Charge-Transfer Complex of a New Acceptor Cyananilate with Tetramethyltetrathiafulvalene, $(TMTTF)_2HCNAL$

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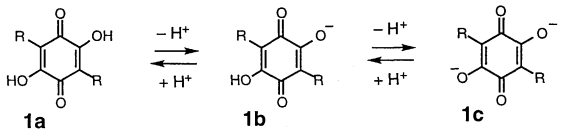
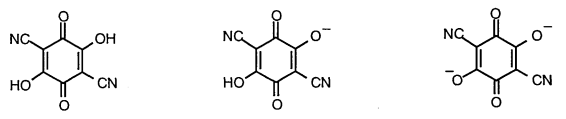
Cyananilic acid (H_2CNAL) gave a charge-transfer complex with tetramethyltetrathiafulvalene, $(TMTTF)_2HCNAL$, in which the acceptor forms a hydrogen-bonded ribbon arrangement and the donor forms a columnar stacking. The ionicity of the donor is estimated as +0.5. The electrical conductivity is 0.03 Scm^{-1} with the activation energy of 0.05 eV. The magnetic spin susceptibility is described in terms of a one-dimensional antiferromagnet.

Benzoquinone-type acceptors[1] possess both electron and proton accepting properties to form the hydrogen-bonded (H-bonded) charge-transfer (CT) complexes. In addition, benzoquinones with dihydroxy groups, **1a**, show an additional feature of multi–stage deprotonation-protonation processes. Three species, **1a** – **1c**, are expected to produce respective characteristic intermolecular H-bonded structures in the crystal. Actually, the neutral species **1a** (R = H, Cl, F),[2–4] were reported to produce a molecular ribbon-type arrangement by a complementary H-bonding. On the other hand, the bis-deprotonated dianionic species **1c** (R = Cl, NO_2)[5,6] form a multiple intermolecular H-bonding through a water molecule, but no direct intercomponent H-bonding. In order to explore new H-bonded CT complexes with electrically conducting properties, we have utilized a cyananilic acid system, **2a** – **2c**, as acceptor components. We now report here the crystal structure and solid state properties of the CT complex of the mono-deprotonated species, HCNAL (**2b**) with tetramethyltetrathiafulvalene, $(TMTTF)_2HCNAL$, which has an H-bonded ribbon-type arrangement of the acceptor component and shows a semi-conductive behavior.

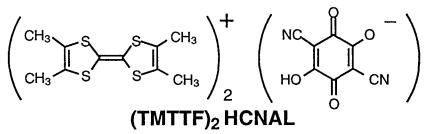


1a **1b** **1c**

R = H, OH, Cl, Br, NO_2



H_2CNAL, 2a **HCNAL, 2b** **CNAL, 2c**



$(TMTTF)_2HCNAL$

Cyananilic acid, 2,5-dicyano-3,6-dihydroxy-1,4-benzoquinone (H_2CNAL, **2a**) was prepared according to the procedure reported in the literature,[7] from 2,5-dibromo-3,6-dicyano-1,4-benzoquinone which is readily accessible by our improved method.[8] Diffusion of a tetrahydrofuran–dichloromethane (2 : 1) solution of H_2CNAL and TMTTF in an H-tube gave a CT complex as single black plate crystals. The donor–acceptor ratio was determined as 2 : 1 by elemental analysis[9] and X-ray crystal structure analysis.[10] Furthermore, the acceptor component was assigned to be HCNAL from the crystal structure. Thus, cyananilic acid was mono-deprotonated under the diffusion condition to form HCNAL.

The crystal structure of the CT complex showed that the anion HCNAL has centrosymmetry, and the H atom of the OH group locates on the two O atoms with 0.5 probability (Figure 1). The anion is linked into molecular ribbons parallel to the *c* axis via OH···O type H-bonds. The O···O distance of the H-bond is 2.81 Å, which indicates the weak nature of H-bonding. The donor TMTTFs form segregated columns with a dimerized stacking along the *c* axis. The overlap patterns of the neighboring TMTTF within the dimer and between the dimers are shown in Figure 2 (a). The mean interplanar spacings are 3.37 and 3.54 Å, respectively. Within the donor column, there are two types of S···S contact (3.651 and 3.784 Å) near the van der Waals contact. The donor column is surrounded by the four H-bonded ribbons of the acceptor (Figure 1b). Therefore, no short intercolumnar S···S contact exists. Thus, the crystal structure indicates one-dimensionality of the TMTTF column. According to the proposed procedure to estimate the ionicity of the TMTTF component in the CT complexes,[11] we obtained the ionicity of the donor component of $(TMTTF)_2HCNAL$ as 0.4 and 0.6 by using the bond length of central C=C (1.371 Å) and the average C–S bond (1.733 Å), respectively. This is consistent with the experimental value of donor-acceptor ratio 2 : 1, which indicates +0.5 formal charge of TMTTF.

The electrical conductivity shows semiconductive behavior with the room temperature resistivity of 31 Ωcm and the activation energy of 0.052 eV. We observed a low energy electronic absorption band at around $5x10^3$ cm^{-1}, which can be assigned to a CT transition between the neutral state and cation radical state of the donor components in the dimeric unit.

The temperature dependence of the static magnetic susceptibility of several single crystals of $(TMTTF)_2HCNAL$ has been studied over the range of 4.5–400 K. The spin susceptibility χ (T) has a broad maximum around T_{max} ~270 K as shown in Figure 3. The feature with a broad peak proves the presence of localized spin (S=1/2) coupled by antiferromagnetic interactions in the one-dimensional frame, taking into account the

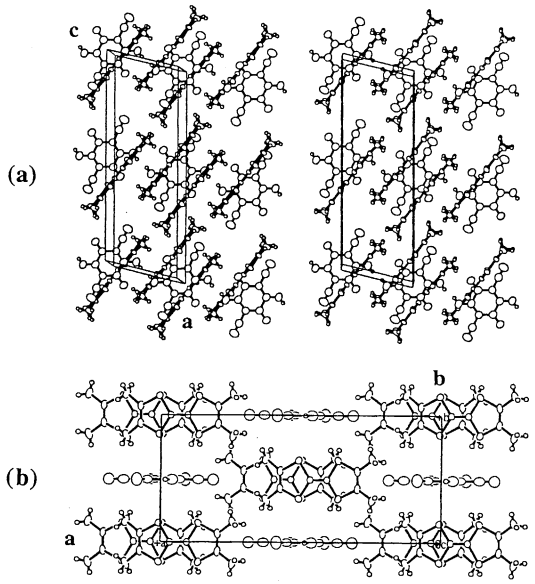


Figure 1. Crystal structure of $(TMTTF)_2HCNAL$: view along the *b* axis (a) and along the *c* axis (b).

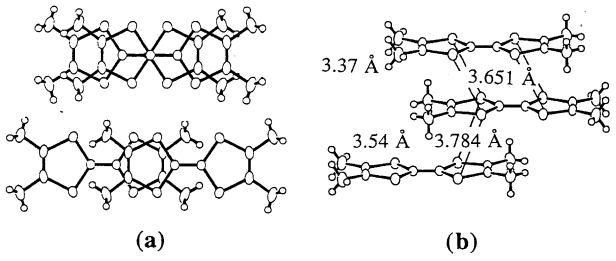


Figure 2. Overlap pattern of TMTTF (a) and interplanar spacings and intra-column S···S contacts.

semiconductive properties of this compound. The intra-chain exchange interaction was roughly estimated at J/k_B ~210 K from the best fitting based on the S = 1/2 antiferromagnetic Heisenberg chain model by Bonner-Fisher with T_{max} ~270 K, although there is a large disagreement in the magnitude from the behavior expected from the linear chain model. We give two possible explanations from this disagreement. One is associated with ambiguity in the estimation of the diamagnetic contribution. The conjugated π-electronic structure of the anions gives a correction in the diamagnetic contribution. The second is related to incomplete-ness of the charge transfer from TMTTF to the anion molecule.

In conclusion, we successfully obtained an electrically conducting CT complex of the mono-deprotonated cyananilic acid, which showed semiconductive behavior and interesting magnetic properties. Generally, the hydroxybenzoquinone type molecules possess multiple proton and electron transfer ability. The effects of such ability on the solid state properties in CT complexes are under investigation. [12]

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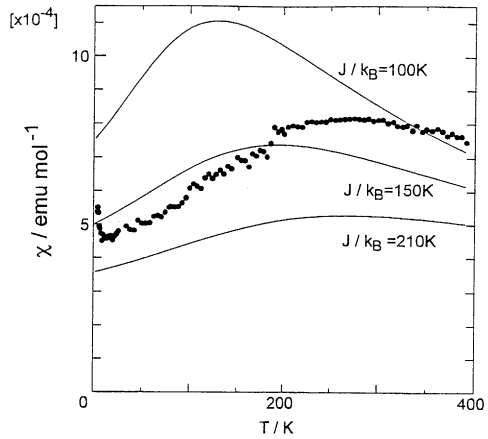

Figure 3. Temperature dependence of static magnetic susceptibility.

References and Notes

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9 $(TMTTF)_2$ HCNAL: black plate, mp 230 ℃ (decomp.). IR (KBr pellet): 2192 (C≡N), 1560 (C=O) cm^{-1}. Anal. Found: C, 47.07; H, 3.67; N, 4.01%. Calcd for $C_{28}H_{25}N_2O_4S_8$: C, 47.36; H, 3.55; N, 3.95%.
10 Crystal data: for $(TMTTF)_2HCNAL$, $C_{28}H_{25}N_2O_4S_8$, FW = 710.00, black crystal, monoclinic, C_2/m (#12), a = 21.691(2) Å, b =9.675(2) Å, c = 7.547(2) Å, β = 103.86(1)°, V = 1537.5(4) $Å^3$, Z = 2, R = 0.027, R_W = 0.031, Goodness of Fit Indicator = 3.17, D(calcd) = 1.533 Mg m^{-3}, μ(Mo$K\alpha$) = 6.91 cm^{-1}, 1611 observed reflections ($Io > 3\sigma(Io)$), T = 23.0 °C, ω–2θ scan, maximum $2\theta_{max}$ = 55.0°. Scan Rate = 8.0 °/min (in ω) up to 5 scans, Scan Width = (1.42 + 0.30 tanθ).
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