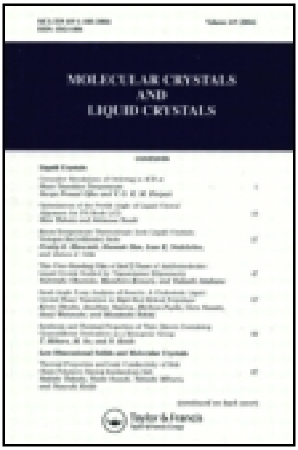

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Structures and properties of ethylenedioxy substituted CH-TTP

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STRUCTURES AND PROPERTIES OF ETHYLENEDIOXY SUBSTITUTED CH-TTP

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Most of the organic conductors based on CH-TTP derivatives, where CH-TTP is 2-(4,5-cyclohexeno-1,3-dithiol-2-ylidene)-5-(1,3-dithiol-2-ylidene)-1,3,4,6-tetrathiapentanlene, behave metallic down to low temperatures. An X-ray crystal structure analysis of CHEO-TTP$(ReO_4)_{0.38}$ revealed that the arrangement of the donors is close to that of the κ-BEDT-TTF salts. The band structure calculated with the tight-binding approximation suggests that the ReO_4^- salt has a closed Fermi surface similar to those of the κ-type superconductors.

Keywords: organic conductor; electrical conductivity; X-ray crystal structure analysis; band calculation

INTRODUCTION

It is important to develop the new κ-type salts in order to research organic superconductors, since the κ-type donor arrangement is considered as one of the structures favorable for organic superconductors. Recently, we have prepared CH-TTP and found that CH-TTP$(I_3)_{0.31}$ is the κ-type salt, which behaved metallic down to 1.5 K [1]. Therefore, CH-TTP derivatives are of considerable interest as donor components for the κ-type salts. In this

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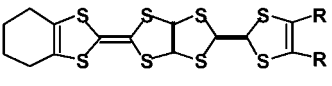
*Corresponding author. E-mail: masateru@mee3.moleng.kyoto-u.ac.jp paper, we describe the electrical properties of the TCNQ complexes and cation radical salts of CH-TTP derivatives **(1a–c)**, and crystal and electronic structures of a new κ-type salts, CHEO-TTP$(ReO_4)_{0.38}$.

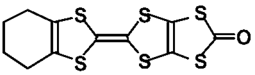


1a-c

1a 2R = -SCH$_2$S-: CHMT-TTP
1b 2R = -S(CH$_2$)$_2$S-: CHET-TTP
1c 2R = -O(CH$_2$)$_2$O-: CHEO-TTP

RESULTS AND DISCUSSION

Target molecules **1a–c** were prepared in 28–62% yields by the trimethylphosphite mediated cross-coupling reaction between 1,3-dithiol-2-one fused with cyclohexeno-TTF **(2)** and the corresponding 1,3-dithiole-2-thiones **(3a–c)** in refluxing toluene [2].



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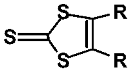

3a-c

a 2R = -SCH$_2$S-
b 2R = -S(CH$_2$)$_2$S-
c 2R = -O(CH$_2$)$_2$O-

The electrical properties of the TCNQ complexes and cation radical salts based on **1a–c** are summarized in Table 1. The resistivity of the AsF_6^- and SbF_6^- salt of CHMT-TTP **(1a)** show metallic temperature dependence down to 4.2 K, though that of the AsF_6^- salt has a maximum around 130 K (Figure 1a). On the other hand, both the I_3^- and ClO_4^- salts of **1a** are semiconductors with the activation energy (E_a) of 0.023–0.037 eV. The TCNQ complex of CHET-TTP **(1b)** exhibits a metallic temperature dependence of the resistivity in spite of a compressed pellet (Figure 1b). Although the resistivity of the AsF_6^- salt slightly increases at low temperature, the salt is essentially a metal down to about 30 K. Among the new CH-TTP derivatives, CHEO-TTP **(1c)** yields most organic conductors preserving metallic state down to low temperatures. The TCNQ complex of **1c** has high conductivity of 210 Scm^{-1}, and its resistivity also shows metallic temperature dependence down to 4.2 K on a compressed pellet. As shown in Figure 1c, the temperature-resistivity curve of the $ReO^{-}{}_{4}$ salt followed T^2-law down to low temperature, while the $ClO^{-}{}_{4}$ salt has a maximum around 120 K. The resistivity of the $PF^{-}{}_{6}$ salt showes weak temperature dependence down to about 170 K, afterwards it is reduced to 30% of the room temperature resistivity at 1.5 K. Among all the salts, the

TABLE 1 Composition and Electrical Properties of the CT Complexes and Cation Radical Salts (Donor)(Acceptor)$_x$

Donor	Acceptor	Solvent	x[a]	σ_{rt}/Scm^{-1}[b]	Conducting behavior
1a	I_3^-	PhCl	0.33(I)	16[c]	$E_a = 0.023\,eV$
	ClO_4^-	PhCl	0.29(Cl)	2.0	$E_a = 0.037\,eV$
	AsF_6^-	PhCl	0.51(As)	120	M[d] down to 4.2 K
	SbF_6^-	PhCl	0.33(Sb)	12	M down to 4.2 K
1b	TCNQ	PhCl	1.0[e]	150	Metallic[f]
	AsF_6^-	PhCl	0.77(As)	0.53	Metallic[f]
1c	TCNQ	PhCl	–[g]	210[c]	M down to 4.2 K
	$Au(CN)_2^-$	THF	0.47(Au)	32	$T_{MI} = 130K$
	ClO_4^-	THF	0.30(Cl)	38	M down to 4.2 K
	ReO_4^-	THF	0.38(X)	11	M down to 4.2 K
	PF_6^-	THF	0.47(P)	8.6	M down to 1.5 K
	SbF_6^-	THF	0.33(Sb)	92	M down to 1.5 K

[a] Determined by the energy dispersion spectroscopy (EDS) from the ratio of sulfur and the elements designated in the parentheses. X designates the value determined from X-ray structure analysis.

[b] Room temperature conductivity measured by four-probe technique on a single crystal.

[c] Measured on a compressed pellet.

[d] M = Metallic.

[e] Determined based on elemental analyses.

[f] The resistivity increases a little at low temperature. See the text.

[g] Not determined because adequate quantity of samples for elemental analyses could not be obtained.

SbF_6^- exhibits the highest conductivity of 92 Scm^{-1} at room temperature and has the largest value of $R_{rt}/R_{4.2\,K}(=40)$. On the other hand, the $Au(CN)_2^-$ salt shows a metal-to-semiconductor transition at 130 K.

An X-ray crystal structure analysis was carried out for the ReO_4^- salt of CHEO-TTP [3]. The stoichiometry of the salt is determined to be CHEO-TTP$(ReO_4)_{0.38}$ on the basis of the population analysis of Re atom. The donors and anions construct the conducting and insulating layers parallel to the *bc* plane, respectively, and their layers are alternately arranged. The donor arrangement is the so-called κ-type [4] as shown in Figure 2. The donor molecules are dimerized in a head-to-tail manner, and the overlap mode of the dimer is a so-called ring-over-bond type. The slip distance along the molecular long axis is 1.4 Å, while the interplanar distance 3.50 Å.

The tight-binding calculation of the ReO_4^- salt was performed on the basis of an extended Hückel approximation [5]. The energy dispersion and Fermi surface are shown in Figure 3. The band structure is degenerated on the ZM and MY zone boundary due to the requirement of the space group.

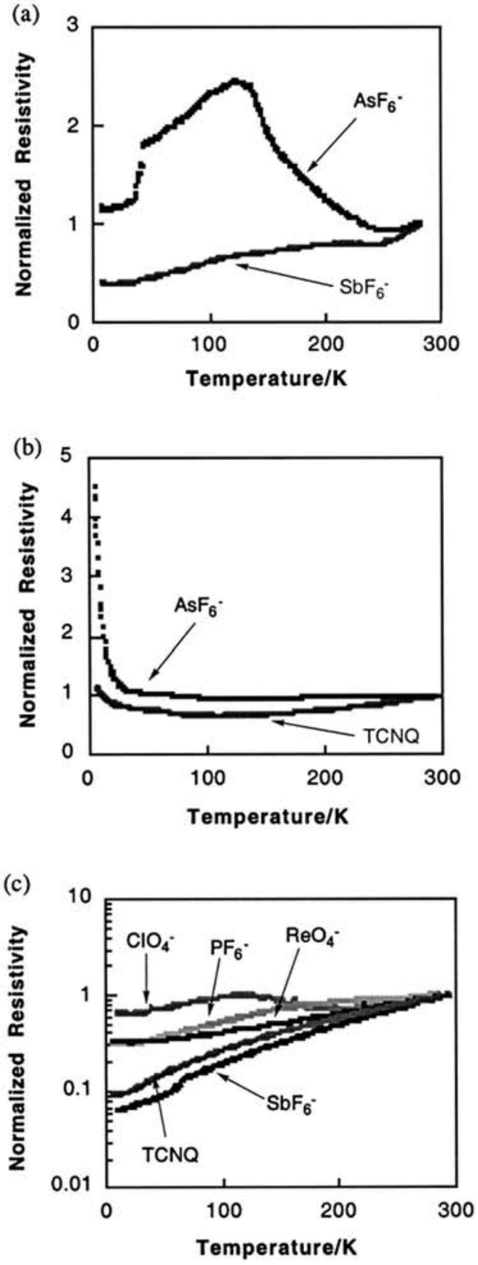

FIGURE 1 Temperature dependence of the normalized resistivity of organic conductors based on (a) CHMT-TTP **(1a)**, (b) CHET-TTP **(1b)**, and (c) CHEO-TTP **(1c)**.

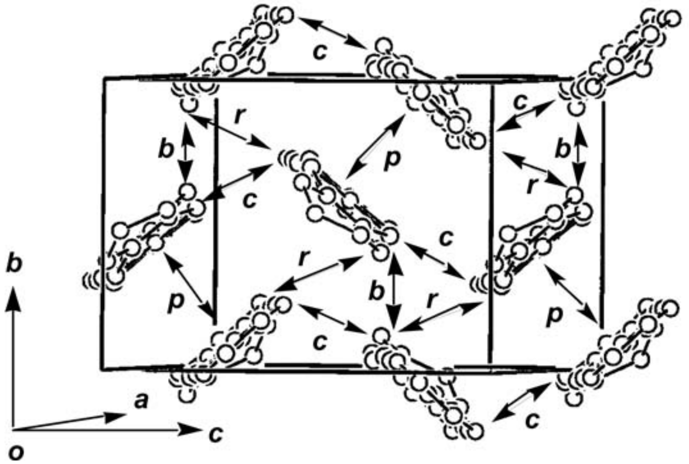

FIGURE 2 Donor arrangement of CHEO-TTP$(ReO_4)_{0.38}$. The intermolecular overlap integrals ($\times 10^3$) are $p = 24.5$, $b = 16.4$, $c = -6.11$, and $r = 6.46$.

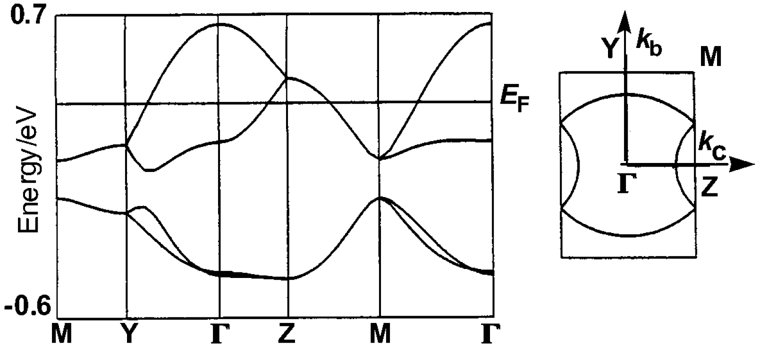

FIGURE 3 The energy dispersion and Fermi surface of CHEO-TTP$(ReO_4)_{0.38}$.

The upper bandwidth is estimated to be 0.66 eV, the value of which is larger than that of CH-TTP$(I_3)_{0.31}$ (0.56 eV). The Fermi surface is essentially closed circle similar to that of κ-(BEDT-TTF)$_2$X. The deviation from the half-filled may prevent this salt from undergoing superconducting transition in spite of the κ-type donor arrangement.

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[3] Crystallographic data of CHEO-TTP$(\mathrm{ReO_4})_{0.38}$: monoclinic, space group $C2/c, a = 45.734(7), b = 8.111(8), c = 11.189(7)$Å, $\beta = 99.08(3)^\circ, V = 4098(4)$Å^3, $Z = 8$, and $R = 0.069$ for 1750 independent reflections with $I > 4\sigma(I)$.

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