Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: S V Batty , D W Clegg , D J Simmonds , D J Craik , S Qureshi & M R Willis (1992): Toluidine Blue Tcnq - A Novel Magnetic Material, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 235-239

To link to this article: http://dx.doi.org/10.1080/10587259208047046

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 235–239
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Printed in the United States of America

TOLUIDINE BLUE TCNQ - A NOVEL MAGNETIC MATERIAL

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Abstract The TCNQ simple salt derived from the Toluidine Blue cation shows highly unusual magnetic properties. The finely powdered material moves in response to a hand held magnet. However the magnetic susceptibility measured on a Faraday balance is largely temperature independent above the Curie tail and is not abnormally large. Unusually the magnetic susceptibility saturates at around 1T, which is consistent with chains of spins having strong ferromagnetic coupling and a high S value, typically around 100.

INTRODUCTION

The magnetic properties of TCNQ complexes have been extensively explored by both esr and magnetic balance techniques[1,2]. Most commonly the materials display a strong temperature dependent paramagnetic susceptibility due to the thermal population of triplet excitons. Alternatively, a near temperature independent paramagnetism is observed[3], particularly in the more highly conducting materials, which is attributed to Pauli-like behaviour. Almost invariably a Curie law[4] paramagnetism dominates at very low temperatures, which is commonly associated with spins isolated at lattice defects. In this paper we make a preliminary report of highly unusual magnetic behaviour, consistent with ferromagnetic coupling, in the TCNQ sample salt derived from Toluidine Blue.

EXPERIMENTAL

(a) Preparation of the material (TB - TCNQ)

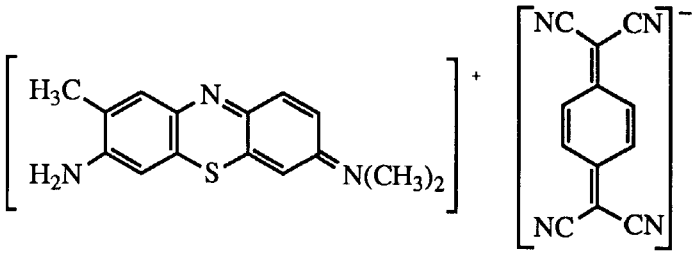

FIGURE 1 TB-TCNQ

Li(TCNQ) (0.5g) was dissolved in acetonitrile on methanol (100 ml) and to the solution was added an equimolar quantity of Toluidine blue chloride. The mixture was refluxed for 5 minutes and filtered hot. The solution was allowed to cool to room temperature and the resulting precipitate was filtered and washed with toluene, water and ether before drying. The product was a purple brown amorphous powder which decomposed above 214°C. UV/visible spectroscopy was consistent with the material being a 1:1 simple salt. The microanalysis (C = 66.75%, H = 4.15%, N = 19.8% and S = 6.46%) was also consistent with a simple salt, but suggested the presence of some lattice water. The best agreement was obtained for TB - TCNQ:0.7H_2O (calculated C ◘ 66.57, H = 4.43, N ◘ 20.12 and S ◘ 6.58). Other samples were recrystallised from acetonitrile.

The absence of metallic contaminants (Al, Fe, Ni) in the material was confirmed using atomic adsorption spectroscopy.

The room temperature electrical conductivity was $1.18 \times 10^{-6} \Omega^{-1}\ cm^{-1}$.

(b) Magnetic Measurements

Magnetic susceptibility measurements were made on a Faraday Balance operative up to 2T equipped with an Oxford Instruments cryostat permitting measurements of susceptibility and magnetisation down to 4k.

RESULTS AND DISCUSSION

Interest in the magnetic properties of this material were aroused by two qualitative observations.

(i) On moving a small hand magnet near a powdered sample some of the particles were seen to move in a somewhat similar manner to iron filings, suggesting a high paramagnetic susceptibility.

(ii) A fragment of compacted material floating on water in the presence of a magnetic field, rotated as the direction of the field was rotated, suggesting that the magnetisation and demagnetisation were not instantaneous.

Measurements of the total magnetic susceptibility as a function of temperature [Fig. 2] show no anomolies. The material is weakly diamagnetic at room temperature, and the weakly temperature dependent susceptibility only becomes paramagnetic at low temperatures.

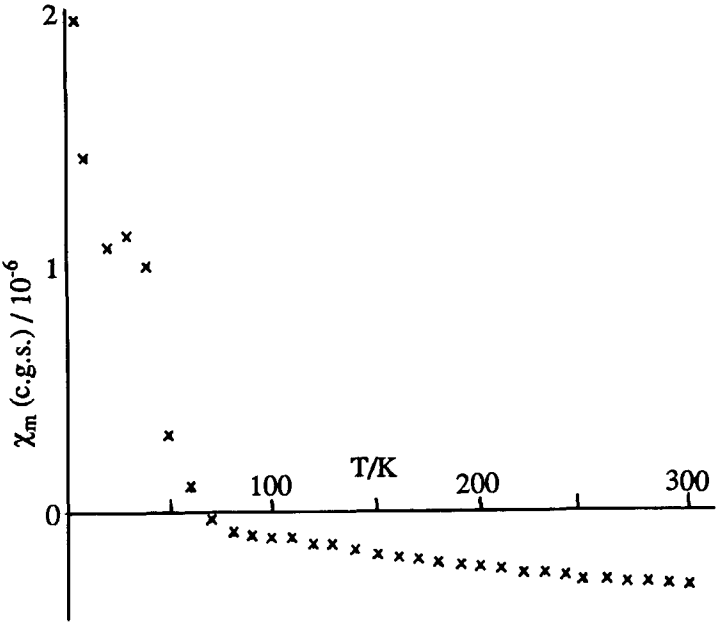

FIGURE 2 Apparent magnetic susceptibility as a function of temperature.

Highly unusual magnetic behaviour is, however, revealed in Fig. 3. The magnetisation (corrected for diamagnetism) is clearly field dependent, showing saturation at around 1T. As a consequence the susceptibility, which is the ratio of magnetisation to field, is high at low fields and low at high fields. The disparity between the qualitative observation and the observed susceptibility can therefore be understood.

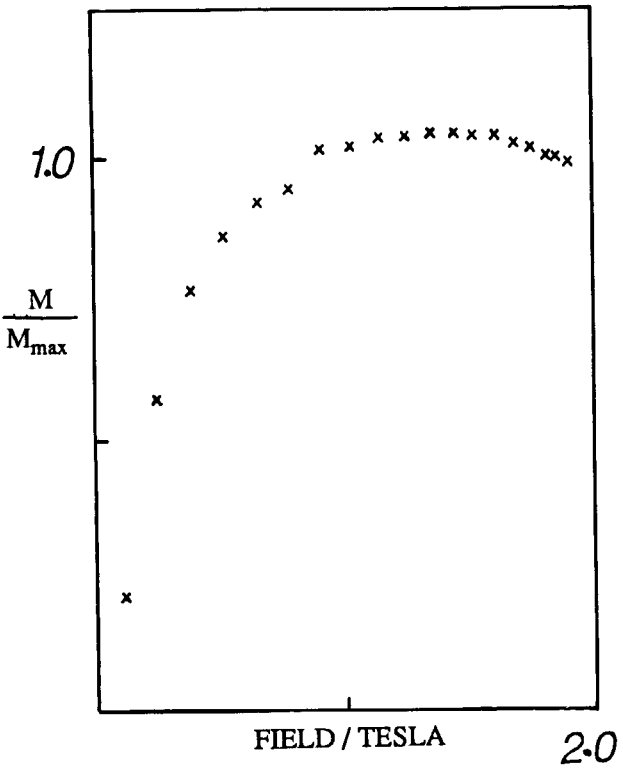

FIGURE 3 The variation of corrected magnetisation with field at 300 K

The saturation of the magnetisation of paramagnetic materials is normally found only at high fields. The field at which saturation occurs is dependent on the value of the total spin, the higher the S the lower the field required for saturation. On this basis a remarkably high value of S of approximately 100 is required. There is some degree of sample to sample variation, suggesting that defects may be involved. We therefore tentatively

propose that the coupling between spins in the ideal lattice is ferromagnetic and that the average chain length between defects (cracks, lattice vacancies or particle surfaces, etc.) is of the order of 100 TCNQ units.

The zero field molar susceptibility is given by

$$\chi = \frac{L\,\mu_o\,g^2\,\beta^2\,S\,(S+1)}{3kT}$$

for $s = \frac{1}{2}$

$$\chi_{(s=\frac{1}{2})} = \frac{L\,\mu_o\,g^2\,\beta^2}{4kT}$$

For a chain of n coupled spins, the total spin S ◘ n x $\frac{1}{2}$. The number of chains N, is L/n for a mole of spins.

Thus $$\chi_{(s=nx\frac{1}{2})} = \frac{L}{n}\,\mu_o\,g^2\beta^2\,\frac{n}{2}\,(\frac{n}{2}+1)\,\frac{1}{3kT}$$

$$= \frac{L\mu_o\,g^2\,\beta^2}{4kT}\;\;\frac{(n+2)}{3}$$

Therefore $$\chi_{(s=nx\frac{1}{2})} = \frac{n+2}{3}\;\;\chi_{(s=\frac{1}{2})}$$

Thus the existence of coupled chains gives an enhancement of the paramagnetic susceptibility of $\frac{n+2}{3}$

Under the saturation conditions the Curie dependence on temperature is not expected to be obeyed.

Experiments are in hand to explore the phenomena further, and in particular to grow single crystals for X-ray crystal structure determination and magnetic measurements.

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