

# 锰 - 稀土单分子磁体的研究进展

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## 摘要

自首例{Mn<sub>12</sub>Ac}单分子磁体(SMMs)报道以来, 对高核含锰单分子磁体的研究引起了人们极大的兴趣, 成为当前介观物理, 磁学, 纳米材料等学科的研究热点。Mn-Ln异金属单分子磁体, 因为体系中含有两种不同属性的金属离子, 其配位特性也不同, 对于同一种配体还经常存在着竞争配位, 反应往往比同核单分子磁体的反应要复杂, 所以相对同核单分子磁体, Mn-Ln异金属单分子磁体报道的相对较少。因此, 本文通过对近年来典型的锰 - 稀土SMMs进行综述, 以期对3d-4f SMMs的发展奠定一定的基础。

## 关键词

锰 - 稀土单分子磁体, 结构, 磁性

# Research Progress in Mn-Ln Single Molecule Magnets

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## Abstract

Since the first {Mn<sub>12</sub>Ac} single molecule magnet (SMMs) is reported, the study of high nuclear Mn-

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containing SMMs has aroused great interest, and has become a research hotspot in mesoscopic physics, magnetism, nanomaterials and other fields. Mn-Ln heterometallic monomolecular magnets, because the system contains two metal ions with different properties, exhibit different coordination characteristics. For the same ligand, there is often competitive coordination, and the reaction is often more complex than that of homonuclear monomolecular magnets. Thus, compared with homonuclear monomolecular magnets, Mn-Ln heterometallic monomolecular magnets have relatively few reports. Therefore, this paper reviews the typical Mn-Ln SMMs in recent years, in order to lay a certain foundation for the development of 3d-4f SMMs.

## Keywords

### Mn-Ln Single Molecule Magnets, Structure, Magnetism

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## 1. 引言

Mn 原子中含有大量的未配对电子,使其具有多变的氧化态。在  $Mn^{III}$  氧化态中,最外层的电子轨道包括四个电子。当三个电子占据  $t_{2g}$  轨道,而唯一的电子位于  $e_g$  轨道,产生高自旋态,有助于获得磁性能较好的配合物。并且,当  $Mn^{II}$  和  $Mn^{III}$  在同一配合物中共存时,会产生不同的自旋中心。首例锰单分子磁体  $\{Mn_{12}Ac\}$  即为混合价态的锰配合物[1],其成功的合成引起了人们的极大关注。随后,大量的锰配合物被合成,如  $\{Mn_{84}\}$  [2]、 $\{Mn_{30}\}$  [3]等。然而随着自旋基态值的增加,磁性能并没有提升。

2008 年 Eliseo Ruiz 等[4]对两个  $\{Mn_6\}$  配合物的磁相互作用及磁各向异性进行了研究,研究结果表明磁各向异性的大小主要决定于自旋轨道耦合的强度,不能通过分别优化自旋基态值及各向异性大小来控制,即高的自旋基态值和大的各向异性不能同时兼得。要获得高的自旋基态值往往需要降低体系中的磁各向异性。因而,在配合物中利用具有高的自旋基态值和大的各向异性的稀土离子是制备具有高能垒单分子磁体的重要途径。但由于稀土离子中的 4f 电子会受到 5s 和 5p 电子的屏蔽,使至金属离子中心之间的磁相互作用较弱,而且稀土离子大多存在磁化强度量子隧穿效应,从而导致磁各向异性能垒降低,这对于构造出具有良好性质的稀土单分子磁体具有一定局限性。因此探索如何抑制稀土离子的量子隧穿效应来提高磁各向异性能垒一直是稀土单分子磁体研究中亟需解决的关键性问题。

近年来,通过在过渡配合物中,引入高的自旋基态值和大的各向异性的稀土离子,提升单分子磁体的磁性能。一方面,由于过渡金属离子磁交换作用较强,另一方面,稀土离子高的自旋基态值和大的各向异性,使 3d-4f 异金属配合物具有异于同金属配合物的磁特性。因此一系列高性能的 3d-4f SMMs 被报道[5][6]。其中, Mn 原子中含有大量的未配对电子,使其具有多变的氧化态,因此 Mn-Ln SMMs 由于其广阔的研究前景受到了科学家们的广泛关注。

## 2. 锰 - 稀土单分子磁体的研究进展

目前,已报道的锰 - 稀土单分子磁体如表 1 所示,本论文仅选其中一些例子进行描述,并根据其核数进行分类,以研究其结构与磁性行为之间的关系。

**Table 1.** The magnetic data of Mn-Ln SMMs  
**表 1.** 锰 - 稀土单分子磁体的磁性数据

Complexes	$H_{dc}/\text{kOe}$	$U_{\text{eff}}/\text{K}$	$\tau_0/\text{s}$	$v/\text{mT/s}$	$T_B/\text{K}$	Ref.
$[\text{Mn}^{\text{II}}\text{Dy}(\text{H}_2\text{L}^1)(\text{NO}_3)_3](\text{CH}_3\text{OH})_2$	1	12.98	$2.33 \times 10^{-7}$			[7]
$[\text{DyMn}(\text{opch})_2(\text{OAc})(\text{MeOH})(\text{H}_2\text{O})_2]$	1	5.3 51.8	$4.9 \times 10^{-5}$ $1.8 \times 10^{-7}$			[8]
$[\text{Mn}^{\text{III}}\text{La}(\text{dpm})_4(\text{MeO})_2(\text{MeOH})_2]$	4	15.0	$4.0 \times 10^{-8}$			[9]
$[\text{Mn}^{\text{III}}\text{Pr}(\text{dpm})_4(\text{MeO})_2(\text{MeOH})_2]$	4	8.2	$4.1 \times 10^{-7}$			[9]
$[\text{Mn}^{\text{III}}\text{Eu}(\text{dpm})_4(\text{MeO})_2(\text{MeOH})_2]$	2	13.0	$3.6 \times 10^{-8}$			[9]
$[\{\text{Dy}^{\text{III}}\text{Na}^{\text{I}}[12\text{-MC}_{\text{sha},\text{Mn}(\text{III})\text{-}4](\text{DMF})_{0.5}(\text{H}_2\text{O})_{3.5}\}_2(\text{odba})_4] \cdot 15\text{DMF} \cdot 4\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$	1	25.5(7) – 30.5(9)	$1.2(4) - 4.7(7) \times 10^{-8}$			[10]
$[\text{Tb}_2\text{Mn}(\text{C}_7\text{H}_5\text{O}_2)_8] \text{ (1)}$	0	18.79 (4)	$2.56 \times 10^{-8}$			[11]
$[\text{Dy}_2\text{Mn}(\text{C}_7\text{H}_5\text{O}_2)_8] \text{ (2)}$	0	15.4 (4) 92.4 (2)	$2.99 \times 10^{-5}$ $5.37 \times 10^{-8}$			[11]
$\text{TBA}_2[\text{Mn}_4\text{Dy}_2(\text{teaH})_4(\text{N}_3)_{12}] \text{ (3)}$	0	43.8	$1.47 \times 10^{-10}$			[12]
$[\text{Tb}_2\text{Mn}(\text{QCl})_8] \cdot \text{CHCl}_3 \text{ (4)}$	0	20.3 (6)	$3.7 \times 10^{-8}$			[13]
$[\text{Dy}_2\text{Mn}(\text{QCl})_8] \cdot \text{CHCl}_3 \text{ (5)}$	0	44.5 (1)	$1.06 \times 10^{-9}$			[13]
$[\text{Mn}_2\text{Dy}_2(\text{L}^1\text{H})_4(\mu\text{-OAc})_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O} \text{ (6)}$	0	24.0	$8.30 \times 10^{-9}$			[14]
$[\text{Mn}_2\text{Tb}_2(\text{L}^1\text{H})_4(\mu\text{-OAc})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{CH}_3\text{OH} \cdot \text{Et}_2\text{O} \text{ (7)}$	0	48.3	$1.63 \times 10^{-8}$			[14]
$[\text{Mn}^{\text{III}}_2\text{Nd}_2(\text{bdea})_2(\text{bdeaH})_2(\text{piv})_6] \cdot 2\text{MeCN}$	0	10.0	$1.4 \times 10^{-6}$			[15]
$[\text{Mn}^{\text{II}}_2\text{Tb}_2(\text{hmp})_6(\text{NO}_3)_4(\text{CH}_3\text{OH})_2][\text{Mn}^{\text{II}}_2\text{Tb}_2(\text{hmp})_6(\text{NO}_3)_4(\text{H}_2\text{O})_2]$	0.5	3.84	$6.43 \times 10^{-7}$			[16]
$[\text{Mn}^{\text{II}}_2\text{Dy}_2(\text{hmp})_6(\text{NO}_3)_4(\text{CH}_3\text{OH})_2][\text{Mn}^{\text{II}}_2\text{Dy}_2(\text{hmp})_6(\text{NO}_3)_4(\text{H}_2\text{O})_2]$	0.5	3.86	$1.24 \times 10^{-6}$			[16]
$[\text{Dy}_2\text{Mn}_2(\text{L}^5)_4(\text{NO}_3)_2(\text{DMF})_2]$	0	11	$1 \times 10^{-8}$			[17]
$[\text{Mn}^{\text{III}}_2\text{Dy}_2(\mu_3\text{-OH})_2(\text{p-Me-PhCO}_2)_6(\text{L}^7)_2]$	0	19.32	$5.64 \times 10^{-8}$			[18]
$[\text{Mn}^{\text{III}}_2\text{Dy}_2(\mu_3\text{-O})_2(\text{O}_2\text{C}^t\text{Bu})_{10}][\text{Et}_3\text{NH}]_2$	0	29	$4.6 \times 10^{-6}$			[19]
$[\text{L}^4\text{DyMn}^{\text{IV}}_3\text{O}_4(\text{OAc})_3(\text{DMF})_2][\text{OTf}]$	0	27	$2.13 \times 10^{-8}$			[20]
	0.8	32	$1.77 \times 10^{-8}$			[20]
$[\text{Mn}^{\text{III}}_2\text{Dy}_3(\text{L}^3\text{H})_4(\text{NO}_3)(\text{HOCH}_3)]\text{ClO}_4 \cdot \text{NO}_3$	2	13	$5 \times 10^{-6}$			[21]
$[\text{Mn}^{\text{III}}_4\text{Dy}(\text{HL}^7)_4\{(\text{py})_2\text{CO}_2\}_2\text{Cl}_2](\text{OH})$	0.8	7.9	$4.67 \times 10^{-4}$			[22]
$[\text{Mn}_2\text{Dy}(\text{HL}^7)_2(\text{hmp})_2(\text{CH}_3\text{COO})_2\text{N}_3]_n \cdot \text{H}_2\text{O}$	1.5	9.6	$5.8(5) \times 10^{-8}$			[22]
$[\text{Mn}^{\text{III}}_6\text{O}_3(\text{saO})_6(\text{OCH}_3)_6\text{La}_2(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_2] \text{ (8)}$	0	32.8	$5.8 \times 10^{-10}$	0.7	1.8	[23]
$[\text{Mn}^{\text{III}}_6\text{O}_3(\text{saO})_6(\text{OCH}_3)_6\text{Tb}_2(\text{CH}_3\text{OH})_4(\text{H}_2\text{O})_2] \text{ (9)}$	0	103	$1.6 \times 10^{-10}$	0.7	4.5	[23]
$[\text{NMe}_4]_2[\text{Mn}^{\text{III}}_2\text{Dy}_2(\text{tmp})_2(\text{O}_2\text{CMe}_3)_4(\text{NO}_3)_4] \cdot 2\text{MeCN} \cdot 0.5\text{H}_2\text{O}$	0	15	$3.31 \times 10^{-7}$			[24]
$[\text{Mn}_4\text{Tb}_2\text{O}_2(\text{O}_2\text{CBu}^t)_6(\text{edteH}_2)_2(\text{NO}_3)_2]$	0	20.3	$1.4 \times 10^{-11}$	35	0.9	[25]
$[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2\text{Tb}_2(\mu_4\text{-O})_2(\text{edteH}_2)_2(\text{benz})_6] \cdot 2\text{MeCN}$	0	21.2	$4.0 \times 10^{-9}$			[26]
$[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2\text{Tb}_2(\mu_4\text{-O})_2(\text{edteH}_2)_2(\text{piv})_6(\text{NO}_3)_2] \cdot 4\text{MeCN}$	0	20.9	$5.7 \times 10^{-6}$			[26]
$[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2\text{Tb}_2(\mu_4\text{-O})_2(\text{edteH}_2)_2(\text{piv})_8] \cdot 4\text{MeCN}$	0	19.9	$1.3 \times 10^{-5}$			[26]
$[\text{Mn}_4\text{Dy}_2(\text{L}^{12})_4(\text{CH}_3\text{O})_2(\text{H}_2\text{O})_6\text{Cl}_6][\text{Cl}] \cdot 2\text{H}_2\text{O}$	0	1.5				[27]

续表

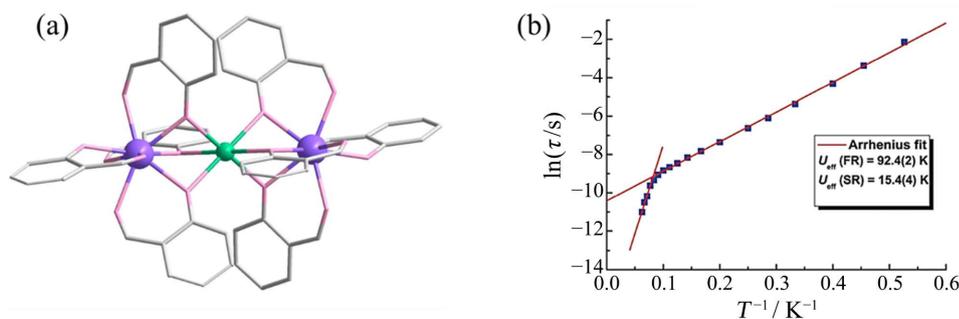
[Mn <sup>II</sup> Mn <sup>III</sup> <sub>2</sub> Dy <sub>4</sub> (mosao) <sub>2</sub> (mosaoH) <sub>4</sub> (piv) <sub>4</sub> (N-mdea) <sub>4</sub> ] $\cdot$ <i>x</i> MeCN	0	9.27	$7.37 \times 10^{-6}$			[28]
[Mn <sup>II</sup> Mn <sup>III</sup> <sub>2</sub> Y <sub>4</sub> (mosao) <sub>2</sub> (mosaoH) <sub>4</sub> (piv) <sub>4</sub> (N-mdea) <sub>4</sub> ] $\cdot$ <i>x</i> MeCN	0	13.83	$3.50 \times 10^{-7}$			[28]
[Gd <sub>2</sub> Mn <sub>6</sub> O <sub>3</sub> (OMe) <sub>4</sub> (Et-sao) <sub>6</sub> (acac) <sub>2</sub> (MeOH) <sub>4</sub> ] $\cdot$ 0.7MeCN ( <b>10</b> )	0	24	$1.7 \times 10^{-9}$			[29]
[Tb <sub>2</sub> Mn <sub>6</sub> O <sub>3</sub> (OMe) <sub>4</sub> (Me-sao) <sub>6</sub> (acac) <sub>2</sub> (MeOH) <sub>3</sub> (EtOH)] $\cdot$ 0.5 H <sub>2</sub> O ( <b>11</b> )	0	46				[29]
[Mn <sub>5</sub> Tb <sub>4</sub> (O) <sub>6</sub> (mdea) <sub>2</sub> (mdeaH) <sub>2</sub> (Piv) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] $\cdot$ 2 MeCN	0	33	$4.5 \times 10^{-9}$			[30]
[Mn <sub>5</sub> Dy <sub>4</sub> (O) <sub>6</sub> (mdea) <sub>2</sub> (mdeaH) <sub>2</sub> (Piv) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] $\cdot$ 2 MeCN	0	38.6	$3.0 \times 10^{-9}$	2	1.9	[30]
[Mn <sub>5</sub> Y <sub>4</sub> (O) <sub>6</sub> (mdea) <sub>2</sub> (mdeaH) <sub>2</sub> (Piv) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] $\cdot$ 2MeCN	4.5	20.2	$2.6 \times 10^{-8}$			[30]
[Mn <sup>III</sup> <sub>4</sub> Tb <sub>4</sub> (OH) <sub>4</sub> (C <sub>4</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> (DMF) <sub>6</sub> (H <sub>2</sub> O) <sub>6</sub> ](OH) <sub>2</sub>	0	3.0	$1 \times 10^{-7}$			[31]
[Mn <sup>III</sup> <sub>4</sub> Dy <sub>4</sub> (OH) <sub>4</sub> (C <sub>4</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>2</sub> (DMF) <sub>6</sub> (H <sub>2</sub> O) <sub>6</sub> ](OH) <sub>2</sub>	0	5.0	$3 \times 10^{-8}$			[31]
[Mn <sub>4</sub> Dy <sub>4</sub> ( <sup>n</sup> Bu-dea) <sub>4</sub> ( $\mu$ -HCOO) <sub>4</sub> ( $\mu$ -OMe) <sub>4</sub> ( $\mu$ -O <sub>2</sub> CET) <sub>4</sub> (O <sub>2</sub> CET) <sub>4</sub> (MeOH) <sub>4</sub> ]	0	12	$3.5 \times 10^{-7}$	140	0.5	[32]
[Mn <sub>4</sub> Sm <sub>4</sub> ( <sup>n</sup> Bu-dea) <sub>4</sub> ( $\mu$ -HCOO) <sub>4</sub> ( $\mu$ -OMe) <sub>4</sub> ( $\mu$ -O <sub>2</sub> CET) <sub>4</sub> (O <sub>2</sub> CET) <sub>4</sub> (MeOH) <sub>4</sub> ]	2	15	$4.9 \times 10^{-8}$			[33]
[ <i>n</i> -PrNH <sub>2</sub> ] <sub>3</sub> [Mn <sub>6</sub> LaO <sub>3</sub> (OMe) <sub>3</sub> (SALO) <sub>6</sub> (SALOH) <sub>3</sub> ]	0	6	$6 \times 10^{-7}$			[34]
[ <i>n</i> -PrNH <sub>2</sub> ] <sub>3</sub> [Mn <sub>6</sub> TbO <sub>3</sub> (OMe) <sub>3</sub> (SALO) <sub>6</sub> (SALOH) <sub>3</sub> ]	0	2	$2 \times 10^{-5}$			[34]
[ <i>n</i> -PrNH <sub>2</sub> ] <sub>3</sub> [Mn <sub>6</sub> DyO <sub>3</sub> (OMe) <sub>3</sub> (SALO) <sub>6</sub> (SALOH) <sub>3</sub> ]	0	1.3	$6 \times 10^{-11}$			[34]
[Mn <sub>8</sub> Tb <sub>2</sub> O <sub>2</sub> (OH) <sub>2</sub> {(py) <sub>2</sub> CO <sub>2</sub> }] <sub>4</sub> (teaH) <sub>4</sub> (CH <sub>3</sub> COO) <sub>6</sub> ] $\cdot$ 6 CH <sub>3</sub> CN $\cdot$ 2H <sub>2</sub> O	0	18.97	$1.71 \times 10^{-9}$			[35]
[Mn <sup>III</sup> <sub>4</sub> Mn <sup>IV</sup> Tb <sub>6</sub> (O) <sub>4</sub> (OH) <sub>4</sub> (OMe) <sub>2</sub> (bemp) <sub>2</sub> (OAc) <sub>10</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	0	17.76	$4.76 \times 10^{-8}$			[36]
[Mn <sup>III</sup> <sub>9</sub> Mn <sup>II</sup> <sub>2</sub> Ho(O) <sub>8</sub> (OH)(piv) <sub>16</sub> (NO <sub>3</sub> )(CH <sub>3</sub> CN)] $\cdot$ 2 CH <sub>3</sub> CN $\cdot$ 0.5C <sub>7</sub> H <sub>16</sub>	0	6.0	$8.6 \times 10^{-4}$	140	1.0	[37]
[Dy <sub>2</sub> Mn <sub>10</sub> O <sub>8</sub> (O <sub>2</sub> CPh) <sub>10</sub> (hmp) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	0	30	$6 \times 10^{-10}$	140	1.6	[38]
[Ho <sub>2</sub> Mn <sub>10</sub> O <sub>8</sub> (O <sub>2</sub> CPh) <sub>10</sub> (hmp) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	0	41	$3 \times 10^{-12}$			[38]
[Tb <sub>2</sub> Mn <sub>10</sub> O <sub>8</sub> (O <sub>2</sub> CPh) <sub>10</sub> (hmp) <sub>6</sub> (NO <sub>3</sub> ) <sub>4</sub> ]	0	42				[38]
[Dy <sub>4</sub> Mn <sub>8</sub> O <sub>8</sub> (O <sub>2</sub> CPh) <sub>16</sub> (dmhmp) <sub>4</sub> ]	0	17.2	$9(2) \times 10^{-8}$	140	1.6	[39]
[Mn <sub>6</sub> Dy <sub>2</sub> ( $\mu$ -OH) <sub>4</sub> ( $\mu$ -O)(Ac) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> (R-L <sup>6</sup> ) <sub>6</sub> ] $\cdot$ NO <sub>3</sub> $\cdot$ OH	0	14.85	$2.38 \times 10^{-7}$			[39]
[Mn <sub>12</sub> GdO <sub>9</sub> (O <sub>2</sub> CPh) <sub>18</sub> (O <sub>2</sub> CH)(NO <sub>3</sub> )(HO <sub>2</sub> CPh)]	0	16.0	$2.4 \times 10^{-12}$	8	0.7	[40]
[Mn <sup>III</sup> <sub>9</sub> Mn <sup>II</sup> <sub>2</sub> Gd <sub>2</sub> ( $\mu$ -O) <sub>7</sub> ( $\mu$ -O)( $\mu$ -OH) <sub>2</sub> (piv) <sub>10.6</sub> (O <sub>2</sub> CC <sub>4</sub> H <sub>3</sub> O) <sub>6.4</sub> (NO <sub>3</sub> ) <sub>2</sub> (OH <sub>2</sub> ) <sub>3</sub> $\cdot$ 13CH <sub>3</sub> CN $\cdot$ 3H <sub>2</sub> O	0	18.4	$2 \times 10^{-12}$			[41]
[Mn <sup>III</sup> <sub>9</sub> Mn <sup>II</sup> <sub>2</sub> Gd <sub>2</sub> (O) <sub>8</sub> (OH) <sub>2</sub> (piv) <sub>10.6</sub> (fca) <sub>6.4</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)] $\cdot$ 13 CH <sub>3</sub> CN $\cdot$ H <sub>2</sub> O	0	18.4	$2 \times 10^{-12}$			[42]
[Mn <sub>11</sub> Dy <sub>4</sub> O <sub>8</sub> (OH) <sub>6</sub> (OMe) <sub>2</sub> (O <sub>2</sub> CPh) <sub>16</sub> (NO <sub>3</sub> ) <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub> ] $\cdot$ 15 MeCN	0	9.3	$4 \times 10^{-8}$	35	1	[43]
[Mn <sub>10</sub> Dy <sub>6</sub> (R/S-L <sup>8</sup> ) <sub>6</sub> (L <sup>9</sup> ) <sub>2</sub> (Ac) <sub>12</sub> ( $\mu$ -O)( $\mu$ -O) <sub>6</sub> ( $\mu$ -OH) <sub>6</sub> ( $\mu$ -H <sub>2</sub> O) <sub>2</sub> ][Mn <sub>6</sub> Dy <sub>2</sub> (R/S-L <sup>8</sup> ) <sub>6</sub> (L <sup>9</sup> ) <sub>2</sub> (Ac) <sub>2</sub> ( $\mu$ -O) <sub>2</sub> ( $\mu$ -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	0	25.1	$2.0 \times 10^{-8}$			[44]
[Dy <sub>10</sub> Mn <sup>III</sup> <sub>4</sub> Mn <sup>II</sup> <sub>2</sub> O <sub>4</sub> (OH) <sub>12</sub> (OAc) <sub>16</sub> (L <sup>10</sup> ) <sub>4</sub> (HL <sup>10</sup> ) <sub>2</sub> (EtOH) <sub>2</sub>	0	11.38	$1.99 \times 10^{-7}$			[45]
[Dy <sub>6</sub> Mn <sub>12</sub> O <sub>7</sub> (OH) <sub>10</sub> (OAc) <sub>14</sub> (mpea) <sub>8</sub> ] $\cdot$ 20H <sub>2</sub> O $\cdot$ 4MeOH ( <b>12</b> )	0	35.1 (5)	$1.00 \times 10^{-8}$			[46]

续表

[Dy <sub>6</sub> Mn <sub>12</sub> O <sub>9</sub> (OH) <sub>8</sub> (OAc) <sub>10</sub> (mpea) <sub>8</sub> (mp) <sub>2</sub> (MeOH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (13)	0	18.2 (5)	$3.02 \times 10^{-8}$			[46]
[Tb <sub>6</sub> Mn <sub>12</sub> O <sub>7</sub> (OH) <sub>10</sub> (OAc) <sub>14</sub> (mpea) <sub>8</sub> ]·13H <sub>2</sub> O·7MeOH	0	36.6 (7)	$4.52 \times 10^{-10}$			[47]
[Tb <sub>6</sub> Mn <sub>12</sub> O <sub>9</sub> (OH) <sub>8</sub> (OAc) <sub>10</sub> (mpea) <sub>8</sub> (mp) <sub>2</sub> (MeOH) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] (14)	0	19.6 (14)	$2.04 \times 10^{-8}$			[47]
[Mn <sup>III</sup> <sub>12</sub> Mn <sup>II</sup> <sub>6</sub> Dy(μ <sub>4</sub> -O) <sub>8</sub> (μ <sub>3</sub> -Cl) <sub>6,5</sub> (μ <sub>3</sub> -N <sub>3</sub> ) <sub>1.5</sub> (HL <sup>2</sup> ) <sub>12</sub> (MeOH) <sub>6</sub> ] (15)				2	0.5	[48]
[Mn <sub>21</sub> DyO <sub>20</sub> (OH) <sub>2</sub> (Bu <sup>t</sup> CO <sub>2</sub> ) <sub>20</sub> (HCO <sub>2</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub> ] (14)	0	74	$2.0 \times 10^{-12}$	70	3	[49]
[Mn <sub>21</sub> GdO <sub>20</sub> (OH) <sub>2</sub> (Bu <sup>t</sup> CO <sub>2</sub> ) <sub>20</sub> (HCO <sub>2</sub> ) <sub>4</sub> (NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>7</sub> ] (14)	0	27.6	$5.0 \times 10^{-12}$			[49]
[Mn <sub>26</sub> Dy <sub>6</sub> O <sub>16</sub> (OH) <sub>12</sub> (O <sub>2</sub> CCHMe <sub>2</sub> ) <sub>42</sub> ] (15)	0	46				[50]

saO = Salicylaldehyde; Hmp = 2-hydroxy-5-methyl-isophthalaldehyde; H<sub>2</sub>mpea = 2-hydroxy-3-((2-hydroxy-ethylimino)methyl)-5-methylbenzaldehyde); H<sub>3</sub>L<sup>1</sup> = 2,2'-(2-hydroxy-3-methoxy-5-methylbenzylazanediy)diethanol; C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> = salicylic aldehyde; TBA = Tetrabutylammonium; H<sub>3</sub>tea = triethanolamine; HQCl = 5-chloro-8-hydroxyquinoline; O<sub>2</sub>CPh = benzoic acid; H<sub>3</sub>tmp = Trimethylol; H<sub>2</sub>mdea = N-methyldiethanolamine; HPiv = pivalic acid; H<sub>2</sub>bdea = N-Butyldiethanolamine; H<sub>3</sub>L<sup>2</sup> = 2,6-bis-(hydroxymethyl)-4-methylphenol; H<sub>3</sub>bemp = 2,6-bis[N-(2-hydroxyethyl)iminomethyl]-4-methylphenol; C<sub>4</sub> = calix[4]arene; <sup>n</sup>Bu-deaH<sub>2</sub> = N-<sup>n</sup>Butyldiethanolamine; C<sub>4</sub>H<sub>3</sub>OCOOH = 2-furan-carboxylic acid; H<sub>4</sub>edte = N,N,N',N'-tetrakis(2-hydroxyethyl)ethylenediamine; H<sub>4</sub>L<sup>3</sup> = (E)-2,2'-(2-hydroxy-3-((2-hydroxyphenylimino)methyl)-5-methylbenzylazanediy)-diethanol; H<sub>2</sub>mosao = 3-Methyloxysalicylaldehyde; H<sub>2</sub>SALO = 3,5-di-*tert*-butylsalicylic acid; H<sub>3</sub>L<sup>4</sup> = 1,3,5-tris(2-di(2'-pyridyl)hydroxymethylphenyl) benzene; HOTf = trifluoromethanesulfonate; Hhmp = 2-(hydroxymethyl)pyridine; (py)<sub>2</sub>CO<sub>2</sub>H<sub>2</sub> = the gem-diol form of di-2-pyridyl ketone; H<sub>2</sub>L<sup>5</sup> = (E)-2-ethoxy-6-(((2-hydroxyphenyl)imino)methyl)phenol; Hdpm = 2,2,6,6-tetramethyl-3,5-heptanodione; fcaH = 2-furan-carboxylic acid; R-H<sub>2</sub>L<sup>6</sup> = (R)-2-[(2-hydroxy-1-phenylethylimino)methyl]-5-methoxy-phenol; dmhmpH = 2-(pyridine-2-yl)propan-2-ol; H<sub>2</sub>opch = (E)-N'-(2-hydroxy-3-methoxybenzylidene)pyrazine-2-carbohydrazide; H<sub>2</sub>L<sup>7</sup> = 2,2'-(pyridin-2-ylmethyl)azanediyl)bis(ethan-1-ol); Ac = acetic acid; H<sub>2</sub>L<sup>8</sup> = (R/S)-2-(((1-hydroxybutan-2-yl)imino)methyl)-5-methoxyphenol; HL<sup>9</sup> = 2-hydroxy-4-methoxybenzaldehyde; H<sub>2</sub>L<sup>10</sup> = 4-bromo-2-[(2-hydroxypropylimino)methyl]phenol; H<sub>4</sub>L<sup>11</sup> = N,N',N'',N'''-tetra(2-hydroxy-3-methoxy-5-methylbenzyl)-1,4,7,10-tetraazacyclododecane; L<sup>12</sup> = ditopic carbohydrazone ligand.

2015年,唐金魁等[11]报道了一类三核异金属配合物 Ln<sub>2</sub>Mn(C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>)<sub>8</sub> (Ln = Tb (1), Dy (2), C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> = 水杨醛)。这些配合物是第一个仅以 Mn<sup>II</sup> 为中心的线性 Mn-Ln SMM 的实例。这 3 个金属离子通过 6 个水杨醛配体上的 6 个 μ<sub>2</sub>-酚酸氧原子连接,形成[Dy<sub>2</sub>Mn(μ<sub>2</sub>-O)<sub>6</sub>]<sup>2+</sup>核(图 1(a))。交流磁化率测试表明,配合物 1 和 2 在外加磁场为零的情况下,其实部和虚部交流磁化率均表现出较强的温度和频率依赖性。对于 1 和 2 利用广义 Debye 模型拟合得出 2 的 α 参数值相对较高,2 表现出双重弛豫途径,这可能是由于 Dy<sup>III</sup> 离子的单离子行为和 Dy<sup>III</sup> 与 Mn<sup>II</sup> 离子之间的弱耦合。在较高温度下,单个 Dy<sup>III</sup> 离子主导的弛豫过程,有效能垒为 92.4 (2) K,弛豫时间为  $5.37 \times 10^{-8}$  s。在较低温度下,由于 Dy 和 Mn 之间存在弱的耦合作用,随着温度的降低,χ''(ν)的最大值逐渐向低频偏移,证实了配合物 1 和 2 在零直流场下存在慢磁弛豫行为,其能量势垒为 15.4 (4) K (图 1(b))。



**Figure 1.** The molecular structure (a) and  $\ln(\tau)$  versus  $T^{-1}$  plot under zero-dc field (b) for **2**. The solid line is fitted with the Arrhenius law

**图 1.** 2 的分子结构(a)和磁化弛豫时间  $\ln(\tau)$  相对于  $T^{-1}$  的图(b)。实线是通过拟合 Arrhenius 定律得到

2017年 Powell 等[12]合成了一种含有叠氮化物的配合物  $\text{TBA}_2[\text{Mn}_4\text{Dy}_2(\text{teaH})_4(\text{N}_3)_{12}]$  (**3**, TBA = 四丁基铵,  $\text{teaH}_3 =$  三乙醇胺)。该配合物由一个中心对称的重阴离子簇  $[\text{Mn}_4\text{Dy}_2(\text{teaH})_4(\mu\text{-N}_3)_2(\text{N}_3)_{10}]^{2-}$  和两个作为电荷平衡的四丁基铵离子组成。在结构上, 每个  $\text{Dy}^{\text{III}}$  与两个去质子化的  $\text{teaH}^{2-}$  配体配位, 将  $\text{Dy1}$  与  $\text{Mn1}$ 、 $\text{Mn1A}$  和  $\text{Mn2}$  离子连接起来。此外, 叠氮化物配体连接  $\text{Dy1}$  和  $\text{Mn1A}$  离子。由于阴离子团簇的中心对称性, 形成了蝴蝶形状的  $\{\text{Mn}_2\text{Dy}_2\}$  内核。其余叠氮化物配体与 4 个 Mn 离子配位, 使  $\text{Mn1}$  和  $\text{Mn2}$  离子分别呈扭曲的八面体构型和四方锥体配位构型, 而  $\text{Dy}^{\text{III}}$  则呈现出单帽四方反棱柱配位构型(图 2)。配合物 **3** 的交流磁化率显示出温度和频率的依赖性行为, 没有出现完整的峰值。利用广义德拜公式进行拟合, 得到有效能垒为 43.8 K, 指前因子  $\tau_0$  为  $1.47 \times 10^{-10}$  s。Cole-Cole 图显示在 **3** 中存在不止一个弛豫过程, **2** 与 **3** 均不止一个弛豫过程。

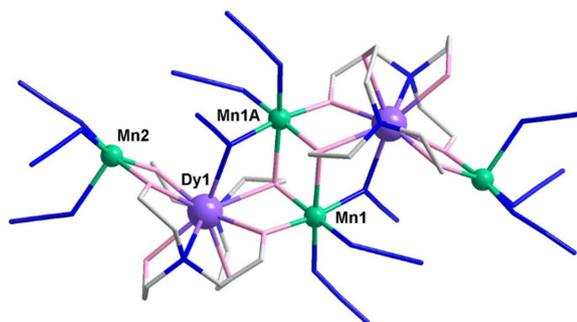


Figure 2. The molecular structure of **3**  
图 2. **3** 的分子结构

2022年, Keith S. M.等[13]报道了一系列三核配合物  $[\text{Ln}_2\text{Mn}(\text{QCl})_8]$  ( $\text{HQCl} =$  5-氯-8-喹啉酸酯;  $\text{Ln} =$  Tb (**4**); Dy (**5**); Er)。在配合物 **4**、**5** 和  $[\text{Er}_2\text{Mn}(\text{QCl})_8]$  中, 三个金属离子呈线性排列, 两个末端的  $\text{Ln}^{\text{III}}$  离子通过三个羧酸氧原子与中心的 Mn 离子相连。在 8 个 QCl 配体中, 两个位于配合物的两端, 并且仅与  $\text{Ln}^{\text{III}}$  离子相连。其余 6 个配体连接  $\text{Ln}^{\text{III}}$  和 Mn 离子, 导致 Mn 离子形成扭曲的八面体配位环境(图 3(a))。配合物 **4**、**5** 和  $[\text{Er}_2\text{Mn}(\text{QCl})_8]$  在 1.8~10 K 范围内进行交流磁化率测试。在零直流场下, **5** 表现出明显的频率依赖信号, 并表现出两个弛豫过程。快速弛豫过程归因于与温度无关的 QTM。在整个温度范围内,  $\ln \tau$  vs  $T^{-1}$  数据呈现出接近线性的趋势, 因此符合 Arrhenius 定律, 得到 **5** 的有效能垒为 44.5 K (图 3(b))。与配合物 **5** 相比, 配合物 **4** 的能量势垒较低, 为 20.3 K, 而配合物  $[\text{Er}_2\text{Mn}(\text{QCl})_8]$  没有出现任何虚部信号。

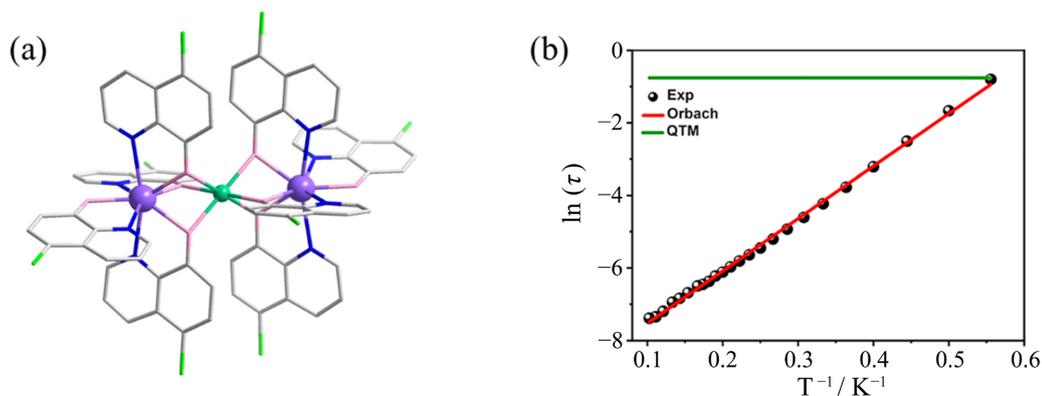
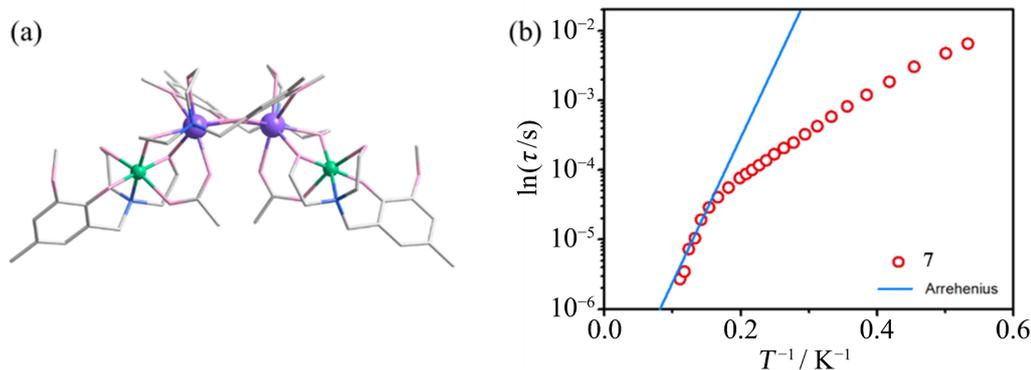


Figure 3. The molecular structure of **4** (a) and plot of  $\ln(\tau)$  vs  $T^{-1}$  for **5** (Black dots) (b). The red line is fitted using an Orbach-only mechanism of relaxation

图 3. **4** 的分子结构图(a)和 **5** 的  $\ln(\tau)$  vs  $T^{-1}$  曲线(黑点) (b)。红线是用 Orbach 弛豫机制拟合的

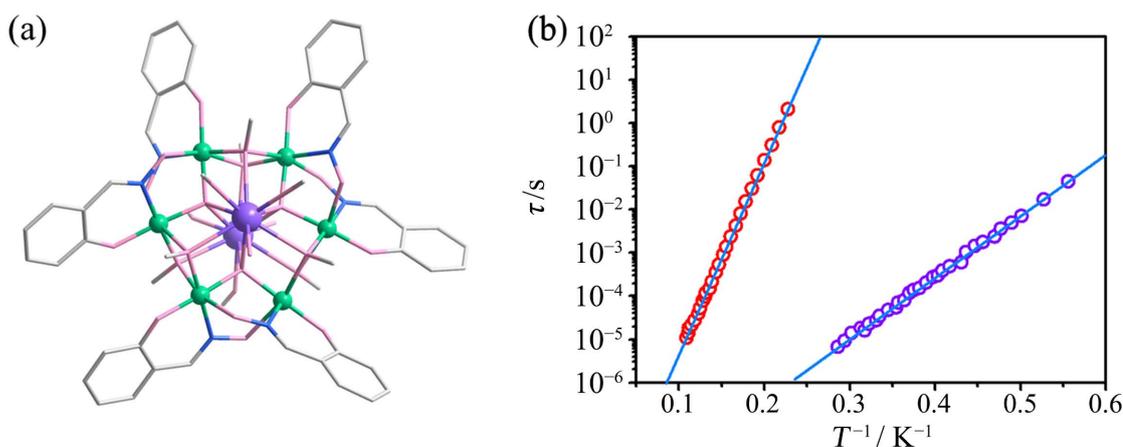
2013 年, Chandrasekhar 研究组[14]成功合成了一例四核配合物  $[\text{Mn}_2\text{Ln}_2(\text{HL}^1)_4(\mu\text{-OAc})_2(\text{NO}_3)_2 \cdot 2\text{CH}_3\text{OH} \cdot 3\text{H}_2\text{O}$  ( $\text{Ln} = \text{Dy}$  (**6**),  $\text{Tb}$  (**7**),  $\text{H}_3\text{L}^1 = 2,2'-(2\text{-羟基-3-甲氧基-5-甲基苄基二基})二乙醇$ )。在  $\text{Ln}^{\text{III}}$  和  $\text{Mn}^{\text{III}}$  之间, 有两种不对称取代多齿配体  $\text{H}_3\text{L}^1$  和醋酸桥桥联; 而两个  $\text{Ln}^{\text{III}}$  通过两个配体的氧原子相互连接, 形成三个连续的四元环, 整体呈梯形的金属骨架(图 4(a))。在交流磁化率测试中, **6** 和 **7** 表现出慢磁弛豫行为, **6**、**7** 的弛豫现象不仅与  $\text{Ln}^{3+}$  中心的  $m_j$  态的零场分裂有关, 而且在一定程度上也受到了 Jahn-Teller 畸变  $\text{Mn}^{3+}$  中心磁各向异性的影响。由于  $\text{Mn-Ln-Ln-Mn}$  主链呈拱型,  $\text{Ln}^{3+}$  离子的各向异性轴和  $\text{Mn}^{3+}$  离子的 Jahn-Teller 轴并非共线取向, 降低了有效能垒(图 4(b))。



**Figure 4.** The molecular structure (a) and Magnetization relaxation time  $\ln(\tau)$  vs  $T^{-1}$  plot (b) for **7** (red dots). The blue solid line is fitting curve with the Arrhenius law

**图 4.** **7** (红点) 的分子结构图(a)和  $\ln(\tau)$  vs  $T^{-1}$  图(b)。蓝色实线是通过 Arrhenius 定律拟合得到

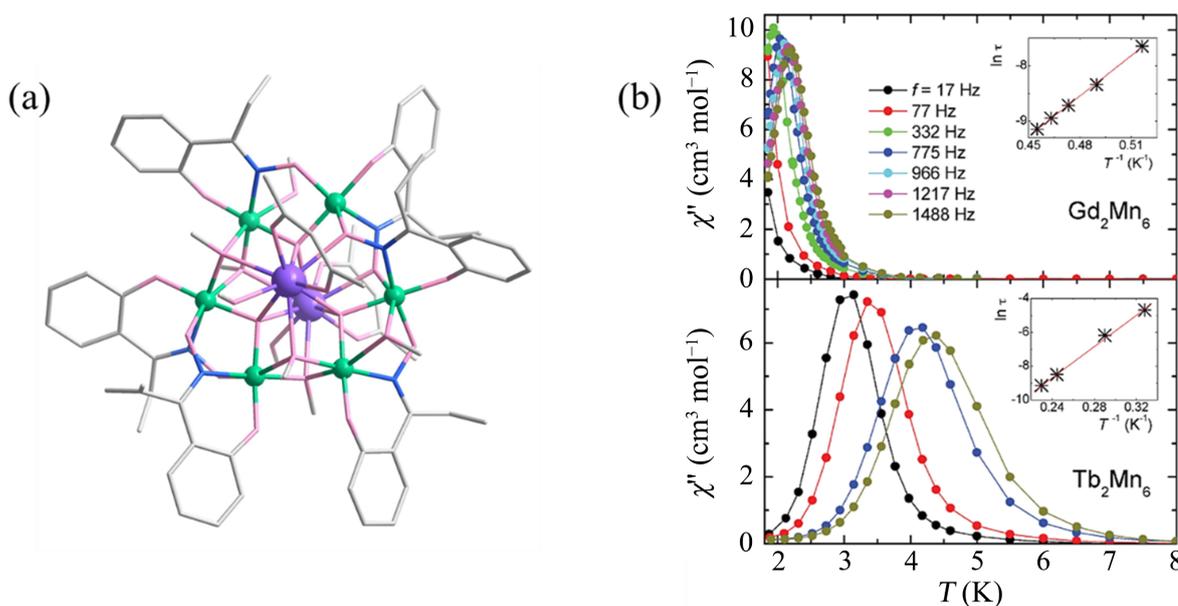
2011 年, Stefanie Dehnen 等[23]成功合成了含有  $\{\text{Mn}^{\text{III}}_6\text{O}_3\text{Ln}_2\}$  ( $\text{Ln} = \text{La}$  (**8**),  $\text{Tb}$  (**9**)) 单元的  $\text{Mn-Ln}$  SMM。在该配合物中, 6 个  $\text{Mn}^{\text{III}}$  离子通过水杨醛肟配体和  $\mu_4\text{-O}$  桥相互连接, 形成近似平面结构。此外, 这 6 个  $\text{Mn}^{\text{III}}$  离子围绕中央  $\text{Ln-Ln}$  轴以循环方式排列(图 5(a))。与类似的  $\{\text{Mn}^{\text{III}}_6\text{O}_3\text{Ln}_2\}$  核配合物相比[36], 配体配位模式在 **8** 和 **9** 内的明显改变导致 6 个  $\text{Mn}^{\text{III}}$  离子的 Jahn-Teller 轴的非共线取向。因此, **8** 和 **9** 表现出近乎完美的  $\text{C}_3$  对称结构, 有效地减弱了量子隧穿的影响。值得注意的是, 由于  $\text{Tb}^{\text{III}}$  离子固有的磁性各向异性, **9** 的有效能垒达到了 103 K (图 5(b)) [13]。



**Figure 5.** The molecular structure (a) and magnetization relaxation time  $\tau$  vs  $T^{-1}$  plot for **8** (violet dots) and **9** (red dots) in zero dc-field (b). The blue solid line is fitting curve with the Arrhenius law

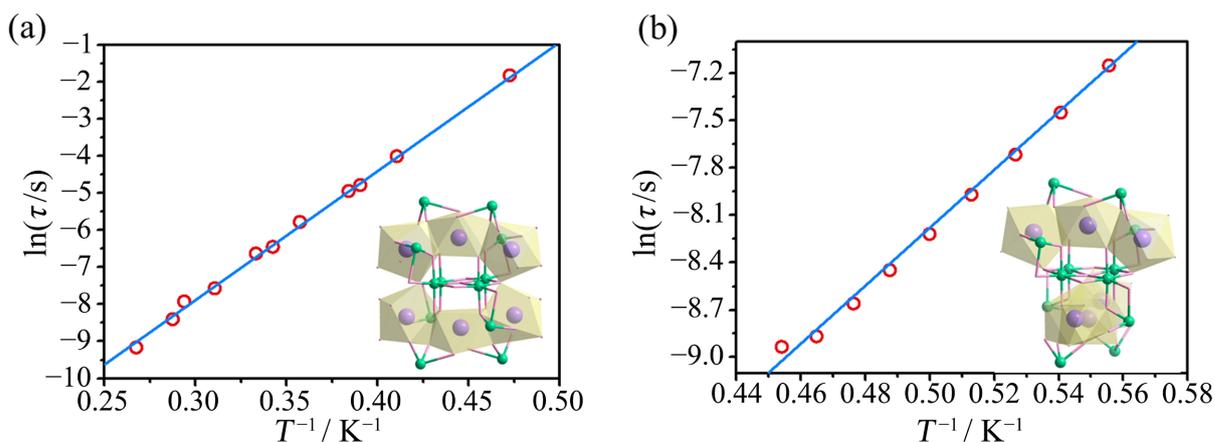
**图 5.** 配合物 **8** 和 **9** 的分子结构(a)和磁化弛豫时间  $\tau$  vs  $T^{-1}$  图(b)。紫点: **8**; 红点: **9**。蓝色实线为通过 Arrhenius 定律得到的拟合曲线

2011年, Euan K. B. [29]利用水杨醛肟衍生配体(R-saoH<sub>2</sub>, R = Me, Et)成功地合成了六方棱柱形 3d-4f 配合物{Mn<sup>III</sup><sub>6</sub>Ln<sup>III</sup><sub>2</sub>} (Ln = Gd (**10**), La, Tb (**11**)). 配合物 **10** 和{Mn<sup>III</sup><sub>6</sub>La<sup>III</sup><sub>2</sub>}的金属骨架由 6 个 Mn<sup>III</sup> 组成的非平面六边形结构, 顶部和底部各有一个 Ln<sup>III</sup>. Ln<sup>III</sup> 通过 3 个 μ<sub>4</sub>-O<sup>2-</sup>和 4 个 μ<sub>3</sub>-MeO 桥联到 Mn<sup>III</sup> 上, 形成[Ln<sup>III</sup><sub>2</sub>Mn<sup>III</sup><sub>6</sub>O<sub>3</sub>(MeO)<sub>4</sub>]<sup>14+</sup>单元。此外, 配体 Et-sao<sup>2-</sup>采用两种不同的配位模式。其中一种模式通过 μ:η<sup>1</sup>:η<sup>1</sup>:η<sup>1</sup> 的方式连接到[Mn<sub>6</sub>]循环结构中的 Mn<sup>III</sup>, 另一种是通过 μ<sub>3</sub>:η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup> 的方式连接 Mn<sup>III</sup> 和 Ln<sup>III</sup> (图 6(a)). 在与配合物 **10** 和{Mn<sup>III</sup><sub>6</sub>La<sup>III</sup><sub>2</sub>}类似的配合物 **11** 中, Et-sao<sup>2-</sup>配体被 Me-sao<sup>2-</sup>取代。磁化率测试结果表明, **10** 和{Mn<sup>III</sup><sub>6</sub>La<sup>III</sup><sub>2</sub>}表现出 SMM 行为。配合物 **10** 的有效能垒为 24 K, τ<sub>0</sub> 值为 1.7 × 10<sup>-9</sup> s。相反, 与配合物 **10** 相比, 配合物 **11** 的能量势垒明显增强, 达到 46.3 K (图 6(b)).



**Figure 6.** The molecular structure of **10** (a) and plot of the out-of-phase ( $\chi''$ ) ac susceptibility for **10** (top) and **11** (bottom) measured at the indicated temperatures and frequencies (b)

图 6. **10** 的分子结构(a)和 **10** (上)和 **11** (下)在指定温度和频率下测量的虚部( $\chi''$ )交流磁化率图(b)



**Figure 7.** Magnetization relaxation time  $\ln(\tau)$  vs  $T^{-1}$  plot for **12** (a) and **13** (b)

图 7. **12** (a)和 **13** (b)的  $\ln(\tau)$  vs  $T^{-1}$  图

同年, 童明良等[46]合成了两种 3d-4f 配合物, 即[Dy<sub>6</sub>Mn<sub>12</sub>O<sub>7</sub>(OH)<sub>10</sub>(OAc)<sub>14</sub>(mpea)<sub>8</sub>·20H<sub>2</sub>O·4MeOH (**12**)

和 $[\text{Dy}_6\text{Mn}_{12}\text{O}_9(\text{OH})_8(\text{OAc})_{10}(\text{mpea})_8(\text{mp})_2(\text{MeOH})_2(\text{H}_2\text{O})_2]\cdot 26\text{H}_2\text{O}\cdot 2\text{MeOH}$  (**13**,  $\text{Hmp}$  = 2-羟基-5-甲基-二苯二醛;  $\text{H}_2\text{mpea}$  = 2-羟基-3-((2-羟乙基)甲基)-5-甲基苯甲醛)。配合物 **12** 和 **13** 的金属骨架由 $[\text{Mn}^{\text{III}}_8\text{O}_{13}]$ 单元组成。这些单元包含一个扭曲的四边形 $[\text{Mn}^{\text{III}}_4\text{O}_5]$ 片段, 其中 $[\text{Mn}^{\text{III}}_4\text{O}_5]$ 的中心氧原子在配合物 **12** 中充当 $\mu_4$ -氧桥, 连接 $[\text{Mn}^{\text{III}}_4]$ 单元, 而在配合物 **13** 中, 它充当 $\mu_5$ -O 桥, 连接 $[\text{Mn}^{\text{III}}_4]$ 单元和 $[\text{Dy}^{\text{III}}_3]$ 三聚体的中心  $\text{Dy}^{\text{III}}$  离子(图 7)。配合物 **12** 和 **13** 之间最显著的区别在于 $[\text{Dy}^{\text{III}}_3]$ 单元的朝向。这些 $[\text{Dy}^{\text{III}}_3]$ 单元在配合物 **12** 和 **13** 中分别几乎平行和垂直。这种差异导致配合物 **12** 和 **13** 中 $[\text{Mn}^{\text{III}}_4\text{O}_5]$ 单元的 Jahn-Teller 轴的取向不同, 导致其基态自旋值和慢磁弛豫行为的明显差异。在交流磁化率测量中, 这两种配合物都表现出单分子磁性行为。值得注意的是, 配合物 **12** 具有更高的自旋和共线的局部各向异性轴, 表现出更高的能量势垒和阻塞温度。

2010 年, Christou 课题组[49]合成了一种多核配合物 $\{\text{Mn}_{21}\text{Dy}\}$ (**14**), 主要由 $[\text{DyMn}^{\text{IV}}_3\text{O}_4]^{7+}$ 立方体构成。立方体的上下部分分别与一个由 7 个  $\text{Mn}^{\text{II}}$  离子组成的非共面环和另一个由 8 个  $\text{Mn}^{\text{III}}$  离子组成的非共面环相连。此外, 三个  $\text{Mn}^{\text{III}}$  离子通过  $\text{O}^{2-}$  桥接(图 8(a))。值得注意的是, 在这个配合物中, 在 Dy 和 Mn 之间存在大量的  $\text{O}^{2-}$ , 促进了有效的磁交换相互作用, 得到有效能垒为 74 K (图 8(b))。与其他报道的多核 Mn-Ln-SMMs 相比, **14** 表现出优异的磁性能。

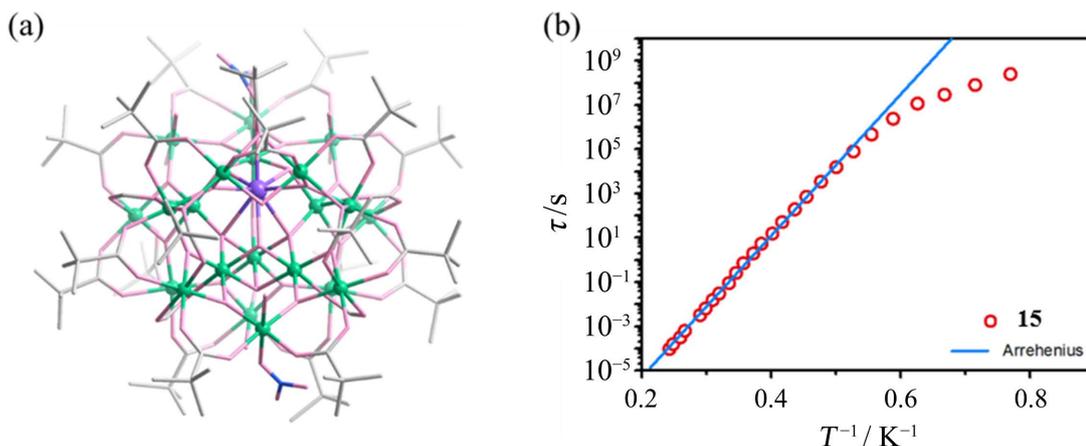


Figure 8. The molecular structure (a) and plots of  $\tau$  vs  $T^{-1}$  (b) for complex **14**

图 8. 配合物 **14** 的分子结构(a)和  $\tau$  vs  $T^{-1}$  图(b)

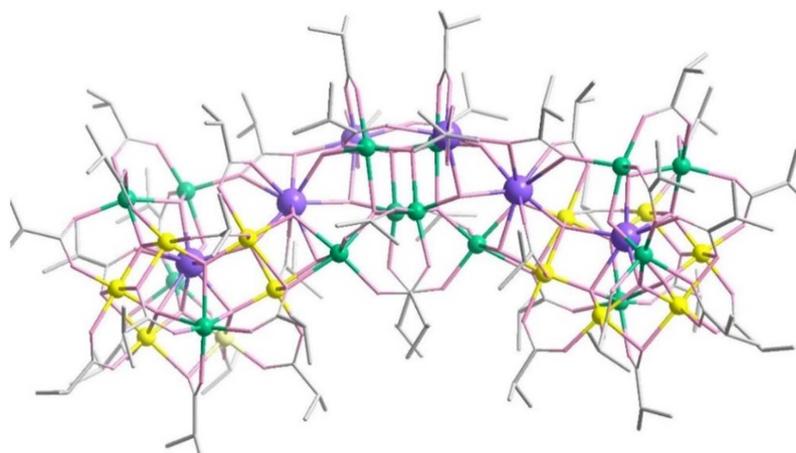


Figure 9. The molecular structure of **15**

图 9. **15** 的分子结构

2019年, Svetlana G. B.等[50]成功合成了一例混价杂金属多核配合物, 其分子式为 $[\text{Mn}_{26}\text{Dy}_6\text{O}_{16}(\text{OH})_{12}(\text{O}_2\text{CCHMe}_2)_{42}]$  (**15**)。该配合物具有 $[\text{Mn}^{\text{II}}_{10}\text{Mn}^{\text{III}}_{16}\text{Dy}^{\text{III}}_6]^{86+}$ 核, 由14个 $\mu_4\text{-O}$ , 2个 $\mu_3\text{-O}$ 和12个OH<sup>-</sup>连接金属离子构成。中心部分包括一个 $[\text{Mn}^{\text{III}}_4\text{O}_4]$ 单元, 而另外的12个 $\text{Mn}^{\text{III}}$ 离子在其周围形成两个外围六角形环。此外, 核心被42个异丁酸基团配位(图9)。配合物内的 $\text{Mn}^{\text{II}}$ 和 $\text{Mn}^{\text{III}}$ 离子呈畸变八面体构型, 而 $\text{Dy}^{\text{III}}$ 离子呈八配位的三角十二面体构型或九配位的单帽四方反棱柱构型。值得注意的是, **15**的 $\chi_{\text{mT}}$ 值随着温度的降低而降低, 在30 K以下迅速下降, 证明配合物内存在反铁磁相互作用, 下降是由于Dy Stark亚能级的热布居减少和磁相互作用。交流磁化率的频率依赖性揭示了液氮温度下的慢磁化动力学, 有效能垒为46 K。

### 3. 结论

$\text{Mn}^{\text{III}}$ 离子含有的未成对d电子数较多, 同时有多种不同的价态可以在同一配合物中形成两种磁性中心, 零场分裂效应也较强, 适合于形成高自旋分子, 从而趋向获得比较强的磁性分子。因此含有锰离子的配合物由于其自身优越性, 是3d-4f配合物中研究最多, 数量最多的。 $\text{Mn-Ln}$ 配合物是3d-4f异金属配合物中研究较早, 原因在于磁各向异性较大的稀土离子引入到过渡金属配合物中可提高单分子磁体的能垒及其阻塞温度。锰-稀土配合物中至少有一个磁各向异性较大的三价锰离子, 合成出的主要有环状八核, 线形三核, 铃形十三核等配合物。人们研究 $\text{Mn-Dy}$ 单分子磁体发现尽管大多数分子都是 $\text{Mn-Dy}$ 异金属配合物表现出较好的单分子磁体性质, 但也有少数配合物的能垒比Dy的要高。这可能与Mn金属的3d轨道与Ln的4f轨道发生一定的磁耦合作用而使分子轨道能级发生变化有关。

综合以上研究进展, 本文综述了不同结构类型且单分子磁体性能优异的 $\text{Mn-Ln}$ 单分子磁体。随着科学技术的不断进步, 期望进一步设计合成新型配体, 能够定向设计合成和优化 $\text{Mn-Ln}$ 单分子磁体的结构, 增强其磁学性能, 为稀土-过渡异金属单分子磁体的应用和发展做出了重要贡献。

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