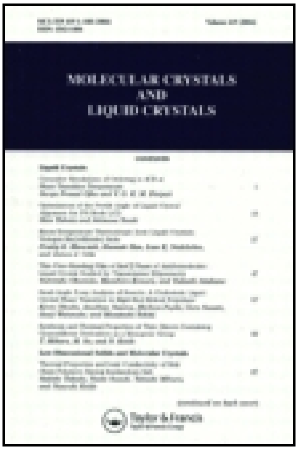

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Crystal Structures and Electrical Properties of Hexacyano-Butadiene (HCBD) Charge Transfer Complexes

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CRYSTAL STRUCTURES AND ELECTRICAL PROPERTIES OF HEXACYANOBUTADIENE (HCBD) CHARGE TRANSFER COMPLEXES

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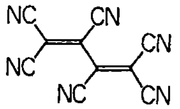
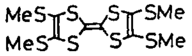
Abstract We have prepared charge transfer (CT) single crystals comprising TTF derivatives and hexacyanobutadiene (HCBD), which is one of the strongest acceptors. TMTTF gave two crystals in different stoichiometry, one is 2:1 semiconductor and the other is 1:1 insulator. In the 2:1 complex, TMTTF molecules form face-to-face segregated columns with dimerized manner and HCBD lies perpendicular to the donor columns to form side-by-side segregated columns in the cavity produced by donor columns. The ground state of this complex is antiferromagnetic. The 1:1 complex has face-to-face uniform segregated columns and shows some phase transition at around 150K. TTMTTF forms a semiconductive 1:1 complex with uniform face-to-face segregated column.

INTRODUCTION

HCBD is a flat, strong acceptor (E_A=3.22eV vs 3.15eV(F_4TCNQ)) which contains six CN groups protruding on the periphery of the molecule. The on-site Coulomb repulsion of HCBD is comparable to that of F_4TCNQ (E_{red}=0.6, 0.02V(HCBD), 0.53, 0.02V(F_4TCNQ)).[1] Furthermore, HCBD is known to form 2:1 conductive complex with TTF ($\rho=10^{-3}\Omega$cm) and 2:1 insulators with pyrene and hexamethylbenzene.[2] From these observations, it is expected that some HCBD complex with increased dimensionality due to the chalcogen-nitrogen atomic contact may be obtained by employing TTF derivatives. In addition to this, it is worth to obtain and investigate 2:1 (D:A) HCBD complex, because an enhanced metallic character



HCBD



TTMTTF

due to partial CT and the possible increased interchain interaction might be expected supposing uniform segregated stack, to seek the possibility of replacing inorganic counter anion X^- in the organic metal; $(D)_2X$, by organic anion; $HCBD^-$. We obtained single crystals of TMTTF·HCBD with different molecular ratio (1:1, 2:1) with very different crystal structures. We also obtained 1:1 crystal of TTM-TTF·HCBD. We report here the structural, electrical, optical, and magnetic properties of these single crystals.

RESULTS

TABLE I

	TMTTF·HCBD (2:1)	TMTTF·HCBD (1:1)	TTMTTF·HCBD (1:1)
	monoclinic-C	monoclinic-C	monoclinic-C
a Å	18.27	12.81	30.16
b	9.82	21.62	4.05
c	9.50	4.03	23.41
β °	102.76	108.01	117.45
V $Å^3$	1662	1061	2535
Z	4	2	4
$\rho_{calc.}$	1.45	1.45	1.55
$\rho_{obs.}$	1.46	1.46	1.53

The crystallographic data are summarized in Table 1.

1. TMTTF·HCBD(2:1) hexagonal prism···TMTTF forms a face-to-face segregated stack along the c-axis in dimerized manner (Figure 1) with the molecular separation of ca.3.5Å within the dimer and ca.3.7Å between the dimer. Overlapping pattern of the neighboring TMTTF within the dimer is different from that between the dimer. Therefore, high conductivity cannot be expected

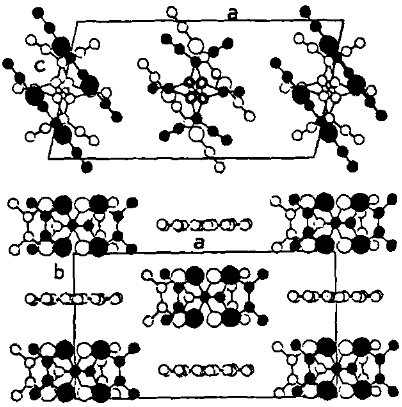


FIGURE 1 Crystal structure of TMTTF·HCBD(2:1)

unfortunatelly, and actually the complex is semiconductive (ρ_{RT}=3.3 x10^3Ωcm, $\mathcal{E}_a$=0.16eV). Interestingly, HCBD makes a novel side-by-side segregated stack along the c-axis in which HCBD lies perpendicular to the donor plane. Each of HCBD is rather independent (N··N≥3.43Å, vdW 3.0Å) in the stack but has appreciable short contact with methyl groups of TMTTF(N··CH_3≥3.43Å vdW 3.5Å). HCBD is disordered *in the orientation. The degree of CT is estimated from the bond* length of the central C=C of TMTTF and the reflection spectra (3200cm^{-1} //c due to $(TMTTF)_2{}^+$) as being +0.5 for TMTTF. ESR measurement shows antiferromagnetic behavior ($1/\chi_{mol}$=A(T+50)) and the ESR signal disappears below 20K.

2. TMTTF·HCBD(1:1) thin plate···This phase grows together with the 2:1 phase but more commonly. TMTTF and HCBD molecules form two independent uniform face-to-face segregated columns along the c-axis (Figure 2). Molecular planes of two kinds of components locate on the plane of (101) approximately and there are short contacts between central nitrogen and sulfur atoms along [10$\bar{1}$] (N··S=3.31Å vdW 3.35Å). Interplanar distance of TMTTF along c is ca.3.6Å and that of HCBD is ca.3.4Å. HCBD is disordered. The complex has high resistivity (ρ>10^{15}Ωcm) because the degree of CT determined from the central C=C of TMTTF is 0.2, which inconceivably small for such strong components. The reflectance of the complex was too weak to measure, and the first absorption band (ca.10000cm^{-1}) has components along c as well as [10$\bar{1}$]. While, second absorption at ca.14500cm^{-1} is solely polarized along [10$\bar{1}$].

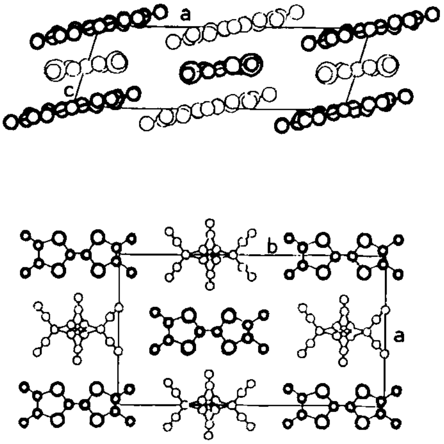


FIGURE 2 Crystal structure of TMTTF·HCBD(1:1)

The assignment of these bands are under investigation. ESR intensity shows a slight decrease at ca.280K and almost diminishes at ca.150K. Below that temperature, the signals reappear to show Curie like behavior.

3. TTMTTF·HCBD(1:1) rod···TTMTTF is distorted considerably about the central C=C bond in the neutral state, but becomes flat except the terminal methyl groups by the formation of the complex. Uniform segregated columns of each component are found along the b-axis (Figure 3). The donor columns are connected by S··S contacts(3.51Å) along the c-axis. HCBD is disordered in this complex too. The first band in reflectance spectrum is at 4600cm^{-1} polarized along the b-axis which is due to partial CT. But this complex is semiconductive($1.1\times10^{4}\,\Omega$cm, 0.22eV, //b). This relatively poor conductivity may be ascribed to the steric hindrance of methyl groups of the donor, since the methyl groups are out of plane and the molecular separationof TTMTTF is 3.65Å. This complex shows Bonner-Fisher type magnetic behavior.

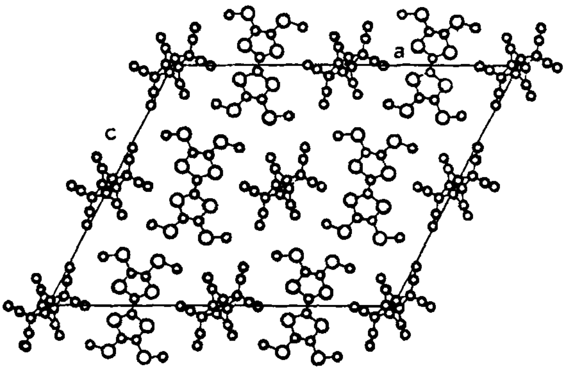


FIGURE 3 Crystal structure of TTMTTF·HCBD (1:1).

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