Inorganic Chemistry

Communication

pubs.acs.org/IC

A New Family of Nonanuclear Lanthanide Clusters Displaying Magnetic and Optical Properties

Dimitris I. Alexandropoulos,[†] Shreya Mukherjee,[‡] Constantina Papatriantafyllopoulou,[‡] Catherine P. Raptopoulou,[§] Vassilis Psycharis,[§] Vlasoula Bekiari,[⊥] George Christou,[‡] and Theocharis C. Stamatatos*[,†,¶]

[†]Department of Chemistry, University of Patras, 26504 Patras, Greece

[‡]Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

[§]Institute of Materials Science, NCSR "Demokritos", 15310 Aghia Paraskevi Attikis, Greece

[⊥]Department of Aquaculture and Fisheries Management, Technological Educational Institute of Messolonghi, 30200 Messolonghi, Greece

[¶]Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, P.O. Box 135, 54124 Thessaloniki, Greece

Supporting Information

ABSTRACT: The initial employment of 2-(hydroxymethyl)pyridine in 4f metal chemistry has afforded a new family of Ln^{III}_9 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 property within the same molecule or family of isomorphous compounds.[1] Toward 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 and large Ising-type magnetoanisotropy. As a result, 4f metal SMMs often possess a significant barrier to magnetization relaxation, and at low enough temperatures, they display out-of-phase alternating-current (ac) magnetic susceptibility (χ_M'') signals and hysteresis in magnetization versus applied direct-current (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] Consequently, population of the emitting levels of the Ln^{III} ion is best achieved by employing light-harvesting ligands that normally strongly absorb 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 containing aromatic group(s) for enhancing the luminescence intensities.[11]

With all of 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, and magnetic and photoluminescence properties of three representative members belonging to a new family of nonanuclear Ln^{III} clusters. None of them display both SMM and photoluminescent properties, but the described work represents important steps toward this objective as the work is extended.

The reaction of $Ln(NO_3)_3 \cdot xH_2O$ (Ln = Eu, Gd, and Dy), hmpH, and NEt_3 in a 1:2:2 molar ratio, in a solvent mixture comprising *N,N*-dimethylformamide (DMF) and CH_2Cl_2 (2:1, v/v), gave yellow solutions that upon layering with Et_2O gave

Received: June 27, 2011
Published: October 20, 2011

dx.doi.org/10.1021/ic2013683 | *Inorg. Chem.* 2011, 50, 11276–11278

colorless crystals of $[Ln_9(OH)_{10}(hmp)_8(NO_3)_8(DMF)_8](OH)$ in 65−70% isolated yield. It should be mentioned that OH^- counterions are with precedent in cluster chemistry.[13] Representative complex $[Dy_9(OH)_{10}(hmp)_8(NO_3)_8(DMF)_8]$-$(OH)\cdot 1.6H_2O\cdot 0.6CH_2Cl_2$ (**1**$\cdot 1.6H_2O\cdot 0.6CH_2Cl_2$) was characterized by X-ray crystallography,[14] and the other analogues (Gd_9, **2**; Eu_9, **3**) were identified by elemental analyses (C, H, and N) and IR spectral and unit-cell comparison with crystals of **1** (see the Supporting Information, SI); thus, only the structure of **1** will be discussed in detail. The structure of **1** has a 4-fold axis passing through the central Dy^{III} atom (Figure 1).

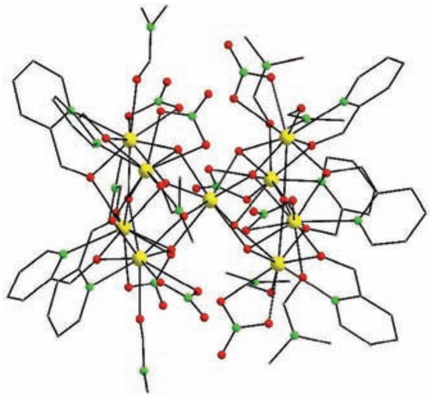

Figure 1. Structure of the cation of **1**, with H atoms omitted for clarity. Color code: Dy^{III}, yellow; O, red; N, green; C, gray.

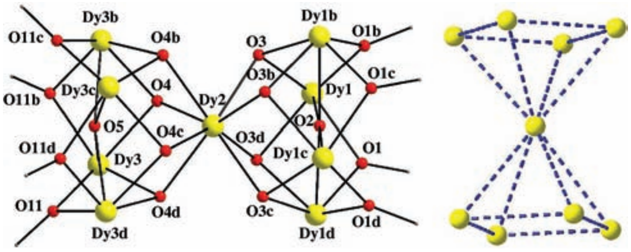

Figure 2. (left) Labeled PovRay representation of the complete $[Dy_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(\mu\text{-}OR)_8]^{9+}$ core of **1**. (right) Dy_9 topology, emphasizing the sandglass description (blue dashed lines). All atoms are related to each other by the 4-fold symmetry. The color scheme is as in Figure 1.

Its cation consists of nine Dy^{III} atoms held together by two μ_4-OH^- (O2 and O5), eight μ_3-OH^- (O3, O4, and their symmetry-related counterparts), and eight η^1:η^2:μ-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 a sandglass consisting of eight Dy^{III} atoms at the apexes and one Dy^{III} ion at the center of a Dy_8 square antiprism (Figure 2, right). Each edge of the $\{Dy_4\}$ 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 $[Dy_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(\mu\text{-}OR)_8]^{9+}$ [R = $(py)CH_2-$] core. Peripheral ligation about the core is provided by eight bidentate chelating NO_3^- groups and eight terminal DMF molecules. All Dy atoms are eight-coordinate, and the protonation level of the OH^- groups was determined by charge-balance considerations and bond-valence-sum (BVS) calculations.[15]

Complexes **1**−**3** are the first structurally characterized homometallic 4f metal clusters to contain any form (neutral or anionic) of the hmpH 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 $Eu^{III}{}_9$ analogue should not exhibit any magnetic moment because Eu^{III} has an $^7F_0$ with $J = 0$, although some contribution from thermally accessible levels such as $^7F_1$ and $^7F_2$ may appear (Figure S1 in the SI).[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**) cm^3 K mol^{-1} as the temperature decreases to ~100 K, where the value starts to steadily decrease to minimum values of 68.71 (for **1**) and 35.19 (for **2**) cm^3 K mol^{-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 cm^3 K mol^{-1} for nine Dy^{III} ($S = {}^5/_2$; $L = 5$, $^6H_{15/2}$, $g = {}^4/_3$) and nine Gd^{III} ($S = {}^7/_2$, $L = 0$, $g = 2$) noninteracting ions, respectively. Given the large spin−orbit coupling of Dy^{III} ions and the fact that the field dependence of magnetization below 10 K is not saturated even at 7 T, it is difficult to conclude 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 the 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 nonzero $\chi_M T$ value at 5.0 K is consistent with an $S \neq 0$ spin ground state. Attempts to fit the magnetization versus 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 the dc studies for determining the ground state of a system because they preclude any complications arising from the presence of a dc field.

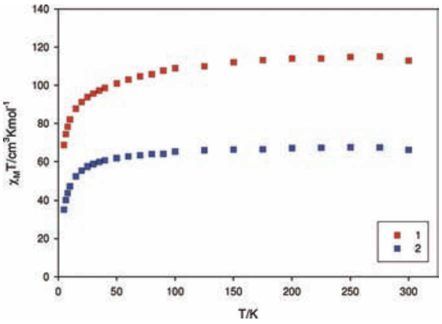

Figure 3. Plot of $\chi_M T$ vs T for complexes **1** (red squares) and **2** (blue squares).

The in-phase ($\chi_M{}'$) ac signal, shown as $\chi_M{}'T$ in Figure S2 in the SI, 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 cm^3 K mol^{-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 in the SI) 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.

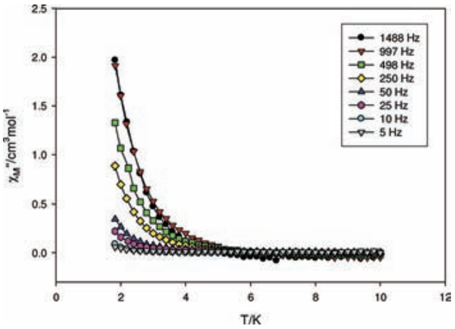

Figure 4. Out-of-phase (χ_M'') vs T ac susceptibility signals for **1** in a 3.5 G field oscillating at the indicated frequencies.

In order to gain any possible access into dual physical properties for this new family of nonanuclear 4f metal complexes, we decided to perform photoluminescence studies on the Eu$^{III}_9$ analogue (**3**). The solid-state emission spectrum of **3** (Figure 5) displays strong red photoluminescence, assigned to the characteristic $^5D_0 \rightarrow {}^7F_n$ (n = 0−4) transitions of Eu^{3+}. Specific assignments are as follows: $^5D_0 \rightarrow {}^7F_{0,1}$ (593 nm), $^5D_0 \rightarrow {}^7F_2$ (616 nm), $^5D_0 \rightarrow {}^7F_3$ (652 nm), and $^5D_0 \rightarrow {}^7F_4$ (697 nm).[8,11] Few emission peaks observed below 590 nm are likely due to transitions from the $^5D_1$ and $^5D_2$ excited states to the ^7F_n levels.[18] Note that the free organic ligand hmpH shows no emission at room temperature.

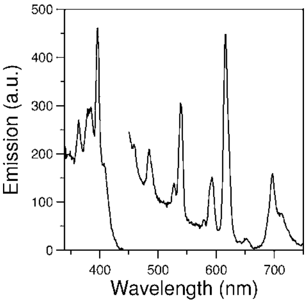

Figure 5. Excitation (at 396 nm) and emission spectra of solid-state complex **3** at room temperature.

In conclusion, a structurally unique family of nonanuclear Ln^{III} complexes of the hmpH 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 magnetization, as seen in SMMs. We are currently investigating the optical and magnetic properties of more members, i.e., the Tb$^{III}_9$ 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.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: thstama@chemistry.upatras.gr.

■ ACKNOWLEDGMENTS

Th.C.S. thanks the Royal Society of Chemistry Research Fund for chemical supply. This work was also supported by the National Science Foundation (Grant CHE-0910472 to G.C.).

■ REFERENCES

(1) (a) Öhrström, L.; Larsson, K. *Molecule-Based Materials*; Elsevier Publishers BV: Amsterdam, The Netherlands, 2005. (b) Gómez-Romero, P.; Sanchez, C. *Functional Hybrid Materials*; Wiley-VCH: Weinheim, Germany, 2004.

(2) Eliseeva, S. V.; Bünzli, J.-C. G. *New J. Chem.* **2011**, *35*, 1165.

(3) Gatteschi, D.; Sessoli, R.; Villain, J. *Molecular Nanomagnets*; Oxford University Press: New York, 2007.

(4) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048.

(5) (a) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *253*, 2328. (b) Lin, P.-H.; Burchell, T. J.; Ungur, L.; Chibotaru, L. F.; Wernsdorfer, W.; Murugesu, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 9489.

(6) (a) Coronado, E.; Day, P. *Chem. Rev.* **2004**, *104*, 5419. (b) Bogani, L.; Wernsdorfer, W. *Nat. Mater.* **2008**, *7*, 179.

(7) For example, see: Silver, J. In *Comprehensive Coordination Chemistry II*; McCleverty, J. A., Meyer, T. J., Eds.; Elsevier: Amsterdam, The Netherlands, 2004; Vol. 9, p 689.

(8) Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons: West Sussex, U.K., 2006.

(9) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201.

(10) Bekiari, V.; Thiakou, K. A.; Raptopoulou, C. P.; Perlepes, S. P.; Lianos, P. *J. Lumin.* **2008**, *128*, 481.

(11) (a) Magennis, S. W.; Parsons, S.; Pikramenou, Z. *Chem.—Eur. J.* **2002**, *8*, 6761. (b) Mancino, G.; Ferguson, A. J.; Beeby, A.; Long, N. J.; Jones, T. S. *J. Am. Chem. Soc.* **2005**, *127*, 524.

(12) Stamatatos, Th. C.; Christou, G. *Inorg. Chem.* **2009**, *48*, 3308 and references cited therein.

(13) Stamatatos, Th. C.; Nastopoulos, V.; Tasiopoulos, A. J.; Moushi, E.; Wernsdorfer, W.; Christou, G.; Perlepes, S. P. *Inorg. Chem.* **2008**, *47*, 10081 and references cited therein.

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

(15) (a) BVS calculations for inorganic O atoms in **1** gave values of 0.96 (O2), 1.02 (O3), 1.06 (O4), and 0.99 (O5), all consistent with an OH$^-$ assignment. (b) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(16) (a) Manseki, K.; Yanagida, S. *Chem. Commun.* **2007**, 1242. (b) Li, X.; Liu, Q.; Lin, J.; Li, Y.; Cao, R. *Inorg. Chem. Commun.* **2009**, *12*, 502. (c) Petit, S.; Baril-Robert, F.; Pilet, G.; Reber, C.; Luneau, D. *Dalton Trans.* **2009**, 6809. (d) Xu, G.; Wang, Z.-M.; He, Z.; Lu, Z.; Liao, C.-S.; Yan, C.-H. *Inorg. Chem.* **2002**, *41*, 6802. (e) Xu, H.-B.; Li, X.-F.; Yan, D. *Inorg. Chem. Commun.* **2008**, *11*, 1187.

(17) (a) Abbas, G.; Lan, Y.; Kostakis, G. E.; Wernsdorfer, W.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2010**, *49*, 8067 and references cited therein. (b) Lin, P.-H.; Korobkov, I.; Wernsdorfer, W.; Ungur, L.; Chibotaru, L. F.; Murugesu, M. *Eur. J. Inorg. Chem.* **2011**, 1535.

(18) Dejneka, M.; Snitzer, E.; Riman, R. E. *J. Lumin.* **1995**, *65*, 227.