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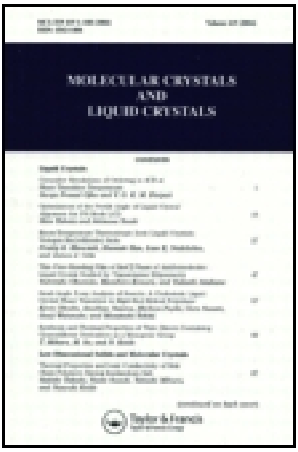

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FERROMAGNETIC INTERACTIONS IN A DECAMETHYLFERROCENIUM SALT OF NICKEL(III) BIS(2-OXO-1,3-DITHIOLE-4,5-DITHIOLATE)

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Abstract. The synthesis, crystal structure and magnetic properties of the title compound are presented : $Fe[C_5(CH_3)_5]_2[Ni(III)(S_4C_3O)_2](CH_3CN)$, Mr= 786.65, crystallizes in the C2/m monoclinic space group with cell parameters a=16.374(4) Å, b=10.84(2)Å, c=19.530(5)Å, β=98.02(2)°, V= 3431 Å^3, Z=4, d_{calc}= 1.523 g.cm^{-3}, Full-matrix least-squares refinements gave R(F)=0.060, Rw(F)=0.077 based on 1068 reflections with $I>3\sigma(I)$. The magnetic behavior is typical of dominant ferromagnetic interactions to which very weak antiferromagnetic interactions are superimposed.

INTRODUCTION.

Following the observation of bulk ferromagnetism in $Fe(Cp^*)_2TCNE$ (TCE= tetracyanoethylene),[1] great efforts have been devoted to these kind of materials[2]. In this context the decamethylferrocenium donor (D) and the metal dichalcogenide acceptors (A) were used as basic building blocks for ferromagnetic charge transfer complexes.[2,3-4] We report herein the preparation, X-ray crystal structure and magnetic behavior of a new magnetic molecular material based on decamethylferrocenium cation and Bis(dithiolato)metalate anion $[Ni(III)(dmio)_2]^-$; dmio^{2-} = $[C_3S_4O]^{2-}$ = 2-oxo-1,3-dithiole-4,5-dithiolate). The $Ni(dmit)_2^-$ based salt showing a ...$D^+D^+A^-A^-D^+D^+A^-A^-$ ...packing has been reported[4]. We found that the oxo anion (X=O) leads in similar crystal growth conditions to significant changes in the crystal structure (see below) but the magnetic behavior remaining very close to the thio based complexe (X=S) (see scheme 1).

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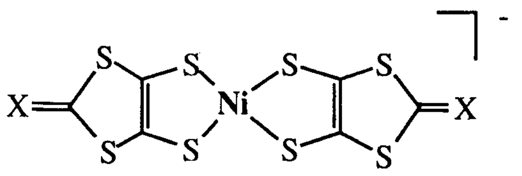

X=O : [Ni(dmio)$_2$]$^-$; X=S : [Ni(dmit)$_2$]$^-$

SCHEME 1

EXPERIMENTAL SECTION :

Synthesis :

1,3,4,6-terathiapentalene-2,5-dione (TPD) and Aliquat 336, from Aldrich, were used as received. Fe(Cp*)$_2$BF$_4$ was prepared using the literature procedure.[5]

The reaction of TPD with sodium carbonate in a heterogeneous media : (1/1) benzene-water mixture containing the phase-transfer catalyst Aliquat 336 produce the anionic [DMIO]$^{2-}$ entities. The transition-metal complexe is easily separated by precipitation of the tetraphenylphosphonium salt P(Ph)$_4$Ni(dmio)$_2$ and recrystallized from Dimethylformamide to give well formed brown crystals.

The solvated complexe Fe(Cp*)$_2$Ni[dmio]$_2$(CH$_3$CN) was obtained by the reaction of equimolar amounts of Fe(Cp*)$_2$BF$_4$ and P(Ph)$_4$Ni(dmio)$_2$ in hot acetonitrile. After filtration shiny brown crystals grew from the filtrate which have been used for the X-Ray crystal structure determination.

X-Ray Diffraction :

The X-ray data collections were performed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromatized MoKα (λ=0.71073Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centred reflections. Data were collected with the θ–2θ scan method. Three standard reflections were measured every hour and revealed no fluctuations in intensities. Intensities were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and successive Fourier difference synthesis. An empirical absorption correction was applied using the DIFABS procedure[6].The refinements (on F) were performed by the full-matrix least squares method [H-atoms, both found by Fourier synthesis and placed at computed positions (C-H: 1.Å, B=5Å^2), were not refined]. The scattering factors were taken from International Tables for X-ray Crystallography (1974). All the calculations were performed on a MicroVAX 3100 using the Molen programs[7]. Selected bond lengths, bond angles and the intermolecular short distances are given in table 1.

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STRUCTURAL and MAGNETIC CHARACTERIZATIONS :

Crystal Structure

The unit cell contains one $[Fe(Cp^*)_2]^+$ cation centered on the miror plane at the 4i position of the C2/m group and two independent $[Ni(dmio)_2]^-$ anions (A and B) with the 2/m symmetry (2c and 2b positions) laying parallel and perpendicular to the miror respectively. The structure of this salt consists of anion (A^-)-cation (D^+) mixed layers parallel to the ab plane separated in the c direction by anionic sheets (figure 1a). These layers are built of alternating one dimensional mixed stacks : $...A^-D^+D^+A^-D^+D^+A^-...$ and the essentially based anionic sheet ensures the charge neutralization. The mean planes of the adjacent anionic units, belonging to the mixed layer and the anionic sheet respectively, are perpendicular in such a way that every side by side cationic dimer is located at the centre of an anionic octahedron while every anionic unit occupies the main diagonal of a cationic parallelepiped. The structure can thus be regarded as an association of centrosymmetrical octahedra sharing edges in the (001) plane and vertices in the [100] direction (figure 1b). The cation-anion Fe-S short distances within this octahedra are 5.499(6), 5.449(1) and 6.093(5)Å in the a, b and c directions respectively. The shortest Fe-Fe distance is 8.332Å while the Fe-Ni distances are 6.003(2)Å, 6.835(2)Å and 7.268(2)Å (figure 1b). A similar structure had been reported[4] for the compound $Fe(Cp^*)_2Ni[bds]_2(CH_3CN)$ [bds^{2-} = 1,2-benzenediselenolate] which gives rise to dominating ferromagnetic interactions with Fe-Fe and Fe-Ni shortest distances of 9.10Å and 5.85Å respectively and Fe-Se distances of 5.60Å and 6.88Å.

Table 1. Selected Bond Distances (Å) for $Fe(Cp^*)_2Ni(dmio)_2(CH_3CN)$.
For distances d1 to d8 see figure 1a.

Ni1 - S1	2.160(5)	C11 - C12	1.31(2)	d1 (Fe-Fe)	8.332(4)
Ni1 - S2	2.116(5)	C13 - O1	1.21(3)	d2 (Fe-Ni2)	6.003(2)
S1 - C11	1.71(2)	Ni2 - S5	2.141(4)	d3 (Fe-Ni1)	6.838(2)
S2 - C12	1.72(2)	S5 - C14	1.72(1)	d4 (Fe-Ni1)	7.268(2)
S3 - C11	1.76(2)	S6 - C14	1.73(1)	d5 (Ni1-Ni2)	11.84
S3 - C13	1.72(2)	S6 - C15	1.77(1)	d6 (Ni1-Ni2	11.17
S4 - C12	1.71(2)	C15 - O2	1.21(3)	d7 (Ni1-Ni1)	9.82
S4 - C13	1.80(2)			d8 (Ni1-Ni2)	13.59

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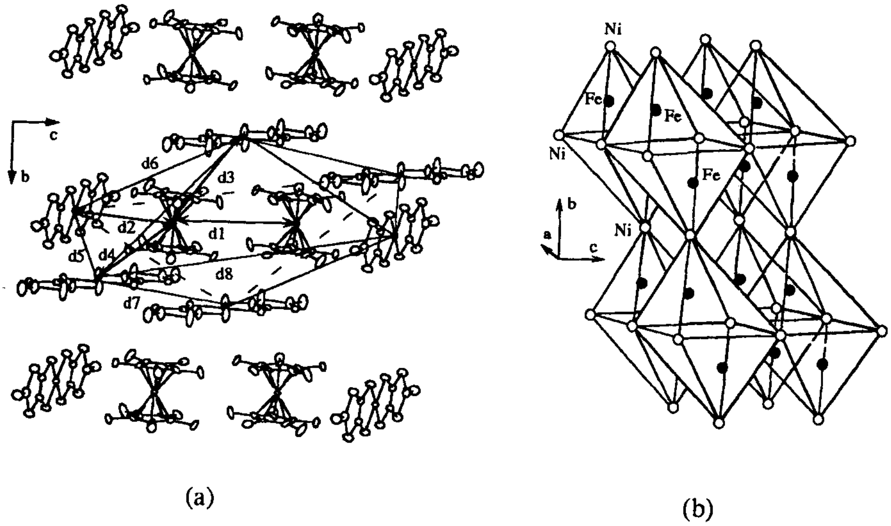

(a) (b)

FIGURE 1 : (a) Structure of the the mixed anion-cation layer and the anionic sheets.
(b) Anionic framework

Magnetic properties

The magnetic properties of the compound are shown in figure 2 in the form of the $\chi_M T$ versus T curve, χ_M being the molar magnetic susceptibility (per FeNi unit) and T the temperature. At room temperature, $\chi_M T$ is equal to 1.50 cm^3 K mol^{-1}, increases first very slowly, then more and more rapidly as T is lowered down to 2.90K and reaches a maximum at that temperature with $\chi_M T=2.60$ cm^3 K mol^{-1}. When T is lowered further below 2.9K, $\chi_M T$ decreases, but the susceptibility χ_M continues to increase and exhibits no maximum down to 1.7K, the lowest temperature we investigated. This behavior is typical of dominant ferromagnetic interactions to which very weak antiferromagnetic interactions are superimposed. The complexity of the crystal structure prevents any qualitative interpretation of the magnetic data. What we can say, it is that down to 3K the magnetic susceptibility data closely follow the Curie-Weiss low χ_M (in cm^3mol^{-1})=1.66/(T-1.97), the Weiss constant $\theta=1.97$ K accounting for relatively large ferromagnetic interactions. A mean-field calculation leads to $zJ=5.5$ cm^{-1}, J being the mean value of the interaction parameter between D^+ and A^- spin carriers (the interaction spin Hamiltonian being expressed in the form $H=-JS_{D+}S_{A-}$), and z being the number of nearest neighbors around a spin carrier.[2a] Our findings are in line with those reported by Broderick et al concerning 1:1 salts with decamethylferrocenium cations and Nickel bis(dichalcogolenes) anions. These authors, however , in 1989 analyzed

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the ferromagnetic nature of the interactions in terms of coupling between D^+A^- ground state and $D^{2+}A^{2-}$ forward charge-transfer excited state (the so-called second McConnell mechanism.[3] We suggest that the interaction occurs through the overlap between the negative spin density on the rings of the $[Fe(Cp^*)_2]^+$ cations (spin polarization effect) and the positive spin density on the sulfur atoms of the $[Ni(Dmio)_2]^-$ anions (spin polarization effect).[8] The weak antiferromagnetic interactions preventing the onset of a long-range ferromagnetic ordering might be dominated by the S-S intermolecular contacts.

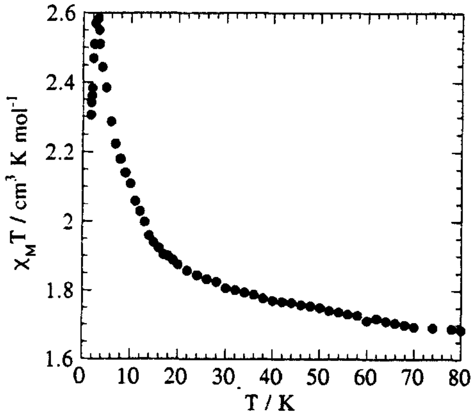

FIGURE 2 : $\chi_M T$ versus T curve, χ_M being the molar magnetic susceptibility (per FeNi unit) and T the temperature.

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