Magnetic interactions in Cu-containing heterospin polymer

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The electronic structure of Cu hexafluoroacetylacetonate, crystallized with a stable nitronyl nitroxide radical [Ovcharenko et al., Russ. Chem. Bull. 53, 2406 (2004)], is calculated from first principles within the density functional theory using the SIESTA method, in two magnetic configurations reflecting parallel or antiparallel setting of \( S = 1/2 \) spins of Cu(II) ions to those of organic radicals. For a given (high-temperature) crystal structure, the interaction is found to be predominantly antiferromagnetic, and its magnitude estimated to be 67 cm\(^{-1}\). This preference is discussed in terms of calculated electronic properties (densities of states, molecular orbitals).

1 Introduction

Over last decades, a large variety of metalloorganic materials has been synthesized, many of them having non-trivial magnetic properties. One often denotes them generally as “molecular magnets”, notwithstanding their affiliation to one or another of two large groups (see, e.g., [1, 2]). The first is referred to as “single molecule magnets”, which are molecular crystals composed of well-defined blocks, stable in a solution and remaining well spatially separated (by solvent molecules) upon crystallization. Such systems gained much attention due to spectacular manifestations of essentially quantum mechanical properties (quantum tunneling of magnetization, spin crossover) in the behaviour of ensembles of identical molecules. Another group of systems, although also being often referred to as molecular magnets, are in fact polymers, because their molecular building blocks gets connected into effectively infinite linear chains, or more sophisticated structures. The properties of a single molecule cannot be easily specified in such systems, but a number of other characteristics become relevant, e.g. conductivity and long-range magnetic order. Among such polymers one finds metalloorganic ferromagnets with respectable values (>300 K) of Curie temperature [3].

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Further on, the magnetism is not necessarily due to transition metal (TM) ions, but it can be brought about by a free radical as well. The study of polymers based on stable free radicals has a long history. Mixing up TM ions and free radicals in a single polymer system opens possibilities of sophisticated tuning of magnetic properties. The chemistry offers certain flexibility in bringing together the localized spins of TM ions and distributed spins of free radicals in a controllable way, in a pattern reproducible throughout the crystal. A recent review to this subject has been offered by Blundell and Pratt [4].

This poses a question to which extent the electronic and magnetic properties of such heterospin systems can be grasped by a first-principles calculation. While in general ab initio calculation schemes based on the density functional theory (DFT) work well (up to certain limitations) in describing the ground-state magnetic structure and certain related properties (magnetic anisotropy etc., see Ref. [5, 6] for reviews), heterospin polymer systems have certain obstacles for a calculation. First, many DFT methods found useful in calculations of single molecular magnets, can work on isolated molecular fragments only, and do not support periodic boundary conditions. The same applies to more accurate quantum chemistry calculation schemes. Second, large number of atoms and lack of symmetry makes an ab initio calculation with any scheme quite demanding. However, a successful calculation may give insight into chemical bonding and its relation with magnetic properties in these heterospin compounds. Moreover one can apply certain constraints in the calculation and force the system into one or another magnetic configuration, which would help to estimate the typical magnetic interaction energies.

2 The system of the present study

We calculate and discuss the electronic structure of one heterospin substance, based on copper (II) hexafluoroacetylacetonate Cu(hfac)$_2$, hfac = CF$_3$–C(O)–CH–C(O)–CF$_3$, in combination with a stable nitronyl nitroxide radical 4,4,5,5,-tetramethyl-2(1-ethyl-1H-pyrazol–4-yl)-imidazoline-3-oxide-1-oxyl, described e.g. in Ref. [7]. Some properties of the resulting crystal were addressed in Ref. [8]. During last years a large variety of related heterospin compounds has been synthesized [7, 9, 10], in which Cu(hfac)$_2$ blocks are connected by spin-labeled pirazoles (L$^{Me}$, L$^{Et}$, L$^{i-Pr}$, L$^{Bu}$ for the above formula with different 1-alkyl substitutions).

The compound in question with the nominal formula C$_{22}$H$_{21}$CuF$_{12}$N$_4$O$_6$, referred to as Cu(hfac)$_2$L$^{Et}$, crystallizes in base-centered monoclinic lattice with the space group $C2/c$ (Nr. 15) and lattice parameters $a$=30.516 Å, $b$=9.540 Å, $c$=25.194 Å, $\beta$=123.96°. The primitive cell contains four above given formula units (264 atoms). The monoclinic unit cell (hosting twice as many atoms)
Figure 1. Monoclinic unit cell of Cu(hfac)$_2$L. One chain of Cu atoms with their embedding (hfac)$_2$ fragments and connecting radical molecules runs along the diagonal of the mid-height cutting plane; of an (equivalent) chain in the basal plane, only Cu atoms are shown. H and F atoms are omitted. 

is shown in Fig. 1 the arrangement and labelling of atoms in the fragments relevant for our discussion, – ‘head-to-head’ coupling of ligands to magnetic Cu atoms, embedded in the (hfac)$_2$ blocks, – in Fig. 2.

3 Calculation method and setup

The calculation have been done within the DFT, by the SIESTA method and computer code [11–13], using atom-centered and strictly confined numerical functions [14, 15] as a basis set for solving the Kohn–Sham equations. Norm-conserving pseudopotentials have been constructed according the Troullier–Martins scheme [16], for the following electron configurations (pseudoization radii in Bohr are given in brackets): C2s$^2$(1.25)2p$^2$(1.25), N2s$^2$(1.25)2p$^3$(1.25), O2s$^2$(1.15)2p$^4$(1.15), F2s$^2$(1.20)2p$^5$(1.20), Cu4s$^{1.50}$(2.08)4p$^0$(2.08)3d$^0$3$^{0.50}$(1.79). The basis set was double-$\zeta$ with polarization orbitals, according to the notation common in tight-binding schemes (see, e.g., Refs. [14,15]) for Cu, N and O, and double-$\zeta$ for C, F and H. The energy shift parameter responsible for the localization of basis functions in SIESTA with its ‘default’ value of 20 mRy resulted in the following maximal extension of basis functions: 2.492 Å (H), 2.577 Å (C), 2.265 Å (N), 2.083 Å (O), 1.899 Å (F), 3.308 Å (Cu). The sampling over the Brillouin zone has been done with 3×5×2 divisions along the reciprocal cell vectors. The
Figure 2. An enlarged view of Cu(hfac)$_2$–L–Cu(hfac)$_2$–L sequence, making a period of the chain in Fig. 1 with labelling of atoms.

real-space grid used for the fast Fourier transform in the process of solving the Poisson equation was generated with the energy cutoff parameter of beyond 300 Ry, that resulted in $144 \times 96 \times 240$ divisions along the lattice vectors. The exchange-correlation was treated in the generalized gradient approximation after Perdew–Burke–Ernzerhof [17].

4 Results and discussion

We used the coordinates of atoms as determined experimentally [7,18] at room temperature, without attempting to adjust the structure in the calculation. In fact the crystal structure, notably Cu1–O2 and Cu2–N4 bonds, slightly vary with the temperature [7]. Apparently this gives rise to an abrupt change of the character of magnetic interaction between Cu1 and radical spin, from predominantly antiferromagnetic (above $\sim 220$ K) to predominantly ferromagnetic (below this temperature), as the Cu1–O2 distance grows from 2.237 Å (293 K) to 2.260 (188 K) to 2.281 (115 K). Ovcharenko et al. [7] emphasize that antiferromagnetic coupling in the axially coordinated $>\text{N}-(\text{O})-\text{Cu(II)}-\text{O}^-\text{N}<$ groups is rather unusual and comes about due to anomalously short Cu–O distance at higher temperatures. It was a major objective of our present study to verify a tendency for antiferromagnetic coupling from a first principles
The calculation can be initialized with different spin configurations on selected atoms; this leads to a set of solutions, representing different metastable configurations. Two observations helped to reduce the amount of work: i) the solutions with opposite setting of magnetic moments of two radicals neighbouring a certain Cu1 atom were impossible to bring to convergence, thus indicating that a symmetry or antisymmetry of hybridized wavefunctions with respect to a central Cu1 are strongly favoured; ii) the energy difference between solutions which correspond to various magnetic order between two chains (shown in Fig. 1), i.e. due to inversion of all spins in one chain, are tiny – at least they are not reliably resolvable within the present calculation setup. This underlines an expected fact that magnetic interaction between two (spatially well separated) chains are negligibly small. Therefore we imposed antiparallel setting of spin moments within one chain with respect to the other, and fixed the total spin moment of the unit cell to zero, which helped to improve the stability and convergency of calculation. This leaves us with several options of mutually setting spins of Cu1, two radicals coupled to it, and Cu2. We keep two most stable solutions, shown in Fig. 3 and discuss their electronic structure in more detail.

The AFM2 case involves the inversion of magnetic moments of all Cu atoms, as compared to AFM1. This leaves the local electronic structure only slightly affected; the Mulliken charges and local magnetic moments (Table I) are the same, within 0.01, for AFM1 and AFM2. One finds $1 \mu_B$ distributed over the radical (referred to as R in the following); similarly, the spin $S=1/2$ can be associated with each Cu site, even as in reality the magnetic density spills over its neighbouring atoms of the (hfac)$_2$ fragment. We found a band dispersion over sampled points in the Brillouin zone to be within 0.1 meV, preserving a band gap of $\sim 16$ mRy in AFM1 and $\sim 36$ meV in the AFM2 configuration.
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Table 1. Partial charges (Mulliken populations) $Q$ (e) and local magnetic moments $M$ ($\mu_B$) in two most stable magnetic configurations. Four oxygen atoms in each Cu(hfac)$_2$ fragment, labeled O3 and O4 in Fig. 2 are in reality subdivided into two inequivalent sites, according to inversion symmetry relative to Cu centers.

|        | Cu1  | O4   | Cu2  | O3   | O1   | N1   | N2   | O2   |
|--------|------|------|------|------|------|------|------|------|
| **AFM1** |      |      |      |      |      |      |      |      |
| $Q$    | 10.64| 6.15 | 10.67| 6.14–6.16| 6.10 | 4.93 | 4.90 | 6.15 |
| $M$    | 0.51 | 0.07 | 0.57 | 0.08–0.09| 0.29 | 0.21 | 0.20 | 0.19 |
| **AFM2** |      |      |      |      |      |      |      |      |
| $Q$    | 10.65| 6.15–6.16| 10.67| 6.15–6.16| 6.10 | 4.93 | 4.90 | 6.15 |
| $M$    | 0.45 | 0.08–0.04| 0.57 | 0.07–0.08| 0.30 | 0.21 | 0.21 | 0.18 |

Although not a strict criterion, a larger band gap is often an indication of a more stable configuration among competitive ones. Indeed, the total energy is lower in the AFM2 case by 35 meV, per unit cell of 256 atoms, which contains two Cu2–L–Cu1–L units. It could be expected that the experimental band gap be larger, because the molecular orbitals just below and above the gap are those with large Cu contribution, and it is known that an inclusion of correlation effects within the (quite localized, in this case) Cu3d shell beyond the conventional GGA would tend to move these states apart.

Assuming the Cu1–R magnetic interaction as dominant and those involving Cu2 as comparably small, one can map the above energy difference onto the Heisenberg model. There are several ways to extract magnetic interaction parameters from a first-principles calculation, e.g., in a form consistent with spin-fluctuation theories, in terms of Green’s function elements [19–21], or via non-local susceptibility [22]. The difficulty in the present case would be a delocalized character of a spin over four atoms (O1–N1···N2–O2) of the radical, and a certain ambiguity in defining the corresponding matrix elements of the Green’s function and/or susceptibility. A less conceptually problematic, although quite ‘old-fashioned’, is comparison of total energies in several representative magnetic configurations. A prerequisite for this approach to be meaningful is that the involved spins retain their ‘identity’ (i.e., magnitude, localization etc.) in the configurations to be compared. This is indeed the case in the compound under study, as follows from the inspection of local densities of states (DOS, shown below) and spatial spin densities.

Given ambiguities in the definitions of sign and prefactor of the Heisenberg model, we introduce the magnetic interaction parameter consistently with Ref. [10], notably Eq. (2) therein for the special case of interaction within the $>N−O−\text{Cu(II)}−O′−N<$ ‘exchange cluster’:

$$\mathcal{H} = -2JS_{\text{Cu}}S′ + (\text{Zeeman term}) + (\text{interaction with more distant ions}),$$

where $S'$ is the total spin of two radicals flanking Cu1. Mapping this onto
total energy values of our calculation yields:

\[ E_{\text{AFM1}} - E_{\text{AFM2}} = -16J S_{\text{Cu}} S_{\text{R}} \]

whence (with \( S_{\text{R}} = 1/2 \) for the spin of one radical) \(-J = 8.3 \text{ meV} = 96 \text{ K} = 67 \text{ cm}^{-1}\). This rough estimate of (antiferromagnetic) coupling between a Cu ion and the radical can be looked at as an upper-bonded value: an inclusion of intraatomic correlation effect beyond the conventional GGA may scale down the energy difference between magnetic configurations by a factor as large as 3–4, depending on a system, according to a previous experience for other molecular magnets [23,24]. Moreover, an explicit inclusion of interactions with Cu2 into the model would slightly renormalize the Cu1–R interaction further down.

We could not find an experimental value to compare with, e.g. that extracted from a Heisenberg-model fit to magnetic measurements data; the value \( J = 26 \text{ cm}^{-1} \) given in Table 3 of Ref. [7] stems from the fit over low-temperature range, where exchange interaction within the R–Cu1–R group is of predominantly ferromagnetic character. (We remind that our calculation has been done in the room-temperature structure, whereas at 220 K the exchange interaction does apparently change sign). Antiferromagnetic type of coupling over large temperature range was observed in chemically related, but structurally different, system Cu(hfac)\(_2\)L\(_{\text{Pr}}\), yielding \( J = -100 \text{ cm}^{-1} \) (see Ref. [7] for details). It is noteworthy that all estimations of “additional” exchange parameters (those incorporating, on the average, interactions to more distant Cu2 atoms and between the chains) are by almost two orders of magnitude smaller. This is consistent with relative unimportance of these more distant interactions also according to the calculation.

An inspection of partial DOS helps to understand the origin of energy preference of the AFM2 configuration. Fig. 4 compares the partial DOS at Cu1 and its neighbours which exhibit a noticeable magnetization, and that of more distant Cu2. For better comprehensibility, a very structured DOS from nondisperse energy bands was broadened with half-width parameter of 0.1 eV. Obviously this completely smears the above-mentioned tiny band gap. Although formally dealing with a non-metal, we refer to the energy which separates occupied and unoccupied states as the Fermi energy (zero in Fig. 4).

Somehow simplifying, but in accord with chemical intuition, the Cu(II) ion has its \( 3d \) majority-states fully occupied, and in the minority-spin one state vacant. This vacant \( 3d \) state is responsible for a narrow peak in the DOS ‘at’ (in fact, just above) the Fermi level. This simple picture seems not quite consistent with nominal magnetic moments at Cu1 and Cu2 sites as shown in Table 1 but that’s merely because the Cu magnetization spills over its neighbours. It is well seen in spin density maps (not shown here) and in the maps of Cu-
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Figure 4. Spin-resolved partial DOS in two AFM configurations. Zero energy separates occupied and unoccupied states. The features marked by thick dots and labeled a and b are explained in the text.

centered molecular orbitals shown below; moreover it is demonstrated by a presence of the Cu-related peak just above the Fermi level in the O4 DOS. Apart from this, we have a magnetic moment of the radical, roughly coming from summing up the values in Table 1 over O1, N1, N2 and O2 atoms where this moment is distributed (with a pronouncedly larger portion residing on the more Cu-distant O1).

As a most coarse observation, the Cu1-DOS is ‘inverted’ when changing from AFM1 to AFM2, but this is accompanied by a noticeable reconstruction of electronic states, responsible to the Cu3d–O2p hybridization. Among Cu-related and R-related orbitals, which share the energy interval of $-4$ to $+1$ eV around the Fermi level, we further concentrate on some, with particular character of bonding. The highest-energy peak among the fully occupied ones in majority-spin panel on the Cu1 site (spin-up for AFM1, spin-down for AFM2) comes from a state which is nonbonding with respect to the radical and antibonding with respect to oxygens of the Cu(hfac)$_2$ group (note its presence in the O4 spin-up DOS). The inversion of Cu1 spin changes merely the position of this peak: from $-0.83$ eV in AFM1 to $-0.68$ eV in AFM2. Further on, there is a state nonbonding with respect to Cu1 and pinned at the radical. It emerges in the DOS of O1, N1, N2, O2 as the lower of two peaks crossed by the Fermi
level. Its wavefunction is shown in Figs. 5 and 6 as that of the last-but-highest occupied molecular orbital (-HOMO). It contains no contribution from Cu1 whatsoever (having in fact a node at the Cu1 position) and is almost identical for AFM1 and AFM2 cases. Then there are two pronounced states which involve both Cu1 and the radical: (a) a feature in the minority-spin DOS at the Cu1 site, i.e., in the spin-down channel of AFM1 (at −0.71 eV) and in the spin-up channel of AFM2 (at −1.13 eV); (b) the ‘just occupied’ part of the highest of those two peaks which make a distinguished two-peak structure best seen in the local DOS of the radical atoms, crossed by the Fermi level. In fact this is the HOMO. This state is antibonding with respect to Cu1–O2 interaction. These (a) and (b) features are marked by thick dots in the DOS figures.

The lowest unoccupied molecular orbital (LUMO) centered at the selected Cu1 site corresponds to spin-down channel (the spin-up LUMO resides at a Cu1 atom in the other polymer chain) and contains no contribution from R. This is understandable, because within ±0.5 eV around the Fermi level there is a gap in the spectrum of spin-down states of the radical. The structure of the Cu3d wavefunction within the LUMO is of the $xy$ type, in contrast to spin-up $z^2$ in the HOMO. The next to LUMO (and higher by 16 meV) is the (also spin-down) orbital centered at Cu2.

When we now turn to the molecular orbitals of the AFM2 configuration (Fig. 6) we notice that the last-but-HOMO orbital, nonbonding to Cu1 and antisymmetric relative to its position, has the same shape as for AFM1. However, the HOMO differs from that of the AFM1 case by its symmetry at the Cu1 site. It bounds two O4 atoms of the Cu(hfac)$_2$ group much stronger than two others; this contributes to much higher disproportionality of magnetic moments over O4 atoms in AFM2 case than in AFM1 (see Table 1). The LUMO of AFM2 does not reflect the Cu1 states nor those of the radical, but instead the Cu2 (see below). The next-to-LUMO contains again the Cu1 contribution in somehow similar shape as in AFM1-LUMO↓, spread over the Cu(hfac)$_2$ plane. However – and this is crucial – the discussed wavefunction spreads over the O2···N2···N1···O1 group, in antibonding setting relative to Cu1.

As a result we see markedly stronger interaction of Cu3d states with the magnetic states of the radical in the AFM2 configuration than in AFM1. This is so because the responsible states which tend to interact, based on their spatial shape, belong now to the same spin channel, namely to spin-up in the notation of Fig. 4. As a single manifestation of this effect, the Cu-R hybridized state (a), on the one side, and (b), but also the ‘(LUMO+1)$\uparrow$’ of Fig. 8 on the other side, move apart. A similar argument applies with respect to other hybridized Cu1–R states, resulting in a slight overall (albeit non-uniform) replacement of occupied bands downwards. As a result, the AFM2 configuration wins over AFM1 due to the gain in band energy; moreover, this
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Figure 5. Highest occupied and lowest unoccupied molecular orbitals corresponding to $k=0$ in the AFM1 configuration. Only the Cu(hfac)$_2$ block and its two neighbouring ligands are shown. Positive and negative values are indicated by two grayscale levels. As in an AFM configuration all orbitals are doubly degenerate, and the figures show the vicinity of a selected Cu1 atom, the spin label is given for those respective orbitals which give a major contribution at the site in question, consistently with Fig. 4. The opposite-spin orbitals at the same energy are prominent at different Cu1 atom in the other polymer chain (see Fig. 6). The plots are created with the XCrySDen program [25].

accounts for a slightly larger band gap in AFM2.

The Cu2-DOS (the bottom panels in Fig. 4) seems largely unaffected by a reversal of its magnetic moment: its 3$d_{\uparrow\downarrow}$ DOS in AFM2 is almost identical to 3$d_{\downarrow\uparrow}$ one in AFM1. There are tiny differences responsible for the coupling of Cu2 to the ‘tail’ of the ligand via N4 (see Fig. 2), but they are left beyond the scope of the present study. It suffices to mention that the interaction with differently magnetized Cu2 changes the sequence of orbitals in the vicinity of the Fermi level, which are anyway nearly degenerate. In the AFM1 configuration, the LUMO has a pronounced contribution at the Cu1 site (shown in the right panel of Fig. 5), with the spin-down orientation, and the next state (higher by 16 meV) is that centered at Cu2. In the AFM2 configuration, the state with Cu2 predominance becomes the LUMO and have no contribution at Cu1, whereas the Cu1-centered orbital is now the next after LUMO (by 4 meV higher, shown in the right panel of Fig. 6), now evidently in the spin-up channel.

Summarizing, we investigated electronic structure, local densities of states and the shape of molecular orbitals responsible for chemical bonding and magnetic interaction in a heterospin polymer, connecting Cu(II) and nitronyl nitroxide radical in a ‘head to head’ configuration. We reproduced in the calcu-
Figure 6. The same as in Fig. 5 for the AFM2 configuration.

ulation and explained at microscopic level the preference for antiferromagnetic coupling between Cu and radical spins, and made an estimate of the magnitude of this coupling. There are certain issues which seem appealing for subsequent study. First, one should elucidate the interaction between Cu2 ion coupled to the ‘tail’ of the ligand and the presently analyzed ‘exchange cluster’. Second, the variation of all interaction parameters with temperature, according to (available by now) crystallographic data [26]. This might help to understand an unusual switch in the character of magnetic interaction, apparently accompanying a structural transition at 220 K described in Ref. [8, 27].

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