

Control of the Barrier in Cyanide Based Single Molecule Magnets Mn(III)₂Mn(II)₃: Theoretical Analysis

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Abstract: The aim of this communication is to probe the possibility of increasing the barrier for reversal of magnetization in the family of new cyano-bridged pentanuclear Mn(III)₂Mn(II)₃ clusters in which single molecule magnet behavior has been recently discovered. In this context, we analyze the global magnetic anisotropy arising from the unquenched orbital angular momenta of ground terms ³T₁(t₂⁴) of the two apical Mn(III) ions. The model takes into account the trigonal component of the crystal field, spin–orbit interaction in ³T₁(t₂⁴), and an isotropic exchange interaction between Mn(III) and Mn(II) ions. The height of the barrier is shown to be sensitive to the change of the trigonal field stabilizing orbital doublet ³E, which carries the first-order orbital magnetic contribution and enhances with an increase of the trigonal field. This result is expected to be useful for the more rational design of new cyano-bridged SMMs with high blocking temperatures.

1. Introduction

The existence of the phenomenon of single-molecule magnetism was first noted in the family of clusters of general formula [Mn₁₂O₁₂(O₂CR)₁₆(H₂O)₄].^{1–3} These systems show very slow relaxation of magnetization and quantum tunneling effects at low temperatures. One of the most important characteristics of single molecule magnets (SMM) is the blocking temperature, which is closely related to the magnitude of the spin reorientation barrier. The blocking temperature for existing magnetic clusters with SMM properties is still not high enough to be used in applications. In fact, the highest blocking temperature observed to date is 3 K (for the Mn₁₂acetate cluster having a barrier of about 60 K). This corresponds to a relaxation time of about 10⁸ s in Mn₁₂acetate; a relaxation time acceptable for applications

should be at least 15 years at room temperature.⁴ Therefore, the increase of the spin reversal barrier remains the central problem in the design of SMMs with higher blocking temperatures.

The magnitude of the barrier is closely related to the global magnetic anisotropy of the system that can arise from single ion anisotropy or/and anisotropic exchange interactions. If the ionic ground states are orbital singlets, both types of anisotropic interactions are relatively small. This is peculiar for most of the known SMMs based on oxo-bridged clusters, in which the orbital angular momenta of the constituent metal ions are quenched by the local low-symmetry crystal fields. Under these conditions, a large spin *S* of the ground state and the axial global magnetic anisotropy described by the Hamiltonian *D_SS_Z²* with *D_S* < 0 are the basic ingredients of SMM behavior. The magnitude of the barrier in the oxo-bridged clusters can be increased either by increasing the spin of the ground state or the axial zero field splitting parameter *D_S*. However, the *D_SS_Z²* term represents a second-order correction with respect to the spin–orbit coupling, and hence *D_S* is usually small. This fact essentially constrains

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the possibility to increase the barrier exhibited by oxo-bridged molecules even if the sizes of the spin clusters are made much larger.

If the ground terms of the ions are orbitally degenerate, the unquenched orbital angular momenta give rise to a strong (first order) anisotropy. The orbitally dependent exchange in this case has been considered in detail in the series of articles,^{5–9} in which the exchange Hamiltonian in the most general form has been constructed, the idea about strong exchange anisotropy was developed, and the magnetic anisotropy has been analyzed. Within this approach the anisotropic pseudo-spin-1/2 Hamiltonian for the Kramers doublet ions in the case of strong spin–orbit interaction has been deduced. The parameters of the anisotropic interaction in a Mo(III)–CN–Mn(II) pair in the case of strong spin–orbit interaction have been evaluated in ref 10. The unquenched orbital angular momentum also promotes a strong (first-order) single ion anisotropy. In general, both types of the anisotropy (single-ion and exchange) contribute to the global magnetic anisotropy of the system, with the relative importance of these two contributions being dependent on the electronic and geometrical structure of the cluster.

As distinguished from the oxo-bridged clusters the highly symmetric ligand network in the metal–cyanide complexes can give rise to the unquenched orbital angular momenta of the constituent metal ions and hence to the strong global magnetic anisotropy. Such a situation takes place in the trigonal bipyramidal cyano-bridged cluster [Mn^{III}(CN)₆]₂–[Mn^{II}(tmphen)₂]₃ (tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline) exhibiting SMM properties.¹¹ Due to a strong cubic crystal field produced by six carbon ions, the ground term of each Mn(III) ion is orbitally degenerate being the low spin–orbital triplet ³T₁(t₂⁴). Under this condition the Mn^{III} ions carry a first-order magnetic contribution that is sensitive to the local crystal fields. This leads to a significant single ion anisotropy governed by the combined action of spin–orbit coupling and trigonal component of the crystal field, which splits the ground orbital triplet of the Mn(III) ion. Such anisotropy represents a first-order effect with respect to the named interactions and thus cannot be described by the term *D_SS_Z²*. Recently we have shown¹² that strong single ion anisotropy of this type is able to create a barrier for the reversal of magnetization. At the same time the anisotropic terms in the exchange Hamiltonian have been neglected. In this way the experimental data on the static magnetic susceptibility of the Mn₅-cyanide cluster have been explained, and the proposed model has been shown to be in accordance with the observed SMM properties of the system. The analysis of the model proposed in ref 12 argues hints at future prospects for the design of new cyano-bridged SMMs with higher blocking temperatures. In this paper we show that the barrier in the family of Mn₅-cyanide clusters should be able to be significantly increased by ligand substitutions that result in the variation of the trigonal crystal field.

2. Hamiltonian of the Mn₅-Cyanide Cluster

The model for the interpretation of the observed temperature dependence of the static magnetic susceptibility has been considered in detail in our paper,¹² so here we briefly describe

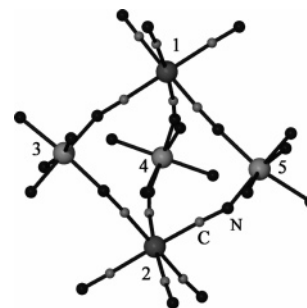


Figure 1. Molecular structure of {[Mn^{II}(tmphen)₂]₃[Mn^{III}(CN)₆]₂}: 1,2-Mn(III), 3,4,5-Mn(II).

only the Hamiltonian of the system. The molecular structure of the Mn₅-cyanide cluster is shown in Figure 1. The metal skeleton represents a trigonal bipyramid containing two Mn(III) ions (1 and 2) in the apical positions and three Mn(II) ions (3, 4, and 5) in the equatorial positions. Each Mn(III) ion is in an almost perfect octahedral surrounding of the carbon atoms (strong cubic crystal field), and the ground term of this ion possesses a fictitious orbital angular momentum *l* = 1, and spin *s* = 1 associated with the low spin cubic term ³T₁(t₂⁴). This state is split into the orbital singlet ³A₂ (orbital basis *m_l* = 0) and the orbital doublet ³E(*m_l* = ±1) due to slight distortions of the carbon octahedra along the common C₃ axis of the molecule. On the contrary, the ground state of each Mn(II) ion coordinated by the nitrogen atoms (weak cubic crystal field) is the orbital singlet ⁶A₁–(t₂³e²). The effective Hamiltonian of the system operating within the ground (³T₁)₁ ⊗ (³T₁)₂ ⊗ (⁶A₁)₃ ⊗ (⁶A₁)₄ ⊗ (⁶A₁)₅ manifold is as follows:

$$H = -\kappa\lambda(s_1l_1 + s_2l_2) + \Delta(l_{1z}^2 + l_{2z}^2 - 4/3) - 2J_{\text{ex}}(s_1 + s_2)(s_3 + s_4 + s_5) \quad (1)$$

Here the first two terms describe the intracenter interactions for the Mn(III) ions including the spin–orbit (SO) coupling and the trigonal component of the crystal field, with *λ*, *κ*, and *Δ* being the many-electron SO coupling parameter, the orbital reduction factor, and the trigonal field parameter, respectively. The trigonal field parameter *Δ* is defined in such a way that ³A₂ becomes the ground term providing *Δ* > 0. Finally, the last term in eq 1 describes the isotropic Heisenberg superexchange between Mn(II) and Mn(III) ions through the cyanide bridges. The results of paper¹² indicate that, in the Mn₅-cyanide cluster, the superexchange is antiferromagnetic, so we will consider only negative values of *J_{ex}*. From now on, for the spin–orbit coupling parameter and orbital reduction factor we use the values *λ* ≈ −180 cm^{−1} and *κ* ≈ 0.8 used in the previous simulations (see ref 12 and references therein).

3. Results and Discussion

The sign of the local magnetic anisotropy is determined by the sign of the trigonal component of the crystal field. Providing relatively strong positive trigonal field (*Δ* > 0) each Mn(III) behaves as a spin *s* = 1 ion with the quenched (to a second order) orbital angular momentum so in this case the Mn₅-cyanide cluster can be considered as a spin-system containing two spins *s*₁ = *s*₂ = 1 and three spins *s*₃ = *s*₄ =

$s_5 = 5/2$. Since the exchange interaction is antiferromagnetic, the spin of the ground state of the whole cluster is $S = 11/2$, and the global magnetic anisotropy can be described by the second-order zero-field splitting Hamiltonian $D(s_{1z}^2 + s_{2z}^2)$, where D is the single ion zero-field splitting parameter. By considering the combined action of SO coupling and trigonal crystal field one obtains the following approximate result for the parameter D (that is valid in the strong trigonal field limit and accurate within λ^3/Δ^2) for a Mn(III) ion:¹²

$$D = \frac{\kappa^2 \lambda^2}{\Delta} - \frac{2\kappa^3 \lambda^3}{\Delta^2}$$

Providing $\Delta > 0$ the parameter D proves to be positive. Since the anisotropy of the Mn(II) ions is negligible, the molecular D_S value for the isolated ground multiplet with $S = 11/2$ (in which two spins of Mn(III) $s_1 = s_2 = 1$ are parallel being antiparallel to three spins of Mn(II) $s_3 = s_4 = s_5 = 5/2$) is also positive, thus precluding the formation of the barrier for the reversal of magnetization in the case of large positive Δ . This conclusion is valid for any positive value of Δ .

A qualitatively different situation occurs when the trigonal crystal field is negative, and the ground state of each Mn(III) ion is the trigonal 3E term that carries first-order orbital magnetism. This orbital magnetism was shown to result in the barrier for the reversal of magnetization.¹² A satisfactory explanation of the observed temperature dependence of the static magnetic susceptibility of the Mn₅-cyanide cluster has been obtained with the best fit parameters $\Delta = -251 \text{ cm}^{-1}$, $J_{\text{ex}} = -3.8 \text{ cm}^{-1}$. The results demonstrate that the trigonal field plays a crucial role in the formation of the barrier in the Mn₅-cyanide cluster. From this point of view the idea to control the SMM properties by changing the crystal field appears attractive. Such a change in the crystal field is expected to be achieved by substituting ligands on the Mn(III) ions to create a mixed-ligand environment in which the terminal ligands are changed meanwhile the bridging ones remain the same in the series of new hypothetical compounds. Provided that such a substitution does not affect the CN-bridges mediating the superexchange between the Mn(II) and Mn(III), one can use the fixed value of the exchange parameter $J_{\text{ex}} = -3.8 \text{ cm}^{-1}$ as a starting point in the subsequent consideration. The role of the exchange will be revealed later.

To clarify the role of the trigonal field in the formation of the barrier we will first discuss the limit of strong negative trigonal field ($|\Delta| \gg \kappa|\lambda|$, J_{ex}), a case for which the ground orbital doublet is well separated from the excited orbital singlet thus preventing spin-orbital and exchange mixing of the ground $(^3E)_1 \otimes (^3E)_2 \otimes ({}^6A_1)_3 \otimes ({}^6A_1)_3 \otimes ({}^6A_1)_5$ manifold of the system with the excited states. In this limit the effective SO coupling operator acting within the $^3E(m_1 = \pm 1)$ term proves to be axial

$$H_{\text{SO}}(^3E) = -\kappa\lambda s_z l_z \quad (2)$$

so the low-lying part of the energy pattern of a single Mn(III) ion contains three equidistant levels with the energies $-\kappa|\lambda|$, 0, and $\kappa|\lambda|$ as shown in Figure 2.

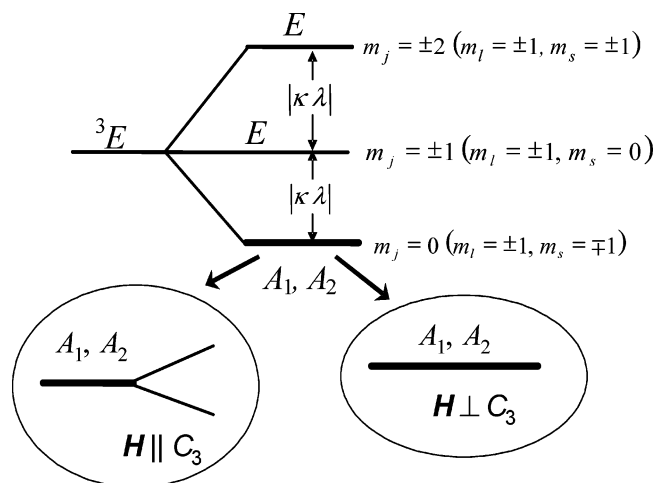


Figure 2. Spin-orbit splitting of the trigonal 3E term and Zeeman splitting of the ground A_1, A_2 doublet.

This set of levels includes the ground accidentally degenerate level A_1, A_2 possessing the total angular momentum projection of the Mn(III) ion $m_j = 0$ ($m_l = \pm 1$, $m_s = \mp 1$) and two non-Kramers doublets E with $m_j = \pm 1$ ($m_l = \pm 1$, $m_s = 0$ and $m_j = \pm 1$, $m_s = \pm 1$). At low temperatures, when only the ground non-Kramers doublets of the Mn(III) ions are populated, one can restrict the exchange problem by considering only the ground $(A_1, A_2)_2 \otimes (A_1, A_2)_2 \otimes ({}^6A_1)_4 \otimes ({}^6A_1)_5$ manifold of the Mn₅-cyanide cluster. Moreover, since $\kappa|\lambda| \gg J_{\text{ex}}$ one can take into account only the matrix elements of the exchange interaction between the states belonging to the ground manifold thus neglecting the mixing of these states with the excited ones. This corresponds to the first order of perturbation theory with respect to the exchange coupling. A remarkable feature of the ground non-Kramers doublet of the Mn(III) ion is that this state is magnetic. In fact, in a magnetic field parallel to C_3 axis the A_1, A_2 level is split into two Zeeman sublevels with the energies

$$\begin{aligned} \langle m_l = \pm 1, m_s = \mp 1, m_j = 0 | \beta(g_e s_z - \kappa l_z) H_z | m_l = \\ \pm 1, m_s = \mp 1, m_j = 0 \rangle = \mp \beta(g_e + \kappa) H_z \quad (3) \end{aligned}$$

This splitting is shown schematically in Figure 2. At the same time, this level is nonmagnetic in a perpendicular magnetic field because all matrix elements of the operators s_x, s_y and l_x, l_y vanish within the A_1, A_2 level. To describe the exchange interaction between the Mn(III) ion in the ground non-Kramers doublet state and the spin-ion Mn(II) (let us say, ions 1 and 3) one can use the following effective Hamiltonian:

$$H_{\text{ex}}^{\text{eff}}(1,3) = -4J_{\text{ex}} \tau_{1z} s_{3z} \quad (4)$$

Here $\tau_{1z} = (1/2)\sigma_z$ (σ_z is a Pauli matrix defined in a basis $|\pm 1/2\rangle$), so that eq 4 defines a pseudo-spin-1/2 Hamiltonian. The two basis states $|+1/2\rangle$ and $|-1/2\rangle$ correspond to the two components $|m_l = +1, m_s = -1\rangle$ and $|m_l = -1, m_s = +1\rangle$ of the ground non-Kramers doublet. Equation 4 shows that the initial isotropic Heisenberg exchange Hamiltonian is reduced to the fully anisotropic Ising one that is operative within the ground manifold.

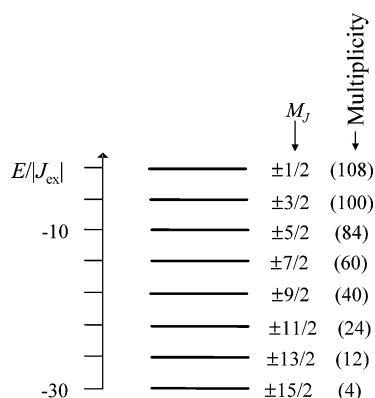


Figure 3. Eight low-lying energy levels of the Mn₅-cyanide cluster calculated with the aid of eq 7.

To find the principal values of g -tensor for the ground A_1, A_2 doublet one must compare the matrix of the Zeeman operator $\beta(-\kappa I + g_e s)H$ defined in the $m_l = \pm 1, m_s = \mp 1, m_j = 0$ basis with the matrix of the effective Zeeman operator $\beta \tau g H$ in the pseudo-spin-1/2 basis. Using eq 3 we obtain

$$g_{||} = 2(\kappa + g_e), g_{\perp} = 0 \quad (5)$$

Then the full effective Hamiltonian of the Mn₅-cyanide cluster is given by

$$H_{\text{eff}} = -4J_{\text{ex}}(\tau_{1Z} + \tau_{2Z})(s_{3Z} + s_{4Z} + s_{5Z}) + \beta g_{||}(\tau_{1Z} + \tau_{2Z})H_Z + g_e \beta(s_3 + s_4 + s_5)H \quad (6)$$

The most suitable choice of the effective basis is the following: $|\sigma_1 \sigma_2 m_{3s} m_{4s} m_{5s}\rangle$, where $\sigma_1, \sigma_2 = \pm 1/2$, and m_{3s}, m_{4s}, m_{5s} take on the values $\pm 1/2, \pm 3/2, \pm 5/2$. The eigenvalues of the exchange part of the Hamiltonian, eq 6, are the following:

$$E(\sigma_{12}, M_S^{345}) = -4J_{\text{ex}}(\sigma_1 + \sigma_2)(m_{3s} + m_{4s} + m_{5s}) = -4J_{\text{ex}}\sigma_{12}M_S^{345} \quad (7)$$

The corresponding eigenvectors are characterized by the total angular momentum projection defined as $M_J = M_S^{345}$, because the effective $|\sigma\rangle$ states correspond to the true $|m_j = 0\rangle$ states of the Mn(III) ions and hence the total angular momentum projection is composed of the spin projection of three Mn(II) ions. The eight low-lying energy levels calculated with the use of eq 7 are shown in Figure 3. The main feature of this energy pattern is that the absolute value of the total angular momentum projection decreases with the increase in energy, so these levels form the barrier for the reversal of magnetization. Each level is 4-fold degenerate over the signs of M_J and σ_{12} , additional factors of multiplicity are related to the spin projection $M_S^{345} = m_{3s} + m_{4s} + m_{5s}$ that can be achieved at different sets of $m_{3s} + m_{4s} + m_{5s}$. Full multiplicities increase with the decrease of M_J as indicated in Figure 3. It is also notable that these levels are equidistant, and in this aspect the present energy pattern is drastically different from that described by the zero-field splitting Hamiltonian $D_S S_Z^2$. Setting $J_{\text{ex}} = -3.8 \text{ cm}^{-1}$ one can roughly estimate the magnitude of the barrier as $\Delta_b = E(|M_J| = 1/2) - E(|M_J| = 15/2) = 106.4 \text{ cm}^{-1}$. This value is approximately 3.5 times larger than the value $\Delta_b \approx 30$

cm^{-1} calculated in ref 12 with the set of the parameters that provide the best fit to the static magnetic susceptibility data. Although the magnitude of the barrier calculated within the simple model operating with the only non-Kramers doublet on each Mn(III) ion proves to be overestimated, the results reported here clearly indicate that the barrier can be significantly increased by variation of the strength of the trigonal crystal field.

One comment should be made concerning the possibility to regard the value Δ_b as the effective height of the barrier. Indeed this definition is approximate because it does not take into account the fact that the degeneracy of the levels rapidly increases with the decrease of $|M_J|$. The increase of degree of degeneracy leads to the population of excited levels at lower temperatures thus facilitating a more rapid magnetic moment reorientation. Despite this the value Δ_b (and especially the ratio between the Δ_b values related to different values of the trigonal field) seems to be useful as a qualitative measure of the barrier.

Now we turn from the above approximate consideration to the analysis of the results obtained by means of the diagonalization of the matrix of the initial Hamiltonian, eq 1 within the full basis set that includes the wave functions:

$$|s_1 l_1(j_1) s_2 l_2(j_2)(J_{12}) s_3 s_4(S_{34}) s_5(S_{345}) J M_J\rangle \quad (8)$$

This basis is defined in such a way that the orbital angular momentum of each Mn(III) ion is coupled with its spin to give the total angular momentum of the ion, the total angular momenta of two Mn(III) ions are coupled to give the total angular momentum J_{12} of the Mn(III) pair, and finally J_{12} is added to the spin S_{345} of the Mn(II) triad leading to the total angular momentum J of the cluster. The matrix elements are calculated with the aid of the irreducible tensor operator technique, and the details are given in ref 12.

Figure 4 demonstrates the low-lying energy levels calculated with three different values of the parameter Δ . The energies depend on the absolute value of the total angular momentum projection $M_J = m_{1j} + m_{2j} + M_S^{345}$ that reflects the axial magnetic symmetry of the system. The level with $|M_J| = 15/2$ is always the ground one, and then M_J is decreased (in general, nonmonotonically) with the increase of the energy and reaches its minimum value $|M_J| = 1/2$. This energy pattern can be associated with the barrier for the reversal of magnetization. One sees that the increase of the negative trigonal field from $\Delta = -250 \text{ cm}^{-1}$ to $\Delta = -10\,000 \text{ cm}^{-1}$ nearly triples the barrier (from 30 cm^{-1} up to 87 cm^{-1}). An additional illustration of this fact is provided by Figure 5, where the effective magnitude of the barrier defined as $\Delta_b = E(|M_J| = 1/2) - E(|M_J| = 15/2)$ is shown as a function of the parameter Δ .

At $\Delta = 0$ (isotropic limit) the energies depend on J rather than on M_J , and no barrier appears ($\Delta_b = 0$); on the contrary, at $\Delta \neq 0$ ($\Delta < 0$) we obtain a barrier that monotonically increases with the increase of $|\Delta|$. This can be realized by inspecting two low-lying energy levels of the Mn(III) ion (the levels A_1 and A_2 with $m_j = 0$). In the limit of strong negative field when these two levels are merged into an accidentally degenerate level (Figure 2) we are dealing with the first-order angular momentum contribution to the mag-

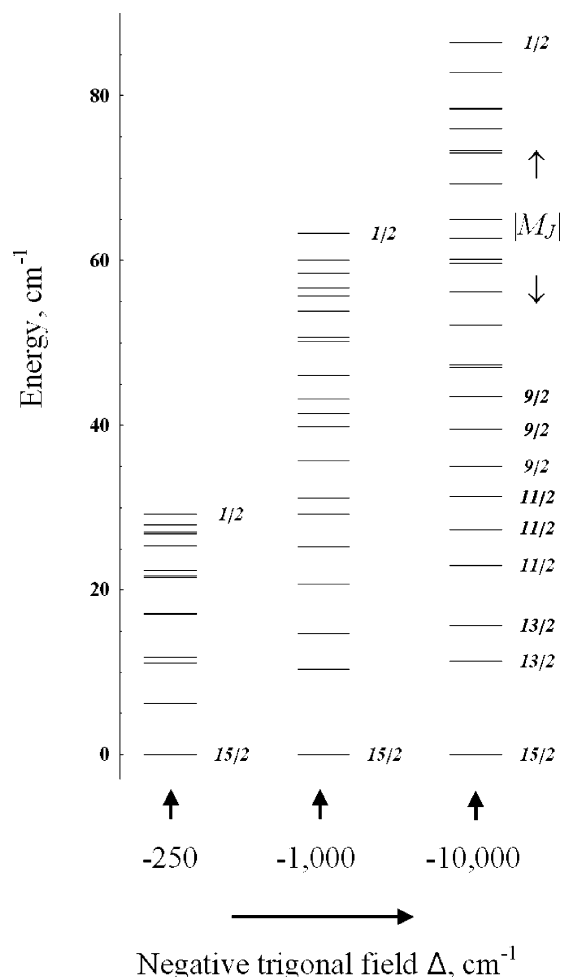


Figure 4. Low-lying energy levels calculated with $J_{\text{ex}} = -3.8 \text{ cm}^{-1}$ and three different values of Δ .

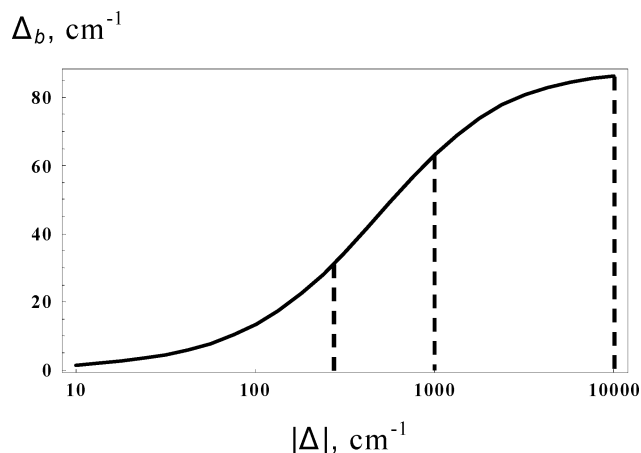


Figure 5. Magnitude of the barrier vs trigonal crystal field.

netic moment that appears due to the mixing of states A_1 and A_2 by the operator $\hat{l}_Z(A_2)$. When we pass from this axial limit toward the more symmetric case (smaller $|\Delta|$ values), this level is split into two singlets, and the first-order effect is transformed into the second-order one thus reducing the single ion anisotropy and hence the global anisotropy. Note in this context that the value $-10\,000 \text{ cm}^{-1}$ for the trigonal crystal field parameter does not appear to be too high as compared to the cubic one. In fact, the latter reaches the value $10 Dq = 30\,000 \text{ cm}^{-1}$ in cyanide complexes.

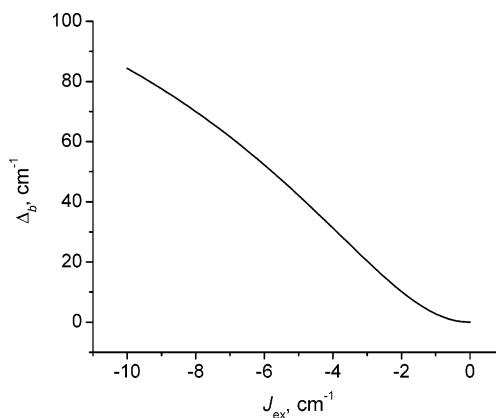


Figure 6. Magnitude of the barrier vs exchange parameter calculated with $\Delta = -250 \text{ cm}^{-1}$.

The possibility to significantly increase the barrier by varying $|\Delta|$ seems to be a specific feature of cyano-bridged SMMs containing metal ions with unquenched orbital angular momenta thus distinguishing such systems from the traditional oxo-bridged SMMs. The variation of the crystal field can be achieved by substitution of the terminal ligands in a controllable way with the aid of cyanide chemistry in order to increase the barrier for magnetization reversal and the blocking temperature.

Although the magnitude of the exchange interaction Mn(II)-Mn(III) is mainly determined by the cyano bridging ligands, the variation of the terminal ligands can also be appreciable. In fact, the substitution of three ligands on the same magnetic center can change metal-metal distances and angles in the first coordination sphere and for this reason influence the exchange interaction through the bridging ligands. This influence can be especially significant when the exchange interaction is relatively small. As it follows from the approximate Hamiltonian, eq 7, the value of the plateau in the dependence height of the barrier vs trigonal field is influenced by the exchange interaction. The magnitude of the barrier as a function of the exchange coupling is shown in Figure 6 providing that the trigonal field is fixed to the value -250 cm^{-1} . One can see that the height of the barrier enhances with the increase of the antiferromagnetic exchange and thus the variation of the exchange (along with the trigonal field) can be also used to increase the barrier, although the electronic factors controlling the exchange are less evident.

Finally, a remark regarding the vibronic interaction is to be made. The adopted model is dealing with the orbitally degenerate (${}^3T_{1g}$) terms of Mn(II) ions for which the vibronic Jahn-Teller (JT) interaction could be active. Accordingly to the JT theorem¹³ the vibronic interaction with the nonsymmetric (JT) vibrations stabilizes the nuclear configuration corresponding to the ground orbital singlet. As it follows from the previous arguments the magnetic anisotropy in this case would be positive precluding thus the formation of the barrier. On the contrary, the orbital doublet ground state that gives the negative magnetic anisotropy cannot be achieved through the JT distortion in the adiabatic limit that justifies the employed static crystal field model. To develop and to justify a more general model that would take into

account both static crystal field and pseudo JT vibronic interaction one needs more experimental data (temperature variable single crystal EPR and magnetic data) that are presently unavailable.

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