Single-Molecule Magnets

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Geometry-Mediated Enhancement of Single-Ion Anisotropy: A Route to Single-Molecule Magnets with a High Blocking Temperature**

*Mamon Dey and Nayanmoni Gogoi**

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Raising the blocking temperature (T_b) of magnetization reversal in single-molecule magnets (SMMs) is a formidable challenge that has to be addressed for their eventual practical application. A SMM displaying characteristic freezing of magnetization along a preferred direction in the absence of external magnetic field at above approximately 14 K has been elusive so far.[1] Tremendous efforts are being devoted to rationalize the parameters governing the energy barrier of magnetization reversal (U) in SMMs. The thermal energy barrier of magnetization reversal between ground $\pm M_s$ levels is related to the axial zero-field splitting D and ground-state spin S through the expression $U = S^2|D|$ (or $U = (S^2-1/4)|D|$ for non-integer spins; Figure 1).

The quadratic dependence of U on the ground state spin (S) initially suggested that increasing S would be a promising route to enhance U. However, this approach turned out to be rather naive and accounts for the lack of concomitant increase of blocking temperature in giant ground-state-spin polynuclear complexes.[2] Therefore, in recent times, efforts to elevate U have been devoted towards enhancing uniaxial anisotropy. Indeed, large uniaxial anisotropy originating from strong spin-orbit coupling in f-block elements facilitates the slow relaxation of magnetization in several single-ion lanthanide/actinide species.[3]

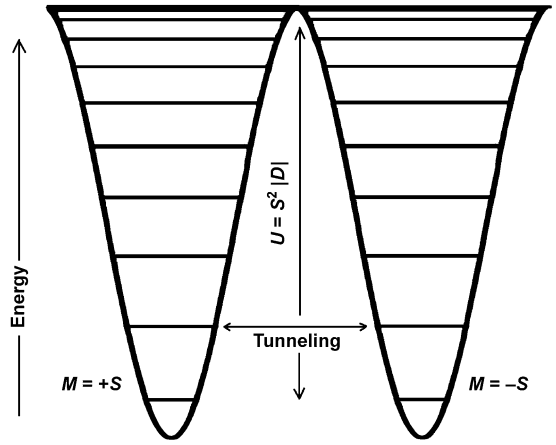

Figure 1. Conventional double-well potential energy diagram showing splitting of M_s levels under uniaxial anisotropy.

The f orbitals remain essentially degenerate in complexes featuring f-block ions and this leads to large spin-orbit coupling. However, for transition elements, pronounced quenching of the orbital angular momentum is observed owing to the influence of the ligand field. This phenomenon limits the occurrence of significantly large D values to a handful of 3d ions for example, Co^{2+} and Mn^{3+} (with octahedral O_h coordination geometry).[4] To prevent the quenching of the orbital angular momentum in transition-metal complexes, the d-orbitals must remain nearly degenerate or lie within a narrow energy gap. This can possibly be achieved if the ligand-field strength is weak. To create such a scenario, the coordination number must be kept low, the coordination environment should be symmetric, and the metal ion should be in a low oxidation state.

Large internal hyperfine fields observed in low-temperature Mössbauer spectra of rigorously linear, homoleptic, two-coordinate Fe^{II} complexes initially demonstrated the presence of unquenched orbital angular momentum in such species.[5] In fact, dynamic susceptibility studies on such two-coordinate Fe^{II} complexes established that the large uniaxial anisotropy originating from unquenched orbital angular momentum effectively increases the energy barrier for magnetization reversal.[6] For $[Fe\{N(SiMe_3)(Ar)\}_2]$ (Ar: diisopropylphenyl), the measured U_{eff} (181 cm^{-1}) is several fold higher than the prototypical SMM $\{Mn_{12}\}$ ($U_{eff} = 46\ cm^{-1}$).[7] Therefore, normally a slow relaxation of magnetization at elevated temperatures would be expected. Surprisingly, none of the reported two-coordinate Fe^{II} complexes displays slow relaxation of magnetization in the absence of an external field bias. This could primarily be attributed to quantum tunneling of magnetization (QTM), which allows quick relaxation of spins without ascending the thermal activation energy barrier for spin reversal. The origin of QTM can be attributed to the

[*] M. Dey, Dr. N. Gogoi
Department of Chemical Sciences, Tezpur University
Napaam 784028, Sonitpur, Assam (India)
E-mail: ngogoi@tezu.ernet.in

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efficient mixing of ground $\pm M_s$ levels, as a result of transverse zero field splitting (E). The applied field bias lifts the degeneracy of $\pm M_s$ levels and thereby suppresses QTM. Nevertheless, according to Kramer's rule, the mixing of $\pm M_s$ states by E is forbidden in half-integer spin systems and thus QTM can be suppressed.[8] Indeed, as a result of the efficient suppression of QTM in non-integer ground-state spin species, the complexes $(Ph_4P)_2[Co(SPh)_4]$ and $[Fe(PNP)Cl_2]$ ($PNP^- = N[2\text{-}P(CHMe_2)_2\text{-}4\text{-methylphenyl}]_2$ anion) display slow relaxation of magnetization in the absence of an external field.[9,10] Therefore, in an attempt to produce linear two-coordinate $3d^7$ complexes, efforts were directed towards the one-electron reduction of $[Fe\{C(SiMe_3)_3\}_2]$.

A reversible Fe^{II}/Fe^{I} reduction peak observed in the cyclic voltammogram of the two-coordinate Fe^{II} complex $[Fe\{C(SiMe_3)_3\}_2]$ initially suggested the possibility to reduce it into its Fe^{I} congener. Indeed, reduction of $[Fe\{C(SiMe_3)_3\}_2]$ by KC_8 in presence of a crown ether, crypt-222, produces the expected two-coordinate Fe^{I} species $[K(crypt\text{-}222)][Fe\{C(SiMe_3)_3\}_2]$ with non-integer ground-state spin, $S = 3/2$ (Figure 2).[11] Owing to the two-coordinate geometry and low

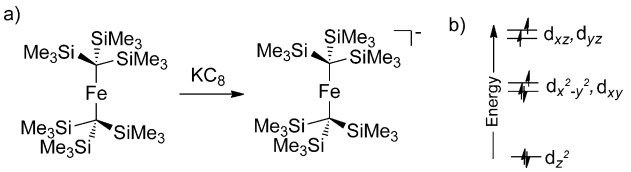

Figure 2. a) The reduction of $[Fe\{C(SiMe_3)_3\}_2]$ using KC_8; b) d-orbital splitting pattern in the $[Fe\{C(SiMe_3)_3\}_2]^-$ ion.

oxidation state of the metal ion, the orbital angular momentum remains almost unquenched. This situation leads to large spin-orbit coupling, and a rise in the energy barrier for magnetization reversal is observed. The measured $U_{eff} = 226\ cm^{-1}$ is unprecedentedly large among transition-metal species. Moreover, as expected for half-integer spin systems, QTM could efficiently be suppressed in this single-ion Fe^{I} species. Thus, the $[Fe\{C(SiMe_3)_3\}_2]^-$ ion shows slow relaxation of magnetization even up to 29 K, in the absence of an external field bias. It is pertinent to note that more than a decade ago, Klatyk and co-workers recognized the existence of unquenched orbital angular momentum for a Fe^{I} ion in a weak axial coordination environment. This investigation was performed on the iron nitridometallate, $Li_2[(Li_{1-x}Fe^{I}_x)N]$ where Fe^{I} is doped within an alkali-metal nitride host matrix.[12] Intriguingly, for $[Fe\{C(SiMe_3)_3\}_2]^-$ and $Li_2[(Li_{1-x}Fe^{I}_x)N]$, computational studies establish that efficient mixing of $3d_{z^2}$ and 4s orbitals stabilizes the $3d_{z^2}$ orbital. Thus, the d-orbital energy-level sequence in $[Fe\{C(SiMe_3)_3\}_2]^-$ (or $Li_2[(Li_{1-x}Fe^{I}_x)N]$) does not follow the conventional trend expected for a linear two-coordinate complex and accounts for the presence of unquenched orbital angular momentum (Figure 2b).

Several other reports on unquenched orbital angular momentum in low-coordinate transition-metal complexes have appeared recently. Significantly increased energy barriers for magnetization reversal have been observed in these species (Table 1).[6,9–11,13–18] However, many of these species with large barrier heights fail to display slow magnetic relaxation in the absence of an external field. Suppression of QTM in half-integer spin species $[Fe^{I}\{C(SiMe_3)_3\}_2]^-$, $[Fe(PNP)Cl_2]$, and $[Co^{II}(SPh)_4]^{2-}$ leads to a slow relaxation of magnetization, even in the absence of any applied field bias. However, several Co^{2+} species with half-integer spin and a large axial zero-field spitting parameter do not display a slow relaxation of magnetization, in the absence of an external field. This situation indicates that in such species QTM is operating through either hyperfine or dipolar coupling.

Table 1: Single-ion transition-metal species with large U_{eff}.

Compound[a]	Spin	Geometry[b]	U_{eff} [cm^{-1}]	Ref.
$[Fe^{I}\{C(SiMe_3)_3\}_2]^-$	3/2	linear	226	[11]
$[Fe^{II}\{N(SiMe_3)(Ar)\}_2]$	2	linear	181	[6]
$[Fe^{II}\{C(SiMe_3)_3\}_2]$	2	linear	146	[6]
$[(tpa^{tBu})Fe^{II}]^-$	2	tpy	65	[13]
$[Fe^{III}(PNP)Cl_2]$	3/2	tbp	32	[10]
$[Fe^{II}\{N(SiMe_3)_2\}_2(PCy_3)]$	2	tpl	29	[14]
$[Fe^{II}(iPr_5Cp)Ar]$	2	unusual	28/99	[15]
$[Co^{II}Cl_2(PPh_3)_2]$	3/2	tetrahedral	25	[16]
$[Co^{II}L^1Cl]$	3/2	tetrahedral	24	[17]
$[Co^{II}(SPh)_4]^{2-}$	3/2	tetrahedral	21	[9]
$[Co^{II}L^2(NCS)_2]$	3/2	sp	11	[18]

[a] tpa = tris(pyrrolylmethyl)amine. [b] tpy = trigonal pyramidal, tpl = trigonal planar, tbp = trigonal bipyramidal, sp = square pyramidal, L^1 = 1,1,1-tris-[2N-(1,1,3,3-tetramethylguanidino)methyl]ethane, $L^2 = [\{ArN{=}CMe\}_2(NPh)]$.

The ability to freeze the relaxation of magnetization, even in single-ion transition-metal species, is an important step towards observing SMM behavior above cryogenic temperatures. Manipulation of the magnetic anisotropy using unconventional coordination geometries and intricate control over QTM emerge as powerful strategies for inducing slow magnetic relaxation. The above examples from recent literature open up new frontiers and are anticipated to trigger a burst of activities in this area.

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