



Review

Toward heterometallic single-molecule magnets: Synthetic strategy, structures and properties of 3d–4f discrete complexes

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Abbreviations: SMM, single-molecule magnet; SCM, single-chain magnet; U_{eff} , effective energy barrier for magnetization reversal; QTM, quantum tunneling of magnetization; HSAB, hard and soft acids and bases; MC, metallacrown; R-saoH₂, salicylaldehyde oxime ligands; H₃shi, salicylhydroxamic acid; (S)-pheHA, (S)-phenylalaninehydroxamic acid; pyCOPy, di-2-pyridyl ketone; dpk[−], di-2-pyridyl ketoximate; dapdoH₂, 2,6-diacetylpyridine dioxime; paoh, 2-acetylpyridine oxime; Hhmp, 2-hydroxymethylpyridine; Hhep, 2-(2-hydroxyethyl)pyridine; pdmH₂, 2,6-pyridinedimethanol; Gly, glycine; pro, proline; H₂mdea, methyl-diethanolamine; piv, pivalic acid; H₂bdea, N-butyl-diethanolamine; H₃tea, triethanolamine; H₄edte, N,N,N',N'-tetraakis-(2-hydroxyethyl)ethylenediamine; Hdmem, 2-((2-(dimethylamino)ethyl)methylamino)ethanol; H₅bis-tris, bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane; H₃tmp, 1,1,1-trihydroxymethylpropane; H₃bemp, 2,6-bis[N-(2-hydroxyethyl)iminomethyl]-4-methylphenol; ovan, o-vanillin; hfac[−], hexafluoroacetylacetone; H₂sal, salicylic acid; Hchp, 6-chloro-2-hydroxypyridine; H₂valdien, N,N'-bis(3-methoxysalicylidene)diethylenetriamine; Hbpca, bis(2-pyridylcarbonyl)amine; HBpz₃[−], hydrotris(pyrazolyl)borate; dto^{2−}, dithiooxalato dianion; DFT, density functional theory; OBz[−], benzoate; 9-An, 9-anthracene-carboxylate; phen, phenanthroline; XMCD, X-ray magnetic circular dichroism; SIM, single-ion magnet; acac[−], acetylacetonate anion; Hdmb, dibenzoylmethane; dae-o^{2−}, open isomers of 1,2-bis(5-carboxyl-2-methyl-3-thienyl)perfluorocyclopentene; pdcaH₂, 2,6-pyridinedicarboxylic acid; H₃tme, 1,1,1-tris(hydroxymethyl)ethane; H₃bemp, 2,6-bis-(((2-(2-hydroxyethoxy)ethyl)imino)methyl)-4-methylphenol; aibH, 2-amino-isobutyric acid; SALOH₂, 3,5-di-tert-butylsalicylic acid; saphH, N-salicylidene-o-amino-phenol; H₂mpea, 2-hydroxy-3-(((2-hydroxyethyl)imino)methyl)-5-methylbenzaldehyde; Hmp, 2-hydroxy-5-methylisophthalaldehyde; fcaH, 2-furancarboxylic acid; MCE, magnetocaloric effect.

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ABSTRACT

3d–4f heterometallic discrete complexes have enjoyed increasing attraction in recent decades because of their potential advantages to create new single-molecule magnets: the moderate magnetic couplings between 3d and 4f spin carriers and significant single-ion magnetic anisotropies of 4f ions. Herein we review the synthetic strategy, structures and magnetic properties of 3d–4f discrete complexes. Particular attention is paid in this review to the examples showing dynamics of the magnetization.

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1. Introduction

Molecular magnetic materials have attracted great attention over the past decades for their great potentials in high-density information storage device, quantum computer, spintronics and magnetocaloric materials [1]. The newly discovered unconventional molecular nanomagnets in 1990s, namely single-molecule magnets (SMMs) and single-chain magnets (SCMs), exhibit magnet-type behaviors without long-range magnetic ordering [2]. The quantum nature of such molecular nanomagnets and the chemically tunable magnetic properties make them the major issues in molecular magnetism.

It is commonly considered that molecular nanomagnet requires significant uni-axial anisotropy and well-defined spin ground state as large as possible to be well separated from the first excited state. Most of the early efforts to generate SMMs with large effective relaxation energy barrier (U_{eff}) focused on synthesizing exchange-coupled metal-oxo clusters for large spin ground state, whereas few SMMs have been designed from the outset to maximize anisotropy through structural control. A large number of metal-oxo clusters have been synthesized using a serendipitous assembly approach [3] and exhibiting classical magnetic blocking behaviors of SMMs, such as Mn_{84} [4], Mn_{30} [5], Fe_{19} [6], Ni_{21} [7] and Co_{24} [8].

However, the lack of geometric control has resulted in some complexes with extremely large spin values that do not behave as SMMs due to the absence of Ising-type magnetic anisotropy [9]. Recent theoretical studies have suggested that large magnetic anisotropy and high spin state cannot coexist in molecular compounds [10], challenging the conventional understanding for 3d-SMMs greatly. The polynuclear complexes with high total spin might not necessarily be fruitful as a strategy for maximizing the magnetic relaxation barrier [11].

The lanthanide-SMMs (4f-SMMs) [12–14] have promoted a growing realization that single-ion anisotropy is the crucial factor when designing SMMs. Because of the significant single-ion anisotropy of lanthanide ion originated from the strong spin–orbit coupling and crystal field effect, lanthanide complexes have already shown considerable potential for SMMs [15].

As discussed above, blocking of the magnetization cannot be easily achieved in pure 3d complexes due to small spin-flip contribution to zero field splitting parameter (D) in the case of large spin value (S) and vice versa [10]. While for 4f spin carriers, the large total angular momentum (J) and significant single ion anisotropy make them the excellent spin carriers for SMMs. However, the obstacles of using lanthanide ions as spin include: (1) the naturally accompanied quantum tunneling always lowers the effective relaxation energy barrier and induces the loss of remnant magnetization [16]; and (2) the limited radial extension of the 4f orbital corresponds to very weak or even no exchange interactions, and consequently goes against to obtain larger spin ground state than that for a single ion [17]. In this context, it is expected to merge 3d

and 4f spin carriers together with appropriate bridging ligands into a singular material with the following advantages: (1) large magnetic moment could be achieved by the intrinsic characteristic of 4f ions instead of by exchange interactions within polynuclear clusters; (2) the uni-axial anisotropy can be satisfied more easily from the single ion anisotropy of 4f ions rather than that of molecular anisotropy; and (3) the intermediate magnetic exchange between 3d–4f ions may effectively suppress zero-field quantum tunneling mechanism (QTM) and improve the energy barrier for spin reversal [13b,e].

Up to now, plenty of 3d–4f complexes have been synthesized and investigated [18], such as binuclear [19–23], trinuclear [24–27] and tetranuclear [28–31] complexes with various Schiff-base ligands (L), the high dimensional magnets constructed by cyano-bridges [32], the polynuclear M_2Ln_2 [33–38], M_3Ln [39–41], M_4Ln_2 [42–46], M_6Ln [47–51], M_4Ln_4 [52–55] with customer designed organic ligands, the heterometallic analogue of the Mn_{12} family [56–60], the unusual discrete molecules with novel topologies like Mn_9Dy_8 [61], $\text{Fe}_{12}\text{Sm}_4$ [62], $\text{Co}_2\text{Dy}_{10}$ [63], Ni_8Dy_8 [64] and so on. These 3d–4f heterometallic clusters based on a great range of organic ligands are synthesized under optimized conditions, exhibiting diverse molecular structures with interesting topologies and various interesting magnetic properties for both theoretical interests and potential applications.

However, it is still a great challenge for chemists to rationally design and synthesize 3d–4f complexes due to the complexity of the reaction system. By exploring a large number of 3d–4f heterometallic complexes documented as far as May 2014, in this review we are trying to promote the booming of synthesizing discrete 3d–4f complexes and impress the researchers by synthetic strategies, summary of various novel complexes with interesting magnetic properties, as well as theoretical results to better understand both chemical and physical nature of 3d–4f systems.

2. Synthetic strategy of discrete 3d–4f complexes

Synthetic strategy toward cluster compounds is to build metal oxide cores surrounded by organic ligands that act simultaneously as bridging and peripheral ligands to enable the stabilization of discrete species. The prerequisites for ligands should include multiple donor atoms to bridge metal ions and bulky groups to isolate molecules from each other [65]. By using such strategy, tremendous homometallic polynuclear complexes were obtained and magnetically studied [66].

The difficulty of rational designing and synthesizing 3d–4f complexes mainly results from the specific chemical nature of 3d and 4f ions and the complicated heterometallic reaction systems. According to *hard and soft acids and bases* (HSAB) [67], 3d and 4f metal ions have priority to coordinate with different donor atoms such as nitrogen and oxygen, respectively. In general cases, simply

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