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<th>Computational Design of Mn-Based Single-Molecule Magnets</th>
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<tr>
<td>Citation</td>
<td>Issue Date: 2009-03</td>
</tr>
<tr>
<td>Type</td>
<td>Thesis or Dissertation</td>
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<td>Text version</td>
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<td>Rights</td>
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1. Introduction

Single-molecule magnet (SMM) is a molecule that can function as magnets below its blocking temperature \(T_B\). This behavior results from a high ground-state spin \(S_G\) combined with a large and negative axial magneto-anisotropy \((D)\). Therefore, SMM is called an anisotropic high spin molecule. Recently, SMMs have received tremendous attention due to both their particular physical properties, such as macroscopic quantum tunneling and related phenomena, and their potential applications, such as quantum bits for quantum computing, and ultrahigh density information storage at molecular level. Another interesting aspect of SMMs is that SMMs are available as magnetic building blocks for developing novel materials [1], i.e. SMM-based materials. They are new classes of multifunctional/hybrid materials such as bi-functional magnetic/conducting materials, and new classes of nano-scale magnetic systems such as single-core magnets (SCMs), and multi-dimensional SMM networks (nano-dots networks). SMM consists of transition metal (TM) atoms and ligands. As described above, \(S_G\) and \(D\) are the important parameters for control of SMM behavior. The \(S_G\) of SMM results from local spin moments at TM ions \((S_i)\) and exchange coupling between them \((J_{ij})\). Moreover, \(J_{ij}\) have to be important to well separate the ground spin state from the excited states; the relative high value of \(T_B\) is dependent on them [2,3]. Therefore, not only \(S_G\) and \(D\), but also \(J_{ij}\) are crucial parameters for control of SMM behavior. Controlling these parameters is the way to develop new SMMs and SMM-based materials. One effective way to tailor these parameters is based on rational variations in ligands and TM atoms of known SMMs. With the advancement of the first principles calculation methods, it becomes feasible to predict many of the important physical quantities of SMMs. However, theoretical prediction of possibilities of controlling these parameters of SMMs is still missing.

2. Purpose and Computational Methods

In the present dissertation, to explore possibilities of controlling \(S_G\), \(D\), and \(J_{ij}\), a systematic study of rational variations in ligands of Mn-based SMMs (especially Mn-based SMMs) has been performed by using Dmol3 and OpenMX codes based on Density-functional theory (DFT). Distorted cubane Mn_4 (Mn^{4+}Mn^{3+}) SMMs have the general chemical formula \([\text{Mn}^{11}\text{Mn}^{9}\text{Mn}^{5}\text{Mn}^{2}]\text{(Mn}^{5}\text{O}^2\text{)}\text{X}^3\text{(O}_2\text{CR)}\text{L}_1\text{L}_2\text{L}_3\text{L}_4\text{X})\text{(X = F, Cl, Br, etc.)}, or variation in the R group (R = a radical such as CH_3 or C_6H_5), or variation in the peripheral-ligands group (L1, L2) = (py,Cl) or (dbm). By these variations, the \(S_T\) of Mn^{4+}Mn^{3+} SMMs is a constant of 9/2 resulting from antiferromagnetic (AFM) couplings between the Mn^{4+} ion at the A site with formal magnetic moment \(3\mu_B\) and the three Mn^{3+} ions at the B sites with their formal magnetic moment \(4\mu_B\), only the exchange coupling parameters between Mn ions \((J_{AB} \text{ and } J_{BB})\), and the axial anisotropy parameter \((D)\) are slightly changed.

Great effort has been paid for synthesizing new distorted cubane Mn^{4+}Mn^{3+} SMMs by variation in the core X^- group (X = F, Cl, Br, etc.), or variation in the R group (R = a radical such as CH_3 or C_6H_5), or variation in the peripheral-ligands group (L1L2) = (py,Cl) or (dbm). By these variations, the \(S_T\) of Mn^{4+}Mn^{3+} SMMs is a constant of 9/2 resulting from antiferromagnetic (AFM) couplings between the Mn^{4+} ion at the A site with formal magnetic moment \(3\mu_B\) and the three Mn^{3+} ions at the B sites with their formal magnetic moment \(4\mu_B\), only the exchange coupling parameters between Mn ions \((J_{AB} \text{ and } J_{BB})\), and the axial anisotropy parameter \((D)\) are slightly changed.

The previous theoretical studies focused on two typical Mn_4 SMMs, i.e. \(\text{Mn}_2\text{O}_2\text{Cl}(\text{O}_2\text{CMe})_2\text{(dbm)})_2\) and \(\text{Mn}_4\text{O}_2\text{Cl}(\text{O}_2\text{Cl})_2\text{(py,Cl)})_2\), and the \(\text{Mn}_4\) dimer \([\text{Mn}_2\text{O}_2\text{Cl}(\text{O}_2\text{Cl})_2\text{(py,Cl)})_2\)]_2. Their \(S_T\), \(J_{AB}\), \(J_{BB}\), \(D\), and local magnetic moments at the A and B sites \((m_A \text{ and } m_B)\) have been calculated. In general, the previous calculated results are in good agreement with experiment [5], although the calculated exchange-coupling parameters are somewhat overestimated compared to the experimental values as common for DFT calculations.
However, in the previous DFT studies of Mn₄ SMMs, there is no discussion about mechanism of exchange coupling between Mn ions, and no suggestion for tailoring Sₚ, J_AB, J_BB, and D was proposed.

In the present dissertation, to explore possibilities of controlling Sₚ, D, J_AB, and J_BB of Mn₄ SMMs, not only variations in X and (L₁,L₂), but also variations in O⁺core and O₃O₃a have been made. These variations are based on deep understanding of the electronic structure, magnetorestrictive correlation, and mechanism of exchange coupling between Mn ions of distorted cubane Mn₄ molecules. The mₐ and mₜ have been calculated by using the Mulliken population analysis. The J_AB and J_BB have been computed by adopting the total energy different method. A qualitative discussion of D is given based on the local electronic and geometric structures at TM sites.

3. Results and Discussion

The electronic structure, geometric structure, Sₚ, mₐ, mₜ, J_AB, and J_BB of three known typical Mn₄ molecules, Mn₄O₂Cl(O₂CMe)₃(dbm)₃ (dbmH = dibenzoyl-methane) and Mn₄O₂Cl(O₂CR)₃(pyCl)₃ (R = Me or Et, py = pyridine), have been deeply investigated by using eight different GGA-based exchange-correlation-energy (Eₓc) functionals: HCTH407, RPBE, VWN-BP, BP, PBE, PW91, BOP, and BLYP. A comparison between the calculated and experimental results shows that the most reliable Eₓc functional is the RPBE. Therefore hereafter, the RPBE functional has been adopted to explore possibilities of tailoring Sₚ, J_AB, and J_BB of Mn₄ SMMs.

3.1. Variations in (L₁,L₂)

In TM complexes, the valence state as well as the formal charge of TM ions is determined by the valence of the ligands. For designing Mn based SMMs, three important valence states of Mn are Mn⁷⁺/Mn²⁺ with a configuration 3d⁶, Mn⁶⁰⁰/Mn⁶⁺ with a configuration 3d⁴, and Mn⁹⁵/Mn⁶⁺ with a configuration 3d³. In these valence/charge states, Mn ions have the advantage of yielding large magnetic moments. Moreover, the high spin (HS) state of Mn³⁺ ion and the intermediate spin (IS) state of Mn²⁺ are expected to produce strongly elongated Jahn-Teller distortion resulting in axial anisotropy of Mn based SMMs.

This subsection is devoted to shed light on possibilities of designing above charge and spin states of Mn in Mn₄ SMMs without destroying the distorted cubane geometry of the Mn₄O₂X core. For this purpose, variation in peripheral ligands (L₁,L₂) is the best way. By variation in (L₁,L₂) [4], twenty four distorted cubane Mn₄ molecules have been designed or reconstructed with a general chemical formula Mn₄O₂Cl(O₂CMe)₃(L₁,L₂)ₙ, in which three types of ligand couple (L₁,L₂) with different valences have been used.

The calculated results show that when L₁ and L₂ are a neutral ligand and an anionic ligand, respectively, Mn₄ molecules are anisotropic high spin molecules [4] with the Sₚ of 9/2 resulting from AFM coupling between the A with magnetic moment mₐ ≃ −3 μₑₗ and three B sites with m_B ≃ +4 μₑₗ. Three B sites are strongly elongated Jahn-Teller distortion, and thus are expected to yield a large and negative D.

When both L₁ and L₂ are anionic ligands, Mn₄ molecules are high-spin molecules with the Sₚ of 6 resulting from ferromagnetic (FM) coupling between the A site with mₐ ≃ +3 μₑₗ and three B sites with m_B ≃ +3 μₑₗ [4]. However, these Mn₄ molecules have the disadvantage of a small D due to no elongated Jahn-Teller distortion at Mn sites.

When both L₁ and L₂ are neutral ligands, Mn₄ molecules have the Sₚ of 3 [4]. The Mn ion at the A site has the formal charge of +4 and the magnetic moment with magnitude of |mₐ| ≃ +3 μₑₗ. The Mn ions at the B sites have the formal charge state of +2, however, their spin state can be an IS state with mₜ ≃ +3 μₑₗ or a low-spin (LS) state with mₜ ≃ ±1 μₑₗ depending on (L₁,L₂) [4]. The LS state is favorable by using CH₃CN as peripheral ligands, while the IS state is favorable by using other ligands. In the later, Mn₄ molecules are anisotropic high spin molecules owing to strongly elongated Jahn-Teller distortion at the B sites [4]. Moreover, this is the first time, possibilities of designing a IS state of Mn³⁺ ion have been found.

As presented above, by rational variations in the peripheral ligands (L₁,L₂), the occupation of 3d orbitals at the B sites is controlled. This brings us an effective way to explore exchange couplings between Mn sites, as well as exchange couplings of 3d orbitals between Mn sites. In Mn⁴⁺Mn³⁺ molecules (both L₁ and L₂ are anionic ligands), the exchange coupling between the Mn⁴⁺ ions at the A and B sites is FM. Here it is noted that, three magnetic electrons of each of these Mn⁴⁺ ions are mainly distributed in three t₂g orbitals. This means that exchange coupling between the t₂g orbitals at the A and B sites is FM. In Mn⁴⁺Mn⁴⁺ molecules (L₁ and L₂ correspond to a neutral and an anionic ligands), the exchange coupling between the Mn⁴⁺ ion at the A and the Mn³⁺ ions at the B sites is AFM. Here, four magnetic electrons of the Mn³⁺ ions are mainly distributed in not only three t₂g orbitals, but also the dₓz orbital. Therefore, exchange coupling between the A and B sites consists of the t₂g-x₂g and the t₂g-dₓz couplings. By adopting the result from Mn⁴⁺Mn⁴⁺ molecules, it is revealed that the t₂g-dₓz coupling must be AFM, and stronger than the FM t₂g-t₂g coupling. By adopting this result, the exchange coupling between Mn ions in Mn⁴⁺Mn⁴⁺ molecules (both L₁ and L₂ are neutral ligands) can be also easy to be understood.

For each type of Mn⁴⁺Mn³⁺ molecules, the effective exchange-coupling parameters between Mn ions are only slightly changed by variations in their peripheral ligands (L₁,L₂) [4] resulting from stabilization of the geometry of exchange pathways Mn-O-Mn with variations in (L₁,L₂). For example, the geometric parameters of exchange pathways Mn-O-Mn of Mn⁴⁺Mn³⁺ molecules are stable with variations in (L₁,L₂), as shown in Fig 2a.
As mentioned above, the exchange coupling between the A and B sites of Mn\(^{4+}\)Mn\(^{3+}\) molecules is determined by the coupling between the d\(_z^2\) orbital at each B site and a t\(_{2g}\) orbital at the A site through a hybridization with s orbitals at oxygen, as shown in Fig. 2b. Here, it is noted that, in this coupling, the hybridization between the t\(_{2g}\) orbital at the A site and orbitals at oxygen is π-like. Therefore, the strength of this coupling is expected to be sensitive to the change of A-O-B angle (α), and strongest with α ≈ 90°. Current Mn\(^{4+}\)Mn\(^{3+}\) molecules have α ≈ 95°. Therefore, looking for Mn\(^{4+}\)Mn\(^{3+}\) molecules with α ≈ 90° is an effective way for developing new superior Mn\(^{4+}\)Mn\(^{3+}\) SMMs with higher blocking temperatures resulting from strong intramolecular exchange coupling. For this purpose, variations in ligand sites O\(_{core}\), X, and O\(_{OAc}\) will be the best ways.

![Fig. 2.](image)

**Fig. 2.** (a) The geometry of exchange pathways A-O-B of synthesized Mn\(^{4+}\)Mn\(^{3+}\) molecules. (b) The coupling between the \(\zeta^2\) orbital at the B site and a \(t_{2g}\) orbital at the A site through a hybridization with orbitals at oxygen.

3.2. Combining Variations in O\(_{core}\), X, and O\(_{OAc}\)

To preserve the distorted cubane geometry of Mn\(^{4+}\)Mn\(^{3+}\) molecules and the formal charges of Mn ions, ligands substituted for the O\(_{core}\) should satisfy following conditions: (i) To have the formal charge of \(-2\); (ii) The ionic radius of these ligands should be not so different from that of O\(^{2-}\) ion. From these remarks, N based ligands, NR' (R' = a radical), should be the best candidates. Moreover, by variation in R' group, the local electronic structure as well as electronegativity at N site can be controlled. As a consequence, the Mn-N bond lengths and the Mn\(^{3+}\)-N-Mn\(^{4+}\) angles (α), as well as \(J_{AB}\) are expected to be tailored. Smaller changes in α are expected to be made by variations in the X\(_{core}\) and O\(_{OAc}\).

By these variations, 42 new anisotropic high spin Mn\(_4\) molecules with the \(S_f\) of 9/2 resulting from the AFM couplings between the Mn\(^{4+}\) ion at the A site and the Mn\(^{3+}\) ions at the B sites, and the α in a range of 88.5°–95.5° have been designed. Three B sites are elongated octahedron resulting in axial anisotropy of these Mn\(_4\) molecules. These molecules have a general chemical formula [Mn\(_4\)L\(_3\)XZ(CH(CH\(_{2}\))O\(_3\))] (hereafter Mn\(_4\)L\(_3\)XZ) with L = O, NH, NCH\(_3\), NCH\(_2\)CH\(_2\), NCH=CH\(_2\), NC=CH, or NC\(_6\)H\(_5\); X = F, Cl, or Br; and Z = (CH\(_3\))COO\(_3\) or CH\(_2\)C(CH\(_2\))NOCOCH\(_3\)). The calculated results show that these Mn\(_4\)L\(_3\)XZ molecules also have C\(_3v\) symmetry with the C\(_1\) axis through the A and X sites, and their Mn\(_4\)L\(_3\)X core also has distorted cubane geometry.

The calculated results confirm that the \(J_{AB}\) tends to become stronger when the α reaches to around 90°, as shown in Fig. 3a, due to enhancement of hybridization between 3d orbitals at Mn sites and ligands orbitals at L sites. The Mn\(_4\)(NC\(_6\)H\(_5\))\(_2\)F(CH\(_2\))(CH\(_2\))NOCOCH\(_3\)) molecule with α = 89.69° has the highest \(J_{AB}/k_B\) of −214.79 K. This value is about three times larger than that of synthesized Mn\(_4\) SMMs.

As shown in Fig. 3b, the AFM coupling between the A and B sites also tends to become stronger when the distance between the A and B sites (\(d_{AB}\)) decreases which can be attributed to increase of direct overlap between 3d orbitals at the A and B sites.

However, the results demonstrate that the strength of \(J_{AB}\) depends on not only the α and \(d_{AB}\) but also the nature of exchange-pathway-ligands which determines delocalization of 3d electrons between Mn sites, especially delocalization of the d\(_z^2\) electrons from the B sites to the A site (\(\Delta m_A = 3 - |m_B|\)). This relation is illustrated in Fig. 3c, in which the strength of \(J_{AB}\) tends to increase with \(\Delta m_A\). A comparison between Figs. 3a–c shows that \(\Delta m_A\) seems to be a better parameter to describe \(J_{AB}\) than α and \(d_{AB}\). The \(J_{AB}\) is nearly linear with \(\Delta m_A\).

![Fig. 3.](image)

**Fig. 3.** (a) The α dependence of \(J_{AB}\). (b) The \(d_{AB}\) dependence of \(J_{AB}\). (c) The \(\Delta m_A\) dependence of \(J_{AB}\).
4. Conclusion
In conclusion, by a systematically rational variation in ligands, we have succeeded in revealing the possibilities of controlling $S_f$, $D$, and $J_{AB}$ of Mn$_4$ SMMs based on DFT, in which $S_f$ and $D$ can be tailored by variations in peripheral ligands, $J_{AB}$ can be controlled by variations in exchange-pathway-ligands. The results also demonstrate that variation in peripheral ligands is an effective method to explore mechanism of exchange coupling between Mn ions of Mn$_4$ SMMs, as well as to reveal a key parameter for control of $J_{AB}$. This result allows us to predict that $J_{AB}$ will be strongest when the Mn-ligand-Mn exchange coupling angle ($\alpha$) reaches to around 90°. By variations in exchange-pathway-ligands, 42 new anisotropic high spin Mn$_4$ molecules with the $S_f$ of 9/2 and the $\alpha$ in a range of 88.5°–95.5° have been designed. The calculated results confirm that, $J_{AB}$ tends to become stronger when $\alpha$ reaches to around 90°, in which $J_{AB}/k_B$ is maximum of -214.79 K with the $\alpha = 89.69^\circ$. This value is about three times larger than that of synthesized Mn$_4$ SMMs. However, the results show that the strength of $J_{AB}$ depends on not only the $\alpha$ but also the nature of exchange-pathway-ligands which determines delocalization of 3d electrons between Mn sites. A new magnetic parameter which can depict delocalization of 3d electrons between Mn sites, $\Delta m_A = 3 - |m_{AB}|$, has been first introduced. The $\Delta m_A$ is better parameter to describe $J_{AB}$ than geometric parameters such as $\alpha$. The $J_{AB}$ is nearly linear with $\Delta m_A$. This is the first time that N based ligands, NR (R = various), have been used to form exchange pathways between Mn ions in Mn$_4$ SMMs. Variation in the R radical is demonstrated as an effective way to tailor and optimize $J_{AB}$. This method can be adopted for other SMMs. We hope the results would give some hints for synthesizing not only new superior Mn$_4$ SMMs, but also a new class of SMMs and SMM-based materials by using N based ligands to form exchange pathways between magnetic ions.

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