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Jiro Tanaka [a], Chuji Katayama [a], Hiroaki Kumagai [a], Gunzi Saito [c a], Toshiaki Enoki [b a] & Hiroo Inokuchi [b a]

[a] Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464
[b] Institute for Molecular Science, Myodaiji, Okazaki, 444
[c] Institute for Solid State Physics, Minato, Tokyo, 106, Japan
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THE CRYSTAL AND ELECTRONIC STRUCTURES OF HEXACYANOBUTADIENE COMPLEXES WITH TETRATHIAFULVALENE DERIVATIVES

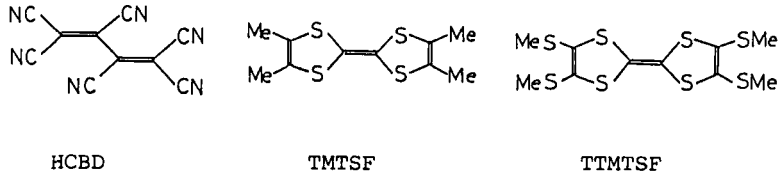
JIRO TANAKA, CHUJI KATAYAMA, HIROAKI KUMAGAI, GUNZI SAITO**, TOSHIAKI ENOKI* AND HIROO INOKUCHI*
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, 464,
* Institute for Molecular Science,Myodaiji, Okazaki,444
**Institute for Solid State Physics, Minato, Tokyo,106, Japan

Abstract The crystal structures and the electronic properties are investigated on the complex crystals made from the acceptor, hexacyanobutadiene (HCBD) and the donors, tetramethyltetrathiafulvalene (TMTTF) and tetramethylthiotetrathiafulvalene (TTMTTF). The electrical conductivity, the optical spectra and the magnetic properties of these crystals are discussed in connection with the crystalline structures and the phase transitions.

INTRODUCTION

HCBD is one of the strongest electron acceptor, and is expected to form molecular complex; a mixed valence complex with a moderate electron donor and an ionic one with a good electron donor. In the previous paper[1] we presented a preliminary account of the crystal structures and electrical properties of some of these complexes. HCBD forms two complexes with tetramethyltetrathiafulvalene (TMTTF); their composition being 2:1 and 1:1 donor to acceptor ratio. HCBD complexes with tetramethylthiotetrathiafulvalene (TTMTTF) with a 1:1 ratio. Precise crystal structures on these complexes are determined[2] and their electronic structures will be discussed based on the

structural, electrical, magnetic and optical properties.



HCBD TMTSF TTMTSF

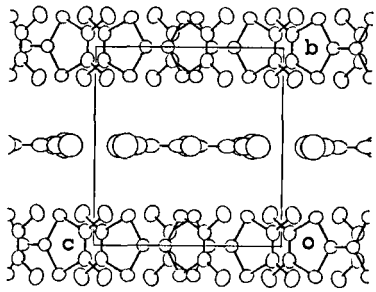


Fig.1 Projection of $(TMTTF)_2$·HCBD crystal onto the (100) plane. The dimer cation stacks along the a axis.

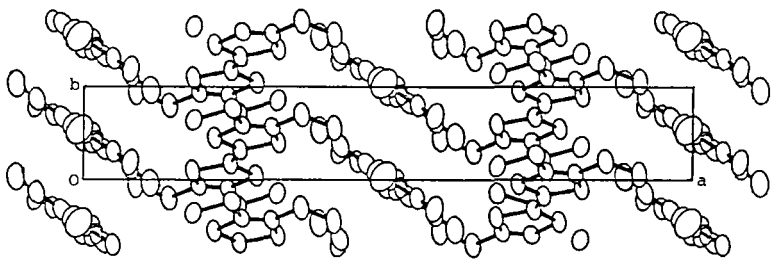


Fig.2 Projection of TTMTTF·HCBD crystal onto the (001) plane. The donor and the acceptor form segregated stacks along the b axis.

DEGREE OF CHARGE TRANSFER

A precise determination of the central C=C and C-S bond lengths of TMTTF in TMTTF·HCBD and $(TMTTF)_2$·HCBD and TTMTTF in TTMTTF·HCBD complex and in its neutral state enables us to estimate the degree of the charge transfer in the ground state. It is found that a formal charge of TMTTF in the 2:1 complex is about +0.5 and that of in the 1:1 complex is +1.0. In TTMTTF·HCBD, the donor and the acceptor form segregated columns and an apparent formal charge is about +0.5 in the donor. Therefore this crystal is considered to contain two columns of the donor and the acceptor stacks of a mixed valence character.

ELECTRICAL CONDUCTIVITY

TMTTF·HCBD is composed of ionic constituents, $(TMTTF)^+$ and $(HCBD)^-$, and the donor and the acceptor form segregated columns. The electrical resistivity of this crystal is very large, $\rho > 10^{15}$ Ω·cm; thus it is an insulator. A full charge both on the donor and the acceptor will exert strong electron correlation within the stacks, hence the crystal is a Mott insulator.

$(TMTTF)_2$·HCBD is composed of a stack of dimer cation, $(TMTTF)_2^+$, and the planar HCBD molecules are arranged in the cavity of the TMTTF column. (Fig.1) The resistivity for the b axis direction is measured as being $\rho = 3.3 \times 10^3$ Ω·cm at ambient temperature and its temperature dependence showed that the crystal is a semiconductor with an activation energy of 0.16 eV.

The resistivity of TTMTTF·HCBD at room temperature is 1.1×10^3 Ω·cm and the temperature dependence showed that the activation energy is 0.22 eV. Although both TTMTTF and

HCBD form segregated regular stacks with a mixed valence character (Fig.2), but the molecular overlap may be so small that a metallic conductivity is not observed.

OPTICAL SPECTRA

$(TMTTF)_2$·HCBD The reflection spectra are measured with the (100) face as shown in Fig.3. A sharp peak at 2800 cm^{-1} might be ascribed to the intradimer charge resonance band polarized along the direction connecting the centers of two molecules. Such a sharp peak is a characteristic of a semiconductive crystal.[3] The peaks at 12000 cm^{-1} and 14000 cm^{-1} might be due to $(TMTTF)^+$ and another peak at 18000 cm^{-1} could be assigned to $(HCBD)^-$ ion.

TTMTTF·HCBD The reflection spectra are measured with the (100) and the (001) faces (Fig.2) with the light polarized parallel to the a, b and c axes.(Fig.4) The peak at 4000 cm^{-1} is found along the stacking axis of the donor and the acceptor columns. The band is again sharp; it is indicative of a semiconductive property of the crystal. The origin of the reflection peak at 9000 cm^{-1} is not so clear but from the polarization character it may be suggested that the band is the short-axis polarized transition of $(TTMTTF)^+$ or the inter-stack transition between the donor and the acceptor. The reflectances around 16000 - 20000 cm^{-1}, strongly polarized parallel to the c axis might be due to $(TMTTF)^+$ and $(HCBD)^-$ ions.

TMTTF·HCBD The electronic absorption spectra of the crystal showed a CT band polarized along the stacking axis of $TMTTF^+$ and $HCBD^-$ at 9000 cm^{-1} region. A full detail of the spectral change accompanied with lowering temperature

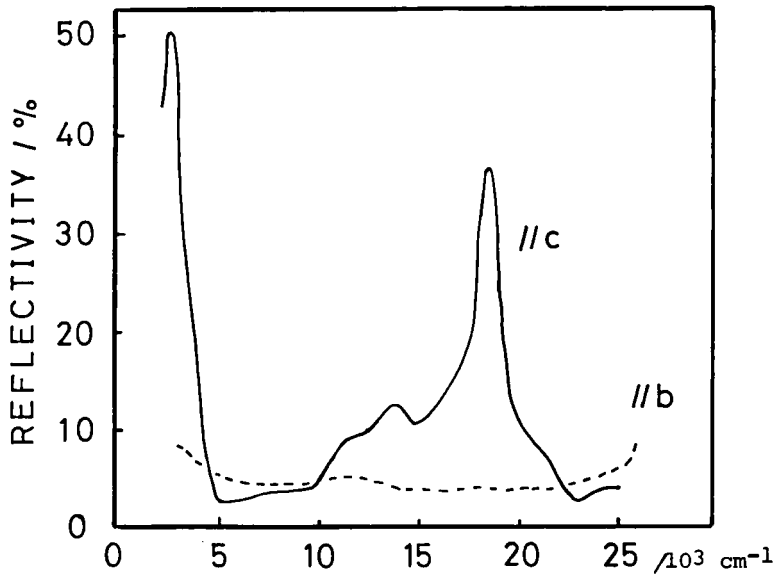


Fig.3 Reflection spectra of $(TMTTF)_2$·HCBD

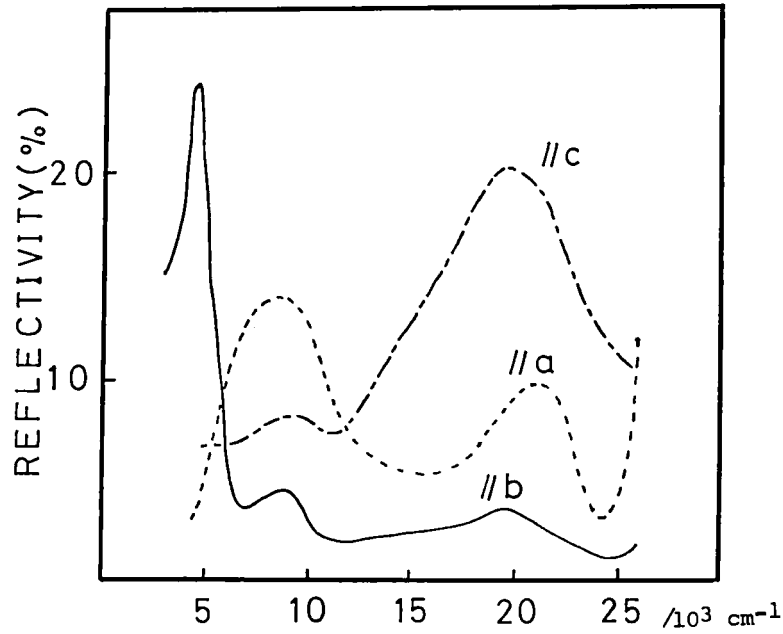


Fig.4 Reflection spectra of TTMTTF·HCBD

will be discussed in the succeeding paper.

MAGNETIC SUSCEPTIBILITY

The ESR absorption intensities of $(TMTTF)_2$·HCBD (I), (TMTTF)·HCBD (II) and (TTMTTF)·HCBD (III) are measured and its absolute intensities calibrated with a known amount of a standard DPPH gives the susceptibility as shown in Fig.5. The static susceptibility is also measured with (II) in order to confirm temperature variation of the susceptibility by a magnetic balance.[4] Both measurements are carried out at the Instrument Center of Institute for Molecular Science.

The magnetic susceptibility χ of (I) is given by Curie-Weiss law in the range of 20 - 300 K as

$$\chi = 1.04C / (T + 45)$$

where $C = 2 N g_B^2 \mu_B^2 S(S + 1)/3k = 0.75$ emu·K/mole. A slight enhancement from a free spin value, which corresponds to 2 moles of free spin, may be within experimental error. Below 20 K, the ESR absorption intensity drops abruptly and vanishes completely at 10 K. The transition below 20 K may be due to an antiferromagnetic ordering of free spins.

The χ of (II) exhibits several transitions in the 2 - 300 K. The ESR absorption intensity is measured after a rapid cooling of the crystal down to 2 K and then at each temperature after gentle warming. A comparison with the static measurement indicated that the observed intensity below 150 K is dependent on sample treatment, therefore this signal may be due to crystalline defect induced by a rapid cooling. The susceptibility above 276 K is represented by Curie-Weiss law for 2 moles of free spin in accordance with other evidences of the electronic structure. The phase transition occurs at 276 K, and almost two third of

the free spin disappeared. At 176 K another magnetic transition is found that the residual active spin is decayed almost completely without changing the crystalline structure.

The χ of (III) shows a little change, a typical of weakly coupled one-dimensional spin system described by a linear Heisenberg model. A J value of 0.015 eV with Bonner-Fisher formula gives excellent agreement with the observed values.

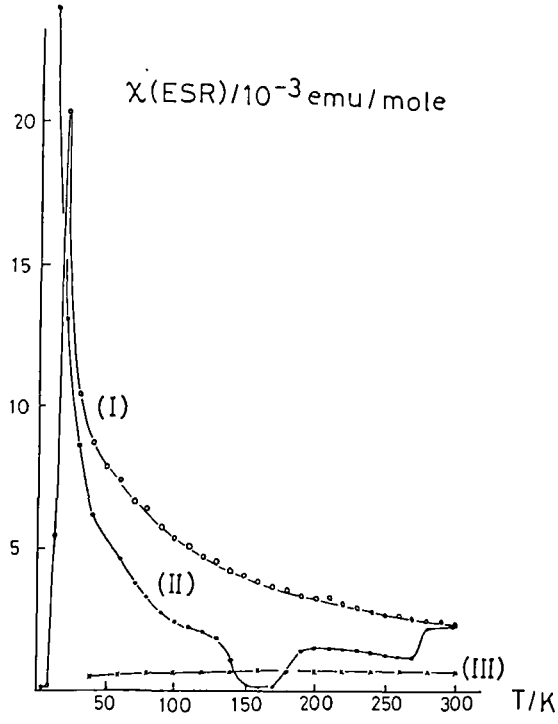


Fig.5 Magnetic susceptibilities of (I) $(TMTTF)_2HCBD$ (II) (TMTTF)HCBD and (III) (TTMTTF)HCBD

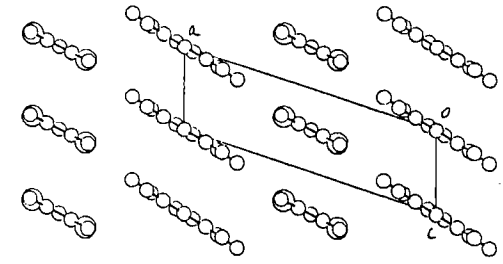


Fig.6 (TMTTF)HCBD α phase projected to (010) plane.

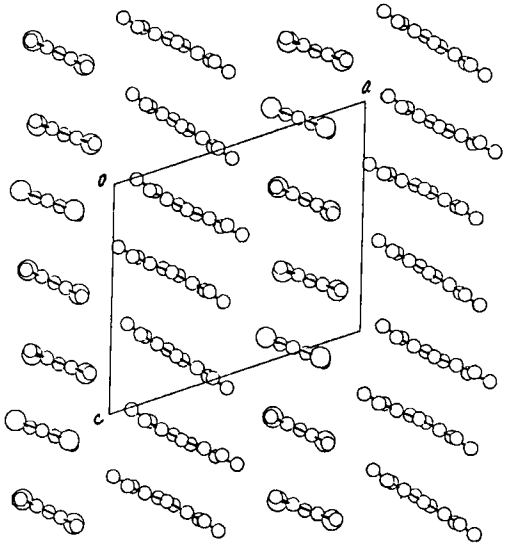


Fig.7 β phase projected to (010) plane.

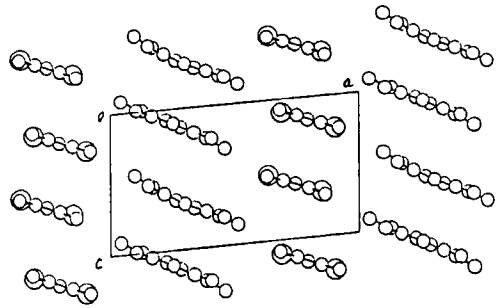


Fig.8 γ phase projected to (010) plane.

PHASE TRANSITIONS AND CRYSTALLINE STRUCTURES OF TMTTF·HCBD

In order to correlate the magnetic phase transitions of TMTTF·HCBD with structural change by other means, the X-ray crystal structure analysis is undertaken below 300 K, and the transition temperatures are found at 276 K and 154 K. We may call the room temperature phase as α phase, the second phase between 276 - 154 K as β phase and the phase below 154 K as γ phase. The structure of the α phase shown in Fig.6 is a segregated regular stack of TMTTF and HCBD, which is a typical of one-dimensional structure with ionic constituents. The structure of the β phase (Fig.7) is characterized by a triple c lattice spacing, and two of three donor and acceptor molecules form dimers and each one of TMTTF and HCBD are left without pairing but they form a flat network linked through -C=N···S contact of ∿ 3.2 Å. The magnetic transition occurring around 175 K may be due to a coupling of unpaired spin in this network. The structure of the γ phase (Fig.8) which is found below 154 K has a doubled c spacing and all the donors and the acceptors are paired by forming dimers. The magnetic susceptibility of this phase is expected to be very small by a coupling of spins in the dimer, but actually residual spins may be found which are left uncoupled during the process of rapid cooling of the crystal in the ESR measurement. Hysteresis of the measured susceptibility is found in this temperature range by a static measurement.[4)]

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