



Chromium–ethynyltetrathiafulvalene complex based magnetic materials

Junichi Nishijo*

School of Science and Engineering, Meisei University, 2-1-1 Hodokubo, Hino, Tokyo 191-8506, Japan

ARTICLE INFO

Article history:

Available online 8 February 2013

Keywords:

Acetylde
Tetrathiafulvalene
Molecule-based magnet
Charge transfer complex

ABSTRACT

New molecule based magnetic materials $[\text{CrCyclam}(\text{C}\equiv\text{C-MeEDT-TTF})_2](\text{TCNQ})_3$ ($[\mathbf{1}](\text{TCNQ})_3$, Cyclam = 1,4,8,11-tetraazacyclotetradecane, MeEDT-TTF = 5-methyl-4',5'-ethylenedithiotetrathiafulvalene, TCNQ = 7,7,8,8-tetracyanoquinodimethane) and $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ (Phen = 1,10-phenanthroline) were prepared by the electrochemical oxidation of $[\mathbf{1}](\text{CF}_3\text{SO}_3)$. Tetrathiafulvalene (TTF)-type ligands and a neutral TCNQ molecule are stacked and form a charge-transfer complex in the crystal of $[\mathbf{1}](\text{TCNQ})_3$, where a weak ferromagnetic interaction was observed between Cr^{3+} and $(\text{TCNQ})_2^-$. The crystal structure of $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ was characterized by ferrimagnetic chain of Cr^{3+} Cyclam units ($S = 3/2$) and $(\text{TTF})_2^+$ ligand dimers ($S = 1/2$), while each $(\text{TTF})_2^+$ dimer is sandwiched between two $[\text{Cr}(\text{NCS})_4\text{Phen}]^-$ anions ($S = 3/2$). The crystal shows ferrimagnetic transition at 4.8 K.

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1. Introduction

In these days, there has been considerable interest in magnetic transition metal complexes containing redox-active tetrathiafulvalene (TTF)-based ligands [1–7]. In transition metal-TTF composite systems, the π -spin ($S = 1/2$) on an oxidized TTF ligand can strongly interact with the d-spin of center transition metal through the coordination bond. Furthermore, we can also expect a strong inter-molecular interaction by using an inter-molecular π - π stacking which frequently brings quite strong spin–spin interaction of $|2J|/k_B > 100$ K [8], where k_B is the Boltzmann constant and J is defined in the following Hamiltonian;

$$H = -2J \sum_{\langle ij \rangle} S_i S_j$$

Recently, the author and co-workers reported a new transition metal–TTF complex $[\text{CrCyclam}(\text{C}\equiv\text{C-MeEDT-TTF})_2]^{n+}$ ($[\mathbf{1}]^{n+}$, Fig. 1) [9] which shows strong intra- and inter-molecular spin–spin interactions. The strong inter-molecular interaction is achieved by the π - π stacking of the TTF-type ligands, resulting in the charge- and spin-delocalization over adjacent molecules. The intra-molecular exchange interaction between localized d- and delocalized π -spins is mediated by the ethynyl group, which directly connects the π -spin of a ligand to the d-spin with the strong exchange interaction of $2J/k_B = -30$ K. Because the observed strong intra- and inter-molecular interactions of $[\mathbf{1}]^{n+}$ are well suited for molecule-based magnets, an attempt was made to construct new molecule-based magnets consisting of $[\mathbf{1}]^{n+}$ and magnetic anions.

In this paper, I report on the two new molecule-based magnetic materials, $[\mathbf{1}](\text{TCNQ})_3$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) and $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ (Phen = 1,10-phenanthroline). The former is a charge-transfer complex owing to the strong π - π interaction between TTF-type ligands and TCNQ molecules. The latter is a ferrimagnet with a transition temperature of 4.8 K, where a cation–anion π - π interaction plays an important role.

2. Experimental

All reagents and solvents were purchased from Aldrich Chemical Co., and used without further purification. $[\mathbf{1}]\text{OTf}$, and $\text{TEA}[\text{CrPhen}(\text{NCS})_4]$ (TEA = tetraethylammonium) were prepared according to the literatures [9,10]. $[\mathbf{1}](\text{TCNQ})_3$ crystals were prepared as follows; 50 mg of $[\mathbf{1}]\text{OTf}$, 20 mg of TCNQ and 20 mg of Li-TCNQ were dissolved in 50 ml of acetonitrile. After standing the solution for a day the precipitate of $[\mathbf{1}](\text{TCNQ})_3$ is filtered and washed with a small amount of diethyl ether. $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ was obtained by the galvanostatic oxidation of $[\mathbf{1}]\text{OTf}$ (12 mg) in 20 ml $\text{TEA}[\text{Cr}(\text{NCS})_4\text{Phen}]$ (30 mg) solution of toluene–acetone 1:1 mixture (0.4 μA , 2 weeks). The crystal structures of the materials were determined by single crystal X-ray diffraction with a Rigaku AFC-7R four-circle diffractometer at 293 K, using Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). The structures were solved using direct methods (SIR2004) [11], then refined with a full-matrix least-squares method (SHELXL-97) [12]. Magnetic susceptibilities were measured by using Quantum-Design MPMS-XL7 SQUID magnetometer for crystals encapsulated in an aluminum capsule. Diamagnetic corrections were estimated from Pascal's constants as -739×10^{-6} and -1024×10^{-6} emu mol^{-1} for $[\mathbf{1}](\text{TCNQ})_3$ and $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$, respectively.

* Tel./fax: +81 42 591 7542.

E-mail address: jun-ichi.nishijo@meisei-u.ac.jp

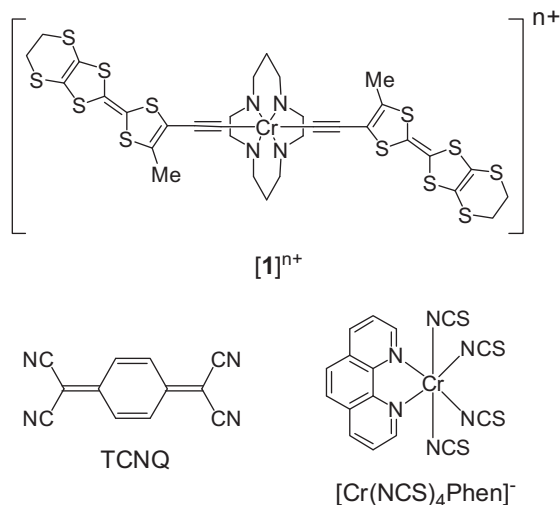


Fig. 1. The molecular structures of $[\text{CrCyclam}(\text{C}\equiv\text{C-MeEDT-TTF})_2]^{n+}$ ($[\mathbf{1}]^{n+}$), TCNQ and $[\text{CrPhen}(\text{NCS})_4]^-$.

3. Results and discussion

3.1. Crystal structures

The crystallographic data of the crystals are summarized in Table 1. The asymmetric unit of $[\mathbf{1}](\text{TCNQ})_3$ contains a half $[\mathbf{1}]^{n+}$, and one and a half TCNQ molecules. One kind of TCNQ molecules, denoted as TCNQ (A), form $(\text{TCNQ})_2$ dimers, while the other TCNQ molecules, TCNQ (B), are isolated. These TCNQ dimers, monomers and TTF-type ligands of $[\mathbf{1}]^{n+}$ are stacked in the manner of $(\text{TCNQ}(\text{A}))_2\text{-TTF-TCNQ}(\text{B})\text{-TTF}$, resulting in a sheet structure parallel to the (111) plane as shown in Fig. 2. Using the empirical relations between the bond lengths in a TCNQ molecule and its charge state [13,14], we can estimate the valence of the TCNQ molecules as -0.56 for TCNQ (A) and -0.28 for TCNQ (B), respectively. Considering the charge compensation and charges of Cr^{3+} and ethynyl groups (-1), the valence of a TTF-type ligand is also determined as $+0.2$. The result indicates that a TCNQ (B) molecule and two adjacent TTF-type ligands form a non-magnetic charge-transfer

Table 1
Crystallographic data.

	$[\mathbf{1}](\text{TCNQ})_3$	$[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$
Molecular formula	$\text{C}_{68}\text{H}_{50}\text{CrN}_{16}\text{S}_{12}$	$\text{C}_{77}\text{H}_{74}\text{Cr}_3\text{N}_{16}\text{O}_2\text{S}_{20}$
Formula weight	1528.04	2052.72
Temperature (K)	293(2)	293(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$
a (Å)	9.2644(9)	30.782(2)
b (Å)	12.8103(11)	15.0938(10)
c (Å)	15.1934(14)	21.2184(16)
α (°)	78.133(5)	90
β (°)	89.715(6)	106.1731(17)
γ (°)	85.234(6)	90
V (Å ³)	1758.4(3)	9468.2(12)
Z	1	4
d_{calc} (g cm ⁻³)	1.443	1.440
Unique reflections	8476	12302
$I > 2\sigma$	6768	8530
Final R_1^a , wR_2^b	0.0522, 0.1351	0.0642, 0.1791

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$.

complex thanks to their π - π stacking, while a TCNQ (A) dimer behaves as a $S = 1/2$ radical anion. The charge transfer state of a TTF-type ligand is also supported by the almost flat shape of the TTF-type ligand which shows off-planar structure in a neutral state [15].

The crystal structure of $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ is shown in Fig. 3. The asymmetric unit of the crystal consists of a half $[\mathbf{1}]^{n+}$ cation, one $[\text{CrPhen}(\text{NCS})_4]^-$ anion, a half toluene and one acetone molecules, where the conformation of a terminal ethylene group in a TTF-type ligand, the orientation of a toluene molecule and the rotational angles of the methyl groups of an acetone and a toluene molecules are disordered. The cation to anion ratio of 1:2 indicates the divalent state of the complex $[\mathbf{1}]^{2+}$, where an additional positive charge is owing to the oxidation state of TTF backbones. Adjacent TTF-type ligands of neighboring $[\mathbf{1}]^{2+}$ cations form a $(\text{TTF})_2^+$ dimer, resulting in one-dimensional chain structures elongated parallel to the $(a+b)$ and $(a-b)$ directions as shown in Fig. 3b. This chain structure is quite similar to that observed in $[\mathbf{1}][\text{ClO}_4]_2(\text{PhCl})_2(\text{MeCN})$ [9], suggesting that a charge and a spin are delocalized over a $(\text{TTF})_2^+$ dimer. In the present case, a $(\text{TTF})_2^+$ dimer is sandwiched between two anions, and cation-anion inter-molecular spin-spin interaction is expected through the π - π stacking. The chains of $[\mathbf{1}]^{2+}$ cations are separated from each other in the c -direction by solvent molecules, while thiocyanate ligands of an anion make several inter-chain contacts in both the b - and the c -directions.

3.2. Magnetic properties

The molar magnetic susceptibility χ of $[\mathbf{1}](\text{TCNQ})_3$ obeys the Curie-Weiss law with the Curie constant of $2.25 \text{ emu K mol}^{-1}$ and small positive Weiss temperature of $\Theta = +0.3 \text{ K}$ as shown in Fig. 4. The observed Curie constant is in good agreement with the sum of the spin-only values of $S = 3/2$ ($1.875 \text{ emu K mol}^{-1}$) and $S = 1/2$ ($0.375 \text{ emu K mol}^{-1}$), and consistent with the crystal structure containing two magnetic species: Cr^{3+} ($S = 3/2$) and $(\text{TCNQ})_2^-$ ($S = 1/2$). The χT value gradually increases as the temperature decreases suggesting the existence of a ferromagnetic interaction, but no magnetic transition was observed down to 1.8 K . The weak ferromagnetic coupling between Cr^{3+} and $(\text{TCNQ})_2^-$ is probably mediated by a π - π stacking of a non-magnetic TTF-type ligand and a $(\text{TCNQ})_2^-$ dimer.

Fig. 5a shows the temperature dependencies of the χ and χT values of $[\mathbf{1}][\text{Cr}(\text{NCS})_4\text{Phen}]_2(\text{acetone})_2(\text{toluene})$ measured under the magnetic field of 0.1 T . The observed value of $\chi T = 5.76 \text{ emu K mol}^{-1}$ at 300 K is obviously smaller than that of the sum of the spin only values of Cr^{3+} ($S = 3/2$), $(\text{TTF})_2^+$ ($S = 1/2$) and two $[\text{Cr}(\text{NCS})_4\text{Phen}]^-$ ($S = 3/2$), suggesting the existence of a strong antiferromagnetic interaction. The χT value gradually decreases as the temperature decreases, and reaches a minimum of $5.47 \text{ emu K mol}^{-1}$ at around 80 K . Below the temperature, the χT value exhibits a rapid rise to a maximum value of $22.51 \text{ emu K mol}^{-1}$ at 4.8 K , and then rapidly decreases as the temperature decreases where the χ exhibits a roughly constant value of 5.0 emu mol^{-1} . The sharp peak of the χT value and the plateau of the χ value below the temperature suggest that this material shows a ferrimagnetic transition at 4.8 K , as evidenced by the magnetization curve at 2 K . In the temperature, applying the external field substantially increases the magnetization M as shown in Fig. 5b, and M reaches a value of $8 \mu_B$ at around 1.5 T , corresponding to the ferrimagnetic system of $3 \times 3/2 - 1/2$. In the low field region, the curve clearly shows a hysteresis loop with the small coercive force and the remanent magnetization of 80 Oe and $0.3 \mu_B$, respectively. The small coercive force related to a small anisotropy is consistent with the almost isotropic nature of the octahedral Cr^{3+} (d^3) complexes.

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