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Theoretical Study on Magnetic Interactions of Mn-π Conjugated System

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Magnetic interaction of Mn-π conjugated system, especially $Mn(II)_2$-py-rimidine was investigated by the *ab initio* UHF, post-UHF, and DFT approximations. The calculated effective exchange integrals (J_{ab}) are negative, even though the m-phenylene type bridge is employed. This indicates that the superexchange effect plays a predominant role to determine the sign of J_{ab} in Mn-π conjugated systems.

Keywords: $Mn(II)_2$-pyrimidine; effective exchange interaction (J_{ab}); charge and spin density distributions; natural orbital analysis; approximate spin-projection procedure

INTRODUCTION

Magnetic interactions of the d-p conjugated systems have attracted a great deal of attention from both the theoretical and experimental viewpoints. Recently experimental studies on these systems have been reported[1-3], while theoretical studies are rather limited. Previously we reported unrestricted Hartree-Fock (UHF), UHF Møller-Plesset nth(n = 2, 4)-order perturbation, UHF Coupled Cluster and DFT (UBLYP and UB3LYP) calculations by the use of several basis sets for the simplest model complexes,

TABLE 1 Basis sets employed for the present calculations.

Type	Metal	C, H, O
I	5333/333/3[a)]	4-31G
II	62111111/3312/32[b)]	6-31G*
III	533(21)/33(21)/41[a)]+ Hay's d diffuse function[c)]	6-31G*
IV	62111111/3312/32[b)]+ Hay's d diffuse function[c)]	6-31G*

a) Ref. [5], b) Ref. [6], c) Ref. [7]

M(4-pyridyl)methylene (M = Mn(II) and Cu(II)), of 1:1 complex of $Mn(II)(hfac)_2$ and $Cu(II)(hfac)_2$ with (4-pyridylmethylene) to elucidate the magnitude of the effective exchange interactions between transition metals and carbene sites.[4]

In this work, we focus the d-p conjugated complex synthesized and measured the magnetic properties by Ishida and his co-workers[1]. We investigate the magnetic interaction of the simplest model complex of this complex, $Mn(II)_2$-pyrimidine(**1**), from the viewpoint of effective exchange interaction (J_{ab}) and charge and spin density distributions by *ab initio* calculations. UHF, UMPn (n=2, 4), UCCSD(T), and DFT(UBLYP, UB3LYP) calculations are employed for this work. Table 1[5-7] lists the basis sets used for calculations.

NUMERICAL RESULTS AND DISCUSSION

Effective Exchange Interactions in $Mn(II)_2$-pyrimidine

We estimated the magnitude of magnetic interactions between the$Mn(II)_2$-pyrimidine (**1**) from energy gaps between low- and high-spin states. The effective exchange integrals (J_{ab}) were calculated using approximate spin-projection (AP) procedure by combination of the UHF, UMPn (n=2,4), UCCSD(T), or DFT method with the Heisenberg model as

$$J_{ab}(AP-X) = \frac{{}^{LS}E_X - {}^{HS}E_X}{{}^{HS}\langle S^2\rangle - {}^{LS}\langle S^2\rangle} \qquad (1)$$

where ${}^{Y}E_X$ and ${}^{Y}\langle S^2\rangle_X$ denote the total energy and total angular momen-

TABLE II Effective exchange integral $(J_{ab})^{a),b)}$ of $Mn(II)_2$-pyrimidine.

Methods	I[c]	II[c]	III[c]	IV[c]
AP-UHF	17.46	14.87	11.26	14.29
AP-UMP2	−182.5	−166.8	−169.5	−166.3
AP-UMP4	−139.9	−126.1	−128.4	−125.3
AP-UCCSD(T)	−15.56	−15.40	−19.72	−15.28
AP-UBLYP	−0.64	-0.13	−1.48	−0.78
AP-UB3LYP	0.21	0.31	−0.11	0.12

a) J_{ab} are shown in cm^{-1}.
b) J_{ab}(exp.)=−0.14cm^{-1}.
c) Basis sets I-IV are given in Table I.

tum of the spin state Y by the calculated method X (X=UHF, UMP, UCCSD(T), DFT), respectively.[8] Here, the geometrical parameters of **1** were taken from the literature as C-C = C-N =1.20Å, C-H = 1.08Å, N-Mn = 2.0Å, C-C-C = C-C-H = C-N-C = Mn-N-C = 120.0°[9] for a qualitative purpose.

Table II summarizes the effective exchange integrals of **1** by approximate spin-projection methods (Eq. (1)). From Table II, the J_{ab} value by AP-UHF is 14.29cm^{-1} using basis set IV, showing ferromagnetic interaction between the Mn(II) ions via pyrimidine group. Judging from this result, AP-UHF overestimates spin polarization (SP) effects. On the other hand, the J_{ab} values estimated by AP-UBLYP, AP-UMPn (n=2,4), and AP-UCCSD(T) show antiferromagnetic interactions, even though the m-phenylene type bridge is employed. Especially, AP-UBLYP calculations estimate J_{ab} value close to the experimental value (−0.14cm^{-1}). The sign of J_{ab} value is negative for $Mn(II)_2$-pyrimidine due to the inclusion of an antiferromagnetic superexchange (SE) effect. AP-UB3LYP calculations evaluate positive J_{ab} values by basis I, II, and IV, because of the inclusion of ferromagnetic UHF character. Finally, it is noteworthy that the difference of J_{ab} value estimated by using different basis sets is not so large in all computations.

Charge Density and Spin Density in $Mn(II)_2$-pyrimidine

We investigated the population of charge and spin densities of **1** in order to elucidate the mechanism of the magnetic interaction. Figure 1 shows

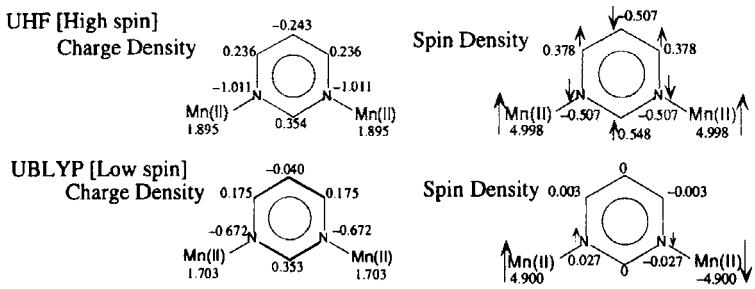

FIGURE 1 Charge Density and Spin Density of $Mn(II)_2$-pyrimidine.

the population of the charge and spin densities estimated by UHF and UBLYP calculations using basis IV. The net charge densities on the Mn(II) ions are 1.895 and 1.703, respectively, and indicate that the charge transfer from pyrimidine ring to Mn(II) ions decreases in order: UBLYP > UHF. Judging from J_{ab} values, this result shows that UBLYP estimates the spin delocalization (SD) effect more appropriately than UHF. Therefore UBLYP calculation results in showing an antiferromagnetic interaction.

The absolute value of the spin densities on C- and N-atoms in the pyrimidine ring are 0.4 to 0.5 by UHF, and their signs change alternatively to show the characteristic of the spin density wave. Therefore, this is in conformity with the SP effect. However, judging from the magnitude of the spin densities, UHF calculation overestimates the SP effect of the pyrimidine ring. On the other hand, the population of spin densities calculated by the UBLYP method does not exhibit the SDW-type spin alternation, namely SP-pattern, but shows the sign of the spin density on Mn(II) ion is similar to that on N-atom in the pyrimidine ring, in other words, SD pattern.

Natural orbital analysis in $Mn(II)_2$-pyrimidine

We examined the singly occupied natural orbitals[10,11] and their occupation number of 1 by UHF and UBLYP calculations, respectively, in order to elucidate the mechanism of the magnetic interaction of this model. Fig. 2 shows that the localized natural orbitals are found on the Mn(II) ions at UHF level, indicating that J_{ab} becomes ferromagnetic due to the overesti-

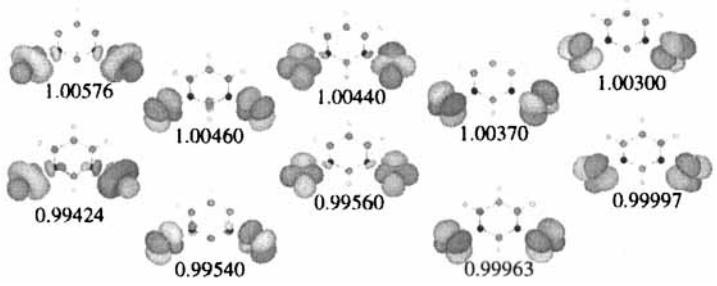

FIGURE 2 Natural orbitals and their occupation numbers of $Mn(II)_2$-pyrimidine by UHF calculation using basis IV.

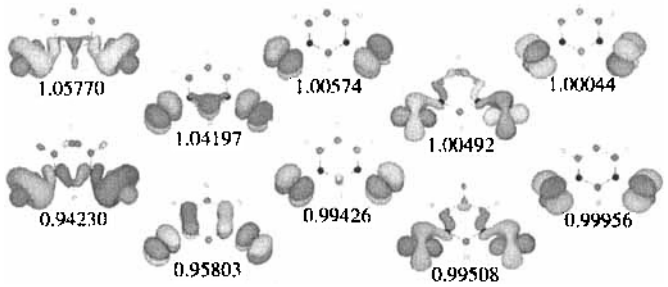

FIGURE 3 Natural orbitals and their occupation numbers of $Mn(II)_2$-pyrimidine by UBLYP calculation using basis IV.

mates of the SP effect by the UHF theoretical treatment. On the other hand, from Fig. 3, we observe the natural orbitals delocalized on the whole molecule at UBLYP level. It is clear that UBLYP calculation provides the antiferromagnetic SE interaction between Mn(II) ions via pyrimidine ring.

CONCLUDING REMARKS

UHF, UMPn (n=2,4), UCCSD(T) and DFT (UBLYP and UB3LYP) calculations were performed for the $Mn(II)_2$-pyrimidine (**1**) in order to elucidate the effective exchange interactions (J_{ab}) between Mn(II) ions. Our main conclusions are as follows; (i) the sign of J_{ab} is negative for $Mn(II)_2$-pyrimidine due to the inclusion of an antiferromagnetic SE effects, (ii)

the UHF method overestimates the SP effect on C- and N-atoms in the pyrimidine ring, (iii) the UBLYP method provides reasonable effective exchange integrals for $Mn(II)_2$-pyrimidine because of the appropriate estimate of the antiferromagnetic SE interaction, and (iv) the single occupied natural orbitals of UBLYP calculation delocalize the whole molecule, indicating that SE interaction affects the magnetic interaction.

It is found that the superexchange effect is crucial to investigate the magnetic interactions of Mn-π conjugated systems.

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