

Complexes of *p*-*tert*-butylcalix[5]arene with lanthanides: synthesis, structure and photophysical properties †

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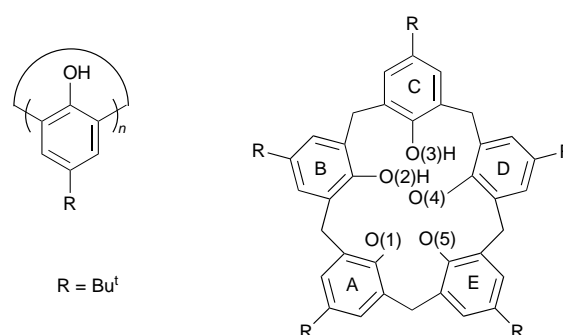
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Spectrophotometric pK_a determination for *p*-*tert*-butylcalix[5]arene (H_5L) in acetonitrile ($pK_{a1} = 11.5 \pm 0.7$, $pK_{a2} = 15.4 \pm 1.0$ at 298 K) evidenced both intra- and inter-molecular stabilisation of the deprotonated forms. Dimeric complexes $[Ln_2(H_2L)_2(dmsO)_4]$ ($Ln = Eu^{III}$, Gd^{III} , or Tb^{III} ; $dmsO =$ dimethyl sulfoxide) were isolated from tetrahydrofuran (thf) in the presence of NaH as base. A single-crystal analysis of $[Eu_2(H_2L)_2(dmsO)_4] \cdot 10thf$ showed the deformation of the cone conformation of the calixarene upon complexation and co-ordination of $dmsO$ molecules by inclusion through the hydrophobic cavity of the ligand. A photophysical investigation revealed a total quenching of the metal luminescence by a ligand-to-metal charge-transfer state in the case of Eu^{III} while luminescence of Tb^{III} is sensitised (quantum yield in thf: 5.1%). The temperature-dependent lifetime of Tb^{III} is analysed in terms of a potential metal-to-ligand back-transfer process.

The cyclic framework of calixarenes,¹ associated with the presence of phenol oxygen donor atoms, affords an interesting platform for the complexation of metal atoms,² while the hydrophobic cavity allows the inclusion of charged³ and neutral⁴ organic guests. The relative facility with which calixarenes can be partially or totally functionalised at the upper or lower rims, coupled with their easy large-scale synthesis, at least for the even members of the series ($n = 4, 6$ or 8), has opened further perspectives for their use in supramolecular chemistry.⁵ In particular, the hard acid character of the lower rim makes calixarenes interesting potential ligands for the complexation of trivalent lanthanide ions, either for extraction purposes⁶ or for the design of efficient lanthanide-based luminescent devices.^{7–9} Antenna effects¹⁰ can be generated directly by the phenol units or by lower or upper rim substitution.

Previous work on the complexation of lanthanides with calix[n]arenes has mainly focused on the four-, six- and eight-membered systems. While *p*-*tert*-butylcalix[8]arenes form bimetallic complexes in which the ligand is six times deprotonated,¹¹ the six-membered parent calixarene is bonded to Ln^{III} by a single phenolate group.¹² In the case of *p*-*tert*-butylcalix[4]arene 2:2 dimeric complexes were obtained, in which the two metal atoms are separated by only 3.91 Å.¹³ In our laboratory we have mainly studied the photophysical properties of bimetallic complexes with *p*-*tert*-butylcalix[8]arene^{14–16} and demonstrated the influence of the low-lying ligand-to-metal charge-transfer state (LMCT) on the Eu^{III} -containing assemblies, which enhances the f–f absorption probabilities through mixing with the 4f orbitals and quenches the $^5D_0(Eu)$ excited level. Moreover, the sensitisation of Eu^{III} and/or Tb^{III} can be conveniently tuned by changing the nature of the *para* substituent.¹⁷

Calix[5]arenes appear to be adequately suited for the complexation of lanthanoid(III) ions in view of the oxygen-rich array displayed by the five phenol groups in the cone conformation,¹⁸ and the possibility of forming multiply charged anions.¹⁹ To our knowledge, the only study on the interaction between lanthanoid(III) ions and a calix[5]arene has been

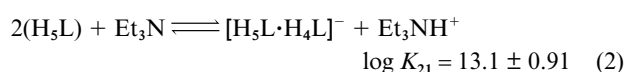
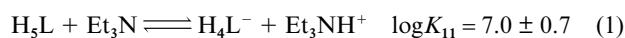


reported by Steed *et al.*¹⁹ who isolated water-soluble inclusion complexes between *p*-sulfonatocalix[5]arene with La, Gd, Eu, Tb and Yb and showed by X-ray crystallography that the interaction is either outer sphere or occurs exclusively *via* one sulfonato functionality, the metal centre acting often as a bridging brick. In this paper we present the isolation and the structural and photophysical properties of lanthanoid(III) ($Ln = Eu, Gd$ or Tb) phenolate-bonded inner-sphere complexes with *p*-*tert*-butylcalix[5]arene (H_5L). The reported data add valuable information on the interaction between lanthanoid(III) ions and *p*-*tert*-butylcalix[n]arenes and demonstrate that multiple bonds between the ligand and the metal ions can be generated only in the presence of a strong base. In addition, the spectrophotometric determination of the first two pK_a values of the ligand is reported.

Results and Discussion

Acid-base behaviour of H_5L in acetonitrile

The compound H_5L was titrated at 298 K by Et_3N in acetonitrile with NEt_4ClO_4 as supporting electrolyte. The evolution of the UV/VIS spectra during titration could be best fitted with the model (standard deviation: 0.007 absorbance unit between calculated and measured values) in equations (1)–(3). The first two acidity constants of *p*-*tert*-butylcalix[5]arene,



† Supplementary data available: UV/VIS and IR spectra, crystallographic numbering scheme. For direct electronic access see <http://www.rsc.org/suppdata/dt/1998/505/>, otherwise available from BLDSC (No. SUP 57328, 4 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (<http://www.rsc.org/dalton>).

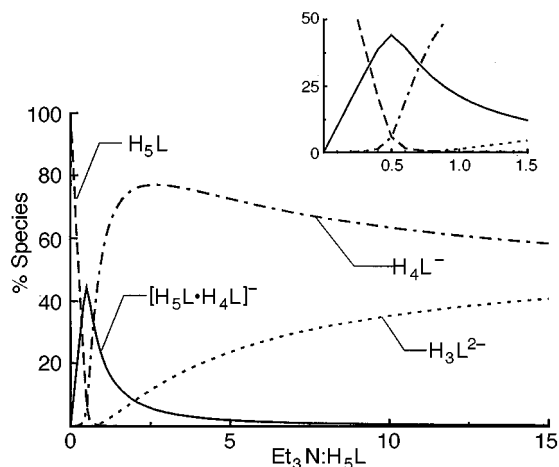
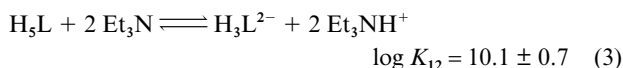


Fig. 1 Species distribution in solutions of H_5L in acetonitrile vs. the $Et_3N:H_5L$ ratio



K_{a1} and K_{a2} , can be evaluated from the relationships $K_{11} = K_{a1}/K_{Et_3NH^+}$ and $K_{12} = K_{a1}K_{a2}/(K_{Et_3NH^+})^2$. With $pK_{Et_3NH^+} = 18.46$ ²⁰ one gets $pK_{a1} = 11.5 \pm 0.7$ and $pK_{a2} = 15.4 \pm 1.0$. The distribution curves as a function of the $Et_3N:H_5L$ ratio are shown in Fig. 1.

For a 1:2 ratio the major species is an adduct formed from two calixarene molecules with one proton removed [equation (2)]. This can be related to the association process (4) with $\log K_{ass} = 6.1 \pm 1.1$.



Adding more base leads to the monodeprotonated calixarene while the dianionic species appears for ratios larger than 1:1. The observed pK_a values can be understood on the basis of the monoanion stabilisation by intramolecular hydrogen bonds forming cyclic arrays, as previously reported for pK_a data measured in water-containing solvents²¹ or in the same solvent but with different calixarenes.²² The reconstructed electronic spectra (SUP 57328) display an increase of the intensity of the low-energy $\pi \rightarrow \pi^*$ transition centred on the ligand at 288 nm upon deprotonation, together with the emergence of a shoulder around 305 nm. We tried to demonstrate the formation of the postulated dimeric adduct $[H_5L \cdot H_4L]^-$ by measuring the electrospray (ES) mass spectrum of a solution with a 1:2 base:calixarene ratio at which the dimer is the major species in solution (88%). The spectrum effectively displays a peak at m/z 1641.1 (15%), which can be attributed to a dimer $[2H_5L \cdot H_2O \cdot H^+]$ ($M_{calc} = 1640.3$). The presence of this species emphasises the possibility of intermolecular hydrogen bonds stabilising the monoanion, a way found by the system to minimise its energy in the absence of highly solvating molecules such as MeOH or water. Further deprotonation leads to Coulombic repulsion between the two parts of the dimer and destabilises it.

Synthesis and characterisation of the complexes (Ln = Eu, Gd or Tb)

Spectrophotometric investigation of the interaction between H_5L and lanthanoid(III) ions in acetonitrile and in the presence of Et_3N revealed a weak interaction leading to the formation of 1:1 and 2:1 species, but the analysis of the data did not converge properly. Given the values of pK_a reported above, triethylamine is not a strong enough base to produce the anionic species necessary for a stable association with the lanthanoid(III) ions. We therefore switched to NaH to deprotonate the calixarene and to tetrahydrofuran (thf) as solvent. Under

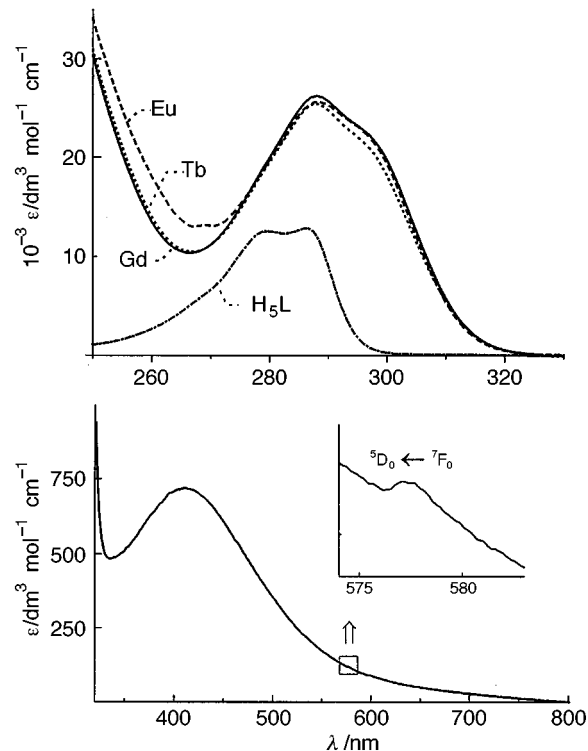


Fig. 2 Top: UV absorption spectra of $[Ln_2(H_5L)_2(dmsO)_4]$ in thf. Bottom: visible absorption spectrum for Ln = Eu showing the LMCT and ${}^3D_0 \leftarrow {}^7F_0$ transitions

these conditions, crystalline complexes were obtained by mixing stoichiometric amounts of H_5L with dimethyl sulfoxide (dmsO) adducts of the lanthanoid(III) nitrates. The elemental analyses are compatible with $[Ln_2(H_5L)_2(dmsO)_x]$ with $x = 4$ for Ln = Gd and Tb and 3 for Eu, which emphasises the tendency of the latter compound to lose 1–2 dmsO molecules upon drying. These analyses confirm the absence of nitrate in the isolated compounds. Infrared spectra of the three solids are very similar, showing an absorption band at 1023 cm^{-1} , not present in the spectrum of free H_5L , and assigned to the S–O stretching vibration of oxygen-bonded dmsO.²³ Upon complexation the broad $\nu(O-H)$ pattern shifts from 3305 cm^{-1} for free H_5L to a band centred around 3409 cm^{-1} with a shoulder at 3305 cm^{-1} (SUP 57328).

The $\pi \rightarrow \pi^*$ absorption bands of the ligand are very similar for the three complexes in thf (Fig. 2). They undergo a red shift with respect to H_5L , with a maximum at 288 nm ($34\,200 \text{ cm}^{-1}$; $\epsilon = 25\,620, 26\,230$ and $25\,420 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ respectively for Eu, Gd and Tb) and a shoulder at 295 nm ($33\,900 \text{ cm}^{-1}$). In the case of Eu^{III} an additional absorption band around 409 nm ($24\,445 \text{ cm}^{-1}$, $\epsilon = 720 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) is attributed to the ligand-to-metal charge-transfer transition, as previously reported for bimetallic complexes with *p*-substituted-calix[8]-arene.^{15,17} The presence of the LMCT transition relaxes Laporte's rule, so that the ${}^3D_0 \leftarrow {}^7F_0$ transition is observed at 577.7 nm ($17\,310 \text{ cm}^{-1}$), with an unusually large absorption coefficient ($\epsilon = 2.4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, after correction for MLCT absorption). The ES mass spectra of thf solutions of the complexes of Gd^{III} and Tb^{III} display base peaks at $m/z = 1932.6$ and 1929.5 respectively, which are typical of the dimeric cations $[Ln_2(H_5L)_2]^+$. No such peak is observed for the europium(III) complex, possibly as a result of reductive reactions on the metal, in accordance with the low-lying LMCT state.

Crystal structure of $[Eu_2(H_5L)_2(dmsO)_4] \cdot 10thf$

Slow concentration of a mixture of the europium(III) complex in thf afforded yellow-orange platelets suitable for X-ray diffraction analysis, with formula $[Eu_2(H_5L)_2(dmsO)_4] \cdot 10thf$.

Table 1 Selected averaged distances (Å) and angles (°) for the co-ordination sphere around the two europium(III) ions in $[\text{Eu}_2(\text{H}_2\text{L})_2(\text{dmsO})_4] \cdot 10\text{thf}$ (a and b refer to the dmsO O atoms, b corresponding to the molecule included in the calixarene cavity)

| | | | | | | | |
|---------------------|-----------|-----------|----------|-----------|----------|----------|----------|
| Eu...Eu' | 3.891(2) | Eu-O(3) | 2.56(2) | Eu-O(5') | 2.32(1) | | |
| Eu-O(1) | 2.33(1) | Eu-O(4) | 2.35(1) | Eu-O(a) | 2.32(1) | | |
| Eu-O(2) | 2.54(1) | Eu-O(5) | 2.48(1) | Eu-O(b) | 2.36(1) | | |
| O(x)-Eu-O(y) angles | | | | | | | |
| y | 1 | 2 | 3 | 4 | 5 | 5' | a |
| x | | | | | | | |
| 2 | 79.8(8) | | | | | | |
| 3 | 134.9(11) | 55.4(6) | | | | | |
| 4 | 144.0(5) | 133.8(7) | 78.8(9) | | | | |
| 5 | 73.2(5) | 132.7(6) | 132.4(7) | 73.0(5) | | | |
| 5' | 78.5(6) | 138.9(13) | 138.7(7) | 79.5(7) | 71.8(13) | | |
| a | 100.4(14) | 74.8(14) | 74.9(11) | 101.0(15) | 147.2(9) | 75.4(10) | |
| b | 92.0(19) | 67.1(7) | 67.5(8) | 91.5(16) | 75.7(8) | 147.5(9) | 137.0(6) |

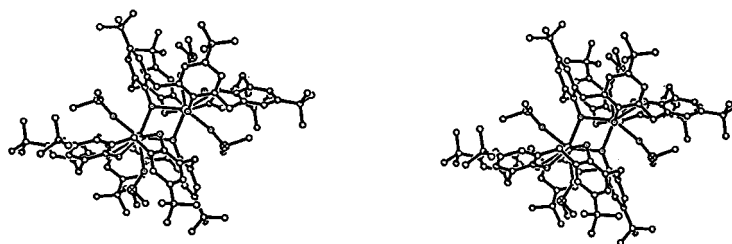


Fig. 3 Stereoscopic view of a dimeric $[\text{Eu}_2(\text{H}_2\text{L})_2(\text{dmsO})_4]$ unit

Details of the experimental conditions, cell data, structure solution and refinement are given in the Experimental section. Selected bond lengths and angles for the co-ordination sphere around Eu^{III} are given in Table 1 (the complete numbering scheme is described in SUP 57328).

The unit cell contains two crystallographically independent and neutral $[\text{Eu}_2(\text{H}_2\text{L})_2(\text{dmsO})_4]$ dimers comprised of two H_2L^{3-} anions, two europium(III) ions and four dmsO molecules co-ordinated to the metal ions. Within a dimer, an inversion centre is located halfway from the two Eu^{III} . Each eight-co-ordinated Eu^{III} is bonded to the five oxygen atoms of a calix[5]arene trianion, two dmsO oxygen atoms and a eighth oxygen from the second calix[5]arene anion (see the ORTEP²⁴ view in Fig. 3). The latter, O(5'), bridges the two europium ions, as does O(5), O(5) and O(5') being related by the inversion centre. The co-ordination polyhedra of the two ions (SUP 57328) are severely distorted as the analysis of the Eu-O bond distances shows.

The Eu-O(2) and Eu-O(3) bond lengths (2.54 and 2.56 Å, respectively) are longer than the other Eu-O (calixarene) bonds. Since two of the five phenol groups remain protonated, we think this lengthening is typical of Eu-OH bonds similarly to what was observed for the parent complex with a calix[4]arene.¹³ The average Eu-O distance is 2.41(10) Å resulting in an effective ionic radius, according to Shannon's definition,²⁵ of 1.10 Å (with $r_{\text{O}} = 1.31$ Å), in reasonable agreement with the literature value of 1.07 Å for eight-co-ordination.²⁶ The two bridging oxygen atoms form a parallelepiped O(5)-Eu(1)-O(5')-Eu(1') in which the metal ions are separated by 3.89 Å. A special feature of the structure is the bonding of one dmsO molecule to Eu^{III} through the hydrophobic cavity of the calixarene, thus combining co-ordination to the metal ion and inclusion in the calixarene, in a similar way to that reported for the co-ordination of pyridine *N*-oxide in $\text{Na}_8[\text{Tb}_4(\text{C}_5\text{H}_5\text{NO})_4(\text{H}_2\text{O})_{18}\text{L}'_4]$ ($\text{L}' = p$ -sulfonatocalix[5]arene).¹⁹

In the acetone and acetate clathrates of H_5L the macrocycle adopts a typical cone conformation,^{18,27} which is not the case in the presently described structure. The phenol rings B and C are strongly bent, with the oxygen atom pointing inside the hydrophobic cavity, while the methylene group bridging

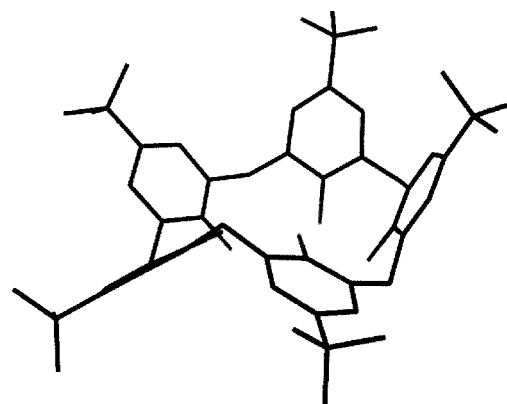


Fig. 4 Conformation of the ligand in $[\text{Eu}_2(\text{H}_2\text{L})_2(\text{dmsO})_4]$ as drawn with the PACHA program²⁸

these rings points outward, in contrast to the four other bridging methylene groups. The phenol rings A, D and E remain in the cone conformation and the whole configuration can be described as distorted toward a 1,2-partial cone conformation (Fig. 4).

This X-ray analysis confirms that the reaction of H_5L with a dmsO adduct of a nitrate salt of europium in the presence of a strong base leads to the isolation of a dimeric complex, as for the parent *p*-*tert*-butylcalix[4]arene complexes with Eu^{III} ¹³ or with Zn^{II} , Al^{III} , Fe^{III} and Ti^{IV} .²⁹ The Eu...Eu' distances in the two dimeric moieties with calix[4]- and calix-[5]arenes are very similar, 3.91 Å for the former and 3.89 Å for H_5L . These distances are also close to those measured in the bimetallic complexes $[\text{Eu}_2\text{L}''(\text{dmf})_5]$ (dmf = dimethylformamide): 3.69 Å ($\text{L}'' = \text{hexaanion of } p\text{-tert-butylcalix[8]arene}^{\text{II}}$) and 3.81 Å ($\text{L}'' = \text{hexaanion of } p\text{-nitrocalix[8]arene}^{\text{III}}$).³⁰

Luminescent properties

Upon excitation through the ligand $\pi \rightarrow \pi^*$ transition, solutions of the three complexes in thf display a sizeable emission band in the range 33 000–27 800 cm^{-1} , with a maximum at 31 150 cm^{-1} , assigned to luminescence from the $^1\pi\pi^*$ state of

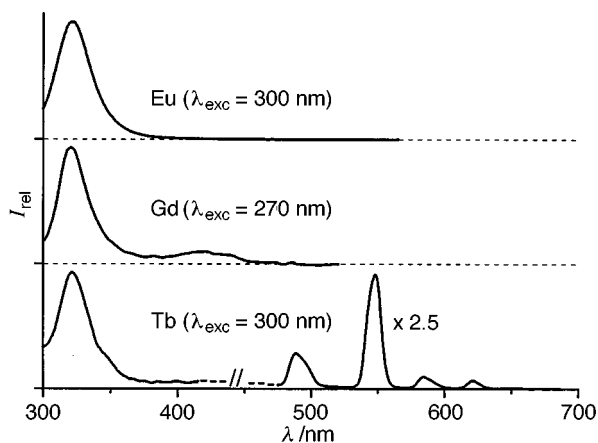


Fig. 5 Luminescence spectra of 10^{-3} M $[\text{Ln}_2(\text{H}_2\text{L})_2(\text{dmsO})_4]$ in thf, at room temperature

the ligand (Fig. 5). In the case of Gd^{III} the triplet-state emission can also be seen as a weaker band in the range $27\,000\text{--}20\,000\text{ cm}^{-1}$ and with a maximum at $23\,640\text{ cm}^{-1}$. Assignment to the $^3\pi\pi^*$ state relies on its decay time (a few tenths of ms). For the europium(III) compound no metal-centred luminescence is observed. Previous studies on *p-tert*-butylcalix[8]arene complexes with Eu^{III} ^{15,17} have pointed to a low-lying LMCT state being responsible for the almost complete quenching of the Eu^{III} -centred luminescence in these compounds and the same explanation probably holds for the calix[5]arene dimeric complex. In contrast to Eu^{III} , the complex of Tb^{III} displays a luminescence pattern characteristic of the metal-centred $^5\text{D}_4 \rightarrow ^7\text{F}_j$ ($J = 0\text{--}6$) transitions (Fig. 5), revealing a ligand-to-metal energy-transfer process. The quantum yield of the dimeric complex 10^{-3} M in thf amounts to 5.1%. Given the absence of specifically designed chromophoric groups attached to the calix[5]arene, this figure appears to be quite encouraging for the development of calix[5]arene-based luminescent stains.

In the solid state the lifetime of the $\text{Tb}(^5\text{D}_4)$ excited state, obtained by direct laser excitation to $^5\text{D}_4$, amounts to 1.12 ± 0.04 , 0.90 ± 0.04 , and 0.21 ± 0.01 ms at 10, 70 and 295 K, respectively. This relatively short lifetime may be partially due to the complexation of the two hydroxyl groups O(2)H and O(3)H. In $[\text{Tb}_2\text{L}'(\text{dmf})_4]$ ($\text{L}' = \text{hexaanion of } p\text{-tert-butylcalix[8]arene}$) where each Tb^{III} is co-ordinated to one phenoxyl group only, $\tau(^5\text{D}_4) = 1.52$ ms at 77 K¹⁴ and similar lifetimes have been reported at room temperature for complexes with lower-rim substituted calix[4]arenes with carbamoyloxy groups (1.5 ms in water for $\text{R} = \text{OCH}_2\text{CONEt}_2$ ³¹ and 1.79 ms in methanol for $\text{R} = \text{OCH}_2\text{CONH}_2$ ³²). The large temperature dependence observed between 10 and 295 K and leading at room temperature to a lifetime shorter than that observed for the aqua-ion (0.42 ms³³) is noteworthy. Such dependence has been assigned to back energy transfer from the terbium(III) ion to the ligand triplet state,³⁴ a phenomenon often observed for Tb^{III} included in supramolecular edifices.^{35,36}

Analysis of the temperature-dependent $\tau(^5\text{D}_4)$ lifetime between 50 and 295 K according to an Arrhenius relation of the type $\ln(\tau^{-1} - \tau_0^{-1}) = A + (E_a/RT)$,³⁴ where τ is the lifetime at temperature T , τ_0 that in the absence of quenching (taken here at 10 K) and E_a the activation energy for the quenching process, is shown on Fig. 6. A linear regression leads to $E_a = 180 \pm 20\text{ cm}^{-1}$, smaller than the values reported³⁴ for triacetate chelates with 1,10-phenanthroline ($900\text{--}2000\text{ cm}^{-1}$). If back energy transfer from the $^5\text{D}_4$ excited state of terbium to the triplet state occurs in $[\text{Tb}_2(\text{H}_2\text{L})(\text{dmsO})_4]$, such a small activation barrier can be related to vibrational motion in the complex and the deactivation pathway may be phonon assisted, for instance by Ln–O vibrations, which occur at around 220 cm^{-1} .³⁷

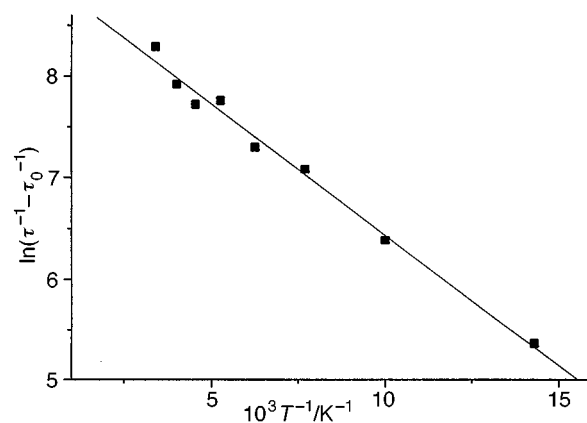


Fig. 6 Arrhenius plot of the $\text{Tb}(^5\text{D}_4)$ lifetime in $[\text{Tb}_2(\text{H}_2\text{L})_2(\text{dmsO})_4]$ vs. the reciprocal temperature (see text)

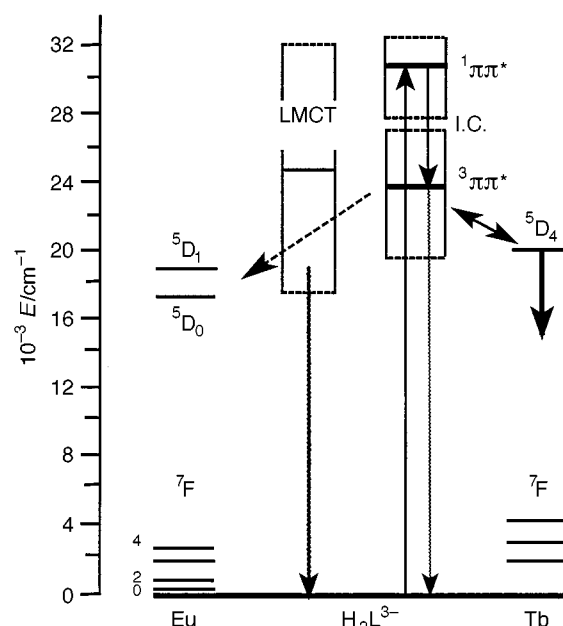


Fig. 7 Schematic energy-level diagram for H_2L^{3-} and its dimeric complexes with Eu^{III} and Tb^{III} (I.C. = intersystem crossing)

Conclusion

The data presented here point to *p-tert*-butylcalix[5]arene being an interesting ligand for lanthanide complexation. In a low-polarity solvent such as acetonitrile, stabilisation of its anionic forms is achieved both by intra- and inter-molecular hydrogen bonds. In the presence of a strong base, such as NaH, deprotonation is favoured and the macrocyclic anion reacts with lanthanide trivalent ions to form dimeric complexes, both in solution and in the solid state, as demonstrated by ES mass spectra and X-ray diffraction data.

The energy-level scheme reproduced in Fig. 7 summarises the photophysical properties of the isolated complexes. If the europium dimer proves to be inefficient as a luminescent probe, the metal-centred luminescence being completely quenched by the LMCT state (*cf.* the respective energy of this state and of the ligand $^3\pi\pi^*$ state), the terbium assembly conveniently absorbs UV light and transfers its energy from the ligand $^3\pi\pi^*$ state to the terbium $^5\text{D}_4$ excited state. The overall efficiency of this transfer remains modest for two reasons. (i) The occurrence of a back-transfer process: Fig. 7 shows the near overlap between the $\text{Tb}(^5\text{D}_4)$ level and the low-energy tail of the $^3\pi\pi^*$ state, so that a low-energy phonon-assisted back transfer will be easily achieved (*cf.* the activation energy of 180 cm^{-1} found for this process). (ii) More significantly, the intersystem $^1\pi\pi^* \rightarrow ^3\pi\pi^*$ conversion

has a poor yield, as exemplified by the persistence of the singlet-state ligand-centred luminescence in the spectrum of the dimeric metal complex. The ligand used in this study does not bear specifically designed chromophoric groups and it may be envisaged that the relatively small quantum yield might be improved by grafting such groups on the calix[5]arene skeleton.

Finally, the inclusion-complexation properties of the calix[5]arene evidenced for dmsO may be of interest to probe the inclusion of organic molecules in the calixarene cavity, since co-ordination to the lanthanoid(III) ions will change the photo-physical properties of the latter.

Experimental

Synthesis and characterisation of the complexes

Solvents and starting materials other than *p*-*tert*-butylcalix[5]arene (Acros) were from Fluka (Buchs, Switzerland) and used without further purification unless otherwise stated. Tetrahydrofuran was distilled over Na and acetonitrile was treated with CaH₂ and P₂O₅.³⁸ The dmsO adducts of the lanthanoid salts were prepared from the oxides (Rhône-Poulenc, 99.99%)³⁹ and their lanthanoid content determined by titration with Titriplex III (Merck) in the presence of urotropine (1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane) and xylene orange.⁴⁰

The complexes were synthesized according to the following general procedure. The compound H₅L (1.3 × 10⁻⁴ mol, 1 equivalent) was dissolved in dry thf (0.12 dm³) under a nitrogen atmosphere. Sodium hydride (4.55 × 10⁻⁴ mol, 3.5 equivalents, 60% in oil) was added and the solution stirred for 2 h before Ln(NO₃)₃·*x*dmsO (*x* = 3.18, 2.97 or 3.25 for Ln = Eu, Gd or Tb) (1.3 × 10⁻⁴ mol, 1 equivalent) was added and the mixture stirred for 18 h at room temperature. A white precipitate of NaNO₃ slowly appeared and was filtered off. The solution was concentrated under reduced pressure until a precipitate formed, which was separated from the mother-liquor by centrifugation, washed with cold thf (2 cm³), centrifuged, and separated from the supernatant liquid. The resulting efflorescent solid was dried under vacuum [12 h, 40 °C, 10⁻² Torr (*ca.* 1.33 Pa)] to yield 66, 68 and 58% (Eu, Gd and Tb) of [Ln₂(H₅L)₂(dmsO)₄] as a white (Tb and Gd) or orange (Eu) powder [Found: C, 65.33; H, 7.12. Calc. for C₁₁₆H₁₅₂Eu₂O₁₃S₃ (*x* = 3): C, 64.67; H, 7.11. Found: C, 63.17; H, 7.16. Calc. for C₁₁₈H₁₅₈Gd₂O₁₄S₄ (*x* = 4): C, 63.18; H, 7.10. Found: C, 62.93; H, 6.92. Calc. for C₁₁₈H₁₅₈O₁₄S₄Tb₂ (*x* = 4): C, 63.08; H, 7.09%]. No nitrogen was found in any compound. Elemental analyses were performed by Dr. H. Eder (Microchemical Laboratory, University of Geneva). Infrared spectra were measured on a Mattson Alpha Centauri FT spectrometer as KBr pellets. The absorption maxima (in cm⁻¹) were identical, within experimental error, for all three complexes: 3305, 3409 (ν_{OH}); 3049 (ν_{CH_{ar}}); 2957, 2868 (ν_{CH_{al}}); 1605, 1482, 1465 (δ_{CH_{al}}); 1461 (ν_{CH_{al}}); 1023 (ν_{dmsO}).

Physicochemical measurements

Electrospray mass spectra were measured on a Finnigan SSQ 710C spectrometer with 10⁻⁴ M solutions in thf or acetonitrile. Spectrophotometric titrations were performed at 298 ± 0.2 K on a UV/VIS Perkin-Elmer Lambda 7 spectrometer with 1 cm quartz cells. In a typical experiment, a 10⁻⁴ M solution (10 cm³) of H₅L in dry acetonitrile containing 7.9 × 10⁻³ M NEt₄ClO₄ as inert salt was titrated by increasing amounts of a 10⁻³ M solution of Et₃N in the same solvent, delivered by a Metrohm Dosimat E 535 and recorded for Et₃N:H₅L ratios between 0 and 40:1. The spectra were fitted using the SPECFIT program.⁴¹ Factor analysis revealed the presence of four different species, which were described according to the model given in the Results and Discussion section.

Luminescence spectra were recorded on a Perkin-Elmer LS-50 spectrofluorimeter, using a 300 nm excitation filter for the terbium-centred emission. The quantum yield was determined in degassed thf (90 ppm water) at room temperature as previously described⁴² using [Tb(terpy)₃][ClO₄]₃ (terpy = 2,2':6',2''-terpyridine) in degassed acetonitrile (100 ppm water) as a secondary standard {absolute quantum yield 4.7%, as determined by the same method with [Ru(bipy)₃][ClO₄]₂ (bipy = 2,2'-bipyridine) in air-saturated water as standard⁴³}. The concentrations used were 10⁻³ M for both the terbium dimer and the reference (to avoid decomplexation), with λ_{exc} = 320.0 (sample) and 365.0 nm (reference). The ⁵D₄ → ⁷F_{*J*} transitions with *J* = 3–6 only were considered to obtain the integrated luminescence intensity. Neglecting the weak transitions to *J* = 0, 1 and 2 (<5% of the total integrated intensity) introduces negligible error and avoids corrections for the Rayleigh diffusion band interfering with these transitions. The luminescence spectra were corrected for the residual non Tb^{III}-centred emission. The Tb(⁵D₄) lifetimes were determined on a previously described instrumental set-up⁴⁴ using microcrystalline samples and selective laser excitation to the ⁵D₄ level (486 nm); the reported lifetimes are averages of at least three determinations; biexponential fitting of the curves was used, revealing a residual short lifetime due to an instrumental artefact, as confirmed by blank measurements.

Crystallography

The compound [Eu₂(H₅L)₂(dmsO)₄]₂·10thf crystallised as yellow-orange platelets which were incorporated into a drop of Hostinert 216 oil and frozen to 170 K (Oxford Cryostream). Such a manipulation prevented observation of the crystals under orthoscopic conditions but an episcopic inspection revealed thin boundaries subdividing the platelets into rectangular blocks which were warped with respect to each other. Data were collected on a Stoe IPDS system equipped with Mo-Kα radiation (λ 0.710 73 Å); 200 images in φ intervals of 1° were exposed for 6 min each. The crystal-image plate distance (80 mm) corresponded to a 1.13 Å⁻¹ resolution. Other experimental details are reported in Table 2. The indexing program of the IPDS system found the cell parameters from 2000 reflections (20 images), but only ¼ of the peaks belonged to the cell, as a result of the poor quality of the crystals (several attempts to produce better crystals failed). The defects of the crystals materialised in diffraction patterns containing large spots and in a large background noise all over the reciprocal space, which made it difficult to evaluate a reasonable effective mosaic spread for the data. Following a referee's suggestion, we attempted to solve the structure in a more symmetrical monoclinic cell. This resulted in a slightly worse agreement factor and did not change the topology of the dimer. We therefore think that the cell proposed in Table 2 soundly describes the important features of the diffraction pattern, despite the large final *R* values.

Data were corrected for Lorentz-polarisation effects (the intensity decay during the measurement was negligible) and the structure was solved with SHELXTL.⁴⁵ A first solution was found in space group *P*1, but after successful refinement the program MISSYM⁴⁶ revealed an inversion centre between the Eu atoms of the dimer. Therefore, we refined two half dimers related by a pseudo-translation (½ *c**). One isotropic displacement parameter was used for all atoms of the phenol rings, one for the atoms from the *tert*-butyl groups and one for the atoms of the methylene bridges. Benzene rings were restrained to be flat and to have literature C–C bond lengths,⁴⁷ and *tert*-butyl groups and dmsO molecules were restrained to conventional bond lengths and angles.⁴⁷ The dmsO molecules were refined using both isotropic and anisotropic displacement parameters.

Table 2 Crystal data and structure refinement for [Eu₂(H₂L)₂·(dmsO)₄]·10thf

| | |
|---|---|
| Formula | C ₁₁₈ H ₁₅₈ Eu ₂ O ₁₄ S ₄ ·10C ₄ H ₈ O |
| <i>M</i> | 2961.87 |
| Colour, shape | Yellow-orange platelets |
| Crystal system | Triclinic |
| Space group | <i>P</i> $\bar{1}$ |
| <i>a</i> /Å | 16.442(3) |
| <i>b</i> /Å | 16.496(3) |
| <i>c</i> /Å | 32.629(7) |
| α /° | 97.97(3) |
| β /° | 97.51(3) |
| γ /° | 114.26(3) |
| <i>U</i> /Å ³ | 7816(3) |
| <i>Z</i> | 2 |
| <i>F</i> (000) | 3088 |
| <i>D</i> _c /g cm ⁻³ | 1.245 |
| μ /mm ⁻¹ | 0.912 |
| θ Range for data collection/° | 1.93 to 24.05 |
| <i>hkl</i> Ranges of reflections | −18 to 18, −18 to 18, −37 to 37 |
| Reflections collected | 44 486 |
| Independent reflections | 22 971 (<i>R</i> _{int} = 0.2389) |
| Refinement method | Full-matrix least squares on <i>F</i> ² |
| Data, restraints, parameters | 22 971, 229, 724 |
| Goodness of fit on <i>F</i> ² | 0.822 |
| <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] (all data) | 0.112, 0.247 0.281, 0.317 |
| Extinction coefficient | 0.000 24(14) |
| Residuals in final difference map/ e Å ⁻³ | 1.106 and −1.179 |

CCDC reference number 186/812.

See <http://www.rsc.org/suppdata/dt/1998/505/> for crystallographic files in .cif format.

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