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$NH_4Ni(mnt)_2.H_2O$. A NEW 1D ORGANIC FERROMAGNET

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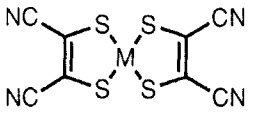
Abstract $NH_4Ni(mnt)_2.H_2O$ shows localized moments with antiferromagnetic coupling at room temperature. The antiferromagnetism persists down to 100K at which point there is an abrupt change in the slope of the susceptibility corresponding to an anomaly observed in the resistivity. Below 100K there is evidence for ferromagnetic coupling between the spins. The crystal has an orthorhombic space group Pnam, with a=12.096Å, b=3.918Å, c=29.216Å, U=1384.8Å^3 and Z=4, and the crystal structure is highly anisotropic, in common with other charge transfer salts of this type. The anions form uniform stacks along the b-axis in which the molecules are tilted by 26° to the stacking axis. Results are presented here on the electrical and magnetic behaviour of this salt .

INTRODUCTION

Most complexes of the type M'M(mnt)$_2$ where M' = Li, Na, K. NH_4, Rb and Cs, M = Ni, Pt and Pd, and mnt = maleonitrile dithiolate, crystallise with a 1:1 ratio of M' to M(mnt)$_2$ molecules, with the M(mnt)$_2$ molecules arranged in one dimensional uniform stacks, and with only minor structural differences between them[1]. All the 1:1 salts are semiconductors at room temperature, and most behave as Heisenberg antiferromagnets, with a transition to an activated susceptibility at low temperatures which is thought to arise from a low temperature dimerisation of the lattice[2]. In particular, the ammonium salt, $NH_4Ni(mnt)_2.H_2O$, was reported by Isett et al[3] to exhibit antiferromagnetic behaviour similar to that of the other mnt salts, but we found that crystals prepared under similar conditions gave very different behaviour, with a transition to ferromagnetic coupling below about 100K, leading to the formation of a ferromagnetically-ordered state below 4.9K. We report here on conductivity, structural and magnetic measurements which we have carried out on this material.



The M(mnt)2 complex (mnt is the maleonitrile dithiolate ligand).

CONDUCTIVITY MEASUREMENTS

The electrical conductivity of the salt was measured along the needle axis of the crystal (b-axis) (Figure 1). The salt is semiconducting, with an activation energy for the conductivity of about 70meV at room temperature, which increases on cooling to 110meV at 170K. From the figure, a small anomaly can be seen just below room temperature (280K), but a clearly defined transition occurs at ~120K on cooling and ~150K on warming and is associated with a factor of two change in the conductivity. The exact temperature of the transition depends on the thermal history of the salt. (Isett et al found a transition between 220 and 180K[3]). Below the transition the salt is still semiconducting, but has a smaller activation energy of about 50meV. The thermal hysteresis of the conductivity is a strong indication that there is a first-order structural phase transition with a significant energy barrier between the two structures.

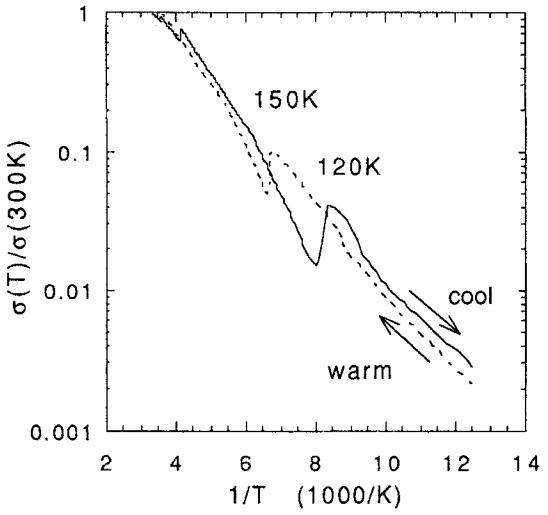


FIGURE 1. The temperature dependence of the conductivity of $NH_4Ni(mnt)_2.H_2O$ along the b-axis at ambient pressure, normalised to $\sigma(300K)$.

MAGNETIC MEASUREMENTS

The magnetic spin susceptibility of $NH_4Ni(mnt)_2.H_2O$ has a room temperature value of $1x10^{-3}$ emu/mol which increases rapidly as the material is cooled. Plots of χ

and $1/\chi$ against temperature are shown in Figures 2 & 3. The material clearly shows antiferromagnetic behaviour between room temperature and ~100K, since a straight line fit to the $1/\chi$ plot has a negative intercept on the temperature axis. In this region the susceptibility can be fitted either to a simple Curie-Weiss law ($\chi = C/(T-\theta)$) with θ = -120 K, or more appropriately by a Bonner-Fisher type fit[4] for a 1D Heisenberg antiferromagnet, with J = 57K and 0.95 spins per molecule (referring to the expected susceptibility of 1 mole of s=1/2 spins with $g_{av} = 2.07$). Below about 100 K the plot of $1/\chi$ tends to zero at a positive temperature, indicating that ferromagnetic coupling between the spins now dominates the magnetic behaviour. A fit to the Curie-Weiss law in the region 20-70K gives C = 0.156 emuK/mol and θ = +7K. By comparison with the Curie constant expected for a mole of s=1/2 electrons (g=2.07, C=0.401 emuK/mol) it can be seen that in the high temperature antiferromagnetic region the Curie constant is approximately that expected for one s=1/2 spin per formula unit, while in the region of ferromagnetic coupling only ~0.4 spins are contributing to the susceptibility, based on fits to both a Curie-Weiss and a ID Ising model.

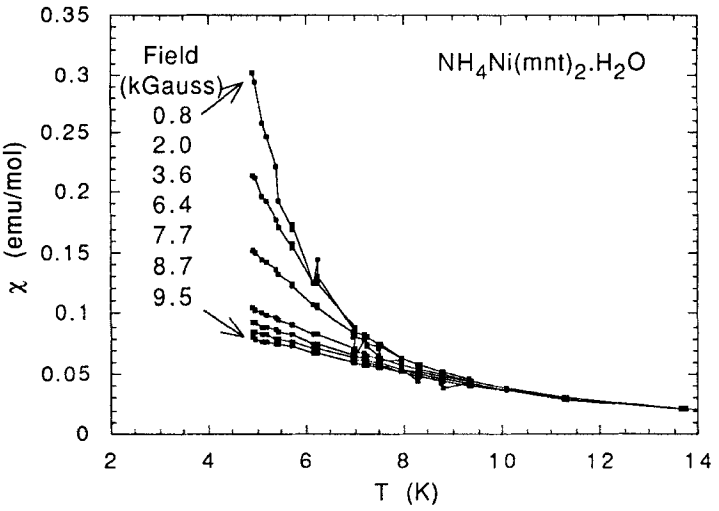


FIGURE 2. The magnetic susceptibility in various fields of polycrystalline samples of NH4Ni(mnt)2.H2O at low temperatures.

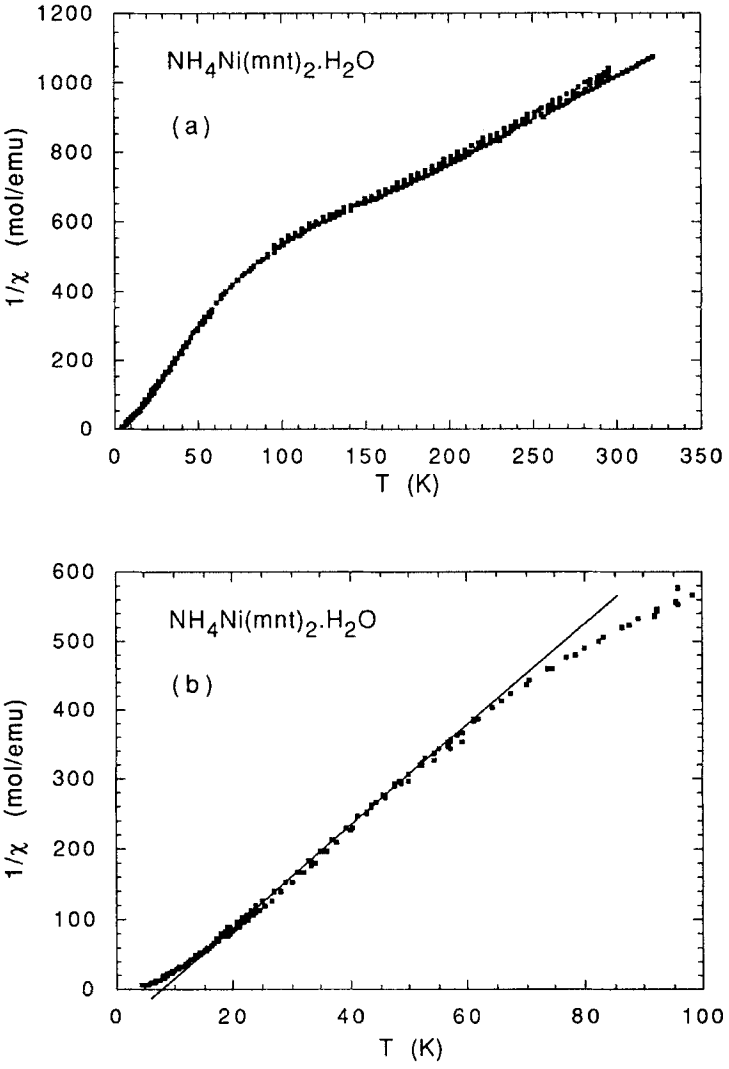


FIGURE 3. The magnetic susceptibility of a polycrystalline sample of $NH_4Ni(mnt)_2.H_2O$. The data are corrected for the calculated contribution of the core electrons (-140×10^{-6} emu/mol). The straight line in (b) is the Curie Weiss fit to the data between 20-70K, which has a positive intercept of 7K.

STRUCTURAL MEASUREMENTS

In view of the unusual magnetic behaviour of this material, a full structure determination was carried out at room temperature using a Stoe four-circle X-ray diffractometer. It was found that the structure was the same as that reported[1] but the quality of the new crystal was sufficient to identify the crystal space group, which was not known previously. The structure is orthorhombic, space group Pnam, with a=12.096Å, b=3.918Å, c=29.216Å, U=1384.8Å^3 and Z=4. The anions form uniform stacks along the b-axis in which the molecules are tilted by 26° to the stacking axis (Figure 4). This gives a perpendicular separation between the anions of only 3.52Å.

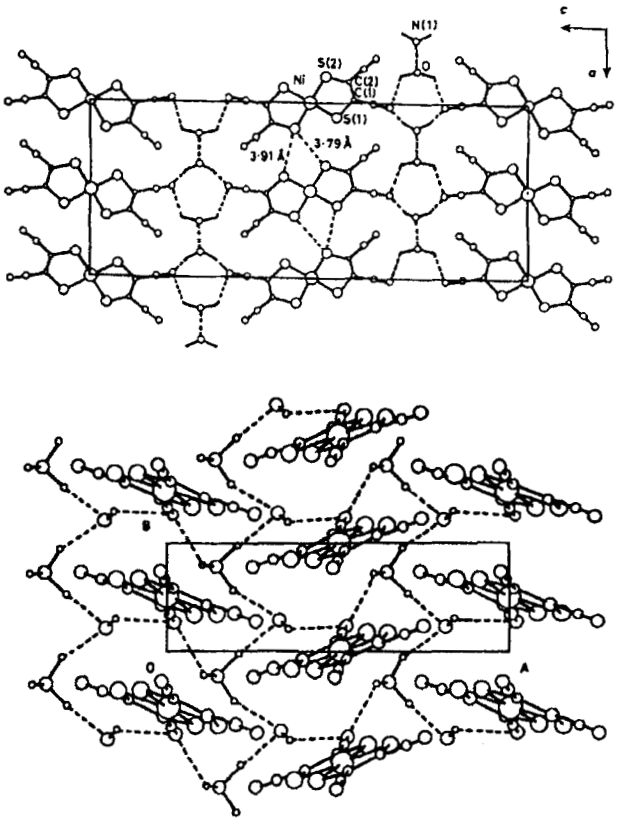


FIGURE 4. The crystal structure of NH4Ni(mnt)2.H2O, viewed (a) down the b-axis, and (b) down the c-axis[1]. The hydrogen-bonding interactions are marked by dashed lines.

The stacks are arranged in sheets parallel to the a-b plane, separated by sheets of hydrogen-bonded cations and water molecules which are hydrogen bonded to one CN group of each (mnt) ligand. Within the anionic sheets the neighbouring stacks are stepped up by b/2 giving interstack distances of 3.79Å and 3.91Å. These contacts are considerably greater than the van der Waals radius, suggesting very little interaction along this direction. In spite of this, the crystal structure of this material is still highly anisotropic, in common with other charge transfer salts of this type. An attempt has been made to determine the structure at 98K but single crystal studies at low temperature have so far been impeded by the crystal fracturing as it passes through the transition. This behaviour supports the resistivity results indicating that a substantial rearrangement of the lattice is taking place.

CONCLUSION

We have shown that at room temperature the spins in $NH_4Ni(mnt)_2.H_2O$ are coupled by 1D antiferromagnetic interactions with an exchange energy J~60K. Between 4K and 70K the salt behaves as a 1D ferromagnet with J~20K, and ~0.4 spins per molecule.

A virtual exchange model[5] cannot account for the ferromagnetic properties of this salt, since the spin on the $Ni(mnt)_2$ anion lies in a non-degenerate orbital. A spin polarisation mechanism predicts antiferromagnetic spin interactions at room temperature, as observed experimentally, and would predict ferromagnetic interactions for certain arrangements of the $Ni(mnt)_2$ molecules. It seems that a structural phase transition at ~120K has distorted the crystal lattice so that ferromagnetic interactions can take place but it is unclear why only some of the spins are contributing to the susceptibility in the ferromagnetic region. Further measurements on the lattice distortion and magnetic behaviour at low temperatures are now being carried out to explain this spin loss and to determine the exact nature of the spin lattice in the ferromagnetic region.

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