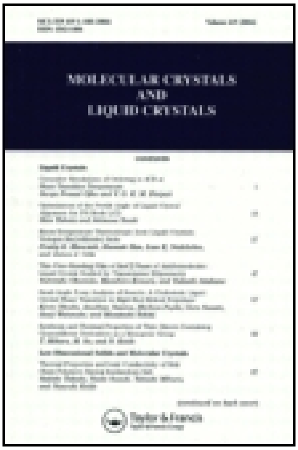

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Synthesis and Magnetic Properties of Decamethylmetallocenium Salts of the Monoanionic Complex $[Ni(tds)_2]^-$

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Synthesis and Magnetic Properties of Decamethylmetallocenium Salts of the Monoanionic Complex $[Ni(tds)_2]^-$

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The synthesis and magnetic properties of $[M(Cp^*)_2][Ni(tds)_2]$, M = Fe, Mn and Cr; tds = bis(trifluoromethyl)ethylenediselenato, are reported. The crystal structure for these compounds consists of an array of parallel stacks of alternating cations, $[M(Cp^*)_2]^+$, and anions, $[Ni(tds)_2]^-$, $\cdots D^+A^-D^+A^-D^+A^-\cdots$.

For $[Fe(Cp^*)_2][Ni(tds)_2]$ and $[Mn(Cp^*)_2][Ni(tds)_2]$ the magnetic behavior is dominated by FM interactions, with θ values of 10.6 and 24.6 K respectively, while for $[Cr(Cp^*)_2][Ni(tds)_2]$ the magnetic behavior is dominated by AFM interactions, with $\theta = -86.4$ K. $[Mn(Cp^*)_2][Ni(tds)_2]$, at low temperatures, shows a metamagnetic behavior, with $T_N = 2.1$ K and $H_C = 60$ G.

Keywords: Electron Transfer Salts; Decamethylmetallocenium Salts; Molecular Magnetic Materials; Metamagnetism

INTRODUCTION

After the report of bulk molecular ferromagnetism in 1986 for $[Fe(Cp^*)_2](TCNE)$[1], a considerable effort has been devoted to molecular magnetic materials, in particular to the electron transfer salts (ETS) based on $[M(Cp^*)_2]^+$ and on planar acceptors exhibiting 1D structural arrangements $\cdots D^+A^-D^+A^-D^+A^-\cdots$[2]. The salts based on $[M(Cp^*)_2]^+$ and on monoanionic planar metal bis-dichalcogenate complexes of transition metals such as Ni, Pd and Pt, with $S = \frac{1}{2}$, seem quite promising in the preparation of new molecular magnets, in special it is expected that the peripheric chalcogen atoms can induce significant extended magnetic interactions. As a consequence a considerable effort was dedicated to this type of ETS and a large number of compounds were studied, but, with a few exceptions, most of them present structural sequences that differ from the 1D $\cdots D^+A^-D^+A^-D^+A^-\cdots$, which is believed to favor FM coupling and bulk ferromagnetism[2]. Although several of these ETS present FM interactions[3], it is not surprising that magnetic ordering was only observed in the cases of $[Mn(Cp^*)_2][M(tfd)_2]$ with M = Ni, Pd, Pt[3c] and $[Fe(Cp^*)_2][Ni(edt)_2]$[3c], which present the above mentioned 1D chain structure. In this work we aim to study the series $[M(Cp^*)_2][Ni(tds)_2]$, M = Fe, Mn and Cr, where we expect to obtain a similar 1D structural arrangement as in the $[Ni(tfd)_2]$ salts[3a, 3c]. In particular, we are interested in the effect of replacing sulfur by selenium on the acceptors, as we hope that the larger selenium atoms should lead to stronger magnetic interactions.

EXPERIMENTAL

Synthesis

$[Fe(Cp^*)_2]BF_4$[4], $[Mn(Cp^*)_2]PF_6$[5]; $[Cr(Cp^*)_2]PF_6$[6] and $TBA[Ni(tds)_2]$[7] were prepared by published procedures. The reactions were performed in an inert atmosphere glovebox. Solvents were dried and distilled under nitrogen. The products were stored and manipulated under nitrogen, as several decompose upon exposure to air.

$[Fe(Cp^*)_2][Ni(tds)_2]$ (**1**) was obtained by the addition of a concentrated MeCN solution of $[Fe(Cp^*)_2]BF_4$ to an equimolar solution of $TBA[Ni(tds)_2]$ in MeOH/DCM. The dark green precipitate was collected by vacuum filtration. Anal. Found (calc) for $FeNiC_{28}H_{30}F_{12}Se_4$: C, 32.94 (32.81); H, 3.12 (2.95). Dark green needle shaped crystals were obtained by slow evaporation from acetone concentrated solutions.

$[Mn(Cp^*)_2][Ni(tds)_2]$ (**2**) and $[Cr(Cp^*)_2][Ni(tds)_2]$ (**3**) were obtained following a similar procedure to the described above for **1**, using

$[Mn(Cp^*)_2]PF_6$ and $[Cr(Cp^*)_2]PF_6$ respectively. Anal. Found (calc) for $MnNiC_{28}H_{30}F_{12}Se_4$: C, 33.17 (32.84); H, 3.25 (2.95). Anal. Found (calc) for $CrNiC_{28}H_{30}F_{12}Se_4$: C, 33.06 (32.94); H, 3.07 (2.96). Crystallizations afforded dark brown needle shaped crystals.

Magnetic Measurements

Magnetization measurements were carried out, with a SQUID magnetometer, on polycrystalline samples, using quartz sample holders. Magnetization data were corrected for sample holder and core diamagnetism contributions.

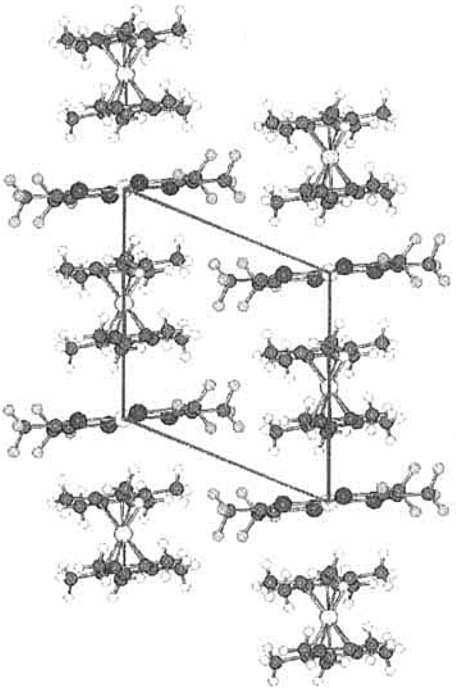

FIGURE 1 Packing diagram of **1** showing a view of two out of registry $\cdots D^+A^-D^+A^-D^+A^-\cdots$stacks in the *bc* plane.

RESULTS AND DISCUSSION

The salts **1**, **2** and **3** are isostructural and the crystal structures consist of an array of parallel alternated 1D stacks of the donor ($[M(Cp^*)_2]^+$) and the acceptor ($[Ni(tds)_2]^-$), $\cdots D^+A^-D^+A^-D^+A^-\cdots$[8], similar to those reported for $[Mn(Cp^*)_2][M(tfd)_2]$ with M = Ni, Pd, Pt[3c] and $[Fe(Cp^*)_2][Ni(tfd)_2]$[3a]. No contacts shorter than the sum of the van der Waals radii between the decamethylmetalloceniums and the dichalcogenide anionic complexes were observed.

At high temperatures ($T > 50$ K), the magnetization data for **1**, at 5 kG, follows the Curie-Weiss expression, $\chi = C/(T\text{-}\theta)$, with $\theta = 10.6$ K. At room temperature the effective magnetic moment, μ_{eff}, has a value of 3.24 μ_B, which is higher than the value predicted for independent spins and random orientation (3.1 μ_B), considering the $\langle g \rangle$ values of $[Fe(Cp^*)_2]^+$, 2.8[3a], and of $[Ni(tds)_2]^-$, 2.1[9]. This enhancement can be attributed to the high g anisotropy of $[Fe(Cp^*)_2]^+$ and orientation effects due to the applied magnetic field. The product χT increases upon cooling, as illustrated in Fig. 2, confirming that down to 2 K the dominant magnetic interactions are ferromagnetic.

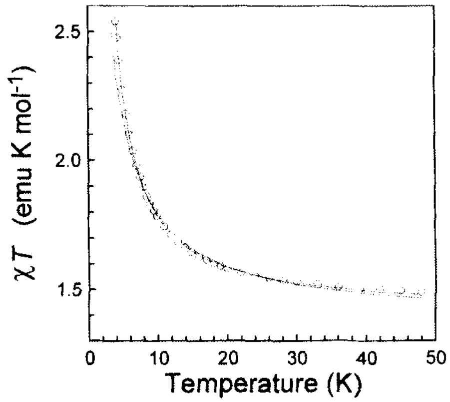

FIGURE 2 χT temperature dependence for **1**, compared to the fits of the 1D Heisenberg (dotted line), with $J = 4$ K, and Ising (solid line), with $J = 2.4$ K, models with FM interactions.

The low temperature dependence of χT can be fitted by a S = ½ 1-D Heisenberg model with ferromagnetic exchange[10]:

$$\chi T = \frac{Ng^2\mu_B^2}{4k}\left[\frac{\left(1 + 5.80\,K + 16.90\,K^2 + 29.38\,K^3 + 29.83\,K^4 + 14.04\,K^5\right)}{\left(1 + 2.80\,K + 7.01\,K^2 + 8.65\,K^3 + 4.57\,K^4\right)}\right]$$

where $K = J/2kT$. Between 7 and 50 K the best fit is obtained with a $J = 3$ K, represented by the dotted line in Fig. 2. However in the case of [Fe(Cp*)$_2$][Ni(tds)$_2$], a better fit to the experimental results could be obtained considering the S = ½ 1-D Ising model[11]:

$$\chi T = Ng^2\mu_B^2 e^{2K}/4k$$

as shown in Fig. 2 by the solid line. Between 7 and 50 K, the best fit in this case gives a smaller value for the FM interaction constant, $J = 2.4$ K. The fits from both models are consistent with a mean g value of the order of 2.7 (2.71 for the Heisenberg and 2.74 for the Ising models) that is consistent with a g value of 2.1 for [Ni(tds)$_2$]$^-$ and a g value of 3.2 for [Fe(Cp*)$_2$]$^+$, which is in good agreement with the obtained value from μ_{eff} at room temperature.

The isothermal magnetization data at 2 K, shown in Fig. 3, confirms the dominating FM interaction in **1**. The magnetization values exceed significantly the calculated from the Brillouin function, represented by the

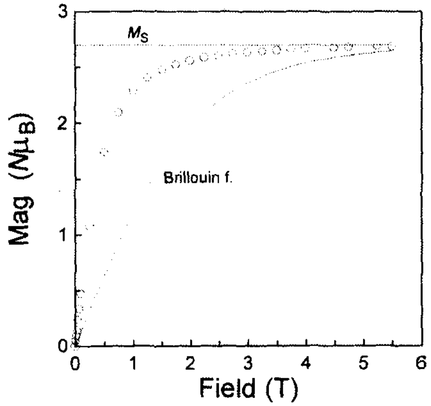

FIGURE 3 Magnetization field dependence at 2 K for **1**

dotted line, where the g value of $[Fe(Cp^*)_2]^+$, $g_D = 3.4$, was estimated from the magnetization value at 5.5 T, $M_S = g_AS_A+g_DS_D = 2.7\ N\mu_B$. Down to 2 K no spontaneous magnetization or hysteresis were observed, which is consistent with either a soft 3D FM or magnetic ordering at lower temperatures.

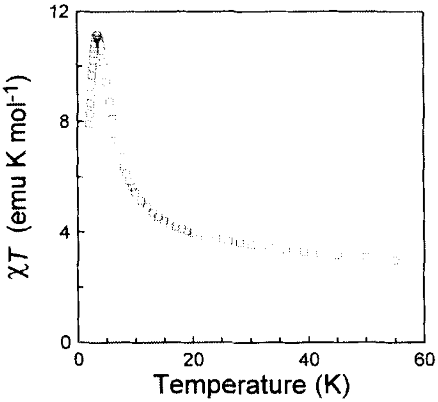

FIGURE 4 χT temperature dependence for **2**.

In the case of **2**, at high temperatures, the magnetization data, at 5kG, follow the Curie-Weiss behavior, with a ferromagnetic θ of 24.6 K. At room temperature μ_{eff} has a value of 4.24 μ_B, which is higher than the value predicted for independent spins and random orientation (3.7 μ_B), considering the ⟨g⟩ values of $[Mn(Cp^*)_2]^+$, 2.2[12], and of $[Ni(tds)_2]^-$, 2.1[9]. This enhancement can be attributed to the high g anisotropy of $[Fe(Cp^*)_2]^+$ and orientation effects due to the applied magnetic field. The product χT increases upon cooling, indicating that down to 2 K the dominant magnetic interactions are ferromagnetic, and it shows a maximum at ca. 3 K, as can be seen in Fig. 4. For compound **2**, at high applied magnetic fields the magnetization increases upon cooling down to 2 K, as can be seen in Fig. 5 for the 500 G applied field, but for low magnetic fields a maximum is observed at ca. 2.1 K, both in the data obtained at 40 and at 2 G, denoting an antiferromagnetic phase transition. As this maximum seems to be nearly field independent it is taken as the Néel temperature, $T_N = 2.1$ K.

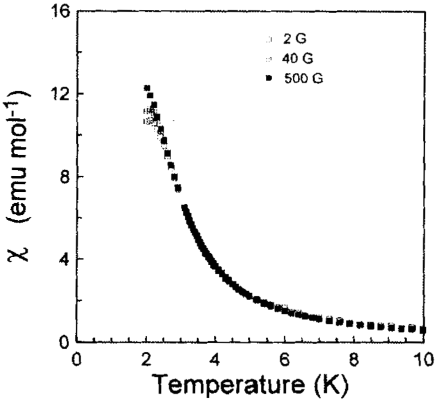

FIGURE 5 Susceptibility temperature dependence for 2, at applied fields of 2, 40 and 500 G

For 2 the magnetization isotherms obtained at 2, 2.6 and 3 K, and the values calculated from the Brillouin function, are shown in Fig. 6. An expansion of the low field region is shown in Fig. 7, where it is possible to observe that for 2 K the magnetization at low fields exhibits a sigmoidal behavior typical of metamagnetism, where a transition from an AFM to a FM ground state occurs. At 2 K, the critical field, HC, defined as the extrapolation

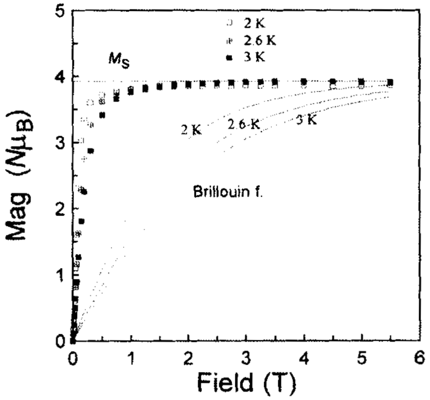

FIGURE 6 Magnetization field dependence at 2 K for 2.

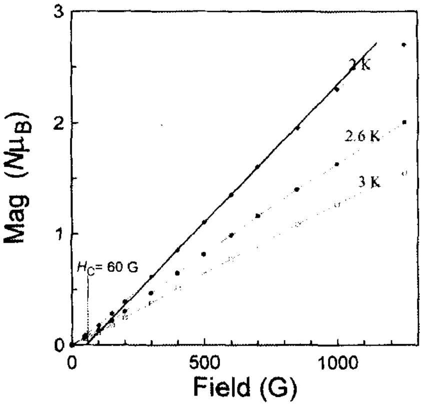

FIGURE 7 Magnetization isotherms for **2**, at 2, 2.6 and 3 K.

of the transition region (the crossover AFM ↔ FM) to $M = 0$, is ca. 60 G. The magnetization increases rapidly with the field and for fields higher than 1 T the magnetization saturates at ca. 3.9 $N\mu_B$.

Above T_N, on the magnetization isotherms up to 2.6 K the same low field upward curvatures and the subsequent inflection points, at ca. 500 G, were detected, as it is possible to observe in Fig. 7 on the 2.6 K isotherm. A similar effect was observed before in other highly anisotropic compounds as in $FeBr_2$ [13] or in $Co(pyr)_2Cl_2$ [14]. An interpretation for this effect was only given for $FeBr_2$, which possess a 2D extended covalent bonding network, and the persistence of residual AFM order above T_N was atributed to the existence of interlayer AFM interactions of the same order or larger than the intralayer FM ones [15]. But in the case of $[Mn(Cp^*)_2][Ni(tds)_2]$ that interpretation does not seem appropriate, as in this compound is highly 1D and the intrachain interactions are expected to be much larger than the interchain interactions, however it seems likely that the relation between intra and interchain interactions can play a role in the persistence of the AFM order above T_N.

At high temperatures, T > 50 K, the magnetization data for **3**, at 5 kG, follows the Curie-Weiss expression, with an AFM Weiss constant of −86.4 K. At room temperature μ_{eff} has a value of 4.1 μ_B, which is agrees reasonably with the value predicted for independent spins and random orientation (4.4 μ_B), with the $\langle g \rangle$ values of [Cr(Cp*)$_2$]$^+$, 2.0[6], and of [Ni(tds)$_2$]$^-$, 2.1[9]. χT decreases upon cooling, as expected for AFM dominant interactions.

CONCLUSIONS

The compounds [M(Cp*)$_2$][Ni(tds)$_2$] (M = Fe, Mn, Cr) are isostructural and present a $\cdots D^+A^-D^+A^-D^+A^-\cdots$ linear chain structural motive. At high temperatures, the compounds **1** and **2** are dominated by strong intrachain FM interactions (θ = 10.6 and 24.6 K, respectively), while **3** is dominated by strong AFM interactions(θ = −86.4 K), which is in a good agreement with the McConnell's configuration interaction mechanism[16].

The magnetization results for **1** adjust quite well to a 1-D Ising model with ferromagnetic interactions, with J = 2.4 K, and reasonably to a Heisenberg model with a ferromagnetic J = 3 K. In the case of this compound, down to 2 K, there is no evidence for 3D magnetic ordering. However in the case of **2** a metamagnetic phase transition was observed with T_N = 2.1 K and H_C = 60 G, at 2 K. The persistence of residual AFM order above T_N up to temperatures of the order of 2.6 K could not be explained, and a more detailed study is required in order to clarify this phase transition.

Although the compounds [M(Cp*)$_2$][Ni(tds)$_2$] are not isostructural with the corresponding sulfur based dichalcogenide salts, [M(Cp*)$_2$][Ni(tfd)$_2$][3a, 3c], they present very similar structures and magnetic properties. The main differences were observed for the Mn compounds, presenting both metamagnetic transitions at low temperatures. [Mn(Cp*)$_2$][Ni(tds)$_2$] shows considerably stronger intrachain ferromagnetic interaction, which can be seen through a Weiss constant of 24.6 K as compared to the one from [Mn(Cp*)$_2$][Ni(tfd)$_2$], θ = 2.6 K[3c]. Also in the case of [Mn(Cp*)$_2$][Ni(tds)$_2$], at low temperatures ($T < 3$ K), the magnetizations saturates at applied fields of the order of 1 T, while in case of [Mn(Cp*)$_2$][Ni(tfd)$_2$], at 1.85 K, with fields of the order 4 T the magnetization is still far from saturation[3c].

Acknowledgments

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