Inorganic Chemistry
Communication
pubs.acs.org/IC

A Strongly Blue-Emitting Heptametallic [Dy^{III}_7] Centered-Octahedral Single-Molecule Magnet

Angelos B. Canaj,[†] Demetrios I. Tzimopoulos,[‡] Aggelos Philippidis,[∥] George E. Kostakis,[§] and Constantinos J. Milios*[,†]

[†]Department of Chemistry, The University of Crete, Voutes, 71003 Herakleion, Greece

[‡]Department of Chemistry, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

[§]Institute of Nanotechnology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

[∥]Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas (IESL-FORTH), P.O. Box 1385, GR 71110 Herakleion, Greece

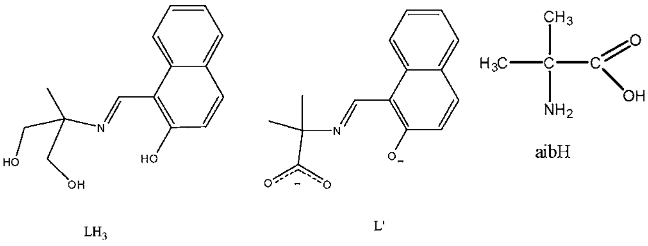
Supporting Information

ABSTRACT: The employment of 2-(β-naphthalideneamino)-2-(hydroxymethyl)-1-propanol and 2-aminoisobutyric acid in dysprosium chemistry has led to the isolation of a novel heptanuclear [Dy^{III}_7] cluster displaying single-molecule-magnetism behavior and blue-emitting properties.

The construction of lanthanide-based clusters has attracted a lot of research interest recently because of the intrinsic magnetic properties that such species display. This is true for both heterometallic 3d–4f and homometallic 4f clusters, which display enhanced magnetic properties.[1] Such properties are due to the magnitude of the spin as well as the spin–orbit-coupling-based magnetic anisotropy that the 4f species display, making them ideal candidates for single-molecule magnets, i.e., molecules that retain their magnetization once magnetized in the absence of an external magnetic field. Indeed, very recently, a [Dy^{III}_2] single-molecule magnet was reported with a record magnetic blocking temperature of 8.3 K and a spin-reversal barrier of 178 K.[2] Furthermore, lanthanide-based clusters find applications in optics as light-emitting diodes, optical fibers, lasers, optical amplifiers, near-IR-emitting materials, and sensory probes[3] because of the well-shielded electronic properties of the inner 4f orbitals from the ligands' crystal field.

We recently initiated a project toward the synthesis of "hybrid" molecular materials that would display both magnetic and optical properties[4] because such materials would be at the interface of magnetism and optics. Herein, we report the synthesis, structure, and magnetic and photoluminescent properties of a heptametallic [Dy^{III}_7] cluster using 2-(β-naphthalideneamino)-2-(hydroxymethyl)-1-propanol (LH_3) and 2-aminoisobutyric acid (aibH; Scheme 1).

Scheme 1. Structure of the Ligands Discussed in the Text



$Dy(NO_3)_2·6H_2O$ (440 mg, 1 mmol), LH_3 (259 mg, 1.0 mmol), aibH (103 mg, 1.0 mmol), and NEt_3 (3.0 mmol) were added in MeOH (10 mL), and the resulting mixture was transferred to a Teflon-lined autoclave and kept at 120 °C for 14 h. After slow cooling to room temperature, yellow crystals of [$Dy^{III}_7(OH)_2(L')_9(aib)$]·4MeOH (**1**·4MeOH) were obtained in ~35% yield and collected by filtration, washed with Et_2O, and dried in air (L′ = dianion of the Schiff base between naphthalene aldehyde and aibH).

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. Its core (Figure 1) consists of a distorted octahedral [Dy_6] cage, which encapsulates the seventh Dy^{III} atom in an off-center manner. The "central" Dy atom is located toward the upper apex of the octahedron at a distance of ~1.3 Å from the basal plane defined by four Dy^{III} atoms. The dimensions of the basal plane are ~3.8 and 6.0 Å, while the upper and lower corners of the octahedron are located at ~5.2 and 4.7 Å above and below the plane, respectively. The upper Dy^{III} center is connected to the four basal Dy^{III} centers, as well as to the "inner" Dy^{III} center, via four $\eta^2:\eta^1:\mu_3$-carboxylates from four $\eta^2_{\text{O-carboxylate}}:\eta^1:\eta^1:\eta^1:\mu_3$ dianionic L′ ligands (Figure 1, bottom, **A**), while the lower Dy^{III} is connected to the basal Dy^{III} centers through four $\eta^1:\eta^1:\mu$-carboxylates from three $\eta^2_{\text{O-hydroxyl}}:\eta^1:\eta^1:\eta^1:\mu_3$ dianionic L′ ligands (Figure 1, bottom, **B**) and one deprotonated $\eta^1:\eta^1:\eta^1:\mu$-*syn,anti*-aib^- ligand. The "inner" Dy^{III} center is further connected to the basal Dy atoms via (i) two μ_3-OH^- groups and (ii) two $\eta^2:\eta^1:\mu_3$-carboxylates from two $\eta^2_{\text{O-carboxylate}}:\eta^1:\eta^1:\eta^1:\mu_3$ dianionic L′ ligands. The Dy^{III} centers in **1** are eight- and seven-coordinate, adopting square-antiprismatic (Dy1 and Dy3), bicapped trigonal-prismatic (Dy2 and Dy6), and pentagonal-bipyramidal (Dy4, Dy5, and Dy7) geometry.

Variable-temperature direct-current (dc) magnetic susceptibility data were collected for **1** in the temperature range 5.0–

Received: May 18, 2012
Published: June 29, 2012

dx.doi.org/10.1021/ic301038q | Inorg. Chem. 2012, 51, 7451−7453

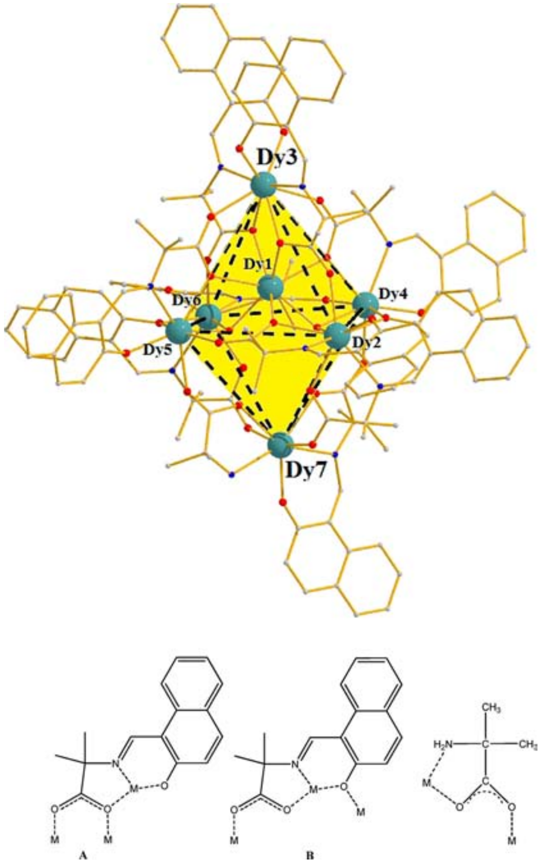


Figure 1. (Top) Molecular structure of complex **1** highlighting the $[Dy_7]$ off-center octahedral topology. Color code: Dy^{III}, gray-blue; O, red; N, blue; C, gold. Inset: Coordination modes of the ligands present in **1**. (Bottom) Coordination modes of the ligands present in **1**.

300 K under an applied field of 0.1 T and are plotted as $\chi_M T$ versus T in Figure 2. The room temperature $\chi_M T$ of 86.41 cm^3 K mol^{-1} is slightly lower than the calculated value of 99.2 cm^3 K mol^{-1} for seven noninteracting Dy^{III} ions ($S = {}^{5}/_{2}$, $L = 5$, $J = {}^{15}/_{2}$, $g_j = {}^{4}/_{3}$). Upon cooling, the $\chi_M T$ product decreases gradually to a minimum value of 63.84 cm^3 K mol^{-1} at 5 K, possibly indicative of weak antiferromagnetic interactions within the cluster and/or depopulation of the Dy^{III} Stark sublevels.[5] The former was further established by a Curie–Weiss analysis of the high-temperature (50–300 K) magnetic susceptibility data with $\theta = -10.3$ K (Figure 2, inset), suggesting the presence of weak antiferromagnetic interactions within the cluster, even though one may not exclude the effect of the Stark sublevels' depopulation on the θ value.

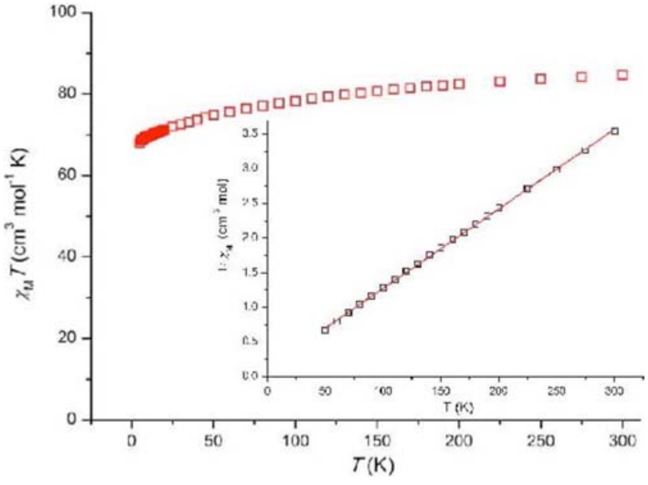


Figure 2. Plot of $\chi_M T$ versus T for complex **1** under an applied dc field of 1000 G; Curie–Weiss plot for **1** for the 50–300 K range (inset).

Alternating-current (ac) magnetic susceptibility measurements were performed on a polycrystalline sample of **1** in the 2.0–10 K range in a zero applied dc field and a 2.5 G ac field oscillating at 50–1500 Hz. The in-phase (χ_M', plotted as $\chi_M' T$ versus T; Figure 3, top) signal decreases upon decreasing temperature, indicating either the presence of low-lying excited states with larger S values than the ground state or the depopulation of the lanthanide Stark sublevels with decreasing temperature, in agreement with dc measurements. Frequency-dependent out-of-phase (χ_M'') signals are observed below ~3 K, but no peaks are seen (Figure 3, bottom), indicating the possibility of single-molecule-magnetism behavior.

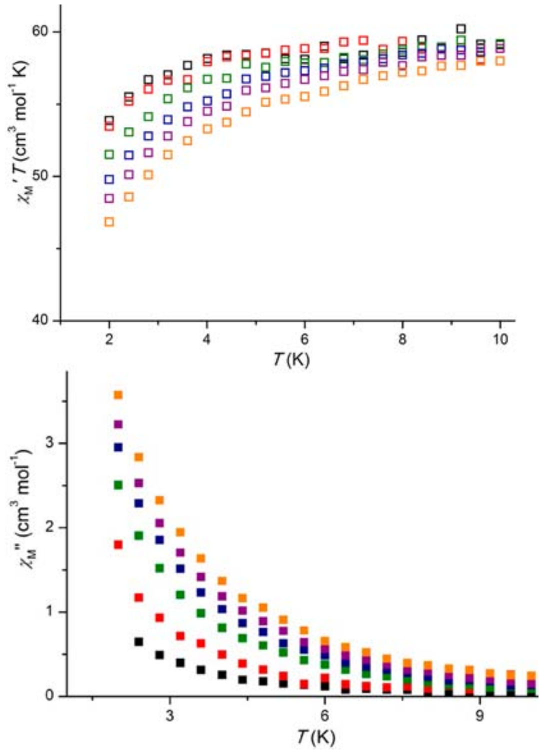


Figure 3. Plot of the in-phase ($\chi_M' T$, top) and out-of-phase (χ_M'', bottom) signals verss temperature for **1** in a 2.5 G field oscillating at 100 (black squares), 250 (red squares), 500 (green squares), 750 (blue squares), 1000 (purple squares), and 1500 (orange squares) Hz frequency.

Figure 4 shows the solid-state UV–vis spectra of complex **1** and LH_3, and it can be observed that the absorbance peaks of the free ligand are shifted when bound in the complex. More specifically, the peaks at 404 and 428 nm are "blue"-shifted at 382 and 400 nm, i.e., 22 and 28 nm, respectively.

Solid-state room temperature fluorescence emission spectra for LH_3 and complex **1** are given in Figure 5. Complex **1** strongly emits blue light (Figure 6) displaying "typical" emission bands for a Dy^{III} complex, one located at 467 nm and the other at 559 nm, corresponding to the two characteristic ${}^4F_{9/2} \rightarrow {}^6H_J$ ($J = {}^{15}/_{2}$, ${}^{13}/_{2}$) emission transitions

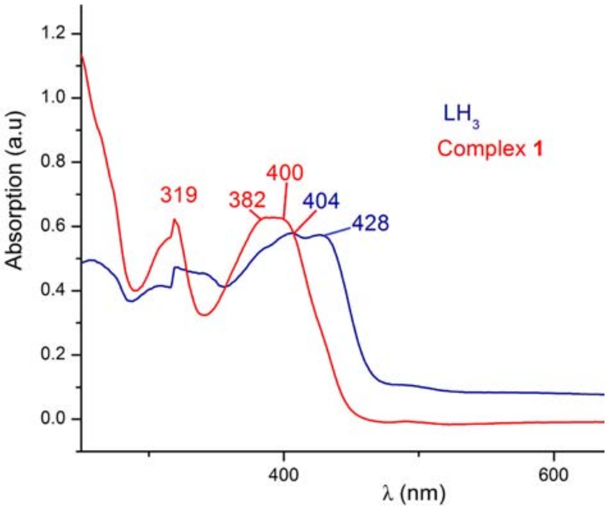


Figure 4. Solid-state UV−vis spectra of LH_3 and complex **1**.

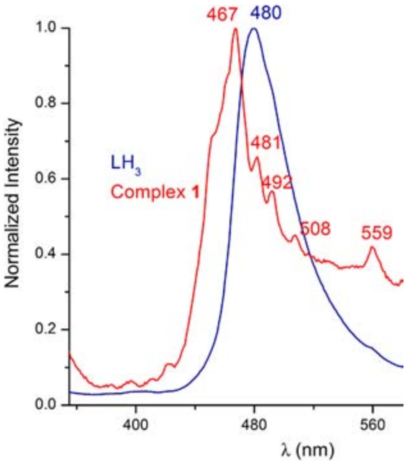


Figure 5. Solid-state room temperature emission spectra for **1** and LH_3 (excitation at 310 nm).

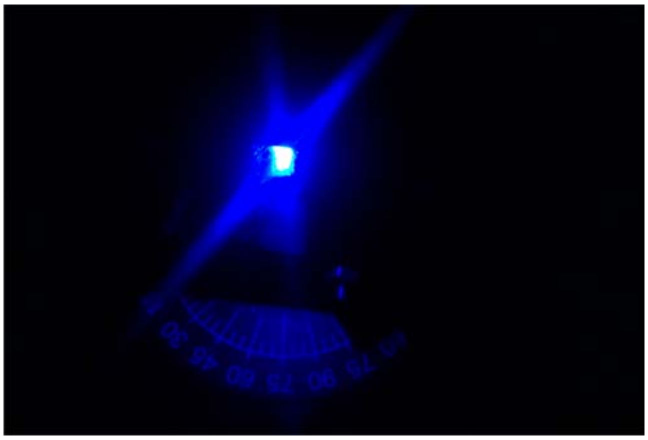


Figure 6. Photograph of complex **1** (in powder) under a UV lamp.

of Dy^{3+} ions.[6] Furthermore, it displays additional peaks at 481, 492, and 508 nm, which may be attributed to other transitions but are difficult to assign at this stage. Therefore, detailed lifetime experiments are underway in order to fully elucidate the origin of the emission properties of **1** and to investigate whether the luminescence is single-ion- or ligand-based.

In conclusion, the initial use of the ligand "blend" consisting of LH_3 and aibH has provided access to a heptametallic [Dy_7] strongly emitting single-molecule magnet. We have now isolated and characterized other lanthanide analogues of **1**, and a complete photophysical as well as magnetic study is underway. Furthermore, our next step is to investigate the photoluminescent properties of **1** under an applied magnetic field throughout the 5−300 K temperature range in order to investigate how the paramagnet-to-single-molecule magnet transition for **1** affects its photoluminescent properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: komil@chemistry.uoc.gr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

C.J.M. thanks The University of Crete (ELKE, Research Grant KA 3089) for funding.

■ REFERENCES

(1) Representative references and refs cited therein: (a) Sessoli, R.; Powell, A. K. *Coord. Chem. Rev.* **2009**, *253*, 2328. (b) Papatriantafyllopoulou, C.; Stamatatos, T.; Efthymiou, C. G.; Cunha-Silva, L.; Paz, F. A. A.; Perlepes, S. P.; Christou, G. *Inorg. Chem.* **2010**, *49*, 9743. (c) Efthymiou, C. G.; Stamatatos, T. C.; Papatriantafyllopoulou, C.; Tasiopoulos, A. J.; Wernsdorfer, W.; Perlepes, S. P.; Christou, G. *Inorg. Chem.* **2010**, *49*, 9739. (d) Mishra, A.; Wernsdorfer, W.; Parsons, S.; Christou, G.; Brechin, E. K. *Chem. Commun.* **2005**, 2086. (e) Mereacre, V.; Ako, A. M.; Clèrac, R.; Wernsdorfer, W.; Hewitt, I. J.; Anson, C. E.; Powell, A. K. *Chem.—Eur. J.* **2008**, *14*, 3577. (f) Abbas, G.; Lan, Y.; Mereacre, V.; Wernsdorfer, W.; Clèrac, R.; Buth, G.; Sougrati, M. T.; Grandjean, F.; Long, G. J.; Anson, C. E.; Powell, A. K. *Inorg. Chem.* **2009**, *48*, 9345. (g) Baskar, V.; Gopal, K.; Helliwell, M.; Tuna, F.; Wernsdorfer, W.; Winpenny, R. E. P. *Dalton Trans.* **2010**, *39*, 4747. (h) Chandrasekhar, V.; Pandian, B. M.; Boomishankar, R.; Steiner, A.; Vittal, J. J.; Houri, A.; Clèrac, R. *Inorg. Chem.* **2008**, *47*, 4918. (i) Rigaux, G.; Inglis, R.; Morrison, S.; Prescimone, A.; Cadiou, C.; Evangelisti, M.; Brechin, E. K. *Dalton Trans.* **2012**, DOI: 10.1039/c1dt10154d.

(2) Rinehart, J. D.; Fang, M.; Evans, W. J.; Long, J. R. *Nat. Chem.* **2011**, *3*, 539.

(3) For example, see: (a) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048. (b) Binnemans, K. *Chem. Rev.* **2009**, *109*, 4283.

(4) Orfanoudaki, M.; Tamiolakis, I.; Siczek, M.; Lis, T.; Armatas, G. S.; Pergantis, S. A.; Milios, C. J. *Dalton Trans.* **2011**, *40*, 4793.

(5) Luzon, J.; Bernot, K.; Hewitt, I. J.; Anson, C. E.; Powell, A. K.; Sessoli, R. *Phys. Rev. Lett.* **2008**, *100*, 247205.

(6) (a) Yan, B.; Zhou, B. *J. Photochem. Photobiol. A: Chem.* **2005**, *171*, 181. (b) Xu, B.; Yan, B. *Spectrochim. Acta A* **2007**, *66*, 236. (c) Yan, B.; Xie, Q. *J. Coord. Chem.* **2003**, *56*, 1285. (d) Yan, B.; Song, Y. S. *J. Fluoresc.* **2004**, *14*, 289.