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Tetrathiafulvalene (TTF) Charge Transfer Compounds of FeCl₂ and Fe₂(SO₄)₃; (TTF)₃FeCl₃·0.5CH₃OH and (TTF)_{2.5}Fe(SO₄)₂·CH₃OH

Eun-Jung Park, Hong-Woo Lee, and Young-Inn Kim*

*Department of Chemistry Education, and Research Institution for Science Education,
Pusan National University, Pusan 609-735, Korea*

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Tetrathiafulvalene (TTF) and its analogues have been used as electron donors to form highly electrical conductive charge transfer compounds.¹ Their electrical properties can be varied over a wide range by changing the nature of the acceptor species. The use of metal chelates as acceptor is expected to be a versatile route for the preparation of a wide variety of conductive TTF compounds which exhibit different electrical properties, because various types of metal chelate anions can be employed with different geometries and oxidation states of the central metal ion. Among the metal complexes, Fe(III) complexes have been widely used as electron acceptors since Fe(III) is readily reduced to Fe(II) due to the relatively high reduction potential (Fe(III) → Fe(II); $E_{1/2}$ =0.771 V in H₂O), for example, (TTF)₂₋₃FeX₃²

and (BEDT-TTF)FeX₄³ (BEDT-TTF: bis(ethylenedithio)tetrathiafulvalene, X=Cl and Br) were reported. However the reported compounds showed different charge transfer process during the reaction. In the former compound, the electron has transferred from TTF to the central Fe(III) ion to form reductive Fe(II) state, whereas in (BEDT-TTF)FeX₄, charge transfer has occurred to the FeX₄⁻ moiety as a result of the addition of halide anion to FeX₃ in solution. In this study, even Fe(II) cannot be reduced readily, we tried to prepare TTF-FeCl₂ charge transfer compound since iron(II) chloro-anion, FeCl₃⁻, can be obtained by interaction of FeCl₂ with chloride anion. TTF-Fe₂(SO₄)₃ compound was also prepared to ascertain the charge transfer behavior. The prepared compounds were characterized by spectroscopic,

Table 1. Vibrational and electronic absorption of Fe-TTF compounds

| Compound | Vibrational mode | λ_{\max} (nm) in |
|--|--|--------------------------------|
| TTF | 1530 (ν_{14} , m), 1090 (ν_{15} , m), 781 (ν_{16} , s), 734 (ν_{17} , m), 427 (ν_{18} , m), 3073 (ν_{22} , m), 1254 (ν_{23} , m), 794 (ν_{25} , s), 639 (ν_{34} , s) | 448, 318 (805, 452, 370, 307) |
| TTF ⁺ | 1478 (ν_{14} , m), 1072 (ν_{15} , m), 836 (ν_{16} , s), 751 (ν_{17} , m), 460 (ν_{18} , m), 3063 (ν_{22} , m), 1237 (ν_{23} , m), 825 (ν_{25} , s), 705 (ν_{34} , s) | |
| (TTF) ₃ FeCl ₃ ·0.5CH ₃ OH | 1494 (ν_{14} , m), 1088 (ν_{15} , w), 822 (ν_{16} , m), 736 (ν_{17} , m), 484 (ν_{18} , m), 3073 (ν_{22} , m), 3057 (ν_{22} , m), 1239 (ν_{23} , s), 803 (ν_{25} , m), 697 (ν_{34} , m) | 585, 442, 318 (1065, 529, 383) |
| (TTF) _{2.5} Fe(SO ₄) ₂ ·CH ₃ OH | 1497 (ν_{14} , m), 1069 (ν_{15} , m), 833 (ν_{16} , s), 739 (ν_{17} , s), 466 (ν_{18} , s), 3074 (ν_{22} , m), 3057 (ν_{22} , m), 1235 (ν_{23} , s), 821 (ν_{25} , s), 687 (ν_{34} , m) | 584, 442, 308 (919, 521, 360) |

magnetic and electrochemical methods.

Experimental

(TTF)₃FeCl₃·CH₃OH and (TTF)_{2.5}Fe(SO₄)₂·CH₃OH were prepared by the direct reaction of TTF with hydrated FeCl₂ and Fe₂(SO₄)₃ respectively in CH₃OH solution, followed by the literature method.² Elemental Analysis were performed by Korean Basic Science Center, in which satisfactory results were obtained for the prepared compounds. Anal. calc. for (TTF)_{2.5}Fe(SO₄)₂·CH₃OH: C, 24.67; S, 50.00; H, 1.81. Found: C, 24.78; S, 52.52; H, 1.81. Calc. for (TTF)₃FeCl₃·0.5CH₃OH: C, 28.08; S, 49.00; H, 1.80. Found: C, 28.69; S, 50.15; H, 1.95.

Infrared (IR) spectra on KBr pressed pellets were measured with a Polari's FT-IR spectrometer. Electronic absorption spectra (200-1100 nm) in DMF solution and in nujol/solid state were obtained with a Shimadzu UV-1601PC spectrophotometer. Cyclic voltammograms in DMF solution were recorded on a Bio Analytical Systems CV 50W Voltammeter. TEAP (0.1 M tetraethyl ammonium perchlorate) was used as supporting electrolyte. Ag/Ag⁺ reference electrode and Pt auxiliary electrode were used for cyclic voltammograms. The room temperature powdered electrical conductivities were determined by compressing the bulk sample between two graphite rods (5 mm in diameter) surrounded by a glass tube sheath. The electrical conductivity measurements were made with CV 50W Voltammeter. EPR spectra in solid and solution (CH₂Cl₂/DMF=1:1) were acquired at 77 K by using a Bruker Instruments ESP-300S of Korea Basic Science Center. Magnetic susceptibility data were collected from 4 K to 300 K using MPMS7 (Magnetic Property Measurement System) of U.S.A. Quantum Design by SQUID method. The data were corrected for temperature independent paramagnetism and for the diamagnetism of the constituent atoms using Pascal's constants.

Results and Discussions

The infrared spectra of Fe-TTF compounds were examined by using KBr pellet technique in the range of 400-4000 cm⁻¹. The frequencies were analyzed tentatively by comparing to TTF, TTF⁺, and some TTF radical compounds.⁴ The vibrational modes and their assignments are listed in Table 1.

The ν_{16} mode represents C-S stretching bond and the ν_{25}

mode is contributed from SCC bending bond in the five membered ring of TTF molecule. The two specific modes (ν_{16} , ν_{25}) of TTF⁰ and TTF⁺ appear in the region of 780-840 cm⁻¹. The former band is more intense than the latter, because ν_{25} band is often masked by the ν_{16} band. Both of them are expected to be shifted by the change of bond orders and bond lengths due to the oxidation of TTF. The ν_{16} mode is apparently indicative of ionization shift of TTF.⁵ The ν_{16} mode of (TTF)₃FeCl₃·0.5CH₃OH and (TTF)_{2.5}Fe(SO₄)₂·CH₃OH are at 822, 833 cm⁻¹ respectively, which are in the middle range of TTF⁺ (836 cm⁻¹) or TTF⁰ (781 cm⁻¹) state. It is supposed that TTF in (TTF)₃FeCl₃·0.5CH₃OH and (TTF)_{2.5}Fe(SO₄)₂·CH₃OH are mixed valence state between neutral and charged state.

Electronic absorption spectra were recorded at the range of 200-1100 nm in DMF solution and solid/nujol state, and also summarized in Table 1. Wudl *et al.*⁶ reported the maximum absorbance (λ_{\max}) of TTF⁺ in H₂O at 340, 435, and 575 nm. The three values were assigned as 340 nm ($b_{3g} \rightarrow b_{1u}$), 435 nm ($b_{1u} \rightarrow b_{2g}$), and 575 nm ($b_{2g} \rightarrow b_{1u}$).⁷ Those electronic transitions are comparable to the results for the prepared compounds in this work. Furthermore, the charac-

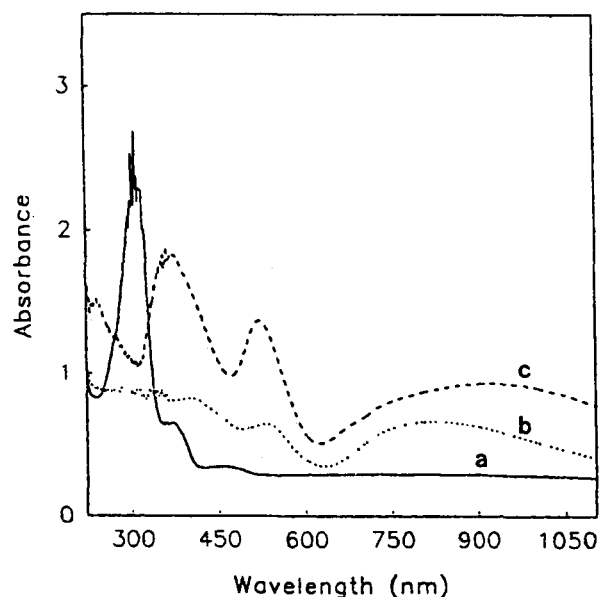


Figure 1. Electronic absorption spectra of Fe-TTF compounds in solid/nujol state. a: TTF, b: (TTF)₃FeCl₃·0.5CH₃OH, c: (TTF)_{2.5}Fe(SO₄)₂·CH₃OH.

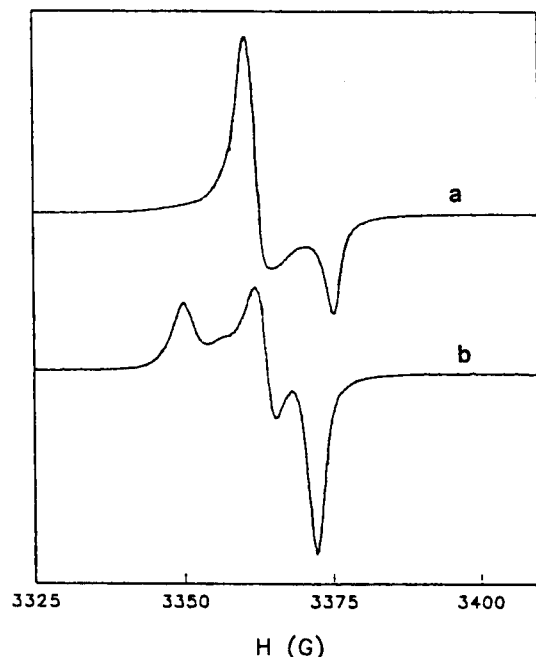


Figure 2. X-band EPR spectra of Fe-TTF compounds in powdered sample. a: $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$, b: $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$.

teristic broad absorbance (λ_{max}) was observed lower than 850 nm in solid/nujol state as shown in Figure 1. This existence of the lower energy band is shown to be due to the mixed-valence nature of the compounds.⁸

The powdered EPR spectrum of $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$ exhibited two components of g values (g_{\parallel} , g_{\perp}) and the spectrum of $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ was well resolved into three g values (g_{xx} , g_{yy} , g_{zz}). Figure 2 shows EPR spectra of the compounds in powdered sample at 77 K, and EPR parameters in solid together with the obtained data in solution are listed in Table 2. The average $\langle g \rangle$ value is nearly equal to the g value of the TTF free radical ($g=2.0083$)⁶ in both solid and solution. This observation implies that the peaks are arisen from the unpaired electron residing on TTF.

The temperature dependence of the magnetic susceptibility data are shown in Figure 3. The magnetic susceptibility of $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$ is almost temperature independent, whereas in $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ the mag-

Table 2. EPR parameters of powder and solution Fe-TTF samples at 77 K

| Compound | EPR | | | |
|---|-----------------------|----------------------------------|-----------------------|---------------------|
| | solid | | solution ^b | |
| | g value | ΔH_{pp} ^a (G) | g value | ΔH_{pp} (G) |
| $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ | $g_{xx}=2.015$ | $A_{xx}=12$ | $g_{xx}=2.015$ | $A_{xx}=11$ |
| | $g_{yy}=2.007$ | $A_{yy}=4$ | $g_{yy}=2.007$ | $A_{yy}=8$ |
| | $g_{zz}=2.002$ | $A_{zz}=7$ | $g_{zz}=2.002$ | $A_{zz}=3$ |
| $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$ | $g_{\perp}=2.008$ | $A_{\perp}=4$ | $g_{\perp}=2.008$ | $A_{\perp}=7$ |
| | $g_{\parallel}=2.001$ | $A_{\parallel}=10$ | $g_{\parallel}=2.002$ | $A_{\parallel}=7$ |

^a Peak to peak EPR linewidth (G: gauss). ^b $\text{CH}_2\text{Cl}_2/\text{DMF}$ (1:1) were used for solution.

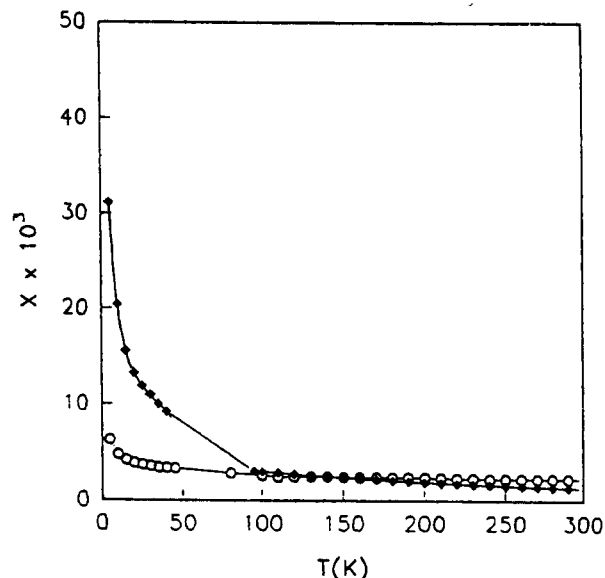


Figure 3. Temperature dependence of magnetic susceptibility for Fe-TTF compounds. ○: $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$, ◆: $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$.

netic susceptibility increases as decreasing the temperature like Curie-Weiss tail. The effective magnetic moments were calculated by using $\mu_{\text{eff}}=2.828(\chi T)^{1/2}$ and listed in Table 3. The diamagnetism of $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$ represents that the oxidation state of Fe is 2+, d^6 low spin configuration with the effective magnetic moment (μ_{eff}) value of 0.36 BM. This observed value is arisen from the unpaired electrons delocalized along TTF in $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5\text{CH}_3\text{OH}$. The effective magnetic moment of $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ is 1.76 BM which is very similar to that of spin-only value of one electron (1.73 BM). It is supposed to be composed of d^5 low spin configuration of Fe(III) in $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$. The magnetic susceptibility of $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ must include a contribution from the unpaired electron on the iron ion, a contribution from the electron on TTF radical, and an exchange interactions between the paramagnetic species.² However, the magnetic susceptibility data were well fit to the Curie-Weiss law from 4 to 150 K, indicating that the localized electron on the Fe(III) ion in $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ dominantly represents the magnetic data, and that the weak temperature independent paramagnetism is arisen from TTF radicals in this case. The paramagnetic $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ also exhibits weak EPR g value at ~ 4.06 which is interpreted as the g value of

Table 3. Electrical conductivity, magnetic moments, and magnetic susceptibility parameters in Fe-TTF compounds

| Compound | σ_{RT} ^a (Scm^{-1}) | μ_{eff} ^b (BM) | parameter ^c | |
|---|---|--------------------------------------|------------------------|----------|
| | | | C | θ |
| $(\text{TTF})_{2.5}\text{Fe}(\text{SO}_4)_2 \cdot \text{CH}_3\text{OH}$ | 6.23×10^{-3} | 1.76 (300 K) | 0.34 | 6.40 |
| $(\text{TTF})_3\text{FeCl}_3 \cdot 0.5 \text{CH}_3\text{OH}$ | 3.07×10^{-4} | 0.36 (210 K) | | |

^a Electrical conductivity at room temperature. ^b Effective magnetic moment: obtained by $\mu_{\text{eff}}=2.828(\chi \cdot T)^{1/2}$. ^c Curie-Weiss law parameter: $\chi=C/(T+\theta)$, obtained from 4 K to 150 K.

Fe(III).

Fe-TTF compounds have an electrical conductivity in the range of 10^{-3} – 10^{-4} S·cm⁻¹. Those values are in semiconductor range. This means that partially oxidized TTF are moderately stacked in solid state, and exhibited the electrical conductivity in stacking direction. The values of electrical conductivity are represented in Table 3.

The mid-peak potentials ($E_{1/2}$) of TTF in the prepared compounds are about 0.00 V for TTF⁺/TTF⁰ couple and +0.23 V for TTF²⁺/TTF⁺ couple. TTF molecule shows similar $E_{1/2}$ values in this work. Similar results were also reported for TTF and some heavy transition metal compounds.⁹

In summary, TTF reacts with hydrated FeCl₂ and Fe₂(SO₄)₃ in methanol to form (TTF)₃FeCl₃·0.5CH₃OH and (TTF)_{2.5}Fe(SO₄)₂·CH₃OH respectively, in both of which charge transfer has occurred to [FeCl₃]⁻ and [Fe(SO₄)₂]⁻ moiety during the reaction. The partially oxidized TTFs are moderately stacked to exhibit relatively high electrical conductivity. Such inter-stack interactions between TTFs are also supported by the temperature-independent magnetic susceptibility arisen from the TTF radicals. This small and temperature independent magnetic susceptibility, Pauli paramagnetism, is well known in low-dimensional semiconductor as a result of band formation.¹⁰

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Extractive Separation of Alkali Metal Ions by Mono- and Bis-*o*-Xylyl Crown Macrocyclic Compounds in an Aquatic Environment

Yong-Ill Lee^{*†}, Dong-Won Kim[‡], Ki-Young Choi[†], Miran Yoo^{*},
Jong Seung Kim^{*}, Young-Jae Yoo^{*}, and Wonbo Sim^{*}

^{*}Department of Chemistry, Changwon National University, Changwon 641-773, Korea

[‡]Department of Chemistry, Chungbuk National University, Cheongju 360-763, Korea

[†]Department of Chemistry, Mokwon University, Taejon 301-729, Korea

^{*}Department of Chemistry, Konyang University, Nonsan 320-711, Korea

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Synthetic macrocyclic multidentate ligands such as crown ethers become the focus of intense scientific interest for the separation of alkali and alkaline earth metal cations from aqueous solutions and synthetic efforts have been successful in obtaining various macrocyclic compounds.¹⁻⁴ Some of the ligands and metal complexes have several potential applications, including medical treatment,⁵ imaging,⁶ analytical separation of metal cations^{7,8} and ion-selective electrodes.^{9,10} Recently, Lee *et al.*¹¹ reported the synthesis of bis-crown ether derivatives, *i.e.* (1,2)(4,5)-bis-*o*-xylyl crown compounds in which the macrocycles are connected to the benzene core *via* Ar-CH₂-O linkages. However, to the best of our knowledge, no details on their alkali metal cation complexation have been appeared yet. Understanding com-

plexation at the molecular level provides the basis for metal selectivity sequence and binding strength which depends on cavity size, steric factors, conformation, ligand basicity, and rigidity.¹² Although there are several reports on the solvent extraction of alkali metal ions with crown ethers, most experiments employed monocyclic crown ethers as organic ligands. Schlotter *et al.*¹³ deduced a qualitative insight in the metal cation complexation properties of benzo-bis-(18-crown-6) from ¹H NMR titration studies using potassium thiocyanate and potassium picrate. They observed the increase of $\Delta\delta$ (Hz) for benzo-bis-(18-crown-6) in going to host/guest ratios 1:2, compared to the corresponding benzo-(18-crown-6).

In the present paper, mono- and bis-*o*-xylyl crown ethers of different cavity sizes, *i.e.*, mono-*o*-xylyl-(17-crown-5) (I), bis-*o*-xylyl-(14-crown-4) (II), and bis-*o*-xylyl-(17-crown-5)

[†]To whom correspondence should be addressed.