Molecular Building Blocks For Magnets



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Indo-French Workshop on Magnetism of Molecular Systems SSCU, IISc Bangalore, November 26-28 2018

Acknowledgements

- Department of Science and Technology
- Council of Scientific and Industrial Research
- IIT Kanpur, TIFR Hyderabad and NISER Bhubaneswar
- Prof. Enrique Colacio, University of Granada, Spain
- Prof. Rodolphe Clérac, CPRP-CNRS, France
- □ Prof. Jean-Pascal Sutter, University of Toulouse, France
- □ Prof. Paul Kögerler, RWTH, Aachen University, Germany
- □ Prof. Paul Goddard, Univeristy of Oxford
- Prof. Floriana Tuna, University of Manchester, U. K.
- Murugesapandian, Atanu Dey, Sakiat Hossain, Joydeb Goura, Prasenjit Bag, Sourav Das, Sourav Biswas, Pankaj Kalita, Joydev Acharya, Arun Kumar Bar

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



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



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



Single Molecule Magnets (SMMs)

First proven example: [Mn₁₂O₁₂(O₂CMe)₁₂(H₂O)₄]



Spins on Mn⁴⁺ sites (S = 3/2) anti-ferromagnetically coupled to spins on Mn³⁺ sites (S = 2)

Spin ground state = $8 \times 2 - 4 \times 3/2 = 10$

Christou et al, J. Am. Chem. Soc., 1993, 115, 1804.

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



Possible Candidates for SMMs

- Homometallic transition metal complexes
- Heterometallic 3d/4f complexes
- •Homometallic Lanthanide Complexes

Coordination Chemistry



C. A. Mirkin

Synthesis by Serendipity: Unpredictable Outcome

✤Use ligands and metal salts that are likely to generate cages or clusters

Ligands should be multifunctional

Metal ion's needs and ligand's need should not match with each other

Disadvantages: Structures of Product(s) not predictable

Advantages: Structures of Product(s) could not have been designed

Planned Synthesis

Design a ligand that can interact with metal ions to afford a compound whose structure can be predicted *apriori*

Disadvantages: you are limited by your imagination; not using the full potential of nature to throw a library of interesting structures

Advantages: you can make a compound whose design is predictable

Polynuclear Transition Metal Complexes

Serendipity

$[Mn_{12}O_{12}(O_2CMe)_{12}(H_2O)_4]$



Dodecanuclear copper cluster



Angew. Chem. Int. Ed. 2000, 39, 2320; Dalton Trans. 2011, 40, 5394; Chem. Rev.2015, 115, 6854.

A Cu₂₆ Phosphonate



Dalton Trans. 2013, 42, 8709; Chem. Rev. 2015, 115, 6854.

Ligands

- **Choice of Ligands**
- The Ideal ligand systems are those that can provide ferromagnetic exchange interactions between the metal ions



Such organic ligands that can propagate ferromagnetic coupling at certain coordination modes when bound to metal centers at specific angles

(More) Polyfunctional Ligands



Inorg. Chem. 2013, 52, 4554-61

Chem. Eur. J. 2015, 21, 16955

Polynuclear 3d Metal Ion SMMs

3d Metal clusters derive their unique magnetic properties due to

- Large spin ground state (S)
- Uniaxial magnetic anisotropy (Negative zero field splitting parameter, D)

U = |D| S² for integer spin= |D| (S² - 1/4) for half-integerspin

Construction of 3d metal SMMs require ferromagnetic exchange interactions leading to a high total spin (S)

> However precise control of local anisotropies is difficult to avoid in clusters results in smaller D values due to mutual cancellation of local anisotropy axes



 $S = 12 U_{eff} \sim 62 \text{ cm}^{-1} \text{ D} = -0.43 \text{ cm}^{-1}$





S = 83/2 $U_{\rm eff} \sim 0.024 \ {\rm cm^{-1}} \ {\rm D} = -0.004 \ {\rm cm^{-1}}$



 $S = 6 U_{eff} \sim 12.5 \text{ cm}^{-1} \text{ D} = -0.21 \text{ cm}^{-1}$

T. Glaser, Chem. Commun., 2011, 47, 116

Polynuclear 3d Metal Ion SMMs

From simple metal precursors



R. E. P. Winpenny and co-workers, Chem. Eur. J., 2002, 8, 4867

Cluster Expansion





Synthetic Scheme



Inorg.Chem. 2011, 50, 1420-28

$4[Mn_{3}O(O_{2}CMe)_{3}(mpko)_{3}](ClO_{4}) + 6 fumH_{2} \xrightarrow{MeCN} [Mn_{12}O_{4}(fum)_{6}(mpko)_{12}](ClO_{4})_{4} + 12 MeCO_{2}H$



 $S = 6 Mn_3 SMM$

Rectangular tetramer of Mn₃ SMM

G. Christou and co-workers, Inorg. Chem., 2013, 52, 12320



At high field, the magnetization is fully saturated and no slope is observed ---- proves the absence of significant anisotropy

Powell, A. K. et al. Angew. Chem. Int. Ed. 2006, 45, 4926.

Criteria for SMMs S vs D





Below 0.5 K, hysteresis loops are observed on the M vs. H plot for sweep rate of 2 mT s⁻¹ confirming slow relaxation of the magnetisation 27

Powell, A. K. et al. Chem. Commun. 2009, 544.

S vs D

- Linear increase of S does not lead to an increase in U_{eff}
- Ferromagnetic exchange between ions leads to a ZFS much smaller than the corresponding single ion
- Conclusion:

Single-Ion Anisotropy is probably an important criterion in design of SMMs

3d Metal-containing Single-Ion Magnets

- (1) To understand and control the magnetic anisotropy of single ions, leading to high U_{eff} and high T_{B} .
- (2)3d metal ions lag behind the 4f metal ions because of
 (i) smaller magnetic moments
 (ii) intrinsically lower spin-orbit coupling constants
 (iii) larger ligand-field splitting energies
- (3) The ligand field effects can partly be supressed by low coordination number which causes the d orbitals to be within a narrow energy range
- (4) Synthetic efforts are therefore made towards isolation of mononuclear 3d metal ion complexes in which possess low coordination numbers and have a half-integer spin ²⁹



E. Ruiz and coworkers, J. Am. Chem. Soc., 2013, 135, 7010

Magnetic anisotropy in 3d SIMs

Theoretical observation: $|D| \propto 1/E_{1st Excitation}$

 $|\Delta m_{\rm I}| = 0$ \implies -ve D



E. Ruiz and co-workers, J. Am. Chem. Soc., 2013, 135, 7010

3d Metal SIMs: Effect of X



Heavy donor atoms (soft bases) with large spin-orbit coupling parameters enhances the magnetic anisotropy of the 3d metal complexes

K. R. Dunbar and co-workers, Chem. Commun., 2014, 50, 12266



E. Ruiz and co-workers, Inorg. Chem., 2014, 53, 676

 $[Fe^{II} \{C(SiMe_3)_3\}_2] + KC_8 + crypt-222 \xrightarrow{THF}_{N_2}$ $[K(crypt-222)][Fe^{I} \{C(SiMe_3)_3\}_3] + 8C$



J. R. Long and co-workers, *Nat Chem.*, 2013, **5**, 577

Ligand induced coordination geometry



T. Mallah and coworkers, *Chem. Sci.* **2014**, *5*, 3418 E. Ruiz and coworkers, *Inorg. Chem.* **2014**, *53*, 676

Pentagonal bipyramidal complexes



J.-P. Sutter and coworkers, *Chem. Commun.*, 2015, **51**, 3616
3d/5d Metal SMMs



J. Faus and coworkers, J. Am. Chem. Soc., 2006, 128, 14218

Thermodynamics of 3d/4f Metal Complexes

Potential energy

Considering the affinity of N-donor and O-donor organic ligands towards 3d and 4f metal ions in general, simply mixing 3d ions, 4f ions and organic ligands together would prefer to produce pure 3d or 4f complexes



Proposed Approaches:

Formation of metal complexes Qualitative model according to HSAB Theory

1) Multi pocket ligands having different kinds of coordination pockets for both 3d and 4f metal ions

2) Suitable co-ligands to assist the self-assembly processes in which 4f ions can combine 3d metal ions at the presence of multidentate ligands

P. Cheng and co-workers, *Coord. Chem. Rev.*, 2014, **289–290**, 74

Compartmental Ligands



Tn= Transition metal ion Ln= Lanthanide ion

Multipocket Ligands



P. Cheng and co-workers, Coord. Chem. Rev., 2014, 289-290, 74





P. Cheng and co-workers, Coord. Chem. Rev., 2014, 289-290, 74



(a) Stepwise synthesis; (b) One pot synthesis

Phosphotrihydrazide



Acyclic Systems



Six Coordination Sites

Inorg. Chem. 2003, 42, 5889; Inorg. Chem. 2005, 44, 4608.

Reaction with M(III) salts



Eur. J. Inorg. Chem. 2008, 1116.

Reaction with M(II) salts



Inorg. Chem. 2003, 42, 5889; Inorg. Chem. 2005, 44, 4608; Chem. Commun. 2005, 459.

Trinuclear Complexes



Structure of L₂M₃

Paddle Wheel View

3d/4f heterometallic compounds

Modified Phosphorus-based multi-dentate ligand $H_3C - N$ - CH₃ нс CH 11 OH CH H ЭМе MeC

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

ЭМе

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





Where [LHM] is metalloligand





Inorg. Chem. 2007, 46, 5140



Cyclo- and Carbophosphazene-Supported Ligands Having Dual Pockets



Inorg. Chem. 2012, 51, 2031.

Cyclo- and Carbophosphazene-Supported Ligands for the Assembly of Heterometallic Complexes



Ferrocene-based Ligands



Dalton Trans., 2014, 43, 8921; Dalton Trans., 2013, 42, 13436

Ferrocene-based Multi-site Ligand



Dalton Trans., 2016, 45, 17633



Inorg. Chem. 2013, 52, 13078-86

Synthetic Scheme of Ni^{II}₂Ln₃ compounds





Designing a Ligand to Expand the Nuclearity of the 3d/4f Complex



Modulation of Nuclearity by Ligand Design





Inorg. Chem. 2011, 50, 1420.



Inorg. Chem. 2013, 52, 2588.

Heptanuclear [Cu₅Ln₂]



= Cu5Ho2

Inorg. Chem. 2013, 52, 2588



Inorg. Chem. 2013, 52, 2588

Cu₅Ln₂: Monomer, 1D and 2D Polymer



Inorg. Chem. 2017, 56, 14612–14623; Eur. J. Inorg. Chem. 2018, 1645–1654

4f Complexes

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	2/2	1/2	514	615
g Value	3/2	4/3	5/4	0/5

Polynuclear 4f Metal Ion SMMs

- (1)Most molecular 4f metal complexes display zero field quantum tunneling of magnetization limiting its practical application
- (2) Strong or relatively strong Ln^{III....}Ln^{III} exchange interactions are necessary to limit the rate of QTM
- (4) The Ln^{III} Ln^{III} exchange interactions are very weak as a result of the efficient shielding of the unpaired electrons in their 4f orbitals and the magnetic coupling is usually of a dipolar nature

Dinuclear Complexes

Dinuclear Complexes

Dinuclear Ln(III) systems: The simplest model to study Ln(III)...Ln(III) interactions



Among these S- and radical-based bridges provides the most promising results in promoting magnetic interactions

M. Murugesu and co-workers, *Chem. Soc. Rev.*, 2013, 42, 3278

Radical Bridged Dinuclear Ln(III) systems



The efficient exchange coupling J = -27cm⁻¹ (Gd₂) between the Ln^{III} ions and the N₂³⁻ bridge hinders zero-field fast relaxation pathways

U_{eff} : 192 K

*T*_B: 14 K

J. R. Long and co-workers, Nature Chem., 2011, 3, 538

Sulfur-Bridged Dinuclear Ln(III) systems



The more diffuse orbitals of S than in Cl allows greater orbital overlap and hence stronger exchange interactions

F. Tuna and co-workers, Angew. Chem. Int. Ed., 201, 51, 6976
N-Bridged and O-Bridged Dinuclear Lanthanide Complexes



R. A. Layfield and co-workers, *Chem. Eur. J.* 2010, **16**, 4442; M. Murugesu and co-workers, *Angew. Chem. Int. Ed.* 2008, **47**,

Synthetic Scheme for Dinuclear Assemblies



Ln = Gd, Tb, Dy, Eu

Dalton Trans. 2015, 44, 4328-40

Dinuclear Lanthanide Complexes



SMM $U_{\rm eff}$ = 80 K (1000 Oe)



Eur J. Inorg. Chem. 2019, 000

Trinuclear Complexes



due to vortex spin chirality

Is it possible to link Lanthanide triangles to make bigger clusters ?

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A. K. Powel, and co-workers, Angew. Chem. Int. Ed., 2006, 45, 1729

Tetranuclear Complexes

Rhombus Shaped Ln₄ complexes



Inorg. Chem. 2013, 52, 6346



Molecular structure of Dy₄ (1)complex



The four dysprosium ions are present in the corners of a perfect rhombus with the inter Dy-Dy distances being 3.79(13) Å

Flexible Compartmental Ligands



 $U_{eff} = 1.3 \text{ K} (\tau_0 \approx 1 \times 10^{-5} \text{ s})$



A pendant -CH₂OH arm at the 6th position of the pyridine ring

Tang et al. Inorg. Chem. 2011, 50, 9705



✓LH₄ has 7 potential coordination sites

✓ This ligand can also undergo keto-enol tautomerism under reaction conditions

 ✓ This ligand can show the flexibility arising out of the conformational isomerism resulting from the C-C bond rotation



Conformational isomerism of the ligand LH₄ showing different coordination pockets.

Fusion of two Dinuclear Sub-units



Inorg. Chem. 2013, 52, 11956

$4 \operatorname{DyCl}_3 + 14 \operatorname{KO}^t \operatorname{Bu} + \operatorname{H}_2 \operatorname{O} \xrightarrow{\text{toluene}} [\operatorname{Dy}_4 \operatorname{K}_2 \operatorname{O}(\operatorname{O}^i \operatorname{Bu})_{12}] + 12 \operatorname{KCl} + 2 \operatorname{Bu}^t \operatorname{H}$





R. E. P. Winpenny and co-workers, Nat. Chem., 2013, 5, 673

Hexanuclear Complexes



due to vortex spin chirality

Is it possible to link Lanthanide triangles to make bigger clusters ?

87

A. K. Powel, and co-workers, Angew. Chem. Int. Ed., 2006, 45, 1729

Coupling of Lanthanide Triangles



A. K. Powel, and co-workers, Angew. Chem. Int. Ed., 2010, 49, 6352; M. Murugesu, and coworkers, Chem. Commun., 2009, 1100

Macrocycles

Polyfunctional Ligand

High nuclearity Lanthanide clusters



✓LH₅ has 9 potential coordination sites

✓This ligand can also undergo keto-enol tautomerism under reaction conditions

Ln₈ Macrocylces



Inorg.Chem., 2013, 52, 4562

Modulation of Nuclearity



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Modulation of Nuclearity



Chem. Eur. J. 2017, 23, 5154

4f SIMs

Single Ion Anisotropy: Prolate and Oblate.....

prolate (axially elongated), oblate (equatorially expanded), or isotropic (spherical).



 $4f_{x(x}^2 - 3y^2)$ orbital is strongly oblate, $4f^1$ electron in this orbital (Ce^{III}), will be oblateshaped electron density.

Highest magnitude of m_l (most oblate shape) and lowest magnitude m_l (most prolate shape).

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
- ✓ For prolate ions an equatorial coordination geometry is preferred

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

An Example





Tang, J. J. Am. Chem. Soc. 2014, 136, 4484-4487

Phthalocyanine-sandwich Complexes as SIMs

 $Na_2CO_3 + 2 Ln(O_2CMe)_3 * xH_2O + 16 C_6H_4(CN)_2^{(i) 340-350 * C, DMF} [Bun_4N][Pc_2Tb]$



[Tb{Pc(OEt)₈}₂] $U_{eff} = 590 \text{ K}$ In this case one of the pc ligand behaves as

radical but can be delocalized across both

the ligands

*U*_{eff} : 331 K

(Buⁿ₄N)[Tb{Pc(OEt)₈}₂] *U*_{eff} = 735 K $[\mathsf{Tb}\{\mathsf{Py}(\mathsf{OEt})_8\}_2][\mathsf{SbCI}_6]$ $U_{\mathrm{eff}} = 790 \text{ K}$

N. Ishikawa, and co-workers, J. Am. Chem. Soc., 2003, **125**, 8694; Inorg. Chem., 2007, **46**, 7250

Lanthanide Single-Ion Magnet



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

Other Examples

 $\text{DyCl}_3 + 2 \text{Na}(\text{O}^t\text{Bu}) + \text{Na}(\text{BPh}_4) + 5 \text{Py} \xrightarrow[-35^{\circ}\text{C}]{\text{THF/Py}}$

 $[Dy(O^tBu)_2(Py)_5](BPh_4) + 3 NaCl$



Bis-trans deposition of anionic charge stabilizes the axiality of Dy^{III} crystal field

R. E. P. Winpenny and co-workers, *Angew. Chem. Int. Ed.*, 2016, **55**, 16071 ¹⁰⁰

PBP 4f Metal Complexes



M. L. Tong and co-workers, *J. Am. Chem. Soc.* 2016, **138**, 5441 M. L. Tong and co-workers, *J. Am. Chem. Soc.* 2016, **138**, 2829 R. Murugavel, and co-workers, *Chem. Sci.* 2016, **7**, 5181

An approach for a rigid pentagonal plane



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Rational design of PBP Ln(III) complexes



The comparatively low energy barrier is mainly due to weaker axial CF

Inorg. Chem., 2018, 57, 2398

An example of High U_{eff} and High T_B SMM



Organometallic SIMs



Cp-Dy-Cp = 147.59° Dy-Cp = 2.296 Å, Dy-Cp* = 2.413 Å

 $U_{\rm eff}$ = 1837 K $T_{\rm B}$ = 60 K



Cp-Dy-Cp = 162.50° Dy-Cp = 2.296 Å, Dy-Cp* = 2.284 Å

$U_{\rm eff} = 1541 \ {\rm cm}^{-1} \ T_{\rm B} = 80 \ {\rm K}$

R. Layfield and co-workers, Angew. Chem. *Int. Ed.*, 2017, **56**, 11445; Science, DOI: 10.1126/science.aav0652

Organometallic SIMs (More Examples)



The combination of a large Cp-Dy-Cp angle and short Dy-Cp bond distances enables a large thermal barrier to magnetic relaxation in $[(\eta^5-Cp^*)Dy(\eta^5 Cp^{iPr5}$][B(C₆F₅)₄]

J. R. Long and co-workers, *Chem. Sci.*, DOI: 10.1039/c8sc03907k

Summary

- Various Synthetic strategies for 3d; 3d/4f and 4f complexes
- > Trend: Moving towards rational design
- > Importance of Anisotropy
- Mononuclear Single-molecule Magnets hold promise.