Coordination Chemistry Reviews 367 (2018) 163–216

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

# Low-coordinate mononuclear lanthanide complexes as molecular nanomagnets

Arun Kumar Bar [a,*], Pankaj Kalita [a], Mukesh Kumar Singh [b], Gopalan Rajaraman [b,*], Vadapalli Chandrasekhar [c,d,*]

[a] School of Chemical Sciences, National Institute of Science Education and Research, HBNI, Bhubaneswar 752050, India
[b] Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India
[c] Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208016, India
[d] Tata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad 500107, India

ARTICLE INFO

*Article history:*
Received 21 December 2017
Accepted 28 March 2018

ABSTRACT

The discovery that some *bis*-(phthalocyaninato)lanthanide complexes are molecular magnets triggered interest in lanthanide ion complexes. Theoretical and experimental observations have shown that the magnetization dynamics of such complexes can be tailored by tuning the coordination geometry and ligand-field around the metal centres. In particular, low-coordinate Ln(III) complexes seem to be quite attractive as molecular magnets, some of them displaying significantly large energy barriers for magnetization reversal with high blocking temperatures. In this *review article*, a concise but comprehensive introductory section to the basics of the magnetic anisotropy of the lanthanide ions is portrayed along with the conventional classifications and quality-check parameters of the molecular nanomagnets. We have elaborated with examples the magneto-structural correlation in various lanthanide-based molecular complexes with coordination numbers ranging from one to seven, and have highlighted the most promising systems as nanomagnets. We have also reviewed various examples of low-coordinate lanthanide-based molecular nanomagnets that are encapsulated inside fullerene cages of various sizes. A short section dealing with the lanthanide ions-based magnetic systems exhibiting slow relaxation of magnetization is also included. A special attention is also paid to the magneto-structural correlation of the lanthanide-based half-sandwich, pseudo-sandwich and a special class of sandwich complexes.



**Contents**



* Corresponding authors at: Tata Institute of Fundamental Research Hyderabad, Gopanpally, Hyderabad 500107, India (V. Chandrasekhar).
*E-mail addresses:* amiakb@gmail.com (A.K. Bar), rajaraman@chem.iitb.ac.in (G. Rajaraman), vc@iitk.ac.in, vc@niser.ac.in (V. Chandrasekhar).

https://doi.org/10.1016/j.ccr.2018.03.022
0010-8545/

## 1. Introduction

The discovery of slow relaxation of magnetization, at very low temperatures, in a $Mn_{12}$ cluster, by Sessoli et al. [1–3] has triggered an intense flurry of research activity in the field of molecular magnetism, with enthusiastic participation from the physics, chemistry and materials science community [4–15]. The ultimate goal of these research activities is to achieve magnetically bi-stable molecular complexes, also known as single-molecule magnets (SMMs) that can exhibit magnetization-blocking at readily accessible temperatures so that such complexes can be utilized in novel applications such as information storage, spintronics, quantum computing, multiferroics, *etc.* [4,6,7,13–16]. While realizing these goals, in full, appears distant at the moment, the focus of immediate endeavours is to understand the fundamental factors that control SMM behaviour and then to translate the understanding gained to come out with better synthetic methodologies for assembling SMMs with improved properties. Through such work, involving both experimental and theoretical research, it has been realized initially that the effective energy barrier ($U_{eff}$) for magnetization reversal in transition metal-based magnetically bi-stable molecular complexes depend linearly on the zero-field splitting parameter, $D$, and quadratically on its ground state spin, $S$; i.e. $U_{eff} = |D|S^2$ for integer spin and $U_{eff} = |D|(S^2 - ¼)$ for half-integer spin [4–16].

The initial efforts looked at the quadratic dependence on $S$ as the main means to prepare high-performance molecular magnets [9,14,17]. Thus, several polynuclear paramagnetic transition metal complexes were prepared and studied with the aim of achieving very large ground-state spins [4,16]. But, while large ground-state spins have been achieved in many complexes, the overall molecular $D$ parameters of such magnetic clusters, in general, are found to be very low [4,16]. It is worth emphasizing here that for the polynuclear molecular nanomagnets, it is very difficult to enhance concomitantly both the $S$ and $D$ parameters. The dependence of $U_{eff}$ on $S$ is essentially linear instead of quadratic for the cluster molecular nanomagnets that incorporate relatively larger number of magnetic centres (metal ions) [18,19]. The overall molecular $D$ parameter, which is a resultant of all the contributions from each and every local anisotropic metal centre in the cluster, is obviously expected to be low where the ionic magnetic anisotropy axes of the constituent metal centres are randomly orientated, which is more like a general phenomenon rather than an exception. The magnitude of the overall molecular $D$ parameter of the cluster molecular nanomagnets follows inverse proportionality to the ground state spin, $S$, i.e., $D \propto 1/S$, and the nature of $D$ parameter (*easy-plane* or *easy-axis*) is largely influenced by the nature of the magnetic exchange interactions (ferromagnetic or antiferromagnetic) among the metal centres in the clusters [19]. Therefore, assembling very large-sized clusters possessing a gigantic spin ground state does not guarantee, in any way, SMM behaviour [16]. It is worth remembering that the expression of $U_{eff}$ associating $D$ parameter and ground state spin, $S$, as mentioned above, is valid only for the transition-metal based molecular nanomagnets. It does not hold for the lanthanide based molecular nanomagnets. However, in transition metal complexes the crystal field (CF) splitting is found to be larger compared to spin–orbit coupling ($\sim 10^3$ $cm^{-1}$ and $\sim 10\ cm^{-1}$ respectively for *3d* series) and the orbital angular moment is quenched in most of the cases (except for the low-coordinate complexes). Contrary to this, in lanthanide complexes, the valence *4f* orbitals are deeply buried and almost non-interacting with ligand field, resulting in a small CF splitting compared to the spin-orbital coupling. As a result, lanthanide ions (except La(III), Gd(III), Lu(III)) possess large unquenched orbital angular moment along with a large magnetic moment. Therefore, lanthanide ions have attracted considerable attention in the arena of single-molecular magnetism [20–32]. However, fine tuning the magnetic anisotropy in polymetallic complexes that are usually prepared via serendipitous synthetic strategies is extremely difficult considering the many variables such as the orientation of the magnetic anisotropy axes, chemical environment, crystal-field strength and coordination geometry of the constituent paramagnetic anisotropic ions. On the other hand, tailoring magnetic anisotropy of paramagnetic metal ions in mononuclear complexes via chemical and geometric tuning appears relatively easier [21,22,27,33].

Notably, significant impact of strong magnetic anisotropy of the Ln(III) ions towards the enhancement of coercive field for the magnetization blocking in *3d-4f* three-dimensional coordination frameworks was well documented as early as in 1976 [34]. Slow relaxation of magnetization of single-ion origin was reported by Gao and co-workers for a *3d-4f* two-dimensional coordination polymer $[Nd^{III}Co^{III}(bpym)(CN)_6(H_2O)_4]\cdot 3H_2O$ (where bpym = 2,2′-bipyrimidine) in 2001 [35]. However, observation of slow relaxation of magnetization in Ln(III) based mononuclear sandwich complexes was first reported by Ishikawa and co-workers in 2003 [36], and this report has since triggered interest in complexes containing Ln(III) ions. As low-coordinate high-symmetry complexes are anticipated to possess large magnetic anisotropy [27,33,37], there has been a natural motivation to explore such compounds. Between low-coordinate lanthanide-based and transition metal ion-containing single-ion magnets, the former are more challenging because of the following reasons. First, as Ln(III) ions are bigger in size and contain shielded *4f* orbitals, they prefer large coordination numbers and hence, stabilization of low-coordinate Ln(III) complexes requires appropriate synthetic strategies [38]. Second, prediction and rationalization of magnetic anisotropy in Ln(III) complexes is more difficult than in transition metal complexes because of the complexities involved in the theoretical studies of the former [39]. Nonetheless, there have been successful efforts at assembling low-coordinate Ln(III)-containing molecular magnets and studying them both experimentally and theoretically.