Multiproperty Molecular Materials: TTF-Based Conducting and Magnetic Molecular Materials

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The chemistry and physics of molecule-based materials are exciting subjects, and due to potential applications this area is being extensively investigated. Considerable effort is currently being made to design and to investigate new materials involving interplay or synergy between multiple physical properties. This microreview examines materials combining magnetism and electrical properties. Some fundamental background material is covered, together with a discussion of constraints on the design of molecular materials with these physical properties. Some examples from the literature are then related, in order to illustrate the achievements in this area.

1. Introduction

Considerable effort is currently devoted to the synthesis and investigation of new molecule-based materials involving interplay and synergy between multiple physical properties.[1] The construction of molecule-based materials which possess two or more such properties is currently a challenging target. Optical properties in particular are of current interest (especially with respect to natural optical activity), but other combinations of properties have also been targeted both for their fundamental scientific interest and for their potential applications. These kinds of combinations of properties lead either to competition, coexistence, or cooperativity between the desired properties; the latter is much more difficult to achieve than the other two. It should be noted that the construction and control of the self-assembly of the molecular building blocks (so that the resulting supramolecular compound has the desired structure, stability and physical properties) is still a major challenge for synthetic chemists working in this area. Nevertheless, some significant achievements have been obtained, namely:

(i) *Light-induced magnetization*.[2] Direct applications of this technology would be photo-induced magnetic memory devices based on the choice of the laser wavelength. As an

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MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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example, some very interesting systems have been obtained by Hashimoto and co-workers, for example, a derivative of Prussian blue, namely the cobalt iron cyanide formulated as $K_{0.2}Co_{1.4}[Fe(CN)_6]6.9H_2O$,[2d,2e] which was found to exhibit photo-induced reversible magnetization. The critical temperature increases from 16 to 19 K under illumination with red light, as a result of oxidation state changes for the metal ions [Co^{III} ($S = 0$) and Fe^{II} ($S = 0$) to Co^{II} ($S = 3/2$) and Fe^{III} ($S = 1/2$)].

(ii) *Synergy between spin-crossover and magnetic interactions.*[3] To the best of our knowledge, $Fe(mnt)_2$-rad [or 2-(*para*-*N*-methylpyridinium)-4,4,5,5-tetramethylimidazoline-1-oxyl iron(III) bis(maleonitrile dithiolate)] is the only compound in which evidence has been found for synergy between the spin cross-over effect and intersite magnetic interactions. It was found the $[Fe(mnt)_2]^-$ moiety exhibits a spin cross-over between $S_{Fe} = 3/2$ at high temperature and $S_{Fe} = 1/2$ at low temperature. At the same time, an antiferromagnetic (AF) interaction operates between the spin of the $[rad]^+$ unit ($S = 1/2$) and the spin of the iron atom ($S_{Fe} = 1/2$) at low temperatures, giving rise to a singlet ground state.

(iii) *Electrical conductivity and magnetic interactions.*[4−13] Conducting materials incorporating localized spins are currently a subject of intense investigation. Numerous research groups are involved in this area, and many compounds of this kind have been isolated and characterized. Some important results obtained are the coexistence of paramagnetism and superconductivity,[5a,12] antiferromagnetism and superconductivity,[5c] ferromagnetism and metallic conductivity[5d] and also field-induced ferromagnetism and superconductivity.[12b,12c]

In this microreview, we focus on materials combining magnetic interactions and electrical properties.

2. Background to the Physics of π-d Interactions

Transition metals such as iron are widely known strong ferromagnetic materials. In such metal ferromagnets, the unpaired d-electrons, which stay in the inner shell, behave as localized electrons having magnetic moments, whereas the s- and p-electrons move freely in the crystal, acting as carriers of electrical charge. Thus, the d-electrons in the free electron jellium interact with the charge carriers through an s-d interaction, expressed by the following equation (when a conduction s-electron approaches a d-electron site):

$$2J_{s\text{-}d}\delta(r)\boldsymbol{sS} \qquad (1)$$

where s and S are the spin operators for a conduction electron and a localized d-electron, respectively, $\delta(r)$ the delta function, and $J_{s\text{-}d}$ is the coupling constant for the exchange interaction between a conduction s-electron and a localized d-electron, and r is the distance between the conduction electron and the localized d-electron.

The interaction expressed by Equation (1) is termed the s-d interaction. In a crystal where the s-d interaction operates, the conduction carriers mediate the interaction between the magnetic moments of the localized d-electrons. Consequently, the mediation of conduction carriers results in a long-range interaction between localized magnetic moments of the d-electrons, expressed by Equation (2):

$$\frac{3N}{16\pi^2}\frac{J_{s-d}^2}{E_F} I(\boldsymbol{R}_{ij}) S_{iz} S_{jz} \qquad (2)$$

where R_{ij} is the distance between d-electrons having the z-components of spins S_{iz} at site i and S_{jz} at site j, E_F is the Fermi energy and $I(R_{ij})$ is the decaying function of R_{ij}, with a spatially oscillatory behavior which depends on the Fermi wave number k_F, as given by Equation (3):

$$I(\boldsymbol{R}_{ij}) = \frac{16\pi k_F^3}{\left(2k_F\boldsymbol{R}_{ij}\right)^4}\left(2k_F\boldsymbol{R}_{ij}\cos 2k_F\boldsymbol{R}_{ij} - \sin 2k_F\boldsymbol{R}_{ij}\right) \qquad (3)$$

The exchange interaction between localized magnetic moments in a metallic medium, described in Equation (2), is called the Rudermann−Kittel−Kasuya−Yoshida (RKKY) interaction, which is the origin of strong ferromagnetism in transition metals such as iron.

The RKKY interaction has strategic importance for the development of organic systems with magnetic interactions similar to the s-d interaction, and for the preparation of molecular versions of metal magnets. This could give new insights into phenomena related to the interplay between conduction carriers and localized magnetic moments.

Recently, a large variety of "organic metal" complexes and superconductors, modeled on organic charge-transfer complexes,[14] have been developed and their interesting novel properties uncovered. In such organic conductors, the constituent donor/acceptor molecules are planar, so that their π-electron orbitals (which protrude perpendicular to the molecular plane) overlap with each other, giving the π-electrons a small kinetic energy (transfer integral) in the 0.1−1 eV range. Therefore, these π-electrons play a role in the electron transport process, in contrast to conventional metals, in which the s- and p-electrons have a kinetic energy of several eV. In other words, organic conductors can be described as highly correlated electron systems, in which the kinetic energy of the π-electrons is smaller than or similar to the on-site Coulomb interaction. Moreover, one of the important features specific to organic complex crystals, associated with molecular stacking, is the one- or two-dimensionality of their lattices. As a consequence, organic conductors have electronic instabilities, resulting in the appearance of insulating states at low temperatures, such as charge density wave (CDW) and spin density wave states (SDW).[14]

The π-d interaction, which is the organic version of the s-d and s-f interactions, results from the introduction of d-electrons into organic conductors. It can be considered to possess a different nature from the s-d interaction, judging from the specific electronic and structural features mentioned above. Here, we present a brief perspective on the magnetism emerging in π-d interaction systems, shown in Figure 1. In this regard, typical π-d based metal magnets appear in the regime where both the transfer integral and the π-d interaction $J_{\pi\text{-}d}$ govern the characteristics of the electronic structures. In the insulating regime, superexchange-mediated π-d composites are expected to provide ferrimagnets, weak ferromagnets or helical magnets, whereas metallic π-d systems only become organic magnetic superconductors if the π-d interaction is not strong enough to bring about pair-breaking against the superconducting state.

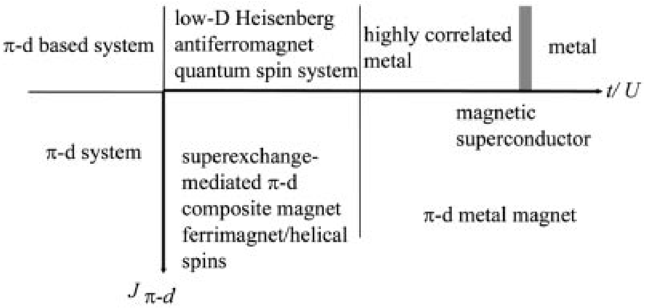


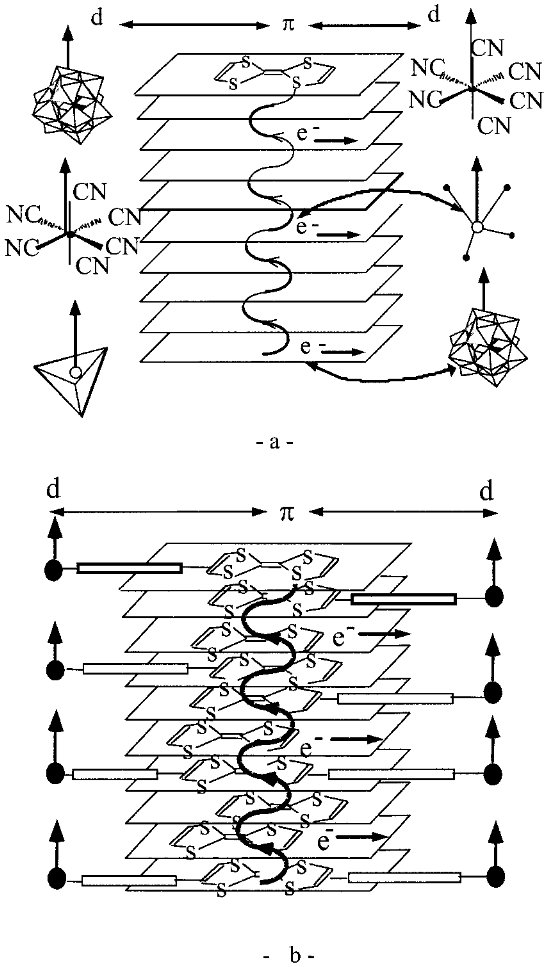
Figure 1. Overview of magnetism appearing in organic charge transfer complexes, depending on t, U and $J_{\pi\text{-d}}$

From the perspective of materials design, the π-d system model is based on the synergy between electrical conductivity and magnetic interactions. In this regard, a combination of TTF-based organic donors and magnetic anions having d-electrons could give rise to an interesting family of materials, classified as organic-inorganic hybrids, in which the spins are localized on the transition metals (d-electrons). In these materials, an interesting interplay between electron transport and magnetism could be produced by a long-range magnetic coupling between localized spins through the mobile π-electrons of the conducting networks (Scheme 1).

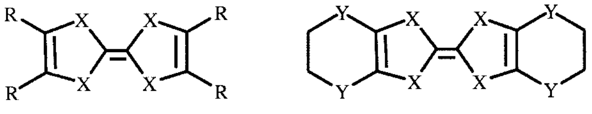
An alternative way of designing a molecule-based magnetic material would be to construct an organic compound in which the localized spins are borne by an organic radical.[11]

3. Conducting and Magnetic Materials

Conducting organic materials incorporating localized spin first appeared in the early 1980s.[4] In particular, (TMTSF)$FeCl_4$ and (TMTTF)$FeCl_4$ [4b] were the first compounds in which it was claimed that the weak antiferromagnetic interactions observed between the localized spins were mediated by the organic system. Since then, many compounds have been synthesized and characterized, but most of these materials show one of the following unfavorable situations between the two properties: (i) Stabilization of the superconducting state with paramagnetic anions, as in (BEDT-TTF)$_4$[$(H_2O)Fe(C_2O_4)_3$]C_6H_5CN (T_c = 8.5 K)[5a] and (BETS)$_2$($FeCl_4$)$_{0.5}$-($GaCl_4$)$_{0.5}$ (T_c = 4.6 K)[12] [BETS = bis(ethylene dithiotetraselenafulvalene)], (ii) Coexistence of two completely independent metallic and ferromagnetic sublattices, as in the recently-reported metal ferromagnets (BEDT-TTF)$_3$[$MnCr(C_2O_4)_3$][5d] and (BO)$_3$ [$FeCr(C_2O_4)_3$],[5e] (iii) The presence of magnetic interactions not mediated by the conducting electrons, as found in some insulating salts of TTF derivatives containing [$Cr(NCS)_4$(phen)]$^-$,[8a] (phen = 1,10-phenanthroline). However, the following interesting examples are worthy of note.



Scheme 1. Representation of the indirect exchange mechanism; (a) through space interaction, (b) through bridge interaction



TTF : X = S, R = H
TMTTF : X = S, R = CH_3
TMTSF : X = Se, R = CH_3

BEDT-TTF : X = Y = S
BEDS : X = Se, Y = S
BO : X = S, Y = O

Scheme 2. Some typical organic donors; TTF = tetrathiafulvalene; TMTTF = tetramethyl-TTF; TMTSF = tetramethyltetraselenafulvalene; BEDT-TTF = bis(ethylenedithio)-TTF; BEDS = bis(ethylenedithio)tetraselenafulvalene; BO = bis(ethylenedioxo)-TTF

3.1. (BEDT-TTF)$_3$(CuCl$_4$)H$_2$O

This compound was the first BEDT-TTF stable organic metal with a paramagnetic anion;[5f] it is metallic down to very low temperatures (200 mK). No superconductivity was observed under pressure (up to 12 kbar) at temperatures down to 2 K. The product of the susceptibility and the temperature ($\chi_M T$), obtained from ESR measurements, shows a gradual increase at low temperature, indicating short-range ferromagnetic interactions between the Cu^{II} atoms. The Cu···Cu distance was found to be greater than 8.5 Å, resulting in insignificant exchange interactions. A more probable explanation for this behavior is the possibility of indirect exchange through the free electrons of the conducting layer.

3.2. (BETS)$_2$(MCl$_4$) (M = Fe^{III}, Ga^{III})

A series of BETS conductors with MX$_4^-$ anions [M = Fe^{III} (S = 5/2) and Ga^{III} (S = 0)] have been reported by Kobayashi et al.[12] These compounds [formulated as (BETS)$_2$(MCl$_4$)] revealed a rich polymorphism and some interesting properties, including superconductivity in the alloy (BETS)$_2$(Fe$_{0.5}$Ga$_{0.5}$Cl$_4$). The compounds λ-(BETS)$_2$(Fe^{III}Cl$_4$), containing a paramagnetic anion with S = 5/2, and its isomorphous salt λ-(BETS)$_2$(Ga^{III}Cl$_4$), containing a diamagnetic anion are worthy of discussion. The crystal structures of these two compounds are identical, but their electrical conductivities are very different. Both salts are metallic between 300 K and 8 K, and have almost identical conductivities. But below 8 K, the Ga^{III}-containing salt has a superconducting transition, whereas the Fe^{III}-containing salt has a metal to insulator (MI) transition. It appears that the presence of paramagnetic species strongly influences the electrical conductivity in the donor layers. In agreement with this hypothesis, it was possible to restore the metallic state below 8 K at high magnetic fields.[12b,12c]

3.3 (DMET)$_2$FeBr$_4$ and (EDTDM)$_2$FeBr$_4$

These two compounds are isostructural.[15] They consist of alternately stacked donor conducting layers and square-lattice magnetic layers of Fe^{3+} with localized spins (S = 5/2). In each donor sheet, donor molecules form 1D chains subjected to weak inter-chain interactions, giving 3/4-filled quasi-1D π-electronic systems. The resistivity shows metallic features down to temperatures of about 40 K and 15 K for (DMET)$_2$FeBr$_4$ and (EDTDM)$_2$FeBr$_4$, respectively, below which the insulating SDW emerges. The magnetism is governed mainly by the Fe^{3+} (S = 5/2) localized spins. In (DMET)$_2$FeBr$_4$ and (EDTDM)$_2$FeBr$_4$, Fe^{3+} spins undergo 3D antiferromagnetic (AF) ordering at T_N = 3.7 and 3 K, respectively.

The magnetization curves are anomalous, as shown for (DMET)$_2$FeBr$_4$ in Figure 2 (a). Application of the external field along the spin-easy axis gives a spin-flop transition when B_{SF} is approximately 2 T. In addition, an anomaly appears around $B_2 \approx$ 5 T in the hard axis direction. This feature cannot be explained only by Fe^{3+} spins, suggesting that donor electrons participate in the magnetization.

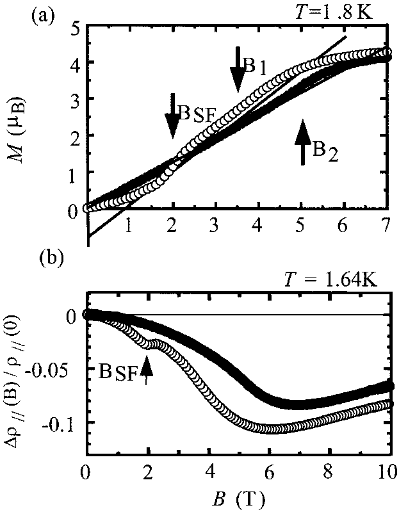


Figure 2. Field dependence of the magnetization; (a) and the in-plane magnetoresistance; (b) for (DMET)$_2$FeBr$_4$; open and closed circles denote the data for the field applied along the spin-easy and spin-hard axes, respectively; B_{SF} is the field of the spin-flop transition; B_1 and B_2 are the fields at which anomalies appear in the magnetization curves

Figure 2 (b) represents the magnetoresistance (MR) vs. field plot below T_N for the in-plane electron transport of (DMET)$_2$FeBr$_4$. The MR is negative in the whole field range up to 15 T with a minimum at around 6 T. Interestingly, an anomalous discontinuity exists at B_{SF}, when the field is applied in the spin-easy axis direction. For the field along the hard axis, the MR shows a discontinuity at $B_2 \approx$ 5 T, at which the magnetization has an anomaly, as we can see by taking the derivative of the MR with respect to B.

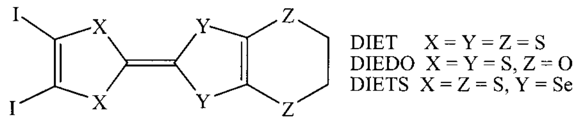
The correlation between the magnetic behavior and the magnetoresistance features can be understood by the formation of SDW in the insulating phase. Below T_{MI}, localized magnetic moments generated in the donor electronic system are spatially ordered. A simple analysis gives the fourfold periodicity in the SDW state along the chain, since the donor is in the 3/4-filled electronic state. In the SDW state, in which the periodicity of the Fe^{3+} AF arrangement is well registered to the SDW, Fe^{3+} spins become antiferromagnetically ordered below T_N. This results in an enhancement of the SDW gap, compared to the case which has no internal magnetic field of Fe^{3+} spins. However, well above the field at which all the Fe^{3+} spins are ferromagnetically arranged, the potential of the Fe^{3+} magnetic lattice does not modify the SDW gap. Therefore, the elevation of the field strength gives negative MR up to the saturation field of Fe^{3+} spins. At fields higher than the field at which the SDW state is destroyed, individual electrons contribute to the transport, resulting in an increase in the MR. The anomaly at B_{SF} in the MR is the consequence of a subtle change in the magnetic energy, which modifies the SDW gap slightly.

4. Current Developments

In order to establish magnetic or (at least) structural interactions between the organic and inorganic sublattices, some ideas are currently being explored in our groups. The first consists of using halogen-substituted organic donors and polycyanide anions.[5b,7b] The second uses an inorganic anion with π ligands[8] and the third (which is very recent) deals with coordination complexes containing TTF or its derivatives as ligands.[9,10,16]

4.1. Halogen-Substituted Donors

The nitrogen-halogen interaction is known from crystal engineering, and was used to construct the molecular pathway.[17] In our case, we used the unsymmetrical halogen-substituted organic donors DIETS [diiodo (ethylenedithio)-dithiadiselenafulvalene], DIEDO [diiodo(ethylenedioxo)-tetrathiafulvalene] and DIET [diiodo(ethylenedithio)tetrathiafulvalene],[18] which have two terminal iodine atoms with paramagnetic polycyanometalates such as $[M(CN)_6]^{3-}$ [7b] and $[Ni(mnt)_2]^-$ [7] as anions (Scheme 3). We describe here two types of compounds containing these anions.



Scheme 3. Organic donors bearing iodine atoms

4.1(a). $(DIETS)_8[Cr(CN)_6]_{0.67}Cl_22H_2O$

This compound has a typical layered crystal structure with extremely short Donor···Anion (I···N) contacts.[7b] These distances (in the range 2.722 to 2.825 Å) are slightly shorter than the sum of van der Waals (vdW) separation of ca. 3.65 Å. From the physical properties (Figure 3) we concluded that this compound is semiconducting and paramagnetic. The dc. electrical conductivity measurements over the range 20−300 K show semiconducting behavior, with $\sigma_{RT} \approx 0.2$ Scm^{-1} and $E_A = 65$ K. The magnetic susceptibility (Figure 3) obeys the Curie−Weiss law ($C = 1.571$ emu K^{-1} mol^{-1}, $\Theta = -0.2$ K), and there is no magnetic ordering down to 1.7 K. The small Weiss temperature and the absence of any magnetic phase transition shows that the exchange interaction between the magnetic anions is small. The decrease of $\chi_M T$ at low temperature is attributed to AF interactions in the organic layer. Therefore, despite the very short contact attained in this compound, no magnetic interactions were observed between the conduction and magnetic systems.

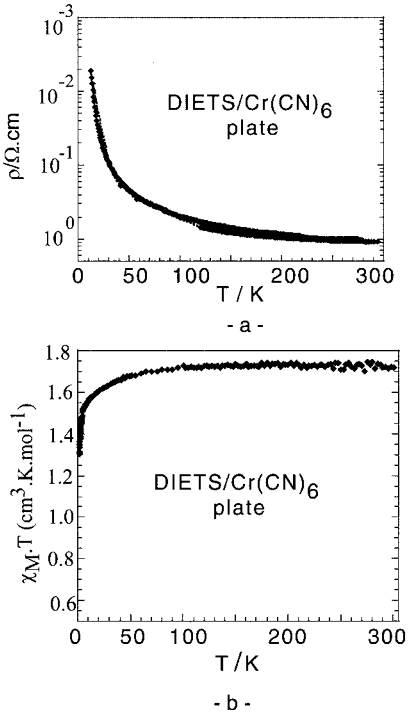


Figure 3. (a) Electrical conductivity and (b) magnetic properties of $(DIETS)_8[Cr(CN)_6]_{0.67}Cl_22H_2O$

4.1(b). $(EDO-TTFI_2)M(mnt)_2$ (M = Ni, Pt): An "Organic Metal" with a Ferromagnetic Interaction

$(EDO-TTFI_2)M(mnt)_2$ (M = Ni, Pt) complexes feature 1D metal chains (the donor $EDO-TTFI_2$ columns) and 1D magnetic chains [the $M(mnt)_2$ anion columns], which are aligned parallel to each other along the *c*-axis, as shown in Figure 4.[7a] The donor chain has a 3/4-filled state; the metal-insulator transition, $T_{MI} = 88$ and 96 K for M = Ni and Pt, respectively.

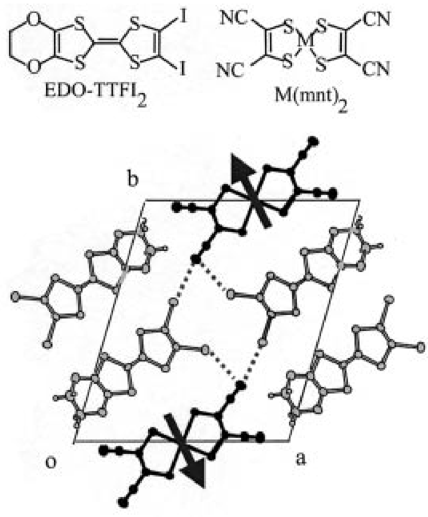


Figure 4. Crystal structure of $(EDO-TTFI_2)_2M(mnt)_2$ (M = Ni, Pt); dotted lines denote close CN−I atomic contacts between donor and anion; localized spins ($S = 1/2$) on acceptors are shown with arrows

The anion is in the half-filled state with a localized moment of $S = 1/2$. The temperature dependence of the magnetic susceptibility is shown in Figure 5. The susceptibility provides evidence for the presence of ferromagnetic interaction, as clearly seen from the increasing trend of χT at low temperatures for M = Ni and Pt. Actually, the observed susceptibility can be satisfactorily explained in terms of the Heisenberg model (for an $S = 1/2$ 1D ferromagnet), with $J = 18$ K for M = Ni, taking into account the absence of anisotropy in the susceptibility as shown in Figure 5 (a). The absence of 3D long-range order is the consequence of the 1D Heisenberg isotropic spin feature. For the Pt complex, the susceptibility has a large anisotropy dependent on the field direction [as shown in Figure 5 (b)], where the fitting is satisfactory with the Ising model (for an $S = 1/2$ 1D ferromagnet), with $J = 20$ K. From the peak in the susceptibility, it is clear that long-range 3D ordering takes place at $T_N = 5.5$ K; the weak inter-chain AF interaction ($J' \approx -0.05$), with the aid of the anisotropy, plays an important role, giving an antiparallel arrangement of ferromagnetic chains.

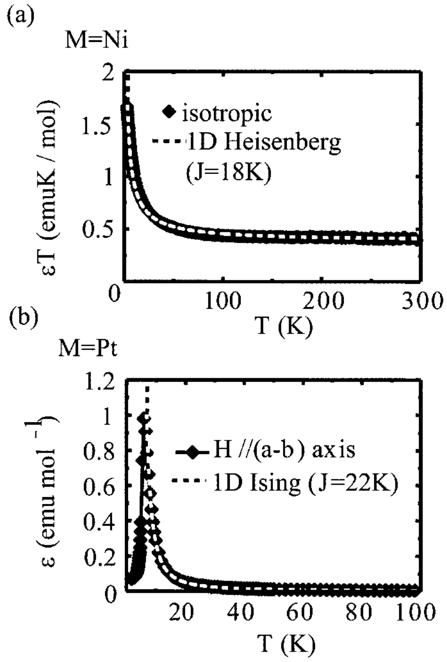


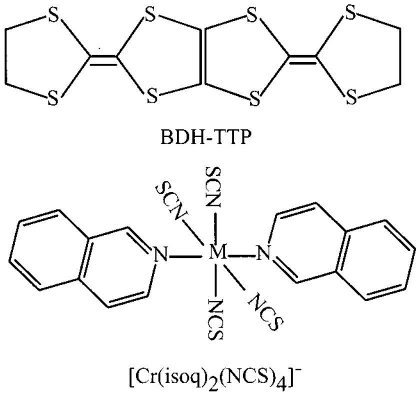
Figure 5. (a) χT vs. T plot for $(\text{EDO-TTFI}_2)_2\text{Ni(mnt)}_2$; the dashed line is the theoretical curve for the Heisenberg model (for a $S = 1/2$ 1D ferromagnet) ($J = 18$ K); (b) χ vs. T plot for $(\text{EDO-TTFI}_2)_2\text{Pt(mnt)}_2$; the solid line represents the curve for the Ising model (for a $S = 1/2$ 1D ferromagnet) ($J = 20$ K).

The origin of the ferromagnetic interaction can be explained in terms of McConnell's theory,[19] namely, that the spin polarization effect causes the ferromagnetic interaction. The slipped metal-over-sulfur configuration of M(mnt)_2 molecules causes an AF interaction between the small negative spin density on the sulfur atom of an M(mnt)_2 unit and a large positive spin density on the metal atom of an adjacent M(mnt)_2 unit. Eventually, this local AF configuration produces a ferromagnetic interaction between the large positive spin densities on the metal atoms of adjacent M(mnt)_2 molecules.

The interaction between π-conduction carriers and localized spins is an important issue in the development of molecular versions of metal magnets. From this viewpoint, the ESR signal featuring a single Lorentzian shape for M = Ni and the absence of an ESR signal for M = Pt indicate the presence of a considerable interaction between conducting donors and magnetic anions.

4.2. Paramagnetic Anions with π Ligands

Recently, TTF- and TTP- (tetrathiapentalene) derived salts containing $[\text{M(NCS)}_4(\text{L})_n]^-$ [where M = Cr^{III}, Fe^{III}, L = 1,10-phenanthroline (phen) or isoquinoline (isoq)] have been reported[8] (Scheme 4). In these compounds, magnetic interactions should be induced by both S···S contacts and π-stacking overlap between the paramagnetic anions and organic radicals. Indeed, a large number of the salts showed long-range ferrimagnetic and weak ferromagnetic order with T_c in the range 4.2–8.9 K.[8]



BDH-TTP

$[\text{Cr(isoq)}_2(\text{NCS})_4]^-$

Scheme 4

As an example, we describe here $(\text{BDH-TTP})[\text{Cr(isoq)}_2(\text{NCS})_4]$ (**3**),[8c] where BDH-TTP = 2,5-bis(1,3-dithiolan-2-ylidene)-1,3,4,6-tetrathiapentalene. As shown in Figure 6, the crystal structure consists of one-dimensional chains parallel to the c-direction, with remarkably short intermolecular S···S distances (in the range 3.264–3.397 Å, vdW = 3.70 Å). The adjacent chains are connected through the π-π overlap of isoquinoline moieties [interplanar separation, $d = 3.600(5)$ Å] between the anions, and short S···S contacts [S(5)–S(5) = 3.640(2) Å] between the donors. In the [101] direction, neighboring anions are related by the c-glide plane, and therefore the orientation of these anions is different; the angle between the molecular axes (defined as isoq–M–isoq) is 6.0(3)°.

As expected from the 1:1 stoichiometry and the alternate stacking of donors and anions, the salt has a low conductivity [$\sigma(300\text{ K}) = 10^{-5}\text{ S cm}^{-1}$]. Its magnetic susceptibility [Figure 7 (a)] obeys the Curie–Weiss law above 50 K, with $\Theta = -20.4$ K and $C = 2.19\text{ emu K mol}^{-1}$, which is close to the corresponding spin-only value ($2.25\text{ emu K mol}^{-1}$) for non-interacting anion ($S = 3/2$) and donor ($S = 1/2$) spins, assuming $g = 2.0$ for each species. Below 50 K, $\chi_M T$ decreases with the temperature down to 8 K, but then it shows a steep increase at $T_C = 7.6$ K due to a magnetic transition. The insets of Figure 7 (a) present the field-cooled magnetization (FCM) measured at 10 mT, and the

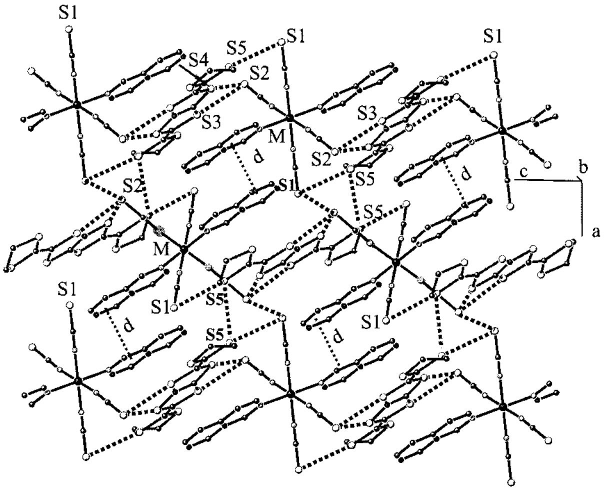


Figure 6. Projection of the crystal structure of (BDH-TTP)[Cr(isoq)$_2$(NCS)$_4$] in the *ac* plane, S···S contacts are shown

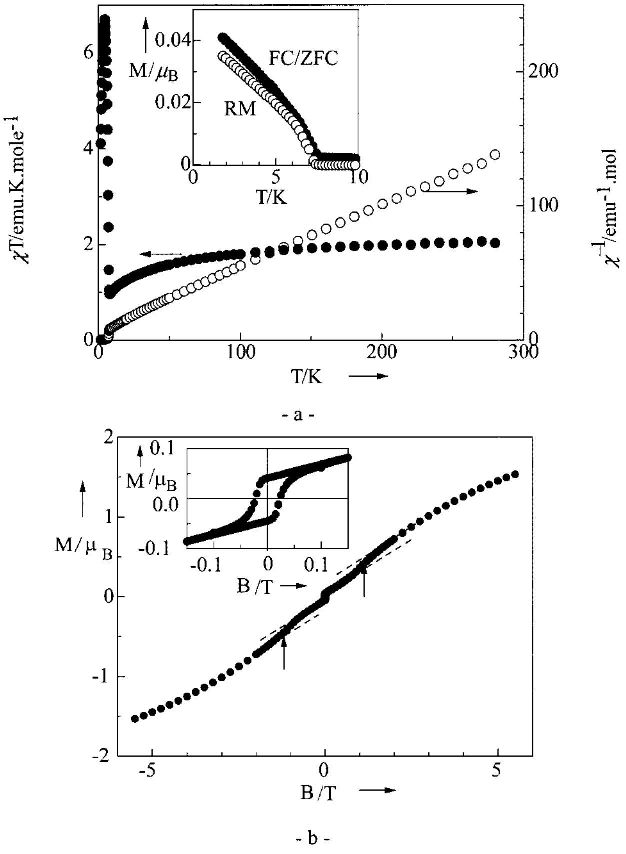


Figure 7. (a) Temperature dependence of $\chi_M T$ (filled circles) and $\chi_M{}^{-1}$ (open circles) for non-oriented samples, measured with an applied field of 10 mT for (BDH-TTP)[Cr(isoq)$_2$(NCS)$_4$]; inset: temperature dependence of the FCM (filled circles) and RM (open circles); (b) magnetization curves at 2 K measured on non-oriented samples; inset: hysteresis loop around B = 0 T

remnant magnetization (RM) observed after the external field of 10 mT is removed at 1.8 K. Below T_C = 7.6 K, the FCMs increase steeply and the RMs also emerge, indicating the presence of spontaneous magnetization. Moreover, in the magnetization curve a hysteresis loop is also observed around B = 0 T [Figure 7 (b)].

This salt has a bulk weak ferromagnetic state, originating from the angled alignment of the one-dimensional ferrimagnetic chains involving d-electrons and π-electrons. The origin of the intra-chain AF coupling are the short intermolecular S···S contacts between donors and anions, whereas the inter-chain coupling comes from the π-π overlap between anions and/or S···S contacts between donors.

4.3. Covalent Links Between Paramagnetic And Conducting Systems

As for the above-described compounds, the strategy commonly used in this area is the assembly of conducting organic sublattices and paramagnetic inorganic sublattices in salts comprising organic ions and paramagnetic inorganic counterions. In general, this yields materials with weak interactions (when they exist at all) between the two systems.

We are currently developing a strategy which consists in preparing new materials where the conducting and magnetic systems are covalently linked through a π-conjugated bridge, as shown in Scheme 1.[9,10] We have therefore synthesized and characterized new paramagnetic coordination complexes containing TTF or BEDT-TTF as ligands, as well as their radical cation salts. We present here as an example [Cu^{II}(hfac)$_2$](TTF-py)$_2$, where hfac = hexafluoroacetylacetonate[10] and TTF-py = 4-(2-tetrathiafulvalenylethenyl) pyridine. Its molecular and crystal structure are shown in Figure 8 (a). The Cu atom is bonded in the equatorial plane to the oxygen atoms of two bidentate hfac anions. The TTF-py ligands occupy the apical positions and are *trans* to each other; they are then bonded to the metal atom through the nitrogen atoms of the pyridyl ring. The crystal structure [Figure 8 (b)], consists of alternate organic (TTF-py) and inorganic [Cu(hfac)$_2$] layers, linked by a conjugated bridge. The two TTF moieties are neutral, and therefore this complex is insulating and paramagnetic, as expected.

The following step of this work was obviously the partial oxidation of these TTF-py ligands to introduce electrical conductivity. A part of this goal has now been achieved by the synthesis and the characterization of the unprecedented radical cation salt [Cu(hfac)$_2$(TTF-py)$_2$][PF$_6$][10] [Figure 9 (a)].

The bond lengths around the Cu atom are very close to those found in the neutral complex, but the central C=C bond length of the TTF-py moiety [1.369(8) Å], which is more sensitive to oxidation, is slightly larger than in the neutral complex [1.317(10) Å]. From the stoichiometry, we can deduce that the charge distribution is [Cu^{2+}(hfac)$_2{}^{2-}$(TTF-py)$_2{}^{+}$][PF$_6$]$^-$. This gives rise to a mixed valence state in the [Cu^{2+}(hfac)$_2{}^{2-}$(TTF-py)$_2{}^{+}$] radical unit. In the crystal structure [Figure 7 (a)], the TTF units form dimers separated by the PF$_6$ anions [Figure 9 (b)]; the isolated dimers are of course in the mixed valence state. Actually, this structural arrangement is not favorable for electrical conductivity, and therefore further work is needed to achieve electrical conductivity. Studies investigating systematic changes in anions, metals and ligands are currently underway.

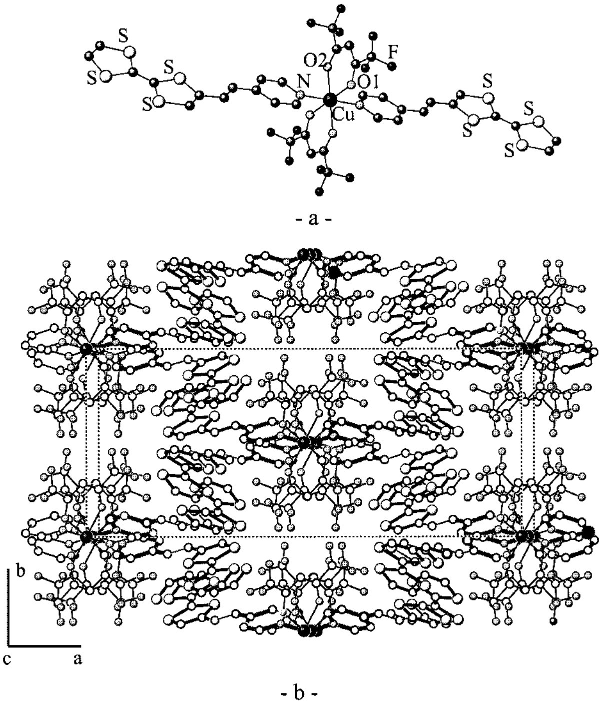


Figure 8. Molecular and crystal structure of $[Cu^{II}(hfac)_2](TTF\text{-}py)_2$, showing separate layers of organic and inorganic units linked by conjugated bridges

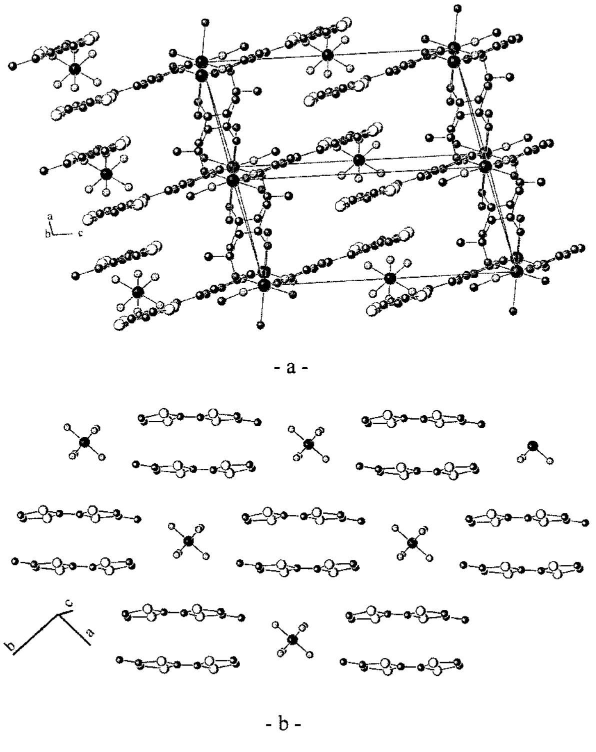


Figure 9. (a) Crystal structure of $[Cu^{2+}(hfac)_2{}^{2-}(TTF\text{-}py)_2{}^{+}][PF_6]^{-}$; (b) projection of the organic layer in the *ab* plane

5. Conclusions

In $(DIETS)_8(Et_4N)[Cr(CN)_6]_{0.66}Cl_22H_2O$, short I···N contacts were observed between donors and anions. This compound is semiconducting and paramagnetic. However, despite these very short contacts, no magnetic exchange interactions between donor π-electrons and anion d-electrons have been observed. $(EDO\text{-}TTFI_2)M(mnt)_2$ complexes (M = Ni, Pt) are metallic with ferromagnetic interactions, and $(BDH\text{-}TTP)[Cr(isoq)_2(NCS)_4]$ belongs to a series of insulating weak ferromagnets with T_c values in the range 5.8−8.9 K.

Finally, new transition metal complexes and their radical cation salts containing organic donor (TTF-py) as ligands covalently linked through π-conjugated bridges have been presented. These compounds are very promising and constitute a new approach for obtaining π-d interactions in bifunctional conducting and magnetic molecular materials.

From the present results, a combination of TTF-based donors and magnetic anions having d-electrons as building blocks should be expected to produce a large variety of molecular magnets having an unconventional interplay of electron transport and magnetism, owing to the hybrid structure of two components with different functions.

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