusions

We prepared the charge transfer (BEDT-TTF)_{1.5}CuX₂ (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}CuBr₂ than in (BEDT-TTF)_{1.5}CuCl₂ 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}CuCl₂ being much greater than that of (BEDT-TTF)_{1.5}CuBr₂. Furthermore, it can be concluded that the ratio of BEDT-TTF to CuX₂ should be more than 2 per formula unit to reduce copper (II) completely to copper(I), leading to a high electrical conductivity.

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