Structure and magnetic properties of two new lanthanide complexes with the 1-((E)-2-pyridinylmethylidene)semicarbazone ligand

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Graphical Abstract

Ref.: “Structure and magnetic properties of two new lanthanide complexes with the 1-((E)-2-pyridinylmethylidene)semicarbazone ligand”

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Synthesis, structural and magnetic characterization of two lanthanide complexes containing 2-formylpyridine semicarbazone (HSCpy) is discussed.
Structure and magnetic properties of two new lanthanide complexes with the 1-((E)-2-pyridinylmethylidene)semicarbazone ligand.

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Abstract

Two novel semicarbazone-lanthanide(III) complexes were prepared and structurally characterized as [Ln (Hscpy)2(NO3)2]NO3·MeOH (Ln = Gd and Tb; Hscpy = 1-((E)-2-pyridinylmethylidene)semicarbazone). The 4f metal ions experience deca-coordination geometry. Each molecular formula contains two neutral Hscpy molecules in the keto form coordinated through two nitrogen atoms and one oxygen atom, while two nitrate ligands are both coordinated in a chelate mode. The 1+ charge of the cation-complex is balanced by a nitrate anion. Extensive intermolecular hydrogen bonds are formed through the methanol solvate molecule, which acts both as a donor and an acceptor molecule. The chemical composition of the compounds was confirmed by high resolution mass spectra (ESI-MS); peaks at m/z = 122.07 and 148.05, assigned to the fragments C6H8N3+ and C7H6N3O+, respectively, are in agreement with the coordination of Hscpy. Alternating current magnetic susceptibility analysis was performed in the 10 – 10000 Hz range, and the terbium-complex showed slow relaxation of the magnetization when immersed in a static magnetic field of 1 kOe and 1.5 kOe, with an activation barrier to the relaxation (21.9(4) cm⁻¹) among the highest found for ten-
coordinated Tb(III) complexes. This behavior of slow relaxation of the magnetization is relevant as a memory effect regarding the development of Single Molecule Magnets (SMM).

Keywords: Lanthanide; Semicarbazone; Crystal structure; Magnetic properties; SMM.

Introduction

The trivalent cations have 4f orbitals shielded by 5s and 5p orbitals; thus the Ln$^{3+}$-ligand interactions are mainly electrostatic, and the magnetic and spectroscopic features of Ln$^{3+}$ ions are determined by ligand symmetry [1-4]. The most common oxidation state for lanthanide ions found in coordination compounds is 3+, with ionic radii in the 1.1-0.85 Å range; gadolinium(III) exhibits a radius of 0.99 Å [5]. The lanthanide cations also show large coordination numbers, typically 8-10. Due to their similar electronic configuration, the lanthanide elements are considered to have similar chemistry, which is often assumed to be less attractive relative to the d-block. Quite the opposite, the chemistry of the lanthanide ions in the solid state and in solution has proven this to be wrong. These ions have distinct magnetic and spectroscopic characteristics in a chemistry dominated by charge, size and steric effects.

The chemistry of lanthanide complexes continues to be intensively investigated due to numerous potential applications. For example, sensitive molecular sensors have been developed exploring the long-lived luminescence of the 4f elements [6-8]. The coordination chemistry determines the sensitivity, and the composition of the lanthanide sensor varies throughout the test as the complex may dissociate and re-assemble.

Among other potential applications of lanthanide complexes, magnetic resonance imaging (MRI) appears as an important field of research [9,10]. Upon chelation by an organic ligand, most of the coordinated solvent molecules are displaced from the inner-sphere. A typical ligand used to create an MRI contrast agent has eight donor
atoms. Any remaining solvent molecule (water, in particular) is important for MRI contrast, since it allows, through chemical exchange, that several other solvent molecules can interact with the lanthanide ion, controlling the relaxation efficiency of the Ln-based MRI contrast agents [11]. Finally, lanthanide ions are of great interest to develop Single-Molecule Magnets (SMMs) due to their strong spin-orbit coupling, large magnetic anisotropy, and large energy barriers of spin reversal, showing slow magnetic relaxation. SMMs are important due to their potential applications in data storage, quantum processing and molecular spintronics [12-14].

In this work we expand on developing novel 4f complexes with chelating ligands, with particular interest in semicarbazones. Semicarbazones are multidonor atom ligands that can bind in a chelate mode, generating interesting coordination compounds that can achieve the most diverse coordination modes and geometric demands of metal ions. Their complexes have been studied for years as potential biologically antifungal agents [15-18]. \(\text{(E)}\)-2-(pyridine-2-ylmethylene)hydrazine-1-carboxamide (Hscpy) (Scheme 1) is a semicarbazone tridentate ligand prepared from the reaction of semicarbazide hydrochloride and 2-pyridinecarbaldehyde in the presence of sodium acetate in ethanol. Hscpy has five potential donor atoms, and it usually binds as a chelate using two nitrogen (pyridinic/pyridiny1 and azomethinic) atoms and one oxygen atom.

The first reports on the coordination chemistry of Hscpy appeared in 1987 by Singh and coworkers, who described the preparation of mononuclear-complexes with vanadium(V), molybdenum(VI), manganese(II), tungsten(VI), antimony(III) and bismuth(III), although no clear structural information was presented [19-28]. Soon after, metal complexes containing the Hscpy ligand, such as the cobalt(II), nickel(II), zinc(II), copper(II) and iron(II) compounds, were structurally characterized [29-33]. Recently we
reported the dinuclear copper(II) complex and its relation with the thiosemicarbazone analogues [34].

Regardless of its great potential to coordinate metal ions, as far as we know, no coordination complexes of Hscpy with lanthanide ions have been reported. Therefore, design, synthesis and characterization of new lanthanide complexes with chelating ligands, as well as the knowledge of their coordination mode, structure, and fundamental properties, continue to be relevant to the multiple potential applications.

Hence, herein we describe the synthesis and structural characterization of two new deca-coordinated gadolinium and terbium complexes with Hscpy.

The dynamics of the magnetization of the Tb derivative have been investigated, in the search for compounds that show slow relaxation of magnetization. This is relevant as a memory effect in the development of Single Molecule Magnets (SMM).

Scheme 1. Tautomeric (keto and enolate) forms of the pyridine-2-carbaldehyde semicarbazone ligand.
Experimental

General

Reagent grade chemicals were used in this work. The ligand Hscpy was prepared according to published procedures [18]. Infrared spectra were obtained with a FTS3500GX Bio-Rad Excalibur series spectrophotometer in the region 4000-400 cm\(^{-1}\) in KBr pellets. Microanalyses were performed with a Perkin Elmer CHN 2400 analyser. Mass spectra were measured in a high resolution ESI-MS on a microTOF QII mass spectrometer (Bruker Daltonics, Billerica, MA) from methanolic solutions. X-band Electron Paramagnetic Resonance (EPR) spectra (See Supporting material) were recorded on a Bruker EMX micro spectrometer equipped with a high quality factor TE102 resonant cavity from solid samples and from aqueous solutions at 77 K. The samples were placed in standard 4 mm o.d. EPR quartz tubes and the low temperature spectra were obtained using an insertion quartz finger Dewar.

Synthesis

Bis(1-((E)-2-pyridinylmethylidene)semicarbazone)(dinitrato)lanthanide(II) nitrate [Ln (Hscpy)\(_2\) (NO\(_3\))\(_2\)]NO\(_3\)·MeOH (Ln = Gd and Tb; herein complexes (1) and (2), respectively). Hscpy (0.49 g, 3 mmol), dissolved in 20 mL of ethanol, was added to a solution of 1 mmol of Ln(NO\(_3\))\(_3\)·xH\(_2\)O dissolved in a minimum volume of boiling ethanol. The solution was kept under reflux for 4 h. Then, the system was kept in the freezer overnight and the product was collected by filtration, washed with cold ethanol and dried under vacuum. Yields were 408 mg (61%) for Gd\(^{3+}\) and 437 mg (65%) for Tb\(^{3+}\).
Single-Crystal X-Ray Analyses

Crystals suitable for X-ray diffraction analysis were obtained by the saturation of a methanolic solution of each complex with diethyl ether vapor. From each sample under oil, a crystal was mounted on a Micro mesh and fixed in the cold nitrogen stream on a Bruker D8 Venture diffractometer, equipped with a Photon 100 CMOS detector, Mo-Kα radiation and graphite monochromator. Intensity data were measured by thin-slice ω- and φ-scans.

Data were processed using the APEX3 program [35]. The structure was determined by the intrinsic phasing routines in the SHELXT program [36] and refined by full-matrix least-squares methods, on F²'s, in SHELXL [37]. The two complexes were found to be isostructural – the two complex molecules and their packing arrangements are essentially identical. The non-hydrogen atoms were refined with anisotropic thermal parameters, except, in complex (1) for O(36A), O(36B), C(37A) and C(37A), which were kept isotropic, due to crystal disorder, leading to a better refinement result. For complex (1), all hydrogen atoms bound to carbon atoms were included in idealized positions with U(iso)'s set at 1.2*U(eq) or, for the methyl hydrogen atoms, 1.5*U(eq) of the parent carbon atoms; hydrogen atoms bound to nitrogen or oxygen atoms were refined freely. For complex (2), the same procedure was followed except that H(38) was also included in an idealized position with U(iso)'s set at 1.5*U(eq) of the parent oxygen atom.

Scattering factors for neutral atoms were taken from reference [38]. Computer programs used in this analysis have been noted above and were run through WinGX [39].

More detailed information about the structure refinements is given in Tables 1, for experimental details, and 2, which shows selected bond distances and angles.
CCDC files 1867407 and 1867408 contain the crystallographic data for 1 and 2 respectively, for this paper at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk].

AC susceptometry.

Alternating current (ac) magnetic susceptibility analysis of pellets made of microcrystalline powders of 2, was performed with a Quantum Design PPMS setup working in the 10 – 10000 Hz range with zero, 0.1 and 0.15 T applied static fields. Magnetic data were corrected for the sample holder contribution and for the sample diamagnetism using Pascal’s constants [40]. The ac susceptibility data were analyzed within the extended Debye model [41], in which a maximum in the out-of-phase component $\chi''$ of the complex susceptibility is observed when the relaxation time $\tau$ equals $(2\pi \nu)^{-1}$. The frequency dependence of $\chi''$ at constant temperature was determined using equation (1):

$$
\chi''(\omega) = (\chi_T - \chi_S)_1[(\omega \tau_1)^{1-\alpha_1}\cos(\alpha_1 \pi/2)]/[1 + 2(\omega \tau_1)^{1-\alpha_1}\sin(\alpha_1 \pi/2) + (\omega \sigma)^{2-2\alpha_1}] + (\chi_T - \chi_S)_2[(\omega \tau_2)^{1-\alpha_2}\cos(\alpha_2 \pi/2)]/[1 + 2(\omega \tau_2)^{1-\alpha_2}\sin(\alpha_2 \pi/2) + (\omega \sigma)^{2-2\alpha_2}] \quad (1)
$$

where $\omega = 2\pi \nu$, $\chi_T$ and $\chi_S$ are the isothermal and adiabatic susceptibilities, i.e., the susceptibilities observed in the two limiting cases $\nu \to 0$ and $\nu \to \infty$, respectively, and $\alpha$ is a parameter which accounts for a distribution of relaxation times. The present function includes two different sets of $\chi_T$, $\chi_S$. $\tau$ and $\alpha$ to reproduce the two overlapping relaxation processes shown by 2.
Results and Discussion

Complexes 1 and 2 have essentially identical chemical structures. Figure 1 shows a molecular representation of complex 2. The crystal structure contains a terbium centre that is deca-coordinated by two Hscpy and two nitrate ligands in chelating mode. Each of the Hscpy ligands is coordinated to the central ion forming two five-membered chelate rings, one through the pyridine and the azomethine nitrogen atoms and the other through the latter nitrogen atom and the oxygen atom from the amide group. The 1+ charge of the cation-complex is balanced by a separate nitrate anion, that of N(33). A methanol molecule completes the chemical environment of the complex.

The tridentate Hscpy ligand in 2 shows bite angles N(py)-Tb-O of 123.64(14)° and 121.48(13)°, while the chelating nitrates show O-Tb-O' angles of 50.50(12)° and 51.38(14)°. The normals to the Hscpy ligand planes in this complex, calculated from the positions of the twelve heavier atoms of each ligand, are 41.29(7)° apart (Supp. Info., Fig S1.).
Figure 1. View of the complex 2, indicating the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Selected bond distances and angles for complexes 1 and 2 are listed in Table 2. The Ln-O(11,23), Ln-N(01,13) and Ln-N(08,20) bond lengths are between 2.392(4) and 2.6568(15) Å, which are values significantly longer than those in a 3d-complex such as the nickel(II)-complex (mean Ni-N bond distance of 2.047 Å and Ni-O 2.137 Å) [33]; this is consistent with the larger radius of the lanthanide ions. Analyzing the bond lengths of the atoms directly bonded to the lanthanide ions in complexes 1 and 2, we observe that all bond lengths follow the general pattern with longer bonds for the Gd complex than for the Tb cation. This is in accord with the ‘Lanthanide contraction’; as we progress through the 4f series, the f electrons suffer a greater attraction from the nucleus due to poor shielding effect, leading to the ion radii decreasing as we advance in the series.
Table 1. Crystal data and structure refinement for complexes 1 and 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Complex 1</th>
<th>Complex 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental formula</td>
<td>$C_{14}H_{16}N_{10}O_{8}$Gd, NO$_3$, CH$_2$O (1)</td>
<td>$C_{14}H_{16}N_{10}O_{8}$Tb, NO$_3$, CH$_2$O (2)</td>
</tr>
<tr>
<td>Formula weight</td>
<td>703.67</td>
<td>705.35</td>
</tr>
<tr>
<td>$T$ / K</td>
<td>302(2)</td>
<td>240(2)</td>
</tr>
<tr>
<td>Radiation, $\lambda$ / Å</td>
<td>0.71073</td>
<td>0.71073</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P-1$</td>
<td>$P-1$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 8.7881(16)</td>
<td>a = 8.7424(8)</td>
</tr>
<tr>
<td></td>
<td>b = 12.105(2)</td>
<td>b = 12.0551(10)</td>
</tr>
<tr>
<td></td>
<td>c = 12.106(2)</td>
<td>c = 12.0572(11)</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 77.544(8)$</td>
<td>$\alpha = 77.268(4)$</td>
</tr>
<tr>
<td></td>
<td>$\beta = 86.075(8)$</td>
<td>$\beta = 86.632(4)$</td>
</tr>
<tr>
<td></td>
<td>$\gamma = 88.102(8)$</td>
<td>$\gamma = 87.882(4)$</td>
</tr>
<tr>
<td>Volume / Å$^3$</td>
<td>1254.3(4)</td>
<td>1236.95(19)</td>
</tr>
<tr>
<td>Z, Calculated density / Mg m$^{-3}$</td>
<td>2.1.863</td>
<td>2.1.894</td>
</tr>
<tr>
<td>Absorption coefficient / mm$^{-1}$</td>
<td>2.725</td>
<td>2.941</td>
</tr>
<tr>
<td>$F(000)$</td>
<td>694</td>
<td>696</td>
</tr>
<tr>
<td>Crystal colour, shape</td>
<td>Colourless, parallelepiped</td>
<td>Colourless, parallelepiped</td>
</tr>
<tr>
<td>Crystal size / mm</td>
<td>0.343 x 0.255 x 0.128</td>
<td>0.242 x 0.135 x 0.044</td>
</tr>
<tr>
<td>$\theta$ range / °</td>
<td>2.9 to 27.5</td>
<td>2.9 to 27.2</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-11$\leq h \leq 11$, -15$\leq k \leq 15$, -15$\leq l \leq 15$</td>
<td>-11$\leq h \leq 11$, -15$\leq k \leq 15$, -15$\leq l \leq 15$</td>
</tr>
<tr>
<td>Completeness to $\theta = 25.2$ °</td>
<td>99.8 %</td>
<td>99.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7461 and 0.6826</td>
<td>0.6985 and 0.5656</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>124952 / 5758 [R(int) = 0.029]</td>
<td>60747 / 5501 [R(int) = 0.200]</td>
</tr>
<tr>
<td>No. of ‘observed’ reflections</td>
<td>5507</td>
<td>4949</td>
</tr>
<tr>
<td>(I &gt; 2$\sigma_{I}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5758 / 0 / 392</td>
<td>5501 / 0 / 378</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.100</td>
<td>1.029</td>
</tr>
<tr>
<td>Final R indices (‘observed’ data)</td>
<td>R = 0.016, wR$_2$ = 0.039</td>
<td>R = 0.048, wR$_2$ = 0.114</td>
</tr>
<tr>
<td></td>
<td>R = 0.017, wR$_2$ = 0.040</td>
<td>R = 0.055, wR$_2$ = 0.118</td>
</tr>
<tr>
<td>Largest diff. peak and hole / e Å$^{-3}$</td>
<td>0.88 and -0.26</td>
<td>1.74 and -1.34</td>
</tr>
<tr>
<td>Location of largest difference peak</td>
<td>near the O(36B) atom</td>
<td>near the Tb atom</td>
</tr>
</tbody>
</table>

$w=[\sigma(Fo)^2+0.0219P+0.5100P]^{-1}$ for complex 1 and $w=[\sigma(Fo)^2+0.0635P+3.800P]^{-1}$ for complex 2.
Table 2. Selected bond lengths (Å) and angles (°) for complexes 1 and 2.

<table>
<thead>
<tr>
<th></th>
<th>Gd (1)</th>
<th>Tb (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ln</strong></td>
<td><strong>Ligand 1</strong></td>
<td><strong>Ligand 2</strong></td>
</tr>
<tr>
<td>Ln-N(01,13)</td>
<td>2.6073(14)</td>
<td>2.6568(15)</td>
</tr>
<tr>
<td>Ln-N(08,20)</td>
<td>2.5801(14)</td>
<td>2.5946(14)</td>
</tr>
<tr>
<td>Ln-O(11,23)</td>
<td>2.4226(14)</td>
<td>2.4035(12)</td>
</tr>
<tr>
<td>Ln-O(27,30)</td>
<td>2.5100(14)</td>
<td>2.4748(14)</td>
</tr>
<tr>
<td>Ln-O(28,31)</td>
<td>2.5399(14)</td>
<td>2.5030(15)</td>
</tr>
<tr>
<td>C(07,19)-N(08,20)</td>
<td>1.274(2)</td>
<td>1.273(2)</td>
</tr>
<tr>
<td>N(08,20)-N(09,21)</td>
<td>1.358(2)</td>
<td>1.361(2)</td>
</tr>
<tr>
<td>N(09,21)-C(10,22)</td>
<td>1.357(2)</td>
<td>1.362(2)</td>
</tr>
<tr>
<td>C(10,22)-O(11,23)</td>
<td>1.242(2)</td>
<td>1.243(2)</td>
</tr>
<tr>
<td>C(10,22)-N(12,24)</td>
<td>1.326(2)</td>
<td>1.325(2)</td>
</tr>
<tr>
<td>N(01,13)-Ln-N(08,20)</td>
<td>61.56(5)</td>
<td>60.61(5)</td>
</tr>
<tr>
<td>N(08,20)-Ln-O(11,23)</td>
<td>61.71(4)</td>
<td>61.62(4)</td>
</tr>
<tr>
<td>N(01,13)-Ln-O(11,23)</td>
<td>123.10(5)</td>
<td>121.14(4)</td>
</tr>
<tr>
<td>N(08)-Ln-N(12,24)</td>
<td>170.65(5)</td>
<td>170.50(14)</td>
</tr>
<tr>
<td>N(25)-Ln-N(29)</td>
<td>172.50(4)</td>
<td>172.61(13)</td>
</tr>
</tbody>
</table>

*Ligand 1 = ligand coordinated through N(01), N(08) and O(11) atoms; ligand 2 = ligand coordinated through N(13), N(20) and O(23) atoms

Support for the proposed neutral form of the Hscpy ligand comes from the analysis of the N(09)-C(10) and C(10)-N(12) bond distances which, in the two ligands of the Tb complex, have mean values of 1.370(7) Å and 1.321(7) Å, respectively; these indicate the keto form of the ligand as shown in Scheme 1. The C(10)-O(11) bond exhibits a double-bond character with a short mean length of 1.241(7) Å, also in accordance with the keto form of the tautomeric equilibrium. The same behavior was also observed for the Gd(III) complex and as seen in
Further, typical bond distances of the semicarbazole [33], namely C(06)-C(07), C(07)-N(08), N(08)-N(09) and N(09)-C(10), are practically the same after coordination to the lanthanide ions despite the rotation of 180° about the N(9)-C(10) bond in the complex molecules. The largest changes were found in angles such as C(06)-C(07)-N(08) and C(10)-N(09)-N(08) that are 4.8° and 6.7° lower, respectively, after coordination.

Recently, Raja and co-workers reported the crystal structure of a similar complex [Ce(BPBH)$_2$(NO$_3$)$_3$], BPBH = 2-benzoylpyridine benzohydrazone [42]. The structure resembles those reported here, but in the Ce complex case all the nitrate ions are directly bound to the cerium(III) ion, leading to dodeca-coordination of the metal centre. Some observed bond distances, for Ce-N(pyridine), Ce-N(azomethinic), Ce-O(BPBH) and Ce-O(NO$_3$), are at 2.9365(16), 2.7706(14), 2.4952(12) and 2.62(2)-2.72(2) Å, respectively. Comparing those with the mean bond distances found in our terbium complex 2, Ln-N(1,13) 2.619 Å, Ln-N(8,20) 2.569 Å, Ln-O(11,23) 2.401 Å and Ln-O(27,28,30,31) 2.491 Å, respectively, one can see that the bonds for the lanthanide complexes have significantly shorter lengths.

The methanol molecules, with the oxygen atom O(38), in both of our complexes act as donors and acceptors in the formation of hydrogen bonds which, with hydrogen bonds from every N-H group, link the various moieties in an extensive hydrogen bond network. Figure 2 shows a section of this supramolecular arrangement in the unit cell of complex 2.
Figure 2. The hydrogen bond networks in complex 2, viewed along the $a$ axis. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen bonds are shown as dashed lines.

FTIR and mass spectra.

Infrared spectra showed bands that are characteristic of group functions expected for these compounds as seen in Figure 3. Mean values, observed in the series are: $\nu$(N-H) at 3379 cm$^{-1}$, $\nu$(C=O) at 1665 cm$^{-1}$, (pyridine ring) at 1547 cm$^{-1}$, $\nu$(C-C) at 1478 cm$^{-1}$, $\delta$(C-H) at 1153 cm$^{-1}$ [43]. The complexes also showed the stretching mode $\nu$(N-O) of nitrate ions at 1383 cm$^{-1}$. 
Figure 3. FTIR spectra of the complexes 1 and 2.

Figure 4 shows high resolution mass spectrum (HRMS-ESI) of compounds 1 and 2 in the positive mode (Full spectra can be seen as Supp. info. Fig S2). They exhibited peaks at m/z = 122.07 and 148.05 assigned to the fragments C₆H₈N₃⁺ and C₇H₆N₃O⁺, respectively, Scheme 2. In addition, several fragments containing lanthanides were also observed as represented in Scheme 2 for both complexes. The assignments are in accordance with the calculated fragmentation patterns, considering the isotopic distribution of the elements, as demonstrated in Figure 4.
Figure 4. HRMS-ESI positive mode of complexes 1 (a1) and 2(b1) dissolved in 9:1 CH$_3$OH/H$_2$O mixture showing the corresponding fragment inset. Calculated fragmentation patterns (a2) and (b2) for Gd and Tb complexes, respectively, showing the most intense peaks, considering the isotopic distribution of the elements.

Scheme 2. Fragments assignments according to the experimental data of complexes 1 and 2.
The largely unquenched magnetic orbital moment of the lanthanide ions, in combination with the crystal field acting on them, makes their magnetic moment relax more slowly than that usually found in paramagnets. Systems featuring slow relaxation of the magnetization are called Single Ion (or Molecule) Magnets (SIM and SMM, respectively), and are widely investigated for the memory effect [44] and quantum coherence associated to their magnetic moment at the level of the magnetically isolated molecular entity [45]. In order to evaluate the relaxation dynamics of complex 2, frequency- and temperature-dependent alternated-current susceptometry was carried out.

With zero static applied magnetic field, complex 2 did not show any out-of-phase signal in the magnetic susceptibility (see Suppl. Info. Fig. S3), similar to previously analyzed ten-coordinated Tb(III) complexes [46-48]. The application of a static field of 1 kOe significantly slows down the magnetization dynamics, allowing the detection of a set of frequency- and temperature-dependent peaks in the investigated range, reported in Figure 5a. Examination of the frequency dependence of the in-phase ($\chi''(\omega)$) and out-of-phase ($\chi'(\omega)$) susceptibilities points to the presence of two distinct relaxation processes. The first one is too slow to present peaks within the investigated frequency range and appears as a tail in the low temperature part of the $\chi''(\omega)$ plot. The second one, on the other hand, shows frequency- and temperature-dependent peaks in the $10^2 - 10^3$ Hz range. In order to extrapolate the magnetic relaxation time of the system, $\tau$, the fitting of the $\chi''(\omega)$ profiles has been carried out with an extended Debye model including two independent relaxation processes (Equation 1). Since no peaks in the frequency dependence of the $\chi'(\omega)$ plot for the slow process have been detected, the parameters describing the slow relaxation process are
affected by great uncertainties and will not be discussed here, but simply used to fit efficiently the complete \( \chi_{M''}(\omega) \) isothermal profiles. The temperature dependence of the relaxation time of the faster process has been plotted as function of the inverse of temperature, according to the Arrhenius relation \( \tau = \tau_0 \exp(\Delta/k_B T) \), in Figure 5b.

Figure 5. a) Frequency dependence of the out-of-phase magnetic susceptibility \( \chi_{M''} \) of 2, measured for different temperatures ranging from 2.0 K (blue points) to 6.0 K (red points) measured with an applied magnetic field of 1 kOe. b) Temperature dependence of the relaxation times measured with a static applied magnetic field of 1 kOe (empty circles) and 1.5 kOe (full circles) along with the corresponding best fitting lines, as described in the text.

The plot describes a temperature dependence of \( \tau \) that is decreasing upon lowering the temperature, indicating a crossover between at least two relaxation mechanisms. To fit this curve, a model including an Orbach process, describing a thermally activated relaxation through an activation barrier, coupled to a temperature independent one (tunneling process) has been used:

\[
\tau(T) = \tau_0 \exp(\Delta/k_B T) + \tau_{\text{tunneling}}
\]
The black line reported in Figure 5b displays the results of the fitting, which yielded $\tau_0 = 2.6(1) \times 10^{-6}$ s, $\Delta = 7.6(2)$ cm$^{-1}$ and a tunneling frequency of $2.60(3) \times 10^4$ Hz as best-fitting parameters. It must be stressed that fitting of the plot with models including a Raman process coupled to a direct or to a tunneling one yielded poorer results or extremely low Raman exponent (2.3), and were thus discarded. In order to have better insights into the relaxation dynamics of 2, the ac susceptibility characterization has been measured with a static magnetic field of 1.5 kOe, yielding the results reported in Figure S4. The frequency-dependent behavior of the $\chi_M''$ exhibits again two different relaxation processes, of which only one presents clear maxima. For this, the plots have been fitted with the same model employed for the 1 kOe measurements. The extracted relaxation times, reported as full dots in Figure 5b, are higher than those previously found at the same temperature in a 1 kOe field, indicating that the increased field suppressed the quantum tunneling relaxation process still present in the 1 kOe field. As observed in the previous case, the higher temperature part displays a steeper dependence on temperature, which is reduced upon cooling, reaching a maximum at about 2.9 K. Below this temperature, a decrease in the relaxation time upon cooling occurs. This phenomenon can be interpreted as result of a decrease in the energy exchange between the molecules and the solid state vibrations responsible for the spin relaxation upon cooling (phonon-bottleneck effect) [49-51]. The curve has been fitted with the same model as used before, joining an Orbach process with a remaining tunneling mechanism. The extracted parameters are $\tau_0 = 8.3(5) \times 10^{-7}$ s, $\Delta = 21.9(4)$ cm$^{-1}$ and a tunneling frequency of $1.92(1) \times 10^4$ Hz. The presence of a quantum tunneling of the magnetization with an applied field may arise from the presence of overlapping processes of direct relaxation and phonon-bottleneck effect. The experimentally determined value of the activation barrier to the magnetic relaxation is among the highest found for ten-coordinated Tb(III) complexes, pointing to the Hscpy ligand as a
good building block from which to prepare lanthanide complexes with slow relaxation of the magnetization [46-48,52].

Conclusion

Two new complexes of the bis-semicarbazone Hscpy series have been prepared and characterized, and both trivalent metal ions (Gd and Tb) showed coordination number 10. The ligand Hscpy is bound as a tridentate chelate, coordinated through two nitrogen atoms and one oxygen atom, while two nitrate ligands are coordinated in a chelate mode. The complexes crystallized with an accompanying discrete nitrate anion as counter-ion, and a methanol mono-solvate molecule; the overall composition is $[\text{Ln(Hscpy)}_2(\text{NO}_3)_2]\text{NO}_3\cdot\text{MeOH}$.

Infrared (FTIR) as well as high resolution mass spectra (HRMS-ESI) of the Gd$^{3+}$ and Tb$^{3+}$ compounds exhibited bands and fragments, respectively, in accordance with the chelate mode of binding of Hscpy, and the calculated fragmentation patterns.

In search for essential magnetic properties required for a possible application as a single molecule magnet (SMM), we have explored the dynamics of magnetization of the terbium complex. It showed slow relaxation of the magnetization under static magnetic fields of 1 kOe and 1.5 kOe, with an activation barrier to the relaxation $(21.9(4) \text{ cm}^{-1})$ among the highest found for ten-coordinated Tb(III) complexes, indicating that the Hscpy ligand is a good building block from which to prepare lanthanide complexes with slow relaxation of the magnetization.
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References

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Ref.: Structure and magnetic properties of two new lanthanide complexes with the 1-((E)-2-pyridinylmethylidene)semicarbazone ligand

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HIGHLIGHTS

1) Structural and Magnetic investigation of semicarbazone Gd(III) and Tb(III) complexes
2) Asymmetric and supramolecular 3D assembly in the solid state
3) Terbium complex shows a high activation barrier to relaxation