Dinuclear lanthanide complexes supported by a hybrid salicylaldiminato/calix[4]arene-ligand: synthesis, structure, and magnetic and luminescence properties of (HNEt₃)[Ln₂(HL)(L)] (Ln = Sm³⁺, Eu³⁺, Gd³⁺, Tb³⁺)†

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The synthesis, structures, and properties of a new calix[4]arene ligand with an appended salicylaldimine unit (H₄L = 25-[2-((2-methylphenol)imino)ethoxy]-26,27,28-trihydroxy-calix[4]arene) and four lanthanide complexes (HNEt₃)[Ln₂(HL)(L)] (Ln = Sm³⁺ (4), Eu³⁺ (5), Gd³⁺ (6), and Tb³⁺ (7)) are reported. X-ray crystallographic analysis (for 4 and 6) reveals an isostructural series of dimeric complexes with a triply-bridged NO₃Ln(μ-O)₂(OH⋯O)LnO₃N core and two seven coordinated lanthanide ions. According to UV-vis spectrometric titrations in MeCN and ESI-MS the dimeric nature is maintained in solution. The apparent stability constants range between log $K$ = 5.8 and 6.3. The appended salicylaldimines sensitize Eu³⁺ and Tb³⁺ emission ($λ_{\text{exc}}$ 311 nm) in the solid state or immersed in a polycarbonate glass at 77 K (for 5, 7) and at 295 K (for 7).

Introduction

Calix[4]arenes have turned out to be versatile backbones for multidentate supporting ligands, and a large number of donor groups have been appended at the lower and upper rim in order to control the properties of the resulting complexes. Lanthanide complexes of such ligands have also been well investigated, particularly for their potential in liquid–liquid extraction. Recently, some research in this area has been directed towards the development of lanthanide-based single-molecule magnets and luminescent probes and materials. The calixarenes are typically designed to saturate the metal’s coordination sphere, and several luminescent complexes have been investigated. Despite the maturity of the field, not many lanthanide complexes of pendant calix[4]arenes were structurally characterized. Most structures are derived from calix[4]arene diamides or tetraamides. Only a handful of structures with triply appended calix[4]arenes have been reported, and as far as we are concerned no structures exist with one-armed calix[4]arenes. To fill this gap, we decided to prepare a mono-substituted calix[4]arene-Schiff base ligand H₄L and investigate its coordination chemistry towards some lanthanide ions. Hybrid ligands of this sort are known to complex first-row transition metals readily, but their lanthanide chemistry remains largely unexplored.

This study demonstrates that H₄L supports dinuclear lanthanide complexes (for Ln = Sm, Gd, Eu, and Tb) – a property which contrasts the mononucleating behavior of the double and fourfold functionalized calix[4]arene amides. Their synthesis and characterization along with the investigation of photophysical, magnetic and structural properties are presented herein.
Results and discussion

Synthesis and characterization of the ligand

The salicylaldimine-appended calix[4]arene H₄L was readily prepared according to a procedure reported by Zhang et al. for related bis(salicylaldimine)-p-tert-butylcalix[4]arenes (Scheme 1).⁵⁸ Alkylation of the parent calix[4]arene 1 with bromoacetonitrile followed by reduction of the nitrile 2 provided the amine 3, which was condensed with salicylaldehyde in the presence of MgSO₄, to provide the title compound as a pale-yellow solid in 21% overall yield. The IR spectrum of H₄L reveals two sharp (3635 and 3500 cm⁻¹) and one broad OH band (3320 cm⁻¹) indicative of hydrogen bonding interactions.⁵⁹ The CN stretch appears at 1635 cm⁻¹, a typical value for salicylaldimines.⁶⁰ The calixarene adopts a cone conformation in CH₂Cl₂ as evidenced by NMR (two characteristic AB systems for the Ar–CH₂–Ar groups).⁶¹–⁶³ The free ligand displays intense absorption bands in the UV (Table 1), attributed to π→π* transitions of aromatic rings of the calix[4]arene (254, 286 nm)⁶⁴ and the salicylaldimine (311 nm).⁶⁵,⁶⁶ A weak band around 403 nm (ε = 117 M⁻¹ cm⁻¹) can be assigned to the n→π* transition of the imine group.

The crystal structure of the free ligand (Fig. 1) shows a cone conformation stabilized by three intramolecular OH⋯O hydrogen bonds (O1⋯O2, O2⋯O3, O3⋯O4). The pendant Schiff-base is almost perfectly planar forming an intramolecular

![Scheme 1](image)

Table 1  Selected analytical data for H₄L and its lanthanide complexes 4–7

<table>
<thead>
<tr>
<th>Compound</th>
<th>ESI-MS(–)</th>
<th>IR/cm⁻¹</th>
<th>λ_max/nm (ε/M⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₄L</td>
<td>570.3</td>
<td>1635, 1338</td>
<td></td>
</tr>
<tr>
<td>4 (Sm)</td>
<td>1439.2, 719.1</td>
<td>1635, 1316</td>
<td></td>
</tr>
<tr>
<td>5 (Eu)</td>
<td>1441.3, 720.1</td>
<td>1636, 1317</td>
<td></td>
</tr>
<tr>
<td>6 (Gd)</td>
<td>1451.3, 725.1</td>
<td>1636, 1325</td>
<td></td>
</tr>
<tr>
<td>7 (Tb)</td>
<td>1453.3, 726.1</td>
<td>1637, 1303</td>
<td></td>
</tr>
</tbody>
</table>

⁴ Concentration of solutions were ~1.0 × 10⁻⁵ M, T = 298 K. ⁵ MeCN solution.
OH⋯N hydrogen bond, as in other o-hydroxyaryl Schiff bases. An intramolecular CH⋯π interaction manifests itself by a short H8b⋯Xt′enantiomeric distance of 2.84 Å. Self-inclusion mediated by intermolecular CH2⋯π interactions of length 2.90 Å occurs. This leads to one-dimensional chains as illustrated in Fig. 1.

The new ligand and all intermediates were characterized by IR, UV-vis, 1H and 13C NMR spectroscopy and electrospray ionization mass spectrometry (ESI-MS). 2D NMR experiments (NOESY, HSQC, HMBCC) were used to correctly assign the chemical shifts of hydrogen and carbon atoms (ESI†).

Synthesis and characterization of complexes

The reaction of H4L with samarium(III) nitrate hexahydrate was performed with NEt3 as a base (pKₐ 18.82, MeCN) to deprotonate the phenol functions. At a ∼1 : 1 : 4.5 molar ratio in a mixed CH2Cl2/MeOH solution at room temperature a pale-yellow solution forms, from which a dinuclear compound of composition [Ln(L)(MeCN)2] (7) could be reproducibly obtained in 82% yield (Scheme 2).

Analogous europium(III) (5), gadolinium(III) (6) and terbium(III) (7) were also synthesized in this manner. According to ESI-MS, mononuclear complexes of composition [LnL]⁻ are also present (Table 1), but all attempts to isolate these entities failed. The exclusive formation of the [Sm2(HL)(L)]⁻ dimers may be due to a lower solubility although other factors such as packing or specific intermolecular interactions cannot be ruled out. All complexes are air-stable but hygroscopic, and may be due to a lower solubility although other factors such as packing or specific intermolecular interactions cannot be ruled out. All complexes are air-stable but hygroscopic, and only sparingly soluble in protic solvents.

The formulation of the complexes was ascertained in all cases by elemental analysis, mass spectrometry, IR and UV-vis spectroscopy, and in case of the Sm(III) and Gd(III) complexes also by X-ray crystallography. The negative ESI-MS spectra of dilute (10⁻³ M) MeCN/CH₂Cl₂ solutions exhibit molecular ion peaks at m/z = 1439.2 (4), 1441.3 (5), 1451.3 (6), and 1453.3 (7), respectively, with the correct isotopic peak pattern for dimeric [Ln₂(HL)(L)]⁻ anions (ESI). Under these conditions, signals at m/z = 719.1 (4), 720.1 (5), 725.1 (6) and 726.1 (7) for monomeric [LnL]⁻ species are also observed. The IR spectra of all complexes reveal a band at 1635–1636 cm⁻¹ for the C==N stretching frequency, a typical value for imine functions coordinated to Ln(III) ions. O–H stretching bands were absent indicative of Ln(III) bound phenolate groups. The C–O stretching frequency observed for H₄L at 1338 cm⁻¹ is shifted to lower frequencies in the complexes (1327–1316 cm⁻¹), indicative of the coordination of the phenol ether moiety as well.

Crystallographic characterization

Single crystals of (HNEt₃)[Sm₂(HL)(MeCN)]₂·MeCN (4·3MeCN) and (HNEt₃)[Gd₂(HL)(MeCN)]₂·MeCN (6·3MeCN) were analyzed by X-ray diffraction. The structure comprises dinuclear [Sm₂(HL)(L)(MeCN)]⁻ anions (Fig. 2), HNEt₃⁺ cations and MeCN molecules. The latter occupy voids in the structure and the calixarene cavities, as in other structures. The HNEt₃⁺ ion is located in a cleft generated by three phenyl rings of the dimer and hydrogen bonds to a MeCN solvate molecule N₃⋯N₆ 2.90 Å (see Fig. S1†). Significant interactions between the HNEt₃⁺ ion and phenolate O atoms are not observed (N₃⋯O₇ 3.43 Å), presumably due to the fact that the latter are buried by the organic residues of the supporting ligand.

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The complex has idealized C₂ symmetry comprising two mononuclear Sm(III) units joined by two phenolato bridges to give a four-membered Sm₂O₂ ring, a motif quite common in lanthanide calixarene structures but herein realized from phenol groups of the salicylidene moieties. This assembly is reinforced by a hydrogen bond between O₄ and O₈ of the ligand and the complexation of the phenolate group by lanthanide ions. Depending on the location of the phenolate group and the size of the lanthanide ion, two different types of interactions are observed: (i) the phenolate group is bound to a lanthanide ion from above (with a C–O⋯Ln distance of 2.97 Å), and (ii) the phenolate group is bound to a lanthanide ion from below (with a C–O⋯Ln distance of 2.94 Å), as is reinforced by a hydrogen bond between O₄ and O₈ of the phenolate group and a lanthanide ion. The ion L₄⁻ is coordinated to the Sm(III) ion from above with a Ln–O distance of 2.32 Å (Fig. 2).
calixarene bowls (O4⋯O8 2.40 Å, O4–H4⋯O8 164°). Each samarium atom is further bonded to four calix[4]arene O atoms and to the imine N atom of the Schiff base unit, giving rise to coordination number seven (Fig. 3).

The calix[4]arene adopts a distorted cone conformation with an “elliptical” rather than a “circular” cross section very similar to that observed in [Eu2(HL)3(dmf)4]·7dmf (where HL represents triply deprotonated p-t-butyl-calix[4]arene). The Sm–O bond lengths vary significantly from 2.18–2.59 Å. Four Sm–O bonds are very short (Sm1–O1, O3; Sm2–O6, O7) ca. 2.18 Å. The Sm–O bonds involving the bridging phenolate oxygen donors are significantly longer at 2.38–2.48 Å (Sm1–O9, O10, Sm2–O9, O10), which is unusual for such bridges. The phenol ether O atoms (O2, O5) are weakly coordinating and form the longest Sm–O bonds (2.58 Å). They compare well with those in samarium complexes [[pic-O]Sm((L–H)

\((\text{HETO})_m\text{C}_2\text{Cl}_2)_n\)]([pic]∙EtOH·2H₂O and [Sm(L-2H)[pic]], where pic = picrate anion and L is a bis- or tris-substituted calixarene.78 The Sm–N bonds in 4 are also quite long at 2.56 Å. The presence of the hydrogen bonding interaction is supported by the relatively long Sm1–O4 and Sm2–O8 distances of 2.372 Å and 2.375 Å.

The structure of the gadolinium compound (HNEt₃)[Sm₂(HL)(L)·3MeCN (6·3MeCN) is isomorphous with 4·3MeCN, having slightly shorter Gd–O and Gd–N distances (Table 2), in agreement with its smaller ionic radius. The Ln⋯Ln distance is 3.9067(3) Å in 4 and 3.8965(4) Å in 6. In essence the NO₃ donor set of H₄L cannot saturate the coordination sphere of the lanthanide ions and so dimerization occurs to share some of the O donors.74 There are no significant intermolecular bonding interactions between the [Ln₂(L)(HL)]⁺ complexes. The shortest intermolecular Ln⋯Ln distances are 10.725 Å in 4 and 10.696 Å in 6.

### Magnetic properties

The lanthanide complexes were further studied by temperature-dependent magnetic susceptibility measurements using a SQUID-Magnetometer (MPMS Quantum Design) in applied magnetic fields of 0.5 T over a temperature range 2–300 K. Plots of χM versus T for 4–7 are shown in Fig. 4.

For the Sm₃⁺ complex 4 the χM/T value is 0.72 cm³ K mol⁻¹ at room temperature, slightly larger than the expected value of 0.64 cm³ K mol⁻¹ for two non-interacting Sm⁺ ions. On lowering the temperature, χM/T decreases and tends to a value of ca. 0.01 cm³ K mol⁻¹ at 2 K. For Sm³⁺, with a ⁶H₁₄ ground state, the multiplet spacing is on the order of ₉/₈ and thermal population of excited ⁴H₁₂ states \((j = 7, 9, 11, 13, 15)\) contributes significantly to the susceptibility. The crystal field, which partially lifts the degeneracy of the J states in zero field, may also affect the susceptibility.

We analyzed the temperature dependence of the magnetic susceptibility of the Sm⁶⁺ complex by utilizing the analytical expression given by Kahn (eqn [S1]²). This model considers only the effect of spin–orbit coupling, which is appropriate given that magnetic exchange interactions are weak as suggested by the results for the analogous Gd complex (see below). Indeed, a reasonable fit was possible (excluding the

### Table 2

<table>
<thead>
<tr>
<th>M</th>
<th>4·3MeCN (M = Sm)</th>
<th>6·3MeCN (M = Gd)</th>
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<tr>
<td>M1–O1</td>
<td>2.186(2)</td>
<td>2.175(3)</td>
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<td>2.572(4)</td>
</tr>
<tr>
<td>M1–O3</td>
<td>2.163(3)</td>
<td>2.158(4)</td>
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<tr>
<td>M1–O4</td>
<td>2.375(2)</td>
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<tr>
<td>M2–N2</td>
<td>2.554(3)</td>
<td>2.525(5)</td>
</tr>
<tr>
<td>M1–M2</td>
<td>3.9067(3)</td>
<td>3.8965(4)</td>
</tr>
</tbody>
</table>

Fig. 4 Temperature dependence of the χM product at 5000 G for the dinuclear complexes 4–7. χM being the molar susceptibility per dinuclear complex defined as M/H. The solid lines correspond to the best fits.
low temperature data). The value of the spin–orbit coupling constant was determined to be $\lambda = 254$ cm$^{-1}$. This value is comparable to that of the free Sm$^{3+}$ ion (284 cm$^{-1}$).81

The $\chi_M T$ value of the Gd$^{3+}$ complex 6 amounts to 16.16 cm$^3$ K mol$^{-1}$ at 300 K, somewhat larger than the expected value 15.77 cm$^3$ K mol$^{-1}$ of two uncoupled $^6S_{7/2}$ centers. Upon cooling, $\chi_M T$ slowly decreases to 15.5 cm$^3$ K mol$^{-1}$ at 23.3 K and drops to 11.2 cm$^3$ K mol$^{-1}$ at 3 K, indicative of a very weak antiferromagnetic exchange interaction as in other phenolato-bridged Gd$^{3+}$ complexes.82,83 For Gd$^{3+}$ ions, first-order spin–orbit coupling is absent ($L = 0$). Therefore, the exchange interaction can be analyzed by using the isotropic spin Hamiltonian $H = -J S_{Gd1} S_{Gd2}$ with $S_{Gd1} = S_{Gd2} = 7/2$. The magnetic susceptibility for a dinuclear Gd$^{3+}$ complex is given by eqn (1), where $g$ is the Landé factor, $\mu_B$ the Bohr magneton, $N_a$ the Avogadro number, $k_B$ the Boltzmann constant, and $x = J/k_BT$.

$$\chi_M T = \frac{2 N_a \mu_B^2}{k_B} \left[ e^x + 5e^{5x} + 14e^{6x} + 30e^{10x} + 55e^{15x} + 91e^{21x} + 140e^{28x} \right]$$

$$\left[ 1 + 3e^x + 5e^{5x} + 7e^{6x} + 9e^{10x} + 11e^{15x} + 13e^{21x} + 15e^{28x} \right]$$

(1)

A good fit of the experimental data is possible applying $J = -0.065$ cm$^{-1}$ and $g = 2.01$. Such a weak antiferromagnetic coupling constant is a typical value for phenolato-bridged Gd$^{3+}$ systems.82,84–87

The $\chi_M T$ value of the Eu$^{3+}$ complex 5 is 2.80 cm$^3$ K mol$^{-1}$ at 300 K, a value which is close to that expected for two non-interacting Eu$^{3+}$ ions (2.65 cm$^3$ K mol$^{-1}$), with non-negligible population of excited $^7F_1$–$^7F_0$ levels. The deviation from the Hund-Landé expectation value ($\chi_{\text{H-L}}$) is also attributable to contributions from the second order Zeeman effect in the ground $^7F_0$ multiplet.88 Upon cooling, the $\chi_M T$ values decrease steadily, reaching 0.03 cm$^3$ K mol$^{-1}$ at 2 K, as in other dinuclear Eu$^{3+}$ complexes.89 The magnetic susceptibility of the Eu$^{3+}$ complex can be fitted to the formula derived by Kahn (eqn (S2)†) by considering only $\lambda$ (multiplet spacing) as a parameter as also done for the Sm$^{3+}$ complex. Again, the magnetic interaction between the Eu$^{3+}$ ions are assumed negligible.

Indeed, an excellent fit was possible over the whole temperature range to give $\lambda = 324$ cm$^{-1}$. The multiplet spacing is within the range of $k_BT$, and significant population of the first excited state at 300 K explains the deviation from the Curie law. The $\lambda$ parameter for 6 agrees with other dinuclear Eu$^{3+}$ complexes. In [Eu$_2$(L)$]_2$, for example, where $L$ is derived from a calixarene ligand with two hydroxyquinolinolato arms, and the Eu$^{3+}$ ions in an N$_2$O$_5$ environment $\lambda = 325$ cm$^{-1}$.90

The $\chi_M T$ value of the dinuclear Tb$^{3+}$ complex at 300 K with 23.87 cm$^3$ K mol$^{-1}$ is slightly higher than the expected value of 23.60 cm$^3$ K mol$^{-1}$ for a $^7F_0$ ground state. Upon cooling the $\chi_M T$ values decrease first slowly to 22.71 cm$^3$ K mol$^{-1}$ at 100 K and then more rapidly to 15.87 cm$^3$ K mol$^{-1}$ at 4 K. Tb$^{3+}$ complexes are known to exhibit significant magnetic anisotropy, and fitting of susceptibility data is therefore difficult.84 The field dependence of the magnetization for complex 7 was determined in order to see whether magnetic anisotropy is present in this complex. Indeed, at 2 K the magnetization values increase rapidly at low fields and then linearly but without a clear saturation, reflecting the presence of a significant magnetic anisotropy (Fig. 5). Moreover, a $M$ vs. $H/T$ plot (Fig. 6) illustrates that the curves are not really superimposed on each other as expected for an isotropic system with a well-defined ground state. Nevertheless, hysteresis effects were not observed in $M$ vs. $H$ data at 2 K. Alternative current (ac) measurements were also undertaken to determine potential SMM behavior. However, neither maxima nor imaginary components of the ac susceptibility were observed in the $\chi_M T$ vs. $T$ plots, ruling out an SMM behavior for 7. This may be attributed to the low local symmetry of the Tb$^{3+}$ ions.91

Spectrophotometric titrations

To study the complexation reactions of H$_4$L with Sm$^{3+}$, Eu$^{3+}$, Gd$^{3+}$, and Tb$^{3+}$ in solution UV-vis spectrophotometric batch titrations were carried out. The experiments were performed at...
room temperature in acetonitrile at constant ionic strength ($10^{-2}$ M $\text{N}^+\text{Bu}_4\text{PF}_6$) and pH value ($5 \times 10^{-4}$ M $\text{NET}_3$ buffer). Data were recorded in the 200–600 nm range. The titration of $\text{H}_4\text{L}$ with $\text{Sm(NO}_3\text{)}_3$·$6\text{H}_2\text{O}$ is representative for all complexes (Fig. 7). For the other compounds, see ESI Fig. S29–S35.† Upon addition of aliquots of $\text{Sm(NO}_3\text{)}_3$·$6\text{H}_2\text{O}$ (0–5 equiv.) clear changes occur in the UV-vis ligand spectra. The bands at 254, 286, and 311 nm for $\text{H}_4\text{L}$ vanish with increasing $\text{Sm}^{3+}$ concentration, while new bands for $\text{[SM}_2\{\text{HL}\}\{\text{L}\}]^+$ develop with maxima at 300 and 345 nm. The final spectra match the recorded spectra of the isolated metal complexes. An isosbestic point at 325 nm indicates that $\text{Sm}^{3+}$ binding occurs to a single equilibrium.

To determine the stoichiometry of the resulting species the mole ratio method was applied.92 The inset of Fig. 7 shows a plot of absorbance values at 345 nm versus molar ratio $[\text{Sm}^{3+}]/[\text{H}_4\text{L}]$. The values increase steadily up to a molar ratio of about unity and then remains constant. No further changes were observed for up to five-fold excess of lanthanide salt, signifying the formation of a complex species with $1:1$ ligand/metal stoichiometry. The other lanthanide ions behave in a very similar fashion. Irrespective of the type of the lanthanide ion, only $1:1$ compounds were systematically detected. Nonlinear least-squares refinements of the titration data converged for a speciation model involving the ligand and its $1:1$ complexes with apparent stability constants of $6.08(4)$ ($\text{Sm}^{3+}$), $6.21(7)$ ($\text{Eu}^{3+}$), $5.81(4)$ ($\text{Gd}^{3+}$), and $6.34(6)$ ($\text{Tb}^{3+}$). The stability constants show a strong affinity of $\text{L}^-$ towards lanthanides and decrease with decreasing ionic radii with the strongest interaction observed for $\text{Sm}^{3+}$ and the weakest interaction observed for $\text{Sm}^{3+}$. There are only very few studies reporting thermodynamic data for $f$-element calixarene complexes in non-aqueous solvents.93–96 Danil de Namor and Jafour have studied the complexation of trivalent cations by $p$-tert-butylcalix[4]arene tetraethanoate, $p$-tert-butylcalix[4]arene tetramethyl ketone, and $p$-tert-butylcalix[4]arene tetraacetamide in acetonitrile.97 Borisova and co-workers have determined stability constants for lanthanide complexes supported by 2,2'-bipyridyl-$6,6'$-dicarboxylic acid diamide and 2,6-pyridinedicarboxylic acid diamide ligands in the same solvent. The binding constants of these complexes were found to lie in a similar range ($\log K \sim 4–6$).98

Spectroscopic and photophysical properties

The new compounds were further characterized by UV-vis absorption and emission spectroscopy. The electronic absorption spectra were measured in acetonitrile (complexes) at room temperature. Table 1 lists the data. All complexes show three intense absorption bands around 220 nm, 300 nm, and 350 nm, respectively. The first two high-energy bands are associated with $(\pi-\pi)^*$ transitions centered on the phenol ether and phenolate groups of the calix[4]arene backbone. The transition at 350 nm can be attributed to the phenyl ring of the salicylidimine unit. Deprotonation and coordination of the lanthanides red-shifts these features by 15 and 40 nm relative to those of the free ligand. The change of the lanthanide ion appears to have little if any impact on the spectrophotometric properties. Hence, upon going from the Sm to the Tb complex a slight blue-shift of the lowest energy band of ca. 2 nm can be detected.

The luminescence properties of the Eu and Tb complexes were investigated in view of literature reports that calix[4]arenes can act as an antenna for the sensitization of lanthanide luminescence.37,41 The free ligand shows a single emission band with a maximum at 455 nm when excited at 285 nm. The two complexes are not emissive in solution ($\text{CH}_3\text{CN}, \text{CH}_2\text{Cl}_2$). However, when embedded in a polymer Eu complex 5 displays four relatively broad and intense transitions (Fig. 8), attributed to $5\text{D}_0 \rightarrow 7\text{F}_J$ transitions ($J = 1$–$2$) when excited at 311 nm at 77 K.99 Both, the $5\text{D}_0 \rightarrow 7\text{F}_1$ (580 nm, 595 nm,) and the $5\text{D}_0 \rightarrow 7\text{F}_2$ transitions (620, 630 nm) appear as doublets. In view of the low local symmetry of the

![Fig. 7 Spectrophotometric titration of $\text{H}_4\text{L}$ with $\text{Sm(NO}_3\text{)}_3$·$6\text{H}_2\text{O}$ in $\text{CH}_3\text{CN}$ ($10^{-2}$ M concentration) at constant ionic strength ($10^{-2}$ M $\text{N}^+\text{Bu}_4\text{PF}_6, T = 298$ K) in the presence of $5 \times 10^{-4}$ M $\text{NET}_3$. The green curve refers to a final molar ratio of $\text{M}/\text{H}_4\text{L} = 5.0$. The inset shows the evolution of absorbance values at 345 nm versus the $[\text{Sm}^{3+}]/[\text{H}_4\text{L}]$ molar ratio.](Image)

![Fig. 8 Luminescence spectrum of ($\text{HNEt}_3$)[$\text{Eu}_2\{(\text{HL})(\text{L})\}$] at 77 K (poly-carbonate thin films doped with 4 wt% Eu). The excitation wavelength is 311 nm. The transitions above 575 nm start from the $5\text{D}_0$ state.](Image)
coordination polyhedron (C₁ in this case), this may be related to crystal-field splitting of the ⁷F₁ and ⁷F₂ levels. Splitting of these levels is not unusual for Eu(III) complexes with such a low site symmetry.⁹⁰ The ⁵D₀ → ⁷F₂ transition (expected in the 570–585 nm range), is a strictly forbidden transition in site symmetries other than Cₘₐ, Cₜ, or Cₛ.⁹⁰ It is also not observed for the present compound.

The intensity of the hypersensitive ⁵D₀ → ⁷F₂ transition (or the ratio R of the intensities I(⁵D₀ → ⁷F₂)/I(⁵D₀ → ⁷F₁)) is also often used as a measure for the asymmetry of the Eu³⁺ site, since the ⁵D₀ → ⁷F₂ signal is strictly forbidden for a Eu³⁺ at a site with inversion symmetry. In our case, there is no inversion symmetry about the Eu³⁺ ion. The ⁵D₀ → ⁷F₂ is observed and is 1.6 times more intense than the ⁵D₀ → ⁷F₁ transition, in good agreement with the theoretical predictions.¹⁰¹⁻¹⁰³

The Tb complex gives rise to four transitions at 490, 545, 584 and 619 nm, assigned to the ⁵D₁ → ⁷F₆ (J = 6, 5, 4, 3) transitions, again split by crystal-field effects. Of these, the “green” ⁵D₁ → ⁷F₆ transition at 545 nm has the highest intensity. Note that the intensity decreases with increasing temperature, which might be traced to quenching via enhanced vibrational relaxation (energy transfer to the O−H⋯O vibration modes).¹⁰⁴,¹⁰⁵

The excited state luminescence decay of the immobilized Tb complex is biexponential, although the first exponential term is dominating (99% of the initializing luminescence intensity, I₀) with a lifetime of about τ₁ = 81 ± 2.5 μs. A small contribution of a second term with a time constant of τ₂ = 305 ± 3 μs was determined. The origin of the second term may be a different conformation of the complex due to the imbedding into the polymer matrix, as often observed for imbedded dyes.¹⁰⁶ This will be further investigated in a subsequent work. The features of the lifetimes are comparable to values reported for other luminescent Tb calixarene complexes (Fig. 9 and 10).¹⁰⁷

The luminescence properties of the Gd compound 6 were examined in order to determine the triplet state energy of the Schiff base ligand. The emission spectrum of compound 6 is further stabilized by an intramolecular OH⋯hydrogen bond established in second sphere of the calixarene bowls. The dimeric units are also present in MeCN solution as suggested by ESI MS. There are little – if any – magnetic exchange interactions in the dimers, and the absence of SMM behavior may be associated with the low local symmetry of the lanthanide ions. The present study enlarges the database, may contribute to current knowledge of structure–property relationship in Ln calixarene containing SMMs, luminescent materials, and chemosensors.

Conclusions

A new monofunctionalized calix[4]arene-Schiff base ligand has been synthesized and its coordination chemistry towards selected lanthanide ions (Sm, Eu, Gd, Tb) investigated in solution and solid state. The chemistry of this ligand system is distinct from that of the well-studied bis- and tetrakis-lower rim functionalized calix[4]arenes, which tend to support only monomeric structures. Dimerization occurs via the salicylidene’s phenolate groups, not via bridging O atoms from the calix[4]arene, as seen for some heteroleptic complexes involving the parent calix[4]arenes to give coordination number 7 with an highly irregular coordination geometry. The assembly is further stabilized by an intramolecular OH⋯O–hydrogen bond established in second sphere of the calixarene bowls. The dimeric units are also present in MeCN solution as suggested by ESI MS. There are little – if any – magnetic exchange interactions in the dimers, and the absence of SMM behavior may be associated with the low local symmetry of the lanthanide ions. The present study enlarges the database, may contribute to current knowledge of structure–property relationship in Ln calixarene containing SMMs, luminescent materials, and chemosensors.

Experimental section

Materials and methods

The calix[4]arene 1 was prepared as described in the literature.¹⁰⁸ All reagents and solvents were commercial grade and used without further purification. Melting points were deter-

Fig. 9 Luminescence spectrum of (HNEt₃)[Tb₂(HL)(L)] (7) at 77 and 298 K (polycarbonate thin film doped with 4 wt% Tb). The excitation wavelength is 311 nm. All transitions start from the ⁵D₄ state.
minded with an Electrothermal IA9000 series instrument using open glass capillaries and are uncorrected. Elemental analyses were carried out on a VARIO EL elemental analyzer (Elementar Analyensysteme GmbH, Hanau). NMR spectra were recorded on a Bruker FT 300 spectrometer or AVANCE DRX 400 spectrometer at 298 K. Chemical shifts refer to solvent signals. Mass spectra were obtained using the negative ion electrospray ionization mode (ESI) on a Bruker Daltonics ESQUIRE 3000 Plus ITMS or Impact II UHR QqTOF instrument. Infrared spectra (400–4000 cm⁻¹) were recorded at 1 cm⁻¹ resolution on a Bruker TENSOR 27 (equipped with a MIRacle ZnSe ATR accessory from PIKE Technologies) FT-IR spectrometer. Solution absorption spectra were collected on a Jasco V-670 UV-vis-NIR device. Steady state fluorescence absorption and emission spectra were recorded on a PerkinElmer LS 50B luminescence spectrometer using 1 cm quartz cells (Hellma). The magnetic susceptibility measurements were performed with the use of a MPMS 7XL SQUID magnetometer (Quantum Design) working between 1.8 and 330 K for applied dc fields ranging from −7 to 7 T. Measurements were performed on polycrystalline samples over the temperature range 2–330 K at applied magnetic field of 0.1, 0.5, 1.0 T. The observed susceptibility data were corrected for the underlying diamagnetism.

Synthesis and analysis of compounds

25-(2-Cyanomethoxy)-26,27,28-trihydroxy-calix[4]arene (2). Cesium fluoride (2.15 g, 14.13 mmol, 1.2 eq.) and tetrahydroxy-calix[4]arene (5.00 g, 11.78 mmol) were dissolved in warm (40 °C) DMF (100 mL). Bromoacetonitrile (8.21 mL, 117.8 mmol, 10 eq.) was added and stirring continued for 2 d at 40 °C. The resulting pale-yellow suspension was acidified with 250 mL aqueous HCl (5 M) and extracted with CH₂Cl₂ (3 × 100 mL). The organic fractions were combined, dried with MgSO₄, and filtered. Evaporation provided an oily residue which was purified by column chromatography (CH₂Cl₂, Rf = 0.41). Colorless solid, yield: 1.59 g (29% based on 1).

M.p. 247 °C. Elemental analysis for C₃₀H₂₉NO₄·1/2H₂O (467.57 + 130.5 (w), 2924 (w), 2868 (w), 1008 (w), 984 (w), 877 (w), 788 (w), 753 (s), 742 (m), 705 (w), 692 (w), 686 (w).

25-(2-Aminoethoxy)-26,27,28-trihydroxy-calix[4]arene (3). The nitrite (2 (1.64 g, 3.54 mmol) was dissolved in dry THF (100 mL). The solution was cooled to 0 °C and a B₃H₆·THF solution (1 M, 37.3 mL, 37.3 mmol, 10.54 eq.) was added dropwise. The reaction mixture was refluxed for 12 h, cooled to r.t., and hydrolyzed with aqueous HCl (1 M, 100 mL). After stirring for 1 h, the solvent was evaporated under reduced pressure. The resulting white solid was taken up in CH₂Cl₂ (100 mL), water (20 mL) was added, and the pH adjusted to 10 by addition of aqueous NaOH solution (2 M). The organic phase was separated and the aqueous phase extracted with CH₂Cl₂ (3 × 50 mL). The organic fractions were combined and evaporated to dryness. Colorless solid, yield: 1.51 g (91% based on 2). M. p. 239 °C. Elemental analysis for C₃₀H₂₆NO₄·1/2H₂O (467.57 + 9.01) calcld: C 75.61, H 6.35, N 2.94%; found C 75.37, H 6.38, N 2.66%. m/z (ESI+), MeCN/CH₂Cl₂): C₃₀H₂₆NO₄ (467.210) [M + H⁺]⁺: 468.217; found 468.3.

1H-NMR (300 MHz, DMSO-d₆, for atom labels see Fig. S6f): δ = 3.17 (δ, 1JCH(1H) = 12.4 Hz, 2H, ArCH₂HAr), C(1′), 4.35 (2H, ArCH₂HAr, C(2′)), 13.9 Hz, 2H, ArCH₂HAr, C(1′)), 4.35 (δ, 1JCH(1H) = 13.9 Hz, 2H, ArCH₂HAr, C(1′)), 4.35 (δ, 1JCH(1H) = 14.9 Hz, 2H, ArCH₂HAr, C(1′)), 5.04 (s, 2H, –OCH₂C₉H₅), 6.17 (t, 1JCH(1H) = 7.5 Hz, 1H, p-AtH, C(11)), 6.72 (t, 1JCH(1H) = 7.5 Hz, 2H, p-AtH, C(1′), 6.93–7.04 (m, 3H, p-AtH, m-AtH, C(29), C(10,12), 7.04–7.17 (m, 6H, m-AtH, C(2,6,16,22,24), 8.43 (s, 2H, Ar–O–H, C(26,28)), 9.13 (s, 1H, Ar–OH, C(27)), 13.6°C (1H) NMR (100 MHz, CH₂Cl₂-d₆, for atom labels see Fig. S2f): δ = 32.0 (ArCH₂Ar, C(2′)), 32.1 (ArCH₂Ar, C(2′)), 61.2 (OCH₂C₉H₅), 115.3 (C(C–N), C(3)), 121.5 (p-AtC C(4a)), 122.6 (p-AtC C(4a)), 127.8 (p-AtC C(4a)), 128.1 (o-AtC C(4a)), 128.6 (o-AtC C(4a)), 129.05 (o-AtC C(4a)), 129.1 (m-AtC C(4a)), 13.1 (m-AtC C(4a)), 129.4 (m-AtC C(4a)), 129.6 (m-AtC C(4a)), 130.5 (m-AtC C(4a)), 130.9 (m-AtC C(4a)), 133.4 (m-AtC C(4a)), 149.3 (ipsopo CAR–OH C(4a), C(27)), 150.9 (ipsopo CAR–O–CH₂ C(4a), C(25)), 151.5 (ipsopo CAR–OH C(4a), C(26,28)). ATR-IR (ZnSe): ν/cm⁻¹ = 3290 (s, br, ν O–H), 3271 (s, br, ν O–H), 3040 (w), 2931 (w), 2866 (w), 1593 (w, ν C=C), 1467 (s, ν C=C), 1454 (s, ν C=C), 1430 (m), 1377 (m), 1349 (m), 1297 (w), 1272 (m), 1260 (m), 1243 (m), 1226 (m), 1210 (m), 1180 (m), 1156 (w), 1146 (w), 1085 (w), 1034 (m), 1029 (w), 976 (w), 959 (w), 949 (w), 895 (w), 841 (w), 806 (w), 796 (w), 778 (w), 753 (s), 742 (m), 705 (w), 692 (w), 686 (w).

25-(2-(Methylphenyl)imino)ethoxy)-26,27,28-trihydroxy-calix[4]arene (H₄L). To a solution of 3 (0.50 g, 1.07 mmol) and salicylaldehyde (144 mg, 1.18 mmol) in CH₂Cl₂/MeOH (150 mL, 1:1, v/v) was added MgSO₄ (100 mg). The resulting mixture was stirred at r.t. for 12 h, filtered, and evaporated in vacuum to ~1/3 of its original volume. The resulting yellow precipitate was filtered, washed with methanol (20 mL) and dried at 60 °C to give 495 mg (81% based on 1) of pure H₄L₁ as a yellow
To a solution of H4L (150 mg, 0.262 mmol) and NEt3 (0.165 mL, 1.18 mmol), and Eu(NO3)3·6H2O (130 mg, 0.289 mmol) were added in analogy to the samarium compound. Pale-yellow powder. Yield: 140 mg (69% based on H4L), mp > 240 °C (decomposes without melting).

This compound was prepared from H2L (150 mg, 0.262 mmol), NEt3 (0.165 mL, 1.18 mmol), and Gd(NO3)3·6H2O (130 mg, 0.289 mmol) were reacted in analogy to the procedure detailed above for the europium compound to give 169 mg (83% based on H4L) of the title compound as pale yellow powder. mp > 245 °C (decomposes without melting).

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tip of a glass fibre using perfluoropolyether oil. The data sets equipped with graphite monochromated Mo-Kα = 15 175.7(10) Å³, Vgroup Pbca 180(2) K, the supplementary crystallographic data for this paper. C86H84Gd2N6O10
Suitable single crystals of H₂L, (HNEt₃)[Sm₂(HL)(L)(MeCN)]·MeCN (4·3MeCN), and (HNEt₃)[Gd₂(HL)(L)(MeCN)]·MeCN (6·3MeCN) were selected and mounted on the tip of a glass fibre using perfluoropolyether oil. The data sets were collected at 180(2) K using a STOE IPDS-2 diffractometer equipped with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were processed with the programs XAREA.† The data were solved by direct methods and refined by full-matrix least-squares techniques on the basis of all data against F² using SHELXL-97. PLATON was used to search for higher symmetry. All non-hydrogen atoms were refined anisotropically. Graphics were produced with Ortep3 for Windows and PovRAY.

Crystal data for H₄L·0.5H₂O. C₃₇H₃₃NO₅.5, Mr = 579.67 g mol⁻¹, orthorhombic space group P2₁2₁2₁, a = 11.516(2) Å, b = 14.372(3) Å, c = 18.060(4) Å, V = 2989(1) Å³, Z = 4, Rcalc = 1.27 g cm⁻³, T = 181 K, μ(Mo Kα) = 0.086 mm⁻¹ (λ = 0.71073 Å), 19399 reflections measured, 5261 unique, 3947 with I > 2σ(I). Final R₁ = 0.0317, wR₂ = 0.093/0.115 e Å⁻³. The Flack x parameter (absolute structure parameter) was calculated to be −0.36(16) for the present structure and 1.36 for the inverted structure. The solvent molecule is disordered over two positions with site occupancy factors of 0.25 each (fixed). Hydrogen atoms were not calculated for this solvate structure. Crystal data for (HNEt₃)[Sm₂(HL)(L)(MeCN)]·MeCN. C₃₈H₄₆N₆O₆Sm₂, Mr = 1662.37 g mol⁻¹, orthorhombic space group Pbca, a = 22.6899(5) Å, b = 25.2258(5) Å, c = 26.5373(5) Å, V = 15 189.2(5) Å³, Z = 8, Rcalc = 1.466 g cm⁻³, T = 180(2) K, μ(Mo Kα) = 1.595 mm⁻¹ (λ = 0.71073 Å), 48009 reflections measured, 14906 unique, 11481 with I > 2σ(I). Final R₁ = 0.0416, wR₂ = 0.1137 (I > 2σ(I)), 945 parameters/0 restraints, min./max. residual electron density = −0.401/0.231 e Å⁻³. The N–H hydrogen atom of the HNEt₃⁺ cation and the OH hydrogen atom of the [Sm₂(HL)(L)(MeCN)]⁻ anion were located unambiguously from final Fourier maps but were refined using a riding model.

Crystal data for (HNEt₃)[Gd₂(HL)(L)(MeCN)]·MeCN. C₃₈H₄₆Gd₂N₆O₆, Mr = 1676.15 g mol⁻¹, orthorhombic space group Pbca, a = 22.7767(8) Å, b = 25.1415(11) Å, c = 26.5012(10) Å, V = 15 175.7(10) Å³, Z = 8, Rcalc = 1.466 g cm⁻³, T = 180(2) K, μ(Mo Kα) = 1.797 mm⁻¹ (λ = 0.71073 Å), 51122 reflections measured, 16712 unique, 10439 with I > 2σ(I). Final R₁ = 0.0485, wR₂ = 0.1160 (I > 2σ(I)), 942 parameters/0 restraints, min./max. residual electron density = −0.383/0.115 e Å⁻³. CCDC 1880057 (H₄L), 1880058 (K₄L) and 1880059 (K₆L) contain the supplementary crystallographic data for this paper.

Spectrophotometric titrations/determination of stability constants
A series of UV-vis spectroscopic studies were performed in order to determine the composition and stability constants of the lanthanide complexes. The stoichiometry of the lanthanide complexes was determined by the mole ratio method. All titrations were performed at 298 K in Hellma 110-QS quartz cells of 1 cm optical path length containing solutions at constant ionic strength (N(nBu)₄PF₆ 0.01 M) and constant ligand concentrations (5 × 10⁻⁵ M) in MeCN. For each experiment, 21 solutions were prepared by combining stock solutions of the ligand and the corresponding Ln(NO₃)₃·6H₂O salts with an Eppendorf micropipette (volume range of 10–100 µL and 100–1000 µL; 0.71–0.10% error) and allowed to stir for 12 h. UV–vis absorption spectra were collected in the 190–650 nm range at uniform data point intervals of 1 nm with a double-beam V-670 (Jobin Yvon) spectrophotometer. The multilength absorption data sets were analyzed by a nonlinear least-squares procedure implemented in the Hyperquad2008 v1.1.33 software.

Synthesis of the polycarbonate films
Polycarbonate Z200 (0.30 g) was dissolved in CH₂Cl₂ (1.5 mL) and stirred for 10 min. A solution of the lanthanide complex (V = 1 mL, 8 × 10⁻³ M) in CH₂Cl₂ was added to the PC solution. The resulting mixture was spread on a Petri dish (d = 5 cm) and the solvent was evaporated in open air overnight.

Luminescence lifetime measurements
The luminescence lifetime of the Tb complex 7 was measured applying a Fluoromax4 (HoribaScientific) equipped with a Fluorohub (Horiba Scientific) and the DataStation (Version 2.7) software package for TCSPC applications. The sample, imbedded in a thin polycarbonate matrix, was installed at an 35° angle towards the incident excitation light beam. Excitation and emission wavelengths of 310 and 545 nm were chosen. The time resolution was 1.33 µs per channel. In order to determine the instrument response function we used the identical setup with a highly reflective spectralon sample. The photon count rate was well below 1 percent of the excitation count rate ruling out pile up effects.

Conflicts of interest
There are no conflicts of interest to declare.

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References


99 The Sm complex 4 is not emissive at 77 K neither in solution nor in polycarbonate.


