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Title	Computational Design of Mn-Based Single-Molecule Magnets
Author(s)	Nguyen, Anh Tuan
Citation	
Issue Date	2009-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/8004
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Description	Supervisor:Prof. Shin-ichi Katayama, マテリアルサイエンス研究科, 博士

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Computational Design of Mn-Based Single-Molecule Magnets

Katayama Lab., 0540203, Nguyen Anh Tuan

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_T) combined with a large and negative axial magnetoanisotropy (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-chain magnets (SCMs), and multi-dimensional SMM networks (nano-dots networks). SMM consists of transition metal (TM) atoms and ligands. As described above, S_T and D are the important parameters for control of SMM behavior. The S_T 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_T 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_T, D, and J_{ij}, a systematic study of rational variations in ligands of Mn-based SMMs (especially Mn_4 SMMs) has been performed by using DMol^3 and OpenMX codes based on Density-functional theory (DFT). Distorted cubane Mn_4 ($Mn^{4+}Mn^{3+}{}_3$) SMMs have the general chemical formula $[Mn^{4+}Mn^{3+}{}_3(\mu_3\text{-}O^{2-})_3(\mu_3\text{-}X^-)(O_2CR)^-{}_3(L1,L2)^-{}_3]$ (X, R, L1, and L2 = various) [4]. The geometric structures of Mn_4 SMMs are schematically displayed in Fig. 1. Previous experimental studies reported that each molecule has C_{3v} symmetry, with the C_3 axis passing through Mn^{4+} and X^- ions. The $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)]$ core can be simply viewed as a "distorted cubane", in which the four Mn atoms are located at the corners of a trigonal pyramid, with a $\mu_3\text{-}O^{2-}$ ion bridging each of the vertical faces and a $\mu_3\text{-}X^-$ ion bridging the basal face. Three carboxylate (O_2CR) groups, forming three bridges between the A and B sites, play an important role in stabilizing the distorted cubane geometry of Mn_4O_3X core. Each peripheral-ligands couple (L1,L2) forms two coordinate bonds to complete the distorted octahedral geometry at each B site, and thus is a crucial factor in controlling the local electronic structure at the B sites, as well as the physical properties of Mn_4 molecules.

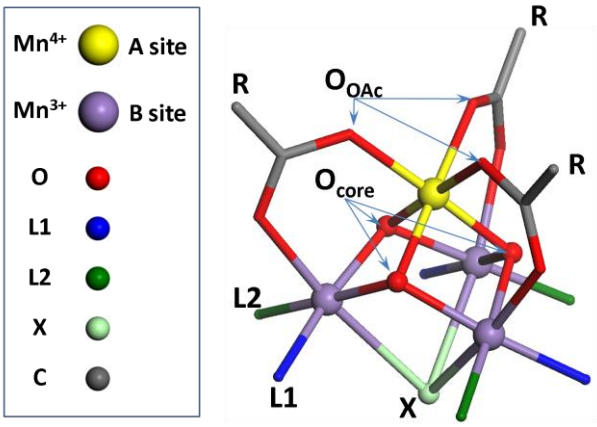

Fig. 1: A schematic geometric structure of $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)(O_2CR)_3(L1,L2)_3]$ SMMs. The $[Mn_4(\mu_3\text{-}O)_3(\mu_3\text{-}X)]$ core is highlighted in balls.

Great effort has been paid for synthesizing new distorted cubane $Mn^{4+}Mn^{3+}{}_3$ 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_2H_5), or variation in the peripheral-ligands group (L1,L2) = (py,Cl) or (dbm). By these variations, the S_T of $Mn^{4+}Mn^{3+}{}_3$ 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} 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. $Mn_4O_3Cl(O_2CMe)_3(dbm)_3$ and $Mn_4O_3Cl(O_2CEt)_3(py,Cl)_3$, and the Mn_4 dimer $[Mn_4O_3Cl(O_2CEt)_3(py,Cl)_3]_2$. Their S_T, J_{AB}, J_{BB}, D, and local magnetic moments at the A and B sites (m_A 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 Mn_4 SMMs, there is no discussion about mechanism of exchange coupling between Mn ions, and no suggestion for tailoring S_T, J_{AB}, J_{BB}, and D was proposed.

In the present dissertation, to explore possibilities of controlling S_T, D, J_{AB}, and J_{BB} of Mn_4 SMMs, not only variations in X and (L1,L2), but also variations in O_{core} and O_{OAc} have been made. These variations are based on deep understanding of the electronic structure, magnetostructural correlation, and mechanism of exchange coupling between Mn ions of distorted cubane Mn_4 molecules. The m_A and m_B 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, S_T, m_A, m_B, J_{AB}, and J_{BB} of three known typical Mn_4 molecules, $Mn_4O_3Cl(O_2CMe)_3(dbm)_3$ (*dbmH* = *dibenzoyl-methane*) and $Mn_4O_3Cl(O_2CR)_3(py,Cl)_3$ (R = Me or Et, *py* = *pyridine*), have been deeply investigated by using eight different GGA-based exchange-correlation-energy (E_{xc}) functionals: HCTH407, RPBE, VWN-BP, BP, PBE, PW91, BOP, and BLYP. A comparison between the calculated and experimental results shows that the most reliable E_{xc} functional is the RPBE. Therefore hereafter, the RPBE functional has been adopted to explore possibilities of tailoring S_T, J_{AB}, and J_{BB} of Mn_4 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 Mn^{II}/Mn^{2+} with a configuration $3d^5$, Mn^{III}/Mn^{3+} with a configuration $3d^4$, and Mn^{IV}/Mn^{4+} with a configuration $3d^3$. In these valence/charge states, Mn ions have the advantage of yielding large magnetic moments. Moreover, the high spin (HS) state of Mn^{3+} ion and the intermediate spin (IS) state of Mn^{2+} ion 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 Mn_4 SMMs without destroying the distorted cubane geometry of the Mn_4O_3X core. For this purpose, variation in peripheral ligands (L1,L2) is the best way. By variation in (L1,L2) [4], twenty four distorted cubane Mn_4 molecules have been designed or reconstructed with a general chemical formula $Mn_4O_3Cl(O_2CMe)_3(L1,L2)_3$, 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, Mn_4 molecules are anisotropic high spin molecules [4] with the S_T of 9/2 resulting from AFM coupling between the A with magnetic moment $m_A \approx -3\ \mu_B$ and three B sites with $m_B \approx +4\ \mu_B$. 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, Mn_4 molecules are high-spin molecules with the S_T of 6 resulting from ferromagnetic (FM) coupling between the A site with $m_A \approx +3\ \mu_B$ and three B sites with $m_B \approx +3\ \mu_B$ [4]. However, these Mn_4 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, Mn_4 molecules have the S_T of 3 [4]. The Mn ion at the A site has the formal charge of +4 and the magnetic moment with magnitude of $|m_A| \approx +3\ \mu_B$. The Mn ions at the B sites have the formal charge state of +2, however, their spin state can be an IS state with $m_B \approx +3\ \mu_B$ or a low-spin (LS) state with $m_B \approx +1\ \mu_B$ depending on (L1,L2) [4]. The LS state is favorable by using CH_3CN as peripheral ligands, while the IS state is favorable by using other ligands. In the later, Mn_4 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 Mn^{2+} ion have been found.

As presented above, by rational variations in the peripheral ligands (L1,L2), the occupation of 3*d* 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 3*d* orbitals between Mn sites. In $Mn^{4+}Mn^{4+}{}_3$ molecules (both L1 and L2 are anionic ligands), the exchange coupling between the Mn^{4+} ions at the A and B sites is FM. Here it is noted that, three magnetic electrons of each of these Mn^{4+} ions are mainly distributed in three t_{2g} orbitals. This means that exchange coupling between the t_{2g} orbitals at the A and B sites is FM. In $Mn^{4+}Mn^{3+}{}_3$ molecules (L1 and L2 correspond to a neutral and an anionic ligands), the exchange coupling between the Mn^{4+} ion at the A and the Mn^{3+} ions at the B sites is AFM. Here, four magnetic electrons of the Mn^{3+} ions are mainly distributed in not only three t_{2g} orbitals, but also the d_{z^2} orbital. Therefore, exchange coupling between the A and B sites consists of the t_{2g}-t_{2g} and the t_{2g}-d_{z^2} couplings. By adopting the result from $Mn^{4+}Mn^{4+}{}_3$ molecules, it is revealed that the t_{2g}-d_{z^2} coupling must be AFM, and stronger than the FM t_{2g}-t_{2g} coupling. By adopting this result, the exchange coupling between Mn ions in $Mn^{4+}Mn^{2+}{}_3$ molecules (both L1 and L2 are neutral ligands) can be also easy to be understood.

For each type of $Mn^{4+}Mn^{n+}{}_3$ 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 $Mn^{4+}Mn^{3+}{}_3$ 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 $Mn^{4+}Mn^{3+}{}_3$ 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 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 with the change of A-O-B angle (α), and strongest with α ≈ 90°. Current $Mn^{4+}Mn^{3+}{}_3$ molecules have α ≈ 95°. Therefore, looking for $Mn^{4+}Mn^{3+}{}_3$ molecules with α ≈ 90° is an effective way for developing new superior $Mn^{4+}Mn^{3+}{}_3$ 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.

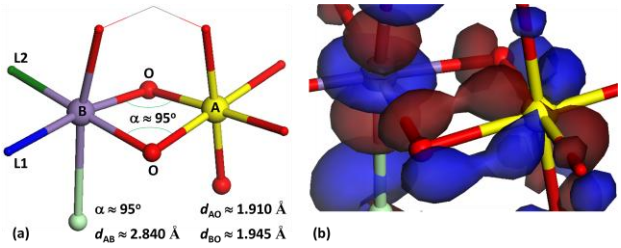

Fig. 2:. (**a**) The geometry of exchange pathways A-O-B of synthesized $Mn^{4+}Mn^{3+}{}_3$ molecules. (**b**) The coupling between the z^2 orbital at the B site and a t_{2g} orbital at the A site through a hybridization with orbitals at oxygen.

3.2. Combining Variations in O_{core}, X, and O_{OAc}

To preserve the distorted cubane geometry of $Mn^{4+}Mn^{3+}{}_3$ 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^{4+}-N-Mn^{3+} 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_T 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 $[Mn_4L_3XZ(CH(CHO)_2)_3]$ (hereafter Mn_4L_3XZ) with L = O, NH, NCH_3, NCH_2CH_3, $NCH{=}CH_2$, NC≡CH, or NC_6H_5; X = F, Cl, or Br; and Z = $(CH_3COO)_3$ or $CH_3C(CH_2NCOCH_3)_3$. The calculated results show that these $Mn_4L_3XZ_3$ molecules also have C_{3v} symmetry with the C_3 axis through the A and X sites, and their Mn_4L_3X 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 $Mn_4(NC_2H_5)_3F(CH_3C(CH_2NOCOCH_3)_3)$ 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 ($\Delta m_A = 3 - |m_A|$). This relation is illustrated in Fig. 3c, in which the strength of J_{AB} tends to increase with Δm_A. A comparison between Figs. 3a–c shows that Δm_A seems to be a better parameter to describe J_{AB} than α and d_{AB}. The J_{AB} is nearly linear with Δm_A.

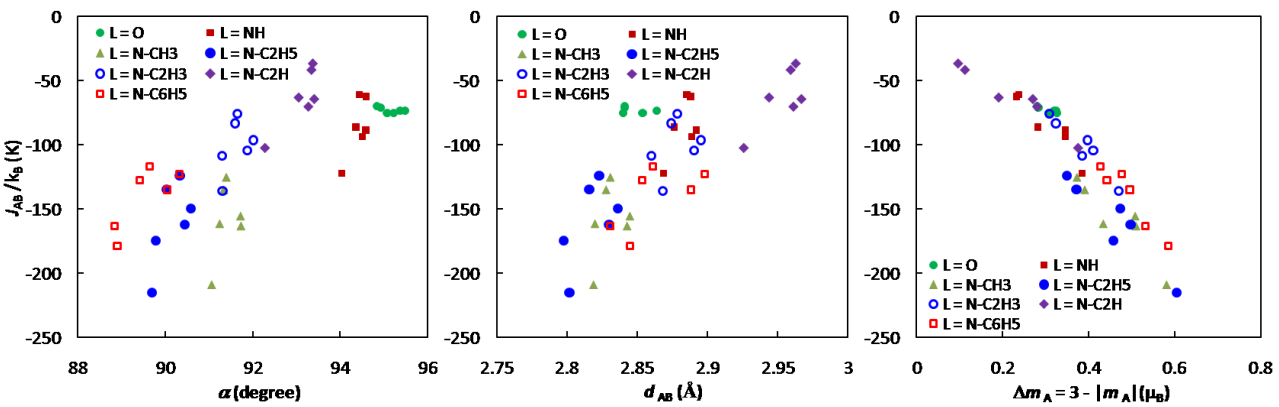

Fig. 3: (**a**) The α dependence of J_{AB}. (**b**) The d_{AB} dependence of J_{AB}. (**c**) The Δm_A dependence of J_{AB}.

4. Conclusion

In conclusion, by a systematically rational variation in ligands, we have succeeded in revealing the possibilities of controlling S_T, D, and J_{AB} of Mn_4 SMMs based on DFT, in which S_T 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 (α) reaches to around 90°. By variations in exchange-pathway-ligands, 42 new anisotropic high spin Mn_4 molecules with the S_T of 9/2 and the α in a range of 88.5^o–95.5^o have been designed. The calculated results confirm that, J_{AB} tends to become stronger when α reaches to around 90°, in which J_{AB}/k_B is maximum of -214.79 K with the $\alpha = 89.69^o$. 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 α 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, $\Delta m_A = 3 - |m_A|$, has been first introduced. The Δm_A is a better parameter to describe J_{AB} than geometric parameters such as α. The J_{AB} is nearly linear with Δm_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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LIST OF PUBLICATIONS

Journal Articles

[1]. **Nguyen Anh Tuan**, Shin-ichi Katayama, Dam Hieu Chi, *The role of complex ligands in controlling ground-state spin of triangle pyramidal Mn_4O_3Cl Single Molecule Magnets*, VNU. Journal of science, Mathematics-Physics Vol. XXII, No. 2AP (2006) 206.

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