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A family of dinuclear lanthanide(III) complexes from the use of a tridentate Schiff base: structural and physical studies, and the case of a Dy\textsuperscript{III}\textsubscript{2} emissive single-molecule magnet\textsuperscript{†}

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The use of \(N\)-salicylidene-\(o\)-aminophenol (\(H\textsubscript{2}\text{saph}\)) in 4f-metal chemistry has led to the isolation of seven new isostructural lanthanide(III) [\(\text{Ln}^{\text{III}}\)] complexes. More specifically the \(\text{Ln}(\text{NO}_3\text{)}\text{\textsubscript{x}}\text{H}_2\text{O}/\text{H}_2\text{saph}/\text{Et}_2\text{N} (1:1:1)\) reaction mixtures in DMF/MeCN gave complexes [\(\text{Ln}_2(\text{NO}_3\text{)}\text{\textsubscript{2}}(\text{saph})_2(\text{DMF})_4\)] (\(\text{Ln} = \text{Sm} (1); \text{Eu} (2); \text{Gd} (3); \text{Tb} (4); \text{Dy} (5); \text{Ho} (6); \text{Er} (7)\)) in good yields (~65%). The structures of the isomorphous complexes 3 and 5 were solved by single-crystal, X-ray crystallography; the other complexes are proposed to be isostructural with 3 and 5 based on elemental analyses, IR spectra and powder XRD patterns. The two \(\text{Ln}^{\text{III}}\) atoms in the centrosymmetric molecules of 3 and 5 are doubly bridged by the deprotonated iminophenolato oxygen atoms of two nearly planar \(\eta^1\text{-}\eta^1\text{-}\eta^2\text{-}\mu\text{saph}\) ligands. The imino nitrogen and five terminal oxygen atoms (the salicylaldiminate, two from one bidentate coordination at each metal centre. The IR spectra of the complexes are discussed in terms of the coordination modes of the ligands present in the complexes. Solid-state emission studies for all 1-7 display identical ligand-based photoluminescence. Dc magnetic susceptibility studies in the 2-300 K range reveal the presence of a weak, intramolecular antiferromagnetic exchange interaction \(J = -0.19(1) \text{ cm}^{-1}\) based on the spin Hamiltonian \(H = -J \text{\boldmath \$g_{\text{Gd}}\text{\boldmath \$g_{\text{Gd}}}})\) for 3 and probably ferromagnetic exchange interaction within the molecules of 4 and 5. Ac magnetic susceptibility measurements in zero dc field show temperature- and frequency-dependent out-of-phase signals with two well defined, thermally-activated processes for 5, suggesting potential single-molecule magnetism character. The \(U_{\text{eff}}\) value is 17.4 cm\(^{-1}\) for the higher temperature process and 16.2 cm\(^{-1}\) for the lower temperature one. The combination of photoluminescence and single-molecule behaviour in the Dy\textsuperscript{III}\textsubscript{2} complex 5 is critically discussed.

Introduction

Molecular mononuclear, dinuclear, polynuclear (coordination clusters\textsuperscript{′}) and polymeric (coordination polymers\textsuperscript{5}) lanthanide(III) (\(\text{Ln}^{\text{III}}\)) complexes are a central research theme in inorganic chemistry. Such complexes currently attract the intense interest of synthetic, physical and theoretical chemists due to their involvement in diverse scientific fields/areas, for example Single-Molecule\textsuperscript{3} and Single-Ion\textsuperscript{4} Magnetism, magnetic refrigeration,\textsuperscript{5} quantum computing,\textsuperscript{6} homogeneous\textsuperscript{7} and heterogeneous\textsuperscript{8} catalysis, optics,\textsuperscript{9} organic transformations,\textsuperscript{10} and in the chemistry of multifunctional (or ‘hybrid’) molecular materials.\textsuperscript{11} A broad range of applications has been envisioned for \(\text{Ln}^{\text{III}}\)-containing molecules, including use as qubits for quantum information processing,\textsuperscript{6} and prototype devices such as molecular spin valves\textsuperscript{12} and transistors.\textsuperscript{13}

The creation of multifunctional molecular materials is currently an extremely important challenge in many high-tech applications.\textsuperscript{14} Such materials are molecular compounds exhibiting more than one property within the same molecule or family of isomorphous complexes. Dinuclear and polynuclear \(\text{Ln}^{\text{III}}\) complexes are ideal candidates for the construction of...
hybrid molecular materials. Restricting further discussion to the combination of photoluminescent (PL) and Single-Molecule Magnet (SMM) properties, the following features are of key importance. The 4f-4f electronic transitions (responsive for the light emission) are narrow and characteristic of each Ln$^{III}$, and the emitting excited states are long-lived. To overcome the limitation of the spin- and parity-forbidden nature of 4f-4f transitions, aromatic ligands can be utilized as sensitizers. Highly luminescent Ln$^{III}$ complexes are attracting attention in a wide variety of photonic applications, such as planar waveguide amplifiers, light-emitting diodes and bio-inspired luminescent probes. In the SMM area, some Ln$^{III}$ ions, with their highly anisotropic magnetic moments, have been responsible for many of the recent advances in this interdisciplinary area, pushing the frontiers to longer relaxation times and higher temperature regimes. Among the Ln$^{III}$ series, the Dy$^{III}$ member has yielded the largest numbers of 4f-based SMMs, which benefit from both the high magnetic moment and the high anisotropy of the spin-orbit Dy$^{III}$ Kramers doublet ground state (S=5/2, L=5, J=15/2).

Dinuclear Ln$^{III}$ complexes represent one of the simplest units which allow the study of multifunctional Ln$^{III}$ molecular materials, i.e., to investigate the dominance of one property over the other and within a given property to answer fundamental questions regarding single-ion behaviour (e.g. magnetic relaxation) versus behaviour arising from the molecule as an entity. Thus Ln$^{III}$ complexes are highly desirable. From the synthetic inorganic chemistry viewpoint, the simplest and most logical route for the isolation of dinuclear 4f-metal ion complexes is the simultaneous employment of bidentate bridging anionic groups (e.g. η¹:η¹:µ or/and η¹:η¹:µ carboxylate groups) and chelating (most often bidentate or tridentate, e.g. bpy, phen, terpy) neutral capping organic ligands, which block two or three coordination sites per Ln$^{III}$ ion and terminate further aggregation or potential polymerization. Another route is the simultaneous employment of capping bidentate nitrato groups and neutral or anionic organic ligands that bridge the two metal centres.

Thus, the choice of organic ligands is of paramount importance for the preparation of Ln$^{III}$ complexes. With all of the above in mind and given the recently initiated interest of our groups in the ‘hybrid’-dual Ln$^{III}$ molecular species, and especially in those displaying both magnetic and electronic-optical properties, we report here the syntheses, structures, magnetism and emission properties of new Ln$^{III}$ complexes, including an emissive Dy$^{III}$ SMM, bearing the tridentate Schiff base N-salicylidene-o-aminophenol (H$_2$saph, Scheme 1) as ligand. This Schiff base is a rather well-known ligand in 3d24 and mixed 3d/4f-metal25 chemistry, but with negligible use26 in homometallic 4f-metal chemistry.

Scheme 1. (left) Structural formula and abbreviation of N-salicylidene-o-aminophenol, and (right) the coordination mode of its doubly deprotonated form (saph$^2$) in complexes 1-7.

Experimental section

Materials and physical measurements

All manipulations were performed under aerobic conditions using materials (reagent grade) and solvents as received. The organic ligand H$_2$saph was synthesized in typical yields of >70% following the reported method. Its purity was checked by microanalyses and $^1$H NMR spectrum. Elemental analyses (C, H, N) were performed by the University of Patras microanalysis service. IR spectra (4000-400 cm$^{-1}$) were recorded using a Perkin Elmer 16PC FT-IR spectrometer with samples prepared as KBr pellets. Solid-state absorbance spectra were recorded on a Perkin Elmer Lambda 950 UV/VIS spectrometer in the 250-800 nm range, with a step of 2 nm. Solid-state fluorescence spectra were recorded on a Jobin-Yvon Horiba, Fluoro Max-P (SPEX) fluorescence spectrometer with excitation from a cw xenon arc lamp. The slit width for excitation was 1 nm and for emission 5 nm. Powder XRD measurements were collected on freshly prepared samples of the complexes on a PANalytical X’Pert Pro MPD diffractometer. Variable-temperature and variable-field magnetic studies of the Gd(III), Tb(III) and Dy(III) complexes were performed using a DSM5 Quantum Design magnetometer operating at 0.3 T in the 300-30 K range and at 0.02 T in the 30-2.0 K range to avoid saturation effects. Diamagnetic corrections were applied to the observed paramagnetic susceptibility using Pascal’s constants.

Synthetic details

Preparation of the representative complex [Gd$_2$(NO$_3$)$_2$(saph)$_2$(DMF)$_4$] (3). To a stirred dark yellow solution of H$_2$saph (0.107 g, 0.5 mmol) and Et$_3$N (0.067 mL, 0.5 mmol) in a solvent mixture comprising MeCN (5 mL) and DMF (5 mL) was added solid Gd(NO$_3$)$_3$$·$6H$_2$O (0.226 g, 0.5 mmol). The solid soon dissolved and the resulting yellow solution was stirred for a further 15 min and filtered. The reaction solution was layered with Et$_2$O (20 mL). Slow mixing gave pale yellow rhombohedral crystals of the product after 4-5 d. The crystals were collected by filtration, washed with MeCN (1 mL) and Et$_2$O (3x2 mL), and dried in air. The yield was ~65%. Analytical data, calcd for C$_{30}$H$_{46}$Gd$_2$N$_2$O$_{14}$ (found values
in parentheses): C 39.57 (39.71), H 4.03 (3.97), N 9.72 (9.56) %.
IR bands (KBr, cm⁻¹): 3140w, 3035w, 2930w, 1666s, 1648s, 1606s, 1582m, 1534m, 1480sh, 1466s, 1452sh, 1380s, 1344m, 1324w, 1284s, 1256m, 1244w, 1170m, 1148s, 1106m, 1042w, 1026m, 974w, 916m, 868m, 855s, 828s, 820sh, 778sh, 760s, 678m, 662m, 598m, 538w, 506sh, 492m, 446w, 410w.

Preparation of complexes [Ln(NO₃)₃(saph)(DMF)] (Ln = Sm, 1; Ln = Eu, 2; Ln = Tb, 4; Ln = Ho, 6; Ln = Er, 7). These complexes were prepared in an identical manner with 3 by simply replacing Gd(NO₃)₃·6H₂O with the corresponding hydrated nitrate salts of the other lanthanides. Typical yields are in the 60-70% range. The IR spectra of 1, 2 and 4-7 are almost superimposable with the spectrum of 3 with a maximum wavenumber difference of ±3 cm⁻¹.

Analytical data, calcd for C₃₉H₆₀Ln₃N₁₄O₁₄ (found values in parentheses): 1: C 40.07 (40.28), H 4.08 (3.96), N 9.84 (9.71); 2: C 39.94 (39.70), H 4.06 (4.00), N 9.81 (9.99); 4: C 39.46 (39.29), H 4.02 (4.11), N 9.69 (9.50); 5: C 39.21 (39.37), H 3.99 (4.07), N 6.93 (9.40); 6: C 39.05 (39.31), H 3.98 (3.87), N 9.59 (9.72); 7: C 38.89 (39.34), H 3.96 (3.87), N 9.55 (9.80).

Single-crystal X-ray crystallography
Crystals of 3 (0.22x0.38x0.79 mm) and 5 (0.30x0.35x0.52 mm) were taken from the mother liquor and immediately cooled to -113 °C. Diffraction measurements were performed on a Rigaku R-AXIS SPIDER Image Plate diffractometer using graphite-monochromated Cu Ka radiation. Data collection (o-scans) and processing (cell refinement, data reduction and empirical absorption correction) were performed using the CrystalClear program package. Important crystallographic data are listed in Table S1. The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques on F² with SHELX-97. H atoms were either located by difference maps and were refined isotropically or were introduced at calculated positions as riding on their respective bonded atoms. All non-H atoms were refined anisotropically. Full details can be found in the CIF files.

Results and discussion
Syntheses and IR spectra
The reactions of Ln(NO₃)₃·xH₂O (x = 5 or 6), H₂saph and Et₃N in a 1:1:1 molar ratio in DMF/MeCN (1:1 v/v) gave yellow solutions that upon layering or vapour diffusion with Et₂O gave yellow crystals or crystalline powders of [Ln(NO₃)₃(saph)(DMF)] (Ln = Sm (1); Eu (2); Gd (3); Tb (4); Dy (5); Ho (6); Er (7)) in good yields (60-70%). The crystals of 3 and 5 were of X-ray quality and their structures were solved by single-crystal X-ray crystallography. The other complexes are proposed to be isostructural with 3 and 5 based on elemental analyses, IR spectra and powder XRD patterns (Fig. S1). In order to investigate how the reaction’s conditions affect the product identity, we tried various metal:ligand:Et₃N ratios (1:1:2, 1:2:2, 1:2:3), but in all cases the same dinuclear complexes were obtained in ~70% yields. Assuming that the dinuclear compounds are the only products from their respective reaction mixtures, the preparation of 1-7 can be represented by eqn (1):

\[ 2 \text{Ln(NO}_3\text{)}_3\cdot x\text{H}_2\text{O} + 2 \text{H}_2\text{saph} + 4 \text{Et}_3\text{N} + 4 \text{DMF} \xrightarrow{\text{MeCN/DMF}} [\text{Ln}_2(\text{NO}_3\text{)}_3(\text{saph})_2(\text{DMF})_2]\ + 4 \text{Et}_3\text{NH(NO}_3\text{)}_2 + 2\text{xH}_2\text{O} \] (1)

The ν(C=O) and δ(OCN) IR modes of coordinated DMF appear at ~1665, ~1650 and ~680 cm⁻¹, respectively, in the spectra of the complexes. Due to coordination, the ν(C=O) and δ(OCN) bands are shifted to lower and higher wavenumbers, respectively, when compared with the corresponding bands in the spectrum of free DMF. The appearance of two ν(C=O) bands in the spectra of 1-7 (which is reproducible) probably reflects the presence of two crystallographically independent DMF molecules in the compounds. The spectra of the complexes exhibit strong bands at 1605-1608 cm⁻¹ which are assigned to the stretching vibration of the Schiff-base linkage, ν(C=N). These bands have been shifted to lower frequencies on going from the free ligand (at 1631 cm⁻¹) to the complexes; this behaviour is typical of the coordination of the imino nitrogen to LnIII. The IR bands at ~1465, ~1285 and ~1025 cm⁻¹ are assigned to the ν(C=O) and δ(OCN) IR modes of coordinated DMF. The separation of the two highest-frequency stretching bands is ~180 cm⁻¹, a typical value for bidentate nitrato groups.

Description of structures
Complexes 3 and 5 are isomorphous and crystallize in the monoclinic space group P2₁/n. The molecular structures of the complexes are shown in Figs. 1 and S2. The dinuclear [Ln₂(NO₃)₃(saph)₂(DMF)₂] molecules possess an inversion centre at the mid-point of the Ln1···Ln1’ distance. The two LnIII atoms are doubly bridged by the deprotonated iminophenolato oxygen atoms (O1, O1’) of two nearly planar, η¹:η²:µ-saph ligands, the LnIII···LnIII distance being 3.784 and 3.738 Å for 3 and 5, respectively. The imino nitrogen and five terminal oxygen atoms (the salicylaldiminate, two from one asymmetric bidentate chelating nitrato group and two from two DMF molecules) complete 8-coordination at each metal site. The Dy-O/N bond lengths are slightly shorter than the corresponding Gd-O/N ones due to lanthanide contraction. A SHAPE analysis reveals that the coordination geometry of the 8-coordinate LnIII centres is square antiprismic (Figs. 2 and S3-S5, Table S2). The two square bases consist of atoms O1, O1’, O2, N1 and O3, O4, O6, O7; the angle between the best mean planes of the square bases is 2.1° for 3 and 1.7° for 5. The square antiprism, along with the bicapped trigonal prism and the triangular dodecahedron seem to be the most common
polyhedra among 8-coordinate complexes\(^{26}\) and were termed by Muettetries and Wright ‘low energy polyhedra’.\(^{26}\)

The lattice structures of the two complexes are built through weak intermolecular C–H···O interactions involving one aromatic carbon atom of the iminophenolate part of saph\(^{2}\) and one coordinated nitrito oxygen atom. The dinuclear molecules form 2D layers extending parallel to the (101) plane (Figs. 3 and S6).

![Fig. 1](image1.png)

Fig. 1 The molecular structure of 5. Unprimed and primed atoms are related by the symmetry operation \(-x+2, -y, -z\). Selected interatomic distances (\(\AA\)) and angles (°): Dy1···Dy1\(^{\prime}\) 3.738(1), Dy1-O1 2.323(2), Dy1-O1\(^{\prime}\) 2.322(3), Dy1-O2 2.200(3), Dy1-N1 2.525(4), Dy1-O(NO\(_3\))\(^{2-}\) (DMF) 2.319(3)–2.482(3) \(\AA\); O1-Dy1-O1\(^{\prime}\) 72.8(1), O3-Dy1-O4 51.7(1), O1···Dy1-O4 163.3(1), O2-Dy1-O6 146.9(1), Dy1-O1-Dy1\(^{\prime}\) 107.2(1)\(^{\circ}\).

![Fig. 2](image2.png)

Fig. 2 The square antiprismatic coordination geometry of Dy1 in the structure of 5. The plotted polyhedron is the ideal, best-fit polyhedron using the program SHAPE.\(^{24}\)

The lattice structures of the two complexes are built through weak intermolecular C–H···O interactions involving one aromatic carbon atom of the iminophenolate part of saph\(^{2}\) and one coordinated nitrito oxygen atom. The dinuclear molecules form 2D layers extending parallel to the (101) plane (Figs. 3 and S6).

![Fig. 3](image3.png)

Fig. 3 A small portion of one 2D layer in the crystal structure of complex 5, resulting from the intermolecular C3-H3···O4 (and symmetry equivalent) hydrogen bonding interaction.

Complexes 3 and 5 join a very small family of structurally characterized Ln\(^{III}\)-containing complexes that possess anionic forms of H\(_2\)saph as ligands. Four of them are 3d/4f-metal complexes\(^{25}\) and only compound [Dy\(_2\)(OH)\(_2\)(C\(_6\)H\(_5\))\(_2\)](saph\(_2\))(H\(_2\)O)(MeOH)\(_2\)]\(^{26}\) is a pure 4f-metal cluster. Since all these complexes were reported only recently, we feel it timely to collect them in Table 1 together with the coordination modes of saph\(^{2}\) and Hsaph\(^{+}\), and basic information about their magnetic behaviour. Thus, complexes 3 and 5 are the first dinuclear Ln\(^{III}\) complexes of saph\(_2^2\)/Hsaph\(^{+}\).

**Table 1** Structurally characterized Ln\(^{III}\)-containing complexes that possess Hsaph\(^{+}\) and saph\(_2^2\) as ligands.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Coordination mode</th>
<th>Magnetic Behaviour</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>(Et(_2)NH)[Me(^{III})Dy(_2)(OH)(_2)(NO(_3))(saph)](_2)</td>
<td>(\eta^6):(\eta^6):(\mu)</td>
<td>AF, SMM</td>
<td>25a</td>
</tr>
<tr>
<td><a href="saph">Mn(^{II})Dy(_2)(OH)(NO(_3))(saph)</a>(_2)(H(_2)O)</td>
<td>(\eta^6):(\eta^6):(\mu)</td>
<td>AFF, SMM</td>
<td>25a</td>
</tr>
<tr>
<td><a href="saph">Ni(_n)Gd(_n)(OH)(OMe)(C(_6)H(_5))(_2)</a>(MeOH)(H(_2)O)</td>
<td>(\eta^2):(\eta^2):(\mu)</td>
<td>F</td>
<td>25b</td>
</tr>
<tr>
<td><a href="saph">Ni(_n)Dy(_n)(OH)(OMe)(C(_6)H(_5))(_2)</a>(MeOH)(H(_2)O)</td>
<td>(\eta^2):(\eta^2):(\mu)</td>
<td>AF, SMM</td>
<td>25b</td>
</tr>
<tr>
<td><a href="saph">Dy(_2)(OH)(OMe)(CMe)</a>(saph)(_2)(H(_2)O)(MeOH)(_2)]</td>
<td>(\eta^2):(\eta^2):(\mu)</td>
<td>AF</td>
<td>26</td>
</tr>
<tr>
<td><a href="DMF">Gd(_n)(NO(_3))(saph)(_2)</a>(_2)](3)</td>
<td>(\eta^2):(\eta^2):(\mu)</td>
<td>AF (a) this work</td>
<td></td>
</tr>
<tr>
<td><a href="saph">Dy(_2)(OH)(OMe)</a>(saph)(DMF)(_2)](5)</td>
<td>(\eta^2):(\eta^2):(\mu)</td>
<td>F, SMM (b) this work</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) For the Hsaph\(^{+}\) ligand. \(^b\) AF= overall antiferromagnetic behaviour, F= overall ferromagnetic behaviour, SMM= Single-Molecule Magnet. \(^c\) The assignment of AF or/and F exchange interactions in the 3d/Dy\(^{III}\) and Dy\(^{III}\) complexes should be considered as tentative and taken into account with skepticism.

**Absorption and emission spectra**

The solid-state electronic absorption spectra of all complexes were recorded; the spectra of the representative complexes 4 and 5, as well as the spectrum of H\(_2\)saph are shown in Fig. S7. The spectra of 1–7 are very similar, dominated by ligand-based bands. Due to deprotonation and coordination, the absorption bands of free H\(_2\)saph at 454 and 486 nm are “blue” shifted by ca. 90 and 80 nm, respectively, in the spectra of the complexes. In accordance with the fact that deprotonation causes “blue” shift, a methanolic solution of H\(_2\)saph containing 2.5 equivalents of LiOH (assumed to contain a high concentration
of saph$^{2-}$) exhibits the two longest wavelength absorptions at 420 and 445 nm.

Solid-state, room-temperature emission spectra of the free ligand H$_2$saph and complexes 4 and 5 are presented in Fig. 4. Upon maximum excitation at 400 nm, a strong emission peak at 616 nm and a shoulder at ca. 650 nm are detected for free solid H$_2$saph. This spectral pattern remains the same upon excitation at 485 and 450 nm (Fig. S8). Since solid “salts” A$_2$(saph), where A$^+$ = Li$^+$, Na$^+$, K$^+$, Et$_3$NH$^+$, Bu$^+$/N$^+$, …, are not known in the literature (our efforts to prepare such “salts” repeatedly failed leading to mixture of products difficult to separate and characterize), we were not able to compare the solid-state emission spectra of the complexes with the corresponding spectrum of the free saph$^{2-}$ ion. However, a methanolic “H$_2$saph·2.5LiOH” solution emits weakly green light displaying a broad peak at ca. 550 nm upon excitation at 400 nm. An almost identical, room-temperature photoluminescence behaviour is observed for solids 1-7 (Fig. 4 for 4 and 5, Fig. S9 for 1). Upon maximum excitation at 400 nm, a broad green emission at ca. 530 nm was recorded; no significant Ln$^{III}$ emission (Ln= Sm, Eu, Tb, Dy) was detected. These experimental facts reveal that the broad green emission at ~530 nm in the spectra of all complexes is saph$^{2-}$-centered.

De magnetic susceptibility studies

Solid-state direct-current (dc) magnetic susceptibility ($\chi_T$) data on powder samples of complexes 3, 4 and 5 were collected under applied fields of 0.3 T (300-30 K) and 0.02 T (30-2.0 K). The data are plotted as $\chi_M/T$ products versus $T$ in Fig. 5. The room-temperature $\chi_M/T$ value for 3 is 16.01 cm$^3$ K mol$^{-1}$, essentially equal to the spin-only value (15.75 cm$^3$ K mol$^{-1}$ for $g$ = 2.00) expected for two noninteracting Gd$^{III}$ ($S$=7/2, $L$=0) ions. The value of the $\chi_M/T$ product remains almost constant down to ~30 K and then decreases rapidly to 6.59 cm$^3$ K mol$^{-1}$ at 2.0 K, suggesting a moderately weak antiferromagnetic exchange interaction. Fit of the experimental data was performed by means of the conventional analytical expression derived from the isotropic spin Hamiltonian shown in eqn (2). The best-fit parameters obtained are $J$=−0.19(1) cm$^{-1}$ and $g$=2.023(1). The $J$ value is typical for dinuclear complexes containing the [Gd$^{III}_2$($\mu$-OR)$_2$] core.$^{3,13a,37,38}$

$$H = -J\hat{S}_{Gd} \hat{S}_{Gd}$$  

(2)

The gradual increase of the $\chi_M/T$ product remains almost constant down to ~30 K and then decreases rapidly to 6.59 cm$^3$ K mol$^{-1}$ at 2.0 K, suggesting a moderately weak antiferromagnetic exchange interaction. Fit of the experimental data was performed by means of the conventional analytical expression derived from the isotropic spin Hamiltonian shown in eqn (2). The best-fit parameters obtained are $J$=−0.19(1) cm$^{-1}$ and $g$=2.023(1). The $J$ value is typical for dinuclear complexes containing the [Gd$^{III}_2$($\mu$-OR)$_2$] core.$^{3,13a,37,38}$

![Figure 5](image-url)
under an external field of 4 G agree with the low-\(T\) \(\chi_M T\) values at higher fields (145 and 3000 G); orientation of the crystals under a field of 4 G can be ruled out.

The lack of a superposition of the reduced magnetization \((M)\) versus \(H/T\) data on a single master curve and the low magnetizations of 11.9 \(\hbar\)β for 4 and 12.8 \(\hbar\)β for 5 at 5 T (Fig. 6) suggest the presence of a moderate magnetic anisotropy and/or low-lying excited states.

### Ac magnetic susceptibility studies

In the light of the dc susceptibility measurements and magnetization responses, alternating-current (ac) magnetic susceptibility measurements were performed on polycrystalline samples of 4 and 5 in the 2.0-12 K range in zero applied dc field and a 4.0 G ac field oscillating in the 10-1488 Hz range (Figs. 7 and S10). No out-of-phase (\(\chi''\)) signals were detected for 4, but well defined frequency-dependent \(\chi''\) signals were observed for 5, indicative of SMM behaviour. The \(\chi''\) ac signals show two peaks corresponding to two well defined, thermally-activated processes around 6 K for frequencies in the 1488-561 Hz range and around 2.5 K for frequencies ranging between 174 and 10 Hz. At intermediate frequencies (462, 380, 356 Hz), the peaks overlap and the position of the maxima are not clearly defined.

Fitting to the Arrhenius law \[\tau = \tau_0 \exp(U_{eff}/K_B T)\] (Fig. 8) afforded values of \(U_{eff} = 17.4\) cm\(^{-1}\) and \(\tau_0 = 3.0 \times 10^4\) s for the process at \(\sim 6\) K, and \(U_{eff} = 16.2\) cm\(^{-1}\) and \(\tau_0 = 4.4 \times 10^7\) s for the lower temperature process. As expected, the flattened (i.e. non-emicircular shape) Cole-Cole plot at 5 K (Fig. 9) confirms the two simultaneous relaxation processes. The relaxation time, \(\tau\), does not become temperature independent even down to 2.2 K, indicating that a pure quantum regime is not yet active.

The observation of more than one relaxation process in Dy\(^{III}\)\(_2\) units has been related either with the presence of two different metal sites in the molecule or with relaxation of the ground state through excited levels.\(^3\)\(^,\)\(^19c\)\(^,\)\(^42\) Since complex 5 is centrosymmetric with a unique metal site, the latter possibility emerges as the reasonable origin of the two processes. The topic of magnetic relaxation in Ln(III) SMMs is of great current interest.\(^3\)\(^b\)\(^,\)\(^18c\)\(^,\)\(^19c\)\(^,\)\(^40b\)\(^,\)\(^43\) Magnetic relaxation is typically controlled by single-ion factors rather than magnetic exchange and proceeds through thermal relaxation of the lowest excited states. For a Kramers doublet Ln\(^{III}\) (like Dy\(^{III}\)) SMM, the lowest energy doublet has high \(|m_j|\), and the complexity of the relaxation phenomena is related to the number of relaxation paths available (reversal mechanism via quantum tunnelling of magnetization within the lowest energy doublet, thermal mechanism via an excited state, thermally activated quantum
tunnelling of magnetization occurring within an excited doublet).

Given that in the absence of high symmetry, the ground state of Dy\textsuperscript{III} is a doublet quantized along the anisotropy axis with \( m_I = \pm 15/2 \), we have determined the orientation of the ground state magnetic anisotropy axis for each Dy\textsuperscript{III} centre of \( 5 \) using a method reported recently, based on an electrostatic model.\textsuperscript{44} The method does not rely on the fitting of experimental data, requiring only the determination of the single-crystal X-ray structure of the complex. Following this method and the program MAGELLAN (a FORTRAN program), the ground state magnetic axis for each Dy\textsuperscript{III} ion in \( 5 \) (the two axes are co-parallel due to the presence of a crystallographically imposed inversion centre in the molecule) was found tilted towards the DMF atom \( O7 \) and the terminal oxygen atom \( O2 \) which belongs to the salicylidene part of saph\textsuperscript{2-} (Fig. 10), i.e. pointing toward the square faces of the approximate antiprism. However, after several decades of studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theories, it is well established that the electrostatic models are not completely valid neither for studies on ligand field theore...
National Resources (to S.P.P.), and by the CICYT (project CTQ2012-30662) and Excellence in Research ICREA-Academic Award (to A.E.).

Notes and references


40 We thank two referees who raised these points.


GRAPHICAL ABSTRACT

The bridging potency of the dianionic form of N-salicylidene-o-aminophenol has been exploited for the preparation of dinuclear lanthanide(III) complexes; the Dy_{II}^{III} complex is bifunctional exhibiting both photoluminescence and slow relaxation of its magnetization.