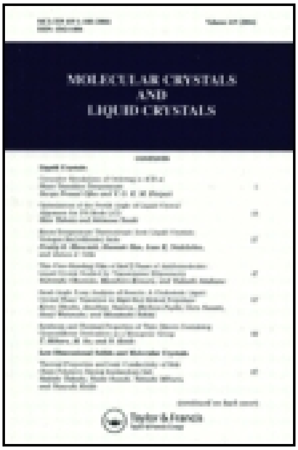

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ET and TTF Salts with Lanthanide Complex Ions Showing Frequency-Dependent ac Magnetic Susceptibility

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We measured conducting and magnetic properties of $(ET)_4[Ln(NCS)_6]\cdot CH_2Cl_2$ *(Ln = Dy, Ho, Er, and Yb),* $(ET)_5[Ln(NCS)_6NO_3]\cdot EtOH$ *(Ln = Tb and Dy), and* $(TTF)_6[Dy(NCS)_6]$*. All of the complexes behaved as semiconductors irrespective of Ln ions used, and also exhibited anomalous frequency-dependence of ac magnetic susceptibility below ca. 10 K, especially for Dy derivatives, indicating blocking behavior as found in single-molecule magnets.*

Keywords: BEDT-TTF; lanthanide ions; lanthanoid ions; magnetic properties; organic semiconductors; single-molecule magnets

INTRODUCTION

Search for suitable counter-ions is one of the main strategic tasks in the preparation of multi-functional organic conductors and superconductors, based on the salts of TTF (tetrathiafulvalene) and ET

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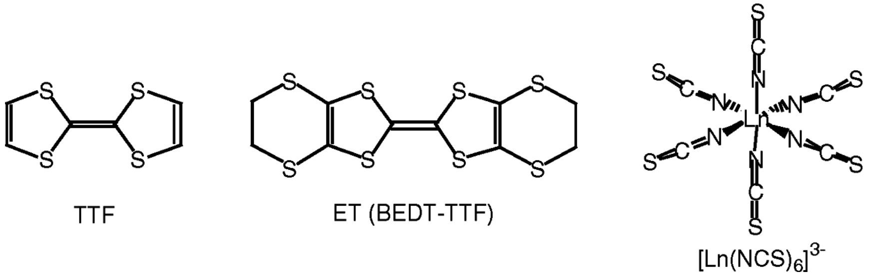


SCHEME 1 Structural formulas.

(BEDT-TTF; bis(ethylenedithio)TTF) (Scheme 1). We have already prepared several lanthanide (Ln) complexes showing frequency-dependent ac magnetic susceptibility [1], which can be observed usually for single-molecule magnets (SMMs) [2]. We then turned our attention to study on conducting SMMs obtained from TTF and ET with lanthanide complex ions.

EXPERIMENTAL

There have been pioneering works on ion-radical salts containing $[Ln(NCS)_6]^{3-}$ [3] and $[Ln(NCS)_6NO_3]^{4-}$ [4]. The present materials, $(ET)_4[Ln(NCS)_6]{\cdot}CH_2Cl_2$ (abbreviated as **1Ln**; Ln = Dy, Ho, Er, and Yb) and $(ET)_5[Ln(NCS)_6NO_3]{\cdot}EtOH$ (**2Ln**; Ln = Tb and Dy), were prepared by means of the electro-crystallization method. We also prepared $(TTF)_6[Dy(NCS)_6]$ (**3Dy**) by a chemical process using $(TTF)_3(BF_4)_2$. The composition was estimated by elemental analysis, IR spectrometry, and/or X-ray crystallographic analysis.

X-ray diffraction data were collected on a Rigaku R-axis RAPID diffractometer with graphite monochromated Mo $K\alpha$ radiation. The structures were solved by direct methods and expanded using Fourier techniques in the CrystalStructure program package [5]. Selected crystal data for **2Tb**:monoclinic, $P2_1/n$, $a = 17.76(1)$, $b = 15.57(1)$, $c = 33.00(2)$ Å, $\beta = 98.09(4)°$, $Z = 4$, $V = 9033(8)$ Å^3, $d_{calc} = 1.867\ \mathrm{g\,cm^{-3}}$, $T = 90$ K.

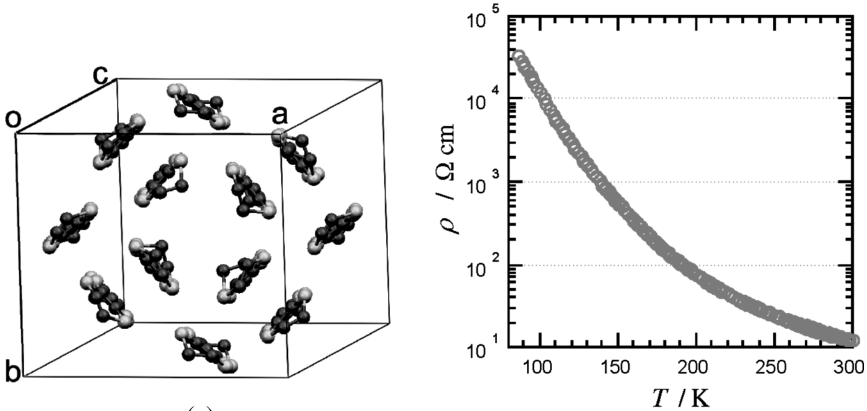
Conductivity and magnetic measurements were performed on a Quantum Design PPMS. Single-crystal conductivities were measured along a long axis of the platelet-shaped crystals of **1Ln** and **2Ln**. Ac magnetic susceptibilities of randomly oriented polycrystalline samples were measured varying the frequency (50–10000 Hz) of an applied ac magnetic field (amplitude: 5 Oe).

RESULTS AND DISCUSSION

The crystal structures of **1Ln** (Ln = Ho, Er, Yb) [3] and **2Dy** [4] are described previously. New complex **2Tb** was isomorphous to **2Dy** [4]. The molecular arrangement in a donor sheet of **2Tb** is shown in Figure 1(a). Salts **3Ln** did not afford good crystals suitable for single-crystal X-ray diffraction study.

The room-temperature resistivity of **1Ln** was ca. 20 Ω cm with the activation energy (E_a) of 0.08–0.4 eV. The resistivities of **2Ln** were ca. 10 Ω cm with $E_a = 0.09$ and 0.1 eV for Ln = Tb and Dy, respectively (Fig. 1(b) for **2Tb**). Compressed pellets of **3Dy** were also semiconducting with $E_a = 0.08$ eV. All of the ion-radical salts investigated here are semiconductors. Tamura *et al.* reported metallic conductors using BO [6] and TTP [7] with $[\mathrm{Ln(NCS)_6}]^{3-}$ and $[\mathrm{LnCl_4(H_2O)_6}]^-$ [8]. The choice of donor molecules is crucial for development of metallic conductors especially when bulky counter anions are incorporated.

Ac magnetic susceptibilities were measured for polycrystalline samples of **1Ln** and **2Ln** and fine powder samples of **3Dy**. Frequency dependence of χ''_{ac} was observed for **1Ln**, where χ'_{ac} and χ''_{ac} denote the in-phase and out-of-phase parts of ac magnetic susceptibility, respectively. As shown in Figure 2 for example, χ''_{ac} of **1Dy** and **1Er** increased with an increase of frequency in a low temperature region ($\leq$10 K). Very slight frequency dependence was found for both **2Tb** and **2Dy** (not shown). Complex **3Dy** showed an appreciable increase of χ''_{ac} with an increase of frequency (Fig. 3). The coordination geometry around



(a)

(b)

FIGURE 1 (a) Packing of ET molecules in the crystal of $\mathrm{(ET)_5[Tb(NCS)_6NO_3]\cdot EtOH}$ (**2Tb**) viewed along the molecular axis. (b) Resistivity of **2Tb** measured along the *ab* diagonal (*a*-*b*) direction.

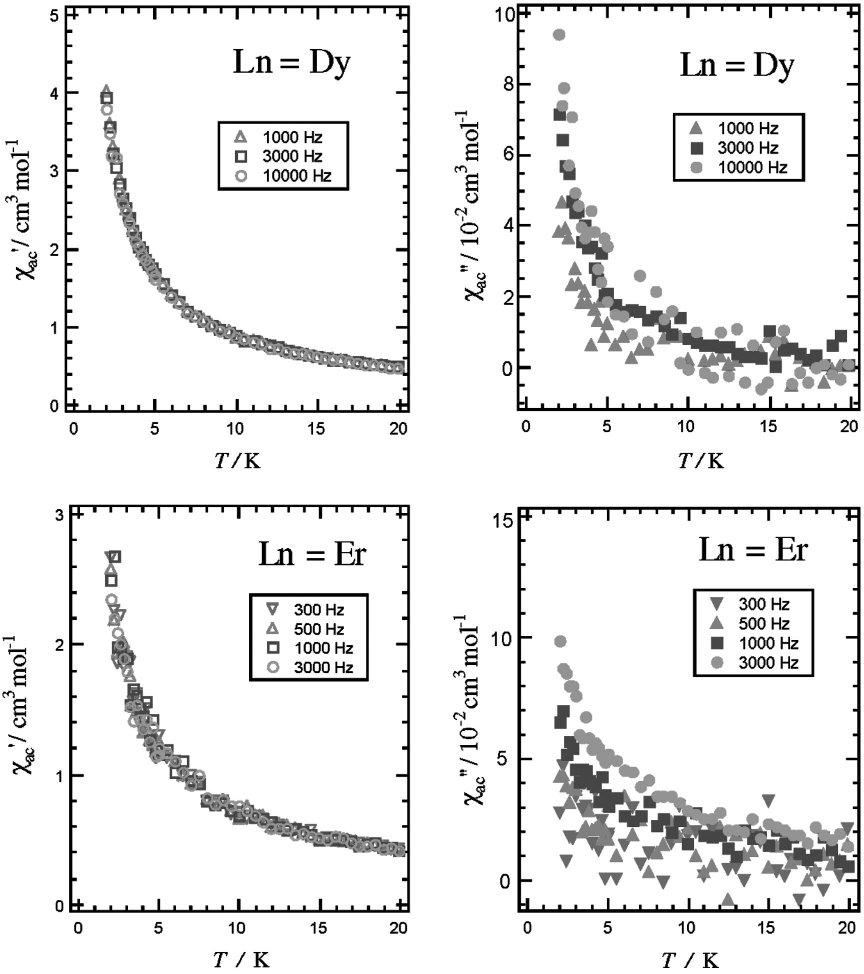


FIGURE 2 Frequency-dependence of χ'_{ac} and χ''_{ac} for $(ET)_4[Ln(NCS)_6]\cdot CH_2Cl_2$ (**1Ln**; Ln = Dy, Er).

the Ln ion in $[Ln(NCS)_6]^{3-}$ is a highly symmetrical octahedron but that of $[Ln(NCS)_6NO_3]^{4-}$ is unsymmetrical octa-coordinate due to additional oxygen atoms of NO_3^-. Irrespective of the symmetries around the Ln ions, all of **1Ln–3Ln** exhibited relatively small frequency dependence of ac magnetic susceptibility. In contrast to our expectation, **1Ln** exhibited larger frequency dependence than **2Ln**.

These frequency dependences were substantial, and can be regarded as an indication of blocking behavior observable for SMMs

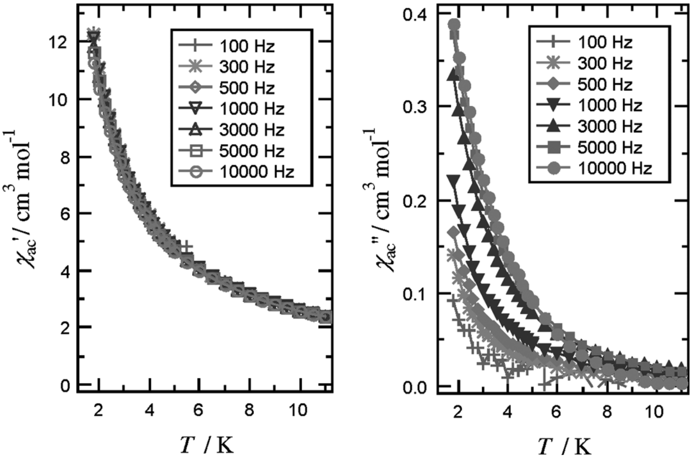


FIGURE 3 Frequency-dependence of χ_{ac}' and χ_{ac}'' for $(TTF)_6[Dy(NCS)_6]$ (**3Dy**). Solid lines are shown for a guide to the eye.

due to slow magnetization relaxation [2]. These complexes might be semiconductors with magnetization blocking, but the blocking will take place at temperatures much lower than 2 K. To raise the possible blocking temperature, we have to turn our attention to other types of Ln-based counter anions with well-designed ligands. The $[Ho(pc)_2]^-$ complex anion behaving as a SMM (pc = phthalocyaninate^{2-}) [9] may afford a clue to development of this study.

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