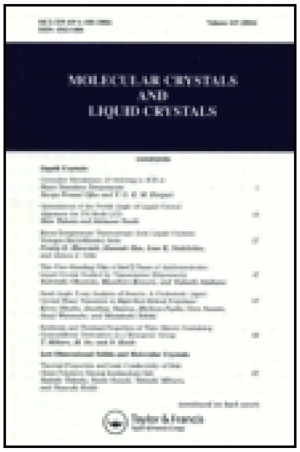

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Ferromagnetism in Charge Transfer Salts Based on Metallocenes and Nickel Bis-Dithiolenes

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To cite this article: Vasco Da Gama, Dulce Belo, Isabel C. Santos & Rui T. Henriques (1997): Ferromagnetism in Charge Transfer Salts Based on Metallocenes and Nickel Bis-Dithiolenes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 306:1, 17-24

To link to this article: http://dx.doi.org/10.1080/10587259708044544

Mol. Cryst. Liq. Cryst., 1997, Vol. 306, pp. 17–24
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FERROMAGNETISM IN CHARGE TRANSFER SALTS BASED ON METALLOCENES AND NICKEL BIS-DITHIOLENES

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Abstract The synthesis and preliminary structural and magnetic studies of several compounds based on $[M(Cp^*)_2]$, with M = Fe; Mn; Cr, and on $[Ni(L)_2]$, where L is a 1,2-dithiolate, as bdt = benzenedithiolate, edt = ethylenedithiolate and tcdt = tetrachlorobenzenedithiolate, are reported. In the charge transfer salts, $[M(Cp^*)_2][Ni(L)_2]$, both 1D and layered structures are observed. From the magnetic behavior of the several charge transfer salts apparently ferro and antiferromagnetic interactions are competing in most compounds. Generally AFM interactions dominate at high temperatures, but in several cases FM interactions become dominant at low temperatures. However magnetic ordering was only clearly observed for $[Fe(Cp^*)_2][Ni(edt)_2]$ and $[Mn(Cp^*)_2][Ni(bdt)_2]$, both presenting metamagnetic transitions with $T_N = 3.2$ K and $H_C \approx 4$ kG, at 2 K, for the first and with $T_N = 2.3$ K and $H_C \approx 200$ G, at 2 K, for the second.

INTRODUCTION

After bulk ferromagnetism was reported for $[Fe(Cp^*)_2](TCNE)$[1], substantial efforts were devoted to this type of materials, namely seeking to obtain ferromagnetically ordered charge transfer salts (CTS)[2]. With this purpose several CTS using metal dichalcogenide as acceptors were prepared[2, 3]. In spite ferromagnetic interactions were observed to be dominant in several cases, no evidence for bulk ferromagnetism was obtained and only the compounds $[Mn(Cp^*)_2][M(tfd)_2]$ (M = Ni, Pd, Pt) were found to exhibit a metamagnetic behavior[3c].

Besides ferromagnetism, an interesting aspect, usually neglected, regarding these metallocene based CTS is related with the possibility of achieving ferrimagnetism, which is possible both through Δg ($|g_D - g_A|$) or ΔS ($S_D - S_A$). In the search for ferro or ferrimagnetic ordered molecular CTS several of these compounds were prepared and we report here the synthesis and magnetic properties of $[M(Cp^*)_2][Ni(bdt)_2]$, with M = Fe, Mn, Cr, $[M(Cp^*)_2][Ni(edt)_2]\cdot x(MeCN)$, with M = Fe (x=0), Cr (x=1) and $[M(Cp^*)_2][Ni(tcdt)_2]$, with M = Fe, Mn, Cr.

EXPERIMENTAL

Synthesis

All the $[M(Cp^*)_2][Ni(L)_2]\cdot xMeCN$ compounds were prepared by the same procedure: saturated equimolar solutions of $[Fe(Cp^*)_2]BF_4$[4]; $[Mn(Cp^*)_2]PF_6$[5]; $[Cr(Cp^*)_2]PF_6$[6] and TBA$[Ni(bdt)_2]$[7]; TBA$[Ni(edt)_2]$[8]; TBA$[Ni(tcdt)_2]$[7] in acetonitrile were combined and the resulting compounds precipitated on standing. Dark brownish green plate shaped crystals were collected by filtration in the case of the bdt derivatives (M1), the edt compounds (M2) were obtained as brown needle shaped crystals, while in the case of the tcdt derivatives (M3) light green powders were obtained. The elemental analysis results from the collected products are shown in Table I.

TABLE I Analytical data (calculated values for given formulation).

Compound	Abrev.	% C	% H	% N
$[Fe(Cp^*)_2][Ni(bdt)_2]$	Fe1	57.36(57.76)	5.84(5.76)	0.00(0.00)
$[Fe(Cp^*)_2][Ni(edt)_2]$	Fe2	50.57(50.99)	6.26(6.06)	0.26(0.00)
$[Fe(Cp^*)_2][Ni(tcdt)_2]$	Fe3	41.48(40.85)	2.79(3.21)	0.34(0.00)
$[Mn(Cp^*)_2][Ni(bdt)_2]$	Mn1	58.11(57.84)	5.18(5.76)	0.00(0.00)
$[Mn(Cp^*)_2][Ni(tcdt)_2]$	Mn3	41.00(40.88)	3.11(3.22)	0.00(0.00)
$[Cr(Cp^*)_2][Ni(bdt)_2]$	Cr1	57.72(58.10)	5.67(5.79)	1.51(0.00)
$[Cr(Cp^*)_2][Ni(edt)_2]\cdot 2MeCN$	Cr2	52.31(52.09)	6.10(6.25)	4.35(4.34)
$[Cr(Cp^*)_2][Ni(tcdt)_2]$	Cr3	41.24(41.01)	3.17(3.23)	0.12(0.00)

Crystallization by slow evaporation from saturated acetonitrile solutions afforded crystals suitable for X-ray analysis, except in the case of the M3 compounds, which were insoluble, and in the case of Mn1, where decomposition took place. Structural characterization of these compounds is still in progress. For $[Fe(Cp^*)_2][Ni(bdt)_2]$[9] (Fe1) and $[Cr(Cp^*)_2][Ni(bdt)_2]$[9] (Cr1) the crystal structure consists of donor (D) - acceptor (A) mixed layers, composed of ···DDADDA··· stacks, separated by acceptor layers, neutralizing the charge. Apart some minor differences, this structure resembles those reported for $[Fe(Cp^*)_2][Ni(bds)_2]MeCN$[3b] and $[Fe(Cp^*)_2][Ni(dmio)_2]MeCN$[3d]. In the case of $[Fe(Cp^*)_2][Ni(edt)_2]$[9] (Fe2) the structure consists of a parallel ···DADADA··· stack arrangement, similar to those reported for $[M(Cp^*)_2][Ni(tfd)_2]$, M = Fe[3a]; Mn[3c].

Magnetization Measurements

Magnetization data of the decamethylferrocene compounds, were obtained with a Faraday system, between 1.8 and 300 K, with polycrystalline samples, using a Teflon sample holder. In the case of the Mn and Cr compounds, magnetization was measured with a SQUID magnetometer, between 2 and 300 K, with polycrystalline samples, using a quartz sample holder. Magnetization data were corrected for contributions due to sample holder and core diamagnetism, estimated from tabulated Pascal constants.

RESULTS AND DISCUSSION

The magnetic susceptibility for most of $[M(Cp^*)_2][Ni(L)_2]$ compounds, follow the Curie-Weiss expression, $\chi = C/(T-\theta)$, at high temperatures (from ca. 50 to 300 K), except for $[Mn(Cp^*)_2][Ni(bdt)_2]$. The room temperature effective magnetic moments, for most of the compounds, have a good agreement with the predicted values. Table II shows the values of the field used in the experiments (ZFC), the experimental values of θ and of room temperature effective magnetic moment, μ_{eff}^{RT}, and the manetic moment predicted values for a random orientation of the crystals, $\langle\mu_{eff}^{calc}\rangle$, considering the $\langle g\rangle$ values of the metallocenes (2.8 for Fe[3a], 2.2 for Mn[10], and 2 for the Cr[6]) and 2.06 for the Ni complexes[11], and for a fully oriented sample, $\mu_{eff}^{calc}{}_{\parallel}$, considering the $g_{\parallel}$ of the Fe and Mn metallocenes, 4.4[3a] and 3.33[10] respectively.

TABLE II θ and μ_{eff} experimental values and μ_{eff} predicted values.

Compound	H (kG)	θ (K)	μ_{eff}^{RT} (μ_B)	$\langle\mu_{eff}^{calc}\rangle$ (μ_B)	$\mu_{eff}^{calc}{}_{\parallel}$ (μ_B)
Fe1	5	-2.4	3.35	3.02	4.21
Fe2	10	-9.8	3.15	3.02	4.21
Fe3	5	-22.9	2.83	3.02	4.21
Mn1	0.5	-----	8.52	3.6	5.04
Mn3	1	-28.5	4.19	3.6	5.04
Cr1	0.5	-7.8	4.51	4.27	4.27
Cr2	0.5	-5.3	4.31	4.27	4.27
Cr3	1	-20.4	4.71	4.27	4.27

Except for Mn1, the observed deviations from the values of μ_{eff}^{RT}, relatively to $\langle\mu_{eff}^{calc}\rangle$, can be attributed to a partial orientation of the crystals due to the magnetic field, in the case of the Fe and Mn compounds (g strongly anisotropic), or to errors in the sample weight determination, mainly in the case of the Mn or Cr compounds, due to the fact that the sample handling had to be done inside a glove box.

As shown in Table II, for Mn1, μ_{eff}^{RT} exceeds largely the calculated values. Similar anomalous values, higher than the predicted for fully aligned spins, were also observed for $[Mn(Cp^*)_2][DDQ]$[10]. Furthermore, as shown in Figure 1, μ_{eff} decreases significantly on cooling, reaching a minimum of 4.2 μ_B, at ca. 25 K. Three possible (simple) explanations for this unusual behavior, which was observed to be reproducible, are: i)- an unusually high, temperature dependent, orbital contribution to the g factor of $[Mn(Cp^*)_2]^+$; ii)- a charge transfer towards a neutral $[Mn^{II}][Ni^{IV}]$ form, involving a high spin (S =5/2) $Mn(Cp^*)_2$, together with a spin transition to a ground state with S = 1/2, in a similar way to what is known to occur for $Mn(MeCp)_2$[12]; iii)- the existence of a "neutral - ionic" equilibrium, that would be displaced towards the neutral form, at high temperatures, and to the ionic form, at low temperatures. The third hypothesis seems more appropriate since the situation i) would imply a rather exaggerated value, ca. 5, for $g_{||}$ and in situation ii) the existence of S = 0, neutral metal dithiolate is not consistent with the magnetic phase transitions, at low temperatures, which would require considerable magnetic interactions between the spins.

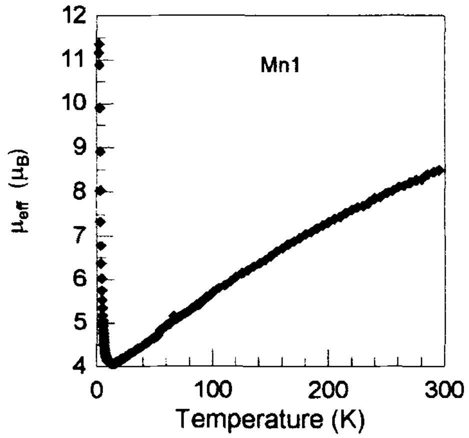

FIGURE 1 μ_{eff} temperature dependence for Mn1.

The observed negative values of θ, clearly show that antiferromagnetism dominates at high temperatures. However, at low temperatures, deviations from the high temperature Curie-Weiss behavior are detected for several compounds and in some cases a crossover to a behavior typical of dominant ferromagnetic interactions is observed. The low temperature magnetic behavior of the $[M(Cp^*)_2][Ni(L)_2]$ compounds is shown in Figures 2 (Fe#), 3 (Mn#), and 4 (Cr#), where both χ^{-1} (a) and χT (b) are represented.

At low temperatures, Fe1 has predominant ferromagnetic interactions, χT rises on cooling and shows a maximum at ca. 4 K (Figure 2b). As it can be seen in Figure 2a, in the case of Fe2 it is possible to detect a minimum in χ^{-1} at 4 K, which is typical of an AFM transition. For Fe3, in spite its general behavior indicates a predominance of AFM interactions, at low temperatures this dominance seems to decrease, as suggested by the deviations below 60 K, from the high temperature Curie-Weiss behavior, represented by the straight line in Figure 2a.

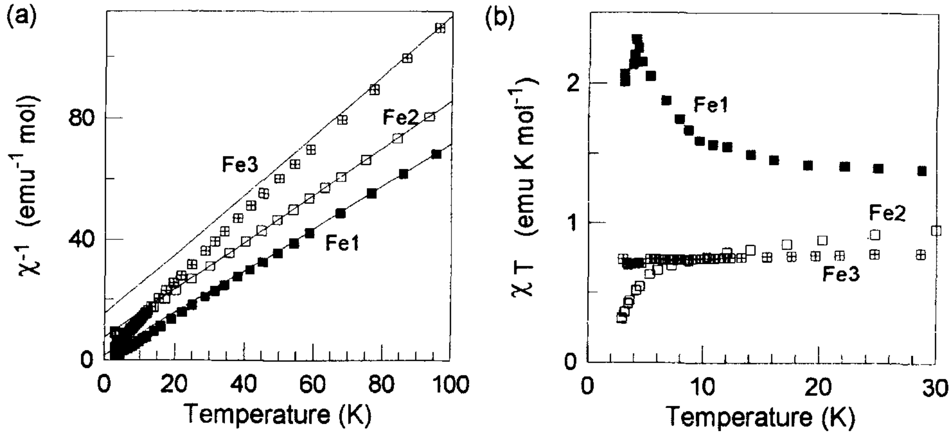

FIGURE 2 (a) χ^{-1} and (b) χT temperature dependences of the Fe# compounds.

In Figure 3b it is possible to see an abrupt increase of χT for Mn1, at ca. 5 K, indicating that FM interactions become dominant. The behavior of Mn3 is similar to the observed for Fe3, and the AFM character of the interactions seems also to decrease at low temperatures, as suggested from the deviations from the high temperature Curie-Weiss behavior, represented by the straight line in Figure 3a.

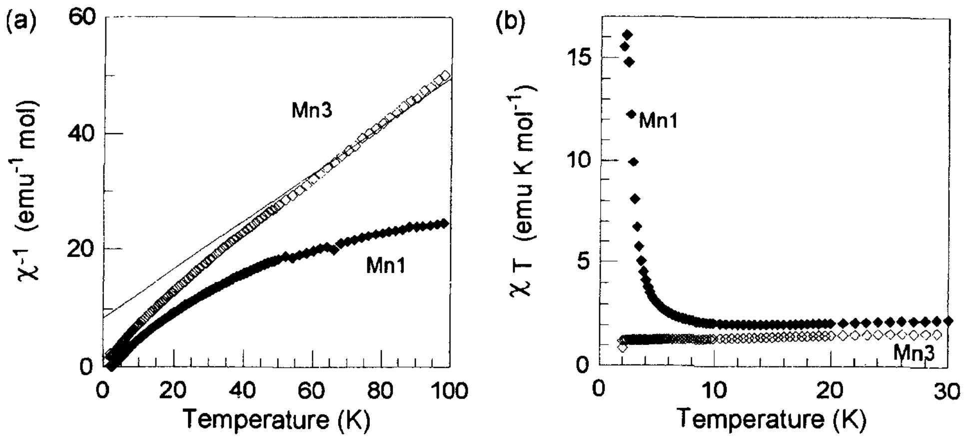

FIGURE 3 (a) χ^{-1} and (b) χT temperature dependences of the Mn# compounds.

As for Fe1 and Mn1, Cr1 has predominant FM interactions at low temperatures, as denoted by an abrupt increase of χT, bellow ca. 3K (Figure 4b). Cr2 follows reasonably a Curie-Weiss behavior down to 2 K (with a small anomaly at 60 - 80 K). In the case of

Cr3, although the AFM character seems to decrease at low temperatures, as suggested by the deviations from the high temperature Curie-Weiss behavior, represented by the straight line in Figure 4a, it was possible to observe the existence of a minimum in χ^{-1}, at 2.5 K, suggesting the existence of an AFM transition.

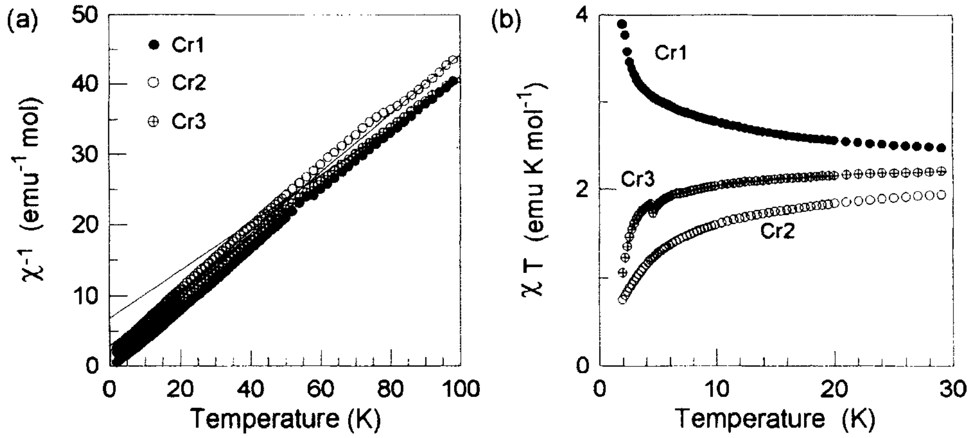

FIGURE 4 (a) χ^{-1} and (b) χT temperature dependences of the Cr# compounds.

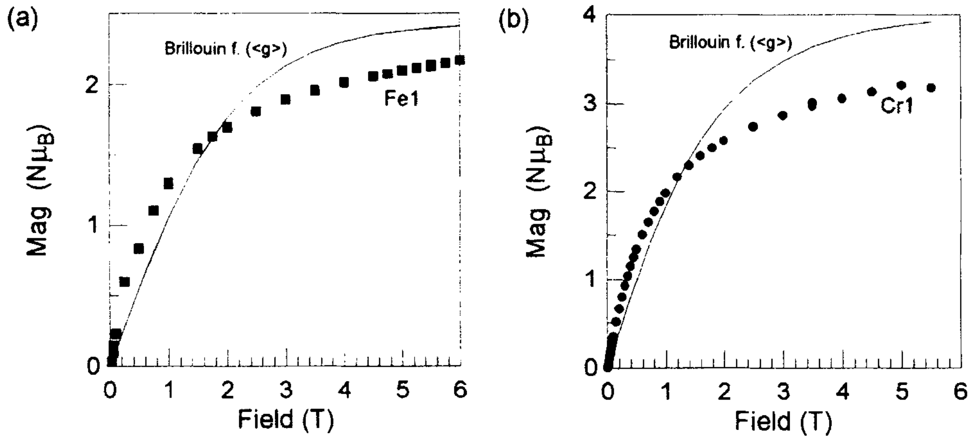

FIGURE 5 Magnetization field dependence, (a) for Fe1, at 1.8 K ; (b) for Cr1, at 2 K.

The magnetization field dependences of the compounds Fe1 and Cr1, at low temperatures, are shown in Figure 5a and 5b respectively, where it is possible to see that, for low fields, the magnetizations rise faster than the Brillouin functions, calculated with $\langle g \rangle = 2.8$ and 2.0, for Fe1 and Cr1 respectively, confirming the dominance of the FM interactions. However no spontaneous magnetization, saturation or hysteresis were observed, which indicates that, at these temperatures, 3D FM order is not yet achieved.

The magnetization field dependences for Fe2 and Mn1, at 2 K, is shown in Figures 6a and 6b, respectively. Both curves show a sigmoidal behavior, with a positive curvature at low fields and a negative one at high fields, which is typical of metamagnetic materials[3c], where a field induced transition from an AFM to a FM ground state occurs. The critical field, H_C, at 2 K, defined as the extrapolation of the transition region (the crossover AFM ↔ FM) to $M = 0$, is 4 kG for Fe2 and 200 G for Mn1.

In the case of Fe2 and Mn1, the FC magnetization curves show that, for high applied magnetic fields, magnetization increases on cooling, while for low magnetic fields, it increases and reaches a maximum (at ca. 4.5 K, for Fe2, and 3 K for Mn1), decreasing sharply for lower temperatures. From the low applied fields magnetization curves it was possible to obtain the Neel temperatures corresponding to a maximum in dM/dT, $T_N = 3.2 \pm 0.1$ K for Fe2 and $T_N = 2.3 \pm 0.05$ K for Mn1.

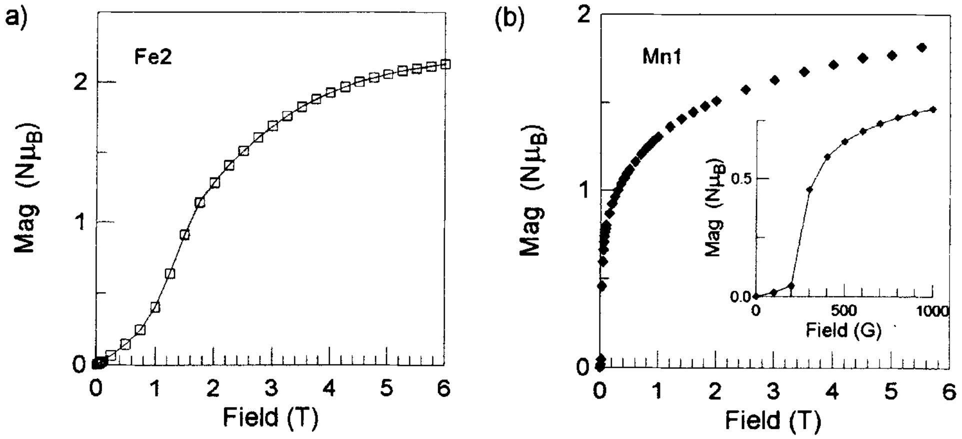

FIGURE 6 Magnetization field dependence, (a) for Fe2, at 2 K ;
(b) for Mn1, at 2 K.

In the case of Mn1 the magnetization at 5.5 T is 1.8 $N\mu_B$, and although it is still not saturated, it is far below $M_{Sat} = g_A S_A + g_D S_D = 3.24\ N\mu_B$, with $g = \langle g_D \rangle = 2.2$. The nature of the high field state seems more consistent with a ferrimagnetic state, as in this case $M_{Sat} = g_A S_A - g_D S_D$, would be 1.16, taking $g_D = \langle g_D \rangle$, or 2.29, with $g_D = g_{||}$. Anyway considering the anomalous high temperature behavior, the nature of this state can not be inferred just through the value of the magnetization in the high field region.

From our results, ferro and antiferromagnetic interactions are competing in most *compounds*. Generally at high temperatures AFM interactions dominate and in several cases at low temperatures FM interactions became dominant. However magnetic ordering was observed only in the cases of [Fe(Cp*)$_2$][Ni(edt)$_2$] and of [Mn(Cp*)$_2$][Ni(bdt)$_2$], presenting metamagnetic transitions. No clear evidence for ferrimagnetism was found, however it may occur in the high field state for [Mn(Cp*)$_2$][Ni(bdt)$_2$], or for the [M(Cp*)$_2$][Ni(tcdt)$_2$] compounds, at lower temperatures than the ones we attained.

The understanding of the reported unusual behavior of [Mn(Cp*)$_2$][Ni(bdt)$_2$] depends on the structural characterization, which is still on progress, as well as on the determinations of both the oxidation states of the metallic elements and the spin value of the [Mn(Cp*)$_2$] species.

Acknowledgment. We acknowledge Prof. M. Godinho, for the access to the SQUID magnetometer at Faculdade de Ciências da Universidade de Lisboa. This work was partially supported by Junta Nacional de Investigação Científica e Tecnológica under the project PBIC/C/QUI/2204/95 and by Fundação Oriente.

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