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Synthesis and characterization of tetrathiafulvalene charge transfer compounds with copper halides

Young Inn Kim* and William E. Hatfield**
Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290 (USA)

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Abstract

Charge transfer compounds with the general formula $(TTF)_4CuX_2$ (TTF = tetrathiafulvalene; X = Cl, Br) may be prepared by the reaction of excess TTF with $Cu(sparteine)X_2$ in methylene chloride. The semiconducting compounds have low activation energies and relatively high electrical conductivities. Magnetic susceptibility, EPR and spectroscopic data provide evidence that copper has been reduced to copper(I) in the complexes, and that the unpaired electrons are delocalized over columnar stacks of TTF. Reaction of TTF with $[Cu(2\text{-aminoethylpyridine})Cl_2]$ or $[Cu(nicotine)Cl_2]$ in methylene chloride yielded $(TTF)_2CuCl_2$, while reaction of TTF with $[Cu_4OCl_6(2\text{-picoline})_4]$ yielded (TTF) $CuCl_2$.

Introduction

Tetrathiafulvalene (TTF) and its analogues have been used as electron donors to form highly electroconductive charge transfer complexes [1], the notable example being TTF–TCNQ [2] (TCNQ = tetracyanoquinodimethane). Other electroconductive charge transfer complexes with TTF contain metal halides [3], simple halides [4] and pseudohalides [5a] as electron acceptors. Some transition metal complexes with typical organic ligands have been used as acceptors [6]. Since the reduction potential of transition metal complexes can be readily modified by the selection of ligands and ligand substitution, such complexes are very good candidates for use in designed syntheses. Here the goal is to prepare charge transfer complexes with fractional electron transfer, per formula unit, since partial electron transfer is among the factors that lead to high electrical conductivity.

Recently Inoue *et al.* [7] have reported a variety of conductive TTF–copper halide compounds by the direct reaction of excess TTF with copper halides in various solvents. They pointed out that the composition of the compounds $(TTF)_nCuX_2$ (X = Cl and Br) was dependent on the solvent employed in the reaction. We describe herein the reaction of TTF with some copper(II) coordination compounds, and give the results of the characterization by magnetic, electroconductive and spectroscopic techniques of the new compounds formed from the reaction of TTF with $Cu(sp)Cl_2$ (sp = (−)-sparteine) [8].

Experimental

Synthesis

A solution of 0.2 g of TTF in 10 ml of methylene chloride was added to a methylene chloride (10 ml) solution of 0.5 g of $Cu(sp)Cl_2$. TTF was obtained from Stream Chemicals and was used without further purification. $Cu(sp)Cl_2$ was prepared by a method that has been described previously [9]. The mixture of TTF and $Cu(sp)Cl_2$ was stirred for 30 min at room temperature. The deep purple solid product that precipitated was filtered off and washed with methylene chloride. The product was dried in vacuum at room temperature. The purple bromide complex was synthesized by a similar method. Element analysis were obtained from Galbraith Laboratories, Inc., in Knoxville, TN. *Anal.* Calc. for $(TTF)_4CuCl_2$: C, 30.28; H, 1.69. Found: C, 30.89; H, 2.02%. Calc. for $(TTF)_4CuBr_2$: C, 27.69; H, 1.55. Found: C, 27.28; H, 1.63%.

Reaction of TTF with $[Cu(2\text{-aminoethylpyridine})Cl_2]$ or $[Cu(nicotine)Cl_2]$ in methylene chloride yielded $(TTF)_2CuCl_2$, while the reaction of TTF with $[Cu_4OCl_6(2\text{-picoline})_4]$ yielded $(TTF)CuCl_2$. These known compounds were characterized by chemical analysis and physical measurements. Our results were

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*Current address: Department of Chemical Education, Pusan National University, Pusan 609-735, Korea.

**Author to whom correspondence should be addressed.

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consistent with known properties, and they will not be discussed here.

Physical measurements

Four probe d.c. electrical resistivities were measured on pressed pellets, 1.3 cm in diameter and about 0.1 cm in thickness, using a CTI-Cryogenics 21SC Cryodine Cryocooler and the Van der Pauw technique [10]. The temperature was controlled by a Lake Shore Cryotronics DRS 80C temperature controller. EPR spectral measurements were made on powdered samples at 77 K and at room temperature by using a Varian E-109 X-band spectrometer. The field strength was calibrated using DPPH ($g = 2.0037$). Magnetic susceptibility data were collected from 77 K to room temperature by using the Faraday method with a Cahn 2000 electrobalance. The magnetometer was calibrated with $HgCo(NCS)_4$ [11]. IR spectra (400–1500 cm^{-1}) were obtained using Nujol mulls on cesium iodide plates with a Nicolet model 200X FT-IR spectrophotometer. Electronic spectra in the UV–Vis range were obtained with a Hewlett-Packard 8451A spectrophotometer on Nujol mulls mounted between quartz plates. Cyclic voltammograms were recorded on a Princeton Applied Research (PAR) model 173 cyclic voltammograph at pH = 7.01 in aqueous solutions at a scanning rate of 200 mV/s. All potentials are reported versus the saturated calomel electrode (SCE).

Results and discussion

$(TTF)_4CuX_2$ (where X = Cl and Br) were obtained by the reaction of TTF and $Cu(sp)X_2$ in methylene chloride. The composition of the products was always four TTF per copper, and the composition was independent of the amount of TTF as long as an excess was used in methylene chloride.

Electrical properties

The electrical conductivity of $(TTF)_4CuX_2$ was measured by using the van der Pauw four-probe d.c. method in the range of 70–300 K. As shown in Table 1, the powdered samples of each compound exhibits high electrical conductivities at room temperature. The conductivities are higher than those of halide salts of TTF [4a, 12] which are known to have columnar structures of partially oxidized TTF. The resistivities of both compounds increases with decreasing temperature in the range of 70–300 K. The negative coefficient $d\rho/dT < O$ reflects the intrinsic semiconductor behavior given by $\rho = \rho_0 \exp(E_a/kT)$. Similar behavior has been found in TTF salts with several transition metal complex anions [3a, 6, 7]. A plot of log ρ versus $1/T$ for $(TTF)_4CuBr_2$ showed a small inflection near 230 K. The data above 230 K may be fitted by the above equation with $E_a = 0.21 \times 10^{-1}$ eV, and the data below 230 K may be fitted with $E_a = 2.40 \times 10^{-1}$ eV. The data for $(TTF)_4CuCl_2$ did not exhibit an inflection.

The mobility model for electrical resistivity is given by [13]

$$\rho(T) = AT^{\alpha} \exp(E_a/kT)$$

The Boltzmann term accounts for an activated generation of charge carriers in a narrow-band gap semiconductor. The preexponential term is associated with a temperature dependence of the mobility. The data for $(TTF)_4CuX_2$ was fitted by the above equation. The best-fit parameters are $A = 8.58 \times 10^1$, $\alpha = 1.48$, $E_a = 1.88 \times 10^{-1}$ eV for $(TTF)_4CuCl_2$, and $A = 1.12 \times 10^2$, $\alpha = 1.47$, $E_a = 1.28 \times 10^{-1}$ eV for $(TTF)_4CuBr_2$. The values for the parameter α are nearly equal to the theoretical value ($\alpha = 1.5$) for the temperature dependence of mobility for the small polaron mechanism [14]. The mobility model has been used to describe the conductivity in other electrical conductors including a series of porphyrinic molecular metals [15–17].

Magnetic properties

EPR spectra for powdered samples were obtained both at room temperature and at 77 K. At room temperature $(TTF)_4CuCl_2$ exhibits a slightly unsymmetrical spectral band with the anisotropic g values, $g_{\parallel} = 2.017$ and $g_{\perp} = 2.010$, while $(TTF)_4CuBr_2$ exhibits a symmetric EPR spectral band with $<g> = 2.007$. The EPR line shapes for both compounds exhibits good resolution of parallel ($g_{\parallel}$) and perpendicular ($g_{\perp}$) components at 77 K.

The average $<g>$ values of $(TTF)_4CuCl_2$ and $(TTF)_4CuBr_2$ at 77 K are 2.010 and 2.003, respectively, values which are close to the g value of the TTF^+ ion in solution ($g = 2.00838$) [18]. These values are also comparable to those of TTF–halides and TTF–pseudohalides as shown in Table 2. The similarity of th g values indicate that the odd electrons reside on TTF in $(TTF)_4CuX_2$. A signal attributable to Cu(II) was not detected in any case, an indication that the copper ions in $(TTF)_4CuX_2$ are in the diamagnetic Cu(I) state. We cannot rule out the possibility that some electron density is delocalized over several copper ions resulting in a broad undetectable band, but we think this is unlikely.

The magnetic susceptibility data also reflect the diamagnetism of copper in each compound. The temperature dependence of the magnetic susceptibilities from 80–300 K are shown in Fig. 1. The magnetic susceptibility of $(TTF)_4CuX_2$ increases somewhat as the temperature decreases, but the data

TABLE 1. Physical properties of TTF–CuX_2 complexes

Compounds	Electrical conductivity (σ) at room temperature ($S\ cm^{-1}$)	Magnetic susceptibility (χ) at room temperature ($emu\ mol^{-1}$)	Redox potential vs. SCE at pH = 7.01 (V)
$(TTF)_4CuCl_2$	1.69×10	7.44×10^{-4} (1.28)[a]	+0.13 +0.43 +0.79
$(TTF)_4CuBr_2$	6.78×10	4.79×10^{-4} (1.08)	+0.13 +0.44 +0.78

[a] Magnetic moments (BM) at room temperature are listed in parentheses.

TABLE 2. Anisotropic g values and linewidths of EPR spectra of some TTF complexes

Compound	Anisotropic g values		EPR linewidth (Gauss)	Reference
	$g_{\parallel}$	$g_{\perp}$		
$TTF \cdot Cl_x$	2.0033	2.0097	9	4b
$TTF \cdot Br_{0.7}$	2.0025	2.0100	40–52	5a and b
$TTF \cdot I_{0.7}$	2.0050	2.0128	180–200	5a and b
$(TTF)_{11}(SCN)_6$	2.0020	2.0088	11	5a
$(TTF)_{11}(SeCN)_6$	2.0022	2.0086	15	5a
$(TTF)_4CuCl_2$	1.9989	2.0049	17	this work
$(TTF)_4CuBr_2$	2.0002	2.0074	12	this work

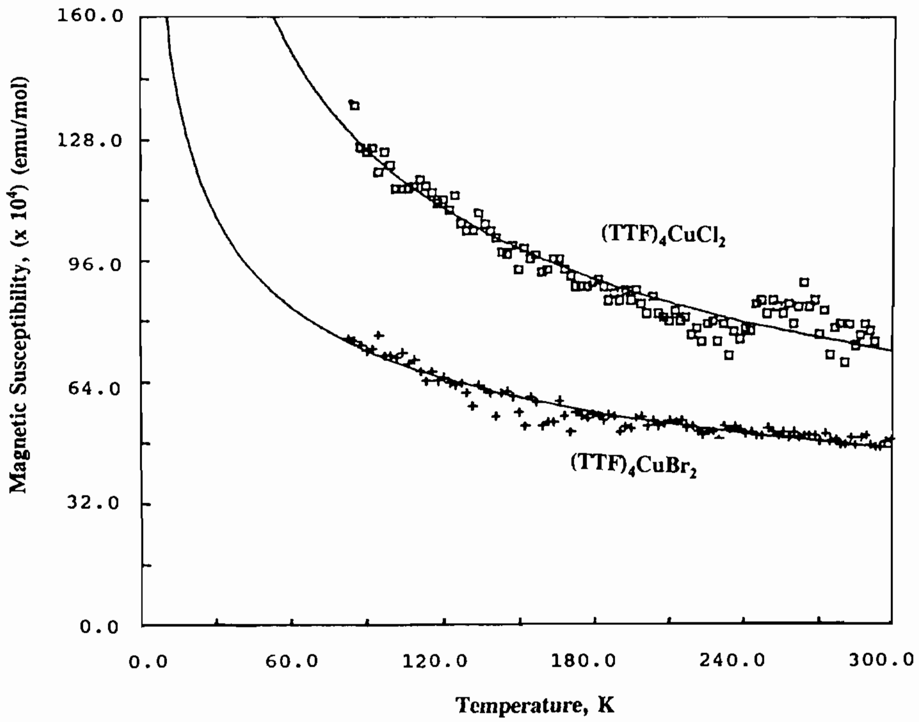

Fig. 1. Temperature dependence of magnetic susceptibility of $(TTF)_4CuCl_2$ and $(TTF)_4CuBr_2$.

are not well described by the Curie law $\chi(T)=C/T$. Weak paramagnetism is well known in highly conducting molecular metals [19]. Here electron delocalization along TTF columns in $(TTF)_4CuX_2$ requires the use of the expression $\chi(T)=C/T^a$, where a is less than 1. The magnetic susceptibility data may be described by the power law with a equal to 0.46 for $(TTF)_4CuCl_2$ and 0.37 for $(TTF)_4CuBr_2$. The best-fit C values are 9.93×10^{-3} and 3.73×10^{-3} for $(TTF)_4CuCl_2$ and $(TTF)_4CuBr_2$, respectively. A power law has been used to describe the magnetic properties of such compounds as quinolinium–TCNQ [20] and the tetramethyl-*p*-phenylene diamine salt (TMPD)–$TCNQF_4$ [21].

The presence of TTF columns in $(TTF)_4CuX_2$ is supported by the narrow peak-to-peak linewidths (ΔH_{pp}) in the EPR spectra. The linewidth of the EPR signals at room temperature is 17 gauss for $(TTF)_4CuCl_2$ and 12 gauss for $(TTF)_4CuBr_2$. This is somewhat larger than that of TTF·TCNQ (~6 G) [22] and similar to that of TTF·SeCN (~15 G) [23]. Line widths of five to fifteen gauss are attributed to spin–orbit interaction of sulfur in TTF columnar chains [12]. The extremely broad linewidth, ~180–200 gauss for $TTF.I_{0.7}$ has been explained as arising from back charge transfer of electrons between TTF and iodide [12].

Spectroscopic properties

The IR spectra of $(TTF)_4CuX_2$ consist of very broad bands extending from 1000–4000 cm^{-1}. These broad absorptions, which arise from the band structure of these semiconductors [24], mask many of the vibrational bands. Vibrational bands of TTF were assigned to the absorptions at 827 (ν_{16}) and 1280 (ν_{23}) cm^{-1} for $(TTF)_4CuCl_2$ and 828 (ν_{16}), 816 (ν_{25}) and 1242 (ν_{23}) cm^{-1} for $(TTF)_4CuBr_2$ by comparison with reported spectra [25]. The ν_{16} vibrational mode is associated with the stretching of the C–S bond in the five membered ring of the TTF molecule. The ν_{23} band arises from CCH, and the ν_{25} band arises from the ring SCC bend. The C–S band as well as the C=C modes are expected to be shifted as a result of variation of bond orders and bond lengths due to the oxidation of TTF. The observed values of ν_{16} in $(TTF)_4CuX_2$ are higher than the value of 781 cm^{-1} for the TTF molecule and lower than 836 cm^{-1} for TTF in TTF·Br [25]. Inoue *et al.* [7] pointed out a linear relationship between the shift in the ν_{16} band and the charge on TTF in TTF–copper halides compounds. Since ν_{16} is shifted here, the IR results confirm partial ionization of TTF in $(TTF)_4CuX_2$.

UV–Vis spectra of solid samples mulled in Nujol revealed absorption maxima (λ_{max}) at 246 and 362 nm for $(TTF)_4CuCl_2$ and at 270, 364 and 486 nm for $(TTF)_4CuBr_2$. The low energy absorption band above 500 nm which is often found in conducting TTF compounds [26] was part of the broad background and a specific wavelength could not be assigned.

Electrochemistry

Cyclic voltammograms of $(TTF)_4CuX_2$ and $TTF\cdot I_{0.7}$ [27] were recorded in aqueous solution at pH = 7.01 versus a saturated calomel electrode (SCE). The results are summarized in Table 1. $(TTF)_4CuCl_2$ exhibited three peaks; at +0.13 V for the Cu^{2+}/Cu^{+} couple, at +0.43 V for the TTF^{+}/TTF couple, and at +0.79 V for the TTF^{2+}/TTF^{+} couple. Similar results were observed for $(TTF)_4CuBr_2$. The potentials ($E_{1/2}$) reported for the couples were estimated by averaging the anodic and cathodic peak potentials. The $E_{1/2}$ potential for the Cu^{2+}/Cu^{+} couple is nearly equal to the standard reduction potential, Cu(II) → Cu(I) (+0.159 V versus SCE) in aqueous solution [28]. Two peaks were found in $TTF\cdot I_{0.7}$, which are the redox potentials for the TTF couples. The experimentally observed $E_{1/2}$ value of $TTF\cdot I_{0.7}$ were +0.42 and +0.73 V. These were assigned to the TTF^{+}/TTF and TTF^{2+}/TTF^{+} couples, respectively and support the assignment in the case of $(TTF)_4CuCl_2$. TTF in CH_3CN solution also exhibits two reversible redox waves at +0.33 (TTF^{+}/TTF) and at 0.70 V (TTF^{2+}/TTF^{+}) versus SCE [29]. Thin films of TTF polymer also show two waves at nearly the same potentials [30]. The cyclic voltammograms were scanned several times and there was no change in the potentials. This is good evidence that the couples are reversible.

Correlation of electrical conductivity with redox potentials has been discussed [31, 32]. With the assumption that electron transfer calculated from solution redox potentials parallels that in the solid phase, it may be concluded that charge transfer compounds with low resistivities ($\rho<0.1$ Ω cm) will result from the combination of moderately strong acceptors with moderately strong donors. Based on studies of TTF complexes with substituted TCNQ, Wheland [32] proposed that the equilibrium constant is related to the difference in redox potentials by the relationship $\log K=E_{1A}-E_{1D}/0.059$, where E_{1A} is the redox potential of acceptor and E_{1D} is that of donor. He noted that electron acceptors which had low K values ($K=10^{0.2}$–10^{-4}) gave highly conducting complexes, whereas acceptors with larger K values ($K=10^{0.2}$–10^{+6}) gave poor conductors. Small K values indicate incomplete electron transfer, and large K values indicate complete electron transfer. A value of $K=\sim10^{-5}$ was calculated by using the above equation for $(TTF)_4CuCl_2$ and $(TTF)_4CuBr_2$. In these compounds there is complete reduction of copper and one electron per four TTF molecules.

Conclusions

Charge transfer compounds $(TTF)_4CuX_2$ prepared from TTF and $Cu(Sp)X_2$ exhibit semiconductor behavior. Magnetic and spectroscopic data reveal that copper(II) has been reduced to copper(I) and that the odd electron is delocalized on TTF molecules in columnar stacks. Orbital overlap between TTF molecules give rise to band formation, low activation energies, and relatively high electrical conductivities. Furthermore, reaction of TTF with copper(II) complexes may provide a convenient method for the preparation of $(TTF)_nCuX_2$ charge transfer compounds with varying ratios of TTF to copper halide.

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