DALTON
FULL PAPER

Lanthanide complexes with a *p-tert*-butylcalix[4]arene fitted with phosphinoyl pendant arms†

Laetitia Le Saulnier,[a] Sabi Varbanov,[b] Rosario Scopelliti,[a] Mourad Elhabiri[a] and Jean-Claude G. Bünzli*[a]

[a] *Institute of Inorganic and Analytical Chemistry, BCH, University of Lausanne, CH-1015 Lausanne, Switzerland. E-mail: jean-claude.bunzli@icma.unil.ch*
[b] *Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria*

Received 23rd September 1999, Accepted 5th October 1999

The lower-rim substituted calix[4]arene, 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene (L) has been synthesized and characterised by the single-crystal structure of its acetonitrile adduct, L·2MeCN (monoclinic, space group $P2_1/c$). The ligand adopts a cone conformation and a Δ enantiomeric form with the four phosphinoyl arms in a δδδδ configuration. The cone conformation is maintained in organic solution where L displays a time-averaged C_4 symmetry. Trivalent lanthanum ions interact with L in acetonitrile to yield both 1 : 1 (log $\beta_1 = 11.4 \pm 1.5$) and 1 : 2 (log $\beta_2 = 19.6 \pm 1.8$) complexes; two forms of the 1 : 1 complex are identified depending on the water content of the solutions. A photophysical study of both the ligand- and metal-centred luminescence of complexes of La, Eu and Tb points to L having a moderate quantum yield (*ca.* 10%, ligand-centred luminescence) and being a poor sensitiser of europium and terbium ions. It confirms the presence of differently solvated 1 : 1 (and 1 : 2) complexes, depending on the solvent composition. The lifetimes of the metal-centred luminescence of the unhydrated 1 : 1 and 1 : 2 complexes are long, in the range 1.4–2.4 ms for Eu and 1.7–7.3 ms for Tb, which indicates that the lanthanide(III) ions are well encapsulated in the cavity formed by the donor groups of the calix[4]arene molecule(s).

The relative facility with which calixarenes can be partially or totally functionalised at the upper or lower rims has opened broad perspectives for their use in supramolecular and coordination chemistry.[1] In particular, the hard acid character of the lower rim substituted calixarenes has been exploited to design polytopic receptors for the complexation of trivalent lanthanide ions, either for extraction purposes[2] and nuclear waste management[3] or for the design of efficient lanthanide-based luminescent devices[4] and probes.[5,6] Previous work in our laboratory has essentially focused on the photophysical properties of bimetallic complexes with *p-tert*-butylcalix[8]arene[7–10] and *p-tert*-butylcalix[5]arene,[11] with main interest in the influence of the *para* substituent on the sensitisation of europium(III) and terbium(III) ions and in unravelling the mechanism of energy transfer processes.

Recently, efficient synthetic technologies have been developed which allow the preparation of calixarenes grafted with phosphorus-containing pendant arms[12] and several of these calixarenes have proved to be better extractants for Ln^{III} and Th^{IV} than trioctylphosphine oxide (TOPO) or the (*N*,*N*-diisobutylcarbamoylmethyl)octylphosphine oxide (CMPO) used in the TRUEX process for nuclear waste retreatment.[13] Most of the studies on the interaction between trivalent lanthanide ions Ln^{III} and calixaryl phosphine oxides rely on extraction methods to determine the stoichiometry of the extracted species where the slope of the logarithm of the extraction coefficient *D* plotted *versus* the logarithm of the "free" ligand concentration yields the metal : ligand ratio. Lanthanide complexes with 1 : 1 and 1 : 2 stoichiometry were recently evidenced by this method.[14,15]

In this paper we present the synthesis and the solid state and solution structure of a new lower-rim substituted calix[4]arene, L = 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis(dimethylphosphinoylmethoxy)calix[4]arene. We then investigate the interaction of L with La^{III} by means of NMR and UV-visible spectroscopy and show the influence of water on the structure of the complexes. Compounds with 1 : 1 and 1 : 2 Ln:L (Ln = La, Eu or Tb) stoichiometry are isolated and their photophysical properties both in the solid state and in acetonitrile solution presented. The 1 : 2 compounds are the first complexes between lanthanide(III) ions and a calixarene isolated with such a stoichiometry.

Results and discussion

Synthesis and structural characterisation of L

Ligand L was prepared with 46% yield *via* a Williamson reaction by refluxing the tetrasodium derivative of *p-tert*-butylcalix[4]arene and chloro(dimethylphosphinoyl)methane in toluene or xylene (Scheme 1). The elemental analysis indicates that the isolated product has a composition $L\cdot 2H_2O$. The IR spectrum displays an intense ν(P=O) band at 1158 cm^{-1}, which moves to 1171 cm^{-1} upon removing the water molecules by heating the KBr pellet at 120 °C for 24 h. The phosphorylated calixarene is soluble at room temperature in methylene chloride, chloroform, methanol, ethanol, dmf, acetonitrile, glacial acetic acid, and sparingly soluble at higher temperature in toluene, xylene, and acetone. It can be recrystallised from various solvent mixtures such as methylene chloride–hexane, acetone–acetonitrile, ethanol–diisopropyl ether, toluene–heptane, xylene–heptane, and acetonitrile–diisopropyl ether. Using the latter mixture, white monoclinic crystals of composition L·2MeCN were obtained which were amenable to crystal

---

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3919/ Also available: ORTEP drawing, NMR and electronic spectra. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3919/, otherwise available from BLDSC (No. SUP 57659, 4 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).

This journal is © The Royal Society of Chemistry 1999

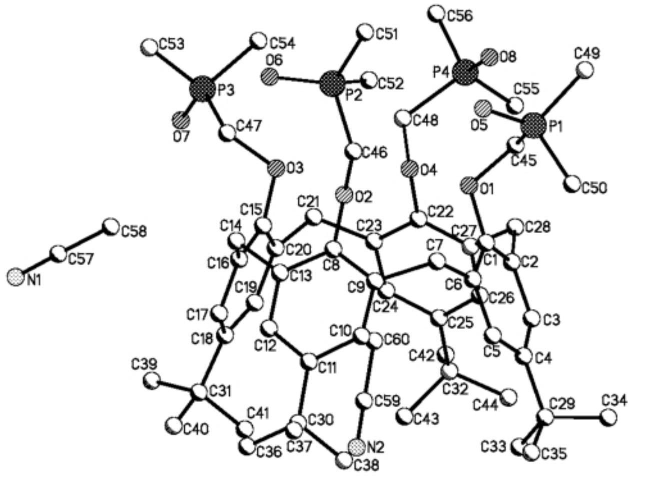
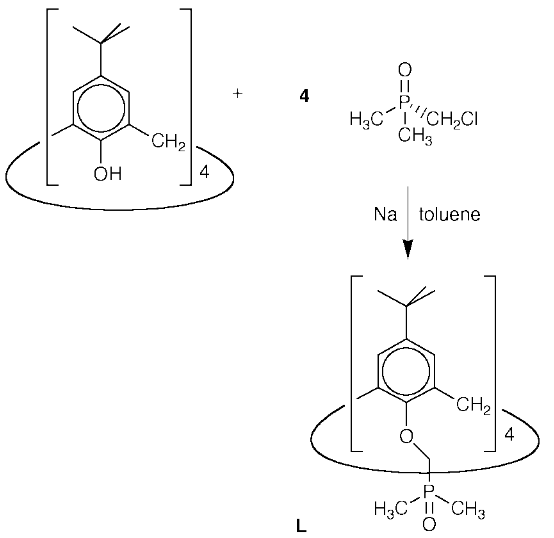


Fig. 1 View of L·2MeCN showing the atom-numbering scheme.



$$H_3C-P(=O)(CH_3)-CH_2Cl$$

Scheme 1

structure determination. The structure is composed of discrete molecules in a cone conformation which incorporate one acetonitrile molecule in the upper rim while the other one is interstitial (Fig. 1). The mean P=O bond length, 1.487(3) Å, is in the range expected for P=O double bonds. All molecules adopt the same enantiomeric form, Δ, with the four phosphinoyl arms in a δδδδ arrangement. The dihedral angle between the aromatic rings A and C amounts to 39° while the angle between B and D is equal to 54°, pointing to a more regular cone than observed in two other related *p-tert*-butylcalix[4]arenes substituted at the lower rim by diphenylphosphinoylethyloxy[16] and diphenylphosphinoylmethoxy[17] arms. In these ligands the A and C rings are almost parallel with φ(A,C) = 2–3° while B and D lie perpendicular to each other with φ(B,D) = 96–97°; the deformation with respect to the cone conformation is due to the steric hindrance generated by the bulky phenyl groups attached to the phosphine oxide substituent.

The ^{1}H-, ^{13}C- and DEPT-135 (distortionless enhancement by polarisation transfer)[18] data point to the ligand displaying a time-averaged C_4 symmetry in acetonitrile and chloroform solutions. For instance, only four singlets are observed for the aromatic carbon atoms in the ^{13}C-{^{1}H} spectrum in CDCl$_3$: δ 125.68 (CH) and 133.57, 146.04 and 153.25 (quaternary C atoms). The cone conformation is also retained in solution, as demonstrated by the AB spin system observed in the ^{1}H NMR spectrum for the bridging methylene protons (SUP 57659) which is characteristic of a blocked cone conformation.[19]

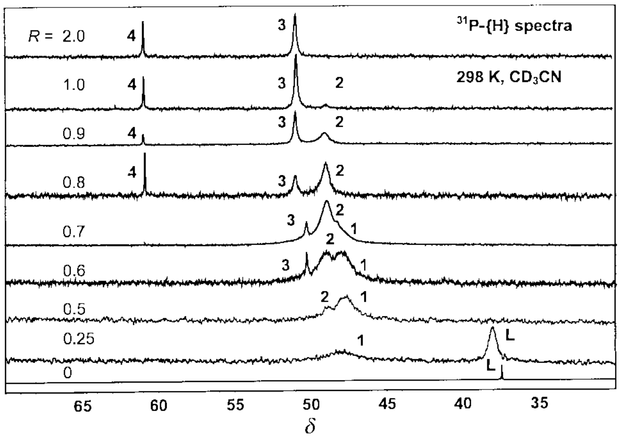


Fig. 2 Titration of L by La(ClO$_4$)$_3$·xH$_2$O in CD$_3$CN as followed by ^{31}P-{^{1}H} NMR spectroscopy at 298 K; R = [La^{III}]$_t$: [L]$_t$.

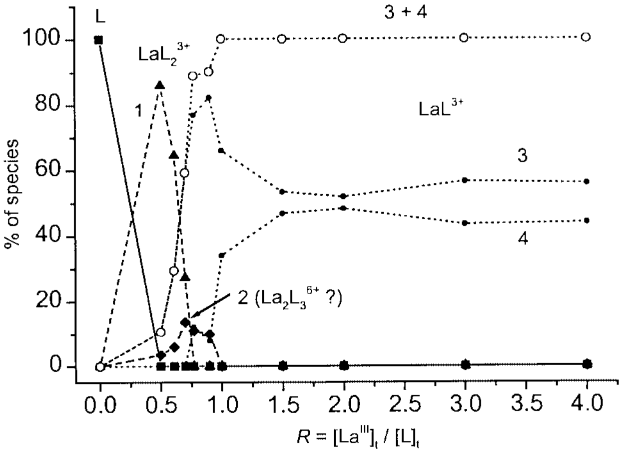


Fig. 3 Titration of L by La(ClO$_4$)$_3$·xH$_2$O in CD$_3$CN: distribution of species based on the integration of the ^{1}H NMR signals.

Interaction of L with lanthanide(III) ions

The titration of 1.6 × 10^{-3} M ligand L in CD$_3$CN by 4.5 × 10^{-3} M La(ClO$_4$)$_3$·xH$_2$O up to a ratio R = [La^{III}]$_t$: [L]$_t$ = 4 : 1 leads to the successive formation of four different species, as monitored by ^{31}P-{^{1}H} (Fig. 2) and ^{1}H NMR (SUP 57659) spectra. Chemical shifts are reported in Table 1 while the distribution of the species *versus* R as determined by integration of the ^{1}H NMR signals from the aromatic protons is represented on Fig. 3. When $R < 0.25$ free and bonded ligands are in rapid exchange, resulting in broad and coalesced ^{1}H NMR signals, which become narrower when the temperature is lowered. When R reaches 0.5 specific signals are observed corresponding to a 1 : 2 (La : L) complex, labelled species 1 on Fig. 2. Between $0.5 < R < 1$ a minor species (2) appears, but its concentration was always too low (<10%) to allow a complete identification of its ^{1}H NMR spectrum; nevertheless, we tentatively assign it to a 2 : 3 complex. In the same R range we observe the growth of two species (3 and 4) the proportions of which stabilise for $R > 1$. One also notices that the accumulated concentration of these two species remains constant for $R > 1$. This may be interpreted in terms of two complexes with 1 : 1 stoichiometry, but with different ligand conformation and/or metal ion environment. In fact, the concentration ratio of species 3 and 4 depends on the amount of water present in solution. Taking into account a simplified model with a 1 : 2 and an "average" 1 : 1 species only, the data of Fig. 3 can be fitted to log β_1 = 13.4 ± 1.3 and log β_2 = 19 ± 1.8. Introducing the 2 : 3 species in the model does not result in a good fit, probably in view of the too large uncertainty on the measured concentration of this species.

Table 1 The ^1H and ^{31}P-{^1H} chemical shifts (δ) and coupling constants (J/Hz in parentheses) for the complexed species identified during the titration of L by $La(ClO_4)_3 \cdot xH_2O$ in CD_3CN at 298 K[a]

Observed nucleus	Species 1 $[LaL_2]^{3+}$	$\Delta\delta$[b]	Species 3[c] $[LaL]^{3+}$	$\Delta\delta$[b]	Species 4[d] $[LaL]^{3+}$	$\Delta\delta$[b]
H(ax)	4.63 (d) (12.2)	−0.19	4.46 (d) (12.8)	−0.36	4.05 (d) (12.8)	−0.77
H(eq)	3.58 (d) (12.8)	+0.28	3.65 (d) (12.8)	+0.35	3.90 (d) (12.8)	+0.60
Aryl H	7.30(s)	+0.22	7.41 (s)	+0.33	7.59 (s) (1.8)	+0.51
$CH_2P(O)$	4.78 (s, br)	+0.14	4.51 (d) (3.6)	−0.13	5.11 (d) (14.0) 4.26 (dd), (14.0, 4.3)	
$P(O)(CH_3)_2$	1.69 (d) (13.4)	+0.26	1.79 (d) (13.4)	+0.36	2.02 (d) (14.0)	+0.59
$C(CH_3)_3$	1.21 (s)	+0.06	1.23 (s)	+0.08	1.21 (s)	+0.06
^{31}P-{^1H}	48.1	+10.7	50.9	+13.5	60.9	+23.5

[a] s = Singlet, d = doublet, dd = doublet of doublets, br = broad. [b] $\Delta\delta = \delta$(bound) − δ(free). [c] In presence of traces of water. [d] Under anhydrous conditions.

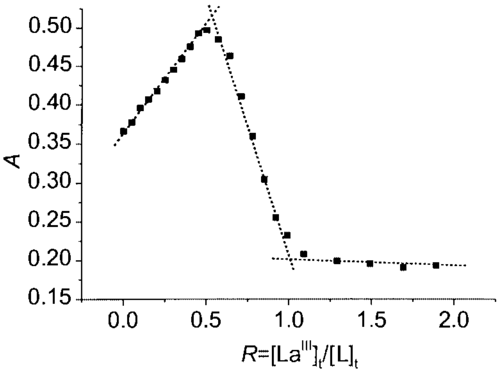


Fig. 4 Spectrophotometric titration of L by $La(ClO_4)_3 \cdot xH_2O$ in MeCN at 295 K: variation of A(280 nm) *vs.* $[La^{III}]_t : [L]_t$.

To confirm the speciation, we have monitored the titration by ES-MS spectroscopy. For $R < 1$ the main species is $[LaL_2]^{3+}$ (m/z 719.1) but $[LaL]^{3+}$ adducts with MeCN are also observed, $[LaL \cdot MeCN]^{3+}$ (m/z 395.6) and $[LaL \cdot 2MeCN]^{3+}$ (m/z 409.6). For larger R values the 1 : 2 complex disappears and the spectra are dominated by the MeCN adducts of the 1 : 1 complex as well as by a $[LaL \cdot ClO_4]^{2+}$ adduct (m/z 623.8). No other La containing species were found. Stability constants were also determined by spectrophotometric titration of L by $La(CF_3SO_3)_3$ in the presence of 0.1 M Et_4NClO_4 0.1 M. When experiments were carried out in the free atmosphere (that is with the water content not controlled) a suitable model could not be fitted to the data. We have therefore conducted the titrations under a controlled atmosphere and using anhydrous acetonitrile (<40 ppm H_2O). Plots of absorbance *versus* R clearly evidence two complexed species (Fig. 4) and factor analysis indicates the presence of 3 or 4 absorbing species, but only a model taking into account 3 species (L, 1 : 1 and 1 : 2) could be fitted to the data with stability constants $\log \beta_1 = 11.4 \pm 1.5$ and $\log \beta_2 = 19.6 \pm 1.8$, in good agreement with the NMR data. Measured band maxima for the absorbing species occur at 278.4 ($\varepsilon = 3780$ M^{-1} cm^{-1}), 276.0 (1660) and 279.5 nm (9970) for L, $[LaL]^{3+}$ and $[LaL_2]^{3+}$, respectively (SUP 57659).

A closer examination of the ^1H NMR spectra gives a clue on the solution structure of the species. First, we note that $[LaL_2]^{3+}$ and hydrated $[LaL]^{3+}$ display the same signal mutiplicity, reflecting a time-averaged C_4 symmetry of the ligand molecules, which is not quite the case for anhydrous $[LaL]^{3+}$ in particular as far as the $CH_2P(O)$ protons are concerned (H_p, Fig. 5). The shift of the aromatic protons with respect to free L reflects the participation of the ether O atoms in the metal ion co-ordination, increasing when the metal–oxygen interaction increases.[20] We find $\Delta\delta = +0.22$ ppm for $[LaL_2]^{3+}$, +0.33 ppm for hydrated $[LaL]^{3+}$ and +0.51 ppm for anhydrous $[LaL]^{3+}$; the latter indicates a strong interaction between La^{III} and the ether O atoms. This is confirmed by the signals of the protons from the ring methylene bridge (H_a, H_e, Fig. 5): $\delta(H_a)$ decreases and $\delta(H_e)$ increases in the order $[LaL]^{3+}$(anh) > $[LaL]^{3+}$(hydr) > $[LaL_2]^{3+}$ a fact consistent with a closer proximity of the metal ion and these protons. Finally, the CH_2PO protons display a different multiplicity for anhydrous $[LaL]^{3+}$ than for the two other complexes; these protons generate a closely spaced doublet in the spectra of L ($J_{HP} = 2.2$ Hz) and hydrated $[LaL]^{3+}$ ($J_{HP} = 3.6$ Hz) and a broad singlet in the spectrum of $[LaL_2]^{3+}$ while they appear as an AB spin system ($J_{HH} = 14$, $J_{HP} = 4.3$ Hz) in the spectrum of anhydrous $[LaL]^{3+}$, pointing to a large geometrical change. These facts may be understood as follows. In the presence of water, co-ordination of the La^{III} is essentially achieved by the four P=O groups and by the strongly co-ordinating H_2O molecules (undried acetonitrile contains about 6–8 mM H_2O) while under anhydrous conditions acetonitrile molecules are unable to compete with ether O atoms and the metal ion shifts deeper into the calixarene cavity (Fig. 6).

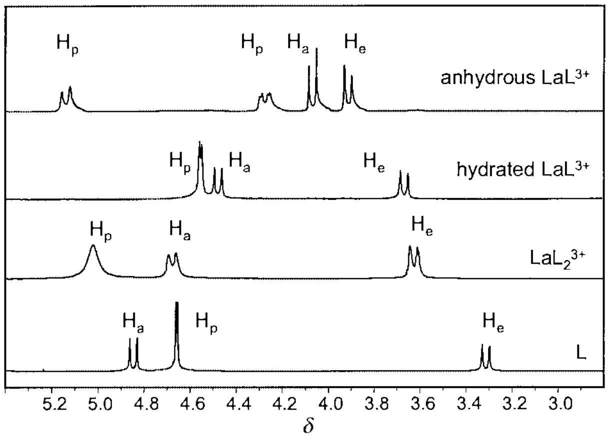


Fig. 5 Part of the ^1H NMR spectra of L and its 1 : 1 and 1 : 2 complexes with La^{III} in CD_3CN at 298 K displaying the signals of the methylene protons (ring, H_a and H_e; arm, H_p).

The 1 : 1 complexes of La, Eu and Tb have been isolated from the chloride and/or perchlorate salts (see Experimental section); the counter ion seemingly plays no role, the only slight differences evidenced lying in the solvation of the isolated compounds. Vibrational spectra clearly show the characteristic absorptions of ionic perchlorate ions but the presence of bonded perchlorate cannot be completely ruled out in view of band overlap. The ν(P=O) vibration is split into two components in the 1 : 1 complexes and red-shifted with respect to its value for an anhydrous sample of L by an amount which depends on the solvation of the complexes; for instance, the $\Delta\nu$ values measured for the chloride 1 : 1 compounds increase from 25 and 5 (La) or 17 and 7 (Eu) to 27 and 18 (La) or 36 and 18 cm^{-1} (Eu) after heating the KBr pellets for 24 h at 120 °C. The ν(P=O) shift is much larger for the 1 : 2 complexes, reaching *circa* 50 cm^{-1} for Tb. These findings are also consistent with the model proposed in Fig. 6.

Table 2 The Eu($^5D_0$) and Tb($^5D_4$) lifetimes (ms) in the $[LnL]X_3{\cdot}solv$ ($X = Cl^-$ or ClO_4^-, solv = EtOH or H_2O) and $[LnL_2][ClO_4]_3{\cdot}H_2O$ complexes obtained under direct laser excitation of the metal excited states ($^5D_0 \longleftarrow {}^7F_0$ and $^5D_4 \longleftarrow {}^7F_6$ transitions)

Conditions	$[EuL]^{3+}$	$[EuL_2]^{3+}$	$[TbL]^{3+}$	$[TbL_2]^{3+}$
Solid, 10 K	1.91 ± 0.01 0.66 ± 0.01	1.68 ± 0.02 0.45 ± 0.01	1.90 ± 0.07 0.84 ± 0.02	7.25 ± 0.03 1.18 ± 0.03
Solid, 77 K	1.87 ± 0.02 0.62 ± 0.02	1.67 ± 0.01 0.45 ± 0.01	1.72 ± 0.06 0.82 ± 0.02	6.27 ± 0.05 1.07 ± 0.01
Solid, 295 K	1.11 ± 0.01 0.75 ± 0.02	1.98 ± 0.02 0.78 ± 0.02	1.75 ± 0.09 0.82 ± 0.02	5.37 ± 0.06 1.07 ± 0.01
5×10^{-4}–10^{-3} M/MeCN/295 K[a]	1.42 ± 0.5 0.51 ± 0.01	1.85 ± 0.01 0.66 ± 0.02	2.13 ± 0.06 0.41 ± 0.04	2.71 ± 0.01 0.67 ± 0.12
2×10^{-2} M/anhydrous MeCN/295 K	1.38 ± 0.02	2.25 ± 0.05 2.40 ± 0.03	[b]	[b]

[a] Excitation through the ligand $^1\pi\pi^*$ state. [b] Not measured.

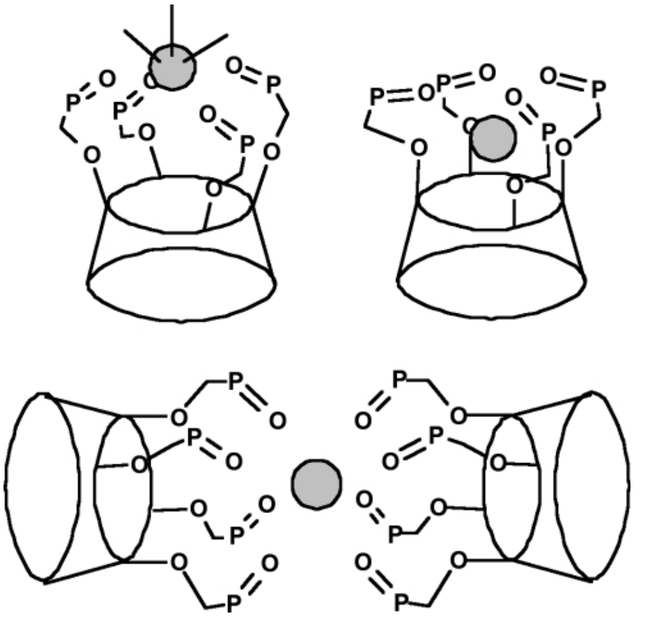


Fig. 6 Schematic representation of the solution structure of both hydrated (top left) and anhydrous (top right) $[LaL]^{3+}$ and of $[LaL_2]^{3+}$ (bottom), as inferred from NMR data.

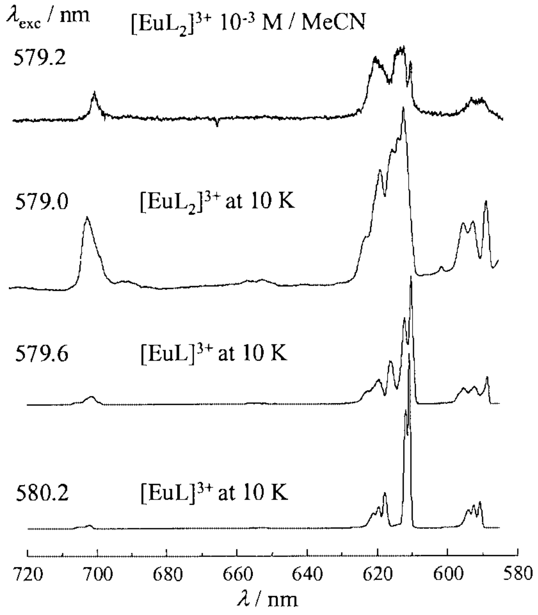


Fig. 7 Emission spectra of $[EuL]Cl_3{\cdot}2EtOH{\cdot}2H_2O$ and $[EuL_2]$-$[ClO_4]_3{\cdot}H_2O$ (vertical scale: arbitrary units).

Photophysical properties

A photophysical study has been undertaken to determine the antenna effect in the complexes of Eu and Tb as well as the extent of the protection against external interactions provided by the metal ion environment. The excitation spectrum of 8×10^{-6} M L in MeCN is essentially identical with its absorption spectrum having an intense band around 205 nm and a weaker and structured one around 280 nm. Excitation at the latter wavelength results in an emission band centred at 308 nm, assigned as arising from the lowest $^1\pi\pi^*$ state. No emission from a triplet state could be evidenced, even at 77 K, but we have determined the quantum yield of the ligand-centred fluorescence Q_L as being 10.4%. Complexation induces a decrease of Q_L to 7.6 (La), 5.9 (Tb) and *ca.* 0.1% (Eu) for solutions of $[LnL]^{3+}$ and to 8.9 (La), 8.5 (Tb) and 1.6% (Eu) for solutions of $[LnL_2]^{3+}$, respectively. The observation of a sizeable ligand-centred fluorescence band in solutions of the complexes of Eu and Tb is indicative of a poor energy transfer, as expected from the high energy of the ligand $^1\pi\pi^*$ state (32 470 cm^{-1}). The quantum yields of the metal-centred luminescence have been measured upon ligand excitation: we find $Q_{Tb} = 2.6$ (1 : 1) and 0.3% (1 : 2), which are reasonable figures in view of the small decrease of Q_L upon complexation to Tb, but $Q_{Eu} = 5 \times 10^{-2}$ (1:1) and 7×10^{-2}% (1 : 2) only. That both the ligand- and metal-centred luminescence are so weak in the europium complexes could be explained by a quenching process arising from a ligand-to-metal charge transfer state, as demonstrated recently for triple helical complexes with bis(benzimidazole)pyridines[21] and for bimetallic europium complexes with calix[8]arenes;[6,7] photoelectron transfer (PET) from the excited $^1\pi\pi^*$ state to the Eu^{III} is also a potential process.

The high-resolution excitation spectrum of a solid sample of $[EuL]Cl_3{\cdot}2EtOH{\cdot}2H_2O$ at 10 K confirms the quasi absence of ligand-to-metal energy transfer, being comprised of transitions to the ^5D_J levels ($J = 0$–4) with, in addition, two weak bands assigned to transitions to the $^5L_6$ and $^5G_2$ levels. The emission spectrum (Fig. 7) is dominated by the hypersensitive $^5D_0 \longrightarrow {}^7F_2$ transition (4.3 times as intense as the magnetic dipole $^5D_0 \longrightarrow {}^7F_1$ transition) and luminescence bands are relatively broad so that assignment of a precise site symmetry is difficult. However, the large relative intensity of the highly forbidden $^5D_0 \longrightarrow {}^7F_0$ transition (10% of the $^5D_0 \longrightarrow {}^7F_1$ transition) may point to a metal ion site with C_n symmetry. This transition occurs at 17 238 cm^{-1}, is broad (full width at half height, fwhh = 22 cm^{-1}) and asymmetric. In the excitation mode it displays one maximum at 17 236 cm^{-1} with a shoulder on the high energy side (17 246 cm^{-1}), pointing to the presence of two different metal environments, but direct laser excitation at these two energies yields very similar spectra. The lifetimes of the Eu($^5D_0$) and Tb($^5D_4$) levels in the 1 : 1 complexes are listed in Table 2. The luminescence decays were found to be bi-exponential for the solid state samples and for dilute solutions (10^{-3}–5×10^{-4} M) in acetonitrile, yielding one long (τ_L) and one short (τ_S) lifetime. For both Eu and Tb complexes, τ_L values correspond to metal environments where no OH oscillator is bound in the inner co-ordination sphere, while the shorter lifetimes are typical of Ln^{III} bonded to two (Eu) or several (Tb) OH oscillators.[22] The temperature dependence of τ_L points to the europium(III) ion being more sensitive to non-radiative deactivation than Tb^{III}, consistent with the larger energy gap in the latter between the ${}^5D_J$ excited level and the ground level. Given the formulae of the isolated complexes, we interpret the lifetime data as reflecting the presence of two species in each case, with and without co-ordinated water and/or alcohol molecules. The ${}^5D_0 \longleftarrow {}^7F_0$ excitation spectrum of the europium 1 : 1 complex has been measured on a more concentrated solution (2×10^{-2} M) in anhydrous acetonitrile (<40 ppm H_2O) in order to minimise the influence of water. It indeed presents one sharp ${}^5D_0 \longrightarrow {}^7F_0$ transition at 17 237 cm^{-1} (fwhh = 4 cm^{-1}) and the luminescence decay is monoexponential with $\tau\ ({}^5D_0) = 1.38 \pm 0.02$ ms. When water is added a new band appears at 17256 cm^{-1} and the lifetime decreases to 0.38 ms. The luminescence data are therefore in line with the interpretation of the previously described NMR and IR data pointing to the occurrence of two differently solvated species for the lanthanum 1 : 1 complex, both in the solid state and in solution.

The low-temperature emission spectra of the 1 : 2 complex, $[EuL_2][ClO_4]_3 \cdot H_2O$, resemble those of the 1 : 1 complex. The ${}^5D_0 \longrightarrow {}^7F_0$ transition occurs at 17 260 cm^{-1}, is relatively intense and asymmetric on the high energy side but again, selective excitation along the profile of the ${}^5D_0 \longleftarrow {}^7F_0$ excitation band produced very similar spectra. The luminescence decays of both the europium and terbium 1 : 2 complexes are more difficult to interpret since bi-exponential fits had to be used. The τ_L values for Tb are unusually long in the solid state, while in acetonitrile solution the lifetime is comparable to the ones reported recently for aqueous solutions of terbium complexes with 1,4,7,10-tetraazacyclododecane grafted with alkylphosphinate arms (3–4 ms).[22] The situation for the europium 1 : 2 complex resembles more that found for the 1 : 1 complex, the shorter lifetimes reflecting the interaction with 1 or 2 water molecules. In anhydrous acetonitrile a more concentrated solution displays a ${}^5D_0 \longleftarrow {}^7F_0$ transition with two clearly separated components, at 17 259 (fwhh = 6 cm^{-1}) and 17 267 cm^{-1} (fwhh ≈ 12 cm^{-1}); the associated lifetimes (single exponential decays) are 2.25 ± 0.05 and 2.40 ± 0.06 ms, respectively, clearly pointing to metal ion sites without OH oscillators in the inner co-ordination sphere. The difference between the two species could be due to the co-ordination of one acetonitrile molecule since the energy difference between the two 0–0 transitions corresponds to the nephelauxetic effect of one MeCN molecule,[23] but we favour another explanation. Indeed, the NMR spectrum of the 1 : 2 lanthenum complex presents somewhat broadened signals (Fig. 5) so that we interpret both the NMR and luminescence data as reflecting the presence of two conformers in rapid equilibrium. Interaction with perchlorate anions cannot be completely ruled out either, but is not likely in view of the larger steric hindrance of these ions.

Conclusion

To the best of our knowledge, the isolated complexes between lanthanide(III) ions and calix[4]arenes described in the literature have either a 2 : 2 stoichiometry, when co-ordination occurs through deprotonated phenol groups,[24,25] or a 1 : 1 stoichiometry when the calixarene is fitted with functional pendant groups on its lower rim.[26,27] The $[LnL_2][ClO_4]_3$ complexes reported in this study in which the metal ion is sandwiched between two lower-rim functionalised calix[4]arenes are therefore the first examples of lanthanide complexes with a calixarene isolated with a 1 : 2 stoichiometry, which substantiates the observations made in extraction studies.[14,15] The 1 : 2 complexes display a good stability in organic solvents and they form because the P=O groups are strong donors, stronger than for instance the carbonyl groups in the tetraamide-substituted calix[4]arene. The phosphinoyl moieties have therefore the tendency to attract the Ln^{III} at the outer rim of the cavity, allowing it to complete its co-ordination sphere either with solvent molecules, like in $[LnL \cdot n\text{solv}]X_3$ (solv = H_2O or EtOH), or with a second ligand molecule. An interaction with the four O atoms of the calixaryl group is only possible in the absence of strong donors, leading to $[LnL]X_3$ species, which limits somewhat the potential application of L in extraction processes. Lifetimes of the $Eu({}^5D_0)$ and $Tb({}^5D_4)$ excited states point to metal ion environments free of OH groups in the latter complexes and in the 1 : 2 edifices in anhydrous acetonitrile, that is providing maximum protection of the encapsulated metal ions. In the solid state, or in acetonitrile containing traces of water, hydrated 1 : 2 complexes are isolated in which a water molecule is probably inserted between the calixarene arms and interacts in the inner co-ordination sphere of the metal ion. On another hand, solutions in anhydrous acetonitrile contain non-hydrated species only.

In conclusion, this study sheds a new light on the interaction between lanthanide(III) ions and small calixarenes. In particular, the demonstration that differently co-ordinated species occur depending upon the water content of the organic solvent is an aspect which should be taken into account when modelling extraction processes.

Experimental

Syntheses and characterisations

Solvents and starting materials other than *p-tert*-butylcalix[4]arene (Acros) and chloro(dimethylphosphinoyl)methane (Hoechst AG) were purchased from Fluka AG (Buchs, Switzerland) and used without further purification unless otherwise stated. Tetrahydrofuran and toluene were distilled over Na and acetonitrile was treated successively by CaH_2 and P_2O_5.[28] Lanthanide chlorides and perchlorates were prepared from the oxides (Rhône-Poulenc, 99.99%) and their metal content determined by titration with Titriplex III (Merck) in the presence of urotropine and xylene orange.[29] Elemental analyses were performed by Dr H. Eder (Microchemical Laboratory, University of Geneva).

L. A solution of chloro(dimethylphosphinoyl)methane (3.59 g, 28.37 mmol) in toluene (50 cm^3) was added dropwise to a refluxing fine suspension of the tetrasodium derivative of *p-tert*-butylcalix[4]arene in toluene, prepared by addition of sodium (0.65 g, 28.37 mmol) to a solution of *p-tert*-butylcalix[4]arene (4.18 g, 6.45 mmol) in methanol (90 cm^3) and toluene (200 cm^3), followed by distillation of the methanol. The resulting mixture was stirred and refluxed under nitrogen for 65 h. After cooling to 50–60 °C the mother-liquor was filtered, the precipitate was washed with three portions of 50 cm^3 each of warm (50 °C) toluene and mixed with 150 cm^3 methylene chloride. Sodium chloride was separated by filtration and the methylene chloride solution washed with 2×50 cm^3 1 M HCl and 3×50 cm^3 water and dried on Na_2SO_4. After evaporation of the solvent, the crude solid product was recrystallised from a methylene chloride–hexane mixture and 3.02 g (yield, 46%) of a white husk-like powder are isolated ($R_f = 0.86$, CH_2Cl_2–MeOH–25%NH_3 2 : 5 : 1 v/v, fusion point 328–330 °C, decomp.) [Found: C, 63.99 ; H, 8.79 ; P, 11.33. Calc. for $C_{56}H_{88}O_{10}P_4$ ($L \cdot 2H_2O$): C, 64.35; H, 8.49; P, 11.85%]. δ_H (400 MHz; solvent CD_3CN) 7.08 (8 H, s, arylH), 4.82 (4 H, d, $J_{HH} = 12.7$, C_6H_2-$CH_2C_6H_2$), 4.64 (8 H, d, $J_{HP} = 2.2$, CH_2PO), 3.30 (4 H, d, $J_{HH} = 12.7$, $C_6H_2CH_2$), 1.43 (24 H, d, $J_{HP} = 13.1$ Hz, $(CH_3)_2PO$) and 1.15 (36 H, s, $C(CH_3)_3$). $\delta_P\{{}^1H\}$ (161.9 MHz, solvent CD_3CN) 37.4. ν(P=O) 1171 cm^{-1} (KBr disk, after heating for 24 h at 120 °C). EI mass spectrum (solvent MeCN–MeOH–HCO_2H): *m*/*z* 1009.5 [$(M + H)^+$ 100] and 1031.5 [$(M + Na)^+$ 10%].

1:1 Complexes. The compound $Ln(ClO_4)_3 \cdot xH_2O$ (Ln = La or Tb) (0.1 mmol) was dissolved in 2 cm^3 EtOH at 40–50 °C and an equimolar amount of L in 4 cm^3 EtOH was added dropwise. A white precipitate appeared and the mixture stirred for 3 h at rt. The precipitate was centrifuged and washed with 2 × 8 cm^3 EtOH. Yields: 80 (La) and 61% (Tb) [Found: C, 45.13; H, 6.29. Calc. for $La(ClO_4)_3 \cdot L \cdot EtOH \cdot 3H_2O$: C, 45.04; H, 6.26. Found: C, 45.52; H, 6.21. Calc. for $Tb(ClO_4)_3 \cdot L \cdot EtOH \cdot 3H_2O$: C, 45.40; H, 6.31%]. ν(P=O) 1122, $\nu(ClO_4)$ 1090, 627 cm^{-1} (KBr disk). δ_H (400 MHz; anhydrous CD_3CN, Ln = La) 7.59 (8 H, s, arylH), 5.11 (4 H, d, J_{HH} = 14, CH_2PO), 4.26 (4 H, dd, J_{HH} = 14, J_{HP} = 4.2, CH_2PO), 4.05 (4 H, d, J_{HH} = 13.0, $C_6H_2CH_2C_6H_2$), 3.90 (4 H, d, J_{HH} = 13.0, $C_6H_2CH_2C_6H_2$), 2.02 (24 H, d , J_{HP} = 14.0 Hz, $(CH_3)_2PO$) and 1.21 (36H, s, $C(CH_3)_3$). A similar procedure was used for $LnCl_3$ (Ln = La or Eu) which required more solvent to dissolve (6 cm^3); addition of L caused a gellification of the solutions; EtOH was evaporated and the resulting white powder was washed with 2 × 10 cm^3 hot acetone and 10 cm^3 Et_2O. Yields: 66 (La) and 78% (Eu) [Found: C, 51.71; H, 7.31. Calc. for $LaCl_3 \cdot L \cdot 2EtOH \cdot 3H_2O$: C, 51.45; H, 7.34. ν(P=O) 1189 and 1198 cm^{-1}. Found: C, 51.97; H, 7.37%. Calc. for $EuCl_3 \cdot L \cdot 2EtOH \cdot 2H_2O$: C, 51.64; H, 7.22%. ν(P=O) 1189, 1207 cm^{-1}]. δ_H (400 MHz, solvent CD_3OD, Ln = La, 295 K): 6.94 (8 H, s, arylH), 4.85 (8 H, s, CH_2PO), 4.60 (4 H, d, J_{HH} = 13.1, $C_6H_2CH_2C_6H_2$), 3.47 (4 H, d, J_{HH} = 13.2, $C_6H_2CH_2C_6H_2$), 1.76 (24 H, d, J_{HP} = 13.1 Hz, $(CH_3)_2PO$) and 1.11 (36 H, s, $C(CH_3)_3$). δ_H (400 MHz, solvent CD_3OD, Ln = Eu, 338 K, broad peaks): 6.99 (8 H, s, arylH), 4.37 (8 H, s, CH_2PO), 3.84 (4 H, s, $C_6H_2CH_2C_6H_2$), 3.70 (4 H, s, $C_6H_2CH_2C_6H_2$), 1.14 (24 H, s, $(CH_3)_2PO$) and 1.11 (36 H, s, $C(CH_3)_3$).

1:2 Complexes. The compound $Ln(ClO_4)_3 \cdot xH_2O$ (Ln = La, Eu or Tb) (0.06 mmol) in 5–6 cm^3 dry MeCN was added dropwise to a solution of 0.1 mmol L in 25 cm^3 dry MeCN heated at 40–50 °C. The resulting mixture was stirred for 4 h at this temperature. The solvent was then partly evaporated (15–23 cm^3) and replaced by diisopropyl ether (15 cm^3) and the solution left for 24 h at −22 °C. The resulting white powder was filtered off and dried. Yields: 66 (La), 88 (Eu), 70% (Tb) [Found: C, 54.15; H, 7.26. Calc. for $La(ClO_4)_3(L)_2 \cdot 2MeCN \cdot 2H_2O$: C, 54.13; H, 6.97. Found: C, 54.01; H, 7.13. Calc. for $Eu(ClO_4)_3(L)_2 \cdot H_2O$: C, 54.10; H, 6.89. Found: C, 53.98; H, 6.93. Calc. for $Tb(ClO_4)_3(L)_2 \cdot H_2O$: C, 53.95; H, 6.87%]. ν(P=O) 1122, $\nu(ClO_4)$ 1090, 627 cm^{-1} (KBr disk, Ln = La, Eu, Tb). δ_H (400 MHz, solvent CD_3CN, Ln = La): 7.30 (8 H, s, arylH), 4.78 (8 H, br s, CH_2PO), 4.63 (4 H, d, J_{HH} = 12.6, $C_6H_2CH_2C_6H_2$), 3.58 (4 H, d, J_{HH} = 12.8, $C_6H_2CH_2C_6H_2$), 1.69 (24 H, d, J_{HP} = 12.6 Hz, $(CH_3)_2PO$) and 1.21 (36 H, s, $C(CH_3)_3$).

Physicochemical measurements

The IR spectra were measured on a Mattson Alpha Centauri FT spectrometer as KBr pellets. The EI-MS spectrum of the ligand was recorded with a Bruker FTMS BioAPEX II spectrometer at the Institute of Organic Chemistry, University of Fribourg; ES-MS spectra of the complexes were measured on a Finnigan SSQ 710C spectrometer on 10^{-4} M solutions in acetonitrile, capillary temperature to 200 °C and acceleration potential 4.5 kV. The ^1H (δ with reference to TMS) and ^{31}P-{^1H} (δ/ppm with reference to H_3PO_4 85%, external) NMR spectra were recorded with a Bruker DRX Avance 400 spectrometer. Analysis of the NMR data in terms of stability constants was done with the program MINEQL$^+$.[30] Spectrophotometric titrations were performed at 298 ± 0.2 K on a UV-Vis Perkin-Elmer Lambda 7 PC-controlled spectrometer with 1 cm quartz cells. In a typical experiment, 10 cm^3 of a 10^{-4} M solution of L in dry acetonitrile containing 10^{-3} M NEt_4ClO_4 as inert salt were titrated in the glove-box by increasing amounts of a 10^{-3} M solution of lanthanum trifluoromethanesulfonate, delivered by a Metrohm Dosimat E 535. Spectra were recorded for Ln:L ratios between 0 and 2:1 and fitted using the SPECFIT program.[31]

Table 3 Crystal data and structure refinement for $L \cdot 2MeCN$

Formula	$C_{60}H_{90}N_2O_8P_4$
M	1091.22
T/K	143(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	12.717(3)
b/Å	18.034(4)
c/Å	26.811(5)
β/°	102.60(3)
U/Å^3	6001(2)
Z	4
Reflections collected	13 510
Independent reflections	7161 (R_{int} = 0.0552)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0550, 0.1207
(all data)	0.1051, 0.1349

Low resolution luminescence spectra were recorded on a Perkin-Elmer LS-50B spectrofluorimeter, using a 300 nm excitation filter. The quantum yields of the metal-centred luminescence were determined at room temperature in phosphorescence mode (time delay 0.05 ms) on solutions in degassed and dried acetonitrile (<40 ppm water) using formula (1) where

$$Q_x/Q_r = [A_r(\lambda_r)/A_x(\lambda_x)][I(\lambda_r)/ I(\lambda_x)][n^2_x/ n^2_r][D_x/D_r] \quad (1)$$

subscript r stands for the reference and x for the samples; A is the absorbance at the excitation wavelength, I the intensity of the excitation light at the same wavelength, n the refractive index (1.343 for solutions in MeCN and 1.333 for solutions in water) and D the integrated luminescence intensity; $[Ln(terpy)_3][ClO_4]_3$ (terpy = 2,2′:6′,2″-terpyridine) in degassed and dried acetonitrile was used as secondary standard (absolute quantum yields: 1.3 (Eu)[32] and 4.7% (Tb)[11]). Concentrations were 10^{-3} M for the reference (to avoid decomplexation) and 5×10^{-4} -10^{-3} M for the samples, with λ_{exc} = 279 nm. The $^5D_0 \longrightarrow {}^7F_J$ (Eu, J = 0–4) and $^5D_4 \longrightarrow {}^7F_J$ (Tb, J = 3–6) transitions only were considered to obtain the integrated luminescence intensity. Neglecting the weak transitions to J = 5–6 (Eu) or 0–2 (Tb) (<5% of the total integrated intensity) introduces negligible error and avoids corrections for the Rayleigh diffusion band interfering with these transitions. Quantum yields of the ligand-centred luminescence were measured with respect to a 3×10^{-5} M solution of quinine sulfate in 0.05 M H_2SO_4 (absolute quantum yield: 54.6%).[33] When needed, emission band areas were corrected for the Rayleigh diffusion band, itself corrected for the absorbance of the solution. High resolution luminescence spectra and lifetimes were determined on a previously described instrumental set-up[23] using microcrystalline samples and selective laser excitation. The reported lifetimes are averages of at least three determinations; biexponential fitting of the curves was used whenever necessary.

Crystal structure determination of L

Suitable crystals of L (white needles) were obtained from MeCN/i–Pr_2O and mounted in glass capillaries. Crystal data and structure refinement details are listed in Table 3. Diffraction data were collected on a mar345 Imaging Plate Detector System. The cell was determined using 101 spots from the first image. Refinement of cell parameters, integration and scaling of data were performed with the program marHKL, release 1.9.1.[34] No absorption correction was applied. Structure solution was performed with *ab initio* direct methods.[35] Space group determination, structure solution, refinement, molecular graphics and geometrical calculation were carried out with the SHELXTL software package, release 5.1.[36]

CCDC reference number 186/1672.

See http://www.rsc.org/suppdata/dt/1999/3919/ for crystallographic files in .cif format.

Acknowledgements

We gratefully acknowledge Professor P. Belser for the EI-MS of L, Cédric Sager for recording ES-MS spectra of the complexes, and Ms. Véronique Foiret for her technical assistance in luminescence measurements. We thank the Fondation Herbette (Lausanne) for the gift of spectroscopic equipment and for a grant to one of us (S.V.). This work is supported through grants from the Swiss National Science Foundation and the Ministry of Education and Science of Bulgaria (Project X-626).

References

1 C. D. Gutsche, *Calixarenes Revisited*, ed. J. F. Stoddart, Monographs in Supramolecular Chemistry, The Royal Society of Chemistry, Cambridge, 1998.

2 F. Arnaud-Neu, S. Cremin, S. Harris, M. A. McKervey, M.-J. Schwing-Weill, P. Schwinte and A. Walker, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 329.

3 F. Arnaud-Neu, R. Arnecke, V. Böhmer, S. Fanni, J. L. M. Gordon, M.-J. Schwing-Weill and W. Vogt, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1855.

4 M. P. O. Wolbers, F. C. J. M. Vanveggel, F. G. A. Peters, E. S. E. Vanbeelen, J. W. Hofstraat, F. J. Geurts and D. N. Reinhoudt, *Chem. Eur. J.*, 1998, **4**, 772.

5 F. J. Steemers, W. Verboom, D. N. Reinhoudt, E. B. Vandertol and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1995, **117**, 9408.

6 J.-C. G. Bünzli, F. Besançon and F. Ihringer, in *Calixarene Molecules for Separation*, ed. G. Lumetta, A. Gopalan and R. D. Rogers, *ACS Symp. Ser.*, 1999, in press.

7 J.-C. G. Bünzli and F. Ihringer, *Inorg. Chim. Acta*, 1996, **246**, 195.

8 P. Froidevaux and J.-C. G. Bünzli, *J. Phys. Chem.*, 1994, **98**, 532.

9 J.-C. G. Bünzli, P. Froidevaux and J. M. Harrowfield, *Inorg. Chem.*, 1993, **32**, 3306.

10 J.-C. G. Bünzli and J. M. Harrowfield, *Calixarenes: A Versatile Class of Macrocyclic Compounds*, eds. J. Vicens and V. Böhmer, Kluwer, Dordrecht, 1991, p. 211.

11 L. J. Charbonnière, C. Balsiger, K. J. Schenk and J.-C. G. Bünzli, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 505.

12 C. Wieser-Jeunesse, D. Matt, M. R. Yaftian, M. Burgard and J. M. Harrowfield, *C. R. Acad. Sci.* (*Paris*), *Ser. C*, 1998, **1**, 479.

13 D. B. Chamberlain, R. A. Leonard, J. C. Hoh, E. C. Gray, D. G. Kalina and G. F. Vandegrift, Report ANL-80/37, Argonne National Laboratory, Argonne, Il, 1990.

14 F. Arnaud-Neu, J. K. Browne, D. Byrne, D. J. Marrs, M. A. McKervey, P. O'Hagan, M.-J. Schwing-Weill and A. Walker, *Chem. Eur. J.*, 1999, **5**, 175.

15 S. Barboso, A. G. Carrera, S. E. Matthews, F. Arnaud-Neu, V. Bohmer, J. F. Dozol, H. Rouquette and M.-J. Schwing-Weill, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 719.

16 J. F. Malone, D. J. Marrs, M. A. McKervey, P. O'Hagan, N. Thompson, A. Walker, F. Arnaud-Neu, O. Mauprivez, M.-J. Schwing-Weill, J. F. Dozol, H. Rouquette and N. Simon, *J. Chem. Soc.*, *Chem. Commun.*, 1995, 2151.

17 C. B. Dieleman, D. Matt and P. G. Jones, *J. Organomet. Chem.*, 1997, **546**, 461.

18 A. Popov and K. Hallenga, *Modern NMR Techniques and Their Applications in Chemistry*, Practical Spectroscopy Series, vol. 11, Marcel Dekker, New York, 1991.

19 C. D. Gutsche, B. Dhawan, J. A. Levine, K. Hyun No and L. J. Bauer, *Tetrahedron*, 1983, **39**, 409.

20 M . R. Yaftian, M. Burgard, D. Matt, C. Wieser-Jeunesse and C. B. Dieleman, *J. Incl. Phenom. Mol. Recogn. Chem.*, 1997, **27**, 127.

21 S. Petoud, J.-C. G. Bünzli, T. Glanzman, C. Piguet, Q. Xiang and R. P. Thummel, *J. Luminesc.*, 1999, **82**, 69.

22 A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. de Sousa, J. A. G. Williams and M. Woods, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 493.

23 J.-C. G. Bünzli and A. Milicic-Tang, *Inorg. Chim. Acta*, 1996, **252**, 221.

24 B. M. Furphy, J. M. Harrowfield, J. S. Ogden, B. W. Skelton, A. H. White and F. R. Wilner, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 2217.

25 A. Bilyk, J. M. Harrowfield, B. W. Skelton and A. H. White, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 4251.

26 S. Pappalardo, F. Bottino, L. Giunta, M. Pietraszkiewicz and J. Karpiuk, *J. Incl. Phenom. Mol. Recogn. Chem.*, 1991, **10**, 387.

27 M. F. Hazenkamp, G. Blasse, N. Sabbatini and R. Ungaro, *Inorg. Chim. Acta*, 1990, **172**, 93.

28 D. D. Perrin and W. L. F. Armarego, *Purification of Laboratory Chemicals*, Pergamon, Oxford, 1988.

29 G. Schwarzenbach, *Complexometric Titrations*, Chapman & Hall, London, 1957.

30 W. Schecher, MINEQL+2.1, Environmental Research Software, Edgewater, MD, 1991.

31 H. Gampp, M. Maeder, C. J. Meyer and A. D. Zuberbühler, *Talanta*, 1985, **32**, 257.

32 S. Petoud, J.-C. G. Bünzli, K. J. Schenk and C. Piguet, *Inorg. Chem.*, 1997, **36**, 1345.

33 S. R. Meech and D. C. Phillips, *J. Photochem.*, 1983, **23**, 193.

34 Z. Otwinowski and W. Minor, *Macromolecular Crystallography, Part A*, eds. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, pp. 307–326.

35 G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 467.

36 SHELXTL 5.1, Bruker AXS inc., Madison, WI, 1997.

Paper 9/07693J