

# What is not required to make a single molecule magnet

Frank Neese<sup>\*ab</sup> and Dimitrios A. Pantazis<sup>ab</sup>

Received 27th April 2010, Accepted 11th May 2010

DOI: 10.1039/c005256f

The widely accepted assumption that the development of more efficient single molecule magnets must involve ever higher total spin values has so far driven synthetic efforts towards molecular clusters of increasing nuclearity. In the present paper it is suggested that it might be worthwhile to reconsider this approach. There is evidence from theory and experiment to suggest that the race for multinuclear complexes with higher total spin might not necessarily be fruitful as a strategy for maximizing the magnetic relaxation barrier. Instead, we propose that more effort should be directed in understanding the parameters involved in maximizing the anisotropy of small, perhaps even mononuclear, molecules. Using multi-reference *ab initio* calculations we demonstrate the theory that can be applied and the principles of the computational approach for representative mononuclear complexes. Such small units may subsequently be employed as building blocks for the controlled assembly of larger and maximally anisotropic single molecule magnets.

## Introduction

Clusters of magnetically interacting open-shell transition metal ions are a subject of persistent interest where different disciplines of chemistry, physics, and biology converge.<sup>1</sup> Manganese-containing systems demonstrate the interdisciplinary and multifaceted nature of the research into molecular magnetism better than any other example. In bioinorganic chemistry, one of the most intensely studied spin-coupled clusters is the oxygen evolving complex (OEC) of Photosystem II, a tetranuclear oxo-bridged calcium-containing manganese cluster ( $\text{Mn}_4\text{O}_x\text{Ca}$ ) of uncertain structure<sup>2–6</sup> that catalyzes the oxidation of water during the first stages of oxygenic photosynthesis.<sup>7,8</sup> In our own studies of several proposed structural models for the  $S_2$  state ( $\text{Mn}_3^{\text{IV}}\text{Mn}^{\text{III}}$ ) of the OEC, we have found that the total ground state spin can vary greatly between different structural models.<sup>9,10</sup> The type of spin coupling (ferromagnetic or antiferromagnetic) between the individual Mn centres depends critically and sensitively on the overall topology of the cluster as well as on the chemical identity and coordination mode of the metal-bridging groups.<sup>11–13</sup> Overall the magnetic coupling for some of the models can lead to an antiferromagnetic  $S = 1/2$  ground state that is in agreement with experimental data,<sup>14–17</sup> whereas for other models ground states of significantly higher total spin are obtained.<sup>10</sup> The first situation is clearly required when one seeks to mimic the  $\text{Mn}_4$  cluster of the OEC. Interestingly, exactly the opposite is true in the field of single molecule magnetism, where the usual goal is instead to maximize the total spin quantum number  $S$ . That

<sup>a</sup>Institute for Physical and Theoretical Chemistry, University of Bonn, Wegelerstrasse 12, D-53115 Bonn, Germany

<sup>b</sup>Max-Planck Institute for Bioinorganic Chemistry, Stiftstr.32–34, D-45470 Mülheim an der Ruhr, Germany. E-mail: neese@thch.uni-bonn.de; Fax: +49 (0)228-739064; Tel: +49 (0)228-732351

intriguing contradiction of purposes has led us to approach the issue from this alternative perspective and to enquire further into some of the assumptions that are central to current research into single molecule magnetism. In the present paper we would like to present our view on one of these assumptions.

Undoubtedly, the intensive quest for the development of zero-dimensional magnets, more commonly known as single molecule magnets (SMMs) is one of the most intellectually captivating and technologically promising topics in molecular magnetism during the last couple of decades.<sup>18–20</sup> SMMs are molecular species that display properties characteristic of bulk magnetic materials: they can be magnetized by an applied field and are able to retain their magnetization for an appreciable amount of time below a certain temperature after the field is removed. This magnetic hysteresis, often referred to as slow relaxation of magnetization, is the most fascinating aspect of SMMs, because it implies that at least in principle—and under the right conditions—these systems can be suitable for information storage of unprecedented high density.

The crucial point about the hysteretic phenomenon is that it does not result from the collective behaviour of a huge number of magnetic particles cooperatively interacting over large distances in a lattice, as in ‘classical’ bulk magnets. Rather, it stems directly from intrinsic properties of the electronic structure of the molecule itself. As such, quantum effects define the behaviour of these systems at a fundamental level.<sup>21</sup> The distinctive feature of a single-molecule magnet is the blocking temperature under which it displays the slow relaxation of magnetization. This, in turn, is related to the height of the spin-reversal energy barrier. Thus, the behaviour of SMMs is understood and discussed in terms of a few fundamental parameters related to the total spin and the magnetic anisotropy of the molecule.

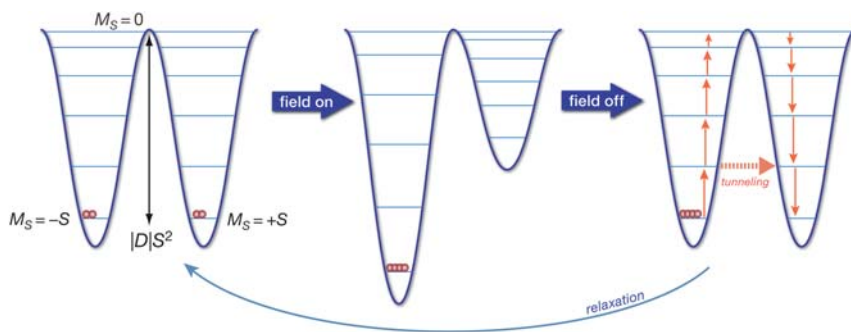
In the following we will provide a short overview of the theory and briefly discuss current approaches. The driving force for the synthesis of high-nuclearity clusters has been the desire to maximize the total spin quantum number  $S$ . This is pursued in the hope that higher  $S$  will lead to increased magnetic anisotropy barriers (*vide infra*), and therefore to better (very slowly relaxing) single-molecule magnets. Our view is that due to fundamental theoretical reasons this approach might not be as successful as expected. It might prove more successful to direct efforts into maximizing the axial anisotropy of smaller units. We demonstrate the potential of this approach with selected examples of mononuclear complexes, using a combination of straightforward ligand-field arguments and high-level *ab initio* calculations of zero-field splitting parameters.

## Fundamental considerations

The magnetic behaviour of SMMs is governed by the anisotropic zero-field splitting parameters  $D$  and  $E$ , according to the Hamiltonian

$$\hat{H} = DS_z^2 + E(S_x^2 - S_y^2) \quad (1)$$

where the axial  $D$  and rhombic  $E$  zero-field splitting parameters reflect the type of symmetry around the magnetic centre. For cubic symmetry both  $D$  and  $E$  are zero, while only  $E$  is zero in the case of axial symmetry. The sign of  $D$  is critical, since it determines the type of magnetic anisotropy associated with the  $S$  multiplet. A positive sign (easy-plane anisotropy) implies that the  $M_S = 0$  state ( $M_S = \pm 1/2$  for half-integer  $S$ ) will have the lowest energy, therefore the magnetic phenomena associated with SMMs cannot be observed. By contrast, a negative value for  $D$  (easy-axis anisotropy) means that the  $M_S = \pm S$  states with the largest component of the spin vector along the quantization axis will be most stable. The latter situation ( $D < 0$ ) is a fundamental requirement for SMMs, since it constitutes the necessary condition for magnetization by allowing differential population of the  $\pm M_S$  manifolds.



**Fig. 1** Schematic diagram demonstrating the magnetization and magnetic relaxation processes in a single molecule magnet.

The magnetization and relaxation processes are traditionally described by the ‘double-well’ diagram of Fig. 1, where the  $\pm M_S$  states are plotted on different wells. At zero-field all  $M_S \neq 0$  levels form degenerate pairs. However, when an external field is applied parallel to the magnetization axis the  $-M_S$  levels are stabilised and the  $+M_S$  levels are destabilised. If the magnetization of the system reaches its saturation value, then only the  $M_S = -S$  level remains populated. Upon removal of the field the system returns to thermal equilibrium through a series of steps depicted on the right diagram of Fig. 1. In a simple approximation, the larger the intrinsic spin-reversal barrier

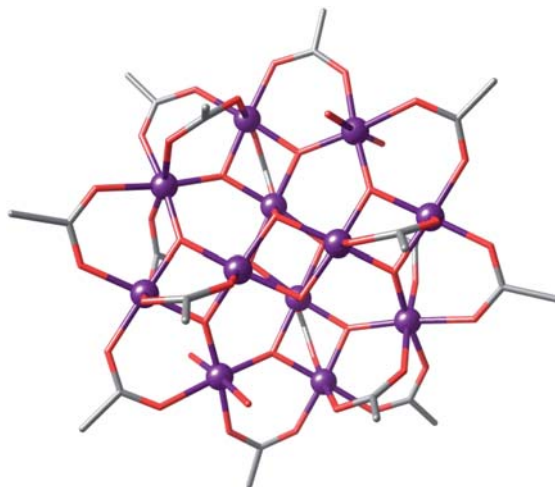
$$U = |D|S^2 \quad (2)$$

the longer the relaxation time will be. This barrier is therefore the most critical determinant for the observation of single-molecule magnetism.

## SMM design and theoretical principles

For various reasons related both to the origins of the field and to synthetic practices, the main focus of SMM research has been placed primarily on manipulating the total spin  $S$  of candidate single molecule magnets. The most fruitful approach in this direction has been to construct polynuclear transition metal entities with predominant ferromagnetic interactions between neighbouring magnetic centres, resulting in high values of the total spin quantum number. Manganese and iron feature prominently in the existing polynuclear SMMs, while numerous examples have been highlighted employing vanadium, nickel, cobalt, and more recently lanthanides.<sup>18,22,23</sup> Single-molecule magnetism was first identified and studied in the ferromagnetic dodecanuclear manganese acetate cluster  $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$  (Fig. 2), a molecule with an  $S = 10$  ground state that exhibits relaxation of magnetization of the order of months at a temperature of 2 K.<sup>24,25</sup> Derivatives of this cluster have been extensively studied and form a large family of SMMs with energy barriers to magnetization reversal up to  $46 \text{ cm}^{-1}$ , while an even higher barrier of  $62 \text{ cm}^{-1}$  was recently achieved in a hexanuclear Mn complex with  $S = 12$ .<sup>26</sup> Driven by the assumption that maximizing the total spin is the most straightforward way to increase the spin-reversal barrier, bigger clusters have and are currently being synthesised, the record presently being  $S = 83/2$  for a mixed-valence manganese aggregate comprising 19 Mn centres.<sup>27</sup>

There is, however, a persistent downside inherent in these and other examples of transition metal clusters that are being explored as candidate SMM platforms: the disconcertingly small value of the ZFS parameter  $D$ . Specifically, the  $\text{Mn}_{12}$  SMM



**Fig. 2** The archetypal single molecule magnet  $[\text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4]$ .

features a  $D$  of only  $-0.46 \text{ cm}^{-1}$ , while even the record-holder  $\text{Mn}_6$  system has a marginally smaller  $D$  of  $-0.43 \text{ cm}^{-1}$ . Hence, despite the relatively high  $S$ , the achievable height of the barrier to magnetization reversal is constrained to  $46 \text{ cm}^{-1}$  and  $62 \text{ cm}^{-1}$  respectively for the  $\text{Mn}_{12}$  and  $\text{Mn}_6$  systems. A comparison of the  $D$  values with those usually observed in mononuclear Mn complexes is revealing in this respect. For an axially elongated  $\text{Mn}(\text{III})$  centre  $D$  is typically around  $-4.5 \text{ cm}^{-1}$ , ten times greater than the  $D$  values associated with the clusters mentioned above. Thus, even with a single metal atom a barrier to reversal of magnetization of  $\sim 18 \text{ cm}^{-1}$  is already possible. When viewed from this perspective, the returns of the synthetic efforts that led the polynuclear SMMs mentioned above appear to fall short of the initial expectations. Unprecedented  $S$  values have not led to obviously better single-molecule magnets in terms of reversal barriers.

Our current understanding of single-molecule magnets points to two factors that lead to small magnetic anisotropy in such polynuclear SMMs. The first one is structural and refers to the topological arrangement of the magnetic centres, or more specifically to the mutual alignment of the local anisotropy axes. In particular, it can be shown that magnetic anisotropy is sensitive to the alignment of the individual Jahn–Teller axes<sup>28,29</sup> and is drastically reduced with increasing nuclearity if the local anisotropy axes become misaligned.<sup>30</sup> This mutual cancellation of local anisotropies is difficult to avoid in clusters containing more than a few metal ions because the potential for rational design and precise local control of the highly symmetric molecular architecture becomes increasingly limited.

The second and most important factor stems from the fundamental realisation that the expression used for the energy barrier (eqn (2)) is misleading in one subtle but crucial respect: it obscures the fundamental connection between  $D$  and  $S$ . The most important point we wish to make is that, despite the appearance of the equation, the height of the magnetic anisotropy barrier is essentially *not* a function of the total spin  $S$ . This is expected on the basis of the known general equations that describe the spin–orbit coupling (SOC) contribution to the  $\mathbf{D}$  tensor<sup>31</sup> (eqn (3)–(5)):

$$D_{kl}^{\text{SOC}(0)} = -\frac{1}{S^2} \sum_{b(S_b=S)} \Delta_b^{-1} \left\langle 0SS \left| \sum_i h_k^{\text{SO}}(i) s_{i,z} \right| bSS \right\rangle \times \left\langle bSS \left| \sum_i h_l^{\text{SO}}(i) s_{i,z} \right| 0SS \right\rangle \quad (3)$$

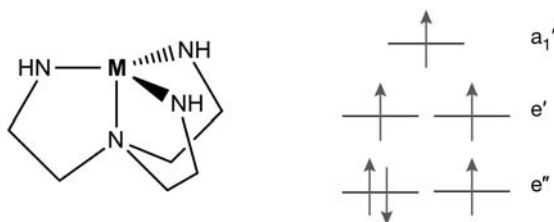
$$D_{kl}^{\text{SOC}(-1)} = -\frac{1}{S(2S-1)} \sum_{b(S_b=S-1)} \Delta_b^{-1} \left\langle 0SS \left| \sum_i h_k^{\text{SO}}(i)_{s_{i+1}} \right| bS-1S-1 \right\rangle \times \left\langle bS-1S-1 \left| \sum_i h_l^{\text{SO}}(i)_{s_{i-1}} \right| 0SS \right\rangle \quad (4)$$

$$D_{kl}^{\text{SOC}(-+1)} = -\frac{1}{(S+1)(2S+1)} \sum_{b(S_b=S+1)} \Delta_b^{-1} \left\langle 0SS \left| \sum_i h_k^{\text{SO}}(i)_{s_{i-1}} \right| bS+1S+1 \right\rangle \times \left\langle bS+1S+1 \left| \sum_i h_l^{\text{SO}}(i)_{s_{i+1}} \right| 0SS \right\rangle \quad (5)$$

where  $\Delta_b = E_b - E_0$  is the energy difference between multiplet  $b$  and the ground-state multiplet in the absence of SOC. It must be emphasized that these expressions are potentially exact: they do not depend on any approximate computational procedure, but derive directly from robust theoretical arguments founded on second-order perturbation theory and are formulated in terms of exact eigenstates of the Born–Oppenheimer Hamiltonian. The equations clearly reveal that  $D$  is inversely proportional to  $S^2$ . This dependence is exact for contributions arising from excited states with the same multiplicity (eqn (3)) and approximate for excited states of different multiplicity (eqn (4) and (5)). Therefore, from purely theoretical considerations it is to be anticipated that  $|D|S^2$  will, to a good approximation, be largely independent of  $S$ . This fact seems to have been generally underappreciated, with few exceptions in the theoretical literature.<sup>32,33</sup> In our view, it implies that attempts to obtain better SMMs by increasing  $S$  may not be the only possible route to follow. Instead, it is worth considering whether directing more research effort into attaining enhanced negative  $|D|$  values might be the best way to eventually achieve higher spin-reversal barriers. In the following we demonstrate how this issue can be explored using theoretical chemistry and also offer a few examples of how it might be possible to work towards this direction using mononuclear complexes.

## Computational approach and examples

The *ab initio* calculation of zero-field splitting<sup>34,35</sup> is particularly challenging in orbitally quasi-degenerate cases or when the spin–orbit coupling is very large. Perturbation theory breaks down in these situations and it is necessary to employ an infinite-order treatment with respect to SOC in the framework of quasi-degenerate perturbation theory (QDPT),<sup>36</sup> as will be outlined below. The models we have used were either partially based on existing experimental structures or designed from scratch and subsequently optimized using the hybrid B3LYP functional<sup>37,38</sup> in combination with the chain-of-spheres approximation to exact exchange (RIJCOSX).<sup>39</sup> The Karlsruhe basis sets of polarized triple- $\zeta$  quality (TZVP) along with the corresponding auxiliary basis sets were used for all atoms.<sup>40,41</sup> Initial wavefunctions were constructed with state-averaged complete active space self-consistent field (CASSCF) calculations employing an active space that comprised the five metal d-based orbitals. For the  $S = 2$  examples all five possible quintet states as well as the 35 triplet states were included in the calculation. The reference CASSCF wavefunctions are subsequently used directly or, in selected cases, corrected for dynamic correlation effects using the difference-dedicated configuration interaction



**Fig. 3** Schematic diagram of a trigonal pyramidal model (left) and the corresponding idealized d orbital configuration for a high-spin Fe(II) system (right).

(DDCI2) method.<sup>42</sup> The spin–orbit coupling contributions to the ZFS are then obtained directly by diagonalization of the SOC operator in the basis of the initial set of roots, employing the Wigner–Eckart theorem for reduction of the SOC matrix elements.<sup>35</sup> In terms of perturbation theory this is equivalent to an infinite-order treatment of spin–orbit coupling. All calculations were performed with ORCA.<sup>43</sup> For orbitally nearly degenerate transition metal systems SOC is the leading interaction and therefore we focus exclusively on this.<sup>35</sup> The direct dipolar spin–spin (SS) coupling becomes non-negligible only for zero-field splitting values much smaller than those considered here.<sup>44</sup>

Turning now to actual examples, it is fair to say that from the perspective of predictive theoretical chemistry a detailed understanding of all the factors that determine the sign and magnitude of  $D$  remains a great challenge. Thus, the rational design of molecules with tailored  $D$  values is a non-trivial task at present.<sup>45</sup> Nevertheless, in order to identify potential candidates for highly anisotropic systems it would be helpful to begin by considering certain coordination geometries and electronic configurations that should be close to orbital near-degeneracies. This would maximize spin–orbit coupling and lead to enhanced zero-field splitting.

An example of this situation is offered by high-spin  $d^6$  systems in trigonal bipyramidal or flat-based trigonal pyramidal environment, where the ligand-field splitting of the d orbitals results in two doubly degenerate sets  $e''$  ( $xz$ ,  $yz$ ) and  $e'$  ( $xy$ ,  $x^2 - y^2$ ), and the  $a_1'$  ( $z^2$ ) highest in energy (Fig. 3). To simulate this situation a model Fe(II) complex ( $S = 2$ ) was studied, using a simple tripodal  $N_4$  tetradentate ligand to define the coordination sphere.

Since the diagonalization of the SOC matrix introduces spin-Hamiltonian terms higher than biquadratic, the results of the QDPT treatment cannot be presented in the same way as those of a simple perturbation theory treatment in terms of a  $\mathbf{D}$  tensor.<sup>44,46</sup> Hence, to obtain values for  $D$  we will use the closed-form solutions of the spin-Hamiltonian problem for  $S = 2$ , for which the eigenfunctions and eigenvalues are<sup>47</sup>

$$|2^s\rangle = \alpha^+(|+2\rangle + |-2\rangle)/2^{1/2} + \alpha^-|0\rangle \quad E_{2s} = 2\sqrt{D^2 + 3E^2} \quad (6)$$

$$|2^a\rangle = (|+2\rangle - |-2\rangle)/2^{1/2} \quad E_{2a} = 2D \quad (7)$$

$$|1^s\rangle = (|+1\rangle + |-1\rangle)/2^{1/2} \quad E_{1s} = -D + 3E \quad (8)$$

$$|1^a\rangle = (|+1\rangle - |-1\rangle)/2^{1/2} \quad E_{1a} = -D - 3E \quad (9)$$

$$|0'\rangle = \alpha^- (|+2\rangle + |-2\rangle)/2^{1/2} - \alpha^+|0\rangle \quad E_{0'} = -2\sqrt{D^2 + 3E^2} \quad (10)$$

where

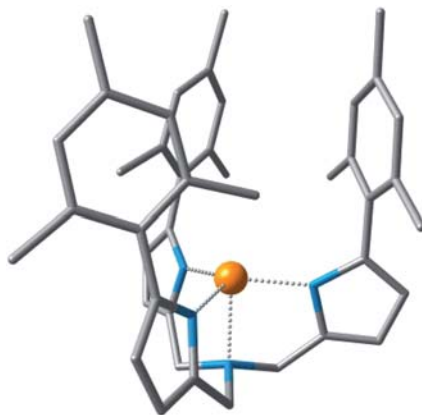
$$\alpha^{\pm} = \frac{1}{4} \sqrt{1 \pm D / \sqrt{D^2 + 3E^2}} \quad (11)$$

According to the results of our calculations the  $D$  value for this model system is predicted to be an impressive  $-26.7 \text{ cm}^{-1}$ . Upon inclusion of dynamic correlation with the DDCI2 approach  $D$  is reduced in magnitude to  $-21.8 \text{ cm}^{-1}$ . The necessity for the QDPT approach described above is starkly revealed when these values are compared with those predicted by perturbation theory, which overestimates the magnitude of  $D$  by a factor of 2–3 in the present case. Regardless of the absolute precision of the predicted figures, even the most conservative values imply an intrinsic spin-reversal barrier ( $|D|S^2$ ) close to  $100 \text{ cm}^{-1}$ .

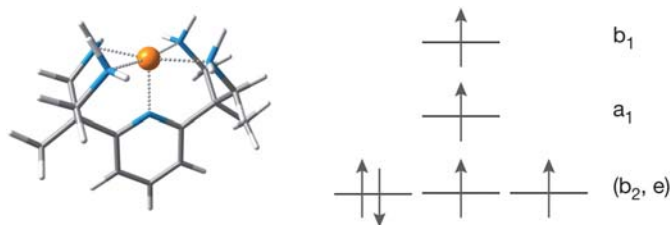
One can envisage that the properties of such a system can be fine-tuned through ligand design, which might determine for example the deviations from co-planarity of the metal and the equatorial donor atoms. Thus, owing to the large anisotropy that can be achieved in this complex, the intrinsic energy barrier to reversal of magnetization could be higher than the corresponding barrier of any polynuclear  $\text{Mn}_{12}$  or  $\text{Mn}_6$  SMM. The anisotropy is maintained to a significant extent when Fe(II) is substituted by Co(III), which retains the same electronic configuration. In this case the SOC contribution is smaller and the predicted  $D$  value is  $-16.3 \text{ cm}^{-1}$ .

It should be pointed out that the situation described above is not a merely theoretical possibility; in a very recent report by Freedman *et al.* the magnetic susceptibility data for the high-spin Fe(II) complex  $\text{K}[(\text{tpa}^{\text{Mes}})\text{Fe}]$  (Fig. 4)<sup>48</sup> were fitted with a  $D$  value of  $-39.6 \text{ cm}^{-1}$ . For the same system, *i.e.* employing the complete ligand at the reported experimental geometry, we calculate a  $D$  of  $-35.1 \text{ cm}^{-1}$ . This excellent agreement confirms that such values are indeed achievable in single-ion systems and predictable with reasonable accuracy by the computational approach used in the present work.

At this point it must be emphasised that the matching procedure between the spin-Hamiltonian and the eigenvalues of the QDPT matrix is valid as long as the zero-order energy difference between the two components of the  $E$ -derived state is recognisably larger than the spread in energy levels induced by spin-orbit coupling. In the present case the spin-orbit coupling yields two distinguishable sets of five magnetic sublevels that can be approximately described by a  $S = 2$  spin-Hamiltonian. However, the system is probably at the limit of applicability of this approach and a more favourable situation is described below.



**Fig. 4** The trigonal pyramidal iron(II) complex  $[(\text{tpa}^{\text{Mes}})\text{Fe}]^-$  (hydrogen atoms omitted for clarity).



**Fig. 5** The square-based pyramidal model using Grohmann's ligand (left) and the idealized d orbital configuration for a high-spin d<sup>6</sup> square-based pyramidal system (right).

Another interesting prospect is that of a square-based pyramidal geometry, as expected from the high-spin d<sup>6</sup> configuration shown in Fig. 5, where partial occupation of the *t*<sub>2g</sub>-derived orbitals should result in high orbital angular momentum. To construct a suitable model for this case, we have used Grohmann's tetrapodal pentadentate N<sub>5</sub>-donor ligand pictured in Fig. 5.<sup>49,50</sup> This ligand has proven valuable for reactivity studies of bond activation processes because it offers a chemically innocent and structurally well-defined environment.<sup>50</sup> For our purposes it is an ideal choice because it defines a rigid and chemically realistic square pyramidal coordination pocket. The model studied was again based on an Fe(II) ion, giving *S* = 2. Importantly, our calculations yielded a large negative value for *D* of −15.5 cm<sup>−1</sup>. Thus, the intrinsic magnetization reversal barrier of such a simple system would be over 60 cm<sup>−1</sup>. For comparison, when Mn(III) is used in a high-spin d<sup>4</sup> configuration for the same ligand, the *D* parameter is predicted to be −4.9 cm<sup>−1</sup>.

The above examples, which have been chosen because they demonstrate the point of this paper with simplicity, are but a very small sample of the possibilities. For instance, another type of mononuclear system that has been experimentally characterized and merits further analysis is the nickel complex [Ni(im)<sub>4</sub>(ac)<sub>2</sub>] (im = imidazole, ac = acetate), for which a simultaneous fitting of susceptibility and magnetization led to a *D* of −22.3 cm<sup>−1</sup>.<sup>51</sup> Many more candidates can be envisaged for a variety of transition metal ions, coordination geometries and oxidation states. Of course, further considerations have to enter the process of investigation, such as control of the rhombic parameter and the tunnelling effect. Lastly, it is worth pointing out that another exciting development in the field of SMMs involves the use of f-block elements. Prominent examples include lanthanide–phthalocyanine systems,<sup>52–54</sup> where terbium and dysprosium have already yielded promising molecules, but also species incorporating actinides. As an example of the latter case, there has been a recent report of slow magnetic relaxation in a trigonal prismatic Uranium(III) complex.<sup>55</sup> Dinuclear species are also potential candidates for highly anisotropic building units, either in the form of 3d–4f clusters or as class III mixed-valence dimers.

## Summary

We propose that a shift of emphasis might be beneficial for research into better single-molecule magnets. The 'hidden' dependence of the zero-field splitting parameter *D* to the spin quantum number implies that maximizing the total *S* through construction of polynuclear entities may not be needed to make better single-molecule magnets. In fact, it might even run counter to the desired outcome. A more promising avenue of research might be to enhance the anisotropy of 'designer' mononuclear species. Combining these building blocks into oligonuclear molecular entities may subsequently be done through a structurally well-controlled manner that does not work against the favourable anisotropy of the individual units.



Through a number of examples studied by multi-reference *ab initio* methods and quasi-degenerate perturbation theory we demonstrated that high axial anisotropy values can indeed be achieved in mononuclear transition metal species. What these examples have in common is an electron configuration that is close to orbital degeneracy. This situation maximises spin–orbit coupling and leads to large zero-field splitting. Determination of the zero-field splitting parameter  $D$  for these systems using MRCI and DDCI2 methods with an infinite-order treatment of spin–orbit coupling (QDPT) yielded negative values for  $|D|$  that are up to two orders of magnitude greater than those observed in polynuclear SMMs. This confirms that a single-ion molecule can in principle have a spin-reversal energy barrier as high as or even higher than that of any polynuclear SMM studied so far. Examples from the recent literature confirm that this approach holds great promise. It remains to be seen whether theoretical chemistry will be able to provide reliable and accurate correlations between structural features and ZFS parameters for a wide range of electronic structure situations, and whether synthetic chemistry will be able to turn these predictions and the properties they promise into real molecules.

## References

- 1 O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.
- 2 J. Barber and J. W. Murray, *Philos. Trans. R. Soc. London, Ser. B*, 2008, **363**, 1129–1137.
- 3 J. Kern, J. Biesiadka, B. Loll, W. Saenger and A. Zouni, *Photosynth. Res.*, 2007, **92**, 389–405.
- 4 J. Yano, J. Kern, K. Sauer, M. J. Latimer, Y. Pushkar, J. Biesiadka, B. Loll, W. Saenger, J. Messinger, A. Zouni and V. K. Yachandra, *Science*, 2006, **314**, 821–825.
- 5 E. M. Sproviero, J. A. Gascon, J. P. McEvoy, G. W. Brudvig and V. S. Batista, *J. Am. Chem. Soc.*, 2008, **130**, 6728–6730.
- 6 P. E. M. Siegbahn, *Chem.–Eur. J.*, 2008, **14**, 8290–8302.
- 7 J. Barber, *Biochem. Soc. Trans.*, 2006, **34**, 619–631.
- 8 W. Lubitz, E. J. Reijerse and J. Messinger, *Energy Environ. Sci.*, 2008, **1**, 15–31.
- 9 D. A. Pantazis, M. Orio, T. Petrenko, S. Zein, E. Bill, W. Lubitz, J. Messinger and F. Neese, *Chem.–Eur. J.*, 2009, **15**, 5108–5123.
- 10 D. A. Pantazis, M. Orio, T. Petrenko, S. Zein, W. Lubitz, J. Messinger and F. Neese, *Phys. Chem. Chem. Phys.*, 2009, **11**, 6788–6798.
- 11 C. Baffert, M. Orio, D. A. Pantazis, C. Duboc, A. G. Blackman, G. Blondin, F. Neese, A. Deronzier and M.-N. Collomb, *Inorg. Chem.*, 2009, **48**, 10281–10288.
- 12 M. Orio, D. A. Pantazis, T. Petrenko and F. Neese, *Inorg. Chem.*, 2009, **48**, 7251–7260.
- 13 D. A. Pantazis, V. Krewald, M. Orio and F. Neese, *Dalton Trans.*, 2010, **39**, 4959, DOI: 10.1039/c001286f.
- 14 G. A. Lorigan and R. D. Britt, *Biochemistry*, 1994, **33**, 12072–12076.
- 15 J. M. Peloquin, K. A. Campbell, D. W. Randall, M. A. Evanchik, V. L. Pecoraro, W. H. Armstrong and R. D. Britt, *J. Am. Chem. Soc.*, 2000, **122**, 10926–10942.
- 16 L. V. Kulik, B. Epel, W. Lubitz and J. Messinger, *J. Am. Chem. Soc.*, 2005, **127**, 2392–2393.
- 17 L. V. Kulik, B. Epel, W. Lubitz and J. Messinger, *J. Am. Chem. Soc.*, 2007, **129**, 13421–13435.
- 18 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, Oxford, 2006.
- 19 D. Gatteschi, R. Sessoli and A. Cornia, in *Comprehensive Coordination Chemistry II*, ed. J. A. McCleverty and T. J. Meyer, Pergamon, Oxford, 2003, pp. 779–813.
- 20 M. R. Pederson and T. Baruah, in *Handbook of Magnetism and Advanced Magnetic Materials*, ed. H. Kronmüller and S. Parkin, Wiley-Interscience, 2007, pp. 643–658.
- 21 D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268–297.
- 22 G. Aromi and E. K. Brechin, *Struct. Bonding*, 2006, **122**, 1–67.
- 23 M. Murrie, *Chem. Soc. Rev.*, 2010, **39**, 1986–1995.
- 24 A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel and M. Guillot, *J. Am. Chem. Soc.*, 1991, **113**, 5873–5874.
- 25 R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141–143.
- 26 C. J. Milios, A. Vinslava, W. Wernsdorfer, S. Moggach, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 2754–2755.
- 27 A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clerac, W. Wernsdorfer, C. E. Anson and A. K. Powell, *Angew. Chem., Int. Ed.*, 2006, **45**, 4926–4929.

- 28 Z. M. Sun, D. Ruiz, N. R. Dilley, M. Soler, J. Ribas, K. Folting, M. B. Maple, G. Christou and D. N. Hendrickson, *Chem. Commun.*, 1999, 1973–1974.
- 29 C. J. Milios, R. Inglis, A. Vinslava, R. Bagai, W. Wernsdorfer, S. Parsons, S. P. Perlepes, G. Christou and E. K. Brechin, *J. Am. Chem. Soc.*, 2007, **129**, 12505–12511.
- 30 J. Cirera, E. Ruiz, S. Alvarez, F. Neese and J. Kortus, *Chem.–Eur. J.*, 2009, **15**, 4078–4087.
- 31 F. Neese and E. I. Solomon, *Inorg. Chem.*, 1998, **37**, 6568–6582.
- 32 O. Waldmann, *Inorg. Chem.*, 2007, **46**, 10035–10037.
- 33 E. Ruiz, J. Cirera, J. Cano, S. Alvarez, C. Loose and J. Kortus, *Chem. Commun.*, 2008, 52–54.
- 34 F. Neese, in *Calculation of NMR and EPR parameters*, ed. M. Kaupp, M. Bühl and V. G. Malkin, Wiley-VCH, Heidelberg, 2004, pp. 541–564.
- 35 D. Ganyushin and F. Neese, *J. Chem. Phys.*, 2006, **125**, 024103–11.
- 36 D. Ganyushin and F. Neese, *J. Chem. Phys.*, 2008, **128**, 114117–13.
- 37 A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652.
- 38 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785–789.
- 39 F. Neese, F. Wennmohs, A. Hansen and U. Becker, *Chem. Phys.*, 2009, **356**, 98–109.
- 40 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
- 41 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.
- 42 J. Miralles, O. Castell, R. Caballol and J.-P. Malrieu, *Chem. Phys.*, 1993, **172**, 33–43.
- 43 F. Neese, *ORCA—an ab initio, Density Functional and Semiempirical Program Package (v. 2.7.0)*, Universität Bonn, 2009.
- 44 F. Neese, *J. Am. Chem. Soc.*, 2006, **128**, 10213–10222.
- 45 R. Boča, *Coord. Chem. Rev.*, 2004, **248**, 757–815.
- 46 D. G. Liakos, D. Ganyushin and F. Neese, *Inorg. Chem.*, 2009, **48**, 10572–10580.
- 47 M. P. Hendrich and P. G. Debrunner, *Biophys. J.*, 1989, **56**, 489–506.
- 48 D. E. Freedman, W. H. Harman, T. D. Harris, G. J. Long, C. J. Chang and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 1224–1225.
- 49 A. Grohmann, *Adv. Inorg. Chem.*, 2004, **56**, 179–210.
- 50 A. Grohmann, *Dalton Trans.*, 2010, **39**, 1432–1440.
- 51 R. Boča, L. Dlhán, W. Haase, R. Herchel, A. Mašlejová and B. Papánková, *Chem. Phys. Lett.*, 2003, **373**, 402–410.
- 52 N. Ishikawa, *Polyhedron*, 2007, **26**, 2147–2153.
- 53 S. Takamatsu and N. Ishikawa, *Polyhedron*, 2007, **26**, 1859–1862.
- 54 N. Ishikawa, Y. Mizuno, S. Takamatsu, T. Ishikawa and S. Y. Koshihara, *Inorg. Chem.*, 2008, **47**, 10217–10219.
- 55 J. D. Rinehart and J. R. Long, *J. Am. Chem. Soc.*, 2009, **131**, 12558–12559.