

Electrical, Magnetic and Spectroscopic Properties of Tetrathiafulvalene Charge Transfer Compound with Copper(II) hexafluoroacetylacetonate, $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$

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Tetrathiafulvalene (TTF) has been used as an excellent electron donor to form electrically conductive charge transfer compounds.¹ TTF salt with the square-planar bis(oxalato) cuprate anion was reported to be a dimer with weak interaction between TTF cations.² The compound exhibited semiconductor behavior with the electrical conductivity in the order of $\sim 10^{-4} \text{ Scm}^{-1}$ as compacted samples at room temperature. However, the increased interaction of TTF cations could enhance the conductivity in the stacking direction. For example, TTF-copper halides compounds having a significant interaction between partially ionized TTF radical cations showed the conductivity of $\sim 10^0 \text{ Scm}^{-1}$ at room temperature.³

Recently, we reported TTF charge transfer compound with metal halides (metal=Fe, Ru, Rh an Ir). It was concluded that the partially ionized TTF salts exhibited greater electrical conductivity than the simple salts.⁴ Therefore, it may be interesting to study the electrical properties of TTF salts in relation to the stacking of partially ionized TTF moieties. This study reports the preparation of TTF charge transfer compound with planar bis(hexafluoroacetylacetonate) cuprate anion and its electrical properties. The stacking of the TTF molecules in the compound as well as the interaction between TTF moieties is discussed based on the magnetic susceptibility measurement, and EPR, electronic, vibrational and X-ray photoelectron spectra. The electrochemical properties are also investigated in this report.

Experimental

Synthesis. 1 mmol of copper(II) (hexafluoroacetylacetonate) was dissolved in a mixture of absolute ethanol (10 ml) and triethylorthoformate (2 ml). A solution of TTF (3 mmol) in a mixture of absolute ethanol (25 ml) and triethylorthoformate (5 ml) was added dropwise with stirring under argon atmosphere. TTF and copper(II) (hexafluoroacetylacetonate) were obtained from Aldrich Chemicals and used without further purification. The reaction solution changed to dark-brown color immediately. The reaction mixture was stirred for *ca.* 4 hrs, and then refrigerated overnight. The deep-brown colored precipitates were isolated by filtration and washed several times with absolute ethanol. The microcrystalline precipitates were dried in vacuum at room temperature (yield; 45.4%). Elemental analysis was performed by Korea Research Institute of Chemical Technology, Daejeon, KOREA. Anal. Calc. for $(\text{TTF})_2 \text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$: C, 29.

57; H, 1.97. Found: C, 29.20; H, 2.22.

Physical measurements. The electrical conductivity was determined on the compressed pellets by van der Pauw's four-probe method in a temperature range of 100-300 K. The sample pellet (2×3×20 mm) was spotted with conductive silver paste (DOTITE D-500) to make a good contact. Low temperature was obtained by using CTI-CRYOGENIS model 8001 cryodine cryocooler. The temperature was measured with a DT-500K silicon diode connected to a Lake Shore Cryotronics, Inc., model DRC-82C temperature controller. Constant current was applied by using a Keithley model 227 current source and the voltage was measured with a Keithley model 181 nanovoltmeter. The EPR spectral measurements were made on powdered sample at 77 K and at room temperature by using a ESP-300S X-band EPR spectrometer. The field strength was calibrated using DPPH ($g=2.0037$). The magnetic susceptibility data were collected from 77 K to room temperature by using Faraday method with a Cahn 2000 electrobalance. The magnetometer was calibrated with $\text{HgCo}(\text{SCN})_4$. Susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constant. The X-ray photoelectron spectra were recorded on a Perkin-Elmer, Physical Electronics model 5400 X-ray photoelectron spectrometer equipped with a magnesium anode X-ray source and a hemispherical analyzer. The residual gas pressure was 5×10^{-9} torr. The binding energies were calibrated using the Au $4f_{7/2}$ peak at 84.9 eV and the $\text{Cu}2P_{3/2}$ peak at 932.2 eV. The adventitious C 1S line at 284.6 eV was used from charge referancing. Electronic spectra were recorded on a Shimadzu 260 spectrometer on solution and solid/nujol mulls mounted between quartz plates. Infrared spectra ($400\text{-}4,000 \text{ cm}^{-1}$) were obtained using potassium bromide pellets with a Polari's FT-IR spectrophotometer. Cyclic voltammograms were recorded on a EG-PAR Inc., model 273 Potentiostat and Galvanostat. The platinum working electrode (0.7 cm diameter) was polished with alumina prior to each run. An Ag/AgCl reference electrode was used. All potentials were reported versus to AgCl electrode and uncorrected for junction potentials. Cyclic voltammograms were recorded in DMF using 0.1 M tetraethylammonium perchlorate as an electrolyte at scanning rate of 100 mV/s.

Results and Discussion

Figure 1 shows the temperature dependence of the powder resistivity of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$. The resistivity increase with decreasing temperature in the experimental temperature range. The negative coefficient $d\rho/dT < 0$ reflects the intrinsic semiconductor behavior given by $\rho = \rho_0 \exp(E_a/k \cdot T)$. The Boltzmann factor describes the thermally activated generation of charge carriers in a narrow bandgap semiconductor, and the activation energy is calculated with $E_a = 0.083 \text{ eV}$. This value is comparable to those of several organic conductors.⁵ The room temperature conductivity is $6.28 \times 10^{-3} \text{ Scm}^{-1}$, which lies in the range of semiconductor. This value is somewhat greater than those of simple ionized TTF salts having a columnar structure ($\sim 10^{-5} \text{ Scm}^{-1}$).⁶ It is similar to those of $(\text{TTF})_n\text{SbX}_4$.⁷ TTF in $(\text{TTF})_n\text{SbX}_4$ is known to be partially ionized and columnar structures are formed. Therefore, such a relatively high electrical conductivity of

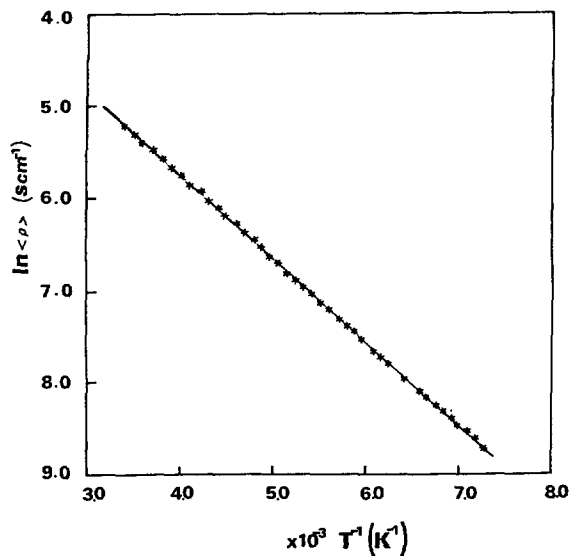


Figure 1. Electrical powder conductivity ($\ln\rho$) plotted against reciprocal temperature (T^{-1}) for $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$.

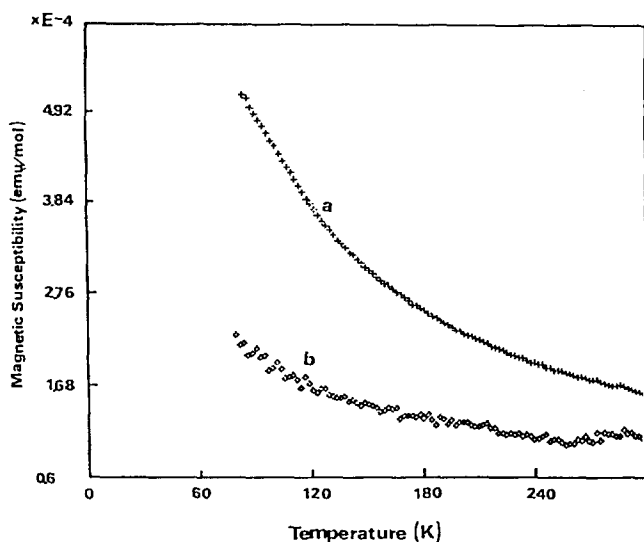


Figure 2. Temperature dependence of magnetic susceptibility for a) $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ and b) $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$.

$(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ implies that TTF is partially ionized and stacked to form chains in the compound. This is also evidenced by the magnetic and spectroscopic properties.

The EPR spectrum of powdered sample gave an unsymmetrical shape with $g_{\parallel} = 2.012$ and $g_{\perp} = 2.006$ at room temperature, and exhibited good resolution of $g_{\parallel} = 2.080$ and $g_{\perp} = 2.137$ upon lowering the temperature to 77 K. The g value is nearly equal to 2.00838 for TTF cation radicals in solution.⁸ A signal attributable to copper(II) ion was not detected. This observation clearly indicates that any unpaired electrons are distributed on TTF chains and the copper atom in the compound is diamagnetic copper(I) oxidation state; the compound, therefore, can be formulated as $[(\text{TTF})_2]^{+} \text{Cu}^{\text{I}}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$.

The temperature dependence of magnetic susceptibility of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ and $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ is shown in

Figure 2. magnetic susceptibility of $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ increases as the temperature decreases, while the magnetic susceptibility of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ increases slowly, roughly constant, with decreasing the temperature. The magnetic moment of $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ at room temperature is 1.95 B.M arising from the odd electron on Cu(II) metal ion.

The effective magnetic moment of $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ is almost constant down to 80 K. On the other hand, in $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$, the value of 1.59 B.M at room temperature decrease slowly down to 1.21 B.M at 80 K. This smaller magnetic moment of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ is rather attributed to the delocalized electrons on $(\text{TTF})_n^{+}$ radicals in the compound.

The magnetic susceptibility data of $\text{Cu}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ do well follow the Curie-Weiss law by the expression, $\chi = C_0 \cdot (T - \theta)^{-1}$ with the value of $C_0 = 0.375$ and $\theta = -63$ K. The data of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$, however, are not described by the Curie law, but fit by the power law, $\chi = C_0 \cdot T^{-\alpha}$, where α is less than 1. The value of $C_0 = 0.039$ and $\alpha = 0.65$ was calculated in $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$. The power law reflects that the magnetic interaction between the unpaired electrons is considerable. This interaction should arise from exchange between the $(\text{TTF})_n^{+}$ radical cations in the stacks. Weak paramagnetism due to the magnetic interaction is well known in conducting materials.⁹

The inter-stack interactions are also indicated by the narrow EPR linewidth of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$. The peak-to-peak EPR linewidth (ΔH_{pp}) is ~ 4 Gauss, very close to that of TTF·TCNQ ($\sim 6\text{G}$).¹⁰ In TTF·TCNQ, the narrow linewidth was explained by the significant spin-orbit interaction of sulfur atoms in one-dimensional TTF chains.

The oxidation state of copper ion was also investigated by X-ray photoelectron spectroscopy (XPS). XPS is an excellent physical method in determining charges on atoms in molecules. The method involves the ionization of the inner core electrons from an atom by X-radiation. The binding energies of the Cu $2P_{1/2}$ and Cu $2P_{3/2}$ core electrons were examined at 952.2 and 932.5 eV respectively. The binding energy of Cu $2P_{3/2}$ is significant smaller than those of several Cu(II) species (935.2–935.4 eV), and comparable to the binding energies of other Cu(I) species (932.5–932.9 eV).¹¹ Diamagnetic Cu(I) oxidation state is also confirmed by the fact that the shake-up satellite peak was not detected in the spectrum. The shake-up satellite peak is known to be the characteristic of paramagnetic Cu(II) oxidation state due to the occurrence of charge transfer from ligand to the unoccupied d orbital of Cu(II) ion.¹²

The IR absorption bands were found at 1082, 828 and 796 cm^{-1} , and were assigned to the ν_{15} (CCH bend in TTF ring), ν_{16} (CS stretch) and ν_{25} (ring SCC bend) modes, respectively.¹³ Inoue, M. B. *et al.*,¹⁴ have mentioned in the TTF-copper halides salts that the shift of the ν_{16} mode can be interpreted in terms of the ionization effect of TTF. The shift of ν_{16} to the higher frequency indicates the higher oxidation state of TTF in the compounds. The observed ν_{16} value of $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$ is between that TTF molecule ($\nu_{16} : 781 \text{ cm}^{-1}$) and TTF free radical ($\nu : 836 \text{ cm}^{-1}$). This result also supports the partial ionized TTF molecule in $(\text{TTF})_2\text{Cu}(\text{hfac})_2 \cdot 1.5\text{C}_2\text{H}_5\text{OH}$.

Electronic spectrum in DMF shows the absorption maxima (λ_{max}) at 306 ($b_{3g} \rightarrow b_{1u}$), 442 ($b_{1u} \rightarrow b_{2g}$), 585 nm ($b_{2g} \rightarrow b_{1u}$) corres-

ponding to the $d-d$ transition. The occurrence of the $d-d$ transition at such a low wavelength is the characteristic of the intramolecular spectra of conjugated π -molecular radicals.¹⁵ The absorption maxima in solid state are shifted to higher energy at 289, 413, 532 nm. This energy shift may be contributed the increased interactions along TTF⁺ stacks in the solid state.

Cyclic voltammogram was recorded in DMF/0.1 M TEAP from -0.2 to $+1.0$ V versus on Ag/AgCl electrode. (TTF)₂Cu(hfac)₂·1.5C₂H₅OH exhibited two cathodic ($E_{p,c}$) and anodic ($E_{p,a}$) peaks at $+0.36$ ($E_{p,c}$), $+0.45$ V ($E_{p,a}$) for the TTF/TTF⁺ couple and at $+0.61$ ($E_{p,c}$), $+0.70$ V ($E_{p,a}$) for the TTF⁺/TTF²⁺ couple. TTF molecule also shows two peaks at nearly the same potential in the same experimental condition. The cyclic voltammograms were scanned several times and there was no change in the potentials, that two couples are reversible. The values of $E_{p,a}/E_{p,c}$ are also nearly equal to 1. A redox peak referred to copper couples were not detected in the experimental conditions.

In summary, charge transfer compound, (TTF)₂Cu(hfac)₂·1.5C₂H₅OH was prepared from the reaction of TTF and Cu(hfac)₂·2H₂O in ethanol solution. The spectroscopic and magnetic properties reveal that charge transfer has occurred to the copper ion resulting in diamagnetic Cu(I) state. The odd electrons are delocalized on TTF⁺ radical cations in the stacks. This inter-stack interaction provides the pathway for the electrical conductivity in the stacking direction. The compound exhibited intrinsic semiconductor behavior with low charge carrier activation energy. A considerable interaction between TTF radical cations is also observed by the magnetic properties, although an X-ray structure determination is necessary for further elucidation of the material.

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Solvent Effects on the Chemical Shift of the Bipyridyl 6'-Proton in [Ru(bpy)₂(*p*-tert-butylpy)(OH₂)]²⁺ Complex

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A novel feature in a series of polypyridyl complexes of ruthenium is the appearance of many oxidation states which are easily accessible over a narrow range. High-oxidation-state [Ru^{IV}=O]²⁺ complexes can be prepared by consecutive proton and electron loss of the corresponding [Ru^{II}-OH₂]²⁺ complexes. Mono-oxo complexes of Ru have been shown as efficient and/or catalytic oxidants toward inorganic and organic substrates and notably as important in understanding the oxidation mechanisms.¹

X-ray crystallographic and in some instances ESR methods have been successfully utilized for the determination of solid phase molecular and electronic structures of metal complexes.² However, question of stereochemistry, fluxional behavior, or substitution dynamics in solutions are best addressed through the application of NMR spectrometry.³ The chemical shift data for the 2,2'-bipyridyl protons of M(II) and M(III) complexes such as [Ir(bpy)₂Cl₂]⁺, *cis*-[Ru(bpy)₂(OH₂)₂]²⁺, [Ru(bpy)₂(py)₂]²⁺, and [Ru(bpy)₃]^{2+/3+}, bpy is 2,2'-bipyridine and py is pyridine) were reported by many workers.⁴ NMR techniques have also been proved as valuable in unravelling mechanistic pathways related to the Ru(IV)-Oxo complexes.⁵

Because most of Ru oxidants are soluble only in polar solvents, we have been interested in the synthesis of Ru-oxo complexes which are also soluble in organic solvents. Considering the extensive and general reactivity of the Ru(IV) oxidants, we initially tried to understand the details of their electronic structures and spectroscopic properties. While examining NMR spectra of new Ru-aqua complexes, we accidentally found out the migration of the chemical shift of the 6'-bipyridyl proton of the *cis*-[Ru^{II}(bpy)₂(*p*-tert-butylpy)(OH₂)]²⁺ (*p*-tert-butylpy is *para*-tert-butylpyridine) complex in various deuteriated solvents. Here we report the initial results of those observations.