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Synthesis, crystal structure and electroconducting properties of a new molecular semiconductor $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$

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The new molecular semiconductor $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$ was synthesised by the electrochemical oxidation of bis(ethylenedithio)tetrathiafulvalene (ET); its crystal structure and electroconducting properties were studied.

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The anions of rare-earth elements[1–3] can be used as non-traditional anions in the synthesis of radical cation salts. Earlier, we obtained and studied molecular conductors with lanthanide complex anions. These are isostructural semiconductors, $(ET)_5[M(NCS)_6NO_3]{\cdot}EtOH$ (M = Dy, Ho or Y) and $(TMTSF)_3[Y(NO_3)_5]{\cdot}2PhCl$;[4] compounds based on an EDT donor, $(EDT)_2[Ho(NCS)_4(H_2O)_4]$ (metal down to 100 K) and a semiconductor, $(EDT)_3[Y(NO_3)_5]$.[5]

In order to investigate the reasons influencing the structure and properties of the conductors, we studied the role of the nature of the ligands bound to rare-earth elements. A number of $(ET)_5[M(NCS)_7]{\cdot}EtOH$ salts (M = Dy, Ho or Y) were synthesised, which differ from the isostructural $(ET)_5[M(NCS)_6NO_3]{\cdot}EtOH$ (M = Dy, Ho or Y) salts obtained earlier by the replacement of the NO_3 group with an NCS group. Here, we describe the compound $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$.

The $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$ salt was synthesised by electrochemical oxidation of ET in the presence of $(Bu_4N)_4[Ho(NCS)_7]$ in a chlorobenzene solution with 15 vol% ethanol. The initial $(Bu_4N)_4[Ho(NCS)_7]$ electrolyte was obtained by the interaction of alcohol solutions of tetrabutylammonium thiocyanate $(Bu_4N)NCS$ with holmium bromide (7:1) on heating with consequent cooling. The electrolyte composition was determined by elemental analysis.

The crystal measured had the form of a thin rectangular plate with the dimensions of $0.7{\times}0.3{\times}0.01$ mm^3. The electrical resistance of the crystals was measured in the *bc* plane by the standard dc-four-probe method at 100–295 K.

The crystal structure of $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$[†] is formed by four ET molecules in general positions and two ET molecules in special central-symmetrical positions, $[Ho(NCS)_7]^{4-}$ complex anion (Figure 1) and two statistically disordered ethanol molecules.

We found that the $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$ salt has a layered structure (Figure 2), where conducting layers consisting of ET radical cations and the molecules of ethyl alcohol alternate with non-conducting anionic layers formed by $[Ho(NCS)_7]^{4-}$ complexes.

Conducting layers in $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$ have the ω-type of donor packing, which was discovered earlier.[4]

Structure of the conducting layer of ω-type is characterised by a clathrate architecture, where the quartets of ET pairs form cavities occupied by ET and EtOH molecules (Figure 3). Note that ethanol molecules are disordered in two positions with approximately similar populations equal to 0.5. Meanwhile the cavities along the *b* and *c* axes are occupied by evenly alternating ET and EtOH molecules, and the cavities along the *bc* diagonale contain only ET and ethanol molecules. The conducting layer has numerous short S···S contacts in the pairs of ET radical cations, between the pairs, between single donors and ET pairs within the range of 3.421–3.634 Å forming a two-dimensional network. The structure has also short interactions S···S of the cation–anion type within the range 3.456(3)–3.622(4) Å and the anion–anion type [3.541(4) Å].

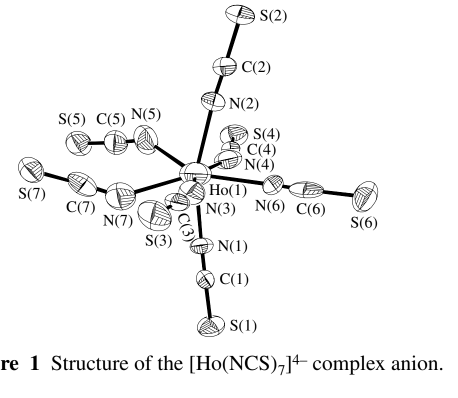

Figure 1 Structure of the $[Ho(NCS)_7]^{4-}$ complex anion.

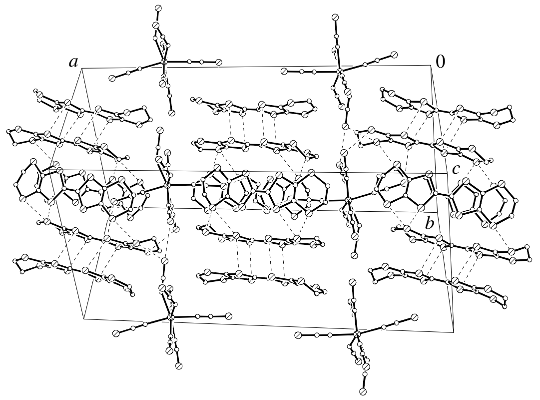

Figure 2 Crystal structure of $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$. Alternation of conducting and non-conducting layers along the *a* axis. Dotted lines show short intermolecular interactions.

The anionic layer has an island structure formed by four-charged $[Ho(NCS)_7]^{4-}$ complexes. The coordination polyhedron of the Ho atom can be presented as a pentagonal bipyramide formed by seven thiocyanate groups, five of which form the equatorial plain and two others take apical positions (Figure 1). The Ho atom in the complex is coordinated by thiocyanate NCS groups along the Ho–N bond. Ho–N bond lengths vary from 2.358(6) to 2.451(9) Å, whereas the Ho–N bond lengths to the

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[†] *Main crystallographic data*: $C_{59}H_{46}HoN_7OS_{47}$, $M = 2540.78$, monoclinic, $a = 32.965(7)$, $b = 15.851(3)$ and $c = 18.007(4)$ Å, $\beta = 98.87(3)°$, $V = 9297(3)$ Å^3, $T = 293(2)$ K, space group $P2_1/n$, $Z = 4$, $\mu = 1.953$ mm^{-1}, $d_{\text{calc}} = 1.81$ g cm^{-3}; the number of measured reflections, 13609; the number of independent reflections, 13177; the number of refined parameters, 1047; $R_{\text{int}} = 0.044$, *R*-factor 0.085 for 8094 reflections with $I > 2\sigma(I)$. X-ray diffraction analysis of $(ET)_5[Ho(NCS)_7]{\cdot}EtOH$ crystals was performed on a KM-4 KUMA DIFFRACTION diffractometer ($\omega/2\theta$-scanning, MoKα radiation, graphite monochromator). Crystal structure was solved by direct methods and following Fourier synthesis using the SHELXS-97 software package.[6] The structure was refined by full-matrix least squares procedures using an anisotropic approximation for all non-hydrogen atoms with the SHELXL-97 program.[7] An absorption correction was applied using the DIFABS program.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 266638. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2005.

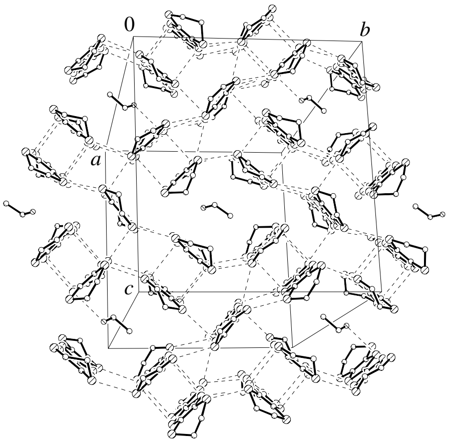

Figure 3 The ω-packing of ET radical cations in conducting layer.

apical N(1) and N(2) atoms are 2.358(6) and 2.367(6) Å, respectively, and bond lengths to the equatorial atoms N(3), N(4), N(5), N(6) and N(7) are 2.358(8)–2.451(9) Å. The N(1)–Ho–N(2) angle is 162.3°. The Ho atom practically does not deviate from the distorted plain of N(3), N(4), N(5), N(6) and N(7) atoms. The deviation makes 0.007 Å in the direction of the N(2) atom.

Note that thiocyanate groups are characterised by different degrees of deviation. The N–C and C–S bond lengths and N–C–S valence angles are within the ranges of 1.02(1)–1.23(1), 1.557(9)–1.78(1) Å and 177.4(9)–179.1(7)°, respectively. The Ho–N–C angles are in the range 147.2(7)–178.5(7)° with maximal non-linearity in Ho(1)–N(7)–C(7) [147.2(7)°] and Ho(1)–N(5)–C(5) [148.6(7)°] groups, respectively.

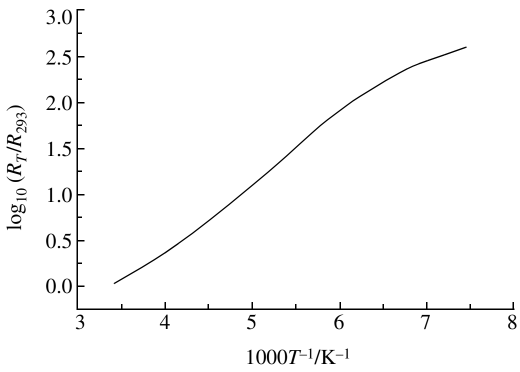

Figure 4 The temperature dependence of the resistance of a single crystal of $(\mathrm{ET})_5[\mathrm{Ho(NCS)}_7]\cdot\mathrm{EtOH}$, $\mathrm{lg}_{10}\,(R/R_{293})$–$1000/T$.

The conductivity of the crystals at ambient temperature in the *bc* plane is 0.5 Ω^{-1} cm^{-1}. The temperature dependence of the resistance of $(\mathrm{ET})_5[\mathrm{Ho(NCS)}_7]\cdot\mathrm{EtOH}$ crystals in the *bc* plane has a semiconductor character with the activation energy $E_\mathrm{a} \cong$ $\cong 0.16$ eV at 150–300 K, as shown in Figure 4. The corresponding activation energy values for the earlier studied crystals of $(\mathrm{ET})_5[\mathrm{M(NCS)}_6\mathrm{NO}_3]\cdot\mathrm{EtOH}$ (M = Dy, Ho or Y) were 0.13–0.15 eV.

Thus, a new molecular $(\mathrm{ET})_5[\mathrm{Ho(NCS)}_7]\cdot\mathrm{EtOH}$ semiconductor was synthesised, and its crystal structure and conducting properties were studied. The compound is isostructural to $(\mathrm{ET})_5$-$[\mathrm{Ho(NCS)}_6\mathrm{NO}_3]\cdot\mathrm{EtOH}$ crystals.[4] It is a semiconductor with the activation energy $E_\mathrm{a} \cong 0.16$ eV. Thus, a comparison between $(\mathrm{ET})_5[\mathrm{Ho(NCS)}_7]\cdot\mathrm{EtOH}$ and $(\mathrm{ET})_5[\mathrm{Ho(NCS)}_6\mathrm{NO}_3]\cdot\mathrm{EtOH}$ allows us to conclude that the substitution of the NO_3 group by the NCS group in the anion does not affect either the structure or the conducting properties of the compounds with the general formula $(\mathrm{ET})_5[\mathrm{M(NCS)}_6\mathrm{X}]\cdot\mathrm{EtOH}$, where M = Dy, Ho or Y; X = NO_3 or NCS.

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