Series of dinuclear and tetranuclear lanthanide clusters encapsulated by salen-type and β-diketionate ligands: single-molecule magnet and fluorescence properties†

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Three dinuclear [Ln2H2OL12(acac)2]·solvent (1, Ln = Gd, solvent = 2CH2Cl2; 2, Ln = Tb, no solvent; 3, Ln = Er, solvent = {C2H5}2O), and two tetranuclear lanthanide clusters [Ln4(μ3-OH)2L2(acac)6]·2(solvent) (4, Ln = Tb, solvent = CH3OH; 5, Ln = Dy, solvent = CH3CN) were characterized in terms of structure, fluorescence and magnetism. The dinuclear lanthanide complexes were constructed by a rigid salen-type ligand H2L1 = N,N′-bis(salicylidene)-o-phenylenediamine and β-diketonate (acac = acetylacetonate) ligands, while the tetranuclear clusters were formed from the flexible ligand H2L2 = N,N′-bis(salicylidene)-1,2-ethanediame. Crystal structure analysis indicates that the rigid ligand favors the double-decker sandwich structure (Ln2L1), in which the two lanthanide ions have different coordination numbers and geometry, while the more flexible ligand (H2L2) leads to planar tetranuclear clusters. The relationship between their respective magnetic anisotropy and ligand-field geometries and their fluorescence properties was investigated. The Dy and Tb-containing clusters exhibit typical visible fluorescence properties, and single-molecule magnet behavior is seen in complex 5.

Introduction

Single-molecule magnets (SMMs) exhibiting slow magnetic relaxation have recently attracted much attention due to their potential for use in high-density information storage, molecular spintronics, quantum computing devices and magnetic refrigeration.1–4 Among them, lanthanide SMMs continue to flourish in these fields due to the presence of the large spin ground state (S,T) and Ising-type magnetoanisotropy (D) in these systems.1,5 Lanthanide(III) ions such as Tb(III), Dy(III), or Ho(III) with a large amount of spin and spin orbital coupling are difficulty in promoting magnetic interactions between the bridging ligand orbital and the 4f orbital of the lanthanide ions. Ligands with orbitals able to overlap the 4f orbitals of the lanthanide ions are preferred for constructing pure lanthanide-based SMMs.6,11 On the other hand, the orbital energy levels of these ligands could match well with the lowest excited state level of lanthanide(III) ions and absorb light in the UV region and transfer the energy via an “antenna effect”, finally resulting in an enhancement of fluorescence emission. Besides the energy matching, a multidentate ligand that can encapsulate the lanthanide(III) ions, protecting them from vibration coupling which may quench fluorescence and keeping them as discrete molecules avoiding intermolecular interaction, is crucial in construction of these fluorescent and magnetic molecule materials.11–13 Thus, a well-selected ligand is one of the key factors in building multifunctional lanthanide-based materials.

Among these ligands, polyalcohols, carboxylic acid derivatives, oximate derivatives and Schiff-base ligands were successfully used in the isolation of high-energy barrier SMMs.14 Especially, Schiff-base and β-diketone ligands have been successfully used in the construction of magnetic and fluorescent materials,8,15,16 while research into bifunctional materials both with SMM and luminescent properties is scarce.17 It is worth noting that the emission spectrum with fine splitting could serve as a means of accessing the magnetism of the lanthanide-based SMMs and these pioneering works attempt to correlate the magnetic and emission properties.
Recently, we successfully developed a useful synthetic strategy involving both salen-type and β-diketonate ligands to isolate tetranuclear planar lanthanide cluster complexes.\(^1\) In these clusters, the salen-type ligand plays a critical role in determining the coordination geometry of lanthanide ions and the β-diketonate ligand mainly plays the role of pushing the lanthanide ions into the \(\text{N}_2\text{O}_2\) coordination pocket of the salen-type ligands, and obviously the steric hindrance of the ligand dominates the formation of this type of lanthanide clusters. In our more recent work, when the rigid salen-type ligands are used, a dinuclear dysprosium complex could be obtained and magnetic analysis demonstrated that it behaves as a Dy\(_2\) SMM with a distinct coordination environment and leads to two unique relaxation modes due to the single-ion type relaxation mechanism. Even the Yb\(_2\) analogue displays a field-induced SMM behavior and as well near-infrared emission was observed.\(^1\) In order to confirm this synthetic strategy and tune the magnetic properties of these SMMs, by changing the coordination ligands, two new salen-type ligands with rigid and flexible backbones are used (Scheme 1). In the present work, three dinuclear lanthanide analogues Gd\(_{\text{III}}\left(\text{H}_2\text{L}_2\right)\) (1), Tb\(_{\text{III}}\left(\text{H}_2\text{L}_2\right)\) (2) and Er\(_{\text{III}}\left(\text{H}_2\text{L}_2\right)\) from the rigid salen-type ligand (H\(_2\text{L}_1\)) and two planar tetranuclear Tb\(_{\text{III}}\left(\text{H}_2\text{L}_2\right)\) (4) and Dy\(_{\text{III}}\left(\text{H}_2\text{L}_2\right)\) (5) from a flexible salen-type ligand (H\(_2\text{L}_2\)) were successfully isolated to illustrate this synthetic strategy. Complex 5 displays SMM behavior and metal-centered emissions. Herein, we report their preparation, structural characterization, and magnetic and fluorescence properties.

**Results and discussion**

Complexes 1–3 were prepared by refluxing H\(_2\text{L}_1\) \((\text{N},\text{N}’\text{-bis(salicilidene)-o-phenylenediamine})\) with solid Ln(acac),H\(_2\text{O}\) as the metal precursor in dichloromethane (CH\(_2\text{Cl}_2\)) solution. In order to obtain crystals of clusters 4 and 5 constructed with H\(_2\text{L}_2\), which is similar to our recently reported ligand (H\(_2\text{L}_1\)),\(^1\) the same experimental conditions were used i.e. refluxing the ligand and Ln(acac),H\(_2\text{O}\) precursor in a mixed solvent of methanol and acetonitrile. It is also noteworthy that these two salen-type ligands act not only as the ligands in this reaction but also as the base, thus promoting the formation of hydroxide ligands from water molecules introduced by the starting materials. Similar bifunctional ligands have been reported in the literature.\(^1,\)\(^2\) Moreover, changes to the molar ratio between the ligand and Ln(acac),H\(_2\text{O}\) as well as using a different reaction solvent result in noncrystalline materials.

**Structural analysis**

Single-crystal X-ray diffraction, IR analysis [Fig. S1, 2]\(^\dagger\) and charge-balance considerations indicate that complexes 1–3 are essentially isomorphous, taking complex 2 as an example to describe the structure, the partially labelled crystal structure is shown in Fig. 1. Complexes are crystallized in a monoclinic crystal system in the space group \(P2_1/n\) (Table 1). Due to both the radii of the Tb\(_{\text{III}}\) ions being large relative to the transition metal ions, and the two imine N atoms and two phenolic O atoms of the rigid ligand H\(_2\text{L}_1\) lying nearly in a plane giving a small pocket, Tb\(_{\text{III}}\) ions could not locate in the center of the inner \(\text{N}_2\text{O}_2\) set. The Tb\(_{\text{III}}\) ions have to coordinate above or below the planar ligands. As shown in Fig. 1, the Tb\(_2\) ion between the two decks of ligands, is placed above one ligand and is ligated by two N atoms and two O atoms from this ligand with Tb\(_2\)–N3, Tb\(_2\)–N4, Tb\(_2\)–O3, and Tb\(_2\)–O4 distances equal to 2.475(3), 2.475(4), 2.238(2) and 2.182(3) Å, respectively. The Tb\(_2\) ion is also located under another ligand and is ligated through two phenolic O atoms of this ligand with Tb\(_2\)–O1 and Tb\(_2\)–O2 distances of 2.377(3) and 2.345(3) Å, respectively. There is one water (O9) atom completing the seven-coordination geometry of the Tb\(_2\) ions, with a Tb\(_2\)–O9 distance of 2.372(3) Å. This leads to a distorted capped trigonal prism, in which O2, O4 and N4, and O1, O3 and N3 form the two triangle planes of the trigonal prism and one water molecule, O9, is located above the distorted square plane formed by O1, O2, O3 and O4 (Fig. 1 bottom). The Tb\(_2\) ion is near to this plane with a 0.2877 Å distance. The Tb1 ion is located above the top ligand and coordinated by two N and two O atoms from this ligand with Tb1–N1, Tb1–N2, Tb1–O1, and Tb1–O2 distances of 2.551(3), 2.563(4), 2.347(2) and 2.352(3) Å, respectively. There are two bidentate acac ligands finishing the...
that the two Tb(III) ions show distinct coordination numbers respectively, as well as Dy2 ions are bridged by the two O7 and O8, and O1, O2, N1 and N2 atoms. The Tb1 and Tb2 bases of the square antiprism for Tb1 consist of the O5, O6, square-antiprismatic geometry (Fig. 1 bottom). The two square bases of 2.394(3), 2.325(3), and 2.303(3) Å. This forms a distorted square-antiprismatic geometry. The two square bases of Tb1 consist of O1, O2, O3 and O3′ atoms. The two Dy2 ions are bridged by the two μ3-phenolic O1 and O2 atoms, with a Tb1–Tb2 distance of 3.8754(3) Å, and Tb1–O1–Tb2 and Tb1–O2–Tb2 angles of 110.23(9) and 111.22(10)°. It is interesting that the two Tb(III) ions show distinct coordination numbers and environments.

Complexes 4 and 5 are constructed with H2L2 and acac ligands. They are crystallographically isostructural and the representative crystal structure of 5 is depicted in Fig. 2. As expected, they give tetranuclear planar lanthanide clusters, all 8-coordinate Dy(III) ions are coplanar and linked by a combination of μ2-hydroxo (O3 and O3′), ketone (O8 and O8′) and phenoxy (O1, O2, O1′, and O2′) oxygen atoms. The two Dy2 and Dy2′ ions are located in the inner N2O2 coordination pocket of the two salen-type ligands (Fig. S2)† with Dy2–O1, Dy2–O2, Dy2–N1 and Dy2–N2 distances equal to 2.372(2), 2.328(2), 2.493(3) and 2.556(3) Å, respectively. Two triply bridging hydroxide (O3 and O3′) atoms lie approximately 0.87 Å above and below the Dy4 plane. The μ3-OH groups form near symmetrical bridges to the metal centers, with Dy2–O3, Dy1–O3 and Dy1′–O3 distances of 2.313(2), 2.370(2) and 2.372(2) Å, respectively, as well as Dy2–O3–Dy1, Dy2–O3–Dy1′ and Dy1′–O3–Dy1 angles of 100.49(8), 111.52(8), and 109.12(8)°, respectively. There are six bidentate anionic acac− groups above and below the planar core chelating to the four Dy(m) ions. In this Dy4 cluster, the 8-coordinate Dy1 and Dy2 ions exhibit a distorted-square-antiprismatic geometry. The two square bases of the square antiprism for Dy1 consist of O1′, O3′, O3 and O6, and O2, O7, O9 and O8, whereas for Dy2, the two square bases are defined by the atoms N1, N2, O1 and O3, and O2, O5, O4 and O8 (Fig. S3 in the ESI).† The two square antiprisms share three oxygen atoms, O2, O3 and O8, which form a triangular face (Fig. 2 and Fig. S3)† with distances of 2.62, 2.78 and 2.85 Å for O2⋯O8, O3⋯O8 and O2⋯O3, respectively. The four Dy(m) ions are located at the corners of a parallelogram with distances and angles between the metal centers described in Fig. S4 in the ESI†.

As expected, these tetranuclear planar Dy4 structures are similar to our recently reported series of Ln4 clusters encapsulated by salen-type H2L and acac ligands (Scheme 1),19 which
results from the similar ortho-diamine backbone of ligand H$_2$L$^1$ and H$_2$L$^3$. The torsion angles of NCCN (ortho-diamine) are 53.34° in cyclohexan-1,2-diamine and 53.91° in the ethane-1,2-diamine backbone, respectively. Thus, this is an efficient synthetic strategy for tetranuclear planer lanthanide clusters incorporating diverse flexible salen-type and β-diketone analogues. However, for complexes 1-3, the torsion angle of NCCN in the benzene-1,2-diamine (H$_2$L$^1$) backbone is 0.07°, nate analogues.20. Thus, this is an are 53.34° in cyclohexane-1,2-diamine and 53.91° in the

Fluorescence properties

The visible photoluminescence (PL) spectra of 2 (Tb$_2$), 4 (Tb$_4$) and 5 (Dy$_4$) in the solid-state were measured at room temperature (Fig. 3 and Fig. S6). They exhibit characteristic metal-centered emission in the visible field.24 The emission spectra of 2 and 5 consist of four main bands centered around 489, 545, 583 and 620 nm that are assigned to the characteristic transitions of $^5$D$_4$ $\rightarrow$ $^7$F$_j$ (j = 6, 5, 4 and 3) for Tb(III) ions (Fig. S6).† In which, the $^5$D$_4$ $\rightarrow$ $^7$F$_5$ transition (545 nm) is clearly the strongest and results in a green emission. It is interesting to note that the lowest excited energy level ($^4$F$_{9/2}$) of the Dy(III) ion (20 830 cm$^{-1}$) is similar to that ($^5$D$_4$) of the Tb(III) ion (20 430 cm$^{-1}$). Thus the ligands suitable for Tb photoluminescent compounds would be efficient for Dy complexes. Like most Dy-containing compounds, the photoluminescence spectrum of 5 shows two sharp emission bands at 480 and 574 nm attributed to the $^4$F$_{9/2}$ $\rightarrow$ $^6$H$_{15/2}$ and $^4$F$_{9/2}$ $\rightarrow$ $^6$H$_{13/2}$ transitions, respectively (Fig. 3). Generally, the later transition is dominant in most Dy(III)-centered emissions. In this case, interestingly, the main emission center changed from 574 nm to 480 nm with the yellow varying to blue emission after formation of the tetranuclear complex, which is likely to be due to the different coordination environment around the lanthanide(III) ions.

The ligand field plays a crucial role both in the fluorescent and the SMM properties, it is challenging to design a ligand field which possesses both the suitable triplet state to match the first exited state of lanthanide(III) ions and the suitable symmetry to stimulate the magnetic anisotropy of the paramagnetic centers displaying SMM behavior. Recently, the fluorescence emission of the 4f-based SMM systems (Dy(III) or Yb(III)) has been proven to be an efficient method of correlating the energy gaps between the ground-state multiplets with the thermal relaxation energy barriers, and further to support the theoretical results of the crystal-field components. Fortunately, we found this system possessed both fluorescent and SMM properties, while the emission line involving the ground-state $^6$H$_{15/2}$ is not sufficiently well resolved to evaluate the fine separation between the two states at highest energy. Nevertheless, according to the present synthetic strategy, the alteration of rigid and flexible backbone ligands is promising to get a bifunctional fluorescent and SMM system for studying the correlation between the fluorescent and SMM properties.

Magnetic properties

The dc magnetic measurements were performed on polycrystalline samples of 1000 Oe (Fig. 4) and the field dependence of the magnetization for 1 to 5 in the temperature range of 2.5 to 8 K were also obtained and are shown in Fig. S7-11.† The values of $\chi T$ at room temperature are 16.05, 21.25, 19.47, 56.08 and 58.81 cm$^3$ K mol$^{-1}$ for complexes 1 to 5 respectively. According to the free-ion approximation of each lanthanide ion, Gd(III) ($^6$S$_{7/2}$, S = 7/2; L = 0, g = 2, $\chi T$ = 7.88 cm$^3$ K mol$^{-1}$), Tb(III) ($^7$F$_{6}$, S = 3, L = 3, g = 3/2, $\chi T$ = 11.82 cm$^3$ K mol$^{-1}$), Dy(III) ($^7$H$_{15/2}$, S = 5/2, L = 5, g = 4/3, $\chi T$ = 14.17 cm$^3$ K mol$^{-1}$), Er(III) ($^7$I$_{13/2}$, S = 3/2, L = 6, g = 6/5, $\chi T$ = 11.48 cm$^3$ K mol$^{-1}$). The theoretical values for two non-interacting lanthanide ions are calculated to be 15.76, 23.64 and 22.96 cm$^3$ K mol$^{-1}$ for 1, 2 and 3, respectively. The theoretical value for four non-interacting lanthanide ions are calculated to be 47.52 and 56.68 cm$^3$ K mol$^{-1}$ for 4 and 5, respectively. The experimental $\chi T$ values at

Fig. 3 Emission spectra of 5 and Dy(acac)$_2$H$_2$O in the solid-state.

Fig. 4 Temperature dependence of the $\chi T$ product for complexes 1-5 under an applied field of 1000 Oe.
room temperature are close to the theoretical values. On lowering the temperature the $\chi T$ product remains fairly constant down to $\sim 50$ K for 1 before dropping rapidly down to 12.29 cm$^3$ K mol$^{-1}$ at 2.5 K. Due to the isotropic nature of Gd(III) ions it is reasonable to assume that the latter behavior is indicative of intramolecular antiferromagnetic interactions. As for complexes 2, 3, 4 and 5, the $\chi \alpha T$ product decreases gradually and more rapidly until a slightly higher temperature of $\sim 70$ K, which is likely to be due to crystal-field effects (i.e. thermal depopulation of the Ln(III) Stark sublevels) and the possible antiferromagnetic dipole–dipole interaction between the molecules is not ruled out.

The $M$ versus $H$ and $H/\chi$ data at high fields for all complexes are given in Fig. S7–11.† For complex 1, the magnetization reaches near saturation at 14.17N/$\chi$ with an applied field of 7 T. This value is close to the expected theoretical value of 14.00N/$\chi$ (g = 2). The magnetization measurements for complexes 2, 3, 4 and 5 show a relatively rapid increase below $\sim 1$ T and a slow linear increase without complete saturation up to 7 T. Their magnetization values (10.86, 9.06, 23.61 and 19.23N/$\chi$) are lower than their theoretically derived values (18.00, 18.00, 36.00 and 40.00N/$\chi$ for 2, 3, 4 and 5, respectively). As aforementioned, the complexes may have low-lying excited states or significant magnetic anisotropy resulting in large differences between experimental and theoretical values. Further confirmation was obtained from the $M$ vs. $H/\chi$ plots (Fig. S7–11),† the non-superposition of the $M$ vs. $H/\chi$ plots at higher field indicates the presence of low-lying excited states or significant magnetic anisotropy.

In order to study the magnetic dynamic behavior of these systems, the alternating-current (ac) susceptibility at various frequencies and temperatures in the absence of dc fields is measured and depicted in Fig. 5 and S12.† For 5, both in-phase ($\chi'$) and out-of-phase ($\chi''$) susceptibilities show a frequency dependence, this clearly indicates the slow relaxation of magnetization arising from single-ion magnet (SIM) behavior. However, no full peak was observed, in the lanthanide systems the tail of a peak generally indicates the presence of quantum tunneling of magnetization (QTM) which is usually systems the tail of a peak generally indicates the presence of quantum tunneling of magnetization (QTM) which is usually seen in 4f-based SMMs. For the frequency dependence of the out-of-phase ac susceptibility ($\chi''$) measurement, the peaks are clearly detected, and the data was fitted to the Arrhenius law ($\tau = \tau_0 \exp(\Upsilon_{eq}/kT)$, Fig. S13)† providing an effective relaxation energy barrier of $\Upsilon_{eq}$ 13.95 K and pre-exponential factor $\tau_0$ 5.01 × 10$^{-6}$ which lies in the normal range of 10$^{-6}$–10$^{-10}$, the relatively large value is indicative of the existence of QTM.

The Cole–Cole plots (Fig. S13 right)† in the form of $\chi''$ vs. $\chi'$ show an asymmetrical shape and can be fitted to the generalized Debye model23 with an $\alpha$ value range of 0.168–0.270 ($\alpha = 0$ for a Debye model). The relatively large $\alpha$ values are in agreement with a wide distribution of relaxation times, and the asymmetric Cole–Cole plots at low temperatures might suggest the occurrence of multiple relaxations most likely associated with distinct anisotropic centres. All these magnetic parameters clearly indicate that the remarkable complex 5 possesses a SMM nature.

**Experimental**

**General information**

All chemicals and solvents were obtained from commercial sources and were used as received, without further purification. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 analyzer. Fourier transform IR spectra were measured on a Perkin-Elmer Spectrum One spectrometer with samples prepared as KBr pellets. Visible and NIR emission and excitation were recorded on an Edinburgh FLS 920 fluorescence spectrophotometer. The salen-type ligands $\text{H}_2\text{L}^1$ and $\text{H}_2\text{L}^2$ were prepared according to the literature report and lanthanide precursors, Ln(acac)$_2$H$_2$O, where Ln = Gd(III), Tb(III), Dy(III), Er(III) and Yb(III) were prepared according to a literature procedure previously described.$^{20a,21}$

**Synthesis of dinuclear complexes (1–3)**

The same procedure was employed in preparing the four complexes; hence, only compound 2 [Tb$_2$H$_2$OL$_2$(acac)$_2$] will be described in detail. To 20 mL of dichloromethane solution of $\text{H}_2\text{L}^1$ (0.159 g, 0.5 mmol), solid Tb(acac)$_3$H$_2$O (0.241 g, 0.5 mmol) was slowly added under stirring. The solution was refluxed for 4 h and the mixture was then cooled to room temperature and filtered. Diethyl ether was layered on top of the filtrate to give yellow single crystals of 2 in one week.
Elemental analyses, infra-red and yields for complexes 1–3

Yields: 0.466 g (70%) for (1), 0.378 g (65%) for (2) and 0.407 g (69%) for (3). Elemental analysis (%) calcd for $\text{C}_63\text{H}_{76}\text{N}_4\text{O}_{19}\text{Tb}_4$: C, 47.02; H, 3.57; N, 4.22; found C, 46.79; H, 3.68; N, 4.05; $\text{C}_63\text{H}_{76}\text{N}_4\text{O}_{19}\text{Tb}_4$ (2): C, 51.65; H, 3.81; N, 4.82; found C, 51.31, H, 3.78, N, 4.45; $\text{C}_63\text{H}_{76}\text{N}_4\text{O}_{19}\text{Tb}_4$ (3): C, 51.78; H, 4.27; N, 4.47; found C, 50.94, H, 3.98, N, 4.58; IR (KBr) for (3): $\nu$ = 1621, 1607, 1583, 1539, 1515, 1474, 1388, 1287, 1260, 1183, 1016, 916, 750, 656, 529 cm$^{-1}$; (2): $\nu$ = 1619, 1607, 1582, 1539, 1516, 1474, 1386, 1286, 1261, 1184, 1149, 1016, 916, 749, 656, 529 cm$^{-1}$; (1): $\nu$ = 1621, 1609, 1583, 1540, 1523, 1475, 1386, 1287, 1264, 1186, 1149, 1018, 917, 748, 657, 531 cm$^{-1}$.

Synthesis of tetranuclear complexes 4 and 5

The same procedure was employed in preparing the two complexes, compound 5 $[\text{Dy}_4(\mu_3\text{-OH})\text{L}_2(\text{aca})]_{2}\text{MeCN}$ will be described in detail. To 10 mL of an acetonitrile solution of $\text{H}_3\text{L}^2$ (0.270 g, 1.0 mmol) 10 mL of a methanol solution of $\text{Dy}(\text{aca})_3\cdot\text{H}_2\text{O}$ (0.485 g, 1.0 mmol) was slowly added under stirring. The solution was refluxed for 3 h, and the filtrate was allowed to crystallize at room temperature by slow evaporation. Yellow crystals, suitable for single-crystal X-ray diffraction analysis, were obtained after 2 weeks.

Elemental analyses, infra-red and yields for complexes 4, 5

Yield: 0.947 g (50%) for 4 and 0.967 g (52%) for 5. Elemental analysis (%) calcd for $\text{C}_{66}\text{H}_{78}\text{Dy}_4\text{N}_6\text{O}_{18}$: C, 51.78; H, 4.27; N, 4.47; found C, 50.94, H, 3.98, N, 4.58; IR (KBr) for (5): $\nu$ = 3577, 1633, 1603, 1516, 1393, 1289, 1016, 922, 756, 644 cm$^{-1}$; (4): $\nu$ = 3577, 1635, 1602, 1517, 1388, 1289, 1018, 921, 759, 644 cm$^{-1}$.

X-ray crystallographic analysis and data collection

Single-crystal X-ray data of the four clusters were collected at 293 K on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct and Patterson methods and refined by the full-matrix least-squares methods on $P^2$, which were performed using the SHELXTL-97 software package.$^{22b,c}$ The location of lanthanide atoms was easily determined, and O, N, C and H atoms were subsequently determined from the difference Fourier maps. The non-hydrogen atoms were refined anisotropically. The H atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. All of the crystal data and structure refinement details for these four compounds are summarized in Table 1. Selected bond lengths and angles for 1–5 are listed in Table S1.$^1$ Crystallographic data for all structures can be obtained from Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 830602 (1), 830603 (2), 830605 (3), 839728 (4) and 837060 (5).

Magnetic measurements

The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 2.5 and 300 K for dc-applied fields ranging from ~7 to 7 T, ac susceptibility measurements were carried out under an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz. Magnetization data were collected at 100 K to check for ferromagnetic impurities which were found to be absent in all samples. A diamagnetic correction was applied for the sample holder.

Conclusions

Three dinuclear and two tetranuclear lanthanide complexes were prepared and characterized in terms of structure, fluorescence and magnetism. It is proved that the use of salen-type and $\beta$-diketone ligands is ideal for isolation of low nuclear lanthanide multifunctional materials. The structural analyses demonstrated that the rigid ligand favors the dinuclear half-decker sandwich structure with different coordination numbers and geometries for the two lanthanide(III) ions, while the more flexible ligand leads to planar tetranuclear clusters. This provides an efficient method by which to tune these double-decker sandwich lanthanide complexes and construct single metal ion complexes and/or multinuclear clusters. The mixed ligands could simultaneously induce the luminescence and single-molecule magnetism of lanthanide(III) ion centers. This gives a facile method with which to investigate the relationship between the structure of lanthanide compounds and their magnetic or luminescent properties. We are currently trying to tune the environments of the lanthanide(III) ions to keep their coordination geometry and vary the ligand field around the lanthanide(III) ion, thus potentially promoting their magnetic or fluorescent properties. This may be the way to elucidate accurately the influence of the ligand field around the lanthanide(III) ions.

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