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Magnetism of 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA) and bis(hexafluoroacetylacetonato)copper(II) ($Cu(hfac)_2$)

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Abstract

An accurate full-potential density-functional method is used to study the mechanism of the origin of magnetism and the magnetic interactions in 1,3,5-Trithia-2,4,6-triazapentalenyl (TTTA) and Bis(hexafluoroacetylacetonato)copper(II) ($Cu(hfac)_2$). The results revealed that the spontaneous magnetic moments for the TTTA·$Cu(hfac)_2$ mainly come from Cu and N_1 atoms, and the O_1, O_2, O_3, O_4 and N_2, N_3, S_1, S_2 atoms also contribute to the magnetism. In TTTA·$Cu(hfac)_2$, there would be ferromagnetic interaction between the Cu(II) ion and the N_1atom of TTTA^{A}, and there exists antiferromagnetic interaction between the intramolecular organic ligands.

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Keywords: Ab initio method; Electronic structure; The magnetic properties

The magnetic properties of organic radical crystals have been extensively studied for a long time [1]. One of the most promising strategies relies on direct exchange coupling between metal ions and coordinated open shell (i.e., radical-based) ligands in clusters or coordination polymers. Among the most intensively studied paramagnetic ligands, in this context, are nitroxide radicals (including nitronyl nitroxides and imino nitroxides) [2], and radical anions such as semiquinones [3] and TCNE [4] and TCNQ [5] radical anions and the stable verdazyl radicals [6]. Recently the thiazyl free radicals represents an attractive alternative ligand system. The radical, 1,3,5-trithia-2,4,6-triazapentalenyl (abbreviated as TTTA), was first prepared in 1989 by Wolmershäuser and Johann [7]. Recently, Fujita and Awaga discovered a first-order phase transition in TTTA that occurs with a drastic change in magnetism and

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with a wide thermal hysteresis loop in the vicinity of room temperature [8]. They also found the TTTA is thermochromic in the phase transition, the high-temperature (HT) and low-temperature (LT) phases of TTTA are purple and green, respectively [8,9]. More recently, Matsuzaki, Fujita, Awaga and Okamoto revealed that the TTTA exhibits optical and magnetic bistability around room temperature with a large hysteresis loop [10]. As a new aspect of thiazyl radicals, the thiazyl radicals have strong electric polarization, leaving positive charges on sulfur atoms and negative charges on nitrogen atoms [11], and it is expected that TTTA operates as a ligand to form polymeric coordination complexes, in which the nitrogen atoms coordinate with metal ions and result in network structures. However, there are currently very few examples of metal-thiazyl complexes. In 2001, Fujita and Awaga reported the crystal structure and magnetic properties of 1:1 complex of TTTA and Bis(hexafluoroacetylacetonato)copper(II) (abbreviated as $Cu(hfac)_2$) in experiment [12]. But to the best of our knowledge, the magnetic properties of $TTTA{\cdot}Cu(hfac)_2$ have not been studied theoretically.

In this paper, we adopt the density-functional theory (DFT) with generalized gradient approximation (GGA) [13] to calculate the electronic band structure and the magnetic properties of $TTTA{\cdot}Cu(hfac)_2$ by the accurate full-potential linearized augmented plane wave (FP_LAPW) method.

The calculations were performed using the Vienna package WIEN2K [14,15]. This is a full-potential (linear) augmented plane wave plus local orbitals method within the density-functional theory (DFT) [16] and the density-functional theory has proved to be a powerful and economical tool for the study of a variety of molecular properties in coordination compound [17–19]. Its efficiency and accuracy have been discussed elsewhere [20,21]. The exchange and correlation effects are treated with the generalized gradient (GGA) approximation according to Perdew–Burke–Ernzerhof [13]. We choose the spin-polarized calculation for titled compounds. We set the expansion up to $l = 10$ in the muffin tins. The self-consistent calculations are considered to be converged only when the integrated charge difference per formula unit, $\int |\rho_n - \rho_{n-1}|\,\mathrm{d}r$, between input charge density $[\rho_{n-1}(r)]$ and output $[\rho_n(r)]$ is less than 0.0001. The complex $TTTA{\cdot}Cu(hfac)_2$ crystallizes in the monoclinic P_{21} space group, in which one unit of $TTTA{\cdot}Cu(hfac)_2$ is crystallographically independent. Fig. 1 depicts the geometry around the Cu(II) ion in this compound, where $Cu(hfac)_2$ and one of the TTTA molecules labeled A forms the independent unit. The other TTTA labeled B is obtained by the symmetry operation from $TTTA^A$. The structure parameters are $a = 6.937\,\text{Å}$, $b = 14.252\,\text{Å}$, $c = 10.699\,\text{Å}$ and $\beta = 103.843^\circ$, $Z = 2$. These data as well as the coordinate of atoms are obtained from the Cambridge Crystallographic Data Center (the CCDC number of PDF file is JA002873Z). We make use of the Vienna package WIEN2K and obtain the electronic structure, the partial density of states and atomic spin magnetic moments of $TTTA{\cdot}Cu(hfac)_2$.

Fig. 2 shows the total density of states (TDOS) of the molecule. Because the DOS distribution

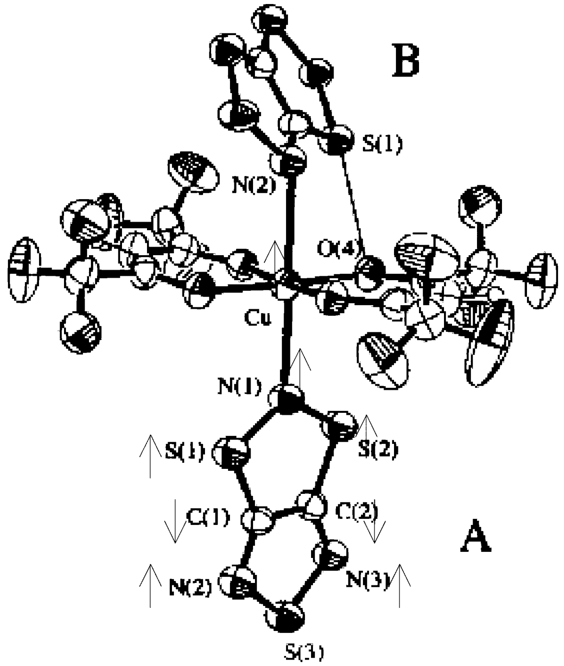

Fig. 1. The structure of $TTTA{\cdot}Cu(hfac)_2$, which achieved in Ref. [12(a)].