Synthesis of Tetrathiafulvalence Charge Transfer Compounds

Bull. Korean Chem. Soc. **1994**, Vol. 15, No. 6   465

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Synthesis and Characterization of Tetrathiafulvalene Charge Transfer Compounds with Iron and Antimony Halides

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The charge transfer compounds $(TTF)_4FeCl_3 \cdot CH_3OH$, $(TTF)_4SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$ were prepared from reactions of the TTF (tetrathiafulvalene) and metal halides. The compounds were characterized by spectroscopic (UV, IR, EPR and XPS) methods, magnetic susceptibility and electrical conductivity measurements. The $d.c$ electrical conductivities of the pressed pellets are in the order of 10^{-1}-10^{-3} Scm^{-1}, which lies in the range of semiconductor region at room temperature. It means that the partially ionized TTF has stacked in low-dimensional chain in each compound. Spectroscopic properties also indicate that TTF molecules are partially ionized and charge transfer has occurred from $(TTF)n$ to Fe(III) center in $(TTF)_4FeCl_3 \cdot CH_3OH$ whereas to the $-SbX_4^-$ entity in $(TTF)_4SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$. The EPR g values are consistent with TTF radical formation and EPR linewidths suggest the delocalization of unpaired electrons along TTF stacks. A signal arised from metal (Fe and Sb) ions were not detected in EPR spectra, indicating that metal ion is in the diamagnetic state in each compound. The diamagnetic state was also examined by the magnetic susceptibility measurement. The magnetic properties reveal the significant interactiion between the TTF^+ radical cations in the stacks. The oxidation state of metal ions was also investigated by XPS spectra.

Introduction

TTF(Tetrathiafulvalene) and its analogues have been used as electron donors to form highly electroconductive charge transfer complexes.[1] The complexes contain simple halides,[2] pseudohalides[3] and some organic materials[1,4] as an electron acceptor. Relatively less work has been done in charge transfer compounds containing transition metals.

Recently we have perpared TTF complexes with the metal halides $FeCl_3$, $FeBr_3$ and the hydrated salts of $RuCl_3$, $RhCl_3$, and $IrCl_4$.[5] TTF π stacks were revealed to exhibit semiconducting behavior in each compound. The compounds formed with $FeCl_3$ and $FeBr_3$ with the formulas $(TTF)_2FeCl_3$ and $(TTF)_3FeBr_3$ were especially interesting since the magnetic interaction along TTF stacks in $(TTF)_3FeBr_3$ was greater than that in $(TTF)_2FeCl_3$ and the electrical conductivity of $(TTF)_3FeBr_3$ was also greater than that of $(TTF)_2FeCl_3$. It was concluded that the magnetic interaction could provide an important information in design of conductive materials.

Furthermore, $(TTF)_5Fe(NO_3)_3$ is also reported.[6] Iron existed in diamagnetic $+2$ state and unpaired electrons were delocalized along TTF stacks in $(TTF)_5Fe(NO_3)_3$. Small temperature-independent paramagnetism was observed as a result of significant magnetic interaction along TTF chains.

In this study, $(TTF)_4FeCl_3 \cdot CH_3OH$ is prepared from TTF and hydrated $FeCl_3$ in methanol solution as the extension of the study of TTF charge transfer compound containing transition metals. $(TTF)_4SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$ are also synthesized in acetone solution. These compounds draw our interest since Fe(III) is reduced to Fe(II) state in $(TTF)_4FeCl_3 \cdot CH_3OH$ as a result of charge transfer from TTF donor to iron, while charge transfer has occured from $(TTF)n$ to the $-SbX_4^-$ ($X=Cl$, Br) entity in $(TTF)_4SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$. Their electrical and magnetic properties are quite different from each other. The compounds are also characterized by EPR, X-ray photoelectron, electronic absorption and vibrational spectroscopy.

Table 1. Electrical and Magnetic Properties of TTF-metal Halides

Compounds	Electrical conductivity (σ) at room temperature (Scm^{-1})	Effective magnetic moment at room temperature (BM)	EPR parameters	
			g values[a]	EPR linewidth[b] (gauss)
(TTF)₄FeCl₃·CH₃OH	5.90×10^{-1}	0.76	$<g> = 2.012$	~15
(TTF)₄SbCl₄	1.42×10^{-3}	0.82	$g_{\parallel} = 2.082$	8
			$g_{\perp} = 2.086$	
(TTF)₅(SbBr₄)₂·CH₃COCH₃	3.27×10^{-3}	1.08	$<g> = 2.021$	4

[a] The listed g values were measured at room temperature. [b] The values are peak-to-peak linewidth (ΔH_{pp})

Experimental

Synthesis. (TTF)₄FeCl₃·CH₃OH was prepared by addition of excess TTF (3.5 mmol) to a solution containing hydrated FeCl₃ (1 mmol) in methanol. The solution was changed to a dark purple color immediately. The mixture was refluxed for ca 1-2 hrs and then refrigerated overnight. The solid was filtered off and washed with absolute methanol several times. The microcrystalline precipitates were dried under vacuum at room temperature. (TTF)₄SbCl₄ and (TTF)₅ (SbBr₄)₂·CH₃COCH₃ were formed by an analogous method using anhydrous SbCl₃ and SbBr₃, respectively, in acetone. All of the compounds were dark purple in color. Elemental analysis was performed by Korea Research Institute of Chemical Technology, Daejeon, Korea.

Anal. Calc. for (TTF)₄FeCl₃·CH₃OH: C, 29.68; H, 1.99; Cl, 10.51. Found: C, 30.53; H, 2.20; Cl, 10.84%. Calc. for (TTF)₄ SbCl₄: C, 26.70; H, 1.49. Found: C, 26.77; H, 1.44. Calc. for (TTF)₅(SbBr₄)₂·CH₃COCH₃: C, 20.21; H, 1.34. Found: C, 19.96; H, 1.37.

Physical Measurements. D. C electrical conductivities were measured on compressed pellets by the Van der Pauw four-probe method[7] at room temperature. EPR spectra of powdered samples were obtained at 77 K and at room temperature by using a Varian E-109 X-band spectrometer (~9.5 GHz). The free radical DPPH (g=2.0036) was used as a field marker. 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 HgCo(SCN)₄.[8] The data were corrected for temperature independent paramagetism and for the diamagnetism of the constituent atoms using Pascal's constants. X-ray photolectron spectra were recorded on 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 calibrate using the Au 4f₇/₂ peak at 84.9 eV and the Cu 2p₃/₂ peak at 932.4 eV. The adventitious C 1s line at 284.6 eV was used for charge referencing. Electronic spectra were taken on a Hewlett Packard 8451A spectrophotometer on solution or solid/nujol mulls between quartz plates. IR spectra were obtained using KBr pellets with a Polari's FT-IR spectrometer.

Results and Discussion

The room temperature d.c powdered electrical conductivity (σₙ) of (TTF)₄FeCl₃·CH₃OH is 5.9×10⁻¹ Scm⁻¹ and those

of (TTF)₄SbCl₄ and (TTF)₅(SbBr₄)₂·CH₃COCH₃ are in the order of 10⁻³ Scm⁻¹. These values are in the range of semiconductor, and somewhat greater than those of simple ionized TTF salts having a columnar structure (~10⁻⁵ Scm⁻¹).[9] This indicates that TTF in each compound is partially ionized and stacked to form chains. The electrical and magnetic properties of the compounds are listed in Table 1. The electrical conductivity of (TTF)₄FeCl₃·CH₃OH is two orders of magnitude greater than those of TTF-SbX₃ compounds. This will be discussed on the basis of magnetic interaction along (TTF)n stacks in the compounds.

The EPR spectrum of a powdered sample of (TTF)₄FeCl₃· CH₃OH at room temperature exhibited a singlet at $<g> = $ 2.012. (TTF)₄SbCl₄ gave an unsymmetrical shaped spectrum with $g_{\parallel} = 2.082$, $g_{\perp} = 2.086$ and $g_{\parallel} = 2.023$, $g_{\perp} = 2.020$ at room temperature and 77 K, respectively. Symmetrical singlets were examined at about $<g> = 2$ both at room temperature and 77 K for (TTF)₅(SbBr₄)₂·CH₃COCH₃. The average $<g>$ values of the compounds are similar to that of TTF in solution[10] ($<g> = 2.00838$) and TTF-copper halides salts[11] containing partially ionized -(TTF)n entity. The EPR peaks of iron and antimony metal ions were not detected. The observed $<g>$ values and the absence of metal ion signals indicate that any unpaired electrons are on TTF radicals and that metal atoms are diamagnetic Fe(II) (d⁶) and Sb(III) (d¹⁰s²) oxidation state. The linewidths of TTF EPR signals (<15G) are comparable to those of TTF·TCNQ (~6G) and TTF· SCN (~15G)[13], the compounds that the magnetic interactions between delocalized electrons along TTF chains are considerable.

The linewidth can be used as a measure of the deviation of a system from one dimensionality.[14] Y. Tomkiewiez and coworkers[15] have explained that the small linewidth of TTF-halides (~10G) is due to the significant interaction between TTF radicals along the stacks and concluded that the smaller the linewidth, the larger the coupling in the TTF stacks. Linewidths of 5 to 15 gauss are known to be the significant spin-orbit interaction of sulfur in TTF columnar chains.[16]

The determined magnetic suscepitivity of (TTF)₄FeCl₃·CH₃ OH (1.60×10⁻⁴ and 1.70×10⁻⁴ emu/mole at room temperature and at 77 K respectively) shows almost temperature-independent paramagnetism. Small temperature-independent, Pauli paramagnetism, is well known in the low-dimensional semiconductors as a result of significant magnetic interaction.[17] The magnetic susceptibility of TTF-SbX₃ salts increases slowly as the temperature decreases. The temperature dependence of magnetic susceptibility data of TTF-SbX₃ salts is shown in Figure 1. The magnetic susceptibility data for
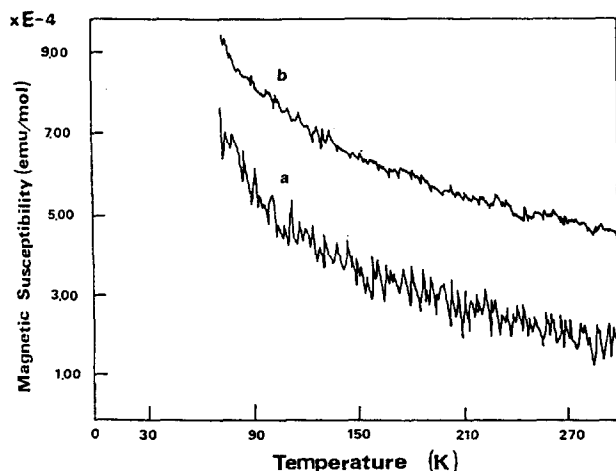
Figure 1. Temperature dependence of magnetic susceptibility for (a) $(TTF)_4SbCl_4$ and (b) $(TTF)_5(SbBr_4)_2CH_3COCH_3$.

$(TTF)_5(SbBr_4)_2CH_3COCH_3$ can not be described by the Curie law $(\chi=C_0T^{-1})$ but do follow the power law, $\chi=C_0T^{-\alpha}$, where α is less than 1. The best fit calculated values are $C_0=4.02$ and $\alpha=0.26$ for $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$. Data were fit using standard linear least-square method. The magnetic properties of some conductive TTF salts[18] and TCNQ salts[19] were also described by this power law, with α ranging from 0.37-0.85. However, the magnetic interaction between TTF radicals in $(TTF)_4FeCl_3 \cdot CH_3OH_3$ is more significant than those in TTF-SbX_3 salts. This observation is reflected in the electrical property with the electrical conductivity of $(TTF)_4$ $FeCl_3 \cdot CH_3OH$ being two orders magnitude greater than those of TTF-SbX_3 salts. Similar result was reported for $(TTF)_2FeCl_3$ and $(TTF)_4FeBr_3$ compounds.[5]

The effective magnetic moments (μ_{eff}) of $(TTF)_4FeCl_3 \cdot CH_3OH$, $(TTF)_3SbCl_4$ and $(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$ are 0.76, 0.82 and 1.08 BM respectively at room temperature. These values, which are contributed from the unpaired electron on $(TTF)n^+$ radical, are somewhat smaller than the spin-only value of 1.73 BM for one unpaired electron. This observation, together with the results of EPR spectra, is consistent with the conclusion that the oxidation states of the metal ions are diamagnetic Fe(III) and Sb(III) state and that the unpaired electrons are delocalized over the $(TTF)n^+$ radicals.

The oxidation state of the metal ion was also investigated by X-ray photoelectron spectroscopy (XPS). XPS detects changes in the electronic environment of an atom, as evidenced by the shifts in the binding energy (BE) of core electrons. The BE data are summarized in Table 2.

A BE of Fe $2p_{3/2}$ core electron in $(TTF)_4FeCl_3 \cdot CH_3OH$ is 710.3 eV, a value which is smaller than that of $FeCl_3$ by 1.2 eV. The value is similar to that of $FeCl_2$, supporting that the oxidation state of iron ion in $(TTF)_4FeCl_3 \cdot CH_3OH$ is +2 as a result of charge transfer reaction by the TTF donor. The BEs of $3d_{5/2}$ (529.8-530.0 eV) are smaller than those of a variety of Sb(III) compounds (529.7-531.2 eV). This is justified by the more electron density on antimony ion in $-SbX_4^-$ entity than is SbX_3. There are essentially little changes in the S $2p$ BE in each compound. The values are comparable to those of TTF molecule and related compounds.[21] It is known that the electron density in the sulfur lone-pair orbitals in TTF is little affected on the oxidation state of sulfur atom.[21,22]

IR spectra in KBr pellets exhibited very broad intense bands extending from 1,000 to 4,000 cm^{-1}. These intense absorptions arise from the electronic transition in the band structure of these semiconductors[23] and mask many of the

Table 2. Binding Energy (eV) of TTF-metal Halides

Compounds	Metal			Halide	S(2p)	O(1s)
	Fe($2p_{3/2}$)	Sb($3d_{5/2}$)	Sb($3d_{3/2}$)			
$FeCl_3$	711.5					
$FeCl_2$	710.8					
$(TTF)_4FeCl_3 \cdot CH_3OH$	710.3			197.9 (Cl $2p_{3/2}$)	164.1	531.9
						540.0
$(TTF)_4SbCl_4$		530.0	539.8	197.8 (Cl $2p_{3/2}$)	164.0	—
$(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$		529.8	539.7	60.1 (Br $3d_{5/2}$)	163.9	—

Table 3. Electronic and Vibrational Spectra of TTF-metal Halides

Compounds	IR spectra (cm^{-1})	Electronic specta	
		λ_{max} (nm)	Solvent
$(TTF)_4FeCl_3 \cdot CH_3OH$	820 (υ_{16})	587, 442, 311	DMF
	1246 (υ_{23})	559, 370, 302	Solid/nujol
$(TTF)_4SbCl_4$	700 (m, υ_{34}), 750 (m, υ_{17}), 830 (m, υ_{16}), 1085 (w, υ_{15})	587, 442, 317	DMF
	1250 (m, υ_{23}), 1350 (s), 1470 (m, υ_{14})	542, 436	Solid/nujol
$(TTF)_5(SbBr_4)_2 \cdot CH_3COCH_3$	700 (m, υ_{34}), 750 (m, υ_{17}), 800 (w), 825 (m, υ_{16})	586, 446, 272	DMF
	1083 (m, υ_{15}), 1260 (m, υ_{23}), 1350 (s),	534, 417	Solid/nujol
	1400 (w), 1463 (m, υ_{14})		

vibrational modes of the compounds. A limited number of vibrational bands of TTF were observed in the absorption tail. The vibrational modes of TTF are tentatively assigned by comparing the reported spectra of conductive TTF salts.[24] The results are summarized in Table 3. In (TTF)$_4$FeCl$_3$·CH$_3$-OH, the absorption bands at 820 and 1246 cm^{-1} were assigned to the υ_{16} and υ_{23} respectively. The υ_{16} vibrational mode is related with the stretching of the C-S in the five membered ring of TTF molecule and the υ_{23} is contribute from CCH bend. The C-S modes are expected to be shifted in terms of the variation of bond orders and bond lengths due to the ionization of TTF. The observed υ_{16} value is between that of TTF° (781 cm^{-1}) and TTF$^+$ (836 cm^{-1}),[24] indicating the partial oxidation of the TTF molecule in (TTF)$_4$FeCl$_3$·CH$_3$-OH. Similar results are observed for the (TTF)$_4$SbCl$_4$ and (TTF)$_5$(SbBr$_4$)$_2$·CH$_3$COCH$_3$ salts. Electronic spectra were recorded from 200-800 nm in both solution and solid state. The results are also listed in Table 3. The observed electronic trasitions are similar to the results of some conductive TTF chage transger compounds[5,11]. The low-energy absorption bands obove 500 nm are typical of the intermolecular spectra of conjugated π-molecular radicals.[25]

Conclusions

We have prepared (TTF)$_4$FeCl$_3$·CH$_3$OH, (TTF)$_4$SbCl$_4$ and (TTF)$_5$(SbBr$_4$)$_2$·CH$_3$COCH$_3$ charge transfer compounds from the reaction of TTF and metal halides. The electroconductivity is in the range of semiconductor in each compound. The spectroscopic (IR, UV, EPR and XPS) results reveal that Fe(III) is reduced to Fe(II) in (TTF)$_4$FeCl$_3$·CH$_3$OH whereas charge transfer has occured from (TTF)n molecules to the -SbX$_4^-$ entity in (TTF)$_4$SbCl$_4$ and (TTF)$_5$(SbBr$_4$)$_2$·CH$_3$COCH$_3$, and that the odd electron is delocalized on TTF$^+$ radicals in columnar stacks. This one-dimemsional inter-stack interactions provide the pathway for the relatively high electroconductivity in the stacking direction. The magnetic properties also indicate the significant interaction between the TTF$^+$ radicals in the stacks. The (TTF)$_4$FeCl$_3$·CH$_3$OH shows greater magnetic interaction than those of (TTF)-SbX$_3$ salts. This interaction is reflected in the electrical properties with the electroconductivity of (TTF)$_4$FeCl$_3$·CH$_3$OH being greater than those of (TTF)-SbX$_3$ compounds. This observation could be used to design conductive materials with prescribed magnetic and electrical properties.

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