

Towards Multifunctional Molecular Materials: A New Family of Enneanuclear Lanthanide Clusters Displaying Magnetic and Optical Properties

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ABSTRACT: The initial employment of 2-(hydroxymethyl)pyridine in 4f-metal chemistry has afforded a new family of Ln^{III} clusters with a sandglass-like topology and dual physical properties; the Dy^{III} member shows single-molecule magnetism behavior, while the Eu^{III}-analogue exhibits intense red photoluminescence.

The current interest of many research groups worldwide is focused on the synthesis of multifunctional (or “hybrid”) molecular materials, which are species exhibiting more than one physical properties within the same molecule or family of isomorphous compounds.¹ Towards this aim, polynuclear lanthanide complexes (4f-metal clusters) appear as promising candidates, given their contributions to various research areas, such as molecular magnetism, optics, catalysis and medicine.² Of particular interest is the ability of 4f-metal clusters to function as single-molecule magnets (SMMs)³ and photoluminescence sensitizers.⁴ In the former field, SMMs derive their properties from the combination of a large magnetic moment in the ground state with a large Ising-type magnetoanisotropy. As a result, 4f-SMMs often possess a significant barrier to magnetization relaxation and at low enough temperatures they display out-of-phase ac magnetic susceptibility (χ_M'') signals, and hysteresis in magnetization *vs* applied dc field loops.⁵ Thus, SMMs have been proposed for several potential applications, such as in very high-density information storage and spintronics.⁶

Furthermore, homometallic 4f-metal clusters have shown intense, long-lived emissions, thus making their complexes of particular interest for a wide range of applications such as display devices, luminescent sensors and probes for clinical use.⁷ This applies particularly to Eu^{III} and Tb^{III}-based clusters with red and green luminescence due to $^5D_0 \rightarrow ^7F_n$ and $^5D_4 \rightarrow ^7F_n$ transitions, respectively.⁸ Luminescence from trivalent lanthanides arises from electronic transitions between the 4f orbitals, which are forbidden on symmetry grounds, thus leading to poor absorption cross-sections and long-lived excited states.⁹ Conse-

quently, population of the emitting levels of the Ln^{III} ion is best achieved by employing light-harvesting ligands that normally absorb strongly UV light and can sensitize the metal ion by intramolecular energy transfer from the ligand-based triplet state.¹⁰

It becomes apparent that the chances of identifying new 4f-metal clusters exhibiting simultaneously interesting magnetic and photophysical properties will benefit from the development of new reaction schemes with suitable organic ligands. In order to synthesize such “hybrid” molecular materials, the choice of the organic ligand becomes of particular importance. This should present (i) an affinity in binding to the oxophilic Ln^{III} ions by containing O-donor atom(s), (ii) an ability to bridge many metal centers but prevent polymer formation, and (iii) a dual role in both promoting strong magnetic exchange interactions between the metal atoms it bridges and in containing aromatic group(s) for enhancing the luminescence intensities.¹¹

With all the above in mind, we decided to use 2-(hydroxymethyl)pyridine (hmpH), a well known ligand for the synthesis of 3d-metal clusters possessing large spin ground states and SMM behavior,¹² but with negligible use in homometallic 4f-metal cluster chemistry to date. Herein we report the syntheses, structures, magnetic and photoluminescence properties of three representative members belonging to a new family of enneanuclear Ln^{III} clusters.

The reaction of Ln(NO₃)₃·xH₂O (Ln = Eu, Gd, and Dy), hmpH, and NEt₃ in a 1:2:2 molar ratio, in a solvent mixture comprising DMF and CH₂Cl₂ (2:1, v/v), gave yellow solutions that upon layering with Et₂O gave colorless crystals of [Ln₉(OH)₁₀(hmp)₈(NO₃)₈(DMF)₈](OH) in 65-70% isolated yields. It should be mentioned that OH⁻ counterions are with precedent in cluster chemistry.¹³ Representative complex [Dy₉(OH)₁₀(hmp)₈(NO₃)₈(DMF)₈](OH)·1.6H₂O·0.6CH₂Cl₂ (1·1.6H₂O·0.6CH₂Cl₂) was characterized by X-ray crystallography,¹⁴ and the other analogues (Gd₉; 2, Eu₉; 3) were identified by elemental analyses (C, H, N), and IR spectral and unit cell comparison with crystals of 1 (see the Supporting Information); thus, only the structure of 1 will be discussed in detail. The

structure of **1** has a fourfold axis passing through the central Dy^{III} atom (Figure 1). Its cation consists of nine Dy^{III} atoms held together by two μ_4 -OH⁻ (O2, O5), eight μ_3 -OH⁻ (O3, O4, and their symmetry-related counterparts), and eight $\eta^1:\eta^2:\mu$ hmp⁻ groups (Figure 2, left). The central Dy^{III} atom (Dy2) is the shared apex of two square pyramids formed by Dy(1,1b,1c,1d) and Dy(3,3b,3c,3d), respectively. An alternative description of the topology of **1** is as a sandglass consisting of eight Dy^{III} atoms at the apices and one Dy^{III} ion at the center of a Dy₈ square antiprism (Figure 2, right). Each edge of the {Dy₄} square bases is bridged by four μ -O atoms (O1 or O11, and their symmetry-related counterparts) of the hmp⁻ ligands, one μ_4 -OH⁻, and four μ -OH⁻ ions; the latter become μ_3 - and are capping the center of the triangular faces of the pyramids, bridging the central Dy atom with two Dy atoms of the square base. The complex thus contains an overall [Dy₉(μ_4 -OH)₂(μ_3 -OH)₈(μ -OR)₈]⁹⁺ [R = (py)CH₂]⁻ core. Peripheral ligation about the core is provided by eight bidentate chelating NO₂⁻ groups and eight terminal DMF molecules. All Dy atoms are eight-coordinate, and the protonation level of OH⁻ groups was determined by charge-balance considerations and bond valence sum (BVS) calculations.¹⁵

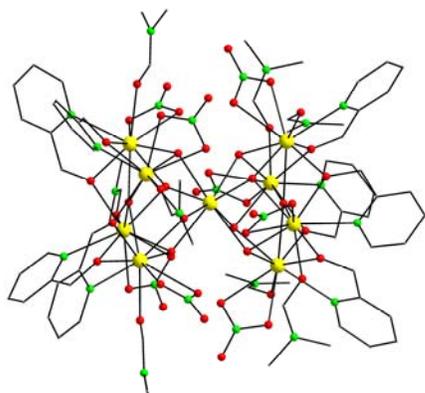


Figure 1. Structure of the cation of **1**, with H atoms omitted for clarity. Color code: Dy^{III} yellow, O red, N green, C gray.

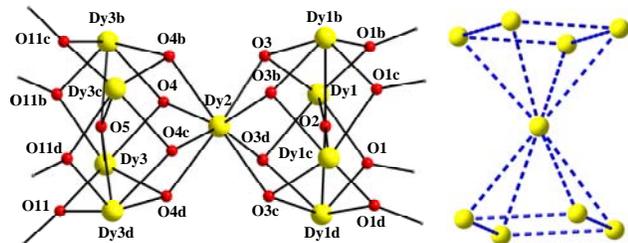


Figure 2. (left) Labeled PovRay representation of the complete [Dy₉(μ_4 -OH)₂(μ_3 -OH)₈(μ -OR)₈]⁹⁺ core of **1**. (right) Dy₉ topology, emphasizing the sandglass description (blue dashed lines). All atoms are related to each other by the fourfold symmetry. Color scheme as in Figure 1.

Complexes **1-3** are the first structurally characterized homometallic 4f-metal clusters to contain any form (neutral or anionic) of the 2-(hydroxymethyl)pyridine ligand. They also join only a handful of previous Ln^{III} clusters with a nuclearity of 9.¹⁶

Variable temperature dc and ac magnetic susceptibility studies were carried out on freshly prepared, crystalline samples of complexes **1-3** in the temperature range 5.0-300 K under an applied field of 0.1 T. Theoretically, the Eu^{III} analogue should not exhibit any magnetic moment, since Eu^{III} has an ⁷F₀ with $J =$

0, although some contribution from thermally accessible levels such as ⁷F₁ and ⁷F₂ may appear (Figure S1).⁸ The obtained data for complexes **1** and **2** are shown as $\chi_M T$ vs. T plots in Figure 3. For both complexes, $\chi_M T$ remains almost constant at a value of ~ 113 (for **1**) and ~ 66 (for **2**) cm³Kmol⁻¹ as the temperature decreases, until ~ 100 K where the value starts to steadily decrease to a minimum value of 68.71 (for **1**) and 35.19 (for **2**) cm³Kmol⁻¹ at 5.0 K. The room-temperature $\chi_M T$ values are slightly less than the expected values of 127.53 and 70.88 cm³Kmol⁻¹ for 9 Dy^{III} ($S = 5/2$; $L = 5$, ⁶H_{15/2}, $g = 4/3$) and 9 Gd^{III} ($S = 7/2$, $L = 0$, $g = 2$) non-interacting ions, respectively. Given the large spin-orbit coupling of Dy^{III} ions and the fact that the field dependence of the magnetization below 10 K is not saturated even at 7 T, it is difficult to conclude on the exact strength and nature of the magnetic exchange interactions between the metal centers in **1**.¹⁷ However, in the case of complex **2**, where contributions from orbital angular momentum and anisotropic effects do not need to be taken into account, the decrease of the $\chi_M T$ value at $T < 100$ K could be assigned to the presence of weak antiferromagnetic interactions between the nine Gd^{III} centers; the non-zero $\chi_M T$ value at 5.0 K is consistent with an $S \neq 0$ spin ground state. Attempts to fit the magnetization vs. field data, assuming that only the ground state is populated in the lowest T - and field-ranges, were all unsuccessful and we thus performed ac susceptibility studies, which are a powerful complement to dc studies for determining the ground state of a system because they preclude any complications arising from the presence of a dc field.

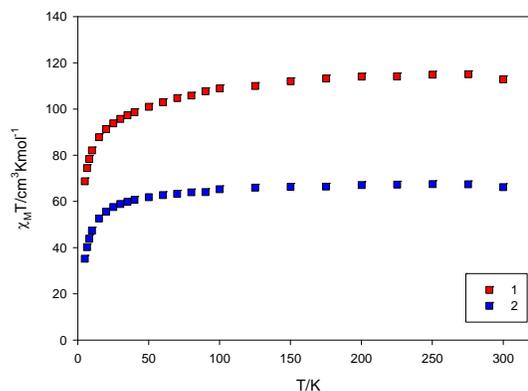


Figure 3. Plot of $\chi_M T$ vs. T for complexes **1** (red squares) and **2** (blue squares).

The in-phase (χ'_M) ac signal, shown as $\chi'_M T$ in Figure S2, is very temperature-dependent in the 1.8-15 K region, consistent with the presence of many very low-lying excited states with S greater than that of the ground state. Extrapolating the plot above 4 K down to 0 K gives a value of ~ 7.5 cm³Kmol⁻¹, suggesting an $S \approx 7/2$ ground state with $g \sim 1.95$. The corresponding plot for **1** shows a similar behavior albeit with the presence of a frequency-dependent decrease in the $\chi'_M T$ (Figure S3) and a concomitant appearance of out-of-phase χ''_M tails of signals at $T < 5$ K (Figure 4). This behavior is indicative of slow magnetization relaxation, suggesting **1** to possibly be a new SMM, the first with such a topology and nuclearity in 4f metal cluster chemistry.

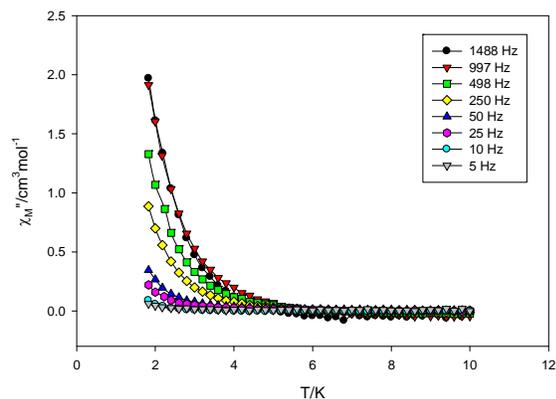


Figure 4. Out-of-phase (χ_M'') vs. T ac susceptibility signals for **1** in a 3.5 G field oscillating at the indicated frequencies.

In order to gain any possible access into dual physical properties for this new family of enneanuclear 4f-metal complexes, we decided to perform photoluminescence studies on the Eu^{III} analogue (**3**). The solid-state emission spectrum of **3** (Figure 5) displays strong red photoluminescence, assigned to the characteristic $^5\text{D}_0 \rightarrow ^7\text{F}_n$ ($n = 0-4$) transitions of Eu^{3+} . Specific assignments are as follows: $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1}$ (593 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (616 nm), $^5\text{D}_0 \rightarrow ^7\text{F}_3$ (652 nm) and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ (697 nm).^{8,11} Few emission peaks observed below 590 nm are likely due to transitions from the $^5\text{D}_1$ and $^5\text{D}_2$ excited states to the $^7\text{F}_n$ levels.¹⁸

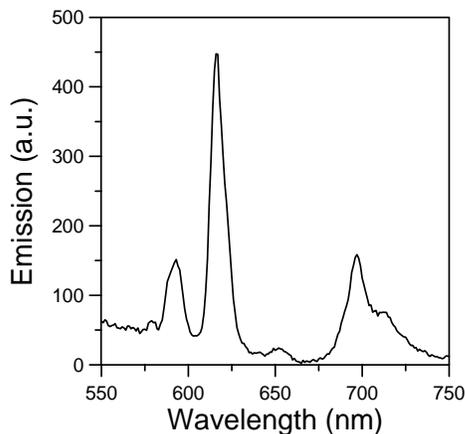


Figure 5. The emission spectrum of **3** in the solid state at room temperature (excitation at 396 nm).

In conclusion, a structurally unique family of enneanuclear Ln(III) complexes of the 2-(hydroxymethyl)pyridine ligand has been isolated and characterized. Despite being isomorphous, members of this family of Ln_9 molecular species demonstrate assorted physical properties; the Eu system was shown to exhibit red luminescence, while the Dy analogue shows slow relaxation of the magnetization, as seen in SMMs. We are currently investigating the optical and magnetic properties of more members, i.e. the Tb^{III} analogue, in order to isolate simultaneously SMM and emissive behaviors in the same molecule.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data (CIF format), microanalyses, and magnetic plots for complexes **1-3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Crystal structure data for $1 \cdot 1.6\text{H}_2\text{O} \cdot 0.6\text{CH}_2\text{Cl}_2$: $\text{C}_{72.60}\text{H}_{119.40}\text{Gd}_9\text{N}_{24}\text{O}_{52.60}\text{Cl}_{1.20}$, $F_w = 3675.16$, tetragonal space group $P4/n$ with $a=b=19.0680(3)$ Å, $c=16.2385(3)$ Å, $V=5904.1(2)$ Å³, $T=160(2)$ K, $Z=2$, $R1 [I > 2\sigma(I)] = 0.0749$, $wR2 (F^2, \text{all data}) = 0.1761$.
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