Ab initio DFT study of magneto-structural correlation of dinuclear mixed-valence Mn complexes

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Abstract. Recently, magnetism of Mn complexes has attracted much attention in relation to the metalloenzymes, in which Mn ions play important roles in the catalytic abilities. The magnetism of them are determined by structures of the Mn complexes part of the enzymes. In particular, the ferromagnetic and antiferromagnetic interactions usually compete with each other for mixed valence states. In this study, we investigated the magneto-structural correlation of a simple mixed valence complex, Mn(II)(µ-O)Mn(III)(H₂O)₁₀ using ab initio density functional method. Describing the landscape of magnetism of this complex for Mn-O-Mn plane, it was found that the spin-state transition occurs near the most stable structure of this complex. We consider why the spin-state transition occurs in the landscape from the viewpoint of natural orbital pictures.

1. Introduction

Recently, magnetism of Mn complexes has attracted much attention in relation to several important enzymes such as oxygen-evolving complex (OEC) in photosystem II [1-9], catalase[10-13], and superoxide dismutase (SOD)[14], in which Mn ions play important roles in the catalytic abilities of these enzymes. One important feature is that the reaction centers of these enzymes contain two or four Mn ions, of which oxidation states could vary during the reaction steps: even if we focus on two centers, there are many common oxidation states, Mn(II)₂, Mn(II)Mn(III), Mn(III)₂, Mn(III)Mn(IV), and Mn(IV)₂. In the models of some oxidation steps for the OEC, Mn(II)Mn(IV) and Mn(IV)Mn(V) states are also involved [4]. In the reaction centers of these enzymes, it is most likely that changes of structures and oxidation states yield Brønsted-Lowry acids and/or bases that catalyze the reactions [15,16]. Oxidation states, structures, and magnetism of Mn complexes are expected to strongly correlate with each other [17-20]. In particular, the coupling between magnetism and structures could be complicated for the mixed valence states, since double-exchange and superexchange interactions [21] compete with each other: magnetism is determined by a balance between them, which must be determined by the structure of the Mn complexes. In fact, we found that the low-lying spin-structures are nearly degenerate for the X-ray structure of OEC in previous studies [3,4], implying that correlations between magnetism and structures (magneto-structural correlations) should be taken into account for predictions or simulations of the enzyme.

Thus, we intend to investigate magneto-structural correlations of Mn complexes. For this purpose, we examined a Mn(II)(µ-O)Mn(III)(H₂O)₁₀ as a simple Mn complex. We calculated energy landscapes of both lowest-spin (LS) and highest-spin (HS) states for various structures of the Mn-O-Mn core. Then the landscapes
of magnetic interactions are calculated, clarifying that the spin-state transition occurs near the most stable point in the LS energy surface. We analyzed the reason for the changes of stable spin states.

2. Computational details

The ab initio density functional theory (DFT) method, which always yields correct results for both stable geometries and electronic structures of manganese complexes, has not been established so far. However, we previously confirmed [22] that the B3LYP functional [23] qualitatively reproduces the magnetism of dinuclear Mn complexes, except the weak ferro and weak antiferromagnetic ones: if the absolute values of magnetic interactions of Mn complexes are more than 10 cm⁻¹, the magnetism estimated with using B3LYP were found to be consistent with their experimental values within ±25% for 16 Mn complexes we examined [22].

The B3LYP functional was reported to reproduce the experimental molecular geometries of Mn complexes when we employed LACVP* basis set [20]. Thus we employed B3LYP and LACVP* respectively for the functional and the basis set in the following all calculations. All ab initio DFT calculations presented in the next section were done with using Gaussian 09 package [24]. The UltraFine grid is used for the numerical integration scheme for DFT terms. In addition, we choose the tight convergence criteria for DFT calculations in both electronic structure calculation and geometry optimization procedures. In addition, normal frequency analyses were implemented in order to ensure that the geometries obtained are minima, not saddle points.

3. Results and discussion

We first optimized molecular geometries of Mn(II)(µ-O)Mn(III)(H₂O)₁₀. The optimized distances between Mn ions are 3.589 Å and 3.559 Å for high-spin (HS) and low-spin (LS) states, respectively. The angle, Mn-O-Mn are also similar, which are 150.136 and 148.483 degrees for HS and LS states respectively, indicating that there is not a significant difference in the optimize geometries between HS and LS states. This fact is reasonable from the viewpoint of Feynman’s electrostatic theorem [25], which ensures that the forces and Hessians on nuclei of molecules are exerted only by other nuclei and by the electrons’ charge distribution. Thus, at the first approximation, it might imply that we could reasonably optimize geometries of Mn complexes with assuming the highest-spin state of the Mn complexes, which in fact have been often employed by the precursors who have investigated the molecular structures of Mn complexes [5,11]. However, strictly speaking, the spin state of the computational targets affects on both the charge distribution and energies due to exchange and correlation effects, resulting in the difference of optimized geometries between spin states.

Thus, focusing on the lower-lying low-spin (LS) state, we illustrated the energy landscape for various Mn-O-Mn geometries around the most stable geometry of the LS state. To this end, we performed partial optimizations of Mn(II)(µ-O)Mn(III)(H₂O)₁₀ with fixing the X and Z coordinates of two Mn ions and the µ-oxygen dianion, which are indicated in figure 1(A). In order to plot the energy landscape, this partial optimization procedure is implemented for the various coordinates (X,Z) of the µ-oxygen dianion: X is from 0.0 to 1.0 Å at 0.05 Å intervals, and Z from 0.00 to 0.25 Å at 0.05 Å intervals. On the other hand, the interatomic distance between two Mn ions is fixed to be the value at equilibrium geometry, 3.559 Å. To validate this partially optimization, we checked the vibration amplitudes of all 93 normal modes at the equilibrium geometry.
Figure 1(B) shows the displacement vectors of a normal mode, in which the amplitudes of the Mn ions are largest among 93 normal modes. The frequency and the intensity of this mode are 203.96 cm⁻¹ and 4.16, respectively. We can see from this figure that the Mn ions do not move so much, being consistent with the fact that the mass of the Mn atom is three times as heavy as that of the oxygen atom.

The calculated energy landscape is illustrated in figure 2 (A). The equilibrium point lies at (X,Z)=(0.499, 0.164) (unit:Å). At this point, the μ-oxygen dianion leans towards Mn(III), which is reasonable from the viewpoint of simple electrostatic interactions. As shown in the optimized geometry of figure 1(B), there are two hydrogen bonds between water molecules, causing the bending Mn-O-Mn line. In fact, the energy of the most stable point within the straight Mn-O-Mn geometries is higher than the equilibrium point by approximately 10 kcal/mol, which is approximately equal to the stabilization energies due to two hydrogen bonds. To check the behavior of magnetism for this landscape, we also calculated the energies of highest spin (HS) state with fixing the optimized geometries obtained for the LS state. The energy landscape of the high-spin state, which is colored in light red, is illustrated in figure 2(B). Comparing figure 2(B) with figure 2(A), we find that the landscapes of the HS state is quite similar to that of the low-spin state, confirming that the Feynman’s electrostatic theorem holds for this system. However, it is also true that there are slight adiabatic energy differences between the LS and HS surfaces. This could be clearly shown in figure 2(C), in which we superimposed LS and HS surfaces in the same coordinate. As can be seen in this figure, there is a phase-transition line near the equilibrium point.

In order to describe the magneto-structural correlation more explicitly, we estimated the magnetic interactions using the Heisenberg model,

\[ H = -2J \hat{S}_1 \cdot \hat{S}_2, \]  

which is usually employed to fit magnetic susceptibility measurements to determine the magnetic interaction, J, experimentally. In order to estimate J theoretically, we use the equation,

\[ J = \frac{E^{LS} - E^{HS}}{\langle \hat{S}_2^2 \rangle^{LS} - \langle \hat{S}_2^2 \rangle^{LS}}, \]  

which can be derived from equation (1) with assuming that the magnitudes of spins at the Mn(II) and Mn(III) sites are equal each other [26]. Here \( E^X \) and \( \langle \hat{S}_2^2 \rangle^X \) are, respectively, energy and expectation value of square of the total spin for the X state calculated with using the B3LYP/LACVP* method. The landscape of the magnetic interaction J on the (X, Z) plane is illustrated in figure 3. Now there is an obvious line where the magnetic transition occurs.

To consider the reason why antiferromagnetic and ferromagnetic states become stable for these two regions, we picked out two optimized geometries for (X, Z) = (0.0, 0.25) and (0.5,0.0), and implemented natural orbital analysis for low-spin solutions at these two geometries. Figure 4 illustrates natural orbitals (NOs), together with occupation numbers of NOs. F1 and A1 are singly occupied molecular orbitals (SOMO) of the LS solutions.
for FM and AFM regions, respectively. It is obvious that the F1 localizes the left hand site, while the A1 delocalizes over two Mn sites.

Figure 3: The landscape of magnetic interaction, J. The coordinates are those indicated in figure 1(A).

Occupation numbers (ONs) of natural orbitals, (F2)~(F5) are 1.002, 1.046, 1.191, and 1.221 respectively. The corresponding ONs of (A2)-(A5) are larger than those of (F2)-(F5). Here we would like to discuss the implications of the NOs and ONs [4]. In figure 4, we only show the bonding type of natural orbitals, \( \{ \phi_i^b \} \), of which occupation numbers (ONs) \( \{ n_i^b \} \) are larger than 1.0. Correspondingly, there are the antibonding type of NOs, \( \{ \phi_i^a \} \), of which ONs are given by, \( \{ n_i^a \} \) with \( n_i^a = 2.0 - n_i^b \). The relation between NOs and spin orbitals, \( \{ \psi_i^\alpha \} \), is given by,

\[
\psi_i^\alpha = \cos \theta_i^\alpha \phi_i^b + \sin \theta_i^\alpha \phi_i^a.
\]

where + and — indicate \( \alpha \) and \( \beta \) spins, respectively. Further the occupation number of the bonding NO, \( n_i^b \), is related to the overlap integral between \( \psi_i^\alpha \) and \( \psi_i^\beta \) as follows:

\[
n_i^b = \left( \psi_i^\alpha \vert \psi_i^\beta \right) + 1.0.
\]

Equation (4) implies that, as the occupation number of bonding type of NO increases, the overlap between \( \alpha \) and \( \beta \) orbitals increases, resulting in the thicker superexchange path. A noteworthy point is that this holds only for active orbitals, not for closed shell orbitals. Of course, there are bonding natural orbitals, of which occupation numbers are nearly equal to 2.0, implying that the orbitals are closed-shell ones, which do not contribute to magnetism of the Mn complex. The key point to increase the overlaps is the relative position among Mn, O, and Mn ions. It is known that p orbitals at the oxygen site intermediate the transfers between two Mn ions, enhancing the orbital overlap between two Mn sites [21]. A bend of the Mn-O-Mn deteriorates this effect, resulting in small orbital overlaps. In fact, there are little amplitude at the oxygen site in (F2) and (F3), corresponding to the localization of the d orbitals at two Mn sites. This NO analysis clarifies that the landscape of the magnetic interaction of this manganese complex exemplifies the Kanamori-Goodenough rule [22,23] on the basis of ab initio calculational results.
Figure 4 Natural orbitals (NOs) of LS solutions for (X, Z) = (0.5, 0.0) (F1~F5) and (X, Z) = (0.0,0.25) (A1~A5). The numbers indicated below the orbitals are occupation numbers of the NOs.

It might be valuable to comment upon the universality of the calculated results we showed, because it is also known that the localizability and delocalizability, and so calculated magnetism, is strongly affected by the DFT
functional we employ [29]. As described above, we previously showed that the B3LYP functional often fails to describe the weak magnetic interactions for dinuclear Mn complexes, but it is also found to be reliable for magnetism of Mn complexes, of which magnitudes are larger than 10 cm$^{-1}$[22]. Thus, the borderline between ferro and antiferromagnetic regions could slightly be shifted if we use another functional, but we can expect that the other qualitative features of this landscape of magnetism hold for other functionals.

4. Conclusion

In this study, we examined magneto-structural correlations of a simple dinuclear Mn complex with calculating the energy landscape and the magnetic interaction landscape. It is expected that this type of landscapes provide a useful guideline to understand and/or to predict the magneto-structural correlation of Mn complexes. At the next step, we will study real synthesized complexes as well as the cores of metalloenzymes with using this approach. For instance, a typical high-valent di-$\mu$-O complex, [Mn(IV)$_2$(µ-O)$_2$($\mu$-OH)$_n$(salpn)$_2$]$^{3m}$(n=0,1,2) is an interesting target: the deprotonated version (n=0) exhibits the catalase activity, and the protonation to this complex deteriorates its activity [13,30]. It was also reported that the J value decreases from -92 cm$^{-1}$ for n=0 to -48 cm$^{-1}$ for n=1 and to -6 cm$^{-1}$ for n=2 as the successive protonations occur. The oxidation state of the synthesized complex is only Mn(IV) so far, but the computational study using the landscape approach with assuming any of various oxidation states, Mn(II)Mn(III), Mn(IV)$_3$ and Mn(III)Mn(IV), is possible, by which we can examine effects of oxidation, protonation, and structural changes. We expect that such typical cases exemplify the correlation among magnetism, protonation modes, and structural changes for the Mn complexes.

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