

First-principles study of the ferromagnetic and half-metallic properties of the fumarate-bridged polymer

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Abstract. Density-functional theory (DFT) with generalized gradient approximation (GGA) is applied to study the electronic structure and the magnetic properties of ferromagnet $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$. The density of states, the electronic band structure and the spin magnetic moment are calculated. The calculations reveal that the compound has a stable half-metal-ferromagnetic ground state, and that there exists a dominant ferromagnetic interaction arising from the alkoxo-bridged dimeric part of the compound. The spin magnetic moment $1.0 \mu_B$ per molecule mainly comes from the Cu ion with little contribution from O, N, C anion.

PACS. 75.50.Xx Molecular magnets

1 Introduction

For the past decades, the molecular-based magnetic materials with paramagnetic metal ions where bridging ligands act as a superexchange pathway between the metal centers have been widely studied both experimentally and theoretically, and some new materials have also been synthesized [1–6]. In the past few years the investigation of organic magnetic materials containing only light elements, typically C, N, O, S and H, has been the subject of a considerable amount of work [7–13]. Pure organic magnetic materials have free radicals, which can supply the magnetic moment, but their transition temperatures are too low for practical applications. The synthesis of the molecular-based ferromagnet with metallic ions has attracted an extensive interest. Recently, the use of organic spacers as superexchange pathways between the metal ions is of growing interest in the field of molecular magnetism.

The compound $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ [14] uses fumarate anions as a bridging block. The significant feature of the complex is that one of the carboxylate acid groups acts as a monatomic bridging ligand linked to two Cu(II), and the remaining group functions as a monodentate coordinating ligand to form a 1-D chain with alternate repetition of 4- and 14-member rings. A dominant ferromagnetic interaction with alternating ferro- and antiferromagnetic chain model exists for $S = 1/2$ local spin Cu(II) systems, where the ferromag-

netic interaction arises from the alkoxo-bridged dimeric part of the compound. For the monatomic bridging behavior of the carboxylic acid group, some papers reported [15,16] that the carboxylic acid group shows the bridging behavior, but that they are not characterized magnetically. In the dimeric Cu-O₂-Cu part of the chain of the compound $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$, one of the bridging oxygens is in the axial position of the first Cu(II) center, whereas the same oxygen is in the equatorial position of the second Cu(II). The other bridging oxygen of this dimeric part is linked to Cu(II) in a reversed manner. Each Cu(II) is in distorted square pyramidal environment. The structure of the polymeric compound $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ for all non-hydrogen atoms is shown in Figure 1 [14]. According to the susceptibility measurement, the present complex is ferromagnetic at low temperatures, and this ferromagnetic interaction arises from the monatomic(alkoxo type) bridged copper (II) dimeric part of the complex through the large Cu-O-Cu angle (104.1°).

In this paper, we adopt the density-functional theory (DFT) with generalized gradient approximation (GGA) to calculate the electronic structure and the ferromagnetic properties of the present compound, using the accurate full potential linearized augmented plane wave (FP-LAPW). The main goals of our work are to investigate the electronic structure and the magnetic coupling, and to analyze the propagation of the observed ferromagnetic interaction via the density of states(DOS) and the electronic band structure. This provides new insights to the origin

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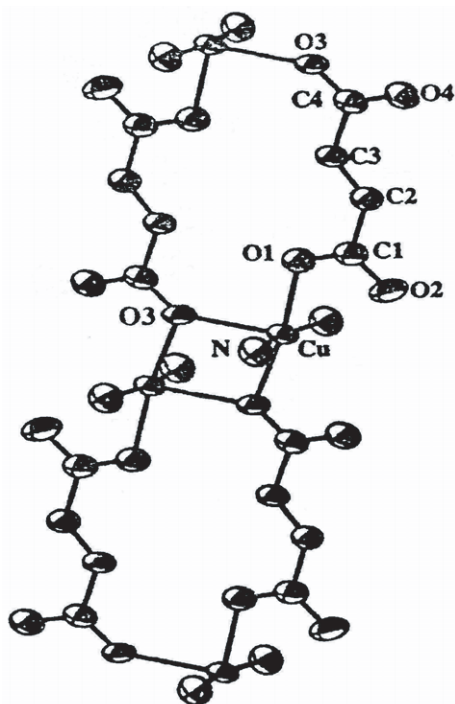


Fig. 1. ORTEP diagram of $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$ with a labeling scheme which shows 50% probability thermal ellipsoids for all non-hydrogen atoms.

of the strong ferromagnetic coupling in the compound, which should be useful for the design of novel ferromagnetic materials.

2 Results and discussion

The calculations presented in this work were performed by employing DFT with GGA using the FPLAPW method, which is among the most accurate band structure methods presently available. In this method, no shape approximation is used for either the potential or the electronic charge density. We use the Wien2k [17] package which allows inclusion of local orbitals in the basis, which upon linearization improves and makes possible a consistent treatment of semi-core and valence in one energy window.

In our case, the self-consistent calculations are based on the following structural parameters: the atomic-sphere radii R_{mt} are chosen as 2.4, 1.3, 1.0, 1.0, 0.6 a.u. for Cu, O (except for O51w), N, C, H (except for H5A) respectively. Since the O51w-H5A bond length is very small, we chose the atomic-sphere radii R_{mt} of O51w and H5A to be 0.8 and 0.5 a.u. respectively. The cutoff parameter is taken to be $R_{mt}K_{max} = 2$, where K_{max} is the maximal value of the reciprocal lattice vector used in the plane wave expansion, which corresponds to about 35724 plane waves at the equilibrium lattice constant. There are two molecules in one primitive cell. Our work is done on the compound $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$. Although the experimental work was on $m=n$, we chose to take $m = n$ and $m = n = 1$. Because the water molecule is

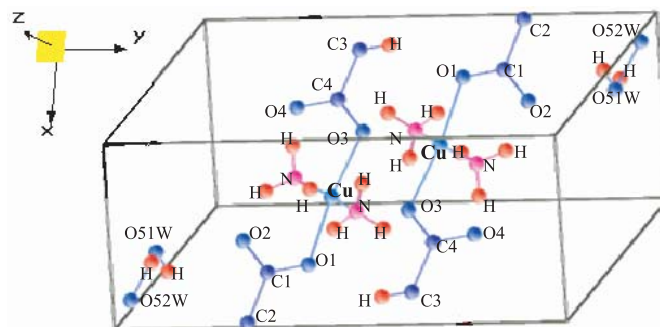


Fig. 2. ORTEP labeled primitive cell for $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_n$.

disordered over two positions with a site occupancy ratio 0.8/0.2, we chose two oxygen atoms (O51w and O52w) occupied positions in one water molecule. We show the primitive cell in Figure 2. When we omit the water molecule in the complex, we get almost the same result; therefore the water molecule has almost no effect on the magnetic properties of the complex.

According to the experiment, the present Cu(II) compound is in the monoclinic structure with the space group $C2/m$, and the lattice parameters are $a = 13.955(5) \text{ \AA}$, $b = 7.330(3) \text{ \AA}$, $c = 8.927(2) \text{ \AA}$, $\beta = 102.39(3)^\circ$. The structure shows a rare monatomic bridging mode of an acid group. The remaining carboxylate group acts as a monodentate coordinating ligand, thereby producing a chain with alternate repetition of 4- and 14-membered rings, and the two copper ions are interlocked by fumarate ligands.

Figure 3 shows the total density of states (DOS) of the molecule, the partial DOS (PDOS) for d -electrons of Cu and p -states of O1, O2, O3, C2, where the plotted energy range is from -6 eV to 4 eV . Because the DOS distribution near the Fermi level determines the magnetic properties, we concentrate our attention on the DOS in the vicinity of the Fermi level, and the Fermi level is set to zero. In the vicinity of the Fermi level, the total DOS, DOS of Cu $3d$ and DOS of O1, O2, O3, C2 $2p$ are clearly split, which means that the ordered spin arrangement is formed by the exchange interaction. Our calculation shows that the spin magnetic moment is $1.0 \mu_B/\text{molecule}$, which is in good agreement with the experimental result. In order to study the origin of the magnetic moment, we have studied the electronic structure of the compound. According to the DOS distribution, we note that the main origin of magnetism is provided by Cu $3d$ orbital, however the O1, O2, O3, C2 $2p$ orbitals also contribute to the spin magnetic moment, and the net spin of Cu $3d$ is parallel to that of O1, O2, O3, C2 $2p$. These phenomena play an important role in the indirect interaction between Cu(II) ions of two molecules, which implies that the monatomic bridge acts as superexchange pathway, and that the ferromagnetic interaction arises from the alkoxo-bridged dimeric part of the chain. In Figure 3 we show that near the Fermi level, the Cu $3d$ spin-up DOS distribution is below the Fermi level, the spin-down DOS distribution crosses the Fermi level, while most is above the Fermi level with peaks

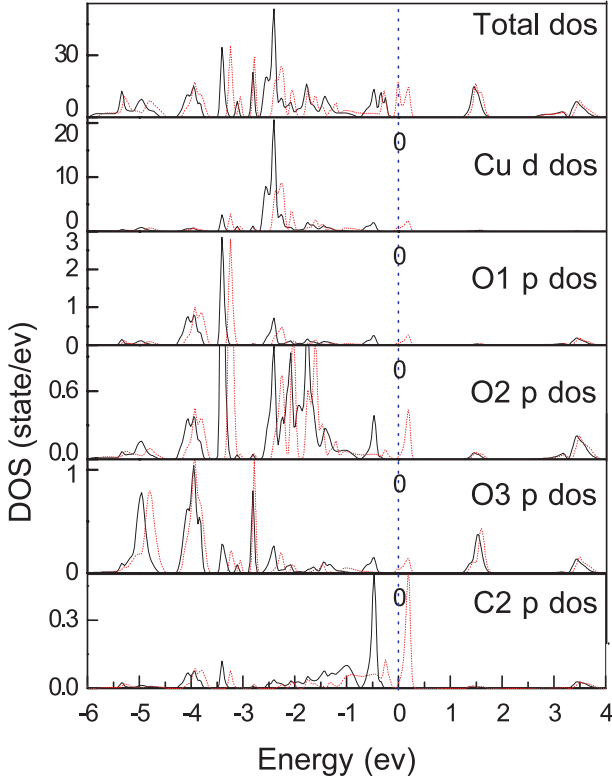


Fig. 3. Fig.3 Density of states for $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ (solid: spin-up states; dotted: spin-down states).

Table 1. Calculated magnetic moments in μ_B for the atoms of $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$.

site	Cu	O1	O2	O3	O4	O51w
Magnetic	0.316	0.043	0.055	0.028	-0.001	0.002
Moment	N	C1	C2	C3	C4	O52w
(μ_B)	0.024	-0.003	0.078	-0.008	0.000	0.058

at -0.46 eV for spin-up states and 0.18 eV for spin-down states respectively. The number of spin-up electrons for Cu is larger than that for the spin-down electrons. The calculations indicate that the unpaired spins mainly come from the d -orbital of Cu atom.

The spin magnetic moments of the complex are given in Table 1. The major part of the spin magnetic moment is from Cu, and there are smaller positive spin populations on the oxygen atoms, which can be explained by the spin delocalization mechanism. In the complex, the Cu^{2+} ion with the $3d^9$ has one unpaired electron; therefore there is a singly-occupied metal orbital. The two singly-occupied metal orbitals of the unit cell along with the two highest-occupied molecular orbitals (MOs) of O_2^- lead to the four molecular orbitals, b_{1g} , b_{1g^*} , b_{2u} , b_{3u} . At the active-electron approximation, the wave function for the $M_s = 1$ unit cell of the triplet state may be written as [18]

$$\Psi(S=1) = |b_{1g} \overline{b_{1g} b_{3u} b_{3u} b_{1g^*} b_{2u}}|.$$

Such a wave function leads to large positive spin populations on the copper atoms and smaller positive spin populations on the oxygen atoms. Because of the spin polarization within the π orbital of the fumarate groups, the sign of the carbon spin population alternates as $-/+/-/+$, the sign along the fumarate anion shows that the coupling between the carbon atoms is antiferromagnetic. In our calculation, the C2 atom has a large magnetic moment whereas the neighbors (C2 and C3) have a much smaller value. If we take the ambience around C2 into account, when choosing two primitive cells along the x and z axis, we found that the Cu atom in the nearest neighbor primitive cells along the z axis is near the C2 atom in the initial primitive cell, and that the Cu atom is the nearest atom to C2 atom. Therefore there must exist a spin delocalization from the Cu^{2+} ion toward the C2 atom, thereby leading to a larger spin magnetic moment of C2 atom. In Figure 1, each copper is in a distorted square pyramidal environment. Two nitrogens and O1, O3 define the equatorial plane of the pyramid, and the bond lengths are the following: Cu-N is $1.975(5)$ Å; Cu-O(1) is $1.973(5)$ Å; Cu-O(3) is $1.994(5)$ Å. The calculated magnetic moments per atom listed in Table 1 show that the ferromagnetic interaction arises from the alkoxo-bridged dimeric part of the chain, which acts as the superexchange pathway in the complex. Although the interaction between the carbon atoms is antiferromagnetic, the ferromagnetic interaction along the monatomic bridged dimeric unit of the molecule is dominant. These phenomena are in agreement with the experimental result, which shows that the title polymer has alternating ferro- and antiferromagnetic chains, and that the complex shows an overall intrachain ferromagnetic interaction. From Table 1, we also find that the magnetic moment of O4 is very small and negative, which is consistent with the experimental result that O(4) forms a hydrogen bond, $\text{N-H}(2\text{N}) \cdots \text{O}(4)$ [14]. According to our calculation, we can define a Heisenberg model which taking into account only the alternating nearest-neighbor interactions, yields the following Hamiltonian

$$H = J_1 \sum_{i=1}^{N/2} \vec{S}_{2i} \cdot \vec{S}_{2i+1} + J_2 \sum_{i=1}^{N/2} \vec{S}_{2i} \cdot \vec{S}_{2i+2}$$

J_1 is negative, corresponding to the antiferromagnetic coupling, while J_2 is positive, corresponding to the ferromagnetic one. In the Heisenberg model, we suppose that the intra-chain coupling is ferromagnetic, and that there exists an antiferromagnetic coupling between the inter-chains. Since the main magnetic moment comes from Cu atom, we just take into account the spin of Cu atom. In our calculation, the calculated exchange energy is $\Delta E = -0.015(7)$ Ry. If we take $J_F = +12 \text{ cm}^{-1}$ and $J_{AF} = -3.8 \text{ cm}^{-1}$, i.e. the same as the experimental ones, the exchange energy is $\Delta E = -0.015(1)$ Ry. Our result is therefore consistent with the experimental result.

In Figure 3 we show that near the Fermi level, the total DOS is clearly split. The Fermi level crosses the gap of the total spin-up DOS, and the top of the occupied spin-up band is 0.23 eV below the Fermi level. There is a 1.35 eV

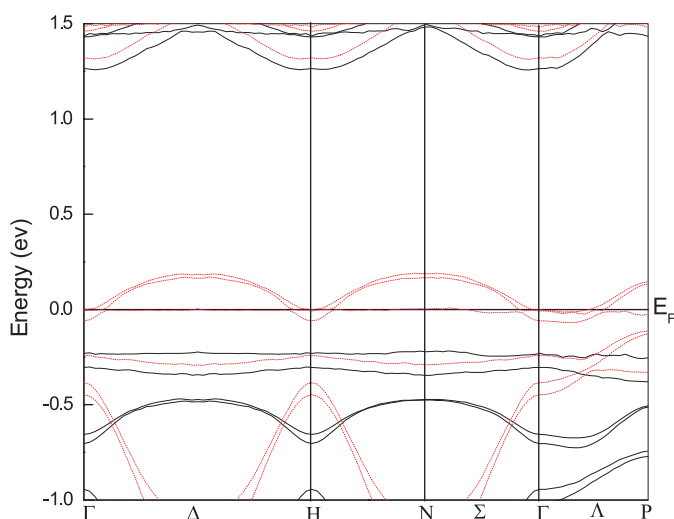


Fig. 4. Electronic bands of $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ along selected symmetry lines within the first Brillouin zone (solid line is spin-up electronic band; dashed line is spin-down electronic band).

energy gap between the spin-up occupied subband and the spin-up unoccupied subband. The total spin-down DOS crosses the Fermi level while most is above the Fermi level, which means the complex has half-metallic properties. In Figure 3 we notice that the bands near the Fermi level are mainly from the Cu $3d$ orbital, therefore the conduction electrons mainly come from the Cu d electrons.

In order to further investigate the magnetic interaction and the half-metallic properties, we also give the electronic band structure in Figure 4 (solid line is spin-up electronic band; dashed line is spin-down electronic band). In Figure 4 we show that the two single occupied molecule orbitals (SOMO) of the two molecules in the spin-up electronic bands are below the Fermi level, but that the spin-down electronic bands cross the Fermi level and are mostly above the Fermi level. This means that there exists a dominant ferromagnetic interaction between the two molecules, where the spin magnetic moment is about $1.0 \mu_B/\text{molecule}$. In Figure 4 we also show that the spin-down valence bands cross the Fermi level, and that there is no gap, however the top of the occupied spin-up band is 0.23 eV below the Fermi level, which implies that the complex has half-metallic properties.

3 Conclusions

In this work, we have investigated the magnetic and the half-metallic properties of a novel $[\text{Cu}(\mu\text{-C}_4\text{H}_2\text{O}_4)(\text{NH}_3)_2]_n(\text{H}_2\text{O})_m$ compound by employing DFT and GGA from the electronic band structure point of view. The results show that the Cu(II) complex has a half-metal-ferromagnetic ground state. An analysis of the DOS and

the electronic band reveals that the spin magnetic moment is $1.0 \mu_B$ per molecule, and that there is a dominant ferromagnetic interaction both for the intra- and the inter-molecules. The spin magnetic moment mainly comes from the Cu ion, and the ferromagnetic interaction is from the alkoxo-bridged dimeric part of the molecule. The conduction electrons are mainly from Cu(II) d orbital, and are located in the valance band.

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