Can large magnetic anisotropy and high spin really coexist?†

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This theoretical study discusses the interplay of the magnetic anisotropy and magnetic exchange interaction of two Mn_6 complexes and suggests that large magnetic anisotropy is not favoured by a high spin state of the ground state.

Single molecule magnets (SMMs) are molecules that show a preferential direction of magnetization imposed by their magnetic anisotropy, associated with a negative zero field splitting (ZFS) parameter D. The SMMs were discovered more than a decade ago[1] and their study has been stimulated since by their potential application in information storage at the molecular level.[2] However, to make technological applications feasible, the energy barrier for the reversal of the molecular magnetic moment should be large enough to prevent thermal jump processes or tunnelling effects. This energy barrier amounts to $|D|\cdot S^2$, where S is the total spin of the molecule. For the first SMM, the Mn_{12} acetate molecule, a D value of -0.46 cm^{-1} and an $S = 10$ ground state give an energy barrier of about 46 cm^{-1}.[3] Up to now, most efforts have been devoted to the synthesis of compounds with large spin through exchange interactions, which are more predictable than the magnetic anisotropy parameter D.[4] It is worth noting that in this kind of polynuclear complexes, the ZFS parameters are rather small in comparison with those in mononuclear complexes. For instance, the D value for $[Mn(acac)_3]$ is -4.52 cm^{-1},[5] an order of magnitude larger than that of Mn_{12}.

Recently, Brechin and coworkers have synthesized a family of polynuclear Mn_6 complexes that show appealing magnetic properties.[6] We wish to stress here that two such molecules have analogous composition and structures, yet one of them has a high total spin, while the other one presents a lower spin but a higher anisotropy parameter. Thus, $[Mn_6O_2(sao)_6(O_2CH)_2(MeOH)_4]$ ($saoH_2$ = salicylaldoxime) (**1**, Fig. 1) has $S = 4$ as a result of ferromagnetic interaction between two antiferromagnetically coupled triangles of Mn^{III} cations, but its D value is one of the largest known so far for a polynuclear complex (-1.39 cm^{-1}).[6c] The second compound, $[Mn_6O_2(Etsao)_6(O_2CPh(Me)_2)_2(EtOH)_6]$ (**2**, Fig. 2), has all its Mn^{III} cations ferromagnetically coupled in an $S = 12$ ground state and has a D value of -0.43 cm^{-1}, resulting in the highest anisotropy barrier (62 cm^{-1}) known for an SMM.[6a] From these data, a question that immediately arises is how to select or modify the ligands to obtain a new complex that combines the high magnetic anisotropy of **1** and the high spin of **2**.

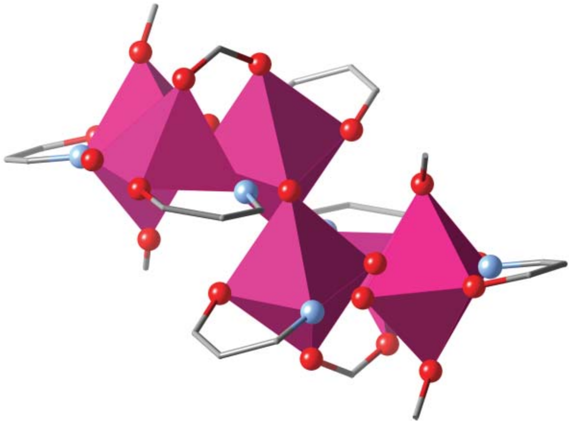

Fig. 1 Polyhedral representation of the structure of $[Mn_6O_2(sao)_6(O_2CH)_2(MeOH)_4]$ (**1**). Mn, O and N atoms represented by pink polyhedra and red and blue spheres, respectively.

A detailed analysis of the molecular structures (Figs. 1 and 2) shows that two coordination octahedra of each Mn_3 triangle are bridged by a formato ligand in **1**, while the corresponding carboxylato ligands in **2** are monodentate. As a result of the small bite of the bridge, one of the octahedra is tilted, thereby resulting in one long Mn··O distance to the neighbouring triangle that makes

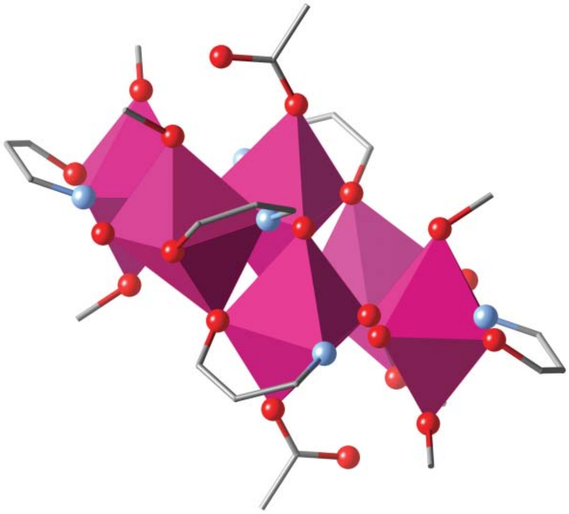

Fig. 2 Polyhedral representation of the structure of $[Mn_6O_2(Etsao)_6(O_2CPh(Me)_2)_2(EtOH)_6]$ (**2**). Colour code as in Fig. 1. The carboxylate structure has been simplified for clarity.

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† Electronic supplementary information (ESI) available: Table S1 showing the S and D values of ferromagnetically coupled SMMs. See DOI: 10.1039/b714715e

one Mn^{III} ion at each triangle effectively five-coordinated with a square pyramidal stereochemistry (Fig. 1). Despite these differences, the Jahn–Teller axes present similar orientations in both complexes, approximately perpendicular to the Mn_3 triangles.

Theoretical methods based on density functional theory have been extensively employed for the study of the exchange interactions that control the total spin of the ground state in polynuclear complexes.[7] Those calculations should be helpful for predicting ferromagnetic coupling and large S values needed for high energy barriers, such as those present in complex **2**. The zero field splitting parameters, on the other hand, can be estimated for polynuclear complexes following the perturbative approach of Pederson[8] that includes spin–orbit effects in density functional calculations. A detailed description of such an approach can be found in the literature.[8a,c] In brief, the D value is obtained from the second order perturbative energy term:

$$E^{(2)} = \sum_{\sigma\sigma'} \sum_{ij} M_{ij}^{\sigma\sigma'} S_i^{\sigma\sigma'} S_j^{\sigma'\sigma} \tag{1}$$

where the M_{ij} matrix elements (i, j = cartesian components x, y, z) are the orbital contributions given by eqn (2), S_i and S_j are spin integrals, φ_l and φ_k are the occupied and empty Kohn–Sham orbitals (labelled σ for the occupied and σ' for the empty functions), respectively, V_i is a spin–orbit related operator and $\varepsilon_{l\sigma}$ and $\varepsilon_{k\sigma'}$ are the orbital energies.

$$M_{ij}^{\sigma\sigma'} = -\sum_{l,k} \frac{\langle \varphi_{l\sigma} | V_i | \varphi_{k\sigma'} \rangle \langle \varphi_{k\sigma'} | V_j | \varphi_{l\sigma} \rangle}{\varepsilon_{l\sigma} - \varepsilon_{k\sigma'}} \tag{2}$$

Thus, for a diagonal form of the D tensor it is possible to obtain the following expression,

$$\sum_{\sigma\sigma'} \sum_{ij} M_{ij}^{\sigma\sigma'} S_i^{\sigma\sigma'} S_j^{\sigma'\sigma} = D_{xx} S_x^2 + D_{yy} S_y^2 + D_{zz} S_z^2 \tag{3}$$

and from the components of the tensor we can obtain the usual D parameter commonly employed in the spin Hamiltonian.

$$D = D_{zz} - \frac{1}{2}\left(D_{xx} + D_{yy}\right) \tag{4}$$

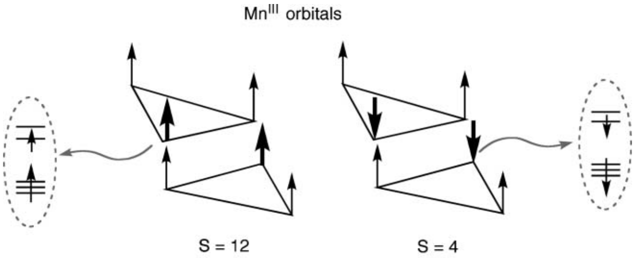
It is convenient to group the terms of eqn (3) according to the spin associated with the involved orbitals. We therefore have four sets of contributions to the D value, called *spin channels*. The D values and the spin channel contributions for complexes **1** and **2**, calculated with the PBE functional[9] and a large Gaussian basis set implemented by default in the NRLMOL code,[10] are presented in Table 1.

Table 1 Experimental and calculated D (cm^{-1}) for complexes **1** and **2** in their S = 4 and S = 12 states indicating the spin channel contributions. The results for two spin states of the Mn_{12} complex are provided for comparison

	S	D_{exp}	D_{calc}	α–α	α–β	β–α	β–β	$\lvert D_{calc}\rvert \cdot S^2$
1	4	−1.39	−2.15	−0.44	−1.05	−0.46	−0.21	34.6
1	12		−0.23	−0.07	−0.16	−0.001	−0.001	33.1
2	4		−2.28	−0.49	−0.96	−0.50	−0.34	36.5
2	12	−0.43	−0.23	−0.07	−0.16	−0.001	−0.001	33.1
Mn_{12}	10	−0.46	−0.40	−0.12	−0.27	−0.006	−0.001	40.0
Mn_{12}	22		−0.08	−0.02	−0.06	−0.0001	−0.0007	38.7

The calculated D values are in fair agreement with the experimental ones, especially taking into account that the exchange coupling in these molecules is not strong as assumed in the perturbative approach used[8] and that the experimental D values are averaged over the low-lying states. We have determined that the lowest energy S = 4 single determinant solution for **1** corresponds to the spin inversion of the two central pentacoordinated Mn^{III} cations (Fig. 1). For complex **2** an equivalent S = 4 system was considered, but in this case the lowest energy S = 4 solution is achieved with the spin inversion of external Mn^{III} cations. For the two Mn_6 complexes the calculated D values for the lower spin state are one order of magnitude larger than in the higher spin state, suggesting that the ZFS parameter depends mostly on the ground state rather than on structural details. Similar results were obtained for the Mn_{12} complex, whose S = 22 high spin state has a relatively small D value in comparison with that of the ferrimagnetic S = 10 ground state. The bad news is that high spin and high magnetic anisotropy seem to be incompatible, and similar energy barriers should be expected for the different spin states in such systems.

The most important contributions to the magnetic anisotropy come from M_{ij} terms involving excitations within d orbitals of the same metal. Thus, a spin flip of two Mn^{III} cations required to transform the S = 12 high spin state into the S = 4 state does not alter the local electronic structure of each cation. The only effect of such a spin flip will be the replacement of the α–α and α–β contributions of these two Mn^{III} cations in the S = 12 state by β–β and β–α terms in the S = 4 state. Thus, the energy barriers for the two states are very similar while the D values are significantly smaller for the state with the larger spin (Table 1).



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These concepts are reflected in the contributions of the different spin channels (Table 1). For the S = 4 state, there are significant contributions from all spin channels and the weights of the α–α and α–β terms are approximately twice as large as the β–β and β–α ones, respectively, consistent with the number of Mn^{III} cations with α and β electrons (**3**). In the high spin states, the β–α and β–β terms are negligible, as expected for the electron configuration with no β electrons in the metal d manifold, since contributions from low lying β electrons localized at the ligands are rather small due to a large denominator in eqn (2). Finally, in the lower spin state, the α–β terms that imply pairing two electrons in the same d orbital result in a larger contribution compared to that from the α–α channel.

The main difference found between Mn_{12} and Mn_6 is that in the former the β–α and β–β contributions are negligible also for the lower spin state. This result is due to the fact that these terms involve spin flip within the isotropic Mn^{IV} cations that do not contribute to magnetic anisotropy. The relatively small D values calculated for Mn_{12} are probably due to a misalignment of the Jahn–Teller axes of the Mn^{III} cations.

In summary, our results for two polynuclear Mn_6 complexes show a very strong dependence of the D value on the spin of the ground state while the energy barriers are practically constant. Thus, complex **2** with a large spin ($S = 12$) favoured by ferromagnetic interactions has a small D value, while the lower spin complex **1** ($S = 4$) has a large D value. An analysis of the D values for ferromagnetically coupled SMMs (see Table S1, ESI†) shows this to be a general trend.

This behaviour suggests that the magnitude of the anisotropy barrier is mainly determined by the strength of the spin–orbit coupling and cannot be engineered by independently optimizing D and S, since the intrinsic relationship between these two parameters prevents this possibility. In the case of large S, the spin flip contributions at the same atom, which give a large contribution to D, become small, because it costs much more energy to flip a spin in the field of the remaining spins compared to a lower spin state. For the same reason one finds very large D in monomers, because there the spin flip excitations cost much less energy.

From this point of view systems with larger energy barriers should be obtained in the case of perfect alignment of the Jahn–Teller axes corresponding to the largest possible number of paramagnetic centres, such as Mn^{III} cations or complexes with f-electrons, due to the stronger spin–orbit coupling. However, the challenge here will be the control of the ferromagnetic exchange.[11]

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