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# Crystal Structures of Organic Superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$, at 298 K and 104 K

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The crystal structures of an organic superconductor $(BEDT\text{-}TTF)_2Cu(NCS)_2$ (Tc=10.4 K) at 298 K and 104 K are determined by X-ray analysis. The packing pattern of donors is nearly analogous to $\kappa$-$(BEDT\text{-}TTF)_2I_3$. The counter anion, $Cu(NCS)_2^-$, has no positional disorder and constructs a peculiar sheet where a copper ion is coordinated with a sulfur and two nitrogen atoms to form a one-dimensional polymer with a permanent dipole moment.

In the previous papers we have described the synthesis, the magnetic susceptibility, the electrical conductivity, the preliminary crystal structure analysis, and the critical field measurements of an ambient pressure superconductor, $(BEDT\text{-}TTF)_2Cu(NCS)_2$ (BEDT-TTF: bis(ethylenedithiolo)tetrathiafulvalene) which has the highest $T_c$ and $H_{c2}$ among organic superconductors so far obtained.[1, 2] However, the conductivity showed some anomaly between around 270 K and 90 K. Also the crystal structure analysis presented in the previous paper at room temperature was not completed concerning about the position of the counter anion. In order to clarify these points and to observe whether there is a structural phase transition or not, we have performed the structure analysis of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 104 K as well as 298 K.

The crystal data at 104 K are summarized in Table 1. Intensity data were collected by $\omega$-$2\theta$ scan technique with a Rigaku automated four-circle diffractometer. The X-ray of Mo $K_\alpha$ radiation monochromatized with graphite was used. The data collections at low temperatures were examined under temperature-controlled $N_2$ gas flow. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares by using independent 4444 reflections ( $|F_0| > 3\sigma(F_0)$, $2\theta < 60°$ ). The hydrogen atoms were included in the final refinement and the anisotropic temperature factors were adopted for non-hydrogen atoms. The final R value is 0.042.

The crystal structure at 104 K shows (Fig. 1) that there are two independent

BEDT-TTF molecules in an asymmetric unit and no inversion center even upon the anion, $Cu(NCS)_2^-$. The molecular packing pattern of BEDT-TTF is almost analogous to that in κ-$(BEDT\text{-}TTF)_2I_3$[3] though the space group is lowered from $P2_1/c$ to $P2_1$. Two BEDT-TTF molecules form a pair with their central tetrathioethylene planes almost parallel (dihedral angle between planes=2.1°, interplanar spacing=3.30 Å) and each pair stacks nearly perpendicularly (83-88°) to one another to construct a donor sheet in the bc plane (Fig. 2). Each donor molecule is linked by several short intra-(3.577 Å) and interpair (≥3.507 Å) S···S contacts in the sheet which forms the two-dimensional conducting layer (Table 2). Every conducting layer is sandwiched by the insulating layers of $Cu(NCS)_2$ along the a-axis. The bond lengths of two independent BEDT-TTF molecules suggest that they have the same formal charge of about +0.5.[4] The BEDT-TTF molecules are slightly bent with the dihedral angles between the least square planes of three tetrathioethylene moieties of 4.52, 10.30, 10.72, and 4.81°. Two ethylene groups of a BEDT-TTF molecule deviate from the least square planes of the outer tetrathioethylene moieties and no significant conformational disorder is observed for the ethylene groups.

Table 1. Crystallographic data of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 298 K/104 K, unit temperature dilation of primary axes upon cooling and specific cation-anion atomic contacts at 104 K

| | | 298 K | 104 K | $\Delta ll^{-1}\Delta T^{-1}/K^{-1}$ |
|---|---|---|---|---|
| a | /Å | 16.248(5) | 16.382(4) | $4.3 \times 10^{-5}$ |
| b | | 8.440(2) | 8.402(2) | $-2.3 \times 10^{-5}$ |
| c | | 13.124(5) | 12.833(4) | $-11.4 \times 10^{-5}$ |
| β | /° | 110.30(3) | 111.33(2) | $4.8 \times 10^{-5}$ |
| V | /Å$^3$ | 1688.0(9) | 1645.3(7) | $-13.0 \times 10^{-5}$ |

monoclinic, $P2_1$, and Z=2

| | | | | | |
|---|---|---|---|---|---|
| o | H9-S51 | 2.87(9) | p | H7-N55 | 2.59(11) |
| q | H8-S51 | 2.84(9) | r | H16-S51 | 2.87(12) |
| s | H4-N55 | 2.46(7) | | | |

The crystal structure at 298 K was refined on the basis of the structural results obtained at 104 K. The final R value is 0.084. The lattice parameters (Table 1) are almost the same as those of κ-$(BEDT\text{-}TTF)_2I_3$. The intramolecular bond lengths and angles are normal compared to those of the ordered BEDT-TTF molecules.[4] However, the thermal motion of one of the ethylene groups of each BEDT-TTF molecule is large which indicates a conformational disorder. The interplanar

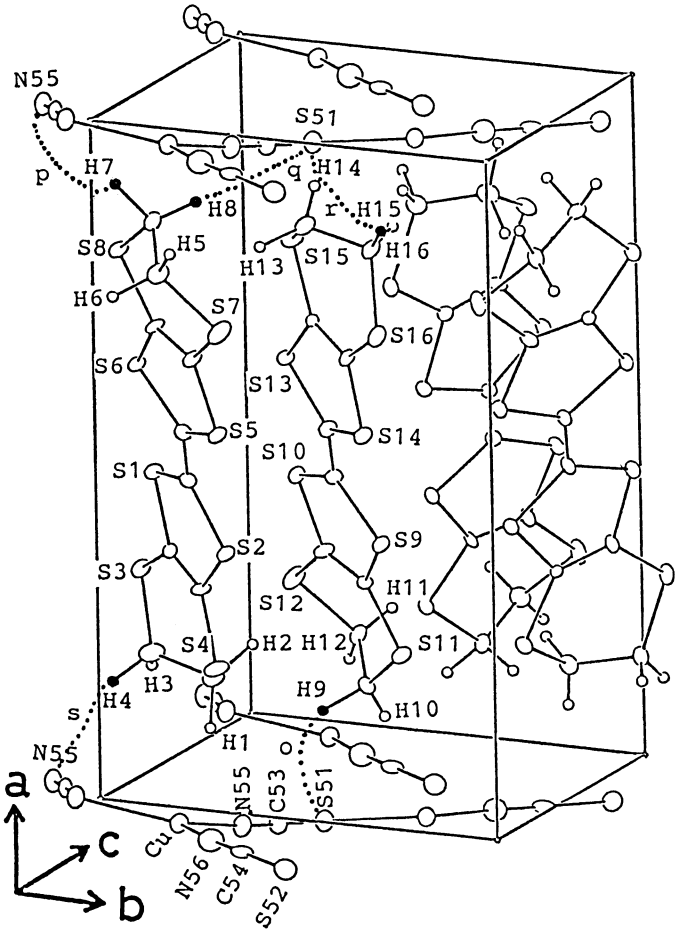


Fig. 1. Crystal structure of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 104 K and specific cation-anion contacts. The shaded circles indicate the H atoms to form contacts.

spacing between the central tetrathioethylene moieties of a pair increases to 3.38 Å and the number of the short intra- and inter-pair S····S contacts (<3.6 Å) decreases on going to 298 K due to the subtle movement of BEDT-TTF molecules (Table 2) but the total features of the donor sheet have little difference from those at 104 K.

Table 2. Short S··S contacts(Å)

| | | 298 K | 104 K |
|---|---|---|---|
| t | S1-S13 | 3.659(5) | 3.577(2) |
| u | S3-S13 | 3.554(7) | 3.507(2) |
| v | S8-S16 | 3.553(8) | 3.548(3) |
| | S6-S16 | 3.574(8) | 3.567(2) |
| | S3-S9 | 3.508(8) | 3.542(2) |
| | S3-S11 | 3.510(9) | 3.520(3) |
| w | S2-S16 | 3.671(7) | 3.589(2) |

Figure 3 shows the arrangement of the anion at 104 K and Table 3 summarizes the bond lengths and angles at 104 K and 298 K. Two crystallographycally independent N-C-S groups (I, II ) are almost linear (175, 179°) and no positional disorder speculated in the previous paper is observed. Three N-C-S groups ( I, I, II) coordinate to a copper cation with two nitrogen and one sulfur atoms to construct a one-dimensional zig-zag polymer along the b-axis in the bc plane. Thus the polymer is represented as $\leftarrow$SCN -Cu(NCS)$\rightarrow_n$. The thermal changes of angles ( $\Delta\theta/\theta$ ) associated with the ligand II are considerably larger than those of the ligand I indicating that the ligand I is under more rigid circumstance than II as expected. However, the corresponding interatomic distances of two kinds of ligands are almost identical to each other despite the different circumstances of them. Moreover the compressibilities ($\Delta l/l$, Table 3) of the corresponding bonds show almost the same temperature dependences between them.

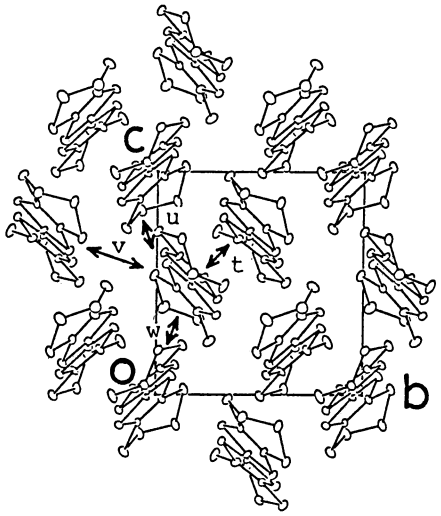


Fig. 2. Molecular arrangement of $(BEDT\text{-}TTF)_2Cu(NCS)_2$ at 104 K.

The trigonal coordination of Cu(I) is very unique. The rare example is $K[Cu(CN)_2]$ where three CN groups are linked to Cu(I) with two carbon and one nitrogen atoms and they form a polymer.[5] According to the similarities of the coordination pattern between them, the anion studied here should be expressed more appropriately as $Cu(NCS)_2$ rather than $Cu(SCN)_2$ in the previous paper. However, the linking pattern makes a difference between $Cu(NCS)_2$ and $Cu(CN)_2$; The former forms a one-dimensional planar chain while the latter extends to be a spiral chain. Since the coordination number of three has not been observed in any Cu(II) compounds, to our knowledge, the crystal data obtained here give an additional strong support to the electronic structure of Cu(I) in the $Cu(NCS)_2$ salt besides the ESCA at room temperature and ESR down to 4 K.[6] The most striking feature of the anion is that each one-dimensional polymer has a permanent dipole moment and the moment cannot be cancelled out in the crystal. There has been only one example of organic superconductors which contain an anion with a permanent dipole moment; $(TMTSF)_2FSO_3$.[7]

Some specific cation-anion contacts in the $Cu(NCS)_2$ salt are observed at 104 K. The meaningfully short atomic contacts of two N····H (<2.6 Å) and three S(anion) ··H (<2.9 Å) are formed by using hydrogen atoms on the both side of ethylene groups of BEDT-TTF molecules (Fig. 1 and Table 1), while such specific contacts were observed on only one side of ethylene groups of BEDT-TTF in $\beta$-$(BEDT\text{-}TTF)_2I_3$.

Table 3. Bond distances (Å) and angles (°) of anion $\leftarrow$SCN-Cu(NCS)$\rightarrow_n$

| | 298 K | 104 K | Δl/l | | 298 K | 104 K | Δθ/θ |
|---|---|---|---|---|---|---|---|
| S51-C53 | 1.622(19) | 1.646(7) | 0.015 | S52-C54-N56 | 175.8(24) | 179.3(8) | 0.020 |
| S52-C54 | 1.606(27) | 1.637(8) | 0.019 | C54-N56-Cu | 160.1(22) | 166.5(7) | 0.040 |
| C53-N55 | 1.196(27) | 1.150(9) | -0.038 | N56-Cu-N55 | 121.0(9) | 117.6(3) | -0.028 |
| C54-N56 | 1.192(34) | 1.163(10) | -0.024 | N56-Cu-S51 | 117.2(7) | 120.8(2) | 0.031 |
| N55-Cu | 1.898(20) | 1.964(6) | 0.035 | N55-Cu-S51 | 121.8(6) | 121.6(2) | -0.002 |
| N56-Cu | 1.885(24) | 1.938(7) | 0.028 | Cu-S51-C53 | 107.0(7) | 107.8(3) | 0.007 |
| S51-Cu | 2.231(7) | 2.198(2) | -0.015 | S51-C53-N55 | 173.8(18) | 175.0(7) | 0.007 |

Therefore every two-dimensional BEDT-TTF sheet in the bc plane is connected to each other by C-H··N··H-C and C-H··S··H-C bonds along the a-axis.

The lattice parameters show gradual changes with lowering temperature indicating that there are no distinct structural phase transition down to 104 K. The thermal compressibility of the b-axis ($\Delta b/b\Delta T=-2.3 \times 10^{-5}$ $K^{-1}$) is a little smaller than those of the two-dimensional axes of β-(BEDT-TTF)$_2I_3$, while the compressibility of the c-axis ( $\Delta c/c\Delta T=-11.4 \times 10^{-5}$ $K^{-1}$) is about five times bigger than that of the b-axis and this value is considerably larger than those of the BEDT-TTF organic superconductors so far known.[8] The thermal dilation of the a-axis is outstanding that it expands upon cooling from 298 K to 104 K by $\Delta a/a\Delta T= +4.3 \times 10^{-5}$ $K^{-1}$. It has been known that the a-axis of β-(BEDT-TTF)$_2I_2Br$ shows the same tendency but the magnitude of which ($+0.1 \times 10^{-5}$ $K^{-1}$) is very small.[8] The temperature dilation of the a-axis of the Cu(NCS)$_2$ salt is not linear with the temperature. The a-axis remains constant down to 260-270 K where it starts to expand gradually with upper curvature down to 104 K, though the real separation of two anion layers (a·sinβ) is almost unchanged. The detail of the variations of the lattice parameters with temperature and other physical properties will be published soon.

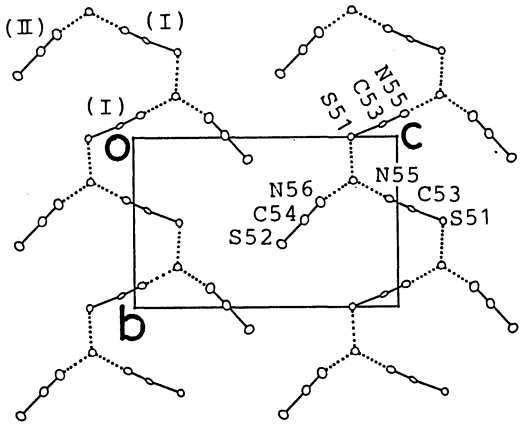


Fig. 3. Anion arrangement of (BEDT-TTF)$_2$Cu(NCS)$_2$ at 104 K.

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