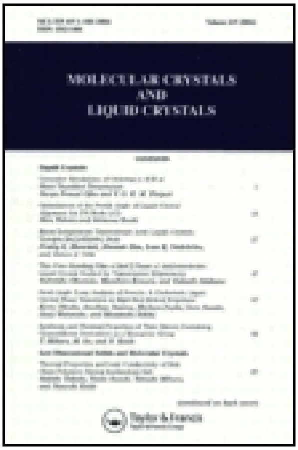

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New Magnetic Iron(II) Chelate and Iron(III) Chelate TCNE$^-$ Complexes with a T_c of 10 K

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New Magnetic Iron(II) Chelate and Iron(III) Chelate TCNE$^{\bullet}$ Complexes with a T_c of 10 K

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The high spin iron(II) chelate complex **Fe1x2MeOH** as well as its 1:1 derivative with TCNE have been investigated with respect to cooperative magnetic properties. **Fe1x2MeOH** represents a magnetic chain compound, wherein an intermolecular interaction via hydrogen bonds between the OH-groups of axially coordinated methanol and the ester groups located on the ligand periphery is observed. The weak spontaneous magnetization below approximately 10 K indicates cooperative magnetic behavior. The reaction of the iron(II) chelate complex with the electron acceptor TCNE leads to a 1:1 charge-transfer complex. The spontaneous magnetization occurs here below 10 K and is significantly higher compared to the magnetic iron(II) chelate chain compound.

Keywords: magnetic chain compound; iron chelate; charge-transfer; TCNE

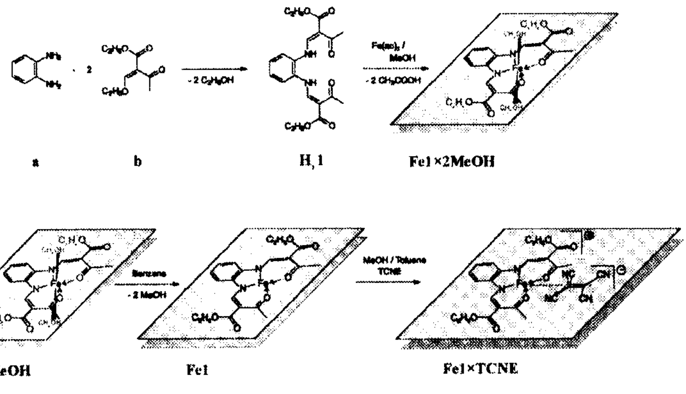
INTRODUCTION

The study of molecule-based magnets is an area of interdisciplinary research and deals with the design, synthesis and magnetic characterization of new materials with enhanced T_c's. In 1992, Miller and co-workers[1] found one class of molecule-based magnets exemplified by $[\mathrm{MnTPP}]^+[\mathrm{TCNE}]^-$ (TPP = meso-tetraphenylporphinato, TCNE = tetracyanoethylene). This complex shows an extended linear chain of alternating donor and acceptor molecules (D^+A^-) which exhibits a long-range magnetic behavior at a critical temperature of $T_c = 18$ K.

In our approach to magnetic materials we have studied an iron(II) chelate complex which forms linear chains and exhibits spontaneous magnetization below $T_c = 9.5$ K. It is noteworthy that this iron(II) complex contains ester groups on the ligand periphery which are essential for the chain formation. Furthermore, this complex is able to react with electron acceptors forming charge-transfer complexes. A new magnetic iron(III) chelate $TCNE^-$ complex with alternating $S = 5/2$ iron(III) high spin and $S = 1/2$ $TCNE^-$ radicals is presented here.

RESULTS AND DISCUSSION

The synthesis of the iron(II) chelate complex and the corresponding charge-transfer salt is schematically illustrated in scheme 1. The chelate ligand **$H_2$1** was synthesized according to literature[2] by 1:2 condensation of 1,2-diaminobenzene (**a**) with ethoxymethylene-ethylacetoacetat (**b**). Iron(II) acetate reacts with the free ligand **$H_2$1** in methanol under inert conditions to form the iron(II) complex **Fe1** [(E,E)-[{diethyl 2,2'-[1,2-phenylenebis-(iminomethylidyne)]bis[3-oxobutanoato]}(2-)-N,N'O^3,$O^{3'}$] iron(II)] as its adduct with two axially coordinated methanols[3], **Fe1×2MeOH**. The removal of the axially coordinated methanol can be performed by extracting this complex in benzene yielding the complex **Fe1**. This solvents free species reacts with TCNE in methanol/toluene solution by a one electron transfer process to give the 1:1 charge-transfer salt **Fe1×TCNE**.



SCHEME 1 Reaction route for the magnetic compounds

The diadduct **Fe1×2MeOH** was characterized by X-ray crystallography. It has been shown that intermolecular interactions via hydrogen bonds between the OH-group of axially coordinated methanols and the ester groups located on the ligand periphery occur forming in this way linear chains. The hydrogen bond length $CH_3\underline{\mathbf{O}}\mathbf{H} \cdots \underline{\mathbf{O}}$=COEt is 2.744(4) Å and indicates a strong interaction[4].

The IR frequencies of the ester groups (C=O valence vibration) for the complex **Fe1** are 1701 and 1685 cm^{-1} (Table 1). In the case of **Fe1×2MeOH**, the bands are significantly shifted to lower wave numbers and occur as a broad band at 1668 cm^{-1}. The shift can be explained by the formation of H-bridges in which the ester groups are involved. In the solvent free **Fe1**, the C=O frequencies are nearly the same as in the analogous nickel and copper complexes[2] where no intermolecular coordinations were observed. Thus, we assume that also in the case of **Fe1** such intermolecular coordinations (interactions) should only be very weak.

TABLE 1 IR frequencies [cm^{-1}] of the ester groups ($\underline{CO}$OEt) located on the ligand periphery and the CN groups of the reduced acceptor TCNE$^-$

Compound	$\nu_{\underline{CO}OEt}$ [cm^{-1}]	ν_{CN} [cm^{-1}]
$H_2$1	1708	-
Fe1	1701/1685	-
Fe1×2MeOH	1668	-
Fe1×TCNE	1654 (broad)	2224/2187/2146/2079

The magnetic behavior of **Fe1** and **Fe1×2MeOH** are illustrated in Fig. 1. The molar susceptibility χ_M for both complexes can be fit by the Curie-Weiss law according to

$$\chi_M = \frac{C}{(T-\theta)}$$

(C: Curie constant; θ: Weiss temperature). The least-squares fit in the temperature range between 300 and 5 K gives for the complex **Fe1** the values $\theta = -4.7$ K and C = 2.93 cm^3 K mol^{-1} and for the **Fe1×2MeOH** the data $\theta = +5.3$ K and C = 3.06 cm^3 K mol^{-1}. This means that the iron(II) chelates are high spin complexes and a spin transition to low spin is not observed in the measured temperature range. The **Fe1×2MeOH** complex shows a very small deviation from the Curie-Weiss plot at T < 12 K indicating a very weak magnetic interaction between the high spin iron(II) d^6 spin states. In contrast to

Fe1 , the diadduct **Fe1×2MeOH** shows a weak spontaneous magnetization below 9.5 K indicating a long-range magnetic ordering behavior for this chain compound (compare the inset in Fig. 1). The disappearance of this long-range behavior for **Fe1** is consistent with the observed IR frequencies of the ester carbonyl groups (Table 1) which give no hints to intermolecular interactions.

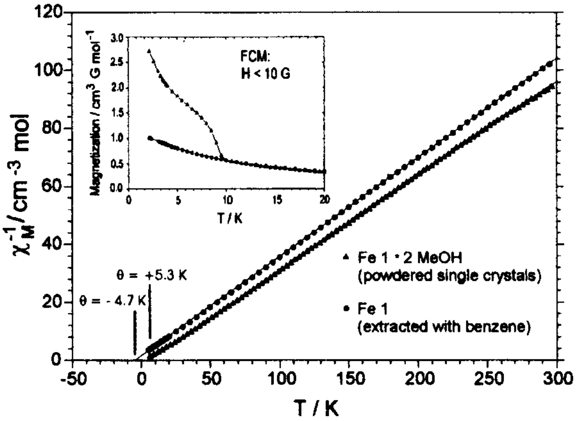


FIGURE 1 Reciprocal molar susceptibility, χ_M^{-1}, as a function of temperature T and field-cooled magnetization (FCM) vs T curve measured under a weak field of H < 10 G (inset) for the complexes **Fe1** and **Fe1× 2MeOH**.

In our synthetic approach to magnetic charge-transfer complexes, we have synthesized a new magnetic iron(III) chelate $TCNE^-$ complex derived by oxidation of the iron(II) chelate **Fe1**. The magnetic properties of this complex are illustrated in Fig. 2. The $\chi_M T$ product is 5.25 K cm^3 mol^{-1} at 300 K. This value corresponds to the high-temperature limit $(\chi_M T)_{HT}$ at T = 300 K calculated from the sum of the local contributions of isotropic and independent g = 2.11, S = 5/2 high spin iron(III) and g = 2.00 and S = 1/2 $TCNE^-$ radicals according to

$$[\chi_M T]_{HT} = \frac{N\beta^2}{3k}[g^2_{iron(III)} S_{iron(III)}(S_{iron(III)} + 1) + g^2_{TCNE} S_{TCNE}(S_{TCNE} + 1)]$$

where N is the Avogadro number, k the Boltzmann constant and ß the Bohr magneton. On cooling, the product $\chi_M T$ decreases, reaching a rounded minimum of 3.51 K cm^3 mol^{-1} at about 20 K, and then increases as the temperature is lowered further to 10 K. Finally, below 10 K, $\chi_M T$ decreases rapidly.

The magnetic behavior in the temperature range between 300 and 20 K can be explained by assuming an antiferromagnetic coupling between the high spin states of iron(III) and the $S = 1/2$ states of the TCNE$^-$ radicals. The formation of the TCNE$^-$ radical was determined by infrared spectroscopy monitoring the shift of the ν_{CN} vibrations. The neutral TCNE shows IR frequencies at 2260 and 2221 cm^{-1} which are shifted to 2224, 2187, 2146 and 2079 cm^{-1} for TCNE$^-$ in the **Fe1×TCNE** complex (Table 1). The observed minimum in the $\chi_M T$ vs T plot, monitored here at 20 K, is characteristic for a ferrimagnetic chain in which two kinds of different magnetic centers alternate.

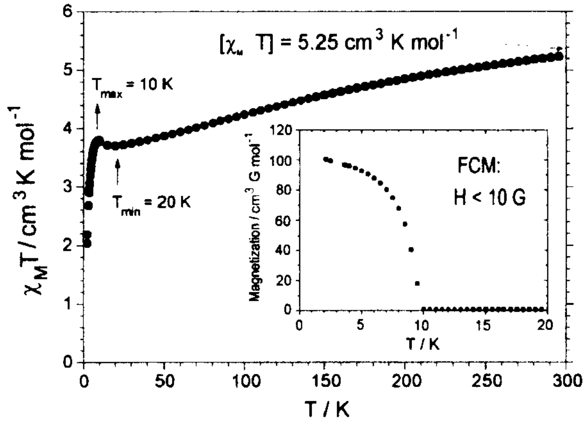


FIGURE 2 $\chi_M T$ vs T plot for the 1:1 charge-transfer complex **Fe1×TCNE**. The inset shows the field-cooled magnetization (FCM) curve measured under a magnetic field of $H < 10$ G.

The field-cooled magnetization (FCM) curve obtained on cooling within a field of $H < 10$ G confirms that a spontaneous magnetization occurs at a critical temperature of $T_c = 10$ K (inset of Fig. 2). The onset of the spontaneous magnetization corresponds to the maximum in the $\chi_M T$ vs T plot observed in the high field magnetic measurement at H = 10.000 G. The rapid decrease of the $\chi_M T$ value below 10 K is field dependent. The relative low spontaneous magnetization below 10 K (inset of Fig. 2) should be an indication for a canting antiferromagnetic behavior of the **Fe1×TCNE** compound

The observed shift of the ν_{co} ester frequencies from 1701 and 1685 cm^{-1} (**Fe1**) to1654 cm^{-1} in **Fe1×TCNE** indicates an intermolecular interaction between the charge-transfer complexes (Table 1).

CONCLUSION

The magnetic ordered iron(II) chelate complex **Fe1×2MeOH** has been characterized by X-ray crystallography and magnetic measurements. It has been shown that this high spin complex builds up a linear magnetic chain in which the ester groups on the ligand periphery are essential for the chain formation. In general, this kind of complex seems to be an interesting candidate in order to study the structure-function relationships of molecular-based magnets because the ligand design and therefore the lewis acidity, the steric demands and the electronic behavior can be controlled by modification of the ligand periphery.

The electron transfer reaction of the iron(II) complex **Fe1** with electron acceptors (e.g. TCNE) leads to charge-transfer salts with 3-D interaction (spontaneous magnetization) at low temperatures. The critical temperature T_c for the charge-transfer complex **Fe1×TCNE** and the magnetic chain **Fe1×2MeOH** are approximately the same. Only for **Fe1×TCNE** the magnitude of magnetization is approximately forty times higher.

Acknowledgments

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