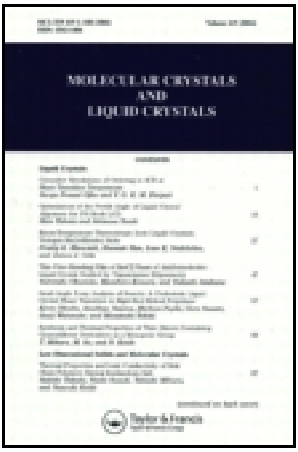

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Characterisation of New Organic Ligand-Based Magnets: [M_NTTP] [TCNE] and [M_NTTP][TCNQ]

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CHARACTERISATION OF NEW ORGANIC LIGAND-BASED MAGNETS: [MNTTP] [TCNE] AND [MNTTP][TCNQ]

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Abstract: We analysed the temperature and field dependence of the magnetisation of the electron transfer salts meso-(Tetratolylporphinato)manganese(III)-tetracyanoethenide, $[\mathrm{Mn^{III}TTP}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$ and meso-(Tetratolylporphinato)manganese(III)-7,7,8,8-tetracyano-p-quinodimethane $[\mathrm{Mn^{III}TTP}]^{\cdot +}[\mathrm{TCNQ}]^{\cdot -}$. They show cooperative magnetic behaviour for temperatures below 10 K.

We have pursued two approaches to attaining cooperative magnetic behaviour in organic materials: (1) creating organometallic complexes with transition elements as complex ions, and (2) using purely organic materials built up of free radicals. The latter was realised by growing single crystals of newly synthesised nitronyl nitroxide radicals. Composed of mono-, di- and triradicals, low and high spin systems were found with an intramolecular exchange much stronger than the intermolecular coupling. This part will be published elsewhere.[1]

MANGANESEPORPHYRIN-COMPLEXES

By using the larger spin moment of manganese larger magnetic susceptibilities and stronger exchange interaction can be obtained compared to purely organic compounds. In order to analyse the influence of small molecular modifications of meso-(Tetraphenylporphinato)manganese(III)-tetracyanoethenide[2], $[\mathrm{Mn^{III}TPP}]^{\cdot +}[\mathrm{TCNE}]^{\cdot -}$, we have synthesised charge transfer salts of the type meso-(Tetratolylporphinato)manganese(III)-7,7,8,8-tetracyano-p-quinodimethane [MnTTP]-[TCNQ] and [MnTTP]-[TCNE]. Both showed magnetic ordering at low temperatures but a significantly different dependence on magnetic field and temperature of the magnetic moment.
Since we expect that the crystallographic structure is similar to systems synthesised earlier by Miller et al.[3], magnetic chains built up by an array of Manganese and TCNQ/TCNE spins with $S^{(Mn)} = 2$ and $S^{(TC)} = 1/2$ may be the appropriate model for a quantitative description of the present system. According to this, the effective moment μ_{eff} per formula unit should be, for independent isotropic g=2, S=2, and S=½ radicals,

$$\mu_{eff} = \mu_B \left\{ \left[\left(g^{Mn}\right)^2 \cdot S^{Mn}(S^{Mn}+1) + \left(g^{TC}\right)^2 \cdot S^{TC}(S^{TC}+1) \right] \right\}^{1/2} = 5.2\mu_B . \qquad (1)$$

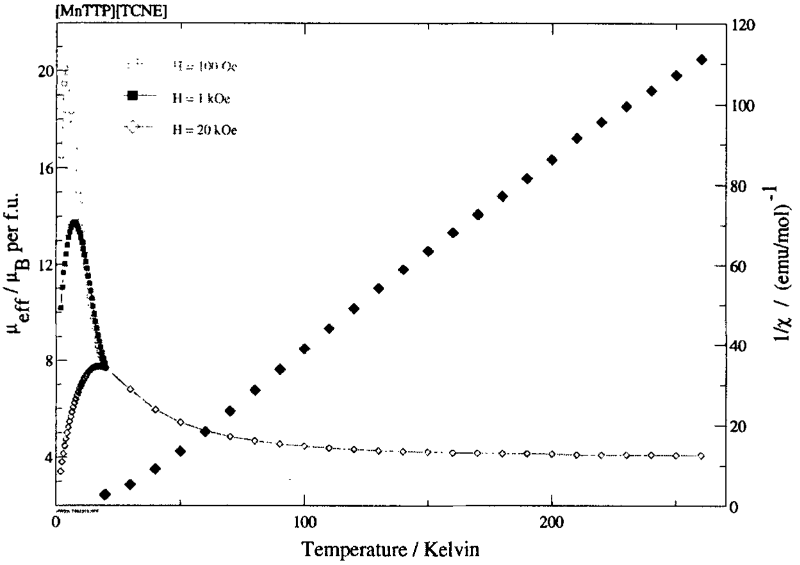

Figure 1: Effective moment per formula unit as function of temperature at three different field strengths of H = 20 kOe, 1 kOe and 100 Oe and reciprocal molar magnetic susceptibility (right scale) at a field strength of 20 kOe, assuming [MnTTP][TCNE] as the molecular unit.

The temperature dependence of the effective magnetic moment of [MnTTP]-[TCNE], measured on a powder sample with a SQUID magnetometer at three different field-strengths of H = 0.1, 1.0 and 20 kOe, is shown in Figure 1.

The observed effective moment shown in figure 1 deviates about 20 % from the nominal value which may be due to built-in solvent molecules and not fulfilling the high temperature limit. The intra- and interchain coupling should also give rise to a pronounced deviation from a simple Curie law. An analysis by fitting of a Curie-Weiß law, reduced by a temperature independent diamagnetic contribution should take that into account:

$$\chi(T) = \frac{C}{T-\theta} + \chi_{dia} \qquad (2)$$

A least-squares fit for temperatures above 200 K gives for the Curie-Weiß temperature θ = -9 K and for the Curie constant C = 2.3 emu K/mol if potential solvent inclusion is neglected when determining the molar weight. At this point it must be remarked that the value as well as the sign of the Curie-Weiß temperature changes if the temperature range is extended to lower temperatures. This behaviour indicates that the spins are coupled antiferromagnetically, leading to a bulk ferrimagnet with competing magnetic interactions between and within the stacks. Below 100 K, the effective moment *increases* (figure 1) and below 5 K magnetic susceptibility revealed no longer a linear field dependence (figure 2). The onset of a three-dimensional ferrimagnetic ordering is proved by a hysteresis loop measured at T = 5 K and T = 2 K (figure 2) and onset of a spontaneous magnetic moment.

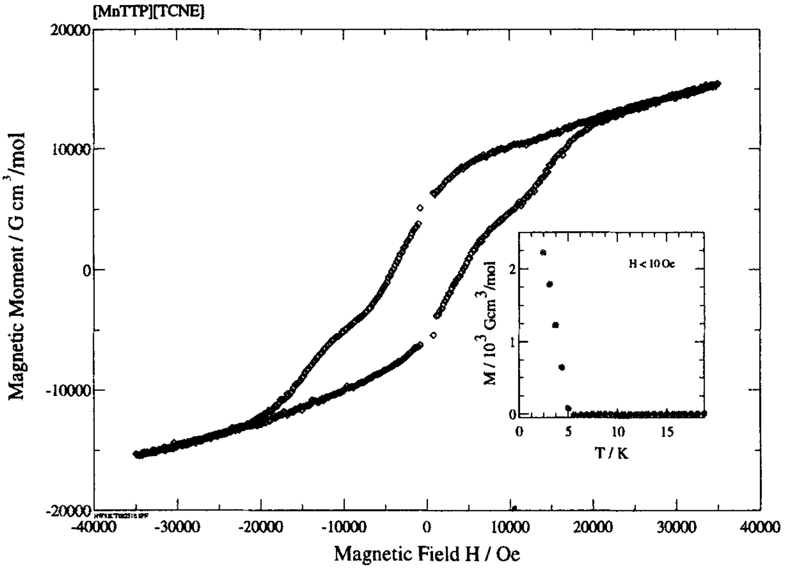

Figure 2: Field dependence of the magnetic moment at a temperature of 2 K. The three-dimensional ferrimagnetic ordering is proved by a hysteresis loop and the onset of a spontaneous moment in a magnetic field of less than 10 Oe.

These experimental data suggest that antiferromagnetic correlations of S=1/2 and S=2 spins in one-dimensional [MnTTP]-[TCNE] chains are established before three-dimensional ferrimagnetic ordering takes place. The coercive field strength is about (4 ± 0.5) kOe. The saturation value $M_S(T=0)$ for a ferrimagnetic coupled spin system of S=1/2 and S = 2 spins should be 16750 Gcm^3/mol which is in agreement with the experimental data. Since these measurements were performed on powder samples no further details could be extracted.

The temperature dependence of the effective magnetic moment of [MnTTP]-[TCNQ] measured on a polycrystalline sample at three different field strengths of H = 0.1, 1.0 and 20 kOe and the reciprocal susceptibility is shown in Figure 3.

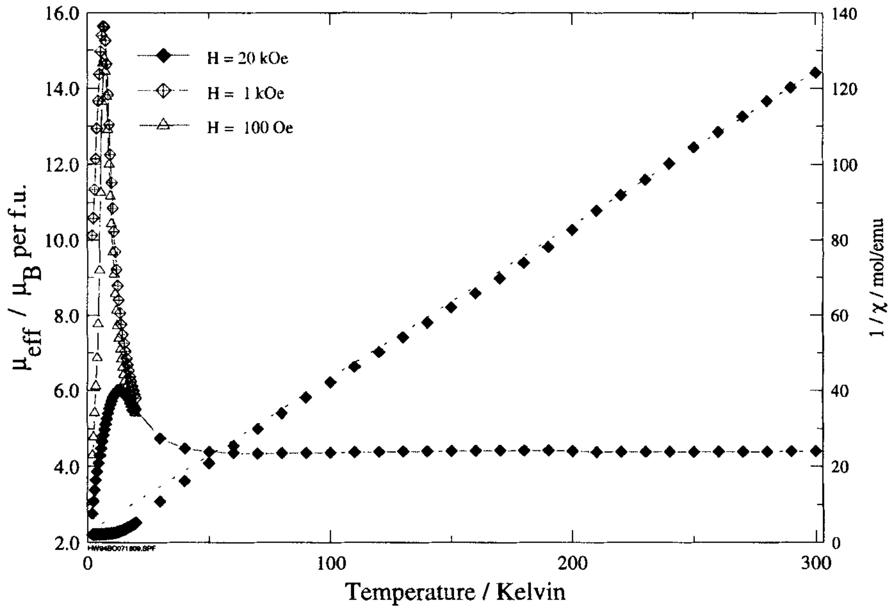

Figure 3: Effective moment per formula unit as function of temperature (left scale) and reciprocal molar magnetic susceptibility (right scale) at three different field strengths of 20 kOe, 1 kOe and 100 Oe, assuming $[Mn^{III}TTP]^{\cdot+}[TCNQ]^{\cdot-}$ as the formula unit.

The high-temperature susceptibility (T › 200 K) was analysed by fitting of a Curie-Weiß law reduced by a temperature independent diamagnetic contribution as mentioned above. A least square fit gives for $\theta = -10$ K and for C = 2.5 emu·K/mol if potential solvent inclusion is neglected when determining the molar weight. The observed effective moment shown in figure 3 deviates about 15 % from the nominal value. The negative Curie-Weiß temperature of -10 K indicates that the predominating exchange interaction must be antiferromagnetic. The onset of a three-dimensional antiferromagnetic ordering takes place, at least for the smallest field of 100 Oe, at a temperature of 7.0 ± 0.5 K (figure 5).

Similarly to the TCNE complex, the effective moment *increases* (figure 3) below 50 K.

These experimental data suggest that ferrimagnetic correlations in one-dimensional [MnTTP]-[TCNQ] chains are established before three-dimensional antiferromagnetic ordering takes place at 7 K. Therefore, we analysed quantitatively the dependence of the magnetic moment on the external field at three different temperatures. At 20 K no deviation from a linear behaviour can be detected[4]. At a closer view one discerns a slight curvature in the field dependence of the magnetic moment at 5 K, but not at 10 K (figure 4).

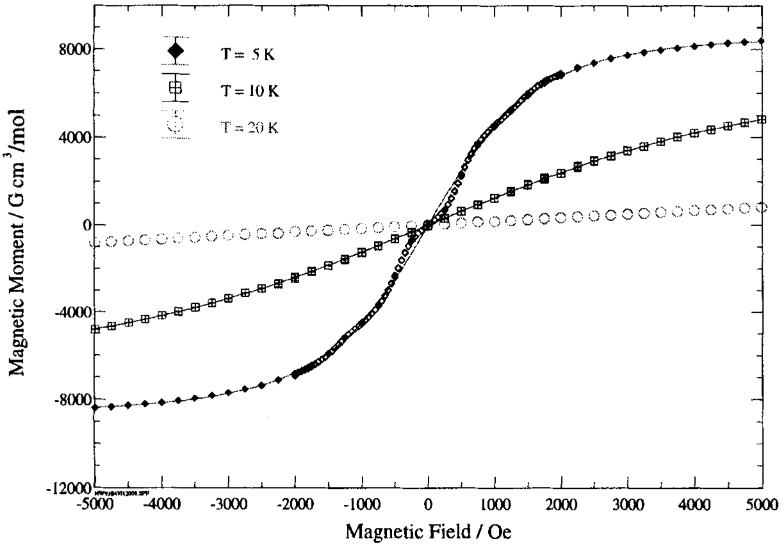

Figure 4: Field dependence of the magnetic moment at three different temperatures. At temperatures of 5 K and lower, a strong deviation from the plotted Brillouin function can be seen.

To allow better insight, the first derivative of the magnetic moment at 5 K is shown in figure 5.

From the maximum of the differential susceptibility, spin flopping of the three-dimensional antiferromagnetic arrangement at 5 K at a field of less than 500 Oe must be inferred. Increasing the field strength may eventually lead from this spin flop phase to a paramagnetic phase.

A comparison of the saturation behaviour (fig. 2 and fig. 4) leads to the interesting result, that the TCNE and TCNQ systems respond quite different. Although the curvatures show similarities in their slopes, but not in their characteristic behaviour and approached values for the magnetic moment (T=2K, H=20kOe: M^{TCNQ} = 9470 Gcm^3/mol, M^{TCNE} = 12100 Gcm^3/mol). At the moment we have no quantitative model of this strange result but it may be connected with the possibility that there remain antiferromagnetically coupled spins in the TCNQ system. Also other energy barriers are conceivable and our field strengths are not high enough to break these couplings.

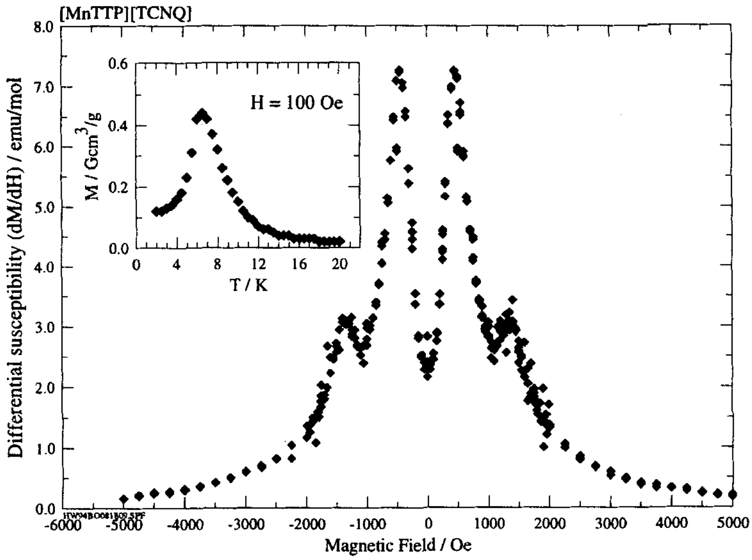

Figure 5: Differential molar susceptibility (dM/dH) calculated as first derivative of the molar magnetic moment as function of magnetic field at a temperature of T = 5 K. INSET: Temperature dependence of the magnetic moment for magnetic field strength of 100 Oe.

This is a further example[2,3] for the observation how important the effect of counterions or minor structural changes (i.e. inclusion of solvent molecules) can be, as it changes in our system the sign of the magnetic interchain interaction of the TCNE system compared to the TCNQ system.

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