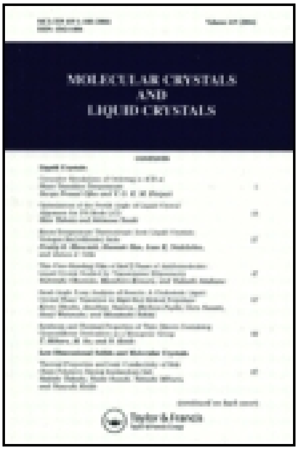

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Molecular Magnets Based on Charge Transfer Complexes

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Version of record first published: 24 Sep 2006.

To cite this article: T. Enoki , M. Enomoto , M. Enomoto , K. Yamaguchi , N. Yoneyama , J. Yamaura , A. Miyazaki & G. Saito (1996): Molecular Magnets Based on Charge Transfer Complexes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 285:1, 19-26

To link to this article: http://dx.doi.org/10.1080/10587259608030773

Mol. Cryst. Liq. Cryst., 1996, Vol. 285, pp. 19–26
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MOLECULAR MAGNETS BASED ON CHARGE TRANSFER COMPLEXES

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Abstract We investigated two classes of organic charge transfer complexes in the TTF family and related materials, in order to aim at the development of novel magnetic systems. The first one is the complexes with transition metal d-electrons having localized magnetic moments, where the π-electrons in organic donors play an important role in the exchange interaction mechanism between the localized magnetic moments of d-electrons. The second class is obtained on the basis of the localized magnetic moments of π-electrons, where the on-site Coulomb interaction in organic donors overwhelms the transfer integral.

INTRODUCTION

Organic donors such as TTF derivatives form charge transfer complexes with various kinds of anions, which give a large variety of low dimensional electronic systems consisting of π-electrons among insulators, semiconductors, metals and superconductors.[1] The appearance of the large variety of electronic states is governed by the competition among the transfer integral, the on-site Coulomb interaction and the electron-phonon interaction. Metallic state appears when the transfer integral overwhelms the on-site Coulomb interaction, while the major contribution of the on-site Coulomb interaction brings about insulating state. From the point of magnetism, there are two kinds of aspects for the development of magnetic systems based on organic charge transfer complexes. One is the employment of the intrinsic π-electronic structure of complexes related to the competition between the transfer integral and the on-site Coulomb interaction, which can generate localized magnetic moments. In the insulating state where the on-site Coulomb interaction overwhelms the transfer integral, π-electrons in the donors are localized, resulting in the appearance of localized magnetic moments. As a consequence, the localized magnetic moments of the π-electrons aligned in the low dimensional lattice of organic donors provide a low dimensional magnetic system. Moreover, the decrease in the strength of the on-site Coulomb interaction makes the role of the transfer integral more emphasized, resulting in the generation of itinerant features in the magnetic π-electrons. Another aspect is the introduction of extrinsic magnetic moments in the complexes. Anions comprising transition metal d-electrons that have localized magnetic moments can be introduced in the formation of charge transfer complexes with organic donors. In this case, there are a variety of electronic structures that we can employ as a counter part to the d-localized magnetic system. The arrangement of the d-localized magnetic moments embedded in insulating phases of the organic donor lattice forms a low dimensional magnet where superexchange interaction between d-magnetic moments mediated by organic molecules plays an important role. In metallic systems, the coexistence of conduction π-electrons and the localized d-magnetic moments is expected to realized organic versions of metal-magnets through the π-d interactions. The low-dimensionality of both the conducting lattice and the magnetic lattice will give rise to novel features associated with the cooperation of the two constituent players, the conduction electrons and localized magnetic moments.

In this paper, we present magnetic properties of molecular-based magnets developed with organic charge transfer complexes of TTF and related donors under the two aspects mentioned above.

MOTT-HUBBARD SYSTEMS

β'-(BEDT-TTF)$_2$X (X=ICl$_2$, AuCl$_2$)

β'-(BEDT-TTF)$_2$X (X=ICl$_2$, AuCl$_2$) have a quasi-two dimensional crystal structure,[2,3] where intermolecular face-to-face S-S atomic contacts between BEDT-TTF molecules play a role in the formation of linear chains of dimerized BEDT-TTF molecules oriented parallel to the *b*-axis. The side-by-side S-S atomic contacts, which are relatively weak in comparison with the face-to-face interactions, give two-dimensional arrays of the linear chains in the *bc*-plane which are separated from each other through an X anion layer. This structural feature provides a quasi-two dimensional antiferromagnetic lattice comprising a localized magnetic moment per BEDT-TTF dimer unit, which has a nature of Heisenberg spin system. Figure 1 shows temperature dependence of magnetic susceptibility for the ICl$_2$ salt. The susceptibility has the similar trend in the behavior of temperature dependence for both salts. Namely, it has a broad peak around 110K which is suggestive of the development of magnetic short range order, and then, it has an anomaly at T_N=22K and 28K for three-dimensional long range order in the ICl$_2$ and AuCl$_2$ salts, respectively. The behavior of the susceptibility can be described in terms of intrachain interaction J_b and interchain interaction J_c as a quasi-two dimensional Heisenberg antiferromagnetic system where structural consideration gives the numbers of nearest neighbors z_b=2 and z_c=2 for J_b and J_c, respectively. The analysis on the basis

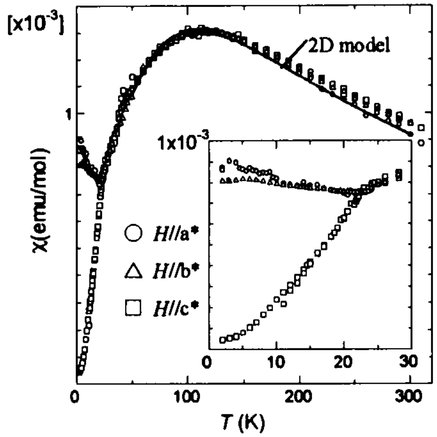

FIGURE 1 The magnetic susceptibility of β'-(BEDT-TTF)$_2$ICl$_2$.

of high temperature series expansion theory[4] gives the estimation of the exchange interactions J~59K, if we assume $J=J_b$~J_c. This two-dimensional feature is in good agreement with the band calculation which gives the estimate J_c/J_b~0.4. From the appearance of anisotropy in the susceptibility below T_N, the easy spin axis in the antiferromagnetically ordered state is found to be oriented parallel to the c-axis.

<u>(BEDT-TTF)$_2$Br·C$_2$H$_4$(OH)$_2$</u>

In (BEDT-TTF)$_2$Br·C$_2$H$_4$(OH)$_2$ (C$_2$H$_4$(OH)$_2$=1,2-ethanediol), BEDT-TTF donors dimerized along the a-axis form a one-dimensional chain structure parallel to the c-axis, where the charge transfer is expected to generate a hole per dimerized unit.[5] The band calculation suggests the feature of a one-dimensional metallic system, consistent with the behavior of resistivity. There is a metal-insulator transition with first order nature at T_{c1}=190K. In the high temperature metallic phase, the resistivity has weak temperature dependence with the room temperature value of ρ_{rt}~0.6Ωcm, while the insulating phase has the energy gap of E_g=660K. Figure 2 shows the temperature dependence of susceptibility. The susceptibility obeys the Curie-Weiss law with the Weiss temperature Θ=-83K above T_{c1}. The spin concentration is estimated at 1spin/2BEDT-TTF, which is in good agreement with the dimerized BEDT-TTF structure. However, the presence of localized magnetic moments contradicts the metallic nature suggested by the conductivity behavior. Consequently, the high temperature phase above T_{c1} is characterized as a highly correlated metallic state. The susceptibility drops abruptly by ca.50% at T_{c1}, shows a weak decrease on the lowering of the temperature until T_{c2}=80K, and then decays exponentially to zero below T_{c2}. The discontinuous change at T_{c1} is caused by the orientational change of BEDT-TTF molecules, judging from the

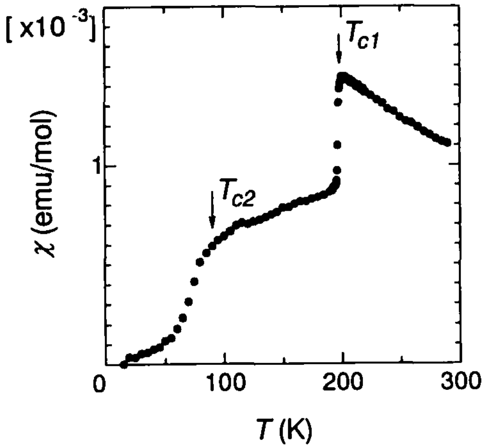

FIGURE 2 The magnetic susceptibility of $(BEDT\text{-}TTF)_2Br{\cdot}C_2H_4(OH)_2$.

observed change in the ESR g-value. The behavior of the susceptibility in the intermediate temperature range $T_{c2}<T<T_{c1}$ is explained by the development of short range order brought about by the one-dimensional exchange interactions which are expected to be enhanced by the structural transition at T_{c1}. The disappearance of magnetism at T_{c2} is considered to be related to a spin-Peierls transition.

MAGNETIC SYSTEMS HAVING π-d INTERACTION

C_1TET-TTF·FeX_4 (X=Cl, Br) and $[Ni(dddt)_2]_3(FeBr_4)_2$

In the insulating phases of charge transfer complexes with anions having transition metal species, the magnetic systems are described in terms of low-dimensional magnets consisting of localized magnetic moments of d-electrons. Since transition metal atoms are coordinated with ligands, the atomic contact between the ligand atom and the peripheral atoms of the donor is expected to participate in the superexchange interaction to realize magnetic interaction in the systems. Here, we introduce two kinds of systems with C_1TET-TTF and $Ni(dddt)_2$ as donors.

The first example is the complexes with asymmetric C_1TET-TTF donor. Figure 3(a) shows the crystal structure of C_1TET-TTF·FeX_4 (X=Cl, Br), that consists of C_1TET-TTF$^+$ monocations and FeX_4^- with the 1:1 composition ratio.[6] The donor molecules coupled as head-to-tail dimers form two-dimensional layers in the (102)-plane, which are separated to each other by the presence of the two-dimensional FeX_4^- anion layers. In the anion layer, zigzag chains are formed with two kinds of FeX_4^- anions located at different heights with respect to the *b*-axis direction, where the anions are intruded into the donor layers to some extent. This situation makes the intermolecular

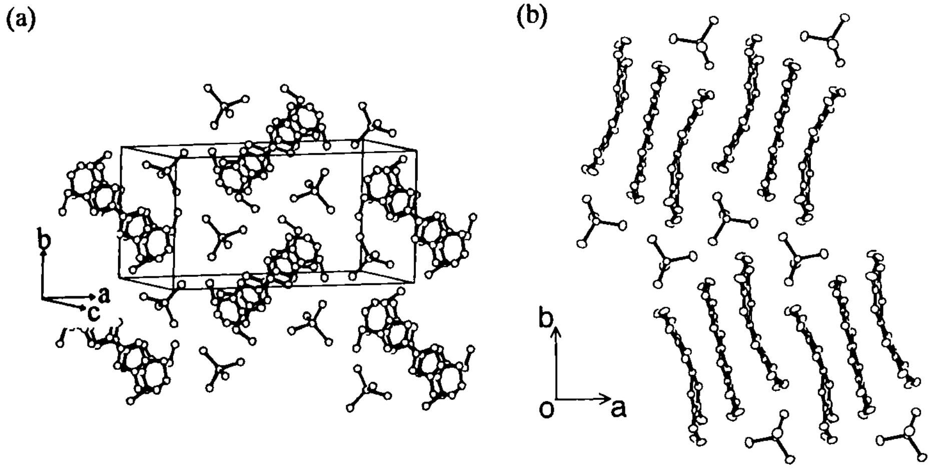

FIGURE 3 The crystal structures of (a) C_1TET-TTF·FeX_4 (X=Cl, Br) and (b) [Ni(dddt)$_2$]$_3$($FeBr_4$)$_2$.

distance between C_1TET-TTFs and FeX_4^- anions enough short to realize superexchange paths. Actually, the shortest interatomic distances between X and S atoms in the donor are estimated at 3.62 and 3.45 Å for X=Br and Cl, respectively, which are shorter than the corresponding van der Waals distances. The nearest intermolecular distances between X atoms in the adjacent FeX_4^- anions; 3.80 Å (Br), 3.67 Å (Cl), are enough short for superexchange interaction in the zigzag chain. The susceptibility obeys the Curie-Weiss law with the antiferromagnetic Weiss temperatures of Θ=-6.5K and -18.3K for the $FeCl_4$ and $FeBr_4$ complexes, respectively. It also indicates the onsets of long range magnetic ordering at 4K and 9K for the $FeCl_4$ and $FeBr_4$ complexes, respectively. The estimation of the Curie constants suggests the unique contribution of Fe^{3+} magnetic moments with S=5/2. Therefore, the system is described in terms of a spin ladder magnet with the exchange interactions associated with Fe-X-X-Fe and Fe-X-(donor)-X-Fe superexchange paths.

Next, we discuss the magnetic properties of [Ni(dddt)$_2$]$_3$($FeBr_4$)$_2$. In Fig.3(b) is shown the crystal structure of [Ni(dddt)$_2$]$_3$($FeBr_4$)$_2$. Ni(dddt)$_2$ donors with the 2/3 filled state form a trimerized structure, which are stacked along the a-axis. $FeBr_4$ anions forming corrugated sheets are sandwiched by the trimerized-donor sheets. There are short intermolecular atomic contacts between ligand Br atoms and S atoms at the peripheries of the donor molecules (Br-S=3.52Å), which are expected to give magnetic interactions. The absence of any detectable ESR signal and the semiconducting properties with ρ_{rt}~2.5Ωcm indicate the singlet state of π-electrons in the trimers, which means the absence of localized magnetic moments originating from π-electrons.

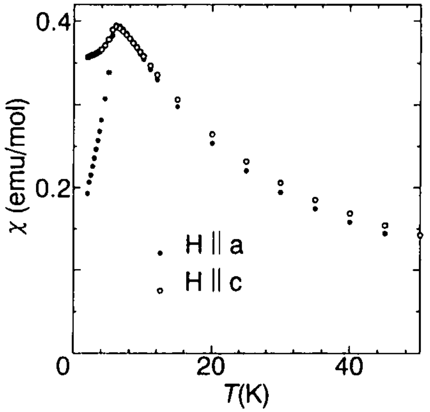

FIGURE 4 The magnetic susceptibility of $[Ni(dddt)_2]_3(FeBr_4)_2$.

Consequently, the magnetic system is described in terms of quasi-two-dimensional FeX_4 lattices coupled to each other by the interlayer interaction associated with the superexchange paths of the trimerized donor units. The susceptibility obeys the Curie-Weiss law with the small antiferromagnetic Weiss temperature Θ=-0.19K as shown in Fig.4. An antiferromagnetic transition takes place at T_N=6K, below which magnetic anisotropy suggests the spin easy axis oriented parallel to the *a*-axis.

<u>$(BEDT\text{-}TTF)_3CuBr_4$</u>

$(BEDT\text{-}TTF)_3CuBr_4$ consists of alternative stacking of conducting BEDT-TTF sheets having π-carriers and $CuBr_4^{2-}$ magnetic sheets with Cu^{2+} magnetic moments S=1/2 of Heisenberg type.[7-9] According to the crystal structure analysis,[7,10] the donor sheet is formed with neutral (A) and cation radical (B) BEDT-TTF species, where the composition ratio of B/A is 2. In ambient pressure, it behaves semiconductive with resistivity of ρ_{rt}~4.1Ωcm accompanied by a first order structural transition at T_c=59K. The susceptibility is described in terms of the contributions of the magnetic moments of both $BEDT\text{-}TTF^+$(B) molecules and Cu^{2+} ions above T_c. The large antiferromagnetic Weiss temperature Θ=-100K proves the presence of strong exchange interactions acting between Cu^{2+} and $BEDT\text{-}TTF^+$(B) moments, that is, the strong π-d interaction. The transition results in the disappearance of the magnetic moments of $BEDT\text{-}TTF^+$(B) donors below T_c, so that the magnetic systems is characterized as a two-dimensional Heisenberg antiferromanget of Cu^{2+} spins, where the exchange interaction is estimated at J=-15.7K. The Cu magnetic layers undergo an antiferromagnetic transition at T_N=7.65K. The low temperature X-ray structural analysis suggesting the homogenization of the charge distribution between A and B donors excludes the

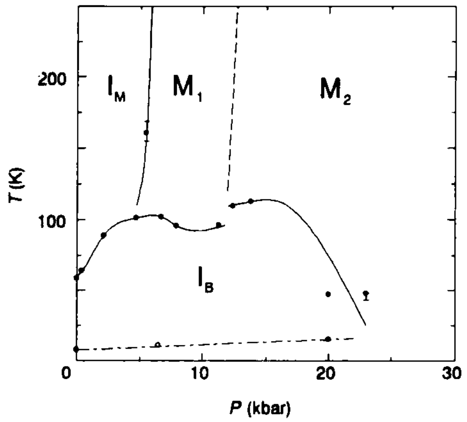

FIGURE 5 The P-T phase diagram of (BEDT-TTF)$_3$CuBr$_4$. I_M and I_B are the Mott and band insulator phases, while M_1 and M_2 are metallic phases. The dot-dash line represents the antiferromagnetic transition.

possibility of a spin-Peierls transition as the origin of the transition at T_c.[10] As a consequence, the transition is ascribed to the transition from a Mott insulator with localized magnetic moments to a band insulator, which is driven by the structural change. Figure 5 shows the P-T phase diagram. The phase boundary between the Mott insulator I_M to the band insulator I_B has a positive slope in the phase diagram, while there is a transition from the insulator I_M to a metallic state M_1 around 5kbar in the high temperature range. Moreover, phase M_1 is adjacent to another metallic phase M_2 on the high pressure side of its boundary around 12kbar, where the M_2 phase prevails in the higher pressure range, resulting in a negative slope of the phase boundary between M_2 and I_B. The antiferromagnetic transition of the Cu magnetic lattice is linearly elevated as the increase of the pressure.[11] Judging from the trends of the phase diagram, it is expected to have a crossing between the magnetic transition of Cu spins and the metal-insulator transition of the donor sheets. Therefore, the magnetic interactions of the Cu^{2+} spin system are expected to be enhanced by the conduction π-carriers in the metallic medium at the high pressures.

SUMMARY

Organic charge transfer complexes are good candidates for the development of molecular based magnets. In this paper, we investigate two classes of these complexes in order to aim at the development of novel magnetic systems. The first one is obtained on the basis of the localized magnetic moments of π-electrons. β'-(BEDT-TTF)$_2$X is described in terms of two-dimensional antiferromagnets of π-electron magnetic moments. In the case of (BEDT-TTF)$_2$Br·$C_2H_4(OH)_2$, the situation of Mott-Hubbard boundary is realized with the coexistence of the π-electron conduction and localized magnetic moments. The second class is the complexes with transition metal d-electrons having localized magnetic moments. The π-electrons in organic donors play an important role in the exchange interaction mechanism between the localized d-electron magnetic moments. Namely, the superexchange paths associated with π-electrons strongly contribute to the magnetic behavior of C_1TET-TTF·FeX_4 and [Ni(dddt)$_2$]$_3$($FeBr_4$)$_2$, while (BEDT-TTF)$_3$$CuBr_4$ shows novel features related to the strong π-d interactions.

ACKNOWLEDGEMENTS

The present work partly supported by the Grant-in-Aid for Scientific Research form the Ministry of Education, Science and Culture of Japan.

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