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▌ Single-Molecule Magnets

Probing the Origin of Magnetic Anisotropy in a Dinuclear {Mn^{III}Cu^{II}} Single-Molecule Magnet: The Role of Exchange Anisotropy

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Abstract: Using ab initio calculations all the components of the magnetic anisotropy in a dinuclear [Mn^{III}Cu^{II}Cl(5-Br-sap)$_2$(MeOH)] single-molecule magnet (SMM) have been computed. These calculations reveal that apart from the single-ion anisotropy, the exchange anisotropy also plays a crucial role in determining the sign as well as the magnitude of the cluster anisotropy. Developed magneto-structural correlations suggest that a large ferromagnetic exchange can in fact reduce the ground-state anisotropy, which is an integral component in the design of SMMs.

Interest in polynuclear clusters has increased tremendously since the discovery of single-molecule magnetic (SMM) behavior in a {Mn$_{12}$} cluster.[1] Since then, a number of potential applications for SMMs have been proposed including information storage devices and solid-state Q bits in quantum computing.[2] The proposed potential applications are related to the bistability observed at very low temperatures due to slow relaxation of magnetization reversal. It has been established that the relaxation of magnetization in SMMs is due to an energy barrier related to spin ground state S and negative axial anisotropy D of the ground state ($|D|S^2$ for an integer spin ground state). Enhancing the energy barrier for SMMs is vital for future developments, and this has been the primary goal for many researchers working in this area.[3] It is a known fact that increasing S and/or D is expected to raise the barrier height; however, there are no rational approaches available to fine tune these parameters to date.[4] Even though individually the S[5] and the D[6] parameters have been raised significantly, the barrier height has not been raised considerably for transition-metal complexes.[4c]

Over the years, a significant development has been done in theoretical and experimental side to understand the factors, which are likely to control the ground state spin S,[7] and at many instances the magnetic anisotropy is suggested as the most important parameter over the total spin to increase the barrier height.[8] Some path-breaking discoveries with a very large D values include report on a monomeric Ni^{II} complex[6a] possessing D value as high as -250 cm^{-1} and a monomeric Co^{II} SMM having D value of -70 cm^{-1}.[6b] However, such large D values for di/polynuclear complexes are unfounded. Understanding the microscopic origin of ZFS parameter in di/polynuclear complexes hold the key to the future success, because experimental,[9,10] as well as theoretical, studies[11a–c,12] targeting to probe the origin of single-ion and cluster anisotropies are relatively scarce. The factors that control D in polynuclear clusters are poorly understood, because there are many competing components, such as single-ion and exchange anisotropy.[9a] By using DFT/ab initio methods, D and E parameters of several mononuclear complexes and some SMMs[13] have been computed, and for mononuclear complexes some efforts has been undertaken to probe the origin of ZFS.[11a–c,14] Recently, Neese and co-workers articulated that effort to understand the parameters involved in maximizing the anisotropy of small nuclearity clusters is crucial for future success in this area.[15] Despite numerous theoretical studies on ZFS of mononuclear complexes, studies on polynuclear complexes are uncommon and particularly how the single-ion anisotropy transforms in the cluster framework is rather limited.

Herein, we address some of these issues and studied in detail the anisotropy of a ferromagnetically coupled dinuclear {Mn^{III}Cu^{II}} SMM[16] by using state-of-the-art ab initio calculations to offer insights on D and also provide some information to enhance the energy barrier. Synthesis, structure, and magnetic properties of the dinuclear {Mn^{III}Cu^{II}} complex [Mn^{III}Cu^{II}Cl(5-Br-sap)$_2$(MeOH)] (**1**, 5-Br-sap = 5-bromo-2-salicylideneamino-1-proanol; see Figure 1a) has been reported earlier.[16] Complex **1** was thoroughly characterized by d.c., a.c., magnetization and high-field (HF) EPR spectroscopy.[16,17] It has been characterized as an SMM and single-crystal HF-EPR studies and low-temperature magnetization data estimate the axial zero-field splitting D$_{5/2}$ as -1.81 cm^{-1}, whereas the rhombic parameter E is assumed to be zero. The effective energy barrier (U$_{eff}$) in **1** was estimated from the relaxation studies to be 10.5 K confirming the SMM characteristic of the complex **1**.[16] Besides, **1** has also been thoroughly investigated by low-temperature NMR experiments,[18] spin-filtering and spin-transport studies.[19]

In complex **1**, the Mn^{III} ion is in an elongated tetragonal environment, whereas the Cu^{II} ion was found to be in a square-planar environment having two μ-alkoxo bridges, which

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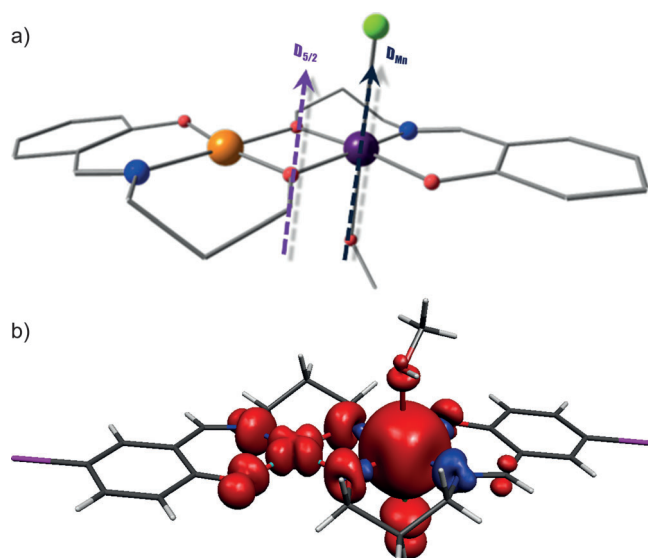*E-mail: rajaraman@chem.iitb.ac.in*

Figure 1. a) NEVPT2-computed orientation for single-ion and cluster-anisotropy (D_{ZZ}) axis; b) DFT-computed spin-density plot for complex **1**. The isodensity surface represented corresponds to a value of 0.003 e⁻ bohr⁻³. The red and blue regions indicate the positive and negative spin densities, respectively.

govern the magnetic exchange. The selected structural parameters, which are likely to govern the J values, are given in Table S1 in the Supporting Information. Initially, we performed the DFT calculations to estimate the exchange coupling (DFT, B3LYP) on the full structure of **1**, and the calculated magnetic coupling of +78 cm⁻¹ is in excellent agreement with experimental one (J +78 cm⁻¹; see the Supporting Information, Table S2). A strong ferromagnetic exchange interaction arises from the orthogonality of the magnetic orbitals of Mn[III] and Cu[II] ions. The magnetic orbitals of Jahn–Teller elongated Mn[III] are e_g (d_{xz} and d_{yz}), b_{2g} (d_{xy}), a_{1g} (d_z^2) and b_{1g} ($d_{x^2-y^2}$), whereas under square-planar environment, the magnetic orbital of Cu[II] is b_{1g}, which is orthogonal to the magnetic orbitals of Mn[III] leading to a strong ferromagnetic exchange. The computed overlap integral also supports this argument (Table S3 and Figure S2 in the Supporting Information). The spin-density plot for the high spin state is given in Figure 1b, and this clearly shows that the unpaired electron lies in $d_{x^2-y^2}$ orbital of Cu[II], whereas the spin densities around Mn[III] ion exhibit spin delocalization/polarization.[20]

The large anisotropy in **1** is due to a significant contribution from the single-ion anisotropy of the Mn[III] ion, and it is known that the orbital degeneracy of the ground state ^5E_g configuration of the Mn[III] ion in an octahedral ligand field is removed by the Jahn–Teller distortion giving rise to a ground state with a large ZFS. At many instances it has been demonstrated that for small nuclearity clusters, the ab initio methods, such as CASSCF and SORCI calculations, are superior in estimating the D and E values compared to DFT methods. Hence, we have performed state-average CASSCF calculations with an active space composed of thirteen electrons in ten orbitals (d electrons in d-based orbitals) with five sextets and 35 low lying quartets states (see the Supporting Information for an elabo-

rate computational details). These calculations gave D value of −1.71 cm⁻¹ with E value 0.13 cm⁻¹, which is in excellent agreement with the experimental parameters. The E value is assumed to be zero in the experiment, whereas calculations revealed a small rhombic E parameter for **1**. The NEVPT2 computed D-tensor orientation is given in Figure 1a, in which the D_{ZZ} was found to align along the Jahn–Teller elongated axis of the Mn[III] ion (Cl-Mn-OH-CH₃). Improving the description of electron correlation further by second-order perturbation theory or including many singlet states does not alter the computed magnitude of D significantly, compared with the CASSCF calculations.

The main contribution to the ZFS is arising from the spin–orbit coupling, which originates due to the presence of low-lying excited states. The maximum contribution arises from $\alpha \rightarrow \beta$ spin-flip excitations (SOMO→SOMO), as well as $\alpha \rightarrow \alpha$ spin-conserving excitations (SOMO→virtual molecular orbital (VMO). The $\alpha \rightarrow \beta$ spin-flip excitations are more pronounced and contribute to approximately 70% of the total D value in this complex. For complex **1**, in strong exchange limit ($J \gg D$), the global anisotropy is given by the following equation:[21]

$$D_s = d_{Mn}D_{Mn} + d_{MnCu}D_{MnCu} \qquad (1)$$

in which D_{Mn} and the D_{MnCu} are the single-ion and exchange anisotropies, respectively, and d_{Mn} and d_{MnCu} are the corresponding coefficients obtain upon solving the equation for ZFS within S manifold.[21]

The ground-state anisotropy of **1** has two contributions, one is the single-ion anisotropy, and the other is the exchange anisotropy due to the presence of Cu[II] ions. The single-ion anisotropy is estimated by replacing Cu[II] by a diamagnetic Zn[II], and then a routine SA-CASSCF calculation have been performed, which gave the D value as −2.73 cm⁻¹ with the E being 0.13 cm⁻¹: both values are in the range expected for a monomeric Mn[III] complex.[11a–c, 22] Generally, the single-ion anisotropies are large and make dominant contribution to the cluster anisotropy. The low-lying excited states, which contribute to ZFS, were found to be higher in energy for the {MnCu} system compared with the {MnZn} model complex. In the {MnZn} model complex, the SOMO→SOMO excitations contribute −1.92 cm⁻¹, whereas SOMO→VMO excitations contribute −0.82 cm⁻¹ to the net D value (see the Supporting Information for details). In the case of the {MnCu} system, the SOMO→SOMO excitations contribute −1.14 cm⁻¹, whereas the SOMO→VMO excitations contribute −0.56 cm⁻¹ (see the Supporting Information for detailed excitation energies and discussion) to the net D value. Incidentally, the D_{ZZ} orientation of the single-ion anisotropy is collinear with the global anisotropy axis of complex **1**, and this allow to compute the exchange anisotropy D_{MnCu} as −0.27 cm⁻¹ for **1** (see Eq. (1) and Figure 1a).

The exchange anisotropy has essentially two contributions, one is through space, and the other is through bond.[10] To further estimate this parameter, calculations have been performed on a fictitious {MnCu} dinuclear complexes, in which

the methoxide bridges were replaced by point charges, and this gave the through-space exchange anisotropy $D_{MnCu(through\ space)}$ as -0.89 cm^{-1} (see the Supporting Information, Table S7). Because for a ferromagnetically coupled dimer, the pure dipolar contribution should be positive (see the Supporting Information for details), the calculations revealed that the computed value is not pure dipolar in origin. From this value, the through bond-exchange anisotropy was estimated to be $+0.62$ cm^{-1}. Interestingly, the signs of the estimated parameters are opposite to each other leading to a decrease in the overall D_{MnCu} value. Our calculations unequivocally demonstrate that the exchange anisotropy is not negligible even for such small nuclearity clusters.

This view has also been reflected by others earlier.[10] In complex **1**, the single-ion and the exchange anisotropies are not competing,[9c] and this leads to a relatively large value for the global anisotropy $D_{5/2}$ for **1**. However, there are cases, in which these two components of anisotropy could antagonize each other leading to a decrease in the total ground-state anisotropy $D_{5/2}$ (see below). Our protocol thus helps to estimate the exchange anisotropy D_{MnCu}, which is otherwise an intricate parameter to extract from the experimental measurements. There are some cases, in which extensive optical and EPR techniques been used to extract this parameter in a cluster environment.[9b,c, 10, 23]

Although both the single-ion, as well the exchange, anisotropies are not competing in case of the original {MnCu} complex, a strong ferromagnetic interaction leads to large energy gap between the ground and excited states, and this led to a decrease in the strength of excitations (see the Supporting Information for details). Furthermore, we have decided to develop magnetostructural correlations for complex **1** to understand the effect of subtle structural parameters on the computed $D_{5/2}$, D_{Mn}^{III}, D_{MnCu}, and the corresponding E values (for E parameter, see the Supporting Information, Table S5 and Figure S13). Because the anisotropy in this complex is strongly correlated to the Mn^{III} ligand environment and related Jahn–Teller elongation, we have developed correlations by varying the axial ligands (compression, as well as elongation) and computed the relevant parameters. It is known that the axial compression leads to positive ZFS, whereas the elongation leads to a negative ZFS.[24,25] In complex **1**, the average Mn–L$_{ax}$ (axial M–L bonds) bond lengths are 2.60 Å, whereas the average Mn–L$_{eq}$ (equatorial M–L bonds) bond lengths are 1.92 Å. We have varied the Mn–L$_{ax}$ bond lengths from 1.80 to 3.0 Å, and the same has been performed also on the {MnZn} model complex. The developed correlation is shown in Figure 2. Upon further elongation from 2.6 to 3.0 Å, all three parameters $D_{5/2}$, D_{Mn}^{III}, and D_{MnCu} only marginally change, which is reflected in the computed d-orbital ordering that are largely unaffected. On the other hand, compression has a larger influence on the computed ZFS. Upon decreasing the Mn–L$_{ax}$ bond lengths to 2.1 Å, the magnitude $D_{5/2}$ increases and reaches a value of -2.35 cm^{-1}. Decreasing the Mn–L$_{ax}$ bond lengths further switch the isomerism to Jahn–Teller compressed Mn^{III} isomer, leading to a ground-state configuration of $(d_{xy})^1(d_{xz})^1(d_{yz})^1$-$(d_{x^2-y^2})^1$. This change leads to positive ZFS for the {MnCu} com-
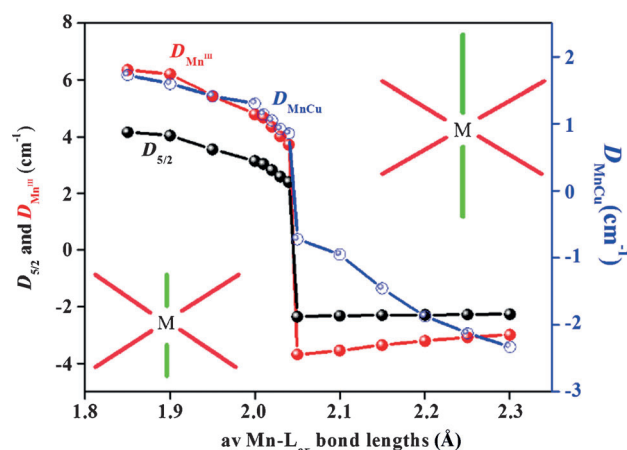

Figure 2. CASSCF-computed D values for complex **1** by varying M–L$_{ax}$ bond lengths (Jahn–Teller distortion).

plex. This is also in accord to the experimental data collected for Jahn–Teller compressed Mn^{III} complexes.[26] Besides, as the magnetic orbitals are now non-orthogonal, this gives an antiferromagnetic interaction and an $S = 3/2$ ground state.

Since antiferromagnetically coupled {Mn^{III}Cu^{II}} dinuclear complex ([Cu^{II}Mn^{III}(L)$_2$(py)$_4$](ClO$_4$)·EtOH) with an $S = 3/2$ ground state has been studied by us recently,[26] we have focused herein on the $S = 5/2$ state resulting for structures with acute M-O-M angles (see the Supporting Information, Table S8 and Figure S12). For the $S = 5/2$ case, the compression increases the magnitude of $D_{5/2}$ reaching a value of $+4.15$ cm^{-1} at the extreme limit tested. Here as well, the D_{MnCu} estimates were found to follow the sign of $D_{5/2}$ values.

Another correlation, in which the octahedral environment around the Mn^{III} ion is allowed to transform into a trigonal prism through Bailar Twist, has also been developed (Figure 3).[27] The computed $D_{5/2}$ value for this complex was found to be -2.00 cm^{-1}, whereas the D_{Mn}^{III} was estimated to be -2.76 cm^{-1} with the D_{MnCu} being -1.9 cm^{-1} (see the Supporting Information for details). The developed correlation for the twist angle of 0 to 60° degrees is shown in Figure 3. The D_{Mn}^{III} increases with the distortion and this is similar to the conclusion reported earlier.[22b] Interestingly, the $D_{5/2}$ decreases with the distortion, and the primary reason for this is that the D_{MnCu} is competing with the single-ion D_{Mn}^{III} as the distortion progresses. The D_{MnCu} values decrease when the angle increases till 45 degrees, after which the D_{MnCu} switches the sign to positive and competes with the D_{Mn}^{III}, and this tremendously diminishes the net $D_{5/2}$ value. Thus, our calculations conclude that, unlike earlier studies on monomeric Mn complexes,[22b] the Bailar twist does not help to bring forth large ground-state anisotropy. This demonstrates the importance of D_{MnCu} in determining the magnitude of ground-state anisotropy in a cluster framework.

A closer look at the contributing factors suggest that spin-flip $\alpha \rightarrow \beta$ transitions decides the sign of D herein. When we move towards trigonal-prism structure, the d-orbital splitting narrows, and this apparently led to an increase in the magnitude of the D_{Mn}^{III}. However, the net $D_{5/2}$ decreases, and this is
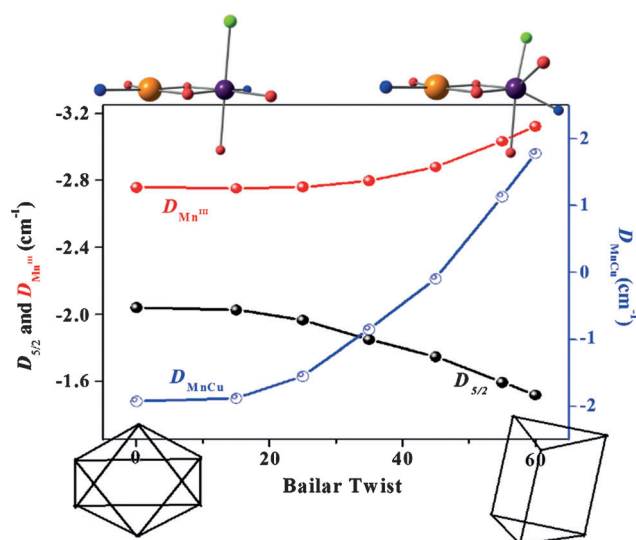
Figure 3. CASSCF computed D values for complex **1 a** as a function of Bailar twist.

due to the antagonizing behavior of the D_{MnCu}, which switches its sign and tend to increase when we move towards trigonal-prismatic structure. The reason for this antagonizing behavior is rooted back to the stronger magnetic coupling and larger gap between the spin-coupled states (see the Supporting Information, Figure S14). This grimly suggests that stronger ferromagnetic exchange led to a smaller magnetic anisotropy, that is, these two most desired parameters for an ideal SMM are unlikely to co-exist in a cluster frame work.

For the first time, we have successfully estimated all the contributions of magnetic anisotropy in dinuclear {MnCu} SMM by using ab initio CASSCF methods. Our results illustrate that the magnetic anisotropy is a delicate parameter in clusters, and the exchange anisotropy can become crucial at a juncture and might even control the sign and strength of global anisotropy and thus cannot be neglected. Efforts to study other experimentally characterized[28] systems by using this methodology are underway in our laboratory.

Acknowledgements

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