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

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Spectrophotometric pKₐ determination for p-tert-butylcalix[5]arene (H₅L) in acetonitrile (pKₐ = 11.5 ± 0.7, pKₐ = 15.4 ± 1.0 at 298 K) evidenced both intra- and inter-molecular stabilisation of the deprotonated forms. Dimeric complexes [Ln₂(H₅L)₄(dmso)] (Ln = EuIII, GdIII, or TbIII; dmso = dimethyl sulfoxide) were isolated from tetrahydrofuran (thf) in the presence of NaH as base. A single-crystal analysis of [Eu₂(H₅L)₄(dmso)]·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 EuIII while luminescence of TbIII is sensitised (quantum yield in thf: 5.1%). The temperature-dependent lifetime of TbIII is analysed in terms of a potential metal-to-ligand back-transfer process.

The cyclic framework of calixarenes, associated with the presence of phenol oxygen donor atoms, affords an interesting platform for the complexation of metal atoms, 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.7,8 Antenna effects9,10 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]arene form bimetallic complexes in which the ligand is six times deprotonated,11 the six-membered parent calixarene is bonded to Ln12 by a single phenolate group.13 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.14 In our laboratory we have mainly studied the photophysical properties of bimetallic complexes with p-tert-butylcalix[8]arene14–16 and demonstrated the influence of the low-lying ligand-to-metal charge-transfer state (LMCT) on the EuIII-containing assemblies, which enhances the f-f absorption probabilities through mixing with the 4f orbitals and quenches the ⁤D₀(Eu) excited level. Moreover, the sensitisation of EuIII and/or TbIII 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 (H₅L). The reported data add valuable information on the interaction between lanthanoid(III) ions and p-tert-butylcalix[5]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 pKₐ values of the ligand is reported.

Results and Discussion

Acid-base behaviour of H₅L in acetonitrile

The compound H₅L was titrated at 298 K by Et₃N in acetonitrile with NEt₃ClO₄ 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, H₅L + Et₃N ⇌ H₄L⁻ + Et₃NH⁺, logKₐ = 7.0 ± 0.7 (1) 2(H₄L⁻) + Et₃N ⇌ [H₃L⁻·H₄L⁻]⁺ + Et₃NH⁺, log Kₐ = 13.1 ± 0.91 (2)
The observed p...while the dianionic species appears for ratios larger than 1 : 1.

But with different calixarenes.

Adding more base leads to the monodeprotonated calixarene...necessary for a stable association with the lanthanoid(III) nitrates. The elemental analyses are compatible with [Ln3(H3L)2(dmso)] 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 H3L, and assigned to the S–O stretching vibration of oxygen-bonded dmso. Upon complexation the broad v(O–H) pattern shifts from 3305 cm\(^{-1}\) for free H3L to a band centred around 3409 cm\(^{-1}\) with a shoulder at 3305 cm\(^{-1}\) (SUP 57328).

The π→π* absorption bands of the ligand are very similar for the three complexes in thf (Fig. 2). They undergo a red shift with respect to H3L, with a maximum at 288 nm (34 200 cm\(^{-1}\); e = 25 620, 26 230 and 25 420 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\) respectively for Eu, Gd and Tb) and a shoulder at 295 nm (33 900 cm\(^{-1}\)). In the case of Eu\(^{III}\) an additional absorption band around 409 nm (24 445 cm\(^{-1}\), ε = 720 dm\(^3\) mol\(^{-1}\) cm\(^{-1}\)) is attributed to the ligand-to-metal charge-transfer transition, as previously reported for bimetallic complexes with p-substituted-calix[8]-arene.\(^{18,17}\) The presence of the LMCT transition relaxes Laporte’s rule, so that the \(\text{D}_{\text{Dy}}\) ← \(\text{F}_{\text{Gd}}\) transition is observed at 577.7 nm (17 310 cm\(^{-1}\)), with an unusually large absorption coefficient (ε = 2.4 dm\(^3\) mol\(^{-1}\) 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 [Ln2(H2L)4]\(^{2+}\). 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 [Eu3(H3L)2(dmso)3]·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 [Eu3(H3L)2(dmso)3]·10thf.
from the second calix
case in the presently described structure. The phenol rings B
would be severely distorted as the analysis of the Eu
The average Eu–O distance is 2.41(10) Å resulting in an
distorted toward a 1,2-partial cone conformation
strong base leads to the isolation of a dimeric complex, as for
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
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 remain in the whole configuration can be
described as distorted toward a 1,2-partial cone conformation.
The Eu–O of 1.10 Å (with
The unit cell contains two crystallographically independent
and neutral [Eu(HL)2(dmso)]3 dimers comprised of two
H2L+ 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 EuIII. Each eight-co-
ordinated EuIII is bonded to the five oxygen atoms of a calix-
arene anion (see the ORTEP25 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
expect this lengthening to be typical of Eu–OH bonds similarly to what was observed for the parent complex with a calix[4]-
arene.28 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 \(r_e = 1.31 \) Å), in reasonable agreement with the
literature value of 1.07 Å for eight-co-ordination.28 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 EuIII 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
In the acetone and acetate clathrates of H2L the macrcro-
cycle adopts a typical cone conformation,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

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Table 1 Selected averaged distances (Å) and angles (°) for the co-ordination sphere around the two europium(III) ions in [Eu2(H2L)2(dmso)12]10thf (a and b refer to the dmso O atoms, b corresponding to the molecule included in the calixarene cavity)

Fig. 3 Stereoscopic view of a dimeric [Eu2(H2L)2(dmso)]12 unit

Fig. 4 Conformation of the ligand in [Eu2(H2L)2(dmso)]12 as drawn with the PACHA program28
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 27 000–20 000 cm⁻¹ and with a maximum at 23 640 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) 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 \( ^4\Delta_4 \rightarrow ^4\Sigma_2 \) (\( J = 0 \)–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 Tb\((^4\Delta_4)\) excited state, obtained by direct laser excitation to \( ^4\Delta_4 \) 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 [TbL\(^4\text{dmf}\)]\(^0\) (L\(^0\) = hexaamin of \( p \)-tert-butylcalix[8]arene) where each Tb(III) is co-ordinated to one phenoxyl group only, \( \tau_0\)\( ^{\text{D}}\text{D}_4 \) = 1.52 ms at 77 K.⁴⁴ and similar lifetimes have been reported at room temperature for complexes with lower-ring substituted calix[4]arenes with carbamoyloxy groups (1.5 ms in water for \( R = \text{OCH}_2\text{CONH}_2 \)⁴⁵ and 1.79 ms in methanol for \( R = \text{OCH}_2\text{CONH}_4 \)). 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 ms)⁴⁴ is noteworthy. Such dependence has been assigned to back energy transfer from the terbium(III) ion to the ligand triplet state,⁴⁴ a phenomenon often observed for Tb(III) included in supramolecular edifices.⁴⁴,⁴⁶

Analysis of the temperature-dependent \( \tau_0\)\( ^{\text{D}}\text{D}_4 \) lifetime between 50 and 295 K according to an Arrhenius relation of the type \( \ln(\tau_0^-\tau_0) = A + (E_a/RT) \) shows that \( \tau_0 \) is the lifetime at temperature \( T \), \( \tau_0^- \) 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 \( E_a = 180 ± 20 \) cm⁻¹, smaller than the values reported⁴⁴ for triacetate chelates with 1,10-phenanthroline (900–2000 cm⁻¹). If back energy transfer from the \( ^4\Delta_4 \) excited state of terbium to the triplet state occurs in [Tb\(^4\text{H}_2\text{L}\)]\(^0\) (dmso)\(^0\), 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⁻¹.⁴⁷

**Conclusion**

The data presented here point to \( p \)-tert-butylcalix[8]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 luminescence 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 \( ^3\Delta_4 \) 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 Tb\(^{(4}\Delta_4)\) 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-

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. Tetra-
hydrofuran was distilled over Na and acetonitrile was treated with CaH2 and P2O5. The dmso adducts of the lanthanoid salts were prepared from the oxides (Rhône-
Poulenc, 99.99%)35 and their lanthanoid content determined by titration with Titrillex III (Merck) in the presence of uro-
tropine (3,1,5,7-tetraazatricyclo[3.3.1.13,7]decanec and xylene)
or.

The complexes were synthesised according to the following general procedure. The compound H2L (1.3 × 10−4 mol, 1 equiv) 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 200 nm (sample) and 750 nm (reference).

The compound [Eu(H2L)3(dmso)3]:6ClO4 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 unwrapped when the crystals had partially effloresced. The compound [Eu(H2L)3(dmso)3]ClO4 was obtained from NaNO3, slowly appeared and was filtered off. The solution was concentrated under reduced pressure until a precipitate formed, which was separated from the mother-liquid by centrifugation, washed with cold thf (2 cm3), centrifuged, and separated from the supernatant liquid. The resulting efferoscent solid was dried under vacuum (12 h, 40 °C). 1023 (dmso); 1023 (bipy-dmso). The concentrations used were 10−3 mol, 1 mol, 80 mm. This resulted in a slightly worse agreement factor (R1, 2) and the reference (to avoid decomplexation), with λexc = 320.0 (sample) and 365.0 nm (reference). The D3µ → F2 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 Tbµ-centred emission. The Tb(D4) lifetimes were determined on a previously described instrumental set-up46 using microcrystalline samples and selective laser excitation to the D4 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 [Eu(H2L)3(dmso)3]: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 unwrapped when the crystals had partially effloresced. The compound [Eu(H2L)3(dmso)3]ClO4 was obtained from NaNO3, slowly appeared and was filtered off. The solution was concentrated under reduced pressure until a precipitate formed, which was separated from the mother-liquid by centrifugation, washed with cold thf (2 cm3), centrifuged, and separated from the supernatant liquid. The resulting efferoscent solid was dried under vacuum (12 h, 40 °C). 1023 (dmso); 1023 (bipy-dmso). The concentrations used were 10−3 mol, 1 mol, 80 mm. This resulted in a slightly worse agreement factor (R1, 2) and the reference (to avoid decomplexation), with λexc = 320.0 (sample) and 365.0 nm (reference). The D3µ → F2 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 Tbµ-centred emission. The Tb(D4) lifetimes were determined on a previously described instrumental set-up46 using microcrystalline samples and selective laser excitation to the D4 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.

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clinic 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 P1, but after successful refinement the program MISSYM revealed an inversion centre between the Eu atoms of the dimer. Therefore, we refined two half dimers related by a pseudo-translation (a/3 1/2 2) and the reference (to avoid decomplexation), with λexc = 320.0 (sample) and 365.0 nm (reference). The D3µ → F2 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 Tbµ-centred emission. The Tb(D4) lifetimes were determined on a previously described instrumental set-up46 using microcrystalline samples and selective laser excitation to the D4 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.
Goodness of fit on Data, restraints, parameters
Refinement method

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References

45 SHEXLTL 5.05, Siemens Analytical X-Ray Instruments, Madison, WI, 1996.