Organic Ferromagnetism

A Thiazyl-Based Organic Ferromagnet**

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In 1928 Heisenberg proposed[1] that bulk ferromagnetic order would only ever be achieved in systems containing heavy atoms, that is, metals, their oxides, and related derivatives. Indeed it was not until 1991 that the first organic ferromagnet was reported; the β-polymorph of the *para*-nitrophenyl nitronyl nitroxide radical (*p*-NPNN, **1**; Scheme 1) was shown to order below 0.6 K.[2] Since then a number of other purely organic radicals have been found to undergo bulk ferromagnetic order, although the majority order below 1 K. Exceptions include the radical cation salts $[C_{60}][TDAE]$[3] (TDAE = tetrakis(dimethylamino)ethylene) and [BBDTA]-$GaCl_4$[4] (**3**; BBDTA = benzobis(1,3,2-dithiazolyl), which order as ferromagnets at 16 and 6.7 K, respectively. Of the neutral radicals, only the nitroxide-based diradical DOTMDAA (**2**; DOTMDAA = *N,N′*-dioxy-1,3,5,7-tetramethyl-2,6-diazaadamantane) orders ferromagnetically above 1 K (T_c = 1.48 K),[5] although the dithiadiazolyl radical *p*-$NCC_6F_4CNSSN^{\bullet}$ (**4**) orders as a weak ferromagnet at 36 K under ambient pressure,[6] the highest reported temperature for magnetic ordering in an organic radical. We have sought to prepare new dithiadiazolyl radicals, closely related to **4**, in which small structural changes may lead to new magnetically ordered systems. Here we report the structure and magnetic properties of **5**, which is only the second neutral organic radical to order as a ferromagnet above 1 K.

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[**] We would like to thank the EPSRC (A.A., R.J.L., C.M.P., and R.D.F.), the CICYT (grant MAT2001-3507-C02-02), and the Gates Cambridge Trust (A.A.) for financial support, and the ESF program "Molecular Magnets" for partial support to the collaborative activities. We are grateful to Dr. N. Feeder for X-ray data collection and analysis and preparation of crystallographic data for deposit.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

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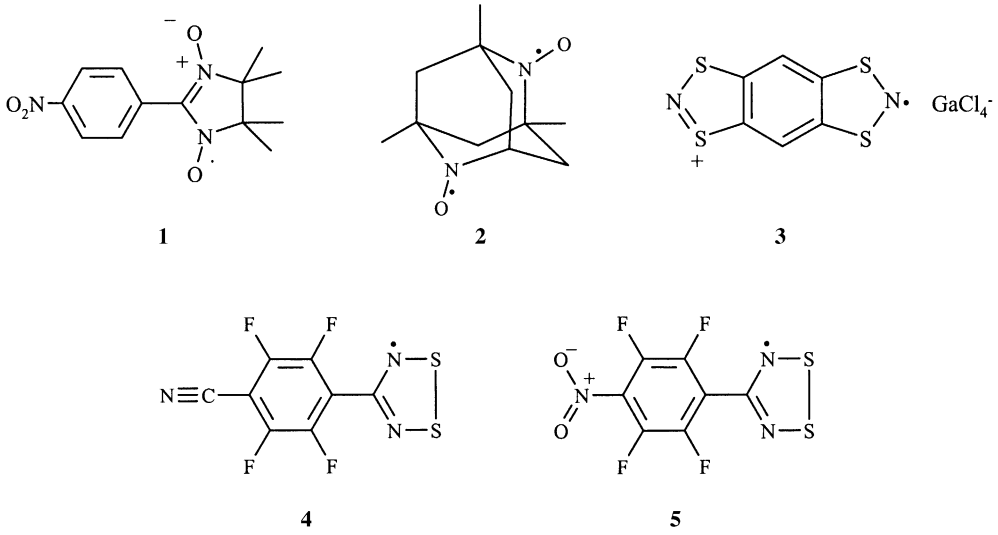

Scheme 1. Organic molecular magnets **1**–**5**.

The radical, p-$O_2NC_6F_4CNSSN^{\bullet}$ (**5**), was synthesized from p-$O_2NC_6F_4CN$ utilizing standard synthetic procedures. X-ray diffraction studies revealed an asymmetric unit[7] comprising half a molecule of **5** located about a crystallographic twofold axis. The molecular dimensions are of unexceptional geometry[8] with a twist angle between the two ring planes of 58.1°. The packing of **5** (Figure 1) can be described in terms of

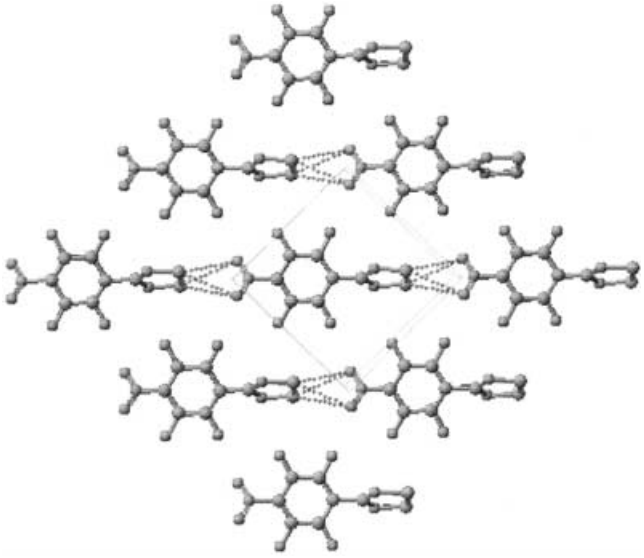

Figure 1. Crystal structure of the p-$O_2NC_6F_4CNSSN^{\bullet}$ radical in the *ab* plane.

chains of molecules linked through electrostatic $S^{\delta+}\cdots O^{\delta-}$ interactions in the [110] plane. These chains are reminiscent of the favorable $CN^{\delta-}\cdots S^{\delta+}$ contacts observed in **4**.[6] Whilst chains in **4** align co-parallel throughout the structure, polar sheets of **5** are related via a 4_1 screw axis down the crystallographic *c* axis, with each molecule forming four symmetry-equivalent S···N contacts of 3.681 Å to neighboring heterocycles, which are nearly orthogonal ($\theta = 97.3°$; Figure 2).

X- and Q-band EPR studies on **5** exhibit hyperfine coupling to the two heterocyclic N atoms and superhyperfine coupling to the two *ortho* F atoms of the phenyl substituent.

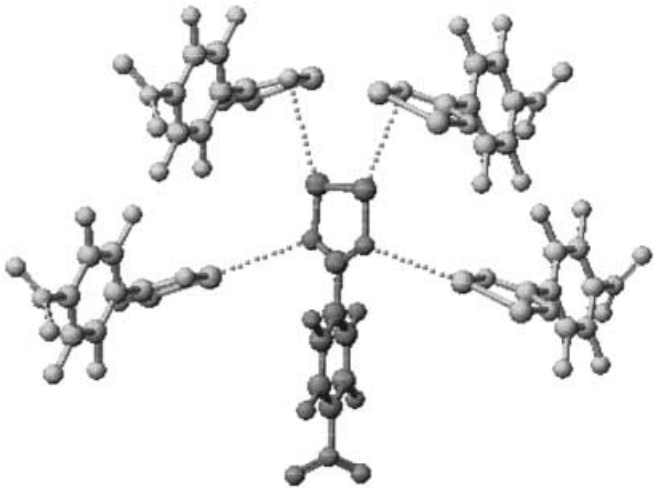

Figure 2. Crystal structure of the p-$O_2NC_6F_4CNSSN^{\bullet}$ radical illustrating close intermolecular S···N contacts between layers.

The coupling constants are similar to those reported for other perfluorophenyl dithiadiazolyl radicals[9,10] and are consistent with substantial localization of the spin density on the dithiadiazolyl ring. The spin-density distribution in **5** extracted from the anisotropic EPR spectra (≈24% on each dithiadiazolyl N atom and less than 0.1% on each of the *ortho* F atoms) is in good agreement with previous DFT calculations.[10]

The magnetic behavior of a polycrystalline sample of **5** (0.104 g) was measured between 1.8 and 300 K using a Quantum Design SQUID magnetometer in an applied field

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of 10 kOe. The sample was corrected for diamagnetism ($\chi_d = -114 \times 10^{-6}$ emu Oe^{-1} mol^{-1}) using Pascal's constants. The compound exhibits Curie–Weiss behavior down to approximately 10 K (Figure 3) with $\theta = +1.6(\pm 0.1)$ K and a Curie constant $C = 0.368$ emu K mol^{-1} Oe^{-1} (compared with 0.375 for an S = 1/2 paramagnet). The positive value of θ is consistent with ferromagnetic exchange interactions between S = 1/2 centers with an upper limit to the ferromagnetic ordering temperature of 1.6 K, based on mean field theory. Below 10 K the data begins to deviate from Curie–Weiss behavior, as expected in the region of T_c because of short-range interactions. The maximum observed in μ_{eff} is due to saturation effects of the applied field on a ferromagnet and cannot be compared with measurements made at very low field (see below).

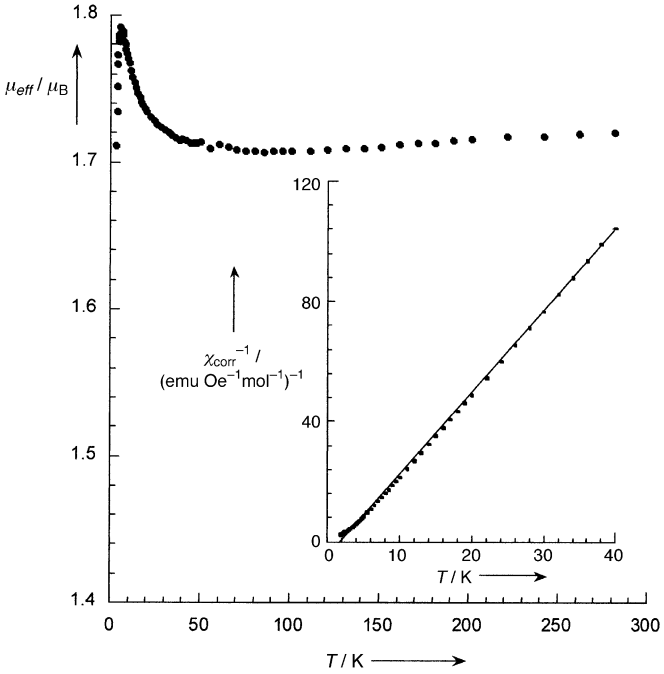

Figure 3. Temperature dependence (5–280 K) of the effective magnetic moment of the *p*-$O_2NC_6F_4CNSSN^{\bullet}$ radical measured in an applied field of 10 kOe. The appearance of the maximum is a consequence of the suppression of the ferromagnetic state by the applied field. Inset: A plot of $1/\chi$ versus *T*.

Low-temperature ac susceptibility measurements on a single crystal of **5** were made between 0.6 and 2.5 K on a low-field SQUID magnetometer in a field of approximately 2 G. The crystal, when oriented both perpendicular and parallel to the [001] axis, showed an abrupt increase in the out-of-phase ac susceptibility below 1.4 K, reaching a maximum at 1.3 K, consistent with the onset of bulk ferromagnetic order with $T_c = 1.32 \pm 0.02$ K (Figure 4). Little anisotropy in *M* versus *H* or χ versus *T* data was observed. The difference in the data corresponding to the crystal orientations shown in Figure 4 is attributed to demagnetizing effects arising from the sample geometry.

Previous magnetic studies on thiazyl radicals[6,11–15] have shown that magnetic interactions propagate through intermolecular S···N contacts. In the case of **5**, the near orthogonal nature of the singly occupied molecular orbitals on neighboring molecules would appear to lead to a ferromagnetic interaction.[16]

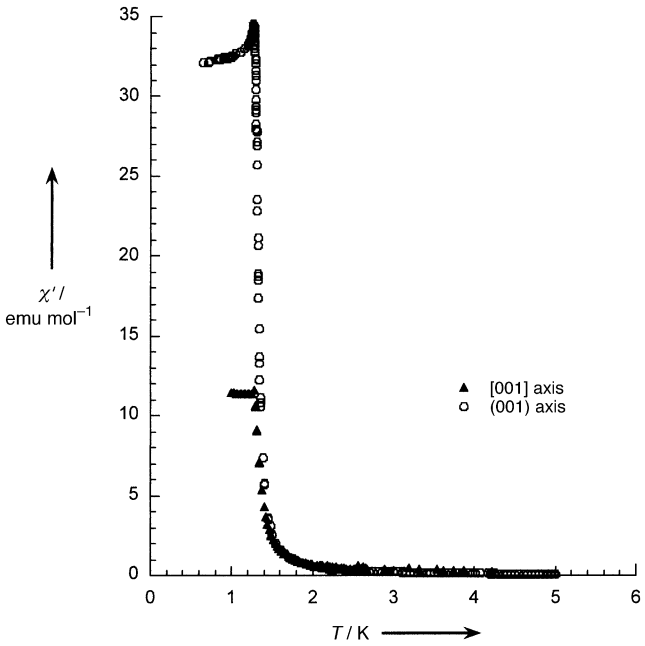

Figure 4. Single-crystal ac susceptibility of the *p*-$O_2NC_6F_4CNSSN^{\bullet}$ radical in an applied field of 2 G and at 1.11 Hz.

These studies provide clear evidence of ferromagnetic order in an organic radical above 1 K. Detailed analysis of the spin-density distribution by polarized neutron diffraction, EPR/ENDOR, and DFT studies, coupled with a determination of the magnetic structure through single-crystal neutron diffraction experiments, a theoretical analysis of the exchange pathway, and determination of the critical exponents of the magnetic behavior will be the subjects of future reports.

Experimental Section

5: *p*-$O_2NC_6F_4CN$ (500 mg, 2.27 mmol) was added to a solution of $Li[N(SiMe_3)_2]$ (380 mg, 2.27 mmol) in dry Et_2O (40 mL). The reaction mixture turned red and was stirred for 18 h at room temperature. SCl_2 (0.40 mL, 660 mg, 5.11 mmol) was then added to the solution at 0 °C. The solution was allowed to warm to room temperature and stirred for a further 5 h. The resultant yellow precipitate was filtered, washed (2×10 mL of dry Et_2O), and dried in vacuo. The yellow salt ([*p*-$O_2NC_6F_4CNSSN$]Cl) was stirred with Ag powder (245 mg, 2.27 mmol) in liquid SO_2 for 18 h, and the purple SO_2 extracts were sublimed (100 °C, 10^{-3} Torr) to yield lustrous black blocks (70 mg, 10%). Positive EI-MS: *m*/*z* 297.9 (M^+), 252.0 (M^+–SN). Elemental analysis (%) calcd: C 28.19, N 14.09; found: C 28.52, N 14.17. X-band EPR (THF, $T = 298$ K): $g = 2.011$, $a_N = 5.2$ G, $a_F = 1.3$ G.

Received: June 23, 2003 [Z52194]
Published Online: September 23, 2003

Keywords: ferromagnetism · magnetic properties · molecular magnetism · radical ions · radicals

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[7] Crystal data for **4**. A crystal of **4** was studied on a Nonius Kappa 4 CCD diffractometer equipped with an Oxford Instruments Cryostream [$T = 220(2)$ K] using $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). Crystal structure solution utilized SHELXTL software. All atoms were refined anisotropically. Chemical Formula: $C_7F_4N_3O_2S_2$, $M_r = 298.22$, tetragonal, space group $P4_12_12$, $a = 8.1380(4)$, $b = 8.1380(4)$, $c = 15.0490(12)$ Å, $Z = 4$, $\rho_{calcd} = 1.987\ g\,cm^{-3}$, $\mu = 0.592\ mm^{-1}$, $F(000) = 588$. All 1145 unique reflections of the 3046 reflections measured, were used in refinement yielding refinement indices wR_2 (all data) $= 0.080$ and R_1 [$I > 2\sigma(I)$] $= 0.035$. The Flack parameter of $-0.18(14)$ is indicative of the correct absolute structure determination. The largest residual electron density was within $\pm 0.3\ e\,Å^{-3}$. CCDC-210990 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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