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Probing magnetic exchange interactions in molecular magnets: an inclusion compound of a dithiadiazolyl radical

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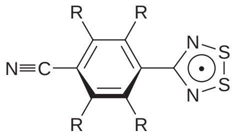
Co-sublimation of the dithiadiazolyl radical, *p*-NCC_6H_4CNSSN **2** with the inclusion-forming host compound perhydrotriphenylene (PHTP) leads to trichroic crystals of the host–guest complex [PHTP–**2**]. Molecules of **2** are linked through a CN···S interaction (*ca.* 3.03 Å) to form polar chains within the channels of the PHTP host lattice. The host–guest ratio is approximately 5 : 1. Pyroelectric and non-linear optic responses indicate that crystals of [PHTP–**2**] are macroscopically polar. A combination of variable temperature solid state EPR spectroscopy and magnetic susceptibility measurements are used to probe the electronic properties of [PHTP–**2**]; whilst [PHTP–**2**] is paramagnetic, no exchange coupling between neighbouring molecules of **2** within the channels could be established. The implications of these results on the magnetic exchange pathway of the weak ferromagnet, β-*p*-NCC_6F_4CNSSN β-**1**, are discussed.

The development of molecular organic ferromagnets, based on open-shell organic radicals, has generated considerable interest in recent years.[1] There are, however, only a few such examples whose magnetic behavior is an intrinsic property of the material.[2] Most of these are based on the nitroxide radical $NO^{\bullet}$ and have ordering temperatures (T_cs) significantly below 5 K.[1b] In comparison, the β-phase of the 1,2,3,5-dithiadiazolyl radical **1**,[3] orders as a weak ferromagnet (canted antiferromagnet) at a remarkable 36 K. In β-**1** the radicals crystallize in a polar space group (*Fdd*2) with the molecules linked together in parallel chains *via* strong, dipolar CN···S interactions.[3] The lack of an inversion center in β-**1** is one of the necessary prerequisites for its observed spin-canted behavior.[3,4] In addition, there must be magnetic exchange between the radicals to facilitate long-range magnetic order.[5]



R = F **1**
R = H **2**

It is often a complex or intractable problem to identify these communication pathways and the magnitude of the magnetic exchange terms. In the case of β-**1**, there appear two close intermolecular contacts (Fig. 1) which are likely to propagate the magnetic exchange pathway; either *via* the close CN···S interactions (at *ca.* 3.0 Å) which link molecules into molecular chains along the crystallographic *c*-axis and/or through the longer inter-chain S···N interactions (at *ca.* 3.5 Å).

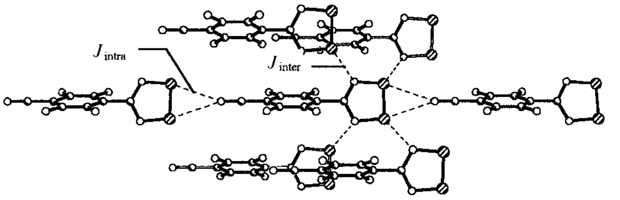


Fig. 1 Crystal structure[3] of β-**1** illustrating the possible exchange pathways, *via intra*-chain CN···S interactions and *via inter*-chain N···S interactions.

Perhydrotriphenylene (PHTP) forms channel-type inclusion host lattices in which polar, rod-like guest molecules (such as **2**) are included as polar chains within the parallel channels.[6,7] The channels are widely separated (*ca.* 15 Å) and, for radicals, magnetic interactions between molecules in different channels can be considered negligible. Inclusion compounds of this type should prove to be novel and ideal models with which to study selected magnetic exchange interactions.[8] Here, we report the synthesis, characterisation and electronic properties of an inclusion complex of PHTP with the dithiadiazolyl radical **2**, [PHTP–**2**].

Results and discussion

The dithiadiazolyl radical **2** was chosen for inclusion in preference to **1**, because of its smaller diameter which facilitated its inclusion into the channels of PHTP. Radical **2**, like **1**, exhibits a strong dipolar CN···S interaction in the solid state[9] which links molecules into polar chains. In addition, previous studies have shown that the electronic properties (*g*-value and N-hyperfine coupling constants and redox behaviour) of the dithiadiazolyl radical are remarkably insensitive to substituents at the carbon atom of the heterocyclic ring.[10] Consequently the inclusion complex [PHTP–**2**] should prove to be a suitable model with which to examine the intra-chain exchange interaction in β-**1**.

Unlike **1**, radical **2** is dimeric and consequently diamagnetic in the solid state.[9] However, the dimerization enthalpy is rather low (*ca.* 35 kJ mol^{-1})[10] and is overcome in the gas phase[11] during sublimation and also upon dissolution.[10] The diameter of the channels within PHTP inclusion compounds[6,7] precludes inclusion as a dimer and **2** must be included in a monomeric form. Whilst the twist angle between heterocyclic and phenyl rings in β-**1** is *ca.* 54°, it averages only 7° in **2**.[3,9] From close-packing considerations and the similarity of the unit cell data (*vide infra*) to that found for a similar [PHTP–guest] crystal whose structure has been fully elucidated,[12] the size of the channels in PHTP should restrict the twist angle to within $\pm 20°$ of planarity. Under these circumstances, any communication between molecules within the channel will be enhanced because of the near coplanarity of the π-systems.

Preparation and structural characterisation of [PHTP–2]

Well formed, trichroitic crystals of the inclusion compound [PHTP–**2**] were prepared by co-sublimation of PHTP and **2**. A rotating crystal photograph of the needle-like crystals (Fig. 2) confirms the 1-D ordering of polar chains of **2** in the PHTP lattice, as observed for many polar guests in PHTP,[6] and for both pure β-**1** and **2**.[3,9] The molar ratio of PHTP : **2** was found to be 5 : 1, and the calculated inter-guest CN···S separation (3.03 Å) is in good agreement with those observed for β-**1** (2.986 Å)[3] and pure **2** (3.04 Å).[9] The polar nature of the chains of **2** in [PHTP–**2**] was confirmed by pyroelectric[12] and second harmonic generation (SHG) responses: from the sign of the pyroelectric current, we conclude that the end faces of the crystals are dominated by cyano groups. The positive SHG response indicates that the majority of the molecules of **2** in the PHTP lattice are all ordered in the same direction within the two polar, but 180° opposed, macrodomains, characteristic of such PHTP inclusion crystals containing polar guests.[7,12,13]

EPR studies on [PHTP–2]

EPR measurements (5–294 K) were made on single crystals of [PHTP–**2**] with the crystallographic *c*-axis aligned parallel to the static magnetic field, B_0. In addition, fluid-solution EPR studies (200–293 K) were performed on solutions of pure **2** dissolved in degassed dichloromethane or 1,2-dimethoxyethane. The solid-state spectra for [PHTP–**2**] (Fig. 3) changed markedly as a function of temperature: at 294 K a sharp singlet ($\Delta B_0 = 0.2$ mT) was observed which broadened considerably on cooling to 5 K ($\Delta B_0 = 4$ mT), although no half-field resonance, expected for an $S = 1$ coupled state, was observed. It was not immediately apparent whether the variation in EPR lineshape could be attributed to an intermolecular exchange process or to a molecular phenomenon.

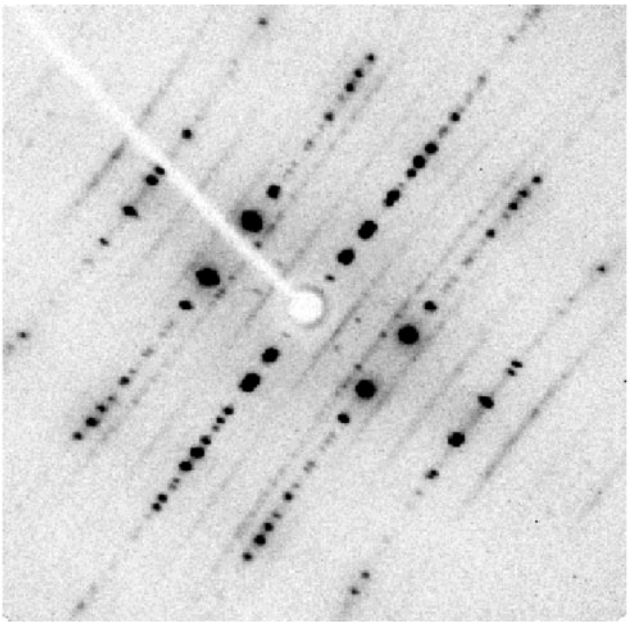


Fig. 2 Rotating-crystal photograph of a [PHTP–**2**] needle crystal recorded on a CCD. There are two distinct, numerically commensurate sets of reflections: one set is composed of Bragg reflections related to the three-dimensionally ordered PHTP lattice; the other is composed of diffuse layers corresponding to the one-dimensionally ordered guest radicals.[7b] Measured translational periods of host and guest along channel-axis *c*: 4.80(2) and 12.00(3) Å, respectively. The intermolecular –S···NC– interaction length was calculated to be 3.03(5) Å.

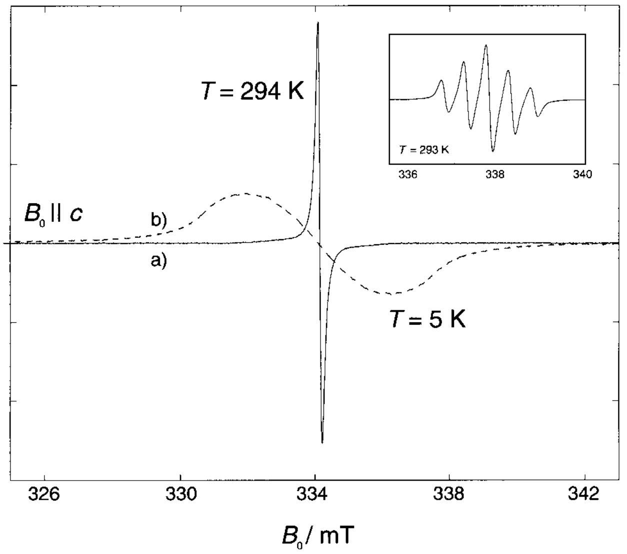


Fig. 3 EPR spectra of a needle-like crystal of [PHTP–**2**] oriented parallel to the static field B_0 at: a) 294 K ($g_c = 2.021$); b) 5 K ($g_c = 2.021$). Intensity in arbitrary units. Note: 1) the lack of resolved hyperfine splittings; 2) the considerable increase in the peak-to-peak linewidth on cooling ($\Delta B_0 = 0.2$ and 4 mT, respectively). Top right inset: solution spectrum of pure **2** in CH_2Cl_2 ($T = 293$ K; $A_{iso}{}^{N} = 0.502$ mT; $g_c = 2.010$).

In order to rationalize the temperature dependence of the EPR signal, the molecular chains of **2** were diluted with diamagnetic *p*-terphenyl by co-sublimation of *p*-terphenyl with PHTP and **2**. The ratio of terphenyl : **2** in the inclusion crystals was estimated at 10 : 1. We can assume from statistical considerations that the radical guests are isolated from each other by several *p*-terphenyl molecules. EPR measurements, with B_0 parallel to the inclusion channel axes, now indicated the presence of isolated $S = 1/2$ spins with a large hyperfine coupling ($A_z{}^{N}$) to N atoms of the dithiadiazolyl ring (Fig. 4). With B_0 perpendicular to the inclusion channel axes, the much smaller splittings $A_x{}^{N}$, $A_y{}^{N}$ are observed, such that the magnitude of $(A_x{}^{N} + A_y{}^{N} + A_z{}^{N})/3$ is of the same order as the isotropic value $A_{iso}{}^{N}$ measured for pure **2** in solution. The orientation dependence of the EPR spectrum is associated with the orientation of the molecules within the channels of the PHTP host. Fluid solution EPR spectra (200–293 K) of pure **2** consisted of a characteristic[10] quintet structure resulting from coupling to two equivalent ^{14}N nuclei (Fig. 3, inset). Within samples of [PHTP–**2**], [PHTP–**2**] diluted with *p*-terphenyl, and in dilute solutions of **2**, the radicals exhibit a complex, strongly temperature-dependent hyperfine splitting pattern, which we attribute to molecular motion. The EPR spectra of other thiazyl radicals also exhibit a marked temperature dependence.[14] Precise orientation- and temperature-dependent EPR measurements are planned to determine exact hyperfine couplings, rotational diffusion times and rotational energetics.

Magnetic studies on [PHTP–2]

Variable temperature magnetic studies showed that [PHTP–**2**] exhibited Curie behavior in the region 1.8–300 K (Fig. 5). The

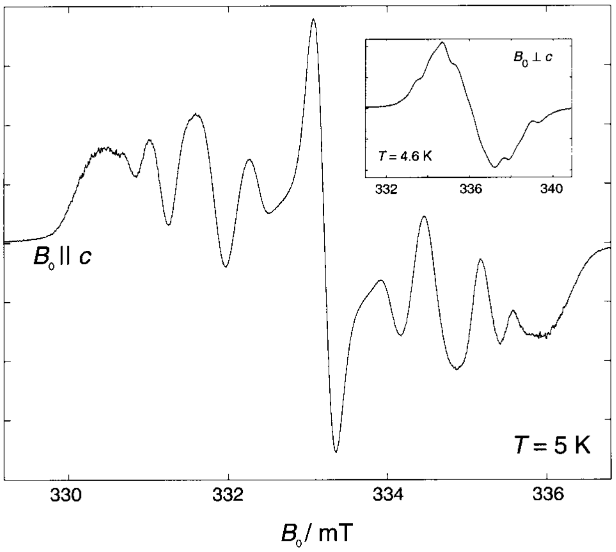


Fig. 4 X-Band EPR spectrum of a needle-like crystal of [PHTP–**2**] diluted with diamagnetic *p*-terphenyl (large excess), oriented parallel to B_0 ($T = 5$ K). Intensity in arbitrary units. Compare with curve b) in Fig. 3 for the pure [PHTP–**2**] crystal and Fig. 3 (inset) for the solution spectrum of pure **2**. The principal *g*-tensor values ($g_c = 2.021$; $g_a = 2.000$; $g_b = 2.006$) were determined ($T = 10$ K) by W-band (cw) measurements on a powdered sample of crystalline [PHTP–**2**–terphenyl]. Top right inset: corresponding spectrum of the crystal oriented perpendicular to B_0 ($T = 4.6$ K).

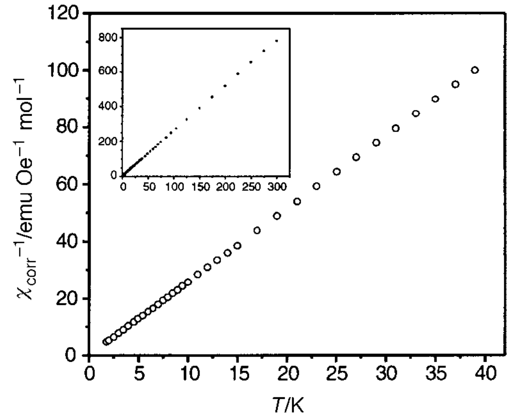


Fig. 5 Variable temperature magnetic susceptibility studies on [PHTP–**2**] recorded in the range 0–50 K (0–300 K inset). χ_{corr} is the dc magnetic susceptibility with a correction made for the diamagnetic component. The inclusion compound displays pure Curie behavior in the region 1.8–300 K, consistent with an $S = 1/2$ paramagnet.

value of $\chi_{(M)}T$ remained constant throughout the entire temperature range and was consistent with an $S = 1/2$ paramagnet in which exchange interactions are negligible.

From the EPR and magnetic studies described above, we conclude that there is no exchange interaction between molecules of **2** within the PHTP host structure. This observation is supported by theoretical calculations.[4] These indicate that, in the ground state,[15] the unpaired spin density is localized on the S and N atoms of the heterocyclic ring and the C atom is nodal, preventing delocalization of the spin density over the rest of the molecule. This is confirmed by a lack of additional hyperfine splittings due to the protons of the phenyl ring or the nitrogen of the CN group; moreover, identical ^{14}N hyperfine coupling constants A_{iso}^{N} [0.5016 mT] were obtained in dichloromethane and dimethoxyethane, and are similar to those found for other dithiadiazolyl derivatives (0.492–0.528 mT).[10]

We can therefore conclude that whilst the close CN···S interactions in [PHTP–**2**], and by logical extension **1**, may be a strong supramolecular synthon, forming polar chains of molecules, they do not support significant intra-chain magnetic exchange interactions. Whilst the crystal polarity induced by the CN···S interaction is essential for the weak ferromagnetism observed in β-**1**, it is the inter-chain S···N interactions which propagate the antiferromagnetic exchange which is responsible for the weak ferromagnetism of β-**1**.

Experimental

Rotating crystal photographs of the inclusion compound were recorded on a Siemens three-circle CCD diffractometer operating at 300 K. Scanning pyroelectric microscopy measurements were performed on the crystals using equipment and techniques described elsewhere.[11] Temperature- (5–300 K) and orientation-dependent solid-state EPR spectra were recorded on a Bruker ESP 300 (X-Band, cw) with a 100 kHz field modulation, a rectangular TE_{102} microwave cavity and an APD He cryostat. Fluid-solution EPR studies (200–293 K) on degassed solutions of pure **2** dissolved in dichloromethane and dimethoxyethane, were performed using a Varian E9 spectrometer equipped with a Marconi Instruments 2440 microwave counter and a Bruker ER 035M NMR Gaussmeter. Temperature-dependent magnetic susceptibility measurements on the crystals were recorded on a Quantum Design SQUID magnetometer. The temperature dependence of the dc susceptibility was measured between 1.8 and 300 K using an external magnetic field of 0.1 T. PHTP and radical **2** were prepared according to the literature methods.[6,9]

Preparation of inclusion crystals

Inclusion crystals of [PHTP–**2**] and [PHTP–**2**–*p*-terphenyl] were formed in a sealed ampoule at 115 °C and 10^{-4} Torr using a co-sublimation technique,[15] on a 50–100 mg scale. Exact amounts of each reagent were not required since the composition of the products (and the ratio of **2**:*p*-terphenyl guest molecules) are dependent on the vapour pressure of each component not the relative quantities.

The crystals of [PHTP–**2**] were identified initially on the basis of their morphology (needles with approx. hexagonal cross-sections) and colour (pale–medium blue; pure **2** and PHTP are intensely dark blue–black and colourless, respectively). The presence of both PHTP and **2** was confirmed by mass spectrometry on washed (EtOH), discrete crystals of [PHTP–**2**] isolated from the sublimation vessel, with the observation of parent ions for both PHTP and **2** (*m*/*z* 246 and 206, respectively). The preparation of [PHTP–**2**] diluted with *p*-terphenyl was accomplished in a similar manner.

Acknowledgments

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