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Microwave assisted synthesis of heterometallic 3d-4f M₄Ln complexes

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In this paper we describe the synthesis and magnetic properties of a series of 3d-4f complexes of general formula [M₄Ln(OH)₂(chp)₄(SALOH)₅(H₂O)(MeCN)(Solv)] (solv = MeOH, MeCN, H₂O; chp stands for deprotonated 6-chloro-2-hydroxypyridine (C₅H₃ClNO), SALOH stands for monodeprotonated 3,5-ditert-butylsalicylic acid (C₁₅H₂₁O₃)) obtained by a solvent-free microwave assisted synthesis method. The Ni(II) complexes (**Ni₄Gd**, Solv = MeOH; **Ni₄Dy**, Solv = MeCN) are not SMMs in the absence of an applied dc field. The replacement of Ni(II) by Co(II) (**Co₄La**, Solv = MeOH; **Co₄Gd**, Solv = H₂O; **Co₄Gd**-MeCN, Solv = MeCN; **Co₄Tb**, Solv = MeOH; **Co₄Dy**, Solv = H₂O) results in improved SMM properties.

Introduction

Interest in molecular nanomagnets due to their potential applications in high-density information storage, molecular spintronics, quantum computing^{1,2,3} or magnetic coolers⁴ has grown in the last 30 years. Since the discovery of the first single-molecule magnet (SMM) Mn₁₂Ac in the 90's by Christou⁵ and Gatteschi,⁶ the synthesis of high nuclearity complexes with SMM properties is a great and challenging target for coordination chemists. An SMM must have a large spin ground state and easy axis anisotropy, leading to slow relaxation of the magnetization below its blocking temperature. Thus, an SMM is able to retain the magnetization and it behaves like a magnet at the molecular level.^{7,8} SMMs were also obtained using other 3d transition metals including manganese, iron, nickel, cobalt or vanadium,⁹ but in these cases higher working temperatures have been elusive. Thus, the anisotropy barrier for the reversal of the magnetization in transition metal SMMs depends on two properties: the total spin of the molecule S and the Ising-type anisotropy. This knowledge has been used to design improved SMMs based on two strategies: rising S or increasing the anisotropy of the molecule. Increasing S by introducing stronger ferromagnetic coupling has been achieved in several examples: Mn₁₈,¹⁰ Mn₂₁,¹¹ Mn₈₄¹² or Mn₁₉.¹³ However, higher nuclearity structures with a large S value is no guarantee of a large molecular anisotropy. A great example is Mn₁₉: it possesses the record spin of 83/2 for a molecular cluster, but it lacks anisotropy and thus it is not an SMM. Focus is set since the early 2000's in increasing the magnetic anisotropy of the prepared complexes in order to improve SMM properties, using metal ions with strong spin-orbit coupling as Co(II) or the lanthanides. Heterometallic 3d-4f compounds as well as pure 4f systems are seen as the route to better SMMs. Rare earths have long been used in magnetism due to their strong magnetic anisotropy. 4f complexes usually have high energy barriers compared with 3d

metals SMMs but their hysteresis loops are usually closed due to fast QTM (Quantum Tunnelling of the Magnetization) and alternative relaxation pathways.^{14,15} Since the first heterometallic 3d-4f SMM was reported in 2004, many groups have devoted much effort to these 3d-4f complexes.¹⁶ Still, in 2018 high operational temperatures for 4f or 3d-4f SMMs remain elusive. In 2018, after his previous work on organometallic lanthanide SMMs,^{17,18,19} Layfield reported a nearly linear Dy metallocenium that displayed hysteresis at 80 K.²⁰ Reta and Chilton offered theoretical insight on the high temperature hysteresis, relating it once again to the coupling with vibrational phonons in the structure.²¹ The last results greatly improved the archetypical lanthanide SMMs, the phthalocyanine lanthanide sandwich complexes first studied as SMMs by Ishikawa et al.^{22,23,24}

The synthetic methodologies are crucial for obtaining homo- or heteronuclear complexes with the desired properties, but most are still based on serendipitous assembly.²⁵ The interest on finding new synthetic methodologies is a challenge in chemistry.²⁶ In the last few years, microwave assisted synthesis has been useful for organic chemists not only to synthesize products that are otherwise unattainable, also to obtain in pure form products that in conventional conditions appear in a mixture that requires taxing purification methods. In the same way, this synthetic method is useful for the synthesis of high nuclearity coordination compounds.²⁷ In general, with microwave assisted synthesis, formation of one species is favoured.²⁸ Microwave assisted synthesis is clean, quick and it is included in green chemistry, because of its partial or in some cases total absence of organic solvents.²⁹ The microwave reactor offers a unique environment, which allows high temperatures and high pressure, generated by the heating of the molecules by the microwave radiation. Microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field.³⁰ Only those substances with a

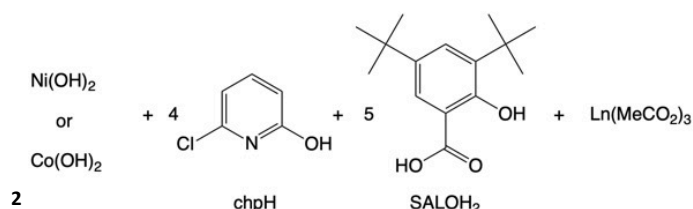
dipolar moment will be excited by microwaves. This energy transfer to some of the species in the reaction mixture is very efficient and the heating rate is homogeneous.³¹ The technique has been used to synthesize polynuclear coordination compounds like Ni_8 and Ni_9 ³² or Mn_3 ,³³ MOF's (Metal-Organic Frameworks)³⁴ and nanoparticles.³⁵ Solvent-free synthetic methods are often used in coordination chemistry, in a melt state^{36–40} or by sublimation of the product.⁴¹ Of particular relevance to spintronics is the archetypical mononuclear single molecule magnet (SMM) TbPc_2 ,²² synthesized by conventional heating over long periods of time and that often produce mixtures of products and require tedious purification methods.^{42,43}

In 2017 we used solvent-free microwave assisted synthesis to obtain $[\text{Ni}_4\text{Tb}(\text{OH})_2(\text{chp})_4(\text{SALOH})_5(\text{H}_2\text{O})(\text{MeCN})(\text{MeOH})]$ (**Ni₄Tb**), and its La analogue, **Ni₄La**.⁴⁴ Clearly, the prepared complexes were very interesting to us and we wanted to extend the synthetic method to other lanthanide ions and other transition metals. We herein exploit this synthetic method to prepare a family of M_4Ln complexes of general formula $[\text{M}_4\text{Ln}(\text{OH})_2(\text{chp})_4(\text{SALOH})_5(\text{H}_2\text{O})(\text{MeCN})(\text{Solv})]$ (solv = MeOH, MeCN, H_2O) (**Ni₄Gd**, Solv = MeOH; **Ni₄Tb**, Solv = MeOH; **Ni₄Dy**, Solv = MeCN; **Co₄La**, Solv = MeOH; **Co₄Gd**, Solv = H_2O ; **Co₄Gd-MeCN**, Solv = MeCN; **Co₄Tb**, Solv = MeOH; **Co₄Dy**, Solv = H_2O) and its by-products. The change of Ni(II) for Co(II) leads to an improvement on the SMM properties of the prepared complexes, as the cobalt complexes display SMM properties in the absence of an applied dc field.

Results and Discussion

Following our work on microwave assisted synthesis in coordination chemistry we decided to apply the method to solvent-free systems. This would provide a clean, cost and time efficient method to obtain heterometallic coordination complexes. The clear limitation of the method is only that the ligands chosen must have easily attainable melting points in order to provide a good molten media for ion diffusion.

Microwave assisted synthesis was used to obtain new 3d-4f molecular nanomagnets with two versatile ligands (2-hydroxy-6-chloropyridine, Hchp, melting point 128–130°C and 3,5-ditertbutylsalicylic acid, SALOH₂, (melting point 157–162°C)) chosen due to their many possible coordination modes and their low melting points. The tert-butyl groups also improve solubility, processability of SMMs and self-organization on a metal surface.^{45–47} The metal salts used are the metal hydroxides, freshly prepared, since they provide useful OH-counterions that are desired bridges in the final products. In 2017 we reported complex **Ni₄Tb** $[\text{Ni}_4\text{Tb}(\text{OH})_2(\text{chp})_4(\text{SALOH})_5(\text{H}_2\text{O})(\text{MeCN})(\text{MeOH})]$ and its La analogue.⁴⁴ Homometallic reactions in a similar ligand system have been reported elsewhere.⁴⁸



Scheme 1. Synthesis scheme showing methods a, b and c and their products. * reported in reference 44.

Following this work on homometallic and heterometallic reactions with a versatile ligand system we decided to extend this chemistry to other transition metals and to study the reaction system in different reaction conditions. Three different reaction methods were studied: (a) solvent-free microwave assisted synthesis, (b) microwave assisted synthesis in solvent and (c) bench-top stirring reactions at room temperature.

The solvent free microwave assisted reaction (method a) was studied with microwave pulses between 100 W and 300 W at the melting point of the ligands. The 300 W pulse was chosen since it consistently produced the best yield of products. Once the reaction was cooled a solid was obtained and characterized by IR spectroscopy: the results were very similar to those of the products after recrystallization. The comparison of the IR of the melt with the IR of the crystals and that of free SALOH₂ (see ESI Figure S05) clearly shows that the organic ligands are already coordinated to the M(II) and Ln(III) ions, a fact that was supported by the formation of acetic acid during the reaction by protonation of the acetate groups from the lanthanide acetate reagent. The solid was extracted with the minimum amount of MeOH/MeCN mixture (1:1 in volume) and the green or pink-purple solution was left undisturbed. Crystals suitable for single crystal X-Ray diffraction were obtained after 15–20 days. For complex **Co₄Gd-MeCN**, crystals of the product were obtained using only MeCN as crystallization solvent.

Met. a

Solvent free
microwave
reaction

Met. b

Microwave
reaction
with solvent

Met. c

Bench-top
reaction
with solvent

Table 1. Crystallographic parameters for the M_4Ln complexes.

	Ni ₄ Dy	Co ₄ La	Co ₄ Gd-MeCN	Co ₄ Gd	Co ₄ Dy
System	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Fdd2	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a/Å	38.0841(17)	20.3125(12)	20.3401(13)	20.390(4)	20.3905(6)
b/Å	65.768(3)	33.4255(19)	33.317(2)	33.367(7)	33.2699(10)
c/Å	21.4176(10)	21.1033(12)	21.0558(13)	21.344(4)	21.2501(7)
α/°	90	90	90	90	90
β/°	90	115.075(3)	115.756(3)	115.83(3)	115.857(2)
γ/°	90	90	90	90	90
Volume/Å³	53645.1(4)	12977.8(13)	12851.3(15)	13070(5)	12972.6(7)
Z	16	4	4	4	4
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0610 wR ₂ = 0.1817	R ₁ = 0.0795 wR ₂ = 0.2124	R ₁ = 0.0782 wR ₂ = 0.2497	R ₁ = 0.0784 wR ₂ = 0.2475	R ₁ = 0.0922 wR ₂ = 0.2805
T/K	293 K	173 K	100 K	100 K	100 K

The complexes obtained all had the general formula $[M_4Ln(OH)_2(chp)_4(SALOH)_5(H_2O)(MeCN)(Solv)]$ (**Ni₄Gd**, **Ni₄Dy**, **Co₄La**, **Co₄Gd**, **Co₄Tb**, **Co₄Dy**). Complex **Co₄La** was always obtained in a mixture of precipitate and very small crystals. Crystals were handpicked for magnetic analysis and elemental analyses.

The alternative microwave assisted reactions with solvent (method b in Scheme 1) were tested but were only successful in some systems (Ni/Tb, Co/Dy and Co/Gd): all reactants and the solvents MeOH/MeCN (2mL, 2mL) were placed into the microwave reactor cavity. A 300 W microwave pulse was applied for 10 minutes at 120°C. The lower temperature if compared to method a is mandated by the boiling point of the organic solvents. The precipitate was filtered and the solution left undisturbed. Crystals suitable for single crystal X-Ray diffraction grew in ca. 15 days in some systems. For the Ni/Tb system **Ni₄Tb-b** was obtained. For the other Ni/Ln systems we were not able to identify the products obtained by method b, however IR analysis of the solids obtained showed they were not the pure known M_4Ln species. The cobalt/Ln (Ln = Gd, Dy) reaction systems produced mixtures of products. Two types of crystals, with very similar colour and shape, appeared at similar times from the solution. The crystals were identified as complex **Co₄Gd-b** and **Co₄Dy-b**, and the new linear species $[Co_2Dy_2(chp)_2(SALOH)_8(MeOH)_4]$ and $[Co_2Gd_2(MeCO_2)(chp)(SALOH)_8(MeCN)_2]$. These by-products are also obtained for some of the Co/Ln systems from method c, doing the reaction on the bench-top, stirring at room temperature (method c in Scheme 1) for Ln = Dy, Tb but they products could not be isolated in pure form from a microwave reaction. Similar complexes have been found in the CSD with the core Co_2Ln_2 and similar organic ligands with N- or O-donors.^{49,50,51} A complete analysis of the new Co_2Ln_2 complexes will be reported elsewhere. The species of general formula

$M_4Ln [M_4Ln(OH)_2(chp)_4(SALOH)_5(H_2O)(MeCN)(Solv)]$ were only obtained from microwave assisted reactions. However, method b in the case of the Co/Gd and Co/Dy systems do not afford a pure product but a mixture of species. In fact, for the Co(II)/Ln(III) system we here observe that the microwave assisted reaction with solvent (method b in Scheme 1) affords a mixture of the products from the solvent-free microwave assisted reaction (method a in Scheme 1) and the bench-top reaction (method c in Scheme 1). To our knowledge, this Co/Ln system is unusual for microwave assisted synthesis which is often used to avoid by-products or mixtures of products.

The solvent-free microwave assisted reaction has been applied successfully to 3d-4f heterometallic coordination complexes in a carefully chosen ligand system. We believe this method can be extended to other metal-ligand systems with good results.

Description of Crystal structure

Crystallographic and data collection details for **Ni₄Dy** and **Co₄La**, **Co₄Gd**, **Co₄Gd-MeCN** and **Co₄Dy** are presented in Table 1. For **Ni₄Tb-b** only the unit cell was checked and it coincided with that of **Ni₄Tb**.⁴⁴ Crystals were often very small and diffracted poorly due to the free-rotation of tert-butyl groups, thus data for complex **Co₄Gd** were collected using synchrotron radiation. Data for **Ni₄Gd** and **Co₄Tb** had low resolution so only unit cells are reported. The unit cell parameters are as expected, very similar to those of the other M_4Ln complexes and can be found in SI Table S-C1.

All complexes crystallize in the monoclinic space group P2₁/c except **Ni₄Dy**. They all have the same $M_4Ln(OH)_2$ core with small differences only in the coordinated solvent molecules. **Ni₄Dy** $[Ni_4Dy(OH)_2(chp)_4(SALOH)_5(H_2O)(MeCN)_2]$ crystallizes in the orthorhombic space group Fdd2. To avoid repetition, a general description of the common features of all M_4Ln complexes will be given. The asymmetric unit contains the whole molecule and disordered non-coordinated solvents, this is also true for

complex Ni_4Dy . The crystal structure and the core of $\text{Co}_4\text{Gd-MeCN}$ are shown in Figure 1.

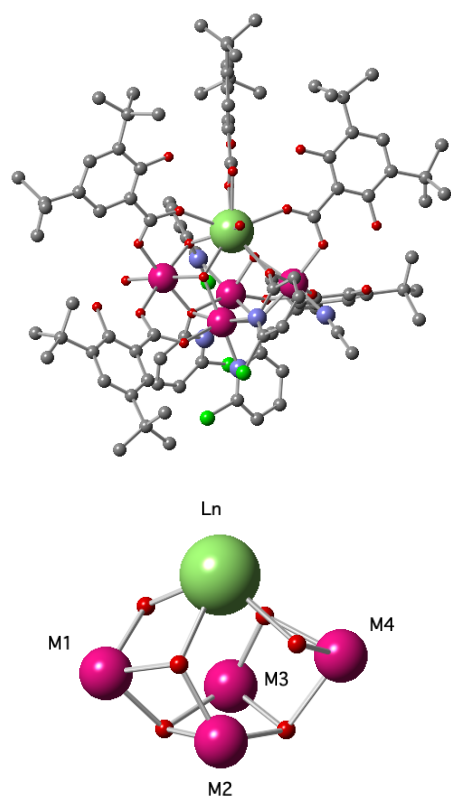
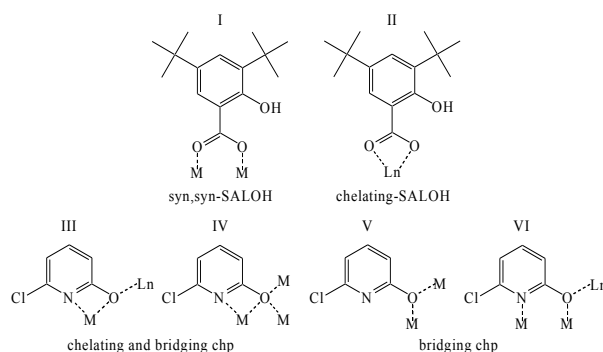


Figure 1. Crystal structure of $\text{Co}_4\text{Gd-MeCN}$ and general labelled core showing the triply bridging OH- and the bridging oxygens from chp ligands. M atoms in purple, Ln in light green, oxygen in red, nitrogen in blue, carbon in gray, chlorine in green. Hydrogen atoms have been removed for clarity.

The core consists of one Ln(III) ion linked to four M(II) ions by oxygen bridging ligands, two of these oxygens are provided by μ^3 -hydroxo groups and the other four are from chp ligands. Scheme 2 shows the observed coordination modes for the chp and SALOH ligands. There are four SALOH ligands bridging every M(II) ion to the Ln(III) ion in coordination mode I. The other SALOH ligand is chelating the Ln(III) in coordination mode II. Two chp ligands are bridging three metals and chelating one metal using the oxygen and nitrogen donors in the coordination mode IV. The two remaining chp ligands are bridging the Ln(III) ion to M1 and M4 in coordination mode VI. The four M(II) ions are hexacoordinated with distorted octahedral geometries. The Ln(III) ion is ennea-coordinated with a distorted geometry. To complete its coordination sphere M1, M4 and the Ln(III) ion are bonded to terminal solvent molecules. For all the series Ln(III) is bonded to a terminal aqua ligand while the solvent molecules for M1 and M4 are either water, MeOH or MeCN. Complexes Ni_4Gd and Co_4Tb have MeOH bound to M1 and MeCN bound to M4. Complexes Co_4Gd and Co_4Dy have the same metal-OH-core as the M_4Ln series but differ in the terminal solvents: they have terminal water bonded to M1 ion. Complex $\text{Co}_4\text{Gd-MeCN}$ has terminal MeCN ligands for M1 and M4.



Scheme 2. Binding modes of the ligands.

Complex Ni_4Dy $[\text{Ni}_4\text{Dy}(\text{OH})_2(\text{chp})_4(\text{SALOH})_5(\text{H}_2\text{O})(\text{MeCN})_2]$ crystallizes in the orthorhombic space group Fdd2 and it has two terminal MeCN bonded to the M1 and M4. Bond valence sum calculations (BVS, calculated values can be found in ESI Tables S-C2 and S-C3)^{52,53,54} confirm the oxidation states of the transition metal ions as M(II) and the lanthanide ion as Ln(III) , as well as the oxygen atoms valence, verifying when necessary the protonation level of OH- bridging ligands, water molecules or terminal alcohol groups.

Magnetic properties

Magnetic data for crushed crystalline samples of complexes Ni_4Gd , Ni_4Dy and Co_4La , Co_4Gd , Co_4Tb and Co_4Dy were collected on a commercial SQUID. Magnetic data for complexes Ni_4La and Ni_4Tb and fitting of the susceptibility for complex Ni_4La were already reported in our ICF paper of 2017.⁴⁴ Magnetic susceptibility vs. temperature are shown as χT vs. T plots for the two families of complexes Ni_4Ln and Co_4Ln in Figures 2 and 3, respectively. The data were collected in the 2-300 K temperature range at an applied field of 3000 Oe and a field of 300 Oe below 30 K. The χT product values at 300 K are collected in Table S01. The χT product values at 300 K are in agreement with the expected values for the Ni_4Ln family: four Ni(II) ions ($S=1$, $g=2.1-2.3$) and one lanthanide ion, Ni_4Dy : Dy(III) ($^6\text{H}_{15/2}$, $S=5/2$, $L=5$, $J=15/2$, $g=4/3$) or Ni_4Gd : Gd(III) ($^8\text{S}_{7/2}$, $S=7/2$, $L=0$, $g=2.0$). In the Co_4Ln family complexes the contribution of Co(II) ions is higher than the expected for a spin-only case ($S=3/2$, $g=2.0$) due to the presence of spin orbit coupling in hexacoordinated Co(II) . For all complexes in the series the χT product values at 300 K are in agreement with four Co(II) with strong spin orbit coupling and one lanthanide(III) ion, Co_4La : La(III) ($S=0$), Co_4Gd : Gd(III) ($^8\text{S}_{7/2}$, $S=7/2$, $L=0$, $g=2.0$), Co_4Tb : Tb(III) ($^7\text{F}_6$, $S=3$, $L=3$, $J=6$, $g=3/2$), Co_4Dy : Dy(III) ($^6\text{H}_{15/2}$, $S=5/2$, $L=5$, $J=15/2$, $g=4/3$).

The susceptibility of the M_4Ln complexes can be understood as the addition of a lanthanide ion weakly coupled to the more strongly coupled tetranuclear transition metal M_4 unit. The couplings between the transition metals in the M_4 unit are easily derived from the La derivative, for the cobalt series, that is Co_4La . For the Ni(II) series, the ferromagnetic coupling between the Ni(II) ions in Ni_4La was described in our 2017 paper as well as the ferromagnetic Ni-Tb coupling in Ni_4Tb , confirmed by XMCD.⁴⁴ For the Co(II) analogue there is some extent of antiferromagnetic coupling between the Co(II) centres of Co_4Ln .

DFT calculations have been used to estimate the exchange coupling between Co(II) ions and between Co(II) and the lanthanide ion.

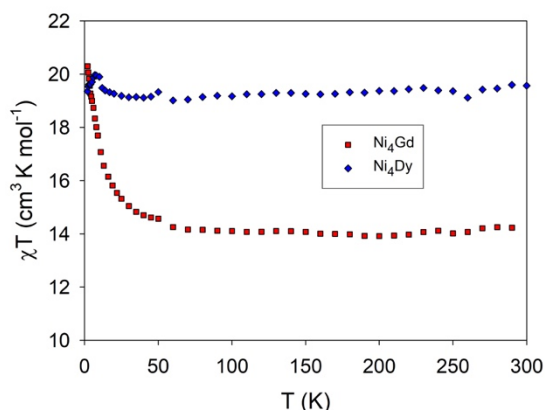


Figure 2. Magnetic susceptibility data for Ni_4Ln complexes shown as χT vs. T plots. Data for complexes Ni_4La and Ni_4Tb can be found in reference 44.

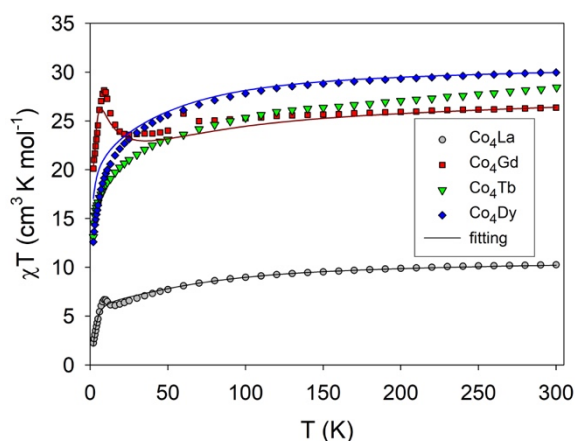


Figure 3. Magnetic susceptibility data for Co_4Ln (right) complexes shown as χT vs. T plots.

Magnetization vs. field data at 2 K for Ni_4Ln and Co_4Ln complexes are shown in Figure S01. For the family of Ni_4Ln complexes saturation is almost reached at 5 T in agreement with the ferromagnetic interactions that lead to the spin ground state. This is not the case of the Co_4Ln complexes. The fact that the magnetization value does not saturate is consistent with magnetic anisotropy associated with strong spin orbit coupling and with a combination of ferromagnetic and antiferromagnetic interactions as calculated using theoretical approaches.

Given the field-induced SMM nature of Ni_4Tb ⁴⁴ and the large spin ground states observed and the anisotropy associated to lanthanide complexes, the dynamic magnetic properties of the new Ni_4Ln and the Co_4Ln complexes were studied. Ac magnetic susceptibility data were collected between 20 K and 1.8 K. The data showed the absence of out-of-phase signals for Ni_4Gd and Ni_4Dy with or without an applied dc field. Ni_4Tb is the only complex of the nickel family that shows clear field-induced

SMM behaviour.⁴⁴ Clearly, the Ni_4 unit, even though it has a large spin does not have enough anisotropy to trigger SMM behaviour. The change of the transition metal from Ni(II) to Co(II) has a clear effect in the magnetic anisotropy of the complex, thus affecting the dynamic magnetic properties of the species.

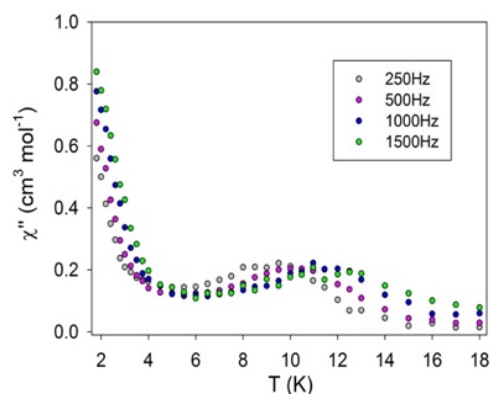
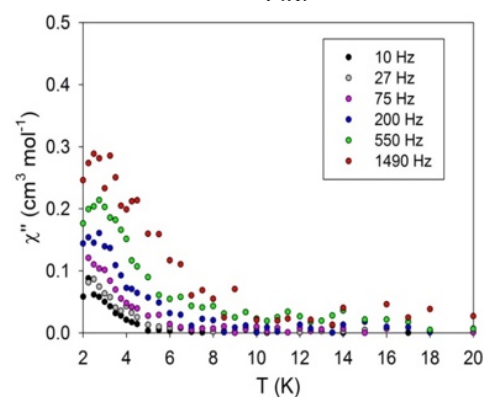
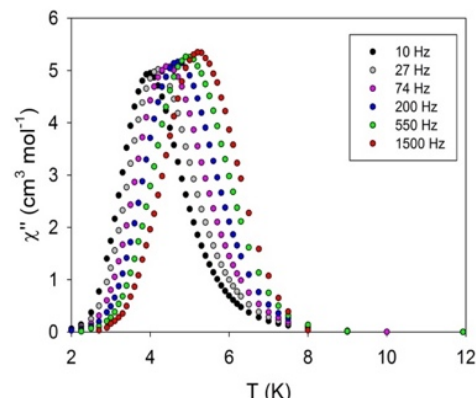


Figure 4. Out of phase AC magnetic susceptibility plots for Co_4Gd (top), Co_4Tb with $d_c = 2000$ G (centre) and for Co_4Dy with $d_c = 2000$ G (bottom).

All Co_4Ln complexes show peaks in the out-of-phase ac magnetic susceptibility, as expected. In a 2009 paper, Boča and Titiš⁵⁵ correlated Ni(II) coordination in Ni(II) monomers with the sign of D : negative D values needed for a transition metal SMM are expected for tetragonally compressed Ni(II). Ruiz and co-workers showed for octahedral Co(II) monomers that D values are larger than for Ni(II) but sometimes positive. In polynuclear systems, an effective negative D for the molecule can be

obtained by the appropriate orientation of the local ZFS tensors with respect to the molecular easy axis.⁵⁶

Gd(III), with a large $S = 7/2$ is ferromagnetically coupled to the Co₄ unit in **Co₄Gd**, the complex has a large magnetic moment. **Co₄Gd** is an SMM and it displays an out-of-phase ac magnetic susceptibility peak at 5 K, as shown in Figure 4 (top). The relaxation data was fitted to Arrhenius' equation with $\tau_0 = 6.95\text{e-}12\text{ s}^{-1}$ and $U_{\text{eff}} = 86\text{ K}$, values typical of a transition metal SMM (Figure S03) as good as the archetypical Mn₁₂Ac.^{9,57} The Argand plots for **Co₄Gd** at different temperatures between 3 K and 6 K are shown in ESI Figures S05–06. The data were fitted to a Debye model for a distribution of relaxation processes with $\tau_0 = 1.06\text{e-}6\text{--}1.53\text{e-}2\text{ s}^{-1}$ and $\alpha = 0.56\text{--}0.69$ between 3 and 6 K. The values for each temperature can be found in the ESI Table S01. **Co₄Tb** and **Co₄Dy** only show tails of out-of-phase ac susceptibility peaks if a dc field is applied. Thus, a static dc magnetic field was applied and ac magnetic susceptibility data were collected for **Co₄Tb** and **Co₄Dy**. The data are shown in Figure 4 (centre) with an applied dc field of 2000 Oe. A peak appears below 6 K for **Co₄Tb** but the maximum is only observed at the highest frequencies (750 to 1500 Hz). If we compare and **Co₄Tb** to **Ni₄Tb**, the ac peak appears at higher temperatures so it is clear that using Co(II) instead of Ni(II) leads to higher energy barriers for the relaxation of the magnetization.

The ac data for **Co₄Dy** with an applied field of 2000 Oe shows two relaxation processes, one centred at 11 K and the other one below 3 K. The high-temperature process can be analysed using the Arrhenius' equation with $\tau_0 = 3.43\text{e-}7\text{ s}^{-1}$ and $U_{\text{eff}} = 66\text{ K}$ (see ESI Figure S03). The low temperature peak is related to the application of a dc field and is important at low temperatures and low frequencies, as discussed for Ni(II), Co(II) and Cu(II) SMMs by Titus and Boca.^{58,59} The ac susceptibility for **Co₄Dy** was also studied as a function of frequency at several temperatures, (ESI Figure S04–05). The data were fitted to a Debye model for a distribution of relaxation processes with $\tau_0 = 8\text{e-}5\text{--}9.4\text{e-}3\text{ s}^{-1}$ and $\alpha = 0.04\text{--}0.31$ between 5 and 13 K. The values for each temperature can be found in the ESI Table S01.

Clearly the combination of a Co₄ SMM with an anisotropic lanthanide ion like Dy(III) or Tb(III) results in this case in worst properties than the combination of the Co₄ unit with Gd(III). The controversy between the importance of spin and anisotropy is clear for this family of Co₄Ln complexes: if anisotropy is good enough, increasing spin wins over increasing magnetic anisotropy in a heterometallic complex and the Co/Gd analogue **Co₄Gd** is the SMM with ac out-of-phase peaks at higher temperatures in the absence of an applied dc field, however, QTM effects are very relevant in all **Co₄Ln** complexes.

Theoretical approach to magnetic properties. For **Co₄La** the magnetic properties were modelled using a theoretical approach that shows that there is a combination of ferromagnetic and antiferromagnetic interactions between the Co(II) ions. In order to study the intramolecular exchange interactions of the Co₄La system, electronic structure calculations at density functional level have been performed using the Heisenberg Hamiltonian (see Computational Details). The computed exchange constants as well as the involved atoms can be found in Table 2.

The overall magnetic behaviour of **Co₄La** is a combination of ferromagnetic and antiferromagnetic contributions.

The ferromagnetic interaction J_3 takes place via two chp ligands coordinated by both the O and N donor atoms (see Figure 1).

Table 2. Calculated exchange interactions (cm⁻¹) for complex **Co₄La**, with the corresponding bridging ligands and geometrical parameters (distances in Å and angles in degrees). Subindexes indicate metal number as shown in Figure 1.

	Atoms involved	d(Co-Co)	Bridging ligands	$\alpha(\text{Co-O}_{\text{ox}}\text{-Co})$	$J_{\text{calc.}}$
J_1	Co ₁ Co ₂	3.119	$\mu_3\text{-OH}$, $\mu_2\text{-RCOO}$	99.37, 92.25,	-2.67
	Co ₃ Co ₄	3.139	OR, $\mu_2\text{-RCOO}$	100.14, 92.74	
J_2	Co ₂ Co ₃	3.388	$\mu_2\text{-OR}$	99.22, 99.06	+0.63
J_3	Co ₁ Co ₃	3.715	$\mu_2\text{-OR}$	117.15	+5.79
	Co ₂ Co ₄	3.746		118.80	

This interaction is responsible of the observed χT value at room temperature. The only antiferromagnetic interaction observed in **Co₄La** corresponds to J_1 , and involves the $\mu_3\text{-OH-}$ bridging ligand, the O-donor atom from the chp ligand (coordination mode IV in Scheme 2) and a *syn,syn*-carboxylato group from SALOH (coordination mode I in Scheme 2). The *syn,syn*-carboxylato bridging mode is well known to favour antiferromagnetic coupling. Additional spin distributions were considered, which allows us to estimate the error on the computed exchange interactions. This statistical data validates the ferromagnetic nature of J_3 and the antiferromagnetic nature of J_1 (see ESI material). The crystal structures of both Ni and Co complexes are very similar, however the strong spin-orbit coupling (SOC) in octahedral Co(II) results in S not being a good quantum number to describe the magnetic properties of Co(II) complexes, and one must consider J and the splitting of the m_j sublevels. Magnetostructural correlations are common for transition metals with quenched SOC like Cu(II) or Ni(II). In particular, Ni(II) cubanes with $\mu_3\text{-O}$ bridges are systems that have been particularly well studied. The complexes reported here are not cubanes, but they could be described as deformed capped cubanes, where the lanthanide caps and separates the two metal ions in one face of the cubane. The M-O-M angles in the Ni(II) series of M₄Ln are between 93° and 117° (mean Ni-O-Ni angle 102°) while for the Co(II) series are between 91° and 116° (mean Co-O-Co angle 101°). The full list of angles in the M₄Ln core can be found in SI Table S-C4. Magnetostructural correlations for cubanes show that the relationship between the M-O-M angle and the sign of the magnetic coupling is clear for Ni(II), with Ni-O-Ni angles below 99° leading to ferromagnetic coupling but not so straight-forward for Co(II): similar angles for Co(II) complexes lead to either ferromagnetic or antiferromagnetic coupling.^{60,61} Additionally, Ni(II) dinuclear complexes bridged by phenoxo ligands display relatively large ferromagnetic coupling constants,⁶² while such a magnetostructural correlation is not reported for Co(II). The theoretical approach supports the fact that an antiferromagnetic exchange pathway via a *syn,syn*-carboxylato bridging ligand is present in **Co₄La**.

Table 3: Calculated exchange interactions (cm^{-1}) for complex **Co₄Gd**, with the corresponding bridging ligands and geometrical parameters (distances in Å and angles in degrees). Sub-indexes indicate metal number as shown in Figure 1.

	Atoms involved	d(Co-Co)	Bridging ligands	$\alpha(\text{Co-O}_{\text{ox}}\text{-Co})$	$J_{\text{calc.}}$
J_1	Co ₁ Co ₂ Co ₃ Co ₄	3.119 3.149	$\mu_3\text{-OH}$, $\mu_2\text{-OR}$, $\mu_2\text{-RCOO}$	98.53, 91.95 99.55, 93.24	-2.43
J_2	Co ₂ Co ₃	3.149	$\mu_2\text{-OR}$	99.55, 93.24	+0.29
J_3	Co ₁ Co ₃	3.363	$\mu_2\text{-OR}$	99.22, 99.06	+0.76
J_4	GdCo ₂ , GdCo ₄	3.516 3.487	$\mu^2\text{-OR}$, $\mu_3\text{-OH}$	102.04, 105.09, 102.03, 104.20	+0.71

In order to assess the Co(II)-Ln(III) coupling the magnetic data for complex **Co₄Gd**, the magnetic properties of **Co₄Gd** have also been calculated using theoretical approach. The magnetic properties of complex **Co₄Dy** have been obtained by rescaling by a factor 5/7 and the anisotropy of Dy(III) studied. Introducing one lanthanide ion with a magnetic moment increases the complexity of the model. DFT calculations have been performed to explore the Co(II)-Co(II) and Co(II)-Gd(III) magnetic exchange interactions in **Co₄Gd**.

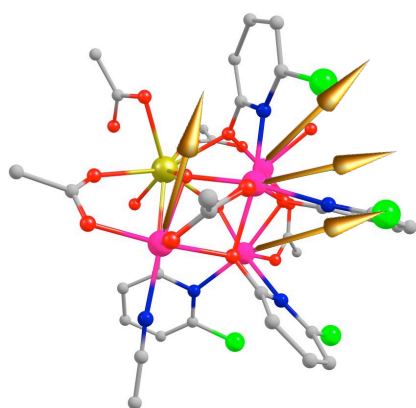


Figure 5. The D_{zz} tensor the four Co(II) metal centres of complex **Co₄Dy**. Colour code: Dy-Greenish yellow, Co-Pink, Cl-Green, O-Red, N-Blue, C-grey. Hydrogens are omitted for clarity.

To estimate four different exchange coupling constants, five spin configurations were chosen (See ESI for details). The exchange coupling constants (Table 3) are estimated to be $J_1(\text{Co-Co}) = -2.43$, $J_2(\text{Co-Co}) = 0.29$, $J_3(\text{Co-Co}) = 0.76$ and $J_4(\text{Co-Gd}) = 0.71 \text{ cm}^{-1}$. The Co-Co coupling constants (J_1 and J_2) are similar to those obtained for **Co₄La**. *Ab initio* calculation predicts that axial zero field splitting parameter of each Co is positive. The anisotropy axis of the Co(II) and Dy(III) in **Co₄Dy** are shown in Figure 5.

Table 4: The axial and rhombic zero field parameter of Co centres.

Metal centre	D (cm^{-1})	E/D
Co1	75.8	0.26
Co2	85.5	-0.03
Co3	61.0	-0.22
Co4	94.9	-0.16

The axial and rhombic zero field splitting parameter estimated are gathered in Table 4. All four Co(II) ions are found to have local positive D value ranging from 61.0 to 94.9 cm^{-1} with significant E/D values. The variations in the magnitude of D are due to the local distortions of octahedral Co(II) with O/N donor ligands. The computed values are in accord with the values reported in the literature.⁶³ The values in Table 4 imply that D value increases with increasing deviation from the octahedral symmetry except Co(3) (see Table S07). The magnitude of E/D value decreases with increasing deviation from the octahedral symmetry except for Co(2). To validate the exchange parameters obtained by DFT calculation we attempted to fit the experimental susceptibility data for **Co₄La**, **Co₄Gd** and **Co₄Dy**. The susceptibility data of **Co₄La** and **Co₄Gd** were fitted using PHI⁶⁴, with the *ab initio* computed D and E tensors of Co(II) ions along with DFT estimated exchange coupling constants as a starting point. The best fits are shown in Figure 3 as solid lines. For complex **Co₄La**, the J_1 and J_3 exchanges were varied to get the best fit. The best fit was obtained with the value of -0.75 cm^{-1} for J_1 and 0.85 cm^{-1} for J_3 , TIP of $0.00150 \text{ cm}^3/\text{mol}$ and $zJ' = 0.01 \text{ cm}^{-1}$. For complex **Co₄Gd**, the susceptibility is found to be sensitive to the exchange coupling J_1 . By fixing all other parameters constant (single-ion D value of the four Co(II) centres and J_2 , J_3 and J_4 interactions), good fit is obtained when J_1 is -0.90 cm^{-1} , intermolecular interaction $zJ' = 0.02 \text{ cm}^{-1}$ and TIP = 0.005 cm^{-1} . For both **Co₄La** and **Co₄Gd**, DFT computed values are overestimated compared to the values obtained from best fitting of the data. While the variation is apparent clear in J_1 for **Co₄La** and **Co₄Gd**, and in J_3 for **Co₄Gd**, since all other parameters are obtained from computational studies, this yields confidence on the estimated spin Hamiltonian parameters. The estimated Co-Ln exchange here are in line with the parameters estimated by us earlier on other [CoLn] clusters.^{65,66}

Although the zero field splitting parameter of the individual Co(II) centres are positive the anisotropy axis of the individual Co(II) centres are not collinear to each other (Figure 5). The overall magnetic behaviour is dominated by the ferromagnetic exchange (J_2 , J_3 and J_4). This leads to $S = 19/2$ ground state for **Co₄Gd** (which is also supported by the experimental value of temperature dependent susceptibility at high temperature) leading to a large barrier for magnetisation reversal in zero field. Figure 6 shows the population of each spin state calculated using PHI.

For complex **Co₄Dy**, simulations were performed using POLY_ANISO routine. The DFT computed exchange coupling constants (re-scaled to Dy(III)) were used for the simulation with

Figure 1 consists of two parts. Part (a) shows the crystal structure of the complex, which is a coordination polymer. It features a central metal atom (yellow sphere) coordinated by several ligands, including a large organic ligand (blue and green spheres) and a smaller ligand (red spheres). The structure is shown in a 3D perspective view. Part (b) is a plot of Energy (cm⁻¹) versus the reaction coordinate $M(\mu_x)$. The plot shows the energy profile of the reaction, with the energy increasing from 0 to 35 cm⁻¹ as the reaction coordinate increases from -3 to 3. The energy profile is shown for two different reaction paths, with the energy values at the reactant, transition state, and product states indicated. The reactant state is at $M(\mu_x) = -3$ with an energy of 0 cm⁻¹. The transition state is at $M(\mu_x) = -2$ with an energy of 30 cm⁻¹. The product state is at $M(\mu_x) = 3$ with an energy of 0 cm⁻¹. The energy difference between the reactant and transition state is 30 cm⁻¹, and the energy difference between the transition state and product is 30 cm⁻¹. The energy difference between the reactant and product is 0 cm⁻¹. The energy profile is shown for two different reaction paths, with the energy values at the reactant, transition state, and product states indicated. The reactant state is at $M(\mu_x) = -3$ with an energy of 0 cm⁻¹. The transition state is at $M(\mu_x) = -2$ with an energy of 30 cm⁻¹. The product state is at $M(\mu_x) = 3$ with an energy of 0 cm⁻¹. The energy difference between the reactant and transition state is 30 cm⁻¹, and the energy difference between the transition state and product is 30 cm⁻¹. The energy difference between the reactant and product is 0 cm⁻¹.

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(m), 815 (m), 795 (m), 724 (m), 668 (m); where strong (s), medium (m), weak (w), broad (b).

Ni₄Dy Yield: 56 mg (7%), based on Dy(MeCO₂)₃. Calculated Elemental Analysis for C₁₁₀H₁₇₁Cl₆DyN₈Ni₄O₄₂: C, 45.8%; N, 3.9%; H, 5.9%. Found Elemental Analysis: C, 45.1%; N, 3.9%; H, 4.6%. IR data (KBr, cm⁻¹): 3628 (w), 2958 (s), 1653 (m), 1595 (s), 1558 (s), 1444 (s), 1361 (s), 1339 (m), 1295 (m), 1244 (m), 1165 (m), 995 (m), 933 (m), 814 (m), 793 (m), 726 (m), 699 (m); where strong (s), medium (m), weak (w), broad (b).

[Co₄Ln(OH)₂(chp)₄(SALOH)₅(H₂O)(MeCN)(Solv)] (**Co₄La** Ln = La, Solv = MeOH; **Co₄Gd**, Ln = Gd, Solv = H₂O; **Co₄Gd-MeCN**, Ln = Gd, Solv = MeCN; **Co₄Tb**, Ln = Tb, Solv = MeOH; **Co₄Dy**, Ln = Dy, Solv = H₂O): Freshly prepared cobalt hydroxide (100 mg, 1.088 mmol), 6-chloro-2-hydroxypyridine (140.94 mg, 1.088 mmol), Ln(III) acetate (**Co₄La**, 85.96 mg; **Co₄Gd**, 90.95 mg; **Co₄Tb**, 91.42 mg; **Co₄Dy**, 92.38 mg; 0.272 mmol) and 3,5-di-tert-butylsalicylic acid (338.84 mg, 1.36 mmol) were homogenized on a mortar and then placed in a microwave reactor. A 300 W microwave pulse was applied for 10 minutes at 170°C. The resulting solid was dissolved in the minimum amount of MeOH/MeCN (1:1) and then filtered warm obtaining a dark pink solution. Pink crystals grew in circa 20 days. Complexes were characterized using single crystal X-Ray Diffraction. Crystals of **Co₄Gd-MeCN** were obtained extracting with only MeCN.

Co₄Gd: Yield: 188.4 mg (31%), based on La(MeCO₂)₃. Calculated Elemental Analysis for C₁₃₀H₁₇₃Cl₄Co₄LaN₆O₂₉: C, 55.7%; N, 3.0%; H, 6.2%. Found Elemental Analysis: C, 55.7%; N, 3.0%; H, 6.4%. IR data (KBr, cm⁻¹): 3274 (m, b), 2960 (s), 2904 (m), 2867 (m), 1646 (s), 1593 (s), 1558 (s), 1506 (w), 1444 (s), 1389 (m), 1360 (m), 1281 (w), 1244 (m), 1220 (w), 1201 (w), 1163 (w), 1083 (w), 988 (m), 922 (m), 890 (w), 815 (m), 793 (m), 745 (w), 722 (w), 637 (w), 529 (w); where strong (s), medium (m), weak (w), broad (b).

Co₄Gd: Yield: 44.9 mg (7%), based on Gd(MeCO₂)₃. Calculated Elemental Analysis for C₁₁₃H₁₆₃Cl₇Co₄GdN₈O₃₉: C, 46.8%; N, 3.8%; H, 5.6%. Found Elemental Analysis: C, 46.7%; N, 3.4%; H, 4.9%. IR data (KBr, cm⁻¹): 3629 (w), 3417 (m, b), 3102 (w), 2955 (m), 1982 (w), 1616 (m), 1594 (s), 1538 (m), 1442 (s), 1339 (m), 1253 (w), 1164 (m), 1068 (w), 1040 (m), 994 (m), 933 (m), 786 (m), 733 (w), 697 (m), 648 (w), 611 (m), 536 (m); where strong (s), medium (m), weak (w), broad (b).

Co₄Tb: Yield: 149.7 mg (24%), based on Tb(MeCO₂)₃. Calculated Elemental Analysis for C₉₈H₁₃₂Cl₄Co₄N₅O₂₅Tb: C, 50.8%; N, 3.0%; H, 5.7%. Found Elemental Analysis: C, 50.8%; N, 2.9%; H, 5.6%. IR data (KBr, cm⁻¹): 3417 (m, b), 2958 (s), 2907 (m), 2869 (m), 1652 (w), 1593 (s), 1558 (s), 1444 (s), 1391 (s), 1361 (m), 1295 (w), 1244 (s), 1202 (m), 1170 (m), 1150 (w), 1118 (w), 1007 (m), 938 (m), 814 (m), 792 (m), 745 (w), 722 (w), 643 (w), 562 (w); where strong (s), medium (m), weak (w), broad (b).

Co₄Dy: Yield: 201 mg (32%), based on Dy(MeCO₂)₃. Calculated Elemental Analysis for C₁₀₂H₁₄₁Cl₅Co₄DyN₆O₃₀: C, 48.8%; N, 3.3%; H, 5.6%. Found Elemental Analysis: C, 48.8%; N, 3.2%; H, 5.6%. IR data (KBr, cm⁻¹): 3627 (w), 3107 (w, b), 2958 (s), 2869 (w), 1652 (w), 1593 (s), 1558 (s), 1444 (s), 1392 (s), 1361 (m), 1295 (w), 1244 (m), 1202 (w), 1168 (m), 1121 (w), 1005 (w), 937 (w), 815 (w), 792 (w), 724 (w), 668 (w), 644 (w), 614 (w), 540 (w), 516 (w); where strong (s), medium (m), weak (w), broad (b).

Method b (Ni₄Tb-b, Co₄Gd-b and Co₄Dy-b): Freshly prepared nickel or cobalt(II) hydroxide (1.088 mmol), 6-chloro-2-hydroxypyridine (140.94 mg, 1.088 mmol), Ln(III) acetate (Ln = Tb, 91.42 mg, 0.272 mmol; Ln = Gd, 90.95 mg, 0.272 mmol; Ln = Dy 92.38 mg, 0.272 mmol) and 3,5-di-tert-butylsalicylic acid (338.84 mg, 1.36 mmol) were homogenized on a mortar and then placed in a microwave reactor with MeOH/MeCN (2ml/2ml). A 300 W microwave pulse was applied for 10 minutes at 120°C. A solution with precipitate was obtained. The precipitate was filtered and the solution left undisturbed. Crystals grew in circa 5 days and the products identified as **Ni₄Tb-b**, mixtures of **Co₄Dy-b** and [Co₂Dy₂(chp)₂(SALOH)₈(MeOH)₄] and

mixtures of **Co₄Gd-b** and [Co₂Gd₂(MeCO₂)(chp)(SALOH)₈(MeCN)₂] by single crystal X-Ray diffraction, IR and elemental analyses.

Characterization

X-Ray diffraction data for complexes **Ni₄Dy**, **Co₄Gd-MeCN**, **Co₄Dy** and unit cells for **Ni₄Gd**, **Ni₄Tb-b**, **Co₄Gd-b**, **Co₄Tb**, and **Co₄Dy-b** were collected on a Bruker APEXII SMART diffractometer using Molybdenum K α microfocus (λ =0.71073Å) radiation source. Single crystal diffraction data for **Co₄Gd** were collected at the XALOC beamline of Alba -CELLS Synchrotron (Spain) (T=100 K, λ =0.729Å). Single crystal diffraction data for **Co₄La** were collected at the Advanced Light Source station, at Berkeley (USA) (T = 173 K, λ = 0.71073Å). The structures were solved by Patterson or intrinsic phasing methods (SHELXS2014 and SHELXT) and refined on F² (SHELXL-2014). Hydrogen atoms were included on calculated positions, riding on their carrier atoms. To calculate solvent accessible voids solvent masks were applied. Cif files can be obtained free of charge from the Cambridge Structural Database (<http://www.ccdc.cam.ac.uk/>, deposition numbers CCDC **Ni₄Dy** (1915070), **Co₄Gd-MeCN** (1878755), **Co₄Dy** (18335341), **Co₄La** (1878760), **Co₄Gd** (1878756)). Elemental analyses (CHN) were performed at Servei de Microanàlisi in CSIC (Consell Superior d'Investigacions Científiques). Infrared spectra were collected on KBr pellets on an AVATAR 330 FT-IR at Departament de Química Inorgànica, Universitat de Barcelona. XPS experiments were performed in a PHI 5500 Multitechnique System (from Physical Electronics) with a monochromatic X-ray source (Aluminium K-alfa line of 1486.6 eV energy and 350 W), placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a full width at half maximum (FWHM) of 0.8 eV. The analysed area was a circle of 0.8 mm diameter, and the selected resolution for the spectra was 187.85 eV of Pass Energy and 0.8 eV/step for the general spectra and 23.5 eV of Pass Energy and 0.1 eV/step for the spectra of the different elements. A low energy electron gun (less than 10 eV) was used in order to discharge the surface when necessary. All Measurements were made in a ultra high vacuum (UHV) chamber pressure between 5x10⁻⁹ and 2x10⁻⁸ torr. Magnetic measurements were performed at the Unitat de Mesures Magnètiques of the Universitat de Barcelona on a Quantum Design SQUID MPMS-XL magnetometer equipped with a 5 T magnet. Diamagnetic corrections for the sample holder and for the sample using Pascal's constants were applied. Hysteresis measurements were performed with an array of micro-SQUIDS. This magnetometer works in the temperature range of 0.04 to 5 K and in fields up to 1.4 T with sweeping rates as high as 0.28

Conclusions

The solvent-free microwave assisted synthesis method can be easily extended to different ligand/metal systems, in this paper we show how we can systematically change the metals in the system using this synthetic approach. The requirements are simple: ligands with low melting points that can serve as a molten reaction media on the microwave reactor. The molten ligand facilitates ion diffusion in the reaction and is key for the formation of a coordination complex. The solvent free reaction drastically reduces the use of organic solvents, being a clean method that is both cost and time efficient. In the particular case reported here, the solvent free microwave assisted synthesis has been applied to the preparation of a family of heterometallic 3d-4f M₄Ln complexes, with the possibility of changing both the transition metal (M = Co(II), Ni(II)) and the lanthanide ion (Ln = La(III), Gd(III), Dy(III), Tb(III)). This produces a family of complexes with tuneable magnetic moment and magnetic anisotropy. The static and dynamic magnetic properties of the complexes reported have been studied showing that the substitution of Ni(II) for Co(II) consistently

leads to better SMMs. In the Co_4Ln series, the largest magnetic moment for Co_4Gd as well as the lack of the spin-orbit coupling in the lanthanide ion are key for obtaining high energy barriers for the relaxation of the magnetization and to avoid relaxation by QTM. The analogues of more anisotropic lanthanide ions like Dy(III) or Tb(III) have relaxation mechanisms dominated by QTM that must be quenched in order to obtain better SMM properties.

Conflicts of interest

In accordance with our policy on [Conflicts of interest](#) please ensure that a conflicts of interest statement is included in your manuscript here. Please note that this statement is required for all submitted manuscripts. If no conflicts exist, please state that “There are no conflicts to declare”.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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