A new family of Ln₇ clusters with an ideal $D_{3h}$ metal-centered trigonal prismatic geometry, and SMM and photoluminescence behaviors†

Eleni C. Mazarakioti, Katye M. Poole, Luis Cunha-Silva, George Christou and Theocaris C. Stamatatos*

The first use of the flexible Schiff base ligand N-salicylidene-2-amino cyclohexanol in metal cluster chemistry has afforded a new family of Ln₇ clusters with ideal $D_{3h}$ point group symmetry and metal-centered trigonal prismatic topology; solid-state and solution studies revealed SMM and photoluminescence behaviors.

One of the current major challenges in molecular nanoscience is the synthesis of new polynuclear metal complexes (clusters) exhibiting more than one physical property within the same entity. Of significant importance is the combination of their magnetic properties with one or more additional properties, such as conductivity, chirality and luminescence. This is due to the fact that such multifunctional (or ‘hybrid’) molecular magnetic materials can find potential applications in the fields of molecular electronics and spintronics. Molecular electronics is undoubtedly an emerging area of research which is based on the construction and fabrication of molecular species with intriguing magnetic properties, pronounced stability, robustness, and capability to be deposited on electrical conducting surfaces. Such deposition of ‘hybrid’ molecular materials is actually one of the ultimate goals, but at the same time one of the most difficult challenges for synthetic chemists to unravel. It primarily requires the molecules to retain their structures and properties in solution, and subsequently to allow anchoring of the peripheral sites.

The unique electronic and physical properties of the 4f-metal ions render polynuclear lanthanide(m) metal clusters as excellent candidates for the construction of dual-acting molecular species. In particular, 4f-metal clusters have shown a remarkable ability to act as single-molecule magnets (SMMs) when the f-block ions are highly anisotropic and carry a significant spin (i.e., Dy, Tb, Ho, Er). SMMs derive their properties from the combination of a large magnetic moment in the ground state with a large magnetoanisotropy originating from the substantial, unquenched orbital angular momenta. An appreciable number of 4f-metal clusters with various interesting structural topologies and SMM behaviors have been reported to date, from linear and linked-triangular to more complex ones such as cubanes, trigonal prismatic and disc-like.

Polynuclear 4f-metal complexes have also shown intense, sharp and long-lived emissions, which make these compounds particularly interesting for a variety of optical uses such as display devices and luminescent sensors. This is also applied to the ‘magnetic’ Tb and Dy-based clusters which show photoluminescence properties with metal-centered emissions at different regions of the visible spectrum. Due to the forbidden electronic transitions between the 4f orbitals on symmetry grounds, which lead to poor absorption cross-sections, population of the emitting levels of the Ln ion is best achieved by employing light-harvesting ligands.

It therefore becomes apparent that one of the most important factors for the construction of new 4f-metal clusters with dual physical properties, unprecedented topologies and possible structural integrity in solution is the choice of the primary organic bridging/chelating ligand. This often dictates not only the topology and the number of paramagnetic metal ions present, but also the nature of the intramolecular magnetic exchange interactions and the efficiency of metal ion’s sensitization by the intramolecular energy transfer from the ligand’s triplet state (‘antenna’ effect). A family of such potentially multi-acting organic ligands is Schiff bases, and particularly the ones which are based on the scaffold of N-salicylidene-o-aminophenol (saphH₂, Scheme 1). The latter is a well-explored precursor in coordination chemistry because of the ability of the relatively soft N atom and the two hard, upon deprotonation, O atoms to bind to a single or multiple metal centers. However, the employment of saphH₂ ligand in 4f-metal chem-
chemistry has been limited to mono- and dinuclear compounds. In the present study, we have decided to slightly “tweak” the o-aminophenol moiety of saphH₂ and replace the bulky phenyl ring with the more flexible cyclohexane functionality. The latter could, in principle, differentiate the electronic and steric properties of the resulting precursor, and subsequently lead to the formation of new polynuclear 4f-metal complexes with unprecedented topologies and interesting physical properties. We herein present the use for a first time of N-salicilidene-2-aminocyclohexanol (sachH₂) discussed in the text.

The Schiff base ligand sachH₂ has been prepared in 85% yield by the condensation of 2-aminocyclohexanol (cis- and trans-mixture) with salicylaldehyde in a 1:1 molar ratio in refluxing absolute methanol. The resulting yellow microcrystalline solid was dissolved in MeCN and circular dichroism studies confirmed its racemic mixture, as was expected owing to the cis-trans-mixture of the starting precursor. The reaction of Ln(CO₃)₃·6H₂O (Ln = Gd, Tb and Dy), sachH₂, and Me₄NOH·5H₂O in a 1:3:3 molar ratio in MeOH gave deep yellow solutions that upon slow evaporation at room temperature afforded yellowish crystals of [Ln₇(OH)₆(CO₃)₃(sach)₃(OH)₆(MeOH)₆] [Ln = Gd (1); Tb (2); Dy (3)] in 25–35% isolated yields. The CO₃²⁻ ions are presumably derived from the fixation of atmospheric CO₂ during aerobic reactions. The pivotal role of carbonates as multidentate bridging ligands in the synthesis of 4f- and 3d/4f-metal clusters with unprecedented topologies has been recently discussed by Brechin et al. The formulas of the compounds are based on metric parameters, charge balance considerations and O BVS calculations; the latter confirmed the assignment of the μ₃-bridging groups as OH⁻ ions (BVS 1.10–1.12). As a result of the calculations, the formulas of 1–3 initially appeared to be [Ln₂(OH)₆(CO₃)₃(sach)₃(MeOH)₆]³⁺, their trionionic nature disagreeing with the absence of three countercations in the crystal lattice. To maintain the neutral charge of each cluster, it is very likely that the crystallographic C₃ axis of the molecule is masking the presence of three protons statically disordered between three sachH⁻/sachH⁺ pairs, or even among other groups (i.e., CO₃²⁻/HCO₃⁻).

Complexes 1–3 are isomorphous and differ only in the number of lattice MeOH solvate molecules; thus, only the structure of representative complex 1 will be described in detail. Complex 1·11MeOH crystallizes in the high-symmetry hexagonal space group P6₃/m and comprises seven GdIII ions linked through six μ₁-OH⁻ and three μ₁:η¹:η²:μ₃-CO₃²⁻ bridges to form an ideal metal-centered trigonal prism with a perfect D₃h point group symmetry (Fig. 1a). Such a metal topology has never been seen before in homometallic 4f-metal cluster chemistry, although heptanuclear LnIII compounds with cage-disc-like and centered-octahedral topologies have been reported. Of interest is also the unusual η¹:η²:μ₃-binding mode of the carbonate group which has been previously seen only in complex [Er₃(CO₃)(MQ)₇] (MQ⁻ = 8-quinolindinolate). The compound has therefore an overall [Gd₂(μ₁-OH)₆-(μ₁-CO₃)]⁺core (Fig. 1b), with peripheral ligation provided by six N,O,O-tridentate chelating sach²⁻/sachH⁻ ligands and six terminally-bound MeOH molecules, each coordinated to one of the external GdIII ions.

The six external, symmetry equivalent GdIII ions (Gd1 and its symmetry-related partners) constitute the two trigonal faces. The two parallel trigonal faces are ideal equilateral triangles with Gd–Gd distances of 4.495 Å and Gd–Gd–Gd angles of 60°. Two GdIII ions from each trigonal face make up three ideal and symmetry-related Gd₄ rectangles with Gd–Gd distances of 4.495 and 5.093 Å, and Gd–Gd–Gd–Gd angles of 90°; these units constitute the three tetragonal faces of the prism (Fig. 1c). The crystallographically unique Gd2 atom is located exactly at the center of the prism (Gd1···Gd2 3.636 Å). All the external Gd atoms are eight-coordinate with slightly distorted triangular dodecahedral geometries whereas the central Gd2 is nine-coordinate with a perfect spherical tricapped trigonal prismatic geometry (Fig. S1†). The Gd₂ molecules, as well as the other members of this family of Lnₙ clusters, are well-isolated in the crystal, with the shortest Gd···Gd intermolecular separation being 12.767 Å.

Variable-temperature direct current (dc) 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. The obtained data for all studied compounds are shown as $\chi_M T$ vs. $T$ plots in Fig. 2. The experimental $\chi_M T$ values at room temperature are in good agreement with the theoretical ones (55.13 cm$^3$ K mol$^{-1}$ for 1; 82.74 cm$^3$ K mol$^{-1}$ for 2; 99.19 cm$^3$ K mol$^{-1}$ for 3) for seven non-interacting Gd$^{III}$ ($S_{7/2}$, $L = 7/2$, $S = 0$, $g = 2$), Tb$^{III}$ ($F_6$, $S = 3$, $L = 3$, $g = 3/2$) and Dy$^{III}$ ($H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$). For the isotropic Gd$^{III}$ (1), the $\chi_M T$ product remains almost constant at a value of $\sim$54 cm$^3$ K mol$^{-1}$ from 300 K to $\sim$50 K and then steadily decreases to a minimum value of 40.82 cm$^3$ K mol$^{-1}$ at 5.0 K indicating the presence of weak intramolecular antiferromagnetic exchange interactions between the seven Gd$^{III}$ centers and/or zero-field splitting. For the anisotropic Tb$^{III}$ (2) and Dy$^{III}$ (3) complexes, the thermal evolution of the magnetic susceptibility is similar, in which the $\chi_M T$ product remains essentially constant at a value of $\sim$81 and $\sim$92 cm$^3$ K mol$^{-1}$ from 300 K to $\sim$140 K and then rapidly decreases to a minimum value of 55.63 and 73.79 cm$^3$ K mol$^{-1}$ at 5.0 K, respectively. Such low temperature decrease of the $\chi_M T$ product is mainly due to depopulation of the excited Stark sublevels of the Tb$^{III}$ and Dy$^{III}$ ions and the weak antiferromagnetic interactions between the metal centers which cannot be quantified due to the strong orbital momentum.$^{7,8}$

The field dependence of magnetization measurements at low temperatures show all the expected characteristics for polynuclear, weakly coupled Ln(III) clusters. Briefly, the lack of saturation in magnetization for complexes 2 and 3 (Fig. S2†) indicates the presence of magnetic anisotropy and/or population of low-lying excited states. In the case of 1, the magnetization reaches a saturation of 48.9$\mu_B$ at the highest fields (Fig. S3†), which is in excellent agreement with the expected value of 49$\mu_B$ for seven non-coupled Gd$^{III}$ ions. The slight deviation of $M$ vs. $H$ for 1 at low temperatures and small magnetic fields is due to the population of low-lying excited states with $S$ larger than the ground state.

Alternating current (ac) magnetic susceptibility studies have been also carried out in order to investigate the magnetization dynamics of the anisotropic Tb$^{III}$ and Dy$^{III}$ clusters under a zero dc magnetic field. Complex 3 shows strong frequency-dependent out-of-phase $\chi_M$ tails of signals at temperatures below $\sim$10 K (Fig. 3), indicative of the slow magnetization relaxation of an SMM with a small energy barrier for magnetization reversal. This is most likely due to the fast tunneling relaxations from the excited Stark sublevels of the Tb$^{III}$ and Dy$^{III}$ ions, which can be assigned to the singly charged anion [Gd$_{7}$(OH)$_{6}$(CO$_{3}$)$_{3}$(sach)$_{4}$(sachH)$_{2}$(MeCN)$_{3}$]$^{-}$, with the volatile coordinating MeOH molecules of the solid-state cluster being partially replaced by three terminal MeCN groups (Fig. S7†).$^{21}$ Isotopic pattern of the molecular ion was used to justify further the compositional assignment. Taking into advantage the characteristic isotopic patterns of molecules containing 4f-elements, a good agreement was observed between the experimentally determined isotopic pattern for 1

Fig. 2 Plots of $\chi_M T$ vs. $T$ for complexes 1–3.

Fig. 3 The out-of-phase ($\chi''$) vs. $T$ ac susceptibility signals for 3 in a 3.5 G field oscillating at the indicated frequencies.

Considering a single relaxation process, the least-squares fit of the experimental data (Fig. S5†) gave an energy barrier of $\sim$1.2 cm$^{-1}$ ($\sim$1.7 K) and a relaxation time of $0.2 \times 10^{-6}$ s which is consistent with the expected $\tau_0$ values for a fast relaxing SMM.

The solution characterization of the free ligand sachH$_{2}$ and complexes 1–3 included UV/Vis, electrospray mass spectrometry (ES-MS) and excitation/emission studies in low-concentration ($\sim$10$^{-5}$ M) MeCN solutions. Such studies have been performed in order to probe the integrity of the structures of 1–3 in solution and elucidate any possible photophysical properties. The absorption spectrum of sachH$_{2}$ exhibits three bands located at 215, 255 and 314 nm, which are characteristic of Schiff-based complexes,$^{22}$ and can be mainly assigned to $\pi \rightarrow \pi^*$ transitions. In all complexes 1–3 these bands have been shifted to slightly higher wavenumbers (222, 263 and 340 nm, respectively) consistent with coordination of the ligand to the metal centers (Fig. S6†).

The negative ion electrospray mass spectrum (ES-MS) of the representative Gd$_{7}$ compound 1 in MeCN shows a strong intensity peak at 2811 m/z which can be assigned to the singly charged anion [Gd$_{7}$(OH)$_{6}$(CO$_{3}$)$_{3}$(sach)$_{4}$(sachH)$_{2}$(MeCN)$_{3}$]$^{-}$, with the volatile coordinating MeOH molecules of the solid-state cluster being partially replaced by three terminal MeCN groups (Fig. S7†).$^{21}$ Isotopic pattern of the molecular ion was used to justify further the compositional assignment. Taking into advantage the characteristic isotopic patterns of molecules containing 4f-elements, a good agreement was observed between the experimentally determined isotopic pattern for 1
and its theoretical one (Fig. S8†). Complexes 2 and 3 showed similar compositions allowing us to confirm the structural integrity of 1–3 in MeCN.

In light of the stability of complexes 1–3 in MeCN, we decided to perform photophysical studies in solution. The free sachH2 ligand shows a broad blue-shifted, fluorescence emission at 466 nm upon maximum excitation at 310 nm (Fig. S9†). The observed emission band is not concentration-dependent and is typical for organic molecules containing aromatic fragments.25 As expected, the Gd7 complex did not produce any metal-centered emission since the emissive state of Gd3+ is too high to accept energy transfer. Indeed, this state (6P7/2) lies at >30 000 cm⁻¹, while that of Tb3+ (5D4) is located at ~20 500 cm⁻¹.11,25 Thus, upon excitation at 340 nm, the Tb7 complex 2 exhibits a strong green luminescence emission with sharp and narrow bands (Fig. 4, top) which can be ascribed to the characteristic 5D4 → 7F(1/2; 5/2) transitions of Tb3+.26 This means that the sachH2 ligand promotes an efficient energy transfer to the Tb3+ ions and can be considered as a prominent “antenna”, although some ligand fluorescence is still observed as a broad band at ~430 nm which is due to back-energy transfer from Tb3+.27 In case of Dy7 complex 3, a strong blue emission is clearly observed upon maximum excitation at 340 nm (Fig. 4, bottom). The broad band at ~438 nm is assigned to a strong energy transfer from DyIII to the ligand’s excited state(s) leading to a ligand fluorescence, whereas the shoulder at 474 nm and the narrow band at 575 nm are ascribed to the characteristic 4F9/2 → 6H15/2 and 4F9/2 → 6H13/2 emission transitions of DyIII ions.28

Conclusions

We have shown herein that flexible analogues of the well-known bulky ligand N-salicylidene-o-aminophenol, such as that of N-salicylidene-2-amino-cyclohexanol, can lead to high-nuclearity and high-symmetry 4f-metal clusters with unprecedented topologies and interesting magneto-optical properties. The reported heptanuclear compounds are very rare examples of polynuclear 4f-metal species which retain their structural conformations in solution. This can potentially allow us to deposit the reported materials on a variety of surfaces, a perspective which is related to the field of molecular electronics. We are currently trying to (i) modify sachH2 ligand by replacing the para-H atom with an anchoring -SR site, and (ii) synthesize the pure cis- and trans-sachH2 ligands and subsequently isolate and use the corresponding enantiomers in an attempt to prepare chiral SMMs.

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Notes and references

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