Notes

Bull. Korean Chem. Soc. 1996, Vol. 17, No. 12 1167

Synthesis and Characterization of Tetrathiafulvalene Compounds with Titanium and Thallium, (TTF)ₙTiXₘ and (TTF)ₙTlXₘ

Mi-Kyung Kim, Young-Inn Kim*, Seong Bae Moon, and Sung-Nak Choi†

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

†*Department of Chemistry, Pusan National University, Pusan 609-735, Korea*

Recently, we have reported some tetrathiafulvalene (TTF) charge transfer compounds[1] with the intention of preparing molecular based electrical conductive materials. TTF is an excellent electron donor to form charge transfer compound and exhibit electrical conductivity due to the delocalized π-bonding through the aromatic ring in TTF stacks.

Some transition metal complexes were also used as electron acceptors because the reduction potential of transition metal complexes can be readily modified by the change of chemical environments.

More recently, electrical conductive Tl(III)-tetracyanoquinodimethane (TCNQ) complexes with the formula of Tl (TCNQ)₃ and TlCl₂(TCNQ)₂.₅ were prepared and characterized.[2] The thermal properties were especially interesting in view that the ligand decomposition and reduction process of the central metal (Tl(III)→Tl(I)) were simultaneously occurred in both compounds above at 200 ℃. This observations imply that Tl(III) can be readily reduced to Tl(I) in the presence of appreciate reductants. This is accountable for the relatively high standard reduction potential of Tl(III)→Tl(I); $E^0 = +1.25$ V in aqueous solution. Therefore, we tried to prepare another electrical conductive charge transfer compounds using TTF electron donor with Tl(III)Cl₃ and Tl(II) (NO₃)₃ in this study.

Furthermore, TTF charge transfer compounds with TiX₄ (X=Cl, Br) were also prepared because [TiX₅⁻] anions are stabilized in solution even Ti(IV) complexes are not readily reduced comparing to Tl(III) complexes. The prepared compounds were characterized by spectroscopic, electrochemical methods, and by electrical conductivity, magnetic susceptibility measurements.

Experimental

Synthesis. (TTF)₃TiCl₅ compound was prepared as follows: A solution of 0.3 mmol of TiCl₄ in 20 mL of dichloromethane was added dropwise with stirring to 1 mmol of TTF dissolved in 10 mL of dichloromethane under argon atmosphere. The reaction mixture was stirred for *ca.* 4 hours at room temperature and then refrigerated overnight. The deep-purple powder was collected by filtration and dried over vacuum. (TTF)₄.₅TiBr₅ was obtained in a similar way using TiBr₄ in dichloromethane. Oxidation of TTF in ethanol with hydrated TlCl₃ and Tl(NO₃)₃ also yielded (TTF)₁.₅TlCl₃ and (TTF)₃Tl(NO₃)₃, respectively. All of the products are

found to be stable in the air. Elemental Analysis was performed by Korea Basic Science Center, Seoul, Korea. Anal. Calc. for (TTF)₃TiCl₅: C, 25.79; H, 1.43. Found: C, 25.36; H, 1.63. Calc. for (TTF)₄.₅TiBr₅: C, 23.72; H, 1.32. Found: C, 23.93; H, 1.33. Calc. for (TTF)₁.₅TlCl₃: C, 17.84; H, 0.92; S, 29.70. Found: C, 17.51; H, 0.98; S, 31.16. Calc. for (TTF)₃Tl(NO₃)₃: C, 23.40; H, 1.51; S, 44.03; N, 3.81. Found: C, 23.85; H, 1.33; S, 42.44; N, 3.82.

Physical Measurements. The electrical conductivities for Ti and Tl-TTF compounds were determined with the compressed pellets using two electrode system connected with a potentiostat at a room temperature.[3] Infrared spectra were obtained with standard KBr pelleting techniques by a Mattson Instruments Polaris FT-IR Spectrometer. The resolution was 4 cm⁻¹. Electronic absorption spectra were taken by using a Shimadzu UV-265 Spectrophotometer on solution or solid/nujol mulls between quartz plates. EPR Spectra were acquired on bulk and solution samples at 77 K and at room temperature using a Bruker Instruments ESP-300S ESR Spectrometer at X-band frequency (9.35 GHz). The complexes were dissolved in CH₂Cl₂/DMF (1 : 1) and then immediately frozen in liquid N₂. The field modulation frequency was 100 kHz.

Magnetic susceptibility data were collected from 5 to 300 K using MPMS7 (Magnetic Property Measurement System) of U.S.A. Quantum Design by SQUID method. The data were collected for temperature independent paramagnetism and for the diamagnetism an the constituent atoms using Pascal' constants.

Cyclic voltammetry was performed using a conventional three electrode system. The working electrode was a Pt disk of 1 mm in diameter. The working electrode was first polished with an alumina powder (0.3 micron) on a polishing cloth attached to a glass plate and rinsed throughly in an ultrasonic bath. The working electrode was inserted in a 0.5 M H₂SO₄ for the electrochemical pretreatment. A Pt wire was used as an auxiliary electrode. The reference electrode was an Ag wire immersed in 0.01 M AgNO₃, 0.1 M TEAP in acetonitrile. All the electrode potentials are reported relative to the Ag/Ag⁺ electrode of non-aqueous system. All the elctrochemical measurements were made with a BAS CV-50 W Voltammetric Analyzer and computer controlled with 50W Electrochemical Software (version : 1.0). The cell solution was made from 0.1 M TEAP/DMF, where TEAP was used as a supporting electrolyte.

Results and Discussion

The powdered electrical conductivities of all TTF-metal (Ti and Tl) compounds are in the order of 10^{-5}-10^{-6} S·cm⁻¹ as shown in Table 1. These values lie in the range of semiconductors, implying that the partially ionized (TTF)ₙ in each compound may be stacked in a low dimensional form. The low dimensional phenomena are discussed in spectroscopic and magnetic properties.

IR spectra of the prepared compounds exhibited very broad intense band in the range of 1,000-4,000 cm⁻¹, and a limited number of vibrational band of TTF in the TTF-metal salts were found in the absorption tail in the range of 400-1,400 cm⁻¹. The vibrational modes of these band were assigned by comparing the frequencies and intensities with

1168 *Bull. Korean Chem. Soc.* **1996**, Vol. 17, No. 12

Notes

Table 1. Physical Properties of TTF-metal compounds

Compounds	σ_{RT} (S·cm^{-1})	vibrational frequencies (cm^{-1})	Electronic frequencies (λ_{max}, nm)
(TTF)$_3$TiCl$_5$	7.16×10^{-5}	ν_{CCH}: 1074(w) ν_{CS}: 829(s) ν_{SCC}: 819(m)	316, 436, 579 (CH$_3$CN) 359, 531 (soild/nujol)
(TTF)$_{4.5}$TiBr$_6$	2.00×10^{-6}	ν_{CCH}: 1074(w) ν_{CS}: 830(s) ν_{SCC}: 818(m)	316, 435, 575 (CH$_3$CN) 358, 553 (soild/nujol)
(TTF)$_{1.5}$TlCl$_3$	4.37×10^{-5}	ν_{CCH}: 1088(w) ν_{CS}: 831(s) ν_{SCC}: 821(m)	317, 435, 578 (CH$_3$CN) 455, 537 (soild/nujol)
(TTF)$_3$Tl(NO$_3$)$_3$	5.69×10^{-5}	ν_{CCH}: 1072(w) ν_{CS}: 830(m) ν_{SCC}: 820(w)	318, 435, 579 (CH$_3$CN) 347, 544 (soild/nujol)

s; strong, m; medium, w; weak

reported spectra of one-dimensional TTF compounds.[4] The spectra assignments are listed in Table 1. The observed values of ν_{15} (ν_{CCH} bending), ν_{16} (ν_{CS} stretching), and ν_{25} (ν_{SCC} bending) modes are between those reported for the TTF molecule (ν_{15}: 1090, ν_{16}: 781, ν_{25}: 794 cm^{-1}) and the TTF free radical (ν_{15}: 1072, ν_{16}: 836, ν_{25}: 825 cm^{-1}). Inoue *et al.*[5] pointed out a linear relationship between the shift in the ν_{16} band and the charge on TTF in TTF-metal compounds. The shifting of ν_{15}, ν_{16} and ν_{25} modes may support the partial oxidation of the TTF molecule.

Electronic spectra of the TTF-metal compounds were recorded in the range of 200-800 nm in both solution and solid state. The results are also summarized in Table 1. The absorption maxima (λ_{max}) of the TTF radical are shown at 340, 435 and 575 nm in H$_2$O and that of neutral TTF molecule exhibited only at 310 nm.[6] These electronic transitions are comparable to the results observed from the TTF-metal salts in this work and such low-energy absorption bands are usually come from the spectra of conjugated π-molecular radicals with intramolecular interaction.[7] TTF^{2+} ion shows a characteristic frequency at 445-460 nm in the solid state.[8] In this work, the λ_{max} in (TTF)$_{1.5}$TlCl$_3$ complex exhibits at 455 nm. This supports that (TTF)$_{1.5}$TlCl$_3$ is regarded as a similar composition of the material containing dicationic TTF^{2+}.

EPR spectra were obtained by using powdered samples at room temperature and 77 K. The EPR line shapes for each compounds exhibited good resolutions of parallel ($g_{\parallel}$) and perpendicular ($g_{\perp}$) components at 77 K. The physical parameters of EPR are summarized in Table 2. The average $\langle g \rangle$ values of these compounds are similar to $\langle g \rangle = 2.00838$ of TTF$^+$ radical in solution[6] and that of TTF-copper halide salts containing partially ionized (TTF)$_n$ entity.[5] This means that the $\langle g \rangle$ values of the EPR signal is arisen from the unpaired electrons distributed on TTF. A signal attributed to metal ions was not detected in any compounds. The observed $\langle g \rangle$ values and the absence of metal ion signals are strongly indicated that any unpaired electrons resided on TTF radicals and the metal atoms in TTF-Tl compounds exist in diamagnetic Tl(I) ($d^{10}s^2$) and Ti(IV) (d^0) state. There-

Table 2. EPR parameters and magnetic properties of powdered samples of TTF-metal compounds

Compounds	EPR parameters				Magnetic moment[c] (BM)
	$\langle g \rangle$[a]	$g_{\parallel}$[a]	$g_{\perp}$[a]	EPR linewidth[b] (Gauss)	
(TTF)$_3$TiCl$_5$	2.0043	2.0090	2.0019	6	0.88
(TTF)$_{4.5}$TiBr$_6$	2.0062	2.0100	2.0047	8	1.09
(TTF)$_{1.5}$TlCl$_3$	2.0040	2.0079	2.0020	7	0.70
(TTF)$_3$Tl(NO$_3$)$_3$	2.0045	2.0090	2.0022	3	0.83

[a] the listed g values were measured at 77 K. [b] the values are peak to peak linewidth (ΔH_{pp}). [c] the magnetic momenta were obtained at room temp.
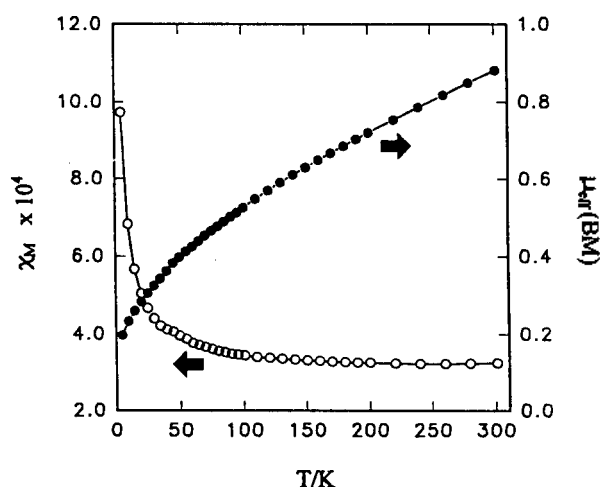
Figure 1. Temperature dependence of the magnetic susceptibility (χ_M) and magnetic effective moment (μ_{eff}) of (TTF)$_3$TiCl$_5$.

fore we can propose that the formula of (TTF)$_3$TiCl$_5$ and (TTF)$_{4.5}$TiBr$_6$ are presumed as [Ti^{IV}Cl$_5$]$^-$ and [Ti^{IV}Br$_5$]$^-$, whereas (TTF)$_{1.5}$TlCl$_3$ and (TTF)$_3$Tl(NO$_3$)$_3$ as [Tl^{I}Cl$_3$]$^{2-}$ and [Tl^I(NO$_3$)$_3$]$^{2-}$, respectively.

The temperature dependence of the magnetic susceptibility (χ_M) for (TTF)$_3$TiCl$_5$ is shown in Figure 1. χ_M is almost temperature- independent and rapidly changes down to 10-20 K as Curie-like tail, but the data do not follow the Curie law. This weak temperature-independent paramagnetism may come from the strong interactions between the stacks of TTF. The effective magnetic moments (μ_{eff}) decrease gradually as decreasing the temperature as shown Figure 1, which are small values compared to that of single unpaired electron (1.73 BM). This relatively small values and the temperature independent paramagnetism provide the evidence of the significant magnetic interaction between the unpaired electron resides on the TTF stacks. Such interstack interactions are also supported by the narrow EPR linewidths. Linewidths below *ca.* 15 Gauss are usually expected in low-dimensional TTF compounds due to the spin-orbit interaction of sulfur in TTF columnar chains.

Cyclic voltammograms of TTF and TTF-metal (Ti and Tl) complexes were performed in dimethylformamide (DMF)/0.1 M tetraethyl-ammonium perchlorate (TEAP) using an Ag/
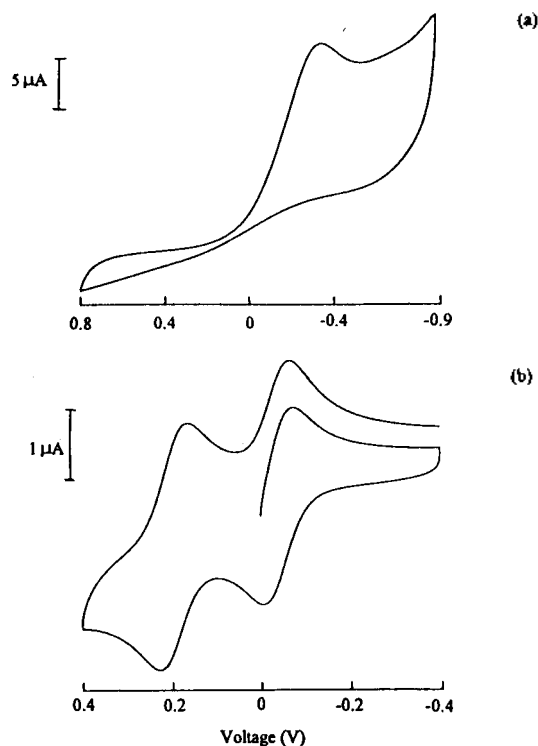
Notes

Bull. Korean Chem. Soc. **1996**, Vol. 17, No. 12 **1169**

Figure 2. Cyclic voltammograms of (a) 5×10^{-4} M $Tl(NO_3)_3$ and (b) 5×10^{-4} M $(TTF)_{3.5}Tl(NO_3)_3$ obtained in 0.1 M TEAP/DMF at the scan rate of 100 mV/s.

Ag^+ reference electrode. The mid-peak potentials $(E_{1/2})$ of the complexes were estimated by averaging the anodic and cathodic peak potentials. The i-V curve of $Tl(NO_3)_3$ shows only cathodic wave, but not for anodic process as shown in Figure 2. This is responsible for the fact that Tl(I) state is much more stable than Tl(III) state. Thus redox couples are irreversible process. However, cyclic voltammogram of $(TTF)_3Tl(NO_3)_3$ complex exhibited two waves at -0.05 V (TTF^+/TTF^0) and $+0.20$ V (TTF^{2+}/TTF^+) as shown in Figure 2. Similar results were observed for other TTF compounds in this work. The peaks related to metals (Ti and Tl) were not detected, hence redox processes of the complexes may be localized to the ligands rather than the metal center. The observed $E_{1/2}$ value of TTF were -0.05 and $+0.20$ V. These values are assigned to TTF^+/TTF^0 and TTF^{2+}/TTF^+ couples, respectively and support the assignment in all compounds. Thin films of TTF polymer also show two waves at nearly the same potentials.[9] The values of E_{pa} and E_{pc} should be identical for simple reversible couple, $E_{pa}/E_{pc} = 1$.[10] The values of E_{pa}/E_{pc} were nearly equal to 1. Cyclic voltammograms were scanned several times and there was no change in the appropriated ranges of the potentials. This result means that the redox couples are quite reversible.

Conclusion

$(TTF)_3TiCl_5$, $(TTF)_{4.5}TiBr_5$, $(TTF)_{1.5}TlCl_3$, and $(TTF)_3Tl(NO_3)_3$

charge transfer compounds were prepared from the reaction of TTF with TiX_4 (X=Cl and Br), TlX_3 (X=Cl and NO_3). The experimental results reveal that TTF is partially ionized and stacked in low-dimensional chain in each compound. The absence of metal ion signals in EPR and the magnetic susceptibility measurements support the diamagnetic Ti(IV) and Tl(I) oxidation state, indicating that charge transfer has occurred from $(TTF)_n$ to Tl(III) center in TTF-Tl compounds and to the $-TiX_4^-$ entity in TTF-Ti compounds. This results are responsible for the fact that Tl(III) compounds are strong oxidants and are easily reduced to the $+1$ oxidation state, whereas titanium chloro- and bromo-anions, $[TiX_5]^-$ can be obtained by interaction of TiX_4 with other cations in solution.[11] Kondo K. *et al* also reported $(TTF)_n[SnX_6]$ (X=Cl, Br) compounds were made from the reaction of TTF and SnX_4 as a result of the stable SnX_6^{2-} anion in solution.[12] This synthetic results could be used to presume and design the electrical conductive TTF compounds with prescribed electrochemical properties.

References

1. (a) Kim, Y. I.; Hatfield, W. E. *Inorg. Chim. Acta*, **1991**, *188*, 15. (b) Kim, Y. I.; Hatfield, W. E. *Inorg. Chim. Acta*, **1991**, *188*, 237. (c) Kim, Y. I.; Hatfield, W. E. *Inorg. Chim. Acta*, **1993**, *204*, 261. (d) Kim, Y. I.; Choi, S. N.; Jung, W. S. *Bull. Kor. Chem. Soc.* **1994**, *15*, 465. (e) Kim, Y. I.; Choi, S. N.; Jung, W. S. *Bull. Kor. Chem. Soc.* **1995**, *16*, 69.
2. Kim, M. K.; Kim, Y. I.; Moon, S. B.; Choi, S. N. *Bull. Kor. Chem. Soc.* **1996**, *17*, 424.
3. Moon, S. B.; Kim, Y. I. *Bull. Kor. Chem. Soc.* **1995**, *16*, 511.
4. Bozio, R.; Zanon, I.; Girlando, A.; Pecile, C. *J. Chem. Phys.* **1979**, *71*, 2282.
5. Inoue, M. B.; Inoue, M.; Fernando, Q.; Nebesny, K. W. *Inorg. Chem.* **1986**, *25*, 3976.
6. Wudl, F.; Smith, G. M.; Hufngel, E. J. *J. Chem. Soc., Chem. Commun.* **1970**, 1453.
7. Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B.* **1979**, *19*, 730.
8. Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of stable Free Radicals*; Academic: New York, 1968; p 352.
9. Coffen, L. D.; Chambers, J. Q.; Williams, D. R.; Garett, P. E.; Canfied, N. D. *J. Am. Chem. Soc.* **1971**, *93*, 2258.
10. Kaufmann, F. B.; Schroeder, A. H.; Engler, E. M.; Kramer, S. R.; Chambers, J. Q. *J. Am. Chem. Soc.* **1980**, *102*, 483.
11. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley& Sons: New York, 1988.
12. Kondo, K.; Matsubayashi, G-E.; Tanaka, T.; Yoshioka, H. *J. Chem. Soc., Dalton Trans.* **1984**, 379.