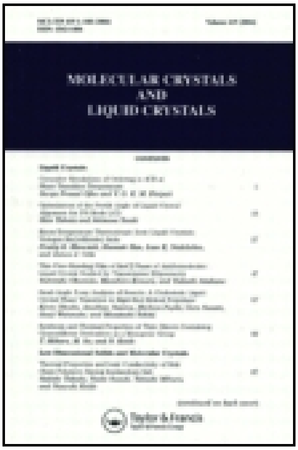

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Metamagnetic Behavior in [M (tvp) $(NCS)_2$] Coordination Polymers (M = Fe(II) and Co(II); tvp = 1,2-di-(4-pyridyl)-ethylene)

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Metamagnetic Behavior in $[M(tvp)(NCS)_2]$ Coordination Polymers (M = Fe(II) and Co(II); tvp = 1,2-di-(4-pyridyl)-ethylene)

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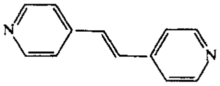
We report the synthesis and magnetic properties of two new coordination polymers of formula $[M(tvp)(NCS)_2]$ (M = Fe(II) and Co(II)). The magnetic data reveal the occurrence of metamagnetic behavior. Switching from bulk antiferromagnetic to ferromagnetic behavior occurs for magnetic fields greater than 1300 G (Fe(II)) and 450 G (Co(II)) at temperatures lower than 4 K. Both compounds are isomorphous. A molecular structure is suggested in the light of the magnetic properties and precedent data on related systems.

Keywords: coordination polymer; magnetic properties; metamagnetism

Introduction

Recently, a new research realm in crystal engineering of supramolecular architectures assembled by means of coordinate covalent bonding, hydrogen bonds or other weak intermolecular interactions has been expanding in order to develop new classes of functional materials [1]. In this regard, coordination chemistry of paramagnetic metal ions provides the synthetic chemist with a useful tool to build a great variety of such structures. That is, the synthesis of coordination polymers by self-assembling of metal ions and suitable ligands. The primary strategy employed is quite simple: propagate a known coordination geometry with rigid linear bifunctional spacer ligands. In addition to their intrinsic structural interest, coordination polymers bearing paramagnetic ions are attractive because they can exhibit some kind of cooperative functions (ferromagnetism or spin cross-over phenomena, for instance) arising from the interaction among their subunits. In this context, the present report deals with the synthesis and magnetic characterization of the coordination polymers of formula $[M(tvp)(NCS)_2]$ (M = Fe(II) (**1**), Co(II) (**2**)).



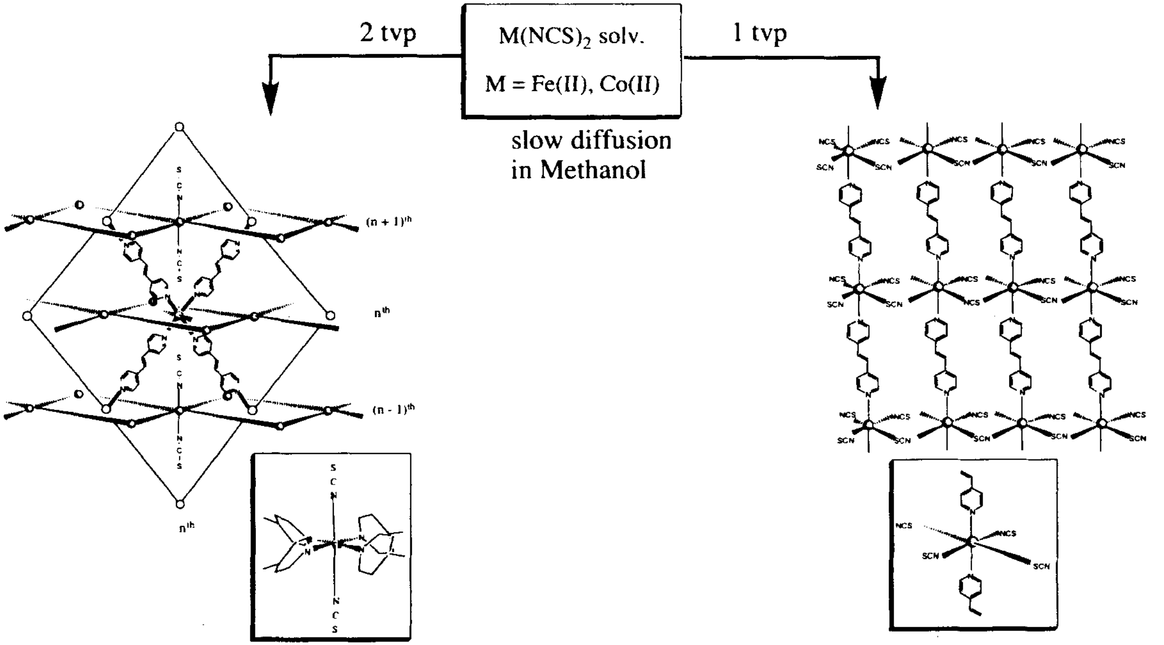
tvp

Preparation and proposed structure

1 and **2** were isolated by slow diffusion in an H-shaped tube from methanolic solutions of Fe(II)/NCS^- (1:2 iron-to-thiocyanate molar ratio) and tvp. Two different crystalline solids were formed: well shaped prismatic crystals of $[M(tvp)_2(NCS)_2]\cdot CH_3OH$ (M = Fe(II), Co(II)) catenane polymeric system [2] (see chart 1, left) and agglomerations of crystals of **1** and **2**. The two different solids were mechanically separated. Unfortunately, the crystals of **1** and **2** were not suitable to single crystal X-ray diffraction studies. However, a reasonable structure for **1** and **2** can be envisaged taking into account their isomorphous character, their magnetic behavior (vide infra) and that of related systems [3, 4]: **1** and **2** would consist of parallel sheets, each sheet being made of an array of M(II) ions in pseudo-octahedral surroundings. The metal ion is connected by four NCS^- groups defining infinite one-dimensional $[M(NCS)_2]_n$ chains whereas the tvp ligands fill the two remaining axial positions of the octahedron and connect two different parallel $[M(NCS)_2]_n$ chains (see chart 1, right).

Magnetic properties

The temperature dependence of the $\chi_M T$ (χ_M being the molar magnetic susceptibility) for **1** (H = 1000 G) and **2** (300 G) is shown in Figure 1. The $\chi_M T$ value at room temperature is 3.4 (**1**) and 2.97 (**2**) $cm^3\ mol^{-1}\ K$. They are as expected for pseudoctahedral high-spin iron(II) and cobalt(II) compounds where the $^5T_{2g}$ (Fe(II)) and $^4T_{1g}$ (Co(II)) ground state orbital degeneracies have been removed partially by a low symmetry crystal field. The $\chi_M T$ value decreases smoothly in the 298-50 K temperature range for **2**, because of the spin-orbit coupling. This effect seems to be negligible for **1**. At temperatures lower than 100 (**1**) and 40 K (**2**) the $\chi_M T$ values increases sharply with decreasing temperature indicating the occurrence of a net ferromagnetic coupling



[M(II)(tvp)$_2$(NCS)$_2$] catenane system

proposed structure for [M(II)(tvp)(NCS)$_2$]

Chart 1

which takes place likely along the $[M(NCS)_2]_n$ chains. In order to get an estimate of the coupling exchange constant we have attempted to fit the data in the 100-4 (**1**) and 40-4 K (**2**) temperature ranges by using the classical spin model of Fisher [5]. The solid lines in Figure 1 represent the calculated $\chi_M T$ values. They match quite well the experimental data in the temperature regions above mentioned. The computed value of the coupling constant is *ca.* $+2\ cm^{-1}$ for both compounds.

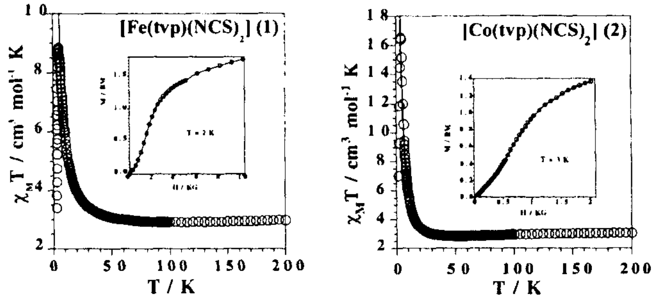


FIGURE 1. $\chi_M T$ versus T plot for compounds **1** and **2** (the inset shows the M versus H plot)

Below 4 K, $\chi_M T$ decreases rapidly and a maximum of χ_M is observed close to 4 K for applied fields lower than 1300 (**1**) and 450 G (**2**). The presence of this maximum is a clear indication that an interchain antiferromagnetic coupling is involved. Interestingly, the bulk magnetic properties of **1** and **2** show field dependence. These peculiar magnetic properties at low temperature are consistent with a metamagnetic behavior.

The temperature dependence of M/H (M and H being magnetization and applied magnetic field, respectively) at various fields is shown in Figure 2. For values of H less than 1300 (**1**) and 450 G (**2**), the M/H versus T curves present a maximun at *ca.* 4 K revealing the occurrence of an interchain antiferromagnetic coupling. This maximum disappears when H reaches 1300 G (**1**) and 450 G (**2**). The interchain antiferromagnetic coupling is destroyed by the field and **1** and **2** behave in a ferromagnetic fashion. This metamagnetic behavior is confirmed by the characteristic inflexion observed in the field dependence of the magnetization depicted in the inset of Figure 1.

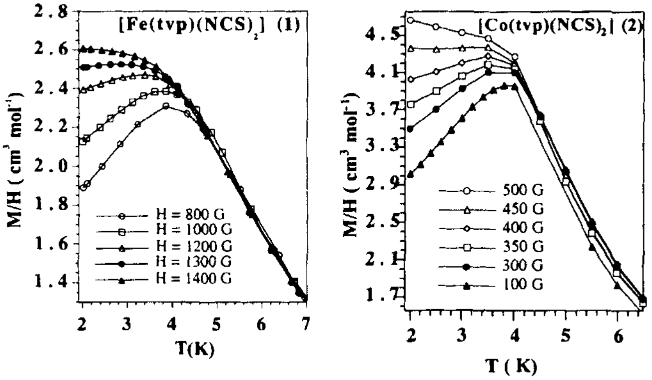
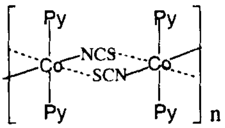


FIGURE 2. M/H versus T plot for compounds **1** and **2**.

Concluding remarks

The magnetic properties of **1** and **2** agree well with those of the related Fe(py)$_2$(NCS)$_2$ (**3**) (py = pyridine) compound reported long ago [3]. **3** also exhibits very low-field (*ca.* 1000 G) metamagnetic behavior. In addition, the molecular structure of **3** was derived indirectly from the single-crystal structure of Co(py)$_2$(NCS)$_2$ (**4**) because of they are isomorphous. Single-crystal studies of **4** revealed that the repeating unit is that shown in the following scheme.



The structure of **4** corresponds thus to a linear chain with trans-axial pyridine groups coordinated to the cobalt(II) ion [4]. Hence, these facts give support to the structure proposed for **1** and **2**.

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