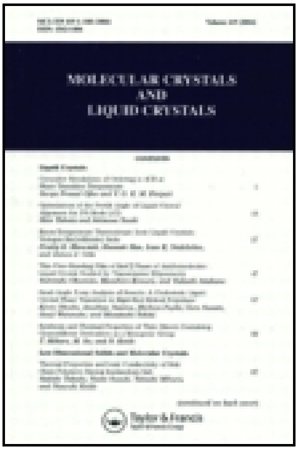

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Magnetic Behaviour of NiFe-Hexacyanates as Influenced by Change of Ligand

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Magnetic Behaviour of NiFe-Hexacyanates as Influenced by Change of Ligand

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Two new ferromagnets belonging to the Prussian Blue family have been synthesized: $[Ni(OCH_2CH_2O)_2]_3[Fe(CN)_6]_2.2.5H_2O$ (I) and $[Ni(SCH_2CH_2O)_2]_3[Fe(CN)_6]_2.7H_2O$ (II), with respective Curie temperatures 21K and 23 K. Their synthesis, and magnetic properties are reported. One of them exhibits a coercive field as high as 1792 Oe.

Keywords: molecule-based magnets; bimetallic assemblies

INTRODUCTION

Recently, much interest has been invoked in the inorganic coordination complexes belonging to the family of Prussian Blue, which offer a potential route towards design and synthesis of high dimensional molecule-based magnets that show bulk properties such as long-range magnetic ordering and ferro(ferri)-magnetism. Prussian Blue, $Fe_4^{III}[Fe(CN)_6]_3.15H_2O$ which is a mixed-valent compound shows long-range ferromagnetic ordering at T_C=5.6K[1, 2]. The magnetic interactions occur through Fe(III)-CN-Fe(II)-NC-Fe(III) linkages between Fe (III) ions which are 10.6 Å away. The presence of strong spin densities on the nitrogen and carbon atoms of the cyano groups has been experimentally observed by polarized neutron diffraction[3], a technique that allows spin-density maps to be plotted. The possibility of below 18.6 K[6,7] where 'en' stands for ethylenediamine. Its structure consists of a polymeric zigzag chain formed by an alternate array of $[Fe(CN)_6]^{3-}$ and cis-$[Ni(en)_2]^{2+}$ ions. The chains align along a line to form a trans-$[Ni(en)_2]^{2+}$. The low-spin $Fe^{III}(t_{2g}^{1})$ and $Ni^{II}(eg^{2})$ orbitals are orthogonal to each other and the ferromagnetic interaction is transmitted through the cyano-bridges. In order to elaborate on the role of the ligand such as 'en', we recently synthesized $[Ni(pn)_2]_3[Fe(CN)_6]_2.12H_2O$ where,(pn=1,2-propanediamine) which shows ferromagnetism at 19 K. With the same goal in mind, we report in this paper the synthesis of two more new compounds in which the ligands were (i) ethylene glycol and (ii) 2-mercapto ethanol viz., $[Ni(OCH_2CH_2O)_2]_3[Fe(CN)_6]_2.2.5H_2O$ (I) and $[Ni(SCH_2CH_2O)_2]_3[Fe(CN)_6]_2.7H_2O$ (II), which show bulk ferromagnetic behaviour below 21K and 23 K, respectively.

EXPERIMENTAL

The compounds (I) and (II) were synthesized by adding 20 mL solution of $K_3Fe(CN)_6$ (prepared by dissolving 2 mmol of $K_3Fe(CN)_6$ in 20 mL water) to a solution of trans-$Ni(OCH_2CH_2O)_2Cl_2$ and trans- $Ni(SCH_2CH_2O)_2Cl_2$ (prepared by dissolving 3 mmol of each in 30 mL water-methanol taken in 1:1 ratio) respectively. The reaction mixture was then heated at 50 C to give immediate precipitation of green-coloured polycrystalline solids in both the cases. The solids were washed with water and methanol. The yield was 42% for compound (I) and 30% for compound (II). The FTIR spectra showed peaks corresponding to -CN stretching frequencies i.e. 2096 and 2164 cm^{-1} for (I) and 2096 and 2148 cm^{-1} for (II). Thermogravimetric measurements were carried out with a Shimadzu DT-300 apparatus in static air environment in the range 25-300 ^{0}C. The elemental analysis and TG results indicated that compound (I) was associated with 2.5 H_2O while compound (II) was associated with $7H_2O$. The C,H,N values calculated for compound (I) and (II) in that order are C, 28.32; H, 2.40; N, 16.71 and C, 24.32; H, 2.04; N, 14.20. Found: C, 29.4; H, 2.40; N,17.1 and C, 26.9; H, 2.6, N, 15.0.

The X-ray powder diffraction patterns were recorded with Ni-filtered Cu Kα radiation on a Phillips PW1710 wide-angle goniometer. AC susceptibility measurements were made using an APD susceptometer with E.G. & G. Model 5208 Lock-in amplifier. The dc magnetization measurements were made both as a function of temperature, and applied magnetic field, $M(T)$, and $M(H)$ using an EG & G P. A. R. Model 4500 Vibrating Sample Magnetometer fitted with an 8.5 kOe Walker electromagnet and Tidewater bipolar power

Magnetometer fitted with an 8.5 kOe Walker electromagnet and Tidewater bipolar power supply. Zero field-cooled magnetization (ZFCM) data was recorded by cooling the sample down to 5 K in zero applied field, switching the applied field (200 Oe) on at this temperature and recording the magnetization while warming the sample up. Field-cooled magnetization (FCM) data was collected after cooling the sample in 200 Oe field and recording the data while warming up, keeping the field on. Next, remanent magnetization (REM) data was taken after cooling the sample in the same field to 5 K, and recording the data while warming up after reducing the field to zero. M(H) hysteresis loop was recorded at 5 K using a field range of ±8500 Oe.

RESULTS and DISCUSSION

X-ray powder diffraction data for compounds (I) and (II) reveal that they are isostructural with triclinic structure (space group $\overline{P}$ 1, matching with reference 7). Fig. 2 gives the powder X-ray diffraction pattern for compound (I). The lattice cell parameters for

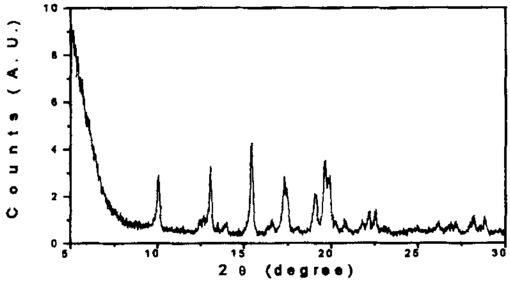
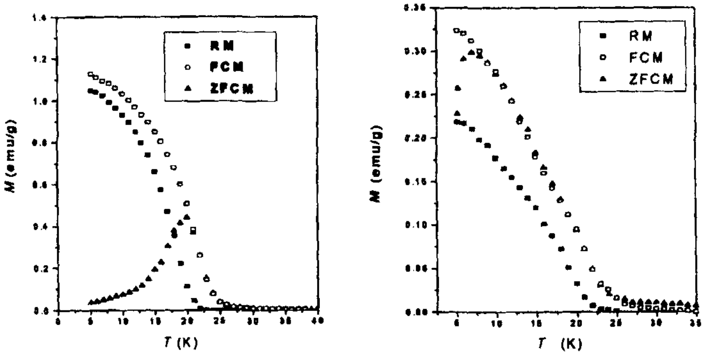


FIGURE 2 X-ray powder diffraction pattern for compound (I)

	a	b	c	α	β	γ
I	9.690(1)Å	15.922(2) Å	7.364(1) Å	90.027(1) °	106.858(2) °	105.422(1) °

TABLE 1 Lattice parameters of compound (I)

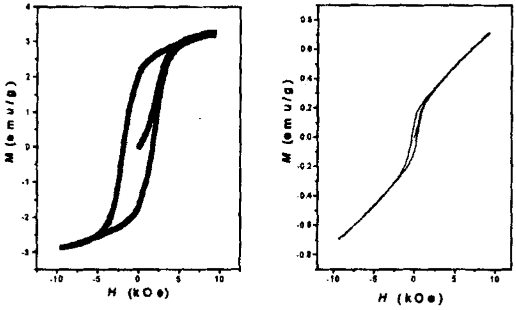
compound (I) are given in Table 1. The compound (II) was not completely single-phase. Therefore, the X-ray diffraction pattern is not given for it. The cell parameter data is also omitted for compound (II) for the same reason.Fig. 3 shows the DC magnetization data for both the compounds in the temperature range 5-35 K and under an applied field of 200 Oe. The field-cooled magnetization (FCM) showed an abrupt increase below the temperatures of 21 K for (I) and 22 K for (II) and thereafter, saturated as the temperature was lowered to 5 K. Since this FCM behavior is typically that of a ferromagnetic material, we take these temperatures to be the Curie temperature (T_C) of the respective compounds. The ZFCM shows a broad peak for compound (I), the maximum of which occurs at ~20K. In contrast, the ZFCM for compound (II) very nearly followed its FCM curve till 5 K after which it began to decrease sharply. The remanence in both the cases vanished at their respective Curie temperatures.



(I) (II)

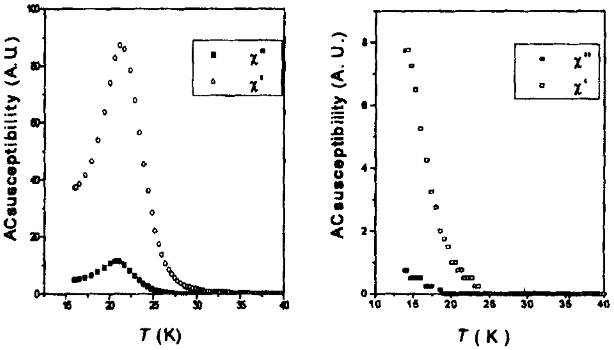
FIGURE 3 DC magnetization study for compounds (I) and (II)

The hysteresis loops recorded at 5 K on powdered samples are plotted in Fig. 4. As is evident from the M(H) curves compound (I) is a rather hard magnet compared to compound (II). The values of coercive field (H_C) and remanent magnetization (M_R) are known to be markedly influenced by the way the sample is prepared and therefore depend on grain size and shape. For both the compounds, the M(H) values did not attain saturation even for an applied field as high as 8500 Oe, which is insufficient to align all the moments in the field direction. This kind of domain-behavior is attributed to the magnetic anisotropy of the low-spin Fe^{III} magnetic ions and to the fact that the hysteresis loops are recorded on powdered samples.



(I) (II)

FIGURE 4 Hysteresis loops for compounds (I) and (II)



(I) (II)

FIGURE 5 AC susceptibility measurements on compounds (I) and (II)

Fig. 5 shows the AC magnetic susceptibility measurements in the temperature range 13-40 K, in zero static field (ν_{ac}=80 Hz, H_{ac}=0.5 Oe), for both the compounds. The out-of-phase χ'' component shows a broad hump with maxima at 18 K for (I) while χ'' continued to rise propagating magnetic interactions through extended bridging networks seems to be specific to molecular compounds and is due to the strong delocalization of the metal-ion spin towards its nearest neighbours. By synthesizing analogues of Prussian blue in which metals with different nonzero spins occupy alternate lattice sites, Bozorth et al., showed in 1956 that magnetic ordering temperatures above 30K can be achieved[4]. Recently, the room temperature barrier was overcome at 315 K with a $Cr^{III}/[V^{II}\text{-}V^{III}]$ compound[5]. These Prussian Blue like complexes can be synthesized in various k/l stoichiometries, $[A^{II}(Ligand)_n]_k[B^{III}(CN)_6]_l.xH_2O$ where A and B are the paramagnetic centres. Depending upon the nature of A-B interaction, these compounds may be three-dimensional ferromagnets, antiferromagnets or ferrimagnets. The nature of the A-B interaction, in turn, is governed by symmetry considerations, in particular, the orbital symmetries of the unpaired electrons on A and B. In this respect, the magnetic properties of the cyano-based solids agree very well with the theoretical models established for molecular magnets.

Ohba et al. have described a novel rope-ladder chain-structured compound $[Ni^{II}(en)_2]_3[Fe^{III}(CN)_6]_2.2H_2O$ (as shown schematically in Fig 1) which is metamagnetic

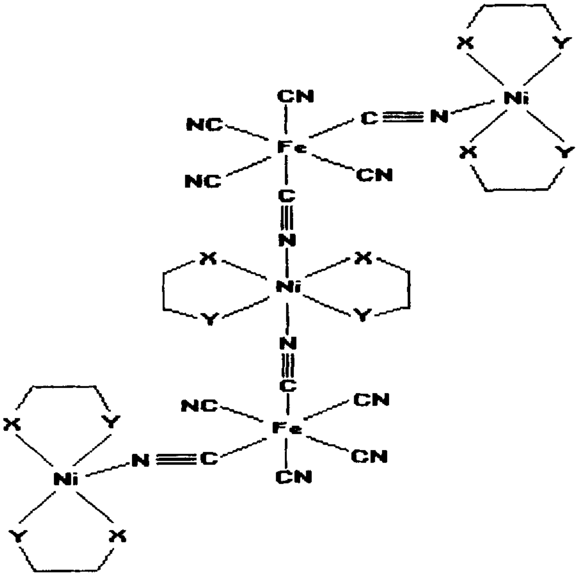


FIGURE 1 Schematic structure for the compounds where, X=Y=N, O, or S.

until 13 K for (II). The non-zero values of χ'' for (I) and (II) confirms the ferromagnetic ordering in the bulk of these materials. The χ' (T) curve for (I) shows a sharp maximum at 18 K. The decrease in χ' below the maxima is possibly due to increasing domain wall stiffness with decreasing temperature, which is common in molecule-based ferromagnets exhibiting anisotropy and low magnetic density. A similar situation was observed for $V(TCNE)_2.0.5\,CH_2Cl_2$[9].

The study of magnetic properties of compounds (I) and (II) indicates that the change of ligand in this cyanide-based system does not make much difference to the value of T_C. The interaction between adjacent Fe^{III} and Ni^{II} ions is ferromagnetic through the cyanide bridge and these momenta get aligned in the direction of the applied field below T_C to give bulk ferromagnetism. Stabilization of ferromagnetic interaction between the two non-zero spins is governed strictly by the orthogonality condition in molecule-based magnets such as (I) and (II). The orbitals bearing the Fe^{III} and Ni^{II} spins, therefore appear to be orthogonal to each other. Any non-orthogonality of these orbitals would have resulted in antiferromagnetic interaction between the two spins. Among molecular magnets, these cyano-based solids belonging to the Prussian Blue type offer a greater scope in exercising considerable control over the nature and magnitude of the local magnetic exchange interactions. The linear A-CN-B bridges promote the formation of strong magnetic interactions between adjacent spin centres. Moreover, a wide range of metals with different spin states and oxidation states can be substituted into the lattice. Lastly, and as is typical of molecular magnets, these solids can be easily prepared at room temperature from well characterized cyanometallate building blocks.

Acknowledgments

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