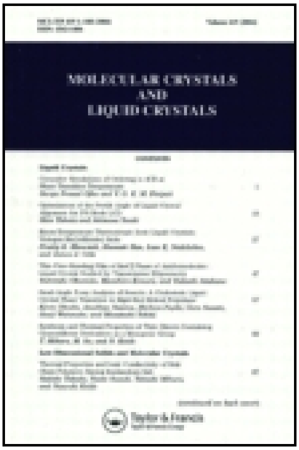

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Interaction Between Free Carriers of Organic Conductors and Localized Moment on Magnetic Anions

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INTERACTION BETWEEN FREE CARRIERS OF ORGANIC CONDUCTORS AND LOCALIZED MOMENT ON MAGNETIC ANIONS

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Abstract Crystals of (BEDT-TTF)$_n$X$_m$, where X is an anion having magnetic moment, have different stoichiometries and structural motifs depending on the size of the anions and their coordination geometry. Their electrical properties are predominantly semiconducting except for one salt which is metallic down to 200mK. The magnetic properties of the large gap semiconducting salts are dominated by the moments on the metal anions and do not show any observable interaction between the spin systems [e.g. for (BEDT-TTF)$_2$FeCl$_4$ θ is -6K). Those of small gap semiconductors indicate there is some exchange [e.g. for (BEDT-TTF)$_6$(CuBr$_4$)$_2$ θ is -107K). In the case of the metallic salt, (BEDT-TTF)$_3$ CuCl$_4$.H$_2$O, the interaction between the two independent spin systems is small (θ~+1K).

INTRODUCTION

Superconductivity and ferromagnetism are mutually exclusive states of matter, which occur independently in many materials.[1] A few compounds have been synthesised such that the two properties can exist. These are interesting to many scientists in various fields; from synthetic chemists to theoretical physicists. In general these few compounds that show this peculiar properties have superconducting critical temperatures greater than the three dimensional magnetic ordering temperature. The main question is what is the interplay between the magnetic ions and the Cooper pairs in the intermediate temperature region. In order to simplify the theoretical problem, we have been searching for materials having lower dimensionality.[2] Our main efforts have been directed to the synthesis of charge transfer salts of the organic donor molecule, BEDT-TTF or ET [bis(ethylenedithio)tetrathiafulvalene] with a range of transition metal complexes. The compounds obtained so far are not superconductors; in two cases, one a metal[3] and the other a narrow gap semiconductor[4], we observed some exchange between the two types of spin. In this paper, we describe the magnetic properties of the electrocrystallised compounds obtained with simple halides of copper (II) and iron (III) and relate them to their crystal and electronic band structures.

RESULT AND DISCUSSION

The interaction of free carriers of organic conductors, based on BEDT-TTF, with localized moments of transition metal anions can be of great value in the understanding of the competition between superconductivity and magnetism, as well as giving us a measure of the superconducting coherent length in the presence of magnetic impurities and defects.These informations are possible through a program of synthesis, determination of the crystal and electronic structures and a study of the electronic transport, magnetic and optical properties.

The compounds were synthesised electrochemically from BEDT-TTF and the tetraalkylammonium salts of the anions in dipolar aprotic solvents. Crystals of dimension as large as $5x1x0.5mm^3$ were harvested for current of 1μA for a period of 15 days.

Crystal Structure

A common feature in the crystal structure of BEDT-TTF salts is the slightly dimerised pair of BEDT-TTF molecules forming the basic unit.[5] These units form stacks which are parallel to each other with close S···S contacts to form layers. Although, these are the pertinent structural motif for some of the salts reported here, we find that in the monocharged BEDT-TTF salts the layer structure is lost. Varying the shape, size and charge of the anion as well as the number of unpaired spins on the transition metal results in several structural packing motifs. In general, the salts having the BEDT-TTF molecules with a non integral charge are layered while those which are monocharged are strongly dimerised and each dimer is separated by the anion.[2,6]

Electrical Transport Properties

The electrical transport properties depend on the crystal as well as the electronic band structures. The $FeCl_4$ salt is semiconducting ($\sigma=10^{-2}Scm^{-1}$ and $E_A=0.21eV$) while the $FeBr_4$ salt is insulating ($\sigma<10^{-6}Scm^{-1}$). The two $CuCl_4$ salts also behave differently; the 2:1 salt is semiconducting ($\sigma=10^{-4}Scm^{-1}$, $E_A=0.32eV$) while the 3:1 salt is metallic down to 200mK ($\sigma=140Scm^{-1}$). The $CuCl_2Br_2$ and $CuBr_4$ salts are as expected very similar to one another; they are semiconducting ($\sigma=0.7(1)Scm^{-1}$, $E_A(300K)=0.09eV$ for $CuCl_2Br_2$ and 0.17eV for $CuBr_4$. Below 200K the activation energies are reduced to 0.027 and 0.036 respectively.[4,7]

Applying pressure on the 3:1 salt of $CuCl_4$ increases the room temperature conductivity by three and do not stabilise a superconducting ground state up to 12kbar and 1.4K.[8] While for the mixed copper halide and copper bromide salts, a metallic state is stablised for pressures above 5kbar and temperature above 100K.[9,10]

Electron Paramagnetic Resonance

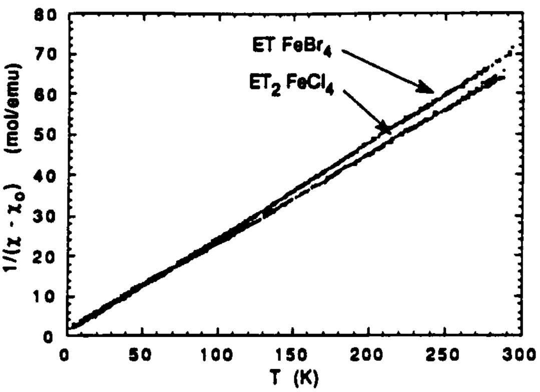
The magnetic properties have been studied by single crystal EPR measurements and on samples of randomly oriented crystals by a Faraday balance. The EPR spectra of the iron halides salts are characterised by very broad lines (700G for $FeCl_4$ and 1400G for $FeBr_4$) whose intensities increase to low temperatures. The spectra of the 2:1 salt of $CuCl_4$ show a single Lorentzian line with a linewidth, H_{pp}, varying between 24 and 65G depending on orientation and a g-values from 2.005 to 2.29. This is consistent with the spectra of $CuCl_4^{2-}$. Those of the metallic 3:1 $CuCl_4$ salt show two lines; one of width 40-120G and g-value 2.005-2.305 corresponding to the spin on the $CuCl_4$ ion and the second line, which is only observed in a limited angular region, with width 60G and g=2.003. The latter being that of the conduction electron resonance. The $CuCl_2Br_2$ and $CuBr_4$ salts have similar spectra; a single Lorentzian line with almost isotropic width of 90(5)G and 115(2)G respectively. The g-values are 2.021-2.086 for the mixed halide and 2.012-2.054 for the bromide salt.

Bulk Magnetic Susceptibility

The data for the salts are given in the Table. Figures 1-4 display the susceptibilities of the six compounds. For ET_2FeCl_4 and $ETFeBr_4$ the Curie constant corresponds to an effective magnetic moment of 5.9(1)μ_B per formula unit. These values are close to that for a S=5/2 ion (5.91μ_B) as would be expected for the high spin $3d^5$ Fe^{3+}. A contribution to the susceptibility is expected from the unpaired spins on the ET dimers in ET_2FeCl_4, similar to the response of ET_2GaCl_4, which has the same structure and conductivity and band gap but with a non-magnetic anion. For example at 80K the susceptibility of ET_2FeCl_4 is ~5.5×10^{-2}emu/mol, about forty times larger than the maximum susceptibility of ET_2GaCl_4.[11] Thus the properties of the spins of $(ET_2)^+$ dimers are obscured by the large magnetic response of the $FeCl_4$ anion. For the $FeBr_4$ salt, the strong dimerisation and one spin per molecule will result in a diamagnetic contribution from the $(ET_2)^{2+}$.The two salts

TABLE: Electrical and magnetic parameters for the BEDT-TTF salts with magnetic anion

Compound	σ/Scm^{-1}	E_A/eV	χ/emu mol^{-1}	θ/K
ET_2FeCl_4	10^{-2}	0.21	1.53×10^{-2}	-6
ET $FeBr_4$	10^{-6}		1.44×10^{-2}	-5
ET_2CuCl_4	10^{-4}	0.32	5.8×10^{-3}	0
$ET_3CuCl_4.H_2O$	140	0		+1
$ET_6(CuCl_2Br_2)_2$	0.7	0.087	4×10^{-4}	-59
$ET_6(CuBr_4)_2$	0.6	0.165	3.8×10^{-3}	-107



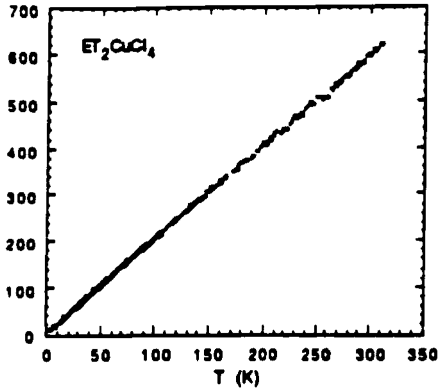


Figure 1: Magnetic susceptibility of ET_2FeCl_4 and $ETFeBr_4$.

Figure 2: Magnetic susceptibility of ET_2CuCl_4.

have antiferromagnetic Weiss constants of ~-5K.The situation for ET_2CuCl_4 is similar to $ETFeBr_4$, where the susceptibility is dominated by the moments on the anion and a Curie value (0.45(3)emuK/mol) is well within the range of values expected for Cu(II).

The susceptibility of the conducting salt $ET_3CuCl_4.H_2O$ is best described by that determined from the EPR intensities as this technique allows the contribution of the two spin systems to be monitored independently. On the one hand, the susceptibility of the Cu(II) signal increases at low temperature. Analysis of the low temperature data give a positive Weiss constant of 1(1)K and a Bleaney-Bowers model for an interacting dimer gives J=4(1)K. On the other hand, the spin susceptibility of the conduction electrons is

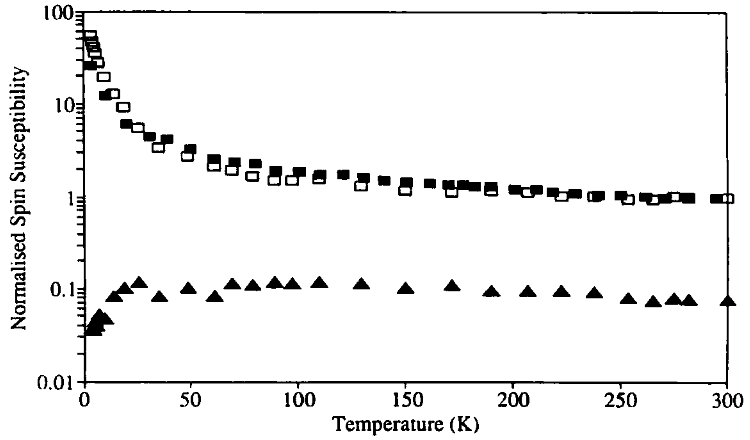


Figure 3: Spin susceptibilities due to the copper electrons (squares) and conduction electrons (triangle) for $ET_3CuCl_4.H_2O$.

Pauli like above 30K and decreases monotonically below 30K to about one fifth of its room temperature value. This indicates that exchange between conduction electron and copper atoms is not negligible. The fact that the Cu centers are more than 8.5Å apart supports the argument of a super-exchange mechanism operating in this compound.

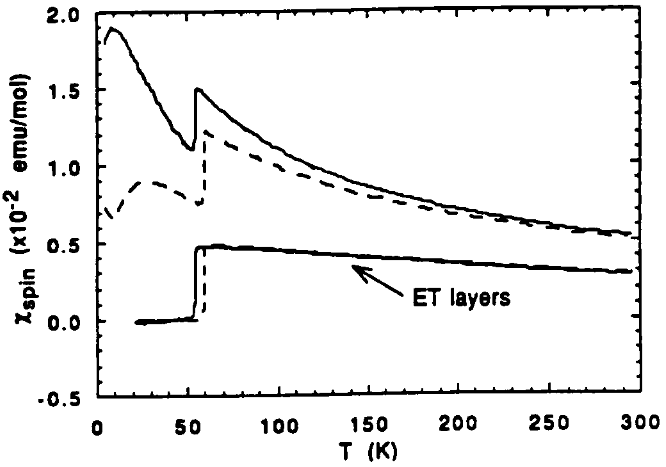


Figure 4: Magnetic susceptibilities of $ET_6(CuCl_2Br_2)_2$ (solid line) and $ET_6(CuBr_4)_2$ (dashed line) and the contribution from the ET moieties.

The susceptibilities of $ET_6(CuCl_2Br_2)_2$ and $ET_6(CuBr_4)_2$ have a certain similarity. The former has a transition at 55K compared to 60K for the latter. The data fit a Curie-Weiss law above the transition with θ=-59 and -107K, respectively. Below the transition, the data show a maximum which can be fitted to a quadratic layer antiferromagnet with J=-8 and -15K, respectively. A second transition at 8K in the bromide salt has been associated with a spin flop transition.[10] Below this temperature the EPR linewidth broadens and the g-value increases. The fact that there is only one EPR signal in the EPR spectra at all temperature is indicative of strong exchange between the conduction electrons and the moment on the copper. Taking the difference between the observed data and the QLAF fit to the low temperature data for 1.9 spins for the bromide and 2.0 spins for the mixed halide gives the contribution from the BEDT-TTF moiety. It is clear that there is a **loss** of almost all the spins of the BEDT-TTF layer at the transition at 60K. Fits to the difference data for T>60K for a QLAF with J=42K is better than for a Bonner-Fisher one dimensional antiferromagnetic Heisenberg chain. Given that the activation energy is only 0.03eV below 60K, there would be some carriers present even at 8K which could enhance the spin flop transition.

CONCLUSION

The products of the electrocrystallisation with transition metal anions have different stoichiometry depending on the size of the anion. The coordination geometry also plays a part in the arrangements in the organic moiety. The physical properties can range from semiconductor to metallic depending on the electronic structures. The exchange interactions between the conduction electrons and the localised moments on the anions appears to be enhanced when chlorine is replaced by more polarisable bromine.

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