

Field-Induced Slow Magnetic Relaxation in a New Family of Tetranuclear Double-Stranded Cu₂^{II}-Ln₂^{III} Metallohelicates

Sergio Caballero, Evangelos Pilichos, Mercè Font-Bardia, Júlia Mayans, and Albert Escuer*

Cite This: Cryst. Growth Des. 2023, 23, 3711–3719



ACCESS	III Metrics & More	E Article Recommendations	Supporting Information
ABSTRACT: A se	ries of tetranuclear $Cu_2^{II}Ln_2^{III}$	(Ln ^{III} from La ^{III} to Yb ^{III}),	
double-stranded me	tallohelicates have been synthe	sized using a bis-bidentate	
flexible ligand obta	ined by condensing <i>o</i> -vanillin	with 4,4'-oxydianiline. The	

flexible ligand obtained by condensing *o*-vanillin with 4,4'-oxydianiline. The complexes exhibit a variety of Ln^{III} environments and decreasing coordination number along the series and several nitrato coordination modes proved by the structural determination of the La^{III} (1La), Sm^{III} (4Sm), Gd^{III} (5Gd), Er^{III} (9Er), and Yb^{III} (10Yb) derivatives. The other members of the family (2Ce, 3Pr, 6Tb, 7Dy, and 8Ho) have been characterized by powder X-ray diffraction to verify their isostructurality. Susceptibility measurements show field-induced slow relaxation of the magnetization for the anisotropic Tb^{III} and Dy^{III} complexes and for the isotropic Gd^{III} system.



■ INTRODUCTION

The construction of helical arrays has been a playground for synthetic supramolecular chemists since the apparition of the first one reported in the mid-1950s.¹ Helical structures are achieved by wrapping molecular strands around a central axis, where this wrapping can be controlled by the coordination to a metallic center or by supramolecular interactions.²⁻⁴ Despite this early example, the term helicate was first introduced by Lehn in 1987.⁵ Metallohelicates are structures that contain metallic centers surrounded by an organic ligand that should fulfill some criteria to properly wrap around the cation: it should have several sets of donor atoms to be able to coordinate to one or more cations and it should have a flexible enough spacer between the coordination sites. The most common case consists of two sets of donor atoms connected by a more or less long but flexible spacer that can yield double-, triple-, or even quadruple-stranded helicates, benefiting the coordination number of the involved cations.

Many supramolecular structures have been used to build systems exhibiting slow relaxation of magnetization (singlemolecule magnets, SMMs), which are, today, one of the main research areas in magnetochemistry because they have been proposed as functional molecules with possible applications in different fields like information storage,⁶ molecular spintronics,⁷ or quantum information processing (QIP).^{8,9} Their characteristic slow relaxation of magnetization arises, in principle, from a high ground spin state (*S*) and a negative axial magnetic anisotropy (*D*), giving rise to a potential energy barrier that the spin has to overcome in order to demagnetize.^{10,11} However, recently, many exceptions to these paradigms have appeared with the rise of slow-relaxing molecules with S = 1/2, which slowly relax without the possibility of the potential barrier to overcome,^{12,13} the apparition of slow-relaxing molecules with a positive value of D,^{14–16} and, more recently, the discovery of this magnetic response for isotropic cations.^{17–21} Among the wide diversity in slow-relaxing molecules, one of the most abundant types is the one using the highly anisotropic lanthanoid cations as paramagnetic centers, a property arising from their large and unquenched orbital angular momentum.^{22,23} Almost any paramagnetic lanthanoid(III) cation can present slow magnetic relaxation under appropriate conditions,^{24,25} but Dy^{III} is today the most used one in molecular magnetism, and, until today, it has given rise to some groundbreaking results.^{26–28}

On the above basis, we chose the Schiff base 2-(((4-(4-((2-((xido)-3-methoxybenzylidene)amino)phenoxy)phenyl)-imino)methyl)-6-methoxyphenolato (H₂L), which contains two sets of three donor atoms separated by a flexible spacer, Chart 1. This ligand provides two cavities at each end, which are able to coordinate two cations (or two groups of cations) bridged by phenolato bridges.

The cascade reaction of H_2L with Cu^{II} and further reaction with lanthanoid nitrates allows one to characterize a series of tetranuclear complexes with the common $\{Ln_2^{III}Cu_2^{II}L_2\}$ helical skeleton $(Ln^{III} = La^{III} (1La), Ce^{III} (2Ce), Pr^{III} (3Pr),$

Received:February 5, 2023Revised:March 2, 2023Published:March 21, 2023





Chart 1. (top) Structural Formula of the H₂L Ligand Employed in This Work to Generate Helical Tetrameric {Ln₂^{III}Cu₂^{II}L₂} Complexes; (bottom) Schematic Plot of the Coordination of Two L²⁻ Ligands to Two Cations at Each End of the Helicate



Sm^{III} (4Sm), Gd^{III} (5Gd), Tb^{III} (6Tb), Dy^{III} (7Dy), Ho^{III} (8Ho), Er^{III} (9Er), and Yb^{III} (10Yb)) and nitrato counteranions linked to the Ln^{III} and Cu^{II} cations in a variety of modes that fulfill their coordination spheres.

The single-crystal structures of complexes 1La, 4Sm, 5Gd, 9Er, and 10Yb were determined, showing the influence of the radii and coordination number of the Ln^{III} cation on the local coordination of the counteranions. The static magnetic properties show weak intramolecular $\mathrm{Cu}^{\mathrm{II}}\!\cdots\!\mathrm{Ln}^{\mathrm{III}}$ interactions mediated by the phenoxo bridges, and alternating current susceptibility measurements reveal slow relaxation of magnetization for the anisotropic Tb^{III} (6Tb) and Dy^{III} (7Dy) complexes and also for the less common isotropic case of $\mathsf{Gd}^{\mathrm{I\!I\!I}}$ (5Gd).

EXPERIMENTAL SECTION

Materials and Methods. All manipulations were performed under aerobic conditions. All reagents and solvents were used as received. The infrared spectra $(4000-400 \text{ cm}^{-1})$ were recorded on a Thermo Scientific Nicolet IS5 spectrophotometer. The magnetic susceptibility and magnetization measurements were performed with a Quantum Design MPMS-XL SQUID magnetometer at the CCiT Magnetochemistry Unit of the University of Barcelona. Single crystals of compounds 1La, 4Sm, 5Gd, 9Er, and 10Yb were set up on a Bruker D8-VENTURE diffractometer equipped with a multilayer monochromator and a Mo microfocus ($\lambda = 0.71073$ Å). The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm, and the structures were solved and refined using the Bruker SHELXTL software package.²⁹ The diffraction for the complex 5Gd was not crystallographically satisfactory due to the poor quality of the crystals and the unsolved disorder of the nitrato ligands around one of the Gd^{III} cations; Figure S1. Several crystallizations were performed, but single crystals of better quality were not obtained; thus, the crystallographic data have been included only as Supporting Information for the readers. However, the core of the complex is well defined and the obtained data have been included in the general descriptions. Crystal and structure refinement data are summarized in Table S1. Powder X-ray diffraction analysis was performed with a PANanalytical X'Pert PRO MPD Θ/Θ powder diffractometer.

Synthesis. H_2L Ligand. The ligand was prepared by the condensation reaction of 2-hydroxy-3-methoxybenzaldehyde and 4,4'-oxydianiline following a slight modification of reported methods.³⁰ A total of 10 mmol (1.52 g) of the aldehyde was dissolved in 50 mL of ethanol and added to a 50 mL ethanolic suspension of 5 mmol (1.00 g) of the diamine. Upon addition, the mixture immediately took a deep-orange color and was refluxed until an orange precipitate appeared (around 30 min). The reaction mixture was left to cool at room temperature. It was vacuum-filtered, and the crude solid was washed several times with cold ethanol and ether. It was allowed to dry in a desiccator. IR (cm^{-1}) : 3445 (br, m),

3712

1615 (sh, s), 1485 (sh, s), 1467 (sh, s), 1286 (sh, s), 1197 (sh, s). ¹H NMR (500 MHz, CDCl₃) δ (ppm): 13.66 (s, ¹H), 8.64 (s, 1H), 7.34-7.28 (m, 2H), 7.12-7.06 (m, 2H), 7.01 (ddd, J = 15.4, 8.0, 1.5 Hz, 2H), 6.89 (t, J = 7.9 Hz, 1H), 3.94 (s, 3H).

Metallohelicates. All of the lanthanoid-derived complexes were prepared following the same procedure using the corresponding lanthanoid(III) nitrate salts. To a stirred suspension of H₂L (58.5 mg, 0.125 mmol) in a solvent mixture of MeOH/MeCN (10 mL, 1:1) was added 0.125 mmol (25.2 mg) of [Cu₂(CH₃COO)₄(H₂O)₂]. The resulting dark-brown solution was stirred until a brown precipitate of $[Cu_2L_2]$ appeared. The corresponding equimolar amount (0.125) mmol) of Ln(NO₃)₃·xH₂O was dissolved in 10 mL of a MeOH/ MeCN (1:1) mixture and added to the suspension of $[Cu_2L_2]$. The mixture was stirred for two hours until the solid dissolved and the solution took a dark-yellow-brown color. The resulting solution was filtered, and diethyl ether vapor was allowed to diffuse until darkbrown prism-like crystals suitable for X-ray diffraction appeared for compounds 4Sm and 5Gd. For complexes 1La, 9Er, and 10Yb, darkorange prism-like crystals (~60% yield) were obtained after layering the corresponding solutions with diethyl ether. We were unable to obtain single crystals of compounds 2Ce, 3Pr, 6Tb, 7Dy, and 8Ho, which give polycrystalline powders in all cases. Infrared spectra are provided in Figure S2, and analytical data are summarized in Table S2.

RESULTS AND DISCUSSION

Structural Description. Powder X-ray Diffraction. Despite the similar synthetic response and the practically



Figure 1. Space filling (top) and ball and stick (bottom) plots of the $\{Cu_2La_2(L)_2\}$ helicate 1La, showing the wrapping of the two L^{2-} ligands around the four cations.

superimposable IR spectra, XRPD spectra demonstrate that the structure of complexes 1-10 evolves along the series. The complexes derived from the larger cations 1La, 2Ce, and 3Pr are isostructural, and also, 5Gd and 7Dy show similar spectra, whereas complexes 4Sm, 6Tb, 8Ho, 9Er, and 10Yb are different; Figure S3. From these preliminary data, the structures of five complexes along the series have been solved to check the origin of the structural differences.

Single-Crystal Diffraction. The structures of complexes 1La, 4Sm, 5Gd, 9Er, and 10Yb were solved, and the five structures, as could be expected, show similarities in their general trends but show local differences in the coordination sphere around the lanthanoid and the Cu^{II} cations. To avoid repetitive descriptions, the structure of complex 1La will be described in detail, and for the remaining complexes, only the main differences will be pointed out.



Figure 2. Top-left, labeled plot of the $\{La(1)Cu(1)\}$ fragment of complex **1La**. For clarity, only this environment is shown because of the similarity to the $\{La(2)Cu(2)\}$ fragment of the helicate. Top-right, plot of the closest ideal polyhedron around the La1 cation. Bottom, plot of the main intermolecular interactions present in the structure of complex **1La** (H-bonds and intercentroid distance are emphasized as dotted red bonds).

Table 1. Selected Bond Distances and Bond Angles for the $\{La(1)Cu(1)\}$ Fragment of Complex 1La

Bond Distances (Å)									
Cu1-O2	1.919(3)	Cu1-N1	1.964(3)						
Cu1-07	1.920(3)	Cu1-N3	1.965(3)						
La1-O1	2.675(3)	La1-06	2.719(3)						
La1-O2	2.506(2)	La1–O7	2.527(2)						
La1-011	2.561(3)	La1-O12	2.855(4)						
La1-014	2.628(3)	La1-015	2.647(3)						
La1-017	2.623(3)	La1-O18	2.675(3)						
La1-O20	2.563(3)								
Bond Angles (deg)									
La1-O2-Cu1	107.0(1)	La1-O7-Cu1	106.2(1)						



Figure 3. Coordination environment and ideal polyhedron of the lanthanoid cation for the Cu1/Ln1 fragments of complexes 1La, 4Sm, 5Gd, and 10Yb. The environments of Er1 and Er2 (complex 9Er) are shown due their different coordination number.

 $[Cu_2La_2(L)_2(MeOH)_2(NO_3)_6]\cdot 1.5CH_3CN\cdot C_4H_{10}O$ (**1La**· 1.5CH_3CN·C_4H_{10}O). Complex **1La** consists of a {Cu_2La_2} tetranuclear double-stranded helicate in which the four cations are held together by the two deprotonated L²⁻ ligands; Figure 1. A labeled plot of **1La** is shown in Figure 2, and the main bond parameters are summarized in Table 1.

 $Eac\hat{h}\ Cu^{II}$ cation is coordinated by one N-iminic atom and one O-phenoxo donor atom from each L²⁻ ligand, resulting in a N_2O_2 chromophore. The Cu^{II} cation is placed in a square planar environment with a significant tetrahedral distortion (the dihedral angle between the OCuO/NCuN mean planes is 30.5°). The Cu–N distances for both Cu^{II} cations vary between 1.957(3) and 1.965(3) Å, and the Cu-O distances are slightly shorter, comprising between 1.914(2) and 1.921(2) Å. The $O_{\mbox{\tiny phenoxo}}$ donors act as bridges between the $\mbox{La}^{\mbox{\tiny III}}$ and Cu^{II} cations, resulting in a bent four-membered $Cu-(O)_2$ -La ring (Cu-O-O-La torsion angles of 19.5(1)° for the Cu1-O2-O7-La1 ring and 23.0(1)° for the Cu2-O4-O9-La2 ring). In addition to the two $\mathrm{O}_{\mathrm{phenoxo}}$ donors, each $\mathrm{La}^{\mathrm{III}}$ cation links two O_{methoxo} donors, three bidentate nitrate anions, and one methanol molecule, resulting in an undecacoordination (LaO₁₁). Intermolecular interactions between clusters comprise $\pi \cdots \pi$ stacking interactions established between neighboring phenyl rings from the diphenyl-ether moieties with a centroid ring distance of 3.576(2) Å and H-bonds between the coordinated methanol molecules and one oxygen of the nitrate from the neighbor clusters with $O \cdots O$ distances of 2.815(5)-2.920(5) Å; Figure 2, bottom.

Continuous shape measurements (CShMs) performed with the SHAPE³¹ program for the La^{III} environment shows that the closest polyhedron is a capped pentagonal antiprism (JCPAPR-11), with an ideal $C_{5\nu}$ symmetry (Figure 2, topright). However, the CShM value of 3.82 implies a severe

	11.5	4Sm	5Gd	9Fr(1)	9Fr(2)	10Vb
	1154	7011	304		\mathcal{F}	1010
Cu ^{II} coord. number	4	5	4	5	5	5
Ln ^{III} coord. number	11	10	10	10	9	9
dCu…Ln (Å)	3.549(1)	3.508(1)	3.485(1)	3.465(1)	3.362(1)	3.349(1)
Ln–O _{phenoxo} (Å)	2.507(3)	2.401(3)	2.378(6)	2.321(3)	2.306(3)	2.256(6)
Ln-O _{methoxo} (Å)	2.726(3)	2.636(3)	2.579(6)	2.545(3)	2.565(3)	2.458(6)
torsion Cu–O–O–Ln (deg)	21.3(1)	10.6(1)	5.3(3)	2.0(1)	20.9(1)	18.02(3)
torsion O-O-N-N (deg)	28.3(1)	21.9(1)	22.30(3)	18.9(1)	11.2(1)	11.8(2)

Table 2. Coordination Numbers and Evolution of the Main Bond Parameters (Mean Values) along the Series of Reported Complexes

Chart 2. (top) Reported Ligands Derived from Aromatic 4,4'-Diamines Employed to Generate Helical Structures; (bottom) Different Reported Cases of 3d (Tr) or Lanthanoid (Ln) Double Strand $\{Tr_2L_2\}$ (a), Triple Strand $\{Tr_2L_3\}$ (b), Quadruple Strand $\{Ln_2L_4\}$ (c), or Double Strand $\{Tr_2Ln_2\}$ (d) Helical Structures



Figure 4. $\chi_{\rm M}T$ product vs temperature for complexes 2Ce, 4Sm, 5Gd, 6Tb, 7Dy, 9Er, and 10Yb. The solid lines show the best fit of the data.

distortion from the ideal polyhedron due to the low O-Ln-O bond angles imposed by the bidentate nitrato ligands that take values lower than 50°. The intramolecular $Cu(1)\cdots Cu(2)$ and $La(1)\cdots La(2)$ distances are 11.863(1) and 18.930(1) Å, respectively.

 ${Cu_2Ln_2(L)_2}$ Complexes $[Ln^{III} = Sm^{III} (4Sm), Gd^{III} (5Gd), Er^{III} (9Er), Yb^{III} (10Yb)]$. The structures of complexes 4Sm, 5Gd, 9Er, and 10Yb are similar in general trends to the described La^{III} complex 1La, with the same distribution of cations and helical shape. However, the flexibility of the L²⁻ Schiff bases



Figure 5. Temperature (top) and frequency (bottom) dependence of $\chi_{M}^{"}$ for the complex **5Gd** at the optimal applied external magnetic field of 0.6 T.

and the radii contraction along the series induce significant differences that are mainly related to the coordination sphere of the Ln^{III} cation; Figure 3.

The decreasing radii of Ln^{III} along the series has, as a consequence, the regular variation of some bond parameters (Table 2) and the concomitant decrease of the coordination number, being 11 the larger one for complexes **1La** and the isostructural Ce^{III} (**2Ce**) and Pr^{III} (**3Pr**) compounds, with a set of four O-donors from the Schiff bases, three bidentate nitrato ligands, and one methanol molecule. For **4Sm** and **5Gd**, the coordination number 10 remains constant but with different nitrato coordination modes. For the complex **4Sm**, the coordination environment is formed by the four O-donors from the L²⁻ ligands, two bidentate nitrato ligands, and two



Figure 6. Temperature (top) and frequency (bottom) dependence of $\chi_{M}^{"}$ for the complex **6Tb** at the optimal applied external magnetic field of 0.3 T.

methanol molecules and one bridging nitrato ligand that links to the axial site of the distorted square pyramidal Cu^{II} cation, which shows a N_2O_3 environment.

The Gd^{III} derivative (5Gd) exhibits a decacoordination around the lanthanoid, formed by the four O-donor atoms from the L²⁻ ligands and three bidentate nitrato ligands and maintaining the pentacoordination around the Cu^{II} cation by coordination of a methanol molecule. The case of the Er^{III} complex (9Er) becomes interesting because Er1 and Er2 cations exhibit different environments, showing the transition to the enneacoordination. Er1 shows the same coordination number 10 and the same set of ligands as the Gd^{III} complex. However, Er2 shows a coordination number of 9, formed by the four O-donors from the L^{2-} ligands, one bidentate nitrato ligand, two methanol molecules, and one O-atom from a nitrato ligand that acts as a bridge with the Cu^{II} cation, which also becomes pentacoordinated. The resulting positive charge of the complex is fulfilled with an ionic nitrate counterion. This case has special interest in future applications because the search for asymmetric dilanthanoid coordination compounds is a hot topic today in the construction of potentially applicable quantum gates.³² Finally, the Yb^{III} complex 10Yb shows a similar enneacoordination as Er2 with the coordination sphere formed by the four O-donor atoms from the L^{2-} ligands, two



Figure 7. Temperature (top) and frequency (bottom) dependence of $\chi_{M}^{"}$ for the complex 7Dy at the optimal applied external magnetic field of 0.5 T.



Figure 8. Left, Arrhenius dependence of the $\chi_{\rm M}^{"}(T)$ maxima plotted as $\ln(1/2\pi\nu)$ vs inverse of temperature. Right, fit of the relaxation times in front of inverse of temperature for complexes **6Tb** (green circles) and **7Dy** (blue diamonds) using data extracted from Cole–Cole plots.

bidentate nitrato ligands, and one O-atom from a nitrato ligand that acts as a bridge with the Cu^{II} cation.

In light of the structural data, the molecular formula for these complexes should be better described as $[Cu(L)La-(MeOH)(NO_3)_3]_2$ (1La), $[Cu(NO_3)(L)Sm-(MeOH)_2(NO_3)_2]_2$ (4Sm), $[Cu(L)Gd(NO_3)_3]_2$ (5Gd),

3715

[{CuLEr(NO₃)₃}{(μ -NO₃)CuLEr(MeOH)₂(NO₃)}] (9Er), and [μ -(NO₃){Cu(L)Yb(NO₃)₂}]₂ (10Yb).

Ligand Overview. The combination of 4,4'-oxydianiline or 4,4'-diaminodiphenylmethane with aldehydes like salicylaldehyde, *o*-vanillin, 2-hydroxy-3-ethoxybenzaldehyde, or 2,3-dihydroxybenzaldehyde results in a family of highly tunable ligands closely related to H₂L. The ligands derived from salicylaldehyde exhibit two bidentate fragments, whereas the 2,3-substituted aldehydes generate ligands with two O,O,N-tridentate fragments with a clearly different coordination capability.

The bis-bidentate ligands derived from salicylaldehyde, H_2L1 and H_2L3 , become adequate for the syntheses of neutral dinuclear helicates containing divalent cations with the general formula $[M_2^{II}L_2]$. Several complexes in which L = L1²⁻, L3²⁻ and $M = Co^{II}$, Cu^{II} , Zn^{II} have been reported, with the cations usually placed in a $\rm N_2O_2$ tetrahedral environment; Chart 2. $^{33-40}$ The ligands with an extra O-donor (–OMe, OEt, or -OH) generate bis-tridentate ligands with two sets of NO₂ donors that can increase the nuclearity of the helicates. However, their reaction with divalent 3d cations does not increase the nuclearity and tends to give helical dinuclear complexes with the $[M_2^{11}L_2]$ general formula like those reported for the ligands H_2L5 with Cu^{II} , 41 H_2L2 with Co^{II} and Zn^{II} , 39 or H_2L with Cu^{II} , Zn^{II} , or Co^{II} , 42,43 in which the extra O-methoxo or O-ethoxo donor atoms remain uncoordinated. Very unusual dinuclear triple and quadruple-stranded helicates or mesocates have been reported in two cases employing H_2L4 and Dy^{III} or H_4L6 and Ti^{IV} .^{44,45}

Despite these ligands possessing two cavities with different donor properties able to place a divalent 3d cation in the inner N_2O_2 cavity and one trivalent 4f cation linked to the O_4 donor atoms, heterometallic 3d–4f systems with the $\{Tr_2Lr_2L_2\}$ core (Tr, divalent 3d cation) have been poorly studied. The reaction of the ligands with the 3d cation acting as a guest generates the helicate topology that acts as a preformed template to bind the 4f cation in a cascade reaction. The scarce examples of this kind of system can be summarized as the $\{Cu_2Gd_2L5_2\}$ complex that revealed the ferromagnetic Cu^{II} ... Gd^{III} interaction⁴⁶ or $\{Zn_2Ln_2L_2\}$ complexes in which $Ln = Eu^{III}$, Nd^{III} , and $\{Zn_2Ln_2L_2\}$ $Ln = Yb^{III}$, Er^{III} , which exhibit luminescent response with potential sensor applications induced by the Zn^{III} cation.^{47,48}

Magnetic Properties. Direct current (dc) magnetic susceptibility and magnetization measurements were performed for compounds 2Ce, 4Sm, 5Gd, 6Tb, 7Dy, 9Er, and 10Yb on polycrystalline samples in the 2-300 K range of temperature; Figure 4. The room-temperature $\chi_{\rm M}T$ values of 2.51, 0.80, 16.40, 24.47, 28.74, 22.53, and 5.75 cm³ mol⁻¹ K are in agreement with the expected values for two $\mbox{Cu}^{\mbox{\scriptsize II}}$ and two Ln^{III} noninteracting cations of 2.35 (2Ce, Ce^{III}, ${}^{2}F_{5/2}$), 1.36 $(4Sm, Sm^{III}, {}^{6}H_{5/2}), 16.50 (SGd, Gd^{III}, {}^{8}S_{7/2}), 24.39 (6Tb,$ Tb^{III}, ⁷F₆), 29.09 (7**Dy**, Dy^{III}, ⁶H_{15/2}), 23.72 (**9Er**, Er^{III}, ⁴I_{15/2}), and 5.90 (**10Yb**, Yb^{III}, ²F_{7/2}) cm³ mol⁻¹ K. On cooling, the $\chi_{\rm M}T$ shows a roughly constant value for the 5Gd and 6Tb complexes, which show a $\chi_{\rm M}T$ maximum at 7 K for 5Gd and 10 K for $\mathbf{6Tb}$, suggesting ferromagnetic interactions. For complexes 2Ce, 4Sm, 7Dy, 9Er, and 10Yb, the $\chi_M T$ plot decreases from room temperature due to the depopulation of the corresponding Stark sublevels.

The Cu^{II}/Ln^{III} pairs are well isolated among them, and thus, the effective magnetic superexchange is mediated by the double diatomic phenoxo bridges between each $Cu^{II}-Ln^{III}$

independent dimeric fragment. On these bases, for the case of the complex **5Gd** (Cu–Gd pair), in which the Gd^{III} cation does not possess orbital momentum (S = 7/2, L = 0), the fit of the experimental data was performed with the PHI program⁴⁹ with the effective spin-only Hamiltonian

$$H = -2J(S_{\rm Cu} \times S_{\rm Gd}) \tag{1}$$

Best-fit values were $J = +1.72(4) \text{ cm}^{-1}$, g = 1.977(1) (including a z'J' intermolecular interaction of -0.01 cm^{-1} to simulate the low *T* decay).

The fit of the $\chi_{\rm M}T$ plot for the remaining complexes in which there is orbital contribution was performed with the PHI program⁴⁹ applying the anisotropic spin Hamiltonian

$$H = -2J(S_{Cu} \times S) + \lambda LS + \Delta [L_z^2 - L(L+1)/3]$$
$$+ \beta H(-kL+2S)$$
(2)

where $S_{\rm Cu}$ and S are the spin operators of the Cu^{II} and Ln^{III} cations, respectively; the J coupling constant describes the strength of the Cu^{II}-Ln^{III} interaction; λ is the spin-orbit coupling parameter; Δ represents the axial zero-field splitting parameter of the Ln^{III} cation; and κ is the orbital reduction parameter, which is related to the grade of covalence (1 for fully ionic compounds). This fitting method was previously used to approximate the sign of the axial zero-field splitting parameter, Δ .^{50,51} Best-fit values for J and Δ (cm⁻¹) were -0.80(2) and -14.1(1) (**2Ce**), -2.03(2) and -23(1) (**4Sm**), 2.3(3) and -14(2) (**6Tb**), 0.25(1) and -21.6(7) (**7Dy**), 1.65 and 26.7(3) (**9Er**), and 3.9(2) and 58.1(8) (**10Yb**).

In light of the susceptibility data, alternate current (ac) measurements were performed for the reported complexes. Compounds **2Ce** and **10Yb** do not show any response, **8Ho** and **9Er** only exhibit very weak $\chi_{M}^{"}(T)$ tails under the applied field (Figure S4), whereas for **5Gd**, **6Tb**, and **7Dy**, no signals were observed at zero field but well-defined out-of-phase $\chi_{M}^{"}(T)$ peaks were found under external applied fields, suggesting the presence of strong tunneling of the magnetization that quenches the slow relaxation when no dc field is applied. Measurements under fields ranging between 0 and 0.6 T were performed to select the optimal field, and thus, ac measurements were performed under 0.6, 0.3, and 0.5 T for **5**, **6**, and **7**, respectively (Figure S4).

Despite the isotropic character of the half-filled 4f⁷ shell of the Gd^{III} cation that excludes orbital contribution, the complex **5Gd** exhibits maxima in the $\chi_{\rm M}''(T)$ plot below 4.5 K (Figure 5), suggesting slow magnetic relaxation. This behavior for a number of mononuclear systems derived from the Gd^{III} cation¹⁷⁻²¹ has been reported during the past recent years, as well as some scarce examples of mononuclear Mn^{II} complexes⁵¹⁻⁵⁶ or even some Cu^{II}-Gd^{III} or Cu^{II}-Mn^{II} complexes with different nuclearities or spin ground states.²¹ For these systems, where weak anisotropy (typically $D \leq 0.1$ cm⁻¹) is present, the conventional double-well potential takes very low DS^2 values, and it is thermally overcome even at 2 K; thus, the Orbach mechanism is not operative and the relaxation is attributed to other spin-lattice relaxation mechanisms. For 5Gd, the $\chi_{\rm M}''(T)$ plot shows frequencydependent peaks for the larger frequencies with an apparent U_{eff} of 22(2) K and τ_0 of 6(1) × 10⁻⁷ s (Figure 5), a very weak response for intermediate frequencies, and intense frequencyindependent peaks at low temperatures and frequencies below 60 Hz. $\chi_{\rm M}''(\nu)$ has a long relaxation time at low frequencies and low temperature close to 0.1 s⁻¹ from the $\chi_{\rm M}''(\nu)$ peaks.

The Argand plot shows limited data, far from a semicircular plot, and the fit of χ_{M}'' vs χ_{M}' does not give reliable values; Figure S5.

The Tb^{III} and Dy^{III} derivatives (complexes **6Tb** and **7Dy**) show well-defined $\chi_{M}''(T)$ peaks between 2–4 K (**6Tb**) and 3–5 K (**7Dy**), Figures 6 and 7, respectively. Fit of the hightemperature data as $\ln(1/2\pi\nu)$ in front of 1/T yields in low barrier values of $U_{\text{eff}} = 21.1(6)$ K and $\tau_0 = 8(1) \times 10^{-8}$ s for **6** and $U_{\text{eff}} = 29(2)$ K and $\tau_0 = 8(3) \times 10^{-8}$ s for **7**; Figure 8, left.

A more precise analysis can be performed using the fit of the relaxation times extracted from the semicircular Argands plots (Figure S6), which reveal an Orbach relaxation mechanism for **6Tb** with $U_{\text{eff}} = 18.8(2)$ K and $\tau_0 = 1.2(1) \times 10^{-8}$ s and Orbach plus tunnel mechanisms for **7Dy**, using the equation $\tau^{-1} = QT + \tau_0^{-1} e^{-U_{\text{eff}}/KT}$, yielding the best fitting values of $U_{\text{eff}} = 10.9(2)$ K, $\tau_0 = 3.46(5) \times 10^{-7}$ s, and QT = 4400 s⁻¹. The order of magnitude of the effective energy barrier is fully comparable to the values extracted from the $\chi_{\text{M}''}(T)$ plot; Figure 8, right.

CONCLUSIONS

A new family of double-stranded metallohelicates has been synthesized following a cascade reaction with the Cu^{II} cation followed by the Ln^{III} cation and structurally and magnetically characterized. The structural data reveal a similar general $\{Cu_2Ln_2L_2\}$ skeleton with important differences in coordination numbers and nitrato coordination modes along the lanthanoid series, while a structural comparison with similar compounds in the bibliography has been done. The static magnetic characterization shows ferromagnetic coupling from the Gd^{III} to Yb^{III} derivatives. Ac measurements show that the anisotropic 6Tb and 7Dy complexes show the usual fieldinduced slow magnetic relaxation and interestingly and following different relaxation mechanisms, slow relaxation was also observed for the isotropic 5Gd complex. The structural and magnetic study of related systems with modified ligands and/or changing the 3d cation will be developed in future works in the search for improved magnetic properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.cgd.3c00121.

Synthetic, crystallographic, and complementary magnetic information (PDF)

Accession Codes

CCDC 2239235–2239238 (1La, 4Sm, 9Er, and 10Yb, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Albert Escuer – Departament de Química Inorgànica i Orgànica, Secció Inorgànica and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, 08028 Barcelona, Spain; orcid.org/0000-0002-6274-6866; Email: albert.escuer@qi.ub.edu

Authors

- Sergio Caballero Departament de Química Inorgànica i Orgànica, Secció Inorgànica and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, 08028 Barcelona, Spain
- **Evangelos Pilichos** Departament de Química Inorgànica i Orgànica, Secció Inorgànica and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, 08028 Barcelona, Spain
- Mercè Font-Bardia Departament de Mineralogia, Cristallografia i Dipòsits Minerals and Unitat de Difracció de R-X, Centre Científic i Tecnològic de la Universitat de Barcelona (CCiT-UB), Universitat de Barcelona, 08028 Barcelona, Spain
- Júlia Mayans Departament de Química Inorgànica i Orgànica, Secció Inorgànica and Institut de Nanociència i Nanotecnologia (IN²UB), Universitat de Barcelona, 08028 Barcelona, Spain; [®] orcid.org/0000-0001-8875-8075

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.cgd.3c00121

Author Contributions

The manuscript was written through contributions of all authors. All of the authors approved the final version of the manuscript. All of the authors contributed equally.

Funding

A.E. and J.M. are thankful for the support from MICINN, Project PGC2018-094031-B-100.

Notes

The authors declare no competing financial interest.

REFERENCES

 (1) Stratton, W. J.; Busch, D. H. The Complexes of Pyridinaldazine with Iron(II) and Nickel(II). J. Am. Chem. Soc. 1958, 80, 1286–1289.
 (2) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. Helicates as Versatile Supramolecular Complexes. Chem. Rev. 1997, 97, 2005– 2062.

(3) Albrecht, M. "Let's Twist Again". Double-Stranded, Triple-Stranded, and Circular Helicates. *Chem. Rev.* 2001, 101, 3457–3498.
(4) Hannon, M. J.; Childs, L. J. Helices and Helicates: Beautiful Supramolecular Motifs with Emerging Applications. *Supramol. Chem.* 2004, 16, 7–22.

(5) Lehn, J.-M.; Rigault, A.; Siegel, J.; Harrowfield, J.; Chevrier, B.; Moras, D. Spontaneous assembly of double-stranded helicates from oligobipyridine ligands and copper(I) cations: structure of an inorganic double helix. *Proc. Natl. Acad. Sci. U.S.A.* **1987**, *84*, 2565– 2569.

(6) Rogez, G.; Donnio, B.; Terazzi, E.; Gallani, J. L.; Kappler, J. P.; Bucher, J. P.; Drillon, M. The quest for nanoscale magnets: The example of $[Mn_{12}]$ Single Molecule Magnets. *Adv. Mater.* **2009**, *21*, 4323–4333.

(7) Bogani, L.; Wernsdorfer, W. Molecular spintronics using singlemolecule magnets. *Nat. Mater.* **2008**, *7*, 179–186.

(8) Wasielewski, M. R.; Forbes, M. D. E.; Frank, N. L.; Kowalski, K.; Scholes, G. D.; Yen-Zhou, J.; Baldo, M. A.; Freedman, D. E.; Goldscmith, R. H.; Goodson, T.; Kirk, M. L.; McCusker, J. K.; Ojilvie, J. P.; Schultz, D. A.; Stoll, S.; Whaley, K. B. Exploiting chemistry and molecular systems for quantum information science. *Nat. Rev. Chem.* **2020**, *4*, 490–504.

(9) Troiani, F.; Affronte, M. Molecular spins for quantum information technologies. *Chem. Soc. Rev.* **2011**, *40*, 3119–3129.

(10) Sessoli, R.; Gatteschi, D.; Caneschi, A.; Novak, M. A. Magnetic bistability in a metal-ion cluster. *Nature* **1993**, *365*, 141–143.

(11) Sessoli, R.; Tsai, H. -L.; Schake, A. R.; Wang, S.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. High-spin molecules: $[Mn_{12}O_{12}(O_2CR)_{16}(H_2O)_4]$. J. Am. Chem. Soc. **1993**, 115, 1804–1816.

(12) Atzori, M.; Tesi, L.; Benci, S.; Lunghi, A.; Righini, R.; Taschin, A.; Torre, R.; Sorace, L.; Sessoli, R. Spin dynamics and low energy vibrations: insights from vanadyl based potential molecular qubits. *J. Am. Chem. Soc.* **2017**, *139*, 4338–4341.

(13) Atzori, M.; Benci, S.; Morra, E.; Tesi, L.; Chiesa, M.; Torre, R.; Sorace, L.; Sessoli, R. Structural effects on the spin dynamics of potential molecular qubits. *Inorg. Chem.* **2018**, *57*, 731–740.

(14) Yu, C.-J.; Krzyaniak, M. D.; Fataftah, M. S.; Wasielewski, M. R.; Freedman, D. E. A concentrated array of cooper porphyrin candidate qubits. *Chem. Sci.* **2019**, *10*, 1702–1708.

(15) Gómez-Coca, S.; Cremades, E.; Aliaga-Alcalde, N.; Ruiz, E. Mononuclear Single-Molecule Magnets: Tailoring the magnetic anisotropy of first row transition metal complexes. *J. Am. Chem. Soc.* **2013**, *135*, 7010–7018.

(16) Świtlicka, A.; Machura, B.; Kruszynski, R.; Moliner, N.; Carbonell, J. M.; Cano, J.; Lloret, F.; Julve, M. Magneto-structural diversity of Co(II) compounds with 1-benzylimidazole induced by linear pseudohalide coligands. *Inorg. Chem. Front.* **2020**, *7*, 4535–4552.

(17) Orendáč, M.; Sedláková, L.; Čižmár, E.; Orendáčová, A.; Feher, A.; Zvyagin, S. A.; Wosnitza, J.; Zhu, W. H.; Wang, Z. M.; Gao, S. Spin relaxation and resonant phonon trapping in $[Gd_2(fum)_3(H_2O)_4: 3H_2O. Phys. Rev. B 2010, 81, No. 214410.$

(18) Martínez-Pérez, M. J.; Cardona-Serra, S.; Schlegel, C.; Moro, F.; Alonso, P. J.; Prima-García, H.; Clemente-Juan, J. M.; Evangelisti, M.; Gaita-Ariño, A.; Sesé, J.; van Slageren, J.; Coronado, E.; Luis, F. Gd-based Single-Ion Magnets with tunable magnetic anisotropy: Molecular design of spin qubits. *Phys. Rev. Lett.* **2012**, *108*, No. 247213.

(19) Mayans, J.; Escuer, A. Correlating the axial zero field splitting with the slow magnetic relaxation in Gd^{III} SIMs. *Chem. Commun.* **2021**, *57*, 721–724.

(20) Pilichos, E.; Bhunia, P.; Font-Bardia, M.; Ghosh, A.; Mayans, J.; Escuer, A. Quasi-isotropic SMMs: Slow relaxation of the magnetization in polynuclear Cu^{II}/Mn^{II} complexes. *Dalton Trans.* **2022**, *51*, 1779–1783.

(21) Ghosh, T. K.; Maity, S.; Mayans, J.; Ghosh, A. Family of Isomeric Cu^{II} – Ln^{III} (Ln = Gd, Tb, and Dy) Complexes Presenting Field-Induced Slow Relaxation of Magnetization Only for the Members Containing Gd^{III}. *Inorg. Chem.* **2021**, *60*, 438–448.

(22) Sorace, L.; Benelli, C.; Gatteschi, D. Lanthanides in molecular magnetism: old tools in a new field. *Chem. Soc. Rev.* **2011**, *40*, 3092–3104.

(23) Liddle, S. T.; van Slageren, J. Improving *f*-element single molecule magnets. *Chem. Soc. Rev.* **2015**, *44*, 6655–6669.

(24) Pointillart, F.; Cador, O.; Le Guennic, B.; Ouahab, L. Uncommon lanthanide ions in purely 4f Single Molecule Magnets. *Coord. Chem. Rev.* **201**7, 346, 150–175.

(25) Mayans, J.; Sáez, Q.; Font-Bardia, M.; Escuer, A. Enhancement of magnetic relaxation properties with 3d diamagnetic cations in $[Zn^{II}Ln^{III}]$ and $[Ni^{II}Ln^{III}]$, $Ln^{III} =$ Kramers lanthanides. *Dalton Trans.* **2019**, 48, 641–652.

(26) Zhang, P.; Guo, Y. -N.; Tang, J. Recent advances in dysprosium-based single molecule magnets: structural overview and synthetic strategies. *Coord. Chem. Rev.* **2013**, 257, 1728–1763.

(27) Goodwin, C. A. P.; Ortu, F.; Reta, D.; Chilton, N. F.; Mills, D. P. Molecular magnetic hysteresis at 60 kelvin in dysprosocenium. *Nature* **2017**, *548*, 439–442.

(28) Guo, F. -S.; Day, B. M.; Chen, Y. C.; Tong, M. L.; Mansikkamäki, A.; Layfield, R. A. A dysprosium metallocene Single-Molecule Magnet functioning at the axial limit. *Angew. Chem., Int. Ed.* **2017**, *56*, 11445–11449.

(29) Sheldrick, G. M. SHELXL-2014/7: Program for the Solution of Crystal Structures; University of Göttingen: Göttingen, Germany, 2014.

(30) Chandra, R.; Manna, A. K.; Sahu, M.; Rout, K.; Patra, G. K. Simple salicylaldimine- functionalized dipodal bis Schiff base

chromogenic and fluorogenic chemosensors for selective and sensitive detection of Al³⁺ and Cr³⁺. *Inorg. Chim. Acta* **2020**, *499*, No. 119192. (31) Lunell, M.; Casanova, D.; Cirera, J.; Alemany, P.; Alvarez, S. SHAPE v.2.0. Barcelona 2010. The Program Can be Obtained by Request to the Authors.

(32) Borilovic, I.; Roubeau, O.; Le Guennic, B.; van Slageren, J.; Lenz, S.; Teat, S. J.; Aromí, G. Three individually addressable spin qubits in a single molecule. *Chem. Commun.* **2022**, *58*, 7530–7533.

(33) Kruger, P. E.; Martin, N.; Nieuwenhuyzen, M. Dinuclear double helicates with a twist: synthesis, structure and supramolecular entanglement in $[M_2L_2]$ metallo-helices {M = Co(II), Cu(II), H₂L = bis(N-salicylidene-4,4'-diaminodiphenyl)methane}. J. Chem. Soc., Dalton Trans. 2001, 1966–1970.

(34) Su, X.-C.; Zhou, Z.-F.; Zhu, S.-R.; Lin, H.-K.; Weng, L.-H.; Leng, X.-B.; Chen, Y.-T. Synthesis and structure of neutral double helicate. *Chin. J. Chem.* **2010**, *18*, 773–776.

(35) Yoshida, N.; Ichikawa, K.; Shiro, M. Supramolecular motifs in metal complexes of Schiff bases. Part 5. Zinc(II)-assisted self-assembly of some bis-N,N- and N,O-bidentate Schiff bases and chiral packing modes in solid state. *J. Chem. Soc., Perkin Trans.* **2000**, *2*, 17–26.

(36) Chu, Z.; Huang, W. Syntheses and structures of two new bis-N,O-bidentate Schiff base ligands and their respective copper(II) complexes with dinuclear double-helical configuration. *J. Mol. Struct.* **2007**, 837, 15–22.

(37) Oshikawa, Y.; Yoneda, K.; Koikawa, M.; Yamada, Y. Syntheses, crystal structures, and solid-state spectroscopic properties of helical and non-helical dinuclear zinc(II) complexes derived from N_2O_2 ligands with different torsion-generating sources. *Inorg. Chim. Acta* **2019**, 495, No. 118979.

(38) Yoshida, N.; Oshio, H.; Ito, T. Copper (II)-assisted selfassembly of bis-N, O-bidentate Schiff bases: new building blocks for a double-helical supramolecular motif. *J. Chem. Soc., Perkin Trans.* **1999**, *2*, 975–984.

(39) Mondal, A. K.; Parmar, V. S.; Biswas, S.; Konar, S. Tetrahedral M^{II} based binuclear double-stranded helicates: single-ion-magnet and fluorescence behaviour. *Dalton Trans.* **2016**, *45*, 4548–4557.

(40) Singh, V. K.; Kadu, R.; Roy, H.; Raghavaiah, P.; Mobin, S. M. Phenolate based metallomacrocyclic xanthate complexes of Co^{II}/Cu^{II} and their exclusive deployment in [2:2] binuclear N,O-Schiff base macrocycle formation and in vitro anticancer studies. *Dalton Trans.* **2016**, *45*, 1443–1454.

(41) Kelly, N.; Schulz, J.; Gloe, K.; Doert, T.; Gloe, K.; Wenzel, M.; Acker, M.; Weigand, J. J. Self-assembly of dinuclear double-stranded copper(II) helicates with 3-ethoxy-2-hydroxyphenyl Substituted diimines. Synthesis, molecular structure, and host-guest recognition of H₂O. *Z. Anorg. Allg. Chem.* **2015**, *641*, 2215–2221.

(42) Cucos, P.; Tuna, F.; Sorace, L.; Matei, I.; Maxim, C.; Shova, S.; Gheorghe, R.; Caneschi, A.; Hillebrand, M.; Andruh, M. Magnetic and luminescent binuclear double-stranded helicates. *Inorg. Chem.* **2014**, *53*, 7738–7747.

(43) Hasi, Q.-M.; Fan, Y.; Yao, X.-Q.; Hu, D.-C.; Liu, J.-C. Synthesis, characterization, antioxidant and antimicrobial activities of a bidentate Schiff base ligand and its metal complexes. *Polyhedron* **2016**, *109*, 75–80.

(44) Habib, F.; Long, J.; Lin, P.-H.; Korobkov, I.; Ungur, L.; Wernsdorfer, W.; Chibotaru, L. F.; Murugesu, M. Supramolecular architectures for controlling slow magnetic relaxation in field-induced single-molecule magnets. *Chem. Sci.* **2012**, *3*, 2158–2164.

(45) Albrecht, M.; Janser, I.; Houjou, H.; Frohlich, R. Long-range stereocontrol in the self-assembly of two-nanometer-dimensioned triple-stranded dinuclear helicates. *Chem. - Eur. J.* **2004**, *10*, 2839–2850.

(46) Novitchi, G.; Costes, J. P.; Tuchagues, J. P.; Vendier, L.; Wernsdorfer, W. A single molecule magnet (SMM) with a helicate structure. *New J. Chem.* **2008**, *32*, 197–200.

(47) Jiang, D.; Yang, X.; Chen, H.; Wang, F.; Wang, S.; Zhu, T.; Zhang, L.; Huang, S. Cation sensing by luminescent high-nuclearity Zn–Eu Schiff base nanoscale complexes: high sensitivity to Ag^+ and Cd^{2+} ions at the ppm level. *Dalton Trans.* **2019**, *48*, 2206–2212.

(48) Chen, H.; Yang, X.; Jiang, D.; Shi, D.; Zhang, L. Construction of NIR luminescent polynuclear lanthanide-based nanoclusters with sensing properties towards metal ions. *Dalton Trans.* **2018**, *47*, 13880–13886.

(49) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. PHI: A powerful new program for the analysis of anisotropic monomeric and exchange-coupled polynuclear *d*- and *f*block complexes. *J. Comput. Chem.* **2013**, *34*, 1164–1175.

(50) Worrell, A.; Sun, D.; Mayans, J.; Lampropoulos, C.; Escuer, A.; Stamatatos, T. C. Oximato-based ligands in 3d-4f metal-cluster chemistry: A family of {Cu₃Ln} complexes with "propeller"-like topology and Single-Molecule Magnet behaviour. *Inorg. Chem.* **2018**, *57*, 13944–13952.

(51) Marinho, M. V.; Reis, D. O.; Oliveira, W. X. C.; Marques, L. F.; Stumpf, H. O.; Déniz, M.; Pasán, J.; Ruíz-Pérez, C.; Cano, J.; Lloret, F.; Julve, M. Photoluminescent and slow-magnetic relaxation studies on lanthanide(III)-2,5-pyrazinedinecarboxylate frameworks. *Inorg. Chem.* **201**7, *56*, 2108–2123.

(52) Benniston, A. C.; Melnic, S.; Turta, C.; Arauzo, A. B.; Bartolomé, J.; Bartolomé, E.; Harrington, R. W.; Probert, M. R. Preparation and properties of a calcium(II)-based molecular chain decorated with manganese(II) butterfly-like complexes. *Dalton Trans.* **2014**, *43*, 13349–13357.

(53) Rajnák, C.; Titis, J.; Moncol, J.; Micova, R.; Boca, R. Field-Induced Slow Magnetic relaxation in a mononuclear manganese(II) complex. *Inorg. Chem.* **2019**, *58*, 991–994.

(54) Da Cunha, T. T.; Barbosa, V. M. M.; Oliveira, W. X. C.; Pedroso, E. F.; Garcia, D. M. A.; Nunes, W. C.; Pereira, C. L. M. Field-induced slow magnetic relaxation of a six-coordinate mononuclear manganese(II) and cobalt(II) oxamate complexes. *Inorg. Chem.* **2020**, *59*, 12983–12987.

(55) Uchida, K.; Cosquer, G.; Sugisaki, K.; Matsuoka, H.; Sato, K.; Breedlove, B. K.; Yamashita, M. Isostructural M(II) complexes (M = Mn, Fe, Co) with field-induced slow magnetic relaxation for Mn and Co complexes. *Dalton Trans.* **2019**, *48*, 12023–12030.

(56) Pilichos, E.; Font-Bardia, M.; Escuer, A.; Mayans, J. Occurrence of slow relaxation of the magnetization in a family of copper(II)/ manganese(II) quasi-isotropic complexes with different ground spin states. *Dalton Trans.* **2022**, *51*, 17653–17663.