有机-无机杂化化合物[Cu(μ-cbdca)(H$_2$O)]$_n$的电子结构及铁磁性

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摘要：　利用基于密度泛函理论(DFT)的第一性原理的 FP_LAPW 方法, 对以铜离子为磁性中心的化合物 [Cu(μ-cbdca)(H$_2$O)]$_n$(cbdca=cyclobutanedicarboxylate)的电子结构及磁性质进行了计算. 对该材料的铁磁性、反铁磁性和非磁性三种状态下的总能量进行了计算. 计算结果表明, [Cu(μ-cbdca)(H$_2$O)]$_n$ 的铁磁态能量最低, 该化合物为稳定的铁磁性物质, 该结果与实验吻合较好. 对原子磁矩的计算结果发现, 铜原子对化合物磁性的贡献较大, 双齿配体上的氧原子和碳原子的贡献相对较小.

关键词：　密度泛函理论；　电子结构；　FP_LAPW
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Electronic Structure and Ferromagnetic Properties of Organic-Inorganic Hybrid Compound [Cu(μ-cbdca)(H$_2$O)]$_n$

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Abstract: The electronic structure and magnetic properties of the molecule-based magnet [Cu(μ-cbdca)(H$_2$O)]$_n$ (cbdca=cyclobutanedicarboxylate) compound with copper ions as the metallic magnetic center were studied using the FP_LAPW(first-principle full-potential linearized augmented plane wave) method of first-principles, based on density functional theory (DFT) with generalized gradient approximation (GGA) method and local spin density approximation (LSDA) method. The total energies of the ferromagnetic, antiferromagnetic, and non-magnetic phases of organic-inorganic metal phosphonoacetate [Cu(μ-cbdca)(H$_2$O)]$_n$ were calculated. The calculations revealed that the compound [Cu(μ-cbdca)(H$_2$O)]$_n$ had a stable metal-ferromagnetic ground state, which was in agreement with the experimental result. There were large and positive spin populations on copper (II) ions, small and positive populations on the oxygen and carbon atoms of the bidentate ligand, which connected to the copper ions.

Key Words: Density functional theory;   Electronic structure;   FP_LAPW

The quest to develop new magnets based on molecule based materials is a growing area of contemporary materials chemistry research. In the meantime, because of the existence of transition ions, numerous one-, two-, and three-dimensional coordination polymers containing transition ions and light elements, typically C, N, O, and H, often show magnetic order at low temperature, which attract increasing interests among theoretical physicists and chemists[1–8], and there have been many theoretical studies on these systems devoting to understand the magnetic and the electronic properties at the microscopic level[9–11]. In order to construct new molecule-based magnetic materials, one needs to study their electronic structure, which is important to study the mechanism of ferromagnetic interactions hidden behind these materials. On the other hand, the spin distributions

are also important to understand the magnetism. For this purpose, we turn our eyes to the bivalent transition metal phosphonoacetates compounds, which have recently attracted much attention as molecular based magnetic crystals[12−17]. Such compounds are composed of transition metal ions (M^{n+}, M=Mn, Fe, Co, Ni, and Cu) and organic amines structure directing ligands. The crystal structures and the magnetic properties have been determined experimentally by Baldoma *et al.*[18]. The complex has been chosen to calculate for two reasons. (1) The main character of spin distributions in the sheetlike arrangement of (aqua)-copper(II) compound has not been determined from experiment, while the theoretical calculation can help us to get it. (2) The compound contains not only the carbon atoms, which are coordinated to two other neighboring copper ions in a bis (monodentate) fashion through the free oxygen atom, but also the carbon atoms of the six-membered chelate ring at the copper atom, which means that the electronic-structure difference can help us further understand the behavior of the sheetlike arrangement of (aqua)-copper(II) unit group in the compound and the magnetic moment contributions of different atoms.

In this work, we report the first-principle calculations on the compound [Cu(μ-cbdca)(H$_2$O)]$_n$. The spontaneous magnetic moment, the total energy of the cell, and the density of states are calculated. This provides new insights to comprehend the mechanism of the weak ferromagnetic coupling in the family of compounds, which is useful for designing of novel ferromagnetic materials, and opens a path to new class of molecule-based ferromagnetic conductors.

1 Structure of the compound and computational details

The molecular crystal structure of [Cu(μ-cbdca)(H$_2$O)]$_n$ (cbdca= cyclobutanedicarboxylate and chemical formula: C$_6$H$_8$CuO$_5$) is shown in Fig.1. The asymmetric unit of the metal phosphonoacetate compounds consists of sheetlike arrangement of (aqua)-copper(II) units bridged by cbdca ligands and the copper atom, which exhibits a perfect square-pyramidal environment, with four carboxylate oxygen atoms in the equatorial positions and a water molecule in the axial one. The molecular fragment of the [Cu(μ-cbdca)(H$_2$O)]$_n$ compound is plotted in Fig.2. Each cbdca ligand forms a six-membered chelate ring at the copper atom, the value of the angle subtended at the metal atom being 89.75 (14). The carboxylate group adopts the *syn-anti* coordination mode, the value of Cu···Cu separation through this bridge being

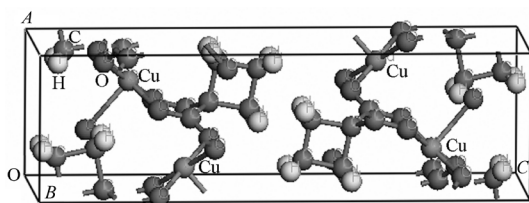48.42(5) nm. The dihedral angle between the basal planes of the consecutive Cu(II) units was found to be 82.3(8)°. According to the experiment of X-ray diffraction[18], the crystal cell has been adopted for the calculation, the optimized values of the compounds, with space group P_{cmn} (Z=4), adopted in the calculations are a=55.24(6) nm, b=70.69(2) nm, c=185.01(8) nm and α=β= γ=90°, more details of the crystal data, including atomic positions, can be obtained from Ref.[18]. The magnetic behavior of [Cu(μ-cbdca)(H$_2$O)]$_n$ has been determined from experiment. The result reveals that it is weak ferromagnetic coupling in the temperature range of 2−300 K.

The first-principle calculation based on the density functional theory (DFT) is one of the most powerful tools to study the ground-state properties of materials. It can give us the information about the electronic structures of complexes. It can also be used to study the spin distribution in malonate bridged compound when their spin distributions have not been measured from experiment. In this article, we use the first-principle full-potential linearized augmented plane wave (FP_LAPW) method based on DFT to calculate the electronic structures of the first six cyclobutanedicarboxylate copper (II) compounds. The calculation has been done with WIEN2K code based on FP_LAPW[19]. In the calculation, the fully relativistic effects of the core states and the valence state are included in a scalar relativistic treatment. For the exchange and correlation interactions, we adopt the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof 96[20]. The muffin-tin sphere radii of Cu, C, O, and H have been chosen as 1.93, 1.09, 0.98, and 0.53 a.u., respectively. Within these spheres, the charge density and the potential are expanded in terms of crystal harmonics up to angular moment l= 6. In the FP_LAPW calculations, the value of $R_{MT} \cdot k_{max}$ (smallest muffin-tin radius multiplied by the maximum k value in the expansion of plane waves in the basis set) determines the accuracy of the basis set used; $R_{MT} \cdot k_{max}$=2.2 was used in this study and $6 \times 5 \times 2$ k-point meshes in the Brillouin zone were adopted in the calculations (27 points in the irreducible part of Brillouin zone) with 30184 plane waves at the equilibrium lattice constant. With these cutoff parameters, the self-consistency was achieved by demanding the convergence of the
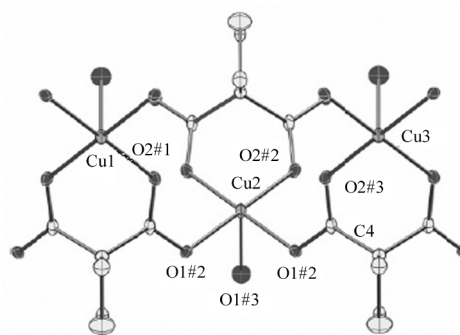

Fig.1 Magnetic structure of ferromagnetic [Cu(μ-cbdca)(H$_2$O)]$_n$ compound, crystallizing with the monoclinic unit cell

Fig.2 Molecular fragment of the [Cu(μ-cbdca)(H$_2$O)]$_n$ compound, showing the asymmetric unit and the numbering scheme

The numbering of hydrogen atoms is omitted for clarity.

integrated charge difference between last 2 iterations ($\int |\rho_n - \rho_{n-1}| dr$) to be smaller than 1.0×10^{-4} electrons. In addition, we checked that the convergence of the total energy was smaller than 1 meV, formula unit for every case.

2   Results and discussion

In the calculation, core states are treated fully relativistically, and the valence states relativistic effects are included in a scalar relativistic treatment. Using the self-consistent total energy calculations, we try to find out the ground state magnetic structure with the ligand-mediated 'superexchange' interaction. In addition, the unit cell described above was doubled in the x direction of the structure, creating a $2 \times 1 \times 1$ supercell containing two copper ions. The initial spin-up and spin-down occupation numbers of the copper ions were inverted, resulting in the pair being antiferromagnetically ordered at the start of the calculation, and the antiferromagnetic calculation was performed. The energy difference of ferromagnetic (FM), antiferromagnetic (AFM) and non-magnetic (NM) structures was determined by performing additional ferromagnetic and non-magnetic calculations with identical parameters as the corresponding antiferromagnetic calculation. In the antiferromagnetic configuration, the two kinds of unequivalent Cu ions, Cu1 and Cu2, are equivalent in non-magnetic and ferromagnetic states. The total energies calculated corresponding to FM, AFM, and NM phases of these three magnetic states for $[Cu(\mu\text{-}cbdca)(H_2O)]_n$ were -36151.673, -36151.631, and -36151.615 Ry. We found the ferromagnetic structure had the lowest energy, which indicated that the FM phase was a stable ground state for this compound. This is consistent with the experimental result. As expected, the copper (II) ions is found to be the main contributor to the magnetic moment of the ferromagnetic structure. The theoretical saturation value for the magnetic moment of one copper (II) ion ($3d^9$ configuration) is $1.000 \mu_B$, and the calculated values for the compound is about $1.000 \mu_B$. The agreement between them is good. The spin populations on different atom sites are listed in Table 1.

The calculation has shown that the spin populations on other atoms are negligibly small, so only the spin populations on copper ion, oxygen and carbon atoms are listed. The main features of the spin distributions in the compound are as follows: (1) Larger positive spin populations of $0.473 \mu_B$ is found on copper (II) ion of the compound. (2) The spin distributions of O1, C4, and O2, which connect the two copper (II) through the O1—C4—O2 bridge plotted in Fig.2, are about one order of

magnitude larger than those of the other atoms of the compound. Here we should mention that in the compound, which contains copper ions, the magnetic moment is not fully restricted to the atoms, but partially expands over the molecule. The cell has been divided into two kinds of regions during the calculation: the non-overlapping atomic spheres surrounding each atom and the interstitial regions[21-26]. The values listed in Table 1 only include the spin populations confined in these atomic spheres, and do not include that distributed in the interstitial regions. So their sum is smaller than the calculated total magnetic moment ($1.000 \mu_B$).

The electronic-structure analysis indicates that the spin populations on copper ion or oxygen and carbon atoms in the compound are dominated by $3d$ or $2p$ states, respectively, while the contributions from other orbitals are negligibly small. Fig.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, C4, and O2, where the plotted energy range is from -6 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, which is set to zero. We find the main features are as follows: (1) The DOSs on copper(II) ions near the Fermi level (between -2 and 1 eV) are obviously larger than that on oxygen and carbon atoms. (2) Near the Fermi level, the DOSs distributed in the O1, C4, and O2 are larger than the
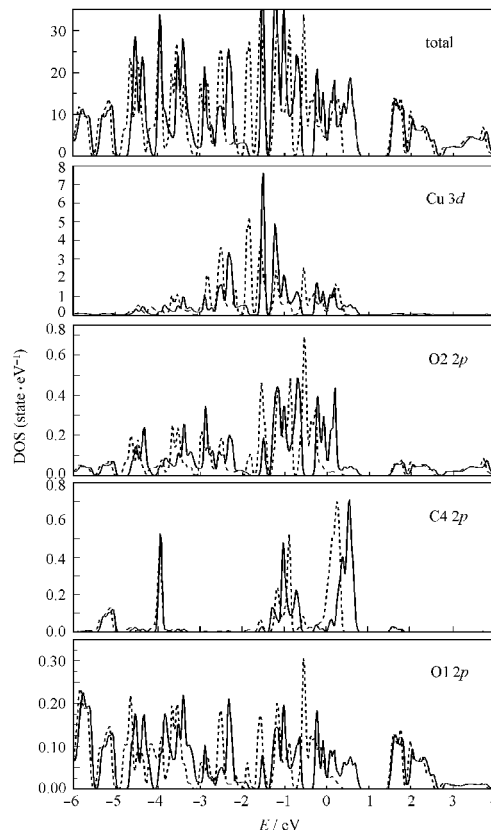
Table 1   Calculated spin populations inside the atomic spheres of different atoms sites in FM configurations

Site	Magnetic moment (μ_B)	Site	Magnetic moment (μ_B)
Cu	0.473	O3	0.003
O1	0.068	C2	0.005
O2	0.044	C3	−0.001
C4	0.033	C5	−0.001

Fig.3   Calculated total and partial DOSs in FM state for $[Cu(\mu\text{-}cbdca)(H_2O)]_n$

solid: spin-up states; dotted: spin-down states

other same atoms whose magnetic moments are negligibly small as shown in Table 1. (3) The distributions of DOSs on the two terminal oxygen atoms of the carboxylate fragments are similar though they occupy different positions: they occupy the same energy range just with different magnitudes, which is due to the hybridization between $2p$ states of the two O2 of different carboxylate fragments. Furthermore, the DOS profiles near the Fermi level (between −1.6 to 0.8 eV) of O1 and O2 are similar with that of copper ion, respectively. This similarity means there is a conjugation effect of the spin delocalization between copper ions and corresponding oxygen atoms due to the hybridization of Cu $3d$ with O $2p$ orbitals. From the above discussion and Table 1, we can see that the signs of the Cu1, O1, C4, O2, and Cu2 spin populations are all positive, which means there exist ferromagnetic exchange interactions between them. As we know that the mechanism based on spin delocalization has been proposed to account for the magnetic coupling. The spin delocalization mechanism[27] can be simply summarized as follows: (1) There is no spontaneous magnetic moment on the bidentate ligand and only the singly occupied orbitals of the magnetic ion provide the net spin of the crystal; (2) When magnetic ions are bridged by the bidentate ligand, their singly occupied electrons are then partially delocalized to the bidentate ligands, which leads to larger positive spin populations on the copper ions and smaller positive spin populations on the two terminal oxygen atoms of the bidentate ligand. From Table 1 one can immediately see that the spin distributions obtained from our calculations are in agreement with that predicted by spin delocalization mechanism and there is no negative spin population on atoms of the bidentate ligand, which cannot be interpreted by spin-polarization mechanism.

From Fig.3, we find that near the Fermi level in FM states there is a DOS distribution crossing the Fermi level. This means that FM state of $[Cu(\mu\text{-}cbdca)(H_2O)]_n$ is a conductor. The metallic character of FM state is related to the chain of Co—O—C—O—Cu as magnetic coupling. This is also due to the fact that the occupied states near the Fermi level are mainly of Cu $3d$ states, then O $2p$ and C $2p$ states.

3 Conclusions

The accurate first-principles calculations on the compound of $[Cu(\mu\text{-}cbdca)(H_2O)]_n$ were reported. The spontaneous magnetic moment, the density of states (DOS), and the electronic band structure were calculated. It is found that the compound $[Cu(\mu\text{-}cbdca)(H_2O)]_n$ has a stable ferromagnetic ground state. The band structure of the compound shows a conductor character and the ferromagnetic coupling through the bidentate ligand should be ascribed to spin delocalization effect. The ferromagnetic compound $[Cu(\mu\text{-}cbdca)(H_2O)]_n$ based on the organic-metal polymer may be a good candidate for the next generation of conductor devices when realized in experiments.

References

1   Escuer, A.; Vicente, R.; Goher, M. A. S.; Mautner, F. A. *Inorg. Chem.,* **1997, 36**: 3440

2   Escuer, A.; Vicente, R.; Mautner, F. A.; Goher, M. A. S. *Inorg. Chem.,* **1997, 36**: 1233

3   Maji, T. K.; Mukherjee, P. S.; Mostafa, G. T.; Mallah, J. C.; Boquera, J. C.; Chaudhuri, N. R. *Chem. Commun.,* **2001:** 1012

4   Mukherjee, P.; Dalai, S.; Zangrando, S.; E.; Chaudhuri, N.; Mostafa, R. G.; Tuchagues, J.; Chaudhuri, N. R. *Chem. Commun.,* **2001**: 1444

5   Maji, T. K.; Mukherjee, P. S.; Koner, S. *Inorg. Chim. Acta,* **2001, 314**: 111

6   Inoue, K.; Hayamizu, T.; Iwamura, H.; Hashizume, D.; Ohashi, Y. *J. Am. Chem. Soc.,* **1996, 118**: 1803

7   Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.,* **1994, 33**: 385

8   Itoh, K.; Miller, J. S.; Takui, T. *Mol. Cryst. Liq. Cryst.,* **1997**: 305

9   Luneau, D. *Curr. Opin. Solid State Mater. Sci.,* **2001, 5**: 123

10 Coord, L. *Coord. Chem. Rev.,* **1998, 178−180**: 1501

11 Miller, J. S.; Epstein, A. *J. Coord. Chem. Rev.,* **2000, 206−207**: 651

12 Escuer, A.; Vicenter, R.; Ribas, J.; El-Fallsh, M. S.; Solans, X.; Font-bardia, M. *Inorg. Chem.,* **1993, 32**: 3727

13 Kurrmoo, M.; Kepert, C. J. *New J. Chem.,* **1998, 22**: 1515

14 Livage, C.; Egger, C.; Ferey, G. *Chem. Mater.,* **1999, 11**: 1546

15 Pan, L.; Ching, N.; Huang, X.; Li, J. *Inorg. Chem.,* **2000, 39**: 5333

16 Das, A.; Rosair, G. M.; Fallah, M.; Salah, E.; Ribas, J.; Mitra, S. *Inorg. Chem.,* **2006, 45**: 3301

17 Zheng, H.; Wang, Z. M.; Gao, S.; Yan, C. H. *Inorg. Chem.,* **2006, 45**: 6694

18 Baldoma, R.; Monfort, M.; Ribas, J.; Solans, X.; Maestro, M. A. *Inorg. Chem.,* **2006, 45**: 8144

19 Blaha, P.; Schwarz, K.; Madsen, G. K.; *et al.* WIEN2k, An augmented plane wave+local orbitals program for calculating crystal properties. Wien, Austria: Technische Universität, 2001

20 Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.,* **1996, 77**: 3865

21 Zhang, Y. S.; Yao, K. L.; Liu, Z. L. *J. Chem. Phys.,* **2005, 123**: 124308

22 Zhang, Y. S.; Yao, K. L.; Liu, Z. L. *J. Magn. Magn. Mater.,* **2006, 301**: 112

23 Zhang, Y. S.; Yao, K. L.; Liu, Z. L. *Phys. B,* **2005, 358**: 216

24 Zhang, Y. S.; Yao, K. L.; Liu, Z. L. *J. Magn. Magn. Mater.,* **2005, 295**: 269

25 Yao, K. L.; Li, Z. B.; Liu, Z. L. *J. Magn. Magn. Mater.,* **2008, 320**: 222

26 Amrani, B.; Hassan, F. E. H.; Zoaeter, M. *Phys. B,* **2007, 452**: 222

27 Aebersold, M. A.; Gillon, B.; Plantevin, O. *J. Am. Chem. Soc.,* **1998, 120**: 52