New Charge-transfer Salts Based on Unsymmetrical Donor DMET and Metal Complex Anions: (DMET)$_3$[Cr(isoq)$_2$(NCS)$_4$] and (DMET)$_3$[Cr(phen)(NCS)$_4$]•CH$_3$CN

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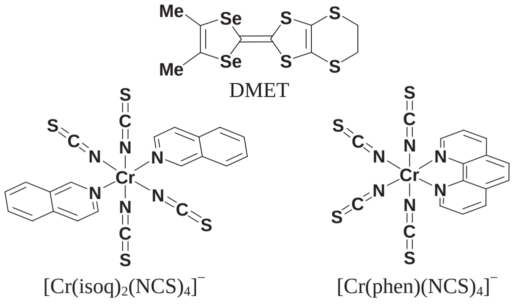
Two charge-transfer salts (DMET)$_3$[Cr(isoq)$_2$(NCS)$_4$] (**1**) and (DMET)$_3$[Cr(phen)(NCS)$_4$]•CH$_3$CN (**2**) have been prepared and characterized. The single-crystal X-ray crystallography revealed that the structures of both salts consist of segregated columns of DMET and metal complex anions. The magnetic and transport properties have shown that these salts are paramagnetic semiconductors.

Hybrid molecular materials combining conducting π electrons with magnetic d electrons have attracted considerable interests from the viewpoints of multifunctionalities.[1] Recently, Day and co-workers reported the charge-transfer salts of TTF derivative with [Cr(L)$_n$(NCS)$_4$]$^-$, L = isoquinoline (isoq) or 1,10-phenanthroline (phen), which behave as ferrimagnetic insulators or paramagnetic semiconductors.[2] For these salts with [Cr(L)$_n$(NCS)$_4$]$^-$, two kinds of structural types have been confirmed, where the first type is the salts with stacks of alternating TTF donors and anions which show long-range magnetic ordering.[2a–2c] The magnetic interactions would be induced by S···S contacts and $\pi \cdots \pi$ interactions between organic radicals and paramagnetic anions. The second type is the salt with segregated columns of donors and anions which does not show long-range magnetic ordering.[2d] But the compound of this type is conductive. If both structural features would coexist in the crystal, the resultant electronic system might behave as ferrimagnetic semiconductor or ferrimagnetic metal. We have focused on unsymmetrical donor DMET [4′,5′-dimethyl-4,5-(ethylenedithio)-1′,3′-diselena-1,3-dithiafulvalene] with the aim of creating a new electronic system (Scheme 1). A DMET molecule constitutes of half of TMTSF and half of BEDT-TTF. According to its hybrid nature, DMET salts provide various species of structures from quasi-one-dimensional structures to two-dimensional κ-typed structures. Moreover, the charge-transfer salts with DMET are expected to have interesting electronic states as the charge density wave (CDW), spin density wave (SDW), Mott insulating, metallic, and superconductivity states.[3] However, a few reports on DMET with magnetic metal anions have been reported.[4] Here, we report the structures, electrical resistivities, and magnetic susceptibilities of (DMET)$_3$[Cr(isoq)$_2$(NCS)$_4$] (**1**) and (DMET)$_3$[Cr(phen)(NCS)$_4$]•CH$_3$CN (**2**).



Scheme 1.

DMET[5] and electrolytes[6] were prepared to according to the previously reported procedure. Single crystals of **1** and **2** were obtained by electrochemical oxidation.[7] The solutions of CH$_3$CN (20 mL) containing the DMET (3 mg, 7.2×10^{-6} mol) and (^{n}Bu$_4$N)$_3$[Cr(L)$_n$(NCS)$_4$](L = isoq and phen) (10–11 mg, 1.4×10^{-5} mol) were applied by a constant current of 0.1 µA.

The structure of **1** is shown in Figure 1. The asymmetric unit contains one and half DMET molecules, and half [Cr(isoq)$_2$-(NCS)$_4$] anion. The structure shows that the atoms of the half of a DMET molecule are disordered onto two sites. The mean values for Cr–N (NCS) distances and Cr–N (isoq) are 1.995(4) and 2.077(3) Å, respectively, which are comparable with those of previously reported salts.[2] From the 3:1 stoichiometry, the

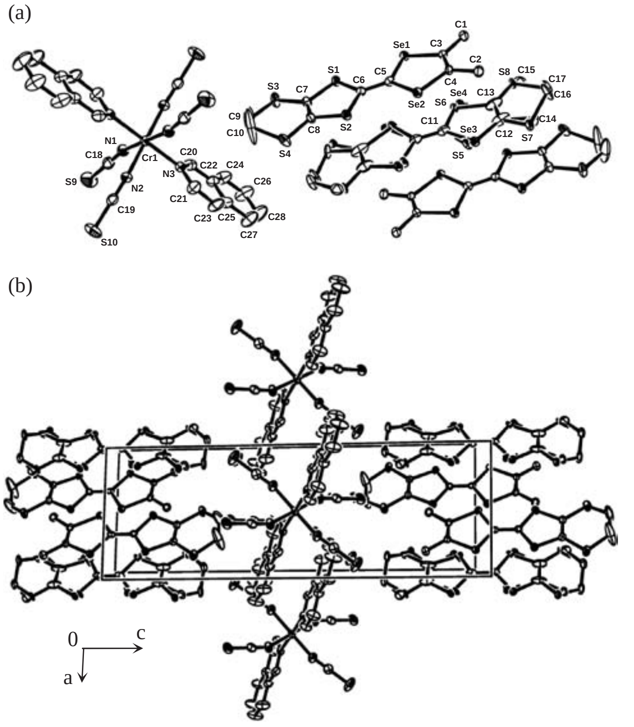


Figure 1. Molecular structure (a) and crystal structure (b) of **1**.

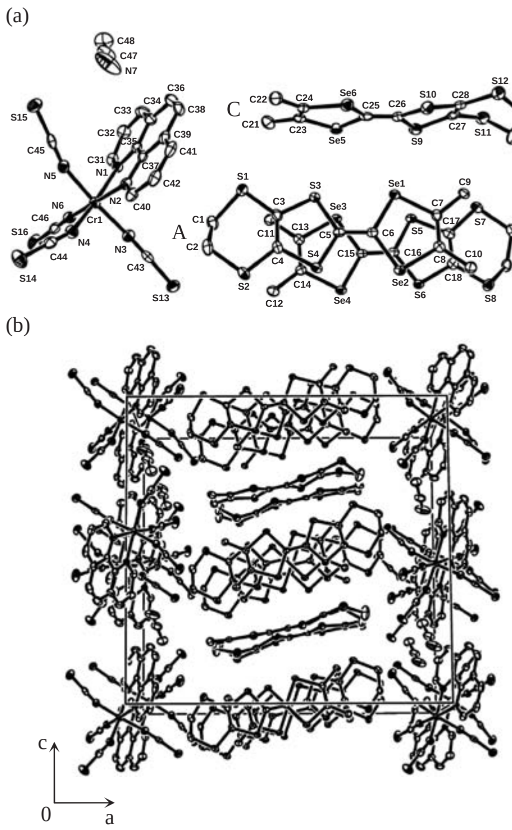


Figure 2. Molecular structure (a) and crystal structure (b) of **2**.

charge on the DMET molecule is assigned as $+1/3$. The crystal structure of **1** consists of columns of DMET molecules separated by sheets of anions. The several intermolecular van der Waals contacts between donors were observed in S atoms (e.g., $S\cdots S = 3.491$ and 3.500 Å). Other meaningful contacts may be considered in hydrogen bonds (e.g., $S\cdots H_C \approx 2.938$ Å). On account of the presence of disordered molecules, it is difficult to calculate the energy band structure of **1**. The structure of **2** is shown in Figure 2. The asymmetric unit contains three DMET molecules [labeled A, B, and C in Figure 2a], and one [Cr(phen)-$(NCS)_4$] anion, and one CH_3CN solvent molecule. The crystal structure of **2** consists of layers of DMET molecules separated by sheets of anions. In the donor layer, molecules A and B form a column along *b* axis, where the molecules are arranged in the sequence ···AABBAABB···, and the molecule C lies orthogonal to the columns. The donor arrangement of **2** is relatively similar to that of $(TMTSF)_3[Cr(phen)(NCS)_4]_2{\cdot}0.5CH_2Cl_2$ and $(BMDT\text{-}TTF)_3PF_6$(1,2-dichloroethane).[8] A calculation of overlap integrals between the HOMOs indicated that the slight dimerization have occurred between B and B within the stacks.[9] A tight-binding band calculation of **2** predicts that the system is a semiconductor. The mean values for Cr–N (NCS) and Cr–N (phen) distances are 1.987(5) and 2.068(4) Å, respectively. The empirical correlation of the bond lengths within the donor molecules is an efficient tool for evaluating the degree of charge transfer. The central C=C bonds lengths of **2** are 1.347(7) Å for molecule A, 1.364(7) Å for molecule B, and 1.334(7) Å for molecule C, respectively. The lengths of the central C=C bonds of molecule are observed to a longer for molecules A and B than for molecule C. Because the bond length of molecule C is similar to that of neutral DMET, the charge on the molecule C is considered to be neutral. Therefore, the charge on the molecules A and B are considered to be $+0.5$. The several intermolecular van der Waals contacts between donors were observed (e.g., $Se\cdots S = 3.657$ and 3.621 Å).

Single crystal conductivity measurements performed on **1** and **2** show semiconducting behaviors [σ_{RT} ($S\,cm^{-1}$) = 1.55 for **1** and 1.23×10^{-1} for **2**]. The transport property of **2** is in agreement with the energy band structure. The changes of the activation energy were observed at ambient pressure; it is 28.6 meV below 210 K and 58.3 meV above 210 K for **1**, it is 71.6 meV below 250 K and 19.8 meV above 250 K for **2**.

The temperature dependence of the magnetic susceptibilities of two compounds obeys the Curie–Weiss law. The values of the parameters were as follows: (**1**), the Curie constant $C = 1.97\,emu{\cdot}K{\cdot}mol^{-1}$, the Weiss temperature $\theta = -1.8$ K; (**2**), $C = 1.94\,emu{\cdot}K{\cdot}mol^{-1}$, $\theta = -1.6$ K. The Curie constant of two compounds is close to the spin-only values of Cr^{3+} species ($1.875\,emu{\cdot}K{\cdot}mol^{-1}$).

In summary, we have prepared the new charge-transfer salts **1** and **2** based on unsymmetrical donor DMET and $[Cr(L)_n(NCS)_4]^-$ (L = isoq and phen) in order to create the new electronic system such as ferrimagnetic semiconductor and ferrimagnetic metal. The structures of **1** and **2** were constructed by the combination of the segregated columns of donors and anions. The meaningful overlaps between the donors and anions have not confirmed. The structural aspects of both salts lead to the paramagnetic semiconducting behavior which is similar to the previous reported salts.[2d]

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7 a) Crystal data for **1**: $C_{52}H_{44}CrN_6S_{16}Se_6$, MW 1791.65, triclinic; $P\bar{1}$ (#2), $a = 7.8600(8)$ Å, $b = 9.1687(9)$ Å, $c = 22.544(2)$ Å, $\alpha = 98.746(2)^\circ$, $\beta = 90.014(2)^\circ$, $\gamma = 102.169(2)^\circ$, $V = 1568.8(3)$ Å^3, $Z = 1$; $D_{calcd} = 1.896\,g{\cdot}cm^{-3}$; $T = 120(2)$ K, $R_1 = 0.0401$ ($I > 2\sigma I$), $wR_2 = 0.0967$ ($I > 2\sigma I$), GOF = 0.994. b) Crystal data for **2**: $C_{48}H_{41}CrN_7S_{16}Se_6$, MW 1754.60, monoclinic; $P2_1/c$ (#14), $a = 21.485(2)$ Å, $b = 14.1419(13)$ Å, $c = 20.4642(19)$ Å, $\beta = 90.256(3)^\circ$, $V = 6217.8(10)$ Å^3, $Z = 4$; $D_{calcd} = 1.874\,g{\cdot}cm^{-3}$; $T = 120(2)$ K, $R_1 = 0.0345$ ($I > 2\sigma I$), $wR_2 = 0.0593$ ($I > 2\sigma I$), GOF = 1.080.

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