Crystal and electronic structure of new organic semiconductors with rare-earth metal counter-anions

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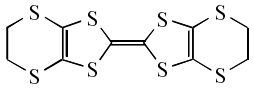
10.1070/MC2001v011n05ABEH001477

The new molecular semiconductors $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) have been studied by X-ray crystallography at 295 and 110 K, and the electronic band structure of these salts has been examined.

A search for suitable counter-ions is one of the main strategic tasks in the preparation of new organic conductors and superconductors based on the salts of bis(ethylenedithio)tetrathiafulvalene (ET) and its derivatives. Here, we report on the use of rare-earth metal-complex anions for the preparation of new ET salts. In addition, changing the filling of the *f* shells along the lanthanide series may influence the electroconducting and magnetic properties of the possible compounds. This paper describes the crystal and electronic band structure of the new salts $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) of dysprosium and yttrium.



ET

The new salts were prepared by the electrochemical oxidation of ET using the salt $(Bu_4N)_3[M(NCS)_4(NO_3)_2]$ as an electrolyte.

A Bruker AXS SMART 1000 instrument[1] with a CD detector (MoKα line, graphite monochromator, *ω* scanning, scanning pitch 0.3°, frame measuring time 30 s, $2\theta \leq 60°$) was used. The crystal structure was solved by direct methods and subsequent Fourier syntheses using the SHELXL-93 program package.[2]

The crystals of salts $(ET)_5[Dy(NCS)_6NO_3]\cdot EtOH$ **1** and $(ET)_5[Y(NCS)_6NO_3]\cdot EtOH$ **2** (Table 1)† are isostructural and have a layered structure (Figure 1). The crystal structure is characterised by the alternation of conducting radical cation layers including ET and ethanol molecules and anionic layers containing the complex units $[M(NCS)_6NO_3]^{4-}$ (M = Dy, Y) along the *c* axis.

The ET layers show a clathrate architecture in which groups of four ET pairs form cavities (Figure 2). The cavities along the *a* and *b* axes are uniformly occupied in an alternating way by

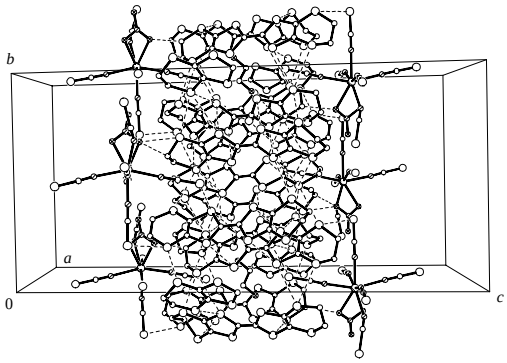


Figure 1 A fragment of the crystal structure of the $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) salts.

† Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2001. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/99.

Table 1 Main crystal data for the $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) salts.

	1	**1**	**2**
Formula	$C_{58}H_{46}DyN_7O_4S_{46}$	$C_{58}H_{46}DyN_7O_4S_{46}$	$C_{58}H_{46}YN_7O_4S_{46}$
M	2542.28	2542.28	2468.69
T/K	295	110	110
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	17.877(4)	17.670(1)	17.749(2)
b/Å	15.863(3)	15.548(1)	15.567(2)
c/Å	33.165(11)	33.002(2)	33.052(2)
β/°	97.62(2)	97.858(2)	97.921(2)
V/Å^3	9322(4)	8981.7(9)	9045(2)
Z	4	4	4
d_{calc}/g cm^{-3}	1.812	1.880	1.813
μ/cm^{-1}	14.332 (CuKα)	1.952 (MoKα)	1.757 (MoKα)
No. of observed reflections $[F_0 > 4\sigma(F_0)]$	2667	4987	7154
GOF	1.209	1.178	1.060
Final *R*, *wR*	0.056, 0.127	0.078, 0.190	0.076, 0.175

ET and EtOH molecules, while the cavities along the *ab* diagonal are occupied by only ET molecules. Note that although the donor layers of $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) remind those of the well-known *κ*-phases, first found in the organic superconductors $(ET)_4Hg_3Cl_8$,[4] $(ET)_4Hg_{2.78}Cl_8$[5] and $(ET)_4Hg_{2.89}Br_8$,[5] in the present case, they contain both dimeric and monomeric ET units (and ethanol molecules). Thus, the radical cation layers have a new packing type which we propose to refer to as *ω*-type. The conducting layers of salts **1** and **2** exhibit many short S···S contacts between ET molecules.

The anionic layer contains isolated four-charged complex units $[M(NCS)_6NO_3]^{4-}$ (M = Dy, Y). The M atom of the complex anion is coordinated to six N atoms from NCS groups and to one bidentate NO_3 group. Thus, the complex anion has an approximately pentagonal bipyramidal shape (Figure 3).

The conductivity of $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) crystals measured along the *b* axis in the plane of the radical

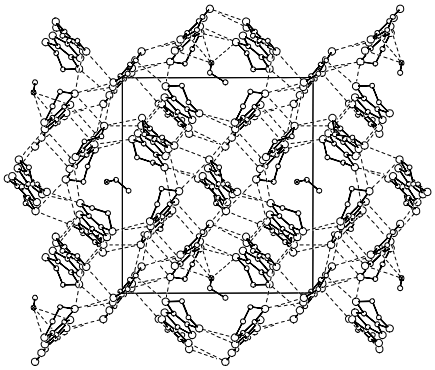


Figure 2 View of the *ω*-packing of the radical cations in the $(ET)_5[M(NCS)_6NO_3]\cdot EtOH$ (M = Dy, Y) salts. The dotted line shows short intermolecular S···S contacts [r(S···S) ≤ 3.68 Å].[3]

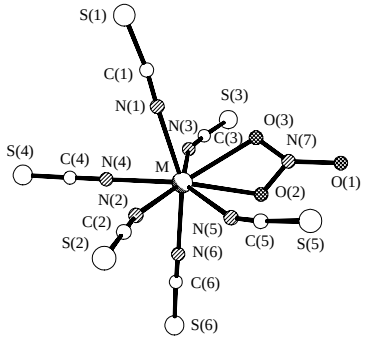


Figure 3 Structure of the $[M(NCS)_6NO_3]^{4-}$ complex anion. The M–N and M–O bond lengths at 110 K for **1** are (Å): Dy–N(1) 2.39(1), Dy–N(2) 2.42(1), Dy–N(3) 2.42(1), Dy–N(4) 2.39(1), Dy–N(5) 2.35(1), Dy–N(6) 2.37(1), Dy–O(2) 2.55(2), Dy–O(3) 2.54(2). The M–N and M–O bond lengths at 110 K for **2** are (Å): Y–N(1) 2.365(5), Y–N(2) 2.433(5), Y–N(3) 2.409(6), Y–N(4) 2.434(7), Y–N(5) 2.410(8), Y–N(6) 2.340(6), Y–O(2) 2.668(9), Y–O(3) 2.57(1).

cation layers is 0.1–0.2 Ohm^{-1} cm^{-1} at room temperature. The salts exhibit a semiconducting behaviour.[6]

The electronic structure of these salts was analysed by tight-binding extended Hückel type calculations[7] for their donor layers using a modified Wolfsberg–Helmholz formula.[8] Double-ζ Slater type orbitals were used for C and S and single-ζ Slater type orbitals, for H. The exponents, contraction coefficients and parameters were taken from ref. 9. The repeating unit of a donor layer contains ten ET donors so that the band structure in the vicinity of the Fermi level contains ten HOMO bands. The calculated band structure for a donor layer of salt **2** is shown in Figure 4. Given the stoichiometry and the tetravalent nature of the anion, there must be eight holes in these HOMO bands. As shown in Figure 4, there is an energy gap between the four upper bands and the lower ones so that, in agreement with the conductivity results, salt **2** should be a semiconductor.

The interaction between the two ET donors of every pair is strong so that the two HOMOs of each of these pairs lead to a low-lying orbital, which we will refer to as (Ψ^+)HOMO, and to an upper-lying orbital, which we will refer to as (Ψ^-)HOMO. The four upper bands in Figure 4 are built from the four (Ψ^-)HOMO orbitals associated with the four ET pairs in the repeating unit of the donor layer. The six filled bands in Figure 4 can be divided into two groups: (*a*) two very flat bands, at the top of this group of filled bands, which are each associated with the HOMO of one of the single ETs and (*b*) four bands, slightly lower in energy, which are built from the (Ψ^+)HOMO orbitals of the four ET pairs. Consequently, since the four empty bands are mostly based on the ET pairs, we can conclude that the paired ET donors must be considered as ET^+, whereas the single ET donors must be considered as ET^0.

At this point the question arises of how the single ET donors should be considered, as a real part of the donor lattice or as just filling the cavities of the donor lattice built from the ET pairs (*i.e.*, like the EtOH molecules). As far as the HOMO···HOMO interactions are concerned, this question can be answered by evaluating the so-called $\beta_{HOMO-HOMO}$ interaction energies, which are a measure of the interaction between two HOMOs in adjacent sites of the lattice.[10] There are three types of HOMO···HOMO interactions: (*a*) intra-pair, (*b*) inter-pair (every ET of one pair interacts with two ETs of adjacent pairs so that every ET pair interacts with four adjacent pairs) and (c) interactions between the single ETs and the paired ones (every single ET makes a total of eight interactions with the eight donors of four adjacent ET pairs). The calculated $\beta_{HOMO-HOMO}$ values for salt **2** are very large for the intra-pair interactions (around 0.8 eV) and quite sizeable for the inter-pair interactions (0.14–0.26 eV). In contrast, of the eight interactions between the single and paired ETs, only one is associated with a sizeable $\beta_{HOMO-HOMO}$ (0.18), whereas the remaining seven are around one order of magnitude smaller. Consequently, these interactions seem to be weak and, as far as the the HOMO··HOMO interactions are concerned (*i.e.*, those determining the shape of the band structure around the Fermi level), the ET sublattice of these salts can be described as a series of ET^+ dimers interacting relatively strongly among themselves but only weakly with single ET^0 units partially filling the cavities of the dimers lattice.

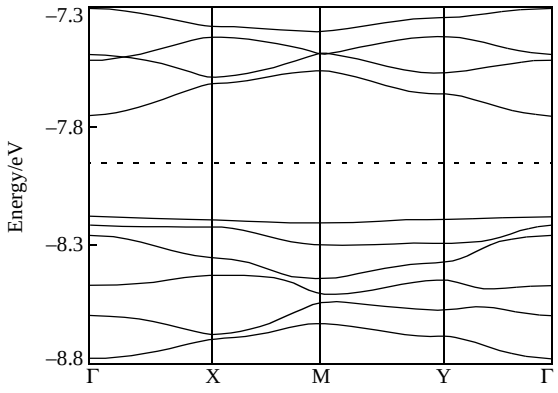


Figure 4 Calculated band structure for the donor layer of **2**; the dashed line refers to the Fermi level. Γ = (0, 0), X = (a^*/2, 0), Y = (0, b^*/2) and M = (a^*/2, b^*/2).

To check this conclusion, we calculated the band structure of the same ET lattice from which the single ETs are removed. The calculated band structure is very similar to that in Figure 4 except for the absence of the two upper filled very flat bands associated with the single ETs. However, as far as the band structure of Figure 4 is correct, it cannot be concluded that the single ETs do not influence the conductivity of the lattice: the holes of these semiconductors are associated with the upper flat bands (*i.e.*, mainly with the HOMOs of the weakly interacting single ETs) and the electrons with the bottom of the more dispersive empty bands [*i.e.*, mainly with the set of interacting (Ψ^-)HOMO orbitals of the ET dimers].

In conclusion, the novel radical cation salts $(ET)_5[M(NCS)_6NO_3]\cdot$EtOH (M = Dy, Y) were prepared and their crystal and electronic structures were examined. These salts have radical cation layers with a new packing type (ω-type) separated by anionic layers. Despite the presence of a great number of intermolecular and intramolecular short S··S contacts in the two-dimensional radical cation layers, the salts exhibit semiconducting properties.

This work was supported by the Russian Foundation for Basic Research (grant no. 00-03-32809), DGI Spain (project no. BFM2000-1312-C02-01) and Generalitat de Catalunya (1999 SGR 207).

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Received: 15th May 2001; Com. 01/1803