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A first-principles *bottom-up* study of the magnetic interaction mechanism in the bulk ferromagnet *p-O$_2$N-C$_6$F$_4$-CNSSN*

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ABSTRACT

The crystals of the *p-nitro perfluorophenyl dithiadiazolyl* radical have been shown to present bulk ferromagnetism below 1.32 K. Using our first-principles bottom-up methodology, the mechanism of the magnetic interactions in these crystals has been studied to gain a rigorous quantitative understanding of such bulk ferromagnetism. The *p-O$_2$N-C$_6$F$_4$-CNSSN* crystal is found to present only two non-negligible interactions ($J(d1)$ = 0.83 cm^{-1} and $J(d3)$ = 0.07 cm^{-1}). The dominant interaction $J(d1)$ generates a three-dimensional (3D) magnetic topology that can be described as a distorted diamond-like arrangement. Using the appropriate minimal magnetic model to describe this topology, the magnetic susceptibility and heat capacity curves were computed. A good agreement is found between the computed and experimental magnetic susceptibility data. Furthermore, the critical temperature obtained from the heat capacity curve (0.6 K) agrees well with the experimental one. A comparison of the magnetic data for *p-O$_2$N-C$_6$F$_4$-CNSSN* and four nitronyl nitroxide bulk ferromagnets indicates that the critical temperature not only depends on the size of the largest J interactions, but also on the corresponding magnetic topology.

1. Introduction

Since the first bulk purely-organic ferromagnet was reported in 1991 (β-*p-nitrophenyl nitronyl nitroxide* [1] with a critical temperature of 0.6 K), many efforts have been directed at synthesizing new purely-organic radicals presenting bulk ferromagnetism at higher critical temperature. These efforts resulted in a variety of new organic bulk ferromagnets, most of them showing transition temperature to ferromagnetic order below 1 K. There are a few known crystals of bulk ferromagnets above 1 K, such as crystals of radical-cations salts [2,3], and neutral nitroxide-based radical [4]. There is also a neutral dithiadiazolyl radical (*p*-cyano perfluorophenyl dithiadiazolyl radical), whose β-phase crystal presents the highest reported critical temperature (T_c = 36 K) for magnetic ordering in an organic radical [5].

Recently, Rawson et al. [6] reported a new example of neutral purely-organic radicals having crystals that behave as bulk ferromagnets above 1 K: the *p-nitro perfluorophenyl dithiadiazolyl* radical (*p-O$_2$N-C$_6$F$_4$-CNSSN*, see Fig. 1a), whose crystal behaves as a bulk ferromagnet below 1.32 ± 0.02 K. Furthermore, these authors also carried out first-principles B3LYP/6-311G(d) calculations on the 160 K structure in order to evaluate the magnetic coupling constants (J_{AB}) for all A–B radical–radical pairs with intermolecular contacts between dithiadiazolyl rings shorter than 7 Å. They reported the existence of four J_{AB} magnetic coupling constants, with values 1.15, 0.04, −0.03, and −0.04 cm^{-1} (using the Heisenberg Hamiltonian $\widehat{H} = -\sum_{A>B} J_{AB}\widehat{S}_A\widehat{S}_B$), and concluded that the J_1 = 1.15 cm^{-1} magnetic interaction was dominant and allowed the propagation of ferromagnetic interactions along the three directions of the crystal, that is, the presence of long-range magnetic order [7].

Although the previous qualitative justification of the *p-O$_2$N-C$_6$F$_4$-CNSSN* magnetic properties seems appropriate, given its relevance as a bulk ferromagnet a quantitative study of the magnetic properties of this radical using our first-principles bottom-up (FPBU) methodology [8] is also needed. Such quantitative study will also allow us to compare the mechanism and magnetic properties for the *p-O$_2$N-C$_6$F$_4$-CNSSN* crystal to other purely-organic bulk ferromagnets previously studied using the FPBU methodology [9].

1.1. Computational details

The first-principles bottom-up procedure consists of the following four steps (for a detailed mathematical and physical discussion see Ref. [8]):

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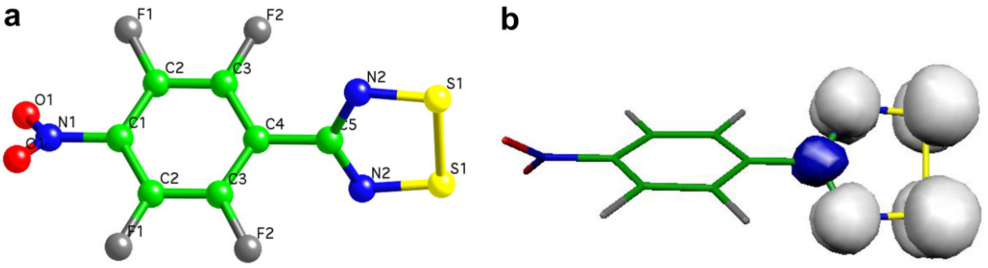

Fig. 1. (a) Structure of the *p*-O_2N-C_6F_4-*CNSSN* radical. (b) Spin distribution computed at the UB3LYP/6-31+G(d) level (isodensity surface of 0.003 atomic units; blue is used for regions of negative spin density, and white for positive spin density). A Mulliken atom population analysis of the radical gives the following non-negligible spin population on the atoms (in atomic units): C5 = −0.11, N2 = 0.27, S1 = 0.29. All other atoms have spin populations whose absolute value is smaller than 0.01 atomic units.

Step 1: Analysis of the crystal structure in order to find all unique *A*–*B* radical–radical pairs that might be responsible for the microscopic magnetic interactions. This selection, in practice, is done by identifying each symmetry-unique radical *A* and, then, choosing all *A*–*B* radical pairs, *di*, whose inter-pair distance is smaller than a given threshold value (above which the magnetic interaction between radicals is expected to be negligible due to its exponential dependence on the distance). The selection procedure of *di* radical pairs is, thus, completely non-biased as it does not make any *a priori* assumptions on the nature or size of the microscopic magnetic interactions.

Step 2: Computation of the microscopic J_{AB} magnetic interactions for all *A*–*B* radical–radical pairs selected in the previous step. Each J_{AB} is evaluated using the total energies computed from first-principles methods for the appropriate high and low spin states of the *di* radical pairs. As *p*-O_2N-C_6F_4-*CNSSN* ground state is a doublet, all radical–radical pairs can either present a singlet or triplet electronic state. Since the singlet state is open-shell, a proper description within the DFT methodology can only be achieved using the broken symmetry approach [10]. Within this approximation, the value of J_{AB} for the Hamiltonian $\widehat{H} = -2\sum_{A>B} J_{AB}\widehat{S}_A \cdot \widehat{S}_B$ is obtained as $2J_{AB} = 2(E^{S}_{BS} - E^{T})$, where E^{T} is the energy of the triplet state and E^{S}_{BS} is the energy of the open-shell singlet computed using the broken symmetry approach (the expression for J_{AB} derives from the original broken-symmetry equations [10] when the SOMO orbitals of the two radicals do not overlap). For magnetic superexchange interactions, although its use has been controversial, it provides results closer to the experimental values in most cases [11]. We computed both energies using the B3LYP functional [12], and the 6-31+G(d) [13] basis set. All B3LYP calculations on the radical pairs were done using GAUSSIAN-03 [14].

Step 3: Definition of the magnetic topology of the crystal and corresponding minimal magnetic model using the non-negligible J_{AB} values. Two neighboring *A*–*B* radical sites are connected whenever its magnetic interaction presents a $|J_{AB}|$ value larger than a given threshold. The magnetic topology is then defined in terms of how non-negligible J_{AB} interactions propagate along the crystal axes. Complementarily, the minimal magnetic model is defined as the smallest set of radicals that include all non-negligible J_{AB} interactions in a ratio as close as possible to that found in the infinite crystal. The repetition of such minimal model along the crystallographic (*a*, *b*, *c*) directions should regenerate the magnetic topology of the full crystal (a useful test to check the validity of the selected model spaces). The radical centers constituting the minimal magnetic model define a spin space that is used to compute the matrix representation of the corresponding Heisenberg Hamiltonian.[1]

Step 4: The Heisenberg Hamiltonian matrix is diagonalized to obtain the energy for all possible spin states. The size of the corresponding basis set increases with the number of doublet radical centers N of the minimal magnetic model as N!/[(N/2)!(N/2)!]. Current computer limitations allow us up to 16 doublet centers. Notice that the only parameters required to compute that matrix representation of the Heisenberg Hamiltonian are the J_{AB} parameters computed in step 2. The obtained energies are then used to compute the magnetic susceptibility $\chi(T)$ and/or heat capacity C_p(T) using the adequate expressions obtained from a Statistical Mechanics treatment.

It should be now clear why such methodological procedure is called first-principles *bottom-up*. It is *bottom-up* because the macroscopic magnetic properties are obtained from the microscopic radical–radical magnetic interactions present in the Heisenberg Hamiltonian. It is *first-principles* because the magnetic exchange J_{AB} interaction for each radical pair is obtained from the difference between the energy of the appropriate states that is computed using the adequate first-principles (either *ab initio* or DFT) methods. We must stress the fact that this first-principles *bottom-up* procedure benefits from the well-known theoretical methods from chemistry (step 2) and physics (step 4) as a part of a global strategy to study molecular magnetism.

2. Results and discussion

The study of the magnetism of *p*-O_2N-C_6F_4-*CNSSN* applying the first-principles bottom-up procedure is now described in separate sections corresponding to each step.

2.1. Identification of all unique radical–radical pairs in the crystal (step 1)

At 220 K, the *p*-O_2N-C_6F_4-*CNSSN* radicals crystallize in the $P4_12_12$ space group, with cell parameters *a* = *b* = 8.138 Å, *c* = 15.049 Å (with *Z* = 4). The five- and six-membered rings of the *p*-O_2N-C_6F_4-*CNSSN* radicals are twisted 58.1°. The same crystal

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[1] We have used the following general form of the Heisenberg Hamiltonian, as it is more convenient for our computer codes: $\widehat{H} = -2\sum_{A>B} J_{AB}(\widehat{S}_A \cdot \widehat{S}_B + \frac{1}{4}\widehat{I}_{AB})$, where *A* and *B* indexes run over all non-negligible different radical pairs in the minimal model space, $\widehat{I}_{AB}$ is the identity operator, and $\widehat{S}_A$ and $\widehat{S}_B$ are the spin operators acting on radicals *A* and *B* of the *A*–*B* radical pair. The energy spectrum computed using this Hamiltonian presents the same energy differences between different eigenvalues than those obtained using the Hamiltonian $\widehat{H} = -2\sum_{A>B} J_{AB}\widehat{S}_A \cdot \widehat{S}_B$ (2).