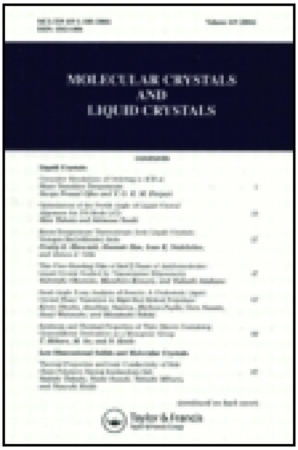

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# Hybrid Materials Formed by Two Molecular Networks. Towards Multiproperty Materials

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# Hybrid Materials Formed by Two Molecular Networks. Towards Multiproperty Materials

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The possibilities offered by hybrid materials formed by two molecular networks in the context of the molecular magnets are illustrated. Molecule-based layered magnets are used as anionic hosts for electroactive molecules, with the aim of obtaining multiproperty materials exhibiting in addition to the cooperative magnetism other interesting properties according to the nature of the inserted molecules. In particular, hybrid molecular compounds containing molecular species giving rise to paramagnetic, conducting, or bi-stable properties are reported.

*Keywords:* Molecular magnets; molecular conductors; bimetallic oxalate complexes; Hybrid materials

## INTRODUCTION

Molecule-based materials with active physical properties are a focus of contemporary materials chemistry research. A current development in this

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area is to design hybrid materials formed by two molecular networks such as anion/cation salts or host/guest solids, where each network furnishes distinct physical properties. Examples include hybrid materials formed by combination of magnetic and conducting molecular networks. The typical compound in this case is a cation radical salt formed by an organic π-electron donor of the tetrathiafulvalene (TTF) type and an inorganic metal complex anion that can act as magnetic component. Several organic/inorganic salts of this kind have been recently reported[1,2,3,4,5]. However, all are based on discrete metal complexes ranging from simple anions of the type $[FeCl_4]^-$, $[Fe(CN)_6]^{3-}$ or $[Fe(ox)_3]^{3-}$, to large metal-oxide clusters (polyoxometalates) incorporating one or more magnetic centers in their structures.[5b] As far as the properties are concerned, the lack of extended magnetic interactions in this kind of inorganic networks prevents the occurrence of collective magnetic properties, such as ferro- or ferrimagnetism. Hence, the only property of interest in these compounds is that arising from the organic component.

Metal complexes able to form infinite extended networks in the solid state are more suitable in this respect. Especially interesting in this context are the two-dimensional bimetallic phases $A[M^{II}M^{III}(ox)_3]$ ($M^{II}$ = Mn, Fe, Co, Ni, Cu; $M^{III}$ = Cr, Fe) which behave as magnets with ordering temperatures comprised between 5 and 44 K[6,7,8,9,10]. Their structure consists of extended magnetic layers of the oxalate-bridged bimetallic complexes $[M^{II}M^{III}(ox)_3]^-$ interleaved by layers of $A^+$, an electronically "innocent" organic cation of the type $[XR_4]^+$ (X = N, P; R = phenyl, n-propyl, n-butyl, etc.) (Figure 1).

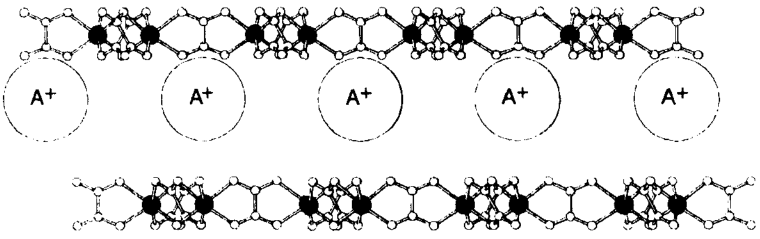
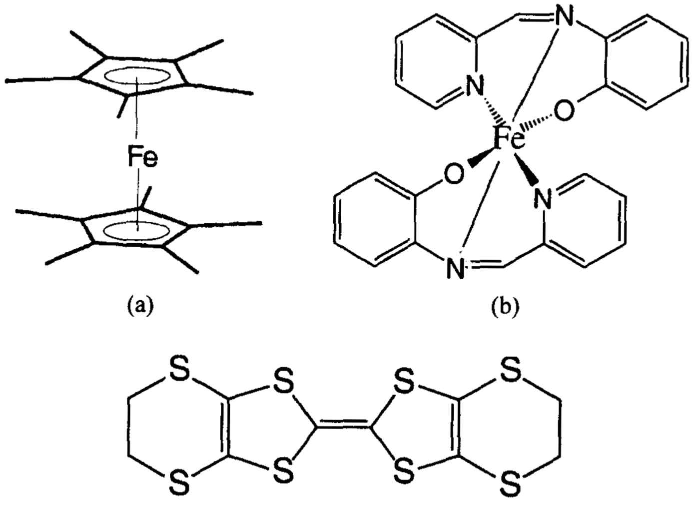


FIGURE 1 Layered structure for the series $A[M^{II}M^{III}(ox)_3]$·

Using these anionic networks as hosts for the insertion of "electroactive" molecular cations we can incorporate to the solid a new property in addition to the spontaneous magnetization. According to this approach here we report the main features of new magnets incorporating molecules with different properties (Figure 2), in particular: (i) the decamethylferrocenium paramagnetic cation $[FeCp^*{}_2]^+$; (ii) the bi-stable $Fe^{III}$ complex $[FeL_2]^+$, where $L = [O(C_6H_4)N{=}C(C_5NH_4)]^-$), as its perchlorate salt shows thermal spin transition [11]; and (iii) the BEDT-TTF (ET) organic radical which has given rise to the largest family of organic conductors and superconductors[12].



(a) (b)

(c)

FIGURE 2 View of the molecular structure of : a) $[FeCp^*{}_2]^+$; b) $[FeL_2]^+$; c) BEDT-TTF.

## INSERTION OF THE ORGANOMETALLIC CATIONS $[FeCp^*_2]^+$ AND $[CoCp^*_2]^+$ IN THE BIMETALLIC OXALATE-BRIDGED LAYERED MAGNETS

The synthesis and structure of this new series of molecular based magnets formed by ferromagnetic (or ferrimagnetic) anionic layers alternating with paramagnetic layers of $[FeCp^*_2]^+$ was previously communicated[13]. The structure exhibits the typical honeycomb lattice for the bimetallic oxalate complex; the interlayer separation is 9.213 Å, similar to that found in the $[XR_4]^+$ derivatives. A distinctive feature of the structure of this family with respect to the other structurally known 2D phases is that now the cation does not penetrate into the honeycomb net. A second difference deals with the stacking of the bimetallic layers. Thus, in contrast with the $[XR_4]^+$ derivatives, all the layers are of the same type so that the metals of one layer lie directly over those in the next layer (Figure 3). Such a difference may have influence in the cooperative magnetic properties of the hybrids.

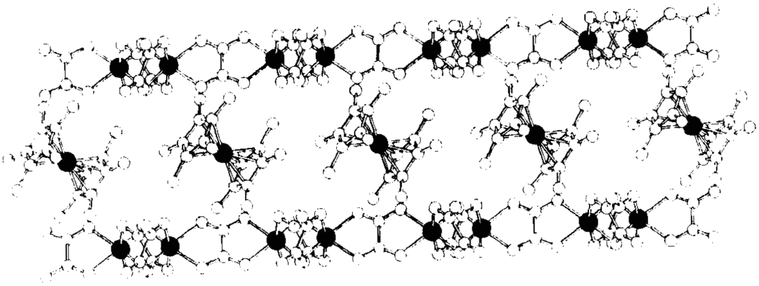


FIGURE 3 View of the structure of the compound $[FeCp^*_2][MnFe(ox)_3]$ showing the eclipsed stacking of the anionic bimetallic layers.

However, at first sight, the relevant magnetic parameters of these molecular magnets -critical temperatures and coercive fields of the hysteresis loops- are found to be roughly the same that those observed in the $[XR_4]^+$ derivatives (Table I). This result emphasizes that the long-range magnetic ordering is essentially 2D as it is controlled by the interactions within the bimetallic layers. It also indicates that the paramagnetic $[FeCp^*_2]^+$ sublattice essentially behaves independently from the magnetically ordered bimetallic sublattice, without a significant cation-layer electronic interaction, in agreement with the structural features. Still, the organometallic cation does have some influence on the coercive fields as it has been observed when the paramagnetic cation $[FeCp^*_2]^+$ is changed by the diamagnetic cation $[CoCp^*_2]^+$. For example in Cr-Fe derivative the coercive field increases from 320 Oe to 750 Oe, while in the Cu-Cr derivative it decreases from 40 Oe to 15 Oe (Table I).

TABLE I Critical temperatures ($T_c$) and coercive fields at 5 K ($H_{coer}$) for the series $[CoCp^*_2][M^{II}M^{III}(ox)_3]$ and $[FeCp^*_2][M^{II}M^{III}(ox)_3]$. Comparison with the $NBu_4^+$ salts[7,9b].

| | $[CoCp^*_2]^+$ | | $[FeCp^*_2]^+$ | | $[NBu_4]^+$ | |
|---|---|---|---|---|---|---|
| $M^{II}M^{III}$ | $T_c$ (K) | $H_{coer}$ (Oe) | $T_c$ (K) | $H_{coer}$ (Oe) | $T_c$ (K) | $H_{coer}$ (Oe) |
| MnCr | 5.1 | - | 5.3 | 10 | 6 | 20 |
| FeCr | 12.7 | 750 | 13.0 | 320 | 12 | 320 |
| CoCr | 8.2 | 50 | 9.0 | 50 | 10 | 80 |
| CuCr | 6.7 | 15 | 7.0 | 40 | 7 | 40 |
| MnFe | 25.4 | 200 | 28.4 | 850 | 28 | - |
| FeFe | 44.0 | 90 | 43.3 | 1235 | 45 | - |

A much more profound effect on the magnetic properties is expected to occur when using mixtures of $Cr^{III}$ and $Fe^{III}$ in the construction of the anionic network as in this case competitive ferromagnetic $M^{II}$-$Cr^{III}$ and antiferromagnetic $M^{II}$-$Fe^{III}$ interactions will coexist within the magnetic layer. Such a possibility was loosely investigated by Bhattacharjee and Ijima[14] who examined the D.C. magnetic susceptibility behavior of the compounds $[NBu_4][Mn^{II}Fe^{III}_{0.5}Cr^{III}_{0.5}(ox)_3]$ and $[NBu_4][Fe^{II}Fe^{III}_{0.5}Cr^{III}_{0.5}(ox)_3]$. We have undertaken a detailed magnetic study of the series of trimetallic compounds of general formula $A[M^{II}Fe^{III}_xCr^{III}_{(1-x)}(ox)_3]$ ($M^{II}$ = Mn, Fe, Co, Ni; $A^+$ = $[NBu_4]$, $[FeCp^*_2]$, $[CoCp^*_2]$). What is quite remarkable in this mixed metal series is the huge increase in the coercive fields. Thus, coercive fields at least one order of magnitude larger than those found for the pure $Cr^{III}$ and $Fe^{III}$ derivatives have been observed. In particular, the series $[NBu_4][Fe^{II}Fe^{III}_xCr^{III}_{(1-x)}(ox)_3]$ exhibits a coercive field as large as 11300-11700 Oe at 2 K for mixtures with x = 0.70 ± 0.05. Bearing in mind that substitution of $[NBu_4]^+$ by $[CoCp^*_2]^+$ resulted in an increase of the coercive field, we have prepared the corresponding $[CoCp^*_2]^+$ salts with the aim of increasing even more this coercive field. This has allowed us to reach a maximum coercive field of 16700 Oe at 2 K for a sample with x = 0.5 (Figure 4). These large $H_{coer}$ values are comparable to those observed in hard magnets[15]. Notice that this effect does not arise from the particle size as it remains in the same range for all the investigated compounds (around 0.5-0.2 μm).

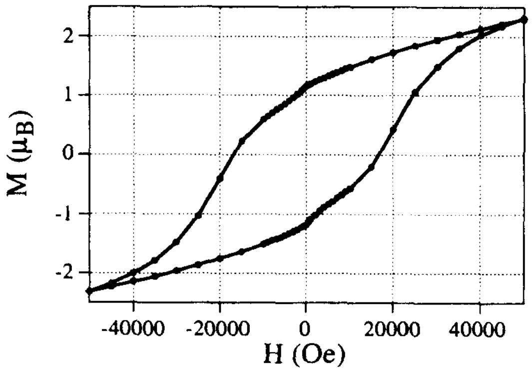


FIGURE 4 Hysteresis loop at 2 K for the compound $[CoCp^*_4][Fe^{II}Fe^{III}_xCr^{III}_{(1-x)}(ox)_3]$ (x = 0.5).

This increase in $H_{coer}$ is rather due to the presence of competing ferro and antiferromagnetic interactions within the layers as these will difficult the motion of domain walls. In fact, these compounds show features which may be associated to a spin glass behavior, as for example a small, but sizeable, frequency dependence of the A.C. susceptibility peak at low temperatures, and the lack of a Lambda peak in the specific heat data which indicates that the compound does not undergo a magnetic transition to an ordered state.

## INSERTION OF THE IRON (III) COMPLEX $[FeL_2]^+$ IN THE BIMETALLIC OXALATE-BRIDGED LAYERED MAGNETS

With the aim of incorporating to the cooperative magnetic properties a spin crossover transition we have used the complex $[FeL_2]^+$ ($L=[O(C_6H_4)N{=}CH(C_5NH_4)]^-$); Figure 2b) as this is monocationic and has a redox stability (the metal ion is Fe(III) instead of Fe(II), as in most of the known spin crossover systems). The perchlorate salt of this complex shows a thermal spin transition at temperatures comprised between 260 and 120 K with a hysteresis of ca. 20 K[11]. The hybrid $[FeL_2][MnCr(ox)_3]$ was prepared by addition of a toluene solution of $[Cr(ox)_3]^{3-}$ to an ethanol solution containing the $[FeL_2]^+$ complex and Mn(II). The X-ray powder pattern of this material can be indexed in the same hexagonal space group as the layered $[NBu_4]^+$ derivative. The unit cell parameters are reported in Table II. The larger volume of the $[FeL_2]^+$ cation has produced an increase in the interlayer spacing which increases from 8.91 Å (in $[NBu_4]^+$)[10] to 13.80 Å. The presence of extended bimetallic oxalate-bridged layers is also demonstrated by A.C. magnetic susceptibility measurements which exhibit a transition to a ferromagnetic state at $T_c = 5.5$ K (Figure 5).

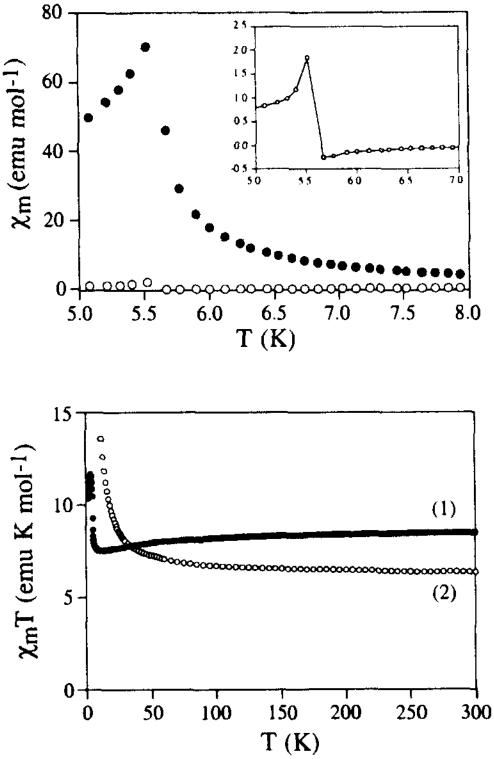


FIGURE 5 up) A.C. magnetic measurements for the salt $[FeL_2][MnCr(ox)_3]$, showing the in-phase (full circles) and out-of-phase (empty circles) signals; down) D.C. magnetic measurements for the compound $[FeL_2][MnCr(ox)_3]$(1) compared to those of $[CoCp^*_2][MnCr(ox)_3]$(2).

As far as the spin crossover is concerned the D.C. magnetic susceptibility measurements indicate that at high temperatures the compound is mainly in its high spin state (Figure 5). When the temperature is decreased the product

$\chi T$ slightly decreases from 8.5 emu.K.mol$^{-1}$ at 300 K to 7.5 emu.K.mol$^{-1}$ at 10 K, suggesting a partial smooth transition to a low spin state. In this sense preliminary Mössbauer measurements show that the intensity of the signal associated to the low spin state of Fe(III) increases upon cooling down at expenses of the high spin signal. On the other hand, a hyperfine magnetic splitting giving rise to a sextuplet is observed below $T_C$. This is a consequence of the internal magnetic field created by the ferromagnetic layers and demonstrates that the $[FeL_2]^+$ cations are inserted in between the layers.

TABLE II Hexagonal unit cell parameters and interlayer separation, d, for the compounds of general formula $A[M^{II}M^{III}(ox)_3]$.

| $M^{II}M^{III}$ | A | *a* (Å) | *c* (Å) | d (Å) |
|---|---|---|---|---|
| MnFe | $[NBu_4]^+$ | 9.482 | 17.827 | 8.91 |
| MnCr | $[FeL_2]^+$ | 9.27 | 27.60 | 13.8 |
| CuCr | $[BEDT\text{-}TTF]_2^+$ | 9.46 | 19.80 | 9.9 |

## INSERTION OF ORGANIC DONORS IN THE BIMETALLIC OXALATE-BRIDGED LAYERED MAGNETS

Much effort has been devoted to this kind of hybrid systems as they are good candidates to show coexistence of cooperative magnetism and electrical conductivity or even superconductivity. In fact, it has been shown that the layered material $[BEDT\text{-}TTF]_4[(H_2O)Fe(ox)_3]$ is a molecular superconductor containing paramagnetic $[Fe(ox)_3]^{3-}$ anions[16]. However, the lack of an extended bimetallic layer in this compound has prevented the occurrence of a magnetic ordering.

A first attempt to combine the bimetallic oxalate-bridged layer with the chemically oxidized organic donor $TTF^+$ resulted in the breaking of the polymer complex into trimeric bimetallic units.[17] Therefore, no long magnetic ordering was observed in this series. As a second attempt we have used the BEDT-TTF donor (Figure 2c). The main chemical challenge was that of making soluble the inorganic precursors while electrochemically oxidizing the donor in an organic solvent. The high insolubility of the final compound made impossible any attempt to grow single crystals but a polycrystalline sample of the salt $[\mathrm{BEDT\text{-}TTF}]_2[\mathrm{CuCr(ox)_3}]$ was collected on a platinum electrode upon electrochemical oxidation of BEDT-TTF in the presence of a dichloromethane / toluene / ethanol solution of $\mathrm{Cu}^{2+}$ and $[\mathrm{Cr(ox)_3}]^{3-}$. X-ray analysis confirms the presence of the extended bimetallic layer. In fact, as in the previous hybrid, the compound crystallizes in a hexagonal space group with an interlayer spacing of 9.90 Å (Table II).

The magnetic properties of this compound show a peak at 2.8 K for both the in-phase and the out-of-phase A.C. susceptibilities (Figure 6). On the other hand, the compound exhibits a magnetic hysteresis below this temperature (Inset of Figure 6).

These magnetic properties strongly differ from those observed when in the Cu-Cr layer the inserted cations are $[\mathrm{XR_4}]^+$ or the metallocenes. Thus, the peak associated to the magnetic transition is shifted from 7 K to 2.8 K, and the magnetization at 2 K diminishes from 2 BM to 0.1 BM and does not saturate at values of the magnetic field as high as 1000 Oe. These significant differences emphasize the strong influence of the inserted BEDT-TTF donors on the magnetic properties.

As far as the electrical properties are concerned, preliminary measurements on a pressed pellet have indicated a semiconducting behavior with a room temperature temperature conductivity of $3.10^{-3}$ $\mathrm{S.cm^{-1}}$ and an activation energy of 12.8 meV. The above results indicate that this organic/inorganic compound shows the coexistence of cooperative magnetism, with a spontaneous magnetization below 2.8 K, and electron delocalization within the organic layer. It represents the first material of this kind.

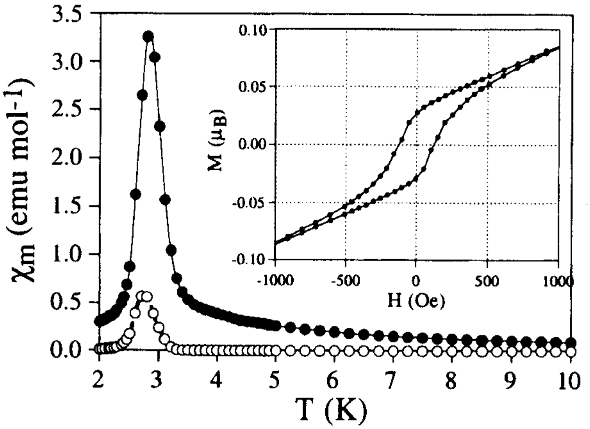


FIGURE 6 A.C. susceptibility showing the in-phase (full circles) and out-of-phase (empty circles) signals, and hysteresis loop at 2 K (inset) for the salt $[\mathrm{BEDT\text{-}TTF}]_2[\mathrm{CuCr(ox)_3}]$.

## CONCLUSION

We have shown in this paper that the bimetallic oxalate-bridged layered complexes can be used as anionic hosts for inserting electroactive molecules, with the aim of obtaining multiproperty materials exhibiting in addition to the cooperative magnetism other interesting properties such as paramagnetism, spin-crossover, or electronic conductivity. This illustrates how the hybrid approach, based on the association of two molecular networks, can be a useful approach to create materials with coexistence of properties. Here we have restricted the discussion to the combination of magnetism with a second electronic property. However other interesting possibilities can be imagined such as the combination of electrical with optical properties. In this case we should mention for example the association of organic donors furnishing electrical conductivity with bi-stable photochromic complexes, as the nitroprusside anion, which can undergo excitation to a long lived excited state upon irradiation[18]. Another possibility worth to mention is that offered by the Langmuir Blodgett technique. So far LB films showing electrical[19], optical[20] or magnetic[21] properties have been obtained. In the near future the design of LB films containing different kinds of electroactive monolayers may be a useful approach to afford novel multilayered molecular films exhibiting different associations of properties.

## Acknowledgments

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