



## Structural Analysis and Single-Crystal EPR Study of Dimeric Cu(I) Complex with TTF Derivative

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**Abstract** : A Cu(I) complex with an asymmetric TTF derivative (CET-EDTTTF) is prepared from the slow-diffusion method using CET-EDTTTF and Cu(I)Br solutions and characterized by X-ray crystallography and EPR spectroscopy. Structural analysis shows Cu(I) ions are tetrahedrally coordinated to two bridging bromides, one terminal bromide, and one S atom from CET-EDTTTF. Detailed geometrical and EPR analysis identified that the dimer molecule contains  $[\text{Cu}_2\text{Br}_4]^{2-}$  anion between two  $[\text{CET-EDTTTF}]^+$  radical cations. Single-crystal EPR investigation of the complex reveals that the  $g$ -anisotropy is unusually big, compared to those of the previously reported TTF<sup>+</sup> cation radicals, implying that there is significant contribution of the Cu d-orbital to the HOMO of the complex.

Key words: Cu(I) complex, TTF-derivative, Radical cation, Crystal EPR

### INTRODUCTION

Great efforts are being made to create new materials with conducting, superconducting, magnetic, and optical properties.<sup>1</sup> TTF (tetrathiafulvalene)-based molecules are one of the central interests in such materials since the observation of metallic properties in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane).<sup>1</sup> Transition metal-TTF hybrids have appeared to exhibit both magnetic and conducting properties.<sup>2</sup> In this research, we extend the search for such material using Cu and an asymmetric TTF-unit.

Cu(II) halides, as an oxidant, with TTF and its derivatives can generate a variety of

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charge-transfer complexes of which structural and physical properties are quite unique. We synthesize a Cu(I) complex with an asymmetric TTF derivative (CET-EDTTTF; 4-Cyanoethylthio-4',5'-ethylenedithiotetrathiafulvalene) using diffusion method.<sup>3</sup> Its crystal structure shows a noble dimeric  $[\text{Cu(I)Br}_2(\text{CET-EDTTTF})]_2$  complex and EPR (electron paramagnetic resonance) reveals the existence of TTF-based cation radical. In the present study, we also carry out single crystal EPR study to further understand the fused d (metal) -  $\pi$  (ligand) electronic structure of the complex.

## Experimental

### Synthesis of 4-Cyanoethylthio-4',5'-ethylenedithiotetrathiafulvalene CET-EDTTTF

4-cyanoethylthio-1,3-dithiole-2-thione (CET-DTT)<sup>1</sup> (220 mg, 1 mmol) and 4,5-ethylenedithio-1,3-dithiole-2-one (EDT-DTO)<sup>2</sup> (208 mg, 1 mmol) was dissolved in freshly distilled  $\text{P}(\text{OEt})_3$  (8 mL) and refluxed for 1 h under Ar. The brown solution was cooled to room temperature and the dark orange precipitate was filtered, washed with methyl alcohol and dried in air. After that, the solvent of filtrate was removed by evaporation. The product was then easily separated by column chromatography ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) due to the high polarity of cyanoethyl group. Yield: 72%, m.p: 121 °C FT-IR (KBr,  $\text{cm}^{-1}$ ) : 3064 (=CH), 2929 (- $\text{CH}_2\text{CH}_2$ ), 2248 ( $\text{C}\equiv\text{N}$ ), 1655, 1637 ( $\text{C}=\text{C}$ ), 1421 ( $\text{CH}_2\text{S}$ ) UV ( $\text{CH}_3\text{CN}$ , nm) : 208 st, 248 m, 310 m, 328 sh <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 500 MHz)  $\delta$  : 6.56 (s, 1H), 3.29 (s, 4H), 2.97 (t, 2H,  $J$  7.0 Hz), 2.69 (t, 2H,  $J$  7.0 Hz).

### Preparation of $[(\text{CET-EDTTTF})\text{CuBr}_2]_2$

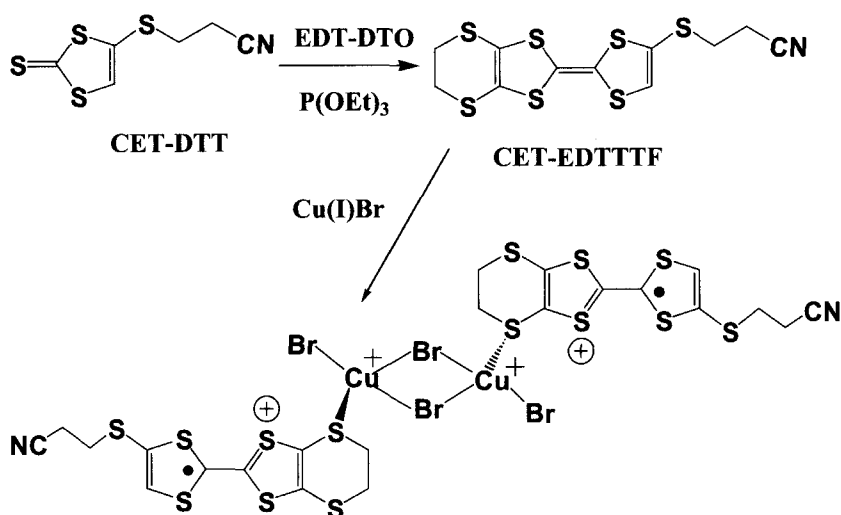
A solution of Cu(I)Br in acetonitrile (25 mM, 2 mL) was poured slowly along the wall of tube into a 0.025 M solution of the TTF derivative (2 mL) in methylene chloride. The reaction occurs immediately at the interface of both solutions. After standing for 7 days in the dark,  $[(\text{CET-EDTTTF})\text{CuBr}_2]_2$  were isolated as black crystals. Yield : 35% FT-IR (KBr,  $\text{cm}^{-1}$ ) : 3051(=CH), 2962, 2860(-CH), 2250 ( $\text{C}\equiv\text{N}$ ), 1654, 1637 ( $\text{C}=\text{C}$ ), 1436( $\text{CH}_2\text{S}$ ), 1345, 1291 ( $\text{C}=\text{C}$ ) Anal. Calc.: C, 21.91; H, 1.50; N, 2.32; S 37.22, Found : C, 22.23; H, 1.65; N, 2.39; S 35.28

### X-ray crystallography

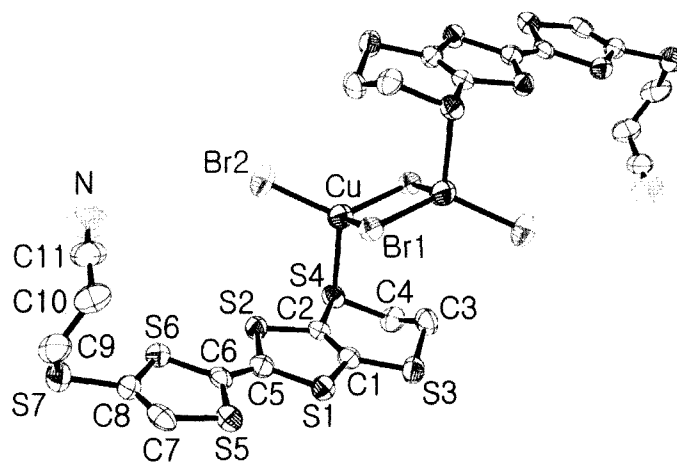
X-ray diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293(2)K. The Structures were solved and refined using SHELXS-86 and SHELXS-93. Hydrogen atoms were theoretically added and included in the final refinement.

### EPR Spectroscopy

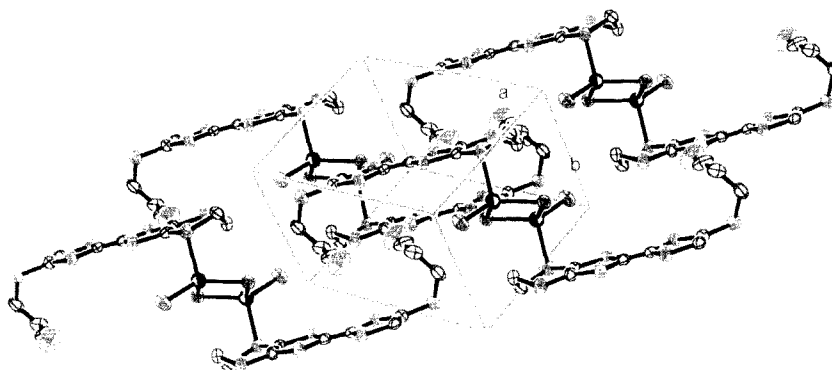
X-band (9 GHz) EPR spectra were recorded on Jeol JES-TE300 ESR spectrometer using 100 kHz field modulation. Low temperature spectra were obtained using Jeol ES-DVT3 variable temperature controller.



Scheme 1



(a)



(b)

Fig. 1. (a) Crystal Structure of  $[(\text{CET-EDTTTF})\text{CuBr}_2]_2$  and (b) unit cell.

## Results and Discussion

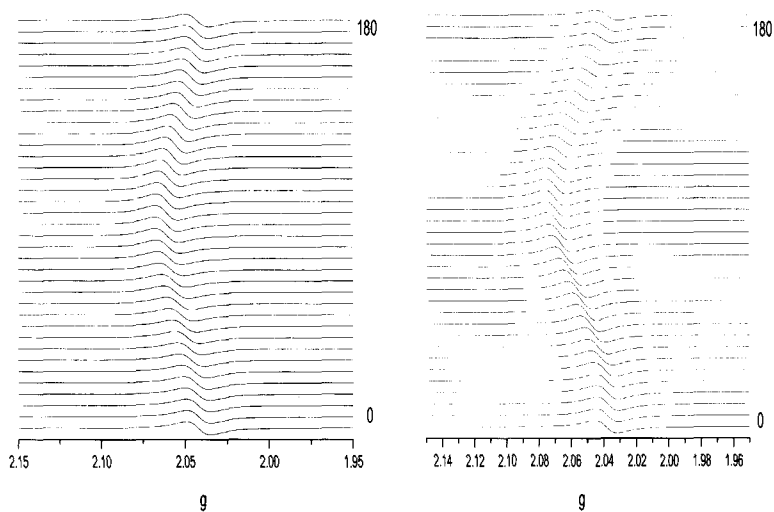
The synthetic step of CET-DTT and general coupling reaction<sup>4</sup> for preparing CET-EDTTTF are illustrated in **Scheme 1**. When CET-EDTTTF was prepared, the equimolar amount of thione (CET-DTT) and oxo-compound (EDT-DTO) was used to be a 0.25 M solution entirely and obtained in high yield. Triethylphosphite used was distilled just prior to use and the precursor of TTF derivative (CET-DTT) was synthesized according to the literature method.<sup>5</sup>

The fine black crystals of Cu(I) complex were prepared by the diffusion method using solutions of TTF unit and Cu(I)Br (**Scheme 1**). The product was not soluble in any common organic solvents. The structure of Cu(I) complex as shown in Fig. 1 is dimeric with the coordination geometry about the metal center distorted from tetrahedral geometry. The centro-symmetric molecule consists of a  $\text{Cu}_2\text{Br}_4$  core located between two CET-EDTTTF cations. In  $[\text{Cu}_2\text{Br}_4]^{2-}$  core, the copper atom is coordinated to the two bridging bromine atoms, one terminal bromine atom and one sulfur atom. A similar feature is also observed in  $[\text{TTF}]_2\text{Cu}_2\text{Br}_4 \cdot 2\text{CH}_2\text{Cl}_2$  where  $[\text{TTF}]$  is the S-position isomer of ethylenedithiodimethylthiotetrathiafulvalene(EDT-DMT-TTF).<sup>6</sup>

The Cu-S bond (C2-S4-Cu :  $98.5^\circ$ , C4-S4-Cu:  $109.5^\circ$ ) is roughly perpendicular to mean plane of CET-EDTTTF ligand, and the dimer molecules are parallel to one another as shown in Fig. 1. The bond angles around a copper atom are  $103\text{--}107^\circ$  (Br#1-Cu-Br1, S4-Cu-Br1 and Br2-Cu-S4),  $112.61^\circ$  (Br2-Cu-Br#1) and  $122.48^\circ$  (Br2-Cu-Br1), which indicates that the geometry around a copper atom is a distorted tetrahedron. In addition, the Cu-Br<sub>terminal</sub> bond (2.373 Å) is slightly shorter than two Cu-Br<sub>bridging</sub> bond, moreover there is a small disparity between two Cu-Br<sub>bridging</sub> (2.444 Å and 2.582 Å).

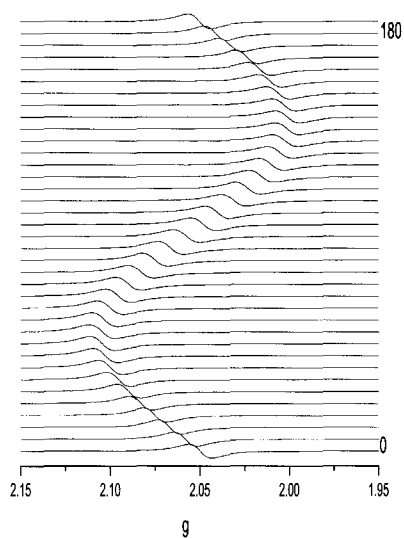
When CET-EDTTTF compound coordinates to Cu(I)Br, the most bond lengths, especially those in the outer six-membered ring in CET-EDTTTF, changed significantly. In case of CET-EDTTTF as an electron donating ligand to copper atom, especially, bonds in six-membered ring neighboring Cu-S bond became longer than those in neutral CET-EDTTTF.

Moreover, it is noteworthy that the central C=C bond length is distinctly increased from 1.337 Å to 1.388 Å when the neutral CET-EDTTTF is oxidized to CET-EDTTTF<sup>+</sup>



(a)

(b)



(c)

Fig. 2. Single-crystal EPR spectra obtained by rotating the Cu(I) complex about three mutually perpendicular (a) x-, (b) y-, and (c) z-axes of the crystal. (x, y, z is arbitrary).

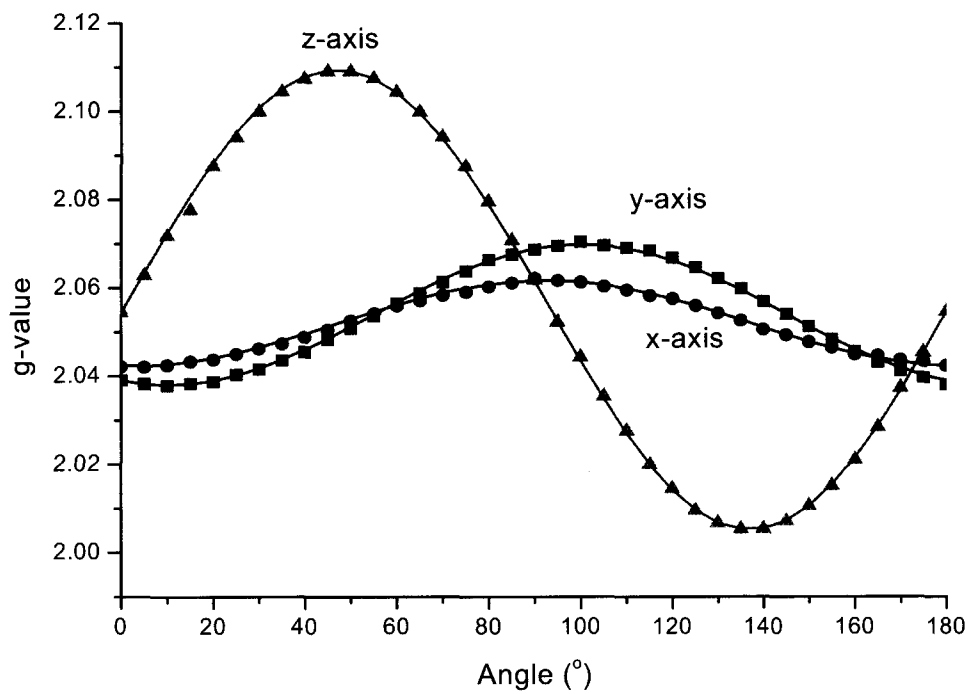


Fig. 3. Experimental g-values ( $\blacktriangle$ ,  $\bullet$ ,  $\blacksquare$ ) and theoretically calculated g-values (solid lines).

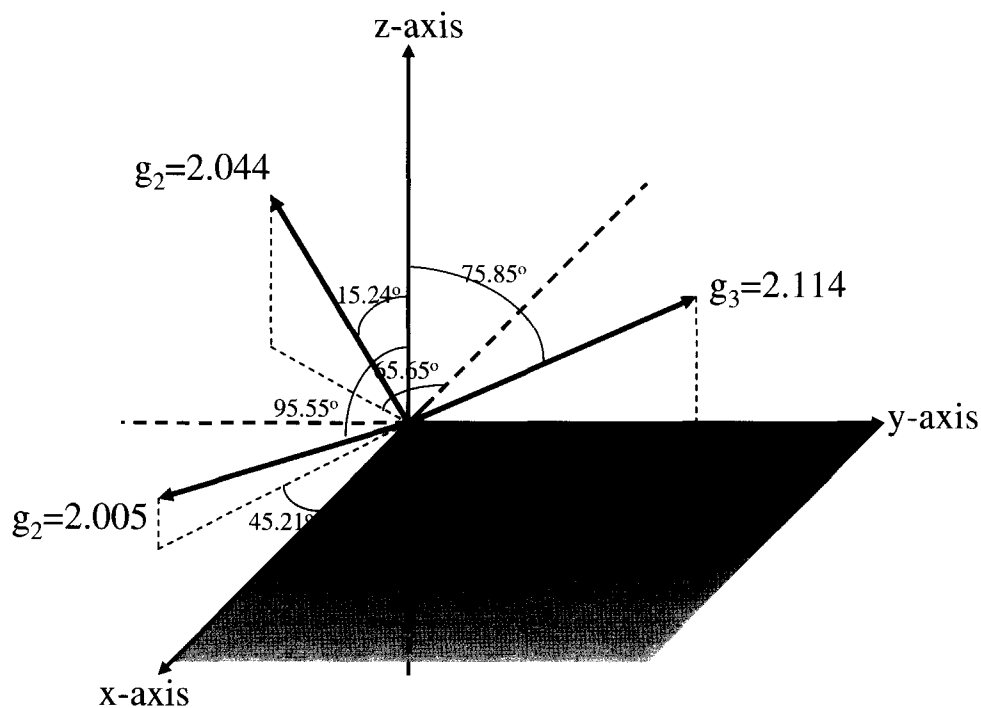


Fig. 4. Principal g-tensor orientations with respect to x-, y-, and z- axes of the crystal.

radical cation in the Cu(I) complex, which corresponds to the well known tendency of TTF-radical salt because the central C=C bond is assigned to the highest occupied molecular orbital (HOMO) of the TTF unit.<sup>7</sup>

Fig. 2 displays the EPR spectra obtained at every  $5^\circ$  by rotating the crystal about three mutually orthogonal axes (x, y, z) of the crystal at room temperature. The EPR spectra did not show any change from room temperature to 110 K. Here, the rotation of the crystal about x-axis means effectively the rotation of the external magnetic field in yz plane of the stationary crystal. The spectra shows two well-defined signals at  $g = \sim 2$ , indicating the presence of paramagnetic species.



X-ray crystal data exposes the bond length of the central C5=C6 bond increases upon the formation of the complex (1.388 Å) from the neutral CET-EDTTTF (1.337 Å) while the bond lengths of C5-S1, C5-S2, C6-S5, and C6-S6 decrease. Previous theoretical studies suggested that HOMO of BEDT-TTF includes C=C bonding and immediate four C-S antibonding orbitals of BEDT-TTF. Lengthening of C=C bond length and lessening of the C-S bond lengths was predicted by removal of one electron from the HOMO generating TTF cation radical.<sup>7,8</sup> The change of the bond lengths of CET-EDTTTF upon the formation of the complex analogously indicates the oxidation of the CET-EDTTTF unit resulting in radical species with one unpaired electron.

The spin density was expected to be largest at the central C=C bond of BEDT-TTF by computational method.<sup>7</sup> To understand detailed electronic structure of the complex, the information of the principal g-tensor values and the g-tensor orientation with respect to the crystal structure is necessary. Fig. 3 is the overlay of the theoretical calculation of g-values according to the rotation angles and the experimental data.<sup>9</sup> Diagonalization of the g-tensor values in the x-, y-, z- axes system revealed the three principal g-values of  $g_1 = 2.005$ ,  $g_2 = 2.044$ ,  $g_3 = 2.114$ . And the orientation of the  $g_1$ ,  $g_2$ , and  $g_3$  axes are depicted in Fig. 4 with respect to the x-, y-, z- axes system. The derived principal g-values exhibit surprisingly large g-anisotropy which is unprecedented in TTF-based cation radicals. The large anisotropy may imply that the delocalized HOMO in the  $\pi$ -system of the ligand is strongly fused with the metal d-orbital of the Cu(I) ion. We are undergoing detailed density functional calculations on the system and are mapping the principal g-tensor orientations into the crystal structure to completely understand the electronic structure of the complex.

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