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A new family of Ln_7 clusters with an ideal D_{3h} metal-centered trigonal prismatic geometry, and SMM and photoluminescence behaviors†

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The first use of the flexible Schiff base ligand *N*-salicylidene-2-aminocyclohexanol in metal cluster chemistry has afforded a new family of Ln_7 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,[1] chirality[2] and luminescence.[3] 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.[4] 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.[5] 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.[6] 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(III) 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)[7] when the f-block ions are highly anisotropic and carry a significant spin (*i.e.*, Dy^{III}, Tb^{III}, Ho^{III}, Er^{III}). 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.[7,8] An appreciable number of 4f-metal clusters with various interesting structural topologies and SMM behaviors have been reported to date, from linear[9a] and linked-triangular[9b] to more complex ones such as cubanes,[9c] trigonal prismatic[9d] and disc-like.[9e]

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.[10] This is also applied to the 'magnetic' Tb^{III}- and Dy^{III}-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^{III} ion is best achieved by employing light-harvesting ligands.[11]

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 ($saphH_2$, 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 $saphH_2$ ligand in 4f-metal chem-

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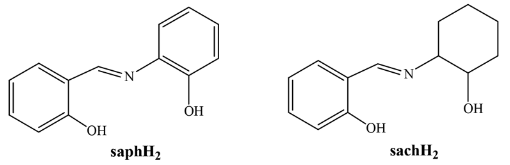

Scheme 1 Structural formulas and abbreviations of the ligands *N*-salicylidene-*o*-aminophenol ($saphH_2$) and *N*-salicylidene-2-aminocyclohexanol ($sachH_2$) discussed in the text.

istry has been limited to mono- and dinuclear compounds.[12] In the present study, we have decided to slightly "tweak" the *o*-aminophenol moiety of $saphH_2$ 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*-salicylidene-2-aminocyclohexanol ($sachH_2$, Scheme 1) in metal cluster chemistry, and particularly the synthesis, structures, and solid-state and solution characterization of a new family of heptanuclear Ln^{III} clusters with an ideal metal-centered trigonal prismatic topology.

The Schiff base ligand $sachH_2$ 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 $Ln(ClO_4)_3{\cdot}6H_2O$ (Ln = Gd, Tb and Dy), $sachH_2$, and $Me_4NOH{\cdot}5H_2O$ in a 1 : 3 : 3 molar ratio in MeOH gave deep yellow solutions that upon slow evaporation at room temperature afforded yellowish crystals of $[Ln_7(OH)_6(CO_3)_3(sach)_3(sachH)_3(MeOH)_6]$ (Ln = Gd (**1**); Tb (**2**); Dy (**3**)) in 25–35% isolated yields.† The CO_3^{2-} ions are presumably derived from the fixation of atmospheric CO_2 during aerobic reactions.[13] 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.*[14] The formulas of the compounds are based on metric parameters, charge balance considerations and O BVS calculations;[15] the latter confirmed the assignment of the μ_3-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 $[Ln_7(OH)_6(CO_3)_3(sach)_6(MeOH)_6]^{3-}$, their trianionic 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 C_3 axis of the molecule is masking the presence of three protons statically disordered between three $sach^{2-}/sachH^-$ pairs, or even among other groups (*i.e.*, CO_3^{2-}/HCO_3^-).[16]

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 $P6_3/m$ and comprises seven Gd^{III} ions linked through six μ_3-OH^- and three $\eta^1{:}\eta^1{:}\eta^3{:}\mu_3$-$CO_3^{2-}$ bridges to form an ideal metal-centered trigonal prism with a perfect D_{3h} point group symmetry (Fig. 1a). Such a metal topology has never been seen before in homometallic 4f-metal cluster chemistry, although heptanuclear Ln^{III} compounds with cage-/disc-like[17] and centered-octahedral[18] topologies have been reported. Of interest is also the unusual $\eta^1{:}\eta^1{:}\eta^3{:}\mu_3$-binding mode of the carbonate group which has been previously seen only in complex $[Er_3(CO_3)(MQ)_7]$ (MQ^- = 8-quinaldinolate).[19] The compound has therefore an overall $[Gd_7(\mu_3\text{-}OH)_6(\mu_3\text{-}CO_3)_3]^{9+}$ core (Fig. 1b), with peripheral ligation provided by six *N*,*O*,*O*-tridentate chelating $sach^{2-}/sachH^-$ ligands and six terminally-bound MeOH molecules, each coordinated to one of the external Gd^{III} ions.

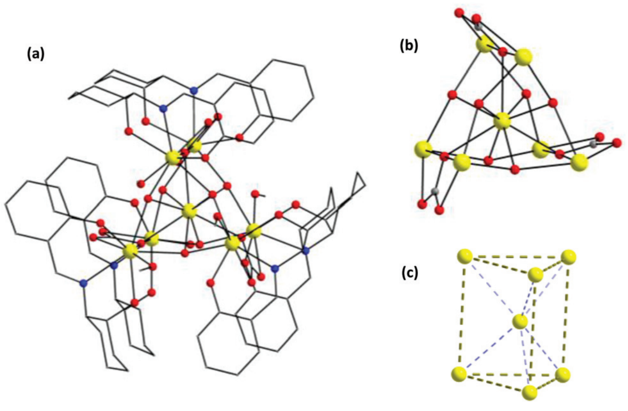

Fig. 1 (a) Molecular structure of complex **1**, (b) the $[Gd_7(\mu_3\text{-}OH)_6(\mu_3\text{-}CO_3)_3]^{9+}$ complete core, and (c) a different view of the ideal metal-centered trigonal prismatic topology. H-atoms and lattice solvate molecules have been omitted for clarity. Green and blue dashed lines indicate the trigonal and tetragonal faces of the prism and their connectivity with the central metal atom, respectively. Color scheme: Gd^{III} yellow, O red, N blue, C gray.

The six external, symmetry equivalent Gd^{III} 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 Gd^{III} ions from each trigonal face make up three ideal and symmetry-related Gd_4 rectangles with Gd⋯Gd distances of 4.495 and 5.093 Å, and 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 Gd_7 molecules, as well as the other members of this family of Ln_7 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

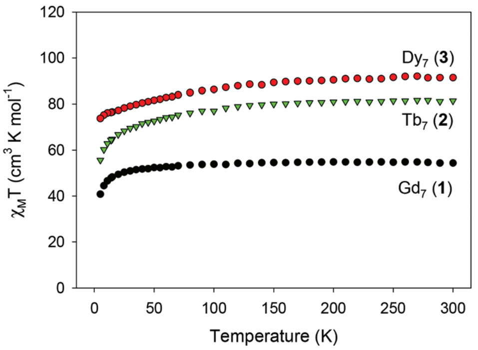

Fig. 2 Plots of $\chi_M T$ *vs.* *T* for complexes **1–3**.

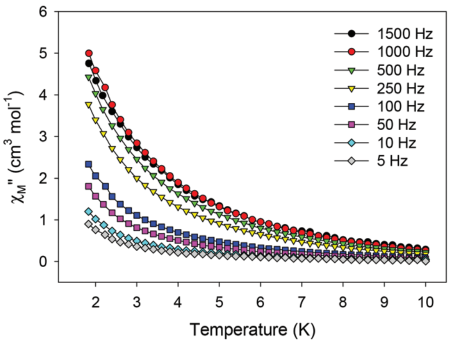

Fig. 3 The out-of-phase (χ''_M) *vs.* *T* ac susceptibility signals for **3** in a 3.5 G field oscillating at the indicated frequencies.

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} ($^8S_{7/2}$, $S = 7/2$, $L = 0$, $g = 2$), Tb^{III} ($^7F_6$, $S = 3$, $L = 3$, $g = 3/2$) and Dy^{III} ($^6H_{15/2}$, $S = 5/2$, $L = 5$, $g = 4/3$) ions. For the isotropic Gd$^{III}{}_7$ (**1**), the $\chi_M T$ product remains almost constant at a value of ~54 cm^3 K mol^{-1} from 300 K to ~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$^{III}{}_7$ (**2**) and Dy$^{III}{}_7$ (**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 ~81 and ~92 cm^3 K mol^{-1} from 300 K to ~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 48.9μ_B at the highest fields (Fig. S3†), which is in excellent agreement with the expected value of 49μ_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$^{III}{}_7$ and Dy$^{III}{}_7$ clusters under a zero dc magnetic field. Complex **3** shows strong frequency-dependent out-of-phase χ''_M tails of signals at temperatures below ~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 which is usually observed in high-nuclearity and high-symmetry Dy^{III} SMMs,[9e,20] and mainly originates from single-ion effects of the individual Dy^{III} Kramer ions.[7,8] There were no out-of-phase ac signals down to 1.8 K for the Tb$^{III}{}_7$ analogue (Fig. S4†). In an attempt to quantify the energy barrier and relaxation time for **3**, and given the absence of χ'' peak maxima, we decided to apply the below equation recently developed by Bartolomé *et al.*[21]

$$\ln(\chi''/\chi') = \ln(\omega\tau_0) + E_a/k_B T$$

Considering a single relaxation process, the least-squares fits of the experimental data (Fig. S5†) gave an energy barrier of ~1.2 cm^{-1} (~1.7 K) and a relaxation time of 0.2 × 10^{-6} s which is consistent with the expected τ_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 (~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 π→π* transitions. In all complexes **1–3** these bands have been shifted to slightly higher wavenumbers (222, 265 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†).[23] 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†).[24] 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 sachH_2 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 Gd_7 complex did not produce any metal-centered emission since the emissive state of Gd^{3+} is too high to accept energy transfer. Indeed, this state ($^6P_{7/2}$) lies at >30 000 cm^{-1}, while that of Tb^{3+} ($^5D_4$) is located at ~20 500 cm^{-1}.[11,25] Thus, upon excitation at 340 nm, the Tb_7 complex **2** exhibits a strong green luminescence emission with sharp and narrow bands (Fig. 4, top) which can be ascribed to the characteristic $^5D_4 \rightarrow {}^7F_J$ (J = 3; 622 nm, J = 4; 583 nm, J = 5; 546 nm, J = 6; 490 nm) transitions of Tb^{III}.[26] This means that the sachH_2 ligand promotes an efficient energy transfer to the Tb^{III} 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 Tb^{III}.[27] In case of Dy_7 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 Dy^{III} 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 $^4F_{9/2} \rightarrow {}^6H_{15/2}$ and $^4F_{9/2} \rightarrow {}^6H_{13/2}$ emission transitions of Dy^{III} ions.[28]

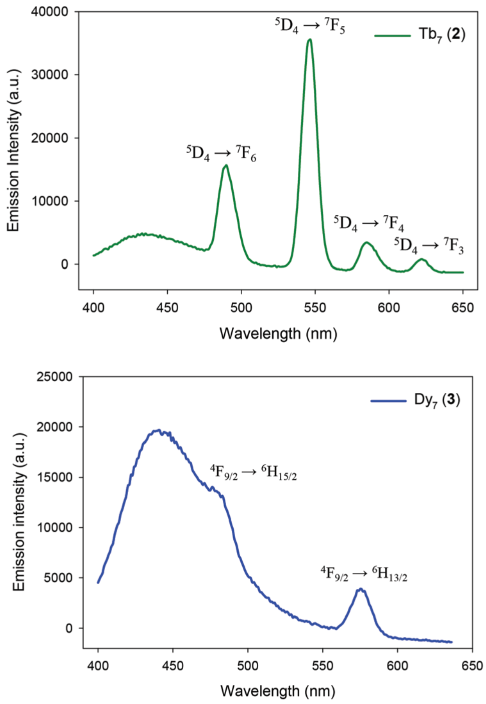

Fig. 4 Room temperature emission spectra for **2** (top) and **3** (bottom) in MeCN (10^{-5} M). The excitation wavelength was 340 nm in both cases.

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-aminocyclohexanol, 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 sachH_2 ligand by replacing the *para*-H atom with an anchoring -SR site, and (ii) synthesize the pure *cis*- and *trans*-sachH_2 ligands and subsequently isolate and use the corresponding enantiomers in an attempt to prepare chiral SMMs.

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