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## Ferromagnetism of the $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$ compounds, where $\text{Me} = \text{Ni}$ and $\text{Co}$

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**Abstract.** We have studied the structural and magnetic properties of two compounds from the  $\text{Me}_3^+[\text{Fe}^{3+}(\text{CN})_6]_2^{3-} \cdot \text{H}_2\text{O}$  family, where  $\text{Me} = \text{Ni}$  and  $\text{Co}$ . From x-ray analysis we find that the compounds crystallize in the face-centred cubic structure with the space group of  $F\bar{4}3m$ . Both the Fe and Me ions are coordinated octahedrally by six carbon atoms and six nitrogen atoms, respectively. The Fe ions are in a strong crystalline field, while the Me ions are in an intermediate field with cubic symmetry. From the magnetic studies a quantitative bulk ferromagnetic behaviour (a spontaneous magnetization and a hysteresis loop) has been established for both complex compounds. In addition, from the magnetization against temperature curves we obtained, for both compounds, the Curie as well as Curie–Weiss temperatures, the Curie constants and the effective moments in the paramagnetic state. From the assumed value of the spin for every cation we fitted the  $\chi T = F(T)$  curves and from the field dependence of the magnetization we determined the high-field susceptibility. The magnetic properties of the compounds were analysed in the framework of the mean-field theory.

### 1. Introduction

In the last few years [1, 2] molecular magnetism has again become the subject of intensive investigations. We can place this field of investigation at the meeting point of three apparently widely separated disciplines, namely molecular materials, biorganic chemistry and solid state physics. Molecular magnets can exhibit cooperative magnetic phenomena, i.e. ferro-, antiferro-, ferri- and metamagnetism.

The lattice dimensionality is of different types: some molecular magnets are one-dimensional (1D) or linear-chain systems, some are two-dimensional (2D) or layer systems and there is also a small group exhibiting three-dimensional (3D) bulk effects. The interest concerning the 1D systems is connected with a number of special features that can occur in them, e.g. the spin Peierls transition, the alternating spin chain, solitons, bound magnons, the Haldane conjecture, etc. [3]. The 2D systems are also interesting from several points of view, e.g. for obtaining examples of unusual models such as 2D-XY (which may exhibit a Kosterlitz–Thouless magnetic phase transition), for the study of 2D magnetic phase diagrams, and for the elucidation of magnetostructural correlations within and between layers. Most recently, two-dimensional Heisenberg-model antiferromagnetism has become of special interest in connection with high-temperature superconductivity in layered high- $T_c$  superconductors or in BEDT-type organic materials.

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As far as the field of molecular materials is concerned, one of the main challenges is to design molecular ferromagnets with bulk ferromagnetic behaviour, such as spontaneous magnetization, a hysteresis loop with a coercive field and well-defined remanence as well as the critical exponents  $\beta$ ,  $\gamma$  and  $\delta$ , for the  $M(T)$ ,  $\chi(T)$  and  $M(H)$  curves, near the Curie point, respectively. One of the approaches consists of first synthesizing the molecular entities with a large spin in the ground state and then to assemble them into a crystal lattice in a ferromagnetic fashion [4–6]. Other strategies have been proposed to favour ferromagnetic interactions within a molecular entity, one of them being the orthogonality of the magnetic orbitals [7, 8]. An interesting idea is that of an irregular spin-state structure of the high-spin molecular units in the crystal lattice, which favours a parallel alignment of the molecular spins and results in a ferromagnetic transition [9]. The strategy for designing molecular ferromagnets evolved from research aimed at preparing TCNQ-based sublimable conducting charge-transfer salts containing organometallic cations:  $[\text{Fe}(\text{C}_5\text{Me}_5)_2][\text{TCNQ}]$  was also successful [10].

One of our goals was to design some molecular ferromagnets. We decided to build a 3D covalent bonding network between the 3d transition metals, with cyanide  $\text{CN}^-$  superexchange bridges which would presumably mediate intra- as well as interplanar magnetic couplings in these systems. Accordingly, we prepared two bimetallic complex systems in the general family of compounds  $\text{Me}_3^+[\text{Fe}^{3+}(\text{CN})_6]_2^-$ , where  $\text{Me} = \text{Ni}$  and  $\text{Co}$ .

Gadet and his co-workers [8] prepared the  $\text{CsNi}[\text{Cr}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$  compound which belongs to the hexacyanometallate family  $[\text{Me}(\text{CN})_6]^{n-}$ . It is a ferromagnet with  $T_c = 90$  K but with a very narrow hysteresis loop; the coercive field is  $B_c = 71 \times 10^{-4}$  T.

The prototypical and classic member of the hexacyanoiron series  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2$ , where  $\text{Me} = \text{Fe}$ , called Turnbull's blue, is known to be a ferromagnet with  $T_c = 5.5$  K [11]. All the complex compounds with different  $\text{Me}$  transition metals exhibit different beautiful colours; the compound with  $\text{Me} = \text{Co}$  is violet and that with  $\text{Me} = \text{Ni}$  is beige.

In this paper we describe preliminary magnetic studies of the systems with trivalent iron ions.

## 2. Experimental details

Powder samples of the  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$ , with  $\text{Me} = \text{Ni}$  and  $\text{Co}$ , were prepared (by one of the authors (GM)) as follows: a solution of  $\text{MeCl}_2 \cdot 2\text{H}_2\text{O}$  ( $0.1 \text{ mol dm}^{-3}$ ) was added to an aqueous solution of  $\text{K}_4[\text{Fe}(\text{CN})_6]$ . Then the mixture was heated in a reflux condenser (1–3 days). The solid was filtered and washed with water till no  $\text{Cl}^-$  ions were detected in the filtrate. Next the solid was dried at a temperature of 90–100 °C under atmospheric pressure.

The x-ray measurements of the lattice parameters and the positions of the atoms in the compounds were carried out in the  $2\theta$  range of 10–70° using a D5000 ( $\theta$ – $\theta$ ) Siemens powder diffractometer with  $\text{Cu K}\alpha$  radiation. In order to minimize statistical errors, the  $\text{K}\alpha$  lines of the high-angle reflections were changed in steps of 0.02° and the computing continuous scan was equal to 10 s. In the crystal structure the positions of Fe, Me, C and N atoms were determined by refinement of the powder diffraction profile lines, using the Rietveld method. The function minimized was  $R = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$ ; the final results for the  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2$  compounds with  $\text{Me} = \text{Ni}$  and  $\text{Co}$  gave  $R$  equal to 3.6% for both compounds.

The static magnetization was measured with an Oxford Instruments vibrating sample magnetometer [12] in magnetic fields up to 12 T. Each sample was pressed gently into a cylinder with diameter 3 mm and height 4 mm.

The field-cooled magnetization,  $M_{FC}$ , was measured during cooling from the temperature  $T = 260$  to  $4.5$  K in a constant field of  $0.2$  T. The cooling rate was  $0.05$  K  $s^{-1}$ . At the lowest temperature the hysteresis loops were measured in the field range  $-5$  T  $< B < +5$  T. The magnetic susceptibility was obtained from  $\chi = \mu_0 M/B$ , where  $\mu_0$  is the permeability of free space.

### 3. Results and discussion

Powder x-ray analysis indicates that the compounds  $Me_3[Fe(CN)_6]_2 \cdot H_2O$  are isostructural. The compounds crystallize in the face-centred cubic lattice with the space group  $F\bar{4}3m$  ( $T_d^2$ ). The lattice can be described as a cubic close-packed array of two different anions: carbon (C) and nitrogen (N), creating the  $(CN)^-$  complex, with the metal ions located in interstitial positions in this array. The positions of the metal ions are fixed by the symmetry of the structure but the anion positions are variable and are specified by the  $x$  parameter. Coordinates of equivalent positions of the cations and anions are as follows:

cation (Fe) 4a ( $\bar{4}3m$ ) 0, 0, 0;

cation ( $Me_1$ ) 4b ( $\bar{4}3m$ )  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ ;

cation ( $Me_2$ ) 4c ( $\bar{4}3m$ )  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ ;

anion (O) 4c ( $\bar{4}3m$ )  $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$  (note: two of the 4c positions are occupied by two  $Me_2$  atoms and the next two 4c positions by two oxygen atoms from the water molecules);

4d ( $\bar{4}3m$ ) positions are unoccupied;

anion (C) 24f (mm)  $x, 0, 0; 0, x, 0; 0, 0, x; \bar{x}, 0, 0; 0, \bar{x}, 0; 0, 0, \bar{x}$ , with  $x = 0.172$  and  $0.096$  for  $Me = Ni$  and  $Co$ , respectively;

anion (N) 24f (mm)  $x, 0, 0; 0, x, 0; 0, 0, x; \bar{x}, 0, 0; 0, \bar{x}, 0; 0, 0, \bar{x}$ , with  $x = 0.284$  and  $0.248$  for  $Me = Ni$  and  $Co$ , respectively;

with translations for a face-centred lattice:

$+(0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0)$ .

Along the cube edge we have the following sequence of atoms:  $Fe-C \equiv N-Me-N \equiv C-Fe$ . The values of the lattice parameters  $a$  and the distances  $d$  between the cations and anions for the compounds studied are listed in table 1.

Table 1. Lattice parameters  $a$  and distances  $d$  between anions and cations in the  $Me_3[Fe(CN)_6]_2 \cdot H_2O$  compounds. All the data are in Å.

Compound	$a$	$d(Fe-C)$	$d(Me-N)$	$d(Fe-N)$	$d(C-N)$	$d(Fe-Me_1)$	$d(Fe-Me_2)$
$Ne_3[Fe(CN)_6]_2$	10.229 $\pm 0.005$	1.761	2.207	2.907	1.145	5.114	4.398
$Co_3[Fe(CN)_6]_2$	10.296 $\pm 0.006$	0.993	2.592	2.556	1.563	5.148	4.427

Each Fe ion has twelve (Fe) nearest neighbours at a distance of  $a/\sqrt{2}$ ; four of these are placed in this same layer and eight in adjacent layers. Each  $\text{Me}_1$  ion has four  $\text{Me}_2$  nearest neighbours at a distance of  $a\sqrt{3}/4$  in adjacent layers. The Fe– $\text{Me}_2$  interlayer separation  $d$  is lower than the intralayer one (see table 1). In the structure we have six vacancies for the internal  $\text{Me}_2$  positions; two of them are occupied by water molecules. Because of this structural (and hence magnetic) disorder some superexchange paths are disconnected.

Both the Fe and Me ions are coordinated octahedrally by six carbon atoms and six nitrogen atoms, respectively. The  $\text{FeC}_6$  and  $\text{MeN}_6$  octahedrons are symmetric (not distorted), but the  $\text{MeN}_6$  octahedrons are always larger than the  $\text{FeC}_6$  ones. For  $\text{Me} = \text{Ni}$  the  $\text{FeC}_6$  octahedron is 1.25 times larger than the  $\text{MeN}_6$  one; for  $\text{Me} = \text{Co}$  this ratio is equal to 2.6. This means that the  $\text{Fe}^{3+}$  ions should be affected by a stronger ligand field than the  $\text{Me}^{2+}$  ions. The ligand field will influence the spin configuration of the transition metal ions directly.

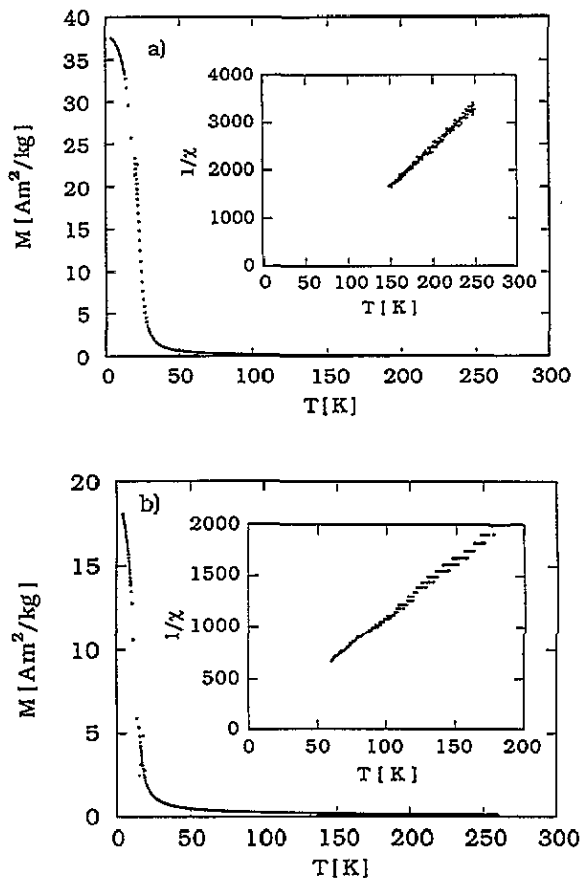


Figure 1. Field-cooled magnetization plotted against temperature for polycrystalline  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$  compounds: (a)  $\text{Me} = \text{Ni}$ , (b)  $\text{Me} = \text{Co}$ . (Note: the inset of each figure shows the inverse susceptibility plotted against temperature.)

Figures 1(a) and (b) show the field-cooled magnetization,  $M_{\text{FC}}$ , plotted against temperature for the  $\text{Me}_3^{2+}[\text{Fe}^{3+}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$  compounds, with  $\text{Me} = \text{Co}$  and  $\text{Ni}$ ,

respectively. For each compound, a substantial departure from Curie–Weiss behaviour is evident at 50 K, and below 15 K the magnetization saturates in the way characteristic of ferromagnets. From the inflection point in the low-temperature  $M_{FC}(T)$  curves (i.e. from the maximum in  $dM/dT$ ) we obtained the critical (Curie) temperatures ( $T_C$ ) for the onset of long-range ferromagnetic order. The most accurate values were determined from an asymptotic critical law of the form [13]

$$\chi_0 = \Gamma(T/T_C - 1)^{-\gamma} \quad (1)$$

where  $\Gamma$  and  $\gamma$  are constants. Fitting equation (1) to the experimental values of  $\chi$ , in the low-temperature range we obtained the critical temperatures with an uncertainty of 1%. The results are shown in table 2.

Table 2. The set of experimental data for the  $Me_3[Fe(CN)_6]_2 \cdot H_2O$  compounds.  $M_s$  is the saturation magnetization,  $\mu_s$  the number of Bohr magnetons per formula unit,  $M(0)$  the spontaneous magnetization,  $B_c$  the coercive field,  $M_r$  the remanence,  $T_C$  the Curie temperature, and  $\Theta_{CW}$  the Curie–Weiss temperature.

Compound	$M_s$ (A m <sup>2</sup> kg <sup>-1</sup> )	$\mu_s$ ( $\mu_B$ )	$M(0)$ (A m <sup>2</sup> kg <sup>-1</sup> )	$B_c$ (T)	$M_r$ (A m <sup>2</sup> kg <sup>-1</sup> )	$T_C$ (K)	$\Theta_{CW}$ (K)
Ni <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	66.0	7.1	53.3	0.25	31.1	23.6	50.6
Co <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	46.8	4.5	30.5	0.07	11.1	14.0	10.0

In the insets of figures 1(a) and (b) the reciprocal susceptibility,  $\chi^{-1}$ , is given as a function of temperature for the compounds with  $Me = Co$  and  $Ni$ , respectively. The Curie–Weiss law is fulfilled above 60 K for  $Me = Ni$  and above 150 K for  $Me = Co$ . From the fitting of  $\chi^{-1} = (T - \Theta_{CW})/C$ , we obtained values of the Curie constant,  $C$ , and the Curie–Weiss temperature,  $\Theta_{CW}$ . The large positive value of  $\Theta_{CW}$  (especially in the case of  $Me = Ni$ ) indicates the presence of net ferromagnetic interactions. Next, by taking into account the relation for the Curie constant [13]

$$C = N_A \mu_0 \rho p_m^2 / 3k_B M' \quad (2)$$

where  $N_A$  is the Avogadro number,  $\rho$  the density of material,  $k_B$  the Boltzmann constant and  $M'$  the molecular weight, we can calculate the effective magnetic moment,  $p_m$ , in a paramagnetic range. The results are given in table 3.

Table 3. The set of calculated data for  $Me_3[Fe(CN)_6]_2 \cdot H_2O$  compounds.  $C$  is the Curie constant,  $p_m$  the effective magnetic moment,  $\chi_{hf}$  the high-field susceptibility,  $\chi_{dia}$  the diamagnetic susceptibility,  $\chi_{VV}$  the Van Vleck susceptibility,  $\alpha$  the effective molecular field constant, and  $J$  the effective exchange constant.

Compound	$C$ (K)	$p_m$ ( $\mu_B$ )	$\chi_{hf}$ (10 <sup>-4</sup> )	$\chi_{dia}$ (10 <sup>-5</sup> )	$\chi_{VV}$ (10 <sup>-5</sup> )	$\alpha$ (m <sup>3</sup> kg <sup>-1</sup> )	$J$ (K)
Ni <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	0.06	5.45	23.88	0.13	0.4	1.1	27
Co <sub>3</sub> [Fe(CN) <sub>6</sub> ] <sub>2</sub>	0.08	6.44	24.41	0.15	0.2	1.0	10

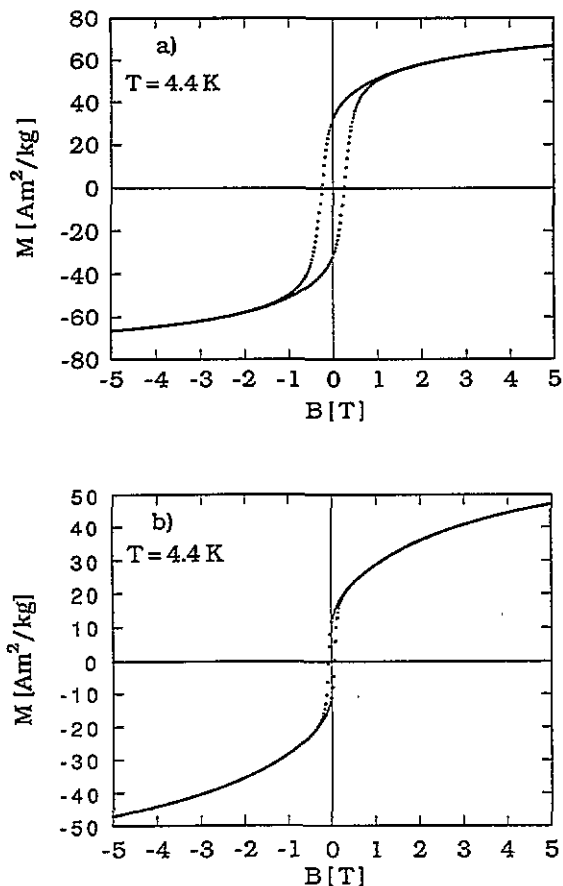


Figure 2. The hysteresis loop for the two members of the  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$  family: (a)  $\text{Me} = \text{Ni}$ , (b)  $\text{Me} = \text{Co}$ .

From the relation  $\Theta_{\text{CW}} = \rho C \alpha$  and the values of  $\rho = 0.77 \times 10^3 \text{ kg m}^{-3}$  and  $0.6 \times 10^3 \text{ kg m}^{-3}$  for  $\text{Me} = \text{Ni}$  and  $\text{Co}$ , respectively, we calculated also the effective molecular constant  $\alpha$ . The data are given in table 3.

The magnetization against applied field for the  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$  compounds exhibits hysteresis loops characteristic for ferromagnetic materials. At 4.4 K a hysteresis loop with a coercive field of 0.257 and 0.07 T and a well-defined remanence of 31.1 and 11.1  $\text{A m}^2 \text{ kg}^{-1}$  is observed for  $\text{Me} = \text{Ni}$  and  $\text{Co}$ , respectively (cf figure 2).

The spontaneous magnetization,  $M(0)$ , was obtained by extrapolation of the linear portion of the magnetization curve to zero field. We determined the differential high-field susceptibility, defined by the relation

$$\chi_{\text{hf}} = \mu_0 \rho \frac{dM}{dB} \quad (3)$$

for  $B > 2.5 \text{ T}$ , where  $M$  depends linearly on  $B$ . The data are given in table 2. From the high-field susceptibility we can extract, by independent calculations [14–16], the diamagnetic susceptibility,  $\chi_{\text{dia}}$  and the temperature-independent Van Vleck paramagnetic contribution. The results are given in table 3.

From a comparison of the values of the saturation magnetization  $\mu_s$ , in Bohr magnetons, per formula unit with the effective magnetic moment,  $p_m$ , we conclude that all the cations in the compounds under study are magnetic.

In our complex compounds all the cations are in an octahedral crystalline field (also called a cubic field) created by the  $CN^-$  ligands. The cubic crystalline field strongly affects the 3d shell electrons of the iron-group ions. This is partly due to the large radius of the 3d shell and partly due to the lack of any outer electronic shells to screen the 3d shell. Thus the orbital moment in many cases becomes quenched and the magnetic properties of these ions are governed by their spins only.

From the spectrochemical series we find that  $CN^-$  ions usually create a strong ligand field and that the  $[Fe^{3+}(CN)_6]^{3-}$  complex exhibits a magnetic moment equal to  $1.7\mu_B$  [17]. This means that the  $Fe^{3+}$  ( $d^5$ ) ion (the only paramagnetic atom in the complex) contains one unpaired electron, and hence it is in the low-spin configuration  $(t_{2g})^5$ ,  $S = \frac{1}{2}$ . This unsymmetric filling of the orbital triplet can lead to a small orbital contribution to the magnetic moment. In the octahedral complexes (in a covalent description) we assume a  $d^2sp^3$  hybridization of a central ion. Because of symmetry, we assume that among the 3d orbitals of the iron, the  $3d_{z^2}$  and  $3d_{x^2-y^2}$  orbitals, which are the  $e_g$  orbitals, take part in the creation of hybridized orbitals of type  $\sigma$ . The remaining three 3d orbitals,  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ , which we will denote by  $t_{2g}$ , do not take part in hybridization nor in the creation of the molecular orbitals type  $\sigma$  (in general, they may create  $\pi$ -type covalent bonds).

As a result of overlapping the six hybridized orbitals of the central ion with the six ligand orbitals, we obtain six bonding localized orbitals of type  $\sigma$  and six antibonding ones of type  $\sigma^*$ . In the  $[Fe(CN)_6]^{3-}$  complex the hybridized molecular orbitals, together with not hybridized  $t_{2g}$  orbitals, contain five valence electrons of the central ion and 12 electrons from ligands. Because each ligand gives two electrons to the molecular complex orbitals, a covalent bond created in this way is called a coordinated bond. Hence, in the low-spin complex of the  $[Fe(CN)_6]^{3-}$  all the bonding orbitals  $(\sigma(CN))^{12}$  are occupied. The energy difference between the  $t_{2g}$  and  $\sigma^*$  orbitals (the crystal field energy) is  $\Delta = 35\,000\text{ cm}^{-1}$  and the bonding energy between electrons with antiparallel spins is  $\Pi = 30\,000\text{ cm}^{-1}$  [18, 19]. The stabilization energy of this octahedral complex is equal to  $2\Delta - 2\Pi$ . From the energy point of view this means that the further five electrons should be placed in three orbitals of  $t_{2g}$ ; a spin one of the electrons is unpaired.

$MeN_6$  octahedrons are always larger than  $FeC_6$  ones (cf table 1), hence the Me ions can be affected by a slightly weaker ligand field than the  $Fe^{3+}$  ions. For  $Ni^{2+}$  ( $d^8$ ) there is only one configuration,  $(t_{2g})^6(e_g)^2$ , with two unpaired electrons, since  $S = 1$ . For  $Co^{2+}$  ( $d^7$ ) either low spin or high spin may occur. For discussion, we choose the low-spin configuration ( $S = \frac{1}{2}$ ), because the ligand field for the  $Co^{2+}$  ions is weaker than for the  $Fe^{3+}$  ones, but it is still a strong field.

If the whole symmetry is high enough to retain the orthogonality of the  $t_{2g}$  and  $e_g$  orbitals ( $(t_{2g} | e_g) = 0$ ), the Me-Fe interaction will be ferromagnetic. Assuming parallel coupling between the spins of the Me and Fe ions and taking into account the values of their spins:  $\frac{1}{2}$ , 1,  $\frac{1}{2}$  for  $Co^{2+}$ ,  $Ni^{2+}$  and  $Fe^{3+}$ , respectively, and the isotropic value of the Landé factor  $g_{Fe} = g_{Ni} = g_{Co} = 2$ , we can estimate the full saturation moment,  $\mu_s$  in Bohr magnetons for the formula unit of  $Me_3[Fe(CN)_6]_2$  at  $T = 0\text{ K}$ . We used the formula  $\mu_s = (n_{Me}g_{Me}S_{Me} + n_{Fe}g_{Fe}S_{Fe})\mu_B$ . The estimation yields  $\mu_s$  values of  $5\mu_B$  and  $8\mu_B$  for Me = Co and Ni, respectively. These values agree well with the experimental data for  $T = 4.2\text{ K}$ , listed in table 2.

We can also use another treatment to find the spins for the magnetic ions, presented in our complex compounds. If we take into account that in the formula unit we have two



different, interacting magnetic ions, Fe and Me, with local spins  $S_1$  and  $S_2$ , respectively, we may write down the relative energies of their low-lying states in a simple way [9]:

$$E_s = -\left(\frac{1}{2}J\right)S(S+1). \quad (4)$$

Here  $S$  denotes the spin of a given state and it varies by an integer value from  $|S_1 - S_2|$  to  $S_1 + S_2$ ;  $J$  is the effective exchange constant of the phenomenological Hamiltonian

$$\hat{H} = -J\hat{S}_1 \cdot \hat{S}_2 \quad (5)$$

which is positive for ferromagnetic interactions. In such a treatment the spin  $S$  varies monotonically with the energy of the states. This regularity yields a simple correspondence between the nature of the interaction and shape of the  $\chi T$  against  $T$  plot.

The high-temperature limit of  $\chi T$ , for  $k_B T \gg |J|$ , is the sum of what is expected for each isolated ion, i.e.

$$(\chi T)_{HT} = (N_A \mu_B^2 / 3k_B) [g_1^2 S_1(S_1 + 1) + g_2^2 S_2(S_2 + 1)] \quad (6)$$

where  $g_1$  and  $g_2$  denote the average values of the local isotropic  $g$  factors. In the absence of interactions ( $J = 0$ ),  $\chi T$  remains constant in the whole temperature range yielding the Curie law.

Upon cooling,  $\chi T$  continuously increases and tends towards the low-temperature limit

$$(\chi T)_{LT} = (N_A \mu_B^2 g_s^2 / 3k_B) [(S_1 + S_2)(S_1 + S_2 + 1)] \quad (7)$$

where  $g_s(S_1 + S_2)$  is related to  $g_1$  and  $g_2$  by [20, 21]

$$g_s = (1 + c)g_1/2 + (1 - c)g_2/2 \quad (8)$$

where

$$c = [S_1(S_1 + 1) - S_2(S_2 + 1)] / S(S + 1). \quad (9)$$

In the low-temperature range  $\chi$  exhibits a plateau, because only there is the ground state thermally populated. If the interaction is ferromagnetic ( $J > 0$ ) the ground state has the largest spin  $S_1 + S_2$  and the highest excited state the smallest spin  $|S_1 - S_2|$ . Taking into account the experimental data of the susceptibility in both temperature limits we fitted the curve of  $\chi T$  against  $T$  to the previously assumed values of the spins:  $S_1 = S_{Fe} = \frac{1}{2}$ ,  $S_2 = S_{Ni} = 1$  or  $= S_{Co} = \frac{1}{2}$  and the isotropic  $g$  value  $g_{Fe} = g_{Ni} = g_{Co} = 2$ . The maximal discrepancy between the experimental data and the calculations, made in the framework of the mean field theory, was about 1%.

For a simple estimation of the effective exchange constant, we apply equation (3), in which the energy of the ground state  $E_g$  should be proportional to the Curie-Weiss temperature,  $\Theta_{CW}$  and the effective spin  $S = S_{Fe} + S_{Me}$ . The results are given in table 2. The positive value of  $J$  is also a measure of the energy separation between the ground state and the first excited state.

Well above  $T_C$  the susceptibility data,  $\chi(T)$ , can be analysed including the effects of axial and rhombic crystal-field distortions, represented by  $D(S_z^2 - \frac{5}{4})$  and  $E(S_x^2 - S_y^2)$  for  $Fe^{3+}$ ,  $D(S_z^2 - \frac{2}{3})$  for  $Ni^{2+}$ , and by the axial field  $D(S_z^2 - \frac{5}{4})$  for  $Co^{2+}$ , with the exchange interactions incorporated in a mean-field approximation. However, it turned out [22], that for the complex compounds, the same  $\chi(T)$  plot can be fitted by a few sets of exchange and crystal-field parameters.

#### 4. Conclusions

The two members of the complex family  $\text{Me}_3[\text{Fe}(\text{CN})_6]_2 \cdot \text{H}_2\text{O}$ , with  $\text{Me} = \text{Ni}$  and  $\text{Co}$ , crystallize in the FCC structure with the space group  $F\bar{4}3m$  ( $T_d^2$ ). Both the Fe and Me ions are coordinated octahedrally by six carbon atoms and six nitrogen atoms, respectively. Because the  $\text{MeN}_6$  octahedrons are larger than the  $\text{FeC}_6$  ones, a crystalline field has a stronger effect on the Fe ions than on the Me ions. The compounds exhibit magnetic properties characterized by a positive Curie–Weiss temperature of 50 and 10 K, a Curie temperature of 23.6 and 14.0 K, a saturation magnetization of 66 and 46.8  $\text{A m}^2 \text{kg}^{-1}$ , a coercive field of 0.25 and 0.07 T, and a remanence of 31.1 and 11.1  $\text{A m}^2 \text{kg}^{-1}$ , for  $\text{Me} = \text{Ni}$  and  $\text{Co}$ , respectively. The data demonstrate that ferromagnetism is achievable in organic-based molecular systems.

We assumed that all the cations contribute to the magnetic properties of these bimetallic compounds. From a knowledge of the details of the crystal structure and using data for other complex compounds described in the literature, we assumed that in the low-spin complexes of  $[\text{Fe}(\text{CN})_6]^{3-}$  the  $\text{Fe}^{3+}$  cations are in a strong crystalline field and the  $\text{Me}^{2+}$  ions are in a slightly weaker field of octahedral symmetry, created by  $\text{CN}^-$  ligands. After taking into account the respective values of the spins and isotropic value of the Landé factor we fitted the experimental plot of  $\chi T$  against  $T$  with about a 1% discrepancy. Also in the framework of the orthogonality of the  $t_{2g}$  and  $e_g$  orbitals, for the same values of the spins, we obtained agreement with the experimental values of the saturation magnetization (in Bohr magnetons) for both compounds.

The results presented in this work we treat as preliminary and we shall confirm this set of data by  $\chi_{ac}$  as well as neutron diffraction studies. We will also attempt to obtain other molecular ferromagnets with higher Curie temperatures.

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