

Synthesis and Characterization of Bis(ethylenedithio)tetrathiafulvalene Charge Transfer Compounds with Gold, Platinum and Osmium Chloride

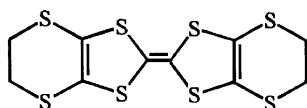
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Recently, we reported the tetrathiafulvalene (TTF) compounds with the hydrogen metal chlorides with the general formula $(\text{TTF})_m\text{MCl}_n$ ($M = \text{Au, Pt, Ir, Os}$).¹ It was reported that the charge transfer occurred from TTF to the metal during the reaction and the powdered electrical conductivities of the reported compounds were in the range of semiconductor ($\sigma_{RT} = 10^{-3} \sim 10^{-5} \text{ S} \cdot \text{cm}^{-1}$). Such electrical conductivities were explicated on the basis of the delocalized electrons over the TTF lattices in each compound.

Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), another modification of the TTF molecule, is also a significant electron donor to the formation of highly conductive charge transfer compounds. Its salts exhibit a wide variety of electrical conductivities depending on the anion present in the material.²



BEDT-TTF

Some of the BEDT-TTF salts exhibited superconductivity at low temperature.² For example, β -(BEDT-TTF)₂I₃ has been known as the first organic superconductor with $T_c = 1.5 \text{ K}$ and κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl was also found to be a superconductor with $T_c = 12.8 \text{ K}$.

In this work, BEDT-TTF compounds with some hydrogen transition metal (gold, platinum, and osmium) chlorides were prepared and compared to TTF compounds. The prepared charge transfer compounds were characterized by electrical conductivity, spectroscopic (IR, UV-Vis, and EPR), magnetic (magnetic susceptibility) and electrochemical (CV) methods.

Experimental Section

BEDT-TTF, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and H_2OsCl_6 were purchased from Aldrich and used without further purification. All solvents used were reagent grade. All reactions were carried out under argon atmosphere in a glove box.

$(\text{BEDT-TTF})_{2.5}\text{AuCl}_2$ was prepared by the direct reaction of BEDT-TTF and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$. $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.3 mmol) was dissolved in 10 mL of acetonitrile (CH_3CN). $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solution was added dropwise to excess BEDT-TTF (1.0 mmol) dissolved in 25 mL of acetonitrile

with constant stirring under an argon atmosphere. The reaction solution changed to dark brown immediately. The reaction mixture was stirred for *ca.* 2 hours, and then refrigerated overnight. The resultant purple precipitates were collected by filtration and washed several times with acetonitrile. The microcrystalline precipitates were dried in a vacuum oven at room temperature. Pt and Os compounds were also prepared by a similar method, using $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ and H_2OsCl_6 in CH_3CN .

Elemental analyses were performed by Korean Basic Science Center (E.A. 1108 Elemental Analyzer).

Anal. Calc. for $(\text{BEDT-TTF})_{2.5}\text{AuCl}_2$: C, 24.78; H, 1.74; S, 51.12. Found: C, 24.46; H, 1.64; S, 52.14. Calc. for $(\text{BEDT-TTF})_3\text{PtCl}_4 \cdot 2\text{H}_2\text{O}$: C, 26.79; H, 2.02; S, 56.02. Found: C, 26.20; H, 1.94; S, 55.85. Calc. for $(\text{BEDT-TTF})_2\text{OsCl}_4 \cdot \text{CH}_3\text{CN}$: C, 22.87; H, 1.99; S, 44.10. Found: C, 23.15; H, 1.68; S, 44.85.

The powdered electrical conductivity was determined by compressing the bulk sample between two graphite rods (5 mm in diameter) surrounded by a glass tube sheath³ and measured with a EG G Model 362 potentiostat in a two electrode configuration at room temperature. EPR spectral measurements were made on powdered samples at 77 K, using a ESP-300S EPR spectrometer at X-band frequency. The field modulation frequency was 100 kHz and DPPH was used as reference. Magnetic susceptibility data were collected from 4 K to 300 K using MPMS7 (Magnetic Property Measurement System) of U.S.A. Quantum Design by the SQUID method. The data were corrected for temperature independent paramagnetism and for the diamagnetism of the constituent atoms, using Pascal's constants.⁴ Solid IR spectra ($400\text{--}4,000 \text{ cm}^{-1}$) were obtained by using potassium bromide (KBr) pellets with a Polari's FI-IR spectrometer. Electronic absorption spectra (200–1,100 nm) were recorded on a Shimadzu 1601PC spectrophotometer in solution or in solid/nujol state. Cyclic voltammograms were recorded on a Bio Analytical Systems CV-50W Voltammetric Analyzer. Cyclic voltammetric measurements were carried out in DMF solution, using a three electrode system. The working electrode was a platinum electrode and the reference electrode was an Ag/Ag^+ (0.01 M $\text{AgNO}_3/0.1 \text{ M TEAP}$ in CH_3CN solution) electrode. A platinum wire was used as an auxiliary electrode. Tetraethylammonium perchlorate (0.1 M) was used as the supporting electrolyte, and the concentrations of metal complexes were in the range of 10^{-3} – 10^{-4} M .

Table 1. The electrical conductivities, EPR parameters and magnetic properties of powdered (BEDT-TTF)_mMCl_n compounds

Compound	σ_{RT}^a (Scm ⁻¹)	EPR parameters		Magnetic moment ^d (BM)
		g value ^b	ΔH_{pp}^c	
(BEDT-TTF) _{2.5} AuCl ₂	1.25×10^{-4}	$g_{\parallel} = 2.014$ $g_{\perp} = 2.007$	20.7	1.07
(BEDT-TTF) ₃ PtCl ₄ ·2H ₂ O	1.43×10^{-2}	$\langle g \rangle = 2.008$	34.5	1.13
(BEDT-TTF) ₂ OsCl ₄ ·CH ₃ CN	6.24×10^{-4}	$\langle g \rangle = 2.004$	19.0	1.21

^aThe powdered electrical conductivity was obtained at room temperature.

^bThe listed g values were measured at 77 K. ^cThe values are peak-to-peak linewidth (Gauss). ^dThe magnetic moments were measured at room temperature.

Results and Discussion

The *d.c.* experimental powdered electrical conductivities at room temperature (σ_{RT}) are 10^{-2} – 10^{-4} S · cm⁻¹ as listed in Table 1. The conductivities of powdered samples are usually smaller than the conductivities of single crystals by a factor of 10^2 – 10^3 due to the interparticle contact resistance effects.⁵ In view of this effect, the electrical conductivities of the prepared compounds are in the range of semiconductor, and these relatively high conductivities are expected for the low-dimensional phenomena of the oxidized BEDT-TTF radicals.

The EPR spectra were obtained for powdered samples at 77 K. The results are summarized in Table 1, and the X-band EPR spectra of powdered samples are shown in Figure 1. The peak-to-peak linewidths are in the range of 19–35G, which is similar to the range of TTF-Fe^{II}X₃ compounds (~25G).⁶ Such relatively narrow linewidths indicate that the interaction along the BEDT-TTF stacks are significant, reflect-

ing the low-dimensional character of the materials.⁶ The EPR spectrum of a powdered (BEDT-TTF)_{2.5}AuCl₂ exhibits an unsymmetrical shaped spectrum with $g_{\parallel} = 2.014$ and $g_{\perp} = 2.007$. This value is nearly equal to the values observed for some salts containing BEDT-TTF donor, which shows $g = 2.000$ – 2.014 .^{7–9} The EPR spectra of (BEDT-TTF)₃PtCl₄ and (BEDT-TTF)₂OsCl₄ · CH₃CN exhibit symmetrical curves with $\langle g \rangle = 2.008$ and $\langle g \rangle = 2.004$, respectively. These observed g values indicate that the EPR signals arose from unpaired electrons distributed on BEDT-TTF. The EPR signals attributed to metal ions were not detected, implying that the metal atoms are diamagnetic.

The temperature dependence of each magnetic susceptibility from 4 K to 300 K is shown in Figure 2. The magnetic susceptibility increases very slightly as the temperature decreases, increasing sharply at low temperature with a Curie-like tail. But the data are not described by $(T) - C/T$ of Curie law. However, the temperature dependence of the magnetic susceptibility is somewhat weaker than in Curie law. This weak temperature dependence implies that the unpaired electrons are delocalized over BEDT-TTF spin lattices. Moreover, the effective magnetic moments (μ_{eff}) are observed to be 1.1–1.2 BM, which is less than the spin-only value of 1.73 BM for one unpaired electron. The somewhat smaller magnetic moments are probably due to the delocalization of the unpaired electron over the BEDT-TTF radicals^{10,11} and indicate that the oxidation states of metal ions are diamagnetic. The oxidation states of metal ions are expected to be low-spin diamagnetic Au(I) d¹⁰, Pt(II) d⁸, and Os(II) d⁶ electronic configuration.

The infrared spectra of the prepared compounds were examined in the range of 400–4,000 cm⁻¹. The frequencies were analyzed by a comparison with BEDT-TTF and the

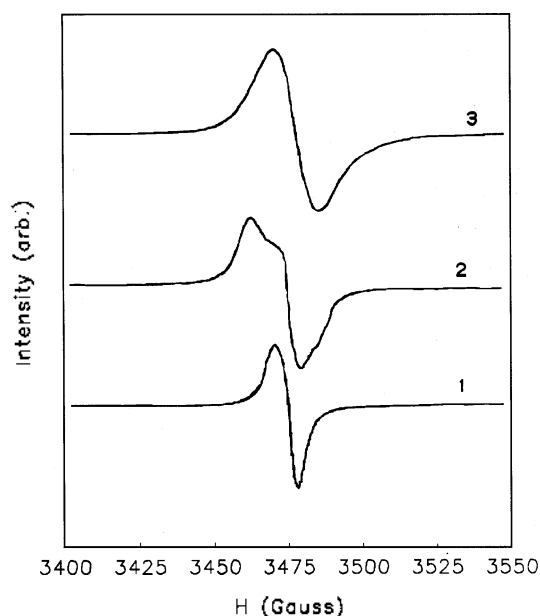


Figure 1. The X-band EPR spectra of BEDT-TTF metal chloride compounds in powdered sample at 77 K. 1: (BEDT-TTF)₂OsCl₄ · CH₃CN, 2: (BEDT-TTF)_{2.5}AuCl₂, 3: (BEDT-TTF)₃PtCl₄ · 2H₂O.

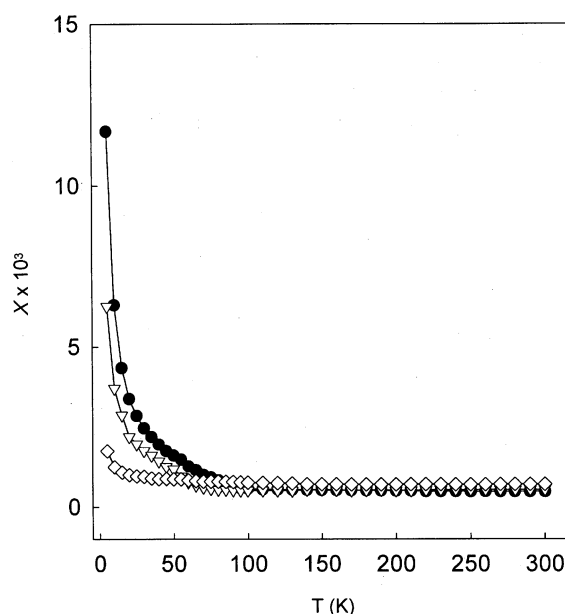


Figure 2. Temperature dependence of magnetic susceptibility for (BEDT-TTF)_mMCl_n compounds. ● : (BEDT-TTF)_{2.5}AuCl₂, △ : (BEDT-TTF)₃PtCl₄ · 2H₂O, ◇ : (BEDT-TTF)₂OsCl₄ · CH₃CN.

Table 2. Vibrational and electronic absorption of BEDT-TTF metal compounds

Compound	Vibrational mode	λ_{max} (nm)
BEDT-TTF	2963(ν_{60}), 2922(ν_{26}), 1422(ν_{28}), 1410(ν_{45}), 1285(ν_{29}), 1262(ν_{46}), 1175(ν_{21}), 1126(ν_{67}), 999(ν_{30}), 918(ν_{48}), 891(ν_{49}), 772(ν_{32}), 500(ν_{34})	267, 324, 477, 848 (DMF) 481, 1003 (solid/nujol)
(BEDT-TTF) I_3^{H}	2947(ν_{60}), 2914(ν_{26}), 1418(ν_{28}), 1410(ν_{45}), 1401, 1331(vibronic), 1282(ν_{29}), 1275(ν_{46}), 1169(ν_{21}), 1119(ν_{67}), 998(ν_{30}), 922(ν_{48}), 888(ν_{49}), 810(ν_{32}), 498(ν_{34})	
(BEDT-TTF) $_2$.5AuCl $_2$	2961(ν_{60}), 2922(ν_{26}), 1408(ν_{45}), 1344(vibronic), 1285(ν_{29}), 1262(ν_{46}), 1175(ν_{21}), 1127(ν_{67}), 999(ν_{30}), 918(ν_{48}), 889(ν_{49}), 772(ν_{32}), 492(ν_{34})	268, 325, 457, 483, 580, 973 (DMF) 414, 538, 801 (solid/nujol)
(BEDT-TTF) $_5$ PtCl $_4$	2964(ν_{60}), 2922(ν_{26}), 1397, 1337(vibronic), 1279(ν_{29}), 1258(ν_{46}), 1175(ν_{21}), 1127(ν_{67}), 1000(ν_{30}), 920(ν_{48}), 880(ν_{49}), 772(ν_{32}), 488(ν_{34})	271, 322, 454, 485, 976 (DMF) 406, 512, 973 (solid/nujol)
(BEDT-TTF) $_2$ OsCl $_4$	2963(ν_{60}), 2922(ν_{26}), 1400(ν_{45}), 1331(vibronic), 1283(ν_{29}), 1263(ν_{46}), 1175(ν_{21}), 1127(ν_{67}), 999(ν_{30}), 918(ν_{48}), 889(ν_{49}), 772(ν_{32}), 500(ν_{34})	267, 326, 345, 424, 487, 965 (DMF) 411, 496, 846 (solid/nujol)

^areference 15.

reported BEDT-TTF radical compounds¹² based on D_{2h} symmetry of BEDT-TTF molecule. The vibrational modes and their assignments are listed in Table 2.

The prepared BEDT-TTF compounds show a broad, intense band extending to *ca.* 1400 cm^{-1} . A similar band was observed for some conducting TTF compounds.¹³ The strong bands at 1410-1330 cm^{-1} are interpreted as vibronic bands, which are related with the interaction between electronic states and intramolecular vibrations. Kozlov *et al.*¹² reported that the pair of vibronic transitions appeared at 1401 cm^{-1} and 1331 cm^{-1} in the IR spectrum of (BEDT-TTF) I_3 . This pair was probably related with the symmetric vibrations of the ring and central C-C bands in BEDT-TTF. The pair of vibronic bands in (BEDT-TTF) $_5$ PtCl $_4$ is observed at 1397 cm^{-1} and 1337 cm^{-1} . In (BEDT-TTF) $_2$.5AuCl $_2$ and (BEDT-TTF) $_2$ OsCl $_4$, only one vibronic band is observed at 1344 cm^{-1} and 1331 cm^{-1} , respectively, as shown in Figure 3. This appearance of the vibronic bands supports the conclusion that BEDT-TTF

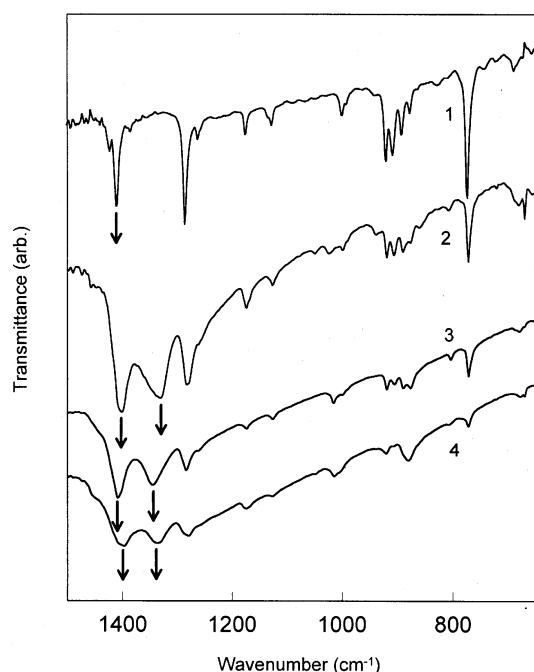


Figure 3. The vibrational spectra BEDT-TTF compounds. 1: BEDT-TTF; 2: (BEDT-TTF) $_2$.5OsCl $_4$ · CH $_3$ CN; 3: (BEDT-TTF) $_2$.5AuCl $_2$; 4: (BEDT-TTF) $_5$ PtCl $_4$.

radical molecular orbitals are partially overlapped and the unpaired electrons are distributed between the adjacent BEDT-TTF radical molecules.¹² It may provide the pathway for the electrical conductivity along these BEDT-TTF radical molecules. The vibronic bands are absent from the IR spectrum of the neutral BEDT-TTF molecule.

Electronic spectra were recorded from 200 nm to 1100 nm both in DMF solution and solid/nujol state. The results are also summarized in Table 2. The characteristic broad absorptions are observed at around 970 nm, although the absorptions are not analyzed in this study. According to Torrance *et al.*,¹⁴ the band in this lower energy region is related with an intermolecular excitation, which is impossible in the isolated molecule.

Cyclic voltammograms were recorded in DMF/0.10 M TEAP from 0.0 to +0.6 V versus an Ag/Ag $^+$ in 0.01 M AgNO $_3$ /0.1 M TEAP CH $_3$ CN solution electrode. The results are given in Table 3. In the cyclic voltammogram of (BEDT-TTF) $_2$.5AuCl $_2$, mid-peak potentials are evaluated at +0.16 V ($E_{\text{pc}} = 0.15$, $E_{\text{pu}} = 0.18$ V) for BEDT-TTF $^{\cdot+}$ /BEDT-TTF couple and at +0.29 V ($E_{\text{pc}} = 0.27$, $E_{\text{pu}} = 0.31$ V) for BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$ couple. The voltammogram of BEDT-TTF exhibits similar values: one at +0.20 V for BEDT-TTF $^{\cdot+}$ /BEDT-TTF couple, and the other at +0.32 V for BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$ couple. Similar results were observed for the other BEDT-TTF-Pt and Os chloride compounds. A peak attributable to the metal was not detected in any case, and hence oxidation/reduction of the prepared compounds is mainly localized to BEDT-TTF radicals rather than the

Table 3. The peak potential values (E_p) versus Ag/Ag $^+$ for BEDT-TTF metal compounds in DMF solution

Compound	E_{pc} (V)	$E_{\text{t}2}$ (V)	E_{pa} (V)	Process
BEDT-TTF	0.17	0.20	0.22	BEDT-TTF $^{\cdot+}$ /BEDT-TTF
	0.29	0.32	0.35	BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$
(BEDT-TTF) $_2$.5AuCl $_2$	0.15	0.16	0.18	BEDT-TTF $^{\cdot+}$ /BEDT-TTF
	0.27	0.29	0.31	BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$
(BEDT-TTF) $_5$ PtCl $_4$	0.12	0.15	0.17	BEDT-TTF $^{\cdot+}$ /BEDT-TTF · 2H $_2$ O
	0.25	0.28	0.30	BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$
(BEDT-TTF) $_2$ OsCl $_4$	0.18	0.20	0.21	BEDT-TTF $^{\cdot+}$ /BEDT-TTF · CH $_3$ CN
	0.31	0.34	0.36	BEDT-TTF $^{2+}$ /BEDT-TTF $^{\cdot+}$

metal center. The π -donor abilities of BEDT-TTF ($E_{12} = +0.20$ V) are smaller than that of TTF ($E_{12} = \sim 0.0$ V).¹⁵ This leads to a smaller charge transfer with metal chlorides in BEDT-TTF compounds than in TTF compounds and hence should decrease the band occupancy.¹⁶

Summary

Charge transfer compounds (BEDT-TTF)₂·₅AuCl₂, (BEDT-TTF)₅PtCl₄·2H₂O, (BEDT-TTF)₂OsCl₄·CH₃CN were prepared from the reaction of BEDT-TTF and the corresponding hydrated hydrogen metal chloride. The experimental results reveal considerable interstack interactions between the oxidized BEDT-TTF radical cations, providing a pathway for the electrical conductivity. The room temperature electrical conductivities of BEDT-TTF metal halides ($\sigma_{RT} = 10^{-2} \sim 10^{-4}$) are somewhat higher than those of the corresponding TTF compounds ($\sigma_{RT} = 10^{-3} \sim 10^{-5}$).¹ This observation may be explained by the more favorable polarizability and band occupancy conditions caused by π -donor BEDT-TTF.

Evidence for this suggestion may be obtained from a structural determination by X-ray crystallography. We have not yet obtained crystals of this quality from our experiments.

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