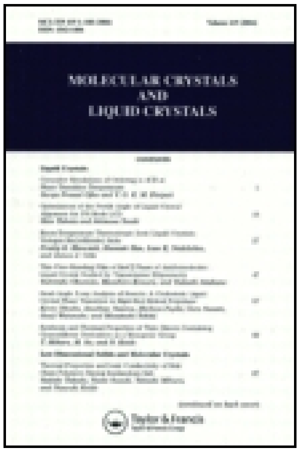

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HYBRID MOLECULAR MATERIALS FORMED BY MAGNETIC AND CONDUCTING NETWORKS BASED ON INORGANIC METAL COMPLEXES AND ORGANIC DONORS

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Abstract. The synthesis and physical characterization of new hybrid molecular materials formed by magnetic and organic networks are reported. The conducting molecular networks have been prepared from TTF and BEDT-TTF type donors. The inorganic magnetic component is formed by anion metal complexes of different nuclearities and dimensionalities (simple metal halides, polyoxometalate clusters and bimetallic oxalates).

INTRODUCTION

One of the goals in molecular magnetism is to create materials in which the magnetic molecules coexist and/or interact with a conducting network in the search for molecular materials combining properties not normally associated with a single material. To reach this goal we are following an organic-inorganic approach[1,2]. As organic component, we are using *TTF-type donor molecules* that constitute the basic ingredient of molecular conductors and superconductors (Figure 1). As inorganic component, we are using metal complexes of various nuclearities and dimensionalities. That includes *simple metal halides* ($FeCl_4^-$), large metal-oxide clusters (*polyoxometalates*) incorporating one or more magnetic centers in their structures, and *bimetallic oxalates* that can form extended ferromagnetic lattices in the solid state. We report here several examples of hybrid organic-inorganic materials of this kind.

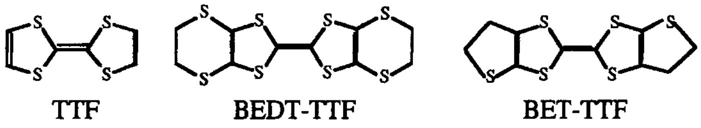

FIGURE 1. Organic donors used in this work

1. HYBRIDS BASED ON POLYOXOMETALATE CLUSTERS

These metal oxide clusters present several characteristics that make them suitable and attractive as inorganic components of hybrid molecular materials: (i) These anions have big sizes and a variety of shapes that can induce new organic packings in the radical salts. In fact, the crystal structures of these organic-inorganic hybrid materials are the result of the tendency of the planar organic molecules to stack and that of the inorganic clusters to adopt closed-packed lattices. Furthermore, the possibility of varying the anionic charge while maintaining the structure of the polyoxometalate may open up the way to modulate the electronic band filling in the resulting salt and, therefore, the physical properties. (ii) They maintain their identities in both aqueous and non aqueous solutions as well as in the solid state. (iii) They can act as ligands incorporating at specific sites of the polyoxoanion structure one or more magnetic transition metal ions.

Very recently we exploited these features to prepare an extensive series of radical salts with the general formula $(BEDT\text{-}TTF)_8[XW_{12}O_{40}]^3$. Keggin polyoxoanions having in the tetrahedral site either diamagnetic ($X = 2(H^+)$, Zn^{II}, B^{III}, Si^{IV}) or paramagnetic ions ($X = Fe^{III}$, Co^{II}, Cu^{II}) were used (Figure 2a). All these materials showed *semiconducting* behaviors with $\sigma_{RT} \approx 10^{-1}$-$10^{-2}$ S.cm^{-1} and $E_a \approx 100$-150 meV, and the magnetic properties indicated that the two magnetic sublattices were quasi-independent.

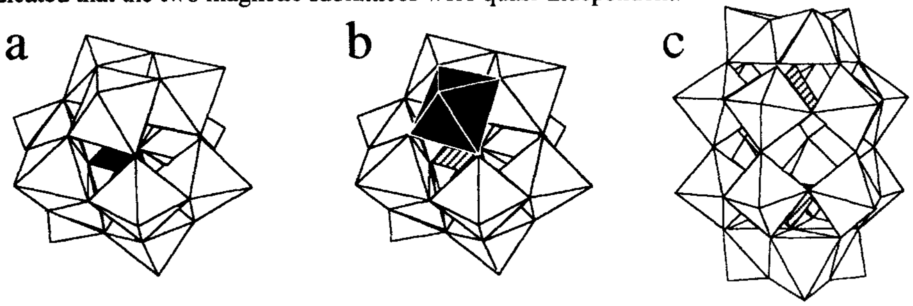

FIGURE 2. Keggin polyoxometalates with a magnetic metal (in black) in the center (**a**) or in the periphery (**b**); Dawson-Wells polyoxometalate (**c**)

With the aim of increasing the magnetic coupling between the two components we have used substituted Keggin anions having a magnetic ion in one of the peripherical octahedral sites (Figure 2b). This has resulted in the preparation of a new series of radical salts of formula $(BEDT\text{-}TTF)_8[XM(H_2O)W_{11}O_{39}]$ ($X = P$; $M = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}. ($X = Si$; $M = Fe^{III}$, Cr^{III}) which maintains the structure of the above family: layers of BEDT-TTF molecules with an α packing mode alternating with layers of the inorganic Keggin anions (Figure 3). The magnetic behavior of the Ni derivative is reported in Figure 4 and compared to that of the tetrabutylammonium salt. Upon cooling down, χT shows a gradual decrease that has to be attributed to a strong antiferromagnetic coupling between the spins of the organic chains, approaching at low temperatures to the behavior of isolated Ni^{II} in such a way that below 10 K the two magnetic curves are coincident. This result is general for all the members of the series and demonstrates that also here the two magnetic components behave independently.

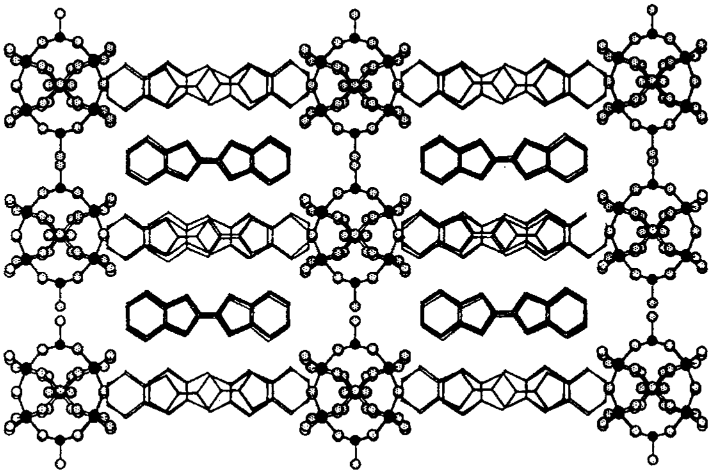

FIGURE 3. Structure of the radical salts $(BEDT\text{-}TTF)_8[XM(H_2O)W_{11}O_{39}]$ ($X = P$; $M = Co^{II}$, Ni^{II}, Cu^{II} and Zn^{II}. ($X = Si$; $M = Fe^{III}$ and Cr^{III}).

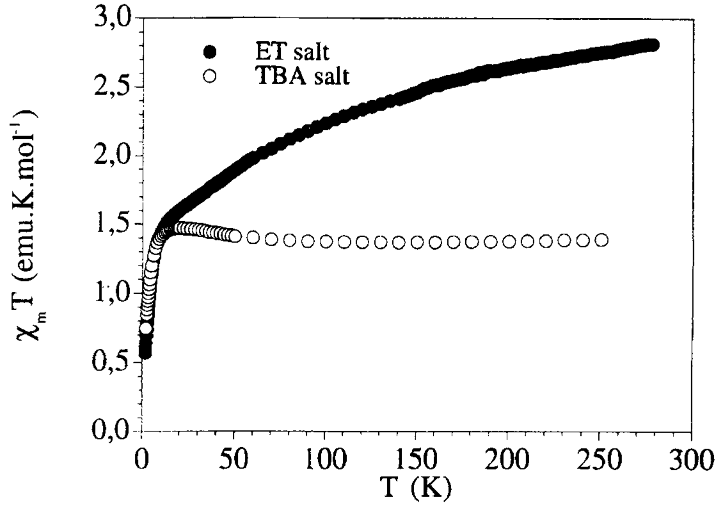

FIGURE 4. Plot of $\chi_m T$ versus T for the $(BEDT\text{-}TTF)_8[PNi(H_2O)W_{11}O_{39}]$ radical salt (filled circles) and for the TBA^+ Ni salt (open circles).

In the two above series the charges on the organic part are strongly localized and therefore, low electrical conductivities and semiconducting behaviors are always observed. This electron localization may be related with the large negative charges on the polyanion, but also with the type of packing (α-phases) adopted by the BEDT-TTF molecules. To change the organic packing we are using polyanions different in size and shape from the Keggin one, as for example the Dawson-Wells heteropolyanion $[P_2W_{18}O_{62}]^{6-}$ (Figure 2c). Crystals of a new radical salt have been then obtained that can be formulated as $\text{BEDT-TTF}_{11}[P_2W_{18}O_{62}].3H_2O$[4]. The structural arrangement of the organic layer is formed by parallel chains of BEDT-TTF molecules. The organic molecules of neighboring chains are also parallel, leading to the so-called β–phase (Figure 5). Another important feature of this structure is the presence of strong intermolecular contacts between the oxygen atoms of the inorganic cluster and the organic molecules via sulfur atoms and ethylene groups of the BEDT-TTF molecules that form hydrogen bonds.

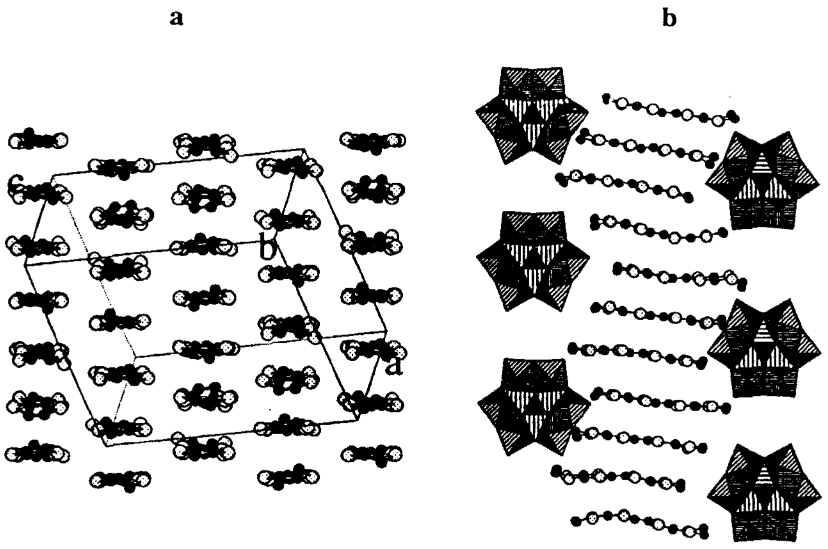

FIGURE 5. $(\text{BEDT-TTF})_{11}[P_2W_{18}O_{62}].3H_2O$: (**a**) Structure of the BEDT-TTF layer showing the β packing of the organic molecules and (**b**) Structure of the organic chains along the [401] direction.

The most attractive characteristic of this salt concerns its electrical conductivity which in the ac plane increases from ca. 5 $S.cm^{-1}$ at room temperature to 5.5 $S.cm^{-1}$ at T ≈ 230 K. Below this T the salt becomes semiconductor with a very low activation energy value of 0.013 eV. This is the first time that a *metallic-like behavior* has been observed in a heteropolyanion-containing radical salt and opens the way for the synthesis of metallic salts with magnetic character by simply replacing one or several W atoms of the Dawson-Wells anion by magnetic d-transition metal atoms. In view of the large electrical conductivity and the strong intermolecular anion-cation contacts, the magnetic salts so obtained may be good candidates to look for an indirect exchange coupling between the magnetic metal centers via the conducting electrons.

2. HYBRIDS BASED ON BIMETALLIC OXALATE-BRIDGED COMPLEXES

The two-dimensional bimetallic phases $A[M^{II}M'^{III}(ox)_3]$ obtained through the reaction of the chelate anions $[Cr^{III}(ox)_3]^{3-}$ or $[Fe^{III}(ox)_3]^{3-}$ with a divalent metal cation ($M^{II} = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}) have shown to behave as ferro or ferrimagnets[5] with critical temperatures ranging from 6 to 44 K. In these compounds, A is an organic cation of the type XR_4 (X = N, P; R = *n*-propyl, *n*-butyl, phenyl) located between the anionic layers that determines the creation of the 2D network and, at the same time, the interlayer separation. This 2D inorganic framework can provide a good support to create new hybrid materials simply by changing the innocent XR_4^+ cation by organic donors that can stabilize conductivity or even superconductivity in between the magnetic inorganic layers. In fact, the first magnetic superconductor that is formed by organic layers of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) molecules alternating with inorganic layers of paramagnetic tris-oxalato-iron(III) complexes and alkali metal ions has recently been discovered[6] In this context, we have synthesized and characterized the reaction products of TTF with $[Cr(ox)_3]^{-3}$ or $[Fe(ox)_3]^{-3}$ in presence of MCl_2 ($M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II} and Zn^{II}).

The two families of isostructural compounds so obtained can be formulated as $(TTF)_4\{M(H_2O)_2[M'(ox)_3]_2\}.nH_2O$ ($M = Mn^{II}$, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}; $M' = Cr^{III}$ and Fe^{III}; $n \approx 14$) . The structure has been solved in the Mn-Cr derivative[7] and consists of alternating layers of the trimeric cluster $\{M(H_2O)_2[M'(ox)_3]_2\}^{-4}$ and the organic donor TTF lying in the ab plane (Figure 6).

The centrosymmetrical linear trimers M'-M-M' are formed by two octahedral $M'(ox)_3$ entities connected through an M atom which is coordinated in a bidentate way by one oxalate group from each $M'(ox)_3$ entity and completes its octahedral coordination with two water molecules in the axial positions. The linear trimers are connected to the four closed neighbors in the layer by four hydrogen bonds involving the axial water molecules of M and one free oxygen atom on each terminal oxalate group (Figure 7).

The organic layers are formed by infinite chains of orthogonal face-to-face dimers of TTF molecules with short S···S distances (3.38 and 3.36 Å), along the a axis. The neighboring chains are displaced in one dimer in such a way that the closest dimers of neighboring chains are also orthonormal. This arrangement is reminiscent of a κ phase, but whereas in this phase inter and intrachain dimer-dimer distances are similar in both directions, in the title compound the intrachain dimer-dimer distances (3.54 and 3.56 Å) are much shorter than the interchain ones (6.60 and 6.61 Å). Thus, this structure can be seen as a pseudo-κ or a one dimensional-κ phase.

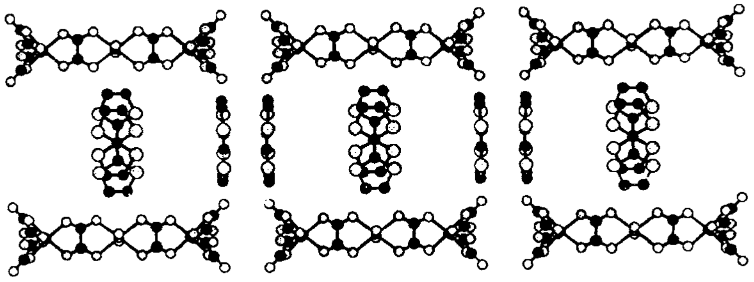

FIGURE 6. Crystal structure of the $(TTF)_4\{Mn(H_2O)_2[Cr(ox)_3]_2\}.14H_2O$ salt showing the alternating organic-inorganic planes.

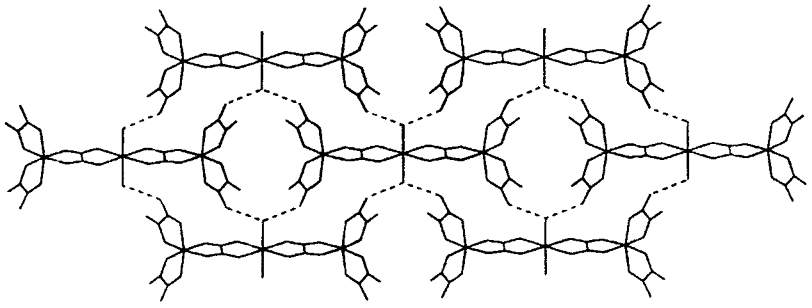

FIGURE 7. Packing of the $\{M(H_2O)_2[M'(ox)_3]_2\}$ trimers in the inorganic layer showing the H bonds between the trimers (dotted lines).

Unfortunately, no electron delocalization is expected to occur in the organic layer since, according with the stoichiometry of the compound, the four TTF molecules should be completely ionized (charge +1), with one unpaired electron on each molecule. Furthermore, the fact that these molecules are dimerized allows us to anticipate that the dimers have no net spin, and therefore all the magnetic contribution is expected to come from the inorganic lattice.

The magnetic measurements do confirm this prediction (Figure 8). Thus, all the compounds exhibit at room temperature the Curie constant expected for magnetically diluted M'-M-M' trimers. When T is lowered the two series (abbreviated as M-Cr and M-Fe) show different magnetic behaviors. Thus, in the chromium series the magnetic moment increases upon cooling, while in the iron series a continuous decrease is observed. This indicates that the exchange coupling M^{II}-Cr^{III} is ferromagnetic, while for the M^{II}-Fe^{III} series this interaction is antiferromagnetic. These data have been adequately fitted with the expressions derived from an exchange hamiltonian of the form $\mathbf{H}_{ex} = -2J(S_1S_2 + S_2S_3)$. where S_1 and S_3 are the spin operators associated to the M^{III} ions, and S_2 is that of the central divalent atom (solid lines in Fig.8). The resulting magnetic parameters are summarized in the table 1.

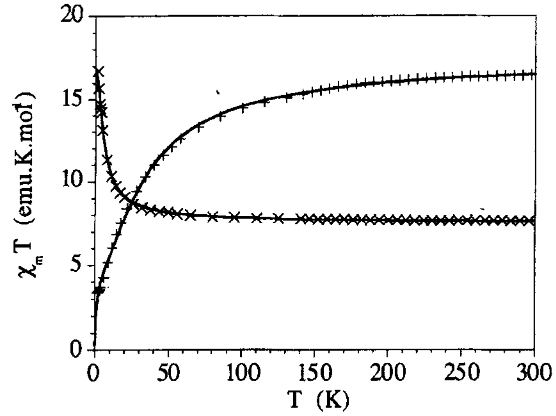

FIGURE 8. Plot of the $\chi_m T$ product versus T for the Mn-Cr (x) and Mn-Fe (+) compounds. Solid lines represent the fits to exchange-coupled trimers Cr^{III}-Mn^{II}-Cr^{III} ($S_{Cr} = 3/2$, $S_{Mn} = 5/2$; $J = 0.54$ cm^{-1}) and Fe^{III}-Mn^{II}-Fe^{III} ($S_{Fe} = S_{Mn} = 5/2$; $J = -1.38$ cm^{-1})

TABLE 1. Magnetic parameters obtained for the series of radical salts $(TTF)_4\{M(H_2O)_2[M'(ox)_3]_2\}.14H_2O$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}; M' = Cr^{III} and Fe^{III}). No fit for the Co^{II} derivatives has been performed, given the orbital degeneracy of this ion. S_T is the ground spin state of the trimeric cluster.

M'-M-M'	S_T	g	J (cm^{-1})
Cr-Mn-Cr	11/2	1.917(2)	0.54(1)
Cr-Fe-Cr	5	1.868(3)	0.48(1)
Cr-Co-Cr	"9/2"	-	-
Cr-Ni-Cr	4	1.837(1)	0.12(5)
Cr-Cu-Cr	5/2	1.885(3)	-0.49(1)
Fe-Mn-Fe	5/2	2.168(1)	-1.38(1)
Fe-Fe-Fe	3	2.217(2)	-2.35(4)
Fe-Co-Fe	"7/2"	-	-
Fe-Ni-Fe	4	1.83(1)	-4.9(6)

No evidence of cooperative magnetic properties has been detected down to 2 K in this family, in agreement with the discrete structure of the inorganic layer (formed by trimeric clusters). However, this family provides nice examples of high spin clusters comprising large numbers of parallel unpaired electrons in the ground states (up to 11). On the other hand, these are the first examples of hybrid materials formed by *bimetallic* oxalate complexes exhibiting magnetic interactions and organic TTF radicals. The change of TTF by other organic donors (as the BEDT-TTF) opens now the way to obtain materials with coexistence of magnetic interactions (or even ferromagnetic ordering) and conducting properties. Another possibility could be to use inorganic donors having a magnetic character as for example the decamethylferrocenium cation. In this context we have just obtained a new crystalline material of composition $[Cp^*{}_2Fe][Mn^{II}Cr^{III}(ox)_3]$. The a.c. magnetic susceptibility shows that this material undergoes a magnetic ordering at $T_c = 4.44$ K, and furthermore, the out-of-phase signal suggests that this ordering is ferromagnetic (Figure 9). The good new of this result is that hybrid materials containing the extended bimetallic lattice can be obtained. The bad new is that despite the magnetic character of the intercalated cation, T_c has decreased from 6 K to 4.44 K with respect to the tetrabutylammonium salt. This is probably due to the larger interlayer separation imposed by these bulk cations.

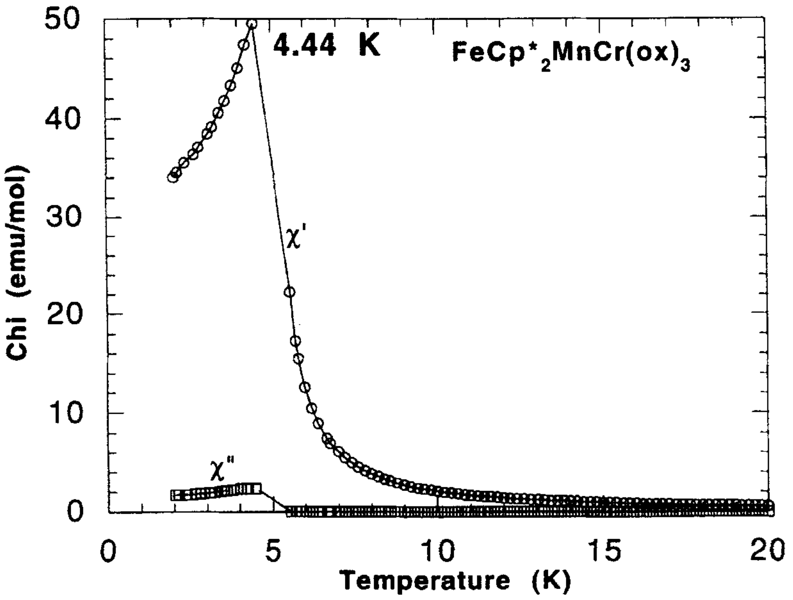

FIGURE 9. a.c.magnetic susceptibility for $[Cp^*{}_2Fe][Mn^{II}Cr^{III}(ox)_3]$.

HYBRIDS BASED ON THE $[FeCl_4]^-$ ANION

Incorporation of these magnetic anions into organic conductors has already been achieved in the recent past although only in a few cases this incorporation has been successful[8]. In view of the good conducting properties exhibited by the radical salts of the BET-TTF donor (Figure 1) with simple monoanions[9] as for example PF_6^-, SCN^- or I_3^-, we have prepared and characterized the radical salt BET-$TTF_2[FeCl_4]$.[10] We report here some preliminar data on this material. The structure consists of layers of the organic donor exhibiting a β-packing which are interleaved by the inorganic anions. These are well separated in the structure. The Fe-Fe distance is 6.2 Å. The electrical properties show a metallic behavior with a conductivity at room temperature of ca. 70 $S.cm^{-1}$. The magnetic properties of this radical salt are reported in figure 10 and compared to those found for the tetraethylammonium (TEA) iron salt. We observe that the two curves are coincident down to 40 K but below this T the magnetic data of the radical salt decrease more strongly than those of the TEA salt. This suggests the presence of antiferromagnetic pairwise Fe-Fe interactions. In fact the fitting of the data to a model that takes into account a value of the single-ion anisotropy parameter for Fe(III) of D = 4.3 K (calculated from the curve for the TEA salt) and an isotropic exchange interaction between the metals, gives an exchange parameter of J = -0.22 K (solid line in the figure). This value is an order of magnitude larger than the dipolar Fe-Fe interactions (of ca. 0.01 K). Therefore, it is reasonable to assume that this interaction, although very weak, can occur through an indirect exchange mechanism invoving the conduction electrons.

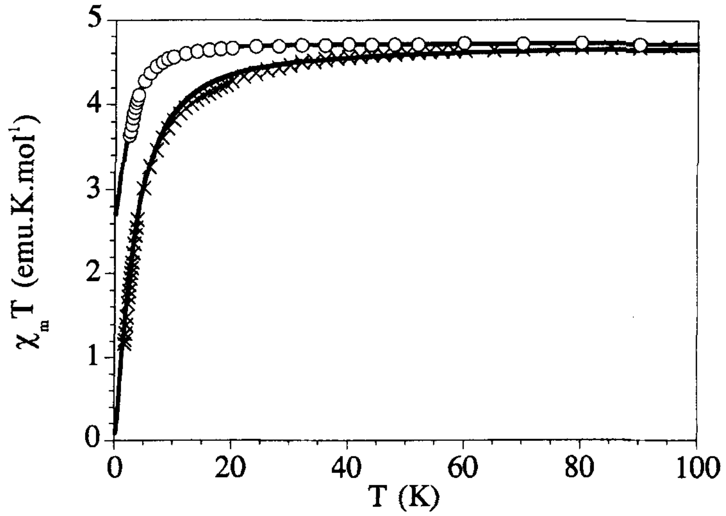

FIGURE 10. Plot of the $\chi_m T$ product versus T for the salt (BET-TTF)$_2[FeCl_4]$ (X) and TEA$[FeCl_4]$ (O). For the TEA salt the solid line represents the behavior of a spin S=5/2 with an axial ZFS (D/k = 4.3 K). For the radical salt the solid line corresponds to the best fit of the data to a model that assumes antiferromagnetically coupled Fe(III) dimers with a ZFS on the Fe(III) ions.

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