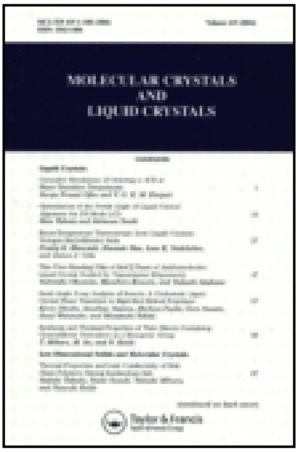

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Theoretical Studies on Magnetic Interactions of Aligned Tetrametal Systems by Using Magnetic Effective Density Functional (MEDF) Method

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Theoretical Studies on Magnetic Interactions of Aligned Tetrametal Systems by Using Magnetic Effective Density Functional (MEDF) Method

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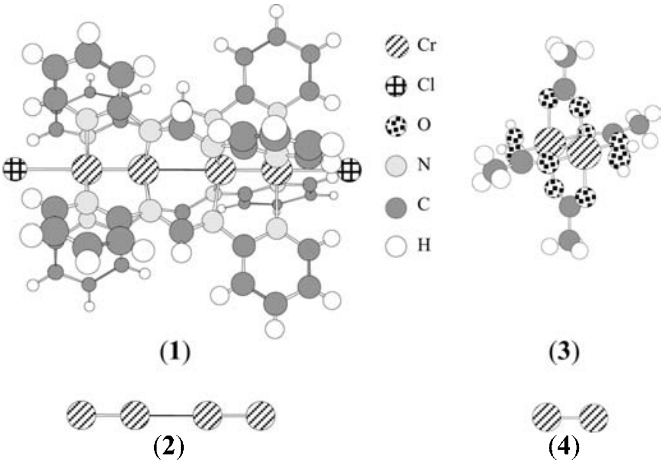
Magnetic interactions between divalent chromium (Cr(II)) ions in tetra Cr(II) complex were estimated by using a magnetic effective density functional (MEDF) method. Those results were discussed in comparison with a di-Cr(II) complex to elucidate the types of magnetic interactions. Charge and spin densities and natural orbitals by MEDF were also examined in terms of the ligand effects.

Keywords aligned tetrametal systems; magnetic interaction; effective exchange integrals; Magnetic Effective Density Functional; MEDF

INTRODUCTION

In recent years, many reports about metal string complexes have been presented[1-3]. Those aligned metal systems are interesting in terms of both fundamental studies of their peculiar characters and applications to functional materials. It has been, however, very difficult to investigate electronic states of those complexes by post Hartree-Fock methods, because the systems are



(1) (3)

(2) (4)

FIGURE 1 $[Cr(II)_4(DpyF)_4Cl_2]^{2+}$ complex model (**1**) , its naked metal tetramer model (**2**) and $Cr(II)_2(O_2CCH_3)_4(H_2O)_2$ complex model (**3**), its naked metal dimer model (**4**)

too large to approach with an quantitative consideration of electron correlation effects. Density functional theory (DFT) methods have been applied to large sized molecules such as metal complexes, biosystems and so on. Although the DFT has an advantage that electron correlation effects are taken into account at low computing costs, there is a week point that usual BLYP and B3LYP overestimate the stability of low-spin state and they indicate large negative effective exchange integrals (J_{ab}) values[4]. Our group has improved the hybrid DFT scheme for the open shell system in terms of the magnetic interactions between radical species, namely a magnetic effective density functional (MEDF) [4-6]. The MEDF reproduced the experimental J_{ab} for $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex[7].

In this study, we focused on aligned tetra chromium(II) systems, $[Cr(II)_4(DpyF)_4Cl_2]Cl_2$ synthesized by Cotton et al[1]. We applied the MEDF method to this system for investigation of electronic states in terms of magnetic interactions between Cr(II) ions. As model systems, we examined $[Cr(II)_4(DpyF)_4Cl_2]^{2+}$ complex model (**1**) and its naked model *i.e.* without ligand model (**2**) as illustrated in Figure1. $Cr_2(O_2CCH_3)_4(H_2O)_2$ complex model (**3**) and its naked model (**4**) were also discussed to make a comparison.

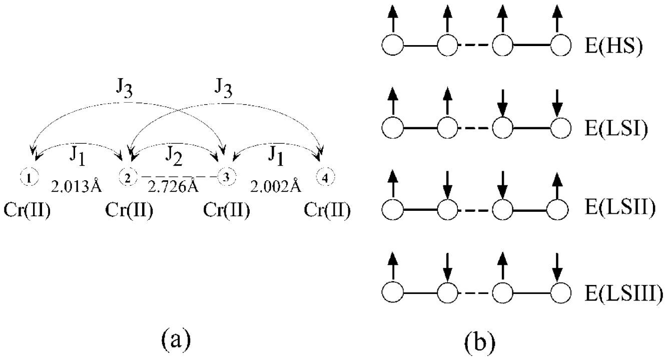


FIGURE 2 (a) The notation for J_1, J_2 and J_3 in model **1** and **2**, (b) The calculated four states to obtain J_{ab} value by eq.(2)

THEORETICAL BACKGROUND

Magnetic Effective Density Functional (MEDF) method

The MEDF method takes an appropriate dynamical correlation into account under the approximation that a non-dynamical correlation is expressed by using unrestricted calculation[6]. Here, we generalized the exchange-correlation potential, which involved both HF and DFT terms as follows,

$$E_{XC} = c_1 E_X(HF) + (1 - c_1)\left(E_X(Slater) + \Delta E_X(Becke88)\right) + \left(E_C(VWN) + \Delta E_C(LYP)\right) \quad (1)$$

The mixing coefficient (c_i=0.5) that was optimized for the Cr(II) dimer was used[7].

Effective Exchange Integrals (J_{ab})

The magnetic interactions between Cr(II) ions; J_1, J_2 and J_3 as illustrated in Figure2(a) were investigated by using the effective exchange integrals (J_{ab}). The J_{ab} values were derived from Heisenberg model

$$H = -2\sum J_{ab} \boldsymbol{S_a} \bullet \boldsymbol{S_b} \quad (2)$$

TABLE1 The J_{ab} values between Cr(II) ions of model **1** and **2**

Type	R(Å)	model **1** J(cm^{-1})	model **2** J(cm^{-1})
J_1	2.013 (2.002)	-1260	-1125
J_2	2.726	-180.2	-39.2
J_3	4.739	-30.4	+4.7

and four types of electronic states were calculated to obtain J_1, J_2 and J_3 as illustrated in Figure2(b).

Computational Details

All atomic coordinations were taken from date of X-ray crystal structure analysis. Each calculation was performed by the use of Tatewaki-Huzinaga MIDI plus p type wavefunctions for Cr atoms and 4-31G basis set for other atoms, respectively. All calculations were carried out by using GAUSSIAN98.

RESULT AND DISCUSSION

Effective Exchange Integrals

Calculated results of J_{ab} values were summarized in Table1. The value of J_1 of full model **1** showed the relatively strong anti-ferromagnetic interactions and was consistent with the naked model **2**. Therefore J_1 mainly originated from metal-metal direct interactions. On the other hand, J_2 and J_3 in model **1** were larger than ones in naked model **2**. Especially, J_3 in model **1** showed small anti-ferromagnetic interaction although the J_3 interaction in model **2** almost disappeared. In previous studies[7], we calculated the J_{ab} values for

TABLE2 The J_{ab} values* between Cr(II) ions of model **3** and **4**

Type	R(Å)	model **3** J(cm^{-1})	model **4** J(cm^{-1})
J_{ab}	2.36	-520	-299
J(direct)		-327	
J(through-bond)		-193	

*in ref [7]

TABLE3(a) The charge densities on Cr(II) ions of model **1** and **2**

atom	model **1**	model **2**
1	-0.19	2.14
2	2.40	1.85
3	2.40	1.86
4	-0.26	2.15

TABLE3(b) The spin densities on Cr(II) ions of model **1** and **2**

atom	model **1**	model **2**
1	3.07	3.75
2	-3.79	-3.56
3	3.76	3.55
4	-3.04	-3.74

$Cr_2(O_2CCH_3)_4(H_2O)_2$ (**3**). A metal-metal direct interaction and a through-bond interaction were also estimated respectively as summarized in Table2. We found that J_2 in model **1** was similar to J(through-bond) in model **3**. From those results, J_2 in model **1** mainly originated from a through-bond interaction. Similarly, it was considered that the J_3 in model **1** was also caused by a through-bond interaction.

Charge and Spin Densities

Charge and spin densities of full model **1** and naked model **2** were also examined to elucidate effects of ligands. The calculated results of most stable state; LS(III) in Figure2(b) were summarized in Table 3(a) and (b). Charge densities and spin densities on edge atoms, atom 1 and 4 in full model **1** in the table, were smaller than ones in naked model **2**. Especially, charges on edge atoms in model **1** were almost zero. From those results, we found that the ligands had a strong influence on spin and charge densities for those complexes.

Density Functional Natural Orbital (DNO) Analysis

The DNOs were also examined to elucidate contributions of orbitals. In Figure3, σ and δ orbitals of LS(III) in Figure2(b) were depicted. The σ

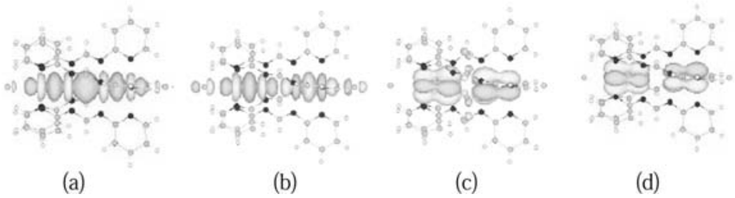

(a) (b) (c) (d)

FIGURE 3 The DNOs of model 1. (a) and (b) are σ orbitals and (c) and (d) are δ orbitals

orbitals were delocalized to axial terminal Cl ligands. It seemed that this delocalization has close relation with the decrease of charges on edge atoms. The δ orbitals had spiral structures reflecting ligand structures. It is considered that the δ orbitals were easily affected by the spiral structure of ligands.

SUMMARY

In this study, we calculated the electronic states of $[Cr(II)_4(DpyF)_4Cl_2]^{2+}$ complex in terms of magnetic interactions between Cr(II) ions by using MEDF method. Three types of magnetic interactions between Cr(II) ions, J_1, J_2 and J_3, were estimated and we discussed the origin of those interaction. The charge and spin densities were also calculated and we found the decrease of charges on edge Cr(II) ions. Finally, DNOs were also examined and we found that σ and δ orbitals were influenced by axial and spiral ligands.

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References

[1] F.A.Cotton, L.M.Daniels and C.A.Murillo, X.Wang, *Chem.Commun.*,**1**,39 (1998)
[2] K.Mashima, M.Tanaka and K.Tani, *J.Am.Chem.Soc.*,**119**,4307 (1997)
[3] M.E.Prater, L.E.Pence, R.Clérac, G.M.Finniss, C.Campana, P.Auban-Senzier, D.Jérome,E.Canadell and K.R.Dunber, *J.Am.Chem.Soc.*,**121**, 8005(1999)
[4] M.Nishino, S.Yamanaka, Y.Yoshioka, K.Yamaguchi, *J.Phys.Chem.A.*, **101**, 705(1997)
[5] Y.Kitagawa, T.Soda, Y.Shigeta, S.Yamanaka, Y.Yoshioka and K.Yamaguchi, *Int.J.Quant.Chem.*,**84**,592(2001)
[6] Y.Kitagawa, K.Kawakami and K.Yamaguchi, *Mol.Phys.*, *in press.*
[7] Y.Kitagawa, T.Soda, T.Onishi, Y.Takano, M.Nishino, Y.Yoshioka and K.Yamaguchi, *Mol.Cryst.Liq.Cryst.*,**343**,145(2000)