Single Molecule Magnets Containing Lanthanide- and Transition Metal Ions



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Single-molecule Magnets

•These are compounds of exchange coupled clusters of paramagnetic metal ions and and are often encapsulated by organic ligands

•These molecules retain their spin orientation *even after switching off the magnetic field*.



•Once magnetized, SMMs show *Slow Relaxation of Magnetization* which is **of purely molecular origin**

•*No intermolecular interaction is necessary* for this phenomenon to occur

Types of Molecular Magnets

Single-Molecule Magnet (SMM)¹

Single-Chain Magnet (SCM)²





 $[Mn_{12}O_{12}(ac)_{16}(H_2O)_4]$

Single-Ion Magnet (SIM)³

Caneschi, A. et al. JACS 1991, 113, 5873
Clerac, R. et al. JACS 2002, 124, 12837
Freedman, D. E. et al. JACS 2010, 132, 1224



Organometallic SMMS



Layfield, R. A., et. al., *Angew. Chemie Int. Ed.* **2017**, *56*, 11445; Mills, D. P. et. al., *Nature*, **2017**, *548*, 439

Organometallic SMMs



Layfield et al., Science, 2018, ASAP

Requirements for SMM

- **Electronic ground state should be bistable**
- ≻Large ground state spin
- Large uniaxial (negative) magnetoanisotropy (Ising-type)
- (Negative zero field splitting parameter D)
- $U = |DS^2|$ (for integer spin); $U = |DS^2|-1/4$ (for non-integer spin)

Higher the barrier the magnetization retained for a longtime



Relaxation by either quantum tunneling magnetization or thermal energy

Magnetization and Magnetic Relaxation





Magnetic Relaxation



Coord. Chem. Rev. 2018, 367, 163

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Experimental Characterization of SMMs

1. AC susceptibility measurements

Due to blocking of magnetization, SMMs show a frequency-dependent

out-of-phase signal in χ'' vs **T** plot (called as slow relaxation of magnetization)

 $\chi_{\rm ac} = \chi' + i\chi''$

2. Hysteresis measurement

Magnetisation vs field plot



Determination of Energy Barrier



Linear Trinuclear 3d-4f-3d Systems

Lanthanides have large ground state spins; many are magnetically anisotropic

Combination of 3d and 4f-metal ions may increase the ground spin state through d–f magnetic interactions

Phosphorus-based multi-dentate ligand



9 Coordination sites; OMe weak donor, but can coordinate to lanthanide ions

Inorg. Chem. 2007, 46, 5140; Inorg. Chem. 2008, 47, 4918; Dalton Trans. 2008, 43, 5962 Inorg. Chem. 2009, 48, 1148





Where [LHM] is metalloligand

Can we use transition metal ion for anisotropy and lanthanide ion for high spin?

Co(II) S = 3/2

Gd(III) S = 7/2





Inorg. Chem. 2007, 46, 5140



AC susceptibility measurement at zero DC field



Temp. dependent AC susceptibility measurement at 1000 Oe at various frequency







 τ vs T^{-1} plot at $H_{dc} = 0$ and 1 k Oe. The solid lines represent an Arrhenius fit of the data

Energy gap Δ = 27.4 K; τ_0 = 1.5 x10⁻⁷s at 1000 Oe field

Energy gap Δ = 27.2 K; τ_0 = 1.7 x10⁻⁷s at zero Oe field



	Energy barrier (K)	τ ₀
Co ₂ Gd	27.2 K at 0 Oe	1.7 x 10⁻⁷ s
	27.4 K at 1000 Oe	1.5 x 10 -7 s
Co ₂ Tb	24.2 K at 0 Oe	5.1 x 10 ⁻⁶ s
	25.8 K at 1500 Oe	3.7 x 10⁻⁶ s
Co ₂ Dy	18.9 K at 0 Oe	5.5 x10 ⁻⁶ s
Co ₂ Ho	8 K at 0 Oe	1.3 x 10⁻⁴ s

Inorg. Chem. 2007, 46, 5140; Inorg. Chem. 2009, 48, 1148

Other Trinuclear 3d/4f Complexes

Other Trinuclear Complexes



Synthetic Scheme of Co^{II}₂Ln Compounds



Molecular Structure



four-membered CoDyO₂ rings

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AC Susceptibility Plot



Ac susceptibility measurements as a function of the temperature at different frequencies and under zero-external field show that only complex 1 exhibits slight frequency dependence

Ac susceptibility for complex 1 measured under 1000 Oe applied dc field.

Probable reasons behind this observation

(i) A comparatively weaker anisotropy of the Ln^{III} ions induced by the ligand-field effects.

(ii) The non-favourable orientation of the main local anisotropies axes of Co^{II} and Ln^{III} ions leading a relatively weak anisotropy for the whole molecule. In fact, complexes 1-4 are not centrosymmetric and the diphenoxo-bridging fragments are turned each other by 64.75° (non parallel main anisotropy axes of the Co^{II} ions), the complexes of the other two series are centrosymmetric (parallel main anisotropic axes of the Co^{II} ions).

(iii) The existence of a very efficient zero-field quantum tunneling of magnetization (QTM) facilitated by an extended 2D network of hydrogen bonds.

Ni^{II}₂Ln^{III}



Molecular Structure: Ni^{II}₂Dy^{III}





The trinuclear core of **3** showing twisted planer fragment of the two four-membered NiDyO₂ rings



Distorted squre aniprism geometry



Distorted octahedral geometry

Magnetic Studies



Replacing the Paramagnetic Ion with Zn^{II}/Mg^{II}



Molecular Structure



AC Susceptibility Plot



 $U_{\rm eff}$ =72(2) K; $\tau_{\rm o}$ = 8 x 10⁻⁹ s (SR) $U_{\rm eff}$ = 61(2)K; $\tau_{\rm o}$ = 4 x 10⁻⁷ s (FR) 1 under 1000 Oe applied *dc* field



 U_{eff} = 67(3) K with τ_{o} = 4.5 x 10⁻⁸ s for 4 under 1000 Oe applied *dc* field

Do Intermolecular Magnetic Dipolar Interactions Influence the relaxation of the magnetization?

Can we unequivocally demonstrate that the relaxation process is single molecular in origin?.

We have performed *ac* susceptibility measurements on 1:10 Dy:Y magnetic diluted samples of of **1** and **4**, named as **1'** and **4'**

These samples were prepared through crystallization with the diamagnetic and isostructural Mg_2Y and Zn_2Y complexes using a Dy/Y molar ratio of 1:10 (the amount of Dy present in the dilute sample was calculated to be 10.8 and 10.2% for **1'** and **4'**

AC Measurements for Dilute Samples Under 1000 Oe DC Field





 $U_{\rm eff}$ = 90(7) K and $\tau_{\rm o}$ = 1.1 x 10⁻⁹ for 1'

 $U_{\rm eff}$ = 106(4) K and $\tau_{\rm o}$ = 5.2 x 10⁻¹⁰ for **4'**

A Bent Co(III)-Dy(III) system



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3d/4f Families

Inorg. Chem. 2016, 55, 8422

Inorg. Chem. 2013, 52, 13078



Inorg. Chem. 2014, 53, 6524



4f Complexes

Inorg. Chem. 2013, 52, 6346



Inorg. Chem. 2014, 53, 3385

Ln₄ Families



Inorg. Chem. 2014, 53, 3417



Macrocycles



Chem. Eur. J. 2015, 21, 16955

Chem. Eur. J. 2017, 23, 5154

Lanthanide Single-Ion Magnet



Ishikawa, N., et. al., J. Am. Chem. Soc. 2003, 125, 8694

Lanthanide (III) Ions in SMMS

Many Lanthanide ions have a large spin and an unquenched orbital angular momentum

	Tb(III)	Dy(III)	Ho(III)	Er(III)
4f ⁿ	4f ⁸	4f ⁹	4f ¹⁰	4f ¹¹
Spin-				
Orbit				
Ground	⁷ F ₆	⁶ H _{15/2}	⁵ I ₈	${}^{4}I_{15/2}$
Term				
Free-ion	3/7	1/3	514	615
g Value	3/2	4/3	5/4	0/3

How to harvest single ion anisotropy of Lanthanide(III) ions in complexes: Ligand design



Figure: Quadrupole approximations of the 4f-shell electron distribution for the tripositive lanthanides

Recipe to maximize the anisotropy:

✓ For oblate ions the crystal field should be such that the ligand electrons are concentrated above and below the xy plane

 \checkmark For prolate ions an equatorial coordination geometry is preferred

Long, J. R. Chem. Sci. 2011, 2, 2078

Pentagonal Bipyramidal (D_{5h}) Ln^{III} complexes

Zero field QTM is inherent in many Ln^{III} complexes.

---- transversal anisotropic components (g_x, g_y)

---- intermolecular magnetic interactions

---- hyperfine interactions

• Strict group-theoretical rules suggests that an ideal axial symmetry can be achieved in point groups $C_{\infty v}$, $D_{\infty h}$, S_8 , D_{4d} , D_{5h} , D_{6d}



Zheng, Y.-Z. et al., Angew. Chem. Int. Ed. **2016**, 55, 16071

Tong, M. L. et al. J. Am. Chem. Soc. **2016**, 138, 5441

Murugavel, R. et al. Chem. Sci., 2016,7, 5181

Pentagonal bipyramidal complexes



J.-P. Sutter and coworkers, Chem. Commun., 2015, 51, 3616

An approach for a rigid pentagonal plane



 $Ln = Tb, Dy, Y_{0.94}Dy_{0.06}$

SCXRD: Solid state structures



め magellan : Magnetic anisotropy axis



AC Magnetic susceptibility



A rigid pentagonal plane



Inorg. Chem. 2018, 57, 2398



> A new family of molecule-based magnetic materials

- Heterometallic trinuclear 3d-4f compounds
- Homometallic lanthanide assemblies: Variation in nuclearity and structures
- Efforts to assemble PBP mononuclear Lanthanide complexes