

Synthesis and Properties of Tetrathiafulvalene Charge Transfer Compound with Antimony(III) Iodide, $(\text{TTF})_7\text{SbI}_4$

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Recently, we prepared TTF(tetrathiafulvalene) charge transfer compounds, $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$, $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ having partially oxidized TTF columnar stacks.¹ The magnetic properties of the compounds were interesting since the magnetic interaction along TTF stacks were significant. The magnetic susceptibility of $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$ was nearly constant from 77 K to 300 K, while those of $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ increase slowly as decreasing temperature. This result indicated the more significant magnetic interaction in $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$. Furthermore the electrical conductivity of $(\text{TTF})_4\text{FeCl}_3 \cdot \text{CH}_3\text{OH}$ is two order of magnitude higher than those of $(\text{TTF})_4\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$. This observation provoked us to investigate the synthesis and properties of TTF-antimony iodide salt since the magnetic interaction could be reduced due to the large size of SbI_4^- entity. SbI_3 was prepared from Sb metal and iodine, and used immediately in the glove box. $(\text{TTF})_7\text{SbI}_4$ was obtained from the reaction of TTF and SbI_3 in ethanol, and found to be stable in the air. The compound was characterized by electrical conductivity and magnetic susceptibility measurements, and by spectroscopic (EPR, optical, vibrational and XPS) methods. Electrochemical properties were also investigated.

Experimental

Synthesis. Anhydrous SbI_3 (0.2 mmol) was dissolved in a mixture of absolute ethanol (5 mL) and triethylorthoformate (1 mL). A solution of TTF (2 mmol) in a mixture of absolute ethanol (25 mL) and triethylorthoformate (5 mL) was added dropwise with stirring under argon atmosphere. TTF was obtained from Aldrich chemical and used without further purification. Antimony triiodide was prepared by the direct reaction of iodine with antimony powder in boiling benzene² and used immediately in the glove box because this material was unstable in the air. The reaction solution was changed to dark-purple color immediately. The resulting mixture was stirred for ca. 2 hours, and then refrigerated overnight. The deep-purple colored precipitates were isolated by filtration and washed several times with absolute ethanol. The microcrystalline precipitate was dried in vacuum at room temperature (yield: 65.73%). Elemental analysis was performed by the Korea Research Institute of Chemical Technology, Daejeon, Korea. Anal. Calc. for $(\text{TTF})_7\text{SbI}_4$: C, 25.02; H, 1.40. Found: C, 24.66; H, 1.49%.

Physical measurements. The electrical conductivity was determined on the compressed pellets by van der Pauw's

four-probe method³ at room temperature. The sample pellet ($2 \times 3 \times 20$ mm) was spotted with conductive silver paste (DOTITE D-500) to make a good contact. 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 a powdered sample at 77 K and at room temperature by using an 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 method⁴ 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.⁴ 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 Cu $2p_{3/2}$ peak at 932.2 eV. The adventitious C 1s line at 284.6 eV was used from charge referencing. Electronic spectra were recorded on a Shimadzu 260 spectrometer on solution and solid/nujol mulls mounted between quartz plates. Infrared spectra ($400 \sim 4,000 \text{ cm}^{-1}$) were obtained using potassium bromide pellets with a Polaris FT-IR spectrophotometer. Cyclic voltammograms were recorded on DMF using 0.1 M tetraethylammonium perchlorate as an electrolyte at scanning rate of 100 mV/s 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.

Results and Discussion

The room temperature *d.c.* powdered sample of electrical conductivity (σ_n) of $(\text{TTF})_7\text{SbI}_4$ is $1.72 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, which lies in the range of semiconductor. It means that the partially ionized TTF has stacked in the compounds.

The determined magnetic susceptibilities of $(\text{TTF})_7\text{SbI}_4$ are 4.90×10^{-4} and $9.10 \times 10^{-4} \text{ emu/mole}$ at room temperature and at 77 K, respectively. The magnetic susceptibility increases as the temperature decreases, but the data cannot fit by the Curie law, $\chi = C_0 \cdot T^{-1}$. The data is described by the power law expressed by $\chi = C_0 \cdot T^{-\alpha}$ ($0 < \alpha < 1$), indicating that the interaction between the TTF^+ radical cations is considerable. Figure 1 shows that $\ln \chi$ versus $\ln T$ of a powdered sample is linear in the experimental temperature range. Data were fit using linear least-squares methods. The best fit parameters are $C_0 = 10.91$ and $\alpha = 0.45$. This obtained α value is somewhat larger than that of $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ ($\alpha = 0.26$).¹ This implies that the magnetic interaction arising from exchange between the TTF^+ radical cations of the stacks in $(\text{TTF})_7\text{SbI}_4$ is smaller than that in $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$. These interactions are reflected in the electrical conductivity of the compounds. The electrical conductivity of $(\text{TTF})_7\text{SbI}_4$ is one order of magnitude smaller than that of $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ ($\sigma_n = 3.72 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$).¹ Similar results were also reported in the electrical and magnetic properties of $(\text{TTF})_2\text{FeCl}_3$ and $(\text{TTF})_3\text{FeBr}_3$ charge transfer

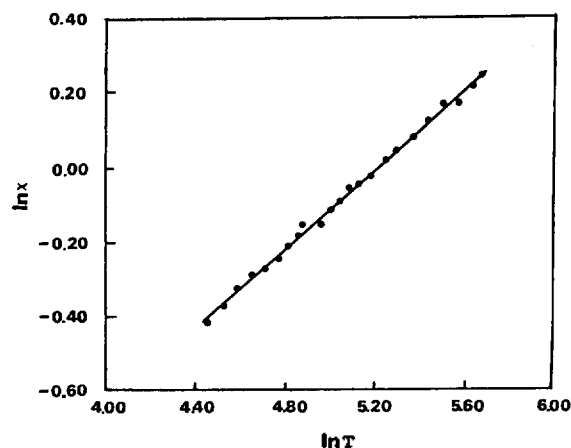


Figure 1. Temperature dependence of magnetic susceptibility for $(\text{TTF})_7\text{SbL}_4$.

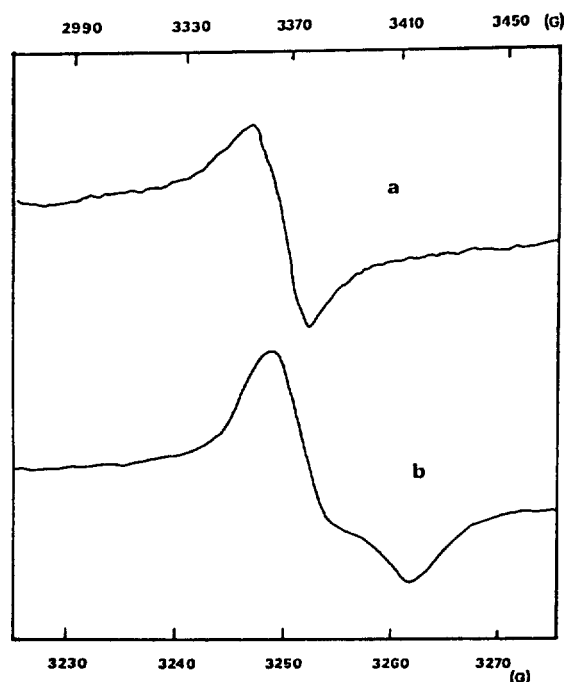


Figure 2. The X-Band EPR spectra of $(\text{TTF})_7\text{SbL}_4$ at (a) room temperature and (b) 77 K in powder sample.

compounds.⁵

The effective magnetic moment (μ_{eff}) is 1.09 B.M for $(\text{TTF})_7\text{SbL}_4$ at room temperature, which is similar to those of $(\text{TTF})_4\text{SbCl}_4$ ($\mu_{\text{eff}}=0.82$) and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ ($\mu_{\text{eff}}=1.08$).¹ This is smaller than the spin-only value of 1.73 B.M for one unpaired electron. This smaller value is arising from the unpaired electron delocalized on TTF^+ radical stacks in $(\text{TTF})_7\text{SbL}_4$.

The EPR spectrum of powdered sample of $(\text{TTF})_7\text{SbL}_4$ exhibited symmetric singlet at $\langle g \rangle = 2.022$ at room temperature and unsymmetric band with the anisotropic g values, $g_{\parallel} = 2.021$ and $g_{\perp} = 2.024$ at 77 K, as shown in Figure 2. The g values are similar to that of TTF^+ ion in solution ($\langle g \rangle = 2.00838$),⁶ and to those of TTF-antimony ($\langle g \rangle = 2.021\text{--}2.085$) and other metal (Fe, Ru, Rh and Ir) halides ($\langle g \rangle = 2.002\text{--}$

Table 1. The peak potential values (E_p) versus Ag/AgCl in cyclic voltammograms for TTF-Sb halide compounds

Compound	E_{pc} (V)	$E_{1/2}$ (V)	E_{pa} (V)	Process
TTF	+0.36	+0.42	+0.47	TTF^+/TTF
	+0.61	+0.66	+0.77	$\text{TTF}^{2+}/\text{TTF}^+$
$(\text{TTF})_4\text{SbCl}_4$	+0.34	+0.39	+0.44	TTF^+/TTF
	+0.57	+0.63	+0.69	$\text{TTF}^{2+}/\text{TTF}^+$
$(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$	+0.35	+0.41	+0.47	TTF^+/TTF
	+0.55	+0.62	+0.69	$\text{TTF}^{2+}/\text{TTF}^+$
$(\text{TTF})_7\text{SbL}_4$	+0.32	+0.41	+0.49	TTF^+/TTF
	+0.57	+0.67	+0.76	$\text{TTF}^{2+}/\text{TTF}^+$

2.175).⁵ This similarity of the g values indicates that the odd electrons reside on TTF in $(\text{TTF})_7\text{SbL}_4$. The EPR peak to peak linewidth (ΔH_{pp}) was observed to be 10 Gauss at room temperature. This narrow linewidth implies that the interaction among the TTF stacks is significant.⁷ An EPR signal attributable to antimony metal ion was not detected. The antimony ion in $(\text{TTF})_7\text{SbL}_4$ is in the diamagnetic Sb(III) state, and the charge transfer has occurred from TTF moiety to the SbL_4^- entity.

The oxidation state of antimony metal ion was also investigated in XPS spectra. The binding energies (B.E) of Sb $3d_{5/2}$ and $3d_{3/2}$ core electrons in $(\text{TTF})_7\text{SbL}_4$ are 529.8 and 539.8 eV, respectively. These values are comparable to the binding energy in TTF-SbX_3 ($X=\text{Cl}, \text{Br}$) salts¹ and in the other Sb(III) species.⁵ However, the binding energies of Sb $3d_{5/2}$, $3d_{3/2}$ are smaller, by 0.1–0.8 eV, than those of SbL_3 (Sb $3d_{5/2}$; 530.6, $3d_{3/2}$; 539.9 eV).⁸ This is justified by the more electron density on antimony metal in SbL_4^- entity than in SbL_3 . The binding energies of S($2p$) and I ($3d_{5/2}$) were measured to be 163.7 and 618.1 eV, respectively. S($2p$) peak was very slightly asymmetric with a tail at the high binding energy side, and the full width at half-maximum height (FWHM) was ~ 2.6 eV. This value is somewhat larger than that of TTF^0 (FWHM=2.1 eV) molecule and completely ionized TTF^+ radical (FWHM=2.5 eV).⁹ Ikemoto *et al* reported⁹ that S($2p$) spectra of the mixed-valence TTF halides were broader (FWHM=2.7–3.1 eV) than TTF^0 and TTF^+ due to the overlap of TTF^0 and TTF^+ components. The relatively large S($2p$) FWHM supported the partially ionized TTF stacks in $(\text{TTF})_7\text{SbL}_4$.

Electronic spectra of $(\text{TTF})_7\text{SbL}_4$ were recorded from 200–800 nm in both solution and the solid state. Electronic spectrum of $(\text{TTF})_7\text{SbL}_4$ shows maximum absorbance (λ_{max}) at 269, 430, 585 nm in DMF solution and at 221, 421, 545 nm in solid/nujol mulls. The electronic transitions are similar to the results reported for the partially ionized conductive TTF salts of metal halides.¹⁰ The vibrational absorption bands were found at 1087, 832 and 798 cm^{-1} and were assigned to the ν_{15} (CCH bend in TTF ring), ν_{16} (CS stretch) and ν_{25} (SCC bend in TTF ring) modes, respectively.¹¹ The observed values are between those of TTF^0 molecule (ν_{15} : 1090, ν_{16} : 781 and ν_{25} : 825 cm^{-1}) and TTF free radical (ν_{15} : 1072, ν_{16} : 836 and ν_{25} : 783 cm^{-1}),¹¹ providing the evidence of the partially ionized TTF molecule in $(\text{TTF})_7\text{SbL}_4$.

Cyclic voltammograms of $(\text{TTF})_7\text{SbI}_4$ were recorded in DMF/0.1 M TEAP (tetraethylammonium perchlorate) from -0.2 to $+1.0$ V versus an Ag/AgCl electrode. Redox potentials of TTF molecule, $(\text{TTF})_7\text{SbCl}_4$ and $(\text{TTF})_5(\text{SbBr}_4)_2 \cdot \text{CH}_3\text{COCH}_3$ were also examined and summarized in Table 1. The half-wave potential ($E_{1/2}$) were estimated by averaging the anodic and cathodic peak potentials. $(\text{TTF})_7\text{SbI}_4$ exhibits two peaks at $+0.41$ and $+0.67$ V. These are assigned to TTF^+/TTF and $\text{TTF}^{2+}/\text{TTF}^+$ couples, respectively. The experimentally observed $E_{1/2}$ value of TTF molecule are $+0.42$ and $+0.66$ V, assigned to TTF^+/TTF and $\text{TTF}^{2+}/\text{TTF}^+$ couples, respectively. The voltammogram of TTF in CH_3CN solution was also reported to show two reversible redox waves at $+0.33$ (TFF⁺/TTF) and at $+0.70$ V (TFF²⁺/TTF⁺) versus SCS,¹² and support the assignment in the case of the present compounds. The cyclic voltammograms were scanned several times and there was no change in the potentials, indicating that the redox couples are reversible. A redox peak attributable to antimony metal was not detected in any case.

Conclusion

$(\text{TTF})_7\text{SbI}_4$ was prepared from TTF and SbI_3 as a result of a charge transfer from $(\text{TTF})_n$ molecules to SbI_4^- entity. Relatively high electrical conductivity and spectroscopic properties lead to the conclusion that partially ionized TTF radical cations have stacked to form low-dimensional chains. Magnetic properties also reveal that the magnetic interstack interaction between TTF radicals is considerable. This magnetic interaction plays an important role in enhancing the electrical conductivity, and furthermore, provides a useful information to design conductive materials.

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Facile Direct *p*-Functionalization of Calix[4]arene through Transmetalation of *p*-Bromocalix[4]arene Tetrahexyl Ether

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Calixarenes have attracted many interests because of their potential diversities for host-guest complexes and enzyme mimics.¹ The diversities are attributable to the various sizes, the chemical reactivities at both rims, and even the easy conformational changes of calixarenes.

Functionalizations of calixarenes both at the phenolic oxygen (lower-rim)² and at the *para* position of aromatic nucleus (upper-rim)³⁻⁷ have been developed extensively. Particularly the functionalizations at "upper-rim" of calix[4]arene have attracted considerable attentions because the upper-rim contains a hydrophobic cavity which could be manipulated for neutral substrate recognition. Shinkai *et al.* achieved the sulfonation and nitration,³ and Gutsche *et al.* performed modification *via* the *p*-Claisen rearrangement route⁴ and *via* the *p*-quinone methide route.⁵ The Parma group introduced the *p*-chloromethylation route⁶ and the selective diametrical functionalization of calix[4]arene at the upper-rim.⁷

Except for Shinkai's direct electrophilic substitutions, however, one has to pass through several steps to introduce an appropriate functional group. In this respect, a direct functionalization method on the upper-rim of a common intermediate has been looked for. Indeed, transmetalation route was attempted by Gutsche *et al.*,⁸ who reported the synthesis of *p*-lithiocalix[4]arene tetramethyl ether from *p*-bromocalix[4]arene tetramethyl ether by treatment with *n*-BuLi at -78 °C. But, tetralithiation of *p*-bromocalix[4]arene tetrahexyl ether in the reported conditions cannot be repeated.⁹ Only when the lithiate solution was warmed up to room temperature, tetralithiation was achieved in a rather low yield.

In this note we report the facile *p*-functionalization through the direct transmetalation of *p*-bromocalix[4]arene tetrahexyl ether using *t*-BuLi at -78 °C followed by quenching with several electrophiles.

Results and Discussion

As shown in Scheme 1, alkylation of calix[4]arene **1** with 1-bromohexane afforded the fixed cone-structured tetrahexyl ether **2** in 84% yield.¹⁰ Bromination of **2** with NBS gave *p*-bromocalix[4]arene tetrahexyl ether **3** in 88% yield.¹⁰

Complete metal-halide exchange of *p*-bromocalix[4]arene **3** was achieved by treatment with excess *t*-BuLi at -78 °C in THF for 2 h. This *p*-lithiocalix[4]arene was quenched with trimethylsilyl chloride, methyl iodide, and *N*-formylmorpholine to give *p*-(trimethylsilyl)calix[4]arene tetrahexyl ether **4** (76%), *p*-methylcalix[4]arene tetrahexyl ether **5** (68%), and *p*-formylcalix[4]arene tetrahexyl ether **6** (60%) res-