

Intercalation of decamethylferrocenium cations in bimetallic oxalate-bridged two-dimensional magnets

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The structure and magnetic properties of novel hybrid molecule-based magnets formed by combination of two magnetically active sublattices, the bimetallic oxalato-bridged honeycomb net $[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]$ ($\text{M}^{\text{II}} = \text{Mn, Fe, Co, Cr, Ni, Cu}$; $\text{M}^{\text{III}} = \text{Cr, Fe}$) and the organometallic cation decamethylferrocenium, are reported.

Much interest has been shown in oxalate complexes in the search for new molecule-based magnets since the discovery at the beginning of the nineties of new polymeric bimetallic phases of variable dimensionality.¹ Especially interesting are the two-dimensional bimetallic phases $\text{A}[\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]$ ($\text{M}^{\text{II}} = \text{Mn, Fe, Co, Cr, Ni, Cu}$; $\text{M}^{\text{III}} = \text{Cr, Fe}$) because they behave as ferro-,² ferri-³ or canted antiferro-magnets⁴ with critical temperatures ranging from 5 up to 44 K. Their structure⁵ consists of extended oxalate-bridged layers of the two metal atoms separated by A^+ , an electronically 'innocent' counter ion of the type $[\text{XR}_4]^+$ ($\text{X} = \text{N, P}$; $\text{R} = \text{Ph, Pr}^n, \text{Bu}^n$), which may act as a template controlling the formation of the net structure and thus determining the interlayer separation.^{4b} The change of this cation to an electroactive one could create new hybrid molecular materials with interesting properties or combinations of properties, depending on the nature of the cation and the possible interactions with the magnetic network. Very recently we reported an example of such hybrid materials: the $[\text{TTF}]_4\{\text{M}^{\text{II}}(\text{H}_2\text{O})_2[\text{M}^{\text{III}}(\text{ox})_3]_2\} \cdot n\text{H}_2\text{O}$ family,⁶ in which the cation is the organic π -donor molecule tetrathiafulvalene (TTF), although instead of the extended two-dimensional network, a molecular layer of oxalato-bridged bimetallic trimeric clusters is formed.

Here we show that it is possible to combine the layered bimetallic oxalate complexes with the magnetically interesting organometallic cation $[\text{Fe}(\text{Cp}^*)_2]^+$ (Cp^* = decamethylferrocenium), which has spin $S = 1/2$. It is to be noticed that other salts formed by decamethylmetallocenium cations and two-dimensional molecule-based magnets have been very recently reported, but the structure of these materials is unknown.⁷

The new family of organometallic-inorganic magnetic compounds has the formula $[\text{Fe}(\text{Cp}^*)_2][\text{M}^{\text{II}}\text{M}^{\text{III}}(\text{ox})_3]$ ($\text{M}^{\text{II}} = \text{Mn, Fe, Co, Ni, Cu, Zn}$; $\text{M}^{\text{III}} = \text{Cr, Fe}$). They were obtained by the one-pot reaction of the tris(oxalato) complex $[\text{M}^{\text{III}}(\text{ox})_3]^{3-}$ with the divalent metal ion M^{II} and $[\text{Fe}(\text{Cp}^*)_2]^+$ cations in water. Crystals of good quality were obtained by diffusion, and the crystal structure was solved for the $\text{Fe}^{\text{III}}\text{Mn}^{\text{II}}$ derivative. The structure[†] consists of anionic layers of the well known honeycomb bimetallic oxalate-bridged network with decamethylferrocenium cations intercalated in between [Fig. 1(a)]. The bimetallic layers are eclipsed by each other creating hexagonal channels running along the c axis. The organometallic cations exhibit a staggered configuration (symmetry D_{5d}). They are ordered within the interlayer space. In fact, they are located at the center of the hexagonal channels forming a pseudo-hexagonal arrangement. These cations are tilted with respect to the layer by an angle of 32.6° (angle defined by the fivefold symmetry axis of the cation with the normal to the bimetallic plane) in such a way that the two pentamethylcyclopentadienyl molecules of each $[\text{Fe}(\text{Cp}^*)_2]^+$ cation are pointing towards the center of the hexagons of two adjacent

layers [Fig. 1(b)]. The interlayer separation is 9.213 Å, similar to that found in previous compounds of two-dimensional phases,^{5,4b} and there is no evidence of hydrogen-bond interactions between the cations and the layers (the minimum $\text{H}\cdots\text{O}$ distance is 2.584 Å). A distinctive feature of this structure with respect to the other structurally known two-dimensional phases is that now the cation does not penetrate into the honeycomb net (the minimum distance of the cation to this plane is 0.88 Å; distance from the mean plane defined by the metals to the closest hydrogen from a methyl group). A second difference deals with the stacking of the bimetallic layers. Thus, in contrast with the $[\text{XR}_4]^+$ derivatives, all the layers are of the same type so that the metals of one layer lie directly over those in the next layer.[‡]

All these compounds are magnets exhibiting spontaneous magnetization below T_c and hysteresis loops. As in the $[\text{XR}_4]^+$ derivatives, the compounds of the $\text{Cr}^{\text{III}}\text{M}^{\text{II}}$ series behave as ferromagnets[§] which have ferromagnetic interactions between Cr^{III} and M^{II} ions through the oxalate group, while in the $\text{Fe}^{\text{III}}\text{M}^{\text{II}}$ series this coupling is antiferromagnetic giving rise to ferrimagnets (for $\text{M}^{\text{II}} = \text{Fe, Co}$) or canted antiferromagnets (for $\text{M}^{\text{II}} = \text{Mn}$). We have performed ac susceptibility measure-

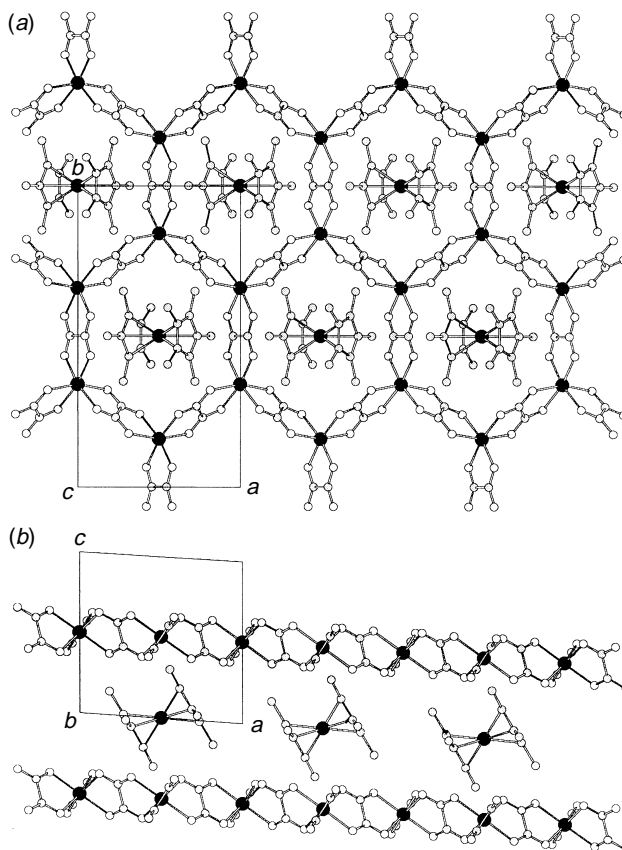


Fig. 1 View of the structure in the ab plane showing the honeycomb magnetic layers (a) and in the ac plane (b)

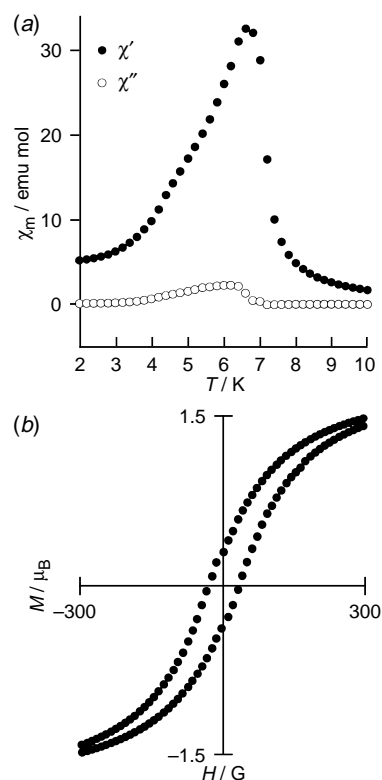


Fig. 2 Magnetic properties of the $\text{Cr}^{\text{III}}\text{Cu}^{\text{II}}$ derivative: (a) ac susceptibility vs. temperature showing the out-of-phase signal (χ''); (b) hysteresis loop at 5 K

ments in order to obtain accurate values of T_c . These data show a sharp peak in both the in-phase and the out-of-phase susceptibility signals at t_c (Fig. 2). The relevant magnetic parameters (critical temperatures and coercive fields for the Cr–M ferromagnets and critical temperatures for the Fe–M ferrimagnets) are summarized in Table 1 and compared to those reported for the $[\text{XR}_4]^+$ derivatives. As we can see, the $[\text{Fe}(\text{Cp}^*)_2]^+$ salt of the $\text{Fe}^{\text{III}}\text{Co}^{\text{II}}$ derivative has no precedent among the $[\text{XR}_4]^+$ salts. This material undergoes ferrimagnetic ordering at $T_c = 19.5$ K. As far as the magnetic ordering is concerned what becomes apparent from the above magnetic results is that the paramagnetic $[\text{Fe}(\text{Cp}^*)_2]^+$ cations are not

Table 1 The series of compounds $[\text{Fe}(\text{Cp}^*)_2][\text{M}^{\text{III}}\text{M}^{\text{II}}(\text{ox})_3]$. Critical temperatures and coercive fields (at 5 K) for $\text{Cr}^{\text{III}}\text{M}^{\text{II}}$ and critical temperatures for $\text{Fe}^{\text{III}}\text{M}^{\text{II}}$. Comparison with the $[\text{XR}_4]^{4+}$ salts

$\text{M}^{\text{III}}\text{M}^{\text{II}}$	T_c / K		$H_{\text{coerc}} / \text{G}$	
	$[\text{Fe}(\text{Cp}^*)_2]^+$	$[\text{XR}_4]^+$	$[\text{Fe}(\text{Cp}^*)_2]^+$	$[\text{XR}_4]^+$
CrMn	5.3	6	10	20
CrFe	13.0	12	320	320
CrCo	9.0	10	50	80
CrNi	14.5	14	250	160
CrCu	7.0	7	30	30
FeMn	28.4	25–29		
FeFe	43.3	33–48		
FeCo	19.5	—		

directly involved in the long-range magnetic ordering, which is essentially controlled by the bimetallic layers. Thus, T_c values are found to be roughly the same as those observed in the $[\text{XR}_4]^+$ derivatives. On the other hand, the coercive fields are also very similar. These results indicate that the two magnetic sublattices essentially behave independently, without a significant cation–layer electronic interaction, in agreement with the structural features. Unusual magnetic effects may arise from the coexistence of these two magnetic sublattices. For example, in the ordered state the magnetic layers are expected to polarize the spins of the metalocene layer and therefore a Zeeman splitting of the $S = 1/2$ spins of the paramagnetic cations may be observed. Complete physical characterization of these and other molecular magnetic multilayers that can be obtained using the same methodology is now in progress.

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Footnotes and References

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† X-Ray crystal structure analyses: Enraf-Nonius CAD4 diffractometer, Mo-K α radiation, $\lambda = 0.71069$ Å, graphite monochromator, 295 K. Lorentz polarization and absorption corrections (ψ scan). Data collection, solution and refinement: ω - 2θ , direct methods using the SIR92 program, followed by Fourier synthesis, SHELXL-93 computer program. $[\text{Fe}(\text{C}_{10}\text{H}_{15})_2][\text{Mn}-\text{Fe}(\text{C}_2\text{O}_4)_3]$ ($\text{C}_{26}\text{H}_{30}\text{O}_{12}\text{Fe}_2\text{Mn}$), monoclinic, space group $C2/m$, $a = 9.0645(8)$, $b = 17.143(3)$, $c = 9.215(4)$ Å, $\beta = 93.66(2)^\circ$, $U = 1429(1)$ Å³, $Z = 2$, $D_c = 1.630$ g cm⁻³, crystal size $0.2 \times 0.05 \times 0.05$ mm. 1909 reflections measured in the range $4 < 2\theta < 64$, 1871 unique and 1434 assumed as observed with $I \geq 6\sigma(I)$. $R = 0.0348$ and wR_2 0.0937. CCDC 182/551.

‡ In the $[\text{XR}_4]^+$ derivatives a graphite-like stacking of the bimetallic layers has been found with a stacking order . . . ABAB . . . (for NBu_4), or . . . ABCABC . . . (for PPh_4^+).

§ The ferromagnetic ordering in the $\text{Cr}^{\text{III}}\text{M}^{\text{II}}$ series is in agreement with the saturation magnetization values which roughly correspond to the total number of unpaired electrons per formula unit.

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