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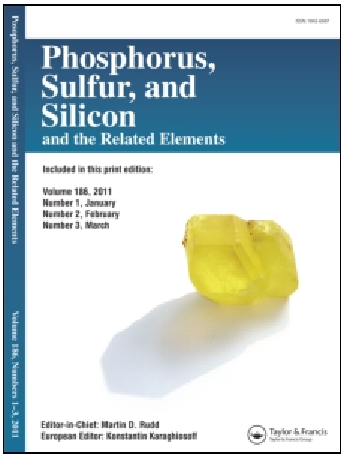

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NOVEL MAGNETIC MATERIALS BASED ON SULFUR-NITROGEN RADICALS

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The application of sulfur-nitrogen free-radicals as molecular 'bricks' for the construction of novel magnetic materials is described and exemplified by the dithiadiazolyl radical, $NCC_6F_4\overline{CNSSN}$, which becomes weakly ferromagnetic at 36K.

Keywords: sulfur; nitrogen; dithiadiazolyl; magnetism

INTRODUCTION

In recent years there has been considerable interest in the synthesis of magnetic molecular materials.[1] These may provide distinct advantages over traditional magnets; combining solubility with other physical properties such as a non-linear optical response which can interact cooperatively with the magnetic properties. Perhaps the most academically challenging area of molecular magnetism is the design and

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preparation of magnetic materials which do not contain any metal atoms. These materials are commonly referred to as *organic magnets.*

The first organic ferromagnet, β-*p*-NPNN was discovered in 1991.[2] Although the magnetic ordering temperature, Tc, below which the compound exhibits magnetic behaviour was only 0.6K, it was the fact that purely organic materials could provide a physical property which previously was associated only with metal-based materials which was so exciting.

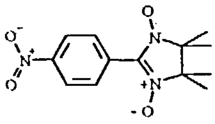	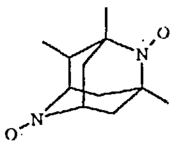	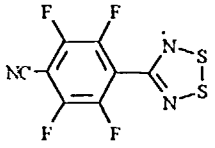
β-*p*-NPNN	DOTMDAA	β-*p*-CTFDD
0.6K	1.7K	36K
$0.503\mu_B$		$0.002\mu_B$

TABLE 1. Some organic magnets, their transition temperatures and spontaneous magnetic moments

Subsequently other workers[3] have produced a number of other organic magnets (Table 1), all of which have Tc's significantly below the temperature of liquid helium (4.2K). In this article we describe how thiazyl-based radicals can act as organic magnets through a phenomenon known as *weak ferromagnetism.*

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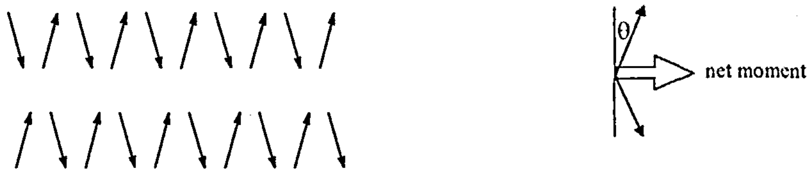
Weak Ferromagnetism

In weak ferromagnets[4] the electrons on adjacent molecules are coupled antiferromagnetically (AF) but due to some magnetic anisotropy and symmetry restraints, imposed by the crystal structure, they cannot align perfectly antiparallel. Consequently the spins are *canted* and this leads to a small net magnetic moment. The alignment of spins in weak ferromagnets is illustrated in Figure 1. There are a number of key features which are essential to a simple understanding of weak ferromagnetism. Firstly there must be no inversion centre between magnetic sublattices in order for canting to occur.



Electron spins are AF coupled but are 'canted', leading to a net magnetic moment The magnitude of the magnetic moment is dependent on the canting angle, θ.

$2\theta = \arctan[(g-g_e)/g]$.

g_e = g-value for free electron
g = observed g-value

FIGURE 1. Electron alignment and canting angles for weak ferromagnets

Structurally, the compound must crystallise in a non-centrosymmetric or polar space group.[5] Provided this can be achieved, then the magnitude of the spontaneous magnetic moment is dependent on the canting angle,θ, which is related to the degree of molecular anisotropy and is manifested in the magnitude of the g-tensor.

For organic radicals, g-values tend to be close to that observed for the free electron and canting angles tend to be rather less than 1°. Despite the small magnitudes of these spontaneous magnetic moments (typically 3 orders of magnitude less than those observed for pure ferromagnets), they can lead to large anomalies in magnetic susceptibility which may be used in magnetic devices. The transition temperature to the magnetically ordered phase is dependent on the strength of the intermolecular magnetic exchange interactions.

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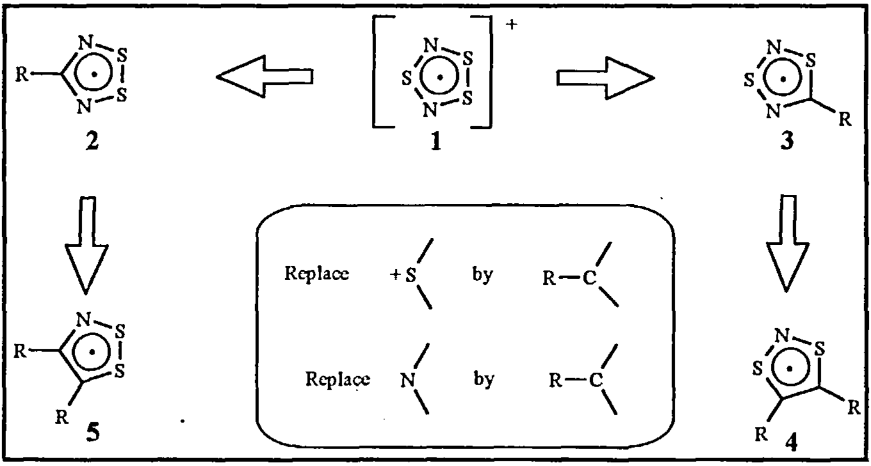
MAGNETISM AND SULFUR-NITROGEN RADICALS

Our work has primarily involved the synthesis and characterisation of a family of sulfur-nitrogen radicals, of which the $S_3N_2^{+\cdot}$ radical (1) is the parent.[6] Other members of the family can be visualised by replacing N or S^+ by R-C (Scheme 1).



SCHEME 1

The diffuse nature of the S orbitals nearly always leads to direct orbital overlap of singly occupied molecular orbitals (SOMOs) and therefore naturally favours AF exchange between radicals. These interactions can often be so strong that, although the compounds exist as radicals in solution, they form spin-paired dimers in the solid state.[6] The dimeric structure[7] of $(p\text{-}O_2NC_6H_4\overline{CNSSN})_2$ is shown in Figure 2a. If we are to use thiazyl radicals as molecular magnets, we must overcome this dimerisation process. In addition, we must exploit the tendancy for AF coupling between thiazyl radicals and attempt to design weak feromagnets. The exchange interactions between thiazyl radicals tend to be large (favouring higher Tc's) and, for weak ferromagnets, the incorporation of sulfur induces a greater anisotropy favouring relatively large canting angles.

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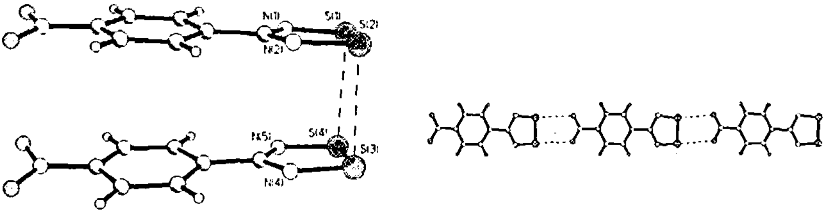

(a) (b)

FIGURE 2 (a) Structure of $(p\text{-}O_2NC_6H_4\overline{CNSSN})_2$; (b) nitro-sulfur interactions in $(p\text{-}O_2NC_6H_4\overline{CNSSN})_2$ induce chain-like structure

Design of a Weak Ferromagnet Based on Sulfur-Nitrogen Radicals

The first pre-requisite for any type of magnetic property is the presence of unpaired spins in the solid state. Consequently it is imperative that the dimerisation process associated with thiazyl radicals such as **1-5** is overcome. Dimerisation energies for **1-4** have been estimated[8-11] from solution ESR studies (Table 2). For **1** and **2**, these dimerisation energies are much weaker than covalent bonds (*c.f.* S-S at 266 kJmol^{-}

[1]), but are very strong on the scale of intermolecular van der Waals forces (the principle instrument of 'crystal engineering'). Electropositive C atoms lead to a drift of unpaired electron density away from the chalcogen and in turn this weakens the dimerisation process. In the case of **4**, the dimerisation energy is approximately zero. No data is presently available for **5**, although we can anticipate that this too will be close to zero. In this paper we will restrict our discussion to consider how derivatives of **2** can be used as weak ferromagnets.

Compound	ΔH_{dim} (kJ/mol)	Compound	ΔH_{dim} (kJ/mol)
$S_3N_2^+$ (**1**)	-45	$\mathrm{Ph\overline{CNSNS}}$ (**3**)	-19
$\mathrm{Ph\overline{CNSSN}}$ (**2**)	-37	$\mathrm{CF_3\overline{CSNSC}CF_3}$ (**4**)	~ 0

TABLE 2. Enthalpies of dimerisation for some thiazyl radicals.[8-11]

Overcoming the Dimerisation Energy

In simple aryl derivatives of **2**, the aryl and heterocyclic rings are approximately co-planar and the aryl group does not hinder dimerisation.[6] However, *ortho*-fluorinated aryl derivatives induce much larger twist angles between aryl and heterocyclic ring, making the aryl group more sterically demanding; Of a number of perfluorinated derivatives of **2**, some are dimeric[12] e.g. $(\mathrm{C_6F_5\overline{CNSSN}})_2$ whereas others are monomeric,[13] e.g. *p*-$\mathrm{NCC_6F_4\overline{CNSSN}}$.

Inducing a Spontaneous Magnetic Moment in Thiazyl Radicals

Recent results from Passmore,[14,15] Oakley[16] and co-workers have indicated that AF exchange interactions (arising from the diffuse orbitals asociated with S, and intermolecular $S^{\delta+}...N^{\delta-}$ interactions) will dominate the magnetic properties of thiazyl radicals. In order to obtain

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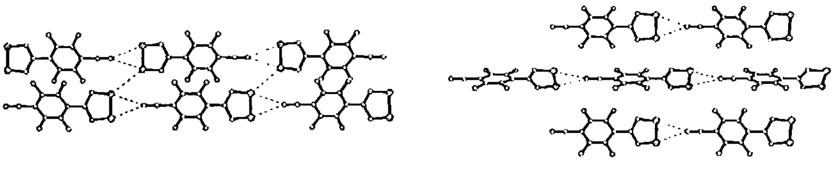
a weak ferromagnet, we must promote the formation of polar or non-centrosymmetric crystals. Our approach to this problem has been to introduce electronegative groups (E) in the *para*-position, such that one-dimensional polar chains of molecules are formed linked together through $S^{\delta+}...E^{\delta-}$ interactions. The chain-like structure of $(p\text{-}O_2NC_6H_4\overline{CNSSN})_2$ is shown in Figure 2b.

Magnetic Properties of $p\text{-}NCC_6F_4\overline{CNSSN}$

The dithiadiazolyl radical, $p\text{-}NCC_6F_4\overline{CNSSN}$, provided the first derivative of **2** which crystallises as a monomer in the solid state. In this compound the *ortho*-fluorine atoms induce a large twist between aromatic and heterocyclic rings, and intermolecular F...F repulsions assist the breakdown of the dimeric structure. The CN group in the *para*-position provides the intermolecular interactions required to produce the desired chain-like structure. In comparison to the intrachain interactions, the inter-chain interactions are weak and this is highlighted by the observation that $NCC_6F_4\overline{CNSSN}$ crystallises in two phases; in the α-phase[13] the chains are related through an inversion centre (Figure 3a) whereas the β-phase crystallises[17] in the polar space group Fdd2 in which the chains are parallel (Figure 3b). The preparation of α or β-phases is dependant on sublimation conditions.



(a) α-phase (b) β-phase

FIGURE 3

Magnetic studies on the α-phase indicate the presence of strong AF interactions,[13] with a broad maximum in the magnetic susceptibility, χ, around 12K indicative of the onset of long-range AF order (Figure 4a). Magnetic studies on the β-phase[17] (Figure 4b) indicate much stronger AF exchange interactions between molecules but below 36K, there is an anomalous increase in χ and the magnetic susceptibility becomes dependent on the applied field, indicative of the presence of a spontaneous magnetic moment. The T_C of 36K is one to two orders of magnitude greater than any other open-shell organic radicals.

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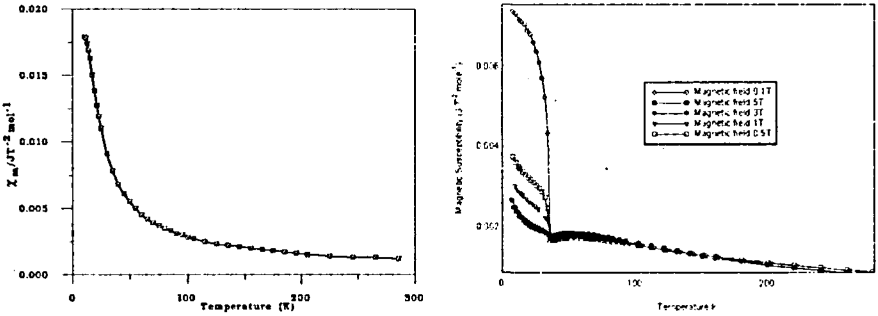

(a) (b)

FIGURE 4. Molar susceptibility as a function of temperature for (a) α-p-NCC$_6$F$_4$CNSSN and (b) β-p-NCC$_6$F$_4$CNSSN

The small magnitude of the spontaneous magnetisation ($1.5\text{x}10^{-3}\mu_B$/mole) is consistent with β-p-NCC$_6$F$_4$CNSSN exhibiting weak ferromagnetism, with a canting angle of about 0.26° and is in agreement with calculations based on solution ESR studies which indicate a canting angle of about 0.15°. Powder neutron diffraction and a.c. calorimetry measurements[17] confirm the onset of long-range magnetic order at 36K. Theoretical calculations[6] on derivatives of **2** indicate that the unpaired spin density is localised on the N/S fragment of the heterocyclic ring and the nodal nature of the heterocyclic carbon effectively inhibits delocalisation of unpaired spin density onto the aromatic substituent. Consequently, although the CN...S interactions play an important role in determining the solid state structure, the aromatic substituents tend to act as magnetic insulators and the magnetic exchange is propogated through the interchain S...N interactions.[17] A careful study of the neutron diffraction data concludes that the magnetic space group is *Fd'd2', in which the spins are fixed in the ab plane and the resultant magnetic moment is likely orientated parallel to the a-axis.[17]

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CONCLUSIONS

Thiazyl radicals exhibit strong AF exchange interactions. Careful manipulation of the solid state structure can overcome the tendancy for dimerisation and weak ferromagnetism can be induced by control of solid state structure. The radical $NCC_6F_4\overline{CNSSN}$ provides the first example of an open-shell 'organic' radical to exhibit a Tc above that of liquid helium.

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REFERENCES

[1] J.S. Miller and A. Epstein, *Chem. Eng. News.*, 1995, **73**, Oct. 2, 30.

[2] H. Tamura, Y. Nakazawa, D. Shiomi, K. Nozawa, Y. Hosokoshi, M. Ishikawa, M. Takahashi and M. Kinoshita, *Chem. Phys. Lett*, 1991, **186**, 401.

[3] R. Chiarelli, M.A. Novak, A. Rassat and J.L. Tholence, *Nature*, 1993, **363**, 147.

[4] F. Palacio, *Mol. Cryst. Liq. Cryst.*, 1997, in press.

[5] R.L. Carlin, *Magnetochemistry*, Springer, Berlin, 1989.

[6] J.M. Rawson, A.J. Banister, and I. Lavender, *Adv. Heterocycl. Chem.*, 1995, **62**, 137.

[7] C.M. Aherne, Ph.D. Thesis, University of Durham, 1995.

[8] E.G. Awere, N. Burford, C. Mailer, J. Passmore, M.J. Schriver, P.S. White, A.J. Banister, M. Oberhammer and L.H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66.

[9] J. Passmore and X Sun, *Inorg. Chem.*, 1996, **35**, 1313

[10] W.V.F. Brooks, N. Burford, J. Passmore, M.J. Schriver and L.H. Sutcliffe, *J. Chem. Soc., Chem. Commun.*, 1987, 66.

[11] S.A. Fairhurst, K.M. Johnson, L.H. Sutcliffe, K.F. Preston, A.J. Banister, Z.V. Hauptman and J. Passmore, *J. Chem. Soc., Dalton Trans.*, 1986, 1465.

[12] J.M. Rawson, unpublished results.

[13] A.J. Banister, N. Bricklebank, W. Clegg, M.R.J. Elsegood, C.I. Gregory and B.K. Tanner, *J. Chem. Soc., Chem. Commun.*, 1995, 679.

[14] T.S. Cameron, R.C. Haddon, S.M. Mattar, S. Parsons, J. Passmore and A.P. Ramirez, *Inorg. Chem.*, 1992, **31**, 2274.

[15] T.S. Cameron, R.C. Haddon, S.M. Mattar, S. Parsons, J. Passmore and A.P. Ramirez, *J. Chem. Soc., Dalton Trans.*, 1992, 1563.

[16] T. Barclay, A.W. Cordes, N.A. George, R.C. Haddon, R.T. Oakley, T.T.M. Palstra, G.W. Patenaude, R.W. Reed, J.F. Richardson and H. Zhang, *Chem. Commun.*, 1997, 873.

[17] F. Palacio, G. Antorrena, M. Castro, R. Buriel, J.M. Rawson, J.N.B. Smith, N. Bricklebank, J. Novoa and C. Ritter, *Phys. Rev. Lett.*, accepted for publication.

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