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# Quasi-three-dimensional network of molecular interactions and electronic structure of a new organic semiconductor, ET(NCS)<sub>0.77</sub>

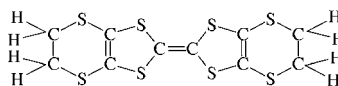
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The radical cation salt ET(NCS)<sub>0.77</sub> [bis(ethylenedithio)tetrathiafulvalene thiocyanate (1/0.77)] has been prepared for the first time by electrocrystallization and its crystal and electronic structure at 110 K was investigated. The unit-cell dimensions are orthorhombic,  $a = 6.638$  (1),  $b = 8.309$  (2),  $c = 28.776$  (6) Å,  $V = 1587.1$  (6) Å<sup>3</sup>, space group *Pbcm*,  $Z = 4$ . The compound has a layered structure. The ET radical cations of the conducting cationic layer build stacks. In the anionic layer the thiocyanate groups form polymeric chains where they are oriented in a 'head-to-tail' mode. The structure has short intermolecular contacts of the cation–cation, anion–anion and cation–anion types, which leads to the formation of a three-dimensional structure of intermolecular interactions. This phenomenon is very rare in molecular conductors. Tight binding band structure calculations suggest, however, that the interlayer interactions through the anions are weak and that the incomplete occupation of the anion sites is the reason for the activated conductivity of the salt.

## 1. Introduction

In the course of our search for new organic conductors and superconductors based on bis(ethylenedithio)tetrathiafulvalene (ET) we have obtained the new radical cation salt



ET

ET(NCS)<sub>0.77</sub>. The NCS group has been frequently used as a ligand in various metal complexes during the synthesis of organic conductors (Mori *et al.*, 1998; Urayama *et al.*, 1988; Coppens *et al.*, 1991; Kepert *et al.*, 1997; Dyachenko *et al.*, 1995). Some salts based on TTF are known (Pyrka *et al.*, 1989; Kobayashi & Kobayashi, 1977), but radical cation salts based on ET with the above group acting as an anion have not been reported. Physical measurements prove that the ET(NCS)<sub>0.77</sub> salt exhibits typical semiconducting properties. This work describes the results of the X-ray crystal structure analysis of the ET(NCS)<sub>0.77</sub> salt at 110 K, as well as the associated tight binding electronic structure.

## 2. Experimental

### 2.1. Synthesis

The ET(NCS)<sub>0.77</sub> crystals were prepared as thin, black rectangular plates of different sizes by electrochemical ET

oxidation in a chlorobenzene–methanol medium. The electrolyte used was composed of 18-crown-6-ether and a mixture of KSCN and  $(\text{Bu}_4\text{N})_3[\text{Y}(\text{NCS})_4(\text{NO}_3)_2]$  (1:1). The concentrations of these components are equal to  $10^{-3}$  mol dm $^{-3}$ . The chemical composition  $\text{ET}(\text{NCS})_{0.77}$  was determined from a low-temperature X-ray study.

## 2.2. X-ray diffraction

The X-ray crystal structure study was performed at 110 K on a Bruker AXS SMART 1000 instrument equipped with a CCD detector (graphite monochromator, scanning pitch 0.3, frame measuring time 30 s). Crystal data for the  $\text{ET}(\text{NCS})_{0.77}$  salt are given in Table 1. The crystal structure was solved by direct methods and subsequent Fourier synthesis using *SHELXL93* (Sheldrick, 1993) software. The structure was refined by full-matrix least-squares procedures by the *SHELXL97* (Sheldrick, 1997a) program using an anisotropic approximation for all non-H atoms, and populations of S1, C1 and N1 atoms of the thiocyanate group were found to be equal to 0.771 (4), 0.81 (2) and 0.70 (2), respectively. Taking into account the population of the heaviest of these three atoms, the S1 atom, the formula of the compound is  $\text{ET}(\text{NCS})_{0.77}$ . An absorption correction was applied using the *SADABS* program (Sheldrick, 1997b). The H atoms were calculated.

## 3. Results and discussion

The radical cation  $\text{ET}(\text{NCS})_{0.77}$  salt has a layered structure (Fig. 1), in which the conducting layers of ET radical cations alternate along the *c* axis with the non-conducting layers of  $\text{NCS}^-$  anions. In the  $\text{ET}(\text{NCS})_{0.77}$  crystals the ET molecules are centrosymmetric ( $4b$  positions) and have a ‘chair’ conformation in which two  $\text{CH}_2$  groups deviate markedly from the average molecular plane (by approximately  $\pm 0.7$  Å), while the deviation of the other two  $\text{CH}_2$  groups is only  $\pm 0.02$  Å. The atoms in the  $\text{NCS}^-$  anion stay in the mirror symmetry plane ( $4d$  positions). The atomic labelling is given in Fig. 2, and the bond lengths and angles are listed in Table 2.

The ET radical cations of the conducting layer (Fig. 3) form stacks along the *b* axis. The neighbouring molecules in the stacks are practically parallel, turned with respect to each other by an angle of  $26.4^\circ$  and shifted along the long molecular axis by approximately  $3/2$  of the length of the central  $\text{C}=\text{C}$  bond (Fig. 4). Along the stacks, the distance between the mean molecular planes going through the S atoms is the same (3.44 Å). The dihedral angle between these planes is  $1.8^\circ$ . The short  $\text{S}\cdots\text{S}$  contacts between ET radical cations in the stacks [3.631 (2) Å] are only slightly shorter than the sum of the van der Waals radii. The ET molecules of the translationally identical stacks form bands along the *a* axis, making ‘side-by-side’ intermolecular interactions with  $\text{S}\cdots\text{S}$  contacts as short as 3.424 (1) and 3.397 (1) Å (Table 3). Thus, the ET radical cations in the conducting layer are packed in a way which is a superposition of the packing types observed earlier in  $(\text{ET})_2\text{FeCl}_4$  (turning of the ET molecules in the stacks; Mallah *et al.*, 1990) and  $(\text{ET})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$  (ET bands with a

**Table 1**

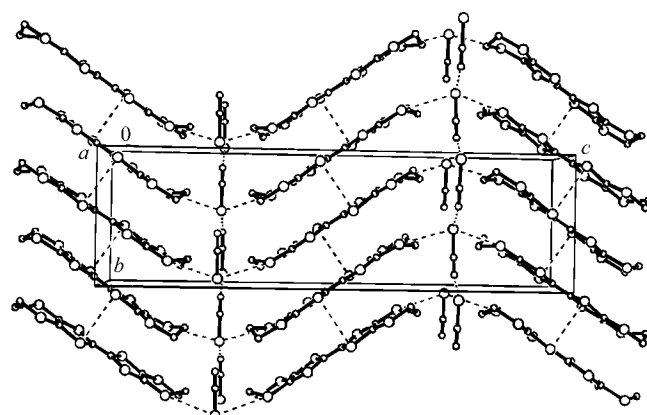
Experimental details.

Crystal data	
Chemical formula	$\text{C}_{10.77}\text{H}_{18}\text{N}_{0.77}\text{S}_{8.77}$
Chemical formula weight	429.37
Cell setting, space group	Orthorhombic, <i>Pbcm</i>
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.638 (1), 8.309 (2), 28.776 (6)
<i>V</i> (Å $^3$ )	1587.1 (6)
<i>Z</i>	4
<i>D<sub>x</sub></i> (Mg m $^{-3}$ )	1.797
Radiation type	Mo <i>K</i> α
$\mu$ (mm $^{-1}$ )	1.212
Temperature (K)	110 (2)
Crystal form, colour	Rhombic plates, black
Crystal size (mm)	0.38 × 0.33 × 0.25
Data collection	
Diffractometer	Bruker AXS SMART 1000
Data collection method	$\omega$ scans
Absorption correction	Semiempirical
No. of measured, independent and observed parameters	3049, 1533, 1288
Criterion for observed reflections	$I > 2\sigma(I)$
<i>R</i> <sub>int</sub>	0.0512
$\theta_{\text{max}}$ (°)	30.07
Range of <i>h</i> , <i>k</i> , <i>l</i>	−9 → <i>h</i> → 4 −11 → <i>k</i> → 5 −39 → <i>l</i> → 15
Intensity decay (%)	0
Refinement	
Refinement on	<i>F</i> <sup>2</sup>
$R[F^2 > 2\sigma(F^2)]$ , <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.0569, 0.1412, 0.884
No. of reflections and parameters used in refinement	1533, 103
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0000P]$ , where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.057

Computer programs used: *SHELXS93* (Sheldrick, 1993), *SHELXL97* (Sheldrick, 1997a).

‘side-by-side’ interaction type; Kobayashi *et al.*, 1983). It should be noted that in  $(\text{ET})_2\text{FeCl}_4$  there are pairs of ET molecules turned with respect to the adjacent ones and there are no individual radical cations as in  $\text{ET}(\text{NCS})_{0.77}$ .

In addition to the intermolecular  $\text{S}\cdots\text{S}$  interactions in the conducting layer, short  $\text{S}\cdots\text{S}$  contacts are also present



**Figure 1**

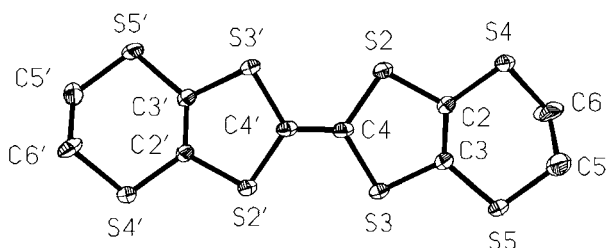
The  $\text{ET}(\text{NCS})_{0.77}$  crystal structure showing the alternation of the conducting radical cation layers and the non-conducting anionic layers along the *c* axis.

**Table 2**  
Bond lengths (Å) and angles (°) for ET(NCS)<sub>0.77</sub>.

S1—C1	1.91 (2)
S2—C4	1.731 (3)
S2—C2	1.745 (3)
S3—C4	1.733 (3)
S3—C3	1.739 (3)
S4—C2	1.741 (3)
S4—C6	1.804 (4)
S5—C3	1.733 (3)
S5—C5	1.776 (4)
N1—C1	1.09 (3)
C2—C3	1.354 (5)
C4—C4 <sup>i</sup>	1.360 (6)
C5—C6	1.434 (6)
C4—S2—C2	95.6 (2)
C4—S3—C3	95.4 (2)
C2—S4—C6	100.4 (2)
C3—S5—C5	103.3 (2)
N1—C1—S1	170 (2)
C3—C2—S4	127.5 (3)
C3—C2—S2	116.5 (2)
S4—C2—S2	116.0 (2)
C2—C3—S5	128.6 (3)
C2—C3—S3	117.1 (2)
S5—C3—S3	114.2 (2)
C4 <sup>i</sup> —C4—S2	123.0 (3)
C4 <sup>i</sup> —C4—S3	121.7 (3)
S2—C4—S3	115.2 (2)
C6—C5—S5	119.7 (3)
C5—C6—S4	116.5 (3)

Symmetry codes: (i)  $-x + 1, -y + 1, -z + 1$ .

between the cationic and anionic layers. All of them implicate the S1 atom of the thiocyanate group and S4 of the ET cation [3.578 (1) Å]. In the anionic layer the thiocyanate groups form polymeric chains where they are oriented in a 'head-to-tail' mode. The distances between the S and N atoms of the neighbouring thiocyanate groups is 2.44 (2) Å, which is shorter by 0.90 Å than the sum of the respective van der Waals radii, 3.34 Å (Zefirov, 1997). Thus, the structure has short intermolecular contacts of the cation–cation, anion–anion and cation–anion types (Table 3), which leads to the formation of a three-dimensional structure of intermolecular interactions (Fig. 5). As far as we know, the formation of a three-dimensional network of intermolecular interactions is very rare in molecular conductors. This may have a significant effect on the physical properties of the compounds, for instance, by lowering the conductivity anisotropy along different directions



**Figure 2**  
Atomic labelling used for the ET(NCS)<sub>0.77</sub> crystal. Symmetry transformations used to generate equivalent atoms: (')  $-x + 1, -y + 1, -z + 1$ .

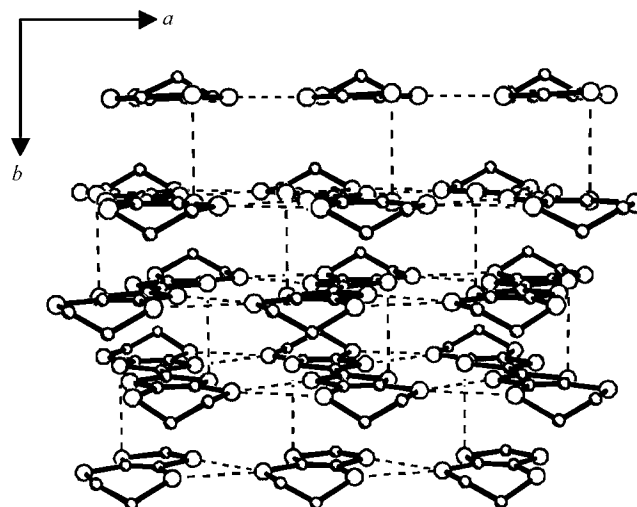
**Table 3**  
Short contacts S...S and S...N [ $r(\text{S}\cdots\text{S}) \leq 3.68$  Å,  $r(\text{S}\cdots\text{N}) \leq 3.34$  Å; Zefirov, 1997] in the ET(NCS)<sub>0.77</sub> salt.

Type of interaction	Contact	Distance (Å)
Cation...cation	S2—S5 <sup>i</sup>	3.424 (1)
	S3—S3 <sup>ii</sup>	3.631 (2)
	S4—S5 <sup>i</sup>	3.397 (1)
Cation...anion	S1—S4 <sup>iii</sup>	3.578 (1)
Anion...anion	S1—N1 <sup>iv</sup>	2.44 (2)

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $x, \frac{1}{2} - y, 1 - z$ ; (iii)  $1 - x, y - \frac{1}{2}, z$ ; (iv)  $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$ .

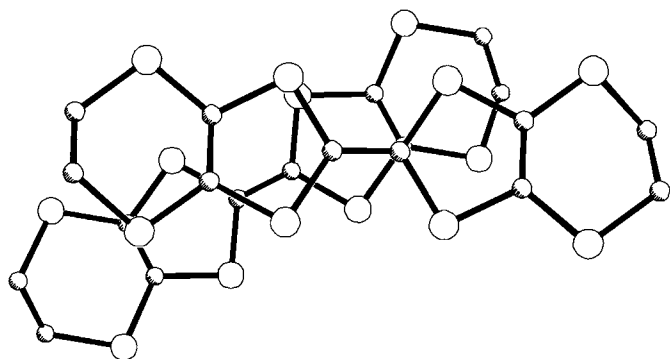
of the crystal lattice. However, it should be kept in mind that only around 77% of the anion positions are occupied.

Tight binding band structure calculations were carried out assuming full occupation of the anion sites. These calculations used an extended Hückel-type Hamiltonian (Whangbo & Hoffmann, 1978) and a modified Wolfsberg–Helmholz formula (Ammeter *et al.*, 1978) to calculate the non-diagonal matrix elements. Double- $\zeta$  Slater-type orbitals were used for C, S and N and single- $\zeta$  Slater-type orbitals for H. The exponents, contraction coefficients and ionization potentials were taken from previous work (Heuzé *et al.*, 2000). As shown in Fig. 6, the HOMO bands (*i.e.* those which will be partially filled and consequently those which should determine the transport properties of the salt) have a practically nil dispersion along the direction perpendicular to the donor layers (*i.e.*  $\Gamma$ -Z). In fact, each band in that figure is really the superposition of two almost indistinguishable bands. This is a consequence of the fact that there are two donor layers per unit cell, but negligible interactions between the layers as far as the HOMO bands are concerned. Consequently, the salt should be considered at most as a two-dimensional conductor. There are two reasons behind this result. First, the dispersion of the HOMO bands in molecular conductors is largely dominated by the direct HOMO...HOMO interactions and

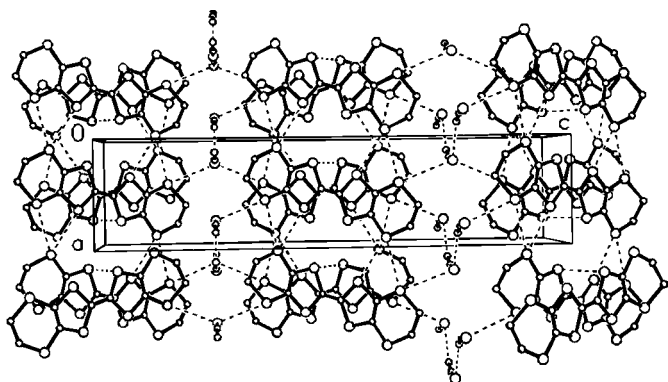


**Figure 3**  
Packing of the ET radical cations in the donor layers of the ET(NCS)<sub>0.77</sub> crystal.

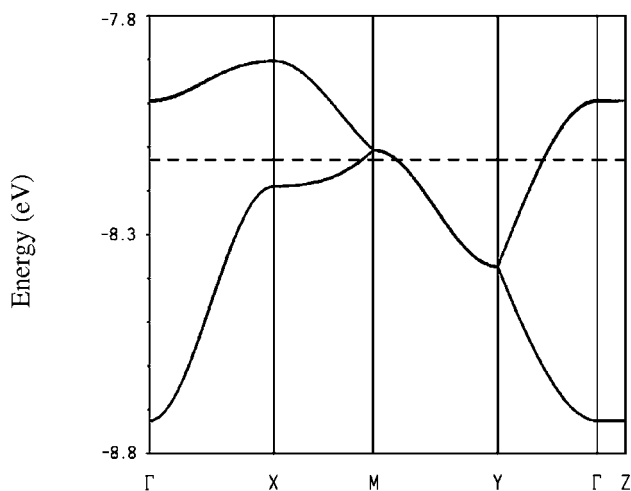
there are no such interactions along the interlayer direction. Second, even if there are interactions through the  $\text{NCS}^-$  anions, these interactions involve an S atom (*i.e.* S4) of the outer six-membered ring of ET and it is well known (Whangbo



**Figure 4**  
Overlap mode of the ET radical cations in the stacks.



**Figure 5**  
A view of the  $\text{ET}(\text{NCS})_{0.77}$  crystal structure along the  $b$  axis.



**Figure 6**  
Calculated HOMO bands for the  $\text{ET}(\text{NCS})_{0.77}$  salt assuming full occupation of the anion sites. The dashed line refers to the Fermi level according to a rigid band scheme and assuming a metallic filling of the bands.  $\Gamma = (0, 0, 0)$ ,  $X = (a^*/2, 0, 0)$ ,  $Y = (0, b^*/2, 0)$ ,  $M = (a^*/2, b^*/2, 0)$  and  $Z = (0, 0, c^*/2)$  in units of the reciprocal lattice vectors.

*et al.*, 1985) that the participation of this atom in the HOMO of ET is small. Note that, for practical reasons, we have assumed full occupation of the anion sites in our calculations, so that the real interlayer interactions should be even weaker than suggested by our calculations.

The HOMO···HOMO interactions within the layers are, however, quite sizeable. The absolute values of the  $\beta_{\text{HOMO-HOMO}}$  interaction energies, which are a measure of the strength of the interactions between two HOMOs in adjacent sites of the lattice (Whangbo *et al.*, 1985), are 0.214 eV for the interactions along the stacks and 0.163 eV for the side-by-side interactions (there is a third non-nil interaction between the HOMO of one ET and that of the second nearest neighbour in the next stack, but this interaction is noticeably smaller, 0.061 eV). Thus, there is a two-dimensional network of relatively strong and uniform HOMO···HOMO interactions, so that it is expected that the HOMO bands of the donor layer exhibit a quite two-dimensional behaviour. This is confirmed by the calculated band structure reported in Fig. 6. The dashed line in that figure refers to the Fermi level appropriate for the  $\text{ET}(\text{NCS})_{0.77}$  stoichiometry, assuming a rigid band scheme and metallic filling of the bands. The band dispersion in Fig. 6 is of the same order as those exhibited by ET salts with metallic and even superconducting properties (Williams *et al.*, 1987). Since these bands must be partially filled, as far as the HOMO···HOMO interactions are concerned there is no reason why the salt should not be metallic also. The reason for the activated conductivity behaviour must originate from the external random Coulomb potential associated with the incomplete occupation of the anion sites.

#### 4. Conclusions

An X-ray crystal chemical analysis of the new  $\text{ET}(\text{NCS})_{0.77}$  semiconductor has shown the existence of a partial three-dimensional structure of intermolecular interactions in this salt. However, tight binding calculations suggest that these interactions should not play a major role in the transport properties of the salt. It is suggested that the random Coulomb potential due to the partial occupation of the anion sites lies at the origin of the activated conductivity.

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