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Communication

A Criterion for the Anisotropy Barrier in Single-Molecule Magnets

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A criterion for the height of the anisotropy barrier $\Delta = |D|S^2$ in single-molecule magnets, and therefore the blocking temperature $T_B \propto \Delta$, is presented. In particular, it is found that the anisotropy barrier does not increase with S as S^2 but as S^0. Consequences concerning the strategies to enhance Δ or T_B, respectively, are discussed.

Single-molecule magnets (SMMs), such as the molecule $[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4]\cdot 2CH_3COOH\cdot 4H_2O$ (Mn_{12}-acetate), have attracted enormous attention recently.[1] At low temperatures, below a blocking temperature T_B, they exhibit slow relaxation of the magnetization, such that each molecule may function as a data-storage unit. However, as yet, T_B does not exceed a few Kelvin, which is too low for applications, and synthesis of new SMMs with larger T_B is an important goal in the area of molecular magnetism. It had been observed earlier that T_B is related to the presence of an anisotropy barrier Δ ($T_B \propto \Delta$), which, in turn, is governed by the molecular ground-state spin S and easy-axis anisotropy parameter D, $\Delta = |D|S^2$.[2] This gave rise to the "golden rule" for enhancing T_B: increase $|D|$ and increase S. Ideally both $|D|$ and S should simultaneously be controlled, which however is obviously extremely difficult. Current synthetic efforts may by and large be characterized so as to aim at controlling either $|D|$ or S (and to hope for the best for the other parameter). Increasing S appears as particularly promising, considering its expected quadratic influence on Δ or T_B, respectively. In this Communication, a criterion for the height of the anisotropy barrier Δ is developed, which implies that enhancing S is not as efficient as suggested by the golden rule.

The discussion is based on the well-known formula[3]

$$\mathbf{D} = \sum_{i=1}^{N} d_i \mathbf{D}_i \qquad (1)$$

where $\mathbf{D}$ is the zero-field-splitting (ZFS) tensor in the ground-state spin multiplet (with spin S), i numbers the N metal centers in the cluster, the d_i values are projection coefficients, and $\mathbf{D}_i$ is the local ZFS tensor on site i. Some comments are appropriate:

(i) Equation 1 is derived in the strong-exchange limit for a spin cluster described by the microscopic spin Hamiltonian

$$\hat{H} = -\sum_{i<j} J_{ij}\hat{\mathbf{S}}_i\cdot\hat{\mathbf{S}}_j + \sum_{i=1}^{N}\hat{\mathbf{S}}_i\cdot\mathbf{D}_i\cdot\hat{\mathbf{S}}_i + \hat{H}' \qquad (2)$$

which consists of the Heisenberg exchange interactions as the dominant term, the local ZFS, and further terms such as dipole−dipole interactions (which are collected in $\hat{H}'$).[3] For the applicability of eq 1, the total spin S should be a good quantum number. However, even if mixing between spin multiplets (S mixing)[4,5] is important, eq 1 is still a good starting point because S mixing does not affect the magnitude of $\mathbf{D}$ much (but crucially affects the value of higher-order parameters, such as B_4^0, B_4^4, etc.).[5] Hence, for the present purpose, it is sufficient that S is "almost" a good quantum number. This is true for almost all SMMs. However, it is clearly stated that the results below do not apply if the anisotropy is so strong that a perturbative treatment breaks down, e.g., for high-spin cobalt(II) or lanthanide ions (writing $\Delta = |D|S^2$ in these cases is then ill-defined anyhow, and the golden rule has to be replaced by something else).

(ii) In general, also dipole−dipole interactions contribute to $\mathbf{D}$.[2] They have been disregarded in eq 1 because the local ZFS is usually the dominant contribution to the magnetic anisotropy, especially in SMMs. Also, their effect is similar to that of the local ZFS and may be considered to be included

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(2) For half-integer spin S, the energy barrier is $|D|(S^2 - 1/4)$, with a negligible correction as compared to $|D|S^2$, which is hence ignored here.
(3) Bencini, A.; Gatteschi, D. *Electron Paramagnetic Resonance of Exchange Coupled Cluters*; Springer: Berlin, 1990. Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: Oxford, U.K., 2006.
(4) Liviotti, E.; Carretta, S.; Amoretti, G. *J. Chem. Phys.* **2002**, *117*, 3361.
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effectively in the tensors D_i. Moreover, and most importantly, ignoring dipole−dipole interactions does not alter the conclusions of this work (see also the Supporting Information).

(iii) Equation 1 is a tensorial relationship; i.e., both the magnitude and orientation of the local ZFS tensors D_i are relevant in determining D. However, this work is interested in exploring the role of S. It is the exchange couplings in the cluster that determine the nature of the ground-state spin multiplet, and therefore the value of S. However, with the ground state, also the values of d_i in eq 1 are determined. Hence, S and the d_i values are linked through the Heisenberg interactions, and exploring the role of S also requires consideration of the behavior of the d_i values. The tensor property of D_i (and D) does not enter into this game (controlling D_i is, so to say, the part of the strategy to "increase $|D|$", which is not considered here). Hence, symbols $|D|$ and $|D_i|$ are introduced, without a further precise definition (their meaning will always be obvious in the actual cases). Accordingly, eq 1 is exploited as $|D| = \sum_i d_i |D_i|$.

The discussion is started by first considering a spin cluster with the ferromagnetic spin multiplet as the ground state, i.e., for which S assumes the maximal value $S_{max} = \sum_i S_i$. The state of this spin multiplet with magnetic quantum number $M = S$ is the product state $|F\rangle = |M_i = S_i, \forall i\rangle$ with all spins "up". The projection coefficients d_i can be calculated through the relations

$$\langle \psi | 3\hat{S}_{i,z}^2 - S_i(S_i + 1) | \psi \rangle = d_i \langle SS | 3\hat{S}_z^2 - S(S + 1) | SS \rangle \quad (3)$$

with $|\psi\rangle = |F\rangle$; the other symbols have the expected meaning (for further details on eq 3, see the Supporting Information). One obtains[3]

$$d_i = \frac{S_i(2S_i - 1)}{S(2S - 1)} \quad (4)$$

Equation 4 already indicates what will become the main conclusion of this work: The projection coefficients, and therefore $|D|$, scale with S as S^{-2}, which compensates for the S^2 factor in $\Delta = |D|S^2$, such that the anisotropy barrier Δ is, in fact, by and large *independent* of S. This is a very robust conclusion; it is traced back to the fact that the matrix elements on the left- and right-hand sides of eq 3 are on the order of S_i^2 and S^2, respectively.

Next, the general case of a cluster with a ground-state multiplet with $S \leq S_{max}$ is considered. The $M = S$ state of this multiplet shall be written as $|\Psi\rangle = \sum_\gamma c_\gamma |\gamma\rangle$, with the product states $|\gamma\rangle = |M_1 M_2 ... M_N\rangle$. The d_i values may be calculated again with eq 3, which requires evaluation of $\langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle$. Because the action of $\hat{S}_{i,z}^2$ is equal for all states $|\gamma\rangle$ with equal values of M_i (these states are denoted as $|\beta M_i\rangle$ and indexed by β), it is useful to split the sum over γ into a sum over M_i and β, i.e., to write $|\Psi\rangle = \sum_{M_i}\sum_\beta c_{\beta M_i}|\beta M_i\rangle$. This yields

$$\langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle = \sum_{M_i} c_{M_i}^2 M_i^2 \quad (5)$$

with $c_{M_i}^2 = \sum_\beta c_{\beta M_i}^2$. The largest possible value of $\langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle$

Table 1. Minimum and Maximum Values of $d_i S(2S - 1)$ for Various S

	$d_i S(2S - 1)$			$d_i S(2S - 1)$	
S_i	minimum	maximum	S_i	minimum	maximum
1	−2	1	5/2	−8	10
3/2	−3	3	7/2	−15	21
2	−6	6	8	−72	120

is then found by maximizing eq 5 under the constraints $\sum_{M_i} c_{M_i}^2 = 1$ and $0 \leq c_{M_i}^2 \leq 1$. It is easy to confirm that $\langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle \leq S_i^2$, i.e., that the maximum value coincides with that of the ferromagnetic state. Similarly, the smallest value is found as $1/4 \leq \langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle$ for half-integer S_i and $0 \leq \langle\Psi|\hat{S}_{i,z}^2|\Psi\rangle$ for integer S_i. These findings establish lower and upper bounds for $\langle\Psi|3\hat{S}_{i,z}^2 - S_i(S_i + 1)|\Psi\rangle = d_i S(2S - 1)$, which are listed in Table 1. Inspection of this table further reveals that one may sum up the findings as

$$|d_i| \leq 2\frac{S_i(2S_i - 1)}{S(2S - 1)}, \quad \forall S_i = 1 \quad (6a)$$

$$|d_i| \leq \frac{S_i(2S_i - 1)}{S(2S - 1)}, \quad \forall S_i > 1 \quad (6b)$$

It is convenient to define a "local anisotropy barrier" of the ith metal center via $\Delta_i = |D_i|S_i^2$ (in the following, $S_i > 1$ will be assumed, the extension of the considerations to $S_i = 1$ is straightforward; see also the Supporting Information). For a cluster with a ferromagnetic spin ground state, the energy barrier is given by $\Delta = \Delta_{max}$, with

$$\Delta_{max} = \sum_{i=1}^N \frac{2 - 1/S_i}{2 - 1/S}\Delta_i \quad (7)$$

According to eq 6, this finding is generalized to $\Delta \leq \Delta_{max}$ for a cluster with $S \leq S_{max}$. The fraction in the sum on the right-hand side of eq 7 is smaller or equal to 1 for $S \geq S_i$ (this restriction is acceptable, being interested in not too small S), which allows one to write $\Delta_{max} \leq \sum_i \Delta_i$. Putting this all together, one finally obtains the criterion

$$\Delta \leq \Delta_{max} \leq \sum_{i=1}^N \Delta_i \quad (8)$$

Because $\Delta = \Delta_{max}$ is obviously reached for $S = S_{max}$, eq 8 seems to clearly support the design rule to "increase S as much as possible". However, although the largest anisotropy barrier is attained for the ferromagnetic spin multiplet, the effect of increasing S is not as large as naively expected because of the S^{-2} scaling of the projection coefficients, as mentioned before. In fact, S does not enter eq 8 (for not too small S, it holds $2 - 1/S \approx 2$).

Indeed, Δ may get close to Δ_{max} already for moderate values of S. An instructive example is the molecule Mn_{12}-acetate, for which $S = 10$ and $S_{max} = 22$. With exchange couplings as in ref 6, exact numerical diagonalization yields the projection coefficients $d_{Mn^{III}} = 0.0252$, and the experi-

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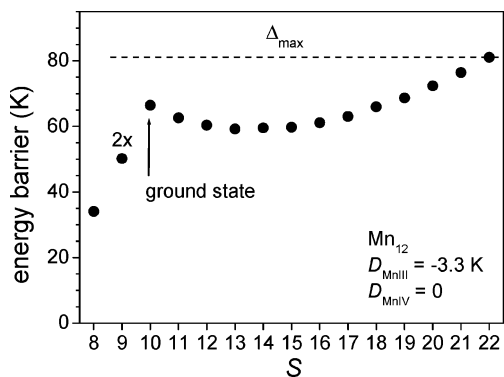
Figure 1. Height of the anisotropy barrier of the lowest spin multiplets for each value of $S \geq 8$ in Mn$_{12}$-acetate (with parameters as discussed in the text). For $S = 9$, the spectrum actually consists of two degenerate lowest-lying multiplets with identical barrier heights.[6]

mentally observed anisotropy barrier is reproduced by $|D_{Mn^{III}}|$ = 3.3 K or $\Delta_{Mn^{III}} = 13.2$ K, respectively (the contribution to the anisotropy from the Mn^{IV} ions is assumed to be zero, i.e., $|D_{Mn^{IV}}| = 0$).[5] Equation 1 then predicts $|D| = 0.665$ K or $\Delta = 66.5$ K, respectively. By increasing S to 22, it is tempting to expect an increase of Δ by a factor of $(22/10)^2$, promising barrier heights of about 250 K. However, for Mn$_{12}$-acetate, $\Delta_{max} = 81$ K. That is, despite a value of S of "only" 10, Mn$_{12}$-acetate already reaches 82% of the optimum (of what is attainable by tuning S without modifying the local ZFS). The situation is visualized in Figure 1, which presents the barrier height for the lowest spin multiplet for each value of $S \geq 8$ (for $S \neq 10$, they are excited states). The trend is complicated but shows that a simple S^2 dependence is not realized, not even approximately. For $S < 10$, it seems as if the barrier height quickly decreases with decreasing S, in a roughly linear fashion, but this conclusion is premature because from eq 6 the anisotropy barrier is expected to become larger again with further decreasing S (for very small values of S, the minimum values in Table 1 are approached).[7]

The example of Mn$_{12}$-acetate also provides a feeling for the accuracy of eq 1, or the strong-exchange limit, respectively, for our purposes: With the same parameters as before, a full numerical diagonalization, which treats S mixing exactly, yielded $|D| = 0.653$ K,[5] which is only 2% smaller than the value reported for the strong-exchange limit in the previous paragraph.

Because $\Delta \rightarrow \Delta_{max}$ for $S \rightarrow S_{max}$, increasing S will generally result in an enhancement of Δ, and doing so remains a good idea, but the possible improvement of Δ is only on the order of S^0, i.e., unity, and not on the order of S^2. On the other hand, eqs 3 and 6 show that the projection coefficients, in general, vary with S_i as S_i^2 (this is implicitly reflected in eq 8 through $\Delta_i = |D_i|S_i^2$). Thus, the criterion suggests the design rule to "increase S_i" (which is, however, intuitively obvious and already almost exhausted by Mn^{III}).

Increasing the number N of metal centers in the cluster appears as a simple approach for enhancing $|D|$ and S simultaneously. Because one might expect both $|D|$ and S to increase linearly with N, the golden rule seems to suggest the very promising scaling $\Delta \propto N^3$. However, having seen that Δ is basically independent of S, one has to conclude the much less favorable scaling $\Delta \propto N$, which is also obvious from eq 8, if one reads it as $\Delta \leq \sum_i \Delta_i$. Another tempting strategy, suggested by the golden rule, is to build a SMM from two "building blocks", where one building block is responsible for providing a large $|D|$ and the other one for providing a large S. However, $\Delta \leq \sum_i \Delta_i$ clearly shows that it is best to have every metal ion in the cluster to contribute as much as possible to the energy barrier.

In conclusion, a rather general criterion for the energy barrier in SMMs has been found. It shows that the widely considered design rule to "increase S" is not as efficient as suggested by $\Delta = |D|S^2$, i.e., that the increase in Δ is on the order of unity and not S^2. This design rule may be replaced by "increase S_i". The criterion further shows that Δ scales only linearly with the number N of metal ions. For obtaining better SMMs, it hence seems most promising to work on the local ZFS tensors $\mathbf{D}_i$ (i.e., to "increase $|D|$") or to work in a limit where the Heisenberg term is not dominant (i.e., to "break the strong-exchange limit"). It is mentioned that our conclusion seems to be supported by the experiment in the sense that the strategy to "increase S", despite impressive achievements in terms of the value of S,[8] has not yet produced better SMMs, while the strategy to "increase $|D|$" has had some significant successes in this regard.[9] The results presented here, of course, do not provide new design rules for the synthesis of SMMs but clarify the status of some of them, which should help in directing future synthetic efforts.

Supporting Information Available: More details of the derivations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Unfortunately, because of the huge dimension of the problem for Mn$_{12}$-acetate, our numerical calculations were limited to $S \geq 8$.

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