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# **Manuscript Revised**

# Slow magnetic relaxation in mononuclear gadolinium(III) and dysprosium(III) oxamato complexes\*\*

Tamyris T. da Cunha,<sup>†</sup> Vitor M. M. Barbosa,<sup>†</sup> Willian X. C. Oliveira,<sup>†</sup> Carlos B. Pinheiro,<sup>‡</sup> Emerson F. Pedroso,<sup>§</sup> Wallace C. Nunes,<sup>∥</sup> Cynthia L. M. Pereira<sup>\*,†</sup>

<sup>†</sup>Departamento de Química, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais. Av. Antônio Carlos 6627, Pampulha, Belo Horizonte, Minas Gerais, 31270-901 Brazil. e-mail: <u>cynthialopes@ufmg.br</u>

<sup>‡</sup>Departamento de Física, Instituto de Ciências Exatas, Universidade Federal de Minas Gerais. Av. Antônio Carlos 6627, Pampulha, Belo Horizonte, Minas Gerais, 31270-901 Brazil;

Scentro Federal de Educação Tecnológica de Minas Gerais, Av. Amazonas 5523, Belo Horizonte, Minas Gerais 30421-169, Brazil;

<sup>II</sup> Instituto de Física, Universidade Federal Fluminense, Av. Gal. Milton Tavares de Souza, s/n°, Campus da Praia Vermelha, 24210-346, Niterói, Rio de Janeiro, Brazil.

\*\*This work is dedicated to Prof. Miguel Julve on the occasion of his 65<sup>th</sup> birthday and for being an example of a generous and nice person and a brilliant scientist who has inspired a generation of chemists worldwide. It is an enormous pleasure for us to collaborate with him.

#### ABSTRACT

A series of lanthanide(III) oxamate complexes of formula Na[Eu(4-HOpa)<sub>4</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O (1), Na[Gd(4-HOpa)<sub>4</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O (2), Na[Dy(4-HOpa)<sub>4</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O (3), and Na[Ho(4- $HOpa_4(H_2O)$ ]·2H<sub>2</sub>O (4) (4-HOpa= N-4-hydroxyphenyloxamate) were synthesized and characterized. The crystal structures of complexes 1-4, as well as the oxamate ligand in the ethyl ester acid form (Et[4-HOpa]), were elucidated by single crystal X-ray diffraction. 1-4 are isostructural, and they crystallize in the  $P2_1/n$  space group of the monoclinic system. The crystal structures of 1-4 consist of mononuclear lanthanide(III) complex anions,  $[Ln(4-HOpa)_4(H_2O)]^-$  (Ln= Eu<sup>3+</sup>, Gd<sup>3+</sup> Dy<sup>3+</sup> and Ho<sup>3+</sup>), coordinated sodium(I) countercations, and crystallization water molecules, resulting in a 2D NaILnIII supramolecular coordination network. The coordination sphere of Ln<sup>3+</sup> ions consists of square-face capped square antiprism (SAPRS-9). Magnetic properties were investigated for 1-4 in the 2-300 K temperature range using polycrystalline samples. Complex 2 exhibits an unusual and rare slow-relaxation of the magnetization for Gd<sup>3+</sup> ions under DC applied field of 1.0 kOe, behaving as a field-induced single-ion magnet as occurs for the  $Dy^{3+}$  complex 3. The Eu<sup>3+</sup> complex 1 has a nonmagnetic ground state, while the Ho<sup>3+</sup> compound 4 behave as a paramagnet, and do not exhibit relaxation of the magnetization with or without an applied field.

**Keywords:** oxamate ligands; lanthanide complexes; crystal structures; slow magnetic relaxation; single-ion magnets

### 1. Introduction

Since the report of the first single-molecule magnet that exhibited magnetic bistability with the potential for data-storage applications at temperatures of a few Kelvin [1], several researchers in the world have directed their efforts to overcome this limitation, increasing the temperature in compounds containing lanthanide ions for which this phenomenon can be detected [2]. The discovery of magnetic relaxation of the magnetization in mononuclear terbium(III)- and dysprosium(III)-bis(phthalocyaninato) complexes at approximately [3] 40 K puts the strategy of using lanthanides ions for the obtention of molecules containing only one magnetic ion, the so-called single ions magnets (SIMs), in the spotlight. A factor in achieving such magnetic effects seems to be the presence of a large single-ion magnetic anisotropy which depends on the type of organic ligand involved. Thus, lanthanides(III) ions can be very promising in quantum information processing and high-data storage at the molecular and atomic level [4].

In this direction, research groups worldwide have been invested their efforts in the discovery of new lanthanide molecules containing different types of ligands with the potential to become a magnetic storage device [5]. Recently, the discovery of dysprosium(III)-based metallocenium cations of general formula  $[Dy(CpR)_2]^+$  (CpR =  $C_5R_5$ ; R = H, alkyl or silyl) that contain a  $Dy^{3+}$  ion sandwiched between two cyclopentadienyl-type aromatic  $\pi$  ligands, namely dysprosocenium, brings back this research in evidence since the magnetic bistability phenomena in this compound was detected at 60 K, is considered very high for such kind of molecule [6,7]. That being so, it is essential to keep looking for new ligand types that can result in high-temperature SIMs for potential data-storage applications.

In our research work we are dealing with *N*-substituted oxamate ligands, which are very versatile ligands that present a large variety of binding modes combined with innumerable possibilities of substituent groups, either aliphatic [8] or aromatic, such as phenyl [9], phenylene [10] and polyaromatics [11]. This ligand versatility brings to these plethora of complexes several different possibilities beyond magnetism [12–17], such as metal organic frameworks for click chemistry catalysis [18] and decontamination of organic pollutants for environmental purposes [19], hybrid materials based in carbon nanotubes [20] and Vycor glass (PVG) [21] for magnetic studies, hybrid catalyst

anticancer agent [22] and amphiphilic catalyst for biphasic process [23], among others [24,25].

The design of oxamate ligands has been mainly focused on the building of molecular edifices with transition metal ions. Some examples of lanthanide-containing oxamate complexes were reported on the literature [26–31], the majority involving the self-assembly of 3d and 4f paramagnetic metal ions. The first report of a compound containing only oxamate ligands and lanthanides ions was described a few years ago [32]. It consisted of mononuclear dysprosium(III) complex with the N-(2,6-dimethylphenyloxamate ligand, resulting in a supramolecular 2D hydrogen-bonded polymer that exhibited a slow magnetic relaxation behavior typical of a SIM at low temperatures [32].

Herein, we present the synthesis, crystal structures and magnetic properties of the first series of mononuclear oxamate-based lanthanide coordination compounds of general formula Na[Ln(4-HOpa)<sub>4</sub>(H<sub>2</sub>O)]·2H<sub>2</sub>O [Ln= Eu<sup>3+</sup> (1), Gd<sup>3+</sup> (2), Dy<sup>3+</sup> (3), and Ho<sup>3+</sup> (4)], where 4-HOpa stands for *N*-4-hydroxyphenyloxamate, obtained from the reaction of corresponding LnX<sub>3</sub> salts [X= Ac<sup>-</sup> or Cl<sup>-</sup>] with the sodium(I) salt of the proligand Na[4-HOpa] (Scheme 1). For the first time, it is reported an unusual slow relaxation of the magnetization for a gadolinium(III)-oxamato complex **2**, behaving as single ion magnet as the related dysprosium(III)-oxamato complex **3**.



Scheme 1. The general chemical structure for the oxamate ligand derivatives Et[4-HOpa] (R = Et) and Na[4-HOpa] (R = Na).

#### 2. Experimental Section

#### 2.1. General procedures

All chemicals and solvents used were of analytical grade and used without further purification in the syntheses. Elemental analyses were carried out with a Perkin-Elmer 2400 analyzer, and IR spectra were recorded from KBr pellets in the range 4000 and 400 cm<sup>-1</sup> on a Perkin Elmer 882 Spectrophotometer. NMR spectra of ligands were obtained with a Bruker AVANCE-III 400 Nanobay spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm concerning dmso-d<sub>6</sub> as the internal standard. Melting points (m.p.) were determined by the digital device MQAPF-302 12038DV from Microquímica. X-ray powder diffraction (PXRD) intensities for polycrystalline samples of **1**–**4** were measured at 293 K on a Shimadzu XRD-7000 X-RAY (Cu K $\alpha$ ,  $\lambda$  = 1.54056 Å) by scanning over the range of 5–40° with steps of 2°/s. Simulated PXRD patterns of **1**–**4** were generated with Mercury® software using crystal data retrieved from CIF file. Magnetic measurements were performed using a Cryogenics SQUID magnetometer model S700X with applied magnetic fields of 0.020 T (for DC measurements) and a Quantum Design PPMS (for AC susceptibility measurements). The AC and DC measurements were

performed in samples placed in gelatin capsules with mineral oil to prevent crystals movement. All diamagnetic corrections of the constituent atoms were estimated from Pascal's constants [33]. All experimental magnetic measurements were also corrected for the sample holder.

#### 2.2. Synthesis of Et[4-HOpa]

The proligand was prepared in a standard manner[34] from the condensation of 4aminophenol (1.08 g, 9.9 mmol) and ethyl oxalyl chloride (1.10 mL, 9.9 mmol) in the presence of triethylamine (1.38 mL, 9.9 mmol) in tetrahydrofuran (THF), and it was isolated as the ethyl ester acid derivative. Crystals of Et(4-HOpa), well-formed colorless needles, were obtained in THF recrystallization. Yield: 57% (1.18 g). M.p. = 182 °C. Selected IR peaks (cm<sup>-1</sup>): 3340 (s), 1732 (s), 1678 (s), 1560 (w), 1516 (m), 1022 (m), 834 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmso-d<sub>6</sub>), 400 MHz, 25 °C:  $\delta$  = 1.3 (t, *J* = 7.1, 3H); 4.2 (q, *J* = 7.1, 2H); 6.7 (d, *J* = 8.9, 2H); 7.5 (d, *J* = 8.9, 2H); 9.4 (s, 1H); 10.5 ppm (s, 1H). <sup>13</sup>C NMR (dmso-d<sub>6</sub>, 101 MHz, 25°C):  $\delta$  = 161.02, 155.13, 154.55, 129.05, 122.28, 115.22, 62.32, 13.90 ppm. Elemental analysis calcd (%) for C<sub>10</sub>H<sub>11</sub>NO<sub>4</sub>: C 57.40 H 5.30, N 6.70; found C 57.65, H 5.10, N 6.94.

#### 2.3. Synthesis of Na[4-HOpa]

The sodium(I) salt of the proligand was synthesized according to literature methods [34, 35]. NaOH (0.19 g, 4.78 mmol) was added to a methanolic solution (20.0 mL) of Et(4-HOpa) (1.0 g, 4.78 mmol). The resulting mixture was refluxed at 80°C for 1 h under continuous stirring. The resultant solid was filtered, washed with methanol and dried at 60°C for 1 h. Yield: 77% (0.747 g). Selected IR peaks (cm<sup>-1</sup>): 3408 (s), 3332 (s), 1670 (s), 1642 (s), 1540 (w), 1522 (m), 1258 (m), 820 (m), 804 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (dmso-d<sub>6</sub>), 400 MHz, 25 °C:  $\delta$  = 6.70 (d, J = 8.8, 2H); 7.55 (d, J = 8.9, 2H); 9.43 (s, 1H); 10.03 (s, 1H). <sup>13</sup>C NMR (dmso-d<sub>6</sub>, 101 MHz, 25°C):  $\delta$  = 163.87, 163.08, 153.65, 130.26, 121.02, 115.03 ppm. Elemental analysis calcd (%) for C<sub>8</sub>H<sub>6</sub>NNaO<sub>4</sub>: C 47.30 H 2.98, N 6.90; found C 47.71, H 2.84, N 7.04.

#### 2.4. Synthesis of $Na[Eu(4-HOpa)_4(H_2O)] \cdot 2H_2O(1)$

An aqueous solution (20.0 mL) of Eu(Ac)<sub>3</sub>·3H<sub>2</sub>O (0.33 mmol, 0.126 g) was added dropwise to an aqueous solution of Na(4-HOpba) (1.0 mmol, 0.203 g) under continuous stirring. The resulting light yellow solution was heated at 60 °C for 15 min. Colorless prismatic single crystals were obtained after 5 days at room temperature. Yield: 68% (0.160 g). Selected IR peaks (KBr/cm<sup>-1</sup>): 3338 (s), 1640 (s), 1552 (w), 1512 (m), 1370 (m), 1272 (m), 836 (m), 812 (w) cm<sup>-1</sup>. Elemental analysis calcd (%) for  $C_{32}H_{30}EuN_4NaO_{19}$ : C 40.48, H 3.18, N 5.90; found C 40.17, H 2.82, N 6.20.

### 2.5. Synthesis of $Na[Gd(4-HOpa)_4(H_2O)] \cdot 2H_2O$ (2)

An aqueous solution (20.0 mL) of Gd(Ac)<sub>3</sub>·4H<sub>2</sub>O (0.33 mmol, 0.134 g) was added dropwise to an aqueous solution of Na(4-HOpba) (1.0 mmol, 0.203 g) under continuous stirring. The resulting light yellow solution was heated at 60 °C for 15 min. Colorless prismatic crystals were obtained after 5 days at room temperature. Yield: 44% (0.112 g). Selected IR peaks (KBr/cm<sup>-1</sup>): 3350 (s), 1650 (s), 1560 (w), 1514 (m), 1386 (m), 1242 (m), 834 (m), 816 (w) cm<sup>-1</sup>. Elemental analysis calcd (%) for C<sub>32</sub>H<sub>30</sub>GdN<sub>4</sub>NaO<sub>19</sub>: C 40.25, H 3.17, N 5.87; found C 40.80, H 3.17, N 5.83.

#### 2.6. Synthesis of $Na[Dy(4-HOpa)_4(H_2O)] \cdot 2H_2O$ (3)

An aqueous solution (20.0 mL) of  $Dy(Ac)_3 \cdot 3H_2O$  (0.33 mmol, 0.129 g) was added dropwise to an aqueous solution of Na(4-HOpba) (1.0 mmol, 0.203 g) under continuous stirring. The resulting light pink solution was heated at 60 °C for 15 min. Light pink prismatic single crystals were obtained after 5 days at room temperature. Yield: 82% (0.195 g). Selected IR peaks (KBr/cm<sup>-1</sup>): 3354 (s), 1654 (s), 1638 (s), 1560 (w), 1514 (m), 1386 (m), 1242 (m), 836 (m), 810 (w). Elemental analysis calcd (%) for  $C_{32}H_{30}DyN_4NaO_{19}$ : C 40.03, H 3.15, N 5.84; found C 39.97, H 3.30, N 5.73.

#### 2.7. Synthesis of $Na[Ho(4-HOpa)_4(H_2O)] \cdot 2H_2O$ (4)

An aqueous solution (20.0 mL) of HoCl<sub>3</sub>·6H<sub>2</sub>O (0.33 mmol, 0.125 g) was added dropwise to an aqueous solution of Na(4-HOpba) (1.0 mmol, 0.203 g) under continuous stirring. The resulting light pink solution was heated at 60 °C for 15 min. Light pink prismatic single crystals were obtained after 5 days at room temperature. Yield: 69 % (0.166 g). Selected IR peaks (KBr/cm<sup>-1</sup>): 3354 (s), 1602 (s), 1554 (m), 1514 (m), 1370 (m), 1244

(m), 836 (m), 812 (w). Elemental analysis calcd (%) for C<sub>32</sub>H<sub>30</sub>HoN<sub>4</sub>NaO<sub>19</sub>: C 39.93, H
3.14, N 5.82; found C 39.29, H 3.29, N 5.77.

#### 2.8. X-ray Crystallographic Measurements

Table 1 provides a summary of the crystal data, data collection and refinement parameters for Et[4-OHpa] and 1-4. All diffraction data were collected on an Oxford-Diffraction GEMINI-Ultra diffractometer at 298 K (Et[4-HOpa], 1, 3) and 150 K (2, 4) using Mo  $K_{\alpha}$ radiation ( $\lambda = 0.71073$  Å). CRYSALIS Pro software [36] was used respectively for data integration, scaling of the reflections and analytical absorption corrections. Space group identification was done with XPREP [37], and structure solution was carried out by direct methods using SUPERFLIP [38]. Refinements were performed using SHELXL-2018 [37] based on F<sup>2</sup> through the full-matrix least square routine. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located in difference maps and included as fixed contributions according to the riding model [39]. Values C–H = 0.97 Å and  $U_{iso}(H) = 1.2 U_{eq}(C)$  were used for aromatic and methylene (*R*-CH<sub>2</sub>-*R*') carbon atoms, C-H = 0.96 Å and  $U_{iso}(H) = 1.5 U_{eq}(C)$  for methyl carbon atoms, N-H = 0.97 Å and  $U_{iso}(H) = 1.2 U_{eq}(N)$  for amide groups, O-H = 0.87 Å and  $U_{iso}(H) = 1.5 U_{eq}(O)$  for the phenyl OH groups and O-H = 0.90 Å and  $U_{iso}(H) = 1.5$  $U_{eq}(O)$  for water molecules. Graphics were prepared with Mercury<sup>®</sup> [40] and VESTA [41]. Crystallographic data for the reported structures have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 1840845 (Et[4-HOpa]), 1840846 (1), 1840847 (2), 1840848 (3) and 1840849 (4).

 Table 1. Summary of Crystallographic Data for Et[4-HOpa] and 1-4.

Compound	Et(4-HOpa)	1	2	3	4
Formula	C <sub>10</sub> H <sub>11</sub> NO <sub>4</sub>	C32H30EuN4NaO19	$C_{32}H_{30}GdN_4NaO_{19} \\$	$C_{32}H_{30}DyN_4NaO_{19}\\$	C <sub>32</sub> H <sub>30</sub> HoN <sub>4</sub> NaO <sub>19</sub>
Fw/g mol <sup>-1</sup>	209.19	949.54	954.83	960.08	962.52
T/K	298	298	150	298	150
$\lambda$ /Å	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> /n	$P2_1/n$	$P2_{1}/n$	<i>P</i> 2 <sub>1</sub> /n	$P2_1/n$
<i>a /</i> Å	5.2065(5)	14.5377(12)	14.5944(11)	14.5856(2)	14.5944(11)
b/Å	15.7243(15)	12.246(4)	12.3188(11)	12.3101(2)	12.3188(11)
<i>c /</i> Å	12.8790(11)	12.246(4)	20.002(3)	20.0288(3)	20.002(3)
α/o	90	90	90	90	90
β/°	95.782(9)	91.106(10)	91.356(9)	91.3570(10)	91.356(9)
γ / °	90	90	90	90	90
V / Å <sup>3</sup>	1049.02(17)	3567.0(12)	3595.1(6)	3595.17(9)	3567.22(9)
Ζ	4	4	4	4	4
ho / mg m <sup>-3</sup>	1.325	1.768	1.764	1.774	1.792
$\mu$ /mm <sup>-1</sup>	0.104	1.861	1.947	2.181	2.321
F(000)	440	1904	1908	1916	1920
Crystal size/ mm <sup>3</sup>	0.69×0.13×0.09	0.47×0.46×0.20	0.30×0.10×0.06	0.22×0.15×0.10	0.88×0.59×0.26
Reflections collected (R <sub>int</sub> )	6862 (0.064)	18610 (0.0432)	26011 (0.0700)	129327 (0.0783)	93721 (0.0468)
Reflections with I≥2σ(I)	2148	7299	7351	7358	7293
Unique Reflections	1346	5115	4999	6616	6378
Goodness- of-fit on F <sup>2</sup>	1.032	1.067	1.064	1.063	1.075
$R^{\rm a}, wR^{\rm b}$	0.0558, 0.1446	0.0377, 0.0836	0.0446, 0.0859	0.0243, 0.0613	0.0253, 0.0615
R <sup>a</sup> , wR <sup>b</sup> (all data)	0.0899, 0.1446	0.0695, 0.0991	0.0815, 0.1017	0.0286, 0.0642	0.0330, 0.0668
Larg. diff. peak and hole / e Å <sup>-3</sup> )	0.207, -0.206	1.651, -0.755	1.738, -1.160	0.993, -0.741	2.607, -0.678

 ${}^{a}R = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR [\Sigma (|F_{o}|^{2} - |F_{c}|^{2})^{2} / \Sigma |F_{o}|^{2}]^{1/2}.$ 

### 3. Results and discussion

#### 3.1. Synthesis and characterization

The proligand Et[4-HOpa] and the corresponding sodium(I) salt Na[4-HOpa] were obtained in a similar way as described previously [34,35]. Crystal structure of Et(4-HOpa) will be described for the first time in the present work. NMR data confirm the molecular formula of both compounds Et(4-HOpa) and Na(4-HOpa). The IR spectra of Et(4-HOpa) and Na(4-HOpa) are very similar, except for the presence of an intense absorption peak at 1732 cm<sup>-1</sup> in the spectrum of Et(4-HOpa) which is attributed to the stretching vibration of the ethyl ester group. This result suggests that the basic hydrolysis of Et(4-HOpa) resulted in Na(4-HOpa), replacing the ethyl substituent by sodium(I) ion (see Scheme 1).

All complexes were synthesized following the same procedure, and single crystals were obtained after five days at room temperature. The yield of products varies from 44 (2) to 82% (3). The analysis and refinement of single-crystal X-ray diffraction data showed that all compounds are isostructural, and the IR spectra of 1-4 are very similar between them also. The main stretching vibrations of 1-4 are observed in the following regions: (i) 3338-3350 cm<sup>-1</sup>, related to N–H and O–H bonds; (ii) 1640-1654 cm<sup>-1</sup>, attributed to the C=O bonds; 1370-1386 cm<sup>-1</sup> reported to the C–N bonds. The PXRD patterns of 1-4 are very similar (See SI, Figure S3). This feature corroborates that 1-4 are isostructural, as revealed by single-crystal X-ray diffraction analysis.

### 3.2. Crystal structures

#### *3.2.1. Crystal structure of Et[4-HOpa]*

The proligand in the form of the ethyl ester Et[4-HOpa] crystallizes in the monoclinic space group P2<sub>1</sub>/n. The asymmetric unit consists of one Et[4-HOpa] molecule featuring a 4-phenol substituent at the nitrogen atom of the ethyl ester oxamic acid moiety, as shown in Figure 1(a). The oxamate group exhibits an s-*trans* conformation being almost coplanar with the aromatic phenyl ring. The dihedral angle between the mean normal vector plane of oxamate group and the normal vector plane of phenyl ring is  $4.7(4)^{\circ}$ , where the phenyl mean plane is defined by C3/C4/C5/C6/C7/C8, and the oxamate means plane involves N1/C2/O3/C1/O1/O2 set of atoms.



**Figure 1.** (a) Representation of hydrogen-bonded dimers with ellipsoids at 50% of probability level and (b) double layers interactions. Hydrogen bonds are represented in dashed green lines along. (c) Packing view along the *a* axis in the spacefilling model and hydrogen atoms were omitted for clarity. Color code: C in gray, N in light blue, O in red.

The oxamate groups from two centrosymmetrically-related Et(4-HOpa) molecules form hydrogen-bonded dimers along crystallographic *a* axis , where the amide N–H group interacts with the ester carbonyl oxygen atom in a double symmetric motif [N1–H1···O1<sup>ii</sup> = 2.55 Å; ii: 1–*x*, 2–*y*, –*z*] which is typical of oxamato derivatives (Figure 1(a)) [42]. Additional hydrogen bonds between the carbonyl oxygen atom of the amide group and the phenol group [O4–H4A···O3<sup>i</sup> = 1.99 Å; *i*: 1/2+*x*, 5/2–*y*,–1/2+*z*] of adjacent hydrogen-bonded dimers are responsible for the resulting crystal packing of Et(4-HOpa) (Figure 1(b)). These hydrogen-bonding interactions lead to interleaved dimers layers along the crystallographic *b* axis, as featured in Figure 2(b). Besides, the double layers pack each other along the crystallographic *b* axis direction driven by aliphatic ethyl to aromatic phenyl group interactions (Figure 1(c)). A 3D supramolecular architecture is achieved taking into account the combination of the interactions between dimers along the axis *a* and the double layers interaction along *b* and *c*. Finally, no  $\pi$ ··· $\pi$  stacking interactions were observed in Et(4-HOpa).

3.2.2. Crystal structures of  $Na[Ln(4-HOpa)_4(H_2O)] \cdot 2H_2O$  ( $Ln^{3+} = Eu$  (1), Gd(2) Dy (3) and  $Ho^{3+}$  (4)

Crystal structure analysis data revealed that complexes **1-4** are isostructural. They crystallize in the monoclinic space group  $P2_1/n$  (Table 1). One crystallographically independent Ln<sup>III</sup> ion, four 4-HOpa ligands and one sodium cation – playing the role of charge balancing counterion – along with three water molecules (one of coordination and the other two cocrystallized) compose the asymmetric unit, as illustrated in Figure 2 for the Europium derivative **1** (see Figure S3 for **2-4**). The nine-coordinated Ln<sup>III</sup> ion of **1-4** presents a square-face capped square antiprism (SAPRS-9) distorted geometry [43] composed by four carboxylate oxygen atoms [O2, O6, O10, O14] and four carbonyl amide oxygen atoms [O3, O7, O11, O15] from the oxamate groups in a bidentate coordination mode, and also by one water molecule [O17] with very similar Ln–O bond lengths (Table 2). The O2 atom occupies the capped position of the square face defined by O6, O7, O11, and O15 atoms, the other square face being composed by O3, O10, O14 and O17 atoms, as illustrated in Figure 2(b) for the europium derivative **1**. The average value of the angles  $\Theta$ , the angle between the diagonals of the two squares faces (skew angle) [2], are 39.05° (**1**), 39.17° (**2**), 39.14° (**3**), and 39.05° (**4**).



**Figure 2.** (a) Asymmetric unit of **1** with ellipsoids at 50% of probability level, hydrogen atoms were omitted for clarity. Color code Eu (pink), Na (purple), C (gray), N (light blue), O (red). (b) Different views of the coordination polyhedron of Eu1 in square-face capped square antiprism distorted geometry.

The five-coordinated Na<sup>I</sup> ion coordination sphere of **1-4** is composed of three carboxylate oxygen atoms [O6, O2<sup>ii</sup>, O14<sup>ii</sup>], one phenol oxygen atom [O8<sup>iii</sup>], and one coordinated water molecule [O18] (*ii*: 1.5–*x*, 1/2+*y*, 1/2–*z*; *iii*: 2–*x*, 2-*y*, –*z*). The sodium coordination polyhedron is better described as square a based distorted pyramid in an anti-Berry conformation , as reflected by the value of the geometric parameter [44]  $\tau$  of 0.28 [O6–Na1–O18 = 156.8(6)° and O8<sup>iii</sup> –Na1–O14<sup>ii</sup> = 140.2(2)°] [45–47]. The sodium atom is lowered by 0.16 Å from the mean basal plane of the pyramid opposite to the apical position occupied by the atom O2<sup>ii</sup>. Different views of the coordination polyhedral of **2**-**4** are depicted in the Supporting Information, Figure S5.



**Figure 3.** Crystal packing views for **1**, highlighting Eu1 (purple) and Na1 (yellow) coordination polyhedrons with the ligand L (light green) along the (a) *a* axis and (b) *b* axis, arrows in green and pink representing the layers of coordinate covalent bond (Eu–O)/ion dipole (Na–O) and intermolecular interactions, respectively.

Bond length or interatomic distance / Å	1	2	3	4
Ln–O2	2.419(3)	2.447(3)	2.434(2)	2.422(2)
Ln–O3	2.387(3)	2.422(3)	2.402(2)	2.389(2)
Ln–O6	2.358(4)	2.393(4)	2.376(2)	2.363(2)
Ln–O7	2.460(3)	2.486(4)	2.473(2)	2.460(2)
Ln-O10	2.402(3)	2.427(4)	2.406(2)	2.399(2)
Ln-O11	2.429(3)	2.452(3)	2.436(2)	2.424(2)
Ln-O14	2.374(4)	2.410(4)	2.382(2)	2.375(2)
Ln-O15	2.423(3)	2.454(3)	2.435(2)	2.423(2)
Ln-017	2.432(4)	2.456(4)	2.435(2)	2.417(2)
Ln…Ln	7.255(2)	7.3014(7)	7.2881(4)	7.255(2)

Table 2. Selected bond lengths and interatomic distances for 1-4.

A 2D Na<sup>I</sup>Ln<sup>III</sup> supramolecular coordination framework composes the crystal packing of **1**-4, as illustrated in Figure 3 for the europium derivative **1**. Along the *b* axis, the Na<sup>I</sup> and Ln<sup>III</sup> ions are connected through oxygen atom bridges leading to a zig-zag chain [Ln1–O6–Na1– $\mu$ –(O14<sup>i</sup>, O2<sup>i</sup>)–Ln1<sup>i</sup>; symmetry code (i)= 3/2–*x*, 1/2+*y*, 1/2+*z*]. The shortest intrachain Ln<sup>...</sup>Ln distances are 7.255(2) (**1**), 7.3014(7) (**2**), 7.2881(4) (**3**), and 7.255(2) Å (**4**) values which are far enough so that no magnetic coupling was observed in the magnetic measurements. Along the *ac* plane, the connection between the Na<sup>I</sup> and Ln<sup>III</sup> ions is established using one unit of the ligand through carboxylate oxygen atom O6 and phenol oxygen atom O8 leading to layers, as shown in Figure 3(b). In addition, there are intermolecular Van der Waals forces, mainly between the stacked phenol rings. Also, the crystal packing of **1-4** is ruled by a complex hydrogen bond network between phenol and carboxylate groups and water molecules maintaining the three-dimensional structure (for compounds **1-4**, see ESI tables S1-S4).

#### 3.3. Magnetic Properties

#### 3.3.1. DC magnetic measurements

Considering the magnetic properties of trivalent lanthanides ions with a first-order orbital momentum (4f<sup>h</sup> electronic configuration with n = 0-14), the spin-orbit coupling (SOC) partially removes the degeneracy of the free ion <sup>2S+1</sup> $\Gamma$  ground term, where *S* and *L* are respectively the quantum numbers associated with the spin and orbital angular momenta and  $\Gamma$  is denoted as S (L = 0), P (L = 1), D (L = 2), F (L = 3), G (L = 4), H (L =5), I (L = 6) and so on. This gives rise to <sup>2S+1</sup> $\Gamma_J$  states, where *J* is the quantum number associated with the total angular momentum defined as J = L + S (Russel Saunders coupling), with *J* varying by an integer value from |L - S| to (L + S).

In general, the  ${}^{2S+1}\Gamma_J$  ground state of the Ln<sup>3+</sup> ion is well separated in energy from the first excited state, so that only the ground state is populated at room temperature and below, and the magnetic susceptibility ( $\chi$  (*J*)) for a mononuclear lanthanide(III) complex obeys the Curie law given by Eq 1:

$$\chi(J) = \frac{Ng_J^2 \beta^2 J(J+1)}{3 \, kT} \quad (\text{Eq 1})$$

Where *T* is the absolute temperature, *N* is the Avogadro constant,  $\beta$  is the Bohr's magneton, *k* is the Boltzmann constant, and *g*<sub>J</sub> is the Zeeman factor. The saturation magnetization is then given by  $M = N\beta g_J J$ , where the *g*<sub>J</sub> value can be expressed by Eq 2:

$$g_J = \frac{3}{2} + \frac{[S(S+1) - L(L+1)]}{2J(J+1)}$$
(Eq 2)

In most cases, however, the  $\chi_M T vs. T$  plot for mononuclear lanthanide(III) complexes deviates from the predicted one from eq 1. This deviation can be understood by analyzing two effects. The first one is the crystal field, which partially removes the 2J + 1 degeneracy of the  ${}^{2S+1}\Gamma_J$  ground state in zero field and the second one is due to the thermal population of excited states.

In this latter case, the presence of excited states not so far in energy from the ground state can add a significant temperature independent magnetic contribution. The magnetic susceptibility considering the free ion approximation [48] can then be described as shown in Eq 3:

$$\chi(J) = \frac{Ng_J^2 \beta^2 J(J+1)}{3 kT} + \frac{2N\beta^2 (g_J - 1)(g_J - 2)}{3 \lambda}$$
 (Eq 3)

where  $\lambda$  is the spin-orbit coupling parameter in the Hamiltonian  $\mathbf{H} = \lambda \mathbf{L} \cdot \mathbf{S}$  ( $\lambda > 0$  for a 4f<sup>n</sup> electronic configuration with n < 7 and  $\lambda < 0$  for n > 7).

The magnetic properties of polycrystalline samples of **1-4** were investigated in the temperature range of 2.0-300 K in the form of  $\chi_M T$  versus *T* plots,  $\chi_M$  being the molar magnetic susceptibility and *T* temperature (Figure 4). The  $\chi_M T$  values at room temperature for **2-4** are in agreement with the calculated values according to Eq 1, as shown in Table 4. At room temperature (see Table 3), the  $\chi_M T$  for **1** is 1.33 emu K mol<sup>-1</sup>, which is different from the expected value of zero. However, since the thermally populated excited states located at least 300 cm<sup>-1</sup> are populated, the observed value is in agreement with the expected value for one isolated Eu<sup>3+</sup> ion (~ 1.5 emu K mol<sup>-1</sup>) in similar situations [48–50]. As T is lowered,  $\chi_M T$  decreases and tends to a value very close to zero.

**Table 3.** Experimental  $\chi_M T$  values at room temperature for 1, 2, 3 and 4 and their expected  $\chi_M T$  values.

Compound	gj	Theory S L Free ion		ory Free ion	Calculated <sub>XM</sub> T(cm <sup>3</sup> K mol <sup>-1</sup> )	Experimental <sub>XM</sub> T(cm <sup>3</sup> K mol <sup>-1</sup> )
		$\boldsymbol{\lambda}$		term		
1	5	6/2	3	$^{7}F_{0}$	0	1.33
2	2	7/2	0	${}^{8}S_{7/2}$	7.88	7.88
3	4/3	5/2	5	<sup>6</sup> H <sub>15/2</sub>	14.17	13.99
4	5/4	4/2	6	<sup>5</sup> I <sub>8</sub>	14.07	13.70

Since the <sup>7</sup>F ground term of the Eu<sup>3+</sup> ion is split by the SOC into seven states, <sup>7</sup>F<sub>J</sub> with *J* taking values from 0 to 6, the energy of the states are given by Eq 4 [48]:

 $E(J) = \lambda J (J+1)/2$  (Eq 4)

Where E(J) is the energy of  ${}^{7}F_{0}$  ground state taken as the origin. In the case of  $Eu^{3+}$  ions, the ground state is nonmagnetic, but the thermal population of the excited states leads to a nonzero and thermally dependent magnetic moment. Considering that  $\lambda$  is small enough for the first excited states to be thermally populated, the equation for the calculation of the magnetic susceptibility of  $Eu^{3+}$  is:

$$\chi_{M} = \frac{\sum_{J=0}^{6} (2J+1) \chi(J) exp \left[-\frac{\lambda J(J+1)}{2kT}\right]}{\sum_{J=0}^{6} (2J+1) exp \left[-\frac{\lambda J(J+1)}{2kT}\right]}$$
(Eq 5)

All of the  $g_J$  factors are equal to 3/2, except  $g_0$  which is equal to 5 (2 + L = 5). The full equation is given in the literature [48]. The least-square fit of magnetic susceptibility data of 1 resulted in  $\lambda$  equal to 355 cm<sup>-1</sup>. The agreement factor is defined by  $\Sigma[(\chi_M T)^{calcd}-(\chi_M T)^{obs}]^2/\Sigma$  [ $(\chi_M T)^{obs}]^2$  and it is equal to 9.2 x 10<sup>-6</sup>, indicating that theoretical curve reproduces quite well experimental data. The calculated  $\lambda$  value is in agreement with that expected for mononuclear Eu<sup>3+</sup> compounds [49].



**Figure 4.** (a)  $\chi_M T$  versus *T* plot for **1** (H= 0.02 T). The solid line represents the best-fit curve of experimental data. (b)  $\chi_M T$  versus *T* plot (o) for **2** (H= 0.02 T). In the inset, it is shown the *M* versus *H* plot of **2** at 3.5 K. Solid line represents the best-fit curve of experimental data through the Curie law. The solid line in the inset corresponds to the Brillouin function. (c)  $\chi_M T$  versus *T* plot (o) for **3** (H= 0.02 T). In the inset, it is shown the *M* versus *H* plot of **3** at 1.7, 3.0 and 3.5 K. The lines in the *M* versus *H* plots are just eye guides. (d)  $\chi_M T$  versus *T* plot (o) for **4** (H= 0.02 T). In the inset, it is shown the *M* versus *H* plot of **4** at 3.5, 4 and 6 K.

The  $\chi_M T$  versus T plot for **2** is shown in Figure 4(b). At room temperature, the  $\chi_M T$  value is 7.88 emu K mol<sup>-1</sup>, which is equal to the expected value for one Gd<sup>3+</sup> ion with no first-order orbital momentum. The magnetic susceptibility is constant and obeys Curie law over a wide range of temperature. The curve of  $\chi_M^{-1}$  versus T plot (see SI, Figure S6) depicted a straight line. The value of C is 7.87 cm<sup>3</sup> K mol<sup>-1</sup>. In this compound, the molecules are very well isolated, and Gd<sup>3+</sup> do not present orbital contribution. The crystal field effects do not perturb the  ${}^8S_{7/2}$  ground state, and the first excited state was located at some 10<sup>4</sup> cm<sup>-1</sup> high in energy [48]. Below 10 K, a small increase of  $\chi_M T$  can be associated with very weak ferromagnetic dipolar interactions or with the reorientation of the crystals in the presence of magnetic field [48,49]. The *M* versus *H* curve at 3.5 K presents a saturation value of 6.75 N $\beta$  at 60 kOe, being a characteristic curve of isotropic compounds with S = 7/2.

The  $\chi_{\rm M}T$  versus T plot for **3** is shown in Figure 4 (c). At room temperature,  $\chi_{\rm M}T$ value is 13.99 cm<sup>3</sup> K mol<sup>-1</sup>, close to the expected value for one paramagnetic Dy<sup>3+</sup> ion  $(\chi_{\rm M}T = 14.17 \text{ cm}^3 \text{ K mol}^{-1})$  using a free ion approximation [49–51]. When the system is cooled down from room temperature, the  $\chi_M T$  value smoothly reduces until it reaches the value of 10.94 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K. Below 5 K, a small increase of  $\chi_M T$  value appears, probably due to the weak ferromagnetic dipolar interactions. The reduction of the  $\chi_{\rm M}T$ product for 3 from room temperature to 5 K, is related with the thermal depopulation of the  $m_J$  levels of the free-ion  ${}^{6}H_{15/2}$  ground state that arrive from spin-orbit coupling that couples the ground state with the excited ones, besides the crystal field splitting effects into these levels [52–55]. The *M* versus *H* measurements in different temperatures show a strong magnetization increase until approximately 5 kOe, and above this value, Mincreases more slowly, and no effects of saturation are verified. At 60 kOe, the magnetization saturation values are 6.02 NB, 5.45 NB e 5.92 NB at 1.7, 3.0 e 3.5 K, respectively. The expected value of saturation magnetization for **3** considering  $g_i = 4/3$ and J=15/2 is 10 NB. The resultants values are different from the expected ones, indicating the presence of anisotropy and strong crystal field splitting of different components of m<sub>1</sub> [51,56] The crystal field effects eliminate the degeneracy of the  ${}^{2S+1}\Gamma_{I}$  ground state at the lanthanide(III) ions [52]. Moreover, the M versus  $HT^{-1}$  curves for 3 at distinct temperatures does not superimpose (see Figure S7), corroborating with the presence of magnetic anisotropy [52] in 3.

At room temperature, the  $\chi_M T$  value for **4** is 13.70 cm<sup>3</sup> K mol<sup>-1</sup>, which is in agreement with the expected one for one isolated holmium(III) ion (14.07 cm<sup>3</sup> K mol<sup>-1</sup>) [53]. The  $\chi_M T$  value remains slightly constant until 100 K, and below this temperature the  $\chi_M T$  product reduces until reaching a value of 8.68 cm<sup>3</sup> K mol<sup>-1</sup> at 3.0 K. This reduction of these values is associated with the splitting of energy levels caused by both spin-orbit coupling and crystal field splitting, as occurs in **3**. The *M* versus *T* curve (inset of Figure 4(d)) shows a strong increase of the magnetization until approximately 10 kOe, and above this value, M increases more slowly. The saturation of the *M* is not reached, and at 60 kOe the following values are obtained: 5.58 (3.5 K), 5.98 (4.0 K) and 6.03 (6.0 K) N $\beta$ . These values are smaller than the expected for holmium(III) ion (10.0 N $\beta$ ). As explained for **3**, this occurs due to the presence of magnetic anisotropy. As the temperature is lowered, the reduction of the saturation magnetization values can be explained by the increase of the thermal population of energy levels with small *J* values. The anisotropy exhibited by **4** is confirmed by the absence of superposition of the *M* versus *HT*<sup>-1</sup> curves at 3.5, 4.0 and 6.0 K (see Figure S8).

### 3.3.2. AC magnetic measurements

The dynamic magnetic behavior for **2-4** was analyzed through AC magnetic susceptibilities measurements under an external DC field of 1.0 kOe. For all compounds, both in-phase ( $\chi_M$ ') and out-of-phase ( $\chi_M$ ') components of the AC molar susceptibility exhibited a dependence with the frequency of the alternating AC field of 5 Oe in the temperature range below 5.0 K. Under zero applied dc field, however, there was no frequency dependence of the AC magnetic susceptibility for **2-4**, more likely because of the occurrence of a fast quantum-tunneling magnetization (QTM) relaxation.

Figure 5 shows the frequency dependence of both  $\chi_M$  '*T* and  $\chi_M$ "*T* for **2** at 1.0 kOe. Frequency dependence of  $\chi_M$ ' and  $\chi_M$ " data obtained at different temperatures were fitted by using the generalized Debye equation [57], resulting in a reasonably good agreement between the calculated and experimental data (Figures 5(a) and (b) and Table S5, SI). The temperature dependence of the relaxation times ( $\tau$ ) afforded from the fit was used to construct an Arrhenius plot (Figure 5(d)). The deviations between experimental data and the linear behavior expected from the Arrhenius law is indicative of the existence of several relaxation processes. The Cole-Cole plots constructed from the  $\chi_M$ "*T* vs.  $\chi_M$ '*T* 

data at different temperatures and fitted curves show semicircular shapes with  $\alpha$  values within the range 0.14-0.21, which corroborate the existence of several relaxation modes in 2 ( $\alpha = 0$  for a single relaxation process).



**Figure 5.** (a) Frequency dependence of  $\chi_M$  '*T* and (b)  $\chi_M$ "*T* for **2** under an applied field of 1.0 kOe in the frequency range of 10-10000 Hz. The solid lines represent the best fit using the generalized Debye equation. (c) Cole-Cole plots for complex **2** under an applied field of 1.0 kOe in the frequency range of 50-10000 Hz. The solid lines represent the best fit based on the generalized Debye equation. (d) Temperature dependence of the average relaxation time for complex **2** at 1kOe dc field. The red line is the best fits obtained according to Eq. 5.

To investigate the temperature dependence of relaxation time of **2** in detail, the experimental data were fitted considering multiple relaxation processes. Since for the externally applied field of 1 kOe, the quantum-tunneling magnetization is expected to be negligible, we adjusted the  $\tau^{-1}$  *vs. T* data by using Eq. 5, which considers the single-

phonon direct process (parameters A and m), Raman process (parameters C and n), and two-phonon Orbach process (parameters U and  $\tau_0$ ) [58].

$$\tau^{-1} = AH^{m}T + CT^{n} + \tau_{0}^{-1}\exp(-U/k_{B}T)$$
 (Eq 5)

To avoid over-parametrization, we fixed the values of m = 1 (direct processes) and n = 9 (Kramer ion). Best-fits results gave the following set of parameters (values in parentheses are the standard errors): A = 2.9 (1),  $C = 2(1) \times 10^{-5}$ , U = 13 (1) K, and  $\tau_0 = 6$  (1) x  $10^{-6}$  s. These values suggest that the relaxation time at a low-temperature region is dominated mainly by the overcome of direct and Orbach processes.

Since the Gd<sup>3+</sup> ion is very isotropic, only gadolinium(III) complexes with particular coordination environments can behave as single-molecule magnets at very low temperatures [59,60], as reported previously by Murugesu and coworkers for the Gd<sup>III</sup>-EDTA complex (EDTA= ethylenediaminetetracetic acid)[61], which shows distinct relaxation processes that each dominate in different regimes. They observed the absence of magnetic relaxation in zero DC field due to the fast QTM promoted by internal dipolar fields by removing Kramers degeneracy. For a relevant applied DC field, the QTM is suppressed, and the slow relaxation of magnetization is observed associated with interlevel spin-phonon transitions of direct and Raman mechanisms on the Gd<sup>III</sup> site [61]. These behaviors seem to be related with the axial symmetry of the coordination sphere of the gadolinium(III) complex, which is nonacoordinated as observed for **2**.

The AC magnetic properties of **3** in the form of in-phase ( $\chi_M$ ') and out-of-phase ( $\chi_M$ '') components of AC molar susceptibility per mononuclear unit evidence the occurrence of field-induced slow magnetic relaxation effects typical of SIMs. At zero DC magnetic field, both  $\chi_M$ ' and  $\chi_M$ ' show no dependence effects with the frequency. However, when a field of 1.0 kOe was applied, relaxation of magnetization phenomena was observed, as has been reported for other dysprosium(III)-based SIMs [32,62]. Figure 6 shows the frequency dependence of both  $\chi_M$ 'T and  $\chi_M$ ''T for **3** at 1.0 kOe. Besides the maximum in  $\chi_M$ '' observed at high frequency, a sort of plateau can be observed in the low-frequency region. This behavior might be associated with two different relaxation modes slightly separated in frequency. The existence of these low relaxation modes is more evident when analyzing the Cole-Cole plots of **3**, that shows a semicircular shape followed by a plateau at lower frequencies (Figure 6(c)). Therefore, the  $\chi_M$ '=f( $\nu$ ) and

 $\chi_{\rm M}$  ''=f(v) data were fitted by taking into account only the high-frequency region of semicircular shape (200-10000 Hz). Quantitative determination of the relaxation rate for this frequency range was obtained by fitting  $\chi_{\rm M}$ '=f(v) and  $\chi_{\rm M}$ ''=f(v) data obtained at different temperatures with the generalized Debye equation, which gave  $\alpha$  values (width distribution of  $\tau$ ) within the range 0.21-0.33, suggesting a narrow distribution of relaxation rates (Table S6, SI). The temperature dependence of  $\tau$  obtained for **3** is shown as the Arrhenius plot in Figure 6(d). Fitting these data using the Equation 10 (assuming that the QTM is effectively quenched under relevant fields), we obtain a negligible value for A, C =2(5), U = 16 (1) K, and  $\tau_0 = 1.4(9) \times 10^{-8}$  s. Therefore, there are only Raman and Orbach processes associated with the high-frequency region (200 - 10000Hz). On the other hand, the second relaxation mode occurring at the low-frequency region can be associated with collective behavior, such as spin-glass-like phase since the process is frequency independent and dominant at low temperature.



**Figure 6.** (a) Frequency dependence of  $\chi_M$  '*T* and (b)  $\chi_M$  '*T* for **3** under an applied field of 1.0 kOe in the frequency range of 10-10000 Hz. The solid lines represent the best fit of experimental results. (c) Cole-Cole plots for complex **3** under an applied field of 1.0 kOe in the frequency range of 50-10000 Hz. The solid lines represent the best fit based on the generalized Debye equation. (d) Temperature dependence of the average relaxation time for complex **3** at 1 kOe dc field. The red line represents the best-fit curve obtained according to Eq. 5.

The holmium(III) derivative 4 displays no frequency dependence of AC magnetic susceptibility, neither without an applied DC field or with a DC field up to 2 kOe. Consequently, it does not exhibit a SIM behavior. The presence of slow relaxation of magnetization in holmium(III) compounds is rare, even if a few examples are described in the literature [63,64].

#### 4. Conclusion

In this work, we described the synthesis and crystal structures of a new proligand, namely 4-hydroxyphenyl-*N*-oxamic acid ethyl ester, and the sodium salts of its corresponding oxamato complexes containing lanthanide ions  $[Ln = Eu^{3+} (1), Gd^{3+} (2), Nd^{3+} (3), and Ho^{3+} (4)]$ . Compounds 1-4 are isostructural and consist of mononuclear lanthanide(III) complexes with four bidentate oxamato ligands coordinated to one metal ion, through the carbonyl amide and carboxylate oxygen atoms, and one water solvent molecule are completing the coordination sphere of lanthanide ions, resulting in square-face capped square antiprism (SAPRS-9) coordination geometry. The supramolecular structure of all complexes consists of an intricate two-dimensional Na<sup>I</sup>Ln<sup>III</sup> coordination network.

Magnetic properties were investigated in the form of AC and DC magnetic measurements. Thus, we discovered the unique features of  $Gd^{3+}$  complex **2**. In the zero-field, the  $Gd^{3+}$  complex behaves as a paramagnetic ion. However, under an applied field, we observed the frequency-dependent magnetic phenomena characteristic of anisotropic field-induced SIMs. The interpretation of this result seems to be the same described by Murugesu et al. [61], in which occurs the interlevel spin–phonon transitions that are not separated by any blocking barrier in  $Gd^{3+}$  ions. The  $Dy^{3+}$  complex **3** also exhibited the relaxation of the magnetic susceptibility under an applied field, behaving as a SIM. The Eu<sup>3+</sup> compound **1** has a nonmagnetic ground state, while the Ho<sup>3+</sup> compound **4** act as a

paramagnet, and do not exhibit relaxation of the magnetization with or without an applied field.

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### Synopsis:

Synthesis, crystal structures and magnetic properties of four mononuclear complexes containing Eu<sup>3+</sup>, Dy<sup>3+</sup>, Gd<sup>3+</sup>, and Ho<sup>3+</sup> with the new hydroxyphenyloxamate ligand were studied. Slow relaxation of magnetization phenomena were observed for Dy<sup>3+</sup> and Gd<sup>3+</sup> A COLORINAL COLO compounds, which can be considered Single-Ion Magnets.