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Hints for the Control of Magnetic Anisotropy in Molecular Materials

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

We resume here a fundamental aspect concerning magnetic anisotropy and show with some examples how it is possible to rationalize it. The results are obtained within the framework of a simple angular overlap approach. The application of this model to idealized systems, real monomer molecules, and clusters behaving as single-molecule magnets is described, showing how even within a simple ligand field approach it is possible to get some clues on how to control the magnetic anisotropy. Finally, we focus our analysis on the calculation of fourth-order anisotropy, which has been shown to be of fundamental importance in determining the quantum tunneling effects in single-molecule magnets. © 2001 Academic Press

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Magnetic molecular materials are a clear indication of the role played by clever design for introducing expected properties in the compounds obtained through chemical techniques (1). The development of the field has indeed been made possible by the availability of simple models that could be used by synthetic chemists in deciding whether to use one metal ion or another, or a bridging ligand rather than another, in order to induce ferro- or antiferro-magnetic coupling in the material. In this sense the role of the Kahn model (2), which translated in the molecular orbital-oriented language of the 1980s the Goodenough–Kanamori rules (3–5), is of fundamental importance. More recently it has also become possible to quantitatively calculate the coupling constants using DFT approaches (6–8), with an accuracy that only a few years ago was unthinkable. Therefore it may be safely stated that the control of the sign of the magnetic interaction between the building blocks of molecular materials is a solved problem, at least at the isotropic level.

The control of the sign of the magnetic interaction is however not sufficient if the magnetic properties of the materials must be efficiently designed. In fact the other important aspect that must be taken into consideration is magnetic anisotropy. This is well known to affect important properties like the hysteresis cycle (9), thus determining whether a material must be considered as a soft or a hard magnet. In recent years an attempt has been made to introduce large anisotropy in molecular materials, and hard magnets have been obtained (10, 11). It may be easily predicted that in the next few years these aspects will be more and more taken into consideration. This is particularly true for the finite size magnetic molecules that show slow relaxation of the magnetization at low temperature (12–17). For these materials, which are currently indicated as single-molecule magnets, SMM (18), the introduction of a large magnetic anisotropy of the easy axis type is a prerequisite. Further it is also necessary to control the transverse anisotropy if quantum tunneling effects must be observed (19, 20). Therefore it is necessary to make available simple rules that help the synthetic chemist to develop suitable strategies for introducing the appropriate anisotropy in the molecules.

The theoretical background for rationalizing the magnetic anisotropy is well developed, even if in this field DFT calculations have not yet been pushed to the required level of sophistication. However ligand field models have long been used to describe the low-symmetry properties of paramagnetic species (21), and they can provide an excellent basis for the description of the magnetic anisotropy of molecular magnets. We wish to resume here a fundamental aspect concerning magnetic anisotropy and show with some examples how it is possible to rationalize it. We will focus on single-molecule magnets, because they have the advantage of the finite size, which makes the understanding of the details easier, but the same considerations apply also to the infinite arrays of molecular magnets.

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SINGLE-ION ANISOTROPY

The contribution of a single building block of the SMM to the global anisotropy of the cluster is the single-ion anisotropy. A system may show anisotropy both in the way it responds to an external field (Zeeman effect) and by making some directions preferable even in the absence of an external field (zero field splitting). Both these situations can occur if an orbital contribution is present in the ground state. It should however be considered that—with the exceptions of the ions that have an orbitally degenerate ground state of T type—orbital degeneracy will be removed by Jahn-Teller distortions (22).[2] One may then assume in first approximation that the ground state does not possess orbital contribution. At this level of approximation the system is isotropic, because it is only orbital components that can feel differences between different orientations. The anisotropy is introduced in the system by spin–orbit coupling that admixes excited states into the ground one. This phenomenon can be described by the Hamiltonian $\mathbf{H} = \lambda \mathbf{L} \cdot \mathbf{S}$, where λ is the spin–orbit coupling within a given Russell–Saunders multiplet (21). It is related to the spin–orbit coupling constant of the ion, ζ, by the relation $\lambda = \pm \zeta/2S$, where the plus sign applies to configuration d^n with $1 \leq n \leq 4$ and the minus sign to $6 \leq n \leq 9$. For high-spin d^5 ions no orbital degeneracy is introduced at this level of approximation.

The effect of the spin–orbit coupling is obviously depending on the magnitude of the coupling constant λ and on the energy difference between the ground state and the admixed one. As λ is small for constituent atoms of organic radicals, the magnetic anisotropy is small in these systems, while it is much larger for transition metal ions (especially for the second and third rows) and lanthanides, which are indeed well known to possess a large anisotropy.

The term zero field splitting identifies the splitting of states belonging to the same S multiplet and different M_S values, which leads to a preferential axis (or plane) for the orientation of the magnetization of the molecule. This kind of anisotropy can be described by a series expansion in terms of magnetic multipoles, most appropriately expressed through the following Hamiltonian (23, 24).

$$\mathbf{H} = \sum_{k,q} B_k^q \mathbf{O}_k^q, \qquad [1]$$

where the operators $\mathbf{O}_k^q$, the so-called Stevens operator equivalents, are defined in Table 1 and the B_k^q coefficients must be determined from experiment. The term corresponding to $k = 2$, which describes the effect of the quadrupolar interaction, can be written also as

$$\mathbf{H}_2 = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}, \qquad [2]$$

where $\mathbf{D}$ is a symmetric traceless tensor that can also be explicitly rewritten as

$$\mathbf{H}_2 = D[\mathbf{S}_z^2 - S(S+1)/3] + E(\mathbf{S}_x^2 - \mathbf{S}_y^2), \qquad [3]$$

where $D = \frac{1}{3} B_2^0$ and $E = B_2^2$.

For cubic symmetry $D = E = 0$. For axial symmetry $E = 0$ and if $D > 0$ the anisotropy is of the easy-plane type while if $D < 0$ it is of the easy-axis type. Indeed, the number of terms to be retained in [1] depends both on the spin value and on the symmetry of the center. Only terms with $k \leq 2S$ will be present; this leads to the conclusion that terms with $k = 4$, describing hexadecupolar interactions, are present only for $S \geq 2$ while for $k = 6$ to be present $S \geq 3$ is necessary: this is only the case of rare-earths and actinides ions. Concerning the symmetry, for a system with $S \geq 2$ in tetragonal symmetry only $k = 0$ and 4 are needed, for trigonal symmetry only $k = 0$ and 3, while for orthorhombic symmetry only 0, 2, and 4. It should be noted here that the $\mathbf{O}_k^0$ operators describe a purely axial anisotropy and does not mix states with different M_S values, while the other terms of Eq. [1] introduce some degree of transverse anisotropy, coupling states differing in M_S by $\pm q$.

TABLE 1
Explicit Form of Stevens Operators up to Fourth Order

$n = 2$	$\mathbf{O}_2^0 = 3S_z^2 - S(S+1)$
	$\mathbf{O}_2^2 = \frac{1}{2}(S_+^2 + S_-^2)$
$n = 4$	$\mathbf{O}_4^0 = 35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2$
	$\mathbf{O}_4^2 = \frac{1}{2}\{(7S_z^2 - S(S+1) - 5), (S_+^2 + S_-^2)\}^{\otimes}$
	$\mathbf{O}_4^3 = \frac{1}{2}\{(S_z, (S_+^3 + S_-^3)\}^{\otimes}$
	$\mathbf{O}_4^4 = \frac{1}{2}(S_+^4 + S_-^4)$

Note. $\{A, B\}^{\otimes}$ is used as a shorthand for $\frac{1}{2}(AB + BA)$. $S_{\pm} = S_x \pm iS_y$ (after Ref. (24)).

MAGNETIC ANISOTROPY IN POLYNUCLEAR COMPOUNDS

In a system where two or more ions with single-ion anisotropy are interacting one must sum all the single-ion contributions:

$$\sum_i \mathbf{S}_i \mathbf{D}_i \mathbf{S}_i. \qquad [4]$$

[2] In the following we will refer essentially to octahedral coordination for the sake of simplicity.

In [4] only the second-order terms have been considered for the sake of simplicity. However, in polynuclear complexes an additional term is needed, describing the pairwise interaction between different spins:

$$\sum_{i<j} \mathbf{S}_i \mathbf{D}_{ij} \mathbf{S}_j. \qquad [5]$$

The $\mathbf{D}_{ij}$ tensors may have two different origins, namely through-space and through-bond (25). The former contribution can be easily calculated using the point dipolar approximation, i.e., assuming that the spins are localized on isolated centers, and that the separation between different centers is large compared to the spatial extension of the magnet dipoles. This approximation is in general good for polynuclear metal ion complexes characterized by low covalency, while it breaks down for polyradicals. The appropriate form of the tensor is

$$\mathbf{D}_{12} = \mu_B^2 \frac{\mathbf{g}_1 \cdot \mathbf{g}_2 - 3(\mathbf{g}_1 \cdot \mathbf{R})(\mathbf{R} \cdot \mathbf{g}_2)}{R^3}, \qquad [6]$$

where $\mathbf{g}_1$ and $\mathbf{g}_2$ are the $\mathbf{g}$ tensors of centers 1 and 2, respectively, and $\mathbf{R}$ is the unitary vector parallel to the line connecting the two centers. For a pair of spins the dipolar interactions tends to align them parallel to each other, giving rise to easy-axis-type anisotropy, with the axis parallel to $\mathbf{R}$.

The through-bond component arises from spin–orbit coupling mixing of excited states into the ground state. To evaluate this term it is customary to use the so-called Moriya approximation (26), which estimates the $\mathbf{D}_{ij}$ tensors through the relation $\mathbf{D}_{ij} \propto (\Delta g/g_e)^2 J$, where Δg is the difference $g - g_e$, g_e is the free electron value, and J is the coupling constant. The main drawback is that J refers to the coupling between the ground states on the two centers, while in the Moriya approximation the coupling between one center in the ground state and the other center in the excited state should be used. Experimental results showed that in many cases the Moriya approximation may provide even the wrong sign (25). In general it must be expected that for centers with $g \approx g_e$ (like organic radicals and S-ion like Mn^{II}, Fe^{III}, Gd^{III}) $\mathbf{D}_{ij} \approx 0$.

Provided that the total spin is a good quantum number, i.e., strong exchange limit is achieved, one can then describe the global anisotropy of the system as:

$$\mathbf{H} = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}. \qquad [7]$$

In this assumption,

$$\mathbf{D} = \sum_i d_i^S \mathbf{D}_i + \sum_{i<j} d_{ij}^S \mathbf{D}_{ij}. \qquad [8]$$

Here, the $\mathbf{D}_{ij}$'s are the dipolar tensors which, in first approximation, can be calculated treating the magnetic centers as point dipoles: the approximation is valid if the distance between the dipoles is large compared to their extension.

Following [8] the single-ion contribution to the magnetic anisotropy of a polynuclear compound can be calculated as a weighted sum of individual contribution if the nature of the total spin state is known. It is important to stress that Eq. [8] is a tensorial one, which means that the principal directions of the various tensors must be taken into account.

A relation relying on the same approach describes the dependence of the global g value on the individual ones:

$$\mathbf{g}_S = \sum_i c_i^S \mathbf{g}_i. \qquad [9]$$

Once the individual, intermediate, and total spin states are definite, the c_i^S, d_i^S, and d_{ij}^S coefficients are readily calculated by projecting the individual spins on the total spin (25). The value of the coefficients can be calculated with recurrent formulas; a computer program for performing these calculations is available from the authors on request.

SAMPLE CALCULATION OF SINGLE-ION ANISOTROPY THROUGH THE ANGULAR OVERLAP MODEL

The angular overlap model (27, 28) is a ligand field approach that is particularly appealing as it allows the use of parameters directly related to the σ- and π-bonding ability of the ligands, which may be easily controlled by the synthetic chemist. Moreover, it is possible to use the real coordination geometry around the metal ion site, thus including effects due to the low symmetry of the ligand field (29). This was applied in the past to the rationalization of spectroscopic, magnetic, and EPR properties of complexes containing Kramers ions such as Cu^{II} and Co^{II} in low-symmetry environments (30, 31).

Recently a more general procedure for calculating the spin Hamiltonian parameters ($\mathbf{g}$ and zero field splitting terms up to fourth order) has been developed (32). The program calculates the ligand field spin–orbit Hamiltonian, considering all the states as originating from a given d^n configuration, and then compares, through a fitting procedure, the obtained energy levels with those resulting from the solution of an appropriate spin Hamiltonian.

It is clear that this could be a very powerful tool to rationalize the anisotropy of metal ions to develop suitable strategies for introducing the appropriate anisotropy in the molecules and thus to get single-molecule magnet behavior at higher temperatures. The starting point is obviously that of getting some clues for the control of the magnetic anisotropy in simple molecules. We will present in the following some sample calculations—whose results are summarized

in Table 2—on both real and model systems that are of interest as constituent of single molecule magnets, containing Fe^{III} and Mn^{III}. In particular, as both of these ions have $S \geq 2$, their description involves the use of fourth-order terms of the spin Hamiltonian, whose calculation will be presented here. This is a very important point, as it has been clearly shown that $\mathbf{O}_4^q$ terms with $q = 2,4$ are of fundamental importance in promoting the quantum tunneling of the magnetization in some single molecule magnets (33, 34).

Fe(III) MONONUCLEAR COMPLEXES

Fe^{III} is a ^6S ion: nevertheless the combined effect of spin–orbit coupling and structural distortion is well known to give rise to appreciable zero field splitting in coordination complexes of this ion (35). We performed some test calculation assuming two kinds of distortion from octahedral geometry in an intermediate ligand field strength ($Dq = 1460\ \text{cm}^{-1}$).

Assuming the quite commonly encountered trigonal distortion, we found that a variation of θ (Fig. 1) by 5° with respect to octahedral geometry (for which $\theta = 54.73°$) leads to $D = 0.383\ \text{cm}^{-1}$ for compression and $D = -0.313\ \text{cm}^{-1}$ for elongation. Conversely, assuming a tetragonal distortion, with a 10% variation of Dq between axial and equatorial ligands, leads to $D = -0.282\ \text{cm}^{-1}$ for compression and $D = 0.308\ \text{cm}^{-1}$ for elongation.

The behavior of fourth-order terms with respect to these two distortions deserves some comment. In particular the D_{3h} symmetry of the trigonal distorted octahedron leads to a zero value of the B_4^4 term and to a nonzero value of the B_4^3 term. Both B_4^3 and B_4^0 are negative, and their absolute value seems not to depend much on the direction of the distortion. For tetragonal distortion the symmetry zeroes the B_4^3 term and leads to a nonzero value of the B_4^4. It must to be noted that, in contrast to what happens for trigonal distortion, in this case both the B_4^0 and B_4^4 terms are positive for elongation and compression.

However the point that is probably of much interest in the perspective of designing new SMM is that several calculations showed that the combination of different distortions, and then of the presence of a resulting

TABLE 2
Summary of the Spin Hamiltonian Parameters Calculated for Different Ions and Distortions on Model Systems Using AOM

Ions[a]	Distortion	Ligand field parameters	Calculated spin hamiltonian parameters
Mn(III)	Tetragonal elongation	$Dq(\text{ax}) = 1520\ \text{cm}^{-1}$ $Dq(\text{eq}) = 1680\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$	$g_z = 1.96$ $g_{x,y} = 1.99$ $D = -4.83\ \text{cm}^{-1}$ $B_4^0 = -4.0 \times 10^{-6}\ \text{cm}^{-1}$ $B_4^4 = 6.57 \times 10^{-3}\ \text{cm}^{-1}$
Mn(III)	Tetragonal compression	$Dq(\text{ax}) = 1680\ \text{cm}^{-1}$ $Dq(\text{eq}) = 1520\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$	$g_z = 2.000$ $g_{x,y} = 1.97$ $D = 4.72\ \text{cm}^{-1}$ $B_4^0 = -5.9 \times 10^{-4}\ \text{cm}^{-1}$ $B_4^4 = 1.8 \times 10^{-3}\ \text{cm}^{-1}$
Fe(III)	Tetragonal elongation	$Dq(\text{ax}) = 1400\ \text{cm}^{-1}$ $Dq(\text{eq}) = 1540\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$	$g_{\text{iso}} = 2.000$ $D = 0.308\ \text{cm}^{-1}$ $B_4^0 = 3.7 \times 10^{-4}\ \text{cm}^{-1}$ $B_4^4 = 1.6 \times 10^{-3}\ \text{cm}^{-1}$
Fe(III)	Tetragonal compression	$Dq(\text{ax}) = 1540\ \text{cm}^{-1}$ $Dq(\text{eq}) = 1400\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$	$g_{\text{iso}} = 2.000$ $D = -0.282\ \text{cm}^{-1}$ $B_4^0 = 4.3 \times 10^{-4}\ \text{cm}^{-1}$ $B_4^4 = 6.6 \times 10^{-3}\ \text{cm}^{-1}$
Fe(III)	Trigonal elongation	$Dq = 1470\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$ $\theta = 49.73°$	$g_{\text{iso}} = 2.000$ $D = -0.313\ \text{cm}^{-1}$ $B_4^0 = -3.6 \times 10^{-4}\ \text{cm}^{-1}$ $B_4^3 = -6.1 \times 10^{-3}\ \text{cm}^{-1}$
Fe(III)	Trigonal compression	$Dq = 1470\ \text{cm}^{-1}$ $2e_\pi/e_\sigma = 0.4$ $\theta = 59.73°$	$g_{\text{iso}} = 2.000$ $D = 0.383\ \text{cm}^{-1}$ $B_4^0 = -4.0 \times 10^{-4}\ \text{cm}^{-1}$ $B_4^3 = -6.0 \times 10^{-3}\ \text{cm}^{-1}$

Note. Further sample calculations may be found in Ref. (32).

[a]The following electronic parameters were used. Mn^{III}: $\zeta = 315\ \text{cm}^{-1}$, $B = 1140\ \text{cm}^{-1}$, $C = 3675\ \text{cm}^{-1}$. Fe^{III}: $\zeta = 450\ \text{cm}^{-1}$, $B = 536\ \text{cm}^{-1}$, $C = 3260\ \text{cm}^{-1}$.

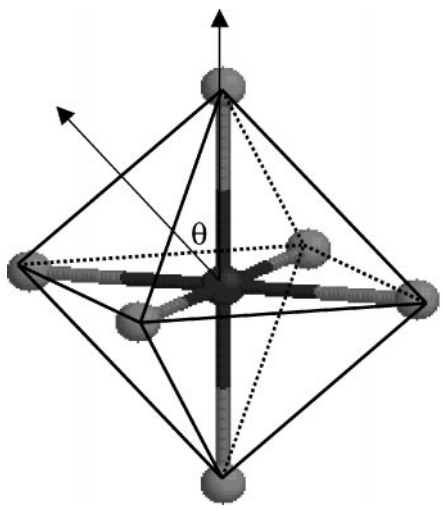

FIG. 1. Scheme of trigonal distortion. The parameter that describes the distortion is the angle between the two arrows (θ in the text).

low-symmetry (i.e., nonregular) distortion, lead to a much smaller value of the anisotropy.

In recent years a relatively large number of clusters containing Fe^{III}–diketonate units bridged by alkoxo-groups, which possess interesting magnetic properties that have been carefully determined by several techniques (HF-EPR, high-field magnetization studies, torque magnetometry), has been synthesized (14, 36–41). Interestingly a series of diketonate complexes of Fe^{III} was fully characterized in terms of spectroscopic parameters by Fatta and Lintvedt in 1971 (42), thus making an analysis in term of AOM feasible. As a first step the validity of this approach in determining the anisotropic characteristic of this kind of system was tested by trying to reproduce the D and E values of the $Fe(acac)_3$ (acac = acetylacetonate) and of the $Fe(dpm)_3$ (dpm = 2,2,6,6-tetramethyl-3,5-heptanedionate) complexes as derived by simulation of EPR (43) and HF-EPR spectra (14), respectively. The results were very promising as, using the real geometry of the chromophore as determined from crystallographic structure and the parameter reported in literature, a very good agreement was obtained in terms of D and E for both these systems (14).

ANISOTROPY IN Mn(III) SYSTEMS

It is well known that the orbital degeneracy of the ground state ^5E_g configuration of Mn^{III} in an octahedral ligand field is removed by the proper Jahn–Teller distortion, giving rise to a ground state with large zero field splitting anisotropy (21). Due to these large values, only in recent years has a relatively large amount of detailed information about the zero field splitting parameters of Mn^{III} mononuclear complexes been made available by HF-EPR spectroscopy (44–46).

A test calculation performed on the hypothesis of a tetragonally distorted system, with $Dq = 1600\,cm^{-1} \pm 5\%$ clearly evidences the much larger zero field splitting of this system with respect to Fe^{III}, giving a D value of $+4.72\,cm^{-1}$ and $-4.83\,cm^{-1}$ for compressed and elongated systems, respectively. The results of the calculation of fourth-order terms for this ion show that the B_4^4 term is quite insensitive to the direction of the distortion, varying only by a factor 3 and maintaining the sign, while the B_4^0 term presents a much larger variation—by a factor 10^2—from elongation to compression. Moreover, the comparison of these results with those obtained for Fe^{III} clearly shows that no straightforward assumption can be made on the relative values of these terms for different ions, in contrast to what has been established for second-order terms.

The AOM approach was satisfactorily tested for real complexes containing Mn^{III}, too: good reproduction of the zero field splitting parameters of $Mn(dbm)_3$ (dbm = 1,3-diphenyl-1,3-propanedionate) as derived by HF-EPR experiments were obtained considering the real structure of this molecule. In particular, a value of the transverse anisotropy in good agreement with those ones obtained by the HF-EPR spectra was easily calculated by assuming only an exponential decrease of the Dq value on the metal–ligand distance and by considering the orthorhombic geometry of the Mn^{III} site in this complex (46).

POLYNUCLEAR COMPLEXES

Much less work has been performed, up to now, on polynuclear compounds using the AOM approach. This is mainly due to three problems: (i) an exact description of the ground state of the cluster is often difficult to obtain, and then the d_i^S and d_{ij}^S coefficients defined in Eq. [8] are not exactly known; (ii) the determination of the ligand field parameters in polynuclear systems is often complicated by the presence of bridging atoms with *misdirected valency*, whose role has long been debated (47–49); and (iii) the number of parameters may be too large to get a meaningful result.

Nevertheless, we have recently obtained some qualitatively interesting results on the single-molecule-magnet $Fe_4(OCH_3)_6(DPM)_6$, hereafter Fe4 (Fig. 2) (14). This relatively simple cluster has an $S = 5$ ground state arising from the antiferromagnetic coupling of the central Fe^{III} with the three external ones. The projection coefficients c_i^S, d_i^S, and d_{ij}^S were calculated assuming a coupling scheme in which the three external iron ions are ferromagnetically coupled together and the resulting intermediate spin (S_{233}) is antiferromagnetically coupled to the central one (S_1) to give the resultant $S = 5$. Using the crystal structure position of the

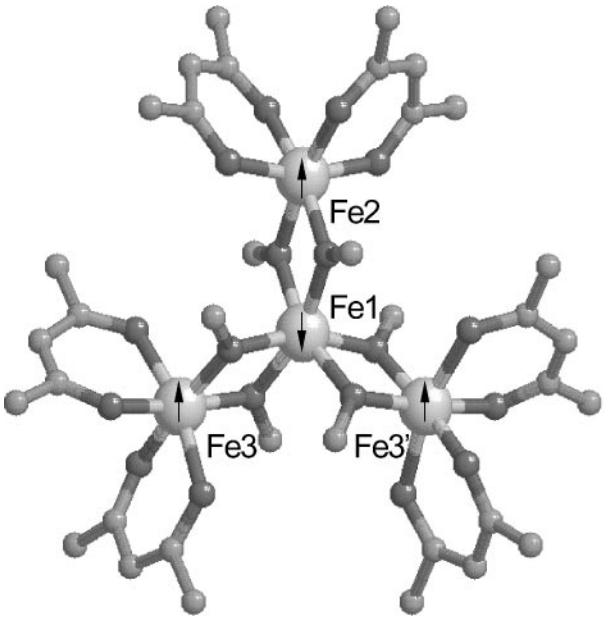

FIG. 2. The structure of the Fe4 cluster. The arrows indicate the spin structure arising from the antiferromagnetic coupling of the central iron with the external ones. The C_2 symmetry axis passes through Fe1 and Fe2.

different ligands for each of the iron centers we were able to get the right sign of the global calculated anisotropy. However the quantitative comparison with the experimental results showed that the calculated value accounted only for 30% of its magnitude. Moreover, a single-crystal HF-EPR analysis has recently shown the calculated direction of the easy axis to be very near to the real one (50). These experiments have shown that fourth-order terms are absolutely necessary to account for a meaningful description of the anisotropy of the system. Unfortunately, as no simple relations between local and cluster fourth-order terms can be derived for this system, the calculated single-ion fourth-order terms cannot be compared with the experimental data.

To get deeper insights into the anisotropy of the Fe^{III} cluster, further calculations on a Ga^{III} doped sample (51) are currently in progress.

Mn12

An estimation of the contribution of single-ion anisotropy up to fourth-order terms in the ground state of Mn12—whose structure is sketched in Fig. 3—was first reported by Villain *et al.* (52) on the basis of two different coupling schemes. No quantitative calculation of the spin levels is possible in Mn12 due to the exceedingly high number of states. It is however possible to make a guess of the prevailing nature of the ground state by choosing appropriate ways of coupling the individual spins to give the total spin S. In the first suggested scheme (Fig. 4a) the eight Mn^{III} of the external ring were ferromagnetically coupled to give an intermediate spin $S' = 16$ and this was subsequently coupled to the intermediate spin $S'' = 6$ resulting from the ferromagnetic coupling of the four Mn^{IV}, to yield the total $S = 10$ state (Fig. 4b). In the second coupling scheme, the four Mn^{III}, which are bridged by two oxide ions to one Mn^{IV}, are antiferromagnetically coupled to the latter (Fig. 5a) to yield four intermediate spins $S' = \frac{1}{2}$. The idea here is that the corresponding coupling constant must be very large. The $S' = \frac{1}{2}$ intermediate spins are then coupled ferromagnetically to the remaining four Mn^{III} to give a resultant spin of $S = 10$ (Fig. 5b).

The two coupling schemes correspond to different wave functions; therefore the relative contributions of the individual spins to the ground state are different from each other: this means that the corresponding c_i^S, d_i^S, and d_{ij}^S values are different in the two cases. In particular for the scheme depicted in Fig. 5 the intermediate spins are $S' = \frac{1}{2}$, and then they do not give any contribution to the zero field splitting of the ground state. In such a way only the four Mn^{III}, which are not coupled to give the intermediate spin S', contribute to the zero field splitting of the cluster. These are the ones bound by two *μ-oxo* bridged oxygens, an apical water molecule, and three acetates, of which two are in the equatorial plane and one is apical: one of these sites is evidenced by an arrow in Fig. 3. On the other hand in the scheme depicted in Fig. 4 all the Mn^{III} spins contribute to the zero field splitting of the ground state.

After calculation of the d_i^S corresponding to the coupling defined by Fig. 5 using spin-projection techniques the axial second-order term of the single-ion anisotropy (D in Eq. [3]) was predicted to be about $-3.3\,cm^{-1}$: this is

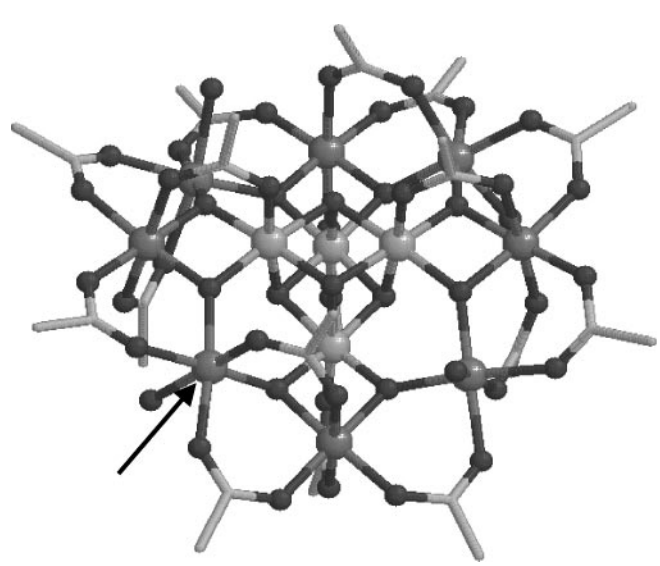

FIG. 3. A picture of Mn12. The arrow evidences the Mn^{III} whose single ion ZFS is relevant to the determination of the cluster anisotropy.

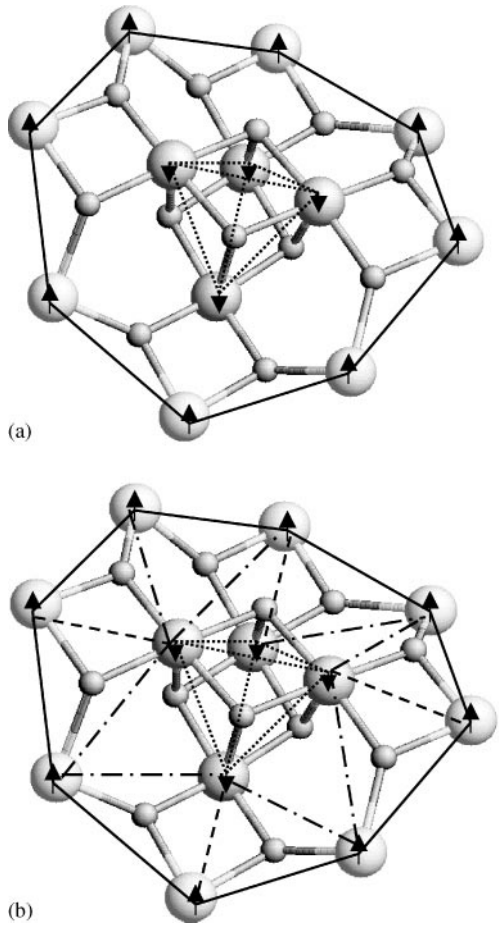

FIG. 4. (a) The eight external Mn^{III} ions are ferromagnetically coupled (continuous line) to yield an intermediate spin $S' = 16$; the four Mn^{IV} are ferromagnetically coupled (dotted line) to give the intermediate spin $S'' = 6$. (b) The two intermediate spins are antiferromagnetically coupled to give the total spin $S = 10$.

a reasonable value on the basis of the literature data concerning the zero dield splitting of Mn^{III}. With the same procedure the absolute values of the single-ion fourth-order terms were estimated to be about 1/1000 of the cluster fourth-order terms, crucial in determining the tunneling process (52).

Given the widespread interest toward this molecule (12, 53–60), we attempted a sample calculation using the above-mentioned AOM-based program. For the sake of simplicity we assumed an orthorhombic geometry for the Mn^{III} site, thus neglecting the angular distortion. While the ligand field parameters concerning acetate and water were easily found in literature (61), we still had the problem of finding a good set of parameters for the two *μ-oxo* groups. We tackled this problem looking for a set of ligand-field parameters that could reproduce the D value of Mn^{III}-doped rutile. The value of $D = -3.4\,cm^{-1}$ reported in the literature (62) for this system was satisfactorily reproduced assuming a small tetragonal elongation, with $Dq = 1560 \pm 10\,cm^{-1}$ and a ratio $2e_\pi/e_\sigma = 0.34$. The Racah parameters B and C and the spin–orbit coupling coefficient ζ were assumed to be that of the free ion, while a small degree of covalence was accounted for by the orbital reduction factor, k, set to 0.75.

The parameter set reported in Table 3 was then employed for the Mn^{III} in Mn12; this yielded $D = -3.2(7)\,cm^{-1}$, $B_4^0 = -3.3 \times 10^{-6}\,cm^{-1}$, and $B_4^4 = 2.2 \times 10^{-3}\,cm^{-1}$. This approach then results in a good reproduction of the second-order parameters, while some more uncertainties are shown for fourth-order parameters. Indeed, on the basis of the HF-EPR results, the value of the cluster parameters

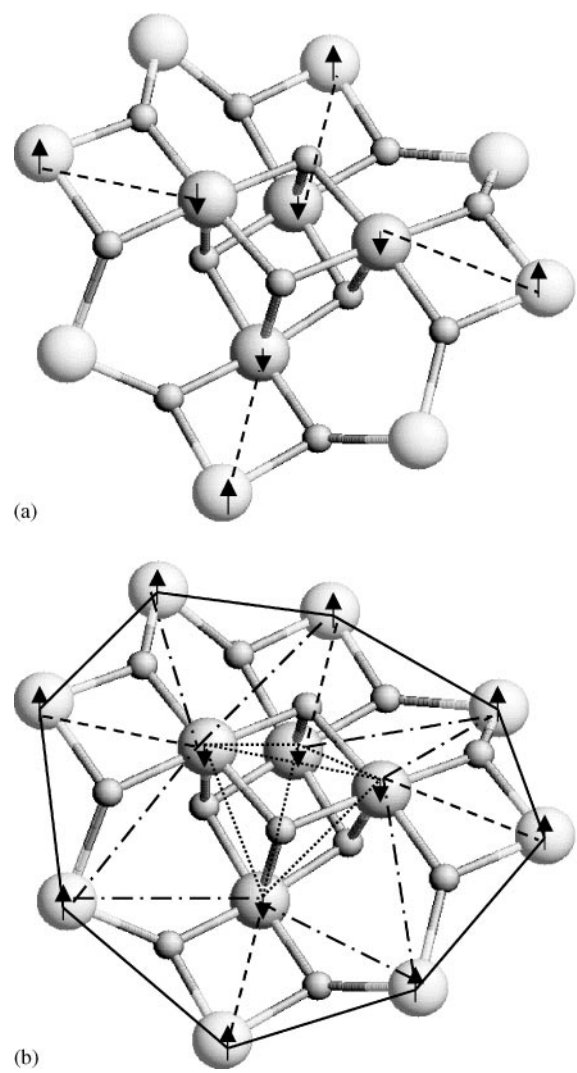

FIG. 5. (a) The spins of the four Mn^{IV} and of four of the external Mn^{III} ion are antiferromagnetically coupled to yield the four intermediate spins $S' = \frac{1}{2}$. (b) The four intermediate spins are ferromagnetically coupled to the four remaining Mn^{III} to give the total spin $S = 10$. In this coupling scheme only the latter Mn^{III} are contributing to the zero field splitting of the ground spin state of the cluster.

TABLE 3
Parameters for the Calculation of Zero Field Splitting Parameters of Mn^{III} in Mn12

Donor atom	Ligand-field parameters
O1(*μ-oxo*)	$Dq = 1570\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$
O2(*μ-oxo*)	$Dq = 1570\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$
O4(basal acetate)	$Dq = 2030\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$
O5(basal acetate)	$Dq = 2030\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$
O3(apical water)	$Dq = 1200\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$
O6(apical acetate)	$Dq = 1700\,cm^{-1}$ $2e_\pi/e_\sigma = 0.34$

Note. k (orbital reduction factor) = 0.75, $\zeta = 315\,cm^{-1}$, $B = 1140\,cm^{-1}$, $C = 3675\,cm^{-1}$. Further details on calculations are reported in the text.

were determined to be $D = -0.46\,cm^{-1}$ $B_4^0 = -2.2 \times 10^{-5}\,cm^{-1}$, $B_4^4 = \pm 4 \times 10^{-5}\,cm - ^{1}$. Thus one would expect values on the order of $10^{-2}\,cm^{-1}$ for the single-ion values of B_4^0 and B_4^4. The observed underestimation of the calculated absolute values of fourth-order terms with respect to the expected ones may be explained on the basis of the approximation done in the derivation of ligand field parameters and in the strong simplification of the distortion of the coordination sphere of Mn^{III}. While this level of approximation seems to be quite good for derivation of second-order parameter, it only works at a qualitative level for higher order terms; for these last ones the calculated sign is correct but their absolute value is not.

CONCLUSIONS

Controlling the magnetic anisotropy is of fundamental importance in molecular magnetism, because the bulk properties of the materials dramatically depend on it. The understanding of the conditions determining the magnetic anisotropy however is very complex, depending on the nature of the individual magnetic building blocks, and on their relative arrangements. We feel that simple ligand field models, which parameterize the energy levels of individual building blocks, can contribute in first-order approximation to help find the appropriate metal ions and coordination geometries which can produce the expected magnetic anisotropy.

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