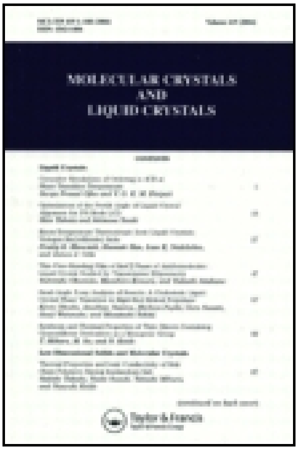

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Theoretical Studies on Magnetic Interaction of Di-μ-oxo Bridged Manganese Dimers

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Theoretical Studies on Magnetic Interaction of Di-μ-oxo Bridged Manganese Dimers

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We performed the density functional theory (DFT) calculations of several manganese model complexes in order to investigate the effective exchange interaction of di-μ-oxo bridged manganese(IV) dimers. We calculated the effective exchange integrals (J_{ab}) of the model molecules and discussed geometry and ligand effects on them.

Keywords: di-μ-oxo bridged manganese dimer; hybrid density functional theory; effective exchange integral; superexchange interaction

INTRODUCTION

The O_2-evolving complex (OEC) in photosystem II consists of a tetranuclear manganese cluster. Extended x-ray absorption fine structure studies suggest that the manganese tetramer is made up of di-μ-oxo dimeric manganese units. In an attempt to reproduce the function of the OEC, many di-μ-oxo manganese dimer have been synthesized[1-6]. Recently, J. Limburg et al. synthesized a functional di-μ-oxo manganese dimer model for the OEC[7], which exhibits the O_2-evolving ability. So, it is important to reveal the nature of the property of these complexes.

Ab initio broken-symmetry calculations of effective exchange interaction (J_{ab}) are current topics in the field of molecular magnetism[8-10].

Previously, we have derived a computational scheme of J_{ab} values on the basis of the broken-symmetry Hartree-Fock and density functional approximations, followed by the approximate spin projection (AP) procedure[11]. The effective exchange interaction between localized spins of a-th and b-th cites with total spin operators S_a and S_b is described by the spin coupling Hamiltonian[12].

$$H(\mathrm{HB}) = -2J_{ab}S_a \cdot S_b \ , \qquad (1)$$

where J_{ab} is the orbital-averaged effective exchange integral. Our computational scheme of this value is

$$J_{ab} = \frac{{}^{\mathrm{HS}}E - {}^{\mathrm{LS}}E}{{}^{\mathrm{HS}}\langle s^2 \rangle - {}^{\mathrm{LS}}\langle s^2 \rangle} \ , \qquad (2)$$

where ${}^{X}E$ and ${}^{X}\langle s^2 \rangle$ denote calculated total energy and total spin angular momentum for the spin state X, respectively. In this paper, we performed the hybrid DFT calculations of di-μ-oxo manganese (IV) dimers with several ligands, H^-, F^-, Cl^-, H_2O, NH_3, and pic^- (picH = picolinic acid). The J_{ab} values of these models are evaluated and compared with the experimental value. By calculating the J_{ab} values of these models varying the geometry parameters of $[Mn_2O_2]$ core, we discussed the geometry effects and ligand effects on J_{ab} value.

COMPUTATIONAL DETAILS

The model complex (**I**) and the full model complex (**II**) of $Mn(IV)_2O_2(pic)_4$ complex are shown in Figure 1. The model complexes $[Mn(IV)_2O_2X_4]$ ($X=F^-$(**III**), Cl^-(**IV**), and H^-(**V**)) are geometrically optimized with D_{2h} symmetry. $[Mn_2O_2(H_2O)_8]^{4+}$ model (**VI**) and $[Mn_2O_2(NH_3)_8]^{4+}$ model (**VIIa**) are optimized with D_2 and C_1 symmetry, respectively. In order to investigate the dependency of J_{ab} on the $[Mn_2O_2]$ core geometry, the J_{ab} values of **VI** and **VIIa** are calculated by varying the geometry parameters, $R_{\mathrm{Mn\text{-}Mn}}$ and $R_{\mathrm{O\text{-}O}}$, and fixing the other parameters. The J_{ab}

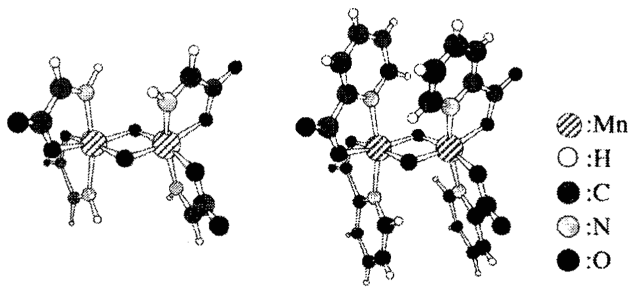


FIGURE 1 Models of $[Mn(IV)_2O_2(pic)_4]^0$. (a)model **I**. (b)model **II**.

values of **VI** and **VIIa** are calculated at 16 different geometries, and two-dimensional surface of two variables, $R_{Mn\text{-}Mn}$ and $R_{O\text{-}O}$, is fitted by least squares as a polynomial of degree 8.

All calculations are performed using the hybrid functionals Becke3-Lee/Yang/Parr91 (UB3LYP) with GAUSSIAN94[13]. Manganese atoms are modeled with a Tatewaki-Huzinaga valence double-ζ GTO basis set[14], while 6-31G basis set is used to describe the others. J_{ab} values computed through Equation 2.

RESULTS AND DISCUSSION

Table 1 summarizes the calculated J_{ab} values and the distances, $R_{Mn\text{-}Mn}$ and $R_{O\text{-}O}$, of model complexes. Table 2 shows the experimental data of several di-μ-oxo manganese complexes[1-6]. All of the calculated J_{ab} values are negative in consistent with the experimental trend. The optimized distance $R_{Mn\text{-}Mn}$ is slightly larger than the experimental data, while $R_{O\text{-}O}$ is comparable with the experiment. The J_{ab} value of pic^- model **II** is reasonable in comparison with the experimental value, but slightly larger in accord with the general tendency[15]. Since the difference between models **I** and **II** is small, the effect of simplification of the ligands is not so significant. The magnitude of the J_{ab} values increases with ligands in the order, H_2O < pic^- < NH_3, in proportion to the number

TABLE 1 Calculated data of di-μ-oxo manganese dimers.

Complex	$R_{Mn\text{-}Mn}$ (Å)	$R_{O\text{-}O}$ (Å)	J_{ab} (cm^{-1})
$[Mn(IV)_2O_2(pic)_4]^0$ (**I**)	2.75[2]	2.39[2]	-124.4
$[Mn(IV)_2O_2(pic)_4]^0$(**II**)	2.75[2]	2.39[2]	-118.4
$[Mn(IV)_2O_2F_8]^{4-}$ (**III**)	2.89	2.37	-36.1
$[Mn(IV)_2O_2Cl_8]^{4-}$ (**IV**)	2.92	2.26	-38.6
$[Mn(IV)_2O_2H_8]^{4-}$ (**V**)	2.85	2.46	-82.3
$[Mn(IV)_2O_2(H_2O)_8]^{4+}$ (**VI**)	2.85	2.27	-99.0
$[Mn(IV)_2O_2(NH_3)_8]^{4+}$ (**VIIa**)	2.89	2.29	-149.3

* optimized on the specified symmetry restraint.

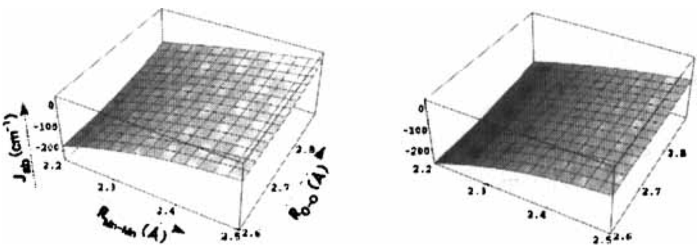
TABLE 2 Experimental data of di-μ-oxo manganese dimers.

Complex	$R_{Mn\text{-}Mn}$ (Å)	$R_{O\text{-}O}$ (Å)	J_{ab} (cm^{-1})	Ref.
$[Mn(IV)_2O_2(salpn)_2]^0$	2.73	2.41	-94	[1]
$[Mn(IV)_2O_2(pic)_4]^0$	2.75	2.39	-86.5	[2]
$[Mn(IV)_2O_2(bispicen)_2]^{4+}$	2.67	2.44	-125.6	[3]
$[Mn(IV)_2O_2(L3)_2]^{4+}$	2.75	2.25	-131	[4]
$[Mn(IV)_2O_2(tmpa)_2]^{4+}$			-137	[5]
$[Mn(IV)_2O_2(phen)_4]^{4+}$	2.75	2.32	-144	[6]

of coordinating nitrogen atoms. This tendency is in accord with the experiments (Table 2).

Figure 2 shows the surfaces of the J_{ab} values of **VI** and **VIIa** with two variables, $R_{Mn\text{-}Mn}$ and $R_{O\text{-}O}$. It is found that J_{ab} values of both models increase in proportion to the both distances $R_{Mn\text{-}Mn}$ and $R_{O\text{-}O}$. The dependency of J_{ab} value on $R_{O\text{-}O}$ is larger than that on $R_{Mn\text{-}Mn}$, and the change of J_{ab} value in **VIIa** is larger than that in **VI**.

J. E. McGrady and R. Stranger discussed the dependency of redox-induced changes in the exchange interaction on changes in the geometry of $[Mn_2O_2]$ core[8]. They performed the approximate density functional calculations of the J_{ab} values of $[Mn(III)_2O_2(NH_3)_8]^{4+}$ (**VIIb**; J_{ab}=-172cm^{-1}) and $[Mn(IV)_2O_2(NH_3)_8]^{2+}$ (**VIIc**; J_{ab}=-274cm^{-1}) model complexes with D_{2h} symmetry, and concluded that the change of J_{ab} values between the two oxidation states predominantly depends on the geometry of $[Mn_2O_2]$ core. In order to confirm this tendency, we estimate the J_{ab} values of



(a) (b)

FIGURE 2 The fitted surfaces of (a)$[Mn(IV)_2O_2(H_2O)_8]^{4+}$ model and (b)$[Mn(IV)_2O_2(NH_3)_8]^{4+}$ model with the variables, $R_{Mn\text{-}Mn}$ and $R_{O\text{-}O'}$

TABLE 3 Evaluated J_{ab} values by using the fitted surface

Geometry	$R_{Mn\text{-}Mn}$ (Å)	$R_{O\text{-}O}$ (Å)	J_{ab} (cm^{-1})
$[Mn(IV)_2O_2(bispicen)_2]^{4+}$	2.67[3]	2.44[3]	-86.6
$[Mn(IV)_2O_2(L3)_2]^{4+}$	2.75[4]	2.25[4]	-201
$[Mn(IV)_2O_2(phen)_4]^{4+}$	2.75[6]	2.32[6]	-146
$[Mn(III)_2O_2(NH_3)_8]^{2+}$ (**VIIb**)	2.72[a]	2.48[a]	-73.6
$[Mn(IV)_2O_2(NH_3)_8]^{4+}$ (**VIIc**)	2.87[a]	2.32[a]	-140

VIIb and **VIIc** by using the our fitted surface in Figure 2(b). We also evaluate J_{ab} values for the several real complexes in Table 2. Table 3 summarizes these estimated J_{ab} values. The tendency of the J_{ab} values on the optimized geometry of **VIIb** and **VIIc** is almost in accord with the calculation in Reference 8, but the evaluated J_{ab} values from the real complexes are not in accord with the experimental data shown in Table 2. This implies that J_{ab} value does not only depend on the geometry of $[Mn_2O_2]$ core, but also on the ligand effects, such as aromaticity and orientation of coordinating ligands.

CONCLUDING REMARKS

The calculated J_{ab} value of pic⁻ model **II** reproduces the experimental value, but slightly overestimates in accord with general tendency[15]. The results of the calculation for the models with variable geometry of $[Mn_2O_2]$ core show that the ligand effect on J_{ab} value is not negligible.

Acknowledgments

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