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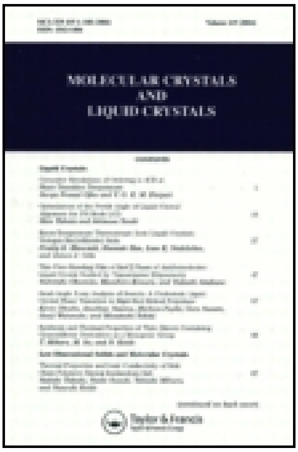

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
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# π- d Interaction-Based Molecular Magnets in TTF-Type Salts

Akira Miyazaki [a], Masaya Enomoto [a], Jun-Ichi Nishijo [a], Kengo Enomoto [a], Toshiaki Enoki [a], Eiji Ogura [b], Takahiro Takano [b], Yoshiyuki Kuwatani [b] & Masahiko Iyoda [b]

[a] Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152-8551, Japan

[b] Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan

Version of record first published: 18 Oct 2010

To cite this article: Akira Miyazaki, Masaya Enomoto, Jun-Ichi Nishijo, Kengo Enomoto, Toshiaki Enoki, Eiji Ogura, Takahiro Takano, Yoshiyuki Kuwatani & Masahiko Iyoda (2002): π- d Interaction-Based Molecular Magnets in TTF-Type Salts, Molecular Crystals and Liquid Crystals, 376:1, 535-542

To link to this article: http://dx.doi.org/10.1080/10587250210751

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*Mol. Cryst. Liq. Cryst.*, Vol. 376, pp. 535-542
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# *π-d* Interaction-Based Molecular Magnets in TTF-Type Salts

AKIRA MIYAZAKI[a], MASAYA ENOMOTO[a],
JUN-ICHI NISHIJO[a], KENGO ENOMOTO[a],
TOSHIAKI ENOKI[a], EIJI OGURA[b], TAKAHIRO TAKANO[b],
YOSHIYUKI KUWATANI[b] and MASAHIKO IYODA[b]

[a]*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo, 152-8551 Japan and*
[b]*Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397 Japan*

Structure, transport properties and magnetism of the following *π-d* systems based on TTF-type salts with magnetic ions are investigated. i) $C_1$TET-TTF·$FeBr_4$: The magnetic anions form zigzag chains, whose property is described in terms of triangular-based ladder systems accompanied with weak ferromagnetism. Its magnetic properties are affected by the sulfur-to-selenium or bromine-to-chlorine substitution. ii) (EDO-TTF$I_2$)$_2$M(mnt)$_2$ (M = Ni, Pt) : Both donor and anion molecules form segregated one-dimensional columns, which are connected via short –CN···I– contacts. These salts show the coexistence of metallic conductivity on the donors and ferromagnetic interaction between localized moments on the anions. iii) (DMET)$_2$Fe$Br_4$: The donor molecules form one-dimensional column with metallic conductivity, whereas the magnetic anions form square-lattice layers and show antiferromagnetic transition. The coincidence of the anomalies on magnetization curves and magnetoresistance supports the presence of *π-d* interaction between these two layers.

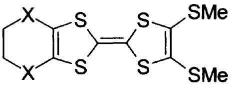
Keywords: molecular conductor; molecular magnet; *π-d* interaction

## INTRODUCTION

Organic molecular conductors having inorganic magnetic counter ions draw attention to the recent research on material science [1]. The organic part has a wide variety of electronic structure ranging from superconductors, low-dimensional metals to insulators. The magnetic anions incorporated into such systems can interact each other via $\pi$-electrons, leading to the realization of novel magnetic systems. The resulted $\pi$-$d$ cooperative system should have physical properties where the $\pi$-$d$ interaction plays an essential role. For example, the application of pressure to $\lambda$-(BEDT-TSF)$_2$FeCl$_4$ reduces the magnitude of the $\pi$-$d$ interaction, leading to the pressure-induced restored metallic state [2].

Here we present the structure and physical properties of three material groups of molecular conductor with magnetic anions that are classified as $\pi$-$d$ cooperative systems. The first one contains $\pi$-electron-based molecules as the exchange network paths connecting the $d$-electron-based localized spins. The second one utilizes strong intermolecular interaction such as –I···X– (X = CN, halogen) contacts [3], which can also be useful for controlling the alignment of molecules with magnetic centers. The last system is based on donor molecule that stabilizes the metallic electronic state, which enables the direct examination of the $\pi$-$d$ interaction by means of the transport property measurements under the magnetic fields at low temperature.

## **C$_1$TEX-TTF·FeY$_4$ (X = S, Se; Y = Cl, Br)** [4,5]



C$_1$TET-TTF (X = S)
C$_1$TESe-TTF (X = Se)

The crystal structure of molecular magnets C$_1$TEX-TTF·FeY$_4$ (X = S, Se; Y = Br, Cl) is characterized as the two-dimensional sheet as shown in Figure 1(a). The anions form zigzag chains using intermolecular halogen–halogen contacts (solid lines), whereas the donor dimers connect the next-nearest neighboring anions using halogen–chalcogen contacts (dashed lines). With these contacts the magnetic anion form a triangular ladder (Figure 1(b)). The magnitudes of the exchange interaction $J_1$, $J_2$ and $J_3$ can be experimentally determined from the Néel and Weiss temperatures [4].

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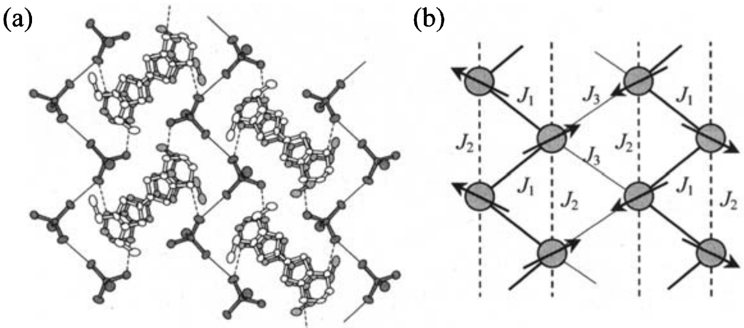

FIGURE 1 (a) The two-dimensional sheet of $C_1$TEX-TTF·Fe$Y_4$ (X = S, Se; Y = Br, Cl). The solid and dashed lines are intermolecular contacts. (b) The schematic drawing of the exchange paths $J_1$, $J_2$ and $J_3$ between the magnetic anions. The spin structure of the $FeBr_4$ salt is also indicated.

The magnetic properties of this system are modified by the atom substitution of the donors [4] or anions [5]. The replacement of the sulfur atoms in the six-membered ring to selenium atoms elongates the intermolecular halogen–halogen distances, resulting in the decrease of $|J_1|$ (1.2 K for X = S, 0.8 K for X = Se). Meanwhile, the variation of the halogen–chalcogen distances is small, hence $|J_2|$ is practically unchanged (0.35 K for X = S, 0.31 K for X =Se).

The bromine-to-chlorine substitution changes the magnetic properties drastically. For the $FeBr_4$ salt, the localized spins lie on the 2-D sheet with the canted spin configuration as illustrated in Figure 1(b). For the mixed salts ($C_1$TET-TTF)($FeBr_{4-x}Cl_x$), the direction of the spin-easy axis begins to tilt from the sheet and the spin canting disappears. For the pure $FeCl_4$ salt, an ordinary antiferromagnetic ordered state is stabilized where the spin-easy axis is ca. 45° tilted from the sheet. This rotation of the spin-easy axis is qualitatively explained from the competition between the single-ion anisotropy that directs the localized moments parallel to the sheet and perpendicular to the anion chain, and the dipole-dipole interaction that directs the spins perpendicular to the sheet. For the $FeBr_4$ salt the single-ion anisotropy determines the spin-

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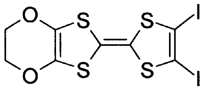
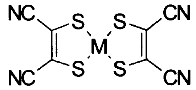
easy axis dominantly due to the larger spin-orbit coupling of Br than Cl. In the same time, the presence of the Dzyaloshinski-Moriya (D-M) interaction gives the canted antiferromagnetic state. For the $FeCl_4$ salt, on the other hand, the contribution of the single-ion anisotropy and the dipole-dipole interaction have the same order in magnitude, hence the spin-easy axis directs to the intermediate direction.

## (EDO-TTFI$_2$)$_2$[M(mnt)$_2$] (M = Ni, Pt) [6]



EDO-TTFI$_2$



M(mnt)$_2$ (M = Ni, Pt)

The crystal of (EDO-TTFI$_2$)$_2$[M(mnt)$_2$] (M = Ni, Pt) consists of segregated one-dimensional stacks connected with short (3.04Å for M = Ni, 3.05Å for M = Pt) –CN···I– contacts as shown in Figure 2(a). The donor column has one-dimensional electronic nature, whereas the M(mnt)$_2$ complexes are stacked with a metal-over-sulfur configuration (Figure 2(b)).

These salts show high conductivity (110~170 $Scm^{-1}$ at room temperature) and metallic behavior down to ca. 90K, regardless of the central metal M of the anion. Figure 3 shows the magnetic properties

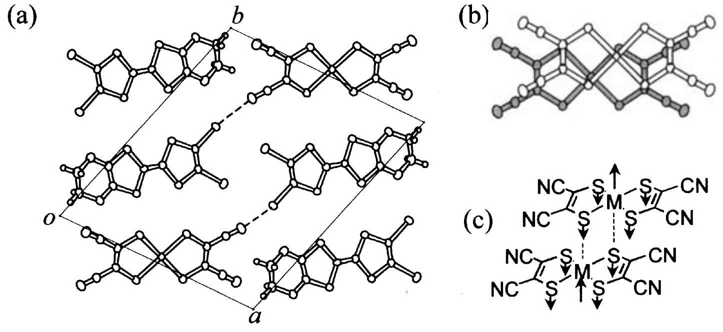


FIGURE 2 (a) The crystal structure of (EDO-TTFI$_2$)$_2$[M(mnt)$_2$] (M = Ni, Pt). The dashed lines are short –CN···I– contacts. (b) Overlap mode of the two adjacent M(mnt)$_2$ molecules. (c) Schematic drawing of the ferromagnetic interaction mechanism. The dashed lines show local antiferromagnetic couplings.

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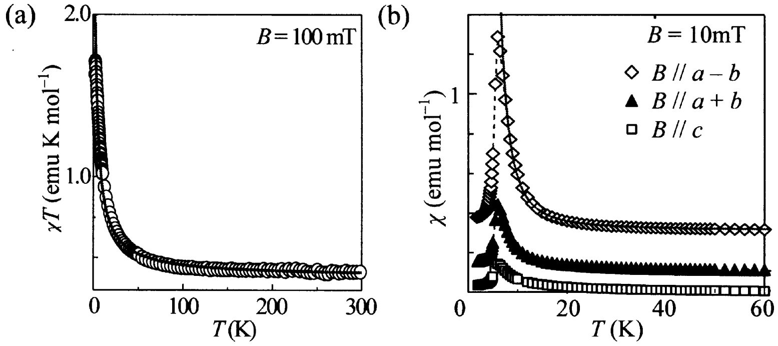

FIGURE 3 The temperature dependence of $\chi T$ for (EDO-TTFI$_2$)$_2$ [Ni(mnt)$_2$]. Solid line: $S$ = 1/2 one-dimensional ferromagnetic Heisenberg model. (b) The temperature dependence of the magnetic susceptibility for (EDO-TTFI$_2$)$_2$[Pt(mnt)$_2$]. Solid line: $S$ = 1/2 one-dimensional ferromagnetic Ising model .

for these salts. The $\chi T$ value at $T$ = 300 K (~0.39 emu K mol$^{-1}$) shows that the susceptibility comes from the localized moments on the anions. The susceptibility of the Ni(mnt)$_2$ salt is well fitted with the one-dimensional $S$ = 1/2 ferromagnetic Heisenberg model [7] with $J$ = 18 K (Fig. 3(a)). Meanwhile, the susceptibility of the Pt(mnt)$_2$ salt obeys the one-dimensional ferromagnetic Ising model [8] reflecting the large spin-orbit interaction of platinum (Fig. 3(b)). The latter salt also undergoes a metamagnetic transition at 5.5 K due to an inter-chain antiferromagnetic interaction.

The metal-over-sulfur overlap mode realized by the strong intermolecular –CN···I– interaction plays an essential role in the origin of ferromagnetic interaction between adjacent M(mnt)$_2$ anions. According to the McConnel model [9], the positive spin on the metal atom induces negative spin on the coordinating sulfur atoms, which then interacts antiferromagnetically with the positive spin on the metal atom of adjacent molecule, resulting in the ferromagnetic coupling between these two anion radicals (Figure 2(c)). The ferromagnetic interaction is also explained with the charge-transfer interaction

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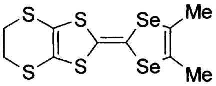
between anion radicals [10]. Due to this overlap mode, the SOMOs of the adjacent M(mnt)$_2$ molecules are nearly orthogonal and the overlap between SOMO and NHOMO is large, hence the admixture of the triplet excited state to the ground state stabilizes a ferromagnetic coupling between two anion radicals.

## (DMET)$_2$FeBr$_4$ [11]



DMET

The crystal structure of (DMET)$_2$FeBr$_4$ is characterized with an alternating stacking of donor layers and anion sheets (Figure 4). The magnetic anions form a quasi-square-lattice by means of Br–Br contacts (solid lines), which is then sandwiched with the donor layer consists of one-dimensional columns along the $a+b$ and $a-b$ directions. These organic and inorganic layers are connected with the Br–S contacts (dashed lines).

This salt is metallic around the room temperature, and a metal-insulator transition takes place at $T_{\mathrm{MI}} \sim 40$ K. In contrast, the localized moments on the anion layer undergoes an antiferromagnetic transition at $T_{\mathrm{N}} = 3.7$ K. The magnetization curve at 1.8 K shows a spin-flop transition at $B_{\mathrm{ST}} = 2$ T for the spin easy axis (= $a$ axis). In addition, anomalies are also observed at $B_1 = 3.5$ T and $B_2 = 5$ T for the easy and hard (= $b$) axis, respectively, which appear as the peaks on the field dependence of the magnetic susceptibilities (Figure 5(a)).

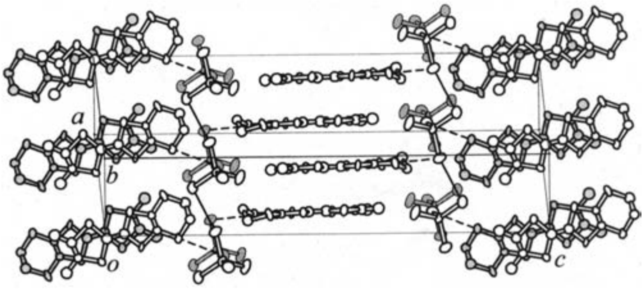


FIGURE 4 The crystal structure of (DMET)$_2$FeBr$_4$. Short intermolecular contacts are shown with solid and dashed lines.

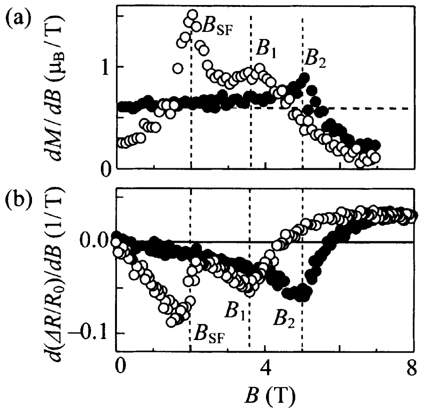


FIGURE 5 (a) Field dependence of the magnetic susceptibility. (b) Derivative of the magnetoresistance as a function of field. Open (○) and filled (●) circles are the data in the field parallel to the easy (= $a$) and hard (= $b$) axes, respectively.

These spin-flop transition and anomalies also appear as the peaks on the derivative curves of the out-of-plane magnetoresistance as a function of a field (Figure 5(b)). This excellent correspondence between the magnetization governed by the $d$-electron and the magnetoresistance that mainly follows the motion of $\pi$-electrons comes from either the internal magnetic field of the magnetic anion, or the presence of the $\pi$-$d$ interactions. In order to check the validity of these hypotheses, an isomorphous salt (EDTDM-TTF)$_2$FeBr$_4$, the all-sulfur-version of this system, is now being studied [12].

## SUMMARY

Structure and physical properties of the following three $\pi$-$d$ interaction-based molecular magnets are investigated: i) C$_1$TET-TTF·FeBr$_4$: The magnetic anions form zigzag chains triangular-based ladder systems, where the highly-tunable $\pi$-electron system participates as bridging ligands. ii) (EDO-TTFI$_2$)$_2$M(mnt)$_2$ (M = Ni, Pt) : Ferromagnetic interaction between anion radical originate from the

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metal-over-sulfur overlapping mode realized with the short intermolecular –CN···I– contacts between donors and anions. iii) $(DMET)_2FeBr_4$: The presence of the $\pi$-$d$ interaction is suggested by the coincidence of anomalies on the magnetization curves ($d$-electrons) and the magnetoresistance ($\pi$-electrons).

## Acknowledgement

This work has been partially supported by Grant-in Aid for Scientific Research on Priority Areas, "Metal-assembled Complexes" from the Ministry of Education, Science and Culture, Japan.

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