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钴－稀土单分子磁体的研究进展

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摘　要

在Co(II)离子中，d轨道上总共有7个电子，其中3个为不成对电子。由于它的轨道角动量未淬灭且自旋轨道耦合相对较强，Co^{II}表现出明显的磁各向异性，使其成为磁性材料中优良且稳定的自旋载体。同时，Co^{II}容易氧化为Co^{III}，在配位环境中通常表现出抗磁性行为。这一特性在3d-4f单分子磁体(SMMs)中被用作磁稀释剂，有效抑制QTM。研究人员利用这些特性合成了许多钴－稀土(Co-Ln)SMMs。因此，本文通过对近年来典型的钴－稀土单分子磁体进行综述，以期为3d-4f单分子磁体的发展奠定一定的基础。

关键词

钴－稀土单分子磁体，结构，磁性

Research Progress in Co-Ln Single-Molecule Magnets

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Abstract

In the Co (II) ion, there are a total of 7 electrons present in the d orbitals, including 3 unpaired electrons. Due to its unquenched orbital angular momentum and relatively strong spin-orbit coupling, Co^{II} exhibits significant magnetic anisotropy, making it an excellent and stable spin carrier within magnetic materials. Simultaneously, Co^{II} readily undergoes oxidation to Co^{III}, which often

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exhibits diamagnetic behavior in coordination environments. This property is harnessed in 3d-4f single molecule magnets (SMMs)to serve as a magnetic diluter, effectively suppressing QTM. Researchers have exploited these characteristics to synthesize numerous Co-Ln SMMs.

Keywords

Co-Ln Single Molecule Magnets, Structure, Magnetism

1. 引言

单分子磁体领域的研究始于 90 年代初，意大利科学家 Sessoli 等[1] [2]报道了一例具有高自旋态的混合价锰的簇合物，并且发现该化合物具有磁体行为。单分子磁体(single-molecule magnets, SMMs)是一类纳米尺度的磁性材料，由于其具有特殊的量子特性，在量子比特、高密度信息存储和分子自旋电子学等方面具有潜在的应用价值而备受关注。相对于传统的磁性存储材料，单分子磁体尺寸通常小于 3 nm，且每个分子高度一致，可以在性质上保证完全一致。此外，单分子磁体在化学上易于调控，且可以溶解在普通溶剂中，易于成膜，可降低成本。

在过去的十几年里，关于 f 元素的配合物发表数量呈指数级增长，这些化合物大多都显示出磁矩的缓慢弛豫。稀土离子具有显著的单离子各向异性，大的磁矩使其成为 SMMs 的优良自旋载体。然而，由于 4f 轨道的有限径向伸展展现出了非常弱，甚至没有交换作用的现象。而其中一种提供强磁交换相互作用的方法是将 3d 离子引入 4f 系统，并且分子的大基态和磁各向异性可以通过控制磁交换相互作用力来引导。通过增加配合物中 3d 和 4f 离子之间的磁耦合，利用 4f 离子的单离子各向异性来增加有效能垒(U_{eff}) [3]。因此，利用 f 元素的大磁矩和各向异性，3d-4f 磁耦合抑制量子隧穿效应(QTM)，从而获得高性能的 3d-4f SMMs [4]-[10]。

在 Co(II)离子中，d 轨道上总共有 7 个电子，其中 3 个为不成对电子。与镧系金属离子相比，虽然 3d 过渡金属离子没有很强的自旋轨道耦合和磁矩，但是其受配体场的影响较大。通常，弱的配体场会导致电子基态和激发态之间的 d 轨道能量分裂能隙变小，进而使自旋轨道耦合最大化，从而增强磁各向异性[11]-[13]。同时，Co^{II}容易氧化为 Co^{III}，在配位环境中通常表现出抗磁性行为。为了实现对于建立 3d-4f 稳定构型的控制，进行大量的实验探究是必不可少的，归根结底，如果结构能够稳定建立，应该是合成显示出某种特定属性的目标配合物，但显然，实现这一目标还是一个漫长的过程。因此，本文通过对近年来典型的钴-稀土单分子磁体进行综述，以期为 3d-4f 单分子磁体的发展奠定一定的基础。

2. 钴－稀土单分子磁体的研究进展

目前，已报道的钴－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。

2.1. [Co_2Dy]型单分子磁体

近年来，随着人们对稀土配合物的不断研究，由镧系金属与有机配体形成的多功能配合物在许多领

域表现出了其特殊的应用价值。2012 年唐金魁研究组利用多齿席夫碱配体成功合成了一例线性四核配合物[$Co_2Dy_2(L^1)_2(CH_3COO)_4(OH)_2(H_2O)_2$] ($ClO_4$)$_2$ 4CH_3CN (**1**，H_2L^1 = N1，N3-双(3-甲氧基水杨亚胺)二乙烯三胺) [14] (图 1)。相较于其他配合物而言，所得配合物 **1** 结构简单。磁性研究表明，在高于 6 K 的弛豫过程中遵循热激活 Orbach 弛豫。根据公式拟合，有效能垒为 33.8 K，τ_0 为 3.73×10^{-6} s。低于 6 K 时，数据偏离了 Orbach 弛豫，表明热激活弛豫过程逐渐被直接过程所取代。由于存在抗磁性 Co^{III}，配合物 **1** 中的磁核可视为由四个乙酸盐配体连接的 Dy_2 系统。抗磁部分有效降低了 Dy_2 二聚体磁核之间的磁相互作用，从而提高了 SMM 的有效能垒。

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

Complexes	H_{dc}/k Oe	U_{eff}/K	τ_0/s	v/m T/s	T_B/K	Ref
[$Co_2Dy_2(L^1)_2(CH_3COO)_4(OH)_2(H_2O)_2$]·($ClO_4$)$_2$·4$CH_3CN$ (**1**)	0	33.8	3.73×10^{-6}			[14]
[Co_2Dy(valdien)$_2(OCH_3)_2$(chp)$_2$] (**2**)	2	71.4(4.2)	$5.6(0.3) \times 10^{-6}$			[15]
[Co_2Tb(valdien)$_2(OCH_3)_2$(chp)$_2$] (**3**)	2	32.3(2.6)	$2.5(1.1) \times 10^{-10}$			[15]
$Dy_2Co_2(L^2)_{10}$(bipy)$_2$ (**4**)	0	118(3)	1.85×10^{-11}			[16]
[$DyCo(CN)_6$(hep)$_2(H_2O)_4$] (**5**)	2	63	7.1×10^{-11}			[17]
[$Dy_2Co^{II}(C_7H_5O_2)_8$]·6H_2O (**6**)	0	127.27(2)	1.69×10^{-9}			[18]
[$Co_2Dy((L^3)^{Br})_2(H_2O)$]$NO_3$·3$H_2O$ (**7**·3H_2O)	0	422	2.4×10^{-11}			[19]
[$Co_2Dy((L^3)^{Br})_2(H_2O)$]$NO_3$ (**7**)	0	600	1.4×10^{-11}			[19]
[$Co_2Dy((L^3)^{Br})_2(H_2O)$]$NO_3$ (**7**·H_2O)	0	522	1.8×10^{-10}			[19]
[$Co_2Dy(TTTT^{Cl})_2$(MeOH)]NO_3·3MeOH (**8**)	0	401(13)	$1.3(6) \times 10^{-10}$			[20]
[$Co_2Dy(TTTT^{Cl})_2$(MeOH)] [$Co(HTTTT^{Cl})$] (**9**)	0	536(10)	$3.8(10) \times 10^{-11}$	20	10	[20]
(PPh_4)[Dy_2(bbpen)$_2${$Co(CN)_6$}]·3.5MeCN (**10**)	2	1075(22)	4.51×10^{-13}			[21]
[$L^4CoYCoL^4$]NO_3·CH_3OH	2	53 K	7.66×10^{-7}			[22]
[$L^5CoYCoL^5$]NO_3·CH_3OH	2	51.3	2×10^{-6}			[22]
[$L^5CoGdCoL^5$]NO_3	0	29.4	1.47×10^{-7}	2	1.1	[22]
[$L^5CoGdCoL^5$]ClO_4·2$CHCl_3$	0	27.4	1.50×10^{-7}	2	1.6	[22]
[$L^5CoGdCoL^5$]($C_5HF_6O_2$)	0	29.5	1.3×10^{-7}	2	1.6	[22]
[$Co_2Dy_2(L^1)_2$(pdm)$_2(CH_3COO)_2(CH_3OH)_2$]	0	64.6(1)	$1.3(7) \times 10^{-6}$			[23]
[$Dy_2Co^{III}_2(OMe)_2$(teaH)$_2(O_2CPh)_4(MeOH)_4$] (NO_3)$_2$·MeOH·H_2O (**11**)	0	88.8(2)	5.64×10^{-8}			[24]
[$Tb_2Co^{III}_2(OMe)_2$(teaH)$_2(O_2CPh)_4(MeOH)_4$] (NO_3)$_2$·MeOH·H_2O (**12**)	1	14.31(1)	2.84×10^{-6}			[24]
[$Dy_2Co^{III}_2(OMe)_2$(dea)$_2(O_2CPh)_4(MeOH)_4$] (**13**)	0	102.9	6.05×10^{-8}			[25]
[$Dy_2Co^{III}_2(OMe)_2$(mdea)$_2(O_2CPh)_4(NO_3)_2$] (**14**)	0	78.6	1.03×10^{-7}			[25]
[$Dy_2Co^{III}_2(OMe)_2$(bdea)$_2(O_2CPh)_4(MeOH)_4$] (**15**)	0	114.4	3.38×10^{-8}			[25]
[$Dy_2Co^{III}_2(OMe)_2$(teaH)$_2$(acac)$_4(NO_3)_2$] (**16**)	0	27	8.1×10^{-6}			[26]
[$Dy_2Co^{III}_2(OH)_2$(teaH)$_2$(acac)$_4(NO_3)_2$]·4H_2O (**17**)	0	28	7.4×10^{-6}			[26]
[$Dy_2Co^{III}_2(OMe)_2$(mdea)$_2$(acac)$_4(NO_3)_2$] (**18**)	0	38	2.6×10^{-6}			[26]
[$Co^{III}_2Dy_2(OMe)_2(O_2CPh$-2-Cl)$_4$(bdea)$_2(NO_3)_2$] (**19**)	0	114.9	$1.8 \times 10{-}8$			[27]
[$Co^{III}_2Dy_2(OMe)_2(O_2CPh$-4-^{t}Bu)$_4$(bdea)$_2(NO_3)$(MeOH)$_3$] (**20**)	0	137.3	5.6×10^{-8}			[27]
[$Co^{III}_2Co^{II}Dy(OH)(O_2CPh$-4-OH)(bdea)$_3(NO_3)_3$(MeOH)] (**21**)	1.5	167.3	3.4×10^{-7}			[27]
[$Co^{III}_2Dy_2(OMe)_2(O_2CPh$-2-$CF_3)_4$(bdea)$_2(NO_3)_2$] (**22**)	0	125.8	1.4×10^{-8}			[27]
[$Co^{III}_2Dy_2$(mdea)$_4$(hfacac)$_3(O_2CCF_3)(H_2O)$] (**23**)	0	32.3	1.4×10^{-6}			[27]
[$Co^{III}_2Dy_2(\mu_3$-OH)$_2$(o-tol)$_4$(mdea)$_2(NO_3)_2$]	0	116.9(2)	9.8×10^{-9}			[28]
[$Co^{III}_2Tb_2(\mu_3$-OH)$_2$(o-tol)$_4$(mdea)$_2(NO_3)_2$]	5	49.2	6.6×10^{-11}			[28]
[$Co_2Dy_2(L^6)_4(NO_3)_2(THF)_2$]·4THF (**24**)	0	117.4	6.2×10^{-7}	235	3	[29]
[$Co_2Dy_2(L^6)_4(NO_3)_2(MeOH)_2$]·2$CH_2Cl_2$	0	104.8	9.2×10^{-7}			[30]

续表

$[Co_2Dy_2(L^6)_4(NO_3)_2(DMF)_2]\cdot 2C_2H_6CO$	0	94.5	$.2 \times 10^{-6}$			[30]
$[Dy_2Co_2(L^5)_4(NO_3)_2(DMF)_2]\cdot 2DMF$	0	125.1	2.67×10^{-6}			[31]
[Dy(4-MMNO)$(H_2O)_5$][Co$(CN)_6$] (**25**)	0	595(3)	1.29×10^{-11}	50	25	[32]
$[CoDy_3(HBpz_3)_6(dto)_3]\cdot 4CH_3CN\cdot 2CH_2Cl_2$ (**26**)	0.8	52	3.6×10^{-8}			[33]
$[Co_4Dy_2(\mu_3\text{-}O)_2(\mu\text{-}N_3)_2(OH)_2(H_2O)_2(HL^7)_4]$	0	73.5	1.86×10^{-8}			[34]
$[L^8{}_2Co^{II}{}_2Gd^{III}][NO_3]$	0	27.2	1.7×10^{-7}			[35]
$[Co_2Dy_{10}(L^9)_4(OAc)_{16}(SCN)_2(MeCN)_2(H_2O)_4(OH)_2(\mu_3\text{-}OH)_4]\cdot 2Co(SCN)_4\cdot H_2O\cdot 2MeCN\cdot 2H_2O$	0	25	3.14×10^{-6}			[36]
$[Co^{III}{}_2Dy_4(OH)_2(ib)_8(bdea)_2(NO_3)_4(H_2O)_2]\cdot 2MeCN$	0	26.6	2.26×10^{-5}			[37]
$[Co^{III}{}_3Dy_3(\mu_3\text{-}OH)_4(O_2C^tBu)_6(teaH)_3]\cdot(NO_3)_2\cdot H_2O$	2	17.5	2.3×10^{-6}			[38]
[Dy_2Co_2(2, 3-DCB)10(2, 2'-bpy)$_2$]	2	2	7×10^{-5}			[39]
$[Dy_2Co_8(\mu_3\text{-}OCH_3)_2(L^{10})_4(HL^{10})_2(OAc)_2(NO_3)_2(CH_3CN)_2]$	0	14.89	1.68×10^{-7}			[40]
$[Dy_4Co_6(L^{10})_4(HL)_2(OAc)_6(OCH2CH2OH)_2(HOCH_2CH_2OH)(H_2O)]$	0	5.49	2.88×10^{-5}			[40]
$[Dy_2Co_4(L^{11})_4(NO_3)_2(OH)_4(C_2H_5OH)_2]\cdot 2C_2H_5OH$	0	27.50	3.36×10^{-8}			[41]
$[Co^{II}{}_4Dy_4(L^{12})_4(\mu_{1,3}\text{-}Piv)_4(\mu_{1,1,3}\text{-}Piv)_2(\eta_1\text{-}Piv)_2(\mu_3\text{-}OH)_4(MeOH)_2]$	0	12.5	1.51×10^{-6}			[42]
$[Co^{III}Dy(CH_3CN)_{0.5}(L^{13})_3(NO_3)_3]$	3	2.58	3.11×10^{-5}			[43]
$[Co^{III}{}_2Dy_4(\mu_3\text{-}OH)_2(NO_3)_4(OAc)_4(L^{32})_4(DMF)_2]\cdot 2C_2H_5OH$	0	27.8	1.94×10^{-7}			[44]
$[DyCo(CN)_6(H_2L^{14})(H_2O)(DMF)]_2\cdot 5H_2O$	1	11.17	1.36×10^{-6}			[45]
$[Co^{III}{}_2Dy_3Na(CH_3CH_2COO)_6(OH)_6(NO_3)_4(H_2O)_2]$	0	60.3	9.6×10^{-8}			[46]
$[Dy_{18}Co^{II}Co^{III}{}_6(OH)_{14}(CO_3)_9(CH_3CH_2COO)_6(dea)_{12}(H_2O)_{30}]$	0	3.53	6.03×10^{-6}			[47]
$[Ni(L^{15})Dy(H_2O)_4][Co(CN)_6]\cdot 3H_2O$	0.8	47.02	6.7×10^{-9}			[48]
$[Dy(pyzic)\{Dy_3Co_2(pyzha)_6(*pyzha)(NO_3)_2(H_2O)(MeOH)_2\}]_2$	0	1.46	2.4×10^{-5}			[49]
$Dy[Co^{III}(CN)_6]$	2	58.3(5)	$1.76(13)\times10^{-6}$			[50]
$[(L^{16})_4Ru_2Co_2](BF_4)_4$	3	12.58	3.1×10^{-5}			[51]
[Nd(18-crown-6)$(H_2O)_4$][Co$(CN)_6$]$\cdot 2H_2O$	0.8	37.0	2.9×10^{-8}			[52]
$[Co^{III}{}_4Dy_3(L^{17})_4(\mu_4\text{-}O)_2(\mu\text{-}OMe)_2(\mu_{1,3}\text{-}OAc)_4(H_2O)_2(NO_3)_2]\cdot NO_3\cdot 3CH_3OH\cdot 1.5H_2O$	0	73.5	9.40×10^{-7}			[53]
$[Co^{II}{}_4Gd(OH)_2(chp)_4(saloh)_5(H_2O)(MeCN)(Solv)]$	2	86	6.95×10^{-12}			[54]
$[Co^{II}{}_4Dy(OH)_2(chp)_4(saloh)_5(H_2O)(MeCN)(Solv)]$	2	66	3.43×10^{-7}			[54]
$[Co^{II}Dy$ (R-HL^{18})(hfac)$_5$]	1.5	297.4	4.7×10^{-10}			[55]
$[Co_2Eu(NO_3)(Piv)_6(EtPy)_2]$	1	4	4.7×10^{-6}			[56]
$Co(\mu\text{-}L^{19})(\mu\text{-}CCl_3COO)Y(NO_3)_2]$	1.2	8.4(6)	$3.2(4) \times 10^{-6}$			[57]
$[Co(\mu\text{-}L^{19})(\mu\text{-}CH_3COO)Y(NO_3)_2]\cdot CH_3CN$	1.2	11.0(4)	$2.5(2) \times 10^{-6}$			[57]
$[Co(\mu\text{-}L^{19})(\mu\text{-}PhCOO)Y(NO_3)_2]\cdot 3CH_3CN\cdot 2H_2O$	1.2	13.7(8)	$2.6(4) \times 10^{-6}$			[57]
$[Co(\mu\text{-}L^{19})\text{-}(\mu\text{-}^tBuCOO)Y(NO_3)_2]\cdot CHCl_3\cdot 2H_2O$	1.2	18.7(6)	$7.4(9) \times 10^{-7}$			[57]
$[Co_6Dy_2(O)_2(dhpb)_6(NO_3)_2(DMF)_2]$	0	11.1	2.8×10^{-7}			[58]
$[Co_6Ho_2(O)_2(dhpb)_6(NO_3)_2(DMF)_2]$	1.5	7.3	2×10^{-7}			[58]
$[Co^{III}{}_2Dy_2(HL^{20})L^{20}\{(py)_2CO_2\}\{(py)_2C(OCH_3)O\}(NO_3)_4CH_3OH]$	0.6	59.4(9)	$3.1(1) \times 10^{-8}$			[59]
$[Co^{III}\{(py)_2C(OH)O\}_2][Co^{II}{}_2Dy^{III}{}_4Dy^{III}(HL^{20})_4(L^{20})_4]$	0.8	10.9(6)	$3.5(3) \times 10^{-8}$			[59]
$[Co_2Dy_2(L^{21})_4(Ac)_2(DMF)_2]\cdot 3CH_3CN$	0	15	2.37×10^{-5}			[60]
$Na[Co^{III}{}_2Co^{II}Ce_{0.65}Dy_{0.35}(H_3L^{22})_2(OAc)_2(NO_3)_2]Cl_2\cdot 4H_2O$	1.5	2.13	1.03×10^{-4}			[61]
$[Co_2La(HL^{42})_4(NO_3)]$ $(NO_3)_2$	1.5	10.65	1.6×10^{-4}			[62]
$[Co_2Pr(HL^{42})_4(NO_3)]$ $(NO_3)_2$	2	15.03	2.63×10^{-7}			[62]
$[Co_2Gd(HL^{24})_4(NO_3)](NO_3)_2$	0	6.69	3.73×10^{-8}			[63]
$[Co_2Tb(HL^{24})_4(NO_3)](NO_3)_2$	0	1.0	3.15×10^{-5}			[63]
$[Co_2Dy(HL^{24})_4(NO_3)](NO_3)_2$	0	0.58 s	3.86×10^{-5}			[63]

续表

$[Co^{III}_2Dy_4(\mu_3\text{-}OH)_2(NO_3)_4(OAc)_4(L^{25})_4(DMF)_2]\cdot 2C_2H_5OH$	0	31.6	5.66×10^{-6}			[64]
$[Dy_2Co(2,3\text{-pzdc})_4(H_2O)_4]\cdot 4H_2O$	2	5	10^{-5}			[65]
$[L^{26}Co^{III}Br_2Dy(acac)_2]\cdot CH_2Cl_2$	0	167.66(0.03)	$8.28(5)\times10^{-8}$	5	3.5	[66]
$[L^{27}Co^{III}Cl_2Dy(acac)Cl(MeO)]$	0	118.72(4.27)	$4.76(2)\times10^{-7}$	5	3	[66]
$[L^{27}Co^{III}Cl_2Dy(acac)Cl(H_2O)]$	0	75.28(13.02)	$3.47(1)\times10^{-6}$	5	3	[66]
$[L^{27}Co^{III}Cl_2\ Dy_{0.05}Y_{0.95}\ (acac)Cl(H_2O)]$	0	128.27(9.61)	$4.51(1)\times10^{-7}$	5	4	[66]
$[Co^{II}_5Eu^{III}_4(OMe)_8(OAc)_{12}(NO_3)_2(MeOH)_6]\cdot 4MeOH$	2	16.4				[67]
$[Co^{II}_5Dy^{III}_4(OH)_2(OMe)_6(OAc)_{10}(NO_3)_4(MeOH)_6]\cdot 4MeOH$	0	7.4				[67]
$[(\mu_3\text{-}CO_3)\{Co^{II}Dy^{III}L^{28}(\mu_3\text{-}OH)(OH_2)\}_3](ClO_4)\cdot 3H_2O$	1	9.2	1.0×10^{-7}			[68]
$[Co(H_{0.5}L^{29})Dy(DBM)_2(H_2O)](ClO_4)_{0.5}\cdot 3H_2O$	2	88.9	1.34×10^{-10}			[69]
$[Tb_2Co_2(hfac)_{10}(NITPhPybis)_2]$	0	7.98	5.4×10^{-6}			[70]
$[Dy_2Co_2(hfac)_{10}(NITPhPybis)_2]$	1	6.03	5.2×10^{-5}			[70]
$[Dy_{45}Co_7(OH)_{68}(CO_3)_{12}(CH_3COO)_{26}(CH_3CH_2COO)_6(H_2O)_{70}]$	0	4.34	3.25×10^{-7}			[71]
$[Co^{III}_6Dy^{III}_6(\mu_3\text{-}OH)_8(n\text{bdea})_6(m\text{-}CH_3C_6H_4COO)_{16}]\cdot 2H_2O\cdot 2CH_3CN$	1	20.8	8.5×10^{-7}			[72]
$[Co^{II}_2Dy_2(Hhms)_2(CH_3COO)_6(CH_3OH)_2(H_2O)_2]\cdot(NO_3)_2$	0.8	13.8	3.2×10^{-6}			[73]
$[Co^{III}_4Dy_4(\mu\text{-}F)_4(\mu_3\text{-}OH)_4(o\text{-tol})_8(mdea)_4]3H_2O\cdot EtOH\cdot MeOH$	0	55.77	1.0×10^{-6}			[74]
$[Co(\mu\text{-}L^{30})(\mu\text{-}NO_3)Y(NO_3)_2]$	1	23.9(8)	1.5×10^{-6}			[75]
$[Zn_{0.9}Co_{0.1}(\mu\text{-}L^{30})(\mu\text{-}NO_3)Y(NO_3)_2]$	1	24.8(1)	1.4×10^{-6}			[75]
$[Zn_{0.9}Co_{0.1}(\mu\text{-}L^{30})(\mu\text{-benzoate})Y(NO_3)_2]$	1	33.2(4)	2.5×10^{-7}			[75]
$[Zn_{0.9}Co_{0.1}(\mu\text{-}L^{30})(\mu\text{-9-anthracenecarboxylato})Y(NO_3)_2]$	1	34.6(9)	2.3×10^{-7}			[75]
$[Co^{III}_2Yb_2(OCH_3)_2(teaH)_2(Piv)_6]$	1.5	32.89	2.1×10^{-6}			[76]
$[Co^{III}_2Ho_2(OCH_3)_2(teaH)_2(Piv)_6]$	3	42.9	6.2×10^{-9}			[76]
$[Co^{III}_2Dy_2(OCH_3)_2(teaH)_2(Piv)_6]$	0	51	6.1×10^{-7}			[77]
$[Dy_4Co_2(\mu_3\text{-}OH)_2(NO_3)_4(CH_3COO)_4(L^{31})_4(DMF)_2]$	0	41.9	1.21×10^{-7}			[78]
$[(vdpyCH_2O)_2Co_2Dy_2ac_8]$	2.4	15.9	2.5×10^{-6}	140	0.5	[79]
$[Co^{III}_2Tb(L^{32})_2(\mu\text{-}O_2CCH_3)_2(H_2O)_3]$	1.5	15.6(4)	1×10^{-7}			[80]
$[Co^{III}_2Er(L^{32})_2(\mu\text{-}O_2CCH_3)_2(H_2O)_3]$	1	9.9(8)	8×10^{-7}			[80]
$[Dy_2Co^{III}_2(OH)_2(teaH)_2(acac)_6]\cdot MeCN$	0	71	2.7×10^{-7}			[81]
$[Dy_2Co^{III}_2(OH)_2(bdea)_2(acac)_6]\cdot 2H_2O$	0.5	38	2.7×10^{-7}			[81]
$[Dy_2Co^{III}_2(OH)_2(edea)_2(acac)_6]\cdot 2H_2O\cdot 4MeCN$	1	16	1.3×10^{-6}			[81]
$[Co^{III}_2Dy(L^{33})_2(\mu\text{-}O_2CCH_3)_2(H_2O)_3]\cdot NO_3\cdot MeOH\cdot 4H_2O$	1	88(8)	1.0×10^{-8}			[82]
$[Co^{II}Y(L^{34})(DBM)_3]$	2	8.56	1.01×10^{-4}			[83]
$[Co_2Dy_4(\mu_3\text{-}OH)_2(piv)_4(hmmp)_4(ae)_2]\cdot(NO_3)_2\cdot 2H_2O$	0.8	32.4	4.2×10^{-7}			[84]
$[(Co^{II})_3(Co^{III})_2Dy_3(\mu_3\text{-}OH)_5(O_2C^tBu)_{12}(L^{35})_2]\cdot 2H_2O$	0	3.8	1.5×10^{-6}			[85]
$[(Co^{III})_3Dy_3(\mu_3\text{-}OH)_4(O_2C^tBu)_6(L^{35})_3](NO_3)_2\cdot 2CH_3CN\cdot 2H_2O$	2	17.4	2.5×10^{-6}			[85]
$[Co(3\text{-MeOsaltn})(MeOH)_x(ac)Tb(hfac)_2]$	1	17.0(4)	$6.1(10)\times10^{-8}$			[86]
$[Co^{III}_2Dy_2(OH)_2(bdea)2(acac)_2(NO_3)_4]$	0	169	1.47×10^{-7}			[87]
$[Co(\mu\text{-}L^{36})(\mu\text{-}OAc)Y(NO_3)_2$	1	22.6	8.9×10^{-7}			[88]
$[Dy_{42}Co^{II}_9Co^{III}(\mu_3\text{-}OH)_{68}(CO_3)_{12}(CH_3COO)_{30}(H_2O)_{70}]$	0	3.67	9.78×10^{-7}			[89]
$[L^{37}CoGdCoL^{37}]NO_3$	0	21.3	1.52×10^{-7}	2	1.1	[90]
$[L^{37}CoTbCoL^{37}]NO_3$	0	14.5	3.0×10^{-6}	140	1.1	[90]
$[\{(S)P[N(Me)N{=}CH\text{-}C_6H_3\text{-}2\text{-}O\text{-}3\text{-}OMe]_3\}_2Co_2Tb]$	1.5	25.8	3.7×10^{-6}			[91]
$[\{(S)P[N(Me)N{=}CH\text{-}C_6H_3\text{-}2\text{-}O\text{-}3\text{-}OMe]_3\}_2Co_2Dy]$	0	14.2	5.1×10^{-6}			[91]
$[\{(S)P[N(Me)N{=}CH\text{-}C_6H_3\text{-}2\text{-}O\text{-}3\text{-}OMe]_3\}_2Co_2Ho]$	0	8	13×10^{-5}			[91]
$[Dy_4Co_2(HL^{38})_2(\mu_3\text{-}OH)_2(piv)_{10}(OH_2)_2]$	0	26.3	8.7×10^{-6}			[92]

续表

H_2L^1 = N1, N3-bis(3-methoxysalicylidene)diethylenetriamine; H_2valdien = N1, N3-bis(3-methoxysalicylidene)diethylenetriamine; Hchp = 6-chloro-2-hydroxypyridine; HL^2 = 3, 5-dichlorobenzoic acid; bipy = 2, 2'-bipyridine; hep = 1-(2-hydroxyethyl)-2-pyrrolidinone; $C_7H_6O_2$ = salicylic aldehyde; $(L^3)^{Br}$ = 2, 2', 2"-(((nitrilotris(ethane-2, 1-diyl))tris(azanediyl))tris(methylene))tris-(4-bromophenol); H_3TTTT^{Cl} = 2, 2', 2"-(((nitrilotris(ethane-2, 1-diyl)) tris(azanediyl)) tris(methylene))tris-(4-chlorophenol); H_2bbpen = N, N'-bis(2-hydroxybenzyl)-N, N'-bis(2- picolyl)ethylene diamine; H_2L^4 = 2-hydroxy-3-methoxybenzaldehyde with 1, 1, 1-tris(aminomethyl)ethane, Me-C(CH_2NH_2)$_3$; H_2L^5 = 2-hydroxy-3-methoxybenzaldehyde with N, N', N"-trimethylphosphorothioic trihydrazide, P(S)[NMe-NH_2]$_3$; H_2L^1 = N1, N3-bis(3-methoxysalicylidene)diethylenetriamine; pdmH_2 = 2, 6-pyridinedimethanol; teaH_3 = triethanolamine; H_3dea = diethanolamine; H_2mdea = N-methydiethanolamine; H_2bdea = N-*n*-butyldiethanolamine; acac = acetylacetonate; hfacacH = hexafluoroacetylacetone; o-tol = o-toluate; H_2L^6 = o-vanillin with 2-aminophenol; H_2L^5 = (E)-2-ethoxy-6-(((2-hydroxyphenyl)imino)methyl)phenol; 4-MMNO = 4- methylmorpholine N-oxide; dto^{2-} = dithiooxalato dianion; $HBpz^{3-}$ = hydrotris(pyrazolyl)borate; H_3L^7 = 2-[Bis(pyridin-2-ylmethyl)amino]-2-(hydroxymethyl)propane-1, 3-diol; H_3L^8 = (S)P[N(Me)NH_2]$_3$ with o-vanillin; H_2L^9 = 2-Bis(2-hydroxy-3-methoxybenzylidene) hydrazine; Hib = isobutyric acid; 2, 3-HDCB = 2, 3-dichlorobenzoic acid; H_3L^{10}= 3-amino-1,2-propanediol with 2-hydroxy-1-naphthaldehyde; H_2L^{11} = 2-(((2-hydroxy-3-methoxybenzyl) imino)methyl)-4-methoxyphenol; H_2L^{12} = 2-((2-hydroxy-3-methoxybenzylidene)amino)benzoic acid; Piv = (μ-OH_2)(O_2CCMe_3)$_4$(HO_2CCMe_3)$_4$; HL^{13} = 8-hydroxyquinoline; H_2L^{32} = (E)-1-(((2-(hydroxymethyl)phenyl)imino)methyl)nap- hthalen-2-ol; H_2L^{14} = 2,6-diylbis(ethan-1-yl-1-ylidene)-di(isonicotinohydrazide); H_2L^{15} = N, N-ethylenebis(3-methoxysalicylaldiimine); H_2pyzha = pyrazinehydroxamic acid; Hpyzic = pyrazinic acid; HL^{16} = bis(tridentate) pyrazolate-bridged ligand; H_2L^{17} = 3-methoxysalicyl-aldehyde with 2-amino-2-methyl-1-propanol; Hchp = deprotonated 6-chloro-2- hydroxypyridine; H_2saloh = 3,5-ditert-butylsalicylic acid; HL^{18} = chiral nitronyl-nitroxide ligands; H_2L^{19} = Fe[(C_5H_4){-C(Me)=N−N=CH-C_6H_3-2-OH-3- OCH_3}]$_2$; H_2dhpb = 6, 6'-dihydroxyl-2, 2'-bipyridine; H_3L^{20} = 2-((2-hydroxy-benzylidene)amino)propane-1, 3-diol; (py)$_2$C(OH)$_2$ = the gem-diol form of di-2-pyridyl ketone (dpk); (py)$_2$C(OCH_3)OH = the hemiacetal form of dpk; H_2L^{21} = (E)-2-((2-hydroxy-3-methoxybenzylidene)amino)-4-methylphenol; H_6L^{22} = bis-tris propane; H_2L^{23} = 2-methoxy-6-[(E)-2'-hydroxymethyl-phenyliminomethyl]-phenol; H_2L^{24} = 2-[(2-hydroxymethyl-phenylimino)-methyl]-6-methoxy-phenol; H_2L^{25} = (E)-4-chloro-2-(((2-(hydroxymethyl) phenyl)imino)methyl)phenol; 2, 3-H_2pzdc = pyrazine-2, 3-dicarboxylic acid; H_2L^{26} = N, N'-bis(2-oxy-3-methoxybenzylidene)-1,2-phenyl-enediamine; H_2L^{27} = N, N'-bis(2-oxy-3-methoxybenzylidene)-1, 2-diaminocyclohexane); H_3L^{28} = 6, 6', 6"-(nitrilotris(methylene))tris(2-methoxy-4-methylphenol); H_4L^{29} = 2, 2'-[1, 2-ethanediylbis[(hydroxyethylimino)methylene]]bis[6-methoxy-4-methyl-phenol]; HDBM = dibenzoylmethane; NIT-PhPybis = 5-(4-pyridyl)-1, 3-bis(1'-oxyl-3'-oxido-4', 4', 5', 5'-tetramethyl-4, 5-hydro-1*H*-imidazol-2-yl)benzene; H_2hms = 1-(2-hydroxy-3-methoxybenzy-lidene)-semicarbazide; H_2L^{30} = N, N', N"-trimethyl-N, N"-bis(2-hydroxy-3-methoxy-5-methylbenzyl)diethylenetriamine; H_2L^{31} = 2-((2-(hydroxymethyl)phenylimino)methyl)-6-methoxyphenol; H_3vdpyCH_2OH = 1, 5-dimethyl-3-[3'- (hydroxymethyl)-2'-pyridine]-6-oxotetrazane; H_3L^{32} = 2-methoxy-6-[{2-(2-hydroxyethylamino)ethyl-imino}methyl]phenol; edeaH_2 = N-ethyldiethanolamine; H_3L^{33} = 2-methoxy-6-[{2-(2-hydroxyethylamino)ethylimino}methyl]phenol; H_2L^{34} = N, N'-dimethyl-N, N'-(2- hydroxy-3-methoxy-5-methyl-benzyl)ethylenediamine; H_2hmmp = 2-[(2- hydroxy-ethylimino)methyl]-6-methoxyphenol; Hae = 2-aminoethanol; H_2L^{35} = *n*-N-butyldiethanolamine; 3-MeOsaltn = N, N'-Bis(3-methoxy-2-oxybenzylidene)-1, 3-propanediaminato; H_2L^{36} = N, N', N"-trimethyl-N, N"-bis(2-hydroxy-3-methoxy-5-methylbenzyl)-diethylenetriamine; H_3L^{37} = N, N', N"-tris(2-hydroxy-3-methoxybenzilidene)-2- (aminomethyl)-2-methyl-1, 3-propanediamine; H_3L^{38} = 2-(2, 3-dihydroxpropyliminomethyl)-6-methoxyphenol.

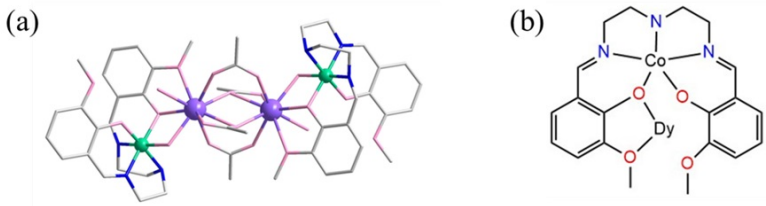

Figure 1. The molecular structure of **1** (a) and structure of ligand H_2L^1 with two types of coordination sites (b). Color code: Co, green; Dy, purple; O, pink; N, blue; C, gray. H atoms are omitted for clarity

图 1. **1** 的分子结构和配体 H_2L^1 具有两种配位位点的结构(b)。颜色代码：Co，绿色；Dy，紫色；O，粉红色；N， 蓝色；C，灰色。为了清晰起见省略了 H 原子

2014 年，研究小组利用邻香兰素衍生的席夫碱配体成功合成了一个三核 Co^{III}-Dy^{III} SMM $[Co_2Ln(valdien)_2(OCH_3)_2(chp)_2]$ ClO_4 $5H_2O$ (Ln = Dy (**2**)，Tb (**3**)，H_2valdien = N1，N3-双(3-甲氧基水杨亚胺)二乙基三胺，Hchp = 6-氯-2-羟基吡啶[15]。在零场交流磁化率测试中，配合物 **2** 和 **3** 均显示出与频率相关的虚部信号，但没有观察到完整的峰值。然而，在施加 2 kOe 的外部场后，这两种配合物的交流磁化率实部和虚部均表现出明显的峰值。利用 Arrhenius 定律拟合，分别得到配合物 **2** 和 **3** 的有效能垒为 71.4 (4.2) K 和 32.3 (2.6) K，τ_0 分别为 $5.6(3) \times 10^{-6}$ s 和 $2.5(1) \times 10^{-10}$ s。因此，与双核 4f 金属的配合物 **1** 相比，单核配合物 **2** 在调控磁各向异性方面更容易实现。

2014 年，研究团队利用 3, 5-二氯苯甲酸(HL^2)作为桥联配体和 2, 2'-联吡啶(bipy)作为末端双齿配体，合成了一种四核链状阳离子团簇 $Dy_2Co_2(L^2)_{10}(bipy)_2$ (**4**) [16]。Dy^{III}与七个 L^{2-}的氧原子配位，采用单帽三角棱柱配位结构。在磁性方面，配合物 **4** 在交流磁化率测量中表现出缓慢的磁弛豫行为。通过拉曼过程、量子隧穿和奥巴赫过程拟合，分别在零磁场和 1 kOe 外磁场下得到有效能垒为 118 (3) K 和 114.2 (7) K，有效能垒相差不大。

2015 年，Powell 等人通过将配合物中的 Fe^{III}替换为 Co^{III}，合成了配合物$[DyCo(CN)_6(hep)_2(H_2O)_4]$ (**5**) [17]。在结构上，与其原来的相似。在磁性方面，直流磁化率测试表明，配合物 **5** 内通过二聚体偶极-偶极相互作用表现出弱的铁磁耦合。在 2 kOe 直流场下进行的交流磁化率试验中，拟合数据得到的有效能垒为 63 K，指数前因子(τ_0)为 7.1×10^{-11} s，与配合物 **2** 相关数据相差不大。由于 Co^{III}的抗磁性和较长的 Dy-Dy 距离，表明配合物 **5** 的磁弛豫行为可能是由单离子 Dy^{III}主导的。

2015 年，唐金魁研究组成功地将配合物中的 Mn^{II}替换为 Co^{II}，合成了配合物$[Ln_2Co^{II}(C_7H_5O_2)_8]$ $6H_2O$ [18]。直流磁化测量结果显示，在配合物自旋载体之间存在显著的磁相互作用。在 1.9 K 至 16 K 的温度范围内，配合物 **6** 表现出两个独立的弛豫过程。利用 Arrhenius 定律拟合，当温度低于 5 K 时，能垒为 16.77 (4) K，其前指数因子 τ_0 为 3.55×10^{-5} s。在高于 5 K 的情况下，获得了能量壁垒为 127.27 (2) K，其前指数因子 τ_0 为 1.69×10^{-9} s，说明温度对其离子之间的作用产生了巨大的影响。在较高温度下，单个 Dy^{III}离子与激发 Kramers 双稳态弛豫有关，而在较低温度下，Dy^{III}和 Co^{III}离子之间的弱耦合占主导地位。因此，通过引入具有基态双稳态和各向异性的 4f 金属离子或选择合适的顺磁性 3d 金属离子，利用 d 和 f 自旋产生的强磁相互作用，可以提高 SMMs 的性能。

在 2015 年，由童明良团队合成了一系列线性型 SMMs，$[Co_2Dy((L^3)^{Br})_2(H_2O)]$ NO_3 $3H_2O$(**7** $3H_2O$)，$[Co_2Dy((L^3)^{Br})_2(H_2O)]$ NO_3 H_2O (**7** H_2O)，以及$[Co_2Dy((L^3)^{Br})_2(H_2O)]NO_3$ (**7**) [19]，形成了一种新的配合物结构。在此系列中，三个配合物中 Dy^{III}离子具有压扁的五角双锥形(D_{5h})配位几何结构。随着水分子损失，沿赤道方向与 Dy^{III}键合的五个氧原子的共面性变得更加明显，将配合物的能量壁垒从 422 K 提高到 600 K(**7**)。这项工作还强调了在合成 SMMs 时，在晶体结构中避免配合物之间的分子间接触的必要性，因为溶剂或水分子可以与磁性单元形成氢键，从而增强晶体中不同[CoDyCo]单元之间的振动耦合，并导致更快的磁性弛豫。

2018 年，该研究团队合成了一个线性三核配合物，$[Co_2Dy(TTTT^{Cl})_2(MeOH)]NO_3{\cdot}3MeOH$ (**8**) [20]。此外，通过$[Co^{III}(TTTTCl)]^+$与$[Co_2Dy(TTTT^{Cl})_2(MeOH)]^+$的共结晶，形成了配合物 **9** (图 2)，从而显著提高了单分子磁体的性能。在交流磁化率测试中，两种配合物均表现出频率依赖性的虚部交流磁化率信号。然而，在较低温度下，温度依赖性的虚部信号显示出长尾现象，这表明两种配合物中都存在量子隧穿或更快的弛豫过程。分析 Cole-Cole 图发现两种情况下都存在多个弛豫过程。通过公式拟合，确定配合物 **8** 和 **9** 的有效能垒分别为 401 K 和 536 K，其前指数因子分别为 $1.3 (6) \times 10^{-10}$ s 和 $3.8 (10) \times 10^{-11}$ s，有效能垒相差不大，但前指数因子有较大差距。配合物 **9** 中的能垒比配合物 **8** 中的高，这可能是由于 Dy^{III}的配位环境更接近五角双锥，并加入了抗磁性 Co^{III}，稀释了磁性相互作用。

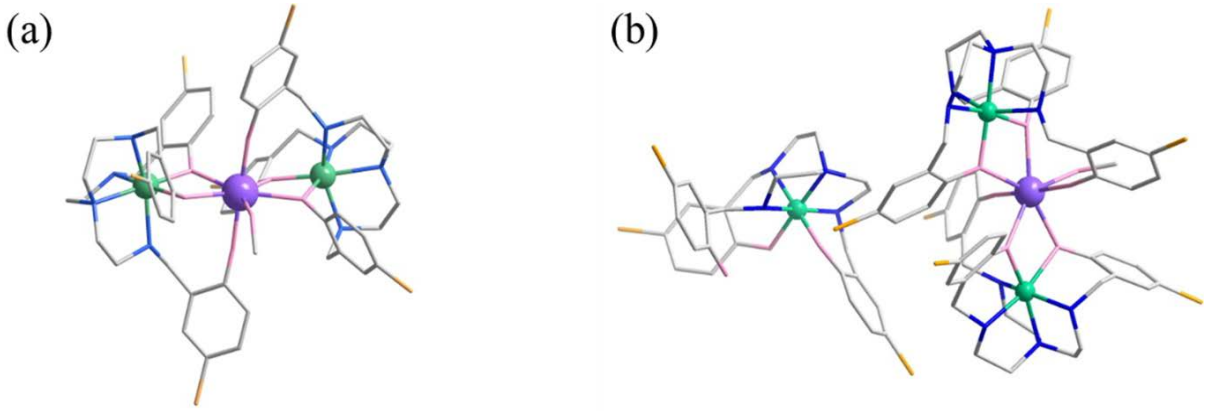

Figure 2. Molecular structures of the complexes $[Co_2Dy(TTTT^{Cl})_2(MeOH)]NO_3{\cdot}3MeOH$ (a) and $[Co_2Dy(TTTT^{Cl})_2(MeOH)][Co(HTTTT^{Cl})]$ (b). Color code: Co, green; Dy, purple; O, pink; N, blue; Cl, orange; C, gray. H atoms are omitted for clarity
图 2. 配合物$[Co_2Dy(TTTT^{Cl})_2(MeOH)]NO_3{\cdot}3MeOH$ (a)和$[Co_2Dy(TTTT^{Cl})_2(MeOH)][Co(HTTTT^{Cl})]$ (b)的分子结构。颜色代码：Co，绿色；Dy，紫色；O，粉红色；N，蓝色；Cl，橙色；C，灰色。为了清晰起见，省略了 H 原子

随后该团队用顺磁低自旋的$[Co(CN)_6]^{3-}$取代了$[Fe(CN)_6]^{3-}$部分，从而合成了配合物{Dy_2Co}(**10**) [21]，该类型的配合物的结构与其他配合物相比，比较复杂。这种改变导致零直流场下的有效能垒显著增加，达到 975 K，磁化磁滞回线的开口温度也上升到 15 K。此外，当施加 2 kOe 的外部磁场时，有效能势垒进一步增强至 1075 (22) K。本研究采用在两个 Dy^{III}离子之间进行顺磁性或抗磁性六氰基金属配合物的选择性整合，以有效调节磁滞。因此，在合成具有高各向异性的 3d-4f SMMs 时，应避免类顺磁离子的并排排列。

2.2. 蝴蝶型单分子磁体

除了$[Co_2Dy]$型配合物外，$[Co_2Ln_2]$型 SMMs 也是 Co-Ln SMMs 领域的重要组成部分。值得注意的是，Langley 研究组合成了一系列$[Co^{III}_2Ln_2]$型单分子磁体。尽管有机配体有所不同，但这些配合物都保持着类似蝴蝶的核结构，表现出非凡的性能。2012 年报道了三种结构相同的 3d-4f 配合物中，每个晶体结构都包含一个不对称单元中的两种不同分子：$[Ln^{III}_2Co^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_4](NO_3)_2$ MeOH H_2O (Ln = Gd, Tb (**11a**)和 Dy (**12a**)，$teaH_3$ = 三乙醇胺)和$[Ln^{III}_2Co^{III}_2(OMe)_2(teaH)_2(O_2CPh)_4(MeOH)_2(NO_3)_2]$ MeOH H_2O (Ln = Gd，Tb (**11b**)和 Dy (**12b**) [24]。在低于 20 K 的条件下，配合物 **12** 的交流磁化率表现出频率和温度依赖性。理论计算表明，由于存在抗磁性的 Co^{III}离子，配合物 **12** 的弛豫行为受 Dy^{III}单离子性质的控制。此外，配合物 **12** 中 Dy 离子之间的弱分子内反铁磁交换相互作用抑制了零场下的 QTM。另一方面，在配合物 **11** 中，在零场下的虚部交流磁化率信号中未观察到的峰值，可见$[Co_2Dy]$型单分子磁体和蝴蝶型单分子磁体在性质上有某些相同之处。然而，在 1 kOe 的外部磁场下，有效能垒上升到 14.3 K，与配合物 **4** 相差较大。

2014 年，他们用二乙醇胺(H_3dea)、N-甲基二乙醇胺(H_2mdea)和 N-正丁基二乙醇胺)取代了 H_3tea (图 3(a))，从而形成配合物 **13** (图 3(b))、**14** (图 3(c))和 **15** (图 3(d)) [25]。这些配合物的主体核心结构与仍然与配合物 **3** 相似。其主要区别在于，在配合物 **13-15** 中，配体采用不同的配位模式，导致金属离子的配位环境发生细微变化。配合物 **12-15** 均表现出 SMM 行为，在零场下能垒分别为 102.9 K、78.6 K 和 114.4 K。这项工作表明，通过简单地调整磁性中心周围的配体以及化学修饰与磁性中心无关的周围配体，可以增强 SMMs 的性能。

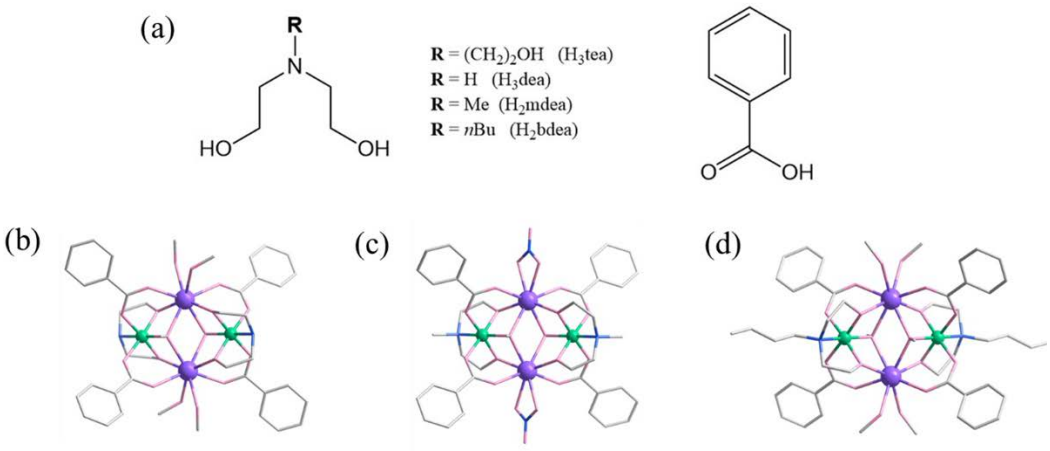

Figure 3. (a) Proligands used towards the synthesis of complexes **13-15**. The molecular structure of **13** (b), **14** (c), **15** (d). Color code: Co, green; Dy, purple; O, pink; N, blue; C, gray. H atoms are omitted for clarity

图 3. (a) 用于合成配合物 **13-15** 的前配体。配合物 **13** (b)，**14** (c)，**15** (d)的分子结构。颜色代码：Co，绿色；Dy，紫色；O，粉红色；N，蓝色；C，灰色。为了清晰起见，省略了 H 原子

此外，他们利用乙酰乙酸(acac)取代苯甲酸配体，得到了三个蝴蝶状的异金属配合物，分别为$[Dy_2Co^{III}_2(OMe)_2(teaH)_2(acac)_4(NO_3)_2]$ (**16**)，$[Dy_2Co^{III}_2(OH)_2(teaH)_2(acac)_4(NO_3)_2]\cdot 4H_2O$ (**17**)和$[Dy_2Co^{III}_2(OMe)_2(mdea)_2(acac)_4(NO_3)_2]$ (**18**) [26]。配合物 **16-18** 的结构核心与 **12** 有相似之处。随后，使用胺－多元醇配体 H_2bdea 和四种羧酸配体：2-氯苯甲酸、4-叔丁基苯甲酸、4-羟基苯甲酸和 2-(三氟甲基)苯甲酸合成了配合物 **19-22**。配合物 **19**、**20** 和 **22** 均呈现出与 **12** 相似的蝴蝶状结构。除此之外，Langley 研究组还成功合成了以先前用于配合体 **7** 的 H_2mdea 和 Hhfacac 为配体的蝴蝶状配合物 **23** [27]。在变温和变频交流磁化率测试中，配合物 **19-23** 表现出频率依赖性和温度依赖性的虚部磁化率信号，与配合物 **6** 相似，其中配合物 **21** 在零场下没有完整的峰值。配合物 **19-22** 分别显示出显著的各向异性能垒为 114.9 K、(110.1 K 和 137.3 K)、167.3 K 和 125.8 K，虽然配合物 **12-15** 也表现出了较强的频率依赖性的实部和虚部信号，但有效能垒没有 **19-22** 的高。在这些配合物中，**19** 和 **22** 中存在的电子吸引基团有助于提高它们的各向异性能垒，而 **20** 则表现出双重弛豫现象。配合物 **19-22** 在 1.8 K 以上没有表现出磁滞现象，而配合物 **7** 的阻塞温度被确定为 2.2 K。这再次证实了在设计 3d-4f SMMs 时，加入吸电子基团和选择具有强交换作用的 3d 和 4f 金属的重要性。

除了上述含有 Co^{III}的蝴蝶型 3d-4f SMMs 外，含有 Co^{II}的 SMMs 也表现出非凡的特性。2012 年，Powell 研究组合成了一种配合物$[Co_2Dy_2(L^6)_4(NO_3)_2(THF)_2]\cdot 4THF$(**24**，$H_2L^6$ 为邻香草醛和 2-氨基酚缩合得到的席夫碱)，其显示出中心对称的排列，其中四个金属离子通过$(L^6)^{2-}$配体连接，形成蝴蝶状(或缺陷立方烷)拓扑结构[29]。直流磁化测量表明，在配合物 **24** 中存在铁磁交换相互作用。在零直流场下，交流磁化率的实部和虚部均表现出温度和频率依赖性，可能是由于配合物 **24** 内单离子 Dy^{III}的贡献所致，而较低温度下的能垒则与 Dy^{III}和 Co^{II}之间的耦合有关。配合物 **24** 中可观察到双弛豫现象，与配合物 **20** 类似，可能是由于 Co^{II}的存在所致，这导致低能级交换分裂比纯$\{Dy_2\}$配合物大十倍。

2.3. 其他类型的单分子磁体

除了线性结构和蝴蝶型配合物外，研究人员还合成了具有其他结构的 Co-Ln SMMs。基于配合物 **8**，高松等人用 Co^{III}代替 Cr^{III}合成了化合物{DyCo}(**25**) [32]。虽然与配合物 **8** 的结构相似，但 **25** 在磁性方面却存在显著差异。在 20 K 时，配合物 **25** 的磁滞回线仍然开口，而低于 10 K 时，与配合物 **8** 相比，其矫

顽力和剩余磁化强度显著提高。此外，由于 Co^{III}的抗磁性，在配合物 **25** 中，弱 Dy^{III}-Dy^{III}偶极相互作用占主导地位。因此，与配合物 **12** 类似，QTM 效应被 Dy^{III}的 D_{5h} 高对称性所抑制。通过对各种弛豫过程的数据拟合，在零直流场下得到 595 (3) K 的有效能垒。

2012 年，唐金魁等人使用二硫代氧杂环二阴离子(dto^{2-})将$[Dy^{III}(HBpz_3)_2]^{2+}$单元($HBpz^{3-}$ = 三(吡唑基)硼酸盐)与过渡金属 Co^{III}组装在一起，从而合成了具有三叶螺旋桨状结构的配合物$[CoDy_3(HBpz_3)_6(dto)_3]$ $4CH_3CN$ $2CH_2Cl_2$(**26**) [33]。在零场条件下，配合物 **26** 表现出频率和温度依赖的交流磁化率，没有明显的峰值，与配合物 **11** 相似，表明存在 QTM 现象。即使在 800 Oe 的最优场下，QTM 仍然很明显。通过拟合得到的配合物 **26** 的有效能垒为 52 K。

3. 结论

单分子磁体作为一类具有独特磁学性质的材料，吸引了研究者们广泛的研究兴趣。目前已报道的 Co 单分子磁体还相对较少，研究主要集中在理解磁体的磁学行为和性质，并改进合成和制备技术。通过研究发现，对 Co-SMMs 的调控归根到底是对其磁各向异性的调控，而其磁各向异性主要来源于基态的零场分裂，还受耦合作用的影响。现阶段已取得了一些重要的进展，但显然，我们对单分子磁体的了解还远不够，有关 Co-Ln 单分子磁体的研究报告没有非常全面，并且大部分 Co-Ln 配合物在奥巴赫、拉曼、量子隧穿这些弛豫过程中的参数(U_{eff}、τ_0、QTM)普遍是利用理性数据拟合所得，并非确切真实数据，其可靠度需要评估。

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 Co-Ln 单分子磁体。随着科学技术的不断进步，相信这些磁构关系不明朗、磁性行为理解片面、工业化生产困难、研究方向单一等一系列问题会被逐个解决。如果可以得到解决，相信对单分子磁体的应用会有更好的指导意义，可以将 Co-Ln 单分子磁体纳入纳米技术中，实现更高级别的磁性控制，并用于纳米电子学和纳米磁性器件，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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