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Theoretical Studies on Magnetic Interactions of Aligned Tetrametal System by Using Hybrid Density Functional Method

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The effective exchange integrals for the naked Cr(II) tetramer are calculated by using post-Hartree-Fock and the improved hybrid density functional method. The calculated values are examined in comparison with naked Cr(II) dimer. The naked Cr(II) tetramer that is arranged similar to $[Cr(II)_4(DpyF)_4Cl_2]Cl_2$ also examined in terms of magnetic interactions.

Keywords effective exchange integrals; hybrid density functional method; aligned tetrametal systems.

INTRODUCTION

In recent years, many syntheses of metal string complexes have been reported. Those aligned metal systems are interested us in both the fundamental study of their peculiar characters and the application to the materials. It has been, however, very difficult to investigate electronic states of those complexes by theoretical approach. Because the systems are too large to calculate with appropriate consideration of the electron correlation effect.

Our group has improved the hybrid density functional theory (DFT) methods for the open shell systems in terms of the effective exchange integrals (J_{ab})[1]. They reproduced the experimental J_{ab} value for Cr-ac-

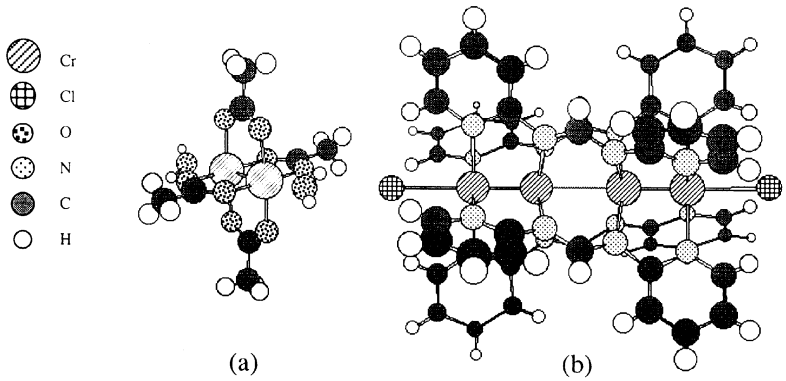

FIGURE 1 (a)$Cr(II)_2(O_2CCH_3)_4(H_2O)_2$(**1**) and (b)$[Cr(II)_4(DpyF)_4Cl_2]Cl_2$(**2**)

etate complex: $Cr_2(O_2CCH_3)_4(H_2O)_2$(**1**) that has quadruple metal-metal bond, while usual BLYP and B3LYP indicate too negative values[1,3,5].

In this work, we focused on the $[Cr(II)_4(DpyF)_4Cl_2]Cl_2$(**2**), where DpyF is bis(2-pyridyl)formamidine by Cotton et al[2]. This complex is considered that there are two Cr(II)-Cr(II) quadruple bonds and little or no bonding between the two inner chromium atoms[2]. we investigated the direct interaction between Cr atoms for the naked Cr tetramer in comparison with naked Cr(II) dimer by using the spin-unrestricted Hartree Fock (UHF), spin-unrestricted post-HF and spin-unrestricted hybrid DFT (UDFT) method.

THEORETICAL BACKGROUND

Hybrid density functional methods

In this study, we generalized the exchange-correlation potential, which involved both HF and DFT terms as,

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

We defined this combination of the functions namely B2LYP. The mixing coefficient (c_i=0.5) that is optimized for the Cr(II) dimer is used[1,3].

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Size-consistent spin projection

In this study, we assumed that the systems have the equivalent spin-spin interaction between each neighboring atom, approximately. In those calculations, we use Heisenberg model (in eq.(2)) and size-consistent spin projection (in eq.(3)) to estimate J_{ab}.[3,4]

$$H = -2\sum J_{ab} \boldsymbol{S}_a \bullet \boldsymbol{S}_b \tag{2}$$

$$J(AP-X) = \frac{\left[{}^{LS}E(X) - {}^{HS}E(X)\right]}{\Delta(Z_{II})} \tag{3}$$

$$\Delta(Z_{II}) = {}^{HS}\left\langle S^2 \right\rangle(X) - {}^{LS}\left\langle S^2 \right\rangle(X) - S_a g(N)\left[{}^{LS}\left\langle S^2 \right\rangle(X) - S_r(S_r+1)\right] \tag{4}$$

where ${}^{Y}E$ and ${}^{Y}\langle S^2 \rangle$ denote the total energy and total angular momentum of the spin state Y. N is the number of spin sites and the S_a and S_b are the sizes of spin at sites a and b. In these even number systems, $g(N)$ and $Sr(N)$ are expresses as follows;

$$g(N) = \frac{(N-2)^2}{N} \tag{5}$$

$$S_r = n(S_a - S_b) \qquad (\mathrm{N} = 2\mathrm{n}), \tag{6}$$

Those spin projected J_{ab} values calculated by the method X called AP - X such as APUHF.

Computational details

Those calculations were performed by the use of Tatewaki-Huzinaga MIDI (533(21)/53(21)/(41)) plus Hay's diffuse d-basis sets. The present computations were carried out by using Gaussian 94 program package.

RESULTS AND DISCUSSIONS

First, we examined the size and the distance dependency of the J_{ab} values

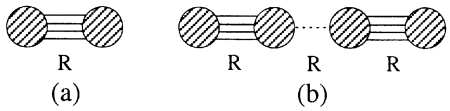

FIGURE 2 (a)naked Cr(II) dimer model **3** and
(b)naked Cr(II) tetramer model **4**

for the naked Cr(II) dimer (**3**) and tetramer (**4**) illustrated as shown FIGURE 2. The calculated state is $\sigma^2\pi^4\delta^2$ for one quadruple bonded unit. TABLE 1 summarizes the J_{ab} values for the dimer and the tetramer. The J_{ab} values for the tetramer model are slightly larger than dimer model. For the both models, J_{ab} values by APUB2LYP correspond to J_{ab} values by APUCCSD(T) in a short distance. On the other hand, the J_{ab} values by APUHF correspond to the J_{ab} values by APUCCSD(T) in a long distance. From this results, the hybrid parameter (c_i=0.5 in eq(1)) is efficacious for the calculations of aligned metal tetramers in a short distance. The interaction between two inner chromium atoms (a broken line in FIGURE2 (b)) is also investigated by estimating the energy difference in comparison with the dimer model. Those energies at interatomic distance R are estimated as in eq. (7) and TABLE 2 summarizes them.

$$E(\text{interaction}) = E_{total}(\text{tetramer}) - 2 \times E_{total}(\text{dimer}) \tag{7}$$

TABLE 1 J_{ab} values[1)] for the Cr(II) dimer(**3**) and tetramer(**4**)

R[2)]	APUHF		APUB2LYP		APUCCSD(T)	
	dimer	tetramer	dimer	tetramer	dimer	tetramer
2.0	-566.	-643.	-918.	-1063.	-887.	-1022.
2.2	-274.	-319.	-490.	-608.	-400.	-502.
2.4	-130.	-151.	-266.	-343.	-181.	-234.
2.6	-60.0	-67.6	-146.	-189.	-80.2	-102.
2.8	-27.0	-29.1	-80.8	-102.	-35.5	-42.6
3.0	-12.0	-12.3	-45.6	-54.8	-15.7	-17.7
3.2	-5.16	-5.11	-26.0	-29.4	-6.82	-7.29
3.4	-2.12	-2.06	-14.9	-16.0	-2.86	-2.96

1) in cm^{-1} 2) in Å

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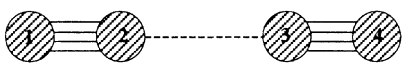
TABLE 2 Repulsion Energy[1)] between two Cr(II) dimers

R[2)]	UHF	UB2LYP	UCCSD(T)
2.0	1492	1448	1464
2.2	1362	1331	1345
2.4	1257	1235	1247
2.6	1167	1153	1162
2.8	1089	1080	1086
3.0	1019	1015	1018
3.2	958	956	957
3.4	903	902	903

1) in kcal mol^{-1} 2) in Å



R(1)=2.013Å R(2)=2.726Å R(3)=2.002Å

FIGURE 3 Cr(II) tetramer model (**5**) that arranged similar to complex **2**

TABLE 3 J_{ab} valeus[1)] for model **5**

method	J_{ab}
APUHF	-423
APUB2LYP	-724
APUCCSD(T)	-700

1) in cm^{-1}

E(interaction) are caused by mainly the interaction between two Cr(II) dimers. From the TABLE2, we found that those interactions are repulsive and the repulsion energies are more than one thousand kcal mol^{-1} at a relatively longer distance.

Next, we examine the J_{ab} values for Cr(II) tetramer model **5** that arranged similar to complex **2** as illustrated in FIGURE 3. TABLE 3 summarizes the J_{ab} values for model **5**. The J_{ab} values by APUB2LYP correspond to the J_{ab} values by APUCCSD(T) well. In terms of magnetic interactions, our hybrid DFT method expresses the appropriate electronic

TABLE 4 Spin density and charge density for model **5** by UB2LYP

atom	spin dinsity	charge density
1	3.75	2.14
2	-3.56	1.85
3	3.55	1.86
4	-3.74	2.15

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states. The spin density and charge density are summarized TABLE 4. From the table, we found that spins are almost localized on Cr(II) atoms but spin density and charge density on the both end Cr(II) atoms are slightly larger than the inner Cr(II) atoms.

CONCLUDING REMARKS

The J_{ab} values by using our hybrid DFT method correspond to the J_{ab} values by using APUCCSD(T) for both naked Cr(II) dimer and tetramer model. It is considered that our method expresses appropriate electronic states for those systems. As mentioned before, the calculated state is $\sigma^2\pi^4\delta^2$, which is found in usual quadruple bonded systems of chromium(II). The real $[Cr(II)_4(DpyF)_4Cl_2]Cl_2$ complex, however, has a helical ligand (see FIGURE 1), therefore it is expected that the electronic states of the complex **2** are more complicated. It is necessary to calculate full model complex for the discussions of the details. In this study, we found that our hybrid DFT method is appropriate to approach these tetrametal systems.

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