

Studies on Electronic Structure and Magnetic Properties of an Organic Magnet with Metallic Mn²⁺ and Cu²⁺ Ions*

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Abstract The electronic structure and the magnetic properties of the non-pure organic ferromagnetic compound $MnCu(pbaOH)(H_2O)_3$ with $pbaOH = 2$ -hydroxy-1, 3-propylenebis (oxamato) are studied by using the density-functional theory with local-spin-density approximation. The density of states, total energy, and the spin magnetic moment are calculated. The calculations reveal that the compound $MnCu(pbaOH)(H_2O)_3$ has a stable metal-ferromagnetic ground state, and the spin magnetic moment per molecule is $2.208 \mu_B$, and the spin magnetic moment is mainly from Mn ion and Cu ion. An antiferromagnetic order is expected and the antiferromagnetic exchange interaction of d-electrons of Cu and Mn passes through the antiferromagnetic interaction between the adjacent C, O, and N atoms along the path linking the atoms Cu and Mn.

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Key words: density-functional theory, non purely organic magnet, electronic structure, ferromagnetic properties

1 Introduction

For the past decades, the synthesis of magnetic materials containing only light elements, typically C, N, O, S, and H, the so-called magnets, has been the subject of a considerable amount of work, both theoretically and experimentally.^[1–5] One of the reasons for this interest was the scientific challenge to achieve a magnetic long range order from s and p electrons, since in conventional magnets this property is related to direct or indirect interactions between electrons of incompletely filled d or f orbitals.^[6] Another reason involves potential technological applications related to the low weight and processing cost of organic materials, and the modulation of properties by means of chemical and electrochemical methods.

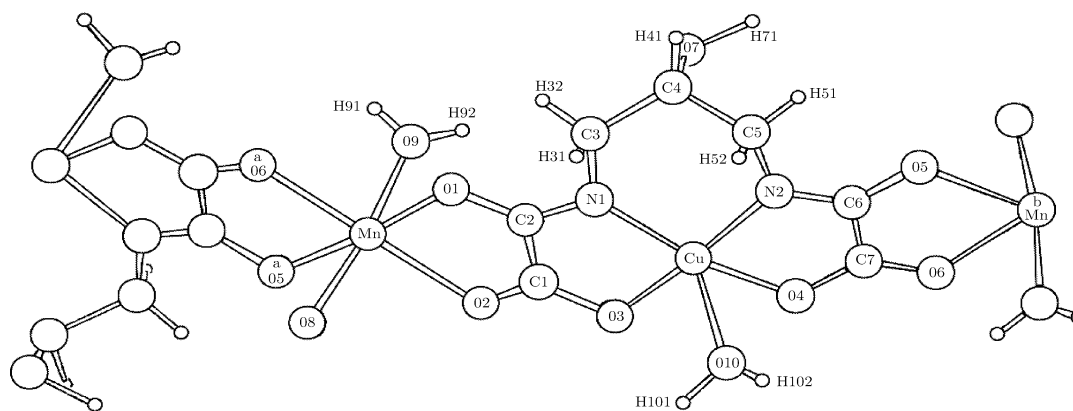


Fig. 1 Section of the bimetallic chain in $MnCu(pbaOH)(H_2O)_3$ as viewed approximately down the crystallographic c axis. The atomic numbering scheme used is shown.

Today, a few materials based on the nitroxide radical^[7–9] and sulfur-nitrogen radicals^[10] are known to display ferromagnetic or ferromagnetic-like properties, but their transition temperatures are still too low for practical applications. The synthesis of organic ferromagnet with the metallic ions^[10–13] has drawn an extensive research interest during the past decades. Some of the organic ferromagnets containing metallic ions have enough high transition temperature to be applied to technological applications. The compound $MnCu(pbaOH)(H_2O)_3$ ^[11] is the one of the non-pure organic ferromagnets synthesized earlier. Its structural formular is shown in Fig. 1. This compound displays a wide variety of magnetic behaviors, including paramagnetism, antiferromagnetism, and ferromagnetism. Down to ~ 30 K, the

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magnetic properties of $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ are identical within experimental uncertainties and are characteristic of one-dimensional (1-D) ferrimagnet. On the other hand, below ~ 30 K, it behaves in opposite fashions. As the temperature is lowered below 30 K, the $\chi_M T$ product of the molar magnetic susceptibility with temperature increases more and more rapidly and reaches extremely high values. The compound $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ exhibits a three-dimensional (3-D) ferromagnetic ordering of the ferromagnetic chains at $T_c = 4.6$ K.^[11]

Although numerous experimental studies have been performed on the compound $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$, its magnetic coupling mechanism is not entirely explained. In this paper, we adopt DFT with LSDA to calculate the electronic band structure and the ferromagnetic properties of the compound $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ by the accurate full potential linearized augmented plane wave (FPLAPW). The magnetic coupling mechanism that gives rise to the antiferromagnetic ordering, as well as the role played by C, N, and O atoms on the magnetic properties of this kind system are also discussed.

2 Result and Discussion

The calculations presented in this work are performed by employing DFT with LSDA, and using the FPLAPW method, which is among the most accurate band structure methods presently available. In this method no shape approximation on either potential or the electronic charge density is made. We use the Wien 97^[14] package, which allows inclusion of local orbitals in basis, improving upon linearization and making possible a consistent of semicore and valence in one energy window, hence ensuring proper orthogonality. The compound $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ crystallizes in the orthorhombic system, space group $\text{P}2_12_12_1$. Room temperature X-ray diffraction measurements indicate that the lattice parameters of the compound $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ are $a = 12.351$ Å, $b = 21.156$ Å, $c = 5.073$ Å. It is too time-consuming to optimize three lattice parameters. In the present calculations, we use these experimental lattice parameters rather than trying to obtain them from the minimum of the total energy.

Figure 2 shows the total density (DOS) of the molecule and the total-atomic DOS of Mn, Cu, N, C, and O atoms. The plotted energy range is from -6 eV to 2 eV, and lower lying semi-core states have been omitted for clarity. The Fermi level is set to zero. The series of bands between approximately -2 eV and -6 eV arises primarily from the O $2p$, N $2p$, and C $2p$ orbitals. The bands between approximately -2 eV and 0 eV are mainly from Mn $3d$ and Cu $3d$ orbitals. The Mn $3d$ and Cu $3d$ orbitals are weakly hybridized with N $2p$, O $2p$, and C $2p$ orbitals. The weak hybridization of these orbitals can play an important role in enhancing the antiferromagnetic interaction between Mn ions and Cu ions of $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$. The total DOS, and Mn-total DOS and Cu-total DOS are obviously split because of the exchange interactions. The total spin-up DOS of Mn is mainly located in the vicinity of the Fermi level and the total spin-down DOS of Mn is mainly distributed above the Fermi level. It is also found that the total-atomic DOS of Mn and the total-atomic DOS of Cu is nearly only from d-orbitals in the energy range from -2 eV to 2 eV, so we do not give the partial DOS of d-orbitals of Mn and Cu, for simplicity. The spin-up DOS distribution of Mn $3d$ is about 1.5 eV lower than the spin-down DOS of Mn $3d$. The splitting causes most of the spin-up Mn $3d$ orbitals to be occupied while most of the spin-down Mn $3d$ orbitals are empty. The DOS of the spin-down Cu $3d$ is shifted down about 0.8 eV from the DOS of spin-up Cu $3d$. The number of spin-up electrons of Cu ion is less than that of the spin-down electrons of Cu ion. The spin magnetic moment of the Mn ion is antiparallel with that of Cu ion. Mn is antiferromagnetically coupled with the nearest intrachain Cu. The present calculations indicate that the unpaired spins mainly reside on d-orbitals of Mn and Cu. By the way, from Fig. 2 we can find that $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ is a conductor. The bands crossing the level are mainly from Mn $3d$ and Cu $3d$ orbitals.

Table 1 Calculated magnetic moments (MM) in μ_B for the atoms of $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$.

Site	Cu	Mn	O1	O2	O3	O4	O5	O6	O7
MM	-0.548	2.773	-0.045	-0.044	0.036	0.033	-0.045	-0.045	-0.023
Site	N1	N2	C1	C2	C3	C4	C5	C6	C7
MM	0.039	0.044	0.000	0.000	0.017	0.029	-0.012	0.000	0.000

In Table 1, the spin magnetic moments of the $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ are given. Alternating $-/+$ spin populations along all paths linking the Cu ion and Mn ion confirm that the $\text{Mn}^{2+}\text{Cu}^{2+}$ bimetallic molecular ferromagnet is deduced from the antiferromagnetic (AFM) interaction between the adjacent atoms along the path linking the Cu ion and Mn ion. Even if the

interaction between nearest neighbors is antiferromagnetic, as it is most frequently, the ground state can be magnetic owing to the noncompensation of the local spins. The ferromagnetic chains within the crystal lattice are formed. Between chains half a unit cell apart in the \mathbf{a} direction, the closest metal-metal separations are $\text{Cu}\cdots\text{Mn}^d(3/2 - x, -y, 1/2 + z) =$

5.751 Å, $\text{Cu}\cdots\text{Mn}^e(3/2 - x, -y, -1/2 + z) = 6.398$ Å, $\text{Mn}\cdots\text{Mn}^d = 6.921$ Å, and $\text{Cu}\cdots\text{Cu}^f(1/2 + x, l/2 - y, 1 - z) = 7.120$ Å. The shortest metal-metal separations between neighboring chains in the \mathbf{a} direction are $\text{Cu}\cdots\text{Mn} = 5.751$ Å and 6.398 Å. The present calculation reveals that the spin magnetic moment per molecule is $2.208 \mu_B$. The present calculations indicate that Cu ion antiferromagnetically coupled with Mn ion in the neighboring chains and with the nearest intrachain Mn ion. We return to a comparison of our results with the experimental values. The saturation magnetization is $M_s = Ng\beta S = 23.3 \times 10^3 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{G}$. Here, N is Avogadro's number and β is the electronic Bohr magneton. We can deduce $S_{\text{Mn}} = 5/2$ and $S_{\text{Cu}} = -1/2$ and $g = 2$ from the saturation magnetization. The experimental spin magnetic moment values suggest $4.0\mu_B/\text{molecule}$, $5.0\mu_B/\text{Mn}$, and $-1.0\mu_B/\text{Cu}$. The present calculation values are not in good agreement with the experimental values. Usually LSDA underestimates splitting energy and magnetic moments. LSDA gives the energetic positions of the shallow d states of transition metals too high and too close to the s or p states. Looking at the total-atomic DOS of atom Mn in Fig. 2, if the d bands of Mn would be about 1.0 eV lower than the LSDA's result, the Fermi level would fall into the gap between spin-up and spin-down d bands, which suggests the half-filled d shell of Mn atom with all spin-up states filled and all spin-down states empty. The spin magnetic moment of Mn would be $5.0\mu_B$. The self-consistent field (SCF) iterations converge to a ferromagnetic state, the total energy in the ferromagnetic state $E = -29\,662.4181$ Ry. An artificial nonmagnetic state is used to obtain the total energy for the nonmagnetic state $E = -29\,662.3827$ Ry. Thus, the total energy difference between the ferromagnetic state and nonmagnetic state is $\Delta = 0.0354$ Ry, so the ferromagnetic state is more stable than nonmagnetic state.

In conclusion, we have studied in this letter the electronic band structure and the ferromagnetic properties of $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ by employing DFT with LSDA. It is shown that $\text{MnCu}(\text{PbaOH})(\text{H}_2\text{O})_3$ has a metal-ferromagnetic ground state. An analysis of the DOS for $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ reveals that the spin magnetic moment is $2.208 \mu_B$ per molecule, and the spin magnetic moment is mainly from the Mn ion and Cu ion. The AFM exchange interaction of d-electrons of the atoms Cu and Mn passes through the AFM interaction between the adjacent C, O, and N atoms along the path linking the Cu and Mn ions.

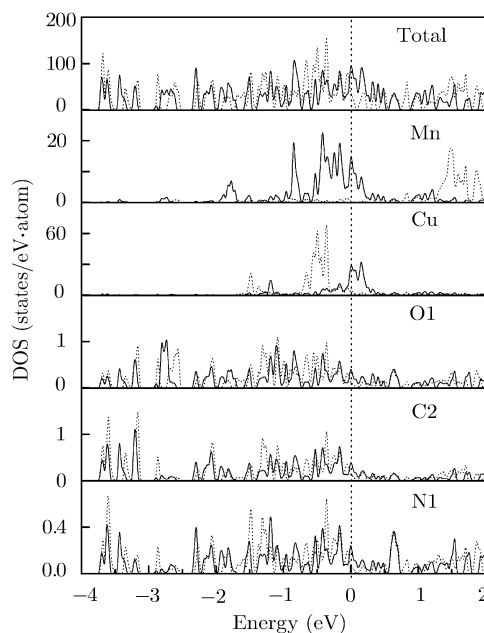


Fig. 2 Density of states for $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$ (solid: spin-up states; dashed: spin-down states).

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